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Annealing-Free Efficient Organic Solar Cells via Alkylbenzene Side-Chain Strategy of Small-Molecule Electron Acceptor

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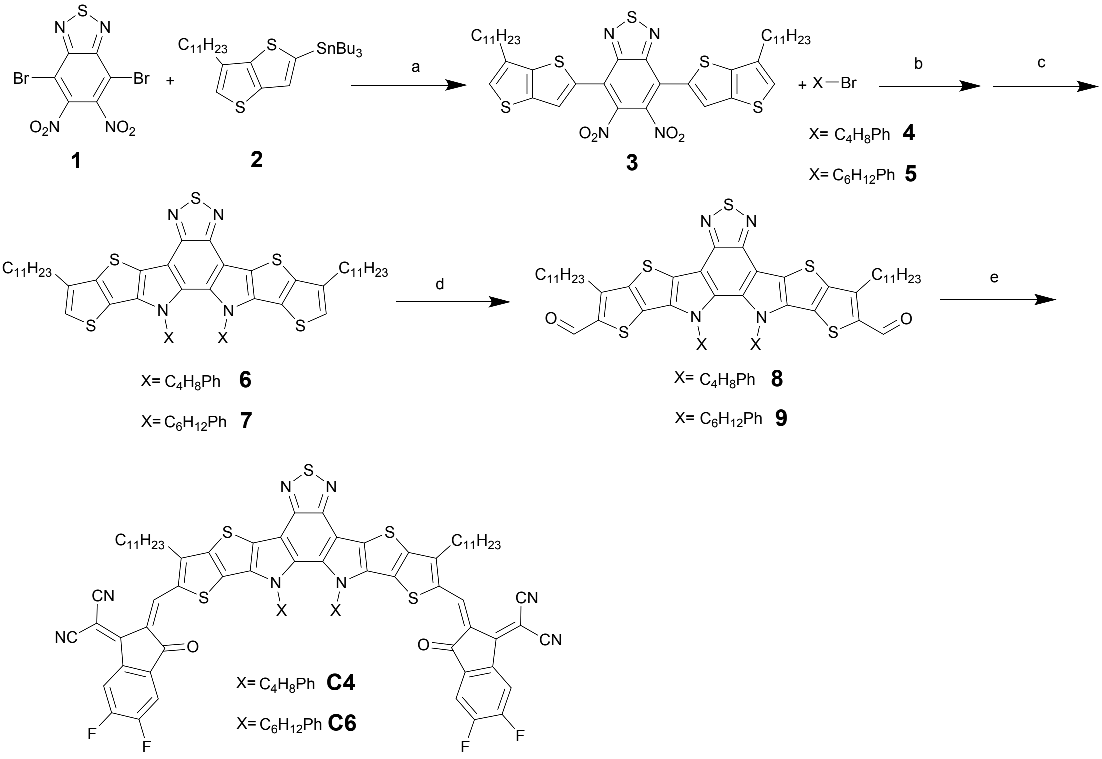
Experiment Section

Materials: poly[4,8-bis(5-(2-ethylhexyl)4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene-alt1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-c:4,5-c']-dithiophene-4,8-dione] (PM6) was purchased from Solarmer Materials (Beijing) Inc and were used without any further purification.

Other chemicals were purchased from J&K Scientific.



Synthesis Procedure of C4 and C6

Compound 3

5,6-dinitro-4,7-bis(6-undecylthieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazole(3)

4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole **(1)** (2.70g, 7.03mmol), tributyl(6-undecylthieno[3,2-b]thiophen-2-yl)stannane **(2)** (10.00g,17.14mmol), $Pd(PPh_3)_4$ (0.30g, 0.43mmol) and Toluene (80ml) put into a 250ml flask filled with argon. The mixture stirred at 80℃ for 8h, After removing the solvent, the resdue was extracted by dichloromethane and H_2O three times, and the organic phases were combined. After remove the solvent under vacuum, the residue was purified by chromatography on silica gel by using petroleum ether/CH_2Cl_2 (6:1, v/v) to give compound **3** (5.20g) as red solid in a yield of 91%. ^{1}H NMR (400MHz, CDCl3) δ 7.71 (2 H, s), 7.18 (2 H, s), 2.82 – 2.73 (4 H, m), 1.79 (4 H, p, J 7.6), 1.43 – 1.35 (6 H, m), 1.27 (26 H, d, J 6.3), 0.91 – 0.84 (6 H, m). ^{13}C NMR (101 MHz, CDCl3) δ: 152.21, 144.27, 141.79, 139.09, 135.12, 130.08, 125.17, 124.12, 124.11, 121.42, 31.91, 29.83, 29.65, 29.63, 29.57, 29.38, 29.34, 28.58, 28.27, 26.77, 22.68, 17.30, 14.11, 13.58. MS (MALDI-TOF): m/z 811.25 (M+)

Compound 6 and 7

Dissolve the mixture of compound **3** and PPh_3 in the flask in 1,2-dichlorobenzene, Then degas the flask. After stirred at reflux under argon for 48h. The mixture pour into water, extracted by dichloromethane three times. The organic layer was dried over $MgSO_4$ and filter. After removing the solvent, the residue solid, compound **4** or **5**, KI, K_2CO_3 and DMF was added into flask under argon, The mixture was stirred at 100℃ for 36h. After remove the solvent, the residue exacted with ethyl acetate and H_2O, then the organic layer dried over $MgSO_4$ and filter. The filtrate purified with column chromatography on silica gel using dichloromethane/petroleum ether (1/10, v/v) as the eluent to give a red solid **6** or **7**

12,13-bis(4-phenylbutyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5'] thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole (6)

Compound **3** (1.00g, 1.23mmol) and PPh_3 (3.23g 12.33mmol) were solve in 1,2-dichlorobenzene(20ml) and usd for reaction to obtain an intermediate, The intermediate, compound **4** (1.31g, 6.16mmol), KI (81.86mg,0.50mmol), K_2CO_3 (1.70g, 12.33mmol) and 20ml DMF was used for reaction. Compound **6** (0.40g) was obtained as red solid in a yield of 32%. ^{1}H NMR (400MHz, CDCl3) δ7.17 – 7.00 (8 H, m), 6.96 – 6.89 (4 H, m), 4.57 (4 H, t, J 7.4), 2.84 (4 H, t, J 7.7), 2.47 (4 H, t, J 7.4), 1.87 (8H, d, J 7.9), 1.42 (16 H, dt, J 22.5, 7.5), 1.29 (20 H, s), 0.93 – 0.86 (6 H, m). ^{13}C NMR (101 MHz, CDCl3) δ: 147.52, 142.21, 141.21, 137.27, 136.94, 130.58, 128.26, 128.20, 125.87, 123.25, 122.62, 119.27, 111.86, 77.22, 50.57, 34.95, 31.93, 29.98, 29.69, 29.64, 29.62, 29.51, 29.47, 29.36, 28.82, 27.90, 22.69, 14.12. MS (MALDI-TOF): m/z 1011.45 (M+)

12,13-bis(6-phenylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5'] thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole (7)

Compound **3** (1.00g, 1.23mmol) and PPh_3 (3.23g 12.33mmol) were solve in 1,2-dichlorobenzene (20ml) and usd for reaction to obtain an intermediate, The intermediate, compound **5** (1.49g, 6.16mmol), KI (81.86mg,0.50mmol), K_2CO_3 (1.70g, 12.33mmol) and 20ml DMF was used for reaction. Compound **7** (0.42g) was obtained as red solid in a yield of 32%. ^{1}H

NMR (400MHz, CDCl3) δ7.25 – 7.18 (4 H, m), 7.17 – 7.10 (2 H, m), 7.08 – 7.02 (4 H, m), 7.01 (2 H, s), 4.58 (4 H, t, J 7.6), 2.81 (4 H, t, J 7.7), 2.45 (4 H, t, J 7.7), 1.86 (8 H, p, J 7.5), 1.52 – 1.38 (12 H, m), 1.30 (24 H, d, J 6.0), 1.21 (8 H, dt, J 25.4, 6.0), 0.94 – 0.86 (6 H, m). ^{13}C NMR (101 MHz, CDCl3) δ: 147.48, 142.31, 142.18, 137.16, 136.93, 130.55, 128.30, 128.20, 125.61, 123.22, 122.60, 119.20, 111.77, 77.22, 50.77, 35.63, 31.94, 31.04, 30.67, 29.70, 29.65, 29.63, 29.52, 29.47, 29.37, 28.80, 28.57, 26.28, 22.70, 14.13. m/z 1067.52 (M+)

Compound 8 and 9

Compound **8** and **9** are easily synthesis by Vilsmeier-Haack reaction, Compound **6** or **7**, DMF were solve in CH_2Cl_2, POCl3 was added at 0℃, the mixture stirred for 2h. Then the mixture was heated to 85℃ for 8h , The ammonium intermediate was formed. Then quenched by cold sodium hydroxide solution. The mixture pour into water and exacted with CH_2Cl_2, the organic layer dried over $MgSO_4$ and filter, The filtrate purified with column chromatography on silica gel using dichloromethane/petroleum ether (1/1, v/v) as the eluent to supply an orange solid 8 or 9.

12,13-bis(4-phenylbutyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (8)

Compound **6** (0.3g,0.30mmol), 0.7ml DMF, 1.5ml $POCl_3$ and 20ml 1,2-Dichloroethanewas used for Vilsmeier-Haack reaction, compound **8** (0.24g) was obtained as an orange solid in a yield of 76%. ^{1}H NMR (400MHz, CDCl3) δ 10.14 (2 H, s), 7.15 – 7.09 (4 H, m), 7.08 – 7.03 (2 H, m), 6.95 – 6.89 (4 H, m), 4.52 (4 H, t, J 7.4), 3.18 (4 H, t, J 7.7), 2.49 (4 H, t, J 7.3), 2.00 – 1.78 (8 H, m), 1.52 – 1.18 (36 H, m), 0.93 – 0.84 (6 H, m). ^{13}C NMR (101 MHz, CDCl3) δ: 181.72, 147.29, 146.78, 143.17, 140.80, 136.95, 136.77, 131.76, 129.16, 128.30, 128.18, 127.21, 126.01, 112.58, 77.22, 50.76, 34.86, 31.90, 30.32, 30.01, 29.65, 29.63, 29.60, 29.53, 29.37, 29.32, 28.13, 27.78, 22.68, 14.11. m/z 1067.45 (M+)

12,13-bis(6-phenylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5'] thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (9)

Compound **7** (0.3g,0.28mmol), 0.7ml DMF, 1.5ml $POCl_3$ and 20ml 1,2-Dichloroethanewas used for Vilsmeier-Haack reaction, compound **9** (0.25g) was obtained as an orange solid in a yield of 79%. ^{1}H NMR (400MHz, CDCl3) δ10.14 (2 H, s), 7.21 (4 H, dd, J 8.1, 6.6), 7.16 – 7.09 (2 H, m), 7.08 – 7.01 (4 H, m), 4.62 (4 H, t, J 7.6), 3.17 (4 H, t, J 7.7), 2.46 (4 H, t, J 7.6), 1.89 (8

