

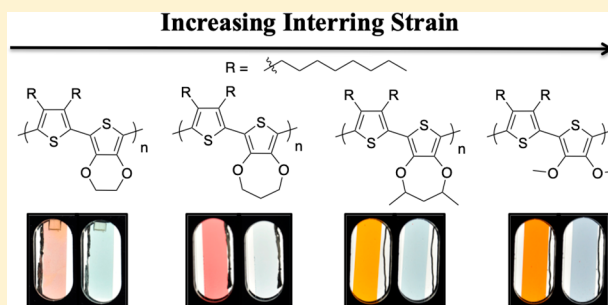
# A Fruitful Usage of a Dialkylthiophene Comonomer for Redox Stable Wide-Gap Cathodically Coloring Electrochromic Polymers

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## Supporting Information

**ABSTRACT:** A series of conjugated polymers are prepared via direct heteroarylation polymerization with the goal of yielding wide-gap, yellow and orange switching to transmissive cathodically coloring electrochromic polymers (ECPs). The polymers are based on repeat units of dialkylthiophene (DAT) in alternation with dioxythiophenes (DOTs) with various side chains to induce differing levels of inter-ring strain yielding 3,4-ethylenedioxythiophene (DAT-EDOT), 3,4-propylenedioxythiophene (DAT-ProDOT), 3,4-(1,3-dimethylpropylene)dioxythiophene (DAT-DMP), and 3,4-dimethoxythiophene (DAT-DMOT) structured polymers. Examination of the optoelectronic properties via UV–vis–NIR spectroscopy, differential pulse voltammetry, and spectroelectrochemistry shows that while increasing the inter-ring strain induced by the side chain of the DOT unit leads to an increased oxidation potential ranging from  $-122$  to  $+288$  mV relative to  $\text{Fc}/\text{Fc}^+$ , this does not decrease the accessibility of the extreme charge states. Through subtle steric interactions between the arylene units, neutral polymer colors were tunable from yellow to deep reds while maintaining transmissive oxidized states. These DAT-based polymers also show increased redox switching stability compared to that of previous generations of wide-gap cathodically coloring ECPs that incorporate phenylene units with DAT-ProDOT and DAT-DMP films showing minimal loss of electrochromic contrast over 1000 switches and a DAT-DMP device showing minimal contrast loss over 10000 cycles. With these properties, these polymers have the ability for subtractive color mixing with other ECPs to create broadly absorbing, color neutral (black and brown) blends that are redox stable.



## INTRODUCTION

Redox-active conjugated polymers have structurally controlled optical properties with redox switching capabilities that make them attractive to study with reference to the application of electrochromism.<sup>1–9</sup> Organic electrochromic polymers (ECPs) can be solution processed under ambient conditions and are lightweight and flexible, while providing a fine degree of structurally induced color control. The electrochromic performance of ECPs has undergone vast improvement over recent years due to an increased understanding of their fundamental electrochemical and spectral/colorimetric properties, solution processing characteristics, thin film morphologies, and interactions with electrodes.<sup>10–22</sup>

The history of research in fully conjugated ECPs has yielded materials that span the entire color palette.<sup>23–29</sup> These polymers can be spray cast to form vividly colored films that upon oxidation become highly transmissive in the visible region. Recently, the approaches toward creating black-to-transmissive electrochromic polymeric materials have been either through the generation of broadly absorbing random copolymers or via subtractive color mixing of polymeric inks.<sup>30–37</sup> The latter of the two approaches has, to date, allowed for finer control, more accurate reproducibility, and higher contrast through the mixing of cyan, magenta, and yellow to create broadly absorbing ECP

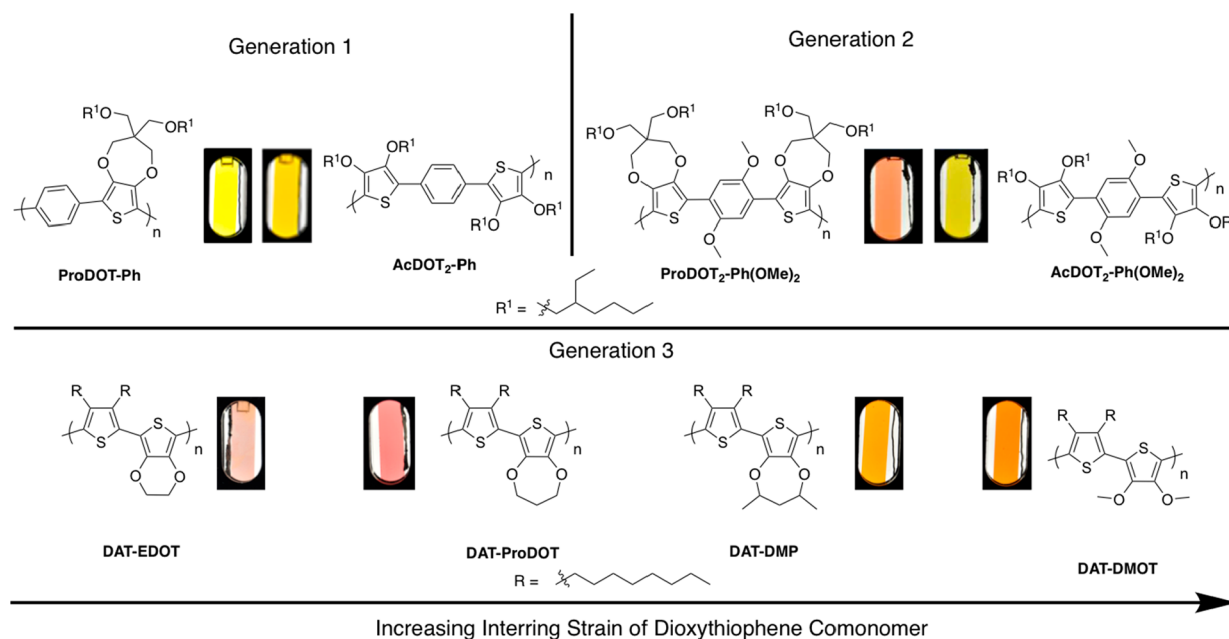
blends. One of the largest challenges to date with using the solution blending technique relates to the short switching lifetime of the yellow to clear switching polymer.<sup>38–44</sup>

