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Benzothiadiazole, hexylthiophen and alkoxy benzene based solution processable copolymer: Effect of the electron withdrawing substituents (fluorine atoms) on electrochemical, optical and electrochromic properties

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ABSTRACT

4,7-Bis(4-hexyl-5-(trimethylstannane) -2-thienyl) −2,1,3-benzothiadiazole (HTBT) coupled with 2,5-bis (decyloxy)-1,4-dibromobenzene to afford the donor-π-bridge-donor-acceptor conjugated poly (4,7-bis (4-hexyl-2-thienyl) −2,1,3-benzothiadiazole-co-p-didecyloxybenzene) (PTBTB). Further, copolymerization of fluorine-functionalized HTBT moiety with alkoxyl benzene π-bridge using Stille crossing-coupling reaction yield PTBTB-F. The optical, electrochemical, fluorescent, spectroelectrochemical and electrochromic switching properties of two polymers with different acceptors are studied in detail. Both polymers exhibit excellent solubility in conventional organic solvents, high thermal stability and favorable fluorescence properties. The combination of a strong electron withdrawing pendant group (fluorine atoms) with benzothiadiazole (BT) backbone significantly influences the electrochemical redox, optical and electrochromic behaviors of conducting polymers. The introduction of fluorine atoms to BT lead to a higher oxidation onset potential, but an improved electrochemical n-doping process. The optical band gaps (E_g) of PTBTB and PTBTB-F films are calculated to be 2.02 eV and 1.91 eV, respectively. PTBTB and PTBTB-F films exhibited obvious and reversible color switching between their neutral and oxidized states with high optical contrasts as well as favorable response times, making the polymers unique candidates for flexible organic electrochromic device applications.

1. Introduction

Organic conjugated oligomers and polymers as kinds of important semiconductor materials have attracted great attention in the field of light emitting diodes [1], organic photovoltaic devices [2], emission transistors [3], electrochromic devices [4–7] and sensors [8,9]. Optimizing the performance of these devices are the major challenges, now a large number of studies have shown that electronic and structural features can be manipulated to improve the material's capabilities (e.g., desired HOMO/LUMO energy levels, low band gap, electron or hole mobility, processability and stability.). For electrochromic polymers (ECPs), the drive is to design and synthesize electrochromic materials with low driving voltage, high optical contrast, high mobility as well as excellent ambient and operating stability. Exploiting liquid crystal properties or incorporating inherently “flat” molecular structure, such as benzene or thiophene derivatives, which was beneficial to intramolecular charge transport and some other optic-electronic properties, particularly through π-stacking [10].

Recently efforts have focused on D-A type conjugated polymers. Hybrid recombination between donor and acceptor unit lead to the polymer with the higher HOMO level and the lower LOMO level, thus resulting in a lower band gap. The donor and acceptor units are alternately arranged and extended indefinitely along the backbone, and the main chain of the molecule exhibits a superlattice structure similar to inorganic semiconductor [11]. Besides, the molecular structure and properties of the polymer can be modified. Change of the monomer repeat unit by considering its electron withdrawing and donating strengths or substitution of functional groups onto the polymer backbone could be used to control the magnitude of the band gap, and further to regulate the color of neutral state and other electrochromic properties.

Fluorinated, π-conjugated polymers are of great interest in the electro-optic field. Incorporating fluorine onto electron-withdrawing groups, which has been proven to be effective in lowering the HOMO

