

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

β -1,3-Glucan (Schizophyllan) Can Act as a One-Dimensional Host for Creating Chirally Twisted Poly(*p*-phenylene Ethynylene)

Munenori Numata^a; Tomohisa Fujisawa^a; Chun Li^b; Shunichi Haraguchi^a; Masato Ikeda^a; Kazuo Sakurai^c; Seiji Shinkai^d

^a Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan ^b Department of Chemistry, Tsinghua University, Beijing, China ^c Department of Chemical Processes and Environments, Faculty of Environmental Engineering, The University of Kitakyushu, Fukuoka, Japan ^d Center for Future Chemistry, Kyushu University, Fukuoka, Japan

To cite this Article Numata, Munenori , Fujisawa, Tomohisa , Li, Chun , Haraguchi, Shunichi , Ikeda, Masato , Sakurai, Kazuo and Shinkai, Seiji(2007) ' β -1,3-Glucan (Schizophyllan) Can Act as a One-Dimensional Host for Creating Chirally Twisted Poly(*p*-phenylene Ethynylene)', *Supramolecular Chemistry*, 19: 1, 107 – 113

To link to this Article: DOI: 10.1080/10610270600982508

URL: <http://dx.doi.org/10.1080/10610270600982508>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

β -1,3-Glucan (Schizophyllan) Can Act as a One-Dimensional Host for Creating Chirally Twisted Poly(*p*-phenylene Ethynylene)

MUNENORI NUMATA^a, TOMOHISA FUJISAWA^a, CHUN LI^{a,b}, SHUNICHI HARAGUCHI^a, MASATO IKEDA^a, KAZUO SAKURAI^c and SEIJI SHINKAI^{a,d,*}

^aDepartment of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan; ^bDepartment of Chemistry, Tsinghua University, Beijing 100084, China; ^cDepartment of Chemical Processes and Environments, Faculty of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, Japan; ^dCenter for Future Chemistry, Kyushu University, Fukuoka 819-0395, Japan

(Received 23 May 2006; Accepted 27 July 2006)

It has been demonstrated that a chiral, insulated poly(*p*-phenylene ethynylene) (PPE) nano-wire can be created by a polymer wrapping method utilizing natural β -1,3-glucan polysaccharide schizophyllan (SPG). Spectroscopic and microscopic measurements have revealed that PPE adopts a rigid conformation and exists as one piece in the helical hollow constructed by two SPG chains. Moreover, the inherent helical structure of SPG can induce the chiral twisting of the insulated PPE backbone. It is believed that the present system is really applicable for designing novel chiral sensors based on PPE.

Keywords: Polysaccharide; Conjugated polymer; Insulated polymer; Chiral sensor

INTRODUCTION

Recently, exploitation of highly sensitive chemosensors based on conjugated polymers (CPs), which can convert chemical and physiological signals into optical emission with signal amplification, has been of much concern. Poly(*p*-phenylene ethynylene) (PPE) is one of such CPs which is suitable to chemosensors due to its excellent optical response to environmental variation through the relatively free rotation of the alkenyl–aryl single bond [1–8]. A particularly challenging aspect of PPE is to design a water-soluble PPE backbone with a one-handed helical structure because it is readily applicable as a sensitive chiral sensor targeting to biologically important molecules and polymers. Accordingly, much effort has been paid to design and synthesis of

various water-soluble PPEs to which chiral substituents are covalently attached. So far, a few attempts have been reported to utilize the chiral PPEs as sensor probes in aqueous solution. However, such water-soluble PPEs have the nature of polymeric “amphiphiles” and strong tendency of the PPE backbone to form interpolymer aggregates has caused serious researchers’ confusion because it induces efficient fluorescence quenching to reduce the sensor sensitivity [9–11]. One potential breakthrough in overcoming this problem is to design the insulated PPE through covalent or noncovalent approaches, in which the PPE backbone is encapsulated by a protective sheath [12]. This intriguing strategy would make it possible to fabricate PPE on a molecular level, avoiding the interpolymer aggregation. Here, one may expect that if the sheath polymers are chiral, they would force the incorporated PPE to adopt a chirally twisted conformation along the sheath polymer chain. We report herein our novel approach toward the creation of a chiral insulated PPE wire through noncovalent inclusion by natural polysaccharide schizophyllan (SPG) acting as a sheath polymer.

