Solution-Processable Neutral Green Electrochromic Polymer Containing Thieno[3,2-b]thiophene Derivative as Unconventional Donor Units

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ABSTRACT: In the quest to develop novel solution-processable neutral green electrochromic polymers, the donor–acceptor (D–A) polymer PBOTT-BTD has been synthesized through direct C–H arylation polycondensation, using 3,6-bis(hexyloxy)thieno[3,2-b]thiophene instead of conventional D units and benzo[c][1,2,5]thiadiazole as the A unit. PBOTT-BTD films obtained through spray-coating were investigated systematically; this green polymer turned blue in the oxidized state, realizing a conversion between two primary colors. PBOTT-BTD exhibited rapid response times, desirable contrasts in both the visible and near-infrared (NIR) regions, favorable efficiencies, and reasonable optical memory and stability, making it a promising candidate for use as a new green electrochromic conjugated polymer. Accordingly, PBOTT-BTD might have applicability not only as an electrochromic material but also in NIR or optical memory devices, perhaps even in supercapacitor applications; the use of thieno[3,2-b]thiophene units presenting alkoxy groups might also allow the preparation of novel D–A conjugated polymers when matched with various acceptor units.

1. INTRODUCTION

Since the breakthrough discovery of the conducting polyacetylene in the 1970s,1 conjugated polymers have attracted considerable attention because of their low cost, flexibility, light weight, easy processing, and tunable intrinsic properties through structural design.2,3 Over the past few decades, they have revealed great potential for use in organic electronic applications, including organic light-emitting diodes (OLEDs),4 organic field effect transistors (OFETs),5,6 organic photovoltaics (OPVs),7,8 and organic electrochromic devices (OECs).9,10 In particular, conjugated polymers used as active layers in electrochromic devices have potential applicability in a variety of fields, including smart windows,11,12 displays,13,14 glasses,15 data-storage devices,16 and camouflage technologies,17 a result of their high processability,18,19 fast switching times,20,21 high optical contrasts,22 and ready tuning of their colors through alteration of their structures.23

Although significant efforts have been devoted to the design and synthesis of electrochromic polymers, most of these conjugated polymers have appeared either red or blue in their neutral states. Attempts at achieving the last (green) of the three primary colors failed because the green polymers typically exhibit dual-band absorptions in both the red and blue regions, obstructing approaches to realize the full color spectrum on the basis of color-mixing theory. Of all attempted approaches, the donor–acceptor (D–A) strategy based on theoretical works24,25 has been the most useful for obtaining green electrochromic polymers. Following the breakthrough studies of the Wudl group,24,25 dozens of neutral green conjugated polymers have been prepared;26–46 Scheme 1 presents the most representative of these polymer structures.

Despite great efforts in the development of neutral green electrochromic polymers, great challenges remain to give consideration to all the properties and to achieve the processability for many polymers due to their poor solubility. Moreover, very few reports have focused on the realization of more than one primary color in a single polymer. Furthermore, the potential applications of neutral green electrochromic polymers, including their use in near-infrared (NIR) absorption and optical memory, remain to be established. Therefore, there is significant scope to realize superior performance and increased applicability, requiring both new materials and deeper investigation. Nevertheless, fewer neutral green polymers have been appearing in recent years. In almost all previous reports of green polymers, thiophene derivatives have been used as the D units; increasing the variety of these polymers has depended mainly on changing their A units. Expanding the range of possible molecular designs would require exploring novel D moieties as replacements for conventional thiophene-based units.

As one of the simplest fused thiophenes, thieno[3,2-b]thiophene provides conjugated systems with low band gaps

Supporting Information

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Scheme 1. Chemical Structures of Representative D–A Neutral Green Electrochromic Polymers Prepared Previously\textsuperscript{34−46}
owing to its stable, electron-rich structure,\textsuperscript{39} accordingly, it has been used as a building block in OPVs\textsuperscript{50,51} and OTFTs.\textsuperscript{52–54} By introducing methoxy groups at the 3,6-positions, poly(3,6-dimethoxythieno\{3,2-b\}thiophene) has been regarded as a possible alternative to poly(3,4-ethylenedioxythiophene) (PEDOT) because of its low potential for electrochemical polymerization, comparable stability, and similar electrochromic properties.\textsuperscript{55,56} Accordingly, thieno\{3,2-b\}thiophene with alkoxy groups might be novel D units for use in neutral green electrochromic polymers.

