Visiting Professors

Visiting Professor
OGOSHI, Sensuke *(from Osaka University)*

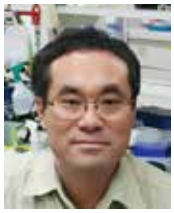
Transformation of Unsaturated Carbonyl Compounds via Nickelacycles

Chemists no longer doubt the importance of a methodology that could activate and utilize aldehydes in organic syntheses since many products prepared from them support our daily life. Tremendous effort has been devoted to the development of these methods using main-group elements and transition metals. Thus, many organic chemists have used an activator–(aldehyde oxygen) interaction, namely, η^1 coordination, whereby a Lewis or Brønsted acid activates an aldehyde. In the field of coordination chemistry, η^2 coordination of aldehydes to transition metals by coordination of a carbon–oxygen double bond has been well-studied; this activation mode, however, is rarely found in transition-metal catalysis. In view of the distinctive reactivity of an η^2-aldehyde complex, unprecedented reactions via this intermediate are a distinct possibility. We have been focusing on the formation of an η^2-aldehyde complex and its application to catalytic reactions. The key to success is efficient formation of oxa-nickelacycles generated by oxidative cyclization with carbon–carbon unsaturated bond. These nickelacycle allow us to develop new transformation of unsaturated carbonyl compounds.

Visiting Associate Professor
SHOJI, Osami *(from Nagoya University)*

Development of Novel Biocatalysts Based on Substrate Misrecognition of Enzymes

Gaseous alkanes such as methane and ethane are important fuels and potential chemical feedstock, but the selective hydroxylation of gaseous alkanes is a long-standing challenge and a current topic of interest considering increasing industrial and economic requirements. Although cytochrome P450s (P450s) are capable of breaking strong C–H bonds of hydrocarbons, the substrate specificity of cytochrome P450s makes them unsuitable for the hydroxylation of gaseous small alkanes, because P450s, especially those isolated from bacteria, recognize their specific substrates by intermolecular interactions to ensure their specificity and efficiency. We focused on the substrate misrecognition of P450s induced by inert dummy substrates (decoy molecules) that have a structural similarity to their natural substrates. We have demonstrated that even wild-type P450BM3 can catalyze the hydroxylation of gaseous alkanes such as ethane and propane by the addition perfluorinated carboxylic acids as decoy molecules. We believe that the catalytic turnover rate and coupling efficiency for hydroxylation of non-native substrates would be further improved by optimizing the structure of decoy molecules based on the crystal structure of P450BM3 with decoy molecules.



Visiting Associate Professor
TOSHA, Takehiko *(from RIKEN SPring-8 Center)*

Elucidation of Mechanism for Effective Chemical Reactions by Supracomplex Formation

Nitric Oxide (NO) plays diverse and significant roles in biological processes such as signal transduction, vasodilation and memory consolidation, despite its high cytotoxicity, raising the essential question of how biological systems control the action of NO to minimize its cytotoxic effect in cells. To answer this question, we focus on microbial denitrification, a form of anaerobic respiration, in which nitrate is reduced to dinitrogen through nitrite, NO and nitrous oxide. In denitrification, cytotoxic NO is produced as an intermediate product, but denitrifying bacteria can grow without any damage from NO, suggesting that there is a system for effective NO elimination. As a possible system, we recently found that NO-generating nitrite reductase (NiR) forms a complex with NO-decomposing nitric oxide reductase (NOR) to suppress the diffusion of NO. On the basis of this result, we further analyze the structure and function of the NOR:NiR complex by X-ray crystallography, mutagenesis, and time-resolved spectroscopic methods.