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From Thiophene [2]Rotaxane to Polythiophene Polyrotaxane

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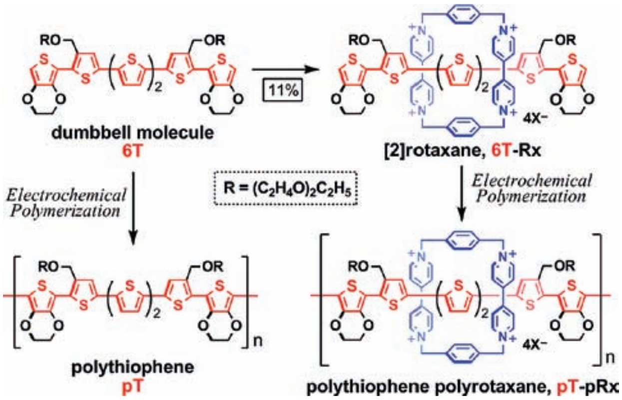
Interlocked molecules such as rotaxanes and catenanes have been studied as promising candidates for molecular machinery due to the mechanical movement between the components.[1] The synthesis of macromolecular interlocked molecules[2] is one methodology to realizing a molecular machine working with macroscale mechanical motion. However, most of the conventional polyrotaxanes[2] and polycatenanes[3] consist of a flexible molecular backbone. The flexible molecular backbone is not desirable because the mechanical motion is dissipated by the conformational changes of the flexible backbone.[4] From this point of view, the oligothiophene is an ideal component to construct macromolecular molecular machinery because of its rigidity and polymerizability.[5] Therefore, we have synthesized the thiophene rotaxanes[6] from the host−guest pair of the electron-rich thiophene derivatives and the electron-poor cyclophane, cyclobis(paraquat-*p*-phenylene)[7] (**CBPQT^{4+}**) developed by Stoddart.

Some groups have challenged the synthesis of the polythiophene (*pseudo-*)polyrotaxanes. Although Swager has reported pioneering studies on the electrochemical synthesis of the macromolecular interlocked compounds,[8] no report has been published on polythiophene polyrotaxanes. The polymetallorotaxane[9] is not regarded as a polythiophene polyrotaxane, because the thread is a copolymer consisting of the thiophene and the ligand units. In the case of the cyclodextrin host, *partially encapsulated* polythiophene is obtainable through the (electro)chemical polymerization of the *inclusion complex*.[10] In the case of the **CBPQT^{4+}** host, however, the conventional protocol is not available because the electrostatic repulsive force between the tetracationic cyclophane and the oligothiophene radical cation dissociates the inclusion complex[11] prior to polymerization. In this study, we applied a new protocol (Scheme 1). First, we synthesized the thiophene [2]rotaxane (**6T-Rx**) consisting of **CBPQT^{4+}** and the dumbbell-shaped sexithiophene derivative (**6T**). Then, we obtained the polythiophene polyrotaxane (**pT-pRx**) film through electrochemical polymerization of **6T-Rx**. This protocol enables us to obtain the polythiophene polyrotaxane with a *well-defined repeating unit*. Here, we report the optical and electrochemical property of the thiophene [2]rotaxane and the polythiophene polyrotaxane film.

The [2]rotaxane **6T-Rx** was synthesized by the template-directed synthesis of **CBPQT^{4+}** on the dumbbell-shaped sexithiophene **6T**. The yield of 11% is comparable to literature results.[4] We confirmed the association constant between the model compound **4T** [thread without two 3,4-ethylenedioxythiophene (EDOT) units of **6T**] and **CBPQT^{4+}** to be 1500 M^{-1} (at 298 K in CD_3CN, Figure S9).

