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Supporting Information

A Polymer acceptor with the grafted small molecule acceptor unit for high efficiency organic solar cells

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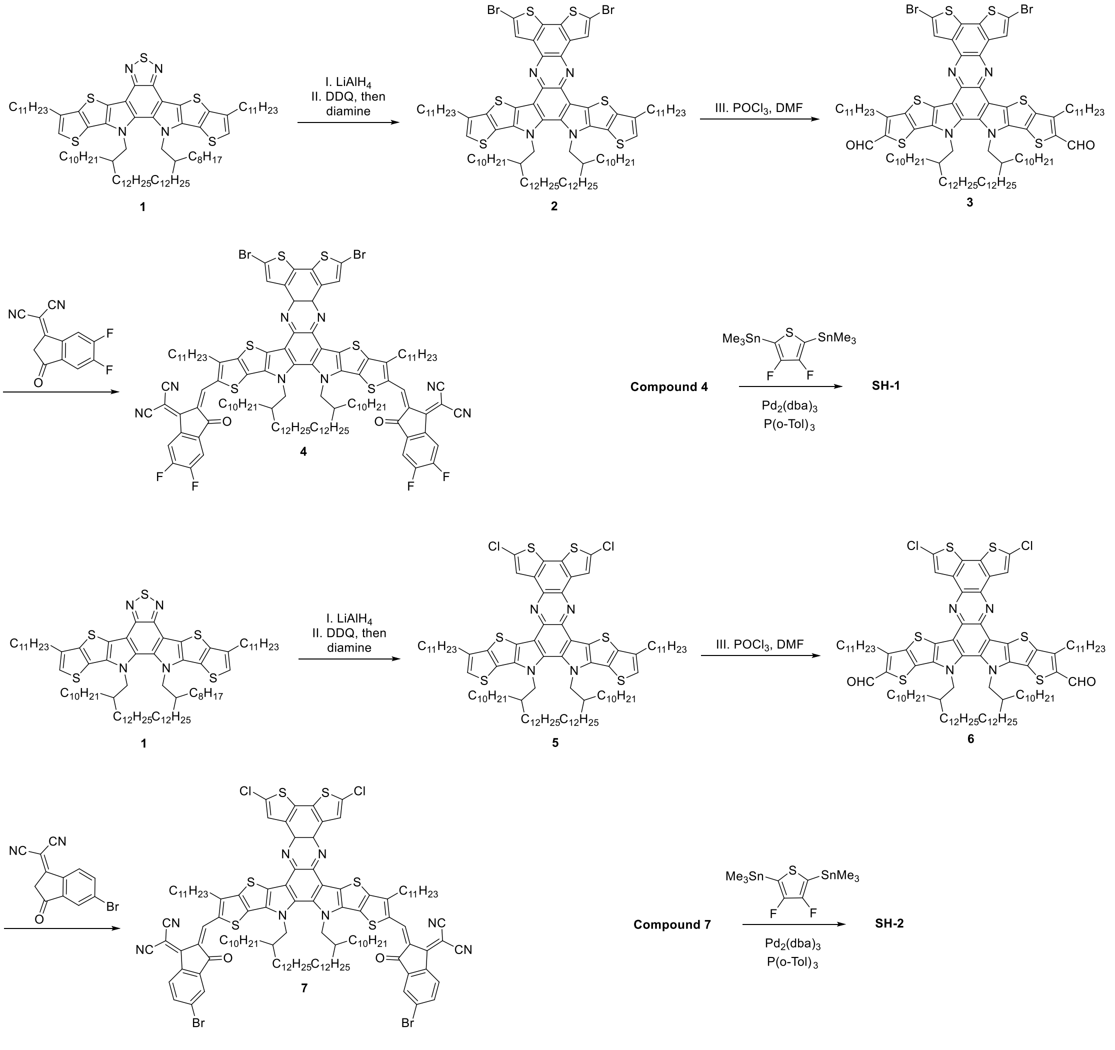
Experimental Procedures

Materials and Synthesis.

Polymer donor PM6, starting material compound 1 and 2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (INCN-Br) were purchased from Solarmer Material (Beijing) Inc, Organtec. Ltd, Woerjiming (Beijing) Technology Development Institute, respectively. All chemicals and other regents, unless otherwise specified, were purchased from commercial suppliers (such as Alfa Aesar, TCl Chemical Co.) and were directly used without further purification.



Scheme S1. The overall synthetic route to SH-1 and SH-2.

Synthesis of Compound 2

Under the protection of argon, $LiAlH_4$ (55 mg, 1.43 mmol, 5.0 eq.) was added to a solution of compound 1 (403 mg, 0.29 mmol, 1.0 eq.) in tetrahydrofuran (THF, 20 mL). The resulting mixture was stirred and heated to reflux for 12 h. After being cooled to 0 °C, water (30 mL) is slowly dropped into the reaction and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 for 1 h. After removal of solvent, the crude product was dissolved in chloroform (45 mL), then 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ, 104 mg, 0.46 mmol, 2.0 eq.) and 2,7-dibromobenzo[2,1-b:3,4-b']dithiophene-4,5-diamine (536 mg, 1.43 mmol, 5.0 eq.) were added to the solution in turn. The reaction was stirred at room temperature for 6 h, and the solvent was removed under vacuum. Finally, the residue was purified by column chromatography to give compound 2 as a red solid. (276 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 7.24 (s, 2H), 4.92 (d, *J* = 7.8 Hz, 5H), 3.15 (t, *J* = 7.9 Hz, 5H), 2.42 (s, 3H), 2.16 (t, *J* = 7.6 Hz, 5H), 1.91 – 0.77 (m, 180H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.40, 137.31, 137.02, 136.11, 135.35, 133.34, 131.42, 127.38, 123.53, 123.09, 118.75, 117.51, 112.56, 55.24, 38.75, 31.99, 31.94, 30.59, 29.79, 29.75, 29.69, 29.63, 29.56, 29.44, 29.36, 28.96, 26.95, 25.67, 22.74, 14.15. MS (m/z, MALDI): Calc. for $C_{98}H_{148}Br_2N_4S_6$ $[M+H]^+$ 1733.84, found: 1733.84.

