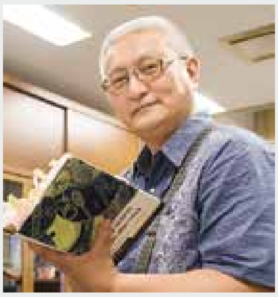
Development of Heterogeneous Catalysis toward Ideal Chemical Processes

Department of Life and Coordination-Complex Molecular Science
Division of Complex Catalysis



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Education

1984	B.S. Hokkaido University
1990	Ph.D. Hokkaido University

Professional Employment

1988	JSPS Research Fellow
1988	Research Associate, Hokkaido University
1990	Assistant Professor, Hokkaido University
1994	Research Associate, Columbia University
1995	Lecturer, Kyoto University
1997	Professor, Nagoya City University
2000	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2007	Research team leader, RIKEN
2014	Distinguished Professor, Three George University
2003	Research Project Leader, JST CREST Project (–2008)
2008	Research Project Leader, NEDO Project (–2012)
2011	Deputy Research Project Leader, JST CREST (–2016)
2014	Research Project Leader, JST ACCEL Project (–2019)

Awards

1991	Eisai Award, Synthetic Organic Chemistry
1998	The Pharmaceutical Society of Japan Award for Young Scientist
2007	The Chemical Society of Japan (CSJ) Award for Creative Work
2007	MEXT Ministerial Award for Green Sustainable Chemistry
2010	Inoue Prize for Science
2014	The Commendation for Science and Technology by the Minister of MEXT (Research Category)

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Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, *etc.*) organic transformation processes. In one active area of investigation, we are developing the heterogeneous aquacatalytic systems. Various types of catalytic organic molecular transformations, *e.g.* carbon–carbon bond forming cross-coupling, carbon–heteroatom bond forming reaction, aerobic alcohol oxidation, *etc.*, were achieved in water under heterogeneous conditions by using amphiphilic polymer-supported transition metal complexes and nanoparticles (**Figure 1**), where self-concentrating behavior of hydrophobic organic substrates inside the amphiphilic polymer matrix played a key role to realize high reaction performance in water.

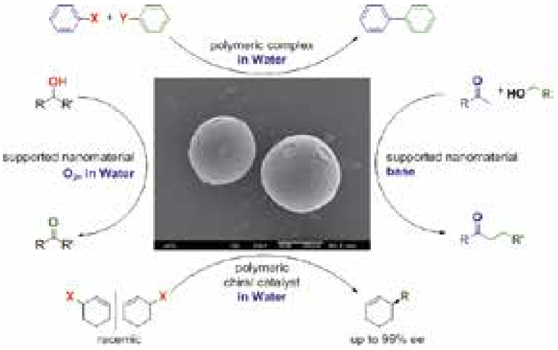

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

Selected Publications

- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Amphiphilic Self-Assembled Polymeric Copper Catalyst to Parts per Million Levels: Click Chemistry," *J. Am. Chem. Soc.* **134**, 9285–9290 (2012).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels," *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Pallasium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, "Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane," *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. The Development of a Vesicular Self-Assembled Amphiphilic Platinum NCN-Pincer Complex and Its Catalytic Application to Hydrosilylation of Alkenes in Water[1)]

An amphiphilic platinum NCN-pincer complex bearing hydrophilic tri(ethylene glycol) and hydrophobic dodecyl chains was designed and synthesized for use as a new aqua-catalytic system. The complex self-assembled in aqueous medium to form bilayer vesicles that catalyzed the hydrosilylation of alkenes by dimethyl(phenyl)silane in water to give the hydrosilylated products in good yields. In contrast, the complex in its amorphous form did not promote the reaction efficiently, and thus, the formation of a vesicular structure was essential to promote the reaction.

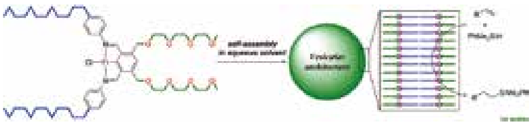

Figure 2. Hydrosilylation of styrene with dimethyl(phenyl)silane in water in the presence of a self-assembled vesicular amphiphilic platinum NCN-pincer complex.

