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Tuning the painter's palette: subtle steric effects on spectra and colour in conjugated electrochromic polymers†

J. A. Kerszulis,^a K. E. Johnson,^a M. Kuepfert,^b D. Khoshabo,^b A. L. Dyer^{ac} and
J. R. Reynolds^{*a}

A series of vibrantly coloured π -conjugated electrochromic polymers (ECPs) were designed and synthesized with the goal of extracting structure–property relationships from subtle changes in steric strain or relaxation. These are soluble all donor, electron rich, alternating polymers based on repeat units of 3,4-ethylenedioxythiophene (**EDOT**), 3,4-propylenedioxythiophene (**ProDOT**), and an acyclic dioxothiophene (**AcDOT**) in varying combinations to tune steric interactions and the subsequent optical absorption for fine colour control. Two families of polymers were formed where **ProDOT**₂–**EDOT**, **ProDOT**–**EDOT**, and **ProDOT**₂–**EDOT**₂ constitute new shades of blues while **AcDOT**₂–**ProDOT**, **AcDOT**–**ProDOT**, and **AcDOT**–**EDOT** yield new hues of magentas with the homopolymers of **ProDOT** and **AcDOT** and the copolymer **AcDOT**₂–**EDOT**₂ serving as comparisons. The polymers were synthesized using direct (hetero)-arylation polymerization. Examinations of the optoelectronic properties *via* cyclic voltammetry, spectro-electrochemistry, and colorimetry show that by subtly varying the level of steric relaxation or strain in the form of **EDOT** or **AcDOT** content, lower or higher energy absorption transitions are produced respectively. This increase in relaxation or strain allows more short or long wavelength light to transmit, giving new shades of blues or magentas respectively. Since these are all donating polymers, they exhibit changes in contrast no less than 70% at the λ_{max} with the exception of **AcDOT**–**EDOT**. The most desirable electrochromic properties were achieved with **ProDOT**₂–**EDOT**₂ and **AcDOT**₂–**ProDOT**, with band gaps (E_g) and neutral state $L^*a^*b^*$ colour values ($-a^*$ and $+a^*$ correspond to green and red and $-b^*$ and $+b^*$ correspond to blue and yellow respectively and L^* represents the lightness) of 1.74 eV, 37, 12, –63 and 2.01 eV, 56, 59, –16 respectively. The highly transmissive oxidized state colour values for **ProDOT**₂–**EDOT**₂ and **AcDOT**₂–**ProDOT** are 92, –3, –3 and 91, –2, –1 respectively. These structure–property relationships grant a greater ability to tune light absorption across the visible, with colour properties similar to ECPs made through other methods without using donor–acceptor effects. This all donor steric tuning method leads to considerably higher levels of transparency when the polymers are fully oxidized.

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Introduction

When comparing electrochromic materials derived from metal oxides¹ with molecular organic^{2–4} and polymeric⁵ electrochromes, the latter stand out for the broad array of colours that can switch to highly transmissive states. Due to their solubility allowing them to be processed *via* spin,^{6–8} spray,^{9,10} blade,¹¹ and slot-die¹² coating along with inkjet printing,^{11,13} fully conjugated

electrochromic polymers (ECPs) provide a full palette of colours from which to develop devices. These polymers all attain highly transmissive states, high electrochromic contrast, rapid (sub-second) switching and long cycle lives (> 10 000). These material properties have allowed ECPs to be incorporated into display and window type devices (ECDs) with potential commercial viability.

Numerous techniques have been employed to control the visible absorption and colour of the neutral state in ECPs. These range from utilizing donor–acceptor (D–A) effects, vinylene and azomethine¹⁴ linkers, the interchange of atoms that constitute heterocycles or reside on the β positions, the variation of comonomer feed ratios or the nature of pendant groups,⁵ and varying the design of the metal–ligand in metallo-supramolecular polymers.^{15–18} The D–A method has proven especially useful as the donor moiety positions the HOMO while the acceptor positions the

^a School of Chemistry and Biochemistry, School of Materials Science and Engineering, Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA. E-mail: reynolds@chemistry.gatech.edu

^b Re-Synthesis Laboratory, NC/IS, BASF Corporation, Tarrytown, NY, 10591, USA

^c Department of Natural Sciences, Clayton State University, Morrow, GA, 30260, USA

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LUMO, retaining low oxidation potentials required for long term redox switching.^{19–21}

Examining the spectra for the transmissive oxidized states of these D–A ECPs shows tailing of charge carrier absorption in the near infrared back into the visible, giving some residual visible absorption and inducing a blue tint in the films. This effect is evident in poly(3,4-ethylenedioxythiophene) (PEDOT)²² and somewhat minimised in poly(3,4-propylenedioxythiophene) (**ProDOT**)²³ ECPs with long and bulky substituents. By retaining the highly electron rich nature of the XDOT polymers (where X represents ethylene, propylene, butylene, *etc.*), we hypothesize that steric control can be the sole “handle” for tuning colour while maintaining outstanding electrochromic switching to highly transmissive states. This is exemplified in the literature by the use of an acyclic dioxothiophene (**AcDOT**) in developing orange and red-coloured ECPs.²⁴

