Supplementary Information

Color Tuning of Black for Electrochromic Polymers Using Precursor Blends

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Materials and instruments

EDOT was purchased from Aldrich, and was distilled under vacuum prior to use. BiEDOT\textsuperscript{1} and 4,7-dibromo-2,1,3-benzothiadiazole\textsuperscript{2} were synthesized according to the literature. Acetonitrile (ACN) was purchased from Fisher Scientific and was distilled over calcium hydride (CaH\textsubscript{2}) under nitrogen atmosphere. Anhydrous N,N-dimethylformamide (DMF), silver nitrate, silver wire, ferrocene, anhydrous magnesium sulfate (MgSO\textsubscript{4}), hexanes, acetone, ethyl acetate, methanol, anhydrous ethanol and chloroform were purchased from Fisher Scientific, and were used as received. 1 M Trimethylstannyl chloride in THF, tetrakis(triphenylphosphone)palladium, tetra-n-butylammonium hexafluorophosphate (TBAPF\textsubscript{6}), lithium trifluoromethane sulfonate (LITRIF), propylene carbonate (PC), polyethylene glycol diacrylate (PEG-DA), and dimethoxyphenylacetophenone (DMPAP) were purchased from Aldrich, and were used as received. Deuterated chloroform (CDCl\textsubscript{3}) was purchased from Cambridge Isotope Laboratories, and was used as received. 2,2'-Bis(3,4-ethylenedioxythiophene) ITO-coated polyethylene terephthalate (PET) substrates (dimensions 50 mm × 60 mm × 0.2 mm, R\textsubscript{s} = 4-10 Ω) were purchased from Delta Technologies and were cleaned by sonication in acetone prior to use. Copper tape was purchased from Newark and UV-sealant glue was purchased from Norland Optics. 50 to 100 μm glass beads were purchased from Polysciences and were used as received. \textsuperscript{1}H and \textsuperscript{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 FT-NMR spectrometer, and chemical shifts (δ) were reported using residue solvent as reference. Gas chromatography mass spectrometer (GCMS) data were recorded on a Hewlett Packard 5890 series instrument. A CH
Instruments 400 potentiostat were used for electrochemical studies. A three electrode cell containing an indium tin oxide (ITO) glass as a working electrode, a platinum wire as a counter electrode, and an Ag/Ag⁺ non-aqueous as a reference electrode, was used for the electrochemistry, absorbance spectrum, colorimetric analysis and spectroelectrochemistry. The calibration was performed by using ferrocene-ferrocenium (Fc/Fc⁺) redox couple, and all reported potentials were reported versus Fc/Fc⁺ redox (i.e. Fc/Fc⁺ = 0). The supporting electrolyte used in the study was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dry acetonitrile (ACN). Thermal analysis was performed using TA Instruments Q-500 and TA Instruments Q-20 for thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC), respectively. Thermal analysis was performed under nitrogen atmosphere at a scan rate of 20 °C/min. The degradation temperature ($T_{\text{deg}}$) corresponds to a 5 % weight loss. Optical properties were measured with a Varian Cary 5000 UV-vis-NIR spectrophotometer with a 150 mm DRA Integrating Sphere and corresponding built-in Color software. Colorimetric data were collected using a 10 degree standard observer angle, a measurement range of 360–860 nm in 1 nm intervals, and a D65 standard illuminant. Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet Magna 560 FTIR spectrometer. Gel permeation chromatography (GPC) was carried out on a Viscoteck GPC MAX using a polystyrene standard calibration. A film of the precursor blends was prepared by using an Iwata spray coater.
Synthesis

