【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： Development of Innovative Molecular Transformations from Molecular Dinitrogen Using Super-Catalysts

NISHIBAYASHI Yoshiaki
(The University of Tokyo, Graduate School of Engineering, Professor)

Research Project Number: 20H05671 Researcher Number：40282579
Keyword：molecular dinitrogen, ammonia, catalyst

【Purpose and Background of the Research】

The principal investigators have recently developed a highly efficient method for the catalytic synthesis of ammonia from nitrogen gas using water as a proton source under extremely mild reaction conditions at ambient temperature and pressure. Based on the research results achieved so far, the main objective of this project is to gain insight into the fundamental technologies for the development of 'super-catalysts' beyond the previously developed series of catalysts and their use to achieve innovative molecular transformations of molecular nitrogen with very low reactivity.

In parallel with the main objective, there is a need to develop a new aspect of ammonia utilization, namely, the use of ammonia as an energy carrier, and we have very recently succeeded in developing a method for extracting energy from ammonia. Based on the research results achieved so far, we will also work to gain knowledge on fundamental technologies to achieve the development of "super-catalysts" that surpass the series of catalysts we have developed so far and to develop ammonia decomposition reactions using them.

【Research Methods】

(1) Development of ammonia synthesis methods

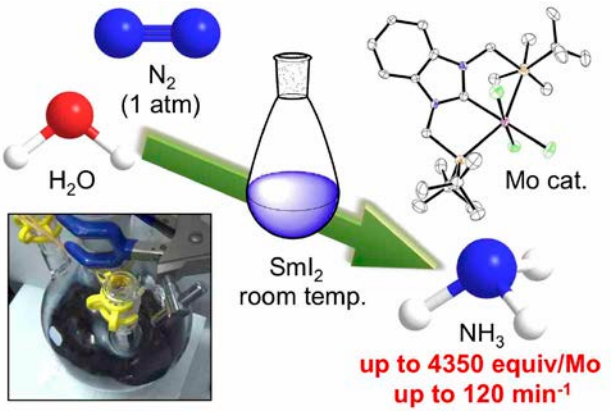
The principal investigator and co-workers have already shown that molybdenum complexes with PCP-type pincer ligands containing carbene skeletons work as effective catalysts for the catalytic ammonia synthesis. In order to gain a detailed insight into the catalytic reaction, DFT calculations are performed for all steps of the catalytic reaction, as well as isolation of key intermediates formed during the catalytic reaction and their stoichiometric and catalytic reactivities. We will attempt to develop new molecular catalysts for more efficient ammonia synthesis by feeding back the findings of the series of investigations into catalyst design.

(2) Development of ammonia decomposition methods

The principal investigator and co-workers have already shown that ruthenium complexes with bipyridine ligands work as effective catalysts for catalytic ammonia decomposition reactions. In order to gain a detailed insight into the catalytic reaction, DFT calculations are performed for all stages of the reaction, as well as isolation of key intermediates formed during the catalytic reaction and their stoichiometric and catalytic reactivities. The findings from the series of investigations will be fed back to the design of the catalysts in an attempt to develop new molecular catalysts for more efficient ammonia decomposition.

【Expected Research Achievements and Scientific Significance】

Results of this research are expected to make a major breakthrough directly in related research fields such as coordination chemistry and catalytic chemistry, as well as having a major impact on a wide range of related research fields such as organic chemistry and organometallic chemistry. The development of a next-generation ammonia synthesis method will not only be an academic achievement, but also a groundbreaking industrial breakthrough, and will be an achievement that will go down in history.



【Publications Relevant to the Project】

- Molybdenum-Catalysed Ammonia Production with Samarium Diiodide and Alcohols or Water, Y. Ashida, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Nature*, **2019**, *568*, 536-540.
- Ruthenium-Catalysed Oxidative Conversion of Ammonia into Dinitrogen, K. Nakajima, H. Toda, K. Sakata, Y. Nishibayashi, *Nature Chemistry*, **2019**, *11*, 702-709.

