

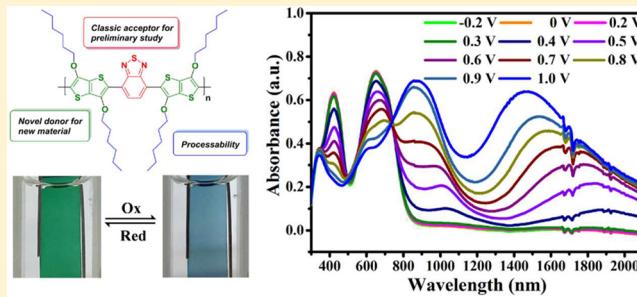
Solution-Processable Neutral Green Electrochromic Polymer Containing Thieno[3,2-*b*]thiophene Derivative as Unconventional Donor Units

Weishuo Li, Yitong Guo, Jingjing Shi, Hongtao Yu, and Hong Meng*

School of Advanced Materials, Peking University Shenzhen Graduate School, Peking University, Shenzhen 518055, China

Supporting Information

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 (OTFTs),^{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 works^{47,48} 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

Received: July 27, 2016

Revised: September 13, 2016

Published: September 27, 2016

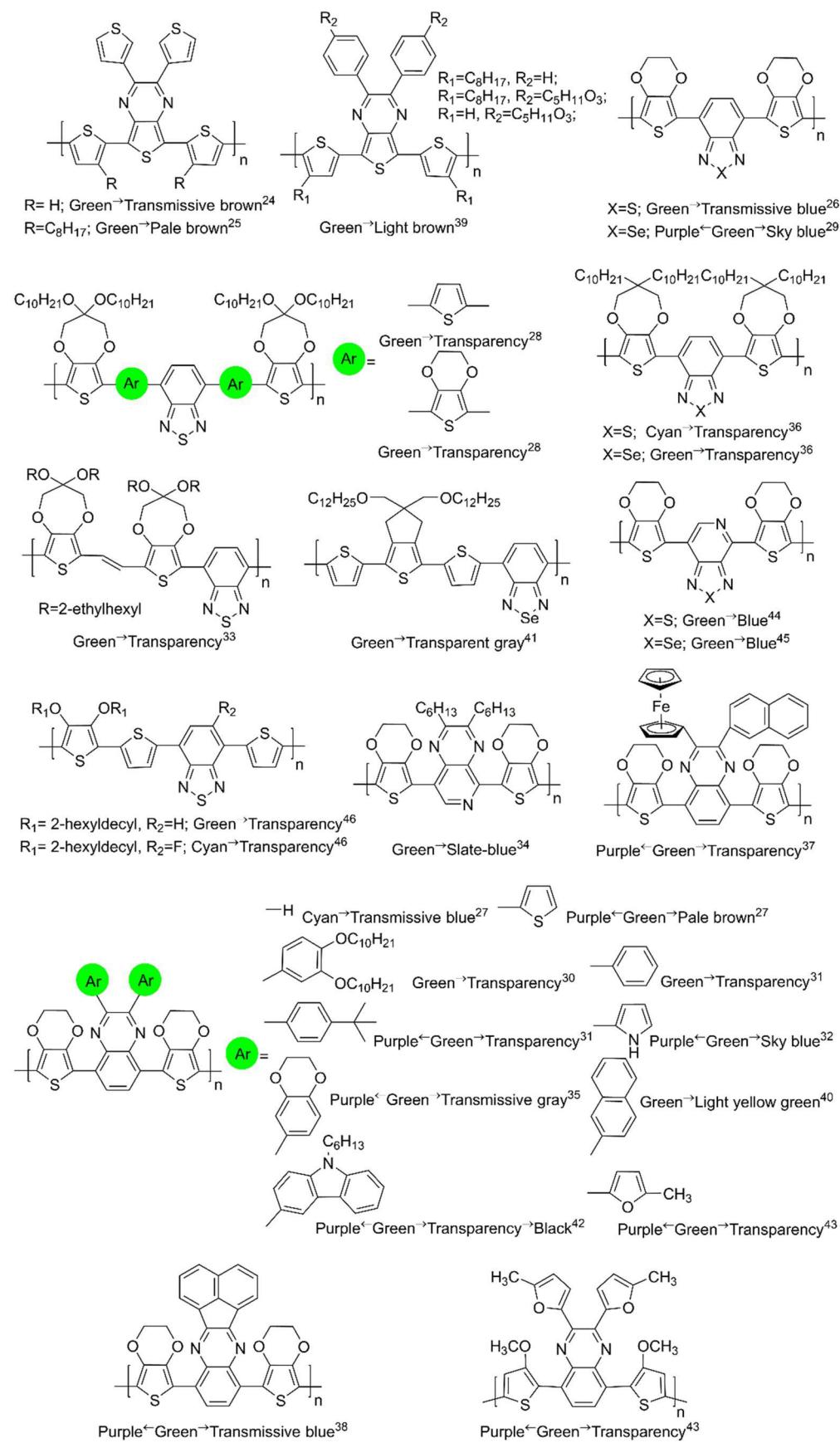


ACS Publications

© 2016 American Chemical Society

7211

DOI: 10.1021/acs.macromol.6b01624
Macromolecules 2016, 49, 7211–7219

Scheme 1. Chemical Structures of Representative D–A Neutral Green Electrochromic Polymers Prepared Previously^{24–46}

owing to its stable, electron-rich structure,⁴⁹ accordingly, it has been used as a building block in OPVs^{50,51} and OTFTs.^{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.^{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).

