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Multichromic polymers of benzotriazole derivatives: Effect of benzyl substitution

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ABSTRACT

Two electroactive monomers 1-benzyl-4,7-di(thiophen-2-yl))-2H-benzo[d][1,2,3]triazole (BBTA) and 2-benzyl-4,7-di(thiophen-2-yl))-2H-benzo[d][1,2,3]triazole (BBTS) were synthesized with satisfactory yields. The effect of substitution site on electrochemical and optical properties was investigated with cyclic voltammetry and spectroelectrochemical studies. Results showed that position of pendant group alters the electronic structure of the resulting polymer causing different optical and electrochemical behaviors. Symmetrically positioned benzyl unit on benzotriazole moiety resulted in a neutral state red polymer, PBBTS, having multi-colored property in its different oxidized and reduced states. Its analogue PBBTA exhibited maximum absorption at 390 nm in its neutral state and also revealed multicolored electrochromic property upon stepwise oxidation. Very different optical band gap values were calculated: 1.55 eV and 2.25 eV for PBBTS and PBBTA, respectively.

1. Introduction

Conjugated polymers are great nominees for plastic electronics due to the fact that the structural modifications on this class of materials enable color-tuning by adjusting band gap [1], high optical contrasts [2], fast switching times [3] and processability [4]. Hence, design of electroactive monomers is a key tool to determine the electrochemical and optical properties of the final conducting polymers. Donor–acceptor (DA) approach is commonly claimed to be a useful method to synthesize low band gap polymers which have multiple red-ox states at low potentials [5,6].

Electrochromic polymers (ECPs) reveal reversible color change upon appropriate external bias. Since energy gap between HOMO and LUMO levels lies in the visible region, most of conducting polymers are colored in their neutral states. Redox switching results in new optical absorption bands due to electronic charge transport and incorporation of counter ions into polymer chains. Upon oxidation or reduction conducting polymers are considered as doped with counter ions and their structures change into a delocalized π-electron band structure [7]. This structural change results in formation of new optical absorption bands in the lower energy part of the spectrum. Rarely, when more than two redox states, absorbing in the visible, are electrochemically accessible, the ECP exhibits multicolored electrochromism [8]. This is a consequence of high energy absorption of polaronic states which also tails into the visible region. It is important to remark that although all conjugated polymers have potential to exhibit two colors, only a few show multi-colored states.

In the context of color tuning concept, DAD type monomers with electropolymerizable heterocyclics at both sides of the A unit symmetrically were studied quite extensively up to date and effects of different D and A groups were investigated. Several examples of electron deficient groups coupled with electron donating groups such as ethylenedioxythiophene (EDOT) and thiophene (Th) revealed either better optical contrast, lower band gap and switching time or both p-type and n-type doping compared to pristine polymers polythiophene (PTh) and PEDOT [9–13]. Recently, synthesis and optoelectronic properties of new DAD type polymers bearing benzotriazole (BTz) as the A unit were reported by our group [14,15]. These BTz based DAD type polymers were seen to be ambipolar due to the electron accepting nature of imine containing triazole ring which also provides a possible alkylation position to improve solubility. BTz containing polymers were also studied by other research groups for solar cell and electrochromic applications recently [16–18]. Poly(2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole) (PTBT) as an example of BTz based polymers revealed multicolored electrochromism with the ability to switch between all RGB colors, black and transmissive states

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which make this polymer unique among numerous electrochromic conjugated polymers [15].

Here we report electrochemical and optical properties of poly(1-benzyl-4,7-di(thiophen-2-yl))-2H-benzo[d][1,2,3]triazole) (PBBTA) and poly(2-benzyl-4,7-di(thiophen-2-yl))-2H-benzo[d][1,2,3]triazole) (PBBTS). Polymers were synthesized electrochemically from their corresponding monomers. Reported spectroelectrochemical results showed that both polymers are multicolored electrochromics with low working potential range. Structural and substitutional effects on electrochromic properties of polymers were highlighted in detail.

