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Tuning of the neutral state color of the π-conjugated donor–acceptor–donor type polymer from blue to green via changing the donor strength on the polymer

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ABSTRACT

Two donor–acceptor–donor types of π-conjugated monomers were synthesized using Stille coupling reaction. Both monomers were found to produce electroactive polymers upon electrochemical oxidation. The effects of different donor substituents on the polymers' electrochemical and spectroelectrochemical properties were examined. Optical characterization revealed that the band gaps of poly(2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-7-yl)-5,8-di(thiophen-2-yl)quinoxaline) (PDBQTh) and poly(2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[*b*]-[1,4]dioxin-7-yl)-5-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)quinoxaline) (PDBQEd) were 1.5 eV and 1.3 eV, respectively. PDBQEd reveals two distinct absorption bands as expected for this type of donor–acceptor–donor polymer at 423 and 738 nm, while PDBQTh has a single absorption band at 630 nm. The colorimetry analysis revealed that while PDBQTh has a blue color, PDBQEd showed a green color in the neutral state. PDBQEd revealed reversible n-doping.

1. Introduction

Research in the area of conducting polymers increased dramatically with the doping of polyacetylene which was the simplest organic polymer with high conductivity [1]. Conjugated polymeric organic materials have attracted considerable attention over the past decades for their potential applications in organic electronic devices, due to their tunable band gaps, redox properties, processability, flexibility and low cost [2–4].

Electron-rich heterocycle based polymers such as polythiophene and its derivatives are the most promising and best studied conducting polymers because of their flexibility towards synthetic modifications. The most useful fundamental property that can be controlled by the structural modification is the polymer band gap, Eg, whose magnitude defines the color of conducting polymer [5]. The different colors observed with these compounds while switching between their different redox states is one of the most important advantages of organic electrochromic materials. Applications that use this property include architectural smart windows, rear-view mirrors for cars, sensors and electrochromic displays [6]. In the history of electrochromic materials, the discovery of third additive primary color green was probably one of the most important steps for the commercialization of full-color electrochromic displays [7]. Recently, conjugated polymers that are green at neutral state were the derivatives of quinoxaline [8,9]. The latest contributions have come from alternation of electron-rich (donor) and electron-poor (acceptor) units in the polyconjugated backbone. A regular alternation of conjugated donor and acceptor moieties in a conjugated polymer that increases double bond character leads to broadening of valence and conduction bands and induces small band gaps [10–13]. Reports on alternating quinoxaline/oligothiophene copolymers show interesting absorption properties revealing independence of the absorption maxima on the length of the oligothiophene [14,15].

In this study, the contributions of donor heterocycles of varying strength on the electrochromic properties of new donor–acceptor–donor polymers were examined. Thiophene and EDOT have been used as the donor moieties. To complete alternation on the monomers, acceptor unit with benzo-1,4-dioxane was inserted in the molecule.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich except anhydrous tetrahydrofuran (THF) and n-butyl lithium which were purchased from Acros. They were used as received without purification. 4,7-

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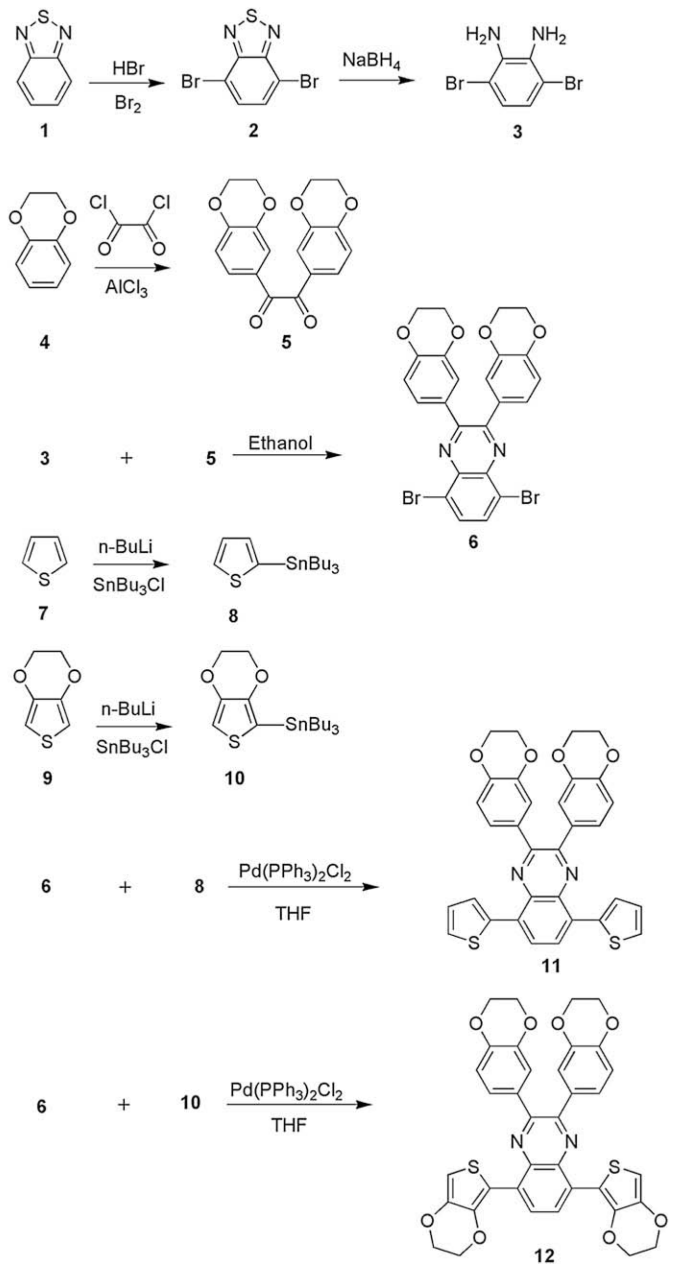

