# Division of Synthetic Chemistry
## – Structural Organic Chemistry –

https://www.scl.kyoto-u.ac.jp/~kouzou/en/index.html


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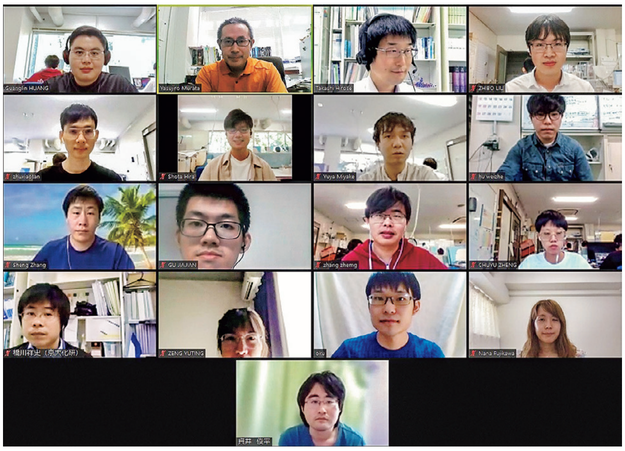
## Scope of Research

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
Functional Materials
Radical Species
Endohedral Fullerenes
Helical Structures



### 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 $C_{65}N$ and $C_{75}N$ 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 $H_2O$ molecule inside the $C_{75}N$ 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 $H_2$ molecule and the embedded N-atom.

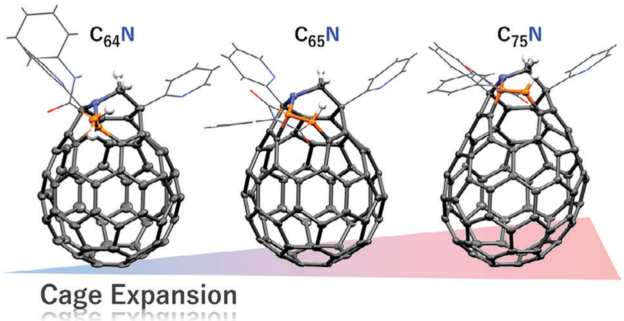


**Figure 1.** Cage-expanded fullerenes.

## 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 $^{13}C$ signals of the Cp ring in $CpIr(CO)_2$ were upfield shifted when compared with the Rh analogue. A missing dinuclear complex, $(CpIr)_2(\mu\text{-}CO)(CO)_2$, was spontaneously generated together with $[CpIr(CO)]_3$ by the loss of CO. The crystallograpgic analyses unambiguously determined their unique structures with one and three Ir–Ir bonds, respectively.

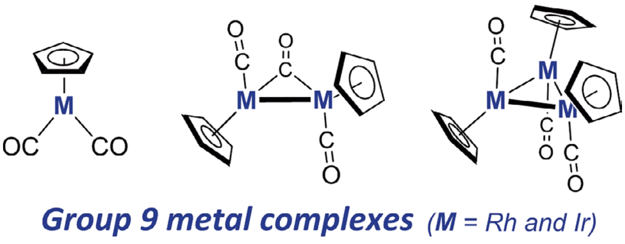


**Figure 2.** Cyclopentadienyl group 9 metal carbonyl complexes.

## 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 $S_1 \rightarrow S_0$ transition. In this work, we designed the $S_1 \rightarrow S_0$ 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 ($k_f = 0.02\ ns^{-1}$) and a large TMDM for the $S_1 \rightarrow S_0$ transition ($|\boldsymbol{m}| = 2.37 \times 10^{-20}$ erg·Gauss$^{-1}$), which are more than 10 times greater than those of unsubstituted [7]helicene ($k_f = 0.001\ ns^{-1}$, $|\boldsymbol{m}| = 0.045 \times 10^{-20}$ erg·Gauss$^{-1}$). As a result, we achieved the [7]helicene derivative whose dissymmetry factor of CPL and fluorescence quantum yield were both high ($|g_{CPL}| = 1.3 \times 10^{-2}$, $\Phi_f = 0.17$) in the solution phase.

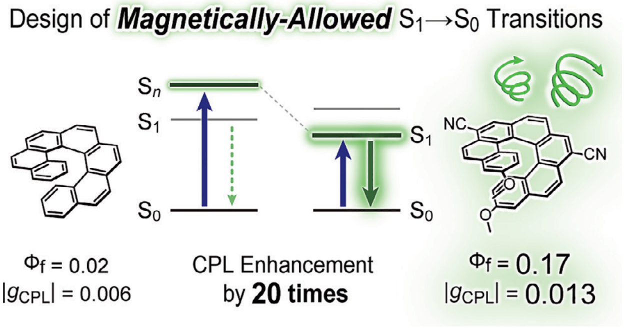


**Figure 3.** A design of emissive [7]helicene with large dissymmetry factor of CPL.