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PAPER

A promising combination of benzotriazole and quinoxaline units: A new acceptor moiety toward synthesis of multipurpose donor–acceptor type polymers

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By combining benzotriazole and quinoxaline units in an acceptor unit, three novel monomers, 2-dodecyl-6,7-diphenyl-4,9-di(thiophen-2-yl)-2*H*-[1,2,3]triazolo[4,5-g]quinoxaline (M_1), 2-dodecyl-4,6,7,9-tetra(thiophen-2-yl)-2*H*-[1,2,3]triazolo[4,5-g]quinoxaline (M_2) and 6,7-bis(4-tert-butylphenyl)-2-dodecyl-4,9-di(thiophen-2-yl)-2*H*-[1,2,3]triazolo[4,5-*g*]quinoxaline (M_3), were synthesized and polymerized electrochemically. All polymers revealed both p- and n-type doping properties under ambient conditions. As found by spectroelectrochemical studies they have small band gaps, *ca.* 1.00 eV. The polymers revealed two distinct absorption bands as all green coloured neutral state donor–acceptor–donor type polymers should have. Besides this, all have broad absorptions covering the region between 700 nm and 1000 nm which is rarely seen in electrochromic polymers. Due to these promising features, they are considered to be potential materials for optoelectronics.

Introduction

Conjugated polymers (CPs) have been investigated over the years for their potential as advanced materials in many optoelectronic applications, including electrochromic devices (ECDs),[1] organic light emitting diodes (OLEDs),[2] organic photovoltaics (OPVs),[3] sensors[4] and organic field effect transistors (OFETs).[5] Due to their extensive use in these areas, production of multipurpose materials mostly relies on newly designed structures. In particular, smart structures are synthesized through molecular architecture, to allow the enhancement of the electronic and optical properties of π conjugated systems *via* controlling structural alterations.[6]

Accordingly, optoelectronic properties can be optimized by structural modification *via* increasing the quinoidal character of the conjugated structure, along with the creation of alternating strong electron donating and withdrawing sites on the polymer backbone.[7] Alternating donor and acceptor units bearing conjugated polymers are thought to be essential to manipulate the band gap. The donor–acceptor approach, one of the most plausible ways for the construction of low band gap systems, is confirmed by assembling an electron rich unit with a high HOMO level and an electron deficient unit with a low LUMO level in the structure. In accordance with these strong electron rich and electron deficient sites on the polymer chain, the combination of monomer segments with higher HOMO levels and lower LUMO levels results in band gap lowering due to interchain charge transfer.[8,9]

Combining donor and acceptor moieties in the polymer backbone enhances D–A interactions and helps in developing the most efficient polymers for OPVs.[7] Besides obtaining low band gap polymers, the D–A approach is also useful in producing polymers with improved optical, mechanical and electronic properties.[10] The band gap can be tuned by changing the donor and acceptor units in the repeating unit.[11] As a result, the structural variations in conjugated systems lead to control of not only the optical and electronic properties of the polymers, but also allow the creation of low band gap polymers.

Changing both or either of the donor/acceptor groups is an effective method to design these alternating systems. Recently, different fused aromatic heterocyclics containing nitrogen and sulfur atoms were used as the electron deficient units, such as benzothiadiazole (BTd), quinoxaline, benzotriazole (BTz), and benzimidazole (BIm). The electron withdrawing ability of these acceptor moieties is the key to obtaining a polymer with the desired band gap and optical properties.[12]

In the literature, the very first examples of BTz-containing conjugated polymers were shown by Yamamoto and coworkers.[13] Later on, in 2009, the electrochromic properties of another BTz derivative (PTBT) were investigated by our group. This fascinating polymer attracted many researchers and it was reported as a multipurpose material due to its solubility, processability and dual type dopability (both p- and n-dopable).[14]

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After this discovery, BTz derivatives were in demand due to the achievement of resulting desired properties such as multichromism, transmissive states and photoluminescence, all combined in a single polymer.[10]

In the meantime, quinoxaline based conjugated polymers, which were widely studied in the literature, attracted considerable attention. The lack of available neutral state green coloured polymers with highly transmissive oxidized states was addressed in 2007 by our group. By virtue of synthesizing these EDOT bearing quinoxaline derivatives, the missing element of the RGB (Red, Green, Blue) puzzle was contrived.[1d,15]

The idea having these two main electron deficient units; benzotriazole and quinoxaline in a single structure leading to the formation of black coloured polymers inspired us to conduct this study. Here, we basically aim to synthesize a new acceptor unit which contains both benzotriazole and quinoxaline moieties. Owing to the increase in imine bonds (two *vs.* four) with this single structure, the molecule is expected to yield higher electron transporting features.[13]

Herein we designed three new monomers namely 2-dodecyl-6,7-diphenyl-4,9-di(thiophen-2-yl)-2*H*-[1,2,3]triazole[4,5-*g*]quinoxaline (M_1), 2-dodecyl-4,6,7,9-tetra(thiophen-2-yl)-2*H*-[1,2,3]triazole [4,5-*g*]quinoxaline (M_2) and 6,7-bis(4-tert-butylphenyl)-2-dodecyl-4,9-di(thiophen-2-yl)-2*H*-[1,2,3]triazole[4,5-*g*]quinoxaline (M_3), in order to have a proper donor–acceptor match. Electrochemical polymerizations of corresponding monomers resulted in the desired polymers P_1, P_2 and P_3 (Fig. 1).