Scheme 1. Synthetic route to monomers, DBQTh (**11**) and DBQEd (**12**).

Dibromo-2,1,3-benzothiadiazole (**2**) [16], 3,6-dibromo-1,2-phenylene-diamine (**3**) [17], 5,8-dibromo-2-(2,3-dihydrobenzo[*b*][1,4]-dioxin-5-yl)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-8-yl)quinoxaline (**6**) [18], tributyl(thiophen-2-yl)stannane (**8**) [19] and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (**10**) [20] were synthesized according to literature methods.

2.2. Methods

^{1}H NMR spectra of DBQTh and DBQEd were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer in $CDCl_3$ at 400 MHz and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard.

Electrochemical studies were achieved with a Voltalab 50 potentiostat. The redox behavior of DBQTh and DBQEd were examined by cyclic voltammetry. The measurements were carried out in a one compartment, three-electrode system in an acetonitrile/dichloromethane (ACN/DCM) solution containing 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) as the supporting electrolyte. A Pt wire and a Ag wire (0.35 V vs SCE) were used as the counter and pseudo-reference electrodes, respectively. The electrochromic measurements; spectroelectrochemistry, and switching studies of the polymer film deposited on ITO-coated glass slide were carried out in the same medium in the absence of monomer using Varian Cary 5000 spectrophotometer. The potentials were controlled using a Solartron 1285 potentiostat/galvanostat. Colorimetry measurements were achieved by a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

*2.3. Synthesis of 1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-(2,3-dihydrobenzo [b][1,4]dioxin-7-yl)ethane-1,2-dione*

Benzo-1,4-dioxane (**4**) was subjected to Friedel–Crafts acylation with oxalyl chloride to give 1,2-dione (**5**). To a suspension of $AlCl_3$ (0.98 g, 7.4 mmol) in CH_2Cl_2 (15 mL), a solution of benzo-1,4-dioxane (1 g, 7.4 mmol) and oxalyl dichloride (0.47 g, 3.7 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 25 °C. The violet mixture was stirred at room temperature for 4 h. The resulting mixture was then poured into 100 mL ice. The yellow organic phase was washed with concentrated $NaHCO_3$ (3×25 mL) and brine, and then dried over $MgSO_4$. After evaporation of the solvent, yellow solid was chromatographed over a bed silica using dichloromethane as the eluent. The solid recrystallized from ethanol yielded 1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-(2,3-dihydrobenzo[*b*][1,4]dioxin-7-yl)ethane-1,2-dione. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 4.24 (s, 8H), 6.77 (d, 2H), 7.43 (d, 2H), 7.50 (s, 2H).

2.4. Synthesis of DBQTh and DBQEd

Access to the monomers, namely 2-(2,3-dihydrobenzo[*b*][1,4]-dioxin-6-yl)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-7-yl)-5,8-di(thiophen-2-yl)quinoxaline (DBQTh) and 2-(2,3-dihydrobenzo[*b*][1,4]-dioxin-6-yl)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-7-yl)-5-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-7-yl)quinoxaline (DBQEd) was afforded by Pd-catalyzed cross coupling reaction of the dibromoquinoxaline derivative with tributyl(thiophen-2-yl)stannane and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane as shown in Scheme 1.