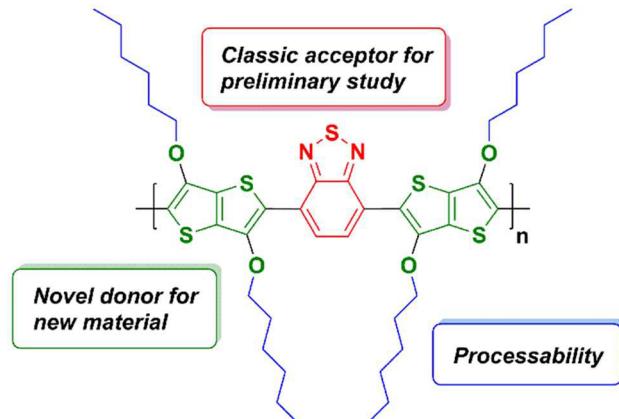


Figure 1. Design concept of PBOTT-BTD.

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 (BTB), 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.⁵⁷ Its structure, optical and electrochemical properties, and specroelectrochemical 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 CaH₂ under N₂. Synthetic steps are described in the Supporting Information. ¹H and ¹³C NMR spectra were recorded using Bruker Avance 300 and Avance-III NMR spectrometers, with CDCl₃ as the solvent and trimethylsilane (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 (TBAPF₆) 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°(Fc/Fc⁺) = 0.54 V (vs Ag wire), in ACN; the HOMO energy level was calculated using the equation⁵⁸

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

The energy level of the lowest unoccupied molecular orbital (LUMO) was estimated by using the equation

$$E_{\text{LUMO}} = (E_{\text{HOMO}} + E_{g,\text{opt}}) \text{ eV}$$

where the optical band gap ($E_{g,\text{opt}}$) was obtained from the onset of the energy band of 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 TBAPF₆/ACN as the supporting electrolyte under ambient conditions. The coloration efficiencies were calculated using the transmittances in the oxidized and neutral states (T_{ox} and T_{neut}) and the injected/ejected charge per unit area (Q_d).⁵⁹ 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.^{56,59,60} 3,6-Bis(hexyloxy)thieno[3,2-*b*]thiophene (4) was obtained through transesterification 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 (M1) was prepared via Stille coupling between 5 and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole in toluene with Pd(PPh₃)₄ as catalyst; the dibromo derivative (M2) was obtained through reaction of M1 with *N*-bromosuccinimide (NBS). The molecular structures of M1 and M2 were confirmed using ¹H and ¹³C NMR spectroscopy and HRMS.

PBOTT-BTD was prepared by typical oxidative polymerization of M1 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 dioxythiophene-based homopolymers by Yu and co-workers,⁵⁷ the direct C-H arylation polycondensation of M1 and M2 was performed in dimethylacetamide (DMAc) using Pd(OAc)₂ as the catalyst and K₂CO₃ 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 ¹H NMR spectroscopy. The number-average molecular weight (M_n) of PBOTT-BTD was 3431 g mol⁻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.

