



THE CHEMICAL
SOCIETY OF JAPAN



The Chemical Society
Located in Taipei

The 5th CSJ-CSLT Joint Symposium

Sustainable Chemical Synthesis via Emerging Designer Catalysts

In conjunction with the 105th Spring Annual Meeting of the Chemical Society of Japan
Room 3202, Floor 2, Bldg. 3, Area 4; Senriyama Campus, Kansai University
Thursday, March 27, 2025

PROGRAM

Session 1 Chen, Yu-Ju (陳 玉如) *Presiding*

- 09:00 **Special Lecture: Proteomics and Mass Spectrometry**
Chen, Yu-Ju (陳 玉如) *CSLT President, Academia Sinica*
- 09:25 **Rational Construction of Molecular Cages and Their Application in Catalysis**
Chan, Yi-Tsu (詹 益慈) *National Taiwan University*
- 09:50 **Development of Artificial Catalytic Systems Inspired by Natural Photosynthesis**
Kondo, Mio (近藤 美欧) *Institute of Science Tokyo*
- 10:15 Break
- 10:25 **Total Synthesis of (±)-Arnicenone via a Stereodivergent Angular Triquinane Synthesis**
Huang, Yu-Wen (黃 郁文) *National Tsing Hua University*
- 10:50 **Synergistic Progress of Living Ionic and Radical Polymerizations via Catalysis for Sustainable Developments**
Kamigaito, Masami (上垣外 正己) *Nagoya University*
- 11:15 **contra-Thermodynamic Positional Isomerization: From Enoates to Alkenyl α -Stereogenic Esters**
Liao, Hsuan-Hung (廖 軒宏) *National Sun Yat-sen University*
- 11:40 Lunch

Session 2 Sawamoto, Mitsuo (澤本 光男) *Presiding*

- 13:00 **Selective CO₂ Conversion to Value-Added Compounds by Heterogeneous Catalysts**
Shishido, Tetsuya (宍戸 哲也) *Tokyo Metropolitan University*
- 13:25 **Palladium-Catalyzed Arylation of Cyclic Vinylogous Esters**
Wu, Yen-Ku (吳 彥谷) *National Yang Ming Chiao Tung University*
- 13:50 **Development of Chiral Catalysts for Asymmetric C-H Functionalization towards Sustainable Synthesis**
Matsunaga, Shigeki (松永 茂樹) *Kyoto University*
- 14:15 **Closing Remarks**
Chen, Yu-Ju (陳 玉如) *President, CSLT*
Maruoka, Keiji (丸岡 啓二) *President, CSJ*

Yi-Tsu Chan

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Education/Career:

2022-present Director, Science Promotion and Engagement Center, National Taiwan University
2021-present Professor, Department of Chemistry, National Taiwan University
2017-2021 Associate Professor, Department of Chemistry, National Taiwan University
2012-2017 Assistant Professor, Department of Chemistry, National Taiwan University
2010-2012 JSPS Research Fellow, Department of Chemistry and Biotechnology,
The University of Tokyo, Japan (Supervisor: Prof. Takuzo Aida)
2005-2010 Ph.D., Department of Polymer Science,
The University of Akron, USA (PhD, Supervisor: Prof. George R. Newkome)
2000-2002 M.S., Department of Chemistry, National Taiwan University
1996-2000 B.S., Department of Chemistry, National Taiwan University

Research Interests

Supramolecular Coordination Chemistry, Polymer Chemistry, and Porous Materials

Representative Publications

- (1) S.-Y. Wang, L.-T. Lin, A. Rani, G.-S. Lee, **Y.-T. Chan**,* “Stepwise Construction of a Metallocatenane Based on Non-labile Bis(terpyridine)-Cd^{II} Complexes”, *Chem. Commun.* **2024**, 60, 7914–7917.
- (2) L. He, L. Li, S.-C. Wang, **Y.-T. Chan**,* “Sequential Self-Assembly of Calix[4]resorcinarene-based Heterobimetallic Cd₈Pt₈ Nano-Saturn Complexes”, *Chem. Commun.* **2023**, 59, 11500–11503.
- (3) L. He, H.-K. Hsu, L. Li, L.-T. Lin, T.-H. Tu, T.-G. Ong, G.-G. Liou,* **Y.-T. Chan**,* “A 10-nm-sized multicompartiment cuboctahedron and its 2D hierarchical arrays observed by cryo-EM”, *Chem* **2022**, 8, 494–507.
- (4) T.-H. Tu, T. Sakurai, S. Seki, Y. Ishida,* **Y.-T. Chan**,* “Towards Macroscopically Anisotropic Functionality: Oriented Metallo-supramolecular Polymeric Materials Induced by Magnetic Fields”, *Angew. Chem., Int. Ed.* **2021**, 60, 1923–1928.
- (5) S.-C. Wang, K.-Y. Cheng, J.-H. Fu, Y.-C. Cheng, **Y.-T. Chan**,* “Conformational Regulation of Multivalent Terpyridine Ligands for Self-Assembly of Heteroleptic Metallo-Supramolecules”, *J. Am. Chem. Soc.* **2020**, 142, 16661–16667.
- (6) L. He, S.-C. Wang, L.-T. Lin, J.-Y. Cai, L. Li, T.-H. Tu, **Y.-T. Chan**,* “Multicomponent Metallo-Supramolecular Nanocapsules Assembled from Calix[4]resorcinarene-Based Terpyridine Ligands”, *J. Am. Chem. Soc.* **2020**, 142, 7134–7144.
- (7) J.-H. Fu, S.-Y. Wang, Y.-S. Chen, S. Prusty, **Y.-T. Chan**,* “One-Pot Self-Assembly of Stellated Metallosupramolecules from Multivalent and Complementary Terpyridine-Based Ligands”, *J. Am. Chem. Soc.* **2019**, 141, 16217–16221.
- (8) Y.-S. Chen, E. Solel, Y.-F. Huang, C.-L. Wang, T.-H. Tu, E. Keinan,* **Y.-T. Chan**,* “Chemical Mimicry of Viral Capsid Self-Assembly via Corannulene-Based Pentatopic Tectons”, *Nat. Commun.* **2019**, 10, 3443.

