Supporting Information for

# F-Substituted Oligothiophenes Serve as Nonfullerene Acceptors in Polymer Solar Cells with Open-Circuit Voltages >1V

Tainan Duan, Maxime Babics, Akmaral Seitkhan, Yuliar Firdaus, Ru-Ze Liang, Federico Cruciani, Shengjian Liu, Sergei Lopatin, and Pierre M. Beaujuge

## **Content:**

1. General Experimental Details	3
2. Synthetic Protocols and Characterizations	4
3. Density Functional Theory (DFT) Calculations	13
4. UV-Vis Spectroscopy	17
5. Photoelectron Spectroscopy in Air (PESA) Measurements	
6. Cyclic Voltammetry (CV) Measurements	19
7. Thermogravimetric Analysis (TGA)	21
8. Differential Scanning Calorimetry (DSC) Measurements	22
9. Device Fabrication	23
10. Additional PV Device Performance Data	25
11. Carrier Mobility Measurements	
12. Transmission Electron Microscopy (TEM) and Electron Energy E Characterization	Loss (EELS) 29
13. Atomic Force Microscopy (AFM) Imaging	
14. X-Ray Diffraction (XRD) Measurements	
15. Transient Photocurrent (TPC) Measurements	
16. Solution NMR Spectra	
17. Supporting Information References	52

## **<u>1. General Experimental Details</u>**

All reactions were performed under nitrogen atmosphere and solvents were purified and dried from appropriate drying agents using standard techniques prior to use. Reagents available from commercial sources were used without further purification unless otherwise stated. Flash chromatography was performed by using Silicycle Silica Flash P60 (particle size 40-63 µm, 60 Å, 230-400 mesh) silica gel. Silica gel on TLC-PET foils from Fluka was used for TLC. Recycling SEC in THF or ethanol-stabilized chloroform was carried out through a set of two JAIGEL-4H-40 preparative SEC columns mounted on an LC-9130NEXT (JAI) system equipped with coupled UV-254NEXT and RI-700NEXT detectors. All compounds were characterized by NMR spectroscopy on Bruker Avance III Ultrashield Plus instruments (400 MHz). The spectra were referenced on the internal standard TMS. High-resolution mass spectrometry (HRMS) data was recorded using a Thermo Scientific-LTQ Velos Orbitrap MS. Note: Spectroscopy-grade CHCl<sub>3</sub> was filtered through basic alumina prior to use in order to suppress solvent acidity and avoid undesired protonation reactions that may influence the spectral absorption of the molecular acceptors described in this study.

#### 2. Synthetic Protocols and Characterizations



Scheme S1. Synthesis of the molecular acceptors D5T6F-M and D7T8F-M.

Note: Compounds  $\mathbf{1}^{[1]}$  and  $\mathbf{9}^{[2]}$  were prepared according to previously report procedures.



**2,5-Bis(trimethylsilyl)-3-fluoro-4-octylthiophene (2):** A solution of *n*-BuLi (2.5 M in hexanes, 41.8 mL, 104.6 mmol) was added dropwise to a solution of **1** (36.6 g, 87.2 mmol) in THF (350 mL) at -78 °C. After stirring for 30 min at -78 °C, NFSI (N-Fluorobenzenesulfonimide) (35.6 g, 113.4 mmol) was added in one portion, and the solution was stirred for another 2 h at -78 °C and was then allowed to return to room temperature. The mixture was stirred overnight, quenched with water (400 mL), extracted with hexanes (3 × 200 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes as the eluent. The solvent was removed by rotary evaporation, affording compound **2** as a pale yellow oil (10.6 g, yield: 34%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 2.57-2.54 (m, 2H), 1.55-1.50 (m, 2H), 1.40-1.28 (m, 10H), 0.89 (t, J

= 5.6 Hz, 3H), 0.33 (s, 9H), 0.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): (164.72, 162.13), (139.25, 139.01), (138.51, 138.48), (119.63, 119.33), 31.92, 30.80, 29.94, 29.44, 29.29, 28.23, 22.72, 14.14, -0.07, -0.49. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ ppm): -121.89. HRMS (+APCI, m/z): calcd. for C<sub>18</sub>H<sub>35</sub>FSSi<sub>2</sub> [M+H]<sup>+</sup>: 329.20548, found 329.20521.



**2,5-Dibromo-3-fluoro-4-octylthiophene(3):** A solution of bromine (3.8 mL, 11.8 g, 73.8 mmol) in chloroform (25 mL) was added dropwise to a solution of **2** (5.31 g, 14.8mmol) in chloroform (30 mL) at 0 °C. After addition of bromine, the mixture was allowed to warm to room temperature and stirred for 3 h in the absence of light. A saturated sodium sulfite solution (80 mL) was added and stirred for another 30 min. The aqueous phase was then extracted with chloroform (2 × 50 mL). The organic phase was combined, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes as the eluent. The solvent was removed by rotary evaporation, affording compound **3** as a colorless oil (3.42 g, yield: 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 2.56 (t, *J* = 7.6 Hz, 2H), 1.56-1.53 (m, 2H), 1.32-1.29 (m, 10H), 0.92 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): (154.76, 152.14), (132.44, 132.21), (107.46, 107.36), (89.53, 89.30), 31.92, 29.32, 29.25, 29.15, 28.54, 27.14, 22.72, 14.16. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -124.24. HRMS (+APCI, m/z): calcd. for C1<sub>2</sub>H<sub>17</sub>Br<sub>2</sub>FS [M+H]<sup>+</sup>: 370.94745, found 370.94774.



