

Electronic Supplementary Information

Performance comparison of fluorinated and chlorinated donor-acceptor copolymers for polymer solar cells

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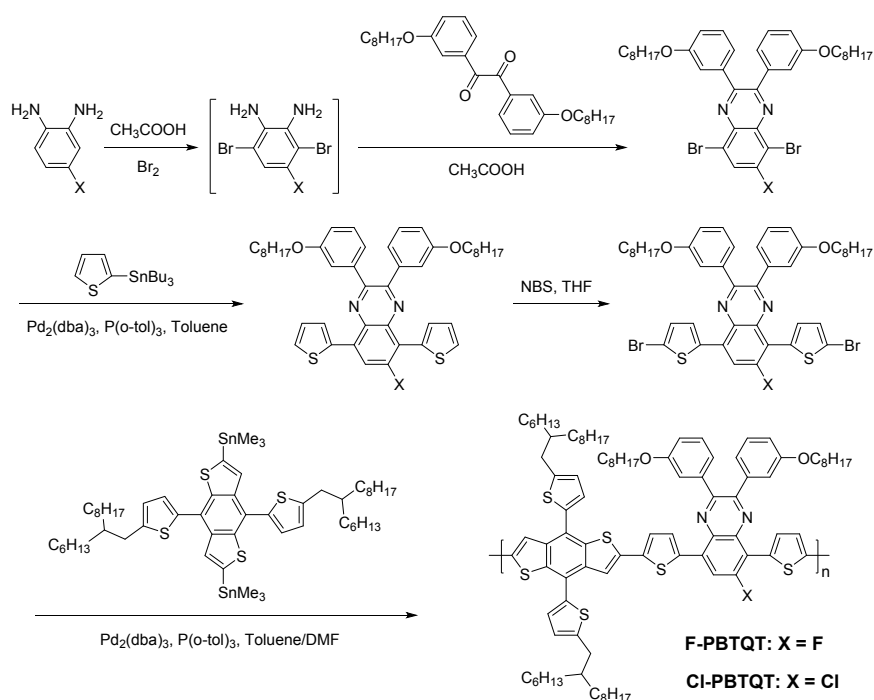
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1. Synthetic procedures and characterizations

1.1 General methods

Chemicals were used as received unless otherwise indicated. Reaction solvents were dried when necessary and purified by distillation. ^1H and ^{13}C NMR spectra were recorded on Bruker 600 MHz spectrometer and chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane standard. Fourier transform mass spectra (FTMS) were recorded on a Bruker Apex Fourier transformation mass spectrometer. Elemental analyses were performed on a German Vario EL III elemental analyzer. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories GPC-50 instrument using tetrahydrofuran as the eluent at 40 °C. The obtained molecular weight is relative to the polystyrene standard.

1.2 General procedures



Scheme S1 Synthesis of F-PBTQT and Cl-PBTQT.

3,6-dibromo-4-fluorobenzene-1,2-diamine. In a 250 mL, flame-dried, two necked,

round-bottomed flask with a condenser, 4-fluorobenzene-1,2-diamine (2.52 g, 20 mmol) was added to glacial acetic acid (100 mL), then liquid bromine (2.36 mL) was slowly added under stirring. The mixture was stirred at room temperature for 2 hours, and poured into sodium sulfite-saturated water solution. The solid was collected via vacuum filtration and washed successively by water, 5% aqueous solution of sodium hydroxide and water. The crude compound was used for next step without further purification.

3,6-dibromo-4-chlorobenzene-1,2-diamine. The compound has been prepared using the same synthetic process as for 3,6-dibromo-4-fluorobenzene-1,2-diamine.

5,8-dibromo-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline. In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, 1,2-bis(3-(octyloxy)phenyl)ethane-1,2-dione (2.33 g, 5 mmol), 3,6-dibromo-4-fluorobenzene-1,2-diamine (1.41 g, 5 mmol) and glacial acetic acid (100 mL) were added. The mixture was stirred at 120 °C for 12 hours, then cooled to room temperature and dropped by water. The organic layer was washed successively by 5% aqueous solution of sodium hydroxide, water and dried over anhydrous MgSO₄. The solvent was evaporated. The product was purified by column chromatography (silica gel, petroleum ether : chloroform = 1 : 1) as eluent. Yield: 44.9%. ¹H NMR (600 MHz, CDCl₃): δ 7.24-7.18 (m, 4H), 7.15-7.12 (m, 2H), 7.02 (d, 1H), 6.94 (m, 2H), 3.83 (t, 4H), 1.70 (m, 4H), 1.42-1.35 (m, 4H), 1.34-1.24 (m, 16H), 0.89 (t, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 161.1, 159.1, 158.8, 153.9, 138.8, 136.1, 129.3, 123.5, 122.4, 120.5, 116.6, 115.7, 109.5, 101.1, 68.1, 31.5, 29.1, 25.6, 22.6, 14.0. FTMS (APCI): found m/z = 714.1683, Calc. for

C₃₆H₄₃Br₂FN₂O₂: 714.1704.

