# Effect of Extended π-Conjugation Structure of Donor–Acceptor Conjugated Copolymers on the Photoelectronic Properties

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**Abstract:** New donor-acceptor conjugated copolymers based on alkylthienylbenzodithiophene (BDTT) and alkoxynaphthodithiophene (NDT) have been synthesized and compared with their benzo[1,2-b:4,5-b']dithiophene (BDT)-based analogues to investigate the effect of the extended  $\pi$  conjugation of the polymer main chain on the physicochemical properties of the polymers. A systematic investigation into the optical properties, energy levels, field-effect transistor characteristics, and photovoltaic characteristics of these polymers was conducted. Both polymers demonstrated enhanced photovoltaic performance and increased hole mobility compared with the BDTbased analogue. However, the BDTTbased polymer (with  $\pi$ -conjugation ex-

**Keywords:** conjugation • donoracceptor systems • photochemistry • polymers • structure-activity relationships tension perpendicular to main chain) gave the highest power conversion efficiency of 5.07% for the single-junction polymer solar cell, whereas the NDT-based polymer (with  $\pi$ -conjugation extension along the main chain) achieved the highest hole mobility of approximately  $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  based on the field-effect transistor; this indicated that extending the  $\pi$  conjugation in different orientations would have a significant influence on the properties of the resulting polymers.

# Introduction

Solution-processable semiconducting polymers have attracted tremendous attention as a result of their unique advantages, including low cost, light weight, and potential applications in flexible and large-area devices, such as polymer solar cells (PSCs)<sup>[1]</sup> or organic field-effect transistors (OFETs).<sup>[2]</sup> Recent advances in the development of new semiconducting polymers have achieved field-effect mobilities of  $> 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and power conversion efficiencies (PCEs) of > 9% in bulk heterojunction (BHJ) devices.<sup>[3,4]</sup> Although optimization of the device has made synergetic

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advancements,<sup>[5]</sup> the development of novel semiconducting polymers still plays a key role in obtaining excellent performance of PSCs or a high charge mobility for OFETs. Thus, a vast number of donor–acceptor (D-A)-type copolymers have been developed because their electronic properties can be easily changed based on the unique combination of the D-A unit, which could promote strong intermolecular interactions and  $\pi$ – $\pi$  stacking, as well as expanding the absorption range.<sup>[6]</sup>

Among the numerous donor units used in the D-A copolymers, benzo[1,2-b:4,5-b']dithiophene (BDT) is one of the most promising electron-donor units for applications in high-performance polymer semiconductors. Its large planar  $\pi$ -conjugated structure promotes facile  $\pi$ - $\pi$  stacking and improves hole mobility.<sup>[7]</sup> On the other hand, quinoxaline (Qx) has been widely used as an electron-acceptor unit owing to the electron-withdrawing properties of the two imine nitrogen atoms and relatively stable quinoid form.<sup>[8]</sup> Nowadays, by choosing BDT and Qx as the building blocks, the resultant polymers with PCEs of up to 8% have been reported; this shows the promising potential of this kind of polymer.<sup>[9]</sup> Although the structure-property relationships of D-A conjugated polymers have been studied extensively, we found that, among the various follow-up works, few studies were carried out on the effect of *n*-conjugated extension orientation on the optical, electrochemical, morphological, OFET, and photovoltaic properties of the copolymers. The existence of the BDT unit allows a selectivity in the construction of polymers through vertical or horizontal  $\pi$ -conjugation extension. For example, by introducing an extended conjugated structure (alkylthienyl) into BDT polymers in the vertical

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direction, significant changes to the charge transport or relative device performance were obtained.<sup>[10]</sup> Prompted by these points, we designed three D-A-type low-band-gap copoly-PBDTmers. named DFDTQX, PBDTT-DFDTQX and PNDT-DFDTQX, respectively (see Scheme 1), based new fluorinated on а alkoxyphenylquinoxaline (DFDTQX) as an acceptor unit and alkoxybenzodithiophene (BDT), alkylthienylbenzodithiophene (BDTT), or alkoxynaphthodithiophene (NDT) moieties as the donor unit. Two electron-withdrawing fluorine atoms were introduced into Qx to lower the HOMO energy levels of the polymers<sup>[11]</sup> to gain a higher open-circuit voltage  $(V_{\rm oc}).$ Moreover, alkoxyphenyl groups were functionalized at the Ox core to ensure solubility. BDTT and NDT possess extended  $\pi$ -conjugation structures perpendicular to or along the main chain compared with their BDT analogues. Thus, using the three donor units to construct different D-A conjugated polymers allows us to study the effect of  $\pi$ -conjugation structures on the properties of the polymers explicitly. Herein, we report the synthesis of three conjugated polymers, their optoelectronic characteristics, and optimal results of field-effect transistors (FETs) and photovoltaic devices.

# **Experimental Section**

Materials and Synthetic Procedures Scheme 2 shows the synthetic routes



Scheme 1. Chemical structures of PBDT-DFDTQX, PBDTT-DFDTQX, and PNDT-DFDTQX.