**3-Fluoro-4-octylthiophene (4):** A solution of tetrabutylammonium fluoride (1 M in THF, 3.8 mL, 11.8 g, 73.8 mmol) was added dropwise to a solution of **2** (5.13 g, 14.2 mmol) in THF (50 mL) at room temperature, and the solution was stirred for 1 h. After quenching the reaction with water (100 mL), the aqueous phase was extracted with chloroform ( $2 \times 50$  mL). The organic phase was collected, dried over Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The crude

product was purified by column chromatography over SiO<sub>2</sub> using hexanes as the eluent. The solvent was removed by rotary evaporation, affording compound **4** as a colorless oil (1.77 g, yield: 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 6.85 (t, *J* = 4.0 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.64-1.58 (m, 2H), 1.33-1.29 (m, 10H), 0.92 (t, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): (132.40, 130.22), (110.16, 109.97), (99.79, 99.73), (85.54, 85.36), 25.52, 23.39, 23.30, 21.22, 17.73, 10.44. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -132.30. HRMS (+APCI, m/z): calcd. for C<sub>12</sub>H<sub>19</sub>FS [M+H]<sup>+</sup>: 215.12550, found 215.12654.



5-Bromo-3-fluoro-4-octylthiophene-2-carbaldehyde (5): In a pre-dried Schlenk tube, a solution of 3 (3.00 g, 8.06 mmol) in anhydrous THF (50 mL) was cooled to 0 °C. A solution of isopropylmagnesium chloride/lithiumchloride complex (1.3 M in THF, 6.2 mL, 8.06 mmol) was added dropwise, and the ice bath was removed. The mixture was stirred for 30 min at room temperature, and was then heated to reflux for 30 min. The heating bath was removed and anhydrous DMF (0.68 mL, 8.86 mmol) was added to the reaction mixture in one portion. After being stirred overnight, the reaction was quenched with HCl (1 M in water, 30 mL) and the aqueous phase was extracted with chloroform  $(2 \times 50 \text{ mL})$ . The organic phase was, dried over Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The crude product was purified by column chromatography over  $SiO_2$  using hexanes/ethyl acetate (8:1) as the eluent. The solvent was removed by rotary evaporation, affording compound 5 as a pale yellow oil (2.02 g, yield: 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 9.93 (s, 1H), 2.59 (t, J = 7.6 Hz, 2H), 1.59-1.56 (m, 2H), 1.34-1.30 (m, 10H), 0.92 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 178.68, (161.20, 158.41), (133.18, 132.97), (122.96, 122.87), (121.97, 121.86), 31.82, 29.22, 29.16, 29.09, 28.37, 26.54, 22.64, 14.09. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ ppm): -118.25. HRMS (+APCI, m/z): calcd. for C<sub>13</sub>H<sub>18</sub>BrFOS [M+H]<sup>+</sup>: 321.03185, found 321.03166.



(3-Fluoro-4-octylthiophen-2-yl)trimethylstannane (6): In a pre-dried Schlenk tube, a solution of 3 (1.65 g, 7.70 mmol) in anhydrous THF (40 mL) was cooled to -78 °C. A solution of LDA (1.0 M in THF, 8.5 mL, 8.50 mmol) was added dropwise, and the mixture was stirred for 2 h at -78 °C. Next, trimethyltin chloride in THF (1.0 M, 9.3 mL, 9.30 mmol) was added to the mixture in one portion. The cooling bath was then removed, the mixture was allowed to warm to room temperature, and was stirred overnight. The reaction was quenched with water (60 mL) and the aqueous phase was extracted with dichloromethane (2 × 50 mL). The organic phase was collected, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and compound **6** was obtained as a yellow oil used in the next step without the need for further purification (2.61 g, yield: 90%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  ppm): 7.13 (d, *J* = 3.2 Hz, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.63-1.60 (m, 2H), 1.34-1.30 (m, 10H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.40 (s, 9H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  ppm): (164.0, 161.5), (132.3, 132.0), (126.1, 126.0), (111.9, 111.5), 31.9, 29.5, 29.4, 29.3, 29.2, 26.7, 22.7, 13.9, -8.8. <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  ppm): -122.84.



**3',4-Difluoro-3,4'-dioctyl-[2,2'-bithiophene]-5-carbaldehyde (7):** In a pre-dried Schlenk tube, **5** (1.28 g, 4.00 mmol), **6** (1.66 g, 4.40 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.20 mmol) were dissolved with degassed toluene (50 mL). The mixture was heated at 110 °C for 24 h. The reaction mixture was allowed to cool down to room temperature, the organic layer was washed with brine, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×40 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and then concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent. The solvent was removed by rotary evaporation, affording compound **7** as a yellow oil (1.54 g, 85%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 10.04 (s, 1H), 7.02 (d, *J* = 4.8, 1H), 2.71 (t, *J* = 7.6, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.67-1.61 (m, 4H), 1.35-1.28 (m, 20H), 0.90-0.88 (m, 6H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 179.44, (162.71, 159.96), (155.30, 152.64), (135.92, 135.87, 135.83, 135.78), (132.87, 132.65), (129.87, 129.66), (121.26, 121.22, 121.17, 121.14), (121.05, 120.97), (112.92, 112.80), 31.86, 31.84, 29.41, 29.32, 29.23, 29.18, 29.08, 29.01, 26.99, 25.90, 22.66, 14.08. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -120.14, -123.41. HRMS (+APCI, m/z): calcd. for C<sub>25</sub>H<sub>36</sub>F<sub>2</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 455.22484, found 455.22455.



**5'-Bromo-3',4-difluoro-3,4'-dioctyl-[2,2'-bithiophene]-5-carbaldehyde (8):** NBS (587 mg, 3.30 mmol) was added slowly into a solution of **7** (1.36 g, 3.00 mmol) in THF (30 mL) at room temperature, and the solution was stirred for 8 h. After quenching the reaction with water (100 mL), the aqueous phase was extracted with chloroform (2 × 50 mL). The organic phase was collected, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent. The solvent was removed by rotary evaporation, affording compound **8** as a yellow oil (1.40 g, yield: 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 10.05 (s, 1H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.57 (br, 4H), 1.34-1.29 (m, 20H), 0.92-0.89 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 179.42, (162.55, 159.80), (153.63, 150.94), (134.42, 134.38, 134.32, 134.28), (132.86, 132.63), (130.35, 130.14), (121.65, 121.61, 121.56, 121.52), (113.16, 113.00), (111.16, 111.06), 31.86, 31.84, 29.37, 29.27, 29.21, 29.16, 29.07, 28.49, 26.89, 25.95, 22.67, 14.10. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -118.66, -119.98. HRMS (+APCI, m/z): calcd. for C<sub>25</sub>H<sub>35</sub>BrF<sub>2</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 533.13535, found 533.13477.