H, dp, J 20.6, 7.5), 1.55 – 1.04 (44 H, m), 0.94 – 0.82 (6 H, m). ^{13}C NMR (101 MHz, CDCl3) δ: 181.66, 147.21, 146.75, 143.14, 142.12, 136.94, 136.67, 131.68, 129.09, 128.28, 128.25, 127.16, 125.69, 112.48, 77.24, 50.99, 35.64, 31.91, 31.06, 30.97, 30.30, 29.65, 29.63, 29.61, 29.53, 29.35, 29.33, 28.62, 28.10, 26.37, 22.68, 14.12. m/z 1123.51 (M+)

Compound C4 and C6

Under argon, a mixture of compound **8** or **9** and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile in were dissolved in chloroform, pyridine was added drop by drop, After stirred at 60℃ for 4h, the mixture was cooled to room and poured into methanol and filtered. The filter residue was purified on silica gel column using petroleum ether/dichloromethane (1:1,v/v) as the eluent to give **C4** or **C6.**

2,2'-((2Z,2'Z)-((12,13-bis(4-phenylbutyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (C4)

C4 (0.18g) was obtained with the reaction of compound **8** (0.15g, 0.14mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.17g, 0.70mmol), 0.5ml pyridine and 39ml $CHCl_3$. The target product is dark blue solid in a yield of 86%.^{1}H NMR (400MHz, CDCl3) δ8.39 (2 H, s), 8.27 (2 H, dd, J 9.8, 6.4), 7.43 (2 H, t, J 7.3), 7.26 – 7.11 (10 H, m), 4.40 (4 H, s), 2.78 (8 H, dt, J 39.5, 8.1), 2.09 (6 H, s), 1.55 – 1.16 (38 H, m), 0.96 – 0.86 (6 H, m). m/z 1491.50 (M+)

2,2'-((2Z,2'Z)-((12,13-bis(6-phenylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (C6)

C6 (0.18g) was obtained with the reaction of compound **9** (0.15g, 0.13mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.15g, 0.66mmol), 0.5ml pyridine and 39ml $CHCl_3$. The target product is dark blue solid in a yield of 86%.^{1}H NMR (400MHz, CDCl3) 8.36 (2 H, d, J 16.9), 8.25 (2 H, dd, J 9.8, 6.4), 7.32 (2 H, t, J 7.5), 7.19 – 7.11 (4 H, m), 7.11 – 7.02 (6 H, m), 4.54 (4 H, t, J 8.2), 2.82 (4 H, d, J 8.3), 2.63 (4 H, t, J 7.7), 2.08 (2 H, s), 1.69 (10 H, p, J 7.3), 1.46 (8 H, p, J 6.8), 1.38 – 1.23 (32 H, m), 0.88 (6 H, t, J 6.5). ^{13}C NMR (101

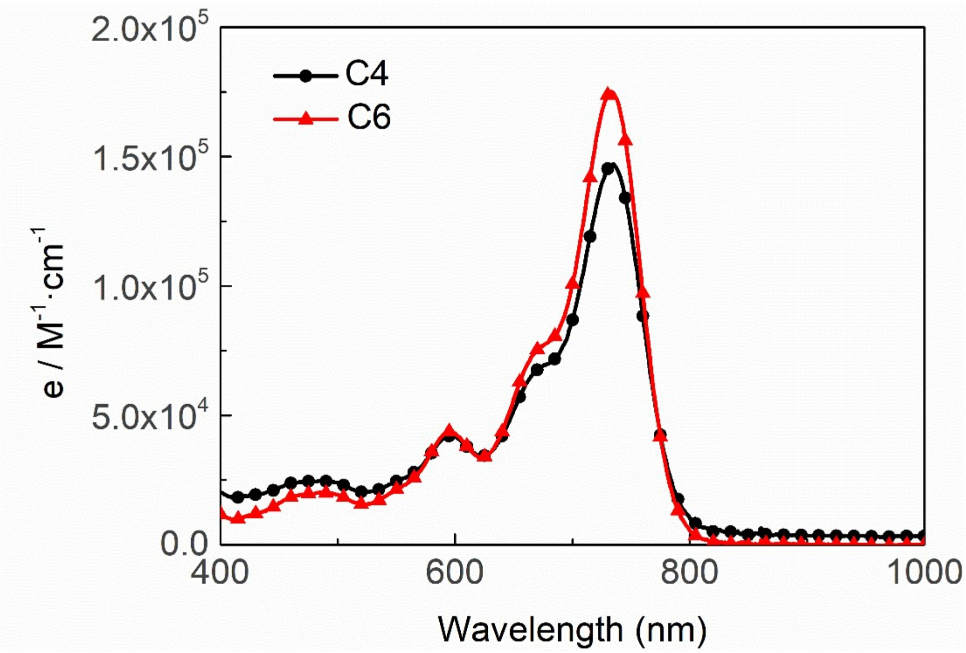
MHz, CDCl3) δ: 185.74, 157.04, 155.19, 153.67, 152.58, 146.69, 144.92, 142.00, 136.86, 136.13, 136.05, 133.74, 133.59, 133.50, 132.33, 131.74, 129.86, 128.35, 128.18, 125.88, 119.44, 114.63, 114.37, 114.24, 113.13, 111.89, 111.71, 69.04, 51.30, 35.73, 31.95, 31.73, 31.17, 30.67, 29.89, 29.69, 29.66, 29.55, 29.39, 29.08, 26.80, 22.72, 14.14. m/z 1547.56 (M+)

Characterization and Measurement

The chemical structure of compounds mentioned in this work were identified by ^{1}H and ^{13}C NMR were recorded on Bruker DMX-400 Spectrometer with $CDCl_3$ as a solvent. The molecular weights of the materials were obtained on a Bruker Autoflex III TOF mass spectrometer. UV-visible absorption spectra were Perkin-Elmer Lambda 950 spectrophotometer. Surface images and the roughness were performed on Veeco Dimension 3100V atomic force microscope. Current density–voltage (*J–V*) characteristics of unencapsulated device were measured in N_2-filled glove box using Keithley 2440 source meter with AM 1.5G solar simulator (Newport-Oriel® Sol3A 450W). The light intensity was calibrated at 100 mW cm^{-2} using a certified reference Si standard cell (SRC-2020 with KG5 filter) obtained from Enli Technology Co., Ltd and the calibration report was traceable to NREL.

Solar Cells Fabrication

OSCs structure is ITO glass/PEDOT: PSS/BHJ blend/PDINO/Al. PEDOT:PSS aqueous solution was filtered through 0.45 μm filter and spin-coated at 3000 rpm for 60s onto the treated ITO substrate and annealed at 130℃ for 15min. The solution of active layer prepared by adding the donor and acceptor with ratio 1:1.2 in chloroform/1-chloronaphthalene (95:5 vol %) mixed solvent, the solution stirred at 35℃ overnight, then spin-coated onto the PEDOT: PSS at 2500 rpm for 60s. The PDINO was dissolved in methanol and their solution were spin-coated onto the active layer at 3000 rpm for 60s. Al as cathode was evaporated in vacuum chamber (3×10^{-6}mbar).



Fig, S1 Absorption spectra of **C4** and **C6** in chloroform.

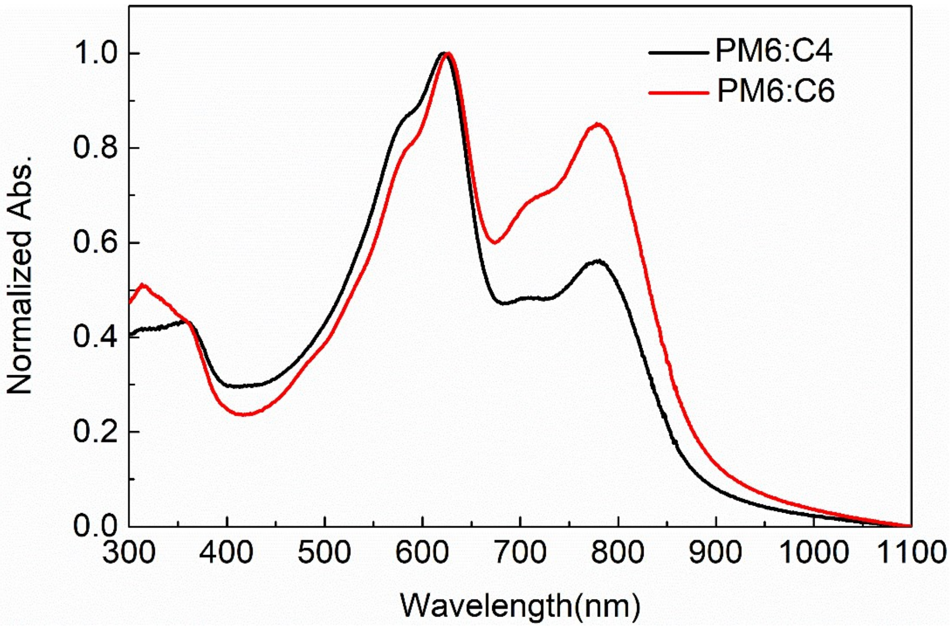


Fig. S2 The normalized UV-Vis-NIR absorption spectra of the optimal PM6:acceptors devices.

