

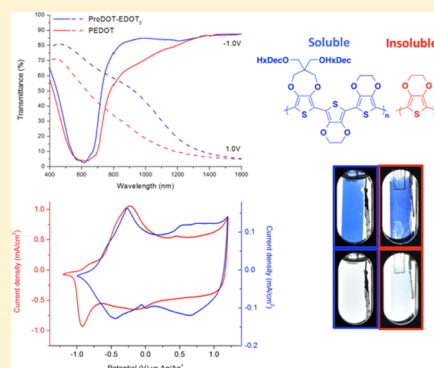
# Designing a Soluble PEDOT Analogue without Surfactants or Dispersants

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## Supporting Information

**ABSTRACT:** Copolymerization of alkoxy-functionalized 3,4-propylenedioxythiophenes (ProDOTs) with unfunctionalized 3,4-ethylenedioxythiophenes (EDOTs) in varying ratios using direct arylation yields a series of solution processable polymers with highly tunable optical and electronic properties. Within this series, we have identified ProDOT–EDOT<sub>2</sub>, a copolymer containing 67% EDOT compositionally, that combines the low oxidation potential, the redox behavior, and the deep-blue neutral color that are characteristic of PEDOT with the high solubility, exceptional electrochromic contrast, and color neutrality in the oxidized state characteristic of alkoxy-functionalized PProDOTs.



## 1. INTRODUCTION

Since its discovery in the 1980s, poly(3,4-ethylenedioxythiophene) (PEDOT) has become one of the most studied and used electroactive polymers because of its redox activity, high conductivity with concurrent visible transmissivity, accompanying thermal, chemical, and environmental stability, as well as organic and, to some extent, aqueous electrolyte compatibility.<sup>1,2</sup> Thin films of PEDOT have been evaluated for use in a variety of applications ranging from transistors to electrolytic capacitors and organic supercapacitors, solar cells, and antistatic coatings.<sup>3–7</sup> In addition, PEDOT was also one of the first cathodically coloring electrochromic polymers, switching from a deep blue neutral form to a sky-blue transmissive oxidized form.<sup>8,9</sup> In the absence of surfactants or dispersants (such as polystyrenesulfonate (PSS<sup>−</sup>)), PEDOT is an insoluble polymer that must be prepared by either electrochemical oxidative polymerization or a vapor phase polymerization, where the properties of the resulting PEDOT films are highly dependent on the precise polymerization conditions and the structural and molecular weight characterizations are difficult.<sup>10–12</sup> Previously, attempts have been made to develop a soluble version of PEDOT by functionalization of the ethylene bridge with alkyl chains, but any direct manipulation of the EDOT unit changes the electrochemical and optical properties of the resulting polymer as a result of the increased steric bulk and regioirregularity induced by the solubilizing groups.<sup>13,14</sup> To facilitate solution processing, EDOT is polymerized in the presence of PSS<sup>−</sup> or another solubilizing salt to form an aqueous dispersion (e.g., PEDOT:PSS) which allows these composites to be deposited by e.g. spin-coating, slot-die coating, or inkjet printing.<sup>1,15–19</sup>

