Macromolecules

Article

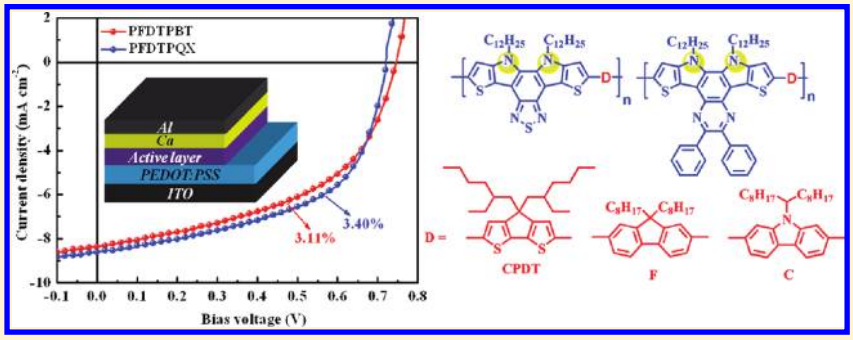
pubs.acs.org/Macromolecules

Synthesis, Photophysical and Photovoltaic Properties of Conjugated Polymers Containing Fused Donor−Acceptor Dithienopyrrolobenzothiadiazole and Dithienopyrroloquinoxaline Arenes

Yen-Ju Cheng,* Yu-Ju Ho, Chiu-Hsiang Chen, Wei-Shun Kao, Cheng-En Wu, So-Lin Hsu, and Chain-Shu Hsu

Department of Applied Chemistry, National Chiao Tung University 1001 Ta Hsueh Road, Hsin-Chu, 30010 Taiwan

Supporting Information



ABSTRACT: We have developed two nitrogen-bridged pentacyclic donor−acceptor dithienopyrrolobenzothiadiazole (**DTPBT**) and dithienopyrroloquinoxaline (**DTPQX**) arenes where the two outer electron-rich thiophene moieties are covalently fastened with the central electron-deficient benzothiadiazole and quinoxaline cores by two nitrogen bridges. These rigid and coplanar **DTPBT** and **DTPQX** building blocks were copolymerized with fluorene (F), carbazole (C) and cyclopentadithiophene (**CPDT**) units via Suzuki or Stille coupling polymerization to afford six new alternating copolymers **PFDTPBT**, **PCDTPBT**, **PCPDTDTPBT**, **PFDTPQX**, **PCDTPQX** and **PCPDTDTPQX**, respectively. The nitrogen bridges not only planarize the structure to induce stronger intermolecular $\pi-\pi$ interaction but also play an important role in determining the electronic and photophysical properties of the polymers. The device based on **PFDTPQX**/$PC_{71}BM$ (1:4, w/w) exhibited a open-circuit voltage (V_{oc}) of 0.72 V, a short-circuit current (J_{sc}) of 8.62 mA/cm^2 and a FF of 0.55 leading to a decent power conversion efficiency (PCE) of 3.40% due to the lower-lying HOMO energy level, and the highest hole-mobility of **PFDTPQX**.

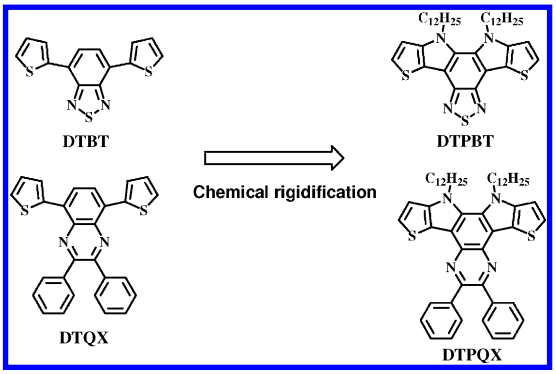
INTRODUCTION

In recent years, all-solution processed polymer solar cells (PSCs) have attracted tremendous academic and industrial interests. To realize low-cost, lightweight, large-area and flexible photovoltaic devices,[1] p-type photoactive conjugated polymer materials play the most important role in boosting high efficiency of PSCs.[2] An ideal p-type conjugated polymer should simultaneously possess low optical band gap (LBG) with strong extinction coefficient to harvest more solar photons and excellent hole mobility for efficient charge transport. Conjugating an electron-rich donor (D) unit with an electron-deficient acceptor (A) unit in an alternating arrangement is the most widely used strategy to produce a low band gap (LBG) polymer.[3] On the other hand, forced planarization by covalently locking neighboring aromatic units is an effective approach to reduce the band gap, because the parallel p-orbital interactions can facilitate π-electron delocalization and elongate effective conjugation length.[4] Furthermore, rigid structures can reduce the rotational disorder around interannular single bonds to lower the reorganization energy, which is beneficial to improve charge mobility.[5] As a result, considerable research effort has been devoted to the development of electron-rich donors having coplanar ladder-type heteroarenes.[6] The D−A polymers based on a series of fascinating fused structures have achieved high-performance solar cells. We envisaged that forced planarization by covalently fastening adjacent electron-rich donor and electron-deficient acceptor units into a coplanar fused D−A assembly may strengthen the electronic interactions between the donor and the acceptor units in a D−A copolymer, leading to more interesting molecular properties.[7] Surprisingly, conjugated polymers consisting of D−A fused moieties are rare in the literatures owing to the challenging synthesis to prepare fused D−A monomer precursor. The benzothiadiazole (BT) and quinoxaline (QX) units are regarded as the superb

Received: December 21, 2011
Revised: February 15, 2012
Published: March 6, 2012

acceptors due to their moderate electron affinity and planar structure.[8] Consequently, nonfused D−A−D structures, 4,7-di(thiophen-2-yl)benzothiadiazole (**DTBT**) or 4,7-di-(thiophen-2-yl)quinoxaline (**DTQX**) units, are the most commonly used components in the D−A polymers for PSCs applications (Scheme 1).[9]

Scheme 1. Chemical Structure of Nonfused DTBT and DTQX Units and Fused DTPBT and DTPQX Units

