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

Title of Project : Development of Innovative Chiral Materials Based on Controlled Helical Nano-Space

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Research Area : Polymer Chemistry
Keyword : Helical Structure, Helical Space, Asymmetric Catalysis, Chiral Recognition

【Purpose and Background of the Research】

Biological polymers, such as proteins and nucleic acids, possess a unique higher-ordered helical structure, which links to their sophisticated functions. Inspired by such exquisite helical structures, remarkable progress has been made in the synthesis of artificial helical polymers and oligomers with a controlled helix-sense in the past two decades. On the other hand, enzymes exhibit elaborate chiral recognition and asymmetric catalysis in specific chiral sites, and channel architectures of membrane proteins play a central role in uptake and transport of substances and signal transduction, mainly derived from its "flexible" and "adaptable" nano-space. Namely, the precise control of chiral "nano-space" has the potential for establishment of innovative and core molecular-technology towards the development of the next generation chiral materials with functions.

With this background in mind, the present research project aims at developing the molecular-technology towards the creation of precisely controlled "helical space" that enables precision polymerization, asymmetric catalysis, and chiral recognition that can not be achieved by conventional methods. In addition, unique molecular machines composed of helical structures showing unidirectional elastic (extension–contraction) motions will be designed and synthesized in order to develop stimuli-responsive chiral materials with specific functions, such as asymmetric catalysis and chiral sensing.

【Research Methods】

1) A rational design and synthesis of chiral molecules, supramolecules, and polymers with a precisely controlled "helical space" that is the key structural feature in this research project will be performed. Using the chiral systems, 2) we will develop novel precision polymerization producing polymers with a controlled stereochemistry and asymmetric catalysis with high enantioselectivity within the helical space, and 3) further develop practically useful chiral materials for separating enantiomers.

Recently, we found a unique optically active double-stranded helicate bridged by two spiroborates that sandwiched a Na^+ ion in the center, which further underwent Na^+ ion-triggered, reversible extension–contraction motion coupled with a twisting motion in one direction upon Na^+ ion release and binding. 4) With the aim at further developments of molecular springs, a series of novel helicates bearing functional units in the middle will be synthesized in order to develop novel stimuli-responsive molecular machines, showing switchable (ON-OFF) asymmetric catalysis and chiral recognition.

【Expected Research Achievements and Scientific Significance】

While a number of studies on helical systems have been reported, development of novel functions derived from helical structures remains a challenge. Furthermore, a limited number of studies have been focused on the "helical space" as well as elastic motions in helical systems. Making the best use of helical structural motif enables to develop the innovative molecular-technology towards the creation of the next generation chiral materials with specific functions, such as asymmetric catalysis and chiral recognition.

【Publications Relevant to the Project】

・H. Yamada, Z.-Q. Wu, Y. Furusho, E. Yashima, Thermodynamic and Kinetic Stabilities of Complementary Double Helices Utilizing Amidinium-Carboxylate Salt Bridges, *J. Am. Chem. Soc.*, **134**, 9506-9520 (2012).
・K. Miwa, Y. Furusho, E. Yashima, Ion-Triggered Spring-like Motion of a Double Helicate Accompanied by Anisotropic Twisting, *Nature Chem.*, **2**, 444-449 (2010).

【Term of Project】 FY2013-2017

【Budget Allocation】 187, 500 Thousand Yen

【Homepage Address and Other Contact Information】

http://helix.mol.nagoya-u.ac.jp/