Bromination of 2,1,3-benzothiadiazole (**1**) was achieved using a mixture of HBr/Br_2 in accordance with the previous reported procedure [16]. To reduce the resulting compound to 3,6-dibromo-1,2-phenyldiamine (**2**), excess amount of $NaBH_4$ was used. Condensation reaction of 3,6-dibromo-1,2-phenyldiamine (**3**) and 1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-(2,3-dihydrobenzo[*b*][1,4]dioxin-7-yl)ethane-1,2-dione (**5**) was performed in ethanol with a catalytical amount of paratoluenesulfonic acid (PTSA). The resulting acceptor unit was characterized via ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 4.23 (s, 8H), 6.7 (d, 2H), 7.0 (d, 2H), 7.33 (s, 2H), 7.78 (s, 2H).

Thiophene (**7**) was converted to its stannyl derivative (**8**) by treatment with n-BuLi followed by Bu_3SnCl. The resulting stannane (7 mmol) was subjected to the Stille coupling reaction with the quinoxaline derivative (1 mmol) in THF (100 mL) using $Pd(PPh_3)_2Cl_2$ (50 mg) as the catalyst. The mixture was stirred at 100 °C under argon atmosphere for 15 h, cooled, and concentrated on the rotary evaporator. The residue was subjected to column chromatography (DCM/hexane, 3/1) to afford a yellow solid. The structure of DBQTh was confirmed by ^{1}H NMR spectroscopy (Fig. 1a). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 4.25 (s, 8H), 6.78 (d, 2H), 7.10 (d, 4H), 7.36 (s, 2H), 7.45 (d, 2H), 7.78 (d, 2H), 8.05 (s, 2H).

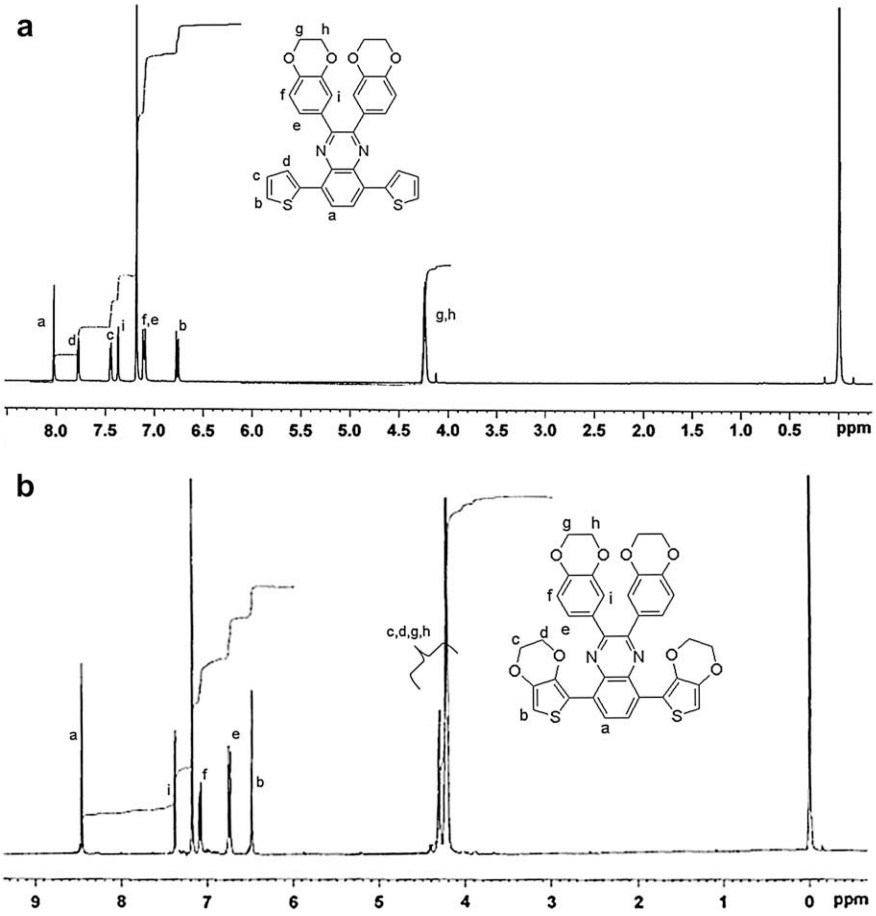

Fig. 1. a. ^{1}H NMR spectrum of DBQTh; b. ^{1}H NMR spectrum of DBQEd.