Scheme 2. Synthetic routes for the preparation of copolymers PBDT-DFDTQX, PBDTT-DFDTQX, and PNDT-DFDTQX.

to the copolymers. Monomers M1, M2, M3 were synthesized according to literature procedures.<sup>[10,12,13]</sup> The synthesis of M4 is described in the Supporting Information. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were of commercial grade and used as received without further purification. All reactions were performed under a nitrogen atmosphere.

Synthesis of poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophenealt-5,8-bis(5-thiophen-2-yl)-6,7-difluoro-2,3bis(4-(dodecyl)phenyl))quinoxaline] (PBDT-DFDTQX)

Monomers M4 (100.9 mg, 0.1 mmol) and M1 (77.2 mg, 0.1 mmol) were dissolved in a 25 mL two-necked flask in degassed toluene (6 mL). The mixture was purged with nitrogen for 15 min, and then  $[Pd(PPh_3)_4]$  (6 mg,0.005 mmol) was added. After being purged for 15 min, the mix-

ture was vigorously stirred at 110 °C for 24 h. After being cooled to room temperature, the reaction mixture was added dropwise to methanol (200 mL) and then collected by filtration and washed with methanol. Then the solid was subjected to Soxhlet extraction with methanol, hexane, and chloroform. Subsequently, the fraction extracted by chloroform was evaporated under reduced pressure, precipitated in methanol, filtered, and dried at 40°C overnight to afford PBDT-DFDTQX as a black solid (82 mg, 63.5%).  $M_{\rm p} = 13.4$  kDa;  $M_{\rm W} = 24.9$  kDa; PDI = 1.86; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.51-7.43$  (br, 6H), 7.08–6.37 (br, 6H), 4.72-3.44 (br, 8H), 2.17-0.57 ppm (br, 78H); elemental analysis calcd (%) for  $(C_{78}H_{98}N_2F_2O_4S_4)_n;$  C 72.29, H 7.78, N 2.61; found: C 72.35, H 7.72, N 2.68.

#### Synthesis of poly{4,9-bis(2-ethylhexyloxy)naphtho[1,2-b:5,6b']dithiophene-alt-5,8-bis(5-thiophen-2-yl)-6,7-difluoro-2,3bis(4-(dodecyl)phenyl))quinoxaline} (PNDT-DFDTQX)

PNDT-DFDTQX was synthesized by a similar processes to that of PBDT-DFDTQX, but monomer M2 (82.2 mg, 0.1 mmol) was used instead of M1. PNDT-DFDTQX was obtained as a greenish-black solid (105.5 mg, 79.6 %).  $M_n = 11.8$  kDa;  $M_W = 23.0$  kDa; PDI = 1.94; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.39-7.42$  (br, 6H), 7.27–5.92 (br, 10H), 4.95–3.34 (br, 8H), 2.42-0.54 ppm (br, 78H); elemental analysis calcd (%) for (C82H100N2F2O4S4)n: C 73.17, H 7.64, N 2.08; found: C 73.12, H 7.67, N 2.10.

#### Synthesis of poly{4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5b']dithiophene-alt-5,8-bis(5-thiophen-2-yl)-6,7-difluoro-2,3bis(4-(dodecyl)phenyl))quinoxaline] (PBDTT-DFDTQX)

PBDTT-DFDTQX was synthesized by a similar processes to that of PBDT-DFDTQX, but monomer M3 (90.4 mg, 0.1 mmol) was used instead of M1. PNDT-DFDTOX was obtained as a black solid (83 mg, 59%).  $M_n = 14.7 \text{ kDa}; M_W = 30.0 \text{ kDa}; \text{ PDI} = 2.04; ^1\text{H NMR}$  (600 MHz,  $CDCl_3$ ):  $\delta = 8.27-7.36$  (br, 6 H), 7.18-6.12 (br, 10 H), 4.67-3.65 (br, 8 H), 3.41-2.64 (br,8H),2.01-0.64 ppm (br, 78H); elemental analysis calcd (%) for (C<sub>86</sub>H<sub>102</sub>N<sub>2</sub>F<sub>2</sub>O<sub>2</sub>S<sub>6</sub>)<sub>n</sub>: C 72.33, H 7.34, N 2.66; found: C 72.22, H 7.27, N 2.78

