



# Donor- $\pi$ -bridge-acceptor type polymeric materials with pendant electron-withdrawing groups for electrochromic applications



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## ABSTRACT

A novel donor- $\pi$ -bridge-acceptor copolymer, PBDTTPA-CHO, containing 4-(Bis(4-bromophenyl)-amino)benzaldehyde (TPA-CHO) and 4,8-bis-(2-ethyl- hexyloxy)-oxybenzo-[1,2-b:3,4-b']dithiophene (BDT), was successfully synthesized using Stille coupling polymerization, and the pendant aldehyde group was modified with cyanoacetic acid to synthesize another polymer, PBDTTPA-COOH. Each of these new polymers are soluble in organic solvents and can be cast onto rigid or flexible substrates. The polymers with different electrophilic groups exhibit different electrochromic behaviors, including different colors, driving voltages and transmittances. The polymer film of PBDTTPA-CHO manifests reversible electrochemical oxidation and reduction accompanied by multicolor changes from its yellow neutral state to a highly absorbent green semi-oxidized state and a gray fully oxidized state, its transmittance change at 601 nm is 43%. PBDTTPA-COOH switches between orange and light green. We fabricated and evaluated electrochromic devices using a PBDTTPA layer as the working electrode and vanadium pentoxide as the counter electrode. With the contribution of counter electrodes, devices of both polymers show similar color changes but higher transmittance than their films.

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## 1. Introduction

The  $\pi$ -conjugated electrochromic polymers [1] have several advantages over transition-metal oxides ( $\text{WO}_3$ ,  $\text{IrO}_2$ ) [2], inorganic coordination complexes (Prussian blue) [3], and small organic molecules (viologens and phthalocyanines) [4,5] in the development of both transmissive and reflective electrochromic devices [6]. The  $\pi$ -conjugated electrochromic polymers reveal facile synthetic procedures [7,8] and offer color fine-tuning [9], high coloration efficiencies [10,11], fast switching capabilities [12], and high optical contrast ratios [13].

In recent years,  $\pi$ -conjugated polymer electrochromic devices (PECDs) have received increasing attention and have become candidate materials in a wide range of application areas, including smart windows [14], sunglasses [15], electrochromic mirrors [16], electronic paper [17], and military camouflage [18]. Such polymers which have intra-molecular charge transfers involving donor-acceptor interactions exhibit broad absorption and low band gaps [19], making them useful for many device applications, including light-emitting diodes [20], field-effect transistors [21],

photovoltaic cells [22], and memory devices [23]. A new family of  $\pi$ -conjugated polymers, donor- $\pi$ -bridge-acceptor copolymers, contain main chains as donor units and side chains as acceptor units; they have proven to have high hole mobility and to optimize spectra and energy levels [24]. Recently, benzo[1,2-b:3,4-b']-dithiophene (BDT) has become a well-known unit in conjugated polymers for large planar, conjugated structures, easily forming  $\pi$ - $\pi^*$  stacking and exhibiting respectable hole mobility and little steric hindrance [25]. Many research groups have reported on the utility of triphenylamine (TPA) derivatives, which are electrochromic materials possessing interesting color transitions and competent electrochromic reversibility in the visible and near-infrared (NIR) ranges [26–28]. In addition, the introduction of aldehyde-group-functionalized polymeric materials has received much attention in optoelectronic devices, because the aldehyde group strongly reacts to a variety of nucleophiles, which can improve solubility and electrochromic properties [29–31]. Nie et al. reported that aldehyde-substituted polyindole showed reversible electrochemical processes and stable color change with high coloration efficiency and optical contrast when switched between its neutral (yellow) and oxidized states (green) [32]. However, the design and synthesis of new donor- $\pi$ -bridge-acceptor copolymers based on BDT and TPA still attract significant attention due to their potential applications in electrochromic devices.

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In this article, we describe an approach to synthesizing multicolored conjugated polymers (PBDTTPAs) by combining the monomers BDT and TPA. Here the PBDTTPAs films with different pendant electron-withdrawing groups were characterized in terms of their absorption, fluorescence, and electrochemical properties. To the best of our knowledge, with the introduction of different electron-withdrawing groups into the polyamide side chains, the polymers revealed interesting electrochromic properties which could prove useful for optoelectronic device applications. Characterization of their electrochromic properties showed that these electrochromic materials lack a transmissive state but may prove useful for display-type applications seeking different colors are in different redox states. Applying potential will oxidize the polymers, causing the color to change. We also fabricated PECs, which demonstrated that creating these polymers with different electron-withdrawing groups give them tunable colors and good electrochromic performance.

## 2. Experimental

### 2.1. Materials and characterization

All chemicals used in this work were commercial products and were used as received without further purification unless otherwise noted. Chlorobenzene (CB) and propylene carbonate (PC) were purchased from Sigma-Aldrich Chemical. Tetrahydrofuran (THF) was dried over Na/K alloy in an argon atmosphere and freshly distilled prior to use. All reactions were performed in argon or in a glove box, unless otherwise stated. 4-(Bis(4-bromophenyl)amino)benzaldehyde [33] and 2,6-Bis-(trimethyltin)-4,8-bis-(2-ethylhexyloxy)oxybenz[1,2-b;3,4-b']dithiophene [25] were prepared according to the methods reported in the literatures.

