

**【Grant-in-Aid for Scientific Research (S)】**  
**Science and Engineering (Chemistry)**



**Title of Project :** Development of High Performance Acid–Base Combined Nanocatalysts

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Research Project Number : 15H05755 Researcher Number : 40221759

Research Area : Organic Chemistry

Keyword : Synthetic Organic Chemistry

**【Purpose and Background of the Research】**

Natural enzyme is the most ideal catalyst which controls high-order selectivity and reactivity of target organic reaction under mild conditions. The exquisite chiral nanosized cavity of enzymes plays an important role for inducing selectivity and reactivity. It is possible to design a nanosized cavity around the active site of catalysts artificially. In this research project, we would like to develop tailor-made high performance catalysts superior to enzymes based on acid–base combination chemistry and supramolecular chemistry.

**【Research Methods】**

In this research project, we would like to establish a new methodology to design supramolecular nanocatalysts by using non-covalent bonding interactions (hydrogen bond, halogen bond, ionic bond,  $n$ -cation, and  $\pi$ - $\pi$  interactions, hydrophobicity, hydrophilicity, fluorophilicity, etc.), resonance effect, inductive effect, and dynamic equilibrium based on acid–base combination chemistry (Figure 1).

The following research tasks will be undertaken:

- (1) Development of high-order selective polyene cyclizations induced by acid-assisted base catalysts
- (2) Development of high-order selective

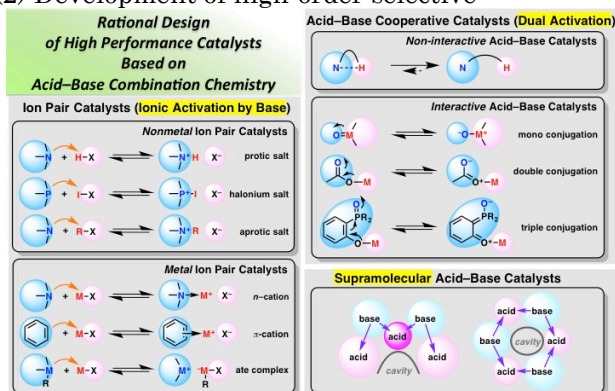


Figure 1 Rational Design of High Performance Catalysts Based on Acid–Base Combination Chemistry  
 cycloaddition reactions induced by base-assisted acid catalysts

- (3) Development of high-order selective dehydrogenative coupling reactions induced by ionic pair catalysts

**【Expected Research Achievements and Scientific Significance】**

The development of tailor-made high performance catalysts contributes to the innovation of technology in organic synthesis and the development of fine chemicals such as new medicines and new organic functional materials.

**【Publications Relevant to the Project】**

- “Enantioselective halocyclization of polyprenoids induced by nucleophilic phosphoramidites,” Sakakura, A.; Ukai, A.; Ishihara, K. *Nature* **2007**, *455*, 900–903.
- “Enantioselective Diels-Alder reactions with anomalous endo/exo selectivities using conformationally flexible chiral supramolecular catalysts,” Hatano, M.; Mizuno, T.; Izumiseki, A.; Usami, R.; Asai, T.; Akakura, M.; Ishihara, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 12189–12192.
- “High-turnover hypiodite catalysis for asymmetric synthesis of tocopherols,” Uyanik, M.; Hayashi, H.; Ishihara, K. *Science* **2014**, *345*, 291–294.

**【Term of Project】** FY2015-2019

**【Budget Allocation】** 153,800 Thousand Yen

**【Homepage Address and Other Contact Information】**

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