

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.; Fujikawa, N.; Murata, Y., π -Extended Fullerenes with a Reactant Inside, *J. Am. Chem. Soc.*, **144**(51), 23292-23296 (2022).
Huang, G.; Hasegawa, S.; Hashikawa, Y.; Ide, Y.; Hirose, T.; Murata, Y., An H_2O_2 Molecule Stabilized inside Open-Cage C_{60} Derivatives by a Hydroxy Stopper, *Chem. Eur. J.*, **28**, e202103836 (2022).
Hashikawa, Y.; Kawasaki, H.; Murata, Y., π -Backbonding in Group 9 Metal Complexes Bearing an η^2 -($H_2O@C_{60}$) Ligand, *Organometallics*, **41**, 354-359 (2022).
Hashikawa, Y.; Okamoto, S.; Sadai, S.; Murata, Y., Chiral Open-[60]Fullerene Ligands with Giant Dissymmetry Factors, *J. Am. Chem. Soc.*, **144**, 18829-18833 (2022).
Nakakuki, Y.; Hirose, T.; Matsuda, K., Logical Design of Small HOMO–LUMO Gap: Tetrabenzo[*fjk,mn,r*][7]helicene as a Small-Molecule Near-Infrared Emitter, *Org. Lett.*, **24**, 648-652 (2022).
Nakakuki, Y.; Hirose, T.; Sotome, H.; Gao, M.; Shimizu, D.; Li, R.; Hasegawa, J.-y.; Miyasaka, H.; Matsuda, K., Doubly Linked Chiral Phenanthrene Oligomers for Homogeneously π -Extended Helicenes with Large Effective Conjugation Length, *Nat. Commun.*, **13**, 1475 (2022).

π -Backbonding in Group 9 Metal Complexes Bearing an η^2 -(H₂O@C₆₀) Ligand

As a measure of d- π^* back-donation, IR stretching modes are, in general, used for metal carbonyl compounds. Once the ligand is replaced with olefins (metal-arene complexes), it can be analyzed crystallographically unless otherwise the C-C bond length falls into values within standard deviation. Herein, we propose a novel measure using an η^2 -(H₂O@C₆₀) ligand in group 9 metal-fullerene complexes, in which the stronger d- π^* backbonding causes enhanced sp³-character on the coordinated olefinic bond and consequently leads to the restricted rotation for the H₂O molecule as detectable by the ¹H NMR relaxation time. The π -backbonding strengths were, therefore, found to follow the ascending order of atomic numbers (Co < Rh < Ir) in CpM(CO)(η^2 -H₂O@C₆₀) (Cp = cyclopentadienyl), associated with the anodic shift on oxidation potentials and hypsochromic shift on absorption edges.



Figure 1. Group 9 metal complexes with a [60]fullerene ligand.

Chiral Open-[60]Fullerene Ligands with Giant Dissymmetry Factors

The optical resolution of open-[60]fullerenes has been limited to only one example since 1998, while the recent advances revealed the excellence of fullerenes as revisited chiral functional materials. Different from conventional chiral induction on [60]fullerene by a multiple-functionalization, a random disruption of the spherical π -conjugation is avoidable for open-[60]fullerenes. Moreover, the macrocyclic orifices enable a metal coordination which endows modulated electronic structures on chiral chromophores. Herein, we showcase Li⁺-coordination behavior and optical resolution of three chiral open-[60] fullerene ligands, showing a giant dissymmetry factor up

to 0.20 owing to a congenital topology of the spherical π -conjugation.

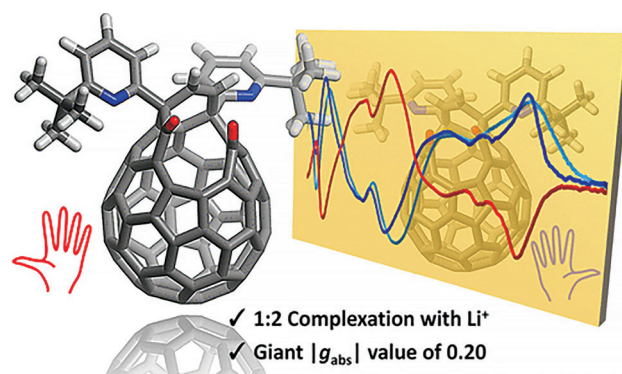


Figure 2. Chiral open-[60]fullerene ligands.

Homogeneously π -Extended Helicenes with Large Effective Conjugation Length as Helical Molecular Wires

π -Conjugated molecules with large effective conjugation length (ECL) are potentially applicable to conductive materials in the nanometer scale, which are called molecular wires. Linear molecular wires have been developed, however, chiral molecular wires with helical structures have been largely undeveloped at the moment. Herein, we report the synthesis of *per-peri*-perbenzo[*n*]helicenes (*n* = 5, 7, and 9), whose HOMO-LUMO gap of the π -extended helicenes decreased significantly from 2.14 to 1.15 eV with increasing helical length. The large ECL of π -extended helicenes is attributed to the large orbital interactions between the phenanthrene subunits at the 9- and 10-positions, which form a polyene-like electronic structure.

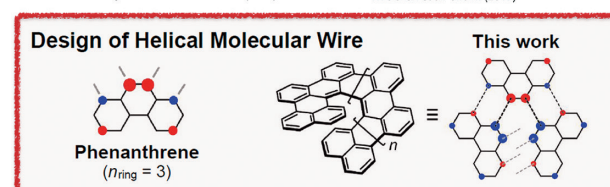
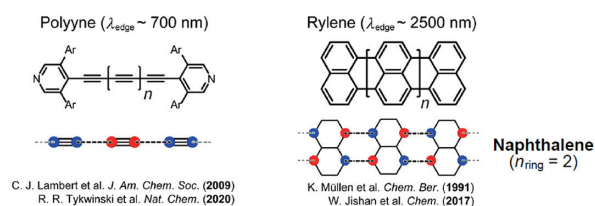


Figure 3. Design of helical molecular wires based on doubly-linked chiral phenanthrene oligomers.