To synthesize DBQEd, tributyltin substituted EDOT (**10**) was prepared. Through the coupling of tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (7 mmol) with the quinoxaline derivative (1 mmol) in THF (100 mL), DBQEd was obtained. Column chromatography (silica, DCM/hexane, 3/1) gave DBQEd as a red solid. The structure of DBQEd was confirmed by ^{1}H NMR spectroscopy (Fig. 1b). ^{1}H NMR (400 MHz, CDCl$_3$): δ: 4.25 (s, 8H), 4.30 (s, 8H), 6.45 (s, 2H), 6.73 (d, 2H), 7.10 (d, 2H), 7.41 (s, 2H), 8.47 (s, 2H).

2.5. *Synthesis of PDBQTh and PDBQEd by electrochemical polymerization*

Polymerization of DBQTh was performed in the presence of 1×10^{-3} M monomer solution, TBABF$_4$ (0.1 M) in acetonitrile (ACN)/dichloromethane (DCM) (90/10,v/v) solvent mixture on an ITO-coated glass slide by using a UV-cuvette as a single-compartment cell equipped with Pt counter electrode, and a Ag/Ag$^+$ reference electrode via potentiodynamic method.

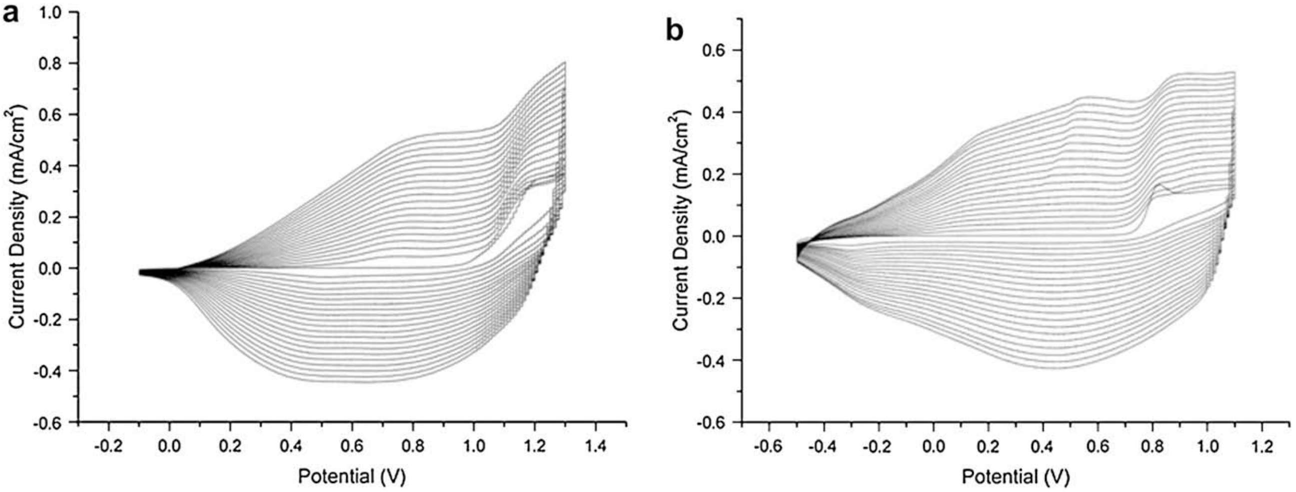

Fig. 2. Repeated potential scan electropolymerization of (a) DBQTh (b) DBQEd at 100 mV/s in 0.1 M TBABF$_4$/ACN/DCM on the ITO electrode.