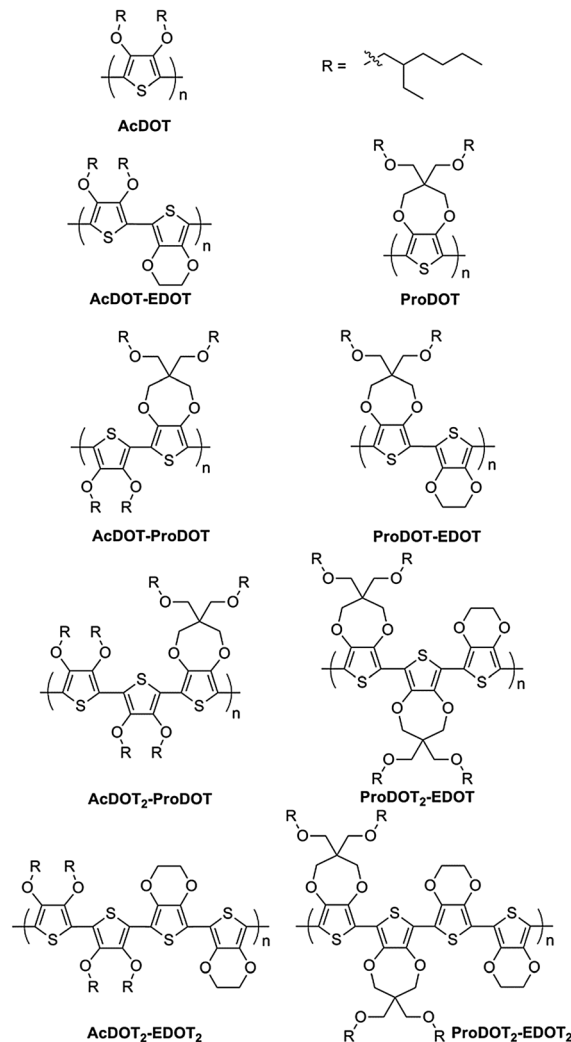
Here, we report a family of **EDOT**, **ProDOT**, and **AcDOT** copolymers, each having regular nonrandom repeat units, and all prepared by direct arylation polymerisation (DAP) where neutral colours can be varied from bright pink, to magenta, purple, periwinkle, and blue solely by steric control. We find these polymers to switch rapidly and reproducibly to highly transmissive oxidised states that are more transmissive and less coloured than previously reported polymers. These ECPs explore the effects of subtle relaxation and torsional strain on spectra for colour control and allow us to address the issue of colour break-in by comparing as-sprayed films to those that have been electrochemically cycled as steric hindrance eliminates the break-in effect making for improved colour consistency.

As illustrated by Scheme 1, steric interactions can be viewed as inducing torsional strain and relaxation along a conjugated polymer backbone, controlling pi-overlap. When **AcDOT** units neighbor another **AcDOT**, strain induces conformational twisting. This breaks conjugation and leads to shorter wavelength absorption. As torsional strain is relaxed through the incorporation of **ProDOT** or **EDOT**, planarity is induced, conjugation is extended, and longer wavelengths of light are absorbed.

Results and discussion

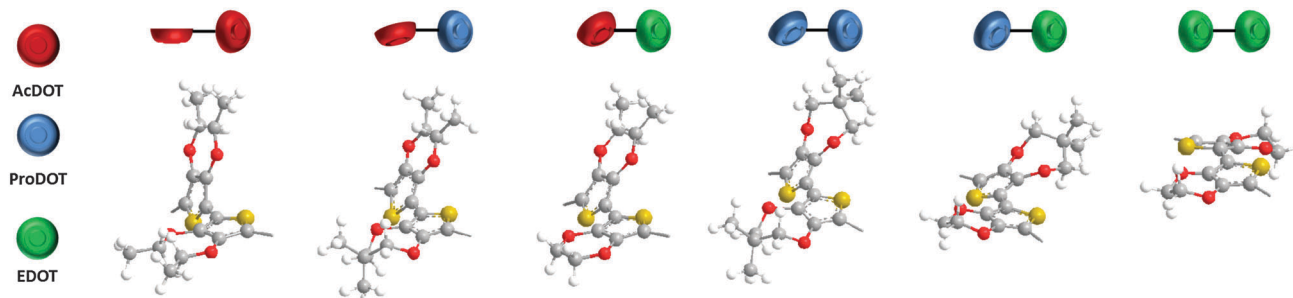
1. Polymer synthesis

All polymers were prepared using optimized DAP^{25,26} from six different monomeric and dimeric XDOTs, as shown in the ESI,[†]



Scheme 2 Family of **EDOT**-, **ProDOT**-, and **AcDOT**-based ECPs prepared for this study using direct arylation.

to yield ECPs with repeat unit structures shown in Scheme 2. With recent developments reviewed by Leclerc *et al.*,²⁷ DAP was chosen as it allows access to the desired electron rich polymer structures without the need to synthesize and purify organotin monomers while maintaining an alternating repeat unit that is not accessible *via* oxidative methods. Characterization by



Scheme 1 Cartoon depicting backbone torsional interactions between neighbouring 3,4-dioxothiophene rings. Strain decreases from left to right through relaxation.