**3',3'',4,4'',4''',4''''-Hexafluoro-3,3''',3'''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''quinquethiophene]-5,5''''-dicarbaldehyde (10):** In a pre-dried Schlenk tube, **8** (650 mg, 1.22 mmol), **9** (227 mg, 0.51 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (55 mg, 0.06 mmol) and tri(o-tolyl)phosphine (91 mg, 0.30 mmol) were dissolved in degassed chlorobenzene (30 mL). The reaction mixture was heated

to 135 °C and stirred for 48 h. Next, the organic layer was washed with brine, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 40 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent. The solvent was removed by rotary evaporation, affording compound **10** as an orange solid (350 mg, 72%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 10.07 (s, 2H), 2.76 (m, 8H), 1.65-1.63 (m, 8H), 1.39-1.27 (m, 40H), 0.90-0.87 (m, 12H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 179.44, (162.60, 159.84), (155.03, 152.37), (143.52, 143.32), (140.86, 140.65), (134.32, 134.28, 134.23, 134.19), (131.94, 131.71), (130.53, 130.32), (124.44, 124.35), (121.86, 121.82, 121.77, 121.73), (114.48, 114.34), 112.90, 31.86, 31.84, 29.52, 29.41, 29.35, 29.25, 29.21, 29.18, 29.16, 29.12, 26.57, 26.08, 22.66, 14.08. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -119.40, -119.98, -130.79. HRMS (+APCI, m/z): calcd. for C<sub>54</sub>H<sub>70</sub>F<sub>6</sub>O<sub>2</sub>S<sub>5</sub> [M+H]<sup>+</sup>: 1025.39571, found 1025.39589.



**3',3'',4-Trifluoro-3,4',4''-trioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde** (**11**): In a predried Schlenk tube, **8** (700 mg, 1.31 mmol), **6**(592 g, 1.57 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (173 mg, 0.15 mmol) were dissolvedin degassed toluene (40 mL). The reaction mixture was heated to 110 °C and stirred for 24 h. Next, the organic layer was washed with brine, extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 40 \text{ mL}$ ), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent. The solvent was removed by rotary evaporation, affording compound **11** as an orange oil (674 mg, 77%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 10.05 (s, 1H), 6.96 (d, *J* = 4.4, 1H), 2.75-2.67 (m, 4H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.67-1.62 (m, 6H), 1.36-1.28 (m, 30H), 0.91-0.89 (m, 9H). <sup>13</sup>C NMR(100 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 179.37, (162.75, 159.99), (155.12, 154.72), (152.46, 152.09), (135.40, 135.35, 135.31, 135.26), (132.67, 132.44), (130.36, 130.13), (129.73, 129.52), (128.83, 128.74), (127.15, 127.12, 127.07, 127.03), (121.24, 121.20, 121.16, 121.11), (119.90, 119.82), (112.67, 112.52), 31.88, 31.85, 29.46, 29.42, 29.36, 29.28, 29.22, 29.17, 29.13, 29.07, 27.1, 26.32, 26.00, 22.68, 22.60, 14.09. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -119.73, -120.20, -126.30. HRMS (+APCI, m/z): calcd. for C<sub>37</sub>H<sub>53</sub>F<sub>3</sub>OS<sub>3</sub> [M+H]<sup>+</sup>: 667.32542, found 667.32675.



5"-Bromo-3',3",4-trifluoro-3,4',4"-trioctyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (12): NBS (191 mg, 1.07 mmol) was added slowly by portions into a solution of 11 (650 mg, 0.97 mmol) in THF (20 mL) at room temperature, and the mixture was stirred for 8 h. After quenching the reaction with water (100 mL), the aqueous phase was extracted with chloroform  $(2 \times 50 \text{ mL})$ . The organic phase was collected, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography over  $SiO_2$  using hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent. The solvent was removed by rotary evaporation, affording compound 12 as a yellow oil (574 mg, yield: 79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 10.05 (s, 1H), 2.72 (t, J = 7.6 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 1.61-1.56 (m, 6H), 1.35-1.29 (m, 30H), 0.90-0.88 (m, 9H). <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>, δ ppm): 179.22, (162.35, 160.14), 154.74, (152.73, 152.62), 150.60, (134.95, 134.91, 134.87), (132.56, 132.38), (130.71, 130.53), (129.77, 129.60), (125.73, 125.70, 125.66, 125.61), (121.35, 121.31, 121.28), (113.20, 113.06), (112.91, 112.79), (109.75, 109.67), 31.88, 31.86, 29.42, 29.31, 29.24, 29.22, 29.19, 29.16, 29.11, 29.06, 28.56, 26.92, 26.33, 25.99, 22.67, 22.57, 14.07. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ ppm): -119.64, -120.15, -121.45. HRMS (+APCI, m/z): calcd. for C<sub>37</sub>H<sub>52</sub>BrF<sub>3</sub>OS<sub>3</sub> [M+H]<sup>+</sup>: 745.20685, found 745.20748.





