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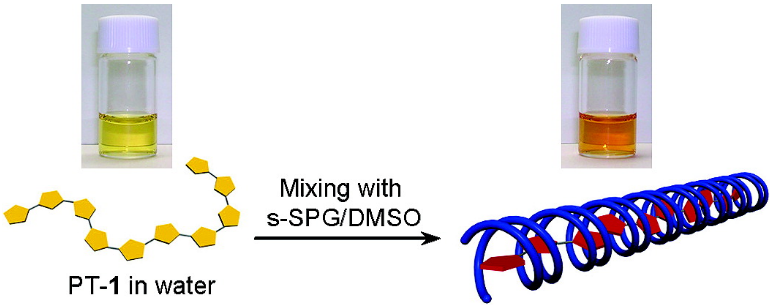

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Self-Assembly of Supramolecular Chiral Insulated Molecular Wire

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Recently, there has been a growing interest in the development of conjugated polymer (CP) molecular wires in view of their theoretical importance for the exploration of new physical properties arising from the π-electron delocalization and for the potential applications to molecular electronics[1] and sensory signal amplification.[2] CPs are often described as one-dimensional molecular wires in current nanotechnology programs, but the relevant physics is usually two- or three-dimensional due to their strong aggregation tendency both in solution and solid phases. This makes it a challenging subject to fabricate CP molecular wires on a single-molecular scale. Hitherto, several intriguing strategies have been developed to solve this problem by designing insulated molecular wires through covalent or noncovalent approaches, in which the CP backbones are encapsulated by a protective sheath, such as threading CPs through cyclophanes[3] or cyclodextrins,[4] wrapping them within dendrimeric wedges,[5] limiting interchain interactions, etc. In this communication, we report our recent findings on the preparation of supramolecular chiral insulated molecular wire by self-assembly between an achiral water-soluble polythiophene (PT-**1**) and a natural polysaccharide, schizophyllan (SPG). To the best of our knowledge, this is the first observation for the insulated molecular wires with the helical structure in a chiral sense.

SPG is a β-1,3-glucan and is known to exist as a right-handed triple helix (t-SPG) in water but as a single random coil (s-SPG) in dimethyl sulfoxide (DMSO).[6] When water is added to its DMSO solution, s-SPG collapses owing to the hydrophobic interaction and retrieves its original triple helix structure (renaturation). These specific structural characteristics make s-SPG form stable water-soluble complexes with certain polynucleotides, single-walled carbon nanotubes, and hydrophobic polymers during its renatured process.[7] It thus occurred to us that SPG can be used as a one-dimensional host to trap single-chain CP to form insulated molecular wire. Typically, the PT-**1**/SPG complex was prepared by adding s-SPG/DMSO solution to PT-**1**/water solution, and then the mixed solution was incubated for 12 h at 60 °C. The ratios of the s-SPG/DMSO and PT-**1**/water solutions were chosen so that, after mixing, the concentrations of PT-**1** and SPG were 1.5×10^{-4} and 6.0×10^{-4} M, respectively, and the volume fraction of water in the mixture (V_w) was 0.95.

Figure 1 compares the absorption, emission (A) and CD (B) spectra between PT-**1** and its mixture with s-SPG at 20 °C. In the absence of SPG, the absorption maximum of 403 nm was attributed to a random-coiled conformation of the PT backbone.[2b] The absorption maximum is red-shifted to 454 nm upon addition of s-SPG into PT-**1** solution, along with a solution color change from yellow to orange. This distinct shift is associated with an increase in the effective conjugation length of the PT-**1** backbone, demonstrating that the interaction between PT-**1** and s-SPG will force the PT-**1** backbone to adopt a more planar conformation.

