11TH SINGAPORE INTERNATIONAL CHEMISTRY CONFERENCE

(SICC - 11)

11th to 14th December 2022

Conference e-Booklet

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FOREWORD

On behalf of the Organizing Committee, it is our great pleasure to welcome all participants to the 11th Singapore International Chemistry Conference (SICC-11), held at Innovis, 2 Fusionopolis Way Singapore. After two years' deferral due to the pandemic, we are excited that it is finally taking place on December 11-14, 2022! We are most grateful to all the conference delegates for your great support towards SICC-11 and for taking time off your busy schedules to join us at this exciting event.

The SICC conference series was initiated and organized by the Department of Chemistry, NUS, in 1999 and it has since been a biennial event dedicated to the promotion of chemical sciences in Singapore. This year would be the eleventh in the series and will cover organic, organometallic, inorganic and material chemistry. The conference serves as a platform for broader discussions on current and new advances in chemistry. We are anticipating over 200 participants, including more than 150 overseas delegates. We hope that all of you will thoroughly enjoy the scientific interactions, renew friendships, make new friends, forge new collaborations during the conference, and bring home fond memories. All members of the Organizing Committee have spent enormous time and effort to ensure a high quality and exceptional event. Needless to say, the conference would not have possibly come to fruition without their dedicated contributions. Generous financial support from our sponsors and professional support from our conference secretariat are very much appreciated. We hope that you will find it fruitful, enjoyable, and rewarding.

Singapore is a unique country, a city-state, and it connects the east to the west. It is just a small dot in the world map, but its influences have been phenomenal. There is much to do on this beautiful island and to our foreign delegates, do find time to explore Singapore, to discover its beauty and uniqueness, and to immerse in our multicultural environment. Most importantly, enjoy yourself, both scientifically and socially, and have a wonderful stay in Singapore!

SICC-11 Chairs

Professor Shunsuke **CHIBA**
Nanyang Technological University

Professor Yu **ZHAO**
National University of Singapore

ORGANISING COMMITTEE

Chairperson	:	Professor Shunsuke CHIBA Nanyang Technological University
Co-Chairperson	:	Associate Professor Yu ZHAO National University of Singapore
Committee Members for Organic Chemistry Symposia	:	Professor Choon Hong TAN Nanyang Technological University Associate Professor Jie WU National University of Singapore Associate Professor Shaozhong GE National University of Singapore Assistant Professor Ming Joo KOH National University of Singapore
Committee Members for Inorganic Chemistry Symposia	:	Professor Rei KINJO Nanyang Technological University Professor Hansen SOO Nanyang Technological University
Committee Members for Material Chemistry Symposia	:	Professor Donglin JIANG National University of Singapore Professor Chunyan CHI National University of Singapore Professor Mihaiela STUPARU Nanyang Technological University
SICC-11 Secretariat	:	Ms. Kimmey POH Singapore National Institute of Chemistry
Event Vendor	:	Spark Planners Pte Ltd.

VENUE

Innovis & Kinesis Building
Address: 2 Fusionopolis Way, Singapore 138634

(Image credits to https://www.a-star.edu.sg/ime/contact-us)

Registration desk: Innovis Building, Multi-Purpose Hall (MPH)

MPH 1 & 2	:	Innovis Building	Level 1
Tech Market Place	:	Innovis building	Level 8
Seminar Room 2	:	Kinesis building	Level 6 (Left Lift Lobby)
Seminar Room 3	:	Kinesis building	Level 7 (Right Lift lobby)

PROGRAMME

Sunday, 11 December 2022

Organic Track

Time	Programme	
1330 - 1430	**MPH 1 & 2** **Registration**	
1430 - 1440	**Opening Ceremony** **LOH Xian Jun**, President of SNIC **Shunsuke CHIBA**, Chairperson of SICC-11	
1440 - 1530	**Plenary talk** (Chair: Donglin JIANG) **Makoto FUJITA** (University of Tokyo) Self-assembly of Gigantic Coordination Polyhedra: From Synthetic to Peptidic	
1530 - 1540	**Transition**	
1540 - 1615	**MPH 1 & 2** Chair: Shunsuke CHIBA **Keynote talk** **Daniele LEONORI** (RWTH Aachen University) Novel Synthetic Methods in Halogen-Atom Transfer and Excited Nitroarene Reactivity	
1615 - 1645	**Tech Market Place** **Tea Break** 🍴 🥤	
	MPH 1 Chair: Ming Joo KOH	**MPH 2** Chair: Shunsuke CHIBA
1645 - 1710	**Ryo TAKITA** (Shizuoka Prefecture University) C–N/C–O/C–D Bonds Formation in H2O or with D2O	**Shaozhong GE** (National University of Singapore) Cobalt-Catalyzed Asymmetric Synthesis of Chiral Organoboroantes
1710 - 1735	**Jun SHIMOKAWA** (Kyoto University) Organosilane Synthesis via New Silicon Species	**Takuji KAWAMOTO** (Yamaguchi University) Synthesis of γ-perfluoroalkylated ketones via β-cleavage
1735 - 1800	**Hiroshi NAKA** (Kyoto University) Transfer (De)hydration Catalysis	**Richmond LEE** (University of Wollongong) Computational-Experimental Approach to Reaction Design of Novel Halide Transfer and Addition (HTA) Process
1800 - 1825	**David NELSON** (University of Strathclyde) Probing Directing Group Effects in C-H Activation Using Hydrogen Isotope Exchange	**Po-Chiao LIN** (National Sun Yat-sen University) Fluorescence Turn-on Strategy for On-Demand Biomolecular Interactions
1830 - 2000	**Tech Market Place** **Networking session and Poster session A** 🍴 🥤 *End of Day 1*	

Legend	**MPH 1 & 2** are located in Innovis building, Level 1 **Tech Market Place** is located in Innovis building, Level 8 **Seminar Room 2** is located in Kinesis building, Level 6 (Left Lift Lobby) **Seminar Room 3** is located in Kinesis building, Level 7 (Right Lift lobby)

Programme updated as of 06 December 2022 and is subjected to changes.

Sunday, 11 December 2022

Inorganic & Materials Track

Time	Programme	
1330 - 1430	MPH 1 & 2	
	Registration	
1430 - 1440	**Opening Ceremony** **LOH Xian Jun**, President of SNIC **Shunsuke CHIBA**, Chairperson of SICC-11	
1440 - 1530	**Plenary talk** (Chair: Donglin JIANG) **Makoto FUJITA** (University of Tokyo) Self-assembly of Gigantic Coordination Polyhedra: From Synthetic to Peptidic	
1530 - 1550	**Transition**	
	Seminar Room 2 Chair: Yanli ZHAO	Seminar Room 3 Chair: Chunyan CHI
1550 - 1625	**Keynote talk** **Hua ZHANG** (City University of Hong Kong) Phase Engineering of Nanomaterials (PEN)	**Keynote talk** **Henrik OTTOSSON** (Uppsala University) Excited State Aromaticity and Antiaromaticity: From Scopes to Pitfalls
1625 - 1645	Outside Seminar Room 2	Outside Seminar Room 3
	Tea Break 🍴 🥤	
	Seminar Room 2 Chair: Yanli ZHAO	Seminar Room 3 Chair: Mihaiela Stuparu
1645 - 1710	**Koji KUBOTA** (Hokkaido University) Mechano-driven main group organometallic chemistry	**Tetsuro KUSAMOTO** (Institute for Molecular Science) Interplay Between Spin and Luminescence in Stable Organic Radicals
1710 - 1735	**Jason DUTTON** (La Trobe University) Synthesis and Reactivity of ArI(OTf)2	**Jishan WU** (National University of Singapore) Synthesis of Some Challenging Molecular Carbons
1735 - 1800	**Ye CHEN** (Chinese University of Hong Kong) Wet-chemical synthesis and electrocatalytic properties of metal nanomaterials with unconventional crystal phases	**Masaichi SAITO** (Saitama University) Lone-pair Interactions between Non-bonded Heavy Atoms to Produce σ- Aromatic Compounds and a Stable σ-Delocalized Radical
1800 - 1825	**Yi-Tsu Chan** (National Taiwan University) 2D Porous Arrays Assembled from Metallo-Supramolecular Giant Cages	**Yoshimitsu ITOH** (University of Tokyo) Dynamic Molecular Assembly of Photo-Aromatizable [4n] Annulene Derivatives
1830 - 2000	Tech Market Place	
	Networking session and Poster session A 🍴 🥤 *End of Day 1*	

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Monday, 12 December 2022

Organic Track

Time	Programme	
0730 - 0820	**MPH 1 & 2** **Registration**	
0820 - 0910	**Plenary talk** (Chair: Choon Hong TAN) **Scott MILLER** (Yale University) Searching for Selective Catalytic Reactions in Complex Molecular Environments	
0910 - 0920	**Transition**	
0920 - 0955	**MPH 1 & 2** **Keynote talk** (Chair: Choon Hong TAN) **Guangbin DONG** (The University of Chicago) Merging C−C and C−H Activation: Palladium/Norbornene Cooperative Catalysis	
0955 - 1025	**Tech Market Place** **Tea Break** 🍴 🥤	
	MPH 1 Chair: Jun SHIMOKAWA	**MPH 2** Chair: Choon Hong TAN
1025 - 1050	**Sunkyu HAN** (Korea Advanced Institute of Science & Technology) Syntheses of High-Oxidation-State Securinega Alkaloids	**Seiji SHIRAKAWA** (Nagasaki University) Design of Chiral Bifunctional Sulfide Catalysts for Asymmetric Halocyclizations
1050 - 1115	**Minami ODAGI** (Tokyo University of Agriculture and Technology) Total Synthesis of Hasubanan Alkaloids Based on Oxidative Phenolic Coupling Reaction and Aza-Michael Reaction	**Sarah Yunmi LEE** (Yonsei University) Catalytic Stereodivergent C–C Bond Formations by Asymmetric Conjugate Additions
1115 - 1140	**Hiroshi TAKIKAWA** (Kyoto University) Silicon-Tethered Benzyne Reactions: A Platform for Exploring New Reactivity	**Hanyong BAE** (Sungkyunkwan University) Augmented Aquacatalysis: Bio-inspired Approaches in Chemical Reactions
1140 - 1205	**Ryan MURELLI** (Brooklyn College) Game of Tropones: Studies on the Synthesis and Function of Cycloheptatrienones	**Taiga YURINO** (Hokkaido University) Catalytic Nucleophilic Isocyanation: Selective N-Terminus Substitution of Ambident Cyanide
1205 - 1315	**Tech Market Place** **Lunch and Poster session A** 🍴 🥤	
1315 - 1405	**MPH 1 & 2** Chair: Shaozhong GE **Plenary talk** **John HARTWIG** (University of California, Berkeley) Selective Catalytic Functionalization of C-H and C=C Bonds	
1405 - 1415	**Transition**	
1415 - 1450	**MPH 1 & 2** Chair: Yu ZHAO **Keynote talk** **Qiu WANG** (Duke University) Copper-Catalyzed Aminofunctionalization of Alkenes and Dienes	
1450 - 1520	**Tech Market Place** **Tea Break** 🍴 🥤	

Cont'd.

	MPH 1 Chair: Hiroshi TAKIKAWA	**MPH 2** Chair: Yu ZHAO
1520 - 1545	**Chihiro TSUKANO** (Kyoto University) Asymmetric Total Synthesis of Shagenes A and B, anti-leishmanial sesquiterpene	**Ye ZHU** (National University of Singapore) Remote Stereocontrol Through Distal Ionic Interactions-Directed Cross-Coupling
1545 - 1610	**Takahiro SUZUKI** (Hokkaido University) Biomimetic Total Syntheses of Chloropupukeananin, Chloropupukeanolide D, and Chloropestolides	**Tetsuhiro NEMOTO** (Chiba University) Silver-Catalyzed Asymmetric Dearomatization
1610 - 1635	**Hirofumi UEDA** (Tohoku University) Synthesis of Substituted Nitrogen-Containing Heterocyclic Compounds via Gold-Catalyzed Cascade Reaction	**Tatsuya UCHIDA** (Kyushu University) Carboxylic Acid Corporative Ruthenium-Catalyzed C–H Oxygenation
1635 - 1645	***Break***	
1645 - 1710	**Yoshio ANDO** (Tokyo Institute of Technology) Asymmetric Total Synthesis of Preussomerins: Stereospecific Photoredox Reaction of Naphthoquinone via 1,6-Hydrogen Shift	**Jun WANG** (Hong Kong Baptist University) Facile Access to Chiral Phosphorus Compounds via Transition Metal-catalyzed Asymmetric Hydrophosphination of Alkenes and Alkynes
1710 - 1735	**Takaaki SATO** (Keio University) Unified Total Synthesis of Stemoamide-Type Alkaloids Based on the Amide-Selective Nucleophilic Addition	**Hong Geun LEE** (Seoul National University) New Horizons in the Activation of Organonboron Compounds
1735 - 1800	**Rong-Jie CHEIN** (Academia Sinica) Carry Forward Anionic Snieckus-Fries Rearrangement	**Hon Wai LAM** (University of Nottingham) New Chiral Dienes for Enantioselective Catalysis
1800	***End of Day 2***	

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Monday, 12 December 2022

Inorganic & Materials Track

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<tr><td>0820 - 0910</td><td colspan="2">Plenary talk (Chair: Choon Hong TAN)
Scott MILLER (Yale University)
Searching for Selective Catalytic Reactions in Complex Molecular Environments</td></tr>
<tr><td>0910 - 0930</td><td colspan="2">Transition</td></tr>
<tr><td rowspan="2">0930 - 1005</td><td>Seminar Room 2
Chair: Han Sen SOO</td><td>Seminar Room 3
Chair: Donglin JIANG</td></tr>
<tr><td>Keynote talk
Han Vinh HUYNH (National University of Singapore)
Coordination Chemistry of Pyrazole-derived N-Heterocyclic Carbenes</td><td>Keynote talk
Shengqian MA (University of North Texas)
Metal-Organic Framework as a New Platform for Heterogeneous Small Molecule Activation</td></tr>
<tr><td rowspan="2">1005 - 1025</td><td>Outside Seminar Room 2</td><td>Outside Seminar Room 3</td></tr>
<tr><td colspan="2">Tea Break</td></tr>
<tr><td></td><td>Seminar Room 2
Chair: Han Sen SOO</td><td>Seminar Room 3
Chair: Yavuz Cafer</td></tr>
<tr><td>1025 - 1050</td><td>Kazuhiko MAEDA (Tokyo Institute of Technology)
Photocatalytic CO2 Reduction and Water Splitting Using Molecule-Containing Solids</td><td>Sang-Young LEE (Yonsei University)
Ionic COF Platforms for Advanced Batteries</td></tr>
<tr><td>1050 - 1115</td><td>Yunho LEE (Seoul National University)
Small Molecule Activation Mediated by Nickel</td><td>Zhengtao XU (Institute of Materials Research and Engineering)
Stable Radicals and Superconductivity from Sulfur Coordination Polymers</td></tr>
<tr><td>1115 - 1140</td><td>Ken SAKAI (Kyushu University)
Advanced Aspects on the Mechanisms of Catalytic Water Splitting and CO2 Reduction</td><td>Michio MATSUMOTO (National Institute for Materials Science)
Introducing heteroatoms in synthetic 2D polymers – sulfur and silicon</td></tr>
<tr><td>1140 - 1205</td><td>Vincent KO (City University of Hong Kong)
Luminescent Mechanochromism and Application of Ir(III) Acyclic Carbene Complexes</td><td>Psaras MCGRIER (The Ohio State University)
Covalent Organic Frameworks for Catalytic and Energy Storage Applications</td></tr>
<tr><td rowspan="2">1205 - 1315</td><td colspan="2">Tech Market Place</td></tr>
<tr><td colspan="2">Lunch and Poster session A</td></tr>
<tr><td rowspan="2">1315 - 1405</td><td colspan="2">MPH 1 & 2
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John HARTWIG (University of California, Berkeley)
Selective Catalytic Functionalization of C-H and C=C Bonds</td></tr>
<tr><td>1405 - 1425</td><td colspan="2">Transition</td></tr>
<tr><td rowspan="2">1425 - 1500</td><td>Seminar Room 2
Chair: Rei KINJO</td><td>Seminar Room 3
Chair: Shengqian MA</td></tr>
<tr><td>Keynote talk
Rebecca MELEN (Cardiff University)
Lewis Acidic Boranes as Catalysts for Carbene Transfer Reactions</td><td>Keynote talk
Donglin JIANG (National University of Singapore)
Covalent Organic Frameworks – The Chemistry for Designing Pores</td></tr>
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Cont'd.

1500 - 1520	**Outside Seminar Room 2**	**Outside Seminar Room 3**
	Tea Break	
	Seminar Room 2 Chair: Rei KINJO	**Seminar Room 3** Chair: Donglin JIANG
1520 - 1545	**Rong SHANG** (Hiroshima University) Bis(borane)-containing ligands: effects on bonding and reactivity	**Yavuz CAFER** (King Abdullah University of Science and Technology) Syngas economy with green hydrogen for rapid decarbonization of fuels and chemicals
1545 - 1610	**Yoshiaki SHOJI** (Tokyo Institute of Technology) Pursuing New Structures and Properties of Organoboron Compounds by Designing Chemical Bonds and Spaces Around Boron	**Ken SAKAUSHI** (National Institute for Materials Science) Coordination Frameworks as Multielectron Transferring Battery Electrode Materials
1610 - 1635	**Ching-Wen CHIU** (National Taiwan University) Catalytic Applications of Boron and Aluminum Cations	**Yanli ZHAO** (Nanyang Technological University) Integrating Supramolecular Interactions into Covalent Organic Frameworks for Catalytic Applications
1635 - 1645	***Break***	
1645 - 1710	**Yangjian QUAN** (The Hong Kong University of Science and Technology) Photoinduced Dehydrogenative Borylation via Dihydrogen Bond Bridged Electron Donor and Acceptor Complexes	**Yi LIU** (Lawrence Berkeley National Laboratory) Functional Covalent Organic Frameworks with "Irreversible" Covalent Bonds
1710 - 1735	**Hairong LYU** (Chinese University of Hong Kong) Boron insertion into alkyl ether bonds via zinc/nickel tandem catalysis	**Kazuhide KAMIYA** (Osaka University) Single-Atom Doped Covalent Triazine Frameworks as Electrocatalysts for Applications in Energy Conversion
1735 - 1800	**Yoichi HOSHIMOTO** (Osaka University) Main-group Catalysis for H2 Purification Based on Liquid Organic Hydrogen Carriers	**Dan ZHAO** (National University of Singapore) Structural Dynamics and Growth Mechanism of Covalent Organic Frameworks
1800	***End of Day 2***	

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Tuesday, 13 December 2022
Organic Track

Time	Programme	
0730 - 0820	**MPH 1 & 2**	
	Registration	
0820 - 0910	**Plenary talk** (Chair: Yu ZHAO) **Mikiko SODEOKA** (RIKEN) Transition Metal Enolate Chemistry: Past, Present, and Future	
0910 - 0920	**Transition**	
0920 - 0955	**MPH 1 & 2** Chair: Shunsuke CHIBA	
	Keynote talk **David NICEWICZ** (The University of North Carolina at Chapel Hill) New Avenues in Synthesis via Organic Photoredox Catalysis	
0955 - 1025	**Tech Market Place**	
	Tea Break 🍴 🥤	
	MPH 1 Chair: Shunsuke CHIBA	**MPH 2** Chair: Shaozhong GE
1025 - 1050	**Takashi KOIKE** (Nippon Institute of Technology) Radical Fluoroalkylation Reactions by Means of OrganicPhotocatalysis	**Takuya KOCHI** (Keio University) Nondissociative Chain Walking of Palladium Catalysts: Applications in Organic Reactions and Mechanistic Analyse
1050 - 1115	**Yoshihiro NISHIMOTO** (Osaka University) Photoredox-Catalyzed Defluoro-Allylation of Perfluoroalkylarenes Using Allylic Stannanes	**Takeshi FUJITA** (University of Tsukuba) Transition-Metal-Catalyzed Allylic and Vinylic C–F Bond Activation via Fluorine Elimination
1115 - 1140	**Sungwoo HONG** (Korea Advanced Institute of Science & Technology) N-Functionalized Pyridinium salts: A New Chapter for Site-Selective Pyridine C–H Functionalization under Visible Light Irradiation	**Jin Kyoon PARK** (Pusan National University) Highly Regio- and Stereoselective Access to Bi- and Trimetallic Skipped (Z,Z)-Dienes
1140 - 1205	**Davide RAVELLI** (The University of Pavia) Merging Decatungstate Photocatalysis with Electrochemistry	**Laurean ILIES** (RIKEN) SpiroBipyridine Ligands for Catalytic C–H Functionalization
1205 - 1315	**Tech Market Place**	
	Lunch and Poster Presentation B 🍴 🥤	
1315 - 1405	**MPH 1 & 2** Chair: Shunsuke CHIBA	
	Plenary talk **Armido STUDER** (University of Münster) Boron an Emergent Element in Radical Chemistry	
1405 - 1415	**Transition**	
1415 - 1450	**MPH 1 & 2** Chair: Ming Joo KOH	
	Keynote talk **James MORKEN** (Boston College) Stereoselective Synthesis with Organoboron Reagents	

Cont'd.

1450 - 1520	**Tech Market Place** **Tea Break**	
	MPH 1 Chair: Jie WU	**MPH 2** Chair: Ming Joo KOH
1520 - 1545	**Julio LLORET-FILLOL** (Institute of Chemical Research of Catalonia) Light-Driven Reduction Chemistry by well-defined complexes	**Xiaodong SHI** (University of South Florida) Gold Redox Chemistry: New Transformations and Asymmetric Catalysis
1545 - 1610	**Nan ZHENG** (University of Arkansas) Harnessing Synthetic Potential of Photogenerated Distonic Radical Cations	**Junqi LI** (Iowa State University) Atom-swapping Reaction Sequences Enabled by Nickel-catalyzed Decarbonylation of Lactones
1610 - 1635	**Hyunwoo KIM** (Pohang University of Science and Technology) Radical-Polar Crossover Strategy in Organic Electrosynthesis	**Hyunwoo KIM** (Korea Advanced Institute of Science & Technology) Hemilabile P,O-Ligands for Pd-Catalyzed Hydrosilylation of Unactivated Alkenes
1635 - 1645	***Break***	
1645 - 1710	**Massimo BIETTI** (University of Rome "Tor Vergata") Diverting Reaction Pathways in Hydrogen Atom Transfer Based C(sp3)□H Bond Oxygenation of Cyclopropane Containing Hydrocarbons	**Rui SHANG** (University of Tokyo) Iron-catalyzed New Transformations and Their Application for Electronic Materials
1710 - 1735	**Eisuke OTA** (Waseda University) σ-Bond Cleavage by Photoredox/Zirconocene Catalysis	**Byunghyuck JUNG** (Daegu Gyeongbuk Institute of Science & Technology) Cu-Catalyzed Regioselective Synthesis of (E)-1-Alkyl/Aryl-3,4-diborabut-1-enes
1735 - 1800	*This section is intentionally left blank*	*This section is intentionally left blank*
1800	**Transportation to Banquet dinner**	
1900 - 2130	**Banquet dinner** 🍴 🥤	

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Tuesday, 13 December 2022

Inorganic and Materials Track

Time	Programme	
0730 - 0820	**MPH 1 & 2**	
	Registration	
0820 - 0910	**Plenary talk** (Chair: Yu ZHAO) **Mikiko SODEOKA** (RIKEN) Transition Metal Enolate Chemistry: Past, Present, and Future	
0910 - 0930	**Transition**	
0930 - 1005	**Seminar Room 2** Chair: Cheuk Wai SO	**Seminar Room 3** Chair: Jishan WU
	Keynote talk **Lili ZHANG** (Institute Of Sustainability for Chemicals, Energy And Environment) Engineering Multifunctional Catalysts for Sustainable Catalysis	**Keynote talk** **Shohei SAITO** (Kyoto University) A Molecular Force Probe for Bridging pico-to-nanoNewton Physics
1005 - 1025	**Outside Seminar Room 2**	**Outside Seminar Room 3**
	Tea Break	
	Seminar Room 2 Chair: Cheuk Wai SO	**Seminar Room 3** Chair: Guillermo BAZAN
1025 - 1050	**Eunsung LEE** (Pohang University of Science and Technology) Stable Organic Radicals (feat. N-Heterocyclic Carbenes)	**Oliver DUMELE** (Humboldt University of Berlin) An All-organic Photomagnetic Switch
1050 - 1115	**Shigekazu ITO** (Tokyo Institute of Technology) Radical Reactions of Phosphorus Heterocycles with Muonium	**Hironobu HAYASHI** (Nara Institute of Science and Technology) Polyazaacene and Cyclazaacene Precursor Synthesis
1115 - 1140	**Roman DOBROVETSKY** (Tel Aviv University) Geometrically Constrained PIII Cations	**Mark CHEN** (Lehigh University) Exploiting Open-Shell Character in Bisphenalenyls for Materials with Radical Optoelectronic Properties
1140 - 1205	**Hiroaki IMOTO** (Kyoto Institute of Technology) Functional Organoarsenic Chemistry Based on Practical Syntheses	**Tetsuo OKUJIMA** (Ehime University) Synthesis of the Soluble Precursors of Tetrabenzoporphyrin and Phthalocyanines
1205 - 1315	**Tech Market Place**	
	Lunch and Poster Presentation B	
1315 - 1405	**MPH 1 & 2** Chair: Shunsuke CHIBA	
	Plenary talk **Armido STUDER** (University of Münster) Boron an Emergent Element in Radical Chemistry	
1405 - 1415	**Transition**	
1415 - 1450	**Seminar Room 2** Chair: Han Sen SOO	**Seminar Room 3** Chair: Shohei SAITO
	Keynote talk **Andy HOR** (A*STAR) The Future of Coordination Chemistry	**Keynote talk** **Chunyan CHI** (National University of Singapore) π-Structures with Different Topologies: Synthesis, Aromaticity and Electronic Properties

Cont'd.

1450 - 1520	**Outside Seminar Room 2**	**Outside Seminar Room 3**
	Tea Break 🍴 🥤	
	Seminar Room 2 Chair: Han Sen SOO	**Seminar Room 3** Chair: Miłosz PAWLICKI
1520 - 1545	**Lan-Chang LIANG** (National Sun Yat-sen University) Mismatched Donor-acceptor Pairs: Serendipitous Reaction and Structural Chemistry	**Hector BARBERO** (University of Valladolid) Corannulene-based Reversible Bistable Molecular Machines for Fullerene Recognition
1545 - 1610	**Hisashi SHIMAKOSHI** (Kyushu University) Bioinspired Catalytic Reactions With and Beyond the Vitamin B12 Enzyme Function	**Tomoko FUJINO** (The University of Tokyo) Oligomer-based Conductors that Modeled Doped PEDOT
1610 - 1635	**Hironobu OZAWA** (Kyushu University) Functional-Molecule-Modified Mesoporous TiO2 Electrodes for Electrochemical and Photoelectrochemical Water Splitting	**Grace HAN** (Brandeis University) Design of Organic Photoswitches for Optically-Controlled Phase Transition and Energy Applications
1635 - 1645	***Break***	
1645 - 1710	**Michael REITHOFER** (University of Vienna) Insight into Carbene stabilized Gold Nanoparticles	**Guillermo Carlos BAZAN** (National University of Singapore) Conjugated Oligoelectrolytes: A Versatile Platform for Membrane Modifications
1710 - 1735	**Chun-Hong Kuo** (National Yang Ming Chiao Tung University) Manipulation of Cu-Based Bimetallic Nanocrystals towards Electrochemical Conversion of Small Molecules	**Shingo ITOH** (Nanyang Technological University) Synthesis of Fully Conjugated Azacorannulene Dimers
1735 - 1800	**Jia Min CHIN** (University of Vienna) Controlling MOF materials across multiple length scales	**Takeshi MAEDA** (Osaka Prefecture University) Unveiling Open-Shell Character of Near-Infrared Absorbing Polymethine Dyes with Oxocarbon Moieties
1800	**Transportation to Banquet dinner**	
1900 - 2130	**Banquet dinner** 🍴 🥤	

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Wednesday, 14 December 2022

Organic Track

Time	Programme	
0730 - 0820	**MPH 1 & 2**	
	Registration	
0820 - 0910	**Plenary talk** (Chair: Yu ZHAO) **Sukbok CHANG** (Korea Advanced Institute of Science & Technology) C-H Amidation Reactions via Nitrenoid Transfer: Scope and Mechanistic Aspects	
0910 - 0920	**Transition**	
0920 - 0955	**MPH 1 & 2** Chair: Ye ZHU	
	Keynote talk **Yoshiaki NAKAO** (Kyoto University) Catalysis across Rh–Al Bonds	
0955 - 1025	**Tech Market Place**	
	Tea Break	
	MPH 1 Chair: Shunsuke CHIBA	**MPH 2** Chair: Ye ZHU
1025 - 1050	**Kanako KUMADA** (Tohoku University) Copper-Catalyzed Aerobic C(sp3)–H Functionalization for the Synthesis of Heterocycles	**Yee Hwee LIM** (Institute Of Sustainability for Chemicals, Energy And Environment) *Title of talk to be updated*
1050 - 1115	**Yusuke SASANO** (Tohoku University) Highly Chemoselective Aerobic Alcohol Oxidation Co-catalyzed by Nitroxyl Radical and Copper	**Seung Hwan CHO** (Pohang University of Science and Technology) Design and Synthesis of New Organoboron Reagents and Their Applications
1115 - 1140	**Kensuke KIYOKAWA** (Osaka University) Amination Using Hypervalent Iodine Reagents Containing (Diarylmethylene)amino Groups	**Tetsuo NARUMI** (Shizuoka University) Peptidomimetic Synthesis via Amide-to-Alkene Isosteric Switching and Beyond
1140 - 1205	**Kentaro OKANO** (Kobe University) “Snapshot” Trapping of Transient Aryllithium in Batch	**Takeshi NANJO** (Kyoto University) Oxidative Functionalization of Peptides Enabled by Catalytic N-Chlorination of Amides
1205 - 1315	**Tech Market Place**	
	Lunch and Poster Presentation B	
	MPH 1 Chair: Jie WU	**MPH 2** Chair: Shingo ITOH
1315 - 1340	**Shinichiro FUSE** (Nagoya University) Highly Efficient Peptide Chain Elongation via One-Flow, Three-Component Coupling Approach	**Crystal CHU** (Lehigh University) Bioinspired Polymer Fibers Drawn from Dynamic Networks
1340 - 1405	**Takahide FUKUYAMA** (Osaka Metropolitan University) Flow C-H Chlorination of Ethylene Carbonate Using a New Photoflow Setup Directed toward Manufacturing	**Koki IKEMOTO** (The University of Tokyo) Design and Synthesis of Nitrogen-Doped Phenine Nanocarbons

Cont'd.

1405 - 1430	**Robert BRITTON** (Simon Fraser University) A de novo Synthesis of Nucleosides and Nucleoside Analogues	**Naoya KUMAGAI** (Keio University) Chemistry Driven by Quinoline Oligomers
1430 - 1455	**Luca CAPALDO** (Universiteit van Amsterdam) Photoinduced Halogen-Atom Transfer (XAT) by N-heterocyclic Carbene Boryl Radicals for C(sp3)−C(sp3) Bond Formation	**Akimitsu NARITA** (Okinawa Institute of Science and Technology Graduate University) Synthesis and Functionalization of Highly Luminescent Polycyclic Aromatic Hydrocarbons toward Photonic Applications
1455 - 1525	**Tech Market Place**	
	Tea Break	
1525 - 1600	**MPH 1 & 2** Chair: Jie WU	
	Keynote talk **Takashi OHSHIMA** (Kyushu University) Controlling and Digitization of Chemoselectivity by Functional Group Targeted Catalyst and by Functional Group Evaluation Kit	
1600 - 1610	**Transition**	
1610 - 1700	**MPH 1 & 2** Chair: Xian Jun LOH	
	Plenary talk **Bin LIU** (National University of Singapore) Accelerating Biomedical Research through Materials Innovation	
1700 - 1715	**Poster award presentation and Closing Remarks** **Shunsuke CHIBA**, Chairperson of SICC-11	

Legend	**MPH 1 & 2** are located in Innovis building, Level 1 **Tech Market Place** is located in Innovis building, Level 8 **Seminar Room 2** is located in Kinesis building, Level 6 (Left Lift Lobby) **Seminar Room 3** is located in Kinesis building, Level 7 (Right Lift lobby)

Programme updated as of 06 December 2022 and is subjected to changes.

Wednesday, 14 December 2022

Inorganic and Materials Track

Time	Programme	
0730 - 0820	MPH 1 & 2	
	Registration	
0820 - 0910	**Plenary talk** (Chair: Yu ZHAO) **Sukbok CHANG** (Korea Advanced Institute of Science & Technology) C-H Amidation Reactions via Nitrenoid Transfer: Scope and Mechanistic Aspects	
0910 - 0930	**Transition**	
0930 - 1005	**Seminar Room 2** Chair: Han Vinh HUYNH	**Seminar Room 3** Chair: Oliver DUMELE
	Keynote talk **Tiow-Gan ONG** (Academia Sinica) Domesticating the Reactivity of Non-Octet Carbon toward Plethora of Chemistry	**Keynote talk** **Mihaiela STUPARU** (Nanyang Technological University) Synthesis of Curved Nanographenes
1005 - 1025	**Outside Seminar Room 2**	**Outside Seminar Room 3**
	Tea Break 🍴 🥤	
	Seminar Room 2 Chair: Han Vinh HUYNH	**Seminar Room 3** Chair: Henrik OTTOSSON
1025 - 1050	**Tsukasa MATSUO** (Kindai University) Ge=O Double-Bonded Species Bearing Rind Groups	**Jordi POATER** (Universitat de Barcelona) Aromaticity and Extrusion of Benzenoids linked to [o-COSAN]-: Clar has the Answer
1050 - 1115	**Michael HAAS** (Graz University of Technology) Recent Advances in the Field of Typ I Photoinitiators	**Hiromitsu MAEDA** (Ritsumeikan University) □-Electronic Ion Pairs: Ordered Arrangement and Radical-Pair Formation
1115 - 1140	**Yusuke SUNADA** (The University of Tokyo) Bond Activation by Silylene Bridged Group 10 Metal Clusters	**Michel Rickhaus** (University of Zurich) Shape-Assisted Self-Assembly of Curved π-Systems
1140 - 1205	**Yumiko NAKAJIMA** (The National Institute of Advanced Industrial Science and Technology) Long-Range Metal-Ligand Cooperation of Co Complexes Bearing a Phenanthroline-Based PNNP Ligand	**Junzhi LIU** (The University of Hong Kong) Rational Synthesis of Nanographenes with Non-Alternant Topologies
1205 - 1315	**Tech Market Place**	
	Lunch and Poster Presentation B 🍴 🥤	
	Seminar Room 2 Chair: Weng Kee LEONG	**Seminar Room 3** Chair: Jordi POATER
1315 - 1340	**Nobuto YOSHINARI** (Osaka University) Migration and Clusterization of Metal Ions in Supramolecular Frameworks of Metal-Organic Carboxylates	**Celedonio ALVAREZ** (University of Valladolid) Supramolecular Interactions with Non-Planar Polyaromatic Species. How Synergistic Arranges of Corannulenes can Increase the Affinity for Fullerenes
1340 - 1405	**Sungho YOON** (Chung Ang University) Heterogenized Catalysts for CO2 conversion into formate	**Yumi YAKIYAMA** (Osaka University) Structures and Properties of Stimuli-responsive Molecular Crystalls Composed of Unique-shaped Building Units

Cont'd.

1405 - 1430	**Edmund TSE** (University of Hong Kong) Steering Oxygen Reduction Electrocatalysts toward 4e/4H Pathway using a Hybrid Membrane with Fuel Cell Implications	**Donghong YU** (Aalborg University) Conjugation break: A new design strategy for electron acceptor polymers towards efficient and thermally stable all-polymer solar cells
1430 - 1455	**Kosei YAMAUCHI** (Kyushu University) Photochemical and Electrochemical Hydrogen Evolution from Water Catalyzed by Co-NHC Complexes	**Jongin HONG** (Chung-Ang University) Wavelength-selective dyes for visibly transparent and colorless solar cells
1455 - 1525	**Outside Seminar Room 2**	**Outside Seminar Room 3**
	Tea Break 🍴 🥤	
1525 - 1600	**Seminar Room 2** Chair: Weng Kee LEONG	**Seminar Room 3** Chair: Chunyan CHI
	Keynote talk **Michael INGLESON** (University of Edinburgh) Forming organoboranes using electrophilic borylation: From arylboronate esters to APIs and organic materials	**Keynote talk** **Miłosz PAWLICKI** (Jagiellonian University) On Delocalisation in Strongly Conjugated Systems
1600 - 1610	**Transition**	
1610 - 1700	**MPH 1 & 2**	
	Plenary talk **Bin LIU** (National University of Singapore) Accelerating Biomedical Research through Materials Innovation	
1700 - 1715	**Poster award presentation and Closing Remarks** **Shunsuke CHIBA**, Chairperson of SICC-11	

Legend	**MPH 1 & 2** are located in Innovis building, Level 1 **Tech Market Place** is located in Innovis building, Level 8 **Seminar Room 2** is located in Kinesis building, Level 6 (Left Lift Lobby) **Seminar Room 3** is located in Kinesis building, Level 7 (Right Lift lobby)

Programme updated as of 06 December 2022 and is subjected to changes.

PLENARY SPEAKERS

Prof. Makoto FUJITA
The University of Tokyo

Plenary 1
Sunday, 11 Dec 2022
1440 – 1530 hrs
MPH 1 & 2

Abstract:

Self-assembly of Gigantic Coordination Polyhedra: From Synthetic to Peptidic

Molecular self-assembly based on coordination chemistry has made an explosive development in recent years. Over the last three decades, we have been showing that the simple combination of transition-metal's square planer geometry (a 90-degree coordination angle) with pyridine-based bridging ligands gives rise to the quantitative self-assembly of nano-sized, discrete organic frameworks. Representative examples include square molecules (1990), linked-ring molecules (1994), cages (1995), capsules (1999), and tubes (2004) that are self-assembled from simple and small components.[1] Originated from these earlier works, one of current interests in our group is focused on giant self-assemblies[2] (Figure 1), as disclosed in this lecture. The organic components can be either simple and rigid bridging ligands or oligopeptides that adopt fixed conformation when folded.[3]

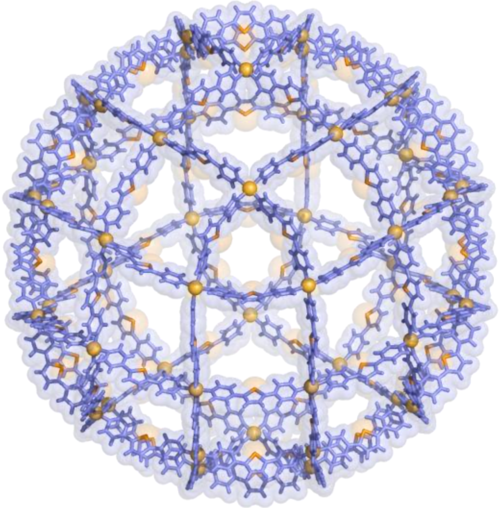

Figure 1. X-ray structure of $M_{48}L_{96}$ complex.

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Prof. Scott MILLER
Yale University

Plenary 2
Monday, 12 Dec 2022
0820 – 0910 hrs
MPH 1 & 2

Abstract:
Searching for Selective Catalytic Reactions in Complex Molecular Environments

This lecture will describe recent developments in our efforts to develop catalysts for asymmetric reactions, in particular for the preparation of densely functionalized, stereochemically complex structures. Over time, our foci have been on enantioselectivity, site-selectivity and chemoselectivity. In much of our current work, we are studying issues of enantioselectivity as a prelude to the extrapolation of catalysis concepts to more complex molecular settings where multiple issues are presented in a singular substrate. Mechanistic paradigms, and their associated ambiguities – especially in light of catalyst or substrate conformational dynamics – will figure strongly in the lecture, raising analogies to enzymes. Finally, several interesting – and often unexpected – collaborations with colleagues in industry will be discussed.

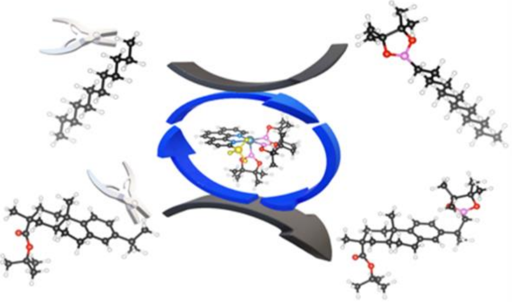
Prof. John F. HARTWIG
University of California, Berkeley

Plenary 3
Monday, 12 Dec 2022
1315 – 1405 hrs
MPH 1 & 2

Abstract:
Selective Catalytic Functionalization of C-H and C=C Bonds

The selective introduction of functional groups at the positions of typically unreactive C-H bonds has been a longstanding challenge in catalysis. Our group has developed practical methods for the catalytic functionalization of C-H bonds with main group reagents.[1-3] These studies have created a general strategy of installing a single transient functional group to form a range of products from one C-H bond functionalization. This research has led us to seek next-generation catalysts for the functionalization of C-H in complex molecules, new classes of functionalization reactions, and new strategies, such as the construction of artificial metalloenzymes to control site selectivity.[4,5]

This lecture will present recent directions of research in our group toward discovering selective reactions of both small and complex molecules with large and small catalysts. The design and selection, as well as the intimate mechanism, of catalysts and catalytic reactions for selective functionalization processes will be presented.



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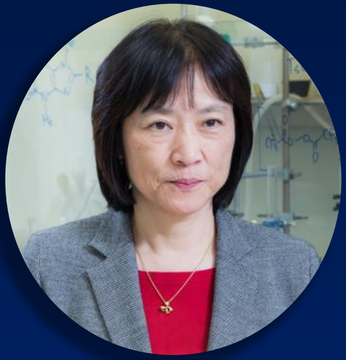

Prof. Mikiko SODEOKA
Riken

Plenary 4
Tuesday, 13 Dec 2022
0820 – 0910 hrs
MPH 1 & 2

Abstract:

Transition Metal Enolate Chemistry: Past, Present, and Future

We have been working on chiral transition metal enolate chemistry for many years. First, we found that chiral palladium enolates act as very mild nucleophiles and developed Pd-catalyzed reactions of carbonyl compounds with various electrophiles. Origin of the high enantioselectivity can be simply explained by steric repulsion between the stable bidentate Pd(II) enolate complex and the electrophile.[1] Recently we are focusing on the reactions using a-ketoesters as pronucleophiles. For this type of substrates, $Ni(OAc)_2$ and $Cu(OAc)_2$ complexes with a chiral diamine ligand were found to act as excellent catalysts for their asymmetric conjugate addition and cycloaddition reactions.[2-5] Mechanistic study revealed completely different principle of the enantiocontrol. Attractive interactions are the key for the high enantio- and diastereo-selectivity.

A notable feature of transition metal catalysts is that they can show various reactivities by the combination of ligands and central metals and can also have redox active properties. The reactions of transition metal enolates that we have developed so far have been based on their reactivity as nucleophiles, but we believe that we can develop even more unique reactions by using the redox properties of the transition metals. Some preliminary finding of this direction would be also discussed.[6]

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Prof. Armido STUDER
University of Münster

Plenary 5
Tuesday, 13 Dec 2022
1315 – 1405 hrs
MPH 1 & 2

Abstract:
Boron an Emergent Element in Radical Chemistry

In the lecture, it will be shown, that readily generated vinyl boron ate complexes, generally used as substrates in the Suzuki-Miyaura coupling, are efficient radical acceptors to conduct electron-catalyzed modular synthesis comprising a radical polar cross over step.[1] Along these lines, dienyl boron ate complexes react with high efficiency with various C-radicals at the □-position, and the polar cross over rearrangement process delivers valuable allyl boronic esters as products.[2] This conceptual approach has recently been successfully also applied to the development of a novel method for the preparation of highly enantioenriched □-chiral ketones.[3] Hydrogen atom transfer induced boron retaining coupling of organoboronic esters and organolithium reagents is discussed as a straightforward method for the □-C-H functionalization of alkyl boronic esters.[4]

In addition, it will be shown that bis(catecholato)diboron (Cat_2B_2) is a highly efficient C-radical trapping reagent.[5-8] For example, this reactivity was applied to establish a transition-metal-free radical alkene 1,2-carboboration reaction.[5] It is further shown that alkyl and aryl iodides react with Cat_2B_2 upon simple irradiation to the corresponding alkyl and aryl boronic esters. Alcohols, if appropriately activated, can also be transformed to boronic esters via radical pathways.[7,8] Finally, migration of boron groups[9] and of aryl moieties[10] from boron in B-ate complexes to C-radicals will be addressed.

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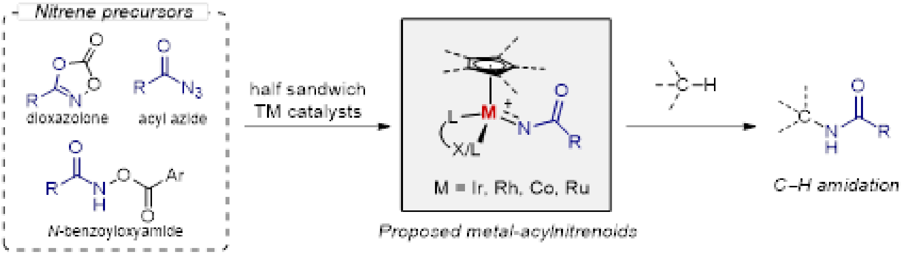
Prof. Sukbok CHANG
Korea Advanced Institute of Science and Technology

Plenary 6
Wednesday, 14 Dec 2022
0820 – 0910 hrs
MPH 1 & 2

Abstract:

C-H Amidation Reactions via Nitrenoid Transfer: Scope and Mechanistic Aspects

Direct amidation of C–H bonds is a highly desirable reaction considering high utility of amidated products in total synthesis, medicinal chemistry and materials science.[1-2] Although tremendous research efforts have been made especially in recent years, the current status enabling such C–H reactions in excellent stereoselectivity and high efficiency is still rather limited. In this context, we have developed a novel methodology that employs tailor-made Ir-based catalysts in combination with dioxazolone substrates to access a short-lived metal-nitrenoid intermediate, thereby eventually leading to a construction of γ-lactams via an outer-sphere C–H insertion pathway.[3] The scope was found to be broad and a range of carboxylic acids could be readily utilized for the lactam formation. More recently, we have successfully introduced an iridium-based catalyst system for asymmetric C−H amidation that enables facile construction of chiral γ-lactams starting from commodity chemicals. Various types of secondary C−H bonds, such as being positioned at the benzylic, unactivated aliphatic, propargylic, and allylic sites, were all smoothly reacted in a regio- and stereoselective manner.[4-5] More recently, this strategy of C-N bond formation has been also successfully demonstrated to work with basic transition metal catalysts.[6-8] The nitrenoid intermedicay was extensively investigated using mechansitrtic experiments, phtocrystallography, and computational studies.[9] The present approach will find broad applications in medicinal chemistry, and the mechanistic insights may provoke further developments in related asymmetric catalysis.