[2,2':5',2'':5'',2''':5''',2''':5'''',2'''':5'''',2'''''-sepithiophene]-5,5'''''-dicarbaldehyde (13): In a pre-dried Schlenk tube, 12 (550 mg, 0.74 mmol), 9 (138 mg, 0.31 mmol),  $Pd_2(dba)_3$  (37 mg, 0.04 mmol) and tri(o-tolyl)phosphine (61 mg, 0.20 mmol) were dissolved in degassed chlorobenzene (30 mL). The recation mixture was heated to 135 °C and was stirred for 48 h. Next, the organic layer was washed with brine and extracted with  $CH_2Cl_2$  (3 × 40 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:2) as the eluent. The solvent was removed by rotary evaporation, affording compound **13** as an orange solid (381 mg, 85%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 10.05 (s, 2H), 2.75-2.72 (m, 12H), 1.65-1.61 (m, 12H), 1.39-1.27 (m, 60H), 0.89-0.86 (m, 18H). <sup>13</sup>C NMR(100 MHz, CHCl<sub>3</sub>,  $\delta$  ppm): 179.32, (162.40, 160.20), (154.88, 152.75), (154.14, 152.02), (143.06, 142.90), (140.94, 140.77), (134.97, 134.93, 134.90, 134.86), (131.62, 131.44), (130.75, 130.57), (129.87, 129.70), (125.82, 125.79, 125.75), (123.31, 123.24), (121.38, 121.34, 121.31, 121.28), (114.37, 114.25), (113.40, 113.30), (112.90, 112.84), 31.89, 31.86, 29.59, 29.48, 29.43, 29.31, 29.26, 29.24, 29.21, 29.18, 29.13, 26.63, 26.48, 26.02, 22.69, 14.09. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -119.60, -120.11, -122.21, -131.33. HRMS (+APCI, m/z): calcd. for C<sub>78</sub>H<sub>104</sub>F<sub>8</sub>O<sub>2</sub>S<sub>7</sub> [M+H]<sup>+</sup>:1449.60263, found 1449.60576.



General procedure for the preparation of the molecular acceptors D5T6F-M and D7T8F-M: The aldehyde 10 or 13 (1.0 equiv.), manolonitrile (10.0 equiv.) and basic Al<sub>2</sub>O<sub>3</sub> (5.0 equiv.) were added into a solution of anhydrous chloroform (20 mL), and the mixture was heated to 68 °C and stirred for 24 h. The reaction mixture was allowed to cool down to room temperature, was filtered, was washed with chloroform (2 × 30 mL), and was concentrated under reduced pressure. The crude product was purified by column chromatography over SiO<sub>2</sub> using chloroform/hexanes (4:1) as the eluent. The solvent was removed by rotary evaporation, affording the desired products (D5T6F-M or D7T8F-M)

**D5T6F-M:** Purple-blue solid (110 mg, 77%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>, δ ppm): 7.94 (s, 2H), 2.79-2.74 (m, 8H), 1.66-1.62 (m, 8H), 1.39-1.28 (m, 40H), 0.90-0.87 (m, 12H). <sup>13</sup>C NMR(100 MHz, CHCl<sub>3</sub>, δ ppm): 162.67, 159.87, 155.72, 153.04, 144.72, (143.72, 143.51), (141.05, 140.84), (136.38, 136.33, 136.29, 136.24), (132.05, 131.82), (129.40, 129.19), (125.62, 125.53),

(115.49, 115.44, 115.38, 115.33), (114.04, 113.93), (113.11, 112.99), 31.86, 31.82, 29.56, 29.40, 29.33, 29.26, 29.21, 29.16, 29.13, 29.01, 26.60, 25.99, 22.65, 14.09. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): -112.06, -116.80, -130.12. HRMS (+APCI, m/z): calcd. for C<sub>60</sub>H<sub>70</sub>F<sub>6</sub>N<sub>4</sub>S<sub>5</sub> [M+H]<sup>+</sup>: 1121.41810, found 1121.41538.

**D7T8F-M:** Purple-blue solid (98 mg, 69%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>, δ ppm): 7.93 (s, 2H), 2.80-2.74 (m, 12H), 1.68-1.61 (m, 12H), 1.40-1.29 (m, 60H), 0.91-0.87 (m, 18H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ ppm): -112.22, -116.77, -121.40, -130.10. HRMS (+APCI, m/z): calcd. for C<sub>84</sub>H<sub>104</sub>F<sub>8</sub>N<sub>4</sub>S<sub>7</sub> [M+H]<sup>+</sup>: 1545.62510, found 1545.62070.

#### **3. Density Functional Theory (DFT) Calculations**

The density functional theory (DFT) calculations were performed at the non-empirically tuned  $\omega$ B97XD/6-31G(d,p) level of theory with the Gaussian 09 (Revision C.01) code.<sup>[3]</sup> The small-molecule side chains were modeled as methyl groups; while side chains play an important role in the organization of small molecules and polymers in the solid state, these have only marginal influence on the electronic and optical properties of the single isolated small-molecule/polymer chain in the gas phase.<sup>[4]</sup> The torsion potential energy surface (PES) plots are shown in Figure **S2**. For the PES modeling, the torsion angles between the various motifs of the small molecules **D5T6F-M** and **D7T8F-M** were scanned at regular intervals of 10° between the  $0^{\circ}$  and  $180^{\circ}$  conformations. Geometries of the ground state were pre-optimized using the B3LYP/6-31G(d,p) level of theory before performing further geometry optimizations using the long-range corrected hybrid functional  $\omega$ B97XD/6-31G(d,p) (here, we note that the B3LYP functional taken alone tends to over delocalize the  $\pi$ -electron wave functions). The range-separation parameter  $\omega$  was optimized following the gap tuning procedure;<sup>[5]</sup> the tuned  $\omega$  value is 0.12 Bohr<sup>-1</sup> for **D5T6F-M** and0.119 Bohr<sup>-1</sup> for **D7T8F-M**. Tables S1 and S2 summarize the gap tuning procedure.



Figure S1. Ball and stick model of the fully optimized ground-state geometries for D5T6F-M and D7T8F-M.

$\omega$ in Bohr <sup>-1</sup>	$E_{\rm IP}$ in eV	<i>E</i> <sub>HOMO</sub> in eV	$\Delta E = E_{\text{HOMO}} - E_{\text{IP}}$
0.1	-6.899	-6.811	0.088
0.119	-7.263	-8.786	-1.524
0.12	-6.966	-6.970	-0.004
0.121	-7.259	-8.787	-1.528
0.14	-7.032	-7.117	-0.085
0.16	-7.096	-7.265	-0.169
0.18	-7.156	-7.378	-0.222

**Table S1**.  $\omega$ -Optimization for **D5T6F-M** using the  $\omega$ B97XD functional; the optimized  $\omega$  value is highlighted in red.

**Table S2.**  $\omega$ -Optimization for **D7T8F-M** using the  $\omega$ B97XD functional; the optimized  $\omega$  value is highlighted in red.