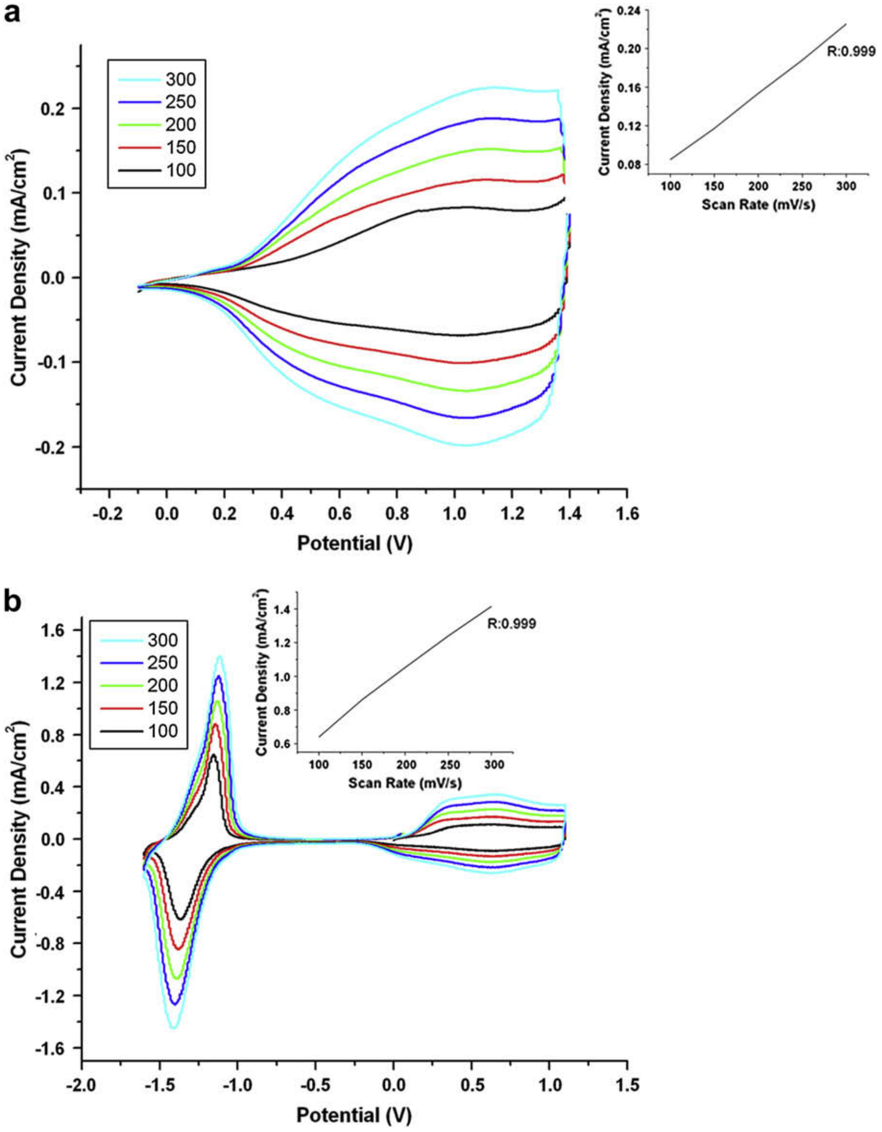

Fig. 3. Cyclic voltammograms of (a) PDBQTh (b) PDBQEd in 0.1 M TBABF$_4$/ACN/DCM at scan rates of 100, 150,200, 250 and 300 mV/s.

Polymerization of DBQEd was performed in the presence of 1×10^{-3} M monomer solution in the same solvent–electrolyte couple system that was used for polymerization of DBOTh on an ITO-coated glass slide by using a UV-cuvette as a single-compartment cell equipped with Pt counter electrode, and a Ag/Ag$^+$ reference electrode via potentiodynamic method.

3. Results and discussion

3.1. Synthesis

Bromination of benzothiadiazole was performed in a mixture of HBr/Br$_2$ to give the dibrominated compound in very high yields [16]. Subsequent reduction of the compound was achieved using excess amount of NaBH$_4$ [17]. A simple condensation reaction was performed with the dibromo diamino and 1,2-dione to give the corresponding dibromoquinoxaline [18]. Stannylation of EDOT and thiophene was achieved by addition of equimolar strong base, n-BuLi followed by addition of Bu$_3$SnCl [19,20]. Lastly a convenient method for formation of carbon–carbon bond, Stille coupling, was used to attach donor moieties to the acceptor quinoxaline unit to give the title compounds.

3.2. Electrochemistry

Multiple cyclic voltammograms for the repeated scanning electropolymerization of DBQTh and DBQEd of these monomers were shown in Fig. 2a and b. Cyclic voltammetry (CV) of DBQTh and DBQEd were carried out in acetonitrile (ACN)/dichloromethane (DCM) (90/10,v/v) solvent mixture using TBABF$_4$ (0.1 M) as the supporting electrolyte. During the first anodic scan, a single peak was observed for DBQTh and DBQEd which corresponds to irreversible monomer oxidation at a bare ITO glass electrode. For DBQTh monomer, the onset of oxidation starts at +1.0 V vs the Ag wire pseudo-reference electrode. The oxidation wave for DBQEd is shifted to +0.7 V due to the presence of electron donating group on donor moiety. The oxidation potential of DBQEd is lower than that of DBQTh measured under the same conditions, thus indicating that the HOMO level of DBQEd is higher than that of DBQTh. On the anodic scans, polymer oxidations were evolved at about +0.7 V for PDBQTh and +0.55 V

