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New, Highly Stable Electrochromic Polymers from 3,4-Ethylenedioxythiophene−Bis-Substituted Quinoxalines toward Green Polymeric Materials

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Two new highly stable electrochromic polymers, poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline) (PDETQ) and poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (PDEQ) were synthesized, and their potential use as neutral state green polymeric materials was investigated. Spectroelectrochemistry showed that both polymers reveal two distinct absorption bands as expected for this type of donor–acceptor polymer, at 410 and 660 nm for PDEQ and 405 and 780 nm for PDETQ. The colorimetry analysis revealed that while PDEQ has a green-blue color, PDETQ showed a saturated green color in the neutral state which is a unique property of conjugated polymers for the completion of the RGB color system. Both polymers have excellent switching properties with satisfactory optical contrasts and very fast switching times. In addition, via both electrochemical and spectral analyses PDETQ was proven to be an n-type dopable polymer. Outstanding optical contrasts in the NIR region, perfect stability, and fast switching times make these polymers excellent candidates for many applications like smart windows and data storage technologies. It should be noted that PDETQ is one of the few examples of neutral state green polymeric materials in literature with a relatively transmissive oxidized state, high stability, and superior switching properties. Hence, PDETQ can be a paramount choice as a green polymeric material for display applications.

Introduction

Since their discovery, conducting polymers[1] have been largely studied for different industrial applications, such as sensors,[2] light emitting diodes,[3] solar cells,[4] field effect transistors,[5] and electrochromic devices.[6] Studies in electrochromic devices started with inorganic compounds such as tungsten trioxide (WO_3) and iridium dioxide (IrO_2).[7] Although many inorganic materials have aroused a great deal of interest in industry over the past 30 years, use of conjugated polymers as active layers in electrochromic devices became popular because of their fast switching times,[8,9] high optical contrasts,[10] processibility,[11] and easy tuning of color with alternations in the structure.[12]

According to the past studies performed in conducting polymers research, there is a huge amount of electrochromic polymers reflecting red and blue color in their neutral states whereas only two studies have been reported related to polymers reflecting green color[13,14]. To reflect red or blue color in reduced state, the materials have to absorb at only one dominant wavelength. On the contrary, to have a green color, there should exist at least two simultaneous absorption bands in the red and blue regions of the visible spectrum where these bands should be controlled with the same applied potential.

The transmissivity in the oxidized state is significantly important in addition to the neutral state color of the polymer. The optical contrast between the states is the decisive point for use of these materials for many electrochromic applications, especially as smart windows and displays. Hence, the material should possess two absorption bands with definite maximum points, and upon oxidation these bands should vanish to have a transmissive state. A donor–acceptor approach can be utilized to solve this puzzle. It has been shown that insertion of alternating donor–acceptor units on the polymer backbone leads to a significant decrease in band gap due to the increased double bond character in the structure.[15]

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Low band gap polymers usually reveal a transmissive oxidized state as a result of even lower energy transitions in the doped state. A further advantage of the approach for green polymeric material synthesis is the double $\pi-\pi^*$ transition nature of the ensuing polymers.[16] Hence, polymers synthesized utilizing the donor–acceptor approach are excellent candidates for neutral state green materials. Polymers bearing 3,4-ethylenedioxythiophene (EDOT) units in the conjugated backbone proved to be exceptional choices for electrochromic applications.[17] Because EDOT moieties are effective donors, a strong acceptor group should be inserted into the molecule to ensure a proper donor–acceptor match for band gap reduction. Hence, EDOT was coupled with two different quinoxaline derivatives to produce electroactive monomers. Monomers were electropolymerized to acquire donor–acceptor type conducting polymers, and electrochromic properties of the polymers were investigated in detail. One of the derivatives was shown to be a reduced state green polymeric material with excellent stability, high optical contrast, superior switching properties, and fine transmissivity in the oxidized state.