Results and discussion

Synthesis

The synthetic route to the monomers was outlined in Scheme 1. 4,7-Dibromo-2-dodecyl-2*H*-benzo[*d*][1,2,3]triazole **3** was synthesized firstly by alkylation of 1*H*-benzo[*d*][1,2,3]triazole 1 and then by bromination with HBr and bromine. Nitration of the resulting brominated product gave 4,7-dibromo-2-dodecyl-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole **4**. Compound **5** was obtained by the Stille coupling reaction of **4** and tributyl(thiophen-2-yl) stannane. The reduction of **5** with iron dust in acetic acid yielded 2-dodecyl-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole-5,6-diamine **6**. Finally, a condensation reaction of **6** with three different diketones, (benzyl **7**, 1,2-di(thiophen-2-yl)ethane-1,2-dione **8** and 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione **9**), in the presence of PTSA and ethanol gave the desired monomers (M_1, M_2, M_3).

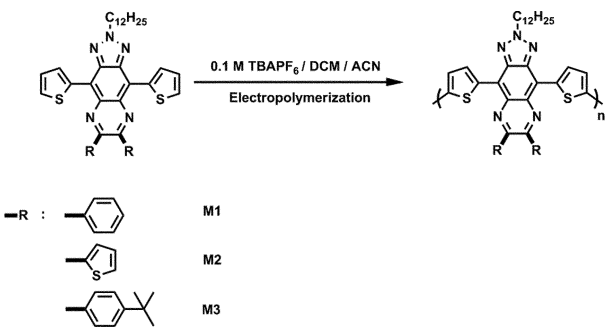


Fig. 1 Electrochemical polymerization of the monomers.

Electrochemistry

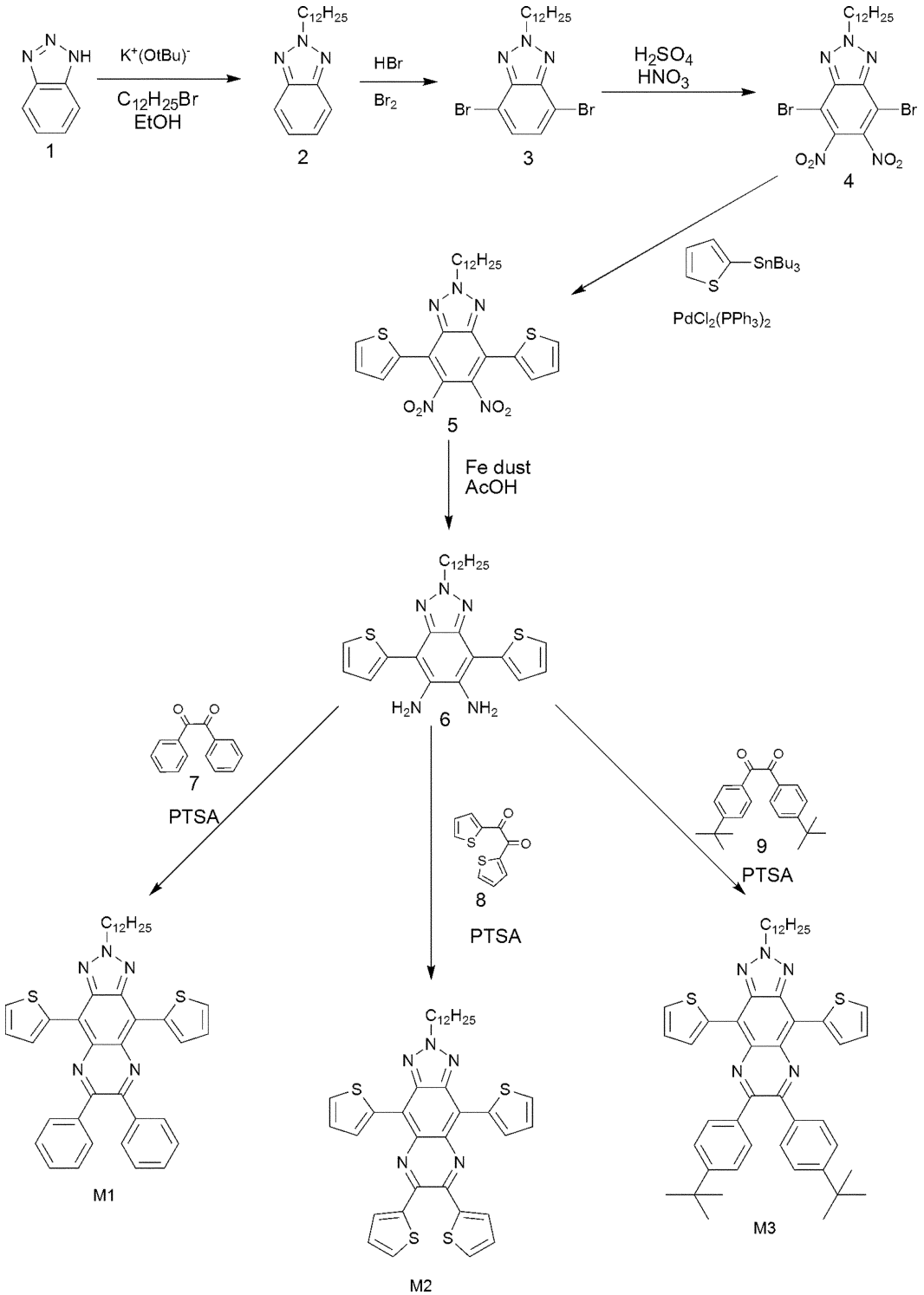
Electrochemical polymerization of the monomers on ITO electrodes was performed in 0.1 M $TBAPF_6$ and 0.01 M corresponding monomer solutions in acetonitrile (ACN)–CH_2Cl_2 (95 : 5, v/v) by applying potentials between 0 V and +1.0 V for M_1 and M_3, and 0 V and +1.2 V for M_2 at a scan rate of 100 mV s^{-1} (Fig. 2). The monomer oxidation potentials were around 1.0 V due to the same electron rich unit, thiophene in their structures. On the other hand, the polymer oxidation potentials were distinct from each other due to the different electron densities of the electrochemically synthesized polymer chains. In all electrochemical polymerizations, reversible redox peaks with increasing current density by repeated cycling were observed.

