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### Facile fabrication of CD-active 1-D polypyrrole by the templating effect of a helix-forming anionic polysaccharide

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## Facile fabrication of CD-active 1-D polypyrrole by the templating effect of a helix-forming anionic polysaccharide

Kouta Sugikawa<sup>ab</sup>, Tomohiro Shiraki<sup>c</sup>, Youichi Tsuchiya<sup>c</sup>, Shuichi Haraguchi<sup>a</sup>, Kazuki Sada<sup>b</sup> and Seiji Shinkai<sup>ac\*</sup>

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We demonstrate the preparation of 1-D nanostructured polypyrrole wrapped by semi-artificial anionic  $\beta$ -1,3-glucans via *in situ* polymerisation. The anionic polysaccharides act as both templating molecules for oxidative polymerisation of pyrrole and 1-D hosts for oligomer or polymer of pyrrole. This system would give a general design strategy for fabrication of 1-D nanostructures.

**Keywords:** polysaccharide; conjugated polymer; insulated polymer; template polymerisation

### Introduction

Recently, significant efforts have been made towards the creation of 1-D nanostructured-conjugated polymers owing to their unique applications in organic field-effect transistors (1), chemical sensors (2), polymer solar cells (3), polymer batteries (4), field emission displays (5) and nanoscale electric devices based on quantum effects (6). Templating techniques have been of interest as an efficient method for directing preparation of various nanostructured-conjugated polymers. Several kinds of templating molecules, such as inorganic materials (7), biomolecules (8–10), carbon nanotubes (11, 12) and others (13–15), have been used, but it is still difficult to design templating molecules suitable for the preparation of nanostructured-conjugated polymers, in particular, those with chiral properties.

Recently, we have demonstrated that natural  $\beta$ -1,3-glucans, such as schizophyllan (SPG) and curdlan (CUR), can wrap various kinds of guest compounds such as single-walled carbon nanotubes (16), conjugated polymers (17) and dyes (18), and act as 1-D hosts for them. More recently, we have reported quantitative and selective modification of the 6-OH group in CUR (19), which gave us a water-soluble ionic CUR, i.e. ammonium-modified CUR (CUR-N<sup>+</sup>) and sulphonate-modified CUR (CUR-SO<sub>3</sub><sup>-</sup>; Figure 1(A)) (19–21). They still maintained their inherent ability as 1-D hosts to create stable complexes with several guest molecules (20–23). We expected, therefore, that CUR-SO<sub>3</sub><sup>-</sup> would act as a templating ‘flask’ molecule, due to the electrostatic interaction, for the reaction of cationic molecules. In order to demonstrate this

anticipation, we attempted to prepare 1-D nanostructured polypyrrole (PPy) using the supramolecular interaction between cationic oxidised PPy and CUR-SO<sub>3</sub><sup>-</sup>.

A common method for preparing PPy involves chemical oxidation of the pyrrole molecules in organic or aqueous solution (24, 25). FeCl<sub>3</sub> is a typical oxidant for this purpose and also used here for templating synthesis of PPy in the presence of CUR-SO<sub>3</sub><sup>-</sup> (26). It is known for PPy that each third constitutional unit can be protonated (Figure 1(B) and see Scheme S1 of the Supporting Information, available online) (26) and this cationic PPy can interact with anionic additives such as anionic surfactants (27), polymers (28, 29) and DNA (9). Thus, the prepared PPy can first interact with CUR-SO<sub>3</sub><sup>-</sup> by electrostatic interactions and can be wrapped efficiently by hydrophobic interactions as in the case of SPG/ionic conjugated polymer complexes (17). Here, we report a novel fabrication method for circular dichroism (CD)-active, 1-D PPy in the presence of CUR-SO<sub>3</sub><sup>-</sup>.