In order for an ECP to be yellow, it requires a high-energy optical absorption, between 380 and 550 nm in the colored state. To then exhibit a high visible light contrast during switching, a cathodically coloring ECP then requires its oxidized state to absorb in the near-infrared ( $>700$  nm). ECPs we have developed that have these optical properties have historically used phenylene units in the backbone of the polymer, which offer both a deep HOMO and a torsional strain that lowers  $\pi$ – $\pi$  overlap along the backbone and widens the gap, relative to their all dioxythiophene counterparts. These phenylene-containing ECPs tend to have higher oxidation potentials than all thiophene polymers due to the larger energy of aromaticity relative to thiophene. These high oxidation potentials are hypothesized to be one of the causes of why yellow ECPs tend to have shorter switching lifetimes. Along with these high oxidation potentials there are open sites for reactivity of the radical cation states when the polymer is oxidized, leaving potential for nucleophilic attack

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**Figure 1.** Key polymers in the progression of designing soluble, wide-gap electrochromic polymers.

and radical–radical coupling. To this end we sought an alternative monomer to use in electron-rich cathodically coloring electrochromic polymers.

Figure 1 shows some key polymers in the progression of designing soluble, yellow and orange electrochromic polymers leading to the design of the current generation. Starting with generation 1, ProDOT-Ph was the first successful synthesis of a yellow to clear ECP using the phenylenes. When this material is sprayed into a film onto an ITO working electrode and subjected to repeated potential square waves that oxidize and reduce the polymer, it shows instability to switching within the first 10–20 cycles due to the high oxidation potential required to switch and the potential reactivity of the phenylene unit itself in the charged state.<sup>45</sup> The design rationale for AcDOT<sub>2</sub>-Ph was to increase the electron-rich dioxithiophene content of the polymer to lower the oxidation potential and maintain the wide gap by using the increased inter-ring strain provided by the acyclic nature of the AcDOT unit. This polymer is slightly more stable than ProDOT-Ph showing significant drops in contrast within the first 100 redox cycles. The second-generation polymers were synthesized to attempt to address these issues by incorporating methoxy groups on the phenylene portion of the polymer to simultaneously lower the oxidation potential to switch and sterically block the open sites from nucleophilic attack and radical coupling.<sup>39</sup> While AcDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> maintains a vibrant yellow color, the increased strain imparted by the Ph(OMe)<sub>2</sub> unit causes the polymer to have a high oxidation potential and only a marginal increase in redox stability. During redox switching, ProDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> lasts over 100 cycles with no drop in contrast, but the decrease in strain red-shifts the absorbance  $\lambda_{\text{max}}$  by 54 nm, leading to a red-orange polymer.

To overcome the issues with the redox switching stability in wide-gap phenylene-containing ECPs, here we report on the use of a dialkylthiophene (DAT) incorporated into alternating copolymers with dioxithiophenes to achieve a wide optical gap. The DAT monomer synthesized and used for the generation 3 study, specifically 3,4-diethylthiophene, provides inter-ring strain with alkyl chains directly appended to the backbone

helping the copolymers to reach wide optical gaps while blocking possible reactive sites for the radical cations. The octyl groups allow for the use of DOT monomers that do not have side chains and still yield soluble polymers than can be spray processed into thin films for characterization and use. The DOT comonomers were designed to vary in the inter-ring strain they provide to the  $\pi$ -conjugated backbone of the system. We show that increasing inter-ring strain can be used to blue-shift the absorption of the polymers by over 70 nm to tune color between yellows, oranges, and reds. We also show that three of the copolymers show increased redox switching stability as films in solution compared to previous wide-gap ECPs with minimal drops in contrast over 1000 cycles in electrolyte solution. Because of its lack of color shifting upon repeated redox cycling, the redox stability of DAT-DMP is investigated further in the construction of an encapsulated device containing DAT-DMP and a charge-storing polymer separated by a gel electrolyte. After an initial equilibration period of 200 switches, this device shows a contrast loss of <5  $\Delta\%$ T after 10000 cycles, which indicates a >81% retention of contrast overall.

## RESULTS AND DISCUSSION

**Polymer Synthesis and Characterization.** The synthetic approach to the monomer and polymer syntheses is shown in Scheme 1. Synthetic procedures, NMR spectra, elemental analyses, and GPC traces are located in the Supporting Information. Starting with commercially available 3,4-dibromothiophene, a Kumada coupling afforded 2, followed by subsequent bromination with NBS to form the desired 2,5-dibromo-3,4-diethylthiophene, 3. The synthetic scheme diverges from here where 3 can be used for direct heteroarylation polymerization with a dioxithiophene monomer to prepare the alternating copolymers DAT-EDOT, DAT-ProDOT, DAT-DMP, and DAT-DMOT.<sup>46–48</sup>

Comparisons of polymerization yields and GPC estimated molecular weights are collated in Table 1, and all GPC traces are shown in Figure S1. All of the polymers are soluble in toluene to at least 20 mg/mL, allowing for airbrush spray processing and drop casting for film formation.