#### Measurements and Characterization

NMR spectra were recorded on a Bruker AV 600 spectrometer in CDCl<sub>3</sub> at room temperature. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to internal tetramethylsilane (TMS;  $\delta = 0$  ppm). Splitting patterns were designated as s (singlet), t (triplet), d (doublet), m (multiplet), and br (broad). The number-average  $(M_n)$  and weight-average  $(M_w)$  molecular weights were measured by the gel permeation chromatography (GPC) method by using polystyrene as a standard and 1,2,4-tricholorobenzene (TCB) as the eluent. Elemental analyses were performed on a Flash EA 1112 analyzer or Elementar vario EL III instrument. Thermogravimetric analysis (TGA; Netzsch TG209C) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were performed by using a MET-TLER differential scanning calorimeter (DSC822e) from 25-250 °C under nitrogen at a heating rate of 10°Cmin<sup>-1</sup>. UV/Vis absorption spectra were measured on solutions of polymer in chloroform and on polymer films cast onto quartz glass by using a Shimadzu model UV-3150spectrometer. Electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with a Pt disk coated with the polymer film, Pt plate, and Ag/Ag+ electrode as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol L<sup>-1</sup> solution of Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile. The film morphology was determined on a Nanoscope V AFM (Digital Instruments) instrument operating in tapping mode. AFM images and blend-film absorption spectra were recorded directly on the tested devices, in the device area out of the Ca/Al electrode. XRD measurements of thin films were performed in reflection mode with  $Cu_{K\alpha}$  radiation ( $\lambda = 0.15418$  nm) by using a Rigaku D/max 2500 V X-ray diffractometer.

#### Fabrication of Photovoltaic Devices

PSCs were fabricated with indium tin oxide (ITO) glass as a positive electrode, Ca/Al as a negative electrode, and a blend film of the polymer/ (6,6)-phenyl C<sub>71</sub> butyric acid methyl ester (PC<sub>71</sub>BM) between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), which was spin-cast from an aqueous solution of PE-DOT:PSS (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer was about 60 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymer and PC71BM in o-dichlorobenzene on the ITO/PEDOT:PSS electrode. Then, the Ca/Al cathode was deposited on the polymer layer by vacuum evaporation under  $3 \times 10^{-4}$  Pa. The thickness of the photosensitive layer was about 100 nm, as measured on an Ambios Tech XP-2 profilometer. The effective area of one cell was about 4 mm<sup>2</sup>. The currentvoltage (J versus V) measurements of the devices were conducted on a computer-controlled Keithley236 source measure unit. A xenon lamp with an AM1.5G filter was used as the white-light source, and the optical power at the sample was 100 mW cm<sup>-2</sup>

External quantum efficiency (EQE) was measured with a homemade system on encapsulated devices: monochromatic light was obtained with a xenon arc lamp from Lot-Oriel (300 W power) coupled with a Spectra-Pro monochromator. The photocurrent produced by the device passed through a calibrated resistance (50  $\Omega$ ) and the voltage drop signal was collected through the resistance with a Lock-In Digital Amplifier SR830. The signal was pulsed by means of an optical chopper (500 Hz frequency). A calibrated silicon UV-enhanced photodiode was used as a reference.

#### Fabrication of FET Devices

Polymer FETs were fabricated in a bottom-gate top-contact (BGTC) configuration. The gold source-drain electrodes were prepared by a vacuum evaporation technique to control the channel length (L) and channel width (W). Before deposition of the polymer semiconductors, octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics, which were placed in a vacuum oven with OTS to form an OTS self-assembled monolayer. Then the polymer thin films were spin-coated on the OTS-modified SiO<sub>2</sub>/Si substrates from solutions in *o*-dichlorobenzene. The OFET devices were annealed on a hot plate for 5 min in air directly and measured in air by using a Keithley4200 semiconductor characterization system. The mobility of the devices was calculated in the saturation regime by using Equation (1):

$$I_{\rm DS} = (W/2L)C_{\rm i}\mu(V_{\rm GS} - V_{\rm Th})^2 \tag{1}$$

in which W is the channel width; L is the channel length;  $C_i$  is the insulator capacitance per unit area; and  $V_{\rm GS}$  and  $V_{\rm Th}$  are the gate voltage and threshold voltage, respectively.

## **Results and Discussion**

The synthetic routes to the polymers are outlined in Scheme 2. Herein, the thiophene  $\pi$  bridge in the main chain of the polymers was introduced to overcome steric hindrance between the adjacent donor and acceptor units, and the 4-(dodecyl)phenyl groups on the Qx core were employed to ensure solubility of the copolymers. All polymers were synthesized by the palladium-catalyzed Stille coupling method. The synthesized polymers were purified by continuous extractions with methanol, hexanes, and chloroform, and the chloroform fractions were recovered. The chemical structures of the polymers were verified by <sup>1</sup>H NMR spectroscopy and elemental analysis. <sup>1</sup>H NMR spectra of the

polymers are shown in the Supporting Information. All polymers exhibited good solubility in common organic solvents, such as chloroform, toluene, and chlorobenzene, and were processed to form smooth and pinhole-free films upon spin-coating. Molecular weights of the polymers were determined by GPC in TCB by using polystyrene as the standard, and the polymers had weight-average molecular weight  $(M_w)$  values ranging from 23.0 to 30.0 kDa with polydispersities (PDIs) of around 1.89–2.04 (see Table 1). The thermal

Table 1. Molecular weights and thermal properties of the polymers.

