Novel Bis-arylPheDOT Synthons for Electrochromic Polymers

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Two terthiophenes incorporating the synthon 3,4-(1,2-phenylenedioxy)thiophene (PheDOT) have been developed. Specifically, 2,5-bisthienyl-3,4-(1,2-phenylenedioxy)thiophene (BTh-PheDOT **1**) and 2,5-bisethylenedioxythienyl-3,4-(1,2-phenylenedioxy)thiophene (BEDOT-PheDOT **2**) were electropolymerized to form electroactive polymer films (**P1** and **P2**) that switched between two highly colored states with the more electron-rich EDOT derivative **P2** observed to switch at a lower potential. Additionally, both **P1** and **P2** displayed moderate to low optical bandgaps of 1.8 and 1.6 eV, respectively. Crystal structures of BTh-PheDOT showed the monomer to be nearly planar with π-stacking observable between monomers. These findings demonstrate the potential of PheDOT as an electroactive synthon for the formation of well-ordered systems.

Keywords: 3,4-(1,2-phenylenedioxy)thiophene, electropolymerization, electrochromic films

1 Introduction

Thiophene and 3,4-ethylenedioxythiophene (EDOT) based polymers have been ubiquitous in the last decade as materials used in electrochromic devices, organic field-effect transistors, and second-order nonlinear optics, to name a few applications (1–4). Functionalized derivatives (5), as well as various multi-ring monomers incorporating the above monomers (6,7), have been thoroughly investigated, and the success, as well as the scope, of these investigations owe much to the stability and tunability of these building blocks. Nevertheless, these synthons have not been without their respective shortcomings. In spite of the conductivities achieved in thiophene-based polymers, undesirable side reactions were observed, such as β-coupling through the 3-position and overoxidation of the polymer, due to the relatively high oxidation potential of the thiophene monomer. EDOT successfully remedied this problem, both because the oxygen substituents effectively blocked the β-position from further reaction, and because the lone pair electrons on oxygen could successfully stabilize the radical cation generated at the 2- and 5- positions upon oxidation of

the monomer, thus lowering the oxidation potential. Conversely however, EDOT oligomers were often too easily oxidized without careful handling.

In response to the problems mentioned above, a novel synthon, 3,4-phenylenedioxythiophene (PheDOT), has been synthesized and employed in electroactive polymers (8,9). As a monomer, PheDOT has been observed to remain stable under ambient conditions and its dimer and trimer derivatives efficiently electropolymerize yielding relatively low oxidation potential polymer derivatives, which should decrease the likelihood of unwanted side reactions. More uniquely however, 2,5-dibromoPheDOT, as well as PheDOT-CN have been found to possess a nearly planar structure (9). This is likely to induce strong aggregation effects in systems incorporating PheDOT via π-stacking interactions, which can lead to highly ordered structures and, by extension, highly conducting materials. Roncali et al. have probed the properties of short-chain PheDOT oligomers and processable PheDOT polymers, and the implications on charge mobility that such a planar system offers (10). Work done in our group has observed the effects of alkyl side chains on the 3- and 4- position of the phenylene ring. Specifically, the effects of two dodecyl chains, not only improved the solubility of the polymer, but induced self-assembly, driven by the fact that the alkyl chains extended in the plane of the PheDOT system as they are attached at sp^2 sites on the phenylene ring (11).

Here, we explore the possibilities that PheDOT offers from a different direction, with the first syntheses

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of multi-ring monomers incorporating PheDOT with other arylene units. Similar systems of EDOT have shown the monomers to have extended conjugation lengths, allowing for significantly lower oxidation potentials relative to single ring monomers and elimination of side reactions, which subsequently leads to better ordered polymers. This paper details the synthesis, electropolymerization, and electrochemical properties of 2,5-bisthienyl-3,4-(1,2-phenylenedioxy)thiophene (BTh-PheDOT **1**) and 2,5-bisethylenedioxythienyl-3,4-(1,2-phenylenedioxy)thiophene (BEDOT-PheDOT **2**) to yield their polymers **P1** and **P2**. The addition of the PheDOT moiety into the multi-ring monomers renders the molecule nearly planar and facilitates ordering in the system.

