

Supporting Information

Low-bandgap small molecule acceptors with asymmetric side chains

Guanhua Zong,^{‡ab} Mingjie Li,^{‡bc} Ke Jin,^b Zhiwei Xu,^{bc} Lixiu Zhang,^b Ning Ma,^{*a} Jilin Wang,^{*d} Guan-Wu Wang,^{*c} Zuo Xiao,^{*b} and Liming Ding^b

^a *Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China. E-mail: mntju@tju.edu.cn*

^b *Center for Excellence in Nanoscience, Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China. E-mail: xiaoz@nanoctr.cn*

^c *Hefei National Research Center for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, China. E-mail: gwang@ustc.edu.cn*

^d *Guangxi Key Laboratory of Optical and Electronic Material and Devices, School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China. E-mail: jilinwang@glut.edu.cn*

[‡] G. Zong and M. Li contributed equally to this work.

* Corresponding authors.

1. General characterization

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag⁺ electrode was used as the reference electrode. The acceptors were coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc⁺. AFM was performed on a Multimode microscope (Veeco) using tapping mode. TEM was performed on a JEM-1400Flash transmission electron microscope at an accelerating voltage of 120.0 kV.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., SunaTech Co. and other commercial suppliers. Diethyl 2,5-dichlorothiopheno[3,2-*b*]thiophene-3,6-dicarboxylate^[1] and tributyl(6-undecylthieno[3,2-*b*]thiophen-2-yl)stannane^[2] were synthesized according to literatures. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.

Compound 1. To a solution of diethyl 2,5-dichlorothiopheno[3,2-*b*]thiophene-3,6-dicarboxylate (600 mg, 1.70 mmol) and tributyl(6-undecylthieno[3,2-*b*]thiophen-2-yl)stannane (2.48 g, 4.25 mmol) in DMF (20 mL) was added Pd(PPh₃)₄ (196 mg, 0.17 mmol) under N₂. The mixture was heated to 130 °C and stirred overnight. After cooling to room temperature, the mixture was poured into methanol. The solid was collected by filtration. The crude product was purified via column chromatography (silica gel) by using CHCl₃ as eluent to give **compound 1** as a yellow solid (1.24 g, 84%). ^1H NMR (CDCl₃, 400 MHz, δ /ppm): 7.83 (s, 2H), 7.06 (s, 2H), 4.43 (q, $J = 7.1$ Hz, 4H), 2.75 (t, $J = 7.5$ Hz, 4H), 1.84-1.69 (m, 6H), 1.43 (t, $J = 7.1$ Hz, 6H), 1.39-1.23 (m, 32H), 0.92-0.84 (m, 6H). ^{13}C NMR (CDCl₃, 100 MHz, δ /ppm): 161.71, 146.81, 141.88, 138.71, 137.44, 135.03, 134.66, 123.27, 122.73, 119.45, 61.43, 31.90, 29.87, 29.65, 29.61, 29.57, 29.39, 29.36, 29.34, 28.61, 22.67, 14.28, 14.11. MALDI-TOF MS (m/z): C₄₆H₆₀O₄S₆ (M⁺) calc. 868.282, found 868.278.

Compound 2. To compound 1 (900 mg, 1.04 mmol) was added phenylmagnesium bromide (5.2 mL, 0.7 M in THF) under N₂. The mixture was heated to 50 °C and stirred for 30 min. After cooling to room temperature, the mixture was quenched with water and extracted with CH₂Cl₂. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:4) as eluent to give **compound 2** as a yellow solid (444 mg, 43%). ^1H NMR (CDCl₃, 400 MHz, δ /ppm): 7.61 (s, 1H), 7.32 (s, 10H), 7.01 (s, 1H), 6.95 (s, 1H), 6.69 (s, 1H), 4.40 (q, $J = 7.1$ Hz, 2H), 3.53 (s, 1H), 2.71 (t, $J = 7.4$ Hz, 2H), 2.64 (t, $J = 7.6$ Hz, 2H), 1.71 (m,

4H), 1.40 (t, $J = 7.1$ Hz, 3H), 1.30 (m, 32H), 0.93-0.82 (m, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 161.90, 146.77, 145.37, 141.76, 141.18, 138.82, 138.49, 138.24, 137.88, 137.78, 135.56, 134.98, 134.84, 134.78, 134.45, 128.28, 128.24, 128.19, 122.95, 122.37, 122.26, 122.08, 119.11, 80.79, 61.25, 31.90, 29.84, 29.81, 29.67, 29.65, 29.62, 29.61, 29.57, 29.56, 29.39, 29.35, 29.34, 29.30, 28.59, 28.53, 22.68, 14.27, 14.12. MALDI-TOF MS (m/z): $\text{C}_{56}\text{H}_{66}\text{O}_3\text{S}_6$ (M^+) calc. 978.334, found 978.370.

Compound 3. To compound 2 (202 mg, 0.21 mmol) was added (4-hexylphenyl)magnesium bromide (2.1 mL, 0.6 M in THF) under N_2 . The mixture was heated to 50 °C and stirred for 1 h. After cooling to room temperature, the mixture was quenched with water and extracted with petroleum ether. After removal of the solvent, the crude product passed through a flash column (silica gel) with CH_2Cl_2 :petroleum ether (1:2) eluent to give a yellow solid. The solid and Amberlyst® 15(H) (200 mg) were dissolved in anhydrous toluene (2.5 mL) under N_2 . The mixture was stirred at room temperature for 2 h. The mixture was purified via flash column chromatography (silica gel) by using petroleum ether as eluent to give **compound 3** as a yellow solid (176 mg, 70%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.28 (m, 10H), 7.17 (d, $J = 8.2$ Hz, 4H), 7.10 (d, $J = 8.3$ Hz, 4H), 6.86 (s, 2H), 2.74-2.67 (m, 4H), 2.59-2.52 (m, 4H), 1.80-1.68 (m, 4H), 1.62-1.55 (m, 4H), 1.42-1.24 (m, 44H), 0.92-0.84 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 147.68, 147.31, 147.22, 146.75, 142.00, 141.23, 140.97, 140.93, 138.40, 138.22, 137.87, 137.63, 137.60, 135.83, 135.78, 134.86, 134.54, 133.36, 133.25, 128.72, 128.61, 128.13, 127.95, 127.39, 120.25, 120.22, 62.73, 62.24, 35.60, 31.91, 31.67, 31.18, 29.66, 29.62, 29.55, 29.46, 29.45, 29.40, 29.34, 29.17, 28.73, 22.69, 22.56, 14.13, 14.07. MALDI-TOF MS (m/z): $\text{C}_{78}\text{H}_{92}\text{S}_6$ (M^+) calc. 1220.552, found 1220.570.

Compound 4. To compound 2 (190 mg, 0.19 mmol) was added (3-hexylphenyl)magnesium bromide (2.6 mL, 0.6 M in THF) under N_2 . The mixture was heated to 50 °C and stirred for 1 h. After cooling to room temperature, the mixture was quenched with water and extracted with petroleum ether. After removal of the solvent, the crude product passed through a flash column (silica gel) with CH_2Cl_2 :petroleum ether (1:2) eluent to give a yellow solid. The solid and Amberlyst® 15(H) 15 (200 mg) were dissolved in anhydrous toluene (2 mL) under N_2 . The mixture was stirred at room temperature for 1.5 h. The mixture was purified via flash column chromatography (silica gel) by using petroleum ether as eluent to give **compound 4** as a yellow solid (192 mg, 81%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.34-7.23 (m, 10H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.12 (s, 2H), 7.07 (d, $J = 7.6$ Hz, 2H), 6.98 (d, $J = 7.8$ Hz, 2H), 6.86 (s, 2H), 2.70 (t, $J = 7.7$ Hz, 4H), 2.55 (t, $J = 7.7$ Hz, 4H), 1.79-1.68 (m, 4H), 1.60-1.52 (m, 4H), 1.42-1.21 (m, 44H), 0.91-0.81 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 147.48, 147.18, 146.75, 143.37, 141.24, 141.13, 140.93, 138.22, 137.92, 137.67, 135.81, 135.71, 134.84, 134.54, 133.38, 133.27, 128.81, 128.72, 128.47, 128.14, 127.48, 127.39, 124.83, 120.27, 62.77, 62.73, 36.01, 31.90, 31.75, 31.31, 29.65, 29.61, 29.55, 29.46, 29.41, 29.34, 28.97, 28.74, 22.68, 22.61, 14.13. MALDI-TOF MS (m/z): $\text{C}_{78}\text{H}_{92}\text{S}_6$ (M^+) calc. 1220.552, found 1220.564.

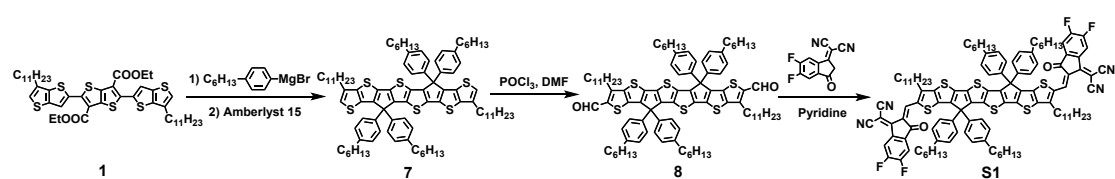
Compound 5. To a solution of compound 3 (141 mg, 0.12 mmol) in 1,2-dichloroethane (5 mL) were added anhydrous DMF (0.18 mL) and phosphorus oxychloride (0.22 mL) in the ice-water bath under N₂. The mixture was stirred at room temperature for 10 min, then heated to 80 °C and stirred for 1.5 h. After that, a saturated sodium acetate solution was added to quench the reaction. The mixture was extracted with petroleum ether. After removal of solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:1.5) as eluent to give **compound 4** as a red solid (135 mg, 92%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 10.00 (s, 2H), 7.35-7.28 (m, 6H), 7.23 (dd, *J* = 7.8, 1.7 Hz, 4H), 7.11 (s, 8H), 3.14-2.96 (m, 4H), 2.60-2.48 (m, 4H), 1.85-1.72 (m, 4H), 1.62-1.51 (m, 4H), 1.45-1.37 (m, 4H), 1.35-1.20 (m, 40H), 0.91-0.81 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 181.65, 181.61, 150.46, 149.98, 147.51, 146.92, 145.82, 144.54, 144.23, 142.61, 142.20, 142.19, 140.09, 139.02, 138.90, 138.25, 138.21, 137.46, 137.45, 137.26, 136.48, 136.19, 129.01, 128.97, 128.91, 127.86, 127.70, 62.87, 62.40, 35.58, 31.88, 31.64, 31.17, 30.27, 29.60, 29.57, 29.44, 29.30, 29.29, 29.11, 27.98, 22.67, 22.54, 14.11, 14.06. MALDI-TOF MS (m/z): C₈₀H₉₃O₂S₆ (M + H⁺) calc. 1277.549, found 1277.608.

Compound 6. To a solution of compound 4 (153 mg, 0.13 mmol) in 1,2-dichloroethane (5 mL) were added anhydrous DMF (0.2 mL) and phosphorus oxychloride (0.24 mL) in the ice-water bath under N₂. The mixture was stirred at room temperature for 10 min, then heated to 80 °C and stirred for 1 h. After that, saturated sodium acetate solution was added to quench the reaction. The mixture was extracted with petroleum ether. After removal of solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:1.5) as eluent to give **compound 6** as a red solid (151 mg, 94%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 10.01 (s, 2H), 7.37-7.27 (m, 6H), 7.24 (dd, *J* = 7.8, 1.7 Hz, 4H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.13-7.06 (m, 4H), 6.95 (d, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.2 Hz, 4H), 2.56 (t, *J* = 7.6 Hz, 4H), 1.80 (p, *J* = 7.8 Hz, 4H), 1.56 (p, *J* = 8.1 Hz, 4H), 1.46-1.37 (m, 4H), 1.36-1.20 (m, 40H), 0.93-0.81 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 181.61, 181.53, 150.24, 149.93, 147.34, 146.92, 145.81, 145.69, 144.53, 144.23, 143.77, 142.20, 142.17, 140.10, 140.00, 138.99, 138.90, 138.33, 138.23, 137.47, 137.45, 136.44, 136.17, 129.02, 128.76, 128.47, 127.95, 127.87, 124.65, 62.93, 62.88, 35.98, 31.87, 31.71, 31.28, 30.27, 29.59, 29.56, 29.44, 29.29, 28.91, 28.00, 22.66, 22.59, 14.12, 14.11. MALDI-TOF MS (m/z): C₈₀H₉₃O₂S₆ (M+H⁺) calc. 1277.549, found 1277.316.

A1. Compound 5 (100 mg, 0.078 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (90 mg, 0.39 mmol) were dissolved in CHCl₃ (10 mL) and pyridine (20 drops). The mixture was heated to 65 °C and stirred for 1 h. After that, the mixture was purified via column chromatography (silica gel) by using CHCl₃ as eluent. Further recrystallization in CHCl₃:methanol gave **A1** as a black solid (100 mg, 75%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 9.00, 8.99 (s, 2H), 8.58-8.49 (m, 2H), 7.69-7.60 (m, 2H), 7.41-7.28 (m, 10H), 7.22-7.11 (m, 8H), 3.16-3.02 (m, 4H), 2.62-2.49 (m, 4H), 1.82-1.68 (m, 4H), 1.62-1.54 (m, 4H), 1.50-1.39 (m, 4H), 1.37-1.19 (m, 40H),

0.92-0.79 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 185.94, 158.92, 158.90, 155.59, 155.45, 153.18, 153.11, 152.96, 152.34, 149.02, 148.91, 148.70, 148.12, 145.45, 145.23, 144.62, 144.56, 143.00, 139.80, 139.64, 139.57, 138.11, 137.87, 136.68, 136.61, 136.58, 136.53, 136.50, 135.01, 134.98, 134.44, 134.40, 134.37, 134.34, 129.25, 129.19, 129.13, 128.23, 127.88, 127.71, 119.71, 119.56, 115.07, 115.04, 114.92, 114.70, 114.65, 112.46, 112.27, 68.16, 68.02, 63.05, 62.60, 35.60, 31.89, 31.65, 31.16, 31.13, 29.75, 29.72, 29.62, 29.59, 29.44, 29.37, 29.32, 29.17, 22.68, 22.55, 14.11, 14.04. MALDI-TOF MS (m/z): $\text{C}_{104}\text{H}_{97}\text{F}_4\text{N}_4\text{O}_2\text{S}_6$ ($\text{M} + \text{H}^+$) calc. 1701.587, found 1701.629.