Table 1 All polymer molecular weight, yield, and solid state spectroscopy data

Polymer	Molecular weight (M_n , PDI, solvent (kDa))	Yield (%)	Absorption onset (eV)	λ_{max} (nm)
ProDOT	12.3, 1.77, THF	40	1.97	555, 606
ProDOT ₂ -EDOT	14.5, 2.00, CHCl ₃	82	1.81	590
ProDOT-EDOT	NA	24	1.75	597
ProDOT ₂ -EDOT ₂	14.1, 4.50, CHCl ₃	70	1.74	606
AcDOT	279.7, 2.08, THF	62	2.10	490
AcDOT ₂ -ProDOT	176.0, 2.20, THF	82	2.01	536, 579
AcDOT-ProDOT	51.8, 2.37, THF	97	2.00	541, 587
AcDOT-EDOT	30.9, 1.21, THF	75	1.84	553
AcDOT ₂ -EDOT ₂	24.2, 4.90, CHCl ₃	60	1.81	557

¹H-NMR and comparative GPC demonstrates all polymers to be correctly structured and of sufficient molecular weight (M_n ranging from 14 kDa to 176 kDa) to produce continuous films where the optical properties are in the polymer limit. A collection of polymerization yields and molecular weights is given in Table 1. All of the polymers were isolated in high yield (>60%) with the exception of ProDOT-EDOT as it was difficult to solubilize. The solubility of the polymers that are composed of EDOTs is relatively low (*ca.* <2 mg mL⁻¹) but sufficient enough to conduct spray casting of solutions at room temperature.

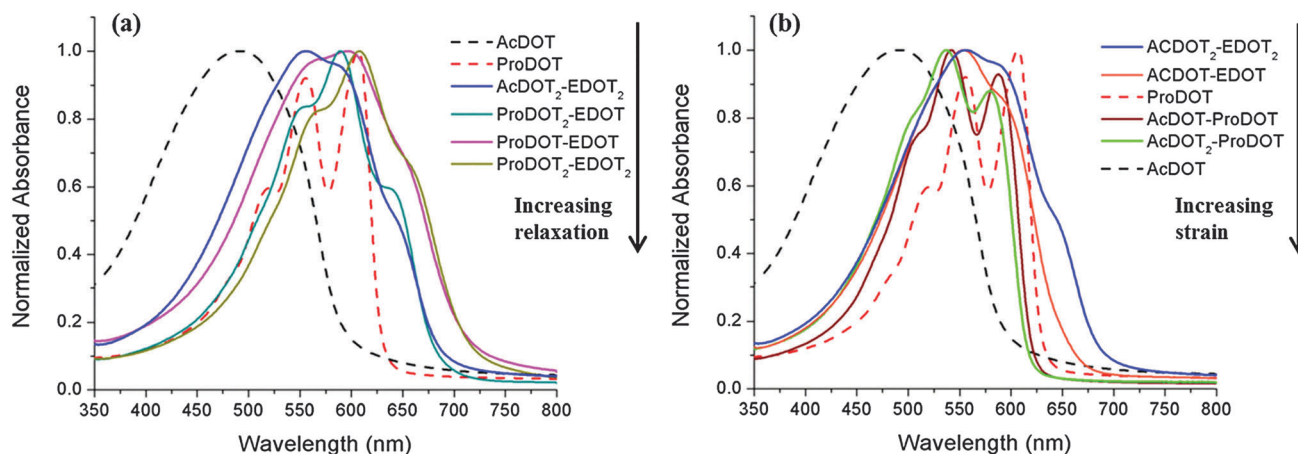
2. Optoelectronic properties

Electrochemistry and break-in. Solutions of the polymers were prepared at a concentration of 5 mg mL⁻¹ in chloroform and then spray cast onto ITO glass at 10 psi yielding films of varying thickness based on optical density (from 0.8 a.u. to 1.2 a.u.) which was then correlated to a physical thickness as measured and averaged by profilometry (see ESI†, Table S1). The polymers are divided into two families: the blue hues (comprised of ProDOT-EDOT, ProDOT₂-EDOT, and ProDOT₂-EDOT₂) and the magenta hues (comprised of AcDOT-ProDOT, AcDOT₂-ProDOT, and AcDOT-EDOT) while AcDOT₂-EDOT₂, ProDOT, and AcDOT (purple and orange hues respectively) stand as comparison structures between the two families. These families of blue and magenta ECPs were developed with the goal of

examining the effects of subtle relaxation and torsional strain on spectra to explore colour control.

Prior to spectroelectrochemistry, the films were electrochemically conditioned (so called “broken in”) with 25 cycles *via* cyclic voltammetry (CV) to the point where the current stabilized to become reproducible. As noted from Fig. S2 (ESI†) there is a considerable change between the first and second cycle, after which the current minimally decreases and is fully reproducible in all cases by the 25th cycle. All of the polymers oxidize easily and, as shown by differential pulse voltammetry (DPV), the onsets for the oxidation potentials range from -490 to 206 mV. AcDOT (ECP-orange) is an exception and has an oxidation potential of 260 mV, attributed to pendant group bulkiness.²⁴ The induction of steric relaxation along the conjugated backbone *via* the alternating addition of EDOT moieties and monomer repeats having large and bulky solubilizing substituents presents drastic changes between the pristine and broken-in film states. As strain is introduced through AcDOT incorporation, this effect is mitigated with a minimal change between the pristine and broken in state exhibited by AcDOT₂-ProDOT (Fig. S2e, ESI†). Examining the differential pulse voltammetry results in Fig. S3 (ESI†), the increase in strain raises oxidation potential onsets while relaxation lowers it.