2 Experimental

NMR spectra were recorded on a Gemini 300 FT-NMR or a VXR 300 FT-NMR. High-resolution mass spectrometry was carried out on a Finnigan MAT 95Q mass spectrometer. Electrochemical studies were carried out using an EG&G PAR model 273A potentiostat/galvanostat in a three electrode cell configuration consisting of an Ag° wire pseudoreference electrode calibrated with Fc/Fc$^+$ couple, a platinum button (S = 0.02 cm^2) as the working electrode, and a Pt flag as the counter electrode. A 0.1 M solution of tetrabutylammonium perchlorate in various concentrations of dichloromethane and acetonitrile was used for all electrochemical experiments. Absorption spectra were carried out on a Varian Cary 500 scan UV-Vis-NIR spectrophotometer.

BTh-PheDOT: To a 3-necked round-bottomed flask equipped with a condenser was added 2-trimethylstannylthiophene (2.1 mmol), 2,5-dibromoPheDOT (1.0 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (0.1 mmol). The flask was purged with argon and degassed dimethylformamide (20 mL) was added via syringe. The reaction was stirred at 80°C overnight, after which it was poured into water and filtered. The solid was concentrated with methylene chloride, dried with MgSO$_4$, filtered, and the solvent removed under vacuum to yield the crude as a brown solid. The crude was purified using column chromatography on silica gel using 3:1 dichloromethane/hexanes as eluent to yield the product as a yellow-orange solid (60% yield); ^{1}H-NMR (300 MHz, (CD$_3$)$_2$CO) (7.54, dd, 2H), 7.41 (dd, 2H), 7.09–7.21 (m, 6H); ^{13}C-NMR (300 MHz, (CD$_3$)$_2$CO) 129.12, 126.99, 126.02, 125.85, 118.59; HRMS [M$^+$] Calcd. for C$_{18}$H$_{10}$O$_2$S$_3$ 353.9843 Found: 353.9840; Elemental Analysis Calcd. for C$_{18}$H$_{10}$O$_2$S$_3$ C 66.99% H 2.84% Found: C 66.72%, H 3.37%.

BEDOT-PheDOT: To a 3-necked round-bottomed flask equipped with a condenser was added 2-trimethylstannylthiophene (6.3 mmol), 2,5-dibromoPheDOT (3.0 mmol), PdCl$_2$ (0.15 mmol), (*t*-Bu)$_3$PBF$_4$ (0.3 mmol), CuI (0.3 mmol), and CsF (6.3 mmol). The flask was purged with argon and degassed dimethylformamide (30 mL) was added via syringe. The reaction was stirred at 80°C overnight, after which it was poured into water and filtered. The solid was concentrated with methylene chloride, dried with MgSO$_4$, filtered, and the solvent removed under vacuum to yield the crude as a brown solid. The crude was purified by recrystallizing from methylene chloride and methanol to yield the product as a yellow-orange solid (90% yield); ^{1}H-NMR (300 MHz, CDCl$_3$) 7.01 (m, 4H), 6.37 (s, 2H), 4.32 (m, 10H); HRMS [M$^+$] Calcd. for C$_{22}$H$_{14}$O$_6$S$_3$ 469.99, Found: 470.14; Elemental Analysis Calcd. for C$_{22}$H$_{14}$O$_6$S$_3$ C 56.16% H 3.00%, Found: C 55.80%, H 2.98%.