【Term of Project】 FY2020-2024

【Budget Allocation】 153,600 Thousand Yen

【Homepage Address and Other Contact Information】

http://park.itc.u-tokyo.ac.jp/nishiba/

【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： **Science of Post-nanocarbons: Structural science of nano π-space**

ISOBE Hiroyuki
(The University of Tokyo, Graduate School of Science, Professor)

Research Project Number: 20H05672 Researcher Number：30302805
Keyword：Nanocarbons, Organic synthesis, Physical organic chemistry, Giant molecules, Curved-π conjugation

【Purpose and Background of the Research】

The science of nanocarbons started by the discovery of fullerenes (1985), carbon nanotubes (1991) and graphenes (2004). Currently, giant nanocarbons such as nanotubes and graphene attract much interest in particular, but there exists one big problem. These nanocarbons are a mixture of various structures and are chemical species, which hampers in-depth understanding as a molecular entity.

This study aims to design and synthesize new "nanocarbon molecules" having discrete molecular structures, which should allow for extensive explorations of their properties/functions. In this project, we wish to answer a fundamental question such as "What is the anomalous property of curved π-systems?" by designing and creating new molecules. We also aim to expand the scope of nanocarbon molecules to be applicable to other fields such as physics and materials science.

【Research Methods】

In this project, three representative topics will be explored for the development of the science of molecular nanocarbons.

(1) Creation of diverse nanocarbon structures. We will explore the scope of concise synthesis of molecular nanocarbons, which should be developed on our ground works of nanocarbon molecules (Figure 1). For example, we have started a new design strategy named "Geodesic Phenine Framework (GPF)", which utilizes a building unit of "phenine = 1,3,5-trisubstituted benzene". This method creates a series of a new class of nanocarbons, and simple chemical compositions of hydrocarbons should be the main targets of this project.

(2) Elucidation of basic characteristics. We will elucidate the basic properties of nanocarbon molecules through physical organic studies. We will employ the state-of-the-art analytical methods in combination with the theoretical and computational chemistry. By applying analytical methods to novel molecules, the characteristics of new nanocarbon molecules will be disclosed.

(3) Development of functions. We develop the unique properties of curved π-systems to functions to be applicable to materials. For instance, we have recently discovered solid-state inertial rotations of the C_{60} guest in our tubular nanocarbon host with rotational frequencies reaching over 200 GHz. The development of a functional molecular machine using such unique dynamics is one of the important subjects to be explored.

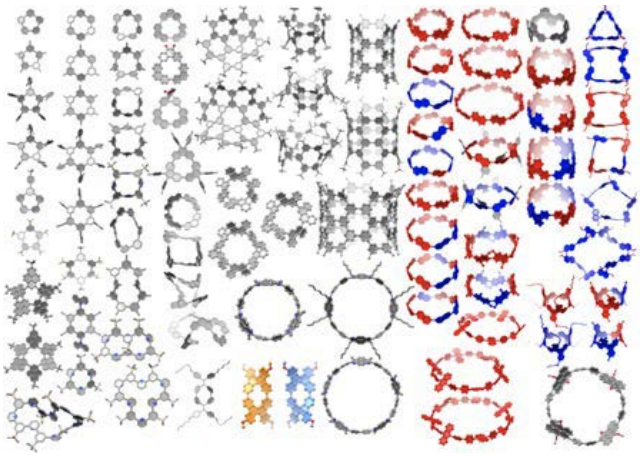


Figure 1. Representative examples of our nanocarbon molecules.

【Expected Research Achievements and Scientific Significance】

We expect the discovery of new properties of gigantic nanocarbons and, which should deepen our understanding of molecular nanocarbons. Atomic precisions that will be brought about by the present project will provide sicentific insight to gigantic and curved π-systems. Anomalous characteristics and functions of nanocarbon molecules should be explored in interdisciplinary fields, which is based on fundamental physical organic studies for (1) creation of diverse structures, (2) elucidation of basic characteristics and (3) development of functions. Design and synthesis of new functional materials shall be expected.