Polymer	$M_n^{[a]}$	$M_{ m w}^{[ m a]}$	$\mathrm{PDI}^{[\mathrm{a}]}$ $(M_{\mathrm{w}}/M_{\mathrm{n}})$	$T_{\rm d}^{\rm [b]}$ [°C]
PBDT-DFDTQX	$13.4 \times 10^{3}$	$24.9 \times 10^{3}$	1.86	345
PNDT-DFDTQX	$11.8 \times 10^{3}$	$23.0 \times 10^{3}$	1.94	404
PBDTT-DFDTQX	$14.7 \times 10^{3}$	$30.0 \times 10^{3}$	2.04	373

[a]  $M_n M_w$ , and PDIs of the polymers were estimated by GPC with TCB as the eluent. [b] The 5% weight-loss temperatures in air.

transition and stability of the polymers were investigated by DSC and TGA under a nitrogen atmosphere. In the DSC measurements (Figure S1 in the Supporting Information), no clear phase transitions were observed in the range of 25–250 °C. The three polymers have good thermal stability with onset decomposition temperatures corresponding to 5%



Figure 1. TGA plots of the polymers with a heating rate of 10°Cmin<sup>-1</sup> under an inert atmosphere.

## **Optical Properties**

The normalized UV/Vis absorption spectra of dilute solutions of PBDT-DFDTQX, PNDT-DFDTQX, and PBDTT-DFDTQX in chloroform, and as thin films deposited on quartz glass, are shown in Figure 2 a and b. Table 2 provides a summary of the optical data, including the absorption peak wavelengths ( $\lambda_{max}$ ), absorption edge wavelengths ( $\lambda_{onset}$ ), and the optical band gap ( $E_g^{opt}$ ). All polymers exhibit a broad and strong absorption spectral feature across the entire UV/Vis region. In Figure 2 a, all of the absorption spectra recorded as dilute solutions in chloroform feature two absorption bands, which are a common feature of D-A copolymers. The absorption band in the short-wavelength region ( $\lambda \approx 423$  nm) originated from the localized  $\pi$ - $\pi$ \* tran-



Figure 2. UV/Vis absorption spectra of polymers in  $CHCl_3$  (a) and as thin films (b).

weight loss at 345, 404, and 373 °C, respectively, as shown in Figure 1. Clearly, the introduction of  $\pi$  conjugation, whether

perpendicular to or along the main chain, significantly improved the thermal stability of the polymers. The high thermal stability of the resulting copolymers is adequate for their applications in PSCs, OFETs, and other electric fields.

Table 2. Optical and electrochemical properties of the polymers.

Polymer	$\lambda_{\rm max}$ [nm]		$\lambda_{\text{onset}}$ film	$E_{g}^{opt[c]}$	$HOMO/E_{ox}$	$LUMO/E_{red}$	$E_{g}^{ec[d]}$
	Solution <sup>[a]</sup>	Film <sup>[b]</sup>	[nm]	[eV]	[eV/V]	[eV/V]	[eV]
PBDT-DFDTQX	416, 569	422, 596	676	1.83	-5.31/0.60	-3.49/-1.22	1.82
PBDTT-DFDTQX	422, 577	421, 609	698	1.78	-5.41/0.70	-3.63/-1.08	1.71
PNDT-DFDTQX	421, 591	427, 632	701	1.76	-5.09/0.38	-3.45/-1.25	1.64

[a] Measured in chloroform. [b] Cast from a solution in chlorobenzene. [c] Band gap estimated from the onset wavelength ( $\lambda_{onset}$ ) of the optical absorption:  $E_g^{opt} = 1240/\lambda_{onset}$ . [d]  $E_g^{ec} = e(E_{ox} - E_{red})$ .

sition of the conjugated backbone, whereas the absorption band at a long wavelength (around  $\lambda = 580$  nm) should be attributed to the strong intramolecular charge-transfer (ICT) interaction between the donor (BDT, NDT, or BDTT) and acceptor (DFDTQX) units.<sup>[14]</sup> The absorption spectra of the three polymers as solid films were similar to the corresponding solution spectra, with clear redshifts of the absorption maximum (Figure 2b), which is often observed in conjugated systems owing to aggregation of the polymer main chains and interchain interactions in the solid film.<sup>[15]</sup> However, the PBDT-DFDTQX film showed a lower redshift than those of the PNDT-DFDTQX or PBDTT-DFDTQX films. This difference can be ascribed to greater aggregation and enhanced  $\pi$ - $\pi$  stacking of NDT- and BDTT-based polymers in the solid state.<sup>[10]</sup> In addition, it is worth noting that only PNDT-DFDTQX displayed a vibronic shoulder at longer wavelength, which indicated that there were some ordered structures in the polymer film, and this should benefit increased charge mobility and photovoltaic performance of the polymer.<sup>[16]</sup> The absorption edges for solid films of PBDT-DFDTQX, PNDT-DFDTQX, and PBDTT-DFDTQX increased from  $\lambda = 676$  nm to  $\lambda = 698$  and 701 nm; this corresponded to optical band gaps  $(E_g^{opt})$  decreasing from 1.83 eV to 1.78 and 1.76 eV, respectively, as shown in Table 2. The band gap of PNDT-DFDTQX was reduced by 0.02 eV in comparison with that of PBDTT-DFDTQX. The reduction of the band gap energy can be mainly attributed to a more planar structure of the NDT unit than that of the BDTT unit.<sup>[17]</sup> Clearly, the vertically extended 2D structure in PBDTT-DFDTQX or horizontally extended conjugated structure in PNDT-DFDTQX imparts more effective intermolecular stacking and a narrower band gap; this is beneficial to increase the light-harvesting capacity for higher short-circuit current density  $(J_{sc})$ .