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and LOMO energy levels due to the high pulling electronegativity of F atom [12]. The fluorine substituents have great influence on the doping properties. For p-doping, introduction of electronegative fluorine caused significant reduction of the doping density, which is likely to increase the energy barrier for p-doping and make it difficult for electrons to remove from the π-conjugated system. As a result, the doping potential shifted to more positive values, and the increase in oxidation potential usually associated with the increase in the number of fluorine atoms [13]. But for n-doping, the increased electronegativity associated with the fluorine groups could result in a lower energy barrier for n-doping, effectively inhibit the degradation reactions of the unstable radical anion at negative voltages with oxygen and trace water in the electrolyte, and improve the stability during the n-doping process. Highly fluorinated systems, such as tetradecafluorosexithiophene [14], perfluoropentacene [15] and perfluoroalkyl end-capped oligothiophenes [16,17] have been successfully prepared and considered to be good n-type semiconductors. Besides, substitution of thiophenes with fluorophenyl group [12,13] or its derivatives [18] has also been shown to reveal improved n-doping property even under ambient conditions. Further, the introduction of fluorine atoms could not cause deleterious steric effects, on the contrary, the noncovalent interactions between F atoms and the components on neighboring thiophene rings can facilitate planarization of the backbone structure and hence promote intramolecular charge transfer [19].

To investigate the effect of fluorine atoms, we incorporated two F atoms onto the 4,8-position of benzothiadiazole (BT) unit to synthesize the difluoro-substituted BT units as acceptor, and used 4-hexylthiophene as donor unit and 2,5-didecyloxybenzene as π-bridge to build the backbone of the target donor-π-bridge-donor-acceptor (D-π-D-A) copolymers. D-π-D-A type polymers, as a new family of π-conjugated polymers, have enhanced planar structures, high carrier transport efficiencies and optimized band gaps, which should be paid attention by researchers. Xu group has synthesized several novel D-π-A polymers [20,21] as EC materials in the last few years, yet the shortcomings, such as low transmittance change, unconspicuous n-doping characteristic or slow response speed, need to be further resolved. So, substitution of fluorine atom onto the BT unit to build the new similar D-π-D-A system is expected to obtain the desired EC materials with the stable p- and n-doping process, low band gap, favorable fluorescent and electrochromic properties, together with excellent solubility. The synthetic route of PTBTB and PTBTB-F is shown in Scheme 1. The structure, thermogravimetry, fluorescence, electrochemical, optical and electrochromic properties of target polymers are characterized in detail.

2. Experimental

2.1. Materials and instrumentation

All chemicals used in this study were purchased from commercial sources (e.g., Aladdin Chemical, Sinopharm Chemical Reagent and Aldrich Chemical.) and used as received without further purification. 4,7-Bis(4-hexyl-5-(trimethylstannane) -2-thienyl) −2,1,3-benzothiadiazole (HTBT, > 98%) and 5,6-difluoro-4,7-Bis(4-hexyl-5-(trimethylstannane) -2-thienyl) −2,1,3-benzothiadiazole (HTBT-F, > 98%) were from Derthon Optoelectronic Materials Science Technology Co., Ltd. (Shenzhen, China). 2,5-Didecyloxy-1,4-dibromobenzene was prepared in exactly the same way as the previous work [22].

^{1}H NMR spectra were measured on Varian AMX 400 with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Average molecular weights and molecular weight distributions were detected by Waters 515 HPLC Pump using HPLC-grade THF as eluent and polystyrene (PS) as standard. The content of each element persisted in the polymer was determined by Vario EL III. TGA were performed in pure nitrogen flow with a Netzsch STA 449C thermogravimetric analyzer with the heating rate of 10 °C/min. The fluorescence spectra were recorded on an F-4500 fluorescence spectrophotometer, where the polymers were dissolved in $CHCl_3$. The light absorption spectra of the polymers in solution or in films were measured with a Varian Cary 5000 UV-vis-NIR spectrophotometer. Cyclic voltammetry, redox reversibility and stability were carried out using a CHI 760C electrochemical analyzer with a three-electrode cell using polymer film coated ITO glasses (the covering area was approximate $1.0 \times 2.0\ cm^2$) as the working electrode, a silver wire (0.02 V *vs.* SCE.) and a platinum wire as the pseudo-reference electrode and the counter electrode, respectively. The three-electrode system was fixed and placed in a colorimetric cell filled with 0.2 M $TBAPF_6$/ACN electrolyte. Spectroelectrochemical experiments were carried out using a Varian Cary 5000 UV-Vis-NIR spectrophotometer connected to the above electrochemical measurement system, as well as colorimetry analysis. Electrochromic film layers were made by spraying the chloroform solution of polymers onto ITO glass, and dried under nitrogen before use. All the photographs in the article were taken with a canon Power Shot A3000 IS Camera.