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Prof. Bin LIU
National University of Singapore

Plenary 7
Wednesday, 14 Dec 2022
1610 – 1700 hrs
MPH 1 & 2

Abstract:
Accelerating Biomedical Research through Materials Innovation

The recent years have witnessed the fast grow of fluorogens with aggregation-induced emission characteristics (AIEgens) in biomedical research. The weak emission of AIEgens as molecular species and their bright luminescence as nanoscopic aggregates distinguish them from conventional organic luminophores and inorganic nanoparticles, making them wonderful candidates for many high-tech applications. In this talk, we summarize our recent AIE work in the development of new fluorescent bioprobes for biosensing and imaging. The simple design and fluorescence turn-on feature of the molecular AIE bioprobes offer direct visualization of specific analytes and biological processes in aqueous media with higher sensitivity and better accuracy than traditional fluorescence turn-off probes. The AIE dot probes with different formulations and surface functionalities show advanced features over quantum dots and small molecule dyes in noninvasive cancer cell detection, long term cell tracing, and vascular imaging. In addition, our recent discovery that AIEgens with high brightness and efficient reactive oxygen species generation in aggregate state further expanded their applications to image-guided cancer surgery and therapy. Recently, we combined accurate prediction of material performance via first-principle calculations and Bayesian optimization-based active learning to realize a self-improving discovery system for high-performance photosensitizers, which can significantly accelerate the materials innovation for biomedical research.

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KEYNOTE SPEAKERS

Prof. Daniele LEONORI
RWTH Aachen University

Keynote 1
Sunday, 11 Dec 2022
1540 – 1615 hrs
MPH 1 & 2

Abstract:
Novel Synthetic Methods in Halogen-Atom Transfer and Excited Nitroarene Reactivity

In this presentation I will discuss two recent research lines from my group focused on the development and understanding of halogen-atom transfer and excited nitroarene reactivity.

Halogen-atom transfer (XAT). Organic halides are valuable building blocks for the generation of alkyl and aryl radicals. However, their applications in photoredox catalysis can be difficult owing to their very negative reduction potentials. I will present our recent work focused on the use of □-aminoalkyl radicals as XAT mediators for the homolytic activation of alkyl iodides and bromides and their application in synthesis.[1,2] Furthermore, I will discuss a non-canonical activation mode in XAT that eludes both kinetic and thermodynamic control.[3]

Photoexcited nitroarenes. Nitroaromatics are widely available feedstocks that are routinely used for the preparation of anilines. I will present our most recent work that demonstrates how these species can be used, upon blue light irradiation, to promote the ozonolysis-style cleave of olefins[4] and also, in a skeletal editing logic, to allow preparation of complex and highly functionalised azepanes.[5]

References

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5. Unpublished results.

Prof. Hua ZHANG
City University of Hong Kong

Keynote 2
Sunday, 11 Dec 2022
1550 – 1625 hrs
Seminar Room 2

Abstract:
Phase Engineering of Nanomaterials (PEN)

In this talk, I will summarize the recent research on phase engineering of nanomaterials (PEN) in my group, particularly focusing on the rational design and synthesis of novel nanomaterials with unconventional phases for various promising applications. For example, by using wet-chemical methods, for the first time, we have successfully prepared novel Au nanostructures (e.g., the hexagonal-close packed (hcp) 2H-Au nanosheets, 4H-Au nanoribbons, and crystal-phase heterostructured 4H/fcc and fcc/2H/fcc heterophase Au nanorods), epitaxially grown metal nanostructures on the aforementioned unconventional Au nanostructures and 2H-Pd nanoparticles, and amorphous/crystalline heterophase Pd, PdCu, Rh and Rh alloy nanosheets. In addition, by using gas-solid reactions, metastable 1T'-phase group VI transition metal dichalcogenides (TMDs), e.g., WS2, WSe2, MoS2, MoSe2, WS2xSe2(1-x) and MoS2xSe2(1-x), have been prepared. Moreover, the phase transformation of TMDs during our developed electrochemical Li-intercalation process has also been observed. Impressively, the lithiation-induced amorphization of Pd3P2S8 has been achieved. Currently, my group focuses on the investigation of phase-dependent physicochemical properties and applications in catalysis, (opto-)electronic devices, clean energy, chemical and biosensing, surface enhanced Raman scattering, waveguide, photothermal therapy, etc., which we believe is quite unique and very important not only in fundamental studies, but also in future practical applications. Importantly, the concepts of phase engineering of nanomaterials (PEN), crystal-phase heterostructures, and heterophase nanomaterials are proposed.

Websites:
https://www.cityu.edu.hk/chem/people/academic-staff/HZHANG
https://scholars.cityu.edu.hk/en/persons/hua-zhang(8f4e048e-884d-4f19-b2b4-ca4d3d53c515).html

Google Scholar: https://scholar.google.com/citations?user=Cgo45S8AAAAJ&hl=en

Prof. Henrik OTTOSSON
Uppsala University

Keynote 3
Sunday, 11 Dec 2022
1550 – 1625 hrs
Seminar Room 3

Abstract:
Excited State Aromaticity and Antiaromaticity: From Scopes to Pitfalls

The use of the excited state aromaticity and antiaromaticity concepts (ESA & ESAA) to rationalize excited state properties and processes has grown rapidly in recent years.[1,2] These concepts are often described by Baird's 4*n* and 4*n* + 2 rules for, respectively, aromaticity and antiaromaticity in the lowest $\pi\pi^*$ excited states, and they have been used to understand various photoreactions,[3] to explore and design photofunctional molecules,[4] and to interpret fundamental excited state properties.[5] They can likely find use in a range of areas; from astrochemistry to biophysics and photovoltaics. Yet, at the same time as they are applied in gradually more areas, it is crucial to explore their limitations, complications and pitfalls. *E.g.*, induced diatropic ring currents in the T_1 state are not always indicative of Baird-aromaticity as molecules also can be Hückel-aromatic in their excited states,[6] and quinoidal compounds can simultaneously be Hückel- and Baird-aromatic.[7] Heterocycles and macrocycles with tentative ESA character further expose conceptual as well as computational challenges.[8,9] My talk will address the scopes of ESA & ESAA as well as their limitations, complications, and pitfalls.

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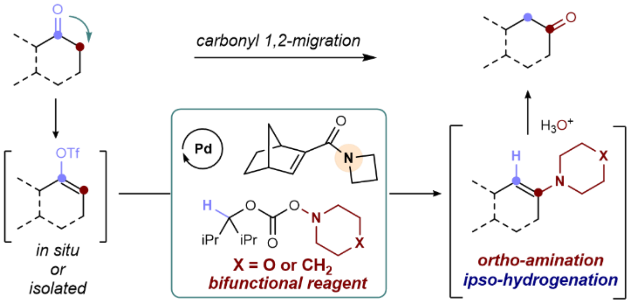
Prof. Guangbin DONG
The University of Chicago

Keynote 4
Monday, 12 Dec 2022
0920 – 0955 hrs
MPH 1 & 2

Abstract:
Merging C−C and C−H Activation: Palladium/Norbornene Cooperative Catalysis

Achieving site-selectivity in arene functionalization that is complementary to the one from electrophilic aromatic substitution (EAS) reactions has been a long-standing quest in organic synthesis. The palladium/norbornene (Pd/NBE) cooperative catalysis potentially offers a unique approach to this problem, but its usage has been hampered by "three constraints": the electrophile constraint, the arene-substrate constraint, which is the requirement of using aryl iodides, and the "ortho constraint", which is the requirement of an ortho substituent for mono ortho functionalization of haloarenes. Here, we show that all these three constraints could be addressed through designing the electrophiles, phosphine ligands and norbornene ligands. Besides Catellani-type ortho alkylation and arylation, new ortho functionalization methods, such as ortho amination, acylation, carboxylation, thiolation and annulation, have been realized. In addition, using a unique phosphine system, various aryl bromides can be employed as the arene substrates. Moreover, a new class of bridgehead-modified NBEs overcomes the "ortho" constraint, thereby enabling a broadly useful strategy for arene functionalization with complementary site-selectivity to EAS reactions. A range of ortho-unsubstituted aryl iodides, previously problematic substrates, now can be employed to provide mono ortho functionalized products effectively. These methods are applicable for late-stage functionalization of complex bioactive molecules at positions that are difficult to be reached by conventional approaches. Beyond arene substrates, we also realized a non-intuitive transformation, that is to migrate ketone carbonyl to its adjacent position in one-pot through α-amination of alkenyl triflate. Conventionally, carbonyl 1,2-migration is a very tedious and less selective process, and generally takes 4-6 steps. This method not only provides a straightforward approach to access oxygen-transposed analogues, but also opens the door for a completely new type of carbonyl transformations.



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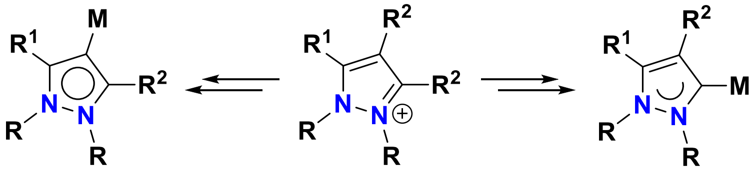
Prof. Han Vinh HUYNH
University of North Texas

Keynote 5
Monday, 12 Dec 2022
0930 – 1005 hrs
Seminar Room 2

Abstract: Coordination Chemistry of Pyrazole-derived N-Heterocyclic Carbenes

In search for less-explored and non-classical N-heterocyclic carbenes (NHCs),[1] we have studied the use of pyrazoles and their benzannulated analogues (indazoles) as ligand precursors. In analogy to complexes of imidazolinylidenes, those of their isomeric pyrazolinylidenes[2] can be conveniently accessed by *in situ* deprotonation or oxidative addition of their N-heterocyclic salts in the presence of suitable metal precursors. The structural and electronic diversity of this rare class of NHC is exemplified by the isolation of non-classical NHC complexes with both normal and mesoionic[1] coordination modes. An overview of our previous and more recent efforts in exploring the chemistry of these rare NHCs will be given including attempts at their stereoelectronic profiling.[3]



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Prof. Shengqian MA
University of North Texas

Keynote 6
Monday, 12 Dec 2022
0930 – 1005 hrs
Seminar Room 3

Abstract:
Metal-Organic Framework as a New Platform for Heterogeneous Small Molecule Activation

The activation of small molecules and their subsequent reactions have been considered as a fundamental pillar of modern catalysis and existing catalysts are dictated by transition metal-based compounds.[1] This is particularly the case for heterogeneous small molecule activation, which primarily relies on precious metal-based catalysts (e.g. Pt, Pd, Rh, Ir) that are rare and costly. Over the past two decades, the rapid growth of metal-organic framework (MOF) that features tunable, designable, and functionalizable nanospace has provided plenty of opportunities for heterogeneous catalysis. Various design approaches will be discussed for the systematic development of MOF as a new and sustainable platform for heterogeneous small molecule activation including dihydrogen activation (Figure 1a) and carbon dioxide chemical transformations (Figure 1b).

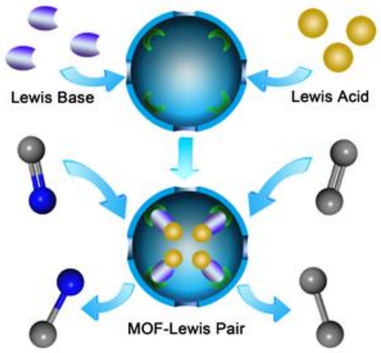

Figure 1a

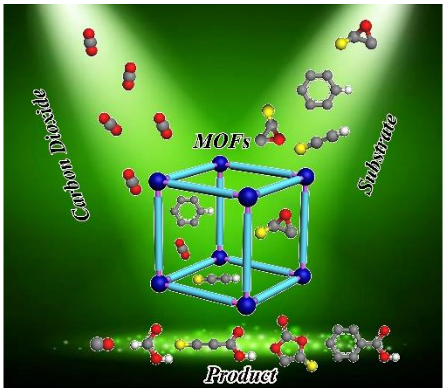

Figure 1b

Figure 1. Illustration of MOF for heterogeneous small molecule activation: (a) dihydrogen activation; (b) carbon dioxide chemical transformations.

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Prof. Qiu WANG
Duke University

Keynote 7
Monday, 12 Dec 2022
1415 – 1450 hrs
MPH 1 & 2

Abstract:
Copper-Catalyzed Aminofunctionalization of Alkenes and Dienes

Aminofunctionalization of alkenes represents a direct and powerful strategy to transform simple and readily available olefins into richly functionalized nitrogen-containing compounds of great value. Toward this end, we have developed copper-catalyzed alkene aminofunctionalization reactions by exploring electrophilic amination and the coupling reactions of versatile nucleophiles. These methods afford a rapid and direct access to a diverse range of 1,2-diamines, 1,2-amino halides, 1,2-amino alcohol derivatives, including highly functionalized lactams and lactones. Mechanistic studies on these reactions have revealed a novel electrophilic amination-initiated activation pathway that has great potentials for a general, powerful platform for designing regio- and stereoselective new functionalization reactions of alkenes and dienes.

Prof. Rebecca MELEN
Cardiff University

Keynote 8
Monday, 12 Dec 2022
1425 – 1500 hrs
Seminar Room 2

Abstract:
Lewis Acidic Boranes as Catalysts for Carbene Transfer Reactions

Reactive carbenes generated from diazo compounds are key intermediates for a range of organic reactions to afford synthetically useful organic compounds. Most of these reactions have been carried out using transition metal catalysts. However, the formation of carbene intermediates using main group elements has not been extensively investigated for synthetic purposes. Recent studies in my group have revealed that triarylboranes can be used for the in-situ generation of a reactive carbene intermediates in both stoichiometric and catalytic reactions. These new reactivities of triarylboranes have gained significant attention in synthetic chemistry particularly in catalytic studies. The variety of organic compounds that have been produced through these reactions are important as pharmaceutics or agrochemicals. In this talk I will highlight the recent progress and ongoing challenges of carbene transfer reactions using triarylboranes as catalysts. I will also highlight the stoichiometric use of triarylboranes in which the boranes not only activate the diazo functionality to afford a carbene intermediate, but also actively participate in the reactions as a reagent.

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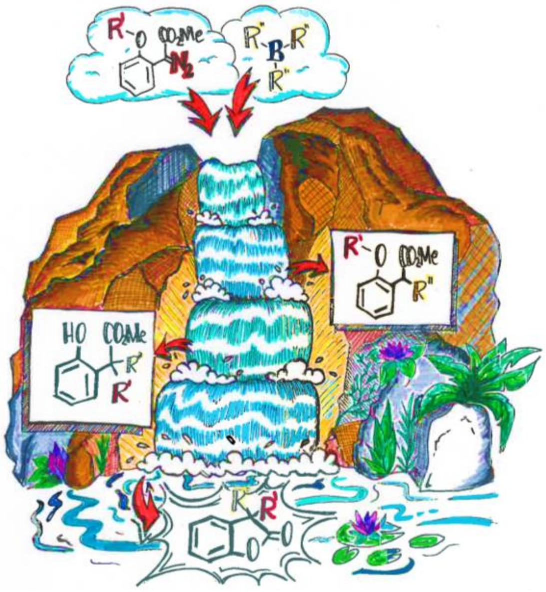

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Prof. Donglin JIANG
National University of
Singapore

Keynote 9
Monday, 12 Dec 2022
1425 – 1500 hrs
Seminar Room 3

Abstract:
Covalent Organic Frameworks – The Chemistry for Designing Pores

Covalent organic frameworks (COFs) are a class of crystalline porous polymer as it combines covalent and non-covalent chemistries to develop long-range ordered polygonal skeletons and discrete permanent pores. Topological diagram – the principle for designing COFs, enables the predesign of not only skeletons but also pores, offering a powerful molecular platform for constructing tailor-made organic/polymeric materials. Over the past decade, progress in chemistry has greatly enhanced our capability of synthesizing COFs to achieve different structures. Looking at the features of COFs, a basic common structure of the pores is the well-defined pore interface, which is constituted by aligned surface atoms and side units at a proximate distance along the pore long-axial direction and distributed periodically over the pores (Figure 1). These features of pore interfaces are specific to COFs and predetermine their functions. In this lecture, we scrutinize the chemistry of pore interface by focusing on pore shape, size, and the aligned atoms and units on pore walls to design unique properties and functions. We highlight pore wall perturbation with surface atoms and side units to demonstrate their decisive roles in structural formation and functional expression.[1,2]

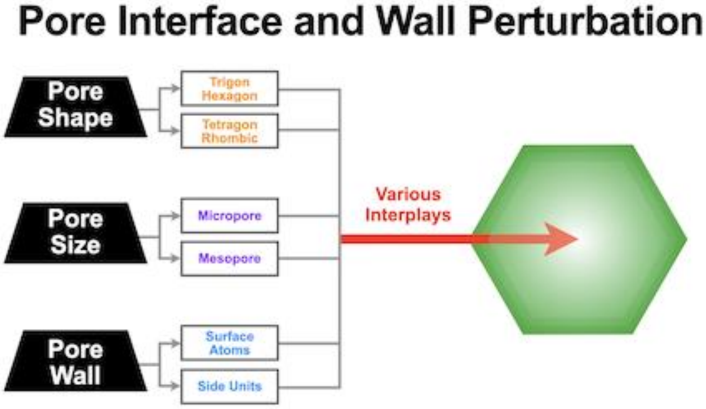

Figure 1. Chemistry of pore interface and wall perturbation for tailor-made pores.

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Prof. David NICEWICZ
The University of North Carolina at Chapel Hill

Keynote 10
Tuesday, 13 Dec 2022
0920 – 0955 hrs
MPH 1 & 2

Abstract:
New Avenues in Synthesis via Organic Photoredox Catalysis

Single electron pathways are common in the biological realm and are integral to photosynthesis and physiological processes in humans. As synthetic chemists, we seek to harness the power of single electron mediated pathways to more efficiently make the pharmaceuticals, agrochemicals, and materials that the modern world requires. My group seeks to use organic salts as excited state catalysts to mediate single electron processes in the development of new chemical transformations. This lecture will give a brief background to organic photoredox catalysis and cover some of the reactivity from my group including C-H functionalization chemistry and applications to radiolabeling technology. Lastly, this lecture will describe how acridinium photooxidants can be transformed to excited state super reductants via two-photon absorption.

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Dr. Lili ZHANG
Institute Of Sustainability for Chemicals, Energy and Environment

Keynote 11
Tuesday, 13 Dec 2022
0930 – 1005 hrs
Seminar Room 2

Abstract:
Engineering Multifunctional Catalysts for Sustainable Catalysis

Multifunctional catalysts with atomically dispersed active centers have been designed. However, how to precisely construct active catalytic sites with precisely defined coordination environment having favorable electronic structure at the atomic level remains challenging. What's more challenging is how to mass produce advanced catalysts with highly dispersed active centers. Single-atom catalysts (SACs) with symmetric charge distribution are not electron-conducting and thus limits the transfer rates. Therefore, breaking the symmetry of electronic density by axially introducing an additional coordinating atom shall improve the catalytic performance. We describe how we achieved multifunctional catalysts with asymmetric electronic structures that lead to good catalytic performance for CO_2 reduction and water splitting. [1-2] In addition, we show how we produced advanced catalysts through high-throughput mechanochemistry method. Ni-N_4-O coordination abundantly anchored on high-surface nitrogen-doped porous graphitic carbon was designed and synthesized.[3] In-depth experimental and theoretical studies reveal that the axial M-O coordination introduces asymmetry to the catalytic center, leading to lower Gibbs free energy for the rate-limiting step, stronger binding with *COOH, and weaker association with *CO in CO_2 reduction. Another SAC achieved electronic regulation of Co active center by near-range coordination with N and long-range interaction with S and exhibited excellent and stable trifunctional electrocatalytic activity for water splitting. The demonstrated strategies can be applied to make various asymmetrically coordinated SACs (M-N4-O/S) to enrich the family of SACs for various catalytic applications.

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Prof. Shohei SAITO
Kyoto University

Keynote 12
Tuesday, 13 Dec 2022
0930 – 1005 hrs
Seminar Room 3

Abstract:

A Molecular Force Probe for Bridging pico-to-nanoNewton Physics

Understanding the transmission of nanoscale forces in the pico-to-nanoNewton range is important in polymer physics. While physical approaches have limitations in analyzing the local force distribution in condensed environments, chemical analysis using force probes is promising. However, there are stringent requirements for probing the local forces generated before structural damage. The magnitude of those forces corresponds to the range below covalent bond scission (from 200 pN to several nN) and above thermal fluctuation (several pN). Here, we report a conformationally flexible dual-fluorescence force probe with a theoretically estimated threshold of approximately 100 pN. This probe enables ratiometric analysis of the distribution of local forces in a stretched/compressed polymer chain network.[1,2] Without changing the intrinsic properties of the polymer, the force distribution was reversibly monitored in real time. Due to the high sensitivity, the percentage of the stressed force probes was estimated to be more than 1000 times higher than that of a conventional mechanophore.

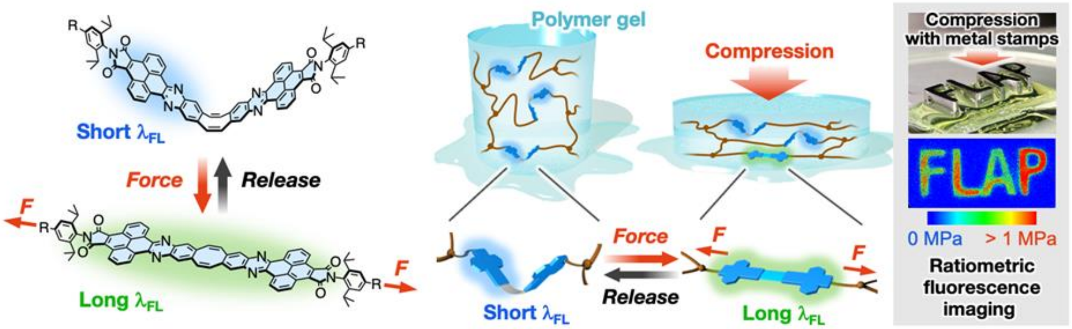

Figure. Flapping molecular probes (FLAPs[1–10]) realize real-time dual-fluorescence responses to the nanoscale force, quantifying the percentage of tensed polymer chains before structural damage.

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Prof. James P. MORKEN
Boston College

Keynote 13
Tuesday, 13 Dec 2022
1415 – 1450 hrs
MPH 1 & 2

Abstract:
Stereoselective Synthesis with Organoboron Reagents

Chiral organoboronic esters are versatile intermediates for chemical synthesis. Not only are these compounds stable under a variety of reaction conditions, they are generally non-toxic and can be transformed with minimal generation of hazardous waste. An important feature of aliphatic organoboronic esters is that the boron atom may be replaced with an array of different functional groups through efficient, stereospecific transformations. This seminar will cover new strategies for the construction of alkylboronic esters from simple starting materials in a catalytic enantioselective fashion and will highlight new methods for the stereospecific coupling of alkylboronic esters with synthetically relevant electrophiles.[1,2]

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Prof. Andy HOR
Agency for Science, Technology and Research

Keynote 14
Tuesday, 13 Dec 2022
1415 – 1450 hrs
Seminar Room 2

Abstract:
The Future of Coordination Chemistry

Coordination Chemistry has undergone many generations of evolutions since the early days of Alfred Werner. It started with the discovery of bonding of seemingly stable small molecules like NH3 or ions like CN- to metal atoms/ions such as Fe and Ni to the current plethora of metallic based or enriched materials, devices, and systems.

While the past seems fulfilling, what about the present and future, given the global challenges that we face? How does coordination chemistry take on global and social challenges? For example, what would be the role of coordination chemistry in climate change, health management, and digital technologies?

The speaker will speak from the discoveries in his laboratory to cite examples and address the above.

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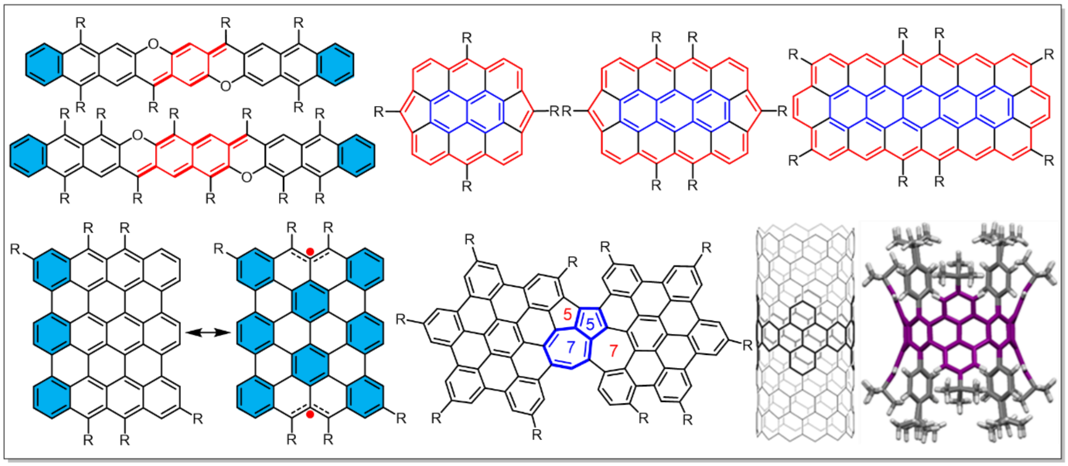
Prof. Chunyan CHI
National University of Singapore

Keynote 15
Tuesday, 13 Dec 2022
1415 – 1450 hrs
Seminar Room 3

Abstract:

π-Structures with Different Topologies: Synthesis, Aromaticity and Electronic Properties

Carbon-based nanostructures have shown revolutionary influence in the area of chemistry, physics and materials science. Recent efforts have been focused on novel topological structures of sp^2-carbons such as carbon nanohoops, nanobelts, molecular cages, and open-shell nanographenes, which provoked new chemistry and materials. However, synthesis of this kind of molecules is extremely challenging mainly due to strain or intrinsic high reactivity. Another issue is that most of these carbon nanostructures have a localized aromatic character; that means, the π-electrons are not globally delocalized along the backbone, which limits their optical and electronic properties and applications. Herein, the synthesis of a series of novel pi-structure with different topologies will be introduced, and their physical properties, aromaticity and diradical character will be discussed.[1-7] Some structures are shown below.



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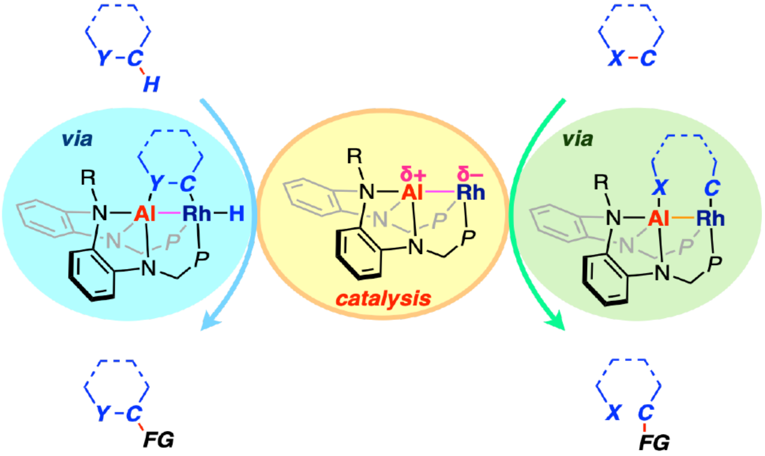
Prof. Yoshiaki NAKAO
Kyoto University

Keynote 16
Wednesday, 14 Dec 2022
0920 – 0955 hrs
MPH 1 & 2

Abstract:
Catalysis across Rh–Al Bonds

Transition-metal complexes that bear a metal–metal bond have attracted considerable interest on account of their unique reactivity. We have been interested in X-type aluminyl ligands because of the low electronegativity and strong Lewis acidity of the Al atom. However, transition-metal complexes that bear X-type aluminyl ligands had until recently remained elusive. In this presentation, the reactivity of Rh complexes that carry a well-designed X-type PAlP pincer-ligand and their characteristic features, i.e., strong σ-donicity, trans-influence, reverse bond polarization, and Lewis acidity will be discussed.1 Catalytic transformations such as site-selective C–H-bond functionalization,2,3 C–F4 and C–O5 bond functionalization will also be demonstrated by using the Rh–Al complexes.



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Prof. Tiow-Gan ONG
Academia Sinica

Keynote 17
Wednesday, 14 Dec 2022
0930 – 1005 hrs
Seminar Room 2

Abstract:
Domesticating the Reactivity of Non-Octet Carbon toward Plethora of Chemistry

Carbodicarbenes (CDCs) are carbones (CL2) repertoire that feature a dicoordinated central carbon (0) atom bearing two lone pairs of electrons, with N-heterocyclic carbenes (NHCs) as ligands (L). Because of the two lone pairs on the central carbon atom, CDCs have been regarded as strong σ-donating surrogates complementary to the well-established NHCs. This presentation will describe the synthetic preparation[1] and chemical properties of the CDC[2] as well as its application toward supporting metallic complexes for catalysis in tandem photoredox[3] cross-coupling reaction via tandem C-H and C-O bond activation[4] and a new spin in diversifying FLP reactivity with comodulator benzyl alcohol. Finally, we also described phosphine-stabilized dicarbon as effective ligand for metal complexes and catalysis.[5] Dicarbon is a reactive carbon allotrope that naturally exists only in the high temperature medium of stellar space.

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Prof. Mihaiela STUPARU
Nanyang Technological University

Keynote 18
Wednesday, 14 Dec 2022
0930 – 1005 hrs
Seminar Room 3

Abstract:
Synthesis of Curved Nanographenes

Corannulene ($C_{20}H_{10}$) is a polycyclic aromatic hydrocarbon that exhibits molecular curvature due to the arrangement of five six-membered rings around a central five-membered ring.[1] It can, therefore, be considered as the cap region of fullerene C_{60}. This is the reason corannulene is sometime referred to as a 'buckybowl'. The nonplanarity of the structure endows corannulene (and C_{60}) with unique electronic properties that are not found in planar aromatic hydrocarbons such as anthracene and pyrene. In contrast to C_{60}, however, corannulene offers high solubility in common organic solvents and an avenue for multiple and well-defined substitutions on the aromatic nucleus. These two attributes are of high relevance to the synthetic and materials chemists as they allow for synthesis and unambiguous structural characterization of the synthesized materials. In this presentation, we will discuss our synthetic work revolving around this beautiful structural motif of carbon. We will focus on the synthesis of curved nanographenes based on the corannulene motif (Figure 1).

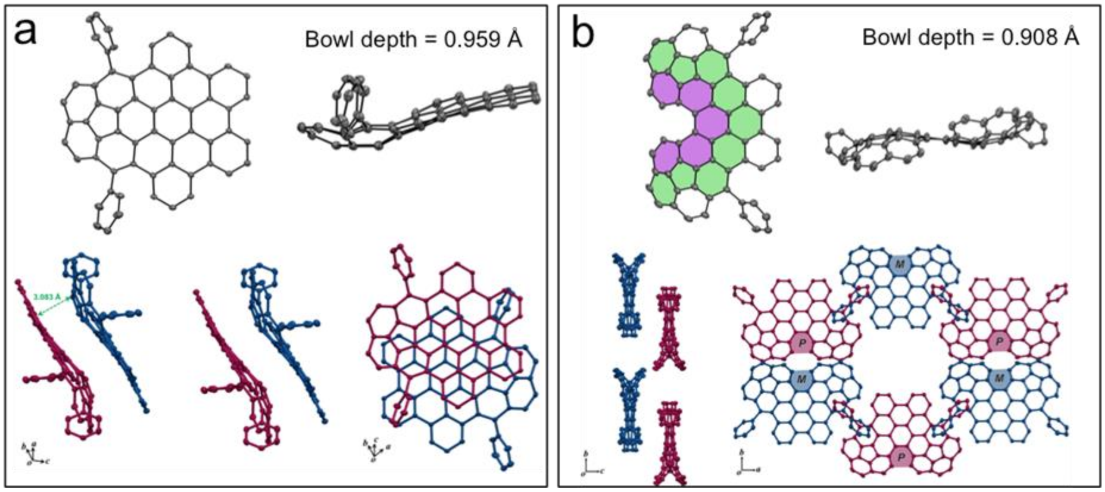

Figure 1. X-Ray crystal structures of nanographenes. Thermal ellipsoids were scaled at 50% probability level. tert-Butyl groups and hydrogen atoms were omitted for clarity. Top view, side view, and packing structures are shown in a clockwise fashion for (a) a corannulene-coronene hybrid and (b) a superhelicene structure.

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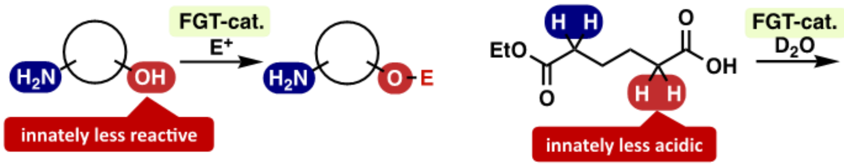
Prof. Takashi OHSHIMA
Kyushu University

Keynote 19
Wednesday, 14 Dec 2022
1525 – 1600 hrs
MPH 1 & 2

Abstract:

Controlling and Digitization of Chemoselectivity by Functional Group Targeted Catalyst and by Functional Group Evaluation Kit

Because complex molecules are highly modified by various functional groups (FGs), controlling the selectivity of the FGs (chemoselectivity) is very important in their synthesis and further functionalization. In general, chemoselectivity is driven by the innate reactivity of the FGs present in the substrate and has been achieved by selectively reacting with more reactive FGs. Therefore, it is difficult to selectively react less reactive FGs in the presence of more reactive FGs. It is common to utilize protective groups (PGs) to reverse the innate reactivity of FGs, but this protection/deprotection strategy leads to an increase in reaction steps, decreasing both step and atom economies. To develop more direct and environmentally friendly PG-free synthetic routes, we are focusing on Functional Group Targeted Catalyst (**FGT-cat.**), which selectively activates low-reactive FGs in the presence of various highly reactive FGs. In fact, we developed various chemoselective reactions, such as Zn-catalyzed *O*-selective acylation[1a] and Cu-catalyzed *O*-selective Michael addition[1b] of aminoalcohols. We also successfully developed chemoselective enolization of carboxylic acid equivalents, such as acylpyrazoles[2a] and acylimidazoles.[2b,c] In this presentation, I will mainly present our recent studies on the chemoselective a–oxidation[3a] and a–deuteration[3b] of carboxylic acids.



Recent efforts using the Functional Group Evaluation Kit (**FGE-kit**)[4] to collect comprehensive data on chemoselectivity and to develop a machine learning-based automatic retrosynthetic analysis method will also be presented.

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Prof. Michael J. Inglesona
University of Edinburgh

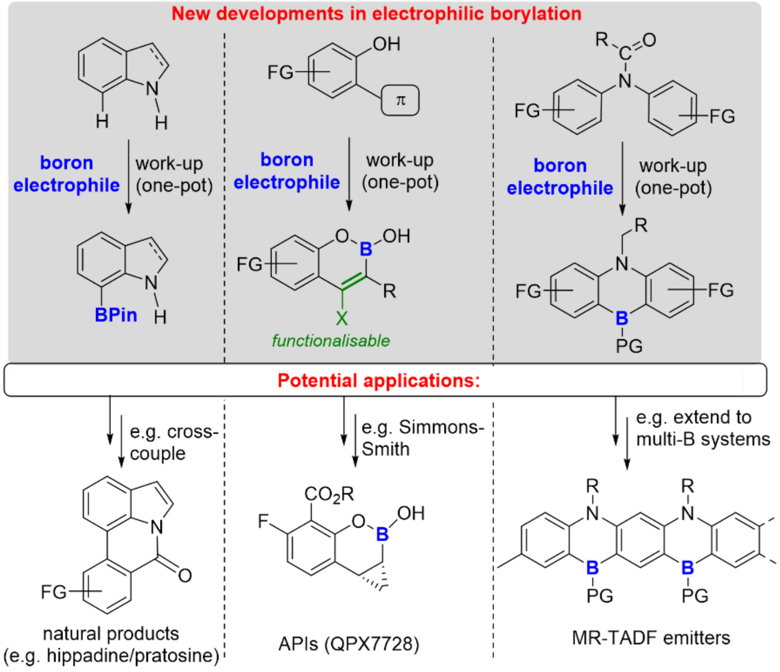
Keynote 20
Wednesday, 14 Dec 2022
1525 – 1600 hrs
Seminar Room 2

Abstract:

Forming organoboranes using electrophilic borylation: from arylboronate esters to APIs and organic materials

Organoboranes are ubiquitous intermediates in synthesis due in large part to the Suzuki-Miyaura cross-coupling reaction. However, there is now a growing realisation that organoboron compounds are useful in their own right. This includes in addressing the rise of infections caused by multidrug-resistant bacteria by combining a β-lactam with a cyclic boronate based broad spectrum β-lactamase inhibitor (e.g. VNRX-5133 and QPX7728).[1] Furthermore, the incorporation of boron into polycyclic aromatic hydrocarbons is now an established approach to modulate the key properties of organic materials to impart useful function, with a recent highlight being their use as MR-thermally activated delayed fluorescence emissive materials.[2]

This talk will focus on our use of boron electrophiles, ranging from bespoke boron-cations to simple reagents (e.g. BCl_3), to effect electrophilic borylation to form C-B bonds. In our recent work, we have used this approach to make otherwise challenging to access useful intermediates,[3] for accessing boron containing APIs[4] and for accessing boron containing organic materials.[5]



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4. Unpublished work
5. For a recent example see: Chem. Sci. **2022**, 13, 1136.

Prof. Miłosz PAWLICKI
Jagiellonian University

Keynote 21
Wednesday, 14 Dec 2022
1525 – 1600 hrs
Seminar Room 3

Abstract:

On Delocalisation in Strongly Conjugated Systems

Modulation of π-electrons in the frames of unsaturated hydrocarbons ready for introducing substantial modifications to observed delocalization, including switching from diatropic to paratropic currents has been diagnosed as a pivotal aspect of π-conjugated derivatives opening a wide scope of potential applications. A separate aspect of planned changes in conjugation, observable in precisely designed unsaturated hydrocarbons is switching between local and global effects of π-conjugation, stabilizing solely global diatropic or paratropic current but also showing two local and opposite dia- and paratropic currents. The extension of conjugation has been realized with an application of several factors (e.g., deprotonation, redox) but also by introducing the rigidifying factor that can be assigned to filling gaps in a *nanographene-like* system by electron accepting or electron donating elements.

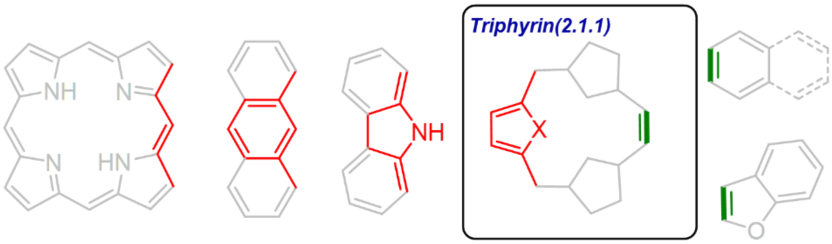

Figure 1

The strategy for formation of hybrid structures linking in one skeleton acene(s) or heteroacenes modulated by a presence of a specific defect i.e. triphyrin(2.1.1) (Figure 1) shows a potential for switching between diatropic and paratropic currents after redox activation.[1] It results in, depending on the complexity of final molecule, observation of local effects of conjugation efficiently influencing properties of each subunit.[2] A specific construction opens a possibility for observation of the reactivity characteristic for isolated unsaturated units[3] in addition creating an opportunity for switching on the global diatropic currents.[4] All those effects will be presented and discussed focusing on the derivatives stabilizing different delocalization paths within precisely designed structural motifs introducing triangular defect(s) open for a post-synthetic modifications either by entrapping of a central ion or redox switching, showing the synthetic approach followed by the spectroscopic behavior extended by XRD analysis and theoretical support.

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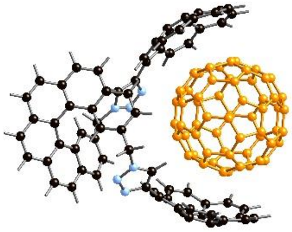
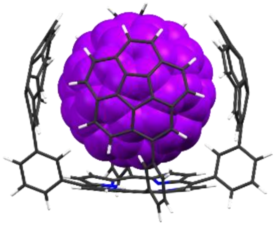
INVITED SPEAKERS

Celedonio ALVAREZ
University of Valladolid

Abstract: Supramolecular Interactions with Non-Planar Polyaromatic Species. How Synergistic Arranges of Corannulenes can Increase the Affinity for Fullerenes

Since its establishment, supramolecular chemistry has been used to design and develop new entities with a wide range of applications in various areas of science.[1] The rational design and development of functional complex architectures capable of interacting with nanometer-sized carbon allotropes, especially fullerenes, in a supramolecular fashion is a challenging current topic. However, the architecture design of efficient systems of this type is not always straightforward since it depends on a delicate balance of favorable and unfavorable interactions and requires an understanding of the different subtle factors at play. Herein I present the results that had been carried out in our laboratory[2] in the last years, focusing on the number of motives that take part in the supramolecular interaction focusing on the non-planar polyaromatic compound corannulene. This will cover a wade range of central structure cores bearing different number of corannulenes ranging from organometallic centers to porphyrin tethers.





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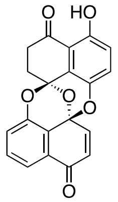
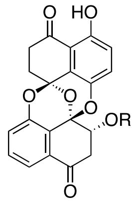
Yoshio ANDO
Tokyo Institute of Technology

Abstract: Asymmetric Total Synthesis of Preussomerins: Stereospecific Photoredox Reaction of Naphthoquinone via 1,6-Hydrogen Shift

Preussomerins are fungal metabolites and possess a variety of biological activities.[1] They pose a dimeric naphthoquinone skeleton, sharing bis-spiroacetal core. These bioactivities and unique architechtures fascinated many synthetic chemists, and several total syntheses have been evoked.[1] On the other hand, the stereoselective construction of the spiroacetal center is remained unsolved.



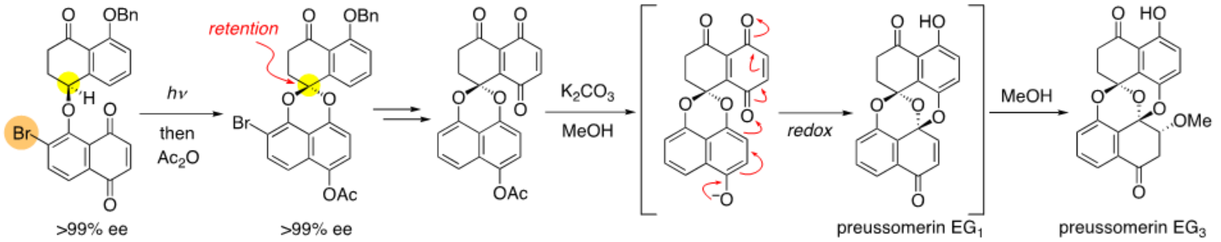
preussomerin EG$_1$



preussomerin EG$_2$: R = H
preussomerin EG$_3$: R = Me

Recently, we reported stereospecific photoredox reaction of naphthoquinone via *1,5-hydrogen shift*,[2,3] enabling the asymmetric total syntheses of spiroxins, dimeric naphthoquinone natural products.[4,5] In addressing the stereoselective synthesis of preussomerins, the key spiroacetal structure would be constructed by stereospecific photoredox reaction of naphtoquinone via *1,6-hydrogen shift*. However, the process involves a 1,6-hydrogen shift is known to be a less facile than its 1,5-couterpart.

The feasibility of the photoredox reaction via 1,6-hydrogen shift has been examined. Upon experimentation, the photoredox reaction worked well by using naphthoquinone having a bromo substituent next to the oxyfunctionality, giving the desired acetal in good yield. Furthermore, the photoreaction proceeded in a stereoretentive manner without loss of the enantiomeric excess, enabling the stereospecific construction of the spiroacetal center in preussomerins. After further transformations, the first asymmetric total syntheses of preussomerin EGs have been accomplished.



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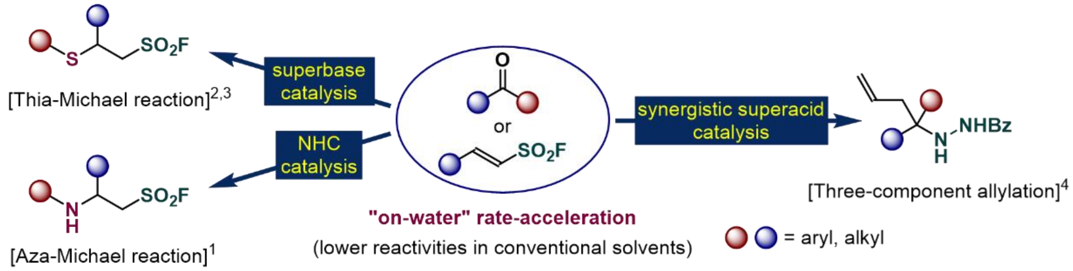
Han-Yong BAE
Sungkyunkwan University

Abstract: Augmented Aquacatalysis: Bio-inspired Approaches in Chemical Reactions

In this presentation, a series of water-accelerated 'aquacatalytic' chemical transformations will be discussed. Firstly, *N*-heterocyclic carbene (NHC)-catalyzed aza-Michael addition reaction is shown to access β-aminosulfonyl fluorides, which are key hubs of the sulfur(VI) fluoride exchange (SuFEx) reaction.[1] Secondly, a new method based on a high-turnover catalytic thia-Michael addition reaction via significant hydrophobic amplification is displayed.[2,3] Finally, the synergistic action of a hydrophobic Brønsted acid in combination with a hydrogen-bonding donor activator enabled the formation of the three-component Petasis-type allylation reaction.[4] The developed exceptionally mild but potent catalytic systems facilitated a broad substrate scope, and enabled efficient multi-gram scalabilities. As a crucial reaction medium in all cases, water considerably augmented the reaction rate with excellent chemo- and site-selectivity (up to >99:1) compared to conventional organic solvents.



