Design and Synthesis of Three-Dimensional Organic Structures

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Education

2005	B.S. The University of Tokyo
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Professional Employment

2009	Assistant Professor, Nagoya University
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2013	Group Leader and Project Coordinator, JST ERATO Itami Molecular Nanocarbon Project (until 2020)
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

2013	RSC PCCP Prize
2014	Akasaki Award
2017	Chemical Society of Japan Award for Young Chemists
2018	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
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Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights (Figure 1).

To achieve our purpose, this group will start electron-diffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultra-small crystals (1 µm or less). There are many fields such as covalent organic crystals with a three-dimensional structure and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

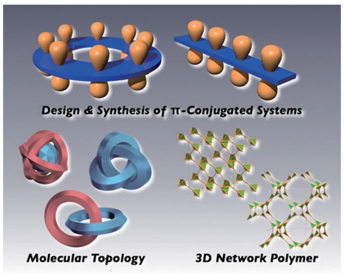

Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- R. Yoshida, H. Sugiyama and Y. Segawa, "Synthesis, Structure, and Properties of a Bay-Fluorinated Triphenylene," *Chem. Lett.* **53**, upae048 (2024).
- S. Hirota, S. Nakano, H. Sugiyama and Y. Segawa "Synthesis of Polycyclic Arenes Composed of Four-, Five-, Six-, and Eight-Membered Rings *via* an Unexpected Four-Membered Ring Formation Reaction," *Org. Lett.* **25**, 8062–8066 (2023).
- M. Nagase, S. Nakano and Y. Segawa, "Synthesis of Penta- and Hexa(3,4-thienylene): Size-Dependent Structural Properties of Cyclic Oligothiophenes," *Chem. Commun.* **59**, 11129–11132 (2023).
- Y. Segawa, "The Transannular Scholl Reaction for the Introduction of Heptagons into Aromatic Hydrocarbons," *Chem* **9**, 2725–2727 (2023).
- Y. Segawa, "Nonplanar Aromatic Hydrocarbons: Design and Synthesis of Highly Strained Structures," *Bull. Chem. Soc. Jpn.* **95**, 1600–1610 (2022).
- Y. Segawa, T. Watanabe, K. Yamanoue, M. Kuwayama, K. Watanabe, J. Pirillo, Y. Hijikata and K. Itami, "Synthesis of a Möbius Carbon Nanobelt," *Nat. Synth.* **1**, 535–541 (2022).
- K. Y. Cheung, K. Watanabe, Y. Segawa and K. Itami, "Synthesis of a Zigzag Carbon Nanobelt," *Nat. Chem.* **13**, 255–259 (2021).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).

1. Synthesis of Hexafluorotetraphenylene Bearing Alkoxy Chains

Triphenylene is one of the polycyclic aromatic hydrocarbons that has been extensively studied for a long time. Triphenylene is a planar π-conjugated molecule with D_{3h} symmetry, consisting of four six-membered rings. As the functionalization of triphenylenes at the peripheral positions is relatively easy, triphenylene derivatives with a variety of structural and electronic properties have been synthesized and applied in materials science.

We synthesized a bay-fluorinated triphenylene and investigated its structural and electronic properties.[1] The synthesis of 2,3,6,7,10,11-hexaethoxy-1,4,5,8,9,12-hexafluorotriphenylene (**1**) was accomplished via a two-step one-pot reaction sequence starting from hexaethoxytriphenylene (**2**) (Figure 2). The bay-selective deprotonation of **2** was carried out using *n*-butyllithium, which was followed by an electrophilic fluorination with NFSI to generate hexafluorinated triphenylene **1**. A single-crystal X-ray diffraction analysis revealed that **1** adopts a distorted C_2 symmetric structure in the single crystal, wherein molecules of **1** arrange into one-dimensional columnar stacks. DFT calculations showed that the C_2 symmetric conformation of **1** is by 5.8 kcal·mol^{-1} more stable than the D_3 symmetric one. Due to the introduction of the fluoro groups, the absorption and fluorescence spectra of **1** showed bathochromic shifts and broadening of the spectra compared to those of **2**. DFT calculations revealed that the energy levels of the HOMOs and LUMOs change due to the introduction of the fluoro groups.

