

Synthesis and Properties of Polymer from Bis-3,4-ethylenedioxythiophene Substituted Acenaphthenequinoxaline

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ABSTRACT: A new electrochromic polymer poly(8,11-bis(3,4-ethylenedioxy thiophen-2-yl)acenaphtho[1,2-b]-quinoxaline) (PBEAQ) was synthesized by electrochemical polymerization of the corresponding monomer (BEAQ) in a 0.1 M tetraethylammonium tetrafluoroborate (TEABF₄) dichloromethane–acetonitrile (2 : 1, v : v) solution. The monomer and polymer were characterized by elemental analysis, ¹H-NMR, IR, and UV-vis spectroscopy. The electrochemical and optical properties of polymer were investigated by cyclic voltammetry and UV-vis spectroscopy. Cyclic voltammetry and spectroelectrochemistry studies

demonstrated that the polymer can be reversibly reduced and oxidized (both *n*- and *p*-doped) between -2 V and $+1.5$ V vs. Ag/Ag⁺. The polymer had a transmissive light blue color in the oxidized state and reddish color in the reduced state. Undoped polymer shows UV-vis absorption peaks at 615 nm in solution, 650 nm in solid state, and has an optical band gap of 1.5 eV. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 74–80, 2010

Key words: electrochemical polymerization; spectroelectrochemistry; quinoxaline; 3,4-ethylenedioxythiophene

INTRODUCTION

Conducting polymers still remain a subject of intense investigation since their discovery¹ because these materials have great potentials in many applications, such as batteries,² light-emitting diodes,³ sensors,⁴ and electrochromic devices.⁵ Electrochromic polymers belong to an important class of conducting polymers, which are able to change colors in response to electronic signals. Conducting polymers became great candidates for electrochromic devices due to the advantages of short switching time, high optical contrasts,^{6,7} and easy tuning of color by changing the structure.⁵ Although a large portion of conducting polymers has colors both in oxidized and reduced states, their relatively high band gap makes it difficult to use them in electrochromic devices.

One successful strategy to achieve low band gap is the “donor–acceptor” approach.⁸ The presence of electron acceptor and electron donor substituents in the same polyconjugated backbone results in a lower band gap due to an intrachain charge transferred from donor to acceptor unit.^{9,10} Besides the “donor–acceptor” interacting factor, several other factors, such as aromaticity, substituent’s effects, intermolec-

ular interactions, and π -conjugation length influence the band gap of conjugated polymers.¹¹

Among the conducting polymers, polymers comprising 3,4-ethylenedioxythiophene (EDOT) unit in the conjugated backbone proved to be exceptional choices for electrochromic applications.¹² Association of EDOT as electron donating system with some of the acceptor groups could lead to polymers with considerable low band gap.¹³ Meanwhile, compounds with quinoxaline aromatic rings which have an electron-deficient nature are used as raw materials for organic light-emitting devices, light-emitting cells, and optoelectronic devices.^{14,15}

Several articles have been published on electrochromic polymers from EDOT or thiophene- bis-substituted quinoxalines.^{16–20} These reports were mainly focused on the increase of the solubility of the resulted polymer. Here we chose a planar fused aromatic ring-substituted quinoxaline derivative as an acceptor with EDOT donor unit for the purpose of increasing aromaticity, π -conjugation length or planarity of the polymer, which may result in low band gap.^{11,21–23}

EXPERIMENTAL

Materials

All the chemicals used were of analytical grade, were obtained from ACROS (China) Chemical Co. and used

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as received unless otherwise stated. THF was distilled over sodium at the presence of benzophenone under an atmosphere of dry nitrogen, and was degassed before use. Acetonitrile (ACN) was distilled from P_2O_5 and kept under nitrogen atmosphere, dichloromethane (DCM) was distilled over calcium hydroxide before use. Acenaphthylene-1,2-dione was recrystallized from ethanol before use. 1,4-dibromo-2,3-diaminobenzene (1),²⁴ 5,8-dibromo[2,3-b]phenanthrenequinoxaline (2),²⁵ and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (3)²⁶ were synthesized according to the previously published procedures.