### Results and discussion

CUR-SO<sub>3</sub><sup>-</sup> was synthesised according to our previous report (21). The optical rotatory dispersion (ORD) spectra were measured to investigate the solution structure of CUR-SO<sub>3</sub><sup>-</sup> in water (Figure 2). In the ORD spectra of  $\beta$ -1,3-glucans, it is known that the triple-stranded helical SPG and CUR show a positive sign with a maximum at around 300 nm (30–32). CUR-SO<sub>3</sub><sup>-</sup> in water, however, gave a negative sign with the monotonous decrease at the wavelength region from 600 to 250 nm, similar to those of

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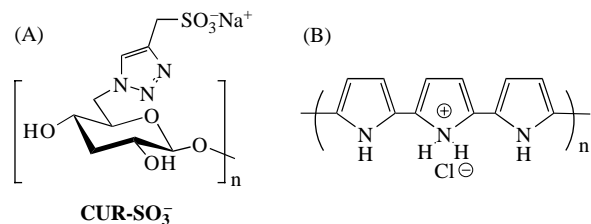


Figure 1. Repeating units of  $\text{CUR-SO}_3^-$  (A) and partially protonated PPy synthesised with  $\text{FeCl}_3$  (B).

single-stranded SPG or single-stranded cationic  $\text{CUR-N}^+$  (20, 31). According to the literature (33), the negative sign of  $\beta$ -1,3-glucans can be generally attributed to the single-stranded form, meaning that  $\text{CUR-SO}_3^-$  exists as the single-stranded form in water as in the case of  $\text{CUR-N}^+$ .

A  $\text{CUR-SO}_3^-$  aqueous solution and a pyrrole aqueous solution were mixed thoroughly, and a  $\text{FeCl}_3$  solution was added to the mixture to initiate polymerisation. Vis–near-infrared (NIR) spectroscopy provided evidence for the polymerisation of pyrrole and formation of  $\text{CUR-SO}_3^-/\text{PPy}$  complexes (Figure 3(A)). Difference spectra of  $\text{CUR-SO}_3^-/\text{PPy}$  complexes are shown in Figure 3(A) (inset), in which the absorption band extended into the NIR region characteristic of an oxidised PPy appears after a few hours of incubation. This indicates that pyrrole was polymerised in the presence of  $\text{CUR-SO}_3^-$  under these conditions (29). The spectral change showed that it took approximately 150 h to complete the polymerisation of pyrrole. When the polymerisation of pyrroles was carried

out in the absence of  $\text{CUR-SO}_3^-$  or in the presence of  $\text{CUR-N}^+$  instead of  $\text{CUR-SO}_3^-$ , little change in the absorption spectra was recognised (Figure S1A and B, respectively, of the Supporting Information, available online). This result implies that the increase in the pyrrole local concentration by interacting with anionic groups of  $\text{CUR-SO}_3^-$  is very important for promotion of the polymerisation under such dilute conditions (27, 29). In addition to this behaviour, a new absorption band appeared at 474 nm after 24–48 h of incubation and increased as the reaction time (Figure 3(A)), which is identified as a  $\pi$ – $\pi^*$  transition of PPy. This  $\pi$ – $\pi^*$  transition absorption observed for  $\text{CUR-SO}_3^-/\text{PPy}$  complexes was red-shifted by 20–25 nm, compared to those of PPy synthesised with  $\text{FeCl}_3$  without special additives (29). This distinct red-shift is associated with an increment of the effective conjugation length in the PPy backbone, which was same as that observed for  $\beta$ -1,3-glucan/conjugated polymer complexes prepared by mixing  $\beta$ -1,3-glucans and conjugated polymers (17, 34). In order to investigate the importance of the wrapping ability of  $\text{CUR-SO}_3^-$ , pyrrole was polymerised in the presence of poly(sodium 4-styrenesulphonate) (PSS) instead of  $\text{CUR-SO}_3^-$  as a templating molecule under the same conditions (35). A notable increment in the absorption in the NIR region originated from the polymerisation of pyrrole was observed, but no characteristic peak at 474 nm was detected (Figure 3(B)). This result strongly supports the idea that the red-shift of the  $\pi$ – $\pi^*$  transition absorption was caused by the wrapping effect of  $\text{CUR-SO}_3^-$ .

