Supporting Information

Discrete Donor−Acceptor Conjugated Systems in Neutral and Oxidized States: Implications toward Molecular Design for High Contrast Electrochromics

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Synthesis Procedures

4,7-bis(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (3). 1 (ProDOT-diethylhexyl) (36.00 mmol, 15.86 g), 2 (dibromo-BTD) (3.0 mmol, 0.88 g), Pd(OAc)$_2$ (8 mol %, 0.050 g), pivalic acid (3.600 mmol, 0.370 g), and K$_2$CO$_3$ (4.50 mmol, 0.620 g) were charged into an oven-dried Schlenk tube fitted with a stir bar, and pumped for 30 min, then purged with Ar three times. Then Ar-bubbled N,N-dimethylacetamide (15 mL) was added to the mixture. The reaction was then placed in an oil bath at 140 °C and stirred until all of the dibromo-BTD is judged consumed by TLC (~ 20 mins). The reaction was then removed from the oil bath, quenched with ethyl acetate (~ 50 mL) and allowed to come to r.t. The mixture is then poured into water and extracted with ethyl acetate. The organics were separated, washed with H$_2$O twice, then brine. The organic layer was separated, dried over MgSO$_4$, filtered, and concentrated. The product was purified via column chromatography, eluting with 3:2 hexanes:CH$_2$Cl$_2$, to yield 2.1 g (69 %) of the pure product. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.31 (s, 2H), 6.66 (s, 2H), 4.21 (s, 4H), 4.09 (s, 4H), 3.55 (s, 8H), 3.31 (d, J = 7.7 Hz, 8H), 1.58 – 1.44 (m, 4H), 1.44 – 1.19 (m, 32H), 0.98 – 0.78 (m, 24H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 152.76, 149.86, 147.97, 127.66, 124.31, 117.70, 106.62, 77.58, 77.16, 76.74, 74.40, 73.96, 70.07, 48.03, 39.75, 30.79, 29.25, 24.14, 23.25, 14.27, 11.31. MS (MALDI, [M+H]$^+$) m/z calcd. for C$_{56}$H$_{88}$N$_2$O$_8$S$_3$ 1012.57; found 1013.53.

4,7-bis(8-bromo-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (4). 3 (0.260 mmol, 0.260 g) was dissolved in CHCl$_3$ (25 mL) and cooled to 0 °C in an ice bath. Then N-bromosuccinimide (0.560 mmol, 0.100 g) was added in one portion as a solid. The reaction mixture was protected from light, stirred, and allowed to come to r.t. overnight. The solvent was removed in vacuo and the concentrate
was passed through a short pad of silica, eluting with 3:2 hexanes:CH$_2$Cl$_2$, to yield 0.22 g (74 %) of the pure product. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.30 (s, 8H), 4.20 (d, J = 13.6 Hz, 8H), 3.68 – 3.43 (m, 4H), 3.31 (d, J = 7.4 Hz, 4H), 1.57 – 1.44 (m, 4H), 1.44 – 1.19 (m, 32H), 0.98 – 0.79 (m, 24H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 152.26, 147.69, 147.13, 127.29, 123.58, 117.41, 96.33, 74.40, 74.21, 70.00, 48.05, 39.76, 30.79, 29.26, 24.14, 23.26, 14.29, 11.33. MS (MALDI, [M+H]$^+$) m/z calcd. for C$_{56}$H$_{86}$Br$_2$N$_2$O$_8$S$_3$ 1168.39; found 1170.38.