3 Results and Discussions

3.1 Synthesis

Bis-arylPheDOTs were synthesized via Stille Coupling between 2 equivalents of mono-stannylated arylene and 2,5-dibromoPheDOT, as detailed in Scheme 1. The mono-stannylated arylenes were synthesized by adding *n*-BuLi to the arylene followed by trimethyltin chloride, as previously detailed in the literature. PheDOT was synthesized from acid-catalyzed nucleophilic aromatic substitution between catechol and 3,4-dimethoxythiophene, while 2,5-dibromoPheDOT was synthesized from *N*-bromosuccinimide and PheDOT, both as previously reported (9).

3.2 Crystal Structure

Figure 1 shows the crystallographic structure of BTh-PheDOT as a nearly planar molecule. Curiously, the molecule is not symmetric: the torsional angle between the left-most thiophene and the central thiophene is 3.4°, yet the torsional angle between the right-most thiophene and the central thiophene is a much larger 13.4°. Both face-to-face and side-to-face packing are observed in the crystal structure of **1** with the molecules packing in a zigzag fashion (Fig. 1c). In the face-to-face packing system the thiophene moiety of one monomer overlaps the thiophene of the central PheDOT moiety of a second monomer (Fig. 1c), giving rise to an intermolecular distance of 3.26 Å, less than the sum of their van der Waals' radii. Significantly, the thiophene participating in this stacking is precisely the one twisted out of the plane of the molecule, raising the possibility that the loss of energy from disrupting the π-conjugation is compensated by energy gained from interaction between the thiophene ring and the dioxyphenylene ring (Fig. 1b). It should also be mentioned that sulfur-oxygen interactions, prevalent in similar thiophene-based systems (13), are absent here. Previous studies have attributed the sulfur-oxygen
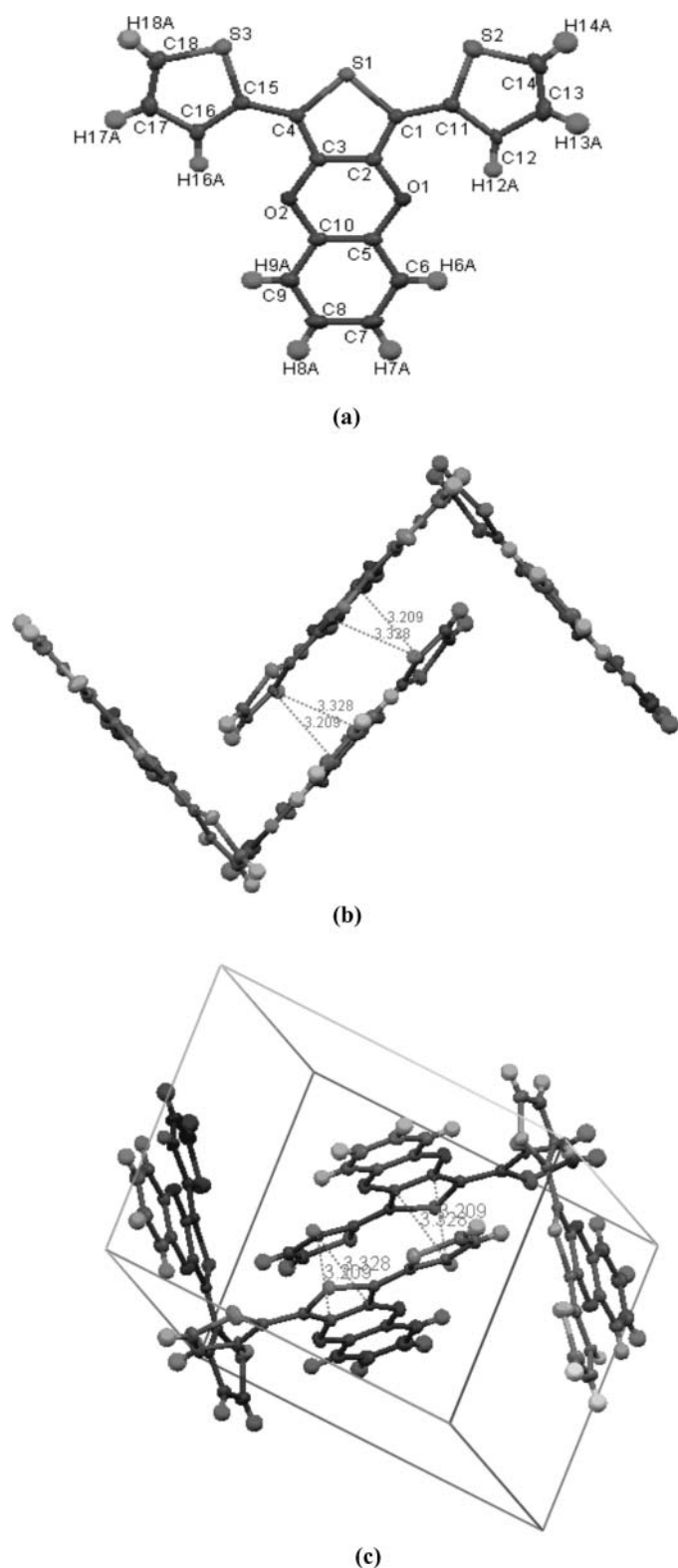
Fig. 1. X-ray crystal structures of BTh-PheDOT (a) displaying atom labels; (b) shows a side-on view displaying the twisting of one thiophene out of the plane of the molecule, as well as the participation by this ring in packing; (c) more clearly illustrates that the molecules participating in π-stacking are the twisted thiophene of one molecule and the central thiophene of another.

