Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
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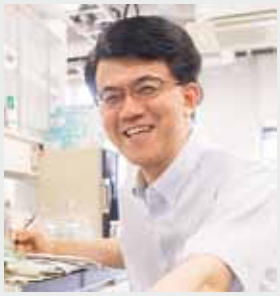

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Graphene and curved graphenes have been extensively investigated by both chemists and physicists because of their unique structures and properties. C_{60} fullerene is spherical and has the positive Gaussian curvature. Carbon nanotubes (CNTs) have the cylindrical structures with the zero Gaussian curvature. The introduction of curvatures to graphene changes the dimensionality and electronic properties. For example, graphene is a two-dimensional zero-gap semiconductor with the ambipolar character (both p- and n-types). C_{60} is a zero-dimensional n-type semiconductor, and CNTs are one-dimensional p-type semiconductors or metals. It is interesting to see how the curvature influences the structure and properties of the graphene molecule. We are currently working on the synthesis of aromatic saddles and belts.

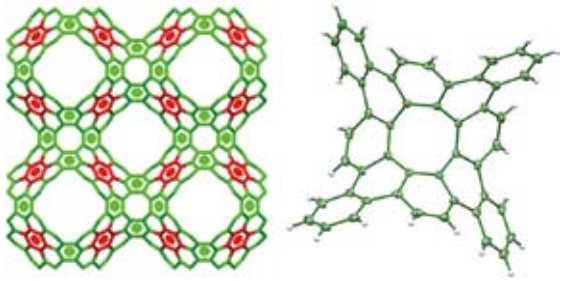

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato and S. Tokito, "Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene," *J. Am. Chem. Soc.* **126**, 8138–8140 (2004).
- T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki and S. Yamago, "Selective and Random Syntheses of [*n*]Cycloparaphenylenes (*n* = 8–13) and Size Dependence of their Electronic Properties," *J. Am. Chem. Soc.* **133**, 8354–8361 (2011).
- Y. Sakamoto and T. Suzuki, "Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene," *J. Am. Chem. Soc.* **135**, 14074–14077 (2013).

1. Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene[1)]

An aromatic saddle was designed from the hypothetical three-dimensional graphene with the negative Gaussian curvature (Schwarzite P192). Two aromatic saddles, tetrabenzo[8]circulene (**TB8C**) and its octamethyl derivative **OM-TB8C**, were synthesized by the Scholl reaction of cyclic octaphenylene precursors. The structure of **TB8C** greatly deviates from planarity, and the deep saddle shape was confirmed by single-crystal X-ray crystallography. There are two conformers with the S_4 symmetry, which are twisted compared to the DFT structure (D_{2d}). The theoretical studies propose that the interconversion of **TB8C** via the planar transition state (125 kcal mol^{-1}) is not possible. However, the pseudorotation leads to a low-energy tub-to-tub inversion via the nonplanar transition state (7.3 kcal mol^{-1}). The ground state structure of **TB8C** in solution is quite different from the X-ray structure because of the crystal-packing force and low-energy pseudorotation. **OM-TB8C** is a good electron donor and works as the p-type semiconductor.

Figure 2. Single-crystal X-ray structure of **TB8C** from the side. The thermal ellipsoids are shown at 50% probability.

2. Synthesis and Physical Properties of a Ball-Like Three-Dimensional π-Conjugated Molecule[2)]

Curved π-conjugated molecules with closed and three-dimensional (3D) structures, such as fullerenes and carbon nanotubes, have been the subject of intensive research due to their potential applications in molecular electronics. However, basic molecular skeletons of 3D molecules are limited because of the lack of a rational and selective synthetic method by organic synthesis. We report the synthesis of a 3D π-conjugated molecule based on the platinum-mediated assembly of four molecules of a stannylated trisubstituted benzene derivative forming a hexanuclear platinum complex with an octahedral shape, from which reductive elimination of platinum gave the target molecule. As many supramolecular transition metal-ligand complexes with 3D cages and polyhedral structures have been synthesized by self-assembly of ligands and metals, the current assembly/reductive elimination strategy could provide a variety of new 3D π-conjugated molecules with different structures and topologies, which are challenging to obtain using conventional synthetic methods.

3. Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effects of Cyclic Structure on the Electronic Properties of Pyrene Oligomers[3)]

A cyclic tetramer of pyrene, [4]cyclo-2,7-pyrenylene ([4]CPY), was synthesized from pyrene in six steps and 18% overall yield by the platinum-mediated assembly of pyrene units and subsequent reductive elimination of platinum. The structures of the two key intermediates were unambiguously determined by X-ray crystallographic analysis. DFT calculations showed that the topology of the frontier orbitals in [4]CPY was essentially the same as those in [8]cycloparaphenylene ([8]CPP), and that all the pyrene units were fully conjugated. The electrochemical analyses proved the electronic properties of [4]CPY to be similar to those of [8]CPP. The results are in sharp contrast to those obtained for the corresponding linear oligomers of pyrene in which each pyrene unit was electronically isolated. The results clearly show a novel effect of the cyclic structure on cyclic π-conjugated molecules.

References

1) Y. Sakamoto and T. Suzuki, *J. Am. Chem. Soc.* **135**, 14074–14077 (2013).
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3) T. Iwamoto, E. Kayahara, N. Yasuda, T. Suzuki and S. Yamago, *Angew. Chem., Int. Ed.* **53**, 6430–6434 (2014).