

Division of Synthetic Chemistry – Structural Organic Chemistry –

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Prof
MURATA, Yasujiro
(D Eng)



Assoc Prof
HIROSE, Takashi
(D Eng)



Assist Prof
HASHIKAWA, Yoshifumi
(D Eng)



PD
ZHANG, Sheng
(Ph D)

Students

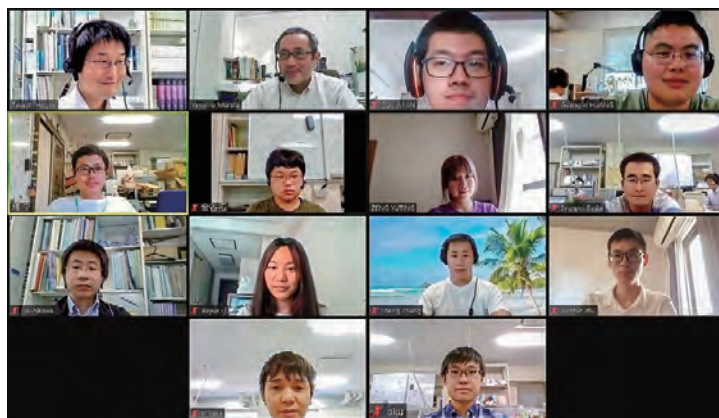
HUANG, Guanglin (D2)	ZHU, Xiaotan (M1)	SADAI, Shumpei (UG)
KANAYA, Taku (M2)	GU, Jiajian (M1)	MIYAKE, Yuya (UG)
LI, Hui (M2)	ZENG, Yuting (RS)	OKUSHIMA, Ryota (UG)
LI, Jiayue (M1)	LIU, Zhibo (RS)	

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.; Fushino, T.; Murata, Y., Double-Holed Fullerenes, *J. Am. Chem. Soc.*, **142**, 20572-20576 (2020).
Hashikawa, Y.; Murata, Y., Cation Recognition on a Fullerene-Based Macrocyclic, *Chem. Sci.*, **11**, 12428-12435 (2020).
Hashikawa, Y.; Hasegawa, S.; Murata, Y., Precise Fixation of an NO Molecule inside Carbon Nanopores: A Long-Range Electron-Nuclear Interaction, *Angew. Chem. Int. Ed.* (in press).
Hashikawa, Y.; Okamoto, S.; Murata, Y., Organophosphorus Zwitterions Engaged in a Conjugated Macrocyclic on Fullerene, *Commun. Chem.*, **3**, 90 (2020).
Kubo, H.; Shimizu, D.; Hirose, T.; Matsuda, K., Circularly Polarized Luminescence Designed from Molecular Orbitals: A Figure-Eight-Shaped [5]Helicene Dimer with D_2 Symmetry, *Org. Lett.*, **22**, 9276-9281 (2020).

Organophosphorus Zwitterions Engaged in a Conjugated Macrocycle on Fullerene

Organophosphorus zwitterions are one of the most important but elusive intermediates for carbon–carbon bond formation in synthetic chemistry and biology. However, a lack of isolated examples due to their lability has hampered in-depth understanding of structures and their reaction mechanisms. In this study, we crystallographically reveal the solid-state structure of a phosha-Michael adduct engaged in a cage-opened C_{60} skeleton, which is formed as a kinetic product. This compound exhibits dark brown colour in solution with an intense absorption band that extends to 1,000 nm, reflecting intramolecular charge transfer transitions. From the 1,2-dicarbonyl moiety on the conjugated orifice, β -oxo-phosphorus ylide is formed as a thermodynamic product. The reaction mechanism that has long been disputed is examined by experimental and theoretical studies, showing a pathway which includes an S_N2 reaction as a key step instead of the hitherto considered carbene pathway.