#### **Electrochemical Properties**

Cyclic voltammetry has been employed and considered as an effective tool in investigating the electrochemical properties of conjugated organic molecules and polymers.<sup>[18]</sup> From the onset oxidation and reduction potentials in the cyclic voltammogram, energy levels of the HOMO and LUMO can be readily estimated; these correspond to ionization potential (IP) and electron affinity (EA), respectively. Cyclic voltammograms of the polymer films are shown in Figure 3. The onset oxidation potentials ( $E_{ox}$ )/onset reduction potentials ( $E_{red}$ ) of PBDT-DFDTQX, PBDTT-DFDTQX, and PNDT-DFDTQX are +0.60/-1.22, +0.70/-1.08 and +0.38/ -1.25 V versus Ag/Ag<sup>+</sup>, respectively. The HOMO and LUMO energy levels of the polymers were calculated from the onset oxidation potential and the onset reduction potential according to Equations (2) and (3):<sup>[19]</sup>

$$E_{\rm HOMO} = -IP = -e(E_{\rm ox} + 4.71)$$
 (in eV) (2)

$$E_{\rm LUMO} = -EA = -e(E_{\rm red} + 4.71)$$
 (in eV) (3)



Figure 3. Cyclic voltammograms of PBDT-DFDTQX, PBDTT-DFDTQX, and PNDT-DFDTQX films on a platinum electrode in a  $0.1 \text{ mol } L^{-1}$  solution of  $Bu_4NPF_6$  in acetonitrile at a scan rate of  $100 \text{ mV s}^{-1}$ .

The  $E_{\rm HOMO}$ ,  $E_{\rm LUMO}$ , and electrochemical band gaps ( $E_{\rm g}^{\rm cc}$ ) of PBDT-DFDTQX, PBDTT-DFDTQX and PNDT-DFDTQX, calculated from the values of  $E_{\rm ox}$  and  $E_{\rm red}$  of the polymers, are -5.31/-3.49/1.82, -5.41/-3.63/1.71, and -5.09/-3.45/1.64 eV, respectively (see Table 2). The electrochemical band gaps of the polymers agree well with their optical band gaps within experimental error. As expected, the incorporation of electron-withdrawing fluorine atoms lowers the HOMO energy levels by about 0.30 eV compared with non-fluorinated Qx-based analogues.<sup>[20]</sup> In contrast to PBDT-DFDTQX, the HOMO ( $-5.41 \, {\rm eV}$ ) and LUMO levels ( $-3.63 \, {\rm eV}$ ) of PBDTT-DFDTQX are lowered by 0.1 and 0.14 eV, respectively (see Figure 4), as a result of replacing the alkoxyl group with an alkylthienyl unit. However,



Figure 4. Energy level diagrams for DFDTQX-based copolymers.

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Among the PSCs, the device based on PBDTT-DFDTQX

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the HOMO (-5.09 eV) and LUMO levels (-3.45 eV) of PNDT-DFDTQX are raised by 0.22 and 0.04 eV, respectively, owing to the more electron-rich capability of NDT relative to the BDT unit. This phenomenon indicates that  $\pi$ -conjugation extension in different orientations significantly affects the HOMO and LUMO levels of the D-A copolymers. Because the open-circuit voltage ( $V_{oc}$ ) of PSCs is dependent on the difference between the HOMO energy level of the electron donor and the LUMO energy level of the electron acceptor, the low-lying HOMO level of the donor polymer is expected to afford a high  $V_{oc}$  for the resultant PSCs. Thus, the highest  $V_{oc}$  for PBDTT-DFDTQX-based PSCs can be anticipated.

### **Photovoltaic Properties**

To investigate the effect of the extended  $\pi$ -conjugation orientation on the photovoltaic properties of the copolymers, BHJ PSC devices with a configuration of ITO/PEDOT:PSS/ polymer:PC<sub>71</sub>BM/Ca/Al were fabricated without any thermal treatment or solvent additives. Figure 5 shows the current density–potential characteristics of PSCs based on blends of polymer:PC<sub>71</sub>BM under illumination of AM1.5G at 100 mW cm<sup>-2</sup>. The open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (FF), and PCEs of the PSCs are summarized in Table 3 for a clear comparison. Blends of the polymers and PC<sub>71</sub>BM at different weight ratios were used to optimize the device performance, and detailed photovoltaic data of the optimization process for the PSCs are listed in Table S1 in the Supporting Information.



