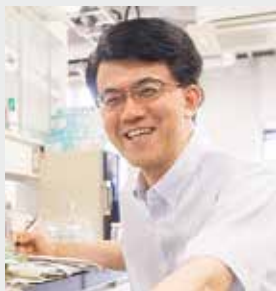


Development of Curved Graphene Molecules as Organic Semiconductors

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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. 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.

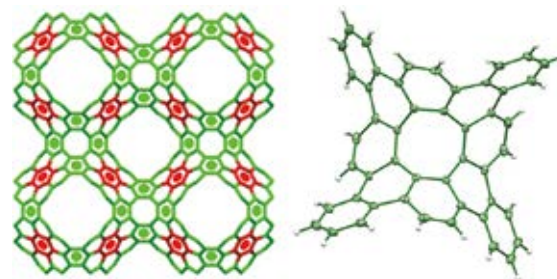


Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

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. Interface Dipole and Growth Mode of Partially and Fully Fluorinated Rubrene on Au(111) and Ag(111)¹

Thin films of fully and partially fluorinated rubrene deposited on Au(111) and Ag(111) were investigated using ultraviolet and X-ray photoelectron spectroscopy. We demonstrate that fluorination of the molecules is an efficient way for tuning the metal–organic interface dipole and the hole injection barrier. Moreover, the results indicate that the pronounced electrostatic dipole moment of partially fluorinated rubrene (F14-RUB) has a strong impact on the growth mode of these molecules. Most notably, we infer that the first layer of F14-RUB on Au(111) and Ag(111) is formed by molecules with alternating orientation of their dipole moments whereas the second layer shows a nearly uniform orientation.

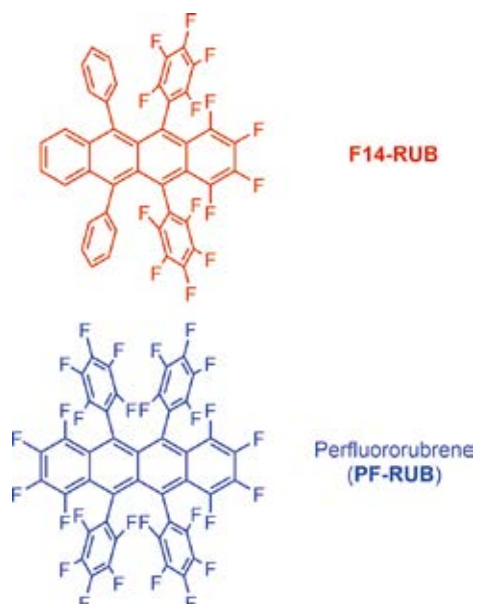


Figure 2. Chemical structures of partially and fully fluorinated rubrene.

2. Tetracyclo(2,7-carbazole)s: Aromaticity in Cycloparaphenylenes

The aromaticity of fullerenes and carbon nanotubes (CNTs) is the key to understand their thermal stability. The total of aromatic (diamagnetic) and antiaromatic (paramagnetic) ring currents can be estimated by the NMR magnetic shielding. In the case of C_{60} , some endohedral derivatives containing atoms (He and Xe) or small molecules (H_2 and H_2O) have been prepared, and their NMR spectra were obtained in solution. For example, the 1H NMR spectrum of $H_2@C_{60}$ showed a singlet at -1.44 ppm, which was shifted by -5.98 ppm compared to free hydrogen in the same solvent. [*n*]Cycloparaphenylenes (CPPs) are the shortest models for armchair (*n,n*) CNTs. The NMR shielding at the ring center would be a good indicator to see the aromaticity of CPPs. Unlike fullerenes, it is difficult to keep atoms or small molecules within CPP rings. Therefore, it is necessary to design a CPP derivative with covalently bonded groups near the ring center. For this purpose, we have synthesized three *N*-substituted tetracyclo(2,7-carbazole)s, which are the derivatives of [8]CPP. Carbazole compounds are also interesting as p-type semiconductors and thermally activated delayed fluorescent materials.

Reference

- 1) F. Anger, H. Glowatzki, A. Franco-Cañellas, C. Bürker, A. Gerlach, R. Scholz, Y. Sakamoto, T. Suzuki, N. Koch and F. Schreiber, *J. Phys. Chem. C* **119**, 6769–6776 (2015).