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Journal of Materials Chemistry A

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Side Chain Modification: An Effective Approach to Modulate the Energy Level of Benzodithiophene Based Polymer for High-Performance Solar Cells [‡]

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In the past few years, it had been proven that deepening the highest occupied molecular orbital (HOMO) levels of conjugated polymer is one of the most successful strategies to develop novel materials for high performance bulk heterojunction polymer solar cells. Here we report an effective approach of side chain modification in donor moiety to modulate the highest occupied molecular orbital (HOMO) energy level of benzo[1,2-b:4,5-b']dithiophene (BDT) based two-dimensional conjugated polymers and hence obtained improved power conversion efficiency. Through introduction 2,3-dioctylthienyl groups instead of conventional 2-ethylhexylthienyl groups as side chain in 4,8-positions of BDT moiety, four mono-fluorinated quinoxaline based alternating polymers: poly{4,8-di(2-ethylhexylthiophene-5-yl)-2,6-benzo[1,2-b:4,5-b']dithiophene-*alt*-5,5-[5',8'-di-2-thienyl-(6'-fluoro-2',3'-bis(3''-octyloxyphenyl)quinoxaline)]} (**PBDTTFTQ-EH**), poly{4,8-di(2-ethylhexythiophene-5-yl)-2,6-benzo[1,2-b:4,5-b']dithiophene-*alt*-5,5-[5',8'-di-2-thienyl-(6'-fluoro-2',3'-bis(3''-octyloxyphenyl)quinoxaline)]}

octylthiophen-2"-yl)quinoxaline)]} (PBDTTFTTQ-EH), poly{4,8-di(2,3-dioctylthiophene-5-yl)-2,6-benzo[1,2-b:4,5-(PBDTTFTO-DO) b']dithiophene-alt-5,5-[5',8'-di-2-thienyl-(6'-fluoro-2',3'-bis-(3''-octyloxyphenyl)-guinoxaline)]} and poly{4,8-di(2,3-dioctylthiophene-5-yl)-2,6-benzo[1,2-b:4,5-b']dithiophene-alt-5,5-[5',8'-di-2-thienyl-(6'-fluoro-2',3'-bis(5''octylthiophen-2"-yl)quinoxaline)]} (PBDTTFTTQ-DO) were synthesized, in which the former two EH-based polymers using 2-ethylhexylthienyl side chain and the latter two DO-based polymers containing 2,3-dioctylthienyl side chain. The results clearly indicated that the variation in the side chain of BDT unit from 2-ethylbexylthienyl group to 2.3-dioctylthienyl group can cause deep HOMO level and slightly enlarged bandgap of the polymer. Consequently, polymer solar cells from PBDTTFTQ-DO and PBDTTFTTQ-DO showed high Voc of 0.88 V and 0.85 V, while that of 0.78 V and 0.72 V were observed in PBDTTFTQ-EH and PBDTTFTTQ-EH based devices, respectively. Both polymers deliver high power conversion efficiency (PCE) exceeding 6.8%, with an outstanding efficiency of 7.61% and an excellent filled factor (FF) of 75.9% for PBDTTFTQ-DO after tetrahydrofuran solvent vapour annealing 30 sec (while PCE of 7.29% for PBDTTFTQ-EH). Similar results were investigated in the PBDTTFTTQ-EH (PCE of 6.82%) and PBDTTFTTQ-DO (PCE of 7.25% with high FF of 75.7%) based solar cells. This finding should provide valuable guideline for the design and synthesis of novel polymer donor materials for highly efficient polymer solar cells via fine tuning the molecular energy levels and absorption spectra through a modulation of the side chain onto the donor moiety.

1. INTRODUCTION

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted much attention due to their advantages of low-cost, lightweight energy sources over large area size on flexible substrates. ^[1-4] In recent years, it witnessed the rapid

developments of the synthesis of novel photoactive materials and their successful applications in high performance PSCs, [5-8] however, the relatively lower power conversion efficiency (PCE) of PSCs when compared with their inorganic counterpart still represent some limitations toward commercialization and widespread utilization. There are many factors limiting the performance of BHJ solar cells, [9,10] in which the polymer electron donor materials play an important role in the whole performances of the device. Ideally, polymers should possess a broad absorption (small bandgap) to ensure effective harvesting of the solar photons and high hole mobility for charge transport. Furthermore, suitable energy levels of the polymers are required to match those of the fullerene derivatives so that excitons (bound electron-hole pairs) can readily dissociate at the donor-acceptor (D/A) interface to produce separated charge carriers. That is, a low-lying highest

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[‡] Electronic Supplementary Information (ESI) available: ¹H NMR and ¹³C NMR

spectra of monomers, TGA plot, absorption spectra of the solutions, SCLC results, J-V characteristics of the polymer: $PC_{71}BM$ devices. This material is available free of charge via the Internet at http://pubs.acs.org.. See DOI: 10.1039/x0xx00000x

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Published on 28 July 2015. Downloaded by California State University at Fresno on 29/07/2015 10:09:49

DOI: 10.1039/C5TA05096K Journal Name

occupied molecular orbital (HOMO) energy level to provide a large open-circuit voltage (V_{oc}) and a suitable lowest unoccupied molecular orbital (LUMO) energy level to ensure enough offset for the charge separation.^[11,12]

Based on these considerations, much effort have been done to tune the optical bandgaps, molecular energy levels and carrier mobilities by incorporating electron-rich (donor) units with the electron-withdrawing (acceptor) units in one conjugated polymer. A variety of donor-acceptor (D-A) polymers that can deliver promising performances have been developed and successfully been used as donor materials in PSCs. ^[13] To further deepen the HOMO levels of the polymer and achieve enhanced device performances, strong electron deficient groups such as ketone groups, sulfonyl groups and fluorine atoms were introduced into the acceptor (A) units in the polymers. ^[14] For instance, significant progress has been achieved by deepening the HOMO levels of benzo[1,2-b:4,5b']dithiophene (BDT)-based conjugated polymers through the substitution of fluorine atoms on various acceptor units, resulting in a high V_{oc} and PCE in PSCs in comparison with the corresponding non-fluorinated derivatives in the past few years. [15]

To ensure good solubility and processability of the conjugated polymers donor for film fabrication, in most cases, 2-ethylhexyloxy groups were usually introduced to the 4,8position of BDT units to build the corresponding polymers. Furthermore, alkylthienyl substituted BDT, especially 2ethylhexylthienyl substituted BDT were designed as electronrich unit and applied in constructing two-dimensional (2D) conjugated polymers for high performance photovoltaic devices because the thienyl-substitution is helpful to broaden the absorption band, lower the HOMO level and improve the hole mobility of the related copolymers. [16] Although many routes have been developed to tailor the energy levels and bandgaps through modification the acceptor of the BDT-based 2D conjugated polymers, there are seldom attempts to modulate the molecular energy level by fine adjusting the flexible side chain (alkyl group or alkoxy groups) on the BDT moiety.^[17] It should be noted that the electron affinity of the flexible side chains affect both HOMO and LUMO levels of the 2D conjugated polymers. In addition, the steric hindrance of long alkyl or alkoxy chains may decrease the π -conjugation degree of the polymer backbone to some extent. Consequently, the flexible side chains on the 2D conjugated BDT moiety play an important role not only in the aspect of solubility but also in their optical and electrical properties. Recently, to tune the molecular energy levels of the polymers, researchers have devoted to finely modify the flexible side chains of the 2D conjugated BDT moiety by replacing the 2ethylhexylthienyl group with meta-alkoxy-phenyl unit, as expected, the resulting polymer showed deeper HOMO level, consequently leading to an enhanced V_{oc} and PCE. ^[18] To modulate the molecular energy levels of BDT based 2D conjugated polymers through another effective side chain modification approach, in this paper, two types of alkylthienyl groups were introduced to the BDT units, meanwhile two mono-fluorinated guinoxaline derivatives were chosen as the