Synthesis of Compound 3

Under the protection of argon, phosphorus oxychloride (0.3 mL) was added to a solution of compound 2 (350 mg, 0.21 mmol) and N, N-Dimethylformamide (DMF, 0.4 mL) in 1, 2-dichloroethane ($ClCH_2CH_2Cl$, 50 mL). The resulting mixture was stirred and heated to reflux for 12 h, then cooled to 0 °C. The resulting mixture was slowly added to a saturated solution of sodium acetate (40 mL), then stirred at room temperature for 2 h. The resulting mixture was extracted with dichloromethane and the organic layer was dried over anhydrous Na_2SO_4 for 1 h. After removal of solvent, the crude product was then purified by column chromatography on silica gel with hexanes/dichloromethane (v/v=1:2) as eluent to afford compound 3 as a red solid (286 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (s, 2H), 8.36 (s, 2H), 4.77 (d, *J* = 8.0 Hz, 4H), 3.33 (d, *J* = 8.3 Hz, 4H), 2.22 (s, 2H), 2.04 (s, 4H), 1.58 (s, 5H), 1.46 (s, 5H), 1.42 – 0.90 (m, 113H), 0.90 – 0.69 (m, 26H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.79, 146.99, 144.40, 137.07, 136.86, 135.98, 135.49, 134.83, 133.75, 132.50, 129.66, 127.76, 127.04, 118.33, 112.97, 55.48, 39.01, 31.94, 31.90, 30.90, 30.55, 29.80, 29.75, 29.67, 29.56, 29.43, 29.38, 29.33, 28.21, 25.66, 22.71, 22.68, 14.15, 14.12. MS (m/z, MALDI): Calc. for $C_{100}H_{148}Br_2N_4O_2S_6$ $[M+H]^+$ 1789.84, found: 1789.83.

Synthesis of Compound 4

Under the protection of argon, dry pyridine (0.5 mL) was added to a solution of compound 3 (279 mg, 0.156 mmol, 1.0 eq.) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (108 mg, 0.468 mmol 3.0 eq.) in chloroform ($CHCl_3$, 45 mL). The resulting mixture was stirred and heated to reflux for 12 h. After being cooled to room temperature, the solvent was removed under a vacuum. The crude product was then purified by column chromatography on silica gel with hexanes/dichloromethane (v/v=1:3) as eluent to afford 4 as a black and green solid (311 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 2H), 8.31 (t, *J* = 8.2 Hz, 2H), 7.93 (s, 2H), 7.71 (t, *J* = 7.7 Hz, 2H), 4.97 (d, *J* = 8.1 Hz, 4H), 3.19 (t, *J* = 8.0 Hz, 4H), 2.40 (s, 2H), 1.85 (t, *J* = 7.9 Hz, 4H), 1.51 (t, *J* = 7.8 Hz, 5H), 1.46 – 0.96 (m, 117H), 0.79 (dq, *J* = 15.7, 7.5, 6.7 Hz, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.95, 158.07, 155.51, 153.88, 146.51, 138.00, 136.44, 136.21, 135.98, 135.41, 134.86, 134.35, 134.11, 133.45, 133.11, 131.40, 126.41, 119.62, 119.24, 114.88, 114.73, 114.43, 113.70, 112.51, 68.18, 56.02, 39.63, 31.88, 31.79, 30.87, 30.13, 29.76, 29.70, 29.65, 29.35, 26.05, 22.65, 22.62, 14.06, 14.02. MS (m/z, MALDI): Calc. for $C_{124}H_{154}Br_2F_4N_8O_2S_6$ $[M+H]^+$ 2214.88, found: 2214.86.

Synthesis of Compound 5

Under the protection of argon, $LiAlH_4$ (55 mg, 1.43 mmol, 5.0 eq.) was added to a solution of compound 1 (348 mg, 0.25 mmol, 1.0 eq.) in tetrahydrofuran (THF, 20 mL). The resulting mixture was stirred and heated to reflux for 12 h. After being cooled to 0 °C, water (30 mL) is slowly dropped into the reaction and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 for 1 h. After removal of solvent, the crude product was dissolved in chloroform (45 mL), then 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ, 113 mg, 0.5 mmol, 2.0 eq.) and 2,7-

dichlorobenzo[2,1-b:3,4-b']dithiophene-4,5-diamine (410 mg, 1.43 mmol, 5.0 eq.) were added to the solution in turn. The reaction was stirred at room temperature for 6 h, and the solvent was removed under vacuum. The resulting product 5 was directly used for the next step without further purification.

Synthesis of Compound 6

Under the protection of argon, phosphorus oxychloride (0.3 mL) was added to a solution of compound 5 (328 mg, 0.20 mmol) and N, N-Dimethylformamide (DMF, 0.4 mL) in 1, 2-dichloroethane ($ClCH_2CH_2Cl$, 50 mL). The resulting mixture was stirred and heated to reflux for 12 h, then cooled to 0 °C. The resulting mixture was slowly added to a saturated solution of sodium acetate (40 mL), then stirred at room temperature for 2 h. The resulting mixture was extracted with dichloromethane and the organic layer was dried over anhydrous Na_2SO_4 for 1 h. After removal of solvent, the crude product was then purified by column chromatography on silica gel with hexanes/dichloromethane (v/v=1:2) as eluent to afford compound 6 as a red solid (248 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 2H), 8.52 (s, 2H), 4.74 (d, *J* = 7.9 Hz, 4H), 3.34 (t, *J* = 7.6 Hz, 4H), 2.17 (s, 2H), 2.11 – 1.99 (m, 4H), 1.59 (s, 11H), 1.53 – 1.44 (m, 4H), 1.42 – 0.73 (m, 111H). MS (m/z, MALDI): Calc. for $C_{100}H_{148}Cl_2N_4O_2S_6$ $[M+H]^+$ 1698.93, found: 1699.93.

Synthesis of Compound 7

Under the protection of argon, dry pyridine (0.5 mL) was added to a solution of compound 6 (302 mg, 0.178 mmol, 1.0 eq.) and 2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (145 mg, 0.534 mmol 3.0 eq.) in chloroform ($CHCl_3$, 45 mL). The resulting mixture was stirred and heated to reflux for 12 h. After being cooled to room temperature, the solvent was removed under a vacuum. The crude product was then purified by column chromatography on silica gel with hexanes/dichloromethane (v/v=1:3) as eluent to afford 7 as a black and green solid (346 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 2H), 8.37 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 1.9 Hz, 2H), 7.78 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.67 (s, 2H), 4.97 (d, *J* = 7.9 Hz, 4H), 3.20 (d, *J* = 7.9 Hz, 4H), 2.37 (s, 2H), 1.85 (t, *J* = 7.9 Hz, 4H), 1.61 – 0.89 (m, 107H), 0.88 – 0.68 (m, 17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.82, 159.07, 153.44, 146.49, 138.18, 138.06, 137.87, 137.38, 136.05, 135.82, 135.11, 133.28, 133.16, 131.39, 131.23, 130.35, 129.46, 126.67, 126.02, 122.35, 119.53, 119.34, 115.26, 114.81, 67.88, 56.12, 39.83, 31.87, 31.11, 30.26, 29.81, 29.78, 29.73, 29.70, 29.65, 29.38, 29.35, 26.30, 22.64, 14.06, 14.03.MS (m/z, MALDI): Calc. for $C_{124}H_{156}Br_2Cl_2N_8O_2S_6$ $[M+H]^+$ 2210.84, found: 2211.83.

The nuclear magnetic resonance (NMR) spectra and High-Resolution Mass Spectra (HRMS).

The 1H/13C nuclear magnetic resonance (^{1}H/^{13}C NMR) spectra of all compounds were obtained from a Bruker AV400 Spectrometer. The High-Resolution Mass Spectra (HRMS) were recorded by Solarix scimax MRMS with high-resolution matrix-assisted laser desorption/ionization (HR-MALDI).

