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Synthesis of new donor–acceptor polymers containing thiadiazoloquinoxaline and pyrazinoquinoxaline moieties: low-band gap, high optical contrast, and almost black colored materials

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ABSTRACT

Two low band gap conjugated polymers, poly[4,9-bis(4-hexylthien-2-yl)-6,7-di(thien-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline] (PHTTQ) and poly[5,10-bis(4-hexylthien-2-yl)-2,3,7,8-tetra(thien-2-yl)pyrazino[2,3-g]quinoxaline] (PHTPQ), consisting of alternating electron-rich 3-hexylthiophene and electron-deficient 6,7-di(thien-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (TTQ) and 2,3,7,8-tetra(thien-2-yl)-2,3-dihydropyrazino[2,3-g]quinoxaline (TPQ) units were synthesized electrochemically. The structures of the π-conjugated monomers were tailored using thiophene as the pendant group on the acceptor units (TTQ and TPQ). The electrochemical and optical properties of the polymers were investigated by cyclic voltammetry and UV–vis–NIR spectroscopy. The absorption spectra of PHTPQ, revealing a 1.0 eV band gap, exhibited three maxima at 352 nm, 535 nm, and 750 nm. Consequently, its absorption spectra cover the region between 400 and 800 nm, which make the polymer almost black in appearance. PHTTQ shows a λ_{max} value of 820 nm and a band gap of 0.8 eV which is very low among other [1,2,5]thiadiazolo[3,4-g]quinoxaline-containing donor–acceptor type polymers.

1. Introduction

Electroactive conducting polymers have been investigated intensively for their conducting, semiconducting, and electrochemical properties. Numerous electronic applications have been proposed and some realized, including electrochromic devices (ECDs),[1] electroluminescent organic light-emitting diodes (OLEDs),[2–4] photovoltaic elements for solar-energy conversion,[5–7] sensors,[8] and field-effect transistors.[9,10]

Due to the fact that the band gap (E_g) is one of the most important factors controlling the opto-electronic properties of electroactive polymers, band structure engineering has become important in the field of materials science. Research on low band gap polymers is of interest due to their electrochemical and optical properties.[11] Low band gap polymers have been defined as conjugated polymers with a band gap below 1.5 eV.[12]

To date, several approaches toward the construction of low band gap systems have been described. One of these involves alternating strong electron-donating and electron-accepting units where mixing monomer segments with higher HOMOs and lower LUMOs is effective in reducing the band gap due to interchain charge transfer.[13,14] The use of fused aromatics as acceptor units, containing benzene-fused heteroaromatic rings with nitrogen atom(s)and/or sulfur atom(s) such as benzothiadiazole, quinoxaline, benzo[1,2-*c*:4,5-*c*′]-bis[1,2,5]thiadiazole, pyrazino[2,3-*g*]quinoxaline, and [1,2,5]thiadiazolo[3,4-*g*]quinoxaline is an effective method to design these alternating systems.[15–22] Both the electron-withdrawing strength of the acceptor unit and the stable geometry contribute significantly to the electronic properties of the alternating donor–acceptor conjugated polymers. Hence, the HOMO level, LUMO level, and the band gap of the polymers can be altered by simply changing the acceptor strength.[23]

Herein we report the synthesis of 4,9-bis(4-hexylthien-2-yl)-6,7-di(thien-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline and 5,10-bis(4-hexylthien-2-yl)-2,3,7,8-tetra(thien-2-yl)pyrazino[2,3-g]quinoxaline. In this study, thiadiazoloquinoxaline (TQ) and pyrazinoquinoxaline (PQ) were selected as the acceptor units since they are excellent building blocks for realizing high electron-affinity organic semiconductors due to the strong electron-withdrawing properties of the four imine groups in their structure.[16,23] Depending on the electron-donating power of the donor units and the bulkiness of

