[Supporting Information]

Fluorinated Thienyl-Quinoxaline-Based D– π –A–Type Copolymer

toward Efficient Polymer Solar Cells: Synthesis, Characterization,

and Photovoltaic Properties

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Experimental Section

Materials.

All other chemicals were purchased from commercial sources (Aldrich, Acros, TCI, and Solarmer Materials Inc.) and were used without further purification unless otherwise stated. reactions were performed under nitrogen atmosphere and All solvents were use. Compound from appropriate distilled drying agents prior to 5,8-Dibromo-6,7- difluoro-2,3-bis(5-hexyl 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene,^{1a} thiophen-2-yl)quinoxaline (M2)^{1b} 6,7-Difluoro-2,3-bis(5- hexylthiophen-2-yl)-5,8-di(thiophen -2-yl)quinoxaline (M3), 5,8-Bis(5- bromothiophen-2-yl)-6,7-difluoro-2,3-bis(5-hexyl thiophen-2-yl)quinoxaline (M4) were synthesized according to the previously literature procedures.¹ The synthetic route of monomer M4 is shown in Scheme S1 and the detailed synthetic processes are illustrated as follows.



Fig. S1 Synthetic route adopted for the preparation of monomers.

1,2-Bis(5-hexylthiophen-2-yl)ethane-1,2-dione (M1).

To a stirred suspension of AlCl₃ (3.30 g, 12.5 mmol) and 2-hexylthiophene (4.20 g, 25.0 mmol) in dry dichloromethane (DCM, 30 mL) was added oxalyl chloride (1.58 g, 12.5 mmol) at 0 °C under nitrogen atmosphere. After the reaction mixture was stirred 3 h at 0 °C, the reaction mixture was poured into saturated aqueous NH₄Cl, extracted with ethyl acetate, and dried with anhydrous MgSO₄. The solvent was removed via rotary evaporation, and was

subsequently purified by column chromatography on silica gel (ethyl acetate/hexane = 1/5) to afford compound M1 (3.03 g, 62.0%).

¹H NMR (CDCl₃, 400 MHz, δ): 7.83 (d, *J* = 4.0 Hz, 2H), 6.85 (dd, *J* =0.8, 4.0 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 4H), 1.72~1.65 (m, 4H), 1.36~1.33 (m, 4H), 1.31~1.24 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ): 182.57, 160.01, 137.70, 136.49, 126.38, 31.42, 31.20, 30.79, 28.86, 22.47, 13.99. HRMS calcd for C₂₂H₃₀O₂S₂: 390.1687, found: 391.1770 [M+H]⁺.

5,8-Dibromo-6,7-difluoro-2,3-bis(5-hexylthiophen-2-yl)quinoxaline (M2).

A mixture of 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene (3.61 g, 10.0 mmol), iron powder (6.70 g, 120.0 mmol) and acetic acid (60 mL) was stirred at 50 °C for 4 h. After filtering, compound M1 (3.90 g, 10.0 mmol) was subsequently added to the filtrate, followed by heating under reflux for 8 h. Afterwards the reaction mixture was poured into water, extracted with dichloromethane (DCM), and dried with anhydrous MgSO₄. The solvent was removed via rotary evaporation, and was subsequently purified by column chromatography on silica gel (DCM/hexane = 1/7) to afford compound M2 (4.47 g, 68 %).

¹H NMR (CDCl₃, 400 MHz, *δ*): 7.38 (d, *J* = 4.0 Hz, 2H), 6.70 (d, *J* = 4.0 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 4H), 1.76~1.68 (m, 4H), 1.53~1.36 (m, 4H), 1.33~1.29 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, *δ*): 152.32, 151.59, 149.03, 147.20, 137.91, 135.12, 130.43, 125.00, 31.52, 31.45, 30.44, 28.83, 22.55, 14.04. ¹⁹F NMR (CDCl₃, 400 MHz, *δ*): -120.77.

HRMS calcd for $C_{28}H_{30}Br_2F_2N_2S_2$: 654.0185, found: 655.0323[M+H]⁺.

6,7-Difluoro-2,3-bis(5-hexylthiophen-2-yl)-5,8-di(thiophen-2-yl)quinoxaline (M3).

A mixture of 2-tri-n-butylstannyl thiophene (3.72 g, 10.0 mmol), compound M2 (3.27 g, 5.0 mmol), and $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol) in toluene (100 mL) was heated under reflux for 48 h under nitrogen atmosphere. After the solvent was removed under reduced pressure, the crude product was subsequently purified by column chromatography on silica gel (DCM/hexane = 1/4) to afford compound M3 (2.37 g, 71.5 %).

¹H NMR (CDCl₃, 400 MHz, δ): 8.00 (d, *J* = 3.2 Hz, 2H), 7.65 (d, *J* = 4.8 Hz, 2H), 7.40 (d, *J* = 4.0 Hz, 2H), 7.25~7.23 (m, 2H), 6.71 (d, *J* = 3.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 4H), 1.79~1.71 (m, 4H), 1.45~1.41 (m, 4H), 1.40~1.34 (m, 8H), 0.92 (d, J = 6.4 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ): 151.00, 144.53, 138.28, 133.72, 130.68, 130.55, 130.09, 129.59, 126.39, 124.59, 31.67, 31.56, 30.49, 28.93, 22.73, 14.24. ¹⁹F NMR (CDCl₃, 400 MHz, δ): -130.47. HRMS Calcd. for C₃₆H₃₆F₂N₂S₄: 662.1729, found: 662.1794.

