



Effect of ring size on benzimidazole unit on electro-optical properties of donor–acceptor–donor type monomers and their polymers



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ABSTRACT

A new series of fluorescent donor–acceptor–donor (D–A–D) type monomers based on benzimidazole acceptor unit bearing various cycloalkane appendages, called 4,7-di-2,3-dihydrothieno[3,4-*b*] [1,4]dioxin-5-ylspiro[benzimidazole-2,1'-cyclopentane] (E5E), 4,7-di-2,3-dihydrothieno[3,4-*b*] [1,4]dioxin-5-ylspiro[benzimidazole-2,1'-cyclohexane] (E6E) and 4,7-di-2-thienylspiro[benzimidazole-2,1'-cyclohexane] (T6T), were synthesized and polymerized via potentiostatic and potentiodynamic methods. The effect of ring size on benzimidazole unit and the kind of donor moiety in D–A–D system on the electrochemical and optical properties have been studied systematically. The optical studies showed that the ring size of the benzimidazole unit has no effect on the absorbance and fluorescence properties, whereas the oxidation potential of the E5E, E6E and T6T monomers varied with respect to both the ring size and the kind of donor unit: 0.89 V, 0.83 V and 1.22 V vs Ag/AgCl, respectively. All polymers have ambipolar (p- and n-type doping) and electrochromic properties. While the polymer films PE5E and PE6E are green at neutral state and transparent at oxidized state, the polymer PT6T has no appreciable color change between its neutral and oxidized states. The polymers PE5E and PE6E bearing 3,4-ethylenedioxythiophene unit as donor units exhibited lower band gap values (1.21 eV and 1.18 eV, respectively) than the polymer PT6T (1.53 eV). When compared to PT6T, PE5E and PE6E polymers are more stable under ambient condition. While PE5E retained 76% of its electroactivity after 4000 cycles, PE6E has 65% of its electroactivity after 2000 cycles.

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1. Introduction

Conjugated polymers continue to be a primary focus of optical and electronic materials to be used in many devices like light emitting diodes [1,2], photovoltaics [3,4], electrochromic devices [5–7] and field effect transistors [8,9]. Electrochromic polymers have a lot of applications because of their various colors in one material at different redox states (multichromism), fast switching times, high optical contrast and coloration efficiencies from the same material [10–12].

One of the major benefits of the conjugated polymers is to improve their electrochemical and optical properties by structural modifications. This approach leads to low oxidation potentials for monomers, fast switching times and low band gaps for the resulting polymers. In order to get polymers with small band gap, for example, electron donor–acceptor–donor (D–A–D) system is one of the most effective processes [13–21]. D–A–D approach is established on the connection of two donor units to one acceptor unit. This design leads to a small band gap and also a larger band-size than the related homopolymers [22,23]. One of the main contributions of this approach is that the monomer structure can be modified. This gives an opportunity to researchers

to control the size of the band gap with appropriate various donor and acceptor units by considering its electron contribution and withdrawing strengths. Thus, the conjugated polymers with donor and acceptor moieties in the main chain have been claimed to have the lowest band gap for a combination with the electronegativity difference between donor and acceptor units [24].

To decrease the band gap and to change the electronic and optical properties by small structural modifications, many different conjugated polymers bearing various acceptor units such as benzimidazole [25], benzoselenadiazole [14], benzoxadiazole [26], benzotriazole [27] and benzothiadiazole [28] have been synthesized and characterized.

Benzimidazole is one of the acceptor units used in D–A–D type polymers having wide absorption spectra. Also, it has been proved that the drugs based benzimidazole have high thermal stability when compared their analogues [29]. Also, benzimidazoles have high transporting ability for electrons due to electron withdrawing imine (CN) bonds in their heterocyclic structures [25].

In literature, the first pioneering examples of benzimidazole based polymers were reported by Yamamoto et al. [30,31]. The polymers are electrochemically active and have ambipolar properties (p- and n-doping processes). Also, the polymers exhibited electrochromic properties: ochre yellow at the neutral state, dark brown at the oxidized state and reddish brown at the reduced state.

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After these studies, the electrochemical and optical properties of benzimidazole based conjugated polymers [30,32–38] were studied in detail and the distinct properties of the polymers make them promising candidates for solar cells [39–45] and electrochromic device applications [36].

On the other hand, functionality ability of the benzimidazole unit is one of the important advantages over other acceptor units. Any group can be substituted on the carbon atom of the benzimidazole ring. Under the light of this advantage, Toppare and his colleagues synthesized a new series of substituted benzimidazole based conjugated polymers in order to understand the effect of substituent on the properties of the corresponding polymers [25]. Imidazole ring was functionalized with phenyl, 3,4-ethylenedioxythiophene (EDOT) and ferrocene. They reported that pendant groups dramatically affected the optical properties of the related polymers.

By the inspiration of these results, Uzun et al. tried to synthesize a novel polymer to construct a biomolecule immobilization matrix [46]. In order to achieve this aim, a benzaldehyde functionalized benzimidazole based conjugated polymer was prepared and performed its biosensor application. The prepared biosensor worked with high accuracy values when it was tested in human real blood serum samples.