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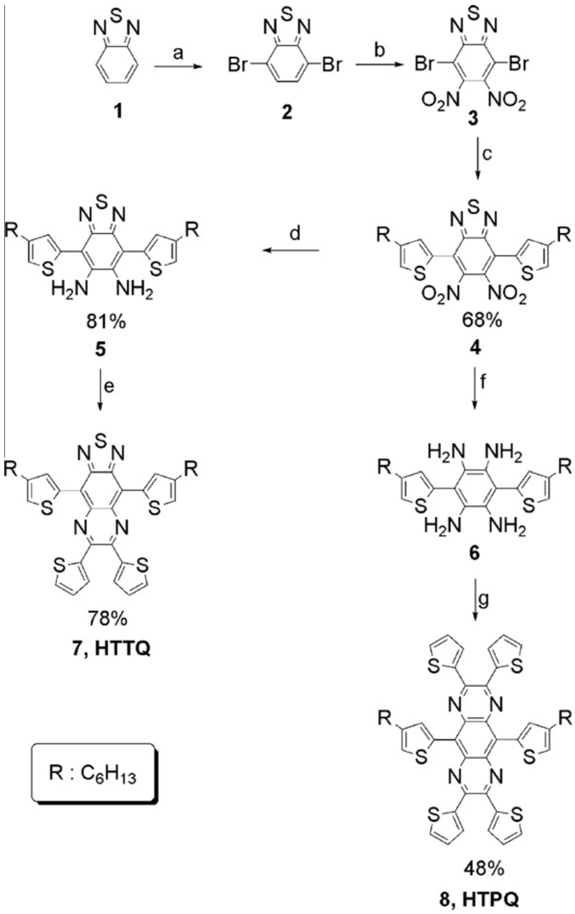
the side group of the acceptor unit, the donor–acceptor alternating polymers containing [1,2,5]thiadiazolo[3,4-*g*]quinoxaline as the acceptor units have been reported to have band gaps between 0.90 and 1.50 eV.[24–27]

Scheme 1 shows the synthetic route to the monomers. The syntheses of 4,9-bis(4-hexylthien-2-yl)-6,7-di(thien-3-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (**7**) (HTTQ) and 5,10-bis(4-hexylthien-2-yl)-2,3,7,8-tetra(thien-2-yl)pyrazino[2,3-g]quinoxaline (**8**) (HTPQ) started with the bromination of 2,1,3-benzothiadiazole followed by nitration to give 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]-thiadiazole (**3**). Compound **4** was obtained by the Stille coupling reaction of **3** with tributyl(4-hexylthien-2-yl)stannane. Reduction of **4** with iron or zinc in acetic acid gave 4,7-bis(4-hexylthien-2-yl)benzo[*c*][1,2,5]thiadiazole-5,6-diamine (**5**) and 3,6-bis(4-hexylthien-2-yl)benzene-1,2,4,5-tetraamine (**6**), respectively. Finally, condensation reactions of compounds **5** and **6** with 2,2′-thenil gave the desired monomers **7**, (HTTQ) and **8**, (HTPQ).



Scheme 1. Synthetic route to monomers **7** and **8**.

The electrochemical behaviors of HTTQ and HTPQ were investigated by cyclic voltammetry (CV). The electroactivity of HTPQ was examined in dichloromethane (CH_2Cl_2)/acetonitrile (MeCN) (95:5) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). As shown in Figure 1a, the cyclic voltammogram of HTPQ exhibited an irreversible monomer oxidation at 0.97 V versus an Ag wire pseudo reference electrode. Moreover, a redox couple with an oxidation potential of 0.95 V and a reduction potential of 0.80 V versus an Ag wire pseudo reference electrode was observed. At first glance, the monomer peak intensity seemed to increase with increasing number of scans. However, the polymer oxidation peak revealed in the second run lies under the monomer oxidation peak. This was confirmed by the single scan polymer cyclic voltammogram in a monomer-free solution. In a monomer-free 0.1 M $TBAPF_6/CH_2Cl_2$/MeCN solution, the characteristic polymer peaks were still observable (Fig. 1b). Hence the present increase refers to the polymer deposition on the electrode upon repetitive scanning. On the other hand, electropolymerization of HTTQ was performed in CH_2Cl_2/MeCN (50:50) using 0.1 M $LiClO_4$ as the supporting electrolyte instead of $TBAPF_6$ in order to satisfy the desired film quality.[28] Figure 2 shows the cyclic voltammogram of HTTQ in which the first cycle represents the irreversible oxidation of the monomer (1.16 V). As the number of cycles was increased, new anodic (0.83 V) and cathodic (0.62 V) peaks were observed due to the evolution of electroactive material on the indium tin oxide (ITO) coated glass surface.