Both benzotriazole and quinoxaline derivatives have strong electron accepting ability.[1d,10] Hence, the combination of these two strong acceptor derivatives resulted in stronger acceptor ability than either benzotriazole or quinoxaline alone. In other words, increasing the number of imine bonds in a structure yields a stronger electron acceptor moiety. As a result, all polymers revealed two reversible peaks as regards to n-doping at ambient conditions. The HOMO–LUMO energy levels of the polymers were estimated using the onset of the corresponding oxidation (Fig. 3) by calibrating the reference electrode against Fc/Fc^+ and calculating the energy levels relative to the vacuum level.[3a]

The LUMO levels differ from each other as regards to the electron density on the quinoxaline units which leads to a decrease in the strength of the acceptor ability with increasing electron density. Although such an assumption was valid for LUMO levels of the polymers, experimentally calculated HOMO levels from their single scan cyclic voltammograms did not reveal plausible results. This may result from the unequal doping features of the polymers, especially for P_3. When the charge injection/ejection is compared, P_3 revealed the lowest charge, as seen in Fig. 3. This is most probably due to the presence of the tertiary butyl group on the phenyl units which obstructs the ejection/injection of the dopant ions. Since all the polymers were both n- and p-type doped, the electrochemical band gap E_g^{ec} and HOMO/LUMO values were calculated experimentally and all the related electrochemistry data were summarized in Table 1.

Electronic and optical studies

To probe the spectral response of the polymers to the doping processes, *in situ* UV-Vis-NIR spectra were monitored in a monomer free, 0.1 M $TBAPF_6$–ACN solution. All three polymers revealed two absorption maxima, the first one in the short wavelength region ranging from 300 to 450 nm is due to the π–π^* transition, whereas the second at the long wavelength region covering 700–1000 nm refers to intramolecular charge transfer transitions between the donor and the acceptor moieties (Fig. 4). The absorption of the polymers covered both red and blue colour regions of the visible spectrum, hence reflecting the evolution of the green color in their neutral state (Fig. 5). As the potential was increased, the short and long wavelength absorption bands were depleted and new transitions in the NIR region were evolved, indicating the formation of charge carriers. At further doping stages, the formation of polarons was followed by the introduction of bipolarons with increasing external potential.



Scheme 1 Synthetic route for the monomers.

Since polaron and bipolaron formations were in the NIR region, all polymers were transparent in their oxidized states. As calculated from the onset of their lowest π–π* transitions, P_1 and P_2 exhibited optical band gaps of 1.02 eV and 0.95 eV, respectively. P_3 revealed the lowest optical band gap of 0.92 eV due to more extensive π–π* transitions at around 882 nm. Electronic band gaps can be higher than the optical ones since electronic band gaps are calculated using CV data where the polymers contain charged species like polarons.