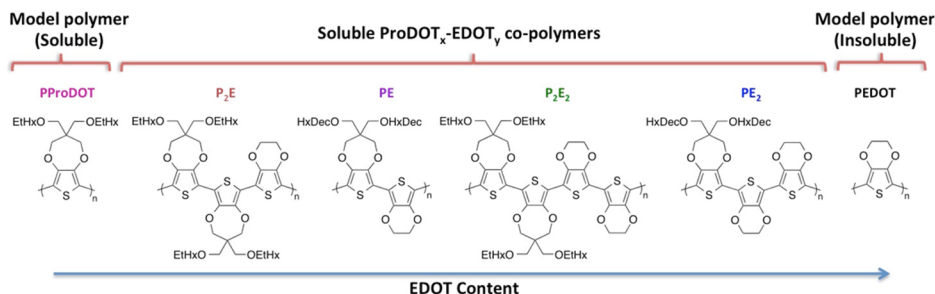
While PEDOT:PSS is used effectively in various solid-state applications where device operation relies on PEDOT maintaining its oxidation state, electrochemical devices such as supercapacitors and electrochromic displays rely on complete and reversible switching between two extreme redox states for optimal device performance (i.e., complete charge/discharge in supercapacitors and optimal color contrast in electrochromic devices). In the presence of an excess of an immobilized counterion, such as PSS<sup>−</sup>, PEDOT cannot be fully reduced to its charge neutral form, limiting its use as an active material in these electrochemical devices. In addition to numerous solvent additives or post-treatment methods that have been evaluated to either remove or segregate the PSS<sup>−</sup>, polyethylenimine (PEI) has been used to chemically reduce PEDOT:PSS for an all-polymer battery application.<sup>16,17,20–22</sup> However, even this method was not able to fully remove polaronic charge carriers from the PEDOT backbone.<sup>22</sup>

Here, we have designed and prepared soluble dioxothiophene polymers (Scheme 1) which are electrochemically equivalent and optically superior to PEDOT with the added advantage of being highly soluble in organic solvents without having to structurally modify the EDOT unit or use any additional surfactants or dispersants. This is achieved by copolymerizing various ratios of EDOT with alkoxy-functionalized 3,4-propylenedioxythiophene (ProDOT) as the solubilizing unit. Alkoxy-functionalized ProDOT was chosen due to its (i) electron richness to maintain a low oxidation potential, (ii) ease of side chain manipulation to tune solubility, and (iii) high

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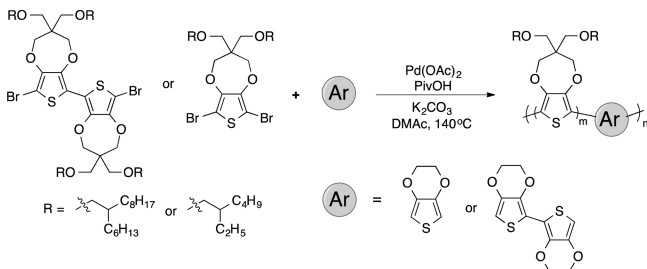
Scheme 1. Full Series of Investigated ProDOT<sub>x</sub>-EDOT<sub>y</sub> (P<sub>x</sub>E<sub>y</sub>) Copolymers as Well as the Parent Homopolymers

electrochromic contrast and color neutral oxidized state.<sup>23</sup> We show that it is possible to combine these two model polymers, PProDOT and PEDOT, to obtain a copolymer with the high solubility and colorless oxidized state of PProDOT and the low onset of oxidation, high electrochemical activity over a broad voltage range, and vibrant blue neutral state color of PEDOT. It has been previously demonstrated in the literature that EDOT readily undergoes direct (hetero)arylation polymerization (DHAP) as either the dihydrogen or dihalide species, allowing for us to avoid the use of more toxic cross-coupling polymerization methodologies such as the tin reagents employed in Stille couplings.<sup>24,25</sup>

## 2. EXPERIMENTAL SECTION

Additional synthetic procedures, characterization, materials, and instrumentation details can be found in the [Supporting Information](#).

**2.1. Materials.** PProDOT was prepared via an oxidative polymerization following a published procedure ( $M_n$ : 12.4 kDa;  $M_w/M_n$ : 1.8).<sup>26</sup> The series of ProDOT<sub>x</sub>-EDOT<sub>y</sub> (P<sub>x</sub>E<sub>y</sub>) copolymers, shown in [Scheme 1](#), were synthesized by DHAP ([Scheme 2](#) and [Figure S1](#)).