As expected, HTPQ and HTTQ were oxidized particularly easily due to their electron-donating side units. The oxidation of HTPQ occurs at lower potential than that of HTTQ. This lower potential can be attributed to the number of electron-rich pendant thiophene units on the acceptor unit, TPQ. Furthermore, the electron-withdrawing ability of the acceptor unit (TTQ) in HTTQ [which is increased due to fusion of the thiadiazole ring onto the vacant sites of the phenyl ring of the quinoxaline unit (QU)] leads to an increase in the oxidation potential (Scheme 2). In the case of the polymer,

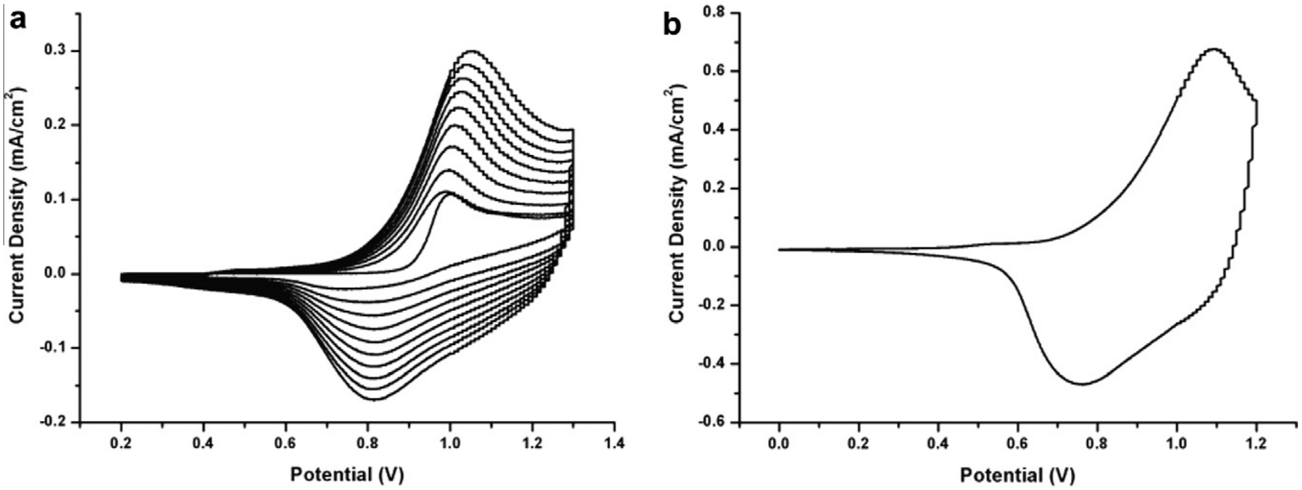


Figure 1. (a) Cyclic voltammogram of HTPQ in 0.1 M $TBAPF_6/MeCN/CH_2Cl_2$ (95/5 v/v) at a scan rate of 100 mV/s. (b) Single scan cyclic voltammogram of PHTPQ in the same solvent-electrolyte system.

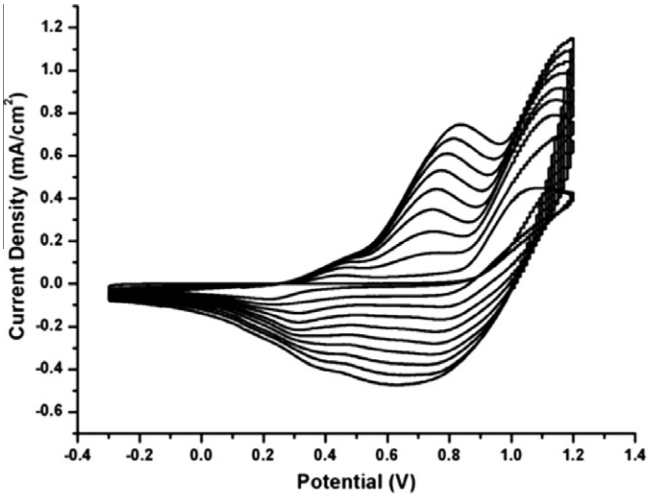
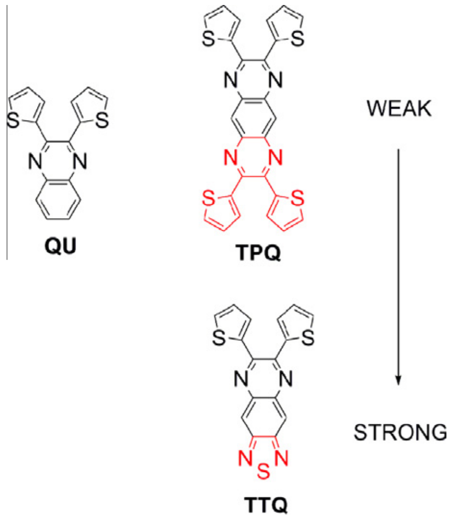