A2. Compound **6** (95 mg, 0.074 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (86 mg, 0.37 mmol) were dissolved in CHCl_3 (9.5 mL) and pyridine (19 drops). The mixture was heated to 65 °C and stirred for 1 h. After that, the mixture was purified via column chromatography (silica gel) by using CHCl_3 as eluent. Further recrystallization in CHCl_3 :methanol gave **A2** as a black solid (115 mg, 91%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 9.01 (s, 2H), 8.59-8.48 (m, 2H), 7.69-7.56 (m, 2H), 7.43-7.29 (m, 10H), 7.25-7.18 (m, 4H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.99 (d, $J = 7.7$ Hz, 2H), 3.19-3.05 (m, 4H), 2.62 (t, $J = 7.7$ Hz, 4H), 1.84-1.72 (m, 4H), 1.66-1.57 (m, 4H), 1.51-1.41 (m, 4H), 1.36-1.20 (m, 40H), 0.87 (t, $J = 6.6$ Hz, 6H), 0.79 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 185.93, 185.70, 158.92, 158.87, 155.58, 155.56, 155.47, 155.43, 152.97, 152.83, 152.61, 152.31, 148.95, 145.42, 144.55, 144.16, 139.77, 139.57, 139.49, 138.06, 137.85, 136.52, 136.50, 134.96, 134.43, 134.41, 134.37, 134.36, 129.25, 129.00, 128.63, 128.33, 128.22, 127.90, 124.42, 119.70, 119.59, 115.07, 115.03, 114.92, 114.70, 114.65, 112.48, 112.29, 112.12, 68.15, 67.99, 63.10, 63.06, 36.08, 31.89, 31.74, 31.37, 31.12, 29.73, 29.61, 29.58, 29.43, 29.37, 29.31, 29.10, 22.67, 22.63, 14.10. MALDI-TOF MS (m/z): $\text{C}_{104}\text{H}_{97}\text{F}_4\text{N}_4\text{O}_2\text{S}_6$ ($\text{M} + \text{H}^+$) calc. 1701.587, found 1701.651.



Scheme S1 The synthetic route of S1.

Compound 7. To compound **1** (140 mg, 0.16 mmol) was added (4-hexylphenyl)magnesium bromide (4 mL, 0.6 M in THF) under N_2 . The mixture was heated to 50 °C and stirred for 1.5 h. After cooling to room temperature, the mixture was quenched with water and extracted with petroleum ether. After removal of the solvent, the crude product passed through a flash column (silica gel) with CH_2Cl_2 :petroleum ether (1:3) eluent to give a yellow solid. The solid and Amberlyst® 15(H) (150 mg) were dissolved in anhydrous toluene (2 mL) under N_2 . The mixture was stirred at room temperature for 3 h. The mixture was purified via flash column chromatography (silica gel) by using petroleum ether as eluent to give **compound 7** as

a red oil (153 mg, 68%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.17 (d, $J = 8.3$ Hz, 8H), 7.10 (d, $J = 8.3$ Hz, 8H), 6.85 (s, 2H), 2.70 (t, $J = 7.6$ Hz, 4H), 2.55 (t, $J = 7.8$ Hz, 8H), 1.79-1.69 (m, 4H), 1.61-1.51 (m, 8H), 1.39-1.23 (m, 56H), 0.91-0.84 (m, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 147.66, 147.21, 141.97, 140.84, 138.45, 137.99, 137.48, 135.76, 134.73, 133.39, 128.60, 127.96, 120.13, 62.24, 35.61, 31.91, 31.68, 31.19, 29.66, 29.63, 29.56, 29.46, 29.41, 29.35, 29.18, 28.74, 22.69, 22.57, 14.13, 14.08. MALDI-TOF MS (m/z): $\text{C}_{90}\text{H}_{116}\text{S}_6$ (M^+) calc. 1388.740, found 1388.757.

Compound 8. To a solution of compound 7 (102 mg, 0.073 mmol) in 1,2-dichloroethane (3.5 mL) were added anhydrous DMF (0.12 mL) and phosphorus oxychloride (0.14 mL) in the ice-water bath under N_2 . The mixture was stirred at room temperature for 10 min, then heated to 80 $^\circ\text{C}$ and stirred for 1 h. After that, saturated sodium acetate solution was added to quench the reaction. The mixture was extracted with petroleum ether. After removal of solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2 :petroleum ether (1:2) as eluent to give **compound 8** as a red solid (89 mg, 84%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 10.00 (s, 2H), 7.11 (m, 16H), 3.05 (t, $J = 7.6$ Hz, 4H), 2.55 (t, $J = 4.4$ Hz, 8H), 1.83-1.72 (m, 4H), 1.61-1.53 (m, 8H), 1.45-1.37 (m, 4H), 1.35-1.21 (m, 52H), 0.91-0.82 (m, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 181.62, 150.48, 147.43, 145.80, 144.37, 142.58, 142.12, 139.08, 138.12, 137.39, 137.31, 136.38, 128.90, 127.72, 62.40, 35.58, 31.88, 31.65, 31.16, 30.28, 29.61, 29.57, 29.45, 29.30, 29.12, 27.99, 22.67, 22.54, 14.10, 14.05. MALDI-TOF MS (m/z): $\text{C}_{92}\text{H}_{117}\text{O}_2\text{S}_6$ ($\text{M} + \text{H}^+$) calc. 1445.737, found 1445.453.

S1. Compound 8 (47 mg, 0.032 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (37 mg, 0.16 mmol) were dissolved in CHCl_3 (4.5 mL) and pyridine (9 drops). The mixture was heated to 65 $^\circ\text{C}$ and stirred for 1 h. After that, the mixture was purified via column chromatography (silica gel) by using CHCl_3 as eluent. Further recrystallization in CHCl_3 :methanol gave **S1** as a black solid (50 mg, 82%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 8.99 (s, 2H), 8.53 (dd, $J = 10.0, 6.5$ Hz, 2H), 7.65 (t, $J = 7.6$ Hz, 2H), 7.16 (m, 16H), 3.08 (t, $J = 7.9$ Hz, 4H), 2.55 (t, $J = 7.9$ Hz, 8H), 1.81-1.67 (m, 4H), 1.61-1.53 (m, 8H), 1.49-1.39 (m, 4H), 1.34-1.20 (m, 52H), 0.90-0.78 (m, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 185.96, 185.95, 158.93, 155.58, 155.56, 155.45, 155.42, 153.19, 152.98, 152.94, 152.87, 152.81, 149.07, 148.65, 145.51, 144.59, 142.99, 139.64, 138.08, 136.72, 136.62, 136.59, 136.53, 136.50, 135.00, 134.44, 134.38, 129.12, 127.71, 119.51, 115.10, 114.92, 114.71, 112.44, 112.25, 67.95, 62.60, 35.61, 31.90, 31.65, 31.17, 31.14, 29.75, 29.72, 29.63, 29.60, 29.45, 29.38, 29.33, 29.17, 22.68, 22.55, 14.11, 14.05. MALDI-TOF MS (m/z): $\text{C}_{116}\text{H}_{121}\text{F}_4\text{N}_4\text{O}_2\text{S}_6$ ($\text{M} + \text{H}^+$) calc. 1869.774, found 1869.827.

3. NMR

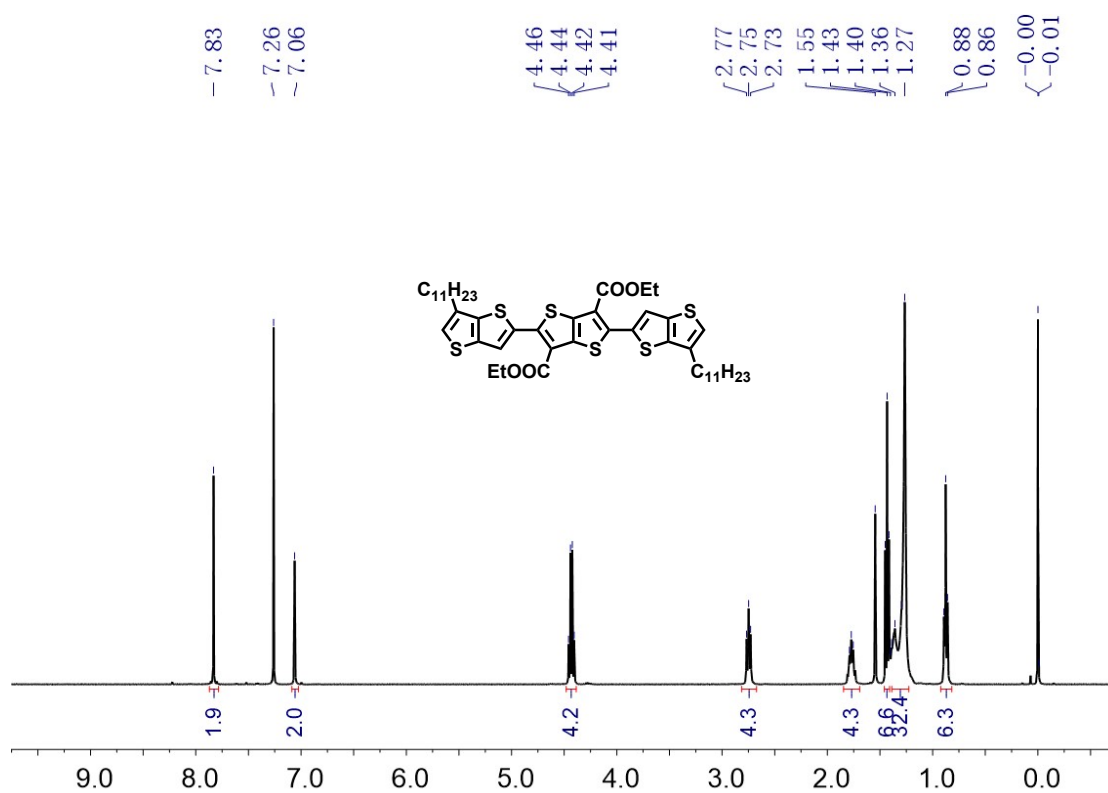


Fig. S1 ^1H NMR spectrum of compound 1.

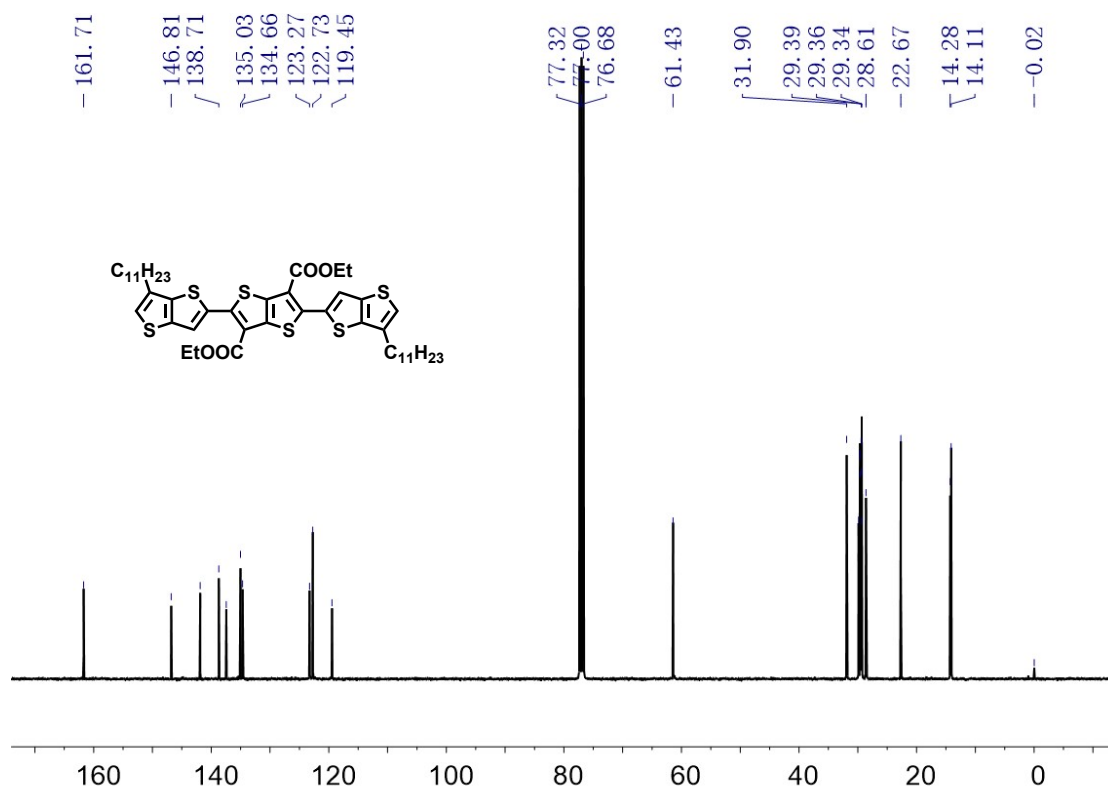


Fig. S2 ^{13}C NMR spectrum of compound 1.