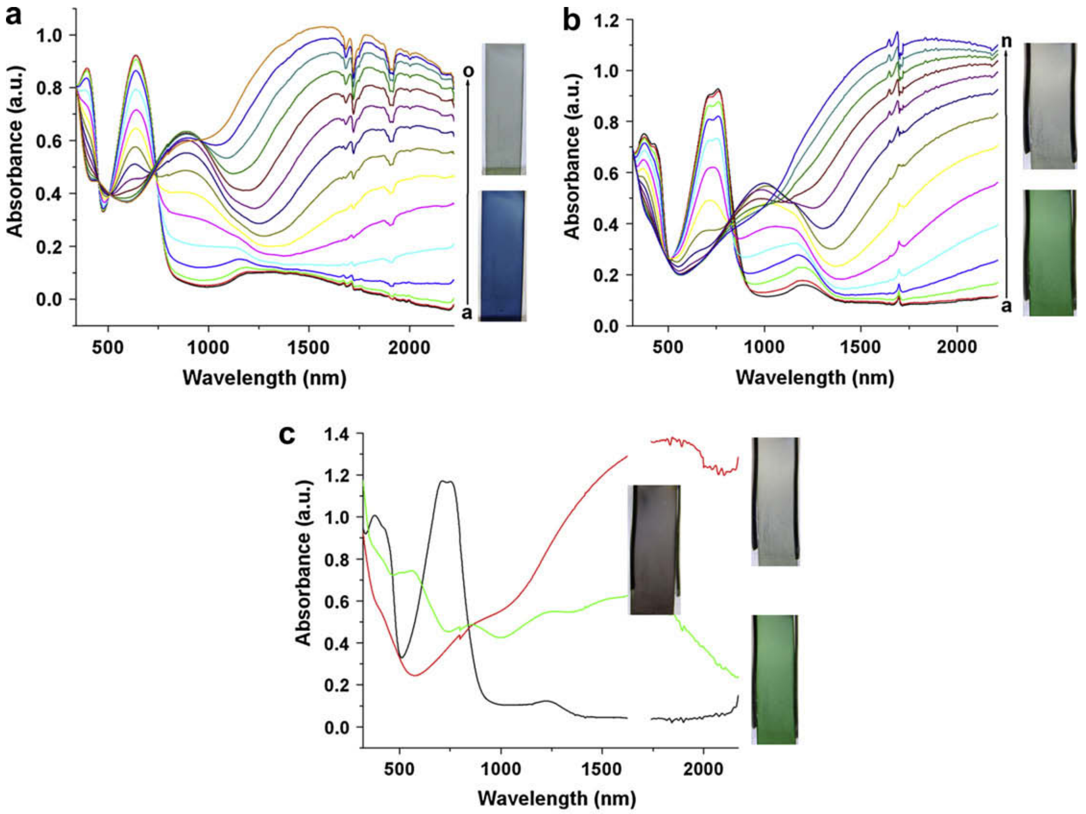

Fig. 4. a. p-Doping spectroelectrochemistry of PDBQTh film on an ITO-coated glass slide in monomer-free, 0.1 M $TBABF_4$/DCM electrolyte–solvent couple at applied potentials (V); (a) −0.1, (b) 0.0, (c) 0.1, (d) 0.2, (e) 0.3, (f) 0.4, (g) 0.5, (h) 0.6, (i) 0.7, (j) 0.8, (k) 0.9, (l) 1.0, (m) 1.1, (n) 1.2, (o) 1.3; b. p-Doping spectroelectrochemistry of PDBQEd film on an ITO-coated glass slide in monomer-free, 0.1 M $TBABF_4$/DCM electrolyte–solvent couple at applied potentials (V); (a) −0.2, (b) −0.1, (c) 0.0, (d) 0.1, (e) 0.2, (f) 0.3, (g) 0.4, (h) 0.5, (i) 0.6, (j) 0.7, (k) 0.8, (l) 0.9, (m) 1.0, (n) 1.1; c. n-Doping spectroelectrochemistry of PDBQEd at −0.2 V, −1.7 V and +1.1. V.

for PDBQEd. The electron donating effect of EDOT group seems to be verified since the p-doping wave of PDBQEd appears at a 0.15 V less positive potential than for PDBQTh. Reduction of the polymers evolved at +0.60 V for PDBQTh and +0.43 V for PDBQEd vs same reference electrode.

The scan rate dependence of the anodic and cathodic peak currents was studied in a monomer-free electrolyte solution (Fig. 3a and b). A linear relationship between the peak current and scan rate demonstrates that the films were well adhered and the electrochemical processes are reversible and non-diffusion-controlled.