Scheme 1. Synthetic Approach to Dialkylthiophene Monomer and Subsequent Direct Heteroarylation Polymerization

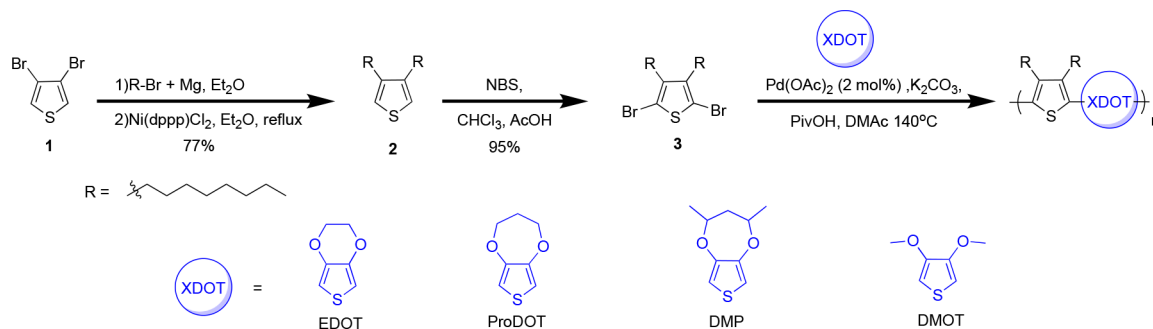


Table 1. GPC Estimated Polymer Molecular Weights and Polymerization Yields

polymer	yield (%)	$M_n$ (kDa)	$M_w$ (kDa)	$\bar{D}$
DAT-EDOT	79	61	143	2.3
DAT-ProDOT	81	32	81	2.6
DAT-DMP	77	25	56	2.2
DAT-DMOT	64	37	150	4.1

**Electrochemical and Optical Properties.** For electrochemical characterization, polymer films were drop cast onto Pt button electrodes from 3 mg/mL solutions in  $\text{CHCl}_3$  to cover the electrode. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured on films of the polymers to gain insight into how the different DOT comonomers affected the electrochemical properties. Upon examining the electrochemical oxidation of the materials via DPV (Figure 2a), the onset of oxidation follows the trend of inter-ring strain imposed by the DOT comonomer (CV for polymers can be found in Figure S2). As inter-ring strain is increased from the least strained EDOT to the most strained DMOT, the resultant onset of oxidation ( $E_{\text{ox}}$ ) ranges from  $-122$  to  $+288$  mV relative to  $\text{Fc}/\text{Fc}^+$ , giving a large window for tuning the desired optical switching potential ( $E_{\text{ox}}$  values are collated in Table 2). These polymers all have  $E_{\text{ox}}$  values below the polymers in the generation one wide-gap polymers (ProDOT-Ph and AcDOT<sub>2</sub>-Ph). Both DAT-EDOT and DAT-ProDOT have  $E_{\text{ox}}$  values below that of the generation 2 polymers (ProDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> and AcDOT<sub>2</sub>-Ph(OMe)<sub>2</sub>) at  $-122$  and  $74$  mV, respectively. The DAT-DMP and DAT-DMOT polymers'  $E_{\text{ox}}$

Table 2. Optical and Electrochemical Properties of ECPs Studied

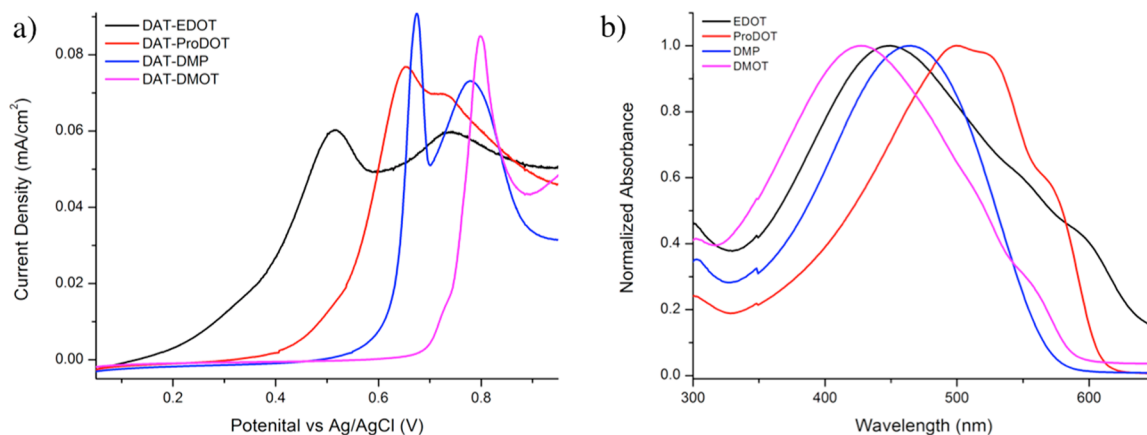
polymer	$E_{\text{ox}}^a$ (mV) vs $\text{Fc}/\text{Fc}^+$	$\lambda_{\text{max}}^b$ (nm)	$E_g^{b,c}$ (eV)
DAT-DMOT	288	427	2.10
AcDOT <sub>2</sub> -Ph(OMe) <sub>2</sub> <sup>d</sup>	330	446	2.38
ProDOT-Ph <sup>d</sup>	451	448	2.44
DAT-EDOT	$-122$	448	1.88
AcDOT <sub>2</sub> -Ph <sup>d</sup>	438	464	2.30
DAT-DMP	180	466	2.19
DAT-ProDOT	74	500	2.03
ProDOT <sub>2</sub> -Ph(OMe) <sub>2</sub> <sup>d</sup>	126	500	2.18

<sup>a</sup>As determined by DPV as the onset of the current for oxidation.