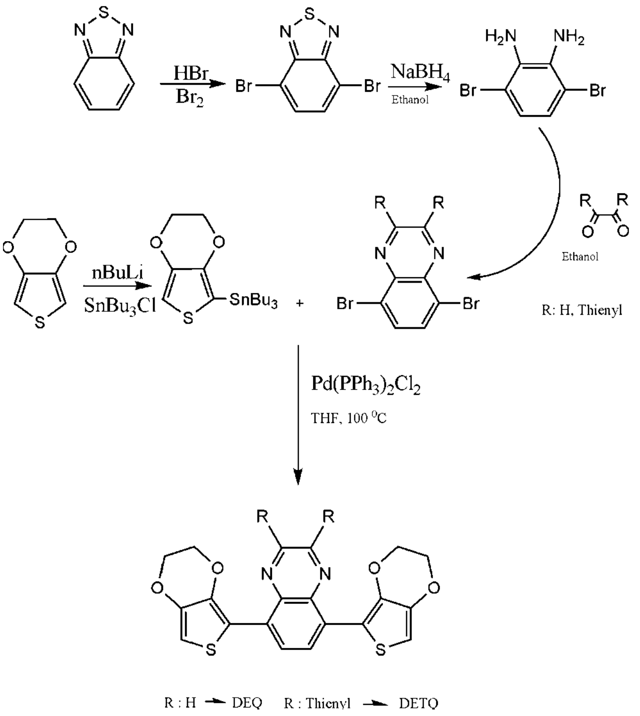
Experimental Section

General Details. All chemicals were purchased from Aldrich. 4,7-Dibromo-2,1,3-benzothiadiazole,[18] 3,6-dibromo-1,2-phenylenediamine,[19] 5,8-dibromoquinoxaline,[20] 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline,[21] and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane[22] were synthesized according to the previously reported methods. Acetonitrile (ACN) was dried and distilled over calcium hydride under nitrogen. All electrochemical studies were accomplished with a Voltalab 50 potentiostat. Electropolymerizations were performed in a three-electrode cell consisting of platinum button or indium tin oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode. The electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (DCM). Electrodeposition was performed from a 0.1 M solution of $TBAPF_6$ at a scan rate of 100 mV/s for 40 cycles.

Cyclic voltammograms of the polymers were obtained using the same electrode setup using monomer-free solution. $TBAPF_6$ was used as the electrolyte in ACN.

UV–vis–NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. A three-electrode cell was utilized consisting of a silver wire pseudo reference electrode, a Pt wire counter electrode, and an ITO coated glass working electrode. The potentials were controlled using a Solartron 1285 potentiostat/galvanostat. Colorimetric measurements were achieved by a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

Scheme 1. Synthetic Route of Monomers DETQ and DEQ



Synthesis. *5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DETQ).* 5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline (200 mg, 0.440 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (948 mg, 2.2 mmol) were dissolved in dry tetrahydrofuran (THF, 80 mL), the solution was purged with argon for 30 min, and $PdCl_2(PPh_3)_2$ (60 mg, 0.85 mmol) was added at room temperature under argon atmosphere. 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 an orange solid (148 mg, yield 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (m, 4 H), 4.28 (m, 4H), 6.5 (s, 2 H), 6.95 (t, $J = 3.97$ Hz 2 H), 7.40 (d, $J = 3.57$ Hz, 2 H) 7.44 (d, $J = 4.8$, 2 H), 8.46 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.35, 63.94, 102.05, 112.04, 126.34, 127.34, 127.48, 128.21, 128.80, 135.56, 139.27, 140.38, 140.68, 142.89. MS: *m*/*e* 574 (M^+).