Rational Construction of Molecular Cages and Their Application in Catalysis

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Recently, 2,2':6',2''-terpyridine (tpy) ligands have garnered significant attention in coordination-driven self-assembly, where multivalent ligands with appropriate geometries are used to create diverse 2D and 3D metallo-supramolecular architectures in a one-pot synthesis.^{1,2} Dynamic heteroleptic coordination with high fidelity has also proven to be a crucial tool for constructing large, discrete structures. In this study, we present the construction of a giant cuboctahedral Cd-48 complex through the cooperative assembly of a multivalent system.³ This Cd-48 coordination cage complex (CCC), with a 5-nm-sized cavity, is assembled from 48 Cd(II) ions, and is highly suitable for hosting ultrafine metal nanoparticles. The cationic framework of the cage accommodates anionic metal sources, and through adsorption and subsequent reduction of these metal sources, we successfully synthesized three hybrid materials: Au@CCC, Pd@CCC, and Pt@CCC. In each case, the resulting nanoparticles of Au, Pd, and Pt are smaller than 4 nm, demonstrating the molecular cage's effectiveness in encapsulating metal nanoparticles. The synergistic effects between the CCC framework and metal nanoparticle surfaces for catalysis are also discussed.

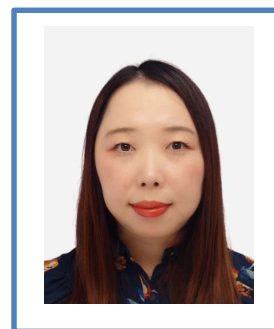
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- [1] Fu, J.-H.; Lee, Y.-H.; He, Y.-J.; Chan, Y.-T. *Angew. Chem., Int. Ed.* **2015**, *54*, 6231–6235.
- [2] Wang, S.-Y.; Fu, J.-H.; Liang, Y.-P.; He, Y.-J.; Chen, Y.-S.; Chan, Y.-T. *J. Am. Chem. Soc.* **2016**, *138*, 3651–3654.
- [3] He, L.; Hsu, H.-K.; Li, L.; Lin, L.-T.; Tu, T.-H.; Ong, T.-G.; Liou, G.-G.; Chan, Y.-T. *Chem* **2022**, *8*, 494–507.

Professor Mio KONDO (近藤 美欧)

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Education

2008 Ph.D. The University of Tokyo, Tokyo, Japan
2003 B.S., The University of Tokyo, Tokyo, Japan

Academic Careers

2024 Professor, Institute of Science Tokyo, Tokyo, Japan
2023-2024 Professor, Tokyo Institute of Technology, Tokyo, Japan
2019-2023 Associate Professor, Osaka University, Suita, Japan
2011-2019 Assistant Professor, Institute for Molecular Science, Okazaki, Japan
2008-2011 Postdoctoral Fellow, Kyoto University, Kyoto, Japan

Awards

2021 FY2021 Mazda Research Grant Encouragement Award
2018 7th NINS Young Researcher Award
2018 6th CSJ Female Chemist Encouragement Award
2016 Morita Science Research Award

Representative Publications

Iron-Complex-Based Supramolecular Framework Catalyst for Visible-Light-Driven CO₂ Reduction, Kosugi, K.; Akatsuka, C.; Iwami, H.; Kondo, M.*; Masaoka, S.* *J. Am. Chem. Soc.* **2023**, *145*, 10451. (Selected as a Back Cover Picture)

Quick and Easy Method for Dramatic Improvement of the Electrochemical CO₂ Reduction Activity of an Iron Porphyrin Complex, Kosugi, K.; Kondo, M.*; Masaoka, S.* *Angew. Chem. Int. Ed.* **2021**, *60*, 22070.

Electrochemical Polymerization Provides a Function-Integrated System for Water Oxidation, Iwami, H.; Okamura, M.; Kondo, M.*; Masaoka, S.* *Angew. Chem. Int. Ed.* **2021**, *60*, 5965. (Selected as a Hot Paper, selected as an Inside Back Cover Picture, Highlighted in *ChemViews*)

Modulation of self-assembly enhances the catalytic activity of iron porphyrin for CO₂ reduction, Tasaki, M.; Okabe, Y.; Iwami, H.; Akatsuka, C.; Kosugi, K.; Negita, K.; Kusaka, S.; Matsuda, R.; Kondo, M.*; Masaoka, S.* *Small* **2021**, 2006150. (Selected as an Inside Back Cover Picture)

Pentanuclear scaffold: a molecular platform for small-molecule conversions, Kondo, M.; Masaoka, S.* *Acc. Chem. Res.* **2020**, *53*, 2140.

A pentanuclear iron catalyst designed for water oxidation, Okamura, M.; Kondo, M., Kuga, R.; Kurashige, Y.; Yanai, T.; Hayami, S.; Praneeth, V. K. K; Yoshida, M.; Yoneda, K.; Kawata, S.; Masaoka, S.* *Nature* **2016**, *530*, 465. (Highlighted in News & Views in *Nature Energy*: "Water oxidation: High five iron")