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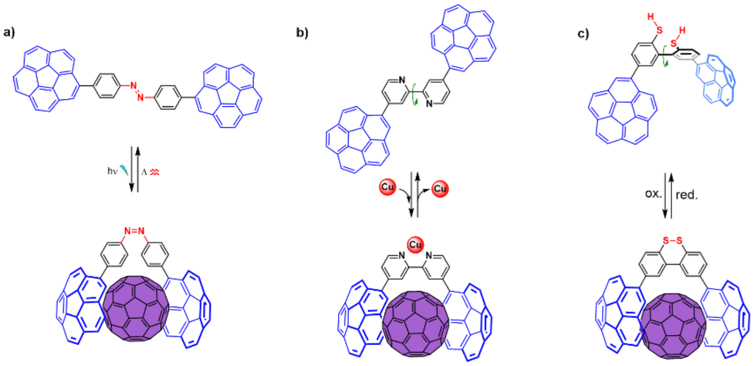
Hector BARBERO
University of Valladolid

Abstract: Corannulene-Based Reversible Bistable Molecular Machines for Fullerene Recognition

A molecular machine refers to a multistable chemical system capable of reversibly modify its structure by a relative movement of its constituent parts as a response to an external stimulus producing observable work.[1] They are actually key functional elements that support life itself in all living beings.

In this talk we will focus on artificial molecular machines which switch their structure between two well-defined conformers/configurational isomers by photoisomerization,[2] metal coordination/decoordination,[3] and redox process.[4] (Error! Reference source not found.). All the species presented bear two units of corannulene ($C_{20}H_{10}$), a geodesic polyarene capable of establishing attractive interactions with fullerenes through concave-convex π-π interactions. The operational principle relies on the formation or disruption of a molecular tweezer by placing two corannulene units in

the right location to establish a cavity for fullerene recognition. Their switching properties, especially the in-situ reversibility, and the impact produced onto their ability to recognize fullerenes (C_{60}, C_{70}) will be shown and discussed.



Scheme 1. Examples of switchable molecular tweezers bearing corannulene groups (in blue) operated by photoisomerization (a), metal coordination (b) and oxidation (c) showing their ability to bind fullerenes (in purple) in one state. Key atoms responsible for the isomerizations are highlighted in red.

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Guillermo Carlos BAZAN
National University of Singapore

Abstract: Conjugated Oligoelectrolytes: A Versatile Platform for Membrane Modifications

Conjugated oligoelectrolytes (COEs) are a class of synthetic molecules characterized by a piconjugated segment and terminal ionic functionalities. The distribution of hydrophobic content and hydrophilic charged groups leads to spontaneous self-assembly within lipid bilayer membranes. One can observe subsequent modification of membrane properties, which correlate to the structural features of the COE. Extended molecular lengths enable rigidification of the membrane and are largely noncytotoxic. As such, one can design molecular probes with a range of optical features for bioimaging and characterization of nano-scale extracellular vesicles, see Figure 1. Specific probes for flow cell cytometry of exosomes can be therefore designed, which offer advantages over commercially available dyes. When the molecular lengths of COEs are shortened relative to the dimensions of lipid bilayers one observes perturbation of membrane properties. Systematic studies have culminated in privileged structures that are specific to bacterial cells, relative to their mammalian counterparts, and that can be tolerated in vivo, either by intravenous or intratracheal delivery methods. The presentation will provide an overview of the structural features of optimal COE antibiotics and their success in lung and wound infection models, see Figure 1.

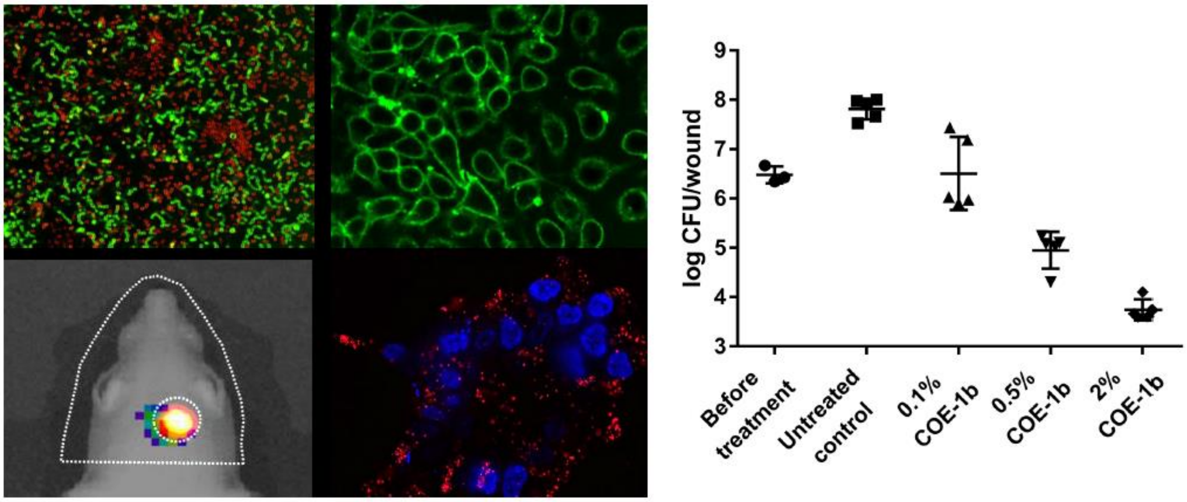

Figure 1. Left: Diverse applications of COE that benefit from the tunable optical properties of the conjugated backbone. Right: Successful wound infection model treatment with an antibiotic COE.

Massimo BIETTI
Università di Roma “Tor Vergata”

Abstract: Diverting Reaction Pathways in Hydrogen Atom Transfer Based C(sp^3)–H Bond Oxygenation of Cyclopropane Containing Hydrocarbons

Site-selective C(sp^3)−H bond functionalization represents an important goal of modern synthetic organic chemistry. By avoiding substrate prefunctionalization associated to traditional functional group manipulation and interconversion, the direct functionalization of these bonds provides access to transformations of high synthetic potential that can offer advantages both in terms of reaction step economy and decreased waste generation. Among the available methodologies, those based on hydrogen atom transfer (HAT) from C(sp^3)−H bonds to radical and radical-like species have attracted considerable interest and accordingly, the factors that govern reactivity and site-selectivity have been discussed in detail. These include bond strengths, electronic, steric and stereoelectronic effects, conjugation and hyperconjugation, as well as medium effects.[1]

Within this framework, cyclopropane containing hydrocarbons are particularly appealing probes for the study of these processes. The presence of the cyclopropyl group has been shown to activate adjacent sites toward HAT via hyperconjugation, providing a powerful handle to implement site-selectivity.[2] Because hyperconjugative effects also account for the stabilization of cyclopropylcarbinyl cations,[3] these substrates offer moreover the opportunity to probe the formation of cationic intermediates via sequential HAT-ET steps. With these concepts in mind, we report on a detailed investigation on C–H bond oxygenation of spiro[2.5]octanes promoted by HAT reagents providing evidence for the involvement of a cationic intermediate and showing how product selectivity can be finely tuned by careful choice of the experimental conditions.[4]

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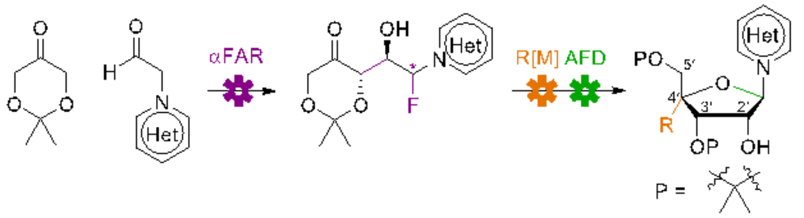
Robert BRITTON
Simon Fraser University

Abstract: A de novo Synthesis of Nucleosides and Nucleoside Analogues

Nucleoside analogues (NAs) are an important class of drugs used most commonly in the treatment of cancer and viral infections, and key building blocks for oligonucleotide synthesis. While several decades of synthetic effort has provided reliable templates for NA synthesis, these processes are often protracted, not amenable to diversification and rely on a limited pool of chiral carbohydrate starting materials. These challenges are manifest for medicinal chemists tasked with lead diversification and can pose additional and significant complications to related process research efforts. Here, a robust platform for rapidly constructing nucleosides and nucleoside analogues from simple achiral starting materials will be presented.[1] Using proline catalysis, we demonstrate that heteroaryl-substituted acetaldehydes can be α-fluorinated then directly engaged in enantioselective aldol reactions in a one-pot reaction (α-fluorination and aldol reaction: αFAR). Carbonyl reduction or a diastereoselective reaction with an organometallic reagent (R[M]) followed by an unprecedented and stereospecific annulative fluoride displacement (AFD) involving a stable N-F aminal provides a fully functionalized NA. The versatility, scalability[2] and broad scope of this process will be highlighted in the construction of D- and L-nucleosides and nucleoside analogues, locked nucleosides, iminonucleosides, C4'-modified nucleosides and C2'-modified nucleosides. We expect this process will become a valuable tool to support both drug discovery and development.



- simple achiral building blocks
- scalable 2-3 step synthesis
- inherent protection of C3′/C5′ alcohols

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Yavuz CAFER
King Abdullah University of Science and Technology

Abstract: Syngas Economy with Green Hydrogen for Rapid Decarbonization of Fuels and Chemicals

Syngas is currently the primary source of hydrogen for fuel cell vehicles and has been the core building block in the chemicals industry for liquids, particularly alcohols, olefins, and low molecular weight fuels. We have recently developed a Ni-Mo-MgO nanocatalyst[1] that facilitates syngas production from the dry reforming of methane without coking or sintering, even after 35 days of continuous operation. Since it is known that switching syngas production from steam reforming to dry reforming could provide gigatons of CO_2 avoidance without significantly altering our lifestyle[2], this emissions relief could provide the necessary time for a successful implementation of future energy technologies. In such a syngas economy, chemicals and transition fuels would be made using syngas from dry reforming of hydrocarbons and green hydrogen water electrolysis. An estimated 15-50% reduction in carbon emissions[3] is possible without any change to the infrastructure. Further reductions would be introduced if syngas was produced from a range of sources, such as biomass, waste, plastics, or paper, and the direct conversion of syngas to more chemicals was feasible.

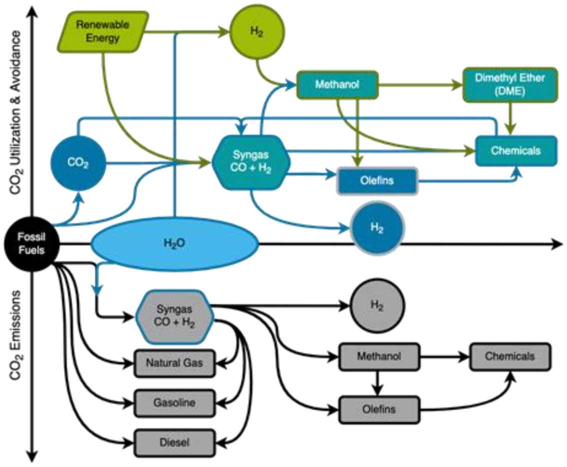

Figure 1. Proposed transitional technologies within the framework of ‘‘syngas economy”, leading to a minimum of 10 Gt CO_2 reuse into a circular carbon economy.

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Luca CAPALDO
Universiteit van Amsterdam

Abstract: Photoinduced Halogen-Atom Transfer (XAT) by N-heterocyclic Carbene Boryl Radicals for $C(sp^3){-}C(sp^3)$ Bond Formation

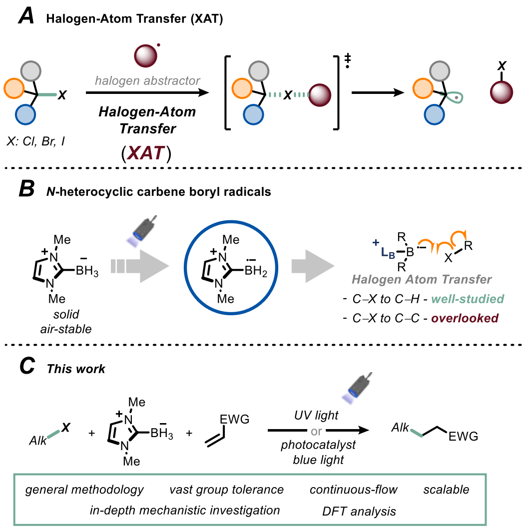

Figure 1

In the realm of radical chemistry, halogen-atom transfer (XAT) is emerging as a powerful activation strategy in synthetic endeavors to engage otherwise recalcitrant organic halides ($R_3C{-}X$).[1] Here, a halogen-abstracting entity is responsible for the formation of a C-centered radical by homolytically cleaving the C−X bond (Figure 1A). Although toxic tin radicals have been in the spotlight as halogen abstractors for decades, the era of photocatalysis has brought to light more sustainable options, such as silyl and a-amino radicals.[2,3] *N*-heterocyclic carbene (NHC)-ligated boryl radicals, i.e. boron-centered radicals where the boron atom is coordinated with a NHC, have been proposed as XAT agents as well. Their use, however, has been mainly restricted to C−X to C−H transformations via a radical chain mechanism (Figure 1B).[4]

Herein, we report a mild and broadly applicable protocol for $C(sp^3){-}C(sp^3)$ bond formation using photoinduced XAT by NHC-ligated boryl radicals under near-UV or blue-light irradiation (Figure 1C). The mildness of the present approach is demonstrated by the fact that derivatives of medicinally-relevant compounds and biologically-active molecules were smoothly functionalized. The key role of the NHC-ligated boryl radicals in the operative reaction mechanism has been uncovered through a combination of experimental, spectroscopic and computational studies.[5]

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Yi-Tsu CHAN
National Taiwan University

Abstract: 2D Porous Arrays Assembled from Metallo-Supramolecular Giant Cages

Surface layers (S-layers) are commonly seen in prokaryotic organisms and play an important role in cell protection and surface interactions. These layers are composed of identical proteinaceous subunits that can self-assemble into ordered porous 2D arrays of 5-15 nm thickness and unit cell sizes in the range of 3-30 nm. To explore how protein motifs can be tiled into 2D crystalline materials, we researched porous layers assembled from artificially synthesized molecules of similar dimensions to explore the construction of giant well-defined building units. Inspired by Buckminster Fuller's concept of tensegrity (tensional integrity), we developed precise coordination-driven self-assembly methodologies[1,2] for the rational construction of a molecular cuboctahedron with a circumscribed sphere diameter of over 10 nm. The result marks a significant breakthrough in the area of chemical mimicry of S-layer self-assembly.[3] The cuboctahedron is assembled from 76 subcomponents and has a double-layered structure, resembling a tensegrity architectural structure. It is worth mentioning that the high stability of the cuboctahedral complex enables small-angle X-ray scattering (SAXS) measurements under dilute conditions, providing crucial structural evidence. Moreover, cryo-EM experiments conducted in vitrified acetonitrile solution clearly indicate that the S-layer-like square arrays of the giant cuboctahedra have a lattice constant of 7.9 nm. Through the cryo-EM analysis, such local packing defects as dislocations and grain boundaries in the 2D arrays are elucidated. The general self-assembly methodology and the serendipitous observation of S-layer-like square arrays presented here may lay the foundation for developing bottom-up techniques for the construction of 2D porous supramolecular materials.

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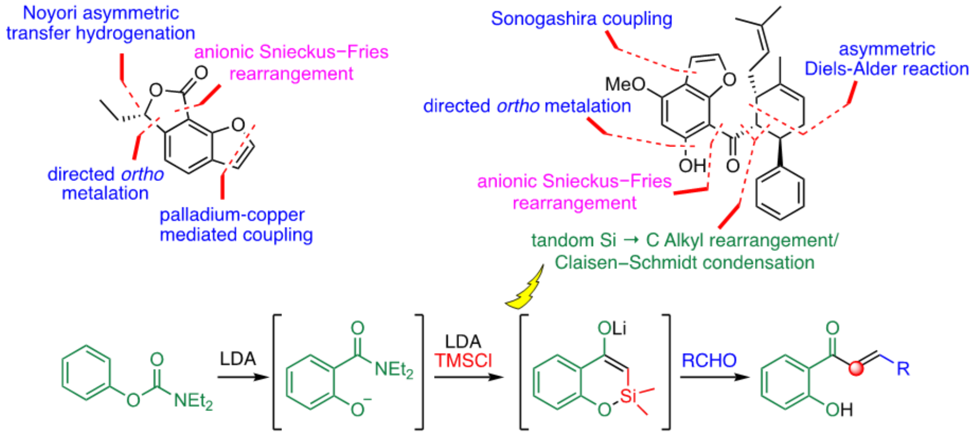
Rong-Jie CHEIN
Academia Sinica

Abstract: Carry Forward Anionic Snieckus-Fries Rearrangement

The anionic Snieckus-Fries rearrangement is a convenient route to ortho-functionalized aromatics. We successfully applied it to the first enantioselective synthesis of (–)-concentricolide[1] and (–)-panduratin D.[2] Further, an extended anionic Snieckus-Fries rearrangement was developed serendipitously for the synthesis of various o-hydroxyacetophenone or 2'-hydroxychalcones from phenyl diethylcarbamate, featuring consecutive Snieckus−Fries rearrangement, anionic Si→C alkyl rearrangement, and Claisen−Schmidt condensation in a single operation.[3-5] The expanding use of silicon reagents in the organic synthesis of a wide range of reactions has greatly increased the prominence of organosilicon chemistry.



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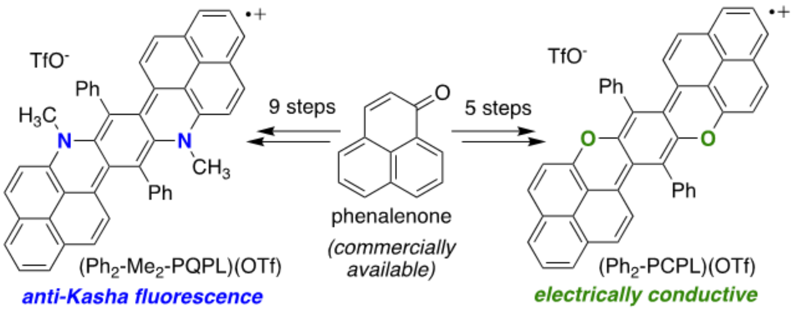
Mark CHEN
Lehigh University

Abstract: Exploiting Open-Shell Character in Bisphenalenyls for Materials with Radical Optoelectronic Properties

Open-shell molecules possess unpaired electron density (radical character), which makes them intriguing candidate materials for many optoelectronic applications. Air-stable structures have been reported, but most require lengthy synthetic sequences with limited generality. Our lab has developed a concise strategy for accessing a variety of bisphenalenyls from commercial starting materials via fragment-coupling with phenalenone.[1] We used this method to synthesize a neutral biradicaloid, Ph_2-*s*-IDPL, and several novel air-stable π-radical cations. One such molecule is a *N*-substituted, cationic bisphenalenyl [(Ph_2-PQPL)(OTf)] that possesses a bent and twisted π-backbone and displays anti-Kasha photoluminescence.[2, 3] In the solid-state, (Ph_2-PQPL)(OTf) is electrically conductive and demonstrates antiambipolar charge transport, likely due to the presence of a half-filled band. We also discovered a *O*-substituted (Ph_2-PCPL)(OTf) that possesses a π-backbone with greater coplanarity, which leads to remarkably close π-stacking distances in single crystals due to electrostatically-enhanced, intermolecular covalent-bonding interactions. Towards developing (Ph_2-PCPL)(OTf) into a functional material, we discovered that mixing soluble PCPL derivatives with polystyrenesulfonate (PSS) enables the formation of water-processable conductive organic films that demonstrate high optical transparency, electrical conductivity, and electron mobility. In these composite n-type materials, PSS not only serves as a counterion, but also promotes n-doping and solution-phase aggregation, which leads to molecular ordering of the π-conjugated molecules in the solid-state.



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Ye CHEN
Chinese University of Hong Kong

Abstract: Wet-Chemical Synthesis and Electrocatalytic Properties of Metal Nanomaterials with Unconventional Crystal Phases

Metal nanomaterials own excellent intrinsic electrocatalytic activities, high conductivity and high stability. While traditional solution-based syntheses mostly focused on morphologies and compositions of the nanocrystals, we made some interesting discoveries on crystal phase controlled synthesis.[1] Instead of getting the normal phase of face center-ed cubic (fcc) structure, we obtain Au nanomaterials in unreported 4H phase and 4H/fcc heterophase with high yield and productivity. These unconventional metastable phases are excellent substrates on which other catalytically active metals like Pd, and Cu can be grown epitaxially. Further study on new metastable phases of these metals can lead to novel physical or chemical properties, such as an enhanced catalytic performance for eletrocatalysis. It provides an alternative strategy of engineering crystal phases of metal nanomaterials via wet-chemical method and exploring their templating effects on various properties.

In this presentation, our recent work on the wet-chemical synthesis of metal nanostructures with unconventional phases and their electrocatalytic properties are introduced. First, epitaxial growth of one-dimensional core-shell metal nanostructures with unconventional crystal phases, including 4H/fcc heterophase Au@Pd nanorods[2] and Au@Cu nanomaterials with 4H and 4H/fcc phases[3], is demonstrated. Then, phase dependence study of metal nanomaterials with novel crystal phases in electrocatalysis, including 4H/fcc Au@Pd nanorods in ethanol oxidation reaction as well as 4H and 4H/fcc Au@Cu nanomaterials in CO_2 reduction reaction, is discussed.

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Jia Min CHIN
University of Vienna

Abstract: Controlling MOF materials across multiple length scales

Biological composites bear complex designs and hierarchical structures that are key to their specific function and exceptional properties. However, the structural and functional complexities of natural materials are difficult to integrate into synthetic composites, as the control of materials across multiple length scales is a major scientific challenge. We work on the preparation[1], assembly, and multi-length scale structuring of Metal-Organic Frameworks (MOFs) and other colloidal materials and composite systems for optical and ion conduction applications, using an interdisciplinary approach. Most MOFs possess non-cubic lattices and anisotropic functionality dependent upon crystallographic direction and are generally synthesized in bulk as loose as microcrystalline powders. As such, for practical purposes, general methods to manipulate and orient free-standing MOF crystals would be useful to harness their anisotropic functionality. This talk will focus on our exploitation of physicochemical interactions at air/liquid/solid interfaces,[2,3] as well as top-down processing methods[4] and external fields[5,6] to manipulate MOF materials, ranging from tuning MOF crystal size and shapes to the dynamic alignment of NU-1000 MOF microrods as well as E-field assisted liquid crystalline assembly of MOF particle superstructures.[7]

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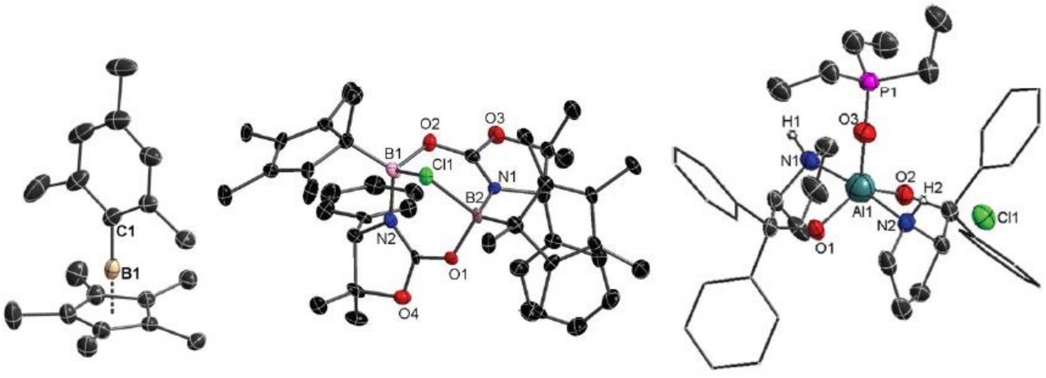
Ching-Wen CHIU
National Taiwan University

Abstract: Catalytic Applications of Boron and Aluminum Cations

As the catalytic applications of halogenated neutral group 13 catalysts continue to expand, the chemistry of cationic group 13 catalysts has also emerged in the past few years. During our study of boron cation catalysts, we discovered that $[h^5\text{-Cp*B-Mes}]^+$ can be viewed as a masked potent Lewis acid that is an efficient catalyst for hydrosilylation of carbonyl, imine, and nitrile compounds.[1] In addition to achiral boron cations, we have also worked on the chiral oxazolidinone functionalized $[\text{BCl- B}]^+$ diboron cations and their application Diels Alder reaction. Interestingly, the enantioselectivity of $[\text{B-Cl-B}]^+$ cation can be further enhanced by $SnCl_4$ coordination at the bridging chloride.[2] Recently, we discovered that Cp* substituent is not essential to realize borinium catalyst. Aryl amino borinium ion, $[\text{TMP-B-Mes}]^+$ is stable enough to catalyze hydrosilylation of ketones and aldehydes.[3] In addition to boron cations, we have prepared a tetra-coordinate chiral aluminum cation that features two chiral prolinol-derived ligands in *C2*-symmetry.[4] Through a competition experiment and fluoride ion affinity calculation, we have confirmed that this prolinol-coordinated aluminum cation is considerably more Lewis acidic than $B(C_6F_5)_3$. To further enhance the Lewis acidity of aluminum cations, we have also prepared a series of chiral BOX-ligand supported alkyl aluminum cations.[5] Although aluminum cation's reactivity is enhanced via reducing the coordination number, the enantioselectivity of the weakly solvated tri-coordinate aluminum cation is also diminished due to the presence of a loose binding pocket.



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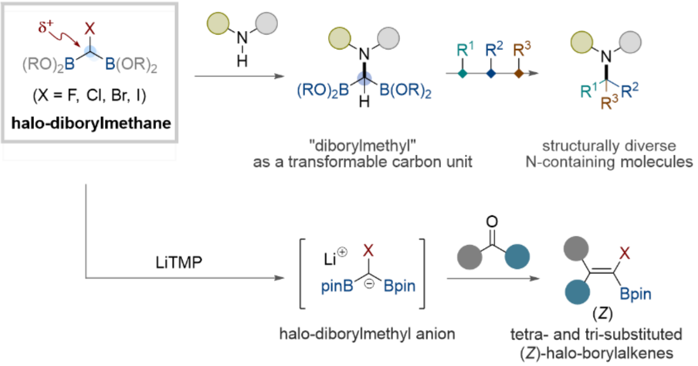
Seung Hwan CHO
Pohang University of Science and Technology

Abstract: Design and Synthesis of New Organoboron Reagents and Their Applications

Chemo- and stereoselective transformations of polyborylalkanes are powerful and efficient methods to access optically active molecules with greater complexity and diversity through programmed synthetic design. In particular, *gem*-diboryl compounds have attracted much attention in organic chemistry as versatile synthetic handles.[1] The notable advantage of *gem*-diboryl compounds lies in their ability to generate two key intermediates, α-borylalkyl anions and (*gem* diborylalkyl)anions. These two different intermediates can be applied to various reactions to rapidly access a diverse set of organoboron compounds, which can be further manipulated to generate various synthetically valuable molecules. In this talk, I will summarize our recent contributions to the design and synthesis of halogen-substituted-*gem*-diboryl compounds and their application to the development of highly chemo- and stereoselective transformations.[2,3]



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Crystal CHU
Lehigh University

Abstract: Bioinspired Polymer Fibers Drawn from Dynamic Networks

Polymer fibers offer tunable structural and mechanical properties in numerous applications including biomaterials, textiles, and composite materials. The demand for tough, biocompatible materials produced by simple processing techniques has led to significant interest in materials inspired by natural fibers such as spider silks.[1,2] Common methods for fiber production often require processes that suffer from high energy costs and are dependent on organic solvents, among other physical limitations due to burdensome protocols and highly viscous polymer solutions.[3,4] This work describes a technique for fabricating polymer fibers that is both operationally simple and performed at room temperature in aqueous solutions.[5] Similar to spider silks, this process incorporates pultrusion, rather than extrusion, to produce fibers several meters in length from a viscous fluid. The liquid-phase precursor consists of a network of polysaccharides

and branched PEGs reversibly bound by dynamic interactions, allowing for fiber formation. Dynamic rheology and tensile testing of the resulting fibers reveal important structure-property relationships for fiber design. Current efforts to prepare additional covalent crosslinks and double network fibers, and characterization of resulting properties, will be presented. Overall, a molecular understanding of how the polysaccharide network translates to macroscopic properties provides a strategy for efficient production and rational design of fibrous biomaterials, opening doors to unexplored stimulus-responsive applications.

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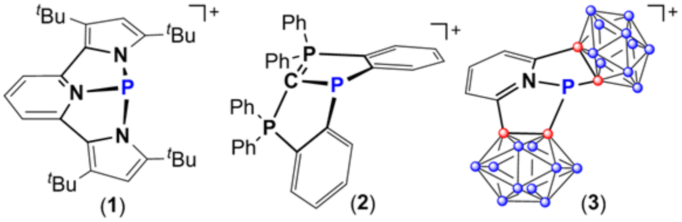
Roman DOBROVETSKY
Tel Aviv University

Abstract: Geometrically Constrained P^{III} Cations

Geometrical constriction of main group elements leading to a change in the reactivity of these main group centers has recently become an important tool in the main group chemistry. A lot of focus on using this modern method is dedicated to group 15 elements and especially to phosphorus. In this talk, I will present our group's recent progress in the synthesis, structure, and reactivity of novel geometrically constrained phosphenium cations (1-3) (Figure 1), which are capable of activating O−H, N−H, Si−H, Ar−F and H−H bonds by oxidative addition type reaction to the phosphorus center or by P-center/ligand cooperation (Figure 1) and their use in catalysis.



(**1**)
Ligand assisted
O−H, N−H, H_3NBH_3
Oxidative addition
Si−H

(**2**)
Oxidative addition
Ar−F

(**3**)
Oxidative addition
O−H, N−H, H−H

Figure 1. Novel geometrically constrained phosphenium cations and small molecules they activate

Oliver DUMELE
Humboldt University of Berlin

Abstract: An All-organic Photomagnetic Switch

Digital data storage relies on the change of a material's electrical, magnetic, or optical properties between two states, indicating 1 and 0. Smaller units of information storage are an interesting research target, because they could lead to higher-density storage. Molecular organic switches are interesting in this context.[1] However, the switching of spin states in all-organic molecules is challenging.

This contribution will focus on the recently developed helical photochemical switch systems.[2] Configurationally stable dimethyl$^{[5]}$helicenes were used in the design of a photochemical magnetic switch with bistable spin states (Figure 1).[2] When introducing quinoidal 4,11-substituents, such as oxo or dicyanomethylidene, the helicene undergoes rapid electrocyclization which can be reversed using light as stimulus (77 K). Upon photochemical ring opening at cryogenic temperatures, the helicene favours a diradical configuration with a triplet ground state and a stable EPR signal. The process is fully reversible under thermal conditions and heating (to 93 K for R = C(CN)$_2$ or 127 K for R = O) recovers the diamagnetic closed-shell form via electrocylization. The system can be cycled without any significant degradation and represents a bistable photomagnetic switch that operates under chemical reactivity.

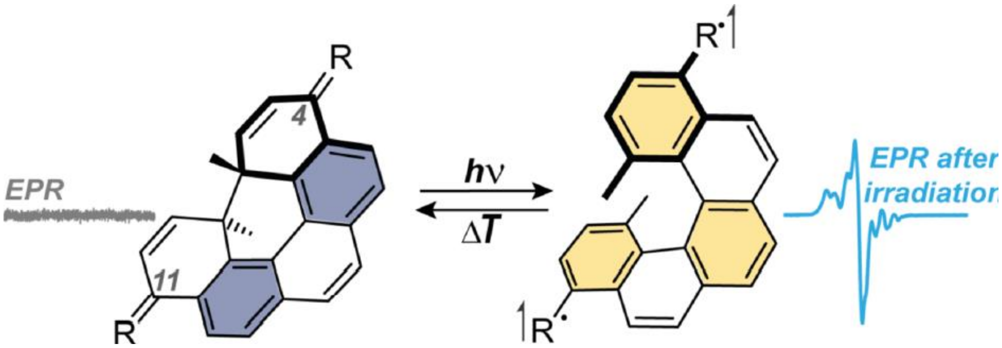


Figure 1. 4,11-Substituted dimethyl$^{[5]}$helicene for photochemical magnetic switching.

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Jason DUTTON
La Trobe University

Abstract: Synthesis and Reactivity of ArI(OTf)$_2$

$PhI(OTf)_2$ was first reported some 30 years ago via the reaction of PhI=O with TMS-OTf. The compound lay fallow for sometime, but with the renaissance of I(III) compounds as useful oxidants for both inorganic and organic chemistry, $PhI(OTf)_2$ was rediscovered by several groups as one of the more powerful I(III) oxidants. The synthetic route employed is by reaction of widely available $PhI(OAc)_2$ with 2 TMS-OTf. However this reaction in fact stops at PhI(OAc)(OTf), and $PhI(OTf)_2$ does not exist. Despite this several groups have persisted in incorrectly invoking $PhI(OTf)_2$, including in detailed theoretical studies on reaction mechanisms. It is clearly a molecule in demand. In this presentation the synthesis, structural characterization and reactivity of a genuine $ArI(OTf)_2$ will be presented. It was determined the Achilles Heel of $PhI(OTf)_2$ was decomposition via electrophilic aromatic substitution with itself. This pathway was shut down by incorporation of a nitro group on the phenyl ring, which renders the target accessible and even more reactive at I(III). A rich reactivity is already being unlocked and preliminary results for what the genuine class of compound can do will also be described.

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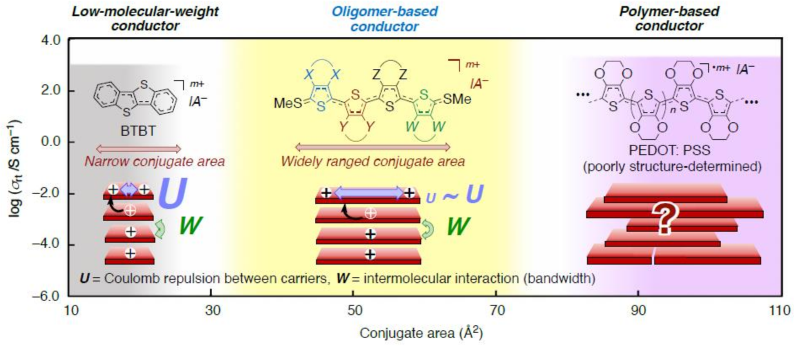
Tomoko FUJINO
The University of Tokyo

Abstract: Oligomer-based Conductors that Modeled Doped PEDOT

Modern organic conductors are either low-molecular-weight- or polymer-based. The low-weight molecules have limited conjugated areas of the donor that hamper precise control of the electronic structure of their salts, while the polymers have wide molecular-weight distributions that make it difficult to investigate the structural details of their doped conductors. These obstacles have severely limited the conductivity range and lowered the reproducibility of the exhibited conductivity. We overcame these obstacles by focusing on less-explored materials that lie between polymers and lowmolecular- weight materials, namely single-molecular-weight oligomer-based conductors possessing expandable conjugate areas. In this study, we developed the oligomer-based conductors that model doped poly(3,4-ethylenedioxythiophene) (PEDOT), the most commercially successful conductive polymer (Figure 1) [1–3]. The rich structure-determining factors, including unit structure, oligomer length and sequence, allowed us to explore the structure–conductivity relationships regarding the electronic parameters such as Coulomb repulsion between carriers (*U*) and intermolecular interaction (bandwidth, *W*), establishing the molecular guidelines toward single-crystalline and highly conductive materials.



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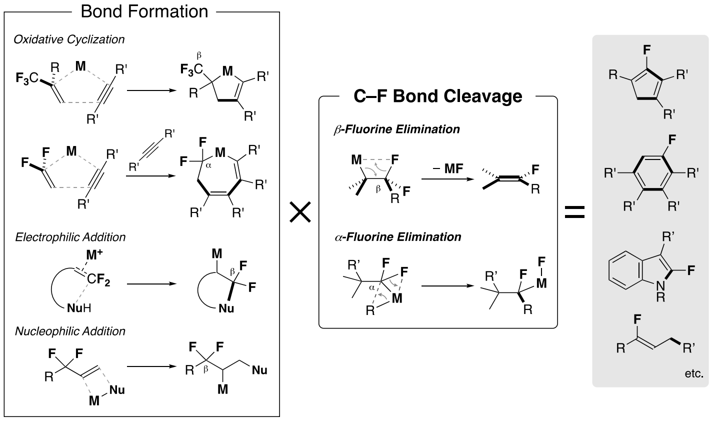
Takeshi FUJITA
University of Tsukuba

Abstract: Transition-Metal-Catalyzed Allylic and Vinylic C–F Bond Activation via Fluorine Elimination

Since the carbon–fluorine (C–F) bond is a stable bond with a high bond energy, chemical transformations via C–F bond cleavage (C–F bond activation) are generally difficult and have been a challenge in organic synthetic chemistry. Recently, various fluorine-containing building blocks possessing multiple fluorine atoms have been developed and readily available. Thus, the development of efficient methods for selective C–F bond activation has become increasingly important in recent years because they can provide fluorinated products, which would serve as promising candidates for pharmaceuticals, agrochemicals, and functional materials.

We have developed highly selective and efficient methods for transition-metal-catalyzed C–F bond activation of fluorine-containing compounds via b- and a-fluorine elimination. b-Fluorine elimination proceeds from organometallic intermediates bearing fluorine substituents on the carbon atoms b to the metal centers to form C–C double bonds. In contrast, a-fluorinated metal species undergo a-fluorine elimination to form new C–C bonds. In these reactions, the bond formation steps via organometallic elementary processes are important to set up intermediates suitable for fluorine elimination. We achieved selective allylic and vinylic C–F bond activation under mild conditions by combining b- or a-fluorine elimination with metal-mediated oxidative cyclization, electrophilic addition, and nucleophilic addition, leading to the syntheses of various fluorine-containing compounds.[1–3]



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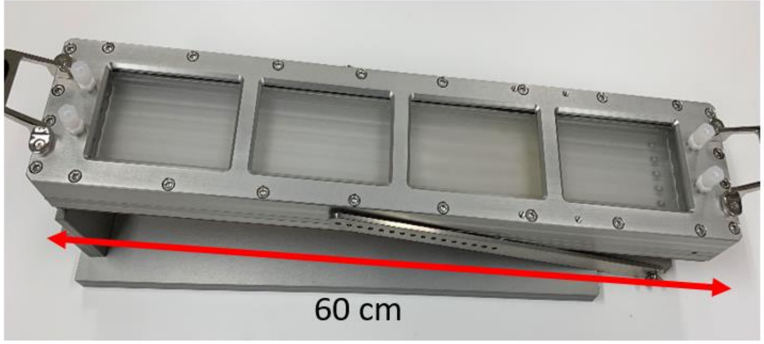
Takahide FUKUYAMA
Osaka Prefecture University

Abstract: Flow C-H Chlorination of Ethylene Carbonate Using a New Photoflow Setup Directed toward Manufacturing

C-H chlorination by molecular chlorine is a highly exothermic reaction that proceeds via a radical chain mechanism and is important in organic synthesis on both laboratory and industrial scales. We have reported a flow C-H chlorination using ex-situ generated Cl_2, in which Cl_2 was generated from HCl and NaOCl.[1] In this study, we investigated the C-H chlorination of ethylene carbonate using gaseous Cl_2, which gives chloroethylene carbonate, a precursor to vinylene carbonate. A novel photoflow setup (photoflow reactor (MiChS L-1) and high-power UV-LED (MiChS LED-s, 60-600 W, 365 nm)) designed for a gas-liquid biphasic reaction turned out to be useful for the direct use of chlorine gas in flow. The setup employed sloped channels to make the liquid phase thinner, ensuring a high surface-to-volume ratio. When the reaction of ethylene carbonate with Cl_2 was carried out at 80 °C with 30 sec residence time, desired mono-chlorinated ethylene carbonate was obtained with 61% conversion and 86% selectivity. If we apply the conditions for continuous operation, around 4.3 kilograms of chloroethylene carbonate can be synthesized per day.[2]



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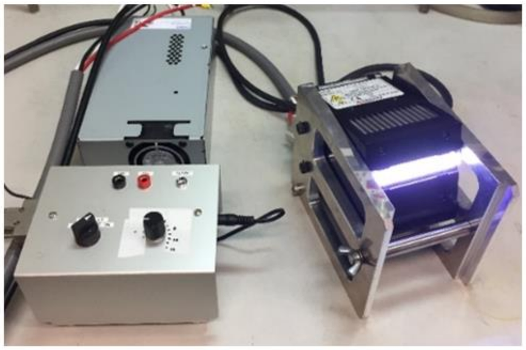
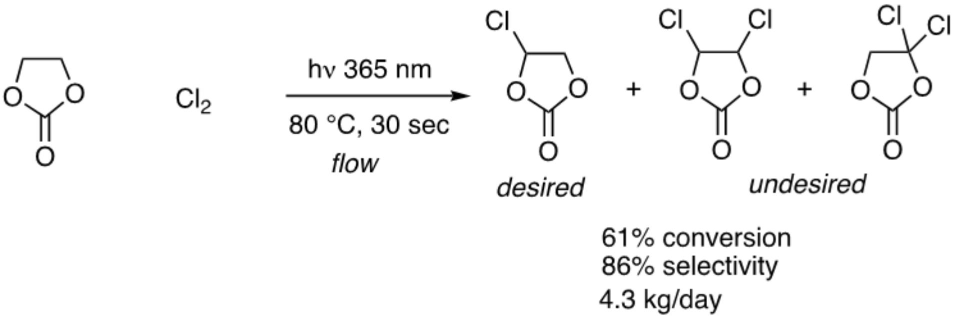


MiChS LED-s



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Shinichiro FUSE
Nagoya University

Abstract: Highly Efficient Peptide Chain Elongation via One-Flow, Three-Component Coupling Approach

Peptides have become increasingly important as drugs. The most conventional peptide chain elongation repeats 1) coupling of an activated *N*-protected amino acid 1 (or 3) with a *N*-terminus free amino acid 2 (or peptide 4), and 2) removal of the *N*-terminus protecting group (Figure 1a). Molecular weights of frequently used coupling agents (DCC: 206, HATU: 380, COMU: 428) and protecting groups (Fmoc: 223, Cbz: 135, Boc: 101) are comparative or larger than the average molecular weight of amino acids (*ca*. 110). Thus, the present peptide synthesis suffered from a large number of synthetic steps, a large amount of waste, and tedious purification.

α-Amino acid *N*-carboxy anhydrides (α-NCAs) 5, that have both nucleophilicity and electrophilicity, have been used as building blocks for the synthesis of oligo/polypeptides. Although the step-wise peptide chain elongation approaches using 5 have been studied, currently, they are rarely used due to difficulty in suppressing undesired reactions of 5.

Micro-flow technology allows precise control of both reaction time and temperature. Our group reported rapid and mild synthetic approaches of NCAs and their derivatization using the micro-flow technology.[1,2] Here, we report a rapid (~ minutes), mild (20 °C) and less wasteful peptide chain elongation via one-flow, three-component coupling of 2, 3 and 5 (Figure 1b). Our developed approach afforded tri- and penta-peptides in high to excellent yields (80-95%). In addition, the highly pure peptides were readily obtained by recrystallization.

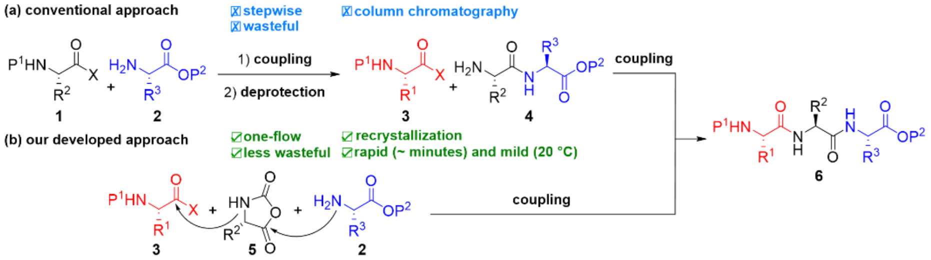

Figure 1. Conventional approach and our developed approach for peptide chain elongation.

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Shaozhong GE
National University of Singapore

Abstract: Cobalt-Catalyzed Asymmetric Synthesis of Chiral Organoboroantes

Enantioenriched organoboron compounds are valuable building blocks in synthetic organic chemistry due to their high stability, low toxicity, and versatile chemical reactivity. Transition-metal-catalyzed enantioselective hydroboration of unsaturated hydrocarbons, such as alkenes, alkynes, and 1,*n*-enyens, is one of the straightforward and atom-economic approaches to access these chiral organoboronates. During our continuous effort in developing cobalt-catalyzed hydrofunctionalization of unsaturated hydrocarbons, we discovered that alkenes, 1,6-enynes and 1,7-enynes could undergo enantioselective diborylation and hydroboration/cyclization in the presence of chiral cobalt catalysts (Figure 1). [1-7] These reactions yielded a series of enantioenriched boryl-functionalized heterocyclic compounds, *gem*-bis(boryl)alkanes, or alkylboronates, and the presence of boryl functionality allows versatile further transformations of these chiral organoboronates. In this presentation, the scope, mechanism, and synthetic applications of these cobalt-catalyzed asymmetric hydroboration and diborylation reactions will be discussed.