interaction to being electrostatic in nature (14). In particular, a net positive charge is observed on the sulfur atom due to delocalization of the lone-pair electrons over the heterocycle π-system; this net positive charge interacts with the electrons of the oxygen atom. While this interaction is observed in similar EDOT and thiophene oligomers, the lone-pair electrons of the oxygen atoms on PheDOT may have a decreased propensity to interact with the net positive charge on the sulfur atom. One possibility is that the phenylene ring serves to delocalize the oxygen electrons, hindering their ability to participate in electrostatic interactions; another is that the planarity of the PheDOT molecule prevents the electrons on oxygen from being oriented in a fashion that would allow them to interact with the sulfur atom. While further studies are needed to probe the reasons underlying these observations, the absence of sulfur-oxygen interactions may have an effect on the ability of polymers containing PheDOT to form a conjugated backbone locked into planarity, with subsequent and interesting implications on the conductivity of these polymers.

Although crystals of sufficient quality for structural analysis of BEDOT-PheDOT could not be obtained, understanding the origin of the sulfur-oxygen interaction leads us to speculate on the presence of these interactions in this multi-ring system. While the oxygen atoms on the central PheDOT may not particpate in an S-O interaction, the oxygen atoms on the peripheral EDOT molecules are fully capable of bonding with the sulfur on the central PheDOT molecule. These interactions could lock the backbone into an even more planar conformation that not only allows the molecule to readily participate in π-stacking interactions but also to exhibit an extended conformation relative to BTh-PheDOT. This speculation finds some support in the electrochemical data below. Additionally, the disparity in melting point values between BTh-PheDOT (165.0–166.5°C) and BEDOT-PheDOT (> 240°C) also suggests that BEDOT-PheDOT possesses much stronger intermolecular interactions.