Molecular weight and polydispersity index measurement.

To measure the molecular weight and polydispersity index of polymer acceptors, gel permeation chromatography (GPC) measurement was carried out on a Waters E2695 instrument using trichlorobenzene (TCB) as eluent at 150 °C.

UV-visible (UV-vis) absorption.

UV-vis absorption spectra and Variable-temperature UV-vis absorption spectra were recorded on a Cary 5000 UV-vis spectrophotometer.

Electrochemical characterizations.

The cyclic voltammetry (CV) was performed on a LK98B II Microcomputer-based Electrochemical Analyzer using a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as reference electrode, and a Pt wire as the counter electrode. The sample film on working electrode was in an acetonitrile solution of 0.1 mol L^{-1} n-Bu_4NPF_6 at a scan rate of 100 mV s^{-1}. The ferrocene/ferrocenium was employed as internal reference. The HOMO and LUMO levels were calculated using the following equations: E_{HOMO}=-(E_{ox}+4.8-E_{Fc/Fc^+}) eV, E_{LUMO}=-(E_{red}+4.8-E_{Fc/Fc^+}) eV.

Photoluminescent (PL).

The steady-state photoluminescence was measured via a FLS1000 equipment. The emission spectra of SH-1 and SH-2 were recorded by NIR 5509 PMT, respectively. The thin-films were prepared by spin-coating their chloroform solutions on the quartz substrate. The polymer acceptors were excited at 750 nm.

Fourier-transform photocurrent spectroscopy EQE (FTPS-EQE).

The OSCs used for the FTPS-EQE spectra measurements are the same with those of the J-V measurements, with a conventional device structure of ITO/PEDOT:PSS/Active layer/PNDIT-F3N/Ag. The FTPS-EQE measurement was carried out on an integrated system (PECT-600, Enli Technology Co., Ltd.), where the photocurrent was amplified and modulated by a lock-in instrument.

Atomic force microscopy (AFM).

The AFM images were obtained from a Bruker Dimension Icon atomic force microscope by using in tapping mode. The film samples were prepared under the same conditions as those used for device fabrication.

Grazing incidence wide angle X-ray scattering (GIWAXS).

The GIWAXS data was obtained at in a Xeuss 3.0 SAXS/WAXS system with a wavelength of λ = 1.341 Å at Vacuum Interconnected Nanotech Workstation (Nano-X). The exposure time was 10 minutes. The film samples on the Si substrate were prepared under the same conditions as those used for device fabrication.

Measurement of charge carrier mobilities.

The hole and electron mobilities were measured by using space-charge-limited (SCLC) method. Hole mobilities were measured with the device structure of

ITO/PEDOT:PSS/active layer/MoO_3/Ag. Electron mobilities were measured with the device structure of ITO/ZnO/active layer/PNDIT-F3N/Ag. The hole and electron mobilities estimated by the following equation: $J=9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant, V is the internal voltage in the device, and d is the thickness of the active layer.

Device Fabrication and Characterization

The OSCs were fabricated with a conventional structure of ITO/PEDOT:PSS/Active layer/PNDIT-F3N/Ag. First, ITO-coated glass was cleaned with deionized water, acetone, and isopropyl alcohol under ultrasonication for sequentially 15 mins. Second, the surface of ITO-coated glass was treated in an ultraviolet-ozone chamber for 15 min. A thin layer of PEDOT: PSS (Baytron PVP AI 4083) was deposited on the ITO substrate at 4300 rpm for 20 s and then dried at 150 °C for 20 mins in air. Then the substrates were transferred to a glovebox filled with nitrogen. The PM6:SH-1 (1:1 *w*/*w*) was dissolved in chloroform at the total blend concentration of 12 mg/mL with 1vt% Chloronaphthalene as additive. The PM6:SH-2 (1:1 *w*/*w*) was dissolved in chloroform at the total blend concentration of 11 mg/mL with 1vt% Chloronaphthalene. All the solutions need to be stirred at room temperature overnight. The active layer was spun onto the PEDOT: PSS layer at 2000 rpm for 30 s, and then the films were treated with thermal annealing at 130°C for 5 min. After cooled down, the methanol solution of PNDIT-F3N (1 mg/mL) was spin-coated on the top of the active layer at 3000 rpm for 20 s. Finally, Ag electrode with the thickness of 150 nm was evaporated under 2×10^{-6} Pa. The active area of device was 4 mm^2.

The current density-voltage (*J*-*V*) curves of the all-PSCs were recorded on a Keithley 2400 source-measure unit in a glove box filled with nitrogen. Enli SS-F5-3A solar simulator with AM1.5 G was used as the light source, and the light intensity was 100 mW cm^{-2} which was calibrated by a standard Si solar cell (made by Enli Technology Co., Ltd., Taiwan, and calibrated report can be traced to NREL). A QE-R Solar Cell Spectral Response Measurement System was used to measure the external quantum efficiency (EQE) values of the devices.

Supporting Figures and Tables

Table S1. The optimal photovoltaic parameters of PM6:SH-1-based devices with different blend concentration under AM 1.5G Illumination (100 mW cm^{-2}).

Concentration	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)$^{a)}$
10mg/mL	0.973	68.14	19.04	12.65
11mg/mL	0.976	69.06	18.99	12.83
12mg/mL	0.973	67.27	20.09	13.18
13mg/mL	0.972	66.50	19.73	12.78

Table S2. The optimal photovoltaic parameters of PM6:SH-1-based devices with different additives under AM 1.5G Illumination (100 mW cm^{-2}).

Additive	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)$^{a)}$
1vt% CN	0.982	68.24	20.60	13.73
1vt% DIO	0.980	66.83	20.21	13.30
100wt% 2-MN	0.981	67.82	20.04	13.39

Table S3. The optimal photovoltaic parameters of PM6:SH-1-based devices with different D:A ratios under AM 1.5G Illumination (100 mW cm^{-2}).

D:A (w:w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)$^{a)}$
1:1	0.976	68.77	20.80	13.86
1:1.2	0.975	68.92	20.26	13.51
1:1.4	0.976	67.11	20.03	13.02

Table S4. The optimal photovoltaic parameters of PM6:SH-1-based devices thermal annealing at different temperature under AM 1.5G Illumination (100 mW cm^{-2}).