5,8-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (DEQ). 5,8-Dibromoquinoxaline (200 mg, 0.70 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1502 mg, 3.50 mmol) were dissolved in dry THF (80 mL), the solution was purged with argon for 30 min, and $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) was added at room temperature under argon atmosphere. 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 an orange solid (172 mg, yield 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (m, 4 H), 4.30 (m, 4H), 6.48 (s, 2 H), 8.50 (s, 2 H), 8.85 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.33, 63.93, 101.91, 111.86, 127.71, 128.46, 138.78, 139.30, 140.35, 141.38. MS: *m*/*e* 410 (M^+).

Results and Discussion

Monomer Synthesis. The synthetic route to the monomers is revealed in Scheme 1.

The reagent 2,1,3-benzothiadiazole was brominated with a HBr/Br_2 mixture in high yields and reduced with $NaBH_4$

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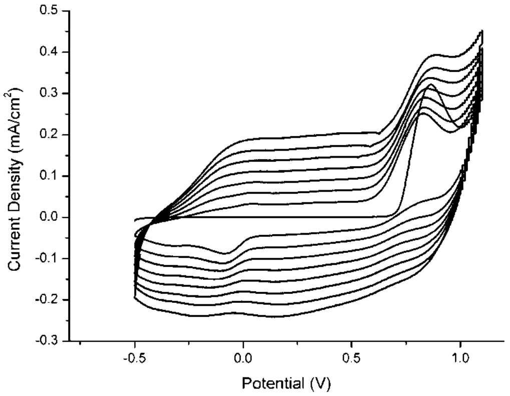

Figure 1. Repeated potential scan electropolymerization of DETQ at 100 mV/s in 0.1 M TBAPF$_6$/DCM on the ITO electrode.

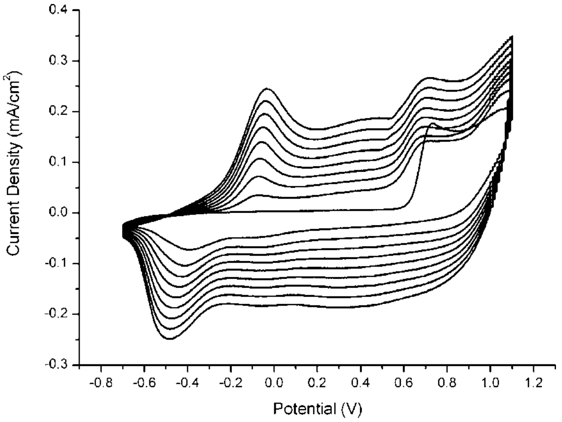

Figure 2. Repeated potential scan electropolymerization of DEQ at 100 mV/s in 0.1 M TBAPF$_6$/DCM on the ITO electrode.

to afford 3,6-dibromo-1,2-phenylenediamine as described previously. Condensation reactions with 2,2-thenil and glyoxal solution (40% in water) in ethanol were performed to give quinoxaline derivatives in high yields. Stannylation of EDOT was achieved in two steps according to previously reported methods. The Stille coupling reaction of dibromoquinoxalines with tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane was performed in dry THF with $Pd(PPh_3)_2Cl_2$ as the catalyst. The reaction proceeded with a short reaction time and relatively high yield to afford the title compounds DETQ and DEQ.

The purity of both monomers was proved with ^{1}H NMR, ^{13}C NMR, and MS analyses. The physical properties of monomers differ slightly form each other. Both monomers are solid in room temperature and have orange color.

Electropolymerization. The potentiodynamic electropolymerizations of monomers (10 mM solutions) were carried out in 0.1 M TBAPF$_6$/DCM supporting electrolyte−solvent couple. The representative electrochemical growth revealing electroactivities of monomers DETQ and DEQ and formation of corresponding polymers are given in Figures 1 and 2, respectively.

