# E-Programme & Abstract Book

## The 9th Asian Conference on Coordination Chemistry (ACCC9)

19-22 February 2024

The Berkeley Hotel Pratunam
Bangkok, Thailand

CONTACT US :

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Organized by

www.accc9.org

# Contents

# Welcome Message from Chair of ACCC9

We extend a warm welcome for you to join us in Bangkok for the 9th Asian Conference on Coordination Chemistry (ACCC9), 19th - 22nd February 2024 at The Berkeley Hotel Pratunam.

We are excited to bring together researchers from around Asia and the world to share and discuss the latest developments in coordination chemistry. The conference will feature a range of presentations, workshops, and networking opportunities, providing a unique opportunity to learn from experts in the field and make valuable connections.

Bangkok is the vibrant and bustling capital of Thailand. Known for its colorful and chaotic streets, delicious food, and rich culture, Bangkok is a must-visit destination. Whether you're interested in history, culture, or simply want to immerse yourself in the energy of the city, Bangkok has something for everyone.

Welcom to ACCC9, 2024 at Bangkok, Thailand!

Professor Thawatchai Tuntulani
Chulalongkorn University
Co-Chairs of ACCC9

Associate Professor David J. Harding
Suranaree University of Technology
Co-Chairs of ACCC9

# ACCC9 Organizing Committee

| | |
|---|---|
| Prof. Dr. Thawatchai Tuntulani | Chulalongkorn University |
| Asst. Prof. Dr. Pannee Leeladee | Chulalongkorn University |
| Assoc. Prof. Dr. Boosayarat Tomapatanaget | Chulalongkorn University |
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| Assoc. Prof. Dr. Preeyanuch Sangtrirutnugul | Mahidol University |
| Asst. Prof. Dr. Teera Chantarojsiri | Mahidol University |
| Assoc. Prof. Dr. Thanthapatra Bunchuay | Mahidol University |
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| Assoc. Prof. Dr. Apinpus Rujiwatra | Chiang Mai University |

The 9th Asian Conference on Coordination Chemistry
The Berkeley Hotel Pratunam, Bangkok, Thailand

Mayfair Ballroom A
Mayfair Ballroom B
Mayfair Ballroom C
Jubilee Ballroom A
Jubilee Ballroom B
Mayfair Ballroom B & C

# Conference Programme

## Day 1: 19th February 2024

| | | | | | |
|---|---|---|---|---|---|
| 7.45-8.30 | Registration | | | | |
| 8.30-9.15 | Open Ceremony | | | | |
| 9.15-10.00 | Plenary 1: Prof. Jonathan Sessler | | | | |
| 10.15-11.20 | | Catalytic coordination chemistry (CA1) | MOF/COF chemistry (MC1) | Coordination cages (CC1) | Frontiers in coordination chemistry (FR1) |
| 11.20-11.35 | Coffee Break | | | | |
| 11.35-13.00 | Supramolecular chemistry (SC1) | Catalytic coordination chemistry (CA2) | MOF/COF chemistry (MC2) | Luminescent compounds (LC1) | Frontiers in coordination chemistry (FR2) |
| 13.00-14.00 | Lunch (Palladium, 10th floor) | | | | |
| 14.00-14.45 | Plenary 2: Prof. Hoi Ri Moon | | | | |
| 15.00-16.40 | Single - molecule magnets and spintronics (SS1) | Catalytic coordination chemistry (CA3) | MOF/COF chemistry (MC3) | Coordination compounds for medical applications (CM1) | Organometallic chemistry (OR1) |
| 16.40-17.00 | | | Flash presentation | | Flash presentation |
| 17.00-18.00 | Reception & Poster session 1 (Mayfair Ballroom A) | | | | |

## Day 2: 20th February 2024

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|---|---|---|---|---|---|
| 8.30-9.15 | Plenary 3: Prof. Partha Sarathi Mukherjee | | | | |
| 9.15-9.45 | RIGAKU-ACCC Rising Star Award: Prof. Nobuhiro Yanai | | | | |
| 10.00-11.25 | Luminescent compounds (LC2) | F-Element chemistry (FE1) | MOF/COF chemistry (MC4) | Single -molecule magnets and spintronics (SS2) | Organometallic chemistry (OR2) |
| 11.25-11.35 | Coffee Break | | | | |
| 11.35-13.00 | Supramolecular chemistry (SC2) | Bioinorganic chemistry (BC1) | MOF/COF chemistry (MC5) | Single -molecule magnets and spintronics (SS3) | Organometallic chemistry (OR3) |
| 13.00-14.00 | Lunch (Palladium, 10th floor) | | | | |
| | International Committee Meeting (The Lounge, 10th floor) | | | | |
| 14.00-14.45 | Plenary 4: Prof. Sally Brooker | | | | |
| 15.00-16.40 | Supramolecular chemistry (SC3) | Bioinorganic chemistry (BC2) | MOF/COF chemistry (MC6) | Single -molecule magnets and spintronics (SS4) | Organometallic chemistry (OR4) |
| 16.40-17.00 | | Flash presentation | | | Flash presentation |
| 17.00-18.00 | Coffee Break & Poster session 2 (Mayfair Ballroom A) | | | | |

## The 9th Asian Conference on Coordination Chemistry

The Berkeley Hotel Pratunam, Bangkok, Thailand

**Mayfair Ballroom A**
**Mayfair Ballroom B**
**Mayfair Ballroom C**
**Jubilee Ballroom A**
**Jubilee Ballroom B**
**Mayfair Ballroom B & C**

## Day 3: 21st February 2024

| | | | | | |
|---|---|---|---|---|---|
| 8.30-9.15 | Plenary 5: Prof. Limin Zheng | | | | |
| 9.15-10.00 | MicrotracBEL-ACCC Award: Prof. Cheng-Young Su | | | | |
| 10.15-11.25 | Main group chemistry (MG1) | Supramolecular chemistry (SC4) | MOF/COF chemistry (MC7) | Switchable magnetic materials (SM1) | Catalytic coordination chemistry (CA4) |
| 11.25-11.35 | Coffee Break | | | | |
| 11.35-13.00 | Bioinorganic chemistry (BC3) | Supramolecular chemistry (SC5) | MOF/COF chemistry (MC8) | Switchable magnetic materials (SM2) | Catalytic coordination chemistry (CA5) |
| 13.00-14.00 | Lunch (Palladium, 10th floor) | | | | |
| 14.00-14.45 | Plenary 6: Prof. Janice Aldrich-Wright | | | | |
| 15.00-16.25 | Frontiers in coordination chemistry (FR3) | Supramolecular chemistry (SC6) | MOF/COF chemistry (MC9) | Switchable magnetic materials (SM3) | Catalytic coordination chemistry (CA6) |
| 16.25-16.35 | Coffee Break | | | | |
| 16.35-18.00 | | | | Switchable magnetic materials (SM4) | Coordination compounds for medical applications (CM2) |
| 18.30-21.00 | Banquet (Mayfair Ballroom C) | | | | |

## Day 4: 22nd February 2024

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|---|---|---|---|---|---|
| 8.45-9.30 | Plenary 7: Prof. Kenneth Kam-Wing Lo | | | | |
| 9.45-11.25 | Main group chemistry (MG2) | Luminescent compounds (LC3) | MOF/COF chemistry (MC10) | Theoretical insights in coordination chemistry (TI1) | Coordination cages (CC2) |
| 11.25-11.35 | Coffee Break | | | | |
| 11.35-13.00 | Main group chemistry (MG3) | Luminescent compounds (LC4) | MOF/COF chemistry (MC11) | Theoretical insights in coordination chemistry (TI2) | Coordination cages (CC3) |
| 13.00-14.00 | Lunch (Palladium, 10th floor) | | | | |
| 14.00-14.50 | Frontiers in coordination chemistry (FR4) | | MOF/COF chemistry (MC12) | Theoretical insights in coordination chemistry (TI3) | Bioinorganic chemistry (BC4) |
| 15.00-15.45 | Plenary 8: Prof. Yoshiaki Nishibayashi | | | | |
| 15.45-16.30 | RIGAKU-ACCC Award: Prof. Mi Hee Lim | | | | |
| 16.30-17.00 | Closing Ceremony & Poster Awards | | | | |

## Plenary & Award winners

### Room: Mayfair Ballroom B&C

### Day 1: 19th February 2024

| | | |
|---|---|---|
| 9.15-10.00 | Plenary 1 | Prof. Jonathan Sessler (The University of Texas at Austin, USA)<br>“Texas-inspired Drug Discovery Efforts”<br>Chair: Prof Masahiro Yamashita |
| 14.00-14.45 | Plenary 2 | Prof. Hoi Ri Moon (Ewha Womans University, Korea)<br>“Tailoring Metal-Organic Framework Characteristics through Controlled Metal Coordination Environments”<br>Chair: Prof Jonathan Sessler |

### Day 2: 20th February 2024

| | | |
|---|---|---|
| 8.30-9.15 | Plenary 3 | Prof. Partha Sarathi Mukherjee (Indian Institute of Science, India)<br>“Chemistry in the Confined Space of Molecular Vessels”<br>Chair: Prof. Makoto Fujita |
| 9.15-9.45 | RIGAKU-ACCC Rising Star Award | Prof. Nobuhiro Yanai (Kyushu University, Japan)<br>“Coordination chemistry for photon upconversion, nuclear hyperpolarization, and quantum sensing”<br>Chair: Prof. Tony James |
| 14.00-14.45 | Plenary 4 | Prof. Sally Brooker (University of Otago, New Zealand)<br>“Discrete spin crossover complexes: solid state and solution phase correlations, tuning and sensing”<br>Chair: Prof David Harding |

### Day 3: 21st February 2024

| | | |
|---|---|---|
| 8.30-9.15 | Plenary 5 | Prof. Li-Min Zheng (Nanjing University, China)<br>“Assembly of Chiral Metal Phosphonates: from Molecular Chirality to Macroscopic Superhelices”<br>Chair: Prof Thawatchai Tuntulani |
| 9.15-10.00 | MicrotracBEL-ACCC Award | Prof. Cheng-Young Su (Lehn Institute of Functional Materials, LIFM, China)<br>“Functionalization of MOCs as Supramolecular Reactors for Cage-Confined Catalysis”<br>Chair: Prof Jack Clegg |
| 14.00-14.45 | Plenary 6 | Prof. Janice Aldrich-Wright (Western Sydney University, Australia)<br>“Unconventional Platinum(VI) Prodrugs”<br>Chair: Prof Jenny Yang |

### Day 4: 22nd February 2024

| | | |
|---|---|---|
| 8.45-9.30 | Plenary 7 | Prof. Kenneth Kam-Wing Lo (City University of Hong Kong, Hong Kong)<br>“Leveraging the Photophysical and Photochemical Properties of Transition Metal Complexes for Bioimaging and Photocytotoxic Applications”<br>Chair: Prof. Khamphee Phomphrai |
| 15.00-15.45 | Plenary 8 | Prof. Yoshiaki Nishibayashi (The University of Tokyo, Japan)<br>“Molybdenum-catalyzed reduction of molecular dinitrogen into ammonia under ambient conditions”<br>Chair: Prof Wonwoo Nam |
| 15.45-16.30 | RIGAKU-ACCC Award | Prof. Mi Hee Lim (Korea Advanced Institute of Science and Technology, KAIST, Korea)<br>“Bioinorganic Strategies to Study Multiple Facets in Dementia”<br>Chair: Prof. Phimphaka Harding |

## Bioinorganic chemistry (BC)

### Day 2: 20th February 2024

| **BC1 Chair: Prof. Takashi Hayashi, Co-chair: Prof. Tsai-Te Lu** | | **Room: Mayfair Ballroom B** |
|---|---|---|
| 11.35-12.05 | BC-K-01 | Prof. Wonwoo Nam (Ewha Womans University)<br>Biomimetic metal-oxygen intermediates in dioxygen activation and formation chemistry |
| 12.05-12.25 | BC-I-01 | Prof. Abhishek Dey (Indian Association for the Cultivation of Science)<br>Factors Deciding the Selectivity of $O_2$, NO, $CO_2$ and $SO_2$ Reduction |
| 12.25-12.45 | BC-I-02 | Prof. Yuma Morimoto (Nagoya University)<br>Effect of Axial-ligand $\pi$-Donor Ability on Reactivity of Compound I Model Complex |
| 12.45-13.05 | BC-I-03 | Prof. Junhyeok Seo (Gwangju Institute of Science and Technology)<br>Modification of NHC Ligand to Make It Suitable for Catalytic Proton Reduction |
| **BC2 Chair: Prof. Wonwoo Nam, Co-chair: Prof. Abhishek Dey** | | **Room: Mayfair Ballroom B** |
| 15.00-15.30 | BC-K-02 | Prof. Takashi Hayashi (Osaka University)<br>Conversion of Myoglobin to Artificial Metalloenzymes |
| 15.30-15.50 | BC-I-04 | Prof. Tsai-Te Lu (National Tsing Hua University)<br>Metal-ligand cooperation in dinitrosyl iron complexes for small molecule activation and biomedical application |
| 15.50-16.10 | BC-I-05 | Prof. Debasis Das (Indian Institute of Science)<br>Deciphering a membrane-bound hydrocarbon-producing metalloenzyme |
| 16.10.-16.40 | BC-K-03 | Prof. Rachel Codd (University of Sydney)<br>Enzyme-mediated assembly of metal chelators: Diversifying structure and function |
| 16.40-16.55 | BC-O-1 | Prof. Yutaka Amao<br>Cationic zinc porphyrin-based photocatalytic system with biocatalyst for fumarate synthesis from $CO_2$ |
| **Flash Presentation** | | |
| 16.55-17.00 | BC-F-01 | Yuma Yamamoto<br>Synthesis and antimicrobial activity of amino acid Schiff base copper complexes with azo groups |
| 17.00-17.05 | BC-F-02 | Dr. Bussaba Pinchaipat<br>Nickel(II) with Schiff base complex: experimental and computational studies of CT-DNA binding |

### Day 3: 21st February 2024

| **BC3 Chair: Prof. Jenny Yang, Co-chair: Prof. Shin Aoki** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 11.35-12.05 | BC-K-04 | Prof. Lee Yun Ho (Seoul National University)<br>Bio-organometallic NOx conversion and utilization |
| 12.05-12.25 | BC-I-06 | Prof. Way-zen Lee (National Taiwan Normal University)<br>Reaction Pathways of a Manganese(III) Superoxo Complex with Various Phenols |
| 12.25-12.45 | BC-I-07 | Prof. Seung Jun Hwang (POSTEC)<br>Unlocking Multi-Electron Oxidation: Harnessing Phosphorus-Ligand Redox Cooperativity |
| 12.45-13.05 | BC-I-08 | Prof. Seung Jae Lee (Jeonbuk National University)<br>Functional and structural roles of supporting components for the methane hydroxylation in sMMO |

### Day 4: 22nd February 2024

| **BC4 Chair: Prof. Way-Zen Lee, Co-chair: Prof. Seung Jun Hwang** | | **Room: Jubilee Ballroom B** |
|---|---|---|
| 14.00-14.30 | BC-K-05 | Prof. Jenny Yang (University of California, Irvine)<br>Chemical Design for Integrated Catalytic $CO_2$ Capture and Utilization" |
| 14.30-14.50 | BC-I-09 | Prof. Shin Aoki (Tokyo University of Science)<br>Optical Resolution of Cyclometalated Iridium(III) Complexes and Its Applications |

## Catalytic coordination chemistry (CA)

**Day 1: 19th February 2024**

| | | |
|---|---|---|
| **CA1 Chair: Prof. Shigeyuki Masaoka** | | **Room: Mayfair Ballroom B** |
| 10.15-10.45 | CA-K-01 | Prof. Han Sen Soo (Nanyang Technology University)<br>Photocatalytic valorization of biomass and non-biodegradable plastics by vanadium coordination complexes |
| 10.45-11.05 | CA-I-01 | Prof. Yasushi Obora (Kansai University)<br>Palladium-complex catalyzed difunctionalization of 1,3-diene with disilane and amine/alcohol |
| 11.05-11.20 | CA-O-01 | Yunyi Pan<br>Electrochemical $CO_2$ reduction on dinuclear complex with square-planar coordination structure |
| **CA2 Chair: Prof. Han Sen Soo** | | **Room: Mayfair Ballroom B** |
| 11.35-12.05 | CA-K-02 | Prof. Shigeyuki Masaoka (Osaka University)<br>Development of Molecular Catalysts for Photosynthetic Reactions |
| 12.05-12.25 | CA-I-02 | Dr. Olivier Siri (Aix-Marseille University)<br>Quinoidal N-ligands in catalysis: from solution to surface |
| 12.25-12.45 | CA-I-03 | Prof. Fakuen Shieh (National Central University)<br>Insights into MOF Chemical Biology: Biocatalysts Encapsulated within MOFs |
| 12.45-13.00 | CA-O-02 | Prof. Sanjib Patra<br>Designing copper(I/II) complexes for developing catalytic fixation of atmospheric $CO_2$ |
| **CA3 Chair: Prof Fa-Kuen Shieh** | | **Room: Mayfair Ballroom B** |
| 15.00-15.30 | CA-K-03 | Prof. Ryota Sakamoto (Tohoku University)<br>2D MOFs Act as Hydrogen Evolution Cocatalysts for Overall Photocatalytic Water Splitting |
| 15.30-15.50 | CA-I-04 | Prof. Chi-How Peng (National Taiwan University)<br>Evolution of the mediators in controlling the radical polymerization of vinyl acetate |
| 15.50-16.05 | CA-O-03 | Prof. Seok Min Yoon<br>Rhenium Redefined as Electrocatalyst for Hydrogen Evolution Reaction |
| 16.05-16.20 | CA-O-04 | Dr. Susanta Hazra<br>Coordination Modulation of Pd Nanoparticles with Heterogenous Phosphine Ligand in Aqueous Micelles |
| 16.20-16.35 | CA-O-05 | China Takeda<br>Development of new methanol oxidation catalyst using iron and study of optimal conditions |
| 16.35-16.50 | CA-O-06 | Wei-Syuan Lin<br>Synthesis and Reactivity of Cobalt Complexes Having Isoindoline-Based Polyprotic Pyrazole Ligand |
| 16.50-17.05 | CA-O-09 | Prof. Ryo Sekiya<br>Metal Nanoparticles on Lipophilic Nanographenes |

## Catalytic coordination chemistry (CA)

**Day 3: 21st February 2024**

| | | |
|---|---|---|
| **CA4 Chair: Prof. Miho Yamauchi** | | **Room: Jubilee Ballroom B** |
| 10.15-10.45 | CA-K-04 | Prof. Bun Yeoul Lee (Ajou University)<br>Development of ethylene tetramerization catalyst: From flask to industrial process |
| 10.45-11.05 | CA-I-05 | Prof. Yuji Kikukawa (Kanazawa University)<br>Synthesis of Octadecavanadate derivatives and oxidation catalysis |
| 11.05-11.25 | CA-I-06 | Prof. Rajib Bandyopadhyay (Pandit Deendayal Energy University)<br>Mononuclear Cu-complex encapsulated hybrid silicoaluminophosphates for enhanced catalysis |
| **CA5 Chair: Prof. Khamphee Phomphrai** | | **Room: Jubilee Ballroom B** |
| 11.35-12.05 | CA-K-05 | Prof. Miho Yamauchi (Kyushu University)<br>Nanocatalysts for a low-carbon society: upgrading chemicals by hydrogenation |
| 12.05-12.25 | CA-I-07 | Prof. Masayuki Yagi (Niigata University)<br>Highly Efficient Water Splitting by an Electrolyzer Fabricated via Mixed Metal Imidazole-Complexes |
| 12.25-12.45 | CA-I-08 | Dr. Yuichiro Himeda (the National Institute of Advanced Industrial Science and Technology (AIST))<br>$CO_2$ Hydrogenation to Methanol Catalyzed by Dinuclear Iridium Complexes at Gas-Solid Phase |
| 12.45-13.00 | CA-O-07 | Dr. Bo Li<br>Encapsulating Copper-based Nanostructures into Metal-Organic Frameworks for $CO_2$ conversion |
| **CA6 Chair: Prof. Yuichiro Himeda** | | **Room: Jubilee Ballroom B** |
| 15.00-15.30 | CA-K-06 | Prof. Takahiko Kojima (University of Tsukuba)<br>Catch-and-release” strategy for selective oxidation of hydrocarbons in aqueous media |
| 15.30-15.50 | CA-I-10 | Dr. Viktor O. Iaroshenko (KTH Royal Institute of Technology)<br>Synthesis of Trifluoromethyl Aryls and Aryl Trifluoromethyl Ethers via Co(II) and Ru(II) Catalysis |
| 15.50-16.10 | CA-O-08 | Md Gulzar Ahmad<br>Cyclometalated Ruthenium Complex Catalyzed Selective Synthesis Of 2-substituted Benzimidazoles |

## Coordination cages (CC)

### Day 1: 19th February 2024

| **CC1 Chair: Prof. Ok-Sang Jung** | | **Room: Jubilee Ballroom A** |
|---|---|---|
| 10.15-10.45 | CC-K-01 | Prof. Makoto Fujita (The University of Tokyo)<br>Molecular Confinement Effects in Self-assembled Cages |
| 10.45-11.05 | CC-I-01 | Prof. David Turner (Monash University)<br>Stability, Ligand Exchange, and Heteroleptic Control in Lantern-Type $Cu_4L_4$ Cages |

### Day 4: 22nd February 2024

| **CC2 Chair: Prof. Jinhee Park** | | **Room: Jubilee Ballroom B** |
|---|---|---|
| 9.45-10.15 | CC-K-02 | Prof. Ok-Sang Jung (Pusan University)<br>Construction and enantioselective discrimination of pairs of new chiral coordination cages |
| 10.15-10.35 | CC-I-02 | Prof. Masahiro Yamashina (Tokyo Institute of Technology)<br>Controlling the assembly of Pd(II)/bianthryl-based $M_2L_4$ and $(M_2L_4)_2$ cages by steric effects |
| 10.35-10.55 | CC-I-03 | Prof. Jamie Lewis (University of Birmingham)<br>Controlling diastereoselectivity in low-symmetry metal-organic cages |
| 10.55-11.10 | CC-O-01 | Prof. Yuya Domoto<br>Skeletal editing of highly entangled polyhedra based on cooperative metal–acetylene coordination |
| **CC3 Chair: Prof. Amilra De Silva** | | **Room: Jubilee Ballroom B** |
| 11.35-12.05 | CC-K-03 | Prof. Jinhee Park (Daegu Gyeongbuk Institute of Science and Technology)<br>Porous cuboctahedral metal-organic cages |
| 12.05-12.25 | CC-I-04 | Prof. Haeri Lee (Hannam University)<br>Stimuli-responsive Cavity Size Control in Palladium(II) Coordination Cages |
| 12.25-12.45 | CC-I-05 | Prof. Dillip Kumar Chand (Indian Institute of Technology Madras)<br>Making of the multi-cavity coordination architectures |
| 12.45-13.05 | CC-I-06 | Prof. Liang Zhao<br>Coenzyme functionalized metal–organic confined supramolecular systems for Cascade Catalysis |

## Coordination compounds for medical applications (CM)

### Day 1: 19th February 2024

| **CM1 Chair: Prof. Jun-Long Zhang** | | **Room: Jubilee Ballroom A** |
|---|---|---|
| 15.00-15.30 | CM-K-01 | Prof. Hong Zhe Sun (The University of Hong Kong)<br>Metallomics approach for deciphering the biological role of metals |
| 15.30-15.50 | CM-I-01 | Prof. Paras Nath Yadav (Tribhuvan University)<br>Anticancer potency of 3-acetylcoumarin thiosemicarbazones and their copper(II) complexes |
| 15.50-16.10 | CM-I-02 | Prof. Ratanon Chotima (Naresuan University)<br>Benzothiazole Schiff Base Complexes: Anticancer Activities and Biological Evaluation Towards Cancer Cells |
| 16.10-16.25 | CM-O-01 | Prof. Samad Khaksar<br>Cytotoxicity and Mechanism of Action of New Pyridine-2,6-Dicarboxylate Ga(III) Complexes |
| 16.25-16.40 | CM-O-02 | Prof. Annie Castonguay<br>Tetraphenylborate-based Ru(II) drug candidates for triple-negative breast cancer therapy |
| 16.40-16.55 | CM-O-03 | Prof. Janusz M. Dabrowski<br>Tuning chemical properties of phthalocyanine and porphyrin metal complexes for photodynamic therapy |

### Day 2: 20th February 2024

| **Flash Presentation** | | |
|---|---|---|
| **BC2 Chair: Prof. Wonwoo Nam, Co-chair: Prof. Abhishek Dey** | | **Room: Mayfair Ballroom B** |
| 17.05-17.10 | CM-F-01 | Yi-Hsin Liu<br>Singlet Oxygen on Material Surface: Energy Transfer via Artificial Defects for Photodynamic Therapy |

### Day 3: 21st February 2024

| **CM2 Chair: Prof. Hong Zhe Sun** | | **Room: Jubilee Ballroom B** |
|---|---|---|
| 16.35-17.05 | CM-K-02 | Prof. Jun-Long Zhang (Peking University)<br>Molecular Ni(II) Phototheranostics: From Biomimetic Models to Metal Drugs |
| 17.05-17.25 | CM-I-03 | Prof. Phil Andrews (Monash University)<br>Bismuth complexes and materials for challenging antimicrobial resistance |
| 17.25-17.45 | CM-I-04 | Prof. Jaclyn Brusso (University of Ottawa)<br>Cluster-based redox responsive MRI contrast agents |
| 17.45-18.05 | CM-I-05 | Prof. Nguyen Thi Thanh Chi (Hanoi National University of Education)<br>Cyclometalated arylolefin complexes of Pt(II): synthesis, characterizations, in vitro cytotoxicity |

## F-Element chemistry (FE)

### Day 2: 20th February 2024

| **FE1 Chair: Prof. George Koutsantonis** | | **Room: Mayfair Ballroom B** |
|---|---|---|
| 10.00-10.30 | FE-K-01 | Prof. Yuichi Kitagawa (Hokkaido University)<br>Photofunctional lanthanide complexes with $\pi$-conjugated polycyclic aromatic ligands |
| 10.30-10.50 | FE-I-01 | Prof. Apinpus Rujiwatra (Chiang Mai University)<br>Lanthanides Coordination Polymers and Their Catalytic Potential in $CO_2$ Capture and Conversion |

## Frontiers in coordination chemistry (FR)

### Day 1: 19th February 2024

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|---|---|---|
| **FR1 Chair: Prof Shie-Ming Peng** | | **Room: Jubilee Ballroom B** |
| 10.15-10.45 | FR-K-01 | Prof. Chen-Wei Liu (National Dong Hwa University)<br>The role of hydrides in ligand-stabilized nanoclusters |
| 10.45-11.05 | FR-I-01 | Prof. Nobuto Yoshinari (Osaka University)<br>Construction of A family of Metal-Organic Carboxylates with L-Cysteine |
| 11.05-11.20 | FR-O-01 | Prof. Qingyun Wan<br>Photo-physics, magnetism, conductivity and self-assembly of d- and f-block metal complexes |
| **FR2 Chair: Prof Mark Humphrey** | | **Room: Jubilee Ballroom B** |
| 11.35-12.05 | FR-K-02 | Prof. Kentaro Tanaka (Nagoya University)<br>Capturing of Fullerenes with Macrocyclic Metal Complexes |
| 12.05-12.25 | FR-I-02 | Dr. Victoria Blair (Monash University)<br>C-F activation and cyclisation of fluoro-imines using bespoke bimetallic reagents" |
| 12.25-12.45 | FR-I-03 | Prof. Marlon Conato (University of the Philippines -Diliman)<br>Crystal engineering of microporous materials for energy applications and catalysis |
| 12.45-13.00 | FR-O-02 | Prof. Xin Bao<br>Advancing solid-state photoswitching with DASA-derived coordination complexes |
| **Flash Presentation** | | |
| **OR1 Chair: Prof. Prof. Han Vinh Hyunh, Co-chair: Prof. Jianfeng Zhang** | | **Room: Jubilee Ballroom B** |
| 16.40-16.45 | FR-F-01 | Dr. Atsushi Okazawa<br>Enhanced-solubility catholytes for redox flow batteries: Carnelley's rule and diverse ion effect |
| 16.45-16.50 | FR-F-02 | Dr. Tetsuya Kambe<br>Chemically synthesized boron-based two-dimensional atomic layers |
| 16.50-16.55 | FR-F-03 | Jeevithra Dewi Subramaniam<br>Constructing lanthanoid double-decker complexes as prototypes of gears |

### Day 3: 21st February 2024

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|---|---|---|
| **FR3 Chair: Prof Chen-Wei Liu** | | **Room: Mayfair Ballroom A** |
| 15.00-15.30 | FR-K-03 | Prof. Shie-Ming Peng (National Taiwan University)<br>From Metal-Metal Multiple Bonds to Helical Metal Strings |
| 15.30-15.50 | FR-I-04 | Prof. Mark Humphrey (Australian National University)<br>Multiphoton absorption at metal alkynyl-based materials |
| 15.50-16.10 | FR-I-05 | Prof. Nak Cheon Jeong (Daegu Gyeongbuk Institute of Science and Technology, DGIST)<br>Intrinsicality of guest molecule coordination in MOF |
| 16.10-16.25 | FR-O-03 | Dr. Ryo Ohtani<br>Functional organic-inorganic hybrids consisting of nitridotetracyanometallate units |

### Day 4: 22nd February 2024

| | | |
|---|---|---|
| **FR4 Chair: Prof Kentaro Tanaka** | | **Room: Mayfair Ballroom A** |
| 14.00-14.20 | FR-I-06 | Prof. Jaeheung Cho (Ulsan National Institute of Science & Technology)<br>A Photo-Responsive Iron-Nitrosyl Complex in Vascular Therapy |
| 14.20-14.35 | FR-O-04 | Prof. Wei-Xiong Zhang<br>Regulating Glass Transitions for Melt-quenched Glasses from Hybrid Crystals |
| 14.35-14.50 | FR-O-05 | Prof. Yoshihiro Sekine<br>Hydrogen-bonding Assembly-induced Thermally Driven Electron Transfer in Cyanide-bridged Complexes |

## Luminescent compounds (LC)

### Day 1: 19th February 2024

| **LC1 Chair: Prof. John Yip Hon Kay** | | **Room: Jubilee Ballroom A** |
|---|---|---|
| 11.35-12.05 | LC-K-01 | Prof. Juyoung Yoon (Ewha Womans University)<br>From fluorescent probes to phoththerapy |
| 12.05-12.25 | LC-I-01 | Prof. Supavadee Kiatisevi (Mahidol University)<br>Bis-BODIPY linked-triazole functional dyes |
| 12.25-12.45 | LC-I-02 | Prof. Youngmi Kim (Kyung Hee University)<br>Tailoring Photophysical Properties of meso-Substituted BODIPY Dyes and Their Applications |
| 12.45-13.00 | LC-O-01 | Dr. Robert Tomala<br>Modification of luminescent properties of carbon dots by synthesis parameters |

### Day 2: 20th February 2024

| **LC2 Chair: Prof. Juyoung Yoon** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 10.00-10.30 | LC-K-02 | Prof. John Yip Hon Kay (National University of Singapore)<br>Developing Metal-Polycyclic-Aromatic-Hydrocarbons As a New Class of Organometallic Emitters |
| 10.30-10.50 | LC-I-03 | Prof. Masaki Yoshida (Kwansei Gakuin University)<br>Photo and Electroluminescence of Platinum Group Metal Complexes with Acyclic Diaminocarbene Ligands |
| 10.50-11.10 | LC-I-04 | Prof. Jaursap Boonmak (Khon Kaen University)<br>Luminescent coordination polymers for the detection of volatile chemicals |
| 11.10-11.25 | LC-O-02 | Dr. Hajime Kamebuchi<br>Emission color control of pH-responsive Pt(II)-NHC complex in highly proton-conductive polymer |

### Day 4: 22nd February 2024

| **LC3 Chair: Prof. Vinich Promarak** | | **Room: Mayfair Ballroom B** |
|---|---|---|
| 9.45-10.15 | LC-K-03 | Prof. Tony D. James (The University of Bath)<br>Fluorescent chemosensors and imaging agents |
| 10.15-10.35 | LC-I-05 | Prof. Songyi Lee (Pukyong National University)<br>A preparation of organic photosensitizers for high efficiency of photodynamic therapy in tumor |
| 10.35-10.50 | LC-O-03 | Anuson Sansee<br>HMPA polymer-tris-cycometalated iridium complex constructs as functional imaging tools |
| 10.50-11.05 | LC-O-04 | Dr. Watcharapol Paritmong<br>Luminescent metal-organic chalcogenolate coordination polymers |
| 11.05-11.20 | LC-O-05 | Dr. Pawel Gluchowski<br>Multifunctional carbon dots: synthesis, characterization, applications |
| **LC4 Chair: Prof. Tony D. James** | | **Room: Mayfair Ballroom B** |
| 11.35-12.05 | LC-K-04 | Prof. Vinich Promarak (Vidyasirimedhi Institute of Science and Technology, VISTEC)<br>Recent Advances in Luminescent Materials for Organic Light-Emitting Diodes |
| 12.05-12.25 | LC-I-06 | Prof. Chun-Guey Wu<br>Photochromic Dyes for Dye-Sensitized Solar Cells" |
| 12.25-12.40 | LC-O-06 | Jan Rzepiela<br>Luminescent thermometry in chiral lanthanide-iridium molecular assemblies |
| 12.40-12.55 | LC-O-07 | Jukkrit Nootem<br>Influence of a B-O-C bond on photophysical and sensing properties toward saccharides of BODIPYs |

## MOF/COF chemistry (MC)

### Day 1: 19th February 2024

| | | |
|---|---|---|
| **MC1 Chair: Prof. Christian Doonan** | | **Room: Mayfair Ballroom C** |
| 10.15-10.45 | MC-K-01 | Prof. Sujit K. Ghosh (Indian Institute of Science Education and Research Pune)<br>Efficient extraction of targeted metal ions from (sea)water using advanced porous materials |
| 10.45-11.05 | MC-I-01 | Prof. Mio Kondo (Tokyo Institute of Technology)<br>Iron-Complex-Based Supramolecular Framework Catalyst for Visible-Light-Driven $CO_2$ Reduction |
| 11.05-11.20 | MC-O-01 | Dr. Anna A. Lysova<br>NIIC-20 family MOFs for hydrocarbon adsorption |
| **MC2 Chair: Prof. Shane Telfer** | | **Room: Mayfair Ballroom C** |
| 11.35-12.05 | MC-K-02 | Prof. Christian Doonan (University of Adelaide)<br>Engineering Flexibility in Metal-organic Frameworks |
| 12.05-12.25 | MC-I-02 | Dr. Takashima Yohei (Konan University)<br>Controlled lattice rearrangement in a metal-organic framework by defect engineering |
| 12.25-12.45 | MC-I-03 | Prof. Dr. Kyriakos C. Stylianou (Oregon State University)<br>Metal-organic Framework Chemistry: Design Strategies to Applications |
| 12.45-13.00 | MC-O-02 | Chieh-Wei Chung<br>Magnetic-Release of NO from MOF-derived Microsphere for Treatment of Bacteria-Infected Wound |
| **MC3 Chair: Prof. Prof. Moonhyun Oh, Co-chair: Prof. Dr. Nanthawat Wannarit** | | **Room: Mayfair Ballroom C** |
| 15.00-15.20 | MC-I-04 | Prof. Hyunchul Oh (Ulsan National Institute of Science and Technology)<br>Mitigation of $LH_2$ tank boil-off losses via adsorption of $H_2$ on metal–organic frameworks |
| 15.20-15.40 | MC-I-05 | Prof. Chia-Her Lin (National Taiwan Normal University)<br>Rapid Desolvation-Triggered Structural Transformation of Metal-Organic Frameworks |
| 15.40-16.00 | MC-I-06 | Prof. Dr. Ryohei Akiyoshi (Kwansei Gakuin University)<br>Polymorphism of two-dimensional photoconductive coordination polymers with lead–sulfur bond |
| 16.00-16.15 | MC-O-03 | Prof. Dr. Intek Song<br>Superprotonic Conductivity of Water-coordinated Metal Hydrogen-bonded Organic Framework Films |
| 16.15-16.30 | MC-O-04 | Dr. Liyuan Qu<br>Charge order in a naphthalenediimide-based porous molecular conductor |
| **Flash Presentation** | | |
| 16.30-16.35 | MC-F-01 | Kotoha Kageyama<br>Phase transition behavior and Li+-ion conductivity of Li+-dinitrile metal–organic frameworks |
| 16.35-16.40 | MC-F-02 | Pattara Siripanich<br>H8-BINOL-Based MOF for Enantioselective Fluorescent Sensors |

## MOF/COF chemistry (MC)

**Day 2: 20th February 2024**

| | | |
|---|---|---|
| **MC4 Chair: Prof. Sujit K. Ghosh** | | **Room: Mayfair Ballroom C** |
| 10.00-10.30 | MC-K-03 | Prof. Dr. Satoshi Horike (Kyoto University/Vidyasirimedhi Institute of Science and Technology)<br>Synthesis and functions of hierarchical metal-organic framework glasses |
| 10.30-10.50 | MC-I-07 | Dr. Lauren Macreadie (The University of New South Wales)<br>Rapid Desolvation-Triggered Structural Transformation of Metal-Organic Frameworks |
| 10.50-11.10 | MC-I-08 | Prof. Wei Shi (Nankai University)<br>Multi-center metal-organic frameworks for sensing applications |
| 11.10-11.25 | MC-O-05 | Dr. Yuki Saito<br>Highly photo-controllable guest release systems using 4-styrylpyridine-coordinated Werner clathrate |
| **MC5 Chair: Prof. Christopher Richardson** | | **Room: Mayfair Ballroom C** |
| 11.35-12.05 | MC-K-04 | Prof. Shuhei Furukawa (Kyoto University)<br>Assembling metal-organic cages as porous materials |
| 12.05-12.25 | MC-I-09 | Prof. Jie-Peng Zhang (Sun Yat-Sen University)<br>Flexible porous coordination polymers for adsorptive separation |
| 12.25-12.45 | MC-I-10 | Prof. Xiao-Ming Chen (Sun Yat-Sen University)<br>Porous Metal-Organic Materials for Electrochemical $CO_2$ Reduction |
| 12.45-13.00 | MC-O-06 | Genki Hatakeyama<br>Ion-Exchangeable Metal-Organic Frameworks for Selective Ammonium Recovery |
| **MC6 Chair: Prof. Dr. Apinpus Rujiwatra** | | **Room: Mayfair Ballroom C** |
| 15.00-15.30 | MC-K-05 | Prof. Tapas Kumar Maji (Jawaharlal Nehru Centre for Advanced Scientific Research)<br>“Title to be announced” |
| 15.30-15.50 | MC-I-11 | Prof. Sarah Park (Pohang University of Science and Technology)<br>Synthesis of conductive metal-organic framework thin films |
| 15.50-16.10 | MC-I-12 | Prof. Ze Chang (Nankai University)<br>Functional Coordination Polymers Based on Donor-Acceptor Systems |
| 16.10-16.25 | MC-O-07 | Dr. Hiroyasu Tabe<br>Photocatalysis of Coordination Polymer Glass Membranes Involving Metalloporphyrins for $CO_2$ Reduction |
| 16.25-16.40 | MC-O-08 | Dr. Bhavesh Parmar<br>Tuning of Singlet Fission Derived Quintet Generation in Acene-based Hetero-linker MOFs |

## MOF/COF chemistry (MC)

**Day 3: 21st February 2024**

| | | |
|---|---|---|
| **MC7 Chair: Prof. Chunying Duan** | | **Room: Mayfair Ballroom C** |
| 10.15-10.45 | MC-K-06 | Prof. Moonhyun Oh (Yonsei University)<br>Components, structures, and metal-organic frameworks |
| 10.45-11.05 | MC-I-23 | Prof. Teppei Yamada (The University of Tokyo)<br>Temperature coefficient of the redox potential of MOF electrodes toward MOF TREC system |
| 11.05-11.25 | MC-I-13 | Prof. Nobuhiko Hosono (The University of Tokyo)<br>A MOFaxane: Threading ultralong polymers through metal–organic frameworks |
| **MC8 Chair: Prof. Mio Kondo** | | **Room: Mayfair Ballroom C** |
| 11.35-12.05 | MC-K-07 | Prof. Shane Telfer (Massey University)<br>A New Concept in Asymmetric Catalysis (Implemented Using MOFs) |
| 12.05-12.25 | MC-I-14 | Prof. Kang Min Ok (Sogang University)<br>Chiral coordination polymers with amplified photoluminescence and second-harmonic generation |
| 12.25-12.45 | MC-I-15 | Prof. Chun-Ting He (Jiangxi Normal University)<br>Molecule-based electrocatalysts and their molecular enhancement catalysis |
| 12.45-13.00 | MC-O-09 | Dr. Pavel A. Demakov<br>Diastereoselective [2+2]-photodimerization of 2-cyclopenten-1-one within a metal-organic framework |
| **MC9 Chair: Prof. Tiexin Zhang** | | **Room: Mayfair Ballroom C** |
| 15.00-15.30 | MC-K-08 | Prof. Chunying Duan (Dalian University of Technology)<br>Enzyme-inspired metal-organic architectures for confined photocatalysis |
| 15.30-15.50 | MC-I-16 | Prof. Christopher Richardson (University of Wollongong)<br>Advances in reactive printing metal-organic framework films |
| 15.50-16.10 | MC-I-17 | Prof. Takashi Okubo (Kindai University)<br>Luminescent Semiconducting Coordination Polymers with Copper(I) Halides and Application to OLEDs |
| 16.10-16.25 | MC-O-10 | Dr. Jey Jau Lee<br>Non-Ambient Single Crystal X-ray Diffraction Beamline at Taiwan Photon Source |

## MOF/COF chemistry (MC)

### Day 4: 22nd February 2024

| | | |
|---|---|---|
| **MC10 Chair: Prof. Dr. Kittipong Chainok** | | **Room: Mayfair Ballroom C** |
| 9.45-10.15 | MC-K-09 | Prof. Baiyan Li (Nankai University)<br>Functional organic framework for pollutant treatment and their batch preparation |
| 10.15-10.35 | MC-I-18 | Prof. Soumyajit Roy (Indian Institute of Science Education and Research)<br>On Soft-oxometalates (SOMs) and Sustainability |
| 10.35-10.55 | MC-I-19 | Prof. Wonyoung Choe (Ulsan National Institute of Science and Technology)<br>New Horizon for Digital Discovery of Metal-Organic Frameworks |
| 10.55-11.10 | MC-O-11 | Prof. Ruey-An Doong<br>Ultra-sensitive detection of levofloxacin with rare earth metal-MOFs as the fluorescent probe |
| 11.10-11.25 | MC-O-12 | Prof. Kenji Okada<br>Oriented film of MIL-53(Al) via epitaxial growth on γ-AlOOH toward soft actuator |
| **MC11 Chair: Prof. Sarah Park** | | **Room: Mayfair Ballroom C** |
| 11.35-12.05 | MC-K-10 | Prof. Tiexin Zhang (Dalian University of Technology)<br>Molecule Device-Inspired "Monodirectional Electron Transfer" of MOF for Photocatalysis |
| 12.05-12.25 | MC-I-20 | Prof. Dr. Raffaele Ricco (Asian Institute of Technology)<br>Encapsulation and Release of Agrochemicals with Porous Materials |
| 12.25-12.45 | MC-I-21 | Prof. Dr. Ken-Ichi Otake (Kyoto University)<br>In situ X-ray Observation of Gate-type Sorption Process of Flexible Porous Coordination Polymers |
| 12.45-13.00 | MC-O-15 | Jakub Józef Zakrzewski<br>Stimuli-responsive frameworks based on luminescent Cr(III) cyanido metal complexes |
| **MC12 Chair: Prof. Lauren Macreadie** | | **Room: Mayfair Ballroom C** |
| 14.00-14.20 | MC-I-22 | Prof. Peng Cheng (Nankai University)<br>Lanthanides Coordination Polymers and Their Catalytic Potential |
| 14.20-14.35 | MC-O-13 | Chantamalinee Chantarangkul<br>Catalytic performance of CuNPs-incorporated MIL-100(Fe) using Cryptolepis Buchanani Roem. & Schult |
| 14.35-14.50 | MC-O-14 | Andrei S. Potapov<br>Multiresponsive highly emissive MOFs for sensing of organic and inorganic pollutants |

## Main group chemistry (MG)

### Day 1: 19th February 2024

| **Flash Presentation** | | |
|---|---|---|
| **MC3 Chair: Prof. Prof. Moonhyun Oh, Co-chair: Prof. Dr. Nanthawat Wannarit** | | **Room: Mayfair Ballroom C** |
| 16.40-16.45 | MG-F-01 | Narisara Tanjedrew<br>Tunable imidazole-benzimidazole-based electrocatalysts for oxygen reduction reaction (ORR) in water |

### Day 3: 21st February 2024

| **MG1 Chair: Prof Eunsung Lee** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 10.15-10.35 | MG-I-01 | Prof. Vadapalli Chandrasekhar (IIT-Kanpur)<br>Metal Complexes of Unsymmetrical N-P-N ligands and Their Utility in Catalysis |
| 10.35-10.55 | MG-I-02 | Dr. Krzysztof Kuciński (Adam Mickiewicz University)<br>Main group compounds as efficient catalysts in the synthesis of organosilicon derivatives |
| 10.55-11.10 | MG-O-01 | Yu-Huei Li<br>Polyantimony chromium complexes: Syntheses, reactivities, paramagnetism, and semiconductivities |
| 11.10-11.25 | MG-O-05 | Prof. Hajime Kameo<br>Square Planar Anionic Pt(0) Complexes Stabilized by Z-type Borane Ligand |

### Day 4: 22nd February 2024

| **MG2 Chair: Prof Sundargopal Ghosh, Co-chair: Prof Ekasith Somsook** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 9.45-10.15 | MG-K-01 | Prof. Chin-Wen Chiu (National Taiwan University)<br>Catalytic Applications of Boron and Aluminum Cations |
| 10.15-10.35 | MG-I-03 | Prof. Hsueh-Ju Liu (National Yang Ming Chiao Tung University)<br>Controllable C–H Bond Activation and P–C Bond Formation on a P4 Moiety Using Novel Dinuclear Iron Hydrido Complexes |
| 10.35-10.55 | MG-I-04 | Prof. Eunsung Lee (Pohang University of Science and Technology)<br>Stable organic radicals derived from carbenes and their applications |
| 10.55-11.10 | MG-O-02 | Dr. Yuniar Ponco Prananto<br>Crystal Structure of 4-picolinyl cyanohydroximinoacetamide Complexes with K(I), Cs(I), Tl(I) |
| 11.10-11.25 | MG-O-03 | Leonardo Santoni<br>Synthesis and structure studies of Aluminium(III) complexes with β-ketoiminate and ethanolamine |
| **MG3 Chair: Prof Vadapalli Chandrasekhar, Co-chair: Prof Hsueh-Ju Liu** | | **Room: Mayfair Ballroom A** |
| 11.35-12.05 | MG-K-02 | Prof. Sundargopal Ghosh (Indian Institute of Technology Madras)<br>Coordination Chemistry of Smaller to Polyhedral Borane Clusters |
| 12.05-12.25 | MG-I-05 | Prof. Shabana Khan (IISER-Pune)<br>N-Heterocyclic silylene supported copper(I) aryl complexes: bond activation to catalysis |
| 12.25-12.45 | MG-I-06 | Prof. Toshiaki Murai (Gifu University)<br>Chirality Transfer Reaction of Organophosphorus Compounds with a Binaphthyl Group and Their Use |
| 12.45-13.00 | MG-O-04 | Ryotaro Yamanashi<br>Synthesis of linear trialumane and unsymmetrical dialumane using Al anion |

## Organometallic chemistry (OR)

### Day 1: 19th February 2024

| | | |
|---|---|---|
| **OR1 Chair: Prof. Prof. Han Vinh Hyunh, Co-chair: Prof. Jianfeng Zhang** | | **Room: Jubilee Ballroom B** |
| 15.00-15.30 | OR-K-01 | Prof. Yi-Chou Tsai (National Tsing Hua University)<br>Catalyst-free [2+2+2] and [2+2+1] Cycloaddition Reactions Involving an Mo−Mo Quintuple Bond |
| 15.30-15.50 | OR-I-01 | Prof. Liang Deng (Shanghai Institute of Organic Chemistry)<br>Advance on the Chemistry of Low-Coordinate Low-Valent Transition-Metal Complexes with NHC Ligation |
| 15.50-16.10 | OR-I-02 | Prof. George Koutsantonis (University of Western Australia)<br>Molecular photochromes for modulating single-molecule conductance |
| 16.10-16.25 | OR-O-01 | Prof. Pengxin Liu<br>Surface Organometallic Chemistry for Single-atom Catalysis |
| 16.25-16.40 | OR-O-02 | Dr. Siti Syaida Sirat<br>Thermolysis of Ru$_3$(CO)$_{10}$(μ-dppp): A New Ru$_4$- Cluster Derived from 1,3-Bis(diphenylphosphino)propane |

### Day 2: 20th February 2024

| | | |
|---|---|---|
| **OR2 Chair: Prof. Yi-Chou Tsai, Co-chair: Prof. Liang Deng** | | **Room: Jubilee Ballroom B** |
| 10.00-10.30 | OR-K-02 | Prof. Hisako Hashimoto (Tohoku University)<br>Synthesis and properties of transition-metal complexes featuring M≡Si triple bonds |
| 10.30-10.50 | OR-I-03 | Prof. Chun-Yi Lin (National Cheng Kung University)<br>Dinuclear chromium complexes of dinitrogen, arene, and a Cr2 quintuple bond enabled by a bulky alkyl ligand |
| 10.50-11.10 | OR-I-04 | Prof. Michel Wong Chi Man (University of Montpellier)<br>Organosilane precursors for silsesquioxane-based materials |
| 11.10-11.25 | OR-O-03 | Prof. Shun Ohta<br>Synthesis of 1,3,5-trisubstituted benzenes from alkynes with bis(indolyl)-ligated Ti-amido catalysts |
| **OR3 Chair: Prof. Hisako Hashimoto, Co-chair: Prof. Chun-Yi Lin** | | **Room: Jubilee Ballroom B** |
| 11.35-12.05 | OR-K-03 | Prof. Andy Hor (The Agency for Science, Technology and Research , A*star)<br>Coordination Chemistry in Asia – Progress, Promise, Potential and Perspectives |
| 12.05-12.25 | OR-I-05 | Prof. Makoto Yamashita (Nagoya University)<br>Synthesis, Structure, and Properties of Aluminum-Early Metal Complexes |
| 12.25-12.45 | OR-I-06 | Prof. Lan-Chang Liang (National Sun Yat-sen)<br>Organometallic chemistry of complexes containing mismatched donor-acceptor pairs |
| 12.45-13.00 | OR-O-04 | Prof. Jinheung Kim<br>Optimal Organization of Photocatalysts and Enzymes on Nanosheets for Efficient CO$_2$ Conversion |
| **OR4 Chair: Prof. Andy Hor, Co-chair: Prof. Makoto Yamashita** | | **Room: Jubilee Ballroom B** |
| 15.00-15.30 | OR-K-04 | Prof. Han Vinh Hyunh (National University of Singapore)<br>Donor Strength Determination of Anionic Ligands |
| 15.30-15.50 | OR-I-07 | Prof. Swadhin Mandal (Indian Institute of Science Education and Research Kolkata)<br>Abnormal N-Heterocyclic Carbene: Organometallic chemistry to metal-free catalysis |
| 15.50-16.10 | OR-I-08 | Prof. Jiangfeng Zhang (Institute of Process Engineering, Chinese Academy of Sciences)<br>4-Phosphorylpyrazolones as tunable receptors for the coordination of s- and f-block elements |
| 16.10-16.25 | OR-O-05 | Prof. Ching Tat To<br>Silicon-hydrogen bond activation of hydrosilanes with perfluoroalkyl rhodium porphyrin complexes |
| 16.25-16.40 | OR-O-07 | Claudia Patrizzia Giarrusso<br>Lewis base alterations of Ag(I) complexes and their catalytic potential |
| **Flash Presentation** | | |
| 16.40-16.45 | OR-F-01 | Masahiro Matsuoka<br>Photoinduced H–H and C–H bond activation by a Cr≡Si triple bonded complex |
| 16.45-16.50 | OR-F-02 | Keita Sato<br>NHC-stabilized hydroaluminylene complexes of tungsten and iron: synthesis and characterization |
| 16.50-16.55 | OR-F-03 | Jingyan Wang<br>Low-temperature deposition of conducting copper through design of molecular precursors |

## Supramolecular chemistry (SC)

### Day 1: 19th February 2024

| **SC1 Chair: Prof. Dillip Kumar Chand, Co-chair: Prof. Shigehisa Akine** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 11.35-12.05 | SC-K-01 | Prof. Amilra De Silva (Queen's University Belfast)<br>From coordination chemistry to medical diagnostics and information processing |
| 12.05-12.25 | SC-I-01 | Prof. Artur R. Stefankiewicz (Adam Mickiewicz University in Poznań)<br>Harnessing pyridine-β-diketones as a scaffold for the generation of supramolecular nanostructures |
| 12.25-12.45 | SC-I-02 | Prof. Ho Yu Au-Yueng (The University of Hong Kong)<br>Coordination Features of Copper-Catenane Complexes |
| 12.45-13.00 | SC-O-01 | Yanisa Sanguansap<br>Pillar[5]arene-based supramolecular nanospheres for long chain aldehyde detection |

### Day 2: 20th February 2024

| **SC2 Chair: Prof. Pradyuth Ghosh, Co-chair: Prof. Yi-Tsu Chan** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 11.35-12.05 | SC-K-02 | Prof. Takashi Kubo (Osaka University)<br>Association Behavior of Organic Radicals and Biradicals with Close π–π Contact |
| 12.05-12.25 | SC-I-03 | Prof. Nanthanit Wanichacheva (Silpakorn University)<br>Modern Fluorescent Sensors as Pollution Monitoring and Strategy to Enhance Theirs Sensitivity |
| 12.25-12.45 | SC-I-04 | Prof. In-Hyeok Park (Chungnam National University)<br>Solvent-Dependent Self-Assembly of Alkali Metal Complexes of Calix[6]-mono-crown-4: Dinuclear Bowls, a Pseudo-Capsule, and a One-Dimensional Polymer |
| 12.45-13.00 | SC-O-02 | Prof. Eunji Lee<br>Influence of guest molecules on pillar[5]arene-based mechanically interlocked polymers by metalation |
| **SC3 Chair: Prof. Takashi Kubo, Co-chair: Prof. In-Hyeok Park** | | **Room: Mayfair Ballroom A** |
| 15.00-15.30 | SC-K-03 | Prof. Pradyut Ghosh (IACS Kolkata)<br>Selective recognition sensing and extraction of oxyanions |
| 15.30-15.50 | SC-I-05 | Prof. Yi-Tsu Chan (National Taiwan University)<br>Self-Selective Metal-Ligand Coordination for Construction of Polymeric Materials |
| 15.50-16.10 | SC-I-06 | Prof. Shigehisa Akine (Kanazawa University)<br>Control of chirality inversion kinetics of helical cage complexes by guest binding |
| 16.10-16.25 | SC-O-03 | Shun Tokuda<br>Synthesis of three-dimensional van der Waals open frameworks |
| 16.25-16.40 | SC-O-04 | Prof. Subinoy Rana<br>Photoresponsive enzyme mimetic using a dissipative supramolecular assembly of Pt(II) complexes |

## Supramolecular chemistry (SC)

**Day 3: 21st February 2024**

| | | |
|---|---|---|
| **SC4** | **Chair: Prof. Jack Clegg, Co-chair: Prof. Vladimir Fedin** | **Room: Mayfair Ballroom B** |
| 10.15-10.45 | SC-K-04 | Prof. Kate Jolliffe (The University of Sydney)<br>Artificial peptides, peptidomimetics and macrocycles for oxoanion recognition and sensing |
| 10.45-11.15 | SC-K-05 | Prof. Mongkol Sukwattanasinitt (Chulalongkorn University)<br>Coordination chemistry of aminoquinoline-based ligands for sensing and photoredox catalysis applications |
| 11.15-11.30 | SC-O-05 | Dr. Rita Ghosh<br>Hydrophobic moiety triggered self-assembly formation for detecting biomarkers in blood |
| **SC5** | **Chair: Prof. Kate Jolliffe, Co-chair: Prof. Mongkol Sukwattanasinitt** | **Room: Mayfair Ballroom B** |
| 11.35-12.05 | SC-K-06 | Prof. Takumi Konno (National Taiwan Normal University)<br>Construction of metallosupramolecular architectures via metalloligand approach" |
| 12.05-12.25 | SC-I-07 | Prof. Xiaopeng Li (Shenzhen University)<br>Pushing the Limits of Coordination-Driven Self-Assembly: Construction of Giant 2D and 3D Supramolecular Architectures |
| 12.25-12.45 | SC-I-08 | Prof. Biing-Chiau Tzeng (National Chung Cheng University)<br>Solvent-Induced and Mechanochromic Luminescence of Au(I)- and Pt(II)-Dithiocarbamate Compounds |
| 12.45-13.05 | SC-I-09 | Prof. Worawat Wattanathana (Kasetsart University)<br>Benzoxazine derivatives: Crystal structures, properties and applications |
| **SC6** | **Chair: Prof. Takumi Konno, Co-chair: Prof. Xiaopeng Li** | **Room: Mayfair Ballroom B** |
| 15.00-15.30 | SC-K-07 | Prof. Jack Clegg (University of Queensland)<br>Crystals under strain: atomic scale understanding of flexibility in molecular crystals |
| 15.30-15.50 | SC-I-10 | Prof. Thanthapatra Bunchuay (Mahidol University)<br>Quinone Funtionalised Pillararenes: Versatile Motifs in Supramolecular Chemistry |
| 15.50-16.10 | SC-I-11 | Prof. Vladimir Fedin (Nikolaev Siberian Branch of the Russian Academy of Sciences)<br>Luminescent Ln-MOFs with tunable color for nanomolar detection of environmental pollutants |

## Switchable magnetic materials (SM)

**Day 3: 21st February 2024**

| **SM1 Chair: Prof David Harding, Co-chair: Prof Peter Weinberger** | | **Room: Jubilee Ballroom A** |
|---|---|---|
| 10.15-10.45 | SM-K-01 | Prof. Sanjit Konar (Indian Institute of Science Education and Research)<br>Spin-State Switching in Dynamic Molecules and Chiral Cages |
| 10.45-11.05 | SM-I-01 | Prof. Shinya Hayami (Kumamoto University)<br>Spin Crossover System with Multifunction |
| 11.05-11.25 | SM-I-02 | Dr. Hoa Van Phan (Hanoi University of Science and Technology)<br>Spin crossover and High spin COFs |
| **SM2 Chair: Prof Colette Boskovic, Co-chair: Prof Abhishake Mondal** | | **Room: Jubilee Ballroom A** |
| 11.35-12.05 | SM-K-02 | Prof. Osamu Sato (Kyushu University)<br>Control of magnetic and electric polarization through external stimuli |
| 12.05-12.25 | SM-I-03 | Prof. Abhishake Mondal (Indian Institute of Science)<br>Redox-active Motifs: Driving the Wheel of Switchable Magnetic Materials |
| 12.25-12.45 | SM-I-04 | Prof. Ho-Chol Chang (Chuo University)<br>Molecular Lattice Engineering for Valence Tautomerism: connecting molecular and macroscopic worlds |
| 12.45-13.00 | SM-O-01 | Dr. Theerapoom Boonprab<br>Crystal engineering in iron(III) spin crossover complexes |
| **SM3 Chair: Prof. Sanjit Konar, Co-chair: Prof. Masayuki Nihei** | | **Room: Jubilee Ballroom A** |
| 15.00-15.30 | SM-K-03 | Prof. Colette Boskovic (University of Melbourne)<br>Towards three-state molecular switches via valence tautomerism and spin crossover |
| 15.30-15.50 | SM-I-05 | Prof. Zhao-Yang Li (Nankai University)<br>Precise Modulation of Spin Transition Behaviors in Fe(III) Spin Crossover Solid Solutions |
| 15.50-16.10 | SM-I-06 | Prof. Peter Weinberger (TU Wien)<br>Tetrazole-substituted carboxylic acids as precursor for luminescent Fe(II) SCO compounds" |
| 16.10-16.25 | SM-O-02 | Prof. Takamitsu Fukuda<br>Synthesis and magnetic properties of halogen-substituted [Mn(taa)] derivatives |
| **SM4 Chair: Prof. Osamu Sato, Co-chair: Prof Shinya Hayami** | | **Room: Jubilee Ballroom A** |
| 16.35-17.05 | SM-K-04 | Prof. Tetsuro Kusamoto (Institute of Molecular Science)<br>Magneto-structural and magneto-luminescence correlations in radical-based coordination polymers |
| 17.05-17.25 | SM-I-07 | Prof. Masayuki Nihei (University of Tsukuba)<br>Structural conversion of supramolecular assembly by intramolecular electron transfer of [Co2Fe2] complex |
| 17.25-17.45 | SM-I-08 | Prof. Zhongyue Zhang (Kumamoto University)<br>Quantum Spin Liquid and Quantum Critical Phenomena in a 2D conjugated Metal-Organic Framework |
| 17.45-18.00 | SM-O-03 | Prof. Takayoshi Kuroda-Sowa<br>Structures and SCO properties of Fe(II) complexes with novel Schiff-base ligands HqapX and Hqan |

## Single molecule magnets (SS)

### Day 1: 19th February 2024

| **SS1 Chair: Prof Sally Brooker, Co-chair: Prof Phimphaka Harding** | | **Room: Mayfair Ballroom A** |
|---|---|---|
| 15.00-15.30 | SS-K-01 | Prof. Shang-Da Jiang (South China University of Technology)<br>Spin Manipulation in Magnetic Molecules |
| 15.30-15.50 | SS-I-02 | Prof. Hitoshi Miyasaka (Tohoku University)<br>Chemo-Switchable MOF Magnets |

### Day 2: 20th February 2024

| **SS2 Chair: Prof Shang-Da Jiang, Co-chair: Prof Gopalan Rajaraman** | | **Room: Jubilee Ballroom A** |
|---|---|---|
| 10.00-10.30 | SS-K-02 | Prof. Muralee Murugesu (University of Ottawa)<br>Slow relaxation of the magnetization in a formally two-coordinate 4f complex |
| 10.30-10.50 | SS-I-03 | Prof. Masahiro Yamashita (Tohoku University)<br>Molecular Spin Qubits for Quantum Computer and High-Density Memory Devices Based |
| 10.50-11.10 | SS-I-04 | Prof. Yan-Zhen Zheng (Xi'an Jiaotong University)<br>Thermally Stable Terbium(II) and Dysprosium(II) Bis-Amidinate Single-Molecule Magnets |
| 11.10-11.25 | SS-O-01 | Dr. Po-Heng Lin<br>Influence of Energy Barriers of Multinuclear Dysprosium SMMs by Different Substitutions of Ligands |
| **SS3 Chair: Prof Annie Powell** | | **Room: Jubilee Ballroom A** |
| 11.35-12.05 | SS-K-03 | Prof. Gopalan Rajaraman (IIT-Bombay)<br>A Key Player in the Design and Evolution of Molecular Nano Magnets |
| 12.05-12.25 | SS-I-05 | Prof. Sanchita Goswami (University of Calcutta)<br>Quest for Single Molecule/Ion Magnets in Mixed Valent (MnII/III, CoII/III) and 3d-4f Systems: Structural Tuning and Observation of Interesting Magnetic Outcomes |
| 12.25-12.45 | SS-I-06 | Кира Е. Вострикова (Nikolaev Institute of Inorganic Chemistry SB RAS)<br>Design of the lanthanide(III) complexes with tripodal nitroxyl radicals |
| 12.45-13.00 | SS-O-02 | Prof. Arun Kumar Bar<br>Impact of the peripheral ligand modifications on the SIM behavior of Dy(III) in PBP coordination |
| **SS4 Chair: Prof Masahiro Yamashita, Co-chair: Prof Muralee Murugesu** | | **Room: Jubilee Ballroom A** |
| 15.00-15.30 | SS-K-04 | Prof. Annie Powell (Karlsruhe Institute of Technology)<br>Exotic spin structures in 4f containing coordination clusters |
| 15.30-15.50 | SS-I-07 | Prof. Ramaswamy Murugavel (IIT Bombay)<br>Enriching Single Ion Magnetism in Lanthanide Phosphate and Phosphonamide Complexes |
| 15.50-16.05 | SS-O-03 | Sukanya Bagchi<br>Tailoring of Slow Dynamics in Magnetization and Luminescence in Mononuclear Lanthanide Complexes |
| 16.05-16.20 | SS-O-04 | Prof. Vignesh Kuduva R.<br>Mixed 3d-4f Single-Molecule Toroics |

## Theoretical insights in coordination chemistry (TI)

**Day 4: 22nd February 2024**

| | | |
|---|---|---|
| **TI1 Chair: Prof. Yuthana Tantirungrotechai** | | **Room: Jubilee Ballroom A** |
| 9.45-10.15 | TI-K-01 | Prof. Jen-Shiang K. Yu (National Yang Ming Chiao Tung University)<br>Mechanistic study on the trimerization of alkyne catalyzed by quintuply-bonded dichromium complex |
| 10.15-10.35 | TI-I-01 | Dr. Jack Evans (Adelaide University)<br>Atomistic simulations to understand the dynamic properties of porous molecules and materials |
| 10.35-10.55 | TI-I-02 | Prof. Tzu-Hsiung Yang (National Tsing Hua University)<br>Designing Transition Metal Complexes with Desirable Spin States Using Generative AI Models |
| 10.55-11.10 | TI-O-01 | Dr. Bing Yin<br>Interpretation and prediction of single-molecule magnet via ab initio calculation |
| **TI2 Chair: Prof. Jen-Shiang K. Yu** | | **Room: Jubilee Ballroom A** |
| 11.35-12.05 | TI-K-02 | Prof. Kyung-Bin Cho (JeonBuk National University)<br>Some examples of DFT applications into inorganic biomimetic compounds |
| 12.05-12.25 | TI-I-03 | Dr. Saurabh K. Singh (Indian Institute of Technology Hyderabad)<br>Correlating Magnetic Anisotropy and Metal-Ligand Covalency in Transition Metal and Lanthanide Complexes using Ab Initio Ligand Field Theory |
| 12.25-12.45 | TI-I-04 | Prof. Joshua Telser (Roosevelt University)<br>Ligand-Field Theory Related to Transition Metal Field/Frequency-Domain Electron Magnetic Resonance |
| 12.45-13.00 | TI-O-02 | Chantalaksana Chantarangkul<br>Theoretical investigations of mononuclear Mn(III) single-molecule magnets |
| **TI3 Chair: Prof. Kyung-Bin Cho** | | **Room: Jubilee Ballroom A** |
| 14.00-14.20 | TI-I-05 | Sergei Ketkov (G.A.Razuvaev Institute of Organometallic Chemistry RAS)<br>Laser ionization spectroscopy and DFT calculations of transition metal sandwich compounds |
| 14.20-14.35 | TI-O-03 | Naphol Witayapaisitsan<br>Computational design of Ni catalysts for C-H activation and hydroarylation of alkenes |
| 14.35-14.50 | TI-O-04 | Kaito Takahashi<br>Learning from multireference calculation on the binding of transition metal atom and CO molecule |

# POSTER PRESENTATION

## POSTER PRESENTATION

| Day 1: 19th February 2024 | Day 2: 20th February 2024 |
|---|---|
| Catalytic coordination chemistry (CA) | Bioinorganic chemistry (BC) |
| Coordination cages (CC) | Coordination compounds for medical applications (CM) |
| Frontiers in coordination chemistry (FR) | F-Element chemistry (FE) |
| Luminescent compounds (LC) | Organometallic chemistry (OR) |
| MOF/COF chemistry (MC) | Supramolecular chemistry (SC) |
| Main group chemistry (MG) | Switchable magnetic materials (SM) |
|  | Single molecule magnets (SS) |
|  | Theoretical insights in coordination chemistry (TI) |

**Note:**

- Poster presenters on 1st day (19th February 2024), please put your poster up on 19th February morning and remove it after you finished poster session on 1st day.
- Poster presenters on 2nd day (20th February 2024), please put your poster up on 19th February evening (after the 1st day session finished) and remove your poster after you finished poster session on 2nd day.

## Day 1: 19th February 2024

## Catalytic coordination chemistry (CA)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| CA-P-01 | Dr. Mahuya Bandyopadhyay | Transition metal complex-based silica materials for the oxidation of benzyl alcohol to benzaldehyde. |
| CA-P-02 | Mr. Yuto Matsuoka | $N_2$ silylation catalyzed by $[Mo_3S_4M]$ (M = Fe, Co, Ni) clusters bearing bulky cyclopentadienyl ligands |
| CA-P-03 | Mr. Hongjin Park | Highly Productive Heterogenized Ru-MACHO POMP Catalyst for $CO_2$ Hydrogenation via Solvothermal Method |
| CA-P-04 | Ms. Jueun Lee | Proton-Coupled Electron Transfer Controlled by Exchange Coupling in Imino-bipyridyl Co Complexes |
| CA-P-05 | Mr. Phurinat Lorwongkamol | Re complexes bearing various bipyridine-derived ligands for photocatalytic carboxylation with $CO_2$ |
| CA-P-06 | Mr. Marc Alec Dominic Ong Yau | Novel, Copper-Based-Complex Framework Catalyst for Photocatalytic $CO_2$ Reduction using Visible Light |
| CA-P-07 | Mr. Dinesh Harijan | Highly Active Higher Coordinated Copper(I)-N-Heterocyclic Chalcogenone Catalysed Click Chemistry |
| CA-P-08 | Mr. Suman Dolai | A cleaner and efficient approach for one pot catalysis by the synthons of heterobimetallic complexes |
| CA-P-09 | Assoc.Prof. Pimpa Hormnirun | Discrete titanium complexes for the polymerization of e-caprolactone and and their copolymerizations |
| CA-P-10 | Mr. Kunanon Jampakaew | Aluminum complexes of tridentate [ONN]-phenolate ligands for the polymerization of rac-lactide |
| CA-P-11 | Ms. Sirawan Kamavichanurat | Controlled (co)polymerization of cyclic ester monomers by β-pyrimidine aluminum complexes |
| CA-P-12 | Ms. Suppakan Vongfak | Tridentate [ONN]-phenolate titanium complexes for the polymerization of cyclic ester monomers |
| CA-P-13 | Mr. Wasan Joopor | Titanium complexes of phenoxy-azo and phenoxy-imine ligands for the polymerization of cyclic esters |
| CA-P-14 | Ms. Phakteema Kongsaktrakul | Methoxy-poly(ethylene glycol)-incorporated quaternary ammonium halide catalysts for $CO_2$ conversion |
| CA-P-15 | Ms. Nur Nabihah Muzammil | Synthesis And Characterization Of Palladium(II) Schiff Base Complexes and Their Catalytic Activity |
| CA-P-16 | Dr. Duyen Thi Le | Removal of $Cd^{2+}$ by hydroxyapatite adsorption granules from aqueous solution |
| CA-P-17 | Ms. Rong Yan | Bioinspired [3Fe-4S] Clusters for Water Oxidation with High TOF |

## Coordination cages (CC)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| CC-P-01 | Mr. Ranit Banerjee | Fullerene induced structural transformation of a metal-organic cage and 1O2-mediated oxidations |
| CC-P-02 | Mr. Rinshad Va | Size-Selective Photoinduced Oxidation of C-H Bonds Within Water-Soluble Coordination Cage |
| CC-P-03 | Mr. Ryota Aoki | Dynamic Behavior of Proton Confined in Pentanuclear Metal Complexes |
| CC-P-04 | Dr. Kaipeng Bai | Record high-nuclearity Mn(II)-Gd macrocycles: syntheses, structures and magnetic behaviors |
| CC-P-05 | Ms. Bogyeong Go | Selective catalytic oxidation of hydrocarbons by Cu-paddlewheel-based metal-organic cages |

## Frontiers in coordination chemistry (FR)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| FR-F-01 | Dr. Atsushi Okazawa | Enhanced-solubility catholytes for redox flow batteries: Carnelley’s rule and diverse ion effect |
| FR-F-02 | Dr. Tetsuya Kambe | Chemically synthesized boron-based two-dimensional atomic layers |
| FR-F-03 | Ms. Jeevithra Dewi Subramaniam | Constructing lanthanoid double-decker complexes as prototypes of gears |
| FR-P-01 | Mrs. Sunita Birara | Resistive Switching Device Based on Redox-Active Bis(Formazanate)Zinc Complex |
| FR-P-02 | Mr. Tatsunari Murakami | Color changes of a bis(benzimidazole)-ligated nickel dichlorido complex by amine vapor adsorption |
| FR-P-03 | Dr. Masaki Donoshita | Constructing an Au electrode modified with an unsymmetrically substituted π-extended TTF derivative |
| FR-P-04 | Mr. Nobuhiro Sato | Porphyrin/Fullerene porous molecular co-crystal featuring one dimensional channel |
| FR-P-05 | Mr. Naohiro Takahashi | Synthesis of Ru complexes with diketopyrrolopyrrole ligands and application to organic solar cells |
| FR-P-06 | Mr. Seongman Lee | Preparation of Poly(acrylic acid)-Assisted MgO Nanoparticles for Dye-Sensitized Solar Cells |

# Luminescent compounds (LC)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| LC-P-01 | Nguyen Hoang Ninh | Zinc(II) complexes bearing π-extended 8-hydroxyquinoline-derived ligands: Synthesis, characterization and photophysical properties |
| LC-P-02 | Ms. Jianyue He | Design and Synthesis of Fluoride-bridged Rare-earth Luminescent Clusters |
| LC-P-03 | Mr. Pitiphoom Sangiamkittikul | Mannose-conjugated BODIPY photosensitizer for photodynamic therapy |
| LC-P-04 | Mr. Yang Y Chiheng | Development of BODIPY-NHC- Au(I) Complexes as Photocage Molecules for Biomedical Applications |
| LC-P-05 | Ms. Chenchira Pherkkhuntod | Synthesis of polyaromatic imidazolium-based on silsesquioxane cages |
| LC-P-06 | Dr. Peng Zhou | A Ratio Fluorescent sensor Based on Carbon Dots for the Detection of Copper Ions |

# MOF/COF chemistry (MC)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| MC-F-01 | Ms. Kotoha Kageyama | Phase transition behavior and Li+-ion conductivity of Li+-dinitrile metal–organic frameworks |
| MC-F-02 | Mr. Pattara Siripanich | H8-BINOL-Based MOF for Enantioselective Fluorescent Sensors |
| MC-P-01 | Dr. Lina He | The potential of UiO-66(Zr) frameworks for the efficient removal of multiple heavy- metal complexes: performance evaluation and mechanistic insights |
| MC-P-02 | Dr. Javier Alonso Salazar Muñoz | UiO-66(Zr) as drug delivery system for non-steroidal anti-inflammatory drugs |
| MC-P-03 | Ms. Xinyu Li | Highly efficient electroreduction of $CO_2$ to ethylene by a metal-organic framework with $CuN_2O_2$ Sites |
| MC-P-04 | Dr. Wei Xue | A Hofmann-type metal-organic framework for $CO_2/N_2$ and $CH_4/N_2$ separation |
| MC-P-05 | Dr. Xue-Wen Zhang | Quasi-open Cu(I) sites for chemical adsorptive separation of CO |
| MC-P-06 | Prof. Tae Hyun Kim | MOF-derived $ZnO/Co_3O_4$/graphene sensor for alfuzosin electrochemical detection |
| MC-P-07 | Mr. Xianjun Li | Iron-porphyrin-based metal organic framework with multifunctional -COO(H) for $CO_2$ photoreduction |
| MC-P-08 | Ms. Gihyun Lee | Conflicted spatial-arrangements of two linkers in MOF and their compromised arrangement |
| MC-P-09 | Ms. Sojin Oh | Surface charge-directed selective catalytic activity of porous M@UiO-66 composites (M = Pt or Ag) |
| MC-P-10 | Mr. Taewaen Lim | Chemical Reconstruction of Bismuth Oxyiodides to Form Oxycarbonate for $CO_2$ Conversion |

| Presentation Code | Name | Abstract Title |
|---|---|---|
|  | Mr. Yuki Sano | Synthesis of porous polymer through thermal treatment of hexaethynylhexaazatrinaphthylene |
| MC-P-12 | Mr. Soochan Lee | Data-driven discovery of zeolitic imidazolate frameworks and their applications in carbon neutrality |
| MC-P-13 | Dr. Tomoki Nishiyama | A Copper(I) Thiocyanate based Photoresponsive Semiconducting 2D Coordination Polymer |
| MC-P-14 | Mr. Yu Kono | MOFs for Decoding the Structures of Single Polymer Chains |
| MC-P-15 | Mr. Kim Seong Su | Metal-Organic Framework(MOF)-based cathodes for next-generation energy storage. : A review. |
| MC-P-16 | Assoc.Prof. Chungwon Park | Al/Zinc-based metal-organic frameworks for atopic dermatitis treatment |
| MC-P-17 | Prof. Tae-Hyung Kim | MOF nanopatterns for controlled autonomous stem cell differentiation |
| MC-P-18 | Ms. Miku Inoue | Quantum sensing by radicals with long coherence time in acene-based metal-organic frameworks |
| MC-P-19 | Dr. Reetu Rani | Adsorption studies of alkali and alkaline earth metal ions on zirconium metal–organic frameworks |
| MC-P-20 | Ms. Asong Byun | Amorphous porous hollow-structured Fe-BTC |
| MC-P-21 | Dr. Bongkyeom Kim | Isostructural Metal-Organic Frameworks based on the Strong Structure-Directing Radical π-Dimers |
| MC-P-22 | Gopalakrishnan Mohan | 3D MOF Derived Nanorods like Cation Defect-rich $Ni_{0.6}Fe_{2.4}O_4$@NC Efficient Electrocatalyst Enables Robust Rechargeable Zinc-air Batteries |

## Main group chemistry (MG)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| MG-F-01 | Ms. Narisara Tanjedrew | Tunable imidazole-benzimidazole-based electrocatalysts for oxygen reduction reaction (ORR) in water |

## Day 2: 20th February 2024

## Bioinorganic chemistry (BC)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| BC-F-01 | Mr. Yuma Yamamoto | Synthesis and antimicrobial activity of amino acid Schiff base copper complexes with azo groups |
| BC-F-02 | Dr. Bussaba Pinchaipat | Nickel(II) with Schiff base complex: experimental and computational studies of CT-DNA binding |
| BC-P-01 | Mr. Suman Patra | Second Sphere Interaction in a Molecular Iron Catalyst Allows Selective CH4 Production from CO |
| BC-P-02 | Mr. Chinmay Dey | Heme-Aβ in SDS micellar environment: Active site environment and reactivity |
| BC-P-03 | Mr. Viet Quoc Nguyen | Reconstitution of a hemophore from Acinetobacter baumannii for applications in antibacterial therapy |
| BC-P-04 | Mr. Yi-Rong Hsiang | Mechanism of NO Generation from $NO_2$- via O-atom Transfer in the Unsymmetrical NacNac Cu(II) complex |
| BC-P-05 | Mr. Youngseob Lee | Tyrosine Activation Study for Di-tyrosine Cross-linking Catalyzed by Transition Metal Ion with ROS |
| BC-P-06 | Mr. Thana Anusanti | Selectivity of C—H oxidation by iron pincer complex with crown ether moiety |
| BC-P-07 | Ms. Tassaneewan Soisuwan | Nickel Schiff base complexes containing pendant proton for catalyzing hydrogen evolution reaction |
| BC-P-08 | Ms. Balqis Auni Binti Badrul Hisyam | Inhibition effects of tridentate hydrazone ligands as corrosion inhibitors on mild steel in $CO_2$ |
| BC-P-09 | Asst.Prof. Jinkyu Park | Iron Speciation and Localization in Yeast: Impact of Growth Phase and Nutrient Composition |
| BC-P-10 | Mr. Ji-Ming Ciou | Metal Ion Induced Dihydro-Imidazopyridium Salts and Their Skin Protection against UVB Irradiation |

## Coordination compounds for medical applications (CM)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| CM-F-01 | Assoc.Prof.Dr. Yi-Hsin Liu | Singlet Oxygen on Material Surface: Energy Transfer via Artificial Defects for Photodynamic Therapy |
| CM-P-01 | Ms. Upala Dasmahapatra | Anti-cancer Property And DNA Binding Interaction Of First Row Transition Metal Complexes |
| CM-P-02 | Dr. Peyman Salahshour | Study on crystallographic structure and antiproliferative effect of a new strontium(II) complex |
| CM-P-03 | Assoc.Prof.Dr. Taishi Higashi | Fabrication of polycatenanes via condensation of two polypseudorotaxanes for drug delivery carrier |
| CM-P-04 | Mr. Kosei Utatsu | Transformable supramolecular material for reversible PEGylation of protein drugs |
| CM-P-05 | Mr. Rin Onaga | Design and evaluation of lactose-modified cyclodextrin as a drug for Niemann-Pick disease type C |
| CM-P-06 | Mr. Toru Taharabaru | Multistep transformable polyrotaxanes for versatile delivery platform of various biopharmaceuticals |
| CM-P-07 | Prof.Dr. Mae Joanne Aguila | Molecular docking analysis of different zinc(II)-salen complexes into amylin |
| CM-P-08 | Nguyen Thi Bang Linh | Mixed olefin/amine Pt(II) complexes: A new class potential for the development of anticancer drugs |
| CM-P-09 | Asst.Prof. Wooram Park | Advancing Cancer Immunotherapy with Metal-Phenolic Framework Nanoparticles and Electrical Ablation |
| CM-P-10 | Mrs. Siti Solihah Khaidir | Green Synthesis, Anticancer Screening and DNA Binding Studies of Polynuclear Schiff base Complexes |

## F-Element chemistry (FE)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| FE-P-01 | Mr. Athip Anupan | Neodymium extraction using deep eutectic solvent |

# Organometallic chemistry (OR)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| OR-F-01 | Mr. Masahiro Matsuoka | Photoinduced H–H and C–H bond activation by a Cr≡Si triple bonded complex |
| OR-F-02 | Mr. Keita Sato | NHC-stabilized hydroaluminylene complexes of tungsten and iron: synthesis and characterization |
| OR-F-03 | Ms. Jingyan Wang | Low-temperature deposition of conducting copper through design of molecular precursors |
| OR-P-01 | Prof. Junghwan Kim | Multicomponent X-ray Shielding Using Sulfated Cerium Oxide and Bismuth Halide Composites |
| OR-P-02 | Ms. Natcha Temnuch | Coordination chemistry of rhenium(I) tricarbonyl derived from derivative 2,6-bis(pyrazolyl)pyridines |
| OR-P-03 | Dr. Jitendra Kumar Bera | Designer Ligand Scaffolds for Metal-Ligand Cooperative Catalysis |
| OR-P-04 | Prof.Dr. Hung Kay Lee | Divalent Cobalt and Nickel Complexes Containing Mono- and Di-anionic Guanidinate Ligands |

# Supramolecular chemistry (SC)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| SC-P-01 | Mr. Kentaro Harada | Circularly Polarized Luminescence of a Biaryl Guest within a Chiral Resorcinarene-based Capsule |
| SC-P-02 | Prof.Dr. Minghuey Shieh | EFe$_3$(CO)9-based (E = Te, Se, S) dipyridyl−Cu polymers: From syntheses to semiconductivities |
| SC-P-03 | Ms. Marryllyn Emma Donaldson | Functionalised zig-zag coordination polymers from tzopz: a new triazole-pyrazine ligand |
| SC-P-04 | Dr. Kazuki Toyama | A redox-responsive multi-ferrocene capsule and its encapsulation-induced CT interactions |
| SC-P-05 | Ms. Seohyeon Yun | Pillar[5]arene-based silver(I) complexes: guest-controlled mechanically interlocked structures |
| SC-P-06 | Asst. Prof. Dr. Boontana Wannalerse | A Fluorescence Sensor Based on Phenolic Derivative for Metal Ion Detection |
| SC-P-07 | Mr. Tanakorn Khongluang | Use of porphyrin derivatives as ionophore in polymeric membrane electrode for ferric ion detection |
| SC-P-08 | Dr. Naoyuki Hisano | Dual redox-responsive supramolecular polymer directed by porphyrin and trinitrofluorenone |
| SC-P-09 | Mr. Kouta Tanabae | Synthesis and Guest Binding Behavior of Macrocyclic Tetrakisporphyrin with Two Cavities |
| SC-P-10 | Mr. Yoshihisa Hashimoto | Strong mechanochromic luminescence of Pt(II)-complexes within aromatic capsules in water |
| SC-P-11 | Ms. Pawares Pornchaiprasartkul | Triazole-Crown Ether Containing QAS and Pyridine-Triazole Ligands via Double-Click Reaction |
| SC-P-12 | Mr. Theerapat Khianjinda | Heteroditopic macrocycles for ion-pair recognition and synthesis of interlocked molecules |
| SC-P-13 | Mr. Pasit Srisawat | Naga[2]rotaxanes in Metallo-Supramolecular Assembly |
| SC-P-14 | Mr. Sutthipoj Vigromsitdet | Functionalised Non-Symmetrical XB triazole/HB amide Macrocycles for Anion Recognition and Sensing |
| SC-P-15 | Asst. Prof. Dr. Praput Thavornyutikarn | Turn-on fluorescence detection of Zn(II) and Cd(II) ions by an anthraquinone-amide-DPA chemosensor |
| SC-P-16 | Mr. Kritanan Junthod | Heteroditopic Lithium Ionophores Capable of Selective Recognition and Recovery of Lithium Salts |
| SC-P-17 | Mr. Pipatpong Laoviwat | Pillararene Supramolecular Assembly in Mechanically Interlocked Molecules (MIMs) |

## Switchable magnetic materials (SM)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| SM-P-01 | Ms. Sakshi Mehta | Stimuli-responsive Magnetic Bistability in Molecular Clusters |
| SM-P-02 | Mr. Sounak Ghosh | Switchable Magnetic Materials Based on Metallosupramolecular Architecture and Discrete Entities |
| SM-P-03 | Mr. Pannawich Jaratape | Structural studies of substituent effects in [Fe(qsal-X)$_2$]OTf complexes |
| SM-P-04 | Mr. Debopam Sarkar | Stimuli-Responsive Molecular Bistability in Di- and Tetranuclear Metallosupramolecular Architectures |
| SM-P-05 | Mr. Yuki Koyama | A novel valence tautomeric phenomenon manifesting in solution at room temperature |

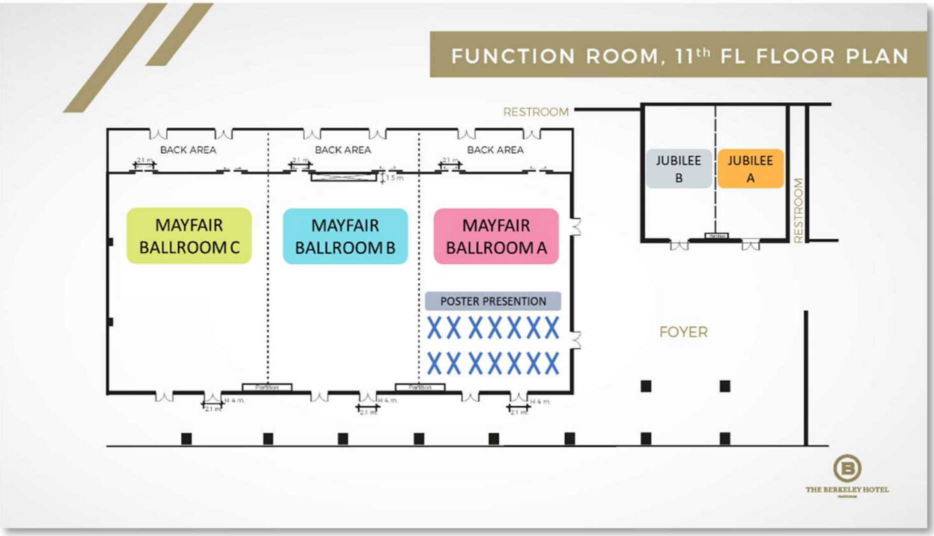
## Single molecule magnets (SS)

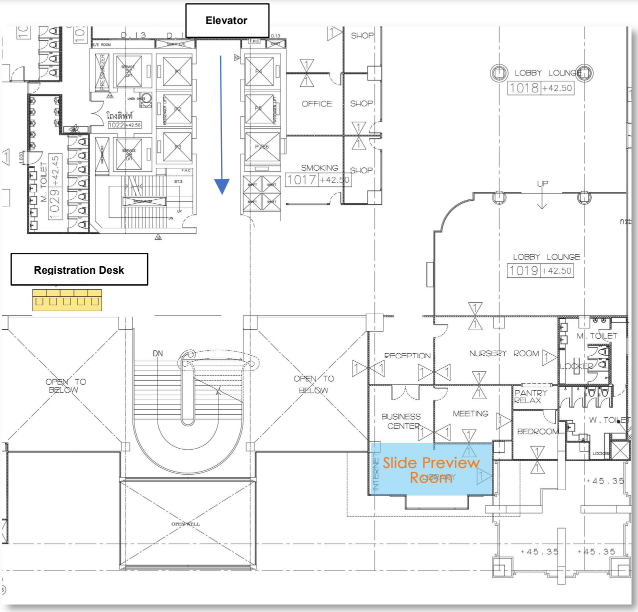
| Presentation Code | Name | Abstract Title |
|---|---|---|
| SS-P-01 | Mr. Pradip Kumar Sahu | Enhancing energybarrier and magneticblocking in Dy-dimer via redoxactive tetraoxolene bridgingligand |
| SS-P-02 | Dr. Toshiharu Ishizaki | Longitudinal relaxation time for an S=1/2 copper(II) incorporated Keggin-type silicotungstate |
| SS-P-03 | Ms. Liu Yeye | Enhancing magnetic properties in bis-$C_5/C_2B_3$ sandwiched geometry by fine charge regulation |
| SS-P-04 | Reo Wada | Magnetic relaxation phenomena of S=1/2 copper(II)-substituted Dawson type phosphotungstate |
| SS-P-05 | Asst.Prof. Kwanghyo Son | Molecular magnetism in structurally flexible metal-organic frameworks |
| SS-P-06 | Dr. Masooma Ibrahim | Polyoxometalate-based building blocks: From ligand to functional materials |

## Theoretical insights in coordination chemistry (TI)

| Presentation Code | Name | Abstract Title |
|---|---|---|
| TI-P-01 | Ms. Steiny Russelisaac Premakumari | Unraveling the Mysteries of Aromatic Oxidation: A DFT investigation into [Fe(IV)OHPor(Cl)] Complex. |
| TI-P-02 | Mr. Kittimeth Thammanatpong | Mechanisms of Hydrogen Evolution by Cobalt Complexes Containing Redox-Active Ligand as Proton Relay |
| TI-P-03 | Ms. Shruti Moorthy | Probing the magnetic anisotropy in tetrahedral CoII SMMs: An Ab-Initio Ligand Field Study |

# Conference Floorplan





# Abstract List by Session

- Plenary Speaker
- Award Winner
- Bioinorganic chemistry
- Catalytic coordination chemistry
- Coordination cages
- Coordination compounds for medical applications
- F-element chemistry
- Frontiers in coordination chemistry
- Luminescence
- Main group
- MOF/COF chemistry
- Organometallics
- Single molecule magnets
- Supramolecular Chemistry
- Switchable magnetic materials
- Theoretical insights in coordination

# Plenary Speaker Abstract

# Texas-inspired Drug Discovery Efforts

Jonathan L. Sessler

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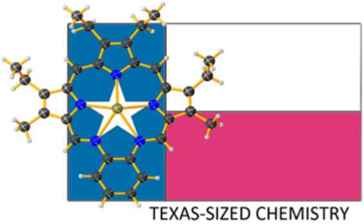
*E-mail: sessler@cm.utexas.edu*

This lecture will present the development of expanded porphyrins--larger analogues of heme pigments--as a class of compounds and as potential drug leads. The presentation will center around my personal story of a 3x cancer survivor and how with the assistance of great coworkers and collaborators an effort has been made to fight back against this disease by studying the chemistry and anti-cancer biology of gadolinium(III) texaphyrins. Texaphyrins were the first of the so-called expanded porphyrins to stabilize a 1:1 complex with a metal cation. Subsequently, effort was made in our laboratories and those of many others to create additional expanded porphyrins. Hundreds are now known. Several from our laboratory show promise in biomedical applications. Recently, efforts have been made to create so-called immunogenic cell death promoters designed to prevent cancer recurrence based on redox-active gold(I) carbenes. This new line of research will be reviewed as time permits.

Profs. Jong Sung Kim, Changhee Lee, Zahid Siddik, Rick Finch, Zhengrong Cui, Dani Gibson, and Zhao-Xi Wang, and Jingqin Chen are gratefully acknowledged. Thanks also go to Jonathan F. Arambula, Gregory Thiabaud, Sajal Sen, Matthew Levine, Adam Sedgwick, and Esther Maier. Current research support is provided by the Robert A. Welch Foundation.

**Keywords**: expanded porphyrins; texaphyrins; cancer; ICD; gold carbenes



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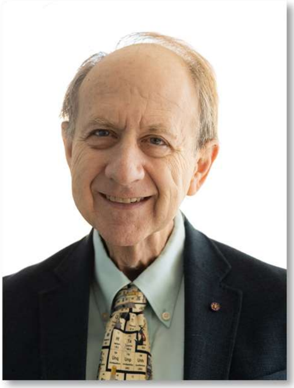
## Biography



Prof. Jonathan L. Sessler was born in Urbana, Illinois, USA on May 20, 1956. He received a B.S. degree (with Highest Honors) in chemistry in 1977 from the University of California, Berkeley. He obtained a Ph.D. in organic chemistry from Stanford University in 1982 (supervisor: Professor James P. Collman). He was a NSF-CNRS and NSF-NATO Postdoctoral Fellow with Professor Jean-Marie Lehn at L'Université Louis Pasteur de Strasbourg, France. He was then a JSPS Visiting Scientist in Professor Tabushi's group in Kyoto, Japan. In September, 1984 he accepted a position as Assistant Professor of Chemistry at the University of Texas at Austin, where he is currently the Doherty-Welch Chair. Dr. Sessler has authored or coauthored over 900 research publications, written two books (with Dr. Steven J. Weghorn and Drs. Philip A. Gale and Won-Seob Cho, respectively), edited two others (with Drs. Susan Doctrow, Tom McMurry, and Stephen J. Lippard, Placido Neri and Mei-Xiang Wang), and been an inventor of record on over 90 issued U.S. Patents. Dr. Sessler was a co-founder (with Dr. Richard A. Miller) of Pharmacyclics, Inc., which was acquired by AbbVie for $21B in 2015. His texaphyrin technology is now the basis for a new company, InnovoTex, Inc. In addition to English, Dr. Sessler speaks French reasonably well, as well as Hebrew and Spanish. He also knows a little bit of German and Japanese, and a couple words of Korean. Dr. Sessler's work has been recognized with several awards, including the American Chemical Society Cope Scholar and Breslow Awards, the Royal Society of Chemistry Centenary Prize, as well as Mond-Nyholm and MASC Supramolecular Chemistry awards, the Molecular Sensors-Molecular Logic Gates Award, the CASE award, the Hans Fischer and Thomas Dougherty Awards in Photodynamic Therapy from the Society of Porphyrins and Phthalocyanines, and the C. David Gutsche Award in Calixarene Chemistry. Dr. Sessler is a member of the U.S. National Academy of Inventors, the European Academy of Sciences, the U.S. National Academy of Sciences, the American Academy of Arts and Sciences, and the Chinese Academy of Sciences (Foreign Member). He has been a Clarivate Highly Cited Researcher for many years.

# Tailoring metal-organic framework characteristics through controlled metal coordination environments

Hoi Ri Moon*

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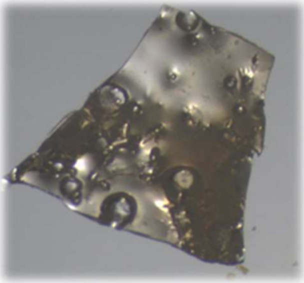
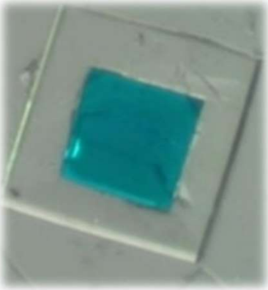
Metal–organic frameworks (MOFs) provide an excellent platform for investigating the correlation of structures with physical properties, given their facile coordination environment changes and responsive structures to external stimuli such as heat, pressure, temperature, and gas sorption. In this talk, we present an understanding of the behavior of MOFs in response to structural variations and the tailoring of MOFs through controlled metal coordination environments for specific purposes. The moisture-triggered proton-conductivity switching behavior, induced by the presence and absence of coordinating solvents in MOFs, reveals that coordinating solvents play a role in conductivity variation.[1] This finding provides a new design strategy for functional solid-state proton conductors. Additionally, we achieved the first example of carboxylate-based melt-quenched MOF glasses comprising $Mg^{2+}$ or $Mn^{2+}$ and an aliphatic carboxylate ligand, adipate by altering their thermal vitrification pathways.[2] To attain new functions, we are intensively studying single crystalline MOF-on-MOF architectures, which are expected to exhibit synergistic effects not present in the original structures.[3] Finally, addressing one of the greatest challenges in modern separation technology, we focus on the isotope mixture separation using well-tailored MOFs by controlling pore environments.[4-6]





**Keywords**: metal-organic frameworks; proton conductivity; MOF glasses; MOF-on-MOF; hydrogen isotope separation

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## Biography

Prof. Hoi Ri Moon is a professor in Department of Chemistry and Nanoscience at Ewha Womans University. She earned her Ph.D in Chemistry from Seoul National University in 2007, followed by postdoctoral research at the Molecular Foundry of Lawrence Berkeley National Laboratory. From 2010 to 2022, she severed as a faculty member at UNIST. In 2023, she joined Ewha Womans University as a Ewha Fellow Professor.

Her contributions to the field have been recognized through various honors, including her election as a member of the Young Korean Academy of Science and Technology (Y-KAST) in 2020 and the receipt of the International Award for Creative Work from the Japan Society of Coordination Chemistry (JSCC) in 2021. Currently, she holds the position of Vice Chair of the Metal-Organic Frameworks-International Commission and serves as an editor for Inorganic Chemistry Communications (Elsevier).

Prof. Moon's research centers on understanding the behavior of metal–organic frameworks in response to structural variations and tailoring MOFs for specific purposes. Her work extends to diverse applications, such as gas separation, storage, molecular sensing, and catalytic reactions.

# Chemistry in the Confined Space of Molecular Vessels

Partha Sarathi Mukherjee*

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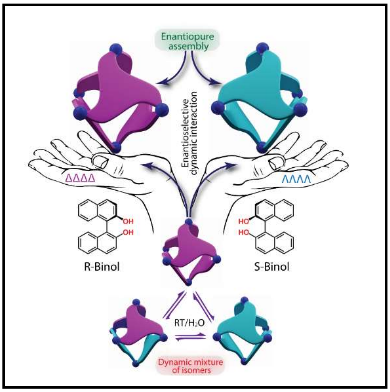
The properties and functions of chemical entities in confined nanospace are expected to be different from their conventional bulk properties due to restricted translational and rotational motions. Such restricted degree of freedom along with other non-covalent interaction/s may allow to stabilize unusual conformations of compounds in confined nanospace of molecular cavity. Our recent efforts on designing chiral molecular vessela including their chiral recognition will be discussed in my lecture. A recently developed strategy on constructing enantiopure cage (Figure 1) without using chiral donor/acceptor will be highlighted in the lecture. My lecture will also focus on the use of confined space for the separation of polyaromatic hydrocarbons by aqueous extraction and stabilization of transient merocyanine in confined space of aqueous molecular vessels.



**Keywords**: Self-assembly; Coordination chemistry; Cage compounds; Chiral recognition

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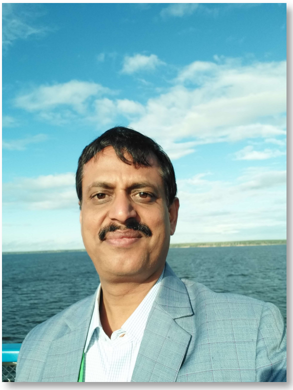

**Partha Sarathi Mukherjee** worked under the supervision of Prof. N. Ray Chaudhuri at IACS (Kolkata) on Cu(II)-coordination polymers including their magnetic studies for his Ph.D. He was a postdoctoral fellow in the group of Prof. Peter Stang at the University of Utah and worked as an Alexander von Humboldt fellow at the University of Göttingen with Prof. Herbert Roesky before joining the Indian Institute of Science (IISc) as a faculty in 2005. Partha is currently a professor of chemistry at IISc (Bangalore). He is a recipient of NASI-SCOPUS young scientist award, INSA-Medal, S. S. Bhatnagar prize, TWAS young affiliateship and Swarnajayanti fellowship of the Govt. of India. He is an elected fellow of the Indian Academy of Sciences and The World Academy of Sciences (TWAS). Partha is/was in the editorial advisory boards of *Inorganic Chemistry*, *Inorganica Chimica Acta*, *Inorganic Chemistry Frontiers*, *The Chemical Records*, and *Scientific Reports*. He is currently serving as an Associate Editor of *Inorganic Chemistry*. He works on self-assembled discrete organic and coordination molecular architectures including their use in catalysis, sensing, and light-harvesting. He has published over 210 papers in peer-reviewed journals with a current *h-index* of 67.

**Homepage:** https://ipc.iisc.ac.in/~psm/

# Discrete spin crossover complexes: solid state and solution phase correlations, tuning and sensing

Sally Brooker*

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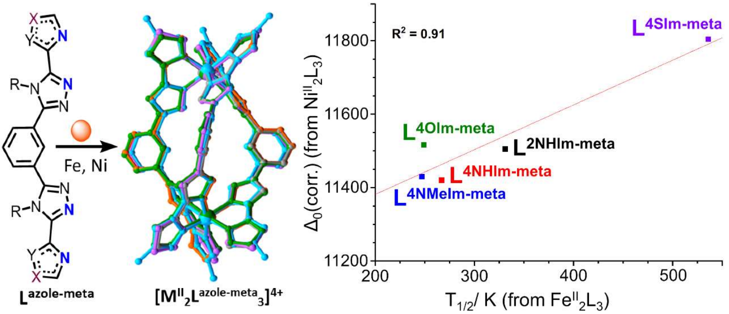
Spin crossover (SCO) occurs only in complexes of metal ions in appropriate *d* electron configurations, and only when an appropriate intermediate ligand field strength is imposed on them. Switching can be induced by application of a variety of stimuli, most commonly change in temperature, but also by change of pressure, light irradiation, application of an electric or magnetic field, or by the presence/absence of a guest. The last of these is of particular interest with regard to the development of guest sensors. For some systems, thermal hysteresis loops are observed: these are of considerable interest for memory applications, for which the lifetime of the sample in the meta stable state is of key importance.

Gaining predictability of field strength, and hence SCO, is also highly desirable, but remains a considerable challenge. This issue is being probed by a number of groups internationally, with some significant breakthroughs, in the solid state and in the solution phase. In the course of these efforts, we have actually *demonstrated* the expected correlation between ligand field strength and spin crossover switching temperature in a family of helicates (Figure).[1]

After an introduction to SCO, we will cover the observation of unusual scan rate dependence of thermal hysteresis loops, pressure-induced SCO, tuning of switching temperature, the development of SCO-based sensors, and finally establishing useful correlations, including some that may enable easy prediction of spin state in solution in advance of synthesis.



**Keywords**: spin crossover; iron(II); cobalt(II); heterocyclic ligands; correlations

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# Biography

**Professor Sally Brooker** (MNZM, FRSNZ, FNZIC, FRSC) studied at the University of Canterbury, New Zealand [BSc(Hons) first class; PhD with Professor Vickie McKee]. After postdoctoral research at Georg-August-Universität Göttingen, Germany, with Professor George M. Sheldrick, she took up a Lectureship at the University of Otago where she is now a full Professor and Sesquicentennial Distinguished Chair, MacDiarmid Institute Principal Investigator, and co-leader of the German NZ Green Hydrogen alliance / He Honoka Hauwai. She has been the recipient of numerous awards, most recently including a Queens Birthday Honour for services to science (MNZM), the Hector Medal (RSNZ) and Burrows Award (RACI). Her research interests concern the design, synthesis and full characterisation of, primarily paramagnetic, di- and poly-metallic complexes of transition metal and lanthanide ions with polydentate acyclic and macrocyclic ligands, as these have interesting redox, magnetic, catalytic and photophysical properties (*otago.ac.nz/brooker*).