Temperature	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)$^{a)}$
As cast	0.984	60.88	20.26	12.08
90°C	0.982	68.24	20.60	13.73
110°C	0.976	68.20	21.03	13.94
130°C	0.975	68.34	21.24	14.10

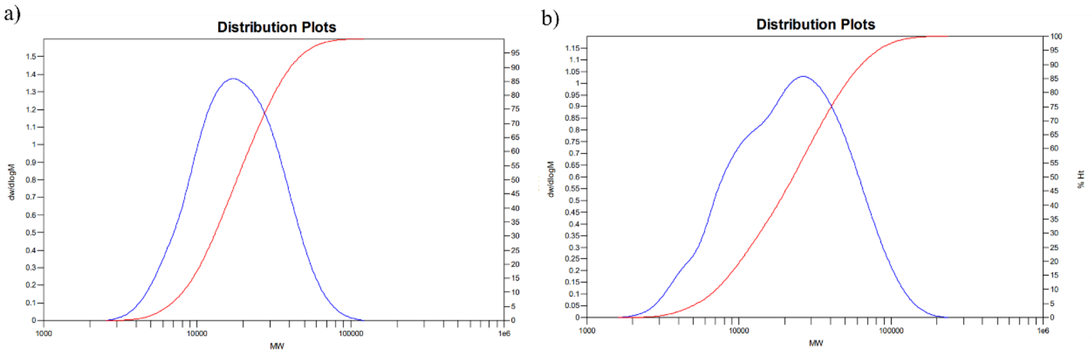


Figure S1. The molecular weight of a) SH-1 and b) SH-2 measured by GPC.

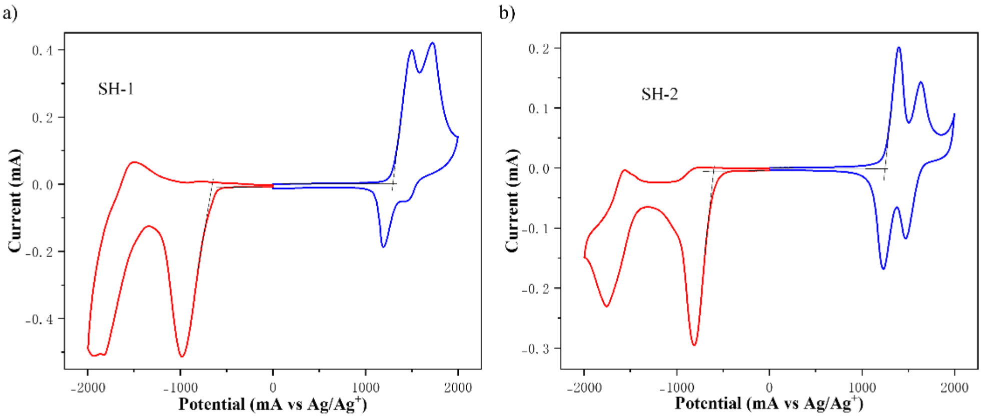


Figure S2. Electrochemical cyclic voltammetry curves of a) SH-1 and b) SH-2.

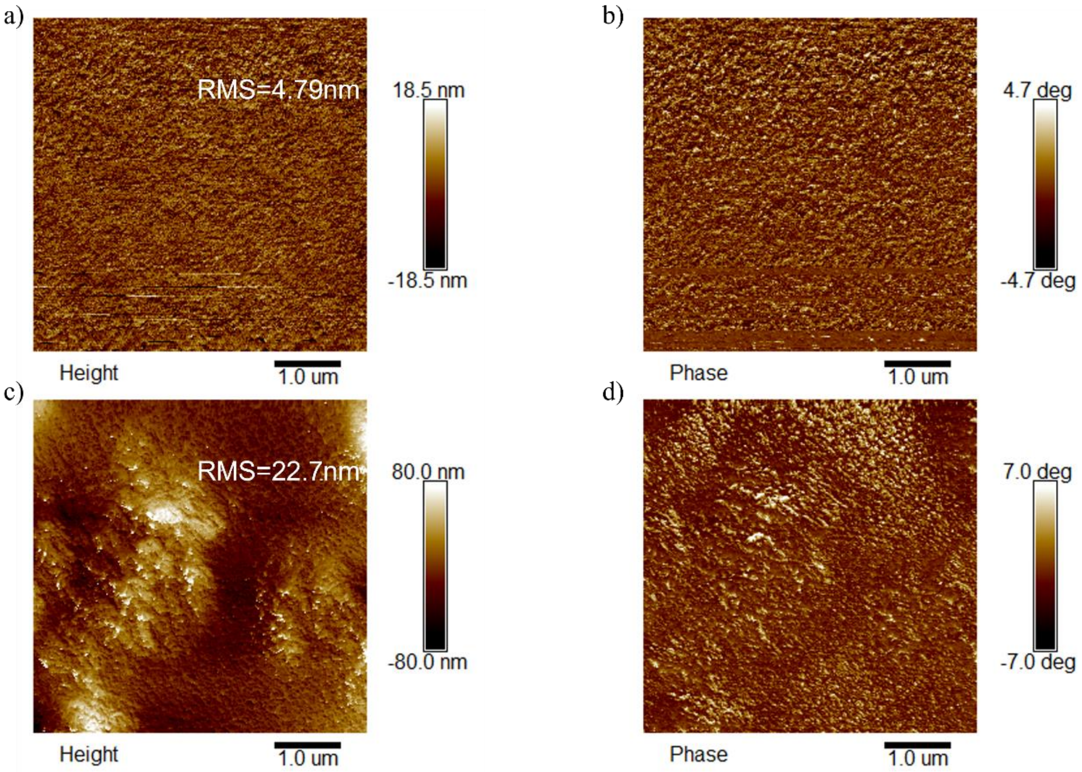


Figure S3. a) AFM height image and b) AFM phase image for SH-1 neat film. c) AFM height image and d) AFM phase image for SH-2 neat film.

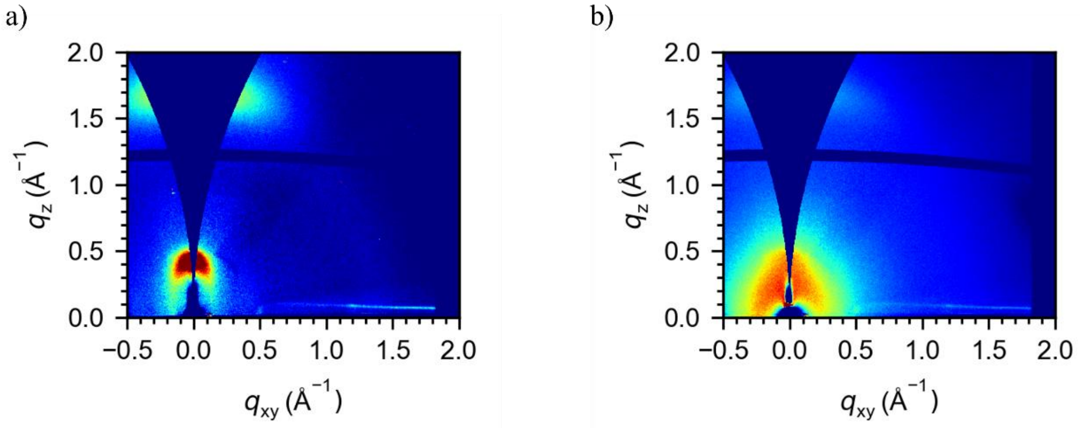


Figure S4. GIWAXS pattern for a) SH-1 neat film and b) SH-2 neat film.

