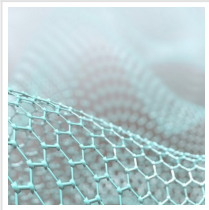
Synthesis and Properties of Wing-shaped Nanographene



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A research group has studied the synthesis and physical properties of hexapyrrolohexaazacoronene (HPHAC), a nitrogen-containing PAH, using pyrroles.

In recent years, various synthetic chemical approaches have been investigated using polycyclic aromatic compounds (PAHs) as "nanographene with precise molecular structure and high purity". If it becomes possible to construct structurally controlled 3D assemblies and spaces from this 2D nano-sized graphene, new materials with unique structural properties can be created. A research group at Ehime University has been studying the synthesis and physical properties of hexapyrrolohexaazacoronene (HPHAC), a nitrogen-containing PAH, using pyrroles. HPHACs, which are composed of electron-rich pyrroles, are easily oxidized and their two-electron oxidized forms exhibit global aromaticity. However, the only reported studies on HPHACs have been on the synthesis of monomers, including analogues, and the elucidation of their structure-property relationships. No studies have been conducted on the synthesis of dimers toward structurally controlled 3D structures.

In this study, a wing-shaped HPHAC dimer was synthesized by employing a bicyclooctadiene skeleton as a structurally rigid crosslinking site. As with the known HPHAC monomer, stable redox properties were observed in the newly synthesized dimer. In addition, the characteristic assembly modes depending on the oxidation state were revealed by single crystal structure analysis and various spectroscopic measurements. Furthermore, in the tetracationic species of the HPHAC dimer, the aromaticity of the 3D space surrounded by the two HPHACs was found to be enhanced. This is a result of the influence of the magnetic and electronic properties of the HPHACs on each other.

In recent synthetic chemical research on nanographene, instead of the conventional planar compounds, high-dimensional compounds with, for example, bowl- and saddle-shaped structures have been reported. On the other hand, there have been few studies on the construction of structurally controlled 3D assemblies and spaces and their use as constituent units. The versatile assembly modes of 3D nanographene can provide high mechanical robustness and a large surface area, and thus are expected to be applied to sensors, bioimaging, and energy conversion materials.