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Synthesis and electrochemical properties of a new benzimidazole derivative as the acceptor unit in donor–acceptor–donor type polymers

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ABSTRACT

A new benzimidazole unit, 4′-(tert-butyl)spiro[benzo[d]imidazole-2,1′-cyclohexane] was synthesized and coupled with different donor units like 3-hexylthiophene and 3,4-ethylenedioxythiophene (EDOT) via Stille coupling. The donor–acceptor–donor (D–A–D) type monomers, 4′-(tert-butyl)-4,7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (BIHT) and 4′-(tert-butyl)-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (BIED) were electrochemically polymerized, their electrochemical and optical properties were investigated by cyclic voltammetry, UV–vis-NIR spectroscopy techniques. Effect of donor groups on the optical and electronic properties of polymer was studied.

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1. Introduction

Applications of conjugated polymers, such as electrochromic devices [1–7], organic light emitting diodes [8–10], organic photovoltaic devices [11–13], and organic field effect transistors [14–16] made them outstanding topics in polymer science. Properties like ease of processability, lightweight and ease of changing the structural properties to alter the absorption, solubility and electrical properties make them superior to their inorganic counterparts [17]. Among these band gap is the most important criterion for the optical and electronic properties of the conjugated polymers. Therefore, most studies focus on tuning the band gap of polymer in order to obtain desired electronic and optical properties of conjugated polymers. There are several parameters affecting the band gap of conjugated polymers, namely resonance effect, planarity, interchain alternation and bond length alternation. These effects can be monitored by donor–acceptor (DA) approach [18–20]. DA theory is the mostly used one in order to tune band gap of a conjugated polymer [21,22].

Recently, low band gap D–A–D type conjugated polymers have attracted great attention with their organic electronic applications [22]. Polymers containing benzotriazole, benzothiadiazole and benzimidazole as the acceptor groups and thiophene derivatives; such as, thiophene, 3-hexyl thiophene, 3,4-ethylenedioxythiophene as the donor groups were synthesized by our group [23–29]. The optical and electronic properties of these polymers are accompanied with low band gaps, low switching times and high optical contrasts. In the literature, there are many examples of benzotriazole and benzothiadiazole moieties used as the electron deficient groups [30,31]. Nevertheless, the properties of donor–acceptor–donor type benzimidazole compounds are still in an early stage of research. In this study, 4′-(tert-butyl)spiro[benzo[d]imidazole-2,1′-cyclohexane] acceptor unit was synthesized for the first time and coupled with strong donor units; 3-hexylthiophene and EDOT to generate donor–acceptor–donor type benzimidazole containing monomers. These new monomers were electrochemically polymerized and their electrochemical and spectroelectrochemical properties were investigated. The new benzimidazole derivative was used as the electron deficient group for the first time where two thiophene derivatives were used as the donor groups. In order to obtain conjugated polymers with good electrical and optical properties, two monomers, namely 4′-(tert-butyl)-4,7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (BIHT) and

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4′-(tert-butyl)-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (BIED) were synthesized and electrochemically polymerized. BIHT and BIED were compared with respect to their different donor groups and their effects on electronic and optical properties of the polymers.

2. Experimental

2.1. General

All chemicals and reagents were obtained from commercial sources and used without any further purification unless mentioned otherwise. THF (tetrahydrofuran) was dried over sodium and benzophenone. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with TMS (tetramethylsilane) as the internal standard and $CDCl_3$ as the solvent and chemical shifts were given in ppm. HRMS studies were done with a Waters SYNAPT MS system. Electrochemical studies were performed in a three-electrode cell consisting of an ITO (indium tin oxide) coated glass slide as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode under ambient conditions using a VoltaLab PST-50 potentiostat. HOMO-LUMO values were calculated taking the value of SHE as -4.75 eV vs. vacuum. Varian Cary 5000 UV–vis-NIR spectrophotometer was used to perform the spectroelectrochemical studies of the polymers. 4,7-Dibromobenzothiadiazole **(1)** [32], 3,6-dibromobenzene-1,2-diamine **(2)** [33], tributyl(4-hexylthiophen-2-yl)stannane **(4)** [34] and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane **(5)** [35] were synthesized according to previously published procedures.