electron-withdrawing moiety to build the D-A polymers, due to their excellent electron-deficient N-heterocycle structure and facile synthesis process. [19-23] The structures of the mentioned alternating polymers: poly{4,8-di(2-ethylhexylthiophene-5-yl)-2,6-benzo[1,2-b:4,5-b']dithiophene-alt-5,5-[5',8'-di-2-thienyl-(6'-fluoro-2',3'-bis(3''-octyloxyphenyl)quinoxaline)]} (PBDTTFTQ-EH), poly{4,8-di(2-ethylhexythiophene-5-yl)-2,6benzo[1,2-b:4,5-b']dithiophene-alt-5,5-[5',8'-di-2-thienyl-(6'fluoro-2',3'-bis(5''-octylthiophen-2''-yl)quinoxaline)]} (PBDTTFTTQ-EH), poly{4,8-di(2,3-dioctylthiophene-5-yl)-2,6benzo[1,2-b:4,5-b']dithiophene-alt-5,5-[5',8'-di-2-thienyl-(6'fluoro-2',3'-bis-(3''-octyloxyphenyl)-quinoxaline)]} (PBDTTFTQ-DO) and poly{4,8-di(2,3-dioctylthiophene-5-yl)-2,6-benzo[1,2b:4,5-b']dithiophene-alt-5,5-[5',8'-di-2-thienyl-(6'-fluoro-2',3'bis(5"-octylthiophen-2"-yl)quinoxaline)]} (PBDTTFTTQ-DO) were shown in Scheme 1, in which the former two EH-based polymers using 2-ethylhexylthienyl side chain and the latter two DO-based polymers containing 2,3-dioctylthienyl side chain. It is worthy to note that the PBDTTFTQ-DO and PBDTTFTTQ-DO possess both deeper HOMO energy levels and slightly larger bandgaps in comparison with those of PBDTTFTQ-EH and PBDTTFTTQ-EH. With the conventional BHJ polymer solar cell device structure, the devices based on PBDTTFTQ-EH and PBDTTFTTQ-EH exhibited remarkable PCEs of 7.29% and 6.82% with corresponding V_{oc} of 0.78V and 0.72V, while PBDTTFTQ-DO and PBDTTFTTQ-DO-based devices showed excellent results of 7.61% and 7.25% with higher V_{oc} of 0.88V and 0.85V.

2. EXPERIMENTAL SECTION

2.1 Materials

All chemicals and solvents were purchased from Aldrich or Alfa & Aesar. Tetrahydrofuran (THF) is dried over Na/benzophenone ketyl and freshly distilled prior to use. 5,8-Bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-

octyloxy)phenyl)quinoxaline (3) ^[24,25] and 1,2-bis(5octylthiophen-2-yl)ethane-1,2-dione (5) ^[26] were synthesized according to the literatures. 2,6-Bis(trimethyltin)-4,8-di(2(2ethylhexyl)thiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophene (2a) ^[16a] and 2,6-bis(trimethyltin)-4,8-di(2,3-dioctylthiophen-5-yl)benzo[1,2-b:4,5-b']dithiophene (2b) ^[27] were prepared through an modification routine of the references. The synthetic routes of monomers and polymers are shown in **Scheme 1**.

4,8-Di(2-(2-ethylhexyl)thiophen-5-yl)-benzo[1,2-b:4,5b']dithiophene (**1a**) and **4,8-Di(2,3-dioctylthiophen-5-yl)benzo[1,2-b:4,5-b']dithiophene** (**1b**). 2-Ethylhexylthiophene (3.92 g, 20 mmol) was dissolved in anhydrous THF (60 ml) under an argon atmosphere, the solution was cooled to 0 °C in an ice water bath, and n-BuLi (2.5 M, 20 mmol) was added slowly dropwise to the mixture, then the reaction was heated and kept at 50 °C for 1 h. Subsequently, 4,8-dehydrobenzo[1,2b:4,5-b']dithiophene-4,8-dione (1.58 g, 7.22 mmol) was added and the mixture was stirred at 50 °C for 2 h. After cooling down to the room temperature, a solution of SnCl₂·2H₂O (13 g,



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Scheme 1. The synthetic routes of the polymers. (a) n-BuLi, THF, 0 °C, then 50 °C; $SnCl_2 \cdot 2H_2O$, 10% HCl aq. (b) n-BuLi, 0 °C, then room temperature; Me_3SnCl , 0 °C, room temperature. (c) CH_3COOH . (d) $Pd(PPh_3)_2Cl_2$, toluene. (e) NBS, THF. (f) $Pd_2(dba)_3$, $P(o-Tol)_3$, toluene.

57.52 mmol) in 10% hydrochloric acid (17 ml) was added, and the reaction was stirred for additional 2 h. The mixture was extracted with ethyl acetate and organic phase was washed with brine and dried over MgSO₄. The crude was purified by silica gel chromatography using hexane as eluent to afford compound **1a** (2.28 g) as a viscous liquid in yield 53.5 %. ¹H NMR (CDCl₃, 500 MHz) δ (ppm): 7.68(d, 2H), 7.44 (d, 2H), 7.34 (d,2H), 6.93 (d, 2H), 2.87 (d, 4H), 1.75 (m, 2H), 1.51–1.17 (br, 16H), 0.92–0.85 (m, 12H). ¹³C NMR (CDCl₃, 125 MHz) δ (ppm): 145.21, 139.07, 137.49, 136.46, 127.61, 127.30, 125.30, 124.03, 123.29, 41.55, 34.33, 32.55, 29.43, 25.83, 23.06, 15.67, 11.02.

For compound 1b. The synthetic route was the same as compound 1a. (2.97g ,51.2%). ¹H NMR (CDCl₃, 500MHz) δ (ppm): 7.70 (d, 2H), 7.45 (d, 2H), 7.22 (s, 2H), 2.82 (t, 4H), 2.61 (t, 4H), 1.73 (dt, 4H), 1.65 (dt, 4H), 1.39 (m, 40H), 0.90 (td, 12H). ¹³C NMR (CDCl₃, 125 MHz) δ (ppm): 140.19, 138.84, 138.13, 136.35, 135.08, 129.86, 127.29, 124.13, 123.61, 77.29, 77.04, 76.79, 31.95, 31.93, 31.88, 30.87, 29.57, 29.55, 29.44, 29.38, 29.31, 28.34, 28.03, 22.74, 14.25.

2,6-Bis(trimethyltin)-4,8-di(2(2-ethylhexyl)thiophen-5-yl)benzo[1,2-b:4,5-b']dithiophene (2a) and 2,6-Bis(trimethyltin)-4,8-di(2,3-dioctylthiophen-5-yl)-benzo[1,2-b:4,5b']dithiophene (2b). Compound 1a (5.8 g, 10 mmol) was dissolved in anhydrous THF (80 mL) under the protection of argon. The solution was cooled to 0 °C and n-BuLi (2.5 M , 24 mmol) was added dropwise to the mixture. Then the reaction was warmed to ambient temperature and stirred for 2 h, SnMe₃Cl (5.5 g, 27.6 mmol) was quickly added in one portion at 0 °C, and then the mixture was warmed to room temperature and stirred for 6 h. The reactant was poured into water and extracted with hexane and the organic layer was washed with brine and dried over MgSO4. The residue was recrystallized with isopropanol for three times and afforded yellow green crystal (5.54 g, 61.5%). ¹H NMR (CDCl₃, 500MHz) δ(ppm): 7.68 (s, 2H), 7.35 (d, 2H), 6.89 (d, 2H), 2.88 (d, 4H), 1.74 (m, 2H), 1.57-1.33 (br, 16 H), 0.94 (m, 12H), 0.42 (s, 18H). ¹³C NMR (CDCl₃, 125MHz) δ(ppm): 145.37, 143.29, 142.22, 138.01, 137.31, 131.18, 127.55, 125.30, 122.42, 41.57, 34.24, 32.52, 28.98, 25.82, 23.04, 15.41, 10.99, -8.35. Anal. calcd for C₄₀H₅₈S₄Sn₂(%): C 53.11, H 6.46; Found (%): C 52.82, H 6.45.