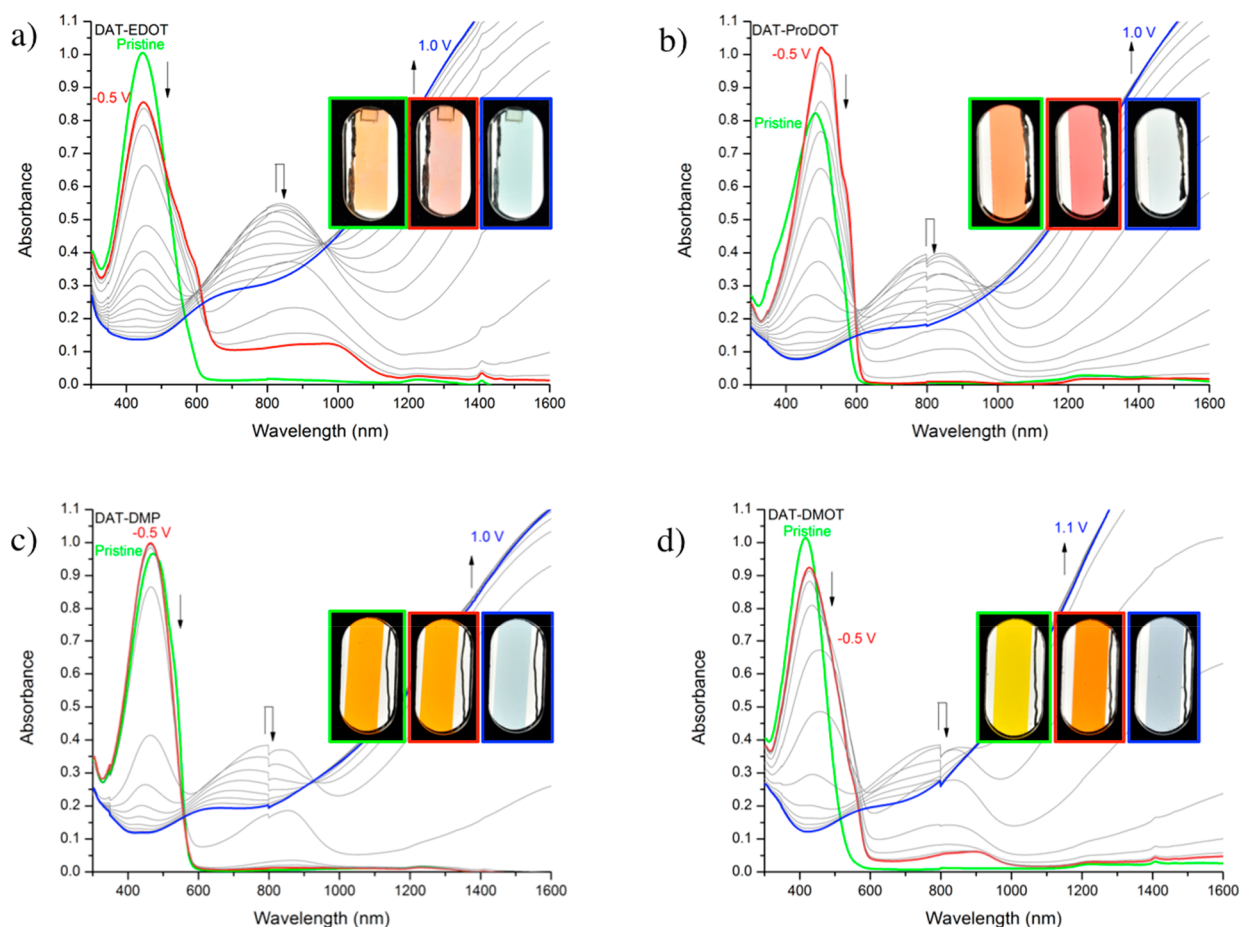
<sup>b</sup>For films cast onto ITO-coated glass measured after 10 CV cycles listed in order of increasing wavelength. <sup>c</sup>Bandgap determined by onset of light absorption. <sup>d</sup>Values from ref 38.

values fall between ProDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> and AcDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> with 180 and 288 mV, respectively.

For optical characterization, polymer films were airbrush sprayed onto glass/ITO electrodes from 3 mg/mL solutions in toluene, and the films subjected to 10 CV cycles before UV-vis spectra were measured. While DAT-ProDOT, DAT-DMP, and DAT-DMOT all formed smooth films from this method, DAT-EDOT films were consistently hazy, which is indicative of induced order during film formation. Figure 2b shows the UV-vis spectra of the films of the polymers after electrochemical conditioning (UV-vis spectra of as-cast films can be found in Figure S3 of the Supporting Information). The UV-vis absorption data are collated in Table 2 in order of



**Figure 2.** (a) Comparison of  $E_{\text{ox}}$  acquired via DPV for polymers on Pt button electrode in 0.5 M TBAPF<sub>6</sub>/PC. Reference:  $-450$  mV vs  $\text{Fc}/\text{Fc}^+$ . (b) Neutral state spectra of DAT-EDOT, DAT-ProDOT, DAT-DMP, and DAT-DMOT on ITO-coated glass in 0.5 M TBAPF<sub>6</sub>/PC electrolyte solution after 10 CV electrochemical conditioning cycles. Films were sprayed to an absorbance of  $1.00 \pm 0.05$  in the as-cast state to best compare the absorption and switching properties.<sup>49,50</sup> Absorbance values are normalized due to the increase/decrease of absorbance upon film break-in.