The oxidation of DETQ on a bare electrode starts at 0.7 V and reveals a peak at 0.85 V versus Ag wire pseudo reference electrode in TBAPF$_6$/DCM. The lower oxidation potential of DEQ (+0.6 V) can be attributed to the quinoxaline unit with a low acceptor capacity compared to 2,3-di(thiophen-2-yl)quinoxaline. Redox couples for both monomers rapidly grow at relatively low potentials (−0.3 V, −0.01 V for DETQ, and −0.5 V, 0.02 V for DEQ vs same reference electrode) which signifies the formation of highly electroactive polymers. The scan rate dependence of the anodic and cathodic peak currents is illustrated in Figures 3 and 4 for the polymers.

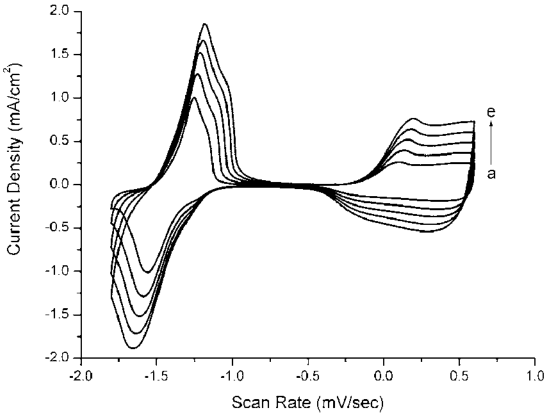

Figure 3. Scan rate dependence of PDETQ film in TBAPF$_6$/ACN at (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 mV/s.

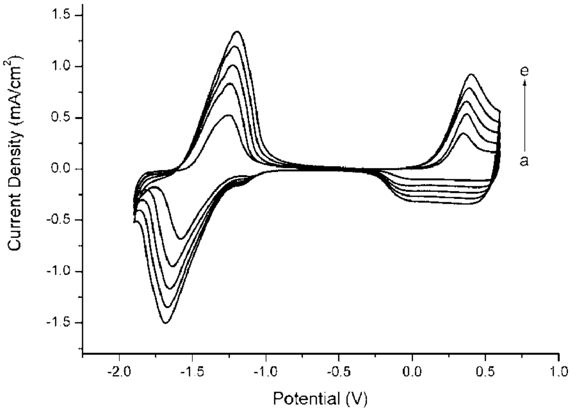

Figure 4. Scan rate dependence of PDEQ film in TBAPF$_6$/ACN at (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 mV/s.

A linear dependence demonstrates that the films were well adhered and the electrochemical processes are reversible and non-diffusion-controlled.[23]

Using cyclic voltammograms of DETQ and DEQ, anodic-to-cathodic peak ratios were calculated. The values are very close to 1.0, which is a significant indication for superior reversibility of the redox processes.

The long-term switching stability between doped and neutral states is a crucial property for electrochromic polymers, because these materials have the potential to be used for commercially important device applications. To investigate this characteristic, PDETQ and PDEQ films were deposited on Pt electrode with repeated scanning in TBAPF$_6$/DCM. The polymer films were washed with monomer-free solution and cycled 5000 times with a scan rate of 200 mV/s in 0.1 M LiClO$_4$/PC (propylene carbonate). The overall charge involved in the electrochemical process was calculated for each voltammogram. Once the polymer electrochemical equilibrations have been reached after 400 cycles, both

