

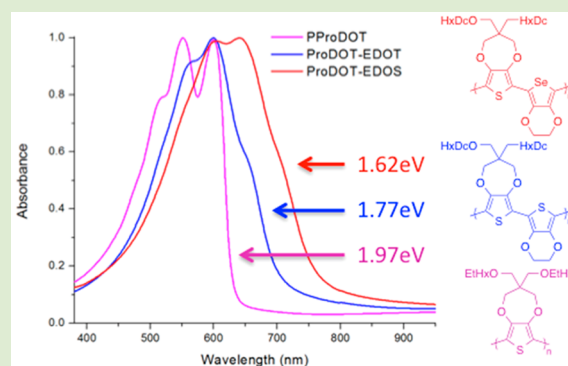
## Heteroatom Role in Polymeric Dioxyselenophene/Dioxythiophene Systems for Color and Redox Control

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## S Supporting Information

**ABSTRACT:** The first example of a solution processable dioxothiophene-*alt*-dioxyselenophene polymer, ProDOT-EDOS, prepared via direct (hetero)arylation polymerization is reported and its optical and electrochemical properties are compared to the all thiophene analog, ProDOT-EDOT, and other relevant dioxothiophene polymers. By substituting the sulfur atom for a selenium atom on one of the monomers in the repeat unit a significant red-shift of both the neutral (41 nm, 132 meV) and polaronic (106 nm, 126 meV) absorbances results, as well as a 160 mV reduction in the onset of oxidation compared to ProDOT-EDOT. Spray-cast films of the polymer electrochemically switch from a vibrant blue charge neutral state to a color neutral and highly transmissive oxidized state.



Polysephenes have received attention in the field of organic electronics due to their similarities and differences to the more widely studied polythiophenes, where they possess reduced aromatic character, leading to increased quinoidal character and planarity between rings and yielding lower electronic band-gaps.<sup>1–4</sup> Of particular note is the computational and experimental work of the late Michael Bendikov on selenophene oligomers and polymers who developed extensive selenophene chemistry and made important comparisons with structurally similar thiophene-based polymers.<sup>1,5–9</sup> Recently, poly(3-alkylselenophenes) and copolymers containing 3-alkylselenophenes<sup>10–12</sup> along with other selenophene containing polymers have found use as both organic field-effect transistor (OFET)<sup>13–15</sup> and organic photovoltaic (OPV)<sup>16,17</sup> materials with enhanced transport properties due to more extensive interchain interactions compared to their thiophene analogs.

In a similar comparison, electrochemically polymerized 3,4-alkylenedioxyselenophenes (XDOSs) and their analogous 3,4-alkylenedioxythiophenes (XDOTs) have been investigated and compared as redox active and electrochromic (EC) materials. This is illustrated in PProDOS, which exhibits a saturated blue hue due to a distinct red-shift<sup>4,18</sup> of the neutral polymer's  $\pi \rightarrow \pi^*$  transition relative to the more purple color observed for the PProDOTs.<sup>19,20</sup> A red-shifted absorption of the PProDOS cation-radical (polaron state) relative to that observed for PProDOT moves the charged material's absorption of light more fully into the near-infrared.<sup>20</sup> These PXDOS materials have low oxidation potentials (as low as  $-0.95$  V vs Ag/AgCl),<sup>6</sup> which is of particular use in EC and electrochemical charge storage devices, such as supercapacitors. For the PXDOS family of materials to become more attractive and useful for redox and