$\omega$ in Bohr <sup>-1</sup>	$E_{IP}$ in eV	$E_{HOMO}$ in eV	$\Delta E = E_{HOMO} - E_{IP}$
0.1	-6.562	-6.519	0.043
0.119	-6.638	-6.671	-0.033
0.12	-6.642	-6.679	-0.036
0.121	-6.646	-6.686	-0.040
0.14	-6.720	-6.826	-0.105
0.16	-6.794	-6.961	-0.167
0.18	-6.864	-7.087	-0.223

Molecule	<i>E<sub>LUMO</sub></i> in eV (B3LYP)	<i>E<sub>HOMO</sub></i> in eV (B3LYP)	<i>E<sub>LUMO</sub></i> in eV (ωB97XD)	$E_{HOMO}$ in eV ( $\omega$ B97XD)
D5T6F-M	-3.48	-5.79	-1.93	-7.53
D7T8F-M	-3.31	-5.54	-1.76	-7.24

**Table S3.** Calculated HOMO and LUMO levels of **D5T6F-M** and **D7T8F-M**with B3LYP/6-31G(d,p) and  $\omega$ B97XD, respectively



**Figure S2 (a-c).** Potential Energy Surface (PES) of the small molecule fragments calculated at the B3LYP/6-31G(d,p) level of theory. All the plots show two minima, corresponding to the fully planar  $0^{\circ}/anti$  and  $180^{\circ}/syn$  conformations for the red fragment, to the  $0^{\circ}/anti$  and  $160^{\circ}/syn$  for the purple fragment, and to the  $0^{\circ}/anti$  and  $110^{\circ}/syn$  for the blue fragment. For the red and purple fragments, the  $0^{\circ}/anti$  conformations are predicted to be more stable than the *syn* conformations by 3-4 Kcal/mol; for the blue fragment, there is only 0.5 Kcal/mol difference between *anti* and *syn* conformers. The minima are separated by energy barriers of ca. 5 Kcal/mol for the blue and red fragments, while up to 12 Kcal/mol separate the minima for the purple fragment. Given the significant energy barrier averages between conformers and the greater stability of the  $0^{\circ}/anti$  conformations.

### 4. UV-Vis Spectroscopy

Temperature-dependent UV-Vis spectra in solution were recorded on a Varian Cary 100 instrument in single beam mode in 1 cm quartz cuvettes.



Figure S3. (a) Room-temperature UV-vis spectra of D5T6F-M and D7T8F-M in chlorobenzene solution. Temperature-dependent UV-vis absorption spectra of (b) D5T6F-M, and (c) D7T8F-M; solutions in chlorobenzene (CB), concentration of  $3.0 \times 10^{-5}$  M. In Figure S3b and S3c, the absence of pronounced aggregation footprints in solution and the relatively modest effect of temperature on the main absorption bands suggest that the molecular acceptors are not forming ordered aggregates in solution.

#### 5. Photoelectron Spectroscopy in Air (PESA) Measurements

Photoelectron Spectroscopy in Air (PESA) measurements were recorded using a Riken Keiki PESA spectrometer (Model AC-2) with a power setting of 10 nW and a power number of 0.2.Samples for PESA were prepared on glass substrates.



**Figure S4**. PESA curves for **D5T6F-M** and **D7T8F-M**; PESA-inferred ionization potentials (IPs) are reported on the plots.

**Table S4**. Summary of optical and electronic parameters for the SM derivatives **D5T6F-M**, **D7T8F-M**, and for the polymer donor PCE10 (model system).

Material	$\lambda_{abs}^{[a]}$	$\lambda_{abs}^{[b]}$	$E_{\mathrm{opt}}^{[\mathrm{c}]}$	$IP^{[d]}$	EA <sup>[e]</sup>		
	System	[nm]	[nm]	[eV]	(eV)	(eV)	
	D5T6F-M	559	642	1.93	6.09	4.16	
	D7T8F-M	561	656	1.81	5.74	3.93	
	PCE10	765	795	1.56	4.95	3.39	

[a] In chlorobenzene (CB) solution (room temperature). [b] Thin film (cast from CB). [c] Optical bandgaps estimated from the onset of the UV-Vis absorption (films). [d] Estimated by photoelectron spectroscopy in air (PESA). [e] Inferred from PESA-obtained IPs and  $E_{opt}$  values.

#### 6. Cyclic Voltammetry (CV) Measurements

Electrochemical measurements were performed with a BAS 100 W Bioanalytical electrochemical workstation, using a glassy carbon button electrode as the working electrode, a platinum wire as the auxiliary electrode, and a porous  $Ag/Ag^+$  glass electrode as the reference electrode. The reference electrode used throughout the study contained a solution of 0.01 M AgNO<sub>3</sub> and 0.1 M TBAP (tetrabutylammonium perchlorate) in acetonitrile (ACN). The oxidation and reduction onsets were measured from a CH<sub>2</sub>Cl<sub>2</sub> solution of the SM acceptors. A 0.1 M solution of TBAPF<sub>6</sub> (tetrabutylammonium hexafluorophosphate) in CH<sub>2</sub>Cl<sub>2</sub> was used as the supporting electrolyte, and a scan rate of 50 mV/s was employed for the measurements. The Ag/Ag<sup>+</sup> reference electrode was internally calibrated using the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. Fc/Fc<sup>+</sup> is taken to be 5.1 eV relative to the vacuum level.<sup>[6]</sup> The electrochemically estimated ionization potential (IP) and electron affinity (EA) values for the SM acceptors were estimated according to the following empirical formulae: IP = (*E*<sub>onset, ox</sub> + 5.10) eV (absolute values). *E*<sub>onset, ox</sub> is taken as the potential inferred from the oxidation onset vs. Fc/Fc<sup>+</sup>, and *E*<sub>onset, red</sub> is taken as the potential inferred from the reduction onset vs. Fc/Fc<sup>+</sup>.



Figure S5. (a) Reduction and (b) oxidation scans of the SM acceptors D5T6F-M and D7T8F-M; vs. Fc/Fc+.

