Development of Novel Catalytic Organic Transformations

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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, Photocatalysis

Our research interests lie in the development of catalytic reaction systems toward ideal (highly efficient, selective, green, safe, simple, *etc.*) organic transformations. In particular, development of a wide variety of the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels, have been achieved. Furthermore, we have recently been developing a novel photocatalysis where, for example, the carbonyl groups underwent two successive one-electron reduction to generate carbinol anion species achieving electrophilic carbonyl substitution. Along this line, in 2024, we have developed a series of novel diazabenzacenaphthenium photocatalysts, denoted as ***N*-BAP**s, which promoted the unprecedented 4-electron photoreduction of esters to form the corresponding alcohols with visible LED light irradiation under aqueous conditions.

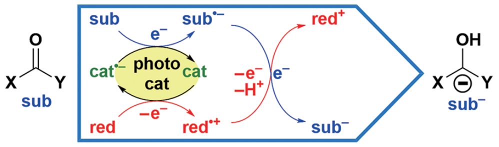


Figure 1. The outlined concept of photocatalytic reductive activation of substrate through two successive one-electron transfer process (*e.g.* carbonyl reduction to carbinol anion).

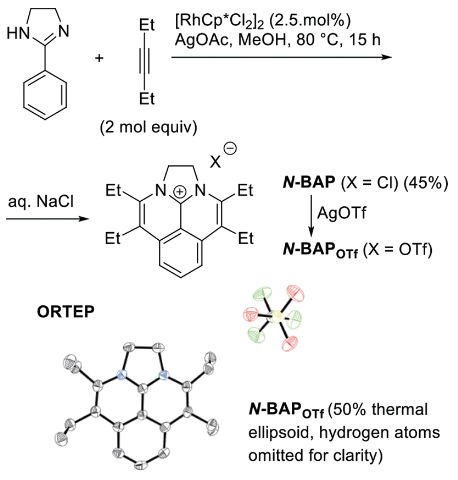
Selected Publications

- S. Okumura, K. Torii and Y. Uozumi, “Electrophilic 1,4-Addition of Carbon Dioxide and Aldehydes to Enones,” *Org. Lett.* **25**, 5226–5230 (2023).
- S. Okumura, T. Takahashi, K. Torii and Y. Uozumi, *Chem. –Eur. J.* **29**, e202300840 (2023). DOI: 10.1002/chem.202300840
- G. Hamasaka, D. Roy, A. Tazawa and Y. Uozumi, “Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate,” *ACS Catal.* **9**, 11640–11646 (2019).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, “Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin,” *ACS Catal.* **7**, 7371–7377 (2017).
- 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).

1. Novel Diazabenzacenaphthenium Photocatalysts[1)]

1-1. Design and Preparation of *N*-BAP

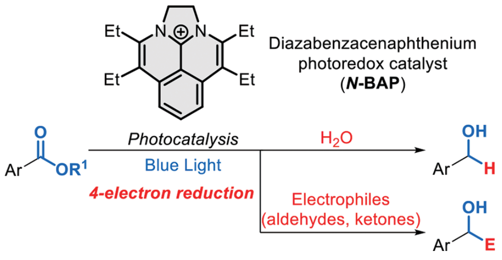
A novel diazabenzacenaphthenium photocatalyst ***N*-BAP** was designed and identified on the basis of an extensive *in silico* screening, with a view to its use as a photocatalyst under visible-light irradiation in photoinduced multielectron-transfer reactions. The photocatalyst was prepared by a rhodium-catalyzed oxidative annulation of 2-phenyl-4,5-dihydro-1*H*-imidazole with hex-3-yne in one step. Single-crystal X-ray analysis of ***N*-BAP**$_{\mathrm{OTf}}$ clearly confirmed the presence of a planar π-conjugated diazabenzacenaphthenium structure.



Scheme 1. Preparation of ***N*-BAP**.

1-2. Multielectron-Reduction of Esters

Under visible-light irradiation, ***N*-BAP** promoted the four-electron reduction of esters in the presence of ammonium oxalate as a "traceless reductant" to generate carbinol anion intermediates that underwent protonation with water to give the corresponding alcohols. The resulting carbinol anions also exhibited nucleophilic reactivity under the photocatalytic conditions to undergo a 1,2-addition to a second carbonyl compound, affording unsymmetric 1,2-diols.



***N*-BAP** reduces ester **I** through SET to give the acetal radical **II** and oxidized ***N*-BAP**. Oxidized ***N*-BAP** oxidizes oxalate anion to afford CO_2 and a CO_2 radical anion, with regeneration of ***N*-BAP**. The acetal radical **II** undergoes a second SET from excited ***N*-BAP** (or a CO_2 radical anion) to form the acetal carbanion **III**; this is followed by protonation with water to give the aldehyde **IV**. A second two-electron reduction of **IV** then generates the carbinol anion **V**. The four-electron-reduction process proceeds almost simultaneously to suppress radical side reactions. Lastly, the resulting carbinol anion **V** reacts with water or a carbonyl electrophile to furnish the final product **VI**.

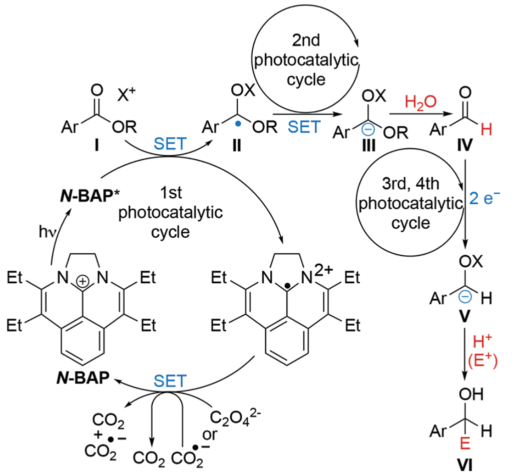


Figure 2. Proposed mechanism.

2. Tetrahydroxydiboron as a Green Reducing Agent Serving in Water[2,3)]

We have developed a transfer hydrogenation of aldehydes and ketones, as well as a transfer hydrogenolysis of O–C and N–C bonds of *O*-, and *N*-benzyl groups with $B_2(OH)_4$ as a reductant and amphiphilic resin-dispersed palladium nanoparticles as a catalyst system in an aqueous medium, where water also serves as a hydrogen donor. A variety of aldehydes and ketones, including aliphatic carbonyl compounds, reacted to give the corresponding primary and secondary alcohols, respectively. Benzyl groups of a variety of benzylic ethers, esters, carbamates, and amines, including benzyl-protected carbohydrates and amino acids, were reductively removed in high yields. The catalyst was recovered by filtration and reused nine times without a significant loss of its catalytic active.

References

1) S. Okumura, S. Hattori, L. Fang and Y. Uozumi, *J. Am. Chem. Soc.* **146**, 16990–16995 (2024). DOI: 10.1021/jacs.4c05272
2) K. Zhang, S. Okumura and Y. Uozumi, *Chem. Lett.* **53**, upae082 (2024). DOI: 10.1093/chemle/upae082
3) K. Zhang, S. Okumura and Y. Uozumi, *Eur. J. Org. Chem.* **27**, e202400322 (2024). DOI: 10.1002/ejoc.202400322