5,8-dibromo-6-chloro-2,3-bis(3-(octyloxy)phenyl)quinoxaline. The compound has been prepared using the same synthetic process as for 5,8-dibromo-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline. The yield of the product was 51.1%. ¹H NMR (600 MHz, CDCl₃): δ 7.26-7.17 (m, 4H), 7.16-7.11 (m, 3H), 6.92 (m, 2H), 3.86 (t, 4H), 1.73 (m, 4H), 1.43-1.26 (m, 20H), 0.89 (t, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 159.2, 158.9, 154.3, 144.1, 138.6, 135.7, 132.5, 129.4, 122.5, 120.6, 116.8, 115.8, 110.2, 101.3, 68.2, 31.8, 29.3, 29.2, 29.1, 26.1, 22.6, 14.1. FTMS (APCI): found m/z = 730.1436, Calc. for C₃₆H₄₃Br₂ClN₂O₂: 730.1410.

6-fluoro-2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline. In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, 5,8-dibromo-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (3.56 g, 5 mmol), tributyl(thiophen-2-yl)stannane (3.93 g, 10.5 mmol), Pd₂(dba)₃ (180 mg, 0.2 mmol), P(o-Tol)₃ (243.5 mg, 0.8 mmol), and anhydrous toluene (120 mL) were added. The mixture was purged with nitrogen gas and heated to reflux for 2 days, then cooled to room temperature and dropped by water. The organic layer was washed successively by 5% aqueous solution of sodium bicarbonate, water and dried over anhydrous MgSO₄. The solvent was evaporated. The product was purified by column chromatography (silica gel, petroleum ether : chloroform = 2 : 1) as eluent. Yield: 76.1%. ¹H NMR (600 MHz, CDCl₃): δ 7.29-7.16 (m, 4H), 7.14-7.06 (m, 3H), 7.03-6.98 (m, 4H), 6.95 (m, 4H), 3.85 (t, 4H), 1.71 (m, 4H), 1.40-1.35 (m, 4H), 1.33-1.22 (m, 16H), 0.90 (t, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 161.0, 159.3, 158.6, 153.5, 151.0, 147.3, 142.2, 138.8, 138.2, 136.1, 129.3,

128.6, 128.1, 127.6, 122.8, 122.5, 120.3, 118.8, 116.5, 115.5, 109.6, 101.1, 68.2, 31.6, 29.0, 25.6, 22.7, 14.1. FTMS (APCI): found $m/z = 720.3204$, Calc. for $C_{44}H_{49}FN_2O_2S_2$: 720.3159.

6-chloro-2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline. The compound has been prepared using the same synthetic process as for 6-fluoro-2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline. The yield of the product was 66.3%. 1H NMR (600 MHz, $CDCl_3$): δ 7.31-7.17 (m, 5H), 7.11 (d, 2H), 7.05-7.00 (m, 4H), 6.96 (m, 4H), 3.83 (t, 4H), 1.72 (m, 4H), 1.39-1.33 (m, 4H), 1.31-1.21 (m, 16H), 0.91 (t, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 158.5, 153.3, 151.0, 147.4, 142.3, 139.7, 138.6, 138.1, 136.3, 129.2, 128.7, 128.0, 127.5, 122.9, 122.5, 121.0, 116.8, 115.6, 109.9, 101.0, 68.1, 31.4, 28.8, 26.0, 23.1, 14.1. FTMS (APCI): found $m/z = 736.2940$, Calc. for $C_{44}H_{49}ClN_2O_2S_2$: 736.2903.

