Development of Graphene Molecules as Organic Semiconductors

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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. 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.

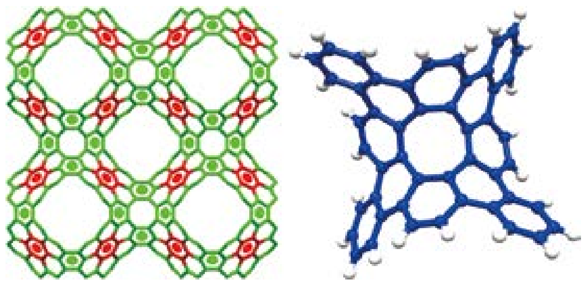

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- 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).
- Y. Sakamoto and T. Suzuki, "Perfluorinated and Half-Fluorinated Rubrenes: Synthesis and Crystal Packing Arrangement," *J. Org. Chem.* **82**, 8111–8116 (2017).

1. Perfluorination of Rylene Compounds for Electronics and Optoelectronics

Perfluorination of aromatic compounds is a simple method of exchanging all hydrogen with fluorine, and it is possible to convert a p-type semiconductor to an n-type one.[1] Although the molecular weight greatly increases, the melting point, sublimation temperature, and stability do not change so much. Therefore, perfluorinated aromatic compounds can be handled under similar conditions. As seen in pentacene ($C_{22}H_{14}$) and perfluoropentacene ($C_{22}F_{14}$), the size and symmetry of the hydrogen molecule and the fluorine form are comparable. Because of this advantage, comparative study is easy and contributes to a deep understanding of molecular properties. In this research, we decided to fluorinate the rylene compound as a new target.

The rylene compound is an oligomer in which the 1,8 and 4,5 positions of naphthalene ($C_{10}H_8$) are connected.[2] Perylene (dimer, $C_{20}H_{12}$), terrylene (trimer, $C_{30}H_{16}$), and quarterrylene (tetramer, $C_{40}H_{20}$) have been known for a long time. Oligomers up to octamer have been reported as derivatives with solubilizing groups. Rylene compounds are interesting in the following three points. (1) High efficiency singlet fission (SF) can be expected. (2) Perylene derivatives such as diindenoperylene (DIP, $C_{32}H_{16}$) and dibenzotetraphenylperiflanthene (DBP, $C_{64}H_{36}$) have been frequently used for organic solar cells, and reports on organic thin films have increased. (3) Polyrylene corresponds to an armchair-type graphene nanoribbon (GNR) with the minimum width.

In collaboration with the Momiyama group, we synthesized some fluorinated naphthalene monomers and are working on perfluorinated perylene.

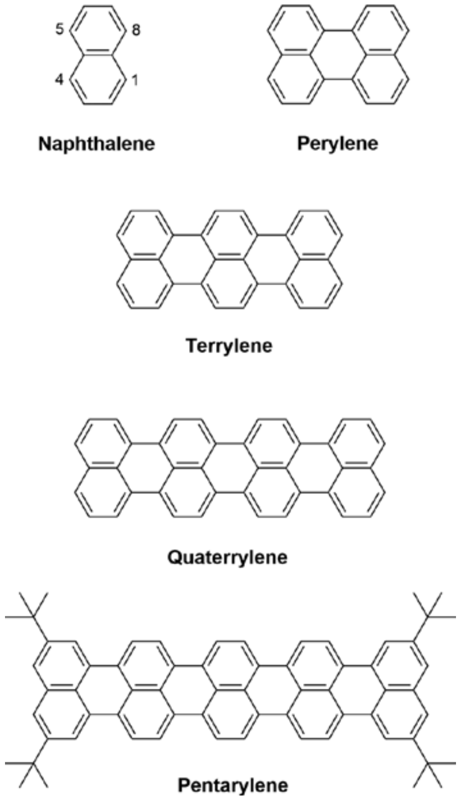

Figure 2. Chemical structures of naphthalene to pentarylene.

References

1) Y. Sakamoto and T. Suzuki, *J. Org. Chem.* **82**, 8111–8116 (2017).
2) J. T. Markiewicz and F. Wudl, *ACS Appl. Mater. Interfaces* **7**, 28063–28085 (2015).