Development of Artificial Catalytic Systems Inspired by Natural Photosynthesis

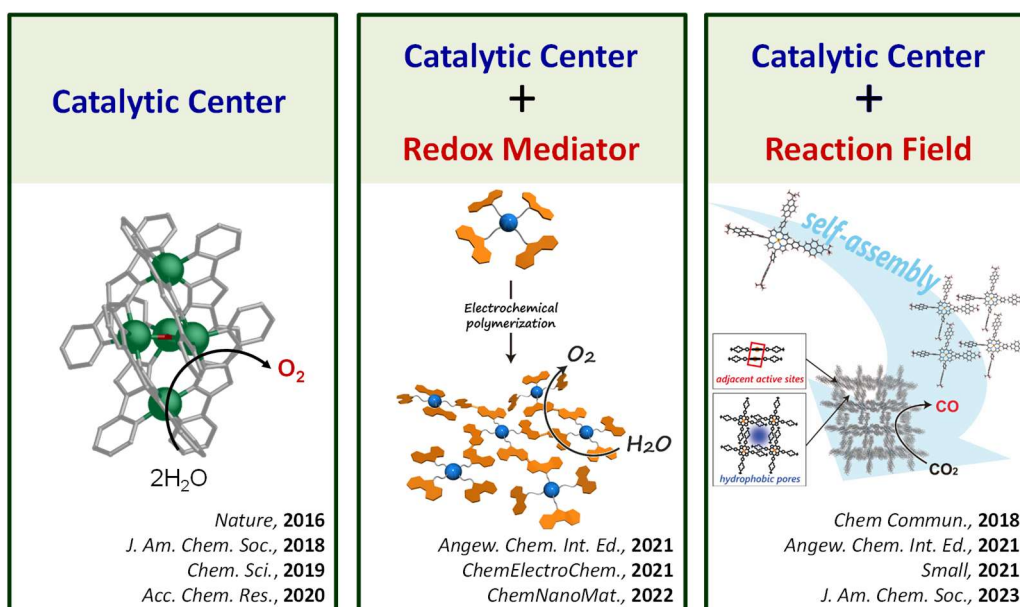
Mio KONDO

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Artificial photosynthesis, a process mimicking natural photosynthetic reactions, is believed to be a viable solution to energy and environmental problems, as it can cleanly produce useful chemical energy sources (e.g., hydrogen and methanol) from earth-abundant substances such as water and carbon dioxide. Among the two half-reactions involved in artificial photosynthesis, the oxidation half-reaction corresponds to oxygen production via the four-electron oxidation of water ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$), while the reduction of carbon dioxide or water by the thus released electrons to afford a chemical energy source constitutes the reduction half-reaction. As both of these half-reactions are small-molecule transformations requiring the presence of catalysts, the development of highly efficient catalysts for small-molecule conversion is important for the realization of artificial photosynthesis. Natural photosynthesis achieves the efficient small molecule conversions by the synergistic effect between (1) an active center with good reactivity, (2) charge-transporting sites close to the active center, and (3) substrate-transporting channels. Inspired by the natural photosynthesis, we have been working on the development of artificial catalytic systems for small molecule conversions. As a result, we have obtained the highly active catalytic centers for water oxidation by the integration of multielectron transfer ability and bond formation ability¹. Moreover, it was revealed that efficient catalytic system for water oxidation can be constructed by the integration of active center and charge transfer site. In addition, we also demonstrated that efficient catalytic system for carbon dioxide reduction can be obtained by the integration of adjacent active center and reaction field.



References

1. Kondo, M.; Tatewaki, H.; Masaoka, S. *Chem. Soc. Rev.* **2021**, 50, 6790.

Curriculum Vitae

Name Yu-Wen Huang (黃郁文)
Birth Taiwan, ROC, 1982, 12, 4.
Education B. Sc. National Cheng Kung University, 2001-2005
M. S. National Tsing Hua University,
(w/ Shang-Cheng Hung), 2005-2007
Ph. D. University of Rochester,
(w/ Alison J. Frontier), 2009-2016



Professional Appointment:

Postdoctoral researcher (w/ John L. Wood), Baylor University, 2016-2019
Assistant Professor, National Tsing Hua University 2019-Present

Research Interests

- (1) Natural product synthesis
- (2) Methodology development

List of Publications (2007-2024)

1. Chen, P.-C.; You, P.-Y.; Wu, L.-Y.; Chin, Z.; Chiu, K.-H.; Hsieh, S.-T.; Huang, Y.-W.* “Diastereodivergent α -Homoallylation of Cyclic Enones”, *Org. Lett.*, **2024**, 26, 553-558. (IF = 5.2, Ranking = 5.17%, 3/58, Chemistry, Organic)
2. Chiou, Y.-J.; Chan, Y.-F.; Yu, S.-P.; Lu, C.-Y.; Hsiao, S. S.-Y.; Chiang, P.-W.; Hsu, T.-C.; Liu, P.-Y.; Wada, N.-H.; Lee, Y.; Jane, W.-N.; Lee, D.-C.; Huang, Y.-W.; Tang, S.-L.* “Similar But Different: Characterization of *dddD* Gene-mediated DMPS Metabolism Among Coral-associated *Endozoicomonas*”, *Sci. Adv.* **2023**, 9, eadk1910. (IF = 13.6, Ranking = 9.58%, 7/73, Sciences, Multidisciplinary)
3. Huang, Y.-W.; Kong, K.; Wood, J. L.* “Total Synthesis of (+)- and (±)-Hosieine A”, *Angew. Chem., Int. Ed.*, **2018**, 57, 7664-7667. (IF = 12.257, Ranking = 9.59%, 17/172, Chemistry, Multidisciplinary, Citations = 17)
4. Huang, Y.-W.; Frontier, A. J.* “Nazarov Cyclization/Internal Redox Cyclization Sequence for the Synthesis of *N*-Heterocyclic Bridged Ring Systems”, *Org. Lett.*, **2016**, 18, 4896-4899. (IF = 6.579, Ranking = 4.24%, 3/59, Chemistry, Organic, Citations = 23)
5. Huang, Y.-W.; Frontier, A. J.* “Enantioselective Nazarov cyclization catalyzed by a Cinchona alkaloid derivative”, *Tetrahedron Lett.*, **2015**, 56, 3523-3526. (IF = 2.347, Ranking = 41.53%, 25/59, Chemistry, Organic, Citations = 23)
6. Patil, P. S.; Lee, C.-C.; Huang, Y.-W.; Zulueta, M. M. L.; Hung, S.-C.* “Regioselective and stereoselective benzyldiene installation and one-pot protection of D-mannose”, *Org. Biomol. Chem.*, **2013**, 11, 2605-2612. (IF = 3.389, Ranking = 21.55%, 13/58, Chemistry, Organic, Citations = 32)
7. Wang, C.-C.; Lee, J.-C.; Luo, S.-Y.; Kulkarni, S. S.; Huang, Y.-W.; Lee, C.-C.; Chang, K.-L.; Hung, S.-C.* “Regioselective one-pot protection of carbohydrates”, *Nature*, **2007**, 446, 896-899. (IF = 28.751, Ranking = 1%, 1/50, Multidisciplinary Sciences, Citations = 418)