Figure 1 shows ^1H NMR spectra of the dumbbell **6T** and the [2]rotaxane **6T-Rx**·$4PF_6$. Compared to free dumbbell **6T**, an upfield shift of the protons **b**, **c**, **d**, and **e** was confirmed in the [2]rotaxane. On the other hand, the protons of the EDOT units (**a**, **f**, **g**) and the ethyleneglycol chains showed a downfield shift. The up- and downfield shifts are attributed to the shielding effect inside the cavity of **CBPQT^{4+}** and the deshielding effect in the periphery of the **CBPQT^{4+}** aromatic units, respectively.[6] These results are consistent with those deduced from the rotaxane structure. We confirmed no spectral change when the solution of the [2]rotaxane **6T-Rx** or the 1:1 mixture of the free dumbbell **6T** and the macrocycle were heated to 70 °C for 24 h (Figures S10 and S11). Since the end part of the dumbbell **6T** is bulky enough to interlock the **CBPQT^{4+}** macrocycle, our obtained product is the rotaxane and not the pseudorotaxane.

Scheme 1. Protocol for Synthesizing Thiophene [2]Rotaxane **6T-Rx** and Polythiophene Polyrotaxane **pT-pRx**



The UV−vis spectra of **6T** and **6T-Rx**·$4PF_6$ (see Figure S12) indicate that rotaxanation results in a red shift (maximum absorption wavelength $\lambda_{max} = 429 \rightarrow 436$ nm) and a smaller absorption of the $\pi-\pi^*$ band of the thiophene units (molar extinction coefficient $\epsilon = 5.2 \times 10^4 \rightarrow 4.3 \times 10^4$ M^{-1} cm^{-1}). This result confirms the electronic interaction between the sexithiophene and the bipyridinium units.[6] The charge-transfer (CT) band is detectable as a small absorption from 500 to 700 nm ($\epsilon = 1500$ M^{-1} cm^{-1} at 550 nm).

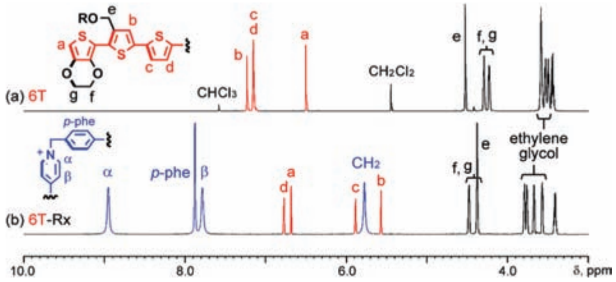


Figure 1. ^1H NMR spectra of (a) **6T** and (b) **6T-Rx**. Solvent: CD_3CN. Temperature: room temperature. Labeling scheme is also depicted.

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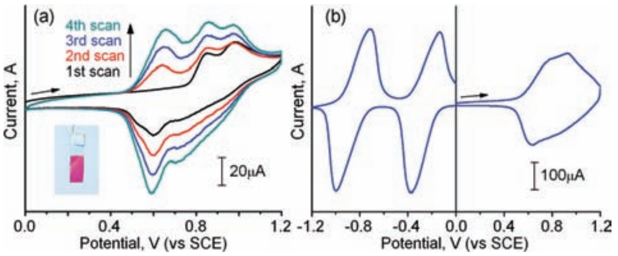

Figure 2. Cyclic voltammograms. (a) [2]Rotaxane **6T-Rx** in MeCN. Sample concentration: 1 mM. Scan rate: 50 mV s^{-1}. Inset: Photograph of the **pT-pRx** film on an ITO electrode. (b) Polythiophene polyrotaxane **pT-pRx** film on glassy carbon. Scan rate: 100 mV s^{-1}.

6T-Rx was electrochemically polymerized by cyclic potential scans (Figure 2a). Since we used tetrabutylammonium·ClO$_4$ (TBA·ClO$_4$) as the supporting electrolyte (Concentration: 0.1 M), the counterion of **6T-Rx** is considered to be ClO$_4^-$.[12] In the first anodic scan, the first oxidation took place at the half-wave potential ($E_{1/2}$) of +0.81 V (Figure S13b). In the second anodic scan, a new oxidation peak appeared around +0.65 V (Figure 2a). The intensity of the new redox peak increased with the number of potential scans. We confirmed the formation of the red-purple film of the polythiophene polyrotaxane (**pT-pRx**) on the indium−tin oxide (ITO) coated glass slide (inset in Figure 2a).