【Publications Relevant to the Project】

・ "Ratchet-free solid-state inertial rotation of a guest ball in a tight tubualr host" Matsuno, T.; Nakai, Y.; Sato, S.; Maniwa, Y.; Isobe, H. *Nat. Commun.* **2018,** *9*, 1907.
・ "Finite phenine nanotubes with periodic vacancy defects" Sun, Z.; Ikemoto, K.; Fukunaga, T. M.; Koretsune, T.; Arita, R.; Sato, S.; Isobe, H. *Science* **2019**, *363*, 151-155.

【Term of Project】 FY2020-2024

【Budget Allocation】 149,800 Thousand Yen

【Homepage Address and Other Contact Information】

https://physorg.chem.s.u-tokyo.ac.jp/
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【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： **Innovative energy storage materials based on the peculiar functions realized by isolated molecules/orbitals.**

YAMADA Atsuo

(The University of Tokyo, Graduate School of Engineering, Professor)

Research Project Number: 20H05673 Researcher Number：30359690

Keyword：Isolated molecule, Isolated orbital, Rechargeable battery, Electrochemical reaction, Molecular dynamics

【Purpose and Background of the Research】

For a coming low carbon society, ultimately with energy self-sufficiency, dispersive use and smart controlling of renewable energy would be of critical importance. On-demand energy storage device is necessary to compensate for the time-dependent energy supply inherent to, for example, sunshine, where rechargeable batteries should serve as an important infrastructure providing a temporary buffer not only for transportation but also for a center of electricity management.

Solids and liquids are the self-condensed systems composed of limited types of atoms and molecules, where many of the electronic/chemical properties emerges as a result of orbital interaction induced by their condensation. Based on the new principles we have recently established, we will intentionally introduce high-density "isolated" molecules/orbitals that are free from the self-interactions in solids or liquids.

Approaching from such "isolated chemistry", we will extract and maximize the hitherto unknown but useful electrochemical super-functions related to the energy storage and conversion.

【Research Methods】

"Isolation strategies" will be applied to organic electrolytes, aqueous electrolytes, solid electrodes, and electrode/electrolyte interface. Target properties are (i) extension of the electrolyte window using modified frontier orbitals induced by the isolated solvent molecule, (ii) increasing the operating voltage and reversible capacity of electrode materials by maximum isolation of electron orbitals related to the redox reactions, (iii) maximizing the double layer capacitance at electrode-electrolyte interface utilizing modified dielectric function of confined and isolated molecules.

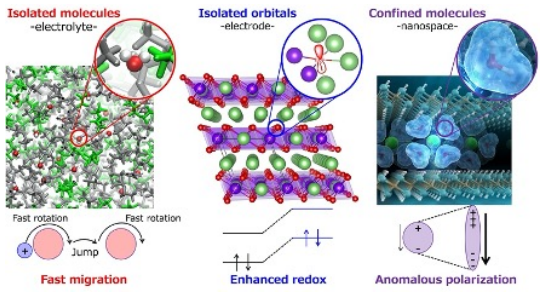

Fig. 1 Isolated molecules and isolated orbital incorporated into condensed solid or liquid systems.

【Expected Research Achievements and Scientific Significance】

The original new concept, "isolation strategies for molecules and orbitals", should be promising toward "realistic" breakthrough, as it still satisfies the essential requirements for highly reversible electrochemical reaction such as, "maintaining original structure and morphology" and "spontaneous formation of electrode/electrolyte interface in a closed system".

