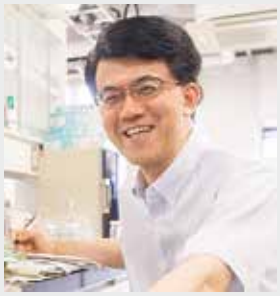
Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



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Keywords Organic Synthesis, Organic Semiconductor, Graphene Molecule

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. Three-dimensional graphenes with the negative Gaussian curvature were proposed as shown in Figure 1. It is interesting to see how the curvature influences the structure and properties of the graphene molecule.

Perfluorination is a simple method to prepare an n-type semiconductor with the same molecular symmetry. It is important to understand the impact of perfluorination on the solid-state structures and charge transport properties. We are currently working on the synthesis of new perfluorinated aromatic compounds.

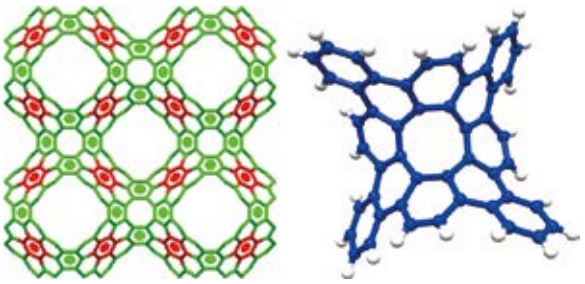

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

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).
- Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara and S. Yamago, "Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops," *J. Org. Chem.* **81**, 3356–3363 (2016).

1. Perfluorinated and Half-Fluorinated Rubrenes: Synthesis and Crystal Packing Arrangements[1)]

Perfluororubrene (PF-RUB) has been synthesized by cycloaddition of perfluorinated 1,3-diphenylisobenzofuran and 1,4-diphenyl-2,3-didehydronaphthalene followed by reductive deoxygenation. This method was easily applied for the synthesis of half-fluorinated rubrene (F_{14}-RUB). The electrochemical measurements and DFT calculations indicate that perfluorination strongly lowers the HOMO and LUMO energies. Recrystallization and sublimation of PF-RUB gave two different crystals with planar and twisted conformations, respectively. In both cases, perfluorination leads to the formation of short C–F and F–F contacts and completely disrupts face-to-face π interactions. Single crystals of F_{14}-RUB were grown by sublimation, and twisted molecules display the two-dimensional π-stacking with a face-to-face distance of 3.54 Å.

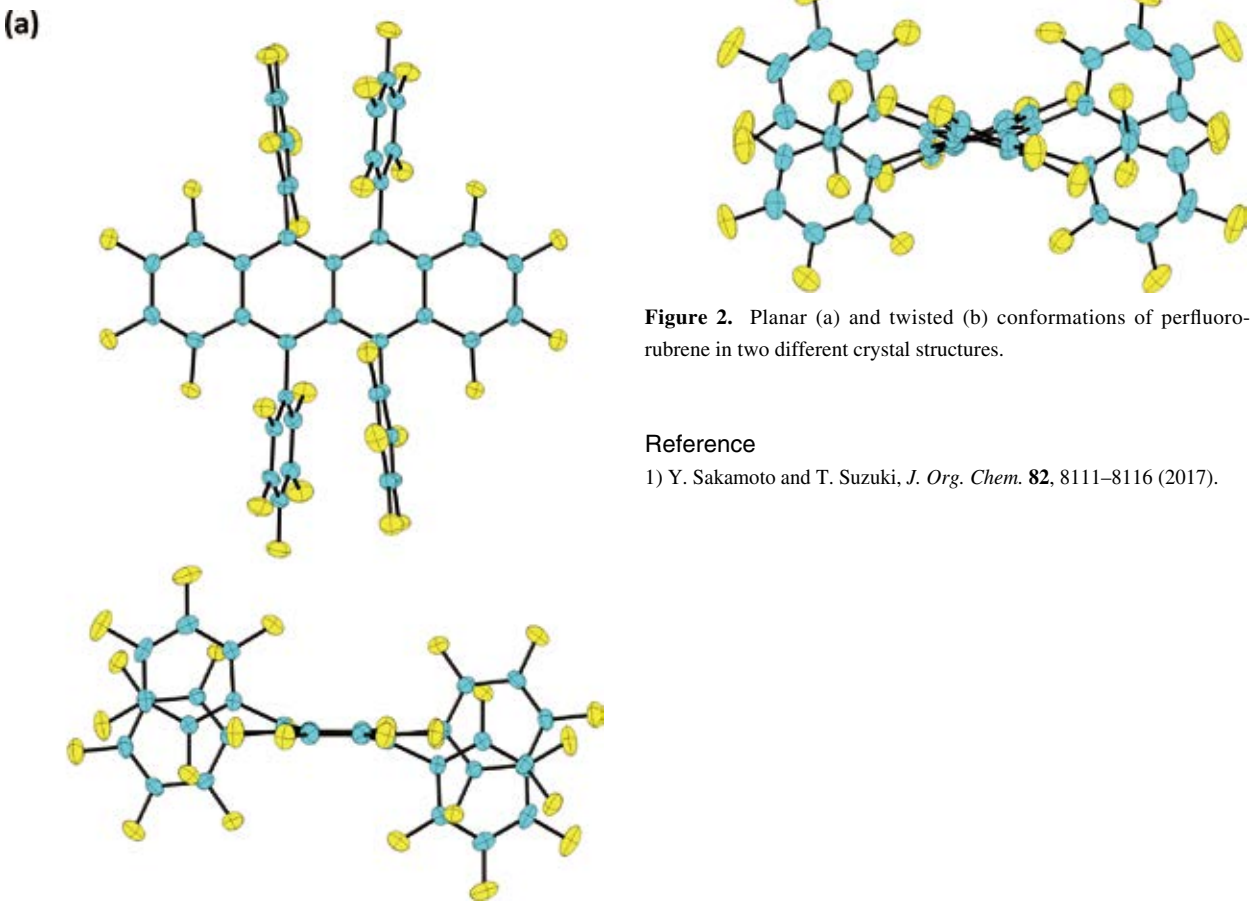

Figure 2. Planar (a) and twisted (b) conformations of perfluororubrene in two different crystal structures.

Reference

1) Y. Sakamoto and T. Suzuki, *J. Org. Chem.* **82**, 8111–8116 (2017).