# Assembly of Chiral Metal Phosphonates: from Molecular Chirality to Macroscopic Superhelices

Li-Min Zheng

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Chirality is a universal phenomenon in nature, and how to amplify chirality from the molecular level to macroscopic aggregates is a highly challenging topic. Related research not only helps to understand the origin of chirality, but also has significant implications for the application of chiral substances in chiral recognition and separation, asymmetric catalysis, and chiral functional materials. Metal phosphonates are an important class of inorganic-organic hybrid materials showing versatile structures and intriguing functions. Although many chiral metal phosphonates have been reported, they usually appear as crystalline materials. Herein we present our recent work on chiral coordination polymer assemblies based on one-dimensional metal phosphonates, including the crystalline chiral materials, the hierarchical helical nanostructures in which the chirality is transferred and amplificated from molecular level to the macroscopic level, and the helicity regulation of superhelices. In addition, we investigated the effect of morphology on the physical properties of phosphonate materials.

**Keywords**: metal phosphonate; superhelix; chirality inversion; coordination polymer

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## Biography

Li-Min Zheng is a professor in the School of Chemistry and Chemical Engineering and the State Key Laboratory of Coordination Chemistry of Nanjing University. She obtained her B.S., M.S. and Ph.D. degrees from Nanjing University in 1986, 1989 and 1992, respectively, and was a postdoctoral fellow at the University of Zurich, Switzerland, from 1994 to 1996, and a visiting scholar at the University of Houston, USA, from 1999 to 2000. She is mainly engaged in the research of functional coordination chemistry, especially the assembly and properties of metal phosphonates, including magneto-optical bifunctional materials and chiral materials. She has published more than 280 papers, and was awarded the Outstanding Youth Fund by the National Natural Science Foundation of China in 2003, and was elected as a Fellow of the Royal Society of Chemistry in 2021. She is currently an Associate Editor of Dalton Transactions, and a member of the international editorial boards of Inorganic Chemistry and ACS Applied Electronic Materials.

# Unconventional Platinum(VI) Prodrugs

Janice R. Aldrich-Wright,[1,2*] Christopher P. Gordon,[1] Kieran Scott,[2,3] Robin I. Taleb,[4] Costantine F. Daher,[5] Jennette Sakoff,[6] Krishant Deo,[1] Brondwyn McGhie,[1] Aleen Khouy,[1] Maria Elias,[1] Angelico Auputen,[1] Ashley Jurisinec,[1] Fatin Rashid,[1] Sarah Soliman[1]

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Conventional platinum(II) anticancer drugs are administered for over 50% of chemotherapy, despite clinical difficulties of acquired resistance, cross-resistance and side effects that frequently result in patients withdrawing from treatment or reducing the therapeutic dose. Combinations of several other medications are used to control the extent of these difficulties. Overcoming these clinical disadvantages has inspired us to create complexes with inherently different modes of action. To this end, we have designed and developed many $\mathrm{Pt^{IV}}$ prodrugs that will facilitate the coordination of bioactive axial ligands. The core coordination scaffolds of $\mathrm{Pt^{IV}}$PHEN*SS*, $\mathrm{Pt^{IV}}$5ME*SS* and $\mathrm{Pt^{IV}}$56ME*SS* have been characterized using HPLC, NMR, UV and CD spectroscopy together with ESI-MS. The potency in human cancer cell lines has been determined to be almost always superior to cisplatin, oxaliplatin or carboplatin, and comparable with their $\mathrm{Pt^{II}}$ precursors, $\mathrm{Pt^{II}}$PHEN*SS*, $\mathrm{Pt^{II}}$5ME*SS* and $\mathrm{Pt^{II}}$56ME*SS* they elicit their potency through mitochondrial and cytoskeletal damage.[1,2]

Figure 1 $\mathrm{Pt^{IV}}$ scaffold with two bioactive axial ligands

**Table 1** Summary of the cytotoxicity of Pt$^{IV}$ complexes

| Pt$^{IV}$ complex | A2780 | ADDP* | MCF-7 | HT29 | Du145 | MIA |
|---|---|---|---|---|---|---|
| | *Ovarian* | *Ovarian* | *Breast* | *Colon* | *Prostate* | *Pancreas* |
| **$[Pt^{IV}56MESS(OH)_2]Cl_2$** | 0.056 ± 0.0071 | 0.17 ± 0.12 | 0.48 ± 0.14 | 0.036 ± 0.0071 | 0.015± 0.003 | 0.043 ± 0.0025 |
| **$[Pt^{IV}PHENSS(OH)_2]Cl_2$** | 0.80 ± 0.084 | 1.3 ± 0.35 | 16 ± 4.5 | 0.71 ± 0.30 | 0.31 ± 0.092 | 3.4 ± 2.2 |
| **$[Pt^{IV}PHENSS(4\text{-}PhB)(OH)Cl_2$** | 0.35 ± 0.038 | 0.30 ± 0.015 | 0.74 ± 0.15 | 0.16 ± 0.026 | 0.35 ± 0.084 | 0.18 ± 0.0033 |
| **cisplatin** | 1.0 ± 0.1 | 28 ± 1.7 | 6.5 ± 0.8 | 11.3 ± 1.9 | 1.2 ± 0.1 | 7.5 ± 1.3 |
| **carboplatin** | 9.2 ± 2.9 | >50 | >50 | >50 | 14.7 ± 1.2 | >50 |
| **oxaliplatin** | 0.16 ± 0.0 | 0.8 ± 0.1 | 0.5 ± 0.1 | 0.9 ± 0.2 | 2.9 ± 0.4 | 0.9 ± 0.2 |

**Keywords**: Platinum; prodrug; anticancer; Pt$^{II}$56ME*SS*; Pt$^{IV}$56ME*SS*

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**PLENARY 6**

**Janice R. Aldrich-Wright**

## Biography

Professor Janice Aldrich-Wright is a Medicinal Bioinorganic Chemist, who has been Deputy Dean of Graduate Research School, Professor of Chemistry in the School of Science, and the Academic Lead for the Science in Australia Gender Equity initiative at Western Sydney University. She undertook a BSc in applied science at University of Technology, Sydney, work in the chemical industry for some years before returning to undertake a PhD at Macquarie University. Her PhD thesis was awarded the Cornforth Medal for the best Chemistry PhD in Australia 1993, and she now has a strong international research reputation in anticancer prodrug design as the focus of her research. She has been awarded the Vice Chancellor's Excellence in Postgraduate research supervision three times and has mentored 36 PhD, 27 Master and 38 Honours candidates during their candidatures. She has published over 140 papers, holds patents, is a fellow of the Royal Australian Chemical Institute and a Fellow of the Royal Society of Chemistry. She is an important mentor to early career academics and a strong advocate for gender equity.

Publications appear in high profile journals with H-index = 39. ORCID ID: https://orcid.org/0000-0002-6943-6908

# Leveraging the Photophysical and Photochemical Properties of Transition Metal Complexes for Bioimaging and Photocytotoxic Applications

Kenneth Kam-Wing Lo

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The coordination of functional ligands to d-block elements facilitates the formation of transition metal complexes with unique properties. We have a long-standing interest in exploiting the intriguing photophysical and photochemical properties of rhenium(I), ruthenium(II), and iridium(III) polypyridine complexes for a range of biological applications. Notably, the highly environment-sensitive and long-lived emission properties of these complexes have led to the development of new photoactive labels, intracellular sensors, and bioimaging reagents. Many transition metal complexes also serve as efficient photosensitizers for singlet oxygen, and have been utilized in the design of novel photocytotoxic agents. The integration of various functional pendants into photofunctional transition metal complexes has paved the way for the development of innovative bioimaging and phototherapeutic agents. In this lecture, I will outline our recent designs of luminescent rhenium(I), ruthenium(II), and iridium(III) polypyridine complexes, utilized as bioorthogonal probes, imaging reagents, and photocytotoxic agents. I will focus on the photophysical and photochemical properties, cytotoxic activity, cellular uptake behavior, and intracellular functions of these photofunctional transition metal complexes.

**Keywords**: bioimaging; bioorthogonal; photodynamic therapy; photosensitizers; transition metal complexes

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5. K. K.-W. Lo, *Acc. Chem. Res.*, 2020, **53**, 32.

## Biography

Prof. Kenneth Lo obtained his BSc (1993) and PhD (1997) degrees at The University of Hong Kong. From 1997 to 1999, he worked as a Croucher Foundation Postdoctoral Research Fellow at University of Oxford. Prof. Lo joined the Department of Biology and Chemistry (currently Department of Chemistry) of City University of Hong Kong as Assistant Professor in 1999 and became Associate Professor (Scale B) in 2003, Associate Professor (Scale A) in 2007, Professor in 2011, and Chair Professor in 2023.

Prof. Lo’s research interest is the utilization of luminescent inorganic and organometallic transition metal complexes as biomolecular and cellular probes, with a focus on the development of intracellular sensors, photoactive labels, and bioimaging reagents. He received The APA Prize for Young Scientist from The Asian and Oceanian Photochemistry Association in 2005 and The Distinguished Lectureship Award from The Chemical Society of Japan in 2011. He was awarded a Croucher Senior Research Fellowship from the Croucher Foundation in 2015 and was admitted as a Fellow of the Royal Society of Chemistry (FRSC) in 2018. He was on the Editorial Advisory Board of *Inorganic Chemistry* (2015 – 2017) and the Advisory Board of *RSC Advances* (2013 – 2015), and has been on the International Advisory Board of *European Journal of Inorganic Chemistry* since 2020 and Editorial Advisory Board of *Chemical & Biomedical Imaging* since 2022. He served as an Associate Editor for *RSC Advances* (2015 – 2020) and has been an Associate Editor for *Inorganic Chemistry* since 2020.

**PLENARY SPEAKER**
**PLENARY 8**
**Yoshiaki Nishibayashi**

# Molybdenum-catalyzed reduction of molecular dinitrogen into ammonia under ambient conditions

Yoshiaki Nishibayashi*

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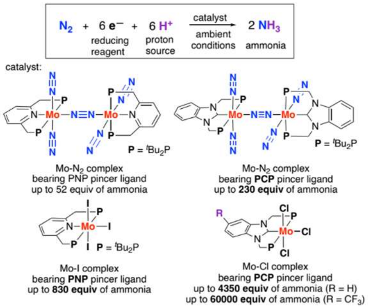
Recently, we found that dimolybdenum-dinitrogen complexes bearing **PNP** and **PCP** pincer ligands worked as effective catalysts for the formation of ammonia from dinitrogen under ambient reaction conditions, where 230 equiv of amount of ammonia were produced based on the catalyst.[1-3] More recently, molybdenum-iodide complex bearing **PNP** pincer ligand has been found to work as a more effective catalyst than the previous dinitrogen complexes, where 830 equiv of amount of ammonia are produced based on the catalyst.[4] This remarkable catalytic activity is induced by a novel reaction pathway via direct cleavage of the nitrogen–nitrogen triple bond of the bridging dinitrogen ligand in the Mo–N≡N–Mo core. Based on these research backgrounds, we have quite recently found that the combination of samarium diiodide (SmI2) and simple alcohol or water realized the unprecedented catalytic activity in molybdenum- catalyzed ammonia production under ambient reaction conditions, where up to 60000 equiv of amount of ammonia are produced based on the catalyst.[5] The high reactivity is achieved by a proton-coupled electron transfer (PCET) process realized by the bond weakening of O–H bonds of alcohols and water coordinated to SmI2.



**Keywords:** molybdenum; reduction; dinitrogen; ammonia; catalytic reaction

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**PLENARY SPEAKER**
**PLENARY 8**
**Yoshiaki Nishibayashi**

## Biography

### Diplomas

March 1991: B.Sc., Kyoto University
March 1993: M.Sc., Kyoto University
November 1995: Ph.D., Kyoto University

### Research Activities

1995-2000: Assistant Professor, The University of Tokyo
2000-2005: Assistant Professor, Kyoto University
2005-2016: Associate Professor, The University of Tokyo
2016-present: Professor, The University of Tokyo

### Awards

2001 The Chemical Society of Japan Award for Distinguished Young Chemists
2005 The Minister Award for Distinguished Young Scientists Japan
2012 The JSPS Prize
2012 The Green & Sustainable Chemistry Honorable Award
2016 The Nissan Chemical Industries Award for Novel Reaction & Method from the Society of Synthetic Organic Chemistry, Japan
2017 The Japan Society of Coordination Chemistry Award for Creative Work
2018 The Inoue Prize for Science
2018 The Prizes for Science and Technology (Research Category) in the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
2021 The Chemical Society of Japan Award for Creative Work

### Recent publications

236 original papers and 103 reviews. Selected recent examples are as follows:
(1) Catalytic Production of Ammonia from Dinitrogen Employing Molybdenum Complexes Bearing N-Heterocyclic Carbene-Based PCP-Type Pincer Ligands, Y. Ashida, T. Mizushima, K. Arashiba, A. Egi, H. Tanaka, K. Yoshizawa, and Y. Nishibayashi, Nature Synthesis, 2, 635–644 (2023).
(2) Catalytic Nitrogen Fixation Using Visible Light Energy, Y. Ashida, Y. Onozuka, K. Arashiba, A. Konomi, H. Tanaka, S. Kuriyama, Y. Yamazaki, K. Yoshizawa, and Y. Nishibayashi, Nature Communications, 13, 7263 (2022).
(3) Direct Synthesis of Cyanate Anion from Dinitrogen Catalysed by Molybdenum Complexes Bearing Pincer-Type Ligand, T. Itabashi, K. Arashiba, A. Egi, H. Tanaka, K. Sugiyama, S. Suginome, S. Kuriyama, K. Yoshizawa, and Y. Nishibayashi, Nature Communications, 13, 6161 (2022).
(4) Molybdenum-Catalysed Ammonia Production with Samarium Diiodide and Alcohols or Water, Y. Ashida, K. Arashiba, K. Nakajima, and Y. Nishibayashi, Nature, 568, 536–540 (2019).
(5) Ruthenium-Catalysed Oxidative Conversion of Ammonia into Dinitrogen, K. Nakajima, H. Toda, K. Sakata, and Y. Nishibayashi, Nature Chemistry, 11, 702–709 (2019).

# Award Winner Abstract

**Award Winner**
**MicrotracBEL-ACCC Award**
**(For Male Researcher)**
**Cheng-Yong Su**

# Functionalization of MOCs as Supramolecular Reactors for Cage-Confined Catalysis

Cheng-Yong Su[3*]

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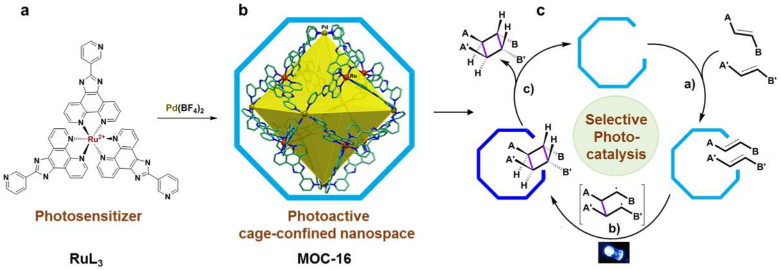
The self-assembly of metal-organic cages (MOCs) and their applications represent an attractive research topic in the field of coordination supramolecular chemistry, owing to their significance as biomimetic artificial blueprints and promises as supramolecular containers and reactors, devices and machines, transporters and separators, as well as enzyme-mimicking supramolecular reactors. We would like to give a briefly introduction of the progress of our research group in the self-assembly of functionalized MOCs, focusing on how to construct the "active MOCs" by integrating chiral, photoactive, catalytic centers in the cage-confined nanospaces to create multi-functional supramolecular nanoreactors for supramolecular catalysis of wide organic transformations.



**Keywords**: metal-organic cages; supramolecular reactor; cage-confined catalysis; supramolecular catalysis; host-guest chemistry

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## Biography

Dr. Cheng-Yong Su is the Cheung Kong Professor of Chemistry at Sun Yat-Sen University. He obtained his Ph. D in 1996 from Lanzhou University. In 2001, he joined Prof. Wolfgang Kaim's group at Stuttgart University as an Alexander von Humboldt Research Fellow, and then moved to the University of South Carolina in 2002 to work with Prof. Hans-Conrad zur Loye as a postdoctoral fellow. In 2004, he was promoted to a full professor in Sun Yat-Sen University. He has authored/coauthored over 400 peer reviewed papers, 30 patents, and 12 books & chapters, receiving > 38000 citations with H-index 93. Prof. Su's research is interdisciplinary in the fields of coordination supramolecular chemistry and materials, focusing on the health and energy relevant metal-organic materials (MOMs) and nanomaterials: (1) self-assembly of metal-organic cage/containers (MOCs), metal-organic frameworks (MOFs) and metal-organic gels (MOGs), (2) supramolecular catalysis in confined nanoscale spaces and artificial photosynthesis, and (3) supramolecular materials for adsorption/separation, luminescence, and theranostics. He is the Highly Cited Researcher during 2018-2022 by Web of Science™, and received the second class National Natural Science Award and the first class Guangdong and MOE Natural Science Awards. He also serves as the co-editor of *IUCrJ* and the member of advisory board of *J. Mater. Chem. A*.

**Award Winner**
**RIGAKU-ACCC Award**
**(For Female Researcher)**
**Mi Hee Lim**

# Bioinorganic Strategies to Study Multiple Facets in Dementia

Mi Hee Lim

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Alzheimer's disease (AD), associated with degeneration of neurons and synapses in the brain, leads to motor impairment and eventual fatality. Neurodegeneration could be related to various interconnected features, including (i) plaque formation from amyloid-β (Aβ) peptide fragments, (ii) metal ion dyshomeostasis and miscompartmentalization, as well as (iii) inflammation and increased oxidative stress due to overproduction of reactive oxygen species (ROS). The inter-relations between some of these pathological factors have been investigated. Metals are found entangled in the Aβ plaque and likely contribute to Aβ neurotoxicity and oxidative stress. ROS have been shown to increase the rate of Aβ plaque formation. Our understanding of the correlation between these elements and AD neuropathogenesis has been very limited, however. There is currently no cure for AD; therapies are focused on symptomatic relief targeting the decrease in the levels of acetylcholine, only one of the multiple factors causing the disease.[1-4] To find a cure for AD, we require a better understanding of the relationship between various causative factors of this devastating disease. Towards this goal, we have been developing suitable chemical tools capable of targeting and regulating multiple underlying factors or identifying the pathogenic networks composed of their direct interactions and reactivities.[5-13]

**Keywords**: Alzheimer's disease; transition metal ions; amyloid-β; reactive oxygen species; small molecule-based chemical tools

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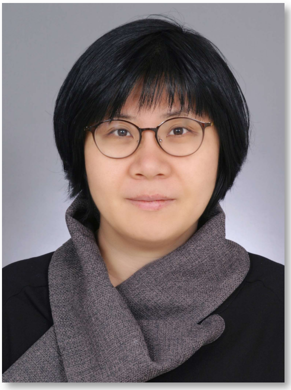
## Biography



Mi Hee Lim is a KAIST Endowed Chair Professor and the Director of the Center for MetalloNeuroProteinoChemistry in the department of chemistry at the Korea Advanced Institute of Science and Technology (KAIST). She received her BS in Chemistry from Ewha Womans University, Seoul, Korea, in 1999 and her MSc in 2001 under the direction of Professor Wonwoo Nam. In 2002, she moved to MIT where she obtained her PhD under the supervision of Professor Stephen J. Lippard. She then pursued her postdoctoral research in the laboratory of Professor Jacqueline K. Barton at Caltech. In 2008, she began her independent career as an Assistant Professor of Chemistry and Research Assistant Professor in the Life Sciences Institute at the University of Michigan, Ann Arbor, USA. In 2013, Mi Hee moved to the Ulsan National University of Science and Technology (UNIST), Ulsan, Korea, as an Associate Professor with tenure. In 2018, Mi Hee joined the Department of Chemistry at KAIST, Daejeon, Korea. Her research interests lie in bioinorganic chemistry, especially focusing on identifying how metal-involved biological networks are linked to dementia, such as Alzheimer’s and Parkinson’s diseases, and establishing new directions for developing chemical reagents as tools, diagnostics, and therapeutics for such diseases. Mi Hee is a Fellow of the Royal Society of Chemistry and has received numerous awards including the Asian Biological Inorganic Chemistry (AsBIC) James Hoeschele Award, the Society of Biological Inorganic Chemistry (SBIC) Early Career Award, the Year Award for Women in Science and Technology, the S-Oil Next-Generation Scientist Award, the Award for "30 Young Scientists of Korea" to Lead Basic Science Research for the Next 30 Years, the Korean Chemical Society (KCS)-Wiley Young Scientist Award, the NSF CAREER Award, the Alfred P. Sloan Fellowship. Mi Hee is a Specialty Chief Editor, *Frontiers in Chemical Biology*, an Associate Editor in *Dalton Transactions*, and an Editorial Advisory Board Member in *Accounts of Chemical Research, Chem*, *ACS Central Science*, *Chemical Science*, *Chemical Communications*, *ACS Applied Bio Materials*, *Journal of Inorganic Biochemistry*, *Journal of Biological Inorganic Chemistry*, and *Metallomics.*

# Coordination chemistry for photon upconversion, nuclear hyperpolarization, and quantum sensing

Nobuhiro Yanai[1,2]

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Photo-excited triplets have interesting features such as long excited state lifetimes and polarized electron spins. The long excited-state lifetime of triplets of milliseconds allows photon upconversion based on triplet-triplet annihilation (TTA-UC) to occur at relatively low excitation light intensities. Recent studies on the triplet sensitizers and emitter materials necessary for TTA-UC have led to the development of new methods for the efficient conversion of near-infrared light to visible light and from visible light to ultraviolet light. In this talk, I will introduce the design of TTA-UC chromophores and their applications.[1-5]

The utilization of the spin degree of freedom of the photoexcited triplet will lead to the connection with quantum technology, which has been gaining a great deal of momentum in recent years. While it is necessary to cool down to cryogenic temperatures of several K to polarize electron spins in thermal equilibrium, the photoexcited triplet can transiently create such a highly polarized state even at room temperature. The polarization transfer of these electron spins to nuclear spins will lead to significantly enhanced sensitivity in NMR and MRI. I would like to introduce our recent research applied to the NMR sensitivity enhancement of biomolecules[6-9] and optical electron spin polarization in MOFs.[10,11]

**Keywords**: photon upconversion, singlet fission, spin polarization

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11. Akio Yamauchi et al., *Science Adv.*, in press.

# Biography

Nobuhiro Yanai is an Associate Professor in the Department of Applied Chemistry at Kyushu University, Japan. He earned his Ph.D. from Kyoto University in 2011 under Prof. Susumu Kitagawa and Prof. Takashi Uemura on guest properties in metal-organic frameworks. He was a postdoctoral fellow with Prof. Steve Granick at the University of Illinois at Urbana-Champaign, experiencing colloid and soft matter sciences. He joined Kyushu University in 2012. He is currently leading a group that creates photo-functional materials for photon upconversion, dynamic nuclear polarization, and quantum sensing. He is serving an Associate Editor of *Chemical Physics Reviews* (AIP) and Advisory Boards of *Chemical Science* (RSC), *Nanoscale Horizons* (RSC), *ChemNanoMat* (Wiley). He received several awards including The Wiley Young Researcher Award, The Asian and Oceanian Photochemistry Association Prize for Young Scientists, Award for Young Chemists, Chemical Society of Japan, Young Scientist Award from MEXT, Research Promotion Award from Quantum Life Science Society, Award for Encouragement of Research in Coordination Chemistry from Japan Society of Coordination Chemistry, and The Japanese Photochemistry Association Award for Young Scientist.

# Bioinorganic Chemistry (BC)

# Abstract

# Biomimetic metal-oxygen intermediates in dioxygen activation and formation chemistry

Wonwoo Nam

*Department of Chemistry and Nano Science, Ewha Womans University*
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Dioxygen is essential in life processes, and enzymes activate dioxygen to carry out a variety of biological reactions. One primary goal in biomimetic research is to elucidate structures of reactive intermediates and mechanistic details of dioxygen activation and oxygenation reactions occurring at the active sites of enzymes, by utilizing synthetic metal-oxygen complexes. A growing class of metal-oxygen complexes, such as metal–superoxo, –peroxo, –hydroperoxo, and –oxo species, have been isolated, characterized spectroscopically, and investigated in various oxygenation reactions. During the past decade, we have been studying the chemical and physical properties of various reactive intermediates in oxygenation reactions, such as high-valent iron(IV)- and manganes(V)-oxo complexes of heme and non-heme ligands in oxo-transfer and C-H activation reactions, non-heme metal-peroxo complexes in nucleophilic reactions, and non-heme metal-superoxo complexes in electrophilic reactions. The effects of supporting and axial ligands on structural and spectroscopic properties and reactivities of metal-oxygen adducts have been extensively investigated as well. In this presentation, I will present our recent results on the synthesis and structural and spectroscopic characterization of mononuclear nonheme metal-dioxygen intermediates as well as their reactivities in electrophilic and nucleophilic oxidation reactions.

**Keywords**: biomimetic chemistry; nonheme iron enzymes; dioxygen activation; dioxygen formation; reactive intermediates

**References**

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# Conversion of Myoglobin to Artificial Metalloenzymes

Takashi Hayashi[1*]

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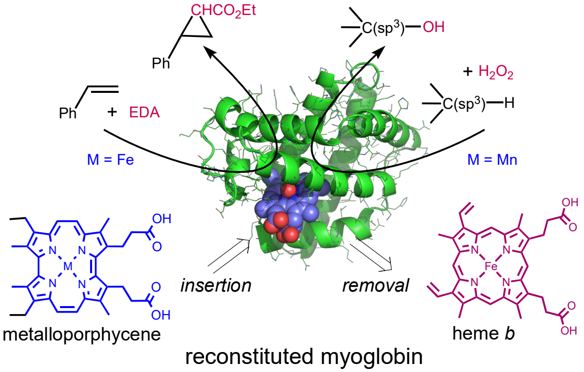
Hemoproteins are ubiquitous metalloproteins with iron porphyrin (heme) as a cofactor. In the case of myoglobin responsible for a molecular oxygen storage protein, the heme cofactor is noncovalently bound to the protein matrix, so removal of heme under acidic conditions can easily yield the corresponding apoprotein. Furthermore, it is known that the reconstituted myoglobin can be obtained by inserting appropriate artificial cofactor into the apoprotein. Our group has focused on the reconstitution of myoglobin by the aforementioned methods and its conversion to artificial metalloenzymes. In this presentation, myoglobins reconstituted with iron porphycene and manganese porphycene, constitutional isomer of porphyrin, will be reported as new artificial metalloenzymes that catalyze the styrene cyclopropanation and alkane hydroxylation reactions, respectively, under mild conditions.



**Keywords**: artificial metalloenzyme; myoglobin; metalloporphycene; cyclopropanation; hydroxylation

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# Enzyme-mediated assembly of metal chelators: Diversifying structure and function

Rachel Codd[1]

*School of Medical Sciences, The University of Sydney, New South Wales 2006, Australia*
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It would be useful if the structural diversity of traditional sets of ligands used in coordination chemistry could be expanded. This would simultaneously open opportunities to expand fundamental knowledge in coordination chemistry and broaden scope in environmental and/or biomedical metal sequestration/delivery applications. Natural products are well established as a reservoir of structurally diverse molecules, which includes metal-binding ligands such as high-iron(III)-affinity bacterial siderophores.[1] We selected hydroxamic acid-containing siderophores as our starting platform towards expanding structural diversity and considered whether we might exploit the bacterial biosynthesis machinery as a facile approach to generate new ligand analogues. This required access to siderophore biosynthesis enzymes and to substrates ideally with a modular synthetic route to allow structural diversification. We produced a set of recombinant siderophore assembly enzymes[2] from a siderophore-producing marine actinomycete[3] and synthesized monomeric *endo*-hydroxamic acid amino carboxylic acids as substrates.[4] Enzyme-substrate incubation resulted in the generation of combinatorial mixtures of linear and macrocyclic siderophore ligands with variable multiplicity, which had differential coordination properties towards solutions of metal ions with different ionic radii. Blending molecular biology, organic synthetic chemistry, and coordination chemistry, is an attractive approach towards the discovery and production of structurally diverse natural product chelators with potential for broader function.

**Keywords**: siderophores; hydroxamic acid; combinatorial chemistry; ligand structural diversity

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# Bio-organometallic $NO_x$ conversion and utilization

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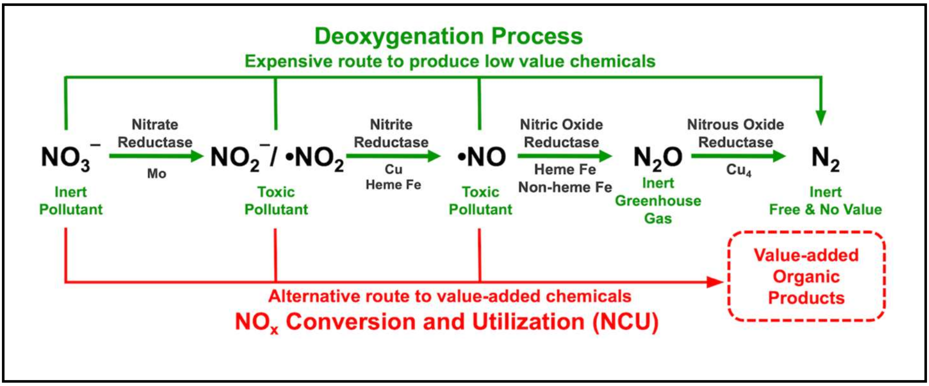
Global nitrogen cycle has been significantly influenced by anthropogenic perturbation. To contribute to re-balance this cycle, a new technology to convert $NO_x$ species to safe and useful chemicals is timely needed. Biological denitrification involving $NO_x$ conversion occurs via a multi-step process to reduce nitrate to dinitrogen ($NO_3^- \rightarrow N_2$). Although the efficient enzymatic reactions attractively operate under mild conditions, four different metalloenzymes are needed to convert a series of intermediate $NO_x$ species, which is, unfortunately, difficult to apply in an industrial process. Recently, we have developed a synthetic approach to this issue by utilizing a bifunctional metal catalyst for producing value-added products from $NO_x$.

In this presentation, a novel catalysis based on a nickel pincer system will be presented. The catalysis starts with converting Ni–$NO_3$ to Ni–NO via deoxygenation with CO(g), which is followed by transfer of the *in-situ* generated nitroso group to organic substrates. The transfer favorably occurs at the flattened Ni(I)–NO site via its nucleophilic reaction. Successful catalytic production of oximes from benzyl halides by using both $KNO_3$ and $NaNO_2$ was presented under mild conditions. Our nickel catalyst effectively fulfils a dual-purpose, namely deoxygenating $NO_x$ anions and catalyzing C–N coupling.



**Keywords**: NOx conversion and utilization; nitrate conversion; nickel catalysis; C-N coupling

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**Bioinorganic Chemistry (BC)**
**Keynote Speaker**
**BC-K-05**
**Jenny Y. Yang**

# Chemical Design for Integrated Catalytic CO2 Capture and Utilization

Jenny Y. Yang, Jared Stanley, Ciara Gillis, Ab Mir

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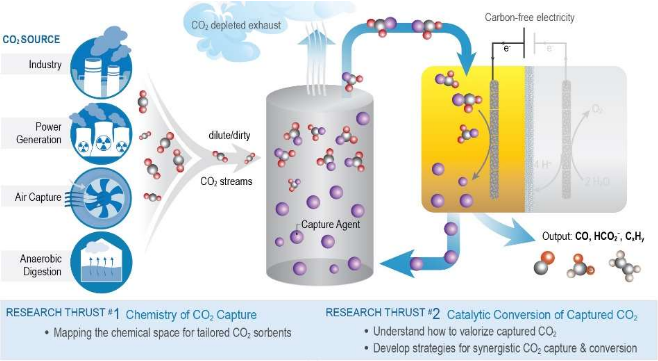
Prof Yang is the Director for the Center for Closing the Carbon Cycle (4C) will advance the foundational science and define key integration parameters for synergistic $CO_2$ capture and conversion, or reactive capture of $CO_2$ (RCC). While there has been significant independent research in either $CO_2$ capture or pure $CO_2$ conversion, it is not well understood what knowledge is translatable to RCC. Specific efforts towards understanding the translatable knowledge between electrocatalytic $CO_2$ reduction and reduction of captured $CO_2$ will be discussed, with particular emphasis on catalysts that normally have high selectivity towards $CO_2$ and $HCO_2^-$.



**Keywords**: transition metal catalysis, electrocatalysis, carbon dioxide

# Factors Deciding the Selectivity of $O_2$, NO, $CO_2$ and $SO_2$ Reduction.

Abhishek Dey

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The talk will describe the intermediates involved in the multiple electron and multiple proton reduction of small molecules like $O_2$, NO ($NO_2^-$), $CO_2$ and $SO_2$. These intermediates are either observed in solution during stoichiometric reaction or in-operando using spectro-electrochemistry and characterized using a combination of spectroscopic techniques like EPR, Mossbauer, FTIR and resonance Raman spectroscopy. These transient intermediates are found to determine the selectivity of $ne^-/nH^+$ reduction of these small molecules which allows predictive design of catalysts for the purpose. While the reactions are very different, there seems to be certain commonalities in these reaction intermediates which can be taken advantage of when designing catalysts for selective reduction of these small molecules.

**Keywords**: $ne^-/nH^+$ reduction, $O_2$, $NO_x$, $CO_x$, $SO_x$

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**Bioinorganic Chemistry (BC)**
**Invited Speaker**
**BC-I-02**
**Yuma Morimoto**

# Effect of Axial-ligand π-Donor Ability on Reactivity of Compound I Model Complex

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In biological systems, lipophilic compounds undergo metabolism through heme enzymes, which generate oxido-iron(IV) porphyrin π-cation radical known as Compound I as the pivotal reactive intermediate. Studies on Compound I model complexes have shown that the axial ligand controls its reactivity toward alkyl amine and allylic substrate by changing the free energy of the iron(III) resulting complex.[1] However, the impact given by the axial ligand on the electronic state of the iron complexes remains elusive. Furthermore, the axial ligand effect on hydroxylation of aliphatic substrates has yet to be explored due to the limited lifetime of Compound I model complexes during the relatively slow reaction. Recently, we discovered a significant extension in the lifetime of Compound I model complexes in a fluorinated carbon solvent system.[2] Capitalizing on this development, we conducted a systematic investigation into the axial ligand effects on the alkane hydroxylation reaction.

An oxidation reaction of cyclohexane by $Fe^{IV}(O)(TMP^{+\bullet})(L)$ (TMP: 5,10,15,20-tetramesityl-porphyrinato dianion, L: $CF_3COO^-$, $CH_2ClCOO^-$, $Cl^-$, $AcO^-$, $BzO^-$, $F^-$) (**2**$^{L}$, 28 μM) was initiated by adding an excess molar amount of cyclohexane (25–400 mM) to the **2**$^{L}$ solution. From the time trace of electronic absorption spectra of the reaction solution, the pseudo-first-order rate constant ($k_{obs}$) was determined, and the second-order rate constant ($k$) of the cyclohexane hydroxylation reaction was determined from the substrate concentration dependence of $k_{obs}$. The obtained $k$ values differed in the rage of $8.0\times10^{-3}$–$1.2\times10^{-1}$ $M^{-1}$ $s^{-1}$. The ln $k$ values does not depend on the one-electron reduction potential of **2**$^{L}$ or p$K_a$ values of conjugate acid of the axial ligands, whereas shows linear dependence on the wavenumber of the stretching vibration of the Fe–O bond ($\nu_{Fe=O}$) of **2**$^{L}$. The ln $k$ value also shows the linear correlation with the N–O stretching vibration ($\nu_{N-O}$) of $Fe^{III}(NO)(TMP)(L)$ (**3**$^{L}$), which solely reflect the p-donor ability of the axial ligand (**Figure 1**). The origin of the axial ligand effect on the reactivity of **2**$^{L}$ will be discussed in this presentation.

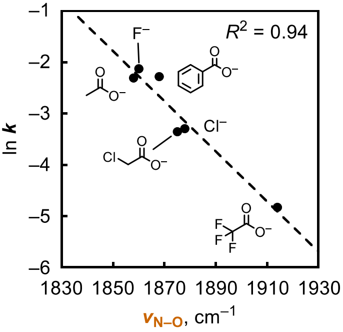

**Figure 1.** Plot of logalism of $k$ (ln $k$) against Raman shift of **3**$^{L}$ asinable to $\nu_{N-O}$ (L: $CF_3COO^-$, $CH_2ClCOO^-$, $Cl^-$, $AcO^-$, $BzO^-$, $F^-$) assigned to Fe–O bond streching vibration ($\nu_{Fe=O}$).

**Keywords**: Compound I Model; Mechanistic Study; Alkane Hydroxylation; p-Donor Ability; Iron-Nitrosyl Complex

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# Modification of NHC Ligand to Make It Suitable for Catalytic Proton Reduction

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N-Heterocyclic carbene (NHC) ligands have the strong σ-donating property that benefits nucleophilic reactions, and in fact, the NHC-transition metal complexes have shown versatile catalytic abilities in organometallic reactions. However, the robust σ-donating property rather becomes a disadvantage in electrocatalysis because it hinders electron transfer from a cathode surface. Thus, new electron transfer pathways need to be devised for NHC complexes, to exploit the strong σ-donating property in electrocatalytic applications. In this talk, we will discuss a unique strategy to modify a NHC type complex to make it suitable for the use in electrocatalytic proton reduction. Typically, strong σ-donating property of NHC ligand requires a large reduction potential energy to form a *trans* metal-hydride, which makes NHC-type complexes inefficient for catalytic proton reduction. A newly synthesized BpyNHC/tpy-Ni complex enabled the formation of catalytically active Ni(II)–H in the *cis* position of the NHC σ-donor. Additionally, we could make a bypass route for electron transfer in BpyNHC/tpy-Ni, without nullifying the NHC's σ-donating ability. The structural features of the complex overcome the intrinsic limitation of NHC complex in electrocatalytic proton reduction; the BpyNHC/tpy-Ni catalyst could show the most efficient catalytic activity among the known NHC-based catalysts.

**Keywords**: NHC; Modified NHC; Electrochemistry; Proton Reduction; NHC-Ni Complex

# Metal-ligand cooperation in dinitrosyl iron complexes for small molecule activation and biomedical application

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Biomimetic study of dinitrosyl iron complexes (DNICs) unravels that the (1) redox-active nature of DNIU, (2) metal-ligand cooperation in DNICs, and (3) facile interconversion between mononuclear and dinuclear DNICs facilitate their reactivity toward small molecule activation, catalysis, and biomedical application.[1-4] In particular, nucleophilic activation of $CO_2$ by dinuclear DNIC $[(NO)_2Fe(-{}^{Me}Pyr)_2Fe(NO)_2]^{2-}$ (**2**, $^{Me}Pyr$ = 3-methylpyrazolate) results in the formation of $CO_2$-captured complex $[(NO)_2Fe(^{Me}PyrCO_2)]^{-}$ (**2-CO₂**, $^{Me}PyrCO_2$ = 3-methyl-pyrazole-1-carboxylate). Single-crystal structure, spectroscopic, reactivity, and computational study unravels **2-CO₂** as a unique intermediate for reductive transformation of $CO_2$ promoted by $Ca^{2+}$. Moreover, sequential reaction of **2** with $CO_2$, $Ca(OTf)_2$, and $KC_8$ established a synthetic cycle, **2** → **2-CO₂** → $[(NO)_2Fe(\mu\text{-}{}^{Me}Pyr)_2Fe(NO)_2]$ (**1**) → **2**, for selective conversion of $CO_2$ into oxalate.[4] In the second part, recent investigation on the ligand control over selective superoxide-mediated NO monooxygenation and superoxide-dioxygen interconversion will be discussed.[1] During the superoxide-induced conversion of DNIC **1** into DNIC $[(K\text{-}18\text{-}crown\text{-}6\text{-}ether)_2(NO_2)][Fe(\mu\text{-}{}^{Me}Pyr)_4(\mu\text{-}O)_2(Fe(NO)_2)_4]$ and an $[Fe^{3+}(^{Me}Pyr)_x(NO_2)_y(O)_z]_n$ adduct, stoichiometric NO monooxygenation yielding $NO_2^-$ occurs without the transient formation of peroxynitrite-derived $\bullet OH/\bullet NO_2$ species. In contrast to DNIC **1**, DNIC $[(NO)_2Fe(\mu\text{-}SEt)_2Fe(NO)_2]$ (**3**) and $[K\text{-}18\text{-}crown\text{-}6\text{-}ether][(NO)_2Fe(\mu\text{-}SEt)_2Fe(NO)_2]$ (**3-red**) display a reversible equilibrium of "**3** + $O_2^-$ ⇋ **3-red** + $O_{2(g)}$", which is ascribed to the covalent $[Fe(\mu\text{-}SEt)_2Fe]$ core and redox-active DNIU.

**Keywords**: Dinitrosyl iron complex; $CO_2$ reduction; superoxide; $H_2$ generation; NO delivery

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# Deciphering a membrane-bound hydrocarbon-producing metalloenzyme

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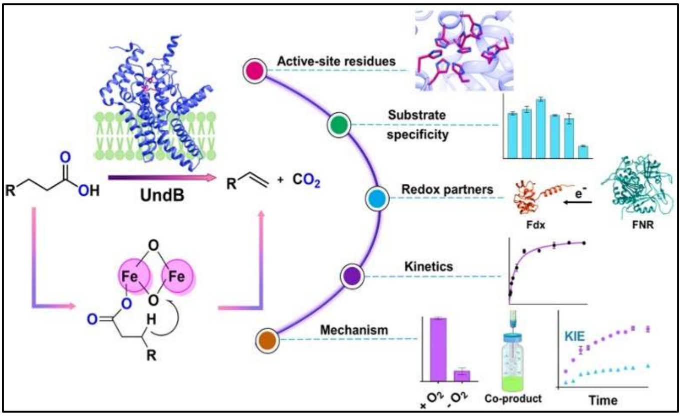
Biosynthetically produced 1-alkenes hold immense value as sustainable alternatives to fossil fuels and find widespread applications in polymer, lubricant, and detergent industries. UndB is the only known membrane enzyme capable of converting naturally abundant fatty acids to 1-alkenes. However, despite diverse applications, UndB remains poorly understood since its discovery nearly a decade ago. We present here insights into the molecular basis of UndB catalysis and the mechanism of UndB reaction at the membrane interface. We unravel UndB as a diiron-enzyme that utilizes a conserved histidine cluster at the active site. We decipher the dependency of UndB activity on molecular oxygen and electrons and identify the most efficient redox partners of UndB. We elucidate the catalytic intricacies of UndB and establish it as the most efficient decarboxylase in producing industrially valuable medium-chain 1-alkenes. Further, we engineer UndB, substantially improve the enzyme's activity, and develop a novel whole-cell biocatalyst utilizing the engineering UndB for highly efficient conversion of naturally abundant free fatty acids to 1-alkenes.



**Keywords**: Metalloenzyme; Biocatalyst; fatty acid decarboxylase; Biofuels

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**Bioinorganic Chemistry (BC)**
**Invited Speaker**
**BC-I-06**
**Way-Zen Lee**

# Reaction Pathways of a Manganese(III) Superoxo Complex with Various Phenols

Yao-Cheng Tian, Kuan-Ting Lin, Chung-Wei Fu, Way-Zen Lee[3*]

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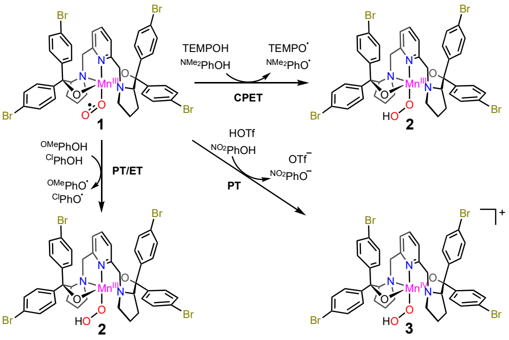
In our long-term investigation on $O_2$ activation facilitated by enzymatic mimics, we have prepared homogeneous Fe$^{III}$-, Co$^{III}$-, and Mn$^{III}$-superoxo complexes via addition of $O_2$ to their divalent precursors at low temperatures.[1-3] The Mn$^{III}$-superoxo complex, Mn(BDP$^{Br}$P)(O$_2^{\bullet}$) (**1**, H$_2$BDP$^{Br}$P = 2,6-bis((2-(S)-di(4-bromo)phenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine), was found to react with TEMPOH yielding a corresponding Mn$^{III}$-hydroperoxo complex, Mn(BDP$^{Br}$P)(OOH) (**2**).[3] Furthermore, treatment of **1** with trifluoroacetic acid (TFA) led to formation of a Mn$^{IV}$-hydroperoxo complex, [Mn(BDP$^{Br}$P)(OOH)]$^+$ (**3**).[4] Reaction of **1** with 4-dimethylaminophenol at −80 °C produces a 4-dimethylaminophenoxy radical, suggesting a concerted proton electron transfer reaction occurs, whereas a high valent Mn$^{IV}$-hydroperoxo **3** is remarkably afforded as complex **1** reacting with 4-nitrophenol in the same reaction conditions, indicating a proton transfer reaction proceeds. Further inspections on the other two phenols, 4-chlorophenol ($^{Cl}$PhOH) and 4-methoxyphenol ($^{MeO}$PhOH), show the reactions of **1** with $^{Cl}$PhOH and $^{MeO}$PhOH via a proton transfer followed by an electron transfer. UV-vis and EPR spectroscopic studies along with DFT calculations were carried out to confirm these three different reaction pathways are proceeded for O-H bond activation of various phenols by the same Mn(III)-superoxo **1**.



**Keywords**: Mn(III)-superoxo; Mn(III)-hydroperoxo; Mn(IV)-hydroperoxo; Concerted Proton Electron Transfer (CPET); Proton Transfer followed by Electron Transfer (PT/ET)

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# Unlocking multi-electron oxidation: harnessing phosphorus-ligand redox cooperativity

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The type of chemistry and catalysis necessary to develop alternative energy sources beyond the C–H bonds found in fossil fuels rely on small molecule (e.g., $H_2$, $O_2$, $CH_4$, etc.) activation processes. These small molecules are potential reservoirs of chemical energies, however, it is challenging to activate these chemicals due to their intrinsically high kinetic barriers accompanying multi-electron, multi-proton reaction sequences. One possible method to circumvent these high-energy pathways is to mediate concerted multi-electron reaction pathways, bypassing high-energy intermediates altogether, thus requiring the development of catalysts capable of mediating multi-electron reactivity. Our group envisioned that the well-established two-electron process in main-group elements, such as phosphorus, would allow four-electron redox reactions when used in combination with a redox cooperative ligand. To test this idea, our group synthesized the geometrically distorted phosphorus complex that can relay two electrons at the phosphorus center and another two electrons at the ligand via an aromatization-dearomatization process. In this symposium, I will introduce how modulation of the electronic structure of main group elements can activate small molecules and establish a connection to the chemistry of cytochrome P450.

**Keywords**: four-electron redox; redox cooperativity; cytochrome P450; oxygen reduction; geometrically distorted complex

# Functional and structural roles of supporting components for the methane hydroxylation in soluble methane monooxygenase

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Methane ($CH_4$), a greenhouse gas, has a higher heat capacity than carbon dioxide ($CO_2$), and reducing this harmful gas is critical to achieve the goal of carbon neutrality. Methanotrophs converts methane gas to methanol through soluble methane monooxygenase (sMMO) in a copper-limited condition. Unlike particulate methane monooxygenase (pMMO), sMMO is a superfamily of bacterial multi-component monooxygenase that requires hydrocarbons, molecular oxygens, electrons, and protons as substrates. For the catalytic functions of sMMO, there is a hydroxylase (MMOH), a regulatory component (MMOB) and a reductase (MMOR), while gene maps of sMMO have conserved components including *mmoR* and *orfY,* which express to MmoR and MMOD, respectively. It was proposed that MMOD works as a copper regulator for the transcriptional regulation of sMMO and pMMOD expression. MmoR is postulated as a transcriptional regulator based on the copper concentration, although the biochemical mechanisms are not fully understood.

In this paper we present its biochemical aspects with the over-expressed MMOD and MMOR from *Methylosinus sproium* 5. The MMOH-MMOD complex indicated that MMOD works as a inhibitor because it disrupts the coordination of the diiron active site and shifts the four-helix bundle including B, C, E, and F helices that house the diiron active site. The purified MmoR indicated that it binds to a specific sequence that positions the promoter sequence of MMOH. It was proved that MmoR regulates transcription with sigma54 ($\sigma^{54}$) in the presence of ATP. It is postulated that these two enzymes coordinate with copper ions, although the purified enzymes did not show evidence of binding to copper ions.

**Bioinorganic Chemistry (BC)**
**Invited Speaker**
**BC-I-09**
**Shin Aoki**

# Optical Resolution of Cyclometalated Iridium(III) Complexes and Its Applications

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Herein we report on the optical resolution of synthesis of optically pure cyclometalated iridium(III) (Ir(III)) complex-peptide hybrids as amphiphilic peptide conjugates (IPH-ACs)[1] and the effect of the stereochemistry with respect to their Ir(tpy)$_3$ (tpy: 2-(4'-tolyl)pyridine) core on their cytotoxicity against cancer cells. Intrinsically, Ir(III) complex cores adopt octahedral or pseudo-octahedral 6-coordinated structures, and hence possess metal-centered chirality, delta (*D*) form and lambda (*L*) forms.[2] In this work, the racemic carboxylic acids of Ir(III) complexes (*fac*-Ir(ppyCO$_2$H)$_3$ (ppy: 2-phenylpyridine), *fac*-Ir(tpyCO$_2$H)$_3$ (tpy: 2-(4'-tolyl)pyridine)), and *fac*-Ir(mpiqCO$_2$H)$_3$ (mpiq: 1-(4'-methylphenyl)isoquinoline)) were converted to the corresponding diastereomers by the condensation with (1*R,*2*R*)-2-aminocyclohexanol, which were separated by HPLC (with non-chiral column) or silica gel column chromatography, followed by the hydrolysis of the ester moieties, as we reported very recently.[3] It was found that both optically pure *D*- and *L*-forms of IPH-ACs induce paraptotic cell death[1,4] in Jurkat cells and the EC$_{50}$ values were evaluated by MTT assays. The measurement of the intracellular uptake of *D*- and *L*-forms of IPH-ACs in the cells and their EC$_{50}$ values against Jurkat cells indicate that the intrinsic cytotoxicity is almost equal for the *D*- and *L*-forms and that their different cytotoxicity against Jurkat cells is due to the selectivity in their intracellular uptake.[5]

**Keywords**: iridium complex; cancer cell death; optical resolution; paraptosis

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# Cationic zinc porphyrin-based photocatalytic system with biocatalyst for fumarate synthesis from $CO_2$

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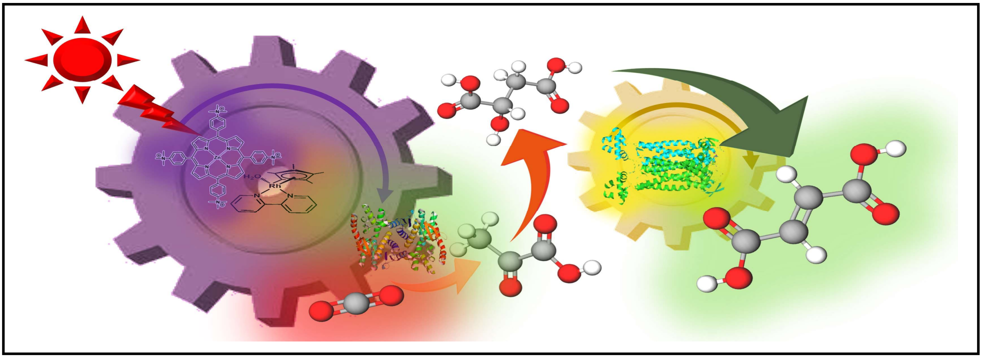
Fumaric acid is a useful unsaturated dicarboxylic acid that serves as a precursor for the biodegradable plastics such as poly(butylene succinate) and poly(propylene fumarate). Fumaric acid is mainly synthesized from oxidation of petroleum resources such as benzene or butene, resulting in large amounts of $CO_2$ emissions during the production process. Thus, it is desirable to construct methods to produce fumaric acid from renewable resources such as biomass derivative pyruvate, $CO_2$ and so on. In this work, an effective visible-light driven fumarate production from gaseous $CO_2$ and pyruvate with the system consisting of triethanolamine, cationic water-soluble zinc porphyrin, zinc tetrakis(4-*N*,*N*,*N*-trimethylaminophenyl) porphyrin ($ZnTMAP^{4+}$), pentamethylcyclopentadienyl coordinated rhodium 2,2'-bipyridyl complex ($[Cp^*Rh(bpy)(H_2O)]^{2+}$), $NAD^+$, malate dehydrogenase ($NAD^+$-dependent oxaloacetate-decarboxylating; MDH) and fumarase (FUM) was developed. In this system, the turnover number and turnover frequency of FUM (1.3 nM) were estimated to be 76769 and 4.3 $s^{-1}$, respectively. It was found that unsaturated dicarboxylate, fumarate was produced from pyruvate and gaseous $CO_2$ by applying dual biocatalysts (MDH and FUM) as a catalyst for the visible-light driven $NAD^+$ to NADH regeneration with $ZnTMAP^{4+}$ and $[Cp^*Rh(bpy)(H_2O)]^{2+}$ for the first example.[1,2]



**Keywords**: zinc porphyrin; dual biocatalysts; $CO_2$ utilization; fumarate; Rh coordination complex

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# Synthesis and antimicrobial activity of amino acid Schiff base copper complexes with azo groups

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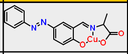
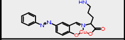
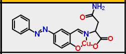
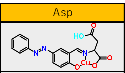
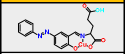
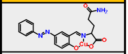
Some copper-based Schiff bases compounds have superoxide dismutase (SOD) mimetic activity; SOD is one of the most important antioxidant enzymes that catalyze the disproportionation of superoxide anions to hydrogen peroxide and molecular oxygen [1]. Our laboratory has also investigated other biological activity of amino acid Schiff base copper complexes [2]. Our previous studies revealed that Schiff base copper(II) complexes, which have been systematically synthesized using amino acids as ligands, showed antimicrobial activity. Among them, copper(II) complexes with Ser, Leu, Ala, and Thr moiety showed predominantly activity. However, the problem in these experiments was that the hydrophilicity was too high.

Therefore, introducing azo groups, we synthesized, identified, and investigated the antimicrobial activity of Schiff base copper(II) complexes with increased hydrophobicity. Indeed, not only the azobenzene moiety in its *trans* form is hydrophobic, but it can change shape, polarity, geometry, and physicochemical properties upon UV illumination. We also investigated antimicrobial activity with ligands to determine the extent to which copper(II) ions affect antimicrobial activity.
As a result, 17 copper(II) complexes were successfully synthesized. The evaluations of antimicrobial activity against *E. coli* in the dark and under UV irradiation will be reported at the conference.

| **Labels** | Ala | Arg | Asn | Asp | Glu | Gln |
|---|---|---|---|---|---|---|
| **Structure** |  |  |  |  |  |  |
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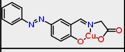
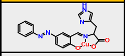
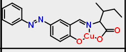
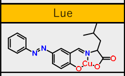
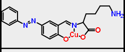
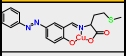
| **Structure** |  |  |  |  |  |  |
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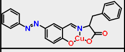
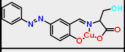
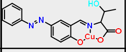
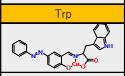
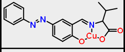
| **Structure** |  |  |  |  |  | - |
| **Molecular weight** | 434 | 374 | 388 | 479 | 386 | - |
| **Amino acid** | Phe | Ser | Thr | Trp | Val | - |

**Keywords**: copper complex; azo-coupled-amino acid Schiff base; antibacterial activity

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# Nickel(II) with Schiff base complex: experimental and computational studies of CT-DNA binding

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3,5-dibromo-*N*-(8-quinolyl)salicylaldimine ($HqsalBr_2$) and its nickel complex, $[Ni(qsalBr_2)_2]$, have been synthesized and characterized. Molecular structure of the complex was determined by single crystal X-Ray crystallography and computationally studied using B3LYP/LANL2DZ level of DFT in Gaussian 09. The optimized bond lengths are in agreement with the reported experimental values. The interaction of the complex with DNA was investigated using calf thymus DNA (CT-DNA) in which electronic absorption and luminescence titration revealed the intercalative mode of binding between the complex and CT-DNA. The study provides great value of binding constant ($K_b$) of $6.02 \times 10^5$ and the quenching constant values ($K_q$) of $7.22 \times 10^{11}$. Anti-lung cancer activity against A549 cell line was examined and compared with standard compounds, Etoposide and Cisplatin. Additionally, the complex was docked into the DNA (PDB: 1bna) and lung cancer (PDB: 7ukv) using molecular docking studies to gain insight into the binding interactions. The result showed the negative binding energy toward both DNA (-9.1 kcal/mol) and lung cancer (-9.3 kcal/mol) through the hydrogen bonds and hydrophobic interactions.

**Keywords**: Schiff base; DNA-binding; Crystal structure; Anti-lung cancer, DFT calculation

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**Bioinorganic Chemistry (BC)**
**Poster Presentation**
**BC-P-01**
**Suman Patra**

# Second Sphere Interaction in a Molecular Iron Catalyst Allows Selective $CH_4$ Production from CO

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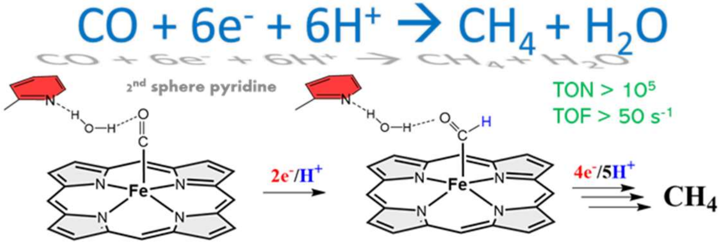
Reduction of oxides of carbon (CO and $CO_2$) into fixed forms of carbon is desirable to achieve sustainable and clean energy. Carbon monoxide (CO), an intermediate product in $CO_2$ reduction, is challenging to reduce which, in turn, jeopardizes the direct reduction of $CO_2$ beyond $2e^-/2H^+$ to products like $CH_3OH$ and $CH_4$. Iron porphyrins can efficiently reduce $CO_2$ to CO by $2e^-/2H^+$ but further reduction is halted by rapid dissociation of CO from the reduced iron center. This work shows that CO can indeed be reduced upon inclusion of a pendent pyridine in the second coordination sphere of an iron porphyrin complex efficiently and selectively to $CH_4$ using water or Phenol as the proton source. In-situ spectro-electrochemistry supported by theoretical calculations indicate that the pendent pyridine moiety imposes a hydrogen bonding interaction between the bound CO and water which stabilizes two low-valent CO adducts, i.e. Fe(I)-CO and Fe(0)-CO, of iron porphyrins, allowing its complete reduction, via a Fe(II)-CHO species, to $CH_4$. The ability to activate and reduce CO by $ne^-/nH^+$ via second sphere hydrogen bonding interaction in a mononuclear iron porphyrin opens newer pathways to valorize both CO and $CO_2$ to valuable $C_1$ products.



**Keywords**: Electrochemical carbon dioxide and carbon monoxide reduction; Iron Porphyrin; Pendent pyridine; Gas Chromatography; Spectro-electrochemistry coupled FTIR

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# Heme-Aβ in SDS micellar environment: Active site environment and reactivity

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Alzheimer's disease (AD), the most common cause of dementia, is a progressive neurodegenerative disorder that causes brain cell death. Oxidative stress derived from the accumulation of redox cofactors like heme in amyloid plaques originating from amyloid β (Aβ) peptides has been implicated in the pathogenesis of AD. In the past our group has studied the interactions and reactivities of heme with soluble oligomeric and aggregated forms of Aβ. In this manuscript we report the interaction of heme with Aβ that remains membrane bound using membrane mimetic SDS (sodium dodecyl sulfate) micellar medium. Employing different spectroscopic techniques, we find that Aβ binds heme using one of its three His (preferentially His13) in SDS micellar medium. We also find that Arg5 is an essential distal residue responsible for higher peroxidase activity of heme bound Aβ in this membrane mimetic environment than free heme. This peroxidase activity exerted by even membrane bound heme-Aβ can potentially be more detrimental as the active site remains close to membranes and can hence oxidise the lipid bilayer of the neuronal cell, which can induce cell apoptosis. Thus, heme-Aβ in solution as well as in membrane-bound form are detrimental.

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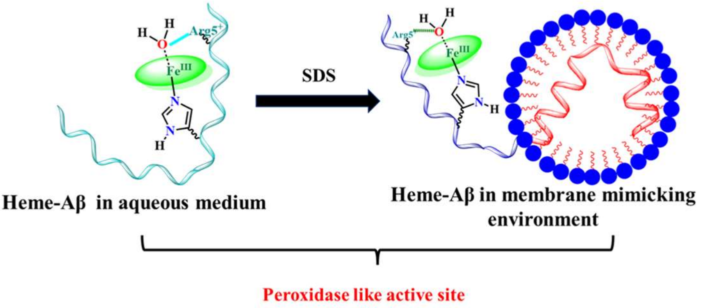

**Keywords**: Amyloid β, Heme, SDS micelle, Alzheimer’s disease, peroxidase activity

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# Reconstitution of a hemophore from *Acinetobacter baumannii* for applications in antibacterial therapy

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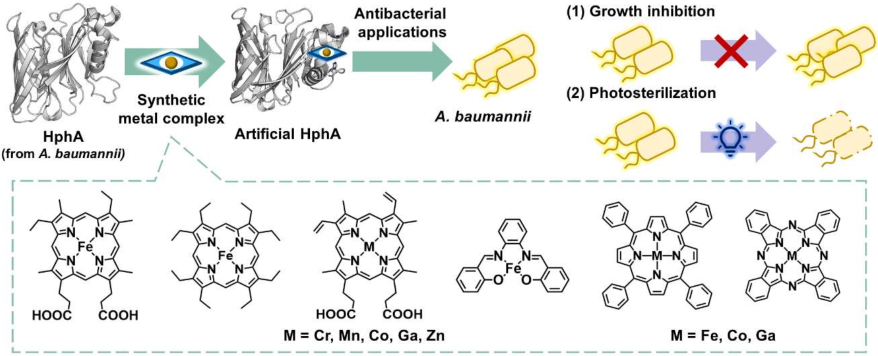
*Acinetobacter baumannii* is a gram-negative and opportunistic bacterial pathogen which is infamous for its multidrug resistance. A recent study has reported that under iron restrictive conditions, *A. baumannii* can secrete a hemophore called HphA to obtain heme from hosts for use as an iron source.[1] Meanwhile, our group has been researching about another hemophore, HasA, which is secreted by some other gram-negative bacteria for the same purpose. We have succeeded in the reconstitution of HasA with various synthetic metal complexes through heme substitution, and applied the artificial HasA proteins to the treatment of *Pseudomonas aeruginosa* by exploiting the bacterial heme uptake system.[2] Although HphA and HasA have significantly different structures and heme coordinating ligands, they share some properties, such as the high exposure of heme binding pocket. Therefore, we proposed that it is possible to also incorporate non-native metal complexes into HphA.

In this work, we first confirmed that HphA can incorporate various synthetic metal complexes, including some tetraphenylporphyrin and phthalocyanine complexes (structures shown below). Then, some of the artificial HphA proteins were investigated for their antibacterial activity against *A. baumannii* (growth inhibitory effect and application in photosterilization), and we discovered some potential candidates for treatment of the pathogen.



**Keywords**: hemoproteins; artificial metalloproteins; *Acinetobacter baumannii*; antibacterial therapy

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# DFT Mechanistic Insights into Nitric Oxide Generation from Nitrite via O-atom Transfer in the Unsymmetrical β-Diketiminato Copper(II) Complexes

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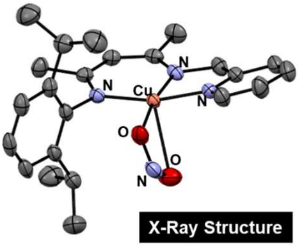
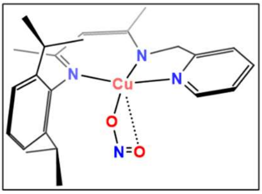
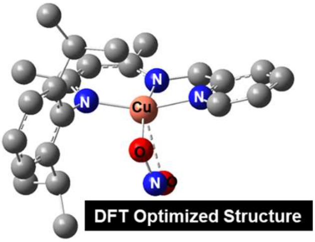
The unsymmetrical ß-diketiminato copper(II) complex **[LCuONO]** has been demonstrated to serve as an effective bioinspired model for copper-containing nitrite reductases (CuNiRs). With the presence of two equivalents of triphenylphosphine ($PPh_3$), **[LCuONO]** undergoes an oxygen atom transfer (OAT) reaction, leading to the conversion of nitrite into nictric oxide (NO) along with $Cu^I$-$PPh_3$ and O=$PPh_3$ formation[1]. In this study, we investigated the mechanism behind the NO generation from nitrite via OAT by density functional theory (DFT) calculation. The computational analysis unfolds in two stages: (a) Introduction of one $PPh_3$ to prompt the OAT, yielding O=$PPh_3$ and Cu-NO as products; (b) Introduction of another $PPh_3$ to facilitate a substitution reaction, liberating NO. Several pathways started from different copper(II) nitrite isomers have been proposed in accordance with the reaction species[2]. To understand how $PPh_3$ induces OAT to produce O=$PPh_3$ and Cu-NO, we explored the distinct approaches involving in $PPh_3$ coordination to Cu(II) center and interaction between $PPh_3$ and O or N atom on nitrite moiety. Given that the final product, $Cu^I$-$PPh_3$, has been observed as a tricoordinate species with an open pyridyl arm, we examined different coordination modes and conducted corresponding orbital analysis on the Cu(I) species engaged in the pathway. Finally, the calculation result will be evaluated by comparing with the previous experimentally kinetic data.



X-Ray Structure



[LCuONO]



DFT Optimized Structure

**Keywords**: Nitrite Reductase; Unsymmetrical β-Diketiminatio Cu(II) Complexes Oxygen Atom Transfer; Mechanism Investigation; DFT Calculation

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# Study of Tyrosine activation for Di-tyrosine Cross-linking Catalyzed by Transition Metal Ion with Reactive-Oxygen Species

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Amyloid fibrils that are considered to be the cause of Alzheimer's disease(AD) are highly stable and insoluble amyloid plaques in the neuropil. Redox-active metal ions such as $Cu^{2+}$, and $Fe^{3+}$ have been suggested to play a key role in many neurodegenerative disorders including Alzheimer's disease1). Metal-protein interactions could result in oxidative stress through generation of reactive oxygen species(ROS) such as $H_2O_2$. In 2013 Al-Hilaly et al. investigated the formation of di-tyrosine cross-links in the amyloid-β (42) peptide by covalent coupling of two tyrosine residues, which has been implied to play a key role in the development of the Alzheimer's disease2). In this point of view, using density functional theory we studied about tyrosine radical formation and di-tyrosine cross-linking catalyzed by several transition metal ions such as Fe(II), Cu(II), Cu(I), Co(II) and Ni(II) with $H_2O_2$ as the ROS in B3LYP/Def2-TZVPP level.

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# Selectivity of C—H oxidation by iron pincer complex with crown ether moiety

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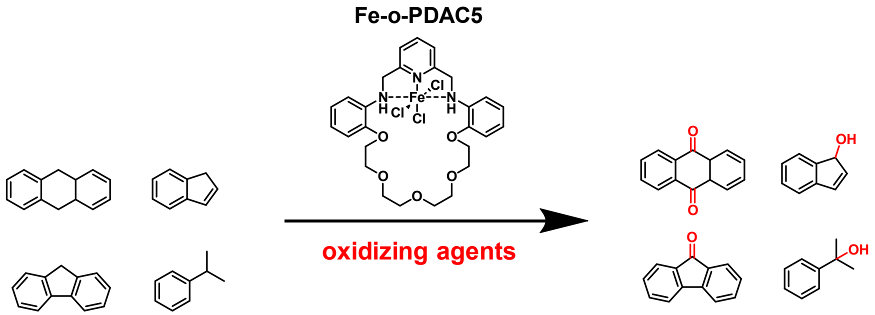
C—H oxidation is a prominent research area due to its various utilization in organic synthesis and functionalization. Without catalysts, the inertness of the C—H bonds usually leads to the low selectivity and inefficiency. Iron complex based on pyridine and amine ligands, with appended crown ether ring, has been reported to enhance catalytic oxidation of C—H bonds in the presence of additional redox inactive cations such as Ba$^{2+}$. Herein, we explored oxidation of C—H bond with various strengths, catalyzed by the same Fe complex. The effects of using multiple oxidants, such as hydrogen peroxide or *meta*-chloroperoxybenzoic acid (mCBPA), toward product selectivity were investigated. Products from oxidation of 9,10-dihydroanthracene, fluorene, indene, and cumene were analyzed to establish trends in selectivity of this Fe catalyst. These results could be developed into a model for C—H oxidation selectivity, for both HAT and OAT, leading to the optimal conditions of the oxidation reaction.



**Keywords**: C—H oxidation; bond dissociation energy; iron pincer complex; oxidizing agents

# Nickel Schiff base complexes containing pendant proton for catalyzing hydrogen evolution reaction

Tassaneewan Soisuwan[1], Teera Chantarojsiri[1*]

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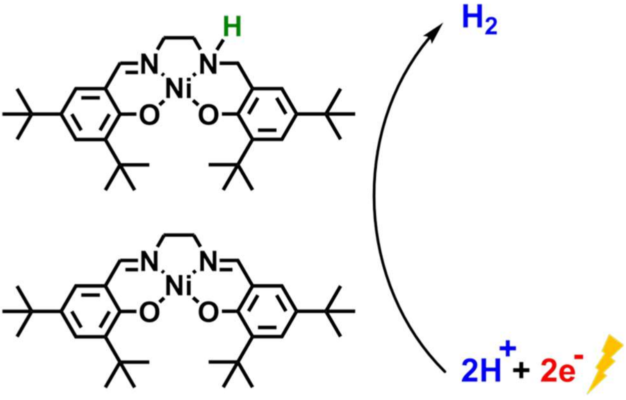
Metal hydrides are important intermediates for electrocatalytic hydrogen evolution reaction (HER). To stabilize the high energy intermediate and to facilitate proton movements during the reaction, secondary coordination sites for proton binding were employed. A series of nickel complexes supported by Schiff base ligand and reduced derivatives, containing pendant proton as a secondary coordination sphere to facilitate proton movement, were synthesized and characterized. Nickel complexes with reduced Schiff base ligands, containing extra N—H moiety exhibited more positive Ni(II/I) reduction potential. Cyclic voltammetry with additional protons showed current enhancement at -1.93 V vs $[Fe(C_5H_5)_2]^{+/0}$. UV-vis spectroscopy titration with acids suggested protonation of Ni complexes occurred before reduction to produce $H_2$. Controlled potential electrolysis in the presence of proton showed the electrocatalytic activities of complexes for $H_2$ evolution. Moreover, the role of pendant proton and catalytic activity of complexes were also investigated by density functional theory (DFT).



**Keywords**: electrochemical hydrogen evolution; pendant proton; nickel Schiff base complexes

# Inhibition Effects of Tridentate Hydrazone Ligands as Corrosion Inhibitors on Mild Steel in $CO_2$ Environment

Balqis Auni Badrul Hisyam[1], Zainiharyati Mohd Zain[2], Nurulfazlina Edayah Rasol[1,3] and Amalina Mohd Tajuddin [1,3*]

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Four tridentate hydrazone ligands (AL01, AL02, AL03, AL04) were synthesized via condensation process between hydrazides; 2-hydroxybenzohydrazide and benzohydrazide with different substituents; OH, and H of aldehydes and ketones. The ligands were characterized by melting point, FTIR, NMR, elemental analysis, UV-Vis, LC-MS and single X-Ray crystallography. The formation of hydrazone ligands was confirmed by the appearance of *v*(C=N) peak in the range of 1605 to 1648 $cm^{-1}$. The mass-to-charge (m/z) $[M+H]^+$ values of AL01 and AL02, which are 242.09 and 226.10, respectively, gave further confirmation of their structures. Compounds AL03 and AL04 were structurally confirmed by single X-ray crystallography with AL03 crystallizes in orthorhombic space group Pbca with a = 12.8190(6) Å, b = 11.8299(6) Å, c = 16.9586(9) Å, and AL04 crystallizes in orthorhombic space group Pbcn with a = 19.116(2) Å, b = 8.0380(12) Å, c = 16.214(2) Å. The influence of hydrazone ligands with different concentrations as corrosion inhibitors on mild steel in 3.5% NaCl solution saturated with $CO_2$ was examined using polarization, electrochemical impedance spectroscopy (EIS). The elemental composition of protective layer forms on mild steel immersed in the solution was further observed using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX).

**Keywords**: $CO_2$; Corrosion Inhibitor; Mild Steel; Protective Layer; Tridentate Hydrazones;

# Iron Speciation and Localization in Yeast: Impact of Growth Phase and Nutrient Composition

Jinkyu Park[1,2*], Yujin Jeong[1], Seeun Kim[1]

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Regulating iron (Fe) homeostasis is crucial for preserving cellular energy metabolism and preventing damage from reactive oxygen species and Fe overload. This study investigates the dynamics of Fe homeostasis in the fungal yeast *Saccharomyces cerevisiae* across various growth modes and nutrient compositions using Mössbauer spectroscopy,[1-3] nano secondary ion mass spectrometry (NanoSIMS), electron microscopy (EM), and diverse techniques.

During the shift from exponential to stationary growth phases, cellular Fe concentration significantly increased. The predominant form, mononuclear nonheme high spin (NHHS) Fe(III), localized within the vacuole, accompanied the accumulation of Fe(III) nanoparticles (NP). Elevated glucose levels promoted NP formation, while increased amino acids and nucleotide bases hindered it. Adenine deficiency induced the reduction of the major Fe form to NHHS Fe(II) in the cytosol. Initially presumed in the vacuole, Fe(III) NP were also detected in the cell wall based on Mössbauer and other evidence. NanoSIMS and EM data strongly supported the hypothesis that the cell wall serves as an additional site for Fe trafficking.

This comprehensive analysis illuminates the intricate mechanisms governing Fe homeostasis, highlighting the dynamic interplay between growth modes and nutrient compositions in *S. cerevisiae*.

**Keywords**: Fe homeostasis; fungal yeast; Fe speciation; Fe localization

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# Metal Ion Induced Dihydro-Imidazopyridium Salts and Their Skin Protection against UVB Irradiation

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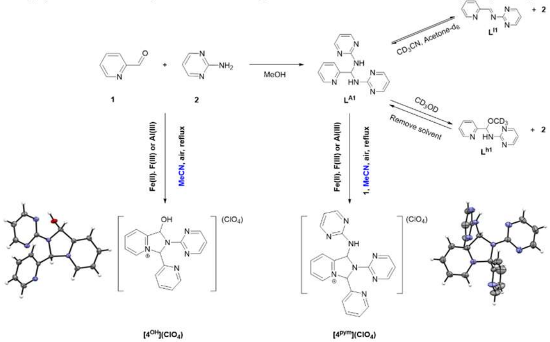
Photoprotection is the process to prevent the skin against damages caused by solar radiation. It involves in two key factors: (a) screening sunlight by reflecting, scattering, or absorbing light; (b) interfering in the sunlight-induced photochemical cascade, such as quenching ROS and repairing DNA. Herein, we synthesized two novel dihydro-imidazopyridium salts **[4$^{pym}$](ClO$_4$)** and **[4$^{OH}$](ClO$_4$)** and examined their potential for photoprotection. **[4$^{pym}$](ClO$_4$)** and **[4$^{OH}$](ClO$_4$)** are derived from the dynamic covalent pyrimidyl aminal $L^{A1}$. In this dynamic aminal system, the ratio of corresponding imine, aminal, hemiaminal, and hemiaminal ether can be modulated by solvent effect.[1] Building upon this property, we further found treatment of 2-pyridinecarboxaldehyde **(1)** with $L^{A1}$, in the presence of Fe(II), Fe(III) or Al(III) in $CH_3CN$, resulted in the formation of **[4$^{pym}$](ClO$_4$)**. When the reaction was carried out in a one-pot manner, the major product was **[4$^{OH}$](ClO$_4$)**, which consists a hemiaminal and **1.** We assessed their cytotoxicity towards HaCaT cells using the alamarBlue Assay and found that **[4$^{pym}$](ClO$_4$)** displayed no significant cytotoxicity at 200 μM, but **[4$^{OH}$](ClO$_4$)** decreased cell viability to 90% at 100 μM. To evaluate the photoprotective potentials of **[4$^{pym}$](ClO$_4$)** and **[4$^{OH}$](ClO$_4$)**, we preliminarily studied the cell viability after UVB exposure and antioxidant activity. Our results indicated both of them exhibited a notable photoprotective effect after UVB irradiation with 20 mJ/cm$^2$. UV-Vis spectra analysis unveiled the UVB-blocking capabilities of both **[4$^{pym}$](ClO$_4$)** and **[4$^{OH}$](ClO$_4$)** through absorption. The DPPH assay demonstrates that **[4$^{pym}$](ClO$_4$)** exhibits superior free radical scavenging activity compared to both ascorbic acid and **[4$^{OH}$](ClO$_4$)**. This study will also include the molecular docking results between the two dihydro-imidazopyridium salts and corresponding proteins to provide insight into the structure-property-activity correlation.



**Keywords**: UVB Irradiation, Photoprotective, Dynamic Aminal System, Metal ions Effect

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# Catalytic Coordination Chemistry (CA) Abstract

# Photocatalytic valorization of biomass and non-biodegradable plastics by vanadium coordination complexes

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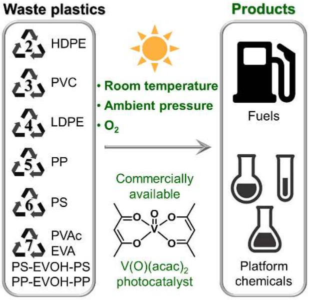
Artificial photosynthesis has been recognized as a sustainable approach to harvest solar energy for energy storage and chemical transformations. In view of this, my team has been working to unify the scalability of artificial photosynthesis with the upcycling of "waste" by photoredox catalysis as alternatives to water oxidation. In this presentation, I will highlight our results in applying vanadium coordination complexes for upcycling materials that are often considered as "waste", such as non-food biomass and plastics, by selective, ambient condition, photoredox C-C cleavage reactions. We used vanadium photocatalysts for the C-C bond activation and functionalization of unactivated, commercially sourced alcohols, polyethylene mono-alcohol,[1] and bioactive small molecules.[2] Recently, we extended our technology to upcycle almost all polyolefins, including polyethylene, polypropylene, polystyrene, polyvinyl chloride, and even multi-layered packaging materials into carboxylic acid platform chemicals at ambient temperatures and pressures.[3] We propose that these photocatalytic reactions illustrate the power of coordination complexes for integrated artificial photosynthetic systems that can be used in the upcycling of plastics and other waste with the concurrent production of solar fuels.



**Keywords**: plastics upcycling; photocatalysis; vanadium complexes; biomass valorization

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# Development of Molecular Catalysts for Photosynthetic Reactions

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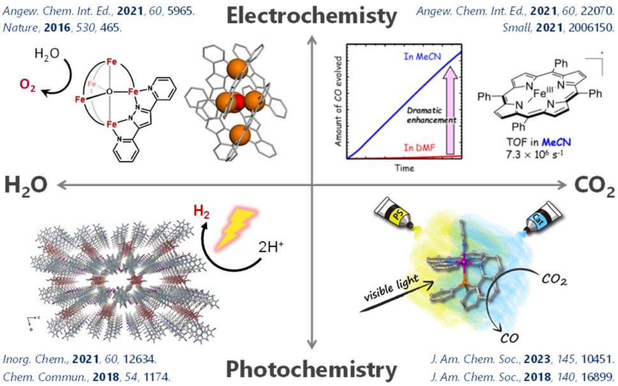
Photosynthesis is a biochemical reaction that converts carbon dioxide and water into carbohydrates and concomitantly stores the energy of sunlight into the products (carbohydrates) as chemical energy. In photosynthetic reactions, solar energy is converted to electrochemical energy via charge separation, and the resulting electrochemical potentials triggers multi-electron redox reactions of small molecules. To artificially reproduce the photosynthetic reactions, our group has investigated the development of molecular catalysts for small-molecule conversions involving multi-electron transfer. These studies can be an important science and technology that contributes to solving energy and resource problems. Recent achievements in our group include (i) development of pentanuclear complexes as active centers for photo- or electrochemical small-molecule conversions, (ii) construction of highly efficient catalytic systems for photo- or electrochemical small-molecule conversions, and (iii) investigation of photo- or electrochemical insertion of small molecules into low-reactive organic molecules.

**Keywords**: Multinuclear metal complex; electron transfer; oxygen evolution; carbon dioxide utilization; artificial photosynthesis



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**Keynote Speaker**
**CA-K-03**
**Ryota Sakamoto**

# 2D MOFs Act as Hydrogen Evolution Cocatalysts for Overall Photocatalytic Water Splitting

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Water-splitting semiconductor photocatalysts require hydrogen evolution reaction (HER) cocatalysts, the majority of which are robust metals and metal oxides. Metal complexes feature designability and reaction selectivity. This feature should be appreciated in the application as HER cocatalysts by suppressing unfavorable back reactions; however, low stability hampers their application. In this research, we demonstrate that a fully π-conjugated and conductive two-dimensional metal–organic framework (2D MOF), which possesses both virtues of metals/metal oxides and metal complexes, serves as an ideal HER cocatalyst candidate. NiBHT, a kind of 2D MOF, is deposited on the photocatalyst $SrTiO_3$:Al with $CoO_x$ as an oxygen evolution cocatalyst to show long-term overall one-step water splitting with an apparent quantum efficiency (AQE) of 6.5% at 350 nm. In comparison to Pt as a representative HER cocatalyst, NiBHT turns out to be a suppressor of back reactions related to oxygen reduction reactions, which is proven both experimentally and theoretically.

**Keywords**: metal–organic framework; nanosheet; photocatalyst; water splitting; low-dimensional material

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**Catalytic coordination chemistry (CA)**
**Keynote Speaker**
**CA-K-04**
**Bun Yeoul Lee**

# Development of Ethylene Tetramerization Catalyst Avoiding Use of MAO: From Flask to Industrial Process

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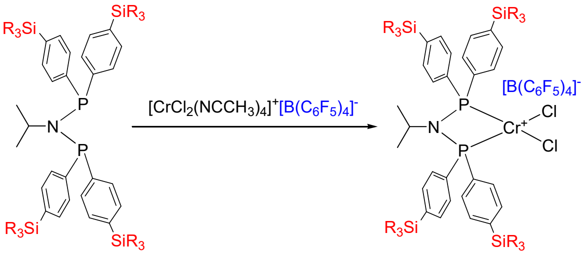
1-Octene is employed as a comonomer in ethylene polymerization processes, and its demand has surged in tandem with the expanded production capacity of linear low-density polyethylene (LLDPE) and polyolefin elastomer (POE). In the early 2000s, Sasol introduced a Cr-based catalytic system that yields 1-octene as the primary product. The original Sasol tetramerization catalyst comprises $Cr(acac)_3$, $iPrN(PPh_2)_2$ (abbreviated as PNP ligand), and a costly modified-methylaluminoxane (MMAO). In large-scale commercial applications employing the original Sasol system, the utilization of excess costly MMAO (Al/Cr, ~500) presents an economic drawback. Despite the notably high reported activity of the typical Sasol system based on Cr (1200 kg/g-Cr), the productivity calculated with respect to the feed amount of MMAO remains unsatisfactory (~2.0 kg/g-MMAO). As a result, endeavors have been undertaken to substitute the expensive MMAO with cost-effective $iBu_3Al$ or $Et_3Al$, in conjunction with stoichiometric quantities of discrete non-coordinating anions (e.g., $[Ph_3C]^+[B(C_6F_5)_4]^-$ or $[PhN(H)Me_2]^+[B(C_6F_5)_4]^-$). However, many of these attempts have unsuccessful. Eventually, we developed active catalytic system that effectively employs the widely available trialkylaluminum $R_3Al$, thus eliminating the need for expensive MMAO.[1–4] Its development story along with activities for its commercialization will be presented.



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# Nanocatalysts for a low-carbon society: upgrading chemicals by hydrogenation

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Hydrogenation reactions using green hydrogen are indispensable for the energy storage and material synthesis without a great deal of $CO_2$ emission. Electrochemical $CO_2$ reduction ($eCO_2R$) or hydrogenation attracts much attention as a technology for carbon circulation on the earth and the selective $eCO_2H$ into high value-added chemicals is increasingly demanded. We demonstrated variable selectivity using hydroxide-derived copper electrodes having a controlled OH amount.[1] Furthermore, CuPd nanoalloys were found to exhibit unique selectivities depending on the mixing pattern of the alloy[2] and $eCO_2R$ from air containing $CO_2$ was achieved on a Cu network electrode[3]. Highly efficient electric power storage is possible by using a structure controlled $TiO_2$ catalysts. Glycolic acid (GC) and oxalic acid (OX) are focused as a redox couple due to their stability and transportability as energy-storage media.[4]
The oxide based electrocatalysts for oxygen evolution reaction were also developed.[5] Furthermore, we demonstrated electrochemical synthesis of amino acids from an organic acid with a nitrogen source by applying the $TiO_2$ electrode highly efficiently.[6]
Efficient thermal hydrogenation reactions such as ammonia synthesis are also demanded. We conducted the highly sensitive modulation-excitation infrared spectroscopy, under reaction conditions for Ru based ammonia synthesis catalysts, which elucidated detailed reaction mechanism of ammonia synthesis.[7, 8]

**Keywords**: Electrochemical $CO_2$ reduction; Amino acid; Ammonia

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# "Catch-and-release" strategy for selective oxidation of hydrocarbons in aqueous media

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As can be seen in enzymatic reactions, selective and efficient conversion of organic substrates to desired products should be important for the construction of sustainable society. So far, tremendous efforts to achieve required reactivity and selectivity have been devoted; however, more improvement should be gained.[1]

Inspired by functionality of oxidation enzymes, we have prepared Fe complexes bearing hydrophobic second coordination spheres (SCSs) made of aromatic substituents and applied them to catalytic oxidation of hydrocarbons including methane in aqueous media. Using $Na_2S_2O_8$ as an oxidant, an Fe(II) complex having hydrophobic SCS made of four anthracenyl groups showed 83% selectivity in methane-to-methanol conversion and high efficiency affording turnover number (TON) of 500 for 3 h in $D_2O/CD_3CN$ (95:5, v/v) at 323 K.[2] This catalytic system has been also applied to oxidation of other gaseous alkanes to obtain the corresponding alcohols as 2-electron oxidized products in high selectivity. In sharp contrast, the corresponding alcohols were not catalytically oxidized, indicating the clear discrimination of hydrophilic substrates. The selectivity is derived from "catch and release" mechanism, in which hydrophobic substrates are captured to be oxidized and hydrophilic products are released to the aqueous medium.

Mechanistic insights into the methane oxidation will be also presented.

**Keywords**: iron complexes; proton-coupled electron transfer; hydrophobic second coordination sphere; catch-and-release strategy; selective oxidation

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# Palladium-complex catalyzed difunctionalization of 1,3-diene with disilane and amine/alcohol

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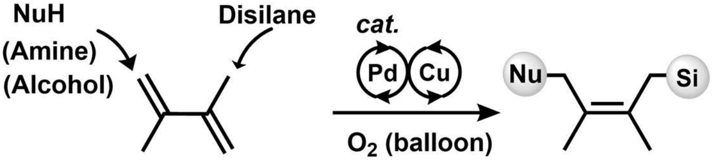
The significance of difunctionalization reactions involving 1,3-dienes has been acknowledged for decades.[1] This recognition stems from the ready availability of diene substrates and the ability to form two chemical bonds in a single step. Such synthetic chemistry can provide complex chemical entries with high control over both regiochemistry and stereochemistry. While most studies of diene chemistry primarily focus on the formation of C-C bonds, some have reported metal-catalyzed reactions to form C-C and C-Si bonds.[2] As an alternative approach, alkene oxidative coupling reactions have emerged as powerful tools in organic synthesis. These reactions have been successfully applied by our group to form C–C, C–N or C-Si bonds.[3] In this presentation, we report a palladium-complex catalyzed difunctionalization of 1,3-dienes (Eq. 1). Specifically, we employed disilane and amine substrate to produce the oxidative coupling product featuring C-N and C-Si bonds in the same molecule.[4] In addition, this strategy can successfully be applied to the reaction of selective oxidative coupling of 1,3-diene with alcohol and dililane, resulting in compounds bearing both C-O and C-Si bonds in the same molecule.[5] This work was supported by the “Development of Innovative Catalytic Process for Organosilicon Functional Materials project” (PL: K. Sato, AIST) from NEDO.



(1)

**Keywords**: Pd-complex-catalyzed reaction; difunctionalization; oxidative coupling; amination; alkoxylation; 1,3-diene

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# Quinoidal N-ligands in catalysis: from solution to surface

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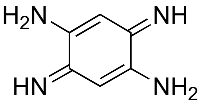
The rich chemistry of molecules exhibiting a quinoid structure has attracted the interest of a large scientific community for decades owing to their implications in a wide range of applications including in catalysis. A critical element in designing and fabricating new ligands in coordination chemistry is the control of the pi-distribution and the nature of the heteroatoms. 2,5-Diamino-1,4-benzoquinonedimine 1 is a very long known molecule (1887)[1] that has been poorly investigated owing to its low solubility and its instability in solution. We decided to revisit the chemistry of **1** in order to elaborate new complexes that are of major interest in many technological sectors including in catalysis. Our strategy is based on the versatile coordination chemistry of **1** in solution depending on the nature of the N-substituents.[2] More recently, these molecules appeared also to be precursors of choice for catalyzed reactions on surface.[3]



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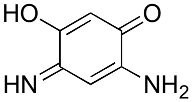

**2**

The different approaches and the key role of the quinoidal precursors will be described and discussed in the presentation. In addition, the related molecule **2** will be also reported in order to highlight the crucial influence of the heteroatoms in coordination chemistry.[4]

**Keywords**: Quinonediimine; transition metal; surface; complexes; zwitterion

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**Catalytic coordination chemistry (CA)**
**Invited Speaker**
**CA-I-03**
**Fa-Kuen Shieh**

# Insights into MOF Chemical Biology: Biocatalysts Encapsulated within MOFs

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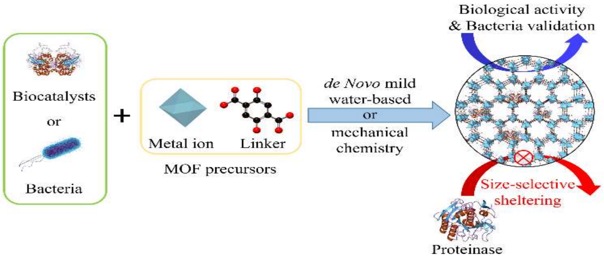
Metal-organic frameworks (MOFs) have found diverse applications in bio-sensing, biomass utilization, and catalysis. This study introduces a novel concept in material biology known as MOF Chemical Biology. It focuses on investigating the impact of containing biomolecules, such as protein enzymes, within synthetic MOF biocomposites, referred to as enzyme@MOFs. These biocomposites are prepared using a *de novo* biomineralization synthesis route, conducted under mild and aqueous conditions. The framework of these biocomposites possesses apertures that enable the free movement of substrates, while the encapsulated enzymes or bacteria remain confined within the structure, thereby shielding them against most structural changes.

Furthermore, we present the first successful demonstration of encapsulating enzymes into robust Zirconium-based MOFs, specifically UiO-66, using a solid-state mechanochemical process. The enzymes encapsulated through this method retain their desired functionality and exhibit resistance to proteases, even under acidic conditions. These innovative approaches provide an alternative system, exploiting the structural confinement effect, for expanding the application of MOFs in studying the biochemical functionalities of prokaryotes, eukaryotes, mammalian cells, and more.

**Keywords**: Metal-organic frameworks; MOF Chemical Biology; Biomineralization; Encapsulation; Biocomposites



Scheme. A *de Novo* mild water-based Synthesis and mechanical chemistry of biocatalysts encapsulated into MOFs.

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# Evolution of the mediators in controlling the radical polymerization of vinyl acetate

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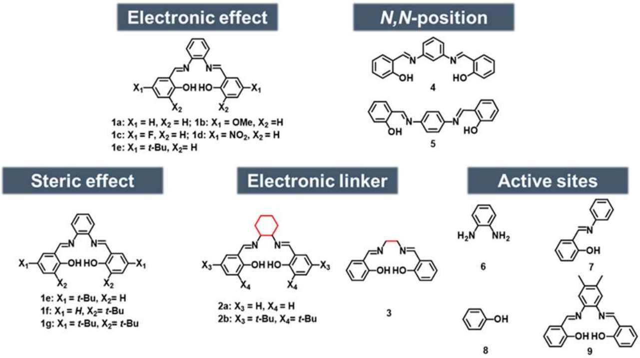
Cobalt-mediated radical polymerization (CMRP)[1] has shown a remarkable capability in controlling the polymerization of vinyl acetate (VAc) and vinyl monomers to produce the homo- and block copolymers with predictable molecular weight and narrow molecular weight distribution. We have devoted ourselves to developing CMRP, including synthesizing novel cobalt complexes, rationalizing the mechanism, and preparing innovative polymer materials. However, the removal of cobalt complexes from the polymeric products is always the barrier for industrial application. Recently, we found a novel aluminum complex that can control the VAc polymerization *via* a mechanism similar to CMRP.[2] Furthermore, an organic compound with only C, H, O, and N atoms, tralen, which was the ligand of the above aluminum complex, was recognized to be the control agent in the RDRP of vinyl acetate and methyl acrylate (MA).[3] Inspired by these results, we reviewed the ligands in CMRP and identified another series of organic compounds, Schiff bases, which could mediate the RDRP of VAc and vinyl monomers. This new methodology using organic compounds as the mediator for the RDRP of VAc and MA, which shows limited toxicity and low cost, demonstrates a great potential to provide the route for the industrialization of PVAc-based homo- and block copolymers



The Schiff bases used to control the radical polymerization

**Keywords**: Reversible-deactivation radical polymerization; vinyl acetate; block copolymer; Schiff bases; cobalt

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# Synthesis of Octadecavanadate derivatives and oxidation catalysis

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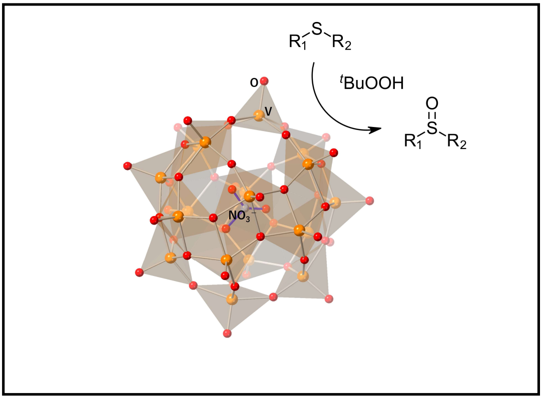
Complexes with vanadium-oxygen units (vanadyl) show the good catalytic performance for various oxidation reactions. The cage-type complexes with vanadyl called polyoxovanadates stabilize an anion at the center of the sphere. Some polyoxovanadates show the catalytic properties for the several oxidation reactions. Generally, it is difficult to determine the accurate active sites in a polyoxovanadate. The local structure control among the related polyoxovanadates leads to understand the reactivity of the specific sites.[1]

The well-defined cage-type octadecavanadonitrate (V18) possesses a nitrate at the center. The shape of V18 is ellipsoid and the top and bottom parts of the ellipsoid are the square pyramidal V4+ units. In this presentation, one-electron-oxidized species of V18 and metal-substituted V18 are prepared. Compound V18 were acted as the efficient catalyst for the selective oxidation of sulfide with tert-butyl hydroperoxide as an oxidant. By the comparison among the derivatives, the possibility of the active sites is investigated.

**Keywords**: Vanadium; Sulfide oxidation; Polyoxometalates; Active site



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# Mononuclear Cu-complex encapsulated hybrid silicoaluminophosphates for enhanced catalysis

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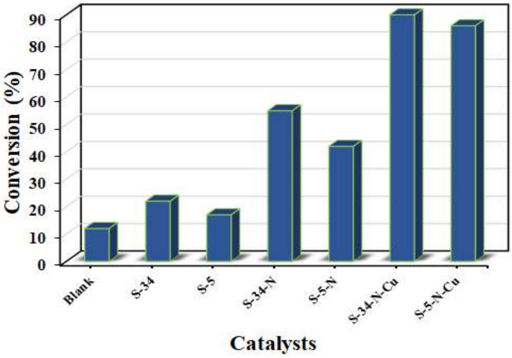
A facile and efficient post-treatment method has been systematically employed to synthesize copper complex immobilized on base-functionalized silicoaluminophosphate molecular sieves. In the present work, a novel mixed ligand copper (II) complex including 2,9-dimethyl-1,10-phenanthroline and nitrate has been successfully synthesized and characterized by single crystal XRD. The effective catalytic activity in epoxide ring opening reaction was achieved when this obtained material was subjected to anchored on amine-functionalized SAPO-34 and SAPO-5 materials. Structure, phase integrity, shape, thermal stability and the existence of functional groups are identified by using different analytical techniques like powder XRD, $N_2$ adsorption-desorption, FT-IR, NMR, SEM, TGA, etc. The hybrid SAPO-34 & SAPO-5 materials were used for the ring opening reaction of propylene oxide with piperidine. Owing to the contributions from both amine groups and copper (II) complex grafted onto the micropore surfaces, the catalytic performance of hybrid materials was found to be superior. 90% and 88% conversion were achieved using copper complex immobilized on base functionalized SAPO-34, and SAPO-5 materials, respectively.



**Keywords**: Copper complex; Functionalized silicoaluminophosphate; Hybrid materials; Epoxide ring opening; Post-treatment

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# Highly Efficient Water Splitting by an Electrolyzer Fabricated *via* Mixed Metal Imidazole-Complexes

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Hydrogen ($H_2$) is a promising sustainable energy carrier alternative to fossil fuels for the future global energy demand due to its high mass energy density (120 MJ $kg^{-1}$) and zero emissions of greenhouse gases. However, over 90 % of $H_2$ is produced from fossil fuels by steam reforming with great emission of $CO_2$ causing global warming up to now. Water splitting driven by a renewable energy source is one of the most promising sustainable and eco-friendly approaches for $H_2$ production with zero $CO_2$ emission. Development of efficient and robust electrolyzer equipped with an anode and a cathode for oxygen and hydrogen evolving reactions (OER and HER), respectively is indispensable for $H_2$ production *via* water splitting. We newly developed a unique technique called “a mixed metal-imidazole casting (MiMIC) method” for preparation of single- or multi-metal oxide films adhering rigidly on various electrode substrates. This is a one-pot procedure to form the metal oxide films by casting precursor methanol solutions (or suspensions) of the corresponding metal ions and imidazole derivatives, followed by calcination. The MiMIC method is useful for mass production of a large variety of metal oxide-based films that are necessary for practical device fabrications due to advantages of its simplicity and scalability.

We report the mixed metal oxide film of $FeNiWO_x$ adhering rigidly on a nickel foam (NF) electrode, showing the very low overpotentials of $\eta_{O2}^{10}$ = 167 mV (The superscripts represent the attained current densities of 10 mA $cm^{-2}$) with a Tafel slope of 49 mV $dec^{-1}$ and at least 100 h stability in OER, which compare advantageously with only a few state-of-the-art OER anodes with excellent $\eta_{O2}^{10} <$ 200 mV. The electrochemical data indicate synergistic coupling among ternary metal centers of Ni, Fe and W to decrease the η value.[1] On the other hand, We also report a Pt/$NiO_x$ composite film deposited on a NF electrode *via* a MiMIC method” to demonstrate extremely efficient and stable HER performance with overpotentials of $\eta_{H2}^{10}$ = 4.2 and $\eta_{H2}^{100}$ = 26.6 mV at geometrical current densities of 10 and 100 mA $cm^{-2}$, respectively in 1.0 M KOH solutions, which are the lowest overpotentials among state-of-the-art cathodes for HER to the best of our knowledge. The mass activity (0.42 A $cm^{-2}$ $mg_{Pt}^{-1}$) of the Pt/$NiO_x$ composite film at $\eta_{H2}$ = 50 mV is 60 times higher than that of the commercial 10 *wt* % Pt/C film on the NF electrode as a commonly used HER electrocatalyst. The extremely stable HER electrocatalysis was first demonstrated at the high current density of -100 mA $cm^{-2}$ for 60 h in 1.0 M KOH solutions. This study opens up a new avenue towards practical application of the electrolyzer equipped with the $FeNiWO_x$ film and the Pt/$NiO_x$ composite film as an efficient OER anode and HER cathode to large-scale and commercial systems for water splitting.

**Keywords**: Water splitting; Oxygen evolving anode; Hydrogen evolving cathode; Electrocatalysis; Artificial photosynthesis

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# $CO_2$ Hydrogenation to Methanol Catalyzed by Dinuclear Iridium Complexes at Gas-Solid Phase

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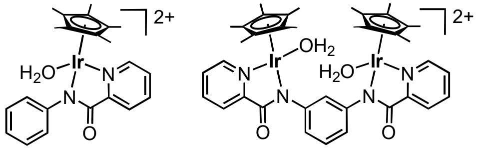
Development of efficient $CO_2$ conversion to methanol as a useful chemical and fuel is intensively in progress. Herein, we describe novel approach for methanol production by catalytic hydrogenation of $CO_2$ using multinuclear iridium complexes in a gas–solid phase reaction under mild reaction conditions.[1]

Conventional homogeneous $CO_2$ hydrogenation using mononuclear iridium complexes **1** in water afforded formic acid but not methanol. To our delight, when the reaction was performed using dinuclear iridium complex **2** under *unconventional heterogenous gas-solid phase*, methanol was produced with high selectivity under mild reaction conditions (Table). A maximum turnover number of 113 was obtained on recycling of the catalyst at 60 °C and 4 MPa of $H_2/CO_2$ (3:1). It is worth noting that methanol was generated catalytically, even at low pressure and low temperature(30 °C, 5 MPa (TON 2.0) and 0.5 MPa, 70 °C (TON 3.0)). This catalytic system opens the door to new possibilities for hydrogenation of $CO_2$ to methanol under mild reaction conditions and heterogenous catalysis of molecular catalyst.

**Keywords**: Methanol; CO2 hydrogenation; iridium complex; Heterogeneous catalysis

$$CO_2 + H_2 \longrightarrow CH_3OH + H_2O$$



**1**

**2**

**Table. $CO_2$ hydrogenation to MeOH**

| T / °C | P / MPa | T / h | TON |
|---|---|---|---|
| 60 | 4 | 47 | 4.0 |
| 70 | 0.5 | 480 | 3.0 |
| 30 | 5 | 168 | 2.0 |
| 60 | 4 | 70day | 113 |

The reaction was carried out $H_2/CO_2$ (3/1) using **2** in gas-solid phase reaction.

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# Synthesis of Trifluoromethyl Aryls and Aryl Trifluoromethyl Ethers via Co(II) and Ru(II) Catalysis

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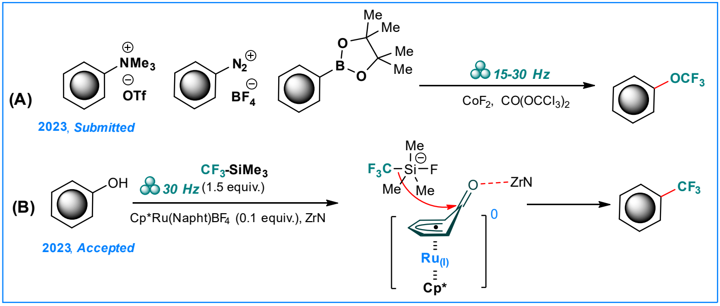
Despite the numerous synthetic methods available, the introduction of many fluorinated functional groups and pharmacophores is still far from being green and benign.[1] Among all the fluorine-containing substituents, the trifluoromethoxy group ($CF_3O$-) is the least-investigated and least-understood moiety.

Continuing our ongoing research program dedicated to the development efficient and concise methodologies towards aromatic and heteroaromatic compounds furnished with $CF_3O$-[2] and $CF_3$-substituents, here we communicate several protocols that permit a straightforward introduction of these groups utilising mechanochemical synthesis as a green tool. Namely: **(A)** $CF_3O$- group was swiftly introduced into aromatic and heteroaromatic scaffolds following the mechanochemical approach based on the selective transformation of aryl pinacol boronates, aryltrimethylammonium triflates, aryldiazonium tetrafluoroborates to aryl trifluoromethyl ethers via the in situ generated $CF_3O$- source using triphosgene and cobalt(II) fluoride ($CoF_2$).[3] Furthermore, we present **(B)** A novel Ru-catalysed transformation of phenols into trifluoromethyl-arenes under mechanochemical conditions.[4] This protocol most probably involves the formation of the $\eta^5$-phenoxo complex with the ligand-to-metal charge transfer between the Ru metal and the phenol, that is stabilized by the interaction with the highly oxophilic ZrN. Of note, the developed here procedures work only in solid-state. Nevertheless, the mechanochemical conditions ensure mild temperature, reduced workup time and solvent economy - corresponding with the principles of green chemistry.