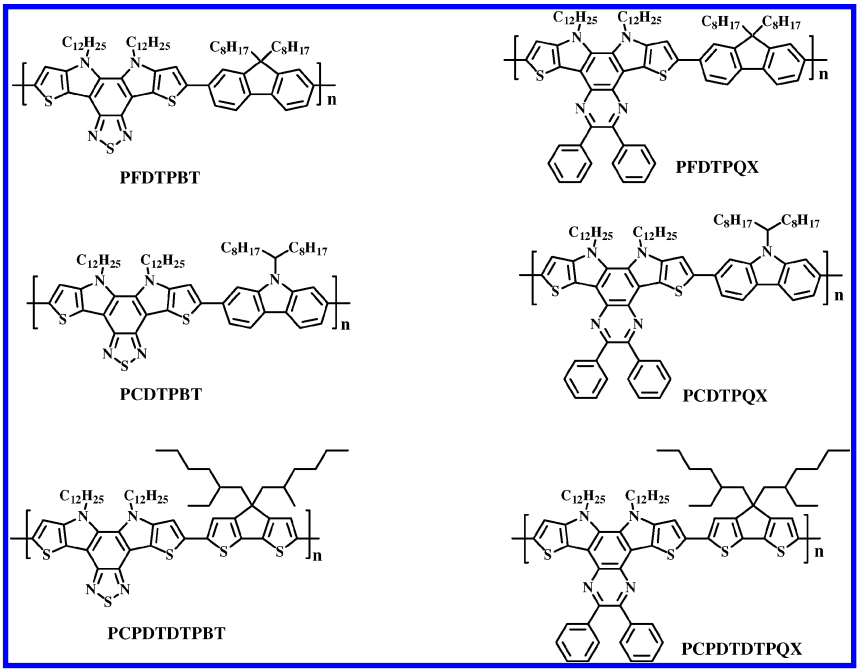


It is of great interest to planarize the **DTBT** structure by connecting 3-positons of the two outer thiophenes with the 5 and 6-positions of the central benzothiadiazole core via two bridging atoms. For this purpose, we have successfully developed a nitrogen-bridged D−A−D dithienopyrrolobenzothiadiazole (**DTPBT**) unit where two pyrrole units are embedded into a multifused pentacyclic structure (Scheme 1).[10] The **DTPBT** structure can be further chemically converted to another new fused D−A−D dithienopyrroloquinoxaline (**DTPQX**) structure. The dibromo-**DTPBT** and dibromo-**DTPQX** monomers were copolymerized with fluorene (F) and carbazole (C) and cyclopentadithiophene (CPDT) donor units, respectively, to prepare six alternating D−A fused conjugated copolymers, poly(fluorene-*co*-dithienopyrrolobenzothiadiazole) **PFDTPBT**, poly(carbazole-*co*-dithienopyrrolobenzothiadiazole) **PCDTPBT**, poly(cyclopentadithiophene-*co*-dithienopyrrolobenzothiadiazole) **PCPDTDTPBT**, poly(fluorene-*co*-dithienopyrroloquinoxaline) **PFDTPQX**, poly(carbazole-*co*-dithienopyrroloquinoxaline) **PCDTPQX** and poly(cyclopentadithiophene -*co*-dithienopyrroloquinoxaline) **PCPDTDTPQX** (Scheme 2). The thermal, photophysical and electrochemical properties of these polymers have been characterized and the nitrogen-bridged effect was carefully investigated. Preliminary tests of the photovoltaic performance based on these polymers show promise for solar cell applications.

RESULTS AND DISCUSSION

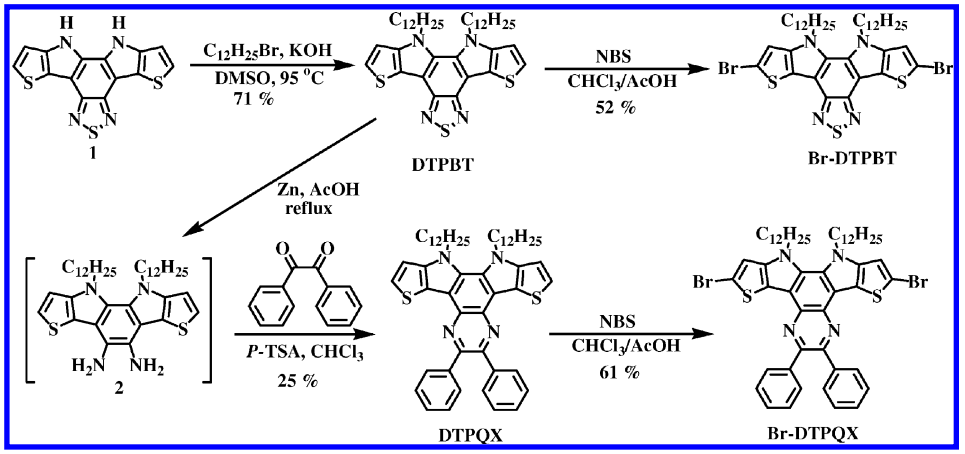
Synthesis. The synthesis of the monomers **Br-DTPBT** and **Br-DTPQX** is depicted in Scheme 3. *N*-alkylation of compound **1** resulted in the formation of **DTPBT**. NBS bromination of **DTPBT** regioselectively occurred at 5-positions of the thienyl moieties to yield the brominated monomer **Br-DTPBT**. Reduction of the thiadiazole moiety in **DTPBT** by Zn/AcOH generated the corresponding diamine intermediate **2** which underwent condensation with benzil to yield dithienopyrroloquinoxaline **DTPQX**. Again, bromination of **DTPQX** selectively occurred at 5-positions of the thienyl moieties to obtain **Br-DTPQX** in 61% yield. With **Br-DTPBT** monomer in hand, the copolymers **PFDTPBT**, **PCDTPBT** and **PCPDTDTPBT** were prepared by reacting **Br-DTPBT** with 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolane-2′-yl)-9,9-dioctylfluorene (**F**) and 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole (**C**) using Suzuki polymerization and 2,6-di(trimethyltin)-4,4-diethylhexylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**CPDT**) via Stille polymerization (Scheme 4). In a similar manner, the copolymers **PFDTPQX**, **PCDTPQX**, and **PCPDTDTPQX** were also synthesized by using **Br-DTPQX** as the monomer (Scheme 4). All the polymerization

Scheme 2. Chemical Structures of Polymers PFDTPBT, PCDTPBT, PCPDTDTPBT, PFDTPQX, PCDTPQX, and PCPDTDTPQX

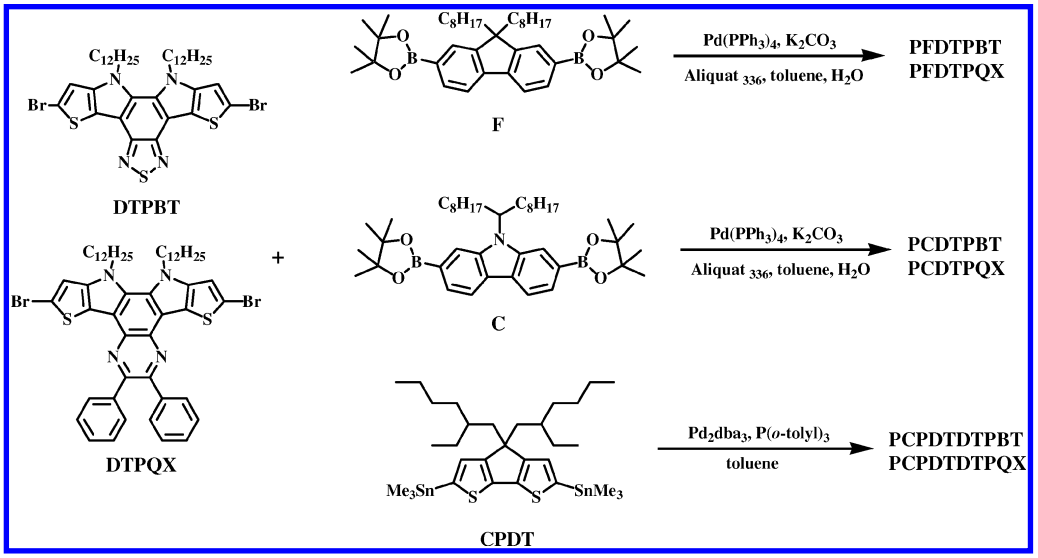


dx.doi.org/10.1021/ma202764v | *Macromolecules* 2012, 45, 2690−2698

Scheme 3. Synthesis of Br−DTPBT and Br−DTPQX Monomer



Scheme 4. Suzuki and Stille Polymerization Toward PFDTPBT, PCDTPBT, PCPDTDTPBT, PFDTPQX, PCDTPQX, and PCPDTDTPQX



reactions were refluxed for 72 h to produce the polymers with reasonably high molecular weights (M_n) ranging from 17 to 34 kDa (Table 1). All of the monomers and corresponding copolymers were fully characterized by NMR spectra (see Supporting Information). The nitrogen bridges allows for introducing aliphatic side chains to promote solubility of the resultant conjugated polymers in common organic solvents, such as chloroform, toluene, chlorobenzene and 1,2-dichlorobenzene.

Table 1. Molecular Weights, Polydispersity Index and Thermal Properties of Polymers

copolymer	M_w[a]	M_n[a]	PDI[a]	T_d (°C)[b]
PFDTPBT	55 000	20 000	2.70	397
PCDTPBT	121 000	27 000	4.47	393
PCPDTDTPBT	58 500	23 400	2.50	388
PFDTPQX	70 000	34 000	2.17	415
PCDTPQX	50 900	30 200	1.68	428
PCPDTDTPQX	36 100	17 000	2.10	408

[a]Molecular weights and polydispersity were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. [b]Decomposition temperature (5% weight loss) measured by TGA.

Thermal Properties. Thermal properties of all copolymers were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) and summarized in Table 1. The decomposition temperatures (T_d) of the polymers are located at 388−428 °C (Figure 1), demonstrating their sufficiently high thermal stability for applications of PSCs. From the DSC measurement, neither melting point nor glass transition temperatures was observed, suggesting that these copolymers tend to be amorphous (see Figure S1, Supporting Information).

