

Division of Synthetic Chemistry – Structural Organic Chemistry –

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Scope of Research

Fundamental studies are being conducted for the creation of new functional π -systems with novel structures and properties, and for evaluation of their application as organic semiconducting materials for photovoltaic and electroluminescent devices. The major subjects are: 1) organochemical transformation of fullerenes C_{60} and C_{70} , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; 2) generation of ionic fullerene species and their application for the synthesis of functional material; 3) synthesis of new carbon-rich materials by the use of transition metal complex; and 4) creation of new functional π -materials with unique photoelectric properties.

KEYWORDS

π -Conjugated Systems Endohedral Fullerenes
Functional Materials Helical Structures
Radical Species



Selected Publications

- Hashikawa, Y.; Murata, Y., Probing the Regioselectivity Using an Entrapped H_2 : Diels-Alder Reaction of a Cage Opened C_{60} Derivative with Anthracene, *Chem. Eur. J.*, **25**, 2482-2485 (2019).
- Suzuki, H.; Nakano, M.; Hashikawa, Y.; Murata, Y., Rotational Motion and Nuclear Spin Interconversion of H_2O Encapsulated in C_{60} Appearing in the Low-Temperature Heat Capacity, *J. Phys. Chem. Lett.*, **10**, 1306-1311 (2019).
- Fujii, S.; Cho, H.; Hashikawa, Y.; Nishino, T.; Murata, Y.; Kiguchi, M., Tuneable Single-Molecule Electronic Conductance of C_{60} by Encapsulation, *Phys. Chem. Chem. Phys.*, **21**, 12606-12610 (2019).
- Hashikawa, Y.; Murata, Y., H_2O /Olefinic- π Interaction inside a Carbon Nanocage, *J. Am. Chem. Soc.*, **141**, 12928-12938 (2019).
- Adachi, K.; Hirose, T.; Matsuda, K., Polymorphism of Porphyrin 2D Assemblies at the Liquid-Graphite Interface: Effect of Polar Solvent Additive and Flexible Spacer on the Face-On and Edge-On Type Molecular Arrangements, *Chem. Commun.*, **55**, 8836-8839 (2019).

Probing the Regioselectivity Using an Entrapped H_2 : Diels-Alder Reaction of a Cage Opened C_{60} Derivative with Anthracene

We have studied the regioselectivity in the Diels-Alder reaction of an open-cage C_{60} derivative with anthracene (Figure 1). By using an encapsulated H_2 molecule as a magnetic probe, we successfully evaluated the product population in detail, indicating the formation of ca. 10 compounds as major components. The NICS calculations showed the close resemblance to the observed 1H NMR spectrum, which realizes facile characterization of the products. We further performed theoretical studies for forming all 29 possible anthracene-adducts. The results indicated that the regioselectivity is strongly governed by steric factor, frontier orbital coefficients, and thermodynamic stabilities. The single crystal X-ray analysis of the most dominant compound exhibited the supramolecular architecture between the anthracene moiety and the π -sphere of a neighbouring molecule.

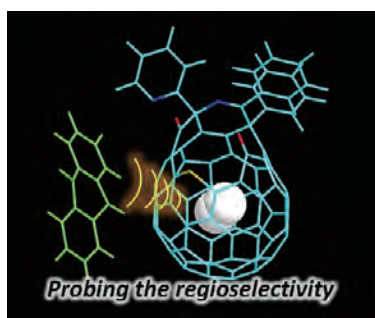


Figure 1. Regioselectivity on the Diels-Alder reaction of an open-cage C_{60} derivative with anthracene, probed by an encapsulated H_2 molecule.

$H_2O/Olefinic-\pi$ Interaction inside a Carbon Nanocage

The $H_2O/CH_2=CH_2$ -type hydrogen-bonding (H-bonding) model was experimentally constructed using a water complex of an open-cage C_{60} derivative, in which an olefinic double bond and a single molecule of H_2O are geometrically confined (Figure 2). To investigate OH/π -type H-bonding, that is, $H_2O\cdots(C=C)$ interaction, we performed 1H NMR spectroscopic studies that demonstrated the monotonic downfield shift of the proton signal corresponding to H_2O with remarkable rotational perturbation by lowering the temperature. From the temperature dependence of the angular momentum correlation time (τ_1), the interaction energy was quantitatively estimated to be ca. 0.3 kcal/mol. Based on comprehensive computational studies, the orientation of H_2O was found to play a prominent role to vary the bonding strength as well as contribution from the

electrostatic attraction and orbital-orbital interaction significantly driven by the favorable orbital overlap identified as $\pi(C=C) \rightarrow \sigma^*(OH)$ interaction.

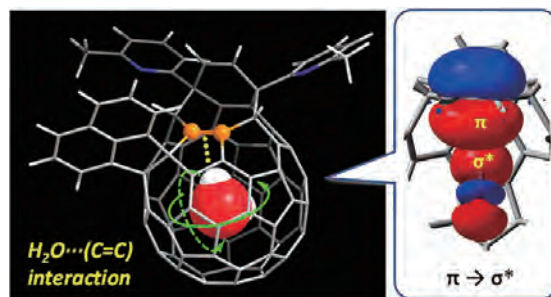


Figure 2. The experimental model of a water-olefin complex based on an open-cage C_{60} derivative encapsulating a water molecule.

Polymorphism of Porphyrin 2D Assemblies at the Liquid–Graphite Interface: Effect of Polar Solvent Additive and Flexible Spacer on the Face-On and Edge-On Type Molecular Arrangements

Precise control over the intermolecular arrangement in ordered assemblies is of primary importance for the development of functional materials in the solid state. In the case where multiple crystal structures are obtained, i.e., so-called polymorphism is observed, selecting a specific molecular arrangement is a straightforward approach to control the solid state properties. In this study, we found that the molecular orientation of porphyrin two-dimensional assemblies at solid-liquid interfaces can be controlled by using intermolecular hydrogen bonds of amide groups (Figure 3). When phenyloctane was used as the solution phase, intermolecular hydrogen bonds were effectively formed and an edge-on orientation was selectively observed. On the other hand, only face-on orientation was observed when octanoic acid was used. Interestingly, the addition of only 0.5 vol% of a polar solvent was found to significantly affect the selectivity of molecular orientation.

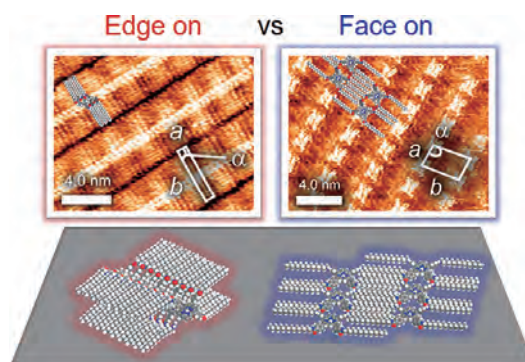


Figure 3. The two-dimensional polymorphs of porphyrin assembly at the liquid/solid interface.