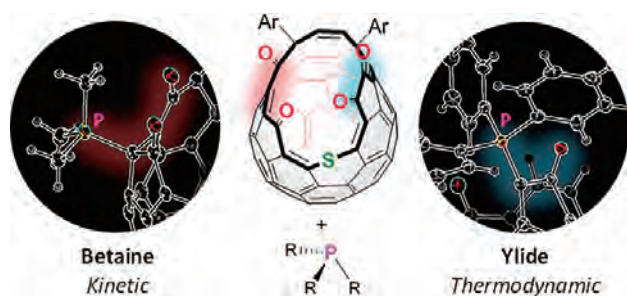


Figure 1. Organophosphorus zwitterions on a cage-opened fullerene derivative.

Double-Holed Fullerenes

Fully-fused caged nanocarbons with multiple orifices are segmental structures of porous carbon frameworks long envisioned as synthetic targets of interest. Conventional bottom-up approaches, however, could not overcome the high strain energies required for graphitic precursors to be rounded up. We demonstrated a top-down approach to produce fully fused carbon nanoelbows as double-holed fullerenes derived from strained C_{60} . The concise one-pot synthesis featuring unique selectivity enabled the isolation of six compounds, while orifice sizes were modifiable from 8- to 12-membered rings and vice versa. The crystallographic analysis confirmed their elbow-shaped structures with different curvatures. Within the crystal, cylindrical nanoporous arrangement were found with the inclusion of solvent guests, reminiscent of hypothetical fullerene sponges.

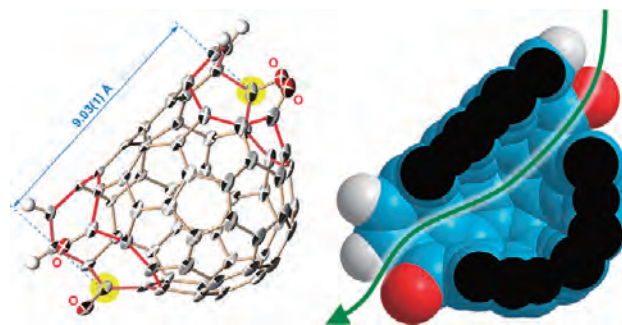


Figure 2. A double-holed fullerene.

Circularly Polarized Luminescence Designed from Molecular Orbitals: A Figure-Eight-Shaped [5]Helicene Dimer with D_2 Symmetry

The shape and symmetry of molecular orbitals determine the photophysical properties of molecules. Although many chiral molecules exhibiting circularly polarized luminescence (CPL) have been reported, few general methods are known to achieve large dissymmetry factor for CPL (g_{CPL}). To maximize the g_{CPL} values, transition electric dipole moment μ and transition magnetic dipole moment m are required to be parallel and of the same magnitude. Regarding the former criterion, from the viewpoint of the group theory, we noticed that D_2 symmetry is the only point group where the directions of μ and m vectors are always parallel for all electronic transitions. We synthesized and demonstrated that a figure-of-eight shaped [5]helicene dimer with the D_2 -symmetry has excellent chiroptical properties ($\Phi_f = 0.08$, $|g_{CPL}| = 1.5 \times 10^{-2}$), which is attributed to the parallel arrangement of μ and m as well as a good $|\mu|/|m|$ ratio.

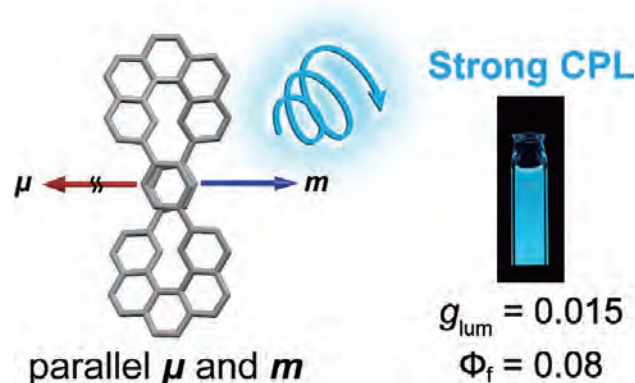


Figure 3. A CPL-active [5]helicene dimer with the D_2 symmetry.