Optical Properties. The absorption spectra of all studied polymers were measured in both dilute chloroform and in the thin films (Figure 2), and the correlated optical parameters were summarized in Table 2. We compared the nitrogen-bridged polymers with the corresponding nonfused **DTBT**- or **DTQX**-based polymers reported in the literatures.[11] There are several interesting and noteworthy observations. Compared to the nonfused polymers, all the *N*-bridged copolymers showed significant band-broadening from the solution state to the solid state, indicating that strong interchain $\pi-\pi$ interactions indeed takes place due to the coplanar and rigid pentacyclic structures.

dx.doi.org/10.1021/ma202764v | *Macromolecules* 2012, 45, 2690−2698

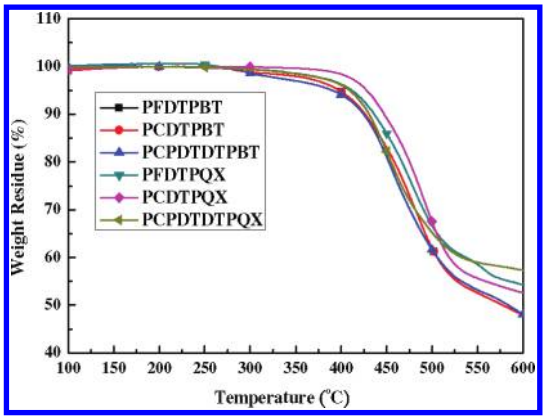


Figure 1. Thermal gravimetric analysis (TGA) measurements of the polymers with a ramping rate of 10 °C/min.

Table 2. Optical Properties of the Copolymers in the Chloroform Solution and in the Thin Film

	chloroform solution			thin film		
polymer	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)
PFDTPBT	517	553	2.24	526	576	2.15
PCDTPBT	518	557	2.23	527	581	2.13
PCPDTDTPBT	588	635	1.95	614	700	1.77
PFDTPQX	518	551	2.25	528	566	2.19
PCDTPQX	513	553	2.24	518	570	2.18
PCPDTDTPQX	582	626	1.98	610	670	1.85

The nonfused **DTBT**-based polymers generally exhibited two distinct absorption bands. One is due to the localized $\pi-\pi$ transition and the other comes from intramolecular charge transfer absorption. However, for the *N*-bridged copolymers, the two bands are merged into a wide absorption window

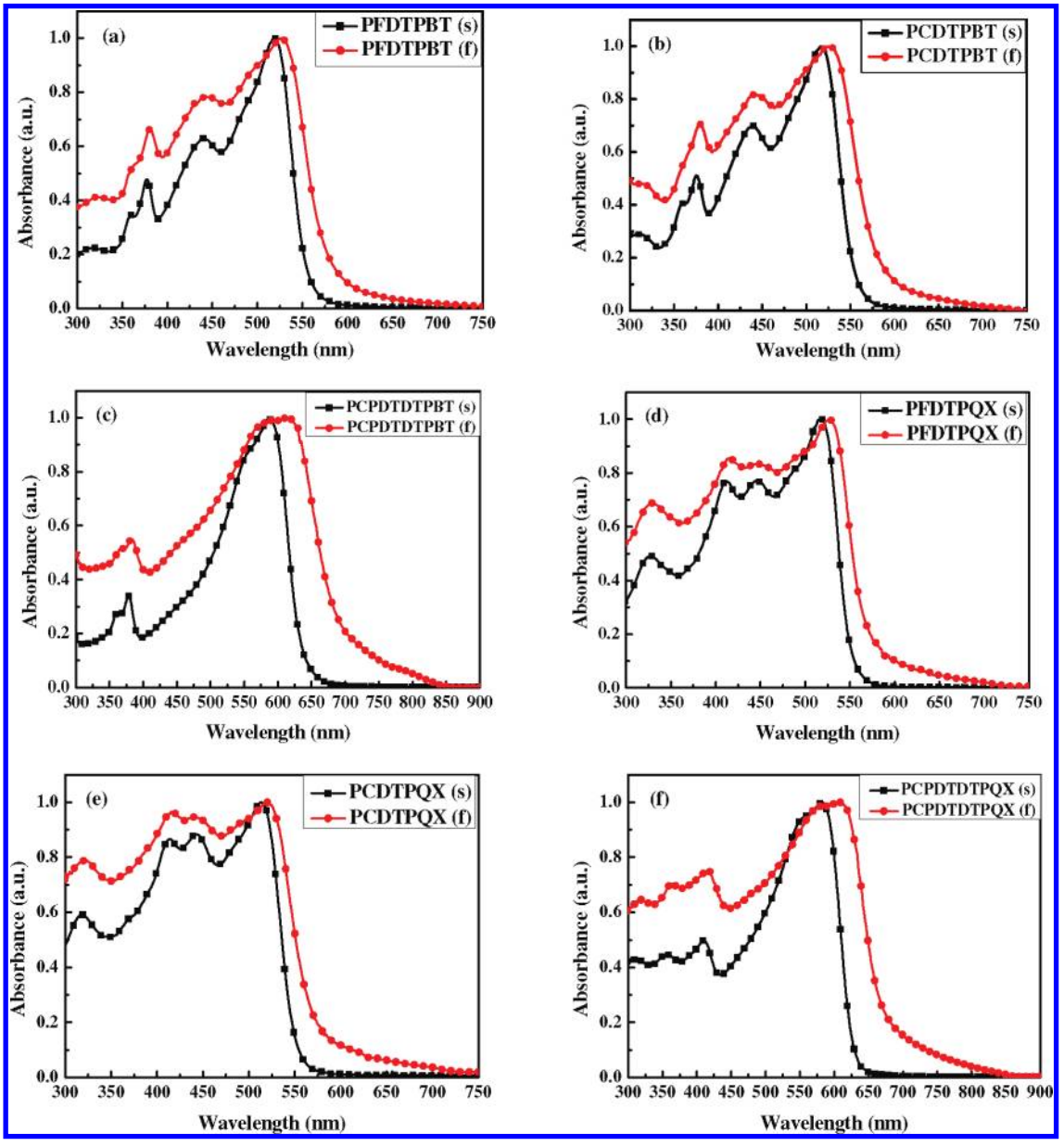


Figure 2. Normalized absorption spectra of all the polymers in the chloroform solution and the thin film.

dx.doi.org/10.1021/ma202764v | *Macromolecules* 2012, 45, 2690–2698

covering from 300 to 700 nm with several vibronic structures. Also note that *N*-bridged polymers exhibited hypsochromic-shifted absorption spectra relative to their corresponding nonfused counterparts. This phenomenon is somewhat different from what we expected previously. To gain deeper insight into the nitrogen effect, we carefully analyzed the absorption spectra of pentacylic nonfused **DTBT** and nitrogen-bridged **DTPBT** small molecules (Figure 3). **DTBT** shows a shorter

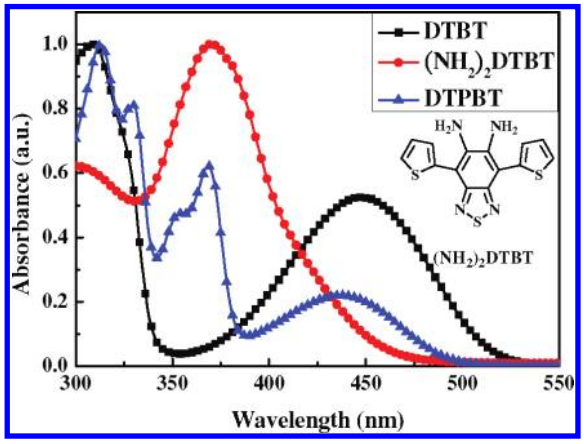


Figure 3. Normalized absorption spectra of **DTBT**, **DTPBT**, and **$(NH_2)_2$DTBT** in the toluene solution.