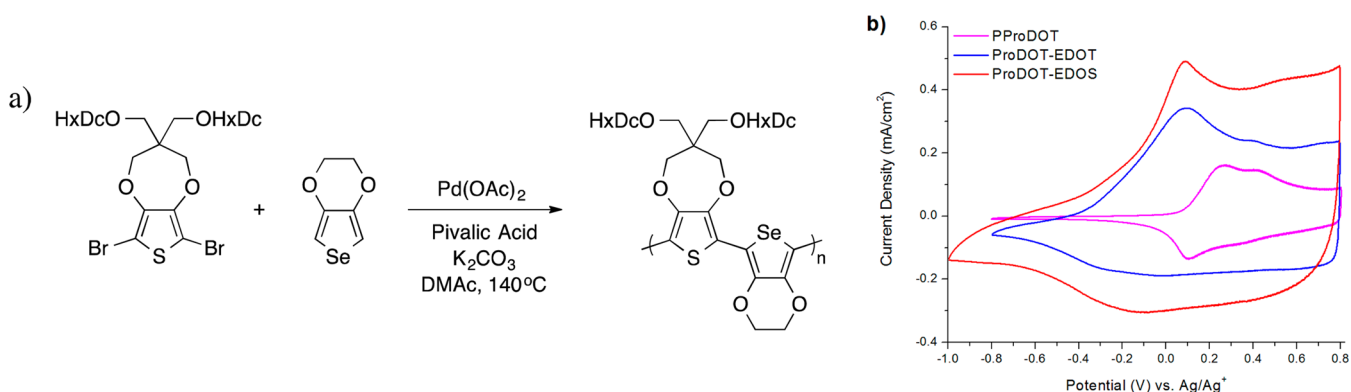
organic electronic applications, it is necessary to move beyond electrochemical polymerizations with the preparation and processing of soluble polymers. To date, there is one example of a PProDOS functionalized with solubilizing side chains that has been electropolymerized to yield a low molecular weight product (7.2–9.3 kDa), which could subsequently be spray cast from a dichloromethane (DCM) solution.<sup>19</sup> During the preparation of this manuscript, the dehalogenative polymerization of dihalo XDOS and XDOT monomers were reported, yielding soluble oligomers with a low molecular weight (5 kDa), but no polymeric materials were presented.<sup>21</sup>

Direct (hetero)arylation polymerization (DHAP) has emerged as one of the most practical and versatile polymerization methods for the synthesis of conjugated polymers.<sup>22–24</sup> DHAP has been previously utilized to synthesize a large number of dioxothiophene-based polymers and copolymers for high contrast electrochromic<sup>25,26</sup> and charge storage applications<sup>27</sup> and here, for the first time, this chemistry has been extended to XDOS-based polymers. Specifically, the first synthesis of an alternating ProDOT-EDOS copolymer, applying standard DHAP conditions, is reported with EDOS serving as the dihydrogen species and a ProDOT derivative with 2-hexyldecyloxy solubilizing chains as the dihalide to yield ProDOT-EDOS, as illustrated in Figure 1a. The polymer was purified via Soxhlet extraction and the repeat unit structure confirmed using elemental analysis and NMR (Figure S1), as outlined in the Supporting Information. The molecular weight of the polymer ( $M_n = 12.5$  kDa,  $\bar{D} = 1.6$ ) was determined via