2. Experimental

2.1. General

All chemicals were purchased from Aldrich except anhydrous tetrahydrofuran (THF) which was purchased from Acros. 4,7-Dibromobenzo[1,2,5]thiadiazole [19], 3,6-dibromo-1,2-phenylenediamine [20], tributyl(thiophen-2-yl)stannane [21], 4,6-dibromo-1,2,3-benzotriazole (**1**) [22] were synthesized according to previously described methods. Electropolymerization was performed with a Voltalab 50 potentiostat in a three electrode cell consisting of platinum wire or indium tin oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode, and an Ag wire as the pseudo reference electrode. Electrodeposition was performed in a 0.1 M solution of tetrabutylammonium hexafluoroborate ($TBAPF_6$) in acetonitrile–dichloromethane mixture (95:5, v/v). UV–vis–NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 spectrometer and chemical shifts were given relative to tetramethylsilane (TMS). Mass analysis was carried out on a Bruker time-of-flight (TOF) mass spectrometer with an electron impact ionization source.

2.2. Synthesis

1-Benzyl-4,7-dibromo-1H-benzo[d][1,2,3]triazole (**2**) and *2-Benzyl-4,7-dibromo-1H-benzo[d][1,2,3]triazole* (**3**): Benzyl bromide (575 mg, 3.4 mmol) was added to a solution of 4,6-dibromo-1,2,3-benzotriazole (500 mg, 1.8 mmol), potassium *t*-butoxide (224 mg, 2 mmol) in ethanol (20 mL) and the reaction mixture was stirred for 12 h at room temperature. The reaction was monitored by thin layer chromatography (TLC). After removal of the solvent by evaporation, the residue was dissolved in CH_2Cl_2 and washed with water and then with brine. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2:hexane = 1:1) to obtain **2** (R_f, 0.23) as a light pink solid in 47% yield (308 mg) and **3** (R_f, 0.43) as a white solid in 28% yield (187 mg). Overall yield is 75%. **2**: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39 (d, 1H, $J = 8$ Hz), 7.33 (d, 1H, $J = 8$ Hz), 7.24 (m, 2H), 7.19 (s, 1H), 7.13 (m, 2H), 6.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 51.71, 100.76, 112.10, 126.00, 127.07, 127.23, 127.83, 130.99, 131.32, 134.75, 145.05. MS (m/z): 367 [M^+]. **3**: ^{1}H (400 MHz, $CDCl_3$, TMS) δ 7.41 (s, 1H), 7.40 (s, 1H), 7.30–7.26 (m, 4H), 7.19 (s, 1H), 5.86 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 59.41, 108.61, 126.94, 127.34, 127.39, 128.23, 132.38, 142.57. MS (m/z): 367 [M^+].

1-Benzyl-4,7-di(thiophen-2-yl))-2H-benzo[d][1,2,3]triazole (BBTA): 1-Benzyl-4,7-dibromo-1H-benzo[d][1,2,3]triazole (**2**) (0.233 g, 0.635 mmol) and tributyl(thiophen-2-yl)stannane (1.185 g, 3.175 mmol) were dissolved in dry THF (50 mL). The solution was purged with argon for 30 min and dichlorobis(triphenylphosphine)-palladium(II) (60 mg, 0.085 mmol) was added at room temperature under an argon atmosphere. The mixture was refluxed for 48 h, cooled, and concentrated on the rotary evaporator. The residue was subjected to column chromatography (hexane/CH_2Cl_2, 1:1, R_f, 0.43) to afford an yellow solid (0.168 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS)) δ 8.27 (d, 1H, $J = 3.7$ Hz), 7.51 (d, 1H, $J = 7.5$ Hz), 7.36 (d, 1H, $J = 5.1$ Hz), 7.32 (d, 1H, $J = 5.1$ Hz), 7.27 (d, 1H, $J = 7.5$ Hz), 7.17–7.15 (m, 1H), 7.13-6.98 (m, 5H), 6.80 (d, 1H, $J = 3.5$ Hz), 6.55 (d, 1H, $J = 6.6$ Hz), 5.66 (s, 2H) ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 52.03, 115.93, 119.44, 125.61, 125.66, 125.71, 125.78, 126.08, 126.67, 127.22, 127.37, 127.48, 129.91, 130.75, 134.63, 136.39, 137.77, 142.59. MS (m/z): 373.5 [M^+].