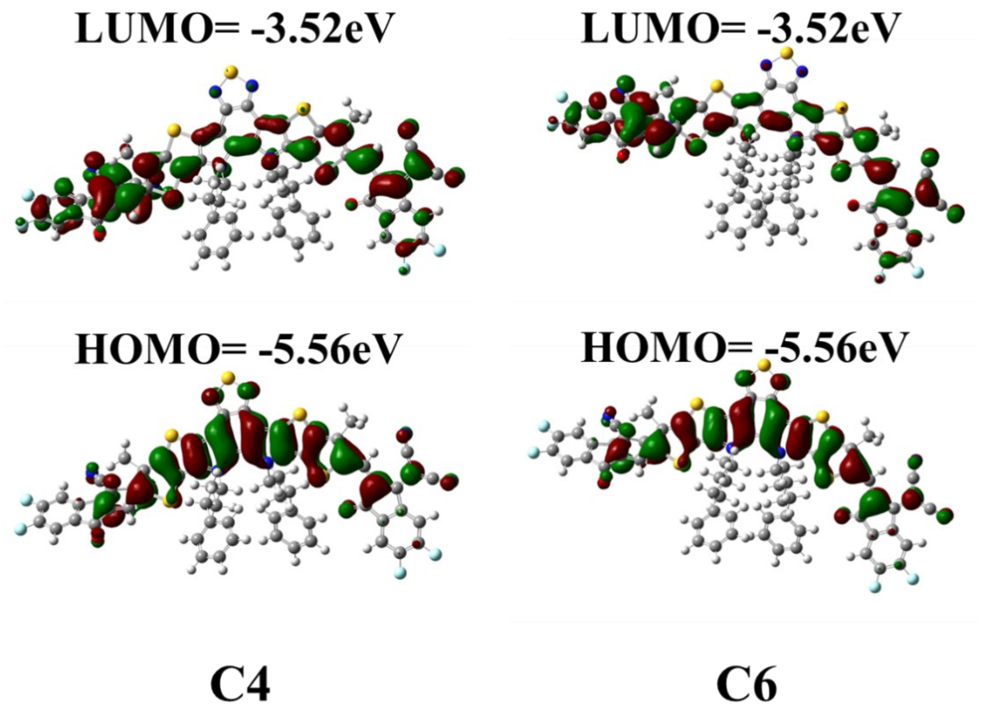


Fig. S3 HOMO and LUMO electron distributions for C4 and C6

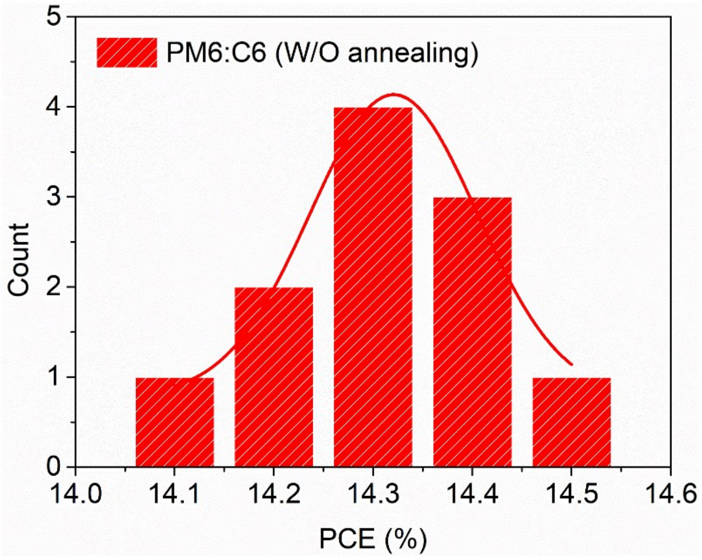


Fig. S4 Histograms of PCEs of counts for 10 individual devices based on annealing-free PM6:C6 devices.

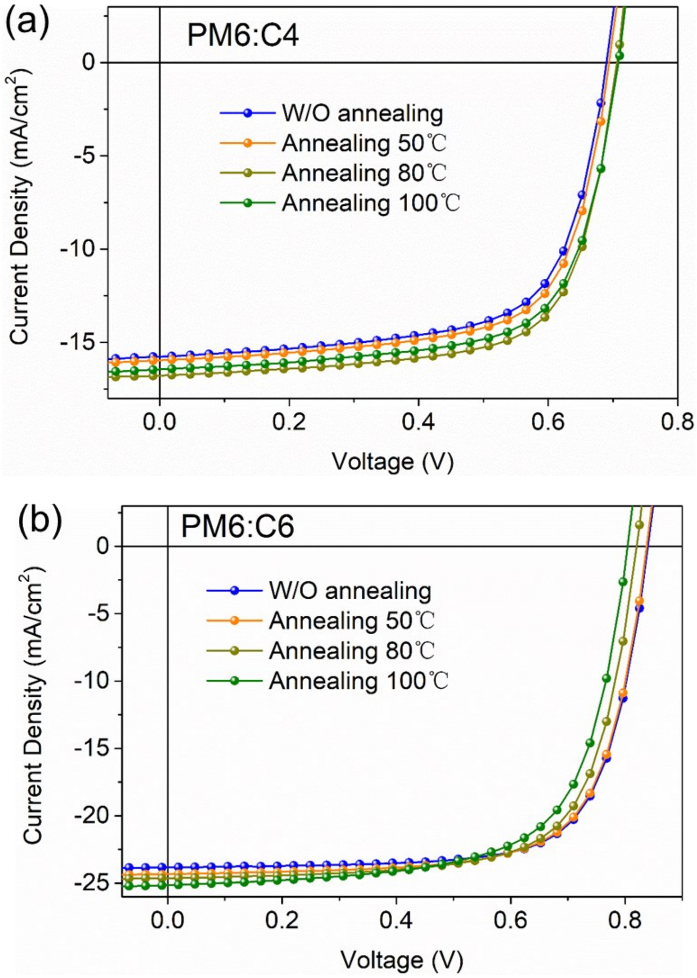


Fig. S5 *J*–*V* curves of (a) PM6:C4-based and (b) PM6:C6-based devices processed with different thermal annealing temperatures.

Table S1. Summary of the device parameters of the **PM6:C4** or **C6** blends with different thermal annealing treatment in solar cells under the illumination of AM 1.5 G, 100 mW/cm^2.

Active layer[a]	Post treatment	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE$_{max}$ (Ave.)[b] [%]
PM6:C4	W/O TA	0.689	15.74	67.01	7.28 (6.46)
	TA 50 °C	0.694	15.94	67.89	7.51 (7.23)
	TA 80 °C	0.706	16.75	69.19	8.18 (7.97)
	TA 100 °C	0.709	16.43	68.00	7.92 (7.62)
PM6:C6	W/O TA	0.84	23.82	72.68	14.54 (14.37)
	TA 50 °C	0.838	24.30	71.07	14.46 (14.19)
	TA 80 °C	0.820	24.60	70.32	14.18 (13.92)
	TA 100 °C	0.804	25.11	67.25	13.58 (13.27)

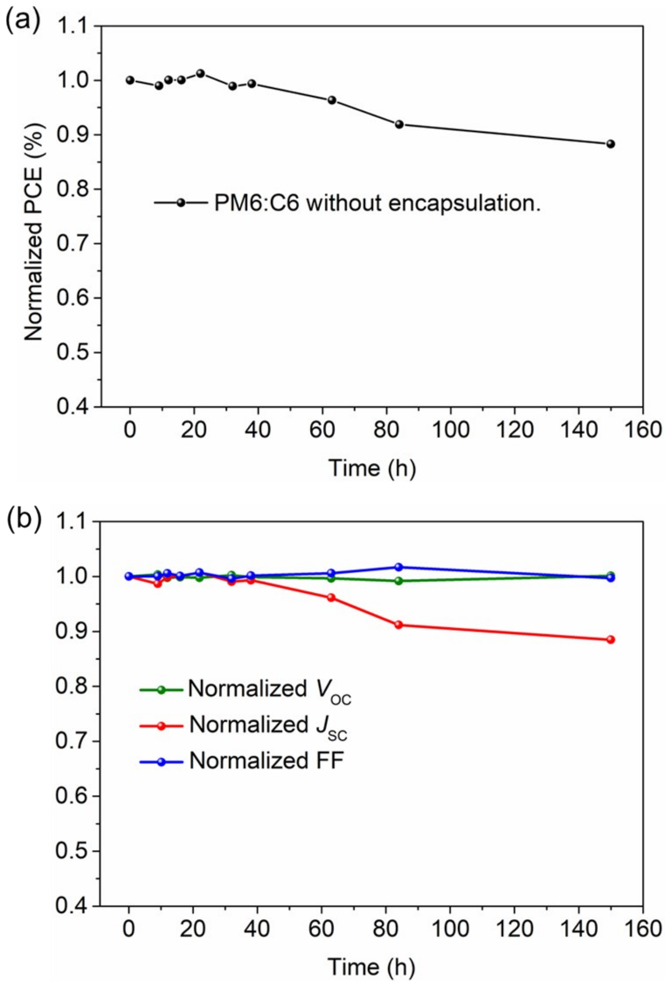


Fig. S6 Stability test of PM6:C6 based optimal devices without encapsulation.

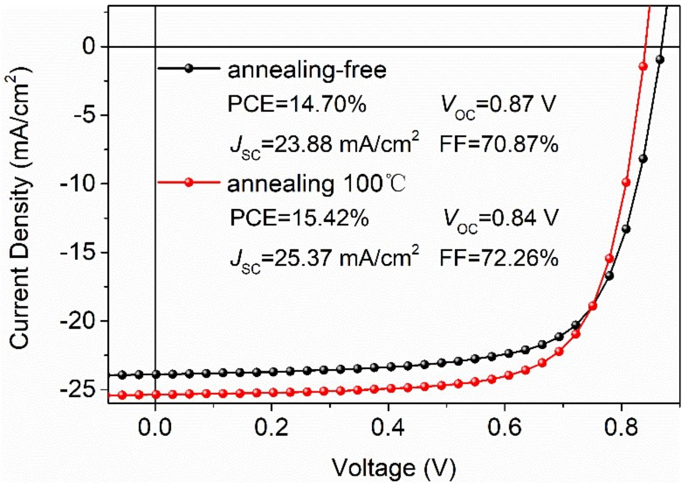


Fig. S7 Photovoltaic performance of the PM6:Y6 (1:1.2, w/w)-based devices, under the illumination of AM 1.5 G, 100 mW/cm^2.

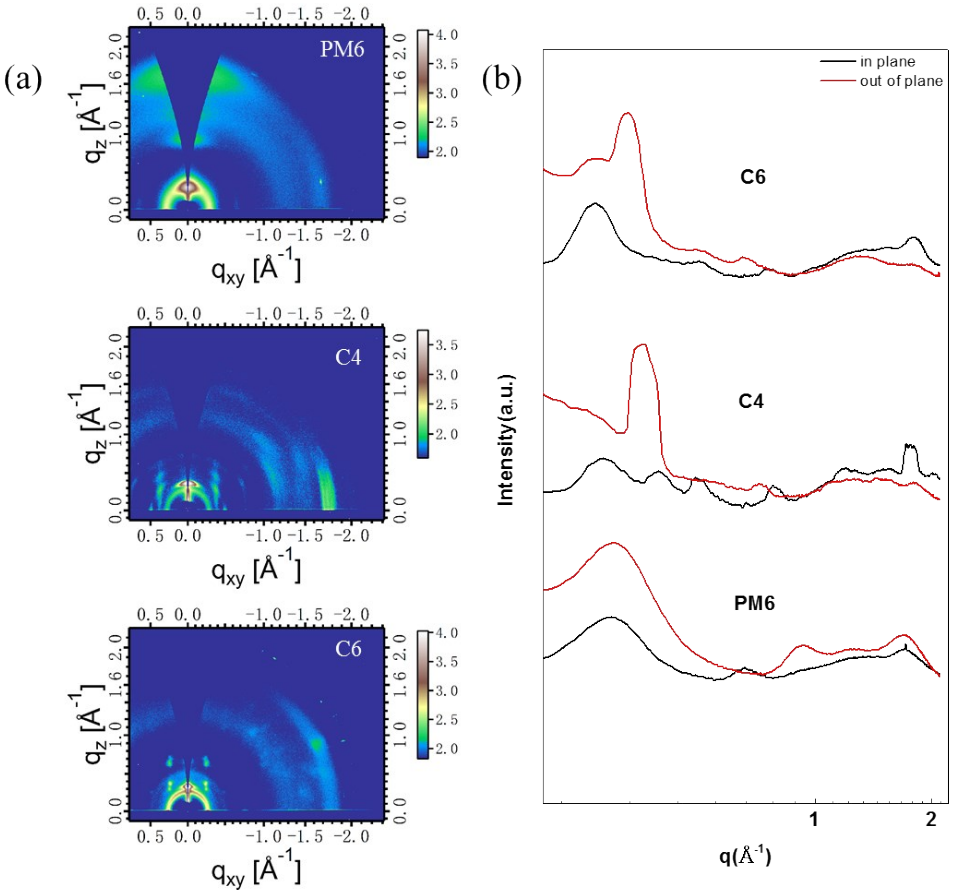


Fig. S8 (a) GIWAXS patterns of PM6, C4 and C6 neat films (b) In-plane (black lines) and out of plane (red lines) line-cut profiles of the GIWAXS results.