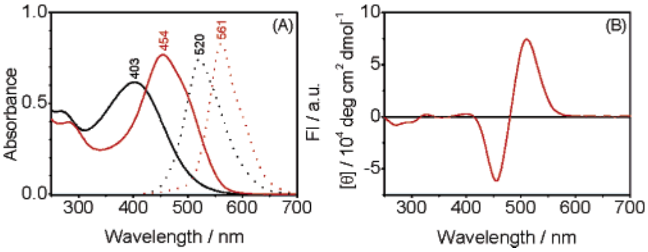
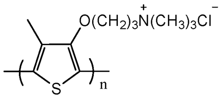
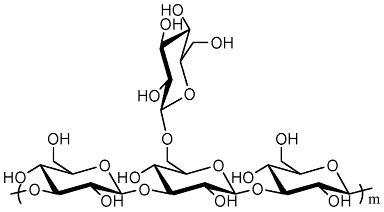


Figure 1. Absorption (solid line, left *y* axis) and emission (dashed line, right *y* axis) (A) and CD (B) spectra of PT-**1** in the absence (black line) and the presence of s-SPG (red line). Excited wavelength: 400 nm.



PT-**1**



SPG

PT-**1** itself is optically inactive, so that no characteristic CD pattern in the $\pi-\pi^*$ transitions was detected, indicating that the PT-**1** backbones adopt an achiral conformation in the mixed solvent. Interestingly, upon addition of s-SPG, an intense split-type induced CD (ICD) in the $\pi-\pi^*$ transition region was observed. Normally, optically active PTs with chiral β-substituents can form intermolecularly π-stacked chiral aggregates in poor solvents at low temperature, accompanied by the appearance of characteristic vibronic bands at the longer wavelength.[8] In our case, upon addition of s-SPG, no vibronic bands were detected. Moreover, the complexes were very stable even at high temperature (only 20% decrease in the CD intensity at 90 °C with respect to the one at 20 °C) (Figure S1), and scarcely exhibited the linear dichroism. These results clearly indicate that the chirality introduction is most probably caused by intrachain effects rather than by interchain π-stacking, and a predominantly one-handed helical structure[9] of PT-**1** is induced by interpolymer complexation with s-SPG. The shape and sign of the ICD pattern are characteristic of a right-handed helix of the PT backbones,[8] reflecting the stereochemistry of SPG which also tends to adopt a right-handed helical structure.[6]

Emission spectra were also used to monitor the conformational transition and interchain interaction of the CP backbones. As shown in Figure 1A, after the addition of s-SPG, an emission maximum of 520 nm is red-shifted to 561 nm, accompanied by a slight increase in intensity. These results indicate that the PT-**1** backbones become more planar and more isolated and the insulated molecular

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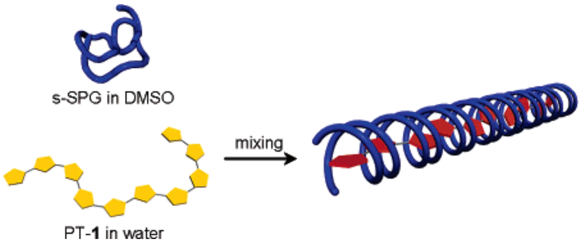

Figure 2. Schematic illustration of the chiral insulated wire formation.

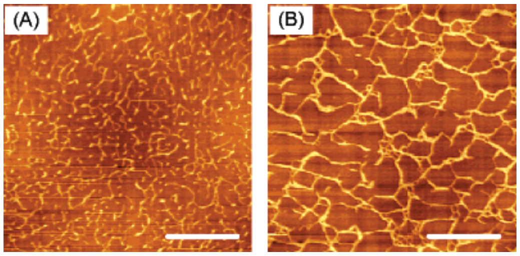

Figure 3. AFM images of the film castings from the PT-**1**/s-SPG complex (A) and renatured t-SPG (B) solutions with the concentration of 0.1 mg mL^{-1}. Scale bar: 500 nm.