Instrumentation

A CHI660C electrochemical workstation (CH Instruments, China) was used for electrochemical studies in a three-electrode cell consisting of an indium tin oxide coated glass slide (ITO) (2.7 cm²) or platinum button (1 cm²) as the working electrode, Pt as the counter electrode, and an Ag/Ag⁺ as the reference electrode. Electropolymerization of monomer (1.2 mM) was performed in a 0.1 M TEABF₄ DCM:ACN (2 : 1, v : v) solution at a scan rate of 100 mV/s for 50 cycles, and applying potentials were controlled between 0 and 1.3 V. UV-vis absorption spectra and electrochromic properties were recorded on a Shimadzu UV-2450 UV-Vis spectrophotometer. FTIR spectra of the copolymers were obtained by using a Bruker Einox-55 Fourier transform infrared spectrometer (frequency range 4000–500 cm⁻¹). ¹H-NMR spectra were collected on a Varian Inova-400 spectrometer operating at 400 MHz in deuterated chloroform solution with tetramethylsilane as reference. Elemental analyses were made on a FLASH EA series 1112 NCHS-O analyzer.

Synthesis

8,11-Bis(3,4-ethylenedioxythiophen-2-yl)acenaphtho[1,2-b]quinoxaline (BEAQ)

5,8-Dibromo[2,3-b]phenanthrenequinoxaline (1.5 g, 3.6 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (3.1 g, 7.2 mmol) were dissolved in dry THF (120 mL), the solution was purged with dry nitrogen for 15 min and PdCl₂(PPh₃)₂ (0.26 g, 0.37 mmol) was added at room temperature and then the mixture was refluxed under nitrogen atmosphere for 24 h. After cooling the reaction mixture to room temperature it was concentrated, and subjected to column chromatography (1 : 1 DCM : hexane) to give the target compound as reddish orange solid (780 mg, 41%). mp > 250°C (air), FTIR (KBr, cm⁻¹): 3100, 3060, 2923, 2867, 1646, 1537, 1490, 1205, 982, 870, 823. ¹H NMR (400 MHz, CDCl₃): δ: 4.34 (m, 4H), 6.63 (s, 1H), 7.86 (t, 1H, J = 7.2 Hz), 8.12 (d, 1H, J = 8.4 Hz), 8.48 (d, 1H, J = 6.8 Hz), 8.63 (s, 1H). Anal. Calcd for

(C₃₀H₁₈N₂O₄S₂): C, 67.40; H, 3.39; N, 5.24; S, 12.00. Found: C, 67.25; H, 3.28; N, 5.43; S, 11.90. MS (ESI): *m/e* 535 (M + H)⁺. UV-vis (CHCl₃) λ: 325, 462 nm.

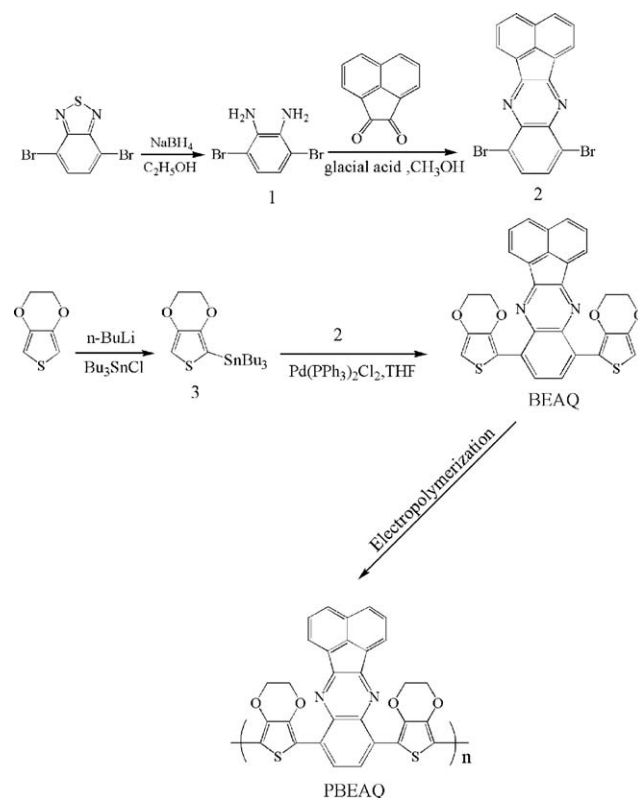
RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic route to the monomer and polymer was showed in Scheme 1.