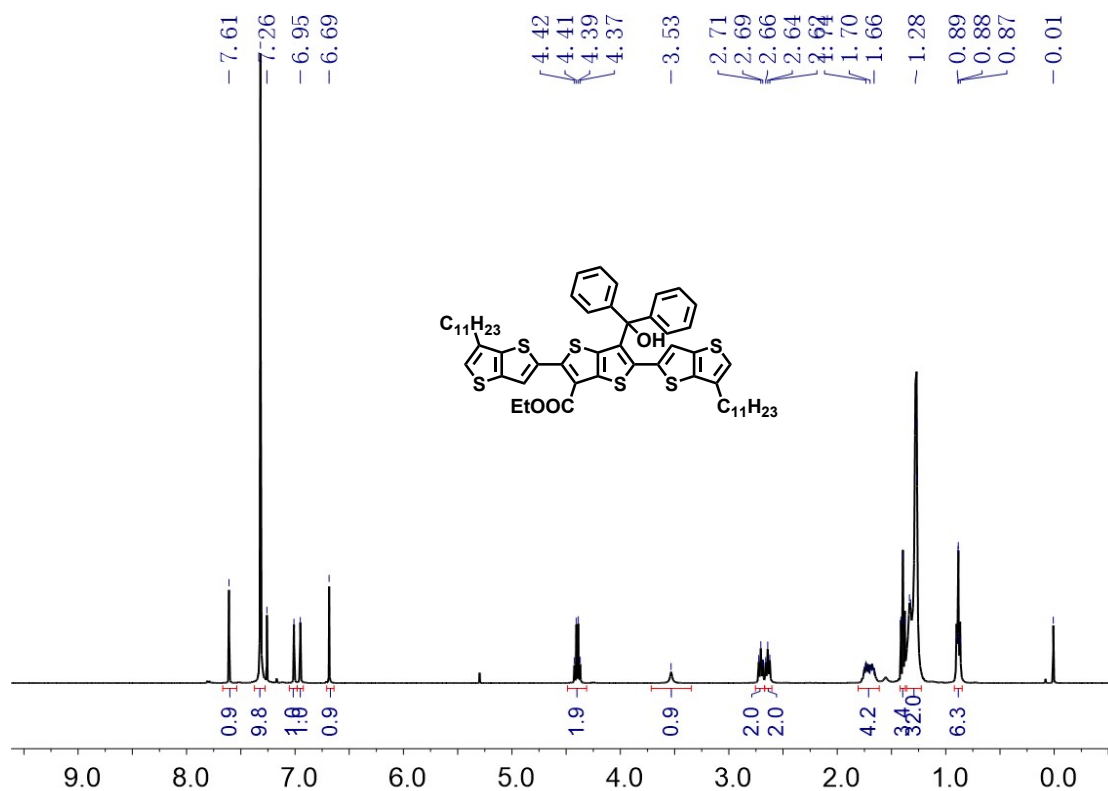


Fig. S3 ^1H NMR spectrum of compound 2.

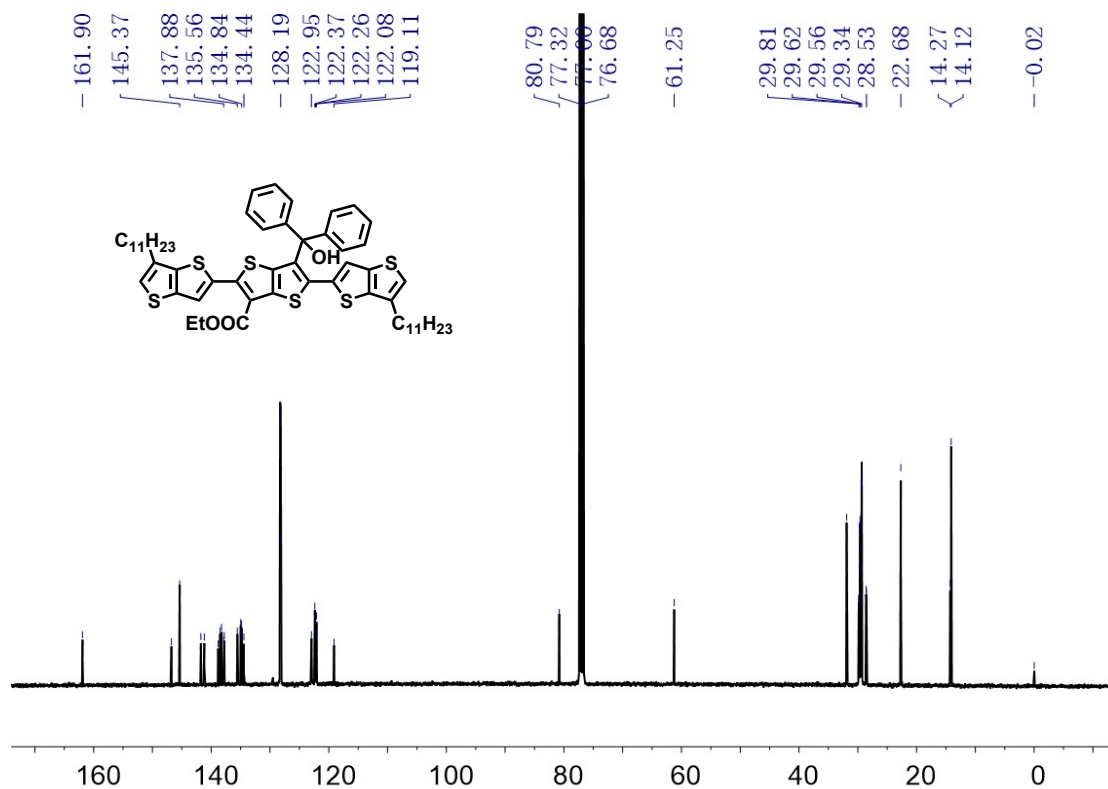


Fig. S4 ^{13}C NMR spectrum of compound 2.

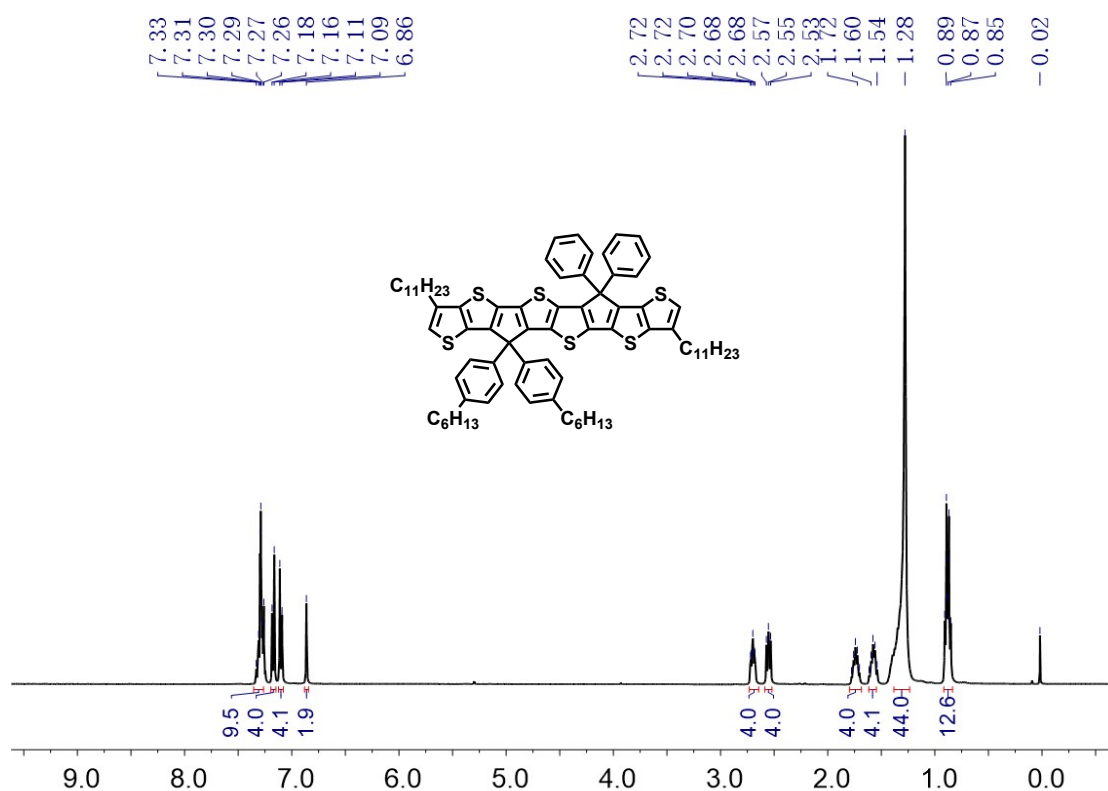


Fig. S5 ¹H NMR spectrum of compound 3.

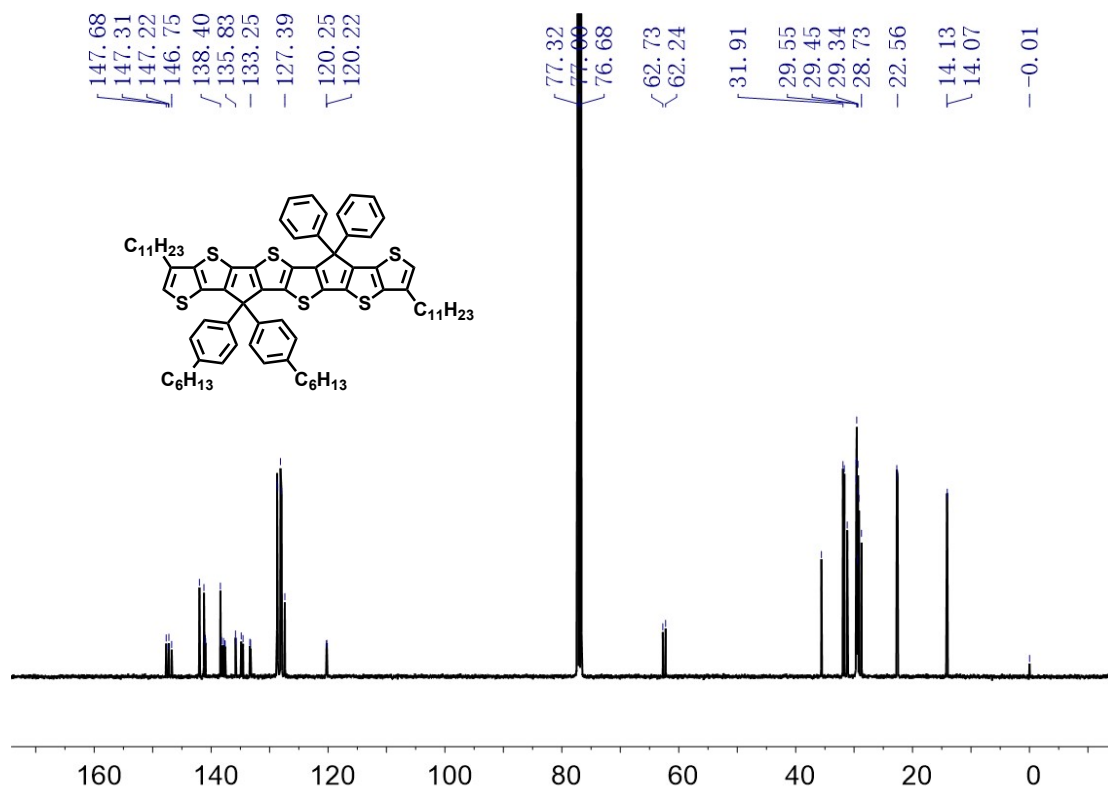


Fig. S6 ¹³C NMR spectrum of compound 3.

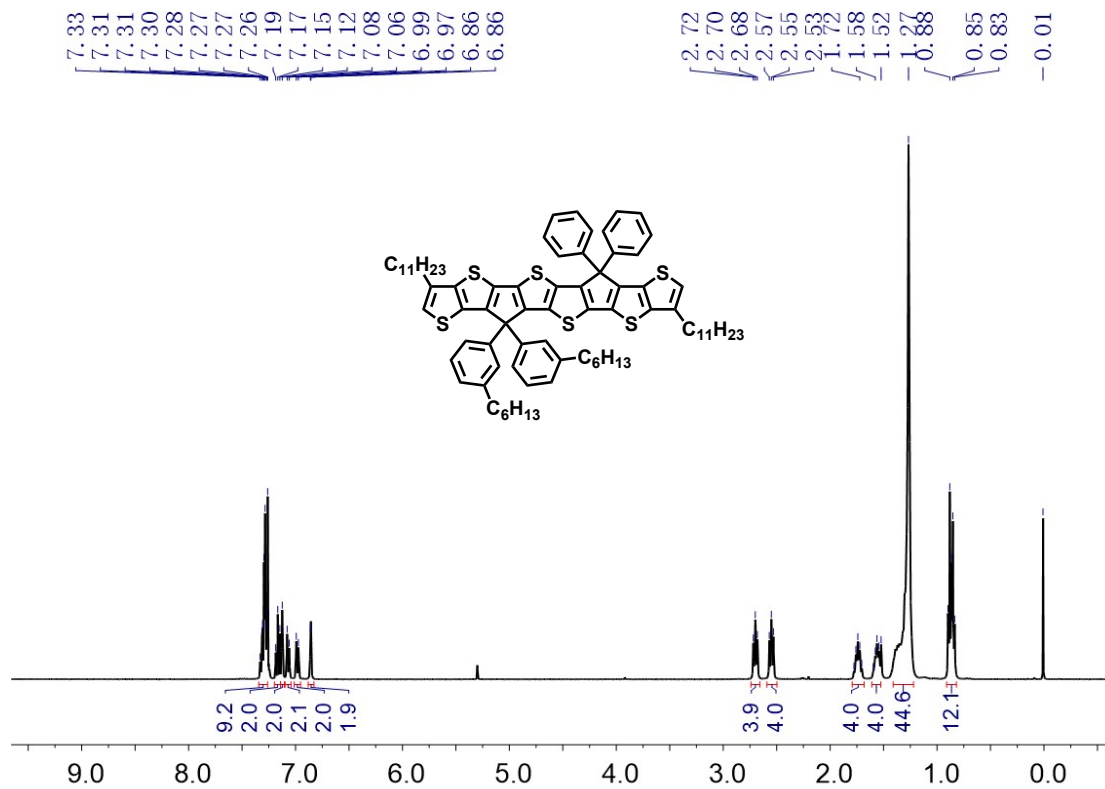


Fig. S7 ¹H NMR spectrum of compound 4.

