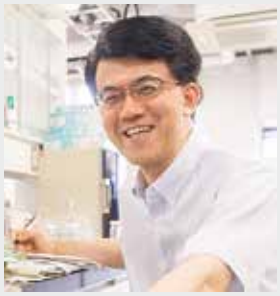
Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



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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.

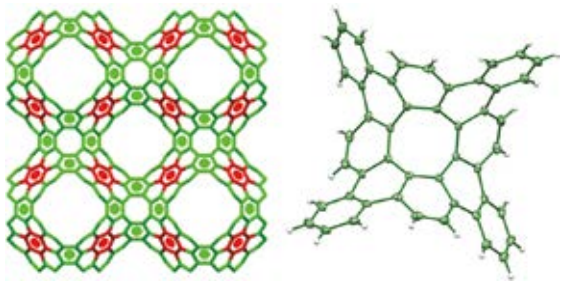

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

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. Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops[1)]

Three *N*-substituted tetracyclo(2,7-carbazole)s have been synthesized to investigate the inner regions of nanohoops. One compound has a 5,5-dimethylnonane bridge between two neighboring *anti* carbazoles, which can be used as covalently bonded "methane probes." These probes near the ring center are strongly shielded by local ring currents and exhibited a singlet at $\delta = -2.70$ ppm in ^{1}H NMR. To visualize local and macrocyclic ring currents separately, we drew NICS (nucleus-independent chemical shift) contour maps of tetracyclo(9-methyl-2,7-carbazole) and [*n*]cycloparaphenylenes (CPPs). Local ring currents make the interior diatropic, and paratropic regions exist only outside the ring. Macrocyclic ring currents in [5] to [7]CPPs generate deshielding cones, which are typical of antiaromatic [4*n*]annulenes.

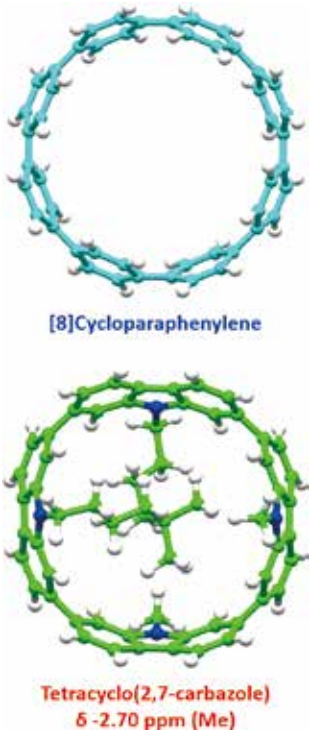

Figure 2. Optimized geometries of nanohoops by DFT calculations at the B3LYP/6-31G(d) level.

2. Ligand-Controlled Synthesis of [3]- and [4]Cyclo-9,9-dimethyl-2,7-fluorenes through Triangle- and Square-Shaped Platinum Intermediates[2)]

The syntheses of [3]- and [4]cyclo-9,9-dimethyl-2,7-fluorenes ([3] and [4]CFRs), cyclic trimer, and tetramers of 9,9-dimethyl-2,7-fluorene (FR), respectively, were achieved by the platinum-mediated assembly of FR units and subsequent reductive elimination of platinum. A triangle-shaped tris-platinum complex and a square-shaped tetra-platinum complex were obtained by changing the platinum ligand. The structure of the triangle complex was unambiguously determined by X-ray crystallographic analysis. Reductive elimination of each complex gave [3] and [4]CFRs. Two rotamers of [3]CFR were sufficiently stable at room temperature and were separated by chromatography. The physical properties of the CFRs were also investigated theoretically and experimentally.

References

1) Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara and S. Yamago, *J. Org. Chem.* **81**, 3356–3363 (2016).
2) E. Kayahara, R. Qu, M. Kojima, T. Iwamoto, T. Suzuki and S. Yamago, *Chem. –Eur. J.* **21**, 18939–18943 (2015).