

Poly(3,4-propylenedioxythiophene)s as a Single Platform for Full Color Realization

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 Supporting Information

Electroactive dyes are an important component in devices such as displays, solar cells, and smart windows.¹ The ability to achieve a variety of colors and color transitions from the same template can offer synthetic ease, facile scale-up, lowered cost, and, more importantly, compatibility to device fabrication. For clarification, the same template material can provide the same voltage switching window and relatively equivalent HOMO energy levels. In the area of electrochromics, there is no single molecular template that has yet provided full color tuning. The results presented here for 1,3-disubstitution, in combination with earlier reports from Reynolds et al. on his various 2,2-disubstitution, demonstrate that full visible spectral tuning for the neutral state of electrochromic polymers can be realized using poly(3,4-propylenedioxythiophene) (ProDOT) as a platform. The majority of the developed materials using the ProDOT platform are neutral-colored to oxidized-transparent electrochromics, which are of high interest to displays and related applications. On the basis of the calculated conformational geometry of the fused propylenedioxy ring (Figure 1), we have found that α -site substitution with respect to oxygen provides a means to precisely disrupt planarity based upon substituent size to provide full visible spectrum realization.

Conducting polymers offer a unique combination of properties which makes them a suitable alternative to current materials for electrochromics (EC),^{1–5} nonlinear optics,⁶ light-emitting diodes (LEDs),⁷ and solar cells.^{8,9} Conjugated polymers based on 3,4-ethylenedioxythiophene (EDOT) and its derivatives have gained much attention for device applications due to their low oxidation potentials, high spectral contrast between their two extreme redox states, and high conductivity.^{10–15}

PEDOT has the ability to transition from deep blue to sky blue upon oxidation with a photopic contrast of 54%.^{16,17} Higher photopic contrasts and more colorless bleached states can be obtained by the incorporation of an additional methylene unit into the bridge between the oxygens, as with 3,4-propylenedioxythiophene (ProDOT).¹⁸ Additionally, polymers have been reported with P22ProDOT-R₂ (ProDOT carrying alkyl substituents beta to the oxygens) showing λ_{max} ranging from 630 to 500 nm (deep blue purple to red) in the neutral state.^{19–21} All previous reports^{22–26} indicate that substitution of ProDOT has been carried out using 2,2-disubstitution, and there are no extensive reports on 1,3-disubstitution (α with respect to oxygen) ProDOT polymer. Walczak et al. reported poly(1,3-dimethyl-ProDOT) (P13ProDOT-Me₂) and poly(1-octylProDOT) with

a band gap of 1.6 eV in both cases and stated that linear substituents are not sufficiently bulky enough to influence the conjugation length as well as the band gap of a conjugated polymer.²⁷ The unavailability of synthetic methodologies for the synthesis of 1,3-disubstituted diols is another reason why 1,3-disubstituted ProDOTs have remained unexplored to date.

In this paper, we have accomplished a facile transesterification procedure for 1,3-disubstitution using *tert*-butyl, hexyl, isopropyl, and methyl groups, resulting in 1,3-di-*t*-butylProDOT (13ProDOT-TB₂), 1,3-dihexylProDOT (13ProDOT-Hex₂), 1,3-diisopropylProDOT (13ProDOT-IP₂), and 1,3-dimethylProDOT (13ProDOT-Me₂), respectively. To date, the largest shift we have observed for disubstituted ProDOT (P13ProDOT) is a ca. 200 nm shift in the λ_{max} . The polymer of P13ProDOT-TB₂ is organic-soluble and can be processed by a variety of solution methods, including spray coating. The remarkable shift in the band gap resulted in a yellow (Y) to green color transition from the neutral to oxidized states, respectively, whereas P13ProDOT-IP₂ is insoluble and showing intermediate band gap with a red color in the neutral and transmissive light blue in the oxidized state. P13ProDOT-Me₂ undergoes a dark blue-purple neutral state to a transmissive light blue oxidized state during switching. The polymer from 2,2-dibenzylProDOT, commonly abbreviated P22ProDOT-Bz₂, was used for comparison with all the reported 1,3-disubstituted ProDOT polymers. The synthesis of these derivatives is shown in Scheme 1.

Generally, there are three strategies for changing optical transitions in conjugated systems. The first is conjugation length; band gap (E_g) decreases with increasing conjugation length, limited by Peierls distortion.^{28,29} A second method is to change the electronic richness or deficiency via incorporation of electron donating (red shift) or withdrawing (blue shift) groups onto the polymer. The third strategy is to introduce steric interactions between repeat units within the polymer backbone, resulting in a larger dihedral angle thereby decreasing π orbital overlap. It is the third approach that has yielded the observed 200 nm blue shift for P13ProDOT-TB₂ as compared to P22ProDOT-Bz₂. The originality of this approach lies in the fact that these substitutions were made to exploit the conformation of the seven-membered fused ring. The ability to tune color transitions via simple

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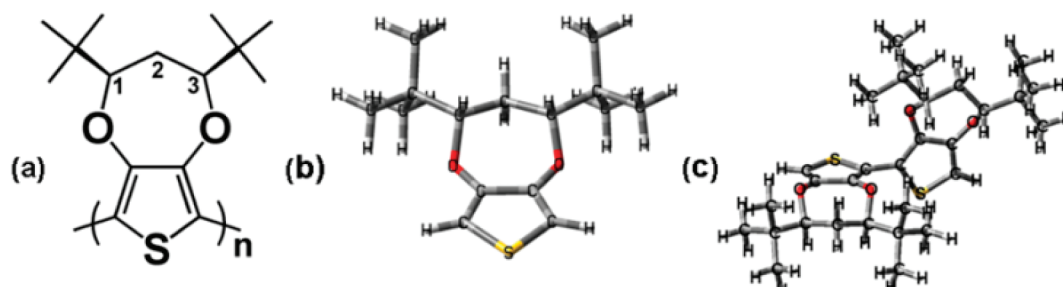
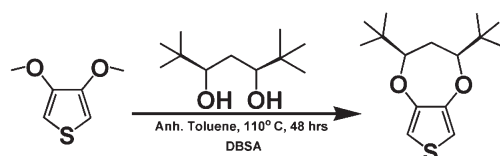


Figure 1. Chemical structure of P13ProDOT-TB₂ with atom labels on the propylenedioxy ring indicating the nomenclature for substitution (a). The optimized calculated structure of 13ProDOT-TB₂ (b) and 13ProDOT-TB₂ dimer (c).