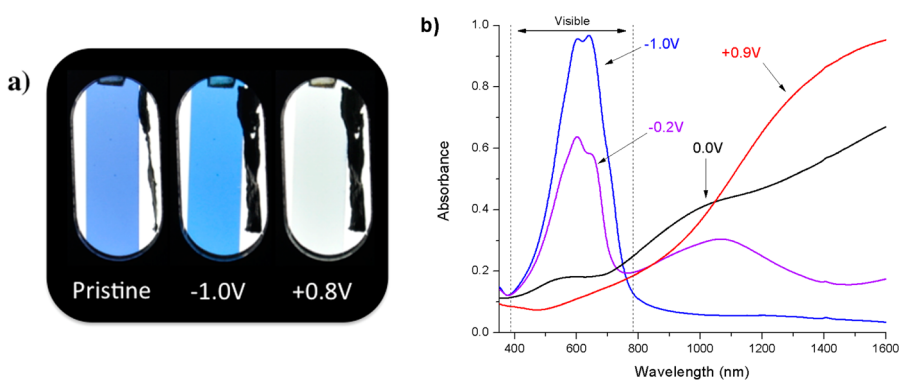
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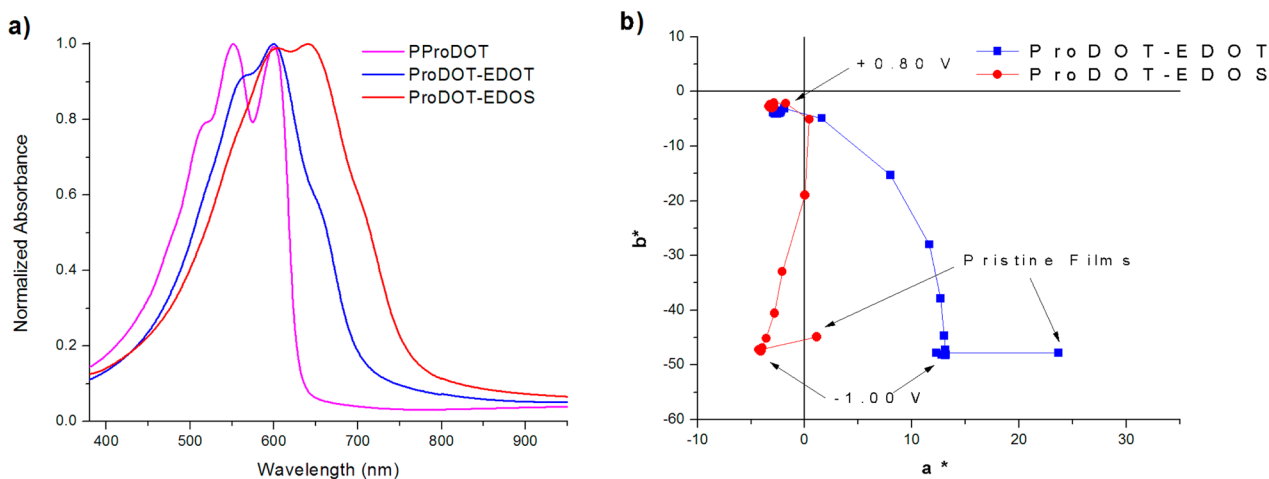
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**Figure 1.** (a) Direct (hetero) arylation polymerization of a dibromo ProDOT derivative and EDOS to yield ProDOT-EDOS and (b) CVs of PProDOT (magenta trace), ProDOT-EDOT (blue trace), and ProDOT-EDOS (red trace) drop cast to equal mass films ( $3 \mu\text{L}$  of  $2 \text{ mg/mL}$  solutions in  $\text{CHCl}_3$ ) on glassy carbon electrodes, demonstrating the reduction in onset of oxidation and broad stable window of the polymer films as well as an increase in redox current.



**Figure 2.** (a) Photographs of a spray-cast film of ProDOT-EDOS on ITO in electrolyte solution in its pristine (as cast), charge neutral ( $-1.0 \text{ V}$ ), and oxidized ( $+0.8 \text{ V}$ ) forms and (b) UV-vis absorption of ProDOT-EDOS on ITO at various applied potentials from the fully reduced, or charge neutral, form (blue trace) to the fully oxidized form (red trace).



**Figure 3.** (a) Normalized absorption spectra of PProDOT (magenta trace) at higher energy, ProDOT-EDOT (blue trace), and ProDOT-EDOS (red trace) at lower energy, and (b)  $a^*b^*$  diagram showing the change in color occurring during electrochemical doping (oxidation) of ProDOT-EDOT and ProDOT-EDOS.

gel permeation chromatography (GPC) relative to polystyrene standards. Cyclic voltammetry (CV) of a dropcast film of the polymer on a glassy carbon electrode exhibited a low onset of oxidation followed by a broad electrochemical response, as shown in Figure 1b. This onset of oxidation is lower than both the PProDOT homopolymer and the ProDOT-EDOT alternating polymer. This is consistent with the low oxidation

potential reported in the literature for electropolymerized XDOS polymers and is confirmed by differential pulse voltammograms (DPVs), as shown in Figure S2, where ProDOT-EDOS shows a reduction in the onset of oxidation of  $160 \text{ mV}$  relative to ProDOT-EDOT simply by changing one of the heteroatoms in the repeat unit from sulfur to selenium.