Table S5. The detailed parameters of corresponding 1D GIWAXS profiles with (100) and (010) diffraction peaks for SH-1, SH-2 and SH-1, SH-2-based blend films, respectively.

Film	(010)		(100)	
	q (Å^{-1})	d^{a} (Å)	q (Å^{-1})	d^{a} (Å)
SH-1	1.625	3.867	-	-
SH-2	1.755	3.581	-	-
PM6:SH-1	1.671	3.760	0.292	21.52
PM6:SH-2	1.653	3.801	0.290	22.05

Stacking distance calculated from the equation: $d = 2\pi/q$.

Table S6. The CCL parameters of corresponding 1D GIWAXS profiles with (100) and (010) diffraction peaks for PM6:SH-1 and PM6:SH-2 blend films, respectively.

Film	π-π stacking	
	FHWM	CCL (Å)
PM6:SH-1	0.164	34.48
PM6:SH-2	0.198	28.56

CCL calculated from the equation: $CCL = 2\pi K/FWHM$ ($K = 0.9$).

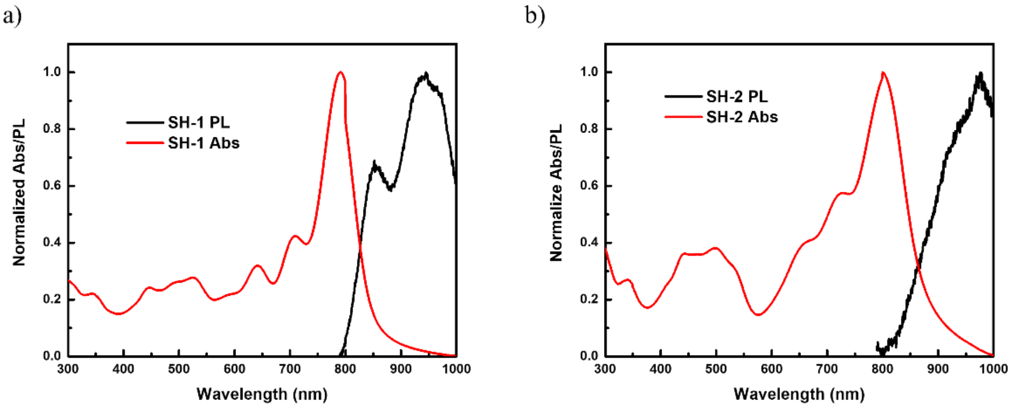


Figure S5. The energy gaps (E_g) of a) PM6:SH-1 and b) PM6:SH-2 estimated from the intersection of normalized optical absorption and PL curves. Excited wavelength at 750 nm and E_g is estimated by the equation $E_g = 1240/\lambda$.

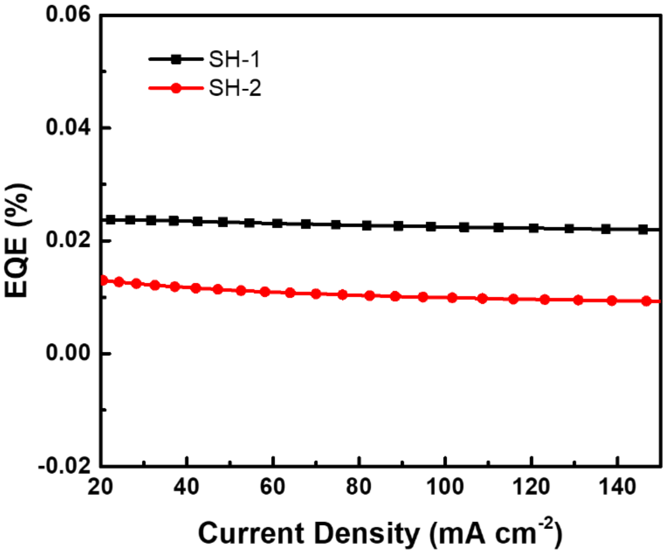


Figure S6. The corresponding EQE_{EL} spectra for optimized all-PSCs.

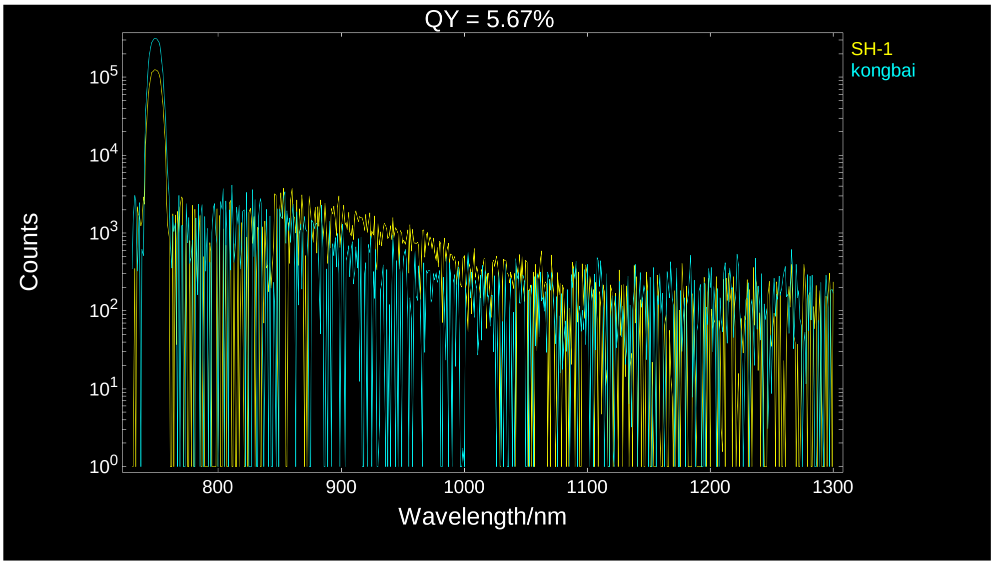


Figure S7. PLQY measurement of SH-1.

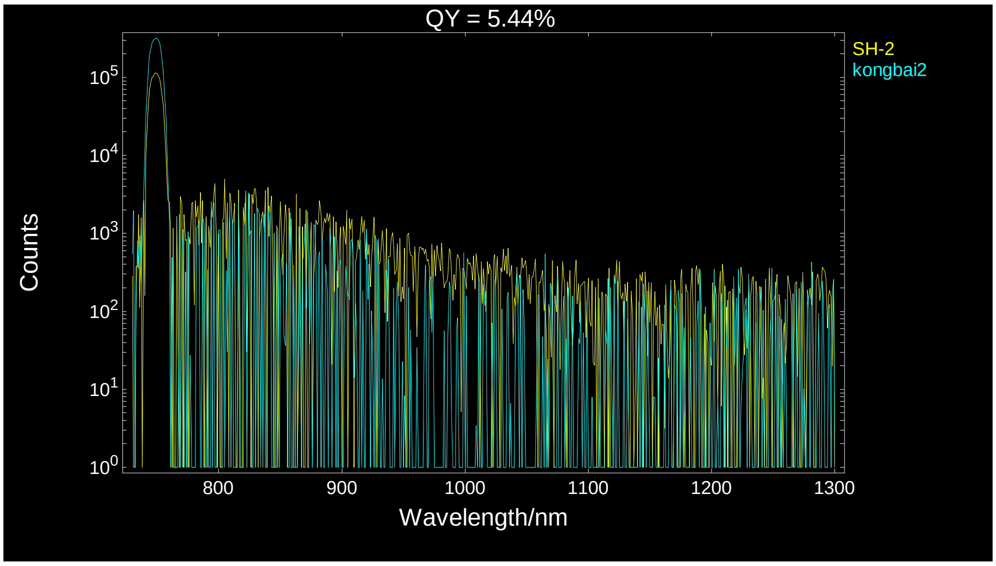


Figure S8. PLQY measurement of SH-2.