2-Benzyl-4,7-di(thiophen-2-yl))-2H-benzo[d][1,2,3]triazole (BBTS): 2-Benzyl-4,7-dibromo-1H-benzo[d][1,2,3]triazole (**3**) (120 mg, 0.327 mmol) and tributyl(thiophen-2-yl)stannane (610 mg, 1.63 mmol) were dissolved in dry THF (40 mL). The solution was purged with argon for 30 min and dichlorobis(triphenylphosphine)-palladium(II) (60 mg, 0.085 mmol) was added at room temperature under an argon atmosphere. The mixture was refluxed for 15 h, cooled, and concentrated on the rotary evaporator. The residue was subjected to column chromatography (hexane/$CHCl_3$, 2:1, R_f, 0.35) to afford an bright yellow solid (118 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (s, 2H), 7.53 (s, 2H), 7.41 (d, 2H, $J = 6.6$ Hz), 7.28 (m, 4H), 7.17 (s, 1H), 7.09 (m, 2H), 5.89 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 60.55, 122.98, 133.74, 125.58, 127.13, 128.13, 128.34, 128.54, 128.82, 134.80, 139.88, 142.50 MS (m/z): 373.5 [M^+].

3. Results and discussion

3.1. Synthesis

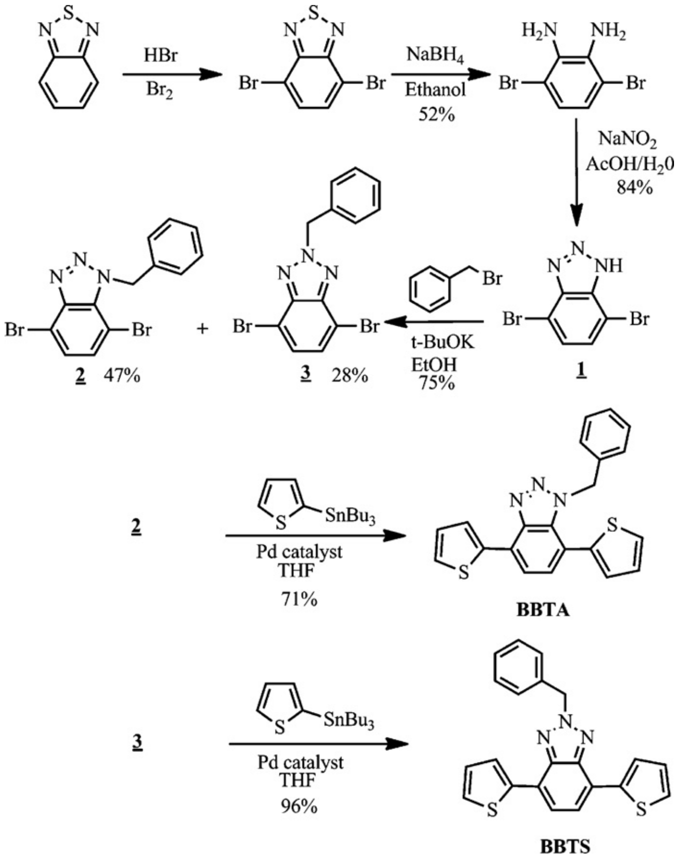
The design of the molecules is based on the donor–acceptor approach. Benzotriazoles are considered to act as electron withdrawing groups owing to electron deficient –N=N– and –C=N– moieties and thiophene acts as the electron rich donor group [23,24]. The substitution pattern of monomers was decided according to previous investigations on alkyl substituted benzotriazoles [15] which have notable properties. Benzyl pendant group was substituted from two available sites of benzotriazole in order to investigate substitution effect.