The reagent 4,7-dibromobenzo[c][1,2,5]thiadiazole was reduced with NaBH₄ to yield 72% of 1,4-dibromo-2,3-diaminobenzene (1) as previously described method,²⁴ and its condensation reaction with acenaphthylene-1,2-dione in methanol in the presence of glacial acid was performed to give quinoxaline derivatives (2) in high yield (86%).²⁵ Stannylation of EDOT (3) was achieved in two steps according to previously reported procedure²⁶ in good yield (81%, determined from ¹H-NMR spectrum) and used without further purification. The Stille coupling reaction of 2 and 3 was performed in dry THF with PdCl₂(PPh₃)₂ as the catalyst under dry nitrogen atmosphere in a moderate yield.

¹H-NMR spectrum of the monomer is shown in Figure 1. All of the detected peaks are consistent with the proposed structure. The protons in the ethylenedioxy group are detected at δ = 4.44–4.32 ppm (8H, m, Hb, and Hc). The protons of a position from



Scheme 1 Synthetic route of the monomer and polymer

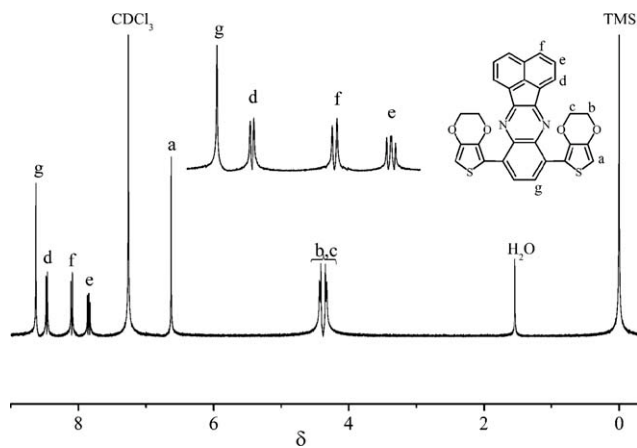


Figure 1 $^1\text{H-NMR}$ spectrum of monomer.

EDOT rings appear at $\delta = 6.63$ ppm (2H, s, Ha). The signals at 8.63 (2H, s, H g), 8.48 (2H, d, H d), 8.10 (2H, d, H f), and 7.84 (2H, t, H e) belong to the Hg, Hd, Hf, and He of acenaphthenequinoxaline ring, respectively.

Figure 2 presents the IR spectra of monomer and polymer. The reduced number of vibration modes and broad peaks in the spectrum of polymer compared to monomer spectrum could be attributed to the existence of additional symmetry in the chemical structure of the repeating units.²⁷ $\text{C}_\alpha\text{-H}$ (EDOT α position) stretching band observed at 3100 cm^{-1} for the monomer was absent in the spectrum of the polymer, this indicated that the polymerization had taken place at EDOT α position.²⁸ The bands at $1200\text{--}1000\text{ cm}^{-1}$ [Fig 2(a-c)] were assigned to the stretching vibration of the C-O-C bond in the ethylenedioxy group and the absorption band at 826 cm^{-1} proved