Table S2. Summarized parameters of the ordered structures.

Blend film	**Blend film**	***π*-*π* stacking**				**Lamellar stacking**	
		q_z	**d_π(Å)**	**FWHM (Å^{-1})**	**CCL**	**q_{xy}**	**d_l(Å)**
PM6:C4	W/O TA	1.72	3.65	0.36	15.7	0.30	20.94
	TA 100 ℃	1.74	3.61	0.44	12.9	0.30	20.94
PM6:C6	W/O TA	1.74	3.61	0.32	17.7	0.30	20.94
	TA 100 ℃	1.77	3.55	0.28	20.2	0.29	21.66

^{1}H NMR, ^{13}C NMR and high resolution mass spectrum

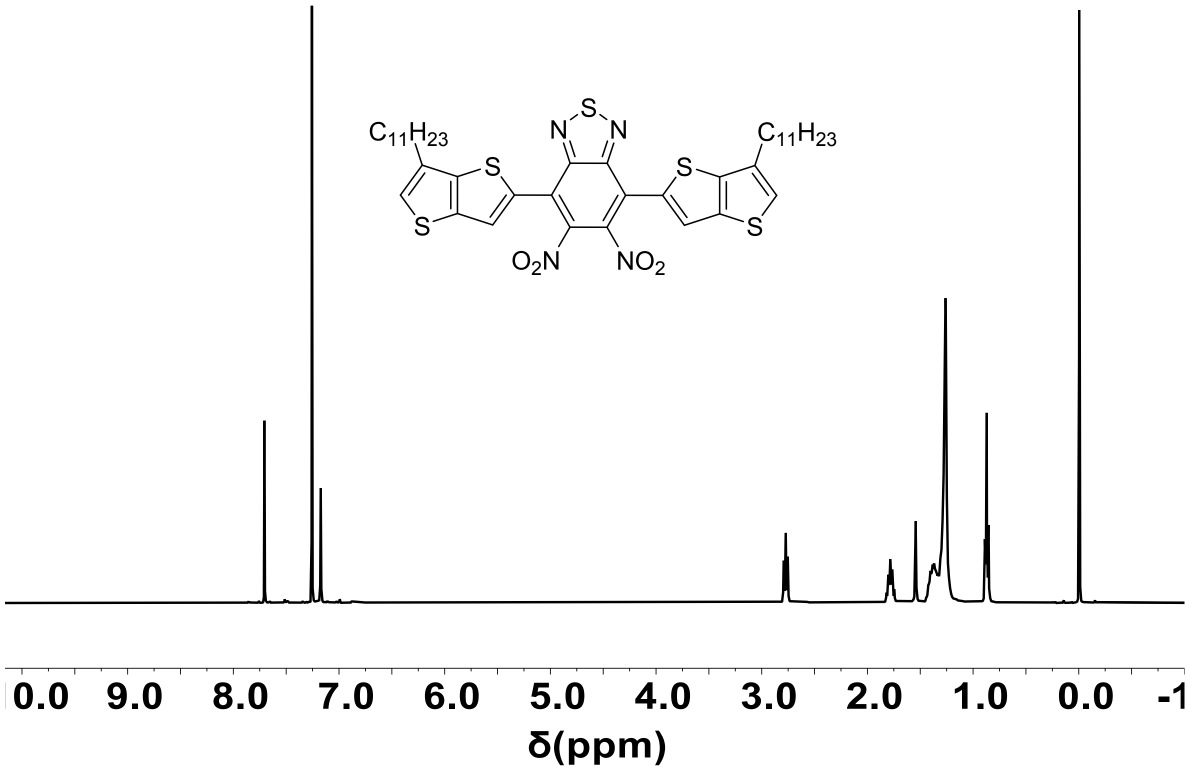


Fig. S8 ^{1}H NMR spectrum of **compound 3**

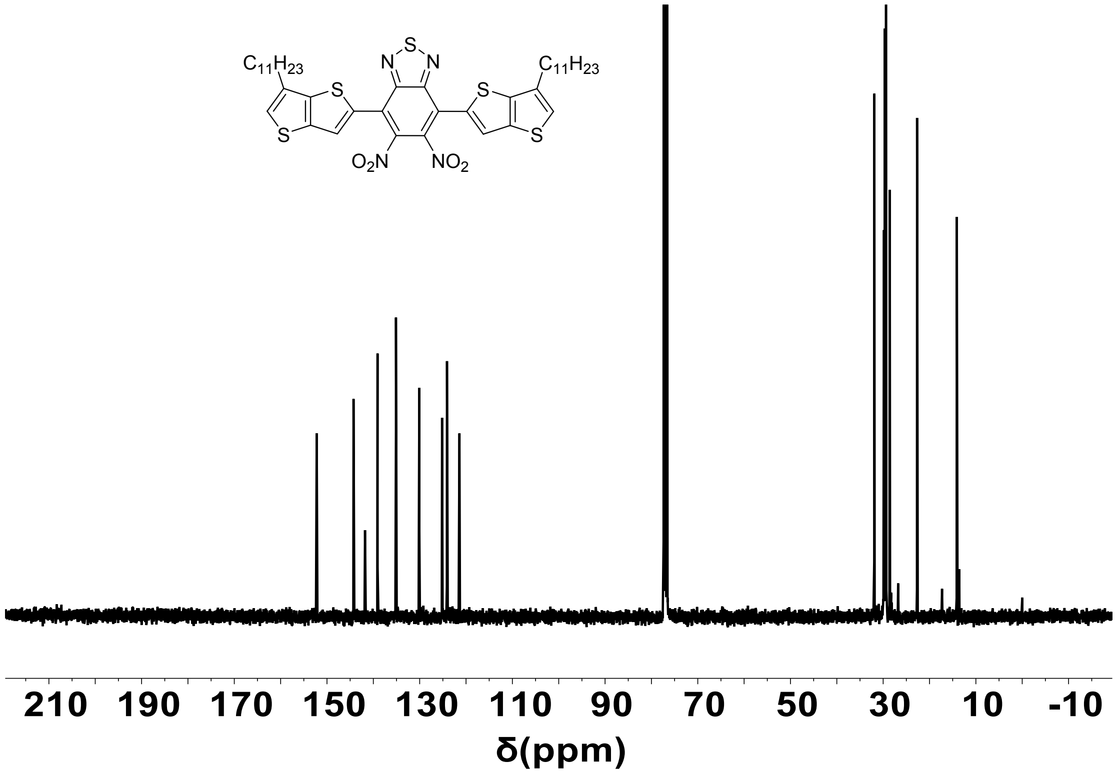