Herein, we report our approach toward a novel solution-processable neutral green electrochromic polymer (Figure 1).

![Figure 1. Design concept of PBOTT-BTD.](image)

3,6-Bis(hexyloxy)thieno\{3,2-b\}thiophene was introduced as a D moiety, displaying properties comparable with those of traditional D units and providing processability as a result of its long alkoxy side chains. Benzo[c]\{1,2,5\}thiadiazole (BTD), a classic A unit, was used as the A moiety. Accordingly, a novel D–A–D conjugated polymer was synthesized through direct C–H arylation polycondensation, which is regarded as a facile and environmentally friendly approach owing to its fewer reaction steps, reduced waste of toxic metal salt byproducts, and achievement of narrow molecular weight distributions.\textsuperscript{57} Its structure, optical and electrochemical properties, and spectroelectrochemical behaviors have been investigated, in addition to a systematic exploration of its electrochromic performances.

2. EXPERIMENTAL SECTION

All chemicals were purchased from Aldrich. Dichloromethane (DCM) and acetonitrile (ACN) were dried and distilled over CaH\textsubscript{2} under N\textsubscript{2}. Synthetic steps are described in the Supporting Information. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded using Bruker Avance 300 and Avance-III NMR spectrometers, with CDCl\textsubscript{3} as the solvent and trimethylsilylamine (TMS) as the internal standard. Mass spectrometry (MS) was performed using a ABI Qstar Elite spectrometer; high-resolution mass spectra (HRMS) were recorded using a Thermo Q-Exactive spectrometer. Average molecular weights and polydispersity indices (PDIs) were measured through gel permeation chromatography (GPC; Shimadzu LC-20AD 230 V). UV–vis spectra were recorded using a PerkinElmer Lambda 750 spectrometer.

Electrochemical experiments were performed using a CHI620E electrochemical workstation. The three-electrode cell consisted of a Ag wire as the reference electrode, a Pt wire as the counter electrode, and a Pt disk as the working electrode, immersed in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) in ACN as the supporting electrolyte. All measurements were performed under ambient conditions, including the stability test. The energy level of the highest occupied molecular orbital (HOMO) was obtained from the onset potential of oxidation, determined from the intersection of the tangent between the baseline and the signal current. The potential was calibrated to the ferrocene redox couple, \(E(\text{Fc/Fc}^+) = 0.54\) V (vs Ag wire), in ACN; the HOMO energy level was calculated using the equation\textsuperscript{36}

\[
E_{\text{HOMO}} = -(E_{\text{onset,ox}} - E_{\text{Fc}} + 5.1) \text{ eV}
\]

where the optical band gap (\(E_{\text{onset,ox}}\)) was obtained from the onset of the energy band in the polymer film.

Spectroelectrochemistry and switching studies were performed using the Lambda 750 spectrometer under control of the CHI620E electrochemical workstation. The three-electrode cell consisted of a Ag wire as the reference electrode, a Pt wire as the counter electrode, and indium tin oxide (ITO)-coated glass slides as working electrodes in a transparent cuvette. All these experiments were performed in 0.1 M TBAPF\textsubscript{6}/ACN as the supporting electrolyte under ambient conditions. The coloration efficiencies were calculated using the transmittances in the oxidized and neutral states (\(T_{\text{ox}}\) and \(T_{\text{neu}}\)) and the injected/ejected charge per unit area (\(Q_{\text{ffil}}\)). Colorimetric measurements were performed using a SN-300 colorimeter.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterizations. Scheme 2 displays the synthesis of PBOTT-BTD from thieno\{3,2-b\}thiophene. Tetrabromothieno\{3,2-b\}thiophene (1), 3,6-dibromothieno\{3,2-b\}thiophene (2), and 3,6-dimethoxythieno\{3,2-b\}thiophene (3) were prepared in satisfactory yields according to previously reported procedures.\textsuperscript{56,59,60} 3,6-Bis(hexyloxy)thieno\{3,2-b\}thiophene (4) was obtained through transetherification from 3. Compound 5, the stannic derivative of 4 at the 2-position, was prepared and used in the next step without further purification. The D–A–D monomer (M\textsubscript{1}) was prepared via Stille coupling between 5 and 4,7-dibromobenzo[c]\{1,2,5\}thiadiazole in toluene with Pd(PPh\textsubscript{3})\textsubscript{4} as catalyst; the dibromo derivative (M\textsubscript{2}) was obtained through reaction of M\textsubscript{1} with N-bromosuccinimide (NBS). The molecular structures of M\textsubscript{1} and M\textsubscript{2} were confirmed using \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy and HRMS.