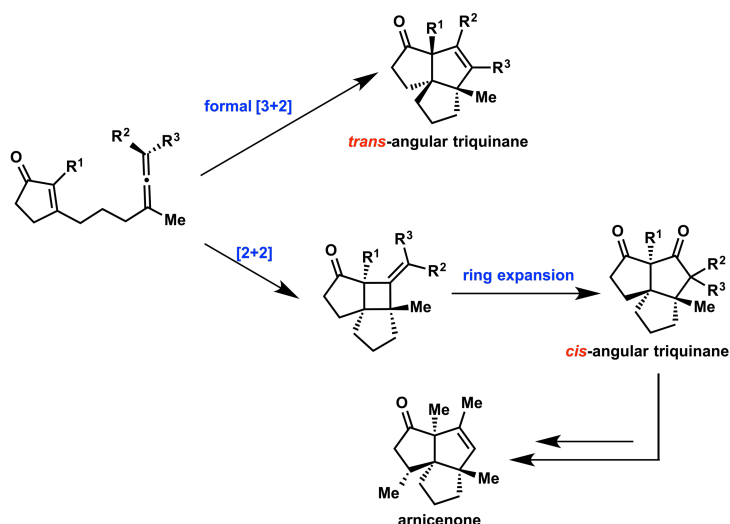
Total Synthesis of (±)-Arnicenone via a Stereodivergent Angular Triquinane Synthesis

Hung-Tse Huang, Li-Yun Wu, Chia-Hou Liu, Shubham Dighe, Yu-Wen Huang*

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Angular triquinane consists of cyclopentanes fused in *cis*-fashions with multiple all-carbon quaternary stereocenters embedded in the ring junctions. Its unique structural complexity possesses a synthetic challenge. Therefore, natural products, such as isocomene, siphenene, arnicenone,^{(1), (2)} waihoensene, and crinipellin A, containing angular triquinane have drawn a great deal of attention in synthetic community. Here, we will discuss our strategy in the total synthesis of arnicenone. During our study, we've developed stereodivergent pathways access to both *cis*- and *trans*-angular triquinane skeletons. These pathways include an acid-promoted formal [3+2] cycloaddition for the synthesis of *trans*-angular triquinane. In addition, a [2+2] cycloaddition followed by a ring expansion route enabled the formation of *cis*-angular triquinane, ultimately leading to the synthesis of arnicenone.



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Yu-Wen Huang (黃郁文)

National Cheng Kung University (BS, 2005)

National Tsing Hua University (MS, 2007)

University of Rochester (PhD, 2016)

Baylor University (postdoctoral, 2016-2019)

Assistant Professor (NTHU, 2019-)

[Field of research] Natural Product Synthesis.

Curriculum Vitae

Name: Masami Kamigaito

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Education:

1988 B.S. Degree, Kyoto University (Prof. Toshinobu Higashimura)
1990 M.S. Degree, Kyoto University (Prof. Toshinobu Higashimura)
1993 Ph.D. Degree, Kyoto University (Prof. Toshinobu Higashimura)

Employment:

1993-1995 Postdoctoral Fellow Sponsored by JSPS (Prof. Mitsuo Sawamoto)
1995-1999 Research Instructor, Department of Polymer Chemistry, Kyoto University
1997-1998 Visiting Scholar, Department of Chemistry, Stanford University (Prof. Robert Waymouth)
1999-2003 Associate Professor, Department of Polymer Chemistry, Kyoto University
2003-2004 Associate Professor, Department of Applied Chemistry, Nagoya University
2004-2017 Professor, Department of Applied Chemistry, Nagoya University
2017- Professor, Department of Molecular and Macromolecular Chemistry, Nagoya University

Other Activities:

2012- Editorial Board, *Progress in Polymer Science*
2019- Advisory Board, *Polymer Chemistry*
2020- Editorial Board, *Journal of Polymer Science*
2020- Executive Editorial Board, *Giant*
2022- Associate Editor, *Macromolecules*
2024- International Advisory Board, *Chinese Journal of Polymer Science*
2024- Editorial Board, *Polymer Science & Technology*

Selected Awards:

2020 The Award of the Society of Polymer Science, Japan
2017 Fellow of the Royal Society of Chemistry
2010 Japan IBM Science Award
2009 SPSJ Wiley Award, Society of Polymer Science, Japan
2001 Arthur K. Doolittle Award, PMSE Division, ACS

Research Interests:

Living Polymerization, Stereospecific Polymerization, Sequence Controlled Polymerization, Precision Polymer Synthesis, Bio-Based Polymers, Degradable Polymers

Selected Representative Publications:

- 1) Kamigaito, M. Step-growth irreversible deactivation radical polymerization: synergistic developments with chain-growth reversible deactivation radical polymerization. *Bull. Chem. Soc. Jpn* **2024**, *97*, uoae069.
- 2) Uchiyama, M.; Ohira, N.; Yamashita, K.; Sagawa, K.; Kamigaito, M. Proton transfer anionic polymerization with C–H bonds as the dormant species. *Nat. Chem.* **2024**, *16*, 1630-1637.