wire may be formed during the complexation with s-SPG, resulting in reduction of interchain interactions.[8] The differences between the absorption spectra of the solid films of PT-**1** and its complex with s-SPG further supported this conclusion (Figure S2): in the absence of s-SPG, the absorption maximum (541 nm) of the film shows a distinct red-shift (by 138 nm) in comparison with that of solution along with the appearance of two shoulders due to the vibronic fine structure,[8] suggesting the strong aggregation of PT-**1** in the film; whereas almost no changes between the spectra of the solution and the solid film of the PT-**1**/s-SPG complex were detected except a slight increase in bandwidth. The finding clearly demonstrates that PT-**1** is well wrapped by s-SPG host and thus can reduce the interchain interactions. Moreover, cyclic voltammograms were recorded for PT-**1** and the PT-**1**/s-SPG complex cast films (Figure S3), in which PT-**1**/s-SPG complex gives a more complex CV pattern than PT-**1** itself because of the wrapping effect of s-SPG.

To elucidate the PT-**1**/s-SPG supramolecular complex formation mechanism, the stoichiometry of the complex formation was determined by means of continuous-variation plots (Job plots) from CD spectroscopic studies in which the total concentrations of PT-**1** and s-SPG were kept constant at 0.4 mM (Figure S4). The stoichiometric ratio ($M_{\mathrm{s-SPG}}/(M_{\mathrm{s-SPG}} + M_{\mathrm{PT-1}})$) is evaluated to be 0.4, which indicates that the molar ratio of glucose residues along the s-SPG main chain to the repeat unit of PT-**1** for the maximum complex formation is around 2.[10] Considering the facts that t-SPG forms a right-handed 6_1 triple helix with a 1.8 nm pitch[6b] and that sexithiophene has a statistically averaged length of 2.0 nm, we suppose that the PT-**1**/SPG complex prepared from s-SPG and PT-**1** is constructed by two s-SPG chains and one PT-**1** chain, in which the PT-**1** chain with a transoid helical conformation[11] is wrapped by two s-SPG chains (Figure 2).

To obtain more direct evidence for the insulated molecular wire formation the atomic force microscopic (AFM) images of the film castings from PT-**1**, its complex with s-SPG in the stoichiometric ratio, and renatured t-SPG solutions on new cleaved mica surfaces were recorded. PT-**1** gives some particles without defined structures (Figure S5). PT-**1**/s-SPG complex forms isolated fibers even for a film casting from a relatively concentrated aqueous solution (0.1 mg mL^{-1} based on SPG), whereas renatured t-SPG fibers aggregate into networks at this condition (Figure 3). These differences can be explained such that the strong electrostatic repulsion between the positively charged PT-**1**/s-SPG fibers suppresses the aggregation which may occur in neutral renatured t-SPG. To get more solid evidence that the fibrous structures in PT-**1**/s-SPG complex are really made from the complex while not from renatured t-SPG, the thickness of the individual fibers obtained from dilute solutions (0.01 mg mL^{-1}) was estimated (Figure S6). The measured mean thicknesses of the PT-**1**/s-SPG complex and renatured t-SPG are 0.43 and 0.99 nm, respectively. Although AFM methods do not yield reliable chain thickness because the molecular chain thickness is convoluted with the thickness of the AFM tip as reported previously,[4a,6b] it does not preclude meaningful observation of the systematic difference between the chain thicknesses of renatured t-SPG and PT-**1**/s-SPG complex. The clear difference indicates that the fibrous structures in these two samples consist of different species and the single-chain PT-**1** is really wrapped by s-SPG to form an insulated molecular wire with a diameter smaller than that of renatured t-SPG.

In summary, we have developed a novel, efficient approach to the preparation of supramolecular chiral insulated molecular wire from a neutral SPG host and a water-soluble PT guest. We expect that the present findings will not only open a door to a new application of polysaccharides but also provide an important clue to prepare stable supramolecular insulated molecular wires with one-handed helical structures.

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Supporting Information Available: Complete ref 4a, detailed experimental procedures, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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