PBOTT-BTD was prepared by typical oxidative polymerization of M\textsubscript{1} initially. But unfortunately, yields of soluble parts were extremely low after the purification through Soxhlet extraction, which might result from the cross-link or superhigh molecular weight of the polymer due to the fairly high activity of its D–A–D monomer. Inspired by the previous work to synthesize dioxothiophene-based homopolymers by Yu and coworkers,\textsuperscript{57} the direct C–H arylation polycondensation of M\textsubscript{1} and M\textsubscript{2} was performed in dimethylacetamide (DMAc) using Pd(OAc\textsubscript{2}) as the catalyst and K\textsubscript{2}CO\textsubscript{3} as the base without any ligands. PBOTT-BTD was obtained in 56% yield with favorable processability after purification through Soxhlet extraction; its structure was confirmed using \textsuperscript{1}H NMR spectroscopy. The number-average molecular weight (\(M_{\text{n}}\)) of PBOTT-BTD was 3431 g mol\textsuperscript{−1}, with a PDI of 1.1, determined using GPC. Compared with oxidative polymerization, PBOTT-BTD prepared by direct C–H arylation polycondensation has advantages of desirable yield for feasibility and narrow PDI for pure color with similar optical and electrochromic properties (Figures S6 and S7). Accordingly, the polymer synthesized by this method is used for further investigation of essential properties and electrochromic performance.
3.2. Optical and Electrochemical Properties. To understand the optical properties of the D−A−D polymer, the UV−vis absorption spectra of PBOTT-BTD were examined both in CHCl₃ solution and as a thin film. Figure 2a reveals that PBOTT-BTD exhibited wide absorption with two distinct bands, characteristic of D−A polymers, in solution and in the film state. The higher energy band (λ max = 404 nm in solution; λ max = 423 nm in the film) can be attributed to the localized π−π* transition of the conjugated systems; the broader, lower energy band (λ max = 588 nm in solution; λ max = 650 nm in the film) is ascribed to intramolecular charge transfer (ICT) between the thieno[3,2-b]thiophene-based D and benzothiadiazole-based A units. Upon proceeding from solution to the film state, obvious red-shifts occurred for both the higher and lower energy bands, suggesting strong interchain interactions, resulting from efficient self-stacking of PBOTT-BTD, in the solid state. The change in the absorption valley from 462 to 510 nm implied that the color of the polymer would be green in the film state and blue in solution, as confirmed experimentally.

The optical band gap (E g,opt) of PBOTT-BTD was 1.51 eV, estimated by measuring the onset of the lower energy band (λ onset) of the polymer film.
Cyclic voltammetry (CV) was used to investigate the electrochemical behavior of PBOTT-BTD in an electrolyte solution of 0.1 M TBAPF₆/ACN. Films of PBOTT-BTD were formed by spray-coating onto Pt disk electrodes from a CHCl₃ solution (ca. 1 mg mL⁻¹) at room temperature; Pt and Ag wires were used as counter and reference electrodes, respectively. Prior to electrochemical characterization, the polymer films were cycled between −0.2 and +1.0 V, at a scan rate of 50 mV s⁻¹, until the electrochemical responses became stable and reproducible. From the cyclic voltammogram in Figure 2b, the polymer film underwent quasi-reversible p-doping/dedoping in the anodic region with half-wave potentials of +0.33 and +0.73 V, whereas it exhibited irreversible n-doping/dedoping in the cathodic region. According to the oxidation onset potential of PBOTT-BTD, the HOMO energy level was −4.79 eV; the LUMO energy level of −3.28 eV was estimated from the HOMO energy level and the optical band gap.