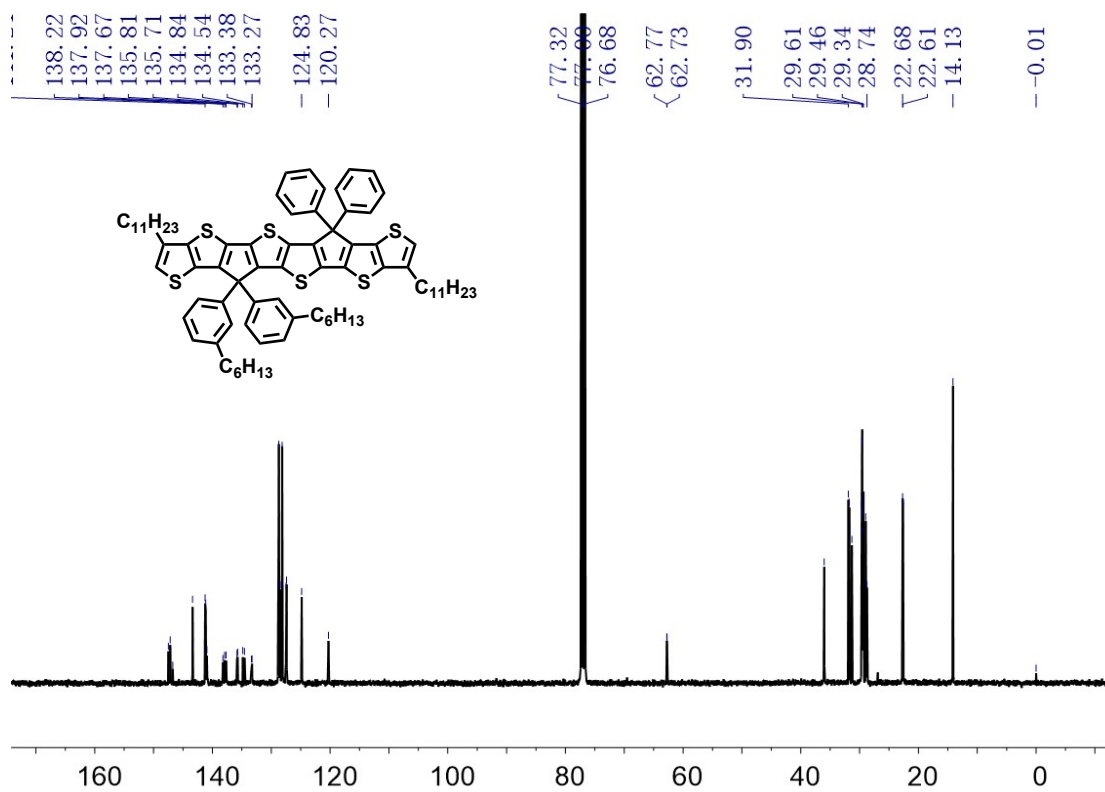


Fig. S8 ¹³C NMR spectrum of compound 4.

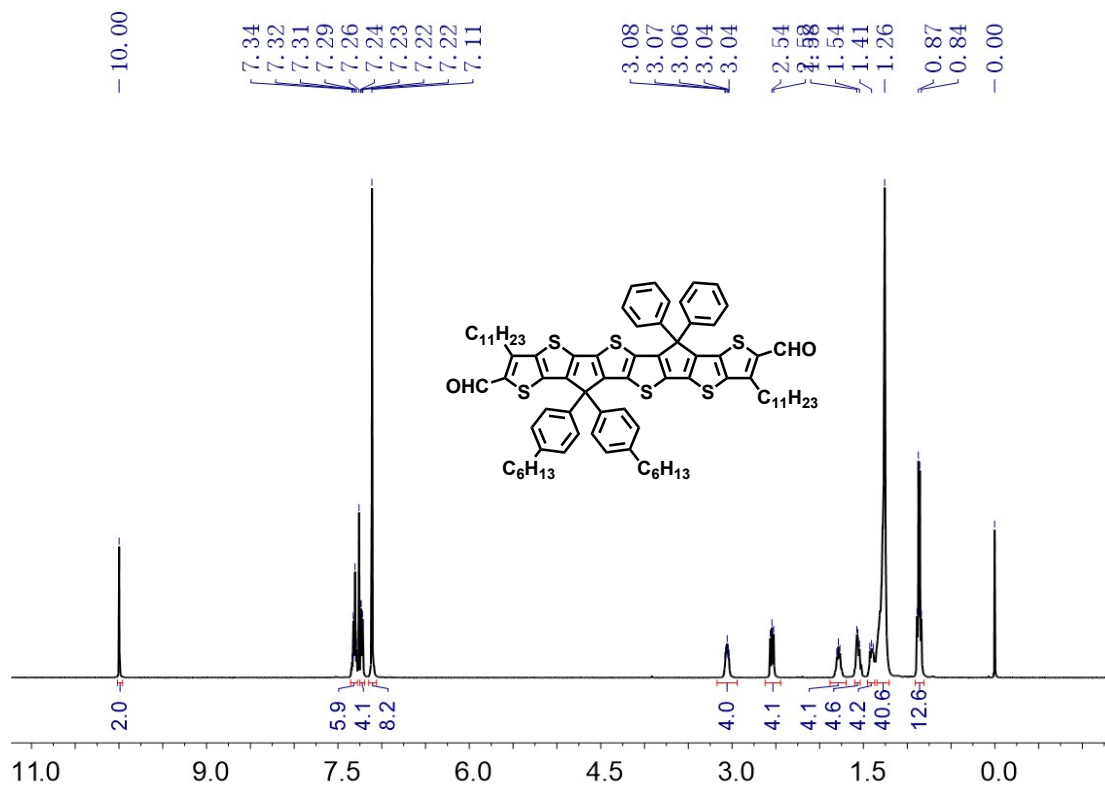


Fig. S9 ¹H NMR spectrum of compound 5.

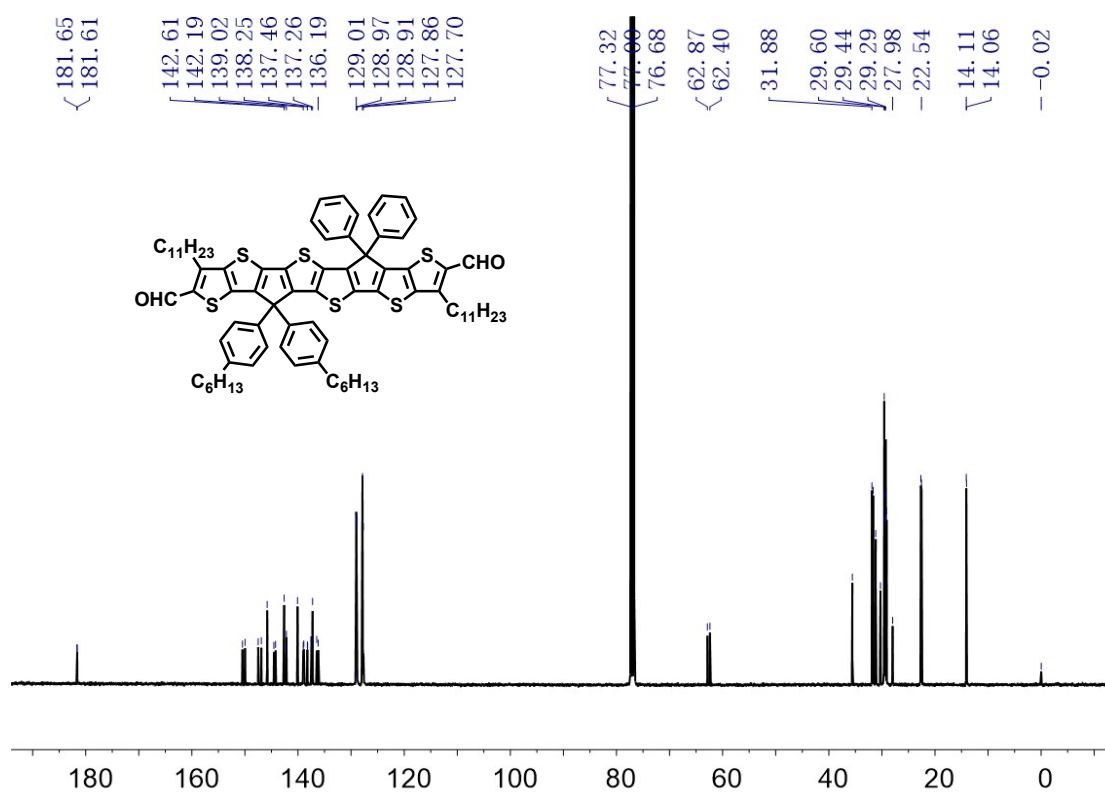


Fig. S10 ¹³C spectrum of compound 5.

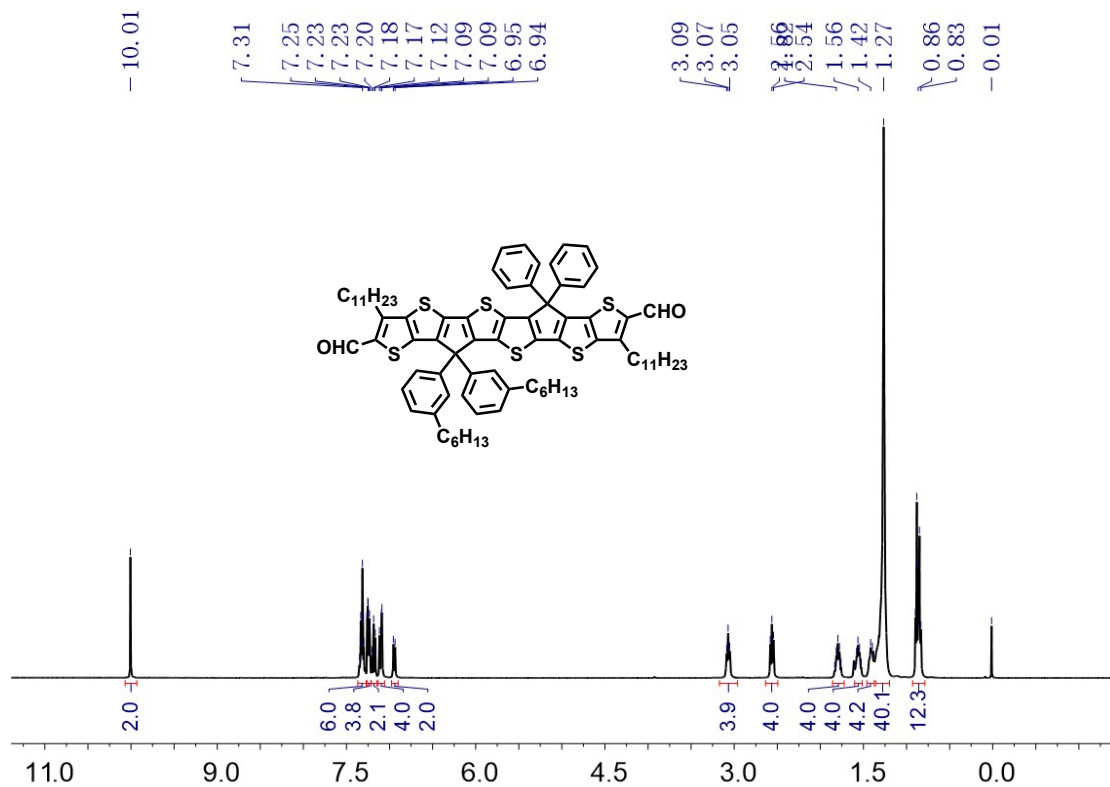


Fig. S11 1H NMR spectrum of **compound 6**.

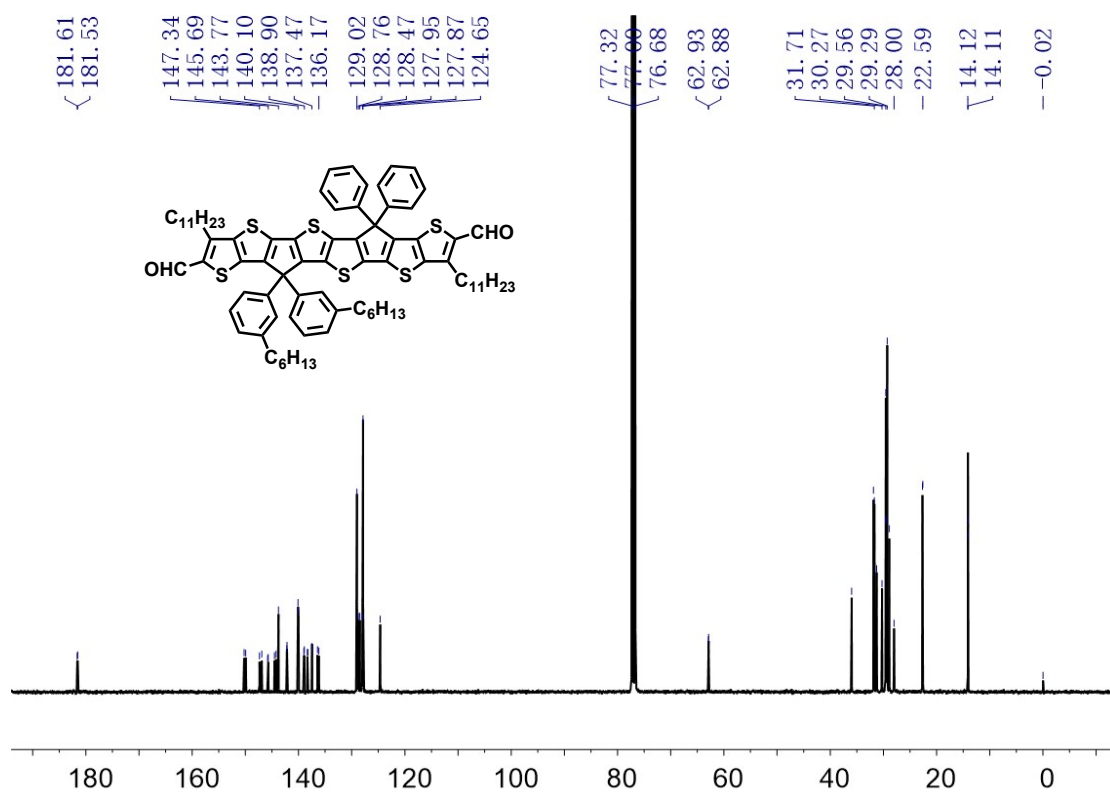


Fig. S12 ^{13}C NMR spectrum of **compound 6**.