As shown in Fig. 3b, the PDBQEd film gives rise to an electrochemically active cycle in the reduction region. A sharp reversible peak corresponding to reversible n-doping of PDBQEd appears at −1.35 V and the corresponding n-dedoping peak appears at −1.14 V vs Ag wire. In contrast with the n-doping/dedoping process, the current associated with the p-doping in the oxidation process of PDBQEd is very small. The results suggest that PDBQEd is a strong electron acceptor and a good n-type conjugated polymer.

Table 1
Measured potentials and calculated band gaps.

	Ox. pot. (V)	Red. pot. (V)	Red. pot. (V)[a]	HOMO (eV)[b]	LUMO (eV)[b]	Eg (eV)[b]	Eg (eV)[c]
DBQTh	+1.0	–	–	–	–	–	–
DBQEd	+0.7	–	–	–	–	–	–
PDBQTh	+0.7	+0.6	–	−5.0	–	–	1.5
PDBQEd	+0.55	+0.43	−1.35	−4.85	−3.50	1.35	1.3

[a] During n-doping.
[b] Calculated from CV measurements (onset potentials).
[c] Spectroelectrochemistry measurements.

3.3. *Spectroelectrochemistry*

Spectroelectrochemical measurements were performed in order to define the changes in optical properties that accompany the redox switching for PDBQTh and PDBQEd. For these measurements, polymer films were electrochemically deposited on ITO-coated glass plates from 1×10^{-3} M monomer solutions in 0.1 M $TBABF_4$/ACN/DCM. The optical changes were investigated by UV–Vis-NIR spectroscopy in $TBABF_4$/DCM electrolytic system by increasing the applied potential.

The evolution of the electronic band structure during electrochemical p-doping of electrochromic polymers were recorded as a function of applied potential and shown in Fig. 4.

In the neutral state, PDBQTh absorbs across the entire visible region, exhibiting blue color with an optical band gap of 1.5 eV as calculated from the onset of the π–π^* transition.

Upon doping, the interband transition decreases, and two new optical transitions (at 896 and 1560 nm) appear at lower energy, corresponding to the polaronic and bipolaronic charge carriers (Fig. 4a). The absorption is enhanced at lower energies.

Table 2
Colorimetry results.

	Color	*Y*	*x*	*y*
PDBQTh	Blue (−0.1 V)	470	0.253	0.296
	Transmissive (+1.3 V)	915	0.302	0.331
PDBQEd (p-doped)	Green (−0.2 V)	486	0.293	0.406
	Transmissive gray (+1.1 V)	293	0.314	0.339
PDBQEd (n-doped)	Red-purple (−1.7 V)	299	0.330	0.340