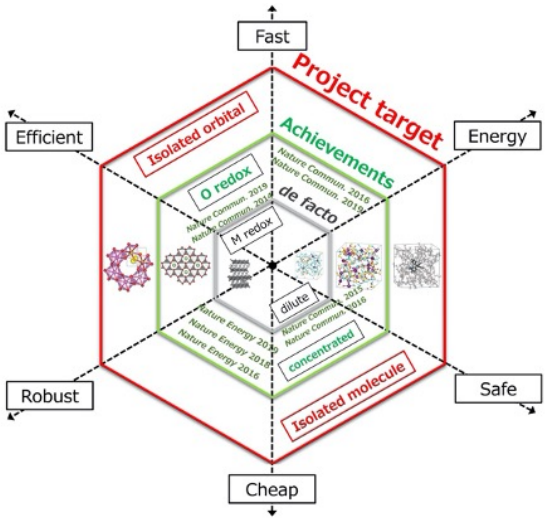

Fig.2 Hirearchy of the originality and its impact. The red line represents the functional frontier we are exploring.

【Publications Relevant to the Project】

· Q. Zheng, Y. Yamada, R. Shang, E. Nakamura, A. Yamada, A cyclic phosphate-based battery electrolyte for high-voltage and safe operation, Nature Energy, 5, 291-298 (2020)

· T. Sudayama, D. Asakura, X. Shi, B. M. Boisse, E. Watanabe, Y. Harada, M. Nakayama, M. Okubo, A. Yamada, Multibond orbital formation for stable oxygen redox reaction in battery electrodes, Energy Environ. Sci., 13, 1492-1500 (2020)

【Term of Project】 FY2020- 2024

【Budget Allocation】 151,100 Thousand Yen

【Homepage Address and Other Contact Information】

http://www.yamada-lab.t.u-tokyo.ac.jp/

【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： **Dynamic Chiral Macromolecular Catalyst for Asymmetric Amplification**

SUGINOME Michinori
(Kyoto University, Graduate School of Engineering, Professor)

Research Project Number: 20H05674 Researcher Number：60252483
Keyword：asymmetric synthesis, chiral catalyst, helical polymer, dynamic chirality, nonbonding interaction

【Purpose and Background of the Research】

In this research project, conceptually new chiral catalysts for asymmetric synthesis that enable asymmetric amplification shall be explored on the basis of helical macromolecules as a catalyst scaffold. The unique structural natures of the helical macromolecules include thermodynamically stable helical structure, which allows accumulation of small free energy differences (ΔG) at each of the monomer units, and its dynamic nature, which makes possible facile inversion between right- and left-handed conformations. Taking advantage of these characteristics, we're going to develop macromolecular catalyst, whose single-handed helical conformation is induced by nonbonding molecular interactions such as chiral dispersion force and dipole-dipole interaction with ubiquitous chiral additives. Unlike conventional asymmetric catalysis, in which "enantiopure" chiral catalysts have to be used, the new system would allow use of chiral sources with "low enantiopurity" by virtue of the asymmetric amplification. Furthermore, such system would lead to the establishment of "self-amplified asymmetric catalysis," where initial small imbalance of the chiral input finally affords enantiopure products.

【Research Methods】

As a particular helical macromolecular scaffold, we utilize poly (quinoxaline-2,3-diyl), which has already been established to provide highly effective chiral reaction space in various catalytic reactions. New modes of helix-sense induction and new asymmetric reactions with the particular macromolecular structure shall be separately examined and optimized in the two independent groups. Since the macromolecular catalysts are designed to be modular, the outcomes of the two groups are merged onto the single macromolecules that show desirable performance in the asymmetric catalysis. In the optimization of screw-sense induction to the macromolecular catalysts, efforts are made for gaining large induction power by tuning structure of the polymer as well as chiral guests. In the exploration of the new catalytic asymmetric reactions, focus is put on the production of chiral molecules that serve as chiral guests in the helix induction. Unifying those results, establishment of new macromolecular catalysts for highly efficient asymmetric amplification is expected.

