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# A Double-Stranded Helix by Complexation of Two Polymer Chains with a Helical Supramolecular Assembly

Takahiro Sugimoto,[†] Takayuki Suzuki,[†] Seiji Shinkai,[†,‡] and Kazuki Sada*,[†]

*Department of Chemistry and Biochemistry and Center for Future Chemistry, Graduate School of Engineering,*
*Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-039, Japan*

Received October 30, 2006; E-mail: sadatcm@mbox.nc.kyushu-u.ac.jp

Multistranded helices are ubiquitous in nature, such as polypeptides,[1] DNA,[2] and polysaccharides.[3] They have been fascinating chemists for many years because of their beautiful three-dimensional structures and functions as entities of biological information, basic structural motifs for proteins, and structural materials in living systems.[4] With respect to the fruitful functions related to their structures, folding into multistranded helices of synthetic polymers and oligomers is still one of the synthetic challenges in organic, inorganic, and supramolecular chemistries. The most facile approach is complementary complexation of a few oligomers or polymers that have both the controlled helical molecular shapes and the mutual recognition sites between the two oligomers or polymers to from multistranded helices such as metal helicates,[5] DNA analogues,[6] aromatic amides foldermers,[6] crescent-shape *m*-terphenyl oligomers,[8,9] and covalently cross-linked synthetic polymers.[10] However, these molecular designs, except the DNA analogues, are so complex that extension to polymeric double helices toward nanodevices and structural materials is not so easy. Thus, a new strategy for constructing the multistranded helices using a wide range of synthetic polymers has been awaited. Herein, we report construction of a double-stranded helix by twisting a polymeric supramolecular ladder as shown in Figure 1. To our best knowledge, this is the first report on the formation of a double helix composed of achiral synthetic organic polymers.

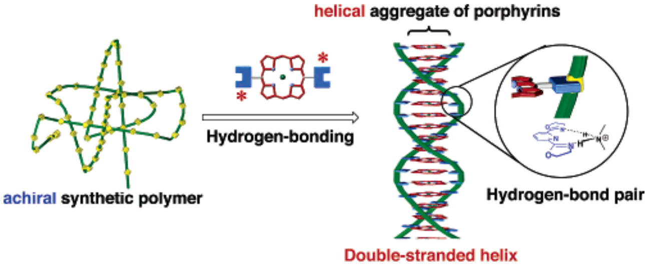

***Figure 1.*** Schematic illustration of the strategy for the construction of the artificial double-helix.

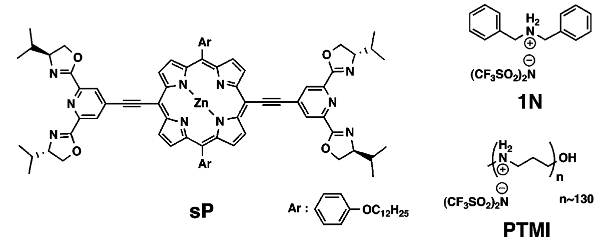

***Figure 2.*** Chemical structure of **sP**, **PTMI**, and **1N**.

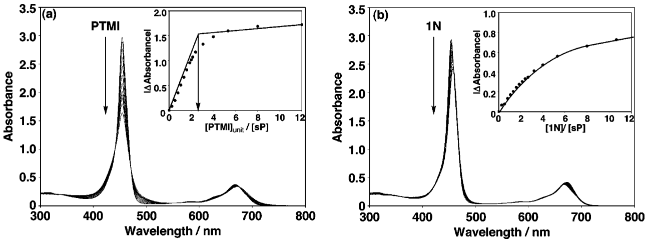

***Figure 3.*** UV spectral changes of **sP** (100 $\mu$M) upon addition of (a) **PTMI** (0~600 $\mu$M), (b) **1N** (0~1.07 mM) in $CHCl_3/CH_3CN$ (40:1) at 25 °C; (inset) plots of the absorption changes at 455 nm.