Figure 5. Current density–voltage characteristics of the PSCs based on polymer: $PC_{71}BM$  blends under illumination of AM1.5G at 100 mW cm<sup>-2</sup>.

Table 3. Photovoltaic performances of the PSCs based on polymer: $PC_{71}BM$  under the illumination of AM1.5G at 100 mWcm<sup>-2</sup>.

Polymer	Polymer/PC71BM	$V_{\rm oc}$	J <sub>sc</sub>	FF	PCE <sub>max</sub> <sup>[a]</sup>
	(w/w)	[V]	$[mA cm^{-2}]$	[%]	[%]
PBDT- DFDTQX	1:2	0.76	5.31	51.98	2.10
PBDTT- DFDTQX	1:1	0.78	12.48	52.03	5.07
PNDT- DFDTQX	1:2	0.68	6.55	51.70	2.30

[a] Optimized data.

demonstrated the best photovoltaic performance, with a PCE of 5.07%, because of a high  $V_{oc}$  of 0.78 V and a  $J_{sc}$  of 12.48 mA cm<sup>-2</sup> at a weight ratio of PBDTT-DFDTQX to  $PC_{71}BM$  of 1:1. It should be noted that this value is one of the highest PCEs of Qx-based copolymers without thermal treatment and solvent additives. When the donor (D)/acceptor (A) weight ratio of PBDTT-DFDTQX to PC71BM increased to 1:2 or 1:3, the PCE decreased to 3.52 or 2.69%, respectively, owing to the reduced  $J_{sc}$  values (from  $12.48 \text{ mA cm}^{-2}$  to  $10.01 \text{ and } 7.24 \text{ mA cm}^{-2}$ ). For PNDT-DFDTQX-based solar cells, the PCE was relatively low (2.30%), with a  $V_{\rm oc}$  of 0.68 V, a  $J_{\rm sc}$  of 6.55 mA cm<sup>-2</sup>, and a FF of 51.7% at a PNDT-DFDTQX/PC71BM ratio of 1:2 (w/w). Moreover, the PCEs preserved about 2% of their values at the other two D/A weight ratios. For the performance of PSCs based on PBDT-DFDTQX, the device exhibited the poorest PCE of 2.10% at a D/A weight ratio of 1:2. We observe that the PCE values of PBDTT-DFDTQX are more sensitive to the D/A weight ratios. As shown in Table 3, all three copolymers demonstrated high FFs above 50%, which indicates that the devices have relatively balanced charge transport and low serial resistance.<sup>[21]</sup> However, it can be seen that the  $V_{\rm oc}$  of PSCs based on PBDTT-DFDTQX, PBDT-DFDTQX, and PNDT-DFDTQX decreased from 0.78 and 0.76 to 0.68 V, as a result of the upshift of the HOMO level of the polymers. In addition, the large decrease in the PCE of PBDT-DFDTQX and PNDT-DFDTQX, relative to PBDTT-DFDTQX, mainly originates from the reduction of  $J_{sc}$ . PBDT-DFDTQX has the lowest  $J_{\rm sc}$  value, partially owing to a relatively broad band gap of 1.82 eV and blueshifted absorption relative to the other two polymers. Although PNDT-DFDTQX possesses the narrowest band gap and broadest light absorption, the relative PSC still exhibits a much lower  $J_{sc}$  than that of PBDTT-DFDTQX. In addition to the absorption spectrum and band gap of the relative polymer, the morphology of the active layer also has a noticeable effect on  $J_{sc.}^{[22]}$  The significant decrease in J<sub>sc</sub> values of PBDT-DFDTQX and PNDT-DFDTQX might be attributed to the poor morphology of the active layer.

To better understand the effect of morphology of the photoactive layers on the photovoltaic performance of the PSCs, the morphological structures of the blend films of polymer:PC71BM were analyzed by tapping-mode AFM. AFM images were recorded directly on the tested devices, in the device area out of the Ca/Al electrode. Figure 6 shows the AFM images of the active-layer surfaces. As observed in Figure 6b and e, a relatively fine and evenly distributed morphological surface appeared with a root-mean-square (RMS) roughness of 1.15 nm when PBDTT-DFDTQX and PC71BM were blended in a 1:1 ratio. Clearly, the uniformity of the phase image for the film of PBDTT-DFDTQX/ PC71BM is beneficial to exciton dissociation and charge-carrier transportation. As a result, the  $J_{sc}$  of the PSC based on PBDTT-DFDTQX:PC71BM exhibited a promising value of 12.48 mA cm<sup>-2</sup>. Compared with PBDTT-DFDTQX:PC<sub>71</sub>BM, 20





Figure 6. AFM phase (top) and topography (bottom) images (5.0 µm× 5.0 µm) of the polymer films of PBDT-DFDTQX:PC71BM 1:2 w/w (a and d), PBDTT-DFDTQX:PC71BM 1:1 w/w (b and e), and PNDT-DFDTQX:PC71BM 1:2 w/w (c and f).