Optical properties. The break-in effect observed results in an alteration of the film spectra after switching as exemplified in Fig. S4 (ESI†). In concert with the changes observed by CV, the film spectra redshift and increase in optical density as relaxation is induced, while the changes in the spectra are reduced with increasing strain. This is exemplified with AcDOT₂-ProDOT where there is no spectral difference between the pristine and broken in state, which can be correlated to a minimal change during CV. To examine the optical properties of the broken-in films, the normalized neutral state absorption spectra for the two families of the all donor polymers are shown in Fig. 1 with the absorption onsets and λ_{max} values reported in Table 1. Examining Fig. 1a, as strain is decreased (relaxation) through increased EDOT content, long wavelength absorption, relative to the ProDOT and AcDOT homopolymers, is increased. All of the copolymers possess considerably lower band gaps relative to ProDOT allowing the

**Fig. 1** Normalized neutral state film spectra of blue (a) and magenta (b) ECPs post break-in.

absorption of long wavelength light, making the materials appear periwinkle-blue to the eye. With this red-shifted absorption onsetting around 700–750 nm, these polymers can be thought of as organic soluble analogues of PEDOT. Turning attention to Fig. 1b, as steric hindrance is increased *via* **AcDOT** addition, shorter wavelength absorption is induced relative to **ProDOT**. These materials with greater strain absorb more of the high energy portion of the visible spectrum, reducing the amount of blue light that reaches the eye, making the materials appear as “reddened” or “hotter” magentas and pinks.

The repeat unit structure has an overall effect on the presence, or lack thereof, of vibronic coupling in the spectra. Increasing the amount of strain *via* shifting from **AcDOT–ProDOT** to **AcDOT₂–ProDOT** only showed a slight decrease in the degree of vibronic coupling, as evidenced by the lower definition in the multiple peaks, relative to **ProDOT** which exhibits a high degree of order.^{22,28–30} Following this, there is a decrease in the extent of vibronic coupling observed for the **EDOT** containing polymers. This indicates that, although **AcDOT** is considerably bulkier than **EDOT**, the low steric hindrance of the latter allows the propylene bridge on neighboring **ProDOT** rings to have more freedom in conformational changes, inducing greater degrees of disorder in the polymer backbone, thereby reducing the extent of vibronic coupling and broadening the spectra.^{31–33}

3. Spectroelectrochemistry

These all-donor polymers exhibit a high electrochromic contrast, switching from a vibrant coloured state to highly transmissive, as illustrated in Fig. 2 for **ProDOT₂–EDOT₂** and **AcDOT₂–ProDOT**, along with the remaining polymers in Fig. S5 (ESI†). The entire family of materials studied exhibit changes in contrast above 60% at λ_{max} as shown in Table 2. **ProDOT₂–EDOT₂** and **AcDOT₂–ProDOT** exhibit the highest contrast values, 75 and 73 $\Delta\%T$ at

λ_{max} respectively, and the least residual absorption in the visible from the fully oxidized transmissive state, even for thicker films. Those that incorporate **EDOT** have a broadened potential range over which the polymer switches with subtle changes over the duration of oxidation while those that utilize **AcDOT** have a narrowing of the potential window with larger changes upon each potential step. As presented by the Leclerc group, this phenomena has been attributed to twiston effects, which are in essence delocalized conformational defects, seen in previous polymer systems.^{24,34,35} Because of the high twist (less planarity) induced in **AcDOT–ProDOT** and **AcDOT₂–ProDOT**, there is a resistance to planarization on initial oxidation. However, at increasing oxidation steps, localized planarization begins to occur, which has a rapid propagation along neighboring repeat units.

Upon examination of the switching kinetics *via* chronoabsorptometry in Fig. S6 (ESI†), all of the polymers synthesized for this study are shown to undergo their full neutral coloured to oxidized transmissive change with switch times as fast as 1 second showing minimal loss in contrast. Upon switching at fast speeds of $\frac{1}{2}$ and $\frac{1}{4}$ second cycles, the polymers exhibit an expected loss in contrast due to diffusion limiting processes of electrolyte migration. After cycling at high speeds, the polymers are all capable of regaining high levels of contrast with no apparent negative effects (delaminating, blistering, *etc.*), demonstrating robustness during rapid changes in switching speeds.

4. Colorimetry

Upon the completion of spectroelectrochemistry the colorimetric properties of each polymer were examined and are presented as a^*b^* colour tracks in Fig. 3 (including photographs), while the colour values of each polymer in the neutral and fully oxidized states are shown in Table 2. The colour trend for the blue hued