2.2. Synthesis of monomers

2.2.1. 4,7-dibromo-4′-(tert-butyl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (3)

A solution of 3,6-dibromobenzene-1,2-diamine (300 mg, 1.13 mmol), 4-tert-butylcyclohexanone (174 mg, 1.13 mmol) and 8 ml toluene was stirred at 130 °C for 24 h under argon (Ar) atmosphere. Then the solvent was removed under reduced pressure. The crude product was dissolved in 11 ml dichloromethane and stirred at room temperature under argon atmosphere. To this solution, 85% activated manganese (IV) oxide (800 mg, 9.16 mmol) was added. After stirring at room temperature for 4 h, the reaction mixture was filtered, diluted with dichloromethane (80 ml), washed with distilled water (3 × 80 ml) and dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography using hexane:ethylacetate (10:1) as the eluent. 4,7-Dibromo-4′-(tert-butyl)spiro[benzo[d]imidazole-2,1′-cyclohexane] was obtained as a yellow solid with a yield of 55%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12 (s, 2H), 2.25 (t, 2H), 2.10 (m, 1H), 1.70 (t, 2H), 1.60 (t, 2H), 1.30 (t, 2H), 0.90 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.00, 156.70, 135.80, 135.60, 119.30, 107.50, 107.50, 107.45, 47.80, 47.85, 47.80, 32.50, 35.80, 35.75, 27.75, 25.7.

2.3. 4′-(tert-butyl)-4, 7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (BIHT)

A solution of 4′,7′dibromo-4-(tert-butyl)spiro[cyclohexane-1,2′-indene] (300 mg, 0.75 mmol) and tributyl(4-hexylthiophen-2-yl)stannane (1715 mg, 3.75 mmol) was refluxed in 41 ml THF at 100 °C under argon atmosphere. After 12 h, solvent was removed under reduced pressure and the residue was purified by column chromatography using dichloromethane:hexane (1:3) as the eluent. 5,5′-(4-(Tert-butyl)spiro[cyclohexane-1,2′-indene]-4′,7′-diyl)bis(3-hexylthiophene) was obtained as a red solid with a yield of 55%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, J = 1.2 Hz, 1H), 7.76(d, J = 1.2 Hz, 1H), 7.20 (s, 2H), 7.15 (s, 2H), 2.60 (t, 4H), 1.60 (m, 4H), 1.50 (m, 2H), 1.48 (m, 2H), 1.38 (m, 1H), 1.30 (m, 4H), 1.29 (m, 8H), 0.94 (s, 9H), 0.88 (t, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.00, 158.50, 145.30, 145.20, 139.55, 139.45, 130.50, 130.30, 129.61, 129.59, 129.20, 129.10, 128.40, 128.30, 122.3, 48.50, 34.85, 34.75, 33.50, 32.67, 31.60, 31.55, 31.40, 31.35, 30.40, 30.30, 28.80, 28.70, 28.60, 27.20, 27.10, 23.61, 23.59, 15.10, 15.00.

HRMS-ESI+ (m/z): [M+] $C_{36}H_{51}N_2S_2$ calculated: 575.3494, found: 575.3495.

2.3.1. 4′-(tert-Butyl)-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)spiro[benzo[d]imidazole-2,1′-cyclohexane] (BIED)