Next, we investigated the CD spectroscopy of the  $\text{CUR-SO}_3^-/\text{PPy}$  complex solution, because the PPy conformation may be affected by a right-handed helical structure of  $\text{CUR-SO}_3^-$ . Previous reports have suggested that induced CD (ICD) signals could be detected in the  $\pi$ – $\pi^*$  transition region from the  $\beta$ -1,3-glucan/conjugated polymer solution (17). However, only a very weak positive CD signal, if it exists, was recognised from the  $\text{CUR-SO}_3^-/\text{PPy}$  complex solution prepared by *in situ* polymerisation (Figure 4, solid red line). This weak ICD was attributed to the rigid conformation of oxidised PPy, which may prevent PPy from forming a stable chiral complex with  $\text{CUR-SO}_3^-$  (34). Then, the  $\text{CUR-SO}_3^-/\text{PPy}$  complex solution was treated with hydrazine in order to reduce the as-prepared PPy. As a result, split-type ICD was clearly detected in the transition region (Figure 4, solid blue line). The shape and sign of the ICD pattern were the characteristic of a right-handed helix of the PPy backbones (36, 37), reflecting a right-handed helical structure of  $\beta$ -1,3-glucans (38). This result strongly supports the view that  $\text{CUR-SO}_3^-$  can wrap PPy in solution and that the helical structure is induced from achiral PPy.

In order to obtain more direct evidence for the formation of  $\text{CUR-SO}_3^-/\text{PPy}$  complexes, the atomic force microscopic (AFM) observation was carried out for the as-prepared  $\text{CUR-SO}_3^-/\text{PPy}$  complex solution incubated for 72 h and for the  $\text{CUR-SO}_3^-$  solution on newly cleaved mica surfaces.

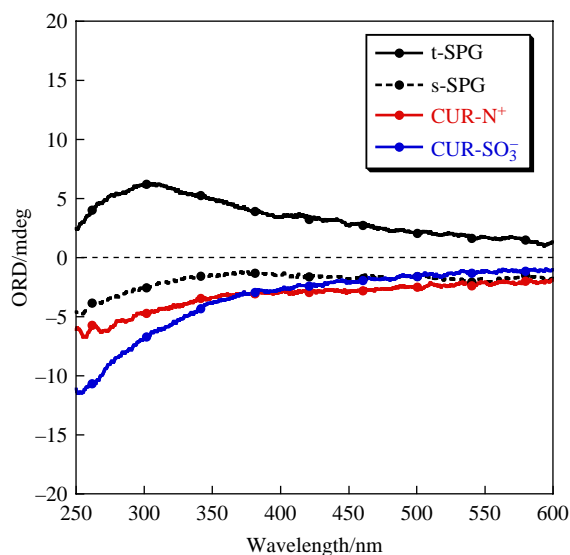


Figure 2. ORD spectra of  $\text{CUR-SO}_3^-$  in water (1 mg/ml, solid blue line),  $\text{CUR-N}^+$  in water (1 mg/ml, solid red line), triple-stranded SPG in water (t-SPG, 1 mg/ml, solid black line) and single-stranded SPG in 0.5 M NaOH (s-SPG, 1 mg/ml, dashed black line).