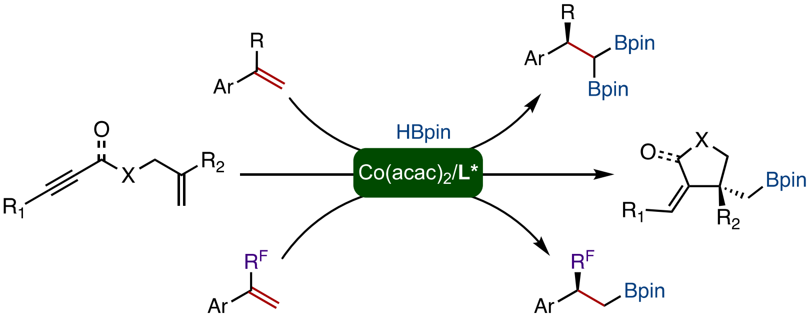

Figure 1. Cobalt-Catalyzed asymmetric diborylation and hydroboration of unsaturated hydrocarbons

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Michael HAAS
Graz University of Technology

Abstract: Recent Advances in the Field of Typ I Photoinitiators

Today, the use of photoinitiators is no longer limited to the field of microelectronics and microlithography, but also applies in the medical field.[1] Consequently, the search for new photoinitiators (PIs) with improved properties are of great interest, but also an enormous challenge. Acyl derivatives (mainly germanium- and phosphorus-based) are important photoinitiators in this context.[2] However, all synthetic strategies towards these compounds rely on classical salt metathesis reactions, where only a moderate complexity of the final products can be achieved. In this lecture we want to go one step further and introduce their electron transfer reactions. Our innovative pathway involves strong bases and alkali-metal reductions, which led to a variety of previously unknown enolates, anions and related compounds that are hitherto hardly producible otherwise. In Figure 1 a typical single electron transfer reaction (SET) towards germenolates and a multiple electron transfer reaction (MET) towards bisgermenolates is depicted.[3]

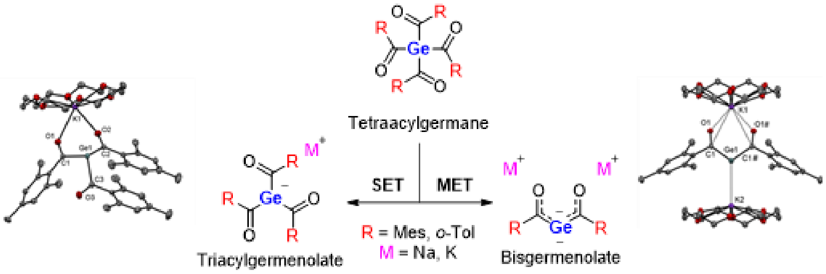

Figure 1. Functionalization Strategy for Ge-Based Precursors

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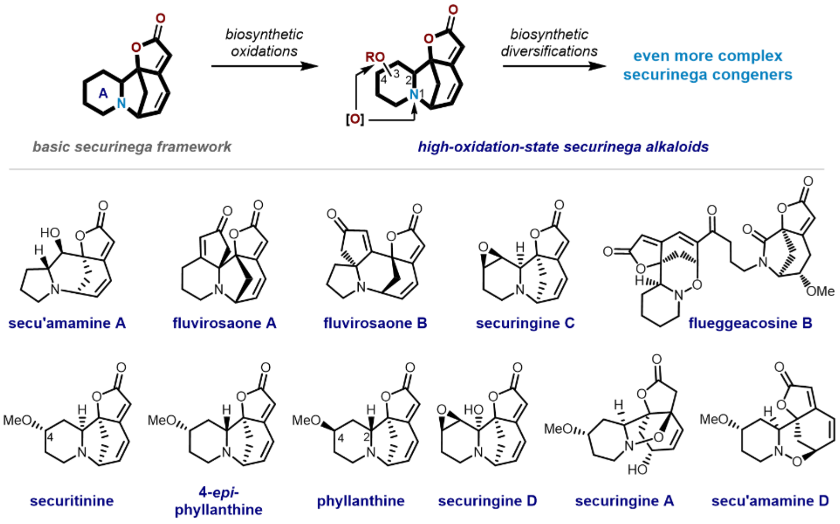
Sunkyu HAN
Korea Advanced Institute of Science & Technology

Abstract: Syntheses of High-Oxidation-State Securinega Alkaloids

Securinega alkaloids have fascinated the synthetic chemical community for over 65 years. Historically, major research foci in securinega natural products synthesis have been on the efficient and innovative construction of the fused tetracyclic framework that bears a butynolide moiety and tertiary amine-based heterocycles. Notably, these "basic" securinega alkaloids have evolved to undergo biosynthetic oxidative diversification, especially on the piperidine core. However, a general synthetic solution to access these high-oxidation state securinega alkaloids is lacking.[1]

In this presentation, our group's recent discoveries centered on the chemical synthesis of securinega alkaloids that are biosynthesized via oxidative diversifications on the piperidine core will be described. More specifically, site selective oxidation of allosecurinine to 2,3-dehydroallosecurinine and its conversion to secu'amamine A, fluvirosaones A and B,[2] collective total synthesis of C4-oxygenated securinine-type alkaloids,[3] and concise synthesis of dimeric securinega alkaloid flueggeacosine B enabled by a newly developed cross-dehydrogenative coupling between aldehydes and electron deficient olefins[4] will be discussed.



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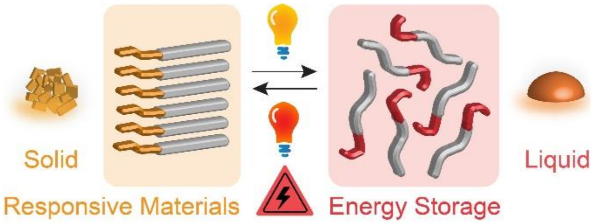
Grace HAN
Brandeis University

Abstract: Design of organic photoswitches for optically-controlled phase transition and energy applications

Light-responsive organic molecules have emerged as a new tool that allows for the optical control over various properties of solid-state materials. Reversible control over the optical, thermal, phase, and mechanical properties of such organic materials enables the applications that involve optical storage, energy storage, and mechanical response. The fundamental understanding of the optically-induced molecular transformation in solids and how such transformation results in phase change, however, is underexplored.

In this talk, the design and synthesis of new organic photoswitches, including azoheteroarenes and hydrazones, that undergo a successful structural transformation in condensed phases will be presented. Various photochromic core structures and functional groups have been explored to yield a deep understanding of the structure-property relationship. We have unraveled the molecular isomerization dynamics in a crowded environment and developed the strategies to alter the conformational freedom around the moving parts of molecular switches. The observation of optically-controlled phase transition of such photoactive molecules sheds light on the types and degree of intermolecular interactions among photoisomers in condensed phases and their applications in solar photon and thermal energy storage.



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Hironobu HAYASHI
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Abstract: Polyazaacene and cyclazaacene precursor synthesis

Polyacenes have attracted a lot of attention due to their potentials as useful building blocks for organic semiconductors. We have synthesized heptacene and nonacene on Au(111) using a precursor method and on-surface synthesis under ultrahigh vacuum (UHV) conditions to provide experimental insight into the chemical and electronic structure.[1] Although the electronic, magnetic, and physico-chemical properties of polyacene could be tuned by the heteroatom substitution, the investigation of polyheteroacenes was less explored. In this study, we synthesized tetraazaundecacene precursor (1) from a key compound (2) (Figure 1).[2] Then, scanning tunneling microscope (STM) tip manipulation afforded tetraazaundecacene, revealing the open-shell character on Au(111). Interestingly, thermal annealing of 1 on Au(111) gave hydrogenated tetraazaundecacene and its analog with two edge-fused five-membered rings. We have also successfully synthesized M[3+3], which can be a cyclazaacene precursor, simply through a dehydration condensation reaction involving 2 and benzene-1,2,4,5,-tetraamine tetrahydrochloride.[3] These results represent a fundamental step toward the precise engineering and tailoring of the unique electronic properties of heteroacene family.

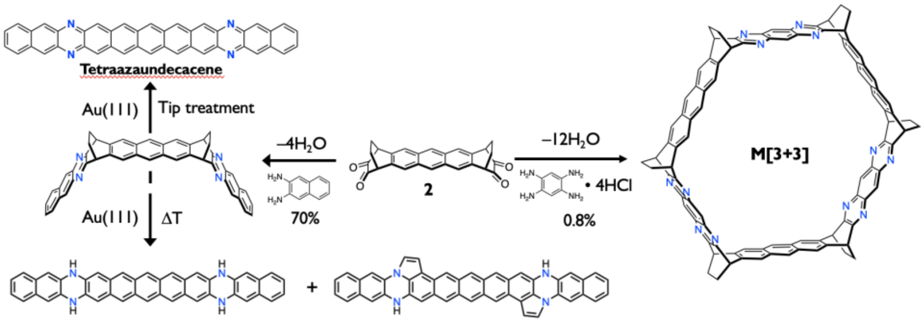

Figure 1. Synthesis of polyazaacene and cyclazaacene precursor.

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Jongin HONG
Chung-Ang University

Abstract: Wavelength-selective dyes for visibly transparent and colorless solar cells

Energy is globally a key consideration in all discussions and meetings on sustainable energy development. Solar energy is the cleanest and most abundant energy source among the renewable energy sources available. Photovoltaics can harness this energy by directly generating electricity from sunlight via the photovoltaic effect, thereby reducing the carbon footprint. Recently, photovoltaic modules have been integrated into the building envelope. Windows have a significant influence on energy demand and heating/cooling load, especially in high-rise buildings with a sizeable window-to-wall ratio, and thus innovative photovoltaic windows are highly anticipated for future zero-energy buildings[1]. Very recently, wavelength-selective technologies, wherein photoactive materials preferentially harvest either ultraviolet (UV) photons (<400 nm) or near-infrared (NIR) photons (>700 nm) or both, have been introduced to achieve the visibly transparent and colorless solar cells as "light-through" solar cells[2]. Among the emerging solar cells, dye-sensitized solar cells (DSSCs) are particularly advantageous because the photosensitizers can be finely modified for wavelength-selective absorption. Herein, I present metal-free organic dyes that selectively harvest UVA (315-400 nm) photons. The dyes have been designed and synthesized to demonstrate the UV-selective and visibly transparent DSSCs exceeding 60% visible light transmittance (VLT)[3]. We also investigate the color perception (chromaticity) and rendering properties (color rendering index (CRI)) of the light transmission through the DSSCs. The color analysis is crucial to predict the color quality of daylight in the building.

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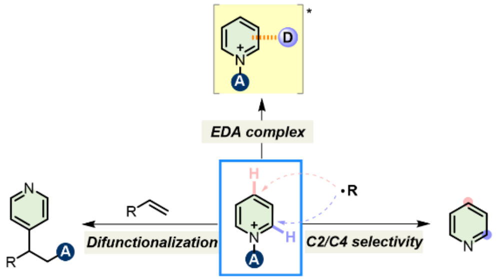
Sungwoo HONG
Korea Advanced Institute of Science & Technology

Abstract: N-Functionalized Pyridinium salts: A New Chapter for Site-Selective Pyridine C–H Functionalization under Visible Light Irradiation

Classically, the synthetic methods for functionalized pyridines often involve radical-mediated Minisci-type reactions under strongly acidic conditions. However, the site-selective functionalization of pyridines in unbiased systems has been a long-standing challenge because the pyridine scaffold contains multiple competing reaction sites (C2 vs. C4) to intercept free radicals. Therefore, prefunctionalization of pyridine is required to avoid issues observed with the formation of a mixture of regioisomers and over-alkylated side products.

The notable advantage of *N*-functionalized pyridinium salts lies in their ability to enhance the reactivity and selectivity for synthetically useful reactions under acid-free conditions. This approach enables exquisite regiocontrol for

nonclassical Minisci-type reactions at the C2 and C4 positions under mild reaction conditions. In addition, a new platform for alkene difunctionalization using *N*-substituted pyridinium salts as bifunctional reagents has been developed, offering an innovative assembly process for complex organic architectures. Intriguingly, strategies involving light-absorbing electron donor–acceptor complexes between pyridinium salts and suitable electron-rich donors further open up new reactivity under photocatalyst-free conditions. We will provide our recent contributions to the development of *N*-functionalized pyridinium salts and summarize the cornerstones of organic reactions that successfully employ these pyridinium salts under visible light conditions.



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Yoichi HOSHIMOTO
Osaka University

Abstract: Main-group Catalysis for H2 Purification Based on Liquid Organic Hydrogen Carriers

Molecular hydrogen (H_2) is an important energy carrier. In the mid-term future, a huge amount of H_2 will be produced from a variety of hydrocarbon sources including wastes and biomass through the in-depth purification of a gaseous mixture of H_2, CO, CO_2, and other components.[1] However, bypassing these purification processes is desirable, given their energy consumption and environmental impact, which ultimately increases the cost of H_2.[2] Here, we demonstrate a strategy to separate H_2 from a gaseous mixture of $H_2/CO/CO_2/CH_4$ that can include an excess of CO and CO_2 relative to H_2 and simultaneously store it in *N*-heterocyclic compounds that act as liquid organic hydrogen carriers (LOHCs),[3] which can be applied to produce H_2 by subsequent dehydrogenation (Figure 1).[4] Our results demonstrate that LOHCs can potentially be used for H_2 purification in addition to their well-established use in H_2 storage.

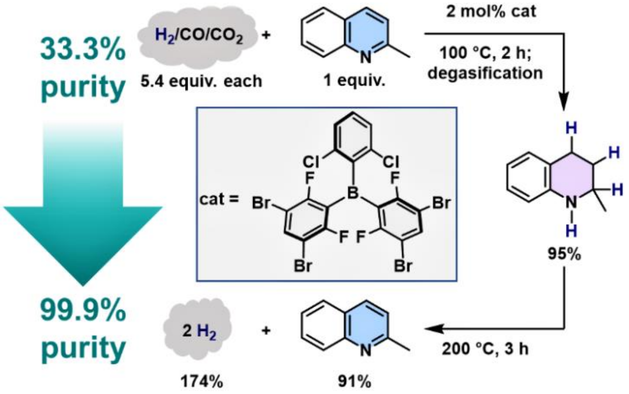

Figure 1. H_2 purification based on the borane-catalyzed hydrogenation of 2-methylquinoline under mixed-gas conditions and subsequent catalytic dehydrogenation.

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Koki IKEMOTO
The University of Tokyo

Abstract: Design and Synthesis of Nitrogen-Doped Phenine Nanocarbons

Doping nitrogen atoms into nanocarbons serves as an effective method to modulate electronic and chemical properties of nanocarbons. Nitrogen dopants are categorized as pyridinic, pyrrolic and graphitic nitrogen, and the types of nitrogen are proposed to have a determinant role for the properties. However, it is difficult to correlate the properties with atomic-level structures of nanocarbons because they comprise mixtures of various structures. Recently, we reported the synthesis of a defective nanotube molecule, phenine nanotubes (pNT), by adopting 1,3,5-trisubstituted benzene (phenine) as a basic trigonal planar unit.[1] Based on the phenine design, in this study, we designed and synthesized nitrogen-doped phenine nanotube molecules (NpNTs), in which the position, number and types of nitrogen atoms are precisely controlled (Figure 1).[2,3] The detailed electronic and optical properties of NpNTs induced by the nitrogen dopants will be discussed.

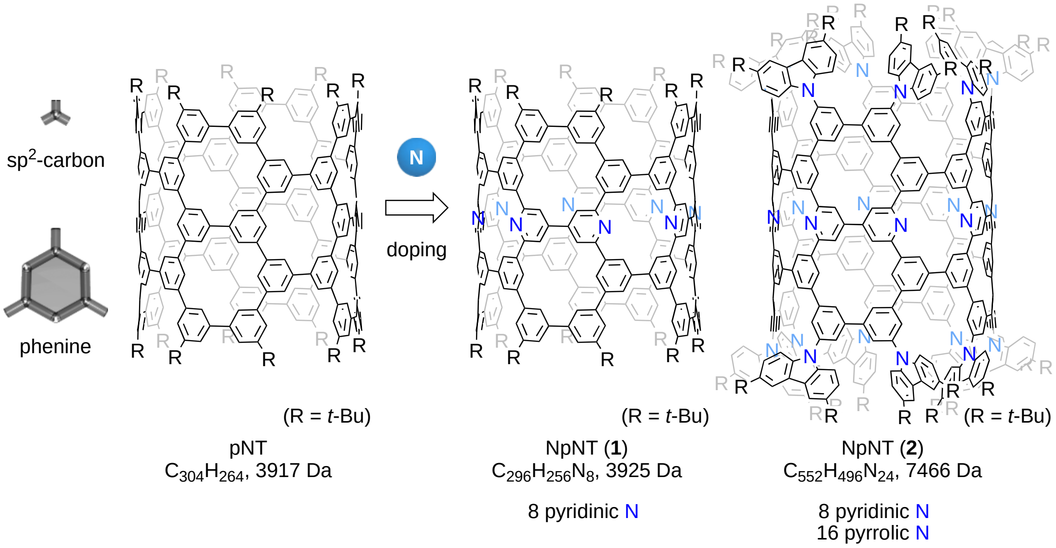

Figure 1. Nitrogen-doping of phenine nanotubes

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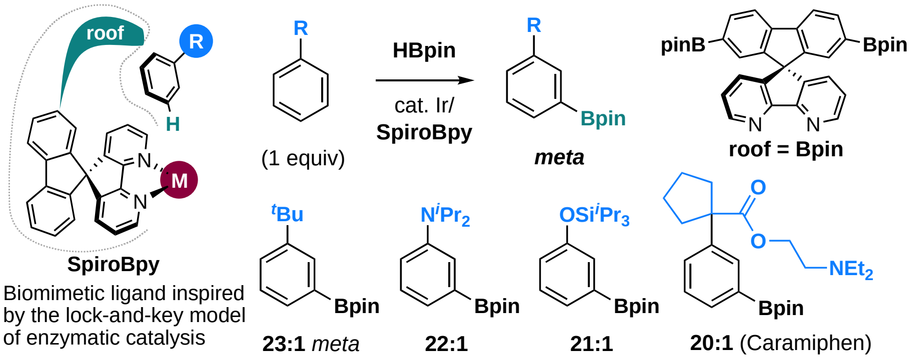
Laurean ILIES
Riken

Abstract: SpiroBipyridine Ligands for Catalytic C–H Functionalization

Modern synthetic chemistry strives to create organic molecules in the most straightforward and efficient manner possible. For this purpose, the use of a metal catalyst to directly introduce functionality into a simple or complex organic molecule has received much attention. However, a serious problem remains largely unsolved: even simple organic molecules have many reaction sites, and controlling the selectivity of the reaction at the desired position is very difficult. Inspired by the lock-and-key model of enzymatic catalysis, we designed a new catalytic system that uses a spirobipyridine "roof" ligand to create a molecular pocket to fit the substrate only in a determined orientation, and thus control the selectivity. We demonstrated this concept for the *meta*-selective functionalization of simple arenes such as alkylbenzenes, anilines, and phenols, and for the late-stage selective functionalization of complex drug molecules (Scheme 1).[1] We also recently found that the spirobipyridine scaffold by itself is capable of accelerating iridium-catalyzed C–H borylation via noncovalent C–H/p interaction between the ligand backbone and the arene substrate.[2]

Scheme 1. Remote steric control using "roof" SpiroBpy



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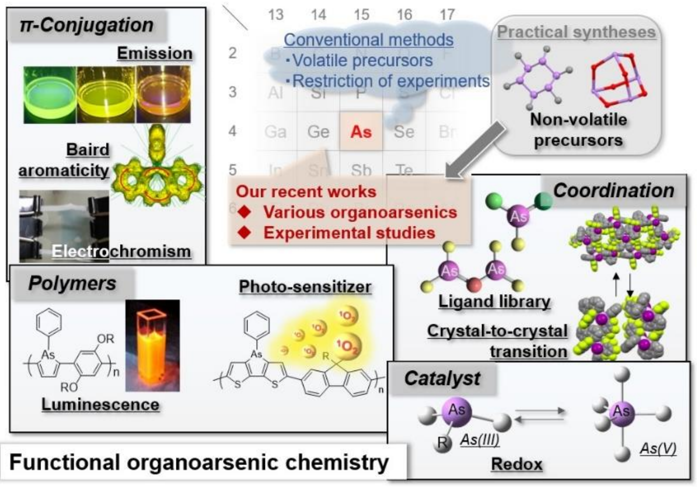
Hiroaki IMOTO
Kyoto Institute of Technology

Abstract: Functional organoarsenic chemistry based on practical syntheses



Background: Hetroatom-containing organic materials have been extensively studied to attain unique structure, functionality, and reactivity. Though various elements are examined, an experimental study on organoarsenic chemistry was highly restricted. In conventional syntheses of organoarsenic compounds, volatile and toxic precursors such as arsenic hydrides and chlorides are necessary, and researchers avoided the experiments. Instead, computational studies on functional organoarsenic compounds were performed to evaluate their optoelectronic properties. We have recently developed practical synthetic methods of organoarsenic compounds, in which non-volatile arsenic precursors are used. These synthetic methods enabled experimental studies on functional organoarsenic chemistry.
Results: We employed cyclooligoarsines (As_5Me_5 or As_6Ph_6) as non-volatile precursors. For example, addition of iodine (I_2) to the cyclooligoarsine gives diiodoarsine ($RAsI_2$), which can be used for arsenic-fused π-conjugated molecules including arsoles and arsepins. While the photophysical and electronic properties of arsoles were computationally predicted, we succeeded in the elucidation of them by experimental means. We developed another synthetic route to generate arsenic electrophile, tribromoarsine ($AsBr_3$) from arsenic oxide (As_2O_3). $AsBr_3$ can be used for synthesis of not only AsR_3-type (C_3-symmetry) compounds but also AsR_2R'-type (C_s-symmetry) ones. Based on the developed synthetic methods, we have constructed "arsenic ligand library", which contains a diverse of arsines and arsine oxides. We synthesized transition metal and lanthanide complexes with the arsenic ligands, and examined their luminescent properties, stimuli-responsiveness, catalytic activities, etc. Moreover, we recently examined trivalent or pentavalent

arsenic compounds as catalysts. For example, it was found that 1-phenylarsolane can work as a catalyst for the arsa-Wittig reaction.

Conclusion: We have studied functional organoarsenic chemistry based on our practical synthetic methods. We would like to introduce the unexplored but fascinating element in the presentation.

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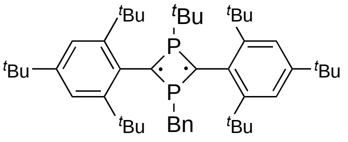
Shigekazu ITO
Tokyo Institute of Technology

Abstract: Radical Reactions of Phosphorus Heterocycles with Muonium

The (positive) muon (μ^+) is an elementary particle of the lepton family and has spin I = 1/2. The mass of the muon is about 1/9 that of proton, and a light isotope of proton can capture an electron in insulators and semiconductors to become muonium (Mu = μ^+e^-), a light isotope of hydrogen atom. The ultralight isotope of hydrogen, Mu, have been utilized as versatile probes for studies on radical reactions of various organic compounds. For example, Mu adds to benzene and provides the corresponding cyclohexadienyl radical whose structure can be characterized by muon spin rotation/resonance (μSR) spectroscopy.[1].

In this talk, our recent μSR studies of intriguing phosphorus heterocycles will be overviewed with discussing the usefulness of μSR for main group chemistry.[2] A 1,3-diphosphacyclobutane-2,4-diyl of singlet biradical (1) shows highly electron-donating character and has stimulated to investigate from the views of materials development. The attractive physical properties of 1 are produced by the particular radical electrons in the 4-membered heterocyclic unit, and thus monitoring radical reactions in 1 would be beneficial to understand nature of the open-shell heterocyclic unit. Muon (avoided) level-crossing resonance (μLCR) of crystalline 1 (Bn = benzyl) showed the regioselective muoniation at the phosphorus atom affording the paramagnetic P-heterocycle including the ylidic skeleton.[3] On the other hand, another 1,3-diphosphacyclobutane-2,4-diyl bearing an electron-deficient heteroaryl substituent promoted direct coupling of muonium and radicalic centre.[4] Next, a *peri*-trifluoromethyl-substituted 9-phophaanthracene 2 (Mes = mesityl) was employed for μSR because radical reactions of anthracene has been important from viewpoints of environmental and combustion sciences. Transverse-field muon spin rotation (TF-μSR) and μLCR of a solution sample of 2 displayed muoniation at the sp^2 phosphorus atom. Subsequent DFT studies characterized the novel muon isotope effect.[5]



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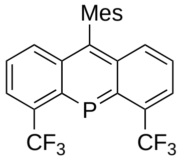

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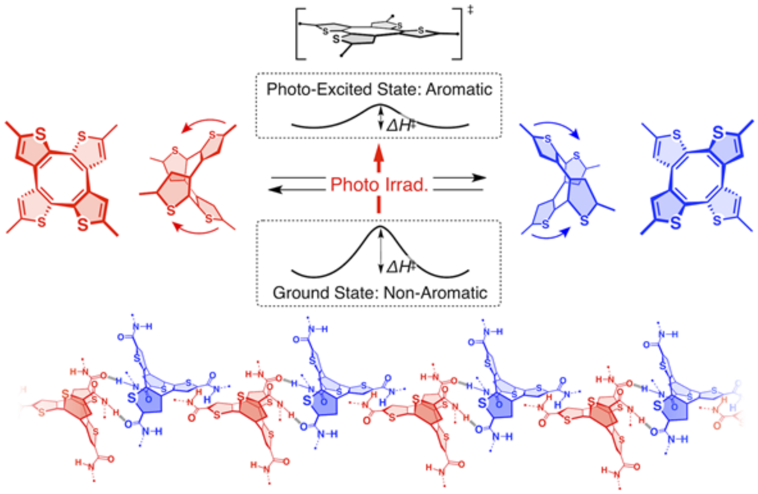
Yoshimitsu ITOH
The University of Tokyo

Abstract: Dynamic Molecular Assembly of Photo-Aromatizable [4n]Annulene Derivatives

Controlling molecular assembling events using light is one of the most important topics in developing photo-responsive materials. Previously, we reported the first experimental demonstration of the energetics of excited-state aromaticity (Baird aromaticity)[1,2] using thiophene-fused cyclooctatetraene derivatives.[3] This molecule undergoes ring inversion through a planar transition state. Under photo-irradiation, the inversion kinetics was significantly enhanced due to the emergence of aromaticity at the [4*n*]annulene core in the planar transition state. By comparing the activation barrier with and without photo-irradiation, we successfully estimated the energetic impact of Baird aromaticity to be 21–22 kcal/mol. By using this photo-responsive molecular motif, we successfully made the first example of an alternating heterochiral supramolecular polymer.[4] As expected, this supramolecular polymerization can be initiated by photo-irradiation to the optically resolved monomer through racemization. Interestingly, we found that the polymerization can proceed only after the removal of the photo-irradiation, even the racemization was completed, due to the rapid fluttering motion of the monomer under photo-irradiation that prevent the monomers to interact with the growing end of the polymer. In fact, we can temporary suspend the polymerization by irradiating light even after the polymerization was initiated. This is the first example of photo-suspendable supramolecular polymerization.[5]



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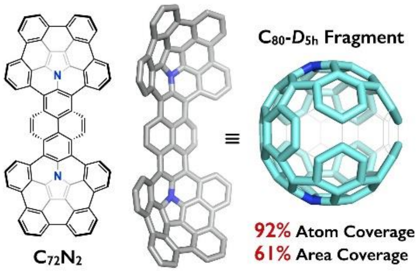
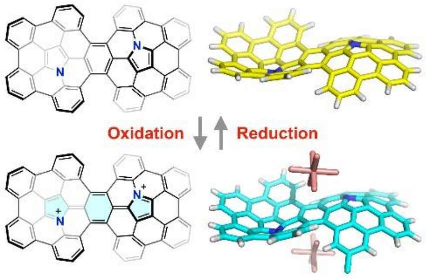
Shingo ITOH
Nanyang Technological University

Abstract: Synthesis of Fully Conjugated Azacorannulene Dimers

Our research group has focused on the development of novel synthetic methods for heteroatom-containing π-functional molecules with unique structures and innovative properties. I would like to present our recent achievements on the synthesis and properties of various nitrogen-embedded polycyclic aromatic molecules enabled by 1,3-dipolar cycloaddition reactions using polycyclic aromatic azomethine ylides.[1] In particular, the lecture will focus on two fused azacorannulene dimers.



One is a fully conjugated azacorannulene dimer with a 76π system, which represents by far the largest diaza[80]fullerene ($C_{78}N_2$) fragment molecule bearing two internal nitrogen atoms. Its boat-shape structure leads to unique selective association with a dumbbell-shaped C_{60} dimer over C_{60} through shape recognition.



The other example is a fully conjugated azacorannulene dimer with a $C_{62}N_2$ core. Due to the steric repulsion between two azapentabenzocorannulene moieties, this molecule shows a rigid *S*-shaped structure where the two azacorannulene bowls face in an opposite direction. Its stepwise chemical oxidation resulted in the formation of the corresponding radical cation and dication, providing an important insight into their aromaticity.

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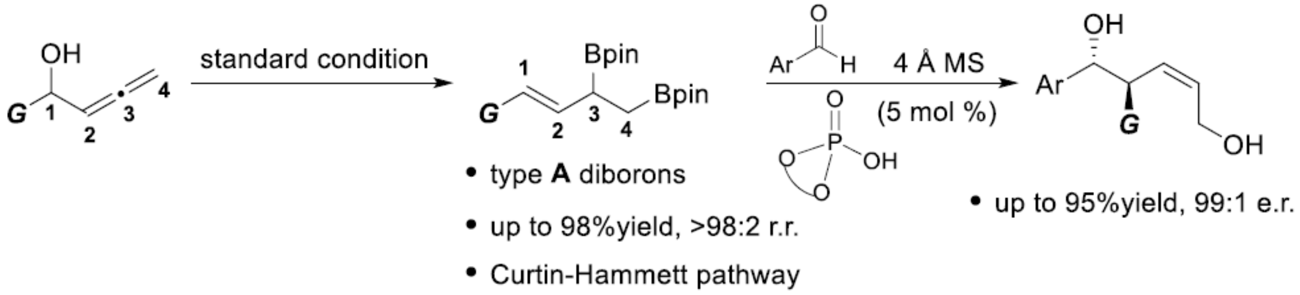
Byunghyuck JUNG
Daegu Gyeongbuk Institute of Science and Technology

Abstract: Cu-Catalyzed Regioselective Synthesis of *(E)*-1-Alkyl/Aryl-3,4-diborabut-1-enes

The installation of an allyl group to carbonyls with allylborons has been an important experimental platform to generate homoallylic alcohol motif in versatile natural products, especially polyketides.[1] Bisallyl diborons have attracted organic chemists by their utility of either double allylation to two carbonyls (dicarbonyls or two carbonyl molecules) or sequential allylation/functionalization of the remained C–B bond for the construction of structural complexity.[2] Among some types of diborons, type A has been less common and studied recently by Morken's and Brown's research group, respectively.[3,4]

The immense screening of various reagents concluded the standard reaction condition. Under this condition, llenols with alkyl- or aryl chains at C_1 position as substrates were transformed into the desired (*E*)-1-alkyl or aryl-substituted 3,4-

diborabut-1-enes up to 98%yield and >98:2 regioisomeric ratio. Computational study unveiled the origin of the regioselectivity, which was governed by Curtin- Hammett kinetics. The synthetic utility of the vicinal diborons was highlighted by the demonstration of enantioselective allyl addition to aldehydes with chiral phosphoric acid catalyst to afford the formation of (*Z*)-diols with high optical purities.[5]



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Kazuhide KAMIYA
Osaka University

Abstract: Single-Atom Doped Covalent Triazine Frameworks as Electrocatalysts for Applications in Energy Conversion

Covalent organic frameworks (COFs) have attracted a keen attention as novel catalyst platforms because of their unique physicochemical properties, including their nano-porous structure, mechanical robustness and high design flexibility. We have recently demonstrated that triazine-based COFs (CTFs) can immobilize metal centers from 3d to 5d groups and exhibit electrocatalytic functions corresponding to these metal centers, such as oxygen reduction, hydrocarbon oxidation and hydrogen oxidation reactions.[1-6]

In this presentation, we will introduce the application of our metal-doped CTFs to the electrocatalysts for CO_2 reduction reactions. We systematically investigate the relationship between the adsorption strength of intermediates and CO_2 reduction activity using a computational and experimental combined approach. As a result, Ni-CTF and Sn-CTF facilitated the reduction of CO_2 to CO and HCOOH, respectively, with a partial current density of over 100 mA/cm^2. First-principle calculations showed that the adsorption strength of intermediates is enhanced by the open-coordination sites, resulting in high catalytic activity.

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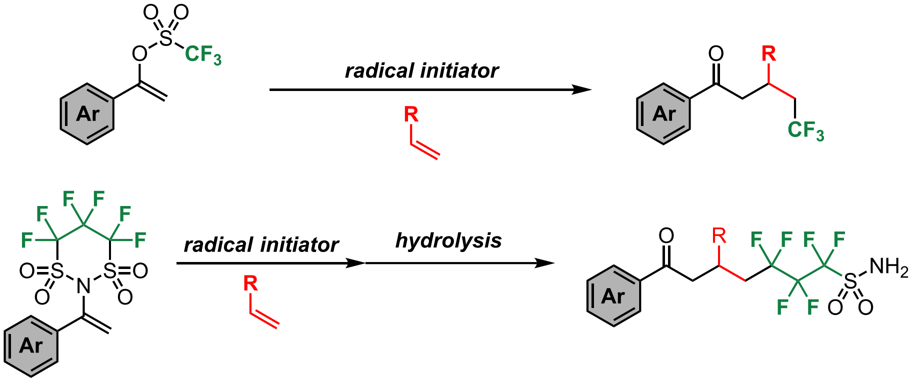
Takuji KAWAMOTO
Yamaguchi University

Abstract: Synthesis of γ-Perfluoroalkylated Ketones via β-Cleavage

Vinyl triflates are valuable electrophiles for transition-metal-catalyzed cross-coupling reactions. In comparison, their use in radical reactions has been scarcely developed. Previously, we have developed the conversion of vinyl triflates into α-trifluoromethylated ketones in the absence of external trifluoromethyl sources.[1,2] In this talk, I will present the radical reactions of vinyl triflates with alkenes leading to γ-trifluoromethylated ketones.[3] The radical reaction of vinyl cyclic perfluoroalkane sulfonyl imides will also be presented.



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Hyunwoo KIM
Pohang University of Science and Technology

Abstract: Radical-Polar Crossover Strategy in Organic Electrosynthesis

Due to the unique reactivity of open-shell intermediates, the development of catalytic transformations driven by single-electron transfer (SET) has been an area of intense research in organic chemistry. In particular, the employment of unconventional means of activation, including photoredox catalysis and electrocatalysis, has provided unique entry to single-electron reactivities and led to new solutions to challenging synthetic problems that are not readily addressed

using existing tools. In the first part of the lecture, an electrochemically driven radical-polar crossover strategy for the stereo- or regioselective alkene functionalization reactions. Compared to the precedent examples, the newly developed system obviates the need for transition metal catalysts or external oxidizing agents, thus providing an operationally simple and efficient route to an array of synthetically valuable organic products. Despite extensive studies on oxidative electrochemistry, reductive electrochemistry has yet to find widespread application in modern organic synthesis. In the second part of the lecture, a key distinction of photoredox catalysis and electroreductively triggered approach will be discussed as well as mechanistic hypotheses that underpin a development of mechanistically distinct and generally valid hydrodifluoromethylation reaction.

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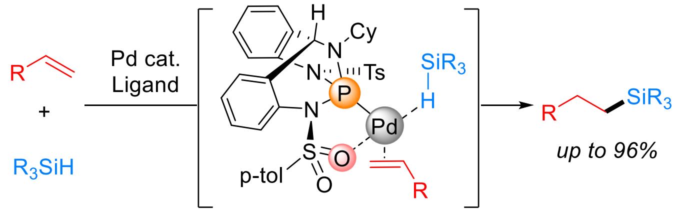
Hyunwoo KIM
Korea Advanced Institute of Science and Technology

Abstract: Hemilabile P,O-Ligands for Pd-Catalyzed Hydrosilylation of Unactivated Alkenes

Alkyl silanes are widely used in the microelectronics and optoelectronics industries and the manufacture of solar cells and flat panel displays. Alkyl silanes are becoming the basis for many new technologies, materials, and devices. In recent years, transition metal catalysts based on Pt, Pd, Fe, Co, and Ni have been developed for the hydrosilylation of alkenes. In the Pd-catalyzed hydrosilylation, the applications are limited to functionalized alkenes and activated silanes such as chlorosilanes.

We recently demonstrated a Pd-catalyzed hydrosilylation of unactivated alkenes and tertiary alkylsilanes. We could achieve such a challenging substrate combination by using a new-designed hemilabile P,O ligand, *N*-ditosyl bicyclic bridgehead phosphorus triamide. This ligand structure is a modification of our ligand platform 'briphos', a tunable and scalable π-acceptor phosphorus ligand.[1-5] DFT computation revealed that the hemilability of *N*-tosyl group facilitated the hydride insertion step, which is known as the turnover-limiting step.



- Unactivated alkenes
- Tertiary silanes

- Intermediate stabilized by Pd-O interaction

- upto 96% yield
- 20 examples

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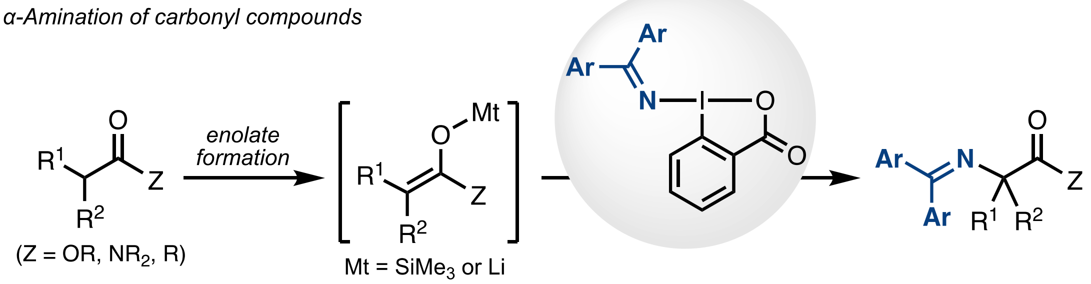
Kensuke KIYOKAWA
Osaka University

Abstract: Amination Using Hypervalent Iodine Reagents Containing (Diarylmethylene)amino Groups

Benzophenone imine derivatives are attractive compounds in organic synthesis because they undergo facile hydrolysis and hydride reduction, providing primary amines and diarylmethylamines, respectively. Hypervalent iodine reagents containing a transferable (diarylmethylene)amino group would offer a promising tool for oxidative amination to deliver modifiable amine products. We report herein the synthesis of new types of hypervalent iodine reagents, (diarylmethylene)amino benziodoxolones, and their use in oxidative amination. The developed amination reactions feature transition-metal-free conditions and simple operation.

The hypervalent iodine reagents enable the α-amination of carbonyl compounds through the formation of enolates such as silyl ketene acetals[1] and lithium enolates. These protocols can provide various types of easily modifiable α-amino carbonyl compounds from esters, amides, and ketones. Mechanistic investigations indicate that the amination proceeds in a radical pathway in which a nitrogen-centered radical is generated through a single-electron transfer between an enolate and the hypervalent iodine reagent.

Decarboxylative carboamination of vinylarenes was found to proceed by using carboxylic acids and the hypervalent iodine reagents in the presence of potassium carbonate under irradiation with blue LEDs. The reaction would be initiated by single-electron oxidation of carboxylates by the photoexcited hypervalent iodine reagent, leading to a radical decarboxylation to provide an alkyl radical species, which could participate in a radical carboamination of alkenes.



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Vincent KO
City University of Hong Kong

Abstract: Luminescent Mechanochromism and Application of Ir(III) Acyclic Carbene Complexes

Luminescent mechanochromism is observed in compounds that would undergo reversible mechanical-induced transformations between two forms having different luminescent behaviors. To date, different types of solid-state luminescent mechanochromic compounds, including simple organic compounds, polymers, and transition metal complexes, have been reported.[1] Their luminescent mechanochromism is mainly derived from reversible switching between the crystalline and amorphous states, through which the intermolecular interactions, such as π-π, H-bonding, dipole-dipole, metal-metal, and metal-ligand interactions, and thus the energy of the electronic states and the luminescence are varied.[1]

As intermolecular interactions are less predictable and difficult to control from the molecular frameworks or substituents, the molecular design of these compounds with tailored luminescent mechanochromism is challenging. Inspired by the strong sensitivity of the emission characteristics of the acyclic carbene complexes to the structural and conformational of the acyclic carbene ligands,[2] herein, we report the design and study of a new class of luminescent mechanochromic transition metal complexes with bidentate acyclic carbene ligands. A detailed study revealed that their mechanochromic behaviors are derived from intramolecular mechanochemical changes.[3] Knowing their mechanochemical changes, it enables the designing of related compounds with tailored mechanochromic properties, including the emission color and the mechanochromic shift.[3] Moreover, their applications in the design of mechanoresponsive, dual-emissive materials and sensors will be reported.[4-6]

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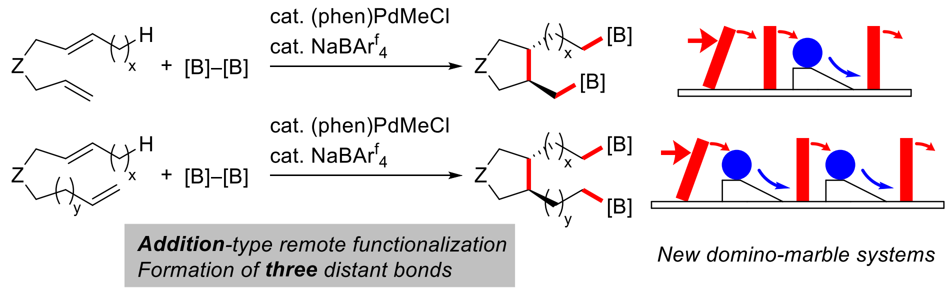
Takuya KOCHI
Keio University

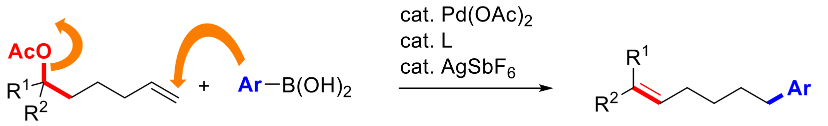
Abstract: Nondissociative Chain Walking of Palladium Catalysts: Applications in Organic Reactions and Mechanistic Analyse

Nondissociative chain walking, a process where an alkylmetal species undergoes repetitive β-hydride elimination and insertion to make a catalyst migrate to a distant position without exchanging alkenes during the process, has been utilized in olefin polymerization. In recent years, the use of the mechanism has also become a powerful strategy in organic synthesis.[1] Since the development of palladium-catalyzed chain-walking cycloisomerization of 1,n-dienes,[2] we have been working on the development of novel reactions using the nondissociative chain walking mechanism. In this talk, I would like to provide our recent developments of new reactions based on the unique features of the nondissociative chain walking mechanism.[3,4] For example, in the remote diborylative cyclization of 1,n-dienes, addition-type remote difunctionalization of alkene substrates were achieved, and in the case of 1,n-dienes (n ≥ 7), sequential formation of three-distant bonds in one catalytic cycle was also accomplished. We also recently developed remote substitution, an new class of remote functionalization reaction, in the remote arylative substitution of alkenes having a distant leaving group. I will also present some mechanistic insights into the chain walking mechanism based on DFT calculations and experiments.

Remote Diborylative Cyclization



Remote Arylative **Substitution**



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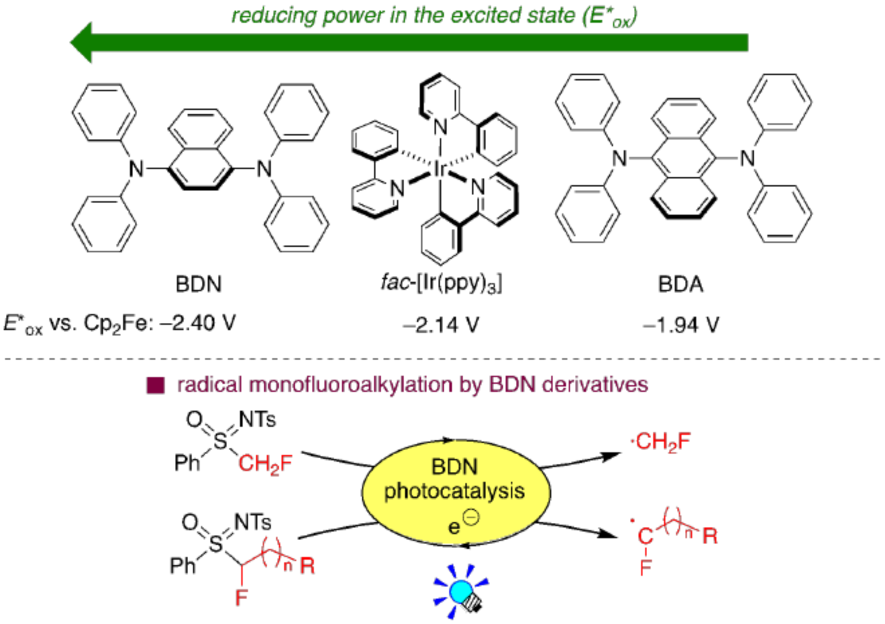
Takashi KOIKE
Nippon Institute of Technology

Abstract: Radical Fluoroalkylation Reactions by Means of OrganicPhotocatalysis

Photoredox catalysis with metal-based complexes and organic dyes has become a useful tool for synthetic radical chemistry.1 Recently, we have found that small aromatics with two diarylamine termini such as 9,10-bis(diphenylamino)anthracene (BDA) and 1,4-bis(diphenylamino)naphthalene (BDN) derivatives serve as efficient organic photocatalysts for a single electron injection against electron-accepting fluoroalkylating reagents.2–5 In particular, BDN derivatives exhibited excellent activity for photocatalytic radical monofluoroalkylation of olefins with sulfoximine-based monofluoroalkylating reagents. In this presentation, new design of highly reducing organic photoredox systems will be discussed.



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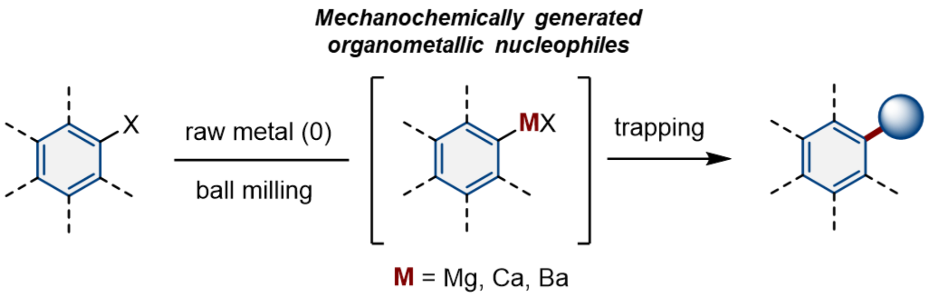
Koji KUBOTA
Hokkaido University

Abstract: Mechano-Driven Main Group Organometallic Chemistry

To date, synthetic organic chemists have typically used external stimuli such as heat, light, or electricity to promote and control desired organic transformations. In contrast, the development of organic reactions promoted by mechanical force has remained unexplored. Recently, mechanochemical synthesis using ball milling has attracted attention as a new tool to carry out organic reactions. The advantages of mechanochemical synthesis include the avoidance of potentially harmful organic solvents, shorter reaction times, and simpler operational handling. Given these attractive features, ball milling techniques have been applied to a wide range of organic transformations, and the number of published papers has significantly increased recently. However, the development of force-driven, conceptually new synthetic strategies with ball milling has not ever been explored.

