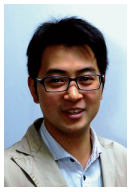
Organic electronic materials, Sensors

Synthesis and investigation of aromatic-rings congested π-cluster systems



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Abstract

Nowadays, variable structures of polycyclic aromatic hydrocarbons (PAHs) composed of benzene ring as a basic unit have been synthesized and some of them have been developed for the organic devises such as organic semiconductors or organic light-emitting diodes. In this work, we have focused on the π-cluster system, having the faces of multiple aromatic rings being shorter than 3.4 Å, which is the sum of the van der Waals radii of carbons, and investigated the unique properties of the π-cluster system that is expressed in congested situation.

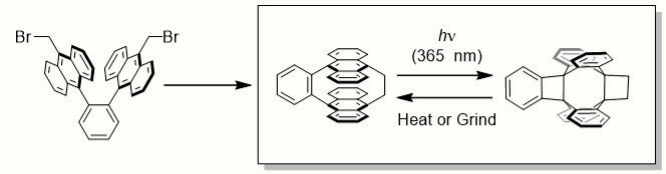
Background & Results

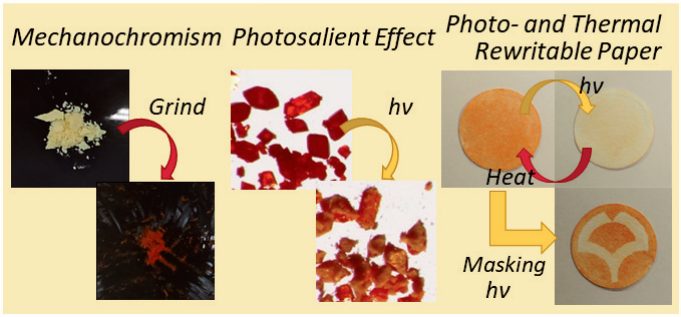
Anthracene-based cyclic π-cluster possessing quite short distance at 2.8 Å between anthracene was effectively synthesized by employing an intramolecular cyclization reaction and it was investigated for disclosing the nature of π-congestion effect. The cyclic anthracene dimer exhibits multi-stimuli responsiveness due to high π-congestion. For example, photoirradiation on the anthracene affords its photoisomer having C–C bonds that are longer than 1.65 Å which can undergo thermal reversion under gentle heating. This enabled mechanochromism of the photoisomer (colorless) to the original anthracene dimer (red). Photoisomerization was also observed in the crystalline state, accompanied by crystal jumping or collapsing, that is, the photosalient effect.

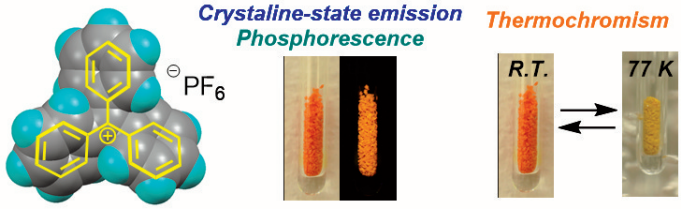
Since the discovery of the triphenylmethyl (TPM) cation 120 years ago, a variety of aromatic cations having various colors and luminescence properties have been rigorously studied. However, the optical properties of non-substituted and highly reactive TPM cation, which was observed to be very weakly luminescent, have not been subjected to detailed investigation. Herein, we explored the optical nature of non-substituted TPM cation in the crystalline state. Investigation of the optical properties revealed that TPM cation shows a crystalline state emission, a distinct color change to yellow upon cooling as a consequence of a change in the nature of the charge transfer interaction between the cation and anion, and phosphorescence.

Significance of the research and Future perspective

By bringing the two aromatic rings closer together at a distance shorter than the sum of the van der Waals radii of the carbon atom, two molecular orbitals of the aromatic rings are hybridized resulting in small HOMO-LUMO gap. Therefore, this simple π-congestion affects the electronic properties of aromatic compounds, leading to the display of unique various properties that cannot be exhibited in the monomeric state. For example, changes in absorption and emission spectra, in electron-donating and accepting properties, isomerization of the molecular skeleton by light irradiation, heating, or mechanical grinding. On the other hand, the construction of such highly congested molecules poses synthetic problems such as low yields. Therefore, we are also focusing on effective synthetic methods for building π-cluster systems with various molecular frameworks for the development of highly versatile functional materials.







Patent

Treatise Nishiuchi, Tomohiko; Kisaka, Kazuki; Kubo,Takashi. Synthesis of Anthracene-Based Cyclic π-Clusters and Elucidation of their Properties Originating from Congested Aromatic Planes. Angew. Chem. Int. Ed. 2021; 60(10): 5400-5406. doi: 10.1002/anie.202013349
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Keyword polycyclic aromatic hydrocarbon, π-cluster, external stimulus responsiveness, luminescent properties, chromism