Although all monomers and polymers contain bulky groups attached to quinoxaline units, P_3 has an additional tertbutyl bulky group on the quinoxaline unit. As a result it may affect the degree of polymerization and arrangement of repeating units in the polymer chains. This may be the reason why the spectral

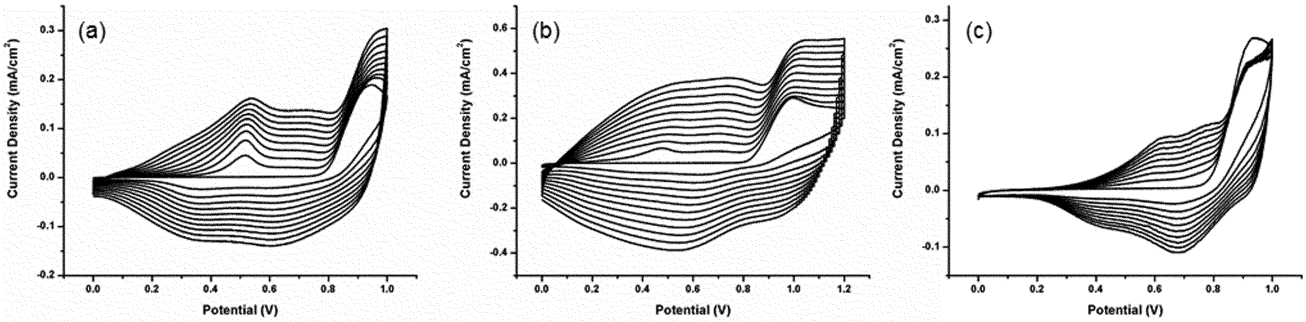


Fig. 2 Electrochemical polymerizations of (a) M_1 (b) M_2 and (c) M_3 at 100 mV s^{-1} in 0.1 M $TBAPF_6/CH_2Cl_2$/ACN on ITO electrodes.

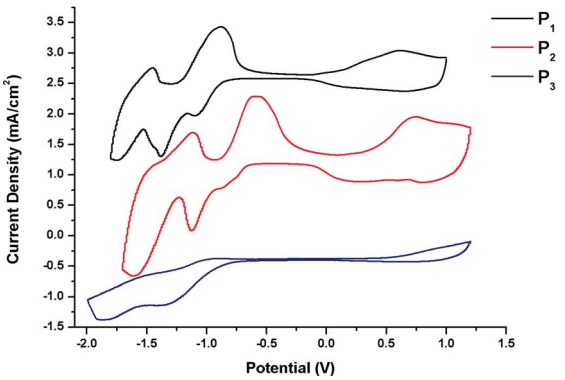


Fig. 3 Single scan cyclic voltammograms of P_1, P_2 and P_3 films using ACN as the solvent and 0.1 M $TBAPF_6$ as the supporting electrolyte at a scan rate of 100 mV s^{-1} and reduction peaks.

behaviours of P_1 and P_2 are different from that of P_3. Recently both p- and n-dopable polymers made several application areas feasible under atmospheric conditions such as light emitting diodes, field-effect transistors and organic solar cells.[2,3,5] Although P_1, P_2 and P_3 revealed reversible n-type redox couples, there should be additional evidence such as considerable structural and especially optical differences after the introduction of charge carries to the conjugated system. Accretion of bands in the NIR absorption region upon n-type doping of P_1, P_2 and P_3 is clear evidence for the formation of negative charge carriers (Fig. 4).

The normalized absorbance spectra of monomers in both CH_2Cl_2 and thin film forms are shown in Fig. 5. In the solution, monomers revealed absorption in visible region centered at 550 nm, 567 nm and 548 nm for M_1, M_2 and M_3, respectively. As regards the ones in thin film form, reduction in conformational freedom, solvent–monomer interactions and a tendency to aggregate in thin film form mostly causes a red shift absorption compared to the ones taken in solutions.[16] In addition to red shift absorption, broadening of absorptions covering between 550 nm and 650 nm were observed.

During the n-doping process, all polymers showed multichromic behaviour which is rarely seen in donor–acceptor type polymers (Fig. 6). This multichromic behaviour of the polymers during the n-doping process may arise from two features: firstly, the presence of two reversible redox couples as given in Fig. 2 and secondly the presence of alkyl chains bonded to triazole units which affects the doping rate.

Electrochromic switching studies

To investigate switching studies, the polymer films on ITO surfaces were studied *via* switching the potentials corresponding to their doped and dedoped states. During the switching, the absorbance at the specific wavelengths determined from the spectra of polymers, were monitored as a function of time with a UV-Vis-NIR spectrophotometer. Due to their high absorption in the NIR region, all polymers showed a high optical contrast in NIR region; P_1 showed 93% contrast at 2000 nm with 2 s of switching time, P_2 revealed 71% with 1.7 s at the same wavelength and P_3 presented 69% with 1.6 s at 1800 nm (Fig. 7). In the studies as the wavelength concerned decreased, the optical contrasts revealed by the polymers were increased; on the other hand, switching times were decreased. Optical contrasts, switching times and percent loss in optical contrasts were summarized in Table 2.

