

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

Recent Selected Publications

Zhang, Z.; Murata, Y.; Hirose, T., Circularly Polarized Luminescence of Hetero[n]helicenes with 2,1,3-Thiadiazole Rings at Both Ends: Design of Magnetically-Allowed Electronic Transitions via Heteroatom Embedding, *Tetrahedron*, **142**, 133514 (2023).

Huang, G.; Ide, Y.; Hashikawa, Y.; Hirose, T.; Murata, Y., $CH_3CN@open-C_{60}$: An Effective Inner-Space Modification and Isotope Effect inside a Nano-Sized Flask, *Chem.-Eur. J.*, **29**, e202301161 (2023).

Hashikawa, Y.; Sadai, S.; Murata, Y., Bilateral π -Extension of an Open-[60]Fullerene in a Helical Manner, *Chem. Commun.*, **59**, 6560-6563 (2023).

Sadai, S.; Hashikawa, Y.; Murata, Y., π -Extended Open-[70]Fullerenes with a Fused Azaacene, *Org. Lett.*, **25**, 2815-2819 (2023).

Hashikawa, Y.; Sadai, S.; Okamoto, S.; Murata, Y., Near-Infrared-Absorbing Chiral Open [60]Fullerenes, *Angew. Chem., Int. Ed.*, **62**, e202215380 (2023).

Near-Infrared-Absorbing Chiral Open-[60] Fullerenes

[60]Fullerene is an achiral molecular nanocarbon with I_h symmetry while it could attain an inherent chirality depending upon a functionalization pattern. The conventional chiral induction of C_{60} relies mainly upon a multiple addition, thus affording a mixture of achiral and chiral isomers. In most cases, however, their chiral function would be largely offset by pseudo-mirror plane(s). These are major obstacles to proceed further study on fullerene chirality and yet leave its understanding elusive. In this study, we developed a carbene-mediated synthesis of C_1 -symmetric chiral open-[60]fullerenes showing an intense far-red to near-infrared absorption. The large dissymmetry factor of $|g_{\text{abs}}| = 0.12$ was confirmed at $\lambda = 820$ nm for circular dichroism in benzonitrile. This is, in general, unachievable by other small chiral organic molecules, demonstrating the potential usage of open-[60]fullerenes as novel types of chiral chromophores.

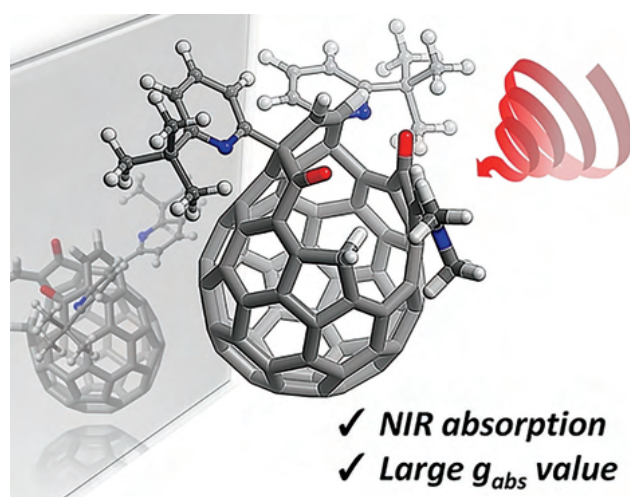


Figure 1. An inherently chiral open-[60]fullerene.

$\text{CH}_3\text{CN}@$ open- C_{60} : An Effective Inner-Space Modification and Isotope Effect inside a Nano-Sized Flask

The large orifice with a ring-atom count of 18 on a [60] fullerene cage was found to allow for a molecule of CH_3CN to be trapped inside the carbon nanocavity under high-pressure conditions. The thus formed molecular complex exhibited a higher polarity than the empty cage on silica gel, reflecting an increased molecular dipole moment. Furthermore, the encapsulation of CH_3CN caused less negative reductions with respect to empty one, being indic-

ative of a strengthened electron-accepting ability which is mainly attributed to a cage deformation as supported by computational studies. These results are demonstrative of trapped species working as a modulator for external properties of [60]fullerenes from the interior.

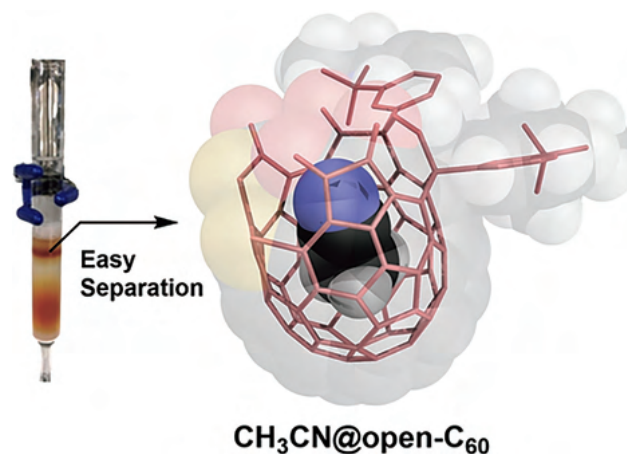


Figure 2. Acetonitrile trapped within a [60]fullerene cage.

Design of Magnetically-Allowed Electronic Transitions by Heteroatom Embedding for an Efficient Circularly Polarized Luminescence (CPL)

Design of excellent circularly polarized luminescence (CPL) emitters requires chiral molecules with large transition magnetic dipole moments (TMDM, $|m|$). In this work [5]-, [7]-, and [9]helicene derivatives with 2,1,3-thiadiazole rings at both ends were designed and synthesized. We revealed that the [9]helicene derivative (**TD[9]H**) showed an excellent CPL with a large g_{lum} of +0.04 at 520 nm in toluene, which was significantly larger than that of unsubstituted carbo[7]helicene ($g_{\text{lum}} = +0.008$). Density functional theory (DFT) calculations suggested that the remarkable g_{lum} of **TD[9]H** was attributed to the magnetically allowed transition with a large TMDM ($|m| = 2.3 \times 10^{-20}$ erg G^{-1}) for the $S_1 \rightarrow S_0$ transition.

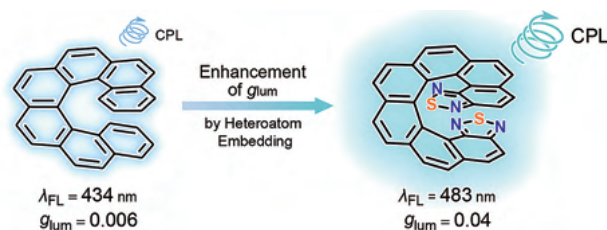


Figure 3. Enhancement of the dissymmetry factor of CPL (g_{lum}) by heteroatom embedding.