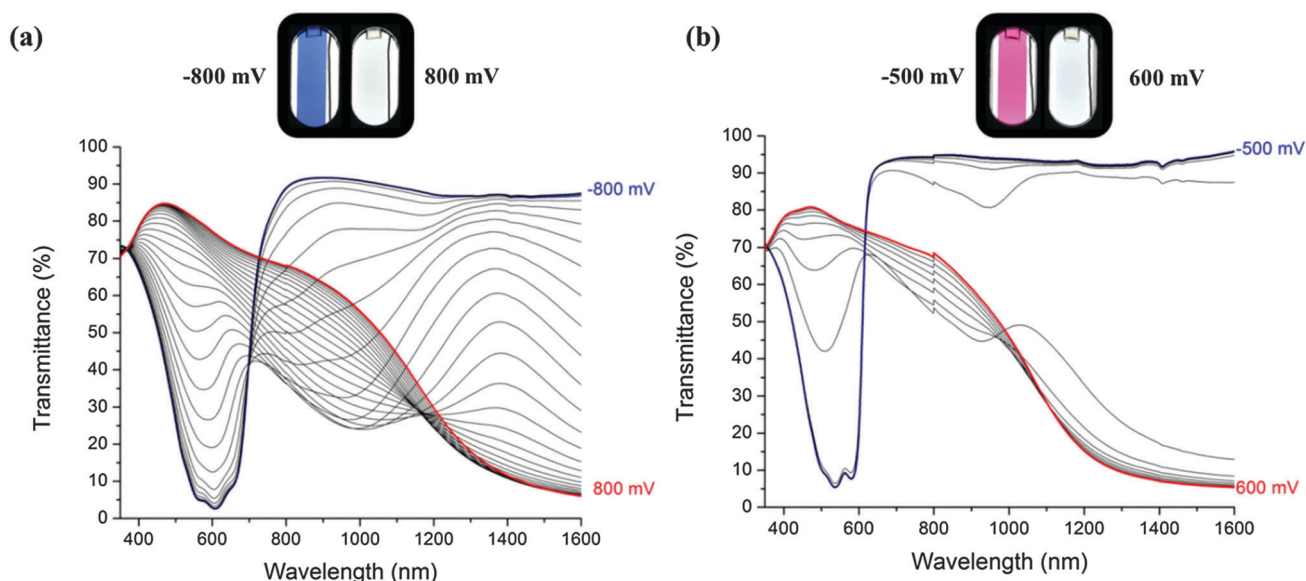
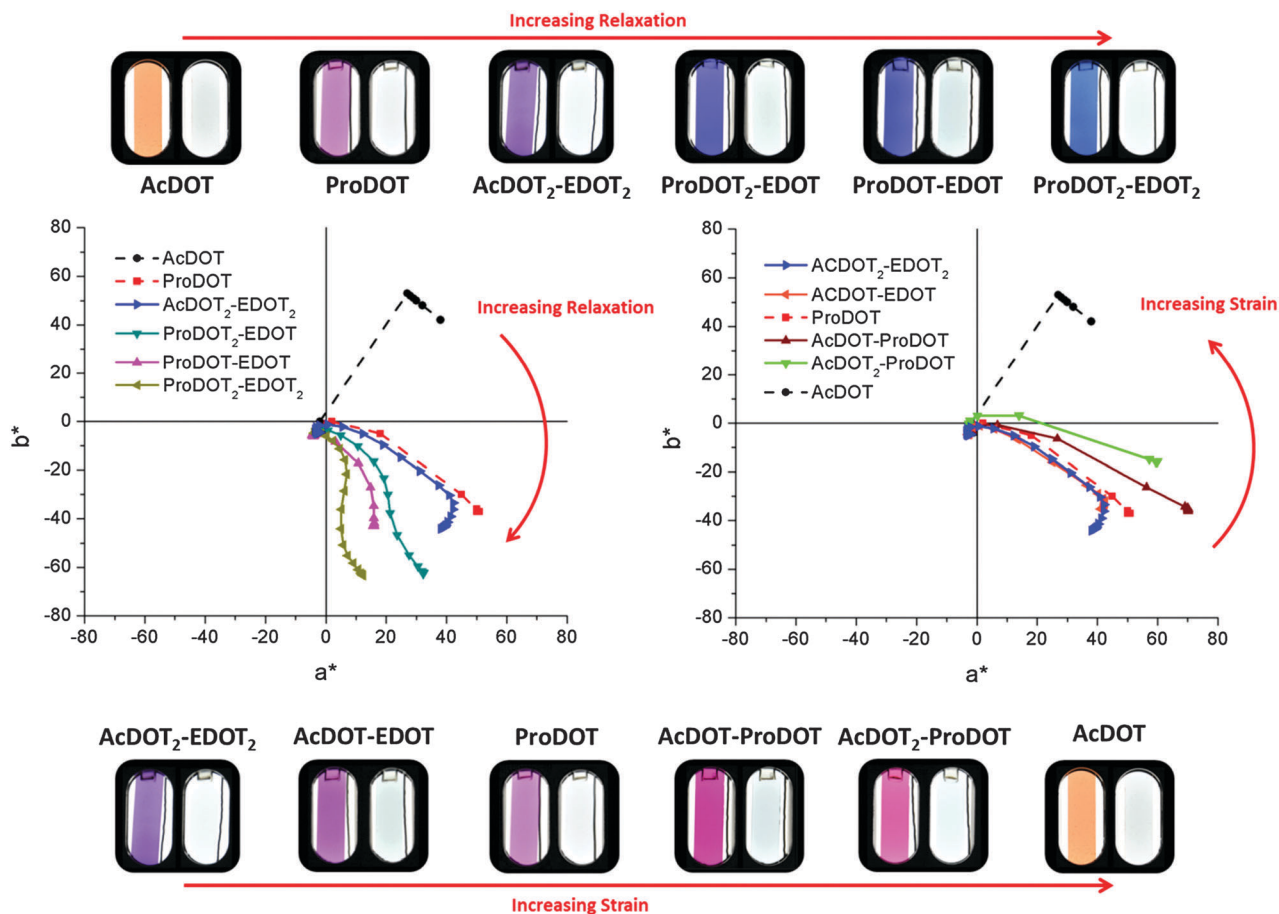


Fig. 2 Electrochromic properties of films sprayed to an optical density of ~ 1.2 a.u. of **ProDOT₂–EDOT₂** (a) and **AcDOT₂–ProDOT** (b). Spectroelectrochemistry performed at potential steps of 50 mV with 0.5 M TBAPF₆ in PC with a Pt wire as counter electrode; Ag/Ag⁺ reference electrode calibrated to Fc/Fc⁺ with a value of 82 mV.