Although benzylation of benzotriazole resulted in substitution from both 1 and 2 positions of the triazole ring, bromination of 1-substituted product was not possible with the previously reported procedures for the bromination of N-functionalized benzotriazoles. In order to obtain 1-benzyl-1H-benzo[d][1,2,3]triazole a more convenient synthetic route was selected where starting material was benzothiadiazole. In this method, benzothiadiazole was brominated from 4,7 positions in high yield and later brominated compound was reduced to 3,6-dibromobenzene-1,2-diamine. Then dibromo benzotriazole (**1**) was formed in the presence of sodium nitride ($NaNO_2$) in acetic acid. From the benzylation of (**1**) both 1-benzyl-1H-benzo[d][1,2,3]triazole and 2-benzyl-1H-benzo[d][1,2,3]triazole were obtained.

The brominated compounds **2** and **3** were coupled with tributyl(thiophen-2-yl)stannane in the presence of Pd catalyst to obtain final desired products, 2-benzyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (BBTS) and 1-benzyl-4,7-di(thiophen-2-yl)-1H-benzo[d][1,2,3]triazole (BBTA). The intermediate products and final products were characterized by ^{1}H ad ^{13}C NMR spectroscopy. The synthetic route was outlined in Scheme 1.

3.2. Cyclic voltammetry

In order to determine redox reactions during electrochemical polymerization and film deposition, monomers; BBTS and



Scheme 1. Synthetic route to monomers BBTA and BBTS.

BBTA were initially subjected to cyclic voltammetry (CV) in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in acetonitrile/dichloromethane (ACN:DCM) (5:95, v:v) on indium tin oxide (ITO) coated glass slides. 5% dichloromethane was used to enhance the solubility of BBTS and BBTA in the electrolytic medium owing to poor solubility of the monomers in acetonitrile.

Fig. 1 shows typical cyclic voltammogram recorded during continuously applied cyclic scans for BBTS. In the first cycle, BBTS exhibited an irreversible monomer oxidation at 1.33 V vs. Ag wire pseudo-reference electrode (50 mV vs. $Fc/Fc^+/V$). After the first run, reversible redox peaks were evolved and the anodic and cathodic currents were increased as a result of regular growth of PBBTS on ITO electrode. The resulting polymer was oxidized and reduced reversibly at 1.05 V and 0.9 V, respectively in a monomer free solution (Fig. 2). The polymer changed colors between red and blue upon p-type doping/dedoping. The whole process requires ca. 24 mC/cm^2. Single scan cyclic voltammetry in monomer free, 0.1 M $TBAPF_6$/ACN solution showed that PBBTS was also n-type dopable (Fig. 2) when the polymer was cycled between negative potentials. The n-type doping property was determined for PBBTS with a reversible couple at −2.02 V and −1.21 V vs. Ag wire reference electrode. The red polymer in the neutral state turned into brown and blue when partially reduced and finally gray color was observed for PBBTS upon further reduction.

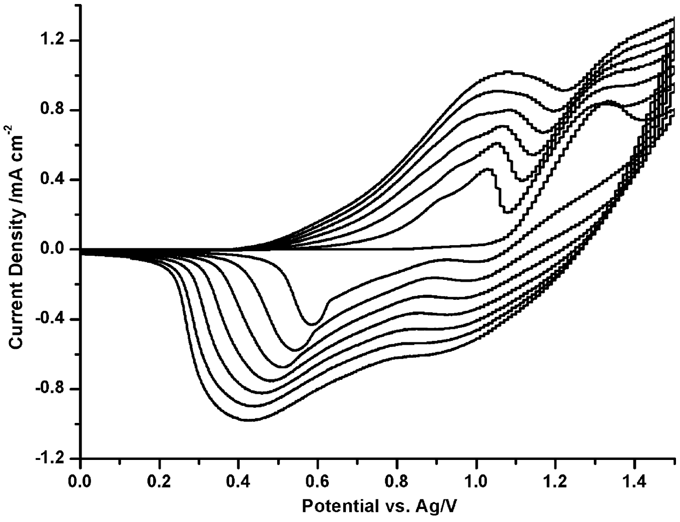


Fig. 1. Repetitive cyclic voltammogram of the 0.01 M BBTS between 0.0 to +1.5 V at 100 mV s^{-1} in 0.1 M $TBAPF_6/CH_2Cl_2$/ACN on an ITO electrode.