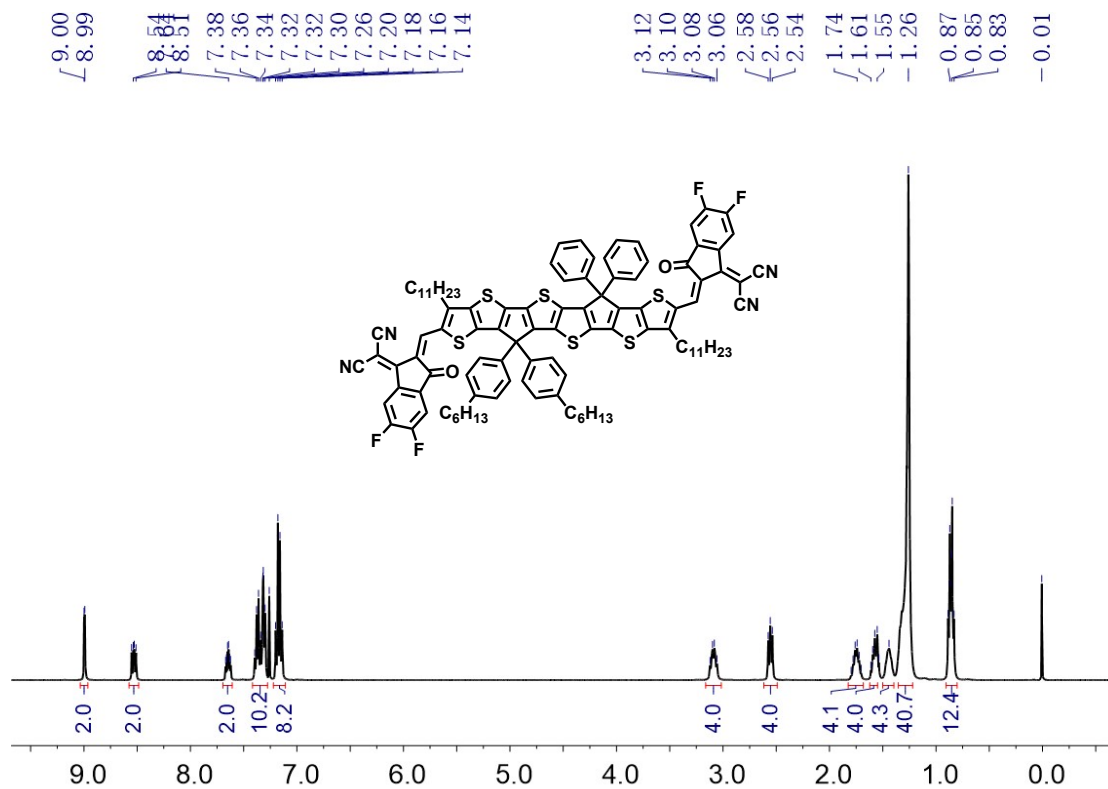


Fig. S13 ¹H NMR spectrum of A1.

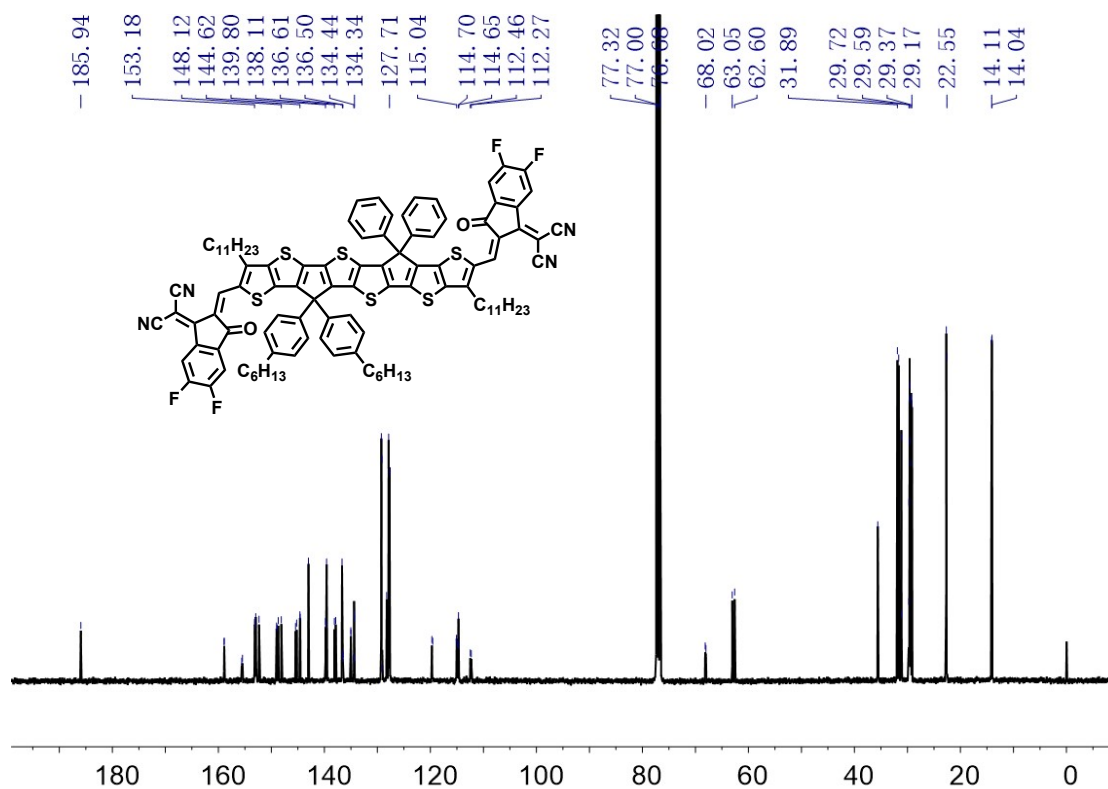


Fig. S14 ¹³C NMR spectrum of A1.

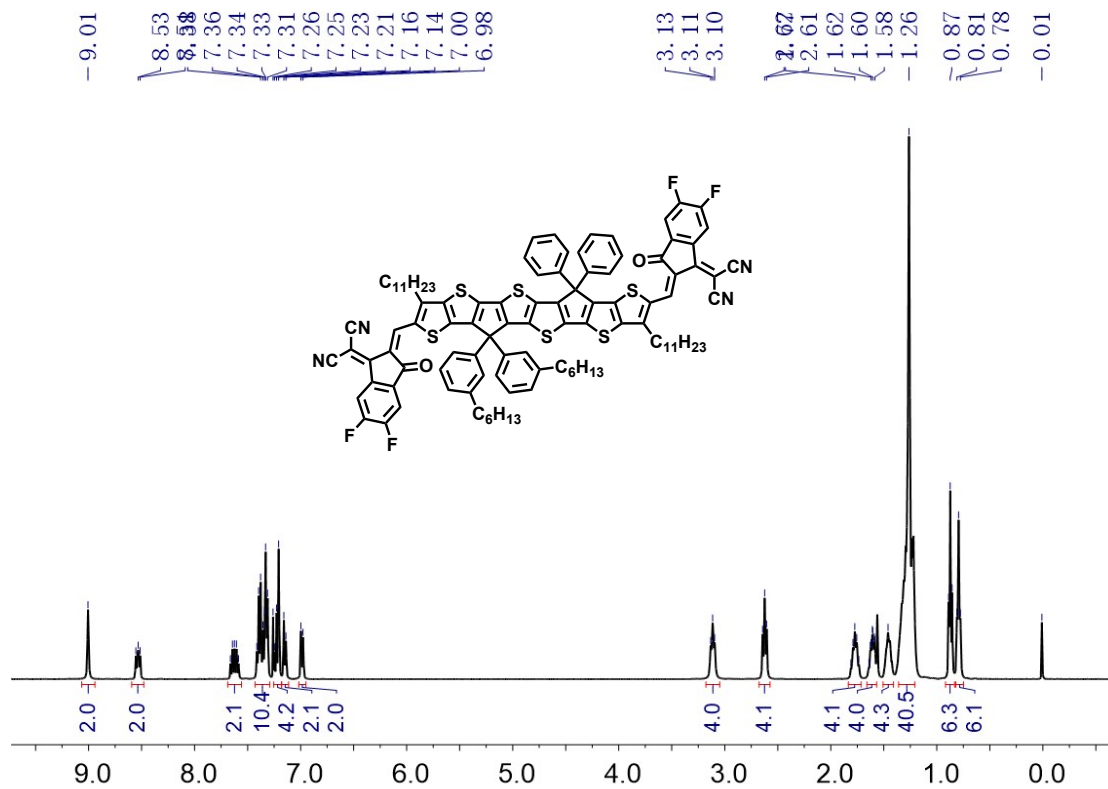


Fig. S15 ¹H NMR spectrum of A2.

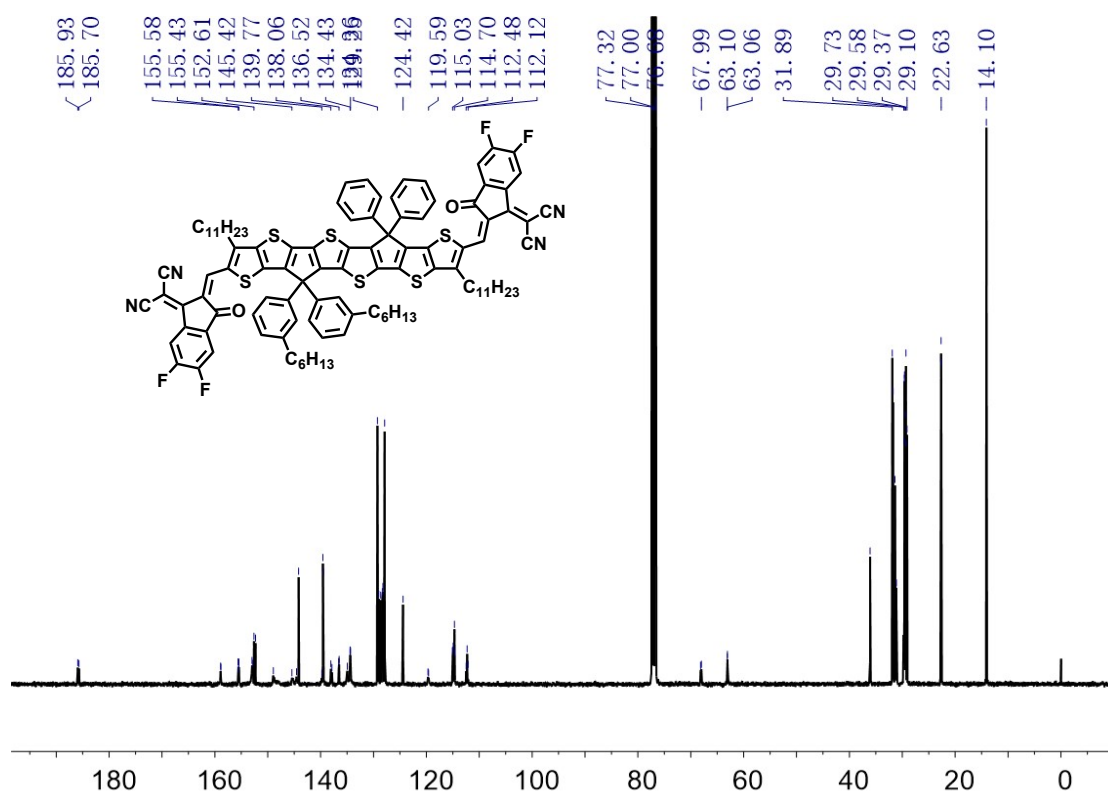


Fig. S16 ¹³C NMR spectrum of A2.

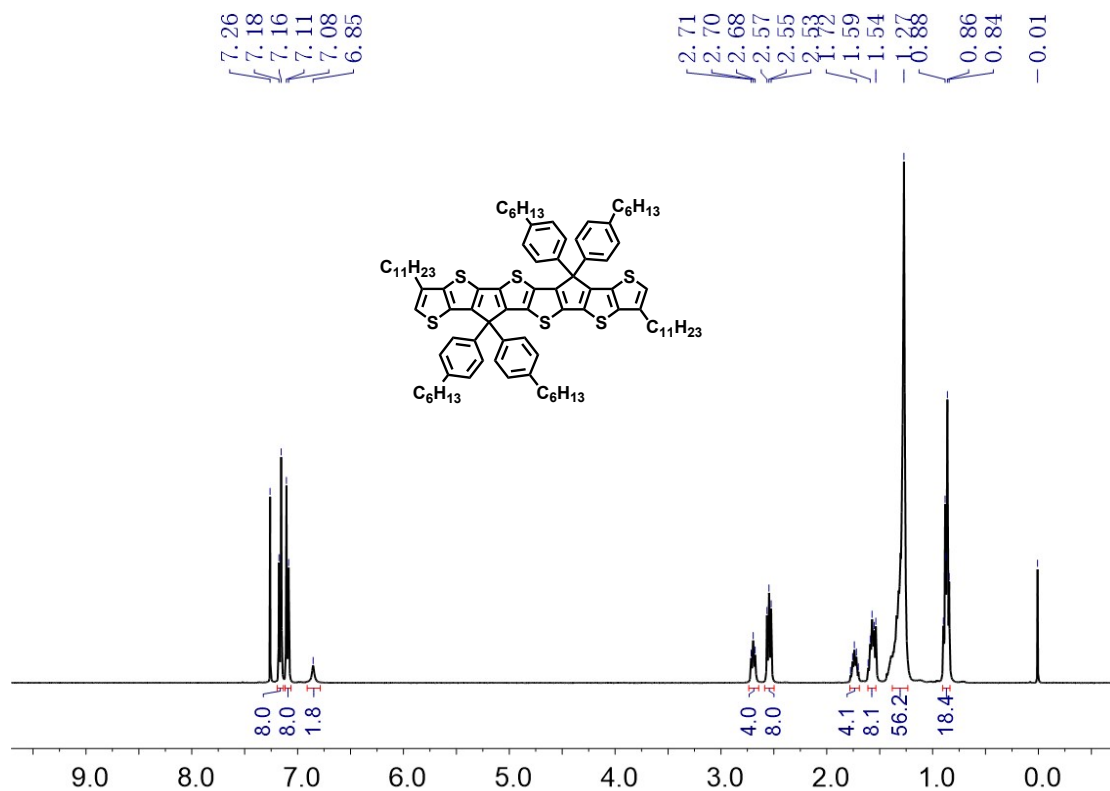


Fig. S17 ¹H NMR spectrum of **compound 7**.