the blend film of PBDT-DFDTQX:PC71BM (w/w 1:2) showed a relatively poor morphology, as shown in Figure 6d (RMS = 2.03 nm). Meanwhile, notable phase separation took shape in the film (Figure 6a). In addition, macro p-n channels formed. The large-phase separation produces a low photocurrent by reducing the charge separation and increasing the exciton diffusion length and recombination of electrical charges.<sup>[23a]</sup> Thus, the lowest photocurrent (5.31 mA cm<sup>-2</sup>) was observed for a PBDT-DFDTQX/  $PC_{71}BM$  ratio of 1:2. As shown in Figure 6 f, it is worth noting that the 1:2 PNDT-DFDTQX:PC71BM blend film forms a larger cluster with an RMS roughness of 5.26 nm. The morphological structure is to destroy the continuous percolating pathway for hole and electron transport to the corresponding electrodes, which inevitably causes the severe charge recombination. Moreover, the rough surface of the PNDT-DFDTQX:PC71BM blend film will also induce high surface resistance, and both of them account for the lower  $J_{\rm sc}$  and PCE of PNDT-DFDTQX-based solar cells.

Figure 7 shows the EQE curves of the PSCs. All of these devices have good response to sunlight in the range from  $\lambda = 350$  to 650 nm, with maximum EQE values of 24% at  $\lambda = 405$  nm, 33% at  $\lambda = 492$  nm, and 63% at  $\lambda = 560$  nm for



Figure 7. EQE spectra of the PSCs based on polymer:PC71BM blends.

PSCs based on PBDT-DFDTQX, PNDT-DFDTQX, and PBDTT-DFDTQX, respectively. Compared with the absorption spectra of pristine polymers, the significantly broadened EQE responses in the visible region can be attributed to both the intrinsic absorption of the polymers and the response of PC71BM. As shown in Figure 7, compared with that of the device based on PBDT-DFDTQX, the PBDTT-DFDTQX-based device exhibits a stronger photoresponse of over 50% in the  $\lambda = 360-640$  nm range; this is consistent with higher  $J_{sc}$  values and is attributed to the alkylthienyl unit being more electron rich than that of the alkoxyl group. The EQE value of the PNDT-DFDTQX-based device only has a slight enhancement, which could be attributed to the high surface resistance. It is clear that introducing vertically extended 2D  $\pi$  conjugation on the BDT can broaden the absorption spectrum, enhance interchain  $\pi$ - $\pi$  interactions, and lower the HOMO energy level of the polymer, especially to acquire a more evenly distributed morphological surface for the blend film with  $PC_{71}BM$ ; therefore, leading to improved PSCs with higher  $J_{sc}$  values and a larger  $V_{oc}$  values. These results indicate that introducing  $\pi$ -conjugation extension perpendicular to the main chain is a helpful method to improve the photovoltaic performance of existing D-A copolymers.

#### **FET Properties of the Polymer**

To fully realize the effect of extended  $\pi$  conjugation in different orientations on the charge-transport properties, the performances of polymer FETs based on PBDT-DFDTQX, PNDT-DFDTQX, and PBDTT-DFDTQX were investigated by using a BGTC configuration. The polymer films were deposited onto OTS-modified Si/SiO<sub>2</sub> (300 nm) substrates by spin-coating. All devices with channel lengths of 80 µm and channel widths of 8800 µm were investigated to optimize the performance at different annealing temperatures. The best performances of the polymer-based devices are listed in Table 4 for comparison.

As shown in Table 4, the OFETs based on PBDT-DFDTQX, PBDTT-DFDTQX, and PNDT-DFDTQX showed maximum mobilities of  $2.63 \times 10^{-3}$ ,  $6.09 \times 10^{-3}$  and  $9.40 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively, after thermal annealing for 5 min at different optimal annealing temperatures. All devices with polymer films spin-coated on OTS-modified Si/ SiO<sub>2</sub> substrates exhibited an  $I_{or}/I_{off}$  ratio of 10<sup>4</sup>-10<sup>5</sup>. Representative output and transfer characteristics of OFETs based on polymer films at optimal annealing temperatures are shown in Figure 8. Compared with PBDT-DFDTQX, the mobility of PBDTT-DFDTQX improved 2.5 times,

Table 4. FET properties of devices with polymer films spin-coated on OTS-modified Si/SiO2 substrates.

Polymer	<i>T</i> <sup>[a]</sup> [⁰C]	$I_{\rm on}/I_{\rm off}$	$V_{ m th}$ [V]	Mobility $[cm^2V^{-1}s^{-1}]$
PBDT-DFDTQX	240	$1.6 \times 10^4$	$\begin{array}{c} 10 \\ -12 \\ 1 \end{array}$	$2.63 \times 10^{-3}$
PBDTT-DFDTQX	160	$1.7 \times 10^5$		$6.09 \times 10^{-3}$
PNDT-DFDTQX	240	$2.5 \times 10^4$		$9.40 \times 10^{-2}$

[a] Annealing temperature.