Scheme 2. Synthesis of PBOTT-BTD

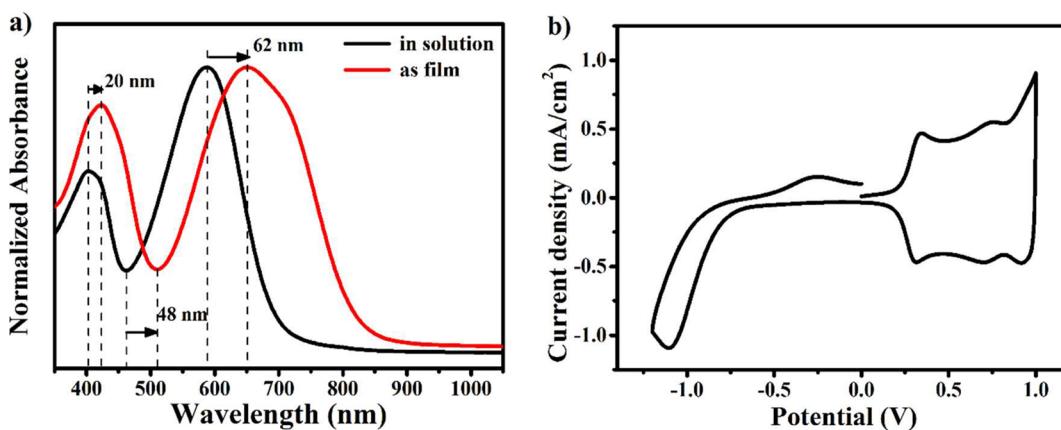
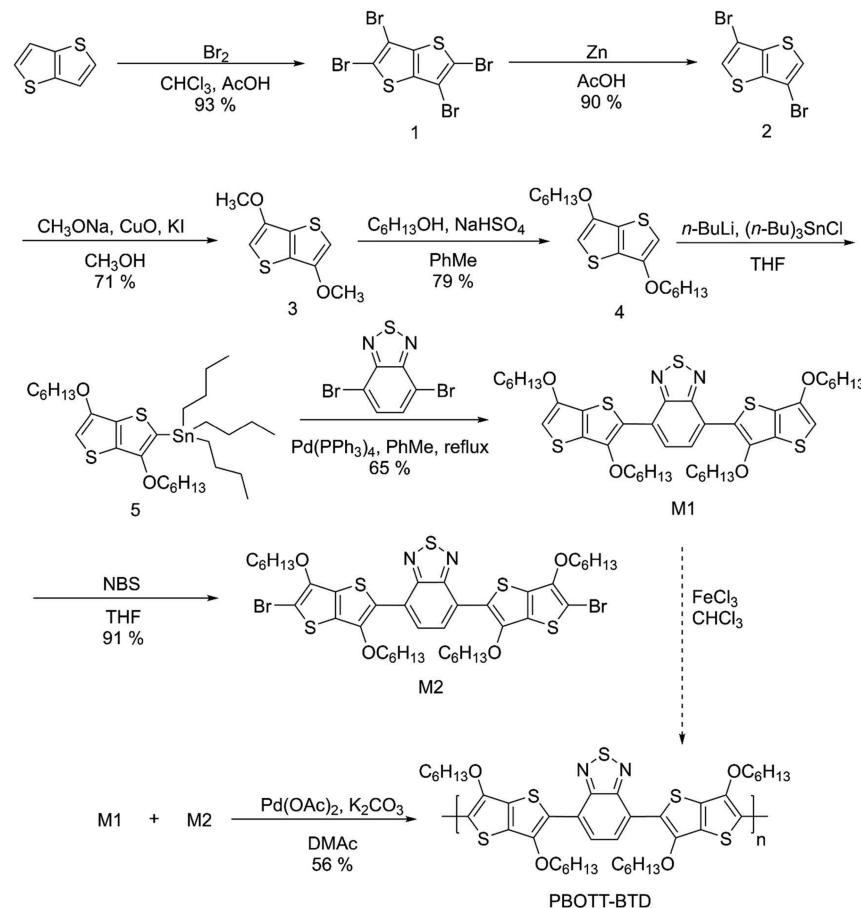


Figure 2. (a) Normalized UV–vis absorption spectra of PBOTT-BTD in CHCl₃ and as a spray-coated thin film. (b) Cyclic voltammogram of PBOTT-BTD spray-coated on the Pt disk electrode in 0.1 M TBAPF₆/ACN, recorded at the scan rate of 100 mV s⁻¹ vs Ag wire electrode.

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 ($\lambda_{\text{max}} = 404 \text{ nm}$ in solution; $\lambda_{\text{max}} = 423 \text{ nm}$ in the film) can be attributed to the localized $\pi-\pi^*$ transition of the conjugated systems; the broader, lower energy band ($\lambda_{\text{max}} = 588 \text{ nm}$ in solution; $\lambda_{\text{max}} = 650 \text{ nm}$ 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 ($E_{\text{g,opt}}$) of PBOTT-BTD was 1.51 eV, estimated by measuring the onset of the lower energy band (λ_{onset}) of the polymer film.