2.2. Synthesis of polymers (PTBTB and PTBTB-F)

HTBT (**4**) and HTBT-F (**5**) were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd, 2,5-didecyloxy-1,4-dibromobenzene (**3**) was synthesized according to the methods from literature [22].

Compound **4** or **5** (1.3 mmol), 2,5-didecyloxy-1,4-dibromobenzene (1.3 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 mmol) and 100 mL dry toluene were successively added into a 250 mL single-necked flask in a short time, then heated at 110 °C and stirred for 48 h in argon. After reaction finished, the solution was naturally cooled to room temperature, and then vacuum rotatory evaporator was used for the concentration. By adding appropriate amount of methanol into the concentrate, crude product that was readily precipitated from the solution. The precipitate was filtered, and repeatedly reflux extracted by Soxhlet extractor to give final products, in which methanol and acetone were used as medium respectively. After vacuum drying, both polymers were collected as deep red solids.

PTBTB (Yield, 75.5%). ^{1}H NMR($CDCl_3$, 400 MHz, ppm): δ = 8.08 (s, 2H, ArH), 7.91 (s, 2H, ArH), 7.05 (s, 2H), 3.97 (t, 4H,–O–CH_2), 2.69 (t, 4H, SF-CH_2), 1.72 (m, 4H,–O–CH_2–CH_2), 1.18–1.38 (m, 44H, –CH_2), 0.84 (t, 12H, –CH_3). (see Supplementary Materials Fig. S1a). GPC: M_n = 32.5 kDa, PDI = 1.10. Elem. Anal. Calcd. For $C_{52}H_{74}N_2O_2S_3$: C, 72.85%; H, 8.93%; N, 3.27%; O, 3.73%; S, 11.22%. Found: C, 72.41%; H, 9.03%; N, 3.32%; O, 3.80%; S, 11.44%.

PTBTB-F (Yield, 73.9%). ^{1}H NMR($CDCl_3$, 400 MHz, ppm): δ = 8.23 (s, 2H, ArH), 7.06 (s, 2H), 3.95 (t, 4H,–O–CH_2), 2.70 (t, 4H, SF-CH_2), 1.70 (m, 4H,–O–CH_2–CH_2), 1.17–1.36 (m, 44H, –CH_2), 0.84 (t, 12H, –CH_3). (see Supplementary Materials Fig. S1b). GPC: M_n = 40.3 kDa, PDI = 1.03. Elem. Anal. Calcd. For $C_{52}H_{72}F_2N_2O_2S_3$: C, 69.91%; H, 8.35%; F, 4.25%; N, 3.14%; O, 3.58%; S, 10.77%. Found: C, 70.28%; H, 8.53%; F, 4.06%; N, 3.07%; O, 3.79%; S, 10.27%.

In addition, further structure characterization of the polymers were carried out by FT-IR and XPS as well as thermal stability by TGA, which were displayed in Supporting Information in detail.

3. Results and discussion

3.1. Electrochemical properties

The electrochemical properties of two polymers films which were spray coated on ITO/glass, were investigated by cyclic voltammetry. The resulting single-cycle CV curves at a scan rate of 100 mV s^{-1} with the potentials range between −2.0 V and 1.8 V for PTBTB, and between −2.0 V and 2.0 V for PTBTB-F can be seen in Fig. 1, in which two polymers showed similar oxidation and reduction behaviors with reversible redox peaks. PTBTB and PTBTB-F in thin films exhibited the unconspicuous oxidation peaks appeared at 1.32 V and 1.50 V, and also the broad reduction peaks with maximum reduction potential of 0.80 V