**Figure 3.** Spectroelectrochemistry and photographs of (a) DAT-EDOT, (b) DAT-ProDOT, (c) DAT-DMP, and (d) DAT-DMOT. The applied potential was increased in 50 mV steps between the fully colored and bleached states in 0.5 M TBAPF<sub>6</sub>/PC. The arrows show the progression of the peak evolution as a function of increasing potential.

increasing  $\lambda_{\max}$  including the previous generation polymers. It is important to note that the  $\lambda_{\max}$  and  $E_g$  do not follow the same trend as there is varying absorption broadness between the different polymers. This varying broadness manifests itself in the color of the polymer films not correlating with  $\lambda_{\max}$  as these polymers span the yellow–orange–red region. It should be noted that when comparing as-cast films to conditioned films, the polymers' absorbances typically exhibit varying degrees of red-shifting and broadening. When a polymer film is sprayed from a high vapor pressure solvent, it is deposited in a kinetically determined morphology as the solvent evaporates.<sup>49</sup> Upon electrochemical oxidation, the conjugated polymer must enter a more quinoid-like structure that causes its backbone to planarize and extend the effective conjugation length of the chromophore. Upon reduction back to the neutral state, the polymer geometry retains a more planar geometry (relative to the as-cast film) leading to a longer effective conjugation length and red-shifted absorbance. This typical red-shifting upon cycling was not observed for DAT-DMP as its absorbance exhibited a small blue-shift of its onset of  $\sim 5$  nm.

**Spectroelectrochemistry and Color Properties.** Spectroelectrochemical measurements were performed on polymer films sprayed on ITO glass in 0.5 M TBAPF<sub>6</sub> in propylene carbonate with a platinum counter electrode and a Ag/AgCl reference electrode with results shown in Figure 3 along with photographs of the films held at potential extremes dictated by the CV results. Optical contrast at  $\lambda_{\max}$  and the  $L^*a^*b^*$  values

are collated in Table 3. Upon electrochemical conditioning of electrochromic polymers, the UV–vis absorption often exhibits

**Table 3.** Color and Switching Properties of ECPs Studied

polymer	$\Delta\%T^{a,b}$ (at $\lambda_{\max}$ )	$L^*, a^*, b^*$ color coordinates <sup>b</sup>	
		neutral state	oxidized state
DAT-EDOT	58	65, 24, 36	83, −5, −8
DAT-ProDOT	63	60, 68, 34	86, −4, −8
DAT-DMP	65	87, 23, 59	90, −2, −4
DAT-DMOT	60	82, 25, 62	85, −1, −7
ProDOT-Ph <sup>c</sup>	67	87, 21, 73	88, −1, −3
AcDOT <sub>2</sub> -Ph <sup>c</sup>	51	87, 9, 76	87, 2, 4
ProDOT <sub>2</sub> -Ph(OMe) <sub>2</sub> <sup>c</sup>	70	80, 47, 36	91, −1, −1
AcDOT <sub>2</sub> -Ph(OMe) <sub>2</sub> <sup>c</sup>	59	89, −4, 85	81, −1, −1

<sup>a</sup>Difference between steady-state transmittance measured at fully oxidized and fully neutral states (all films sprayed to 10%T at  $\lambda_{\max}$ ).

<sup>b</sup>For a film cast onto ITO-coated glass. <sup>c</sup>Values from ref 38.

a characteristic red-shift of the absorbance as the polymer extends its effective conjugation length in the charge neutral state.

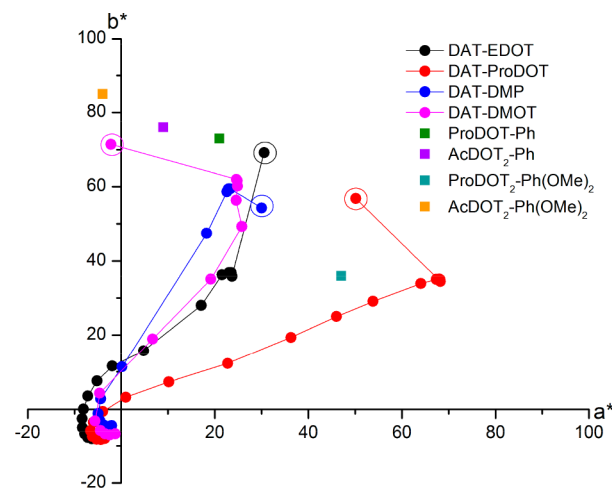
As a pristine film, DAT-EDOT shown in Figure 3a absorbs with a  $\lambda_{\max}$  of 448 nm giving rise to the orange color of the material. As can be seen in the photography it can be noted that this polymer forms relatively hazy films. Upon electrochemical break-in, there is a red-shifting of the onset of



absorbance with the appearance of a shoulder at 650 nm, but there is a drop in absorbance at  $\lambda_{\text{max}}$  and a low intensity, broad absorbance between 600 and 1100 nm indicative of polaron trapping. This broad absorption gives rise to the observed muted pink color of the material. It is unknown whether this phenomenon is caused by either chemical or morphological differences from the other polymers. The trapping in DAT-EDOT is hypothesized to be due to the oxidation of this polymer causing the formation of local potential wells where the polaron is energetically trapped. Upon oxidation, the polaronic peak is still present, and leads to a fairly asymmetric tailing across the visible and a slightly blue hue remains compared to the other polymers. The as cast film of DAT-ProDOT shown in Figure 3b absorbs with a  $\lambda_{\text{max}}$  of 491 nm, thus giving rise to a vibrant orange color. Upon break-in this polymer exhibits an increase in absorbance along with the characteristic red-shifting to a  $\lambda_{\text{max}}$  of 500 nm leading to a red colored polymer with no peaks indicating trapped polarons. Upon oxidation, this polymer's spectrum is flat across the visible giving a highly color neutral and transmissive state. DAT-DMP as a pristine film, shown in Figure 3c, absorbs with a  $\lambda_{\text{max}}$  of 466 nm. Upon break-in this spectrum exhibits a negligible blue-shift in onset with a  $\lambda_{\text{max}}$  and observable color that remained unchanged as a vibrant orange is observed in both states. Note that this polymer also does not show any indication of trapped polarons. In the oxidized state this polymer shows the highest color neutrality with a spectrum that is flat across the visible region. The as cast film of DAT-DMOT, shown in Figure 3d, has the highest energy  $\lambda_{\text{max}}$  of 421 nm and a vibrant yellow color, which was expected due to the increased inter-ring strain compared to the other polymers. Upon break-in the red-shift caused by relief of ring strain can be observed with the color shifting to an orange. There is also a small amount of absorbance between 600 and 1000 nm indicative of slight polaron trapping. This polaronic absorption can be seen again in the oxidized state with slight increased tailing into the visible from the NIR similar to that of DAT-EDOT, and leading to a slightly blue hued transmissive state.