**Table 1.** Optical, Colorimetric, and Electrochemical Comparisons of PProDOT, ProDOT-EDOT, ProDOT-EDOS, and PEDOT

polymer	$\lambda_{\max}$ neutral (nm)	$\lambda_{\max}$ polaron (nm)	$L^*, a^*, b^*$ (neutral)	$L^*, a^*, b^*$ (oxidized)	$E_g$ (eV)	onset of oxidation (V) by DPV
PProDOT	550	937	42, 58, -38	89, -3, -3	1.97	0.08
ProDOT-EDOT	600	970	52, 12, -48	93, -3, -3	1.77	-0.36
ProDOT-EDOS	641	1076	53, -4, -47	92, -3, -3	1.62	-0.52
PEDOT	629	923	35, 10, -54	81, -6, -10	1.66	-0.95

When spray cast from a chloroform solution (4 mg/mL) onto ITO glass, the resulting ProDOT-EDOS film appears as a slightly muted blue film ( $L^*a^*b^* = 53, 1, -45$ ). However, it can be seen in Figure 2a and S3a that following an electrochemical break-in with 5 CV cycles the neutral form of the film is converted to a deep blue color ( $L^*a^*b^* = 53, -4, -47$ ). Upon oxidation of the polymer the blue color disappears and a colorless and transmissive state ( $L^*a^*b^* = 92, -3, -3$ ) is formed, as seen in Figure 2a. The spectroelectrochemical series of the film in Figures 2b and S3b allows us to observe the gradual oxidation of the polymer and the depletion of the charge neutral state as polarons are formed, followed by bipolarons, and ultimately bipolaron band formation<sup>28,29</sup> with complete disappearance of the neutral state absorption by 0.8 V.

The UV-vis-NIR absorbance profiles of PProDOT, ProDOT-EDOT, and ProDOT-EDOS shown in Figure 3a demonstrate a red-shift in both peak and onset of absorbance for this family of polymers. Insertion of the less sterically encumbering EDOT in alternation with ProDOT leads to a relaxation of the torsional angles along the polymer backbone, as demonstrated previously in studies directed to color tuning in EC polymers (ECPs).<sup>26</sup> With the subsequent substitution of the sulfur atom for a selenium atom in the EDOS repeat unit, a further 41 nm red-shift in peak absorbance is observed (Table 1). Using the energy for the onset of the  $\pi \rightarrow \pi^*$  transition in the polymer as an estimation of the optical bandgap, we see a decrease from 1.97 to 1.77 eV and, finally, to 1.62 eV across this series. Tracking the hue and saturation of the films during oxidation, the colorimetry results in Figure 3b, Figure S4, and Table 1 show how the materials transition from deeply colored states to highly transmissive, near neutral hued forms. The  $a^* = -4$  value for ProDOT-EDOS is unusual, as it does not contain a red component as we typically see in blue XDOT ECPs (specifically in ProDOT-EDOT<sub>2</sub> and PEDOT), which have small positive  $a^*$  values.<sup>26,27</sup> As the polymer is oxidized, the colorimetry results track the  $b^*$  axis relatively closely, minimizing secondary colors observed during electrochemical switching. This switch is relatively rapid with a 95% switch, calculated from the chronoabsorptometry in Figure S5, of 0.60 s.