**Table S5.** Summary of electrochemical parameters of the SM acceptors **D5T6F-M** and **D7T8F-**M.

Material	Eonset, ox <sup>[a]</sup> [V]	Eonset, red <sup>[a]</sup> [V]	IP <sup>[b]</sup> (eV)	EA <sup>[c]</sup> (eV)
D5T6F-M	1.01	-1.10	6.11	4.00
D7T8F-M	0.96	-1.18	6.06	3.92

[a] Potentials vs. Fc/Fc<sup>+</sup>, [b] IP = ( $E_{\text{onset, ox}}$  + 5.10) eV, [c] EA = ( $E_{\text{onset, red}}$  + 5.10) eV

## 7. Thermogravimetric Analysis (TGA)

Thermogravimetric Analyses (TGA) were performed with a NETZSCH TG 209 F1 Iris under nitrogen atmosphere, with a set ramp rate of 10 K/min, and using Al<sub>2</sub>O<sub>3</sub> crucibles.



**Figure S6**. Thermogravimetric analyses (TGA) of **D5T6F-M** and **D7T8F-M**. The molecular acceptors show high thermal-stability under nitrogen atmosphere; *ca.* 5% weight loss observed at 396 °C and 409 °C, respectively.

## 8. Differential Scanning Calorimetry (DSC) Measurements

Differential Scanning Calorimetry (DSC) measurements were performed on a NETZSCH DSC 204F1 Phoenix under a nitrogen atmosphere, using aluminum crucibles.



**Figure S7**. Differential Scanning Calorimetry (DSC) traces of (**a**, **b**) **D5T6F-M**, (**c**, **d**) **D7T8F-M** and (**e**, **f**) the two molecular acceptors overlaid on the same plots. Analyses carried out with a scan rate of 10 °C/min between 30 °C and 300 °C. Both molecular acceptors show an apparent phase transition in the range 160-190 °C, suggesting a melt transition in light of the presence of a first order solidification peak on the cooling scan.

#### 9. Device Fabrication

The BHJ solar cellswere prepared on glass substrates with tin-doped indium oxide (ITO, 15  $\Omega$ /sq) patterned on the surface (device area: 0.1 cm<sup>2</sup>). Substrates were prewashed with isopropanol to remove organic residues before immersing in an ultrasonic bath of dilute Extran<sup>®</sup> 300 for 15 min. Samples were rinsed in flowing deionized water for 5 min before being sonicated (Branson 5510) for 15 min each in successive baths of deionized water, acetone and isopropanol. Next, the samples were dried with pressurized nitrogen before being exposed to a UV-ozone plasma for 15 min. Meanwhile, a precursor solution of zinc acetate dihydrate (200 mg), 2-methoxyethanol (4 ml), and ethanolamine (55 µl) was prepared and stirred vigorously in ambient atmosphere for at least 12h. For the fabrication of inverted devices, the resulting solution was spun-cast at 3000 rpm onto the cleaned ITO substrates, affording smooth amorphous ZnO thin films (a-ZnO). This step was followed by an annealing of the a-ZnO thin film at 150 °C for 20 min. Immediately after that, the baked a-ZnO-coated substrates were transferred into a glovebox ( $< 3 \text{ ppm O}_2$ ) for active layer deposition. For the fabrication of direct devices, a thin layer of PEDOT:PSS (~35nm) (Clevios AL4083) was spun-cast onto the UVtreated substrates, the PEDOT-coated substrates were subsequently annealed on a hot plate at 150 °C for 15 min, and the substrates were then transferred into the glovebox for active layer deposition. All solutions with the polymer donor PCE10 (purchased from Solarmer) and the fluorinated molecular acceptors **D5T6F-M** or **D7T8F-M** were prepared in the glovebox. PCE10 and the molecular acceptors were dissolved in chlorobenzene, and the solutions were stirred at 50 °C for at least 4 h. Optimized devices were prepared using blend solutions with a concentration of 15 mg/mL, a PCE10:SM Acceptor ratio of 4:6 (wt:wt) with D5T6F-M, and 3:7 (wt:wt) with D7T8F-M. The effects of various light intensities, film thicknesses, blend ratios and device structures (direct or inverted) on device performance were also examined (Figure S8 to S10, Table S6-S8). The active layers were spun-cast from the blend solutions at 50 °C at an optimized spin speed of 4000 rpm for 45 s, using a programmable spin-coater from Specialty Coating Systems (Model G3P-8), resulting in films of ca. 50 nm in thickness. The samples were then dried under vacuum for at least 1 h. The samples were placed in a thermal evaporator for evaporation of a 7 nm thick molybdenum oxide (MoO<sub>3</sub>) layer evaporated at 0.5 Å/s, and a 100 snm thick layer of silver evaporated at 5 Å/s for inverted devices; a 4 nm thick calcium layer

evaporated at 0.2 Å/s, and a 100 nm thick layer of silver evaporated at 5 Å/s for direct devices; pressure of less than  $2x10^{-6}$  torr. Following electrode deposition, samples underwent *J*-*V* testing.

*J-V* measurements of solar cells were performed in the glovebox with a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to AM 1.5 G, with a KG-5 silicon reference cell certified by Newport. The external quantum efficiency (EQE) measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST.

## **10. Additional PV Device Performance Data**



**Figure S8**. *J-V* curves of BHJ solar cells made with (a) **D5T6F-M** and (b) **D7T8F-M** under eight different light intensities: 0.05, 0.13, 0.24, 0.34, 0.47, 0.65, 0.90, and 1.25 times of one-sun equivalent.



**Figure S9**.  $J_{sc}$  vs. light intensity for optimized PCE10:**D5T6F-M** and PCE10:**D7T8F-M**. The solid lines correspond to the fits derived from the expression  $J_{sc} \propto I^{\alpha}$ . With  $\alpha$ =0.96, and  $\alpha$ =0.94 for PCE10:**D5T6F-M** and PCE10:**D7T8F-M** respectively. Note: bimolecular recombination is not the main limiting factor suppressing efficiency for the optimized blends.



