

Supporting Information

Preventing isomerization of the fused-ring core by introducing methyl group for efficient non-fullerene acceptors

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1. OSCs fabrication and measurements
2. Materials and Instruments
3. Synthesis and characterizations of BTMe-C6-2F and BTMe-C8-2F
4. Other characterizations

1. OSCs fabrication and measurement

An inverted-type device with the configuration of ITO/ZnO/active layer/MoO₃/Al was utilized for photovoltaic characterization. Patterned ITO glass was carefully washed with acetone, water, ethanol and isopropanol, then subjected to UV-ozone treatment for 15 min. The thin ZnO layer was spin-coated onto the ITO glass from the ZnO precursor solution, and then annealed at 220°C for 30 min in the air. The D: A blend solution in chloroform (12 mg mL⁻¹ in total) was spin-coated by varying spin rates on the ZnO layer to form a photoactive layer. Finally, the MoO₃ layer and Al electrode were sequentially evaporated onto the surface of the active layer in a vacuum chamber with a pressure of 2.2×10⁻⁴ Pa. The *J-V* characteristics were measured using a Keithley 2602 Source Meter and an Oriel Sol3A solar simulator equipped with an AM 1.5G solar spectrum filter with an intensity of 100 mW cm⁻² as the light source. The EQE spectrum was measured using a Zolix Solar Cell Scan 100 QE/IPCE measurement system. The mobilities were determined by fitting the dark current under low voltage, which is described as $J=(9/8)\epsilon_0\epsilon_r\mu((V^2)/(L^3))$, where J is the current, μ is the electron mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material,

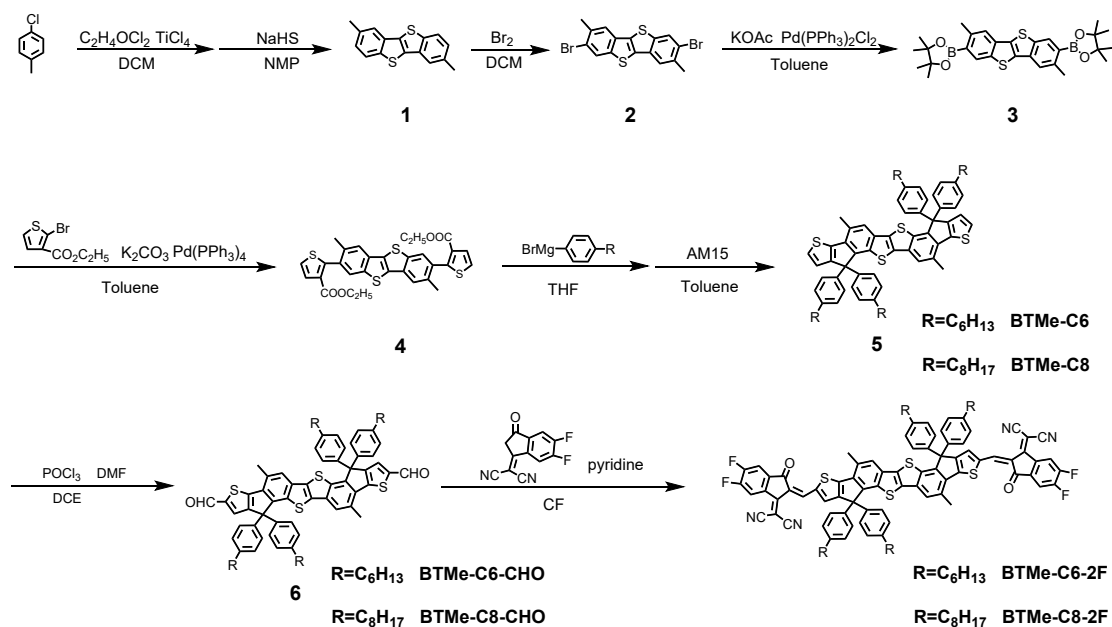
V is the effective voltage, and L is the thickness of the blend films. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The charge transport of blend film was investigated by the space-charge-limited current (SCLC) method, and the structure of electron-only devices is ITO/ZnO/active layer/PFN-Br/Al, while the hole-only device configuration is ITO/PEDOT: PSS/active layer/MoO₃/Al.

2. Materials and instruments

Unless stated otherwise, solvents and chemicals were obtained commercially and used without further purifications. All materials and solvents were purchased from Tianjin Kemiou Chemical Reagent, Alfa Aesar and used without further purifications. PM6 was purchased from Solarmer Inc. Nuclear magnetic resonance (NMR) spectra of the compounds were collected using a Bruker AVANCE 400 MHz spectrometer with deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal reference. Mass spectrometry (MS) data were obtained on a Bruker Aupoflex III MALDI-TOF analyzer with α -cyano-4-hydroxycinnamic acid as a matrix. The thermogravimetric analyses (TGA) measurements were carried out on a TA TGA 50 instrument under nitrogen gas flow with a 20 °C min⁻¹ heating rate. The photophysical and electrochemical properties were characterized by UV–visible–near infrared spectroscopy (Perkin–Elmer Cary 60 UV–Vis–NIR) and cyclic voltammetry (electrochemistry workstation CHI660A, Chenhua Shanghai), respectively. Atomic force microscopy (AFM) images were measured on a Dimension Icon AFM

(MULTIMODEPICOFOREE) in a tapping mode. Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were acquired by detector Pilatus3R 1M, Dectris (X-ray Source: MetalJet-D2, Excillum).

3. Synthesis and characterization of BTMe-C6-2F and BTMe-C8-2F



Scheme S1. Synthetic routes to BTMe-C6-2F and BTMe-C8-2F.

3.1 Synthesis of compound 1

P-chlorotoluene (2.500 g, 20.00 mmol, 1 eq), 1,1-dichloromethyl ether (4.540 g, 40.00 mmol, 2 eq), and dichloromethane (15 mL) were added to a dried 250 mL flask, then titanium tetrachloride (7.500 g, 40.00 mmol, 2 eq) which was dissolved in 10 mL of dichloromethane into the reaction solution at 0°C, and then moved to room

temperature to react for 15 h. After the reaction was completed, the reaction solution was poured into an iced sodium bicarbonate solution and reacted for 0.5 h. Then extracted with dichloromethane, took the organic phase, spun dry and used petroleum ether as eluent for preliminary purification by column chromatography. The crude product was spin-dried and used directly in the next step.

Add the crude product (2.000 g) from the previous step, sodium hydrosulfide (4.000 g) and N-methyl-2-pyrrolidone (10 mL) into a 100 ml flask, stirred at 85 °C for 2 h, and then stirred and refluxed at 180 °C for 8 h. After the completion of the reaction, the reaction solution was added to saturated ammonium chloride solution, stirred for 0.5 h. The precipitated solid was recrystallized with dichloromethane to obtain yellow solid (1.237 g, the total yield of the two steps was about 23%).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.79 (2H, d, $J=8.3$ Hz), 7.68 (2H, s), 7.23 (2H, d, $J=8.2$ Hz), 2.53 (6H, s). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 139.16, 134.71, 133.29, 133.22, 126.50, 123.56, 121.59, 21.41.