Fig. S9 ^{13}C NMR spectrum of **compound 3**

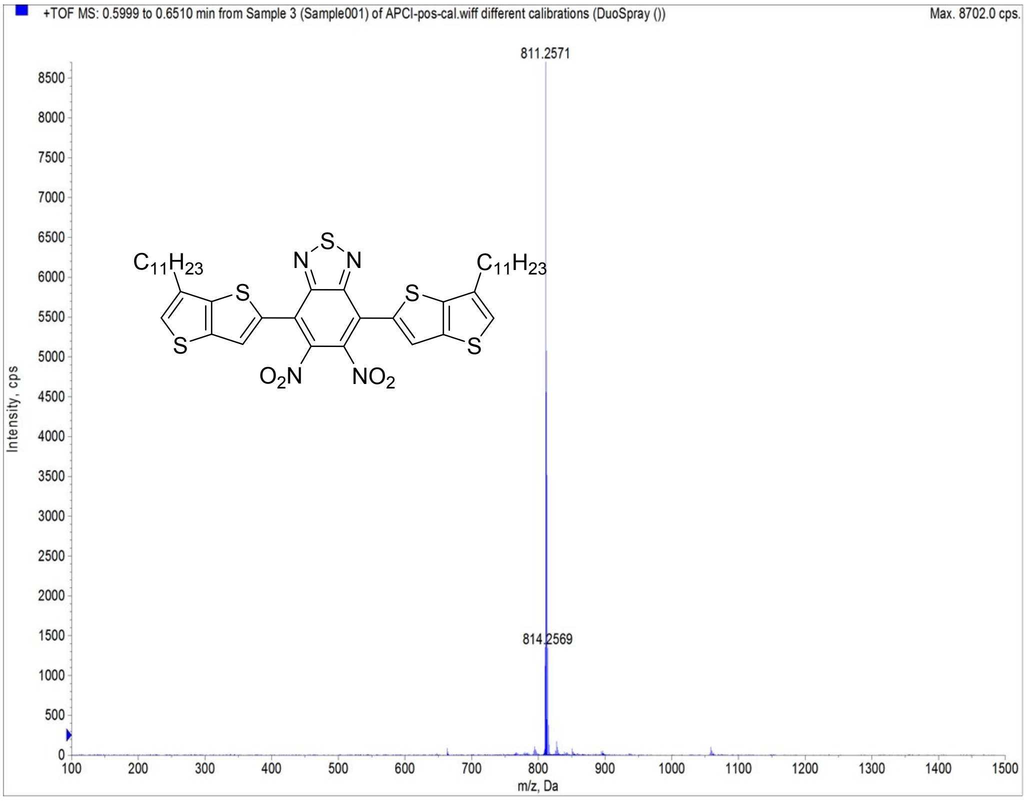


Fig. S10 The high resolution mass spectrum (MALDI-TOF) of **compound 3**

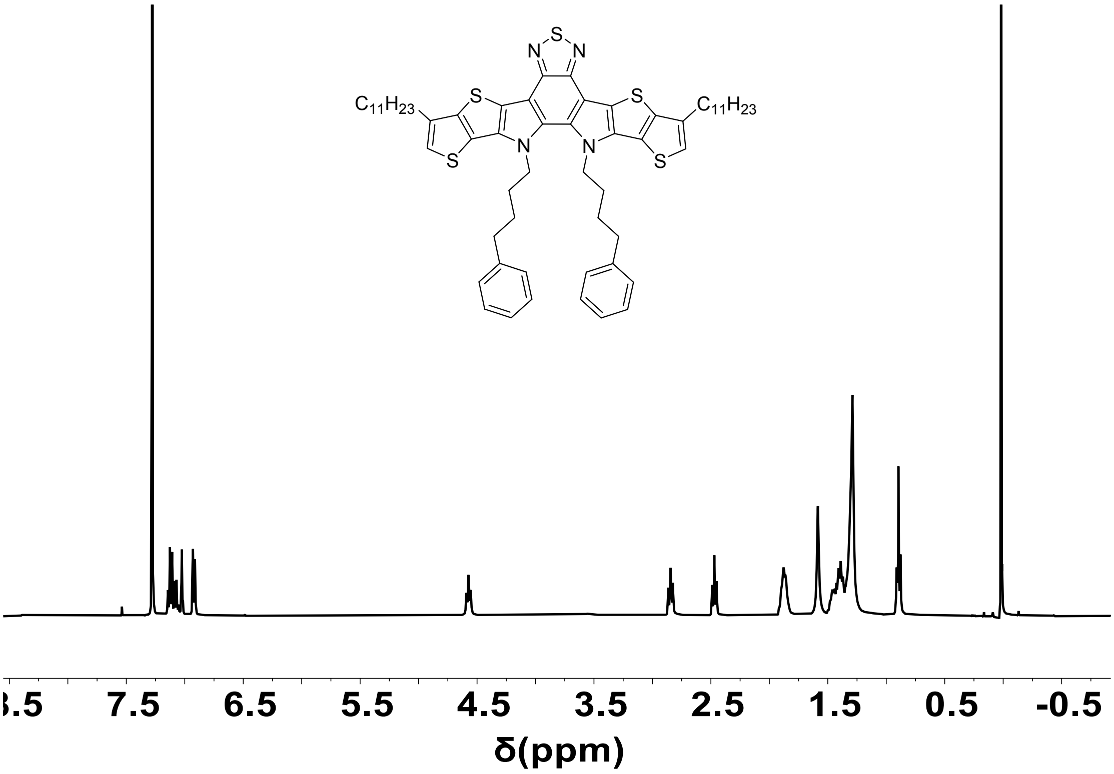


Fig. S11 ^{1}H NMR spectrum of **compound 6**

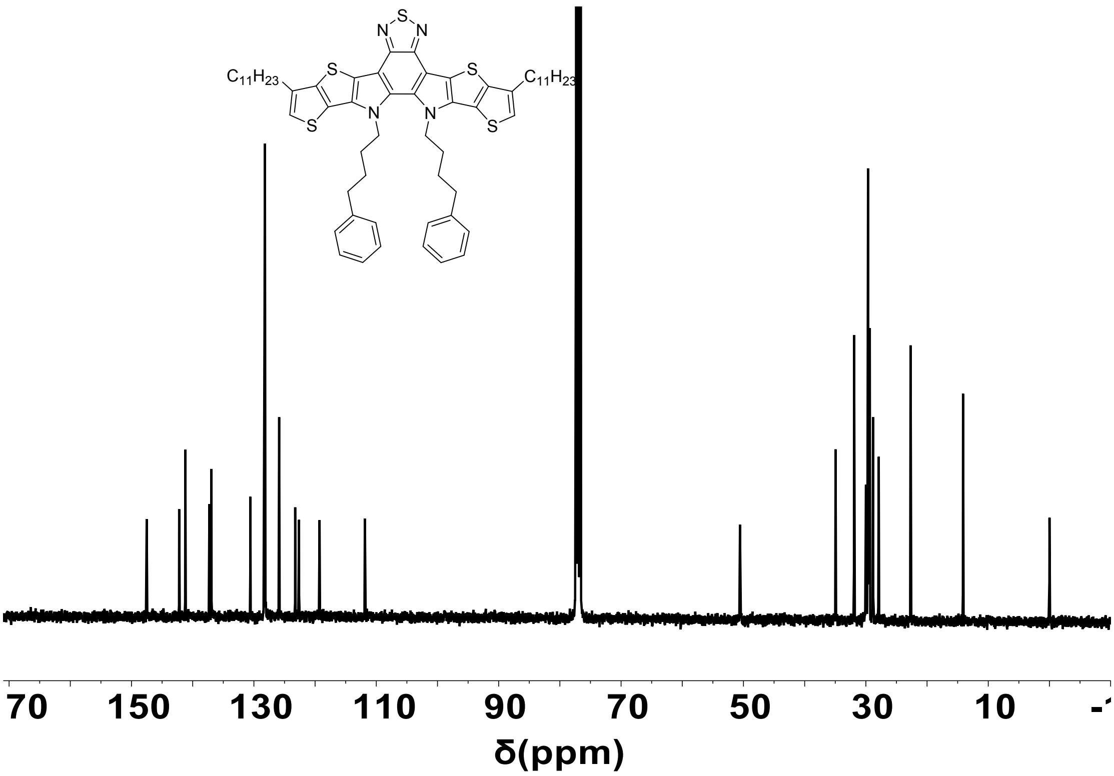


Fig. S12 ^{13}C NMR spectrum of **compound 6**

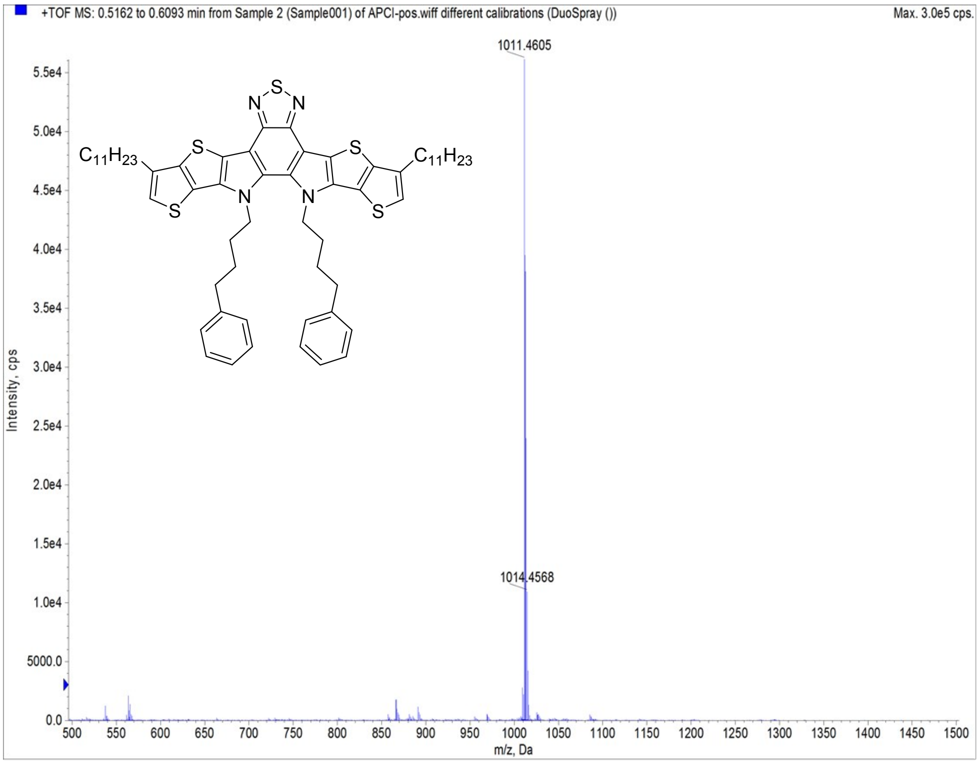


Fig. S13 The high resolution mass spectrum (MALDI-TOF) of **compound 6**

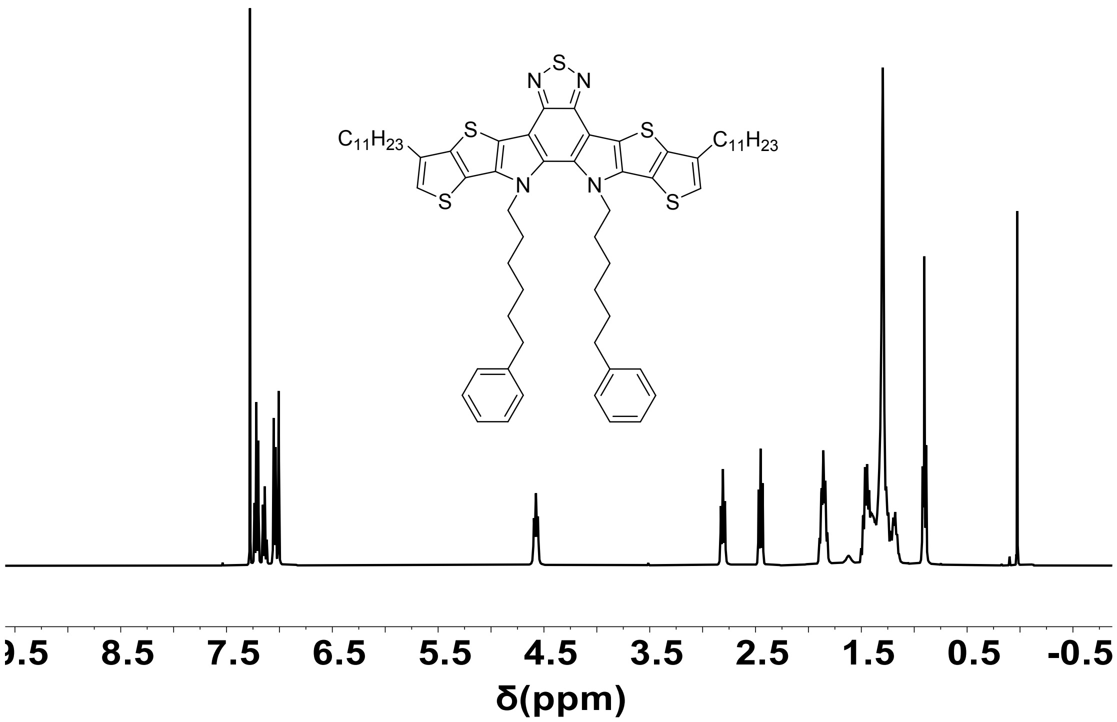