3.3 Oxidative Polymerization

The oxidative electrochemical polymerizations of **1** and **2** were performed via cyclic voltammetry (CV) in mixtures of dichloromethane and acetonitrile (DCM:ACN) with 0.1 M lithium perchlorate as electrolyte. The first-scan CV of BTh-PheDOT shows a sharp onset of oxidation occurring at ~0.60 V versus Fc/Fc$^+$ while the corresponding CV of BEDOT-PheDOT monomer displays a broader onset at ~0.2 to 0.3 V (Fig. 2a). Similarly, the peak observed upon reduction of the **P1** that formed on the first scan occurs sharply, while the corresponding peak of **P2** is again broadened and more poorly defined. It has been postulated that the sharpness of these processes are indicative of the tendency of the counterion to diffuse freely through
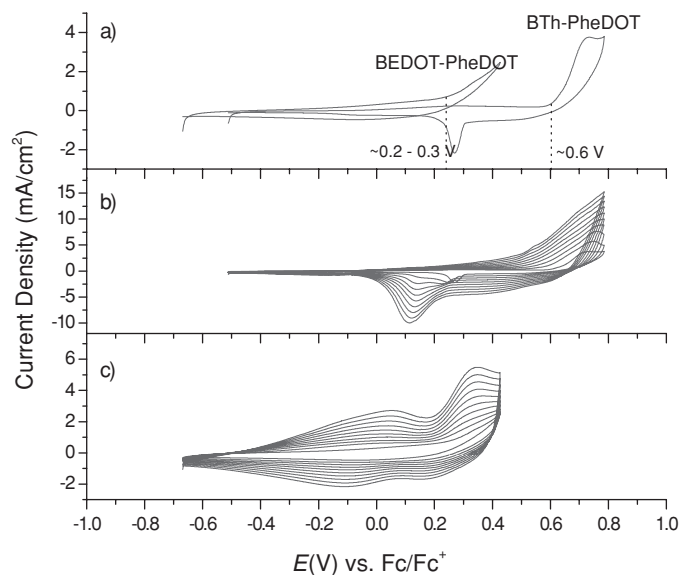
Fig. 2. CV electropolymerizations of 7.5 mmol BTh-PheDOT (b) and 5 mmol BEDOT-PheDOT (c) in 0.1 M lithium perchlorate ACN:DCM solution cycled at 25 mV/s. The first scans of BTh-PheDOT and BEDOT-PheDOT are shown overlaid in (a).

Fig. 3. Single scan CV of PBTh-PheDOT (b) and PBEDOT-PheDOT (c) in the same solutions as those used for electropolymerization after the respective polymer films had stabilized. (a) Shows the overlay of the first scan of both PBTh-PheDOT and PBEDOT-PheDOT. The arrows in (a) denote peaks corresponding to the presence of monomeric species, which are subsequently shown to be absent in (b) and c).

the system. The thiophene rings of BTh-PheDOT offer less steric bulk than the EDOT moieties in BEDOT-PheDOT, which should allow diffusion of the counterion to proceed more freely through the oligomers. Additionally, the twisted thiophene ring in BTh-PheDOT may also prevent strong interchain interactions and aggregations, or it may induce a greater degree of flexibility in the system, both of which would be expected to facilitate the diffusion of counterions. In contrast, the proposed rigidity and interchain interactions for BEDOT-PheDOT would be expected to impede the diffusivity, resulting in the broad processes observed in the CV.

The significantly lower oxidation potential of BEDOT-PheDOT can be attributed to two factors: on the one hand, the oxygen substituent present at the 3-position of BEDOT-PheDOT serves to stabilize the radical cation formed upon oxidative doping, lowering the oxidation potential of **2** relative to **1**; additionally, the out-of-plane twisting tendency of one of the thiophene rings in BTh-PheDOT, as observed above in the crystal structure, decreases the conjugation by breaking the orbital overlap and thus increasing the oxidation potential of the monomer.