For compound **2b**. The synthetic route was the same as compound **2a**. (6.21g, 55%). ¹H NMR (CDCl₃, 500MHz) δ (ppm): 7.73 (s, 2H), 7.23 (s, 2H), 2.84 (t, 4H), 2.62 (m, 4H), 1.75 (dt, 4H), 1.67 (m, 4H), 1.46 (dt, 8H), 1.34 (m, 32H), 0.89 (m, 12H), 0.40 (m, 18H). ¹³C NMR (CDCl₃, 125 MHz) δ (ppm): 139.81,

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137.99, 137.18, 135.76, 131.42, 129.82,122.49, 31.97, 31.91, 31.84, 30.85, 29.62, 29.53, 29.46, 29.35, 29.32, 28.34, 28.05, 22.70, 14.14, -6.87, -6.94, -8.35, -9.76, -9.82. Anal. calcd for $C_{56}H_{90}S_4Sn_2$ (%): C 59.58, H 8.03; Found (%): C 59.31, H 8.01.

5,8-dibromo-6-fluoro-2,3-bis(5-octylthiophen-2-

yl)quinoxaline (6) 3,6-dibromo-4-fluorobenzene-1,2-diamine (4) (2.84 g, 10 mmol) and 1,2-bis(5-octylthiophen-2-yl)ethane-1,2-dione (5) (4.46 g,10 mmol) were dissolved in acetic acid (300 ml), the mixture was briefly warmed to 60 °C and stirred for 10 min, then stirred at room temperature for 2 h. The precipitate was collected by filtration, washed with ethanol, and dried to afford 5,8-dibromo-6-fluoro-2,3-bis (5-octylthiophen-2-yl)quinoxaline (6) (6.28 g) as a yellow solid in yield 90.5%. ¹H NMR(500 MHz, CDCl₃) δ(ppm): 7.79 (d, 1H, J=5Hz), 7.41 (dd, 2H, J=5Hz), 6.72 (m, 2H), 2.87 (t, 4H, J=7.5Hz), 1.75 (m, 4H), 1.42-1.25 (m, 20H), 0.89 (t, 6H, J=5Hz). ¹³C NMR (125 MHz, CDCl₃) δ(ppm): 160.01, 158.06, 151.87, 147.73, 135.45, 130.13, 124.91, 122.58, 58.48, 31.90, 31.51, 30.43, 29.22, 22.66, 18.44, 14.11. Anal. calcd for C₃₂H₃₉Br₂FN₂S₂ (%): C 55.33, H 5.66, N 4.03; Found (%):C 55.46, H 5.64, N 3.98.

5,8-bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(5-

octylthiophen-2-yl)quinoxaline (8). A mixture of compound 6 (3.48 g, 5 mmol), tributyl(thiophen-2-yl)stannane (4.10 g, 11 mmol), dichlorobis-(triphenylphosphine)palladium(II) (0.14 g) and toluene (150 ml) were heated under reflux overnight. It was then cooled and the toluene was removed under reduced pressure and the residue was recrystallized by hexane and obtained compound 7 (2.87 g) in 82% yield. To a suspension of compound 7 (0.70 g, 1 mmol) in THF (30 ml) was added NBS (0.37 g, 2.1 mmol), the mixture was heated at 40 $^{\circ}$ C for 3 h and poured into methanol, the precipitate was collected by filtration and purified by column chromatography on silica gel using hexane/ethyl acetate (100:1) as eluent to afford compound 5,8-bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(5octylthiophen-2-yl)quinoxaline (8) (0.56 g) in yield 65%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.70 (m, 2H), 7.48 (d, 1H, J=5Hz), 7.39 (dd, 2H, J=5Hz), 7.11 (dd, 2H, J=5Hz), 6.73 (d, 2H, J=3Hz), 2.91 (t, 4H, J=5Hz), 1.79 (m, 4H), 1.37-1.26 (m, 20H), 0.90 (t, 6H, J=5Hz). ¹³C NMR (CDCl₃, 125MHz) δ(ppm):159.68, 157.67, 151.87, 145.67, 138.36, 132.94, 130.35, 129.24, 126.35, 124.80, 117.94, 115.39, 58.50, 31.92, 31.50, 30.45, 29.26, 22.71, 18.46, 14.15. Anal. calcd for C₄₀H₄₃Br₂FN₂S₄ (%): C 55.94, H 5.05, N 3.26; Found (%):C 56.21, H 5.05, N 3.12.

Synthesis of the polymers

Compound **2a** (91 mg, 0.1 mmol) and compound **3** (87.8 mg, 0.1 mmol) were dissolved in degassed toluene (20 ml) and purged with argon for 30 min, tris(dibenzylideneacetone) dipalladium(0) ($Pd_2(dba)_3$) (1.8 mg) and tri(otolyl) phosphine ($P(o-Tol)_3$) (3.5 mg) were added and flushed with argon for another 30 min, then the mixture was vigorously stirred at 100 °C for 24 h under argon. After cooling down to the room temperature, the solution was poured into the methanol. The polymer was collected by filtration and soxhlet-extracted in order with methanol, hexane and chloroform, the chloroform solution was concentrated to a small volume and precipitated by pouring into methanol again. Finally, the polymer was collected by filtration and dried under vacuum at 50 °C

overnight and afforded **PBDTTFTQ-EH** (110 mg) as purple-black fiber in yield 86%. GPC (tetrahydrofuran, polystyrene standard): M_n =64.74 kDa, M_w =181.08 kDa, PDI=2.79. **PBDTTFTQ-EH:** ¹H NMR (CDCI₃, 500MHz) δ(ppm): 7.93-7.49(br, 7H), 7.02-6.67(br, 12H), 3.72(m, 4H), 2.96(m, 4H), 1.74-1.57 (br, 26H), 1.28-1.23(br, 16H), 0.91(m, 18H). Anal. calcd for C₇₈H₈₇FN₂O₂S₆ (%): C 72.29, H 6.77, N 2.16; Found (%): C 72.03, H 8.02, N 2.00.

For **PBDTTFTQ-DO.** This polymer was synthesized according to the same route as that for **PBDTTFTQ-EH**. (128 mg, 84.7%). GPC (tetrahydrofuran, polystyrene standard): M_n =75.96 kDa, M_w =250.07 kDa, PDI=3.29. ¹H NMR (CDCl₃, 500MHz) δ (ppm): 8.01 (s, 1H), 7.84 (s, 2H), 7.45-7.31 (br, 4H), 7.19-7.06(br, 6H), 7.02-6.86 (br, 4H), 3.74(m, 4H), 2.78(m, 8H), 1.84-1.63 (br, 12H), 1.41-1.14(br, 60H), 0.89(m, 18H). Anal. calcd for C₉₄H₁₁₉FN₂O₂S₆ (%): C 74.26, H 7.89, N 1.84; Found (%): C 73.66, H 8.03, N 1.57.

For **PBDTTFTTQ-EH.** This polymer was synthesized basing on compound **8** and compound **2a** according to the same route as that for **PBDTTFTQ-EH** with a high yield (82.3%). GPC (tetrahydrofuran, polystyrene standard): M_n =18.45 kDa, M_w =101.38 kDa, PDI=5.49. ¹H NMR (CDCl₃, 500MHz) δ (ppm): 7.92-7.36 (br, 7H), 7.15-6.40 (br, 8H), 2.89 (m, 8H), 1.88-1.65 (br, 8H), 1.46-1.20(br, 34H), 0.92(m, 18H). Anal. calcd for C₇₄H₈₃FN₂S₈ (%): C 69.66, H 6.56, N 2.20; Found (%): C 69.11, H 6.70, N 1.95.