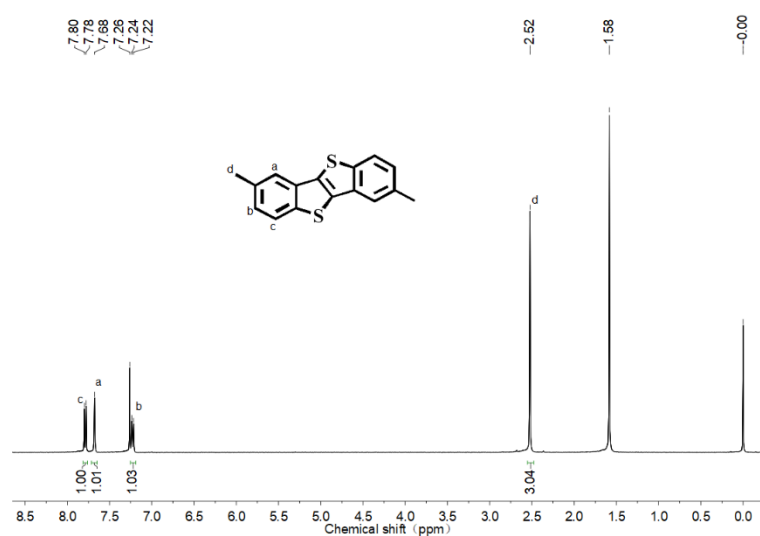


Fig. S1. ^1H NMR spectrum of compound 1.

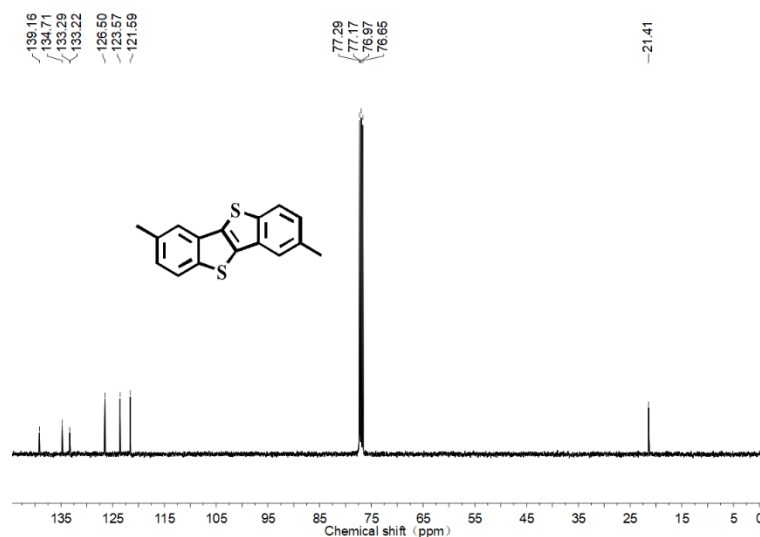


Fig. S2. ^{13}C NMR spectrum of compound 1.

3.2 Synthesis of compound 2

Compound 1 (268 mg, 1.00 mmol, 1 eq) and dichloromethane (150 mL) to a dried 500 mL flask, and then bromine (352 mg, 2.20 mmol, 2.2 eq) in dichloromethane (50 mL) was added dropwise to reacted flask at 0 °C. After reacting at 0 °C for 2 h, it was transferred to room temperature and react for 8 h. After the reaction completed, methanol was added to settle, filtered, and washed with ethanol and dichloromethane three times to obtain a white solid (330 mg, yield 70%). Due to the poor solubility of the compound 2, it could not be characterized by NMR and mass spectrometry, so it is directly used in the next step.

No ^1H and ^{13}C NMR measurements because it is hard to dissolve.

3.3 Synthesis of compound 3

Compound 2 (213 mg, 0.50 mmol, 1 eq), bis(pinacolato)diboron (508 mg, 2 mmol, 4 eq), bistriphenylphosphine palladium dichloride (35 mg, 0.05 mmol, 0.1 eq),

CH₃COOK (392 mg, 4.00 mmol, 8 eq) and toluene (30 mL) were added to a dried 100 mL flask. The mixture was deoxygenated with argon for 30 min and stirred for 24 h at 90 °C under argon. Water and dichloromethane were added, and the organic layer was separated and washed with water three times. After removing of the solvent, it was recrystallized with dichloromethane and methanol to obtain white solid (180 mg, yield about 69%).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.34 (2H, s), 7.67 (2H, s), 2.69 (6H, s), 1.39 (24H, s). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 141.03, 138.92, 135.04, 134.69, 131.67, 122.36, 83.62, 24.88, 22.36. MALDI-TOF MS(m/z): calcd for C₂₈H₃₄B₂O₄S₂: 520.316; Found: 520.272.

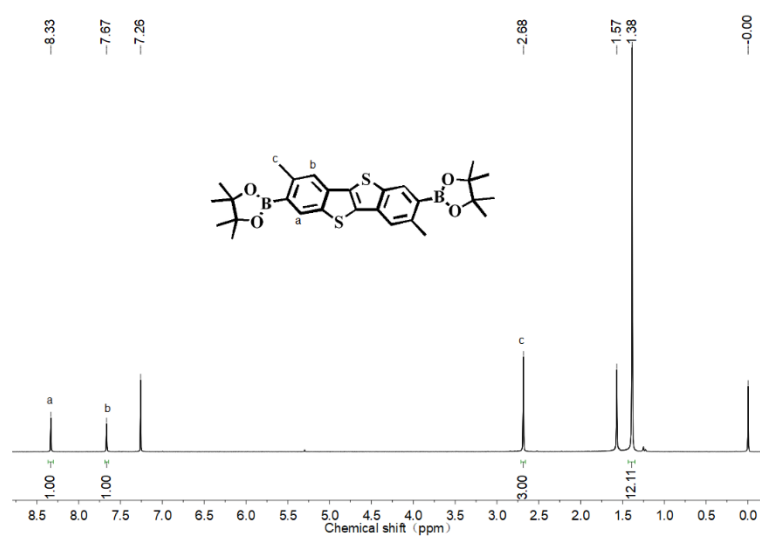


Fig. S3. ¹H NMR spectrum of compound 3.

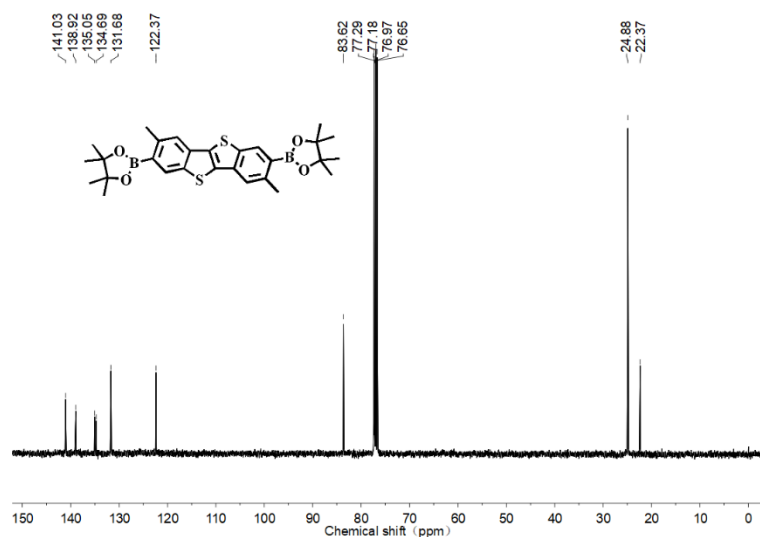


Fig. S4. ^{13}C NMR spectrum of compound 3.