We previously demonstrated the well-defined supramolecular ladders constructed by complexation between the oligomers having two or three secondary dialkylammonium cations as the rails for the ladder and BisPYBOX (2,6-bis(2-oxazolyl)pyridine (PYBOX)) ligands, dimers of PYBOX bridged by a porphyrin ring, as the bars for the ladder.[11] The stable supramolecular ladder was ascribed to stacking of the bridging porphyrins in the BisPYBOX ligands and the complementary hydrogen bonds between two nitrogen atoms of the PYBOX and two protons of the secondary dialkylammonium cation.[12] More recently, we demonstrated the supramolecular organogel of poly(trimethylene iminium) (**PTMI**), a linear polymer with one secondary ammonium cation in the repeating unit, cross-linked by the BisPYBOX ligands.[13] These results prompted us to construct a double-stranded helix by introducing chiral and bulky units into the BisPYBOX ligand that is expected to twist the supramolecular ladder by steric repulsion. The porphyrin was used owing to its ability of self-aggregation and as a detector function of the supramolecular assembly and chirality.[14] The C2 chiral BisPYBOX ligand (**sP**) was prepared according to the method previously reported.[11] First of all, we investigated the formation of the supramolecular ladder between **sP** and **PTMI** by UV−vis absorption spectroscopy in chloroform−acetonitrile (40/1, v/v), as shown in Figure 3. This solvent mixture had high solubility for the **sP**−**PTMI** complex and did not interfere with the complexation. The addition of **PTMI** provided a drastic decrease in the Soret band at 455 nm and induced no apparent shift in the absorption maximum. The decrease in the absorption is attributed to the stacking of the porphyrin rings of **sP** in the presence of **PTMI**.[11,15] On the other hand, the addition of **1N** as a monomeric reference induced a slight decrease in the absorption accompanied by a red-shift of the Soret band (458 nm). Moreover, the titration curve was saturated at a nearly 2:1 ratio of the concentration of the secondary ammonium cation unit in **PTMI** to that of **sP**, suggesting that the stoichiometric amount of PYBOX sites was complexed with the secondary ammonium sites in **PTMI**. The results strongly suggest formation of the supramolecular ladders by complexation of **sP** and **PTMI**.

To reveal the three-dimensional structure and supramolecular chirality, we investigated the CD spectral changes of **sP** induced by **PTMI**, as shown in Figure 4. Without **PTMI**, **sP** exhibited a positive Cotton effect in the Soret band. This Cotton effect should be ascribed to dipole coupling between the porphyrin ring and chiral PYBOX ligands at the terminals through the acetylene groups but not by inducing the CD by the aggregation of **sP**. This was confirmed by the linearity in the Lambert−Beer plot under these con-

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[†] Department of Chemistry and Biochemistry.
[‡] Center for Future Chemistry.

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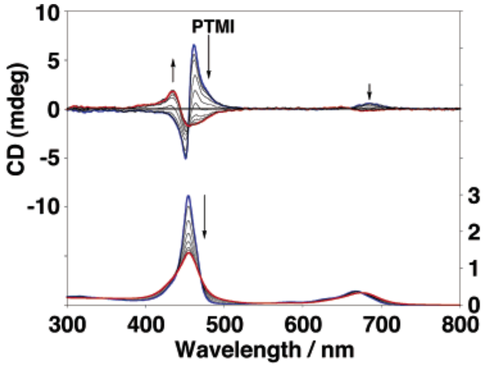

***Figure 4.*** CD spectral changes of **sP** (100 $\mu$M) upon addition of (a) **PTMI** (0∼700 $\mu$M), (b) **1N** (0∼1.4 mM) in $CHCl_3/CH_3CN$ (40:1) at 25 °C; **sP** only (blue line); [**PTMI**]/[**sP**] = 7, [**1N**]/[**sP**] = 14 (red line).