For **PBDTTFTTQ-DO**. This polymer was synthesized according to the similar route as that for **PBDTTFTTQ-EH** with a high yield of 88.5%. GPC (tetrahydrofuran, polystyrene standard): M_n =135.95 kDa, M_w =863.63 kDa, PDI=6.35.¹H NMR (CDCl₃, 500MHz) δ (ppm): 7.93 (s, 1H), 7.77-7.34 (br, 6H), 7.17-6.96(br, 2H), 6.84-6.60 (br, 2H), 3.28-2.24(m, 12H), 1.99-1.63 (br, 12H), 1.44-1.16(br, 60H), 0.89(m, 18H). Anal. calcd for C₉₀H₁₁₅FN₂S₈ (%): C 72.04, H 7.73, N 1.87; Found (%): C 72.31, H 7.77, N 1.93.

2.2 Measurements

All compounds were characterized by nuclear magnetic resonance spectra (NMR) recorded on a Bruker AV 500 spectrometer in CDCl₃ at room temperature. Molecular weights and distributions of the copolymers were estimated by gel permeation chromatography (GPC) method, THF as eluent and polystyrene as standard. The absorption spectra were determined by a Unico UV-2102 scanning spectrophotometer. Thermogravimetric analysis (TGA) of the polymers was investigated on a Universal V2.6D TA instruments. The electrochemical cyclic voltammetry was conducted on a CHI 660D Electrochemical Workstation with glassy carbon, Pt wire, and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF_c) acetonitrile solution. Polymer thin films were formed by dropcasting chloroform solution (analytical reagent, 1mg/mL) onto the working electrode, and then dried in the air. Atomic force microscopy (AFM) images were collected in air under ambient conditions using the MultiMode scanning probe microscope (AFM, Veeco MultiMode V).

2.3 THF solvent vapour annealing (SVA)

SVA was conducted in ambient conditions at room temperature in glove box. THF (2 ml) was injected into a 30 mm glass Petri dish. The Petri dish was closed for 1 min to let the THF vapour saturate the treatment chamber. Then the ascast film was transferred to the Petri dish. The film was about 1 cm above the solvent level during the SVA. After 30 sec, the film was removed from the treatment chamber.

2.4 Fabrication and characterization of PSCs

The device structure was ITO/PEDOT:PSS/polymer:PC71BM/PFN/AI, 40-nm-thick а PEDOT:PSS anode buffer layer was spin-cast on the ITO substrate, then dried in a vacuum oven at 100 $^\circ C$ overnight. The polymer:PC₇₁BM active layer was prepared by spin-coating their 1,2-dichlorobenzene solution with various weight ratios. A 5 nm PFN layer was then spin-coated from methanol solution in presence of a trace amount of acetic acid onto the active layer. Subsequently, the films were transferred into a vacuum evaporator and 100 nm of Al were deposited as cathode. The effective area of a device was 0.16 cm² as determined by the shadow mask used during deposition of Al cathode. PCE values were determined from J-V curve measurements (using a Keithley 2400 source meter) under 1 sun, AM 1.5G spectrum from a solar simulator (Oriel model 91192; 1,000 W m⁻²). External quantum efficiency (EQE) measurements were taken using a monochromator (Newport, Cornerstone 130) joined to the same xenon lamp and a lock-in amplifier (Stanford Research Systems, SR 830) coupled to a light chopper.

2.5 Hole mobility measurement

The device structure of space charge limited current (SCLC) studies is ITO/PEDOT:PSS/polymer/MoO₃(10nm)/Al. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation: J= $(9/8)\epsilon_0\epsilon_r\mu((V^2)/(d^3))$, where J is the current, μ is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}) , $V=V_{appl}-V_{bi}-V_s$. The hole-mobility can be calculated from the slope of the J^{1/2} \sim V curves. The effective area was also 0.16 cm².

2.6 Transient photovoltage and transient photocurrent measurements

Transient photovoltage measurement was performed by holding the devices at open-circuit condition under illumination of a 100W tungsten halogen lamp. The devices were connected to an oscilloscope (Tektronix DPO4104, 1GHz) that has an input impedance of the oscilloscope of 1 M Ω to hold the device at open circuit. The excitation pulse was generated using a pulsed laser (OPOTEK Vibrant 355, with a 5 ns optical pulse). The perturbation light intensity was attenuated by a set of neutral density filter so that the

amplitude of TPV is much less than V_{oc} . Transient photocurrent measurement was performed with the device being held at short circuit condition by connecting the device to the ground through a small resistor. The resulting current transient was measured using an oscilloscope (Tektronix DPO4104, 1GHz) in parallel with a small resistor of 50 Ω . The excitation pulse was generated using a pulsed laser (OPOTEK Vibrant 355, with a 5 ns optical pulse).

3. RESULTS AND DISSCUSSION

3.1 Materials design and synthesis

The synthetic routes of the four polymers are shown in Scheme 1. In our synthetic design, the two octyl groups were introduced to the 2,3-position of the side chain conjugated thiophene rings to replace the 2-ethylhexyl groups. The 5-octyl thienyl and 3-octyloxyphenyl groups were chosen to build the quinoxaline units for their good performances in the donoracceptor polymers for PSCs.^[19] The four polymers were synthesized through typical Stille-coupling reaction with good vield (>82 %). using toluene as solvent. tris(dibenzylideneacetone) dipalladium (Pd₂(dba)₃) and tri(otolyl)phosphine (P(o-tol)₃) as catalyst. Both four polymers showed good solubility in chloroform, o-dichlorobenzene (oDCB) and other common solvents, especially the two polymers containing two octyl groups in the BDTT units (PBDTTFTQ-DO and PBDTTFTTQ-DO). The number-average molecular weight of **PBDTTFTQ-EH**, PBDTTFTQ-DO, PBDTTFTTQ-EH and PBDTTFTTQ-DO are 64.74, 75.96, 18.45 and 135.95 kDa, with corresponding polydispersity index (PDI) as 2.79, 3.29, 5.49 and 6.35, respectively, which were measured by gel permeation chromatography (GPC).

3.2 Properties of the polymers

All of the polymers have decomposition temperature (defined as the 5% weight-loss temperature, T_d) over 300 °C and the **PBDTTFTQ-EH** shows the highest T_d (427 °C for **PBDTTFTQ-EH**, 329 °C for **PBDTTFTQ-DO**, 399 °C for **PBDTTFTQ-EH** and 370 °C for **PBDTTFTTQ-DO** respectively, see **Figure S8** in **ESI**) under nitrogen as determined by thermogravimetric analysis (TGA), indicating their excellent thermal stabilities.