Colorimetry utilizing the  $L^*a^*b^*$  color space, where  $a^*b^*$  values correlate to the chroma or saturation of a color (note:  $-a^*$  and  $+a^*$  correspond to green and red and  $-b^*$  and  $+b^*$  correspond to blue and yellow, respectively) and  $L^*$  depicts the lightness (a value of 0 would be black and 100 would be white), was used to demonstrate the control over colors in the neutral states. The  $a^*b^*$  color space results for the polymer films under study are presented graphically in Figure 4. In the neutral state, after electrochemical break-in, the polymers had  $L^*$  values ranging from 60 to 87,  $a^*$  values ranging from 23 to 68, and  $b^*$  values ranging from 34 to 62, thus remaining in the yellow-orange-red color space similar to the color coordinates for the previous generations' ECPs also shown in Figure 4. In the oxidized states, the transmissive forms had  $L^*$  values increased to range from 83 to 90, with low  $a^*$  values ranging from  $-5$  to  $-1$  and  $b^*$  values ranging from  $-8$  to  $-4$ . As the magnitudes of  $a^*$  and  $b^*$  increase, the colors become more saturated, and as one traverses between color points, the hue changes.

In this figure, the as-cast films are represented in this graph by the encircled points while the rest of the points are postconditioning. Upon break-in the change in color coordinates is greatest for DAT-ProDOT and DAT-DMOT with a increase in  $a^*$  and decrease in  $b^*$  indicating a red-shifting absorbance, while DAT-EDOT and DAT-DMP do not exhibit this characteristic change in color coordinates.



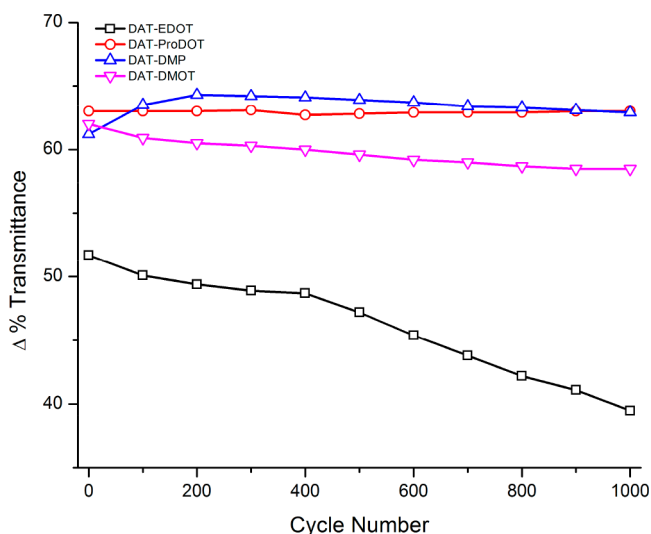
**Figure 4.** Colorimetric analysis of all the polymers. Plots of  $a^*b^*$  color coordinates at increasing applied potentials in 0.1 V steps from neutral (0 V vs Ag/AgCl) to fully oxidized states (1.0 V for DAT-EDOT, 1.0 V for DAT-ProDOT, 1.0 V for DAT-DMP, and 1.1 V for DAT-DMOT). Measurements were performed in 0.5 M TBAPF<sub>6</sub>/PC of films spray-cast onto ITO/glass electrodes. The polymer neutral states are furthest from the origin, and the values track toward the origin as the polymer is oxidized to the bleached state. The encircled points indicate the  $a^*b^*$  coordinates of the as-cast/pristine polymer before electrochemical cycling. The points not connected by lines are the neutral state  $a^*b^*$  coordinates of the previous generations' polymers.

DAT-EDOT's color coordinates move toward the origin upon break-in, showing a drastic decrease in color vibrancy caused by the apparent polaron trapping seen in the spectroelectrochemistry. DAT-DMP's color coordinates actually show a slight decrease in  $a^*$  and increase in  $b^*$  which can be explained by the slight blue-shift in the onset of absorbance of the film upon break-in. This is observed as only a small shift in color of the material upon break-in (remaining orange), which allows for ease of predicting the polymer's usefulness in color mixing.