In this study, our group is aiming to establish a new synthetic concept in which inorganic materials, polymers and zero-valent metals are used as mediators connecting the scale gap between mechanical force and small organic molecules, opening a new field of mechano-driven organic synthetic chemistry.[1-7] This lecture will maily highlight our recent progress of mechano-driven main group organometallic chemistry.



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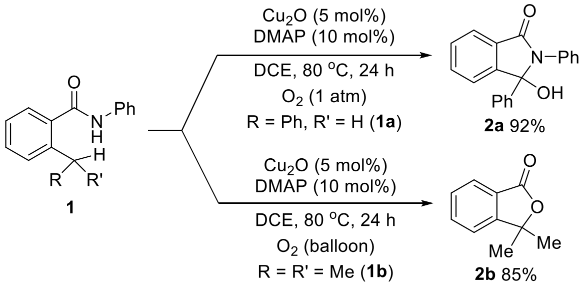
Kanako KUMADA
Tohoku University

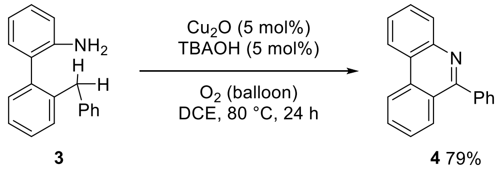
Abstract: Copper-Catalyzed Aerobic C(sp3)–H Functionalization for the Synthesis of Heterocycles

Oxidative C(sp^3)–H functionalization has attracted much attention because it enables straightforward transformation of organic compounds. Most of existing methods require the use of stoichiometric amount of oxidants such as metal oxidants, peroxides, and hypervalent iodines.[1] From safety, economical, and environmental viewpoints, molecular oxygen is one of the most ideal oxidants for these methods because it is without risk of explosion, easily available, and affords water as a by-product. Recently, we developed copper-catalyzed aerobic C(sp^3)–H functionalization for the syntheses of heterocycles such as 3-hydroxyisoindolinones (2a, double C(sp^3)–H functionalization),[2] benzolactones (2b, single C(sp^3)–H functionalization),[3] and phenanthridines (4, double C(sp^3)–H functionalization) (Schemes 1 and 2). Details will be discussed in this presentation.

Scheme 1



Scheme 2



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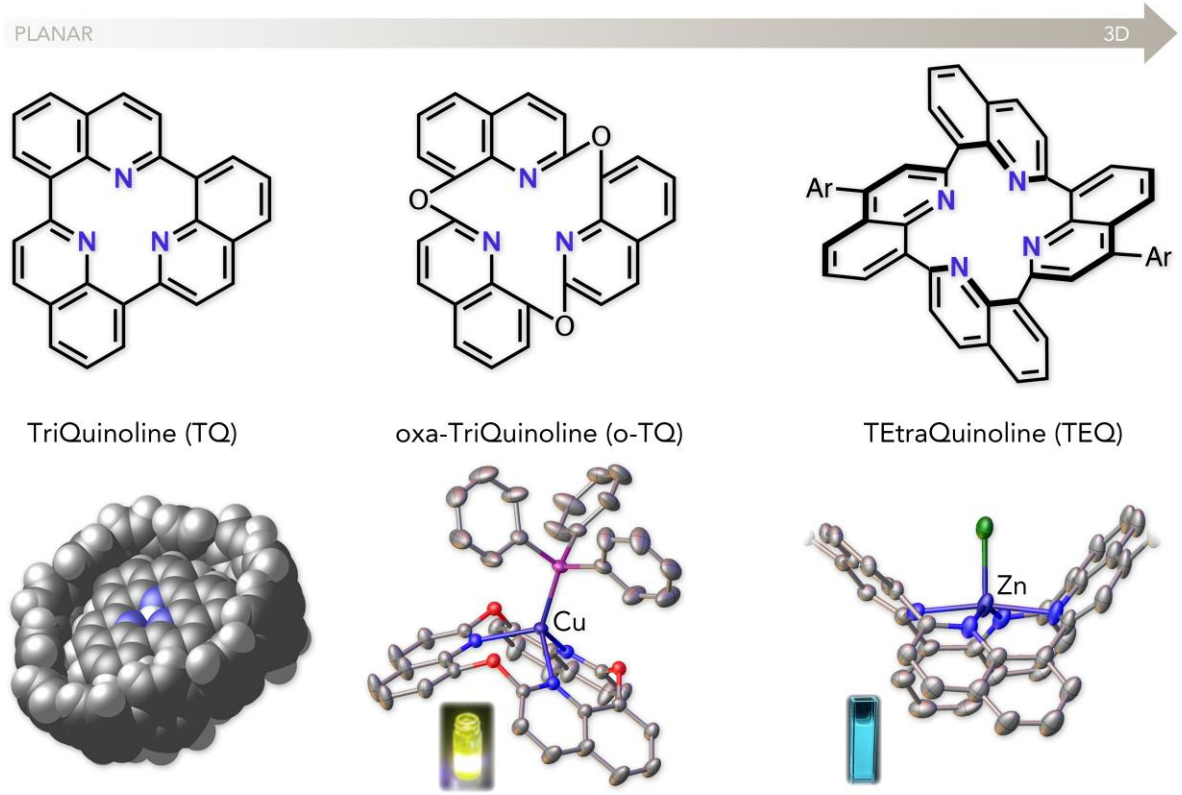
Naoya KUMAGAI
Keio University

Abstract: Chemistry Driven by Quinoline Oligomers

Structure-property or structure-function relationships are the basis for molecular design and engineering to develop new compounds with custom-tailored functionality. We have designed TriQuinoline (TQ) as a miniaturized model of nitrogen-doped graphene with an atomic size void, i.e., a cyclic quinoline trimer concatenated at the 2 and 8 positions in a head-to-tail fashion. TQ turned out to be a super-binder to protons and the resulting positively charged pseudo-planar TQ•H$^+$ exhibited supramolecular complexation via π-π and CH–π interactions.[1] TQ can be converted to a non-flat oxa-TriQuinoline (o-TQ) by the embedment of three oxygen atoms. Flexible o-TQ architecture was fixed by the complexation with metals featuring tetrahedral coordination mode, furnishing bowl-shaped complexes capable of aggregation induced emission. Concatenation of four quinoline units afforded TEtraQuinoline (TEQ), a rigid saddle-shaped macrocycle that features four inwardly oriented four nitrogen atoms like porphyrins. Physicochemical and catalytic properties of these planar and three dimensional quinoline oligomers will be discussed.



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Chun-Hong KUO
National Yang Ming Chiao Tung University

Abstract: Manipulation of Cu-Based Bimetallic Nanocrystals towards Electrochemical Conversion of Small Molecules

Bimetallic surfaces on nanocrystals usually exhibit superior catalytic activities for energy-conversion reactions due to the enhancement by the electronic effect. In addition, integration of plasmonics and catalysis in bimetallic nanocrystals provides more benefits for the creation of novel catalyst systems. In this talk, selected stories about utilization of CuM bimetallic nanocatalysts for catalytic energy-conversion reactions will be introduced.[1-3] The talk will start with the synthesis of Cu nanocubes which serve as the templates for further surface engineering. On the Cu nanocubes, we reduce various kinds of noble metallic ions to form CuM surfaces with a controlled thickness about 2 nm (7-8 atomic layers). In our works, the atom-level surface modulation on the surfaces of Cu nanocubes was achieved by chemical approaches, which exhibited unconventional morphological transformation of nanocrystals after formation of CuM shells. Moreover, treating Cu-CuM core-shell nanocrystals with acid to remove Cu cores triggers further morphological transformation, leading to final nanocages in a specific shape. Those nanocages are eventually applied to electrocatalysis (oxygen reduction reaction, ORR) and photocatalytic synthetic reaction (4-nitrophenol reduction reaction). The results show that these nanocages possess at least triply high mass activities than that of commercial catalysts.[1, 3] Apart from surface-coated shells, fabrication of CuM nanoframes on the Cu nanocubes via selective deposition of metallic ions will be also introduced. These nanoframes have 3D-open skeletons with highly exposed surface area and, more importantly, surface defects (i.e. adatoms and terraces).[2] The characteristics make CuM nanoframes excellent catalysts in both electro- and photocatalysis.

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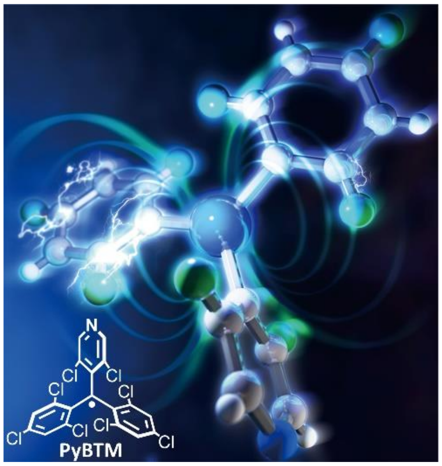
Tetsuro KUSAMOTO
Institute for Molecular Science

Abstract: Interplay Between Spin and Luminescence in Stable Organic Radicals



Organic radicals attract growing interest as novel molecular emitters with unique characteristics, such as efficient electron-photon conversion in OLEDs and the absence of heavy atom effect, attributed to their doublet spin states.[1] One of the important challenges that remain unexplored in the studies of luminescent radicals is to develop photofunctions based on the interplay between spin and luminescence, which are difficult or impossible for conventional closed-shell molecules to achieve. Our group developed magnetic-field-controlled luminescence (magnetoluminescence, MagLum) of radicals as their novel spin-correlated luminescence properties.

We have shown that PyBTM 10 wt%-doped into host molecular crystals shows monomer-like and excimer-centered emission bands in the emission spectrum upon photoexcitation, and the intensity ratio of these two bands changes drastically by applying a magnetic field of up to 18 T at 4.2 K.[2] This is the first demonstration of MagLum in radicals. Detailed investigations allowed us to establish a plausible mechanism of the MagLum and the role of the magnetic field; it dominantly affects the spin sublevel population of radical dimers in the ground states.[3] The MagLum was observed in the other radical-doped materials and radical-based coordination polymers.[4] These results show that the spin degree of freedom in the ground state of open-shell molecules can be a key for achieving spin-correlated photofunctions.

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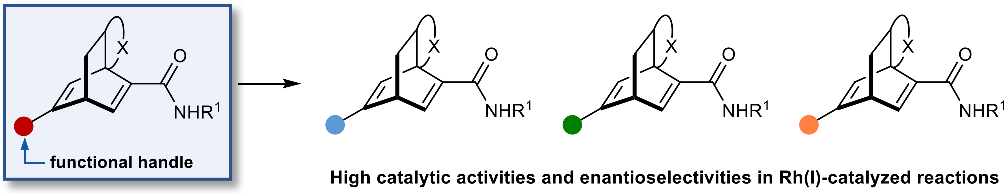
Hon Wai LAM
University of Nottingham

Abstract: New Chiral Dienes for Enantioselective Catalysis

Chiral dienes are important ligands used in asymmetric catalysis that often exhibit higher catalytic activities than other, more commonly used ligands such as chiral bisphosphines.[i] A wide variety of chiral dienes have been designed and synthesized,[i] and a few are commercially available. However, the synthesis of these important ligands can often be lengthy. In addition, their preparation as single enantiomers often requires separation by chiral HPLC, enzymatic kinetic resolution, resolution of the corresponding rhodium complexes with chiral auxiliaries, catalytic asymmetric reactions, or the use of chiral pool starting materials that can result in unequal access to both enantiomeric (or pseudoenantiomeric) series. These inconvenient access issues hamper the wider adoption of chiral dienes in asymmetric catalysis. Therefore, there remains a need to develop concise, straightforward, and efficient syntheses of chiral dienes.



High catalytic activities and enantioselectivities in Rh(I)-catalyzed reactions

- Readily available in multigram quantities
- Equal access to either pseudoenantiomer

In this talk, we describe a scalable synthesis of a new class of chiral dienes that can be accessed on multigram scales and in both pseudoenantiomeric series. In addition, they can be diversified at a late stage to enable fine-tuning for a particular reaction. The new chiral dienes exhibit high performance in various enantioselective rhodium(I)-catalyzed reactions such as 1,4-additions and 1,2-additions.

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Eunsung LEE
Pohang University of Science and Technology

Abstract: Stable Organic Radicals (feat. N-Heterocyclic Carbenes)

For the past decade, there have been developed numerous organic/main group radicals with an aid of N-heterocyclic carbenes (NHCs). 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-based organic radicals, which include unique structural platforms or nitric oxide.[1] As our continuous efforts to access stable organic radicals, we have designed, synthesized, and characterized 1,2-dicarbonyl radical cations derived from NHCs.[2] 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.

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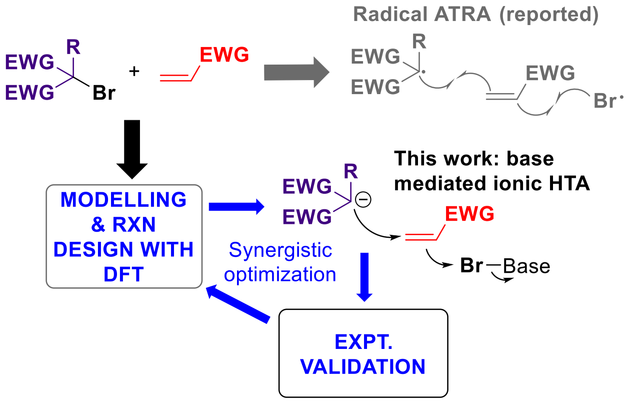
Richmond LEE
University of Wollongong

Abstract: Computational-Experimental Approach to Reaction Design of Novel Halide Transfer and Addition (HTA) Process

In this work, we seek to develop a new synthetic method instigated by halogenophillic substitution (S_N2X) reactivity using our deep understanding of this chemistry.[1,2] Atom transfer radical addition (ATRA) process allows the concurrent construction of $C(sp^3)$–$C(sp^3)$ bond and $C(sp^3)$–X bonds (X is halide) from α-halo carbonyls and unsaturated compounds through radical pathway,[3] but the ionic form is unreported to the best of our knowledge. Exploiting the powerful combination of theory-experimental driven approach, we developed an ionic pathway to concurrently access C(sp3)–C(sp3) and C (sp3)–X bond instigated by halide transfer. We term this ionic ATRA equivalent as Halide Transfer and Addition (HTA) process. Computational studies were done first to predict and establish the viability of the proposed HTA, and experiments were conducted next to verify the theory. More importantly, experimental results also helped shape and improve the theory resulting in a synergistic feedback loop.



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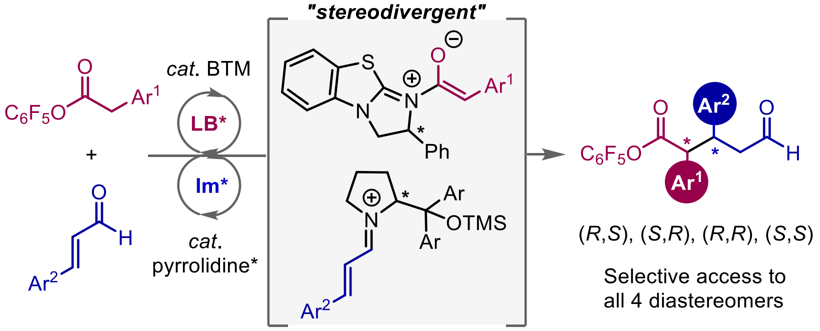
Sarah Yunmi LEE
Yonsei University

Abstract: Catalytic Stereodivergent C–C Bond Formations by Asymmetric Conjugate Additions

The control of stereoselectivity has been one of the central goals in synthetic organic chemistry due to the presence of chiral molecules in a wide range of natural products and pharmaceuticals. Despite remarkable advances in asymmetric synthesis, the development of catalyst-controlled processes that precisely control relative and absolute configurations of multiple stereocenters has been a persistent challenge. In this seminar, I describe methods for the enantio- and diastereodivergent carbon-carbon bond formation catalyzed synergistically by two chiral catalysts that furnishes 1,5-difunctionalized compounds containing two adjacent stereocenters. Specifically, a chiral pyrrolidine in conjunction with either a chiral Lewis acid or a chiral Lewis base can achieve stereoselective conjugate additions of carbon nucleophiles to α,β-unsaturated aldehydes *via* chiral enolate and iminium intermediates. By altering the relative chirality of catalyst combinations, all four stereoisomers of the products are accessible with high enantio- and diastereoselectivity.



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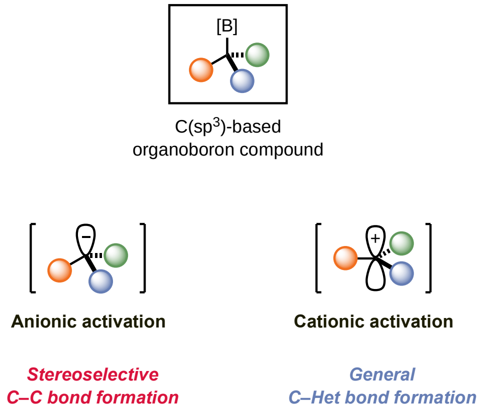
Hong Geun LEE
Seoul National University

Abstract: New Horizons in the Activation of Organonboron Compounds

Novel reactivities of organoboron reagents for the formation of covalent bonds at a carbon atom with sp^3 or sp^2 hybridization are explored. In the first part of the presentation, an integrated synthetic platform of organoboron compounds for the introduction of heteroatoms will be discussed. Based on systematic electrochemical analysis, the electrochemically mediated bond-forming strategy was advanced to be highly effective for the functionalization of sp^3-hybridized carbon atoms with significant steric hindrance. The second half of the presentation covers a stereospecific cross coupling of chiral organoboron reagents. Based on highly stereospecific convey of stereochemical information, enantiopure alph-aryl carbonyl compounds could be synthesized in a straightforward manner.



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2. DOI: 10.26434/chemrxiv-2022-x7ggk-v2

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Yunho LEE
Seoul National University

Abstract: Small Molecule Activation Mediated by Nickel

Activation of small molecules such as NO_x and CO_2 mediated by transition metals is drawing much attention not only due to its importance in understanding various enzymatic reactions but also because they are related to the environmental issues. In this presentation, two topics based on the low-valent nickel chemistry will be discussed. The first topic is about a study focusing on selective CO_2 conversion to CO with synthetic nickel species. Since the binding and reactivity toward CO_2 is controlled in part by the geometry of a L_3Ni scaffold, we have explored the chemistry of low-valent nickel supported by pincer systems (E = N, P or Si), in which the site trans to an E atom is occupied by various ligands, such as NO_x and CO_x. With a structurally rigidified ^{acri}PNP ligand, the Ni(0)-CO species reveals the selective addition of CO_2 to give a nickel(II)-carboxylate species with the expulsion of CO. The closed synthetic cycle for CO_2 reduction to CO was established with a (^{acri}PNP)Ni system.[1] The second topic is about structurally rigidified nickel species utilized to explore NO_x conversion. A unprecedented nickel catalysis for the NO_x conversion and utilization (NCU) technology will be presented. The catalysis starts with converting Ni–NO_x to a nickel nitrosyl species via deoxygenation with CO(g), which is followed by transfer of the in-situ generated nitroso group to organic substrates. Successful catalytic production of oximes from benzyl halides using $NaNO_x$ under mild conditions will be presented. In a key step of the catalysis, a nickel(I)–•NO species activates alkyl halides, which is carefully evaluated by both experimental and theoretical methods.[2]

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Sang-Young LEE
Yonsei University

Abstract: Ionic COF Platforms for Advanced Batteries

With the advent of ubiquitous energy era, which will find the widespread use of smart portable electronics, electric vehicles, and grid-scale energy storage systems, the demands for advanced rechargeable batteries with high energy density and reliable electrochemical performance are rapidly growing. Among numerous material approaches undertaken to address this issue, porous crystalline materials such as covalent organic frameworks (COFs) and metal–organic frameworks (MOFs) have been pioneered as promising alternatives to covnentional battery materials, owing to their versatile structural design, high surface area, long-range ordered structure, and directional ion conduction pathways. Intrigued by this unique chemistry and molecular architecture of COFs, we synthesized a class of ionic COFs and explored their application to batteries, which were rationally designed to act as solid-state electrolytes, electrode materials, and electrode additives. Solid-state electrolytes are needed as a key-enabling material for all-solid-state batteries that have recently garnered considerable attetnion as an attractive candidate for post lithium (Li)-ion batteries. Previous studies on solid-state electrolytes have mostly focused on inorganic-based ionic conductors (*e.g.*, sulfides and oxides). Different from the inorganic electrolytes that have been struggling with practical uses, we synthesized a Li-sulfonated COF (TpPa-SO_3Li) as a solvent-free single Li-ion conductor. Benefiting from its directional pathways, covalently tethered sulfonates, and high number density of Li$^+$, the Li-sulfonated COF showed single-ion conduction behavior without adding Li salts and organic solvents. In addition, this anionic COF structure was coupled with other charge carriers (including zinc ions (Zn^{2+}) as a versatile platform for an ion-conducting medium. For electrode material applications, a redox-active COF (TP–OH–COF) that can accommodate 30 Li$^+$ ions was synthesized for use as a long-cyclable high-capacity Li-ion battery electrode material. This unusual accommodation of Li$^+$ ions in the TP–OH–COF was achieved by alternately tethering redox-active hydroxyl and carbonyl sites on the pore walls. Additionally, we synthesized bipyridine-based COF and quaternized bipyridine-based COF as on-demand electrode additives. These customized COF electrode additives regulated intermolecular electrostatic interactions in the electrodes, thus improving electrochemical performance by simultaneously fulfilling the different requirements of anodes and cathodes.

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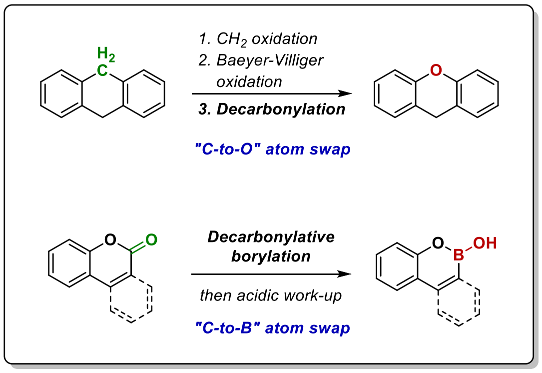
Junqi LI
Iowa State University

Abstract: Atom-Swapping Reaction Sequences Enabled by Nickel-Catalyzed Decarbonylation of Lactones

Single atom changes in a molecule are known to dramatically impact its biological activity, but methods that enable substitutions of atoms embedded in the carbon framework of a molecule remain sparse. We present the development of nickel-catalyzed decarbonylation reactions as the key step towards carbon-to-heteroatom "atom swapping" reaction sequences. By understanding ligand effects in the key elementary organometallic steps, we have expanded the scope of decarbonylative coupling processes to enable atom-swapping transformations in different types of natural products and pharmaceutically relevant molecules.



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Lan-Chang LIANG
National Sun Yat-sen University

Abstract: Mismatched Donor-Acceptor Pairs: Serendipitous Reaction and Structural Chemistry

Ligand design plays an important role in exploratory research on contemporary coordination 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. In particular, 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.

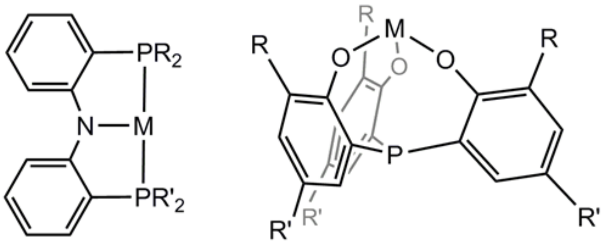

Figure 1. Representative examples of *o*-phenylene derived hybrid ligands

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Yee Hwee LIM
Institute Of Sustainability for Chemicals, Energy And Environment

Abstract: Accessing halogenated molecules through Nature’s catalysts

There are more than 4000 known naturally occurring halogenated molecules.[1] These halogenated natural products can display potent biological activities and specificities, and as such, this feature of halogen incorporation has been exploited commonly in medicinal chemistry to fine tune bioactivities and potency. Chemical halogenation typically requires harsh reagents and often leads to undesired polyhalogenated products. On the other hand, Nature incorporates halogens chemoselectively via a metal halide salts and halogenating enzymes under generally benign conditions.[2] One limitation of Nature’s enzymes is their limited diversity (especially in the case of fluorinase) and substrate specificity. Here, we present our studies on two classes of halogenases – fluorinase FlA1[3,4] and pyrrolic halogenase PrnC[5] which have been applied to access a range of halogenated molecules, including a agrochemical fungicide analog, fludioxonil.

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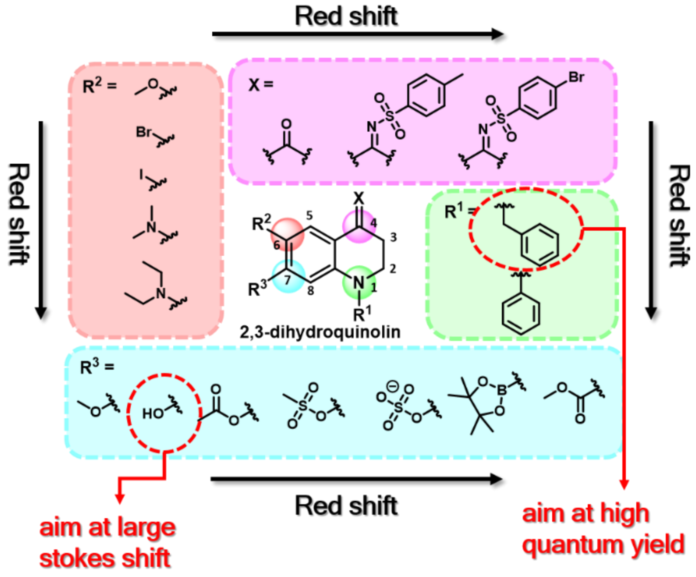
Po-Chiao LIN
National Sun Yat-sen University

Abstract: Fluorescence Turn-on Strategy for On-Demand Biomolecular Interactions

A systematic study in the synthesis and characterization of the environment-sensitive fluorophore, 2,3-dihydroquinolin-4-imine (DQI),[1] allows for expanding structural complexity with significant photophysical properties. The DFT calculation further provides a guideline for preparing DQI analogs with the tailored emission. The solvatochromic property allows the DQI molecule to detect biomolecular interaction with the fluorescence turn-on mechanism. The fluorescence-enrichment strategy has been used in the monitoring of dynamic CAII expression during the growth of zebrafish larvae, as well as cell membrane staining.[2] With the success in tracking proteins of interest, the DQI structure has been further modified for metal ion detection[3] and pH sensing corresponding to chemical and biological stimulation.



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Junzhi LIU
The University of Hong Kong

Abstract: Rational Synthesis of Nanographenes with Non-Alternant Topologies

Incorporation of the non-hexagonal rings into nanographenes (NGs) can significantly affect their electronic and optoelectronic properties, as well as the chemical reactivities.[1-3] Here, we report the first bottom-up synthesis of dicyclohepta[*a*,*g*]heptalene-embedded NG (1, Figure 1), which containing four continuous heptagons and two additional pentagons. To gain new insight into the effect on their electronic and optical properties via the introduction of two continuous heptalenes, various experimental measures, including cyclic voltammetry, Raman, steady UV-vis absorption, and theoretical calculations were carried out on 1 and its structural isomer bischrysene (1R) with only hexagonal rings. Compared with the aromatic 1R, compound 1 presents a distinct anti-aromatic character with a narrower HOMO-LUMO energy gap. Interestingly, this two-heptalenes-inserted 1 exhibited radiative transitions from the S_3 high-lying excited state with bleaching two low-lying excited states emission, which verified by variable-temperature steady-state fluorescence spectrophotometers, as well as supported by the theoretical calculations. Our work reported herein not only provides a new way to the synthesis of novel nanographenes with non-alternant topologies, but also offers the possibility to tune their electronic and optical properties.

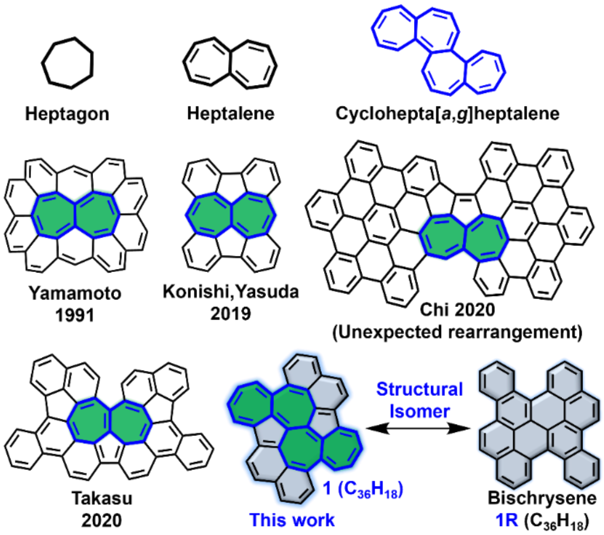

Figure 1. NG 1 with two contiguous heptalene units reported in this work.

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Yi LIU
Lawrence Berkeley National Laboratory

Abstract: Functional Covalent Organic Frameworks with “Irreversible” Covalent Bonds

Covalent organic frameworks (COFs) are functional porous crystalline materials composed of light elements and held together by covalent bonds. Historically, the success of their synthesis has capitalized on reversible covalent bond formation, whose dynamic nature ensures a thermodynamic pathway to periodicity and crystallinity. The intrinsic reversibility however lives within the COFs after its formation, at times becoming the throttling factor that limits the chemical and physical properties of COFs. Considerable research efforts have been devoted to remedying the reversibility of the linkages in recent years.[1] Notable strategies include using less reversible chemical bonds, modifying the linkage post-synthetically, and employing cascade reaction sequences.

Herein I will present our efforts in this direction by highlighting a few examples using the above strategies. In one example, we explored the unusual reversibility of a pyrazine formation reaction and its utilization to build crystalline porous graphitic frameworks, which have shown excellent energy storage properties when employed as cathode materials for lithium ion batteries.[2] We have further employed the Povarov reaction to transform the ubiquitous imine linkages into aromatic quinoline linkages.[3] In the latest example, we utilized the Cadogan reaction to form irreversible heterocyclic linkages via either stepwise or one-pot reactions. The resulting COF has shown excellent intrinsic proton conductivity.[4] We envision such synthetic advances may inspire broader interests in combining new reaction motifs with the reticular concept of COFs for functional porous crystalline materials.

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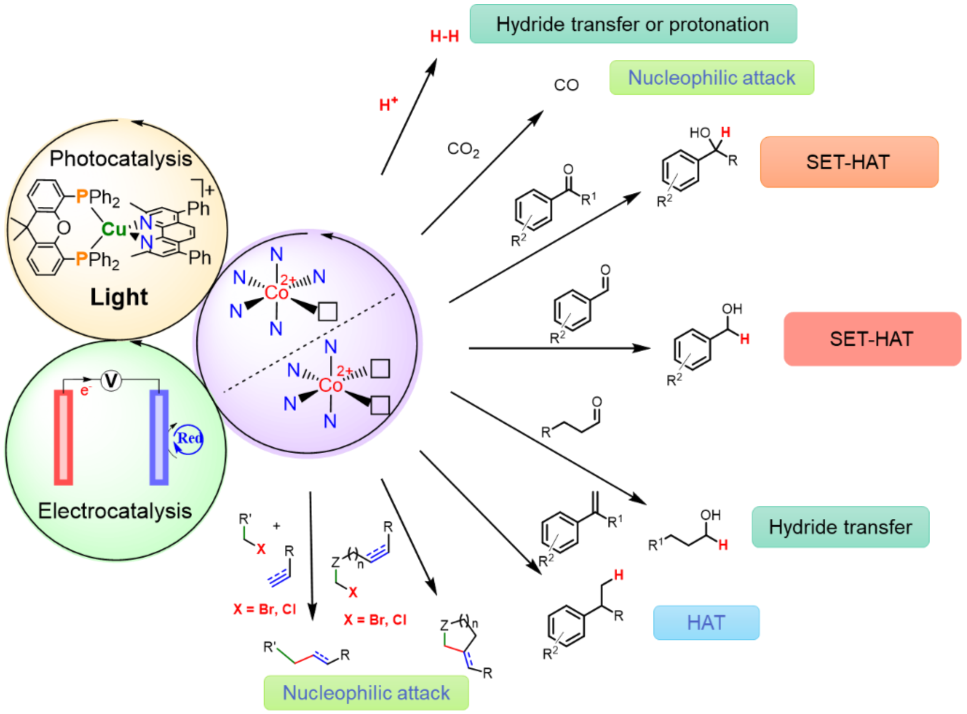
Julio LLORET-FILLOL
Institute of Chemical Research of Catalonia

Abstract: Light-Driven Reduction Chemistry by well-defined complexes

One of the most appealing research areas is the mechanistic understanding of multi-electron multi-proton processes, which is central to transforming small molecules. In this line, we have discovered that well-defined coordination complexes based on the tacn moiety are highly efficient homogeneous catalysts for reducing water,[1] and CO_2[2] and organic substrates such as ketones, aldehydes and olefines.[3] The low valent metal intermediates also promote the challenging visible-light reductive radical C-C bond formations from unactivated chloroalkanes, which open new avenues in photoredox catalysis.[4]

This presentation will discuss these aspects, and how to control the selectivity between water reduction and the reduction of organic functionalities. Mechanism understanding was employed to develop new reactivity and even unlock the reactivity of the Ir-based photosensitizers.



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Hairong LYU
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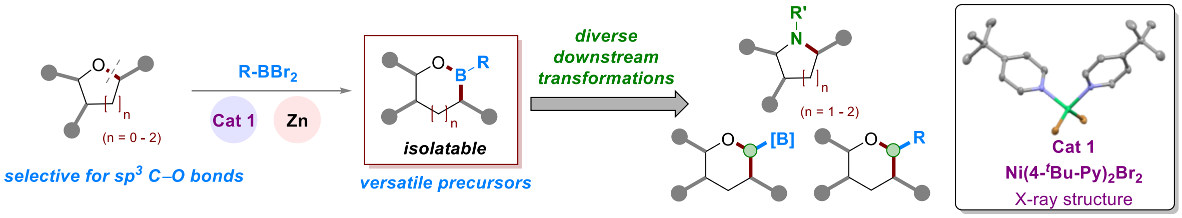
Abstract: Boron Insertion into Alkyl Ether Bonds via Zinc/Nickel Tandem Catalysis

Ether moieties widely exist in feedstock and natural molecules. The inherent robustness and chemical stability of ether carbon-oxygen bonds enable them to serve as structural linkers and protecting groups in organic molecules, while on the other hand bring challenges to their degradation and derivatization. Herein, we report a mild method to cleave and functionalize unactivated ethers through insertion of a boron into the C-O bond. The reaction of cyclic/linear alkyl ethers with dibromoarylboranes in the presence of a tetrahedral Ni(II) catalyst and zinc reductant affords various oxaborinanes (boron-mediated heterocycles) and alkyl boronic acids.[1] Taking the advantage of the versatile C-B bonds, convenient transformations of unactivated ethers into various other functional groups have been achieved, leading to new synthetic applications including "O-to-N" editing, "one-carbon" homologation of cyclic ethers, and ultimately streamlined preparation of bioactive compounds. Experimental and computational mechanistic studies reveal a distinct "cleavage-then-rebound" pathway via Zn/Ni tandem catalysis.



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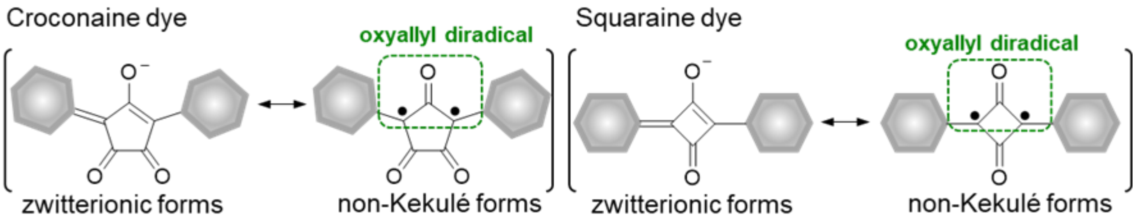
Takeshi MAEDA
Osaka Prefecture University

Abstract: Unveiling Open-Shell Character of Near-Infrared Absorbing Polymethine Dyes with Oxocarbon Moieties

Organic molecules showing near-infrared (NIR) absorption include not only the dyes and polymers with extended π-conjugated systems but also quinoidal polycyclic aromatic hydrocarbons that have intermediate electronic structures between closed-shell and open-shell singlet (diradical) states.[1] According to the perturbation theory, molecules that have sufficiently reduced electronic transition energies corresponding to the near-infrared (NIR) region possibly have a diradical character.[2] In this context, croconaine and squaraine dyes consisting of 4- and 5-membered oxocarbon moieties, respectively, with sufficiently reduced electronic transition energies, are expected to have an intermediate open-shell character. From the structural perspective, these dyes can be described by the resonance between zwitterionic and non-Kekulé oxyallyl diradical forms, as shown below. Nevertheless, the contribution of diradicals has not been experimentally proven so far. Herein, we demonstrate the open-shell character of NIR absorbing croconaine and squaraine dyes with chalcogenopyrylium components through ^{1}H-NMR, ESR spectroscopy and SQUID magnetometric analysis, and X-ray crystallography. We found that the open-shell character impacts the structure and magnetic and photophysical properties of the chromophores. Moreover, these dyes exhibited not only one-photon NIR absorption but also substantial two-photon absorption owing to the diminishment of covalency at the π-bonds.



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Kazuhiko MAEDA
Tokyo Institute of Technology

Abstract: Photocatalytic CO2 Reduction and Water Splitting Using Molecule-Containing Solids

CO_2 reduction into carbon feedstocks through photocatalysis is an attractive means of addressing the problems of global warming and the depletion of fossil fuels. Of particular importance is the development of a photosystem workable under visible light, which accounts for the main component of solar spectrum, toward artificial photosynthesis.[1,2] Along with this, the use of abundant elements as the components of a photocatalytic CO_2 reduction system is also important, and a solid material that is active, recyclable, nontoxic, and inexpensive is strongly demanded.

A hybrid of a visible-light-responsive semiconductor and a metal complex is of interest for application in CO_2 photoreduction, because of the excellent electrochemical (and/or photocatalytic) activity of metal complexes during CO_2 reduction and the ability of semiconductors to efficiently oxidize water to O_2. For example, hybrid systems constructed from a semiconductor (e.g., C_3N_4) and a binuclear metal complex having a redox photosensitizer and a catalytic unit are capable of reducing CO_2 into HCOOH (or CO) according to two-step photoexcitation of the semiconductor and the photosensitizer unit of the metal complex, with high selectivity to a desired product (Figure 1).[2]

We also recently demonstrated that a widespread soil mineral, α-FeOOH (goethite), loaded onto an Al_2O_3 support, functions as a recyclable catalyst for a photocatalytic CO_2 reduction system under visible light ($\lambda > 400$ nm) with the aid of a Ru(II) photosensitizer and an electron donor.[3] This photosystem produced HCOOH as the main product with 80–90% selectivity and an apparent quantum yield of 4.3% at 460 nm. The origin of the produced HCOOH was confirmed by isotope tracer experiments with $^{13}CO_2$ to be the CO_2 introduced in the reaction system. The present work highlights that the use of a proper support material (here, Al_2O_3) is another method of catalyst activation toward the selective reduction of CO_2.

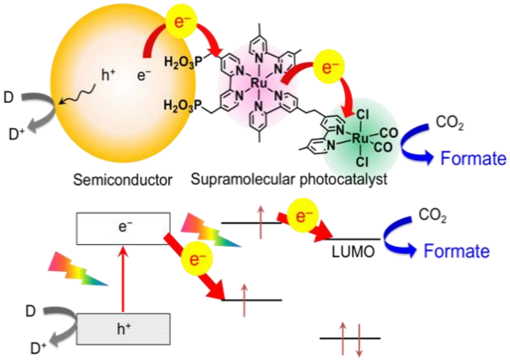

Figure 1. CO2 reduction using a hybrid of a semiconductor and a binuclear metal complex.

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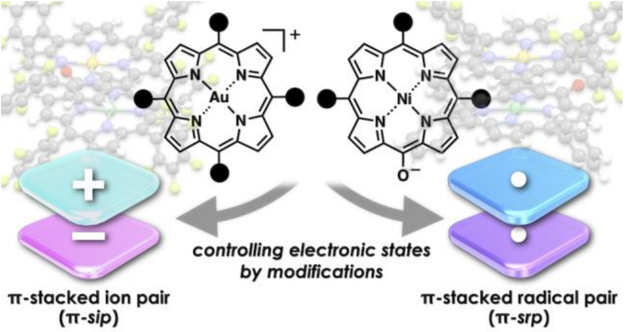
Hiromitsu MAEDA
Ritsumeikan University

Abstract: π-Electronic Ion Pairs: Ordered Arrangement and Radical-Pair Formation



π-Electronic ions with appropriate geometries and peripheral substituents provide assemblies through the interactions between charged building subunits, resulting in fascinating electronic properties. Structures and properties of the assemblies can be controlled by the combined positively and negatively charged species in the assemblies.[1,2] In fact, π-electronic ion pairs comprising porphyrin-based π-electronic anions[3] have exhibited characteristic assembling modes via $^{i}\pi$–$^{i}\pi$ interactions and resulting electronic properties such as solid-state absorption, which was correlated with the arrangement of constituent charged π-systems, and photoinduced electron transfer.[4] On the other hand, ion pairs of porphyrin–Au$^{\mathrm{III}}$ complexes as π-electronic cations, prepared with the combination of various anions including π-electronic anions, formed assemblies as crystals and thermotropic liquid crystals, whose ionic components were highly organized by $^{i}\pi$–$^{i}\pi$ interactions (mainly electrostatic and dispersion forces).[5] Among various combinations of these porphyrin cations and anions (Figure), the "activated" ion pair of *meso*-EWG (electron-withdrawing group)-substituted cation and *meso*-EDG (electron-donating group)-substituted anion exhibited the electron transfer in the steady state according to solvent polarity, resulting in the production of the radical pair. The ESR in frozen toluene revealed the formation of a heterodiradical in a close stacking structure by the antiferromagnetic dipolar interaction and temperature-dependent spin transfer behavior.[6]

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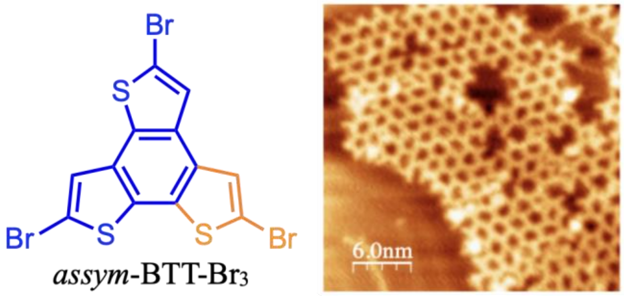
Michio MATSUMOTO
National Institute for Materials Science (Japan)

Abstract: Introducing heteroatoms In Synthetic 2D Polymers – Sulfur and Silicon

The on-surface covalent organic framework (COF)[1] synthesis, often using the Ullmann-coupling type carbon-carbon bond formation reaction on metal surfaces, connects aromatic planar monomers in two-dimensional (2D) geometry and affords π-conjugated 2D crystalline polymers in one atomic thickness.[2] This bottom-up on-surface method enables the precise arrangement of heteroatoms in 2D polymers by introducing the heteroatoms in the monomers with organic synthetic chemistry techniques and offers various synthetic 2D materials. We recently found that these atomic arrangements in the 2D π-conjugated polymer significantly affect the band structures of 2D polymers made from fused thiophenes. Benzotrithiophene (BTT) has two structural isomers, *sym*-BTT and *assym*-BTT (Fig.), by the relative positions of its three sulfur atoms. Unlike the COF structure of *sym*-BTT shows flat band structures, the *assym*-BTT COF structure exhibited distorted band structures.[3] Based on this finding, we synthesized brominated *assym*-BTT (*assym*-BTT-Br$_3$) and obtained 2D polymers made from *assym*-BTT on the Au(111) surface.[4] In this talk, we discuss the importance of arranging heteroatoms in 2D polymers with the atomic preciseness. Furthermore, our recent development arranging silicon atoms in 2D polymers by connecting aromatic monomers with 1,4-disilabenzene will be shared.[5]



assym-BTT-Br$_3$

Fig. Chemical structure of *assym*-BTT-Br$_3$ (right) and STM image of 2D polymer made from *assym*-BTT (left).

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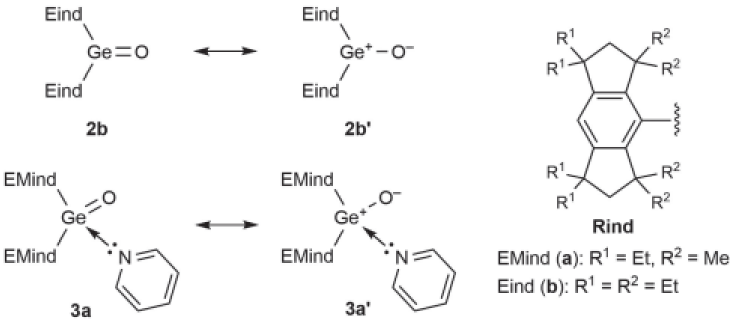
Tsukasa MATSUO
Kindai University

Abstract: Ge=O Double-Bonded Species Bearing Rind Groups

In 2012, we reported the isolation of a monomeric germanone, $(Eind)_2Ge{=}O$ (2b), with a tricoordinate Ge atom bound to a terminal O atom, supported by the bulky Eind (b: $R^1 = R^2 = Et$) groups.[1] DFT calculations and chemical reactions indicate that the Ge=O double-bond is highly polarized with a contribution of the charge-separated form, $(Eind)_2Ge^+–O^–$ (2b'). In the past decade, great progress has been made in the chemistry of the heavier group 14 carbonyl compounds.[2] The discrete molecules of the silanones featuring a free Si=O double-bond were obtained by Kato's, Inoue's, and Iwamoto's groups with the introduction of the appropriate substituents,[3–5] thus Kipping's dream was realized more than a century later.

