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

Broad Section E

Title of Project： Dynamic Chiral Macromolecular Catalyst for Asymmetric Amplification

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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.

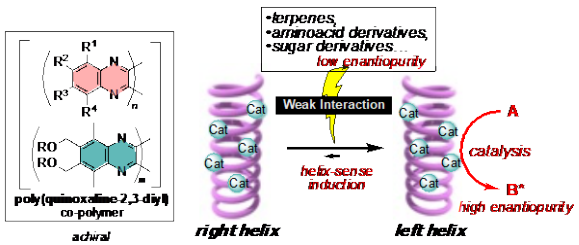

Figure 1. Poly (quinoxaline-2,3-diyl)s as new catalysts featuring dynamic chirality with asymmetric amplification.

【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.

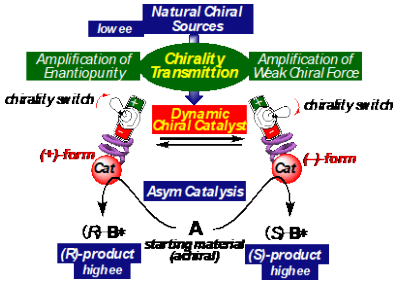

Figure 2. The concept on new chiral catalyst system featuring asymmetric amplification

【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/