SPG is a natural polysaccharide produced by fungus *Schizophyllum commune* and its repeating unit consists of three β -(1-3) glucoses and one β -(1-6) glucose side chain linked at every third main-chain glucose. SPG adopts a triple helix (t-SPG) in nature, which is stabilized by the hydrogen-bonding

*Corresponding author. E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

interaction among 2-OH groups, but can be dissociated into a single chain (s-SPG) by dissolving in dimethylsulfoxide (DMSO) [13]. The s-SPG chain can retrieve the original triple helix by exchanging DMSO for water. The computer-generated structure for this triple helix revealed that the 2-OH side along the main-chain glucoses is more hydrophobic, whereas the 6-OH or the side glucose face is more hydrophilic (Fig. 1) [14]. Therefore, one may image that the one-dimensional hydrophobic cavity is constructed inside the SPG triple helix, like a one-dimensional cyclodextrin array [15–20]. It thus occurred to us that the polymer wrapping by SPG could be a novel approach toward the creation of the chiral insulated PPE wire, in which the PPE backbone is isolated from others and twisted along the SPG polymer chain, reflecting the right-handed SPG helical motif [12,22]. So far, the creation of chiral phenylene ethynylene backbones has been achieved only by inter- or intrapolymer interactions among phenylene ethynylene units with chiral substituents; the typical examples are (1) helical aggregate

formation through interpolymer stacking of PPE [3] and (2) intrapolymer folding of poly(*m*-phenylene ethynylene) [23–27]. To the best of our knowledge, therefore, the present system is the first example for the insulated chiral molecular wire based on PPE.

RESULTS AND DISCUSSION

The complex was prepared according to the following procedure: a DMSO solution of PPE (1.0 g L^{-1}) was mixed with a DMSO solution containing s-SPG (5.0 g L^{-1} , $M_w = 150,000$). At this stage, the mixed solution contained $200 \mu\text{g}$ of PPE and 1.0 mg of SPG. In this concentration range, PPEs are dissolved in DMSO homogeneously without forming the aggregate. This fact was confirmed by Lineweaver-Burk plot (LB plot) using UV–vis spectroscopy (Fig. 2). To the resultant DMSO solution, water was gradually added with stirring to avoid the precipitation of PPE. The final composition of water/DMSO (v/v) was adjusted to 95/5 (v/v). The clear solutions thus

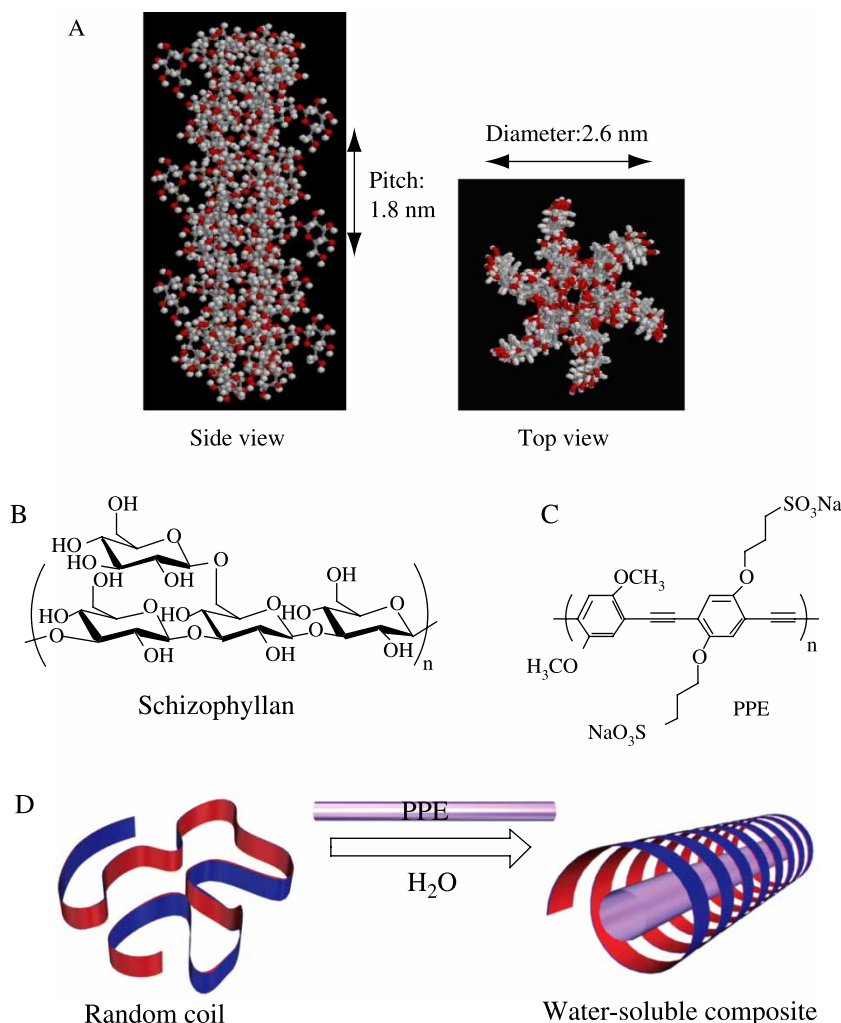


FIGURE 1 (A) Representative models of SPG triple helix, (B) repeating unit of SPG, (C) repeating unit of PPE, and (D) entrapping of PPE into the SPG hydrophobic cavity during the renaturing process.