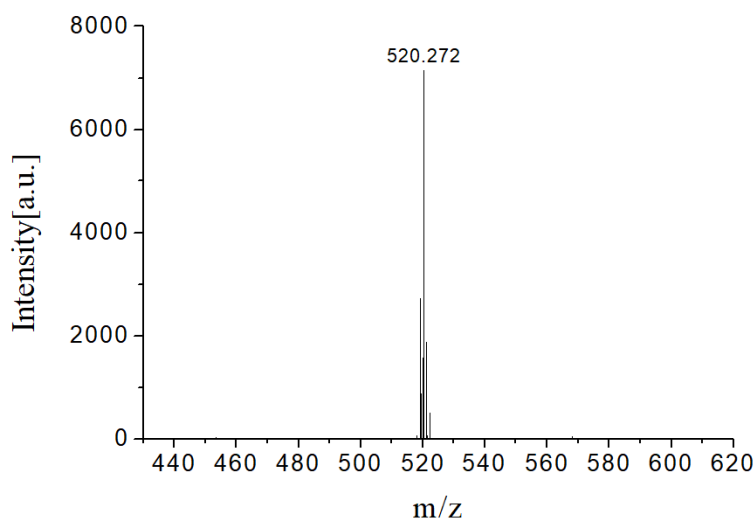


Fig. S5. MALDI-TOF spectrum of compound 3.

3.4 Synthesis of compound 4

Compound 3 (492 mg, 1.00 mmol, 1 eq), 2-bromothiophene-3-carboxylate (705 mg, 3.00 mmol, 3 eq), potassium carbonate (828 mg, 6.00 mmol, 6 eq), $\text{Pd}(\text{PPh}_3)_4$ (30 mg, 0.03 mmol, 0.03 eq) and toluene (50 mL) were added to a 100 mL dried flask. The mixture was deoxygenated with argon for 30 min and stirred for 48 h at 90 °C under

argon. Water and dichloromethane were added, and the organic layer was separated and washed with water three times. After removing of the solvent, it was recrystallized with dichloromethane and methanol to obtain a yellow-white solid (228 g, yield 40%).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.80 (2H, s), 7.76 (2H, s), 7.58 (2H, d, $J=5.4$ Hz), 7.33 (2H, d, $J=5.4$ Hz), 4.12 (4H, q, $J=7.1$ Hz), 2.32 (6H, s), 1.06 (6H, t, $J=7.1$ Hz). No ^{13}C NMR measurements because it is hard to dissolve. MALDI-TOF MS(m/z): calcd for $\text{C}_{30}\text{H}_{24}\text{O}_4\text{S}_4$: 576.758; Found:576.564.

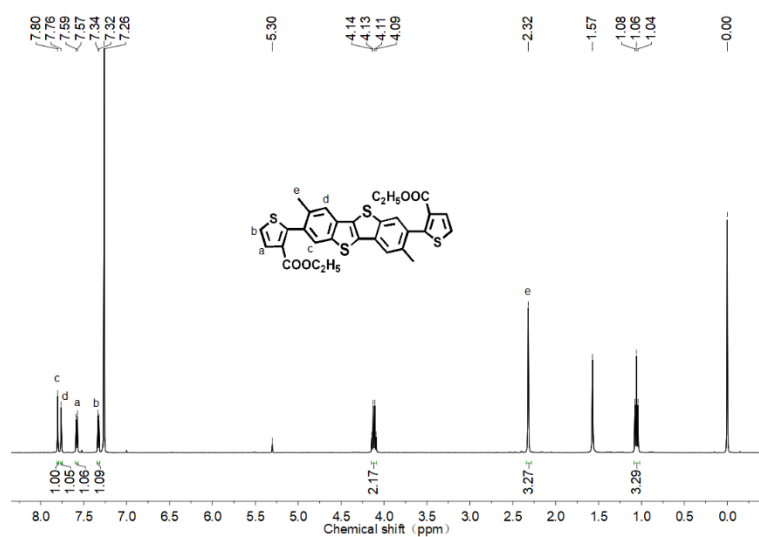


Fig. S6. ^1H NMR spectrum of compound 4.

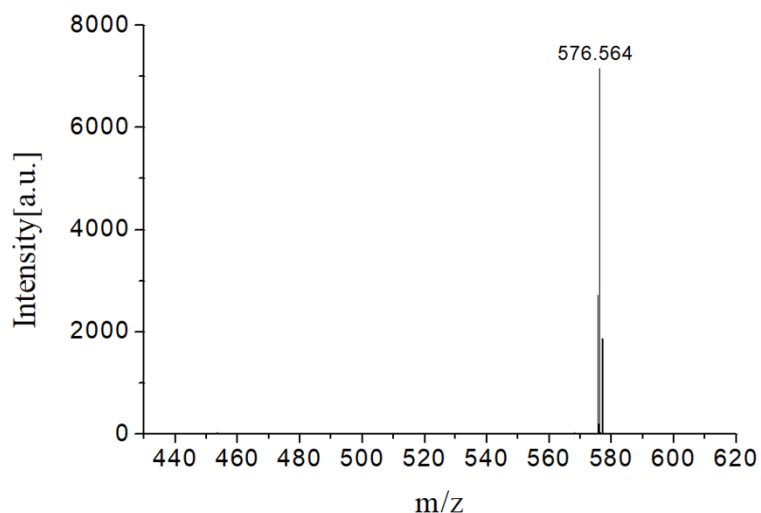


Fig. S7. MALDI-TOF spectrum of compound 4.

3.5 Synthesis of compound 5

Preparation for the Grignard reagent: aromatic halogenated hydrocarbon was slowly added to the suspension of magnesium turnings and catalytic amount of iodine in dry THF at room temperature, and the mixture was stirred for 2 h at 60 °C.

Compound 5 was synthesized by two steps: firstly, to a solution of compound 4 (288 mg, 0.50 mmol, 1 eq) in dry THF (10 mL) under nitrogen were added the prepared Grignard reagent (6.00 mmol, 12 eq) dropwise at room temperature. The resulting mixture was stirred and refluxed for overnight reaction. After the reaction was completed, the reaction solution was added to a saturated ammonium chloride solution and stirred for 0.5 h, and then extracted with dichloromethane, and the organic phase was collected and dried over anhydrous MgSO_4 . After removing of the solvent under reduced pressure, a yellow oil was obtained and directly was used for next step reaction without further purification. Secondly, AM15 ion exchange resin (500 mg) was added

to the solution of the yellow oil in toluene (15 mL). The resulting solution was stirred at 90 °C for 4 h. After removing of the toluene under reduced pressure, the residue was washed with sodium carbonate saturated aqueous solution and extracted by dichloromethane. Then, after removing of the solvent under reduced pressure, BTMe-C6 was recrystallized with dichloromethane and methanol to obtain a yellow solid, and BTMe-C8 was purified by column chromatography (petroleum ether/dichloromethane, v/v=10:1) to obtain a yellow sticky solid. The cyclization products with two different alkyl chains, BTMe-C6 (360 mg, yield about 66%) and BTMe-C8 (420 mg, yield about 69%), was obtained.

BTMe-C6: ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.57 (2H, s), 7.33 (2H, d, $J=4.9$ Hz), 7.12 (2H, d, $J=8.2$ Hz), 7.10 (8H, d, $J=4.9$ Hz), 7.03 (8H, d, $J=8.2$ Hz), 2.68 (6H, s), 2.52 (8H, t, $J=7.5$ Hz), 1.50-1.54 (4H, m), 1.27 (28H, m), 0.83-0.84 (12H, m). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 157.05, 147.87, 141.63, 140.54, 138.22, 136.11, 134.28, 134.09, 131.94, 128.69, 128.48, 128.18, 127.32, 122.57, 121.85, 63.31, 35.57, 31.70, 31.26, 29.71, 29.07, 22.59, 19.77, 14.08. MALDI-TOF MS(m/z) calcd for $\text{C}_{74}\text{H}_{80}\text{S}_4$: 1097.694; Found: 1097.412.