After the initial electrochemical break-in, all of the polymers lie within the desired yellow–orange–red color space (positive  $a^*$  and positive  $b^*$ ), and upon electrochemical oxidation the color coordinates are shifted close to the origin, indicating color neutrality. In the neutral state, DAT-EDOT shows the least saturation of color with an  $L^*a^*b^*$  of 65, 24, and 36 but does reach a highly transmissive oxidized state with an  $L^*a^*b^*$  of 83,  $-5$ ,  $-8$ , further evidence that polaron trapping is the cause of the loss of contrast as the oxidized state of the material is still highly transmissive. DAT-DMOT and DAT-DMP both show similar neutral state color coordinates of 82, 25, 62 and 87, 23, 59, respectively. DAT-DMP does show a slightly more color neutral and transmissive oxidized state with color coordinates of 90,  $-2$ ,  $-4$  compared to 85,  $-1$ ,  $-7$  for DAT-DMOT. The polymer film of DAT-ProDOT has a high  $a^*$  with color coordinates at 60, 68, 34, giving rise to its vibrant orange-red color. This polymer still oxidizes to a highly transmissive and color neutral state with color coordinates of 86,  $-4$ ,  $-8$ .

The small structural changes allowed for varying inter-ring steric strain between these polymers and led to small, yet distinct changes in color. The human eye is sensitive to small changes in absorption, making this approach to color tuning advantageous. Increasing inter-ring steric strain causes blue-shifting absorbance at the cost of increasing oxidation potential. This trade-off must be balanced when attempting to control color and redox activity.

**Film Switching Stability.** Redox switching stability of these wide-gap systems has been one of the larger hurdles for obtaining useable materials, both as vibrant color switching ECPs and for creating high contrast black to transmissive polymer blends. To this end examining the contrast as a function of the number of switches gives a platform to compare materials. To examine the electrochemical redox stability of these polymers, films of each were sprayed to 10%T on ITO glass, and the transmittance at  $\lambda_{\max}$  was monitored over the course of 1000 repeated square-wave potential steps for 1000 cycles in 0.5 M TBAPF<sub>6</sub>/PC electrolyte solution that had been thoroughly dried and degassed with argon. Figure 5 details the



**Figure 5.** Contrast loss of ECP films measured relative to a glass/ITO background at  $\lambda_{\max}$  as a function of number of switches in 0.5 M TBAPF<sub>6</sub>/PC electrolyte solution with repeated square-wave potential steps for 1000 cycles. DAT-EDOT measured  $-0.5$  to  $1.0$  V at  $5$  s steps, DAT-ProDOT measured  $-0.5$  to  $1.0$  V at  $5$  s steps, DAT-DMP measured  $-0.5$  to  $1.0$  V at  $5$  s steps, and DAT-DMOT measured  $-0.5$  to  $1.1$  V at  $7$  s steps.

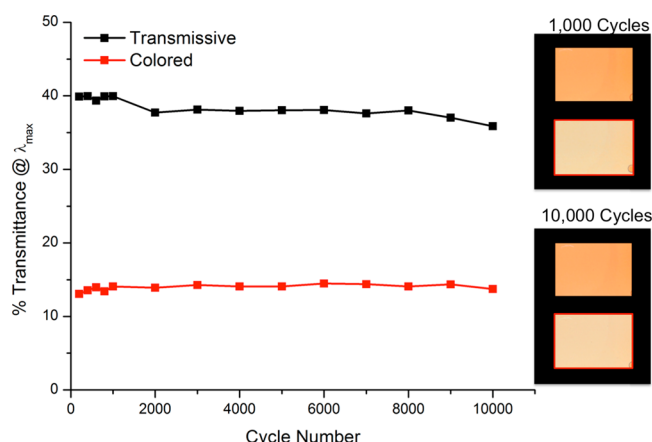
relationship between optical contrasts of the polymer films as a function of the number of electrochemical switches (the %T at  $\lambda_{\max}$  was monitored over the course of the cycles and can be found in Figure S4). It should be noted that the experiment was started after an electrochemical break-in of 10 CV cycles to monitor the proper peak maxima.

This break-in explains why DAT-EDOT has an initial contrast of only  $53 \Delta\%T$ . The polymer shows signs of a large amount of polaron trapping after the first electrochemical switch, as seen in the spectroelectrochemistry. The film only loses more contrast over the course of the 1000 electrochemical switches, ultimately dropping below  $40 \Delta\%T$ . This polymer shows the most rapid decrease in contrast, which is attributed to the observations of polaron trapping, which becomes more pronounced over the course of repeated electrochemical cycling. The other polymers all show initial contrasts above  $60 \Delta\%T$ . DAT-DMOT shows an initial contrast of  $64 \Delta\%T$  and over the course of the experiment only sees a slight drop in contrast to  $59 \Delta\%T$  on the final switch. DAT-ProDOT shows an initial contrast of  $65 \Delta\%T$  and maintains this contrast over the course of the experiment with no measurable loss. DAT-DMP shows an initial contrast of  $63 \Delta\%T$ , and over the course of the experiment there is a slight increase in contrast in the first few

hundred switches that levels off at  $65 \Delta\%T$ . This indicates that there is a larger break-in period required for this polymer to reach an equilibrium state, but the films retain a high contrast with minimal color change throughout. Especially important DAT-ProDOT, DAT-DMP, and DAT-DMOT all show significant increases in film switching stability compared to previous generations of wide-gap electrochromic polymers, with only ProDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> showing redox stability for up to 100 switches.