Figure 2. Cyclic voltammogram of HTTQ in 0.1 M $LiClO_4$/MeCN/CH_2Cl_2 (50/50 v/v) at a scan rate of 100 mV/s.



Scheme 2. Electron-withdrawing strength of TQ and PQ.

the increase in effective conjugation of the PHTTQ main chain due to less steric hindrance from the thiadiazole moiety compared to the thiophene units in the pyrazinequinoxaline unit resulted in a lowering of the redox potentials of the corresponding polymer, PHTPQ.

The scan rate dependences of the polymer films of PHTTQ and PHTPQ were also investigated by CV. There was a linear relationship between the scan rate and current intensity of the anodically electropolymerized polymers, which indicated the presence of well-adhered films on ITO (Fig. 3).

In order to investigate the optical responses upon doping, PHTTQ and PHTPQ films were electrodeposited on ITO-coated glass electrodes in the presence of a suitable solvent/electrolyte couple. Changes in the optical properties of the polymer films were investigated by UV–vis–NIR spectroscopy in a monomer-free, 0.1 M supporting electrolyte/solvent system applying different voltages.

The spectroelectrochemistry and the corresponding colors of the polymer films in their neutral and oxidized states are shown in Figure 4. Three absorption bands centered at 310 nm, 370 nm, and 820 nm were observed in the electronic absorption spectra of PHTTQ (Fig. 4a). The band gap of PHTTQ was found to be 0.8 eV which was calculated from the onset of the π–π^* transition. Similarly, PHTPQ showed three absorption bands at 352 nm, 535 nm, and 750 nm (Fig. 4b). The peak at 750 nm also corresponds to the π–π^* transition of neutral PHTPQ, the onset of which was used to calculate the band gap as 1.0 eV. The lower band gap of PHTTQ can be attributed to the nature of the thiadiazole unit (TQ) in several aspects; the TTQ unit containing a hypervalent sulfur atom has higher electron affinity. Secondly, steric repulsion between the TTQ unit and the adjacent 3-hexylthiophene is lower than that between the TPQ unit and 3-hexylthiophene, which leads to a planar geometry. The last aspect is strong interchain interactions which may be caused by the smaller TTQ unit compared to TPQ spatially. These arguments conclude that PHTTQ has a coplanar backbone, enhanced π-delocalization, and intramolecular charge transfer, which lead to a red-shifted absorption maximum in the visible region and a smaller band gap compared to PHTPQ.

As shown in Figure 4, upon electrochemical doping, there was a slight decrease in the π–π^* transitions and charge carrier states emerge with the majority of light absorption being in the near infrared region (1700 nm for PHTTQ and 1800 nm for PHTPQ).

Colorimetry measurements were performed to define precisely the color of the polymer films at their neutral and oxidized states