Subsequent potential scanning for both monomers (Fig. 2b,c) resulted in an increase in current density, signifying deposition of electroactive species onto the platinum electrode. Additionally, a second peak associated with the polymer species is shown to grow in more rapidly in BEDOT-PheDOT than BTh-PheDOT. This is most likely due to the greater solubility of oligomers of **1** which prevents efficient deposition onto the platinum surface.
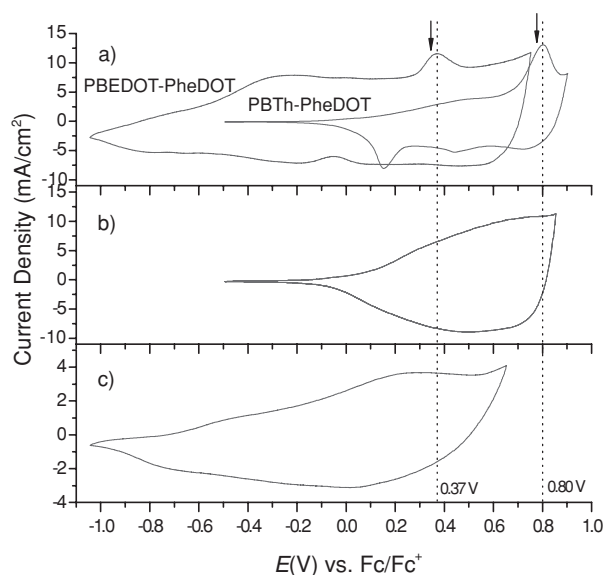
3.4 Electrochemical Properties of Polymers

The electrochemistry of both polymers exhibited a peculiar yet similar pattern of peaks. In electrochemically-polymerized films of both species, initially a broad oxidative process is observed, followed by a sharp oxidation peak occurring with nearly identical onset and peak potentials as their respective monomers (Fig. 3a). In the case of **1** the sharp oxidation peak depletes gradually after approximately 40 scans, while for **2** over 200 scans were needed to observe this depletion (Fig. 3b). We attribute these peaks to monomers trapped in the polymer films due to the rigidity of both materials. The fewer scans required to observe this depletion in PBTh-PheDOT again supports our conjecture that the twisted thiophene ring allows for freer diffusion, not just of electrolyte but also trapped monomer, while the more rigid and aggregated PBEDOT-PheDOT hinders this process.

Films of **P1** and **P2** were electrochemically deposited onto ITO-coated glass slides and analyzed via colorimetry and spectroelectrochemistry. Films of **P1** were observed to change from a dark red in the neutral state to a deep blue in the oxidized state (Fig. 5a). A sharp change in both color and transmittance is observed during this progression as well. This suggests that upon reaching the oxidation potential, electrolyte is able to quickly and freely diffuse through the film to effect such a change in properties. This in turn supports the previous contention that owing to the distorted thiophene ring of **1**, and the reduced planarity
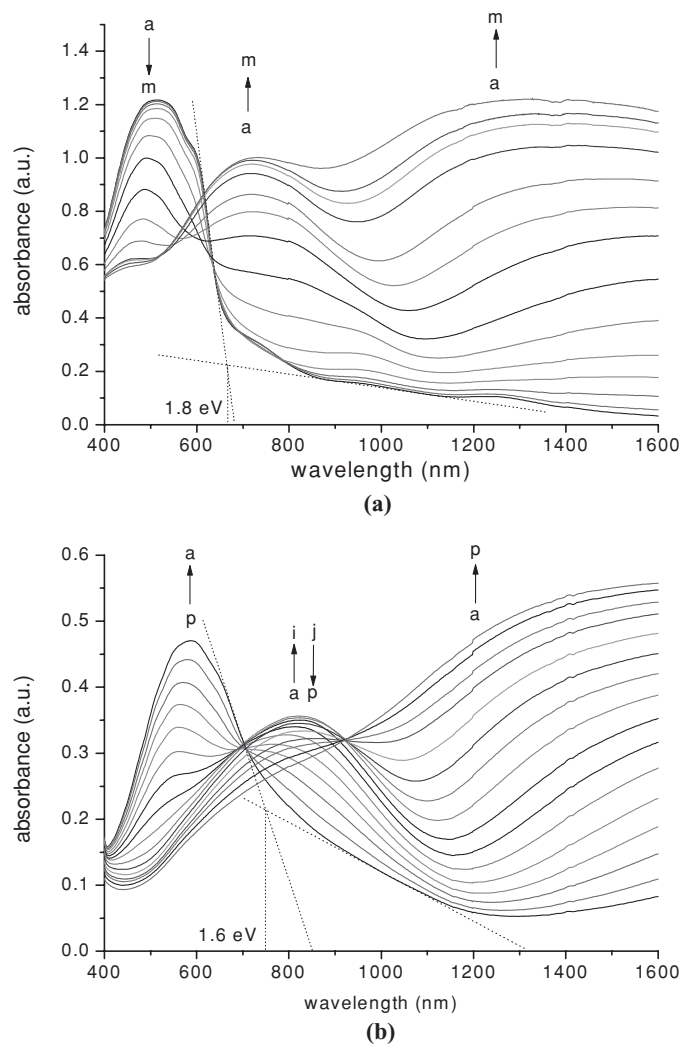
(a)