Interestingly, it can be seen in Table 1 that the absorption maximum of ProDOT-EDOS and PEDOT are similar and the difference in bandgap between the two is small (0.04 eV), suggesting that the materials will appear similar in perceived color. However, a quantitative comparison of the colorimetry values of the two polymers show that this is not true and the materials appear as distinct hues. The color difference equation ( $\Delta E^*_{ab}$ ) presented in the Supporting Information was used to compare the colors, thereby determining if they are distinguishable to a standard observer.<sup>30,31</sup> If the value of  $\Delta E^*_{ab}$  is greater than 2.2, two colors are distinguishable from each other. Despite the similarities in peak absorbance and onset, ProDOT-EDOS and PEDOT have a  $\Delta E^*_{ab}$  value of 24,

meaning that while they are both blue polymers they appear as distinctly different hues of blue. In contrast, ProDOT-EDOT<sub>2</sub> ( $\lambda_{\max} = 613$  nm,  $E_g = 1.71$  eV) has a  $\Delta E^*_{ab}$  value of 2.2 relative to PEDOT, making these two materials indistinguishable to a standard observer in spite of the larger difference in peak absorbance and optical bandgap.<sup>27</sup> Comparing these polymers nicely demonstrates how perceived color is more complex than the bandgap and peak absorbance, but is dependent on the overall absorbance profile.

While altering the backbone structure in dioxothiophene polymers shifts the neutral absorbance, it generally does not have a significant effect on the polaronic absorption, which tends to be found between 780 and 980 nm. This is exemplified in PProDOT and ProDOT-EDOT with a 50 nm difference in the neutral, and a 33 nm difference in the polaronic peak absorbance, corresponding to decreases in energy of 188 and 45 meV, respectively. Substitution of the sulfur for selenium on the EDOT unit leads to a smaller energy reduction of 132 meV (a 41 nm red-shift) in the neutral absorbance and a larger energy reduction of 126 meV (a 106 nm red-shift) in the polaron absorption relative to ProDOT-EDOT. By moving the polaron further into the IR, it may be possible to reduce the extent of tailing of the charged state absorption into the visible, which may ultimately increase the EC contrast observed.

Given the large effect that substitution of a selenium atom in place of sulfur in these structures has on the redox behavior, neutral state absorbance, and polaron absorbance of the resulting copolymer, we envision that these dioxyselenophenes will be of practical use in color mixing of electrochromic polymers. The XDOS family of polymers can provide the long wavelength absorbance needed for brown and black blends without leading to the higher oxidation potential and lower EC contrast that donor-acceptor ECPs (e.g., ProDOT-*alt*-benzothiadiazole) typically exhibit.<sup>32</sup> Additionally, the significant reduction in oxidation potential and broad electroactive response make this polymer, and others of its kind, of interest in charge storage research in both types I and II supercapacitors.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00250.

Experimental procedures and additional polymer characterizations (PDF).