BTMe-C8: ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.57 (2H, s), 7.33 (2H, d, $J=4.9$ Hz), 7.12 (2H, d, $J=8.0$ Hz), 7.09 (8H, d, $J=4.9$ Hz), 7.03 (8H, d, $J=8.0$ Hz), 2.68 (6H, s), 2.52 (8H, t, $J=6.7$ Hz), 1.52-1.54 (4H, m), 1.23-1.26 (28H, m), 0.83-0.86 (12H, m). Pure ^{13}C NMR measurements were not obtained because the product cannot be separated with a small amount of raw material compound and could be explained by

the ^1H NMR. MALDI-TOF MS(m/z): calcd for $\text{C}_{82}\text{H}_{96}\text{S}_4$: 1209.910; Found: 1209.619.

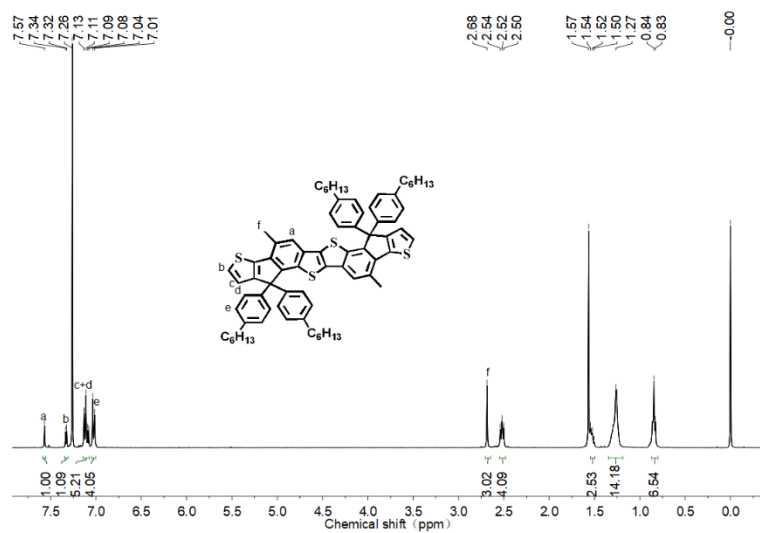


Fig. S8. ^1H NMR spectrum of BTMe-C6.

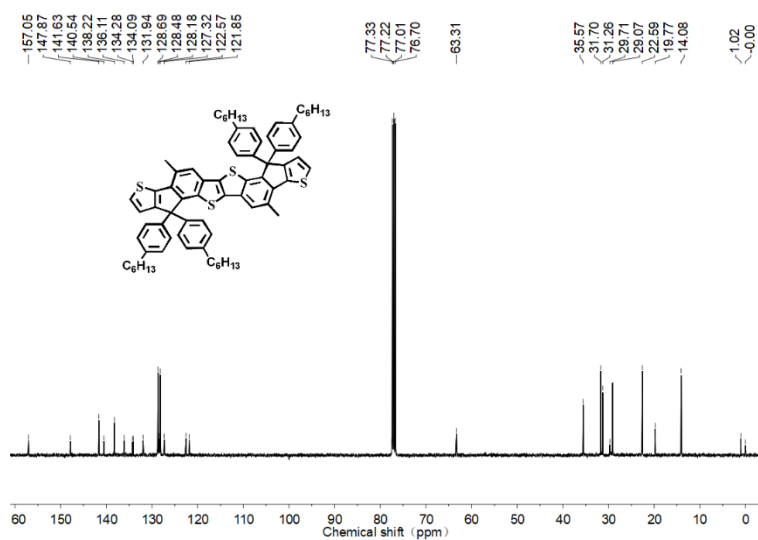


Fig. S9. ^{13}C NMR spectrum of BTMe-C6.

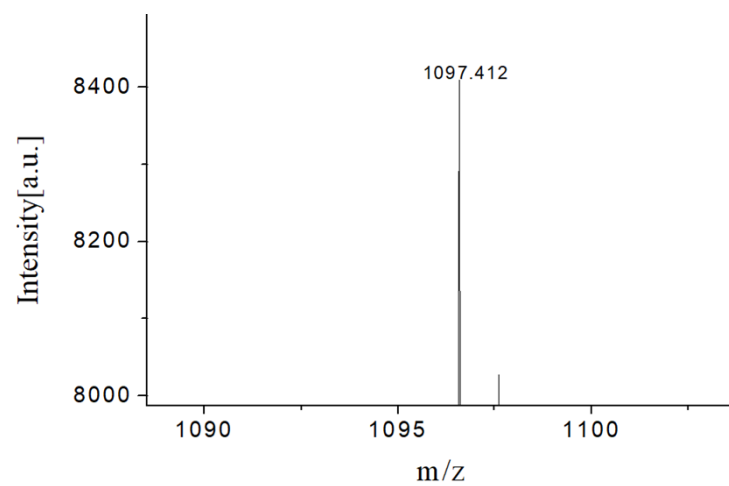


Fig. S10. MALDI-TOF spectrum of BTMe-C6.

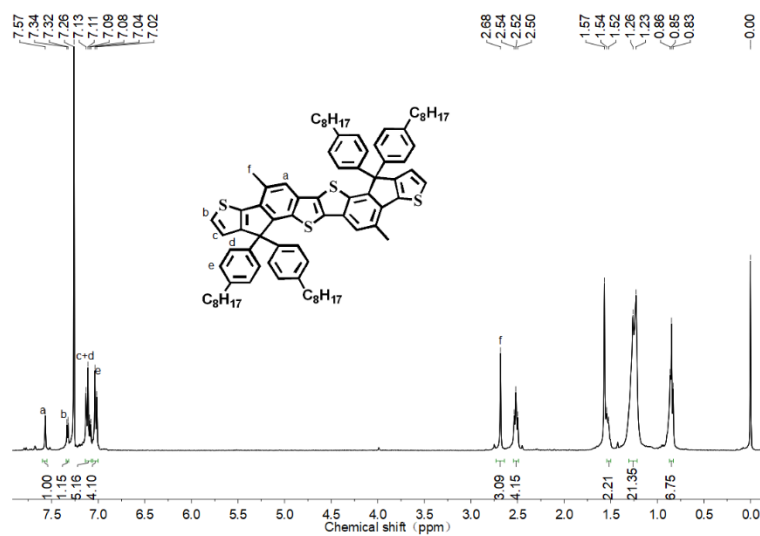


Fig. S11. ¹H NMR spectrum of BTMe-C8.

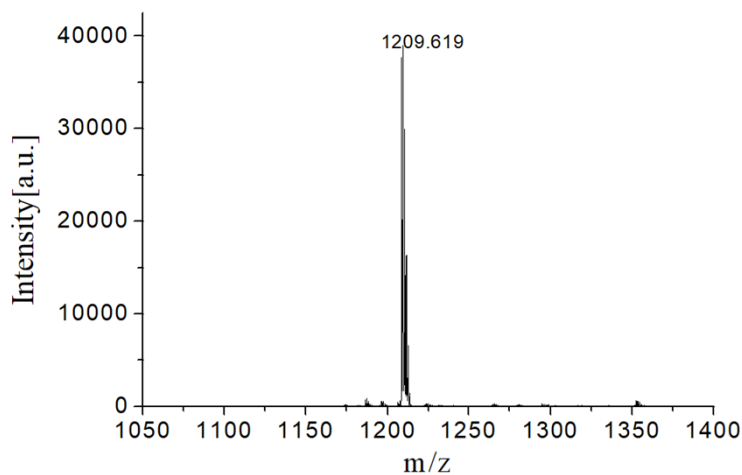


Fig. S12. MALDI-TOF spectrum of BTMe-C8.