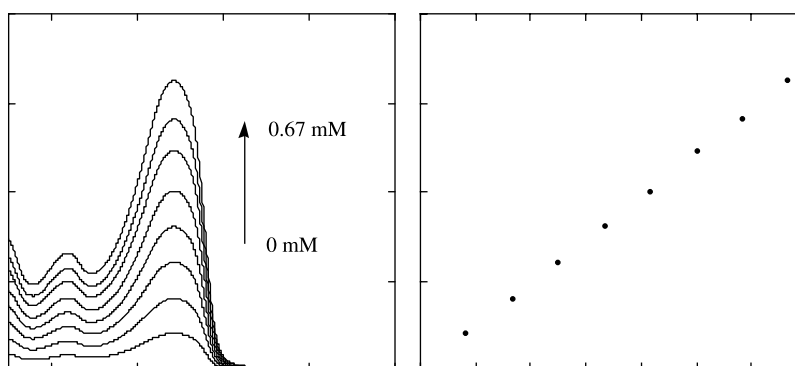


FIGURE 2 UV-vis spectra of PPE as a function of concentration (concentration range: $0\text{--}6.7 \times 10^{-4}$ M) and LB plot at 442 nm, 0.10 cm cell length, r.t.

obtained were characterized by UV-vis fluorescence and CD spectroscopies.

Figure 3 compares the absorption spectra between PPE itself and its mixture with s-SPG. The absorption maximum of 442 nm, observed in the absence of SPG, is attributed to a random-coiled conformation of the PPE backbone. Upon mixing with s-SPG, the absorption maximum is red-shifted to 470 nm, indicating that the effective conjugation length of the PPE backbone is increased. The shift clearly shows that the interpolymer interaction between PPE and s-SPG, which would force the PPE backbone to adopt the more planer and rigid conformation. It is already known that the similar red-shift in the UV-vis spectra can be observed when PPEs form interpolymer aggregates in a poor solvent, but this type of red-shift is always accompanied by fluorescence quenching in the emission spectra. Fluorescence emission spectra of the SPG/PPE complex are shown in Fig. 4. In Fig. 4,

one can recognize that the emission intensity dramatically increases upon addition of s-SPG. The finding indicates that the PPE backbones do not aggregate by themselves but become more planer and more isolated through the complexation with s-SPG. These results support the view that the red-shift in the UV-vis spectra is caused by the insulation of PPE in the one-dimensional SPG cavity.

PPE itself is optically inactive, so that no characteristic CD pattern in the $\pi\text{--}\pi^*$ transition region was detected in the mixed solvent. Interestingly, upon addition of s-SPG, an intense split-type induced CD (ICD) appeared in the $\pi\text{--}\pi^*$ transition region (Fig. 5). The shape and ICD pattern are characteristic of a right-handed helix of the PPE backbone, indicating that the right-handed stereochemistry characteristic of SPG is transcribed to the PPE backbone. Taking all spectroscopic results obtained into consideration, we can conclude that one piece of PPE polymer is incorporated into

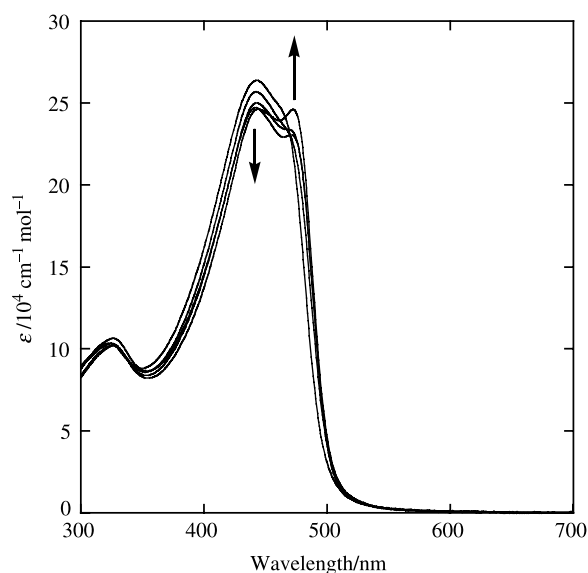


FIGURE 3 UV-vis spectral change of PPE as a function of SPG concentration (concentration range of s-SPG : $0\text{--}6.7 \times 10^{-4}$ M). The concentration of PPE was kept at 1.5×10^{-4} M. $\text{H}_2\text{O}/\text{DMSO} = 95/5$ (v/v), 1.0 cm cell length, r.t.