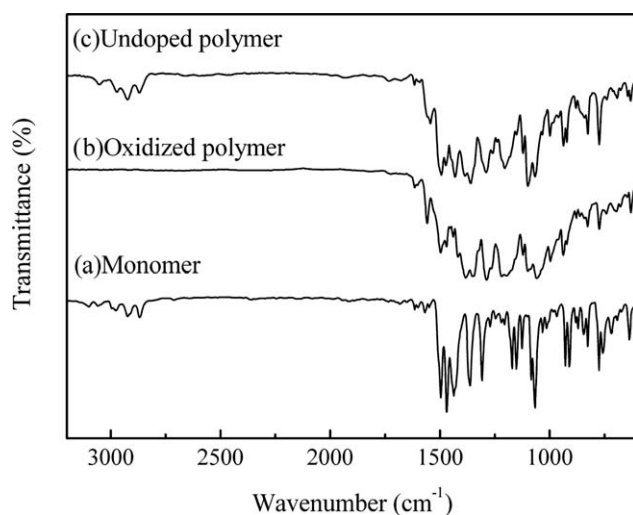


Figure 2 IR spectra of monomer and polymer. (a) monomer (BEAQ), (b) *p*-doped polymer (electrochemically oxidized in 0.1 M TEABF_4 DCM-ACN (2 : 1, v : v) solution), and (c) undoped PBEDAQ (electrochemically oxidized polymer after treated with hydrazine).

the existence of a 1,2,3,4-tetrasubstituted benzene ring. Spectral changes between the doped and undoped polymer were observed with the changes of $\nu(\text{C-H})$ peaks of the ethylenedioxy side chain. In the case of *p*-doped polymer (b), the disappearance of the aliphatic $\nu(\text{C-H})$ absorption peaks of ethylenedioxy unit suggests that the *p*-doping leads to great changes in electronic state of ethylenedioxy unit. Similar IR changes of $\nu(\text{C-H})$ peaks have been reported for *p*-doped poly(3,4-ethylenedioxy thiophene)²⁹ and poly(3-alkoxy thiophene).³⁰ Miller and Mann³¹ also reported that a *p*-dopant (PF_6^-) can locate near an alkyl side chain of a *p*-doped alkyl-substituted oligothiophene which is investigated by X-ray crystallography.³¹

Optical properties

Figure 3 shows UV-vis spectra of the monomer and electrochemically oxidized polymer in solution and film state (mainly the lower-energy peak). Both monomer and polymer give two distinct absorption peaks. For monomer, the first peak appears at 320 nm in solution and 400 nm in solid state (film), while the second peak appears at 462 nm in solution and 515 nm in solid state. The former peak is assigned to a $\pi\text{-}\pi^*$ transition and the lower-energy peak is mainly associated with electronic transition from the end-capping EDOT donor rings to the central electron withdrawing acenaphthenequinoxaline unit, which may form CT-type structure.³² Thus, the optical data reveals that this π -conjugated trimer has a small HOMO-LUMO separation. For polymer, the lower-energy peak occurred at 615 nm indicates that it has an expanded π -conjugated system. Film of the polymer shows UV-vis peak at a longer wavelength,

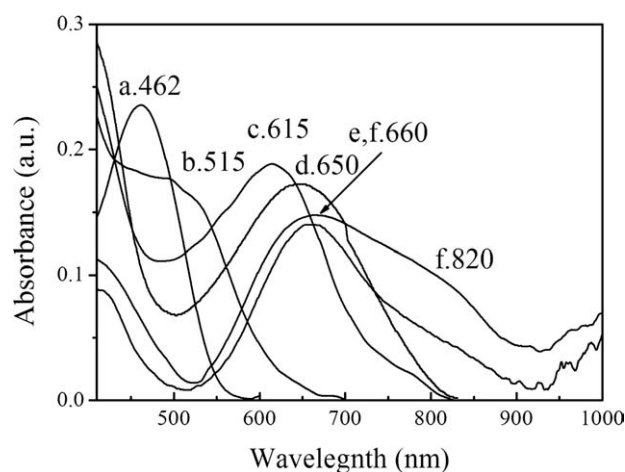


Figure 3 UV-vis spectra of monomer and polymer. (a) monomer in DMSO, (b) monomer in film state, (c) undoped polymer in DMSO, (d) undoped polymer film on ITO glass slide, (e) *p*-doped polymer in DMSO, (f) *p*-doped polymer film on ITO glass slide.

