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.

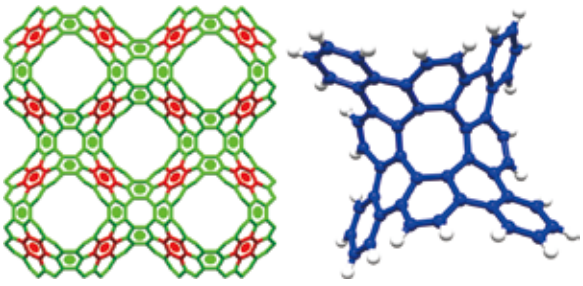

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

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

1. Brønsted Acid-Initiated Formal [1,3]-Rearrangement Dictated by β-Substituted Ene-Aldimines[1)]

The rearrangement of ene-aldimines is a useful reaction for affording homoallylic amines. Despite their utilities in synthetic chemistry, the rearrangement for accessing homoallylic amines substituted at the 2-position remains elusive. In this study, the Brønsted acid-initiated formal [1,3]-rearrangement of ene-aldimines was developed to synthesize 2,4,4-substituted homoallylic amines that were otherwise inaccessible previously. Our study reveals an intermolecular pathway in which the rearrangement proceeds via a protonation-mediated 2-azaallenium cation.

2. Widely Dispersed Intermolecular Valence Bands of Epitaxially Grown Perfluoropentacene on Pentacene Single Crystals[2)]

Strong intermolecular electronic coupling and well-ordered molecular arrangements enable efficient transport of both charge carriers and excitons in semiconducting π-conjugated molecular solids. Thus, molecular heteroepitaxy to form crystallized donor–acceptor molecular interfaces potentially leads to a novel strategy for creating efficient organic optoelectronic devices via the concomitance of these two requirements. In the present study, the crystallographic and electronic structures of a heteroepitaxial molecular interface, perfluoropentacene (PFP, $C_{22}F_{14}$) grown on pentacene single crystals (Pn-SCs, $C_{22}H_{14}$), were determined by means of grazing-incidence X-ray diffraction (GIXD) and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), respectively. GIXD revealed that PFP uniquely aligned its primary axis along the $[1\bar{1}0]$ axis of crystalline pentacene to form well-crystallized overlayers. Valence band dispersion (at least 0.49 eV wide) was successfully resolved by ARUPS. This indicated a significant transfer integral between the frontier molecular orbitals of the nearest-neighbor PFP molecules.

References

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