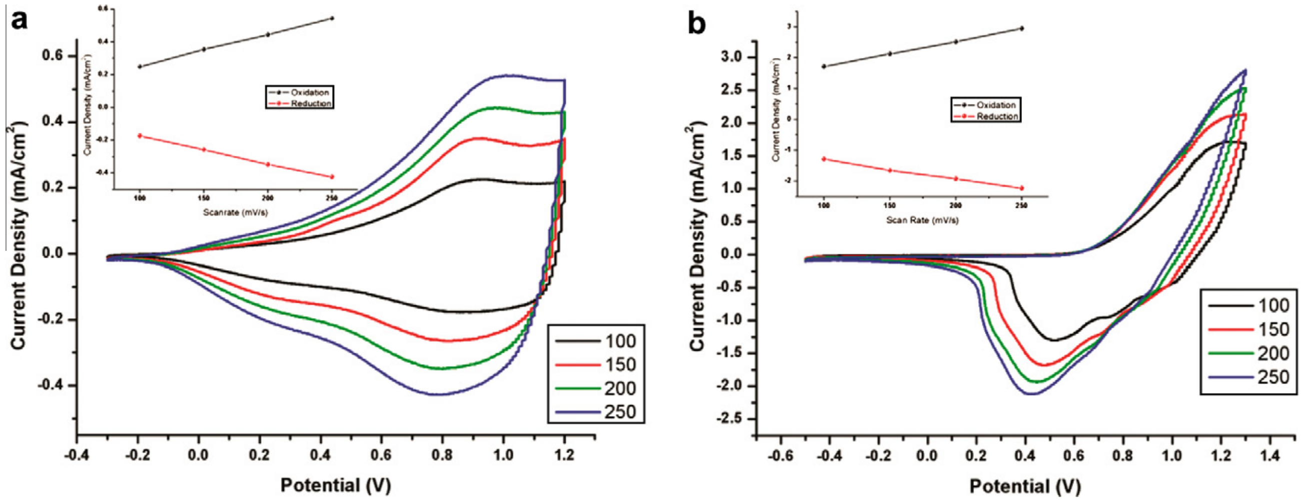


Figure 3. Scan rate dependence of (a) PHTPQ in 0.1 M $TBAPF_6$/MeCN/CH_2Cl_2 (95/5 v/v) and (b) PHTTQ in 0.1 M $LiClO_4$/MeCN/CH_2Cl_2 (50/50 v/v) at scan rates of 100, 150, 200, and 250 mV/s. Insets: the linearity of the current density versus voltage scan rate indicates the presence of well-adhered films on the ITO surface.

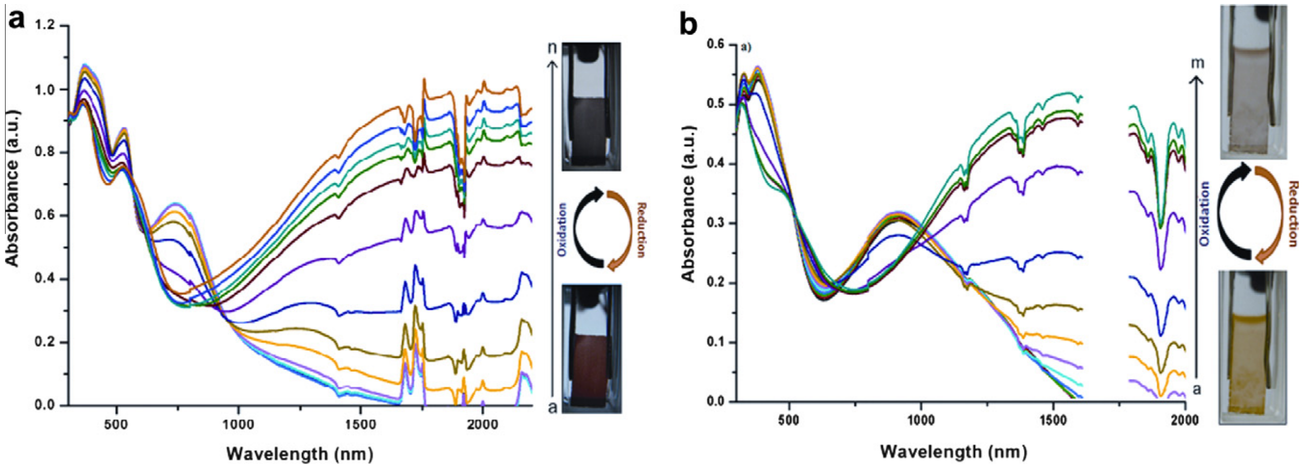


Figure 4. Spectroelectrochemical spectra of (a) PHTPQ with applied potential between 0.0 V and +1.3 V in MeCN/CH_2Cl_2/$TBAPF_6$. (b) PHTTQ with applied potential between −0.1 V and +1.2 V in MeCN/CH_2Cl_2/$LiClO_4$.