suggesting the presence of certain intermolecular electronic interaction in solid state.³³ lower-energy. The optical band gap of the polymer is calculated as 1.5 eV according to the onset position (815 nm) of the lower-energy peak of undoped polymer film. As shown by curves (e) and (f) in Figure 3, *p*-doped polymer exhibits an absorption maxima (λ_{max}) at ca. 660 nm both in solution and solid (film) states. However, *p*-doped polymer film gives a shoulder at ca. 820 nm, due to the presence of certain intermolecular interaction.^{29,33} Interestingly, the doped polymer film gives no shift, while undoped polymer film has a red shift of 35 nm resulting from the presence of *p*-dopant (BF_4^-) in doping polymer structure. UV-vis spectra of *p*-doped polymer both in solution and solid states give absorption onset at a lower-energy band than the dedoped polymer's (c,d), and give a free-carrier tail extending into the infrared which is typical for a conducting polymer.³⁴

Electrochemistry

The redox behavior of BEAQ (6 mM) was tested in 0.1 M TEABF_4 DCM solution with one circle scanning between -2.5 and $+2.5$ V at the scan rate of 100 mV/s (Fig. 4, scatter line), and deep green thin film of polymer was obtained on Pt working electrode due to the reactivity of the radical cation formed at 0.73 V (Fig. 4, scatter line).³⁵ The cyclic voltammetry of the formed polymer film was carried out using the same electrode set up in a monomer-free 0.1 M TEABF_4 acetonitrile solution at 100 mV/s scan rate (Fig. 4, solid line).

In Figure 4 the onset oxidation potential of monomer was observed at 0.73 V . A similar quinoxaline derivative¹⁹ namely, 8,11-bis(4-hexylthiophen-2-yl)-

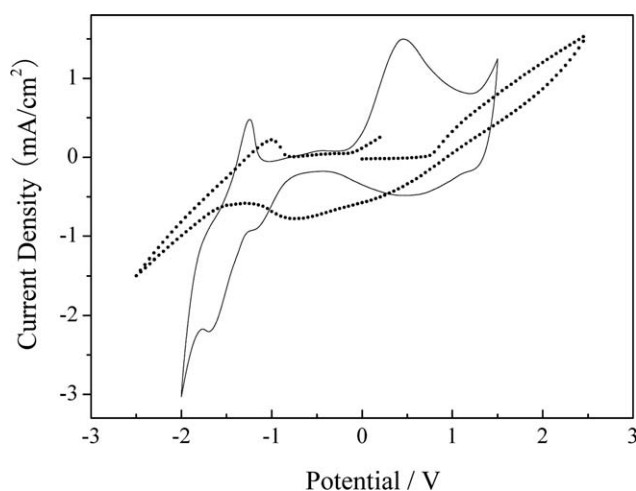


Figure 4 CV of BEAQ (scatter line) in 0.1 M CDM/ TEABF_4 and corresponding polymer (solid line) in a monomer-free 0.1 M ACN/ TEABF_4 solution at 100 mV s^{-1} .