A solution of 5,5′-(4-(tert-butyl)spiro[cyclohexane-1,2′-indene]-4′,7′-diyl)bis(2,3-dihydrothieno[3,4-b][1,4]dioxine) (400 mg, 0.70 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (151 mg, 3.5 mmol) was refluxed in 41 ml THF at 100 °C under argon atmosphere. After 12 h, solvent was removed under reduced pressure and the residue was purified by column chromatography using dichloromethane:hexane (3:1) as the eluent. 5,5′-(4-(tert-butyl)spiro[cyclohexane-1,2′-indene]-4′,7′-diyl)bis(2,3-dihydrothieno[3,4-b][1,4]dioxine) was obtained as a purple solid with a yield of 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.8 (dd, $J1$ = 7.7 Hz, $J2$ = 13.3 Hz, 2H), 6.45 (s, 1H), 6.38 (s, 1H), 4.3 (t, 4H), 4.2 (t, 4H), 1.6 (m, 1H), 1.4 (t, 4H), 1.35 (m, 4H), 0.95 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.60, 156.58, 143.50, 143.40, 140.50, 140.40, 139.50, 139.40, 134.20, 134.15, 124.5, 106.60, 106.55, 102.50, 101.50, 64.10, 63.90, 63.35, 63.30, 45.80, 40.31, 40.29, 31.46, 26.65, 26.60, 26.55, 21.65, 21.60.

HRMS-ESI+ (m/z): [M+] $C_{28}H_{31}N_2O_4S_2$ calculated: 523.1725, found: 523.1733.