1,3-Bis(EDOT)tetramethyldisiloxane. To a vacuum dried three-necked 250 mL round-bottom flask, was added 1.50 mL of EDOT (2.00 g, 14.0 mmol) in 40 mL of THF under nitrogen atmosphere. The reaction mixture was cooled to -78 °C for 1 h. Then 5.94 mL of n-BuLi in hexanes (15.4 mmol) was added dropwise for a period of 30 min. The reaction mixture was stirred at -78 °C for 2 h and 1.36 mL of 1,3-dichlorotetramethyldisiloxane (1.41 g, 6.95 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 3 h. Excess of n-BuLi in THF was quenched by addition of methanol, then the solvent was evaporated. The crude product was dissolved in diethyl ether and transferred to a separatory funnel. The organic layer was washed with water three times and dried with anhydrous MgSO₄. The solvent was evaporated and the reaction mixture was purified by column chromatography using ethyl ether/hexanes (1:4) as eluent to afford 4.50 g of clear liquid product with 77 % yield. ¹H-NMR (CDCl₃, δ, ppm): 6.57 (2H, s), 4.16 (8H, s), 0.39 (12H, s). ¹³C-NMR (CDCl₃, δ, ppm): 147.3, 142.6, 111.7, 105.3, 64.6, 64.5, 1.39. GCMS (m/z⁺): 414.
1,3-Bis(trimethylstannylEDOT)tetramethyldisiloxane. To a vacuum dried three-necked 250 mL round-bottom flask, was added 3 g of 1 (7.24 mmol) in 50 mL of THF under nitrogen atmosphere. The reaction mixture was cooled to -78 °C for 1 h. Then 5.70 mL of n-BuLi in hexanes (14.8 mmol) was added dropwise for a period of 30 min. The reaction mixture was stirred at -78 °C for 3 h and 15.2 mL of 1 M trimethylstannyl chloride in THF (15.2 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 30 min. The reaction was quenched by addition of methanol. The solvent was evaporated and the residue was dried in vacuo. The residue was dissolved in diethyl ether and transferred to a separatory funnel. The organic layer was washed with water three times and dried with anhydrous MgSO₄. The solvent was evaporated and the reaction mixture was recrystallized in ethanol to afford 2.9 g of white crystal with 54 % yield. ¹H-NMR (CDCl₃, δ, ppm): 4.13 (8H, s), 0.36 (12H, s), 0.35 (18H, s). ¹³C-NMR (CDCl₃, δ, ppm): 148.6, 147.8, 118.4, 115.4, 64.6, 64.5, 1.5, -8.5.

Precursor 1. To a vacuum-dried three-neck round-bottom flask with a condenser, 1.00g of 2 (1.35 mmol), 0.397 g of 4,7-dibromo2,1,3-benzothiadiazole (1.35 mmol), 40 mg of tetrakis(triphenylphosphine)palladium(0) (0.034 mmol), 15 mL of anhydrous DMF, and 15 mL of ACN were added under nitrogen atmosphere. The reaction mixture was heated to 60 - 63 °C, and stirred for 3 days. The solvent was removed and the crude product was precipitated in methanol. The precipitants were washed on Soxhlet apparatus with methanol and hexanes and the precursor polymer recovered with chloroform to afford 0.35 g of red powder with 47 % yield. ¹H-NMR (CDCl₃, δ, ppm): 7.94 (2H, b), 4.27 (8H, b), 0.47 (12H, b). FTIR (cm⁻¹): 2957, 2926, 1713, 1553, 1495, 1468, 1436, 1359, 1254, 1166, 1110, 1094, 1069, 1033, 956, 931, 877, 845, 825, 794. T_g = 132°C. T_deg = 348°C.

Precursor 2. To a vacuum dried three-necked round-bottom flask with a condenser, were added 2.00 g of BiEDOT (3.54 mmol) and 20 mL of THF under nitrogen atmosphere. The reaction mixture was cooled to -78°C for 1 h, and 2.72 mL of n-BuLi in hexanes (7.08 mmol) was added. The mixture was warmed up to room temperature and stirred for 2 h. The reaction mixture was cooled to 0°C, then 0.69 mL of 1,3-dichlorotetramethyldisiloxane (0.720 g, 3.54 mmol) was added. The reaction mixture was heated to 55-60 °C and stirred for 3 days. The reaction was quenched via addition of methanol. The
solvent was evaporated and the crude product was dissolved in chloroform and transferred to a separatory funnel. The chloroform layer was washed with water three times and dried with anhydrous MgSO$_4$. The mixture was filtered and concentrated. The crude product was precipitated in hexanes and in methanol respectively. The precipitants were collected and dried in vacuo overnight to yield 1.70 g of light yellow solid with 58 % yield. $^1$H-NMR (CDCl$_3$, $\delta$, ppm): 4.24 (4H, b), 4.16 (4H, b), 0.36 (12H, b). $^{13}$C-NMR (CDCl$_3$, $\delta$, ppm): 146.7, 138.1, 115.4, 109.0 64.9, 64.5, 1.54. FTIR (cm$^{-1}$): 2957, 2921, 1464, 1431, 1357, 1254, 1169, 1079, 1049, 966, 938, 920, 903, 862, 821, 792. $T_g = 83$ °C. $T_{\text{deg}} = 382$ °C.