The optical properties of the polymers were investigated by ultraviolet-visible (UV-vis) absorption spectroscopy both in CHCl₃ solutions (see Figure S9 in ESI) and in thin films (see Figure 1a and 1b). The detailed data obtained from these absorption spectra are summarized in Table 1. As shown in Figure S9 and Figure 1, in comparison with the two EH-based polymers, the DO-substituted polymers (PBDTTFTQ-DO and PBDTTFTTQ-DO) exhibited slightly blue-shifted spectra both in solution and in solid film; i.e. the films of PBDTTFTQ-EH and PBDTTFTTQ-EH showed absorption peaks at 625 nm and 644 nm, however, the corresponding absorption peaks of PBDTTFTQ-DO and PBDTTFTTQ-DO were located at 608 nm and 626 nm, respectively, implying that the replacement of PBDTTFTQ-EH and PBDTTFTTQ-EH with PBDTTFTQ-DO and PBDTTFTTQ-DO slightly increases the optical bandgaps. The absorption edges ($\lambda_{\text{edge}})$ of the four polymer films are 740 nm



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'a of PBDTTFTTQ-EH and cyclic voltammograms of J₄NPF₆ solutions at a scan



Figure 2. Schematic illustration of relative positions of HOMO/LUMO energy levels of the materials in the PSCs

(PBDTTFTQ-EH), 720 nm (PBDTTFTQ-DO), 745nm (PBDTTFTQ-EH) and 722nm (PBDTTFTTQ-DO) respectively, from which the corresponding optical bandgaps (E_g^{opt}) can be calculated as 1.68 eV, 1.72 eV, 1.66eV and 1.72 eV separately, according to the equation $E_g^{opt}=1240/\lambda_{edge}$. It is found that the absorption edges of DO-substituted polymers (PBDTTFTQ-DO and PBDTTFTTQ-DO) are slightly smaller than that of the

corresponding **EH**-based polymers **(PBDTTFTQ-EH** and **PBDTTFTTQ-EH)**, which are ascribed to the big steric hindrance of the two octyl groups on the side chains. Furthermore, it should be noted that when replacing the pendent moctyloxyphenyl side groups **(PBDTTFTQ-EH** and **PBDTTFTQ-DO)** by 5-octylthiophene rings **(PBDTTFTQ-EH** and **PBDTTFTTQ-EH** and **PBDTTFTQ-EH** and **PBDTTFTTQ-EH** and **PBDTTFTQ-EH** a



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Figure 3. Calculated HOMO (a, c) and LUMO (b,d) distribution for PBDTTFTQ-EH (a,b) and PBDTTFTQ-DO (c, d)



Figure 4. Calculated HOMO (a,c) and LUMO (b,d) distribution for PBDTTFTTQ-EH(a,b) and PBDTTFTTQ-DO (c,d)
Table 1. Optical, electrochemical properties of the polymers

Polymer	λ_{edge}	Eg ^{opt a)}	HOMO ^{b)}	LUMO ^{b)}	Eg ^{b)}	E _{ox} c)	E _{red} c)	HOMO ^{c)}	LUMO ^{c)}	Eg ^{c)}
	[nm]	[eV]	[eV]	[eV]	[eV]	[V]	[V]	[eV]	[eV]	[eV]
PBDTTFTQ-EH	740	1.68	-4.79	-2.27	2.52	0.58	-1.66	-5.29	-3.05	2.24
PBDTTFTQ-DO	720	1.72	-4.83	-2.22	2.61	0.66	-1.68	-5.37	-3.03	2.34
PBDTTFTTQ-EH	745	1.66	-4.76	-2.28	2.48	0.41	-1.68	-5.12	-3.03	2.09
PBDTTFTTQ-DO	722	1.72	-4.77	-2.25	2.52	0.60	-1.72	-5.31	-2.99	2.32

^{a)} estimated from the onset of electronic absorption of the polymer films ($E_g^{opt} = 1240/\lambda(nm)$). ^{b)} calculated results from the DFT at B3LYP/6-31G(d) level. ^{c)} cyclic voltammetry results.

DO), red-shifted absorption spectra and decreased bandgaps were achieved, which were in good agreement with the literatures. $^{\left[23\right] }$

Cyclic voltammetry (CV) was employed to measure oxidation and reduction potentials of the polymers (Figure 1c and 1d). The HOMO and LUMO energy levels of the polymers were determined from the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) according to the following equations: HOMO=-e(E_{ox} + 4.71) (eV); LUMO=-e(E_{red}+4.71) (eV), where the unit of potential is V vs Ag/Ag^{+} [28] As shown in Figure 1c and 1d, the onset oxidation potential (E_{ox}) and the onset reduction pontential (E_{red}) are 0.58 V/-1.66 V (PBDTTFTQ-EH), 0.66 V/-1.68 V (PBDTTFTQ-DO), 0.41 V/-1.68 V (PBDTTFTTQ-EH) and 0.60 V/-1.72 V (PBDTTFTTQ-DO) vs. Ag/Ag⁺, corresponding to a HOMO/LUMO level of -5.29 eV/-3.05 eV, -5.37 eV/-3.03 eV, -5.12 eV/-3.03 eV and -5.31 eV/-2.99 eV, respectively. Obviously, when the 2-ethlyhexyllthienyl group was replaced by the 2,3-dioctylthienyl unit, HOMO level of the corresponding polymer can be significantly reduced, 0.08eV for PBDTTFTQ-DO and 0.19 eV for PBDTTFTTQ-DO. To the best of our knowledge, this finding had never been reported in scientific literatures that with similar structure. [29] Thus, this strategy can be a guideline for the design of highly

efficient polymer materials with enhanced photovoltage. Because V_{oc} of BHJ PSCs is closely related to the gap between the HOMO of the donor polymer and the LUMO of the acceptor material in their blended films, higher V_{oc} can be expected in the PSCs based on **PBDTTFTQ-DO** and **PBDTTFTQ-DO** compared to the devices based on **PBDTTFTQ-EH** and **PBDTTFTQ-EH**. ^[30] To make a clear comparison, the energy levels diagrams of the materials used in this study were summarized in **Figure 2**. It is obvious that the LUMO energy levels of the four polymers are both significantly higher than that of PC₇₁BM, which facilitate electron transferring from the polymers to the PC₇₁BM at the photoactive layer of PSCs.

In order to explore the electronic properties of the polymers, molecular simulations were performed on single repeated donor-acceptor unit with all alkyl chains reserved using the Density Functional Theory (DFT) at B3LYP/6-31G(d) level.^[30] As shown in **Figure 3** and **4**, the localization of HOMOs distributed along the polymer backbone while the LUMOs of both polymers were somewhat more localized on the acceptor units, indicating the significant charge-transfer character between BDT and quinoxaline unit, which was consistent with the observed strong low-energy absorption band in **Figure 1**. From the simulation data it can be seen that deeper HOMO levels

DOI: 10.1039/C5TA05096K



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Figure 5. (a) The J-V curves of PSCs based on PBDTTFTQ-EH:PC71BM (1:1.5, w/w ; 2% CN, v/v) and PBDTTFTQ-DO:PC71BM (1:3) with THF-SVA for 30 sec under the illumination of AM 1.5G, 100 mW cm⁻²; (b) the corresponding EQE curves of PBDTTFTQ-EH and PBDTTFTQ-DO devices; (c) the J-V curves of PSCs based on PBDTTFTQ-EH:PC71BM (1:2) and PBDTTFTTQ-DO:PC71BM (1:3) with THF-SVA for 30 sec under the illumination of AM 1.5G, 100 mW cm⁻²; (d) the corresponding EQE curves of PBDTTFTTQ-EH and PBDTTFTTQ-DO devices.

Table 2. Photovoltaic performances of copolymers measured under illumination of AM 1.5 G condition, 100 mW cm⁻²

Polymer	Polymer:PC71BM	THF SVA Time	V _{oc}	J _{sc}	FF	PCE _{max} (PCE _{ave} ^{a)})
	[w/w]	(sec)	[V]	[mA cm ⁻²]	[%]	[%]
PBDTTFTQ-EH	1:1.5(2%CN, v/v)	30	0.78	13.2	70.8	7.29 (7.15)
PBDTTFTQ-DO	1:3	30	0.88	11.4	75.9	7.61 (7.42)
PBDTTFTTQ-EH	1:2	30	0.72	13.4	70.8	6.82 (6.65)
PBDTTFTTQ-DO	1:3	30	0.85	11.3	75.7	7.25 (7.09)

^{a)} Calculated from 5 individual PSCs.

for **DO**-based polymers and smaller calculated bandgap for **EH**based polymers were investigated, which were consistent with the measured HOMO levels and optical bandgaps in Figure 1. The absorption parameters and energy levels of the four polymers were also listed in Table 1.