3.6 Synthesis of compound 6

In a 100 ml two-necked round bottom flask, compound 5 (BTMe-C6 110 mg or BTMe-C8 112 mg, 0.10 mmol) was dissolved in anhydrous 1,2-dichloroethane (20 mL), and the mixture was deoxygenated with argon for 30 min. Then anhydrous DMF (5 mL) was added to this flask. Then the solution was cooled to 0 °C and stirred when phosphorous oxychloride (POCl_3) (0.5 mL) was added by syringe under argon protection. The reaction was kept at 0 °C for 2 h. Then, the mixture solution was allowed to reflux overnight. After the reaction was completed, the reaction solution was poured into a saturated sodium acetate solution and stirred for 1 h, and then the organic phase was extracted with dichloromethane and dried with anhydrous MgSO_4 . After removing of the solvent under reduced pressure, the residue was purified by recrystallization with dichloromethane and methanol to obtain a yellow solid (BTMe-C6-CHO 100 mg, yield about 87% or BTMe-C8-CHO 105 mg, yield about 83%).

BTMe-C6-CHO: ^1H NMR (400 MHz, CDCl_3) δ (ppm): 9.83 (2H, s), 7.73 (2H, s), 7.65 (2H, s), 7.12 (8H, d, $J=8.2$ Hz), 7.06 (8H, d, $J=8.2$ Hz), 2.74 (6H, s), 2.54 (8H, t, $J=8.9$ Hz), 1.53-1.57 (8H, m), 1.26 (24H, m), 0.83-0.86 (12H, m). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 182.92, 157.40, 149.48, 146.43, 142.27, 137.00, 136.34, 135.64, 133.57, 132.94, 129.47, 128.55, 122.60, 63.48, 35.54, 31.68, 31.26, 29.10, 22.58, 19.85, 14.09. MALDI-TOF MS(m/z): calcd for $\text{C}_{76}\text{H}_{80}\text{O}_2\text{S}_4$: 1153.714; Found:1153.570.

BTMe-C8-CHO: ^1H NMR (400 MHz, CDCl_3) δ (ppm): 9.82 (2H, s), 7.73 (2H, s), 7.65 (2H, s), 7.12 (8H, d, $J=8.0$ Hz), 7.06 (8H, d, $J=8.2$ Hz), 2.73 (6H, s), 2.53 (8H, t, $J=7.5$ Hz), 1.55 (8H, m), 1.25 (24H, m), 0.84 (12H, m). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 182.89, 157.42, 150.25, 149.49, 146.45, 142.28, 137.02, 136.37, 135.65, 133.58, 132.96, 131.39, 129.48, 128.56, 128.46, 122.60, 63.51, 35.55, 31.86, 31.29, 29.43, 29.22, 22.64, 19.84, 14.10. MALDI-TOF MS(m/z): calcd for $\text{C}_{84}\text{H}_{96}\text{O}_2\text{S}_4$: 1265.930; Found:1265.876.

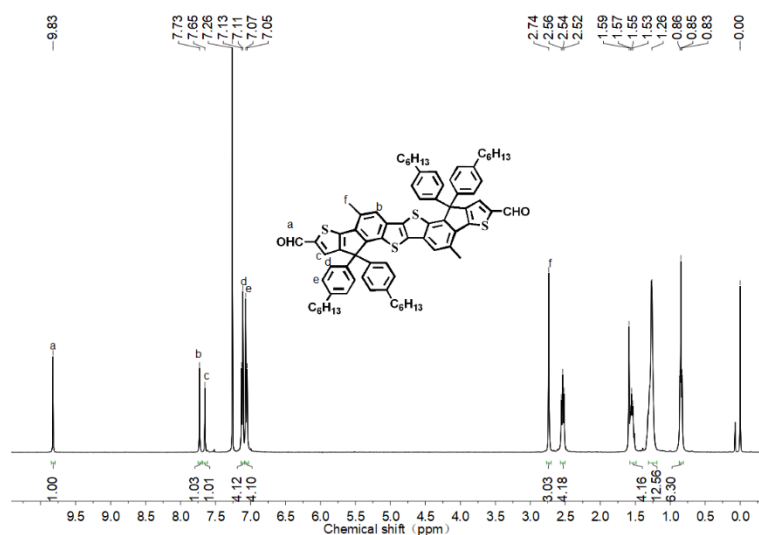


Fig. S13. ^1H NMR spectrum of BTMe-C6-CHO.

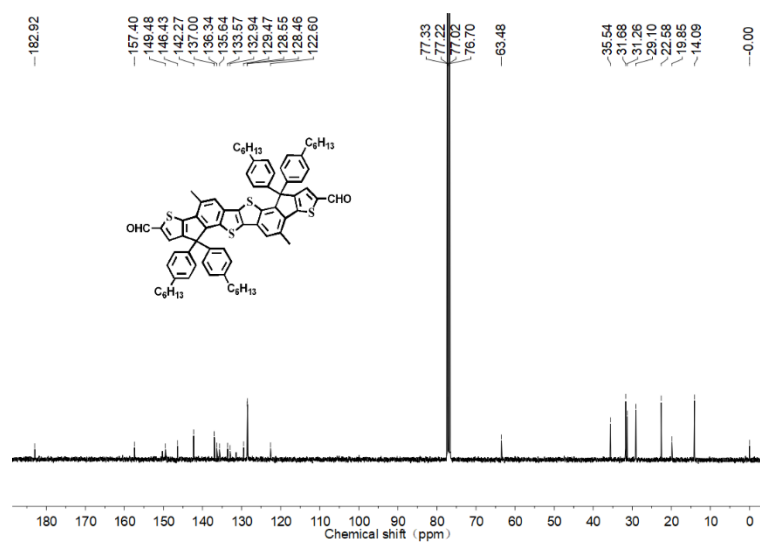


Fig. S14. ^{13}C NMR spectrum of BTMe-C6-CHO.

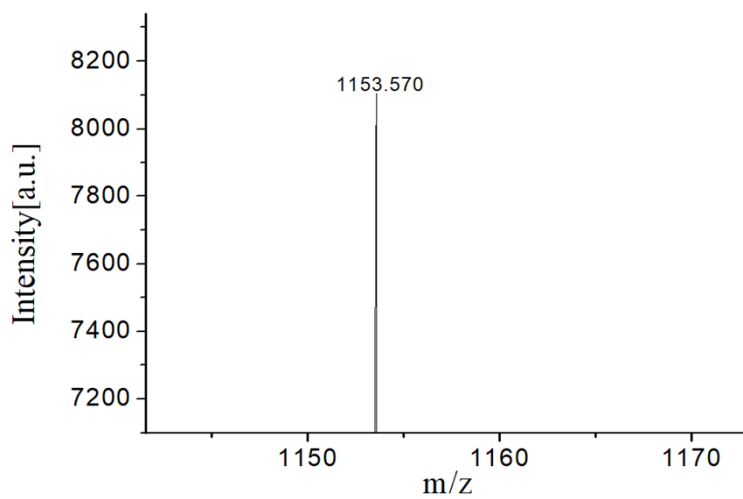


Fig. S15. MALDI-TOF spectrum of BTMe-C6-CHO.

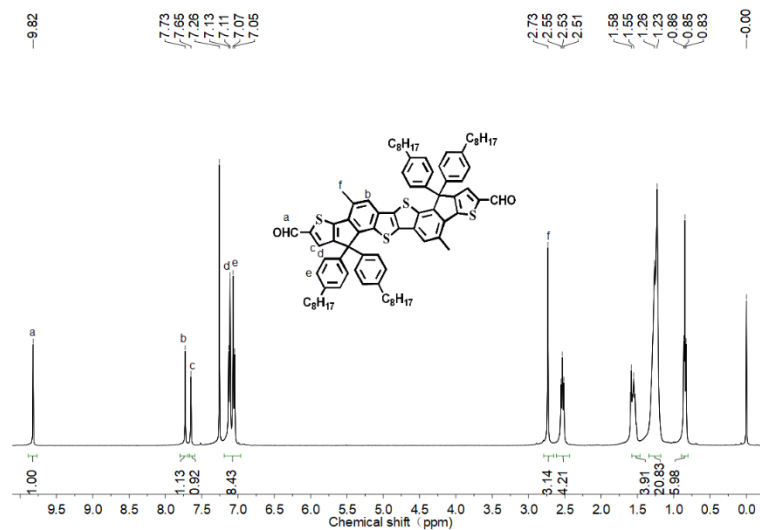


Fig. S16. ^1H NMR spectrum of BTMe-C8-CHO.