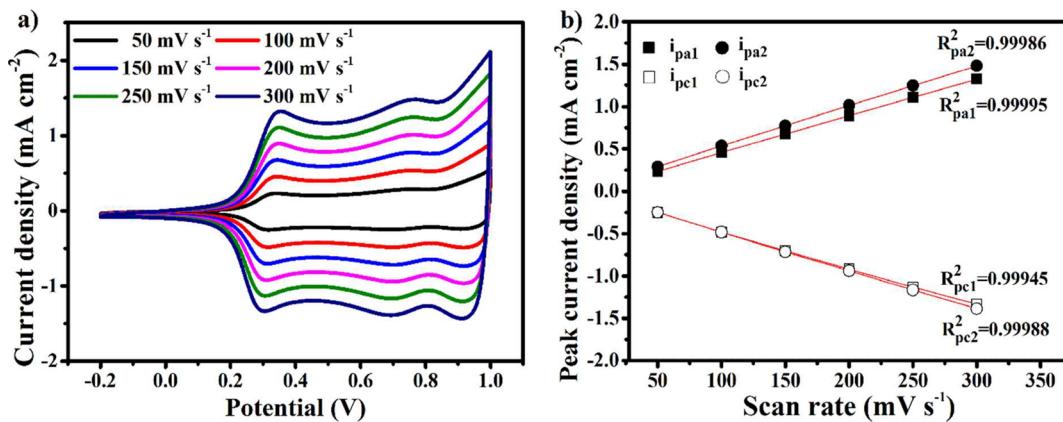


Figure 3. (a) Cyclic voltammograms of PBOTT-BTD spray-coated on the Pt disk electrode in 0.1 M TBAPF₆/ACN, recorded at scan rates of 50, 100, 150, 200, 250, and 300 mV s^{-1} vs Ag wire electrode. (b) Linear relationship between peak current density and scan rate.

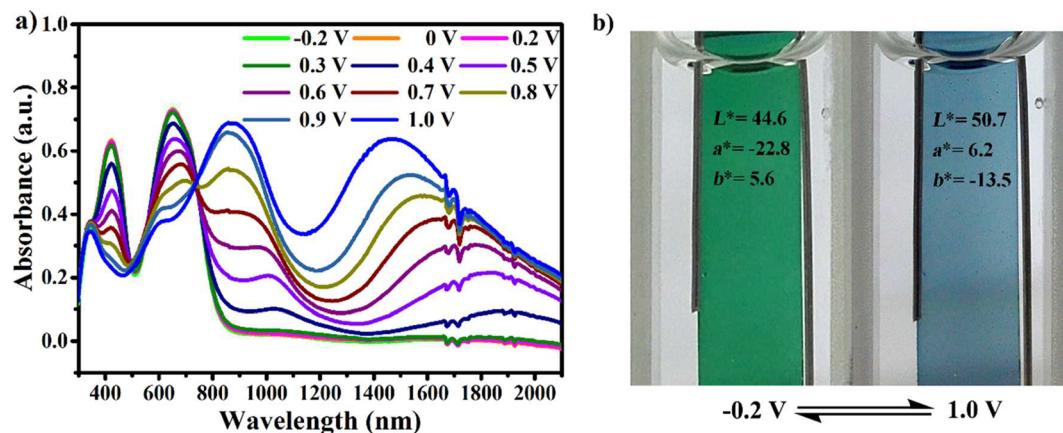


Figure 4. (a) SEC of PBOTT-BTD spray-coated on an ITO-coated glass slide in 0.1 M TBAPF₆/ACN at applied potentials from -0.2 to $+1.0$ V. (b) Colors and colorimetric measurements of PBOTT-BTD at different potentials.

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 ($i_{\text{pa}1}$ and $i_{\text{pa}2}$) and cathodic ($i_{\text{pc}1}$ and $i_{\text{pc}2}$) 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.⁴² 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

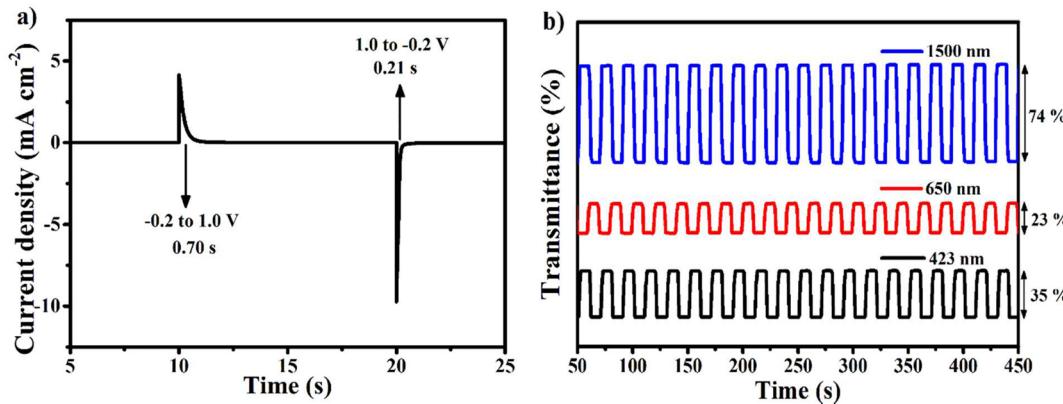


Figure 5. (a) Chronoamperometry and (b) transmittance changes of PBOTT-BTD spray-coated on an ITO-coated glass slide in 0.1 M TBAPF₆/ACN with a 10 s delay between -0.2 and +1.0 V.