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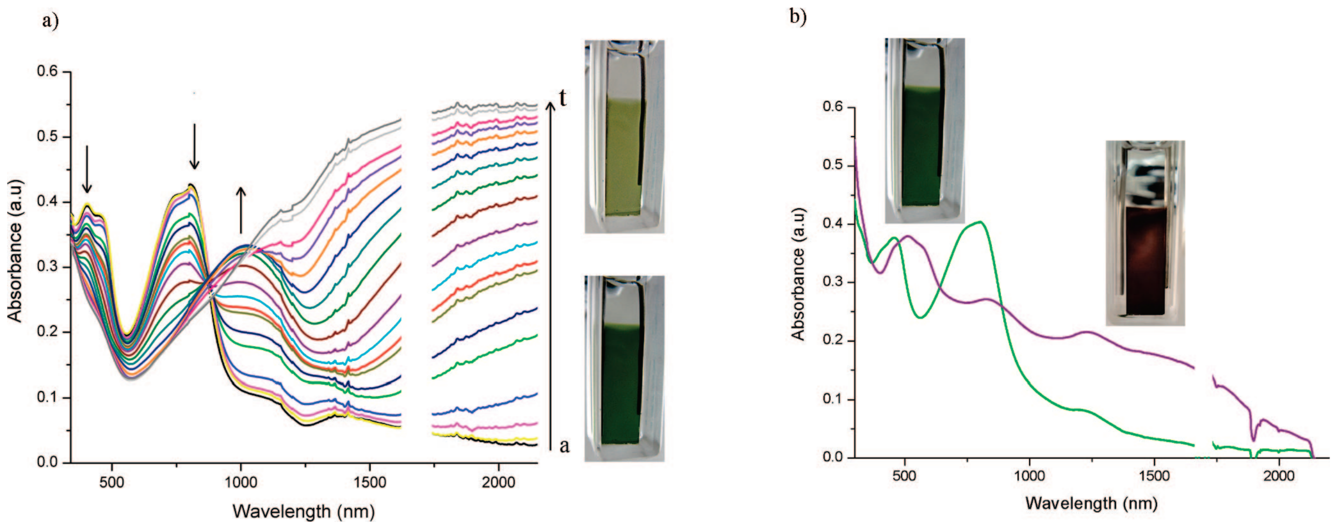

Figure 5. a. p-Doping. Spectroelectrochemistry of PDETQ film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF$_6$/ACN electrolyte−solvent couple at applied potentials (V): (a) −1.0, (b) −0.8, (c) −0.5, (d) −0.4, (e) −0.3, (f) −0.25, (g) −0.2, (h) −0.15, (i) −0.1, (j) −0.05, (k) 0, (l) 0.1, (m) 0.2, (n) 0.3, (o) 0.4, (p) 0.5, (q) 0.6, (r) 0.7, (s) 0.9, and (t) 1.0. b. n-Doping. Spectroelectrochemistry of PDETQ at −1.0 and −1.7 V.

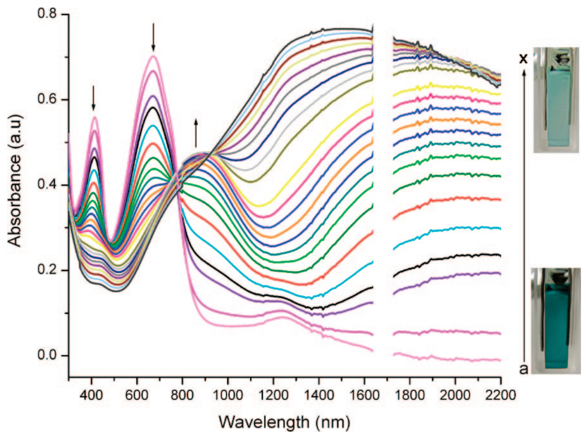

Figure 6. Spectroelectrochemistry of PDEQ film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF$_6$/ACN electrolyte−solvent couple at applied potentials (V): (a) −1.0, (b) −0.6, (c) −0.5, (d) 0.0, (e) 0.05, (f) 0.1, (g) 0.15, (h) 0.2, (i) 0.25, (j) 0.3, (k) 0.35, (l) 0.4, (m) 0.45, (n) 0.5, (o) 0.55, (p) 0.6, (q) 0.65, (r) 0.7, (s) 0.75, (t) 0.8, (u) 0.85, (v) 0.9, (w) 0.95, and (x) 1.0.

polymers showed less than 5% decrease upon cycling for 5000 times. Because the charge under the curves remains intact after 5000 cycles, we did not proceed with further cycling. These results indicate that both polymers are extremely stable toward redox cycling, which makes them outstanding candidates for commercial device applications.