NMR spectra were recorded on a Bruker Avance AV400 instrument. Infrared (IR) spectra were recorded on a Nicolet 8700 Fourier-transform infrared (FT-IR) spectrometer. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped using a Waters 1515 pump and a Waters 2414 differential refractive index detector. The eluent was  $\text{CHCl}_3$  at a flow rate of 1.0 mL/min. Thermogravimetric analyses (TGA) were performed on a Q5000IR. Experiments were carried out on samples of approximately 4 to 6 mg in flowing nitrogen (flow rate = 20  $\text{cm}^3/\text{min}$ ) heated at the rate of 20  $^\circ\text{C}/\text{min}$ . Ultraviolet-visible-NIR (UV-vis-NIR) spectra were obtained on a JASCO V-670 spectrophotometer. Photoluminescence (PL) spectra were measured with a JY Fluorolog-3-Touffluorescence spectrophotometer. Cyclic voltammograms were collected using a CHI 660D electrochemical analyzer with a three-electrode cell using ITO (polymer films area approximately 0.7  $\text{cm} \times 3 \text{ cm}$ ) as the working electrode, a silver wire as the reference electrode (calibrated vs  $\text{Fc}/\text{Fc}^+$ ), and a platinum wire as the counter electrode in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAP)/PC. Spectroelectrochemical analyses were carried out with electrolytic cells using a 1 cm UV-cuvette, ITO as the working electrode, a platinum wire as the counter electrode, and a silver wire for the reference electrode. Photographs of the polymer films and devices were taken with a Canon (PowerShot SX20) digital camera.

### 2.2. Synthesis of $\pi$ -conjugated polymer PBDTTPA-CHO

In a 50 mL two-necked flask, 4-(Bis(4-bromophenyl)amino)benzaldehyde (1.7244 g, 4 mmol), 2,6-Bis-(trimethyltin)-4,8-bis-(2-ethylhexyloxy)oxybenzo-[1,2-b;3,4-b']-dithiophene (2.9852 g, 4 mmol),  $\text{Pd}_2(\text{dba})_3$  (2 mol%), and triphenylphosphine (16 mol%)

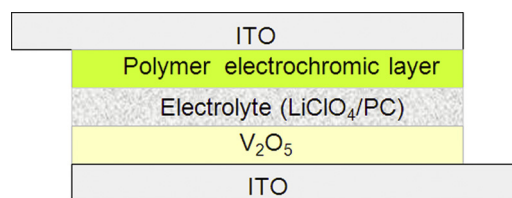


Fig. 1. Structural diagram of PBDTTPA polymer devices.

were degassed with argon before, adding chlorobenzene (5 mL). The mixture was further purged with argon and heated to 120  $^\circ\text{C}$  for 48 h. Then the reactant was cooled to room temperature and the crude polymer was precipitated in methanol, filtered and extracted using a Soxhlet extraction with methanol, hexane, and chloroform in succession. The final product was obtained by precipitating the chloroform solution in methanol as a yellow solid with a yield of 81.6% (235 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 9.82 (s, 1H), 7.72 (d, 2H), 7.66 (d, 4H), 7.21 (d, 4H), 7.19 (s, 2H), 7.14 (d, 2H), 4.17 (d, 2H), 1.35–1.58 (m, 16H), 0.98 (t, 6H), 0.87 (t, 6H). IR (KBr, thin film,  $\text{cm}^{-1}$ ): 1694 (C–H), 2725 (C=O).

### 2.3. Synthesis of $\pi$ -conjugated polymer PBDTTPA-COOH

PBDTTPA-CHO (160 mg, 0.14 mmol of basic units) was completely dissolved in 25 mL pyridine, and then cyanoacetic acid (20 equiv, 464 mg) was added to the solution and heated to 55  $^\circ\text{C}$  for 72 h. After concentrating the solution under reduced pressure, the residue was added dropwise to excess methanol to precipitate the polymer as a red solid with a yield of 85% (94 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.5 (s, 1H), 7.74 (d, 2H), 7.66 (d, 4H), 7.58 (s, 1H), 7.21 (d, 4H), 7.19 (s, 2H), 7.12 (d, 2H), 4.17 (d, 2H), 1.33–1.58 (m, 16H), 0.98 (t, 6H), 0.87 (t, 6H). IR (KBr, thin film,  $\text{cm}^{-1}$ ): 2217 ( $\text{C}\equiv\text{N}$ ), 1710 (C=O).

### 2.4. Preparing working and counter electrodes

The polymer electrochromic films were spin-coated onto the ITO glass (1.5  $\text{cm} \times 2 \text{ cm}$ ) from the chlorobenzene (CB) or N,N-dimethylacetamide (DMAc) solution (10 mg/mL) and thermally treated to attain working electrodes (PBDTTPAs/ITO) that were approximately 100 nm thick. A gel of vanadium pentoxide ( $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) was synthesized using a method reported in our group [34,35].  $\text{V}_2\text{O}_5$  film was electro-deposited onto ITO glass (1.5  $\text{cm} \times 2 \text{ cm}$ ) using the chronoamperometric method (3.65 V for 30 s) in a  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  sol-gel solution and then thermally annealed at a thickness of about 40 nm as the counter electrode.

### 2.5. Fabrication of polymer electrochromic devices

The PECs were assembled by sandwiching an electrolyte (0.1 M  $\text{LiClO}_4/\text{PC}$ ) between PBDTTPAs/ITO glass and  $\text{V}_2\text{O}_5/\text{ITO}$  glass. An epoxy (LOCTITE 9460 Epoxy Adhesive) served as a hermetic barrier to seal the device, which had an effective size of 1  $\times$  1  $\text{cm}^2$ . The assembly process took place in a glove box filled with nitrogen gas and the structural diagram was shown in Fig. 1.

## 3. Results and Discussion

### 3.1. Synthesis and characterization

The synthetic routes leading to the polymer side chains with different electron-withdrawing groups are shown in Scheme 1. The chemical structures of the PBDTTPAs were characterized by  $^1\text{H}$  NMR (Fig. S1). A peak at 9.82 ppm in the  $^1\text{H}$  NMR

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