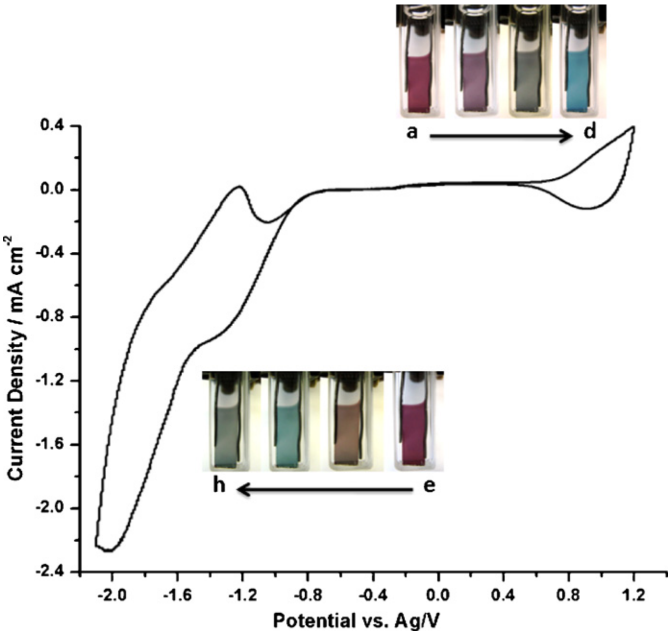


Fig. 2. Single scan cyclic voltammograms of PBBTS films between 1.2 V and −2.1 V using ACN as the solvent and 0.1 M $TBAPF_6$ as supporting electrolyte at a scan rate of 100 mV s^{-1}. Colors observed for p-type doping (a) red; (b) purple; (c) gray; (d) blue. And n-type doping (e) red; (f) brown; (g) blue; (h) gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Cyclic voltammetry of BBTS led to the formation of the corresponding polymer PBBTS, whereas BBTA did not form well adhered film on ITO even continuous scans were applied (Fig. 3a). Therefore, BBTA was polymerized at 1.5 V constant potential vs. the same reference electrode where the homogenous film formation took place on ITO. This process takes 2 min with a total of 220 μA comprising ca. 26 mC/cm^2. Later, the p-doping electrochemistry was probed by oxidative cycling of the polymer film, PBBTA between 0.5 V and 1.65 V in a monomer free environment (Fig. 3b). PBBTA has a broad oxidation peak at 1.30 V and a clear reduction peak at 1.05 V. PBBTA does not have n-type doping property due to differences in the electronic characteristic and enhanced possibility of π interaction on the polymer backbone with respect to the PBBTS.

3.3. Spectroelectrochemistry

In order to observe the polymer characteristics upon applied external bias, spectroelectrochemistry studies of PBBTS and PBBTA were performed in a monomer free 0.1 M $TBAPF_6$ solution.