wavelength absorbance at 310 nm resulting from the $\pi-\pi^*$ transition of the pentacyclic units and a lower energy band at 450 nm attributed to the intramolecular charge transfer (ICT) between the thiophene units and the benzothiadiazole segment. In addition to the two typical bands observed in **DTBT**, an extra band at 368 nm was observed in the nitrogen-bridged **DTPBT** analogue. This band is highly associated with an internal charge transfer transition from a short D−π−A diaminobenzothiodiazole chromophore embedded in **DTPBT**. To confirm this hypothesis, we also synthesized an open-chain nitrogen-substituted **$(NH_2)_2$DTBT** for comparison (structure see in Figure 3). Indeed, **$(NH_2)_2$DTBT** also shows a strong absorption band at 368 nm due to the push−pull dipolar diaminobenzothiadiazole structure. Note that the ICT band at 450 nm observed in **DTPBT** is diminished in **$(NH_2)_2$DTBT**. The electronic and steric effects are responsible for the weak thiophene/BT communication in **$(NH_2)_2$DTBT**. First, the D−π−A push−pull effect decreases the electron deficiency of the BT unit. Second, the two amino groups in **$(NH_2)_2$DTBT** cause structural twisting between the BT and thiophene units. Interestingly, when the coplanarity is fastened in **DTPBT**, a ICT band at 438 nm is regained with relatively weaker intensity.

Although the electronic effect of nitrogen induces an extra absorbance at shorter wavelengths, it also attenuates the electron-accepting ability of the BT and QX units in the polymers. Therefore, the photoinduced charge transfer transition from the electron-rich units to the BT or QX units in the nitrogen-bridged polymers is shifted to higher energy. It is highly intriguing if the nitrogen bridges can be replaced by carbon bridges with more insulating character. This related research is currently underway in our lab. Furthermore, the **DTPBT**-based copolymers showed more red-shifted absorption spectra than the **DTPQX**-based copolymers, indicating that the accepting strength of **DTPBT** is slightly stronger than that of **DTPQX**. The optical band gaps (E_g^{opt}) deduced from the absorption edges of thin film spectra are in the following order: **PCPDTDTPBT** (1.77 eV) < **PCPDTDTPQX** (1.85 eV) < **PCDTPBT** (2.13 eV) < **PFDTPBT** (2.15 eV) < **PCDTPQX** (2.18 eV) < **PFDTPQX** (2.19 eV).

Electrochemical Properties. Cyclic voltammetry (CV) was employed to examine the electrochemical properties and evaluate the HOMO and LUMO levels of the polymers (Table 3 and Figure 4). All of the polymers showed stable and

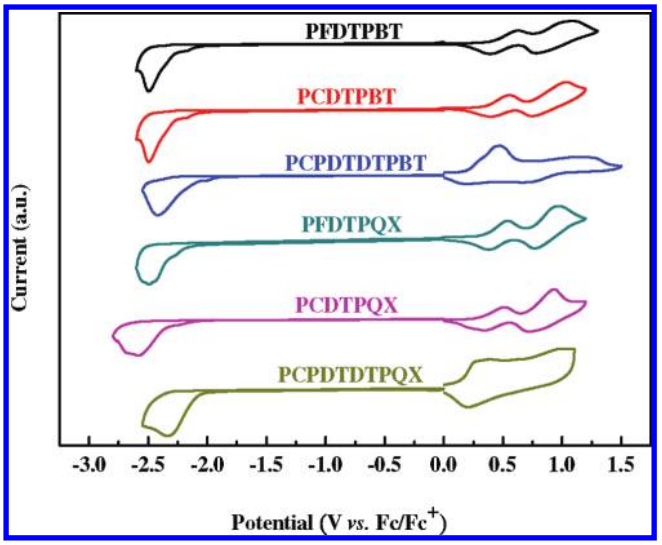


Figure 4. Cyclic voltammograms of the polymers in the thin film at a scan rate of 80 mV/s.

reversible p-doing and n-doing processes, which are important prerequisites for semiconductor materials. The HOMO energy level is estimated to be −5.11 and −5.06 eV for **PFDTPBT** and **PFDTPQX**, −5.06 and −5.02 eV for **PCDTPBT** and **PCDTPQX**, and −4.90 and −4.88 eV for **PCPDTDTPBT** and **PCPDTDTPQX**, respectively. **PCPDTDTPBT** and **PCPDTDTPQX** with higher-lying HOMO energy levels

Table 3. Electrochemical Onset Potentials and Electronic Energy Levels of the Polymers

copolymer	E_{ox}^{onset}(V)	E_{red}^{onset}(V)	HOMO[a] (eV)	LUMO^{el} [b] (eV)	LUMO^{opt} [c] (eV)	E_g^{el} (eV)
PFDTPBT	0.39	−2.08	−5.11	−2.64	−2.96	2.47
PCDTPBT	0.34	−2.05	−5.06	−2.67	−2.93	2.39
PCPDTDTPBT	0.18	−1.90	−4.90	−2.82	−3.13	2.08
PFDTPQX	0.34	−2.11	−5.06	−2.61	−2.87	2.45
PCDTPQX	0.30	−2.08	−5.02	−2.64	−2.84	2.38
PCPDTDTPQX	0.16	−2.01	−4.88	−2.71	−3.03	2.17

[a]HOMO= $-(E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$; $E_{(ferrocene)}^{onset}$ = 0.08 V. [b]LUMO= $-(E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$; $E_{(ferrocene)}^{onset}$ = 0.08 V. [c]LUMO levels of the polymers were obtained from the equation LUMO = HOMO + E_g^{opt}.

dx.doi.org/10.1021/ma202764v | *Macromolecules* 2012, 45, 2690−2698

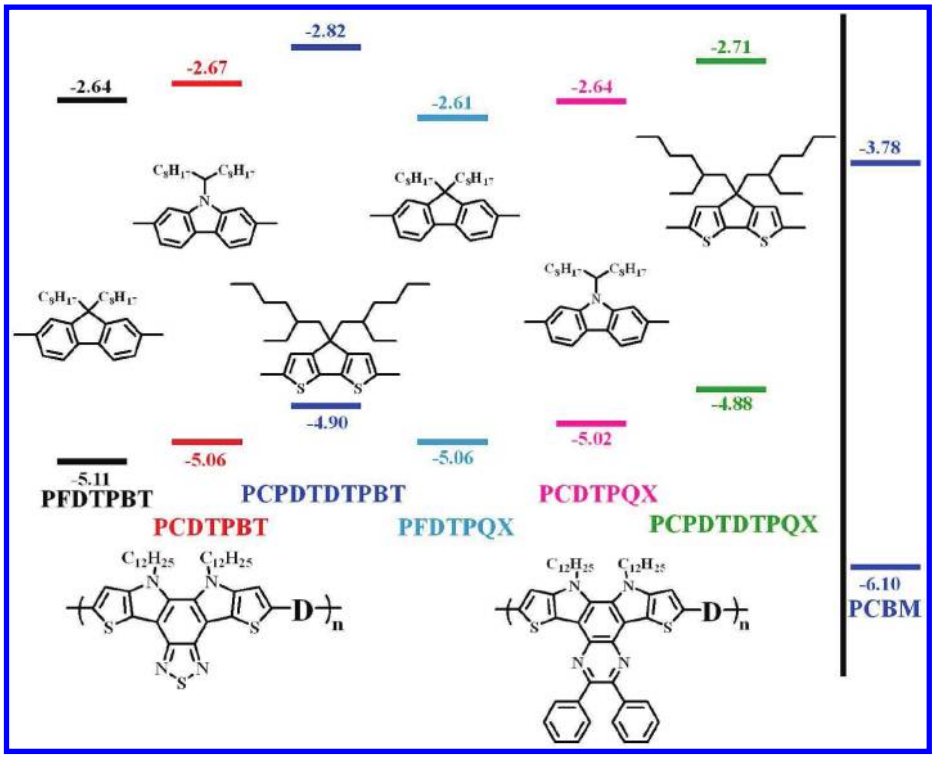


Figure 5. Energy diagram of HOMO–LUMO levels for the polymers and $PC_{71}BM$.