Scheme 2. Synthetic Route to ProDOT<sub>x</sub>-EDOT<sub>y</sub> (P<sub>x</sub>E<sub>y</sub>) Copolymers via DHAP

Each of the copolymers was designed to achieve a solubility exceeding 30 mg/mL to be suitable for a wide range of coating methods yielding films with varied thicknesses. To achieve this solubility, PE and PE<sub>2</sub> were functionalized with 2-hexyldecyloxy (HD) side chains, whereas shorter 2-ethylhexyloxy (EH) side chains were sufficient for the other copolymers. P<sub>2</sub>E ( $M_n$ : 14.5 kDa;  $M_w/M_n$ : 2.0) and P<sub>2</sub>E<sub>2</sub> ( $M_n$ : 14.1 kDa;  $M_w/M_n$ : 4.5) were synthesized via previously reported methodologies.<sup>27,28</sup> PE ( $M_n$ : 43.8 kDa;  $M_w/M_n$ : 1.4) and PE<sub>2</sub> ( $M_n$ : 56 kDa;  $M_w/M_n$ : 1.8) were also polymerized using direct arylation polymerization and are described in detail in the [Supporting Information](#).

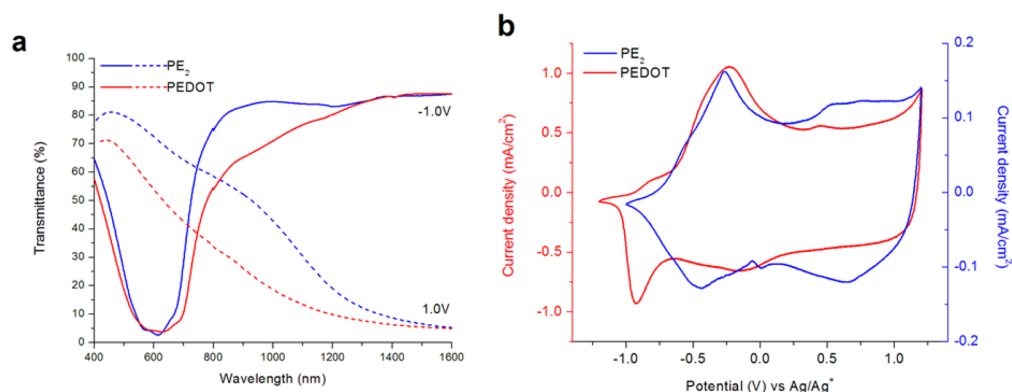
**2.2. Film Preparation.** In this study, the copolymers and PProDOT were spray coated onto ITO/glass (25 × 75 × 0.7 mm<sup>3</sup>, sheet resistance: 8–12 ohm/sq, Delta Technologies) using a simple hand-held airbrush (Iwata-Eclipse HP-BC, 15 psi) from 5 mg/mL polymer–chloroform solutions (BDH, 99.8%) to an optical density of 1.4–1.6. ITO-coated glass slides were cleaned with toluene, acetone, and isopropanol and used as the working electrode for the spectroelectrochemical measurements. Propylene carbonate was used as the electrolyte solvent (PC, Acros Organics, 99.5%) and was

purified and dried using a solvent purification system from Vacuum Atmospheres. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Alfa Aesar, 98%) was used as the supporting electrolyte for the electropolymerization of EDOT as well as the electrochemical and spectroelectrochemical measurements. TBAPF<sub>6</sub> was purified by recrystallized from hot ethanol. Glassy carbon button electrodes (0.07 cm<sup>2</sup>) were used for the cyclic voltammetry and differential pulse voltammetry measurements. For the electrochemical measurements the polymers were drop cast on the glassy carbon electrodes with a fixed volume of 3 μL from a 2 mg/mL solution. PEDOT was potentiostatically polymerized on ITO and glassy carbon at 1.0 V for 30 s in a solution containing 50 mM EDOT dissolved in 0.5 M TBAPF<sub>6</sub>-PC.