Table 2 $L^*a^*b^*$ colour coordinates for all polymers in the neutral and transmissive states and total change in contrast upon switching between the extremes

Relaxed polymers	$\Delta\%T$ (at λ_{\max})	Neutral state L^*, a^*, b^*	Oxidized state L^*, a^*, b^*	Strained polymers	$\Delta\%T$ (at λ_{\max})	Neutral state L^*, a^*, b^*	Oxidized state L^*, a^*, b^*
AcDOT	48	72, 42, 53	81, -2, -7	AcDOT ₂ -EDOT ₂	70	38, 38, -44	91, -2, -4
ProDOT	71	50, 51, -37	88, -1, -2	AcDOT-EDOT	63	49, 41, -35	88, -3, -4
ProDOT ₂ -EDOT ₂	70	38, 38, -44	91, -2, -4	ProDOT	71	50, 51, -37	88, -1, -2
ProDOT ₂ -EDOT	71	33, 32, -63	90, -2, -3	AcDOT-ProDOT	72	47, 70, -36	91, -2, -3
ProDOT-EDOT	68	40, 16, -43	85, -4, -5	AcDOT ₂ -ProDOT	73	56, 59, -16	91, -2, -1
ProDOT ₂ -EDOT ₂	75	37, 12, -63	92, -3, -3	AcDOT	48	72, 42, 53	81, -2, -7

**Fig. 3** Colorimetry of blue and magenta hue ECPs. All films sprayed to ~ 1.0 a.u. Direction of the arrow indicate increasing relaxation or strain.

ECPs with increasing relaxation progressing from orange, through purple, to blue a^*b^* values are as follows:

AcDOT (42, 53) \rightarrow ProDOT (51, -37) \rightarrow
 AcDOT₂-EDOT₂ (38, -44) \rightarrow ProDOT₂-EDOT (32, -63) \rightarrow
 ProDOT-EDOT (16, -43) \rightarrow ProDOT₂-EDOT₂ (12, -63)

Referring to the neutral state spectra in Fig. 1a, as long wavelength absorption transitions are induced through relaxation from the increased content of EDOT, colour values in the neutral state progress to lower a^* , indicating less purple colour and more blue hue. This is due to the progressive transmission

or passing of more blue and less red light. The colour trend for the magenta hue ECPs with increasing strain progressing from purple, through pink, to orange a^*b^* values are as follows:

AcDOT₂-EDOT₂ (38, -44) \rightarrow AcDOT-EDOT (41, -35) \rightarrow
 ProDOT (51, -37) \rightarrow AcDOT-ProDOT (70, -36) \rightarrow
 AcDOT₂-ProDOT (59, -16) \rightarrow AcDOT (42, 53)

Again, connecting to the neutral state spectra in Fig. 1b, as moderate and short wavelength light absorption is induced through the increase in strain from the addition of AcDOT, colour values in the neutral state progress to higher b^* , decreasing

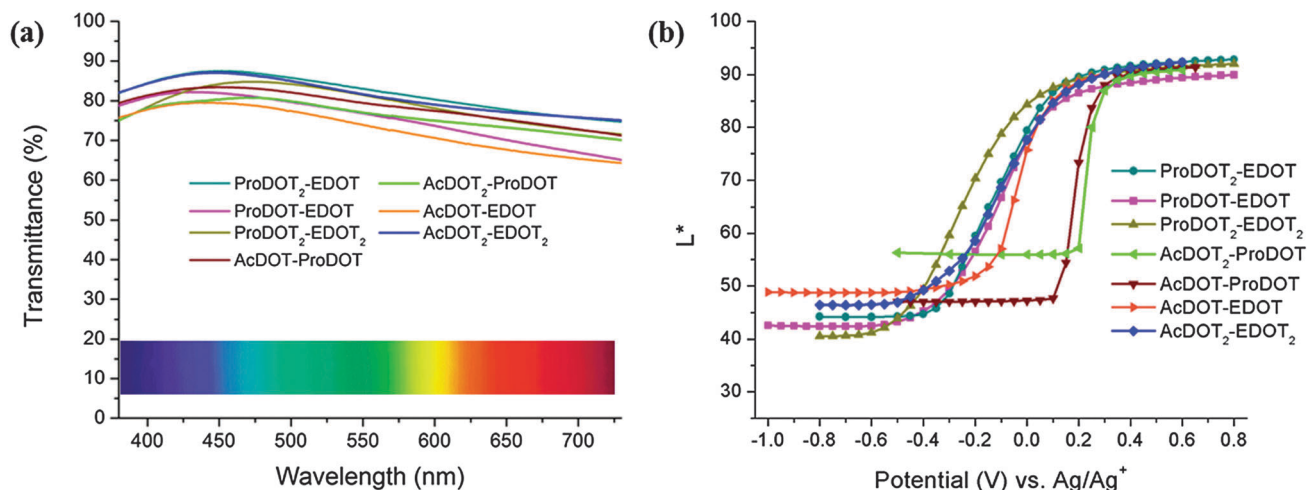


Fig. 4 Most transmissive oxidized state absorption for all polymers across the visible with spectrum as inset (380–730 nm) (a). Lightness values (L^*) for all polymers as a function of voltage (b). All films sprayed to ~ 1.0 a.u.

“purpleness” and yielding truer magenta and pink colours due to more absorption of blue light and increasing transmission or passing of red light. Importantly, **AcDOT₂-ProDOT** nearly matches the colour values of a standard magenta as defined by Munsell (L^* , a^* , b^* = 52, 50, -15)³⁶ whereas **ProDOT** is a bit too “purple” after break-in. This will allow for more accurate colour mixing in the cyan-magenta-yellow (CMY) subtractive regime using these soluble polymers.³⁷ Complete colorimetry and arrays of photographs for each polymer at a variety of thicknesses can be found in Fig. S7 (ESI†).