**Keywords**: Catalysis; Cobalt; Ruthenium; Fluorine; Mechanochemistry.

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# Electrochemical $CO_2$ reduction on dinuclear complexes with square-planar coordination structure

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To mitigate global warming and achieve recycle-oriented society, extensive studies have been conducted on the utilization of $CO_2$ as a carbon source for the production of value-added compounds. Electrochemical $CO_2$ reduction ($ECO_2R$) is a promising method because of its potential capability to utilize renewable electricity. Among various types of $ECO_2R$ catalysts, metal complexes are advantageous because of their well-defined local structures and the tunability of local structures around active sites by ligand modifications. To date, mononuclear complexes such as metal phthalocyanines and metal porphyrins have been primarily applied for $ECO_2R$[1,2]. Meanwhile, multinuclear complexes have not been fully studied but may exhibit unique catalytic properties originated from adjacent catalytic sites. Inspired by a well-known mononuclear complex, metal tetraphenylporphyrin (MTPP, M=metal; **Fig.1**a top), we focused on dinuclear complexes with square-planar coordination structure, including $(M_2L_2)(A)_2$ (M=metal, HL=3,5-bis(2'-pyridyl)pyrazole, A=anion; **Fig. 1**a bottom). We synthesized $(Co_2L_2)(NO_3)_2{\cdot}2.5H_2O$ and characterized it via thermogravimetry and elemental analysis. The molecular structure was confirmed by single-crystal X-ray diffraction. Cyclic voltammetry revealed the catalytic activity for $ECO_2R$ (**Fig.1**b), and controlled potential electrolysis subsequently clarified the product selectivity, which was compared with that of CoTPP.

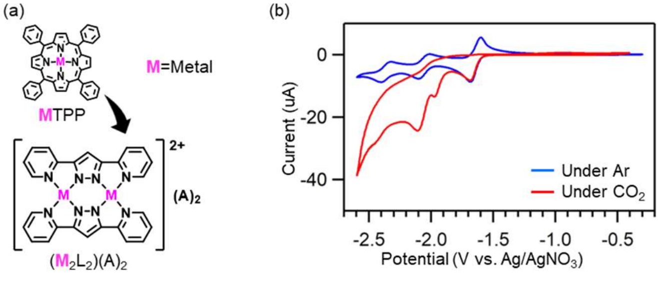

**Fig.1** (a) Molecular structure of MTPP (top) and $(M_2L_2)(A)_2$ (bottom). (b) Cyclic voltammograms of $(Co_2L_2)(NO_3)_2{\cdot}2.5H_2O$ under Ar (blue) and $CO_2$ (red).

**Keywords**: electrochemical $CO_2$ reduction; multinuclear complex; cyclic voltammetry

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# Designing copper(I/II) complexes for developing catalytic fixation of atmospheric $CO_2$

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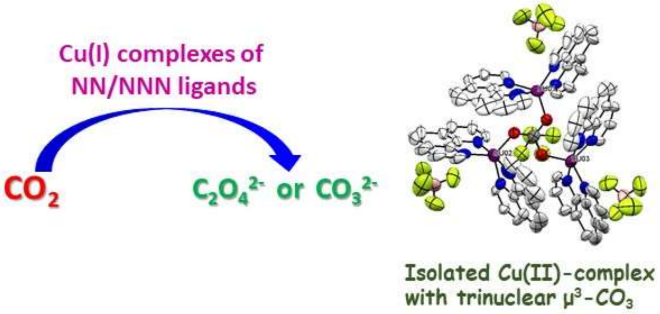
Reduction of enhanced level of carbon dioxide ($CO_2$) is highly necessary to address the current global challenge of climate change. Converting $CO_2$ into $C_1$ or $C_2$ feedstock refers to the process of utilizing carbon dioxide as a raw material to produce value added chemicals and fuels. This strategy has gained great attention as a potential and sustainable solution. In this context of sustainable development and environmental preservation, developing simple and earth abundant transition metal based catalysts for $CO_2$ fixation and sequestration is now a potential topic of considerable interest.[1] In this direction we aim to design and develop Cu(I) and Cu(II) complexes of N-heterocylic ligands to convert $CO_2$ to $C_2$ and $C_1$ derivatives such as oxalate and carbonate.[2,3] We have developed a series of NNN-Cu(I) pincer complexes with judicious variation of ligands. Our aim is to make the conversion process catalytic by chemical or electrochemical way. A systematic approach has been undertaken by tracing the intermediates to construct the conversion cycle.[4] Our attempt is to develop simple but efficient catalysts for fixation and sequestration of atmospheric $CO_2$ at mild condition will be discussed in the presentation.



**Keywords**: Cu(I/II) complexes, $CO_2$ fixation, sequestration, catalytic.

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# Rhenium Redefined as Electrocatalyst for Hydrogen Evolution Reaction

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Rhenium-based catalysts has great potential for green hydrogen production via water electrolysis. Re's electrocatalytic activity for the hydrogen evolution reaction (HER) can be rival with platinum group metals (PGMs) theoretically, and Re is much more cost-effective than Pt. Despite the expected advantages of Re as a catalyst for HER, metallic-Re-based electrocatalysts have exhibited lower HER performances than PGMs-based catalysts experimentally.[1] Herein, to improve Re's electrocatalytic activity, minuscule amount of Pt- and Ni (5 mol%) were doped to Re nanoparticle clusters interconnected by amorphous carbon (Pt-Ni@Re/C NPCs), which were superb than Pt/C. Pt-Ni@Re/C NPCs achieved phenomenally enhanced electrocatalytic HER performance in both acidic and alkaline media. Particularly in alkaline media, Pt-Ni@Re/C NPCs outperformed Pt/C or Pt-NiO/Ni with low overpotential (36 mV at 10 mA cm$^{-2}$), a Tafel slope (30 mV dec$^{-1}$), and excellent stability. The Faradaic efficiency for HER reached 98.63%. Pt-Ni@Re/C NPCs also possessed a low overpotential (419 mV) and high TOF value (195.6 s$^{-1}$) for vigorous evolution of hydrogen gas at a high current density (1000 mA cm$^{-2}$). This design holds promise for advancing industrial green hydrogen production.

**Keywords**: Rhenium; Electrocatalytic Hydrogen Evolution Reaction; Nanoparticle Clusters keyword 4; keyword 5

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# Coordination Modulation of Pd Nanoparticles with Heterogenous Phosphine Ligand in Aqueous Micelles

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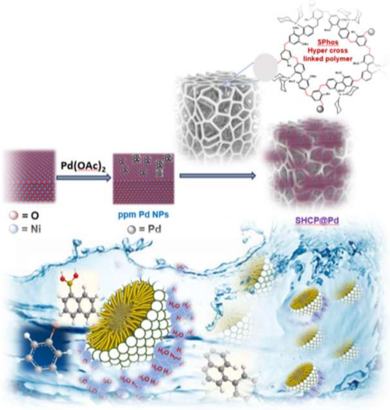
Ligated palladium has been and continues to be a privileged catalyst in the realm of organic synthesis [1]. Palladium-catalysed cross-couplings have been pursued actively in fields ranging from pharmaceuticals to agrochemicals and in the fine chemical industries [1,2]. Mostly C-C cross-couplings are carried out under harsh conditions with the use of high temperature, toxic solvents like 1,4-dioxane, DMF, and high catalyst loading. Coordination on the Pd-sites plays a significant role in tuning the catalytic efficiency. However, there are always challenges to module the surface of nanoparticles, and in most cases, it was achieved with the scarification of expensive phosphine ligands [3].

In the present study, we have synthesized hypercrosslinked polymer (HCP) with catalytic sites to module the ppm level Pd on the NiO surface. Due to the inherent hydrophobic nature of these HCP catalysts, the cooperative effect of micelles and metal HCPs was harnessed to construct C-C bonds in water under very mild conditions. The material was found to be highly efficient (), recyclable, stable, and water-dispersible under ambient conditions. The catalysts were characterized by various spectroscopic/imaging techniques (HR-TEM, SEM, XPS, PXRD, BET, Solid state-NMR).



**Keywords**: Heterogeneous; Catalysis; Micellar Catalysis; Coordination modulation; Recyclable

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# Development of new methanol oxidation catalyst using iron and study of optimal conditions

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Nowadays, methanol is focused on as an anode active material of fuel cells because of its stability, low toxicity, and storability. Hence, direct methanol fuel cells are expected to be a clean energy source of the next generation[1]. However, the anodic catalysts are composed of expensive metals. In this context, methanol oxidation catalysts composed of low-cost metals are required. In this study, three iron(III) complexes with different substituents (Figure 1, R : H, Br, OMe) are prepared as methanol oxidation catalysts, and revealed their spectroscopic and electrochemical properties. Furthermore, the catalytic activities of the iron(III) complexes are evaluated using DNPH method. The catalytic ability of each iron(III) complex for methanol oxidation was evaluated by detection of formaldehyde. As a result, formaldehyde was detected in methanol solution and under dioxygen atmosphere. On the other hand, formaldehyde was not detected in acetonitrile solution and in methanol solution under nitrogen atmosphere. These results indicate that the iron(III) complexes oxidize methanol and promote the formation of formaldehyde, and dioxygen is necessary for the oxidation of methanol. In order to further research for optimal conditions, catalytic activities of iron(III) complexes were evaluated under various conditions.

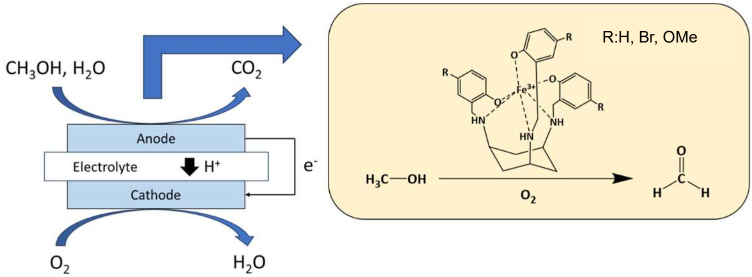

Figure.1 Schematic diagram of direct methanol fuel cells and iron(III) complexes prepared as methanol oxidation catalyst in this study.

**Keywords**: Direct Methanol Fuel Cells; iron(III) complex; methanol oxidation

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# Synthesis and Reactivity of Cobalt Complexes Having Isoindoline-Based Polyprotic Pyrazole Ligand

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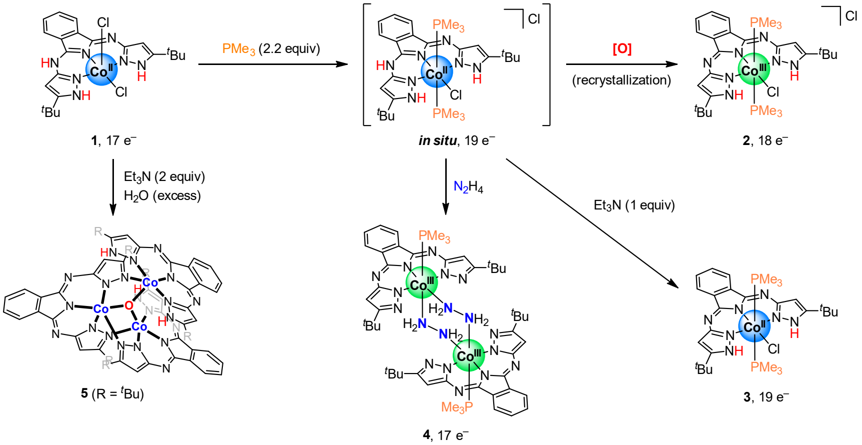
Protic pyrazole has been attractive ligands in coordination chemistry owing to their proton-responsive nature.[1] Recently, our group has introduced two protic pyrazoles into diiminoisoindoline framework to synthesize a new type of pincer ligand, $^{t\mathrm{Bu}}\mathrm{LH}_3$ (5-*tert*-butyl-1,3-bis(pyrazol-3-ylimino)isoindoline), which has a total of three ionizable NH groups. We have also isolated a series of its iron complexes and explored their reactivity.[2] In this work, we investigated the coordination of this ligand to a cobalt center and explored their redox properties and reactivity.

Treatment of $\mathrm{CoCl_2}$ with an equimolar amount of $^{t\mathrm{Bu}}\mathrm{LH}_3$ afforded the cobalt(II) dichlorido complex $[\mathrm{CoCl_2}(^{t\mathrm{Bu}}\mathrm{LH_3})]$ (**1**). Upon coordination, the isoindoline NH group in the free ligand migrated to the pincer backbone. The reaction of **1** with two equivalents of trimethylphosphine yielded the octahedral complex $[\mathrm{CoCl}(^{t\mathrm{Bu}}\mathrm{LH_2})(\mathrm{PMe_3})_2]\mathrm{Cl}$ (**2**) through unexpected oxidation to cobalt(III) and ligand deprotonation. In contrast to the above reaction with Schlenk techniques, the reaction performed in a glove box gave a paramagnetic transient species. Subsequent treatment with triethylamine and anhydrous hydrazine resulted in the formation of cobalt(II) biphosphine complex with monoanionic, $\mathrm{L_2X}$-type ligand $[\mathrm{CoCl}(^{t\mathrm{Bu}}\mathrm{LH_2})(\mathrm{PMe_3})_2]$ (**3**) and hydrazine-bridged cobalt(III) dinuclear complex $[\{\mathrm{Co}(^{t\mathrm{Bu}}\mathrm{L})(\mathrm{PMe_3})(\mu_2\text{-}\mathrm{N_2H_4})\}_2]$ (**4**), respectively. On the other hand, double deprotonation of **1** in the presence of water afforded the trinuclear oxido-bridged complex $[\{\mathrm{Co}(^{t\mathrm{Bu}}\mathrm{LH_2})\}\{\mathrm{Co}(^{t\mathrm{Bu}}\mathrm{LH})\}\{\mathrm{Co}(^{t\mathrm{Bu}}\mathrm{L})\}(\mu_3\text{-O})]$ (**5**), which highlights the multiproton-responsive nature of the $^{t\mathrm{Bu}}\mathrm{LH}_3$ ligand.



**Keywords**: Cobalt; Pincer Ligand; Pyrazole; Isoindoline; Hydrogen Bond

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# Encapsulating Copper-based Nanostructures into Metal-Organic Frameworks for $CO_2$ conversion

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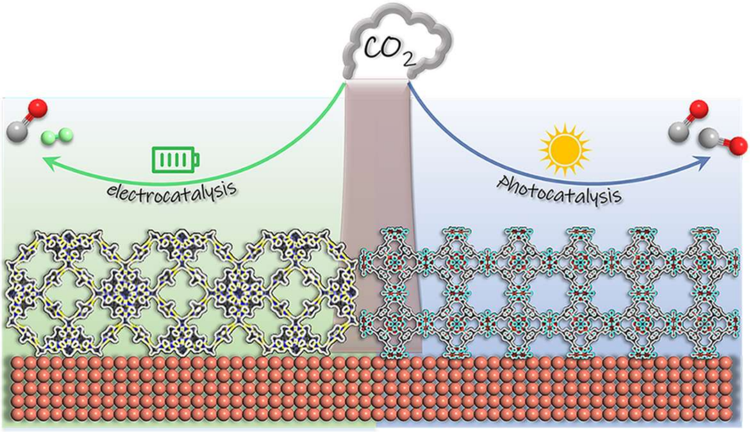
The integration of metal/metal oxide nanoparticles (NPs) into metal–organic frameworks (MOFs) to form composite materials has attracted great interest due to the broad range of applications. However, to date, it has not been possible to encapsulate metastable NPs with high catalytic activity into MOFs, due to their instability during the preparation process. Nanosized Cu catalysts have been leading the catalytic $CO_2$ reduction due to their low cost, abundant reserves and specific activity, and the relatively low stability and the selectivity of target products hinders further applications. For the first time, we have successfully developed a template protection–sacrifice (TPS) method to encapsulate metastable nanostructures such as $Cu_2O$/Cu NWs into MOFs. In addition, the catalytic activity (activity, selectivity) of $Cu_2O$ and Cu NWs is regulated by MOFs through crystal engineering and interface engineering in $CO_2$ reduction.



Cu based nanostructure@MOFs

**Keywords**: $CO_2$ reduction; Metal-Organic Frameworks; Cu-based Nanostructures

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# Cyclometalated Ruthenium Complex Catalyzed Selective Synthesis Of 2-substituted Benzimidazoles

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The catalytic activity of cyclometalated ruthenium complex is investigated for the selective synthesis of 2-substituted benzimidazole motifs through acceptor less dehydrogenative coupling of primary alcohols and diamines. Due to the various biological activity shown by the benzimidazole moiety, an efficient and selective method for the synthesis of benzimidazole is the need of the hour. A series of C−N cyclometalated 2*H*-indazole Ru(II) complex have been synthesized and characterized to investigate their catalytic activity. The merit of this current catalytic protocol is advantageous due to its high selectivity over other conventional methods. Overall, the synthesis of substituted benzimidazole is achieved in excellent yield under microwave irradiation without formation of unwanted side products using the ruthenium catalyst. To the best of our knowledge, this type of selectivity and specificity have not been reported earlier in case of metal catalyzed benzimidazole synthesis.

**Keywords**: ruthenium, catalyzed, benzimidazole, selectivity, microwave

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# Metal Nanoparticles on Lipophilic Nanographenes

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Nanographenes (NGs) are graphene fragments with tens of nanometers. Carboxy groups on the edge of NGs allow their chemical modification to produce NG-organic hybrid materials. Our group has developed a variety of hybrid materials.[1-5] A possible application is catalysis by utilizing their sp$^2$ domains for anchoring metal nanoparticles (NPs). Metal NP-doped lipophilic NGs are expected to catalyze chemical reactions in organic solvents. This background led us to design metal-NPs doped lipophilic NGs carrying octadecyl chains at the edge (Metal NP-**NG1**, Figure 1a).[6]

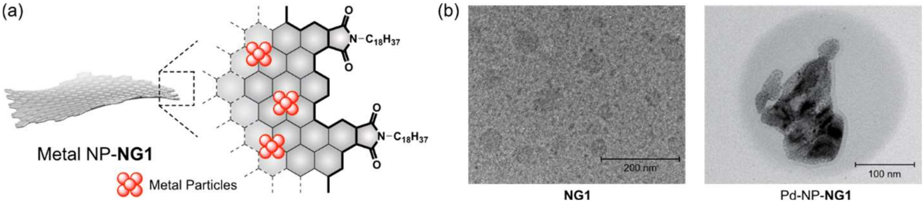

**Figure 1**. (a) Edge structure of NP-**NG1** and (b) TEM images of Pd-NP-**NG1**.

NGs were modified with stearyl amine to yield **NG1**. **NG1** had a size distribution of 40-70 nm in diameter (Figure 1b). The reduction of **NG1** with Na followed by the addition of metal salts ($FeCl_3$, $CuCl_2$, $AgNO_3$, $AuCl_3$, $NiCl_2$, $PdCl_2$) produced metal-NP doped lipophilic **NG1**. The mixtures were filtered to remove undissolved solids. The filtrates were drop-cast onto Cu substrates. TEM images demonstrated the formation of NPs. The average diameters were calculated to be Ni-NPs (15±4 nm), Au-NPs (9±3 nm), (8±2 nm (Ag), 3.5±0.8 nm (Pd), and 2.9±0.4 nm (Fe). We investigated the catalytic activity of Pd-NP-**NG1** in cross-coupling reactions. Detailed will be discussed.

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**Keywords**: graphene; nanographene; metal nanoparticle; catalyst; coupling reaction

# Transition metal complex based silica materials for the oxidation of benzyl alcohol to benzaldehyde.

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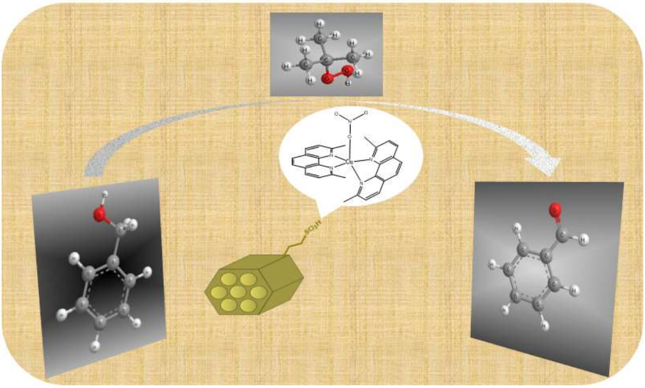
3d transition metal complexes are well known for its homogeneous catalytic activity. Homogeneous catalysts can be transformed into heterogeneous by immobilizing, grafting, anchoring, encapsulating, or grafting them into an inert solid support such a mesoporous silica. Copper (II) complex from mixed ligand having 2,9-dimethyl-1,10-phenanthroline and nitrate has been synthesized and characterized by single crystal XRD followed by anchoring this complex onto the acid functionalized mesoporous materials such as MCM-41-$SO_3H$ and SBA-15-$SO_3H$. A series of characterization techniques such as FT-IR, PXRD, BET, SEM, TG were employed to confirm the phase purity, porosity as well as successful anchoring of the guest moieties into the surface of porous silicas. These modified mesoporous materials (MCM-41-$SO_3H$-Cu and SBA-15-$SO_3H$-Cu) were finally used as oxidation catalysts in solvent-free selective benzyl alcohol oxidation with TBHP (Tert-Butyl Hydroperoxide) as an oxidant. MCM-41-$SO_3H$-Cu was found to be a potential catalyst in terms of benzyl alcohol conversion and benzaldehyde selectivity for the reaction.



**Keywords**: Nano-porous materials; Cu-complex; Benzyl alcohol; TBHP; Oxidation

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# $N_2$ silylation catalyzed by $[Mo_3S_4M]$ (M = Fe, Co, Ni) clusters bearing bulky cyclopentadienyl ligands

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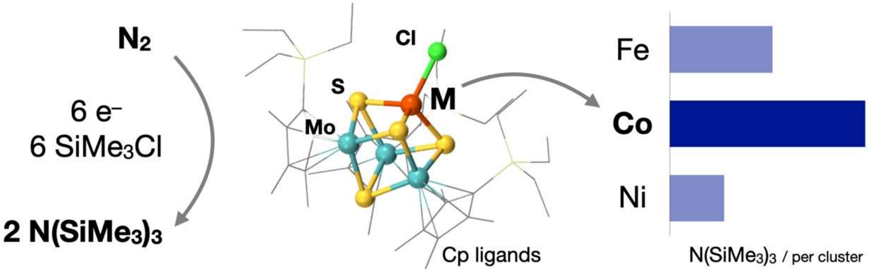
Nitrogenase is an enzyme that catalyzes the multi-electron reduction of $N_2$. This enzyme employs a metal-sulfur cluster called FeMoco ([*R*-homocitrate)$MoFe_7S_9C$]) as its active site [1]. Inspired by this cofactor, we have developed $[Mo_3S_4Fe]$ catalysts and reported the first catalytic $N_2$ reduction (silylation) by synthetic metal-sulfur clusters [2]. This study focuses on improving the $N_2$-reducing activity through the substitution of the Fe reaction site by other transition metals such as Co and Ni. The $[Mo_3S_4M]$ catalysts ($[Cp^{XL}{}_3Mo_3S_4MCl]$; M = Fe (**1**), Co (**2**), Ni (**3**); $Cp^{XL}$ = $C_5Me_4SiEt_3$) were prepared by the metal incorporation into the corresponding $[Mo_3S_4]$ clusters [3]. When Na and $ClSiMe_3$ were treated under $N_2$ atmosphere in the presence of each cluster, 188 (**1**), 358 (**2**), and 100 (**3**) equiv. $N(SiMe_3)_3$ per cluster were formed. For the most active catalyst **2**, a similar reaction with the increased reagent amount gave 951 equiv. $N(SiMe_3)_3$ that represents the highest yield in the known $N_2$ silylation reactions. These results demonstrate that metal-sulfur clusters can achieve high stability and reactivity towards catalytic $N_2$ reduction even compared to molecular catalysts in general.



**Keywords**: $N_2$ reduction; metal-sulfur cluster; base metal, molybdenum.

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# Highly Productive Heterogenized Ru-MACHO POMP Catalyst for $CO_2$ Hydrogenation via Solvothermal Method

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We synthesized a new Ru-MACHO POMP catalyst using a solvothermal method and applied it in $CO_2$ hydrogenation. The catalyst exhibited high catalytic activity for both hydrogenation and dehydrogenation reactions. The homogenous Ru-MACHO catalyst had low solubility in water, limiting its activity. We overcame this by polymerizing the Ru-MACHO POMP catalyst via Friedel-Crafts polymerization, resulting in a heterogeneous catalyst with improved solubility. The resulting catalyst had significantly higher activity than the previously reported $RuCl_3@TN_{20}Bpy_1$-CTF catalyst, with a formate productivity of 8700 ($kg_{For.}/kg_{Cat.}$/day), over 10 times higher. We also investigated the effects of reaction conditions and found that a solvothermal method using a glass-autoclave produced a highly porous catalyst with a formate productivity of 20100 ($kg_{For.}/kg_{Cat.}$/day). This catalyst has the potential to be economically competitive for formic acid production, pending further improvements in stability and recyclability.

**Keywords**: Organometallic catalyst; porous organometallic polymer; $CO_2$ hydrogenation into formate; high productivity; recyclable catalyst

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# Proton-Coupled Electron Transfer Controlled by Exchange Coupling in Imino-bipyridyl Co Complexes

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In the electrochemical hydrogen evolution reaction, 2 protons and 2 electrons are required. Proton-coupled electron transfer (PCET) associated with the step in which they are involved can be modulated through changes in both external and internal methods. External methods involve adjusting proton transfer (PT) by manipulating the p$K_a$ of the proton source or controlling electron transfer (ET) by applying different potential. Internal methods incorporate proton-relaying moieties to assist in PT. As an alternative internal method, we aimed to control PCET by inducing exchange coupling within a complex. To achieve this, we introduced 2,2'-bipyridine to modify the coordination structure. The change in coordination chemistry upon receiving electrons leads to different exchange couplings. Through this approach, we observed that pathways occurring in the electrochemical hydrogen evolution reaction can be controlled, either following stepwise ET/PT or concerted proton-electron transfer (CPET). We tried to elucidate the mechanism using NMR, UV/vis spectroscopy, and DFT calculations. This poster will elucidate the process of modulating PCET by inducing distinct exchange coupling in Imino-bipyridyl Co complexes.

**Keywords**: Proton-coupled electron transfer (PCET); exchange coupling

# Development of Re complexes bearing various bipyridine-derived ligands for photocatalytic carboxylation reactions of organic molecules with $CO_2$

Phurinat Lorwongkamol[1], Masaki Kitada[1], Taito Watanabe[1], Yutaka Saga[1*], Tetsuya Kambe[1], Mio Kondo[1,2,3], Shigeyuki Masaoka[1*]

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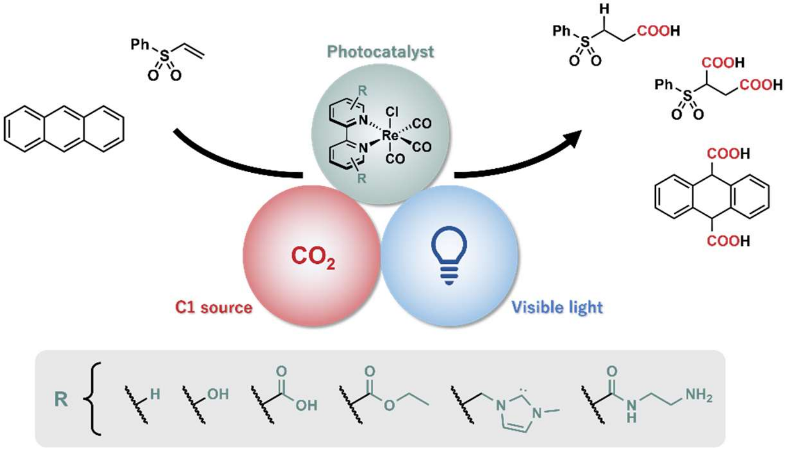
Carboxylic acid moieties are one of the most important structural motifs in numerous bioactive molecules, pharmaceuticals, and functional materials. A carboxylic acid group can be directly installed using $CO_2$ as an abundant and non-toxic C1 resource. However, the use of this highly stable molecule is challenging, and conventional methods for installing $CO_2$ into organic molecules require strong nucleophilic reagents or harsh conditions. In this work, we aim to develop the photochemical carboxylation of organic molecules with $CO_2$ using metal-complex-based catalysts under mild conditions. We employed *fac*-[Re(2,2'-bipyridine)$(CO)_3$Cl], which has been widely known to promote $CO_2$ reduction,[1,2] as a catalyst. Our photocatalytic system achieved the carboxylation reaction of phenyl vinyl sulfone in 86% yield with 2.4/1 selectivity of di- and mono-carboxylation products at room temperature and visible-light irradiation conditions. This is a rare example of the dicarboxylation of organic molecules with $CO_2$.[3] Furthermore, we accomplished the control of selectivity for mono- and di-carboxylation products simply by changing the solvents. Collectively, this study offers a new and unique catalytic system for the carboxylation of organic molecules with $CO_2$ by using the Re complex as a catalyst. Development of novel Re complexes for improving the reactivity is ongoing, and the details will be given.



**Keywords**: visible light; photocatalysis; carboxylation; Re complex

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# Novel, Copper-Based-Complex Framework Catalyst for Photocatalytic $CO_2$ Reduction using Visible Light

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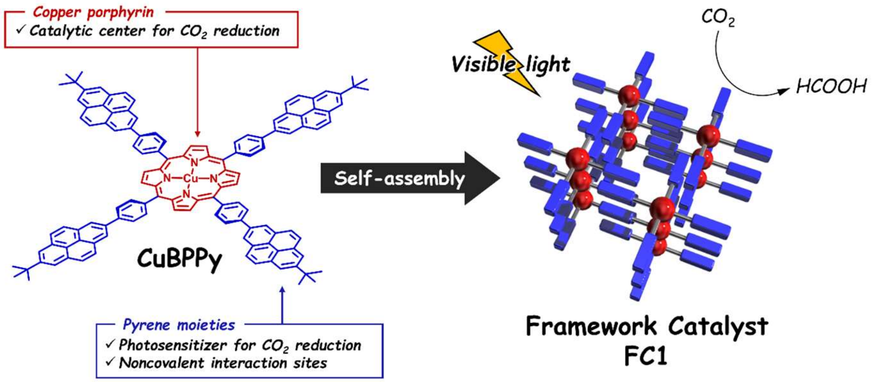
The photochemical reduction of $CO_2$ to value-added carbon products is a promising pathway to address global environmental and energy demand issues simultaneously. To develop a highly active, selective, and stable photocatalyst for $CO_2$ reduction, following elements are important: a catalytic center, light-harvesting units, and a porous structure. To introduce these key elements into one catalyst, we used the concept of a supramolecular framework catalyst[1], which is constructed by the self-assembly of discrete catalyst modules bearing a catalytic center and intermolecular interaction sites via noncovalent interactions. It was also revealed that the framework catalyst combines the advantages of both homogeneous and heterogeneous systems. Here, we developed a novel supramolecular framework catalyst using a copper porphyrin bearing pyrene moieties as the catalyst module. The module, **CuBPPy** (5,10,15,20-tetrakis(4-(7-(tert-butyl)pyren-2-yl)phenyl)porphyrinato copper(II)), was synthesized and characterized by elemental analysis, UV-vis absorption spectroscopy and cyclic voltammetry. Then, by simple recrystallization, the framework catalyst **FC1** was successfully obtained and its structure was clarified by single crystal X-ray diffraction. The powder X-ray diffraction, solid-state UV-vis absorption, and catalytic activity of **FC1** were investigated. **FC1** exhibited high $CO_2$ reduction activity to formic acid under visible-light irradiation in a noble-metal-free system. This catalytic performance is comparable to the best-in-class relevant works.



**Keywords**: $CO_2$ reduction; photochemistry; framework catalyst; self-assembly; porphyrin

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# Highly Active Higher Coordinated Copper(I)-N-Heterocyclic Chalcogenone Catalysed Click Chemistry

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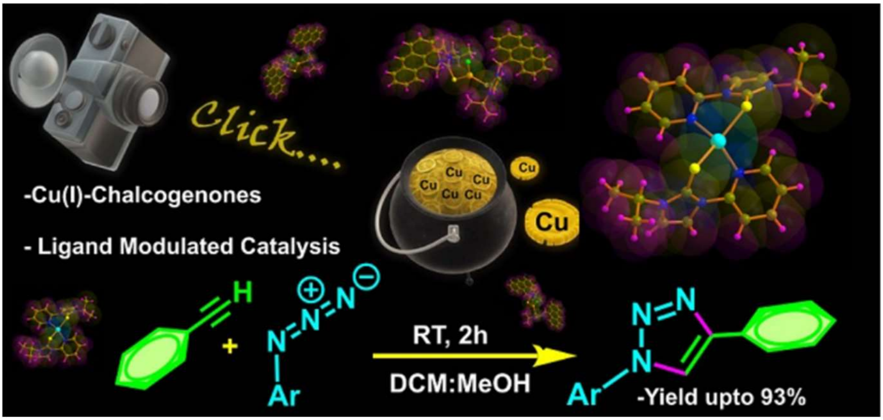
The catalytic efficiency of Cu(I) *N*-heterocyclic chalcogenone complexes is quite amazing compared to Cu(I) *N*-heterocyclic carbene complexes because of the good σ-donor and π-acceptor character of imidazole-2-chalcogenone [1]. The tri-coordinated and tetra-coordinated copper(I) *N*-heterocyclic chalcogenone catalysed [3+2] cycloaddition reaction has been reported to understand the role of ancillary ligands and the coordination environment of the catalyst. A series of tri-coordinated mononuclear copper(I)-*N*-heterocyclic chalcogenone catalysts have been synthesized and structurally characterized along with a cationic tetra-coordinated mononuclear copper(I)-*N*-heterocyclic chalcogenone catalyst. These new catalysts were characterized by FT-IR, NMR, and single-crystal X-ray diffraction techniques. Subsequently, these catalysts were screened for [3+2] cycloaddition catalytic reaction between aryl azide, alkyne tagged with carbazole, and phenylacetylene. However, the tetra-coordinated ionic catalyst is depicted excellently. The mechanistic study disclosed the crucial roles of a six-membered cyclic transition state of the copper(I) catalyst for high reactivity.



**Keywords**: NHC-Chalcogenone; Click chemistry; Catalyst.

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# A cleaner and efficient approach for one pot catalysis by the synthons of heterobimetallic complexes.

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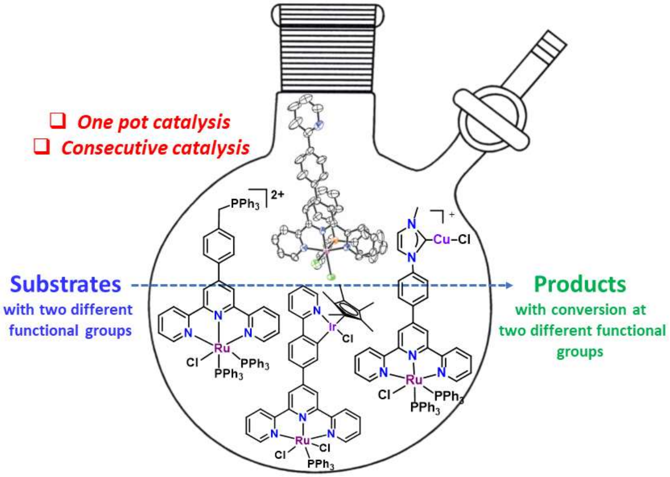
Heterobimetallic complexes are a novel category of catalysts made up of two distinct metal centers that may work together or individually to catalyze various multiple reactions.[1,2] There is a challenge to design the ligand scaffolds and to synthesize the desired hetero-bimetallic complexes. In this context, we have developed a series of hetero-bimetallic synthons with heteroleptic multi-dentate ligand sites, where one catalytic center is Ru(II) and the other metal center is Ir(III/I), Cu(I/II) or Fe(II). All the hetero-bimetallic complexes have been characterized by multinuclear NMR, HRMS, IR including SCXRD studies. In order to develop a better strategy for a cleaner and more convenient route map of catalysis, investigation of various tandem and parallel catalysis reactions with these synthons are underway.[3] Our attempt to develop heterobimetallic catalysts and its preliminary application will be presented and discussed.

**Keywords:** hetero-bimetallic complexes, tandem catalysis, one-pot catalysis



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# Discrete titanium complexes for the polymerization of ε-caprolactone and their copolymerizations

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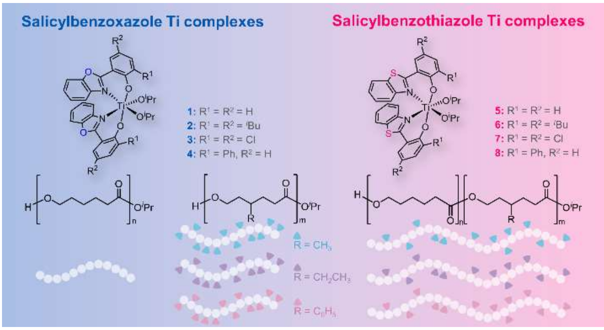
Two series of titanium complexes, including salicylbenzoxazole titanium complexes (**1**−**4**) and salicylbenzothiazole titanium complexes (**5**−**8**), were successfully synthesized and characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction crystallography (for **2** and **5**). The $^1$H NMR spectra of complexes **7** and **8** reveal fluxional behavior in solution at room temperature, and the activation parameters were determined by lineshape analysis of variable-temperature (VT) NMR spectra in toluene-$d_8$: for **7**, $\Delta H^{‡} = 73.0 \pm 1.8$ kJ mol$^{-1}$, $\Delta S^{‡} = 22.1 \pm 5.5$ J mol$^{-1}$K$^{-1}$; for **8**, $\Delta H^{‡} = 73.7 \pm 1.2$ kJ mol$^{-1}$, $\Delta S^{‡} = 20.3 \pm 3.8$ J mol$^{-1}$K$^{-1}$. The positive values of $\Delta S^{‡}$ suggested that the isomerization occurred *via* a dissociative mechanism. All complexes were active initiators for the ring-opening polymerization of ε-caprolactone (ε-CL) and three substituted ε-CLs: γ-Methyl-ε-caprolactone (γMeCL), γ-ethyl-ε-caprolactone (γEtCL), and γ-phenyl-ε-caprolactone (γPhCL)). Of all complexes, complex **5** was found to be the most active initiator in this study. The copolymerizations between ε-CL and three substituted ε-CLs produced completely random copolymers. The polymerization was proposed to proceed *via* a dissociative coordination-insertion mechanism. The catalytic activity of the salicylbenzoxazole titanium complex was lower than that of its closely related salicylbenzothiazole titanium congener.



**Keywords**: Titanium complexes; ring-opening polymerization; ε-caprolactone; salicybenzoxazole; salicylbenzothiazole

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# Aluminum complexes of tridentate [ONN]-phenolate ligands for the polymerization of *rac*-lactide

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A series of aluminum complexes supported by [ONN]-phenolate ligands were successfully synthesized and characterized using NMR spectroscopy. In the presence of benzyl alcohol, all aluminum complexes effectively initiated the ring-opening polymerization (ROP) of *rac*-lactide (LA) and ε-caprolactone (ε-CL) in toluene at 70 °C. All polymerizations proceeded in a controlled manner, as evidenced by a good agreement between the experimental and theoretical molar masses and the observed narrow dispersity values. Kinetic studies revealed first-order kinetics in the monomer for both *rac*-LA and ε-CL polymerizations. The effects of ligand structure on the catalytic activity and stereoselectivity were discussed. A good isoselectivity control was achieved for the polymerizations, with a $P_m$ value up to 0.72.

**Keywords**: aluminum complex; single-site catalyst; ring-opening polymerization; polylactide; polycaprolactone

# Controlled (co)polymerization of cyclic ester monomers by β-pyrimidine aluminum complexes

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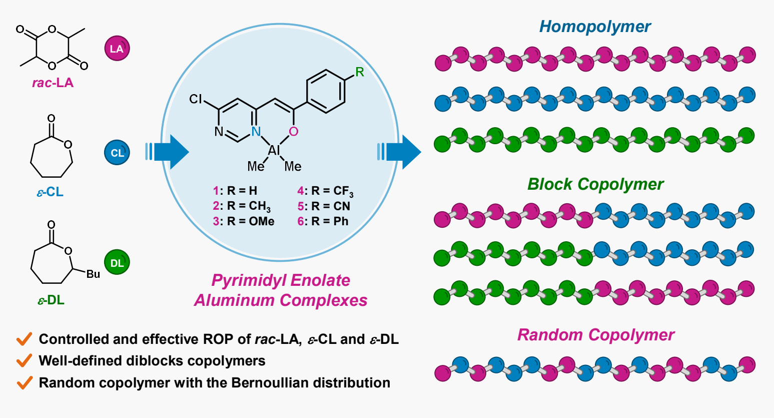
This work describes a series of β-pyrimidyl enolate aluminum complexes with the general formula LAlMe$_2$ (**1**–**6**) {L = $[(2\text{-}C_4H_2N_2Cl)\text{-}CH{=}C(O)C_6H_4R]$, R = H (**1**), Me (**2**), OMe (**3**), CF3 (**4**), CN (**5**), Ph (**6**)} that efficiently produce PLA, PCL, and PDL with controlled molar masses and narrow dispersity values. While the electronic characteristics of the ancillary ligands had no substantial influence on the catalytic activity for the *rac*-LA polymerization, the catalytic activity of the ε-CL and ε-DL polymerizations was affected by the ligand substituent (R), with complex **4** exhibiting the highest catalytic performance in both cases. In addition, six different types of well-defined block copolymer between *rac*-LA, ε-CL, and ε-DL were successfully prepared *via* a sequential-feed approach and the second monomer could be polymerized to complete conversion regardless of the order of the first monomer. The results unveiled that the order of monomer addition was not crucial in this catalytic system. Moreover, the perfect random copolymer between ε-CL and L-LA, poly(L-LA-*r*-CL), with a strict Bernoullian distribution, was successfully produced by complex **3** *via* a single-feed polymerization without the transesterification side reactions. The electronic influence from the pyrimidine ring of the ligand framework was believed to play an important role in the formation of the random copolymer.



✓ Controlled and effective ROP of *rac*-LA, ε-CL and ε-DL
✓ Well-defined diblocks copolymers
✓ Random copolymer with the Bernoullian distribution

**Keywords**: Aluminum catalyst; Ring-opening polymerization; Polylactide; Polycaprolactone; Polydecalactone

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# Tridentate [ONN]-phenolate titanium complexes for the polymerization of cyclic ester monomers

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In this work, twelve titanium complexes supported by tridentate [ONN]-phenolate ligands were synthesized and characterized by NMR spectroscopy. All titanium complexes were active initiators for the ring-opening polymerization of *rac*-lactide (*rac*-LA) and ε-caprolactone (ε-CL) in toluene at 70 °C. The polymerization of ε-CL was found to be faster than that of *rac*-LA. All polymerizations exhibited living characteristics, as evidenced by narrow dispersity values. The theoretical molar mass values were in good agreement with the theoretical values calculated based on three initiating groups per titanium center. It was discovered that no significant stereocontrol was achieved for the *rac*-LA polymerizations, *i.e*., all complexes produced atactic PLAs ($P_m$ = 0.50–0.52). The effects of electronic and steric from ligand substituents were found to have a significant impact on polymerization activities. Kinetic investigations revealed that the zeroth-order and first-order kinetics in monomer concentration were exhibited for the ROP of *rac*-LA and ε-CL, respectively.

**Keywords**: titanium complexes; ring-opening polymerization; polylactide; polycaprolactone; *rac*-lactide; ε-caprolactone

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# Titanium complexes of phenoxy-azo and phenoxy-imine ligands: a comparative study for the ring-opening polymerization of *rac*–lactide and *ε*–caprolactone

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Two series of titanium complexes, bis(phenoxy-azo)titanium(IV) complexes and bis(phenoxy-imine)titanium(IV) complexes, were prepared by the reactions between one equivalent of $Ti(O^{i}Pr)_4$ precursor and two equivalents of the corresponding ligand in hexane at room temperature. The synthesized titanium complexes were characterized by $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectroscopy and X-ray crystallography. The X-ray structures revealed that the two ligands were $\kappa^2$-coordinated to the titanium center, with the two phenoxy groups in *trans* positions and the two nitrogen atoms in *cis* positions. All complexes were active initiators for the ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) and *ε*-caprolactone (*ε*-CL) with living fashions. The results indicated that the complex featuring the least bulky p-methyl phenoxy substituents exhibited the highest catalytic activity. The polymerizations mediated by all titanium complexes were well-controlled, affording polymers with predetermined molar mass and narrow dispersity values. Kinetic studies demonstrated that polymerization was first-order kinetics with respect to monomer concentration. The bis(phenoxy-azo)titanium complexes exhibited higher catalytic activity than their bis(phenoxy-imine)titanium counterparts.

**Keywords**: Titanium complexes; phenoxy-azo ligand; phenoxy-imine ligand; ring-opening polymerization

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# Methoxy-poly(ethylene glycol)-incorporated quaternary ammonium halide catalysts for $CO_2$ conversion

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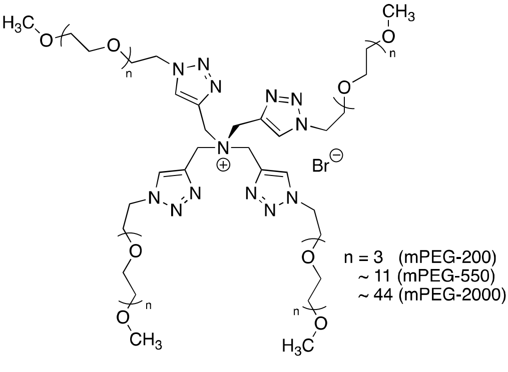
Development of simple, efficient, and low-cost catalysts for converting $CO_2$ and epoxides to the value-added cyclic carbonate products provides both economic and environmental benefits. In this work, a new class of quaternary ammonium species (QAS), functionalized with methoxy-poly(ethylene glycol) (mPEG) of varying chain lengths, mPEG-200, mPEG-550, and mPEG-2000, were synthesized and investigated as catalysts for $CO_2$/epoxide cycloaddition to cyclic carbonates. The synthesis involved the use of copper-catalyzed azide–alkyne cycloaddition (CuAAC) or click reactions to functionalize QAS with mPEGs, resulting in QAS-mPEGn (n = 200, 550, 2000). The polymers were characterized by $^1$H NMR, FT-IR, XRF, TGA, MALDI-TOF, and ESI-MS techniques. In the presence of a catalytic amount of KX (X = Br, I), QAS-mPEGn stabilizes $K^+$ ions and consequently provides more potent nucleophilic $X^-$ ions to promote $CO_2$/epoxide cycloaddition. The catalyst system QAS-mPEG2000/KI mediated a quantitative conversion of $CO_2$ with styrene oxide to styrene carbonate at 120 °C, 1 atm $CO_2$ at 48 h according to $^1$H NMR spectroscopy.

**Keywords**: $CO_2$ conversion; Click reaction; Quaternary ammonium species; Poly(ethylene glycol); Cyclic carbonate



Structures of QAS-mPEGn ( n = 200, 550, 2000)

# Synthesis And Characterization Of Palladium(II) Schiff Base Complexes and Their Catalytic Activity For Stille Reaction

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Schiff bases with different substituents at para-position phenylamines (B1OMe and B1C), and their palladium(II) complexes, (PdB1OMe and PdB1C) were synthesized and characterized by elemental analysis, FTIR, $^1$H NMR, magnetic susceptibility measurements and UV-Visible spectroscopy. The shifting of *v*(C=N) and *v*(C-O) band to lower frequencies in FTIR indicated that the complexation to palladium(II) occurred through these moieties. PdB1OMe is structurally characterized using single crystal X-ray diffraction. PdB1OMe crystallizes in orthorhombic with space group P-1, with a = 7.123(3) Å, b = 8.326(4) Å and c = 11.625(5) Å. The palladium(II) complexes were screened for their catalytic activity in Stille reaction. The reaction was monitored by measuring the % conversion of iodobenzene using GC-FID, where the reaction conditions used were 1.0mmol% catalyst loading in the presence of triethylamine as base and DMSO as solvent at 80°C within 6 hours reaction time. It was observed that PdB1OMe displayed the best catalytic performance for the Stille reaction, indicated by 65% conversion of iodobenzene.

**Keywords**: Catalysis; Palladium(II); Schiff base; Stille reaction; single X-ray Crystallography

# Removal of $Cd^{2+}$ by hydroxyapatite adsorption granules from aqueous solution

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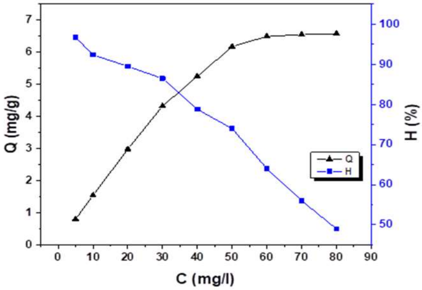
In recent years, water environment pollution caused by heavy metals, which existed mainly in industrial waste, become one of the most serious problems. There have been many materials used for adsorption of heavy metals from aqueous solution, such as the activated carbon, clays, zeolites, apatite, chitosan, bioadsorbents and agricultural wastes. Among them, calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, noted as HAp), is interested by many researchers due to its remarkable adsorption efficiency and extensive application. HAp adsorption granules with average size of 2×10 mm was fabricated from HAp powder and polyvinyl alcohol (PVA) additive by sintering for removing of $Cd^{2+}$ ions from aqueous solution. The effect of some factors on the $Cd^{2+}$ adsorption efficiency and capacity were investigated. The adsorption efficiency and capacity reached 86.5 % and 4.33 mg/g, respectively, at stable condition: HAp granule mass of 0.3 g, initial $Cd^{2+}$ concentration of 30 mg/L, contact time of 40 minutes and $pH_0$ of 5.7 at 30 °C. The adsorption process of $Cd^{2+}$ followed Langmuir adsorption isotherm model and pseudo-second order adsorption kinetic equation. The obtained result will open a potential application direction in the column adsorption with adsorbent of HAp granule for the treatment of $Cd^{2+}$ ions in polluted water.



**Keywords**: Hydroxyapatite granule, adsorption, removal of $Cd^{2+}$

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# Bioinspired [3Fe-4S] Clusters for Water Oxidation with High TOF

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The utilization of earth-abundant low-toxicity metal ions in the construction of highly active and efficient molecular catalysts promoting the water oxidation reaction is important for developing a sustainable artificial energy cycle. However, the majority of current iron-based molecular water oxidation catalysts (MWOCs) exhibit insufficient kinetic properties. Herein we report a newly synthesized trinuclear sulfur-bridged iron complex $[Fe_3(Sip)_4][CF_3SO_3]_2$ which is inspired by iron-sulfur cluster. It showed decent catalytic activity to oxygen evolution reaction (OER) in acetonitrile and water mixed solution. Mechanism research suggested that it participated in the reaction as a pre-catalyst, which is further confirmed by ESI-MS. The catalytic function of sulfur bridged iron complex is unusual in water oxidation, which will provide new insights into the water oxidation catalyst for the structural design.

**Keywords**: Iron Sulfur Cluster; Molecular Catalysts; Biomimetic; Homogeneous Catalysis; Water Oxidation

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# Coordination Cages (CC)

# Abstract

# Molecular Confinement Effects in Self-assembled Cages

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Since our first report on a self-assembled coordination cage in 1995,[1] we and other have been developing the molecular confinement effects of the self-assembled cages (Fig. 1). The cavities of our cages are extraordinarily large and are capable of binding neutral guests. Through molecular recognition, new properties, reactions, and functions have been created.[2,3] One of the recent topics in the course of our study is protein encapsulation in a self-assembled gigantic cage.[4]

**Keywords**: Self-assembly; coordination cages; molecular confinement; molecular recognition

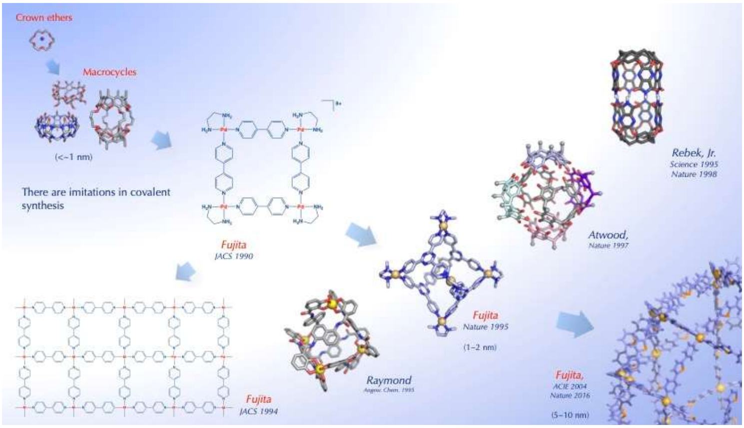

**Figure 1**. An overview on the history of chemically defined cavities.

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**Coordination Cages (CC)**
**Keynote Speaker**
**CC-K-02**
**Ok-Sang Jung**

# Construction and enantioselective discrimination of pairs of new chiral coordination cages

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Reaction of $PdX_2$ ($X^- = ClO_4^-$ and $PF_6^-$) with $C_3$-symmetric tridentate *l*- and *d*-L in the 3:4 mole ratio gives rise to chiral nano-cube pairs $[Pd_6(l\text{-L})_8](X)_{12}$ and $[Pd_6(d\text{-L})_8](X)_{12}$ ($X^- = ClO_4^-$ and $PF_6^-$, respectively) with an inner cavity of 12.3 × 12.3 × 12.3 Å$^3$.[1] Self-assembly of $Hg(ClO_4)_2$ with a pair of new $C_3$-symmetric chiral ligands, *s*,*r*-L and *r*,*s*-L, produces a pair of chiral cages $C_4H_8O_2@[(Hg_2^{II})_3(ClO_4)_6(s,r \text{ or } r,s\text{-L})_2(H_2O)_7](C_4H_8O_2)_7$ via straightforward formation of the reduced $Hg_2^{II}$ species with an inner cavity in which a single dioxane molecule is nestled. The pair of chiral cages are transformed into their downsized pair of cages, $[Hg^{II}_3(ClO_4)_6(s,r \text{ or } r,s\text{-L})_2]$, in the presence of hydrochloric acid.[2] Furthermore, self-assembly of $M(ClO_4)_2$ ($M^{2+} = Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$) with *s*,*r*-L and *r*,*s*-L in the 3:2 mole ratio produces pairs of chiral cages $M_3L_2$. These cages include a single acetone molecule in the inner cavity.

These chiral coordination cages are effective for enantio-recognition of various chiral matrials via electrochemical technique and photoluminescence (PL). The site of enantio-recognition was confirmed by DFT-calculated interactions between each chiral coordination cages and the chiral martials, and the calculated interactions were coincident with the shifts of electrochemical oxidation potentials.

**Keywords**: Chiral cage; Molecular recognition; Photoluminescence; Oxidation potentials

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# Porous cuboctahedral metal-organic cages

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Metal-organic cages (MOCs) are known for their unique structures, intrinsic porosity, and designability. However, their practical applications have been constrained by issues such as loss of porosity due to weak inter-cage interactions. Our research introduces bridging and fixing strategies to address these challenges. Interconnecting cages with short methylene bridges via electrophilic aromatic substitution, followed by post-synthetic solvothermal treatments, effectively retains and enhances the structural integrity of MOCs. These methodologies lead to MOCs with superior porosity. Additionally, the solvothermal treatments result in the formation of mixed-valenced Cu(I)/Cu(II) MOCs. The catalytic activities of these MOCs, particularly in copper(I)-catalyzed hydrative amide synthesis, have been examined. The study also encompasses the synthesis of solvato- and vapochromic MOC nanocrystals and aerogels, demonstrating varied porosities and the capability for colorimetric sensing of common organic solvents. These advancements highlight the potential for broader applications of MOCs in fields such as catalysis and sensing, broadening their relevance and impact across multiple scientific areas.

**Keywords**: Metal-organic cages; metal-organic polyhedra; porous materials; solvato/vapochromism

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# Stability, Ligand Exchange, and Heteroleptic Control in Lantern-Type $Cu_4L_4$ Cages

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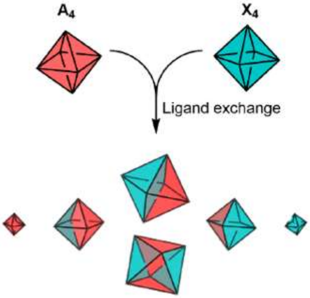
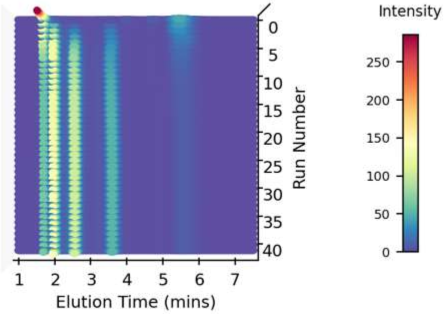
Lantern-type MOCs, containing two copper paddlewheels connected by four dicarboxylate ligands, are the smallest prototypical member of the paddle-wheel MOC family. Understanding factors involved in their stability, and controlling mixed-ligand species, therefore has impact across the larger MOC series and potentially impacts on the synthesis of paddlewheel-based MOFs.

We have studied lantern-type MOCs that comprise ligands based on amino acids, often imparting helical chirality into the final assemblies depending on the nature of the acid.[1] We have shown that ligand exchange between homoleptic cages can be followed and quantified using HPLC, allowing speciation and relative stability to be assessed. Using this method, the steric bulk of the amino acid side-chains was found to control the formation of heteroleptic cages and skew equilibration of cage mixtures away from a simple statistical mixture; the correct ligand combination forms only a single heteroleptic species.[2] The steric bulk also slows the rate of ligand exchange and can alter the half-life of the cage by an order of magnitude.[3] The core group of the ligand, forming the 'belt' around the equatorial ring of the cage also plays a significant role in solution stability, highlighting the complexity associated with the design of MOCs.





**Keywords**: metal-organic cage; ligand exchange; HPLC; heteroleptic

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# Controlling the assembly of Pd(II)/bianthryl-based $M_2L_4$ and $(M_2L_4)_2$ cages by steric effects

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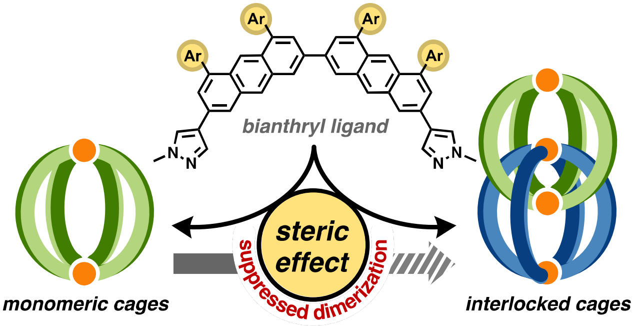
In the energy landscape of coordination-driven self-assembly processes, the isolation of kinetically formed supramolecular cages has long been identified as a challenging task.[1] Herein, we report a reliable strategy for the selective isolation of kinetically or thermodynamically preferred stable coordination cages, whose formation depends on the degree of steric protection[2] offered by the exterior side chains. The combination of Pd(II) ions with arc-shaped 2,2′-bianthryl-based ligands that contain different numbers of methoxyethoxy side chains led to the quantitative formation of both kinetically favorable monomeric $M_2L_4$ cages and thermodynamically favorable dimeric $(M_2L_4)_2$ interlocked cages. These assemblies were structurally fully characterized via NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis. Although the monomeric cages with fewer exterior side chains can reassemble into interlocked cages, the cages with more exterior substituents remain monomeric cages under similar conditions. A computational study revealed that this different behavior is mainly governed by the destabilization of the interlocking assemblies due to the steric repulsion among the side chains on the overcrowded exterior. Furthermore, the kinetically stabilized monomeric $M_2L_4$ cages exhibit permanent host abilities toward sulfonate guests, while the cages with lower steric protection undergo dimerization accompanied by guest release.[3]



**Keywords**: self-assembly; coordination cage; kinetic control; steric effect; host–guest chemistry

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# Controlling diastereoselectivity in low-symmetry metal-organic cages

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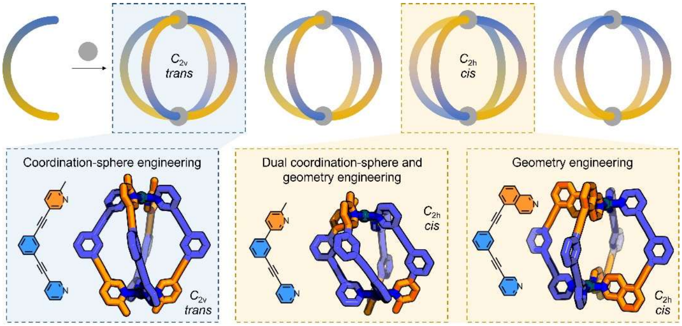
Metal-organic cages (MOCs) are host architectures[1] of interest for applications in catalysis, sensing and stabilisation of reactive species, amongst others. The vast majority of MOCs reported employ symmetrical ligands to facilitate the self-assembly process, as lower symmetry ligands have the potential to form mixtures of isomeric products.[2] Control of this self-assembly process, however, would allow access to more structurally sophisticated architectures, with implications for advanced functionality and guest-binding selectivity.[3]

We have been interested in developing design strategies to bias the formation of particular MOC isomers from unsymmetrical ligand scaffolds. Towards this, we have successfully used covalent tethering[4] as well as geometric[5] and coordination-sphere[6] design parameters to induce diastereoselective assembly of palladium(II)-based MOCs from ligands lacking bilateral symmetry. We have also begun to develop high-throughput computational methodologies to aid in the design of such systems, reducing costly trial-and-error synthetic discovery.[7] Ongoing work is focused on extending our toolbox of design principles for accessing structurally complex, low-symmetry MOCs, and exploiting the observed correlation between experimental and computational results to allow in silico analysis for effective computational forecasting to aid in the design of future systems.



**Keywords**: metallo-supramolecular, cages, capsules, low-symmetry, self-assembly

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# Stimuli-responsive Cavity Size Control in Palladium(II) Coordination Cages

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Coordination cages, with their inherent internal spaces, serve as valuable tools for exploring confined effects. The ability to manipulate the structure and functionality of coordination compounds through external stimuli is a key approach in stabilizing reactants, catalysis, and drug delivery systems. Therefore, the development of stimuli-responsive supramolecules has proven to be a highly challenging topic. In this presentation, we will explore the assembly of coordination complexes, emphasizing an understanding of the driving forces that govern component aggregations, and the functionalization achieved through external stimuli.

**Keywords**: stimuli-responsive; palladium(II); nitrogen donors

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# Making of the multi-cavity coordination architectures

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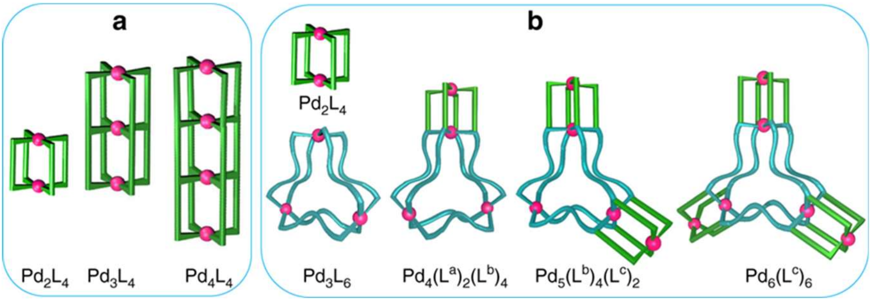
A self-assembled coordination cage usually possesses one well-defined three-dimensional (3D) cavity whereas infinite number of 3D-cavities are crafted in a designer metal-organic framework (or coordination polymer). Construction of a discrete coordination architecture possessing multiple but finite number of 3D-cavities is a challenging task. Complexation of Pd(II) with a nonchelating bi- or poly-dentate ligand is a known strategy for the construction of one-cavity containing 3D-cages of various shapes and sizes. We introduced a double-decker shaped two-cavities based architecture of [$Pd_3L_4$] formulation (Figure 1a), that was prepared using Pd(II) and a designer "E-shaped" tridentate ligand.[1] Subsequently, we decorated a trinuclear [$Pd_3L_6$] core with one, two and three units of the [$Pd_2L_4$] entity to achieve multi-3D-cavity conjoined-cages of [$Pd_4(L^a)_2(L^b)_4$], [$Pd_5(L^b)_4(L^c)_2$] and [$Pd_6(L^c)_6$] formulations, respectively (Figure 1b).[2] In contrast to the double-decker shape of now well-known [$Pd_3L_4$] formulation, one of our recent reports demonstrated an hour-glass shape architecture having the same $Pd_3L_4$ formulation but alternate arrangement of ligand units around metal centers.[3] We are involved in making of single cavity-based cages using known strategies, multi-cavity conjoined-cages using new strategies, and exploiting functional aspects of the isolated nano-space present in the coordination architectures.[4,5]



**Keywords**: palladium(II); multidentate ligand; self-assembly; multi-cavity cages

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# Coenzyme functionalized metal−organic confined supramolecular systems for Cascade Catalysis

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Catalytic strategies inspired by prototypes of natural enzymes have recently attracted interest because they may lead to important tools for efficient chemical conversions. To match the high efficiency and selectivity of enzymatic systems, chemists have used small molecules with defined hydrophobic cavities that mimic the remarkable properties of enzyme active sites and emulate their enzymatic activities in catalyzing specific chemical transformations. Supramolecular chemistry using Werner-type hosts has displayed interesting recognition properties and reactivity reminiscent of natural enzymes. Nature has developed millions of redox systems in which the redox process is participated by numerous coenzymes. We modulated the properties of active center of nicotinamide adenine dinucleotide (NADH) in a redox-active molecular flask to combine various chemical transformation with in situ regeneration of the active site in a one-pot reaction using light as a clean energy source. In terms of the availability, atom economy, and by-product removal, the combination of photocatalysis or enzymatic catalysis reaction to regenerate the active sites is a promising approach. From a catalytic perspective, the challenges in developing one-pot catalytic processes include the combination of photocatalysis or enzymatic catalysis and redox catalysis, in addition to the compatibility between the reaction intermediates and dynamic kinetics and the synergy of the inside and outside redox processes.

**Keywords**: Metal−organic cages; Cofactors; Supramolecular catalysis; Enzymatic catalysis

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# Skeletal editing of highly entangled polyhedra based on cooperative metal–acetylene coordination

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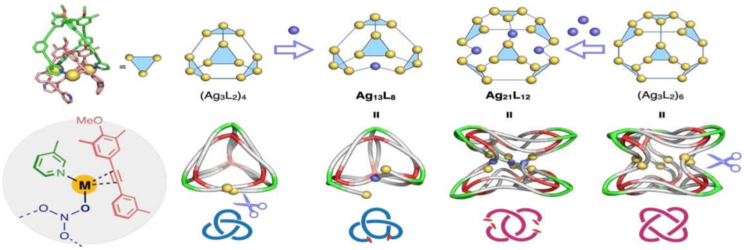
Interconversion of discrete coordination nanostructures is a useful approach for (i) constructing some specific structures accessible only by a multi-step process, or (ii) modifying properties and functions derived from their frameworks, e.g. molecular containers, reactors, or optoelectronic devices. However, atomically precise transformation of huge structures of ca. >3 nm in diameter, comparable in size to inorganic nanoparticles or proteins, is still a challenge and is attracting much attention for the development of artificial nanomaterials which can be precisely manipulated at the atomic level. Recently, we have reported the construction of $(M_3L_2)_n$ polyhedral ($n$ = 2,4,6,8, M = Cu(I) or Ag(I)) based on metal–acetylene pi-coordination cooperatively working with conventional metal–pyridyl coordination.[1,2]

Herein we describe the ‘huge-to-huge’ transformation of the pi-coordinated cage frameworks, through formal metal insertion into the reported $(M_3L_2)_n$ polyhedra to form concave polyhedra.[3] This type of skeletal change was achieved by partial conversion of the binary cooperative coordination system (Ag···pyridyl and Ag···acetylene) into a ternary one, incorporating Ag···$ONO_2$ coordination into the main framework. In addition, the current interconversion into a ternary coordination system has led to a unique secondary phenomenon – the local dissociation of the entangled motifs comprising the polyhedral frameworks, which opens up the way to precise post-assembly modification of three-dimensional molecular entanglements.



**Keywords**: coordination polyhedra; pi-coordination; molecular entanglements; acetylene coordination; anion exchange

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# Fullerene induced structural transformation of a metal-organic cage and $^1O_2$-mediated oxidations

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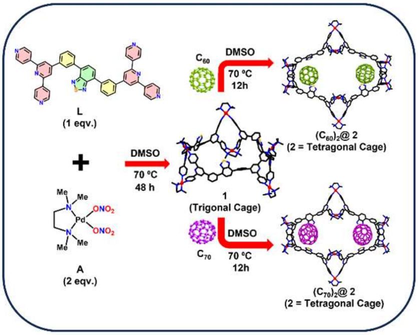
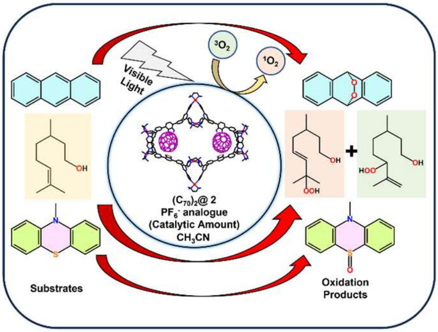
Designing 3D macromolecular systems with unique architectures and internal pockets for guest binding that show stimuli-responsive structural modulation is important but at the same time challenging. Herein, we have successfully synthesized an unusual distorted trigonal cage (**1**) via coordination-driven self-assembly of a 90º *cis*-blocked Pd(II) acceptor and a twisted tetratopic donor (**L**). Interestingly, in presence of fullerene guests $C_{70}$/$C_{60}$, **1** exhibited a structural transformation to its higher homologue tetragonal cage **2** that could stabilize two $C_{70}$/$C_{60}$ molecules within its enlarged cavity forming $(C_{70})_2$@**2** /$(C_{60})_2$@**2** respectively.[1] We recently reported similar fullerene induced transformation of a symmetric trifacial barrel to a tetrafacial barrel.[2] However, by using twisted building units (**L**) here, we could suitably tune the cavity size of the parent cage **1** as well as the transformed cage **2**.

Fullerenes are well-known photosensitizers; however, they fail to generate singlet oxygen ($^1O_2$) in solvents like acetonitrile due to poor solubility. The $PF_6^-$ analogue of $(C_{70})_2$@**2** was soluble in acetonitrile and effectively catalyzed different varieties of $^1O_2$-mediated oxidations. Although free cage **1** contains multiple photosensitizing “benzothiadiazole” moieties, $(C_{70})_2$@**2** showed multi-fold enhancement of $^1O_2$ generating ability, highlighting the importance of fullerene encapsulation for utilizing their photosensitizing properties in acetonitrile.





**Keywords**: Metal-organic cages; Host-guest chemistry; Structural transformation; Singlet oxygen generation

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# Size-Selective Photoinduced Oxidation of C-H Bonds Within Water-Soluble Coordination Cage

Valiyakath Abdul Rinshad[1], Medha Aggarwal[1], Mangili Venkateswarulu[1], Jack Clegg[2], Partha Sarathi Mukherjee[1*]

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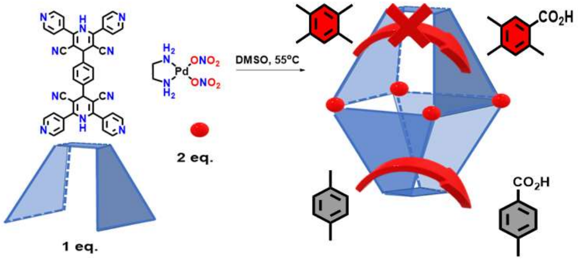
The oxidation of the primary carbon-hydrogen bond is a long-sought-after goal for the sustainable exploitation of petrochemical products. From an industrial point of view, heterogeneous catalysis using transition metal oxidant is often preferred for the oxidation of alkyl aromatics owing to its easy separation.[1] Nevertheless, all such metal complexes exhibited poor turnover numbers even at elevated temperatures. However, such transformation can be performed in a homogenous condition by encapsulating water-insoluble molecules within a water-soluble coordination cage.[2] Herein, we report the design and the synthesis of water-soluble $M_4L_2$ coordination architecture with the self-assembly of the dihydropyridine-based tetradentate ligand with a cis-blocked Pd (II) acceptor. The hydrophobic cavity of the capsule showed the encapsulation of xylene isomers. The oxidation of the xylene isomers within the cage showed selective formation of aromatic mono-carboxylic acids. The use of benign water as a solvent for such transformation helped ease separation and high turnover numbers. Moreover, the molecular $O_2$ has been used as the oxidant for the transformation under ambient temperature upon photoirradiation. Further, the hydrophobic cavity of the cage exhibited molecular sieving with the higher analogues of the alkyl aromatic molecules, which did not undergo such oxidation reactions in water.



**Keywords**: Coordination Cages; Photooxidation; Size-selectivity; Xylene isomers; Host-guest chemistry

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# Dynamic Behavior of Proton Confined in Pentanuclear Metal Complexes

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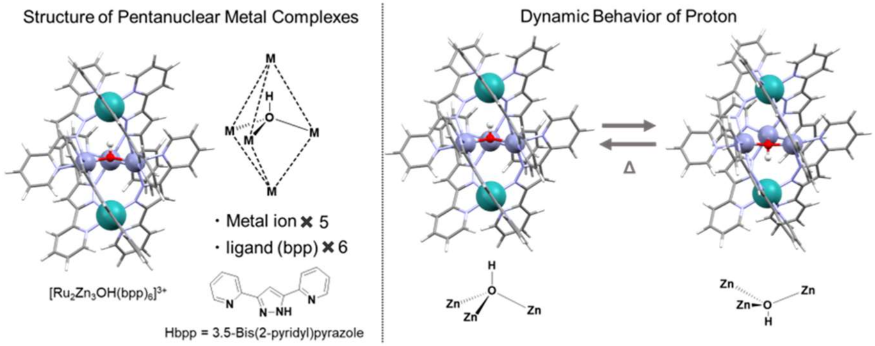
Control of the movement of $H^+$ within materials is of great significance for developing smart functional materials. We previously clarified that a pentanuclear scaffold, which is composed of five metal ions and six $bpp^-$ ligands (Hbpp: 3,5-bis(2pyridyl) pyrazole), possess internal cavity suitable for confinement of $H^+$.[1] In this study, we aimed to control the movement of $H^+$ using this unique nature of the pentanuclear scaffold.

A heterometallic pentanuclear complex, $[Ru_2Zn_3OH(bpp)_6]^{3+}$, was synthesized using a stepwise complexation method.[2] The obtained complex was characterized by $^1H$ NMR and IR spectroscopy, ESI-TOF MS, single crystal X-ray structural analysis, and elemental analysis, and the existence of $H^+$ at the central oxygen atom of its triangular core was confirmed. Subsequently, the dynamic behavior of the complex was investigated by variable temperature (VT) NMR spectroscopy. The results of VT-NMR measurements indicated that the OH moiety of the complex can flip between upper and lower sides of its triangular core, and the rate of the flipping increases as the temperature rises. Furthermore, it was also demonstrated that the movement of $H^+$ can be tuned by the constituting metal ions; changing metal ions at the apical positions from Ru(II) to Zn(II) decreased the activation energy of the flipping.

**Keywords**: Proton movement; Multinuclear complex



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# Record high-nuclearity Mn(II)-Gd macrocycles: syntheses, structures and magnetic behaviors

Kai-Peng Bai[1], Yu Wang[1], Cai-Hong Fan[1], Yuan-Qi Zhai[1], Qian-Cheng Luo[1], Mohamed Saber Lassoued[1], Wei-Peng Chen[1,*], Yan-Zhen Zheng[1,*]

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Three high-nuclearity oxo/alkoxo-bridged cyclic nanosized clusters $\{Mn_{12}Gd_{12}\}$, $\{Mn_{14}Gd_{12}\}$ and $\{Mn_{16}Gd_{16}\}$ were successfully synthesized. Notably, these huge aggregates are rare examples of Mn(II)-contained 3d–4f clusters because the divalent manganese ions are easily oxidized in air under alkaline conditions. In addition, $\{Mn_{16}Gd_{16}\}$ is the largest known member of the fascinating family of Mn–Gd complexes. Magnetic studies indicate that the above three compounds do not exhibit the expected larger magneto-caloric effect (MCE). This may be attributed to the relatively Mn(II)···Mn(II)/Gd(III) antiferromagnetic coupling and magnetic anisotropy of the metal ions, which were further verified by theoretical modelings. Moreover, the ring-like pore structures and the large molecular weight of $H_2$dpga ligands may also cause a low metal/ligand mass ratio for clusters, so as to have a negative influence on the increase of their MCEs.

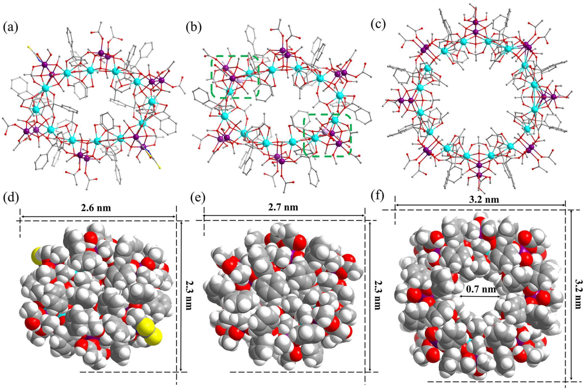

**Figure 1.** Ball-and-stick views (with H atoms removed for clarity) (a–c) and the space filling diagrams (d–f) for **1**–**3**, respectively. Color codes: Gd, cyan; Mn(II), purple; Mn(III), pink; S, yellow; N, blue; O, red; C, grey; H, white.

**Keywords**: 3d-4f cluster, Ring-like nanoscale, Magnetocaloric effect, Antiferromagnetic interactions.

# Selective catalytic oxidation of hydrocarbons by Cu-paddlewheel-based metal-organic cages

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Selective catalytic oxidation, such as the conversion of hydrocarbons into their aldehyde counterparts, is a pivotal step in synthesizing valuable precursors for the chemical industry. Traditional metal-based catalysts, such as metals, alloys, and metal oxides, are commonly used for the oxidation of organic compounds but often require high temperature conditions and suffer from limited reaction selectivity. To address these challenges, we propose the use of Cu-paddlewheel-based metal-organic cages (MOCs) as heterogeneous catalysts for the selective oxidation of mesitylene/xylene. MOCs, comprised of metal clusters coordinated to organic ligands, can be designed with specific sizes, shapes, and functionality through the strategic selection of metal ions and ligands. A series of MOCs featuring various functional groups on isophthalate ligands were prepared to elucidate the influence of these functional groups on catalytic oxidation. Their catalytic performances were further compared with those of the Cu-paddlewheel based metal-organic framework, HKUST-1. The MOCs enable a highly selective catalytic conversion of mesitylene/xylene to aromatic aldehydes. Importantly, the inherent loose arrangement of MOCs promotes mass transport of reactants, such as mesitylene/xylene and oxygen, to the catalytically active sites, thereby expediting the oxidation process. This research highlights the potential of MOCs as heterogeneous catalysts.

**Keywords:** Metal-organic cage; heterogeneous catalysts; selective oxidation

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# Coordination Compounds for Medical Applications (CM)

# Abstract

# Metallomics approach for deciphering the biological role of metals

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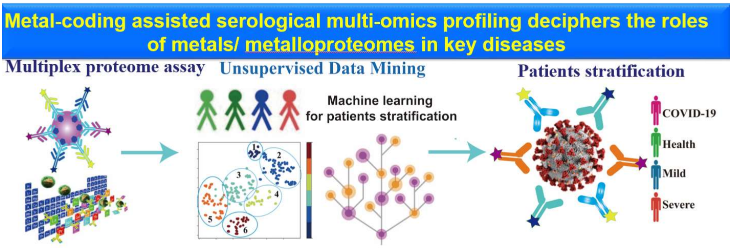
Your Metals are essential for all lives and certain metal compounds have long been used in medicine and healthcare. It is important to identify metal-protein interactions at a proteome-wide scale which are difficult due to diversity of metal-protein interactions.[1,2] We have integrated metallomics with metabolomics, transcriptomics and deep learning to examine multiple cellular changes to the numerous intracellular process affected3 and to quantify the metals for rapid metallome/proteome-wide profiling of metal-binding proteins.

By integrating a home-made fluorescence imaging with a proteomic approach, we visualized the Cr(III) proteome being mainly localized in the mitochondria, and subsequently show that Cr(III) binds to ATP synthase at its beta-subunit.[3] Such a long-standing question of how Cr(III) ameliorates hyperglycaemia stress at the molecular level opens a new avenue for the pharmacological effects of Cr(III). We have built up a metal-coding assisted systematic multi-omic platform, i.e. serological metallome, immunoproteome integrated with single-cell proteome.[4] We constructed a correlation network between the host Metallome/ Metalloproteome–Immunoproteomes, providing a holistic view of the links between the host metallome and immunity of COVID-19. Our metallomic approach can be readily extended to other essential biometals, opening a new horizon for metallobiology, inorganic chemical biology and precision medicine.

*We thank the RGC (SRFS2122-7S04, C7034-20E, 17306323) of Hong Kong SAR; and the University of Hong Kong (URC and Norman & Cecilia Yip Foundation) for support.*



**Keywords**: chromium; metallomics; biocoordination chemistry; metalloproteomics; imaging

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# Biomimetic Nickel (II) Molecular Phototheranostics

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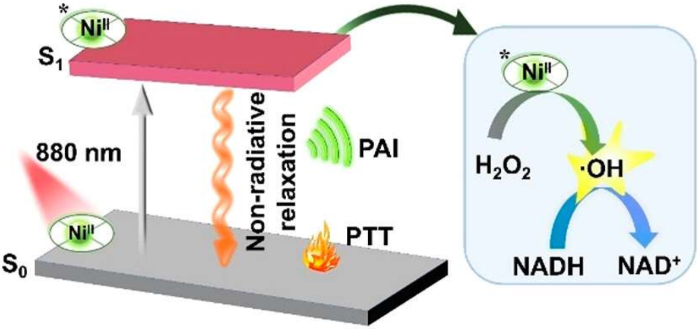
Phototheranostics have emerged as a promising subset of cancer theranostics[1-2] owing to their potential to provide precise photoinduced diagnoses and therapeutic outcomes by undergoing excited-state deactivation via photosubstitution reactions. Here we report a set of macrocyclic organonickel(II) complexes.[3] Ultrafast transient absorption spectroscopy combined with theoretical calculations revealed that, upon photoexcitation, a higher population of ligand-centered and 3MLCT states was studied. Proof-of-principle experiments involving thrombus treatment or photoimmunology demonstrated their potential application and the benefits as as "all-in-one" phototheranostics that can accrue from manipulating the excited-state features of early transition-metal complexes.[4]



**Keywords**: Nickel; **Phototheranostics**; excited-state; metal medicine

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**Coordination compounds for**
**Medical applications (CM)**
**Invited Speaker**
**CM-I-01**
**Paras Nath Yadav**

# Anticancer potency of 3-acetylcoumarin thiosemicarbazones and their copper(II) complexes

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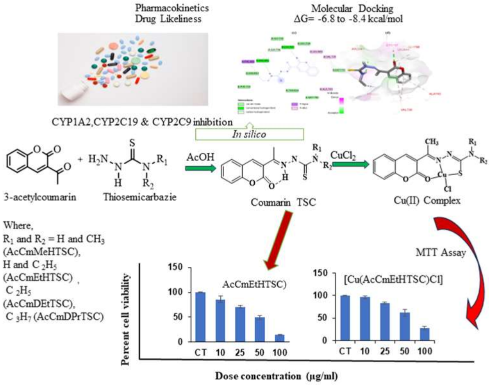
3-Acetylcoumarin N(4)-alkyl i.e. methyl, ethyl, diethyl and dipropyl, thiosemicarbazones; H***AcCmMeTsc, HAcCmEtTsc***, H***AcCmDEtTsc*** and ***HAcCmDPrTsc*** and their copper(II) complexes ***[Cu(AcCmMeTsc)Cl], [Cu(AcCmEtTsc)Cl]***, ***[Cu(AcCmDEtTsc)Cl]*** and ***[Cu(AcCmDPrTsc)Cl],*** respectively were synthesized and characterized by elemental analysis, UV-Vis, FTIR, $^1$H and $^{13}$C NMR, EPR and HR-ESI Mass spectrometry and single crystal XRD study. Single crystal study of the compounds; ***AcCmDEtHTsc*** and ***AcCmDPrHTsc*** revealed the existence of *E* tautomer and partial double bond length along the thiosemicarazide skeleton. The MTT *in vitro* cytotoxicity of the compounds against MCF-7 and MDA-MB-231, exhibited strong anticancer activity in dose dependent manner with IC50 value in the range of 13.01-48.31 µg/mL against MCF-7 cells and 32.84-71.86 µg/mL against MDA-MB-231 cells. Western Blot analysis exhibited upregulation of pro-apoptotic protein Bax and down regulation of anti-apoptotic protein Bcl2.



**Keywords**: Anticancer, Copper(II) complexes, Coumarin-thiosemicarbazone, Molecular Docking, Western Blot analysis.

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# Benzothiazole Schiff Base Complexes: Anticancer Activities and Biological Evaluation Towards Cancer Cells

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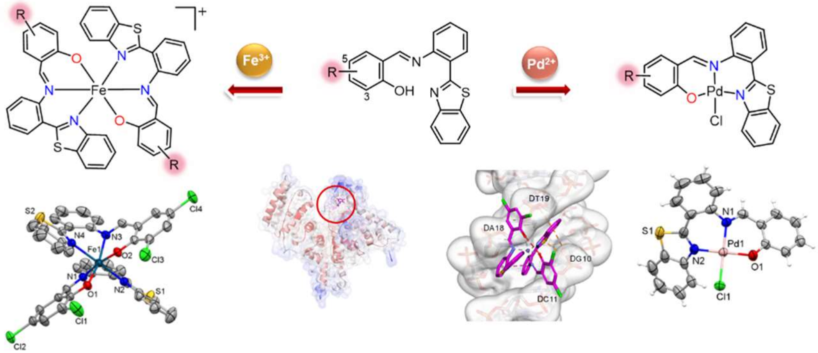
A series of of novel Fe(III) and Pd(II) complexes containing benzothiazolylazo-type Schiff base ligands were successfully synthesized. The X-ray structures of the Pd(II) complexes show distorted square planar geometry with two six-membered metallocyclic rings. The complexes possessed good binding affinity towards CT-DNA and BSA protein. These results were further confirmed by molecular docking. The anticancer activities of the ligands and complexes against three human cancer cell lines (A549, HepG2, and T47D) were determined. The complexes of Fe(III) demonstrated the highest antiproliferative effect against three cancer cell lines compared with cisplatin and inhibit cell migration through the induction of apoptosis, intracellular ROS production and cell cycle arrest. While the Pd(II) complexes show highest effect against HepG2. Interestingly, these complexes are less toxic to normal lung cells (IMR-90), as compared to the cancer cells, suggesting a promising model for novel anticancer drug development.



**Keywords**: benzothiazole Schiff base; Pd(II) complex; Fe(III) complex; anticancer activities

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# Bismuth complexes and materials for challenging antimicrobial resistance

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The *World Health Organisation (WHO)* and the *United Nations (UN)* have identified Antimicrobial Resistance (AMR) as being critical health and economic challenges which require urgent scientific, administrative, and governmental action. Since the introduction of antibiotics 80 years ago, the quantum of effective drugs for managing infections has diminished dramatically.[1]

As a sustainable and enduring strategy our work centres on the development of metal-based rather than natural or organic antimicrobial agents and is predicated on the difficulty microbes face in evolving mechanisms which allow resistance to metal-based compounds to emerge.

Bismuth(III) is known to mimic common Fe(II/III) binding, transport and uptake processes in biological systems but lack the important redox chemistry. This exemplifies the 'Trojan horse' approach in using the target microbes natural iron acquisition and utilization processes to introduce an exogenous metal which, because of fundamental chemical differences, can impact negatively on critical processes in the cell, such as enzyme function and oxidative stress.[2,3]

This presentation will focus on our recent findings into the formation, toxicity, biological activity and selectivity of new bismuth-based antimicrobial complexes, composite materials and coatings, and provide some insight into different and possibly new mechanisms-of-action.[4-6]

**Keywords**: bismuth; antibacterial; complexes; materials; gels

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# Cluster-based redox responsive MRI contrast agents

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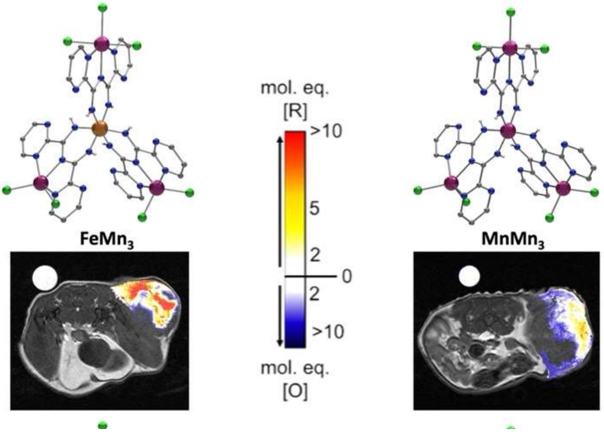
Molecular clusters hold great promise as MRI contrast agents (CA), where selective design can afford control over the cluster size, shape and total spin state. A key characteristic that can endow these complexes with advanced *in situ* reactivity to biomolecular changes in their environment is that the collection of metal ions are linked electronically and can act as a single entity. Yet the potential of clusters as MRI CA has not been realized due to challenges associated with dissociation/speciation in biological media. To resolve this, we employed *N*-2-pyrimidylimidoyl-2-pyrimidylamidine to selectively bind 3d metal ions to form highly stable mixed metal clusters. This presentation will focus on these biologically stable chelates, wherein the microenvironment-responsive chemical activities of our clusters enable us to map biochemical redox potentials spanning reducing and oxidizing environments. Through spectroscopic, electrochemical and magnetic analysis along with *in vitro* and *in vivo* studies, application of iron and manganese homo- and heterometallic metal clusters as MRI CA capable of mapping tumor redox status through a simple $T_1$w/$T_2$w ratiometric approach is demonstrated. This design strategy introduces heteropolynuclear complexes suitable for semi-quantitative *in vivo* MR imaging of tissue redox status, opening new avenues for non-invasive characterization of biochemical microenvironments by MRI.



**Keywords**: redox responsive MRI contrast agents; polynuclear 3d complexes; heteromultinuclear contrast agent design; smart MRI probes; MRI-based redox mapping *in vivo*

# Cyclometalated arylolefin complexes of Pt(II): synthesis, characterizations, *in vitro* cytotoxicity

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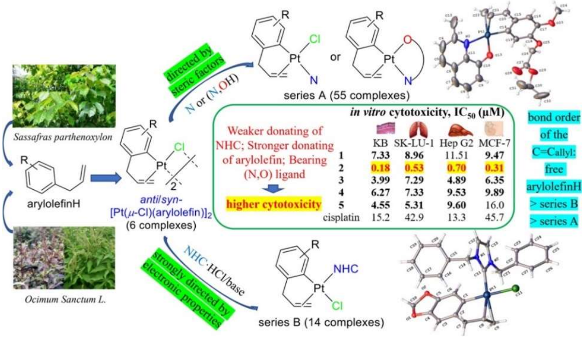
Three generations of platinum(II) based drugs have been playing a critical role in cancer chemotherapy worldwide [1]. However, these drugs still cause severe side effects [2]. Herein, several natural arylolefins originated from plant oils were activated at the *ortho*-C–H of the phenyl ring to furnish dimer complexes, [Pt($\mu$-Cl)(arylolefin)]$_2$, which possess two *syn*/*anti* isomers [3a]. The reaction of these dimers with various either amines (N/N,OH) or N-heterocyclic carbenes (NHCs) produced [PtCl(arylolefin)(N)] and [Pt(arylolefin(N,O)] (series A) or [PtCl(arylolefin)(NHC)] (series B), respectively. The reaction directions are decided by the nature of the reactants, and not by the reaction conditions. The analyses of the NMR spectra, XRD and DFT results indicated that the formation of series B is strongly dominated by electronic properties, while steric factors direct the reaction to form series A. In addition, the olefinic character of the C=Callyl group is exposed as following: free arylolefin > series B > series A [3b]. The result of testing *in vitro* anticancer activity showed that the complexes bearing (N,O) chelator or containing a more weakly donating NHC and the strongest arylolefin donor exihibit 19–147 times more toxicity than cisplatin on four tested human cancer cell lines [3c,d].



*in vitro* cytotoxicity, IC$_{50}$ (µM)

| | KB | SK-LU-1 | Hep G2 | MCF-7 |
|---|---|---|---|---|
| **1** | **7.33** | **8.96** | 11.51 | **9.47** |
| **2** | **0.18** | **0.53** | **0.70** | **0.31** |
| **3** | **3.99** | **7.29** | **4.89** | **6.35** |
| **4** | **6.27** | **7.33** | **9.53** | **9.89** |
| **5** | **4.55** | **5.31** | **9.60** | 16.0 |
| cisplatin | 15.2 | 42.9 | 13.3 | 45.7 |

**Keyword:** Platinum(II) complexes, natural arylolefin, quinoline-8-ol derivatives, *N*-heterocyclic carbenes, *in vitro* cytotoxicity.

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# Cytotoxicity and Mechanism of Action of New Pyridine-2,6-Dicarboxylate Ga(III) Complexes

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Two Ga(III) complexes, derived from pyridine-2,6-dicarboxylic acid and aminopyridine derivatives, share a common structure but differ in extra-nuclear cations. The complexes feature ($pydc^{2-}$) units bound to Ga(III), forming a distorted octahedral geometry, while ($apyH)^+$ units act as extra-nuclear cations. This combination results in enhanced electrostatic interactions and overall stability of the crystal structure, supported by various interaction types. Thermal analysis (TGA) shows both compounds remain stable up to 135°C.

In cancer cell lines, the complexes exhibit distinct $IC_{50}$ values, attributed solely to the $NH_2$ substitution position in the aminopyridine-derived extra-nuclear cations. This emphasizes the profound impact of small extra-nuclear cation variations on the cytotoxicity of metal complexes. Cellular penetration differences are likely due to distinct noncovalent interactions between the extra-nuclear cation and the anionic complex, contributing to varying $IC_{50}$ values.

Notably, these complexes exhibit potent inhibitory effects on A431 cells. Mechanistic investigation through expression assays of apoptosis and autophagy-related proteins suggests bimodal cell death, involving mitochondria-mediated apoptosis and autophagy, in A431 cells treated with both complexes.

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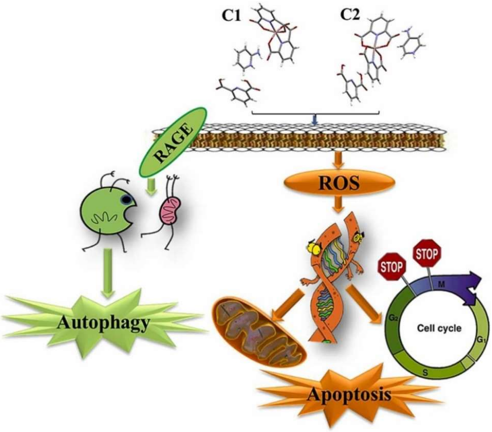

**Keywords**: Ga(III) complex; Extra-nuclear cation; Cytotoxicity; Apoptosis; Autophagy

# Tetraphenylborate-based Ru(II) drug candidates for triple-negative breast cancer (TNBC) therapy

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Organoruthenium complexes are known to exhibit a wide range of biological activities. Some of them have shown great promise in cancer therapy and have successfully entered clinical trials.[1] Notably, cyclopentadienyl ruthenium (CpRu) complexes have shown to be particularly active against triple negative breast cancer, an aggressive type of breast cancer that is difficult to treat.

We and others have recently shown that $BPh_4$ displays a synergistic anticancer activity with cationic organoruthenium complexes when used as counterions.[2] In order to further investigate the role of the $BPh_4$ in these complexes, we have designed two families of cyclopentadienyl ruthenium (CpRu) complexes in which $BPh_4$ is either a counterion or is covalently linked to the ligand, resulting in a zwitterion. For both families, the Ru zwitterion-functionalized cyclopentadienyl complexes demonstrated enhanced anticancer activity against the triple-negative breast cancer cell line compared to their ruthenium cation counterparts. Moreover, preliminary results indicate that both types of boron-containing complexes preferentially accumulate in different organelles, providing insights into their mechanism(s) of action. Further studies are warranted to elucidate the exact pathways through which these complexes exert their cytotoxic effects and to explore their potential as anticancer drug candidates.

This presentation will discuss our latest results regarding the synthesis, characterization and the biological properties of these boron-based organoruthenium complexes.

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# Tuning chemical properties of phthalocyanine and porphyrin metal complexes for photodynamic therapy

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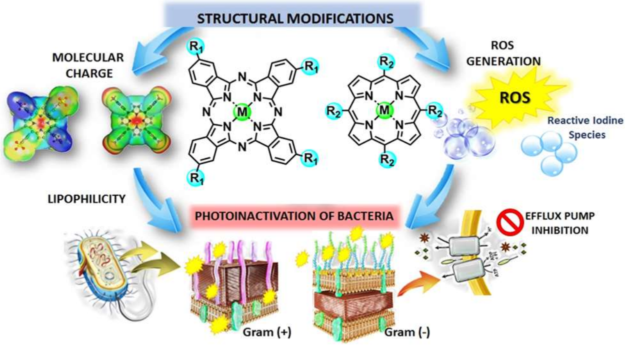
The global pandemic of COVID-19 has been raging during the last 3 years, but medical experts warn another health crisis is looming - antibiotic resistance of bacteria and development of "superbugs." These have trigged an increasing interest in the search for different antimicrobial action mechanisms for which low to no resistance has yet been observed. To address this issue, photodynamic inactivation (PDI) is a promising light-dependent alternative therapy for the treatment of localized infections. [1-2] Herein we present our research on two families of metal complexes with modified porphyrin and phthalocyanine ligands (**Figure 1**).

Aiming towards comprehensive structural-activity relationships, various derivatives were synthesized and characterized. The effects of the polarity, size of the chains, number and distribution of molecular charges and central coordinating metal ions on their photophysical and photochemical properties as well as biological activity will be discussed. [2-3]

We found unique and insightful structure-activity relationships for these families of coordination compounds, which may contribute to the rational design of photosensitizers for use in photodynamic inactivation of microorganims. Furthermore, strategies that combine multiple approaches (the use of nanoparticles, surface modification of $TiO_2$ with selected metalloporphyrins, and addition of inorganic salts) to increase antimicrobial efficacy will be discussed.[4-5] Finally, our latest findings on the use of investigated photosensitizers/photomaterials for photodynamic inactivation of resistant Gram-positive and Gram-negative bacteria using *in vivo* bacterial infection models (Balb C mice) will be presented.



**Keywords**: metal complexes; porphyrins; phthalocyanines; photodynamic therapy

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**Coordination compounds for**
**Medical applications (CM)**
**Flash Presentation**
**CM-F-01**
**Yi-Hsin Liu1**

# Singlet Oxygen on Material Surface: Energy Transfer via Artificial Defects for NIR Photodynamic Therapy

Yi-Hsin Liu[1*], Ping Yi Jiang[1], Ming-Kang Tsai, Yi-Chun Yeh

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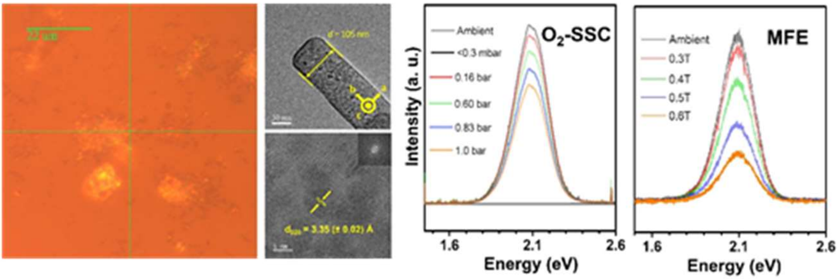
Spin states of molecular oxygen ($O_2$) toward perturbing species are a long-standing, mysterious, and hidden phenomenon. For rare cases of forbidden electric dipole processes, singlet oxygen, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, can be observed after an intersystem crossing (ISC) process in the photosensitizers followed by a triplet-triplet annihilation (TTA) process. Recent works of creating in-gap bound states in quantum architectures, such as $Mn^{2+}$ ($d^5$) in monolayer CdSe, produce intense phosphorescence, directly pumping ambient oxygen to singlet states. By varying doping concentration, temperature, and magnetic fields, relatively rare NIR emission (1200-1300 nm) of singlet $O_2$ was observed accordingly after spin-spin entangled interaction between paramagnetic $O_2$ and $Mn^{2+}$. Modern photodynamic therapy (PDT) requires spatial energy transfer from the photosensitizer's triplet excited state ($T_1$) to the excited state of oxygen. The interaction is a quantum dynamic process, mainly sensitive to paramagnetic species (e.g., $O_2$), resulting in a long $T_1$ lifetime and enhanced SNR for spectral imaging applications like fluorescence lifetime imaging microscopy (FLIM). By incorporating less toxic $Mn^{2+}$ into the photosensitizers, cancerous cells can be relocated by NIR-emission probes and MRI contrast agents as dual imaging techniques, followed by intracellular and vascular developments, even photo-oxidation of amyloid-β fibrils via PDT.

**Keywords**: Singlet oxygen; phosphorescence; defects; nanosheets; photodynamic therapy



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# Anti-cancer Property and DNA Binding Interaction of First Row Transition Metal Complexes

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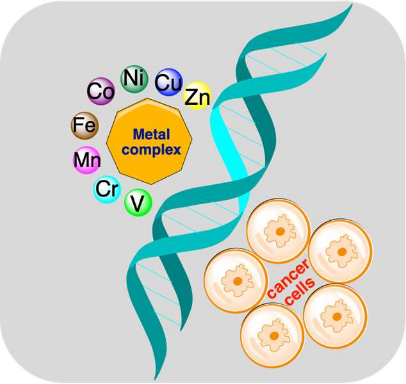
Metal ions carry out a wide range of functions, including redox and acid-base catalysis, signaling, electron transport, and structural work. Metals can interact actively with enzymes through strong or weak bindings to biomacromolecules. The kind of interaction that directs the metal's binding process to macromolecules might vary depending on the type of metal, from pure electrostatic for main group metals to suitable coordination chemistry in transition metals. Since the accidental discovery of cisplatin, the importance of these metal complexes in medical biology has been the focus of primary research. Numerous metal complex libraries produced through the tuning of coordinated ligands have been documented and are currently being studied for the potential to treat various illnesses in humans. The review's scope encompasses the most noteworthy instances of first-row transition metal complexes that have been reported, with a focus on a variety of synthetic procedures to generate possibly novel complexes and investigate their interactions with biological macromolecules.

**Keywords**: Transition metals, coordination, interaction, biological macromolecules, DNA, protein, enzyme, therapeutics.



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**Coordination compounds for**
**Medical applications (CM)**
**Poster Presentation**
**CM-P-02**
**Peyman Salahshour**

# Study on crystallographic structure and antiproliferative effect of a new mixed-ligand strontium(II) complex

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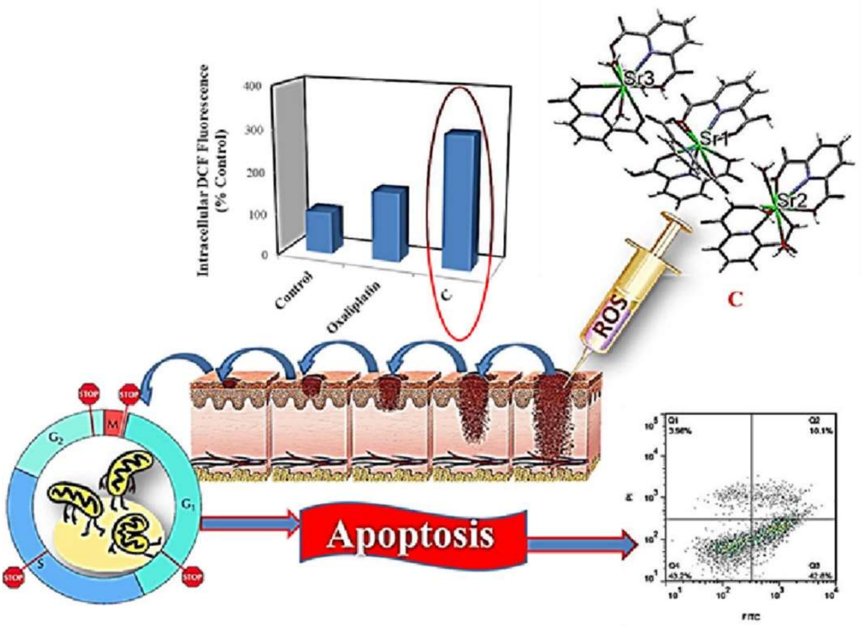
A novel mixed-ligand Sr(II) complex was synthesized from the reaction between N,N´–bis(2–hydroxy-5-methylphenyl) pyridine- 2,6-dicarboxamide and $Sr(NO_3)_2 \cdot 4H2O$ metal salt. The X-ray crystallographic studies indicated that the ligand was hydrolyzed on complexation. The nature of metal, ligand structural features, and reaction conditions were suggested as effective agents for the hydrolysis of the ligand. The complex showed a more strong inhibitory effect compared to both amidic ligand and pyridine-2,6- dicarboxylic acid molecule against cancer cell lines. The most potent anticancer activity of the complex was shown against the A375 cell line. The rise of ROS and loss of MMP proved that the apoptosis pathway may be a remarkable mechanism for cell death.