(b)

Fig. 4. (a) depicts the spectroelectrochemical analysis of PBTh-PheDOT in a 0.1M lithium perchlorate solution of 4:1 ACN:DCM. Measurements were taken in 100 mV intervals from (a) −0.26 V to (m) 0.94 V; (b) shows the spectroelectrochemical analysis of PBEDOT-PheDOT in a 0.1M lithium perchlorate solution of 1:1 ACN:DCM. Measurements were taken at 100 mV intervals from (a) −0.75 V to (p) 0.75 V.
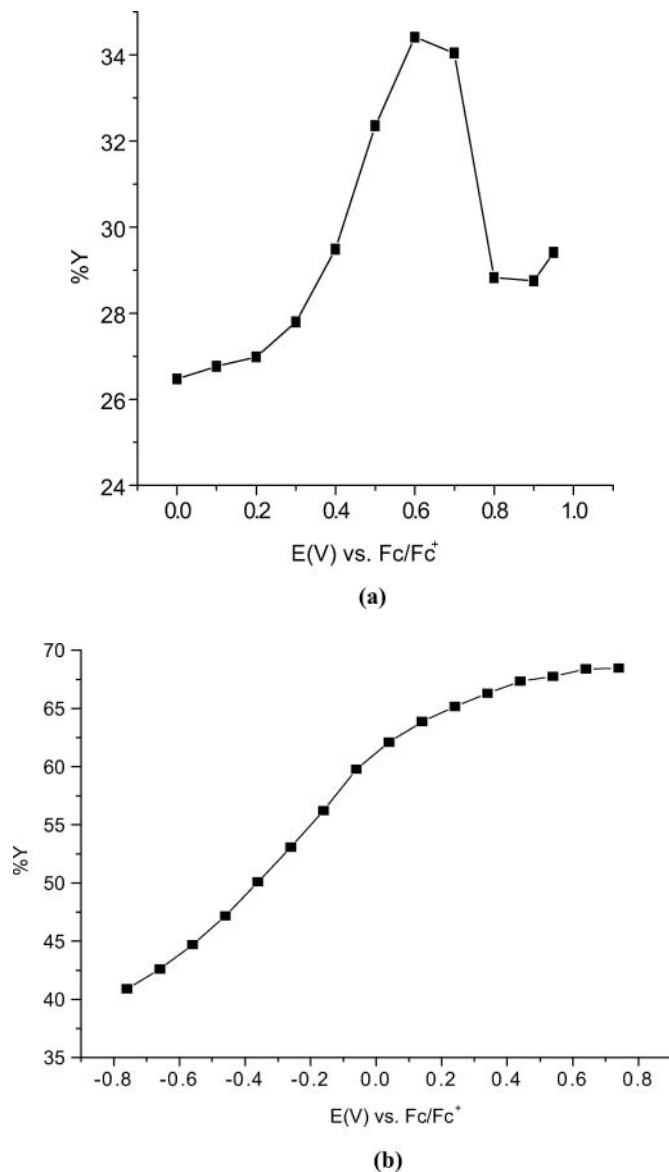