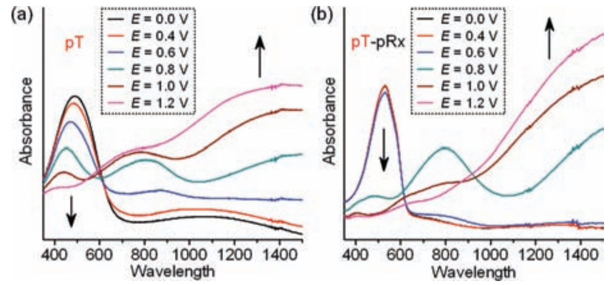

Figure 3. Spectroelectrochemistry of (a) polythiophene **pT** and (b) polythiophene polyrotaxane **pT-pRx** films on ITO electrode. *E*: Applied potential vs Ag wire.

Compared to **6T-Rx**, the **pT-pRx** film shows a large red shift of the $\pi-\pi^*$ band ($\lambda_{max} = 436 \rightarrow 530$ nm, Figure S12), indicating the extension of the π-conjugation. The CT band of the **pT-pRx** film is detectable at ~700 nm.

The polythiophene polyrotaxane film is electrochemically active. The cyclic voltammogram (CV) of the **pT-pRx** film shows reversible redox waves of the polythiophene and **CBPQT^{4+}** in the oxidation and the reduction regions, respectively (Figure 2b). We characterized the oxidation process of the polythiophene (**pT**) and the **pT-pRx** films by spectroelectrochemistry (Figure 3). The intensity of the $\pi-\pi^*$ band for the **pT** film ($\lambda_{max} = 490$ nm) gradually changed at an applied potential of ~+0.7 V (vs Ag wire pseudoreference electrode, Figure S14). In the case of the **pT-pRx** film, we noticed a steep absorption change at +0.7 V (Figure S14). The steep absorption change in response to the applied potential is due to the localization of the redox process.[9a] When we applied +0.8 V to the **pT-pRx** film, the $\pi-\pi^*$ band disappeared and two absorption bands were detectable at 800 nm and the NIR region (Figure 3b). This spectral change is assigned to the generation of the radical cations (polarons) in the polythiophene.[13] Further oxidation ($E = +1.2$ V) resulted in the appearance of the single absorption band in the NIR region, indicating the generation of the dications (bipolarons).[13] The spectrum at +1.2 V returned to its original shape when we applied 0.0 V on the **pT-pRx** film (Figure S15). In the CV trace of the **pT-pRx** film, the peak area for the two-electron oxidation of the polythiophene is almost the same as that for the two-electron reduction of **CBPQT^{4+}** (Figure S16). This result indicates that the polythiophene generates a dication per one **CBPQT^{4+}**. Presumably, the electrostatic repulsive force of the tetracationic **CBPQT^{4+}** confines the radical cation and dication between two **CBPQT^{4+}**s on the polythiophene, which results in the lower degree of charge delocalization in the **pT-pRx**.

In conclusion, we succeeded to synthesize the polythiophene polyrotaxane **pT-pRx** from the thiophene [2]rotaxane **6T-Rx**. Since the polythiophene provides electrochemically active, long, and multidentate binding sites, the synthesis of **pT-pRx** is an important milestone to fabricate the electrochemically controllable polyrotaxane. The **pT-pRx** is attractive not only as a component for constructing macromolecular machinery but also as new type of insulated molecular wire[14] having donor−acceptor interaction between the macrocycle and the conductive polymer. The detailed electronic property of **pT-pRx** is now under investigation.

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Supporting Information Available: Experimental procedures, full spectroscopic data for all new compounds, ^{1}H NMR titration, and electrochemical data. This material is available free of charge via Internet at http://pubs.acs.org.

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