**Keywords**: Strontium complex; Amide ligand; Cytotoxicity; Production of ROS; Apoptosis

Coordination compounds for
Medical applications (CM)
Poster Presentation
CM-P-03
Taishi Higashi

# Fabrication of polycatenanes via condensation of two polypseudorotaxanes for drug delivery carrier

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Recently, interlocked supermolecules, such as polyrotaxanes and polycatenanes, have attracted considerable attention, and cyclodextrins (CyDs) are often used as building blocks. Moreover advanced materials using CyD-based polyrotaxanes have been developed extensively. However, few reports are available on CyD-based polycatenanes. We previously prepared β- or γ-CyD polycatenane through cyclization of the polypseudorotaxane[1]. In the present study, we prepared α-CyD polycatenanes through the condensation of two polypseudorotaxanes, and evaluated their potentials as drug delivery carriers for biopharmaceuticals.

To prepare polycatenane, polypseudorotaxanes consisting of α-CyD and amino- or carboxyl-terminated polyethylene glycol (PEG) were prepared. Then, both polypseudorotaxanes were condensed by BOP reagent/1-hydroxybenzotri-azole/*N*- ethyldiisopropylamine (Fig. 1). Formation of the polycatenane was confirmed by $^1$H-NMR. To prepare the cationic polycatenane, diethylenetriamine was modified to the resulting polycatenane.

Polycatenane was successfully prepared through cyclization of the two polypseudorotaxanes. In addition, cationic polycatenane was successfully prepared by modification of polycatenane with diethylenetriamine. Interestingly, cationic polycatenane was efficiently formed complexes with biopharmaceuticals such as Cas9 RNP and siRNA. Moreover, the intracellular delivery efficiency of cationic polycatenane was greater than that of cationic polyrotaxane. These results indicate the potentials of cationic polycatenane as drug delivery carriers for biopharmaceuticals.

**Fig. 1. Preparation of Polycatenane via Condensation of Two Polypseudorotaxanes**

**Keywords**: cyclodexterin; polyethylene glycol; polycatenane; supramolecular chemistry; drug delivery

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# Transformable supramolecular material for reversible PEGylation of protein drugs

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In recent years, protein drugs have been developed aggressively; however, they often show insufficient physicochemical stabilities and short blood retention. Thus, polyethylene glycol (PEG)-modification are often used. However, covalent PEGylation dramatically reduces the bioactivity of protein drugs. Polyrotaxanes (PRXs) are mechanically interlocked molecules obtained by threading linear compounds through a number of cyclodextrins (CyDs) and capping their terminals with bulky compounds. Importantly, CyDs in PRX are movable onto an axile molecule. Thus, the movable properties of functionalized PRXs allow efficient complexation with protein. We herein prepared a PRX possessing both amino groups and PEG chains (PEG-$NH_2$-PRX). We expected that PEG-$NH_2$-PRX provides amino groups to interact with proteins on demand because the mobility of amino groups in PEG-$NH_2$-PRX was high (Fig. 1). In fact, PEG-$NH_2$-PRX formed complexes with proteins efficiently compared to PEGylated amino-dextran (PEG-$NH_2$-DEX), a control material fabricated with a macromolecular backbone polymer. Moreover, PEG-$NH_2$-PRX markedly improved the stability of antibodies and prolonged the hypoglycemic effects of insulin without loss of bioactivity, compared to PEG-$NH_2$-DEX. In conclusion, a transformable mixing-type material, PEG-$NH_2$-PRX, was developed for reversible PEGylation of protein drugs. These findings suggest that the supramolecular material, PEG-$NH_2$-PRX, is a promising PEGylation material for protein drugs compared to macromolecular materials.

**Keywords**: supermolecule; PEGylation; polyrotaxane; cyclodextrin; protein

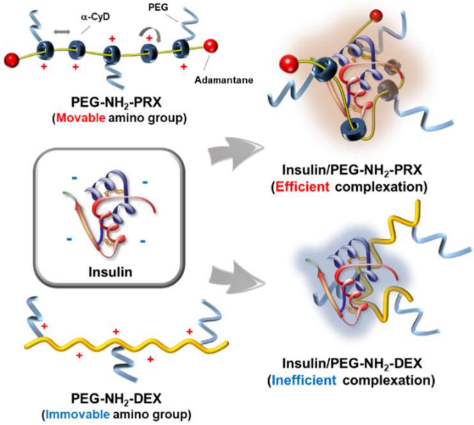

**Fig. 1. Proposed Scheme for Insulin Complexation with PEG-$NH_2$-PRX or PEG-$NH_2$-DEX**

# Design and evaluation of lactose-modified cyclodextrin as a drug for Niemann-Pick disease type C

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Niemann-Pick disease type C (NPC) is characterized by the accumulation of free cholesterol in late endosomes/lysosomes due to dysfunction of NPC1 or NPC2 protein. The main symptoms of NPC are hepatosplenomegaly and neurological symptoms accompanied by decreased motor, cognitive, and mental functions. Namely, target tissues for NPC treatment are liver and brain. Recently, hydroxypropyl-β-cyclodextrin (HP-β-CyD) has been utilized as a treatment agent for NPC because of its lowering effects on cholesterol accumulation in NPC model mice. However, HP-β-CyD has lack of targeting ability to liver and brain. In the present study, we developed lactose-modified HP-β-CyD (Lac-HP-β-CyD) to target for liver and brain. In addition, the lowering effect of Lac-HP-β-CyD on cholesterol accumulation was evaluated in NPC model mice. As a result, Lac-HP-β-CyD decreased cholesterol accumulation in both liver and spleen through the host-guest interaction between Lac-HP-β-CyD and cholesterol. Lac-HP-β-CyD also decreased the amount of free cholesterol in the cerebrum, improving motor dysfunction and the survival period. These results suggest that Lac-HP-β-CyD has potential as a treatment agent for NPC.

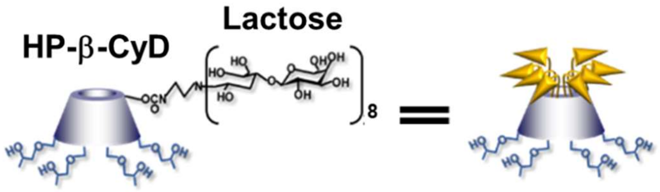

**Fig. 1. Schematic Structure of Lac-HP-β-CyD**

**Keywords**: Niemann-Pick disease type C; cyclodextrin; liver targeting; spleen; cholesterol

# Multistep transformable polyrotaxanes for versatile delivery platform of various biopharmaceuticals

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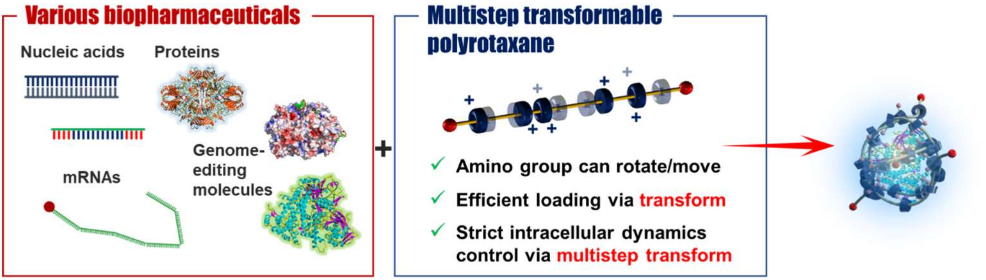
Numerous biopharmaceuticals, including nucleic acids, proteins, and genome-editing molecules, have been developed. Typically, specific carriers are designed for each biopharmaceutical to enable intracellular delivery, but this approach is resource-intensive, time-consuming, and costly.

In this study, we aimed to develop versatile and universal delivery carriers using cyclodextrin (CD)-based polyrotaxanes (PRXs). PRXs are supramolecular polymers consisting of CDs threaded onto the axile molecule (polyethylene glycol: PEG) as the carrier backbone. CDs in PRXs can rotate and move along the axial molecular chain. Thus, we developed aminated PRXs (amino-PRXs) to interact with anionic functional groups in proteins or nucleic acids. Furthermore, we optimized amino groups and degradable bonds in amino-PRXs to endow the endosomal escape and controlled drug release properties.

Amino-PRXs efficiently formed complexes with proteins and nucleic acids than the unmovable control polymers. Optimized amino-PRX (5th generation; 5G) enhanced intracellular uptake and controlled intracellular dynamics, improving delivery for siRNA, antisense oligonucleotides, mRNA, β-galactosidase, and Cas9/Cpf1 genome-editing ribonucleoproteins over commercial reagents.

In summary, amino-PRX (5G) can serve as a versatile and universal platform for delivering various biopharmaceuticals, overcoming the limitations associated with individualized carrier design and offering a cost-effective solution for intracellular delivery.



**Keywords**: protein drugs; nucleic acid drugs; genome editing; drug delivery; polyrotaxane

# Molecular docking analysis of different zinc(II)-salen complexes into amylin

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Recent studies show that one possible cause of hyperglycemia, which in turn results to type 2 diabetes mellitus (T2DM), is the formation of misfolded human islet amyloid polypeptide (hIAPP) aggregates, destroying pancreatic β-cells. Zinc supplementation is a generally used as a part of the treatment because of the insulin-mimetic property of zinc. For this reason, we present molecular docking studies of different zinc salen-based complexes with varying the electronics and sterics of the substituents, into the protein amylin. We look into the nature of their interactions and binding affinity, as an insight into the structure-activity relationships of the zinc(II)-salen complexes and amylin. We found that sterics, rather than electronics, has greater effect on the number of the conventional hydrogen bonds present in the docked structure. Exploring these inhibition studies on the aggregation of amylin using these zinc(II) salen-based complexes gives new avenues for T2DM treatment.

**Keywords**: Amylin aggregation; electronics; molecular docking; type 2 diabetes mellitus; zinc salen

# Mixed olefin/amine Pt(II) complexes: A new class potential for the development of anticancer drugs

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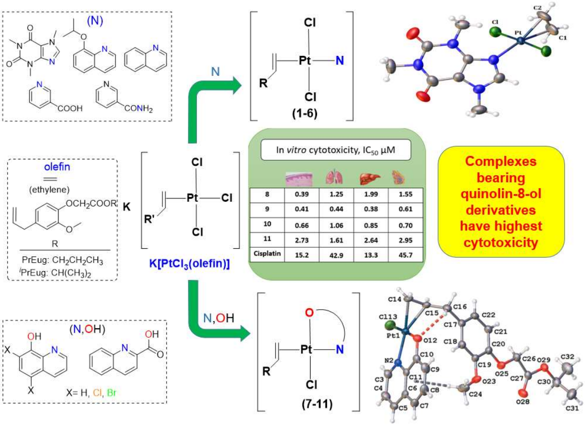
Since Zeise's salt, the first organometallic compound, was isolated in essentially pure form in 1827, various olefin ligands have been introduced into the coordination entity of platinum(II) for different purposes, especially in the field of catalysis [1]. In contrast to the well-known platinum(II) complexes in chemotherapy as cisplatin, carboplatin and oxaliplatin, studies evaluating the biological activity of organoplatinum complexes bearing olefin are very limited [2]. In our research, two series of organoplatinum complexes *trans*-[$PtCl_2$(olefin)(N)] and [PtCl(olefin)(N,O)] are synthesized by the reaction between K[$PtCl_3$(olefin)] (olefin: ethylene, propyl eugenoxyacetate, isopropyl eugenoxyacetate) and various either amines (N/N,OH) under the mild conditions with high yields [3]. The analyses of the NMR spectra and XRD results have showed that all the complexes are square-planar, in which the N atom of amine is in *trans* position to the C=C group of olefin. The tested result of *in vitro* anticancer activities indicated that the complexes bearing the chelator ligand derived from quinolin-8-ol exhibit the best cytotoxicity with values $IC_{50}$ of 0.39-2.95 μM, which are 5 ÷ 95 times more than cisplatin on four tested human cancer cell lines.



In *vitro* cytotoxicity, $IC_{50}$ μM

| | | | | |
|---|---|---|---|---|
| 8 | 0.39 | 1.25 | 1.99 | 1.55 |
| 9 | 0.41 | 0.44 | 0.38 | 0.61 |
| 10 | 0.66 | 1.06 | 0.85 | 0.70 |
| 11 | 2.73 | 1.61 | 2.64 | 2.95 |
| Cisplatin | 15.2 | 42.9 | 13.3 | 45.7 |

Complexes bearing quinolin-8-ol derivatives have highest cytotoxicity

**Keywords**: Organoplatinum(II) complexes, olefin, amines, *in vitro* cytotoxicity.

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# Advancing Cancer Immunotherapy with Metal-Phenolic Framework Nanoparticles and Electrical Ablation

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To advance beyond the constraints of traditional cancer immunotherapy, activating antigen-presenting cells (APCs) to initiate the cancer-immune cycle is essential. This study introduces an innovative method that merges metal-phenolic frameworks (MPF)-based immunoactive nanoparticles with electrical ablation, aiming to amplify the efficacy of cancer immunotherapy. We develop MPF nanoparticles by binding tannic acid with manganese (Mn) ions, which are then coated with CpG-oligodeoxynucleotides (CpG-ODNs) via hydrogen bonds. These CpG-ODN-coated Mn-phenolic framework (CMF) nanoparticles excel in penetrating macrophages, key APCs, and induce M1 polarization, leading to the release of proinflammatory cytokines. Significantly, these CMF nanoparticles demonstrate prolonged retention in tumors compared to standalone CpG-ODN. The therapeutic effectiveness is further boosted by employing electrical ablation, tailored to the tumor microenvironment. This approach markedly enlarges the ablation zone, thereby enhancing immunogenic cell death. The simultaneous use of CMF nanoparticles and electrical ablation not only efficiently suppresses tumor growth but also prolongs survival in a mouse tumor model. This novel combination of Mn and CpG-ODN-infused CMF nanoparticles with customized electrical ablation offers a promising new strategy for the effective treatment of resistant cancers through immunotherapy.

# Green Synthesis, Anticancer Screening and DNA Binding Studies of Mono- and Polynuclear Schiff base Complexes

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The Schiff base ligand 3,3'-((1E,1'E)-(propane-1,3-diylbis(azaneylylidene))-bis(methaneylylidene))bis(benzene-1,2-diol) (AD) was synthesized via microwave-assisted synthesis and subsequently complexed with Pd(II) and Ni(II) ions, resulting in mononuclear, dinuclear, and tetranuclear complexes. The compounds were characterized through elemental analysis, melting point determination, conductivity measurements, and spectroscopic techniques. Notably, IR spectroscopy indicated coordination of metal ions with the ligand, as evidenced by shifts in phenolic (C-O) and azomethine (C=N) peaks. The aforementioned finding was further supported by the deprotonation of the phenolic oxygen and the shifting of the azomethine proton towards a downfield region in the $^1$H NMR spectra of the complexes. The compounds were further assessed for cytotoxicity against HCT116 cells, revealing that higher nuclearity complexes, especially Pd(II) derivatives, exhibited greater anticancer activity. The tetranuclear complex $Pd_4AD$ displayed the highest potency with an $IC_{50}$ value of 2.77 μM. Additionally, electronic absorption spectroscopy and circular dichroism measurements elucidated the ligand and its metal complexes' intercalation mode binding with calf thymus DNA (ctDNA), demonstrating moderate to strong DNA binding affinity with intrinsic binding constants ranging from $3.5 \times 10^6$ to $5.3 \times 10^4$. These findings provide insights into the potential biomedical applications of the synthesized complexes.

**Keywords**: Schiff base; polynuclear complexes; Anticancer; DNA binding; Microwave-assisted synthesis

# F-Element Chemistry (FE)

# Abstract

**Keynote Speaker**
**FE-K-01**
**Yuichi Kitagawa**

# Photofunctional lanthanide complexes with π-conjugated polycyclic aromatic ligands

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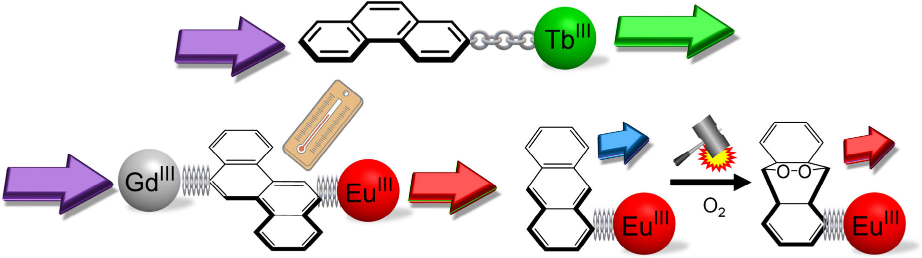
Highly luminescent compounds with high color purity have become increasingly important for developing display and sensing materials. Among the reported luminophores, trivalent lanthanide (Ln(III)) complexes (especially in Eu(III) and Tb(III) complexes) are promising candidates for achieving pure color luminescence owing to their 4f–4f transition, which has a high emission quantum yield.[1] The brightness of the Ln(III) emission is defined as the product of the light absorption coefficient of the organic ligands and the emission quantum yield due to the excitation of the organic ligands.[2] Thus, controlling the ligand electronic structure is crucial for developing luminescent Ln(III) complexes with high brightness.

Recently, model systems of bright luminescent Ln(III) complexes bearing phosphine-oxide ligands based on polyaromatic hydrocarbons, such as phenanthrene, triphenylene, chrysene, and coronene, were constructed.[3–6] The constructed model systems were based on long triplet lifetime originating from the polyaromatic system, which allow for efficient energy transfer to the Ln(III) ions. The polyaromatic ligand can also possess physical-sensing capabilities.[6–7] Herein, a novel molecular-design strategy for developing strongly luminescent Ln(III) complexes with polyaromatic ligands is presented.

**Keywords**: Europium; Terbium; Emission; Display; Sensing



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**Invited Speaker**
**FE-I-01**
**Apinpus Rujiwatra**

# Lanthanides Coordination Polymers and Their Catalytic Potential in $CO_2$ Capture and Conversion

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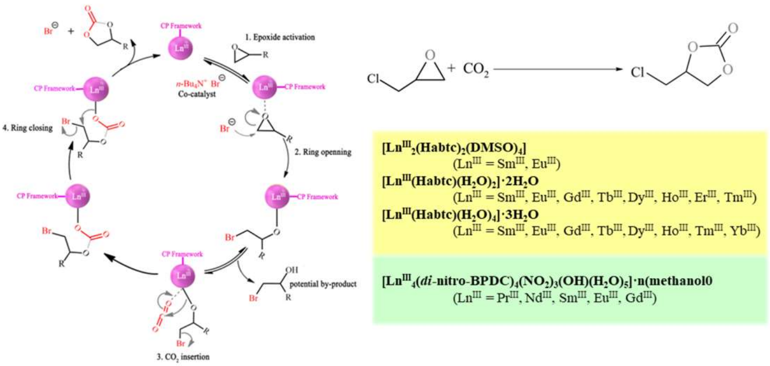
To mitigate atmospheric accumulation of $CO_2$ and its adverse effect, the *in situ* capture and conversion of $CO_2$ to important chemicals has appeared as one of the most sustainable approach. Efficient catalysts are, nonetheless, essential. Aiming at $CO_2$ cycloaddition reactions with epichlorohydrin as a modelled epoxide, lanthanide with their unique coordination chemistry and hard acidity as well as the capability to be tailor-made at molecular level and crystalline nature of coordination polymers have captured our interest. Here, crystal structures and catalytic properties of new lanthanide coordination polymers fabricated using 3,3′,5,5′-azobenzenetetracarboxylic acid ($H_4$abtc) and 2,2′-dinitrobiphenyl-4,4′-dicarboxylic acid (*di*-nitro-$H_2$BPDC) are presented. Under the solvent-free conditions, ambient $CO_2$ pressure and temperatures below 100 °C, moderate to excellent performances have been achieved. The best turn-over number and turn-over frequency of 7,682 and 1,921 $h^{-1}$, respectively, could be achieved from the reaction at 80 °C for 4 using 0.025 %mol of the catalyst. Common issues with the pre-activation and robustness have been successfully dealt with. Relation between structure and property is proposed.



**Keywords**: Lanthanide; Coordination polymer; Metal organic framework; Catalysis; $CO_2$ conversion

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# Neodymium extraction using deep eutectic solvent

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While the demand of neodymium (Nd), an important element of permanent magnets used in many technologies, has been high, the production of Nd is rather limited due to its scarce resource. This makes a separation of Nd from electronic waste being interesting. This research explored a possibility of using di(2-ethylhexyl)phosphate acid (DEHPA), a known lanthanide extractant, to prepare a deep eutectic solvent (DES) as an alternative organic phase to extract Nd from water. It was found that a 1 to 1 mixture of DEHPA and menthol resulted in immiscible DES, however, a formation of emulsion occurred during Nd(III) extraction. Addition of $NaNO_3$, known as salting-out effect, solved this problem thus making extraction possible. The conditions of extraction were studied in terms of organic to aqueous phase ratio (O:A), concentration of Nd(III), concentration of $NaNO_3$, solution pH, and vortex time. The optimal extraction condition was obtained using 1 mL DES to extract 10 mL of 10 mM $Nd(NO_3)_3$ with 0.5 M $NaNO_3$ at pH 4 and 2 min vertexing to reach an extraction efficiency of 97.44 ± 0.08%. This result offers a potential use of DEHPA-menthol DES as an alternative solvent for Nd extraction from aqueous medium such as electronic waste.

**Keywords**: neodymium, rare earth elements, permanent magnets, deep eutectic solvent, solvent extraction

# Frontiers in Coordination Chemistry (FR)

# Abstract

**Keynote Speaker**
**FR-K-01**
**Chen-Wei Liu**

# The role of hydrides in ligand-stabilized nanoclusters

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In our systematic studies of coinage metal hydrides protected by dichalcophosphate ligands ($[E_2P(OR)_2]^-$: E = S, dtp; Se, dsep),[1] we have demonstrated that interstitial hydrides in nanoclusters can reduce M(I) to M(0) and form stable superatoms.[2] Surprisingly, hydride-containing eight-electron alloy nanoclusters, $PtHAg_{19}(dtp/dsep)_{12}$, which hydride position was unequivically confrimed by single crystal neutron diffraction, were rationalized by DFT calculations that the encapsulated H atom provides its electron to the superatomic system to behave as a metallic hydrogen.[3] Subsequently the 8-electron Pd/Ag superatomic alloys with an interstitial hydride $[PdHAg_{19}(dtp)_{12}]$ and $[PdHAg_{20}(dtp)_{12}]^+$ are reported. The targeted addition of a single Ag atom to $PdHAg_{19}$ is achieved by the reaction of one equivalent of trifluoroacetic acid, resulting in the formation of $PdHAg_{20}$ in 55 % yield.[4] Importantly we succeeded to demonstrate hydride doping effects on the structure and properties of eight-electron Rh/Ag superatoms: the $[RhH_x@Ag_{21-x}\{S_2P(O^nPr)_2\}_{12}]$ (x = 0-2) series.[5] The scope of metallic hydrogen can be extended to the thiolate-protected copper-rich alloys. Examples are the first hydride-containing 2-electron palladium/copper alloys, $[PdHCu_{11}\{S_2P(O^iPr)_2\}_6(C{\equiv}CPh)_4]$ and $[PdHCu_{12}\{S_2P(O^iPr)_2\}_5\{S_2PO(O^iPr)\}(C{\equiv}CPh)_4]$, synthesized via the treatment of $[PdH_2Cu_{14}\{S_2P(O^iPr)_2\}_6(C{\equiv}CPh)_6]$ with trifluoroacetic acid.[6] These alloy nanoclusters are rare examples which interstitial hydrides are "metallic" not typically observed one-negative charge ligands.

**Keywords**: hydride; copper; silver; superatomic alloys; X-ray diffraction

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**Keynote Speaker**
**FR-K-02**
**Kentaro Tanaka**

# Capturing of Fullerenes with Macrocyclic Metal Complexes

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Fullerenes and their derivatives have received significant attention due to their wide-ranging applications that include semiconductive materials for solar cells, transistors, and photodynamic therapy. By organizing fullerenes, it is expected that a higher-order molecular organization function based on intermolecular communication between fullerenes, which is not found in monomers, will be expressed. Since such properties of fullerenes are due to their π-electron system, it is desired to develop a methodology for assembling them without direct chemical modification.

Herein, we describe molecular capturing of fullerenes with macrocyclic metal complexes through CH-π interactions. First topic is selective encapsulation of ellipsoidal fullerene $C_{70}$ with a supramolecular double-decker cage composed of shape-persistent metallomacrocycles and pillar ligands [1]. And second topic is an environmentally stable discrete array of $C_{60}$ on an electrode surface with the aid of periodic molecular pits composed of shape-persistent macrocycles [2].

**Keywords**: molecular recognition; fullerene; molecular cage; molecular pit; macrocycle

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# From Metal-Metal Multiple Bonds to Helical Metal Strings

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The study of metal string complexes with 1-D transition metal frameworks (Fig.1) began in the early 1990s. Since these complexes provide great insight into multiple metal-metal bonds, and may have potential applications as molecular wires (Fig.2), this field of research has grown in the past 20 years. As such, the electronic structure of the simplest trinuclear complexes, the supporting ligand systems, and single molecular conductance of metal string complexes are discussed. This review will introduce the development of this field and summarize some important results in the newly designed heteronuclear metal string complexes (HMSCs). These molecules may be of great interest in studying the nature of heterometallic electronic effects and molecular electronic applications.

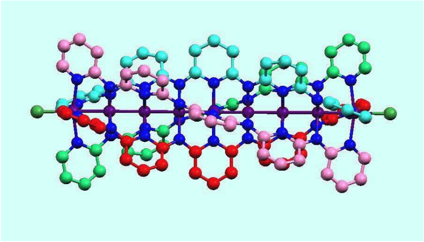

**Figure 1:** Molecular Model of Metal String Complex with Quadruple Ligands

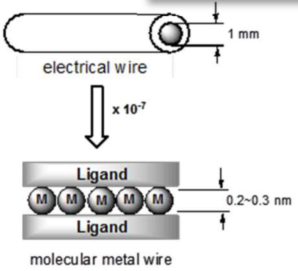

**Figure 2:** An Electric Wire and a Miniature Molecular Wire

**Keywords**: Metal String Complexes; Electric Wire; Metal-metal Multiple Bonds

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**Invited Speaker**
**FR-I-01**
**Nobuto Yoshinari**

# Construction of A family of Metal-Organic Carboxylates with L-Cysteine

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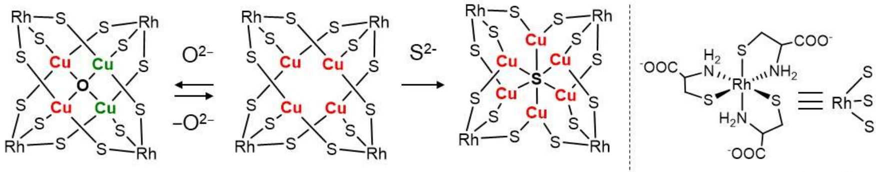
Organic carboxylates are fundamental building units for constructing coordination and hydrogen-bonded frameworks in supramolecular chemistry. Recently, discrete metal complexes with non-coordinating carboxy moieties (Metal-Organic Carboxylates; MOCs) have attracted increasing attention as alternatives to organic carboxylates because of their simple synthetic procedures and structural diversity, as well as the functionality due to transition metal centers.[1] Inspired by the historically important $Cu_{14}$ cluster with D-penicillamine, which is the first MOC,[2] we have developed a variety of metallosupramolecular aggregates based on MOCs using metalloligand approach.[1,3] For example, we have reported that an octanuclear $Rh^{III}_4Zn^{II}_4$ complex anion with 12 free COO- groups, $K_6[Zn_4O(L^{Rh})_4]$ ($L^{Rh}$ = $[Rh(\text{L-cys})_3]^{3-}$) reveals room-temperature superionic conduction in the solid state.[4] Moreover, we found an unusual condensation reaction for aqua lanthanide ions ($Ln^{3+}$) inside the crystal lattice of $K_6[Zn_4O(L^{Rh})_4]$.[5] In this presentation, I will explain our continuing study on the creation of new MOCs by reacting $L^{Rh}$ with $Ag^I$ and $Cu^I$ ions.[6] These reactions were found to afford octanuclear $Rh^{III}_4M^I_4$ complex anions $[M_4(L^{Rh})_4]^{8-}$ (M = $Ag^I$, $Cu^I$), whose molecular structure is quite similar to $[Zn_4O(L^{Rh})_4]^{6-}$. Thanks to the absence of the central O atom, these $Rh_4M_4$ clusters could show interesting reactivity with oxide and sulphide ions.



$[Cu^I_2Cu^{II}_2O(L^{Rh})_4]^{8-}$ $[Cu^I_4(L^{Rh})_4]^{8-}$ ($[\mathbf{1}]^{8-}$) $[Cu^I_6S(L^{Rh})_4]^{8-}$ ($[\mathbf{3}]^{8-}$) $\Delta$-$[Rh(\text{L-cys})_3]^{3-}$ ($L^{Rh}$)

**Keywords**: Metal-organic carboxylates; metalloligands; Redox; Copper

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**Invited Speaker**
**FR-I-02**
**Victoria L. Blair**

# C-F activation and cyclisation of fluoro-imines using bespoke bimetallic reagents

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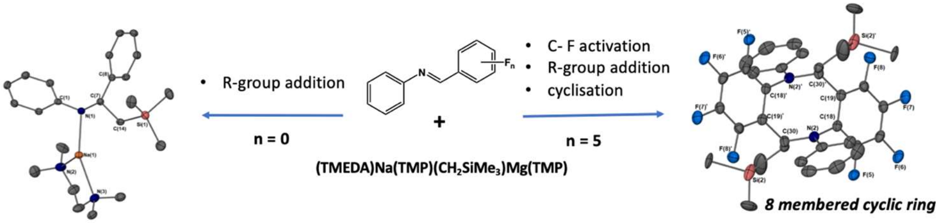
Imines are versatile and synthetically useful molecules that are used for the synthesis of many complex molecules. Their ease of synthesis and functionalisation makes Schiff's bases valuable building blocks in an array of reactions including the synthesis of amines, building pharmaceutical-based scaffolds and in multifunctional ligand design for metal complexation.[1] In this regard fluorinated imine synthons have peaked our interest, owing to their medicinal relevance and prominence of the C-F bond in almost 20% of new drug candidates.[2] One such strategy for synthetically expanding the pool of fluoro organic molecules is C-F activation. Dominated by transition metal complexes,[3] recently s-block and main group species have begun to show success.[4]

In this work, we present the synergistic relationship that exists upon employing our bimetallic sodium-magnesiate base in the functionalisation of a series of imine substrates. Focusing on fluoro-substituted imines, initial studies have revealed selective *ortho*-C-F activation, leading to the unprecedented cyclisation of two imine species and a resultant novel 8-membered carbon-nitrogen ring (Figure 1). The scope of the reaction has been investigated by varying the fluoro-ring-substitution pattern allowing the mechanistic pathway to be probed. Highlighting the synergistic relationship of the bimetallic base in the ring formation comparative studies on the mono-metallic counterparts result in either C-F activation or 1, 2 nucleophilic addition products being isolated.



**Keywords**: C-F activation; bimetallic; alkali metals; cyclisation; main group

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**Invited Speaker**
**FR-I-03**
**Marlon T. Conato**

# Crystal engineering of microporous materials for energy applications and catalysis

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Optimization of the architecture and morphology of metal-organic framework materials towards improved property has been the primary focus of our research. In particular, our interest is on targeted new structures and crystal morphologies towards quality materials for energy applications and catalysis. Herein, we report key developments of our work on the synthesis, structures, and property of MOFs as catalysts for asymmetric reactions or materials for fuel cells. Structures based on inherent chiral linkers such as amino acids improved could improve enantiomeric excess in chiral reactions. On the other hand, structures involving cationic supramolecular networks could facilitate enhanced proton conduction. Another interest in our group is on influencing the growth habits of MOF crystals towards improved design of catalysts. Some MOFs could exhibit a variety of crystal morphology depending on the synthesis conditions and the use of growth modulators could be an important advancement in heterogenous catalysis.

**Keywords**: metal organic frameworks; chiral catalysis; proton conduction; crystal engineering; growth modulators

**Invited Speaker**
**FR-I-04**
**Mark G. Humphrey**

# Multiphoton absorption at metal alkynyl-based materials

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The nonlinear optical (NLO) properties of new materials and their demonstrated or potential applications are of exceptional contemporary interest. Our recent contributions to this area include second-harmonic generation-active inorganic crystals functioning in the IR and deep-UV regions (in conjunction with the Australia-China *Joint Research Centre for Functional Molecular Materials*), and two-photon absorption-active bio-compatible molecules (in conjunction with the CNRS International Associated Lab *REDOCHROM* and the CNRS International Research Project *MAITAI*).[1] We have also approached nonlinear optics from a more fundamental perspective, and have a long-standing interest in the NLO properties of diverse molecular architectures.[2] In a continuation of our studies in the latter domain, this presentation will summarize some of our recent research into certain NLO properties that are of significant current interest, namely multiphoton absorption. We will present studies of (a) metal alkynyl-based dendrimers, including very rare examples of molecular five- and six-photon absorption, (b) heptazine-cored octupolar metal alkynyl complexes, including strongly red-shifted four-photon absorption, and (c) metal alkynyl-porphyrin hybrids, including record NLO coefficients and the first four-photon absorption seen with porphyrins.[3]

**Keywords**: nonlinear optics; multi-photon absorption; metal alkynyl complex; organometallic; porphyrin.

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2. See, for example: (a) *J. Am. Chem. Soc.* **2006**, *128*, 10819. (b) *Angew. Chem. Int. Ed.* **2006**, *45*, 7376. (c) *J. Am. Chem. Soc.* **2007**, *129*, 11882. (d) *Angew. Chem. Int. Ed.* **2007**, *46*, 731. (e) *Adv. Mater.* **2009**, *21*, 2318. (f) *J. Am. Chem. Soc.* **2009**, *131*, 10293. (g) *Angew. Chem. Int. Ed.* **2009**, *48*, 7867. (h) *Angew. Chem. Int. Ed.* **2010**, *49*, 4209. (i) *Adv. Mater.* **2011**, *23*, 1433. (j) *Angew. Chem. Int. Ed.* **2016**, *55*, 2387.
3. (a) *Angew. Chem. Int. Ed.* **2022**, *61*, e202116181. (b) *Angew. Chem. Int. Ed.* **2022**, *61*, e202208168. (c) *Angew. Chem. Int. Ed.* **2023**, *62*, e202301754.

**Invited Speaker**
**FR-I-05**
**Nak Cheon Jeong**

# Intrinsicality of guest molecule coordination in MOF

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Open metal sites within metal-organic frameworks (MOFs), typically hosting Lewis-basic guest molecules through coordination bonding, exhibit pivotal characteristics in their chemical reactivity. In this talk, we elucidate the intrinsic nature of coordinative bonds established at MOF's open metal sites, dependent on the strength of bonding with guest molecules, differentiating between (i) weak and (ii) strong coordination bonds.

For instance, the exchange of relatively stronger coordination bonds, such as water, methanol, ethanol, and DMF, with chloroalkanes results in weak coordination bonding, leading to the activation of metal centers.[1-5] This activated state, induced by chloroalkanes, augments the catalytic activity of these metal centers. In contrast, strong coordination bonding with compounds like hydroquinone and aniline initiates catalytic reactions, such as the "coordinative reduction" of the framework metals or the "catalytic polymerization" of coordinated substances.[6] Specifically, hydroquinone induces the coordinative reduction of Cu(II) ions within the $Cu_3BTC_2$ MOF (BTC=benzenetricarboxylate), while aniline triggers polymerization. Furthermore, we demonstrate that the polymerized aniline (pAni) substantially enhances the hydrolytic stability of the $Cu_3BTC_2$, which is inherently vulnerable to humid conditions due to its low coordination valency. Finally, we illustrate how the stabilized $Cu_3BTC_2$ significantly enhances its performance in atmospheric water harvesting.

**Keywords**: Metal-organic Framework; Open-metal Site; Weak Coordination Bonding; Polyaniline; Atmospheric Water Harvesting

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# A photo-responsive iron-nitrosyl complex in vascular therapy

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The development of metallodrugs, a class of therapeutic agents containing metal ions, has emerged as a crucial avenue in modern medicinal chemistry. Their unique properties and interactions offer distinct advantages, revolutionizing the landscape of drug design, and opening new possibilities for targeted treatments and enhanced therapeutic efficacy.

Retinal vascular occlusion is a prevalent cause of visual impairment. While various approaches, including vasodilators, have been investigated for the treatment, there is currently no effective method available. Herein, we present a novel strategy for treating vascular occlusions by using a photo-responsive iron-nitrosyl complex, $[Fe(TBDAP)(NO)(H_2O)]^{2+}$ (**1**), which acts as a spatiotemporally controllable nitric oxide transporter. Complex **1** was synthesized and characterized using various chemicophysical techniques including X-ray crystallography. Its ability to selectively dilate normal retinal blood vessels and reperfuse the occluded vessels was demonstrated in animal disease models.

Oral Presentation
FR-O-01
Qingyun Wan

# Photo-physics, magnetism, conductivity and self-assembly of d- and f-block metal complexes

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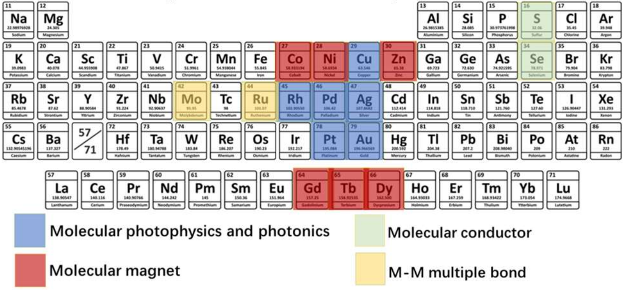
Functional d- and f-block complexes have a wide range of applications in luminescent and light-harvesting materials, magnetic and conductive materials. In order to fully utilize their potential, it is crucial to have a fundamental understanding of their electronic structures, a controllable method to direct their self-assembly process into the solid state, and a comprehensive understanding of their physical properties and functionalities. Our extensive research activities have yielded significant achievements in these three directions which include: (1) We used high-level computational methods and molecular orbital (MO) analysis to **firstly** identify the **repulsive nature** of metal-metal (M-M) closed-shell interaction. It challenged the mainstream belief of "attractive" M-M interaction in the academic community since 1970s (***PNAS***. 2021. 118, e2019265118 ). (2) For the first time, we utilized the **counteranion-cation electrostatic interaction** to regulate the self-assembly bbehaviors of metal complexes (***Chem***. *2020, 6, 945-967;* ***ACIE***. *2018, 57, 17189*). (3) We identified **new triplet-emitting excited state** in Pd(II) and Au(III) assemblies through a combined computational study and spectroscopic investigation (***ACIE***. *2018, 57, 3089;* ***JACS***. *2019. 141. 11572*). These research findings provided new insights into the photo-physics of Pd(II) and Au(III) complexes, besides of conventional $d^8$ systems such as Pt(II) and Rh(I). We studied the **exciton diffusion process, photonic waveguide** and **non-linear optical properties** of Pt(II), Pd(II), Au(III), Au(I), and Cu(I) complexes' assemblies. (***ACIE***. *2022, 10. e202114323.* ***AM***. *2022, 45, 2204839.* ***ACIE***. *2023, 62, e202216523*). We also developed a series of Co(II), Ni(II), Zn(II), Dy(III), Tb(III), and Gd(III) **molecular magnets** and **conductors** (***JACS***. *2023, 145, 26, 14288-14297*).



**Keywords**: Metallophilicity; MMLCT excited state; Exciton dynamics and photonics; Molecular magnets; Strongly correlated molecular conductors

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# Advancing solid-state photoswitching with DASA-derived coordination complexes

Peng Xuan Zheng, Di Yu Dou, Xin Bao*

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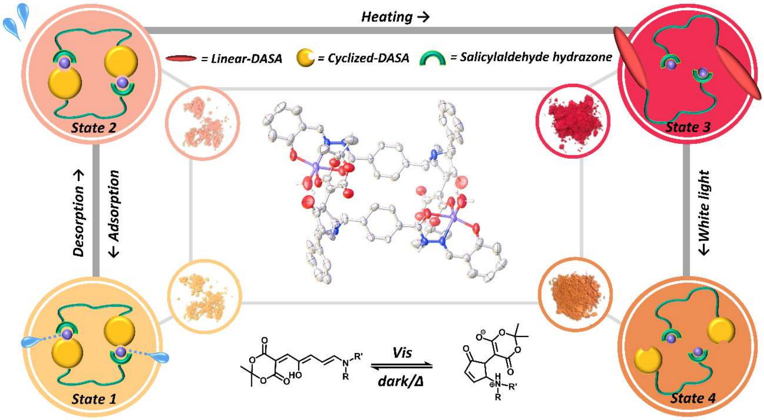
The integration of photoswitchable molecules into coordination chemistry has emerged as a promising avenue for advancing the field of smart materials. This study focuses on Donor-Acceptor Stenhouse Adducts (DASAs), a new class of organic photoswitches with negative photochromism and visible-light switching capabilities. By grafting DASA onto a co-coordinating salicylaldehyde hydrazone, we successfully overcame solvent compatibility and concentration restrictions, resulting in the first well-defined crystalline DASA-derived coordination complex. Notably, the dynamic variation of the coordination structure endowed the sample with distinct responses to various stimuli at different stages, resulting in the creation of multiple accessible states with modulated physical properties. Of particular significance, this complex exhibited exceptional solid-state photoswitching capabilities, which is a remarkable advantage considering the inherent lack of such properties in the DASA ligand itself. This sets it apart from spiropyran families that lose their switching abilities when confined within coordinated structures. Our achievement underscores the remarkable potential of utilizing DASA-derived coordination systems to achieve solid-state photoswitching capabilities independently of intrinsic pores, presenting exciting prospects for the field of smart materials.



**Keywords**: Photoswitchable molecules; Coordination chemistry; Donor-Acceptor Stenhouse Adducts (DASAs); Solid-state photoswitching; Salicylaldehyde Hydrazone

**Oral Presentation**
**FR-O-03**
**Ryo Ohtani**

# Functional organic-inorganic hybrids consisting of nitridotetracyanometallate units

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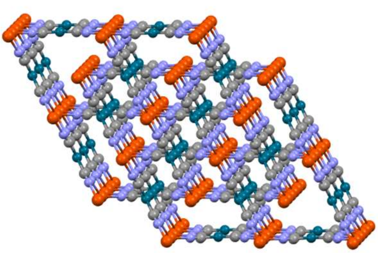
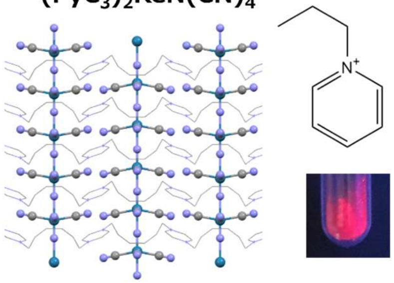
Cyanide-based solid-state materials have been studied actively. In addition to the conventional Prussian-blue analogues, recent advances have expanded the family to functional organic-inorganic hybrid materials functionalized with flexible organic cations. Our group investigates such functional materials synthesized by the anionic four-coordinate/penta-coordinate molecules with cyanides combined with various metal ions or organic cations. In particular, we found that the penta-coordinate mixed-anion units $[MN(CN)_4]^{2-}$ (M = Mn, Cr, Re) produce several 'self-clustering' forms such as tetranuclear cluster, cyanide-bridged chains and nitrido-bridged chains in $A_2X$ type hybrids (A = organic cations). The $A_2X$ type hybrids consist of more dynamic structural characteristics than the conventional perovskite-type hybrids, thus, they exhibit various phase transition behavior and chemical responsivity. For example, $(PyC3)_2[ReN(CN)_4]$ shows a water induced large transformation where re-arrangements of $[ReN(CN)_4]^{2-}$ units occur between chain-type assembly and tetranuclear cluster form. This transformation gives rise to a switching of luminescent properties between visible (560 nm) and near-infrared (740 nm) emissions.

$FePd(CN)_4$



*Angew. Chem. Int. Ed.* 2020, 59, 19254

$(PyC_3)_2ReN(CN)_4$



*Angew. Chem. Int. Ed.* 2023, 62, e202306853

**Keywords**: cyanido; organic-inorganic hybrid; phase transition; chemical response

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# Regulating Glass Transitions for Melt-quenched Glasses from Hybrid Crystals

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The melt-quenched glasses from organic-inorganic hybrid crystals, named hybrid glasses, have gained increasing interests due to their advantageous processability and formability. However, the occurrence of such glasses remains scarce, primarily due to the irreversible decomposition that takes place prior to reaching the melting point in the majority of hybrid crystals. Based on our comprehensive regulation of structural phase transition through intermolecular interactions in hybrid crystals [1-2], we have recently focused on designing the reversible solid-liquid transitions in the hybrid crystals consisting of organic cations and inorganic coordination anions, then to create glasses or glass-ceramics from these crystals and to regulate their glass transitions through the intermolecular interactions [3-5]. For instance, we recently obtained a polar crystal, $(Ph_3PEt)_3[Ni(NCS)_5]$, revealing thermal-induced reversible crystal-liquid-glass-crystal transitions with relatively low melting temperature of 132 °C, glass-transition temperature of 40 °C, and recrystallization on-set temperature of 78 °C, respectively [5]. Then we fabricated an unprecedented hybrid glass-ceramic thin film, *i.e.*, a thin glass uniformly embedding inner polar micro-crystals, which exhibits 25.6 times enhanced intrinsic second-harmonic generation (SHG) effect than its poly-crystalline form. In virtue of convenient process conditions and the intrinsic strong SHG effect without poling treatment, such kind of glass-ceramics can serve as a new promising materials bypassing the technical difficulties in crystal growth for traditional SHG materials.

**Figure 1**. A polar hybrid glass-ceramic with much enhanced intrinsic SHG effect

**Keywords**: Hybrid Crystals; Solid-Liquid Transitions; Hybrid Glasses; Glass-Ceramics

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**Oral Presentation**
**FR-O-05**
**Yoshihiro Sekine**

# Hydrogen-bonding Assembly-induced Thermally Driven Electron Transfer in Cyanide-bridged Complexes

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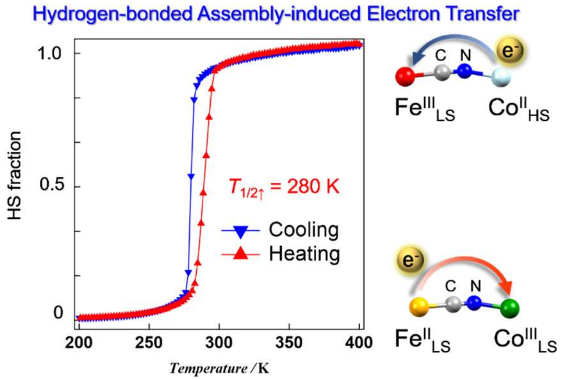
The exploration of new functional compounds based on coordination chemistry is an important subject in the field of materials science. Finely tuning structure, electronic, and spin states in molecular materials, namely flexible charge/spin compounds, is an attractive theme for developing external stimuli-responsive coordination metal complex-based materials.[1-3] Thermally driven electron transfer systems are a class of “smart” and “frontier” materials among such material systems that lead not only to change their oxidation states but also their electronic states, enabling switching of physical properties. Cyano-bridged polynuclear metal complexes, in which cyanide ions bridge multiple metal ions, exhibit unique electronic and magnetic properties due to their metal ions. This presentation demonstrated the synthesis of new Co/Fe complexes for exploring external stimuli-responsive materials. After self-assembling **1** (non-responsive complex) with hydrogen-bonding donor molecules, the supramolecular assembly **2** was successfully constructed. Temperature-dependent structural analyses for **2** revealed that the coordination bond distances around metal ions are significantly changed due to the electron transfer occurrences. Consequently, we have demonstrated a new strategy for complete phase transition behavior using the hydrogen assembly method. Crystal engineering of hydrogen-bonded architecture can influence their packing motif and electronic state variation, yielded in the fine-tuning of the electron transfers.



**Keywords**: Supramolecular assembly; Electron transfers; External-stimuli-responsiveness; Multinuclear coordination metal complexes; Functional materials

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**Flash Presentation**
**FR-F-01**
**Atsushi Okazawa**

# Enhanced-solubility catholytes for redox flow batteries: Carnelley's rule and diverse ion effect

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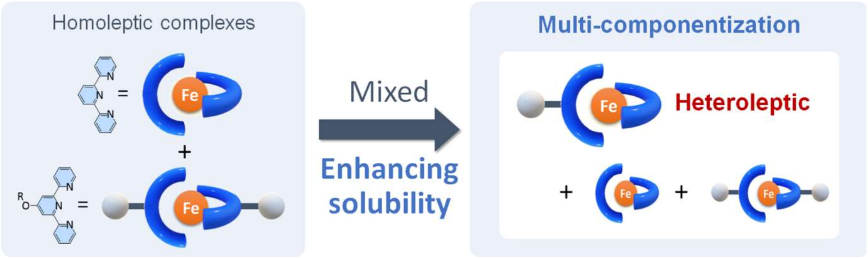
Redox flow batteries (RFBs) are a promising stationary energy storage device. In this system, anolyte/catholyte in tanks store energy as chemical one and an electrochemical cell converts electric and chemical energies, allowing for flexible RFB system design. In commercial vanadium RFBs, the use of vanadium causes severe disadvantages such as cost. To replace the vanadium RFB system, we focus on less expensive terpyridine iron complexes that have higher redox potential of approximately 1 V (vs. SHE) as an active material for the catholyte of nonaqueous RFBs. However, terpyridine iron complexes generally possess low solubility in nonaqueous solvents. In this study, we improved the solubility of the complexes by asymmetrizing their molecular structures, and then explored an application as active materials in catholytes. The mixing of parent terpyridine iron complex, $[Fe(tpy)_2]^{2+}$, and the homoleptic BuO-substituted one, $[Fe(BuOtpy)_2]^{2+}$, in acetonitrile produced a mixture containing a new heteroleptic complex $[Fe(BuOtpy)(tpy)]^{2+}$. The solubility of the mixture increased to 0.49 M, which enhances a theoretical volumetric capacity of catholytes three times than those of the single-component ones. Further solubility improvement was achieved using complexes substituted with poly(ethylene glycol)-type chains.



**Keywords**: Redox flow battery; Solubility; Iron complex; Heteroleptic; Diverse ion effect

# Chemically synthesized boron-based two-dimensional atomic layers

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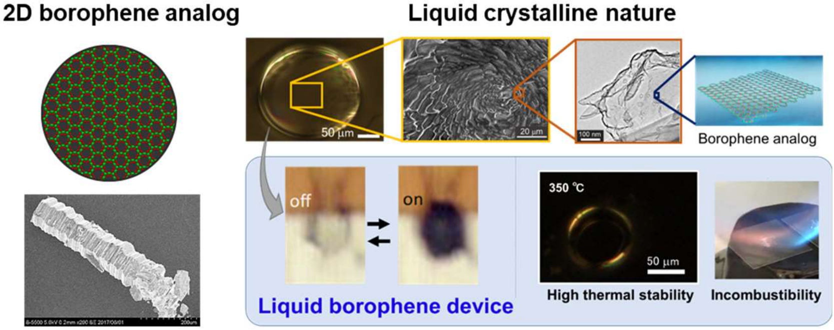
Graphene, which is a thin sheet of carbon with a thickness of one atom, has been the focus of much research efforts across multiple fields. These days, various 2D materials with unique properties have been reported. Regarding the 2D materials, chemical bottom-up synthesis has enough possibility to design the functions of the materials for the application.[1-3] For example, coordination nanosheets composed of metal ions and flat ligands can introduce or tune the electronic functions. In this study, we have achieved the atomically-thin 2D nanosheet liquid material, “Liquid borophene” and its use in an inorganic optical device.

An atomically flat boron network skeleton was synthesized through a simple solution-based method from $KBH_4$. X-ray analysis revealed the 2D material, in which layers of boron atoms bridged with oxygen atoms to form a hexagonal 2D network were intercalated with layers of potassium atoms. Various types of measurements including electron microscopy, spectroscopy, and atomic force microscopy confirmed that the proposed method was effective in producing the desired atomically flat borophene oxide sheets.[4] The characteristic conducting properties of stacked borophene sheets were also revealed from the temperature dependence experiments. In addition, the liquid crystalline feature was achieved by chemical modification of the edge part. The obtained liquid crystal exhibited high thermal stability and optical switching behavior even at low voltages.[5] These findings highlight the strong potential of borophene oxide-derived liquid crystals for use in widespread applications.



**Keywords**: nanosheet; atomic layered material; borophene; liquid crystal

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# Constructing lanthanoid double-decker complexes as prototypes of gears

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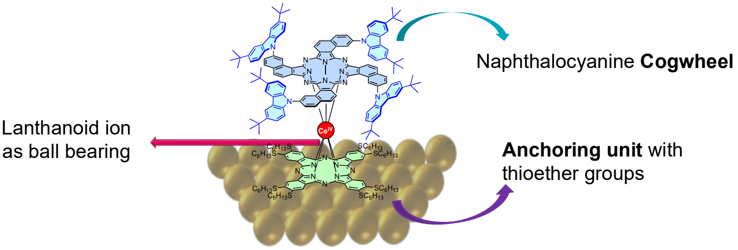
Molecular gear is one of the representatives of artificial molecular machines[1]. Among various molecular gears[2], double-decker complexes, with a lanthanoid ion between two rotating ligands like porphyrin, phthalocyanine, or naphthalocyanine, represent promising molecular gear structures due to the ligands' rotational capability around metal ions[3].

This study introduces cerium(IV) double-decker complexes as a new molecular gear prototype. We achieved the construction of these complexes by utilizing phthalocyanines with π-planar bulky substituents at the α-position. The incorporation of these rigid substituents is anticipated to create a gear-like mechanism, with the upper and lower ligands tightly engaging in coordinated movements. A $C_{4h}$ symmetric phthalocyanine ($H_2$Pc1) having 3,6-di-tert-butyl-carbazole at the α-position was employed and synthesized as a sub-unit of the gearing system. Homoleptic Ce(Pc1)$_2$ was obtained in 40% yield through the complexation of $H_2$Pc1 with Ce(acac)$_3$·n$H_2O$ under microwave irradiation. The structure was confirmed by single-crystal X-ray structure analysis. A desymmetrized $A_3B$-type phthalocyanine complex was also synthesized similarly to Ce(Pc1)$_2$.

For STM-based molecular gearing studies, we designed an heteroleptic double-decker with a thioether-functionalized phthalocyanine as anchor and a helicoidal carbazole-functionalized 1,2-naphthalocyanine as cogwheel (**Fig.1**). The helical chirality of the complex aims to assemble a train of gear with consecutive molecules exhibiting opposite chirality.



Naphthalocyanine **Cogwheel**

Lanthanoid ion
as ball bearing

**Anchoring unit** with
thioether groups

**Fig.1** Gear to be studied on surface with STM

**Keywords**: Molecular Gear; Double-decker Complex; Lanthanoid; Porphyrinoid; Helicity

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# Resistive Switching Device Based on Redox-Active Bis(Formazanate)Zinc Complex

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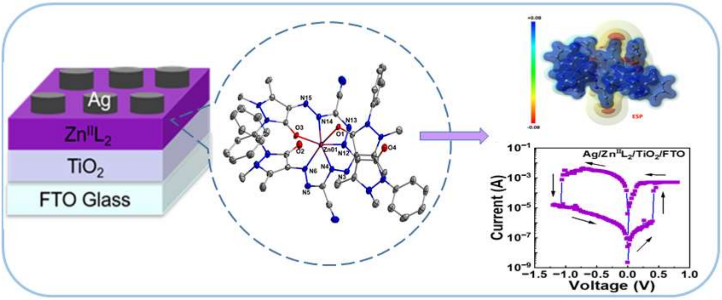
Resistive random access memory (RRAM) devices with MIM (Metal insulator metal) sandwich structures have attracted a lot of interest as prospective candidates for high-performance data storage, mainly because of their potential for data storage with low power consumption, good scalability, and high storage density. Transition-metal complexes (TMCs), among other alternatives, have lately become one of the active materials most often employed in RRAM devices since they are reliable, solution-processable, and robust molecular materials. In this context, we have designed a new mononuclear zinc complex [$Zn^{II}L_2$] containing redox-active 3-Cyano-1,5-(4-antipyrinyl)formazan (LH) ligand and a set of techniques, such as NMR, SC-XRD, elemental analysis, etc., were used to characterize it. Further, the resistive memory device was designed using this solution-processable bis(formazanate) Zn(II) complex leading to the facilitating the development of molecular memory devices based on transition metal complexes. A trap-controlled space charge limited current mechanism is proposed for the observed resistive switching behavior in the designed device, and the role played by p-type [$Zn^{II}L_2$] complex that comprises of redox-active extended conjugate ligand backbone is revealed by corroborating DFT calculations and the experimental studies. Interesting results from the device have shown multilayer switching and low current operation, both of which are advantageous for memory applications. [1]



**Keywords**: Redox active formazans; Single crystal XRD; DFT; Memory Device; Multilevel switching

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# Color changes of a bis(benzimidazole)-ligated nickel dichlorido complex by amine vapor adsorption

Tatsunari Murakami[1], Takahiro Homma[1], Atsunobu Masuno[2], Masaaki Okazaki[1], Shun Ohta[1*]

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As raw materials, pyridine (py) and ammonia ($NH_3$) have widely been used in manufacturing processes.[1] However, py and $NH_3$ are both volatile, and their vapors may give us some health issues;[2] therefore, their sensing materials are required. We have recently reported the adsorption properties of the crystals of complex **1** (Figure 1a) for carbonyl compounds, chloroalkanes, and ethers.[3] In these adsorption processes, the color does not change. In contrast, this study revealed that the color of **1** changed by the adsorption of py- or $NH_3$-vapor (Figure 1a).

Exposure of the crystals of **1** to py vapor for 20 h at room temperature gave deep green solids. According to powder X-ray diffraction, UV-Vis diffuse reflection, and IR spectroscopic studies, complex **2** was found to be included in the green solids. In the case that the crystals of **1** were exposed to aqueous $NH_3$ vapor, light purple solids were obtained and found to include complex **3** in similar manners used for the identification of **2**. This study also revealed that crystals of **1** can adsorb py or $NH_3$ vapor even in low concentrations (Figures 1b and 1c).

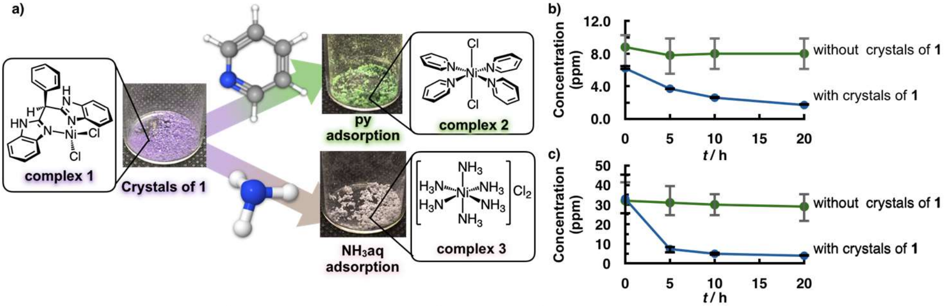

Figure 1. (a) The color changes of crystals of **1** induced by py or $NH_3$ vapor; (b, c) Time-dependent concentration changes of (b) py and (c) $NH_3$.

**Keywords**: Nickel; Adsorption; Pyridine; Ammonia; Color change

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# Constructing an Au electrode modified with an unsymmetrically substituted π-extended TTF derivative

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Chiral electrodes can be used for various purposes such as asymmetric electrosynthesis and spin filtering. Towards applications, systems capable of inverting chirality (handedness) are advantageous. However, the reports on such chirality-switchable electrodes are limited, including DNA-based[1] and molecular-motor-based[2] systems. We aim to construct chirality-switchable metal electrodes based on chiral/achiral conversion. We focused on π-extended tetrathiafulvalene derivatives, which exhibit molecular shape changes upon reduction/oxidation (**Fig. 1**a).[3] In an unsymmetrically substituted derivative, neutral/dication conversion is expected to result in chiral/achiral conversion, and the addition of external chirality sources during the redox processes may lead to the induction of chirality, which can be used for chirality switching. Here, we have newly designed and synthesized an unsymmetrically substituted π-extended tetrathiafulvalene derivative bearing thiol anchors (**Fig. 1**b) and prepared gold substrates modified with this molecule. Details of the synthesis and characterization are presented.

**Keywords**: thiolate-modified electrode, extended TTF

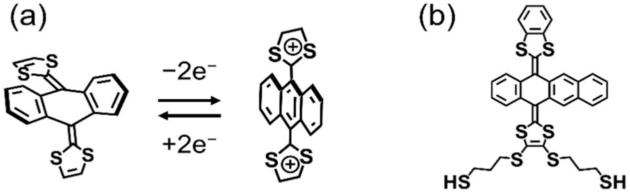

**Figure 1**. (a) Change in molecular shape of π-extended tetrathiafulvalene derivative on redox process. (b) Molecular structure of the target compound.

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# Porphyrin/Fullerene porous molecular co-crystal featuring one dimensional channel

Nobuhiro Sato[1], Tetsu Sato[1], Ryojun Toyoda[1] Shinya Takaishi[1] Ryota Sakamoto[1]

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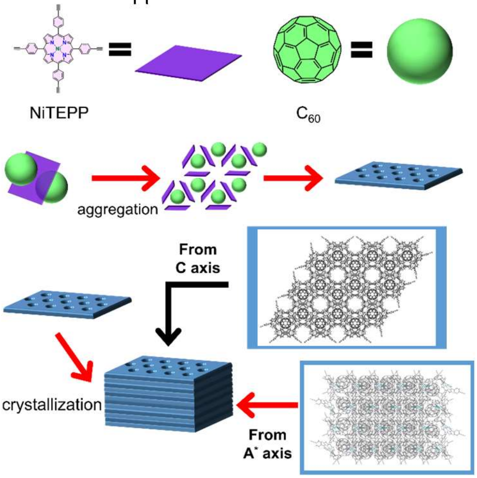
In recent years, porous materials constructed using a bottom-up approach have found applications in various fields, including batteries, catalysts, and gas storage. However, conventional materials face limitations such as decomposition under the influence of acids, bases, or heat. Molecular crystals, which rely on non-covalent interactions, are examples of bottom-up porous materials and offer greater stability against these stimuli.

This study focuses on the interaction between porphyrin and fullerene[1] aiming at developing porous molecular crystals. Through liquid-liquid diffusion, a co-crystal of Ni porphyrin derivative (NiTEPP) and $C_{60}$ was obtained. Its single crystal structure revealed that NiTEPP/$C_{60}$ featured a two-dimensional porous honeycomb network with $C_{60}$ encapsulated by NiTEPP.

NiTEPP/$C_{60}$ demonstrated the ability to reversibly adsorb and desorb solvent vapor in its pores while maintaining its crystalline structure, as shown by in-situ powder X-ray diffraction. To assess its durability, NiTEPP/$C_{60}$ underwent 24-hour reflux under conditions of acid, and base. The material retained its single crystal structure, demonstrating its stability even in the presence of these harsh conditions.

In summary, this research achieved the construction of molecular co-crystals with a designable structure and pores, while maintaining stability against acids, bases, and heat, showcasing the potential of such materials in various applications.



**Keywords**: co-crystal; molecular crystal; porous structure; porphyrin;

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# Synthesis of ruthenium complexes with diketopyrrolopyrrole ligands and application to organic solar cells

Naohiro Takahashi[1], Tomoki Nishiyama[1], Senku Tanaka[1], Hirotaka Kitoh-Nishioka[1], Masahiko Maekawa[1], Takayoshi Kuroda-Sowa[1], Takashi Okubo[1*]

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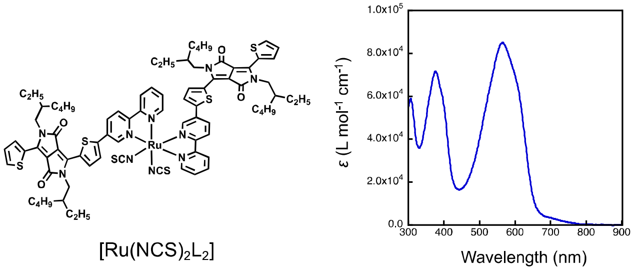
Organic solar cells (OSCs) have the great potential to be lightweight, flexible, and printable next-generation solar cells. In the OSC materials, molecules containing both donor and acceptor units have an advantage for high efficiency OSC materials because of the extended absorption to the near-infrared region by the intramolecular charge transfer. Diketopyrrolopyrrole (DPP) is a promising dye unit used as acceptor molecules in organic semiconductors due to the various features such as strong visible absorption, photochemical stability, formation of column structures by intermolecular π-π stacking and easy chemical modification.[1] In this work, we synthesized ruthenium complexes with the DPP derivatives and attempted them to apply to OSCs because Ru (II) complexes had broad absorption expanding to the NIR region via MLCT and long lifetimes due to the triplet excitons. Figure 1 shows a Ru (II) complex [Ru(NCS)$_2$L$_2$] (**1**) with a new ligand containing DPP and bipyridine units showing strong absorption and luminescence properties. The physical properties of complex **1** were investigated by UV-vis absorption spectroscopy and cyclovoltammetry, and it was found that strong absorption in the visible region and redox activity are suitable for OSCs. We also fabricated OSCs using complex **1**, showing that the ruthenium complex contributed to photoelectric conversion.



[Ru(NCS)$_2$L$_2$]

Figure 1. Chemical structure and UV-vis spectrum of Ru complex **1**

**Keywords**: Organic solar cells; Ruthenium complex; Diketopyrrolopyrrole

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Poster Presentation
FR-P-06
Seongman Lee

# Preparation of Poly(acrylic acid)-Assisted MgO Nanoparticles for Dye-Sensitized Solar Cells

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Magnesium oxide (MgO) nanoparticles are commonly employed to enhance the reactivity and performance of devices and systems across various applications, owing to MgO's heat resistance, binding capabilities, and alkaline properties. Nonetheless, most methods used for synthesizing MgO nanoparticles suffer from non-uniform particle size distributions, making it challenging to produce stable particles. In this study, we developed uniform MgO nanoparticles for the $TiO_2$ photoelectrode in dye-sensitized solar cells (DSSCs) to enhance their interfacial resistances. These uniform MgO nanoparticles were synthesized from 93% pure MgO using a poly(acrylic acid) template-assisted approach (Figure 1). The particle size and crystalline structure of these MgO nanoparticles were thoroughly characterized through NANOPHOX particle size analysis, transmission electron microscopy, and X-ray diffraction. Multilayered $TiO_2$ photoelectrodes, featuring interlayers of MgO nanoparticles, were fabricated for use as photoelectrodes in DSSC devices, and their photovoltaic performance was investigated. The introduction of the MgO interlayer into the multilayered $TiO_2$ photoelectrode not only increased the photocurrent in the DSSC device but also enhanced its power conversion efficiency. This resulted in an overall solar energy conversion efficiency of 6.94%. The application of an MgO interlayer in the DSSC device improved conductivity and charge transfer capability, showcasing exceptional device performance.

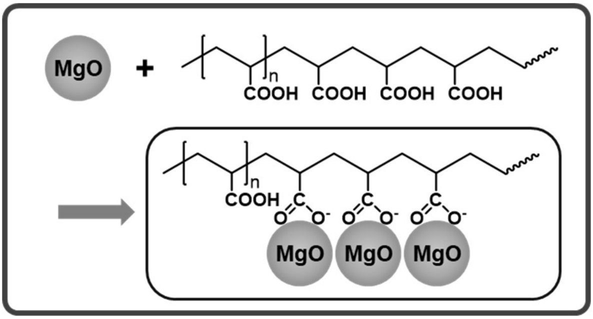

**Figure 1.** Preparation process of MgO nanoparticle by PAA template-assisted method : reaction of MgO nanoparticles and poly(acrylic acid).

**Keywords**: MgO nanoparticles, Poly(acrylic acid), Dye-sensitized solar cells (DSSCs), Template-Assisted Method, Photovoltaic performances.

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# Luminescent Compounds (LC)

# Abstract

**Keynote Speaker**
**LC-K-01**
**Juyoung Yoon**

# From fluorescent probes to phoththerapy

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The development of fluorescent probes for various analytes has been actively pursued by chemists. Recently, a near-infrared two-photon fluorescent probe was developed to not only specially image carboxylesterase (CE) activity *in vivo* and *in situ* but also target orthotopic liver tumor after systemic administration.[1]

On the other hand, photodynamic therapy (PDT) and photothermal therapy (PTT) have attracted considerable interest as a noninvasive treatment method. We devised a novel molecular design approach to create heavy-atom-free photosensitizers for thionapthalimides.[2] The *in vivo* specific binding between albumin and PcS, arising from the disassembly of injected NanoPcS, was also confirmed using an inducible transgenic mouse system.[3]

Photodynamic antibacterial therapy is also regarded as an innovative and promising antibacterial approach due to its minor side effects and lack of drug resistance.[4] Recently, we suggested that reactive differences may pave a general way to design selective photodynamic agents for ablating Gram-positive bacteria-infected diseases.[5]

**Keywords**: Fluorescent probes; photodynamic therapy; activatable photosensitizers; photothemal therapy; phthalocyanines

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# Developing Metal-Polycyclic-Aromatic-Hydrocarbons As a New Class of Organometallic Emitters

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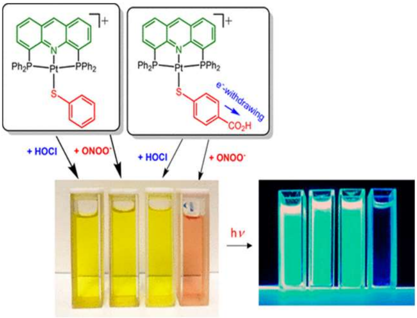
Polycyclic aromatic hydrocarbons (PAHs) such as anthracene, pyrene and tetracene are well known organic chromophores. Combining metals and PAHs may lead to a new class of robust organometallic chromophores and emitters that could have potential applications in solar energy conversion and photocatalysis. Our laboratory has synthesized and studied the electronic spectroscopy of a series of □-complexes of Pt(II) and Au(I) and anthracene, pyrene, tetracene and pentacene. Our results showed metalation can influence electronic structures, photophysics and photochemistry of the PAHs. Perturbations of the metals on the electronic structures of the PAHs are evident from intensification of the otherwise pseudo-parity forbidden $^1L_b$ transition and red-shift of absorption and fluorescence displayed by the metalated PAHs. Notably, phosphorescence of pyrene is switched by heavy atom effect of the metals.[1] Platination and auration of tetracene and tetracenyldiacetylide can red-shift fluorescence energy up to 0.52 eV[2] and move the fluorescence of pentacene to NIR region. Our recent work on Pt-PNP pincer complexes (PNP = 4,5-bis(diphenylphosphino)acridine) shows that emission of $[Pt(PNP)(SPh)]^+$ can be switch on by hypochlorous acid,[3] and a *mer*-$W^0(PNP)(CO)_3$ which exhibits low energy MLCT absorption and anti-Kasha emission.



**Keywords**: Luminescence; platinum; gold; aromatic hydrocarbons; electron spectroscopy

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**Keynote Speaker**
**LC-K-03**
**Tony. D. James**

# Fluorescent chemosensors and imaging agents

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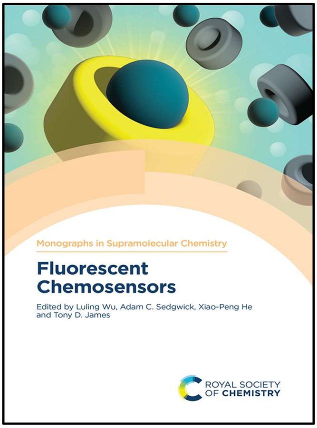
Sensors and imaging agents can be used to monitor analytes within physiological, environmental, and industrial scenarios. The interactions between the "chemosensor" and an analyte of choice occurs on a molecular level and as such gathering and processing the information is challenging. Therefore, I will outline the trials and challenges encountered in the development of several robust chemical molecular sensors "chemosensors" able to detect such analytes selectively and signal or map their concentration in a biological or environmental scenario. During the talk you will be introduced to a variety of fluorescent probes designed for diols (D-glucose), anions, and redox imbalance. With the goal being the development of chemosensors capable of determining the concentration (and location) of a target species in any medium.

Particular attention will be paid to the underlying chemistry associated with the construction of practical chemosensors for both sensing and imaging applications.



Monographs in Supramolecular Chemistry

Fluorescent Chemosensors

Edited by Luling Wu, Adam C. Sedgwick, Xiao-Peng He and Tony D. James

ROYAL SOCIETY OF CHEMISTRY

doi.org/10.1039/9781839167324

**Keywords**: Fluorescence; Chemosensors; Imaging agents.

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Keynote Speaker
LC-K-04
Vinich Promarak

# Recent Advances in Deep Red to Near-Infrared Luminescent Materials for Organic Light-Emitting Diodes

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Recently, fluorophores with efficient deep red/near-infrared (DR/NIR) emission properties ($\lambda_{em}$ = 650–900 nm) have received much attention due to their potential applications in several different fields such as chemosensing, bioimaging/biosensing, photodynamic therapy, optical communication, NLO materials, laser dyes, and DR/NIR electroluminescent devices. However, DR/NIR chromophores typically suffer from low photoluminescent quantum yields (PLQY) because of their intrinsic small band-gap energy causing larger vibronic coupling between the ground and excited states, particularly when they are applied as emitters in organic light-emitting diodes (OLEDs). Hence, the development of highly efficient DR/NIR emitters is still a challenging task. In this presentation, I will share our recent progress in deep red to near-infrared luminescent materials capable of producing high intrinsic quantum efficiency (IQE) through both singlet and triplet exciton emissions (thermally activated delayed fluorescence (TADF) and hybridized local and charge-transfer excited state (HLCT), and hot exciton) for high-performance DR/NIR-OLEDs. Some examples of DR/NIR emissive materials will be discussed in terms of the structure-property relationships, with particular attention to the molecular design that affects the OLED device performance. Our latest achievement in developing and utilizing DR/NIR fluorescence metal-organic framework (MOF) as advanced luminescent materials for OLEDs will be also conferred.

**Keywords**: luminescent materials; deep red/near-infrared emissions; thermally activated delayed fluorescence (TADF); hybridized local and charge-transfer excited state (HLCT); hot exciton; organic light-emitting diodes

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**Invited Speaker**
**LC-I-01**
**Supavadee Kiatisevi**

# Bis-BODIPY linked-triazole functional dyes

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Bis-BODIPY linked-triazole fluorescent and colorimetric sensors based on catechol (BODIPY-OO) and phenylenediamine (BODIPY-NN) for recognition of cations and anions are reported. BODIPY-OO displays turn-on fluorescence upon addition of Ag$^{+}$ and Hg$^{2+}$ ions in methanol media. This is likely caused by the restriction of the intramolecular rotations in BODIPY-OO and chelation-enhanced fluorescence (CHEF) effect. In contrast, BODIPY-NN provides a marked color change from pink to colorless and a remarkable turn-off fluorescence in the presence of F$^{-}$ and CN$^{-}$ ions. Spectroscopic analysis and DFT calculations reveal the sensing mechanism of deprotonation at pseudo-benzylic carbons attached to BODIPY cores by F$^{-}$ and CN$^{-}$ ions. Deionized water was used to demonstrate the discrimination of F$^{-}$ and CN$^{-}$. The CN$^{-}$ detection ability of the sensor in aqueous solution could be improved via the addition of CTAB. Furthermore, BODIPY-NN displays a turn-on fluorescence toward the Cu$^{2+}$ ion. Cu$^{2+}$ acts as both a coordination center and catalyst for oxidative C–N cyclization of phenylenediamine–triazole to in-situ form benzimidazole–triazole receptor. It was successfully applied for monitoring trace of copper in environmental water samples and live cells. Further structural modification of the bis-BODIPY linked-triazole compounds enables them promising fluorescent sensors selective for other analytes and probes for biomedical applications.

**Keywords**: fluorescent sensor; optical sensor; BODIPY; imaging

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# Tailoring Photophysical Properties of *meso*-Substituted BODIPY Dyes and Their Applications

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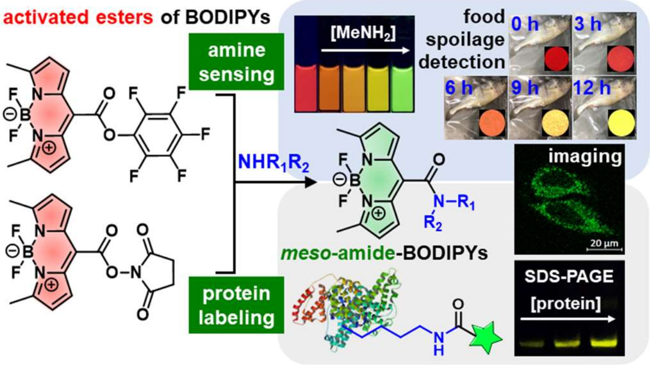
The pursuit of highly sensitive and selective molecular sensory materials with easily detectable recognition events is a compelling endeavor across the realms of chemical, biological, and pharmaceutical sciences. Among the diverse array of available sensory platforms, fluorescence-based sensors have emerged as a central focus, owing to their remarkable capabilities in optical transduction. These encompass fluorescence intensity modulation, wavelength shifts, and alterations in fluorescence lifetime upon analyte binding, collectively forming a versatile toolkit for molecular recognition. These phenomena orchestrate changes in the fluorescence properties of the materials, leading to a transition from fluorescence 'off' to 'on' or vice versa. In this presentation, I will discuss the systematic studies on the photophysical properties of organic fluorophores that have recently been developed in our group.[1-2] Through strategic manipulation of electronic and steric effects of substituents, alongside an exploration of the formation of emissive aggregates, we aim to unveil the fundamental factors governing the optical properties of these fluorophores in both solution and the solid state. Building upon our insights into the optical properties of organic fluorophores, the design and application of fluorescent probes as valuable chemical tools for elucidating biological events in living systems will be demonstrated.



**Keywords**: chemical tools; fluorophore; luminescence; recognition; sensing

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**Invited Speaker**
**LC-I-03**
**Masaki Yoshida**

# Vapor-induced assembly of a luminescent Pt(II) Complex on layered double hydroxide nanoparticles

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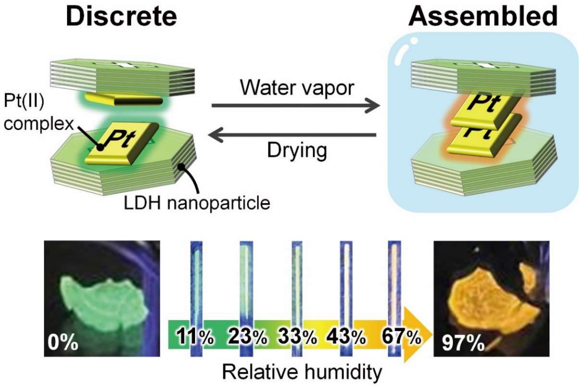
The controlled self-assembly of Pt(II) complexes is key to the development of optical and stimuli-responsive materials. However, the design of self-assembly is still difficult due to weak intermolecular interactions. To overcome this problem, motivated by our recent interest in the cation-controlled assembly of Pt(II) complexes,[1] we have focused on the cationically charged layered double hydroxide (LDH) nanoparticles as a versatile platform to assemble Pt(II) complexes.

In this work, we report a stimuli-responsive nanohybrid material based on $[Pt(CN)_2(ppy)]^-$ (Hppy = 2-phenylpyridine) and the LDH consisting of $Mg^{2+}$ and $Al^{3+}$ ions (hereafter referred to as **Pt-LDH**), in which $[Pt(CN)_2(ppy)]^-$ assembled under water vapor and disassembled under drying. Target **Pt-LDH** has been synthesized by heating $K[Pt(CN)_2(ppy)]$ together with $MgCl_2{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$, and tris(hydroxymethyl)aminomethane. Importantly, the obtained **Pt-LDH** exhibited obvious vapochromic luminescence between green and orange. Variable-temperature luminescence, differential scanning calorimetry (DSC), and water vapor adsorption measurements revealed that the assembly/disassembly of the Pt(II) complex molecules was due to the capillary condensation of water between the nanoparticles. This method of assembling Pt(II) complexes on LDH nanoparticles should not be limited to the work presented here, but is expected to be widely applicable to the assembly of various anionic complexes.[2]



**Keywords**: Layered double hydroxides; luminescence; nanoparticles; Pt(II) complexes; vapochromism

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Invited Speaker
LC-I-04
Jaursup Boonmak

# Luminescent coordination polymers for the detection of volatile chemicals

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The use of vapor-responsive chromic materials in sensing applications for the detection of hazardous volatile chemicals is growing rapidly. Stimuli-responsive luminescent coordination polymers (CPs) have attracted continuous attention owing to their tunable luminescence properties by rationally selecting a luminophore as a building block for their structural assembly. The active sites for specific chemical responses can be designed in CPs. Two examples of luminescent coordination polymers for the detection of volatile chemicals are presented in this work. (1) A phosphorescent Pb(II) 2D-coordination polymer with 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol (pzt) shows a quantum yield of 21.6% and a lifetime of 25.5 μs. Its naked-eye solid-state photoluminescence significantly changes in response to acidic vapors and thermal treatment. Acid protonation of the pzt ligand's heteroatoms can cause structural changes, resulting in emission color changes.[1] (2) A series of luminescent Cu(I) 2D/3D-coordination polymers of iodo-based polymorphs, $[CuI(pyt\text{-}NH_2)]_n$ (**1**-**2**), and thiocyanato-based polymorphs, $[CuSCN(pyt\text{-}NH_2)]_n$ (**3**-**4**) (where $pyt\text{-}NH_2$ = 2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole), show a variety of color and luminescence based on the structural diversity. The iodo-based polymorphs **1** and **2** undergo a change of color and naked-eye solid-state luminescence in response to formaldehyde vapor, demonstrating simultaneous vapochromism and vapoluminescence. For the responsive mechanism, the formation of carbinolamine species via the specific reaction between formaldehyde and the active amino groups of $pyt\text{-}NH_2$ was clarified.[2]

**Keywords**: coordination polymers; Cu(I); Pb(II); acidochromism; vapochromism

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# A preparation of organic photosensitizers for high efficiency of photothermal/photodynamic therapy in tumor

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In this work, we designed and synthesized the thionated NpImidazole derivatives BS and NS, new heavy-atom-free photosensitizers, which efficiently generate a triplet excited state with high singlet oxygen quantum yield. The introduction of the C=S bond to the NpImidazole core is essential for increasing spin-orbit coupling (SOC). The fluorescence emission of BS and NS was quenched at standard ambient temperature, accompanied with the increase in the ISC process from the singlet states to triplet excited states via thionation. BS and NS showed negligible dark cytotoxicity against HeLa cells in working concentration. In contrast, BS and NS rapidly induced cell death under blue light irradiation both under normoxia and hypoxia conditions. Our current study demonstrates that the C=S group can play an important role in type I ROS generation of PSs, which are unprecedented in the previous reports. Finally, the photophysical changes were assigned to the oxidative desulfurization of the C=S group of BS and NS to the C=O group of the corresponding BO and NO via hypochlorite. The combined results demonstrated the dual function of BS and NS as a fluorescent imaging agent for $ClO^-$ and an anti-cancer therapeutic by PDT that showed the potential strategy for “one-for-all” and multifunctional agents.

**Keywords**: photosensitizers; photodynamic therapy; photothermal therapy; antitumor

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LC-I-06
Chun-Guey Wu

# Photochromic dye for dye-sensitized solar cell

Chun-Guey Wu

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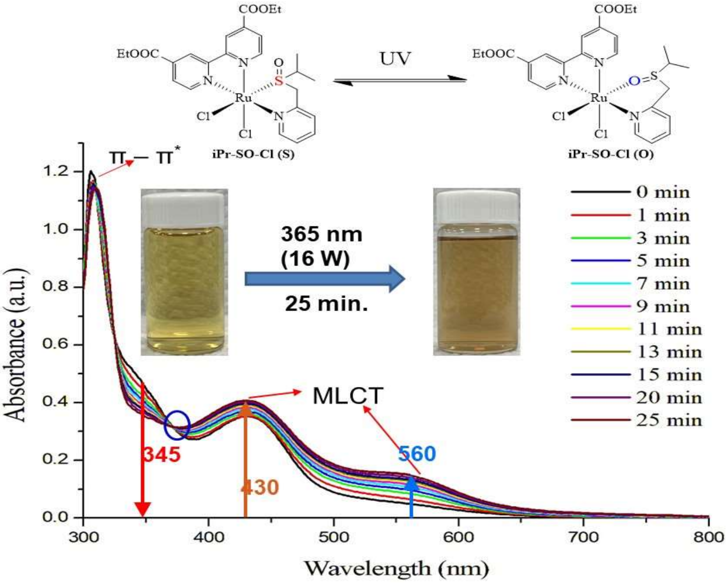
Dye-sensitized solar cell (DSC) is one of the representative third generation photovoltaic technology. The merit of DSC is that it can be designed with a high degree of freedom such as shape, color, and size for unique applications, although the power conversion efficiency of DSC is still lower than the other two representative third generation photovoltaics such as organic solar cell and perovskite solar cell. A new type of sensitizer called photochromic dye was development for DSC recently. The characteristic property of the photochromic dye is that it can turns the color (absorbing light with different wavelength) by absorbing light with certain wavelength (most probably UV light). In this talk we will present the designed organic and ruthenium based photochromic dyes and their photovoltaic performance when applied in DSC. Furthermore, the important parameters, such as the kinetic and reversibility of the color change as well as the structure related photochromic property, for photochromic dyes existed in a DSC will be studied.



**Keywords**: dye-sensitized solar cell; ruthenium dye; photochromic

# MODIFICATION OF LUMINESCENT PROPERTIES OF CARBON DOTS BY SYNTHESIS PARAMETERS

Robert Tomala, Natalia Jastrzębska, Daniela Kujawa, Katarzyna Hałubek-Głuchowska, Paweł Głuchowski, Mateusz Oleszko, Oleksii Bezkrovnyi

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Fluorescent patterning has attracted significant attention due to its potential applications, particularly in the domain of anti-counterfeiting technology. A noteworthy candidate in this field is the utilization of fluorescent Carbon Dots (CDs), a type of fluorescent dye that holds promise for invisible patterning owing to its exceptional optical characteristics. This study aims to introduce green fluorescent CDs as a compelling component in the realm of product coding. Accordingly, methods have been developed to synthesize CDs using the solvothermal technique, which exhibit unique spectroscopic properties depending on the excitation radiation's wavelength. These CDs demonstrate high values of quantum efficiency, enabling a reduction in the required amount of marker inserted into the protected product.

The studies show how by modifying the synthesis parameters, such as annealing temperature, pH, substrate concentrations, or the use of modifiers, the spectroscopic properties of the obtained CDs can be controlled

The project also involves the development of a device that enables clear confirmation of the authenticity of the labeled product, utilizing laser diode technology as the excitation source and a CCD detector.

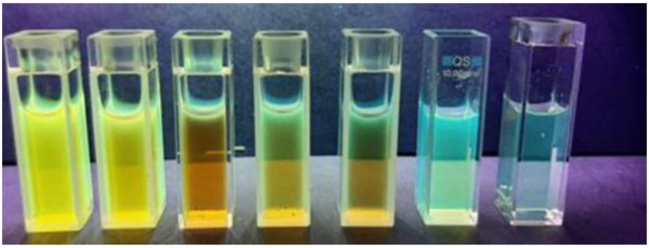

**Figure 1.** The influence of reagents ratio on emission color of CDs under UV excitation

**Keywords**: carbon dots, luminescence, luminescent markers

**Acknowledgements**: This research was funded by the National Centre of Research and Development as part of the LIDER XII program, project number LIDER/26/0121/L-12/20/NCBR/2021

# Emission color control of pH-responsive Pt(II)-NHC complex in highly proton-conductive polymer

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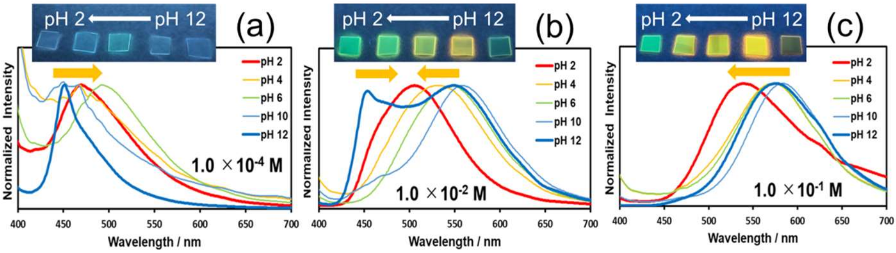
We have proposed a method to control the emission color from red to green by introducing proton-responsive Eu$^{III}$ and Tb$^{III}$ complexes into a highly proton-conductive polymer (Nafion).[1] In this conference, efforts to control a wider range of emission colors, including blue emission, will be presented.

A blue light-emitting platinum(II) *N*-heterocyclic carbene complex, $[(^{i}\mathrm{Pr}\text{-}\mathrm{NHC})\mathrm{Pt}^{II}(\mathrm{C{\equiv}C\text{-}3Py})_2]$ (**1**; $^{i}$Pr-NHCH$^{+}$ = 1-(1-methylethyl)-3-(2-pyridinyl)-1*H*-imidazolium, HC≡C-3Py = 3-ethynylpyridine), and its protonated form, $[(^{i}\mathrm{Pr}\text{-}\mathrm{NHC})\mathrm{Pt}^{II}(\mathrm{C{\equiv}C\text{-}3PyH})_2](\mathrm{PF}_6)_2$ (**1·H₂**), have been successfully synthesized and crystallized. Furthermore, the emission behavior of a transparent film incorporating **1** in Nafion was investigated. The emission spectra of **1**@Nafion showed a red shift from 451 to 593 nm with increasing luminophore content, which suggests Pt-Pt interactions between adjacent molecules. Upon treating **1**@Nafion films with pH 2 buffer, the emission wavelengths of the films with low concentrations of **1** ($10^{-4}$ M) showed a red shift, while those with high concentrations ($10^{-1}$ M) showed a blue shift. The distinctive pH response behavior of discrete and aggregated molecules has allowed us to tune a wide range of emission wavelengths in our transparent films. Additionally, some efforts have been made to control the emission wavelength by applying DC voltage with **1**@Nafion.



**Keywords**: Pt Complex; *N*-Heterocyclic Carbene; Nafion; Proton Conductivity; Multicolor Emission

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# HMPA polymer-tris-cycometalated iridium complex constructs as functional imaging tools

Anuson Sansee[1], Libor Kostka[2*], Adéla Marcalíková[3], Júlia Kudláčová[2], František Sedlák[3,4], Lenka Kotrchová[2], Pavel Šácha[3], Tomáš Etrych[2], Filip Kielar[1]*

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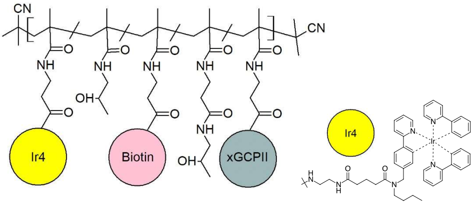
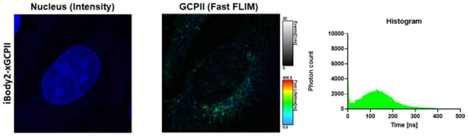
Multifunctional imaging probes are necessary for the investigation of biological systems. Polymers, such as those based on *N*-(2-hydroxypropyl)methacrylate (HMPA), offer the possibility to include several functional components in a single system. We have constructed such a system (iBody) using an HMPA based copolymer equipped with an iridium based luminescent probe, glutamate carboxypeptidase II (GCPII) targeting ligand, and a biotin affinity tag. The synthesized macromolecular probes differed in the structure of the polymer and content of the iridium complex. The applicability of the synthesized probes has been tested in flow cytometry (FACS) based assay, laser confocal microscopy, and fluorescence lifetime imaging (FLIM). The FACS analysis has shown that the targeted iBodies labelled with the iridium luminophore exhibit selective labelling of GCPII expressing cells. This observation was confirmed in the imaging experiments with laser confocal microscopy. Finally, the FLIM experiment has shown that the iBodies with the iridium label exhibit a lifetime greater thatn 100 ns, which distinguishes them from typically used systems labelled with organic fluorophores exhibiting short fluorescence lifetimes. Our results indicate that the synthesized probe exhibits interesting properties, which supports the development of additional biological tools utilizing the key components (iridium complexes, iBody concept) used in this system.




FLIM in U251-GCPII cells

**Keywords**: HPMA; iridium complex; imaging; iBody

# Luminescent metal-organic chalcogenolate coordination polymers

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Metal-organic chalcogenolates (MOCs) are an emerging family of luminescent hybrid coordination polymers that combine the robustness of inorganic materials with the fabrication convenience and tunability of organic molecules. Silver phenylselenolate (AgSePh), a prototypical member of the MOC family, is a 2D semiconductor that features multiple exciting properties including narrow blue luminescence, in-plane anisotropy, large exciton binding energy, robust stability, non-toxic chemical composition, and scalable synthesis methods that are compatible with modern thin-film microelectronics manufacturing. Compared to other 2D semiconductors like layered perovskites and transition metal dichalcogenides, MOCs are distinguished by the presence of organic ligands covalently bound to their inorganic cores, which provides a unique handle to control their structures and electronic properties.

In this presentation, I will present advancement in the synthesis of MOCs, show the impacts of organic modification on their optoelectronic properties, provide examples of their applications in light emission and sensing, and discuss the insights into the exciton physics of this novel material family.

**Keywords**: Coordination polymers, Semiconductors, Luminescent materials, Optoelectronics, 2D materials.

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**Oral Presentation**
**LC-O-05**
**Pawel Gluchowski**

# Multifunctional carbon dots: synthesis, characterization, applications

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Luminescent carbon dots discovered in the early 2000s, often abbreviated as CDs, represent a class of nanomaterials that have garnered significant attention in recent years [1, 2]. These nanoparticles, typically less than 10 nanometers in size, exhibit remarkable luminescent properties, making them a subject of intense research in various scientific and technological fields. CDs evolved into a versatile and promising materials with a wide range of potential applications. Their unique properties, including excellent biocompatibility, low toxicity, and tunable emission wavelengths, have led to investigations in fields as diverse as bioimaging, sensing, catalysis, optoelectronics, and environmental monitoring.

This work aims to provide a brief overview of luminescent and phosphorescent carbon dots, showing their synthesis methods, structural characteristics, and the underlying principles governing their luminescence. The morphology of the CDs, and results of IR, absorption, emission and luminescence kinetics will be presented in terms of their impact on the photocatalytic activity of hybrids. Additionally, it will highlight some of the prominent applications. In particular, we will focus on showing the possibilities of tuning the optical properties of CDs in order to use them in anti-counterfeiting applications, and the use of phosphorescent CDs in photocatalysis process.

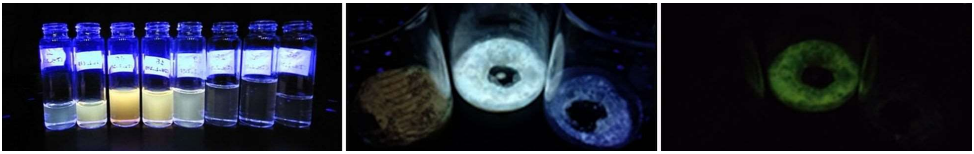

Figure. Photo of CDs with tuned luminescence color (left) and phosphorescent CDs under UV light (middle) and in dark (right)

**Keywords**: carbon dots, optical marker, color tuning, anti-counterfeiting, photocatalyst

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# Luminescent thermometry in chiral lanthanide-iridium molecular assemblies

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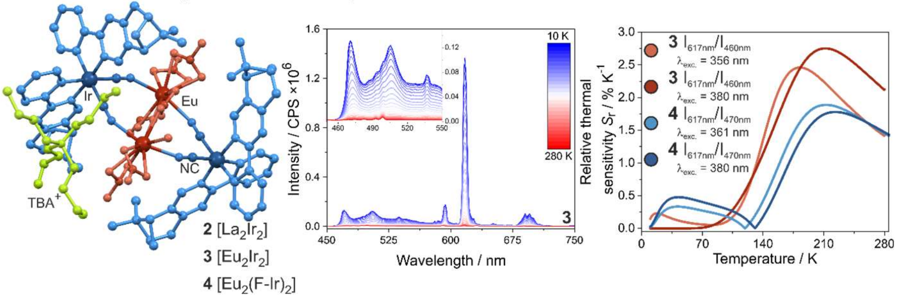
Recently in the literature, a new trend appeared, in which a strong dependence of luminescent is generated and used in the construction of contactless and reliable devices for temperature measurement. In this topic, lanthanide(3+) ions are often used due to their sharp emission bands and strong temperature dependence of emission related to, e.g., thermosensitive energy transfer processes.[1] Such systems found their use in biological studies and chemical reactors.[2,3] Molecular materials based on cyanido metal complexes could exhibit a wide range of functionalities such as magnetic, optical, and magneto-optical, e.g., magneto-chiral dichroism or magnetization-induced second harmonic generation (MSHG).[4–6] In our work, we focused on a combination of chiral cyclometalated cyanidometallate ions with f-block element complexes to obtain a new class of molecular materials exhibiting not only luminescent thermometry but also SHG activity. We report the family of molecular materials with the general formula of $(\mathrm{TBA})_2\{[\mathrm{Ln^{III}}(\mathrm{NO_3})_3(\mathrm{H_2O})]_2[\mathrm{Ir^{III}}(\mathrm{CN})_2(R,R\text{-pinppy})_2]_2\}$ consisting of two Ir(III) and two lanthanide(III) centers (see figure below). They exhibit strong *T*-dependence of luminescence and SHG. The modification of the ligand enables the modulation of the optical thermometry.



**Keywords**: lanthanides; cyanido metal complexes; luminescence; chirality; non-linear optics

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**Oral Presentation**
**LC-O-07**
**Jukkrit Nootem**

# Influence of a B-O-C bond on photophysical and sensing properties toward saccharides of BODIPYs.

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Saccharides are part and parcel of living cells as they play an essential role in the storage of genetic information and are commonly used in the food industry. However, monosaccharides, especially fructose, can be reacted with proteins or lipids affording advanced glycation end-products which may be involved in diabetic vasculature and contribute to the development of atherosclerosis. Thus, monitoring of the concentration of sugars is essential in both clinical and biological applications. In this work, we modified a fluorescent probe for saccharides through displacement of fluorine atoms with methoxy groups on BODIPY molecule affording dimethoxy-BODIPY fluorophore with a phenylboronic acid group at the *meso-* position. Upon addition of sugars, a fluorescent turn on was observed as a result of cyclic ester formed by the interaction between the boronate and the hydroxyl groups of the sugar. The results indicated that the B-O-C bond does not influence photophysical properties of a BODIPY molecule in organic solvents, but dramatically affected their fluorescent signal in aqueous media as it is relatively quenched in buffers, which was then restored when sugars were introduced to the solution. Additionally, it also impacted their sensing properties toward sugars by showing more selective binding with fructose in potassium phosphate buffer at pH8.

**Keywords**: BODIPY; O-BODIPY; boronic acid; fluorescent sensor; saccharides

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**Poster Presentation**
**LC-P-01**
**Nguyen Hoang Ninh**

# Zinc(II) complexes bearing π-extended 8-hydroxyquinoline-derived ligands: Synthesis, characterization and photophysical properties

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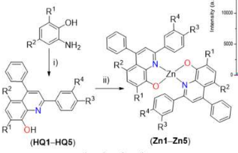
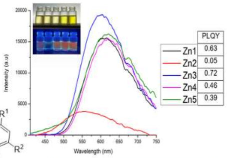
Among the materials showing promising properties for organic light-emitting diode (OLEDs), fluorescence materials based on Zn(II) complexes are potential candidates due to their advantageous properties such as higher emission intensity, less toxicity, high thermal stability, low molecular weight, easy color tunability with simple synthetic procedures and higher reaction yields [1]. In this work, we have investigated the preparation and structural characterization of five new Zn(II) complexes (**Zn1**-**Zn5**) from 2,4-diaryl-8-hydroxyquinoline derivartives. The structures of these compounds were confirmed based on ESI-MS, $^1$HNMR spectra and SC XRD. The analysis of NMR and XRD results revealed that all the complex geometries are tetrahedral and the ligands coordinated with Zn(II) via the N and O atoms. The investigation of optical properties shown significantly stronger fluorescence in the solid state compared to that in solutions. In THF solvent, all the complexes, except **Zn2**, displayed a strong emission at 559-621 nm, characterized by a fluorescence quantum yield of 0.39-0.72 with a large Stokes shift of 173-194 nm. Notably, the quantum yields of the complexes in THF solution tend to increase in the presence of electron-donating substituents. The experimental findings are consistent with the theoretical results calculated by using time-dependent density functional theory (DFT).

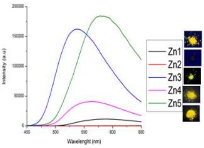


**HQ1/Zn1**: $R^1 = R^2 = R^3 = R^4 = H$
**HQ2/Zn2**: $R^1 = R^2 = R^4 = H$; $R^3 = NO_2$
**HQ3/Zn3**: $R^1 = R^2 = H$; $R^3 = R^4 = OCH_3$
**HQ4/Zn4**: $R^1 = R^2 = Cl$; $R^3 = R^4 = H$
**HQ5/Zn5**: $R^1 = R^2 = R^3 = Cl$; $R^4 = H$

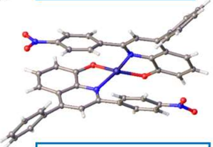
i) phenylacetylene, benzaldehyde derivatives, trifluoroacetic acid, silver(I) trifate, 1,2-dichloroethane; ii) $ZnCl_2$, ethanol, 70 °C, 8 hours.



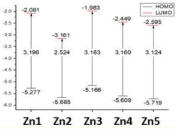
Emission spectra in THF



Emission spectra in solid state



The molecular structure of **Zn2**



Frontier molecular orbital energy (eV)

**Keywords**: Zn(II) complexes; diaryl-8-hydroxyquinoline; fluorescence; effects of substituents.

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**Poster Presentation**
**LC-P-02**
**Jian-yue He**

# Design and Synthesis of Fluoride-bridged Rare-earth Luminescent Clusters

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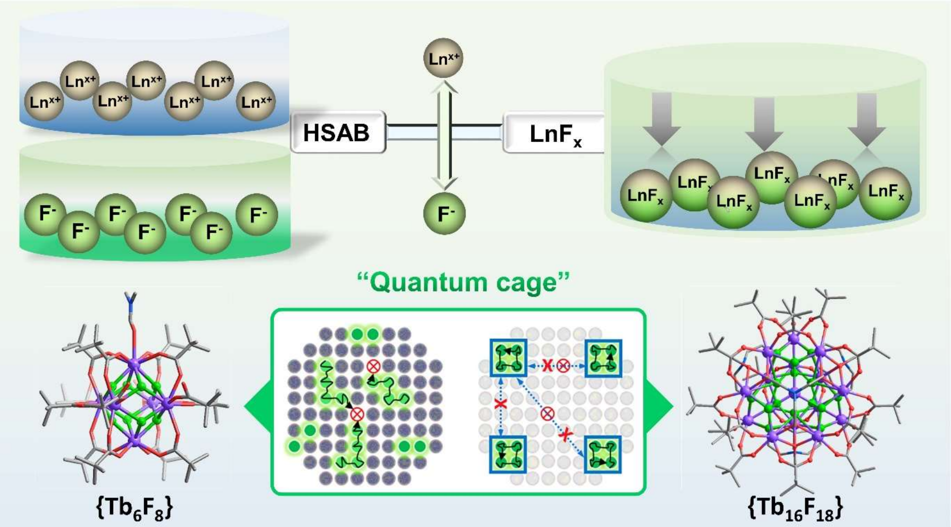
Fluoride-bridged rare-earth clusters that possess precise molecular structures and low phonon energies combine the advantages of both pure inorganic materials and organic molecules. By replacing the $OH^-$ with $F^-$, not only are the rare earth ions more tightly bound, but the energy loss due to molecular vibration is also reduced. The hard base $F^-$ with the greatest electronegativity and small radius should be given priority as the bridging group to coordinate with the rare earth center in the construction of rare-earth clusters. Unfortunately, the direct reaction of the above two usually produces extremely insoluble rare-earth fluoride ($LNF_x$), which has posed great challenges to the synthesis of fluoride-bridged rare-earth clusters. Nevertheless, the fluoride-bridged rare-earth cluster is still seen as a more valuable option for exploring luminescent material. To address this, our research group prepared the fluoride-bridged rare-earth clusters $\{Tb_6F_8\}$[1] and $\{Tb_{16}F_{18}\}$ via a solvothermal method with a high yield of 81 %. As the materials are neutral organic-inorganic assembled molecules, they demonstrate strong resistance to water and thermal stability. Under 365 nm excitation, they exhibit high color purity (green emission) and quantum yield (~ 90%).