Table 4. Photovoltaic Characteristics

copolymer	wt % ratio of Copolymer and $PC_{71}BM$	mobility (cm^2/V s)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PFDTPBT	1:3	4.7×10^{-5}	0.74	−8.37	50	3.11
PCDTPBT	1:3	1.8×10^{-5}	0.72	−7.47	47	2.54
PCPDTDTPBT	1:2	1.3×10^{-5}	0.48	−6.23	45	1.35
PFDTPQX	1:4	5.9×10^{-5}	0.72	−8.62	55	3.40
PCDTPQX	1:3	3.2×10^{-5}	0.70	−8.27	51	2.95
PCPDTDTPQX	1:3	7.8×10^{-6}	0.50	−5.64	49	1.38

should have poorer air-stability. The fluorene-based polymers exhibited a slight deeper HOMO energy levels compared to the corresponding carbazole-based polymers, while the **CPDT**-based polymers showed the highest-lying HOMO levels. On the other hand, the LUMO energy levels of these polymers are located at relatively higher-lying positions from −2.6 to −2.8 eV. This behavior is consistent with the fact that the donating effect of the nitrogen weakens the electron-accepting ability of BT and QX, thereby lifting up the LUMO energy levels of the polymers. According to the HOMO–LUMO energy difference, the band-gaps (E_g^{el}) obtained from CV measurements are greater than the corresponding optical band-gaps (E_g^{opt}), which is a phenomenon consistent with the reports in the literatures.[12] The HOMO–LUMO energy diagram of the polymers is shown in Figure 5 for comparison.

Hole-Mobility and Photovoltaic Characteristics. Bulk heterojunction PSCs were fabricated on the basis of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al configuration and their performances were measured under 100 mW/cm^2 AM 1.5 illumination. Hole-only devices (ITO/PEDOT:PSS/polymer/Au) were also fabricated in order to estimate the hole mobilities of these polymers via space-charge limit current (SCLC) theory. The characterization data of the optimized device conditions are summarized in Table 4 and the $J-V$ curves of these devices are shown in Figure 6. The hole mobility of the

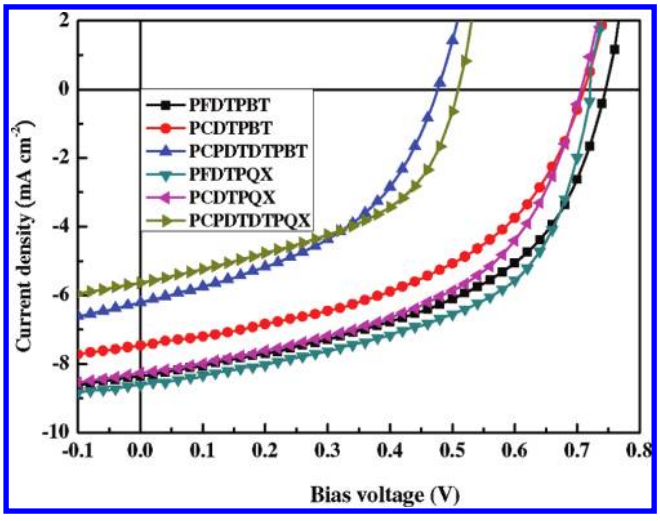


Figure 6. $J-V$ characteristics of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al under illumination of AM1.5, 100 mW/cm^2.

polymer follows the trend: **PCPDTDTPQX** (7.8×10^{-6} cm^2/V s) < **PCPDTDTPBT** (1.3×10^{-5} cm^2/V s) < **PCDTPBT** (1.8×10^{-5} cm^2/V s) < **PCDTPQX** (3.2×10^{-5} cm^2/V s) < **PFDTPBT** (4.7×10^{-5} cm^2/V s) < **PFDTPQX** (5.9×10^{-5} cm^2/V s). This result suggests that the **DTPQX**-based

dx.doi.org/10.1021/ma202764v | *Macromolecules* 2012, 45, 2690–2698

polymers generally have higher hole mobilites than their corresponding **DTPBT**-based polymers. The device based on the **PCPDTDTPBT**/$PC_{71}BM$ blend (1:2, w/w) exhibited a V_{oc} of 0.48 V, a J_{sc} of 6.23 mA/cm^2, a FF of 45% and a PCE of 1.35%, which is very similar to the device based on **PCPDTDTPQX**/$PC_{71}BM$ blend (1:3, w/w) (V_{oc} = 0.50 V, J_{sc} = 5.64 mA/cm^2 and a FF = 49%, PCE = 1.38%). The relatively lower V_{oc} values of the devices are mainly owing to the higher-lying HOMO values of the polymers, and the lower J_{sc} might be due to the unfavorable morphology of the active layer.[13] The device incorporating **PCDTPBT**/$PC_{71}BM$ (1:3, w/w) blend and **PCDTPQX**/$PC_{71}BM$ (1:3, w/w) blend delivered an improved PCE of 2.54% and 2.95%, respectively. This enhancement is ascribed to the **PCDTPBT** and **PCDTPQX**'s higher hole-mobilities and lower-lying HOMO values to obtain higher V_{oc}. The **PFDTPBT**/$PC_{71}BM$ (1:3, w/w) based device showed a V_{oc} of 0.74 V, a high J_{sc} of 8.37 mA/cm^2 and a FF of 50%, with a PCE of 3.11%. More encouragingly, **PFDTPQX**/$PC_{71}BM$ (1:4, w/w) based device exhibited a V_{oc} of 0.72 V, a J_{sc} of 8.62 mA/cm^2 leading to a highest PCE of 3.4%. This performance has outperformed the device based on a nonfused **PFDTQX** polymer reported in the literature.[11d]

CONCLUSIONS

We have successfully developed two novel donor−acceptor multifused **DTPBT** and **DTPQX** unit where two outer thiophene rings are covalently fastened with the central benzothiadiazole and quinoxaline rings by nitrogen bridges. These rigid and coplanar **DTPBT** and **DTPQX** building blocks were copolymerized with electron-rich donors, fluorene (**F**), carbazole (**C**), or cyclopentadithiophene (**CPDT**), via Suzuki or Stille coupling polymerization. The D−π−A diaminobenzothiodiazole and diaminoquinoxaline chromophores embedded in **DTPBT** and **DTPQX** segments induce internal charge transfer transitions upon photoexcitation, resulting in enhanced light-absorption ability in the UV region. Meanwhile, this electronic effect of nitrogen also reduces the electron-deficiency of the BT or QX acceptors. Therefore, the intramolecular charge transfer along the polymer backbones is attenuated. The optimized performance of the devices incorporating these polymers follows the trend: **PFDTPQX** > **PFDTPBT** > **PCDTPQX** > **PCDTPBT**, which is in good agreement with the trend of their hole-mobilities. The device based on **PFDTPQX**/$PC_{71}BM$ (1:4, w/w) exhibited a J_{sc} of 8.62 mA/cm^2 and a highest PCE of 3.4%. This research has gained a deep insight of the steric and electronic effects of the nitrogen bridges on the donor−acceptor fused systems, providing a useful guidance for future molecular design of conjugated polymers in PSCs applications.

EXPERIMENTAL SECTION

General Measurement and Characterization. All chemicals are purchased from Aldrich or Acros and used as received unless otherwise specified. ^{1}H and ^{13}C NMR spectra were measured using Varian 300 MHz instrument spectrometer. The molecular weight of polymers was measured by the GPC method (Viscotek VE2001GPC), and polystyrene was used as the standard (THF as the eluent). Differential scanning calorimeter (DSC) was measured on TA Q200 Instrument and thermal gravimetric analysis (TGA) was recorded on Perkin-Elmer Pyris under a nitrogen atmosphere at a heating rate of 10 °C/min. Absorption spectra were taken on a HP8453 UV−vis spectrophotometer. The electrochemical cyclic voltammetry was conducted on a Bioanalytical Systems Inc. analyzer. A carbon glass-coated with a thin polymer film was used as the working electrode and an Ag/AgCl as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile was the electrolyte. CV curves were calibrated using ferrocence as the standard, whose HOMO is set at −4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO = $-(E_{ox}^{onset} - E_{(ferrocene)}^{onset}+4.8)$ eV. The LUMO levels of polymer were obtained from the equation LUMO = $-(E_{red}^{onset} - E_{(ferrocene)}^{onset}+4.8)$ eV.