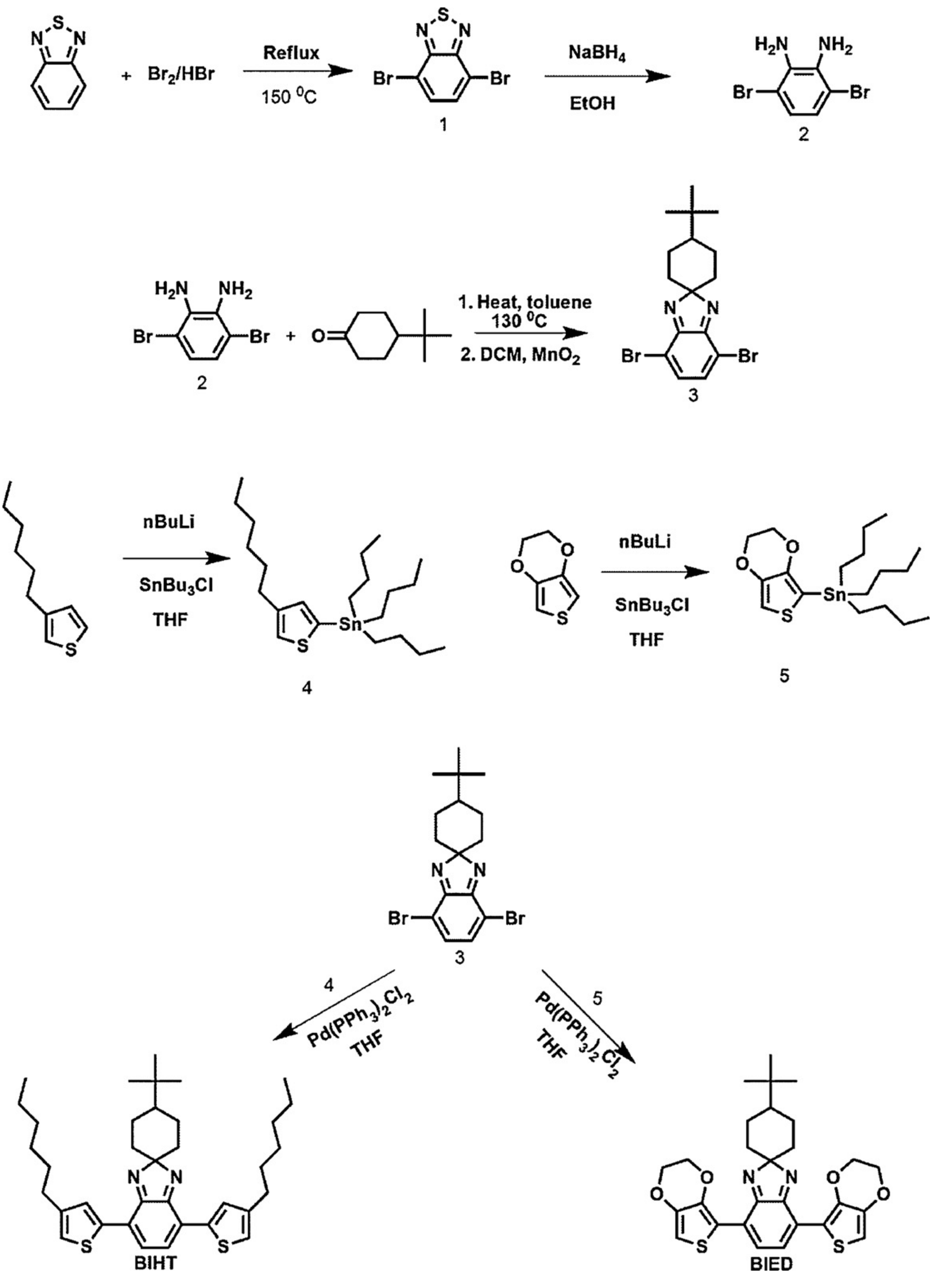
3. Results and discussion

3.1. Synthesis

Synthetic route was outlined in Scheme 1. Benzimidazole group with an electron deficient —C=N— moiety was used as the electron acceptor while electron rich thiophene groups were used as the electron donating moieties [36,37]. Benzothiadiazole was brominated, and then reduced to brominated diamine according to the previously published procedures [32,33]. After that in the presence of manganese dioxide, benzimidazole compound was formed. For the coupling reactions, 3-hexylthiophene and 2,3-dihydrothieno[3,4-b][1,4]dioxine were stannylated in the presence of n-BuLi and $SnBu_3Cl$ [34,35]. All monomers were synthesized via Stille coupling in the presence of palladium catalyst. The structure of monomers was confirmed by NMR and HRMS.

3.2. Cyclic voltammetry

To investigate the electrochromic behaviors of polymers, monomers (BIHT and BIED) were electrochemically polymerized by applying potentials between 0.2 V to 1.1 V and -0.3 V to 1.5 V respectively on indium tin oxide (ITO) coated glass in 0.1 M of $TBAPF_6$/DCM/ACN (5:95, v:v). In order to enhance the solubility of BIHT and BIED 5% dichloromethane was used in the electrolytic medium due to poor solubility of the monomers in acetonitrile.



Scheme 1. Synthetic route to monomers.

In the first cycles, the irreversible monomer oxidation of monomers revealed at 1.04 V for BIHT, 1.26 V for BIED at a bare ITO glass as given in Fig. 1. Difference in their monomer oxidation potentials was found to be 0.22 V, which may be due to the different electronic nature of the donor units. After the first cycle, oxidation peaks and their reverse cathodic peaks emerged at lower potentials than the monomer oxidation potentials and their current densities increased with the increasing number of cycles indicating that corresponding insoluble polymer film was well adhered on the ITO surface. As seen in Fig. 1, while PBIHT shows one redox couple, PBIED revealed two redox couples during the electropolymerization process, which proved higher electron donating ability of EDOT moiety than 3-hexylthiophene. p- and n-doping abilities of both polymer films were investigated in a monomer free 0.1 M $TBAPF_6$/ACN solution by cyclic voltammetry technique as given in Fig. 2.

