

# Design and Synthesis of Three-Dimensional Organic Structures

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



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### 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

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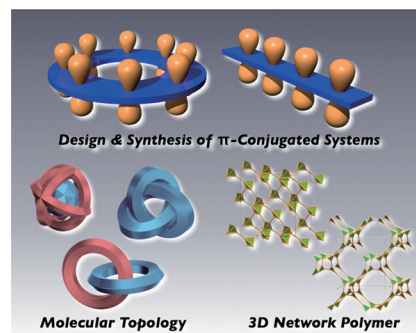
### Keywords

$\pi$ -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  $\sim 0.1$  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 ( $1\ \mu\text{m}$  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.



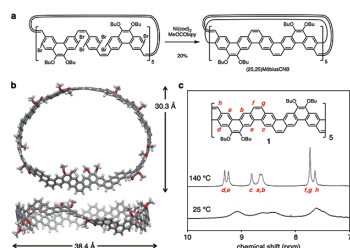
**Figure 1.** Design and synthesis of  $\pi$ -conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

### Selected Publications

- 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). DOI: 10.1038/s44160-022-00075-8
- 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, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," *Acc. Chem. Res.* **52**, 2760–2767 (2019).
- 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).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).

## 1. Möbius Carbon Nanobelt

Technologies for the creation of topological carbon nanostructures have greatly advanced synthetic organic chemistry and materials science. Although simple molecular nanocarbons with a belt topology have been constructed, analogous carbon nanobelts (MCNBs), have not yet been synthesized owing to their high intrinsic strain. Herein, we report the synthesis, isolation and characterization of a MCNB. Calculations of strain energies suggest that large MCNBs are synthetically accessible. Designing a macrocyclic precursor with an odd number of repeat units led to a successful synthetic route via Z-selective Wittig reactions and nickel-mediated intramolecular homocoupling reactions, which yielded (25,25) MCNB over 14 steps (Figure 2a). NMR spectroscopy and theoretical calculations reveal that the twist moiety of the Möbius band moves quickly around the MCNB molecule in solution (Figure 2b,c). The topological chirality originating from the Möbius structure was confirmed experimentally using chiral HPLC separation and CD spectroscopy.



**Figure 2.** (a) Synthesis of (25,25)MCNB. (b) Structure of (25,25) MCNB. (c)  $^1\text{H}$  NMR spectra of (25,25)MCNB.

## 2. Perfluorocycloparaphenylene

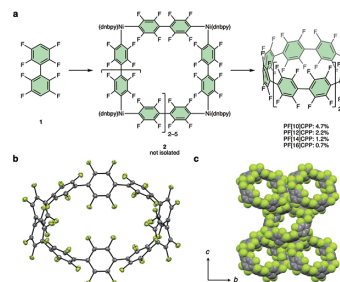
Perfluorinated aromatic compounds, the so-called *perfluoroarenes*, are widely used in materials science owing to their high electron affinity and characteristic intermolecular interactions. However, methods to synthesize highly strained perfluoroarenes are limited, which greatly limits their structural diversity. Herein, we report the synthesis and isolation of perfluorocycloparaphenylenes (PFCPPs) as a class of ring-shaped perfluoroarenes. Using macrocyclic nickel complexes, we succeeded in synthesizing PF[n]CPPs ( $n = 10, 12, 14, 16$ ) in one-pot without noble metals (Figure 3a). The molecular structures of PF[n]CPPs ( $n = 10, 12, 14$ ) were determined by X-ray crystallography to confirm their tubular alignment (Figure 3b,c). Photophysical and electrochemical measurements revealed that PF[n]CPPs ( $n = 10, 12, 14$ ) exhibit wide HOMO–LUMO gaps, high reduction potentials, and strong phosphorescence at low temperature. PFCPPs are not only useful as electron-accepting organic materials but can also be used for accelerating the creation of topologically unique molecular nanocarbon materials.

### Awards

SEGAWA, Yasutomo; Chemist Award BCA 2021 (2021).

SEGAWA, Yasutomo; Thieme Chemistry Journals Award 2022 (2022).

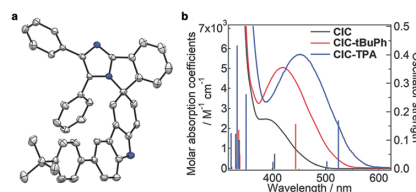
SEGAWA, Yasutomo; 62<sup>nd</sup> Academic Encouragement Award from the Ube Industries Foundation (2022).



**Figure 3.** (a) Synthesis of PFCPPs. (b) ORTEP of PF[10]CPP. (c) Packing structure of PF[10]CPP.

## 3. A Photochromic Carbazolyl-Imidazolyl Radical Complex

Optical phenomena which occur on a timescale of microseconds to milliseconds are instantaneous or invisible for human visions, whereas they can be easily detected by conventional photodetectors. Therefore, fast photoswitching materials that work in these time ranges have received considerable attention for the applications to bioimaging, anti-counterfeiting, and dynamic holographic materials. Here we report the synthesis of carbazole-incorporated photochromic radical complex.<sup>3)</sup> The molecular structure of **CIC-tBuPh** was determined by X-ray crystallography (Figure 4a). The long-wavelength photosensitivity of the photochromic reaction of the molecule is enhanced up to  $\sim 580$  nm by substituting a triphenyl amine group to the 3-position of the carbazole moiety. These photochromic reactions are investigated by subpicosecond-to-microsecond transient absorption measurements (Figure 4b).



**Figure 4.** (a) ORTEP representation of **CIC-tBuPh** with thermal ellipsoids (50% probability), where the nitrogen atom is highlighted in blue. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Steady-state absorption spectra of **CIC**, **CIC-tBuPh** and **CIC-TPA** in benzene at room temperature. Vertical lines indicate the theoretical spectra of each molecule.

### References

- 1) Y. Segawa, T. Watanabe, K. Yamanoue, M. Kuwayama, K. Watanabe, J. Pirillo, Y. Hijikata and K. Itami, *Nat. Synth.* **1**, 535–541 (2022).
- 2) H. Shudo, M. Kuwayama, M. Shimasaki, T. Nishihara, Y. Takeda, N. Mitoma, T. Kuwabara, A. Yagi, Y. Segawa and K. Itami, *Nat. Commun.* **13**, 3713 (2022).
- 3) Y. Kawanishi, Y. Segawa, K. Mutoh, J. Abe and Y. Kobayashi, *Chem. Commun.* **58**, 4997–5000 (2022).