The minimal hue and saturation of colour in the oxidized form for all of these polymers comes from their ability to exhibit minimal residual absorption in the visible spectrum because of their electron rich, all-donating character, as shown by Fig. 4a and Fig. S8 (ESI†). The L^* for all of the polymers as a function of voltage during switching can be seen in Fig. 4b. Upon oxidation all values of lightness are high.

5. Comparing all-donor and donor-acceptor systems

Through relaxation, the subtle steric tuning in all donor polymers can yield materials with low band gaps (**ProDOT₂-EDOT₂**) that are blue in the neutral state with colour values that are comparable to those of a blue-to-transmissive ECP designed by donor-acceptor (D-A) methods.²⁰ A comparison between the neutral states for **ProDOT₂-EDOT₂** and the previously reported ECP-blue (**ProDOT-BTD**) is presented in Fig. 5a. This comparison was chosen as the two materials possess similar colour values while employing distinctly different structures to tune optical transitions. From Fig. 5a it can be seen that using a D-A approach between alternating **ProDOT** and **BTD** (benzothiadiazole) a dual band absorption results where the shorter wavelength absorption is attributed to the π to π^* and the longer wavelength absorption is from the donor-acceptor charge transfer interactions.²¹ Using the method of steric relaxation in **ProDOT₂-EDOT₂**, an absorption was attained with an onset at shorter wavelengths (1.74 eV), remaining at the edge of the visible spectrum. Through the D-A approach, a much lower

onset was achieved (1.53 eV) with a window of transmission at 431 nm between the two bands. The two different absorption spectra give two unique neutral state colours. As shown earlier, **ProDOT₂-EDOT₂** allows a majority of blue light, and a minimal amount of red light, to transmit, giving a saturated blue colour. With ECP-blue, its more redshifted onset from the CT absorption allows more green than red light to transmit however, the higher energy π to π^* filters out blue and violet light, making it a less saturated sky-blue colour. Though they have similar numerical colour values, **ProDOT₂-EDOT₂** appears more saturated in colour because more blue light is reaching the highly sensitive S cones in the human eye.

The electron rich character of the all donor polymers developed here allow them to be fully bleached (oxidized to a point where a^*b^* colour values approach zero and L^* is high) at potentials that are lower than those exhibited by donor-acceptor systems. In the oxidized transmissive states, for the all donor polymer (**ProDOT₂-EDOT₂**), the π -electron donating character of the oxygens residing on the β -position of thiophene impart stabilization to the oxidized form, red-shifting the overall absorption (see Fig. 5a) and leading to a repression of the absorption between 700–1000 nm relative to the donor-acceptor system (ECP-blue). The ability for S and O to interact between neighboring dioxothiophene units and induce planarization may also assist in this redshift.^{32,33} In Fig. 5a it can be seen that when ECP-blue is fully oxidized to the transmissive state there is a significant absorption tailing into the long wavelength portion of the visible (600–720 nm) with a peak in the NIR at ~ 1460 nm, showing a blue tint when oxidized (Fig. 5c) while **ProDOT₂-EDOT₂** exhibits minimal tailing in the same portion with a peak beyond 1600 nm, being nearly colourless when oxidized.

From the comparisons presented in Fig. 5, one can see that lower gaps can be attained with donor-acceptor effects, but at the cost of electrochromic contrast as a consequence of tailing absorption due to the incorporation of electron deficient acceptors. All donor systems would require significant synthetic design of new relaxed rings to achieve comparably low gaps, but as the state