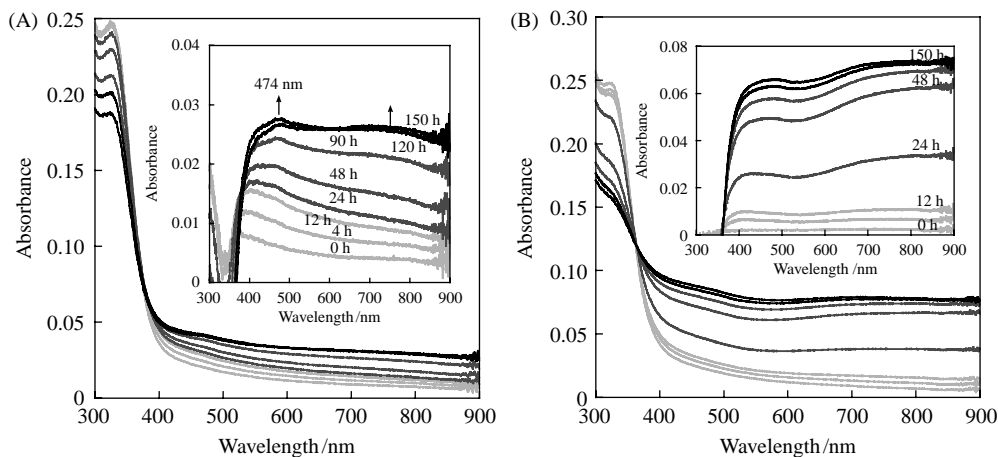


Figure 3. Time dependence of vis-NIR spectra of pyrrole oxidised in the presence of CUR-SO<sub>3</sub><sup>-</sup> (A) and PSS (B). Inset: difference spectra.

Fibrous structures having the uniform 1.3 nm height in average and the 20–400 nm length were observed from the AFM image of CUR-SO<sub>3</sub><sup>-</sup>/PPy complexes (Figure 5(A)). The transmission electronic microscopy (TEM) image of CUR-SO<sub>3</sub><sup>-</sup>/PPy complexes also presented the similar fibrous structure (Figure S2). These results were much different from that of CUR-SO<sub>3</sub><sup>-</sup> itself, but the average height of the observed structure was approximately 0.4 nm (Figure 5(C)). This height was comparable with that of CUR-N<sup>+</sup> existing as a single-stranded form in water (20). This distinct structural change was caused by polymerisation of pyrrole, implying that *in situ*-prepared oligomers or polymers of pyrrole would interact with CUR-SO<sub>3</sub><sup>-</sup> through supramolecular interactions and form 1-D fibrous structures.

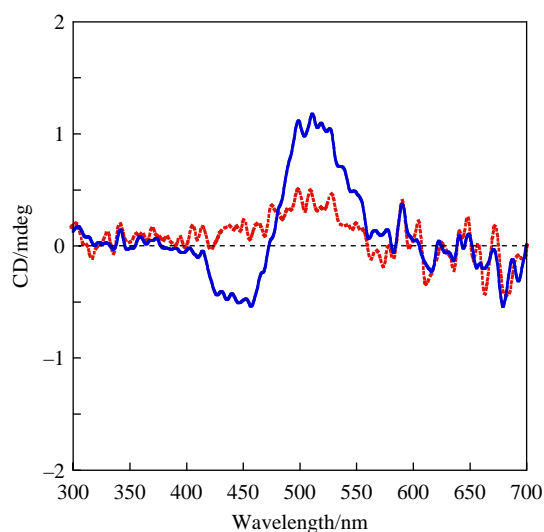


Figure 4. CD spectra of as-prepared (solid red line) and reduced (solid blue line) CUR-SO<sub>3</sub><sup>-</sup>/PPy complex solution incubated for 150 h; [hydrazine] = 14 mM, *d* = 1.0 mm, 25°C.

Time dependence of the morphological change observed by AFM was also investigated. When the incubation time of the solution was prolonged to 150 h, the fibrous structure and its height were scarcely changed any more (Figure 5(B)), even