4,7-bis(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (EPBPE). 4 (0.150 mmol, 0.170 g), 5 (0.340 mmol, 0.080 g), Pd(OAc)$_2$ (2.0 mol %, 0.0021 g), pivalic acid (0.30 mmol, 0.0050 g), and K$_2$CO$_3$ (0.300 mmol, 0.0410 g) were charged into an oven dried Schlenk tube fitted with a stir bar, and pumped for 30 min, then purged with Ar three times. Then Ar-bubbled N,N-dimethylacetamide (5 mL) was added, and the mixture was placed in an oil bath at 140 °C, and stirred for 12 hrs. The reaction mixture was then cooled to r.t. and precipitated in cold methanol. Then the product was collected and redissolved in 1:1 hexanes:CH$_2$Cl$_2$. Column chromatography in silica gel was done to purify the product, eluting with 1:1 hexanes:CH$_2$Cl$_2$, to yield 0.18 g (81 %) of pure product. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.35 (s, 2H), 4.38 (s, 4H), 4.24 (s, 8H), 4.20 (s, 4H), 3.68 – 3.51 (m, 8H), 3.33 (d, J = 5.6 Hz, 8H), 2.66 (s, 4H), 1.71 – 1.56 (m, 4H), 1.56 – 1.45 (m, 4H), 1.45 – 1.20 (m, 44H), 0.99 – 0.80 (m, 30H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 152.72, 148.02, 144.26, 138.01, 137.19, 127.10, 123.79, 117.96, 117.31, 114.73, 106.36, 74.39, 74.17, 70.27, 65.44, 64.71, 48.06, 39.77, 31.72, 30.82, 30.79, 29.27, 29.25, 29.07, 24.16, 23.28, 22.76, 14.31, 14.26, 11.33. MS (MALDI, [M+H]$^+$) m/z calcd. for C$_{80}$H$_{120}$N$_2$O$_{12}$S$_5$ 1460.74; found 1461.75. Elem. Anal. calcd. C, 65.72; H, 8.27; N, 1.92; S, 10.96 found: C, 65.71; H, 8.13; N, 1.97; S, 10.95.
4,7-bis(3,3',3'-tetrakis(2-ethylhexyl)oxy)methyl)-3,3',4,4'-tetrahydro-2H,2'H-[6,6'-bithieno[3,4-b][1,4]dioxepin]-8-yl)benzo[c][1,2,5]thiadiazole (6). 4 (0.590 mmol, 0.600 g), 1 (7.000 mmol, 3.190 g), Pd(OAc)$_2$ (8.0 mol%, 0.010 g), pivalic acid (0.700 mmol, 0.0720 g), and K$_2$CO$_3$ (0.880 mmol, 0.120 g) were charged into an oven dried Schlenk tube fitted with a stir bar, and pumped for 30 min, then purged with Ar three times. Then Ar-bubbled N,N-dimethylacetamide (3 mL) was added, and the mixture was placed in an oil bath at 140 °C, and stirred for 12 hrs. The reaction mixture was then cooled to r.t. and precipitated in cold methanol. Then the product was collected and redissolved in 1:1 hexanes:CH$_2$Cl$_2$. Column chromatography in silica gel was done to purify the product, eluting with 1:1 hexanes:CH$_2$Cl$_2$, to yield 0.49 g (45%) of pure product. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.30 (s, 2H), 6.43 (s, 2H), 4.24 (s, 4H), 4.18 (s, 8H), 4.18 (s, 8H), 4.07 (s, 4H), 3.61 (s, 8H), 3.54 (s, 8H), 3.32 (dd, J = 5.3, 3.4 Hz, 16H), 1.59 – 1.45 (m, 8H), 1.44 – 1.15 (m, 64H), 1.01 – 0.76 (m, 48H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 152.84, 149.54, 147.78, 145.62, 145.39, 127.63, 124.12, 117.06, 115.81, 115.36, 103.71, 74.39, 74.19, 70.21, 39.75, 30.79, 29.27, 26.96, 24.15, 23.26, 14.28, 11.30. MS (MALDI, [M+H]$^+$) m/z calcd. for C$_{106}$H$_{172}$N$_2$O$_{16}$S$_5$ 1889.13; found 1890.08.

4,7-bis(8'-bromo-3,3',3'-tetrakis(2-ethylhexyl)oxy)methyl)-3,3',4,4'-tetrahydro-2H,2'H-[6,6'-bithieno[3,4-b][1,4]dioxepin]-8-yl)benzo[c][1,2,5]thiadiazole (7). 6 (0.110 mmol, 0.220 g) was dissolved in CHCl$_3$ and cooled to 0 °C in an ice bath, and stirred for 20 mins under light protection. Then N-bromosuccinimide (0.25 mmol, 0.045 g) was added as a solid in one portion. Then the reaction mixture was stirred at 0 °C under light protection for 40 mins. Then the reaction mixture was concentrated at reduced pressure and filtered through a silica plug, eluting with 1:1 hexanes:CH$_2$Cl$_2$. Then column chromatography in silica gel was repeated, eluting with 7:3 hexanes:CH$_2$Cl$_2$, to yield 0.12 g (55%) of the pure product. $^1$H NMR (300 MHz, CDCl$_3$) δ
8.30 (s, 2H), 4.18 (d, J = 20.7 Hz, 16H), 3.58 (d, J = 5.3 Hz, 16H), 3.31 (dd, J = 12.6, 8.7 Hz, 16H), 1.54 (t, J = 13.3 Hz, 8H), 1.45 – 1.17 (m, 64H), 1.04 – 0.78 (m, 48H). $^{13}$C NMR (75 MHz, CDCl3) δ aromatic protons were not resolved, 74.42, 70.43, 69.89, 39.78, 30.80, 29.91, 29.27, 24.16, 23.27, 14.30, 11.32. MS (MALDI, [M+H]$^+$) $m/z$ calcd. for C$_{106}$H$_{170}$Br$_2$N$_2$O$_{16}$S$_5$ 2044.95 found 2048.87.