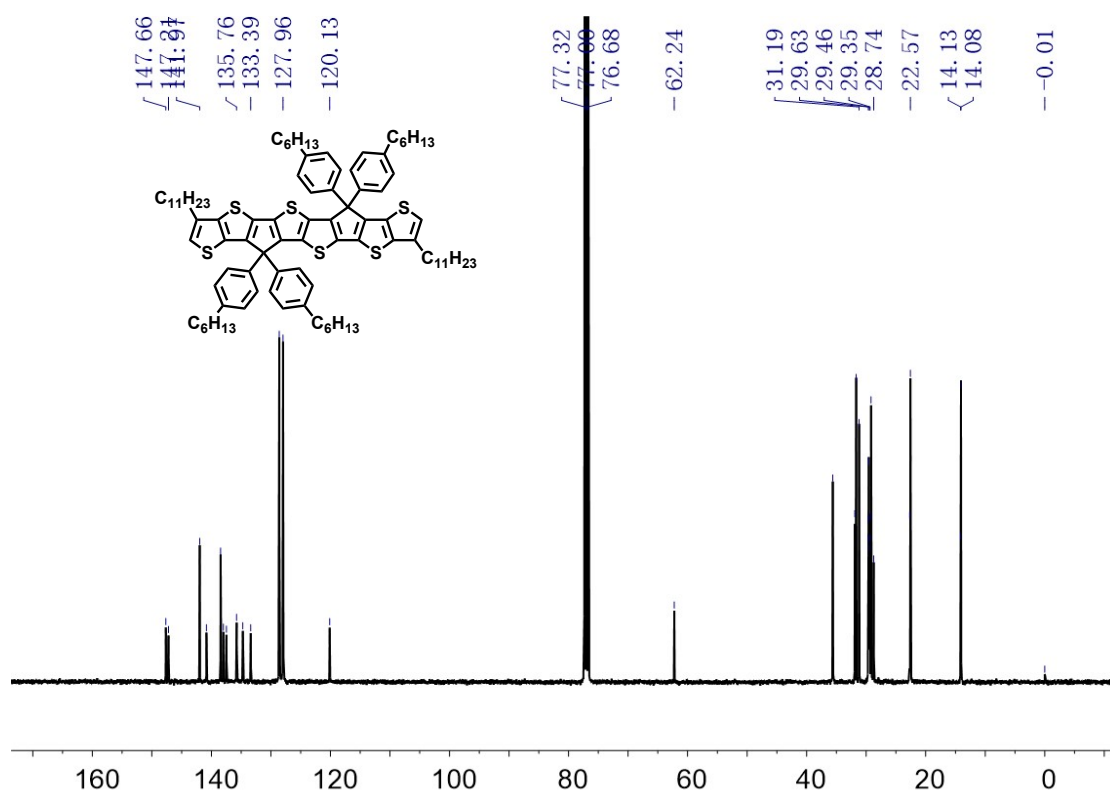


Fig. S18 ¹³C NMR spectrum of **compound 7**.

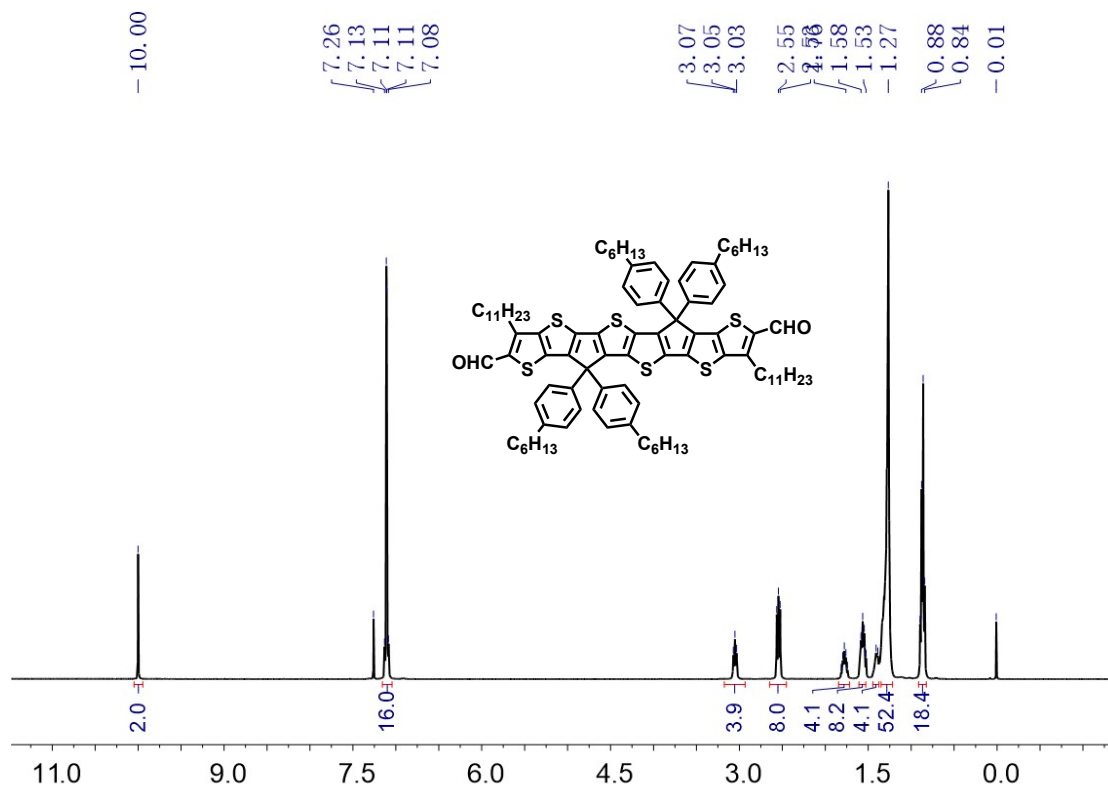


Fig. S19 ^1H NMR spectrum of compound 8.

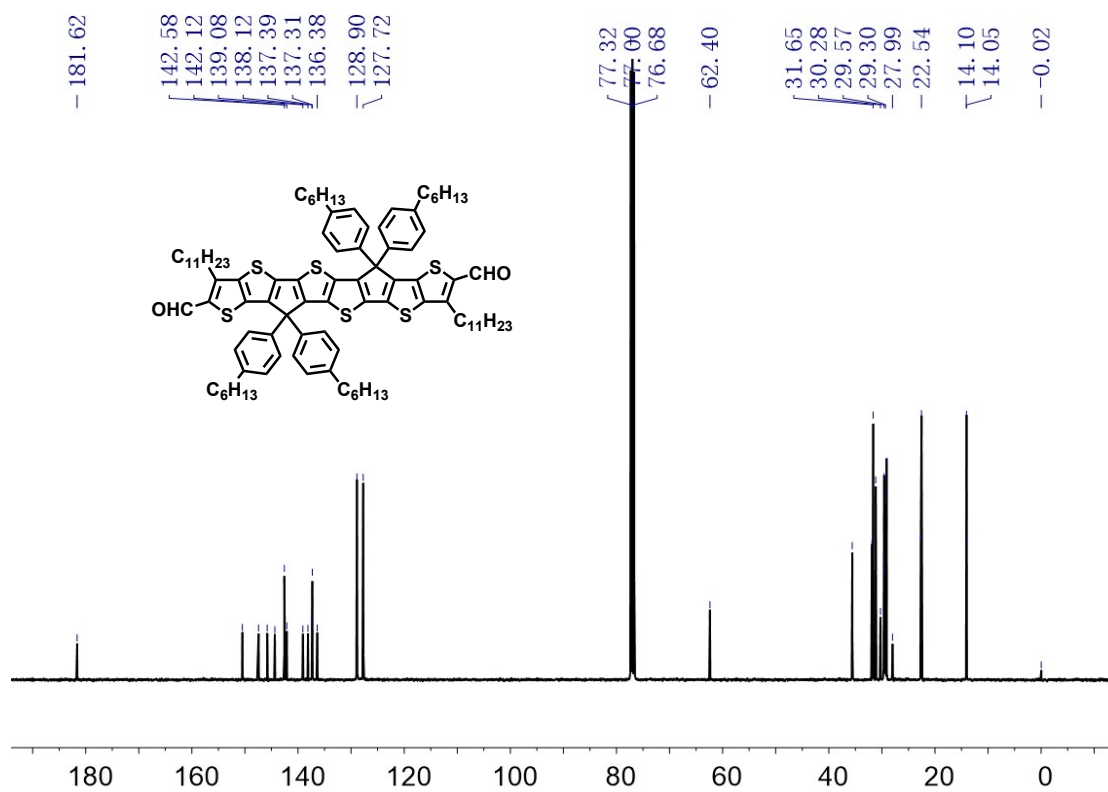


Fig. S20 ^{13}C NMR spectrum of compound 8.

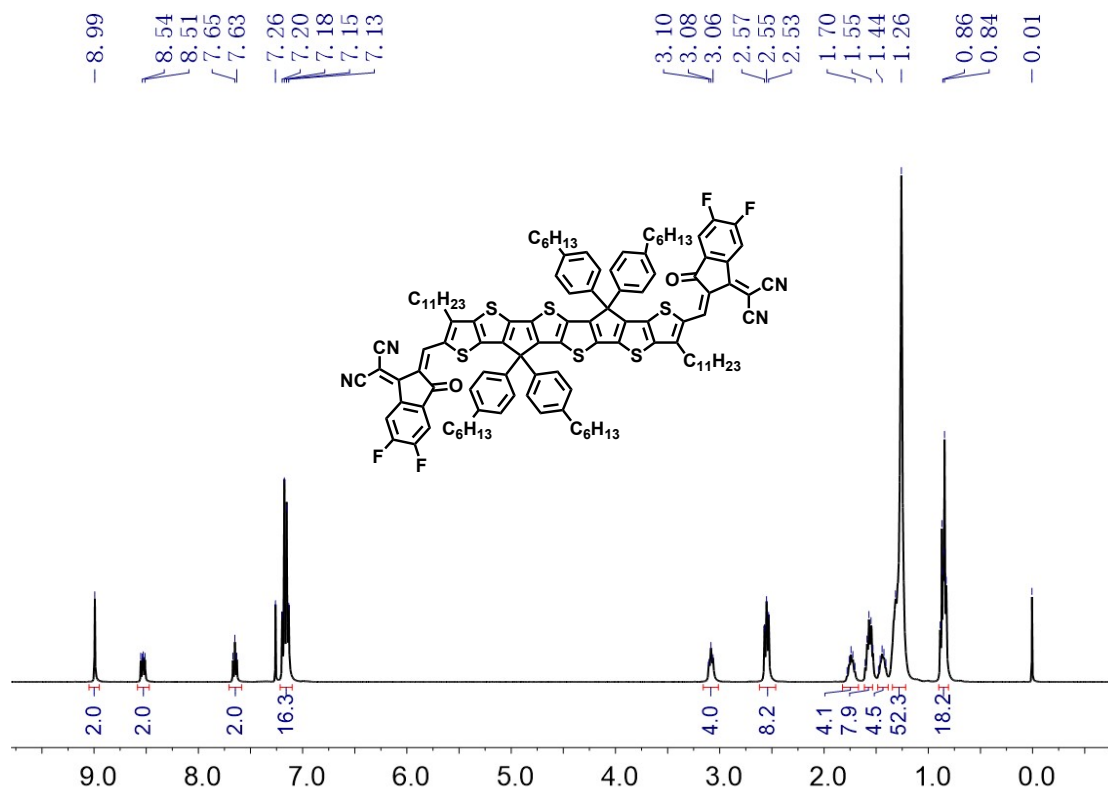


Fig. S21 ¹H NMR spectrum of S1.

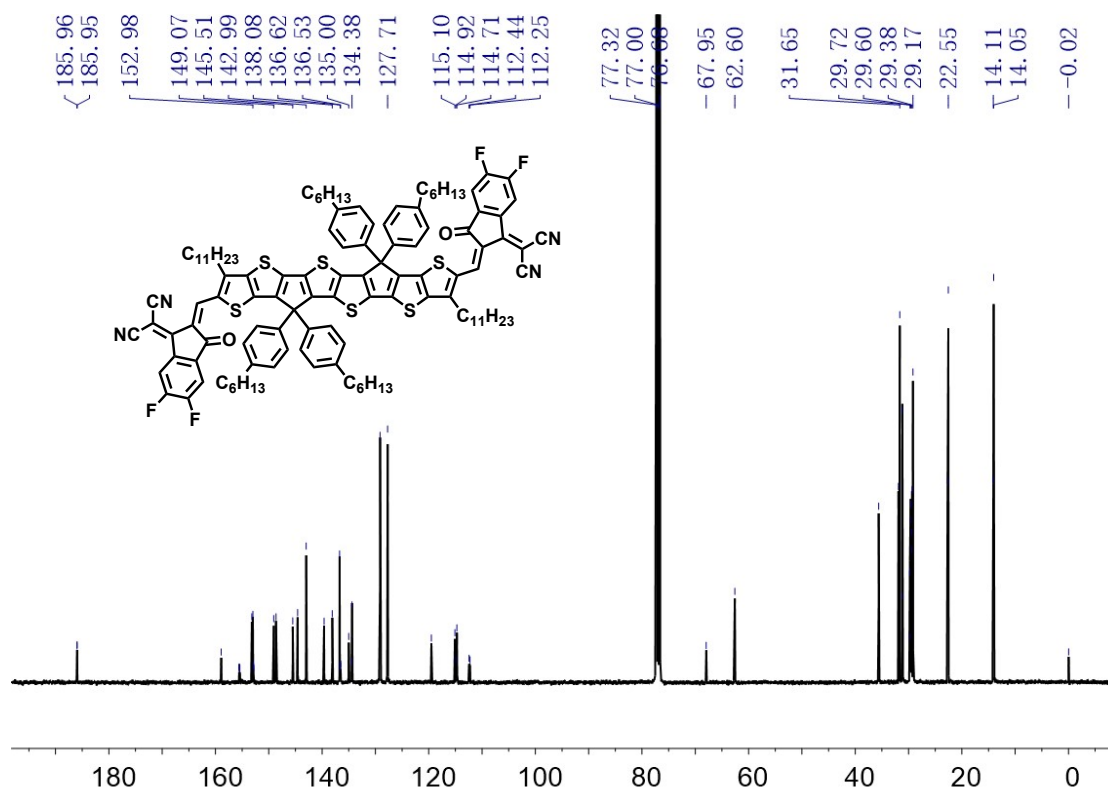


Fig. S22 ¹³C NMR spectrum of S1.