**Device Fabrication and Switching Stability.** With the results obtained and discussed above, DAT-DMP was identified as the best candidate for further examination when considering the use of these polymers as the high-energy absorption component to create black to transmissive switching films.<sup>51</sup> DAT-EDOT is not as redox stable as the other materials, and DAT-ProDOT absorbs at too low an energy to serve this purpose. While both DAT-DMOT and DAT-DMP absorb the high energy portion of the spectrum, DAT-DMP does not shift in absorbance after redox cycling, making it the best candidate for further examination. To further probe the material's redox stability, an electrochromic device was fabricated, and switching stability was tested over 10000 cycles. The device architecture and charge storage layer's structure are detailed in Figure S5. The device construction involves airbrush spraying a film of DAT-DMP from 3 mg/mL toluene solution onto glass/ITO with dimensions of  $5 \text{ cm} \times 6 \text{ cm}$  to an absorbance of 1 and using poly(isobutylene) tape to create a double seal around the polymer active area and around the edge of the slide. On another glass/ITO slide another film of minimally color changing polymer (MCCP) is air-brush sprayed to the same dimensions to act as a charge storage layer but with a thickness dictated by balancing the amount of charge stored by the electrochromic polymer.<sup>52</sup> The MCCP slide is then immersed into 0.5 M TBAPF<sub>6</sub>/PC electrolyte solution in a three-electrode cell and oxidized for 10 s at  $0.8$  V relative to Ag/AgCl. Both slides are then brought into a glovebox with an argon atmosphere, and gel electrolyte (0.5 M TBAPF<sub>6</sub> in 5% w/w PMMA in PC) is drop cast over the active area of the electrochromic polymer. The slide coated with the MCCP film is placed on top and placed on a hot plate set to  $90^\circ\text{C}$  to allow for the poly(isobutylene) sealant to adhere. The device is cooled to room temperature before removing from the glovebox.

Spectra for each 1000 switches can be found in Figure S6. There is minimal change in the spectra of the neutral state over the course of the experiment, indicating the color is not changing over the course of the cycles. The oxidized state spectra do show small decreases in transmittance at 380 and 470 nm indicative of charge imbalance in the device and/or degradation of the MCCP as the decrease in absorbance corresponds to absorbance from the DAT-DMP film. A lack of charge in the charge storage layer, by either degradation or imbalance relative to the amount of DAT-DMP, would cause the DAT-DMP layer to retain absorbance. The disappearance of the peak at 380 nm upon reduction indicates that the MCCP is not degrading to give rise to this peak. This peak is likely due to imbalance in the device. Figure 6 details the evolution of the transmittance at  $\lambda_{\max}$  in both the neutral and oxidized states every 1000 cycles. There is an initial 200 cycles for device equilibration of the MCCP and ECP charge storages. After this device's electrochemical conditioning the oxidized state the device remains consistent over the course of 10000 switches, showing a drop in contrast of  $4.7 \Delta\%T$ . Most noteworthy is that the %T in the colored state



**Figure 6.** Transmittance of the transmissive and colored states measured relative to an air background at  $\lambda_{\max}$  versus number of switching cycles in DAT-DMP device with repeated square-wave potential steps for 10000 cycles measured  $-0.5$  to  $+0.6$  V at 5 s steps and pictures at 1000 and 10000 cycles.

remains consistent over the course of the entire cycling period, indicating that the polymer electrochrome is redox stable in the encapsulated device over this cycling range.

## CONCLUSION

Here, we have reported on the structure–property relationships of wide-gap electrochromic polymers based on repeat units of electron-rich dioxythiophenes of varying steric bulk in alternation with dioctylthiophene. ECPs were obtained with yellow, orange, and red neutral states that switch to colorless oxidized states. The understanding of how small changes in structure allow control of absorption properties in this color space allows for a more informed approach to accessing yellow, orange, and red ECPs with a specific target hue in mind.

We show that the synthetic effort of incorporating dioctylthiophene units in place of the phenylenes improves redox stabilities, lowers oxidation potentials, and allows for the use of DOTs without long side chains as comonomers while maintaining a wide optical gap and solution processability. However, with the EDOT system, the presence of trapped polarons causes a fast degradation of the colored state in an electrochemical cell. Moving to more strained systems allowed for tuning the color to a more orange hue, while maintaining low oxidation potentials and redox stabilities that last over 1000 switches as a film in electrolyte solution. From this understanding, an absorptive/transmissive electrochromic device with DAT-DMP was made to show that there is minimal contrast loss over 10000 switches. This redox cycling stability is enhanced by 2 orders of magnitude in number of cycles than previous generation wide-gap ECP-based devices. This approach could be adapted to other systems by incorporating moieties that block potential reactive sites on the polymer backbone to improve redox stability. The incorporation of the dioctylthiophenes in place of phenylene rings improved upon previous designs of high-bandgap ECPs, bringing the field closer to having a full color palette of stable, high-performance ECPs.

## EXPERIMENTAL SECTION

Reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. THF, toluene, and propylene carbonate were all purified through a Bruker or Vacuum Atmospheres solvent purification system. The

synthetic procedures for new compounds and polymers as well as the corresponding NMR spectra can be found in the [Supporting Information](#). The synthesis and characterization of PProDOT-Ph(OMe)<sub>2</sub> ( $M_n$  = 16.6 kDa,  $M_w$  = 24.4 kDa,  $\bar{D}$  = 1.5), PProDOT-Ph ( $M_n$  = 20.2 kDa,  $M_w$  = 34.4 kDa,  $\bar{D}$  = 1.7), PAcDOT<sub>2</sub>-Ph(OMe)<sub>2</sub> ( $M_n$  = 24.1 kDa,  $M_w$  = 56.2 kDa,  $\bar{D}$  = 2.3), and PAcDOT<sub>2</sub>-Ph ( $M_n$  = 130.5 kDa,  $M_w$  = 468.2 kDa,  $\bar{D}$  = 3.6) can be found in refs 37 and 38. All reactions were performed under an argon atmosphere unless otherwise mentioned.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.macromol.8b01789](#).

Supplementary figures, experimental details, synthesis, and primary characterizations ([PDF](#))

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### Notes

The authors declare the following competing financial interest(s): Electrochromic polymer technology developed at the Georgia Institute of Technology has been licensed to NXN Licensing. J.R.R. serves as a consultant to NXN Licensing.

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