4,7-bis(3,3,3',3'-tetrais(2-ethylhexyl)oxy)methyl)-8'-((7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-3,3',4,4'-tetrahydro-2H,2'H-[6,6'-bithieno[3,4-b][1,4]dioxepin]-8-yl)benzo[c][1,2,5]thiadazole (EPPBPPE). 7 (0.044 mmol, 0.090 g), 5 (0.11 mmol, 0.026 g), Pd(OAc)$_2$ (8.0 mol %, 0.0010 g), pivalic acid (0.013 mmol, 0.0020 g), and K$_2$CO$_3$ (0.090 mmol, 0.012 g) were charged into an oven dried Schlenk tube fitted with a stir bar, and pumped for 30 min, then purged with Ar three times. Then Ar-bubbled N,N-dimethylacetamide (2.5 mL) was added, and the mixture was placed in an oil bath at 140 °C, and stirred for 16 hrs. The reaction mixture was then cooled to r.t. and precipitated in cold methanol. Then the product was collected and redissolved in 1:1 hexanes:CH$_2$Cl$_2$. Column chromatography in silica gel was done to purify the product, eluting with 1:1 hexanes:CH$_2$Cl$_2$, to give 0.070 g (69 %) of pure product. $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 8.38 (s, 2H), 4.47 – 3.96 (m, 24H), 3.75 – 3.50 (m, 16H), 3.35 (d, J = 3.7 Hz, 16H), 2.64 (s, 4H), 1.61 (d, J = 7.5 Hz, 4H), 1.54 (s, 8H), 1.47 – 1.13 (m, 76H), 1.02 – 0.76 (m, 54H). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 153.04, 148.39, 146.10, 145.37, 144.37, 137.87, 137.51, 133.84, 127.44, 124.19, 117.82, 116.02, 114.93, 112.66, 106.33, 74.70, 70.37, 65.72, 65.01, 48.36, 40.08, 31.98, 31.08, 31.05, 30.09, 29.53, 29.25, 24.41, 23.53, 23.02, 14.30, 11.39, 11.36. MS (MALDI, [M+H]$^+$) $m/z$ calcd. for C$_{139}$H$_{204}$N$_2$O$_{20}$S$_7$ 2337.31; found 2338.29. Elem. Anal. calcd. C, 66.74; H, 8.79; N, 1.20; S, 9.59; found: C, 68.13; H, 9.27; N, 1.33; S, 8.31.
1,10-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)decane (8). EDOT (2.30 mmol, 0.330 g) was dissolved in anhydrous THF (10 mL) and the solution was cooled to −78 °C in an isopropyl/dry ice bath, and stirred for 15 mins. Then n-BuLi (1.6 M, 2.41 mmol, 1.51 mL) was added dropwise and the reaction mixture stirred at −78 °C for 1 hr. Then 1,10-diiododecane (1.00 mmol, 0.390 g) dissolved in anhydrous THF (5 mL) was added dropwise to the deprotonated EDOT solution at −78 °C. Then the reaction mixture was allowed to come to r.t. slowly. The reaction mixture was allowed to come to r.t. overnight. Then the reaction was quenched with H₂O, and the organics were extracted with ethyl acetate, washed with NH₄Cl, H₂O, then brine. The organic layer was separated, dried over Na₂SO₄, and concentrated. The product was purified via column chromatography in silica gel, eluting with 95:5 hexanes:ethyl acetate, to yield 0.070 g (17%) of pure product. H NMR (300 MHz, CD₂Cl₂) δ 6.08 (s, 2H), 4.20 – 4.10 (m, 8H), 2.61 (t, J = 15.1, 7.4 Hz, 4H), 1.68 – 1.50 (m, 4H), 1.29 (d, J = 3.7 Hz, 12H). C NMR (75 MHz, CD₂Cl₂) δ 142.00, 137.92, 118.70, 95.14, 65.11, 30.91, 29.92, 29.70, 29.51, 26.23. MS (EI, [M+H]) m/z calcd. for C₂₂H₃₀O₄S₂ 422.16; found 422.1.