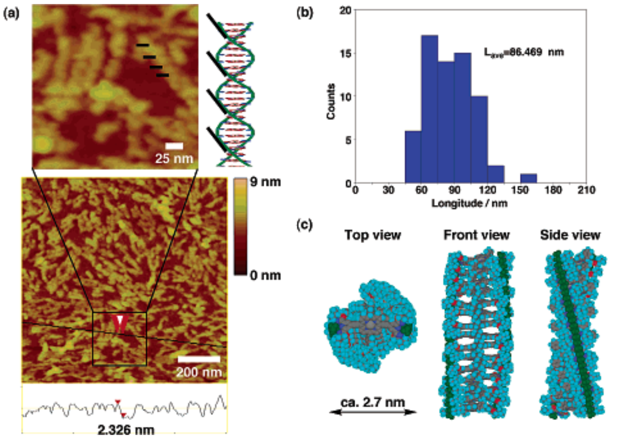

***Figure 5.*** (a) AFM images of **sP**−**PTMI** complex deposited from solution of $CHCl_3/CH_3CN$ = 2:1 onto HOPG; (b) histogram analysis of the longitude of double-helices structure from the AFM image; (c) CPK model of a double-helix structure of the **sP**−**PTMI** complex (**PTMI**, in green).

ditions. Upon the addition of **PTMI** under the same conditions as the UV titration, the positive Cotton effect of **sP** in the Soret band was inverted to negative with a decrease in intensity. Such an inversion was not observed during the addition of the monomeric **1N**, which exhibited a slight decrease in the intensity according to the decrease in the UV absorption. Therefore, this negative Cotton effect suggested that the porphyrin rings aggregated to form supramolecular assemblies in a helical fashion along the **PTMI**.[14] The helical aggregation of the porphyrin rings was caused by the twisted orientation to remove the steric hindrance between the isopropyl groups of **sP**. Consequently, a pair of **PTMI** seemed to construct the double-stranded helix along the helical assemblies of **sP**.

Finally, the complex solution (0.67 mM in $CHCl_3-CH_3CN$ at 2/1 (v/v)) was cast on a highly oriented pyrolitic graphite (HOPG) substrate and subjected to atomic force microscopy (AFM) observations as shown in Figure 5. For the cast samples of **PTMI** and **sP** alone, random molecular assemblies were observed. However, the stoichiometric mixture of **PTMI** and **sP** yielded linear helical assemblies. The height was ca. 2.3 nm, which was consistent with the width of **sP** estimated by the molecular model. This suggests that the helical assemblies were not bundled. More interestingly, the averaged length was ca. 86 nm. This agreed well with the estimated length of **PTMI** from the polymerization degree (ca. 62 nm in length estimated from the length of the repeating unit for the averaged degree of polymerization; 130 mer). These results suggest that the linear helical supramolecular assemblies observed by AFM correspond to the supramolecular complex of the **sP**−**PTMI**. It is understood, therefore, that the complexation of **PTMI** and **sP** provides the double-stranded helix.

In conclusion, we demonstrated that the chirality of **sP** twisted the supramolecular ladder of **PTMI**−**sP** complex to yield the double-stranded helix of **PTMI**. It is regarded as the secondary structure of **PTMI** induced by **sP**. This is a quite rare example of controlling the secondary structure of the common organic synthetic polymers that generally forms a random coil in solution.[16] Variations in the numbers of the binding sites and the size of the bridging groups would provide the multistranded helices with various diameters and pitches. Since a large number of organogelators are known to form helical fibrous aggregates,[17] they have the potential to be cores of such helical structures by association with polymers. Finally, the close-packed stacking of the bridging groups in the core is quite interesting as the method to place functional groups in a one-dimensional array toward nanowires wrapped by the polymers. Therefore, we believe that this strategy would be a powerful tool for the construction of multistranded helices and well-ordered one-dimensional supramolecular assemblies.

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