**Keywords**: rare-earth cluster; Luminescence; fluoride-bridged; quantum yield

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# Mannose-conjugated BODIPY photosensitizer for photodynamic therapy

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Photodynamic therapy (PDT) stands out as a promising strategy for treating diverse diseases, prominently cancer. This study pursues an advancement in the selectivity and efficacy of PDT by designing and synthesizing a BODIPY-based photosensitizer conjugated with mannose. Mannose, chosen for its high affinity towards mannose receptors, particularly overexpressed in certain cancer cells such as MDA-MB-231 breast cancer cells, serves as the targeting moiety. In this work, a new mannose-conjugated BODIPY photosensitizer was synthesized via a click reaction and characterized using NMR and UV-Vis spectroscopy, and mass spectrometry. Study of photophysical properties of the new photosensitizer revealed a significant enhancement in singlet oxygen generation upon exposure to light. This research is currently ongoing, aiming to evaluate the potential of mannose-conjugated BODIPY photosensitizer in both *in vitro* and *in vivo.* The mannose-conjugated BODIPY photosensitizer may exhibit promising potentials in photodynamic therapy applications.

**Keywords**: Photodynamic therapy, photosensitizer, mannose, singlet oxygen generation

# Development of BODIPY-NHC- Au(I) Complexes as Photocage Molecules for Biomedical Applications

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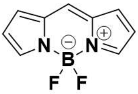
Boron-dipyrromethene (BODIPY) has been a well-matured fluorophore due to its prolific, high extinction coefficients, and excellent quantum yield, leading to numerous applications, including biomedical technology, organic materials, and imaging. N-Heterocyclic carbenes (NHCs) are important ligands for organometallic complexes, and one of the important applications is being utilized as a metallodrug. A photocage is a light-sensitive chemical protecting group that provides precise control using targeted light irradiation in releasing specific molecules. However, several limitations are non-real drug utilizations and limited light absorptions. In this presentation, we are designing a new type of photocage by combing a BODIPY fluorophore with NHC-metallodrug. The photophysical property and structural information were fully characterized. Additionally, the photo-releasing property is evaluated, and cytotoxicity is examined. On the other hand, we are also trying to extend the light absorption of our BODIPY fluorophore by extending the conjugation. Our ultimate goal is to utilize these BODIPY derivatives for achieving both the detection and treatment of cancer.

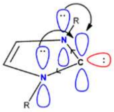
**Keywords:** BODIPY; NHC carbene; Photocage; Fluorescent; NIR

Boron dipyrromethene (BODIPY)：



- ✓ Good photostability
- ✓ High molar absorption efficiency
- ✓ High fluorescence yield and reactive oxygen species yield
- ✓ Low biological toxicity

*N*-heterocyclic carbene (NHC) ：



- ✓ Excellent σ-donor and moderate π-acceptor
- ✓ Great Ligands for transition metal complexes
- ✓ Au-NHC complexes demonstrate multiple potentials in medicinal chemistry

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# Synthesis of polyaromatic imidazolium-based on silsesquioxane cages

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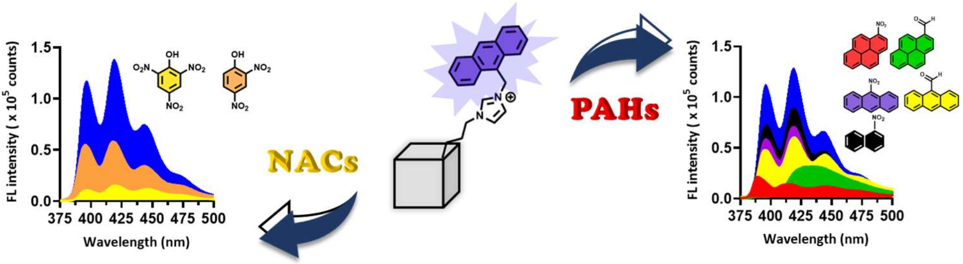
Polyhedral oligomeric silsesquioxane (POSS) was functionalized with polyaromatic-based imidazolium as a sensor (POSS-im-An) that dissolves in polar solvents including EtOH, MeOH, DMSO, DMF, MeCN, DCM, and partially dissolves in $H_2O$ by using simplified synthesis. Aggregation-caused-quenching (ACQ) was found when water in DMSO was more than 15%. The highest fluorescence intensity and clear solution were found at 15% water/DMSO; therefore, was chosen as an optimized condition for study. The sensor is “turn-off” with an excellent selectivity among polycyclic aromatic hydrocarbon (PAH) and nitroaromatic compounds (NACs) including CHO-Ant, CHO-Pyr, $NO_2$-Ant, $NO_2$-Pyr and $NO_2$-Nap, PA, and DNP versus others.[1, 2] The quenching mechanism is related to hydrogen bonding, **π-π** stacking, and Photoinduced electron transfer (PET). POSS-im-An also demonstrated good sensitivity and rapid response and can quantitatively detect PAHs and NACs with low detection limits.



**Keywords**: Nitroaromatic compounds; Polycyclic aromatic hydrocarbons; Imidazolium; Fluorescence quenching; Sensors

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# A Ratio Fluorescent sensor Based on Carbon Dots for the Detection of Copper Ions

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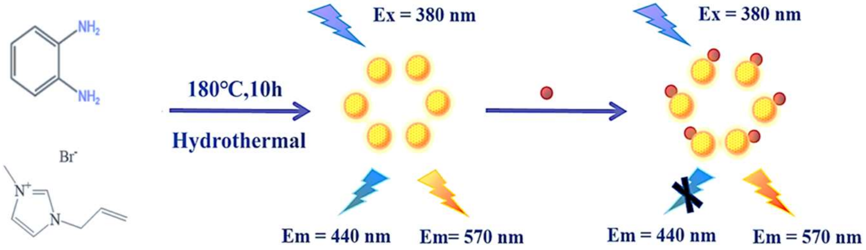
Highly selective and sensitive detection of copper ions in water samples is critical for human health, as excess copper ions in the human body can lead to many neurodegenerative diseases. In this study, a ratiometric fluorescent sensor were prepared by one-step hydrothermal method using o-phenylenediamine and 1-methyl-3-allylimidazole bromide as precursors. The -$NH_2$ and -OH on the surface of the carbon dots can coordination with copper ions to form complexes, which reduces the fluorescence emission intensity at 440 nm and increases the fluorescence emission intensity at 570 nm. The fluorescence intensity ratio showed a good linear correlation with the concentration of copper ion in the range of 2-15 mg/L with a limit of detection (LOD) of 0.04 mg/L. The ratio fluorescence sensor was successfully applied to detect copper ions in water samples with satisfactory recoveries, indicating potential applications of this sensor.



Schematic diagram of preparation of ratio fluorescence sensor and strategy for copper ion detection

**Keywords**: Fluorescent sensor; Carbon dots; Ratio fluorescence; copper ions

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# MOF/COF Chemistry (MC)

# Abstract

**Keynote Speaker**
**MC-K-01**
**Sujit K. Ghosh**

# Efficient extraction of targeted metal ions from (sea)water using advanced porous materials

Sujit K. Ghosh*

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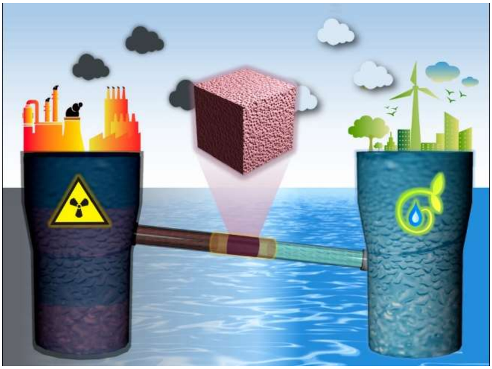
World Economic Forum documented safe drinking water crisis and affordable clean energy are the worldwide major issues. Due to accelerating urbanization along with rapid industrialization, an ever growing number of toxic contaminants are entering the fresh water supplies. In the priority list, the U.S. Environment Protection Agency (EPA) listed metal-based oxoanions as potential toxic inorganic pollutants in waste water. Among them, adsorption followed by ion exchange based purification techniques are emerging, and are considered as promising over other conventional methods. In my lecture, I will discuss about advanced porous materials for highly selective and efficient extraction of various hazardous metal based oxoanions such as, $HAsO_4{}^{2-}$, $SeO_4{}^{2-}$, $ReO_4{}^{2-}$ (surrogate for radioactive $TcO_4{}^{2-}$), $CrO_4{}^{2-}$ etc. from water, in the presence of excess of other coexisting ions. I will also discuss about highly selective and efficient Uranyl ion extraction, from natural seawater for potential applications of Uranium as renewable and clean nuclear energy source, and also from ground water for safe drinking water [1-2].



**Keywords**: Safe-drinking-water; Clean-energy; Contaminants; Advanced-porous-materials

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# Engineering Flexibility in Metal-organic Frameworks

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Metal-organic frameworks are well known to retain crystallinity after experiencing significant changes in unit cell volume. Such flexibility has given rise to unique gas storage and separation properties (1). In recent years we have designed a MOF material that takes advantage of framework flexibility to facilitate catalytic reactions within the pore network with retention of crystallinity. This feature allows for precise characterization of the catalytically active sites along with reactive intermediates (2). In this presentation our groups recent work focused on engineering flexibility in metal organic frameworks will be highlighted.

**Keywords**: Metal-organic framework; flexibility; catalysis

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**Keynote Speaker**
**MC-K-03**
**Satoshi Horike**

# Synthesis and functions of hierarchical metal-organic framework glasses

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Crystal−Liquid−Glass transformation of metal-organic frameworks has been recognized in the last decade.[1,2] Macro-scale structurization and properties of metal-organic framework glasses are correlated with medium-range order of networks and local coordination geometries. Here I describe the update of the synthesis approach of MOF glasses composed of carboxylate/pyridyl ligands to control their structures for porosity and conductivity.[3] Glass materials' design for photo-responsive charge transport, heterogeneous catalysis by the ability of molecular doping and transparency will also be discussed.[4]

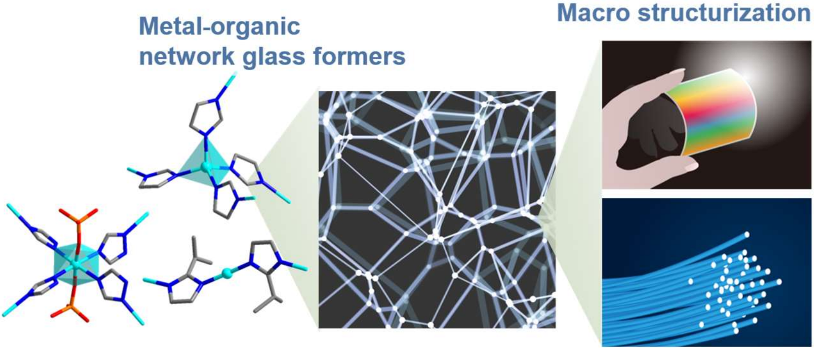

**Figure.** Illustrations of hierarchical structures of metal-organic framework glasses.

**Keywords**: metal-organic frameworks; glass; phase transition; conductivity; porosity

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**Keynote Speaker**
**MC-K-04**
**Shuhei Furukawa**

# Assembling metal-organic cages as porous materials

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A gel is a soft material containing a cross-linked three-dimensional network and a continuous phase like a liquid. Most gel materials reported so far are composed of cross-linked organic polymers or silica-based networks. Recently, metal-organic network systems started contributing to this class of materials. In this case, either amorphous metal-organic networks or colloidal networks based on metal-organic frameworks (MOFs) are used; however, it has been challenging to control their cross-linked network structures. Our group recently reported another type of metal-organic network to form gels, in which well-defined metal-organic cages (MOCs) are used as building blocks and their inter-cage linkage is tuned by coordination chemistry. This network further produces colloidal spheres, followed by connecting them to form colloidal networks. This hierarchical nature of metal-organic networks based on MOCs gives us an opportunity to control their cross-linked networks across multiple length scales.[1-8] In this presentation, we will discuss the strategies to regulate the cross-linked networks of MOCs and tune the resulting properties including porosity.

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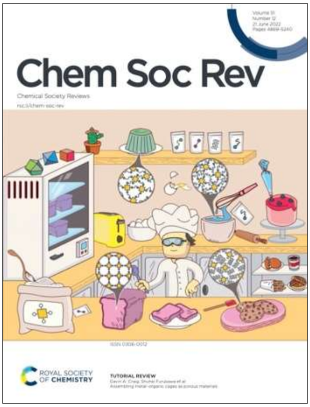

**Keywords**: Metal-organic polyhedra; Porosity; Soft materials; Self-assembly

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**Keynote Speaker**
**MC-K-06**
**Moonhyun Oh**

# Components, structures, and metal-organic frameworks

Moonhyun Oh[1*]

[1]*Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea*
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Metal-organic frameworks (MOFs) have attracted many attentions not only due to their various structural topologies and chemical tunabilities but also their useful properties and applications. The development of more useful MOFs with desired property is vital interest. Components and structures of materials are critical in determining their representative properties and applications. Thus, people are trying to achieve ideal materials having optimal properties by synthesizing materials that have a desired structure with chosen components. A similar strategy applies to MOF. During MOF construction, appropriate components with ideal functionalities are relatively easy to gain from many existing chemicals or by designing new ones. However, the construction of MOFs with a desired structure is rather challenging. Normally, nature decides a structure to have thermodynamically and/or kinetically preferred one from the chosen components. Here I present the understanding on the precise MOF-on-MOF growth process and so the controlled construction of complicated MOFs or naturally non-preferred MOFs. Moreover, I provide an inspiration for the design and construction of MOFs to have a structure that people prefer instead of a structure determined by nature. This work will eventually offer a way to access the ideal MOFs, that should facilitate their use in practical applications.

**Keywords**: induced growth; MOF-on-MOF growth; complicated MOF

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**Keynote Speaker**
**MC-K-07**
**Shane Telfer**

# A New Concept in Asymmetric Catalysis (Implemented Using MOFs)

Shane Telfer, Ludwig Petters, Mohana Arul & Subo Lee

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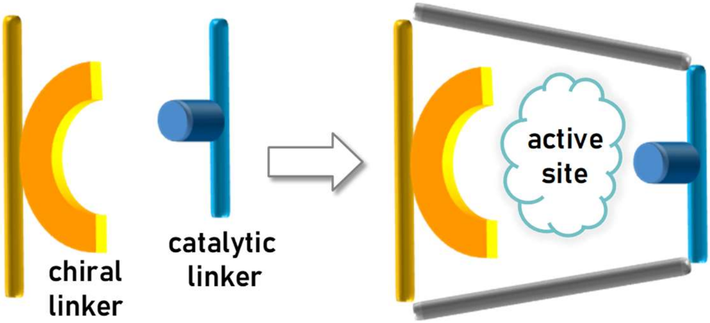
Catalysis rules the chemical kingdom and asymmetric catalysis occupies the throne. However, creating effective asymmetric catalysts remains a formidable challenge. We propose a new concept that is freed from the constraints of conventional design. Here, catalytic activity and chiral induction arise from motifs that are *entirely independent*. To implement this concept, we draw on multicomponent metal-organic frameworks. A catalytic unit is installed on one linker while a chiral unit is installed on another. The space between them is an active site for asymmetric catalysis. Catalysis in these sites delivers ee's of up to 75% (and counting).



**Keywords**: metal-organic frameworks; catalysis; asymmetry

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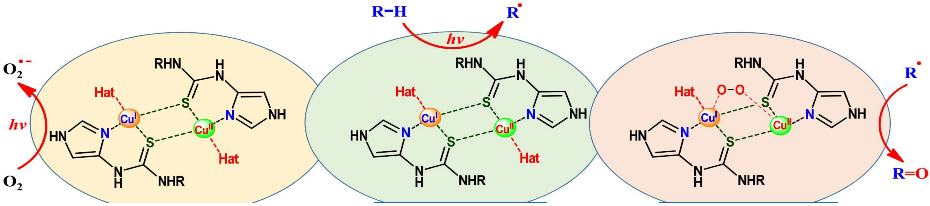
**Keynote Speaker**
**MC-K-08**
**Chunying Duan**

# Enzyme-inspired metal-organic architectures for confined photocatalysis

Xu Jing[1], Liang Zhao[1], Tiexin Zhang[1] and Chunying Duan[2]

*[1]School of Chemistry, Dalian University of Technology, Dalian, 116024, China*
*[2]State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, China.*
**E-mail: cyduan@dlut.edu.cn*

Enzyme provides the fundamental principles for expanding the use of abundant metals in catalysis. Mimicking the structure and function of enzymes in artificial system for converting inert molecules like $H_2O$, $CH_4$, $CO_2$, and $N_2$ is highly valuable but still faces marked challenges. Installing electron transfer pairs in both the ground and excited states and transition-metal clusters into Werner-typed metal-organic architecture hosts is a way to mimic the roles of coenzyme and enzymatic center, respectively. Prof. Duan' group has established a promising protocol to mimic natural enzyme systems in redox transformations of inert bonds by confined photocatalysis. The electron transfer behavior within enzyme-like confined environment differed from both the classical inter- or intramolecular photoinduced electron transfer steps that obey Rehm-Weller or Marcus theory. It has been proposed that this new confined photocatalysis benefits to stabilize the charge-separated pair and enhance the long-range charge delocalization, which helps the high-energetic excited-state processes to realize the energy-demanding inert bond conversions in the consecutive multi-photon & multi-charge processes, such as in the realm of C-H bond activation, $CH_4$ oxidation, $CO_2$ reduction, and $N_2$ reduction.



**Keywords**: metal-organic architecture; photocatalysis; enzyme-inspiration

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# Functional organic framework for pollutant treatment and their batch preparation

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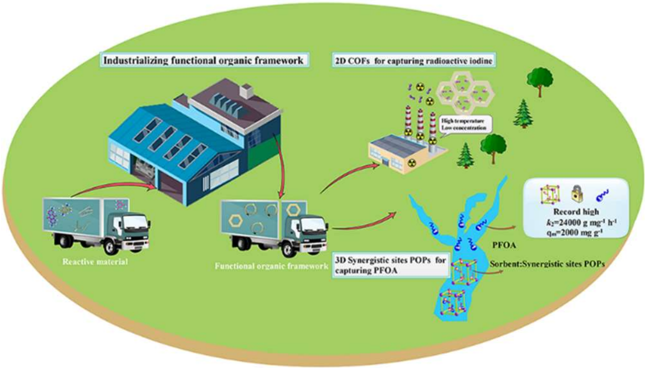
Functional organic framework materials have been widely applied in pollutant treatment with outstanding performances. In this regards, we developed a series of functional organic frameworks as adsorbents for capturing radioactive iodine as well as perfluorooctanoic acid (PFOA). The reported COFs including TGDM and 4F-iCOF-TpBpy-I$^-$ demonstrated a breakthrough $I_2$ capturing performance (~30 wt % for TGDM, and 37 wt % for 4F-iCOF-TpBpy-I$^-$) compared with industrial silver based adsorbents Ag@MOR (17 wt %) under industrial operating conditions (150 °C, ~150ppmv of $I_2$). Moreover, the highly efficient PFOA adsorbents by installing synergistic electrostatic/hydrophobic sites onto porous organic polymers (POPs) have also been illustrated. The constructed PAF-1-NDMB (NDMB = N,N-dimethyl-butylamine) demonstrates an exceptionally high PFOA uptake capacity over 2000 mg $g^{-1}$, which is 14.8, 32.0 and 24.1 times enhancement compared with its parent material (PAF-1) and benchmark materials of DFB-CDP (β-cyclodextrin (β-CD)-based polymer network) and activated carbon. Furthermore, the batch synthesis of functional organic framework were further investigated by high pressure homogenization approach, which can realize large-scale synthesis of functional organic framework materials under benign conditions. These works opens a new avenue for designing functional organic frameworks toward pollutant treatment and their potential application in industrials.

**Keywords**: Functional organic framework; batch preparation; pollutant treatment



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**Keynote Speaker**
**MC-K-10**
**Tiexin Zhang**

# Molecule device-inspired “monodirectional electron transfer” of metal-organic framework for confined photocatalysis with added value

**Tiexin Zhang**[1,*], Mochen Li[1], Yusheng Shi[1], Chunying Duan[1]

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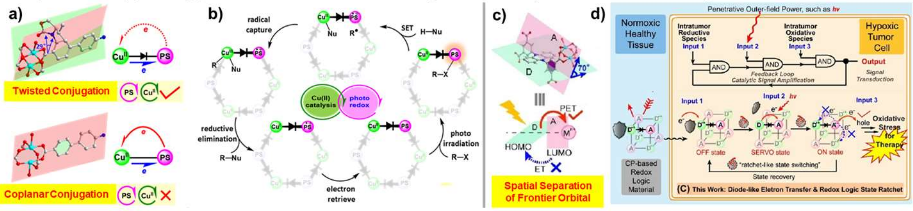
Light energy is a sustainable source of clean energy for catalytic conversion. Under the realm of Marcus theory for homogeneous photocatalysis, the uncontrollable molecular thermal motion and multiple undesirable routes of photoinduced-electron transfer (PET) can cause self-quenching of photo-excited states and side-reactions. Inspired by "molecular devices" and enzymatic electron transfer chains, a "monodirectional electron transfer" system based on metal-organic frameworks (MOFs) is developed to resolve these issues. The dye-based ligands with characteristics of "spatially separated frontier orbital" were used to coordinate with transition metal nodes for constructing MOFs. The anisotropic electronic structures of MOFs were also tuned through "high polarity" and spatially forced "twisted conjugation" of coordination between metal node and ligand. This strategy could mimic the function of “molecular diode” to regulate direction and efficiency of PET, as well as tuning the reactivity of active species such as free radicals in confined pores, which resulted in different selectivities compared with homogeneous photocatalysis, in high value-added transformations such as CF$_3$ protection of aryl metabolic susceptible positions, C-N/O/S coupling, olefin difunctionalization, radical cross-coupling, and inert C-halide bond cleavage. This protocol was further applied in logic-gate-controlled photo-Fenton catalytic therapy of hypoxic tumor models in high bio-compartment selectivity.



**Keywords**: metal-organic framework; confined photocatalysis; unidirectional electron transfer; molecular device

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**Invited Speaker**
**MC-I-01**
**Mio KONDO**

# Iron-Complex-Based Supramolecular Framework Catalyst for Visible-Light-Driven $CO_2$ Reduction

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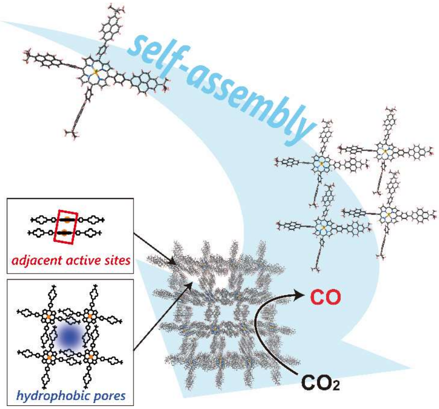
Molecule-based heterogeneous photocatalysts without noble metals are one of the most attractive systems for visible-light-driven $CO_2$ reduction. However, reports on such photocatalysts are still limited, and their activities are quite low compared to those containing noble metals. Herein, we report a noble-metal-free porous crystalline photocatalyst that exhibits high activity for $CO_2$ reduction driven under visible-light irradiation. The key to our success is the use of a supramolecular framework composed of iron porphyrin complexes bearing pyrene moieties at *meso* positions (**FC1**). The rationale for selecting **FC1** as a photocatalyst was based on the following three attributes: (i) an iron porphyrin complex, which serves as a catalytic center, (ii) pyrene-based substituents that operate as light-harvesting units and non-covalent interaction sites, and (iii) a crystalline porous structure to readily accumulate $CO_2$. Our material utilizes iron, which is an earth-abundant and nontoxic transition metal, and promotes catalysis without the addition of external photo-sensitizing molecules or a co-catalyst. Owing to the synergistic effect of these aforementioned properties, **FC1** exhibited high $CO_2$ reduction activity (maximal production rate for CO is 29,100 μmol $g^{-1}$ $h^{-1}$, which is more than 100 times higher than those of the currently available best-in-class porous-crystalline-solid-based photocatalysts without noble metals[1].

**Keywords**: Iron porphyrin; carbon dioxide reduction; framework catalyst; photochemical reaction; heterogeneous catalyst



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# Controlled lattice rearrangement in a metal-organic framework by defect engineering

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Metal-organic frameworks (MOFs) are a series of crystalline porous materials that are composed of metal clusters and organic linkers. The advantage of MOFs is that various functionalities and flexible nature can be easily introduced by proper choice of metal ion and synthetic design of organic linker. Many MOFs with flexible nature that is originated from volume and bond angle change have been synthesized for extensive applications such as gas storage and separation. In contrast, the examples of flexible MOFs based on bond switching mechanism are very few because the synthetic strategy is not clearly established.[1-4]

In this talk, I will present defect engineering method to achieve the connectivity change of coordination bond in a MOF for lattice rearrangement. From the systematic studies in our system, the rearrangement was completed when the amount of defects originated from missing likers range from 5 to 10%; no rearrangement was observed in the case of higher defect levels. In addition, the crystal size of the MOF was also important to control the rearrangement behavior.

**Keywords**: metal-organic framework; lattice rearrangement; defect

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**Invited Speaker**
**MC-I-03**
**Kyriakos C. Stylianou**

# Metal-organic Framework Chemistry: Design Strategies to Applications

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Metal-organic frameworks (MOFs) are crystalline materials prepared by the self-assembly of metal ions/clusters with organic ligands to form three-dimensional porous structures. The scientific importance of these materials stems from the limitless choice of metal ions and potential ligands available, which provide an ideal platform for a systematic study of materials containing specific functionality for a targeted application. In this presentation, I will describe our approaches for the design and synthesis of MOFs for the selective capture of $CO_2$ from dilute sources.[1, 2] I will provide a detailed description of how the sequential pore functionalization in a carborane-based metal-organic framework, utilizing Lewis basic ammonia molecules, leads to the chemisorption of $CO_2$ and the subsequent formation of carbamic acid. Throughout this presentation, I aim to demonstrate how molecular-level features within the MOF structures can be used to tune function, providing solutions in the area of carbon capture.

**Keywords**: metal-organic frameworks, design, carbon dioxide, capture, chemisorption

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**Invited Speaker**
**MC-I-04**
**Hyunchul Oh**

# Mitigation of LH2 tank boil-off losses via adsorption of H2 on metal–organic frameworks

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Liquid hydrogen (LH2) is the best way of transporting hydrogen in terms of volumetric energy density. These benefits translate into a significant reduction in hydrogen transportation and refueling station operations expenses. However, the phase transformation from liquid to gaseous hydrogen is accompanied by a considerable volume change, making long-term storage or transportation problematic. Any heat leakage of the LH2 vessel will result in boil-off and a strong pressure increase, which finally has to be released. These boil-off losses are a severe drawback for continental (long-distance) transportation through truck tube trailers having evaporative losses of about 3-15 % per day depending on the volume. Herein, low-temperature hydrogen storage by cryo-adsorption using crystalline porous adsorbents is proposed as an alternative to reduce boil-off losses and enhance dormancy during long continental transportation. The volumetric H2 uptake in metal-organic frameworks (MOFs) at 20 K can be comparable to the LH2 due to the stronger van der Waals adsorbate-adsorbent interaction than between adsorbate-adsorbate, leading to a higher H2 density inside the pores. As a result, the higher H2 density sufficiently compensates for the skeleton volume of the adsorbent, resulting in a volumetric storage capacity comparable to that of LH2 tanks (~ 96 %). Depending on the textural properties of MOFs, H2 desorption can start from 45 K, resulting in an extended dormancy time of the tank system. In addition, the observation of hindered rotational transition (J : 0→1) signal in neutron scattering analysis indicates that the H2 molecules are firmly attached and highly immobile on the adsorption sites. The hindered rotation by adsorption at 20 K on MOFs also suggests that the intermolecular separation is less than the bulk liquid phase. Considering those above, these results can be exploited to design MOFs and optimize cryo-adsorbent-based H2 transportation and storage

**Keywords**: MOF, Liquid hydrogen, Neutron scattering

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**Invited Speaker**
**MC-I-05**
**Chia-Her Lin**

# Rapid Desolvation-Triggered Structural Transformation of Aluminum Metal-Organic Frameworks

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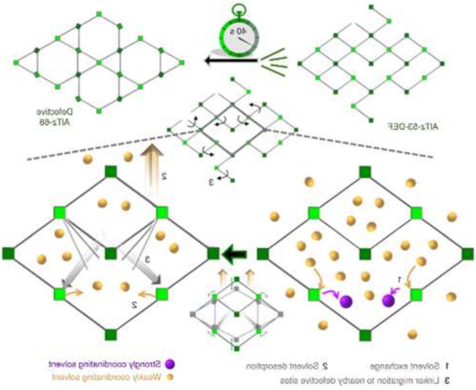
Topological transitions between significantly different phases typically require extreme conditions to collectively break chemical bonds and overcome the stress caused to the original structure by altering its correlated bond environment. In this work, we present a case system that can achieve rapid rearrangement of the whole lattice of a metal–organic framework (MOF) through a ‘domino’ alteration of the bond connectivity under mild conditions. The system transforms from a disordered amorphous MOF with low porosity to a highly porous and crystalline isomer within minutes upon activation (solvent exchange and desorption), resulting in a significant increase in surface area, from about 700 to 2,700 m2/g. Spectroscopic measurements show that this counter-intuitive lattice rearrangement involves a metastable intermediate that results from solvent removal on coordinately unsaturated metal sites.



**Keywords**: Aluminum; Metal-Organic Framework; Structural Transformation

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# Polymorphism of two-dimensional photoconductive coordination polymers with lead–sulfur bond

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Sulfur-coordinated coordination polymers (S-CPs) possess unique optoelectronic properties, making them an emerging class of materials.[1,2] The inorganic $(–M–S–)_n$ structures formed in the S-CPs significantly affect the bandgap energies and charge mobilities. Although the $(–M–S–)_n$ network structures in S-CPs may have a strong influence on the semiconductor nature of S-CPs, there have been no systematic studies on the correlation between network structures and electronic properties. In this study, we synthesized and characterized two polymorphs of a two-dimensional Pb(II) S-CP. Our findings revealed that the thermodynamic product (**KGF-26**) possesses $(–Pb–O–)_n$ chains only, whereas the kinetic product (**KGF-27**) has both one-dimensional $(–Pb–O–)_n$ chains and two-dimensional $(–Pb–S–)_n$ layers (Figure 1). The results of time-resolved microwave conductivity measurements and first-principles calculations confirmed that **KGF-27** exhibits higher photoconductivity than **KGF-26**, which establishes that the inorganic $(–Pb–S–)_n$ networks formed in S-CPs are crucial for achieving high photoconductivity. This was the first experimental demonstration of the impact of the $(–M–S–)_n$ networks in S-CPs on photoconductivity through the comparison of the crystal polymorphisms.

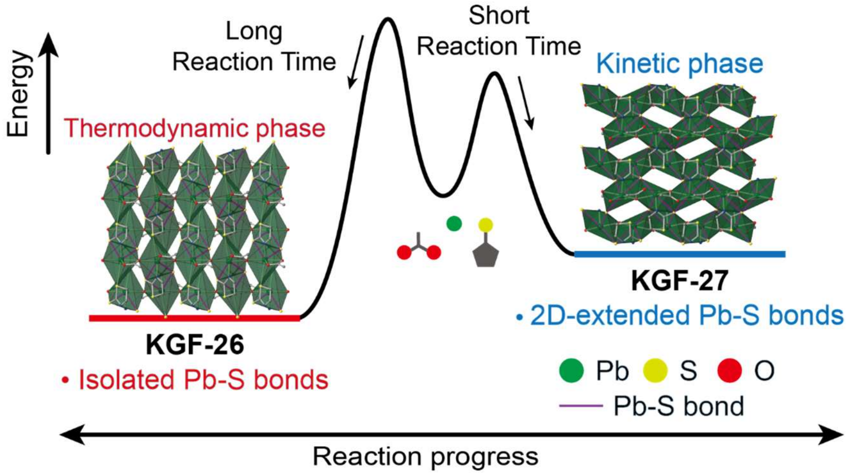

**Figure 1.** Synthesis and schematic structures of **KGF-26** and **KGF-27**.

**Keywords**: Coordination Polymer; Polymorph; Lead Thiolate Network; Secmiconductor

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**Invited Speaker**
**MC-I-07**
**Lauren Macreadie**

# Understanding the structural behaviour of negative thermal expansion in 3DL-MOFs

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Upon heating within a single phase temperature range, the vast majority of known materials experience an increase in their volume, i.e., positive thermal expansion (PTE).[1] This arises due to the anharmonic nature of chemical bonds, which leads to an increase in average interatomic and intermolecular distances with increasing temperature. In contrast to PTE, negative thermal expansion (NTE) results in a decrease in volume with increasing temperature. While NTE was originally seen in metal oxide materials, zeolites and metal cyanide materials, the recent observation of NTE in metal-organic framework (MOF) materials highlighted additional factors contributing to NTE in these structurally more complex materials.

This research describes a strategy to adjust NTE by using linkers that include additional rotational degrees of freedom in 3D-linker MOFs (3DL-MOFs).[2] Specifically, we employ cubane-1,4-dicarboxylate and bicyclo[1.1.1]pentate-1,3-dicarboxylate to form isoreticular MOFs (IRMOFs) CUB-5 and 3DL-MOF-1, respectively, where each linker has low torsional energy barriers. The core of these non-conjugated linkers is decoupled from the carboxylate functionalities, which frees the relative movement of these components. This results in enhanced NTE compared to the analogous, conjugated system. These results identify a new route to enhanced NTE behaviours in IRMOF materials, influenced by low energy molecular torsion of the linker.

**Keywords**: Metal-organic framework; negative thermal expansion; powder X-ray diffraction

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# Multi-center metal-organic frameworks for sensing applications

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Function-oriented coordination chemistry has been at the forefront of the intersection of chemistry and materials science. Focusing on the structure design and function regulation, we have carried out a series of studies recently, to systematically study the efficient synthesis, molecular and energy level structures of multi-component complexes, as well as the dynamic luminescence properties under external chemical stimuli. The main research achievements include: 1) The development of a series of novel multicenter luminescent complexes. By precise regulation of the composition and structure of several important systems, the detailed synthesis rules and luminescence properties of these complexes were studied; 2) Multicenter luminescent complexes were used as advanced sensing materials to realize efficient sensing of functional organic molecules such as biomarkers and environmental pollutants, and the sensing mechanism of these systems was studied.

**Keywords**: Multi-center; metal-organic frameworks; sensing; mechanism

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# Flexible porous coordination polymers for adsorptive separation

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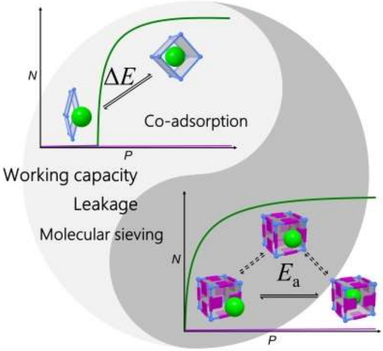
Porous coordination polymers (PCPs), also known as metal-organic frameworks (MOFs), are molecule-based crystalline adsorbents showing ordered, diversified, designable, tailorable, and switchable/flexible structures. Adsorptive separation is a straightforward application for utilization of these unique structural characteristics. Particularly, structural transformations can give rise to unique adsorption/separation mechanisms not available for conventional adsorbents that are generally considered as rigid. In recent years, we have paid particular attention on the role of flexibility for adsorptive separation, which is the main topic of this presentation.



**Keywords**: Molecular sieving; Selectivity; Co-adsorption; Leaking; Purity

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# Porous Metal-Organic Materials for Electrochemical $CO_2$ Reduction

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In recent years, electrocatalytic $CO_2$ reduction reaction (e$CO_2$RR) driven by renewable energy has attracted extensive attention due to its potential role in mitigating green-house effect and energy crisis. However, due to the extremely stable chemical bond in $CO_2$, competing hydrogen evolution reaction in the presence of water, as well as reduction of $CO_2$ involving a multi-electron stepwise process with several intermediates generated from different chemisorbed species, the design of highly efficient and selective catalysts for e$CO_2$RR, especially to produce hydrocarbons, is challenging.

With many useful characteristics, such as well-defined structures, high porosity, structural diversity, designable and modifiable frameworks/pore surface, metal-organic frameworks (MOFs) and relevant metal-organic materials can serve as a platform to provide precise structure-property relationship, and regulate the catalytic sites and chemical micro-environment for better performance.

In this talk, our recent investigations on the design and modification of MOFs and relevant metal-organic materials for e$CO_2$RR to give products of CO,[1] $CH_4$,[2] acetate,[3] and $C_{2+}$ hydrocarbons[4] will be presented, focusing on the regulation and understanding of the coordination and supramolecular interactions between the active site/microenvironment and $CO_2$/specific intermediate species for the catalytic performance.

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**Invited Speaker**
**MC-I-11**
**Sarah S. Park**

# Synthesis of conductive metal-organic framework thin films

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Developing conducting metal−organic frameworks (MOFs) provides an avenue for creating high surface area conductors with potential applications ranging from electrocatalysts and chemiresistive sensors to supercapacitors. Highly ordered and infinite charge transport pathways could be realized in conducting MOF platforms to yield high conductivity. However, it is challenging to engineer electrical conductivity in MOFs because these materials generally have flat bands determined by highly localized organic states and weak hybridization with the inorganic units. Based on using intermolecular π-stacking interactions as topology defining factors of MOFs, strategies for synthesizing and utilizing the conductive and microporous MOFs will be discussed.

In addition, the synthesis of a conductive two-dimensional MOF thin film by single-step all-vapor-phase chemical vapor deposition will be presented.[1] The large-area thin film of $Cu_3(C_6O_6)_2$ synthesized in this study has high crystallinity and an edge-on-orientation. Using e-beam lithography, microdevices based on $Cu_3(C_6O_6)_2$ thin film were fabricated, which showed an electrical conductivity of 92.95 S/cm. The synthesis of conductive MOF thin films through all-vapor-phase CVD could provide insights into the physical properties of these materials and pave the way for their practical applications.

**Keywords**: MOFs; thin films; electrical conductivity; chemical vapor deposition

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**Invited Speaker**
**MC-I-12**
**Ze Chang**

# Functional coordination polymers based on donor-acceptor systems

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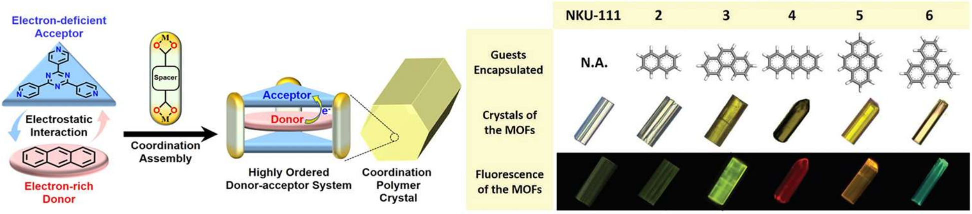
Organic donor-acceptor (D–A) systems based on charge transfer interactions have emerged as an attractive class of materials due to their potential applications in optoelectronic devices.[1] However, since the assembly of D and A species toward donor-acceptor system is complicated and usually affected by many factors, it is usually difficult to precisely predict and control the arrangement of these molecules in the long-range order for the attainment of the required performance of complexes. Therefore, the rational construction and modulation of highly ordered donor–acceptor systems could be a challenge due to the complicated self-assembly process of donor and acceptor species.

On the basis of our continuous investigation in coordination polymers (CPs), we have noticed that CP could be an ideal platform for the rational construction of crystalline donor–acceptor systems. The well-defined arrangement of species in CPs at the molecule level and their readily crystallization nature allow for the rational construction and tuning of donor–acceptor systems. Accordingly, the CPs could reveal highly tunable donor–acceptor properties such as charge transfer based emissions. In addition, the donor-acceptor interaction could be utilized for the structural modulation of CPs. Herein, we will introduce our very recent achievements in this field.[2]



**Keywords**: coordination polymer; donor-acceptor system; charge transfer; emission properties; crystal engineering

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# A MOFaxane: Threading ultralong polymers through metal–organic frameworks

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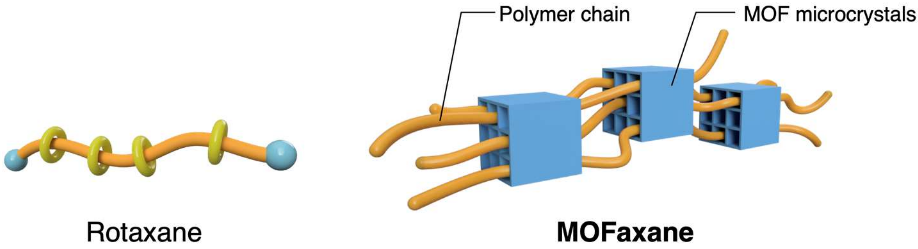
Polyrotaxane is a mechanically interlocked polymer consisting of many macrocyclic rotary elements threading on an axle polymer chain. Although such fascinating architecture of polyrotaxane has inspired chemists to synthesize many functional materials, the studies in this field have only used molecular-scale elements to realize its unique penetrating structure.[1–3]

Here we report synthesis of a new polyrotaxane analogue comprised of ultralong polymers that penetrate through microcrystals of metal-organic frameworks (MOFs), providing a mechanically interlocked organic-inorganic hybrids, MOFaxane.[4] In its bulk state, MOFaxane exhibits a polythreaded structure, where multiple polymer chains thread through a single MOF microcrystal, forming a topologically crosslinked structure. This networked structure is achieved by simply mixing polymers and MOFs, and it exhibits unique characteristics not found in conventional polyrotaxane materials, such as the suppression of unthreading reactions. We anticipate that MOFaxanes will encourage the development of organic-inorganic hybrid materials with interlocked architectures, which can be extended from the molecular scale to the macroscopic scale, as a new family of polyrotaxanes.



**Keywords**: MOF; rotaxane; interlock; penetration complex; polymer hybrid

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**Invited Speaker**
**MC-I-14**
**Kang Min Ok**

# Chiral coordination polymers with amplified photoluminescence and second-harmonic generation

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A series of homochiral coordination polymers (HCPs) was synthesized using solvothermal reactions. The newly synthesized HCPs, characterized by three-dimensional framework structures, crystallized in the extremely rare triclinic space group, *P*1. The structural arrangement was obtained through the self-assembly of metal cations, chiral ligands, and linkers featuring π-conjugated bipyridyl groups. The frameworks of the reported HCPs are composed of robust intermolecular interactions, fostered by hydrogen bonds and π–π stacking. The unique crystal structures, enriched with diverse functional groups within the ligands, confer upon the title compounds the ability to exhibit efficient photoluminescence (PL) over an extensive range within the visible spectrum. The PL emissions reveal significant brightness, and their colors can be tailored by adjusting the excitation wavelength. In addition, the title compounds display enhanced phase-matched second-harmonic generation (SHG) combined with high laser-induced damage thresholds. These attributes are essential prerequisites for their applications in high-power nonlinear optical (NLO) devices. Also, the title compounds demonstrate a distinctive difference in SHG response when the compounds are excited with right- and left-handed circularly polarized light. This phenomenon represents a unique instance of second-harmonic generation circular dichroism (SHG-CD) attributed to the chiral centers present in ligands within a noncentrosymmetric environment.

**Keywords**: Homochiral coordination polymer; Tunable photoluminescence; Second-harmonic generation

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**Invited Speaker**
**MC-I-15**
**Chun-Ting He**

# Molecule-based electrocatalysts and their molecular enhancement catalysis

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Designing efficiently catalytic materials is of great significance for realizing the conversion of energy small molecules and promoting the global carbon neutrality. However, painting a clear physicochemical picture of the catalytic process to achieve accurate synthesis of the catalyst structure remains challenging. Based on molecule-based materials such as structurally regulable metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), we have prepared several highly efficient electrocatalysts through the confinement effect of these porous materials, and developed the concept of molecular enhancement catalysis to remolding the reactivities of various confined active sites. In addition, by establishing series of new catalytic structure models, we have simulated and understood the electronic structure of catalysts, the intermediate sorption, the breaking and recombination of chemical bonds on the atomic level. Our work provides useful guidance for the understanding of catalytic behavior at the surface/interface of molecule-based materials and their derivatives and the rational design of new generation energy catalysts.

**Keywords**: molecule-based materials; molecular enhancement; catalysis; catalytic structure models

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**Invited Speaker**
**MC-I-16**
**Christopher Richardson**

# Advances in reactive extrusion printing metal-organic framework films

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We introduced reactive extrusion printing (REP) for the simultaneous crystallization-deposition of metal-organic framework (MOF) films.[1] This technique co-delivers separate inks of metal ion and ligand starting components directly-to-surface and on-location for rapid nucleation into MOF films at room temperature.

This presentation will focus on advances and improvements for films of $Cu_3btc_2$, also known as HKUST-1, brought about through precision mechanization. The impact of nozzle geometry on ink delivery and the identification of the factors underpinning REP from Design of Experiments (DoE) led to improvements in printing speed and film quality without compromise in particle properties.

An image of the 3D REDI printer from TRICEP[2] used in this work.

**Keywords**: metal-organic framework; reactive extrusion printing; HKUST-1; thin film

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**Invited Speaker**
**MC-I-17**
**Takashi Okubo**

# Luminescent Semiconducting Coordination Polymers with Copper(I) Halides and Application to OLEDs

Takashi Okubo[1,2*], Sota Nakano[1], Tomoki Nishiyama[1], Ami Ito[1], Naohiro Takahashi[1], Hirotaka Kitoh-Nishioka[1], Senku Tanaka[1,2], Masahiko Maekawa[2], Kunihisa Sugimoto[1], Takayoshi Kuroda-Sowa[1]

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Development of organic-inorganic hybrid materials such as coordination polymers or metal-organic frameworks (MOFs) is one of the most attractive subjects in the field of materials science because of their versatile chemical and physical properties due to the flexible frameworks formed by bridging organic ligands. Semiconducting coordination polymers or MOFs are of particular interest both in terms of fundamental knowledge and for applications in organic optoelectronic devices such as organic field-effect transistors (OFETs) and organic photovoltaic (OPV). From this viewpoint, we have investigated the semiconducting and luminescent properties of halide–bridged coordination polymers, showing unique luminescent properties with various mechanisms such as $^3$CC, phosphorescence, and TADF (Thermally Activated Delayed Fluorescence). We utilized a solvent annealing method to fabricate coordination polymer thin films; that is, coordination polymers were fabricated by exposing a layered film of copper(I) iodide and nitrogen-containing π-conjugated ligands deposited on a substrate to acetonitrile vapor. In addition, we fabricated the OLED devices with a coordination polymer $[CuI(phend)]_n$, and we obtained orange electroluminescence from the OLED devices. In this symposium, we will report on the crystal structures, luminescence and semiconductor properties, thin film formation, and application to OLED devices of Cu(I)-halide coordination polymers with nitrogen-containing π-conjugated ligands.

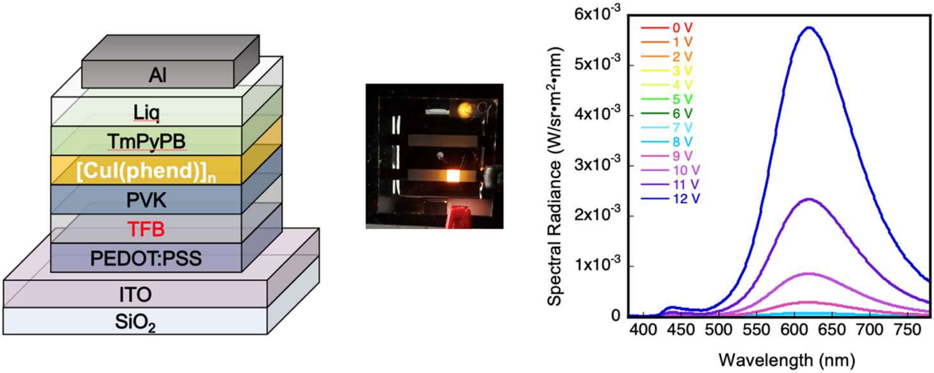

Fig. 1 A device structure and EL properties of an OLED including CP

**Keywords**: coordination polymer; semiconductor; photoluminescence; electroluminescence

**Invited Speaker**
**MC-I-18**
**Soumyajit Roy**

# On Soft-oxometalates (SOMs) and Sustainability

Soumyajit Roy[1],

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Over recent years, we have been exploring sustainable catalytic systems, particularly those involving charged metal oxides known as soft-oxometalates (SOMs). These studies have shed light on how time influences SOMs, leading to the development of technologies ranging from catalytic micro-chips to plastic conductors. Understanding the temporal dynamics of these systems is valuable, especially in catalyzing $CO_2$ reduction into C1 and C2 products such as formic acid, formaldehyde, methanol, ethanol, and ethanoic acid. In our presentation, we will explore a chalcogenide system centered around $MoS_2$, emphasizing the crucial role of sulfur vacancies in $CO_2$ conversion. We will illustrate how these vacancies contribute to the formation of $CO_2$ reduction products like Formic Acid and Methanol, and discuss the dynamic factors affecting product distribution in $CO_2$RR. The presentation will wrap up by outlining the future research directions our lab intends to pursue.

**Keywords**: Soft-oxometalate; CO2RR; Sustainable Sciences.

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# New Horizon for Digital Discovery of Metal-Organic Frameworks

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The demand for high-performance materials to address the ongoing global and energy challenges is significant. To expedite the discovery of innovative materials, we must adopt new approaches in design, synthesis, and characterization practices. In this context, data science is poised to play a crucial role in propelling materials discovery towards sustainable future. Among the notable advancements, Metal-Organic Frameworks (MOFs) stand out as a new class of promising transformative materials, targeting applications in carbon neutrality. Despite the fact that MOFs offer virtually limitless combinations of metal nodes and organic building blocks, optimizing these materials to attain peak performance is a sophisticated endeavor, challenging both computational and synthetic chemists.

In light of these serious challenges, there is a growing trend toward digitizing chemical insights.[1] The advanced digital archives could greatly accelerate the process of identifying groundbreaking future materials. In this presentation, we show detailed case studies, particularly emphasizing Zeolitic Imidazolate Frameworks(ZIFs), Zirconium-based MOFs and Metal-Organic Polyhedra (MOPs).[1-3] Leveraging comprehensive databases—actively utilizing both hypothetical and experimentally confirmed entries—we elucidate their pivotal role in identifying synthetic targets, and further align with specific application goals in carbon neutrality.

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**Invited Speaker**
**MC-I-20**
**Raffaele Ricco**

# Encapsulation and Release of Agrochemicals with Porous Materials

Raffaele Ricco,[1]* Jyotirmoy Pathak,[1] Ranjita Saikia,[1] Md Abdul Kaiyum,[1,2] Suriyan Cha-Um,[3]
Pranab Dutta,[4] and Tanujjal Bora[1]

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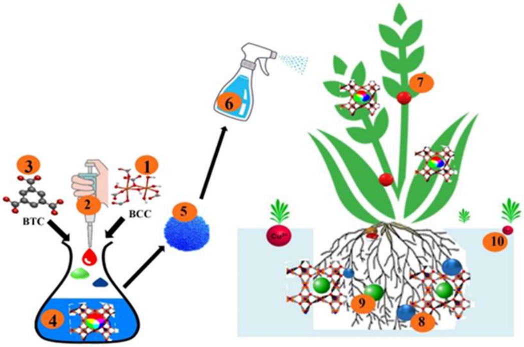
Agrochemicals (e.g., fertilizers, pesticides, growth hormones, etc.) are essential to meet the global need for food, both quantitatively and qualitatively, but their often unsafe, unselective, and repeated administration pose environmental, health, and economical threats.[1]

Researchers are looking into ways to increase agricultural production, simultaneously aiming at the reduction of pesticide wastes.[2] In this regard, delivery methods based on Metal-Organic Frameworks (MOFs) are recently gaining consideration in agricultural applications. Recent studies have already been performed on MOFs as delivery agents in the agricultural sector.[3] Moreover, the use of copper salts is already established (e.g., $CuSO_4$ as fungicide), and it is also an essential element for plants, therefore showing a dual nature of nutrient and pesticide.

This communication reports the fabrication of HKUST-1 via a convenient one-step procedure involving the utilization of basic copper carbonate (BCC), a natural component of malachite or azurite minerals,[4] with and without guest species like fertilizers (e.g., Urea), growth regulators (e.g., Gibberellic Acid), insecticides (e.g., Imidacloprid), and fungicides (e.g., Mancozeb, Propineb). The encapsulation capacities and long term release profile of the aforementioned guest@HKUST-1 systems under different simulated soil parameters of pH, temperature, and salinity, as well as exposure to environmental conditions, are also evaluated.



**Keywords**: Agrochemicals; Pesticides; Metal-Organic Frameworks; Precision agriculture; Long-term release

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**Invited Speaker**
**MC-I-21**
**Ken-ichi Otake**

# In situ X-ray Observation of Gate-type Sorption Process of Flexible Porous Coordination Polymers

Ken-ichi Otake[1*], Yifan Gu[1,2], Mohana Shivanna[1], Jia-jia Zheng[1,3], Susumu Kitagawa[1*]

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[2]*Tongji University*
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Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are crystalline framework materials constructed from the coordination bonds of metal ions/clusters and organic linkers. Since their discovery of porous functionalities, PCPs/MOFs have been extensively studied as promising adsorptive materials due to their designable structures. Among them, flexible PCPs/MOFs, also known as structurally responsive PCPs/MOFs, exhibit fascinating structural properties as they can adopt different interconvertible structures depending on external stimuli.[1,2] In particular, the characteristic known as "gate-opening behavior," which exhibits a rapid increase in adsorption at a certain pressure depending on the type of gas, is expected to enable efficient gas separation and recovery through pressure swing adsorption. However, many aspects of the detailed mechanism behind the gate-opening behavior of PCPs/MOFs remain unclear, making it challenging to control the behavior through structural design. Since gate-opening behavior arises from the balance between structural deformation energy and adsorption energy, understanding this mechanism requires essential structural analysis of the dry structure and gas adsorption state.[2,3]

We have systematically designed and developed a variety of new flexible PCP/MOF materials by systematically varying pore sizes and chemical properties. Our efforts have focused on exploiting their structural responsiveness for functional expansion and conducting detailed mechanistic investigations into such dynamic behaviors. For example, we have achieved successful development of flexible PCP/MOF materials exhibiting unusual adsorption behaviors, such as those showing different adsorption characteristics under varying activation conditions [4]. Additionally, we have developed interpenetrated PCP/MOF materials [5] that exhibit exclusive adsorption behaviors, separating $CO_2$ from a mixture of similar gas molecules, and that show crossover-type sorption behaviors [6].

We have conducted detailed investigations into the origins of the unique functionalities of these flexible PCP/MOF materials. To elucidate the structural changes occurring before and after gas adsorption, as well as during intermediate states, we have utilized in situ and operando X-ray diffraction measurements at SPring-8's BL02B1 (single crystal samples), BL02B2 (powder samples), and BL19B2 (thin film samples). In this presentation, we introduce a series of our research findings related to the structural and mechanistic insights gained through the in situ observations of the dynamic behavior of these flexible PCP/MOF materials.

**Keywords**: Metal–organic framework; Porous coordination polymer; structural flexibility; crystal structure; separation

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# Lanthanide molecular materials towards luminescent and magnetic application

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Lanthanide molecular materials have plenty of applications in the fields of luminescence and magnetism due to their unique features of the f-electron layer.[1] We have synthesized a series of lanthanide molecular materials, the studies of luminescent properties reveal that these molecular materials can be used as luminescent sensors and play an important role in chemical and biological analysis as well as environmental monitoring[2]. Furthermore, we also synthesized a series of Dy-based single molecular magnets (SMMs) that exhibit SMM behavior and ferroelectric properties[3]. And the magnetodielectric effect has also been observed[4]. Therefore, these molecular materials are excellent candidates in the fields of high-density information storage and quantum computing.

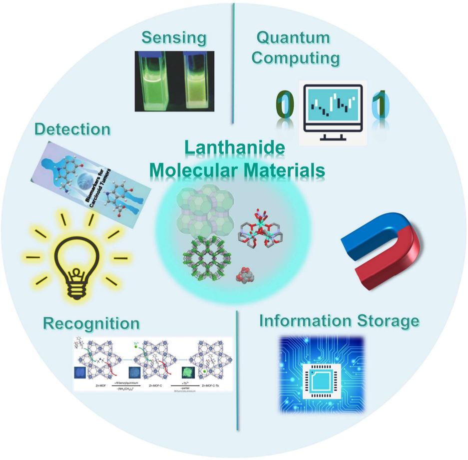

Figure 1 Schematic diagram of the application of lanthanide molecular materials for luminescence and magnetism.

**Keywords**: lanthanide; molecular materials, luminescence; magnetism

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**Invited Speaker**
**MC-I-23**
**Teppei Yamada**

# Temperature coefficient of the redox potential of MOF electrodes toward MOF TREC system

Teppei Yamada[1]*, Chihoko Fukakusa[1], Yuta Takahashi, Hongyao Zhou[1]

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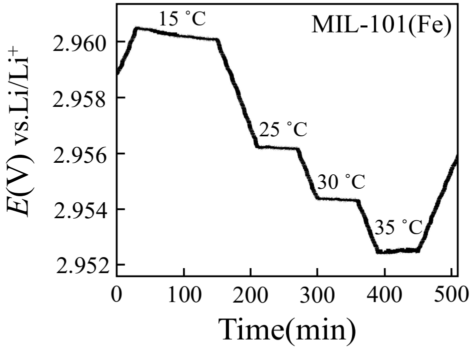
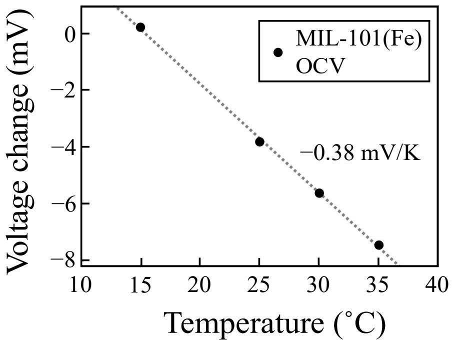
Recovery of waste heat is an essential technology for the effective usage of energy. Thermally regenerative electrochemical cycle (TREC) has attracted much attention recently due to its high thermoelectric conversion efficiency. TREC system is based on the rechargeable battery.

It generates electrochemical energy by charging the rechargeable cell at $T_1$ before discharging it to a different temperature, $T_2$. The difference in the temperature dependency of the electrochemical potentials of the cathode and anode gives the difference in voltage between charging and discharging. As a result, electrochemical energy was obtained during the cycle. The conversion efficiency of the TREC system can be extremely high because it does not have a temperature gradient during the charging and discharging processes, and heat leakage is negligible. The ratio between the obtained energy and the amount of heat supplied determines the thermoelectric conversion efficiency of the TREC system. For the high thermoelectric conversion efficiency of TREC, a pair of electrode materials with low heat capacity and high charge/discharge capacity is desired. In addition, the difference in the temperature coefficient α between the cathode and anode is desired for the high voltage with a small temperature change.

Here, we report the temperature coefficients of various MOFs and PBA in organic electrolytes, including MIL-100(Fe) and MIL-101(Fe), and discuss the origin of the temperature coefficient.





**Keywords**: thermoelectric conversion; MOF; lithium ion battery; TREC; MIL-101(Fe)

# NIIC-20 family MOFs for hydrocarbon adsorption

Anna Lysova*, Denis Samsonenko, Konstantin Kovalenko, Danil Dybtsev, Vladimir Fedin

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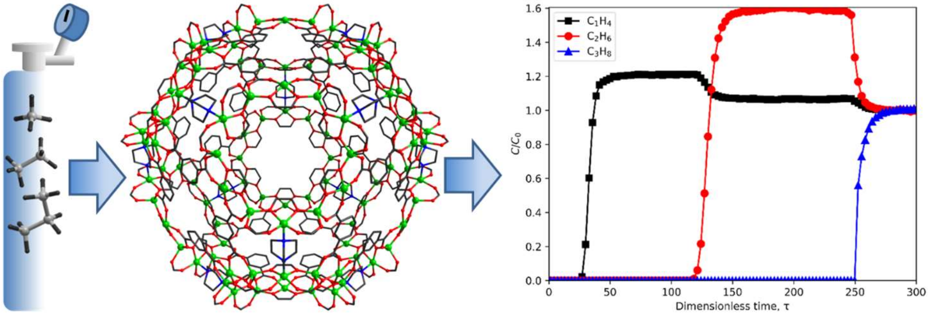
A series of new mesoporous MOFs based on the $Zn_{12}$ carboxylate wheels demonstrate excellent performance in adsorption and separation of various hydrocarbons. Firstly, the compounds demonstrate excellent IAST adsorption selectivities towards ethane in comparison to ethylene and acetylene (up to 15.4 and 10.9 at 298 K and 1 bar for the equimolar gas mixture, correspondingly [1]), which is a rare phenomenon since adsorption of unsaturated hydrocarbons on porous adsorbents is usually preferable. The same trend is observed for adsorption of propane and propylene (IAST adsorption selectivity factors are up to 3.9 at 298 K for the equimolar gas mixture at reduced pressure). Secondly, the compounds demonstrate excellent selectivity towards propylene in comparison to ethylene (with IAST adsorption selectivity factors up to 19.7 at 298 K for the equimolar gas mixture at reduced pressure), which is important for the industrial methanol-to-olefine-process. Thirdly, the compounds demonstrate excellent separation ability towards heavier saturated hydrocarbons ($C_3H_8$ *vs* $C_2H_6$, $C_3H_8$ *vs* $CH_4$ and $C_2H_6$ *vs* $CH_4$), which is confirmed by reproducible breakthrough experiments for binary and triple gas mixtures with the composition close to that of natural, shale and associated petroleum gas [2].

The work was supported by the Russian Science Foundation (project № 23-13-00310).



**Keywords**: metal-organic frameworks; hydrocarbon adsorption

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# Magnetic-Responsive Release of Nitric Oxide from a MOF-derived $Fe_3O_4$@PLGA Microsphere for the Treatment of Bacteria-Infected Cutaneous Wound

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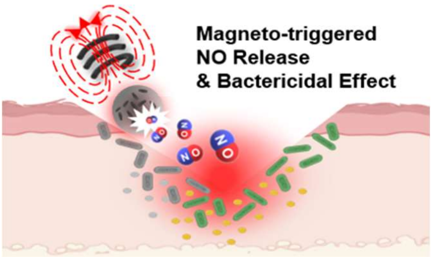
Nitric oxide (NO) is an essential endogenous signaling molecule regulating multifaceted physiological functions in the (cardio)vascular, and immune systems. Due to the short half-life of NO, translational application of NO as a novel therapeutic approach, however, awaits a strategy for spatiotemporal control on the delivery of NO. Inspired by the magnetic hyperthermia and magneto-triggered drug release featured by $Fe_3O_4$ conjugates, in this study, we aim to develop a magnetic-responsive NO-release material (MagNORM) featuring dual NO-release phases, namely burst and steady release, for the treatment of bacteria-infected cutaneous wound. After conjugation of NO-delivery [Fe(□-S-thioglycerol)(NO)$_2$]$_2$ with a metal-organic framework (MOF)-derived $Fe_3O_4$@C, encapsulation of obtained conjugates within PLGA microsphere completes the assembly of MagNORM. Through continuous/no application of alternating magnetic field (AMF) to MagNORM, moreover, burst/slow release of NO from MagNORM demonstrates AMF for temporal control on the delivery of NO. Under continuous application of AMF, burst release of NO from MagNORM triggers an effective anti-bacterial activity against both *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). In addition to the magneto-triggered bactericidal effect of MagNORM against *E. coli*-infected cutaneous wound in mice, steady release of NO without AMF promotes the subsequent collagen formation and wound healing in mice.



**Keywords**: nitric oxide, metal-organic framework, magnetic-responsive drug delivery, magnetic hyperthermia, anti-bacterial

# Superprotonic Conductivity of Water-coordinated Metal Hydrogen-bonded Organic Framework Films

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Hydrogen-bonded organic frameworks (HOFs) are promising due to their distinct hydrogen bond networks that facilitate proton transfer. While they provide design versatility and support solution-based processes, their stability remains a concern. Introducing metals into these structures results in metal hydrogen-bonded organic frameworks (MHOFs) with enhanced functionality and stability. Yet, their common pelletized forms pose challenges in scalability and robustness, and they also require high temperature and humidity to demonstrate proton conductivity. This underscores the demand for MHOF films that operate under milder conditions. In this study, a unique MHOF film is fabricated using a solution-based spin coating technique. This material shows excellent thermal and vacuum stability. The inclusion of a water ligand in its composition enables superprotonic conductivity under mild conditions. The material's expansive hydrogen bond network and coordination bonds collectively contribute to its stability and proton conductivity.

**Keywords**: Hydrogen-bonded organic frameworks; Solution process; Superprotonic conductivity; Hydrogen bond; Film

# Charge order in a naphthalenediimide-based porous molecular conductor

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Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have recently emerged as a class of electron-conductive porous materials which are promising for practical applications such as the active materials for batteries, supercapacitors and sensors.[1] Several strategies have thus been established to engender conductivity in framework materials in the past decade. Most works has been based on MOFs with through-bond conduction pathway, whereas their electronic states have not been well studied because of the difficulty in growing high quality crystals. Thus, the exploration of rational design and novel synthetic methods of highly crystalline conducting MOFs are necessary to understand their intricate nature. We previously proposed the concept of porous molecular conductor (PMC) as the fusion of MOFs and molecular conductors, utilizing the redox-active naphthalenediimide (NDI)-based ligand.[2] This PMC forms π-stacking columns with uniform distance. However, its semiconducting nature suggests the existence of charge-ordering state. In this work, we obtained new PMCs (**PMC-3**) containing crystallographically independent two NDI moieties and two different π-stacking distances. Employing numerous characterization techniques, we will discuss the charge-ordering state and the electronic properties of **PMC-3**.

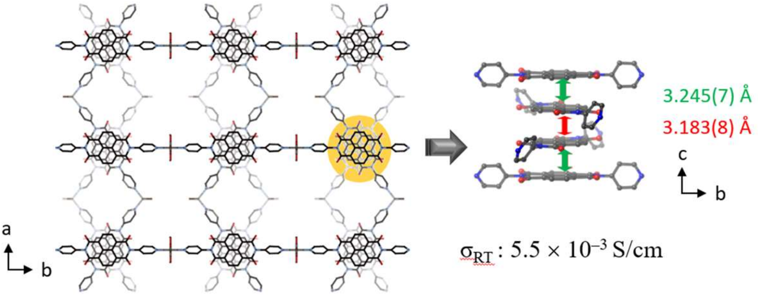

Figure 1. crystal structure of **PMC-3**

**Keywords**: MOFs; conductivity; charge ordering; spectroelectrochemistry; electrochemical synthesis

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# Highly photo-controllable guest release systems using 4-styrylpyridine-coordinated Werner clathrate

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Controlled release of guest molecules by external stimuli has been widely studied because of its possible applications in various fields such as remote-controlled materials, sensors, and drug deliveries.[1] Many types of external stimuli such as heat, light, pH, and pressure have been used to release guest molecules. Among them, a light stimulus has great advantages due to its high controllability. In this study, we investigated the photo-controlled release of guests using Werner clathrates as hosts. The 4-styrylpyridine (4-spy) coordinated Werner clathrate $[Zn(CF_3SO_3)_2(4\text{-}spy)_4]\cdot 2THF$ showed photo-responsive dynamic structural changes caused by the photodimerization of C=C bonds of 4-spy under UV light irradiation (Figure 1). This transformation of the host involved the release of guest THF molecules included in the cavity, and the release amount was highly controllable by changing light intensity. Furthermore, we also investigated the control of the guest release by repeatedly turning on/off UV light and found that the guest THF molecules are only released under UV light irradiation. Werner clathrates with different guest molecules will be discussed in the presentation.

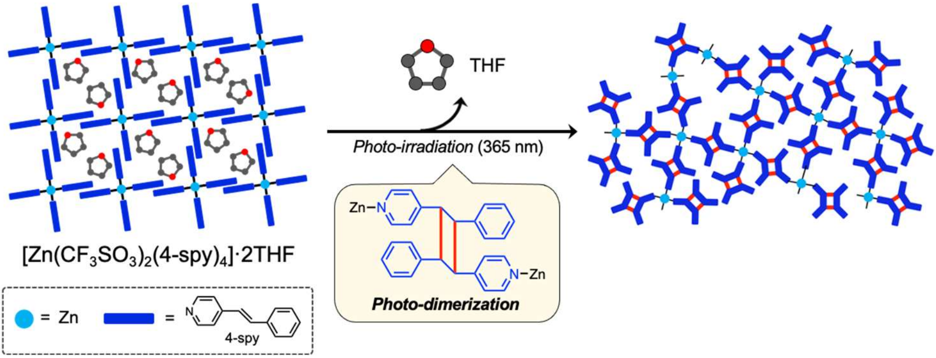

Figure 1. Schematic illustration of the photo-controlled release of THF guests from $[Zn(CF_3SO_3)_2(4\text{-}spy)_4]$.

**Keywords**: Werner clathrate, Guest release, Photodimerization, Porous material

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2.

# Ion-Exchangeable Metal–Organic Frameworks for Selective Ammonium Recovery

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The accumulation of nitrogen compounds in the soil and ocean has become a global issue.[1] The recovery and reuse of ammonium cation from wastewater is highly required. We focused on the uniform nano-porous structure of metal-organic frameworks (MOFs). Although ammonia gas adsorption of MOFs has been reported, reversible ammonium capture of MOFs has not been reported yet due to their instability toward aqueous ammonia.

In this work, we report a novel MOF robustness and strong acidity, Zr-mellitate, synthesized from zirconium and mellitic acid with the presence of aqueous ammonium cation. Single-crystal XRD analysis revealed that the MOF has a lattice length approximately twice that of UiO-66 and has periodic defects (Fig. 1a). A couple of carboxy groups of each mellitate ligand bridges zirconium clusters and the other four carboxy groups remain uncoordinating. The pristine MOF contains one equivalent of ammonium cation per linker, that was liberated by the acid treatment. The reversible ion exchange was executed for ammonium, proton, sodium, and potassium cations. The ion exchange capacity of the MOF was maintained after a repeated ion exchange experiment. Furthermore, the protonated MOF selectively accumulates ammonium from the equimolar mixture of aqueous ammonium and sodium cations (Fig. 1b).

**Keywords**: ion-exchange; ammonium cation; UiO-66; nitrogen cycle

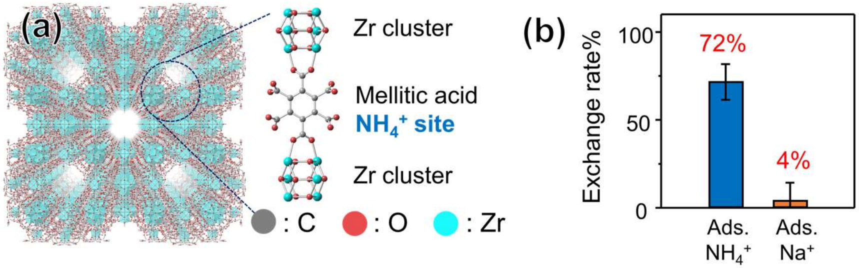

Figure 1. (a) Crystal structure and (b) $NH_4^+$/$Na^+$ adsorption selectivity of protonated MOF

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# Photocatalysis of Coordination Polymer Glass Membranes Involving Metalloporphyrins for $CO_2$ Reduction

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Immobilization of metal complex photocatalysts in solid substrates is an essential technique for catalyst separation and stabilization, but immobilized photocatalysts exhibit moderate activity due to an unexpected light scattering by the substrates. Such a problem can be solved by immobilizing the photocatalysts in transparent and grain boundary-free membrane substrates.

We herein focused on transparent, grain-boundary free coordination polymer (CP) glasses, which have high formability compared with conventional crystalline CPs. Iron(III) 5,10,15,20-tetraphenyl-21H,23H-porphine chloride (Fe(TPP)Cl) was added to $[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$ (**ZnPIm**, Im = imidazolate, Fig. 1A) liquid followed by cooling to room temperature (Fe/g-**ZnPIm**).[1] High formability of Fe/g-**ZnPIm** resulted in fabrication of membranes with 3-9 μm thicknesses (Fig. 1B). The Fe/g-**ZnPIm** membranes exhibited photocatalytic activity for carbon dioxide ($CO_2$) reduction to carbon monoxide (CO) in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole (BIH) as a sacrificial electron donor. The activity in proportional to membrane thickness and $CO_2$ permeability test of the membranes indicated that Fe(TPP)Cl immobilized in the subsurface of membraes contributed to the photocatalytic reaction (Fig. 1C).

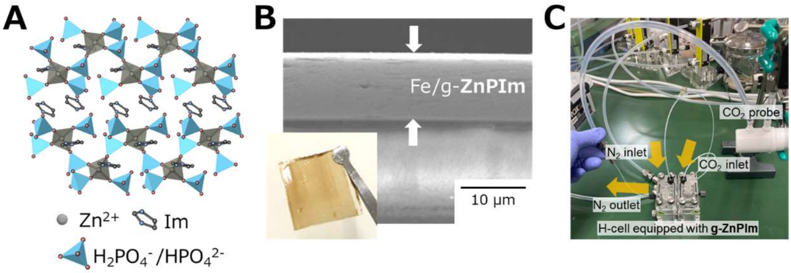

Fig.1. (A) Crystal structure of **ZnPIm**.[2] (B) SEM image of Fe/g-**ZnPIm** with the thickness of 9 μm. (C) Set up of $CO_2$ permeation experiment of g-**ZnPIm**.

**Keywords**: metal-organic framework; photocatalysis; carbon dioxide; artificial photosynthesis

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**Oral Presentation**
**MC-O-08**
**Bhavesh Parmar**

# Tuning of Singlet Fission Derived Quintet Generation in Acene-based Hetero-linker MOFs

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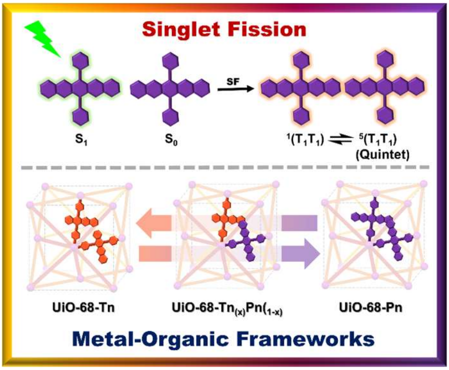
Singlet Fission (SF) process is the splitting of one singlet-exciton into two triplet-excitons. Acene (Tetracene/Pentacene) molecules are well-known to undergo exciton fission. The chromophore pair upon excitation undergoes SF to generate two independent triplet excitons with half energy of one singlet. These triplet-excitons generate exciton pairs, and their net-spin is classified as singlet, triplet or quintet.[1] Particularly quintet $^5(T_1T_1)$ is more interesting as spin qubits due to its higher spin nature. But in practical applications, tuning the quintet and understanding its dynamics are challenging. In literature, acene-based organic dimers are dominant and major studies involving high magnetic fields or cryogenic temperatures limit their practical applicability.[1] Our main goal is focused on tuning quintet generation in solid-state materials applicable at mild conditions for quantum and photonics applications.[1] Metal-organic frameworks (MOFs) are well-known for their inherent tailorability, ordered-structure, porosity, and guest-accessibility. The acene-based chromophores can be introduced as linkers in MOFs to generate well-ordered nets and dynamics control of chromophores.[2] We have designed tetracene/pentacene-based linkers and successfully utilized them to engineer UiO-68-type MOFs. The homo/hetero-linker MOFs have been synthesized, and their photophysical properties have been accessed by different spectroscopic techniques. The SF-derived quintet generation has been analyzed/monitored by Tr-EPR spectroscopy.



**Keywords**: Metal-Organic Frameworks; Singlet Fission; Quintet; Acene; Tr-ESR

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3.

# Diastereoselective [2+2]-photodimerization of 2-cyclopenten-1-one within a metal-organic framework

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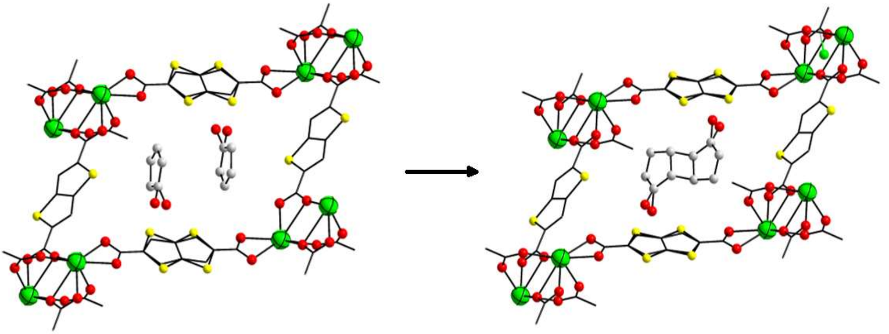
A selective dimerization of 2-cyclopenten-1-one, which proceeds through the [2+2]-cycloaddition mechanism, was successfully carried out under soft UV irradiation with a reagent trapped within the pores of the metal-organic framework. Such approach allowed achieving very high (up to 98%) selectivity of the formation of its head-to-tail *anti*- dimer among other possible diastereomeric dimers, while similar selectivity rarely exceeds 60% using other known approaches [1]. The used metal-organic framework [$Eu_2(DMF)_4(ttdc)_3$] (DMF = N,N-dimethylformamide; $H_2$ttdc – *trans*-thienothiophene-2,5-dicarboxylic acid), containing regular nano-sized pores, acted as a matrix - a “reaction vessel” - which adsorbed the reagent molecules. A highly ordered arrangement of 2-cyclopenten-1-one molecules in the MOF pores, provided by host-guest hydrogen bonds, predetermines the geometry of its dimer at the molecular level and subsequently extremely high selectivity of its formation, confirmed by $^1$H NMR spectroscopy. The stability and geometric rigidity of the porous coordination network structure excludes the formation of other possible product isomers in the reaction. A crystal structure for the inclusion compound of target product with MOF was determined by single crystal X-ray diffraction analysis, providing an unambiguous confirmation for the reaction passing distinctively within the voids of the coordination framework and additional insights into the reaction selectivity in terms of host-guest interactions. Similar results were obtained for 2-methyl-2-cyclopenten-1one, while for 3-methylated derivative its diastereoselective [2+2] dimerization was found to be impeded due to the different guest orientation in the MOF pores, not providing a specific product-like pre-organization of the reagent molecules [2].



**Keywords**: MOF; photochemistry; selectivity; single crystal XRD; host-guest interactions

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# Non-Ambient Single Crystal X-ray Diffraction Beamline at Taiwan Photon Source

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A dedicated small-molecule single-crystal X-ray diffraction beamline is under construction at TPS (Taiwan Photon Source). The Cryogenic Tapered Undulator CUT18 will be used as Xray source to generate high brilliance X-ray. The energy of this beam line is tunable within 8-35 keV. Monochromatic and pink beam modes both will be available at this beamline. The monochromatic beam mode will be selected by a “Double Crystal Monochromator” (DCM) and the pink beam mode will be achieved by Pd/B4C and W/Si (DMM) multilayers (with bandwidth ~ 3-5 % relatively). A Kirkpatrick-Baez (KB) mirror will be used to focus the beam size down to few microns in diameter at sample position. This beamline is designed for advanced and non-ambient crystallographic requests, techniques used at this beamline will include (1) quick data collection for Micro-crystal and large porous structure determination (2) Extreme condition that included low temperature high pressure structural studies (3) Photo-induced excited state structural studies (4) Time-resolved dynamic structural studies with ~50 ps time resolution via Laue diffraction technique. (5) Ultra-high resolution charge density analysis (6) Resonance diffraction. These techniques of this beamline will be able to cover physics, chemistry, and material science

**Keywords**: Electron density ; Single crystal diffraction ; Time-resolved ; High pressure; Non-ambient

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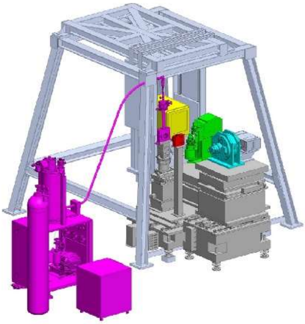

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**Oral Presentation**
**MC-O-11**
**Ruey-An Doong**

# Ultra-sensitive detection of levofloxacin with rare earth elements functionalized MOF as the fluorescent probe

Pooja Somnath Dayma[2], Prashanth Venkatesan[1], Deblina Roy[1], Parthivi Aloni[1], and Ruey-An Doong*[1]

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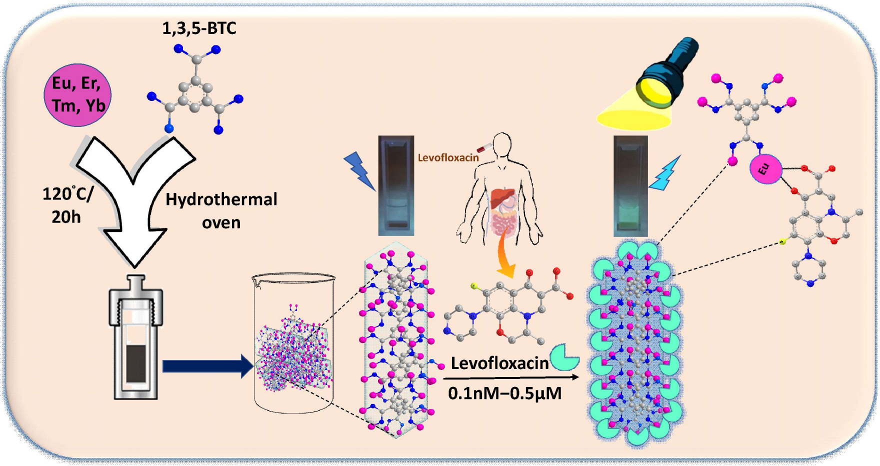
Herein, the 2-dimensional rare earth element-based metal-organic frameworks (MOFs) have been fabricated at 120 °C for the ultra-sensitive and selective detection of levofloxacin (LEV) in phosphate-buffered saline (PBS) and human serum. The nanorod-shaped lanthanide-MOFs including europium (Eu)-, erbium (Er)-, thulium (Tm)-, and ytterbium (Yb)-MOF with an average width of 180–200 nm and length of 0.8 – 1 □m are successfully synthesized by a simple one-step hydrothermal method. The addition of LEV produces a strong fluorescence intensity at 360 nm in Eu-MOF in comparison with other Ln-MOFs and can achieve the maximum intensity within 1 min. The β-diketone structure in LEV can coordinate with Eu ions, resulting in the ultra-sensitive and rapid detection of LEV. The Eu-MOF exhibits an excellent linear response in the concentration range of 100 pM–0.5 μM with the limits of detection of 40 pM in PBS and 0.11 nM in human serum. Moreover, the promising platform is successfully applied to the detection of LEV in water and human serum samples and shows excellent selectivity over 47 interferences including different antibiotics, metals, and biomolecules. Results in this study clearly corroborate that $Eu^{3+}$ plays a vital role in the whole detection system, and rare-earth element-based MOFs can lead the way to develop high-performance and efficient detection probes for LEV and other antibiotics.



**Keywords**: Rare earth element; metal-organic frameworks (MOFs); turn-on sensing; levofloxacin; fluorescent probe.

# Oriented film of MIL-53(Al) via epitaxial growth on γ-AlOOH toward soft actuator

Kenji Okada[1*], Risa Mashita[1], Arisa Fukatsu[1], Masahide Takahashi[1*]

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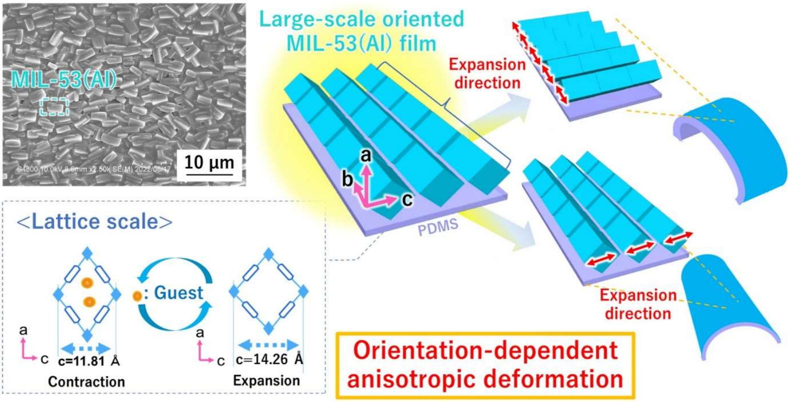
Metal organic frameworks (MOFs) have recently demonstrated high potential for use in high-value technology areas (e.g. thin-film devices, soft actuators), due to their 'designable' chemical/physical properties from the ordered micropores and framework. Towards the use of MOFs for such applications, we have reported the fabrication of three-dimensionally oriented Cu-based MOF thin films by epitaxial growth on $Cu(OH)_2$ as a substrate[1,2]. The three-dimensionally oriented MOF film showed unique in-plane anisotropic electrical/optical properties [3-5]. In the present study, we report on the fabrication of oriented film of Al-based MOF, Al(OH)(bdc) (bdc: 1,4-benzenedicarboxylate), so-called MIL-53(Al), on γ-AlOOH by the epitaxial growth approach. MIL-53(Al) is known to be gas-, solvent-responsive MOFs where the framework structure exhibits anisotropic deformation along the direction perpendicular to the 1D nanopore by absorbing guest molecules. The MIL-53(Al) oriented films on polydimethylsiloxane (PDMS) substrates showed solvent- and gas-dependent deformation. And more importantly, the anisotropic structural change in a lattice of MIL-53(Al) upon guest molecules absorption/desorption resulted in the anisotropic deformation of the film. Therefore, soft actuators with crystal orientation-dependent reversible deformation were achieved. The present responsive film with controllable deformation direction and solvent- and gas-stimuli responsiveness is expected for next-generation soft robotics.



**Keywords**: Oriented film; epitaxial growth; Deformation; Soft actuator; anisotropy

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**Oral Presentation**
**MC-O-13**
**Chantamalinee Chantarangkul**

# Catalytic performance of CuNPs-incorporated MIL-100(Fe) using *Cryptolepis Buchanani* Roem. & Schult extract

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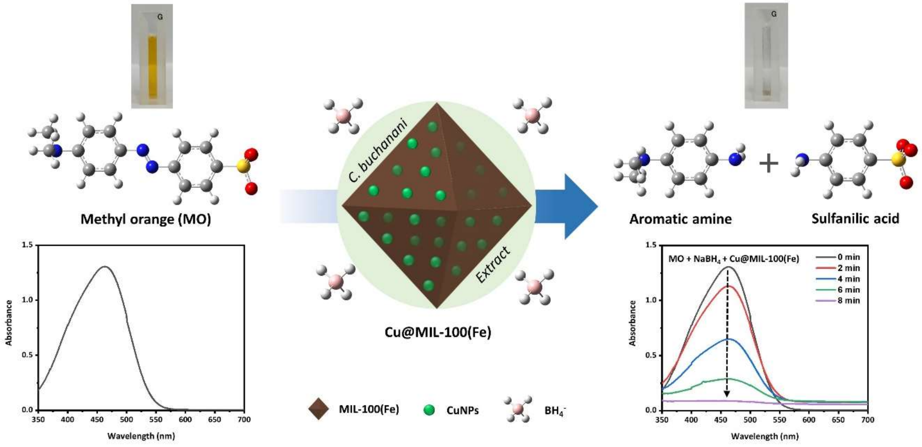
Environmental pollution demands innovative and efficient solutions. Leveraging nanotechnology, this study explores the potential of a new catalyst created by incorporating copper nanoparticles (CuNPs) into the metal-organic framework MIL-100(Fe) using *Cryptolepis buchanani* Roem. & Schult extract. The resultant nanocomposite, Cu@MIL-100(Fe), was characterized using transmission electron microscopy (TEM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) analysis. This characterization confirmed the integration of CuNPs, averaging 4.28 ± 0.87 nm in size, uniformly distributed within the MIL-100(Fe) structure. The composite demonstrated notable catalytic activity, degrading methyl orange dye with a pseudo-first-order rate constant between 0.4237 and 0.5160 $\text{min}^{-1}$, achieving total degradation within 8 minutes. This sustainable, non-toxic, and cost-effective synthesis of CuNPs shows promising potential for water purification.



**Keywords**: Copper nanoparticles, *Cryptolepis buchanani* Roem. & Schult, Iron-based metal-organic frameworks, Catalytic activity

# Multiresponsive highly emissive MOFs for sensing of organic and inorganic pollutants

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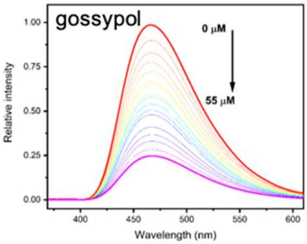
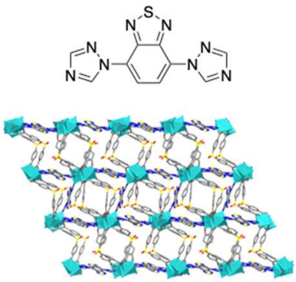
Metal-organic frameworks (MOFs) are porous materials with promising gas adsorption, catalytic and sensing properties. Luminescent MOFs are especially perspective for sensing applications since the quenching or enhancement for the emission may be accurately measured and in most cases detected even by the naked eye allowing the development of portable test kits. The focus of our work is the introduction of highly emissive ligands into the structure of MOFs to achieve high quantum yields and selective luminescent response towards organic and inorganic pollutants.

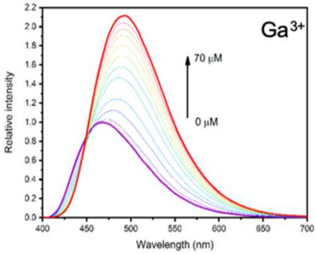
Thus, MOF $\{[Cd_8(tr_2btd)_5(dcdps)_8(H_2O)(EtOH)]\cdot 5DMF\}_n$ ($H_2dcdps$ = di(p-carboxyphenyl)sulphone, $tr_2btd$ = 4,7-di(1,2,4-triazol-1-yl)-2,1,3-benzothiadiazole) demonstrated a high photoluminescence quantum yield of 70 % and a sensitive emission "turn-on" response towards $Ga^{3+}$ cations (LOD 1.1 μM) and a "turn-off" response to the cottonseed phytotoxicant gossypol (LOD 0.17 μM).

Water-stable and high-temperature resistant zirconium-organic framework $[Zr_6O_4(OH)_4(bpbodc)_6]_n$ ($H_2bpbodc$ = 4,7-bis(4-carboxypyrazol-1-yl)-2,1,3-benzoxadiazole) featured a luminescence "turn-on" response to aliphatic amines making it promising for the fabrication of materials for detection of spoiled seafood.

This work was supported by the Russian Science Foundation, grant No. 23-43-00017 "Novel metal-organic frameworks with high luminescence for the detection of biologically active substances and environmental pollutants", https://rscf.ru/project/23-43-00017/.







**Keywords**: 2,1,3-benzoxadiazole; 2,1,3-benzothiadiazole; metal-organic frameworks; luminescence; sensing

# Stimuli-responsive frameworks based on luminescent Cr(III) cyanido metal complexes

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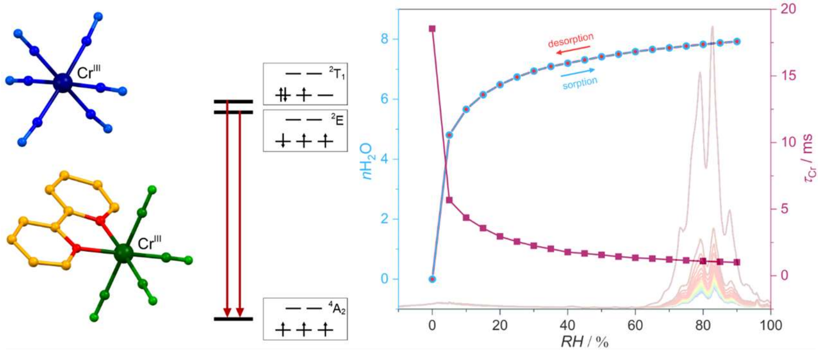
Coordination frameworks based on d- and f-block metal ions are recognized as an infinite source of functional materials incorporating various physical features, including magnetism, ferroelectricity, luminescence, non-linear optical (NLO) properties, and responsivity toward sorption of solvent vapors or gases.[1–4] The latter can be observed for three-dimensional metal-organic frameworks (MOFs) showing high porosity, as well as for coordination systems with reduced coordination connectivity.[5] Other external stimuli, such as temperature, pressure, or light irradiation may also affect the initial properties of coordination systems, including luminescent properties manifested by the emission signal in the visible or near-infrared (NIR) range.[6] For such purposes, the intrinsic emissive properties of f-block metal ions or luminescence of organic ligands involved in the formation of the coordination skeleton are often applied. On the contrary, we tested the strategy involving the use of the spin-flip emissive Cr(III) cyanido complexes, such as hexacyanidochromate(III), $[Cr^{III}(CN)_6]^{3-}$, which generate a sharp emissive band in the edge of visible and NIR regions. Such an approach allows us to obtain bimetallic systems with s- and f-block metal centers, maintaining the original optical property of employed Cr(III) complexes. Moreover, the resulting materials show the signal tunable by the application of external stimuli, such as temperature or pressure, and especially, by the change of relative humidity, due to the high sorption capacity of the framework itself. Therefore, we would like to present our recent results on this topic, which may lead to a better understanding of how to control the emissive properties of spin-flip emitters and use them for the construction of advanced optical sensors.



**Keywords**: chromium; metal-organic frameworks; luminescence; sensors; thermometry

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**Flash Presentation**
**MC-F-01**
**Kotoha Kageyama**

# Phase transition behavior and $Li^+$-ion conductivity of $Li^+$-dinitrile metal–organic frameworks

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Lithium ions ($Li^+$) in dinitrile-based metal–organic frameworks (MOFs) have high mobility.[1,2,3] They are promising candidates as solid electrolytes for Li-ion batteries. In this study, five MOFs were synthesized from lithium bis(fluorosulfonyl)imide (LiFSI) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and succinonitrile (SN) and glutaronitrile (GN) as dinitrile ligands to discuss the relationship between crystal structures, phase transition, and $Li^+$ conductivity. $[Li(SN)_2](FSI)$ (**1**) has a three-dimensional crystal structure.[2] $[Li(GN)_2](FSI)$ (**2**), [Li(SN)(GN)](FSI) (**3**, Fig. 1a), $[Li(SN)_{1.5}(TFSI)]$ (**4**), and $[Li(SN)(GN)][(FSI)_{0.5}(TFSI)_{0.5}]$ (**5**) have two-dimensional (2D) crystal structures. The coordination geometry of $Li^+$ is tetrahedral in all MOFs. **3** was also obtained by mechanically mixing **1** and **2**. All MOF crystals melt below 100 °C confirmed by differential scanning calorimetry (DSC). **4** showed a glass transition at −42 °C. Alternating current (AC) impedance spectroscopies in solid and liquid states indicated that **5** have 10 times higher $Li^+$ conductivity than other MOFs in solid state (Fig. 1b), while **4** showed the lowest activation energy ($E_a$ = 30 kJ $mol^{-1}$) for the $Li^+$ conduction.

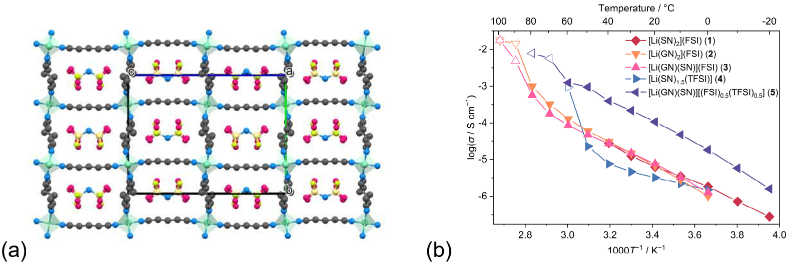

Fig. 1. (a) 2D crystal structure of [Li(SN)(GN)](FSI) (**3**). Li, S, F, O, C, and N atoms are represented as green, yellow, light green, red, grey, and blue, respectively. (b) Arrhenius plots of the ionic conductivity of MOFs obtained from AC impedance spectroscopies on the heating steps. Open markers indicate $\sigma$ above the melting points.

**Keywords**: lithium-ion conductivity; metal-organic framework; crystal structure; melt; glass

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Flash Presentation
MC-F-02
Pattara Siripanich

# $H_8$-BINOL-Based MOF for Enantioselective Fluorescent Sensors

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1,1'-Binaphthol, also known as BINOL, is a well-known fluorophore for its specific property of axial chirality. Consequently, BINOL is a suitable precursor for enantioselective luminescence sensors.[1] Recently, attention has been drawn to $H_8$-BINOL, a partially reduced form of BINOL, due to its potential for asymmetric catalysis.[2] The reactive catalytic reactivity is achieved through alkyl ring electron donation. Enantioselective fluorescence, however, remains largely unexplored with $H_8$-BINOL,[3, 4] particularly within extended supramolecular structures. Metal-Organic Frameworks (MOFs) are notably attractive due to their high porosity, chemical tunability, and stability. Furthermore, MOF-based fluorescent probes have demonstrated rapid responses and high sensitivity.[5, 6] A $H_8$-BINOL-based MOF was designed for use as a chiral fluorescent sensor in this work. Various organic functional groups were installed at different positions on $H_8$-BINOL before being combined with various metal ions with the aim of obtaining a MOF with optimal enantioselective fluorescent sensor properties.

**Keywords**: MOF; Metal-Organic Frameworks; Chiral; Fluorescence Sensors; $H_8$-BINOL

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# The potential of UiO-66(Zr) frameworks for the efficient removal of multiple heavy-metal complexes: performance evaluation and mechanistic insights

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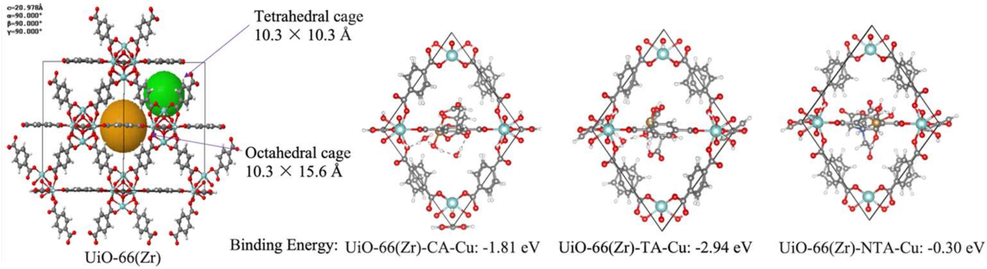
Wastewater from electroplating and other industries contains a large amount of low-concentration of heavy-metal complexes. They usually possess high stability, complicated species, and a concentration level that cannot meet the ever-increasing environmental discharge standards and pose a severe threat to human health. Metal-organic frameworks (MOFs) represented by UiO-66(Zr) have better purification performance of water pollutants than conventional adsorbents, owing to their extremely high surface areas, stable and tunable structures, and abundant active sites. In this work, the removal performance and mechanism of copper citrate (CA-Cu), copper tartrate (TA-Cu), and copper subazotriacetate (NTA-Cu) by UiO-66(Zr) is reported. The removal efficiency of three complexed heavy metals is stable in a wide pH range (4-10). Under the neutral condition, the adsorption capacities of three complexed heavy metals are 18.81, 103.31, and 24.87 mg·g-1, showing that MOFs can selectively purify heavy-metal complexes in low concentration. The results of DFT theoretical calculation, X-ray absorption spectrum, and nitrogen adsorption and desorption show that van der Waals forces, electrostatic interaction, and molecular size matching are the main adsorption mechanisms. This research provides a new idea for the development of highly efficient adsorption materials based on MOFs for the advanced treatment of heavy-metal complexes in wastewater.



**Keywords**: Metal-organic frameworks; UiO-66(Zr); heavy-metal complex; adsorption

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**Poster Presentation**
**MC-P-02**
**Javier Salazar**

# UiO-66(Zr) as drug delivery system for non-steroidal anti-inflammatory drugs

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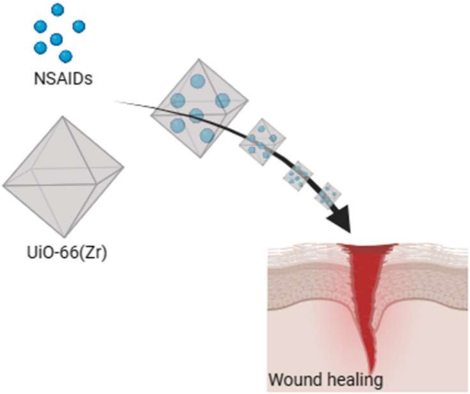
The toxicity for the human body of non-steroidal anti-inflammatory drugs (NSAIDs) overdoses is a consequence of their low water solubility, high doses, and facile accessibility to the population. New drug delivery systems (DDS) are necessary to overcome the bioavailability and toxicity related to NSAIDs. In this context, UiO-66(Zr) metal-organic framework (MOF) shows high porosity, stability, and load capacity, thus being a promising DDS. In this work, we used the biocompatible UiO-66(Zr) MOF to study the absorption and release conditions of ibuprofen, naproxen, and diclofenac using a theoretical and experimental approximation. DFT results showed that the MOF-drug interaction was due to an intermolecular hydrogen bond between protons of the groups in the defect sites, and a lone pair of oxygen carboxyl functional group of the NSAIDs. Also, experimental results suggest that the adsorption process is affected by the solvent. On, the release kinetics assay showed a solvent dependence kinetics whose maximum liberation capacity is affected by the interaction between the drug and the material. Finally, the biological assays show that all the systems studied are not cytotoxic for HMVEC. Additionally, the wound healing assay suggests that the UiO-66(Zr) material has potential application on the wound healing process.



**Keywords**: Metal-organic framework, UiO-66(Zr); Non-steroidal anti-inflammatory drugs; drug delivery system, wound healing

**Poster Presentation**
**MC-P-03**
**Xin-Yu Li**

# *Highly efficient electroreduction of $CO_2$ to ethylene by a metal-organic framework with $CuN_2O_2$ Sites*

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Electroreduction of $CO_2$ into value-added chemical feedstocks is a highly promising approach to alleviating environmental problems and achieving a global carbon neutral economy. Among the various $CO_2$ reduction products, ethylene ($C_2H_4$) is considered the most important vapor product due to its wide range of applications and remarkable energy density. However, highly selective production of ethylene from electrochemical $CO_2$ reduction reaction ($eCO_2RR$) is very difficult because of the sluggish asymmetric C−C coupling reaction and competition of methane production. Therefore, it is urgently necessary to develop more efficient catalysts and to improve the understanding of the mechanisms that promote ethylene production from $eCO_2RR$. Herein, we synthesized a stable two-dimensional metal-organic framework (MOF) **Cu-TABTO** (TABTO = 1,3,5-triamino-2,4,6-benzenetriol). Notably, **Cu-TABTO** shows a high selectivity for ethylene ((FE($C_2H_4$) = 30%) and less methane production ((FE($CH_4$) = 17%) at -1.2 V *vs.* RHE with a current density of 67 mA $cm^{-2}$, surpassing most reported copper-based and all non-Cu metal based catalysts. This work provides a new insight to the catalytic activity on the metal–organic framework and a new design perspective for electroreduction of $CO_2$ to $C_2H_4$ product.