Experimental

Materials

All chemicals and reagents were obtained from commercial sources and used without further purification. THF was dried over sodium and benzophenone. 2-Dodecyl-2*H*-benzo[*d*][1,2,3]triazole (**2**),[14] 4,7-dibromo-2-dodecyl-2*H*-benzo[*d*][1,2,3]triazole (**3**)[14] and tributyl(thiophen-2-yl)stannane[17] were synthesized

Table 1 Summary of electrochemical and spectroelectrochemical properties of P_1, P_2 and P_3

	E_{mon}^{ox}/V	$E_{p\text{-doping}}$/V	$E_{p\text{-dedoping}}$/V	$E_{n\text{-doping}}$/V	$E_{n\text{-dedoping}}$/V	HOMO/eV	LUMO/eV	λ_{max}/nm	E_g^{op}/eV	E_g^{ec}/eV
P_1	0.95	0.54	0.36	−1.38/−1.75	−0.88/−1.46	−5.00	−3.77	450/950	1.02	1.23
P_2	1.00	0.70	0.52	−1.13/−1.60	−0.60/−1.11	−5.07	−3.89	432/1020	0.98	1.18
P_3	0.94	0.78	0.70	−1.38/−1.91	−1.04/−1.54	−5.37	−3.88	400/886	0.92	1.49

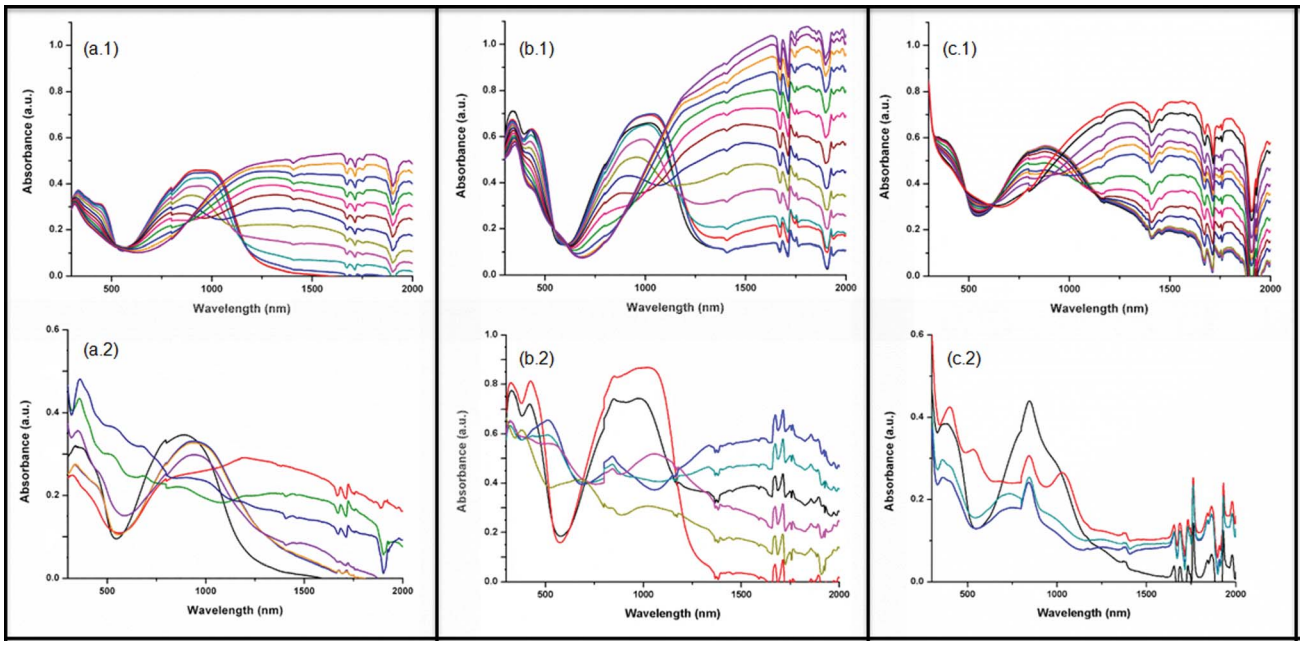


Fig. 4 p-Type doping spectra for P_1 (a.1), P_2 (b.1) and P_3 (c.1) and n-type doping spectra for P_1 (a.2), P_2 (b.2) and P_3 (c.2).

according to previously published procedures. All condensation reactions were conducted with respect to the known procedures.[18]

Synthesis of 4,7-dibromo-2-dodecyl-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole (4)

Compound **4** was synthesized by the modification of a previously published procedure.[19] A mixture of concentrated sulphuric acid (15 ml) and fuming nitric acid (15 ml) was used for the nitration of 4,7-dibromo-2-dodecyl-2*H*-benzo[*d*][1,2,3]triazole (**3**). The acid mixture was cooled to 0 °C and compound **3** (1.5 g, 3.37 mmol) was added to the mixture in small portions to keep the temperature below 5 °C. This heat control prevents over-nitration. After the addition was completed, the reaction mixture was stirred at room temperature for 3 h and then poured into an ice-bath. The precipitate was collected by filtration and recrystallized with an acetone-water mixture to yield 4,7-dibromo-2-dodecyl-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole (**4**) as a yellow solid (1.0 g, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (t, $J = 7.3$ Hz, 2H), 2.31 (m, 2H), 1.35–1.02 (m, 18H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.5, 105.7, 33.2, 30.4, 28.5, 28.2, 28.1, 27.9, 27.8, 27.7, 27.3, 24.9, 21.2, 12.6.