Spectroelectrochemistry of PBBTS showed λ_{max} at 504 nm which corresponds to red color for the neutral polymer. As the potential was increased gradually, new electronic transitions pro-

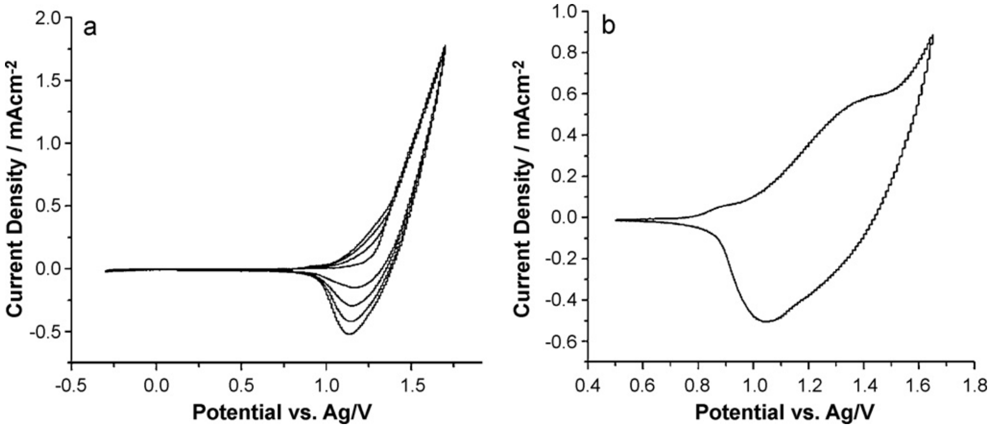


Fig. 3. (a) The cyclic voltammogram of the 0.01 M BBTA between −0.3 to +1.7 V at 100 mV s^{-1} in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$/ACN on an ITO electrode. (b) Single scan cyclic voltammogram of PBBTA film between 0.5 V and 1.65 V at 100 mV s^{-1} in 0.1 M TBAPF$_6$/ACN on an ITO electrode.

gressively intensified at 685 nm owing to the formation of charge carriers such as polarons. Since these transitions lie in the visible region of the electromagnetic spectrum, PBBTS showed multicolored states in its intermediate doping levels. Red color of the polymer film turned into purple and than gray upon oxidation. Moreover, further oxidation of PBBTS resulted in blue color due to increased absorption at 685 nm together with a diminished neutral state absorption. Compared to previously reported polymer PTBT [15], green color was not detected for PBBTS in its partially oxidized forms since the absorptions were not distinct at around 500 and 680 nm, which is essential for green color. Band gap of PBBTS was determined as 1.55 eV from the onset value of lowest energy transition in the visible region (Fig. 4). Additionally, since PBBTS is both p and n dopable, its band gap was also calculated from CV data as 1.9 eV. The electrochemical band gap of PBBTS is higher than its optical gap. This is a common trend observed in conjugated polymers and is usually attributed to the creation of free ions in the electrochemical experiment rather than a neutral optically induced excited state. The most important property of PBBTS is that it shows multicolored charged states during n-doping process. Normally both p and n type dopable polymers tend to have multicolored states however, these kind of polymers are rather rare. PBBTS showed three different reduced state colors and

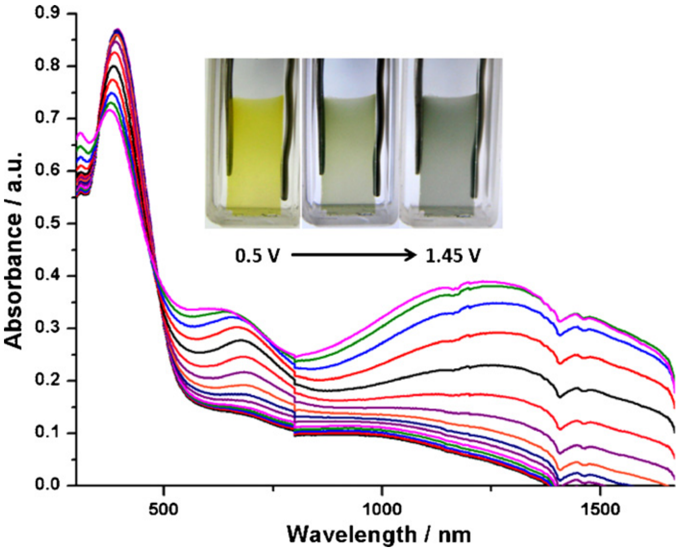


Fig. 5. Spectroelectrochemistry of PBBTA film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF$_6$/ACN electrolyte–solvent couple at applied potentials and corresponding color observed at neutral and doped states.