3.3 Characteristics and Optimization of Photovoltaic Devices

To investigate the photovoltaic properties of the obtained polymers, PSCs with a device structure of ITO/poly(3,4ethylenedioxythiophene):poly(styrene sulfonic acid (PEDOT:PSS)/polymer:PC71BM/poly[(9,9-dioctyl-2,7-fluorene)alt-(9,9-bis(3-N,N-dimethylamino)propyl)-2,7-fluorene]) (PFN, 5 nm)/Al that followed our previous work,^[31] were fabricated. The photoactive layer were spin-coated on top of prefabricated PEDOT:PSS layer from their 1,2-dichlorobenzene solution. After that, the blend film was pre-thermal annealed

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at 90 °C for 10 min and followed by a THF-SVA of 30 sec. Then a thin layer of 5 nm water/alcohol soluble PFN that can serve as the electron-collecting layer was spin-coated atop photoactive layer from methanol solution in the presence of a trace amount of acetic acid before deposition of cathode.

Optimal weight ratios between polymers: PC71BM were found to be 1:1.5 for PBDTTFTQ-EH, 1:3 for PBDTTFTQ-DO, 1:2 for PBDTTFTTQ-EH, and 1:3 for PBDTTFTTQ-DO respectively (Figure S10 and Table S1). In order to optimize morphology of the blend films and thus to improve the photovoltaic properties, 2% (v/v) of 1-chloronaphthalen (CN) was used as additive for PBDTTFTQ-EH based devices. The device performances of both polymers are critically dependent on the processing conditions (donor/acceptor blend ratios, additive and solvent-vapour annealing (SVA) ^[32]), which were detailed summarized in Figure S10-12 and Table S1-3. The current density versus voltage (J-V) characteristics and the external quantum efficiency (EQE) curves of the corresponding optimized PSCs under AM 1.5 G at 100 mW cm⁻² illumination are presented in Figure 5. Photovoltaic parameters deduced from the corresponding J-V curves in Figure 5a and 5c are summarized in Table 2. It is interesting to note that PBDTTFTQ-EH exhibited optimized device performance when combination of CN and THF-SVA were used, while PBDTTFTQ-DO reached its highest PCE (~7.61 %) in case of a simple THF-SVA process. For the PSCs devices prepared under the optimal conditions, the **PBDTTFTQ-DO** based devices showed a V_{oc} of 0.88 V, which is 0.10 V larger than that of the device of PBDTTFTQ-EH. Like PBDTTFTQ-DO, higher V_{oc} of 0.85V (about 0.13V larger than that of PBDTTFTTQ-EH) with relative high PCE (7.25%) was also achieved for the optimized PBDTTFTTQ-**DO** based devices after THF SVA 30 sec. The enhanced V_{oc} of the DO-substituted polymer based devices were ascribed to the deeper HOMO energy levels as discussed above.

As shown in Figure 5b and 5d, the devices of these four polymers processed under each optimal conditions showed similar EQE peak values of >60 %, while the response peaks were 461 nm with the corresponding EQE peak value of 63.50% for PBDTTFTQ-DO, 572 nm for PBDTTFTQ-EH (60.35%), 454 nm for PBDTTFTTQ-DO (63.99%), and 455nm for PBDTTFTTQ-EH (62.42%), respectively. Nevertheless, the response range of the PBDTTFTQ-EH and PBDTTFTTQ-EH-based devices at long wavelength region are 22 nm and 24 nm red-shifted compared to that of the corresponding PBDTTFTQ-DO and PBDTTFTTQ-**DO**-based devices, which are in accord with the film absorption spectra of the polymers as shown in Figure 1a and 1b. As a result, the PBDTTFTQ-EH and PBDTTFTTQ-EH devices showed relatively higher short-circuit current densities (Jsc) of 13.2 mA cm^{$^{-2}$} and 13.4 mA cm^{$^{-2}$}, while the **PBDTTFTQ-DO** and **PBDTTFTTQ-DO** devices exhibited decreasing J_{sc} of 11.4 mA cm^{-2} and 11.3mA cm^{-2} . Except for the differences in V_{oc} and J_{sc} FF values of the devices from these four polymers are essentially high (same 70.8 % for the two EH-based polymers vs. 75.9 % for PBDTTFTQ-DO and 75.7% for PBDTTFTTQ-DO), both implying very good charge separation, transporting and collecting efficiency in these optimal devices. The higher FF of the two **DO**-based polymers might be resulted from their good solubility and film processibility. More importantly, the overall efficiency of the devices from both polymers exceeds 6.8%. The best PCE is 7.61 % for PBDTTFTQ-DO, 7.29 % for PBDTTFTQ-EH, 7.25% for PBDTTFTTQ-DO and 6.82% for PBDTTFTTQ-EH respectively, while the average PCE over 5

individual PSCs from each polymer are 7.42 %, 7.15 %, 7.09% and 6.65%, separately. Obviously, the slightly better photovoltaic performances in the **PBDTTFTQ-DO** and **PBDTTFTQ-DO** devices mainly attributed to the higher FF and enhanced V_{oc} resulting from their deepened HOMO levels compared with that of **PBDTTFTQ-EH** and **PBDTTFTTQ-EH**.

To illuminate the effects of SVA on the device performances, atomic force microscopy (AFM) study was carried out to investigate the phase-separated morphologies of the polymers:PC₇₁BM blends corresponding to the best performance, which were shown in Figure 6-8. The light and dark domains correspond to the aggregations of polymer and PC71BM, respectively. For the pristine films of PBDTTFTQ-EH and PBDTTFTQ-DO, it can be observed clearly that both two blend films exhibit interpenetrating feature with bicontinuous network between polymer and PC71BM. In addition, smooth surface with a root-mean-square roughness (RMS) value of 0.54 nm for PBDTTFTQ-DO and 1.75 nm for PBDTTFTQ-EH were recorded, respectively. As described ahead, the devices from PBDTTFTQ-DO showed strong dependence on the THF-SVA (see Figure S12 and Table S3), which should correlate the change of film morphology upon treatment. As seen in Figure 6, the RMS roughness and the domain size of the films exhibit a continuous enlargement as the SVA time increase. The optimal THF-SVA time is found to be around 30 sec for the PBDTTFTQ-DO blend film. Under this treatment process, the film showed a RMS roughness of 1.35 nm with an ideal domain size of 10-20nm (Figure 6b), which is pretty favorable for efficient diffusion of excitons to donor-acceptor interface. [33,34] Annealing duration exceeding this optimized condition could lead to significantly increased domain size in the PBDTTFTQ-DO blend film, resulting in a reduction in overall performance (see Figure S12 and Table S3). When the THF-SVA duration reached 3 min, the resulting film showed unexpected phase separation with corresponding domain size over 200 nm, which is much larger than typical exciton diffusion length of ca. 10 nm, ^[35] thus is not desired for efficient excitons dissociation at the D/A interface. We also found that in order to obtain optimal performance in PBDTTFTQ-EH device, SVA in conjunction with incorporation of additive, such as CN (2%, v/v) into the blend solution is required (see Figure S11 and Table S2). This combination was found to be able to promote the demixing of the polymer and PCBM in the blend film, so as to optimize film morphology. [36] Optimal phase-separated morphologies were also investigated in Figure 8 for PBDTTFTTQ-EH and PBDTTFTTQ-DO blend films after THF SVA 30 sec, excepted for the RMS values of the treated films decreasing slightly.