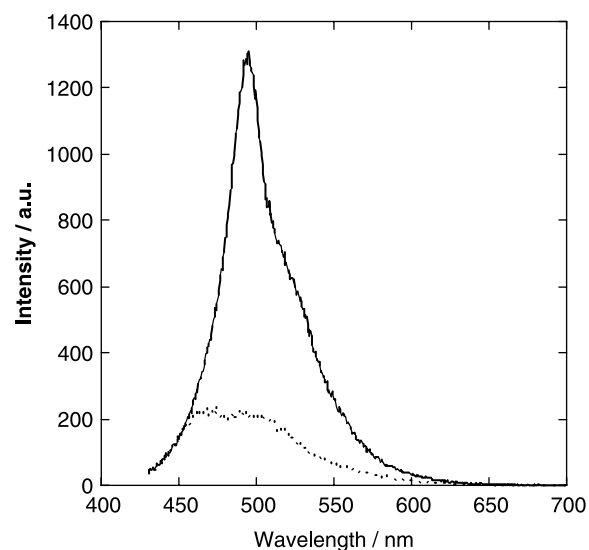


FIGURE 4 Emission spectra of PPE in the absence of s-SPG (dashed line) and in the presence of 15.0 eq. (2.3×10^{-3} M) of s-SPG (solid line), excited at 400 nm. The concentration of PPE was kept at 1.5×10^{-4} M. $\text{H}_2\text{O}/\text{DMSO} = 95/5$ (v/v), r.t.

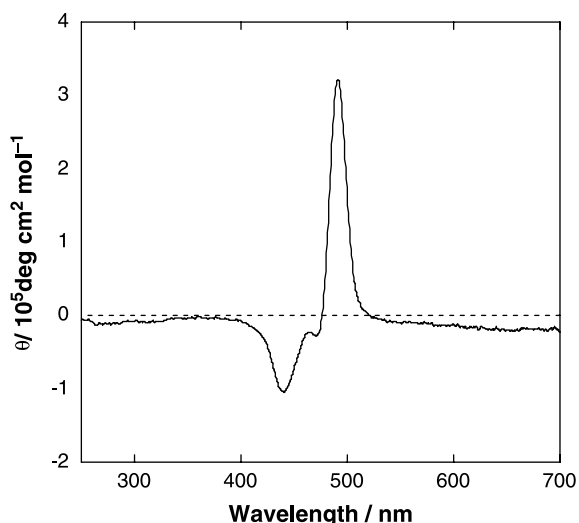


FIGURE 5 CD spectra of PPE in the absence of 15.0 eq. (2.3×10^{-3} M) of s-SPG (dashed line) and in the presence of PPE (solid line). The concentration of PPE was kept at 1.5×10^{-4} M. $\text{H}_2\text{O}/\text{DMSO} = 95/5$ (v/v), 1.0 cm cell, r.t.

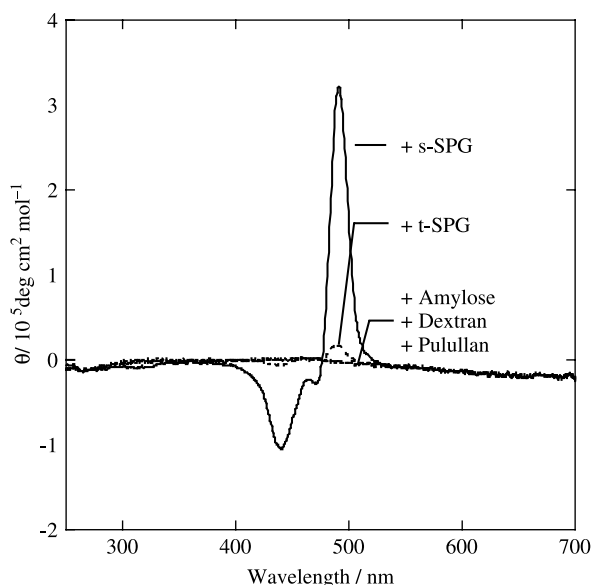


FIGURE 6 Comparison of CD spectra obtained from several PPE solutions containing polysaccharide. The concentration of PPE was kept at 1.5×10^{-4} M. $\text{H}_2\text{O}/\text{DMSO} = 95/5$ (v/v), 1.0 cm cell, r.t.

the SPG one-dimensional cavity and its backbone adopts a right-handed twisted conformation along the SPG polymer chain.

As a reference experiment, we mixed an aqueous solution containing t-SPG with PPE. However, the mixture did not give any CD signal around the same wavelength region. This result supports the view that the renaturing process via s-SPG is indispensable for the effective interaction between SPG and PPE. Moreover, to differentiate the inclusion ability of SPG over other polysaccharides, several polysaccharides (i.e., amylose, dextran, and pulullan) were tested for the reference experiments. However, none of the reference solutions gave a significant CD signal, indicating that among natural polysaccharides, only SPG has the special ability to create the insulated molecular wire (Fig. 6).