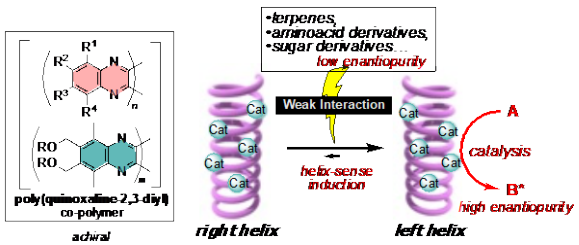

Figure 1. Poly (quinoxaline-2,3-diyl)s as new catalysts featuring dynamic chirality with asymmetric amplification.

【Expected Research Achievements and Scientific Significance】

Establishment of the new catalysts for asymmetric amplification immediately leads to new class of asymmetric synthesis in which ubiquitous chiral organic compounds serve as chiral sources even if their enantiopurity is not 100%. Furthermore, it also opens up the possibility of "absolute asymmetric synthesis," where none of chemical chiral source is used. As mentioned above, "self-amplified asymmetric catalysis" is one of the ultimate goals of this research project.

Even though this research project is directed toward the development of new asymmetric catalysis, the material and concept obtained in the project would have immediate impact on other research areas including studies on new material development and clarification of the origin of the homochirality.

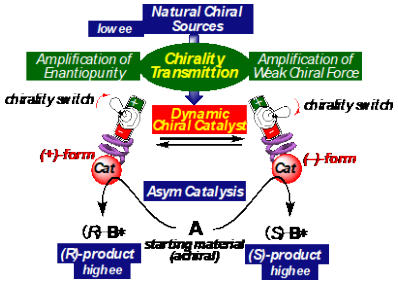

Figure 2. The concept on new chiral catalyst system featuring asymmetric amplification

【Publications Relevant to the Project】

・ Nagata, Y.; Takeda, R.; Suginome, M., *ACS Central Science* **2019**, *5*, 1235-1240.
・ Yamamoto, T.; Murakami, R.; Komatsu, S.; Suginome, M., *J. Am. Chem. Soc.* **2018**, *140*, 3867-3870.

【Term of Project】 FY2020- 2024

【Budget Allocation】 152,700 Thousand Yen

【Homepage Address and Other Contact Information】
http://www.sbchem.kyoto-u.ac.jp/suginome-lab/

【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： **Elucidation of glycan function by synthetic glycans and glycan remodeling systems and their application to new immunotherapies**

FUKASE Koichi
(Osaka University, Graduate School of Science, Professor)

Research Project Number: 20H05675 Researcher Number：80192722
Keyword：glycan, glycoconjugate, chemical synthesis, innate immunity, inflammation, cancer, adjuvant, vaccine

【Purpose and Background of the Research】

Glycans function as key substances for self and nonself recognition in both innate and acquired immunity. We have studied the structure and synthesis of glycans and glycoconjugates that activate or modulate immune systems, and clarified the mechanism of immune activation and inflammation by using synthetic compounds.

In this study, we will clarify new glycan recognition molecules and elucidate new functions of glycans in inflammation and immunity by using synthetic compounds and synthetic biology methods. Furthermore, treatments for cancer and immune diseases will be investigated by development of therapy candidates such as vaccine, cancer immunotherapy, and targeted α-particle therapy, and etc.

【Research Methods】

Structural complexity and heterogeneity are major features of glycans. Most classes of glycans exist as complex glycoconjugates such as glycoproteins, glycolipids, glycosaminoglycans, and etc. The biological functions of glycans have not yet been sufficiently elucidated due to their inherent complexity. Synthetic studies of glycans have greatly contributed to the functional studies of glycans by supplying homogeneous glycans to determine the active units or active principles.