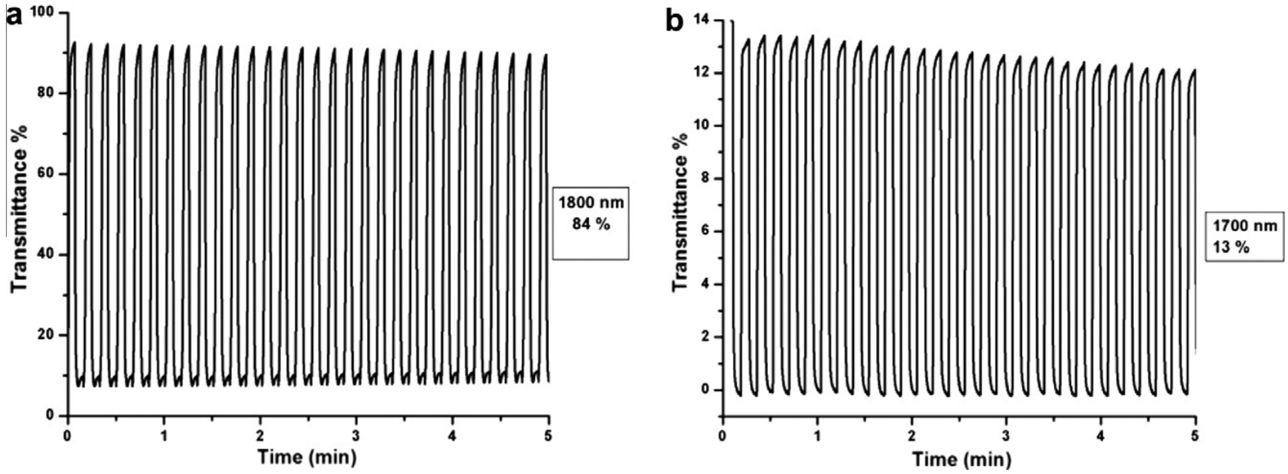


Figure 5. Electrochromic switching, optical absorbance changes monitored (a) at 1800 nm for PHTPQ between 0.0 V and +1.3 V (b) at 1700 nm for PHTTQ between −0.1 V and +1.2 V.

using the CIE 1931 Yxy color space. PHTTQ had a pale yellow color (Y: 60.8; x: 0.350; y: 0.390) in the neutral state (−0.1 V) and a pale brown (Y: 68.4; x: 0.32; y: 0.35) in the oxidized state (+1.2 V). PHTPQ is brown in color (Y: 14.9; x: 0.310; y: 0.346) in its neutral state (0.0 V). When the polymer is oxidized (+1.3 V), it turns into deep purple, almost black (Y: 25.1; x: 0.376; y: 0.363). A polymer with a black color in any state is a significant candidate for smart windows applications.[29]

The ability of a polymer to switch rapidly and exhibit a striking color change is crucial for electrochromic applications. Electrochromic switching studies were performed to monitor the percent transmittance changes as a function of time and to determine the switching time of the polymer at the stated wavelengths by stepping the potential repeatedly between the neutral and oxidized states.

The optical contrast of PHTPQ in the NIR region (at 1800 nm) was found to be 84% with a switching time of 2.0 s (Fig. 5a). This high optical contrast makes this polymer a powerful candidate for NIR electrochromic applications. NIR applicable materials are of particular interest since they are used for optical data transmission and as NIR dyes.[30,31] The optical contrasts for PHTTQ were measured at 1700 nm as 13% with switching times of 1.6 s (Fig. 5b). This low value is consistent with the absorption spectra of PHTTQ in which the emerged electronic state also has an absorption in the visible region at +1.2 V. This means that the polymer film could not be oxidized completely.