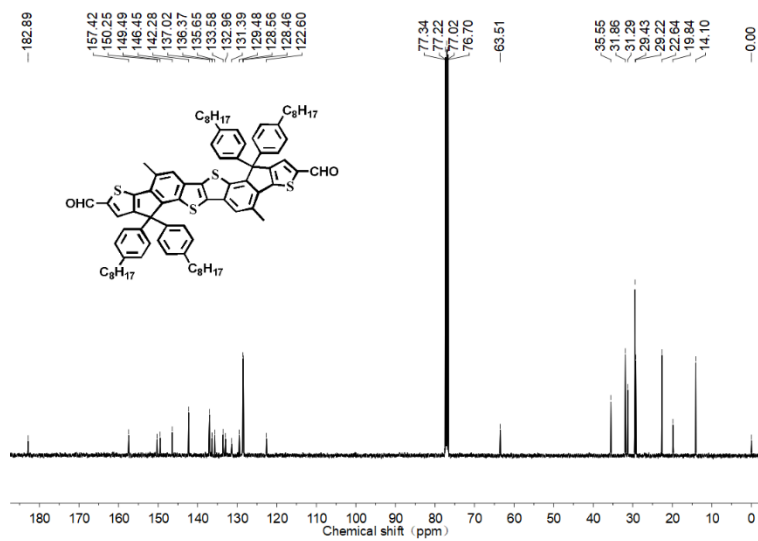


Fig. S17. ^{13}C NMR spectrum of BTMe-C8-CHO.

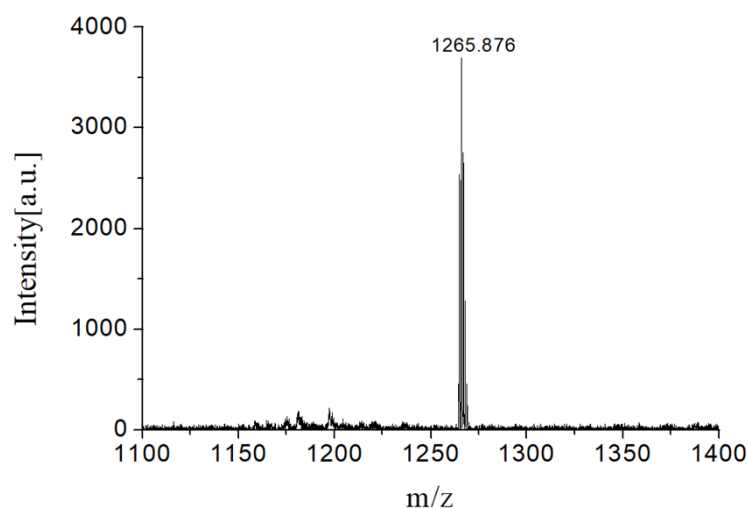


Fig. S18. MALDI-TOF spectrum of BTMe-C8-CHO.

3.7 Synthesis of BTMe-C6-2F and BTMe-C8-2F

Compound 5 (BTMe-C6-CHO 115 mg, 0.10 mmol or BTMe-C8-CHO 126 mg, 0.10 mmol, 1 eq), 2FIC (69 mg, 0.30 mmol, 3eq), pyridine (0.5 mL) and chloroform (25 mL) were added to a three-necked round bottom flask. The mixture was deoxygenated with argon for 30 min and then stirred and refluxed for 4 h. After the reaction was completed, the mixture was poured into methanol (100 mL) and filtered. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 3/1) to give a blue solid (130 mg of BTMe-C6-2F, yield of about 82% or 140 mg of BTMe-C8-2F, yield of about 83%).

BTMe-C6-2F: ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.87 (2H, s), 8.53 (2H, m), 7.81 (2H, s), 7.71 (4H, s), 7.12 (8H, d, $J=7.7$ Hz), 7.08 (8H, d, $J=8.3$ Hz), 2.87 (6H, s), 2.54 (8H, t, $J=6.5$ Hz), 1.25 (32H, m), 0.85 (12H, m). No ^{13}C NMR measurements

because it was hard to dissolve. MALDI-TOF MS(m/z): calcd for $C_{100}H_{84}F_4N_2O_2S_4$: 1578.031; Found:1577.490.

BTMe-C8-2F: 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.88 (2H, s), 8.53 (2H, m), 7.81 (2H, s), 7.69 (4H, s), 7.13 (8H, d, $J=8.0$ Hz), 7.08 (8H, d, $J=8.1$ Hz), 2.87 (6H, s), 2.54 (8H, t, $J=7.6$ Hz), 1.57 (8H, m), 1.23 (40H, m), 0.85 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.04, 160.79, 158.91, 158.37, 155.74, 153.16, 153.02, 150.88, 142.56, 141.31, 139.48, 138.67, 137.03, 136.72, 136.58, 134.76, 134.44, 133.57, 130.87, 128.61, 123.10, 120.72, 115.10, 114.35, 114.28, 112.66, 112.48, 35.57, 31.86, 31.30, 29.71, 29.44, 29.23, 22.65, 20.57, 14.11. MALDI-TOF MS(m/z): calcd for $C_{108}H_{100}F_4N_4O_2S_4$: 1690.248; Found:1689.242.

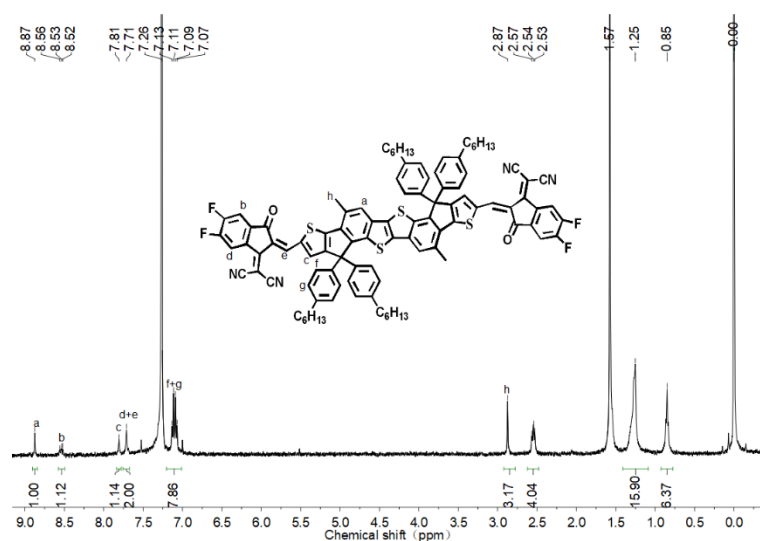


Fig. S19. 1H NMR spectrum of BTMe-C6-2F.