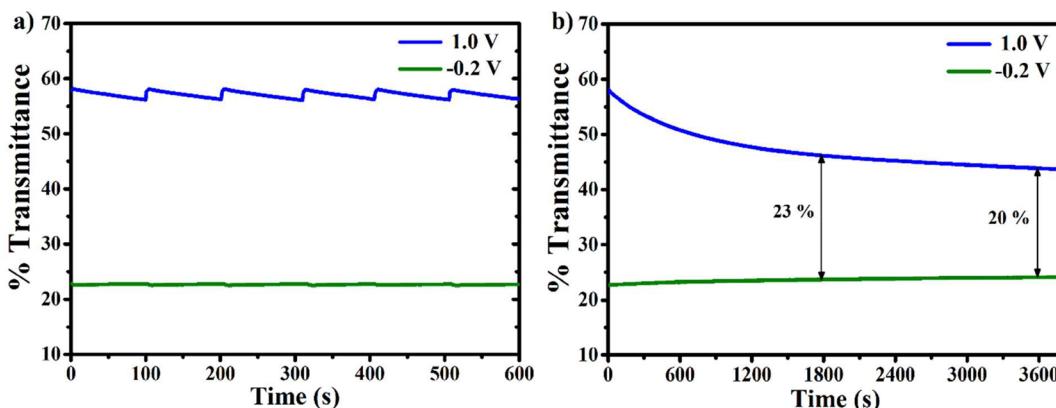


Figure 6. Open-circuit memory tests of PBOTT-BTD spray-coated on an ITO-coated glass slide in 0.1 M TBAPF₆/ACN at 423 nm: (a) short- and (b) long-term performance.

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 (ΔT), 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 TBAPF₆/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 cm² C⁻¹ at 423 nm, 303 cm² C⁻¹ at 650 nm, and 588 cm² 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 cm² 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,⁴⁴ 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).⁹ 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

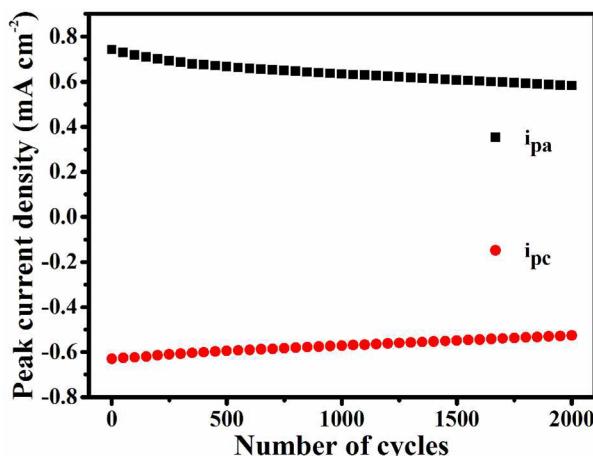


Figure 7. Stability of PBOTT-BTD spray-coated on a Pt disk electrode in 0.1 M TBAPF₆/ACN at a scan rate of 200 mV s⁻¹ vs Ag wire electrode under ambient conditions.

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, evaporation of the electrolyte, or resistive heating under repeated switching.⁹

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.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.macromol.6b01624](https://doi.org/10.1021/acs.macromol.6b01624).

Synthesis details; NMR spectra of monomers and PBOTT-BTD ([PDF](#))

■ AUTHOR INFORMATION

Corresponding Author

*(H.M.) E-mail: menghong@pkusz.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by Shenzhen Key Laboratory of Organic Optoelectromagnetic Functional Materials of Shenzhen Science and Technology Plan (ZDSYS20140509094114164), the Shenzhen Peacock Program (KQTD2014062714543296), Shenzhen Science and Technology Research Grant (JCYJ20140509093817690, JCYJ20160331095335232), Nanshan Innovation Agency Grant (No. KC2015ZDYF0016A), Guangdong Key Research Project (Nos. 2014B090914003 and 2015B090914002), Guangdong Talents Project, National Basic Research Program of China (973 Program, No. 2015CB856505), Natural Science Foundation of Guangdong Province (2014A030313800), and Guangdong Academician Workstation (2013B090400016).

■ REFERENCES

- (1) Shirakawa, H.; Louis, E. J.; Macdiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)_X. *J. Chem. Soc., Chem. Commun.* 1977, 578–580.
- (2) Yoshino, K.; Kaneto, K.; Takeda, S. Applications of conducting polymers as electronics and opto-electronics devices. *Synth. Met.* 1987, 18, 741–746.
- (3) Forrest, S. R. The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* 2004, 428, 911–918.
- (4) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chem. Rev.* 2009, 109, 897–1091.
- (5) Chen, H.; Guo, Y.; Yu, G.; Zhao, Y.; Zhang, J.; Gao, D.; Liu, H.; Liu, Y. Highly pi-extended copolymers with diketopyrrolopyrrole moieties for high-performance field-effect transistors. *Adv. Mater.* 2012, 24, 4618–4622.
- (6) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting pi-conjugated systems in field-effect transistors: a material odyssey of organic electronics. *Chem. Rev.* 2012, 112, 2208–2267.
- (7) Facchetti, A. π -Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications†. *Chem. Mater.* 2011, 23, 733–758.
- (8) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.* 2015, 115, 12666–12731.