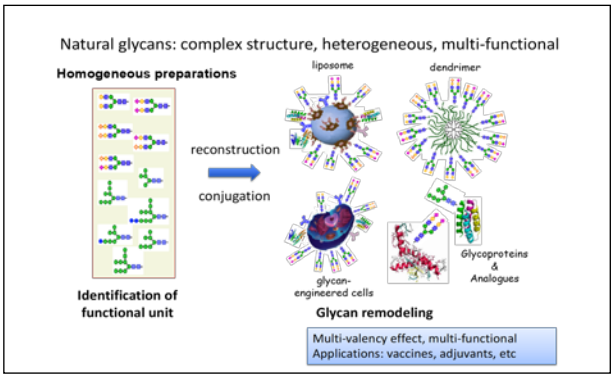

Figure 1 Functional analysis of glycans

In this study, we will investigate immunological functions of bacterial glycoconjugates as well as asparagine-linked glycans on glycoproteins (*N*-glycans) based on chemical synthesis. We will identify the glycan structure (functional unit) responsible for recognition, and elucidate the interaction between glycans with recognition proteins. A reconstruction model of glycans, e.g., glycodendrimers, glycan engineered cells, adjuvant-antigen conjugates will be used to investigate glycan functions in complex systems and to develop new candidates for treatments of cancer and immune diseases.

【Expected Research Achievements and Scientific Significance】

Glycan functions in inflammation and immune response will be clarified. We will also develop immunoadjuvants, self-adjuvanting cancer vaccines consisting of an immunoadjuvant and an antigen, glycosyl transferase inhibitors as regulatory molecules for inflammatory diseases, and new molecular targeting agents for cancer immunotherapy. Furthermore, we aim at developing the new treatment methods of intractable diseases, such as inflammatory bowel disease and pancreatic cancer.

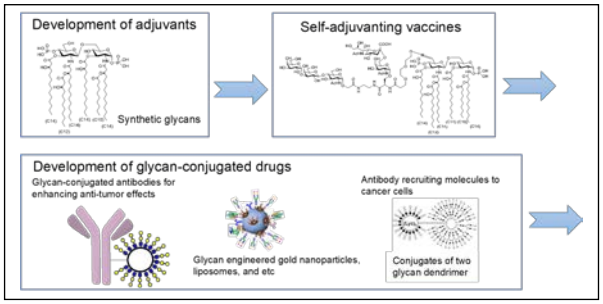

Figure 2 Development of immunotherapy candidates

【Publications Relevant to the Project】

・ Manabe, Y.; Marchetti, R.; Kabayama, K.; Fukase, K.; Molinaro, A. *et al.*, The Core Fucose on an IgG Antibody is an Endogenous Ligand of Dectin-1. *Angew. Chem. Int. Ed.* **2019**, *58*, 18697-18702.
・ Chang, T.-C.; Manabe, Y.; Kabayama, K.; Lin, C.-C.; Fukase, K. *et al.*, Syntheses and immunological evaluation of self-adjuvanting clustered *N*-acetyl and *N*-propionyl sialyl-Tn combined with a T-helper cell epitope as antitumor vaccine candidates. *Angew. Chem. Int. Ed.* **2018**, *57*, 8219-8224.

【Term of Project】 FY2020- 2024

【Budget Allocation】 154,300 Thousand Yen

【Homepage Address and Other Contact Information】

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【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project： **Molecular Systems Chemistry for the Efficient Utilization of Photon Energy**

KIMIZUKA Nobuo
(Kyushu University, Graduate school of Engineering, Professor)

Research Project Number: 20H05676 Researcher Number：90186304
Keyword：Self-Assembly, Molecular System's Chemistry, Singlet Fission, Photon Upconversion

【Purpose and Background of the Research】

Photon energy conversion materials and devices - such as semiconductor photocatalysts and solar cells- suffer from the limitation in the wavelength of sunlight that can be used. As a method for solving this problem, (1) singlet fission (SF) and (2) photon upconversion based on the triplet-triplet annihilation (TTA-UC) mechanism have been attracting attention.

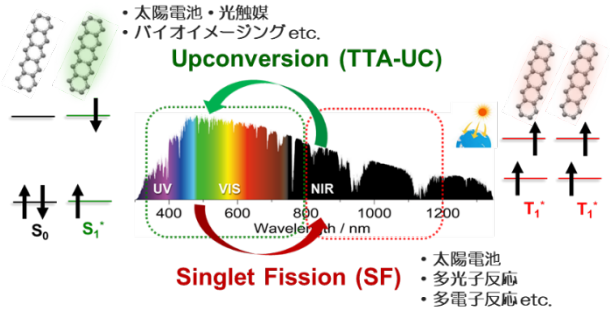

Figure 1 Photon upconversion and Singlet fission.