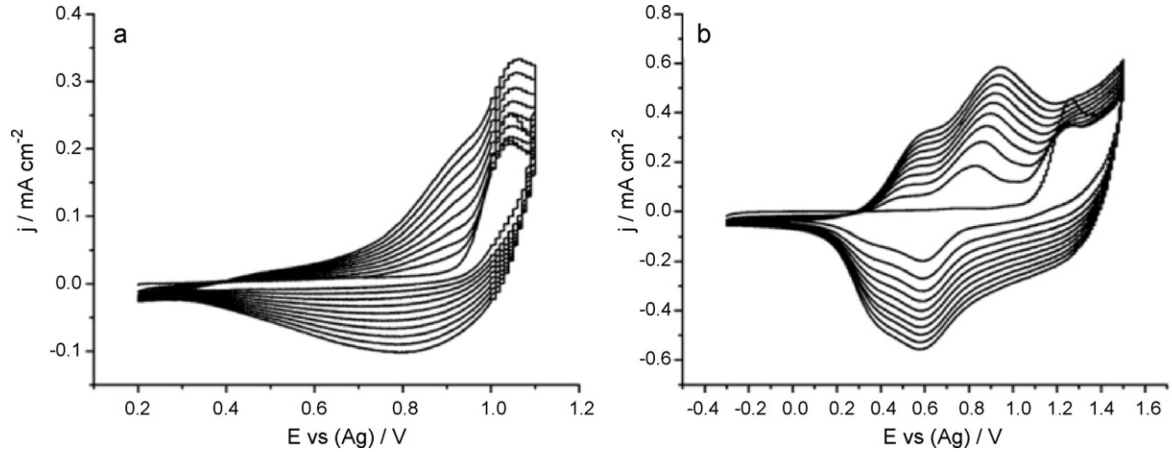


Fig. 1. Repeated potential scan polymerization of (a) 0.01 M BIHT between 0.2 and +1.1 V and (b) 0.01 M BIED between −0.3 and 1.5 V at 100 mV s^{-1} in 0.1 M TBAPF$_6$ CH$_2$Cl$_2$/ACN (5:95, v:v) on an ITO electrode.

Table 1
Summary of electrochemical studies of PBIHT and PBIED.

	E_m^{ox}	E_p^{ox}	E_p^{red}	$E_{n\text{-dope}}$	$E_{n\text{-dedope}}$	HOMO	LUMO	E_g^{op}	E_g^{ec}
PBIHT	1.04 V	0.93 V	0.79 V	−1.9 V	−1.04 V	−5.56 eV	−3.83 eV	1.19 eV	1.73 eV
PBIED	1.26 V	0.55 V/0.82 V	0.34 V/0.59 V	−1.49 V	−0.6 V	−5.31 eV	−4.42 eV	1.15 eV	0.89 eV

Sharp reversible peaks corresponding to reversible n-doping of PBIHT and PBIED appear at −1.9 V/−1.04 V and −1.49 V/−0.6 V, respectively. The current associated with the p- and n-type doping processes for both polymers were nearly same, indicating that PBIHT and PBIED have nearly equal p- and n- type doping ability. Their HOMO and LUMO energy levels were calculated from onset of the corresponding oxidation and reduction potentials vs. Fc/Fc$^+$ reference electrode taking the value of SHE as −4.75 eV vs. vacuum [23] and reported in Table 1. Although both polymers contain same acceptor unit, their LUMO levels were quietly different than each other. PBIED has higher n-doping capacity than PBIHT due to its high capacity of stabilizing negative charges on polymer chains, which leads to lower LUMO energy level. LUMO energy levels of resulting polymers were in accordance with the donor–acceptor match of donor and acceptor units. EDOT is known as a more efficient donor unit than 3-hexylthiophene [2,38], hence PBIED yields in a better donor–acceptor match which lowers the LUMO level.

3.3. *Spectroelectrochemistry and color studies*

Spectroelectrochemistry studies were performed in situ by measuring the absorption behavior of electrochemically deposited polymer films onto ITO coated glass slides in 0.1 M TBAPF$_6$/ACN. During p-doping, the evolution of the free charge carrier bands of the polymers was measured (Fig. 3). These pre-determined potentials were applied to the polymers with 10 mV increments at each step.