Fig. S14 ^{1}H NMR spectrum of **compound 7**

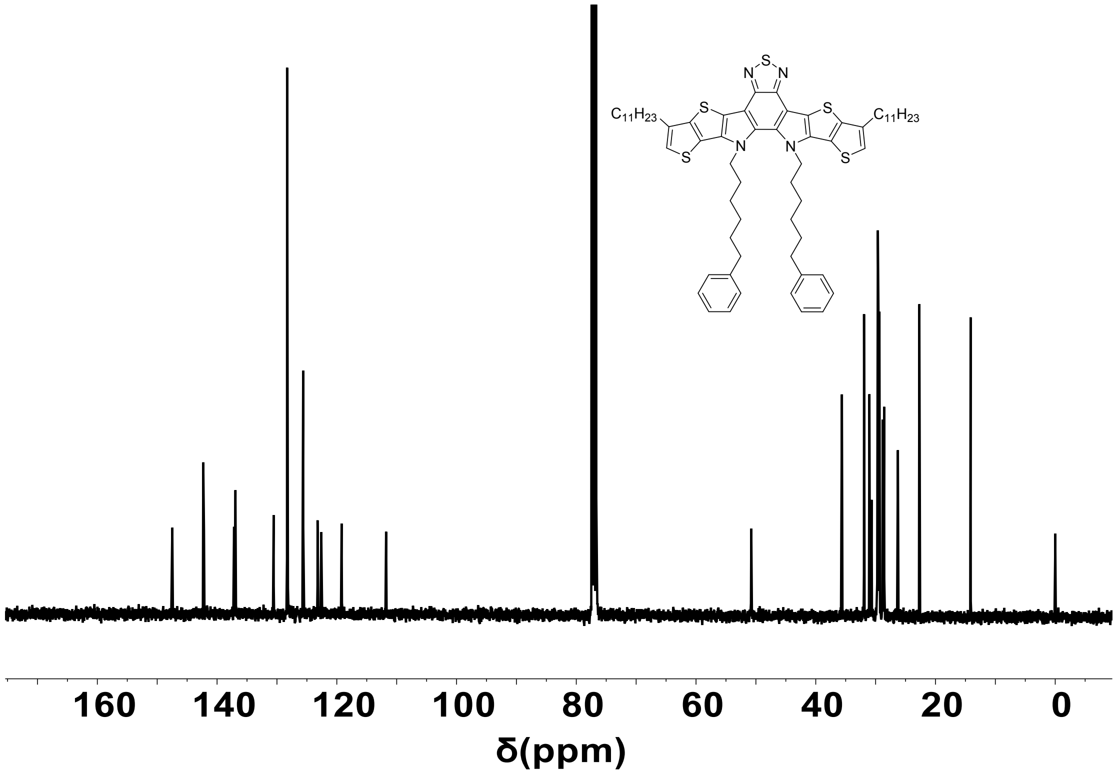


Fig. S15 ^{13}C NMR spectrum of **compound 7**.

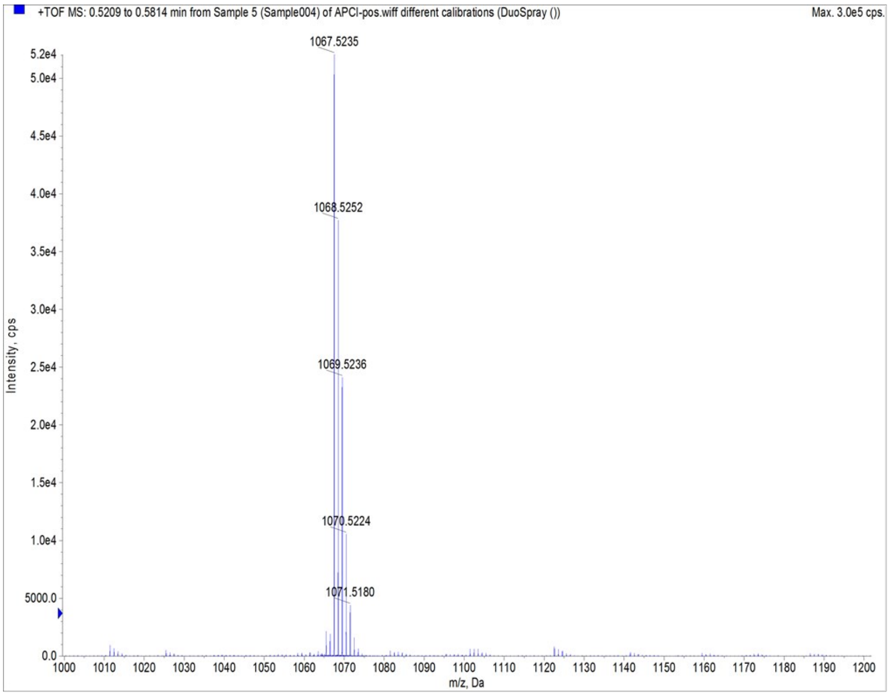


Fig. S16 The high resolution mass spectrum (MALDI-TOF) of **compound 7**.

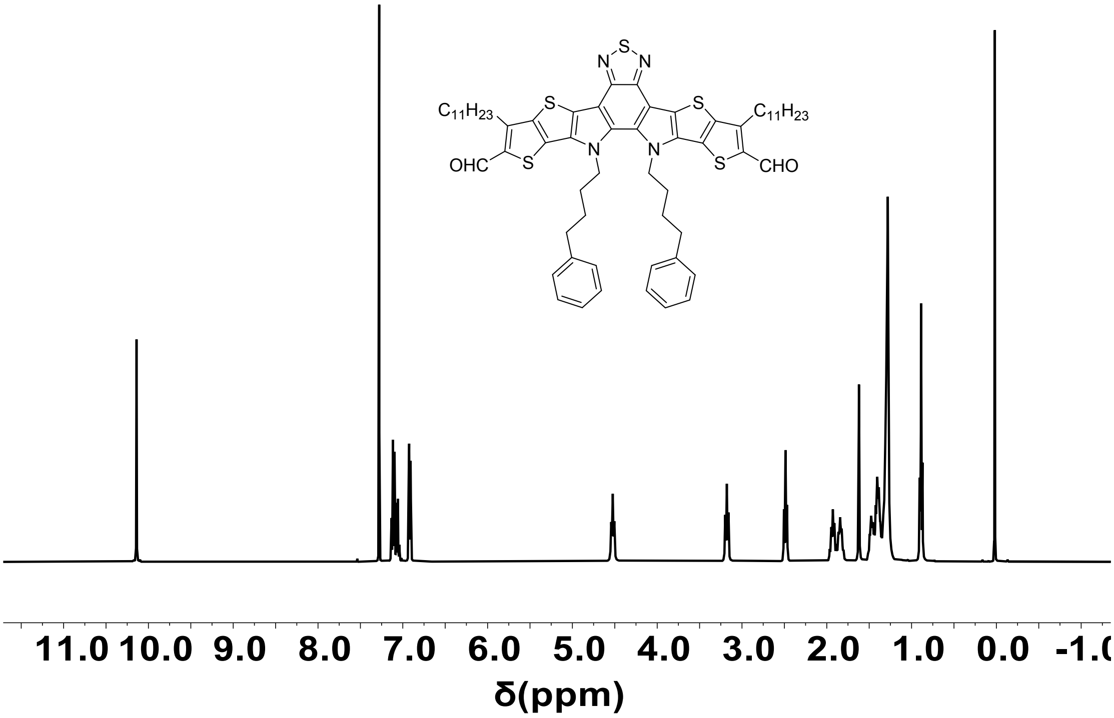


Fig. S17 ^{1}H NMR spectrum of **compound 8**.

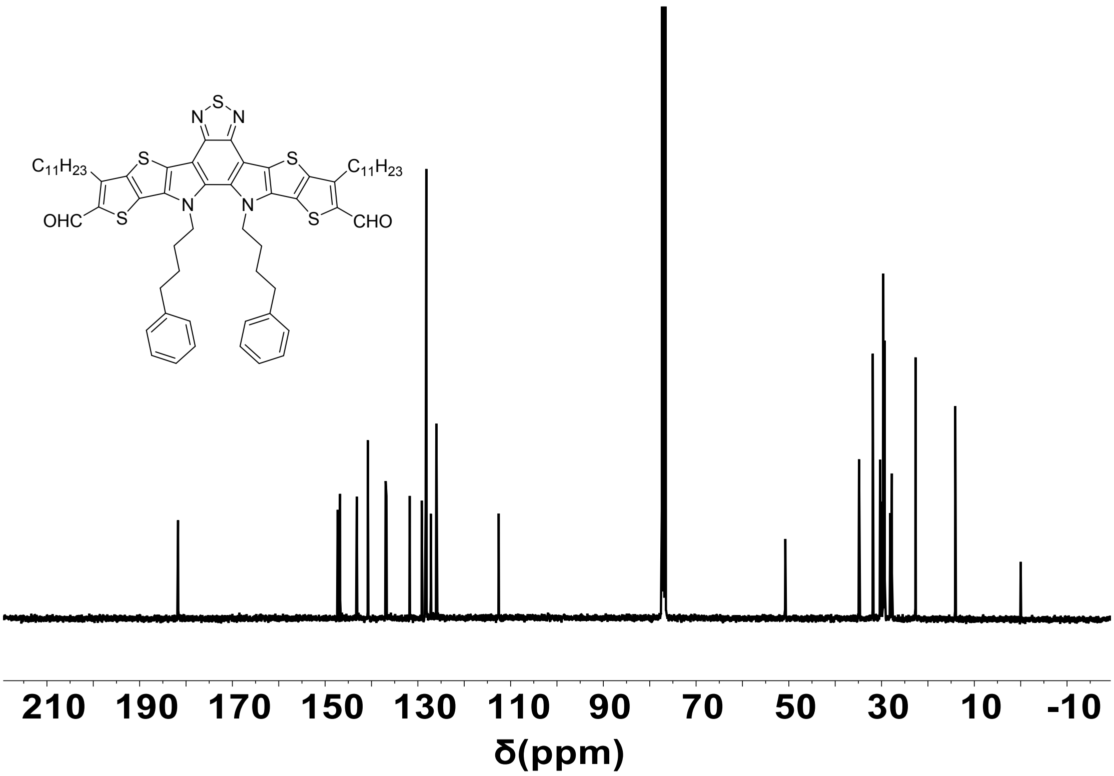


Fig. S18 ^{13}C NMR spectrum of **compound 8**.

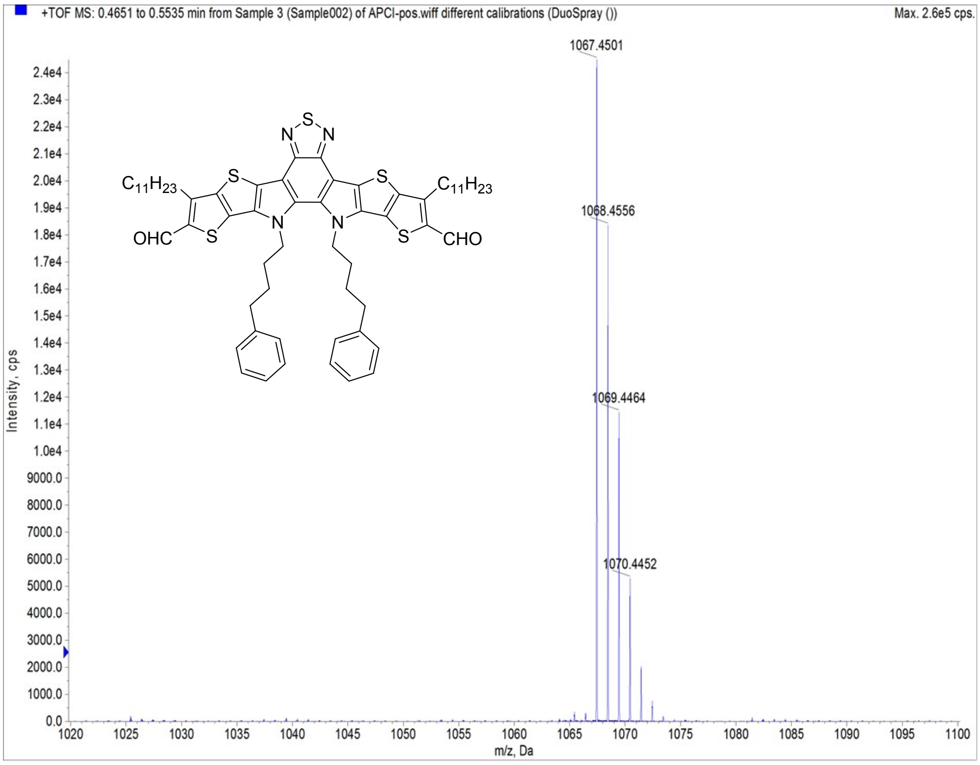


Fig. S19 The high resolution mass spectrum (MALDI-TOF) of **compound 8**.

