

Design and Synthesis of Three-Dimensional Organic Structures

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry



SEGAWA, Yasutomo
Associate Professor
[segawa@ims.ac.jp]

Education

2005 B.S. The University of Tokyo
2007 M.S. The University of Tokyo
2009 Ph.D. The University of Tokyo

Professional Employment

2009 Assistant Professor, Nagoya University
2013 Designated Associate Professor, Nagoya University
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
2019 Nozoe Memorial Award for Young Organic Chemists
2021 Chemist Award BCA

Member

Assistant Professor
SUGIYAMA, Haruki*
JSPS Post-Doctoral Fellow
TSUKAMOTO, Kenji
Graduate Student
NAGASE, Mai
HIROTA, Soshi
WATANABE, Kosuke
YOSHIDA, Ryu
Technical Fellow
NAKANO, Sachiko
HIRATA, Nao
Secretary
TANIWAKE, Mayuko

Keywords

π -Conjugated Molecules, Molecular Topology, 3D Network Polymer

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.

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.

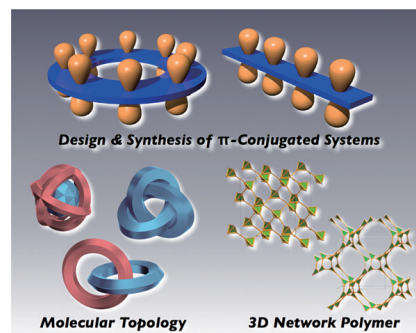


Figure 1. Design and synthesis of π -conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- 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, "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. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, "Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes," *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).
- 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 Cyclic β -Thiophenes

Macrocyclic polyaromatic molecules are interesting materials that exhibit a wide variety of electronic and optical properties derived from their structures, but they are often synthetically challenging because of the ring strain associated with their macrocyclic structures. In this study, we have succeeded in synthesizing 3,4-pentathienylene (**5T**) and 3,4-hexathienylene (**6T**), in which all five and six thiophenes are linked at the 3,4-positions (β -positions), using Ni-catalyzed borylation, Pd-catalyzed cross-coupling and Ni-mediated homocoupling reactions (Figure 2).¹⁾

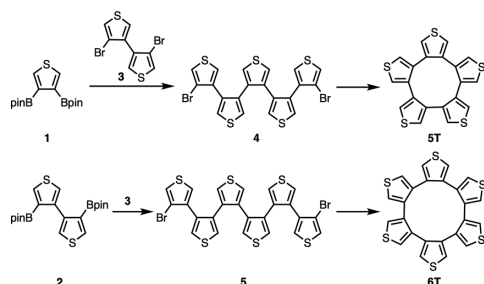


Figure 2. Synthesis of penta(3,4-thienylene) (**5T**) and hexa(3,4-thienylene) (**6T**).

X-ray crystallographic analysis confirmed the C_2 and D_2 symmetries of **5T** and **6T**, respectively (Figure 3). Interestingly, the ^1H NMR spectra of the two molecules were very different: **5T** had a single singlet, whereas three different signals were observed for **6T**, and these remained unchanged at both low and high temperatures (Figure 3).

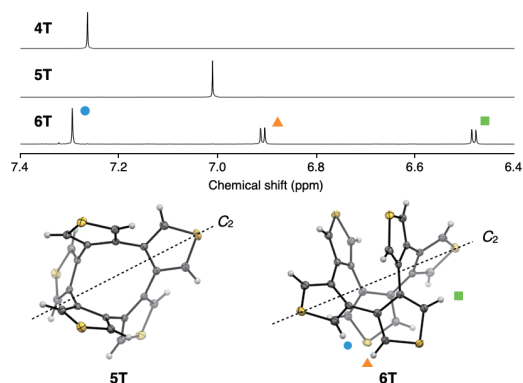


Figure 3. ^1H NMR spectra of **4T**–**6T** in CD_2Cl_2 , and X-ray structures of **5T** and **6T** with thermal ellipsoids at 50% probability.

The isomerization barriers of **5T** and **6T** calculated by DFT method were 5.0 kcal/mol and 26.5 kcal/mol, respectively, and the difference in isomerization rate was the reason for the difference in NMR spectra (Figure 4). The synthesized **5T** and **6T** are useful as a platform for the synthesis of novel polycyclic π -conjugated compounds utilizing the macrocyclic nonplanar structures and the active α -positions.

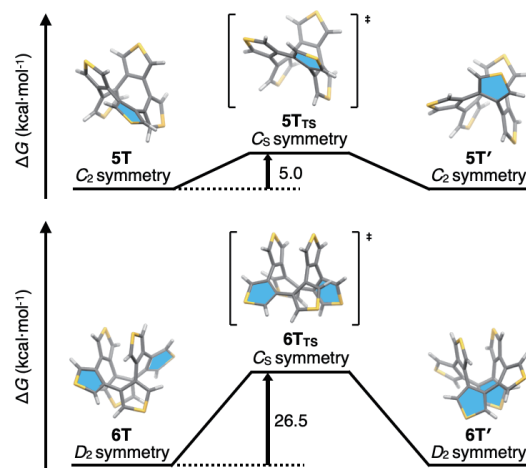


Figure 4. Energy diagrams for the enantiomerization of **5T** and **6T**.

2. An Electron-Deficient Cp^{E} Iridium(III) Catalyst for Ether-Directed C–H Amidation

The synthesis, characterization, and catalytic performance of an iridium(III) catalyst with an electron-deficient cyclopentadienyl ligand ($[\text{Cp}^{\text{E}}\text{IrI}_2]_2$) are reported.²⁾ The $[\text{Cp}^{\text{E}}\text{IrI}_2]_2$ catalyst was synthesized by the complexation of a precursor of the Cp^{E} ligand with $[\text{Ir}(\text{cod})\text{OAc}]_2$ followed by oxidation, desilylation, and removal of the COD ligand. The electron-deficient $[\text{Cp}^{\text{E}}\text{IrI}_2]_2$ enabled C–H amidation reactions assisted by a weakly coordinating ether directing group. Experimental mechanistic studies and DFT calculations suggested that the high catalytic performance of $[\text{Cp}^{\text{E}}\text{IrI}_2]_2$ is due to its electron-deficient nature, which accelerates both C–H activation and Ir(V)-nitrenoid formation.

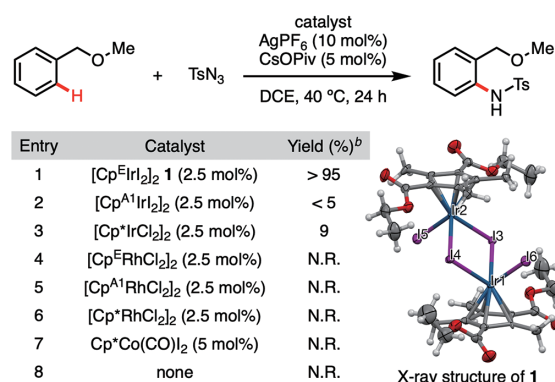


Figure 5. Optimized reaction conditions and control experiments for the Ir-catalyzed ether-directed C–H amidation reaction.

References

- M. Nagase, S. Nakano and Y. Segawa, *Chem. Commun.* **59**, 11129–11132 (2023).
- E. Tomita, M. Kojima, Y. Nagashima, K. Tanaka, H. Sugiyama, Y. Segawa, A. Furukawa, K. Maenaka, S. Maeda, T. Yoshino and S. Matsunaga, *Angew. Chem., Int. Ed.* **62**, e202301259 (2023).

* Present Address; CROSS