In their neutral states, PBIHT and PBIED revealed blue (L: 49.92, a: 1.02, b: −7.41) and green colors (L: 55.54, a: −49.86, b: 35.04) respectively owing to the broad absorption range of PBIHT at around 640 nm and two distinct absorptions of PBIED at 430 nm and 837 nm. In most donor–acceptor–donor type polymers there are two distinct absorption bands since π–π* transition of the polymer and intramolecular charge transfer transitions between donor and acceptor units absorb at different wavelengths [1,2]. Although PBIHT has two absorption maxima similar to PBIED, the short

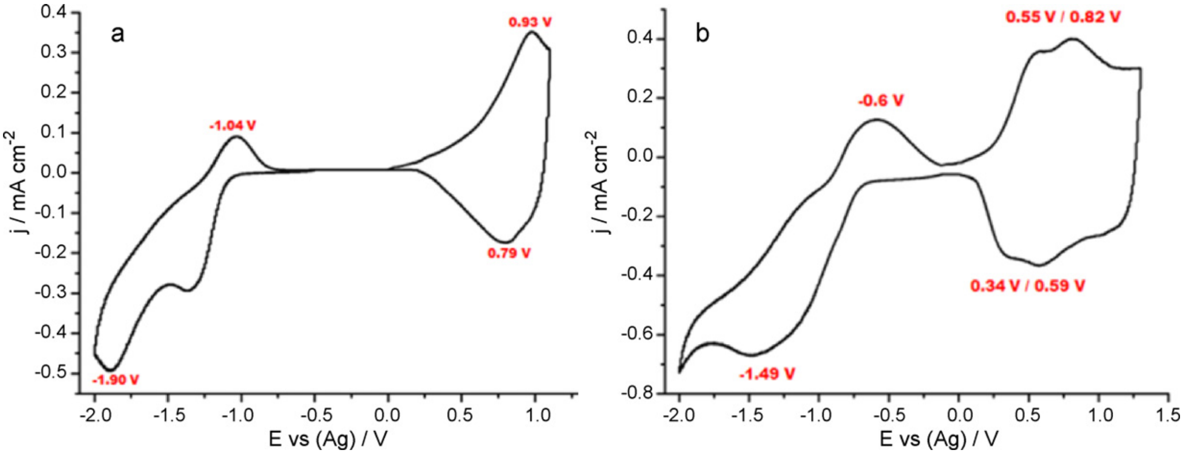


Fig. 2. Single scan cyclic voltammograms of (a) PBIHT between 1.1 V and −2.0 V and (b) PBIED between 1.4 V and −2.0 V using ACN as the solvent and 0.1 M TBAPF$_6$ as the supporting electrolyte at a scan rate of 100 mV s^{-1}.

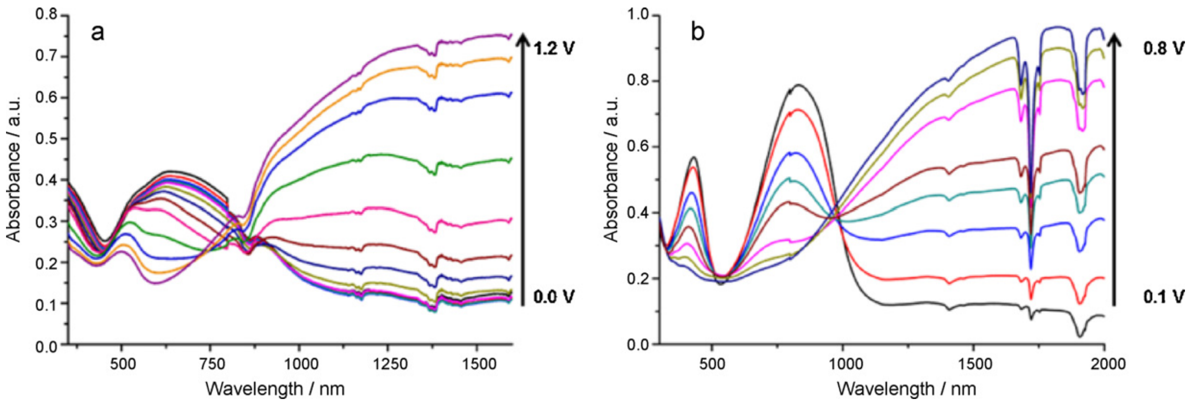


Fig. 3. Spectroelectrochemistry of (a) PBIHT and (b) PBIED films on an ITO coated glass slide in monomer-free, 0.1 M $TBAPF_6$/ACN electrolyte-solvent couple.