Spectral Charts of NMR and HR-MS

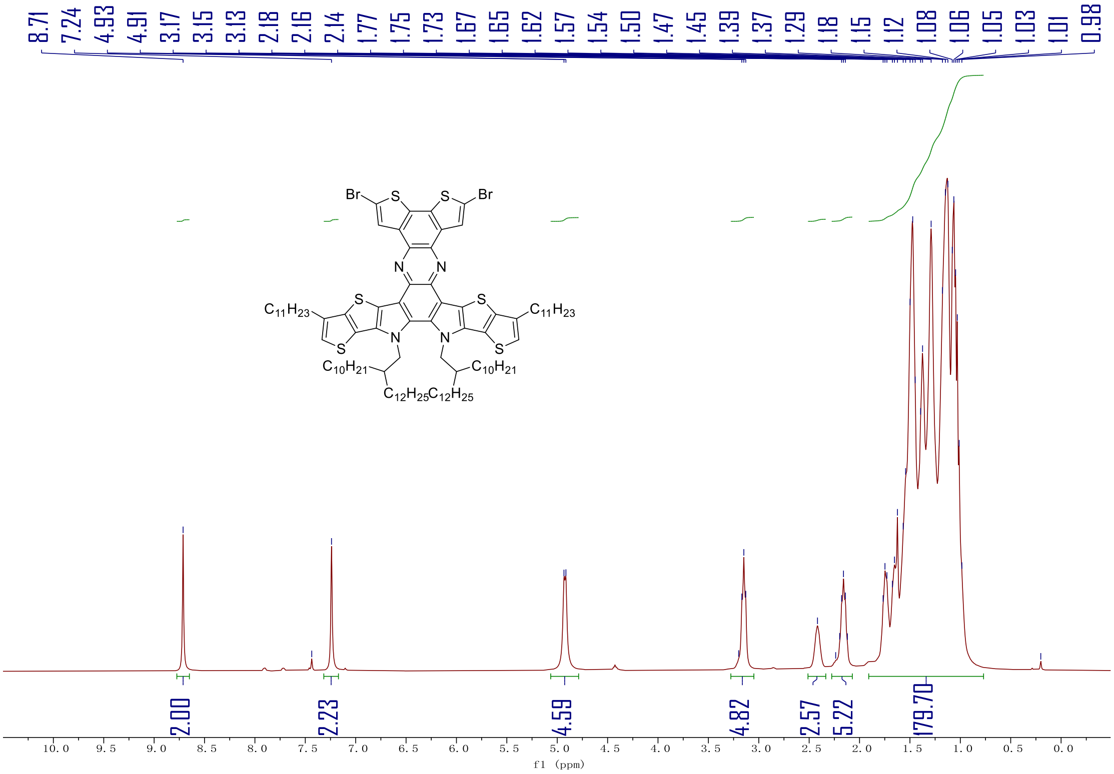


Figure S9. ^{1}H NMR spectra of compound 2 in $CDCl_3$.

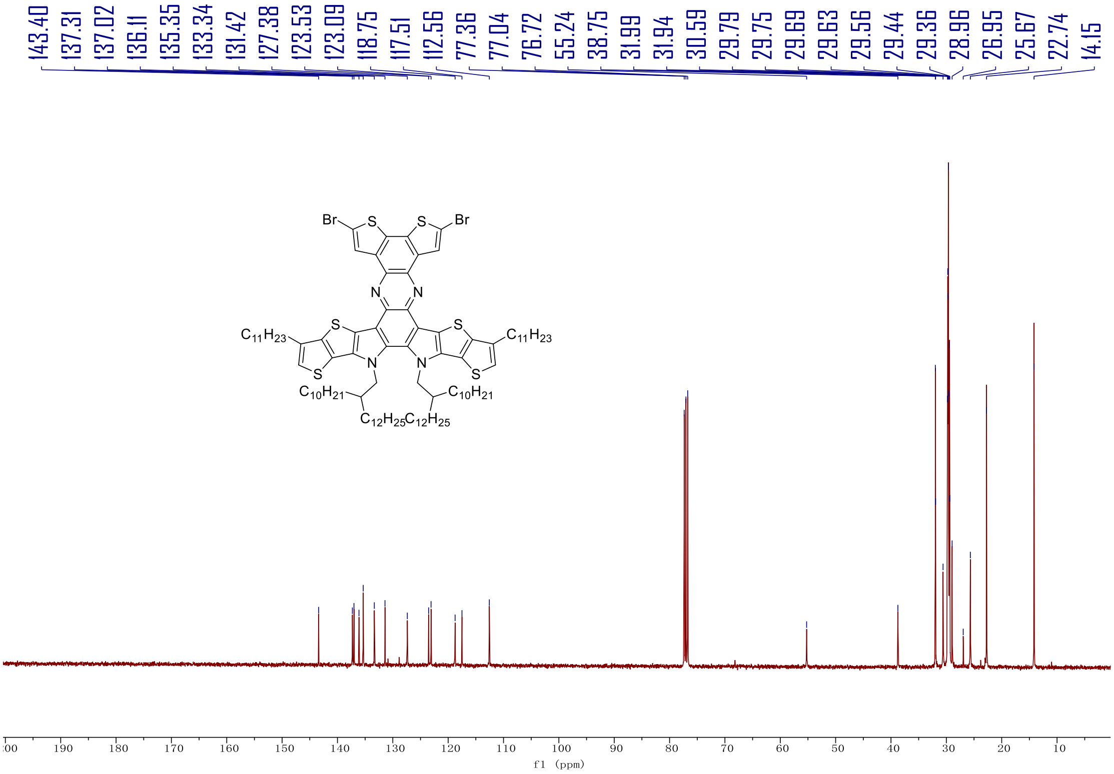


Figure S10. ^{13}C NMR spectra of compound 2 in $CDCl_3$.