Poly-EPBPE. 4 (0.450 mmol, 0.530 g), 8 (0.445 mmol, 0.190 g), Pd(OAc)₂ (2.0 mol %, 0.0060 g), pivalic acid (0.013 mmol, 0.014 g), and K₂CO₃ (0.890 mmol, 0.120 g) were charged into an oven dried Schlenk tube fitted with a stir bar, and pumped for 30 min, then purged with Ar three times. Then Ar-bubbled N-methylpyrrolidone (2.5 mL) was added, and the mixture was placed in an oil bath at 145 °C, and stirred for 24 hrs. Then 5 (0.048 g) was added to the reaction mixture, and stirred for 1.5 hrs. Then the reaction was cooled to r.t., and precipitated in methanol, and stirred for 1.5 hrs. Then the solids were filtered out, and air-dried under vacuum overnight. Then the solids were transferred to a cellulose thimble and placed in a Soxhlet extraction set-up. The solids were washed successively with methanol, acetone, hexanes, and CHCl₃. The CHCl₃
fraction was concentrated, then redissolved in toluene (25 mL). Then diethylammonium diethylndithiocarbamate (Pd scavenger), and 18-Crown-6 (K⁺ scavenger) were added, and the mixture was stirred at 65 °C overnight. Then the reaction mixture was cooled to room temperature, and the solvent reduced in vacuo. The mixture was then reprecipitated in methanol, filtered, and dried under vacuum, to yield 0.46 g (72 %) of polymer. ¹H NMR (300 MHz, CD₂Cl₂) δ 8.40 (s, 2H), 4.54 – 3.97 (m, 16H), 3.73 – 3.46 (m, 8H), 3.35 (d, J = 5.5 Hz, 8H), 2.66 (t, J = 7.2 Hz, 4H), 1.72 – 1.58 (m, 4H), 1.58 – 1.46 (m, 4H), 1.46 – 1.19 (m, 48H), 1.01 – 0.79 (m, 24H). ¹³C NMR (75 MHz, CD₂Cl₂) δ 152.94, 148.44, 144.54, 138.34, 137.59, 127.17, 123.98, 118.27, 117.62, 114.79, 106.42, 74.60, 74.53 – 74.14, 70.32, 65.87, 65.03, 48.31, 40.11, 31.06, 30.94, 30.01, 29.77, 29.64, 29.52, 26.24, 24.44, 23.55, 14.35, 11.39. Elem. Anal. calcd. for (C₇₈H₁₁₄N₂O₁₂S₅)n C, 65.42; H, 8.02; N, 1.96; S, 11.19; found: C, 65.13; H, 7.93; N, 2.14; S, 10.54. GPC: Mₙ: 23.1 kDa, Mₘ: 54.0 kDa, D: 2.33, in CHCl₃ vs. PS.

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<th>Equivalents</th>
<th>ProDOT</th>
<th>BTD</th>
<th>Pd(OAc)₂</th>
<th>Pivalic Acid</th>
<th>Reaction Time</th>
<th>Yield (%)</th>
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<td>47</td>
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<tr>
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<td>4 mol %</td>
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<td>8 mol %</td>
<td>1.2</td>
<td>20 mins</td>
<td>69</td>
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*BTD was dissolved in the solvent and added dropwise to the heated reaction mixture.
Figure S1. Electrochemical stability of EPBPE (A), EPPBPPE (B), Poly-EPBPE in solution (C), and Poly-EPBPE film at 5 mV s\(^{-1}\) (D) and 50 mV s\(^{-1}\) (E) as determined from repeated cyclic voltammetry.
Figure S2. Difference spectra showing absorption changes during addition of one equivalent (A) and two equivalents (B) of oxidant to EPBPE.

Figure S3. Changes in absorption spectra of EPBPE with NOBF₄ oxidation (A). Comparison of neutral and oxidized state spectra obtained from oxidation with NOBF₄ and AgPF₆.
Figure S4. Plots of the absorbances of neutral and polaronic transitions against equivalents added dopant for EPBPE, and their best fit lines.

Table S2. Results of linear regression analysis of the absorbance changes of the different transitions against the equivalents added dopant, and the derived stoichiometric factor, y.

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<th>Transition</th>
<th>Slope</th>
<th>Standard Error (%)</th>
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<th>A_{\lambda p}</th>
<th>y</th>
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Figure S5. (A) Comparison of EPBPE cyclic voltammograms obtained in a bulk electrochemical cell with a Pt button electrode, and an OTTLE cell with a Pt mesh electrode. (B) Schematic diagram and photograph of OTTLE cell used in solution spectroelectrochemistry.
Figure S6. Comparison of absorption spectra of neutral and oxidized states at different concentrations during chemical doping (A) and electrochemical doping (B) of EPBPE.

Figure S7. Comparison of neutral and oxidized state spectra obtained via chemical (solid lines) and electrochemical (dashed lines) doping of EPBPE.

Figure S8. EPR spectra of the neutral, mono-, and di-oxidized states of EPBPE (solid lines) and EPPBPPE (dashed lines).
Figure S9. Comparison of neutral and oxidized state absorption spectra between EPBPE (dashed lines) and Poly-EPBPE (solid lines) obtained via chemical doping.

Figure S10. Morphology of a spray-cast Poly-EPBPE film from on ITO substrate obtained from optical microscopy (A) and atomic force microscopy (1 × 1 μm) (B) height, and (C) phase images.

Figure S11. Difference spectra showing optical changes occurring in Poly-EPBPE film during oxidation to 300 mV (A) and to 600 mV (B) vs. Ag/Ag⁺ reference electrode.