To elucidate the mechanism for s-SPG/PPE supramolecular complex formation, the stoichiometry of the complex was determined by means of a continuous-variation plot (Job plot) from its CD spectroscopic change, where the total repeating unit concentrations of PPE and s-SPG were maintained constant at 0.4 mM. From the Job plot (Fig. 7), we can evaluate the stoichiometric ratio ($M_{\text{s-SPG}}/(M_{\text{s-SPG}} + M_{\text{PPE}})$) to be 0.4, indicating that the maximum complex formation is attained at around 2, which corresponds to the molar ratio of the glucose residue along the s-SPG main chain to the repeating unit of PPE. Furthermore, considering the facts that t-SPG forms a right-handed 6_1 triple helix with a 1.8 nm pitch and that three *p*-phenylene ethynylene unit has statistically 1.6 nm length in average, we suppose that the SPG/PPE complex prepared from a mixture of s-SPG and PPE is constructed by two s-SPG chains and one

PPE chain in which the two s-SPG chains enforce the PPE chain to be twisted [28].

To obtain more direct evidence for the insulated molecular wire formation, the atomic force microscopic (AFM) images of the film prepared by casting a PPE and SPG/PPE composite solution were recorded. It is seen from Fig. 8a that the height of t-SPG itself is ca. 1.0 nm. In Fig. 8b, one can recognize that PPEs themselves form dot-like aggregates reflecting their amphiphilic nature and the height is estimated to be more than 10 nm. On the other hand, as seen in Fig. 8c, the SPG/PPE composites are well dispersed and isolated from each other on the mica surface and most of them have less than 1.0 nm

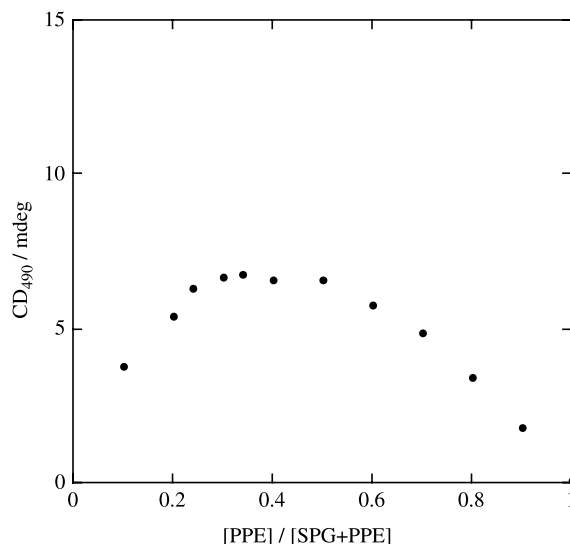


FIGURE 7 Job plot of PPE with s-SPG in the $V_w = 0.95$ mixed solvent at 25°C: $M_{\text{s-SPG}} + M_{\text{PPE}} = 0.4$ mM.