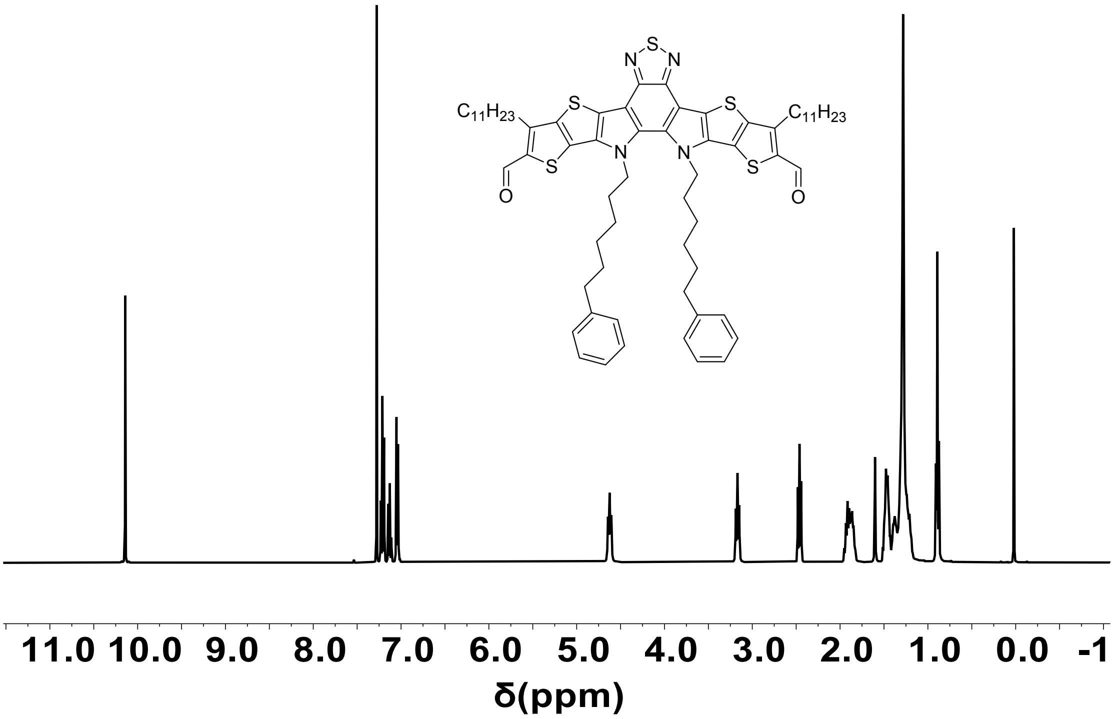


Fig. S20 ^{1}H NMR spectrum of **compound 9**.

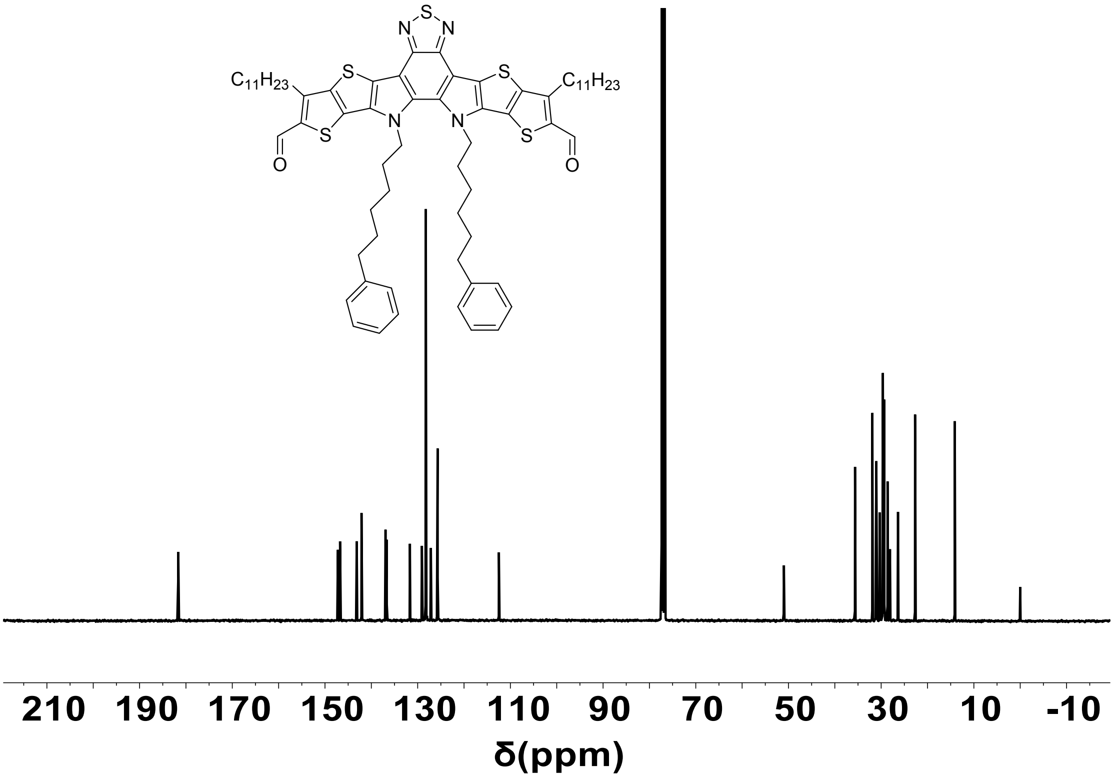


Fig. S21 ^{13}C NMR spectrum of **compound 9**.

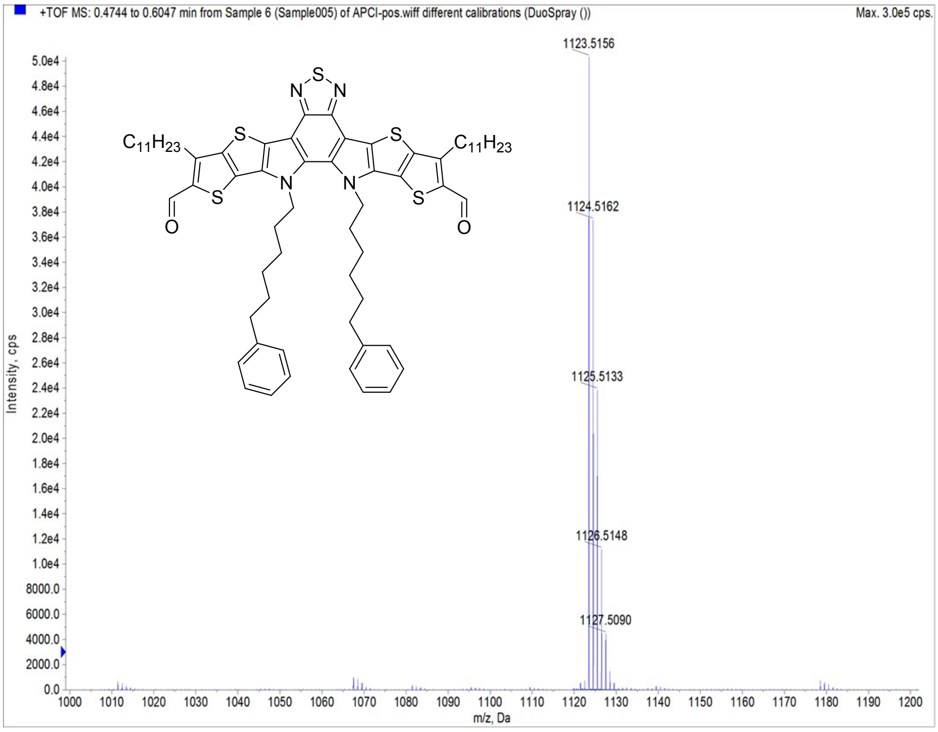


Fig. S22 The high resolution mass spectrum (MALDI-TOF) of **compound 9**.

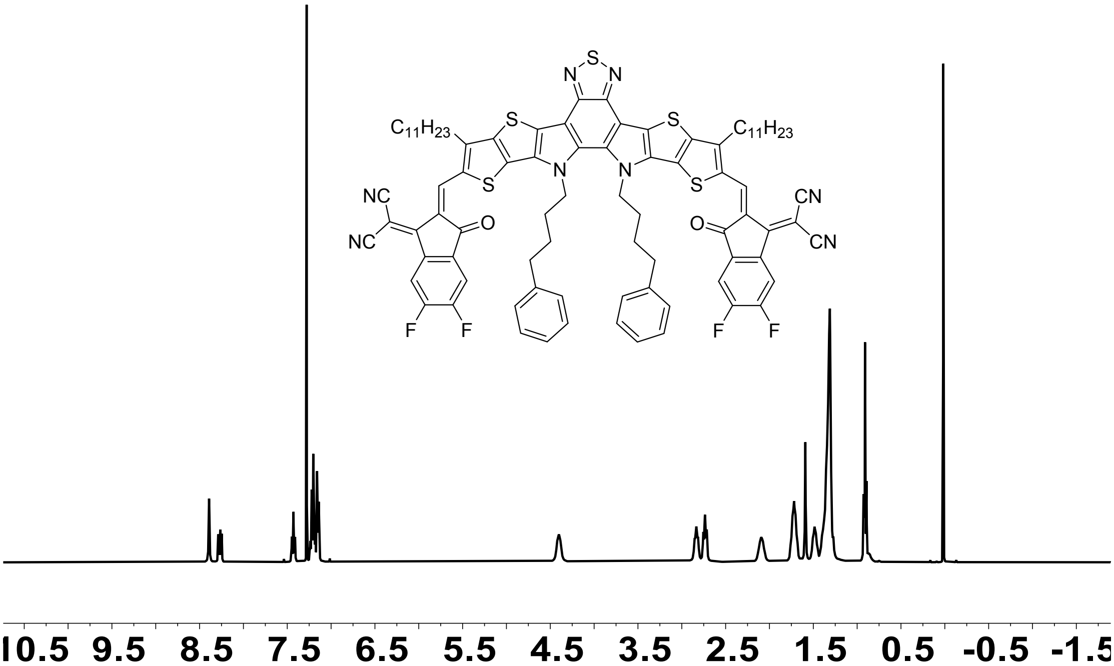


Fig. S23 ^{1}H NMR spectrum of **C4**.