3.4 Effects of Solvent Vapour Annealing on Charge Transport Properties

To get insight into the effects of the SVA on charge transporting, the hole mobilities, μ_{hole} of the blends of polymers and PC₇₁BM were measured using the space-charge-limited current (SCLC) method (**Figure S13-S15**) for the four polymers with different treatment and film thickness. For **PBDTTFTQ-DO** blend films, a high hole mobility (up to $5.28 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was achieved after the THF-SVA 30 sec, while the pristine film only showed a moderate μ_{hole} of $1.45 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ s⁻¹ (**Table S5**). These results were consistent with the

DOI: 10.1039/C5TA05096K



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Figure 6. Surface topographic AFM images (size: 5µm×5µm) of **PBDTTFTQ-DO**:PC₇₁BM blend films with a weight ratio of 1:3 obtained at tapping mode, (a) as cast (RMS:0.54 nm), (b)THF-SVA 30 sec (RMS:1.35 nm), (c) THF-SVA 60 sec (RMS: 1.61 nm), (d) THF-SVA 180 sec (RMS: 3.89 nm).



Figure 7. AFM topography images (5 μ m ×5 μ m) of ITO/PEDOT:PSS/**PBDTTFTQ-EH**:PC₇₁BM (1:1.5) films.(a): Without CN , As cast film (RMS:1.75 nm); (b): Without CN, THF-SVA 30 sec (RMS:4.63 nm); (c): With CN(2%, v/v%), As cast (RMS:1.39 nm); (d): With CN(2%, v/v%), THF-SVA 30 sec (RMS:1.76 nm).



Figure 8. AFM topography images (5 μ m ×5 μ m) of ITO/PEDOT:PSS/**PBDTTFTTQ-DO**:PC₇₁BM (1:3) films.(a): As cast film (RMS:0.79 nm); (b): THF-SVA 30 sec (RMS: 0.64 nm); and ITO/PEDOT:PSS/**PBDTTFTTQ-EH**:PC₇₁BM (1:2) films; (c): As cast film(RMS:0.80 nm); (d): THF-SVA 30 sec (RMS: 0.73 nm).

performance of each device and the film morphology induced by the THF-SVA as shown in **Figure 6b.** Similar results were observed for **PBDTTFTQ-EH** film except that the hole mobility showed a decrease after the CN addition $(3.14 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ vs. } 1.29 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, see **Table S4**). Furthermore, the corresponding hole mobilities of the other two polymers after THF SVA 30 sec (**Figure S15**) are $1.14 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**PBDTTFTTQ-EH**) and $1.49 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**PBDTTFTTQ-EH**) are consistent well with their photovoltaic performances.

To further shed light on the role of SVA, we performed transient photovoltage (TPV)^[37] and transient photocurrent (TPC)^[38] measurements to probe the charge recombination in the **PBDTTFTQ-DO** devices with/without the SVA. The TPV

technique has previously been used to study the charge decay dynamics in organic solar cells under a given steady-state illumination, ^[38] while TPC was used to determine the charge density in the devices. ^[39] For the TPV measurement, the perturbation from pulsed laser was attenuated by a set of neutral density filter so that the amplitude of TPV is much smaller as compared to V_{oc}. Since there is no charge collected under the V_{oc} condition, the excess charge carriers that excited by the pulsed laser are recombined and their lifetime can be extracted from the exponential fitting on the decay of the transient photovoltage. **Figure 9a** shows the typical results of TPV measurement for the **PBDTTFTQ-DO** devices before and after THF-SVA for 30 sec, as obtained under 1 sun illumination and open-circuit voltage conditions, and the extracted carriers



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Figure 9. (a) Transient photovoltage and (b) transient photocurrent signals for the **PBDTTFTQ-DO** devices before and after 30 sec SVA, measured under 1 sun illumination and open-circuit voltage conditions using the same intensity laser pulse. The dashed lines in **Figure 9a** are mono-exponential decay fits.

Lifetimes are 0.187 us and 0.320 us for the **PBDTTFTQ-DO** devices with/without SVA, respectively. The observed shorter carrier lifetime in the device with SVA is consistent with its relatively lower Voc than that of the device without the treatment (0.88 V vs 0.98 V, **Table S3**). On the other side, the device underwent SVA showed higher charge carrier density than that without SVA (**Figure 9b**), which are in good agreement with the observed higher J_{sc} after 30 sec treatment (**Table S3**) and was ascribed to a more preferable morphology for efficient excitons dissociation as shown in **Figure 6b**. By taking the extracted lifetime and mobility together, the calculated carrier diffusion length in the device after 30 sec SVA is obviously higher than that of the control device, which is expected to be responsible for the largely improved FF after the SVA.

3. CONCLUSION

In summary, four D-A polymers based on side chain modified 2D conjugated BDT and mono-fluorinated quinoxaline derivatives, **PBDTTFTQ-EH**, **PBDTTFTQ-DO**, **PBDTTFTQ-EH** and **PBDTTFTTQ-DO** were synthesized and characterized. The results clearly indicated that the variation in the side chain of BDT unit from 2-ethylhexylthienyl group to 2,3-dioctylthienyl group can cause big impact on their optical properties and electronic HOMO levels. This finding should provide valuable guideline for the design and synthesis of novel polymer donor materials for highly efficient polymer solar cells with high open-circuit voltage via fine tuning the molecular energy levels and absorption spectra through a modulation of the side chain onto the donor moiety. In good agreement with the deeper HOMO level of **PBDTTFTQ-DO** (-5.37 eV) and **PBDTTFTTQ-DO** (-5.31 eV) than that of

PBDTTFTQ-EH (-5.29 eV) and **PBDTTFTTQ-EH** (-5.12 eV), the devices from **PBDTTFTQ-DO** and **PBDTTFTTQ-DO** showed high V_{oc} values of 0.88 V and 0.85V, while that of 0.78 V and 0.72V were observed in **PBDTTFTQ-EH** and **PBDTTFTTQ-EH** devices. Both polymers deliver high power conversion efficiency, with an outstanding efficiency of 7.61% and an excellent filled factor of 75.9% in **PBDTTFTQ-DO** as obtained via solvent vapour annealing, which mainly resulted from the improved carrier diffusion length of the devices after proper SVA process.

Acknowledgements

We would like to thank the financial support of the National Natural Science Foundation of China (Nos. 61177031, 61274054, 51225301, and 91333206).

References

- [1] Y. Li, Accounts Chem. Res. 2012,45, 723
- [2] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science*. 1995, **270**, 1789.
- [3] S. H. Liao, H. J. Jhuo, Y. S. Cheng, S. A. Chen, *Adv. Mater.* 2013. **25**, 4766.
- [4] Z. B. Henson, K. Mullen, G. C. Bazan, *Nat. Chem.* 2012, **4**, 699.
- [5] Z. C. He, C. M. Zhong, S. J. Su, M. Xu, H. B. Wu, Y. Cao, *Nat. Photo.* 2012, **6**, 591.
- [6] Y. Liang, Z. Xu, J. Xia, S-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv Mater*, 2010, **22**, E135.
- [7] S-H. Liao, H-J. Jhuo, P-N. Yeh, Y-S. Cheng, Y-L. Li, Y-H. Lee, S. Sharma, S-A. Chen. *Sci. Rep.* 2014, **4**, 6813
- [8] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Common*. 2014, **5**, 5293
- [9] C. J. Brabec, A. Cravino, D. Meissner, N. S. Saricici, T. Fromherz, M. T. Rispens, L. Sanchez, J. C. Hummelen, *Adv. Funct. Mater.* 2001, **11**, 374.

[10] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat. Mater.* 2007, **6**, 497.

[11] G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* 2005, **4**, 864.

[12] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, *Adv. Mater.* 2006, **18**, 789.

