Control of polythiophene redox potentials based on supramolecular complexation with helical schizophyllan

Shuichi Haraguchi, Youichi Tsuchiya, Tomohiro Shiraki, Kazuki Sada and Seiji Shinkai*

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, 819-0395, Japan

[b] RIKEN, Saitama, 351-0198, Japan.

[c] Infomation Technologies and Nanotechnology (ISIT), Fukuoka, 819-0385, Japan.

[d] Department of Nanoscience, Sojo University, Kumamoto, 860-0082, Japan.

shinkai_center@mail.cstm.kyushu-u.ac.jp

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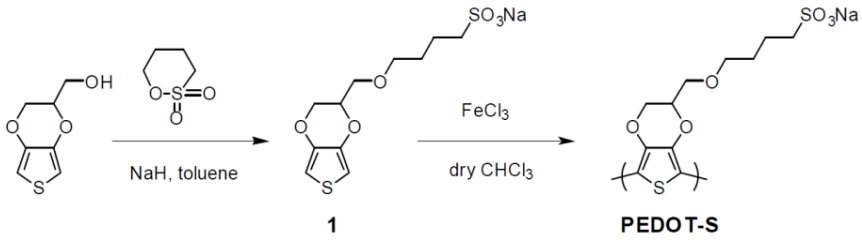
1. Experimental details

Native schizophyllan (Mw = 1.5×10^5) was kindly supplied by Mitsui Seito, Co., Ltd. (Japan). Other chemicals were purchased from Aldrich or Tokyo Kasei Chemicals. The synthesis and characterization of a polythiophene derivative, PT-1, were previously reported.[1] UV-vis spectra were acquired on a Shimazu UV-2500PC spectrometer. All circular dichroism (CD) spectra were measured on a JASCO 720WI spectropolarimeter using a cylindrical quartz cell with a path length of 10 mm. Voltammetric experiments were performed in a one-compartment, three-electrode electrochemical cell with the use of an electrochemical analyzer (BAS 100B). Measurements were performed with a Pt working electrode in anaerobic 0.1 M NaCl aq. solutions with a Pt wire counter electrode and a Ag/AgCl reference electrode at 20 ^{o}C. The pulse amplitude maintained at 50 mV for DPV at a scan rate of 10 mV/s and a pulse width of 50 msec. The potential scan was performed from positive to negative potential. Size exclusion chromatography (SEC) was performed with a Jasco PU-980 Plus liquid chromatograph system equipped with a UV–visible detector (UV-970 Plus), an RI detector (RI-2031 Plus) and a column oven (CO-2060 Plus). A SEC column (Shodex OHpak SB-806M HQ) was connected and H_2O containing 100 mM of $NaNO_3$ was used as the eluent at a flow rate of 0.5 mL/min at 40 °C.

2. Chemical synthesis of PEDOT-S

PEDOT-S was prepared according to the following scheme.[2,3]



4-(2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid, sodium salt (**1**); A solution of 200 mg of 2,3-dihydrothieno [3,4-b][1,4]dioxin-2-yl methanol was added to a suspension of 34 mg (1.42 mmol) sodium hydride in 10 ml of dry toluene under argon atmosphere. A solution of 158 mg (1.26 mmol) of butane sulfone in 5 ml of dry toluene was added slowly. The mixture was heated at reflux temperature for 2 h. After cooling, acetone was added to the mixture, which was

filtered through a fine porosity frit (0.45 μm). The recovered precipitate was washed with acetone under an argon blanket. Pale yellow powder, 300 mg (0.93 mmol), 80 % yield. ^{1}H NMR (400 MHz, D_2O, 25 ^oC, TMS): δ = 6.41 (m, 2H), 4.32 (d, 1H), 4.17 (m, 1H), 4.02 (m, 1H), 3.65 (m, 2H), 3.51 (m, 2H), 2.82 (m, 2H), 1.62 (m, 4H).

Polymer (PEDOT-S); EDOT-S (**1)** (15 mg, 0.04 mmol) and ferric chloride (20 mg, 0.12 mmol) were mixed in 10 mL of chloroform. The reaction was carried out under argon at room temperature over 24 h. The solution was then poured into methanol, containing a few drops of hydrazine solution. After filtration, the recovered dark precipitate was stirred in a 1 M sodium hydroxide methanolic solution (200 mL) for 2 days in order to exchange the iron complexed with the sulfonate groups for sodium ion. The solution was filtered again, and the black polymer powder was stirred in 200 mL of deionized water for 1 day and then filtered again. The polymer was then precipitated in acetone and dried under vacuum. Finally, the polymer was dialyzed with deionized water for 3 days using a 3,500 g/mol cutoff membrane prior to use. SEC (Shodex OHpak SB-806M HQ, 0.1 M $NaNO_3$ aq, 40 ^oC, pullulan standards) M_w (M_w/M_n) = 7.7 x 10^3 (2.06). ^{1}H NMR in D_2O gave very broad peaks possibly due to low segment mobility.[4]

3. Preparation of the SPG/PEDOT-S complex

A few drops of hydrazine solution were added to PEDOT-S aqueous solution and the mixture was left for 2 days. After stabilizing reductive reactions, DMSO solution containing SPG was added to the reduced PEDOT aqueous solution and then the mixed solution was left for 3 days at room temperature. After this operation, the complex was precipitated by adding a large amount of acetone and collected through a centrifuge (3,500 rpm, 30 min). A SPG/oxidized-PEDOT-S mixture was prepared, according to the same procedure, by adding SPG DMSO solution to the PEDOT-S (partially oxidized) aqueous solution.