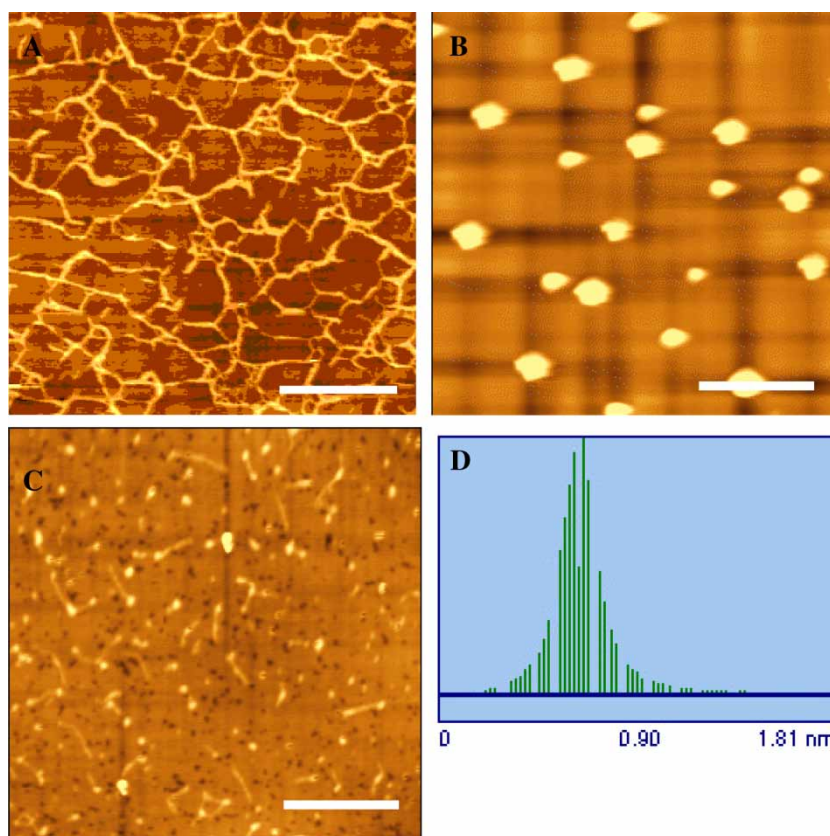


FIGURE 8 AFM image of (A) t-SPG, (B) PPE aggregates, (C) SPG/PPE composite, and (D) height distribution of the SPG/PPE composites. The composite was prepared at the stoichiometric ratio (SPG/PPE = 2/1). Scale bar: 500 nm.

height. This result is supported more quantitatively by the histogram (Fig. 8d): the peak maximum appears at 0.6 nm with narrow distribution. Although AFM observation does not give a reliable polymer thickness because the height is convoluted with the tip thickness, the clear differences in the height between the t-SPG and SPG/PPE composite support the view that the fibrous composite consists of one PPE chain and two s-SPG chains.

CONCLUSIONS

A novel approach toward the preparation of the supramolecular chiral insulated wire of PPE owing to the polymer wrapping effect of SPG has been demonstrated. The ICD pattern of the composite is attributed to formation of the characteristic right-handed helix of the PPE backbone, reflecting the inherent stereochemistry of SPG. Furthermore, UV-vis and fluorescence spectra of the composite revealed that PPE exists as one piece in the helical hollow constructed by two SPG chains. This finding was also supported by AFM observation. To the best of our knowledge, this is the first example to create the helical and isolated PPE nano-fiber, which is expected to be readily applicable for a chiral sensor that is not affected by the analyte-induced

aggregation-deaggregation drawback of PPE. It is believed that the present system will provide a novel concept for chiral PPEs and play an important role to establish a novel sensing system in conjugated polymers.

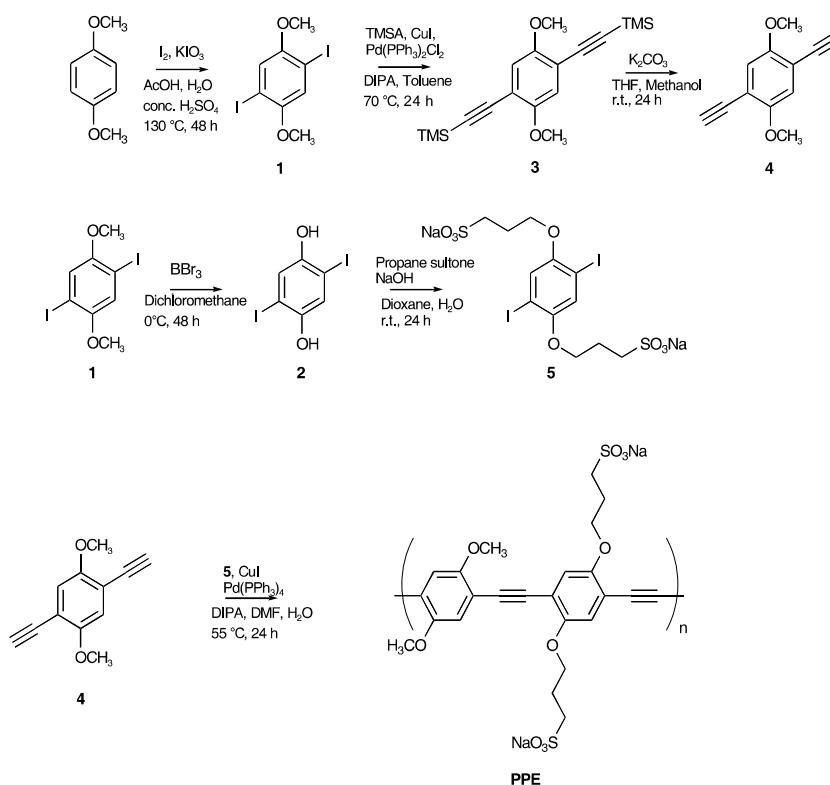
EXPERIMENTAL

Measurements

UV-vis spectra were acquired on a Hitachi U-3000 spectrophotometer. The fluorescence spectra were recorded on a Perkin Elmer LS 55 luminescence spectrometer. CD spectra were measured on a Jasco J-720 WI spectropolarimeter using a cylindrical quartz cell with a pathlength of 1.0 cm. AFM observation was carried out using Topo METRIX SPM2100.