Spectroelectrochemistry. Polymer films were synthesized on ITO coated glass slides by oxidative electropolymerization in DCM containing 10^{-2} M monomer and 0.1 M TBAPF$_6$. UV–vis−NIR spectra were obtained as a function of applied potential and proved the typical bipolaronic nature of the charge carriers. Both polymers revealed two well-separated absorption maxima, which is a necessity for obtaining a green reduced state.[13]

As seen from Figures 5 and 6, for PDEQ the absorption maxima were centered at 410 and 660 nm, whereas for PDETQ they were at 405 and 780 nm.

This observation is attributed to the donor–acceptor match capacity of the polymer backbones. The higher acceptor capacity of 2,3-di(thiophen-2-yl)quinoxaline over quinoxaline, which is a result of extended conjugation, leads to a better donor–acceptor match because EDOT has been known to have a high donor capacity. As observed from the spectra, PDEQ absorption maxima (both higher and lower energy transitions) shifted toward 600 nm which is the absorption maximum of EDOT itself. Hence, the polymer is blue-green (*Y*, 433; *x*, 0.254; *y*, 0.321) in the neutral state. These results imply that as the donor–acceptor match decreases, the resultant polymer is more like the one with the higher capacity. Hence, after examining the spectroelectrochemistry of DEQ we decided to insert a higher acceptor capacity unit in the polymer backbone to synthesize a green polymeric material. This approach worked quite nicely and DETQ exhibited a saturated green color (*Y*, 236; *x*, 0.319; *y*, 0.481) in the neutral state.

The band gaps of the polymers were calculated as 1.4 and 1.2 eV (DEQ and DETQ) according to the onset of the lower energy $\pi-\pi^*$ transitions. The intensities of both absorption bands decreases for both polymers by stepwise oxidation, and a new absorption band in the NIR region appears because of the formation of charge carriers. The PDETQ becomes pale brown (*Y*, 361; *x*, 0.330; *y*, 0.380) in the oxidized state whereas DEQ has a transmissive blue color (*Y*, 683; *x*, 0.283; *y*, 0.326).

Although the conjugated polymers have significant potential to be n-doped, only a little fraction can exhibit this unique property. The n-type polymers are expected to have a major contribution to organic electronics because it will be possible for the fabrication of light emitting p(*i*)n diodes, bipolar transistors, and the polymeric analogue of the silicon npn, pnp field-effective transistors.[24]

An important aspect is to realize that n-doping of a conjugated polymer system is not only formation of a redox couple at a negative potential. There should exist considerable structural and especially optical differences after the

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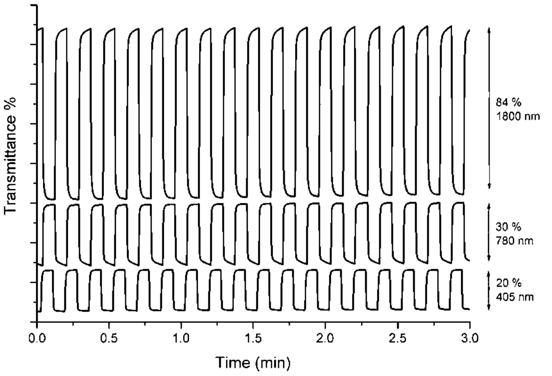

Figure 7. Electrochromic switching and optical absorbance change monitored at 405, 780, and 1800 nm for PDETQ in 0.1 M TBAPF$_6$/ACN.