wavelength absorptions are at UV region, hence the polymer revealed blue color. On the other hand, PBIED has two distinct absorption maxima at around 400 nm and 700 nm; as a result the neutral state color was observed as green. The optical band gaps (E_g^{op}) were calculated from the onset of their long wavelength absorptions as 1.19 eV and 1.15 eV for PBIHT and PBIED, respectively. The broad absorption of PBIHT leads to the onset of π–π^* transition in longer wavelength, hence the optical band gap of the polymer is approximately that of the band gap of its EDOT moiety containing one. As the potentials increased, the absorption in the NIR begun to arise, whereas absorptions in the visible region were depleted, indicating the creation of lower energy polaron and bipolaron charge carriers for both PBIHT and PBIED. When the polymers are fully oxidized, strong absorptions in the NIR region were observed. Absorption tail of the polaron band for PBIED is adjacent to the visible region, resulting a gray color (L: 72.99, a: −3.03, b: 27.34) and a blue color (L: 59.87, a: −1.36, b: −6.59) in doped state, whereas PBIHT revealed transmissive-gray color (L: 59.43, a: −10.57, b: 14.06) (Fig. 4).

PBIHT revealed transmissive-gray color (L: 58.35, a: −4.39, b: 8.56) in n-doped state, whereas PBIED showed multichromism during n-doping; light green (L: 58.67, a: −40.01, b: 74.03), orange (L: 53.99, a: 44.01, b: 58.97) and brick-red (L: 20.99, a: 21.99, b: 24.89) (Fig. 4). Both polymer films turned back to their neutral state colors after dedoping.

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 neutral and fully oxidized states within 5 s time intervals. The switching time was calculated from the kinetic