The scan rate dependence of PBOTT-BTD was studied in the same system. The film was scanned in the anodic region at rates from 50 to 300 mV s⁻¹ (Figure 3a). Based on linear regression fitting, the relationships between the anodic (iₚa1 and iₚa2) and cathodic (iₚc1 and iₚc2) peak current densities and the scan rates (Figure 3b) all had coefficients of determination extremely close to 1, suggesting that PBOTT-BTD had adhered well to the electrodes and that the redox processes were non-diffusion-controlled. The linear behavior indicated that this redox-active polymer followed the characteristics of a surface-confined electrochemical process. Therefore, the spray-coated films did not diffuse into the electrolyte solution even under high scan rates, while charges could diffuse through the polymer films during the redox processes. In addition, the CV curves were nearly rectangular with wide potential windows, suggesting that PBOTT-BTD might be a promising candidate for use in supercapacitors.

3.3. Spectroelectrochemical Analysis. The optoelectronic properties of the polymer film were studied using in situ UV–vis–NIR spectroelectrochemistry (SEC). PBOTT-BTD was spray-coated onto ITO-coated glass slides from a CHCl₃ solution (ca. 1 mg mL⁻¹) at room temperature. Prior to spectroelectrochemical analysis, the polymer film was cycled between −0.2 and +1.0 V at a scan rate of 50 mV s⁻¹ until it exhibited stable and reproducible switching. The changes in the optical absorption spectra, from the neutral to the oxidized state, were recorded in 0.1 M TBAPF₆/ACN under different applied constant voltage pulses (Figure 4a). As the applied potential increased, the two absorption bands at 423 and 650 nm began to decrease in intensity simultaneously with the increase of polaron and bipolaron absorption, with obvious and broad absorption bands observed in the NIR region for the oxidized state. Moreover, the open gap in the visible region became broader, and a blue-shift of the absorption valley occurred from 510 to 460 nm, indicating that the film could...
turn blue in the oxidized state from green in the neutral state. This change in the absorption spectra was consistent with the color change from green to blue observed experimentally (Figure 4b). Accordingly, conversion between two primary colors was achieved. Additionally, the CIE 1976 color coordinates ($L^*, a^*, b^*$, where $L^*$ represents lightness, $a^*$ the red/green balance, and $b^*$ the yellow/blue balance) of the polymer film were determined in both its neutral and oxidized states (Figure 4b).45

3.4. Electrochromic Properties. To determine the potential applicability of the electrochromic performance of PBOTT-BTD, its relative and fundamental parameters were analyzed, including response time, optical contrast ($\Delta T$), coloration efficiency (CE), optical memory, and stability.

The switching behavior of the polymer film was studied by the double-step chronoamperometry method with a switching interval of 10 s in 0.1 M TBAPF$_6$/ACN. From the chronoamperometry analysis shown in Figure 5a, the polymer switched very rapidly between the neutral and oxidized state. And the response times were measured as 0.70 and 0.21 s, which were defined as the times required to reach 95% of the full responses. Meanwhile, the transmittance changes at the dominant wavelengths were monitored as well (Figure 5b). Moderate optical contrasts between redox states were found to be 35% for 423 nm and 23% for 650 nm in the visible region. These values are similar to the contrasts of PBDT (37% for 428 nm and 23% nm for 755 nm),26 which is regarded as one of the most representative green-to-blue polymer with EDOT as donor and BTD as acceptor. Furthermore, PBOTT-BTD exhibited a considerable optical contrast of 74% at 1500 nm, which is significant for many applications in the NIR region, and only a few green D–A polymers, ever known, have shown such high contrasts over 70% in this region.24,26,27,30