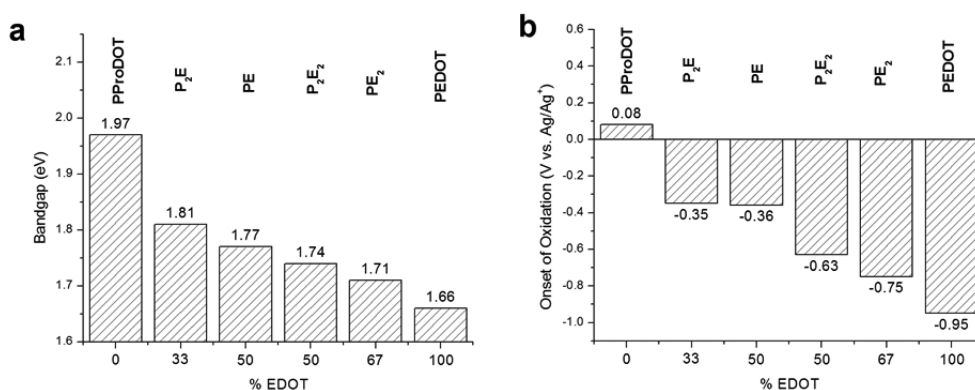
**2.3. Film Characterization.** Electrochemical measurements were performed in a three-electrode cell with a Pt flag as the counter electrode, a Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub> in 0.5 M TBAPF<sub>6</sub>-ACN,  $E_{1/2}$  for ferrocene: 68 mV) as the reference electrode, and a polymer-coated glassy carbon button electrode as the working electrode. The voltage and current were controlled and monitored with an EG&G PAR 273A potentiostat/galvanostatic under CorrWare control. All films were characterized via cyclic voltammetry between −0.8 and 0.8 V at 50 mV/s for 25 cycles; the onset of oxidation was determined by differential pulse voltammetry. The *in situ* spectroelectrochemical measurements were carried out using the same potentiostat/galvanostatic in combination with Varian Cary 5000 UV–vis–NIR spectrophotometer. The switching speeds were determined by square-wave potential absorptiometry (chronoabsorptiometry). Change in absorption was monitored at  $\lambda_{max}$  for the given polymer switched between two potentials (−1.0 to 1.0 V in the case of PE and PE<sub>2</sub>). All colorimetric values were quantified by converting the absorbance spectra to CIELAB  $L^*a^*b^*$  color coordinates where the  $L^*$  represents the white–black balance,  $a^*$  the green–red balance, and  $b^*$  the blue–yellow balance of a given color. Photography was performed using a Nikon D90 SLR camera with a Nikon 18–105 mm VR lens. The photographs are presented without any manipulation apart from cropping. The degree of color saturation for the different polymers was estimated using eq S1 of the [Supporting Information](#) where the color saturation ( $S_{ab}$ ) is defined as the ratio of chromatic color ( $C_{ab}^*$  to the total color sensation on a scale of 0 to 100 where 100 is the pure color).

## 3. RESULTS AND DISCUSSION

From the structures shown in [Scheme 1](#), PE<sub>2</sub> has the highest EDOT content of all the copolymers. However, even with every third heterocycle in PE<sub>2</sub> being an alkoxy-functionalized ProDOT unit, we found this copolymer to be optically (in the charge neutral state) and electrochemically essentially identical to electrochemically polymerized PEDOT as shown in the transmittance spectra and cyclic voltammograms in [Figure 1](#). In the charge neutral state (−1.0 V in [Figure 1a](#)), both PE<sub>2</sub> and PEDOT exhibit a transmittance minimum at ca. 615 nm, giving them both a deep blue color. Despite the similarities in the neutral state color, there is a remarkable difference in the oxidized state spectra (+1.0 V in [Figure 1a](#)). PE<sub>2</sub> has a narrower



**Figure 1.** (a) Transmittance spectra of PE<sub>2</sub> (blue curves) and electrochemically polymerized PEDOT (red curves) on ITO/glass in their charge neutral (−1.0 V vs Ag/Ag<sup>+</sup>, solid lines) and oxidized states (+1.0 V vs Ag/Ag<sup>+</sup>, dashed lines) in 0.5 M TBAPF<sub>6</sub>/PC. (b) Cyclic voltammograms of PE<sub>2</sub> (blue line) and PEDOT (red line) on glassy carbon electrodes at a sweep rate of 50 mV/s.