3-1. UV-vis and CD spectra of the SPG/PEDOT-S complex

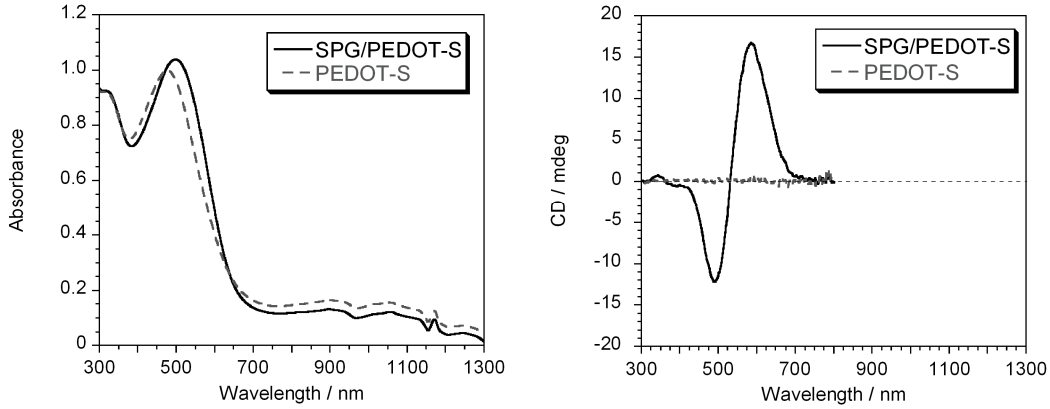


Fig. S1 UV-vis (left) and CD (right) spectra of the aqueous solution of the SPG/PEDOT-S complex (solid line) and PEDOT-S itself (dash line); [SPG] = 1.3 mM (4 glucose units), [PEDOT-S] = 0.8 mM, [hydrazine] = 50 mM, water/(water+DMSO) = 0.89, *d* = 10 mm, 25 ^{o}C.

3-2. UV-vis and CD spectra of SPG/oxidized-PEDOT-S mixture

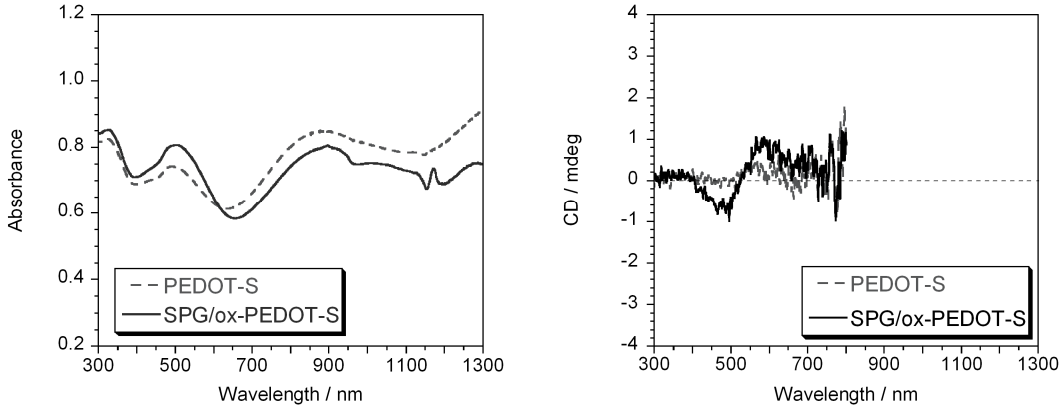


Fig. S2 UV-vis (left) and CD (right) spectra of the aqueous solution of SPG/oxidized-PEDOT-S mixture (solid line) and oxidized-PEDOT-S itself (dash line).