We now present the formation and reactions of Ge=O double-bonded species having the less bulky EMind (a: $R^1 = Et$, $R^2 = Me$) groups, such as a pyridine (Py) adduct of germanone, $(EMind)_2Ge({=}O)(Py)$ (3a).[6]



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Psaras MCGRIER
The Ohio State University

Abstract: Covalent Organic Frameworks for Catalytic and Energy Storage Applications

Covalent organic frameworks (COFs) are a class of advanced materials that are composed of light elements (C, H, O, N, and B) linked via strong covalent bonds. COFs are generally constructed by using reversible bond forming reactions to yield crystalline materials with high surface areas, low densities, and high thermal stabilities. These features make COFs useful for a variety of applications. This presentation will discuss employing a bottom-up approach to create novel functional COFs that can bind small metal cations (e.g., Li, Ca, etc.), and some low-oxidation state transition metals (e.g., Ni(0), Ag(I), Co(II), etc.). The prospect of utilizing these COFs for applications related to catalysis[1] and energy storage[2,3] will be highlighted.

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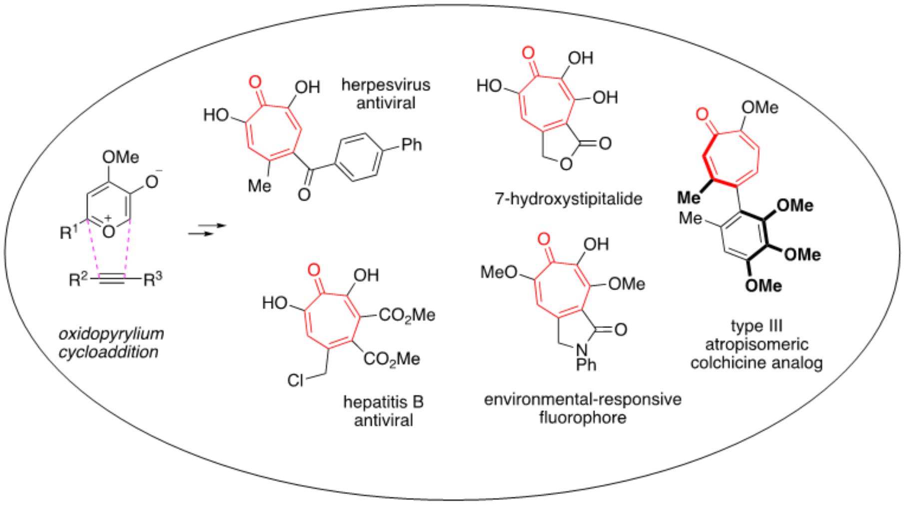
Ryan MURELLI
Brooklyn College

Abstract: Game of Tropones: Studies on the Synthesis and Function of Cycloheptatrienones

Cycloheptatrienone – or tropone – is one of the most well-known non-benzenoid aromatic ring structures, and is described in virtually every undergraduate organic chemistry textbook. Despite this prominence, however, tropone-containing molecules are far less common in the literature than those containing naturally-biased 5- and 6-membered aromatic ring-structures. Never-the-less, they have been identified as key structural elements in a variety of natural products with novel and valuable functions, and thus their synthesis is of active interest to the synthetic organic chemistry community. The following seminar will provide an overview of the Murelli lab's research on the synthesis of troponoids – largely enabled by advances in the intermolecular oxidopyrylium [5 + 2] cycloaddition reaction – and how these synthetic strategies have aided several interdisciplinary programs relevant to medicinal chemistry, chemical-biology, and beyond.[1] More specifically, the talk will touch on our more established studies on the dinuclear metalloenzyme-inhibiting a-hydroxytropolone fragment, disclose some of our recent work on environmental-responsive fluorophores and photoactivatable tags, and describe a new synthetic strategy for accessing and studying colchicine's tubulin-binding AC ring.



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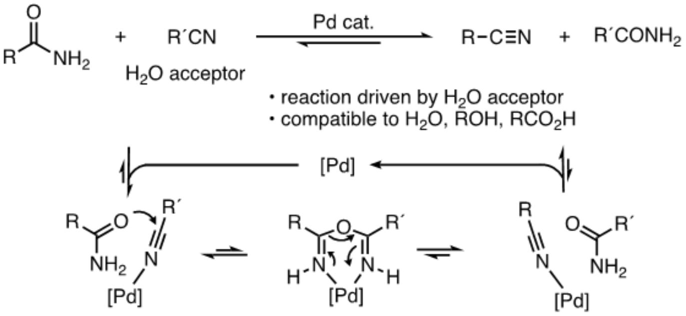
Hiroshi NAKA
Kyoto University

Abstract: Transfer (De)hydration Catalysis

New strategies to dehydrate organic molecules in water are one of the primary interests in synthetic organic chemistry, especially in converting highly hydrophilic biomolecules. While classical dehydration protocols generally require strictly anhydrous conditions, palladium(II)-catalyzed dehydration of amides to nitriles using acetonitrile proceeds under aqueous conditions.[1] This dehydration is chemoselective and reversible, where water is formally transferred from the amide to acetonitrile. However, the range of applicable amides has been limited to relatively electron-rich carboxylic acid amides due to the limited reactivity of acetonitrile. We focused on the reversibility of this reaction and clarified that the use of electron-deficient nitriles (R´CN) as a water acceptor dramatically expands the scope of applicable substrates (Scheme 1).[2] Also, close investigation of the reversible nature in the transfer dehydration catalysis led us to develop transfer hydration of nitriles to amides using carboxamides as a water donor.[3] This method enables the hydration of challenging nitriles (*e.g.* ketone-derived cyanohydrins) to afford the corresponding amides under mild conditions. The talk will cover the development, impact, and mechanism of the transfer (de)hydration catalysis.



Scheme 1. Working model of transfer dehydration catalysis

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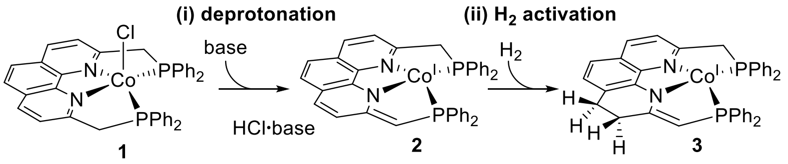
Yumiko NAKAJIMA
National Institute of Advanced Industrial Science and Technology

Abstract: Long-Range Metal-Ligand Cooperation of Co Complexes Bearing a Phenanthroline-Based PNNP Ligand

The concept of the metal-ligand cooperation (MLC), which can achieve various bond cleavage, is recognized as one of the most important tools in catalysis.[1] In this study, the MLC behavior of the PNNP-Co complexes (PNNP = 2,9-bis((diphenylphosphanyl)methyl)-1,10-phenanthroline) were examined.

PNNP-Co chloride 1 underwent deprotonation on the treatment of 1 equiv NaO*t*Bu at ambient temperature, forming 2 bearing a typical useful scaffold for bond cleavage via MLC, a dearomatized ligand backbone with an *exo*-methylene carbon (Scheme 1, step (i)). Complex 2 achieved H–H bond cleavage of H_2 (1 atm) at ambient temperature, to form [Co(PNNP'')] (3), in which two H termini were incorporated in the endocyclic double bond of the PNNP'' ligand backbone (Scheme 1, step (ii)). As a result, rearomatization of the ligand backbone did not proceed through the reaction. This observation is diferent from the previously reported MLC of the acridine- and pyridine-based PNP and PNN pincer systems, where rearomatization of the ligand backbone facilitates the bond cleavage process. By utilizing this intrinsic MLC, we have achived hydrogenolysis of various substrates, such as esters, aryl halides, including fire retardants, under mild conditions.[2] Detailed will be discussed at the presentation.



Scheme 1. H_2 activation via metal-ligand cooperation of the PNNP-Co system.

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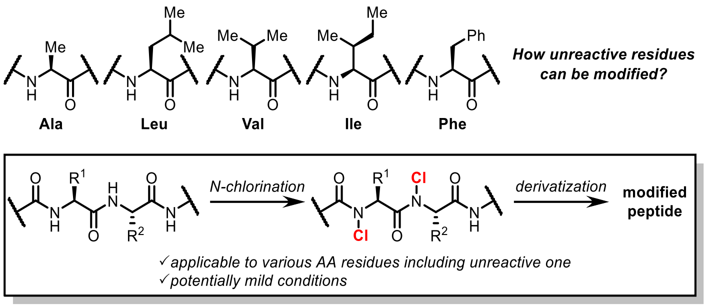
Takeshi NANJO
Kyoto University

Abstract: Oxidative Functionalization of Peptides Enabled by Catalytic N-Chlorination of Amides

Peptide is one of the biopolymers produced by the dehydration of amino acids (AAs) and may play a wide variety of roles in biological organisms. And recently, the peptide is becoming one of the central players in pharmaceutical sciences due to the rapidly increasing interest of middle molecules-based drug discovery. Therefore, synthetic chemists have intensively pursued the efficient methods for chemical modification of peptide chains as well as for the formation of peptide bonds. Now it is relatively easy to modify the peptide chains at specific residues containing reactive functional groups such as amino and sulfide group,[1] however, the less reactive aliphatic AA residue in peptide is still hard to touch.

Based on the background, we started to explore a new synthetic approach for chemical modification of unreactive peptides which do not contain polar functional groups (Figure 1). The key to success is how oxidize such less reactive peptide chain and we envisaged that *N*-chlorination of amide would be a powerful tool for the oxidative functionalization of peptides. Secondary amide is ubiquitous in peptides and some precedent reports shows that *N*-chlorination of conventional amides proceeds via a simple treatment with an electrophilic chlorinating agent,[2] in contrast to the most of *N*-functionalization reactions requiring harsh conditions. We envisioned that a *N*-chloropeptide, which has never been investigated before, would be easily prepared from the native peptide, and converted to a wide variety of non-proteinogenic amino acid structure by the following transformation. This approach does not need any pre-installation of special AAs and we expected that this feature enables not only the shortening of the synthetic route for unusual amino acid-containing peptide fragments but also the late-stage modification of peptide molecules. Herein, we describe a novel *N*-chloropeptide strategy that promotes the late-stage installation of unnatural amino acid motifs into peptide chains.

Figure 1. Strategy for chemical modification of unreactive AA residues



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Akimitsu NARITA
Okinawa Institute of Science and Technology Graduate University

Abstract: Synthesis and Functionalization of Highly Luminescent Polycyclic Aromatic Hydrocarbons toward Photonic Applications

Large polycyclic aromatic hydrocarbons (PAHs) have been attracting renewed attentions for their exceptional optical, electronic, and magnetic properties, both as functional organic materials and as molecular (nano)graphenes.[1] Such PAHs can also be regarded as atomically precise graphene quantum dots (GQDs), which are promising as an environmentally friendly alternative of semiconductor quantum dots, in particular for various photonic applications. We have recently developed a synthesis of dibenzo[*hi*,*st*]ovalene (DBOV) as a PAH with zigzag and armchair edges.[2] DBOV revealed high stability, strong red emission, and stimulated emission (SE), showing the potential, e.g., for lasing. However, absorption losses have suppressed the SE of DBOV derivatives, compromising their optical gain properties. To this end, DBOV was functionalized with two fluoranthene imide (FAI) groups through regioselective bromination and Suzuki coupling.[3] The obtained DBOV-FAI demonstrated red-shifted emission with larger Stokes shift due to the conformational flexibility, and enhanced SE signals with significantly reduced excited state absorption, thus enabling efficient lasing at 720 nm. Moreover, we have more recently obtained dibenzo[*a*,*m*]dinaphtho[3,2,1-*ef*:1',2',3'-*hi*]coronene (DBDNC) with armchair, zigzag, and fjord edges.[5] DBDNC displayed a SE at 710 nm with a longer lifetime than that of DBOV, which was ascribed to the suppression of intermolecular interactions by the nonplanarity. These results provide a further insight into the relationship between the PAH structures and their photophysical properties towards photonic applications.

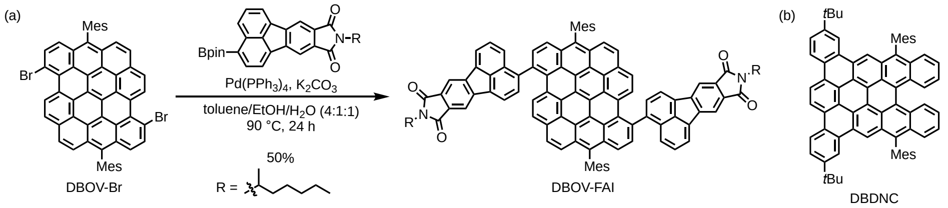

Figure 1. (a) Synthesis of DBOV-FAI and (b) structure of DBDNC.

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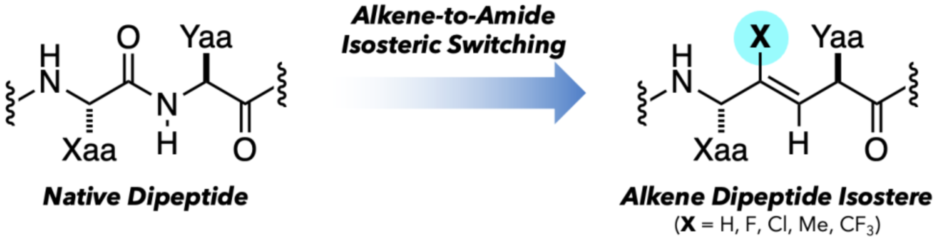
Tetsuo NARUMI
Shizuoka University

Abstract: Peptidomimetic Synthesis via Amide-to-Alkene Isosteric Switching and Beyond

Isosteric switching of a peptide bond with a peptide bond isostere is one of the promising strategies to modify the properties of peptides, including conformation, biological activity, and chemical stability. Halogen-substituted alkenes such as fluoroalkene and chloroalkene have been thought of as one of the ideal surrogates of scissile amide bonds. However, the lack of suitable stereoselective synthetic methods toward those isosteres has hampered their application. As our continuing study on the alkene dipeptide isosteres (ADIs) for ground state mimetics of amide bonds, we have developed multi-gram preparable and diastereoselective synthetic strategies toward (*Z*)-chloroalkene dipeptide isosteres (CADIs),[1-3] including the first stereoselective synthesis of highly functionalized CADIs containing an α,α-disubstituted amino acid (ααAA).[4] Here, we will present the synthetic methods that allow rapid construction of valuable architectures of (*Z*)-CADIs in high yields with excellent (*Z*)-selectivity and diastereoselectivity. In addition, we will demonstrate the peptidomimetic study to probe the contributions of H-bonding interactions in □-sheets by the combination use of (*Z*)-chloroalkene-type and (*E*)-methylalkene-type ADIs. By using the two-type isosteres that are structurally similar but differ in electronic properties, we have been able to examine the contribution of both *interstrand* and *intraresidue* H-bonding interactions on their self-assembly. Details of the synthesis and AFM studies of the peptidomimetics containing ADIs will be presented.



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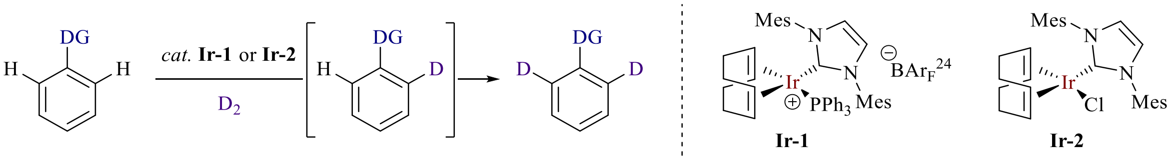
David NELSON
University of Strathclyde

Abstract: Probing Directing Group Effects in C-H Activation Using Hydrogen Isotope Exchange

The successful application of C-H activation in organic synthesis and catalysis relies on overcoming the low reactivity of the C-H bond and achieving selectivity for one such bond amongst the many that are present in most organic molecules. The necessary selectivity can often be achieved using a directing group which is most often a Lewis basic functional group such as an *N*-heterocycle or carbonyl-containing functional group. However, many substrates have multiple such functional groups and so an understanding of selectivity in these systems is desirable.

We have carried out a series of structured competition experiments to assess selectivity in this class of reaction. Initial work deployed a ruthenium-catalysed C-H arylation reaction,[1] but the directing group scope is somewhat limited. More recently, we have used iridium-catalysed hydrogen isotope exchange (HIE) reactions as well-established and operationally simple model reactions to probe selectivity (see Scheme); these rely on a Lewis basic directing group to selectively label the *ortho* aryl C-H position, and can be executed using a very wide range of directing groups.



This presentation will cover some of our recent efforts to use HIE as a model reaction to probe selectivity in directed C-H activation reactions. This will include: the construction of a directing group 'reactivity scale' using competition experiments;[2] the analysis of the kinetic behaviour of these reactions;[3] and new insights into the binding event in the catalytic cycle.[4]

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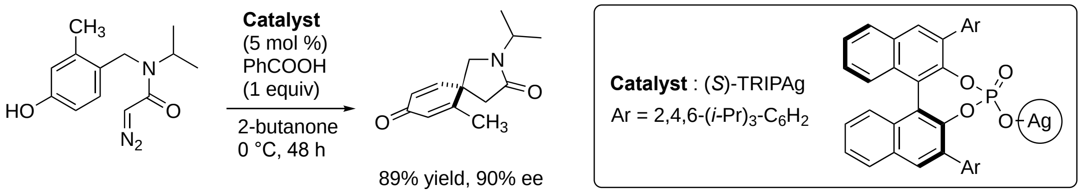
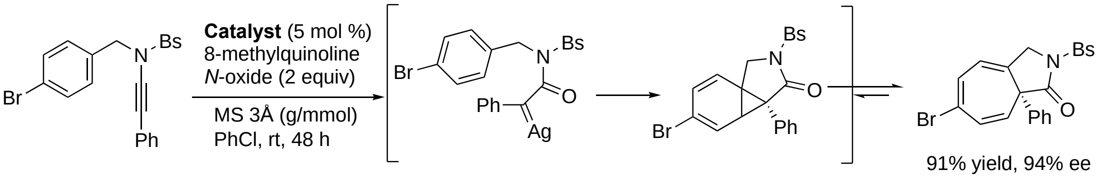
Tetsuhiro NEMOTO
Chiba University

Abstract: Silver-Catalyzed Asymmetric Dearomatization

para-Substituted phenols can react with chirally-modified electrophiles at the *ipso*-position to give spirocyclohexadienones with a quaternary stereocenter. Recently, considerable efforts have focused on developing catalytic asymmetric dearomatization reactions based on this strategy. In addition, chemo- and enantioselective reactions of non-activated arenes with metal carbenoids remain a challenge in the field of organic synthesis because of the divergent reactivity of metal carbenoids. We envisioned chemoselective dearomatization reactions of phenols and non-activated arenes could be realized by using an electrophilic metal carbenoid if the competing reactions such as C–H insertion could be controlled by selection of metal and ligands.

This hypothesis led us to first examine intramolecular phenol dearomatization reaction. The metal screening revealed that, in contrast with the reactions using Rh or Cu catalysts, the reaction using Ag catalyst provided the dearomatized product chemoselectively. Furthermore, when using 5 mol % of chiral Ag catalyst: (*S*)-TRIPAg in 2-butanone in the presence of benzoic acid, the corresponding aza-spirocyclic compounds were obtained in good yield with high enantiomeric excess.[1] We also examined the dearomatization reaction via Büchner reaction using the same catalyst system. When using 5 mol % of the catalyst, the corresponding cycloheptatriene derivatives with a quaternary stereocenter were obtained in good yield with high enantiomeric excess using ynamide derivatives and quinoline *N*-oxide as substrates. Further functionalization based on the norcaradiene-cycloheptatriene equilibrium was performed in the presence of a dienophile, affording the polycyclic-fused molecules via [4+2]-cycloaddition in a highly diastereoselective manner.[2]





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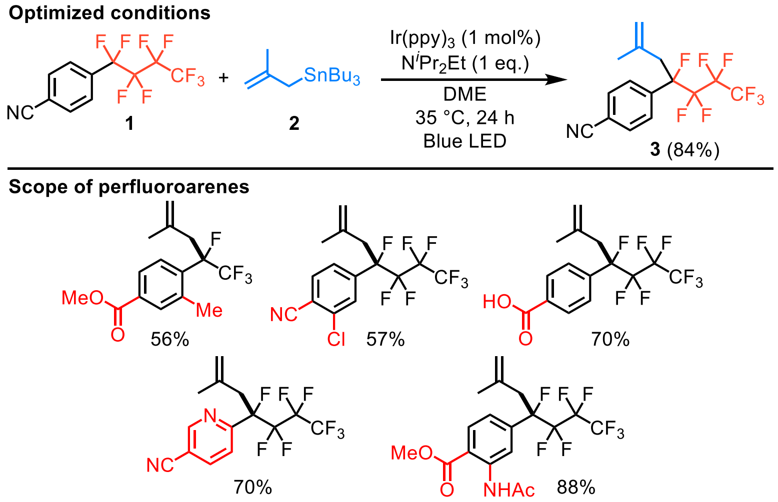
Yoshihiro NISHIMOTO
Osaka University

Abstract: Photoredox-Catalyzed Defluoro-Allylation of Perfluoroalkylarenes Using Allylic Stannanes

Organofluorine compounds have been widely used in pharmaceutical, agrochemical, and material sciences since introducing flurorine atoms brings about specific effects. A selective transformation of selective carbon–fluorine (C–F) bond is straightforward strategy for the synthesis of multi fluorinated compounds from perfluorinated compounds. In the last few years, various type of methods for C–F bond transformation has been reported. There are, however, few reports for mono-defluorination of perfluoroalkyl compounds because of large steric hindrance of perfluoroalkyl group. In this study, photoredox-catalyzed mono defluoro-allylation of perfluoroalkylarenes have been achieved.[1]

The reaction of nonafluorobutyl arene 1 with methallylstannane 2 in the presence of Ir(ppy)$_3$ (1 mol%) and *i*Pr$_2$EtN under blue LED irradiation gave the allylated product 3 in 84% yield. Various perfluoroalkylarenes were applicable and the reaction system exhibits a good compatibility of functional groups.



Next, oxyl free radical as a radical trap reagent for transformation of perfluoroalkylarenes was used. Blue LED irradiation of the mixture of nonafluorobutylarene 1 and an oxyl free radical reagent with a photocatalyst afforded a defluoro-aminoxylated product in a good yield. Further C–F bond transormation of the aminooxylated product with various organo silicone reagents was achieved to give functionalized perfluoroalkyl alcohols.

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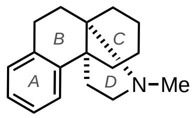
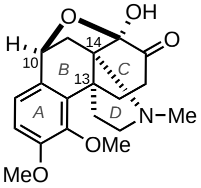
Minami ODAGI
Tokyo University of Agriculture and Technology

Abstract: Total Synthesis of Hasubanan Alkaloids Based on Oxidative Phenolic Coupling Reaction and Aza-Michael Reaction

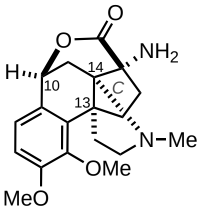
Hasubanan alkaloids are a large family of natural products isolated mainly from plants of the genus *Stephania*, and have a common tetracyclic skeleton containing a pyrrolidine ring (Hasubanan skeleton, 1, ABCD-ring). To date, more than 40 congeners with different oxidation states and functional groups have been identified, and they show a wide range of biological activities, such as antivirus, antimicrobial, and cytotoxicity.[1] With the synthetically challenging structures of these alkaloids as well as their important biological activities, numerous synthetic efforts have been reported in the past several decades.[1] In this presentation, our synthetic approaches for hasubanan alkaloids will be discussed based on the oxidative phenolic coupling reaction and subsequent intramolecular aza-Michael reaction. In particular, synthesis of (+)-stephadiamine (3) was achieved from (–)-metaphanine (2) using a bioinspired "aza-benzilic acid-type rearrangement" as a key reaction.[2] In the synthesis of (–)-cepharatine A (4), the construction of its characteristic azabicyclo[3.3.1]nonane motif (C,D-rings) was attained based on a cascade reaction involving the retro-aza-Michael reaction/ hemiaminal formation.[3]



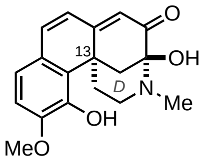
Hasubanan skeleton **1**



(–)-Metaphanine (**2**)



(+)-Stephadiamine (**3**)



(–)-Cepharatine A (**4**)

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Kentaro OKANO
Kobe University

Abstract: “Snapshot” Trapping of Transient Aryllithium in Batch

Microflow chemistry allows the use of highly unstable organolithium compounds, facilitating the development of previously “impossible” chemical transformations in synthetic organic chemistry, and this presentation will describe our recent advances in this area. Our approach toward a selective trapping of these organolithium compounds in a batch reactor led to the development of a finely tuned in situ transmetalation using zinc halide diamine complexes. The reaction rate is controlled by the appropriate choice of diamine ligand. This method was applicable to a wide range of brominated azoles enabling deprotonative functionalization, which was used for a divergent synthesis of both a biologically active azole and its constitutional isomer.1 The scope and selectivity of the related reactions in the context of the total synthesis of biologically active natural products will be also discussed.

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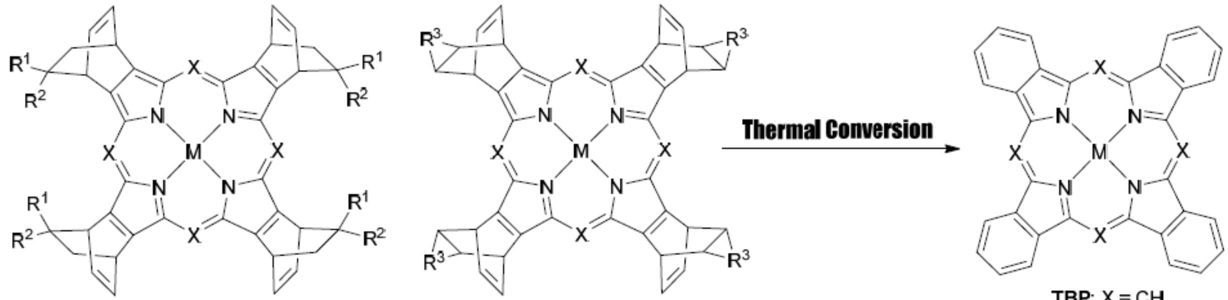
Tetsuo OKUJIMA
Ehime University

Abstract: Synthesis of the soluble precursors of tetrabenzoporphyrin and phthalocyanines

Much attention has been focused on the organic semiconducting molecules due to their potential applications for organic light emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic field effect transistors (OFETs). Tetrabenzoporphyrin (TBP) and phthalocyanine (Pc) have the advantage of easy optimization of molecular structure, low HOMO-LUMO energy gap, and thermal and chemical stability. We have reported the synthesis of tetrabenzoporphyrins (TBPs) by retro Diels– Alder reaction of the corresponding bicyclo[2.2.2]octadiene-fused precursors 1 and their application for OFET fabricated by solution process.[1] A development of the solution process for these materials is necessary in order to provide low-cost and large-area of OFETs and OPVs with high performance. In 2008, We have reported synthesis of extremely soluble TBP-precursors 2 and Pc-based OFET heating after spin-coating of 9.[2] In order to control the solubility and the conversion temperature, thermally convertible precursors 3–6, 7, 8 and 10 were synthesized. The precursors 3, 4, 7 and 8 showed high solubility and were converted into TBPs by heating at 180–330 °C. OFETs based on TBP were fabricated by thermal conversion after spin-coating of the precursors to show good carrier mobility of 10^{-6}–10^{0} cm^{2} V^{-1} s^{-1}.[3]



1: $R^1 = R^2 = H$, X = CH
2: $R^1 = R^2 = Me$, X = CH
3: $R^1 = Et$, $R^2 = Me$, X = CH
4: $R^1 = R^2 = Et$, X = CH
5: $R^1 = R^2 = H$, X = N
6: $R^1 = R^2 = Me$, X = N

7: $R^3 = CH_2$, X = CH
8: $R^3 = CH_2CH_2$, X = CH
9: $R^3 = OCMe_2O$, X = N
10: $R^3 = CH_2CH_2$, X = N

TBP: X = CH
Pc: X = N

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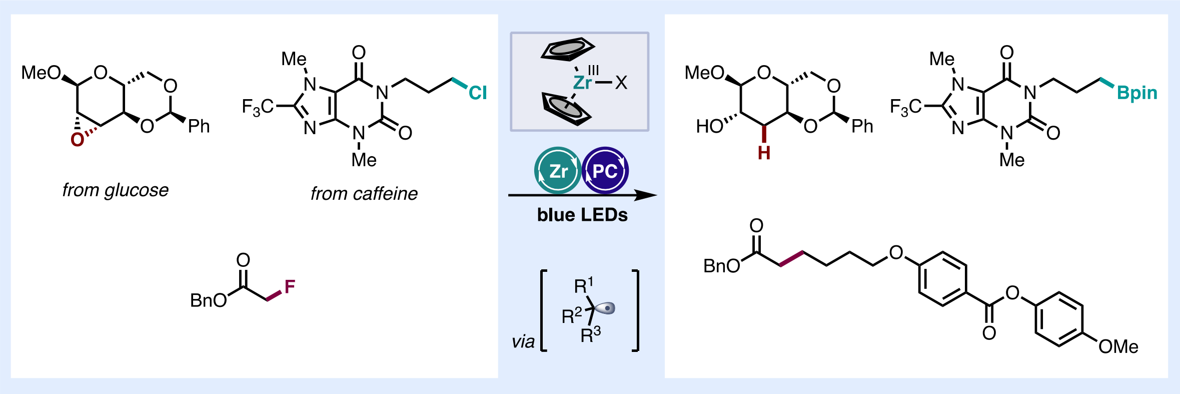
Eisuke OTA
Waseda University

Abstract: σ-Bond Cleavage by Photoredox/ Zirconocene Catalysis

Carbon-centered radicals intrigued intermediates in organic synthesis have been generally formed from well-designed radical precursors. The methodologies to produce carbon-centered radicals by σ-bond cleavage of the previously inaccessible bonds would significantly contribute to the expansion of synthetic strategy. Particularly, the mild methods applicable to highly-functionalized compounds may minimize synthetic steps and have inherent advantages in the context of the rapid construction of complex molecules. In parallel, σ-bond cleavage would serve as a powerful tool to tailor the sp^3 carbon-rich architecture. In this regard, we have sought to develop redox-neutral and mild bond cleavage by photoredox catalysis activating challenging σ-bonds.
Herein, we achieved the cleavage of C–O, C–Cl, and C–F bonds by zirconocene/photoredox catalysis. These protocols are proposed to be engaged with zirconocene (III) and affords carbon-centered radicals, which can undergo numerous functionalization with different radical trapping agents. The processes proceeded under mild conditions and accommodated a wide range of substrates, including derivatives of natural products and pharmaceuticals.



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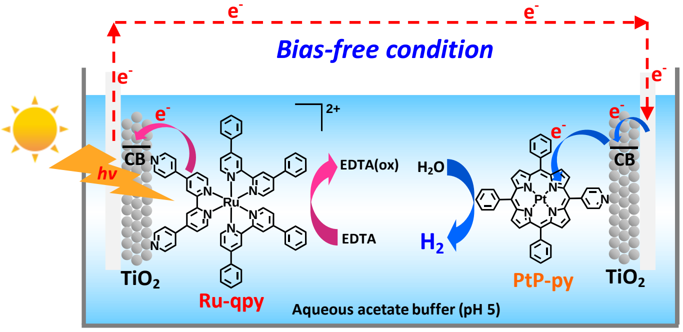
Hironobu OZAWA
Kyushu University

Abstract: Functional-Molecule-Modified Mesoporous TiO2 Electrodes for Electrochemical and Photoelectrochemical Water Splitting

Photoelectrochemical water splitting has attracted considerable attention since H_2 and O_2 can be obtained separately by this method. In this regard, extensive efforts have been thus far devoted in this decade to develop a “molecular-based” photoelectrochemical cell (PEC) for water spitting. Efforts have been also made in our group to achieve such a molecular-based PEC consisting of two mesoporous TiO_2 electrodes modified with functional molecules having pyridine rings as anchor units.[1-4] Solar-driven bias-free H_2 production in the presence of a sacrificial reagent is achieved by the molecular-based PEC consisting of two TiO_2 electrodes individually modified with a molecular photosensitizer (Ru-qpy) and a water reduction molecular catalyst (PtP-py) as shown below.[3] In addition, electrochemical overall water splitting with a relatively small applied overpotential (ca. 1.0 V) is also achieved by using two TiO_2 electrodes individually modified with PtP-py and a water oxidation molecular catalyst.[5] In the presentation, several recent results of our studies on the functional-molecule-modified TiO_2 electrodes for photoelectrochemical water oxidation[6] and electrochemical CO_2 reduction[7] will be discussed.



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Jin Kyoon PARK
Pusan National University

Abstract: Highly Regio- and Stereoselective Access to Bi- and Trimetallic Skipped (Z,Z)-Dienes

While multi-component coupling reactions are successful in regio- and stereoselective assemblage, incorporation of metallic group in skipped dienes is scarce. For instance, Trost group reported pioneering work on Ru-catalyzed two-component alkene-alkyne coupling in 2015.[1a] Relevant to a three-component coupling approach, Mastral group discovered a synergistic copper/palladium catalytic system to couple allyl carbonate and alkyne with bis(pinacolato)diboron (B_2Pin_2).[1b] Ge group has also reported an elegant atom-economic catalytic method to access boryl-functionalized (*E*,*Z*)-1,4-dienes by taking advantage of a chromium(I) hydride intermediate.[1c] To our knowledge, however, analogous coupling strategies between two types of electronically-differentiated C−C π systems employing unsymmetrical interelement reagents (e.g. [Si]-[B]) remain unknown. Herein, a highly stereo- and regioselective multicomponent approach to access (*Z*,*Z*)-skipped 1,4-dienes decorated with silyl and boryl functionalities has been described.[2] This Pd-catalyzed orchestrated atom economy union proceeds without the use of phosphine ligand via a neighboring amide group chelation. A variety of alkynes, as well as allenamides, could be employed to react with Me_2PhSi−Bpin in good yield and excellent selectivity.

Acknowledgement

This study was supported financially by the National Research Foundation of Korea (NRF) (2019R1A2C2004902 and 2022R1A4A2000778)

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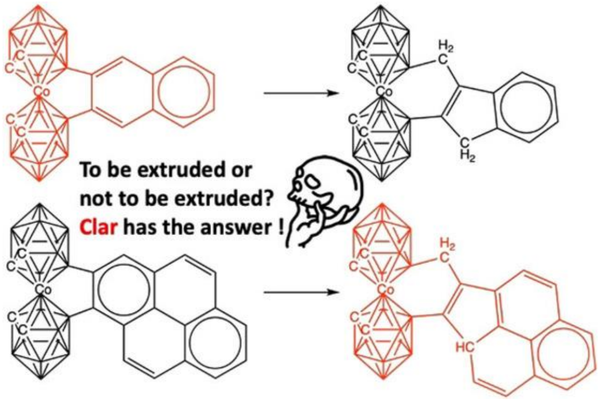
Jordi POATER
Universitat de Barcelona

Abstract: Aromaticity and Extrusion of Benzenoids linked to [o-COSAN]-: Clar has the Answer

Experimentally, benzenoids linked to [*o*-COSAN]$^-$ in some cases suffer extrusion (i.e., naphthalene and anthracene), whereas in other cases do not (i.e., benzene, pyrene, and perylene).[1] We have shown that benzenoids linked to [*o*-COSAN]$^-$ are prone to be extruded only in the case the number of π-sextets is not reduced during the extrusion. This is consistent with two opposing forces that coexist at the junction between the metallacarborane and the aromatic ring. One tends to make the metallacarborane more comfortable, with less strain energy, and the other tends to make the aromatic ring more comfortable, with higher Aromatic Stabilization Energy, ASE. If the ASE is greater, the aromatic ring will be retained, but if part of the ASE can be secured by localizing it elsewhere in the molecule by sliding the aromaticity, then extrusion takes place. Therefore, the answer to the question to be or not to be extruded is found in a simple model such as the Clar's π-sextet theory. Clar has the answer.[2-6]



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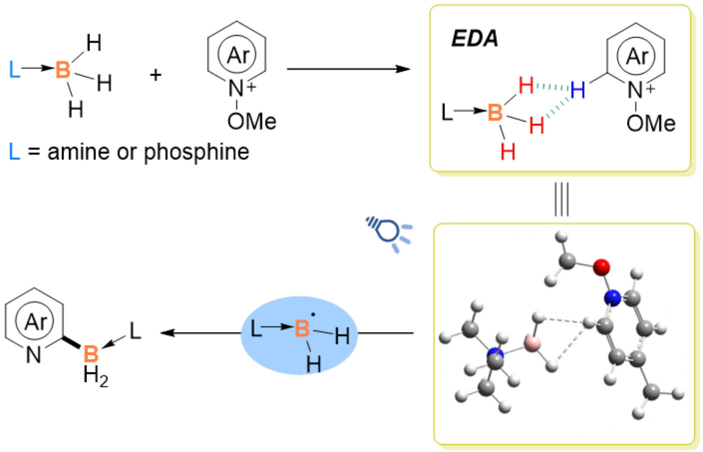
Yangjian QUAN
Hong Kong University of Science and Technology

Abstract: Photoinduced Dehydrogenative Borylation via Dihydrogen Bond Bridged Electron Donor and Acceptor Complexes

The versatile applications of organoboron compounds ranging from synthons to pharmaceuticals promote the development of methodologies for their preparation. Boron-centered radial has exhibited promising potential for C-B bond construction.[1] Very recently, we developed a photochemical electron-donor-accepter (EDA) system for the convenient access to boron-centered radical with no need of external radical initiator and photosensitizer. Amine or phosphine borane was *first* disclosed as the electron donor to integrate with pyridinium acceptor via a B–H$^{\delta-}$···H$^{\delta+}$–C dihydrogen bond. Upon illumination, single electron transfer from borane to pyridinium ion afforded the boryl radical, which then reacted with pyridinium salt to deliver α-borylated pyridine derivatives. This investigation is anticipated to pave an innovative avenue towards boryl-radical-intermediated borylation with good functional group compatibility.



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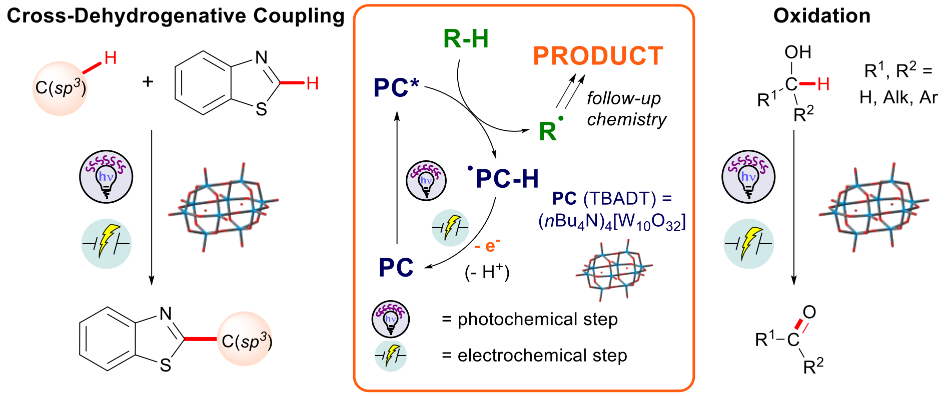
Davide RAVELLI
The University of Pavia

Abstract: Merging decatungstate photocatalysis with electrochemistry

Photocatalyzed hydrogen atom transfer (HAT)[1] is a powerful tool in organic chemistry for the smooth manipulation of C–H bonds via highly reactive radical species. Our group is interested in the development of methodologies based on this reaction manifold through the use of tetrabutylammonium decatungstate (TBADT, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$)[2] as the photocatalyst (PC in Scheme 1). Upon irradiation, the excited PC* cleaves homolytically (often with high chemo- and regioselectivity) the C(sp^3)–H bond in a variety of organic derivatives (R–H),[2] being converted in a singly-reduced form featuring one extra electron (H-PC$^\bullet$, $H^+[W_{10}O_{32}]^{5-}$). Intriguingly, the merging of photocatalysis and electrochemistry offers a smart option to turn-over the spent PC, avoiding the need to employ a (sacrificial) chemical oxidant (framed mechanism in Scheme 1).[3]



Scheme 1. General mechanism of decatungstate-based photoelectrochemical processes (framed) and relevant synthetic applications for cross-dehydrogenative couplings (left) and oxidations (right).

Along this line, we hereby report our recent results in the realization of net-oxidative, photoelectrochemical processes based on decatungstate photocatalysis. Thanks to this strategy, the cross-dehydrogenative coupling of unactivated aliphatic hydrogen donors (e.g., alkanes) with a range of benzothiazoles has been developed (left part in Scheme 1).[4] In a different application, we developed a strategy for the mild oxidation of both benzylic and aliphatic alcohols (either primary or secondary) under chemical oxidant-free conditions, selectively leading to the corresponding carbonyls.[5]

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Michael REITHOFER
University of Vienna

Abstract: Insight into Carbene stabilized Gold Nanoparticles

In the quest to develop highly stable nanoparticles, *N*-heterocyclic carbenes (NHC) have emerged as an alternative to thiol-based ligands for stabilizing metal nanoparticles (NPs), as the metal-NHC bond is usually much stronger than the corresponding metal-thiol bond. This should result in more stable NPs which are less susceptible to ligand exchange reactions. Over the last decade an increasing number of NHC stabilized NPs have been reported and significant effort was made in utilizing these compounds, such as for bioimaging, sensing and also heterogeneous catalysis.[1]
We are interested in NHC-stabilized AuNPs whereby the NHC is derived from the natural chiral pool.[2,3] For this, L and D- histidine was converted into its imidazolium salt using methyl iodine. Subsequent reaction with Ag_2O followed by the addition of $[Au(SMe_2)Cl]$ yields the corresponding organometallic gold chloride complex, which can subsequently

be reduced to histidine-2-ylidene stabilized AuNPs. Due to the chiral nature of histidine, dichroic effects can be detected in circular dichroism spectroscopy. Further water-soluble and pH-responsive histidine-2-ylidene stabilized AuNPs can be obtained through a free unprotected C-terminus of the employed histidine.[4]
This talk will also touch on the first examples of protic acyclic diamino carbene stabilized AuNPs (ADCAuNPs).[5] Compared to NHCs, which are often challenging to asymmetrically functionalize, ADCs have high synthetic flexibility allowing not only the fine adjustment of steric and electronic properties, but also the ease of access of non-symmetric substitutions. Through a series of ADC-stabilized AuNPs, we demonstrate that ADC can be an alternative to NHCs to access functionalized carbene-stabilized AuNPs, with comparable stability but often better structural flexibility.

Acknowledgements
Financial support by the University of Vienna is gratefully acknowledged. This work was supported by the Austrian Science Fund (FWF) Stand-alone grant no. P-34662

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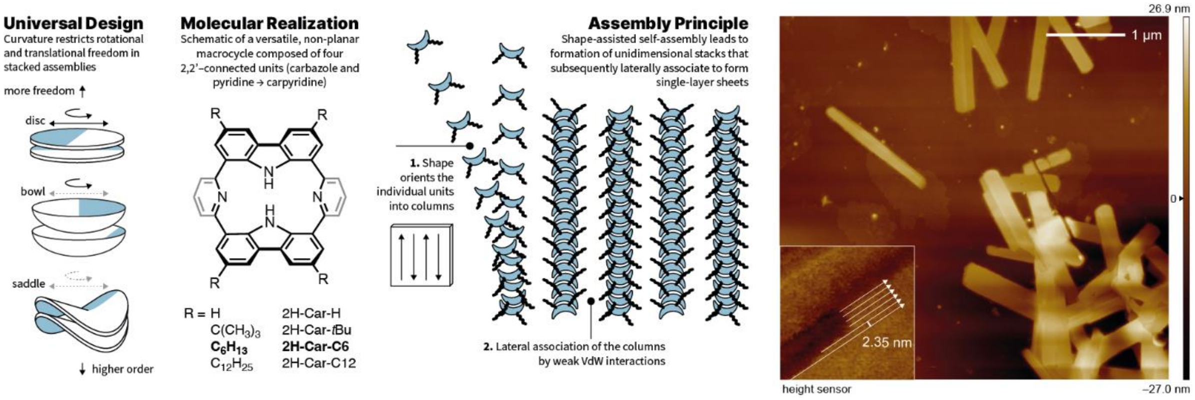
Michel RICKHAUS
University of Zurich

Abstract: Shape-Assisted Self-Assembly of Curved π-Systems

In a typical self-assembly setting, a core is decorated by suitable sidechains that induce supramolecular polymerization. While this approach has led to spectacular assemblies, the core has almost always been seen as a rigid platform from which to append functionality rather than as an integral, defining part of the unit. The core mission of our (young) group is to investigate the role that molecular topography – the form– plays in the assembly process. With emphasis on synthetic solutions, we construct molecular core topographies that we think to be beneficial to supramolecular polymerization - we coined this approach shape-assisted self-assembly (SASA).



We were very recently able to demonstrate[1] that indeed, a simple negatively curved polyaromatic building block (about 2 nm wide, including sidechains) can instigate order on the micrometer(!) scale with astonishing aspect ratios (about 1:1000:100’000) and edge-definition – directly in a common organic solvent (toluene). The paradigmatic shift is that these soft matter monolayered sheets/flakes are not held together by conventionally employed non-covalent interactions like hydrogen-, ionic, or coordinative-bonding. By bringing the shape of the core into the third dimension, we succeeded in driving these assemblies to high order mainly by curved π–π interactions. I will share key (form)-concepts for π-systems to act as information carriers for SASA, insights into our current systems and strategies beyond to obtain control over the – in our case predicted – secondary structure to yield tertiary superstructures.

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Masaichi SAITO
Saitama University

Abstract: Lone-pair Interactions between Non-bonded Heavy Atoms to Produce σ- Aromatic Compounds and a Stable σ-Delocalized Radical

The extension of electronic delocalization has long been one of the important research topics in various fields of chemistry, and π-delocalization in double-bond conjugation and σ-delocalization in polysilanes have maily been investigated. On the other hand, σ-delocalization is also possible between non-bonded atoms. In a geometric constraint, lone-pair interactions on non-bonded atoms can produce σ-delocalization without a bonding framework.1 To closely orient lone pairs on non-bonded atoms, the utilization of rigid platforms such as aromatic skeletons is of great use.2 We have focused on a benzene platform and synthesized multi-arylselenyl-substituted benzenes. As the number of adjacent selenium atoms increases, the HOMO energy level increases (Figure 1). Increase in steric congestion makes the HOMOs composed of σ-symmetric delocalized orbitals with anti-bonding intereactions. Oxidation of the hexa-substituted compound affords a dication bearing (σ+π)-double aromaticity,3 while that of the penta-substituted one provides a stable σ-delocalized cation radical.