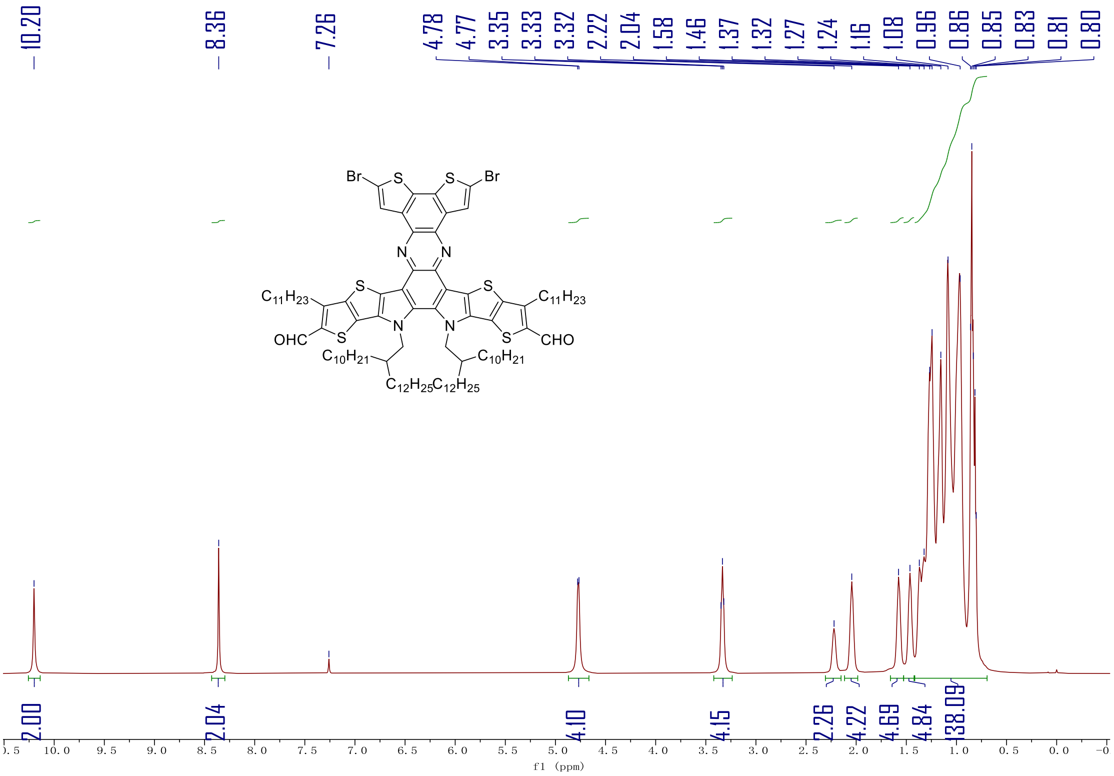


Figure S11. ^{1}H NMR spectra of compound 3 in $CDCl_3$.

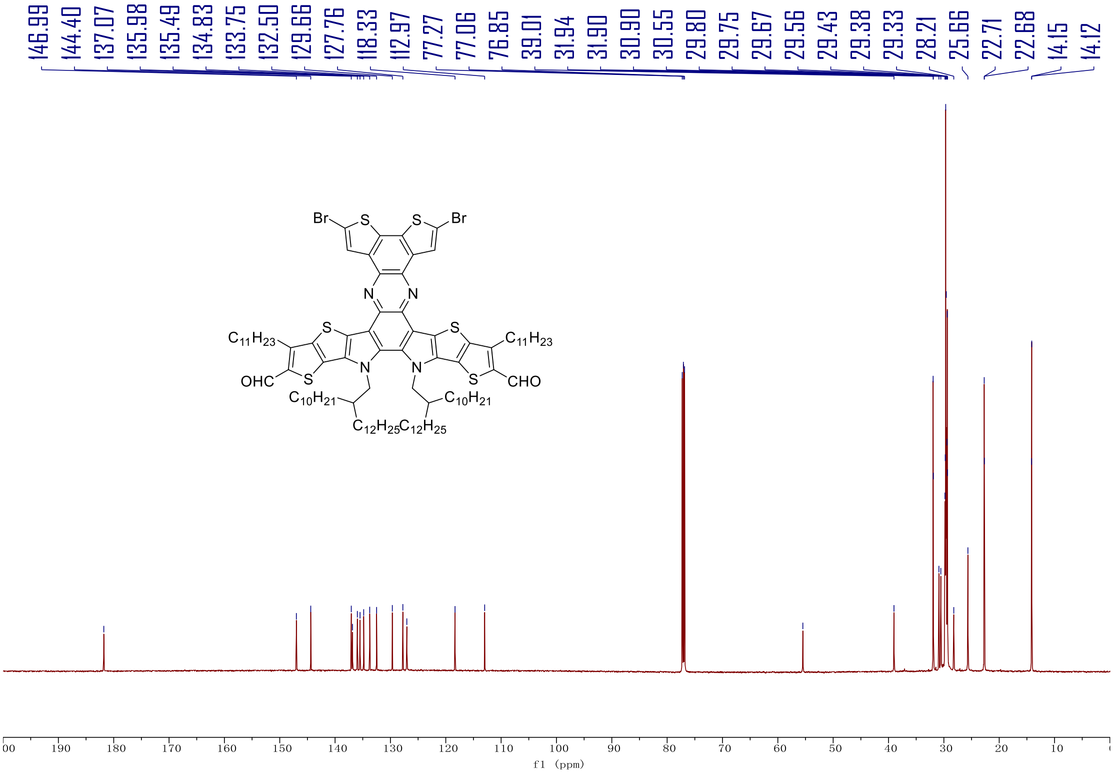


Figure S12. ^{13}C NMR spectra of compound 3 in $CDCl_3$.