In conclusion, two different electroactive donor–acceptor type π-conjugated monomers consisting of 3-hexylthiophene as the donor unit and 6,7-di(thien-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline and 2,3,7,8-tetra(thien-2-yl)-2,3-dihydropyrazino[2,3-g]-quinoxaline as the acceptor units were synthesized via a Stille coupling reaction. Incorporating the electron-deficient TTQ and TPQ units with 3-hexylthiophene in an alternating fashion results in lowering of the band gap of the resulting polymers. Moreover, introduction of 3-hexylthiophene units to the monomer structures leads to easier handling in electrochemical studies by enhancing the solubility. Spectroelectrochemical analysis showed that polymer films have high π to π* electronic transitions (750 nm for PHTPQ and 820 nm for PHTTQ) and low band gaps (1.0 eV for PHTPQ and 0.8 eV for PHTTQ), which mainly depend on the properties of the acceptor units, TPQ and TTQ. PHTPQ is almost black in color in its oxidized state and demonstrates nearly 84% optical contrast in the NIR region with remarkable stability. Due to the almost black color in the oxidized state and high optical contrast in the NIR region, PHTPQ may potentially be used for smart windows applications and NIR electrochromic applications.

2. 4,9-Bis(4-hexylthien-2-yl)-6,7-di(thien-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (7, HTTQ)

4,7-Bis(4-hexylthien-2-yl)benzo[*c*][1,2,5]thiadiazole-5,6-diamine (**5**) (100 mg, 0.20 mmol) was dissolved in EtOH (5 ml). 2,2′-Thenil (44.56 mg, 0.20 mmol) and a catalytic amount of *p*-TsOH were added to the reaction medium. The mixture was stirred at room temperature for 6 h. The solvent was evaporated under vacuum and the crude product was purified by column chromatography over silica gel, eluting with 1:1 (CH_2Cl_2/hexane) to give **7** as a green solid (106 mg, 78%). ^{1}H-NMR (400 MHz $CDCl_3$): δ (ppm) 8.62 (d, $J = 1.1$ Hz, 2H), 7.51 (dd, $J_1 = 5.0$, $J_2 = 0.9$ Hz, 2H), 7.44 (dd, $J_1 = 3.7$, $J_2 = 0.9$ Hz, 2H), 7.19 (br s, 2H), 6.97 (dd, $J_1 = 5.0$, $J_2 = 3.7$ Hz, 2H), 2.68 (t, $J = 7.7$ Hz, 4H), 1.68 (m, 4H), 1.32 (m, 12H), 0.84 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.4, 144.3, 141.5, 140.2, 133.9, 133.3, 132.7, 129.9, 129.2, 126.0, 125.0, 119.1, 30.3, 29.2, 29.21, 27.7, 21.2, 12.7. MS (*m*/*z*) 685.2 $[M+1]^+$. IR $\nu = 3099$, 2919, 1650, 1520, 1453, 1373, 1243, 1189, 1060, 901, 845, 706, 579 cm^{-1}.

3. 5,10-Bis(4-hexylthien-2-yl)-2,3,7,8-tetra(thien-2-yl)pyrazino[2,3-g]quinoxaline (8, HTPQ)

A mixture of 4,7-bis(4-hexylthien-2-yl)-5,6-dinitrobenzo[*c*]-[1,2,5]thiadiazole (**4**) (200 mg, 0.36 mmol) and Zn dust (489 mg, 7.48 mmol) in glacial AcOH (3 mL) was stirred at 60 °C for 1 h until the reaction mixture turned white. After cooling to room temperature, 2,2′-thenil (0.159 g, 0.72 mmol) was added to the solution and the mixture was stirred for 1 h. The solvent was evaporated under vacuum and the crude product was purified by column chromatography over silica gel, eluting with 1:1 (CH_2Cl_2/hexane) to give **8** as a shiny-black solid (145 mg, 48%). ^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) 8.16 (s, 2H), 7.48 (d, $J = 3.7$ Hz, 4H), 7,46 (d, $J = 5.0$ Hz, 4H), 7.27 (s, 2H), 6.94 (dd, $J_1 = 5.0$, $J_2 = 3.7$ Hz, 4H), 2.75 (t, $J = 7.7$ Hz, 4H), 1.77 (m, 4H), 1.35 (m, 12H), 0.84 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.0, 141.3, 141.1, 135.2, 134.8, 132.7, 129.5, 129.2, 126.5, 125.9, 124.7, 30.8, 29.8, 28.2, 21.6, 13.1. MS (*m*/*z*) 843 $[M+1]^+$. IR: $\nu = 3088$, 2925, 1520, 1426, 1310, 1233, 1173, 1060, 853, 701, 598 cm^{-1}.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.03.078.

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