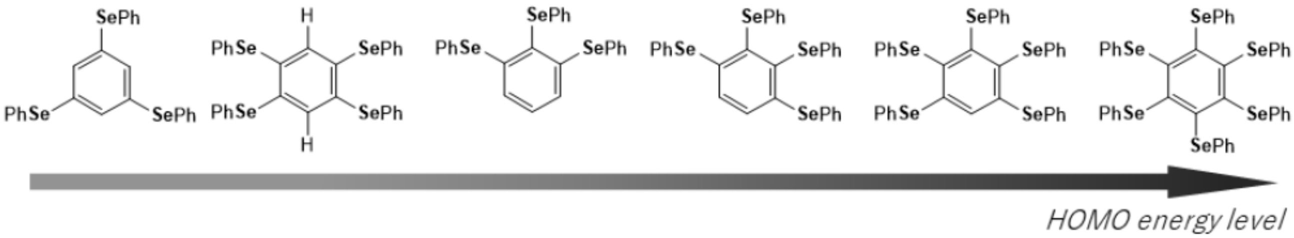

Figure 1. The multi-arylselenyl-substituted benzenes in this study.

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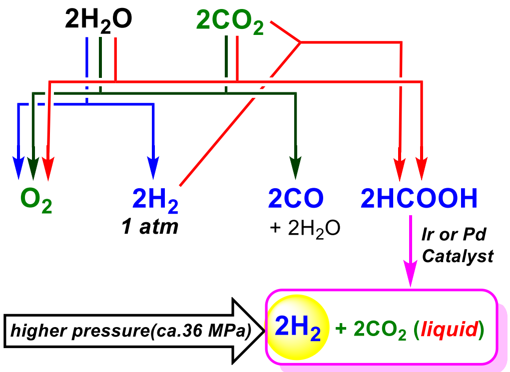
Ken SAKAI
Kyushu University

Abstract: Advanced Aspects on the Mechanisms of Catalytic Water Splitting and CO^2 Reduction

Among various approaches attempting to develop renewable energy sources, solar hydrogen production via water splitting has received an increasing attention in relation to the recent advancement in the hydrogen fuel cell technology. The combustion energy after storing two reductive equivalents (2e) decreases in the order of H_2 (he/2e) > CO (0.99he/2e), HCHO (0.99he/2e) > HCOOH (0.89he/2e) > CH_3OH (0.85he/2e) > CH_4 (0.78he/2e) (he/2e =286 kcal/mol). The source of electrons and protons can be produced in the artificial photosynthetic water oxidation process ($2H_2O + 4h\nu \rightarrow O_2 + 4H^+ + 4e^-$). Among these fuels, only formic acid and methanol are liquid and possess superior characteristics from a viewpoint of energy density together with the feasibility in refueling and transportation in ambient conditions. Further, formic acid has a remarkable potential as a source of *high-pressure* H_2 because of its reversible conversion capability: HCOOH ↔ $H_2 + CO_2$ (ΔG = -12 kcal/mol; see figure). The production of $\{O_2+2HCOOH\}$ is advantageous owing to the spontaneous separation of the two products into the gas and aqueous phases, while the production of $\{2H_2+O_2\}$ or $\{2CO+O_2\}$ yields a flammable gas mixture. With these perspectives in mind, our recent interests still concentrate on the basic studies towards the improvement of our understanding on the mechanisms of water oxidation and reduction together with CO_2 reduction using various transition metal molecular to heterogeneous catalysts.[1-6] We succeed to develop and investigate the environmentally friendly photocatalytic CO_2 reduction in fully aqueous media.[1-3] We have advanced our understanding on the mechanisms of



catalytic CO_2 reduction by DFT.[2-4] We have also advanced our studies on two-electrode solar water splitting systems which permit H_2 separation at a dark cathode.[5] A quite new topic in our group is the mechanistic studies on the electrocatalytic hydrogen evolution reaction by platinum subnanoclusters.[6]

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Ken SAKAUSHI
National Institute for Materials Science (Japan)

Abstract: Coordination Frameworks as Multielectron Transferring Battery Electrode Materials

High-performance yet cost-effective advanced rechargeable battery is a game-changing device for effective use of electricity supplied from wind and sun and achieve "carbon neutrality". The criteria of advanced battery are extraordinarily challenging: (1) Energy density of 500 Wh/kg in a battery pack form; (2) Price with < 100 $/KWh; (3) Duration with > 10 years.[1] In addition, because enormous number of devices are necessary, this battery should be constituted of sustainable elements. However, so far, there is no such battery system to satisfy whole these criteria. Here coordination frameworks (CFs) are shown to be one of possible candidate electrode materials for such advanced batteries.[2-5] A key property in CFs is the designer electronic structure: we can tune their electronic properties by selection of metal cation and linkers;[6,7] therefore, we can also control the electrochemical properties of CFs. As the result, the bis(diimino)copper framework was found to show electron-transfer-number of 3.5 with cation/anion co-redox mechanism together with a dual-ion mechanism. In this talk, the role of the cation–anion interactions for this property will be shown by using an experiment/theory collaboration applied to a series of the model electrode systems based on different metal–nitrogen bonds. These models provide designer multielectron-transfer due to the tunable π-d conjugated electronic structures. In this work, we show that, in addition to tunable electronic structures, it is found that the specific cation-anion bonds in CFs show a unique reversible rearrangement upon electrochemical Li-intercalation. This dynamic structural change can be seen as an analogue to the well-known flexibility to host-guest interactions of this type of materials, for example, upon uptaking various small molecules,[8,9] and this dynamic process is also an essential for a significant reversible multielectron-transfer property.

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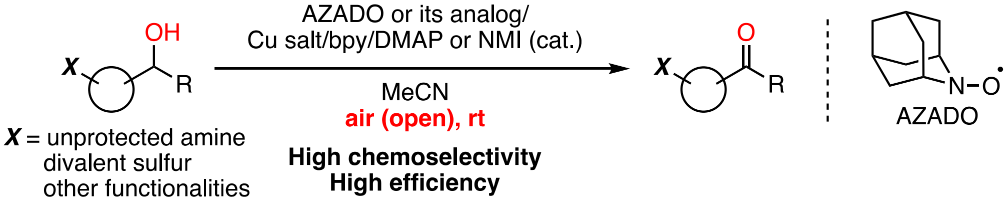
Yusuke SASANO
Tohoku University

Abstract: Highly Chemoselective Aerobic Alcohol Oxidation Co-catalyzed by Nitroxyl Radical and Copper

The oxidation of alcohols into their corresponding carbonyl compounds is one of the most fundamental transformations in organic chemistry, and thus numerous selective alcohol oxidation methods have been developed. Nevertheless, the direct oxidation of alcohols having unprotected amino groups to their corresponding amino carbonyl compounds often suffers from poor yield owing to either the non-productive or destructive interaction between an electron-rich amino group and the oxidant, which reflects immature state-of-the-art of alcohol oxidation.

We have disclosed a highly chemoselective aerobic oxidation of unprotected amino alcohols featuring 2-azaadamantane *N*-oxyl (AZADO)/copper cooperative catalysis.[1] The catalytic system developed enables the selective oxidation of alcohols in the presence of unprotected tertiary, secondary, and primary amines to afford amino carbonyl compounds in good to high yields in open air at room temperature. AZADO/copper-catalyzed aerobic alcohol oxidation can also tolerate other oxidation-prone functional groups, such as sulfides and dithianes.[2] Careful optimization of reaction conditions with several alcohols has revealed that judicious combinations of nitroxyl radicals, copper salts, and additives lead to efficient oxidation of various types of secondary and primary alcohols to afford the corresponding carbonyl compounds in high yields.[3,4]

In the presentation, if possible, an asymmetric aerobic oxidation of alcohols based on AZADO/copper catalysts will also be presented.



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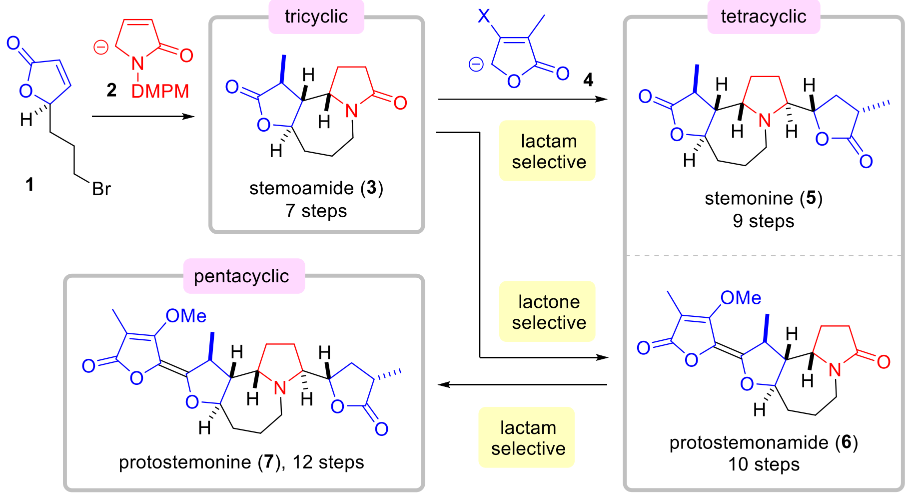
Takaaki SATO
Keio University

Abstract: Unified Total Synthesis of Stemoamide-Type Alkaloids Based on the Amide-Selective Nucleophilic Addition

Modern organic synthesis especially for drug discovery has resulted in the need for compounds of ever-increasing complexity. Our research group has been investigating practical methods for the application to the total synthesis of complex natural products on the basis of “nucleophilic addition to amides” and “chemoselectivity”. In this presentation, I will talk about a unified total synthesis of stemoamide-type alkaloids by chemoselective nucleophilic addition.[1]
Toward the unified total synthesis of stemoamide-type alkaloids, we envisioned three coupling events using five-membered rings. The first coupling reaction was the vinylogous Michael addition of 2 to chiral butenolide 1. After the formation of the seven-membered ring, the second coupling reaction was chemoselective nucleophilic addition to stemoamide (3). While the lactam-selective nucleophilic reaction provided stemonine (5), the lactone-selective reaction gave protostemonine (6). Finally, the lactam-selective coupling reaction with protostemonine (6) accomplished the total synthesis of pentacyclic protostemonine (7). The key to success was iridum-catalyzed hydrosilylation of lactams, which enabled direct installation of five-membered rings to lactams without affecting the lactones.



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Rong SHANG
Hiroshima University

Abstract: Bis(borane)-containing ligands: effects on bonding and reactivity

Since the first structural characterization of metal to borane dative bond,[1] ER_3 (E = B, Al, Ga and In) has attracted increasing interest to be used as a $2e^-$ s-acceptor (Z-type ligand) to electron-rich metal fragments for studies of metal-ligand cooperativity.[2] However, ligand scaffolds utilizing other types of boron-metal bonding remain limited, presumably due to the synthetic challenges and highly reactive nature of M-B bonds.[3]

Our research group are systematically exploring boron's electronic effect on metal centres as a strong s donor and π acceptor through boryl, and borane moieties. We found that more than one reactive boron centre in the metal ligand would permit more metal, ligand and substrates interplay during reactions, allowing a higher level of complexity in controlling regioselectivity and tuning the structure of the resulting complex.[4] In addition, through conjugated π systems, the diverse valences and electronegativity of Group 13-15 elements (B, C, N) shows potential in tunning redox properties of T.M. complexes through orbital interactions as redox-active non-innocent ligands.[5]

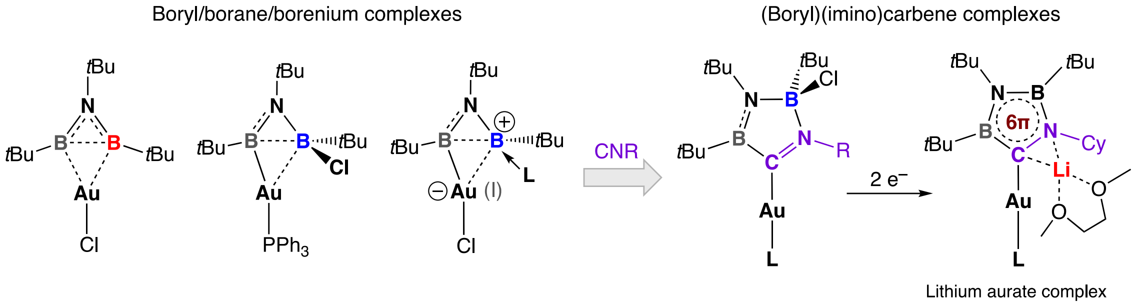

Figure 1. Reactivity of metal diboron complexes and redox tuning power of diboron carbene ligands.

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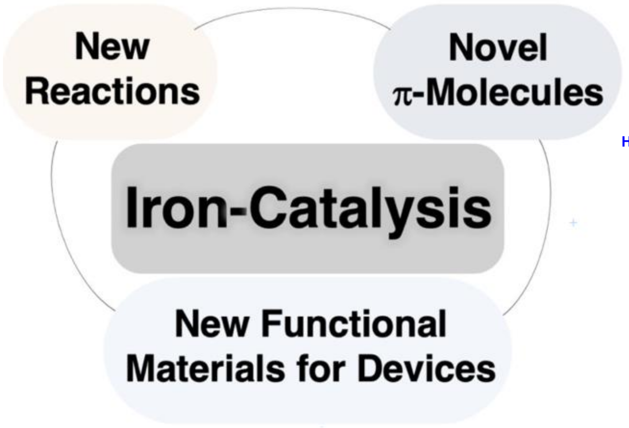
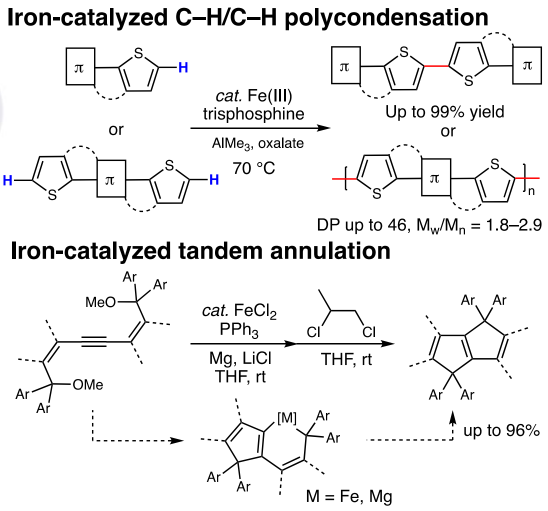
Rui SHANG
University of Tokyo

Abstract: Iron-Catalyzed New Transformations and Their Application for Electronic Materials

As the most abundant metal on the Earth, iron has the merits of use as catalyst for synthesis of conjugated organic molecules of electronic materials interests. Iron's low cost, toxicity, abundance, and ubiquity ideally conform to the spirit of sustainable development goals. However, the synthesis of organic electronic materials so far mostly relies on using precious metals such as palladium and rhodium as catalysts. The cost and scarcity issues of precious metals cause serious problems in material mass production. In this talk, two new types of recently developed iron-catalyzed transformations for accessing conjugated molecules, namely thienyl C–H/C–H couplings[1] and polycondensation[2], and tandem annulation[3] to construct strained 1,4-dihydropentalene frameworks will be introduced. The material properties of several new molecules made by the developed iron catalysis, and their electronic device applications in perovskite solar cells[4] and organic photodetectors will also be discussed.




Iron-catalyzed C–H/C–H polycondensation

Iron-catalyzed tandem annulation

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Xiaodong SHI
University of South Florida

Gold Redox Chemistry: New Transformations and Asymmetric Catalysis

Homogeneous gold catalysis has been developed explosively during the past two decades. Despite the remarkable electrophilic activation of alkynes by cationic Au(I) catalysts [LAuI]+, one exciting new direction is the redox catalysis, allowing gold(I)/gold(III) interconversion in the catalytic cycle. The main challenge to achieve gold redox catalysis is the high oxidation potential between Au(I) and Au(III), ca. ~1.4 eV. Therefore, strong oxidants are required with at least stoichiometric amount, which caused limited substrate scope and many side reactions. To achieve gold redox catalysis under mild conditions, with low cost and mild oxidants, is highly desired to make the overall process practical with improved functional group tolerability. Herein, we disclosed some novel approaches to facilitate oxidation of Au(I) to Au(III) through 1) Aryldiazonium salts as the mild coupling partner/ oxidant, gold catalyzed cross-coupling reactions are accomplished without any external oxidants under photocatalyst-free condition. 2) Employing sulfonium or diselenium cation as mild oxidants for the alkyne functionalization. 3) Electrochemical approach in promoting gold-catalyzed oxidative coupling. These approaches open an opportunity for gold redox catalysis.

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Hisashi SHIMAKOSHI
Kyushu University

Abstract: Bioinspired Catalytic Reactions with and Beyond the Vitamin B12 Enzyme Function

Bioinspired catalyst system was developed in the interdisciplinary fields of bioorganic chemistry and bioinorganic chemistry. In nature, enzymes catalyze various molecular transformations under mild conditions at room temperature and physiological pH with a high efficiency and selectivity. Therefore, we can learn about many excellent systems from nature. As for the catalyst design, a metal complex inspired from the active site of a metal enzyme has been developed. Since metal enzymes catalyze a variety of molecular transformations by the action of the metal ion, they have been considered as one of the desirable catalyst in organic synthesis. Among the metal enzymes, tetrapyrrole pigments, such as porphyrin, chlorophyll, and corrin, that have emerged in nature concerned with various metabolisms have attracted a lot of attention. The characteristic feature of the tetrapyrrole metal complex is its abundant redox property both at the metal center and macrocyclic ligand. Various intermediates for the reaction could be formed in the redox active metal complex. Therefore, the combination of the metal complex with a redox system should form an excellent catalytic

system. Based on this concept, we can utilize various redox systems such as electrochemistry and photo-excited chemistry, for construction of a catalyst system1. Among the metal complexes inspired from natural metal enzymes, the cobalt ion containing the B_{12} (cobalamin) derivative is the focus of this lecture. The development of a hybrid catalyst with the B_{12}-dependent enzyme-inspired photochemical and electrochemical reactions are introduced.

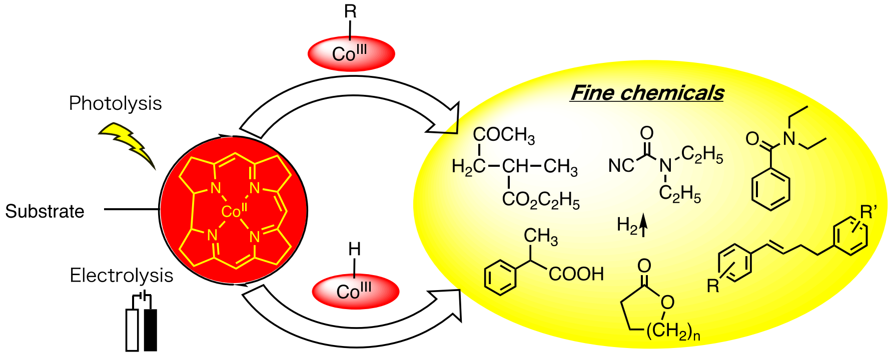

Figure 1 Bioinspired reactions catalyzed by vitamin B_{12} derivatives.

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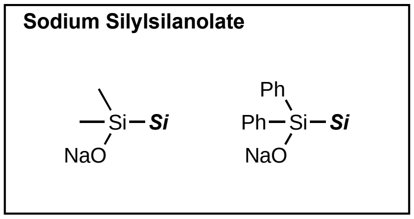
Jun SHIMOKAWA
Kyoto University

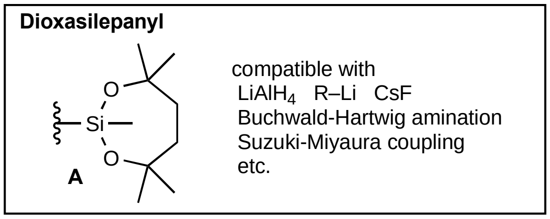
Abstract: Organosilane Synthesis Via New Silicon Species

Organosilanes have gained significant attention in the areas of material, agrochemical, and medicinal sciences due to their well-known low toxicity and distinctive chemical characters. Despite recent developments in silicon chemistry, the search for suitable precursors for the silylmetal species needed for the reaction to create C–Si bonds continues to be a significant challenge.

With this background, we developed sodium silylsilanolates as new precursors for silylmetal species.[1] One Si–Si bond joins the silyl group to be delivered with the silicon atom of a nucleophilic silanolate that serves as a “catapult” in the molecular structure of sodium silylsilanolate. Application of silylsilanolates to palladium-catalyzed silylation of aryl halides afforded silylated products under mild conditions. We also confirmed the reagent could be used in nickel- and copper-catalyzed transformations.[2,3]

Dioxasilepanyl group A has a bulky, seven-membered dialkoxy ring structure that is chemically stable for functional group conversions under a variety of conditions for functional group transformations.[4] It is even compatible with $LiAlH_4$ or alkyllithiums that are usually incompatible with conventional alkoxysilyl groups. A can also be activated under appropriate conditions for coupling reactions with arenes or oxidative transformation to an aromatic hydroxy group. These interesting characteristics of this silyl group make it suited for use in multi-step organic syntheses. In the current study, we investigated the features of such seven-membered dialkoxysilyl groups and newly found 1) silylpotassium species bearing a dioxasilepanyl group could be generated from the corresponding disilanes and potassium *tert*-butoxide, and 2) diarylsilanediols could be synthesized based on the sequential substitution reactions of a seven-membered tetraalkoxysilane with aryl Grignard reagents.





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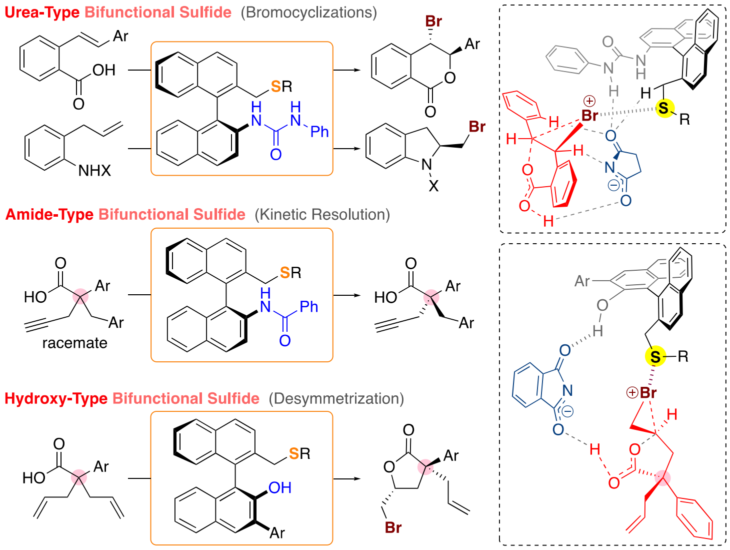
Seiji SHIRAKAWA
Nagasaki University

Abstract: Design of Chiral Bifunctional Sulfide Catalysts for Asymmetric Halocyclizations

Catalytic asymmetric reactions with modularly designed organocatalysts are recognized as one of the most effective methods to produce important chiral molecules in a highly enantioenriched form. Various types of chiral organocatalysts have been designed and applied to highly stereoselective transformations over the past two decades. Among these organocatalysts, chiral amines and phosphines are some of the most widely utilized catalysts in catalytic asymmetric synthesis. By comparison with an exorbitant number of reactions using chiral amine and phosphine catalysts, examples of efficient asymmetric reactions with chiral sulfide catalysts have remained limited and under-developed. In this context, we became interested in the design of effective chiral sulfide catalysts. Herein, we report the development of chiral bifunctional sulfide catalysts for regio-, diastereo-, and enantioselective halocyclizations. The importance of the bifunctional design of chiral sulfide catalysts was clearly demonstrated in the present work.[1]



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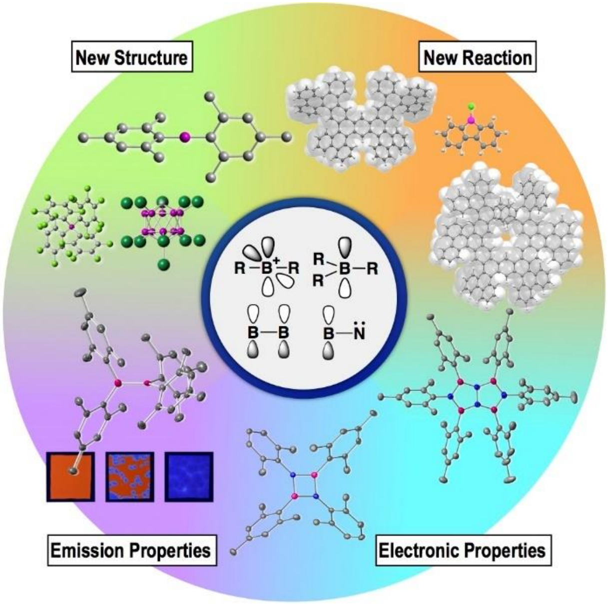
Yoshiaki SHOJI
Tokyo Institute of Technology

Abstract: Pursuing New Structures and Properties of Organoboron Compounds by Designing Chemical Bonds and Spaces Around Boron



Since the structures, reactivity, and properties of organoboron compounds are characterized by the electron deficiency and low electronegativity of boron, the design of the chemical bonds of boron and the space provided by substituents around boron is the key for particular reactivity and functions of organoboron compounds. We have developed new organoboron compound displaying exotic reactivity and properties, based on the concept of vacant boron p-orbital engineering as well as peripheral space design for boron (Figure).[1] In this presentation, we focus on the development of boron compounds by making use of (i) a close interaction between boron and π-systems that leads to new organic transformations[2] and (ii) an interplay between boron vacant p-orbitals that provides new electronic properties. The molecules and reactions appearing in above topics demonstrate intrinsic and new potential of organoboron compounds, since they feature very simple systems.

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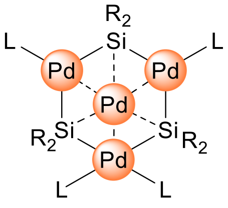
Yusuke SUNADA
University of Tokyo

Abstract: Bond Activation by Silylene Bridged Group 10 Metal Clusters

Transition metal clusters have attracted much attentions due to their unique chemical properties derived from the cooperative functions among multiple metal centers. Recently, we have found that the oligosilanes consisting of multiple silicon-silicon bonds can act as the template to afford the silicon-bridged metal clusters through insertion of the metal species into silicon-silicon bonds.[1] In this presentation, we wish to report the construction of a series of silylene bridged metal clusters by the reactions of low valent group 10 metal precursors with oligosilanes. Bond activation on the obtained group 10 metal clusters will also be demonstrated.

Treatment of palladium(0) precursor, $[Pd(CN^tBu)_2]_3$, with alkyl-substituted cyclotetrasilanes, $(SiR_2)_4$ (R = ^{i}Pr or cyclopentyl), afforded the planar tetrapalladium clusters, $Pd_4(SiR_2)_3(CN^tBu)_4$ (1), in high yield. The obtained cluster 1 effectively activated H_2, thus cluster 1 could act as the active catalysts toward hydrogenation of various alkenes including sterically hindered ones.[2]

It was also found that the denitrogenative coupling of two molecules of CN^tBu proceeded on a multinuclear silylene-bridged nickel cluster framework. First, the cleavage of the C≡N bond of one molecule of CN^tBu took place in the reaction of $(SiPh_2)_4$ with 2:5 mixture of $Ni(cod)_2$ and CN^tBu, giving dinuclear nickel cluster 2 with a silylene-supported carbide and an N^tBu moiety. Further metalation induced the coupling between the carbide moiety and an additional molecule of CN^tBu to afford a pentanuclear nickel cluster 3 bearing a ($\square_3$-$\square^2$-$R_3Si–C≡C–NR'_2$) moiety.[3]



(R = ^{i}Pr, cyclopentyl)

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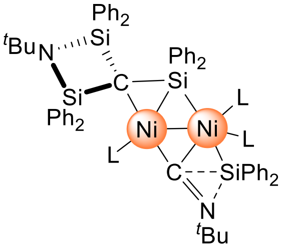

(L = CN^tBu)

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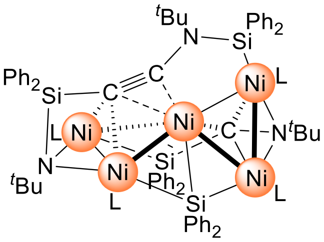

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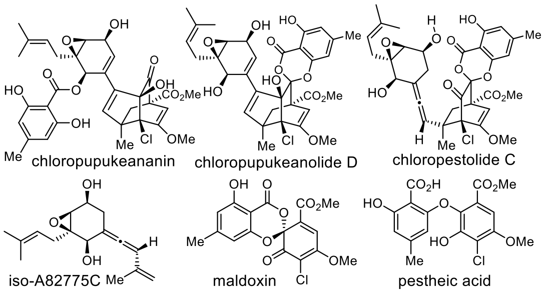
Takahiro SUZUKI
Hokkaido University

Abstract: Biomimetic Total Syntheses of Chloropupukeananin, Chloropupukeanolide D, and Chloropestolides



Chloropupukeananin, chloropupukeanolides, and chloropestolides are a family of structurally complex bioactive natural products that possess highly functionalized tricyclo[4.3.1.0^{3,7}]decane or bicyclo[2.2.2]octane skeletons. Biosynthesis of the chloropupukeananin family is triggered by the intermolecular heterodimeric Diels−Alder reaction between maldoxin and iso-A82775C to produce chloropestolides.[1,2] The subsequent intramolecular carbonyl-ene reaction and migration of the *p*-orsellinate moiety are postulated to lead to the biosynthesis of chloropupukeananin.

We first performed the asymmetric total synthesis of both biosynthetic precursors, namely iso-A82775C and maldoxin. We succeeded in the total synthesis of optically pure iso-A82775C using the cinchonine-catalyzed asymmetric Diels-Alder reaction of α-pyrones and the construction of the vinylallene moiety by the S_N2' reaction using organoindium reagents in the presence of Pd catalyst as key reactions.[3] In addition, after the synthesis of pestheic acid, the precursor of maldoxin, in seven steps including the intermolecular S_NAr reaction as a key reaction, the asymmetric oxidative dearomatization reaction of pestheic acid using the second-generation Ishihara catalyst successfully provided maldoxin in 99% ee.[4]

We next conducted the total synthesis of chloropupukeananin using both biosynthetic precursors.[5] When an equimolar mixture of iso-A82775C and maldoxin was placed under solvent-free conditions, the intermolecular Diels-Alder and carbonyl-ene reactions proceeded to give chloropupukeanolide D and chloropestolide B. Finally, the one-pot migration reaction of the *p*-orsellinate moiety was successfully carried out to achieve the biomimetic total synthesis of chloropupukeananin.

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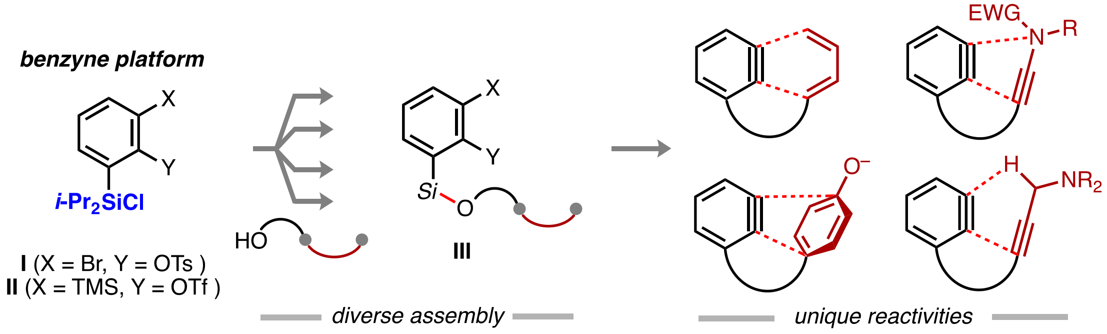
Hiroshi TAKIKAWA
Kyoto University

Abstract: Silicon-Tethered Benzyne Reactions: A Platform for Exploring New Reactivity

Silicon tethers have long been recognized in organic synthesis as easily installable and removable auxiliaries for various intramolecular transformations. The advantages of intramolecular reactions over their intermolecular variant are high reaction efficiency, regioselectivity, and stereoselectivity. But most importantly, unique reactions that do not proceed in intermolecular manner can be realized by setting a suitable spatial relationship between the reactants. Over the past few years, we developed and employed silicon tethers for intramolecular reactions of benzyne, a powerful tool for the introduction of functionalized aromatic rings into target molecules.[1–4] Our strategy has empowered various unique intramolecular reactions, i.e., regio- and peri-selective (4+2) cycloadditions with dienes,[1,3] dearomative (4+2) cycloaddition with phenolates,[2] (3+2) cycloaddition with ynamides, and ene reactions with propargylamines.[4]
o-Bromoaryl tosylate I[1] or *o*-silylaryl triflate II,[3] having a chlorodiisopropylsilyl group, are exploited as a platform to combine various arynophiles. Silyl chloride I and II allow a facile and diverse assembly with various arynophiles with a hydroxy group via a Si–O bond to give silylether III. Upon generation of benzyne, various intramolecular reactions proceed to afford various products. After the reaction, the silyl tether can be easily removed or converted into a hydroxy group under Tamao–Fleming conditions. In this talk, the reaction details and the application to natural product syntheses will also be discussed.



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Ryo TAKITA
Shioka Prefecture University

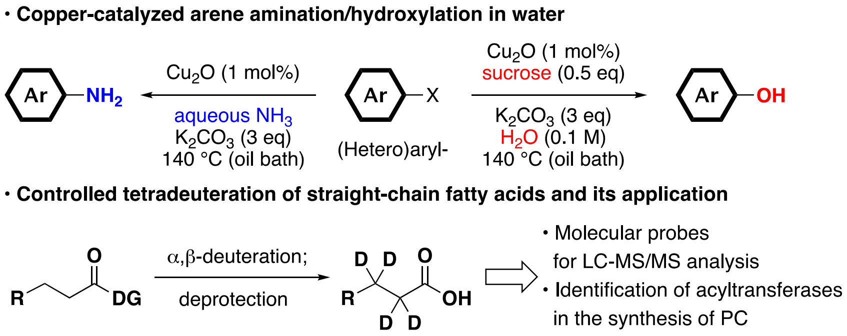
Abstract: C–N/C–O/C–D Bonds Formation in H2O or With D2O

Copper-catalyzed arene amination/hydroxylation in water

Given that water and ammonia are among the cheapest and most abundant sources of oxygen and nitrogen, we investigated a Cu-catalyzed carbon–heteroatom bond-forming reaction with these molecules to develop robust catalytic processes. For the C–N bond formation, a concise protocol for copper(I)-catalyzed arene amination using aqueous ammonia without any additional ligands and organic coordinating solvents has been developed. The C–O bond formation has been achieved in the hydroxylation of aryl halides catalyzed by copper(I) and sucrose in neat water. The roles of aqueous ammonia and sucrose, the reaction pathways, and the high selectivity for both amination and hydroxylation were investigated using a combination of experimental and theoretical techniques.

Controlled tetradeuteration of straight-chain fatty acids and its application

We have also developed a concise and reliable protocol for the precisely controlled tetradeuteration of straight-chain fatty acids (FAs) at the α- and β-positions that is generally applicable to a variety of FAs. The precisely controlled introduction of four deuterium atoms into the FAs enables their persistent and quantitative tracking by LC–MS/MS analysis based on their molecular structures. In addition, the phosphatidylcholine (PC) species prepared from the tetradeuterated FAs thus obtained give a diagnostic peak, namely, a phosphocholine fragment that contains deuterium, in the LC–MS/MS analysis. With these features, the metabolism of a representative oxidized linoleic acid, that is, hydroxyoctadecadienoic acid (HODE), was investigated, leading to the identification of acyltransferases that transfer the acyl moiety derived from HODE to lysophosphatidylcholine.



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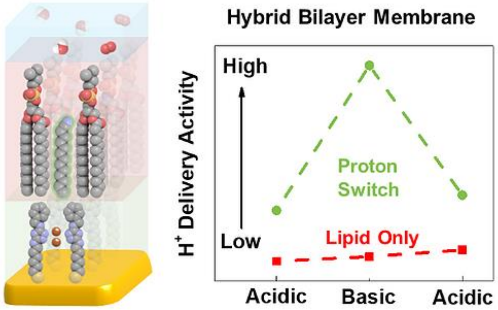
Edmund TSE
University of Hong Kong

Abstract: Steering Oxygen Reduction Electrocatalysts toward 4e/4H Pathway using a Hybrid Membrane with Fuel Cell Implications

Proton-coupled electron transfer (PCET) processes are instrumental to catalytic reactions and energy applications. In this talk, I will showcase our efforts in designing and constructing a nanoscale electrochemical platform (see figure) to modulate the proton and electron transfer rates independently for oxygen reduction reaction (ORR). ORR is the reaction that limits the performance of fuel cells and related energy conversion technologies. Our electrocatalytic nanoplatform features a hybrid bilayer membrane (HBM) comprising of a self-assembled monolayer (SAM), an ORR catalytic motif, a phospholipid layer, and a proton transfer agent.[1] Each of these four controls one aspect of ORR, and together they dictate the overall catalytic performance. Utilizing this modular system, the electron transfer rate can be adjusted by the SAM length, and the proton transfer rate can be tuned by the proton transfer agent in the lipid layer.[2] By regulating the relative rates of proton and electron transfer using our nano-architecture, we achieve higher selectivity for the four-electron process to generate water as the desired product without compromising the activity of the electrocatalyst.[3] New data will also be presented on triggering proton delivery against a pH gradient.[4] In summary, our electrochemical system will provide unique insights into the optimal thermodynamic and kinetic parameters not only for ORR catalysts,[5] but also offer new opportunities to enhance the performance of other catalysts involved in fuel generation and energy storage.[6]



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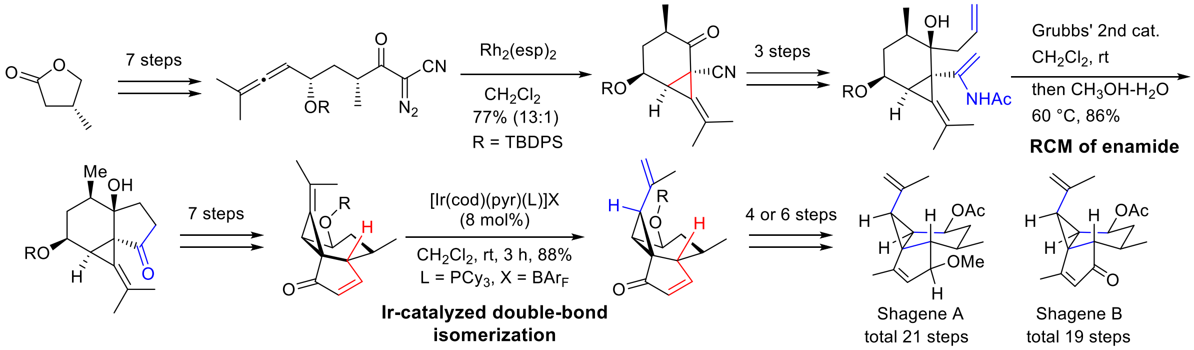
Chihiro TSUKANO
Kyoto University

Abstract: Asymmetric Total Synthesis of Shagenes A and B, Anti-Leishmanial Sesquiterpene

Shagenes A and B were isolated from a soft coral in the Scotia Sea by Baker and coworkers while searching for natural products that exhibited strong toxicity against *Leishmania donovani*, a protozoan that causes leishmaniasis.[1] The structure and relative stereochemistry of these natural products have been determined by high-resolution MS and extensive NMR spectroscopy studies, but their absolute stereochemistry has yet to be determined. These compounds are characterized by a novel tricyclic skeleton with a 3/6/5-membered ring system, six or seven contiguous chiral centers, and a *cis*-substituted cyclopropane. Shagene A exhibited strong toxicity against *L. donovani* (IC_{50} = 5 □M) and had no toxicity towards mammalian cells, while shagene B had no activity against *L. donovani*. Because of its biological activity and high selectivity, the shagene skeleton is expected to be a novel seed for drug development. Despite the importance of shagenes, no total synthesis has yet to be reported. Therefore, we started synthetic studies of shagenes to provide a sample for further biological studies.

In this presentation, we would like to report the first enantioselective total synthesis of shagenes A and B.[2] The keys to success for the synthesis were ring-closing metathesis (RCM) of an enamide and Ir-catalyzed double-bond isomerization of an alkylidenecyclopropane. Chemo- and diastereoselectivity in the distorted *cis*-substituted structures were controlled by the alkylidenecyclopropane reactivity and using the ketone functionality as a remote directing group for the Ir catalyst, respectively. The total synthesis also disclosed the absolute stereochemistry of shagenes.



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Tatsuya UCHIDA
Kyushu University

Abstract: Carboxylic Acid Corporative Ruthenium-Catalyzed C–H Oxygenation

C–H oxygenation is a highly atom- and step-economic organic material transformation, have been recent topics in organic chemistry. In this field, various methodologies are introduced and developed. Especially, metal(oxo) intermediates, an electrophilic oxidant, have attracted much attention and intensively studied due their high usefulness in C–H oxygenation. However, truly practical C–H oxygenation is still limited. Herein, we described a novel catalytic practical C–H oxygenation. Recently, we found that ruthenium[bis(pyridyl-2-methyl)glycinamide] [Ru(bpga)] complexes are efficient catalysts in site-selective unactivated C–H bond oxygenation. Ru(bpga) complex shows excellent catalysis such as high site-selectivity and high turnover number under acidic condition.[1,2] Kinetic studies under acidic conditions indicated that Ru(bpga)-catalyzed C–H oxygenation rates can be controlled depending on the acidity of carboxylic acid in situ (Figure 1), and the nature of that carboxylic acid corporation is thought to be a hydrogen bond between the oxygen atom of oxo ligand and carboxylic acid. Based these considerations, we intrigued the carboxylic acid cooperative (AC) C–H oxygenation and designed AC-Ru(bpga) complex. To the best of our knowledge, AC-Ru(bpga) presented the best catalysis in C–H oxygenation (Figure 2). AC-Ru(bpga)-catalyzed C–H oxygenation using hydrogen peroxide as the terminal oxidant proceeded immediately with excellent site-selectivity at even only 0.1 mol% catalyst loading. The reaction is applicable to the only simple model substrates but also complicate natural products.

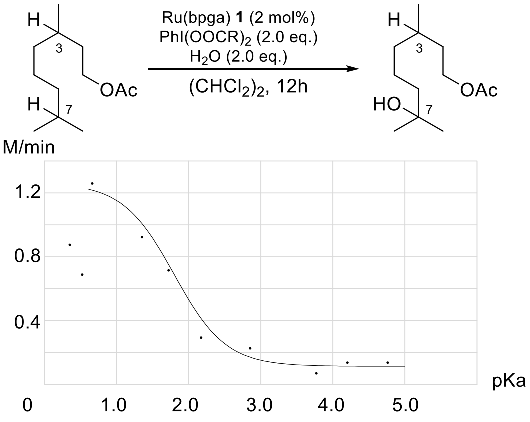

Figure 1. Correlation of reaction rates with carboxylic acids

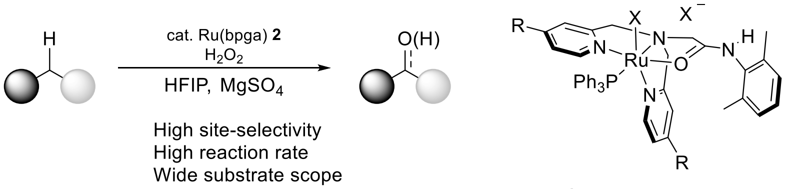

Figure 2.

1: R = CF_3, X = Cl
2: R = H, H-maleate

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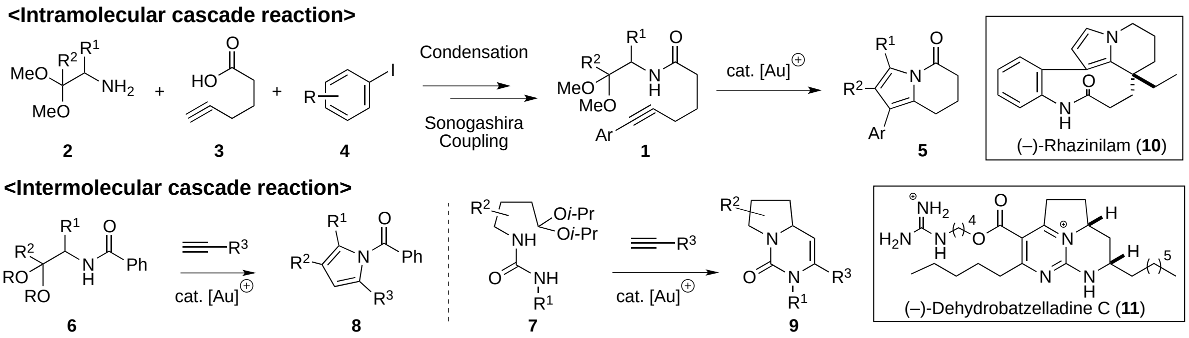
Hirofumi UEDA
Tohoku University

Abstract: Synthesis of Substituted Nitrogen-Containing Heterocyclic Compounds via Gold-Catalyzed Cascade Reaction

Among nitrogen-containing heterocycles, indolizine, pyrrole, and pyrrolopyrimidine are particularly important because these skeletons are found in biologically active natural products, pharmaceutical substances, and functional materials. While a number of synthetic methods for these heterocycles have been developed to date, there are few versatile methods available to synthesize compounds bearing substituents at the desired positions. In the course of our research program directed toward construction of substituted nitrogen-containing heterocycles, we have developed three cationic gold catalyzed cascade reactions to construct highly substituted indolizines, pyrroles, and pyrrolopyrimidines using acyclic substrates with pre-installed substituents at the appropriate position.

First, we developed a cationic gold-catalyzed intramolecular double cyclization of acyclic ynamide 1, which was prepared by assembling aminoacetaldehyde dimethylacetal 2, 5-hexynoic acid 3, and aryl iodide 4, to synthesize the multi-substituted indolizines 5.[1] We next expanded it utility to intermolecular version and established a gold catalyzed-cascade reactions using acetalamide 6 or acetalurea 7 in the presence of acetylenes for synthesis of substituted pyrroles 8[2] or pyrrolopyrimidines 9. Mechanistic investigation of these intermolecular reactions revealed that the reaction involved an auto-tandem catalysis in which the cationic gold catalyst works as a dual catalyst to activate not only electrophilicity but also nucleophilicity of the acetylene. In this presentation, details on development of these three cascade reactions and the application to total synthesis of natural products including (–)-rhazinilam (10) and (–)-dehydrobatzelladine C (11) will be also discussed.