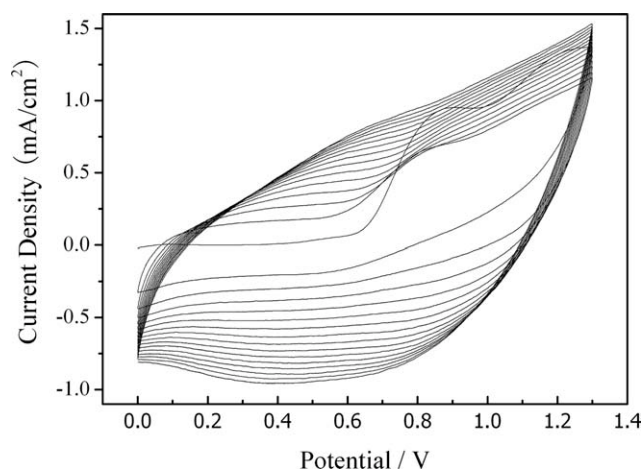


Figure 5 Electrochemical synthesis of PBEAQ in 0.1 M TEABF_4 DCM-ACN (2 : 1, v : v) at 100 mV s^{-1} scan rate on Pt working electrode.

acenaphtho-[1,2-b]quinoxaline (HTAQ) has a monomer oxidation potential of 1.1 V , which was the result of a better donor-acceptor match because EDOT has higher donor capacity than thiophene. In the negative potential interval, a reversible reduction peak was appeared at -0.73 V which was most likely the one-electron reduction of the quinoxaline ring, indicating stable radical anion.^{8,36} The monomer has a calculated electrochemical band gap of 1.43 eV (difference between onset potentials of oxidation and reduction) and this value is 2.3 times lower than bis-3,4-ethylenedioxythiophene (BEDOT) (3.93 eV ³⁷), and rather close to PEDOT (1.35 eV ³⁸). The CV of the polymer film (Fig. 4, solid line) clearly exhibits reversible characteristic broad redox waves of the EDOT backbone of the polymer³⁵ at 0.45 V (oxidation) and 0.40 V (broad, reduction). By scanning negative potential, the reversible reduction peak at -1.68 V was observed. The polymer has an electrochemical band gap of 1.2 eV and this value is little lower than the calculated optical band gap. Calculated electrochemical and optical band gap of the polymer are lower than that of PEDOT as expected, but in comparison to monomer, the decreasing value of polymer's band gap was not distinct and it might be associated with lower π -conjugated degree of PBEAQ.

Oxidative polymerization of BEAQ ($1.2 \times 10^{-2} \text{ M}$) was carried out by potentiodynamic cycling on Pt electrode in 0.1 M TEABF_4 solution. DCM-ACN (2/1, v/v) mixture was chosen as the solvent because of the very poor solubility of the monomer in pure ACN. The growth of the polymer (Fig. 5) on working electrode is reflected by gradually increasing currents in subsequent potential cycling.^{36,39} The onset oxidation potential of monomer (Fig. 5, first scan) was observed at 0.65 V , which is little lower than that of observed in Figure 4 (scatter line), and it

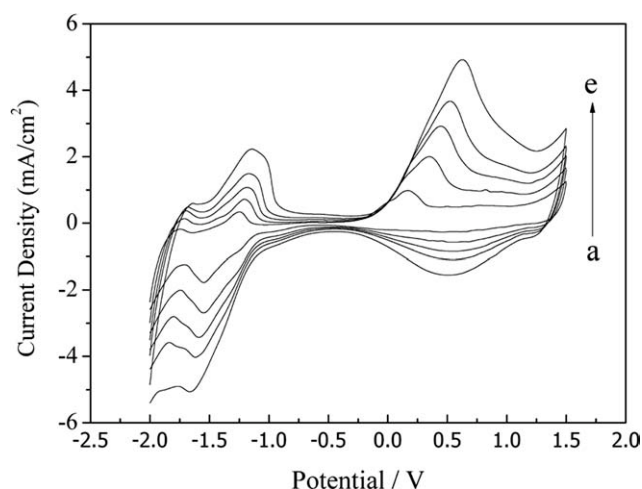


Figure 6 CVs of PBEAQ in monomer-free 0.1 M TEABF₄ ACN solution at different scan rate (a) 50, (b) 100, (c) 150, (d) 200, and (e) 300 mV s⁻¹.

is due to the different monomer concentrations of the two systems.