**Keywords**: metal-organic framework; electrocatalytic; carbon dioxide; $C_2H_4$ product;

# A Hofmann-type metal-organic framework for $CO_2/N_2$ and $CH_4/N_2$ separation

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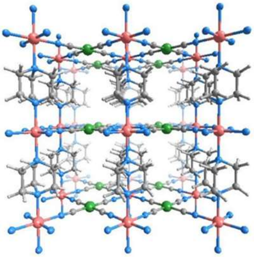
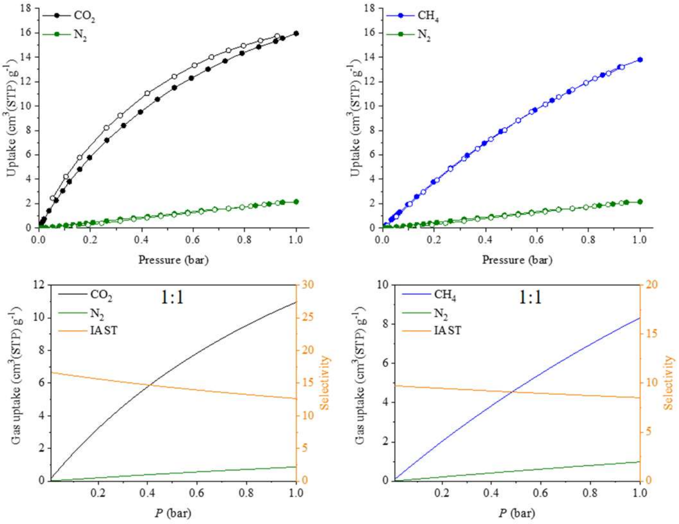
Hofmann-type metal-organic frameworks typically consist of transition metal ions, organic ligands, and cyanide ions[1]. Their structure can be modulated by selecting different transition metal ions and organic ligands to meet various application requirements. This tunability gives them significant potential for applications in gas adsorption, separation, energy storage, catalysis[2,3]. In this study, a Hofmann-type MOF $[CoNi(CN)_4(dabco)]$ was synthesized through the solvothermal reaction of 1,4-diazobicyclo(2,2,2)octane (dabco), $K_2[Ni(CN)_4]$, and Co(II) salts. Single-component adsorption experiments revealed distinct differences in $CO_2/CH_4$ and $N_2$ adsorption. The IAST selectivities at room temperature and 1 bar for $CO_2/N_2$ and $CH_4/N_2$ were calculated to be 13 and 9, respectively, indicating its potential value in $CO_2/N_2$ and $CH_4/N_2$ separation.



$[CoNi(CN)_4(dabco)]$



**Keywords**: Hofmann-type metal-organic framework; $CO_2/N_2$ and $CH_4/N_2$ separation

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# Quasi-open Cu(I) sites for chemical adsorptive separation of CO

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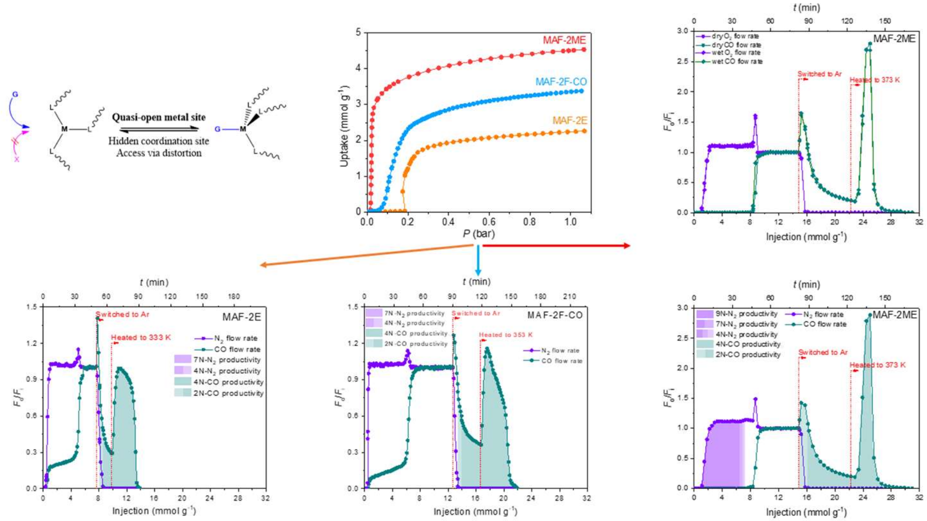
Chemical adsorption holds great promise for the separation and purification of carbon monoxide, but it faces challenges related to desorption difficulties and the instability of open metal sites in the presence of $O_2$, $H_2O$, etc[1-3]. In this study, we demonstrate quasi-open metal sites with hidden or shielded coordination sites as a promising solution. Adopting the trigonal coordination geometry (*sp*$^2$), Cu(I) ions in porous frameworks show weak physical adsorption for nontarget guests. Rational regulation of framework flexibility enables geometry transformation to tetrahedral geometry (*sp*$^3$), generating an additional coordination site for chemical adsorption of CO. Quantitative breakthrough experiments at ambient show CO uptake up to 4.1 mmol $g^{-1}$ and CO selectivity up to 347 against $CO_2$, $CH_4$, $O_2$, $N_2$, and $H_2$. Moreover, the adsorbents can be effectively regenerated at 333-373 K, resulting in CO recovery with purity > 99.99%. Notably, the separation performance remains stable even in the presence of high concentrations of $O_2$ and $H_2O$.



**Keywords**: chemical adsorption; carbon monoxide; open metal sites; quasi-open metal sites

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**Poster Presentation**
**MC-P-06**
**Tae Hyun Kim**

# MOF-derived ZnO/$Co_3O_4$/graphene sensor for alfuzosin electrochemical detection

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We present an electrochemical sensor for detecting alfuzosin (AFZ), an alpha1-adrenoceptor (α1-AR) antagonist, using a metal–organic framework (MOF)-derived nanocomposite of zinc oxide/cobalt oxide (ZnO/$Co_3O_4$) decorated on graphene (Gr) (*Inorg. Chem. Front.,* 2023, **10**, 4829). The ZnO/$Co_3O_4$@Gr nanocomposite was synthesized using the co-precipitation method and ultrasonication. The nanocomposite was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), attenuated total reflectance-infrared (ATR-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM), and high-resolution transmission electron microscopy (HR-TEM). The nanocomposite was modified on a glassy carbon electrode (GCE) to construct an electrochemical AFZ sensor, which exhibited a linear range of 0.05–40 μM and a low limit of detection (LOD) of 0.004 μM. The sensor showed good selectivity, reproducibility, and storage stability. The modified electrode was used to detect AFZ in pharmaceutical tablets, human serum, and urine samples, which delivered adequate recoveries. The ZnO/$Co_3O_4$@Gr nanocomposite-based electrochemical sensor is a promising candidate for the efficient and accurate detection of AFZ, owing to its superior sensitivity, selectivity, reproducibility, and stability.

**Keywords**: MOF; ZnO; $Co_3O_4$; Graphene; Electrochemical Sensor

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**Poster Presentation**
**MC-P-07**
**Xianjun Li**

# Iron-porphyrin-based metal organic framework with multifunctional -COO(H) for $CO_2$ photoreduction

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To address both challenges of global warming and energy scarcity, visible light driven $CO_2$ reduction (e.g., $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$) can be a viable solution, and the development of catalytic systems for the reaction is widely studied. In this work, we aimed to construct a novel catalytic system for photochemical $CO_2$ reduction. An iron porphyrin complex bearing carboxyl groups (-COOHs) at its peripheral positions (Fe(III) meso-tetra(4-carboxyphenyl) porphyrin chloride), **[FeCl($H_4$P)]**, Figure 1) was employed as the basic unit. Self-assembly of **[FeCl($H_4$P)]** afforded a framework catalyst, ***d*-[Fe($H_2$P)]$_n$** (Figure 2), which possesses fixed carboxylate groups and free carboxyl groups. ***d*-[Fe($H_2$P)]$_n$** shows a very high photocatalytic $CO_2$ reduction at under visible-light irradiation in a $CO_2$-saturated acetonitrile (MeCN) solution containing Ir(ppy)$_3$ (Hppy = 2-phenylpyridine, 20 μM), as a photosensitizer, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH, 0.2 M) as a sacrificial electron donor and trifluoroethanol (TFE, 0.2 M) as a proton source. During a 3-hours experiment, the amount of CO increased extremely fast while $H_2$ evolution was negligible (Figure 3), showing an average production rate of $1.8\times10^6$ /μmol $g^{-1}$ $h^{-1}$ (selectivity 100%). This rate is a new record among molecule-based heterogeneous photocatalytic systems for $CO_2$ reduction to produce CO reported up to now.

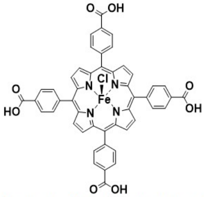

Figure 1. Chemical structure of **[FeCl($H_4$P)]**

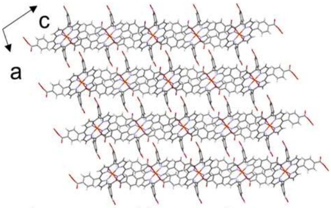

Figure 2. Crystal packing structure of ***d*-[Fe($H_2$P)]$_n$**

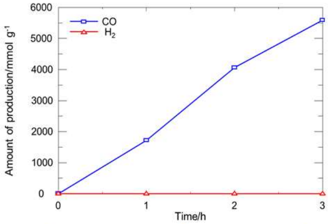

Figure 3. Production amounts of CO and $H_2$ generated from $CO_2$ saturated MeCN solution, which contained 16 μg **d-[Fe($H_2$P)]$_n$**, 20 μM Ir(ppy)$_3$, 0.2 M BIH and 0.2 M TFE, being irradiated with a Xe lamp ($400 \leq \lambda \leq 750$ nm) over 3 h at 20 °C.

**Keywords**: $CO_2$ photoreduction; Iron porphyrin complex; Heterogeneous catalyst

# Conflicted spatial-arrangements of two linkers in MOF and their compromised arrangement

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Metal–organic frameworks (MOFs) offer unique properties through the adjustment of their components and structures. Among these factors, the ability to manipulate the structure of MOFs is crucial for tailoring MOFs to specific applications. Nevertheless, designing an MOF with desired structure and cell lattice remains challenging due to the limited understanding on the fine-tuning of the MOF structures. Herein, we present a novel strategy to control the structure of an MOF by merging two MOF structures into a single MOF. Benzene-1,4-dicarboxylate ($BDC^{2-}$) and naphthalene-1,4-dicarboxylate ($NDC^{2-}$), the two coexisting organic ligands, have conflicting spatial-arrangement preferences within an MOF structure, Kagomé and square lattices, respectively. The final MOF structures are determined depending on the relative contributions of these two organic ligands during MOF construction. Also, the competitive influence between $BDC^{2-}$ and $NDC^{2-}$ is effectively regulated to produce specific MOF structures with a Kagomé or rhombic lattice. In particular, MOFs with rhombic lattices exhibit specific lattice angles representing a compromise between the conflicted spatial-arrangements of the two mixed organic ligands.[1]

**Keywords**: metal–organic framework; structural compromise; hybrid MOF; MOF tunning

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# Surface charge-directed selective catalytic activity of porous M@UiO-66 composites (M = Pt or Ag)

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Metal nanoparticles have garnered significant interest due to their many useful applications such as in catalysis, energy conversion, and gas sensing. However, because of their high surface energy, they are easily agglomerated during the reactions; thus, their activity after a reaction is typically considerably less than their original activity. The construction of porous composites incorporating these active metal nanoparticles is crucial for stabilizing them. Within this aspect, metal–organic frameworks (MOFs) are excellent candidates as supports to stabilize these unstable metal nanoparticles. Herein, we report the fabrication of porous composites based on UiO-66 (M@UiO-66, M = Pt or Ag) containing catalytically active metal nanoparticles. UiO-66-based porous composites incorporating decorated metal nanoparticles are achieved by converting metal ions into metal nanoparticles through a one-step thermal treatment of UiO-66/$M^{n+}$ ($M^{n+}$ = $Pt^{2+}$ or $Ag^{+}$). The M@UiO-66 composites feature well-dispersed metal nanoparticles within the well-developed micropores of UiO-66. Notably, these composites possess the specific surface charge attributed to the presence of metal nanoparticles. As a result, M@UiO-66 exhibits not only exceptional selective catalytic performance in the reduction of organic pollutants but also demonstrates outstanding recyclability.[1]

**Keywords**: metal–organic framework; hybrid MOF; porous composite; catalytic performance; metal nanoparticle

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# Chemical Reconstruction of Bismuth Oxyiodides to Form Oxycarbonate for $CO_2$ Conversion

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Reconstructing heterogeneous catalysts through electrochemical conditions is critical for enhancing the catalytic performance of $CO_2$ reduction. This reconstruction induces changes in the coordination of metal centers at the surface and within the bulk of catalysts, which can significantly affect catalytic performance. Therefore, it is essential to thoroughly investigate these reconstructed species to improve catalysis. In this study, we examined the chemical reconstruction of bismuth oxyiodides using a $KHCO_3$ electrolyte and evaluated the catalytic performance of the reconstructed catalysts for formate production. The $KHCO_3$ electrolyte transformed tetragonal and orthorhombic bismuth oxyiodides (*t*-BiOI and *o*-$Bi_5O_7I$) into $(BiO)_2CO_3$ (BOC-*t* and BOC-*o*) under mild conditions. The $K^+$ reacted with interlayered $I^-$, leading to the removal of iodine in bismuth oxyiodides, while $CO_3^{2-}$ ions easily intercalated between the $[BiO]_2^{2+}$ layers. The BOC-*o* catalyst exhibited sharp edges, exposing $CO_3^{2-}$ species and outperformed BOC-*t* at low overpotential ranges. This superior performance is attributed to bismuth-coordinated $CO_3^{2-}$, which is highly active in formate production. This study highlights the significant influence of electrolytes on the catalysis of $CO_2$ reduction and underscores the role of bismuth-coordinated $CO_3^{2-}$ in enhancing the performance of electrochemical $CO_2$ conversion into formate.

**Keywords**: $CO_2$ reduction; Bismuth oxycarbonate; Reconstruction; Bismuth oxyiodide

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# Synthesis of porous polymer through thermal treatment of hexaethynylhexaazatrinaphthylene

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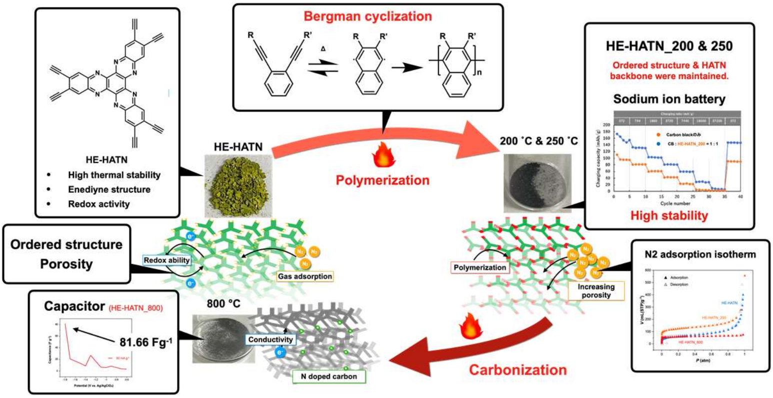
Porous materials have diverse applications. Activated carbon, a prime example, boasts exceptional porosity but presents challenges in controlling atomic arrangement and structure. On the other hand, Ordered Carbonaceous Frameworks[1] (OCFs), synthesized by calcination of precursor molecules with thermally stable π-conjugated backbones and thermal polymerization moieties, represent the new functional porous materials. Due to preserved structural regularity and molecular backbones in the molecular crystal, they offer clear designability and exhibit chemical and thermal stability.

In this study, HE-HATN was synthesized as a precursor molecule of OCFs with an enediyne structure and a thermally stable π-conjugated backbone. It shows promise for applications in secondary batteries[2], capacitors[3], and catalysts, thanks to its multiple-electron redox and coordination sites for metal ions.

As a result, it was suggested that Bergmann cyclization and solid-phase polymerization proceeded by thermal treatment of HE-HATN. The regular structure and HATN backbone were partially retained post-calcination. Notably, HE-HATN exhibited pre-calcination porosity, with an increased specific surface area after calcination. Moreover, it demonstrated high cycle stability as an active material for secondary batteries, highlighting its potential as a functional porous material through calcination, while preserving structure and HATN backbone. The Bergmann cyclization reaction will be a new method for synthesizing OCFs.



**Keywords**: porous material; COFs; Bergman cyclization; secondary battery; capacitor

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# Data-driven discovery of zeolitic imidazolate frameworks and their applications in carbon neutrality

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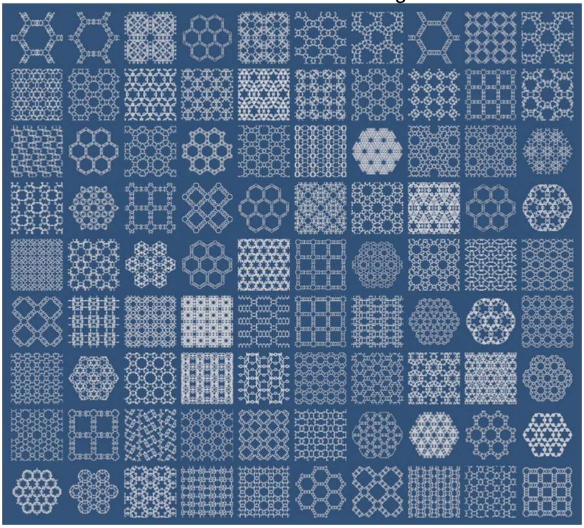
The discovery of functional materials has rapidly increased, thanks to computational techniques that offer a multitude of potential materials. However, the vast number of predictions poses challenges in transitioning from computational models to experimental confirmations. Addressing this, we digitized chemical intuition to streamline the discovery process, focusing on zeolitic imidazolate frameworks (ZIFs)[1] – promising alternatives to zeolites with extensive applications in gas separation. Despite their potential, the limited topologies by the “zeolite conundrum” and an unclear synthetic roadmap have hindered novel ZIF discoveries. We propose a data-driven approach for ZIF discovery, leveraging structural descriptors of known materials as a screening tool for vast hypothetical databases.[2] From over 4 million zeolite structures, we identified potential ZIF candidates based on O−T−O angle difference, vertex symbol, and T−O−T angle. Energy calculations enabled the ranking of synthesizable ZIFs, resulting in the successful synthesis of three new ZIFs with two novel topologies, **uza**-ZIF-1 and **uzb**-ZIF-2, -3. Notably, **uzb**-ZIF-3 demonstrated remarkable $CO_2$ adsorption selectivity over $CH_4$. This work underscores the synergistic potential of computational predictions and chemical intuition in advancing material science.



**Keywords**: Zeolitic Imidazolate Frameworks; Porous materials; Carbon neutrality; Digital discovery; Topology

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**Poster Presentation**
**MC-P-13**
**Tomoki Nishiyama**

# A Copper(I) Thiocyanate based Photoresponsive Semiconducting 2D Coordination Polymer

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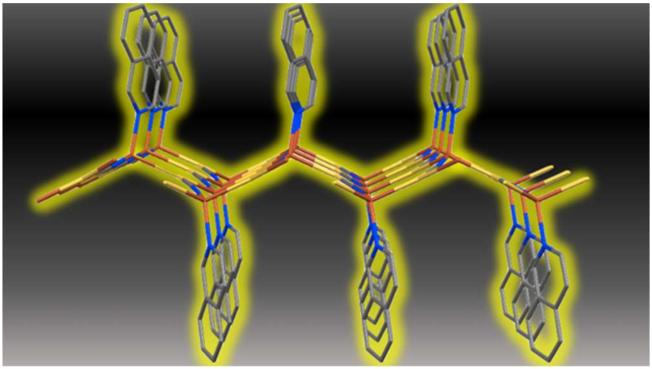
Metal-organic frameworks (MOFs) or coordination polymers (CPs) featuring characteristic infinite structures constructed by the self-assembly of metal ions and a variety of organic bridging ligands are among the most attractive materials. However, most reported CPs are insulators, which is difficult to apply in electronic devices. Especially, for application to optoelectronic devices such as organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs), we need to create CPs having both photoluminescent and electrically conductive properties because the photoactive materials without thermal decay of the excitons due to improve the performance. Therefore, we are working on developing new CPs having both conductivity and photoluminescence properties with copper(I) thiocyanate, which has high hole transport properties.

In this work, we focused on CPs consisting of copper(I) thiocyanate with hole transport ability and nitrogen-containing heterocyclic ligands. we synthesized a coordination polymer $[Cu(SCN)(iqi)]_n$ (**1**) (iqi = isoquinoline) exhibiting both photoluminescent and electrical conductivity properties. The crystal structure was determined by X-ray diffraction, and the electrical conductivity, photoluminescence, and photoconductivity were measured for CP **1**. The band states of CP **1** are determined by density functional theory (DFT) calculations. CP**1** consists of a two-dimensional (2D) sheet structure of copper(I) thiocyanate and shows the photoluminescence derived from $^3$MLCT and photoconductive properties.



**Keywords**: Coordination Polymer; Semiconducting; Photoluminescence; Photoconductivity

# MOFs for Decoding the Structures of Single Polymer Chains

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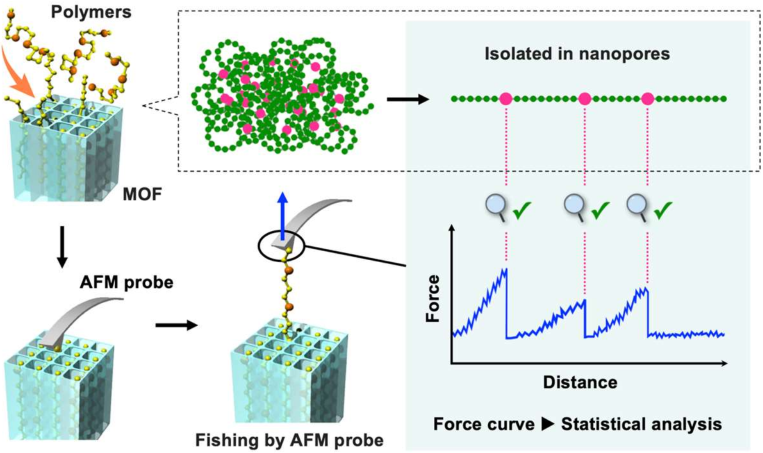
While sequencing of biopolymers, as typified by nanopore sequencer, has become a standard technology in recent years, sequencing of synthetic copolymers remains a formidable challenge because of the lack of fundamental techniques available for accessing the local monomer array structures in a long and coiled polymer chain.1) Recently, our research group has discovered a phenomenon that polymer chains spontaneously enter the nanopores of MOFs, even in the solution phase, while uncoiling their entangled conformations.2)

In this study, we focused on the feature of polymer adsorption into MOFs and developed a novel approach to polymer sequencing by combining a single-molecule analysis technique using an Atomic Force Microscope (AFM). A single polymer chain encapsulated and isolated in the nanopores of a single crystal of MOF with one-dimensional pores was mechanically pulled out with an AFM probe. The force on the probe was monitored during the pulling event, providing a force curve that reflects the local chemical structures of the polymer chain.

This method will make it possible to directly read out the primary structure information of synthetic polymers and create a new trend in polymer analysis technology.



**Keywords**: Metal-Organic Framework; Polymer Adsorption; Atomic Force Microscope; Single Molecule Force Spectroscopy; Polymer Sequencing

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# Metal-Organic Framework(MOF)-based cathodes for next-generation energy storage. : A review.

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In recent years, metal-organic frameworks (MOFs) have emerged as promising cathode materials for various energy storage applications due to their exceptional properties such as high surface area, controlled architecture, porosity, and tunability. The recent methods of MOF synthesis can easily control porosity, particle morphology, electrical conductivity, and stability, which can be tailored to meet specific needs, and also take advantages such as selective metal sources, easy customization. This comprehensive review aims to thoroughly explore MOF-based cathodes, their uniqueness, and their historical development across various synthesis methods. It also discusses brief history, notable advantages and disadvantages of MOFs and their adaptability across multiple applications, with a special emphasis on their vital role in various battery applications such as lithium, sodium, and zinc batteries, and other batteries such as potassium-, magnesium-, and aluminum-ion batteries are discussed. Additionally, MOFs have shown potential in multivalent-ion batteries (MIBs), offering higher energy density compared to traditional lithium-ion batteries. It aims to optimize MOF-based and -derived materials for enhanced battery performance.

**Keywords**: Metal-Organic Frameworks(MOFs); Cathode Materials; Energy Storage

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**Poster Presentation**
**MC-P-16**
**Chun Gwon Park**

# Al/Zinc-based metal-organic frameworks for atopic dermatitis treatment

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Aluminum (Al) and zinc (Zn)-based materials have demonstrated efficacy in promoting wound healing [1,2]. Furthermore, these materials can be applied in anti-inflammatory therapy by targeting mast cell-mediated allergic inflammatory signaling pathways [3]. In this study, Al/Zn-based metal-organic frameworks (MOFs), specifically Al/Zn-MIL-101-$NH_2$, were synthesized as potential therapeutic agents for skin inflammation. Al/Zn-MIL-101-$NH_2$ demonstrated the sustained release of $Zn^{2+}$ and $Al^{2+}$ along with biodegradability. Atopic dermatitis (AD), characterized by persistent inflammation and itching, lacks a definitive cure despite current relief-oriented treatments. In this context, we treated AD using Al/Zn-MIL-101-$NH_2$ as an effective drug delivery platform for modulating immunity. The cytotoxicity of Al/Zn-MIL-101-$NH_2$ was evaluated by exposing L929 cells to them, confirming their biosafety. To assess antioxidant properties, bone marrow-derived dendritic cells were incubated with Al/Zn-MIL-101-NH2. Subsequently, cell-permeable 2,7-dichlorodihydrofluorescein diacetate was employed to detect intracellular reactive oxygen species, revealing the antioxidant capabilities of Al/Zn-MIL-101-$NH_2$. Moreover, in a 1-chloro-2,4-dinitrobenzene -induced AD-like mouse model, Al/Zn-MIL-101-$NH_2$ treatment mitigated inflammation symptoms, leading to reduced epidermal hyperplasia and inflammatory factors. Overall, our findings highlight the therapeutic versatility of Al/Zn-MIL-101-$NH_2$, particularly in the context of treating skin inflammatory diseases.

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**Keywords**: MOF; Transdermal delivery system; Atopic dermatitis treatment; Anti-oxidant; Anti-inflammatory properties

**Poster Presentation**
**MC-P-17**
**Tae-Hyung KIM**

# MOF nanopatterns for controlled autonomous stem cell differentiation

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Ensuring a consistent and reliable provision of essential biomolecules is crucial for replicating in vivo microenvironments that facilitate the spontaneous generation of diverse cell types. In this study, we introduce a novel platform, metal-organic framework (MOF) nanoparticle–embedded nanopatterns, designed for highly efficient neuronal cell generation from neural stem cells. Through careful optimization of the physical parameters governing homogeneous periodic nanopatterns, each nanopit is engineered to encapsulate single nanoscale MOFs. These nanoscale MOFs are specifically tailored for the sustained storage and release of retinoic acid (RA), a key factor in neurogenesis. The platform demonstrates a successful mitigation of physical interactions with cells, ensuring the remarkable stability of the nanoscale MOF structure while avoiding nanoparticle-induced toxicity issues. Leveraging the continuous and long-term release of RA, neural stem cells cultivated on the developed platform exhibit heightened mRNA expressions associated with various neurogenesis-related activities. The versatility of this deplatform extends its applicability to diverse stem cell sources and differentiation lineages, making it a valuable tool for a range of stem cell-based regenerative therapies. Acknowledgements: This research was supported by grants from the National Research Foundation of Korea (NRF) (Grant Nos. NRF-2019M3A9H2031820, NRF-2022R1A4A2000776, and NRF-2022R1A2C4002217) and the Korean Fund for Regenerative Medicine funded by the Ministry of Science and ICT, as well as the Ministry of Health and Welfare (Grant No. RS-2022-00070316).

# Quantum sensing by radicals with long coherence time in acene-based metal-organic frameworks

Miku Inoue[1], Akio Yamauchi[1], Bhavesh Parmar[1], Kana Orihashi[1], Mizue Asada[2], Toshikazu Nakamura[2], Nobuhiro Yanai[1, 3*]

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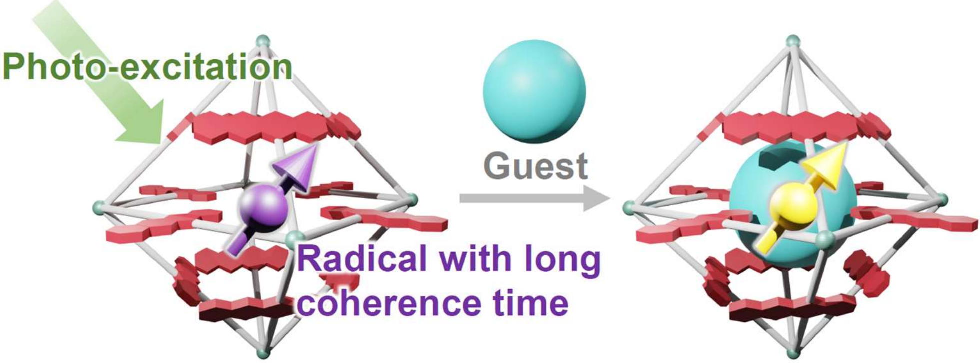
The qubit is the basic unit in quantum information science and utilizes the superposition of multiple quantum states. Quantum sensing is a method of measuring physical quantities using quantum effects and is expected to achieve higher sensitivity than conventional sensing. For such sensing applications, qubits must have a long spin-spin relaxation time or coherence time. Recently, metal-organic frameworks (MOFs) have attracted attention as a useful platform for quantum sensing, because molecular qubits can be integrated as ligands of MOF, and qubits can be close enough to interact with guest molecules. We have previously observed radicals with long coherence time of persistent radicals in a MOF with diazatetracene (DAT) as a ligand after photoirradiation [1]. However, it was difficult to introduce various guest molecules into that MOF due to the limited structural stability. In this study, we synthesized a new UiO-type MOF with a DAT-containing ligand, which enables the stable introduction of guest molecules and evaluates the effect of guest inclusion on coherence time of photo-generated radicals.



**Keywords**: Quantum sensing; Coherence time; Metal-organic frameworks; Radical; Molecular qubits

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**Poster Presentation**
**MC-P-19**
**Reetu Rani**

# Adsorption studies of alkali and alkaline earth metal ions on zirconium metal–organic frameworks

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Zirconium based metal-organic frameworks (Zr-MOFs) including UiO-66, UiO-66-$NH_2$ and UiO-66-$(COOH)_2$ were employed for the adsorption of alkali and alkaline earth metal ions (Li, Na, K, Mg, Ca, Sr) from aqueous solutions. Zr-MOFs exhibit high water stability, a high surface area, and a significant pore volume, all of which contribute to their enhanced adsorption capacity. Adsorption behavior of Zr-MOFs was tested for alkali and alkaline earth metals at different solution pH, different initial concentration of metal ions and contact time, activation time and doses of MOF materials and in the presence of multi-elements. Among three MOFs, the carboxyl-functionalized Zr-MOF; UiO-66-$(COOH)_2$ showed better adsorption capacity towards divalent ions compared to monovalent ions at natural pH of the solution which can be assigned to higher electrostatic attraction of divalent ions compared to monovalent ions. The study delved into the possible mechanisms and adsorption behavior of metal ions onto carboxyl functionalized Zr-MOF. The experimental findings of the present study suggest that carboxyl functionalized zirconium-based MOF hold significant potential towards the preparation of suitable sorbents for extraction of metal ions and therefore, in future UiO-66-$COOH_2$ modified membranes will be tested for selective transfer/extraction of metal ions from aqueous samples.

**Keywords**: Metal Organic Frameworks; Adsorption; Zr-MOFs; Alkali metal ions; Alkaline earth metal ions

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# Amorphous porous hollow-structured Fe-BTC

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Hollow-structured materials, with their well-defined internal void, low density, and increased surface-to-volume ratio, have garnered increasing interest. The synergistic effects of the hollow structure in metal-organic frameworks (MOFs) enhance mass transport and accessibility to active sites, broadening their applications in adsorption/separation, electrochemical energy storage, and catalysis. Despite the structural benefits of hollow MOFs, the inherent crystallin nature of the MOFs can limit their practical applications. To augment MOFs' capabilities, defect engineering has been explored to functionalize pores and modify pore size distributions. Nevertheless, a significant drawback associated with defect generation is that increasing defects often reduces a MOF's surface area, resulting in amorphous MOFs with diminished porosity.

Herein, we have synthesized a hollow-structured, defect-rich, but porous material, h-Fe-BTC (BTC = 1,3,5-benzenetricarboxylic acid), *via* post-synthetic metal-ion metathesis (PSMM) of CuZn-HKUST-1 with $Fe^{3+}$. Once abundant $Fe^{3+}$ ions envelop the labile CuZn-HKUST-1, $Cu^{2+}/Zn^{2+}$ are readily replaced with $Fe^{3+}$, forming a more thermally stable phase, h-Fe-BTC, with an inner cavity. h-Fe-BTC exhibits a significantly higher adsorptive capacity for guest molecules compared to its non-hollow, bulk counterpart, Fe-BTC, owing to its hollow structure, increased metal-defect sites, and enhanced surface area.[1]

**Keywords**: metal-organic framework; defects engineering; hollow structures; amorphous materials; porous materials

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# Isostructural Metal-Organic Frameworks based on the Strong Structure-Directing Radical π-Dimers

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Isostructural metal-organic frameworks (MOFs) provide an ideal platform for investigating the influence of metal nodes on chemical and physical properties of MOFs. However, constructing isostructural MOFs with diverse metal ions remains challenging. Even with identical ligands, differences in the preferred coordination geometry of metal ions yield diverse MOF structures.[1] Herein, we designed radical anionic π-dimers of naphthalenediimide (NDI) based ligands, which form through the reduction of NDI to $NDI^{•-}$ during a solvothermal process. These π-dimers, owing to their low formation energy and strong intermolecular interactions, served a strong structure-directing role in the construction of series isostructural radical anionic MOFs, $M^{2+}$-DGIST-7 (M = Mg, Ca, Mn, Fe, Co, Cd).[2] Single-crystal X-ray diffractometry revealed distinct structural transitions influenced by metal ion types during the oxidative quenching of $NDI^{•-}$. The flexibility of metal ion's oxidation states significantly impacts the properties of $M^{2+}$-DGIST-7. $M^{2+}$-DGIST-7 with inert oxidation states and relatively strong coordination bonds (e.g., Mg, Ca, Cd, Co) exhibited microporosity verified by $N_2$ sorption analysis. $M^{2+}$-DGIST-7 with variable oxidation states (e.g., Mn, Fe, Co) demonstrated superior photocatalytic abilities under visible light. This study elucidated the correlation between the metal ion types and the MOF properties, enabling the tailored MOF design for specific functions.

**Keywords**: Metal-organic framework; Isostructural MOF; Naphthalenediimie; Radical; Photo-responsive

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# 3D MOF Derived Nanorods like Cation Defect-rich $Ni_{0.6}Fe_{2.4}O_4$@NC Efficient Electrocatalyst Enables Robust Rechargeable Zinc-air Batteries.

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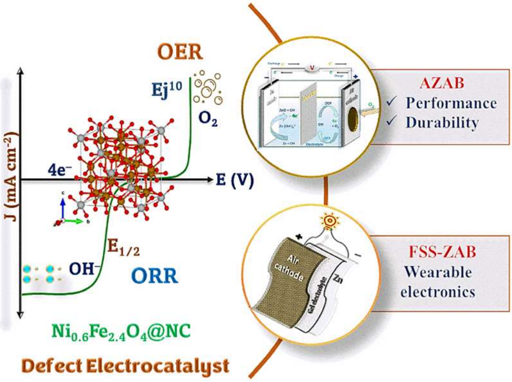
Electrochemical energy storage devices with stable performance, high power output, and energy density are urgently needed to meet the world's energy demand. Recently, Zinc-air batteries are becoming increasingly popular as potential energy sources for green energy storage technologies. The air electrodes which combine with some oxygen electrocatalysts, play a significant role in determining the cost and performance of Zn-air batteries. However, designing and fabricating efficient electrocatalysts still remains challenging. Because of their unique structural flexibility and uniformly dispersed active sites, metal-organic frameworks (MOFs) have emerged as appealing precursors for the synthesis of a wide range of advanced functional materials. Our study proposes the use of flexible multi-carboxylic acids and bipyridine ligands to construct nanorods like NiFe@MOFs with multiple coordination modes and fascinating architectures. Post-annealing of MOF precursors in argon at 750 °C resulted in a cation deficiency Ni0.6Fe2.4O4@NC electrocatalyst. This 3D electrocatalyst has effective activity for the oxygen reduction reaction ORR (E1/2 = 0.85 V) and the oxygen evolution reaction OER (η10 = 207 mV@10 mA cm-2). Furthermore, a rechargeable zinc-air battery with Ni0.6Fe2.4O4@NC as the cathode demonstrated a high open circuit voltage (OCV) of 1.5 V, a peak power density of 194.6 mW cm-2, and exceptional long-term cycling stability over 300 h (1800 cycles, 10 mA cm-2). The flexible solid-state zinc-air battery demonstrated power density of 68.5 mW cm-2 and long-term durability over 35 h at 5 mA cm-2. The proposed strategy allows for the rational design of cation defect-rich spinel structures attached to ultra-thin, N-doped graphitic carbon sheets in order to enhance active site availability and mass electron transport.



**Key words**: MOFs derived, Spinel structures, Cation defect, ORR/OER, Rechargeable ZABs

# Main Group Chemistry (MG)

# Abstract

# Catalytic Applications of Boron and Aluminum Cations

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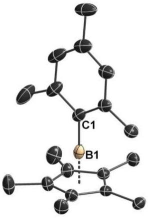
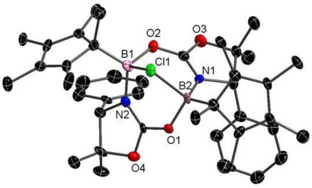
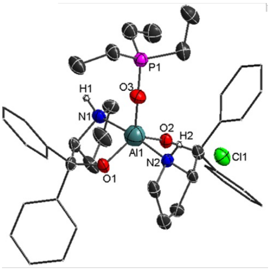
As the catalytic applications of halogenated neutral group 13 catalysts continue to expand, the chemistry of cationic group 13 catalysts has also emerged in recent years. Consequently, we reported that hypercoordinate boron cation ($[Cp^*B\text{-}R]^+$),[1] a readily manageable and robust Lewis acid, efficiently catalyzes the hydrosilylation and cyanosilylation of carbonyl derivatives. In addition to achiral catalysts, chiral functionalities can be incorporated into the Cp*-stabilized boron cation system, leading to a series of chiral $[B\text{-}Cl\text{-}B]^+$ diboron cations and hypercoordinate boron cations.[2] Subsequently, we discovered that the Cp* substituent is not essential to realize a borinium catalyst. An aryl amino borinium ion, $[TMP\text{-}B\text{-}Mes]^+$,[3] can also catalyze the hydrosilylation of ketones and promote Si-H/Si-C cross metathesis at room temperature. Furthermore, in addition to boron cations, we have prepared a series of prolinol-derived tetra-coordinate chiral aluminum cations, which exhibit considerably higher Lewis acidity compared to $B(C_6F_5)_3$.[4] These aluminum cations are effective in catalyzing the C2-alkylation of indole through asymmetric Michael addition and the hydrophosphination of alkenes. Mechanistic studies of the indole C2-alkylation suggest that the rate-determining step of the entire process is the formation of a CAAC-Al intermediate via the cleavage of the C2-H bond.







**Keywords**: boron cation, aluminum cation, asymmetric catalysis

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**Keynote Speaker**
**MG-K-02**
**Sundargopal Ghosh**

# Coordination Chemistry of Smaller to Polyhedral Borane Clusters

Sundargopal Ghosh

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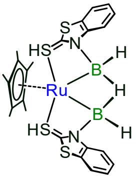
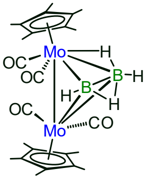
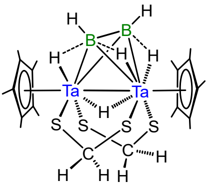
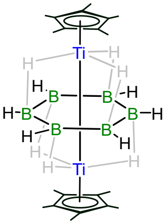
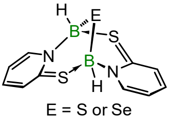
The fascinating aspect of metallaborane chemistry is that several classic organometallic complexes that defined fundamental structural and bonding paradigms are mimicked by many isoelectronic metallaborane analogues.[1] These clusters have been extensively explored for the broad understanding of the chemical bonding and catalysis.[2] For example, we have recently synthesized and structurally characterized a bimetallic diborane(4) which mimics Cotton's dimolybdenum–alkyne complex $[\{CpMo\text{-}(CO)_2\}_2C_2H_2]$.[3] Also, we have isolated the first classical diborane(5) $[B_2H_5]^-$, in which the $sp^2$-B center is stabilized by the electron donation from tantalum.[4] By utilizing the ability of early transition metals to participate in higher degree connectivity, we have isolated the first planar $[B_6H_6]$ ring stabilized by two {Cp*Ti} fragments and a 16 vertex oblate hypho titanaborane cluster.[5] Very recently, we have developed an uncatalysed synthetic pathway to generate the doubly base stabilised symmetrical and unsymmetrical diborane(4) species from the thermolysis reaction of 2-mercaptopyridine with $[BH_3.THF]$. The key results of this work will be described.











**Keywords**: Boron; Metallaborane; Diborane; Polyhedral borane

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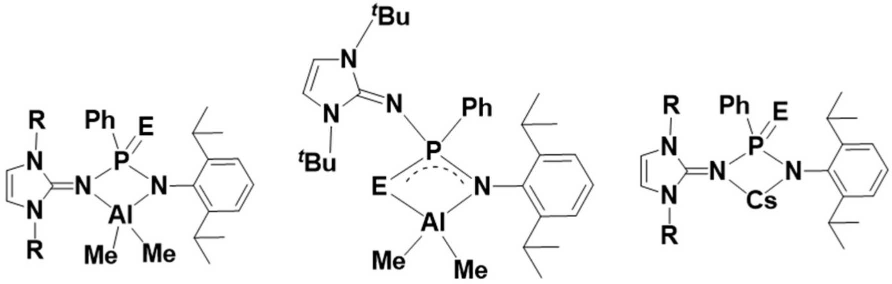
**Invited Speaker**
**MG-I-01**
**Vadapalli Chandrasekhar**

# Metal Complexes of Unsymmetrical N-P-N ligands and Their Utility in Catalysis

V. Chandrasekhar

*Tata Institute of Fundamental Research Hyderabad and Indian Institute of Technology Kanpur*

In this talk we will describe the use of some of our recent efforts in main-group chemistry. We will describe the use of unsymmetrical phosphorus-supported ligands which could be deprotonated to afford a monoanionic chelating N-P-N motif that can bind to metal centres affording four-membered rings (Figure). In these systems the phosphorus centre is in a formal oxidation state of +3. This can be oxidized to a P(V) centre by reaction with chalcogens. The resulting ligands can bind to the metal centre by a N^E coordination (Figure). We describe the utility of Al(III)[1] and Cs(I)[2] complexes in homogeneous catalytic reactions.



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Invited Speaker
MG-I-02
Krzysztof Kuciński

# Main group compounds as efficient catalysts in the synthesis of organosilicon derivatives

Krzysztof Kuciński[1*]

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Silylation of organic and organometalloidal compounds offers a strategic method to produce valuable siloxanes and silyl-protected intermediates, including silyl ethers and silylacetylenes [1-2]. While derivatives with acidic protons, such as alcohols, phenols, and silanols, can be readily silylated, halosilanes are typically employed for this purpose [3]. However, given the challenges associated with these reagents, including high moisture sensitivity, stoichiometric base requirements, and the formation of corrosive byproducts, there is a growing interest in more sustainable alternatives. Accordingly, catalysts rich in naturally abundant elements have been gaining attention. As a result, several methods emphasizing main group species and/or Earth-abundant 3d metals are under investigation. In this study, we highlight the catalytic silylation of alcohols, silanols, terminal alkynes, and primary amines using bis(trimethylsilyl)acetylene. This process facilitates the formation of C–Si, O–Si, and N–Si bonds in a single step. Notably, we employ potassium bis(trimethylsilylamide), a readily available precatalyst for this synthesis (Figure 1) [4-6].

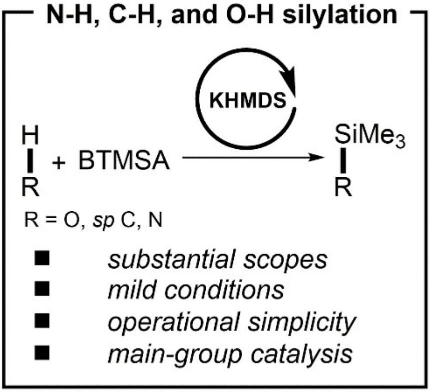

**Figure 1.** C–Si, N–Si, and O–Si bonds formation *via* dealkynative coupling.

**Keywords**: base catalysis; potassium disilazide; silylation; alkynylsilanes; aminosilanes

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Invited Speaker
MG-I-03
Hsueh-Ju Liu

# Controllable C–H Bond Activation and P–C Bond Formation on a $P_4$ Moiety Using Novel Dinuclear Iron Hydrido Complexes

Hao-Yuan Lan[1], Han-Jung Li[1], Tzu-Hsiung Yang[2], Hsueh-Ju Liu[1*]

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Phosphorus is essential for life, which is the basic component in DNA, RNA, ATP, and phospholipids in all living cells, also used in fertilizers, detergents, and pesticides. Functionalization of phosphorus with a controlled manner is particularly challenging. It is necessary to find a renewable and ecologically friendly pathway to produce high value organophosphorus. In this research, we demonstrate functionalization of $P_4$ by preorganized diiron hydrido complexes. $P_4$ reacts with an diiron hydride complex $LFe_2(\mu\text{-}H)_2$ (**1**; L = 1,3-bis(cyclopentadienyl)dimethysilyl)benzene) cleanly to give complex **2** $(L\text{-}H)Fe_2(\mu\text{-}P_4H_3)$, which is fully characterized by multinuclear NMR spectroscopy and X-ray diffraction. This reaction involves a direct hydrogenation reaction of white phosphorus with concurrent C–H bond activation and P–C bond formation events on the phenyl ring of the ligand backbone, and this novel activation/functionalization of $P_4$ molecule is unprecedented in literature to our knowledge. Monitoring the reaction of $P_4$ and complex **1** by NMR spectroscopy, together with DFT calculations, were employed to understand how these fundamentally important bond activation/formation event occur on the $P_4$ moiety.

**Keywords**: phosphorus activation; C–H activation; iron hydrides; main group chemistry

# Stable organic radicals derived from carbenes and their applications

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For the past decade, there have been developed numerous organic/main group radicals with an aid of N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino) carbenes (CAACs). Novel reactivity and properties of them expand further applications of radical chemistry such as new catalysis, and electronic/magnetic materials. However, current synthetic efforts to obtain highly stable organic radicals are based on aminoxyl (TEMPO) or trityl derivatives. A new structure for highly stable organic radicals is, therefore, a priority in the radical chemistry field. Our group has been exploring diverse NHC/CAAC-based organic radicals, which include unique structural platforms or nitric oxide. As our continuous efforts to access stable organic radicals, we have designed, synthesized, and characterized 1,2-dicarbonyl radical cations derived from NHCs and CAAC. Most notably, air-, water-, chemical-, and thermal stability of the presented radicals are comparable or higher than the state-of-the-art organic radicals (TEMPO, trityl, and other radicals). We believe our 1,2-dicarbonyl radical cations would serve as a good complement to the well-known stable organic radicals in various fields, which will be presented in detail.

**Keywords**: N-heterocyclic carbenes; cyclic (alkyl)(amino) carbenes; 1,2-dicarbonyl radical; stable organic radicals; spin density

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# N-Heterocyclic silylene supported copper(I) aryl complexes: bond activation to catalysis

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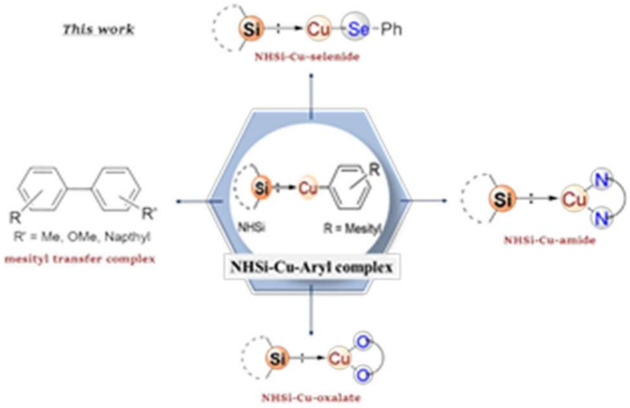
Despite recent advancements in N-heterocyclic carbene (NHC) and cyclic alkyl amino carbene (CAAC) coordinated copper amide complexes, the isolation of the N-heterocyclic silylene (NHSi) coordinated copper amide complexes has remained elusive.[1,2] In this work, we have developed a synthetic methodology for the isolation of N-heterocyclic silylene coordinated organocopper(I) complexes and exploited them towards a variety of functionalized N-H, B-H and Se-Se bond cleavage. Further, we also used N-heterocyclic silylene coordinated organocopper(I) as a mesityl transfer reagent for the C-C coupling reaction, which afforded coupled products in excellent yields.[3]



**Keywords**: N-heterocyclic silylene; Copper complexes; C-C coupling; Bond activation

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# Chirality Transfer Reaction of Organophosphorus Compounds with a Binaphthyl Group and Their Use

Toshiaki Murai*

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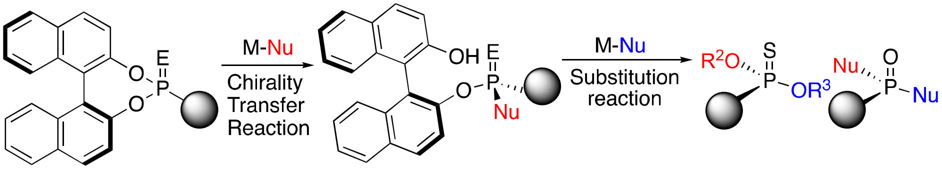
P-Chirogenic organophosphorus compounds play a crucial role due to their extensive applicability as drugs, prodrugs, optically active ligands, and organocatalysts. Over the past three decades, a variety of synthetic methods have been developed, including kinetic resolutions, desymmetrization of prochiral organophosphorus compounds, and the separation of diastereomixtures. In this context, we have developed axis-to-central chirality transfer reactions involving pentavalent four-coordinate organophosphorus compounds bearing a binaphthyl group.[1] We have also explored the conversion of the resulting compounds into enantiomerically enriched P-chirogenic organophosphorus compounds. As an illustrative example, the sequential substitution reaction of phosphonates with a binaphthyl group using aromatic Grignard reagents and methyl Grignard reagents proceeded smoothly, yielding enantiomerically enriched P-chirogenic phosphine oxides in high yields with high enantiomeric ratios. [2] These two-step reactions entail the transfer of axial chirality from the binaphthyl group to the central chirality of the phosphorus atom, coupled with a stereoselective substitution reaction of the initial products with Grignard reagents. Key substrates employed in these reactions included phosphinates,[3] phosphates,[4] phosphorothioates,[4] and phosphonothioates[5] with a binaphthyl group, which reacted with hydroxides and alkoxides as nucleophiles. Further details regarding these reactions will be provided.



**Keywords**: P-chirogenic; organophosphorus compounds; axial chirality; central chirality; chirality transfer

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# Polyantimony chromium complexes: Syntheses, reactivities, paramagnetism, and semiconductivities

Yu-Huei Li, Chia-Hsien Lin, Minghuey Shieh*

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Two novel chromium carbonyl fragment-protected $Sb_4$- and $Sb_{12}$-centered complexes, $[Sb_4Cr_6(CO)_{28}]^{4-}$ (**1**) and $[Sb_{12}Cr_6(CO)_{28}]^{4-}$ (**2**), were synthesized from the reactions of different ratios of $Sb_2O_3$ and $Cr(CO)_6$ under appropriate conditions. X-ray analysis showed that cluster **1** consisted of a central tetrahedral $Sb_4$ core coordinated with four terminal $Cr(CO)_5$ fragments and two bridging $Cr(CO)_4$ moieties. Cluster **2** displayed a central $Sb_{12}$ core bound with four $Cr(CO)_5$ and bridged by two $Cr(CO)_4$ fragments to give a di-$Sb_6Cr$-norbornane-like structure with four $Sb_5$ and four $Sb_4Cr$ faces. Interestingly, complex **1** was found to have versatile reactivities toward groups 7−9 metal carbonyls or metal oxidants, forming transmetallated or oxidized $Sb_4$-based chromium clusters. Also, cluster **1** had a high affinity toward $O_2$ to generate a rare di-oxo-bridged $Sb_4$-centered product. The magnetic measurement showed that these polyantimony chromium complexes **1** and **2** and the $Sb_4$-based heterometallic derivatives exhibited unexpected paramagnetic properties with $S = 1$, where their magnetic centers were determined to be located at the participated transition metals. Detailed paramagnetism of these polyantimony-based transition metal clusters was fully understood by SQUID, EPR, XPS, and XANES, with the aid of DFT calculations. The relationship between their electronic structures and electrical conductivity is also discussed.

**Keywords**: antimony; chromium; transition metal carbonyl clusters; paramagnetism; semiconductivity

# Crystal Structure of 4-picolinyl cyanohydroximinoacetamide Complexes with K(I), Cs(I), Tl(I)

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Synthesis of 4-picolinyl cyanohydroximinoacetamide ($H_2$-4pcha) with kalium(I), caesium(I), and thallium(I), and their crystal structures are reported here. The ligand was prepared from methyl cyanoacetate precursor and the picolinyl group was incorporated to facilitate the construction of coordination polymers. Upon reaction between the ligand and the respected alkali base, metal complexes of $[K(\mu_6\text{-H-4pcha})]_n$ and $[Cs(\mu_6\text{-H-4pcha})]_n$ were obtained in a considerably good yield. Meanwhile, the $[Tl(\mu_4\text{-H-4pcha})]$ was obtained upon metathesis reaction between thallium(I) nitrate and the $[K(\text{H-4pcha})]_n$. Crystal structures of all complexes were solved in the monoclinic space group $P2_1/c$. The crystal packing of both kalium and caesium metal complexes forms 3D networks, with 7-coordinate metal centre, whereas the thallium metal complex only forms 2D sheets due to Tl(I) has a stereoactive lone pair. If the oximate group of the ligand is considered as one coordination bond, the Tl(I) displays an asymmetric square-pyramidal coordination environment.

**Keywords:** *alkali complex, coordination polymers, picolinyl, crystal structure, main group element.*

# Synthesis and molecular structure studies of Aluminium (III) complexes with $\beta$-ketoiminate and ethanolamine ligands

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Aluminium, a cost-effective and abundant metal with high conductivity, holds promise for use in printed electronic films. However, its tendency to oxidize has hindered its industrial usage. There is a lack of research on using aluminium-based complexes for the conversion to aluminium metal due to handling difficulties originating from their reactivity towards moisture and air. Recent precursor design and synthesis advancements have shown significant progress in this field. Notably, the use of bidentate ligands, such as β-ketoiminates and ethanolamine ligands resulted in more stable molecules that can serve as effective precursors.[1] In this study, we present the synthesis, and potential applications of β-ketoiminate and ethanolamine aluminium precursors, whilst retaining a reasonable shelf-life. Compounds of the type [$AlL_3$] have been synthesized from trimethylamine alane (TMAA) with the β-ketoiminate ligands.[2] The reaction of $LiAlH_4$ with the $\beta$-ketoiminate resulted in [$AlL_3$], Li-cages[3] and chelated aluminates.[4,5] Additionally, using TMAA and ethanolamine formed [$L_3(L'Al)_3Al$]. To date, these reactions have been applied to L = $^t$Bu-acnac, Ph-acnac, Me-acnac, L', and L"= N, N-$(Me)_2$ ethanolamine (Figure 1). These reactions have been explored with different ratios between the starting materials, revealing exciting results.

**Keywords**: precursors; aluminium; $\beta$-ketoiminate; decomposition; deposition.

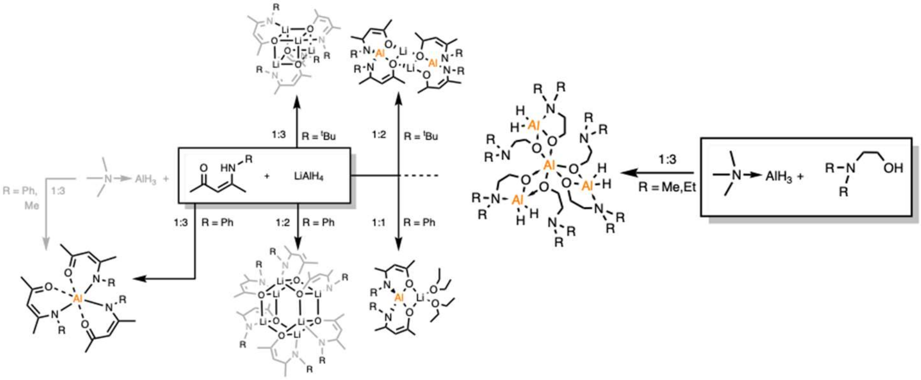

Figure 1. Reactions scheme: $\beta$-ketoiminate Ligands (Left) vs. Ethanolamine Ligands (Right) with Aluminium

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# Synthesis of linear trialumane and unsymmetrical dialumane using Al anion

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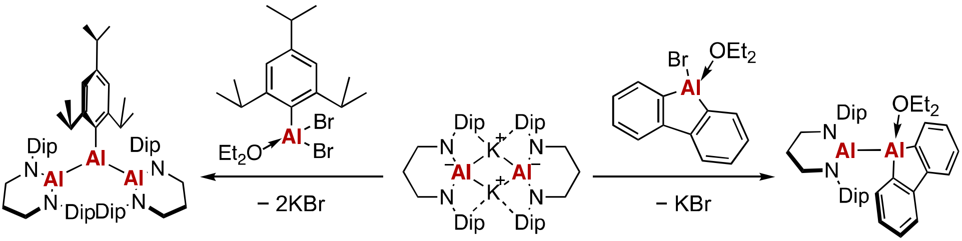
Catenation is a term that refers to a property of an element to form the linear linkage of bonds between identical elements. It is a common phenomenon for group 14 elements as found in polyolefins and polysilanes. In contrast, no linear aluminum linkage with three or more aluminum atoms has been reported. In molecular chemistry of aluminum, three methods have been known to construct Al-Al bonds: (1) reduction of Al-H or -halogen bonds;[1] (2) insertion of alumylene, neutral Al(I) species, into the Al-halogen bond;[2] (3) generation of neutral CpAl species and its spontaneous oligomerization to form Al clusters.[3] Recently, the first nucleophilic Al anion was reported to initiate a rapid advance in chemistry of Al nucleophiles.[4] Herein, we report the synthesis of dialumane and trialumane using our newly reported amino-substituted Al anion[5] and electrophilic aluminum reagents.

A linear trialumane was synthesized by reaction of our amino-substituted Al anion with $TipAlBr_2\cdot OEt_2$ (Tip = $2,4,6\text{-}{}^{i}Pr_3C_6H_2$) (Scheme 1, left). Following the same strategy, we synthesized an unsymmetrical dialumane by reaction of the Al anion with *Al*-bromoaluminafluorene-ether complex (Scheme 1, right). In the presentation, the synthesis, structure, and reactivity of the resulting alkyl-, aryl substituted trialumanes and the unsymmetrical dialumane will be discussed.



Scheme 1. left: Synthesis of trialumane, right: Synthesis of unsymmetrical dialumane

**Keywords**: aluminum; dialumane; trialumane; catenation

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# Square-Planar Anionic Pt(0) Complexes Stabilized by Z-type Borane Ligand

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Anionic M(0) complexes (M = Group 10 metals) are widely recognized as key intermediates in versatile catalytic cross-couplings. Nonetheless, such complexes to be characterized and/or isolated remain limited, and only anionic Ni(0) and Pd(0) species have been authenticated essentially.[1] This is probably attributed to the higher Lewis basicity of Pt(0), which hampers the isolation of such anionic electron-rich zerovalent complexes. Z-type ligands are useful for stabilizing low-valent electron-rich complexes. In this study, a coordinatively unsaturated T-shaped Pt→borane complex **1** was synthesized as an appropriate precursor for anionic Pt(0) complexes in two steps, ie the reaction of diphosphine-borane DPB with Pt(II) precursor (COD)PtCl$_2$, followed by reduction with LiHBEt$_3$ (Figure 1). The coordination of the borane moiety to Pt is expected to enhance its electrophilicity, and we studied the addition of anionic ligands such as CN$^-$, Cl$^-$, Br$^-$, and I$^-$ in the presence of 18-crown-6. Gratifyingly, the corresponding anionic Pt complexes [(DPB)PtX][K(18-crown-6)] (X = CN(**2**), Cl(**3**), Br(**4**), I(**5**)) were readily obtained in good yields, and X-ray diffraction analysis on **2**-**5** revealed the first anionic Pt(0) structure.[2] X-ray photoelectron spectroscopy (XPS) and DFT calculations unequivocally authenticated **2**–**5** as d$^{10}$ Pt(0) complexes.

**Keywords**: platinum; borane; anionic complex; Z-type ligand; palladium

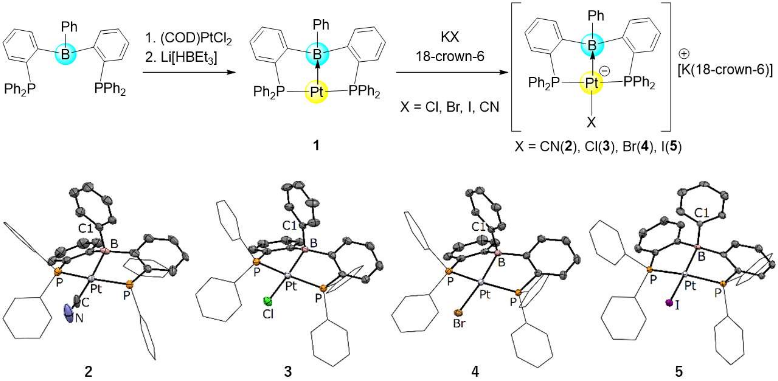

**Figure 1.** Synthesis and structures of anionic Pt(0) complexes (the cation parts were omitted for clarity)

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# Tunable imidazole-benzimidazole-based electrocatalysts for oxygen reduction reaction (ORR) in water

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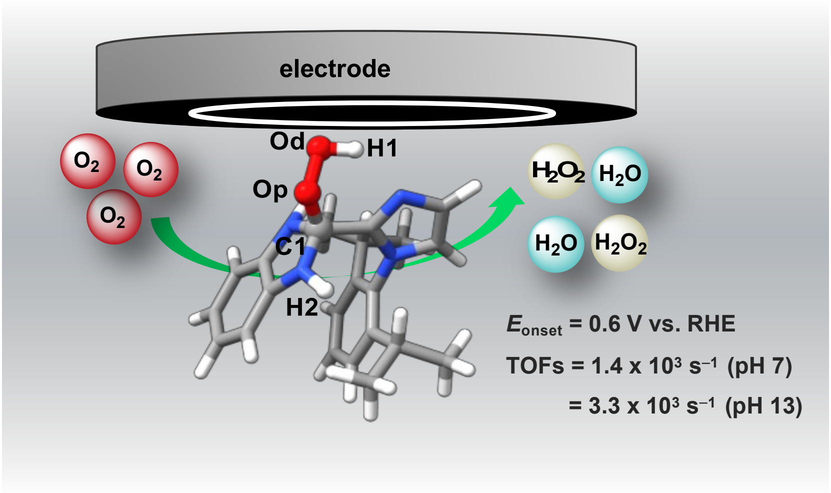
A series of redox-active metal-free imidazole-benzimidazole-based electrocatalysts with different substituents (ImBenz-H, ImBenz-$NO_2$, and ImBenz-$OCH_3$) were successfully synthesized through Cu-catalyzed oxidative C–N cyclization for tunable catalytic activity of oxygen reduction reaction (ORR) in aqueous media. All ImBenz catalysts demonstrated ORR catalysis with high onset potentials ($E_{onset}$), approximately 0.63 and 0.65 V vs. RHE in pH 7 PB and pH 13 KOH solutions, respectively. ImBenz-$NO_2$, featuring an electron-withdrawing group exhibited remarkable selectivity for $H_2O$ production through the 4-electron ORR pathway in a neutral condition. On the other hand, the highest 2-electron ORR selectivity for $H_2O_2$ production was catalyzed by ImBenz-H under alkaline condition. The ORR kinetics study using FOWA indicated that ImBenz-H yields the highest turnover frequencies (TOFs) around $10^3$ $s^{-1}$ in both pH. In addition, the DFT calculation disclosed the redox-active properties of imidazole-benzimidazole catalysts influencing the binding of $O_2$ molecules to produce $H_2O_2$ as a first product.



**Keywords**: benzimidazole; oxygen reduction reaction; metal-free electrocatalyst; redox-active; electrocatalysis

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# Organometallic Chemistry (OR)

# Abstract

**Keynote Speaker**
**OR-K-01**
**Yi-Chou Tsai**

# Catalyst-free [2+2+2] and [2+2+1] Cycloaddition Reactions Involving an Mo−Mo Quintuple Bond

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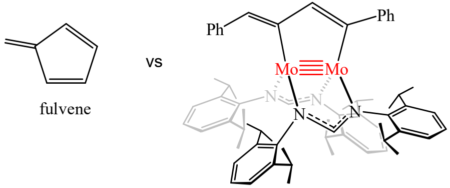
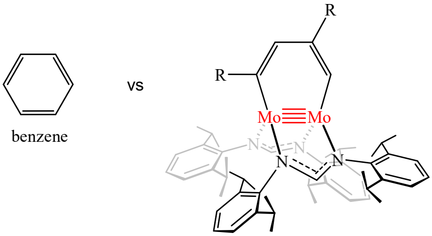
Since the prediction of metal-benzenes in 1979, metallaromatic chemistry has developed rapidly and is of great importance in both experimental and theoretical fields. Metallaromatic compounds contain one metal atom and mainly comprise six major types: metallabenzenes, metallabenzynes, heterometallaaromatics, dianion metalloles, metallapentalenes and metallapentalynes, and spiro metalloles.[1] These unique systems not only enrich the large family of aromatics, but also broaden and extend our understanding of the concept of aromaticity. For the first time, we reported that the amidinate-supported quintuply bonded dimolybdenum complexes $[Mo_2\{HC(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}_2]$ (**1**) are excellent synthons for the construction of a new type of metallaromatic compounds comprising a $C_4Mo_2$ six-membered aromatic ring produced from **1** and terminal alkynes via the [2+2+2] cycloaddition reactions.[2] In addition, **1** undergoes three-component [2+2+2] cycloaddition reactions with two different alkynes. The unusual [2+2+1] cycloaddition involving **1** and two equivalents of terminal alkynes will be presented as well.





**Keywords**: [2+2+1]; [2+2+2]; cycloaddition; catalyst-free; metal−metal quintuple bond

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**Keynote Speaker**
**OR-K-02**
**Hisako Hashimoto**

# Synthesis and properties of transition-metal complexes featuring M≡Si triple bonds

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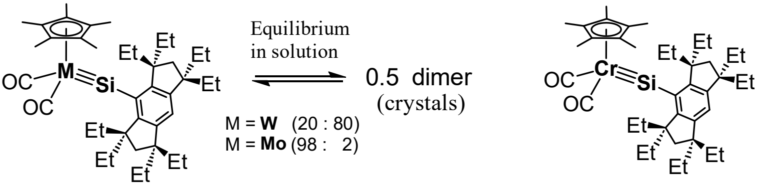
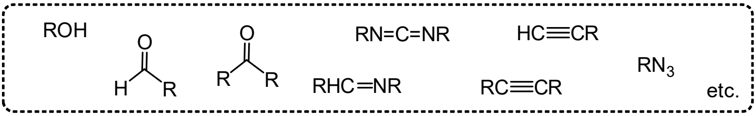
The molecular design based on kinetic stabilization as well as development of various synthetic methods have brought a great progress in the chemistry of tetrylyne complexes featuring triple bonds between a metal and a heavier group 14 element (Si, Ge, Sn, and Pb), which have been challenging synthetic targets for many years.[1] Interest of these complexes is associated with their relationship to carbyne complexes with M≡C bonds, which are utilized for organic synthesis. Thus, the reaction chemistry of tetrylyne complexes is of current interest.

Our group have succeeded in synthesizing metal-germanium and -silicon triple bonded complexes and revealed their structures and peculiar reactivities. In this presentation, I would like to show our recent work, focusing on silylyne complexes of Group 6 metal (W, Mo, Cr) featuring M≡Si triple bonds.[2] Our study includes synthesis, structures, bonding analysis, as well as nucleophilic addition and cycloaddition reactions with various unsaturated organic substrates (aldehydes, ketones, carbodiimide, imines, alkynes, organic azides, etc.)



*Reactivity toward:*



**Keywords**: metal-silicon triple bond; silylyne complex; nucleophilic addition; cycloaddition

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**Keynote Speaker**
**OR-K-03**
**Andy Hor**

# Coordination Chemistry in Asia – Progress, Promise, Potential and Perspectives

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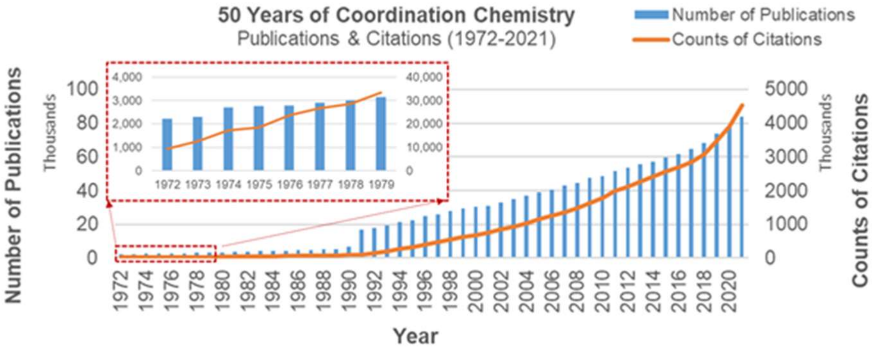
Coordination Chemistry has evolved over nearly six decades from a field of predominantly academic interest (Ref 1 and Figure below) to one that serves as the bedrock of a number of global challenges and industrial revolutions; these stretch from climate change to Industry 4.0 to healthcare in an urbanized society. The field has been advancing in varying paces and directions in Asia, depending on many factors, such as research funding, society needs, industry challenges, institutional strategies, capacity building, talent demands and drivers from intersecting areas. In this lecture, we shall take a deeper dive to analyse the advent of coordination chemistry in different systems, highlight areas of synergy and potential of collaboration among Asian countries, as well as that with the global community. We shall also take this opportunity to propose areas of future growth and new research opportunities for coordination chemists.



**Keywords**: Coordination chemistry; metal complexes; challenges; opportunities; development

## References

1. Manual analysis of over 1.45 million publications using Web of Science @ Clarivate.

**Keynote Speaker**
**OR-K-04**
**Han Vinh Huynh**

# Donor strength determination of anionic ligands

Han Vinh Huynh

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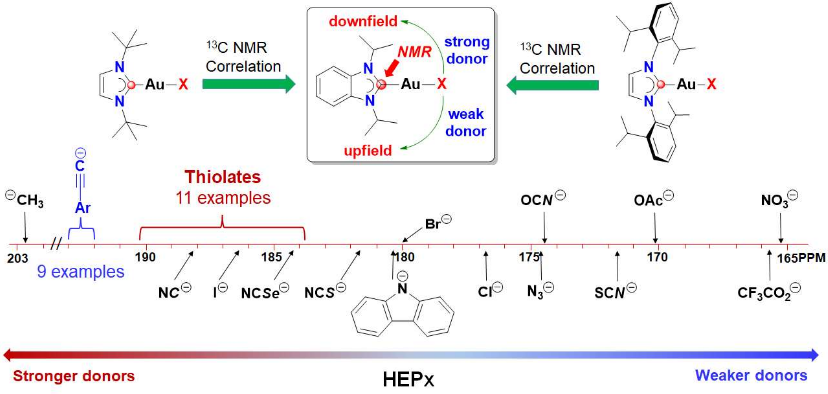
It is well accepted that ligands have an innate influence on the activities and properties of metal complexes. The donors' impact can be traced back to a unique combination of their steric and electronic factors. To understand and systematically tune the reactivities of metal complexes for specific applications, it is therefore important to know these factors. Common methodologies for the experimental determination of ligand donor strength include the $Ni^0$-carbonyl based Tolman electronic parameter (TEP), its $Rh^I$ and $Ir^I$ variants, and the Huynh electronic parameter (HEP). TEP has found widespread use in organometallic chemistry for the evaluation of phosphines, NHCs and related ligands using IR spectroscopy, while HEP employs $^{13}C$ NMR spectroscopy of Pd-NHC complexes and can be applied across many different ligand families on a truly unified scale.[1] However, most monodentate ligands on both scales are formally charge-neutral, while anionic X-type ligands have essentially been left out. In general, attempts to parametrize anionic ligands are rare. Here, we demonstrate that the donating abilities of anionic ligands can be easily determined by $^{13}C$ NMR spectroscopy of [AuX(NHC)] complexes akin to the workings of the HEP.[2] The application and versatility of this new 'HEPx' methodology is demonstrated with several anionic ligands.



**Keywords**: ligands; donor strength; anions; gold; NMR spectroscopy

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# Recent Advance on the Chemistry of Low-Coordinate Low-Valent Transition-Metal Complexes with NHC Ligation

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The knowledge on the formation, structure, and reactivity of low-coordinate 3d metal species forms the basis for the development of new 3d metal-catalyzed organic transformations and also disclosing the mysterious mechanisms of enzymatic catalysis and "single-atom" catalysis. Aiming to deepen our knowledge on this type of reactive metal species, we have been working on the chemistry of low-coordinate zero-valent cobalt, iron and manganese complexes with N-heterocyclic carbene (NHC) and olefin ligation for years. This ligand set is found effective in stabilizing three-coordinate cobalt(0, -I), iron(0, -I), and manganese(0) complexes in the forms of $[(NHC)M(olefin)_2]^{0,1-}$. In this presentation, the synthesis, electronic structure, and reactivity of the three-coordinate zero-valent metal complexes, as well as their synthetic applications in new metal complexes, will be discussed. [1-4]

**Keywords**: cobalt; iron; palladium; N-heterocyclic carbene; imido

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**Invited Speaker**
**OR-I-02**
**George A. Koutsantonis**

# Molecular photochromes for modulating single-molecule conductance

George A. Koutsantonis
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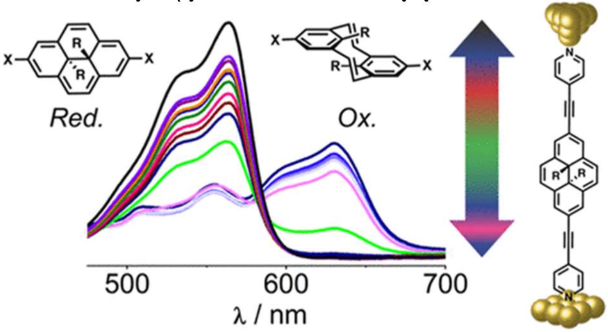
The semiconductor industry's ability to scale silicon-based transistors has been a technological constant,[1] with each new generation of integrated circuits exponentially outperforming the previous generations. With the shrinking of transistor gate length from 10 μm to 3 nm and increasing clock speeds from MHz to the GHz regime allowing more and faster transistors to be exploited on a single chip. The delicate feedback cycle in the semiconductor industry to progress this transistor scaling, linking the miniaturisation of transistors to further investments is facing challenges that could interrupt the constant of Moore's Law. Molecule-scaled electronics uses materials assembled from atoms and molecules and has been touted as a potential solution to problems associated with current CMOS technology.

Controlling the transition between different conductance states of single-molecule junctions is a coveted functionality. Stimuli, including chemical,[2] electrochemical,[3,10] mechanical,[2] and light,[10] have been used to switch the conductance of single-molecule junctions.
In this presentation I will discuss our efforts to use molecular photochromes to modulate single-molecule conductance through a variety of stimuli. We have explored both dihydropyrenes and spiropyrans incorporating them into organic and organometallic scaffolds for conductance measurement in single molecule junctions. These have undergone considerable evolution through iterations of molecular structure.

**Keywords**: Photochromes; Dihydropyrenes; Ruthenium alkynyls; molecular conductance



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# Dinuclear chromium complexes of dinitrogen, arene, and $Cr_2$ quintuple bond enabled by a bulky alkyl ligand

Po-Chun Yang[1], Hsin-Kuan Liu[2], Chun-Yi Lin[1*]

[1]*Department of Chemistry, National Cheng Kung University, Tainan, Taiwan*
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Low-coordinate transition metal complexes are pivotal in advancing our understanding of magnetic properties, small molecule reactivities, and catalytic activities.[1,2] In this study, we report a dimeric square planar Cr(II) halide complex supported by a new bulky alkyl ligand. Upon chemical reduction by a strong reducing agent under a dinitrogen atmosphere, we obtained a low-oxidation state, dinuclear Cr dinitrogen complex.[3] Interestingly, an intermediate was observed prior to the formation of the dinitrogen complex. When the reaction was conducted under an argon atmosphere in a benzene solution, an inverted sandwich dichromium complex was formed, which gradually converted to the dinitrogen complex under a dinitrogen atmosphere. Remarkably, a complex containing a Cr-Cr quintuple bond[4] was isolated when the reduction reaction was performed in a tetrahydrofuran solution. We also discovered that the Cr dinitrogen complex and the inverted sandwich dichromium complex could convert to the quintuple bond dichromium complex. The relationship and relative stability between these complexes were elucidated through multiple spectroscopic experiments, the results of which will be discussed in this presentation. Our findings provide valuable insights into the behavior of low-coordinate transition metal complexes and have potential implications for their use in various chemical applications.

**Keywords**: alkyl ligand; chromium; dinitrogen ligand; arene ligand; quintuple bond

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**Invited Speaker**
**OR-I-04**
**Michel WONG CHI MAN**

# Organosilane precursors for silsesquioxane-based hybrid materials

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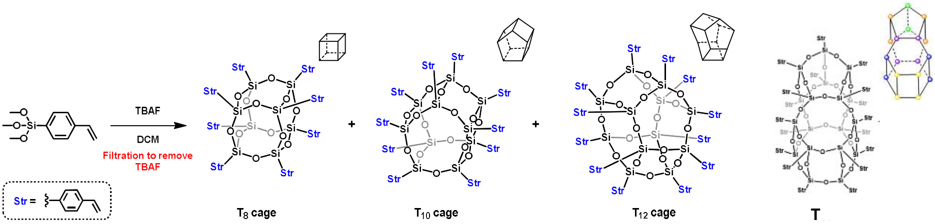
A wide variety of organosilane precursors, typically trialkoxysilylated organics [$(RO)_3SiR'$, $R=CH_3$, $C_2H_5$; R'= organic moiety] are commercially available and commonly used for many applications such as coating/protecting layers on surfaces, flame retarding, catalysis, optics, etc… They can also be hydrolyzed to produce cage compounds known as POSS cages (PolyhedralOligoSilSesquioxanes). POSS consists of a well-defined polyhedral core [$(SiO_{1.5})_n$,$T_n$] (see Graphical Abstract below) surrounded by organic functions which are covalently bonded to the silicon atoms found at the vertices of the cage. We have synthesized and characterized a whole family of styryl-functionalized POSS compounds ($T_8$, $T_{10}$, $T_{12}$ and $T_{18}$, consisting respectively of 8, 10, 12 and 18 silicon atoms).[1,2] The latter ($T_{18}$) is the largest POSS cage isolated pure to date. Moreover a fluoride anion is known to be specifically sequestered in the $T_8$ cage. We have prepared the corresponding styryl-functionalized $T_8F$ cage and investigated its properties.[3] The multinuclear NMR studies (liquid and solid state) demonstrate for the first time a fluxional interaction between the fluoride anion and the 8 silicon atoms. Some of these cages have been post-functionalized with peripheral triethoxysilyl groups which allows subsequent polymerization to form hybrid silica materials. The hydrolysis-condensation of these trialethoxysilylated-POSS leads to silsesquioxane-based materials.[4,5]



**Keywords**: organosilane precursors; sol-gel; silsesquioxane; hybrid silica; POSS

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Invited Speaker
OR-I-04
Michel WONG CHI MAN

# Synthesis, Structure, and Properties of Aluminum-Early Metal Complexes

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Aluminum contains three valence electrons and is the most electropositive element in the p-block. Examples of synthesizing transition-metal complexes with a three-coordinated aluminum ligand remain limited. They can be classified to the following methods: (a) A nucleophilic attack of anionic transition-metal complexes to an aluminum electrophile,[1] (b) the coordination of a base-stabilized Al(I) species to a metal,[2] (c) elimination of alkane via a metathesis reaction,[3] (d) an oxidative addition of an Al–H bond to a metal center in a low oxidation state,[4] (e) insertion of Al(I) species into a metal-halogen bond,[5] and (f) transmetallation of the Al anions to metal halides.[6] In the presentation, our latest contribution to the chemistry of early transition metal-aluminum complexes[7] will be discussed.

**Keywords**: aluminum; early transition metal; metal-metal bond; catalysis

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Invited Speaker
OR-I-05
Lan-Chang Liang

# Organometallic chemistry of complexes containing mismatched donor-acceptor pairs

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Ligand design plays an important role in exploratory research on contemporary organometallic chemistry and catalysis. This presentation describes the origin and accumulative development of PNP amido phosphine complexes and their isoelectronic analogues constructed with an *o*-phenylene backbone.[1] With the incorporation of both soft and hard donors in the hybrid ligands, these complexes are inherently characteristic of having mismatched donor-acceptor pairs. Complexes containing ligands having meridional and facial coordination modes (Figure 1) are exemplified with their physical preferences and chemical activities in bond-forming and bond-breaking transformations. The effects of P-substituents and ligand backbones of these complexes on reaction and structural chemistry are presented.

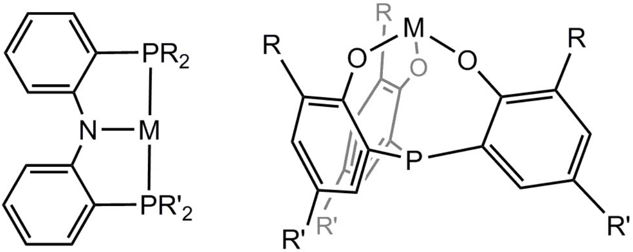

Figure 1. Representative examples of *o*-phenylene derived hybrid ligands

**Keywords**: HSAB; transition metal; main group metal; olefin insertion; b-hydrogen elimination

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**Invited Speaker**
**OR-I-06**
**Swadhin K. Mandal**

# Abnormal N-Heterocyclic Carbene: Organometallic chemistry to metal-free catalysis

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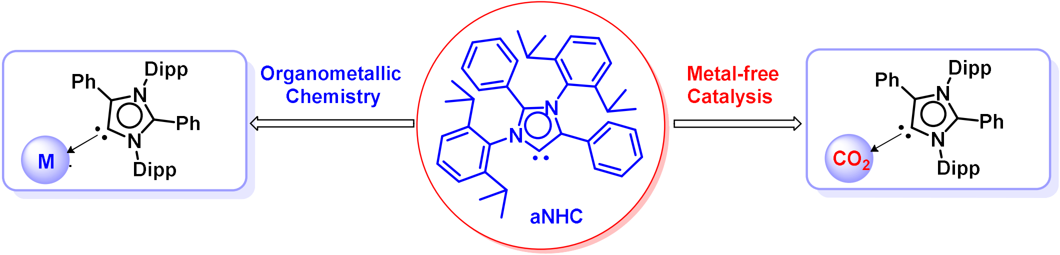
N-heterocyclic carbenes (NHCs) have attracted a great deal of attention as ligands for organometallic chemistry since Arduengo *et al.* reported their isolation in 1991.[1] In 2009, Bertrand and coworkers isolated a new class of NHC known as abnormal NHC, in which the carbene centre was generated between N and C atoms by blocking the C-2 position of an imidazolium salt.[2] Over the last decade, we have used this isolated aNHC as a building block for designing a range of organometallic catalysts employing various earth-abundant and main group elements.[3] In recent efforts,[4-10] we have shown that the aNHC and its derivatives successfully accomplished the metal-free catalytic functionalisation of chemically inert primary amides and thiols using $CO_2$. This talk will showcase our recent efforts on how this new class of isolated abnormal NHC has emerged as a spectacular building block for designing organometallic as well as metal-free catalysts for a number of very important organic transformations.



**Keywords**: abnormal carbene; $CO_2$ activation; catalysis; organometallics; metal-free

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**Invited Speaker**
**OR-I-08**
**Jianfeng Zhang**

# 4-Phosphorylpyrazolones as tunable receptors for the coordination of s- and f-block elements

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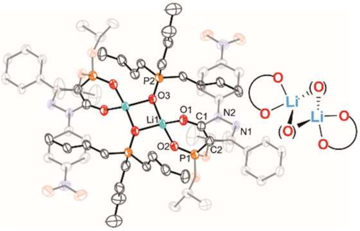
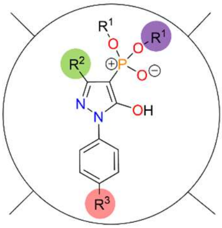
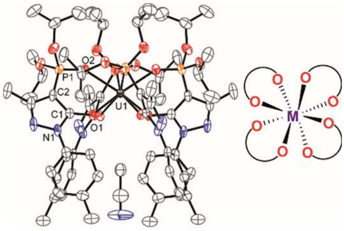
In order to develop highly tunable and selective chelating agents for various metal cations, 4-phosphorylpyrazolones as a new type of ligands were synthesized and employed as the selective receptors for the coordination and separation of s- and f-block elements. The steric requirements, lipophilicity, bite size between the chelating O-donor atoms and the electronic properties can be tuned by changing the substituents $R^1$, $R^2$ and $R^3$.[1-4]



**$[Li_2(L)_2(TBPO)_2]$ complex**



**Ligands (HL)**



**$[U(L')_4]\cdot CH_3CN$ complex**

The structure-function relationships were clearly elucidated using various characterization techniques, such as X-ray, NMR, EXAFS etc., and extraction performance studies. Structural analysis of complexes revealed different coordination modes including monomer, dimer and trimer as well as the strong binding ability of ligands towards various elements, such as lithium, lanthanum, europium and uranium.[1-4] Liquid-liquid extraction results demonstrated that these pH-regulated receptors are promising extraction reagents for the selective separation of lithium from acidic brines and rare earth elements from ores. The studies performed in this work provide a fundamental yet more comprehensive understanding, ranging from the synthesis of 4-phosphorylpyrazolone ligands to their practical applications from an industrial perspective.

**Keywords**: 4-phosphorylpyrazolones; pH-regulated receptor; structure-function relationships; lithium recognition; rare earth separation

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# Surface Organometallic Chemistry for Single-atom Catalysis

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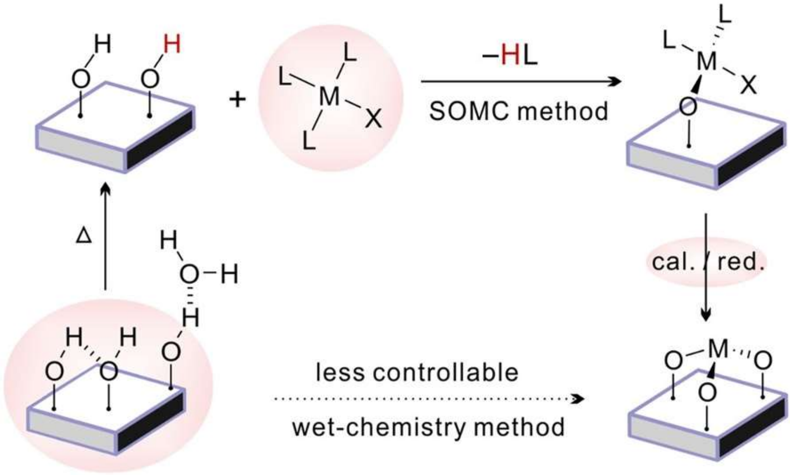
Although extensive efforts have been made to bring homogeneous and heterogeneous catalysis closer, the gap between these two research fields still stands. Surface organometallic chemistry (SOMC) method has been developed along with organometallic chemistry and surface science from the 1970 s. We showed that applying SOMC on single-crystalline MgO(111) two-dimensional nanosheets is an ideal way to prepare single atom catalysts with uniform catalytic sites with identical coordination structures, for fundamental interests. The single crystallinity of the support, the exposed ordered crystalline planes and the SOMC method are ideally suited to minimize the surface heterogeneity for anchoring atomically dispersed species.



**Keywords**: Surface organometallic chemistry; Single-atom catalyst; Single-site catalyst; Atomically dispersed catalyst; Surface coordination structure

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# Thermolysis of $Ru_3(CO)_{10}$(μ-dppp): A New $Ru_4$- Cluster Derived from 1,3-Bis(diphenylphosphino)propane

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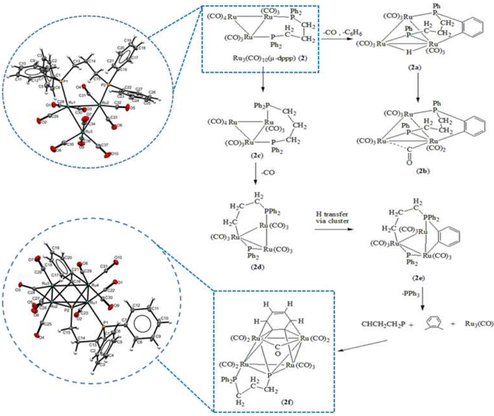
The reaction of $Ru_3(CO)_{12}$ and dppp [dppp = 1,3-bis(diphenylphosphino)propane/ $Ph_2PCH_2CH_2CH_2PPh_2$] with the present of benzophenone ketyl radical afforded $[Ru_3(CO)_{11}]_2$(μ-dppp) (**1**) $Ru_3(CO)_{10}$(μ-dppp) (**2**), $Ru_3(CO)_9$(μ-dppp)($\eta^1$-dppp) (**3**) and $Ru_3(CO)_8(\mu\text{-dppp})_2$ (**4**). Refluxing **2** in octane yields new triruthenium clusters $Ru_3(CO)_9(\mu_3\text{-}PPhCH_2CH_2CH_2PPh(C_6H_4))$ (**2b**) and $Ru_4(CO)_9(\mu\text{-}CO)\{\mu_4\text{-}\eta^2\text{-}PCH_2CH_2CH_2PPh_2\}(\mu_4\text{-}\eta^4\text{-}C_6H_4)$ (**2f**) as a result of P–C and C–H bonds activation involving the $Ph_2PCH_2CH_2CH_2PPh_2$ ligand. However, only compounds **2** and **2f** have been structurally determined by single crystal X-ray diffraction. As expected, the $Ph_2PCH_2CH_2CH_2PPh_2$ ligand in **2** equatorially bonded to Ru-Ru bond in $\mu_2$-$\eta^2$ mode. In contrast, the X-ray structure of **2f** shows an $\mu_4\text{-}\eta^2\text{-}PCH_2CH_2CH_2PPh_2$ and a benzyne group coordinated to a square of Ru atoms. A rotation of benzyne group on a square of Ru atoms was supported by variable temperature NMR studies. The topological analysis was performed on **2f** to further elucidated their chemical bond properties.



**Keywords**: tetraruthenium cluster; triruthenium; benzyne; diphosphine; topological analysis

# Synthesis of 1,3,5-trisubstituted benzenes from alkynes with bis(indolyl)-ligated Ti-amido catalysts

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Transition-metal-catalyzed alkyne cyclotrimerization is an efficient tool for the synthesis of multisubstituted benzenes.[1] When the substrates are terminal alkynes, in principle, two regioisomers (1,2,4- and 1,3,5-trisubstituted benzenes) are formed. The 1,2,4-isomer is often the major product of the cyclotrimerization reactions of terminal alkynes, and numerous reactions that selectively yield the 1,2,4-isomers are known (Figure 1, left). On the other hand, the methods to obtain the 1,3,5-isomers are still rare.[2]

We have previously studied the organometallic chemistry of titanium and zirconium complexes supported by a deprotonated 2,2'-bis(indolyl)methane (henceforth: bis(indolyl)).[3] In these works, the 1,3,5-favored cyclotrimerization reaction of trimethylsilylacetylene using a catalytic system composed of a bis(indolyl)-coordinated titanium dichlorido complex and magnesium is included.[3b] In the present study, we found the corresponding diamido complexes can be promising catalyst precursors to synthesize the 1,3,5-trisubstituted benzenes from terminal alkynes (Figure 1, right). Arguably the most interesting aspect is that the catalyst precursors can adapt to halogen-substituted terminal alkynes (e.g. 1-chloro-4-ethylnylbenzene), as the 1,3,5-trisubstituted benzenes derived from these alkynes are expected to be precursors for further functionalization by cross-coupling reactions.

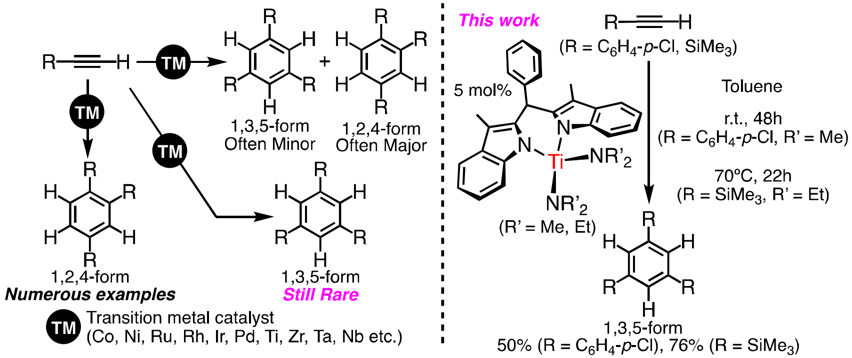

Figure 1. (Left) Current state of transition-metal-catalyzed cyclotrimerization of terminal alkynes. (Right) Synthesis of 1,3,5-trisubstituted benzenes from terminal alkynes by using bis(indolyl)-coordinated titanium diamido complexes as catalyst precursors.

**Keywords**: Titanium complex; Homogeneous catalyst; Cyclotrimerization; Alkyne; Regioselectivity

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# Spatial Immobilization of Photocatalysts and Enzymes on Biocompatible Nanosheets for Efficient $CO_2$ Conversion

**Jinheung Kim**

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Artificial photosynthetic systems composed of photocatalysts and enzymes are a notable framework for converting $CO_2$ to high value chemicals. However, catalyst and enzyme deactivation, poor electron transfer kinetics in multi-step photochemical processes, and non- biocompatible substrates severely limit their catalytic efficiencies. In this study, biocompatible DNA nanosheets (NSs) composed of two different DNA sequences on each face were utilized as a support for selective immobilization of a Rh complex and formate dehydrogenase (FDH) for concerted catalytic reactions for $CO_2$ reduction. Based on the unique face-selectivity, DNA-conjugated Rh complex and FDH were immobilized on NSs into four different configurations. The catalytic system exhibited $CO_2$ conversion efficiencies highly dependent on the spatial organization of Rh complex and FDH, showing the reactivity for the formate production in the order of Rh complex on NS (NS1) coupled with free FDH > Rh complex and FDH on opposite faces of NS (NS3) > FDH on NS (NS2) coupled with free Rh complex > FDH and Rh complex on the same face of NS (NS4) > free Rh complex and FDH. The NS1 coupled with free FDH showed turnover number (TON) of 1,360 for the formate production based on $NAD^+$, which is the highest value reported thus far for Rh-based photocatalyst/enzyme coupled systems. The results demonstrate that the well-organized immobilization of photocatalysts and biological enzymes is a viable approach for improving the efficiency of $CO_2$ conversion and provide important design directions for building efficient artificial photosynthetic systems.

**OR-O-05**

**Ching Tat To**

# Silicon-hydrogen bond activation of hydrosilanes with perfluoroalkyl rhodium porphyrin complexes

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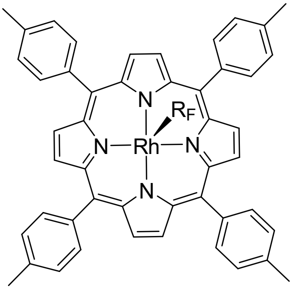
The activation of hydrosilanes with transition metal complex is fundamental to access upgraded organosilane products via the cleavage of silicon-hydrogen bond. In most cases, the interaction of hydrosilane with transition metal leads to oxidative addition process and the formation of a silyl metal species.[1]

Previously, our group has reported the synthesis of the first family of perfluoroalkyl rhodium(III) porphyrin complexes, $Rh^{III}(ttp)R_F$.[2] It was found that these complexes can cleave the silicon-hydrogen bond in hydrosilanes, $R_1R_2R_3SiH$, to yield the corresponding silyl rhodium(III) complexes, $Rh^{III}(ttp)SiR_1R_2R_3$. The organic co-product hydrofluorocarbons, $R_FH$, have been detected. Mechanistic studies suggested the Si-H bond cleavage process was dependent on the perfluoroalkyl ligand. A dual mechanistic pathway involving a direct □-bond metathesis and a prior □-F elimination has been proposed.

$$Rh^{III}(ttp)R_F + \underset{\text{75 equiv}}{R_1R_2R_3SiH} \xrightarrow[\text{benzene}]{120\ ^{o}C\text{, air}} \underset{\text{43-98\%}}{Rh^{III}(ttp)SiR_1R_2R_3} + R_FH$$



$Rh^{III}(ttp)R_F$

$R_F = {}^{n}C_3F_7, {}^{i}C_3F_7, CF_2C_6F_5$

**Keywords**: silicon-hydrogen bond activation; perfluoroalkyl; rhodium; reaction mechanism

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**Oral Presentation**
**OR-O-06**
**Claudia P. Giarrusso**

# Lewis base alterations of Ag(I) complexes and their catalytic potential

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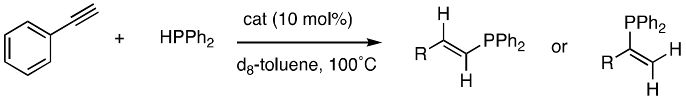
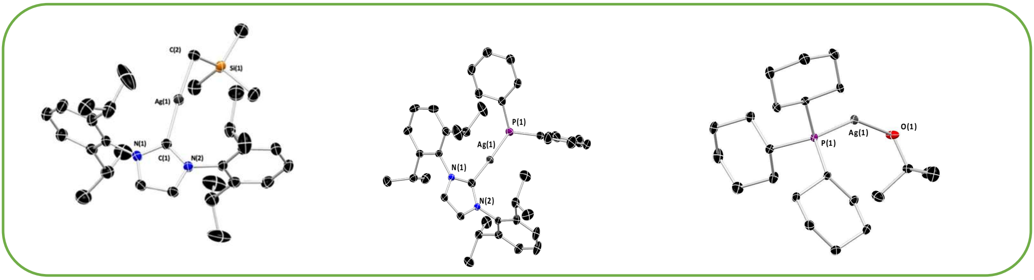
Interest in the use of silver in catalysis has increased tremendously over the past few decades, owing to silvers low cost, selectivity, and low toxicity in comparison to other late transition metals.[1,2] The synthetic versatility and application of N-Heterocyclic carbene (NHC) and phosphine stabilised Ag(I) complexes has since been assessed against a wide range of catalytic and organic transformations including hydroboration, hydrosilylation, $A^3$ coupling, alkynylation, $CO_2$ insertions and cyclisation reactions.[3-9]

Previous studies by the Blair group highlighted the catalytic potential of NHC and phosphine stabilised Ag(I) amido complexes in both the hydroboration and hydrosilylation of carbonyls.[6,7] Encouraged by these studies and seeking to improve upon our previously reported pre-catalysts. We now report the synthesis and characterisation of three Ag(I) complexes with alternating Lewis bases ($CH_2SiMe_3$, $PPh_2$ and $O^tBu$), alongside substrate screenings of these potential pre-catalysts in hydrofunctionalisation reactions (Figure 1).





**PRE-CATALYSTS**

**Keywords**: silver; catalysis; hydrophosphination; solid state

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# Photoinduced H–H and C–H bond activation by a Cr≡Si triple bonded complex

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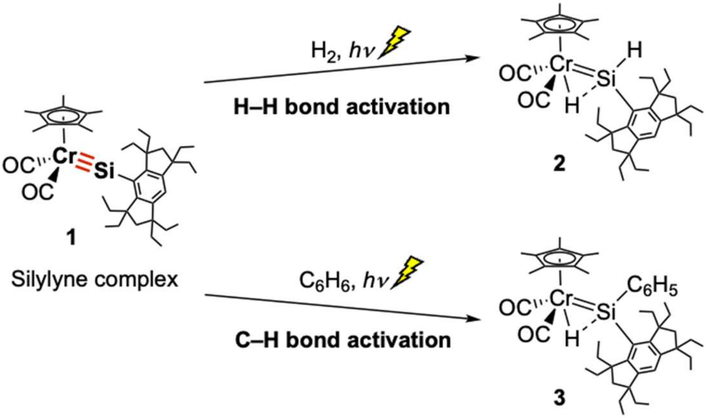
Inspired by important performance of carbyne complexes in organic synthesis,[1] analogous complexes with triple bonds between metal and heavy congeners of carbon (Si, Ge, Sn, Pb), called as tetrylyne complexes, have attracted great attention over the last two decades.[2] Indeed, tetrylyne complexes have been increasingly synthesized and their unique properties including reactions with unsaturated organic substrates have been extensively investigated.[2,3] However, activations of inert bonds such as H–H and C–H bonds using silylyne complexes have not been reported up to now.

In this study, we demonstrate that neutral chromium–silicon triple bonded complex **1** underwent H–H and C–H bond activation. Complex **1** reacted with atmospheric $H_2$ under 365 nm LED irradiation to afford a hydrido(hydrosilylene) complex **2**. In a similar way, **1** also reacted with a benzene to give a hydrido(phenylsilylene) complex **3**. The formation of **3** indicates the occurrence of C–H bond activation of benzene during the reaction. It is notable that silylyne complex **1** bearing generally electron-poor 3d metal, chromium, enables these difficult reactions.



**Keywords**: chromium; silylyne complex; C–H bond activation; photoreaction; dihydrogen

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**Flash Presentation**
**OR-F-02**
**Keita Sato**

# NHC-stabilized hydroaluminylene complexes of tungsten and iron: synthesis and characterization

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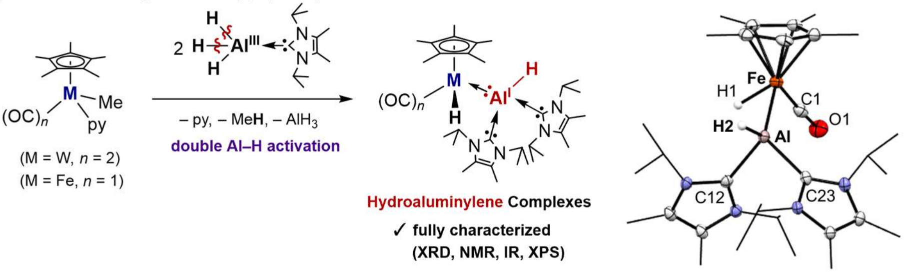
Transition-metal complexes ligated by aluminylenes (:AlR), monovalent species of earth-abundant aluminum, have attracted considerable attention due to unique M–Al bonding characters and expected reactivity based on the strong s-donating and Lewis acidic properties of the :AlR ligands.[1] However, these complexes are thermodynamically unstable, and only a limited number of complexes has been isolated. In particular, metal complexes ligated by the simplest hydroaluminylene (:AlH) have remained elusive.[2] This time, we succeeded in synthesizing of base-stabilized hydroaluminylene complexes.

Reactions of half-sandwich methyl complexes with $H_3Al$•NHC (NHC = *N*-heterocyclic carbene) afforded hydroaluminylene complexes $Cp^*(CO)_n(H)M \leftarrow :AlH(NHC)_2$ (**1**: M = W, *n* = 2; **2**: M = Fe, *n* = 1) in 63 and 43% yields, respectively, through double Al–H activation. Complexes **1** and **2** are regarded as the first isolated hydroaluminylene complexes. These complexes were fully characterized by X-ray crystallography (XRD) and multiple spectroscopies (NMR and IR). The CO stretching bands in the IR spectrum of **1** and **2** appeared in lower wavenumber (1711–1782 $cm^{-1}$), which indicates strong s-donating ability of the $:AlH(NHC)_2$ ligand. Moreover, the monovalent oxidation state of the Al center of complexes **1** and **2** was strongly supported by the X-ray photoelectron spectroscopy (XPS).