- (9) Beaujuge, P. M.; Reynolds, J. R. Color control in pi-conjugated organic polymers for use in electrochromic devices. *Chem. Rev.* **2010**, *110*, 268–320.
- (10) Gunbas, G.; Toppore, L. Electrochromic conjugated polyheterocycles and derivatives—highlights from the last decade towards realization of long lived aspirations. *Chem. Commun.* **2012**, *48*, 1083–1101.
- (11) Yeh, M. H.; Lin, L.; Yang, P. K.; Wang, Z. L. Motion-driven electrochromic reactions for self-powered smart window system. *ACS Nano* **2015**, *9*, 4757–4765.
- (12) Dyer, A. L.; Bulloch, R. H.; Zhou, Y.; Kippelen, B.; Reynolds, J. R.; Zhang, F. A vertically integrated solar-powered electrochromic window for energy efficient buildings. *Adv. Mater.* **2014**, *26*, 4895–4900.
- (13) Remmele, J.; Shen, D. E.; Mustonen, T.; Fruehauf, N. High Performance and Long-Term Stability in Ambiently Fabricated Segmented Solid-State Polymer Electrochromic Displays. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12001–12008.
- (14) Moon, H. C.; Lodge, T. P.; Frisbie, C. D. Solution Processable, Electrochromic Ion Gels for Sub-1 V, Flexible Displays on Plastic. *Chem. Mater.* **2015**, *27*, 1420–1425.
- (15) Osterholm, A. M.; Shen, D. E.; Kerszulis, J. A.; Bulloch, R. H.; Kuepfert, M.; Dyer, A. L.; Reynolds, J. R. Four shades of brown: tuning of electrochromic polymer blends toward high-contrast eyewear. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1413–1421.
- (16) Sonmez, G.; Sonmez, H. B. Polymeric electrochromics for data storage. *J. Mater. Chem.* **2006**, *16*, 2473–2477.
- (17) Yu, H. T.; Shao, S.; Yan, L. J.; Meng, H.; He, Y. W.; Yao, C.; Xu, P. P.; Zhang, X. T.; Hu, W. P.; Huang, W. Side-chain engineering of green color electrochromic polymer materials: toward adaptive camouflage application. *J. Mater. Chem. C* **2016**, *4*, 2269–2273.
- (18) Ye, Q.; Neo, W. T.; Lin, T.; Song, J.; Yan, H.; Zhou, H.; Shah, K. W.; Chua, S. J.; Xu, J. W. Pyrrolophthalazine dione (PPD)-based donor–acceptor polymers as high performance electrochromic materials. *Polym. Chem.* **2015**, *6*, 1487–1494.
- (19) Us, C. N.; Ozkut, M. I. Expanding the Realm of Soluble Narrow Band Gap Polymers with a Benzobisthiadiazole Derivative. *Macromolecules* **2016**, *49*, 3009–3015.
- (20) Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. High contrast ratio and fast-switching dual polymer electrochromic devices. *Chem. Mater.* **1998**, *10*, 2101–2108.
- (21) Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. Conducting poly(3,4-alkylenedioxythiophene) derivatives as fast electrochromics with high-contrast ratios. *Chem. Mater.* **1998**, *10*, 896–902.
- (22) Groenendaal, L.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. Electrochemistry of poly(3,4-alkylenedioxythiophene) derivatives. *Adv. Mater.* **2003**, *15*, 855–879.
- (23) Kerszulis, J. A.; Amb, C. M.; Dyer, A. L.; Reynolds, J. R. Follow the Yellow Brick Road: Structural Optimization of Vibrant Yellow-to-Transmissive Electrochromic Conjugated Polymers. *Macromolecules* **2014**, *47*, 5462–5469.
- (24) Sonmez, G.; Shen, C. K.; Rubin, Y.; Wudl, F. A red, green, and blue (RGB) polymeric electrochromic device (PECD): the dawning of the PECD era. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498–1502.
- (25) Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Jost, R. W.; Rubin, Y.; Wudl, F. A processable green polymeric electrochromic. *Macromolecules* **2005**, *38*, 669–675.
- (26) Durmus, A.; Gunbas, G. E.; Camurlu, P.; Toppore, L. A neutral state green polymer with a superior transmissive light blue oxidized state. *Chem. Commun.* **2007**, 3246–3248.
- (27) Durmus, A.; Gunbas, G. E.; Toppore, L. New, highly stable electrochromic polymers from 3,4-ethylenedioxythiophene-bis-substituted quinoxalines toward green polymeric materials. *Chem. Mater.* **2007**, *19*, 6247–6251.
- (28) Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. Spray Processable Green to Highly Transmissive Electrochromics via Chemically Polymerizable Donor–Acceptor Heterocyclic Pentamers. *Adv. Mater.* **2008**, *20*, 2772–2776.