3.91 Å) between coplanar con-

jugated polymers. In the case of

PNDT-DFDTQX, a clear dif-

fraction peak and a relatively

weak one can be observed at

about 24.6-26.6°, which corre-

sponds to  $d_{\pi-\pi} \approx 3.53$  Å. More-

over, multiple diffraction peaks

of PNDT-DFDTQX indicate

that relatively ordered crystals

formed,<sup>[23b]</sup> in contrast to the

broad diffraction peaks of

PBDT-DFDTQX and PBDTT-

DFDTQX. Thus, we can con-

clude that introducing an ex-

tended  $\pi$  system, whether per-

pendicular to or along the main

chain, is advantageous to en-

hance  $\pi-\pi$  cofacial overlap<sup>[24,25]</sup>

and reduce  $\pi - \pi$  stacking distan-

ces. Therefore, both PNDT-

DFDTQX exhibit higher hole

mobilities than that of PBDT-

DFDTQX. However, polymer

semiconductors are quasi-one-

though the carriers can migrate within the molecules or hop be-

tween the molecules, charge-

carrier motion within the mole-

cules has a greater contribution

to the mobilities of polymers.

For PBDTT-DFDTQX, side-

chain  $\pi$ -conjugation extension

reduces the hopping distance,

which is more helpful for carriers to transport by hopping be-

materials.

and

PBDTT-

Al-

DFDTQX

dimensional



Figure 8. Output (left) and transfer (right) characteristics of the spin-coated film of polymer FETs based on OTS-modified Si/SiO<sub>2</sub> substrates: a), b) PBDT-DFDTQX with annealing at 240 °C for 5 min; c), d) PBDTT-DFDTQX with annealing at 160 °C for 5 min; and d), e) PNDT-DFDTQX with annealing at 240 °C for 5 min.

owing to enhanced intermolecular  $\pi$ - $\pi$  interactions, whereas a much higher hole mobility of approximately 0.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> was achieved for PNDT-DFDTQX. Clearly, the  $\pi$ -conjugated structure of polymers has a significant effect on the mobilities of charge carriers.

To understand the influence of  $\pi$ -conjugated architectures on the mobilities of the corresponding polymers, XRD was used to characterize the microstructures and topographies of the polymer thin films. Figure S2 in the Supporting Information shows XRD patterns of the polymer thin films deposited on OTS-modified Si/SiO<sub>2</sub> substrates at room temperature and after annealing. As shown in Figure S2 a in the Supporting Information, for all polymers, no diffraction peaks were detected before the samples were annealed. However, when PBDT-DFDTQX and PBDTT-DFDTQX were annealed for 5 min (Figure S2b in the Supporting Information), weak diffraction peaks emerged at 22.3 and 23.8°, respectively, which corresponds to the  $\pi$ - $\pi$  stacking distances ( $d_{\pi-\pi}$ =3.99 and tween the pendent conjugated units.<sup>[26,27]</sup> However, for PNDT-DFDTQX, main-chain  $\pi$ conjugation extension enhances the length of effective conjugation and the planarity of the main chain, leading to a highly ordered structure and  $\pi$ - $\pi$  stacking, which mainly contributes to efficient charge transport along the main chain.<sup>[28]</sup> Hence, PNDT-DFDTQX exhibits the highest hole mobility. Based on the obtained experimental results, we can conclude that varying the orientation of  $\pi$ -conjugated extension on the donor unit could significantly influence the photoelectronic properties of these new fluorinated Qx-containing copolymers.

## Conclusion

Three new D-A copolymers, namely, PBDT-DFDTQX, PBDTT-DFDTQX, and PNDT-DFDTQX, were synthesized and characterized. All copolymers possessed good solubility

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and thermal stability as well as low band gaps for efficient photon harvesting. The difference in  $\pi$ -conjugation structures of the donor units led to different properties of the three polymers. Compared with PBDT-DFDTQX, extended  $\pi$ -conjugation perpendicular to the main chain of PBDT-DFDTQX not only downshifted its HOMO energy level, but also enhanced  $\pi\text{-}\pi$  stacking. The PSC made from PBDTT-DFDTQX exhibited a promising PCE of 5.07%, which was 2.5 times higher than that from PBDT-DFDTQX (2.10%). On the other hand, the PSC made from PNDT-DFDTQX, which possessed extended  $\pi$  conjugation along the main chain compared to PBDT-DFDTQX, showed a slightly improved PCE of 2.30%, but much higher carrier mobilities of approximately  $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ; this is the highest value currently reported for fluorinated Qx-based copolymers. The results confirmed that the big difference in properties of the three polymers derived from different  $\pi$ -conjugation structures of these polymers; this indicates that a rational choice of  $\pi$ -conjugation structure is very important for the construction of D-A copolymers with high PSC or OFET performances.

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