



Multichromic and soluble conjugated polymers containing thiazolothiazole unit for electrochromic applications

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ARTICLE INFO

Article history:

Received 28 November 2014

Accepted 22 December 2014

Available online 29 December 2014

Keywords:

Multichromism
Conducting polymers
Thiazolothiazole
Benzotriazole
Electrochromism

ABSTRACT

Here we report the preparation of two solution processible polymers; poly(2-(5-(2-(2-octyldecyl)-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole) (PBTTz) and poly(2-(5-(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole) (PFTTz) which are multichromic electroactive polymers. PBTTz was synthesized via Stille coupling polymerization whereas PFTTz was synthesized via Suzuki coupling polymerization. Both polymers were coated on ITO slides and their electrochromic properties were investigated. The results of the PBTTz were also compared with a previously published polymer to investigate the linear and branched alkyl chain effect. The polymers were compared through their optical properties and UV–Vis spectroelectrochemistry.

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1. Introduction

Conjugated polymers are indispensable materials for organic electronics due to their superior advantages over inorganic counterparts. Consequently, it is a special topic having special interest from quite a number of researchers all over the world and published several works on their properties and application areas since their discovery [1–9]. Electrochromism is one of these application areas due to its exciting potential application fields such as flexible displays [10] and military camouflage [11].

After well understanding of polymer engineering in structure modification, alternating donor and acceptor

group containing conjugated polymers attracted great attention. One of the most desirable properties of these types of polymers is their low band gap, which is necessary for applications especially in photovoltaics. Narrow band gap is also important for electrochromism since it makes easier to switch between the two extreme states of the polymers using small potential differences. That is why, recent effort on conjugated polymers are focused on arranging energy levels of the resulting polymer which is the characteristic that should be determined before further investigation.

Such low band gap polymers with broad long wavelength absorbances, where the photon flux is maximum, are crucial for organic photovoltaics. Using both donor and acceptor units in the same chain alternatively may result in ambipolarity which is essential for organic semiconductors for the development of integrated micro-electronic organic circuits. Additionally, they have several accessible energy states between HOMO–LUMO levels,

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which make the charge transport easy. Small applied potential differences enable the control of the hue and shade of the polymer color. Moreover, tunable energy levels make possible to control the absorption and emission wavelengths of the polymers for use in organic light emitting diodes.

In the class of organic semiconductors designed and synthesized so far, fluorene and thiazolothiazole containing copolymers come forth as essential materials due to their high chemical stability, exclusive electronic and optical properties, and the possibility of introducing appropriate side-groups on the backbone. One of the biggest advantages of the polyfluorenes (PFs) is their tunability of C-9 position. Alkyl chain substitution to the fluorene molecule enabled to obtain a large number of soluble conducting polymers with various physical and chemical properties [12–14]. Additionally, fluorene containing polymers show good film forming and hole transporting properties [15].

In our previous study we examined the effect of thiazolothiazole containing polymer on electrochromism with altered electron donor spacers; thiophene and furan [16]. In this report, the effect of fluorene and benzotriazole on electrochromic behavior of thiazolothiazole containing polymers was firstly discussed in terms of their electrochromic and optical properties. Additionally, the results of the poly[2-(5-(2-decyl-2Hbenzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)-5-(thiophen-2-yl)thiazolo[5,4-d]thiazole] (BTzTh) were also compared with that of PBTTz to have a better understanding of branched chain effect on optoelectronic properties.

2. Results and discussion

2.1. Synthesis and thermal properties

PBTTz was prepared using Stille coupling while PFTTz was prepared via Suzuki coupling reactions as shown in Scheme 1. All monomers were synthesized except for diocetyl-substituted fluorene, which was purchased from commercial sources. Previously published procedures were used for the preparation of alkylated benzotriazole unit as well as brominated (for PFTTz) and stannylated (for PBTTz) thiazolothiazole derivatives. After preparation of polymers they were firstly precipitated in cold ethanol and purified using Soxhlett extraction with ethanol, hexane and acetone respectively and polymers were collected using dichloromethane. For further purification both polymers were recrystallized. They firstly dissolved in minimum amount of dichloromethane and poured into cold ethanol. The molecular weights and the polydispersity indices of the polymers were characterized with gel-permeation chromatography (GPC) with polypropylene glycol universal calibration method. Number average molecular weights of the polymers were found as 12,370 and 21,885 g mol⁻¹ for PFTTz and PBTTz with associated M_w values of 18,025 and 21,932 g mol⁻¹, respectively.

Substituted alkyl chains are significant units to obtain a soluble polymer. However, alkyl chain grafted polymers usually have low decomposition temperatures. The thermal

properties of the polymers were investigated to explore their decomposition temperatures and figure out if they can resist during optoelectronic device construction. Thermal gravimetry analysis (TGA) (Fig. 1) results revealed that both polymers are thermally stable with decomposition temperatures of (5% weight loss) 274 °C and 291 °C for PFTTz and PBTTz, respectively. Branched chain substituted benzotriazole containing polymer showed higher thermal resistivity since it lost its 10% by weight at 360 °C whereas PFTTz revealed the same at 290 °C. Additionally, 50% residual weights for polymers recorded at 430 °C for PFTTz and at 720 °C for PBTTz. It can be concluded that, both PFTTz and PBTTz are suitable polymers for organic electronic device constructions. GPC and TGA results of the polymers are listed in Table 1.

2.2. Electrochemistry

In order to investigate the electron transfer of the polymer films, the redox potentials were measured by cyclic voltammetry. Polymers, PFTTz and PBTTz, were dissolved in DCM (10 mg/mL) and spray casted on ITO coated glass slides, which were used as working electrodes in characterization. The CV curves of the two polymers are shown in Fig. 2 in the potential range of 0–1.7 V for PFTTz and 0–1.5 V for PBTTz versus pseudo reference silver wire. All CV measurements of the polymers were determined using platinum wire as the counter electrode in 0.1 M TBAPF₆/acetonitrile (ACN). Anodic scan doping/dedoping potential couple was detected for PFTTz as 1.38 V and 0.95 V at a scan rate of 100 mV/s. Similar redox potentials were recorded for PBTTz as 1.35 V/1.10 V. Same anodic doping potentials reveal that oxidation of the polymers are highly dependent on the electron rich thiophene unit [17].

Energy levels of the conducting polymers play a crucial role in their applications. To calculate the HOMO levels of the polymers, the onset doping potentials of the polymers were determined from the anodic region of the cyclic voltammogram. Onset oxidation potentials of the polymers were determined as 0.99 V for both polymers as their E_{ox} potentials. Eventually, they have same HOMO level as -5.34 eV which was calculated using the empirical formula $E_{\text{HOMO}} = -(E_{\text{ox,ONSET}} - 0.35) - 4.7$ eV taking SCE as 4.7 eV versus vacuum [18] and Fc/Fc⁺ as 0.35 V versus SCE [19].

LUMO levels of the polymers were calculated subtracting the optical band-gap values from the HOMO energy levels of the polymers, which are listed in Table 2. LUMO levels are found as -3.19 eV for PFTTz and -3.55 eV for PBTTz. From these results it can be concluded that presence of the benzotriazole unit, which is more electron deficient than fluorine, lowers the LUMO energy level and hence the band gap as expected [20].

In Table 2 the electrochemical results of the previously published polymer (BTzTh), were also inserted to discuss the effect of the linear and the branched alkyl chain. The similarity of the HOMO energy levels is in consistence with the similarity of the oxidation potentials. It is concluded that the substitution of linear or branched alkyl chain into the polymer backbone has almost no effect on the electrochemical behavior of the polymers [21].

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