Fabrication and Characterization of BHJ Devices. ITO/glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone and isopropyl alcohol. Then, the substrates were covered by a 30 nm thick layer of PEDOT:PSS (Clevios P provided by H. C. Stark) by spin coating. After annealing in air at 150 °C during 30 min, the samples were cooled down to room temperature. Polymers were dissolved in *o*-dichlorobenzene (ODCB) (0.47 wt %) and $PC_{71}BM$ (purchased from Nano-C) was added to reach the desired ratio. The solution was then heated at 110 °C and stirred overnight. Prior to deposition, the solution was filtrated through a 0.45 μm filter and the substrates were transferred in a glovebox. The photoactive layer was then spin coated at different spin coating speed in order to tune its thickness. After drying, the samples were annealed during 15 min. The detailed processing parameters (spin coating speed; annealing temperature) are shown as follows: **PFDTPBT**/$PC_{71}BM$ (1000 rpm; 130 °C), **PCDTPBT**/$PC_{71}BM$ (1000 rpm, without annealing), **PCPDTDTPBT**/$PC_{71}BM$ (700 rpm; without annealing), **PFDTPQX**/$PC_{71}BM$ (1000 rpm; without annealing), **PCDTPQX**/$PC_{71}BM$ (700 rpm; 130 °C), **PCPDTDTPQX**/$PC_{71}BM$ (700 rpm; without annealing). The cathode made of calcium (35 nm thick) and aluminum (100 nm thick) was evaporated through a shadow mask under high vacuum (<10^{-6} Torr). Each device is constituted of 4 pixels defined by an active area of 0.04 cm^2. Finally, the devices were encapsulated and *I*−*V* curves were measured in air.

Electrical Characterization under Illumination. The devices were characterized under 100 mW/cm^2 AM 1.5 simulated light measurement (Yamashita Denso solar simulator). Current−voltage (*J*−*V*) characteristics of PSC devices were obtained by a Keithley 2400 SMU. Solar illumination conforming the JIS Class AAA was provided by a SAN-EI 300W solar simulator equipped with an AM 1.5G filter. The light intensity was calibrated with a Hamamatsu S1336-5BK silicon photodiode. The performances presented here are the average of the 4 pixels of each device.

Hole-Only Devices. In order to investigate the respective hole mobility of the different copolymer films, unipolar devices have been prepared following the same procedure except that the active layer is made of pure polymer and the Ca/Al cathode is replaced by evaporated gold (40 nm). The hole mobilities were calculated according to space charge limited current theory (SCLC). The *J*−*V* curves were fitted according to the following equation:

$$J = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3}$$

Here ε is the dielectric permittivity of the polymer, μ is the hole mobility, and L is the film thickness (distance between the two electrodes).

Synthesis of DTPBT. To a suspension solution of **1** (1.00 g, 3.06 mmol), 1-bromododecane (4.58 g, 18.38 mmol) and potassium iodide (20 mg) in DMSO (100 mL) was added potassium hydroxide (2.00 g, 35.64 mmol) in one portion at 80 °C. The resulting solution was stirred for 16 h at 80 °C and then was extracted with ethyl acetate (400 mL × 3) and water (200 mL). The combined organic layer was dried over $MgSO_4$. After removal the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 10/1) to give an orange-red solid **DTPBT** (1.44 g, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37 (d, J = 5.1 Hz, 2 H), 7.12 (t, J = 5.1 Hz, 2 H), 4.44 (t, J = 7.5 Hz, 4 H), 1.81−1.65 (m, 4 H), 1.30−0.90 (m, 36 H), 0.80 (t, J = 6.9 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.5, 145.5, 132.1, 126.8, 121.2, 111.7, 110.9, 50.3, 31.9, 30.0, 29.53, 29.51, 29.4, 29.30, 29.28, 29.0, 26.5, 22.7, 14.1. MS (EI,

dx.doi.org/10.1021/ma202764v | Macromolecules 2012, 45, 2690−2698

$C_{38}H_{54}N_4S_3$): calcd, 663.06; found, 663. Anal. Calcd for $C_{38}H_{54}N_4S_3$: C, 68.83; H, 8.21; N, 8.45; Found: C, 68.93; H, 8.17; N, 8.00.

Synthesis of Br-DTPBT. To a solution of **DTPBT** (1.50 g, 2.26 mmol) in chloroform (31 mL)/acetic acid (31 mL) was added *N*-bromosuccinimide (0.85 g, 4.76 mmol) in one portion at 0 °C. The flask was wrapped with alumiunm foil and stirred for 1 h at 0 °C and then was stirred for another 1 h at room temperature. The reaction was quenched by water (100 mL). The mixture solution was extracted with dichloromathane (300 mL × 3) and water (100 mL). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 30/1). The product was recrystallized from hexane to give an red solid **Br-BTDTP** (0.96 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.20 (s, 2 H), 4.41 (t, J = 7.5 Hz, 4 H), 1.79 (t, J = 6.3 Hz, 4 H), 1.28−1.13 (m, 36 H), 0.87 (t, J = 6.9 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.1, 143.2, 130.9, 121.3, 115.0, 113.6, 110.8, 50.4, 31.9, 30.0, 29.6, 29.56, 29.53, 29.4, 29.3, 29.0, 26.5, 22.7, 14.1. MS (EI, $C_{38}H_{52}Br_2N_4S_3$): calcd, 820.85; found, 820. Anal. Calcd for $C_{38}H_{52}Br_2N_4S_3$: C, 55.60; H, 6.39; N, 6.83; Found: C, 55.51; H, 6.52; N, 6.87.

Synthesis of DTPQX. To a solution of **DTPBT** (1.20 g, 1.81 mmol) in acetic acid (60 mL) was added zinc powder (2.40 g, 36.71 mmol) in one portion at room temperature. The mixture solution was heated to 140 °C for 15 min. After the solution was cooled at room temperature, the solid was removed by filtration. The mixture solution was extracted with ethyl acetate (500 mL × 3) and sodium hydroxide solution until the organic layer was basic. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, a black liquid **2** was obtained without further purification. To a solution of **2** and benzil (0.46 g, 1.63 mmol) in chloroform (36 mL) was added catalytic *p*-TSA in one portion at room temperature. The resulting mixture was heated to 65 °C and stirred for 16 h. The reaction solution was quenched by sodium bicarbonate solution, and then extracted with dichloromethane (300 mL × 3) and water (150 mL). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) and washed by ethanol to give a yellow solid **DTPQX**. (0.38 g, 25%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78−7.81 (m, 4 H), 7.47 (d, J = 5.1 Hz, 2 H), 7.37−7.40 (m, 6 H), 7.21 (d, J = 5.1 Hz, 2 H), 4.58 (t, J = 7.5 Hz, 4 H), 1.89 (s, 4 H), 1.15−1.29 (m, 36 H), 0.86 (t, J = 6.6 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.3, 146.2, 140.6, 133.8, 131.9, 130.8, 128.4, 127.7, 121.0, 117.4, 111.8, 50.6, 32.2, 30.6, 29.9, 29.8, 29.71, 29.65, 29.5, 27.0, 23.0, 14.5; MS (EI, $C_{52}H_{64}N_4S_2$): calcd, 809.22; found, 809. Anal. Calcd for $C_{52}H_{64}N_4S_2$: C, 71.09; H, 6.71; N, 10.36; Found: C, 71.30; H, 6.64; N, 10.35.