Synergistic Progress of Living Ionic and Radical Polymerizations via Catalysis for Sustainable Developments

Masami Kamigaito

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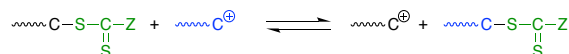
Most of the controlled/living polymerizations developed recently are based on a similar strategy via reversible activation of dormant species into propagating species. This paper focuses on the synergistic progress of living ionic and radical polymerizations.¹ Metal-catalyzed living radical polymerization was developed by analogy with Lewis-acid catalyzed living cationic polymerization, where both are based on the reversible activation of dormant carbon-halogen bonds with metal catalysts. Cationic RAFT polymerization has also been achieved using a similar strategy to radical RAFT polymerization with dormant thioester bonds via degenerative chain-transfer process.² More recently, sulfur-free radical and cationic RAFT polymerizations have been developed using *exo*-olefin compounds as RAFT agents.^{3,4} These polymerizations enable the synthesis of novel polymers, such as chiral polymers⁵ and degradable polymers⁶ with controlled molecular weights. Furthermore, this strategy has also recently been used to develop proton transfer anionic polymerization by base-catalyzed activation of C–H dormant terminals.

Living Cationic Polymerization

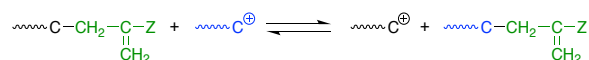
Lewis Acid-Catalyzed Living Cationic Polymerization



Cationic RAFT Polymerization



Sulfur-Free Cationic RAFT Polymerization

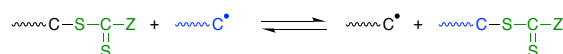


Living Radical Polymerization

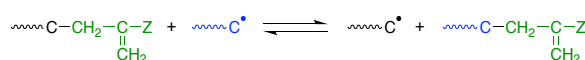
Metal-Catalyzed Living Radical Polymerization Atom Transfer Radical Polymerization



Radical RAFT Polymerization



Sulfur-Free Radical RAFT Polymerization



References

1. Kamigaito, M.; Sawamoto, M. *Macromolecules* **2020**, *53*, 6749–6753.
2. Uchiyama, M.; Satoh, K.; Kamigaito, M. *Prog. Polym. Sci.* **2022**, *124*, 101485.
3. Amano, M.; Uchiyama, M.; Satoh, K.; Kamigaito, M. *Angew. Chem. Int. Ed.* **2022**, *61*, e202212633.
4. Tanimoto, T.; Uchiyama, M.; Kamigaito, M. *Angew. Chem. Int. Ed.* **2023**, *62*, e202307791.
5. Uchiyama, M.; Watanabe, D.; Tanaka, Y.; Satoh, K.; Kamigaito, M. *J. Am. Chem. Soc.* **2022**, *144*, 10429–10437.
6. Uchiyama, M.; Murakami, Y.; Satoh, K.; Kamigaito, M. *Angew. Chem. Int. Ed.* **2023**, *62*, e202215021.
7. Uchiyama, M.; Ohira, N.; Yamashita, K.; Sagawa, K.; Kamigaito, M. *Nat. Chem.* **2024**, *16*, 1630–1637.

Dr. Hsuan-Hung, Liao

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Brief Summary

Hsuan-Hung Liao finished his Ph.D. in Organic Chemistry (Summa Cum Laude, 2016) at RWTH Aachen University in Germany, through DAAD Scholarship, under the guidance of Prof. Magnus Rueping. He was a recipient of the Marie Skłodowska-Curie Individual Fellowship and became a postdoctoral researcher (2017-2019) at the University of Bristol, United Kingdom, in the group of Prof. Varinder Aggarwal. Currently, he is an Associate Professor in the Department of Chemistry, National Sun Yat-sen University (NSYSU), Taiwan. Hsuan-Hung Liao is a recipient of the 2023 Thieme Chemistry Journals Award.

Career

2024-present	Chair of International Ph.D. Program for Science (IPPS), National Sun Yat-sen University
2023-present	Associate professor in Chemistry, National Sun-Yat sen University
2019-2022	Assistant professor in Chemistry, National Sun Yat-sen University
2017-2019	Marie Skłodowska-Curie individual fellow at the University of Bristol
2016-2017	Postdoctoral fellow and subgroup leader, RWTH Aachen University

Education

2012-2016	PhD in Organic Chemistry, RWTH Aachen University, Germany. Grade: Summa Cum Laude
2008-2010	Master of Science in Chemistry, National Tsing Hua University, Taiwan.
2004-2008	Bachelor of Science in Chemistry, National Tsing Hua University, Taiwan.

Selected Honor and Awards

2024-2028	Emerging Young Scholar for the NSTC 2030 Cross-Generation Young Scholars Program
2024-2029	Ministry of Education Yushan Young Scholar (Phase 2)
2023	Asian Core Program Lectureship Award, Korea and Thailand
2023	Outstanding Award for the Young Scholar Innovative and Development in the Taiwan Comprehensive University System
2023	Thieme Chemistry Journal Award
2019-2024	Ministry of Science and Technology young scholar fellowship (the Einstein program)
2019-2024	Ministry of Education Yushan Young Scholar (Phase 1)
2017-2019	EU Horizon 2020 Marie Skłodowska-Curie Individual Fellowship
2017	Borchers-Plakette for outstanding PhD dissertation
2013-2016	Research Grants for Doctoral Candidates and Young Academics and Scientists (DAAD Scholarship)
2012-2013	Taiwan Ministry of Education Studying Abroad Scholarship

contra-Thermodynamic Positional Isomerization: From Enoates to Alkenyl α -Stereogenic Esters.