The CV of the electrocoated polymer film was taken in monomer-free 0.1 M TEABF₄ acetonitrile solution (Fig. 6). The polymer is electrochemically active in both anodic and cathodic regions. Two reversible redox couples at 0.35 V, 0.30 V (broad) and -1.60 V, -1.19 V were observed for the *p*- and *n*-type doping and dedoping processes respectively. These peaks' potential values were little different from the values observed in Figure 4 (solid line), which is probably resulted from the different potential interval used in oxidation process of the monomer.

The dependence of the anodic and cathodic peak currents at the scan rates (between 50 and 300 mV/s) is shown in Figure 6. A linear relationship was found between the peak current and the scan rate both for *p*- and *n*-doping, which indicates that the film was well-adhered and charge transfer process was not dominated by diffusion according to previous reports.^{40,41}

Spectroelectrochemistry

Spectroelectrochemistry experiments were performed to investigate the optical changes upon doping process. For optoelectrochemical studies, after homogeneous polymer film was electrochemically deposited on ITO coated glass slide, UV-Vis spectra were taken in a 0.1 M TEABF₄/ACN solution at various potentials to monitor the changes in absorbance when the polymer film was oxidized or reduced. As shown in Figure 7(a), stepwise oxidation of the polymer film shows the fading of absorption at ca.435 and 670 nm whereas the evolution of an absorbance peak corresponding to polaronic band is observed at ca.920 nm. Meanwhile the color of the polymer film

changes from more green to transmissive light blue. PBEAQ film gives double π - π^* transitions due to the presence of acenaphthenequinoxaline acceptor unit in PBEAQ back bone while PEDOT has one π - π^* transition, and this kind of polymer belongs to neutral state green materials.¹⁶

The reduction of a polymer is not necessarily an *n*-doping process. Electrochemical behavior in the cathodic region cannot be a direct evidence for *n*-type doping. To state that the process is *n*-type doping, after the introduction of charge carries to conjugated system there should be considerable differences in structure, conductivity, and optical properties. Thus, to be able to demonstrate the presence of *n*-type doping process, spectroelectrochemistry or *in situ* conductivity measurements should be studied.^{16,42} Similar to *p*-doping studies, spectroelectrochemistry was performed to probe the optical changes that occurred during the *n*-doping of the polymer