Coloration efficiency (CE) is a fundamental measure used to identify electrochromic performance; it is defined as the change in optical density per unit of inserted charge. Based on the switching studies of PBOTT-BTD, its CE values were calculated to be 370 cm$^2$ C$^{-1}$ at 423 nm, 303 cm$^2$ C$^{-1}$ at 650 nm, and 588 cm$^2$ C$^{-1}$ at 1500 nm. To the best of our knowledge, very few green D–A polymers have attained fairly high CE values over 300 cm$^2$ C$^{-1}$ previously.42,46,61

The optical memory, or open-circuit memory, is a measure of the propensity of a polymer to maintain its redox state upon removal of the external bias. The short-term memory was investigated first. A potential pulse of +1.0 V was applied to the polymer film for 2 s prior to forming the open-circuit state for 100 s; the transmittance change at 423 nm was monitored simultaneously. The same procedure was repeated in the neutral state (−0.2 V). As revealed in Figure 6a, the transmittance was almost unchanged from the neutral state, while a mild fluctuation occurred in the oxidized state, suggesting that PBOTT-BTD displays a promising optical memory. For deeper exploration, the long-term memory was investigated as well (Figure 6b). Initially, the transmittance contrast at 423 nm decreased sharply, dropping to 23% after 30 min; the contrast became constant (ca. 20%) and maintained
over 57% of the initial contrast (35%) in the absence of an applied voltage for 1 h. More visually, the film turned green—blue ($L^* = 49.6; a^* = -6.9; b^* = -5.8$) after 1 h in the absence of an applied potential. In comparison, PBOTT-BTD kept higher contrasts than PBDT (about 15% at 428 nm after 1 h) in the long-term test by Xu and co-workers, which is the best result for green electrochromic polymers ever known. The optical memory tests demonstrated that PBOTT-BTD adhered well to the ITO electrode, minimizing the self-erasing effect (the diffusion and exchange of electrons in the absence of an applied voltage). Thus, it appears to be a promising green OEC material for application in optical or electrochromic memory.

Stability is a measure of the guaranteed electrochromic performance under repeated switching; it is evaluated by monitoring the changes in peak currents. To investigate this fundamental property, PBOTT-BTD was spray-coated onto a Pt disk electrode from a CHCl$_3$ solution (ca. 1 mg mL$^{-1}$) at room temperature; Pt and Ag wires were used as counter and reference electrodes, respectively. Figure 7 reveals that the polymer film exhibited decreases of approximately 20% in both its anodic ($i_{pa}$) and cathodic ($i_{pc}$) peak current densities after 2000 redox cycles under ambient conditions, which revealed the stability of PBOTT-BTD. These decreases might have been caused by the influence of water and/or oxygen, vaporization of the electrolyte, or resistive heating under repeated switching.

4. CONCLUSION

A novel solution-processable neutral green electrochromic polymer, PBOTT-BTD, containing 3,6-bis(hexyloxy)thieno[3,2-b][thiophene instead of conventional D units, has been prepared through direct C-H arylation polycondensation. The optical and electrochemical properties, spectroelectrochemical analysis, and electrochromic performance of PBOTT-BTD films were examined after spray-coating. This material appears to be a promising candidate for use as a green electrochromic conjugated polymer, with processability, conversion between two primary colors, rapid response times, desirable contrasts in both the visible and NIR regions, favorable efficiencies, and reasonable optical memory and stability. Taking these factors into consideration, PBOTT-BTD might have applications not only in electrochromic devices but also in NIR or optical memory devices, possibly even supercapacitor applications. Furthermore, thieno[3,2-b]thiophene units presenting alkoxy groups might also be useful for the preparation of novel D−A conjugated polymers when matched with various A units. Related studies are underway in our laboratories; the results will be reported in due time.

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REFERENCES


(37) Salzner, U. Does the Donor–Acceptor Concept Work for Designing Synthetic Metals? 1. Theoretical Investigation of Poly(3-


