A Dual-Polymer Electrochromic Device with High Coloration Efficiency and Fast Response Time: Poly[3,4-(1,4-butylene-(2-ene)dioxy)thiophene]–Polyaniline ECD


asia_201000763_sm_miscellaneous_information.pdf
Figure S1. Cyclic voltammograms for the PBueDOT and PEDOT electrodes.

CV profiles were processed in a 10 wt % LiTFSI-EtMeImTFSI hydrophobic electrolyte (monomer-free electrolytic medium) under a potential range between -1.2 V and 0.5 V (vs. Pt) at a scanning rate of 50 mV s⁻¹. This excitation cycle was repeated several times.

Figure S2. UV-vis absorbance spectra of the single PBueDOT ECDs: The solid lines (−), dashed lines (−−), and dotted lines (···) represent the single PBueDOT10, PBueDOT20, and PBueDOT30 ECDs, respectively. The spectrum of PBueDOT ECDs in the doped state (lower line for each sample) was recorded at ~ 0.5 V and that in the neutral state (upper line for each sample) at ~ -1.2 V.
The structure of single PBueDOT devices was ITO │ PBueDOT │ ITO. These were operated under potentiostatic conditions between -1.2 V and 0.5 V for 30 s / half cycle. The voltage was controlled to only allow the formation of one redox-couple.

![Graph](image)

**Figure S3.** Percent UV-vis transmittance spectra (%T) of the single PBueDOT ECDs. The solid lines (−), dashed lines (−−), and dotted lines (⋯) represent the single PBueDOT10, PBueDOT20, and PBueDOT30 ECDs, respectively. The upper and lower lines show the bleached and colored states for each sample.

![Graph](image)

**Figure S4.** Exchange charge during cyclic voltammetry of Figure 3.

The cyclic voltammetry was performed as a good preliminary study on the stability of the ECDs. The profile of the oxidation charge ($Q_{\text{ox}}$) and the reduction one ($-Q_{\text{red}}$) across the ECD as a function of cycle number would be, in turn, highly related to the device stability. Thus, we have calculated the $Q_{\text{ox}}$...
and \( Q_{\text{red}} \) (vs. Cycle number) during 600 cycles as depicted the Figure. As expected, this result shows that the reversible redox reactions are indeed occurred between the two conducting polymer electrodes.

**Synthesis**

![Chemical Structure](image)

**Synthesis of 2b**

Using the same procedure as that for 2a, combining 1 (130 mg, 0.5 mmol) and 2,3-\( o \)-isopropylidene-D-threitol (90 mg, 0.55 mmol) produced 166 mg of 2b (86% yield) as white solid. Mp: 146 °C. \( ^1\text{H-NMR} \) (CDCl\(_3\), 250 MHz) \( \delta \) 1.36 (m, 12H), 3.89 (d, \( J = 9.6 \) Hz, 2H), 4.16 (d, \( J = 9.6 \) Hz, 2H), 4.35 (m, 4H), 4.65 (m, 1H), 4.70 (m, 1H); \( ^{13}\text{C-NMR} \) (CDCl\(_3\), 62.5 MHz) \( \delta \) 14.16, 26.59, 61.70, 73.91, 110.24, 122.20, 152.31, 160.23; HRMS (EI) calcd for C\(_{17}\)H\(_{22}\)O\(_8\)S [M]\(^+\) 386.1035, found 386.1040.

![Chemical Structure](image)

**Synthesis of 3b**

Using the same procedure as that for 3a, the product is white solid and the yield is 82%. Mp: > 250 °C. \( ^1\text{H-NMR} \) (DMSO, 250 MHz) \( \delta \) 1.30 (s, 6H), 3.86 (m, 2H), 4.16 (m, 2H), 4.52 (s, 1H), 4.56 (s, 1H), 13.66 (s, 2H); \( ^{13}\text{C-NMR} \) (DMSO, 62.5 MHz) \( \delta \) 26.42, 73.07, 77.28, 109.49, 122.62, 151.56, 161.19; HRMS (FAB) calcd for C\(_{15}\)H\(_{14}\)O\(_8\)S [M]\(^+\) 330.0409, found 330.0406.