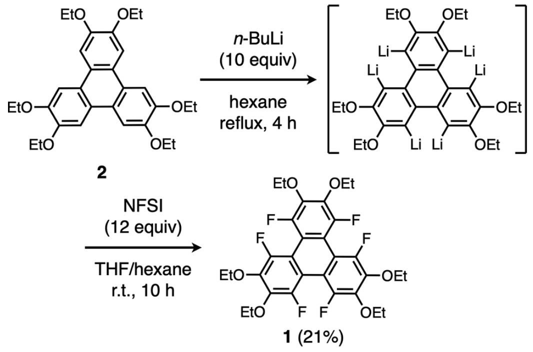

Figure 2. Synthesis of hexafluorotriphenylene **1** (NFSI: *N*-fluoro benzenesulfonimide).

2. Synthesis of Polycyclic Arenes Composed of 4-5-6-8-Membered Rings *via* an Unexpected 4-Membered-Ring Formation Reaction

Aromatic compounds having four-membered rings attract considerable interest owing to their unique structural and physical properties. Biphenylene, a simple four-membered-ring-containing arene, comprises aromatic benzene moieties fused to an antiaromatic cyclobutadiene moiety. In biphenylenes, the fused benzene rings decrease the antiaromaticity of the central four-membered ring relative to that of cyclobutadiene.

We have synthesized and characterized tricarbonylated **1**, which contains four-, five-, six-, and eight-membered rings and tetracarbonylated compound **2** *via* the carbonylation reaction of a tetraphenylene derivative.[2] When dimethyl carbonate was used as the carbonyl source, the carbonylation of tetraphenylene yielded tricarbonylated product **1** *via* an unexpected four-membered ring formation reaction. In contrast, using dimethylcarbamoyl chloride afforded tetracarbonylated compound **2** selectively (Figure 3). The structures of the as-obtained compounds **1** and **2** were determined by X-ray crystallography, revealing one-dimensional stacking structures in the solid state in both cases. UV–vis absorption spectroscopy, CV, and DFT calculations suggested that the HOMO–LUMO gap of **1** is narrower than that of **2** (Figure 4). NICS and ACID calculations indicated that the four-membered ring of **1** and the eight-membered rings of **1** and **2** exhibit antiaromatic characteristics. The reaction reported here provides a new method for introducing a four-membered ring into polyaromatic structures at the late stage of the synthetic process.

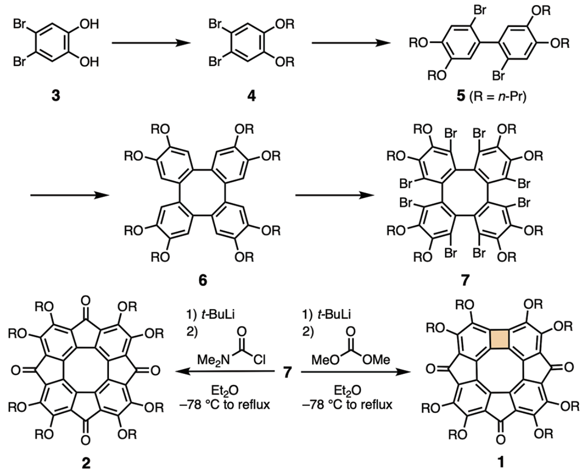

Figure 3. Synthesis of **1** and **2**.

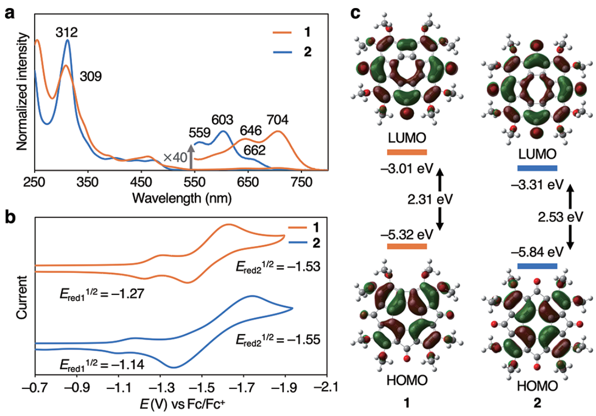

Figure 4. (a) UV–vis absorption spectra of **1** and **2**. (b) Cyclic voltammograms of **1** and **2**. (c) Frontier molecular orbitals of **1** and **2** calculated at the B3LYP/6-31G(d) level.

References

1) R. Yoshida, H. Sugiyama and Y. Segawa, *Chem. Lett.* **53**, upae048 (2024).

2) S. Hirota, S. Nakano, H. Sugiyama and Y. Segawa, *Org. Lett.* **25**, 8062–8066 (2023).