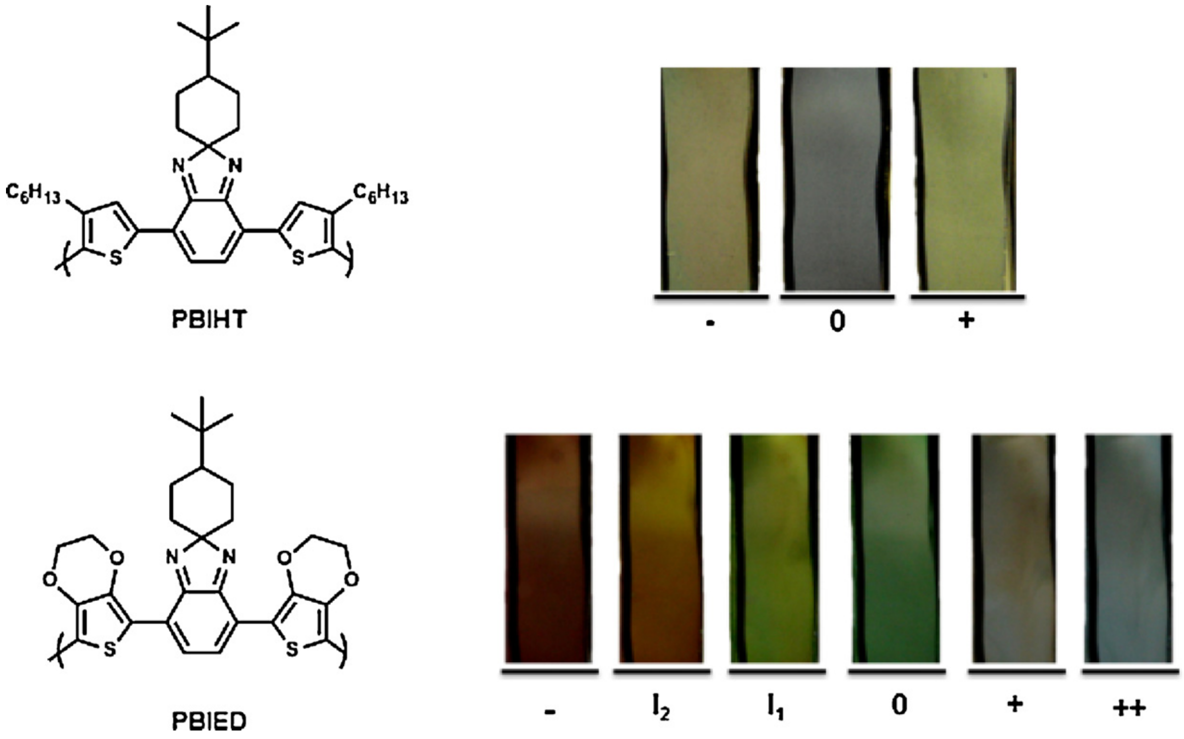


Fig. 4. Chemical structures of PBIHT and PBIED and their color changes. under p- and n-type doping processes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

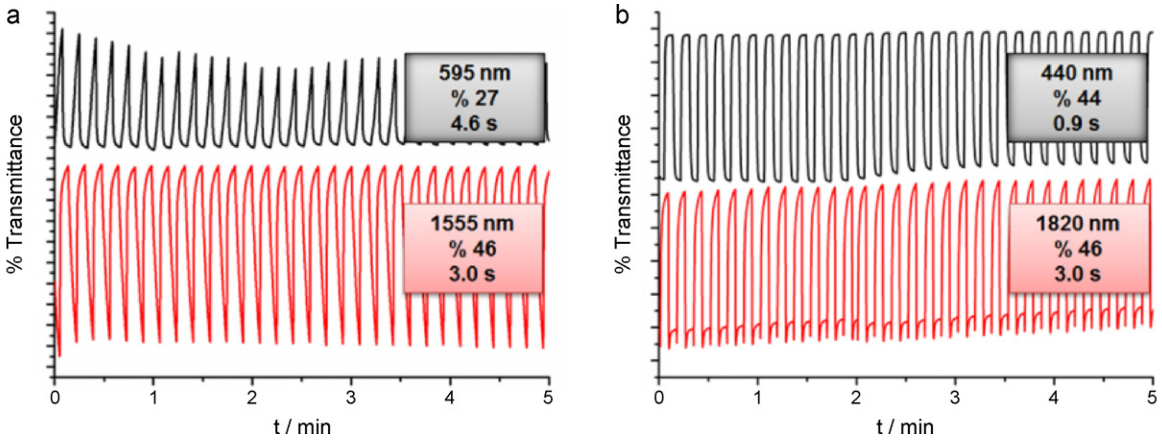


Fig. 5. ΔT% change monitored at different wavelengths for (a) PBIHT and (b) PBIED in 0.1 M $TBAPF_6$/ACN.

studies to determine the time required for 95% of full switches between their colored and bleached states.

At their dominant wavelengths in the visible region, PBIHT showed 27% percent transmittance change with a high switching time (4.6 s) at 595 nm, whereas PBIED revealed $\Delta T\%$ of 44% at 440 nm with a sub second switching time (0.9 s) (Fig. 5). Also PBIED loses 9% of its original contrast in visible region; on the other hand PBIHT loses ca. 32% of the initial contrast upon sequential 30 full switches. The alkyl chain group on the donor moiety leads to a difficulty in charge injection/ejection processes for PBIHT. PBIED revealed notable switching properties in visible region. In NIR region, PBIHT and PBIED revealed 46% (1555 nm) and 46% (1820 nm) transmittance with high switching times (Fig. 5).

4. Conclusions

Two benzimidazole containing donor–acceptor–donor type polymers were synthesized successfully and polymerized electrochemically. Their electrochemical and optical properties were characterized by cyclic voltammetry and spectroelectrochemistry. For PBIED, switching time was less than a second. Both PBIHT and PBIED showed high optical contrast in NIR region and both of them have a broad absorption band making them a possible candidate for solar cell applications. The solar cell applications of these polymers will be the subject of an incoming study.

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