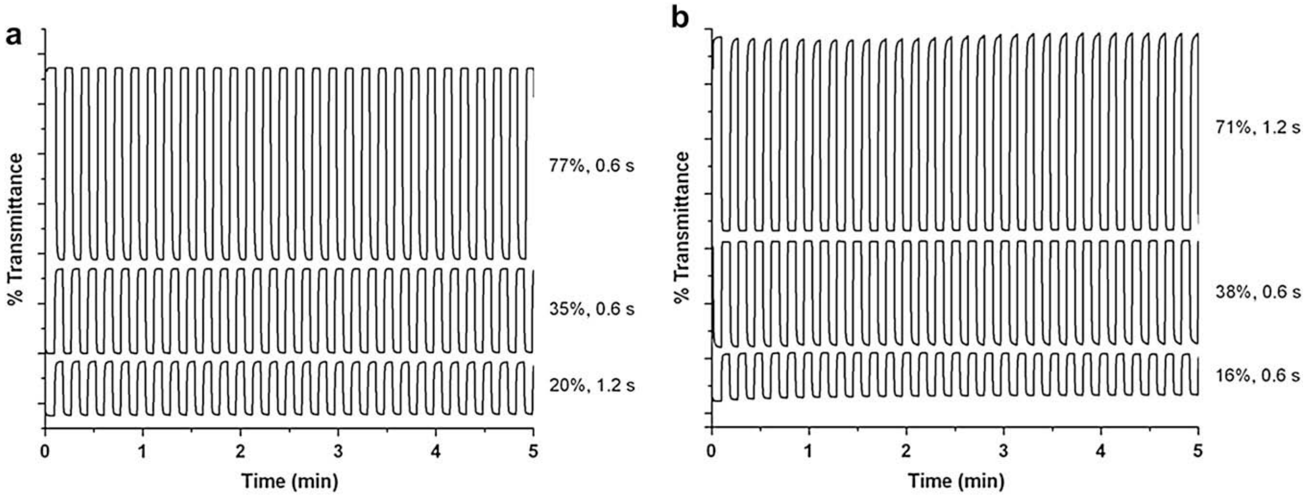

Fig. 5. a. Electrochromic switching and optical absorbance change monitored at 395, 630 and 1560 nm for PDBQTh in 0.1 M $TBABF_4$/ACN. b. Electrochromic switching and optical absorbance change monitored at 423, 738 and 1780 nm for PDBQEd in 0.1 M $TBABF_4$/ACN.

As seen from Fig. 4b, for PDBQEd two well-separated absorption maxima were centered at 423 and 738 nm which is a necessity to maintain a green reduced state. The intensity of both absorption bands decreases and a new absorption band in the NIR region arises due to the formation of charge carriers upon oxidation of the PDBQEd. The band gap calculated from the onset π–π^* transition is 1.3 eV.

Both polymers show absorptions at around 1200 nm in their neutral state which may indicate that the films can not be fully reduced. Both polymers show similar absorption patterns in the UV–vis region with a somewhat better resolved vibronic structure for PDBQEd probably due to an increased planarity (Table 1).

The color changes were further investigated by colorimetry using the CIE 1931 *Yxy* color space to define color precisely. The DBQTh becomes blue (*Y*, 470; *x*, 0.253; *y*, 0.296) in the neutral state, while the oxidized state is transmissive (*Y*, 915; *x*, 0.302; *y*, 0.331). PDBQEd film changed from a green neutral state (*Y*, 486; *x*, 0.293; *y*, 0.406) to a transmissive gray oxidized state (*Y*, 293; *x*, 0.314; *y*, 0.339).

Our studies showed that PDBQEd film was n-dopable due to high capacity to stabilize negative charge on the polymer chain with the presence of a better donor–acceptor match.

That is to say hybridization between the energy levels, especially the HOMO of the donor and the LUMO of the acceptor plays an important role.

The optical change that occurs during the n-doping of the polymer was examined to prove the introduction of charge carries to the conjugated system (Fig. 4c). The reductive absorption spectrum of DPQEd was recorded at −1.7 V, which is the cathodic potential of the redox couple observed in the reduced state. The PDBQEd film shows a green color at its neutral state and turned to red-purple (*Y*, 299; *x*, 0.33; *y*, 0.34) at its n-doped state after reduction (Table 2).

3.4. Electrochromic switching studies

Electrochromic switching studies were carried out to obtain an insight into changes in the optical contrast with time during repeated potential stepping between reduced and oxidized states. In these studies, the transmittance (%T) of the polymer films was recorded as a function of time at constant wavelengths.

Fig. 5a shows the switching of PDBQTh between −0.1 and + 1.3 V with a switching interval of 5 s in 0.1 M $TBABF_4$/ACN at three different wavelengths. In this instance, both the fully oxidized and fully reduced states are reached as evidenced by the leveling off of the optical response. At 395 nm, the optical contrast for PDBQTh was calculated as 20% and the switching time was 1.2 s. The polymer switches rapidly and achieves 35% and 77% of its total optical change in 0.6 s at 630 and 1560 nm, respectively.

PDBQEd was switched from −0.2 V to +1.1 V at 5 s step intervals in 0.1 M $TBABF_4$/ACN while the change in transmittance was monitored. The optical contrasts for PDBQEd were calculated as 16% at 423 nm, 38% at 738 nm, and 71% at 1780 nm. PDBQEd revealed switching times of 0.6 s at 423 nm and 738 nm, 1.2 s at 1780 nm (Fig. 5b).

4. Conclusion

Target monomers based on 2-(2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-8-yl)quinoxaline as the common acceptor unit were synthesized to understand the effects of donor strength on the optoelectronic and redox properties of the resulting electropolymerized materials. The electrochemical cyclic voltammograms of the polymers showed a distinct reversible redox peaks. The band gap of the resulting polymers was found from the investigation of optical absorption properties of PDBQTh and PDBQEd. A stronger donor EDOT unit with the quinoxaline derivative as an acceptor unit has lower band gap relative to the thienyl derivative. Also, a donor–acceptor–donor type of π-conjugated polymer contains electron-rich EDOT as donor moiety has the possibility of being n-type doped. The PDBQEd film showed a color change between green at neutral state and gray at reduced (n-doped) state.

Acknowledgments

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