Supplementary Information

Electrochemical synthesis, optical, electrochemical, and electrochromic characterizations of indene and 1,2,5-thiadiazole-based poly(2,5-dithienylpyrrole) derivatives

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Contents:

1. The synthetic procedures of the SNS derivatives and DTP (Fig. 1)

1.1. Synthesis of 1-(2,3-dihydro-inden-4-yl)-2,5-di(thiophen-2-yl)-pyrrole (DIT)

1,4-Di(2-thienyl)-1,4-butanedione (1.25 g, 5 mmol), 2,3-dihydro-inden-4-amine (0.93 g, 7 mmol), PTSA (0.1 g, 0.58 mmol), and toluene (20 mL) were stirred at 110 °C overnight in a 100 mL round bottom flask equipped with a N_2 inlet. Toluene was evaporated under reduced pressure and crude product was purified with column chromatography (silica gel, dichloromethane:hexane = 1:1) to give the desired compound. Yield: 71 %. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.35 (d, 1H, phenyl-H), 7.23 (dd, 1H, phenyl-H), 7.12 (d, 1H, phenyl-H), 7.00 (d, 2H, Th-H), 6.80 (d, 2H, Th-H), 6.55 (d, 4H, Th-H and Py-H), 2.95 (t, 2H, phenyl-C$\underline{H}_2$-), 2.50 (t, 2H, phenyl-C$\underline{H}_2$-), 1.97−1.90 (m, 2H, phenyl-CH$_2$-C$\underline{H}_2$-). Elem. anal. calcd. for $C_{21}H_{17}NS_2$: C, 72.58 %; H, 4.93 %; N, 4.03 %. Found: C, 72.52 %; H, 4.88 %; N, 3.97 %.

1.2. Synthesis of 4-(2,5-di(thiophen-2-yl)-pyrrol-1-yl)benzo[c][1,2,5]thiadiazole

(BDTA)

BDTA was synthesized using a similar method of DIT, yield: 62 %. ^{1}H-NMR (400MHz, DMSO-d_6): δ 8.32 (d, 1H, phenyl-H), 7.86 (m, 2H, phenyl-H), 7.18 (d, 2H, Th-H), 6.80 (d, 2H, Th-H), 6.70 (d, 4H, Th-H and Py-H). Elem. anal. calcd. for $C_{18}H_{11}N_3S_3$: C, 59.15 %; H, 3.03 %; N, 11.50 %. Found: C, 59.02 %; H, 2.96 %; N, 11.54 %.

*1.3. Synthesis of 4-(tridecan-7-yl)-dithieno[3,2-b:2',3'-d]pyrrole (**DTP**)*

3,3'-Dibromo-2,2'-bithiophene (1.00 g, 3.09 mmol) was added in a 100 mL round bottom flask followed by the addition of *t*-BuONa (0.71 g, 7.41 mmol) and 50 mL toluene at room temperature. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane (49 mg, 0.06 mmol) was added to this reaction mixture followed by the addition of 1,1'-ferrocenediyl-bis(diphenylphosphine) (133 mg, 0.24 mmol) and tridecan-7-amine (0.62 g, 3.09 mmol) at room temperature. Reaction mixture was stirred for 0.5 h and then heated to reflux overnight. The solvent was evaporated under reduced pressure to get crude solid, which was purified with column chromatography (silica gel, hexane/dichloromethane = 10:1) to give DTP, yield: 70 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.10 (d, 2H, Th-$\underline{H}$), 7.01 (d, 2H, Th-$\underline{H}$), 4.22-4.18 (m, 1H, N-C$\underline{H}$-), 2.03-1.98 (m, 2H, N-CH-C$\underline{H}_2$-), 1.85-1.79 (m, 2H, N-CH-C$\underline{H}_2$-), 1.19-1.06 (m, 16H, -C$\underline{H}_2$-), 0.81 (t, 6H, -C$\underline{H}_3$). Elem. Anal. Calcd. for $C_{21}H_{31}NS_2$: C, 69.75 %; H, 8.64 %; N, 3.87 %. Found: C, 69.61 %; H, 8.61 %; N, 3.75 %.

2. Electrochemical and spectroelectrochemical characterizations

Electrochemical studies were implemented on a three-component cell with a CHI660a electrochemical analyzer (U.S.A.). An Ag/AgCl electrode, platinum wire, and ITO coated glass plate were used as reference, counter, and working electrodes, respectively. Spectroelectrochemical studies were performed with V-630 and V-670 JASCO UV-Visible spectrophotometer to record in situ UV-Visible spectra by operating in a time course mode. UV-Visible spectroelectrochemical experiments were carried out in a quartz cuvette of 1 cm path length assembled as an electrochemical cell with an ITO working electrode, a Pt wire as counter electrode, and Ag/AgCl as reference electrode.

3. Electrolytes in ECDs

Electrolyte membranes were prepared using the solution casting method. 0.2 g poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP), 0.6 g EPIDIL, and 0.4 g propylene carbonate (PC) were mixed thoroughly with 100 mL acetone for 24 h. This mixture was poured into a flat Petri dish, and the acetone in the mixture in the Petri dish was then evaporated for 24 h at an ambient temperature in order to obtain dry transparent films. The films were stored in a desiccator to eliminate traces of the solvent and avoid moisture contamination.

4. Construction of ECDs

ECDs were constructed using two complementary polymers. PDIT, PBDTA, P(DIT-co-DTP), or P(BDTA-co-DTP) was employed as the anodically coloring material and PProDOT-Et_2 was used as the cathodically coloring material. The PProDOT-Et_2 films were electrodeposited onto ITO-coated glasses at +1.4 V. ECD was built by arranging the two polymer films (one oxidized, the other reduced) facing each other to be separated by an electrolyte membrane.

5. Electrochemical switching

5.1. Electrochemical switching of polymer films in solutions

The coloration switching time (τ_c) and bleaching switching time (τ_b) estimated at various double-step potential cycles are summarized in Table 5, the switching time was calculated at 90 % of the full-transmittance change because it is difficult to recognize any further color variation with the naked eye beyond these points. For PDIT film in EPIDIL solution, the optical switching time at 886 nm was found to be 1.84 s from the bleaching state to the coloring state and 1.78 s from the coloring state to the bleaching state at 100th cycles. P(DIT-co-DTP) and P(BDTA-co-DTP) films present shorter τ_c and longer τ_b than those of PDIT and PBDTA, respectively, indicating the incorporation of DTP unit into the polymer backbone facilitates color change from the dedoped to the doped state when we use EPIDIL as a supporting electrolyte.

5.2. Switching of ECDs

Upon switching the ECDs between −0.6 V and +1.2 V with a time interval of 5 s, the PBDTA/PProDOT-Et_2 ECD shows a switching time of 1.67 s at 590 nm from the bleaching state to the coloring state and 1.52 s from the coloring state to the bleaching state at 100th cycles. τ_c and τ_b of the ECDs were smaller than those in an ionic liquid solution, indicating the ECDs changed color faster from the neutral to the oxidation state than those in EPIDIL solution. Moreover, P(BDTA-co-DTP)/PProDOT-Et_2 ECD shows low switching times than those for PDIT/PProDOT-Et_2, PBDTA/PProDOT-Et_2, and P(DIT-co-DTP)/PProDOT-Et_2 ECDs, implying the P(BDTA-co-DTP) shortens the switching time between the reduction state to the oxidized state more than those of PDIT, PBDTA, and P(DIT-co-DTP) when we employ them as anodic polymers in ECDs.

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