Synthesis of 2-dodecyl-5,6-dinitro-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole(5)

4,7-Dibromo-2-dodecyl-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole (**4**) (1.5 g, 2.80 mmol) and tributyl(thiophen-2-yl)stannane

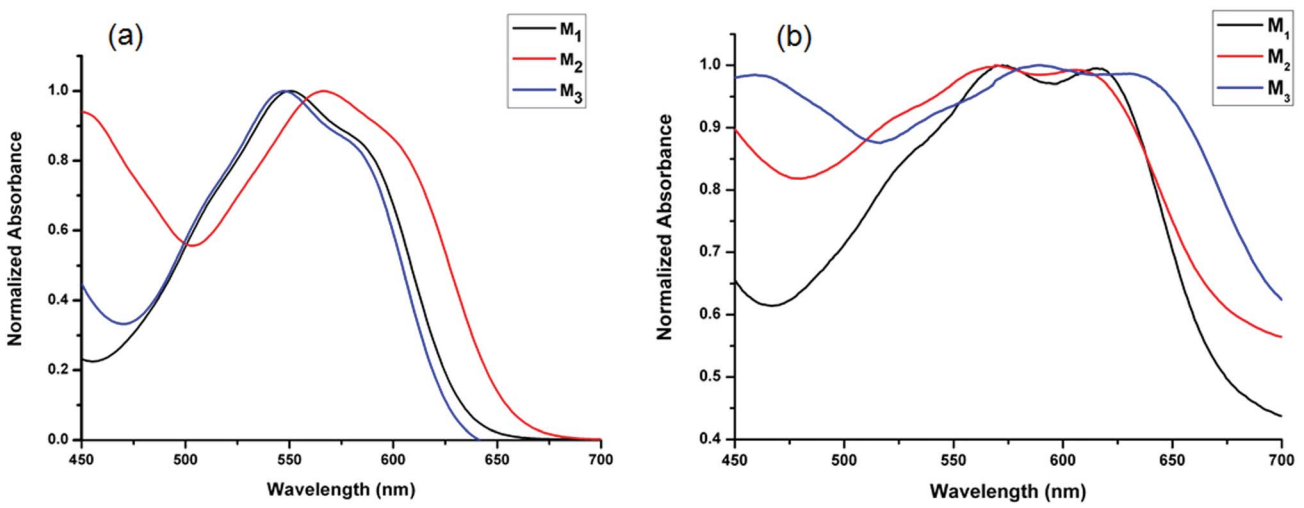


Fig. 5 Absorption spectra of monomers in solution (a) and thin film form (b).

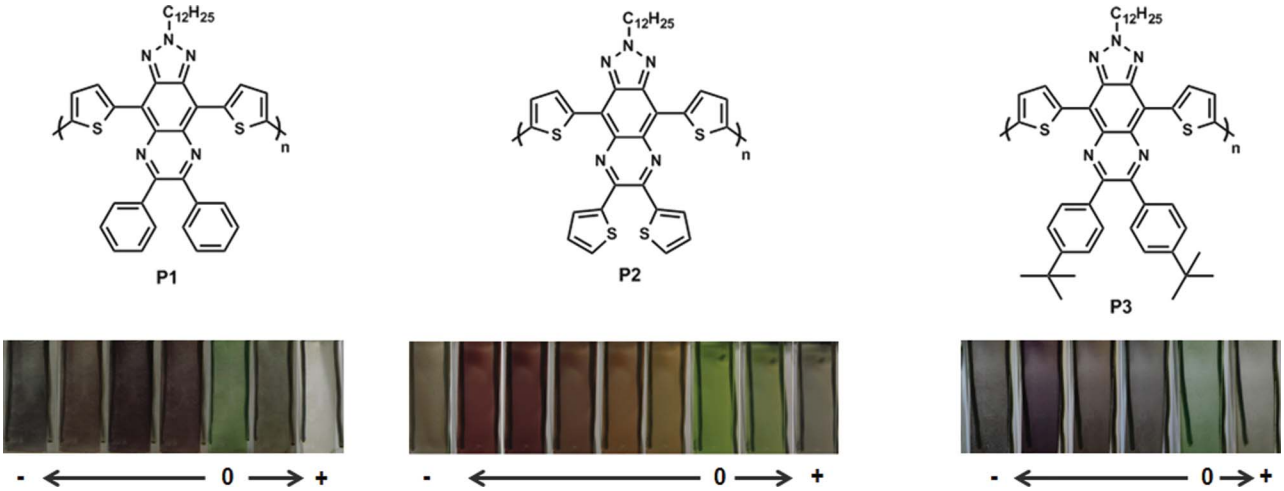


Fig. 6 Structures of the polymers and their colors under different applied potentials.