Synthesis of Br-DTPQX. To a solution of **DTPQX** (0.30 g, 0.36 mmol) in chloroform (7 mL)/acetic acid (7 mL) was added *N*-bromosuccinimide (0.14 g, 0.78 mmol) in one portion at 0 °C. The flask was wrapped with alumiunm foil and stirred for 1 h at 0 °C and then was stirred for another 1 h at room temperature. The reaction was quenched by water (50 mL). The mixture solution was extracted with dichloromathane (100 mL × 3) and water (50 mL). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 100/1). The product was recrystallized from hexane to give an red solid **Br-DTPQX** (0.22 g, 61%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75−7.12 (m, 4 H), 7.28 (m, 6 H), 7.21 (s, 2 H), 4.44 (t, J = 7.5 Hz, 4 H), 1.83 (s, 4 H), 1.21−1.15 (m, 36 H), 0.86 (t, J = 6.6 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.3, 143.4, 139.9, 133.1, 130.3, 130.1, 128.2, 128.0, 120.6, 116.9, 114.7, 114.1, 50.2, 31.9, 30.2, 29.5, 29.4, 29.35, 29.3, 29.1, 26.5, 22.7, 14.1; MS (EI, $C_{52}H_{62}Br_2N_4S_2$): calcd, 967.01; found, 967. Anal. Calcd for $C_{52}H_{62}Br_2N_4S_2$: C, 64.59; H, 6.46; N, 5.79; Found: C, 64.37; H, 6.48; N, 6.13.

Synthesis of PFDTPBT. To a 25 mL round-bottom flask was introduced **Br-DTPBT** (100 mg, 0.12 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolane-2′-yl)-9,9-dioctylfluorene **F** (78 mg, 0.12 mmol), $Pd(PPh_3)_4$ (5.6 mg, 0.0049 mmol), K_2CO_3 (126 mg, 2.36 mmol), Aliquat336 (22 mg, 0.054 mmol), degassed toluene (7 mL), and degassed H_2O (1.5 mL). The mixture was heated to 90 °C under nitrogen gas for 72 h. Then, 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (6.1 mg, 0.03 mmol) was added to the mixture solution and reacted for 24 h at 90 °C. Finally, 1-bromobenzene (4.7 mg, 0.03 mmol) was added to the mixture solution and reacted for 24 h at 90 °C. The solution was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with methanol, acetone, and chloroform sequentially for 1 week. The Pd−thiol gel (Silicycle Inc.) was added to above chloroform solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was redissolved in THF and added into methanol to reprecipitate out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark red solid (110 mg, 86%, M_n = 20000, PDI = 2.70). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.90−7.60 (m, 6 H), 7.60−7.40 (m, 2 H), 4.40−7.80 (m, 4 H), 1.80−2.20 (m, 8 H), 1.50−1.00 (m, 60 H), 0.85−0.75 (m, 12 H).

Synthesis of PCDTPBT. The procedure is following the synthesis of **PFDTPBT**. **Br-DTPBT** (100 mg, 0.12 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole **C** (80 mg, 0.12 mmol), $Pd(PPh_3)_4$ (5.6 mg, 0.0049 mmol), K_2CO_3 (126 mg, 2.36 mmol), Aliquat336 (22 mg, 0.054 mmol), degassed toluene (7 mL), degassed H_2O (1.5 mL), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (6.1 mg, 0.03 mmol), and 1-bromobenzene (4.7 mg, 0.03 mmol). The purified polymer was collected by filtration and dried under vacuum for 1 day to give a orange-red solid (113 mg, 87%, M_n = 27000, PDI = 4.47). ^{1}H NMR ($CDCl_3$, 300 MHz): 8.20−8.05 (m, 2 H), 8.00−7.85 (m, 2 H), 7.80−7.60 (m, 4 H), 7.60−7.50 (m, 2 H), 4.80−4.40 (m, 5 H), 2.60−2.30 (m, 2 H), 2.20−1.80 (m, 2 H), 1.30−1.10 (m, 60 H), 0.90−0.75 (m, 12 H).

Synthesis of PFDTPQX. The procedure is following the synthesis of **PFDTPBT**. **Br-DTPQX** (87 mg, 0.09 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolane-2′-yl)-9,9-dioctylfluorene **F** (58.5 mg, 0.09 mmol), $Pd(PPh_3)_4$ (4.2 mg, 0.0036 mmol), K_2CO_3 (94.5 mg, 0.68 mmol), Aliquat336 (16.5 mg, 0.045 mmol), degassed toluene (5 mL), degassed H_2O (1 mL), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (4.9 mg, 0.023 mmol), and 1-bromobenzene (3.7 mg, 0.023 mmol). The purified polymer was collected by filtration and dried under vacuum for 1 day to give an orange-red solid (100 mg, 93%, M_n = 34000, PDI = 2.17). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.90−7.70 (m, 10 H), 7.60−7.35 (m, 8 H), 4.80−4.50 (m, 4 H), 2.15−1.80 (m, 8 H), 1.50−1.05 (m, 60 H), 0.95−0.75 (m, 12 H).

Synthesis of PCDTPQX. The procedure is following the synthesis of **PFDTPBT**. **Br-DTPQX** (100 mg, 0.10 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole **C** (68 mg, 0.10 mmol), $Pd(PPh_3)_4$ (4.8 mg, 0.0041 mmol), K_2CO_3 (108 mg, 0.78 mmol), Aliquat336 (16 mg, 0.04 mmol), degassed toluene (6 mL), degassed H_2O (1 mL), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (5.3 mg, 0.026 mmol), and 1-bromobenzene (4.1 mg, 0.026 mmol). The purified polymer was collected by filtration and dried under vacuum for 1 day to give an orange-red solid (119 mg, 95%, M_n = 30200, PDI = 1.68). ^{1}H NMR ($CDCl_3$, 300 MHz): 8.30−8.10 (m, 2 H), 8.00−7.65 (m, 10 H), 7.60−7.40 (m, 8 H), 4.80−4.60 (m, 1 H), 2.70−2.30 (m, 2 H), 2.20−1.80 (m, 6H), 1.40−1.00 (m, 60H), 0.90−0.75 (m, 12 H).

Synthesis of PCPDTDTPBT. To a 25 mL round-bottom flask was introduced **Br-DTPBT** (50 mg, 0.06 mmol), 2,6-di(trimethyltin)-4,4-diethylhexylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene **CPDT** (44 mg, 0.06 mmol), $Pd_2(dba)_3$ (4.5 mg, 0.0049 mmol), tri(*o*-tolyl)phosphine (11.8 mg, 0.038 mmol), and dry chlorobenzene (2.2 mL). The mixture was then degassed by bubbling nitrogen for 10 min at room temperature. The round-bottom flask was placed into the microwave reactor and reacted for 45 min under 270 W. Then, tributyl(thiophen-2-yl)stannane (5.6 mg, 0.015 mmol) was added to the mixture solution and reacted for 10 min under 270 W. Finally, 2-bromothiophene (2.4 mg, 0.015 mmol) was added to the mixture solution and reacted for 10 min under 270 W. The solution was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane, and chloroform sequentially for 1 week. The Pd-thiol gel (Silicycle Inc.) and Pd-TAAcOH were added to above chloroform solution to remove the residual Pd catalyst and Sn

metal. After filtration and removal of the solvent, the polymer was redissolved in chloroform again and added into methanol to reprecipitate out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark purple solid (50 mg, 78%, M_n = 23400, PDI = 2.50). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.25−7.10 (m, 4 H), 4.70−4.30 (m, 4 H), 2.10−1.70 (m, 8 H), 1.30−0.90 (m, 54 H), 0.90−0.60 (m, 18 H).