Materials

SPG was kindly supplied by Mitsui Sugar Co., Japan. The molecular weight and the number of repeating units were evaluated to be 1.5×10^5 and 231, respectively. Other polysaccharides used here were purchased from Tokyo Kasei Kogyo Co., ($M_w = 15,000$ for amylose, 70,000 for dextran, 200,000 for pullan and starch).



SCHEME 1 Synthesis of PPE.

Synthesis of PPE

PPE was synthesized according to Scheme 1.

2,5-Diiodo-1,4-dimethoxybenzene (1)

1,4-Dimethoxybenzene (10.0 g, 72.4 mmol), iodine (20.2 g, 79.6 mmol, 1.1 eq.) and potassium iodate (6.35 g, 29.7 mmol, 0.41 eq.) were dissolved in a mixed solvent (acetic acid/water = 10/1 (v/v)). To the solution, 3 mL of sulfuric acid was added and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into a large amount of water to give a crude product as a precipitate. After recrystallization with hot ethanol to give **1** as a colorless crystal (16.3 g, 58%). ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.17 (2H, s), 3.78 (6H, s). MALDI-TOF MS calculated for C₈H₈I₂O₂⁺: 389.9; found: 391.0.

2,5-Diiodo-1,4-dihydroxybenzene (2)

2,5-Diiodo-1,4-dimethoxybenzene **1** (4.0 g, 10.24 mmol) was dissolved in 120 mL of dichloromethane. After cooling to -78 °C, BBr₃ dichloromethane solution (1 M, 27.0 mmol, 2.2 eq.) was added to the mixture under argon atmosphere. The reaction mixture was gradually warmed to room temperature and allowed to stirring for 24 h. To the solution, 150 mL of water was added to give **2** as a white precipitate. This precipitate was used to the next

reaction without further purification (3.58 g, 97%). ¹H NMR (600 MHz, CDCl₃, TMS) δ 7.12 (s, 2H); MALDI-TOF MS calculated for C₆H₄I₂O₂⁺: 362.8; found: 362.8.

2,5-Dimethoxy-1,4-trimethylsilyl ethynylbenzene (3)

2,5-Diiodo-1,4-dimethoxybenzene **1** (5.0 g, 12.8 mmol), Pd(PPh₃)₂Cl₂ (0.54 g, 0.77 mmol, 0.06 eq.) and CuI (0.13 g, 1.28 mmol, 0.10 eq.) were dissolved in a dry mixed solvent (toluene/diisopropylamine = 2/1 (v/v)). To the mixture trimethylsilylacetylene (2.75 g, 28.2 mmol, 2.2 eq.) was added and the mixture was stirred at 70 °C for 4 h under argon atmosphere. After cooling to room temperature, the reaction mixture was washed with water several times and the separated organic layer was dried over anhydrous MgSO₄. After removing the solvent, the residue was purified with flash column chromatography (hexane/ethyl acetate = 5/1 (v/v)). After moving the solvent, **3** was obtained as a white powder (3.04 g, 72%). ¹H NMR (600 MHz, CDCl₃, TMS) δ 6.64 (s, 2H), 3.59 (s, 6H); MALDI-TOF MS calculated for C₁₈H₂₆O₂Si₂⁺: 331.2; found: 331.2.

Monomer Unit for PPE (4)

The solution containing **3** (0.90 g, 2.72 mmol) and K₂CO₃ (3.8 g, 27.5 mmol, 10 eq.) in a mixed solvent (20 mL of THF and 15 mL of methanol) were stirred for 24 h. After removing K₂CO₃ by filtration, the

solvent was evaporated to dryness. The obtained yellow powder was recrystallized with benzene and ethanol to give a pale yellow powder (285 mg, 55%). ^1H NMR (600 MHz, CDCl_3 , TMS) δ 6.92 (s, 2H), 3.82 (s, 6H); MALDI-TOF MS calculated for $\text{C}_{12}\text{H}_{10}\text{O}_2^+$: 187.1; found: 187.1.

Monomer Unit for PPE (5)

2 (3.58 g, 9.9 mmol) was dissolved in a mixed solvent (200 mL of 1 M NaOH and 50 mL of dioxane). To the solution, propanesulfone (3.02 g, 24.7 mmol, 2.5 eq.) was added and followed to react for 24 h at room temperature. After cooling the solution in an ice bath, acetone was added to the mixture to give **5** as a white precipitate (1.26 g, 19%). ^1H NMR (600 MHz, $\text{DMSO}-d_6$, TMS) δ 7.29 (s, 2H), 4.03 (t, 4H), 2.59 (t, 4H), 1.98 (m, 4H).