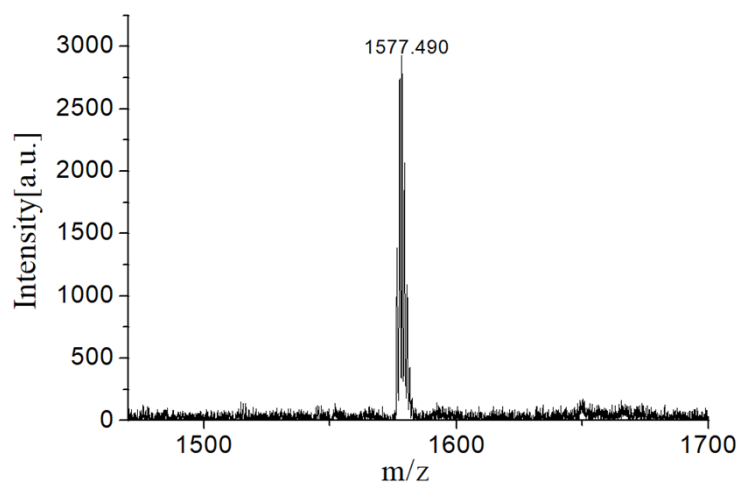


Fig. S20. MALDI-TOF spectrum of BTMe-C6-2F.

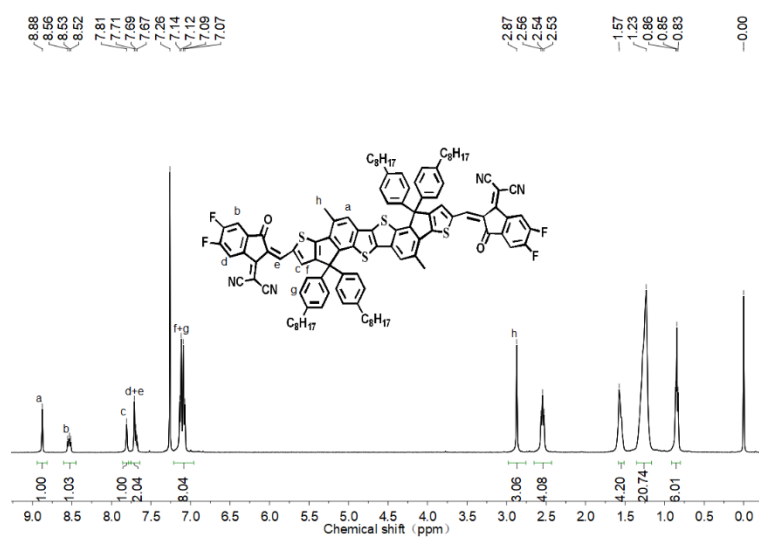


Fig. S21. ¹H NMR spectrum of BTMe-C8-2F.

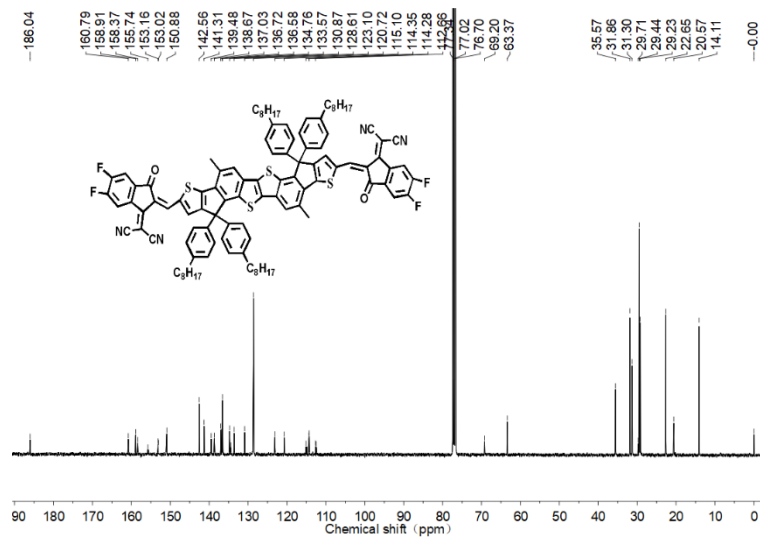


Fig. S22. ^{13}C NMR spectrum of BTMe-C8-2F.

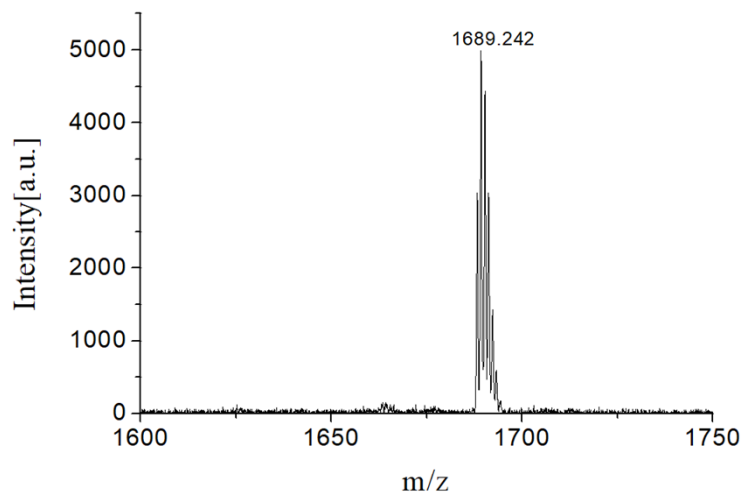


Fig. S23. MALDI-TOF spectrum of BTMe-C8-2F.

4. Other characterizations

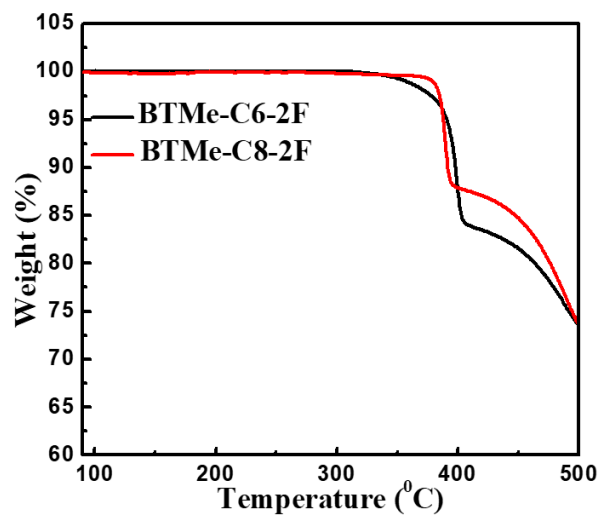


Fig. S24. TGA curves of BTMe-C6-2F and BTMe-C8-2F.

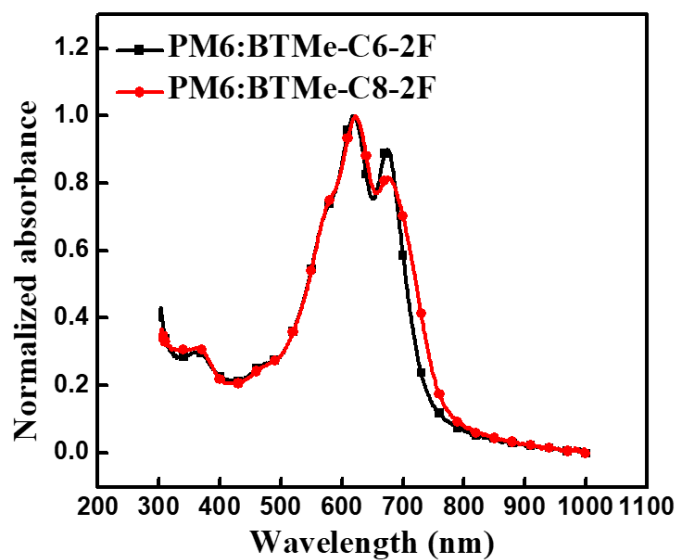


Fig. S25. Normalized absorbance of blend films.

