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 semi-conducting 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
Organic Solar Cells
Endohedral Fullerenes
Perovskite-Based Solar Cells

Selected Publications

Zhang, R.; Murata, M.; Aharen, T.; Wakamiya, A.; Shimoaka, T.; Hasegawa, T.; Murata, Y., Synthesis of a Distinct Water Dimer inside Fullerene C_{70}, *Nat. Chem.*, **8,** 435-441 (2016).

Nishimura, H.; Fukushima, T.; Wakamiya, A.; Murata, Y.; Kaji, H., The Influence of Quasiplanar Structures of Partially Oxygen-Bridged Triphenylamine Dimers on the Properties of their Bulk Films, *Bull. Chem. Soc. Jpn.*, **89,** 726-732 (2016).

Hashikawa, Y.; Murata, M.; Wakamiya, A.; Murata, Y., Synthesis and Properties of Endohedral Aza[60]fullerenes: $H_2O@C_{59}N$ and $H_2@C_{59}N$ as Their Dimers and Monomers, *J. Am. Chem. Soc.*, **138,** 4096-4104 (2016).

Satou, M.; Nakamura, T.; Aramaki, Y.; Okazaki, S.; Murata, M.; Wakamiya, A.; Murata, Y., Near-Infrared Emissive Donor–Acceptor-Type Molecules Containing Thiazole-Fused Benzothiadiazole as an Electron-Acceptor Moiety, *Chem. Lett.*, **45,** 892-894 (2016).

Murata, M.; Kaji, S.; Nishimura, H.; Wakamiya, A.; Murata, Y., Efficient Synthesis of One- and Two-Dimensional Multimetallic Gold-Bis(dithiolene) Complexes, *Eur. J. Inorg. Chem.*, **2016,** 3228-3232 (2016).

Hashikawa, Y.; Murata, M.; Wakamiya, A.; Murata, Y., Water Entrapped inside Fullerene Cages: A Potential Probe for Evaluation of Bond Polarization, *Angew. Chem. Int. Ed.*, **55,** 13109-13113 (2016).

Synthesis of a Distinct Water Dimer inside Fullerene C_{70}

The water dimer is an ideal chemical species with which to study hydrogen bonds. Owing to the equilibrium between the monomer and oligomer structure, however, selective generation and separation of a genuine water dimer has not yet been achieved. We have developed a synthetic method that leads to the successful encapsulation of one or two water molecules inside fullerene C_{70}. These endohedral C_{70} compounds offer the opportunity to study the intrinsic properties of a single water molecule without any hydrogen bonding, as well as an isolated water dimer with a single hydrogen bond between the two molecules. The structure of $H_2O@C_{70}$ was unambiguously determined by XRD analysis, showing that the H_2O molecule was located at the off-center position of C_{70}. Furthermore, in the case of $(H_2O)_2@C_{70}$, a hydrogen bond was observed between the two H_2O molecules, and their rapid interchange was supported by NMR measurements and theoretical calculations. Infrared spectroscopy suggested the possible qualitative recognition of each water-encapsulating C_{70} species based on their unique and characteristic spectra.

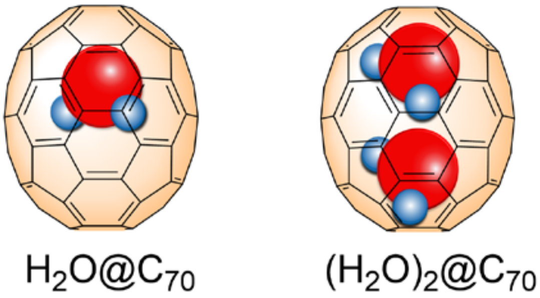

Figure 1. The structures of $H_2O@C_{70}$ and $(H_2O)_2@C_{70}$.

Near-infrared Emissive Donor-Acceptor-type Molecules Containing Thiazole-fused Benzothiadiazole as an Electron-acceptor Moiety

Fluorophores with strong emission in the near-infrared (NIR) region have received attention as NIR organic light-emitting diodes (OLEDs), which find applications in night vision-readable displays and sensors, as well as in fluorescent probes for bioimaging. In addition to conventional dyes, donor (D)‒acceptor (A)-type molecules have attracted considerable interest, as their optical properties can be easily tuned by varying the D and A units. In this work, two D–A-type molecules containing thiazole-fused benzothiadiazole (BT) as the acceptor moiety were designed and synthesized. The thiazole-fused BT skeleton enables fine-tuning of the solubility and the electronic structure as well as two-dimensional extension of the π-conjugation. The combination with common donor units such as diphenylaminothiophene or triphenylamine-substituted thiophene resulted in the formation of D–A–D-type molecules, which exhibited fluorescence in the NIR region.

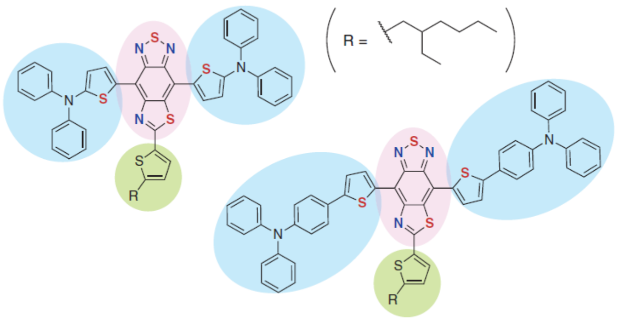

Figure 2. The structures of model compounds for the D–A–D type molecules based on a thiazole-fused BT skeleton.

Efficient Synthesis of One- and Two-Dimensional Multimetallic Gold–Bis (dithiolene) Complexes

Multimetallic complexes having π-conjugated dithiolate ligands have recently received attention because of their unique solid-state properties, which include high conductivity and magnetism, as well as their potential use in organic thermoelectric materials. We demonstrated efficient and versatile methods for the synthesis of 1D and 2D multimetallic gold–bis(dithiolene) complexes with well-defined structures by using a dichlorogold(III) complex having a benzene-1,2-dithiolate ligand as a terminal unit. By using benzene-1,2,4,5-tetrathiolate as a bridging unit, a 1D rod-shaped dimetallic complex was synthesized in good yield. Furthermore, on the basis of this synthetic strategy, we prepared a 2D trimetallic complex with a starburst structure by using a benzenehexathiolate bridging unit. The new synthetic methods can offer a way to prepare a wide variety of unprecedented 1D and 2D multimetallic gold–bis(dithiolene) complexes.

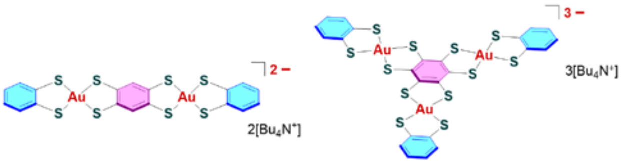

Figure 3. The structures of 1D dimetallic and 2D trimetallic gold–bis(dithiolene) complexes.