2. Detailed Structural Analysis of a Self-Assembled Vesicular Amphiphilic NCN-Pincer Palladium Complex by Using Wide-Angle X-Ray Scattering and Molecular Dynamics Calculations[2)]

Wide-angle X-ray scattering experiments and all-atomistic molecular dynamics calculations were performed to elucidate the detailed structure of bilayer vesicles constructed by self-assembly of an amphiphilic palladium NCN-pincer complex. We found an excellent agreement between the experimental and calculated X-ray spectra and between the membrane thickness determined from a TEM image and that calculated from an electron-density profile, indicating that the calculated structure was highly reliable. The analysis of the simulated bilayer structure showed that the bilayer membrane could act as a nanoreactor. The self-assembled vesicles were shown to be catalytically active in a Miyaura–Michael reaction in water.

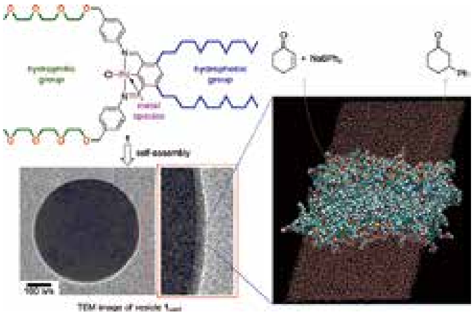

Figure 3. A self-assembled vesicular palladium NCN-pincer complex.

3. Palladium-Catalyzed Asymmetric Suzuki–Miyaura Cross Coupling with Homochiral Phosphine Ligands Having Tetrahydro-1*H*-imidazo[1,5-*a*]indole Backbone[3)]

Amphiphilic polystyrene-poly(ethylene glycol) resin-supported chiral imidazoindole phosphines (PS-PEG-L*) bearing PPh_2, P(*t*-Bu)$_2$, and P(*c*-Hex)$_2$ groups were designed and prepared with a view toward using them in aqueous heterogeneous asymmetric Suzuki–Miyaura biaryl coupling. The asymmetric coupling of 2-substituted 1-iodonaphthalenes and 2-substituted naphthalen-1-ylboronic acid took place in water under heterogeneous conditions in the presence of 10 mol% palladium of PS-PEG-L*-Pd complexes to give up to 94% ee of (*S*)-2,2’-disubstituted 1,1’-binaphthyls.

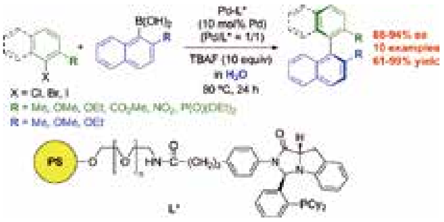

Figure 4. Palladium-catalyzed asymmetric biaryl coupling in water with a PS-PEG resin-supported imidazoindolephosphine.

4. Huisgen Cycloaddition with Acetylene Gas by Using an Amphiphilic Self-Assembled Polymeric Copper Catalyst[4)]

A copper-mediated Huisgen cycloaddition of flammable acetylene gas and a variety of organic azides proceeded smoothly by using our amphiphilic self-assembled polymeric copper catalyst MPPI-Cu to give the corresponding triazoles in high yield. MPPI-Cu was readily reused without loss of catalytic activity.

Figure 5. Huisgen cycloaddition of azides and acetylene in the presence of self-assembled polymeric copper catalyst.

References

1) G. Hamasaka and Y. Uozumi, *Chem. Lett.* **45**, 1244–1246 (2016).
2) G. Hamasaka, T. Muto, Y. Andoh, K. Fujimoto, K. Kato, M. Takata, S. Okazaki and Y. Uozumi, *Chem. –Eur. J.* **23**, 1291–1298 (2017).
3) Y. Uozumi, Y. Matsuura, T. Suzuka, T. Arakawa and Y. M. A. Yamada, *Synthesis* **49**, 59–68 (2017).
4) Y. M. A. Yamada, H. Yoshida, A. Ohno, T. Sato, T. Mase and Y. Uozumi, *Heterocycles* **95**, 715–721 (2017).

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