- (29) Cihaner, A.; Algi, F. A Novel Neutral State Green Polymeric Electrochromic with Superior n- and p-Doping Processes: Closer to Red-Blue-Green (RGB) Display Realization. *Adv. Funct. Mater.* **2008**, *18*, 3583–3589.
- (30) Gunbas, G. E.; Durmus, A.; Toppore, L. A unique processable green polymer with a transmissive oxidized state for realization of potential RGB-based electrochromic device applications. *Adv. Funct. Mater.* **2008**, *18*, 2026–2030.
- (31) Gunbas, G. E.; Durmus, A.; Toppore, L. Could Green be Greener? Novel Donor–Acceptor-Type Electrochromic Polymers: Towards Excellent Neutral Green Materials with Exceptional Transmissive Oxidized States for Completion of RGB Color Space. *Adv. Mater.* **2008**, *20*, 691–695.
- (32) Algi, F.; Cihaner, A. An ambipolar neutral state green polymeric electrochromic. *Org. Electron.* **2009**, *10*, 704–710.
- (33) Beaujuge, P. M.; Vasilyeva, S. V.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. Unsaturated Linkages in Dioxythiophene-Benzothiadiazole Donor–Acceptor Electrochromic Polymers: The Key Role of Conformational Freedom. *Macromolecules* **2009**, *42*, 3694–3706.
- (34) Nikolou, M.; Dyer, A. L.; Steckler, T. T.; Donoghue, E. P.; Wu, Z.; Heston, N. C.; Rinzler, A. G.; Tanner, D. B.; Reynolds, J. R. Dual-andp-Type Dopable Electrochromic Devices Employing Transparent Carbon Nanotube Electrodes. *Chem. Mater.* **2009**, *21*, 5539–5547.
- (35) Tarkuc, S.; Udum, Y. A.; Toppore, L. Tuning of the neutral state color of the π-conjugated donor–acceptor–donor type polymer from blue to green via changing the donor strength on the polymer. *Polymer* **2009**, *50*, 3458–3464.
- (36) İçli, M.; Pamuk, M.; Algi, F.; Önal, A. M.; Cihaner, A. Donor–Acceptor Polymer Electrochromes with Tunable Colors and Performance. *Chem. Mater.* **2010**, *22*, 4034–4044.
- (37) Özdemir, S.; Balan, A.; Baran, D.; Doğan, Ö.; Toppore, L. A ferrocene functionalized multichromic p and n dopable donor–acceptor–donor type conjugated polymer. *J. Electroanal. Chem.* **2010**, *648*, 184–189.
- (38) Pamuk, M.; Tirkes, S.; Cihaner, A.; Algi, F. A new low-voltage-driven polymeric electrochromic. *Polymer* **2010**, *51*, 62–68.
- (39) Hellström, S.; Cai, T.; Inganäs, O.; Andersson, M. R. Influence of side chains on electrochromic properties of green donor–acceptor–donor polymers. *Electrochim. Acta* **2011**, *56*, 3454–3459.
- (40) Ozdemir, S.; Balan, A.; Baran, D.; Dogan, O.; Toppore, L. Green to highly transmissive switching multicolored electrochromes: Ferrocene pendant group effect on electrochromic properties. *React. Funct. Polym.* **2011**, *71*, 168–174.
- (41) Das, S.; Pati, P. B.; Zade, S. S. Cyclopenta[c]thiophene-Based D–A Conjugated Copolymers: Effect of Heteroatoms (S, Se, and N) of Benzazole Acceptors on the Properties of Polymers. *Macromolecules* **2012**, *45*, 5410–5417.
- (42) Karabiyik, E.; Sefer, E.; Koyuncu, F. B.; Tonga, M.; Ozdemir, E.; Koyuncu, S. Toward Purple-to-Green-to-Transmissive-to-Black Color Switching in Polymeric Electrochrome. *Macromolecules* **2014**, *47*, 8578–8584.
- (43) Xu, Z.; Wang, M.; Zhao, J.; Cui, C.; Fan, W.; Liu, J. Donor–acceptor type neutral green polymers containing 2,3-di(5-methylfuran-2-yl) quinoxaline acceptor and different thiophene donors. *Electrochim. Acta* **2014**, *125*, 241–249.
- (44) Ming, S.; Zhen, S.; Lin, K.; Zhao, L.; Xu, J.; Lu, B. Thiadiazolo[3,4-c]pyridine as an Acceptor toward Fast-Switching Green Donor–Acceptor-Type Electrochromic Polymer with Low Bandgap. *ACS Appl. Mater. Interfaces* **2015**, *7*, 11089–11098.
- (45) Ming, S.; Zhen, S.; Liu, X.; Lin, K.; Liu, H.; Zhao, Y.; Lu, B.; Xu, J. Chalcogenodiazolo[3,4-c]pyridine based donor–acceptor–donor polymers for green and near-infrared electrochromics. *Polym. Chem.* **2015**, *6*, 8248–8258.
- (46) Neo, W. T.; Ong, K. H.; Lin, T. T.; Chua, S. J.; Xu, J. W. Effects of fluorination on the electrochromic performance of benzothiadiazole-based donor–acceptor copolymers. *J. Mater. Chem. C* **2015**, *3*, 5589–5597.
- (47) Salzner, U. Does the Donor–Acceptor Concept Work for Designing Synthetic Metals? 1. Theoretical Investigation of Poly(3-