(a)

(b)

Fig. 5. Colorimetric analysis of PBTh-PheDOT (a) and PBEDOT-PheDOT (b) in a.1M lithium perchlorate solution of ACN:DCM. (a) Measurements were taken at 100 mV intervals from −0.16 V to 0.94 V; (b) Measurements were taken at 100 mV intervals from −0.75 V to 0.75 V.

of the monomer, a more open morphology is observed in **P1** which allow charges to pass more freely through the system.

The spectroelectrochemical curves of **P1** display a $\pi \rightarrow \pi^*$ transition centered at 514 nm (Fig. 4). Increasing the applied potential depletes this peak while giving rise to a polaronic peak centered at 719 nm. The optical bandgap was estimated from the onset of the $\pi \rightarrow \pi^*$ transition to be 1.8 eV. It should be noted that the long wavelength absorbance beyond the gap could not be eliminated in the near-IR region, even upon addition of hydrazine as a reducing agent. We propose two theories as possible explanations. Couplings through the β position of thiophene, rather than through the desired α position, has been ob-

served in systems incorporating thiophene. These undesired couplings introduce defects into the backbone of the polymer, leading to a loss of structural regularity and planarity, and giving rise to a broad distribution of absorbing species. More likely however, this baseline tailing is due to the prevalence of trapped charges, polarons and bipolarons, within the film, due to π-stacking interactions. A closely packed morphology would prevent facile diffusion of charge both in and out of the system, resulting in the presistence of absorbace in the polaron and bipolaron regions.

These results were also observed in **P2** (Fig. 4). Neutral films of **P2** were a dark blue color, while oxidized **P2**

films were a more transmissive light blue (Fig. 5b). Unlike **P1**, films of **P2** displayed a more gradual change in color properties and transmissivity. This suggests the more gradual diffusion of charge through the film and supports the proposal of a more packed and π-stacked system in relation to films of **P1**. The spectroelectrochemistry displayed a band gap at approximately 1.6 eV, an estimation complicated by the presence of a more pronounced absorbance in the near IR region than was observed in **P1**. Attempts to remove this absorption by reductively de-doping the polymer with hydrazine proved unsuccessful. Here, the explanation is more likely solely attributed to charge trapping, as undesirable couplings through alternative positions is not allowed. The improved π-stacking expected in this system would cause even more charges to be trapped in the polymer film, and would explain the large absorbances both around 900 nm and at higher wavelengths in the supposedly neutral state. Oxidative doping of the polymer resulted in a gradual depletion of the $\pi \rightarrow \pi^*$ peak centered at 585 nm and a gradual onset of the polaron and bipolaron peaks, with a polaron peak centered at 821 nm.

4 Conclusions

This work marks the first syntheses of PheDOT incorporated into bis-arylene activated monomers for electropolymerization and electroactive polymer formation. Crystal structures of **1** demonstrated both a tendency to π-stack intermolecularly but also a loss of conjugation as well as some planarity along the intramolecular backbone due to ring twisting. Electrochemical analysis showed that both bis-arylPheDOTs possessed the requisite solubilities and reactivities to electrochemically polymerize, with their respective polymers capable of switching between two colored states. Additionally, insight into the morphologies of the films were gathered from the electrochemical data, leading us to believe that incorporation of EDOT and PheDOT synthons into a polymer chain allows access to highly π-stacked, low bandgap polymers while polymers incorporating thiophenes and PheDOTs allow for more open morphologies. While the insolubilities of both polymer species currently precludes further investigation, the ability to attach solubilizing groups at non-stereogenic centers on PheDOT should remedy this problem and permit further studies. Specifically, the ability to spin-cast thin films will allow us to observe how these strong interchain interactions correlate with conductivity.

Acknowledgements

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