**Keywords**: monovalent aluminum; aluminylene ligand; tungsten complex; iron complex; X-ray photoelectron spectroscopy; synthesis

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**Flash Presentation**
**OR-F-03**
**Jingyan Wang**

# Low-temperature deposition of conducting copper through design of molecular precursors

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Printed electronics are widely used in various fields, from gas sensors to cloth tagging;[1,2] while conductive ink is a vital factor in enhancing production efficiency and component performance. However, the high processing temperature of inks has limited their industrial usage and application on low-cost flexible substrates. Recent research aims to lower the decomposition temperature of conductive inks during the sintering process.[3] Copper as a cost-effective metal with high conductivity, holds promise for use in printed electronic films.[4] Notably, the use of alkanolamine as a ligand in copper precursors results in a reduction of decomposition temperature and can be formulated into alcohol-soluble inks.[5] In this study, we describe the successful development of two novel copper metal-organic decomposition (MOD) precursors (Figure 1.) that were used as inks for the deposition of highly conductive copper films on flexible substrates. Through the reaction of copper (II) formate with excess alkanolamines, tris-coordinated copper precursor ions: "[$CuL_3$]", each with a formate counter-ion are isolated and their thermal decomposition mass spectrometry profiles are collected to assess their suitability for use in inks. Furthermore, we explored different deposition methods and formed highly conductive copper device interconnects on paper and polyimide substrates.

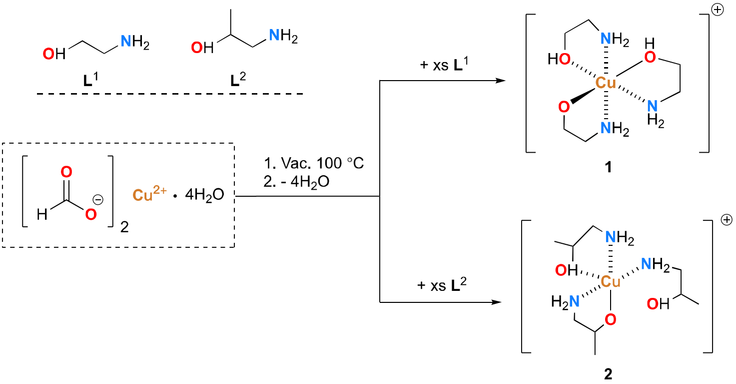

Figure 2 Synthetic routes to compounds 1 and 2. Formate counter ions omitted for clarity.

**Keywords**: precursors; copper; alkanolamine; decomposition; deposition

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**Poster Presentation**
**OR-P-01**
**Junghwan Kim**

# Multicomponent X-ray Shielding Using Sulfated Cerium Oxide and Bismuth Halide Composites

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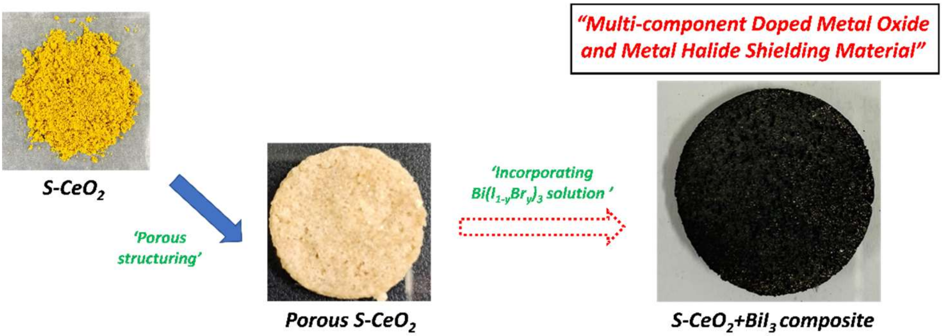
Lead is the most widely used X-ray-shielding material, but it is heavy (density ≈ 11.34 g/cm$^3$) and toxic. Therefore, the replacement of Pb with lightweight, ecofriendly materials would be beneficial, and such materials would have applications in medicine, electronics, and aerospace engineering. However, the shielding ability of Pb-free materials is significantly lower than that of Pb itself. To maximize the radiation attenuation of non-Pb-based shielding materials, a high-attenuation cross-section, normal to the incoming X-ray direction, must be achieved. In this study, we developed efficient X-ray-shielding materials composed of sulfated cerium oxide (S-CeO2) and bismuth halides. Crucially, the materials are lightweight and mechanically flexible because of the absence of heavy metals (for example, Pb and W). Further, by pre-forming the doped metal oxide as a porous sponge matrix, and then incorporating the bismuth halides into the porous matrix, uniform, compact, and intimate composites with a high-attenuation cross-section were achieved. Owing to the synergetic effect of the doped metal oxide and bismuth halides, the resultant thin (approximately 3 mm) and lightweight (0.85 g·cm$^{-3}$) composite achieved an excellent X-ray-shielding rate of approximately 92% at 60 kV, one of the highest values reported for non-heavy-metal shielding materials.



**Keywords**: sulfated; cerium oxides; porous matrix; bismuth halides; X-ray shielding

# Coordination chemistry of rhenium(I) tricarbonyl derived from derivative 2,6-bis(pyrazolyl)pyridines

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Hidehiro Sakurai[2*]

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A novel selective bidentate Re(I) tricabonyl coordination complexes were synthesized by employing based on 2,6-bis(pyrazol-1-yl)pyridine (Bpp) and compared with 2,6-bis(pyrazol-1-yl)pyridine carboxylic acid (BppCOOH), 4-amino-2,6-bis(pyrazol-1-yl)pyridine($BppNH_2$) and 2,6-bis(pyrazol-1-yl)pyridine methyl carboxylate ($BppCOOCH_3$) for investigation effects of electrons with drawing and donating group of Re(I) complexes. Moreover, inquired photoproperties of the triplet metal-to-ligand charge transfer ($^3$MLCT) excited state. This work aimed to prepare the active metal Re(I) tricarbonyl precursors under the photoirradiation. All the obtained complexes were well characterized by the single-crystal X-ray diffraction, Infrared (IR) spectroscopy, Nuclear Magnetic Resonance (NMR), UV-Vis spectroscopy and Phosphorescence. Furthermore, the potential reduction in exhibiting catalytic activity was investigated to facilitate the carbon dioxide reduction.

**Keywords**: Re(I) tricarbonyl complexes, 2,6-bis(pyrazol-1-yl)pyridine, Metal-to-ligand charge transfer excited state.

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# Designer Ligand Scaffolds for Metal-Ligand Cooperative Catalysis

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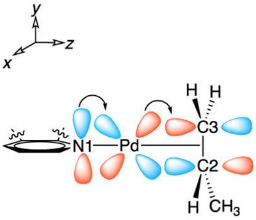
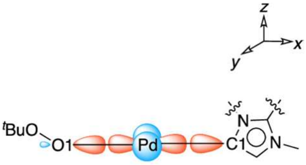
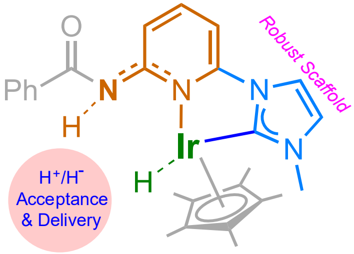
Two donor modules in a ligand with different sigma and pi-bonding characteristics offer prospect for uniting and managing two electronically disparate substrates on a metal center. In this talk, I will provide an orbital perspective on the origin of ligand electronic asymmetry. A Pd(II)-catalyzed Wacker-type oxidation of terminal olefins to methyl ketones will be taken as a test case to highlight the role of the ligand. Proton/hydride management at the ligand/metal assembly for reductive amination of aldehyde and alkylation of ketones will be discussed. Further, new ligand scaffolds that display metal-ligand cooperation will be disclosed.[1-5]



(a) π–corridor



(b) σ–corridor



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# Divalent Cobalt and Nickel Complexes Containing Mono- and Di-anionic Guanidinate Ligands

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Divalent cobalt and nickel complexes supported by monoanionic $[(\mathrm{DippNH})\mathrm{C}(\mathrm{NDipp})_2]^{-}$ $([\mathrm{H}\mathbf{L}^{1}]^{-})$[1] and $[\{(4\text{-}\mathrm{ClC_6H_4})\mathrm{NH}\}\mathrm{C}(\mathrm{NDipp})_2]^{-}$ $([\mathrm{H}\mathbf{L}^{2}]^{-})$ (Dipp = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$), and the corresponding dianionic $[\mathrm{C}(\mathrm{NDipp})_3]^{2-}$ $([\mathbf{L}^{1}]^{2-})$[1] and $[(4\text{-}\mathrm{ClC_6H_4N})\mathrm{C}(\mathrm{NDipp})_2]^{2-}$ $([\mathbf{L}^{2}]^{2-})$ guanidinate ligands, respectively, have been synthesized through metathesis reactions of anhydrous $\mathrm{MCl_2}$ (M = Co, Ni) and lithium salts of the corresponding guanidinate ligands in an appropriate stoichiometric ratio. The solid-state structures of these complexes have been structurally characterized by single-crystal diffraction analysis.

## Acknowledgments

This work was supported by the Hong Kong Research Grants Council in the form of a GRF Grant (Project No.: 14300020). We are grateful to Professor Thomas C. W. Mak and Ms. Hoi-Shan Chan for assistance in X-ray crystallographic determination.

**Keywords**: Cobalt(II) and nickel(II); mono- and di-anionic ligands; guanidinate complexes; synthesis; structures

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# Supramolecular Chemistry (SC)

# Abstract

**Keynote Speaker**
**SC-K-01**
**AP de Silva**

# From coordination chemistry to medical diagnostics and information processing

AP de Silva

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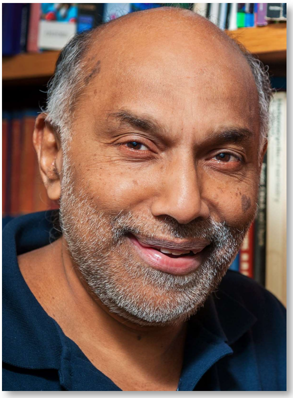
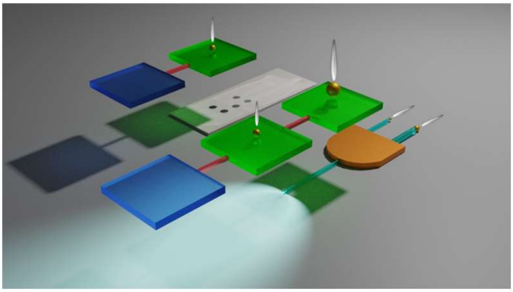


Molecular logic gates,[1,2] introduced[3] from Belfast, Northern Ireland, now have contributions from chemists, molecular biologists, geneticists and computer scientists in over 1600 laboratories. Some of these use the fluorescent PET (photoinduced electron transfer) sensing/switching design tool.[4] Since its generalization in Colombo, Sri Lanka, it has grown to involve chemists and physiologists in more than 1200 laboratories. Some of these sensing systems are serving in hospitals and ambulances by performing blood diagnostics. These form the basis of a half-billion dollar industry.[5] A short video on this topic is available at www.youtube.com/watch?v=sLGnZDP5Ecg

These ideas can also be applied to molecular capture/release systems.[6] We use dimeric and trimeric cyclophanes with redox-switchable 'corners' so that their 'walls' can be erected or collapsed. This alters the geometry and nature of the cavities so that suitable guests like aromatic cations and (polypyridine)Ru(II) complexes can be bound or unbound.



**Keywords**: Fluorescent sensing; photoinduced electron transfer; molecular logic-based computation; blood gas and electrolyte analyzer

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**Keynote Speaker**
**SC-K-02**
**Takashi Kubo**

# Association behavior of organic radicals and biradicals with close π–π contact

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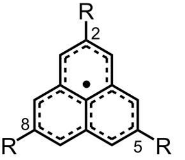
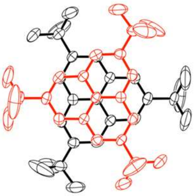
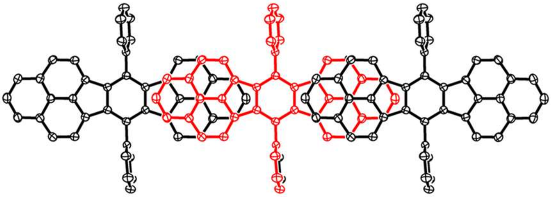
As predicted by Haddon in 1975,[1] one-dimensional (1D) stacks of neutral radicals are potentially endowed with electroconductive property. A widely accepted criterion for a metallic behavior is a $U/W$ value < 1, where $U$ is on-site Coulomb repulsion energy and $W$ is bandwidth. The $W$ is closely related to the degree of molecular orbital (MO) overlap between molecules and the straightforward way to increase the overlap integral of the MOs is the shortening of the interplanar distance of stacked molecules. We have revealed that 2,5,8-tri-*tert*-butyl phenalenyl radical (**1**) affords a π-dimer with a π–π separation distance of 3.2 Å, which is shorter than van der Waals contact of carbon atoms.[2] In the π-dimer, a strong spin–spin interaction is responsible for the short contact. To further decrease a π–π separation distance, we prepared triphenyl (**2**),[3] tris(perfluorophenyl) (**3**),[4] and tris(trifluoromethyl) (**4**) derivatives of the phenalenyl radical. These studies revealed that a phenalenyl radical scaffold provides strong intermolecular attractive force, leading to large MO overlaps between molecules. Due to the strong association nature of phenalenyl radicals, bisphenalenyl biradical molecules form 1D stacks with a short π-π contact.[5,6,7] In this lecture I will presents various association modes of phenalenyl radicals and discuss the factors contributing to the strong intermolecular interactions.[8,9]



R = $^t$Bu (**1**), Ph (**2**), $C_6F_5$ (**3**), $CF_3$ (**4**)



π-dimer of **1**



1D-stack of bisphenalenyl

**Keywords**: phenalenyl radical; intermolecular interactions; covalent bonding interaction; one-dimensional stack; electroconductive property

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Keynote Speaker
SC-K-03
Pradyut Ghosh

# Selective recognition sensing and extraction of oxyanions

Pradyut Ghosh*

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In this century, recognition, sensing and extraction of anions by synthetic hosts have received enormous research attention with promising analytical, industrial and environmental applications. In this regard, encapsulations of oxyanions like phosphates, carbonate, sulphate, chromate, arsenate and perrhenate (chemical surrogate of pertechnetate) are very important area of research. During last two decades, a wide variety of tris(2-aminoethyl)amine, benzene-based, cyanuric acid platform-based receptors containing ammonium, amide, urea groups as anion recognition elements with increasing complexity from tripodal, macrobicycle, molecular capsule to hexapodal have been synthesized by us. In this lecture, the work on capturing aerial $CO_2$ as $CO_3^{2-}$ in a molecular capsule and liquid-liquid extraction of $SO_4^{2-}$ / $CrO_4^{2-}$ will be discussed briefly.[1] However, the main focus of the talk is based on our recent works on (i) selective recognition, sensing and extraction of phosphates by utilizing bis-heteroleptic Ru(II) complexes of pyridyl triazole and bis-heteroleptic Ir(III) complexes of imidazolium bipyridine as selective and sensitive enhancement based phosphates probes;[2-8] (ii) imidazolium functionalized multipodal monomeric and polymeric receptors for selective and efficient removal of $ReO_4^-$ from water (Figure 1).[9-11]

**Keywords**: Anion; Receptors; Molecular Recognition; Phosphates; Perrhenate

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**Keynote Speaker**
**SC-K-04**
**Katrina A. Jolliffe**

# Artificial peptides, peptidomimetics and macrocycles for oxoanion recognition and sensing

Katrina A. Jolliffe[1*]

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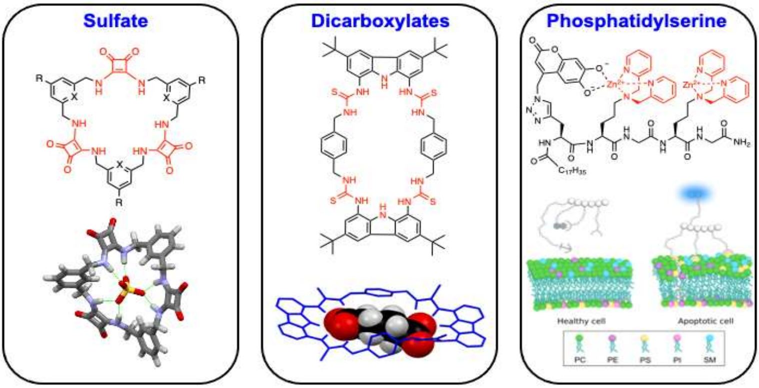
The selective recognition of anions has numerous applications in areas as diverse as the environment and medicine. Most of these applications require anion recognition to occur in a competitive aqueous environment, but the design of receptors capable of selective binding to anions in water is difficult, predominantly as a result of the high hydration energy of anionic species.

The binding of anionic species by peptides and proteins is a crucial recognition event in biological systems, with downstream effects ranging from structural stabilisation to catalysis. In natural systems, highly efficient and selective anion recognition is achieved through the use of large peptides and proteins that take advantage of the numerous H-bonding interactions available from a variety of amino acid side chains with additional contributions from the amide protons in the protein backbone. Metal-ligand interactions from protein-bound metal ions to anions are also common in biological anion binding. This has inspired our research into the development of synthetic anion receptors that combine both natural and non-natural binding motifs. We present here novel anion receptors based on macrocyclic and linear peptidic and peptidomimetic scaffolds, that are capable of selective anion recognition, extraction or transport.



**Keywords**: molecular recognition; anions; macrocycles; peptides

# Coordination chemistry of aminoquinoline-based ligands for sensing and photoredox catalysis applications

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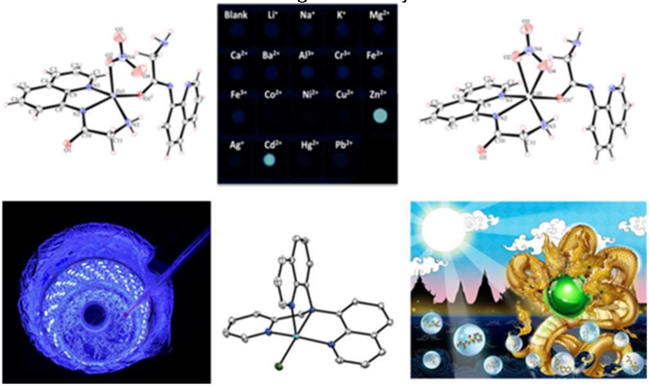
With their pre-organized nitrogen (N) atoms, 8-aminoquinolines excel as chelating ligands for transition metal ions like $Zn^{2+}$, $Cd^{2+}$ and $Cu^{2+}$. The resulting coordination complexes exhibit remarkable tunability in binding affinity and selectivity through strategic N-substitution. For d10 metal ion such as $Zn^{2+}$ and $Cd^{2+}$, strong chelation enhanced fluorescence (CHEF) is useful for the development of highly sensitive "turn-on" fluorescent sensors for these metal ions. In contrast, $Cu^{2+}$ induces photoinduced electron transfer (PET), due to ligand-to-metal charge transfer (LMCT) transitions, quenching the fluorescence. This "turn-off" mechanism forms the basis for selective $Cu^{2+}$ detection. Beyond detection, the complex can initiate atom transfer radical addition (ATRA) reactions by harnessing the transferred electron in the PET process, facilitating the formation of C-C and C-S bonds under visible light irradiation. Their tailored chelation properties and leverage photoinduced electron transfer offer immense potential for advancements in chemical sensing and catalysis.



**Keywords**: aminoquinoline; coordination complex, fluorescent sensor; photoredox catalyst

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**Keynote Speaker**
**SC-K-06**
**Takumi Konno**

# Construction of metallosuparmolecular architectures via metalloligand approach

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Recently, heterometallic coordination compounds that contain more than one kind of metal ions, together with their supramolecular aggregates, have attracted increasing attention in the fields of coordination chemistry and supramolecular chemistry. This class of compounds is commonly synthesized via the one-step self-assembly of organic ligands assisted by metal ions, which often results in the formation of undesired products. On the other hand, we have been interested in the metalloligand approach, in which a pre-designed metal complex with several donor sites is treated with metal ions.[1,2] Previously, we have shown that $[\mathrm{Au}(\mathrm{D}\text{-pen-}S)_2]^{3-}$ ($\mathrm{H_2pen}$ = penicillamine) and $[\mathrm{Au_2(dppe)}(\mathrm{D}\text{-pen-}S)_2]^{3-}$ (dppe = 1,2-bis(diphenylphosphino)ethane) act as multidentate metalloligands to produce a variety of polynuclear and supramolecular coordination compounds.[3] Recently, this gold(I) system was extended to a trigold(I) metalloligand system by introducing a triphosphine ligand that links three $\mathrm{Au^I}$ centers.[4] Here we present the coordination functionality of these metalloligands, which lead to the construction of unique metallosupramolecular architectures.

**Keywords**: metallosupramolecules; metalloligands; coordination compounds; gold(I)

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Keynote Speaker
SC-K-07
Jack K. Clegg

# Crystals under strain: atomic scale understanding of flexibility in molecular crystals

Amy J. Thompson, [1] Arnaud Grosjean[1] John C. McMurtrie[2] and Jack K. Clegg[*1]

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A crystal is normally thought of as *a homogenous solid formed by a periodically repeating, three-dimensional pattern of atoms, ions, or molecules.* Indeed, the regular arrangement of molecules, in a single crystal lead to many useful characteristics (in addition to diffraction!) including unique optical and electrical properties, however, molecular crystals are not typically mechanically robust, particularly compared to crystals of network solids like diamond. Upon the application of stress or strain, these crystals generally irreversibly deform, crack or break resulting in the loss of single crystallinity. We have recently discovered a class of crystalline compounds that display the intriguing property of elastic flexibility – that is they are capable of reversibly bending without deforming, cracking or losing crystallinity. A number of these crystals are flexible enough to be tied into a knot! (See Figure 1). We have developed a unique approach to determine the atomic-scale mechanism that allows the bending to occur which employs mapping changes in crystal structure using micro-focused synchrotron radiation. We have applied this technique to understand the deformation in both elastically and plastically flexible crystals. Most recently we have used to determine the atomic-scale origin of flexibility in crystalline materials.

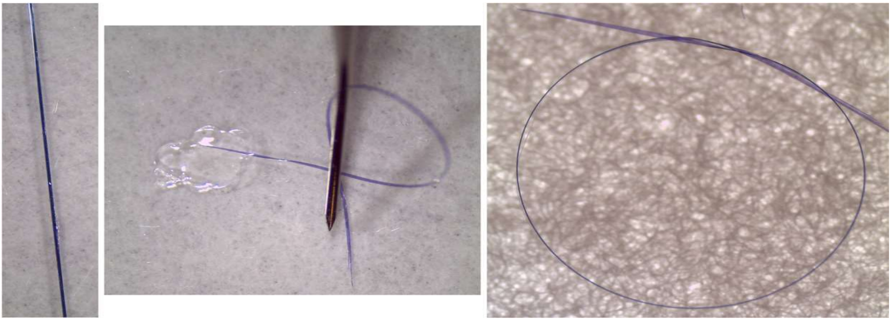

**Figure 1**: A crystal of [Cu(acac)$_2$] showing elastic flexibility.

**Keywords**: Crystal; Flexible; Mechanism; Inorganic; X-ray

# Harnessing pyridine-β-diketones as a scaffold for the generation of supramolecular nanostructures

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[2] *Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poland*
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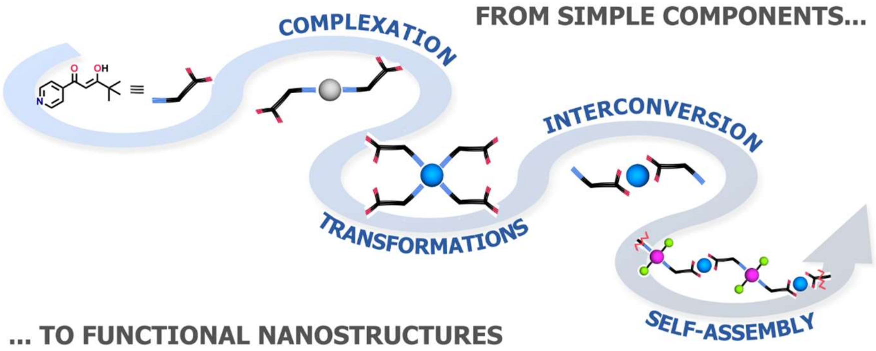
The design and assembly of metallosupramolecular nanostructures have gained significant interest in recent years due to their potential applications in various fields, including catalysis, drug delivery, and materials science. Pyridine-functionalized β-diketones have emerged as versatile and promising ligands for the construction of such nanostructures. The unique properties of these building blocks, such as acid/base responsiveness or their ability to coordinate with a wide range of metal ions, make them ideal candidates for the controlled assembly of metallosupramolecular architectures. During my talk I will present the recent findings of my team on the use of pyridine-functionalized β-diketones as a scaffold for the generation of functional metallosupramolecular nanostructures.[1-7]



**Keywords**: pyridine-functionalized β-diketones; cages; polymers; catalysis; nanomaterials

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**Invited Speaker**
**SC-I-02**
**Ho Yu Au-Yeung**

# Coordination Features of Copper-Catenane Complexes

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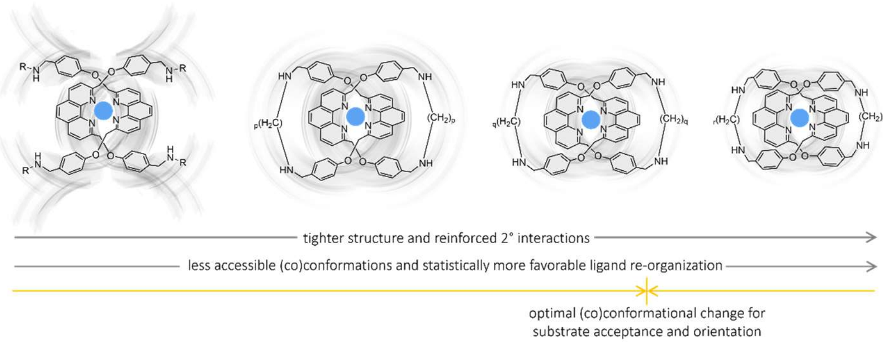
Ligands are central to the structures, properties and chemical reactivity of transition metal complexes. Although many metal complexes supported by mechanically interlocked ligands such as rotaxanes and catenanes have been reported in the literature, systematic understandings on the effects of ligand interlocking on the coordination features and catalytic properties of transition metal complexes are yet to be investigated.

In this talk, the synthesis, characterization and catalytic applications of a series of Cu(I) complexes supported by phenanthroline-derived catenane ligands will be discussed. Focus will be placed on how the different size of the interlocked rings will affect the coordination structures, spectroscopic properties and catalytic activities of the Cu(I) catenane complexes.



**Keywords**: catenane; copper; catalysis; coordination chemistry

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**Invited Speaker**
**SC-I-03**
**Nantanit Wanichacheva**

# Modern fluorescent sensors as pollution monitoring and strategy to enhance their sensitivities

Nantanit Wanichacheva[1, *], Nirawit Kaewnok[1], Jitnapa Sirirak[1], Pattanawit Swanglap[1], Thanasat Sooksimuang[2], Anyanee Kamkaew[3], Adisri Charoenpanich[4]

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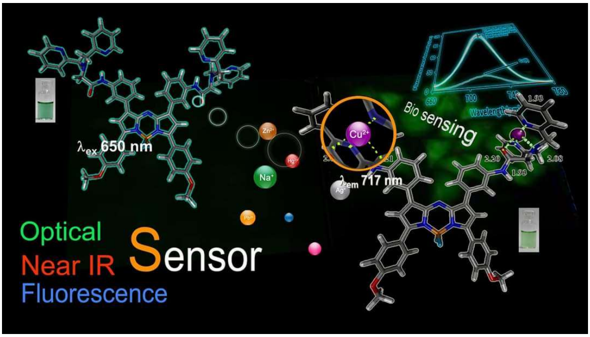
Contamination outbreaks of hazardous ions lead to adverse effects on environment and living species including fatal human health problems. Consequently, the sensing methods for hazardous ions are required to prevent these undesirable circumstances. Fluorescent sensors for toxic ions can provide high selectivity and sensitivity, therefore, are great tools for pollution monitoring and endorsing the well-being of mankind. Herein, several fluorescence sensors and near-infrared sensors were designed and developed. The sensors were prepared based on several high quantum yield fluorophores including, [5]helicene, NBD, fluorescein, rhodamine, aza-BODIPY and cyanin. Importantly, the detection limits of these sensors were lower than the recommended values of the hazardous metal contaminants in drinking water, specified by U.S. EPA and WHO. Additionally, plasmonic enhancement of the synthesized silver nanoparticles (AgNPs) were employed to the sensor systems, resulting in higher sensing sensitivity. Furthermore, the practical uses of the developed sensors were demonstrated in real samples such as foods, vegetables, pharmaceutical products, drinking water, river water, and sea water.



**Keywords**: Fluorescent sensor; Optical sensor; Heavy metals; Near-infrared sensors

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**Invited Speaker**
**SC-I-04**
**In-Hyeok Park**

# Solvent-Dependent Self-Assembly of Alkali Metal Complexes of Calix[6]-*mono*-crown-4: Dinuclear Bowls, a Pseudo-Capsule, and a One-Dimensional Polymer

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1,4-Bridged calix[6]-*mono*-crown-4 ($H_4$**L**) capable of metal binding was employed, and the influence of solvent variations on the formation of alkali metal complexes (**1**–**6**) was investigated.[1] In the crystal, the bowl-shaped $H_4$**L** host contains one water molecule in a good-fit fashion via H-bonds. When the $H_4$**L** host was reacted with alkali metal hydroxides in chloroform/methanol (solvent-A), anion-free dinuclear bowl-shaped complexes of type [$M_2$($H_2$**L**)] were isolated regardless of the metal ions. In the dinuclear bowl complexes **1**–**4**, two metal ions show different binding behaviors. When chloroform/acetonitrile (solvent-B) was used in potassium(I) complexation, interestingly, an elegant pseudo-capsule-type quadrunuclear complex **5** was isolated. In **5**, two dipotassium(I) bowls in a rim-to-rim arrangement are triply bridged by solvent molecules like a magic glue. However, in dichloromethane/methanol (solvent-C), cesium(I) yielded an infinite product **6** in which dicesium(I) bowls are linked by cation−π interactions, giving rise to a one-dimensional zigzag coordination polymer. Taken collectively, all products share a dinuclear bowl unit, some of which are further extended to the pseudo-capsule or polymeric array, depending on the solvents. The results suggest the solvent variation as a versatile engineering tool and present a perspective on the metallosupramolecules of calix[6]-*mono*-crowns with monomer, dimer, and polymer topologies.

**Keywords**: self-assembly; alkali metal complexes; calixarenes; crown ether; coordination polymers

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**Invited Speaker**
**SC-I-05**
**Yi-Tsu Chan**

# Self-Selective Metal-Ligand Coordination for Construction of Polymeric Materials

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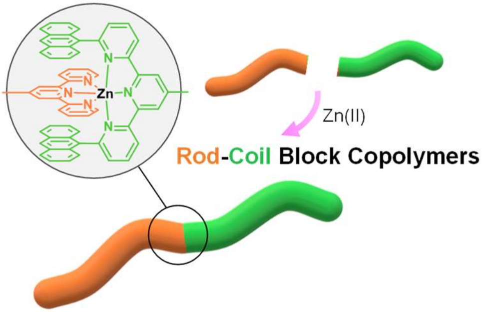
To address the synthetic challenges associated with the preparation of precisely defined copolymers, a complementary complexation pair of terpyridine-based ligands with $Zn^{II}$ ions was designed and synthesized.[1] This selective metal-ligand coordination process was characterized through $^1H$ NMR experiments and X-ray crystallography. The presence of sterically hindered 9-anthracenyl substituents at the terpyridyl 6,6″-positions not only slowed down the formation rate of the homoleptic complex but also provided additional π-stacking stabilization in the heteroleptic complex. This supramolecular approach, akin to click chemistry, was employed for the efficient construction of various rod-coil block copolymers, including P3HT-*b*-PEO,[2] P3HT-*b*-PS,[3,4] and P3HT-*b*-PtBA. The coil segments were synthesized through either direct chain-end functionalization or controlled radical polymerizations.[5] The resulting copolymers exhibited self-assembly and phase-separation behaviors similar to their covalent counterparts. Notably, the labile metal-ligand junctions between polymer blocks allowed for the manipulation of self-assembled nanostructures or phase-separated thin films through a decomplexation-recomplexation process. This reversible coordination interaction endowed the polymeric materials with dynamic functionalities. The presentation will delve into the synthetic strategies, molecular structure characterization, and the physical properties of these materials.



**Keywords**: terpyridine; self-assembly; heteroleptic complexation; supramolecular polymer

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# Control of chirality inversion kinetics of helical cage complexes by guest binding

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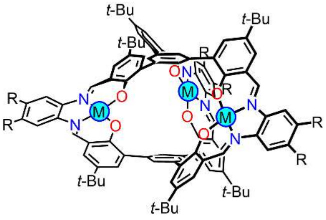
Helical molecules that undergo reversible helicity inversion are useful as a platform for switchable chiral functional molecules. In particular, helical metal complexes generally have a dynamic feature for the switching behavior due to the reversibility of coordination bonds. The chirality inversion of these molecules has mostly been discussed from the viewpoint of the initial and final diastereomeric ratios of the right- and left-handed forms. However, control of the response kinetics has rarely been studied so far.

We designed a triple-helical metallocryptand [$LNi_3$], which has a cavity for recognition of cationic guests. We found that some amino acid derivatives efficiently biased the helicity inversion equilibrium and that the helix inversion was decelerated by recognition of guanidinium ion (Figure 1a).[1] Chirality inversion of a related helical complex, which has chiral auxiliaries, can be both accelerated and decelerated by alkali metal ion binding.[2]

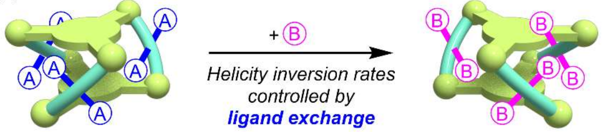
We also developed new helical complexes [$LCo_3X_6$] (X = axial amine ligand), in which the helicity inversion is associated with slow ligand exchange reactions[3] on the inert cobalt(III) centers. We found that the helicity inversion kinetics were controlled by selecting different combinations of achiral and chiral amines as the starting and entering ligands, respectively (Figure 1b).[4,5]



$LM_3$: R = OMe

(a) M = $Ni^{II}$

(b) M = $Co^{III}$



**Keywords**: Helical complex; molecular cage; chirality inversion; guest recognition; ligand exchange

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**Invited Speaker**
**SC-I-07**
**Xiaopeng Li**

# Pushing the Limits of Coordination-Driven Self-Assembly: Construction of Giant 2D and 3D Supramolecular Architectures

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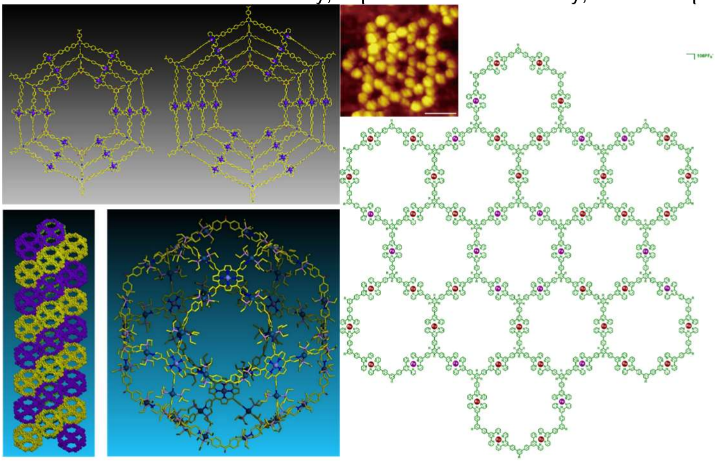
Due to its highly directional and predictable feature, coordination-driven self-assembly has evolved into a well-established methodology for constructing metallo-supramolecules. Up to date, this field has matured in the context of a large variety of macrocycles and polyhedra, which however, still suffered from a lack of complexity and thus were unable to reach the high degrees of functionality found in natural systems. With the goal of assembling structures with high complexity, we pushed the limits of coordination self-assembly through constructing a series of giant 2D and 3D supramolecular architectures. First, multi-armed ligands were synthesized using pyrylium and pyridinium salts chemistry for the self-assembly of concentric hexagons, or Kandinsky circles, which showed high antimicrobial activity. Second, step-wise strategy was utilized to combine folding and self-assembly together to construct hexagonal grids (diameter > 20 nm, MW > 65 kDa) with intrinsically ordered and disordered domains. Third, pre-assembled supramolecular polyhedra with precisely-controlled shapes and sizes could further assemble into double-helical nanowires with a non-natural parastichy pattern. In conclusion, through further understanding of self-assembly, our research could advance the design, and synthesis of new synthetic materials with molecular level precision.

**Keywords**: coordination-driven self-assembly; supramolecular chemistry; metallo-supramolecules



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**Invited Speaker**
**SC-I-08**
**Biing-Chiau Tzeng**

# Supramolecular Assembly, Solvent-Induced and Mechanochromic Luminescence of Au(I)- and Pt(II)-Dithiocarbamate Compounds

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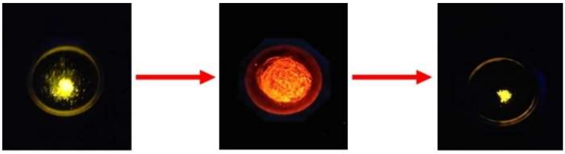
Interpenetrating polyrotaxanes were recognized as an interesting class of metal-organic materials.[1,2] In this context, a 1-D double-zigzag framework, $\{[Zn(paps)_2(H_2O)_2](ClO_4)_2\}_n$ (**1a**; paps = N,N'-bis(pyridylcarbonyl)-4,4'-diaminodiphenyl thioether), was synthesized by the reaction of $Zn(ClO_4)_2$ with paps. However, a similar reaction, except that dry solvents were used instead, led to the formation of a novel 2-D polyrotaxane framework, $[Zn(paps)_2(ClO_4)_2]_n$ (**1b**). Notably, both frameworks can be interconverted by heating and grinding with water and interesting mechanochromism was also observed.[2] Moreover, $[Au_2(O_5NCS_2)_2]$·solvates (**2**·solvates; $O_5NCS_2$=(aza-18-crown-6)dithiocarbamate) with nine different solvates can be successfully isolated from different crystal-growing processes and their crystal structures are all determined by X-ray diffraction as well.[3] It is noted that there are different intermolecular Au(I)···Au(I) contacts in combination with various luminescence for **2**·solvates and indeed there is close relationship between intermolecular Au(I)···Au(I) contacts and luminescence energies. The B3LYP/LanL2DZ calculation results can help clarify the relationship between intermolecular Au(I)···Au(I) contacts and luminescence energies for **2**·solvates. Furthermore, $Pt(phen)Cl_2$ (phen=1,10-phenan-throline) reacted with $NaO_4NCS_2$ or $NaO_5NCS_2$ to give mononuclear $[Pt(phen)(O_4NCS_2)]ClO_4$ (**3**), $[Pt(phen)(O_5NCS_2)]ClO_4$ (**4a**), and dinuclear $[Pt_2(phen)_2(NaO_5NCS_2)_2(ClO_4)_3]ClO_4$ (**4b**), respectively.[3e] In fact, only **4b** shows a remarkable mechanochromic shift from 558 to 603 nm upon grinding (see Fig. 1). In addition, the related *di(4-pyridylmethyl)-aminedithiocarbamate* ($DPMACS_2$) system was also presented.[3f,g]



as synthesized    grinding    immersed in MeOH

Fig. 1. Mechanochromic luminescence for **4b**.

**Keywords**: Supramolecular Assembly; Solvent-Induced; Mechanochromic; Au(I)···Au(I)

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# Benzoxazine Derivatives: Crystal Structures, Properties, and Applications

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Kantapat Chansaenpak[2], Suttipong Wannapaiboon[3], and Apirat Laobuthee[1]

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Dihydro-1,3,*2H*-benzoxazines (or benzoxazine monomers) are a class of compounds that have been widely utilized in many areas, such as the production of functional polybenzoxazines, optoelectronic materials, antimicrobial agents, and medicinal agents. Moreover, the benzoxazine monomers can be used to synthesize benzoxazine dimers, which are a group of compounds with a variety of properties, such as anticancer properties and good chelating behaviors. The structure variety of the benzoxazines plays a vital role in their desired properties. In order to gain a full understanding of the effects of the benzoxazine structures on their properties, the crystal structures of benzoxazines obtained from X-ray crystallography are required. According to the crystal structures of the benzoxazine monomers, it was found that the oxazine ring adopts a half-chair conformation to locate all the members of the benzoxazine ring as planar as possible by employing the expansion of the bond angles within the ring, which is the origin of the photoluminescent properties of the benzoxazine monomers. The intramolecular O–H···N hydrogen bond with the *S*(6) graph set motif is observed in all the derivatives for the benzoxazine dimers. This activates the phenol moieties when forming the coordination compounds, so the benzoxazine dimers are very good chelating agents for several metal ions in ambient conditions. Apart from the intramolecular hydrogen bonds, O–H···O hydrogen bonds with different patterns are observed in the crystal structure of the benzoxazine dimers. It was noticed that the substituent groups play significant roles in the intermolecular hydrogen bonding motifs. Moreover, the effect of substituent groups on thermal, electronic, optical, and anticorrosion properties is also investigated and discussed.

**Keywords**: benzoxazines; crystal structures; optical properties; electronic properties; antimicrobial properties

# Quinone Functionalised Pillararenes: Versatile Motifs in Supramolecular Chemistry

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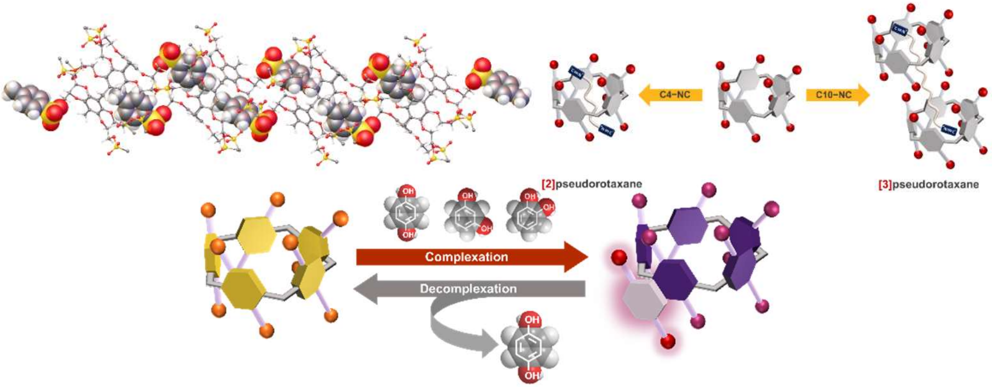
In 2008, Ogoshi and co-workers reported their seminal work on the synthesis of a series of novel macrocycles, coined pillararenes, the multifaceted exterior surface of which bears resemblance to their namesake. Structurally, these macrocycles are cyclic oligomers (n = 5-15) of dialkylated hydroquinone monomers covalently linked by methylene spacer units at the 2,5-positions, forming a highly symmetric and rigid cavity. Pillararenes have become a key player in supramolecular chemistry and nanomaterials. Courtesy of recent synthetic advances in pillar[5]arene chemistry, the electron-donating properties of the dialkyl hydroquinone aromatic panels can be reversed by oxidation to pillar[n]arene[m]quinone (P[n]A[m]Q). This subsequently changes the electronic properties as well as the host-guest binding bahaviour of the resulting macrocyclic hosts. Herein, our recent advances in pillararene research ranging from synthetic chemistry aspects, host-guest chemistry, molecular assembly, and applications will be described



**Keywords**: Pillararene; Quinone; Supramolecular Chemistry; Rotaxane; Macrocycles

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**Invited Speaker**
**SC-I-11**
**Vladimir Fedin**

# Luminescent Ln-MOFs with tunable color for nanomolar detection of environmental pollutants

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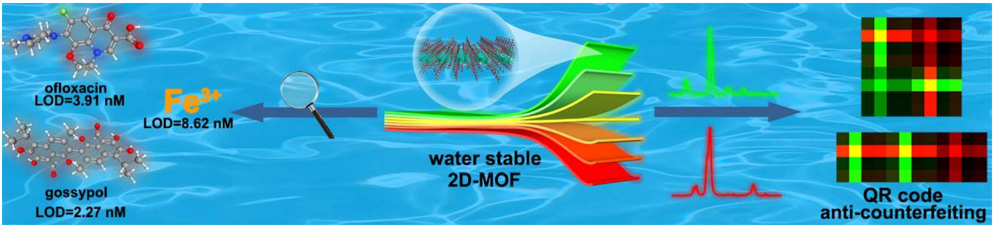
With further industrialization, development of medical and sanitary requirements, heavy metal pollution and organic toxicant poisoning are endangering the natural environment and physical health. Therefore, there is an urgent need to develop sensing materials that can rapidly detect very low amounts of organic and inorganic toxicants. A series of monometallic and bimetallic Ln-MOFs with efficient and tunable photoluminescence was designed based on 5,5'-(pyridine-2,6-diylbis(oxy))diisophthalic and 4-(3,5-dicarboxyphenoxy)isophthalic acids. They demonstrate superior water stability, high temperature resistance and high photoluminescence quantum yields. Moreover, they exhibited top-performing sensing properties through luminescence quenching effect with exceptionally low detection limits towards $Fe^{3+}$, ofloxacin antibiotic and cotton phytotoxicant gossypol. Significantly, Tb-MOF is the first highly efficient sensor that uses water as a solvent to detect trace amounts of gossypol, and it can visualize and quantify gossypol in edible-grade cottonseed oil as well, which proves its great potential for practical application [1-3].

The authors are grateful to the Ministry of Science and Higher Education of the Russian Federation for financial support (Agreement No. 075-15-2022-263), and for providing access to the large-scale research facility “EXAFS spectroscopy beamline”.



**Keywords**: MOF; luminescence; lanthanides; structure; gossypol

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**Invited Speaker**
**SC-I-12**
**Andrew C.-H. Sue**

# Twisted pentagonal prisms: $M_nL_2$ metal-organic pillars

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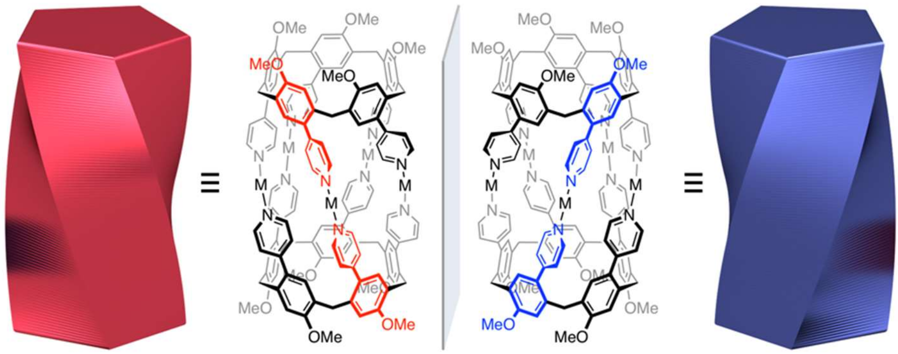
The field of metal-organic cage assembly, which employs organic ligands and metal clusters to create unique polyhedral structures, offers significant opportunities for the design of functional materials. This approach allows for precise customization of building blocks in terms of size, geometry, and functionality, enabling the tailoring of internal spaces within these molecular containers for specific applications. While many macrocyclic compounds like calixarenes have found extensive use in constructing various molecular capsules, cages, and frameworks due to their high symmetries, predefined structures, and versatile functionalization schemes, pillararenes, characterized by their straight pillar-like conformations and identical functional groups on both rims, do not naturally lend themselves to the formation of discrete containers. Our research group focuses on the design and synthesis of "rim-differentiated" pillar[5]arenes[1] and tiara[5]arenes,[2] featuring distinct functional groups on the "upper" and "lower" rims. This presentation provides an overview of how the desymmetrization of these macrocyclic scaffolds enables the development of innovative ligand designs, driving the exploration of new coordination-driven molecular architectures[3] and their emerging properties.



**Keywords**: coordination-driven assembly; pillar[*n*]arene; tiara[*n*]arene; metal-organic pillars; deep-cavity cavitand.

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# Pillar[5]arene-based supramolecular nanospheres for long chain aldehyde detection

Yanisa Sanguansap[1], Vithaya Ruangpornvisuti[1], Thassanant Atithep[2], Thanthapatra Bunchuay[3]*, Boosayarat Tomapatanaget[1]*

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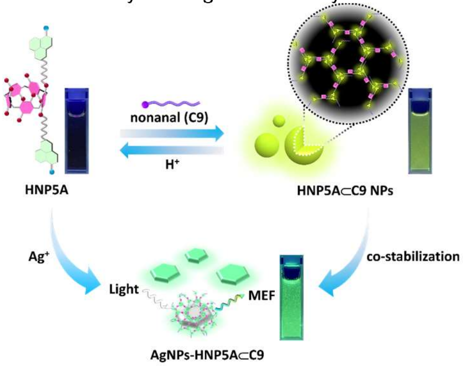
Lung cancer has consistently recorded the greatest mortality rate among cancer-related diseases over the past few years. The development of rapid and accessible methods is required for diagnosing the seriousness of disease. A prior study has identified long-chain aldehyde compounds, particularly octanal (C8) and nonanal (C9), as potential lung cancer indicators.[1] Herein, a novel fluorescence sensor **HNP5A**, which was constructed from bis-hydrazine naphthalimide decorated pillar[5]arene, was designed for sensitive and specific detection of long-chain aldehydes.[2] This sensor demonstrated the ability to detect long-chain aldehydes, particularly C9, and then generated supramolecular pseudorotaxane polymeric nanoparticles within 15 minutes in acetate buffer pH 4, resulting in an enhanced fluorescence emission. The limit of detection (LOD) value of **HNP5A** towards C9 displayed a low concentration at $8.16 \times 10^{-7}$ M without interference from the short-chain aldehydes and lung fluid matrices. Additionally, this as-produced **HNP5A⊂C9** revealed an unanticipated reduction of $Ag^+$ in an aqueous media to form AgNPs with hexagonal shape, and the resulting **AgNPs-HNP5A⊂C9** displayed a considerable fluorescence enhancement under metal-enhanced fluorescence (MEF) phenomenon. Hence, the present work highlights a new fluorescence chemosensor that forms distinctive supramolecular polymeric nanoparticles and provides high sensitivity and selectivity for long-chain aldehyde detection.



**Keywords**: long chain aldehyde; pillar[5]arene; hydrazine napthalimide; supramolecular self-assembly; silver nanoparticles

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# Influence of guest molecules on pillar[5]arene-based mechanically interlocked polymers by metalation

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We continue to examine the possibility of generating the metalation-triggered approach to achieve the synthesis of a new family of mechanically interlocked polymers of pillar[5]arenes. The guest molecules can induce the preparation of mechanically interlocked polymers (MIPs) based on the host–guest interactions between macrocyclic host and guest molecules. In this presentation, the preparation of mechanically interlocked polymers via the guest control of supramolecular coordination platforms is reported. The reaction of dithiopyridyl-armed pillar[5]arene and a silver(I) ion in the absence and presence of the dinitrile guests leads to formation products that range from the one-dimensional (1D) coordination polymer through the 1D poly-pseudo-rotaxane to the 2D poly-pseudo-rotaxane. In the assembly reaction of dibenzonitrile-bearing pillar[5]arene with silver(I) ion afforded a 1D poly-pseudo[1]catenane, which has self-included pseudo[1]rotaxane-type pillars[5]arene. Furthermore, a 1D poly-pseudo-catenane and a 1D poly-pseudo-rotaxane were obtained in the presence of the linear dinitrile guest molecule with different lengths, respectively.

**Keywords**: pillar[5]arene; mechanically interlocked polymers; guests; metalation

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# Synthesis of three-dimensional van der Waals open frameworks

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Strong bonds such as coordination and covalent bonds between molecular building blocks are the prerequisites for the assembly of permanently porous frameworks. Conversely, van der Waals (vdW) interaction is believed to be irrelevant for the framework construction due to its weak force and low directionality. In this study, we demonstrate that vdW interaction drives the assembly of open frameworks from supramolecular building blocks, so-called metal-organic polyhedra (MOPs), a group of metal complexes with well-defined polyhedral shapes.[1] We synthesized a novel octahedral MOP by linking 12 naphthalenediimide-based dicarboxylate with 6 dirhodium(II) paddlewheels. These MOPs formed diamond-like sparse packing upon crystallization, generating a three-dimensional continuum void space that fills 30% of the crystal volume. $N_2$ gas sorption experiment supported this low packing density with the calculated BET surface area of 1437 $m^2/g$, the highest record for MOP-based materials. The high crystallinity was maintained without solvent up to ca. 320°C until MOPs thermally decomposed. DFT calculations elucidated that the interaction energy between two MOPs is over 400 kJ/mol, mostly accounted by dispersion forces (>80%). We also demonstrated analogous frameworks can be prepared in the same design principle. This discovery highlights an overlooked potential of vdW interactions toward the design of permanently porous frameworks.

**Keywords**: metal-organic polyhedra (MOPs); van der Waals interaction, molecular crystals; permanent porosity; naphthalenediimide (NDI)

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# Photoresponsive enzyme mimetic using a dissipative supramolecular assembly of Pt(II) complexes

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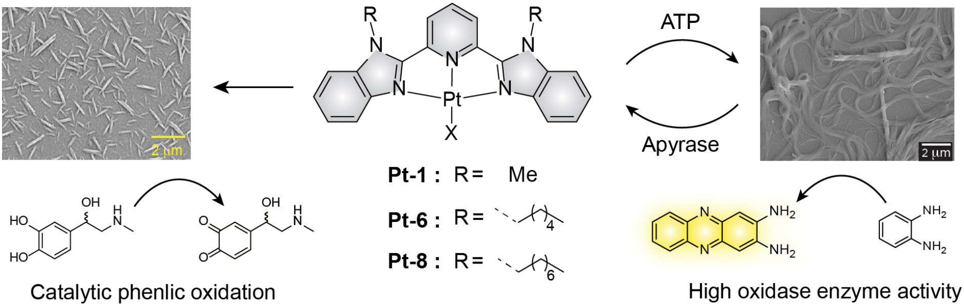
Artificial enzyme equivalents known as nanozymes offer a practical solution for sustainable environmental remediation compared to natural enzymes owing to their remarkable efficiency, operational stability, and cost-effectiveness. We introduce a self-assembling Pt(II) complex stabilized by designed pincer ligands. These supramolecular assemblies in water emit light and mimic oxidase enzyme activity. The luminescent self-assembled structure assists in photogenerating singlet oxygen via a long-lived $^3$MMLCT excited state, conferring specific oxidase-like instead of traditional peroxidase-like activity with light. Our studies demonstrate efficient photocatalytic degradation of various polyphenols and azo dyes within 5-10 minutes of light irradiation. Notably, the system exhibits reusability over twenty cycles and unaltered performance for more than 6 months, providing a robust system for sustainable environmental remediation. Inspired by nature, we further developed a transient assembly using triphosphates that clip the Pt(II) complexes to form fibrous networks. Incorporation of a phosphate-cleaving enzyme (apyrase) into the system, enables temporal regulation of the assembly fueled by triphosphate. Accordingly, the oxidase-like activity is reversibly controlled by the dissipative cycle. We demonstrated efficient programmable logic gate arrays using photochemical inputs. These modular metal complex based supramolecular assemblies offer great opportunity in sustainable environmental remediation, bioactivity, and biocomputing.

**Keywords**: Pt(II) complex; pincer ligands; self-assembly; photoregulated; enzyme mimetic



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**Oral Presentation**
**SC-O-05**
**Rita Ghosh**

# Hydrophobic moiety triggered self-assembly formation for detecting biomarkers in blood

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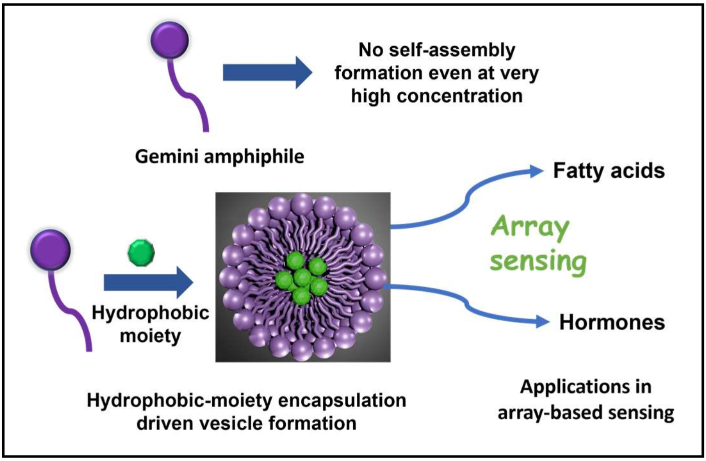
In our study, we have introduced a gemini amphiphile (GA) that exhibits a remarkable self-assembly behavior triggered by any hydrophobic moieties. Unlike most amphiphiles that can self-assemble independently, even at high concentrations, this particular GA does not form self-assembled structures by itself. However, it undergoes self-assembly when it encounters a hydrophobic moiety, forming vesicles. It has been anticipated that in the presence of a hydrophobic moiety, these molecules surround the hydrophobe, effectively trapping it and forming larger vesicles. To analyze these vesicles, we employed various characterization techniques such as fluorescence, dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). What makes this self-assembly property especially intriguing is its potential application in detecting exclusively hydrophobic molecules. Hence, we have developed a multichannel sensor system using three dye mixtures. Surprisingly, these GAs effectively sense a range of biomarkers, including hormones and fatty acids. Notably, array sensing for these biomarkers has not been explored previously. Our GAs excel in distinguishing between different types of fatty acids, including cis, trans, and saturated ones, when used in an array format. This study represents the inaugural demonstration of array-based sensing for fatty acids, achieved through a straightforward and uncomplicated procedure.



**Keywords:** Array sensing; vesicles; fatty acids; hormones; hydrophobicity

**Poster Presentation**
**SC-P-01**
**Kentaro Harada**

# Circularly Polarized Luminescence of a Biaryl Guest within a Chiral Resorcinarene-based Capsule

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Our group has reported that two resorcinarene-based cavitands bearing four bipyridyl arms at the wide rim are self-assembled by metal coordination to give rise to $D_4$ symmetric supramolecular capsule **1** [1]. **1** allows dynamic interconversion between (*P*)- and (*M*)- helicity in the solution containing a small portion of acetonitrile. The enforced cavity of **1** can encapsulate several guest molecules possessing acetyl methyl substituent, which forms CH-π interaction to the electron-rich aromatic rings of resorcinarene scaffold. A chiral hydrogen bonding complex $(AcOH)_2$・*L*(+)-**G1** was well fitted within the cavity of **1**, resulting in the mixture of the two diastereomer $(AcOH)_2$・L(+)-**G1**⊂(*P*)-**1** and $(AcOH)_2$・*L*(+)-**G1**⊂(*M*)-**1**. The ratio of the two diastereomers were biased through the helicity interconversion to give rise to $(AcOH)_2$・*L*(+)-**G1**⊂(*P*)-**1** in 91%*de*. An enantiomerically enriched capsule (*P*)-**1** was prepared by the removal of the chiral template.

Achiral 4,4'-diacetoxybiphenyl guest **G2** was synthesized bearing two fluorescent benzothiadiazole units. CD spectra and DFT calculation of **G2**⊂(*P*)-**1** demonstrated that the dynamic axial chirality of **G2** within (*P*)-**1** was biased to (*S*)-helicity, producing circularly polarized luminescence from benzothiadiazole units in the NIR region [2].

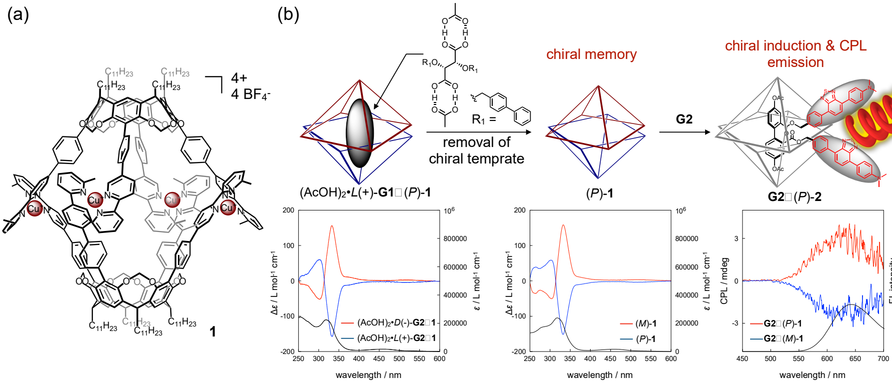

**FIGURE 1.** (a) Molecular structure of capsule **1**. (b) Preparation of enantiomerically enriched capsule **1**, which imposes the axial chirality on guest **G2** to produce CPL in the NIR region.

**Keywords**: Supramolecular Chemistry; Host-Guest Chemistry; Supramolecular Capsule; Molecular Recognition; Circularly Polarized Luminescence

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# $EFe_3(CO)_9$-based (E = Te, Se, S) dipyridyl−Cu polymers: From syntheses to semiconductivities

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A novel family of 1D and 2D $EFe_3(CO)_9$ (E = Te, Se, S) cluster-based Cu polymers were synthesized from the liquid-assisted grinding (LAG) of a predesigned compound $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ or a mixture of $[Et_4N]_2[EFe_3(CO)_9]$ (E = Se, S) and $[Cu(MeCN)_4][BF_4]$ with rigid or flexible dipyridyls. The synthesized polymers possessed various $EFe_3(CO)_9$ (E = Te, Se, S) bonding modes within their frameworks, resulting in the chalcogen-directed structural features. Besides, these polymers could undergo reversible structural transformations upon treatment with appropriate dipyridyls or $[Et_4N]_2[EFe_3(CO)_9]$ (E = Se, S)/$[Cu(MeCN)_4][BF_4]$ components. Importantly, these novel series of $EFe_3(CO)_9$-based Cu-dipyridyl polymers exhibited extraordinary semiconducting properties with ultra-narrow energy gaps and nearly parallel optical (dc) or electrical conductivities. The trend of the semiconductivities for these polymers was closely related to their $EFe_3(CO)_9$−Cu (E = Te, Se, S) bonding modes, which was affected by numerous secondary interactions between COs of clusters $EFe_3(CO)_9$ and dipyridyls within polymeric frameworks. The efficient electron transport was further elucidated by XPS, XAS, and DFT calculations as well as solid-state electrochemistry especially in the sulfur system. Notably, the water- and light-stable Se-containing polymers exhibited unique photodegradation activity toward nitroaromatics and organic dyes, where the efficiency was rationalized by their structural features and energy gaps.

**Keywords**: coordination polymers; metal clusters; ligands; semiconducting behaviors

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**Poster Presentation**
**SC-P-03**
**Marryllyn E. Donaldson**

# Functionalised zig-zag coordination polymers from tzopz a new triazole-pyrazine ligand

Marryllyn E. Donaldson, Gareth J. Rowlands, Brodie E. Matheson, Tyson N. Dais, and Paul G. Plieger

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Coordination polymers (CPs) are metallo-supramolecular systems built from simple units of geometrically controlled metal ions (or metal clusters) and poly-topic organic ligands, held together by coordination bonds or other weak intermolecular bonds. They can expand infinitely in one or more dimensions, as 1D chains, 2D sheets or 3D MOFs (metal organic frameworks).

The design and synthesis of new chelation motifs and modular ditopic ligands is the basis for exploring new polymeric coordination complexes. This approach leads to the consistent synthesis of a larger supramolecular assembly, that can then act as a functionalisable backbone. From this, new materials can be created that can be systematically tuned for function.

Here we present a series of binucleating tridentate ligands, consisting of a new triazole-pyrazine motif. The subsequent complexation of this ligand into 1D zig-zag coordination polymers has been investigated by UV-vis spectroscopy and single crystal X-ray crystallography, revealing a remarkably consistent self-assembly process that is metal cation independent. This work demonstrates an approach to forming a backbone for future materials from ‘clickable’ functional groups.

**Keywords**: coordination polymers; click chemistry; pyrazine; triazole

# A redox-responsive multi-ferrocene capsule and its encapsulation-induced CT interactions

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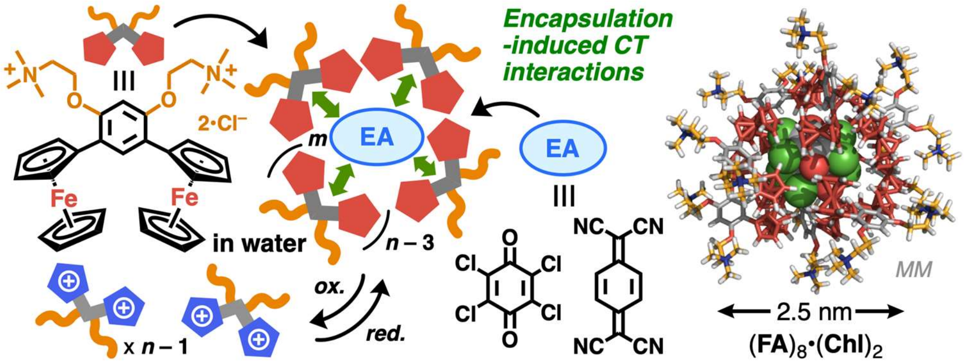
Multiple ferrocene-based capsules are expected to exhibit unusual electrochemical properties. However, the capsules displaying host-guest electric/electrostatic communications have been rarely explored so far. Our group have reported anthracene-based micellar capsule, formed from bent amphiphiles in water, with wide-ranging host ability.[1,2] Here we report the formation of a new multi-ferrocene capsule $(\mathbf{FA})_n$ and its host-guest composites, displaying unusual encapsulation-induced charge-transfer (EICT) interactions.[3]

Ferrocene capsule $(\mathbf{FA})_n$ was quickly and quantitatively formed by the self-assembly of bent amphiphile **FA** in water. The capsule responded to redox stimuli and showed its fully reversible disassembly and assembly. Chloranil (**Chl**) is a representative electron acceptor (EA) yet the combination of **FA** and **Chl** displayed no CT interactions in organic solvent. In contrast, the host-guest composite $(\mathbf{FA})_n\bullet(\mathbf{Chl})_m$ displaying strong EICT interactions was efficiently obtained by the grinding protocol.[2] DLS, UV-visible, and molecular modeling studies indicated the selective formation of $(\mathbf{FA})_8\bullet(\mathbf{Chl})_2$, with a core diameter of ~2.5 nm. Notably, the composite exhibited a new, relatively wide visible-NIR band in the range of 650 to 1350 nm, derived from characteristic EICT interactions between $(\mathbf{FA})_n$ and **Chl**. Moreover, these interactions within the capsule could be readily released by an external stimulus.



**Keywords**: ferrocene; charge-transfer interaction; capsule; bent amphiphile; redox

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# Pillar[5]arene-based silver(I) complexes: guest-controlled mechanically interlocked structures

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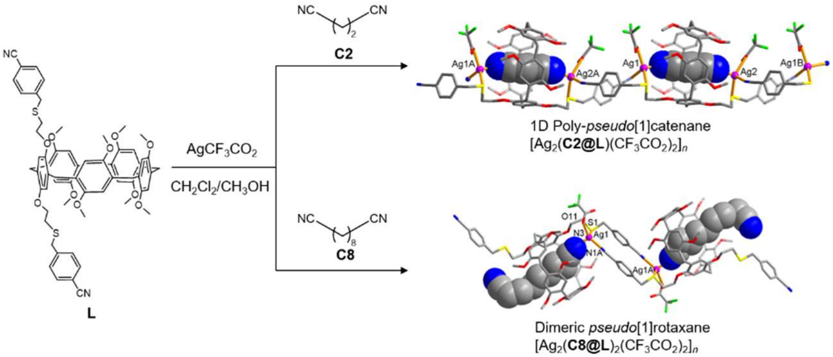
To examine the metal and/or guest-induced mechanically interlocked molecules,[1-3] we employed the pillar[5]arene derivative (**L**), incorporating a (mercaptomethyl)benzonitrile group. The reaction of **L** with $AgCF_3CO_2$ afforded a one-dimensional (1D) poly-*pseudo*[1]catenane, $[Ag_2(\mathbf{L})(CF_3CO_2)_2]_n$), which shows the linkage of self-included *pseudo*[1]rotaxane-type pillars[5]arene with silver(I) ions. In the presence of the linear 1,2-dicyanoethane (**C2**) guest molecule, an 1D poly-*pseudo*[1]catenane, $[Ag_2(\mathbf{C2@L})(CF_3CO_2)_2]_n$ was also obtained. Interestingly, a self-included pillar[5]arene converted to a de-threaded form by a **C2** guest. The guest molecule **C2** threads into the pillar[5]arene cavity and forms the pseudo[1]catenane with the silver(I) ion. Meanwhile, reaction of **L** with $AgCF_3CO_2$ in the presence of 1,8-dicyanooctane (**C8**) afforded a dimeric *pseudo*[1]rotaxane, $[Ag_2(\mathbf{C8@L})_2(CF_3CO_2)_2]_n$, in which **C8** guest threads into the pillar[5]arene cavity. In addition, fluorescence properties were examined by using a fluorescent indicator to examine the host-guest interaction between **L** and the metal ion or guest molecules.



1D Poly-*pseudo*[1]catenane
$[Ag_2(\mathbf{C2@L})(CF_3CO_2)_2]_n$

Dimeric *pseudo*[1]rotaxane
$[Ag_2(\mathbf{C8@L})_2(CF_3CO_2)_2]_n$

**Keywords**: pillar[5]arene; coordination networks; mechanically interlocked molecules

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# A Fluorescence Sensor Based on Phenolic Derivative for Metal Ion Detection

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3-(((5-(dimethylamino)naphthalen-2-yl)sulfonyl)oxy)-5-(hexyloxy)phenyl6 (dimethylamino)naphthalene-1-sulfonate (**1**) was synthesized and characterized using $^{1}$H-NMR, $^{13}$C-NMR, Fourier-transform infrared (FT-IR) and High-resolution mass (HRMS) techniques. The complexation behavior between the sensor **1** and various metal ions ($Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Pb^{2+}$ and $Hg^{2+}$) was studied by fluorescence titration. Sensor **1** preferred $Fe^{3+}$ ion rather than other metal ions. Sensor **1** interacted with $Fe^{3+}$ ion, resulting quenching fluorescence emission. The 1:1 ratio complex between sensor **1** and $Fe^{3+}$ was identified by Job' analysis. Moreover, the limit of detection (LOD) between sensor **1** and $Fe^{3+}$ ion was calculated as $2.58 \times 10^{-8}$ M.

**Keywords**: fluorescent sensor; quenching; metal ion

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Poster Presentation
SC-P-07
Tanakorn Khongluang

# Use of porphyrin derivatives as ionophore in polymeric membrane electrode for ferric ion detection

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In this work, tetrakis(4-dodecyloxyphenyl)porphyrin (**L**) was synthesized in 34% yield from the reaction between 4-n-dodecyloxybenzaldehyde and pyrrole in propionic acid.**L** was then used as ionophore in the fabrication of a polymeric membrane electrode for detection of $Fe^{3+}$ in drinking water. Different ratios of membrane composition were studied to prepare membranes containing a total mass of 220 mg. The membrane prepared using polyvinyl chloride (PVC) 33% wt, bis(2-ethylhexyl)sebacate (DOS) 66% wt, ionophore 0.18 %wt (0.3 μmol) and potassium tetrakis(4-chlorophenyl)borate (KTClPB) $2.71 \times 10^{-3}$ %wt (40 mol% relative to ionophore) as membrane additive showed the best response to $Fe^{3+}$, judging from the selectivity coefficients of the polymeric membrane electrode against other interfering ions measuring by a separate solution method (SSM). This electrode can detect $Fe^{3+}$ at a concentration range of $1.00 \times 10^{-6}$ M - $1.00 \times 10^{-2}$ M with a Nernstian slope of 48.1 mV decade$^{-1}$ ($R^2 = 0.9995$) and has a detection limit of $9.53 \times 10^{-7}$ M. The electrode has a pH working range of 4.3 - 9.0, response time of about 5 seconds and can be used for at least 1 month. This electrode can be used to analyze for $Fe^{3+}$ in drinking water with satisfactory results.

**Keywords**: electrode, ionophore, porphyrin derivatives, ferric ion

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# Dual Redox-Responsive Supramolecular Polymer Directed by Porphyrin and Trinitrofluorenone

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Stimuli-responsive supramolecular polymers have been significantly attracted to developing smart materials due to their regulable fascinating functions, e.g. gelation, self-healability, shape-memory etc. Our group has reported that the supramolecular polymerization of a head-to-tail monomer possessing a bisporphyrin head (bisPor) and a trinitrofluorenone tail (TNF) via the donor-acceptor host-guest interaction.[1] The π-stacked donor-acceptor host-guest complex bisPor-TNF was dissociated by electrochemical and chemical oxidations and reductions. Thus, applying redox stimuli can determine the macroscopic properties of the supramolecular polymer with the dissociation of the host-guest complex. In this study, we will report detailed insights into the supramolecular polymerization behavior of **1** in response to the dual redox stimuli.

A log–log plot of the specific viscosities versus the concentrations of **1** gave rise to a transition at a critical polymerization concentration (CPC) of 10.3 mmol L$^{-1}$. The transition from dilute regime to semidilute regime clearly describes that the supramolecular polymer chains are long enough to be entangled with viscus drag. Upon the addition of tris(2-bromophenyl)aminium hexachloroantimonate or cobaltocene were added to the solution of **1**, the CPC was disappeared with the slopes being consistent. Thus, the supramolecular polymer chains are completely disrupted through the redox stimuli.[2]

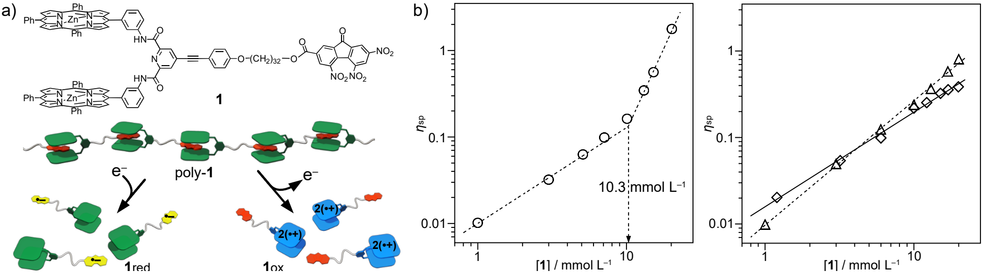

**Figure 1.** (a) Molecular structure of head-to-tail monomer **1** and schematic illustration of dual redox-responsive supramolecular polymer. (b) Plots of specific viscosity ($\eta_{sp}$) of **1** (○), **1** with oxidant (△), and **1** with reductant (◇) versus concentrations.

**Keywords**: Supramolecular Chemistry; Host-Guest Chemistry; Molecular Recognition; Redox Responce; Porphyrin

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# Synthesis and Guest Binding Behavior of Macrocyclic Tetrakisporphyrin with Two Cavities.

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*[2] International Institute for Sustainability with Kotted Chiral Meta Matter / SKCM$^2$, 2-313 Kagamiyama, Higashi-Hiroshima City, Hiroshima, Japan*
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Our group has developed S-shaped tetrakisporphyrin possessing two cavities connected with a butadiyne linker. The cavities encapsulated electron-deficient aromatic molecules.[1,2] In this study, we newly synthesized a novel macrocyclic tetrakisporphyrin molecule **1** with rigid linkers. The macrocyclic tetrakisporphyrin molecule showed positive cooperativity in the guest binding.

The guest binding behavior in the solution was investigated using $^1$H NMR spectroscopy. When **1** was added to a solution of **G1**, the upfield-shifts of the aromatic protons of **G1** were observed, indicating that **G1** was located within the cavities of tetrakisporphyrin, where the aromatic protons of **G1** experienced the strong shielding effect of the porphyrin rings. The detailed insight into guest binding behavior was studied using UV/vis spectroscopy. Upon the addition of **G1** to a solution of **1**, the Soret band at 419 nm decreased and a new absorption band emerged (Figure 2b). The results of the Job plot revealed that the host-guest coplex was formed in a ration of 1:2 (Figure 2c). Nonlinear fitting analysis was performed to obtain association constants for **G1.** A cooperativity parameter ($\alpha = 4K_2/K_1$) of 3.4 suggested that strong positive cooperativity was appeared in the binding process of **G1**. Due to the conformational rigidity of the two cavities, the first guest binding causes the preorganization of the remaining binding cavity.

The metalation of macrocyclic tetrakisporphyrin encapsulated coordinative donor ligand **G2**. In the presentation, we will also discuss the binding behavior of **G2**.

**Keywords**:Supramolecular Chemistry; Host-Guest Chemistry; Molecular Recognition; Cooperativity; Zinc Porphyrin

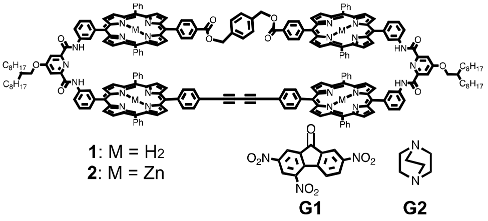

**Figure 1**. Molecular structures of **1, 2** and **G1, G2**.

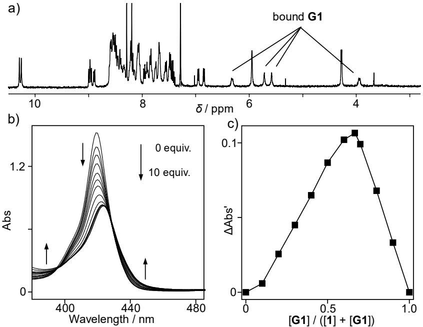

**Figure 2.** (a) $^1$H NMR spectrum of a 1:2 mixture of **1** and **G1**. (b) UV/vis spectra and (c) Job plots of **1** with **G1**.

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# Strong mechanochromic luminescence of Pt(II)-complexes within aromatic capsules in water

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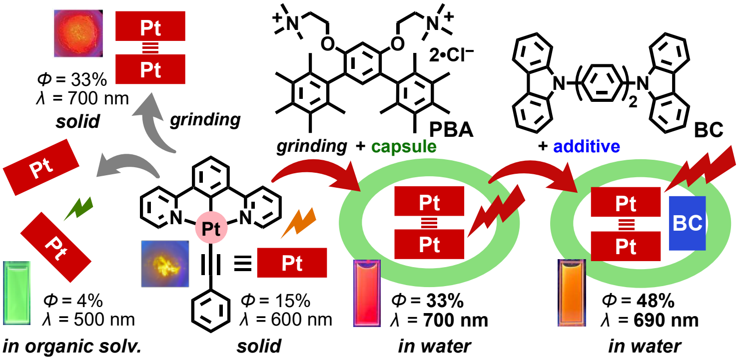
Metal-complexes providing mechanochromic luminescent (MCL) properties have received increasing attention over the last decade.[1] However, MCL can be observed only in the solid state and hardly observed in solution so far owing to the dissociation of MCL state. Our group has reported pentamethylbenzene-based aromatic capsule (**PBA**)$_n$, formed from bent amphiphiles in water, with wide-ranging host ability.[2] Here we report the efficient encapsulation of arylethynyl Pt(II)-complexes (**Pt**) with an NCN-pincer ligand by the aromatic capsule and its strong MCL behavior in water.[3]

Host-guest composite (**PBA**)$_n$•(**Pt**)$_m$ was facilely obtained by manually grinding a 1:1 mixture of **PBA** and **Pt** and the addition of $H_2O$ to the resultant mixture at room temperature. A $CH_2Cl_2$ solution of **Pt** showed weak green emission ($l_{max}$ = 500 nm), derived from its monomeric state, upon irradiation at 450 nm. In sharp contrast, the obtained aqueous solution of (**PBA**)$_n$•(**Pt**)$_m$ exhibited a prominent red emission ($l_{max}$ = 700 nm) with a quantum yield ($\Phi$) of 33% under aerobic conditions. Moreover, enhancement of the MCL (up to $\Phi$ = 48%) could be achieved by coencapsulation of the Pt(II)-complexes with carbazole derivatives **BC** as additive by the capsule in water.



**Keywords**: mechanochromic luminescence, aromatic capsule, bent amphiphile, Pt(II)-complex, encapsulation.

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# Triazole-Crown Ether Containing Quaternary Ammonium Species and Pyridine-Triazole Ligands *via* Double-Click Reaction

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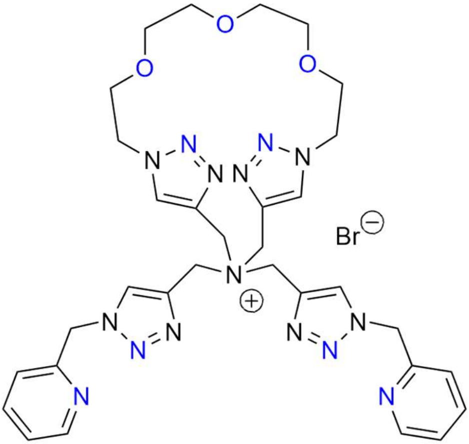
Crown ethers are widely recognized for their capacity to bind selectively with cationic species (host-guest binding). The triazole-crown ether derivatives can be synthesized from Cu-catalyzed azide–alkyne cycloaddition (CuAAC or click) and have recently been investigated for their potential applications as ion-pair sensors. In this work, triazole-crown ether featuring a quaternary ammonium ion and N-based pyridine-triazole chelating ligands was generated *via* simultaneous double-click reaction in the presence of a $Ba^{2+}$ ion template under dilute conditions. The resulting triazole-crown ether derivative should behave as a ditopic ligand with two different metal binding sites, one at the triazole-crown ether ring and the other at the pyridine-triazole ligands. Complexation of this ligand with alkali ($Na^+$, $K^+$), alkaline earth ($Mg^{2+}$, $Ca^{2+}$), and transition metal ($Cu^{2+}$, $Zn^{2+}$, $Ag^+$) ions was determined using $^1H$ NMR spectroscopy, ESI-mass spectrometry, and UV-visible spectroscopy.



**Keywords:** Triazole-crown ethers, Double-click reaction, Pyridine-triazole ligand, Selective binding

# Heteroditopic macrocycles for ion-pair recognition and synthesis of mechanically interlocked molecules (MIMs)

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Charge species are ubiquitous and play significant roles in a broad field of applications ranging from salt extraction and metal recovery to nanotechnology[1]. Not surprisingly, in the past few decades ion-pair recognition has emerged as the prime research field in host-guest supramolecular chemistry. In this study, a series of heteroditopic macrocycles was synthesized by attaching polyether chains of different lengths to bis-triazole derivatives with hydrogen bonding and halogen bonding donor groups. These macrocycles were designed to exhibit simultaneous recognition of both cations and anions in highly competitive organic solvents. The synthesis of the macrocycles was accomplished using the macrocyclization reaction of Williamson ether synthesis, followed by comprehensive characterization using spectroscopic techniques such as $^{1}$H NMR, $^{13}$C NMR, and HRMS. The binding affinities of the cation, anion, and ion-pair for each macrocycle were examined through the use of $^{1}$H-NMR and UV-visible spectroscopic titration experiments. This study revealed that binding affinities of anion to the macrocycle can be increased when alkali metal cations are present. Furthermore, these macrocycles showed their potential in the extraction of alkali metal halide salts by solid-liquid and liquid-liquid methods. Additionally, these macrocycles were utilized in the synthesis of mechanically interlocked molecules (MIM) using active metal template synthesis[2].

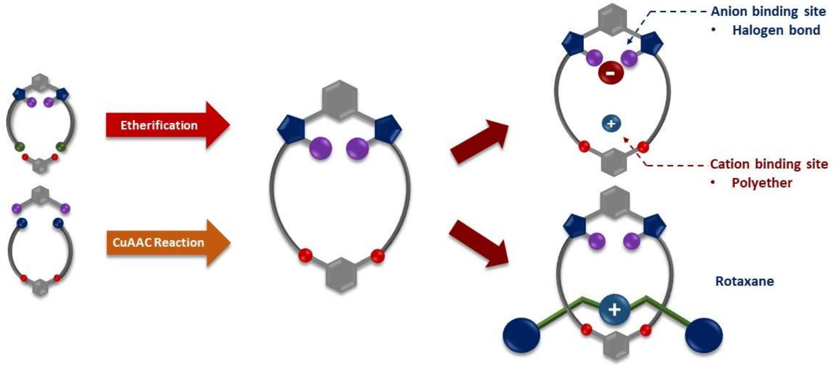

Fig. 1. Synthesis of aryl bis-triazole polyether macrocycle

**Keywords**: Heteroditopic macrocycles; Ion-pair recognition; Salt extraction; Metal recovery; Mechanically interlocked molecules

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# Naga[2]rotaxanes in Metallo-Supramolecular Assembly

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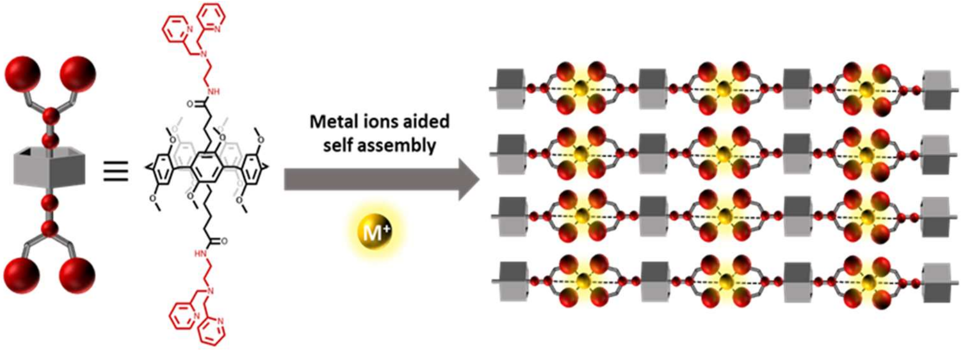
The naga, a legendary serpent, holds cultural significance within the mythological traditions of various Southeast Asian countries. Influenced by the architectural style of Naga in Thai temples, we present a collection of rotaxanes with pillar[5]arene as the central component and including tripodal ligand stoppers, which we refer to as Naga[2]rotaxanes. The synthesis of rotaxanes was achieved by employing the stopper exchange reaction[1] between the pillar[5]arene-containing compound and activated ester stoppers. An excessive quantity of $Zn(ClO_4)\cdot 6H_2O$ was introduced into the solution containing the prepared metallo-supramolecular rotaxane. The $^1$H-NMR spectra exhibit variations in response to the presence of metal ions complexed with the ligands. The rotaxane will undergo additional investigation of its physical properties and will be utilised in supramolecular assembly facilitated by metal ions.



**Keywords**: Pillar[5]arene-based rotaxane, Supramolecular assembly, Supramolecular polymer, [2]Rotaxane, Tripodal ligand stopper

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# Transition Metal Complexes Functionalised Non-Symmetrical XB triazole/HB amide Macrocycles for Enhanced Anion Recognition and Sensing in Aqueous Media

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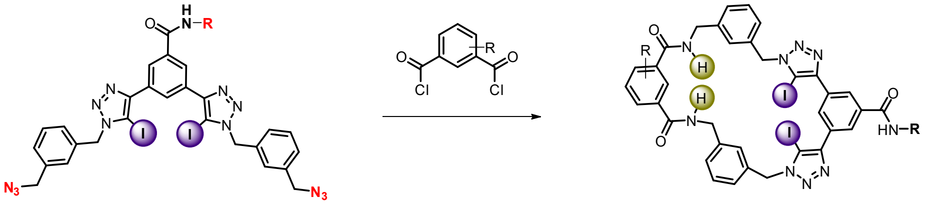
Halogen bonding sigma-hole interaction (XB), described as a highly attractive noncovalent contact between Lewis bases and electron-deficient halogen atoms, has emerged as a key noncovalent interaction that has been widely used in anion coordination during the last several decades. In general, integrating XB scaffolds into receptors can increase anion binding affinities, particularly in watery conditions.[1] Spectroscopic methods were used to thoroughly characterise a collection of tetradentate-macrocyclic hosts containing XB triazole/HB amide donors. The bis-iodotriazole arene appended the bis-amine precursors were first synthesised through a copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) process, followed by amide condensations with the target bis-acyl chloride to provide the target macrocycles (Figure 1). This versatile technique enables the inclusion of optical and redox active groups for anion sensing through UV-visible, fluorescence, and cyclic voltammetry (CV).[2]



**XB Macrocycle Precursor**

**Asymmetric XB-Amide macrocycles**

Figure 1. The series of asymmetric HB/XB macrocyclic molecules for anion recognition.

**Keywords**: anions; halogen bonding; electrochemical; fluorescence; supramolecular chemistry

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**Poster Presentation**
**SC-P-15**
**Praput Thavornyutikarn**

# Turn-on fluorescence detection of Zn(II) and Cd(II) ions by an anthraquinone-amide-DPA chemosensor

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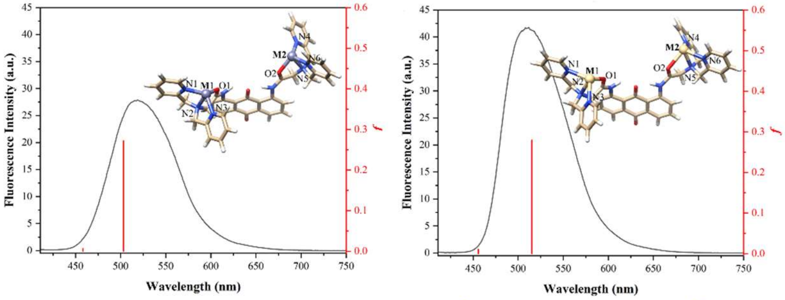
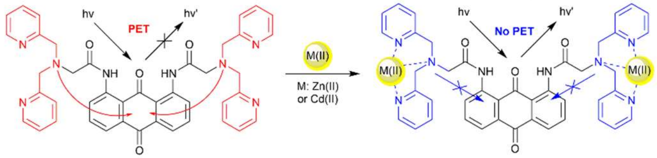
Two turn-on fluorescent chemosensors (**1** and **2**), based on an anthraquinone moiety linked with dipicolylamine units through amide bonds, were successfully synthesized with the overall yields of 61% and 90%, respectively. Structures of both chemosensors **1** and **2** were elucidated using several spectroscopic techniques such as 1D- and 2D-NMR, FTIR and HRMS. Sensor **1** exhibited a significant fluorescence enhancement *via* a turn-on photoinduced electron transfer (PET) mechanism in the presence of Zn(II) and Cd(II) ions. By using the TD-DFT calculations, the predicted binding structures and corresponding fluorescence spectra of complexes between sensor **1** with Zn(II) and Cd(II) ions were investigated and the results were in good correspondence with the experimental findings. Chemosensor **1** binds with Zn(II) or Cd(II) in a 1:2 ligand-to-metal ratio complex. The estimated detection limit values of sensor **1** were 0.408 µM and 0.246 µM, for Zn(II) and Cd(II), respectively.





1 (Turn-Off)

1-M(II) (Turn-On)

**Keywords**: florescence; chemosensor; turn-on PET mechanism; cation sensing

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Poster Presentation
SC-P-16
Kritanan Junthod

# Heteroditopic Lithium Ionophores Capable of Selective Recognition and Recovery of Lithium Salts

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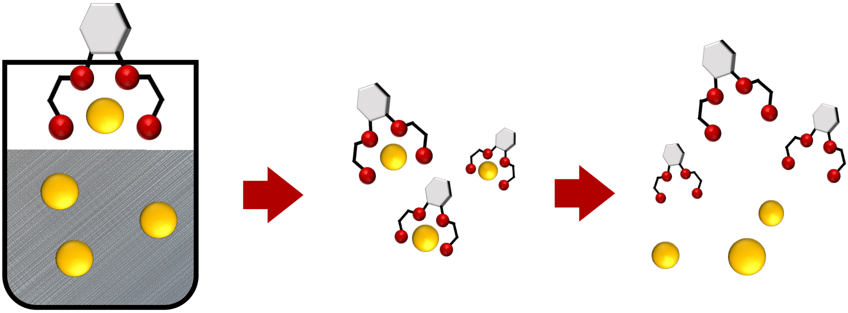
Since lithium is a key component in the production of batteries, effective and environmentally friendly techniques for lithium recovery are required to meet the increasing demand for lithium-ion batteries. In this study, we designed a series of supramolecular ligands containing both cation and anion binding motifs, coined as heteroditopic receptors, for selective recognition and extraction of lithium salts from aqueous solutions. The receptors were synthesised via nucleophilic substitution reaction of 2-chloro-*N,N*-dicyclohexylacetamide with a range of dihydroxybenzene derivatives. Furthermore, the lithium binding properties were investigated using $^1$H-NMR titrations and solid-liquid extraction experiments. It is worth mentioning that the enhanced recyclability of ligands resulting from the reversibility of lithium complexation with these ligands can facilitate their multiple uses of ligands.



Solid-Liquid Extraction

**Keywords**: Lithium recovery; Lithium extraction; Recognition; Supramolecular chemistry; Host-guest interaction.

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Poster Presentation
SC-P-17
Pipatpong Laoviwat

# Pillararene Supramolecular Assembly in Mechanically Interlocked Molecules (MIMs)

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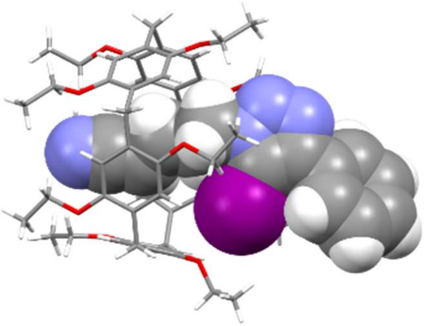
For the past few years, supramolecular chemistry has made advanced progress in broad research fields including material[1], sensing, and drug delivery. The design of macrocyclic hosts capable of forming strong and selective host-guest complexes is the key to manipulating interactions which are used in molecular organization, Pillararene is a pillar-shape macrocycle that has electron-rich aromatic cavities and properties to construct host-guest complementary[2]. In this work, we aim to investigate host-guest complexation properties of ethoxy pillar[5]arene (EtP5A) with a series of triazole-nitrile threads, a common organic linking motif for molecular assembly. Substituents at the 3, 4, and 5 of triazole play significant modulation of binding affinities with EtP5A. X-ray crystallographic analysis of suitable crystals revealed a successful encapsulation of the thread with EtP5A which is stabilized by hydrogen bonds. These results are important information for designing other complex supramolecular architecture in advanced material applications.



**Keywords**: Mechanically interlocked molecules (MIMs); Supramolecular Organic Frameworks (SOFs)

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# Switchable Magnetic Materials (SM)

# Abstract

**Keynote Speaker**
**SM-K-01**
**Sanjit Konar**

# Spin-State Switching in Dynamic Molecules and Chiral Cages

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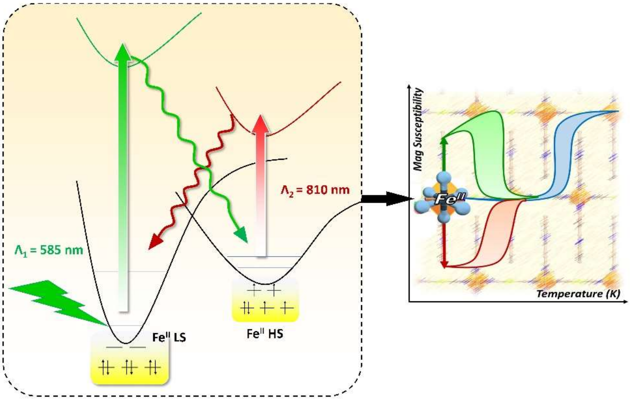
The development of molecular materials that can be switched between two different spin states through the application of external stimuli is of great interest owing to their potential use in molecular devices and information technology[1,2]. This switching behavior can be triggered by different reasons such as a charge/proton transfer, a change in the solid-state structure, or molecular orientation. When the *cooperativity* between spin centres is strong enough, a region of bistability opens, in which either of the two states can be found depending on the material's immediate past. This *memory* effect has been widely exploited in transition metal complexes. Some exciting recent discoveries[3-4] of spin-state switching in the Fe(II) based Hofmann type frameworks and Prussian Blue analogues(PBAs) in presence of external perturbation would be discussed in this presentation. In the second part, I will discuss the self-assembled enantioselective formation Fe(II) chiral cages, where, the guest molecules determines the chirality of the host system, by a relatively new approach known as "Reverse Chiral Recognition"[5].



**Keywords**: Spin-state switching; Hofmann framework; ETCST; LIESST; PBAs

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# Control of magnetic and electric polarization through external stimuli

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The design and synthesis of novel molecular compounds with physical properties that can be controlled via external stimuli have attracted considerable attention.[1] We have synthesized several functional compounds,[1-5] of which the electric polarization can be switched via electron transfer or spin transition process. A typical example is the [CoGa] heterometallic dinuclear complexes.[2] The [CoGa] complex exhibits thermally-induced electron transfer between the metal and ligands, which involves changes in the molecule's dipole moment. Since the [CoGa] complexes are designed to be oriented in the same direction within the crystal via chiral ligands, intramolecular electron transfer causes the polarization to switch at the crystal level. This polarization switching could also be induced by incident photons. Changes in polarization are normally mediated by ion displacement and molecular reorientation, whereas the polarization switching in the [CoGa] complex is realized via electron transfer. Another example is the [FeCo] heterometallic dinuclear complexes, the mechanism of which is the spin transition.[3] The [FeCo] dinuclear complex exhibits a magnetic field-induced spin crossover process, resulting in a significant polarization change of 0.45 μC $cm^{-2}$. Mössbauer spectroscopy and theoretical calculations suggest that the asymmetric structural change, coupled with electron redistribution, leads to the observed polarization change.

**Keywords**: Electric Polarization; Electron Transfer; Spin Crossover

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**Keynote Speaker**
**SM-K-03**
**Colette Boskovic**

# Towards three-state molecular switches via valence tautomerism and spin crossover

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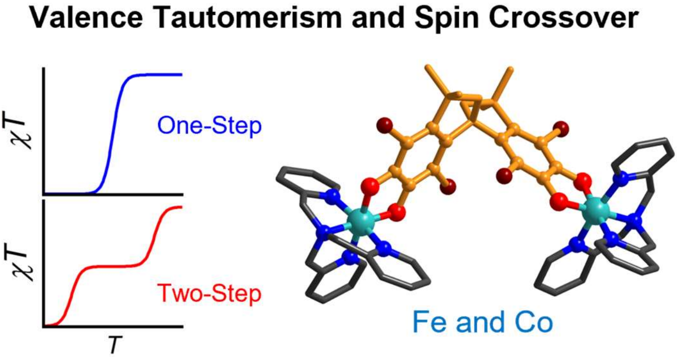
Molecular materials that can be switched between distinguishable forms by application of an external stimulus are of interest for future applications in display devices, sensing and molecular electronics and spintronics. Promising examples include spin crossover (SCO) complexes that can be interconverted between low and high spin states of a metal ion and valence tautomeric (VT) complexes, which undergo a stimulated intramolecular electron transfer between a metal centre and a redox-active ligand. Molecules that offer the possibility of switching between three or more states are of interest for accessing more complex logic processes in molecular electronics/spintronics and potential high density ternary data storage. Our work in this area has focused on the investigation of dinuclear Co and Fe complexes bridged by bis(dioxolene) ligands, towards two-step VT and SCO.[1–3]



**Keywords**: spin crossover; valence tautomerism; redox-active ligand; molecular switch, dinuclear complex

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**Keynote Speaker**
**SM-K-04**
**Tetsuro Kusamoto**

# Magneto-structural and magneto-luminescence correlations in radical-based coordination polymers

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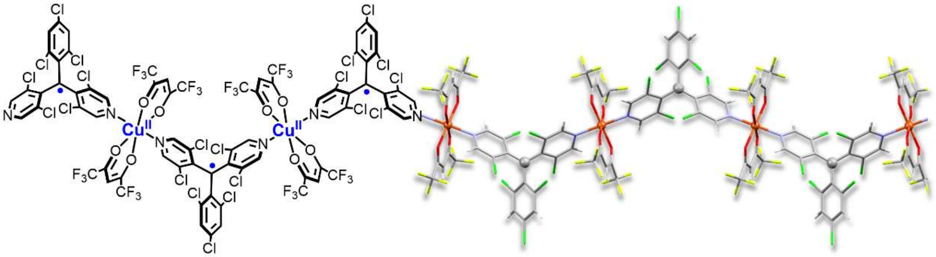
Magnetic coordination polymers (CPs) composed of magnetic building blocks such as paramagnetic transition metal ions and open-shell ligands (i.e., radical ligands) are promising candidates for future spin-related technologies. They exhibit a variety of unique magnetic functions attributed mainly to efficient exchange interactions between electronic spins, responsiveness to chemical and physical stimuli, and structural flexibility. Our group developed pyridyl-containing triarylmethyl radicals as a novel class of molecules demonstrating luminescence and magnetism.[1] Magnetic CPs composed of these radicals have shown distinct magneto-structural and magneto-luminescence correlations.[2,3]

A radical-$\text{Cu}^{\text{II}}$ 1D CP displayed temperature-dependent Jahn-Teller-like structural distortion around $\text{Cu}^{\text{II}}$, which modulated the p-conjugation mode at the ligand. The distortion caused a reorientation of the spin-orbital on $\text{Cu}^{\text{II}}$, enhancing the ferromagnetic radical-$\text{Cu}^{\text{II}}$ magnetic interaction at low temperature.[2]

Radical-$\text{Zn}^{\text{II}}$ 1D and 2D CPs were the first magnetoluminescent pure radical crystals, where the emission intensities of the materials increased with an applied magnetic field.[3] We proposed that weak but negligible magnetic interactions between the spins are the key to achieving magnetoluminescence.



**Keywords**: Magnetic CP; Radical; Jahn-Teller distortion; Luminescence

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# Spin Crossover System with Multifunction

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Ferroelectrics that display electrically invertible polarization are attractive materials because of their potential for wide-ranging applications. To date, considerable effort has thus been devoted towards developing ferroelectric materials, particularly those comprising organic/inorganic compounds. In these systems, structural dynamics such as atomic displacement and reorientation of polar ions/molecules play a key role in the generation of reversible spontaneous polarization. Although there are many reports concerned with organic/inorganic ferroelectrics, ferroelectrics based on coordination metal complexes have been largely unexplored despite their often unique electronic and spin state properties. In this feature article, we discuss recent progress involving coordination metal complex-based ferroelectrics where the reversible polarization originates not only from structural dynamics (represented by proton transfer, molecular motion, and liquid crystalline behavior) but also from electron dynamics (represented by electron transfer and spin crossover phenomena) occurring at the metal center. Furthermore, unique synergy effects (i.e., magnetoelectric coupling) resulting from the structural and electron dynamics are described.

**Keywords**: Spin Crossover; Ferroelectricity; Multifunction; Iron; Cobalt

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**Invited Speaker**
**SM-I-02**
**Hoa Van Phan**

# Spin crossover and High spin COFs

Hoa Phan[1], Jishan Wu[2], Michael Shatruk[3], Vinh The La[1], Chinh Dang Huynh[1]
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*2. Department of Chemistry, National University of Singapore*
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1. Spin crossover is a class of molecular switchable materials, which has attracted much attention due to its interesting properties and potential applications. Herein, we report a series of 2,2′-biimidazole (BIM) derivatives SCO complexes, including mono, binuclear complexes, the complexes for surface functionalization, and multifunctional SCO-conductivity materials.

2. In the second part of the talk, we present our findings associated with high-spin organic and coordination materials. Syntheses of ferro/ferri-magnetically coupled covalent organic frameworks have been a daunting task due to the highly reactive nature of organic radicals, especially when they are ferromagnetically coupled. These species have electrons occupying relatively high energy SOMO orbitals, resulting in rich chemistry. In addition, the unpaired electrons lead to interesting, unique properties that give rise to many potential applications in magnetism, rechargeable batteries, conductivity spintronics, MRI, or switches. Especially, these classes of materials pave the way for carbon-based magnets. In this talk, our recent findings on high-spin polymers/COFs will be reported. Those include fluorenyl radical polymers, triazine-linked trimethylenecyclopropanide radical frameworks, and fluorenyl-based coordination polymers. The structural characterizations, such as FTIR, powder XRD, XPS, and magnetic properties, such as FC, ZFC, EPR, will be presented.