4. Solubility measurements

The solubility of materials was measured according to literature.^[3] The experimental procedure for A1 is given for illustration. A1 chloroform solutions with different concentrations (1 $\mu\text{g/mL}$, 2 $\mu\text{g/mL}$, 4 $\mu\text{g/mL}$ and 8 $\mu\text{g/mL}$) were prepared. The absorption spectra of the solutions were measured (**Fig. S23a**). A linear correlation between the concentration and the absorbance (@787nm) was found, agreeing well with Beer-Lambert law (**Fig. S23b**). Then, a saturated solution of A1 in chloroform was prepared. The solution was diluted 30000 times. The absorption spectrum of the diluted solution was measured. With the aid of **Fig. S23b**, the concentration of the diluted solution was found to be 4.98 $\mu\text{g/mL}$. Finally, the solubility of A1 was calculated to be 149 mg/mL ($4.98 \times 30000 \mu\text{g/mL}$). The solubility for A2 and S1 were measured similarly.

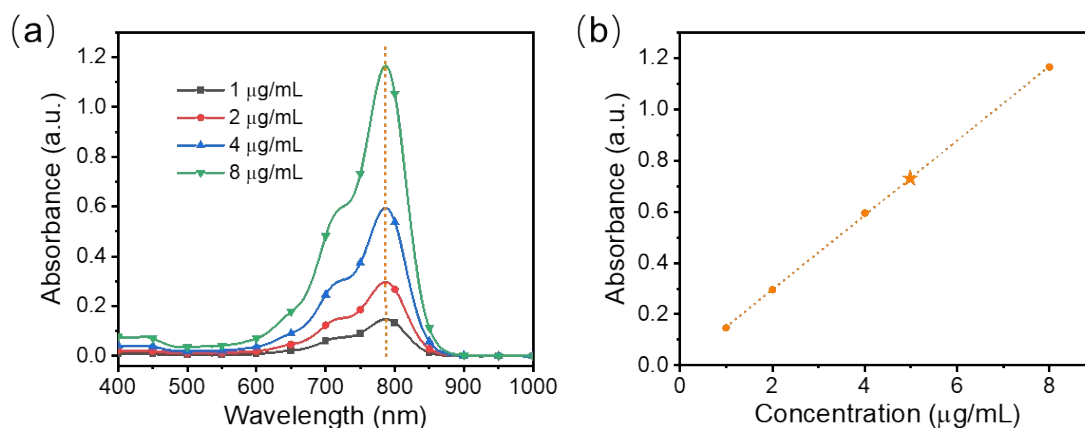


Fig. S23 (a) Absorption spectra for A1 solution with different concentrations; (b) the absorbance-concentration plot.

Table S1 The solubility of acceptors in CHCl_3 at room temperature.

Acceptor	A1	A2	S1
Solubility (mg/mL)	149	113	166

5. XRD

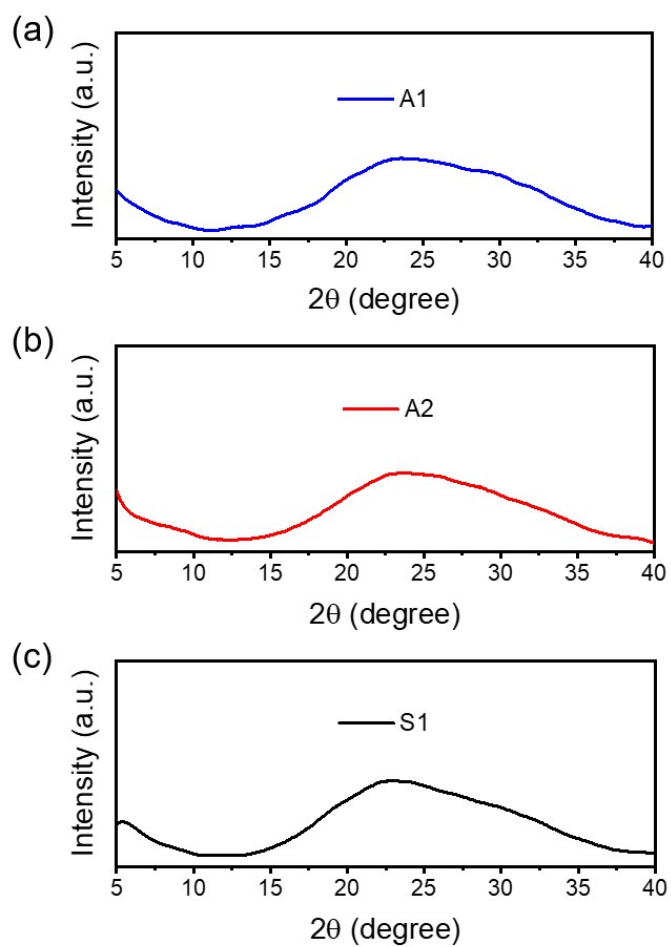


Fig. S24 XRD profiles for pure A1 (a), A2 (b) and S1 (c) films.

Table S2 XRD data for the π - π stacking diffraction peak.

Films	2θ	d -spacing
A1	23.5°	3.78 Å
A2	23.6°	3.77 Å
S1	22.8°	3.90 Å

6. CV

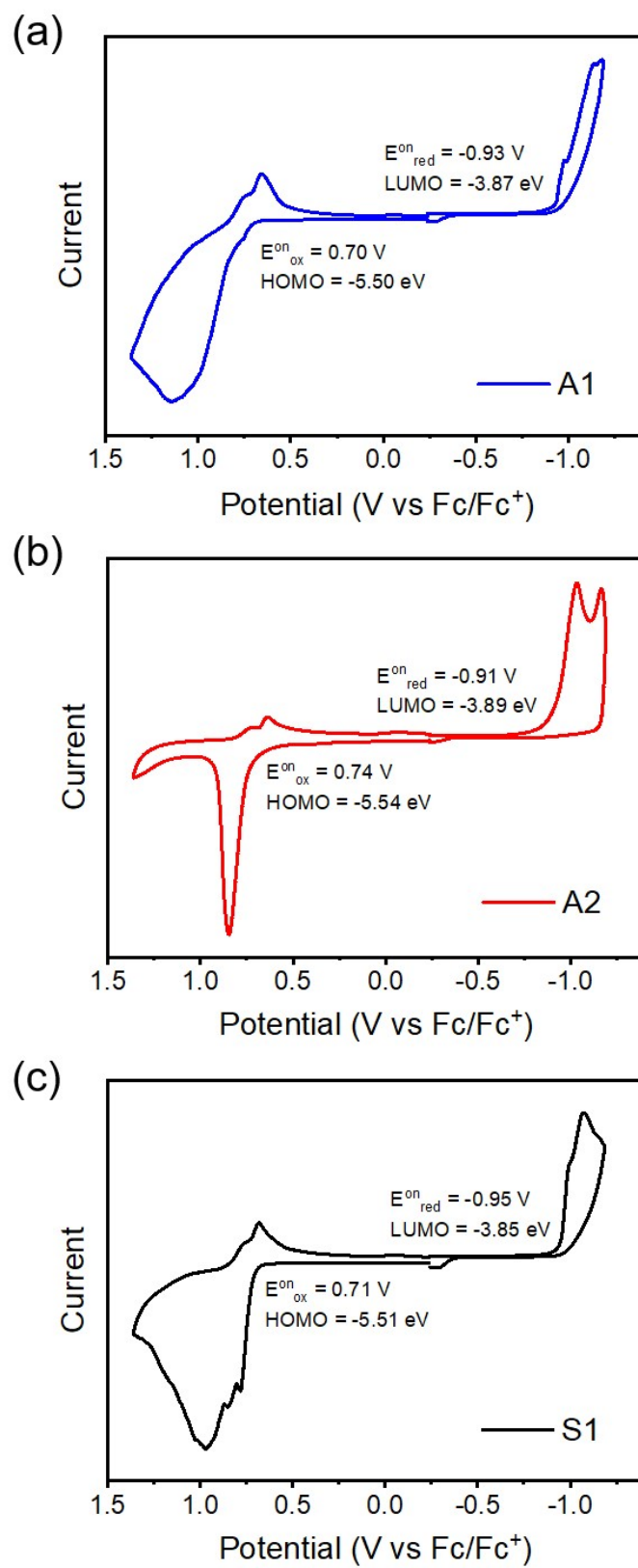


Fig. S25 Cyclic voltammograms for A1 (a), A2 (b) and S1 (c).

7. Device fabrication and measurements

Conventional solar cells

Indium-doped tin oxide (ITO) patterned glass substrate was cleaned by sequential treatment with detergent, deionized water, acetone and isopropanol in an ultrasonic bath for 20 min, respectively. The cleaned ITO glass was sent to UV-ozone treatment for 15 min. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 25 s). PEDOT:PSS substrates were dried at 150 °C for 15 min. An active blend solution (L1-S:acceptor in CF) was spin-coated onto PEDOT:PSS. PDIN (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Ag (~80 nm) was evaporated onto PDIN through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm². The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm²). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by the National Institute of Metrology (NIM). The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Al. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 25 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A blend solution of L1-S:acceptor in CF was spin-coated onto PEDOT:PSS layer. Finally, MoO₃ (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is ZnO/active layer/PDIN/Al. The ZnO precursor sol-gel was obtained from stirring the solution of 1.0 g Zn(CH₃COO)₂·2H₂O in 10 mL ethylene glycol monomethyl ether and 275 μL ethylenediamine. The ZnO films were prepared by spin-coating the ZnO precursor onto ITO glass followed by annealing at 200 °C for 20 min in atmosphere. Then, a pure acceptor or an active blend (L1-S:acceptor) solution in CF was spin-coated onto PEDOT:PSS layer. PDIN (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Finally, Al (~100 nm) was evaporated onto PDIN layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

8. SCLC measurements for pure A1, A2 and S1 films

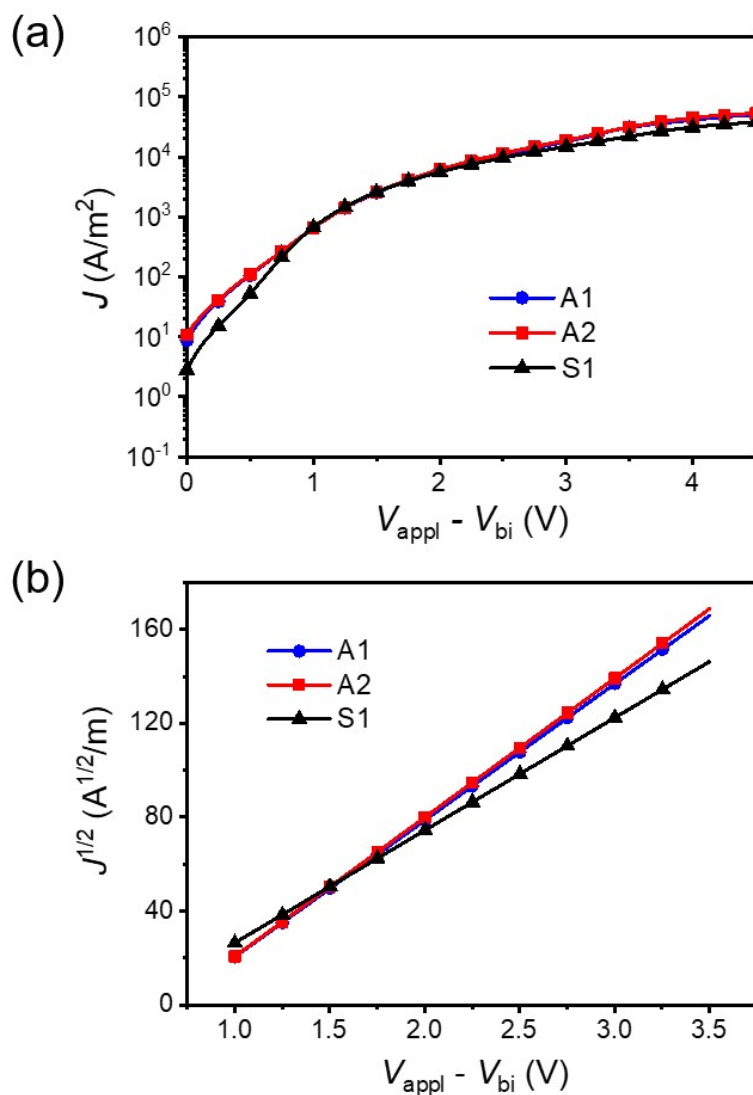


Fig. S26 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the electron-only devices (in dark). The thicknesses for A1, A2 and S1 films are 82 nm, 89 nm and 90 nm, respectively.

Table S3 Electron mobility for A1, A2 and S1.