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitius, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130* (21), 6734–6736.
- (2) Patra, A.; Bendikov, M. *J. Mater. Chem.* **2010**, *20* (3), 422–433.
- (3) Hollinger, J.; Gao, D.; Seferos, D. S. *Isr. J. Chem.* **2014**, *54* (5–6), 440–453.
- (4) Patra, A.; Bendikov, M.; Chand, S. *Acc. Chem. Res.* **2014**, *47* (5), 1465–1474.
- (5) Zade, S. S.; Bendikov, M. *Org. Lett.* **2006**, *8* (23), 5243–5246.
- (6) Li, M.; Sheynin, Y.; Patra, A.; Bendikov, M. *Chem. Mater.* **2009**, *21* (12), 2482–2488.
- (7) Wijsboom, Y. H.; Patra, A.; Zade, S. S.; Sheynin, Y.; Li, M.; Shimon, L. J. W.; Bendikov, M. *Angew. Chem., Int. Ed.* **2009**, *48* (30), 5443–5447.
- (8) Zade, S. S.; Zamoshchik, N.; Bendikov, M. *Chem. - Eur. J.* **2009**, *15* (34), 8613–8624.
- (9) Poverenov, E.; Sheynin, Y.; Zamoshchik, N.; Patra, A.; Leitius, G.; Perepichka, I. F.; Bendikov, M. *J. Mater. Chem.* **2012**, *22* (29), 14645–14655.
- (10) Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S. *J. Am. Chem. Soc.* **2010**, *132* (25), 8546–8547.
- (11) Gao, D.; Hollinger, J.; Seferos, D. S. *ACS Nano* **2012**, *6* (8), 7114–7121.
- (12) Lai, Y.-Y.; Tung, T.-C.; Liang, W.-W.; Cheng, Y.-J. *Macromolecules* **2015**, *48* (9), 2978–2988.
- (13) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabiny, M. L.; Gordeyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, No. 47, 5061–5063.
- (14) Lin, H.-W.; Lee, W.-Y.; Chen, W.-C. *J. Mater. Chem.* **2012**, *22* (5), 2120–2128.
- (15) Kang, I.; An, T. K.; Hong, J.-a.; Yun, H.-J.; Kim, R.; Chung, D. S.; Park, C. E.; Kim, Y.-H.; Kwon, S.-K. *Adv. Mater.* **2013**, *25* (4), 524–528.
- (16) Ballantyne, A. M.; Chen, L.; Nelson, J.; Bradley, D. D. C.; Astuti, Y.; Maurano, A.; Shuttle, C. G.; Durrant, J. R.; Heeney, M.; Duffy, W.; McCulloch, I. *Adv. Mater.* **2007**, *19* (24), 4544–4547.
- (17) Hollinger, J.; Sun, J.; Gao, D.; Karl, D.; Seferos, D. S. *Macromol. Rapid Commun.* **2013**, *34* (5), 437–441.
- (18) Cihaner, A. *Synlett* **2015**, 26 (04), 449–460.
- (19) Atak, S.; İçli-Özkut, M.; Önal, A. M.; Cihaner, A. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (20), 4398–4405.
- (20) Karabay, B.; Pekel, L. C.; Cihaner, A. *Macromolecules* **2015**, *48* (5), 1352–1357.
- (21) Patra, A.; Agrawal, V.; Bhargava, R.; Shahjad; Bhardwaj, D.; Chand, S.; Sheynin, Y.; Bendikov, M. *Macromolecules* **2015**, *48* (24), 8760–8764.
- (22) Mercier, L. G.; Leclerc, M. *Acc. Chem. Res.* **2013**, *46* (7), 1597–1605.
- (23) Okamoto, K.; Zhang, J.; Housekeeper, J. B.; Marder, S. R.; Luscombe, C. K. *Macromolecules* **2013**, *46* (20), 8059–8078.
- (24) Rudenko, A. E.; Thompson, B. C. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53* (2), 135–147.
- (25) Estrada, L. A.; Deininger, J. J.; Kamenov, G. D.; Reynolds, J. R. *ACS Macro Lett.* **2013**, *2* (10), 869–873.
- (26) Kerszulis, J. A.; Johnson, K. E.; Kuepfert, M.; Khoshabo, D.; Dyer, A. L.; Reynolds, J. R. *J. Mater. Chem. C* **2015**, *3* (13), 3211–3218.
- (27) Ponder, J. F.; Österholm, A. M.; Reynolds, J. R. *Macromolecules* **2016**, *49* (6), 2106–2111.
- (28) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18* (10), 309–315.
- (29) Bubnova, O.; Crispin, X. *Energy Environ. Sci.* **2012**, *5* (11), 9345–9362.
- (30) Günther Wyszecki, W. S. S. *Color Science: Concepts and Methods, Quantitative Data and Formulae*, 2nd ed.; Wiley: Hoboken, NJ, U.S.A., 2000.
- (31) Mahy, M.; Van Eycken, L.; Oosterlinck, A. *Color Res. Appl.* **1994**, *19* (2), 105–121.
- (32) Amb, C. M.; Beaujuge, P. M.; Reynolds, J. R. *Adv. Mater.* **2010**, *22* (6), 724–728.