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

Renovation of the chemistry of antiaromatic compounds

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Project Information	Project Number : 22H04974　Project Period (FY) : 2022-2026 Keywords : Aromaticity, Supramolecule, DFT Calculation, Single Molecule Observation

Purpose and Background of the Research

●Outline of the Research

Aromatic compounds with 4n+2 π electrons are stable and used for many applications. Although antiaromatic compounds with 4n π electrons are unstable, they readily accept and release electrons as compared to aromatic ones. This feature is attractive for electronic applications. However, existing antiaromatic compounds often possess bulky substituents for stabilization, which hamper the proximity of molecules in the solid state (Figure 1).

In this project, we will create novel antiaromatic compounds without steric congestion to elucidate the different intermolecular interactions from aromatic ones. We will also explore the properties and functions of antiaromatic compounds in their assembled states. We hope to establish a novel design concept of stable antiaromatic compounds and develop their valuable functions for application in organic electronic materials.

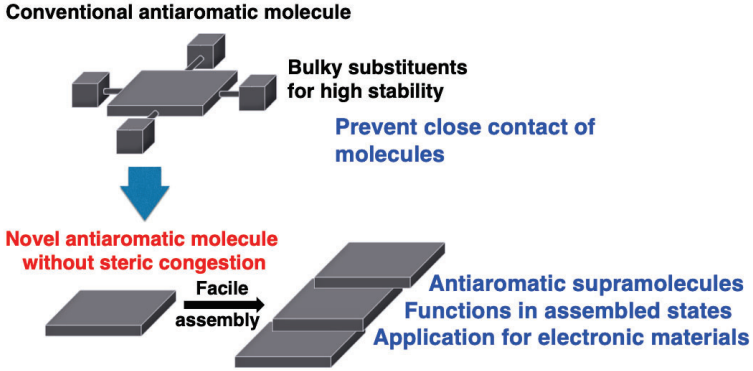

Figure 1. Conventional antiaromatic molecules and novel antiaromatic molecules without steric congestion

●Research Background

Electronic functions of organic materials depend on electron transport among molecules (Figure 2). The key to achieving high performance is a close contact of molecules, where electrons are mobile smoothly. Our previous research has revealed that antiaromatic compounds can assemble more closely than aromatic compounds. The use of antiaromatic compounds would enhance the property of organic materials.

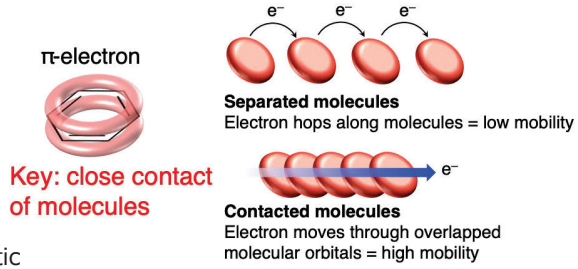

Figure 2. Electron transport in organic materials

●The circumstances leading to the conception of the present research proposal

Antiaromatic compounds are generally unstable and require bulky substituents for stabilization. In contrast, we have developed a stable antiaromatic compound, norcorrole (Figure 3). We have also revealed that norcorrole forms closely stacking structures to exhibit three-dimensional aromaticity. These findings motivated us to explore extremely close contact among antiaromatic molecules. In this project, we will develop novel antiaromatic compounds and attempt to achieve close stacking with various antiaromatic compounds.

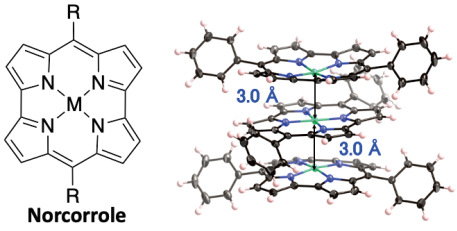

Figure 3. Antiaromatic norcorrole and its close stacking

Expected Research Achievements

●Design and synthesis of antiaromatic molecules without steric congestion

We will elucidate the origin of the stable nature of norcorroles. We will also establish a design concept of stable antiaromatic compounds without steric congestion.

●Better understanding of interactions between antiaromatic molecules

Antiaromatic compounds exhibit stronger intermolecular interactions than aromatic ones due to their unique electronic structure (Figure 4). Based on experiments and calculations, we will clarify the intermolecular interactions. Three-dimensional aromaticity will also be explored (Figure 5).

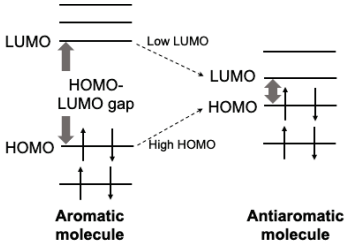

Figure 4. Molecular orbitals of aromatic and antiaromatic molecules

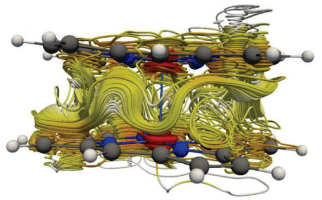

Figure 5. Induced electron stream in stacked norcorrole

●Control of aggregated states of antiaromatic molecules

We will control the aggregated states of antiaromatic compounds based on non-covalent interactions (Figure 6). We will create antiaromatic supramolecules using hydrogen bonding to control the assembling structures.

●Exploration of properties and functions of antiaromatic molecules

We will investigate the mechanism of the electron transport among antiaromatic compounds by single molecular measurements and theoretical calculations.

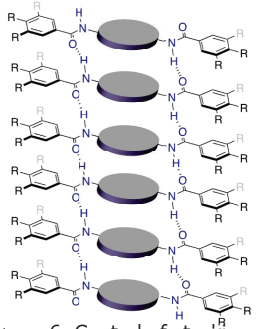

Figure 6. Control of stacking structures by hydrogen bonding

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