**Keywords**: spin crossover, high-spin COFs, fluorenyl radical.

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**Invited Speaker**
**SM-I-04**
**Abhishake Mondal**

# Redox-active Motifs: Driving the Wheel of Switchable Magnetic Materials

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The pursuit of smart multifunctional materials with stimuli-responsive magnetic and optical response has drawn escalating interest in both fundamental science and potential applications to switches, sensors, and intelligent devices.[1] Spin Crossover (SCO) materials are ideal candidates for developing smart multifunctional materials and are promising components in nanotechnological devices.[2]

The development of stimuli-responsive flexible coordination polymers (CP) whose porous structures can be reversibly altered in response to the sorption of guest molecules has attracted growing attention. Also, the rational design of stimuli-responsive multifunctional CP by incorporating one or more additional cooperative properties, *e.g.*, magnetic, electric, optical, with the intrinsic properties, *e.g.*, permanent and tunable porosity, versatile structural topologies, and physicochemical properties have recently gained significant attention.[3] On this aspect, the simultaneous incorporation of both SCO and luminescence properties in CP is challenging but highly attractive as modulation of luminescence signal can signify LS/HS population during the spin-state switching.[4]

Here, I will present the versatility of redox-active Ethylenedioxythiophene (EDOT) based ligands to form a series of 2D CP and monomeric complex (Figure 1). The 2D Fe(II)-based CP exhibits cooperative SCO, luminescence properties, and ON/OFF photo-switching behavior.[5] Co(II)-based monomeric complexes exhibit a Spin Crossover between low-spin (LS) ($S = 1/2$) and high-spin (HS) ($S = 3/2$) states modulated by the counter anions.[6]

**Keywords**: Spin Crossover; Coordination Polymer; Luminescence; Photo-switching

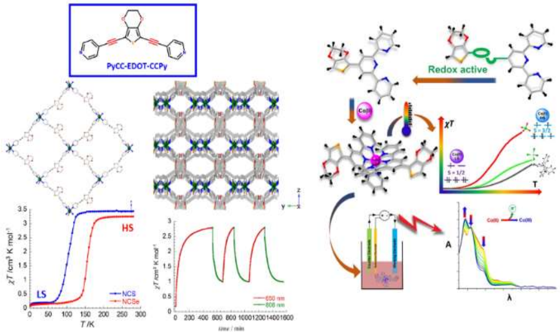

**Figure 3:** (Left) 2D structural, magnetic, and photomagnetic features of the Fe(II)-based CP; (Right) Structural, magnetic, and spectroelectrochemistry features of the Co(II) monomer with redox-active EDOT-Terpy ligand.

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**Invited Speaker**
**SM-I-05**
**Ho-Chol Chang**

# Molecular Lattice Engineering for Valence Tautomerism: connecting molecular and macroscopic worlds

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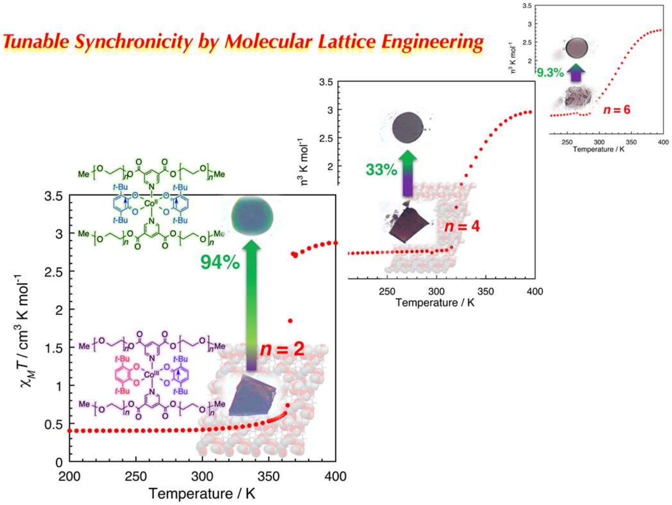
Valence tautomerism (VT) is a molecule-based form of bistability that involves reversible intramolecular electron transfer between two tautomers with different charge distributions. Triggered by the first example of this intriguing phenomenon on a Co-dioxolene complexes reported by Pierpont and co-workers,[1] extensive research has revealed the mechanism of VT, resulting in the development of molecular designs toward the fine-tuning of VT-based molecular bistability by, for example, changing the nature of the metal ion, the substituents on both the dioxolene and ancillary ligands, or the solvent molecules in the lattice.

Motivated by the high degree of cooperativity derived from first-order phase transitions in the solid state, we aimed to combine VT with solid-liquid transitions as an alternative strategy to create cooperativity within a given system. In order to experimentally verify the tunability of the synchronicity, the stability of the solid should be rationally controlled by means of well-defined molecular design. This paper will report the synthesis, VT, and macroscopic properties of a series of new VT complexes bearing two ancillary pyridine ligands with substituents that can effectively tune the molecular lattices of VT complexes.[1]



**Keywords**: valence tautomerism; molecular lattice; solid; liquid; cooperativity

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**Invited Speaker**
**SM-I-06**
**Zhao-Yang Li**

# Precise Modulation of Spin Transition Behaviors in Fe(III) Spin Crossover Solid Solutions

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A vital aspect of spin crossover (SCO) materials is the tunability of their spin transition behaviors. Although few tuning strategies have been implemented, systematic and quantitative tuning of the SCO behavior, including the spin transition temperature ($T_c$) and the number of spin transition steps, remains challenging in crystalline SCO materials[1-4]. This study reports a new Fe(III) SCO solid solution system in which the $T_c$ could be quantitatively tuned over 180–270 K in cooling mode by varying the doping ratio ($\boldsymbol{x}$) of the doped ligand by chemical doping. Upon increasing $\boldsymbol{x}$, a complete and reversible SCO conversion from two-step to one-step conversion was observed. The linear relationship between $T_c$ and $\boldsymbol{x}$ was divided into two stages with the occurrence of an inflection point at $\boldsymbol{x} = 0.6$, and $T_c$ first moved to lower temperatures and then moved to higher temperatures. According to the single-crystal, the dopants were located in the interlayers, and there were C–H⋯$X$ hydrogen bonds between layers. Thus, a correlation between the intermolecular interaction force and $\boldsymbol{x}$ could be established in the new Fe(III) SCO solid solution system. For the first time, $T_c$ and the number of steps were continuously and quantitatively controlled by regulating the intermolecular interaction force in an SCO solid solution with a two-dimensional layered structure.

**Keywords**: magnetic bistability; spin crossover; molecular solid solution; two-dimensional structures

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**Invited Speaker**
**SM-I-07**
**Peter Weinberger**

# Tetrazole-substituted carboxylic acids as precursor for luminescent Fe(II) SCO compounds

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N1-substituted tetrazoles are extremely versatile ligands forming Fe(II) SCO compounds. The family of ω-(1H-tetrazol-1-yl) carboxylic acids such as 2-(1H-tetrazol-1-yl)acetic acid (2COOHTz) yields Fe(II) spin crossover complexes (see Figure left) [1] and can be used as precursor for the synthesis of luminescent tetrazole-meso-substituted borondipyrromethene (BODIPY) as new ligands for Fe(II) SCO complexes.(see Figure right). Synthesis and characterization of this new family of luminescent Fe(II) SCO complexes will be presented.

**Keywords**: iron(II); spin crossover; tetrazoles; BODIPY; luminescence

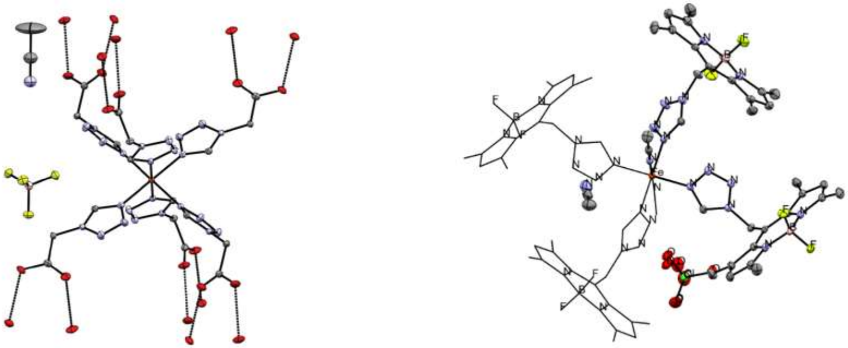

Figure: (left) [Fe(2COOHTz)$_6$](BF$_4$)$_2$·2 MeCN and (right) Fe[(2TzBODIPY)$_4$(MeCN)$_2$](ClO$_4$)$_2$·MeCN

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**Invited Speaker**
**SM-I-08**
**Masayuki Nihei**

# Structural conversion of supramolecular assembly by intramolecular electron transfer of [$Co_2Fe_2$] complex

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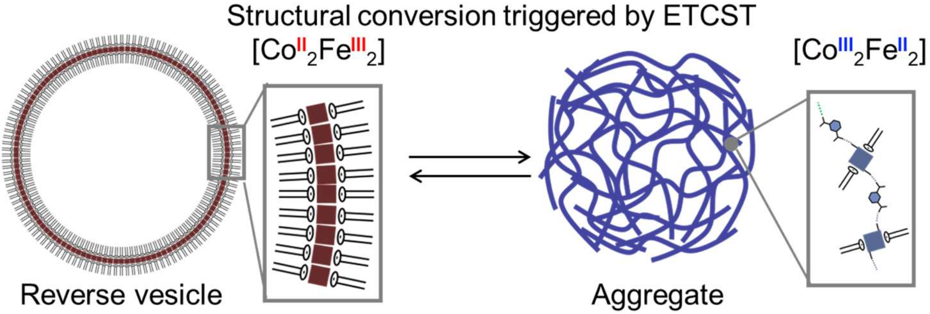
Prussian blue analogues (PBAs) are three-dimensional bulk solids constructed by bridging cyanide and metal ions. Discrete cyanide-bridged multi-nuclear clusters can be considered as zero-dimensional PBAs. We have prepared a series of cyanide-bridged multi-nuclear clusters exhibiting an electron-transfer-coupled spin transition (ETCST).[1,2] In addition, dimensionally controlled assemblies of the cyanide-bridged clusters with multi-stability have been reported so far.[3,4] On the other hand, combining metal complexes with amphiphilic molecules leads to a wide variety of functional self-assembled nanostructures. Metal complexes exhibiting spin transitions can be good candidates as the trigger to cause structural conversion of such assembly because they respond to various external stimuli. In this work, we studied a structural conversion of a supramolecular assembly containing a [$Co_2Fe_2$] complex through a thermally induced ETCST. The [$Co_2Fe_2$] complex formed reverse vesicles with amphiphilic anions in solution and showed reversible thermal ETCST. In contrast, thermal ETCST in the presence of a bridging hydrogen-bond donor caused structural conversion from the reverse vesicle structure to entangled one-dimensional chains through hydrogen bond formation.



**Keywords**: intramolecular electron transfer; supramolecular assembly; spin transition; external stimuli; switching

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**Invited Speaker**
**SM-I-09**
**Zhongyue Zhang**

# Quantum Spin Liquid and Quantum Critical Phenomena in a 2D conjugated Metal-Organic Framework

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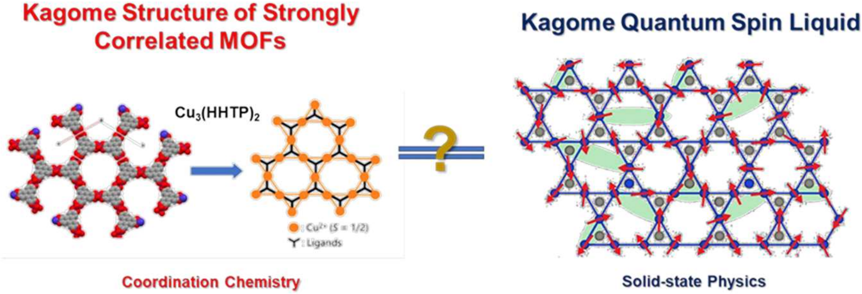
Metal-organic frameworks (MOFs) have been widely studied for their potential applications in gas separation, catalysis, sensors and drug deliveries, however, none of these applications take the advantage of the structural topologies of MOFs. This situation is overturned by the development of 2D π-d conjugated MOFs in recent years, in which the electrons and spins are strongly interacted, and emerging physics could be expected. Herein, using advanced measurement techniques, we unveiled a Kagome Heisenberg antiferromagnet (KHAF) spin liquid state in 2D MOF $Cu_3(HHTP)_2$, which adapts a honeycomb structure but with a Kagome lattice composed by Cu(II) $S$=1/2 lattices. Using ultralow temperature physical measurements, including susceptibility measurements, heat capacity measurements, proton NMR and field dependent measurements, we observed an absence of secondary phase transition, which validated the assumption of quantum spin liquid; the field dependent measurements further unearthed the quantum phase transition behavior and unique phase diagram of this MOF. These research results emphasized the potential of new research paradigm that translates the crystal engineering design of coordination chemistry to the prediction of properties in solid-state physics (Fig.1)

**Keywords**: 2D Metal-Organic Framework; Solid-State Physics; Quantum Spin Liquid; Quantum Critical.



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# Crystal engineering in iron(III) spin crossover complexes

Theerapoom Boonprab[1], Upeksha Habarakada[2], Warisa Thammasangwan[2],
Guillaume Chastanet[3], Phimphaka Harding[1*], David J. Harding[1*]

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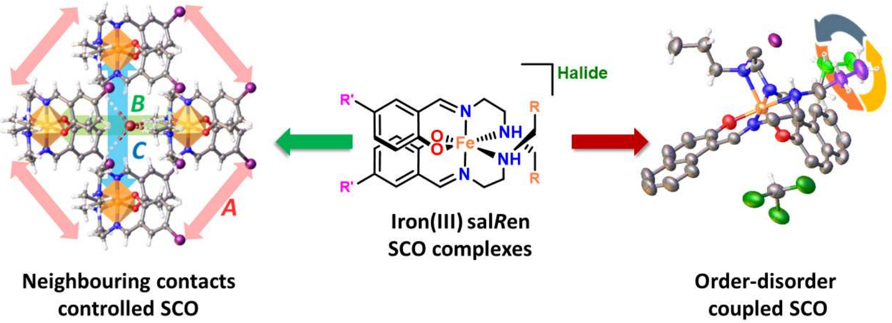
One of the key factors in successful spin-crossover (SCO) materials is control over solid-state cooperativity.[1][2] In this work, we demonstrate that variation of the amino alkyl and substituents on the aryl of Hsal*R*en ((*E*)-2-(((2-(*alkyl*amino)ethyl)imino)methyl)phenol) allows for tuning of the supramolecular packing and SCO capability. Firstly, three solvates of [Fe(naphPren)$_2$]I·sol {naphPren = (2-(((2-(*propyl*amino)ethyl)imino)methyl)naphthalen-2-olate); sol = $CH_2Cl_2$ **1**, $CHCl_3$ **2** and $C_2H_6O$ **3**} were successfully synthesized and characterized. The abrupt SCO in **1** and **2** is tied to a reversible order-disorder in the propyl group, while in the acetone solvate **3** which possesses no disorder shows SCO to a hidden LS state *via* **reverse**-LIESST. The three isostructural compounds [Fe(salEen-5-I)$_2$]halide {salEen-5-I = 2-(((2-(*ethyl*amino)ethyl)imino)methyl)-4-iodophenolate); halide = $Cl^-$ **4**, $Br^-$ **5** and $I^-$ **6**} compounds reveal packing into *2*-D rhomboidal sheets with Fe-Fe distances described by the parameters *A-C* defining the nearest and next-nearest neighbours.[3] These parameters rationalize not only the abruptness of spin crossover, but also the stepped nature of the SCO in **5**. In both cases, crystal engineering is vital in the design and understanding of SCO.



**Keywords**: Spin crossover; Iron(III) complexes; Crystal engineering; Light-induced excited spin-state trapping (LIESST); Order-disorder transitions

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**Oral Presentation**
**SM-O-02**
**Takamitsu Fukuda**

# Synthesis and magnetic properties of halogen-substituted [Mn(taa)] derivatives

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Yuji Miyazaki[2], Motohiro Nakano[2*]

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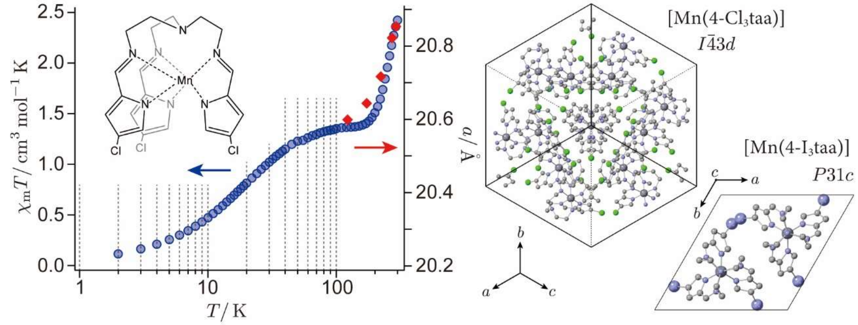
Thermally driven spin crossover (SCO) proceeds in the manner where the complex takes the maximum spin multiplicity (Hund-rule configuration) in the high-temperature range, whereas the number of paired spins is maximized at low temperatures because of diminishing occupation of anti-bonding $e_g$-orbitals. [$Mn^{III}$(taa)] ($H_3$taa = tris(1-(2-azolyl)-2-azabuten-4-yl)amine), which exhibits an abrupt spin transition from the quintet ($S$ = 2) to the triplet ($S$ = 1) below ca. 48 K, is one of the $d^4$ SCO complexes found in the early stage of the SCO study.[1] The entropy changes associated with the SCO of [Mn(taa)] could not be accounted for in terms of spin degeneracy and vibrational softening only, but should also the reorientation motion due to the dynamic Jahn-Teller effect in the high-spin species be considered as an essential entropy source, indicating that the chemical structure of the taa ligand plays a pivotal role in the SCO.[2,3] In this study, a series of halogen-substituted [Mn(taa)] derivatives, [Mn(4-$X_3$taa)] (X = Cl, Br, I), were synthesized, and their crystal structures and SCO properties were elucidated. All the derivatives give cubic *I*-43d crystals similar to the unsubstituted complex, but only [Mn(4-$I_3$taa)] provides another polymorph with the polar trigonal *P*31*c* space group. Either of the cubic crystals showed gradual SCO and the cooperativity appears to be altered by chemical modifications. The magnitude of the demixing interactions was estimated using the Slichter-Drickamer model.



**Keywords**: spin crossover; manganese(III); magnetostructural correlation, Jahn-Teller effect

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# Structures and SCO properties of Fe(II) complexes with novel Schiff-base ligands Hqap$^{X}$ and Hqan

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We have been interested in Fe(II) spin crossover (SCO) complexes with qsal$^{X}$ ligands with various substituents X.[1,2] In this paper, a new tridentate ligand, Hqap (2-[(8-quinolinylmethylene)amino]-phenol) has been synthesized from Schiff-base condensation of 2-Aminophenol and 8-Formylquinoline. The molecular structure of Hqap is resemble to that of Hqsal exept for the direction of the imine (C=N) moiety. The iron(II) complexes, [Fe(qap$^{X}$)$_2$] (X = F, Cl, Br) have been synthesized as black plate crystals and the crystal structure of [Fe(qap$^{Cl}$)$_2$] was determined at 100 K, which is consistent with the low-spin iron(II) spin state. Their magnetic properties were measured by SQUID from 5K to 400 K, which show SCO at $T_{c1/2}$=380 K for [Fe(qap$^{Br}$)$_2$], SCO at $T_{c1/2}$=400 K for [Fe(qap$^{Cl}$)$_2$], and LS state for [Fe(qap$^{F}$)$_2$]. These variations in $T_c$'s are completely different from those for [Fe(qsal$^{X}$)$_2$] system, in which the $T_c$ of [Fe(qsal$^{F}$)$_2$] is the lowest one.

Two-steps SCO at around 210 K was observed for [Fe(qan-2)$_2$], where Hqan-2 is another novel tridentate Schiff base ligand derived from 2-Amino-1-naphthol and 8-Formylquinoline.

**Keywords**: Iron(II) spin crossover; aminophenol; crystal structure; two-step spin transition

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# Stimuli-responsive Magnetic Bistability in Molecular Clusters

Sakshi Mehta,[1] Sujit Kamilya,[1] Rodolphe Clérac*,[2] and Abhishake Mondal*[1]

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The transformation of magnetochemistry into an interdisciplinary field led to the birth of **Molecular Magnetism**, a fruitful association of chemists, physicists and material scientists studying multifunctional magnetic materials. The design and synthesis of switchable molecular materials that can reduce the size of electronic devices have a long-standing promise in the field of molecular sensors, switches, electronics, data processing / storage & spintronics.[1] These materials allow access near room temperature bistability by optimized use of an external stimulus (light, pressure, and electrical field *etc*.).

Cyanide-based chemistry has led to the synthesis of an array of polymetallic systems based on "building block" approach. Amongst them, a particular interest has been given to various molecular model complexes of mixed valence [FeFe] Prussian Blue (PB) and [FeCo] Prussian Blue Analogues (PBAs), *e.g.*, molecular cubes, squares, and dinuclear units exhibiting interesting bistable properties.[2]

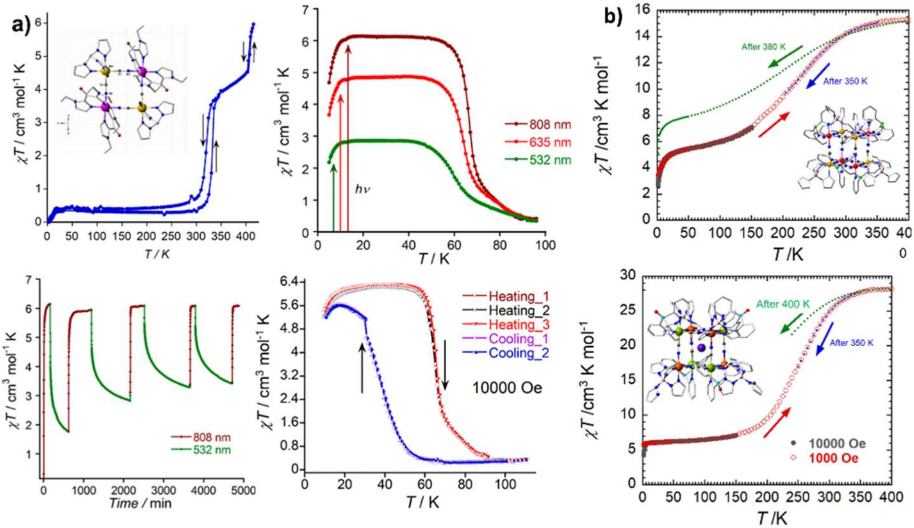

**Figure 4: (a)** Perspective view of $Fe_2Co_2$ molecular square undergoing thermo- and photo-induced MMET and LITH effect, **(b)** Reversible thermo-induced MMET in molecular $Fe_8$ cube and Alkali-inserted $Fe_8$ cube

**Switchable Magnetic Materials (SM)**

**Poster Presentation**
**SM-P-01**
**Sakshi Mehta**

Here, I will present some [$Fe_2Co_2$] molecular squares exhibiting reversible thermo- and photo-induced metal-to-metal electron transfer (MMET) and ON/OFF switching.[3,4] Also, I will present octanuclear $Fe_8$ complexes, where combined structural, magnetic, and spectroscopic studies reveal that applying magnetic field, temperature, and light irradiation could trigger MMET.

**Keywords**: Molecular Magnetism; Bistability; Building block approach; Metal-to-Metal Electron Transfer; ON/OFF switching

**Acknowledgments:** We thank the Indian Institute of Science (IISc), the Solid State and Structural Chemistry Unit (SSCU), the Department of Science & Technology-Science & Engineering Research Board (DST-SERB), the Scheme for Transformational and Advanced Research in Sciences (STARS, MHRD) for the financial support.

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Poster Presentation
SM-P-02
Sounak Ghosh

# Switchable Magnetic Materials Based on Metallosupramolecular Architecture and Discrete Entities

Sounak Ghosh[1], Subrata Ghosh[1], Sujit Kamilya[1], Sukanya Bagchi[1], Sakshi Mehta[1], Yanling Li[2], Rodrigue Lescouëzec[2], Santosh Panjikar[3], Abhishake Mondal[1*]

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The era of modern technology demands the betterment of existing technology, leading to the advancement in the field of molecular magnetism. Thus the molecular magnetic materials having enormous possibilities in future electronic devices. On particular "Spin Crossover (SCO)" systems can fulfill the demands. SCO arises due to the switching between two easily accessible electronic spin-states in $3d^4$ to $3d^7$ octahedral systems *i.e.*, high spin (HS) and low spin (LS) by applying external stimuli *e.g.*, change in temperature, pressure, light irradiation, magnetic and electrical field, presence, or absence of a guest molecule *etc.*[1] In contrast, Single Molecule Magnets (SMMs) are a class of paramagnetic molecular entity exhibiting slow dynamics in their magnetization due to their bistable magnetic states, separated by an energy barrier ($U_{eff}$). Herein, I will present the effect of counter anions in thermal SCO property of mononuclear cobalt(II) complexes using versatile redox-active Ethylenedioxythiophene based terpyridine ligand system.[2] Also, how the various counter anions and different substituents in the $N_4O_2$ type Schiff base ligands result gradual / abrupt / step-wise SCO in mononuclear manganese(III) complexes.[3] I will also show when we move from mononuclear to multinuclear complexes such as $Co^{II}_4L_4$ tetrahedral cage, it exhibits field-induced SMM at 1000 Oe dc field along with SCO in both solid and solution states, evident from solid-state magnetic measurements ($T_{1/2} \approx 360$ K) and solution-state Evans $^1$H-NMR method ($T_{1/2} \approx 398$ K).[4]

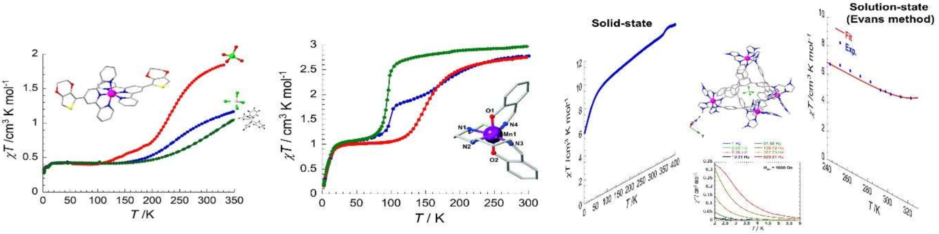

**Figure 5:** Structural representation of mononuclear Co(II), Mn(III) based SCO systems and the corresponding physical

**Acknowledgements:** We thank the Indian Institute of Science (IISc), Solid State and Structural Chemistry Unit (SSCU), the Scheme for Transformational and Advanced Research in Sciences (STARS, MHRD), Govt. of India.

**Keywords**: tetrahedral cobalt(II) cage; symmetry breaking, spin crossover; single molecule magnets, Evans' method

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SM-P-03
Pannawich Jaratape

# Structural studies of substituent effects in [Fe(qsal-X)$_2$]OTf complexes

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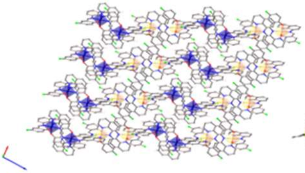
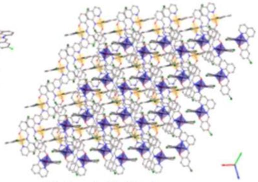
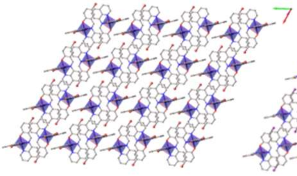
Spin crossover (SCO) behavior is known to be significantly impacted by crystal packing. In this work, we investigated the influence of the halogen substituent on the crystal structure and magnetic behavior in the series, [Fe(qsal-X)$_2$]OTf (qsal-X = 4-X-2-[(8-quinolylimino)methyl]phenolate; X = F **1**, Cl **2**, Br **3**, and I **4**; OTf = $CF_3SO_3$). Two new compounds in the series, **2** and **3•MeOH** were successfully synthesized and characterized. All compounds crystallized in the triclinic $P\bar{1}$ space group with **1** and **2** exhibit two independent iron(III) centers in the asymmetric unit, while **3•MeOH** and **4•MeOH** reveal only one iron(III) center with one molecule of methanol. Gradual SCO was detected in **1** whereas the SCXRD structures reveal that **2** is stabilized in the low spin state (LS). 3D networks in **1** are formed by stacking of the corrugated planes. Alternatively, **2** shows a stacking of 2D planes with alternating Fe1 and Fe2 planes (Fe1-Fe2-Fe1). Meanwhile, abrupt SCO in **4•MeOH** has been reported, and the SCXRD structures reveal that **3•MeOH** also exhibits SCO. **3•MeOH** and **4•MeOH** are isostructural, with highly cooperative 2D networks.



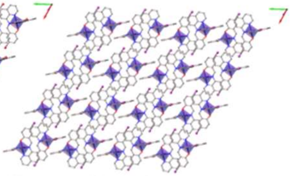
[Fe(qsal-F)$_2$]OTf



[Fe(qsal-Cl)$_2$]OTf



[Fe(qsal-Br)$_2$]OTf•MeOH



[Fe(qsal-I)$_2$]OTf•MeOH

**Keywords**: Spin crossover(SCO); Iron(III) complexes; Single Crystal X-ray Diffraction

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# Stimuli-Responsive Molecular Bistability in Di- and Tetranuclear Metallosupramolecular Architectures

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The application of molecular magnetic materials in electronic devices depends on the “molecular bistability” that arises from switching between two easily accessible electronic spin states of the metal ion *i.e.*, high spin (HS) S = 2 and low spin (LS), S = 0 under the influence of external stimuli (light, temperature, pressure etc) as well as chemical stimuli (*pH*, change of chemical potential)**[1]**. On the other side, following nature mimicking self-assembly process metal ligand coordination entity gives us a library of metallosupramolecular architectures that are employed to design switchable molecular magnetic materials with the strong co-operativity between metal centres inside supramolecular framework**[2]**. These discrete complexes are useful for application in sensing and separation of gases, catalysis and biotechnology**[3]**. Our research is focusing mainly on the rational design and synthesizing Metallosupramolecular self-assembled architectures based on 3d metals, for exploring stimuli-responsive switching phenomenon e.g. Photoluminescence, Spin-State Switching[4] and Single-Molecule Magnets (SMM)[5].

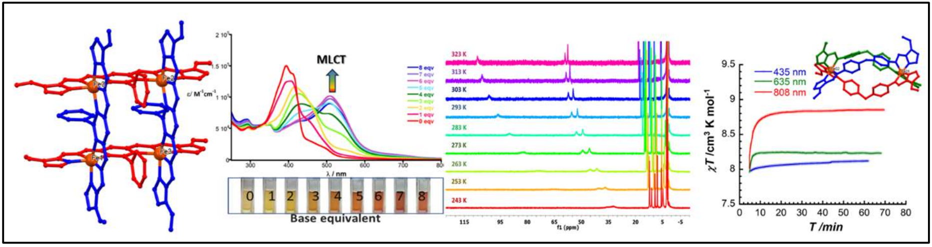

Figure 1: SCXRD structure of the grid and helicate complexes along with their physical properties

Here, I will present several tetranuclear [2x2] grids and dinuclear helicates consisting of Fe(II) exhibiting molecular bistability. A series of Fe(II) [2x2] grids have been synthesized involving ionizable bis-hydrazone moiety in the structure and an exciting Spin State Switching phenomena have been observed both in solid state and solution with change of pH in the medium. The dinuclear Fe(II) helicates also show Spin State Switching with varying ligand field with exciting photomagnetic properties.

**Keywords**: [2x2] Grids; Spin State Switching; Metallosupramolecular Chemistry; Photomagnetism

**Acknowledgement:** The authors thank the Solid State and Structural Chemistry Unit, Indian Institute of Science, Scheme for Transformational and Advanced Research in Sciences (STARS), MHRD, Government of India and Prime Minister’s Research Fellowship, Ministry of Education, Government of India for the research support.

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# A novel valence tautomeric phenomenon manifesting in solution at room temperature

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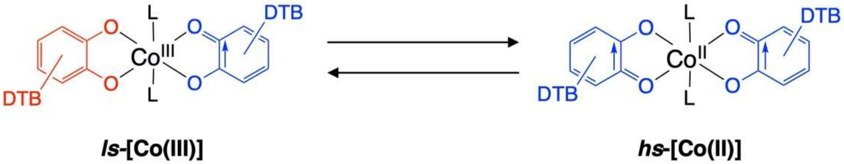
Molecular-based systems responsive to external stimuli, such as heat, light, and magnetic/electric fields, hold significant scientific and technological promise for low-energy driven switches, memories, and information storage applications.[1] The phenomenon of valence tautomerism (VT) is particularly intriguing in this context, as it involves intramolecular charge transfer, potentially leading to drastic changes in optical and/or magnetic property among two or more tautomers (Scheme 1). While VT is commonly induced by heat, light and pressure,[2] most studies have been conducted under variable temperature conditions. In contrast, there are few documented instances of VT occurring under constant room temperature conditions.[3]

In this study, we have identified the inaugural instances of valence tautomeric transitions at room temperature within a series of complexes, encompassing both newly synthesized and previously reported compounds. We will present the synthesis, along with structural and spectroscopic characterizations, of the complexes, highlighting their distinctive VT behaviors at room temperature.

**Scheme 1.** Valence tautomeric equilibrium



**Keywords**: Bistability; Valence tautomerism; Cobalt dioxolene complex; Substituent dependence; Molecular magnetism

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# Single Molecule Magnets (SS)

# Abstract

**Keynote Speaker**
**SS-K-01**
**ShangDa Jiang**

# Spin Manipulation in Magnetic Molecules

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Quantum information technology can realize a new information processing based on quantum mechanics principles. The main systems currently used for quantum computing research include superconducting circuits, semiconductor quantum dots, diamond color centers, and topological insulators. Chemical design can control the quantum behavior of magnetic molecules and obtain a larger Hilbert space. Therefore, studying the quantum coherence of magnetic molecules, performing novel and complex quantum coherence manipulations, and trying to use magnetic molecules for quantum computing are important contents of quantum information materials chemistry. This report will firstly introduce the relevant basic concepts and research ideas of the "Magnetic Molecular Coherence Manipulation", and introduce the "cage structure protection" proposal to enhance the magnetic molecular coherence. The report will also introduce our experiments on efficient coherent manipulation of magnetic molecules using transient electric fields and lasers. The quantum phase interference phenomenon of multi-level molecules of fullerene molecules shows that magnetic molecules have richer physical connotations than traditional quantum systems.

**Keywords**: magnetic molecules; quantum coherence; quantum information processing;

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# *Slow relaxation of the magnetization in a formally two-coordinate 4f complex*

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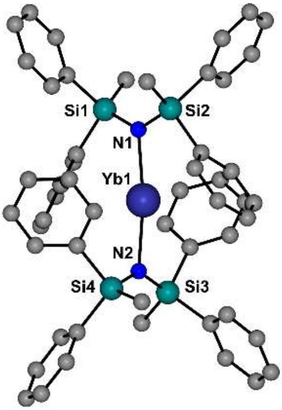
Molecules that exhibit the super-paramagnet-like property of slow magnetization relaxation and thus behave as magnets below their magnetic blocking temperature are termed Single-Molecule Magnets (SMMs). These molecular systems are promising candidates for molecular electronics such as high-density memory storage and quantum computers. Yet, the design of high-performance SMMs has been an ongoing challenge for the last three decades. Low-coordinate lanthanide complexes with strong magnetic anisotropy could afford high-performance SMMs but are challenging to synthesize. Now, through a clever ligand design, a near-linear pseudo-two-coordinate Yb(III) complex that exhibits slow magnetic relaxation is reported for the first time.[1] The complex has a large ground-state splitting arising from the crystal field imposed by the ligands. These results represent an important first step towards SMMs with record bocking temperatures.



**Keywords**: Lanthanide; Single-Molecule Magnets; low-coordinate; magnetism

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# Molecular Modelling: A Key Player in the Design and Evolution of Molecular Nano Magnets

**Gopalan Rajaraman**

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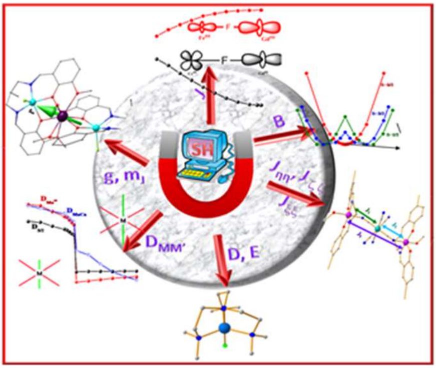
Molecular magnetism is one of the vastly growing research fields with an aim to design molecules and materials with tunable magnetic and electronic properties.[1] Their synthesis, characterization and implementation as devices create a lively crossroad among chemistry, physics and material science: a multidisciplinary research field. These molecules have widespread potential applications ranging from magnetic storage devices, spintronics, and Q-bits in quantum computing to magnetic coolants.[2] Single-molecule magnets (SMMs) are the molecules which show slow relaxation of magnetization below the critical temperature and exhibit a hysteresis loop similar to classical magnets. SMMs offer key advantages over classical magnets due to their lightweight, solubility and multifunctional behaviour. Theoretical tools are indispensable in this arena[2] for understanding the observed magnetic properties. The strength of these methods is not only limited rationalization but also the prediction of novel molecules which can exhibit superior magnetic properties. In this presentation, I will research the effort undertaken by our group towards achieving these goals.[2, 3]



**Keywords**: Ab initio calculations, Single-molecule Magnets, Machine learning, spin-phonon relaxation.

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Keynote Speaker
SS-K-04
Annie Powell

# Exotic spin structures in 4f containing coordination clusters

Annie Powell[1*]

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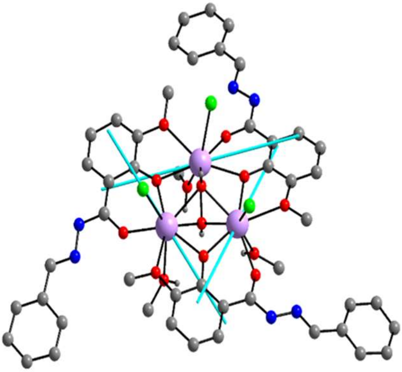
Coordination clusters containing 4f metal ions can show a number of remarkable magnetic behaviors beyond that of acting as Single Molecule Magnets (SMMs). This is a consequence of strong spin orbit coupling effects which lead to unusually anisotropic spins for many of the 4f electron configurations. The dysprosium 3+ ion is the most famous example of an ion with an oblate anisotropy ellipsoid, which leads to an Ising spin ground state, i.e. with the spin oriented along the z-axis and with tiny spin components in the xy plane. This in turn can lead to exotic spin systems such as the first identified molecular realization of a toroidal spin system in a molecule containing a $Dy_3$ triangle produced in our laboratory.[1-3] Further such toroidal $Dy_3$ triangles will be presented, including ones where the triangular arrangement is supported and/or induced by the presence of 3d transition metal ions. In addition, two cyclic $Fe^{III}$-$Dy^{III}$ systems will be described where a solenoidal toroidal moment can be disrupted into what is possibly a molecular realization of an anyon-based[4] arrangement of spin partners.



**Keywords**: Dysprosium; Toroidal moment; Transition metal ion; Magnetism; Coordination cluster

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# Chemo-Switchable MOF Magnets

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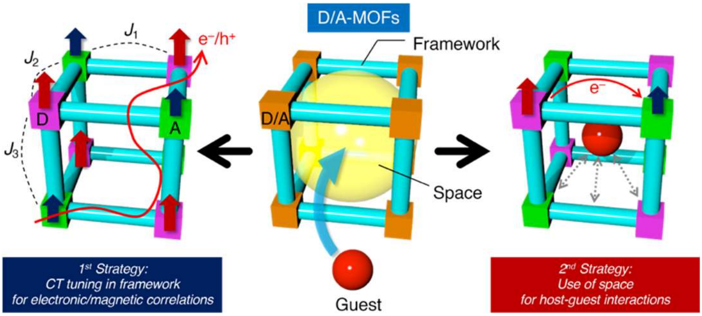
Developing materials with multiple sensing capabilities that can be controlled by chemical and physical stimuli is a significant challenge in the field of materials science. A class of electron-conjugated metal-organic frameworks (MOFs) composed of electron-donors (D) and/or –acceptors (A): we call this class of materials as "D/A-MOFs", is one of the favorable candidates for such materials [1,2], because the charge transfer (CT) of $D^0A^0 \leftrightarrow D^{\delta+}A^{\delta-}$ is tunable based on the parameters of the ionization potential of D, electron affinity of A, and Madelung stabilization of ionic $D^+A^-$ set and could be sensitive to stimuli. Thus, D/A-MOFs are intriguing targets for guest-sensitive electronic, magnetic, and dielectric functional materials as well as their porous nature for gas/solvent sorption or ionic transportation. Multidimensional frameworks were designed using paddlewheel-type diruthenium(II, II) complexes ($[Ru_2^{II,II}]$) as D and TCNQ or DCNQI derivatives as A, and the ability to control CT in D/A-MOFs to achieve electronic and magnetic functionalities has been demonstrated [2]. The magnetic properties of porous $D_2A$ layered systems with void spaces between layers are highly responsive to interlayer environments, which are relevant to guest molecules that are present or inserted between layers and often impact the charge-ordered state of the materials [3–12].



**Keywords**: charge-transfer; MOF magnet; gas adsorption; chemo-switching; phase change

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# Molecular Spin Qubits for Quantum Computer and High-Density Memory Devices

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Spintronics, based on the freedoms of charge and spin of the electron, is a key technology in the 21st century. Magnetic random access memory (MRAM), which uses giant magnetoresistance (GMR), has several advantages compared with electronics. Although conventional magnets composed of transition metals are normally used, in our study, we use molecule-based nano-magnets and single-molecule magnets (SMMs) to overcome "Moore`s Limitation". SMMs are also available for quantum computer. I will talk about the molecular spin qubits for quantum computer according the following four approaches such as [1]Crystal Engineering Method, [2]g-Tensor Engineering Method, [3]Orbital Engineering Method, and [4]Molecular Technology Method. We have realized the spin qubits and Rabi nutation even at room temperature by using MOF. Next, I will talk about the high-density memory devices such as single-molecule memory performance, SMMs encapsulated into SWCNT with the negative magnetoresistance and Coulomb blockade oscillation, and metallic conducting SMMs with negative magnetoresistances to overcome "Moore`s Limitation".

**Keywords**: Molecular Spin Qubits, Quantum Computer, Single-Molecule Magnets,

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**Invited Speaker**
**SS-I-03**
**Yan-Zhen Zheng**

# Thermally Stable Terbium(II) and Dysprosium(II) Bis-Amidinate Single-Molecule Magnets

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Single-molecule magnets (SMMs) are molecules that can store binary data and serve in future ultra-high-density information storage devices. Recently $Dy^{III}$ based SMMs are proven to be the most potential candidates while the design rules are clear for approaching the upper performance limit in static properties. Most investigations of Ln SMMs to date have focused on complexes containing Ln ions in the most common +3 oxidation state.[1] The Kramers ion Tb(II) complex $[Tb(C_5{}^iPr_5)_2]$ has $U_{eff}$ = 1738 K, $T_H$ = 55 K and $T_{100}$ = 52 K.[2] To the best of our knowledge this is the only Ln(II) SMM to date with a measured energy barrier, and all these parameters are currently record-high values for any mononuclear Tb SMM; a $U_{eff}$ value for the non-Kramers ion Dy(II) complex $[Dy(C_5{}^iPr_5)_2]$ could not be determined. Conversely, the mixed-valent Ln complexes $[Ln_2(C_5{}^iPr_5)_2(\mu\text{-}I)_3]$ (Ln = Tb, Dy) exhibit one-electron Ln–Ln σ bonds, leading to large coercive fields and favorable SMM properties for both Tb and Dy; the Dy analog currently holds record values for $U_{eff}$ (2347 K), $T_H$ (80 K), and $T_{100}$ (72 K) amongst all SMMs.[3]

Here we report the thermostable four-coordinate divalent lanthanide (Ln) bis-amidinate complexes $[Ln(Piso)_2]$ (Ln = Tb, Dy; Piso = $\{(NDipp)_2C^tBu\}$, Dipp = $C_6H_3{}^iPr_2$-2,6),[4] which were prepared by the reduction of parent five-coordinate Ln(III) precursors $[Ln(Piso)_2I]$ (Ln = Tb, Dy) with $KC_8$; halide abstraction of $[Ln(Piso)_2I]$ with $[H(SiEt_3)_2][B(C_6F_5)]$ gave the respective Ln(III) complexes $[Ln(Piso)_2][B(C_6F_5)]$. All complexes were characterized by single crystal and powder XRD, SQUID magnetometry UV-vis-NIR, ATR-IR, NMR and EPR spectroscopy, and *ab initio* CASSCF-SO calculations. These data consistently show that $[Ln(Piso)_2]$ formally exhibit Ln(II) centers with $4f^n5d_{z2}{}^1$ (Ln = Tb, $n$ = 8; Dy, $n$ = 9) valence electron configurations. The coordination geometry of $[Ln(Piso)_2]$ is intermediate between square planar and tetrahedral, however projecting from the quaternary carbon atoms of the $CN_2$ ligand backbones show near-linear C···Ln···C arrangements. This results in strong axial ligand fields to give effective energy barriers to magnetic relaxation of 1863(210) K for the Tb(II) analog and 1973(240) K for Dy(II), the highest values observed to date for any mononuclear Ln(II) SMM.[2]

**Keywords**: Single-molecule magnets; divalent lanthanide; amidinate; magnetic anisotropy;

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**Invited Speaker**
**SS-I-04**
**Sanchita Goswami**

# Quest for Single Molecule/Ion Magnets in Mixed Valent (Mn$^{II/III}$, Co$^{II/III}$) and 3d-4f Systems: Structural Tuning and Observation of Interesting Magnetic Outcomes

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The construction of mixed valence and 3d-4f heterometallic species have witnessed a steady growth in the fields of coordination chemistry and magnetochemistry, as evident by a constantly increasing number of publications in this area.[1] The quest for molecular magnetic materials possessing potential applications in information storage, spin−dependent electronics and quantum computing is one of the most challenging topics in chemistry, which leads to the generation of single−molecule magnets (SMM) and single ion magnets (SIM). In addition to potential technological applications, the understanding of the fundamental concept to master the design principle and structure-magnetism correlation also serves as the driving force. A rich library of compounds provides the crucial knowledge to synthetic chemists for the tailor-made design of systems of desirable magnetic outcomes.

In this lecture, I wish to provide a glimpse of our laboratory experience in quest of SMMs/SIMs regarding Mn$^{II}$-Mn$^{III}$,[2] Co$^{II}$-Co$^{III}$,[3] Ln$^{III}_2$ (Ln = Gd, Tb, Dy, Ho),[4] Cu$^{II}$-Dy$^{III}$,[5] Co$^{II/III}$-Dy$^{III}$,[6] Cd$^{II}$-Ln$^{III}$ (Ln = Ce, Nd, Sm, Gd, Ho) systems. A few compounds have exhibited SMM/SIM behavior whereas a couple of systems depicted only slow relaxation of magnetization.

**Keywords**: Single Molecule Magnet (SMM); Single Ion Magnet (SIM); Slow Relaxation of Magnetization

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# Design of the lanthanide(III) complexes with tripodal nitroxyl radicals

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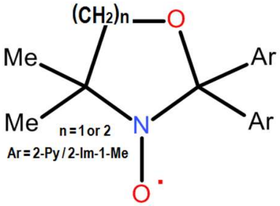
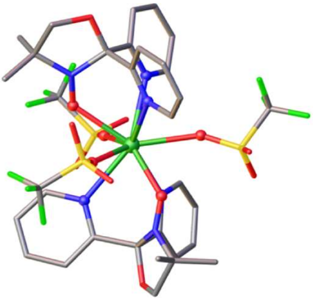
Nitroxyl radicals functionalized with aryl heterocycles (Rad$^{5-6}$) (see picture) are promising in design of molecular magnets due to directly linked N—O group bearing spin density and predictable coordination mode. This is critical to obtain magnetically anisotropic Ln$^{3+}$ complexes with prescribed geometry and ligand field strength. This is crucial to suppress magnetization tunnelling in SMMs. The recently obtained complexes [Ln(Rad$^{5-6}$)(NO$_3$)$_3$] (**1**) possess strong magnetic exchange coupling in a Ln←O—N fragment [1], which also contributes to the suppression of the tunnelling effect. The latter is greater than the lower a polyhedron symmetry characteristic for coordination-capacious lanthanides. Therefore, rational design of paramagnetic ligands for the complexes with a geometry suitable for either prolate or oblate type of Ln$^{3+}$-ions is a challenging task.

In the sandwich-like complexes [Ln(Rad$^{5-6}$)$_2$(OTf)$_3$] (**2**) [2], the equatorial anions are well suited for oblate Ln$^{3+}$-ions, while their absence fits better prolate ones. Magnetic behaviour of **2** can be tuned: tripod should be more sterically demanding and symmetrical. It is possible by varying tripod's organization: combination of 5-membered cycle of *oxazolidine*-N-oxide with 2-imidazoline-1-methyl as Ar (5-5 arrangement) or 6-membered cycle of *oxazinane*-N-oxide with 2-pyridyls (6-6 arrangement). The methyl addition to Ar should lead to the formation of 6-coordinate complexes.

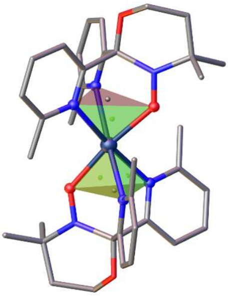


n=1 – 4,4'-dimethyl-2,2'-di(Ar)-oxazolidine-N-oxide
n=2 – 4,4'-dimethyl-2,2'-di(Ar)-oxazinane-N-oxide

**TRIPODAL RADICALS**



**[Ln(Rad$^{5-6}$)$_2$(OTf)$_3$]**



**[Ln(Rad$^{6-6}$)$_2$](anion)$_3$**

**Keywords**: nitroxide radicals; tripodal ligands; Ln(III) complexes; SMMs; keyword 5

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# Enriching Single Ion Magnetism in Lanthanide Phosphate and Phosphonamide Complexes

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Precipitously changing current information technology demands energy and cost efficient tools that not only can efficiently store but also swiftly process large data. The miniaturization technology that was being used to boost the performance of the electronic devices (to keep up with the pace as estimated by Moore's law) is however reaching its limit. To overcome these challenges, several alternative routes are being proposed. Single molecule magnets (SMMs), being considered as one of the potential alternatives, have gone through significant progress during the last two decades and the focus has shifted from the use of polynuclear clusters to mononuclear complexes in recent years. The current frenzy in the field of SMMs is driven by a better understanding of the effects of crystal field (CF) and molecular symmetry on the magnetic properties, especially in the case of mononuclear paramagnetic complexes, apart from other controlling factors. This has led to the advent of highly anisotropic single-ion magnets (SIMs) with magnetic blocking temperatures as high as 60 K and anisotropic energy barriers over 1800 K. This talk would summarize our recent research in the light of the emergence of the importance of CF and symmetry in 4f ion based single-ion magnets (SIMs), especially in the context of SIMs with D5h symmetry, apart from commenting on the synthetic efforts adopted to place these metal ions in unusual coordination geometries.

*The authors thank Prof. G. Rajaraman and his group for an active collaboration in modelling our systems. For further details, please refer to our key publications in this area:* S.K. Gupta et al. *Dalton Trans.* **2015**, *44*, 5961; *Chem. Sci.* **2016**, 7, 5181; *Chem. Commun.* **2016,** *52*, 7168; *Inorg. Chem.* **2017**, *56*, 3946; *Inorg. Chem.* **2017**, 56, 9071; *Dalton Trans.* **2018**, *47*, 357; *Chem. Commun.* **2018**, *54*, 3685; *Dalton. Trans.* **2019**, 48, 15928. *Coord. Chem. Rev*. **2022,** *453***,** 214288; *Chem. Euro. J.* **2022,** e202103585**,** *Dalton Trans***. 2023,** *52***,** 8943**;** *Inorg. Chem.* **2023**, *62*, 8435

# Influence of Energy Barriers of Multinuclear Dysprosium SMMs by Different Substitutions of Ligands

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Single-Molecule Magnet (SMM) displays slow relaxation of magnetization at the molecular dimension which has led to worldwide research interest owing to potential applications in many fields, such as high-density information storage, quantum computations, molecular spintronic devices, as well as multiferroic materials and magnetic refrigerants. For almost two decades, $Dy^{3+}$-based SMMs have been exhibiting the best magnetic performances in an axial environment which stabilizes the $Dy^{3+}$ oblate 4f electronic density. To date, major breakthroughs have been reported in organometallic and coordination complexes showing such axiality. Indeed, mononuclear complexes have been shown a direct correlation between relaxation barriers and electron-withdrawing groups on terminal ligands. However, the examples of multi-nuclear pure lanthanide complexes were relatively rare due to the variable and high coordination numbers as well as the poor directionality of rare earth metals. Therefore, our research was focused on synthesizing similar core structures with a series of electron-donating/withdrawing substitutions and mono-, di- tri-, and tetra-nuclear dysprosium complexes were all obtained. Despite the core structures were identical, minor variations in the number and/or positioning of substituents on primary or secondary ligands led to profound alterations in the magnetic properties.

**Keywords**: Single Molecule Magnet; Dysprosium, structural-magnetic correlations,

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# Impact of the peripheral ligand modifications on the SIM behaviour of Dy(III) in PBP coordination

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The paramagnetic metal complexes, especially the characteristic transition- and late transition metal-based complexes, can display magnetic bistability and slow relaxation of magnetization. Such a complex is generally referred as a Single-Molecule Magnet (SMM). The key quality parameter of an SMM is the critical temperature below which the complex exhibits the SMM behavior, which is commonly known as the blocking temperature ($T_B$). The SMMs have immense applications in various crucial areas of human societies such as quantum computing, memory storage, spintronics, bionics, etc. However, rational design and syntheses of such high-demand molecular complexes is non-trivial.[1-2] The central dictating factors are the nature and magnitude of magnetic anisotropy of the metal-ions, the energy landscape of the magnetic microstates, symmetry and magnitude of the crystal-field of the ligands, nature of electronic communication between the metal ions and the ligands. Our research group has been focusing on multi-pronged synthetic strategies to accomplish potential SMMs and SCMs, especially the air-stable systems. In this presentation, it will be discussed how the relatively simple Schiff base ligands could be employed to tailor the SMM behavior of lanthanide-based complexes by tuning the crystal-field and electronic property.[3-5] For example, the slow relaxation of magnetization and effective energy barrier for magnetization reversal improves markedly upon changing the peripheral -OH substituent with -H of the Schiff base ligands in the pseudo pentagonal bipyramidal mononuclear Ln(III) complexes, as depicted in Figure 1 for the Dy(III) analogues.

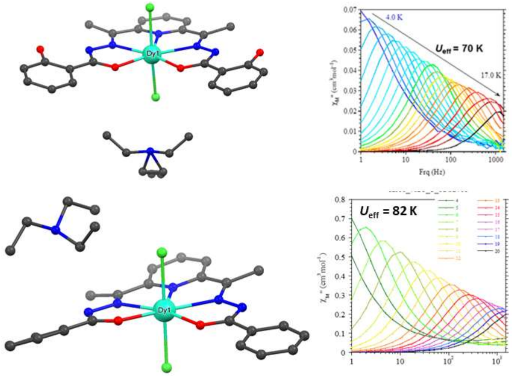

**Figure 1:** Single crystal X-ray structures (left) and *out-of-phase* ac magnetization susceptibilities (right) of the Dy analogues displaying noticeable improvement of energy barrier upon peripheral ligand substitution from -OH to -H.

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# Tailoring of Slow Dynamics in Magnetization and Luminescence in Mononuclear Lanthanide Complexes

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Single Molecule Magnets (SMMs) display slow dynamics of magnetization due to their bistable magnetic states separated by an energy barrier ($U_{eff}$). SMMs find application in molecular spintronics, high-density information storage and quantum computing.[1, 2] They can be used in luminescence thermometry by proper tuning of the temperature dependence of the luminescence.[3, 4] The credit of slow relaxation of magnetization is given to magnetic anisotropy (*D*) and ground state spin (*S*).[b, c] The contemporary idea is to enhance the anisotropic barrier of a single metal center. Thereby, the lanthanide complexes attracted a lot of attention due to their large orbital angular momentum and high spin ground state.[1, 2]

Herein, several novel complexes of Lanthanides, namely, $[Dy(acac)_3(bik\text{-}Et)]$ (1) (acac = acetylacetonate and bik-Et = bis(1-ethyl-1H-imidazol-2-yl)methanone), $[RE(dbm)_3(bik\text{-}Et)]$ (RE = Dy (2), Er (3), Nd (4); dbm = 1,3-diphenyl-1,3-propanedione), $[RE(dbm)_3(bik\text{-}Me)]$ (RE = Dy (5), Tb (6) bik-Me = bis(1-methyl-1H-imidazol-2-yl)methanone) were synthesized and characterized by single crystal X-ray diffraction analysis, spectroscopic and magnetic investigations. AC magnetic susceptibility studies show slow magnetic relaxation behaviour under zero Oe external dc magnetic field for the complexes of Dy (1, 2, 5)[5] and under an applied magnetic field for complexes of Er (3), Nd (4) and Tb (6).[6]

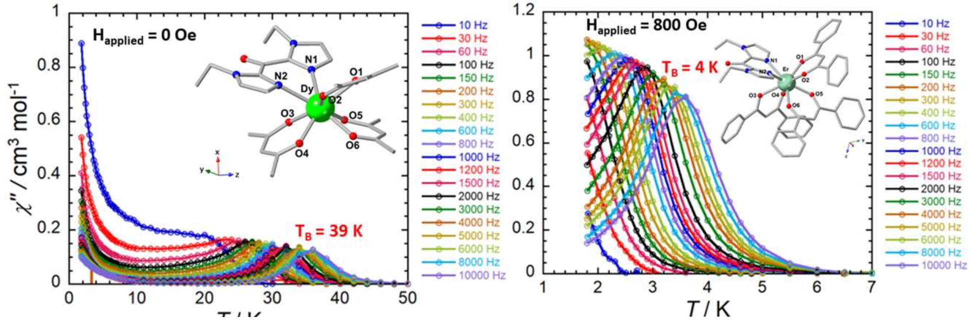

Figure 6: Structural representation and the corresponding physical properties of mononuclear Ln systems

**Keywords**: single molecule magnet; high $T_B$ magnets, luminescence; lanthanides

**Acknowledgement:** We thank the SSCU, IISc; the Ministry of Human Resource Development (MHRD); Ministry of Education (MoE); the Department of Science and Technology (DST); Mission on Nano Science and Technology, Govt. of India.

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**Oral Presentation**
**SS-O-04**
**Kuduva R. Vignesh**

# Mixed 3d-4f Single-Molecule Toroics

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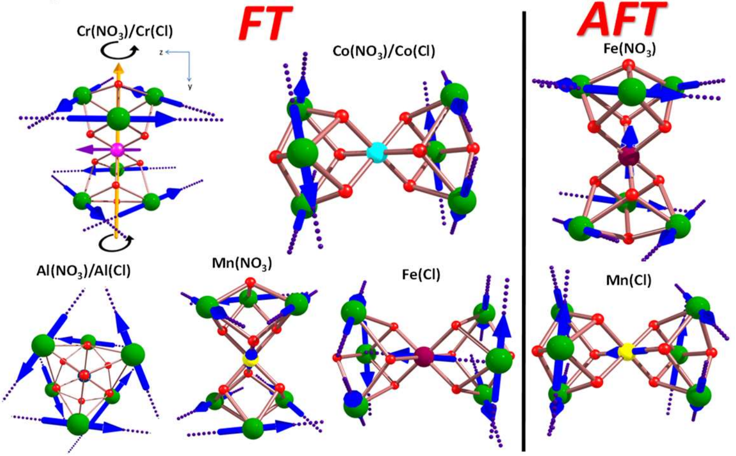
Single Molecule Toroics (SMTs) are defined as molecules that display a toroidal magnetic state that can potentially be used in multiferroic materials, and also in information storage devices and spintronics devices.[1] The observation of toroidal magnetization is dependent on the topology, and it is realized in topologies such as $Dy_3$ triangles, planar/cubic $Dy_4$, wheel $Dy_6$, a snub-square $Dy_8$, and double $Dy_3$+$Dy_3$ triangles.[1] Toroidicity has been mainly observed for $Dy^{III}$ clusters; however, we recently reported SMTs containing $Tb^{III}$ and $Ho^{III}$ ions as well. To enhance toroidicity, we reported {3d-$Ln^{III}$} complexes connecting two molecular triangles, for example, a heptanuclear cluster containing $Cr^{III}$ linked to two $Dy_3$ triangles ({$CrDy_6$}) offering a rare phenomenon called ferrotoroidicity.[2] This effect is required to realize a ferrotoroidically ordered phase, paving the way for the advancement of multiferroics, which could be addressed using magnetoelectric coupling.[1] In addition, we observed such con-rotating ferrotoroidal (FT) ground state behavior in $Tb^{III}$ and $Ho^{III}$ examples but not in the $Er^{III}$ analog, extending the possibility of observing toroidal behavior in non-Dysprosium (III) complexes.[3] We also looked at how to cancel such a toroidal behavior and how the connecting trivalent ions, counterions, and solvents influence ferrotoroidal and antiferrotoroidal (AFT) behavior. Additionally, the magnetic anisotropy directions of Dy ions in a non-cyclic {$Ni_8Dy_4$} complex are investigated; suggesting the toroidal magnetic ground state.

**Keywords**: Single-Molecule toroics; 3d-4f SMTs; Ferrotoroidal; double $Dy_3$ triangles.



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# Enhancing energy barrier and magnetic blocking in Dy-dimer via redox-active tetraoxolene bridging ligand

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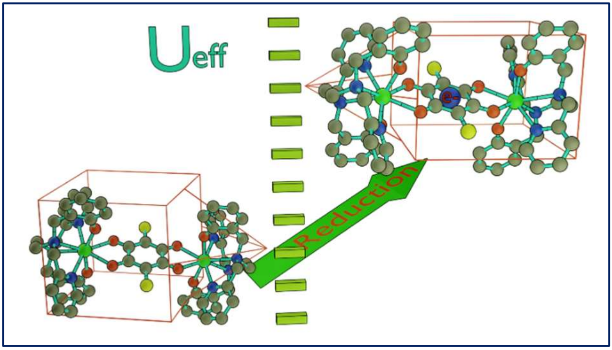
The promising future of storing and processing quantized information at the molecular level has been attracting the study of Single-Molecule Magnets (SMMs) for almost three decades.[1] Coupling high-performance SIMs into SMMs is a natural extension, which however requires rational design.[2] Using a redox-active ligand as a bridging moiety can generate magnetic coupling between the metal ions via its open shell radical form.

In this approach, we have synthesized chloranilic acid (CA) bridged Dy-dimer, [{(bbpen)Dy($\mu_2$-CA)Dy(bbpen)}] (**1Dy**). The chemical reduction of **1Dy** generates a radical bridged analog of the Dy-dimer (**2Dy**). The presence of high electronegative phenoxide ions in the axial position and high axial bond angles enhances the axial anisotropy of Dy(III) centres. Further, the magnetic study reveals the elimination of quantum tunelling of magnetization (QTM) in the magnetic relaxation dynamics of **2Dy** due to efficient coupling between the diffused spin of radical and anisotropic Dy(III) centres. This results in a higher thermal spin reversal energy barrier ($U_{eff}$ = 700 K) of **2Dy** than **1Dy**. In addition, **2Dy** shows a high blocking temperature and remains magnetized till 8 K. Remarkably, this radical-bridged Dy-dimer (**2Dy**) has the highest thermal energy barrier among all radical-bridged lanthanide systems reported to date.



**Scheme:** The radical-induced magnetic coupling enhances the effective energy barrier

**Keywords**: Single-molecule magnet; radical-bridged single-molecule magnet; ferromagnetic interaction; blocking temperature; effective energy barrier

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# Longitudinal relaxation time for an *S*=1/2 copper(II) incorporated Keggin-type silicotungstate

Toshiharu Ishizaki[1*], Tomoji Ozeki[1]

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Mononuclear *S*=1/2 first-row transition metal coordination compounds carrying nuclear-spin free organic ligands have intensively investigated as a potential molecular spin qubits for quantum computation.[1,2] Also, a molecular metal oxides or polyoxometalates are expected as good candidates for spin qubit supporting materials, since some of them serve low abundant nuclear-spin coordination environments.[3] As a first step to investigate spin coherence of *S*=1/2 polyoxometalate systems, spin-lattice relaxations of an *S*=1/2 copper(II)-substituted Keggin-type silicotungstate [(*n*-$C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Cu]$ (**1**) is reported.[4]

To investigate electronic structure of **1**, continuous-wave electron spin resonance (ESR) measurements were performed. The room temperature ESR signal of **1** showed four hyperfine signals between 250 to 280 mT even in pristine powder of **1**. This indicates that the intermolecular magnetic interaction among the copper ions is effectively reduced. The extracted *g* value ($g_{//}$=2.434, $g_{\perp}$=2.107) and hyperfine splitting value *A* ($A_{//}$=12.68 mT (177.5 MHz, $A_{\perp}$=1.0 mT (14 MHz) indicate five-coordinated square-pyramidal geometry around the copper atom.[5]

AC susceptibility measurements were performed for 5% magnetically diluted **1**, [(*n*-$C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Cu_{0.05}Zn_{0.95}]$ (**dil.1**). The out-of-phase signals were successfully observed in an applied static magnetic field, which indicates slow magnetic relaxation of this compound. The longitudinal relaxation processes will be discussed in detail.

**Keywords**: Polyoxometalate; Copper(II); *S*=1/2; Slow magnetic relaxation; spin qubit

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**Note**: A part of this work was conducted in Institute for Molecular Science, supported by "Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Proposal Number JPMXP1222MS1035 and JPMXP1223MS1054. We also acknowledge for Japan Society for the Promotion of Science (JSPS) KAKENHI Grant number 23K13769 and JSPS Core-to-Core program (International Network in Polyoxometalate Science for Advanced Functional Energy Materials).

**Poster Presentation**
**SS-P-03**
**Liu Ye-ye**

# Enhancing magnetic properties in bis-$C_5/C_2B_3$ sandwiched geometry by fine charge regulation

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Three sandwich type Dy-based single-molecule magnets (SMMs) consisting of carboranyl (Cb) and/or cyclopentadienyl (Cp) ligand, $[Dy\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}_2][Li(DME)_3]$ (**1**) $[Dy(\textit{nido-m-}7,9\text{-}C_2B_9H_{11})Cp^*(\mu_2\text{-}Cl)][Li(THF)_3]$ (**2**) and $[Dy(\textit{nido-o-}7,8\text{-}C_2B_9H_{11})(Cp^*)(THF)_2]$ (**3**) were prepared. The negative charges at the equatorial coordination sites of the three complexes show a decreasing trend from two negative charges for complex **1** to zero negative charge for the neutral complex **3** to give the monoanionic and neutral framework, respectively. The bending angle of complex **2** and **3** are 133.41° and 126.45° to exhibits similar axial magnetic anisotropy and effective energy barrier ($U_{\mathrm{eff}}$) for magnetic reversal 615.8(1) K and 612.5(1) K. However, complex **3** performs slower magnetic relaxation at low temperature region and the highest blocking temperatures $T_B$ (ZFC) up to 6 K among **1-3**, which attribute to the well suppressed QTM process as the decreasing of equatorial charge density.

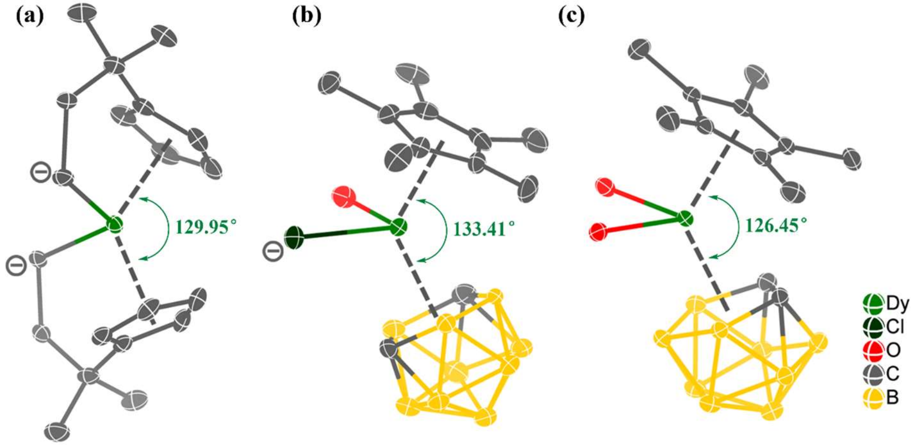

**Figure 2.** Crystal structures of **1** (a), **2** (b) and **3** (c), with thermal ellipsoid drawing at 30% probability level, all hydrogen atoms and the equatorial coordination section are omitted except for atoms connected to dysprosium ions.

**Keywords**: single-molecule magnets (SMMs); bis-$C_5/C_2B_3$ sandwiched geometry

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**SS-P-04**
**Reo Wada**

# Magnetic relaxation phenomena of *S*=1/2 copper(II)-substituted Dawson type phosphotungstate

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Recently, mononuclear *S*=1/2 complexes have attracted attention as a potential quantum bit (qubits) for quantum computation.[1] Since the lifetime of superposition of the spin state is governed by longitudinal relaxation time is valuable. We have revealed that a *S*=1/2 copper(II)-substituted Keggin-type silicotungstate $[SiW_{11}O_{39}Cu]^{6-}$ exhibits long spin-lattice relaxation time in applied static magnetic field ($H_{dc}$) and at low temperatures.[2] In polyoxometalate (POM) chemistry, a larger structure than the Keggin-type, namely Dawson-type POM, is also known. Like the Keggin-type POMs, the Dawson POMs also form the lacunary and transition metal substituted ones.[3]

In this presentation, we report magnetic relaxation phenomena of a *S*=1/2 copper(II)-substituted Dawson-type phosphotungstate $K_8[P_2W_{17}O_{61}Cu(H_2O)]\cdot 15H_2O$ measured by Magnetic Property Measurement System (MPMS). The AC susceptibility measurements of 5% magnetically diluted powder $K_8[P_2W_{17}O_{61}Cu_{0.05}Zn_{0.95}(H_2O)]\cdot 15H_2O$ showed slow magnetic relaxation in an applied $H_{dc}$. The longest relaxation time of 91 ms (1.8 K and $H_{dc}$=5000 Oe) is larger than that of copper (II)-substituted Keggin-type silicotungstate (64 ms). We concluded that the larger molecular skeleton of the Dawson-type POM effectively reduces the intermolecular dipolar interaction among the copper ions, which fasten the magnetic relaxation at low temperature and low $H_{dc}$.

**Keywords**: Polyoxometalate; Qubit; Dawson-type; *S*=1/2 copper(II)

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# Molecular magnetism in structurally flexible metal-organic frameworks

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Crystalline Metal-organic frameworks (MOFs) have attracted increasing attention in recent years owing to their tunable magnetic exchange coupling. This coupling can vary based on factors such as metal ions, ligands, or crystal structures. The magnetic properties of DUT-8(Ni), which consists of a Ni(II) dimer paddle wheel, are significantly influenced by its flexibility. DUT-8(Ni) exhibits two distinct structures: an open structure with porosity and a closed structure without pores. We observed that the Ni(II) dimer's basic unit displays antiferromagnetic interaction. The magnetic state of DUT-8(Ni) is altered from antiferromagnetic or spin-canting to superparamagnetic according to structures, temperature or external magnetic fields. The interactions between intra- and inter- units in the structure are obtained from measured magnetic data. For a fundamental understanding, the M-H data is analyzed using a modified Langevin function. Furthermore, the magnetic phase diagram illustrating the magnetic transition for DUT-8(Ni)_closed is obtained from a series of field-dependent magnetization at various temperatures and AC/DC magnetic susceptibilities.

**Keywords**: Molecular magnets; Metal-organic frameworks; magnetic property; Crystal structure;

**Poster Presentation**
**SS-P-06**
**Masooam Ibrahim**

# Polyoxometalate-based building blocks: From ligand to functional materials

Masooam Ibrahim[1], Christopher E. Anson[1], Gisela Guthausen[1], Steffen Krämer[2], Wolfgang Wernsdorfer[1], Jürgen Schnack[3], Annie K. Powell[1]

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*[2]LNCMI-EMFL, CNRS, INSA-T and UPS, Université Grenoble Alpes, 38042 Grenoble, France*
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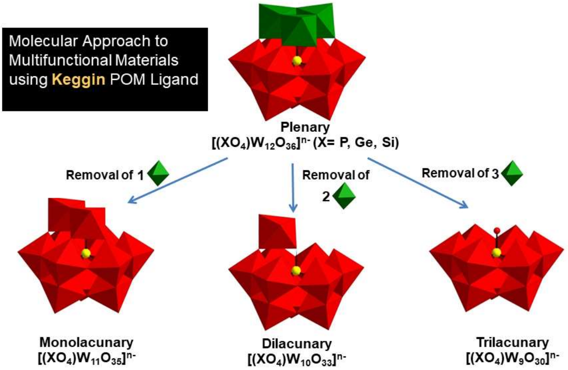
Polyoxometalates (POMs) constitute a distinct category of soluble metal oxides, occupying an intermediary state between monomeric metal oxides and infinite metal oxides. These nanosized metal–oxygen clusters exhibit remarkable structural diversities and electronic properties, finding applications in catalysis, medicine, and magnetochemistry (***Chem. Soc. Rev.***, 2012, **41**, 7403). Moreover, POMs can undergo derivatization by directly conjugating organic or bio-molecules. This process serves to enhance their physicochemical properties and distinctive structural and morphological characteristics (***Chem. Soc. Rev.***, 2012,**41**, 7605. In recent decades, the rapid development of new POMs has been driven by the versatility of preformed lacunary POM fragments: Lacunary POMs, characterized by unoccupied metal sites, serve as valuable rigid multidentate inorganic ligands for constructing multinuclear metal oxo clusters and inorganic-organic hybrid materials. The use of lacunary POMs as building blocks facilitates the creation of advanced functional materials with specific and enhanced properties (*Chem. Soc. Rev.* 2020, **49**, 382).These fragments provide abundant active sites, allowing for the capture of additional metal ions (transition metal (TM), rare earth (RE) or mixed metal ions (TM-RE)) to generate TM/RE-added POMs with unpredictable functionalities (*Chem. Commun.* 2016, **52**, 4418; A*ngew. Chem. Int. Ed.* 2015, **54**, 15574*).*

I focus on synthesizing and characterizing functional POMs using Lacunary Keggin and Dawson building blocks. These play a crucial role in enriching POM chemistry with unique structural features and broad applications.

**Keywords**: polyoxometalates; functional; lacunary POMs; catalysis; magnetism



# Theoretical Insights in Coordination Chemistry (TI) Abstract

**Keynote Speaker**
**TI-K-01**
**Jen-Shiang K. Yu**

# Mechanistic study on the trimerization of alkyne catalyzed by quintuply-bonded dichromium complex

Gou-Tao Huang[1], Jen-Shiang K. Yu[123*]

[1]*Department of Biological Science and Technology,* [2]*Institute of Bioinformatics and Systems Biology, and* [3]*Center for Intelligent Drug Systems and Smart Bio-devices, National Yang Ming Chiao Tung University, Hsinchu City 300, TAIWAN*
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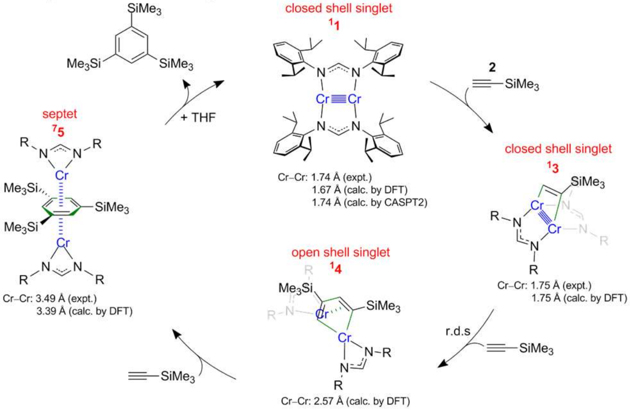
Trimerization of alkyne is one of the synthetic protocols to generate aromatic compounds, and the reaction is able to be catalyzed by the quintuply-bonded dichromium complex of $^{1}$**1**,[1] which has been investigated experimentally and theoretically to demonstrate two types of bonding motifs depending on the Cr–Cr bond length. Within the shorter length ranging from 1.7 to 1.8 Å, δ–δ bonding is dominant but while the Cr–Cr bond is elongated to ca. 2.5 Å the coupling becomes antiferromagnetic.[2] These flexible bonding schemes enable the binding and coupling of alkynes during the reaction. Density functional theory (DFT) and multireference approach of CASPT2 are performed to investigate the electronic structures of intermediates in the catalytic cycle and to construct the energy profile. During the catalytic cycle, the distance between the two Cr atoms varies from 1.7 to 3.5 Å, and meanwhile the Cr–Cr bonding character changes from the primary δ–δ interaction to (anti)ferromagnetic coupling. Calculations indicate that the rate-determining step is the addition of the second alkyne ($\Delta G^{\ddagger}$: 21.7 kcal mol$^{-1}$) to form the dinuclear chromacyclopentadiene complex ($^{1}$**4**), which rationalizes experimental findings that $^{1}$**4** was isolable.



**Keywords**: Regioselectivity; Cyclotrimerization; Antiferromagnetism; Multiconfiguration; Quintuple Bond

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**Keynote Speaker**
**TI-K-02**
**Kyung-Bin Cho**

# Some examples of DFT applications into inorganic biomimetic compounds

Kyung-Bin Cho

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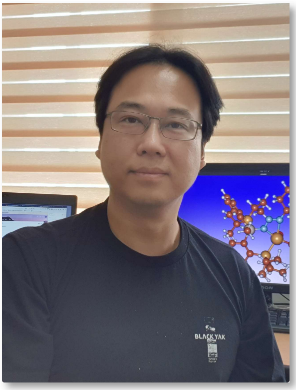

Density Functional Theory is nowadays successfully used in many applications, albeit not always with quality. Our lab has performed many projects in the field of inorganic biomimetic compounds, in order to explain bioenzymatic reactions on an elementary level. The simplification of enzymes into small synthetic model complexes emulates the core reactions occurring in the active site of enzymes, and we may draw some fundamental conclusions from this. Of special interest is metal-oxygen catalyzed reactions of organic substrates, such as C-H activation, hydroxylation or other oxygen addition reactions. The current talk will center around several of our projects highlighting our research: the importance of spin states,[1] C-H activation reactions by Mn(IV)O systems,[2] Ni catalyzed $NO_x$ conversion[3] and synthetic iron-imido complexes catalyzing oxidation reactions.[4] The results are always carefully correlated to experimental results without compromises in theoretical rigor.

**Keywords**: Density Functional Theory; Biomimetics; Reaction Mechanisms

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**Invited Speaker**
**TI-I-01**
**Jack D. Evans**

# Simulations to understand the dynamic properties of porous molecules and materials

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Porosity is an important feature of materials that empowers interactions with atoms, ions and molecules beyond a simple surface. As the number of compounds known and characterised in the literature grows, it is apparent that some can carry properties beyond that expected by conventional, dense inorganic materials. Among these compounds with unusual physical or chemical properties are porous crystals, such as metal-organic frameworks. Many of these porous materials are dynamic and respond to stimulation by displaying structural and property changes that range from counter-intuitive to thermodynamically forbidden. Computational approaches are crucial to understanding these challenging phenomena by calculating the specific thermodynamic driving forces using quantum chemical calculations, force field-based molecular dynamics and Monte Carlo simulations. These approaches have underpinned a new understanding of three curious directions: gating, motorised pores and molecular cages. This has led to the design of new materials, with properties far beyond static limitations.

**Keywords**: porosity; thermodynamics; atomistic simulations

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**Invited Speaker**
**TI-I-02**
**Tzuhsiung Yang**

# Designing Transition Metal Complexes with Desirable Spin States Using Generative AI Models

Tzuhsiung Yang

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Transition metal (TM) complexes exhibit diverse structural and electronic properties that are highly modulable owing to their tunable coordination spheres, wide range of accessible oxidation states, and adjustable spin states.

Herein, we devised a deep generative model—semi-supervised variational autoencoder and transfer learning model (LiveTransForM)—for the generation of transition metal complexes (TMCs) with desirable spin states (SSs). The transfer learning model demonstrates excellent test set accuracy of 90.5% and precision of 91% for low spin and 96% for high spin. 77 novel TMCs with specific SSs were generated. Their SSs were validated by six different approximate density functionals and found to be 77.6% consistent.

We further introduced two design strategies using LiveTransForM: *single mutation* and *seeded generation*. The first strategy optimizes, *via* gradient descent, the spin state of provided complexes by systematically modifying part of the complex. The second strategy performs local modification of provided complexes.

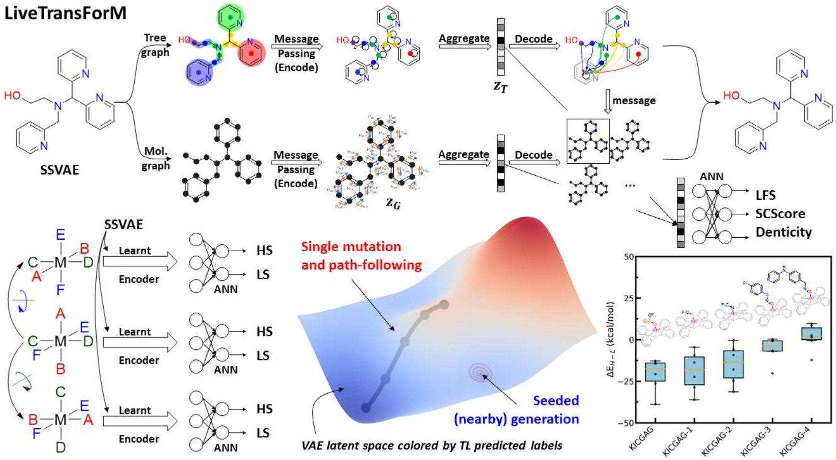

**Figure 7.** LiveTransForM, a semi-supervised variational autoencoder and transfer learning model for the design of transition metal complexes.

**Keywords**: Generative AI models, Molecule Design, Transition Metal Complexes, Property Optimization, Spin States.

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**Invited Speaker**
**TI-I-03**
**Saurabh K. Singh**

# Correlating Magnetic Anisotropy and Metal-Ligand Covalency in Transition Metal and Lanthanide Complexes using Ab Initio Ligand Field Theory

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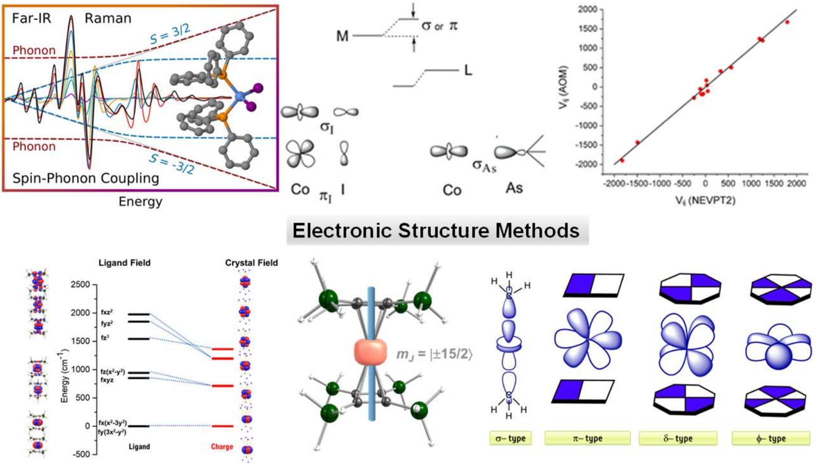
Highly anisotropic mononuclear complexes of the transition metal and lanthanides show a peculiar property of the slow relaxation of magnetization in the absence of the magnetic field and display hysteresis of the molecular origin.[1] These highly anisotropic mononuclear complexes are called Single-Ion Magnets (SIMs), which are highly attractive to explore the quantum effects and have numerous potential applications in information storage devices and molecular spintronics. Accurate modelling of electronic structure and magnetic anisotropy of open-shell d/f-elements is challenging for modern quantum chemistry methods due to the high density of electronic states arising from degeneracy or near degeneracy of the orbitals, proper treatment of the relativistic effects, and subtle metal-ligand covalency.[2] In my presentation, I will describe the use of ab initio-based ligand field theory (AILFT)[3] in conjunction with multireference ab initio methods to analyze the metal-ligand covalency (symmetry adapted and central field covalency) in transition metal and lanthanide complexes and how it plays a crucial role in controlling the magnetic anisotropy of these metal complexes.[4]



**Keywords**: CASSCF/PT2, DFT, Chemical Bonding, d/f elements, Magnetic Anisotropy

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**Invited Speaker**
**TI-I-04**
**Joshua Telser**

# Ligand-Field Theory Related to Transition Metal Field/Frequency-Domain Electron Magnetic Resonance

Joshua Telser*

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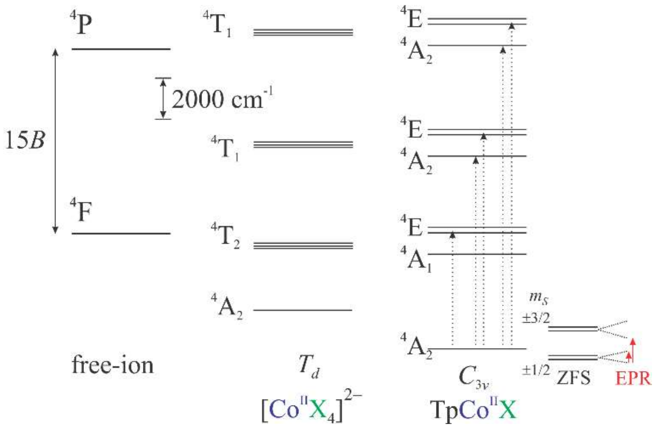
Crystal-field theory, invented by Bethe a century ago and followed by ligand-field theory (LFT) developed by Ballhausen,[1] Schäffer,[2] and others were widely used to understand the electronic absorption spectra of transition metal complexes.[3] With the introduction of quantum chemical theory (QCT), in particular density functional theory (DFT) and more recently *ab initio* methods in this century, combined with readily available software, such as ORCA by Neese,[4] such semi-empirical methods have fallen into disfavour. Nevertheless, there is still place for LFT in concert, not in competition with QCT. This is due to the growing interest in single molecule magnets (SMMs) for which a complete understanding of the electronic structure is needed.[5] In particular, the zero-field splitting (ZFS) behaviour is crucial in determining SMM utility. ZFS can be measured using a variety of techniques,[6] but paramount among these is high-frequency and -field electron paramagnetic resonance (HFEPR), which is typically performed in the field-domain, but can also be fruitfully performed in the frequency domain (far-infrared magnetic spectroscopy – FIRMS). We describe here the use of these techniques combined with LFT and QCT to understand potential SMMs such as 3d ion scorpionate complexes of $Fe^{II}$, $Co^{II}$ (electronic structure diagram shown in the graphic), and $Ni^{II}$.



**Keywords**: electronic spectra; transition metals; magnetic resonance; paramagnetism; molecular magnetism.

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Invited Speaker
TI-I-05
Sergei Ketkov

# Laser ionization spectroscopy and DFT calculations of transition metal sandwich compounds

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Transition metal sandwich compounds play key roles in various fields of fundamental and applied chemistry including studies of the metal–ligand bonding, electrochemistry, biomedicine, catalysis, metallopolymers, nanoelectronics, and molecular machines. A wide number of unique properties of sandwich complexes arise from their ability to form stable or reactive ions. The accurate parameters of ionization processes in sandwich molecules are, therefore, crucial for understanding their reactivity. High-resolution methods of laser threshold ionization spectroscopy provide unprecedented opportunities for comprehensive studies of the sandwich ion formation. Precise ionization energies (IEs) of neutral species and vibrational frequencies of free ions can be obtained by mass-analyzed threshold ionization (MATI) techniques. Vibronic structures of the MATI spectra give unique information on structural transformations of sandwich molecules on ionization. In combination with DFT calculations, laser threshold ionization spectroscopy reveals surprisingly different structural variations accompanying the detachment of an electron from sandwich molecules[1] as well as new aspects of substituent influence on the sandwich electronic structures.[2] Electron density analysis throws lights into the nature of these amazing effects. Recent results in this field are discussed in our presentation.

**Keywords**: sandwich compounds; transition metals; photoionization; electronic structure; DFT calculations.

**Acknowledgements:** This work was supported by the Russian Science Foundation (Project 23-13-00139).

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Oral Presentation
TI-O-01
Bing Yin

# Interpretation and prediction of single-molecule magnet via *ab initio* electronic structure calculation

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The SMM performance of a given system is determined by the underlying microscopic process, i.e., magnetic relaxation. However, this process could be quite complicated due to the co-existence of various pathways, including Orbach, Raman, QTM and etc. Via *ab initio* electronic structure calculation, we have proposed a concise criterion for high-performance SMM and related theoretical methods In recent years,.[1-5] This criterion is the co-existence of long QTM time $t_{QTM}$ and high $U_{eff}$. Strictly, this criterion only covers QTM and thermally-activated (TA) Orbach/TA-QTM directly. However, when applying it in systems of similar coordination environment, satisfactory results can be obtained. The computational cost of this criterion can be minimized to one *ab initio* electronic structure calculation for one system.[3-5] Thus it is easy to apply this criterion to a large number of systems to give a screening of candidates of high-performance SMM. This could largely reduce the burden of subsequent study wherein more accurate but more complicated and computationally expensive method is unavoidable.

**Keywords**: *ab initio*; SMM; QTM; energy barrier

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# Theoretical investigations of mononuclear Mn(III) single-molecule magnets

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Single-molecule magnets (SMMs) are molecular nanomagnets that exhibit slow magnetic relaxation, enabling molecular switching. In this study, we investigate how the anion and the alkyl group impact the magnetic properties of four mononuclear Mn(III) complexes; $[Mn(salEen\text{-}Br)_2]Y$ (salEen-Br = 2-{[2-(ethylamino)ethylimino]methyl}-4-Br-phenol; Y = $ClO_4^-$ **1** and $BF_4^-$ **2**) and $[Mn(salBzen\text{-}Br)_2]Y$ (salBzen-Br = 2-{[2-(benzylamino)ethylimino]methyl}-4-Br-phenol; Y = $ClO_4^-$ **3** and $BF_4^-$ **4**). The magnetic results reveal that presence of the benzyl group on the salBzen-Br ligand plays a key role in observing SMM behaviour under an applied field, while the $ClO_4^-$ and $BF_4^-$ anions have a small impact on the energy barrier. Complete active space self-consistent field (CASSCF) with N-electron valence state perturbation theory (NEVPT2) calculations were performed to gain insight into the magnetic behaviour in **1-4**. These show that the alkyl group influences the order of the *d*-orbitals and therefore the observed SMM properties.

**Keywords**: manganese(III) Schiff base complexes, single-molecule magnets (SMMs), CASSCF calculation

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**Oral Presentation**
**TI-O-03**
**Naphol Witayapaisitsan**

# Computational design of Ni catalysts for C-H activation and hydroarylation of alkenes

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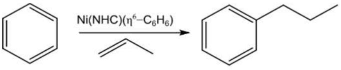
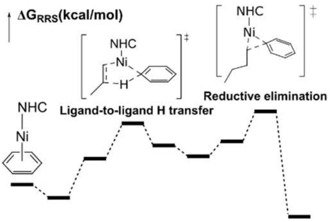
Nickel N-heterocyclic carbene (Ni–NHC) complex-catalyzed hydroarylation of alkenes is a promising method for linear alkylbenzene synthesis. For unsubstituted arene, i.e., benzene, the reaction yields are still moderate. The structural modification of the ligand can potentially improve the catalytic activity. In this work, free energy profiles and linear free energy scaling relationships (LFESRs) for 70 Ni catalysts were explored by varying the NHC ligand structures. An activity map was plotted linking the energy span to two descriptors: (i) the relative free energy of an intermediate formed from ligand-to-ligand hydrogen transfer ($\Delta G_{RRS}$(INT3P)) and (ii) the relative free energy of an intermediate undergoing reductive elimination ($\Delta G_{RRS}$(INT5P)). Achieving a relatively low energy span requires minimizing $\Delta G_{RRS}$(INT5P) while maintaining $\Delta G_{RRS}$(INT3P) within a certain range. Additionally, linear relationships between buried volume and energy span were observed within groups of NHC ligands sharing common structural characteristics. Overall, the favorable NHC characteristics for Ni catalysts were those with substantially large backbone, and with a diisopropylphenyl group or larger substituent group at the nitrogen on the backbone of the NHC. These insights pave the way for optimizing the catalytic activity of Ni catalysts in the hydroarylation of alkene with benzene facilitating the catalyst design process.

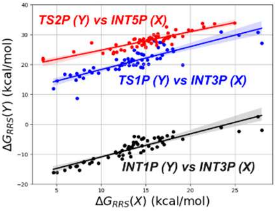
**Keywords**: Ni catalysts; hydroarylation of alkene; linear free energy scaling relationships; activity map; catalyst design



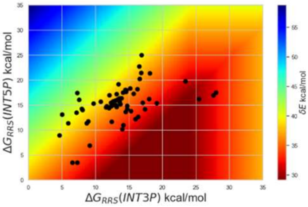
**Ni-NHC catalyzed hydroarylation of alkene**



**Free energy profiles of Ni-NHC catalysts**



**Linear free energy scaling relationships**



**Activity map**

**Oral Presentation**
**TI-O-04**
**Kaito Takahashi**

# Learning from multireference calculation on the binding of transition metal atom and CO molecule

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The interaction between CO molecule and transition metal surfaces has interested chemists in two aspects: 1. due to practical applications in catalytic reactions and 2. due to the nature of bonding given by the Dewar-Chart-Duncanson model[1,2] of $\sigma$ and $\pi$ back donation. The interaction between a single transition metal atom and CO has been extensively studied using various quantum chemistry methods to understand the basic bonding motif. Thereby, many previous calculations utilize density functional theory (DFT) to understand this bonding interaction. On the other hand, DFT studies have shown that in the binding between 3d transition metal (TM) atoms and CO, the electronic spin state of the infinitely separated TM atom and CO have a different spin state from the TM-CO adduct. Therefore, this reaction is the most basic "spin crossover" reaction, where spin states change during the reaction. To treat such spin crossover reactions, one needs to consider the coupling of multiple electronic states. In this study, we used the multireference configuration interaction method with spin-orbit interaction to elucidate the importance of electronic state coupling. We also provide a multireference picture for $\pi$ back donation.

**Keywords**: multireference quantum chemistry; electronic excited state; spin-orbit interaction; transition metal; back donation

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# Unraveling the Mysteries of Aromatic Oxidation: A DFT investigation into [Fe(IV)OHPor(Cl)] Complex’s Reaction Mechanism.

Steiny Russelisaac Premakumari, Kyung-Bin Cho*

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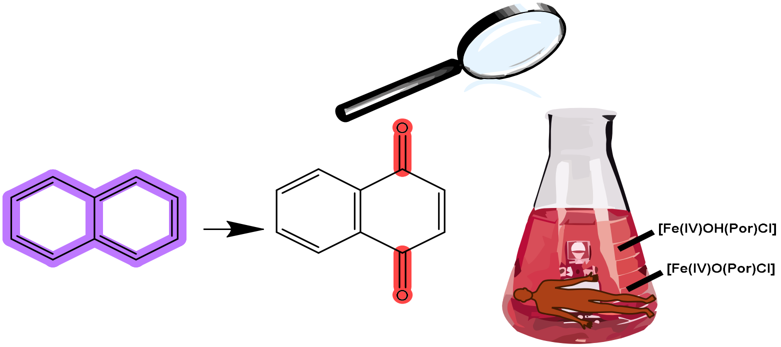
Developing organometallic catalysts that are green, efficient and stable for the selective direct oxidation of aromatic C-H bonds under mild conditions is a challenging task due to their high stability. Despite this challenge, scientists worldwide are making persistent efforts to improve both catalytic activity and selectivity. We focus on a series of structurally diverse metalloporphyrin compounds, with particular attention given to the high-valent iron and manganese complex. These complex serves as a key oxidative intermediate in heme and non-heme enzymes, which catalyze essential biochemical processes[1]. The study investigates the direct hydroxylation of aromatic C-H bond using the active catalyst [Fe(IV)OH(Por)Cl]. Through theoretical analysis, the study uncovers the reaction mechanism for the simple aromatic hydroxylation of naphthalene to naphthalene-1,4-diol and its subsequent oxidation to naphthalene-1,4-dione. The investigation reveals that both oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) mechanisms are involved in the studied process.[2] Moreover, a contracting reactivity pattern is observed during the investigation, where the $\text{Fe}^{IV}$OH species is more reactive than the $\text{Fe}^{IV}$O species. The study also examines the relative oxidative abilities of these two species in a congruent reaction. These findings provide valuable insights into the mechanism of the oxidation reaction and demonstrate the potential of [Fe(IV)OH(Por)Cl] as a catalyst for the efficient production of naphthalene-1,4-dione.



**Keywords**: C-H activation; aromatic hydroxylation; organometallic catalyst; OAT;

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TI-P-02

**Kittimeth Thammanatpong**

# Mechanisms of Hydrogen Evolution by Cobalt Complexes Containing Redox-Active Ligand as a Proton Relay

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Hydrogen evolution reaction is an important process for energy storage. The six-coordinate cobalt complex $[\mathrm{Co^{III}}(\mathrm{L}^{1-})(\mathrm{LH})]^{2+}$ (LH = N-(4-amino-6-(pyridin-2-yl)-1,3,5-triazin-2-yl)benzamidine) was found to catalyze photocatalytic hydrogen evolution. In this work, we performed density functional calculations to obtain the reduction potentials and the proton-transfer free energy of possible intermediates to determine the preferred pathways for proton reduction. The mechanism involves the metal-based reduction of Co(III) to Co(II) before the protonation at the amidinate N on the pyridinyl-substituted diaminotriazine benzamidinate ligand $\mathrm{L}^{1-}$ to form $[\mathrm{Co^{II}}(\mathrm{LH})(\mathrm{LH})]^{2+}$. Essentially, the subsequent electron transfer is not the metal-based reduction, but rather the ligand-based reduction to form $[\mathrm{Co^{II}}(\mathrm{LH})(\mathrm{LH}^{\bullet 1-})]^{1+}$. Through the proton-coupled electron transfer process, the cobalt hydride $[\mathrm{Co^{II}}\mathrm{H}(\mathrm{LH})(\mathrm{LH}_2^{\bullet})]^{1+}$ is formed as the key intermediate for hydrogen evolution. As the cobalt hydride complex is coordinatively saturated, the structural change is required when the hydride on Co is coupled with the proton on pyridine. Notably, the highly redox-active nature of the ligand results in the low acidity of the protonated pyridine moiety of $\mathrm{LH}_2^{\bullet}$, which impedes its function as a proton relay. This should be considered in the development of metal catalysts for $H_2$ evolution when the ligand takes the role as both electron reservoir and proton relay.

**Keywords**: Hydrogen evolution reaction; Cobalt; Pyridine; Redox-active ligand; Proton relay

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# Probing the magnetic anisotropy in tetrahedral Co$^{II}$ SMMs: An Ab-Initio Ligand Field Study

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In the quest for improved Single-Molecule Magnets (SMMs), magnetic anisotropy emerged as a critical factor influencing slow magnetization relaxation. Molecular symmetry and the ligand field were identified as key contributors to magnetic relaxation. Enhancing the single-ion anisotropy of molecular materials involved incorporating larger transition metal ions from the 4d and 5d elements.[1] Another strategy focused on boosting magnetic anisotropy by introducing heavy atoms into the ligand environment, impacting spin-orbit coupling and metal-ligand covalency.[2] Geometric manipulation also played a significant role, as observed in instances where it affected the slow relaxation of magnetization in transition metal-based mononuclear complexes, influencing magnetic anisotropy in metal complexes.[3] Our study delves into two series of Co(II) tetrahedral ligands, utilizing ab-initio methods to assess how ligand modifications influenced magnetic anisotropy in the complexes. The first series examined the impact of varying bond angles on magnetic anisotropy, employing $[Co(pdms)_2]^{2-}$ as our motif (pdms = N,N'-1,2-phenylenedimethanesulfonamide). In the second series, we explored the effect of heavy atoms on zero-field splitting by varying the donor atom from N-Bi (2p – 6p) in a series of $Co(ER_2)I_2$ molecules. This comprehensive investigation aims to shed light on the nuanced factors governing magnetic properties in these molecular systems.

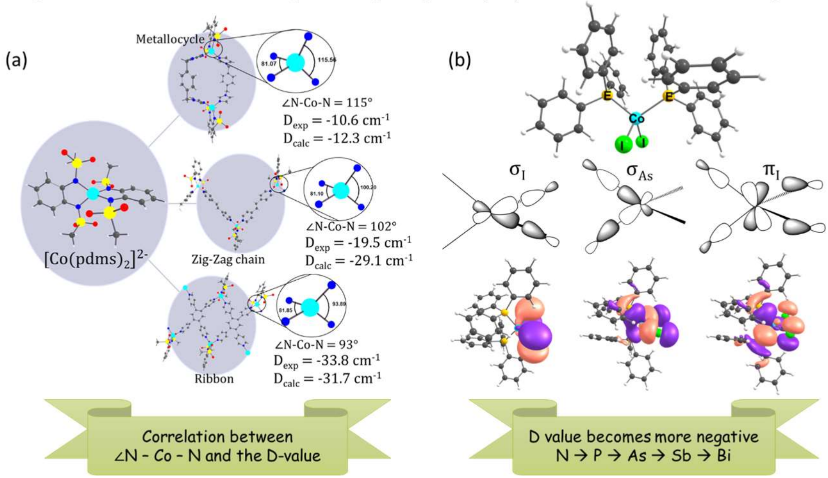

Figure 1. (a) Variation of D with change in the bond angle (b) Variation of D with change in the ligand donor atom.

**Keywords**: CASSCF/NEVPT2, DFT, Single Molecule Magnets, ab-initio ligand field theory

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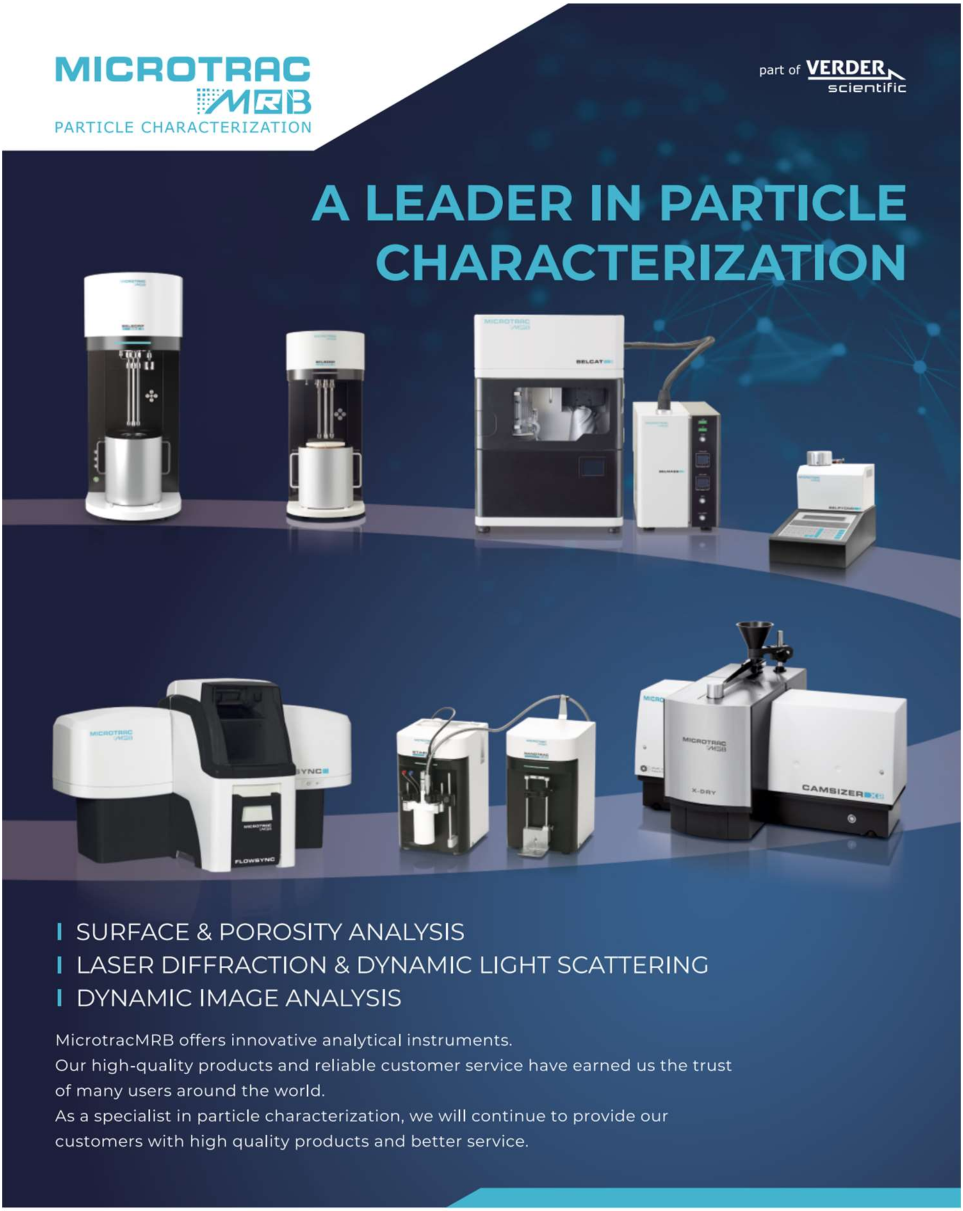


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