5,8-bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline. In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, 6-fluoro-2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline (3.60 g, 5 mmol), NBS (1.87 g, 10.5 mmol), and THF (100 mL) were added. The mixture was purged with nitrogen gas and stirred at room temperature for 12 hours, then dropped by water. The organic layer was washed by saturated sodium chloride solution and dried over anhydrous Na_2SO_4 . The solvent was evaporated. The product was purified by column chromatography (silica gel, petroleum ether : chloroform = 1.5 : 1) as eluent. Yield: 67.4%. 1H NMR (600 MHz, $CDCl_3$): δ 7.26-7.15 (m, 5H), 7.12 (m, 2H), 6.99 (d, 2H), 6.88 (m, 4H), 3.90 (t, 4H), 1.74 (m, 4H), 1.41-1.26 (m, 20H), 0.88 (t, 6H). ^{13}C NMR (150 MHz,

CDCl₃): δ 161.5, 159.6, 158.9, 153.6, 151.3, 147.0, 142.1, 140.5, 138.9, 136.5, 131.5, 129.1, 128.9, 122.7, 122.4, 120.3, 119.0, 117.1, 115.6, 111.9, 110.2, 101.3, 68.7, 31.2, 29.5, 29.1, 25.9, 22.7, 14.1. FTMS (APCI): found m/z = 878.1374, Calc. for C₄₄H₄₇Br₂FN₂O₂S₂: 878.1449.

5,8-bis(5-bromothiophen-2-yl)-6-chloro-2,3-bis(3-(octyloxy)phenyl)quinoxaline.

The compound has been prepared using the same synthetic process as for 5,8-bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline. The yield of the product was 61.8%. ¹H NMR (600 MHz, CDCl₃): δ 7.30-7.18 (m, 5H), 7.10 (m, 2H), 7.01 (d, 2H), 6.80 (m, 4H), 3.88 (t, 4H), 1.72 (m, 4H), 1.39-1.25 (m, 20H), 0.90 (t, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 157.9, 156.8, 152.1, 150.5, 146.3, 141.0, 140.5, 139.1, 138.0, 137.5, 134.9, 131.1, 129.1, 122.5, 122.1, 120.8, 116.5, 115.3, 111.7, 109.2, 100.7, 68.2, 31.6, 29.2, 29.0, 25.9, 22.7, 14.1. FTMS (APCI): found m/z = 894.1134, Calc. for C₄₄H₄₇Br₂ClN₂O₂S₂: 894.1078.

F-PBTQT. To a 25 mL flask, 5,8-bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-(octyloxy)phenyl)-quinoxaline (0.5 mmol), (4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (0.5 mmol), Pd₂(dba)₃ (15 mg) and P(*o*-Tol)₃ (25 mg) were dissolved in degassed toluene (10 mL) and DMF (2.5 mL). The reaction mixture was heated to reflux and maintained at the same temperature for 2 days. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected by thimble and Soxhlet-extracted with methanol, acetone, hexane, ethyl acetate, dichloromethane, and chloroform in order. The final fraction was precipitated in methanol. Finally, the polymer was

collected by filtration and dried under vacuum at 40 °C overnight. The yield of the product was 82.5%. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.78-7.51 (br, 5H), 7.26-7.20 (br, 6H), 7.07-7.04 (br, 4H), 6.89 (br, 2H), 6.65 (br, 2H), 3.89-3.85 (br, 4H), 2.87-2.62 (br, 4H), 1.76-1.69 (br, 6H), 1.31-1.19 (br, 68H), 0.89(br, 18H). Element analysis: Theory: C, 74.37; H, 8.13; N, 1.81; S, 12.41; Found: C, 74.52; H, 8.01; N, 1.89; S, 12.18.

Cl-PBTQT. The compound has been prepared using the same synthetic process as for F-PBTQT. The yield of the product was 71.3%. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.85-7.53 (br, 5H), 7.28-7.21 (br, 6H), 7.11-7.08 (br, 4H), 6.91 (br, 2H), 6.68 (br, 2H), 3.90-3.85 (br, 4H), 2.85-2.63 (br, 4H), 1.75-1.66 (br, 6H), 1.30-1.17 (br, 68H), 0.90 (br, 18H). Element analysis: Theory: C, 73.59; H, 8.04; N, 1.79; S, 12.28; Found: C, 73.38; H, 7.91; N, 1.83; S, 12.04.