3-3. UV-vis and CD spectra of dextran/PEDOT-S mixture

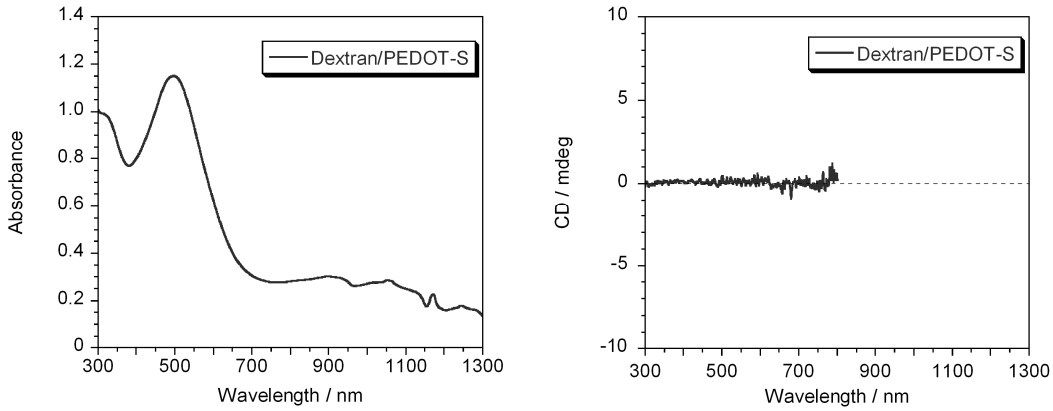


Fig. S3 UV-vis (left) and CD (right) spectra of the aqueous solution of dextran/PEDOT-S mixed solution; [dextran] = 1.7 mM (one repeating unit consists of 3 glucose units), [PEDOT-S] = 0.8 mM, [hydrazine] = 50 mM, water/(water+DMSO) = 0.89, *d* = 10 mm, 25 ^{o}C.

3-4. AFM observation of the SPG/PEDOT-S complex

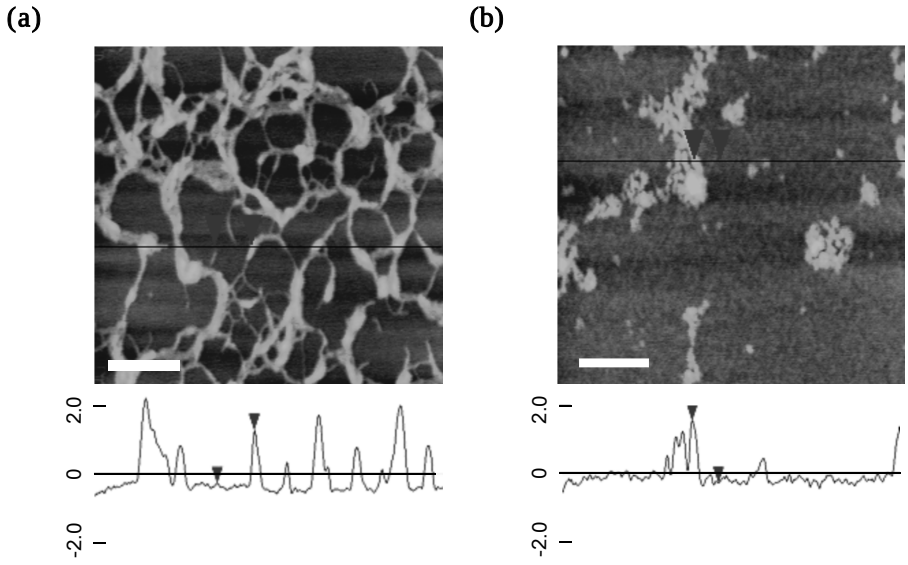


Fig. S4 AFM images of the films of (a) SPG/PEDOT-S complex and (b) PEDOT-S cast from dilute aqueous solutions. Scale bar: 200 nm

4. Preparation and characterization of the SPG/PT-1 complex

The SPG/PT-1 complex was prepared according to our previous reports.[1] DMSO solution containing SPG was added to the PT-1 aqueous solution and then the mixed solution was left for 3 hours at room temperature. After preparation, the complex was precipitated by adding a large amount of acetone and collected through a centrifuge (3,500 rpm, 30 min). A mixture of t-SPG and PT-1 was prepared by adding t-SPG aqueous solution to the PT-1 aqueous solution.

4-1. Change of UV-vis spectra during the p-doping reaction

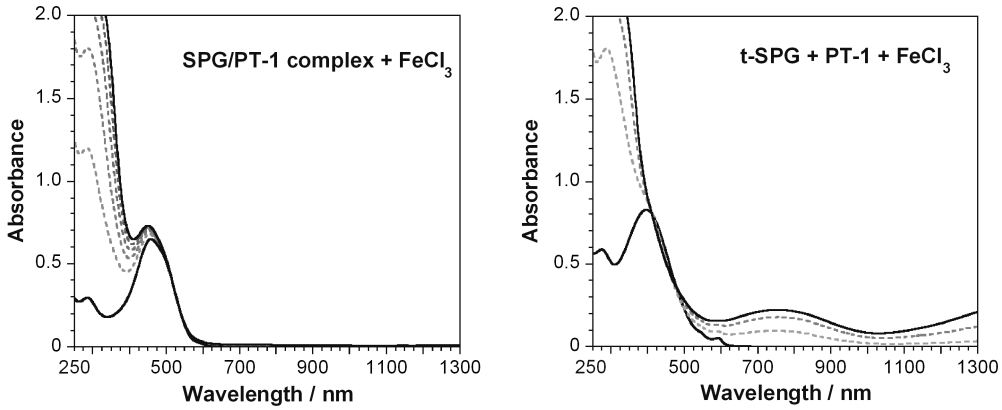


Fig. S5 UV-vis spectral change during the p-doping reaction of the SPG/PT-1 complex (left) and mixture of t-SPG and PT-1 (right), with adding $FeCl_3$ in aqueous solution.

References

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