【Grant-in-Aid for Specially Promoted Research】

Asymmetric Synthesis of Chiral Nonplanar Polycyclic Aromatic Molecules and Application to Materials Chemistry

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Project Information	Project Number : 24H00005　　Project Period (FY) : 2024-2030 Keywords : synthetic organic chemistry, asymmetric synthesis, aromatic compounds, materials chemistry

Purpose and Background of the Research

● Outline of the Research

π-Conjugated molecules are expected to be applied to next-generation organic electronics materials, and the development of synthetic methods and the creation of their functions have been actively studied to date. Nonplanar π-conjugated molecules with non-central chirality would have new chemical and physical functions based on their chirality, but it has been extremely difficult to control the non-central chirality. To overcome this problem, the Tanaka group developed a method to construct non-central chirality by the catalytic asymmetric [2+2+2] cycloaddition and reported many examples of asymmetric synthesis. In this study, we will develop new methodologies and catalysts for the asymmetric synthesis of chiral nonplanar polycyclic aromatic molecules with novel properties and functions using the catalytic asymmetric [2+2+2] cycloaddition.

● Background and Objectives of the Research

The development of catalytic asymmetric reactions is important as a means of providing useful optically active substances. However, versatile catalytic reactions that induce non-central chiralities in aromatic compounds (Figure 2) have not yet been explored. Principal investigator Tanaka has reported numerous reports on applying benzene ring construction via [2+2+2] cycloadditions of alkynes to construct non-central chiralities of aromatic compounds in a unified manner.

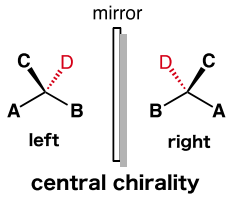

Figure 1. Central Chirality

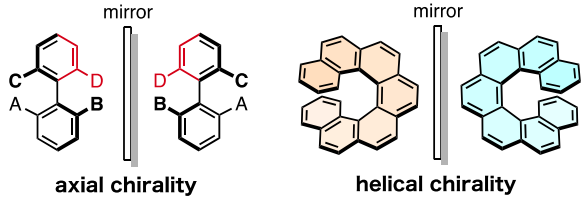

Figure 2. Non-Central Chirality

Planar polycyclic aromatic molecules are attracting attention as next-generation nanocarbon materials because of their unique physical properties that depend on their two-dimensional structure. On the other hand, nonplanar polycyclic aromatic molecules have an additional element of three-dimensional structure and are of interest for their electronic properties, supramolecular properties, and dynamic behavior, which are different from those of planar molecules. However, the synthesis of chiral nonplanar polycyclic aromatic molecules is difficult due to the need to control the chirality and the increase in strain, leaving many unexplored molecules. In this study, we will develop new methodologies and catalysts that enable the construction of unexplored higher-order asymmetric structures and explore new phenomena and new functions based on novel skeletons.

● Research Methodology

The [2+2+2] cycloaddition reaction is inherently more advantageous for realizing this objective than the coupling reaction that has been used universally in the synthesis of aromatic molecules. While coupling reactions require carbon-carbon bond formation with maximum steric hindrance, [2+2+2] cycloadditions are energetically favorable and irreversible reactions using alkynes with minimum steric hindrance (Figure 3).

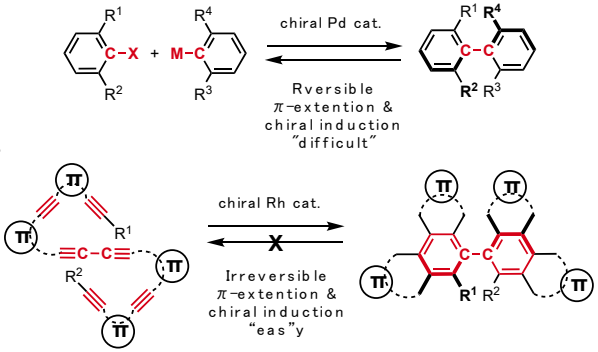

Figure 3. Coupling vs. [2+2+2] Cycloaddition Reactions

Expected Research Achievements

In this project, we will focus on the following three items to construct unexplored higher-order chiral structures and create their functions.

(1) Catalytic asymmetric synthesis of flexible chiral aromatic molecules containing sp^3 atoms: We will develop catalytic asymmetric synthesis methodologies of unexplored cyclic and cage-shaped aromatic molecules.

(2) Catalytic asymmetric synthesis of rigid chiral molecules consisting only of sp^2 atoms: We will develop catalytic asymmetric synthesis methodologies for unexplored helical and saddle-shaped aromatic molecules.

Then, we will develop chiral material and supramolecular chemistry using the chiral non-planar polycyclic aromatic molecules synthesized in (1) and (2) above.

(3) Creation of new highly active catalysts: We will develop new catalysts that enable the challenging asymmetric catalytic reactions described in (2) above.

Development of new methodologies and new catalysts" → "Exploration of new phenomena and functions based on novel skeletons"

(1) Catalytic asymmetric synthesis of "flexible" chiral aromatic molecules

- cyclic molecules (multi-twisted belts) — Möbius aromaticity, helical assembly
- caged molecules (polyhedral cages) — porous organic crystals, Inclusion-adsorption
- helical Molecules (3D π-extended helicenes) — CPL, single-molecule measurements
- saddle molecules (circulenes) — organic semiconductor

asymmetric synthesis of chiral non-planar polycyclic aromatic molecules

(2) Catalytic asymmetric synthesis of "rigid" chiral aromatic molecules

(3) "Highly active new catalysts" for difficult [2+2+2] cycloadditions

Figure 4. Targets in the Research

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