5,8-Bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(5-hexylthiophen-2-yl)quinoxaline

(M4).

Compound M4 (2.65 g, 4.0 mmol) was dissolved in 40 mL of N,N-dimethyl- formamide (DMF) under nitrogen atmosphere, and NBS (1.42 g, 8.0 mmol) was added in one portion. The mixture was stirred at room temperature for 12 h. After the solvent was removed under

reduced pressure, the solution was poured into water, extracted with DCM, and dried with anhydrous MgSO₄. The solvent was removed via rotary evaporation subsequently purified by column chromatography on silica gel (DCM/hexane = 1/4) to afford compound M4 (2.13 g, 65.0 %).

¹H NMR (CDCl₃, 400 MHz, δ): 7.71 (d, J = 4.0 Hz, 2H), 7.36 (d, J = 3.6 Hz, 2H), 7.13 (d, J = 4.0 Hz, 2H), 6.71 (d, J = 3.6 Hz, 2H), 2.88 (t, J = 7.6 Hz, 4H), 1.79~1.72 (m, 4H), 1.45~1.40 (m, 4H), 1.37~1.32 (m, 8H), 0.89 (d, J = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ): 151.71, 145.00, 137.95, 133.23, 132.38, 130.85, 130.78, 130.49, 129.30, 124.80, 118.46, 116.77, 31.57, 31.42, 30.43, 28.81, 22.56, 14.09. ¹⁹F NMR (CDCl₃, 400 MHz, δ): -130.20. HRMS Calcd. for C₃₆H₃₄Br₂F₂N₂S₄: 817.9940, found: 817.9956.

Poly{4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-*alt*-[5, 8-bis(5'-thiophen-2'-yl)-6,7-difluoro-2,3-bis(5-hexylthiophen-2-yl)quinoxaline-5,5'-diyl]} (PBDTT-TTFQ).

To a reaction mixture of compound M4 (205 mg, 0.25 mmol), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithio-phene (226 mg, 0.25 mmol), and Pd(PPh₃)₄ (5.8 mg) with toluene (40 mL), and the solution was heated under reflux for 48 h. Iodobenzene (20 mg) was added, and was allowed to reflux for 12 h. Then, tributylphenyltin (20 mg) was introduced and the solution was refluxed for 12 h. After cooling to room temperature, and the polymer was precipitated by slowly dropwise into MeOH (250 mL), filtered off and dried. The crude polymer was Soxhlet extracted with subsequently with methanol, ethyl acetate, hexane, CH₂Cl₂, and CHCl₃. The CH₂Cl₂ and CHCl₃ solutions were concentrated to a small volume, and the polymers different molecular weight were reprecipitated from MeOH, filtered off, and dried to afford PBDTT-TTFQ. Obtained as a dark purple shining solid (270 mg, 62.6 %), GPC: $M_w = 68 \text{ kg mol}^{-1}$, and $M_n = 43 \text{ kg mol}^{-1}$; PDI = 1.58. ¹H NMR (C₂D₂Cl₄, 400 MHz, δ): 8.03~6.77 (br, 14H), 2.91 (br, 8H), 1.68~0.94(br, 52H).



Fig. S2 ¹H-NMR spectrum of compound M1.



Fig. S3 ¹³C-NMR spectrum of compound M1.



Fig. S4 ¹H-NMR spectrum of compound M2.



Fig. S5 ¹³C-NMR spectrum of compound M2.



Fig. S6¹⁹F-NMR spectrum of compound M2.



Fig. S7 ¹H-NMR spectrum of compound M3.



Fig. S8¹³C-NMR spectrum of compound M3.



Fig. S9¹⁹F-NMR spectrum of compound M3.



Fig. S10 ¹H-NMR spectrum of compound M4.



Fig. S11 ¹³C-NMR spectrum of compound M4.



Fig. S12 ¹⁹F-NMR spectrum of compound M4.



Fig. S13 ¹H-NMR spectrum of copolymer PBDTT-TTFQ.



Fig. S14 Cyclic voltammogram of PBDTT-TTFQ in the thin film at a scan rate of 50 mV s⁻¹.



Fig. S15 UV–vis spectra of PBDTT-TTFQ:PC₇₁BM blend films. The presence of vibronic features at 658-nm in the absorption spectra of the polymer blends further corroborates ordering of the polymer.



Fig. S16 TEM images of a) 1:1 and b) 1:2 PBDTT-TTFQ:PC₇₁BM films bulk morphology after thermal annealing at 150 °C for 10 min. The scale bar is 0.2 μ m in each panel.



Fig. S17 Two-dimensional grazing incidence X-ray scattering (GIWAXS) patterns of the a) neat PBDTT-TTFQ film and b) 1:1 PBDTT-TTFQ:PC₇₁BM blend film without thermal annealing. GIWAXS out-of-plane diffractograms of the corresponding c) neat PBDTT-TTFQ film and d) 1:1 PBDTT-TTFQ:PC₇₁BM blend film.



Fig. S18 Overlay of GIWAXS out-of-plane diffractograms of pristine PBDTT-TTFQ film and 1:1 PBDTT-TTFQ:PC₇₁BM blend film without thermal annealing.

References

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