The study of TTA-UC phenomena has been conducted in organic media by taking advantage of molecular diffusion of the donor (D) and acceptor (A) molecules. However, the use of volatile organic solvents limits their applications. To overcome this issue, we have developed TTA-UC based on the self-assembly of acceptor molecules that harvest singlet and triplet excited energies by energy migration. We have pioneered the molecular self-assembly based TTA-UC in the visible light region in various molecular systems. On the other hand, TTA-UC from the near-infrared light (NIR) region to the visible light (VIS) region is more important, which has not yet been obtained by the molecular organization. In addition, "molecular-organized SF" based on the self-assembly of designed molecules remains an undeveloped field. In this project, we aim to achieve (1) singlet fission in well-designed, self-assembled molecular systems, and (2) NIR-to-Vis TTA-UC in self-assembled molecular systems on nanoplasmonic surfaces.

【Research Methods】

In this study, we mainly examine the following items.

(1) The concept of molecular self-assembly is introduced to the field of singlet fiction (SF). More specifically, we develop a methodology to promote SF by precisely aligning chromophores in self-assemblies. In order to improve the efficiency of SF, it is essential to simultaneously achieve (i) "asymmetric chromophore arrangement" for the efficient formation of triplet pairs and (ii) to facilitate separation of the two excited triplet states so that their recombination is avoided. To achieve both of these issues, we propose a chiral molecular organization. The SF characteristics of the chiral chromophore arrays will be evaluated by ultrafast spectroscopy, and the effect of the chiral organization on SF will be elucidated.

In addition, we will introduce nano-gap plasmonics to the field of self-assembly-based UC, and a methodology for enhancing low-intensity excitation light for NIR-To-Vis UC will be developed. The relative arrangement of D and A is defined by immobilizing Os complexes and stable organic radicals on the surface of metal nanocrystal arrays arranged at nano-gap intervals, and by depositing the acceptor self-assemblies on them.

【Expected Research Achievements and Scientific Significance】

Through the realization of molecular self-assembly-based SF and TTA-UC in the NIR-to-Vis region, a field of molecular systems chemistry will emerge that contributes to the control of the dynamics and functions of excited triplet states and the advanced utilization of light energy. It will lead to a paradigm shift in supramolecular chemistry and in photofunctional materials chemistry

【Publications Relevant to the Project】

・ Y. Yanai, N. Kimizuka, *Acc. Chem. Res.*, **50**, 2487-2495 (2017).
・ P. Bharmoria, S. Hisamitsu, Y. Yanai, N. Kimizuka et al, *J. Am. Chem. Soc.*, **140**, *34*, 10848-10855 (2018).
・ Y. Sasaki, A. H-Takagi, I. Ajioka, N. Yanai, N. Kimizuka et al, *Angew. Chem. Int. Ed.*, **49**, 17827-17833 (2019).

【Term of Project】 FY2020- 2024

【Budget Allocation】 149,900 Thousand Yen

【Homepage Address and Other Contact Information】

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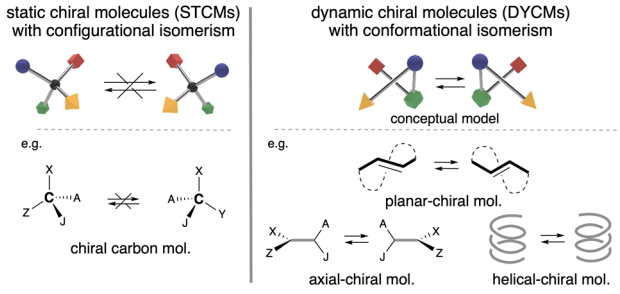
Title of Project : Development of DYASIN: Novel Approach to Enantioenriched Chiral Molecules