**Figure S10**. Device performance of the molecular acceptor **D5T6F-M** in BHJ solar cells with PCE10 as the polymer donor (model system); measurements under AM 1.5G (100 mW/cm<sup>2</sup>). The variations in figures of merit ( $J_{SC}$ ,  $V_{OC}$ , FF, PCE) are provided to show the thickness dependence of PCE10:**D5T6F-M** devices made from "as-cast" films, indicating 45-50 nm is the best thickness. For this system, the markers denote the average values and error bars show the high and low values across 20 devices for PCE10:**D5T6F-M**.

 Table S6. Donor-Acceptor ratio dependence for PCE10:D5T6F-M devices. Performance

 includes standard deviation across at least 10 devices.

D-A ratio	$J_{ m SC}$	Voc	FF	Avg. PCE	Max. PCE
(wt:wt)	$[mA cm^{-2}]$	[V]	[%]	[%]	[%]
5:5	$6.6\pm0.1$	$1.00\pm0.01$	$37.7\pm 0.4$	$2.5\pm0.1$	2.55
4:6	$8.7\pm0.3$	$1.05\pm0.01$	$46.9\pm1.3$	$4.3\pm0.1$	4.55
3:7	$7.9\pm0.2$	$1.04\pm0.01$	$49.5\pm0.4$	$4.1\pm0.1$	4.18

D-A ratio	$J_{ m SC}$	Voc	FF	Avg. PCE	Max. PCE
(wt:wt)	$[mA cm^{-2}]$	[V]	[%]	[%]	[%]
4:6	$3.5\pm 0.2$	$1.05\pm0.02$	$33.0\pm0.6$	$1.2\pm0.1$	1.34
3:7	$4.4\pm0.2$	$1.11\pm0.01$	$34.5\pm0.1$	$1.7\pm0.1$	1.83
2:8	$2.9\pm0.1$	$1.13\pm0.01$	$33.7\pm0.2$	$1.1\pm0.1$	1.13

 Table S7. Donor-Acceptor ratio dependence for PCE10:D7T8F-M devices. Performance includes standard deviation across at least 10 devices.

**Table S8**. Direct and inverted PCE10:**D7T78-M** and PCE10:**D5T6F-M** devices. Performance includes standard deviation across at least 10 devices.

Material	Structure	$J_{ m SC}$	V <sub>OC</sub>	FF	Avg. PCE	Max. PCE
System	Structure	$[mA cm^{-2}]$	[V]	[%]	[%]	[%]
PCE10: D7T78-M	Normal	$2.5\pm0.4$	$1.11\pm0.01$	$30.5\pm0.6$	$0.8\pm0.2$	1.10
	Inverted	$4.4\pm0.2$	$1.11\pm0.01$	$34.5\pm0.1$	$1.7\pm0.1$	1.83
PCE10: <b>D5T6F-M</b>	Normal	$5.7\pm0.3$	$1.01\pm0.01$	$41.7\pm0.6$	$2.4\pm0.1$	2.49
	Inverted	$8.7\pm0.3$	$1.05\pm0.01$	$46.9\pm1.3$	$4.3\pm0.1$	4.55

#### **11. Carrier Mobility Measurements**

The MIS-diodes were fabricated to measure the carrier mobility in blend films of PCE10 and fluorinated acceptors. In MIS-diode structure, a dielectric insulator  $MgF_2$  is deposited on the top or bottom of the blend film, which is sandwiched between two metal electrodes. It will effectively block both electrons and holes. By applying a forward bias voltage to these diode structures, only one type of carrier can be injected depending on the position of the insulator layer (i.e., beneath the cathode or anode).



**Figure S11**. MIS-CELIV transients for (a) PCE10:D5T6F-M blend hole-only, (b) PCE10:D5T6F-M blend electron-only, (c) PCE10:D7T8F-M blend hole-only, and (d) PCE10:D7T8F-M blend electron-only under distinct voltage gradients.

## **12. Transmission Electron Microscopy (TEM) and Electron Energy Loss** (EELS) Characterization

Films were spun-cast on PEDOT:PSS-coated glass substrates. The PCE10:SM BHJ films were floated off the substrates in deionized water and collected on lacey carbon coated TEM grids (Electron Microscopy Sciences). TEM images in a combination with Electron Energy Loss Spectroscopy (EELS) were performed using an FEI Titan 80-300 TEM equipped with an electron monochromator and a Gatan Imaging Filter (GIF) Quantum 966. The microscope was operated at 80 kV to minimize electron beam induced damages of polymers and to increase EELS signal/noise ratio. The EELS maps were acquired in Scanning TEM (STEM) mode as so called spectrum imaging (SI). To resolve spectral features clearly the monochromator was exploited to obtain energy resolution of 150 meV.



Figure S12. Morphology analyses of "optimized" BHJ active layers with PCE10 and SM acceptors. (a, d) Energy loss spectrum (b, e) Dark-field STEM images; (c, f) EELS maps emphasizing the donor-acceptor network. Green: PCE10-rich domains, Red: SM acceptor-rich domains. Scale bar: 500nm.

## 13. Atomic Force Microscopy (AFM) Imaging

A 5400 Agilent Atomic Force Microscope (AFM) was used to image the active layers in tapping mode (topography and phase images).



Figure S13. Magnified AFM topography (a, b) and phase (c, d) images (tapping mode) for optimized BHJ film composed of PCE10:Acceptor (a,c: D5T6F-M; b,d: D7T8F-M). Root mean square (RMS) roughness: D5T6F-M, 4.65 nm; D7T8F-M, 13.95 nm. AFM images show smooth features with modest RMS roughness for both BHJ blend films. Comparing D5T6F-M and D7T8F-M, an increase of roughness was observed in D7T8F-M, which is probably due to its higher crystallinity (Figure S7).