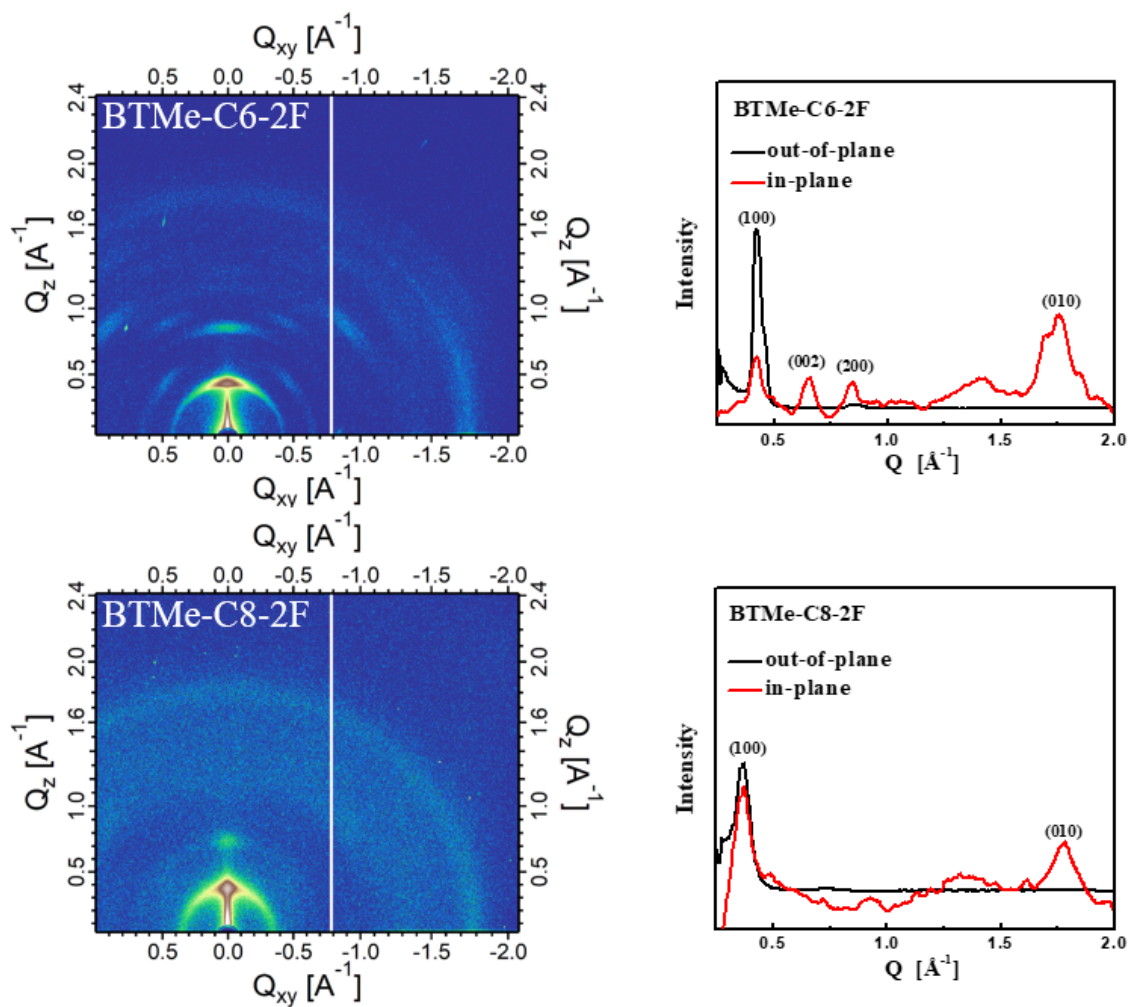


Fig. S26. 2D GIWAXS patterns (left) and line-cut scattering profiles along IP and OOP directions (right) for pure films.

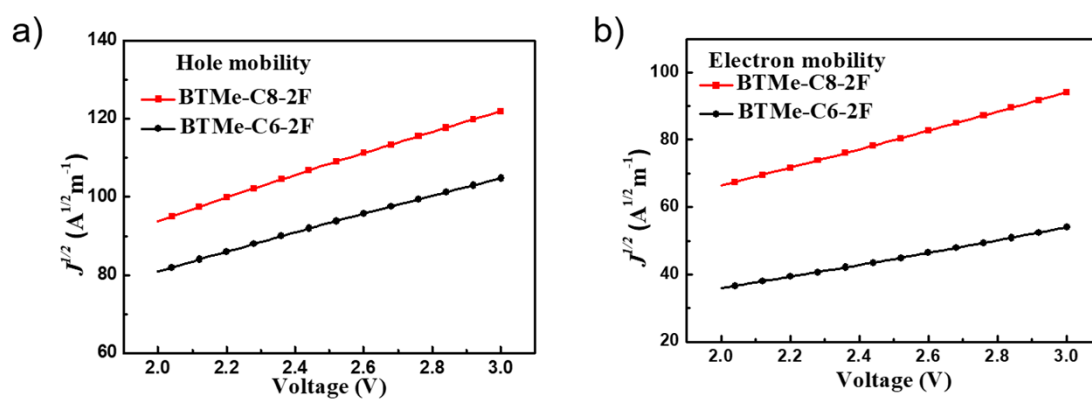


Fig. S27. $J^{0.5}$ - V curves of (a) hole-only and (b) electron-only devices based on PM6: BTMe-C6-2F and PM6: BTMe-C8-2F blend films.

Table S1. Summary of photovoltaic parameters under the illumination of AM 1.5G (100 mW cm⁻²) based on PM6/acceptor (D/A=1/1) with different additive content in chloroform.

Blend films	Additive	V_{oc}	J_{sc}	FF	PCE_{max} (PCE_{ave}^a)
	(vol)	(V)	(mA cm⁻²)	(%)	(%)
PM6: BTMe-C6-2F	--	1.00	17.32	62.00	10.68 (10.32)
PM6: BTMe-C6-2F	0.5%DIO	0.98	16.55	59.18	9.60 (9.34)
PM6: BTMe-C6-2F	0.5%CN	0.90	14.78	59.58	7.92 (7.83)
PM6: BTMe-C8-2F	--	1.01	17.00	68.35	11.70 (11.36)
PM6: BTMe-C8-2F	0.5%DIO	1.00	18.38	66.29	12.24 (12.02)
PM6: BTMe-C8-2F	0.5%CN	0.98	19.01	68.40	12.68 (12.35)
PM6: BTMe-C8-2F	1%CN	0.97	19.65	66.76	12.72 (12.50)
PM6: BTMe-C8-2F	1.5%CN	0.98	16.76	67.21	10.98 (10.58)

^a The average values with standard deviations were obtained from ten devices.

Table S2. Data of the peak analysis of GIWAXS in the OOP direction.

Sample	Q_z (Å⁻¹)	d-spacing (nm)	intensity
BTMe-C6-2F	0.43, 1.79	1.47, 0.35	606.91, 7.94
BTMe-C8-2F	0.37, 1.79	1.71, 0.35	364.04, 8.28
PM6: BTMe-C6-2F	0.31, 1.79	2.00, 0.35	192.08, 13.75
PM6: BTMe-C8-2F	0.35, 1.79	1.78, 0.35	314.48, 46.33

Table S3. Data of the peak analysis of GIWAXS in the IP direction.

Sample	Q_{xy} (Å⁻¹)	d-spacing (nm)	intensity
BTMe-C6-2F	0.42, 1.76	1.50, 0.36	10.14, 12.28
BTMe-C8-2F	0.37, 1.78	1.69, 0.35	17.22, 11.31
PM6: BTMe-C6-2F	0.32, 1.72	1.96, 0.37	35.04, 12.05
PM6: BTMe-C8-2F	0.32, 1.74	1.96, 0.36	66.91, 11.98