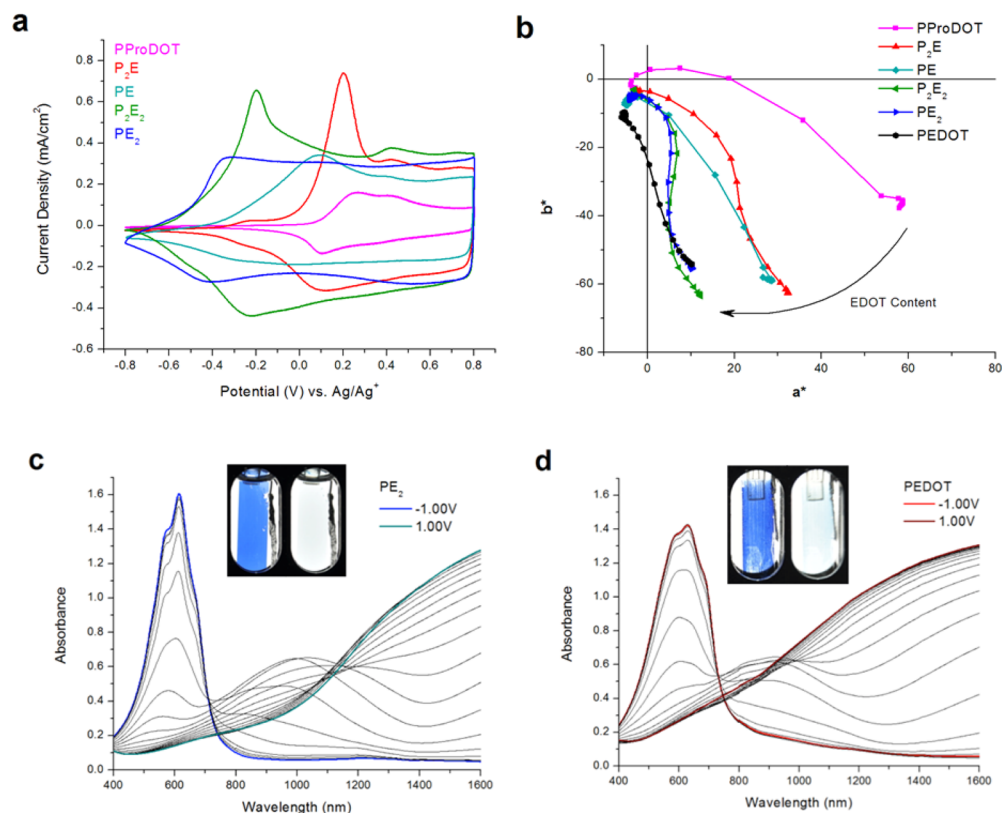
**Figure 2.** Progression of the (a) optical band gap and the (b) onset of oxidation (determined by differential pulse voltammetry) as a function of EDOT content in P<sub>x</sub>E<sub>y</sub> copolymers compared to their parent polymers PProDOT and PEDOT.

and more defined absorbance profile in the visible range with far less tailing into the near-IR in its oxidized state when compared to PEDOT. This results in both a more neutral color and a significantly more transmissive oxidized state. A comparison of the cyclic voltammetry of these two polymers (Figure 1b) shows a remarkable similarity between them in both the onset of oxidation and voltage range of electroactivity. Such low potentials for current onsets demonstrate the highly electron-rich nature of the soluble copolymer film, as desired for applications where accessing the oxidized and conducting form of the polymer is important. In addition, both polymers exhibit high capacitive currents beyond the reversible redox process over a broad potential range (>1.5 V), which is a desirable attribute when considering these polymers for charge storage applications. This broad redox response is not typically seen in soluble ProDOT-based polymers, as they typically tend to exhibit both a much higher onset of oxidation and a more defined, Faradaic redox behavior. Interestingly, even though the ProDOT moieties with their solubilizing groups (i.e., that are significantly different from unfunctionalized EDOT) make up a third of the polymer chain, the electrochemical properties and the color in the charge neutral state bear little resemblance to the ProDOT homopolymer and many similarities to unfunctionalized PEDOT.