cyano-3'-hydroxybithiophene). *J. Phys. Chem. B* **2002**, *106*, 9214–9220.

(48) Salzner, U.; Köse, M. E. Does the Donor–Acceptor Concept Work for Designing Synthetic Metals? 2. Theoretical Investigation of Copolymers of 4-(Dicyanomethylene)-4H-cyclopenta[2,1-b:3,4-b']dithiophene and 3,4-(Ethylenedioxy)thiophene. *J. Phys. Chem. B* **2002**, *106*, 9221–9226.

(49) Cinar, M. E.; Ozturk, T. Thienothiophenes, dithienothiophenes, and thienoacenes: syntheses, oligomers, polymers, and properties. *Chem. Rev.* **2015**, *115*, 3036–3140.

(50) Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Tuladhar, P. S.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I. Thieno[3,2-b]thiophene-diketopyrrolopyrrole-containing polymers for high-performance organic field-effect transistors and organic photovoltaic devices. *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275.

(51) Chen, L.; Wu, F. Y.; Deng, Z. Q.; Feng, L. L.; Gu, P. C.; Dong, H. L.; Hu, W. P.; Chen, Y. W. High charge mobility polymers based on a new di(thiophen-2-yl)thieno[3,2-b]thiophene for transistors and solar cells. *Polym. Chem.* **2015**, *6*, 7684–7692.

(52) Chen, Z.; Lee, M. J.; Shahid Ashraf, R.; Gu, Y.; Albert-Seifried, S.; Meedom Nielsen, M.; Schroeder, B.; Anthopoulos, T. D.; Heeney, M.; McCulloch, I.; Sirringhaus, H. High-performance ambipolar diketopyrrolopyrrole-thieno[3,2-b]thiophene copolymer field-effect transistors with balanced hole and electron mobilities. *Adv. Mater.* **2012**, *24*, 647–652.

(53) Wang, L.; Zhang, X. J.; Zhang, J. D.; Tian, H. K.; Lu, Y. F.; Geng, Y. H.; Wang, F. S. Synthesis and characterization of oligo(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene)s: effect of the chain length and end-groups on their optical and charge transport properties. *J. Mater. Chem. C* **2014**, *2*, 9978–9986.

(54) Chao, P. Y.; Wu, H. C.; Lu, C.; Hong, C. W.; Chen, W. C. Biaxially Extended Conjugated Polymers with Thieno[3,2-b]thiophene Building Block for High Performance Field-Effect Transistor Applications. *Macromolecules* **2015**, *48*, 5596–5604.

(55) Turbiez, M.; Frere, P.; Leriche, P.; Mercier, N.; Roncali, J. Poly(3,6-dimethoxy-thieno[3,2-b]thiophene): a possible alternative to poly(3,4-ethylenedioxythiophene) (PEDOT). *Chem. Commun.* **2005**, 1161–1163.

(56) Hergue, N.; Frere, P.; Roncali, J. Efficient synthesis of 3,6-dialkoxythieno[3,2-b]thiophenes as precursors of electrogenerated conjugated polymers. *Org. Biomol. Chem.* **2011**, *9*, 588–595.

(57) Zhao, H.; Liu, C.-Y.; Luo, S.-C.; Zhu, B.; Wang, T.-H.; Hsu, H.-F.; Yu, H.-h. Facile Syntheses of Dioxythiophene-Based Conjugated Polymers by Direct C–H Arylation. *Macromolecules* **2012**, *45*, 7783–7790.

(58) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical considerations for determining absolute frontier orbital energy levels of conjugated polymers for solar cell applications. *Adv. Mater.* **2011**, *23*, 2367–2371.

(59) Grenier, C. R. G. Organic Electronic Devices, Including Organic Photovoltaic Devices, Polymers, and Monomers. U.S. Patent 9,062,152, June 23, 2012.

(60) Fuller, L. S.; Iddon, B.; Smith, K. A. Thienothiophenes. Part 2.1 Synthesis, metallation and bromine→lithium exchange reactions of thieno[3,2-b]thiophene and its polybromo derivatives. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3465–3470.

(61) Beaujuge, P. M.; Vasilyeva, S. V.; Liu, D. Y.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. Structure-Performance Correlations in Spray-Processable Green Dioxythiophene-Benzothiadiazole Donor–Acceptor Polymer Electrochromes. *Chem. Mater.* **2012**, *24*, 255–268.