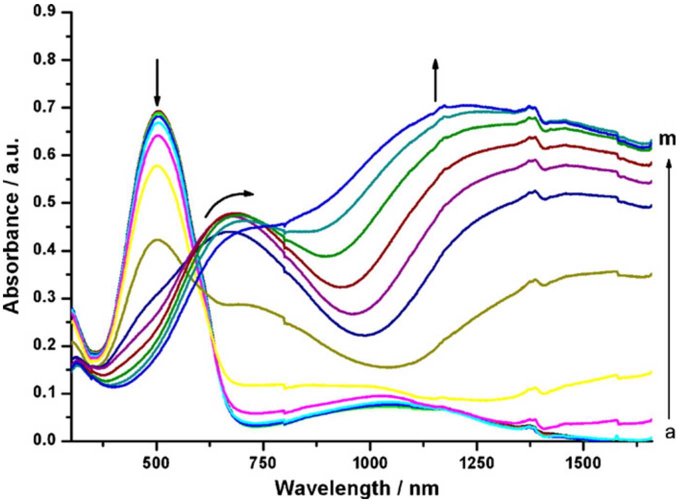


Fig. 4. Spectroelectrochemistry of PBBTS film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF$_6$/ACN electrolyte–solvent couple at applied potentials (V) (a) 0.0; (b) 0.1; (c) 0.2; (d) 0.3; (e) 0.4; (f) 0.5; (g) 0.6; (h) 0.7; (i) 0.8; (j) 0.9; (k) 1.0; (l) 1.1; (m) 1.2.

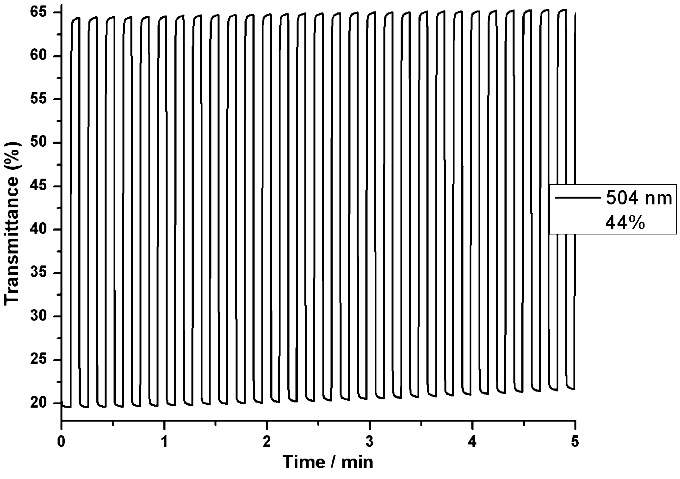


Fig. 6. Δ*T*% change monitored at 504 nm for PBBTS in 0.1 M TBAPF$_6$/ACN.

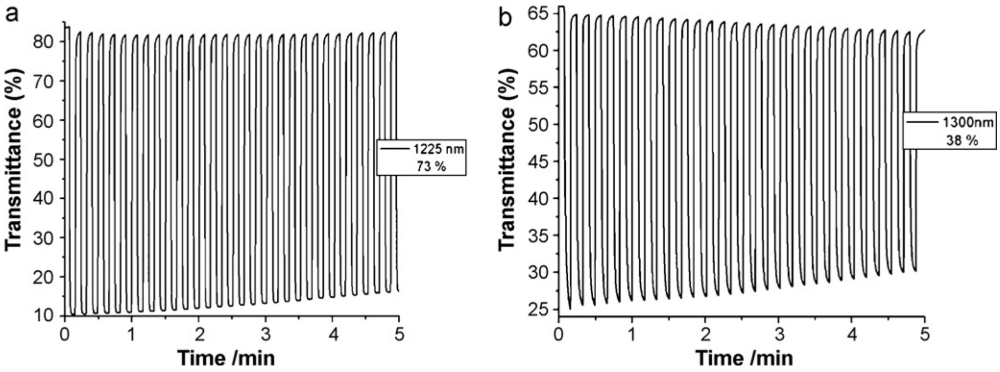


Fig. 7. Δ*T*% change monitored at 1225 nm and 1300 nm for (a) PBBTS and (b) PBBTA in 0.1 M $TBAPF_6$/ACN, respectively.