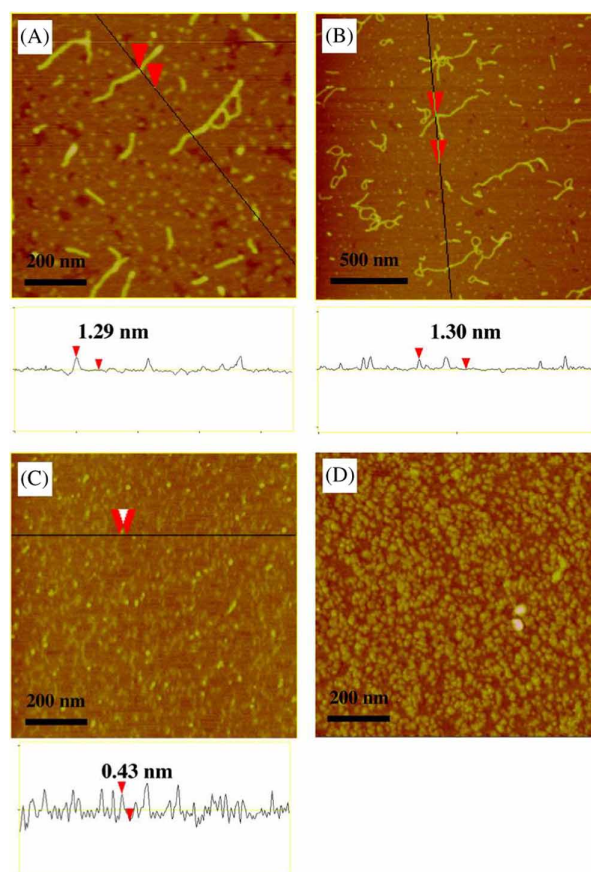


Figure 5. AFM height images of CUR-SO<sub>3</sub><sup>-</sup>/PPy complexes incubated for 72 h (A) and 150 h (B), CUR-SO<sub>3</sub><sup>-</sup> (C) and PSS/PPy complexes (D).



though absorption spectra characteristic of pyrrole polymerisation further increased in this time range (Figure 3(A)). On the other hand, PSS/PPy complex prepared under the same conditions as CUR-SO<sub>3</sub><sup>-</sup>/PPy complex showed no such fibrous structure but the granulated structure (Figure 5(D)), implying that the wrapping ability of CUR-SO<sub>3</sub><sup>-</sup> is very important to fabricate nanowires from polymer complexes. These results suggest that the *in situ* polymerisation of pyrrole can proceed under the template effect of CUR-SO<sub>3</sub><sup>-</sup>.

From these results, the following mechanism can be proposed; partially protonated oligomers or polymers of pyrrole are formed gradually in solution under dilute concentrations. The formed cationic oligomers or polymers of pyrrole can electrostatically interact with anionic groups of CUR-SO<sub>3</sub><sup>-</sup> and are integrated into the hydrophobic cavity of CUR-SO<sub>3</sub><sup>-</sup> and fibrous structures are formed eventually. Then, the concentrated oligomers can be further polymerised efficiently in the host cavity to form the fibrous structure to extend the effective conjugation length of the PPy backbone (39).

## Conclusion

We demonstrate the *in situ* preparation of helical 1-D nanostructured-PPy wrapped by anionic semi-artificial CUR, CUR-SO<sub>3</sub><sup>-</sup>, that acts as both a templating molecule and a 1-D host. In the present system, introduction of functional groups into 6-position of CUR by click chemistry was a key idea for modification of β-1,3-glucans. This indicates that various semi-artificial templating molecules can be easily designed and synthesised from β-1,3-glucans. We believe, therefore, that this system would be applicable more fruitfully to design the templating molecules bearing various functions for both organic and inorganic materials.

## Experimental

### Chemical preparation of PPy

An aqueous solution of distilled pyrrole (30 mM, 50 μl) was added to 620 μl of CUR-SO<sub>3</sub><sup>-</sup> solution (2.4 mM to monomer unit), and the solution was mixed. Aqueous FeCl<sub>3</sub> (50 mM, 30 μl) was added as an oxidant to initiate the polymerisation of pyrrole. The mixed solution was incubated at room temperature to obtain CUR-SO<sub>3</sub><sup>-</sup>/PPy complexes. Other additives, such as CUR-N<sup>+</sup> and PSS, were used in the same procedure.

### Vis-NIR and CD spectroscopy

Vis-NIR and CD spectroscopic studies were performed on a JASCO V-570 spectrophotometer and JASCO JW-720, respectively. Optical length: 1.0 mm, solvent: purified water and temperature: 25°C

### AFM observation

AFM imaging was performed in air using the tapping mode on a Veeco Nanoscope IIIa and NanoProbe tips. Each sample solution was cast on a mica substrate and dried for more than 6 h under reduced pressure before AFM observation.

### TEM observations

TEM image was acquired using a JEOL TEM-2010 microscope (accelerate voltage 120 kV). Each solution was placed on a copper TEM grid, and the TEM grid was dried under reduced pressure for more than 6 h before TEM observations.

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