

International Research Center for Elements Science – Organic Main Group Chemistry –

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Prof
NAKAMURA, Masaharu
(D Sc)



Assoc Prof
TAKAYA, Hikaru
(D Eng)



Assist Prof
HATAKEYAMA, Takuji
(D Sc)

Students

HASHIMOTO, Toru (D3)

OGATA, Kazuki (D3)

KAWAMURA, Shintaro (D3)

NAKAGAWA, Naohisa (D3)

HASHIMOTO, Sigma (D2)

OBA, Tsuyoshi (M2)

IMAYOSHI, Ryuji (M1)

YOKOI, Tomoya (M1)

KAWABATA, Tatsuya (M1)

NAKAJIMA, Sho (UG)

Visitor

Prof HOU, Xue-Long Shanghai Institute of Organic Chemistry, China, P.R., 10 March

Scope of Research

Our research activity is focused on the development of molecular transformation reactions, which can provide new ways to exploit chemical resources, such as haloalkanes, alkenes, alcohol etc. The present research subjects are (1) metal-catalyzed C–C bond forming reactions by using universal metals such as iron, magnesium and aluminum (2) development of smart materials based on synergistic effect of various metals on artificial peptide (3) synthesis of heteroatom-fused π -conjugated molecules toward optoelectronics (4) understanding of synergistic effects of multi-element center interactions for the catalysis with the help of quantum chemical methods and spectroscopy.

KEYWORDS

Carbon–Carbon Bond Formation

Iron Catalyst

Cross-Coupling Reaction

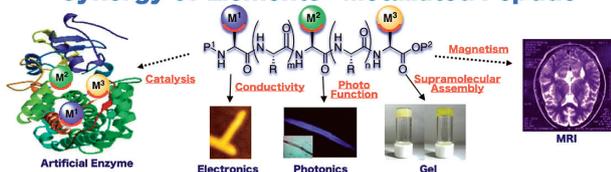
Metallated Peptide

π -Conjugated Molecule



Pursuit of Elements : Catalysis and Synthesis

Synergy of Elements : Metallated Peptide



Selected Publications

Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M., Synthesis of BN-fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation, *M. J. Am. Chem. Soc.*, **133**, 18614-18617 (2011).

Hatakeyama, T.; Okada, Y.; Yoshimoto, Y.; Nakamura, M., Tuning Chemoselectivity in Iron-Catalyzed Sonogashira-type Reaction Using a Diphosphine Ligand with Peripheral Steric Bulk: Selective Alkynylation of Non-activated Alkyl Halides, *Angew. Chem. Int. Ed.*, **50**, 10973-10976 (2011).

Ito, S.; Itoh, T.; Nakamura, M., Diastereoselective Carbometallation of Oxa- and Azabicyclic Alkenes under Iron Catalysis, *Angew. Chem. Int. Ed.*, **50**, 454-457 (2011).

Ishizuka, K.; Seike, H.; Hatakeyama, T.; Nakamura, M., Nickel-Catalyzed Alkenylative Cross-Coupling Reaction of Alkyl Sulfides, *J. Am. Chem. Soc.*, **132**, 13117-13119 (2010).

Hatakeyama, T.; Hashimoto, T.; Kondo, Y.; Fujiwara, Y.; Seike, H.; Takaya, H.; Tamada, Y.; Ono, T.; Nakamura, M., Iron-Catalyzed Suzuki-Miyaura Coupling of Alkyl Halides, *J. Am. Chem. Soc.*, **132**, 10674-10676 (2010).

Tuning Chemoselectivity in Iron-Catalyzed Sonogashira-type Reaction Using a Diphosphine Ligand with Peripheral Steric Bulk

A chemoselective Sonogashira-type coupling of primary and secondary alkyl halides with alkynyl Grignard reagents have been developed by using an iron catalyst. The key to success is the use of diphosphine ligand bearing peripheral steric bulk, which dramatically switches chemoselectivity from the C_{sp^2} -selective coupling to C_{sp^3} -selective coupling. The present reaction can be applicable to secondary alkyl halides, including less-reactive alkyl chlorides, which are difficult substrate with the previous methods. These synthetic advantages, as well as the non-hazardous nature of the catalyst and reagents make the present reaction suitable for facile synthesis or production of various functional molecules bearing alkyne moieties.

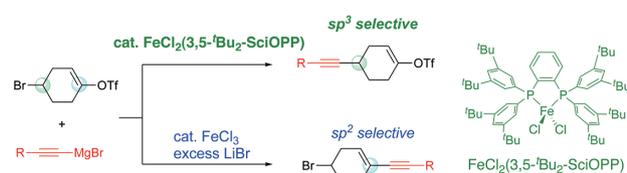


Figure 1. Chemoselective cross-coupling using a novel iron-diphosphine complex.

Programmable Metal Unit Arrangement on Peptides to Create Composition- and Configuration-Controlled Heterometallic Hybrid Materials

This project focuses on the following challenges: i) Development of fundamental methodology for creating composition- and configuration-controlled heterometallic hybrid molecules using metallated-amino acids and peptides as metal units. Chemical synthesis and self-assembly process of the metal units is currently employed, in complementary, to control the composition, 1D/2D array, and 3D configuration of metals on peptides i.e., programmable metal unit arrangements. ii) Exploring the function of heterometallic hybrid molecules. Applications to supra-molecular gelators, molecular electronic devices, photo-chemical devices, advanced catalysts, artificial enzymes, and MRI contrast agents are ongoing with a diverse library of metallated-amino acids and peptides.

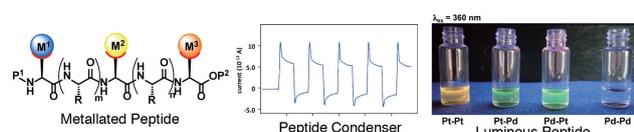


Figure 2. Preparation of metallated peptide and self-assembly of the peptide.

Synthesis of BN-fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation

A tandem intramolecular electrophilic arene borylation reaction has been developed for the synthesis of BN-fused polycyclic aromatic compounds such as 4b-aza-12b-boradibenzo[*g,p*]chrysene **A** ($n=0$) and 8b,11b-diaza-19b,22b-diborahexabenzo[*a,c,f,g,j,l,op*]tetracene **B** ($n=1$). These compounds adopt a twisted conformation, which results in a tight and offset face-to-face stacking array in the solid state. Time-resolved microwave conductivity measurements prove that the intrinsic hole mobility of **A** ($0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is comparable to that of rubrene ($0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), one of the most commonly used organic semiconductors, indicating that BN-substituted PAHs are potential candidates for organic electronic materials.

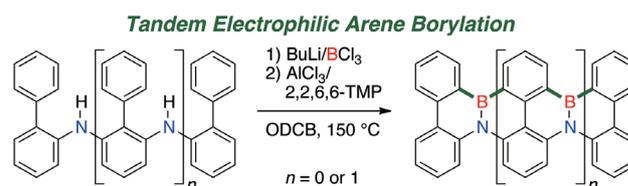


Figure 3. Synthesis of BN-fused polycyclic aromatics.