Scheme 1. Synthetic Scheme for 13ProDOT-TB₂



derivatization would be an attractive approach toward achieving a larger swath of the color gamut.

The monomer oxidation potential of the 1,3-disubstituted ProDOTs were similar to other 2,2-disubstituted alkyldioxythiophenes (ca. +1.03 to 1.10 V), indicating that substituents do not have a significant effect on the HOMO energy level. The redox behavior of all the polymers was studied through the recording of cyclic voltammograms. The resulting electrochromic polymer, P13ProDOT-TB₂, was yellow (λ_{max} of 365 nm) in the neutral state, blue-shifted by ca. 180 nm from P13ProDOT-Me₂, which is deep blue-purple in the neutral state (λ_{max} of 546 nm), whereas P13ProDOT-Hex₂ was orange and P13ProDOT-IP₂ was red (λ_{max} of 496 nm) in the neutral state (see Figure 2). Spectroelectrochemical measurements were taken for all with the results briefly summarized. The P13ProDOT-TB₂ film switches between an absorbing yellow neutral state to a green oxidized state. The band gap of P13ProDOT-TB₂ (assigned as the onset of the π - π^* transition) was found to be 2.50 eV (495 nm), and its λ_{max} was 365 nm, which is about 0.53 eV higher than that of corresponding P13ProDOT-Me₂ ($E_g = 1.91$, 678 nm). P13ProDOT-Hex₂ has a band gap of 1.91 eV with a λ_{max} of 435 nm, and P13ProDOT-IP₂ was found to have a band gap of 2.0 eV with a λ_{max} of 496 nm. The color coordinates for all P13ProDOTs are available in the Supporting Information. The chemically polymerized 13ProDOT-TB₂ gave a number-average molecular weight 6240 g mol⁻¹ with polydispersity of 1.7, whereas the electrochemically generated polymer was found to be 2700 g mol⁻¹ with polydispersity of 1.5. The chemically polymerized 13ProDOT-Hex₂ gave a number-average molecular weight 4833 g mol⁻¹ with polydispersity of 1.2. The polymer oxidation potentials remain essentially the same for each derivative. The HOMO energy levels are not significantly altered by these substituents, although there is some effect even with 1,3-disubstitution. For 2,2-disubstitution, neither the HOMO nor the LUMO levels change at all, based on density functional theory (DFT) calculations. The largest effect on band gap due to these derivatizations, therefore, is attributed to changes in the LUMO energy level.

DFT calculations for these materials were carried out in order to model these effects (see Supporting Information for more

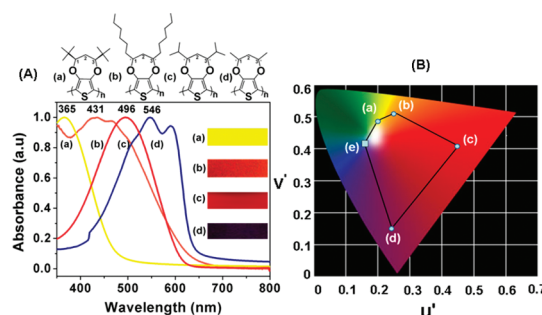


Figure 2. (A) Spectral comparison of neutral P13ProDOT-TB₂ (a), P13ProDOT-Hex₂ (b), P13ProDOT-IP₂ (c), and P13ProDOT-Me₂ (d) electrochemically deposited on ITO-glass with the exception of P13ProDOT-Hex₂, which was spray-coated. (B) CIE u' - v' coordinate plot of the neutral states of the five chromophores (a), (b), (c), (d), and P22ProDOT-Bz₂ (e, square) reported by Reynolds et al.³

details). The large difference in band gap, 0.73 eV (experimentally measured), between PProDOT-Me₂ and P13ProDOT-TB₂ can be explained by distortion of backbone planarity. The dihedral angles of dimers were calculated to give quantitative information about dihedral angles in the polymer. The optimized calculated structure of the 13ProDOT-TB₂ dimer shows a dihedral angle of 76.1°, signifying that there would be a clear distortion of planarity along the polymer backbone (Figure 1C).

In conclusion, we have shown that 1,3-disubstituted ProDOT derivatives exhibit excellent characteristics for EC applications, most notable being the 200 nm shift in λ_{max} from P13ProDOT-Me₂. Fine tuning of color is possible by simply changing the size of the substituents at the 1,3-positions, which is one of the most important aspects of this system. A distinct structure–property relationship was observed for P13ProDOT-TB₂, P13ProDOT-IP₂, and P13ProDOT-Me₂ with respect to conventional PProDOT-Me₂. The bulky substituents used were designed to increase the solubility of the polymer without compromising the electrochromic properties. Currently, we are working on other derivatives in order to fully explore the color gamut that can be achieved by this method. This simple synthetic approach to color tuning will make it easier for electrochromic display applications, among other color-transition-based applications, to be realized in the future.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details, synthesis, characterization of all the 13ProDOT monomers as well

as polymers, and a video of P13ProDOT-IP₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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