From these results, we focused on understanding how the P<sub>x</sub>E<sub>y</sub> copolymers differed from the parent PProDOT and PEDOT homopolymers as well as elucidate how changing the heterocycle ring ratios affected the optical and electrochemical properties. Surprisingly, the addition of just one EDOT unit for

every three heterocycles drastically altered the band gap and oxidation onset compared to the homopolymer PProDOT, as shown in Figure 2. P<sub>2</sub>E has an optical band gap ( $E_{g,opt}$ ) of 1.81 eV, which is significantly narrower than the PProDOT homopolymer with an  $E_{g,opt}$  of 1.97 eV. Similarly, the onset of oxidation is lowered by 0.43 V when exchanging every third ProDOT unit for an EDOT. Increasing the amount of EDOT further from 33% to 50% and finally to 67% results in a progressive decrease in both the band gap (Figure 2a) and the onset of oxidation (Figure 2b), albeit at a more gradual rate. PE<sub>2</sub>, with an EDOT content of 67%, has an  $E_{g,opt}$  that is 0.26 eV smaller than PProDOT but only 0.05 eV larger than electrochemically polymerized PEDOT. Compared to PProDOT, the oxidation potential is almost 0.8 V lower for PE<sub>2</sub>. The lower oxidation potential and narrower  $E_{g,opt}$  is the result of reduced steric interactions between adjacent rings as the amount of solubilizing groups decrease, which leads to a planarization of the polymer backbone.<sup>28</sup>

As demonstrated in Figure 3a, adding just one EDOT unit to the ProDOT system (P<sub>2</sub>E) not only lowers the onset of oxidation but also results in a significant, almost 5-fold, increase in the current density compared to the ProDOT homopolymer. The high current density is also maintained for the other EDOT containing copolymers. Another interesting observation is found when comparing PE and P<sub>2</sub>E<sub>2</sub>; even if the overall EDOT content in one repeat unit is the same (50%), the incorporation of a biEDOT unit results in a significant, almost 0.3 V decrease in the onset of oxidation. This is likely due to the planar, electron-rich nature of the biEDOT unit, which, in



**Figure 3.** (a) Cyclic voltammograms of PProDOT and the P<sub>x</sub>E<sub>y</sub> copolymers in 0.5 M TBAPF<sub>6</sub>-PC at 50 mV/s. (b) *a\*b\** diagram showing the color change occurring during electrochemical oxidation of the polymer series from -1.0 V to 0.8 or 1.0 V vs Ag/Ag<sup>+</sup> in 0.1 V increments. Absorbance as a function of potential recorded between -1 and +1 V vs Ag/Ag<sup>+</sup> of (c) PE<sub>2</sub> and (d) electrochemically polymerized PEDOT in 0.5 M TBAPF<sub>6</sub>/PC.

**Table 1.** Colorimetry and Optical Comparisons of P<sub>x</sub>E<sub>y</sub> Polymer Series

polymer	<i>L*</i> , <i>a*</i> , <i>b*</i> (neutral)	<i>L*</i> , <i>a*</i> , <i>b*</i> (oxidized)	color saturation (neutral)	$\Delta E_{ab}^*$ of P <sub>x</sub> E <sub>y</sub> vs PEDOT (neutral)	$\Delta E_{ab}^*$ of P <sub>x</sub> E <sub>y</sub> vs PProDOT (neutral)
PProDOT	42, 58, -38	89, -3, -3	86	51.1	0.0
P <sub>2</sub> E	33, 32, -63	89, -2, -3	91	23.9	37.2
PE	30, 27, -58	87, -2, -3	91	18.2	38.8
P <sub>2</sub> E <sub>2</sub>	37, 12, -63	92, -3, -3	87	9.4	52.6
PE <sub>2</sub>	34, 10, -56	83, -3, -5	86	2.2	51.9
PEDOT	35, 10, -54	81, -6, -10	84	0.0	51.1

comparison to a single EDOT unit, is able to more efficiently stabilize the positive charge carriers formed during oxidation.