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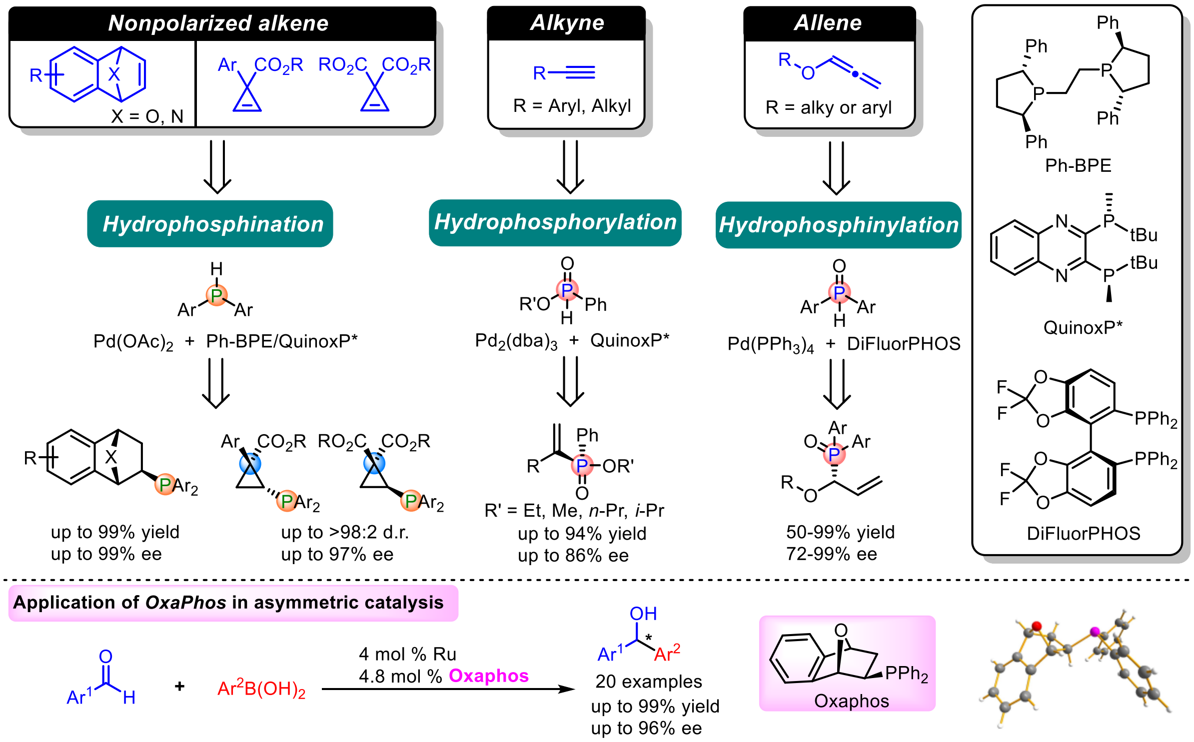
Jun WANG
Hong Kong Baptist University

Abstract: Facile Access to Chiral Phosphorus Compounds via Transition Metal-catalyzed Asymmetric Hydrophosphination of Alkenes and Alkynes

Asymmetric catalysis is a very broad and exciting field. In spite of hundreds of chiral ligands developed, phosphine ligands are keeping their prestigious role as the most powerful and frequently-used ligands. With the exceptionally high demand of chiral phosphine ligand, it is significant to develop efficient methods for construction these chiral organophosphorus compounds. Transition metal-catalyzed asymmetric hydrophosphination is the most direct pathway for the synthesis of chiral phosphine compounds. Recently, our group developed asymmetric hydrophosphination of alkenes, alkynes, allenes and cyclopropenes.[1-4] These approaches allowed concise, direct, modular and unprecedented accesses to potentially valuable chiral phosphorus compounds. In addition, the easily accessible monophosphine products-Azaophos and Oxaphos were successfully used in asymmetric transformation.



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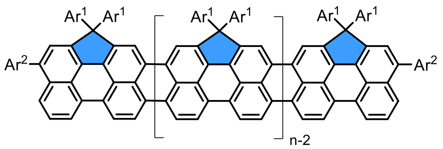
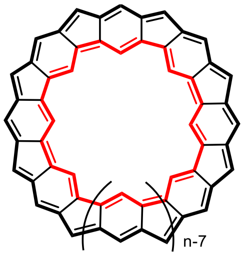
Jishan WU
National University of Singapore

Abstract: Synthesis of Some Challenging Molecular Carbons

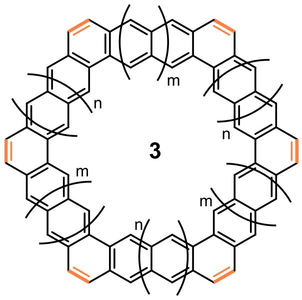
We report the successful synthesis of some challenging molecular carbons that have troubled synthetic chemists for a long time. This includes: (1) long rylene ribbons (1),[1] (2) macrocyclic polyradicaloids with alternatively fused six- and five-membered rings;[2] (3) kekulenes, expanded keulenes and cycloarenes (3);[3-4] (4) twisted carbon nanobelts with persistent chirality (4);[5] and (5) a γ-graphyne spoked wheel molecule (5).[6] Their unique electronic properties will be also discussed.



1 (n=2-12)



2 (n=8, 10)



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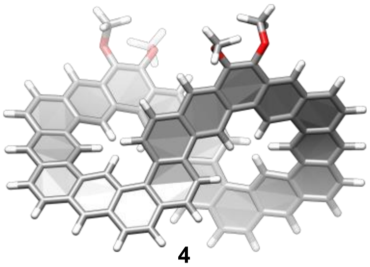

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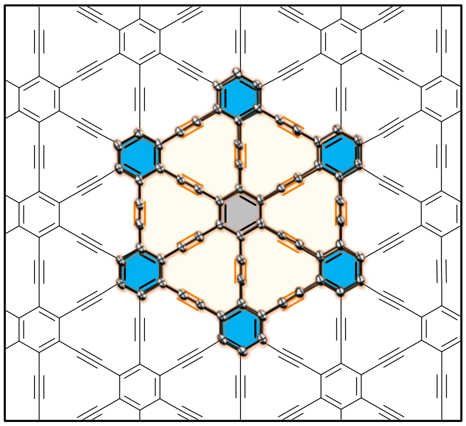

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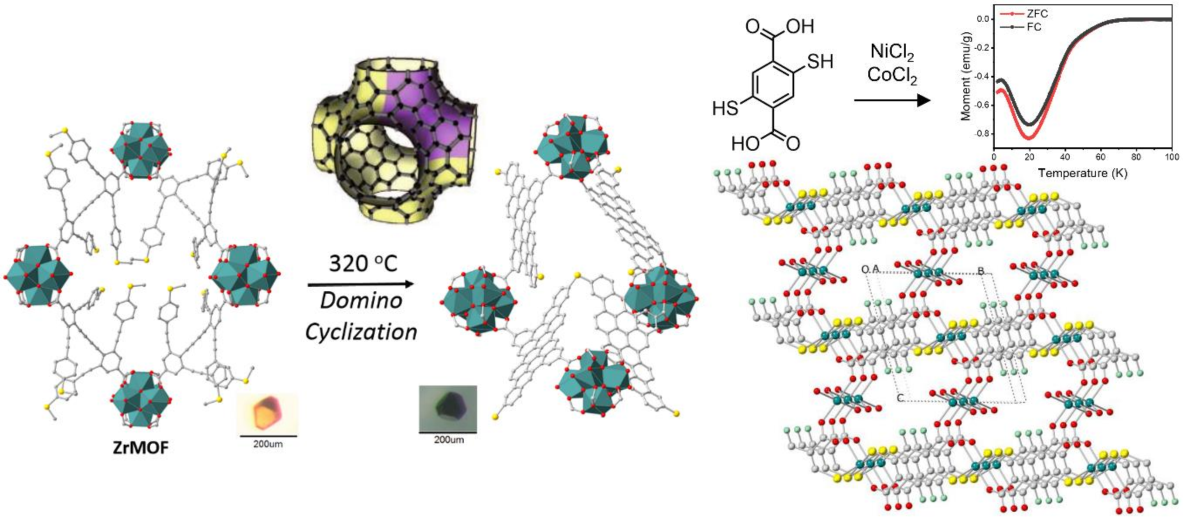
Zhengtao XU
Institute of Materials Research and Engineering

Abstract: Stable Radicals and Superconductivity from Sulfur Coordination Polymers

In the first part, we present organic radical systems that are stable even above 350 °C, surpassing the upper temperature limit (200 °C) observed for other organic radicals (www.nature.com/articles/s41467-022-33948-9). The coordination networks build on alkyne- or sulfur-rich organic linkers which, upon heating, facilitates the formation of the radical centers while preserving the overall crystalline order. Such a post-synthetic thermal treatment also enables a strategy for accessing crystalline porous covalent networks of highly conjugated π-electron systems emulating the coveted 3D graphenes (Figure, left, a), achieving greatly enhanced stability, electroactivity and charge transport. In the second part, we report breakthrough in the modular synthesis of MOF solids extensively equipped with the mercaptan function, in order to fully exploit the unique metal-uptake, catalytic and electronic properties afforded by the thiol function, e.g., potential superconductivity observed of a designer coordination polymer system sporting the chemically soft mercaptan and hard carboxyl groups (Figure, right; www.tandfonline.com/doi/full/10.1080/21663831.2022.2057822).

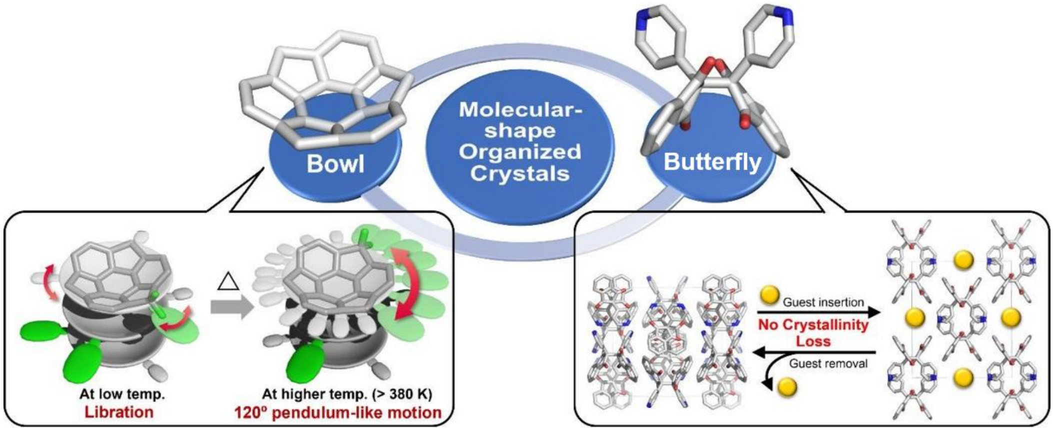


Yumi YAKIYAMA
Osaka University

Abstract: Structures and Properties of Stimuli-responsive Molecular Crystalls Composed of Unique-shaped Building Units

Stimuli-responsive materials, which can change their physical and structural properties by light irradiation, the addition of heat and/or stress, vapor exposition etc., are not only attractive research targets but also one of potential sources of future innovations. Especially the molecular crystalline materials which maintain high crystallinity before and after the response to the stimulus are important in terms of obtaining the structure-property relationship because the many critical aspects of their selective preparation still remain unclear. Indeed, the proper choice of the main building block, whether itself possesses the stimuli responsibility or not, is definitely one of the critical issues, and the precise understanding of the resulting packing structure holds the key to success for the further application of the system.

In this talk, our recent works, which focus on the preparation of stimuli-responsive molecular crystalline materials using bowl-shaped sumanene derivative[1,2] and butterfly-shaped indanedione dimers[3,4], as well as their physical properties, will be shown.



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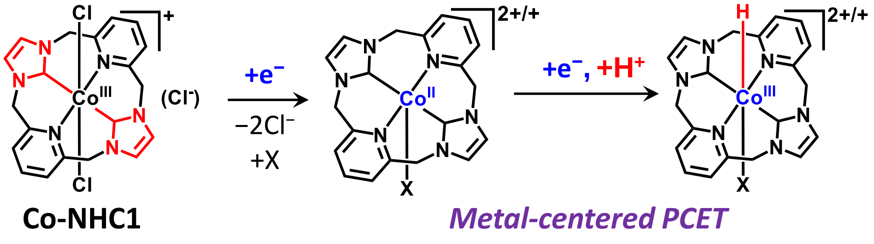
Kosei YAMAUCHI
Kyushu University

Abstract: Photochemical and Electrochemical Hydrogen Evolution from Water Catalyzed by Co-NHC Complexes

Artificial photosynthesis based on splitting water into H_2 and O_2 with solar energy has attracted recent years. In order to realize the overall water-splitting reaction based on molecular systems, it is crucial to develop highly active molecular catalysts for both hydrogen and oxygen evolution reactions (HER and OER). In this context, we have focused on molecular catalysis for H_2 evolution from water by employing a photochemical system comprising of EDTA, $[Ru(bpy)_3]^{2+}$, electron relay and the catalyst, where one-electron-reduced species of methylviologen MV^{2+} (i.e., MV^{+}•) only has a driving force (DF) of 150 meV for HER at pH 5.0. Within these studies, we succeeded in demonstrating that a macrocyclic cobalt-NHC complex Co-NHC1 serves as a catalyst for HER using MV^{+}• as a reductant via the metal-centered PCET process.[1] This is the first example of the 1st row transition metal complex showing the catalysis in this system. Upon changing the electron mediator, we have improved the photosystem which shows 70 times higher rate of HER compared with that of MV^{2+}.[2] A similar approach has been effective even for the molecular photocatalyst having the electron relay within the molecule.[3] On the other hand, we have recently conducted the detailed analyses on the homogeneous electrocatalysis of Co-NHC1 in aqueous media. Importantly, the turnover frequency



Co-NHC1

(TOF) of HER catalyzed by Co-NHC1 has turned out to be extremely high even in neutral media, in which some other cobalt-based molecular catalysts have been previously examined under the similar conditions.[4] Our recent finding includes the development of the highly efficient molecular system based on new cobalt-NHC complex in photochemical H_2 evolution from alkaline water, which will be discussed in the presentation.

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Sungho YOON
Chung Ang University

Abstract: Heterogenized Catalysts for CO2 conversion into formate

Homogeneous catalysts, represented by organometallic compounds, have been studied extensively in the chemical field for a long time by controlling both electronic potential state of active site and steric restriction of peripheral environment due to the clarity of their molecular structure, and excellent research results in terms of catalyst selectivity and activity have already been reported. However, except for a few special cases, it has not yet been widely applied in terms of industrial use. The cause of this limitation may be various, but the difficulty in separating the catalyst after the reaction is one of the representative reasons. On the other hand, the heterogeneous catalyst, which has been mainly studied in chemical engineering, relatively has a lower clarity of structure of the active site, and the activity and selectivity of the catalyst are also not relatively high compared to the homogeneous catalyst. However, it has excellent advantages in terms of catalyst separation after reaction. For this reason, it can be said that more industrialization took place.

In this talk, I would like to present recent research results on heterogenized catalysts to utilize the advantages of previously reported catalysts and simultaneously to overcomes the disadvantages. In particular, the process development of hydrogenation using a heterogenized catalyst to produce formic acid from CO_2 will be presented.[1]

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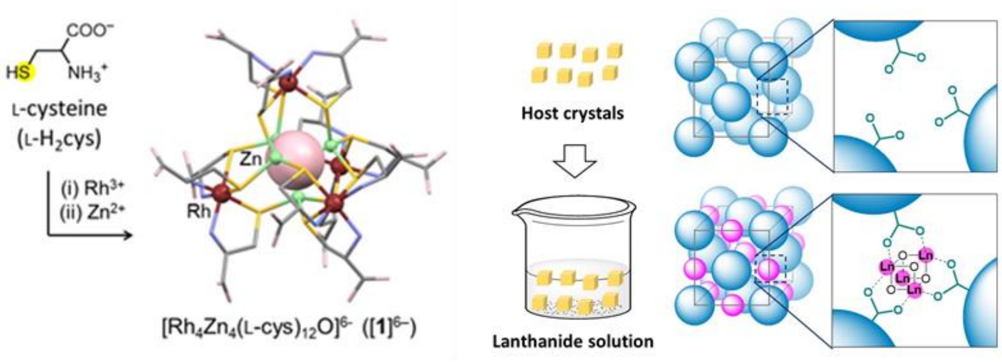
Nobuto YOSHINARI
Osaka University

Abstract: Migration and Clusterization of Metal Ions in Supramolecular Frameworks of Metal-Organic Carboxylates

Organic carboxylates are fundamental building units for constructing coordination and hydrogen-bonded frameworks in supramolecular chemistry. Recently, discrete metal complexes with noncoordinating 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] We have developed various metallosupramolecular aggregates based on MOCs using sulfur-containing amino acids, such as d-penicillamine and l-cysteine ($l\text{-}H_2cys$).[1] Herein, I will describe our recent achievements about the migration and condensation reaction of aqua metal species in the supramolecular frameworks.

Firstly, I introduce the fast ion migration of metal ions over metal cluster aggregates, which comprise alkali metal ions (M) and metal cluster anions having l-cys, $M_6[Rh_4Zn_4O(l\text{-}cys)_{12}]$ ($M_6[1]$) (Fig. left).[2] The conductivities of these ionic crystals increased in the order of $Li^+ < Na^+ < K^+$, which implies the movement of hydrated metal ions in the crystalline state. As the second topic, I will explain an unusual condensation reaction for aqua lanthanide ions (Ln^{3+}) inside the crystal lattice of $M_6[1]$.[3] Soaking single crystals of $K_6[1]$ in a water/ethanol solution containing Ln^{3+} results in the exchange of K^+ by Ln^{3+} with retention of the single crystallinity, producing hydroxide-bridged cubane clusters inside the crystal lattice (Fig. right).



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Donghong YU
Aalborg University

Abstract: Conjugation break: A New Design Strategy for Electron Acceptor Polymers Towards Efficient And Thermally Stable All-Polymer Solar Cells

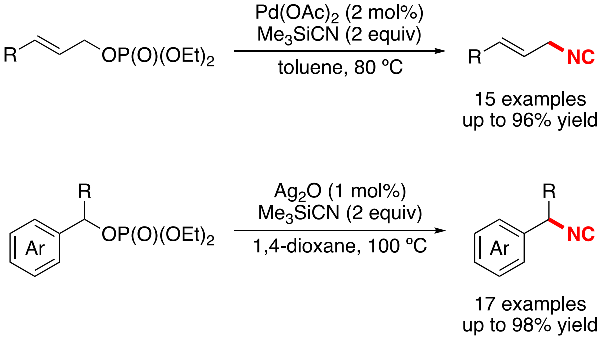
A non-conjugated polymer acceptor PF1-TS4 was synthesized by embedding a thioalkyl segment in the mainchain, which presents excellent photophysical properties like a fully conjugated polymer with a low optical bandgap of 1.58 eV and a high absorption coefficient of 1.28 × 105 cm-1, a high LUMO level of -3.89 eV, and suitable crystallinity. Matched with a polymer donor PM6, the PF1-TS4-based all-PSC achieved a power conversion efficiency (PCE) of 8.63%, which is ~1.5 times higher than that of device based on the small molecule acceptor counterpart IDIC16. Moreover, the PF1-TS4-based all-PSC has good thermal stability with ~70% of its initial PCE retained after being stored at 85 °C for 180 h, while the IDIC16-based device only retain ~50% of it when stored at 85 °C for only 18 h. This work provides a new strategy to develop efficient polymer acceptor materials by linkage of conjugated units with non-conjugated thioalkyl segments.

Taiga YURINO
Hokkaido University

Abstract: Catalytic Nucleophilic Isocyanation: Selective N-Terminus Substitution of Ambident Cyanide

Isonitriles (R–NC) are well-known surrogates of carbon monoxide in organometallic chemistry, whose *C*-termini show carbene-like property. These compounds are also regarded as important building blocks in organic transformations because they can react with both nucleophiles and electrophiles at their *C*-sites. In contrast the side applicability of isonitriles, the preparation of isonitriles is still limited in traditional dehydration of the corresponding *N*-formamide. The conditions are harsh, and thus highly functionalized isonitriles are hardly achieved by those preparation methods. Nucleophilic isocyanation is an alternative protocol for the synthesis of isonitriles, using cyanide (CN^-) as *N*-nucleophile.[1] Cyanide is one of the most typical ambident nucleophiles, whose *C*- and *N*-terminus are both reactive. Generally, its *C*-terminus is kinetically and thermodynamically more reactive than its *N*-terminus. So that, some tricks are necessary for achieving nucleophilic isocyanation.

Herein we report transition metal-catalyzed nucleophilic isocyanation. Allylic phosphates were converted into the corresponding allylic isonitriles in the presence of catalytic amount of palladium salt.[2] In this reaction, no π-allyl-Pd(II) intermediate was included in the catalytic cycle, even though it is the allylic substitution using palladium catalyst. Silyl cyanopalladate complex $(Me_3Si)[Pd(CN)_3]$ generated in situ from $Pd(OAc)_2$ and the excess amount of Me_3SiCN was a possible catalytic active species in this transformations. We also successfully achieved benzylic isocyanation with use of Ag_2O as a catalyst precursor.[3] Both primary and secondary benzylic phosphates were smoothly consumed to afford benzylic isonitriles in high yield. In this case, silyl cyanoargentate complex $(Me_3Si)[Ag(CN)_2]$ generated in equilibrium promoted the catalytic reaction.



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Yanli ZHAO
Nanyang Technological University

Abstract: Integrating Supramolecular Interactions into Covalent Organic Frameworks for Catalytic Applications

Linkage chemistry is important for the synthesis of covalent organic frameworks (COFs), since it not only plays vital roles in the formation of COFs, but also has a significant impact on the properties of resulting materials.[1,2] Although a considerable effort has been devoted to developing novel linkages via covalent modification of mine bond, the resultant COFs often suffer from decreased porosity, irreversible transformation and limited functionalities. Thus, developing more general strategies for improving the crystallinity, stability and functionalities of COFs is highly desired. In this study, we reported supramolecular interaction-integrated linkage engineering to fabricate 2D hydrazone-linked COFs for the coordination of diverse transition metal ions, and demonstrated that different coordination modes in 2D COs have a significant influence on the properties of the resultant frameworks toward advanced catalysis.[3] Multiple supramolecular interactions, including intra-/intermolecular hydrogen bonding, electrostatic interactions in antiparallel stacking as well as metal coordination interactions, were utilized to restrict the bond rotation of linkages in COFs. After coordination with suitable divalent transition metal ions (M), the resultant M/COFs exhibited extended π-conjugation, improved crystallinity, enhanced stability and additional functionalities as compared to the parent COFs. In particular, the coordination mode in Pd/COF endowed it with excellent catalytic activity and cyclic stability for Suzuki-Miyaura cross-coupling reaction, outperforming its amorphous counterparts. This work not only demonstrates that subtle changes in the scaffolds of COFs could greatly affect the corresponding catalytic performance, but also provides a strategy for modulating physicochemical properties of 2D COFs via supramolecular linkage engineering.[4]

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Dan ZHAO
National University of Singapore

Abstract: Structural Dynamics and Growth Mechanism of Covalent Organic Frameworks

Covalent organic frameworks (COFs) are an exciting family of functional porous materials. They feature uniform yet tunable porosity, rich chemical composition, and potentially high stability suitable for various applications. However, their structural dynamics are less explored than other porous materials, and their growth mechanism remains unclear. In this talk, I will introduce our group's recent progress in studying the structural dynamics and growth mechanism of several COFs. The results provide new approaches to design, synthesis, and applications of new functional COF materials and devices.

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Nan ZHENG
University of Arkansas

Abstract: Harnessing Synthetic Potential of Photogenerated Distonic Radical Cations

Amines are routinely used in photoredox catalysis as an electron donor to reduce the photoexcited state of organometallic complexes or organic dyes while oxidizing to amine radical cations. Taking advantage of this facile redox process, we have applied it to the ring opening of cyclopropylanilines and cyclobutylanilines, which produces distonic radical cations. These reactive species bearing a spatially separated iminium ion and a carbon radical undergo [3+2][1] or [4+2][2] annulation reactions with various types of pi bonds to yield a range of aniline-substituted five- or six-membered carbocycles. However, these annulation reactions have not fully taken advantage of the distonic radical cations‘ bimodal reactivity. Using a combination of a nucleophile and a radical acceptor, we are able to orthogonally intercept the iminium ion and the carbon radical and thus fully capture the bimodal reactivity.

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Ye ZHU
National University of Singapore

Abstract: Remote Stereocontrol Through Distal Ionic Interactions-Directed Cross-Coupling

Catalytic construction of a chiral molecule relies on seamless communication between chirality of catalyst and prochirality of substrate. Spatial separation of a prostereogenic center from either the reaction sites or the prochirality-revealing groups (i.e., points of difference between geminal substituents) presents a universal hurdle in asymmetric catalysis. Here, we describe an enantioselective, catalytic transformation where both the enantiotopic reaction sites and the prochirality-revealing groups are distant from a prostereogenic quaternary carbon.[1] We addressed the challenges arising from the twofold spatial separations by innovating a unique anionic, axially chiral catalyst and developing a general strategy employing distal electrostatic interactions (Figure 1). This study demonstrates that, contrary to general expectation, it is viable to achieve precise long-range enantioinduction by engaging electrostatic interactions at a remote position, even as distant as 12 connecting atoms away from the reaction site. In addition, our recent studies demonstrates the adaptability of the ionic stereocontrol strategy in construction of axially chiral biaryls[2] and mechanically planar chiral rotaxanes.[3]

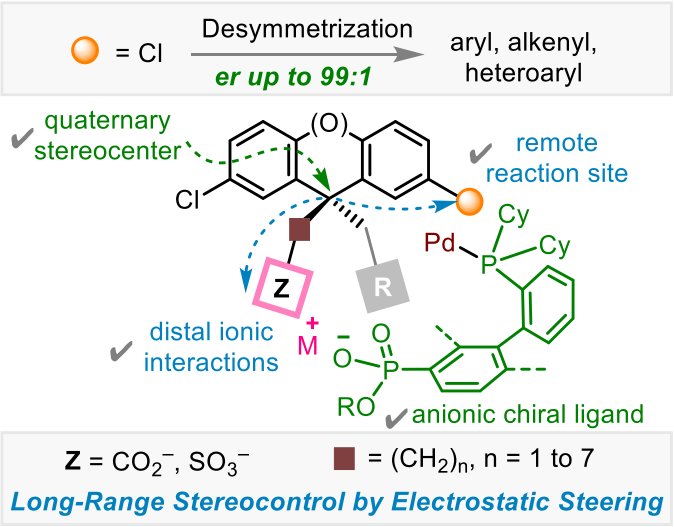

Figure 1. Distal Ionic Substrate–Catalyst Interactions Enable Long-Range Stereocontrol

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POSTER PRESENTERS

Organic Chemistry

Poster No.	Session	Full name	Organization	Abstract title
PO-1	**A**	Yaru GAO	National University of Singapore	Chiral Acid-Catalyzed Enantioselective Condensation Reactions
PO-2	**A**	Ran TAO	National University of Singapore	Enantioconvergent Alkylation of Heterocycles Using Unactivated Alcohols through Borrowing Hydrogen Catalysis
PO-3	**A**	Jiaoting PAN	National University of Singapore	Access to chiral medium-sized heterocycles via Pd-catalyzed enantioselective (4 + n) cycloaddition of azadienes
PO-4	**A**	Huanlin DIAO	National University of Singapore	Enantioconvergent N-Heterocycle Synthesis through Borrowing Hydrogen Catalysis
PO-5	**A**	Xiaoxu YANG	National University of Singapore	Ligand-Enabled Stereodivergence in Nickel-Catalyzed Regioselective Hydroboration of Internal Allenes
PO-6	**A**	Jia LI	National University of Singapore	Copper-Catalyzed Quadruple Borylation of Terminal Alkynes to Access sp3-Tetra-Organometallic Reagents
PO-7	**A**	Junqiang WEI	National University of Singapore	Distal Ionic Substrate−Catalyst Interactions Enable Long-Range Stereocontrol: Access to Remote Quaternary Stereocenters through a Desymmetrizing Suzuki−Miyaura Reaction
PO-8	**A**	Keng Wee Ivan ON	National University of Singapore	Ionic interactions enable atroposelective Suzuki−Miyaura coupling: stereocontrol directed by ortho- and meta-groups
PO-9	**A**	Chi LIU	National University of Singapore	Constructing P-stereogenic center through long-range recognition of the para-position
PO-10	**A**	Kevin Timothy FRIDIANTO	National University of Singapore	Development of cationic naphthoquinoneimidazoles as novel antimycobacterial agents
PO-1	**B**	Quanquan WANG	National University of Singapore	Visible light activation enables desulfonylative cross-coupling of glycosyl sulfones
PO-2	**B**	Yi JIANG	National University of Singapore	Synthesis of C-Glycosides by Ti-Catalyzed Stereoselective Glycosyl Radical Functionalization
PO-3	**B**	Chenfei LIU	National University of Singapore	Nickel/NHC-catalyzed regio- and stereoselective functionalization of alkenes
PO-4	**B**	Lei DAI	National University of Singapore	Asymmetric multifunctionalization of alkynes via photo-irradiated organocatalysis
PO-5	**B**	Qingqin HUANG	National University of Singapore	Nickel-Hydride-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes

PO-6	**B**	Jiami GUO	National University of Singapore	Light-Induced Phosphine-Catalyzed Asymmetric Functionalization of Benzylic C–H Bonds
PO-7	**B**	Haidi TANG	National University of Singapore	Sustainable synthesis of thioesters from feedstock chemicals and elemental sulfur
PO-8	**B**	Qingyao LI	National University of Singapore	Photomediated reductive coupling of nitroarenes with aldehydes for amide synthesis
PO-9	**B**	Mingyue WU	National University of Singapore	Serendipitous Discovery of Photoinduced Hydroxyl Radical Formation Enabled by a Micro-Tubing Reactor Facilitating C(sp3)-H Bond Activation
PO-10	**B**	Jinhui XU	National University of Singapore	Unveiling Extreme Photoreduction Potentials of Donor-Acceptor Cyanoarenes to Access Aryl Radicals from Aryl Chlorides
PO-11	**A**	Cai Xia Esther ANG	Nanyang Technological University	Synthesis of Chiral Tertiary Amine N-oxides
PO-12	**A**	Ziqi YANG	Nanyang Technological University	Chiral Pentanidium and Anionic Pyridinyl-Sulfonamide Ion Pair as Enantioselective Catalyst
PO-13	**A**	Yuan XU	Nanyang Technological University	Combatting Pathogenic Bacteria with Synthetic Immunotherapeutics: Antibody Recruiting at Engineered Bacterial Surface with Peptidoglycan Analogs
PO-14	**A**	Xiaolin ZHANG	Nanyang Technological University	Rapid Access to Bacterial Cell Wall Feedstock: GlcNAc-1,6- anhydro-MurNAc-muropeptide as a Glycosyl Acceptor of Transglycosylase
PO-15	**A**	Han DING	Nanyang Technological University	Catalytic Glycosylation of Glycosyl ortho-2,2-Dimethoxycarbonylcyclopropyl Benzoates Driven by Ring-Strain Release
PO-16	**A**	Adisak THANETCHAIYAKUP	Nanyang Technological University	Photocatalytic Deconstructive Aliphatic Carbon–Carbon Bond Cleavage and Functionalization of Unactivated Alcohols
PO-11	**B**	Wenxin LYU	Nanyang Technological University	Programmable Selective Acylation of Saccharides Mediated by Carbene and Boronic acid
PO-12	**B**	Hongling WANG	Nanyang Technological University	Chiral Oxidants and Oxygen-Atom Transfer Reactions
PO-13	**B**	Feddro Gilbert WIJAYA	Nanyang Technological University	Concise Synthesis of Sophisticated Oligosaccharides such as Fondaparinux
PO-14	**B**	Eugene Yew Kun TAN	Nanyang Technological University	Pyrrolo[2,1-a]isoquinolines as multitasking organophotocatalysts in chemical synthesis
PO-15	**B**	Sekiguchi YOSHIYA	Nanyang Technological University	Base-induced dehydrogenative and dearomative transformation of 1-naphthylmethylamines to 1,4-dihydronaphthalene-1-carbonitriles

PO-16	**B**	Jiahua CHEN	Nanyang Technological University	Synthesis of a-tertiary amines via iterative addition of carbon nucleophiles to N,N-dialkyl carboxamides
PO-17	**A**	Shun KAWANO	Tohoku University	Total Syntheses of Acochlearine and Related Alkaloids
PO-18	**A**	Yuma SHIRATORI	Hokkaido University	Stereoselective Synthesis of Tetrasubstituted Alkenyl Boronates via Alkylboration of gem-Disubstituted Allenes
PO-19	**A**	Jian ZHOU	Hong Kong Baptist University	Enantio- and Regioselective Construction of 1,4-Diamines via Cascade Hydroamination of Methylene Cyclopropanes
PO-20	**A**	Natsuki OYAMA	Hokkaido University	Cu(I)-catalyzed Enantioselective γ-Boryl substitution of Trifluoromethyl- and Silyl-substituted Alkenes
PO-21	**A**	Soojin KWAK	Yonsei university	Regio- and Stereoselective Addition of Secondary Phosphine Oxides to Allenoates Catalyzed by Main Group Lewis Pairs
PO-22	**A**	Byungjun KIM	Yonsei Univerisity	Asymmetric Organocatalytic Diels–Alder Reaction of α,β-Unsaturated Esters via Dual HOMO and LUMO activation
PO-23	**A**	Aidan KERCKHOFFS	University of Oxford	Red-shifting azobenzenes: periodic trends, tuneable half-lives and chalcogen bonding
PO-24	**A**	Daniella CHEANG	University of Oxford	New Methods for Stereocontrol in Hydrogen Borrowing Catalysed Enolate Alkylation
PO-26	**A**	Sophie RODRIGUES	ICMMO - LCM Team	Bimolecular Vinylation of Arenes in HFIP
PO-27	**A**	Yuta KONDO	Kyushu University	Development of Direct Catalytic Synthesis of N-Unprotected Ketimines
PO-28	**A**	Taiki HASHIMOTO	Osaka university	Triaryl Boranes for Catalytic Hydrogenation of N-Heteroaromatics with H2/CO/CO2 Mixed Gas
PO-31	**A**	He-Xin XIAO	Academia Sinica	Synthesis and Characterization of Chiral BINAP-Carbone Palladium Complexes and Their Application in Catalysis
PO-17	**B**	Amy CHAN	Princeton University	Carbon–Nitrogen Cross-Coupling via First-Row Photoredox Catalysis
PO-18	**B**	Cesar Prieto KULLMER	Princeton University	A Phenotypic Approach to Reaction Generality and Mechanistic Insight
PO-19	**B**	Hikaru NAKAHARA	Waseda University	A Functional Group Metathesis between Ketones and Esters via sequential Claisen/retro-Claisen Condensation
PO-20	**B**	Hiroki KATO	Waseda University	Pd-Catalyzed Dearomative Alkylation of Bromoarenes: Development of Reaction and Chiral Ligands through Molecular Field Analysis

PO-21	**B**	Holt SAKAI	Princeton University	Nontraditional Fragment Couplings of Alcohols and Carboxylic Acids
PO-22	**B**	Olivia GARRY	Princeton University	Rapid Access to 2-Substituted Bicyclo[1.1.1]pentanes
PO-23	**B**	Keiichiro LIZUMI	Waseda University	Denitrative Cyanation of Nitroarenes and Organocyanides by a Palladium Catalyst
PO-24	**B**	Kotaro ASAHARA	Waseda University	Pd-Catalyzed Intramolecular Denitrative Mizoroki–Heck Reaction
PO-25	**B**	Miki KUROSAWA	Waseda University	Synthesis of Multiply Arylated Alkanes by Catalytic Deoxygenative Transformation of Diarylketones
PO-26	**B**	Ryuya MIYAZAKI	Waseda University	Synthesis and Reaction of Chloromethylboryl-N-tosylhydrazone as a Multiply Convertible Building Block
PO-27	**B**	Shun NAGAI	Osaka University	N-Phosphine Imide-Substituted Imidazolylidenes (PimIms) and N-Borane-Substituted Cyclic Phosphine Imides (BCPIs)
PO-28	**B**	Xiang LYU	Korea Advanced Institute of Science & Technology	Inter/intra-molecular Alkyne Hydroamidation Enabled by NiH Catalysis
PO-29	**B**	Chen-Hsun HUNG	Academia Sinica	Coupling with Heteroarene and Arenol via Ni-catalyzed C-H/C-OH activation
PO-30	**B**	Myojeong KIM	Korea Advanced Institute of Science & Technology	Site-Selective Pyridylic C–H Functionalization by Photocatalytic Radical Cascades
PO-31	**B**	Changseok LEE	Korea Advanced Institute of Science & Technology	Regio- & Enantioselective Hydroamination of Unactivated Alkenes via Chelateion-Assisted Nickel-Hydride-Catalysis
PO-32	**B**	Wooseok LEE	Korea Advanced Institute of Science & Technology	Regioselective C–H activation of Pyridine by Using N-N Pyridinium Derivatives
PO-33	**B**	Sanghoon SHIN	Korea Advanced Institute of Science & Technology	Strain-Release AminoPyridylation of [1.1.1]Propellanes Using N-Aminopyridinium Salts with Electrophilic Radicals under Visible Light Irradiation

Inorganic Chemistry

Poster No.	**Session**	**Full name**	**Organization**	**Abstract title**
PI-1	**A**	Dinh Cao Huan DO	National University of Singapore	Controlled Access to Four- and Six-Membered Palladacycles via Fine-Tuning Donor Abilities of b-Ketiminato Ligands
PI-2	**A**	Sara AGUIAR	National University of Singapore	Mono- and Bis(Benzimidazolin-2-ylidene) Complexes of Molybdenum(0)
PI-3	**A**	Chak Yu Richard CHAN	National University of Singapore	Selective Monodefluorination of the α-Trifluoromethylstyrene System via Alane Frustrated Lewis Pair
PI-4	**A**	Teresa Yu Ping LIM	Nanyang Technological University	Metal Carbonyl Complexes As Theranostic Corms
PI-5	**A**	Xin LIANG	Nanyang Technological University	A New Class of Triosmium Carbonyl Clusters with Anti-Cancer Properties
PI-6	**A**	Zhen Xuan WONG	Nanyang Technological University	Protein Interactions with Ruthenium Structural Mimics of [Fe]-Hydrogenase
PI-1	**B**	Chenting YAN	Nanyang Technological University	A Three-membered AlN2 Heterocycle to Access an Al=C π Bonding Species
PI-2	**B**	Lizhao ZHU	Nanyang Technological University	Inorganic Huisgen Reaction between 1,2-Diboraallene and Azide to Access a Diboratriazole
PI-3	**B**	Yeow Chuan Nicholas TEO	Nanyang Technological University	A NHC-Silyliumylidene Cation for Catalytic Chemoselective Hydroboration of Isocyanates using Hbpin
PI-4	**B**	Jiawen LEE	Nanyang Technological University	An Amidinato Isopropylmethylamidosilylene for Catalytic Hydroboration of Carbonyl Compounds
PI-5	**B**	Jun FAN	Nanyang Technological University	A Pyridine-Stabilized N-Phosphinoamidinato NHC-Diboravinyl Cation: Boron Analogue of Vinyl cation
PI-7	**A**	Gil Sun LEE	Kookmin University	CO 2 is used to kinetically resolve Mg 2+ ion from Ca 2+ ion in CaMg(CO 3) 2 Dolomite
PI-8	**A**	Seung Jae LEE	Jeonbuk National University	Complex formation for electron transfer pathway from soluble methane monooxygenase
PI-9	**A**	Darren OULD	University of Cambridge	Synthesis and Electrolyte Design for Sodium-Ion Batteries
PI-10	**A**	Hao ZHAO	Okinawa Institute of Science and Technology Graduate University	Water-Soluble Nanoparticles with Twisted Double[7]Carbohelicene for Lysosome- Targeted Cancer Photodynamic Therapy

PI-6	**B**	James OAKLEY	Princeton University	Radius measurement via super-resolution microscopy enables the development of a variable radii proximity labeling platform
PI-7	**B**	Jinheung KIM	Ewha Womans University	*Title to be updated*
PI-8	**B**	Thomas LAINER	Graz University of Technology	New single-source precursors for thin-film deposition
PI-9	**B**	Chao-Hsien LEE	Academia Sinica	Reshaped Bonding in Pincer Anionic Carbodicarbene Metal Complexes

Material Chemistry

Poster No.	Session	Full name	Organization	Abstract title
PM-1	**A**	Tianyu JIAO	National University of Singapore	Synthesis of monolayer and persistent bilayer graphene fragments via a radical-radical coupling approach
PM-2	**A**	Wei FAN	National University of Singapore	Synthesis of topological molecular carbons by Bi(OTf)3-mediated cyclization
PM-3	**A**	Qifeng ZHOU	National University of Singapore	Facile Synthesis of a Twisted Figure-Eight Carbon Nanobelt
PM-4	**A**	Yi HAN	National University of Singapore	Atomically Precise Synthesis of Single-Walled Carbon Nanotube Fragments
PM-5	**A**	Qing JIANG	National University of Singapore	Circumpentacene: Synthesis, Crystal Structure and Redox Properties
PM-6	**A**	Tingting XU	National University of Singapore	Antiaromatic Dicyclopenta[b,g]/[Antiaromatic Dicyclopenta[b,g]/[a,f]naphthalene Isomers Showing Open-shell Singlet Ground State with Tunable Diradical Character
PM-7	**A**	Jiawei SHAO	National University of Singapore	Formation of a tetraazulene fused [10]annulene dication through oxidation-controlled C-C single bond dissociation
PM-1	**B**	Shanshan TAO	National University of Singapore	Hydroxide Anion Transport in Covalent Organic Frameworks
PM-2	**B**	Ke Tian TAN	National University of Singapore	Water cluster in hydrophobic crystalline porous covalent organic frameworks
PM-3	**B**	Lei SUN	National University of Singapore	Rational design of microporous biochar based on ion exchange using carboxyl as an anchor for high-efficiency capture of gaseous p-xylene
PM-8	**A**	Xiaodong ZHANG	Nanyang Technological University	Thiolate-Assisted Route for Constructing Chalcogen QuaNanyang Technological Universitym Dots with Photoinduced Fluorescence Enhancement
PM-9	**A**	Xiaokai CHEN	Nanyang Technological University	Synthesis of tumor extracellular matrix-targeted nanoscavengers to reserve the tumor suppressive microenvironment
PM-10	**A**	Ting HE	Nanyang Technological University	Porphyrin-Based Covalent Organic Frameworks Anchoring Au Single Atoms for Photocatalytic Nitrogen Fixation
PM-4	**B**	Xinjiang ZHANG	Nanyang Technological University	Synthesis of a pi-Extended Azacorannulenophane Enabled by Strain-Induced 1,3-Dipolar Cycloaddition

PM-5	**B**	Fiona HANINDITA	Nanyang Technological University	Fully Conjugated Azacoranulene Dimer as Large Diaza[80]fullerene Fragment
PM-6	**B**	Hamamoto YOSUKE	Nanyang Technological University	Diazapentabenzocorannulenium: A Hydrophilic/Biophilic Cationic Buckybowl
PM-7	**B**	Gabor Bati	Nanyang Technological University	Mechanochemical Synthesis of Curved Nanographenes
PM-8	**B**	Jovana Stanojkovic	Nanyang Technological University	Regioselective chlorination of extended corannulene structures - Mechanochemical approach
PM-9	**B**	Zhongbo Zhang	Nanyang Technological University	Synthesis of Corannulene-Based QuiNanyang Technological Universityple Helicene
PM-11	**A**	Davin Tan	Institute of Materials Research and Engineering	Towards a Low-Carbon Hydrogen-Based Economy: The Issue of Fugitive Emissions
PM-12	**A**	Jaime Pang	Institute of Materials Research and Engineering	Inorganic/Organic Duplex Coating for Corrosion Protection of Al Alloys
PM-13	**A**	Jason Lim	Institute of Materials Research and Engineering	Upcycling Waste Plastics into Functional Materials
PM-14	**A**	Pek Yin Michelle Yew	Institute of Materials Research and Engineering	Electrospun PLA-lignin nanofibers for cartilage regeneration scaffold
PM-10	**B**	Qianyu Lin	Institute of Materials Research and Engineering	High molecular weight hyper-branched PCL-based thermogelling vitreous endotamponades
PM-11	**B**	Tristan Tan	Institute of Materials Research and Engineering	Using Adipic Acid as a Linker in the Benchmark MOF UiO-66
PM-12	**B**	Wenbin Jiang	Institute of Materials Research and Engineering	Single Iron Sites Doped Photocatalyst for Solar-Driven Wastewater Treatment
PM-13	**B**	Constantin Eisen	Institute of Materials Research and Engineering/ University of Vienna	Development of PEG-NHC@AuNPs for Biomedical Sensing
PM-17	**B**	Yoshinobu KAMAKURA	Tokyo Institute of Technology	Visible-Light-Driven Photocatalytic CO2 Reduction into Formate Using Nonporous Coordination Polymer without Precious Metals
PM-16	**A**	Mengqing CHEN	The University of Tokyo	Iron-Catalyzed Tandem Cyclization of Diarylacetylene to a Strained 1,4-Dihydropentalene Framework for Narrow-Band-Gap Materials
PM-17	**A**	Sorachi MIWA	Kyoto University	Synthesis and optical properties of helicene–xanthene hybrid dyes
PM-14	**B**	Takayoshi AKIYAMA	The University of Tokyo	Supramolecular Depolymerization by Homochiral Polymer Solution Mixing

PM-15	**B**	Takumi SAKAMAKI	The University of Tokyo	Two Spiro–Conjugated Carbon–Bridged p–Phenylenevinylene: Synthesis and Properties
PM-16	**B**	Kamonwad NGAMCHUEA	Suranaree University of Technology	Electrocatalysis of hydrogen peroxide at copper hexacyanoferrates: mechanistic insights from experimental and computational studies

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