## 14. X-Ray Diffraction (XRD) Measurements



Figure S14. X-Ray powder diffraction (XRD) spectra of: (a) neat film of D5T6F-M and D7T8F-M; (b) neat film of D5T6F-M, PCE10 and blend film of PCE10:D5T6F-M; (c) neat film of D7T8F-M, PCE10 and blend film of PCE10:D7T8F-M. Note: D7T8F-M is clearly a more crystalline material compared with D5T6F-M, and the blend film has the signature of the neat film of molecular acceptor due to the amorphous character of PCE10.

## **15. Photocurrent Transients Measurements**



**Figure S15**. Normalized photocurrent transients of devices based on (**a**) **D5T6F-M** and (**b**) **D7T8F-M** at short-circuit current condition under nine different light intensities: 0.15, 0.29, 0.43, 0.56, 0.70, 0.84, 0.98, 1.11 and 1.25 times of one-sun equivalent. Transients show excellent device behavior of fast turn-on and turn-off characteristics in both cases, with no evidence of significant trap or blocking layer effects.

## **16. Solution NMR Spectra**



Figure S16. <sup>1</sup>H NMR spectrum of 2 in CDCl<sub>3</sub>.



Figure S17. <sup>13</sup>C NMR spectrum of 2 in CDCl<sub>3</sub>.



Figure S18. <sup>19</sup>F NMR spectrum of 2 in CDCl<sub>3</sub>.



Figure S19. <sup>1</sup>H NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S20. <sup>13</sup>C NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S21. <sup>19</sup>F NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S22. <sup>1</sup>H NMR spectrum of 4 in CDCl<sub>3</sub>.



Figure S23. <sup>13</sup>C NMR spectrum of 4 in CDCl<sub>3</sub>.



Figure S24. <sup>19</sup>F NMR spectrum of 4 in CDCl<sub>3</sub>.



Figure S25. <sup>1</sup>H NMR spectrum of 5 in CDCl<sub>3</sub>.



Figure S26. <sup>13</sup>C NMR spectrum of 5 in CDCl<sub>3</sub>.



Figure S27. <sup>19</sup>F NMR spectrum of 5 in CDCl<sub>3</sub>.



Figure S28. <sup>1</sup>H NMR spectrum of 6 in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S29. <sup>13</sup>C NMR spectrum of 6 in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S30. <sup>19</sup>F NMR spectrum of 6 in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S31. <sup>1</sup>H NMR spectrum of 7 in CDCl<sub>3</sub>.



Figure S32. <sup>13</sup>C NMR spectrum of 7 in CDCl<sub>3</sub>.



Figure S33. <sup>19</sup>F NMR spectrum of 7 in CDCl<sub>3</sub>.



Figure S34. <sup>1</sup>H NMR spectrum of 8 in CDCl<sub>3</sub>.



Figure S35. <sup>13</sup>C NMR spectrum of 8 in CDCl<sub>3</sub>.



Figure S36. <sup>19</sup>F NMR spectrum of 8 in CDCl<sub>3</sub>.



Figure S37. <sup>1</sup>H NMR spectrum of 10 in CDCl<sub>3</sub>.



Figure S38. <sup>13</sup>C NMR spectrum of 10 in CDCl<sub>3</sub>.



Figure S39. <sup>19</sup>F NMR spectrum of 10 in CDCl<sub>3</sub>.



Figure S40. <sup>1</sup>H NMR spectrum of 11 in CDCl<sub>3</sub>.



Figure S41. <sup>13</sup>C NMR spectrum of 11 in CDCl<sub>3</sub>.



Figure S42. <sup>19</sup>F NMR spectrum of 11 in CDCl<sub>3</sub>.



Figure S43. <sup>1</sup>H NMR spectrum of 12 in CDCl<sub>3</sub>.



Figure S44. <sup>13</sup>C NMR spectrum of 12 in CDCl<sub>3</sub>.



Figure S45. <sup>19</sup>F NMR spectrum of 12 in CDCl<sub>3</sub>.



Figure S46. <sup>1</sup>H NMR spectrum of 13 in CDCl<sub>3</sub>.



Figure S47. <sup>13</sup>C NMR spectrum of 13 in CDCl<sub>3</sub>.



Figure S48. <sup>19</sup>F NMR spectrum of 13 in CDCl<sub>3</sub>.



Figure S49. <sup>1</sup>H NMR spectrum of D5T6F-M in CDCl<sub>3</sub>.



Figure S50. <sup>13</sup>C NMR spectrum of D5T6F-M in CDCl<sub>3</sub>.



Figure S51. <sup>19</sup>F NMR spectrum of D5T6F-M in CDCl<sub>3</sub>.



Figure S52. <sup>1</sup>H NMR spectrum of D7T8F-M in CDCl<sub>3</sub>.



Figure S53. <sup>19</sup>F NMR spectrum of D7T8F-M in CDCl<sub>3</sub>.

#### **<u>17. Supporting Information References</u>**

- Z. P. Fei, P. Boufflet, S. Wood, J. Wade, J. Moriarty, E. Gann, E. L. Ratcliff, C.
   R. McNeill, H. Sirringhaus, J. S. Kim, M. Heeney, J. Am. Chem. Soc. 2015, 137, 6866-6879.
- [2] S. J. Liu, Z. P. Kan, S. Thomas, F. Cruciani, J. L. Bredas, P. M. Beaujuge, *Angew. Chem. Int. Edit.* 2016, 55, 12996-13000.
- [3] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.;Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*, Gaussian, Inc.: Wallingford, CT, USA, **2009**.
- [4] a) Risko, C.; McGehee, M. D.; Brédas, J.-L., *Chem. Sci.* 2011, 2, 1200-1218; b)
   Pandey, L.; Risko, C.; Norton, J. E.; Brédas, J.-L., *Macromolecules* 2012, 45, 6405-6414.
- [5] a) Körzdörfer, T.; Brédas, J.-L., Acc. Chem. Res. 2014, 47, 3284-3291; b) Stein,
   T.; Kronik, L.; Baer, R., J. Am. Chem. Soc. 2009, 131, 2818-2820.
- [6] J. D. Douglas, M. S. Chen, J. R. Niskala, O. P. Lee, A. T. Yiu, E. P. Young, J. M. J. Frechet, *Adv. Mater.* 2014, *26*, 4313-4319.