The narrowing of the  $E_{g,opt}$  and a red-shift of the  $\lambda_{max}$  (Figure S2) that is observed as the EDOT content is increased translate into a color change that progresses from the distinct purple-magenta color of alkoxy-functionalized PProDOT to the vibrant deep blue color of PEDOT. To accurately quantify and compare the colors, the absorbance spectra were converted to CIELAB *L\*a\*b\** coordinates. The *a\*b\** representation in Figure 3b allows us to quantify both the hue and saturation of the color where *a\** represents the red-green balance and *b\** the yellow-blue balance of a given color. Further, the *L\** coordinate represents the white-black balance (i.e., the lightness or darkness). All the copolymers fall in the +*a\** and -*b\** (red-magenta-purple-blue) quadrant of the color space, as shown in Figure 3b and Figure S3. The red-shift observed in the  $\lambda_{max}$  translates into the color of the polymer becoming more blue as indicated by the high negative *b\** and the progressive lowering of the *a\** (red) component with increasing EDOT content and increased chain relaxation. The color coordinates for all the copolymers are summarized in Table 1. From the

*L\*a\*b\** values we can determine the degree of color saturation (see eq S1 in Supporting Information), which defines the ratio of chromatic color to the total color sensation on a scale of 0–100, where 0 is gray and 100 a pure color.<sup>29</sup> All the soluble copolymers, as well as PProDOT, exhibit a color saturation between 86 and 91 (see Table 1); these values represent exceptional degrees of color saturation and color purity for a material. As seen graphically in Figure 3b and Figure S3 and numerically in Table 1, the color coordinates of the charge neutral states of PE<sub>2</sub> and PEDOT are very similar. The difference in color can be quantitatively compared using eq 1 to calculate the color difference ( $\Delta E_{ab}^*$ ).<sup>29–31</sup> As shown in Table 1, the value of  $\Delta E_{ab}^*$  for PE<sub>2</sub> and PEDOT is 2.2 in the colored state. A  $\Delta E_{ab}^*$  lower than 2.3 means that two colors (in this case of PE<sub>2</sub> and PEDOT) are indistinguishable to a standard observer.<sup>29,30,32</sup>

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

In addition to a high color saturation and vibrancy, the copolymers all switch to a highly transmissive and color neutral state upon electrochemical oxidation as can be seen in Table 2



**Table 2. Summary of Electrochemical and Optical Properties of P<sub>x</sub>E<sub>y</sub> Copolymers**

polymer	EDOT content (%)	$\lambda_{\max}$ (nm)	contrast (%T)	switching speed <sup>a</sup> (s)
PProDOT	0	552 (600) <sup>b</sup>	71	1.1
P <sub>2</sub> E	33	590	71	0.64
PE	50	596	71	1.1
P <sub>2</sub> E <sub>2</sub>	50	606	75	0.53
PE <sub>2</sub>	67	613	71	0.51
PEDOT	100	629	46	0.66

<sup>a</sup>95% of full switch from colored-to-bleached, calculated from chronoabsorptiometry. <sup>b</sup>Secondary vibronic peak.

and in the color tracks in Figure 3b. In comparison to PEDOT, all copolymers are more color neutral in their oxidized states as indicated by the lower  $a^*b^*$  values and the higher  $L^*$ .<sup>33,34</sup> The slightly negative  $a^*b^*$  values recorded for the oxidized states are due to tailing of charge carrier bands into the visible as will be discussed in more detail below.