[13] a) M. Svensson, F. Zhang, S. C. Veenstra, W. J. H. Verhees, J.
C. Hummelen, J. M. Kroon, O. Inganas, M. R. Andersson. Adv. Mater. 2003, **15**, 988; b) J. You, L. Dou, K. Yoshimura, T. Kato, K.
Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang. Nat. Commun. 2013, **4**,1446; c) M. Zhang, X. Guo, W. Ma, S.
Zhang, L. Huo, H. Ade, J. Hou. Adv. Mater. 2014, **26**, 2089; d) S.
H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D.
Moses, M. Leclerc, K. Lee, A. J. Heeger. Nat. Photo. 2009, **3**, 297

[14] a)D. Dang, W. Chen, R. Yang, W. Zhu, W. Mammo, E. Wang, *Chem. Commun.* 2013, **49**, 9335; b) N. Wang, Z. Chen, W. Wei, Z. Jiang. *J. Am. Chem. Soc.* 2013, **135**, 17060; c) Y. Deng, J. Liu, J. Wang, L. Liu, W. Li, H. Tian, X. Zhang, Z. Xie, Y. Geng, F. Wang. *Adv. Mater.* 2014, **26**, 471. d) Y. Huang, X. Guo, F. Liu, L. Huo, Y. Chen, T. P. Russell, C. C. Han, Y. Li, J. Hou. *Adv. Mater.* 2012, **24**, 3383

[15] a) H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li. *Nat. Photo*, 2009, **3**, 649; b) J. Hou, H.-Yu Chen, S. Zhang, R. I. Chen, Y. Yang, Y. Wu, G. Li. *J. Am. Chem. Soc.* 2009, **131**,15586; c) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu. *J. Am. Chem. Soc.* 2009, **131**, 7792; d) Y. Huang, L. Huo, S. Zhang, X. Guo, C. C. Han, Y. Li, J. Hou, *Chem. Commun.* 2011, **47**, 8904; e) H. J. Son, B. Carsten, I. H. Junga, L. P. Yu, *Energy Envir. Sci*, 2012, **5**, 8158.

[16] a) L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, J. Hou. Angew. Chem. Int. Ed. 2011, 50, 9697; b) C. Cui, W.-Y. Wong, Y. Li. Energy Environ. Sci, 2014, 7, 2276.

[17] a) Z. G. Zhang, Y. F. Li. Side-chain engineering of highefficiency conjugated polymer photovoltaic materials. *Sci China Chem*, 2015, **58**,192;b) Li. Chen, P. Shen, Z. G. Zhang, Y. Li. *J. Mater. Chem. A*, 2015,**3**,12005

[18] M. Zhang, X. Guo, W. Ma, S. Zhang, L. Huo, H. Ada, J. Hou, *Adv. Mater.* 2014, **26**, 2089

[19] a) H.-C. Chen,Y.-H Chen, C.-C. Liu, Y.-C. Chien, S.-W. Chou, P.-T. Chou. *Chem. Mater.* 2012, **24**, 4766; b) H.-C. Chen, Y.-H. Chen, C.-H. Liu, Y.-H. Hsu, Y.-C. Chien, W.-T. Chuang, C.-Y. Cheng, C.-L. Liu, S.-W. Chou, S.-H. Tung, P.-T. Chou. *Polym. Chem.* 2013, **4**, 3411.

[20] A. Iyer, J. Bjorgaard, T. Anderson, M. E. Kose. *Macromolecules* 2012, **45**, 6380.

[21] a) E. Wang, L. Hou, Z. Wang, S. Hellström, F. Zhang, O. Inganäs, M. R. Andersson. *Adv. Mater.* 2010, **22**, 5240; b) A. Gadisa, W. Mammo, L. M. Andersson, S. Admassie, F. Zhang, M. R. Andersson, Olle Inganäs. *Adv. Funct. Mater.* 2007, **17**, 3836; c) L. Huo, Z. Tan, X. Wang, Y. Zhou, M. Han, Y, Li. *J. Polym. Sci. Pol. Chem.* 2008, **46**, 4038; d) M.-H. Lai, C.-C. Chueh, W.-C. Chen, J.-L. Wu, F.-C. Chen, *J. Polym. Sci. Pol. Chem.* 2009, **47**, 973.

[22] Y. Huang, M. Zhang, L. Ye, X. Guo, C. C. Han, Y. Li, J. Hou. J. Mater. Chem. 2012, **22**, 5700.

[23] R. Kroon, A. Lundin, C. Lindqvist, P. Henriksson, T. T. Steckler, M. R. Andersson. *Polymer*. 2013, **54**, 1285

[24] H. Wu, B. Qu, D. Tian, Z. Cong, B. Gao, J. Liu, Z. An, C. Gao, L. Xiao, Z. Chen, Q. Gong, W. Wei, *React. Funct. Polym.* 2013, **73**, 1432

[25] Y. Lu, Z. Xiao, Y. Yuan, H. Wu, Z. An, Y. Hou, Chao Gao, J. Huang, *J. Mater. Chem. C.* 2013,1,630

[26] F. Babudri, V. Fiandanese, G. Marchese, A. Punzi, *Tetrahedron Lett*. 1995, **36**, 7305.

[27] M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang, Y. Cao, J. Am. Chem. Soc. 2011, **133**, 9638.

[28] J. Hou, Z. Tan, Y. Yan, Y. He, C. Yang, Y. Li, *J. Am. Chem. Soc.* 2006, **128**, 4912

[29] Y. Dong, X. Hu, C. Duan, P. Liu, S. Liu, L. Lan, D. Chen, L. Ying,

S. Su, X. Gong, F. Huang, Y. Cao. *Adv. Mater.* 2013, **25**, 3686. [26] G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, C. J. Brabec. *Adv. Mater.* 2008, **20**, 579.

[30] a) R. Kroon, R. Gehlhaar, T. T. Steckler, P. Henriksson, C. Muller, J. Bergqvist, A. Hadipour, P. Heremans, M. R Andersson. Sol. Energ. Mat. Sol C. 2012, **105**, 280; b) G. K. Dutta, T. Kim, H. Choi, J. Lee, D. S. Kim, J. Y. Kim, C. Yang. Polym. Chem, 2014, **5**, 2540.

[31] Z. C. He, C. M. Zhong, X. Huang, W. Y. Wong, H. B. Wu, L. W. Chen, S. J. Su, Y. Cao. *Adv. Mater.* 2011, **23**, 4636.

[32] a) J. Liu, L. Chen, B. Gao, X. Gao, Y. Han, Z. Xie, L. Wang, J. Mater. Chem. A, 2013, 1, 6216, b) B. Kan, Q. Zhang, M. Li, X. Wang, W. Ni, G. Long, Y. Wang, X. Yang, H. Feng, Y. Chen, J. Am. Chem. Soc. 2014, 136, 15529

[33] J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, A. J. Heeger. *J. Am. Chem. Soc.* 2008, **130**, 3619.

[34] J. Liu, L. Chen, B. Gao, X. Cao, Y. Han, Z. Xie, L. Wang. J. Mater. Chem. A, 2013, 1, 6216.

[35] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan. *Nat. Mater.* 2007, **6**, 497

[36] C. G. Shuttle, B. O'Regan, A. M. Ballantyne, J. Nelson, D. D. C. Bradley, J. de Mello, J. R. Durrant. *Appl. Phys. Lett.* 2008, **92**, 093311.

[37] Y. Kim, H. R. Yeom, J. Y. Kim, C. Yang. *Enegry Environ. Sci*, **2013**, 6, 1909.

[38] A. Maurano, C. G. Shuttle, R. Hamilton, A. M. Ballantyne, J. Nelson, W. M. Zhang, M. Heeney, J. R. Durrant. *J. Phys. Chem. C*, 2011, **115**, 5947.

[39] C. G. Shuttle , N. D. Treat , J. D. Douglas , J. M. J. Fréchet , M. L. Chabinyc. *Adv. Energy Mater.* 2011, **2**, 111119.