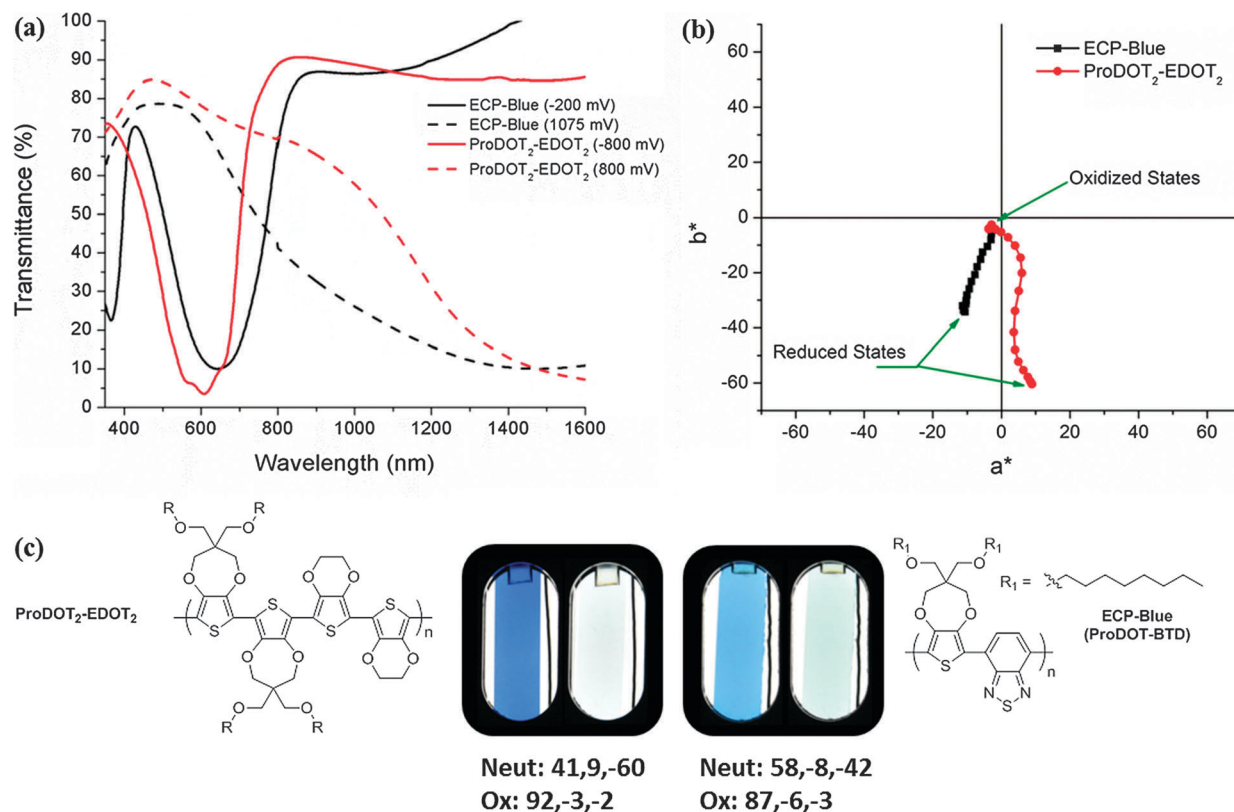


Fig. 5 Comparison between **ProDOT₂-EDOT₂** and ECP-blue (**ProDOT-BTD**) spectra of the extreme states (a), colorimetry (b), and structurally and photographically ($L^*a^*b^*$ colour values below photos, Munsell blue: 29, 14, -50) (c). Both polymers sprayed to ~ 1 a.u.

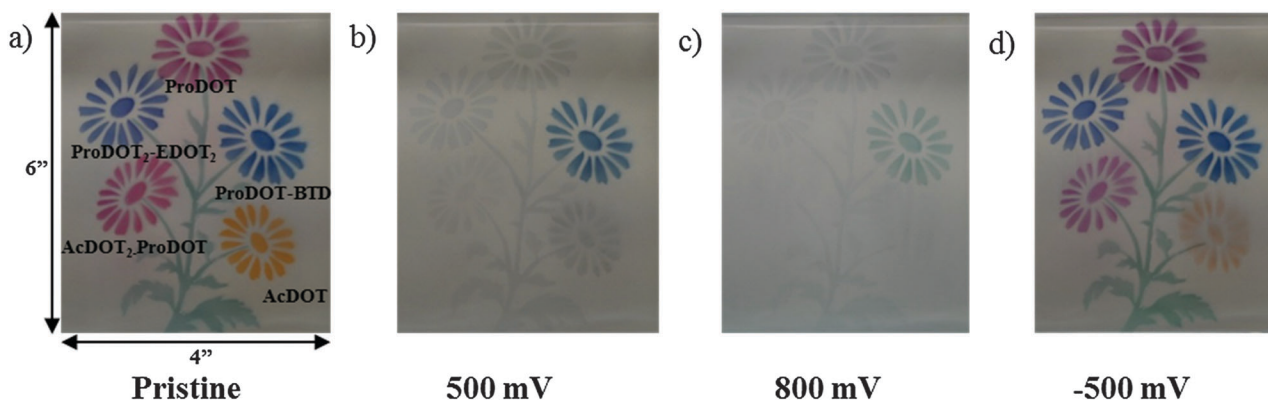


Fig. 6 One electrode comparison of optical properties of all donor and donor-acceptor polymer films in 0.04 M TBAPF₄ in acetonitrile (ACN). Counter electrode is an ITO coated glass pane of equal size with reference electrode that is the same used for other studies herein.

of the art stands with DOTs, the attainable gaps are sufficient for colour applications with high electrochromic contrast from all donor structures nearly eliminating residual visible absorption when fully oxidized.

For improved visualization of the enhanced properties of the all donor systems, Fig. 6 shows a patterned film comparing several of the all donor polymers examined here (**ProDOT₂-EDOT₂**, **ProDOT**, **AcDOT₂-ProDOT**, and **AcDOT**) side by side with the donor-acceptor **ProDOT-BTD**. It is evident that each of the polymers, save for **ProDOT-BTD**, switch to the bleached state in a

similar voltage window, as desired for simultaneously colouring-bleaching displays. The **ProDOT-BTD** remains coloured until higher voltages are applied due to its higher oxidation potential. Also it is worth noting in Fig. 6, the polymer that makes up the stem and leaves of the flower, is also a donor acceptor system, **ProDOT₄-BTD** (structure shown in Fig. S9, ESI†); however, it qualitatively shows behavior that is comparable with the all donor systems. This can be explained by the fact that it has significantly more donor character than acceptor, containing four times the donor amount of **ProDOT-BTD**.

Conclusions

Through modulating the strain along the backbone of all donating dioxithiophene ECPs the colour of the neutral state was controlled, making new, desired shades of blues and magentas with high electrochromic contrast. Blue hues (low band gaps) could be attained by utilizing relaxation in the form of EDOT content while magenta hues (mid gaps) could be acquired through increasing steric hindrance with AcDOT. This steric approach was used to achieve a polymer with a magenta neutral state as defined by Munsell, allowing more accurate subtractive CMY colour mixing. These polymers exhibit significant changes in spectra between the pristine and electrochemically broken-in neutral state, which can be minimized through increased steric strain. Compared to the donor-acceptor method of colour control, sterically tuned all donors can achieve similar vibrantly coloured neutral states but with the advantage of greater contrast when oxidized. Based on this revelation it would be advantageous to minimize the use of donor-acceptor architectures in ECPs where possible or to develop new acceptors that would minimize the tailing from fully oxidized states.

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