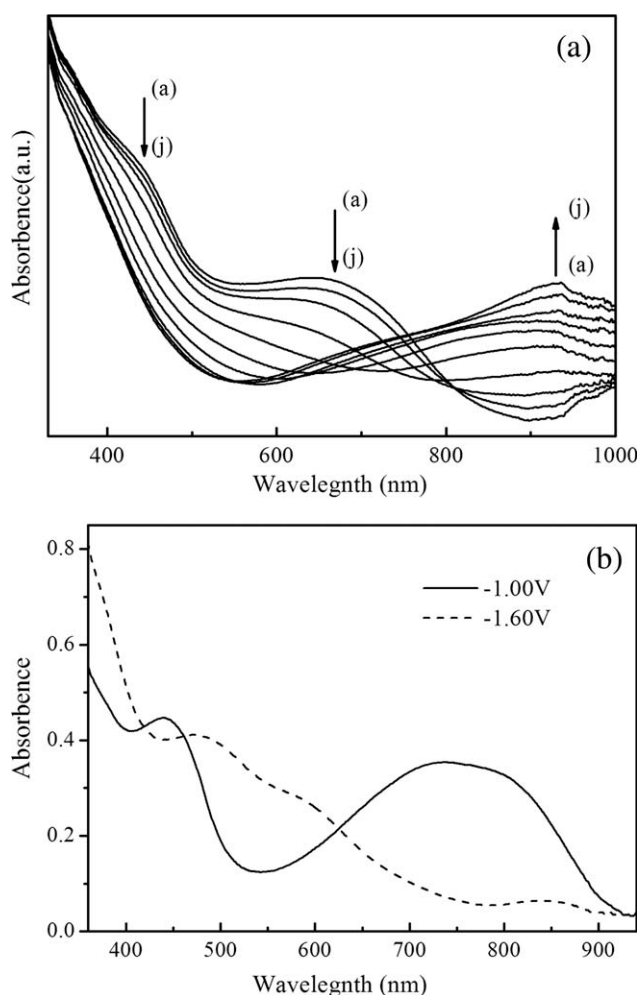


Figure 7 Spectroelectrochemistry of PEDAQ film on an ITO coated glass slide in monomer-free, 0.1 M TEABF₄/ACN electrolyte-solvent at applied potentials (V). a. *p*-Doping (a) -0.4, (b) -0.2, (c) 0.0, (d) +0.2, (e) +0.4, (f) +0.6, (g) +0.8, (h) +0.9, (i) +1.0, and (j) +1.1 V; b. *n*-Doping.

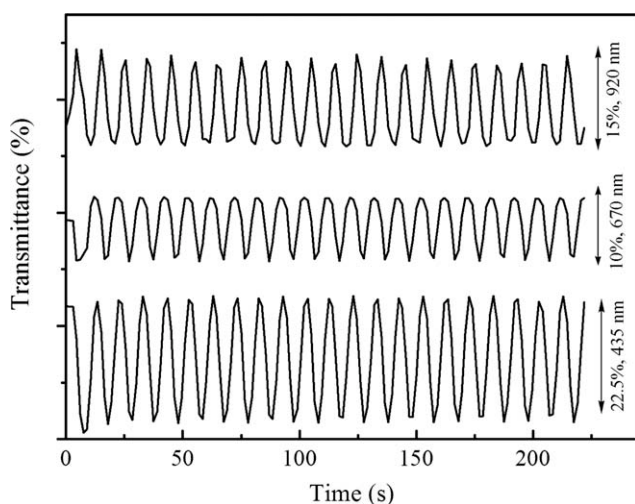


Figure 8 Electrochromic switching, optical absorbance changes monitored at 435, 670, and 920 nm in TEBAF₄/ACN solution.

[Fig. 7(b)]. For PBEAQ the absorption spectrum was recorded at -1.6 V, which was the potential of the redox couple observed in the reduced state. The optical spectrum was drastically changed to produce a reddish color. It could be concluded that charge carriers were formed and a true n-type doping process occurred.

Kinetic studies

Optical switching studies were examined for probing changes in transmittance with time while repeatedly stepping the potential between reduced and oxidized states. Throughout the experiment, the percent transmittance ($T\%$) values at different wavelengths were measured using a UV-vis spectrophotometer as the polymer film was switched between -0.4 V and $+1.2$ V with a residence time of 5 s. The results are shown in Figure 8. The optical contrasts for PBEAQ were calculated as 22.5% at 435 nm, 10% at 670 nm, and 15% at 920 nm. PBEAQ switches between its reduced and oxidized states in 1.5 s at both absorption maxima (435 and 670 nm) where PEDOT needs at least 2.2 s to achieve full switching.

CONCLUSION

In summary, a new EDOT-substituted acenaphthene-quinoxaline was synthesized via Stille coupling reaction, which has a low oxidation potential of 0.73 V vs. Ag/Ag^+ , and was electrochemically polymerized. Undoped polymer shows UV-vis absorption peaks at 615 nm in solution, 650 nm in film state, and has a calculated optical band gap of 1.5 eV. The electrochemically coated polymer film exhibited electrochromic behavior upon p - and n -doping. The film color changed from more green (neutral) to trans-

missive light blue in the oxidized state and reddish in the reduced state. PBEAQ was shown to be neutral state green polymeric material. Considering these advanced properties, PBEAQ can be utilized in electrochromic device applications.

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