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Carbonyl compounds bearing α -stereogenic centers are ubiquitous motifs found in bioactive natural products and pharmaceutical drugs, which attracts chemists' interest to devote in the synthetic field.¹ Among the most utilized methods to build this valuable motif is through asymmetric alkylation of enolates which often employs chiral auxiliaries or chiral catalysts.² Despite its notoriety, this route suffers from common disadvantages like the formation of undesirable side products. Consequently, Norrish Type II Rearrangement has been developed as an alternative route toward constructing quaternary centers. Although Norrish Type II Rearrangement has long been established, the successful case of asymmetric Norrish Type II rearrangement is still limited. Moreover, a step- and atom-economy reaction known as photodeconjugation which involved Norrish Type II rearrangement has been developed. Photodeconjugation reaction mechanistically proceeds through *E/Z* isomerization, followed by 1,5-HAT and keto-enol tautomerization to afford the target motif utilizing enones as substrates. In this study, the chiral phosphoric acid-catalyzed asymmetric Norrish type II rearrangement of acyclic α , β -unsaturated ester under UV light irradiation has been developed. The reaction afforded various acyclic enoates with excellent enantioselectivities and moderate to good yields.

References

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2. Ricard, R.; Sauvage, Paul; Wan, C. S. K.; Weedon, A. C.; Wong, D. F. Photochemical Enolization of Acyclic β -Alkyl- α , β -unsaturated Ketones. *J. Org. Chem.* **1986**, *51*, 62–67.

Tetsuya Shishido received his PhD at Hokkaido University in 1997. He began his career as an Assistant Prof. at the Department of Applied Chemistry, Hiroshima University, in 1997 and then moved to the Graduate School of Engineering, Department of Molecular Engineering, Kyoto University, in 2005. In 2013, he was promoted to full Professor at Tokyo Metropolitan University (Graduate School of Urban Environmental Sciences, Department of Applied Chemistry for Environment). His research focuses on heterogeneous catalysis, such as supported metal/metal oxide catalysts, and solid acid-base catalysts for hydrogen production and storage, CO₂ utilization, and biomass conversion. He also works on *in situ* spectroscopic methods to elucidate the reaction mechanism of heterogeneous catalysts at the molecular level. He published more than 280 publications. He is the director of the Research Center for Hydrogen Energy-based Society, TMU, and a fellow of the Royal Society of Chemistry (FRSC). He also works as a board member of the Catalysis Society of Japan, HESS (Hydrogen Energy Systems Society of Japan), Hydrogenomics Alliance Japan, and The Japan XAFS Society.



2009 Catalyst Society of Japan Award for Young Researchers

2009 The Japan Petroleum Institute Award for Encouragement of Research and Development

2022, 2023 The Japan Petroleum Institute Award for Distinguished Papers

Recent publications

1. Phosphorus-Enhanced Ru/TiO₂ Catalysts: A Leap in Selective CO₂ to CO Conversion, M. Li, H. Miura, T. Shishido, *Energy & Fuels*, **2024**, 38, 10050.
2. Methane activation with nitric oxide at low temperatures on supported Pt catalysts: effects of the support, N. Suganuma, T. Shishido et al., *Catal. Sci. Tech.*, **2023**, 13, 3927.
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Selective CO₂ conversion to value-added compounds by heterogeneous catalysts

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The catalytic conversion of CO₂ into value-added chemicals such as CO, CH₄, CH₃OH, C₂+OH, and hydrocarbons using green H₂ derived from renewable energy sources is important for the development of a carbon recycling system (Fig. 1).

Both the Sabatier reaction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) and the reverse water-gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) proceed competitively at ambient pressure. To achieve the selective formation of CH₄ or CO by CO₂ hydrogenation, it is necessary to reveal the dominant factor for changing the selectivity in CO₂ hydrogenation. We reported that the RWGS reaction proceeds selectively by phosphorus-loaded metal (various 3d, 4d, and 5d metals) catalysts while the Sabatier reaction proceeds mainly on TiO₂-supported metal catalysts (Fig. 2). Structural analysis revealed that metal phosphide NPs were formed on the phosphorus-loaded catalyst. The cationic metal species in metal phosphides were found to selectively produce CO by preventing the cleavage of the C-O bond of the CO molecule.

The direct synthesis of CH₃OH from the hydrogenation of CO₂ attracted significant interest. The methanol synthesis is an exothermic reaction ($\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$; $\Delta H_{298}^0 = -49.5 \text{ kJ mol}^{-1}$), therefore, lower temperature and higher pressure conditions are thermodynamically more favorable. Therefore, the development of versatile heterogeneous catalysts that can operate at low temperatures ($\leq 220 \text{ }^\circ\text{C}$) is extremely important. We found that Pt/MoO_x/TiO₂ catalysts showed a high selectivity to CH₃OH at low temperatures. The addition of MoO_x to Pt/TiO₂ improved both CO₂ conversion and CH₃OH selectivity. Generally, activation and cleavage of the stable C=O bond of CO₂ to form intermediate species is considered to be the crucial step in catalytic CO₂ hydrogenation. The assistance of oxygen vacancies in MoO_x may activate molecular CO₂ and weaken the C=O double bond.

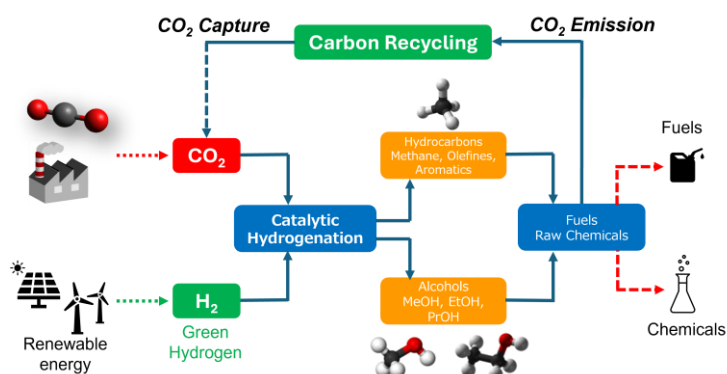


Fig.1 CO₂ hydrogenation to value-added compounds in the carbon recycling process.