(5.22 g, 13.97 mmol) were dissolved in dry THF (60 ml). $PdCl_2(PPh_3)_2$ catalyst was added after the reaction mixture was refluxed for 1 h. Then it was stirred at 100 °C under argon atmosphere for 18 h. At the end of this period, the residue was subjected to column chromatography (silica gel, $CHCl_3$–hexane, 1 : 2) to afford compound **5** in 45% yield (660 mg, 1.22 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, $J = 5.1$ Hz, 2H), 7.54 (dd, $J = 3.7$ Hz, 2H), 7.21 (dd, $J = 5.0$ Hz, 2H), 4.81 (t, $J = 7.2$ Hz, 2H), 1.62 (m, 2H), 1.38–1.29 (m, 18H), 0.94 (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.1, 130.4, 130.4, 130.1, 127.9, 119.8, 32.1, 30.0, 29.6, 29.4, 29.3, 29.0, 28.3, 26.7, 26.5, 22.7, 17.3, 13.5.

Synthesis of 2-dodecyl-6,7-diphenyl-4,9-di(thiophen-2-yl)-2*H*-[1,2,3]triazolo[4,5-*g*]quinoxaline (M1)

Iron dust (350 mg) in acetic acid (25 ml) was used for the reduction of 2-dodecyl-5,6-dinitro-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (240 mg, 0.44 mmol) at 50 °C. The mixture was poured into cold NaOH solution and then extracted three times with ether. 2-Dodecyl-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole-5,6-diamine (**6**) was used without any purification. A previously published procedure was modified for compound **6**.[20] Then a condensation reaction was performed to get the desired monomer. A solution of compound **6** (200 mg, 0.42 mmol) and benzil **7** (230 mg, 1.09 mmol) in EtOH (40 ml) was refluxed overnight with a catalytic amount of *p*-toluene sulfonic acid. The mixture was cooled to 0 °C and concentrated on a rotary evaporator. The residue was purified by flash column chromatography (silica gel, $CHCl_3$–hexane, 1 : 1) to yield a purple oily product in 40% yield (110 mg, 0.17 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, $J = 3.9$ Hz, 2H), 7.76–7.70 (m, 4H), 7.56 (dd, $J = 5.2$, 2H), 7.37–7.32 (m, 6H), 7.23 (dd, $J = 5.1$ Hz, 2H), 4.91 (t, $J = 7.3$ Hz, 2H), 1.48–1.45 (m, 2H), 1.21–1.16 (m, 18H), 0.80–0.78 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 142.9, 138.8, 136.2, 134.8, 133.0, 131.7, 130.7, 129.9, 129.0, 128.1, 126.5, 57.9, 47.1, 32.0, 30.1, 30.0, 29.6, 29.5, 29.4, 29.4, 29.1, 26.7, 22.8. HRMS (EI) for $C_{40}H_{41}N_5S_2$ calculated 656.2882, found 656.2880.

Synthesis of 2-dodecyl-4,6,7,9-tetra(thiophen-2-yl)-2*H*-[1,2,3]triazolo[4,5-*g*]quinoxaline (M2)

2-Dodecyl-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole-5,6-diamine was synthesized according to a previously described procedure.[20] A solution of compound **6** (250 mg, 0.52 mmol) and 1,2-di(thiophen-2-yl)ethane-1,2-dione (**8**) (115 mg, 0.52 mmol) in EtOH (40 ml) was refluxed overnight with a catalytic amount of *p*-toluene sulfonic acid. The mixture was cooled to 0 °C and concentrated on the rotary evaporator. The residue was purified

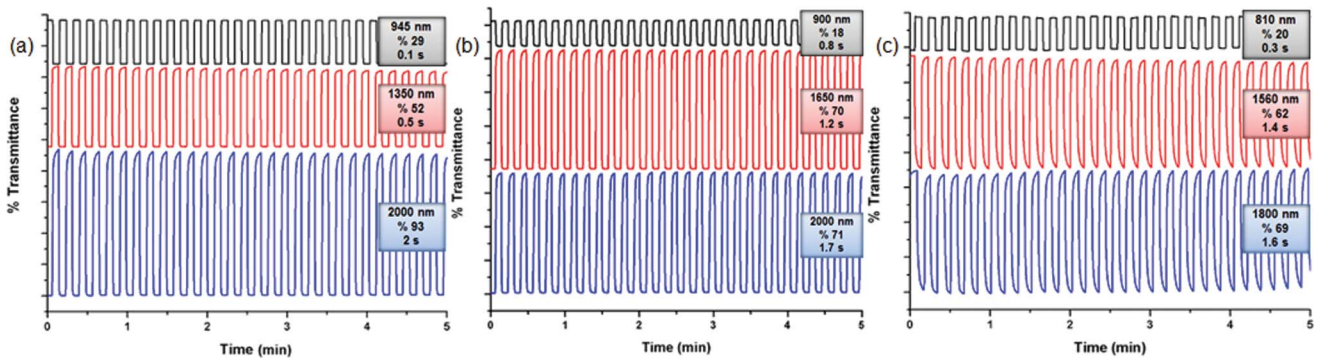


Fig. 7 Optical contrasts and switching times of (a) P_1, (b) P_2 and (c) P_3 at different wavelengths.