PPE

The mixture of **4** (152.6 mg, 0.82 mmol) and **5** (537 mg, 0.83 mmol, 1.01 eq.) was dissolved in 10 mL of mixed solvent (water/DMF = 1/1 (v/v)). To the solution, diisopropylamine (10 mL), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 25 mmol, 0.03 eq.) and CuI (5.6 mg, 25 mmol, 0.03 eq.) were added and stirred at 55°C for 24 h. After cooling to room temperature, the reaction mixture was slowly poured into 1 L of a mixed solvent (methanol/acetone/diethylether = 1/4/5 (v/v/v)). The formed precipitate during this procedure was collected by filtration and dissolved in DMSO. The DMSO solution was subjected to dialysis against water (MWCO: 3,500). After freeze-dry treatment, PPE was obtained as a yellow solid (275 mg, 47%). ^1H NMR (600 MHz, $\text{DMSO}-d_6$, TMS) δ 7.16 (br, 4H), 4.15 (br, 4H), 3.88 (s, 6H), 2.70 (br, 4H), 2.08 (br, 4H).

Acknowledgements

We thank Mitsui Sugar Co., Japan, for providing the schizophyllan samples. This work was supported by The Japan Science and Technology Corporation, SORST Project, a Grant-in-Aid for the 21st Century COE Program "Functional Innovation of Molecular Informatics" from the MEXT and a Grant-in-Aid for Scientific Research S (15105004).

References

- [1] Kim, J.; McQuade, D. T.; McHugh, S. K.; Swager, T. M. *Angew. Chem. Int. Ed.* **2000**, *39*, 3868.
- [2] Tan, C.; Atas, E.; Müller, J. G.; Pinto, M. R.; Kleiman, V. D.; Schanze, K. S. *J. Am. Chem. Soc.* **2004**, *126*, 13685.
- [3] Zahn, S.; Swager, T. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 4226.
- [4] DiCesare, N.; Pinto, M. R.; Schanze, K. S.; Lakowica, J. R. *Langmuir* **2002**, *18*, 7785.
- [5] Kumaraswamy, S.; Bergstedt, T.; Shi, X.; Rininsland, F.; Kushon, S.; Xia, W.; Ley, K.; Achyuthan, K.; McBranch, D.; Whitten, D. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 7511.
- [6] Pinto, M. R.; Schanze, K. S. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 7505.
- [7] Fan, C.; Plaxco, K. W.; Heeger, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 5642.
- [8] Wosnick, J. H.; Mello, C. M.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 3400.
- [9] Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 3826.
- [10] Khan, A.; Müller, S.; Hecht, S. *Chem. Commun.* **2005**, 584.
- [11] Lavigne, J. J.; Broughton, D. L.; Wilson, J. N.; Erdogan, B.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 7409.
- [12] Jiang, D. -L.; Choi, C. -K.; Honda, K.; Li, W. -S.; Yazawa, T.; Aida, T. *J. Am. Chem. Soc.* **2004**, *126*, 12084.
- [13] Yanaki, T.; Norisuye, T.; Fujita, M. *Macromolecules* **1980**, *13*, 1462.
- [14] Miyoshi, K.; Uezu, K.; Sakurai, K.; Shinkai, S. *Chem. Biodiversity* **2004**, *1*, 916.
- [15] Li, G.; McGown, L. B. *Science* **1994**, *264*, 249.
- [16] Gattuso, G.; Menzer, S.; Nepogodiev, S. A.; Stoddart, J. F.; Williams, D. J. *Angew. Chem. Int. Ed.* **1997**, *36*, 1451.
- [17] Ashton, P. R.; Cantrill, S. J.; Gattuso, G.; Menzer, S.; Nepogodiev, S. A.; Shipway, A. N.; Stoddart, J. F.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 1299.
- [18] Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456.
- [19] Michishita, T.; Okada, M.; Harada, A. *Macromol. Rapid Commun.* **2001**, *22*, 763.
- [20] Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2003**, *36*, 6422.
- [21] Numata, M.; Hasegawa, T.; Fujisawa, T.; Sakurai, K.; Shinkai, S. *Org. Lett.* **2004**, *6*, 4447.
- [22] Li, C.; Numata, M.; Bae, A. -H.; Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4548.
- [23] Prince, R. B.; Barnes, S. A.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 2758.
- [24] Prince, R. B.; Moore, J. S.; Brunsveld, L.; Meijer, E. W. *Chem. Eur. J.* **2001**, *7*, 4150.
- [25] Stone, M. T.; Fox, J. M.; Moore, J. S. *Org. Lett.* **2004**, *6*, 3317.
- [26] Prince, R. B.; Brunsveld, L.; Meijer, E. W.; Moore, J. S. *Angew. Chem. Int. Ed.* **2000**, *39*, 228.
- [27] Hill, D. J.; Morre, J. S. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5053.
- [28] We have found that when s-SPG interacts with relatively hydrophilic polymers, the resultant composites always consist of one polymer chain and two SPG chains. See: reference [7] and Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 4520.