

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

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.*, **60**, 2866–2870 (2021).

Hashikawa, Y.; Kizaki, K.; Murata, Y., Pressure-Induced Annulative Orifice Closure of a Cage-Opened C_{60} Derivative, *Chem. Commun.*, **57**, 5322–5325 (2021).

Zhang, S.; Hashikawa, Y.; Murata, Y., Cage-Expansion of Fullerenes, *J. Am. Chem. Soc.*, **143**, 12450–12454 (2021).

Hashikawa, Y.; Sadai, S.; Murata, Y., Reductive Decarbonylation of a Cage-Opened C_{60} Derivative, *Org. Lett.*, **23**, 9495–9499 (2021).

Hashikawa, Y.; Murata, Y., Synthesis and Oligomerization of $CpM(CO)_2$, *ACS Omega*, **6**, 34137–34141 (2021).

Kubo, H.; Hirose, T.; Nakashima, T.; Kawai, T.; Hasegawa, J.-Y.; Matsuda, K., Tuning Transition Electric and Magnetic Dipole Moments: [7] Helicenes Showing Intense Circularly Polarized Luminescence, *J. Phys. Chem. Lett.*, **12**, 686–695 (2021).

Cage-Expansion of Fullerenes

Despite the first proposal on the cage inflation of fullerenes in 1991, the chemical expansion of fullerenes has been still a formidable challenge. Herein, we provide an efficient methodology to expand [60] and [70] fullerene cages by the inclusion of totally C5N unit, giving nitrogen-containing closed structures as C₆₅N and C₇₅N with double fused heptagons. This method consists of two steps commenced with the construction of an opening by the reaction with triazine as a C3N source, followed by the cage reformation using *N*-phenylmaleimide as a C2 source. We also synthesized endohedral cages, demonstrating that the encapsulated H₂O molecule inside the C₇₅N cage prefers the orientation which maximizes the intramolecular interaction with the carbon wall. Additionally, we revealed the existence of a through-space magnetic dipolar interaction between the encapsulated H₂ molecule and the embedded N-atom.

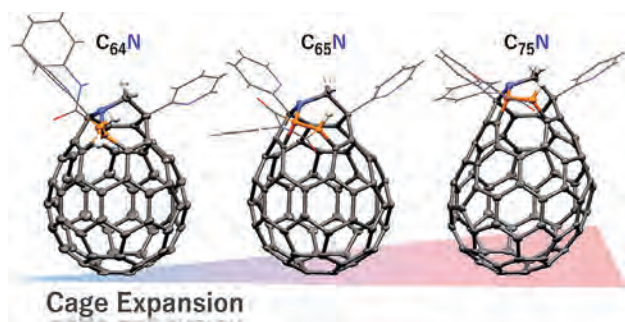


Figure 1. Cage-expanded fullerenes.

Synthesis and Oligomerization of CpM(CO)₂

We showcase efficient synthetic protocols of cyclopentadienyl metal dicarbonyl, CpM(CO)₂ (M = Rh and Ir). Reflecting the relativistic effect, the ¹H and ¹³C signals of the Cp ring in CpIr(CO)₂ were upfield shifted when compared with the Rh analogue. A missing dinuclear complex, (CpIr)₂(μ-CO)(CO)₂, was spontaneously generated together with [CpIr(CO)]₃ by the loss of CO. The crystallographic analyses unambiguously determined their unique structures with one and three Ir–Ir bonds, respectively.



Figure 2. Cyclopentadienyl group 9 metal carbonyl complexes.

Tuning Transition Electric and Magnetic Dipole Moments: [7]Helicenes Showing Intense Circularly Polarized Luminescence

Helicenes are promising candidates for chiral optoelectronic materials, however, the emission intensity of unsubstituted helicenes is very weak ($\Phi_f < 0.05$) due to a small oscillator strength for the S₁→S₀ transition. In this work, we designed the S₁→S₀ transition of [7]helicene derivatives so that it has a large transition magnetic dipole moment (TMDM) and is partially symmetry-allowed. A [7]helicene derivative thus designed showed a large fluorescence emission rate ($k_f = 0.02 \text{ ns}^{-1}$) and a large TMDM for the S₁→S₀ transition ($|m| = 2.37 \times 10^{-20} \text{ erg} \cdot \text{Gauss}^{-1}$), which are more than 10 times greater than those of unsubstituted [7]helicene ($k_f = 0.001 \text{ ns}^{-1}$, $|m| = 0.045 \times 10^{-20} \text{ erg} \cdot \text{Gauss}^{-1}$). As a result, we achieved the [7]helicene derivative whose dissymmetry factor of CPL and fluorescence quantum yield were both high ($|g_{\text{CPL}}| = 1.3 \times 10^{-2}$, $\Phi_f = 0.17$) in the solution phase.

Design of *Magnetically-Allowed* S₁→S₀ Transitions

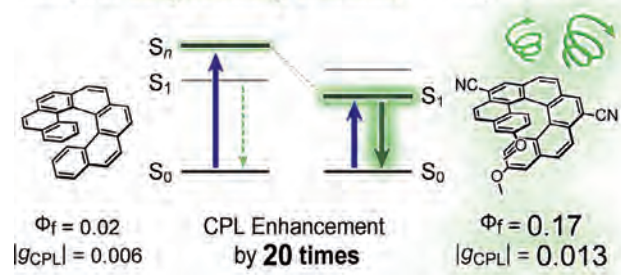


Figure 3. A design of emissive [7]helicene with large dissymmetry factor of CPL.