![Chemical Structure](image)

**Synthesis of 4b**

Using the same procedure as that for 4a, the product is pale yellow oil in 73% yield. \( ^1\text{H-NMR} \) (CDCl\(_3\), 250 MHz) \( \delta \) 1.34 (s, 6H), 3.80 (m, 2H), 4.16 (m, 2H), 4.40 (d, \( J = 4.0 \) Hz, 1H), 4.44 (d, \( J = 4.0 \) Hz, 1H), 6.75 (s, 2H); \( ^{13}\text{C-NMR} \) (CDCl\(_3\), 62.5 MHz) \( \delta \) 26.62, 74.94, 78.00, 109.76, 110.66, 149.14. HRMS (EI) calcd for C\(_{11}\)H\(_{14}\)O\(_4\)S [M]\(^+\) 242.0613, found 242.0609.
Synthesis of 2c

Using the same procedure as that for 2a, combining 1 (130 mg, 0.5 mmol) and 4,5-Dimethylbenzene-1,2-dimethanol (93 mg, 0.55 mmol) produced 190 mg of 2c (97% yield) as white solid. Mp: 148 °C. 1H-NMR (CDCl3, 250 MHz) δ 1.27 (t, J = 7.1 Hz, 6H), 2.13 (s, 6H), 4.26 (m, J = 7.1 Hz, 4H), 5.49 (s, 4H), 6.93 (s, 2H); 13C-NMR (CDCl3, 62.5 MHz) δ 14.24, 19.37, 61.17, 73.65, 117.84, 131.33, 132.19, 137.71, 150.94, 160.63; HRMS (EI) calcd for C20H22O6S [M]+ 390.1137, found 390.1140.

Synthesis of 3c

Using the same procedure as that for 3a, the product is white solid and the yield is 79%. Mp: > 250 °C. 1H-NMR (DMSO, 250 MHz) δ 2.17 (s, 6H), 5.50 (s, 4H), 7.10 (s, 2H), 13.31 (s, 2H); 13C-NMR (DMSO, 62.5 MHz) δ 19.33, 73.43, 118.80, 131.54, 132.71, 137.75, 150.68, 161.93; HRMS (FAB) calcd for C16H14O6S [M]+ 334.0511, found 334.0513.

Synthesis of 4c

Using the same procedure as that for 4a, the product is white solid in 44% yield. Mp: 116 °C. 1H-NMR (CDCl3, 250 MHz) δ 2.23 (s, 6H), 5.30 (s, 4H), 6.50 (s, 2H), 6.97 (s, 2H); 13C-NMR (CDCl3, 62.5 MHz) δ 19.33, 74.37, 106.57, 130.97, 133.08, 136.99, 147.91. HRMS (EI) calcd for C14H14O2S [M]+ 246.0715, found 246.0717.
$^{1}$H-NMR spectra of compound 2a in CDCl$_3$.

$^{13}$C-NMR spectra of compound 2a in CDCl$_3$. 
$^1$H-NMR spectra of compound 3a in DMSO.

$^{13}$C-NMR spectra of compound 3a in DMSO.
$^1$H-NMR spectra of compound 4a in CDCl$_3$.

$^{13}$C-NMR spectra of compound 4a in CDCl$_3$. 
$^1$H-NMR spectra of compound 2b in CDCl$_3$.

$^{13}$C-NMR spectra of compound 2b in CDCl$_3$. 

Chemical structure of compound 2b is shown.
H-NMR spectra of compound 3b in DMSO.

\[ \text{\^{1}H-NMR spectra of compound 3b in DMSO.} \]

\[ \text{\^{13}C-NMR spectra of compound 3b in DMSO.} \]
$^1$H-NMR spectra of compound 4b in CDCl$_3$.

$^{13}$C-NMR spectra of compound 4b in CDCl$_3$. 
$^1$H-NMR spectra of compound 2c in CDCl$_3$.

$^{13}$C-NMR spectra of compound 2c in CDCl$_3$. 
$^1$H-NMR spectra of compound 3c in DMSO.

$^{13}$C-NMR spectra of compound 3c in DMSO.
$^1$H-NMR spectra of compound 4c in CDCl$_3$.

$^{13}$C-NMR spectra of compound 4c in CDCl$_3$. 