2. Thermogravimetric analysis

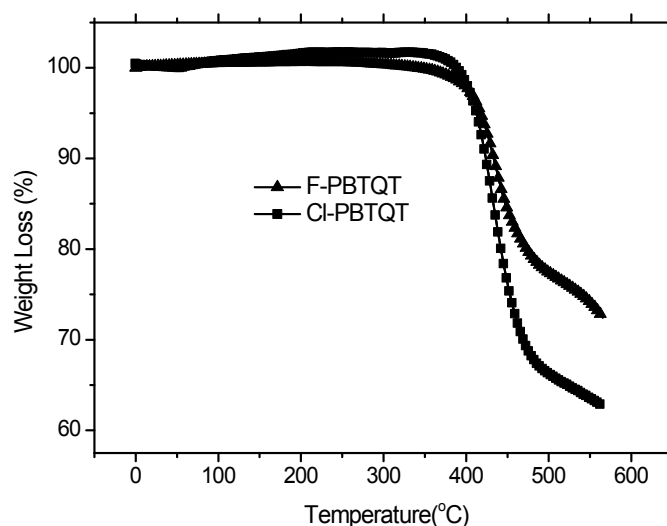


Fig. S1 TG curves of F-PBTQT and Cl-PBTQT.

3. Density functional theory calculations

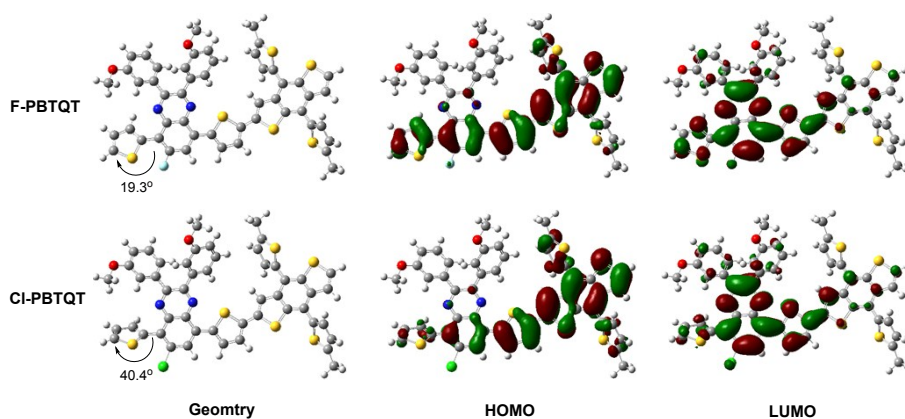


Fig. S2 Geometry and frontier molecular orbitals of F-PBTQT and Cl-PBTQT.

4. X-ray diffraction

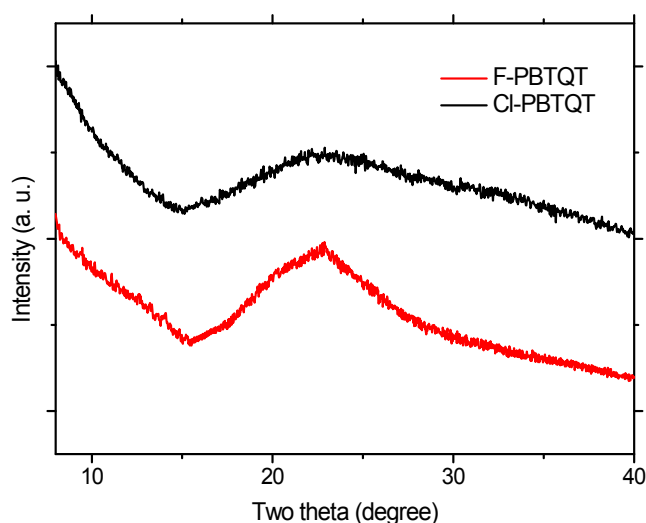


Fig. S3 XRD patterns for F-PBTQT and Cl-PBTQT.

5. Device fabrication and characterization

The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by a nitrogen blow, then a ZnO film was spin-coated onto the ITO surface, followed by baking at 200 °C for 30 min. Polymer was blended with PC₇₁BM in chlorobenzene with the polymer concentration at 10 mg mL⁻¹. 1,8-diiodooctane (DIO) was used as additive in the blended solutions. The active layer was

obtained by spin-coating the blend solution in a glove box. Finally, 10 nm MoO₃ and 100 nm Ag were thermally evaporated atop the active layer in vacuum chamber. The current-voltage (*J-V*) characteristics of the devices were measured using a Keithley 2400 source-measure unit under illumination of a simulated sunlight (AM 1.5G, 100mW/cm²) provided by an Oriel Sol3A solar simulator.