As shown in Table 2 and demonstrated for PE<sub>2</sub> in Figure 3c, all the copolymers exhibit high electrochromic contrasts ( $\Delta\%T$ , defined as the change in transmittance between the neutral and oxidized states measured at  $\lambda_{\max}$ ) exceeding 70% with switching times on the order of 0.5–1 s (the chronoabsorptiometry data for PE and PE<sub>2</sub> are shown in Figure S4 and in ref 28 for P<sub>2</sub>E and P<sub>2</sub>E<sub>2</sub>). Even though comparable electrochromic contrasts could not be obtained here for PEDOT using our electrolyte system and polymerization method, a contrast of 71  $\Delta\%T$  at 635 nm has been reported for electrochemically deposited PEDOT by Bendikov and co-workers using highly optimized film thicknesses and polymerization conditions.<sup>12</sup> The main difference in the electrochromic switching performance of this family of copolymers we observed was that with increasing EDOT content the potential at which the  $\pi$ – $\pi^*$  absorption band is completely bleached out decreases following a similar trend as observed for the  $E_{g, \text{opt}}$  with PE<sub>2</sub> essentially reaching its fully bleached state at just 0.0 V, as shown in the spectra in Figure 3c. Interestingly, even if little electrochromic change is observed at higher potentials, PE<sub>2</sub> and P<sub>2</sub>E<sub>2</sub> are still able to maintain a high redox current up to potentials exceeding 1 V vs Ag/Ag<sup>+</sup>.

A more careful comparison of the spectroelectrochemistry of PE<sub>2</sub> and PEDOT (Figures 3c and 3d) shows that the absorption spectra are nearly identical in the charge neutral states including the same vibronic features, and this accounts for the similarity in the color of the two polymers as discussed above. The noticeable difference in the electrochromic contrast and in the chromaticity of the oxidized states (with a  $\Delta E_{ab}^*$  of 6.2 for PE<sub>2</sub> vs PEDOT in their oxidized states) is due to the charge carrier bands in PEDOT tailing into the visible, leaving more residual color and reducing contrast. In PE<sub>2</sub>, the higher energy charge carrier band originating from polaronic charge carriers is red-shifted by 100 nm from 923 nm to approximately 1038 nm. Also, the bipolaron absorption ( $\lambda_{\max}$  outside the recorded wavelength range) is shifted to a lower energy in PE<sub>2</sub>, which significantly reduces the tailing into the visible and accounts for a more color neutral oxidized state. The positions of the charge carrier bands in PE<sub>2</sub> are more similar to those found in alkoxy-functionalized PProDOT than those in PEDOT. This red-shift of charge carrier bands is an interesting observation as it differs from the trends observed for the  $E_{g, \text{opt}}$ , the color, and the oxidation potential where the copolymers

exhibit properties more closely resembling those of PEDOT than those of PProDOT.

#### 4. CONCLUSIONS AND PERSPECTIVES

In summary, we have developed a highly soluble dioxothiophene-based polymer using direct arylation copolymerization that mimics the electrochemical and optical properties of PEDOT, and we have been able to accomplish this without additional surfactants or dispersants. Using this copolymerization method, we have prepared a family of polymers that combines the attractive properties of PEDOT (low oxidation potential, broad electrochemical window) with those of alkoxy-functionalized PProDOTs (high solubility and exceptional electrochromic contrast) with a range of accessible colors. The polymer with the highest EDOT content (PE<sub>2</sub>) possesses a neutral state color that is optically indistinguishable from electrochemically prepared PEDOT while achieving a higher contrast and a more color neutral oxidized state. This polymer also possesses the lowest oxidation potential we have observed for a soluble thiophene-based polymer and a stable electrochemical window of over 2 V. Having these polymers in hand provides numerous possibilities in various applications presently being investigated in our laboratory that extend beyond electrochromism, including highly electrically conducting (>100 S/cm), hole-transporting and charge dissipating films, along with charge storing supercapacitors, and active bioelectronic circuit elements.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02638.

Synthetic procedures, characterization, materials, and instrumentation details (PDF)

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##### Notes

The authors declare no competing financial interest.

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