International Research Center for Elements Science – Synthetic Organotransformation –

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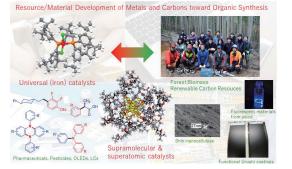
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Scope of Research

Our research activity focuses on the development of new molecular transformations, which can contribute to better or ideal synthesis of functional molecules as well as to exploitation of new chemical (metal and carbon) resources. The present research subjects are (1) metal-catalyzed carbon–carbon and carbon–heteroatom bond forming reactions by using universal metals such as iron (2) development of small metallic nanocluster catalysts based on supramolecular approaches (3) utilization of woody biomass as the renewable carbon resources by mild catalytic transformations of wood molecules into useful compounds and materials.



KEYWORDS

Iron Catalysis Organotransformation

Woody Molecular Transformation Supramolecular & Superatomic Catalysis

Recent Selected Publications

Isozaki, K.; Ueno, R.; Ishibashi, K.; Nakano, G.; Yin, H.; Iseri, K.; Sakamoto, M.; Takaya, H.; Teranishi, T.; Nakamura, M., Gold Nanocluster Functionalized with Peptide Dendron Thiolates: Acceleration of the Photocatalytic Oxidation of an Amino Alcohol in a Supramolecular Reaction Field, *ACS Catal.*, **11**, 13180-13187 (2021).

Adak, L.; Jin, M.; Saito, S.; Kawabata, T.; Itoh, T.; Ito, S.; Sharma, A. K.; Gower, N. J.; Cogswell, P.; Geldsetzer, J.; Takaya, H.; Isozaki, K.; Nakamura, M., Iron-Catalysed Enantioselective Carbometalation of azabicycloalkenes, *Chem. Commun.*, **57**, 6975-6978 (2021).

Iwamoto, T.; Okuzono, C.; Adak, L.; Jin, M.; Nakamura, M., Iron-Catalysed Enantioselective Suzuki-Miyaura Coupling of Racemic Alkyl Bromides, *Chem. Commun.*, **55**, 1128-1131 (2019).

Agata, R.; Takaya, H.; Matsuda, H.; Nakatani, N.; Takeuchi, K.; Iwamoto, T.; Hatakeyama, T.; Nakamura, M., Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and FeII/FeIV Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations, *Bull. Chem. Soc. Jpn.*, **92**, 381-390 (2019).

Adak, L.; Kawamura, S.; Toma, G.; Takenaka, T.; Isozaki, K.; Takaya, H.; Orita, A.; Li, H. C.; Shing, T. K. M.; Nakamaura, M., Synthesis of Aryl C-Glycosides via Iron-Catalyzed Cross Coupling of Halosugars: Stereoselective Anomeric Arylation of Glycosyl Radicals, *J. Am. Chem. Soc.*, **139**, 10693-10701 (2017).



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Iron-Catalyzed Organic Synthesis

Transition-metal-catalyzed carbon–carbon and carbon– heteroatom bond forming reactions are powerful tools for the synthesis of functional molecules. Our group focuses on use of iron as a catalyst, and so far developed a variety of iron-catalyzed cross-coupling reactions, some of which can't be achieved by conventional transition-metal catalysts such as palladium. As a recent representative example, we developed the iron-catalyzed enantioselective carbometalation of azabicycloalkenes (Figure 1a), which is of significant interest due to the facile installation of four stereocenters retaining the azabicyclic skelton. By the combination of X-ray absorption spectroscopy and DFT calculation, we proposed a catalytic cycle of diaryliron complex involving coordination of azabicyclic alkene, olefin insertion, and transmetalation steps (Figure 1b).

Wood Molecular Transformation

Woody biomass is renewable and the most abundant carbon resouce on the earth, thus expected to utilize as a feedstock to chemicals and energy toward a sustainable society. This project focuses on the chemical transformation of woody biomass into useful materials under mild catalytic conditions. To achieve this purpose, we have developed two key technologies; 1) direct transformation of woody lignin to fluorescent molecules, 2) one-pot disintegration of wood powder into nanocellulose. As a recent representative example, we reported the development of artificial urushi-coating materials by installing trienyl side chains from natural linolenic acid to the bio-renewable phenoxypropanone compounds obtained from enzymatic degradatio of woody lignin.

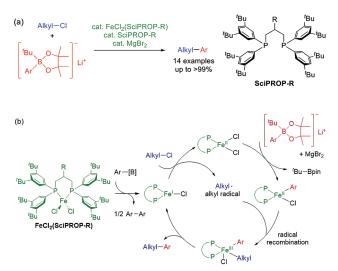


Figure 1. Iron-catalyzed Suzuki-type cross coupling between alkyl chlorides and arylboronates. (a) General reaction scheme and (b) proposed catalytic cycle.

Supramolecular & Superatomic Catalysis

This project focuses on development of smart materials based on synergistic effect of various metals on artificial peptides. Based on this concept, we have developed novel ruthenium complex bound with norvaline, which catalyze efficient and selective oxidation of several methoxybenzene analogues to quinones. Now we are trying further modification of the catalysts toward investigation of future chemical resources.

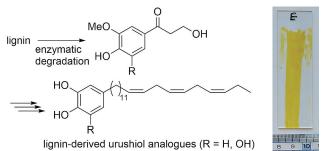


Figure 2. Artificial urushi-coating materials derived from renewable woody lignin.