Table 2 Summary of kinetic and optic studies of P_1, P_2 and P_3

	P_1			P_2			P_3		
	945 nm	1350 nm	2000 nm	900 nm	1650 nm	2000 nm	810 nm	1560 nm	1800 nm
$\%T^a$	29	52	93	18	70	71	20	62	69
t/s[b]	0.1	0.5	2	0.8	1.2	1.7	0.3	1.4	1.6
$\%T$ lost[c]	1.7	4.9	2.8	3.1	0.8	1.5	3.7	7.2	1.9

[a] $\%T$ is the optical contrast difference revealed by polymers during square-wave voltammetry technique at certain wavelengths. [b] t is the switching time at certain wavelengths. [c] $\%T$ lost is the percent contrast of the polymers lost after 30 full switches.

by flash column chromatography (silica gel, $CHCl_3$–hexane, 1 : 1) to yield a bluish purple solid in 26% yield (90 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, $J = 3.8$ Hz, 2H), 7.56 (dd, $J = 9.6$ Hz, 2H), 7.50 (dd, $J = 5.0$ Hz, 2H), 7.41 (dd, $J = 3.7$ Hz, 2H), 7.19 (dt, $J = 7.1$ Hz, 2H), 6.98 (dd, $J = 5.0$ Hz, 2H), 4.83 (t, $J = 7.3$ Hz, 2H), 2.24–2.16 (m, 2H), 1.23–1.07 (m, 18H), 0.80 (t, $J = 4.7$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 141.7, 140.7, 134.7, 131.9, 130.7, 129.7, 129.5, 128.8, 126.3, 125.6, 118.3, 30.9, 29.0, 28.9, 28.6, 28.5, 28.4, 28.3, 28.0, 26.0, 24.3, 21.9, 13.5. HRMS (EI) for $C_{36}H_{37}N_5S_4$ calculated 668.2010, found 668.1979.

Synthesis of 6,7-bis(4-tert-butylphenyl)-2-dodecyl-4,9-di(thiophen-2-yl)-2*H*-[1,2,3]triazolo[4,5-*g*]quinoxaline (M3)

2-Dodecyl-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole-5,6-diamine was synthesized according to the previously described procedure. A solution of compound **6** (250 mg, 0.52 mmol) and 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione **9** (170 mg, 0.52 mmol) in EtOH (40 ml) was refluxed overnight with a catalytic amount of *p*-toluene sulfonic acid. The mixture was cooled to 0 °C and concentrated on a rotary evaporator. The residue was purified by flash column chromatography (silica gel, $CHCl_3$–hexane, 1 : 2) to give a purple oily product in 20% yield (80 mg, 0.10 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, $J = 3.9$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 4H), 7.57 (dd, $J = 5.1$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 4H), 7.23 (dd, $J = 5.1$ Hz, 2H), 4.90 (t, $J = 7.3$ Hz, 2H), 2.25–2.19 (m, 2H), 1.36–1.24 (m,18H), 1.30 (s, 18H), 0.78 (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 151.8, 142.3, 135.9, 135.7, 131.5, 130.5, 130.4, 126.5, 125.0, 124.0, 122.6, 34.8, 33.7, 33.5, 33.4, 31.9, 31.3, 30.1, 29.6, 29.5, 29.4, 29.3, 29.0, 27.0, 26.7, 26.6, 26.5. HRMS (EI) for $C_{48}H_{57}N_5S_2$ calculated 768.4134, found 768.4134.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with TMS as the internal standard and $CDCl_3$ as the solvent. All chemical shifts were given in ppm and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet. Electrochemical studies were performed in a three-electrode cell consisting of an Indium Tin Oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode under ambient conditions using a Voltalab 50 potentiostat. Before each measurement, solutions were purged with nitrogen gas for 5 min. A Cary 5000 UV–Vis-NIR spectrophotometer was used to perform the spectroelectrochemical studies of polymers. HRMS studies were done with a Waters SYNAPT MS system.

Conclusion

Three new donor–acceptor type monomers bearing combined benzotriazole and quinoxaline units as the acceptor and thiophene as the donor group were synthesized. Although both quinoxaline and benzotriazole derivatives were widely studied in the literature, their combination in one acceptor unit, in order to have a more electron deficient acceptor unit, was designed for the first time. After the characterization of the monomers, their polymers were electrochemically synthesized on ITO coated glass slides to investigate their electrochemical and optical properties. All polymers are both p- and n-dopable. Furthermore, the multicoloured n-doped state of all polymers is a rare property that widens their use in several applications. Spectroelectrochemical studies illustrate the broad absorptions between 700 nm and 1000 nm which in return refer to low band gap polymers with about 1.00 eV. Another attractive character of the prepared polymers is their high optical contrast in the NIR region, especially for P_1 which has 93% contrast at 2000 nm which makes it a promising candidate for NIR electrochromic applications.

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