It is well-known that when compared to other familiar acceptor units, benzimidazole unit has great advantages over them since it has ability of functionalization from its 2-carbon position. Therefore, functionalized benzimidazoles in D–A–D system can tune the electrochemical and optical properties of the corresponding polymers. This approach can open up new doors for benzimidazole based polymers to use in electro-optical applications. Under the light of this approach, in this study, by using the functionality ability of the benzimidazole unit, the effect of ring size on benzimidazole unit on the optical and electrochemical properties of the monomers (E5E, E6E and T6T) and their corresponding polymers (PE5E, PE6E and PT6T, respectively) will be investigated systematically (Scheme 1). In order to achieve this aim, the monomers will be synthesized by using D–A–D approach. Two acceptor units with various ring sizes (cyclopentane and cyclohexane) and two donor units called thiophene and EDOT will be used to synthesize monomers. Therefore, it would be possible to study the effect of acceptor and donor units on the properties of the obtained polymers.

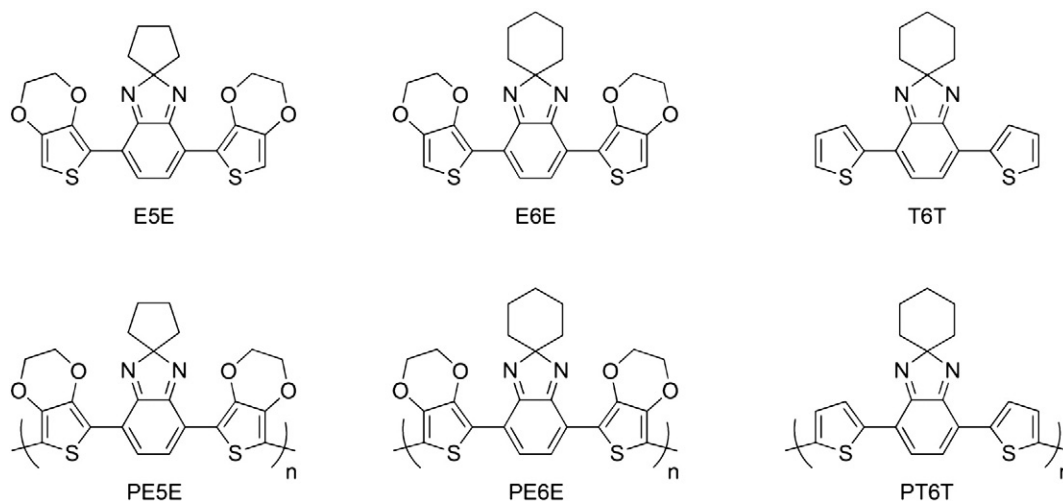
2. Experimental

All chemicals were purchased from Sigma-Aldrich Chemical and used as received unless otherwise noted. For electrochemical and optical studies, dichloromethane, toluene and acetonitrile were freshly

distilled over CaH_2 under nitrogen atmosphere. Ethyl alcohol was distilled over iodine and magnesium wire under argon atmosphere. The molecular sieves (4 Å) were activated at 250 °C for several hours.

^1H and ^{13}C NMR spectra of obtained monomers were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with CDCl_3 and chemical shifts were given relative to tetramethylsilane as the internal standard. Chemical shifts are reported in terms of ppm and that of CDCl_3 is 7.26 ppm. The spectrum of high resolution mass spectrometry was recorded on A Water, Synapt HRMS. Photographs of the polymer films were taken using a Nikon (D600) digital camera. Colorimetric measurements were recorded on Specord S600 (standard illuminator D65, field of width 10° observer) and color space was given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references for colorimetric measurements.

Cyclic voltammetry and electrolysis were performed by using a Gamry PCI4/300 and Gamry Reference 600 potentiostat–galvanostat. The electro-optical spectra were monitored on a Specord S600 spectrometer. The optoelectrochemical spectra of the films were recorded in-situ under applied different potentials. Also, a square wave potential method was used to investigate the ability of switching of the polymer films at various redox states. Tetrabutylammonium hexafluorophosphate (TBAH) was used as an electrolyte. Redox properties and polymerization were performed in an electrolyte solution of 0.1 M TBAH dissolved in dichloromethane, whereas electrochemical and optical properties of the polymer were studied in acetonitrile containing 0.1 M TBAH. In a three-electrode system, platinum disc (0.03 cm^2) and platinum wire electrodes were used as working and counter electrodes, respectively. A Ag/AgCl electrode in 3 M NaCl(aq) solution was used as a reference electrode calibrated externally using 0.36 mM solution of ferrocenium/ferrocene (Fc^+/Fc) redox couple in 0.1 M TBAH/ CH_2Cl_2 solution. The oxidation onset potential of Fc^+/Fc was found as 0.38 V vs Ag/AgCl. Electrochemically obtained polymer films were synthesized by both repetitive cycling and constant potential electrolysis. After electropolymerization, the polymer coated on the working electrode was washed with CH_2Cl_2 to remove the unreacted monomers and oligomeric species. Then, the polymer film was broken by switching several times between its redox states to get repeatable results for electrochemical and optical studies. Optical properties were investigated in situ by using an indium–tin oxide (ITO, Delta. Tech. 8–12 Ω , $0.7 \times 5.0 \text{ cm}^2$) electrode as a working electrode in a UV cuvette. A platinum (Pt) and a silver (Ag) wire were used as a counter and a pseudo-reference electrode, respectively.



Scheme 1. Chemical structures of benzimidazole based monomers and their polymers.

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