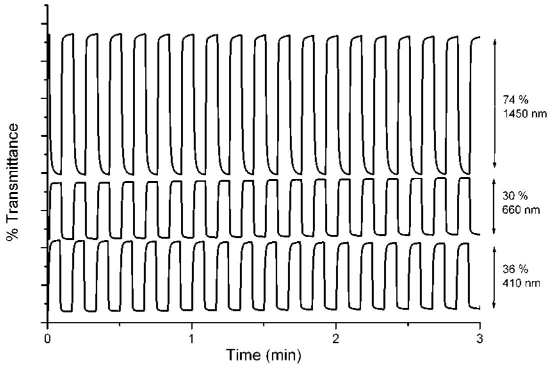

Figure 8. Electrochromic switching and optical absorbance change monitored at 410, 660, and 1450 nm for PDEQ in 0.1 M TBAPF$_6$/ACN.

introduction of charge carries to the conjugated system. Spectroelectrochemistry studies were performed to probe the optical changes that occur during the n-doping of the polymer. However, this property was hardly ever investigated in literature with an exception of a few studies.[25] The n-type doping process could not be observed for PDEQ films because EDOT moieties in the structure lead to an electron rich system. For PDETQ the absorption spectrum was recorded at −1.7 V, which is the cathodic potential of the redox couple observed in the reduced state. The optical spectrum was drastically changed to produce a purple color (*Y*, 423; *x*, 0.319; *y*, 0.325). It can be concluded that charge carriers are forming and a true n-type doping process occurs. The reason that PDETQ has an n-type character is most likely the higher capacity of stabilizing negative charge carriers by means of extended conjugation and a better donor–acceptor match. As more negative potentials were applied, the polymer film degrades because of over-reduction.

Kinetic Studies. Optical switching studies were examined for probing changes in transmittance with time while repeatedly stepping the potential between fully neutral and oxidized states. The polymer films were deposited on ITO glass slides by repeated scanning (40 cycles) in TBAPF$_6$/DCM. Throughout the experiment, the percent transmittance (*T%*) values at different wavelengths including both of the absorption maxima of both polymers were measured using a UV–vis−NIR spectrophotometer as the polymer films were switched between −1.0 V and +1.0 V with a residence time of 5 s. The results are shown in Figures 7 and 8.

The optical contrasts for PDETQ were calculated as 20% at 405 nm, 30% at 780 nm, and 84% at 1800 nm. The optical contrast for the second transition at around 780 nm is excellent while the other two are almost the same compared to that of the first example of green polymeric material[13] (12% at 725 nm, 23% at 370 nm, and 85% at 1600 nm). The optical contrast values for PDEQ are even better than those of PDETQ in the visible region in with 36% transmittance change at 410 nm and 30% at 660 nm. The PDEQ film revealed a 74% optical contrast in the NIR region. The polymers switch very rapidly between their neutral and oxidized states and achieve 95% of their optical contrasts in the visible region in less than 1 s. PDETQ revealed impressing switching times of 0.72 s at 405 nm and 0.9 s at 780 nm. The polymer achieves an outstanding optical contrast of 84% in the NIR region in only 1.5 s. PDEQ has exceptional switching times of 1 s at 410 nm and 0.72 s at 660 nm as well. No more than 1 s is required for PDEQ films to accomplish an excellent optical contrast of 74% at 1450 nm.

Conclusion

Two novel EDOT-bis-substituted quinoxaline monomers were synthesized via Stille coupling reaction. They were electrochemically polymerized to investigate their potential use as neutral state green electrochromic material. PDEQ has a bluish green color in the neutral state and a highly transmissive light blue oxidized state. The polymer revealed high optical contrasts in both visible and NIR regions with excellent switching properties and stability. PDETQ was shown to be one of the few examples of neutral state green polymeric materials in literature. The polymer revealed relatively high optical contrasts in the visible region and an excellent optical contrast of 84% in the NIR. Exceptional stability and very fast switching times make this neutral state green polymer a robust candidate for completion of RGB color space. Moreover, the existence of the n-type doping process was proved by both electrochemical and spectral analysis for PDETQ films. Considering these advanced properties, many quinoxaline derivatives can be utilized in the polymer backbone for synthesis of new superior polymers for electrochromic device applications. Specifically, the introduction of substituents having long alkyl chains can drastically improve solubility and might be of high interest for the production of processable green electrochromics for many display applications.

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