**SI Figure 1.** CVs in the first scan of (a) precursor 1 and (b) precursor 2.
SI Figure 2. Chronocoulometry of the conversion of precursor blends. (a) B1, (b) B2, (c) B3, (d) B4, (e) B5, and (f) B6.
SI Figure 3. CVs (a) PB1, (b) PB2, (c) PB3, (d) PB4, (e) PB5, and (f) PB6. Scan rates was 100 mV s$^{-1}$. 
SI Figure 4. Scan rate studies of (a) PB1, (b) PB2, (c) PB3, (d) PB4, (e) PB5, and (f) PB6. Scan rates were 100 mV s\(^{-1}\), 200 mV s\(^{-1}\), 300 mV s\(^{-1}\), 400 mV s\(^{-1}\), and 500 mV s\(^{-1}\).
SI Figure 5. Spectroelectrochemistries of (a) PB1, (b) PB2, (c) PB3, (d) PB4, (e) PB5, and (f) PB6 in the redox potential window (-0.8 V to 0.6 V with 0.2 V step)
SI Figure 6. Comparison of absorption spectra of PB4, bilayer (P1+P2), P1 and P2. The ratio of 1 and 2 to prepare bilayer was 1 : 2.5, to be the same to prepare PB4. Bilayer was prepared as follows: 1 mL of 5 mM precursor 1 solution in chloroform was spray-coated on an ITO-coated glass and converted to P1. 2.5 mL of 5 mM precursor 2 solution in chloroform was spray-coated on the P1 coated ITO substrate and converted to P2. P1 was prepared by spray-coating 1 mL of 5 mM precursor 1 solution in chloroform on a ITO-coated glass and the film was converted to P1.

SI Figure 7. Absorption spectra in the neutral and oxidized states of three set of PB4 films prepared by using same volume of B4 solution.
**SI Table 1.** L*a*b* of three PB4 films in neutral and oxidized state. The maximum absorbance intensities of the films in the neutral state were 0.291, 0.294 and 0.286 a. u. for set 1, 2, and 3, respectively.

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
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<tr>
<td>Set 1 Neutral</td>
<td>77.6</td>
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</tr>
<tr>
<td>Set 2 Neutral</td>
<td>77.4</td>
<td>1.01</td>
<td>-2.91</td>
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<td>Set 3 Neutral</td>
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<tr>
<td>Set 1 Oxidized</td>
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<td>Set 2 Oxidized</td>
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<td>Set 3 Oxidized</td>
<td>90.5</td>
<td>-4.10</td>
<td>-3.84</td>
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**SI Figure 8.** Square-wave potential step absorptiometry of PB4 film. % Transmittance at 500 nm of PB4 film (absorbance = 0.46 a. u) was recorded as the function of time. Step times and % transmittance changes are noted on the figure.

**Fabrication of Flexible Window-Type EC Device**

A gel electrolyte was prepared in accordance to the literature. An ITO-coated polyethylene terephthalate (PET) substrates was spray coated with B4 solution, using an Iwata spray coater and dried at 80 °C under nitrogen atmosphere for 10 min. The B4 film (40 mm × 45 mm) on the PET substrate was converted to conjugated polymer (PB4) in 0.1 M TBAPF6/ACN electrolyte bath by applying the
potential of 0.6 V vs. Fc/Fc\(^+\) for 5 s. Prior to device assembly, the PB4 (absorbance = 0.48 a. u.) on PET substrate was washed with ACN and dried at ambient atmosphere. The gel electrolyte solution described above was poured over the PB4 on PET substrate, and another ITO-PET substrate was placed on top of the gel electrolyte solution such that the ITO-coated sides face one another. The glass beads in a gel electrolyte and insulating tape maintained an even distance between two ITO electrodes and thereby prevented the shorting of the two ITO substrates. The sides of the device were then sealed using UV adhesive. A 365 nm UV light compartment was used to cure the gel electrolyte and UV adhesive.

**SI Figure 9.** Schematic diagram of the flexible window-type two-electrode PB4 EC device. Upper ITO-coated PET substrate was used as counter electrode, and PB4 deposited bottom ITO-coated PET substrate was used as working electrode

**SI References**