Design and Synthesis of Three-Dimensional Organic Structures

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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 has 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.

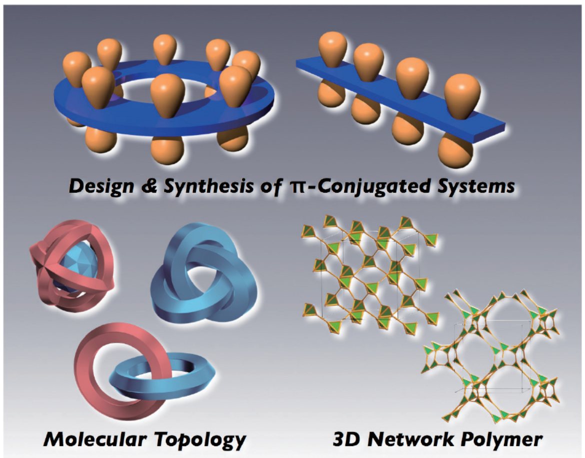

Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- M. Nagase, R. Yoshida, S. Nakano, T. Hirose and Y. Segawa, *Chem. Commum.* **61**, 11187–11190 (2025).
- K. Watanabe, H. Sugiyama and Y. Segawa, *CrystEngComm* **27**, 3552–3559 (2025).
- K. Watanabe, T. Toya, Y. Toyota, Y. Kobayashi, J. Usuba, Y. Hijikata, R. Matsuda, K. Nishimura, H. Sugiyama and Y. Segawa, *Chem. Commun.* **61**, 2822–2825 (2025).
- H. Sugiyama, K. Watanabe, C. Song, K. Murata and Y. Segawa, *Chem. Lett.* **53**, upae192 (2024).
- R. Yoshida, H. Sugiyama and Y. Segawa, *Chem. Lett.* **53**, upae048 (2024).
- S. Hirota, S. Nakano, H. Sugiyama and Y. Segawa, *Org. Lett.* **25**, 8062–8066 (2023).
- M. Nagase, S. Nakano and Y. Segawa, *Chem. Commun.* **59**, 11129–11132 (2023).
- Y. Segawa, *Chem* **9**, 2725–2727 (2023).
- Y. Segawa, *Bull. Chem. Soc. Jpn.* **95**, 1600–1610 (2022).

1. Twisted π-Conjugated Molecules Featuring 3D π–π Interactions in Solid States

Electronic devices based on organic materials are lightweight, flexible, and can display a wide variety of properties by subtle changes in molecular structure, making them promising environmentally friendly next-generation devices. Most organic electronic materials developed to date are made of planar molecules, so charge transport is confined to limited directions; as a result, devices require strict control of molecular orientation. The team wondered whether "twisting" molecules could yield a new material architecture in which charge carriers move easily in three dimensions.

We attached methyl groups to molecules containing multiple thiophene units, thereby synthesizing twisted molecules. X-ray crystallography confirmed the twisted geometry and revealed that, in the solid state, the molecules stack in a three-dimensional fashion. Computational analysis of charge-transport pathways predicted an aggregated structure in which holes can migrate in several directions. When the molecule was fabricated into an organic field-effect transistor, it exhibited a hole mobility of 1.85×10^{-4} cm^2 V^{-1} s^{-1}, experimentally confirming its behavior as an organic semiconductor.

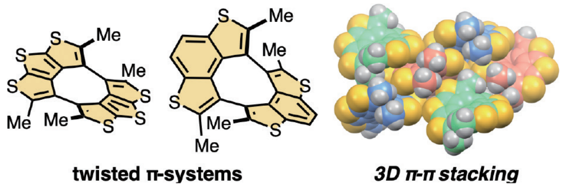

Figure 2. Structures of twisted π-conjugated molecules, and their 3D π–π stacking mode.