turned back to its original neutral state color when compensated. This clearly confirms that the negative charge formation is taking place on the polymer backbone and n-doping process is reversible.

The in situ spectroelectrochemistry of PBBTA was performed between 0.5 V and 1.45 V in a monomer free ACN/0.1 M $TBAPF_6$ solution. The λ_{max} for the π–π^* transition in neutral state was found to be 390 nm and the electronic band gap (E_g) was calculated as 2.25 eV from the onset potential for the neutral film at 551 nm. Although the maximum absorption is not totally in the visible region, since absorbance tails into 450 nm, PBBTA reveals yellow color in its neutral state. Upon stepwise oxidation, the intensity of absorptions corresponding to charge carriers simultaneously increased and observed at around 640 nm and 1230 nm for polarons and bipolarons, respectively (Fig. 5). As a result of the structural change of the polymer film upon oxidation, PBBTA altered its color from yellow to gray. For PBBTA, the increase in the NIR region was not as high as the symmetric PBBTS. Since benzyl unit was placed to 2-position of benzotriazole unit, it may resulted in a steric hindrance for counter-ion injection and increased the possibility of π interaction between pendant groups and the polymer backbone. Thus, the insertion of dopant ions to the polymer structure upon oxidation became less preferred.

Higher band gap and blue shifted absorptions of PBBTA compared to PBBTS suggested that the effective conjugation length is shorter in PBBTA than that of PBBTS [25].

3.4. Electrochromic contrast and switching studies

Electrochromic switching studies were carried out in order to monitor the percent transmittance changes as a function of time and to calculate the switching times of the polymers at their maximum absorptions (λ_{max}) by stepping potentials repeatedly between their fully neutral and oxidized states within 5 s time intervals. The switching time is calculated from the kinetic studies to determine the time required for switching between oxidized and neutral states.

At its dominant wavelength in the visible region (504 nm), PBBTS showed 44% percent transmittance change (Fig. 6). On the contrary to PBBTS, PBBTA has no worthy difference in percent transmittances since the PBBTA film could not be reduced and oxidized successively due to the difficulty in charge injection/ejection processes. In NIR region PBBTS and PBBTA revealed 73% (1225 nm) and 38% (1300 nm) transmittance which are significant for electrochromic materials to be used for NIR applications (Fig. 7) [26,27]. Optical stabilities of the polymers are reasonable since PBBTS loses 5% of its original contrast whereas PBBTA loses ca. 8% of the initial contrast upon consecutive 30 full switches.

In addition to percent transmittance changes of electrochromic materials upon doping/dedoping processes, how quickly these materials change their colors and achieve full contrast are also important. Considering that the PBBTS is a multicolored electrochromic, PBBTS showed notable switching properties in visible region. The switching times at 504 nm and 1225 nm were calculated as 0.6 s and 1.2 s for PBBTS which refer to four different color transitions within that period. For PBBTA, the switching time was recorded as 0.9 s at 1300 nm.

4. Conclusions

Two benzotriazole and thiophene containing DAD type monomers (BBTS and BBTA) with benzyl pendant groups were synthesized successfully and polymerized electrochemically. Their electrochemical and optical properties were characterized by cyclic voltammetry and spectroelectrochemistry. The results revealed that the position of pendant group clearly alter the optoelectronic properties of the resulting polymers. All studies confirmed that symmetrical substitution of pendant groups results in better electrochemical properties, percent transmittance changes, faster switching times and repetitive doping/dedoping processes.

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