Films	μ_e [cm ² /Vs]
A1	6.22×10^{-4}
A2	8.33×10^{-4}
S1	5.57×10^{-4}

9. Optimization of device performance

Table S4 Optimization of D/A ratio for L1-S:A1 solar cells.^a

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.6	0.820	24.10	55.2	10.91 (10.67) ^b
1:1	0.819	24.48	62.3	12.49 (12.37)
1:1.4	0.805	22.60	66.4	12.07 (11.98)
1:1.8	0.809	23.79	62.2	11.97 (11.34)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of the active layer thickness for L1-S:A1 solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
158	0.808	23.74	55.7	10.69 (10.48) ^b
121	0.814	24.44	61.6	12.26 (12.05)
98	0.819	24.48	62.3	12.49 (12.37)
78	0.822	22.97	64.6	12.21 (12.03)

^aD/A ratio: 1:1 (w/w); blend solution: 12.5 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of CN content for L1-S:A1 solar cells.^a

CN [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.819	24.48	62.3	12.49 (12.37) ^b
0.5	0.816	23.51	66.2	12.70 (12.39)
0.7	0.814	24.49	66.5	13.25 (13.06)
0.9	0.812	23.82	65.8	12.74 (12.47)

^aD/A ratio: 1:1 (w/w); blend solution: 12.5 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of D/A ratio for L1-S:A2 solar cells.^a

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.6	0.808	25.36	58.5	11.98 (11.75) ^b
1:1	0.806	25.69	67.3	13.93 (13.50)
1:1.4	0.805	23.88	67.5	12.96 (12.82)
1:1.8	0.800	22.36	66.9	11.94 (11.68)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of the active layer thickness for L1-S:A2 solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
173	0.803	24.52	66.6	13.11 (12.91) ^b
143	0.806	25.69	67.3	13.93 (13.50)
112	0.807	23.62	68.1	12.98 (12.90)
75	0.811	22.49	66.4	12.11 (11.49)

^aD/A ratio: 1:1 (w/w); blend solution: 12.5 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S9 Optimization of CN content for L1-S:A2 solar cells.^a

CN [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.806	25.69	67.3	13.93 (13.50) ^b
0.3	0.813	25.42	68.0	14.05 (14.01)
0.5	0.800	25.09	71.9	14.43 (14.34)
0.7	0.793	25.20	71.0	14.19 (14.08)

^aD/A ratio: 1:1 (w/w); blend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S10 Optimization of D/A ratio for L1-S:S1 solar cells.^a

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.6	0.841	21.65	59.7	10.87 (10.78) ^b
1:1	0.833	22.60	64.8	12.20 (12.08)
1:1.4	0.831	21.57	66.8	11.99 (11.67)
1:1.8	0.833	19.75	66.6	10.96 (10.69)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells

Table S11 Optimization of the active layer thickness for L1-S:S1 solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
164	0.827	22.78	62.8	11.84 (11.54) ^b
139	0.831	22.22	64.5	11.91 (11.86)
123	0.833	22.60	64.8	12.20 (12.08)
100	0.832	21.88	65.6	11.95 (11.80)
72	0.833	21.68	65.8	11.88 (11.69)

^aD/A ratio: 1:1 (w/w); blend solution: 12.5 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S12 Optimization of CN content for L1-S:S1 solar cells.^a

CN [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.833	22.60	64.8	12.20 (12.08) ^b
0.3	0.830	22.99	65.1	12.42 (12.30)
0.5	0.828	23.26	66.5	12.82 (12.66)
0.7	0.827	23.66	65.3	12.77 (12.49)

^aD/A ratio: 1:1 (w/w); blend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

10. SCLC measurements for L1-S:A1, L1-S:A2 and L1-S:S1 blend films

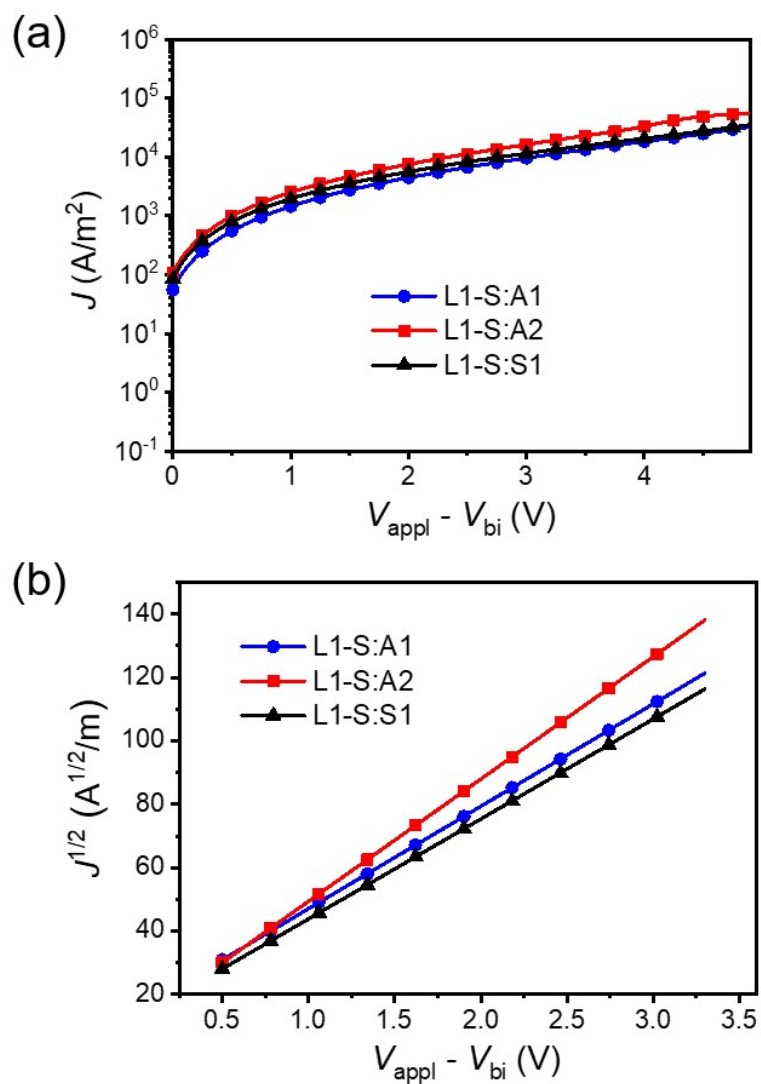


Fig. S27 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the hole-only device (in dark). The thickness for L1-S:A1 (1:1), L1-S:A2 (1:1) and L1-S:S1 (1:1) blend films is 116 nm, 106 nm and 117 nm.

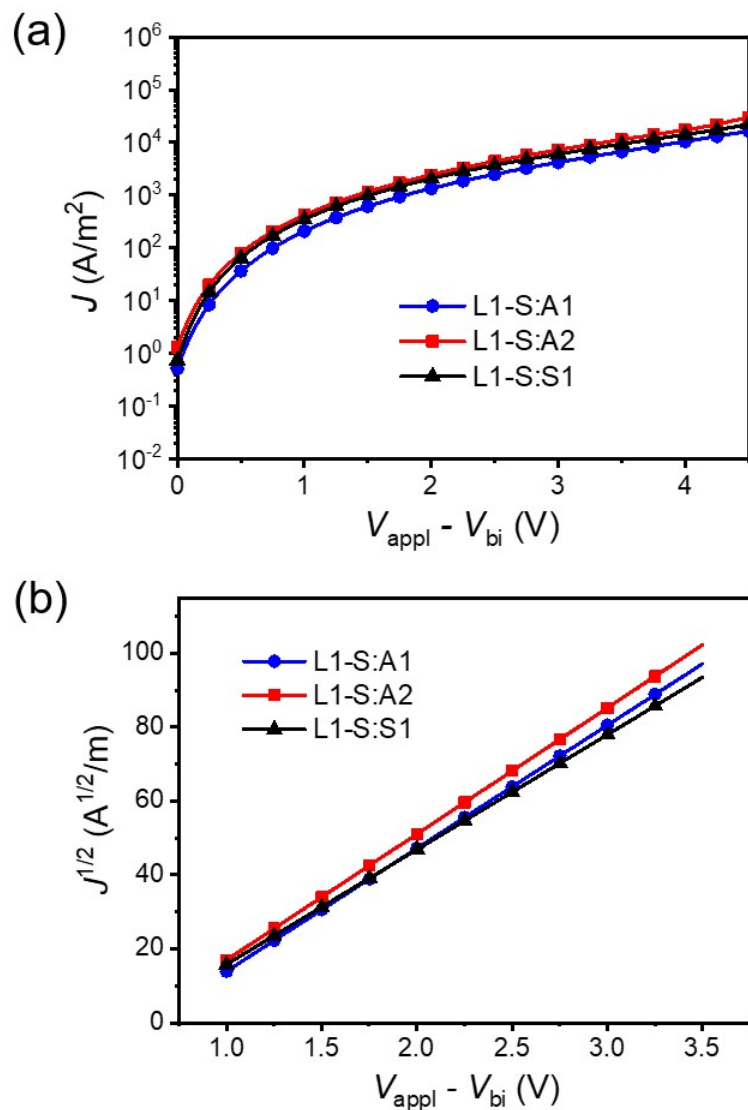


Fig. S28 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the electron-only devices (in dark). The thickness for L1-S:A1 (1:1), L1-S:A2 (1:1) and L1-S:S1 (1:1) blend films is 143 nm, 142 nm and 128 nm.

Table S13 Hole and electron mobility for L1-S:A1, L1-S:A2 and L1-S:S1 blend films.

Films	μ_h [cm ² /Vs]	μ_e [cm ² /Vs]	μ_h/μ_e
L1-S:A1	5.11×10^{-4}	4.23×10^{-4}	1.21
L1-S:A2	6.09×10^{-4}	5.50×10^{-4}	1.11
L1-S:S1	5.40×10^{-4}	4.61×10^{-4}	1.17

11. Surface free energy measurements

The experiments were performed on a KRUSS DSA100S contact angle goniometer. Droplets of two different liquids, water and ethylene glycol (EG) were cast onto the films with the drop size of 2 μ L. Contact angle images were taken at 1 s after the whole droplet was deposited onto the sample surface. The surface free energy of each sample was calculated by:

$$\begin{aligned}\gamma_{\text{water}}(\cos\theta_{\text{water}} + 1) &= 2(\gamma_{\text{sample}}^{\text{d}}\times\gamma_{\text{water}}^{\text{d}})^{1/2} + 2(\gamma_{\text{sample}}^{\text{p}}\times\gamma_{\text{water}}^{\text{p}})^{1/2} \\ \gamma_{\text{EG}}(\cos\theta_{\text{EG}} + 1) &= 2(\gamma_{\text{sample}}^{\text{d}}\times\gamma_{\text{EG}}^{\text{d}})^{1/2} + 2(\gamma_{\text{sample}}^{\text{p}}\times\gamma_{\text{EG}}^{\text{p}})^{1/2} \\ \gamma_{\text{sample}}^{\text{total}} &= \gamma_{\text{sample}}^{\text{d}} + \gamma_{\text{sample}}^{\text{p}}\end{aligned}$$

where θ is the droplet contact angle on the sample film; $\gamma_{\text{sample}}^{\text{total}}$ is the surface free energy of the sample, which is equal to the sum of the dispersion ($\gamma_{\text{sample}}^{\text{d}}$) and polarity ($\gamma_{\text{sample}}^{\text{p}}$) components; $\gamma_{\text{water}} = 72.8 \text{ mJ/m}^2$, $\gamma_{\text{water}}^{\text{d}} = 21.8 \text{ mJ/m}^2$, $\gamma_{\text{water}}^{\text{p}} = 51.0 \text{ mJ/m}^2$, $\gamma_{\text{EG}} = 48.0 \text{ mJ/m}^2$, $\gamma_{\text{EG}}^{\text{d}} = 29.0 \text{ mJ/m}^2$, $\gamma_{\text{EG}}^{\text{p}} = 19.0 \text{ mJ/m}^2$.^[4,5]

Table S14 The contact angles and surface free energy parameters.

Film	Contact Angle ($^{\circ}$)		$\gamma_{\text{sample}}^{\text{d}}$ [mJ/m ²]	$\gamma_{\text{sample}}^{\text{p}}$ [mJ/m ²]	$\gamma_{\text{sample}}^{\text{total}}$ [mJ/m ²]
	Water	Ethylene glycol			
L1-S	100.2	73.6	24.28	0.94	25.2
A1	88.6	63.6	22.07	4.62	26.6
A2	88.0	62.1	23.29	4.49	27.7
S1	91.1	63.3	26.26	2.71	28.9

12. TEM

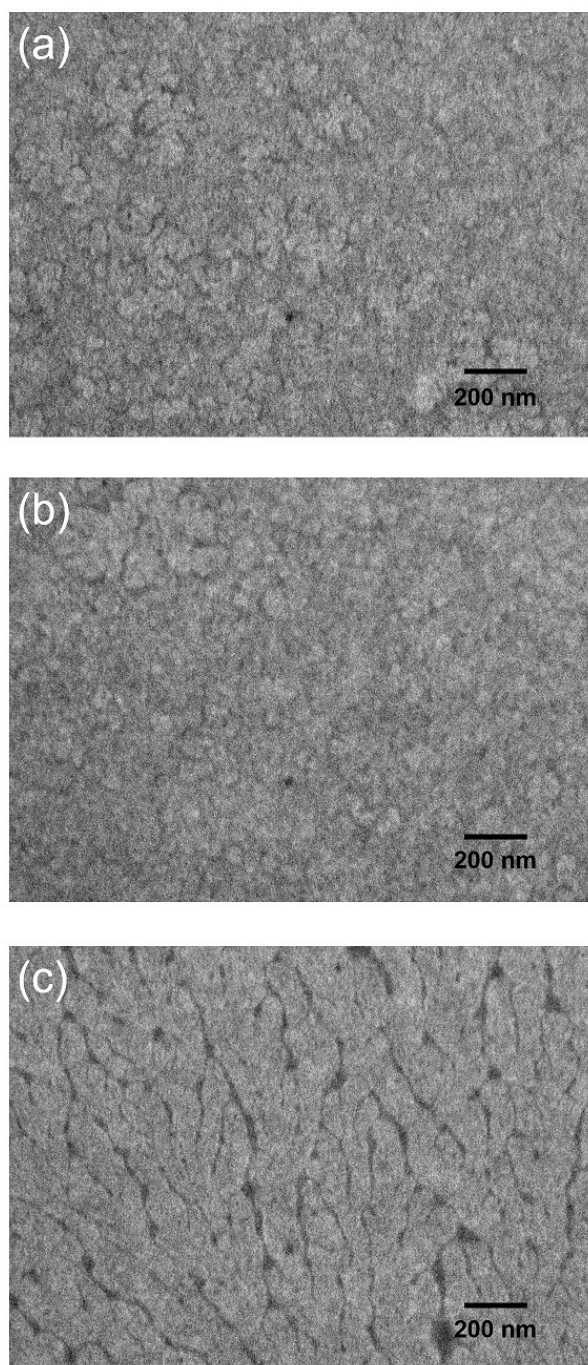


Fig. S29 TEM images for (a) L1-S:A1, (b) L1-S:A2 and (c) L1-S:S1 blend films.

References

- [1] T. Kunz and P. Knochel, Selective Multiple Magnesiations of the Thieno[3,2-b]thiophene Scaffold, *Chem. Eur. J.*, 2011, **17**, 866-872.
- [2] K. Jiang, Q. Wei, J. Y. L. Lai, Z. Peng, H. K. Kim, J. Yuan, L. Ye, H. Ade, Y. Zou and H. Yan, Alkyl chain tuning of small molecule acceptors for efficient organic solar cells, *Joule*, 2019, **3**, 3020-3033.
- [3] N. Sivaraman, R. Dhamodaran, I. Kaliappan, T. G. Srinivasan, P. R. V. Rao and C. K. Mathews, Solubility of C₆₀ in organic solvents, *J. Org. Chem.*, 1992, **57**, 6077.
- [4] D. K. Owens and R. C. Wendt, Estimation of the Surface Free Energy of Polymers, *J. Appl. Polym. Sci.*, 1969, **13**, 1741.
- [5] M.-C. Michalski, J. Hardy and B. J. V. Saramago, On the Surface Free Energy of PVC/EVA Polymer Blends: Comparison of Different Calculation Methods, *J. Colloid Interface Sci.*, 1998, **208**, 319.