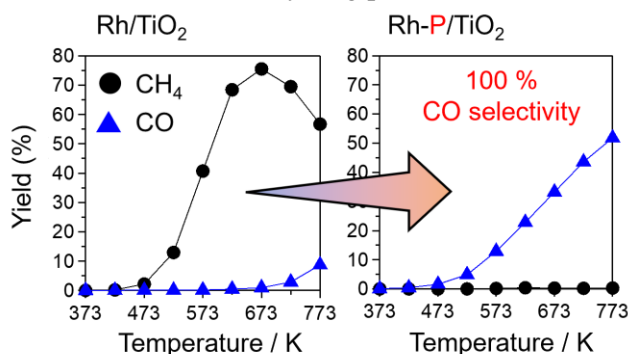


Fig. 2 Phosphorus-Enhanced Rh/TiO₂ Catalysts:
A Leap in Selective CO₂ to CO Conversion.

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Education

Ph.D. (2008-2013) w/ Fred West: The University of Alberta
M. Sc. (2004-2006) w/ Hsing-Jang Liu: National Tsing Hua University
B. Sc. (2000-2004): National Tsing Hua University

Academic Career

2021-: Associate Professor of Applied Chemistry, National Yang Ming Chiao Tung University
2019-2021: Associate Professor of Applied Chemistry, National Chiao Tung University
2015-2019: Assistant Professor of Applied Chemistry, National Chiao Tung University
2013-2015: Postdoc Scholar w/ Viresh Rawal, The University of Chicago

Awards

2024 Outstanding Young Scholar Award (Shui-Mu Foundation of Chemistry)
2023 Ta-You Wu Memorial Award (NSTC, Taiwan)
2023 Thieme Chemistry Journals Award (Thieme Chemistry)
2022 Asian Core Program Lectureship Awards (Japan & Malaysia)
2019 Asian Core Program Lectureship Awards (China)
2018 MOST Young Scholar Fellowship (MOST, Taiwan)

Representative Publications

- 1 Lin, Y.-C.; Yen, K.-W.; Lin, H.-J.; Yang, Y.-C.; Wu, Y.-K. *Chem. Commun.* **2021**, 57, 12119.
- 2 Chien, C.-C.; Kao, S.-C.; Chen, C.-J.; Wu, Y.-K. *Chem. Commun.* **2020**, 56, 15470.
- 3 Chang, Y.-H.; Peng, W.-L.; Chen, I.-C.; Hsu, H.-Y.; Wu, Y.-K. *Chem. Commun.* **2020**, 56, 4660.
- 4 Yang, Y.-C.; Lin, Y.-C.; Wu, Y.-K. *Org. Lett.* **2019**, 21, 9286.
- 5 Chang, C.-Y.; Lin, Y.-H.; Wu, Y.-K. *Chem. Commun.* **2019**, 55, 1116.
- 6 Hou, W.-Y.; Wu, Y.-K. *Org. Lett.* **2017**, 19, 1220.

Research Interests

Total synthesis of natural products by pattern recognition analysis. Updating chemical reactions in continuous-flow reactors. Fragment-coupling approaches to explore biomedicinally relevant chemical space.

Palladium-Catalyzed Arylation of Cyclic Vinylogous Esters

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We recently developed the catalytic monoarylation and polyarylation of cyclic vinylogous esters.^{1,2} The deprotonative arylation reactions occur at the relatively acidic α and/or γ' carbons of cyclic vinylogous esters (Figure 1). Significantly, the regioselectivity of these processes could be well controlled under customized conditions. Overall, this collection of arylation reactions has offered a unique opportunity to rapidly assemble a variety of functionalized aryl-containing scaffolds.

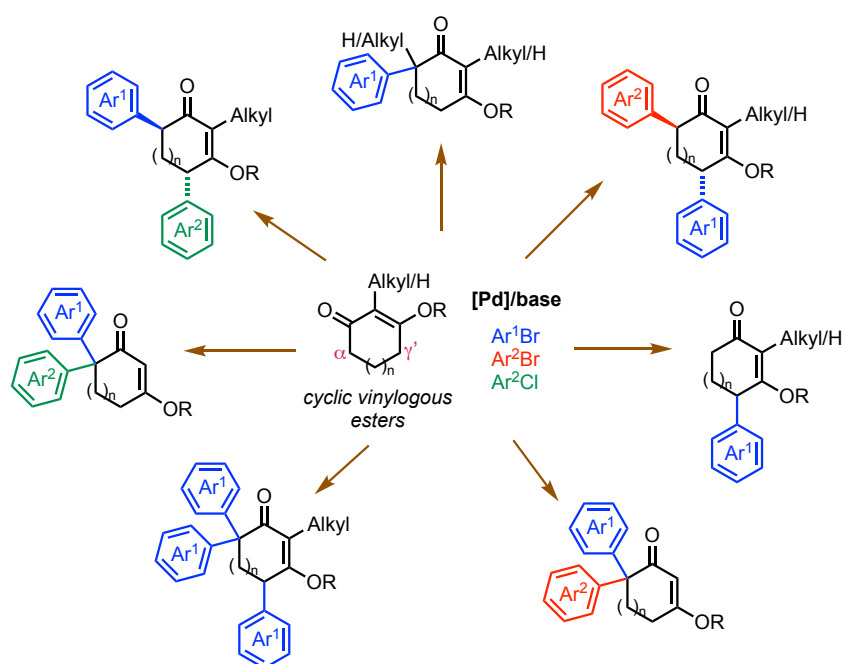


Figure 1. Arylation Reactions of Cyclic Vinylogous Esters.

