

# 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

#### Member

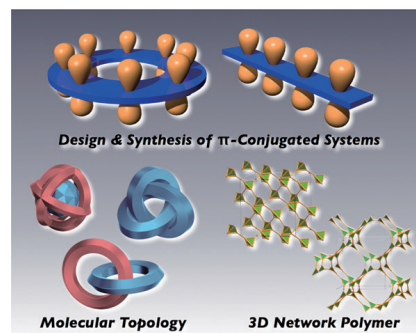
Assistant Professor  
SUGIYAMA, Haruki  
Graduate Student  
NAGASE, Mai  
WATANABE, Kosuke\*  
Technical Fellow  
NAKANO, Sachiko  
Secretary  
TANIWAKE, Mayuko

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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.

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

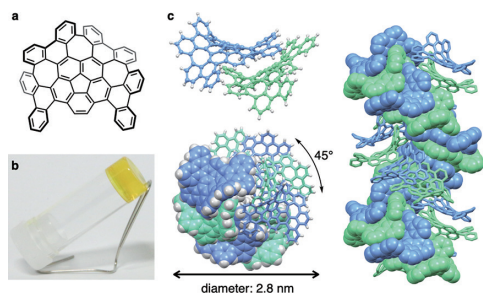
- K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, "Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes," *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).
- K. Y. Cheung, K. Watanabe, Y. Segawa and K. Itami, "Synthesis of a Zigzag Carbon Nanobelt," *Nat. Chem.* **13**, 255–259 (2021).
- Y. Saito, K. Yamanoue, Y. Segawa and K. Itami, "Selective Transformation of Strychnine and 1,2-Disubstituted Benzenes by C–H Borylation," *Chem* **6**, 985–993 (2020).
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- 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).
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- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).

## 1. Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes

The layered structures of graphite and related nanographene molecules play a key role in their physical and electronic properties. The well-ordered molecular alignment of nanographenes and its structural determination are of interest in order to gain insight into a variety of carbon materials. It is well known that the one-dimensional (1D) assembly of planar nanographenes can be achieved by introducing suitable peripheral substituents that tune solubility. The 1D assembly of bowl-shaped nanographenes was also achieved by convex-concave  $\pi$ - $\pi$  stacking along with non-covalent interactions. However, the stacking modes of negatively curved nanographenes remain unclear, owing to the lack of suitable nanographene molecules.

We developed the synthesis and 1D self-assembly of a newly designed nanographene **1-H** ( $C_{68}H_{28}$ ), a negatively curved nanographene with 12 carbon atoms fewer than WNG (Figure 2a).<sup>1)</sup> Serendipitously, we discovered that **1-H** self-assembles in various organic solvents and works as a highly efficient gelator that forms organic gels at concentrations of <1 wt% (Figure 2b). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements confirm that **1-H** forms fibers with diameters of  $\sim 2.8$  nm. The presence of efficient  $\pi$ - $\pi$  interactions in the fiber structures is supported by a bathochromic shift in the fluorescence spectrum of the gel state relative to that of dilute solutions of **1-H**. Finally, using three-dimensional electron diffraction crystallography, the double-helix  $\pi$ - $\pi$  stacking mode of **1-H** in the supramolecular nanofiber was revealed (Figure 2c).

Based on this discovery and its revelation of a new guiding principle in supramolecular self-assembly, we expect that a number of negatively curved nanographenes can be developed for new applications in materials science and biology. Moreover, this work not only reports the discovery of an all- $sp^2$ -carbon supramolecular  $\pi$ -organogelator with negative curvature, but it also showcases the power of 3D electron diffraction crystallography for the structural determination of submicrometer-sized hydrocarbon molecular assemblies.



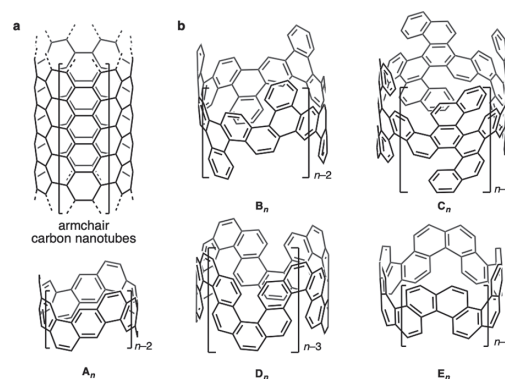
**Figure 2.** The negatively curved nanographene (**1-H**) that forms double-helix nanofibers. (a) Chemical structure of **1-H**. (b) Photo of organogel made of dichloromethane with 0.3 wt% of **1-H**. (c) The double-helix packing structure of **1-H** revealed by microcrystal electron diffraction crystallography (MicroED).

## 2. Theoretical Studies on the Strain Energy of Helicene-Containing Carbon Nanobelts

Carbon nanobelts (CNBs), the sidewall segment molecules of carbon nanotubes (CNTs), have attracted growing attention owing to their radial  $\pi$ -conjugation, strain-induced reactivity and potential applications in template CNT synthesis. Various CNB structures have been proposed and investigated by both theoretical and synthetic organic chemists. Recently, our group synthesized armchair-type  $(n,n)$ CNB (**A<sub>n</sub>**, Figure 3a) and a zigzag-type (18,0)CNB. Apart from these known CNBs, other CNBs with more complex structures can also be designed by cutting the CNTs differently. CNBs with helicene structures (**B<sub>n</sub>**–**E<sub>n</sub>**, Figure 3b) are the representative examples of these complex structures, and the structural properties of such unexplored CNBs have been of interest.

To estimate the feasibility of synthesizing strained belt-shaped compounds, the calculation of strain energy (SE) is effective. While homodesmotic reaction method using reference molecules is generally used for strained molecules, we previously found that conventional homodesmotic reactions using small reference molecules could not be applied to CNBs.

Here we have successfully estimated the strain energies of CNBs containing helicene moieties.<sup>2)</sup> Through the calculation of CNB **B<sub>n</sub>**, we revealed that our previously reported method is not applicable to helicene-containing CNBs. The newly developed method, combining the conventional homodesmotic reactions and linear regression analysis, was successful for the determination of the strain energies of CNBs **B<sub>n</sub>** and **C<sub>n</sub>** that have helicene moieties in their side chains. By changing the reference molecules, the strain energies of CNBs with helicene structures in the main chains (**D<sub>n</sub>** and **E<sub>n</sub>**) were also determined.



**Figure 3.** (a) Structures of armchair CNTs and CNBs (**A<sub>n</sub>**). (b) CNBs containing helicene structures (**B<sub>n</sub>**–**E<sub>n</sub>**).

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- 2) K. Watanabe, Y. Segawa and K. Itami, *Chem. Commun.* **56**, 15044–15047 (2020).