Synthesis of PCPDTDTPQX. To a 25 mL round-bottom flask was introduced **Br-DTPQX** (100 mg, 0.10 mmol), 2,6-di(trimethyltin)-4,4-diethylhexylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene **CPDT** (75.3 mg, 0.10 mmol), $Pd_2(dba)_3$ (7.6 mg, 0.0083 mmol), tri(*o*-tolyl)phosphine (20.1 mg, 0.066 mmol), and dry chlorobenzene (3.6 mL). The mixture was then degassed by bubbling nitrogen for 10 min at room temperature. The round-bottom flask was placed into the microwave reactor and reacted for 45 min under 270 W. Then, tributyl(thiophen-2-yl)stannane (19.2 mg, 0.026 mmol) was added to the mixture solution and reacted for 10 min under 270 W. Finally, 2-bromothiophene (8.4 mg, 0.026 mmol) was added to the mixture solution and reacted for 10 min under 270 W. The solution was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane, and chloroform sequentially for 1 week. The Pd−thiol gel (Silicycle Inc.) and Pd-TAAcOH were added to above chloroform solution to remove the residual Pd catalyst and Sn metal. After filtration and removal of the solvent, the polymer was redissolved in chloroform again and added into methanol to reprecipitate out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a red purple solid (88 mg, 70%, M_n = 17000, PDI = 2.10). ^{1}H NMR ($CDCl_3$, 300 MHz): 8.00−7.70 (m, 4 H), 7.60−7.30 (m, 10 H), 4.80−4.30 (m, 4 H), 2.20−1.80 (m, 6 H), 2.00−1.40 (m, 52 H), 1.00−0.70 (m, 18 H).

■ ASSOCIATED CONTENT

Supporting Information

DSC measurements and ^{1}H and ^{13}C NMR spectra of all the intermediates, monomers, and corresponding copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yjcheng@mail.nctu.edu.tw.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Council and the "ATU Program" of the Ministry of Education, Taiwan, for financial support.

■ REFERENCES

(1) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (c) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.

(2) (a) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868. (b) Chen, J.; Cao, Y. *Acc. Chem. Res.* **2009**, *42*, 1709.

(3) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (b) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng. Res.* **2001**, *32*, 1.

(4) Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761 and reference therein.

(5) (a) Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804. (b) Ando, S.; Nishida, J.-I.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 5336.

(6) (a) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638. (b) Li, L.; Xiang, J.; Xu, C. *Org. Lett.* **2007**, *9*, 4877. (c) Bounchard, J.; Wakim, S.; Leclerc, M. *J. Org. Chem.* **2004**, *69*, 5705. (d) Cheng, Y.-J.; Wu., J.-S.; Shih, P.-I.; Chang, C.-Y.; Jwo, P.-C.; Kuo, W.-S.; Hsu, C.-S. *Chem. Mater.* **2011**, *23*, 2361. (e) Wu., J.-S.; Cheng, Y.-J.; Dubosc, M.; Hsieh, C.-H.; Chang, C.-Y.; Hsu, C.-S. *Chem. Commun.* **2010**, *46*, 3259. (f) Chen, C.-H.; Cheng, Y.-J.; Dubosc, M.; Hsieh, C.-H.; Chu, C.-C.; Hsu, C.-S. *Chem. Asian. J.* **2010**, *5*, 2483. (g) Chen, C. H.; Hsieh, C.-H.; Dubosc, M.; Cheng, Y.-J.; Hsu, C.-S. *Macromolecules* **2010**, *6973*, 697. (h) Wong, K.-T.; Chao, T.-C.; Chi, L.-C.; Chu, Y.-Y.; Balaiah, A.; Chiu, S.-F.; Liu, Y.-H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5033. (i) Wang, J.-Y.; Hau, S. K.; Yip, H.-L.; Davies, J. A.; Chen, K.-S.; Zhang, Y.; Sun, Y.; Jen, A. K.-Y. *Chem. Mater.* **2011**, *23*, 765. (j) Zhang, M.; Sun, Y.; Guo, X.; Cui, C.; He, Y.; Li, Y. *Macromolecules* **2011**, *44*, 7625. (l) Forster, M.; Annan, K. O.; Scherf, U. *Macromolecules* **1999**, *32*, 3159. (k) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895. (n) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853. (l) Patil, S. A.; Scherf, U.; Kadashchuk, A. *Adv. Funct. Mater.* **2003**, *13*, 609. (m) Cheng, Y.-J.; Chen, C.-H.; Lin, Y.-S.; Chang, C.-Y.; Hsu, C.-S. *Chem. Mater.* **2011**, *23*, 5068. (n) Chen, C.-H.; Cheng, Y.-J.; Chang, C.-Y.; Hsu, C.-S. *Macromolecules* **2011**, *44*, 8415.

(7) (a) Guégano, X.; Kanibolotsky, A. L.; Blum, C.; Mertens, S. F. L.; Liu, S.-X.; Neels, A.; Hagemann, H.; Skabara, P. J.; Leutwyler, S.; Wandlowski, T.; Hauser, A.; Decurtins, S. *Chem.—Eur. J.* **2009**, *15*, 63. (b) Jia, C.-Y.; Liu, S.-X.; Tanner, C.; Leiggener, C.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem. Commun.* **2006**, *42*, 1878. (c) Loosli, C.; Jia, C.-Y.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, *70*, 4988. (d) Jaggi, M.; Blum, C.; Dupont, N.; Grilj, J.; Liu, S.-X.; Hauser, J.; Hauser, A.; Decurtins, S. *Org. Lett.* **2009**, *11*, 3096. (e) Balaji, G.; Shim, W. L.; Parameswaran, M.; Valiyaveettil, S. *Org. Lett.* **2009**, *11*, 4450. (f) Zhu, G.; Conner, S. E.; Zhou, X.; Shih, C.; Li, T.; Anderson, B. D.; Brooks, H. B.; Campbell, R. M.; Considine, E.; Dempsey, J. A.; Faul, M. M.; Ogg, C.; Patel, B.; Schultz, R. M.; Spencer, C. D.; Teicher, B.; Watkins, S. A. *J. Med. Chem.* **2003**, *46*, 2027. (g) Wang, H.; Shi, Q.; Lin, Y.; Fan, H.; Cheng, P.; Zhan, X.; Li, Y.; Zhu, D. *Macromolecules* **2011**, *44*, 4213.

(8) Hou, J.; Park, M.-H.; Zhang, S.; Yao, Y.; Chen, L.-M.; Li, J.-H.; Yang, Y. *Macromolecules* **2008**, *41*, 6012.

(9) (a) McNeill, C. R.; Halls, J. J. M.; Wilson, R.; Whiting, G. L.; Berkebile, S.; Ramsey, M. G.; Friend, R. H.; Greenham, N. C. *Adv. Funct. Mater.* **2008**, *18*, 2309. (b) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988.

(10) Cheng, Y.-J.; Chen, C.-H.; Ho, Y.-J.; Chang, S.-W.; Witek, H. A.; Hsu, C.-S. *Org. Lett.* **2011**, *13*, 5484.

(11) (a) Zhang, F.; Jespersen, K. G.; Björström, C.; Svensson, M.; Andersson, M. R.; Sundström, V.; Magnusson, K.; Moons, E.; Yartsev, A.; Inganäs, O. *Adv. Funct. Mater.* **2006**, *16*, 667. (b) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295. (c) Moulé, A. J.; Tsami, A.; Bünnagel, T. W.; Forster, M.; Kronenberg, N. M.; Scharber, M.; Koppe, M.; Morana, M.; Brabec, C. J.; Meerholz, K.; Scherf, U. *Chem. Mater.* **2008**, *20*, 4045. (d) Lindgren, L. J.; Zhang, F.; Andersson, M.; Barrau, S.; Hellström, S.; Mammo, W.; Perzon, E.; Inganäs, O.; Andersson, M. R. *Chem. Mater.* **2009**, *21*, 3491. (e) Wang, E.; Hou, L.; Wang, Z.; Ma, Z.; Hellström, S.; Zhuang, W.; Zhang, F.; Inganäs, O.; Andersson, M. R. *Macromolecules* **2011**, *44*, 2067.

(12) (a) Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, R. A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3371. (b) Yao, Y.; Shi, C.; Li, G.; Shrotriya, V.; Pei, Z.; Yang, Y. *Appl. Phys. Lett.* **2006**, *89*, 153507.

(13) Zhang, J.; Cai, W.; Huang, F.; Wang, E.; Zhong, C.; Liu, S.; Wang, M.; Duan, C.; Yang, T.; Cao, Y. *Macromolecules* **2011**, *44*, 894.