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- [2] For related leading works in the field, see: a) Shao, L.-D.; Chen, Y.; Lin, H.-J.; Wang, M.; Xiao, N.; Zhang, Z.-J.; Li, D.; Li, R.-T. Palladium-catalyzed direct γ -C(sp³)-H arylation of β -alkoxy cyclohexenones: reaction scope and mechanistic insights. *Org. Chem. Front.* **2022**, 9, 2308-2315. b) Johnson, T.; Pultar, F.; Menke, F.; Lautens, M. Palladium-Catalyzed α -Arylation of Vinylogous Esters for the Synthesis of γ,γ -Disubstituted Cyclohexenones. *Org. Lett.* **2016**, 18, 6488-6491. c) Zhao, Y.; Zhou, Y.; Liang, L.; Yang, X.; Du, F.; Li, L.; Zhang, H. Palladium-Catalyzed Sequential Arylation and Allylic Alkylation of Highly Functionalized Ketones: A Concise Synthesis of Mesembrine. *Org. Lett.* **2009**, 11, 555-558.

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Shigeki Matsunaga received his Ph.D. degree from the University of Tokyo in 2003 under the supervision of Professor Masakatsu Shibasaki. He started his academic career in 2001 as an assistant professor at the University of Tokyo working with prof. Shibasaki. He was promoted to senior lecturer in 2008, and then associate professor in 2011 (with prof. Kanai). He began his professor career at Hokkaido University in 2015 before moving to Kyoto University in 2023. He received The CSJ Award for Young Chemists (2007), Mitsui Chemicals Catalysis Science Award of Encouragement (2008), Merck-Banyu Lectureship (2011), Thomson Reuters Research Front Award (2016), Mukaiyama Award (2020) and others.

Selected Recent Publications:

- [1] Enantioselective Synthesis of 1,2-Benzothiazine 1-Imines via Ru^{II}/Chiral Carboxylic Acid-Catalyzed C–H Alkylation/Cyclization, Huang, L.-T.; Kitakawa, Y.; Yamada, K.; Kamiyama, F.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2023**, 62, e202305480.
- [2] An Electron-Deficient Cp^E Iridium(III) Catalyst: Synthesis, Characterization, and Application to Ether-Directed C–H Amidation, Tomita, E.; Kojima, M.; Nagashima, Y.; Tanaka, K.; Sugiyama, H.; Segawa, Y.; Furukawa, A.; Maenaka, K.; Maeda, S.; Yoshino, T.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2023**, 62, e202301259.
- [3] Photocatalytic Deuterium Atom Transfer Deuteration of Electron-Deficient Alkenes with High Functional Group Tolerance, Suzuki, A.; Kamei, Y.; Yamashita, M.; Seino, Y.; Yamaguchi, Y.; Yoshino, T.; Kojima, M.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2023**, 62, e202214433.
- [4] Formation of Isolable Dearomatized [4 + 2] Cycloadducts from Benzenes, Naphthalenes, and N-Heterocycles Using 1,2-Dihydro-1,2,4,5-tetrazine-3,6-diones as Arenophiles under Visible Light Irradiation, Ikeda, K.; Kojima, R.; Kawai, K.; Murakami, T.; Kikuchi, T.; Kojima, M.; Yoshino, T.; Matsunaga, S. *J. Am. Chem. Soc.* **2023**, 145, 9326.

Development of Chiral Catalysts for Asymmetric C-H Functionalization Towards Sustainable Synthesis

Shigeki Matsunaga

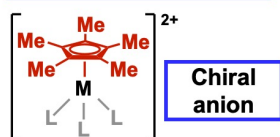
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Our research group is interested in the development of new catalysts/molecules to streamline organic synthesis. Several projects, like asymmetric C-H functionalization under $\text{Cp}^*\text{M(III)/organo-hybrid}$ catalysts, bimetallic Schiff base catalysis, paddlewheel chiral bimetallic catalysis, and metal/photoredox dual catalysis for deuterated building block synthesis, dynamic covalent bonding chemistry with new TETRAD molecules, hypervalent iodine for chemo-selective cleavage of stable C-Si bond, radio labeling of α -emitting astatine element (At-211) for cancer therapy, and others, are ongoing.

In this lecture, recent advances in asymmetric C-H functionalization under $\text{Cp}^*\text{M(III)/organo-hybrid}$ catalysis and chiral paddle-wheel Ru(II)-Ru(III) catalysis will be introduced. The Ru(II)-Ru(III) complexes show unique and distinct catalytic activity in comparison with well-known chiral paddle-wheel Rh(II)-Rh(II) complexes. Basic properties of Ru(II)-Ru(III) complexes as well as application to asymmetric C-H amination and others will be explained.

Selected Ongoing Projects in Matsunaga Group

**$\text{Cp}^*\text{Co(III)/Rh(III)/Ir(III)}$
with
external chiral acids**



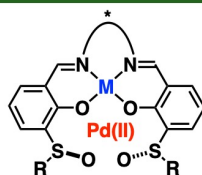
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**Radio labeling via
hypervalent iodine**

CEJ, 2019, 25, 1217.
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Cancer Therapy

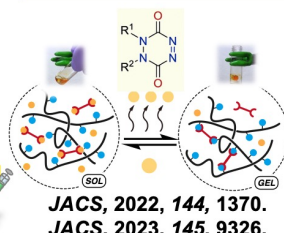


**bimetallic Schiff base
catalysts**



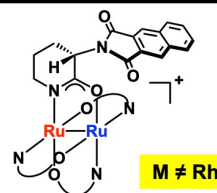
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dynamic covalent bond



JACS, 2022, 144, 1370.
JACS, 2023, 145, 9326.

**paddlewheel
chiral bimetallic cat.**



Nature Catal. 2020, 4, 851.

**photoredox-Cobalt
dual catalysis**

Co(II) + organo-PC



low valent Co/Fe

ACIE, 2019, 58, 9199.
Nature Commun. 2021, 12, 966.
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ACIE, 2023, 62, e202214433.