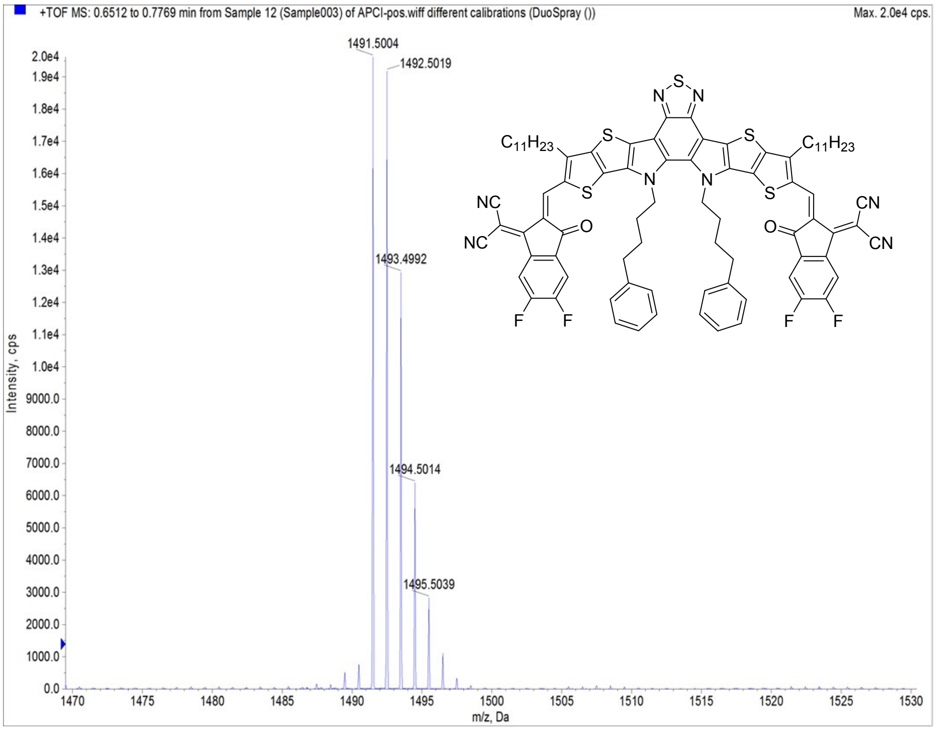


Fig. S24 The high resolution mass spectrum (MALDI-TOF) of **C4**.

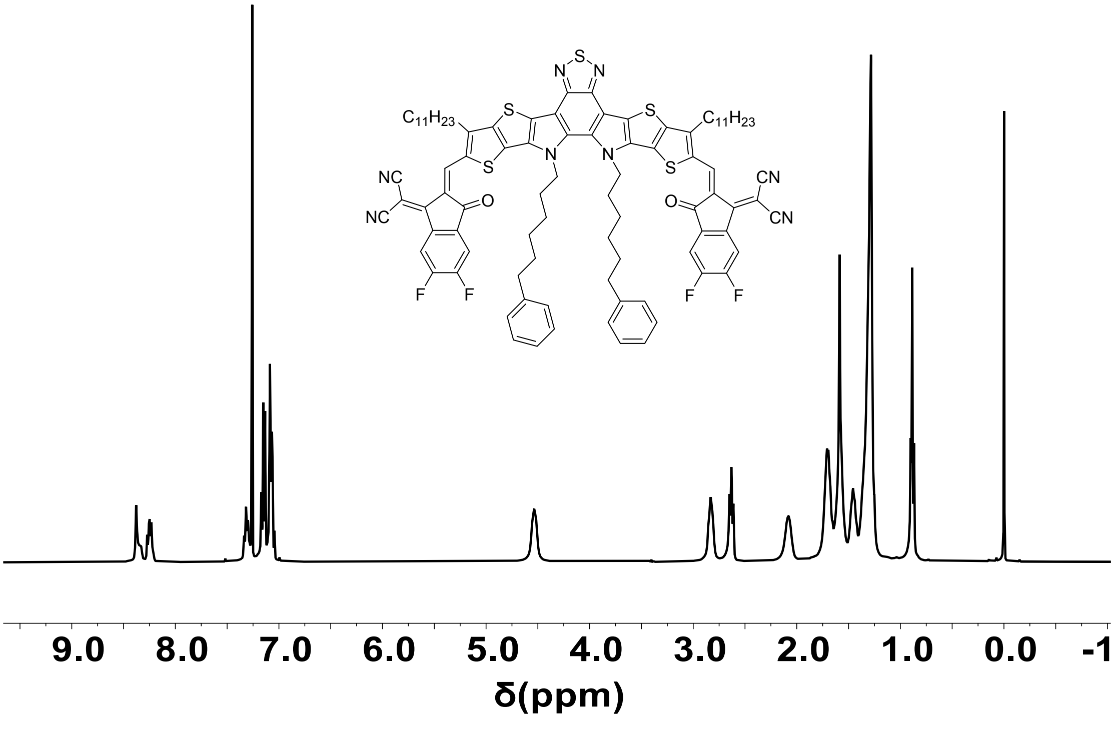


Fig. S25 ^{1}H NMR spectrum of **C6**.

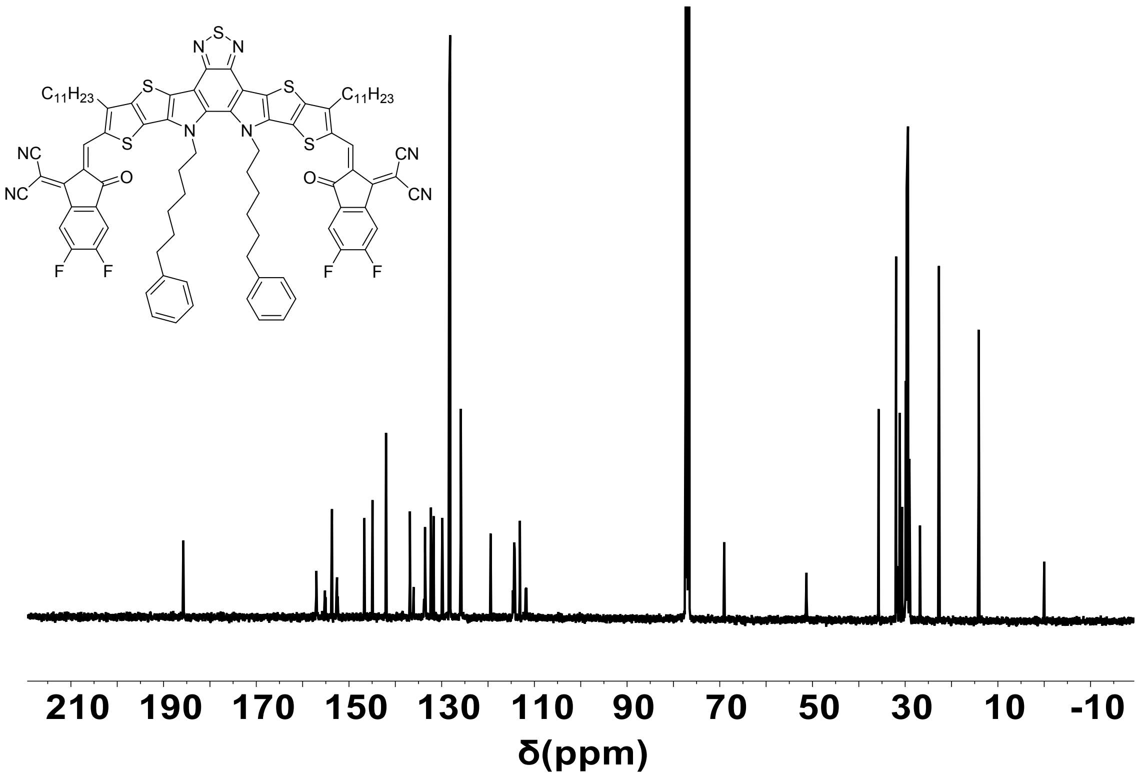


Fig. S26 ^{13}C NMR spectrum of **C6**.

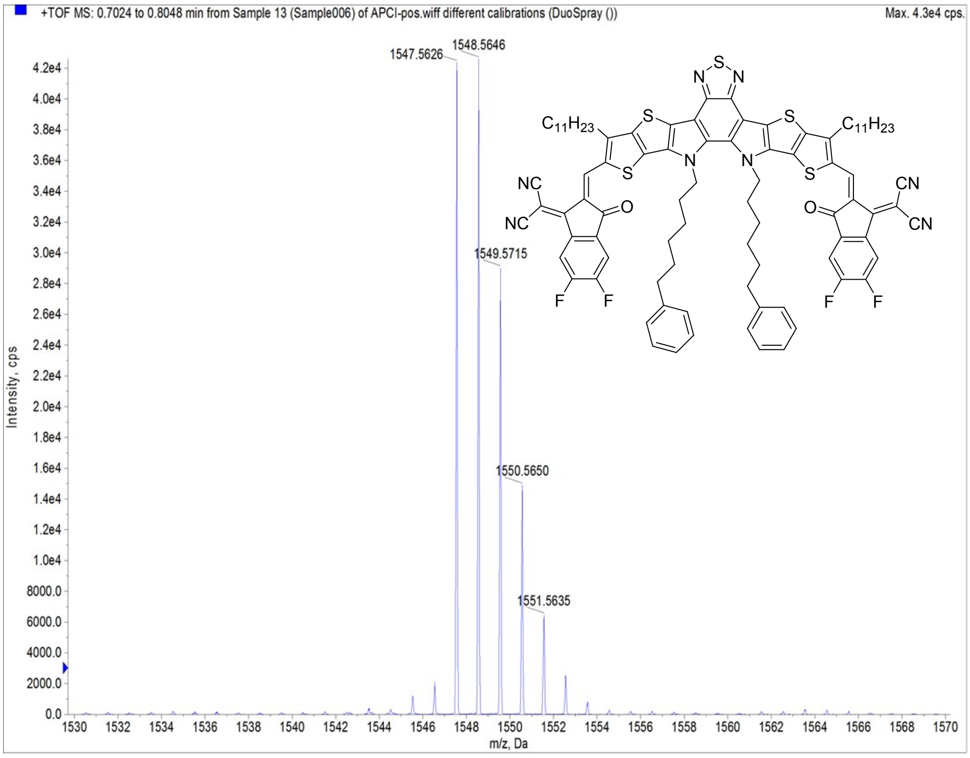


Fig. S27 The high resolution mass spectrum (MALDI-TOF) of **C6**.