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– Structural Organic Chemistry –

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Scope of Research

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

KEYWORDS

π-Conjugated Systems
Open-Cage Fullerenes
Endohedral Fullerenes
Functional Dyes
Organic Solar Cell

Selected Publications

Morinaka, Y.; Sato, S.; Wakamiya, A.; Nikawa, H.; Mizorogi, N.; Tanabe, F.; Murata, M.; Komatsu, K.; Furukawa, K.; Kato, T.; Nagase, S.; Akasaka, T.; Murata, Y., X-ray Observation of a Helium Atom and Placing a Nitrogen Atom inside He@C_{60} and He@C_{70}, *Nat. Commun.*, **4,** 1554/1-1554/5 (2013).

Morinaka, Y.; Nobori, M.; Murata, M.; Wakamiya, A.; Sagawa, T.; Yoshikawa, S.; Murata, Y., Synthesis and Photovoltaic Properties of Acceptor Materials Based on the Dimerization of Fullerene C_{60} for Efficient Polymer Solar Cells, *Chem. Commun.*, **49,** 3670-3672 (2013).

Shimogawa, H.; Mori, H.; Wakamiya, A.; Murata, Y., Impacts of Dibenzo- and Dithieno-Fused Strctures at the *b*, *g* Bonds in the BODIPY Skeleton, *Chem. Lett.*, **42,** 986-988 (2013).

Futagoishi, T.; Murata, M.; Wakamiya, A.; Sasamori, T.; Murata, Y., Expansion of Orifices of Open C_{60} Derivatives and Formation of an Open C_{59}S Derivative by Reaction with Sulfur, *Org. Lett.*, **15,** 2750-2753 (2013).

Zhang, R.; Murata, M.; Wakamiya, A.; Murata, Y., Synthesis and X-ray Structure of Endohedral Fullerene C_{60} Dimer Encapsulating a Water Molecule in Each C_{60} Cage, *Chem. Lett.*, **42,** 879-881 (2013).

Expansion of Orifices of Open C_{60} Derivatives and Formation of an Open $C_{59}S$ Derivative by Reaction with Sulfur

Developments of open-cage fullerenes have been attracting considerable attention from the viewpoints of host–guest chemistry as well as novel endohedral fullerenes when closing of the opening is successful with keeping the encapsulated species inside the fullerenes. We synthesized new sulfur –containing open-cage C_{60} derivatives with a huge opening by using a sulfur insertion as a key reaction. Furthermore, open-cage $C_{59}S$ derivative, in which one carbon atom was replaced by a sulfur atom, was also found to form by simply changing the reaction conditions. The structures of these derivatives were determined by the single crystal X-ray analyses, which showed the encapsulation of a water molecule inside the fullerene cages. These fullerene derivatives would be nice host compounds for other small molecules as well as potential precursors for novel endohedral fullerenes in near future.

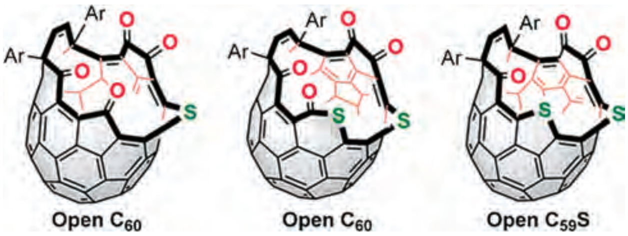

Figure 1. Novel open-cage fullerene C_{60} and $C_{59}S$ derivatives with a large opening.

Synthesis and X-ray Structure of Endohedral Fullerene C_{60} Dimer Encapsulating a Water Molecule in Each C_{60} Cage

It is well known that the chemical reactivities of endohedral metallofullerenes are very different from those of empty fullerenes due to electron transfer from the encapsulated metals to the outer fullerene cages. However, in the case of endofullerenes encapsulating electrically neutral molecule(s), very few studies have been carried out on the chemical reactivity of the outer fullerene cages. We have demonstrated that the cross dimerization of $H_2O@C_{60}$ and empty C_{60} gave three dimers of C_{60}, two of which encapsulate one or two molecules of water. Although similar reactivities toward dimerization were observed for $H_2O@C_{60}$ and empty C_{60}, the encapsulation of water molecules affected the elution order upon HPLC analysis. In addition, a small difference in the volume of the unit cell was observed in the solid state.

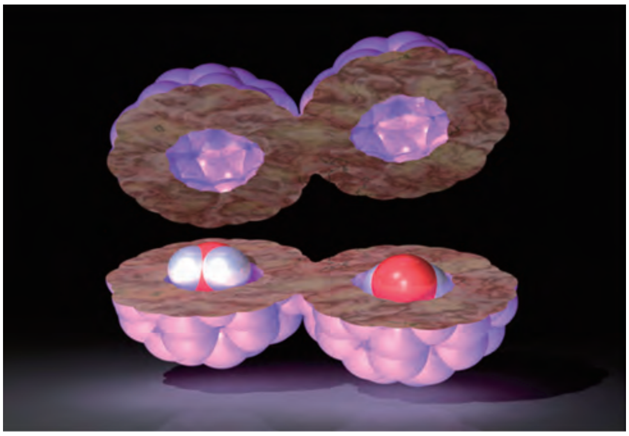

Figure 2. Space filling representation of inner space of C_{60} dimer encapsulating a water molecule in each cage.

Impacts of Dibenzo- and Dithieno-Fused Structures at the *b*, *g* Bonds in the BODIPY Skeleton

BODIPY (4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene) skeleton has unique electrochemical and optical properties, such as intense absorption profiles, high photostability, and high electron accepting ability. We recently reported that monobenzo-fusing at the *a* bond of the BODIPY skeleton effectively increases the HOMO level, whereas monobenzo-fusing at the *b* bond decreases the LUMO level. The latter is important for the molecular design toward NIR dyes or electron-transporting materials with air stability. As the fully π-expanded systems, we synthesized dibenzo[*b*,*g*]-fused and dithieno[*b*,*g*]-fused BODIPY derivatives **1** and **2**, respectively. Electrochemical and photophysical measurements demonstrated that these structural modifications effectively enhance the electron accepting ability of the BODIPY skeleton leading to the red-shifted absorption. We revealed that the impacts of the dibenzo[*b*,*g*]-fusing are more significant compared to that of the monobenzo[*b*]-fusing.

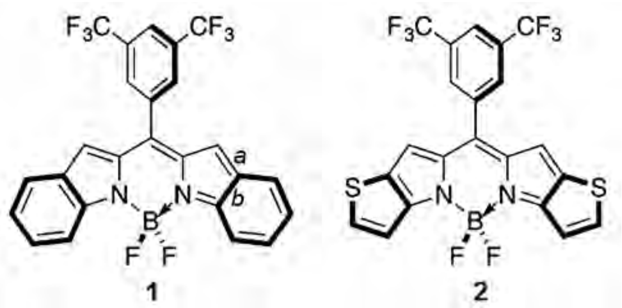

Figure 3. Ring-fused BODIPY derivatives.