2. Diverse Clathrate Crystals Assembled from Weak Intermolecular Interactions

Tetracyanodihydrodipyrazinopyrazines with two mesityl (2,4,6-trimethylphenyl) groups formed clathrate crystals with 15 kinds of organic solvents. Two common types of host molecular networks were observed in the crystals. Theoretical calculations indicated that these host networks are constructed from π–π and CN–π interactions. As these intermolecular interactions are relatively weak, the host network can change flexibly in response to guest molecules. Guest-free crystals can be reversibly transformed into clathrate crystals through crystal-to-crystal phase transitions via the adsorption/desorption of solvent vapor.

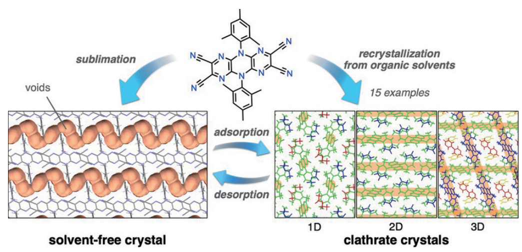

Figure 3. Solvent-free and clathrate crystals of tetracyanodihydrodipyrazinopyrazines.

3. Fully Fused 3D π-Conjugated Polymers Controlled by Steric Repulsion

The synthesis and characterization of fused aromatic networks composed of zinc tetrapyrazinoporphyrazines are reported. The steric repulsion of bulky substituents induced the formation of three-dimensional structures. Thus-obtained insoluble polymers adsorbed CO_2 and had near-infrared absorption indicating their porosity and extended π-conjugation.

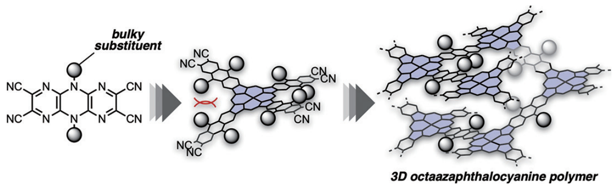

Figure 4. Synthesis of fully fused 3D π-conjugated polymers.

4. Structure Determination of π-Extended Tetraphenylenes by MicroED

The structure determination of large π-conjugated molecules using microcrystal electron diffraction (MicroED) was demonstrated. The poorly soluble solids of the tweezer-shaped molecules were subjected directly from the reaction vessel to MicroED to determine their structures and packing modes. This work validated the efficiency of MicroED in determining the structures of such compounds.

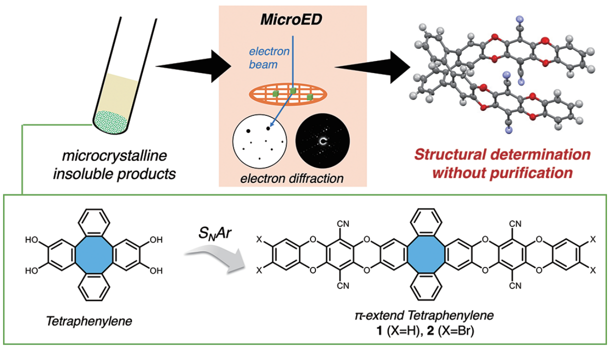

Figure 5. The synthesis and structure determination of π-extended tetraphenylene **1** and **2**.

References

1) M. Nagase, R. Yoshida, S. Nakano, T. Hirose and Y. Segawa, *Chem. Commun.* **61**, 11187–11190 (2025).
2) K. Watanabe, H. Sugiyama and Y. Segawa, *CrystEngComm* **27**, 3552–3559 (2025).
3) K. Watanabe, T. Toya, Y. Toyota, Y. Kobayashi, J. Usuba, Y. Hijikata, R. Matsuda, K. Nishimura, H. Sugiyama and Y. Segawa, *Chem. Commun.* **61**, 2822–2825 (2025).
4) H. Sugiyama, K. Watanabe, C. Song, K. Murata and Y. Segawa, *Chem. Lett.* **53**, upae192 (2024).