TOMOOKA Katsuhiko
(Kyushu University, Institute for Materials Chemistry and Engineering, Professor)

Research Project Number: 20H05677 Researcher Number : 70207629
Keyword : dynamic asymmetric induction, optically active, dynamic chiral molecule, static chiral molecule, outer chiral source

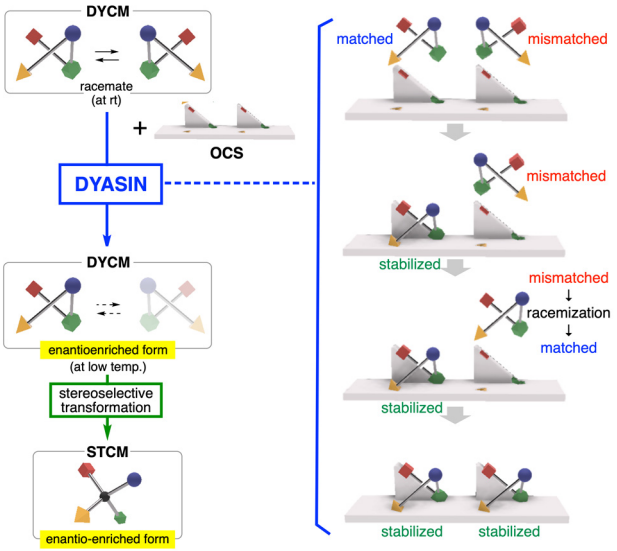
【Purpose and Background of the Research】

In modern organic chemistry, chemists have put forth considerable efforts in order to obtain the desired enantiomers selectively. Chiral molecules with configurational isomerism of an asymmetric carbon represent a principal motif in this field. In general, the chirality of an asymmetric carbon is thermally stable, and hence it can be called "static chirality". Developed approaches towards enantioenriched static chiral molecules (STCMs) are generally classified by i) the separation of enantiomers from racemates, also known as "optical resolution" or ii) the synthesis of chiral molecules with stereoselective bond formation, so called "asymmetric synthesis". On the other hand, it is well known that molecular chirality can also be caused by conformational isomerism and many examples are dynamic, i.e., conversion of enantiomers via bond rotation, in sharp contrast to STCM. This dynamic chirality often causes difficulties in handling the enantioenriched forms of molecules due to stereochemical instability. Meanwhile, dynamic chiral molecules (DYCMs) have a potential advantage in that the enantioenriched forms can be prepared in a very different way from STCM.



【Research Methods】

In this regard, we envisioned that if the chirality was adequately dynamic at ambient temperature, DYCMs could be influenced by an enantioenriched outer chiral source (OCS), and the effect would not be the same between enantiomers; thus, racemic DYCMs could be converted into their enantioenriched forms via thermodynamically controlled isomerization. If the bias towards one enantiomer was sufficiently high, the process would be practically useful. This process is hereafter referred to as "dynamic asymmetric induction (DYASIN)" where DYCMs and an OCS are presented in a conceptual rendering. Although the resulting enantioenriched DYCM is stereochemically labile, it can be isolated without racemization from the system by quick separation at appropriately low temperatures, and would be converted into stereochemically more stable molecules, i.e., STCM or semi-STCM, via proper transformations.



DYASIN would be the efficient technology for the preparation of enantioenriched chiral molecules and open new avenues in the chemistry of chiral molecules.

【Publications Relevant to the Project】

1. Preparation of Enantioenriched Chiral Organic Molecules by Dynamic Asymmetric Induction from Outer Chiral Source. Igawa, K.; Kawasaki, Y.; Ano, Y.; Kashiwagi, T.; Ogawa, K.; Hayashi, J.; Morita, R. Yoshioka, Y.; Uehara, K.; Tomooka, K. *Chem. Lett.* **2019**, *48*, 726-729.

【Term of Project】

FY2020-2024

【Budget Allocation】

152,800 Thousand Yen

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