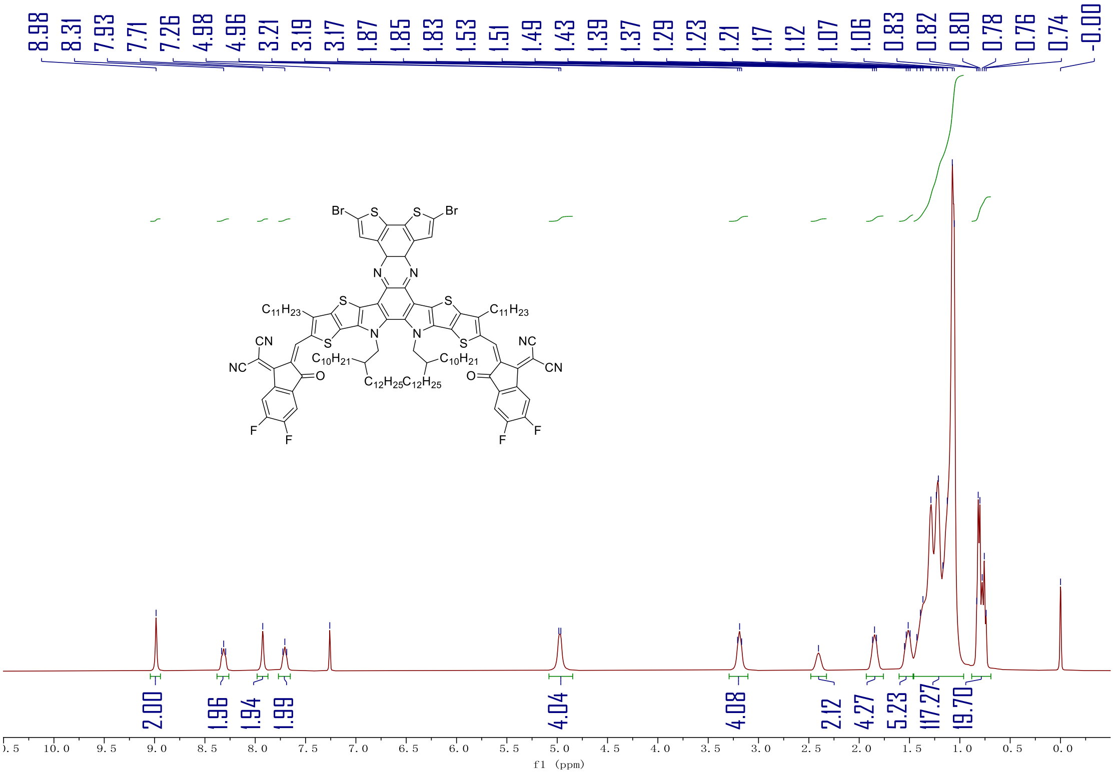


Figure S13. ^{1}H NMR spectra of compound 4 in CDCl$_3$.

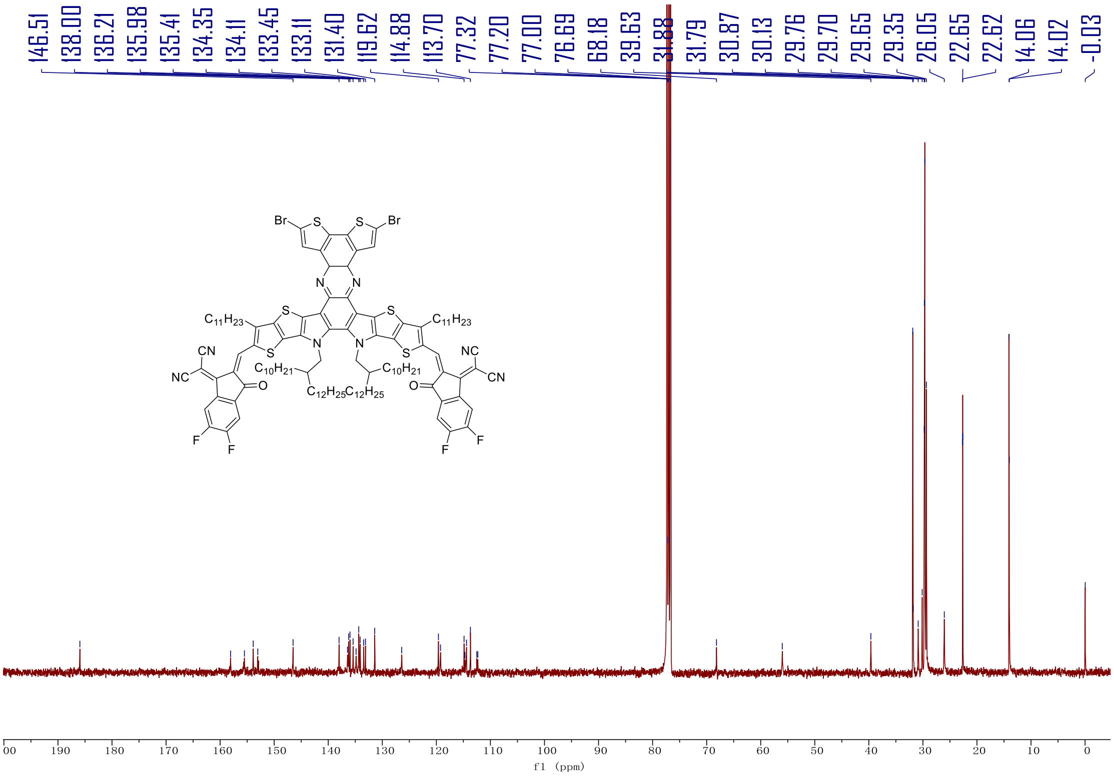


Figure S14. ^{13}C NMR spectra of compound 4 in CDCl$_3$.

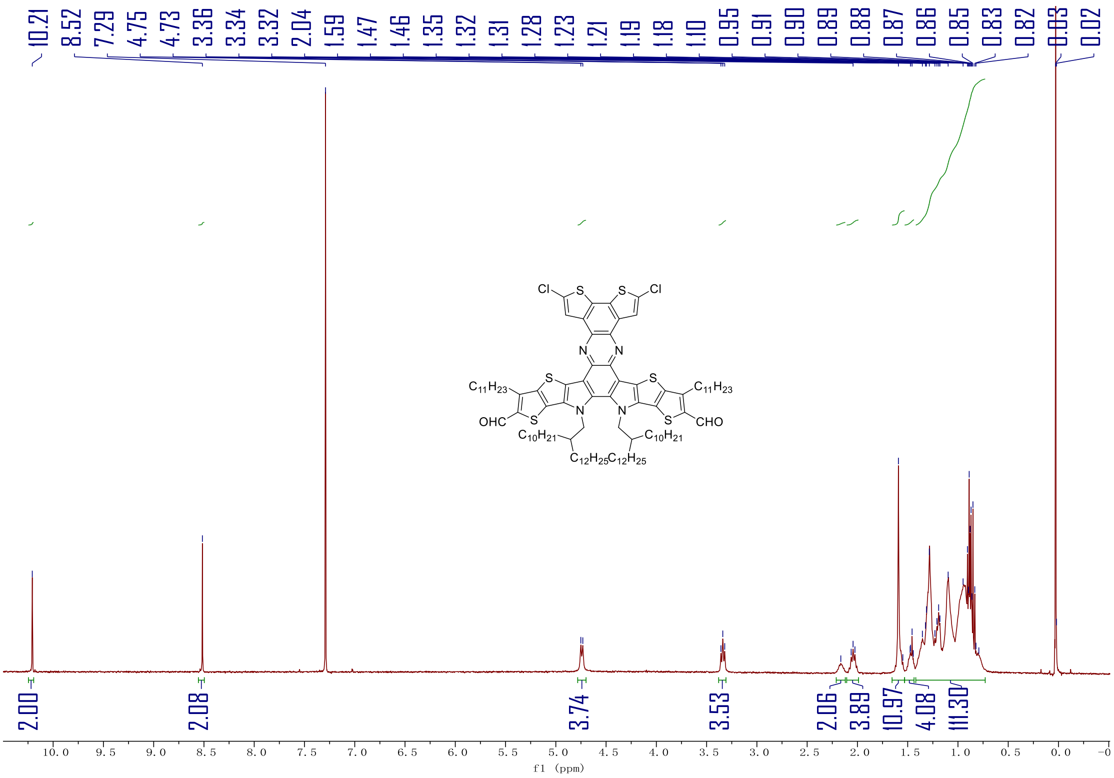


Figure S15. ^{1}H NMR spectra of compound 6 in $CDCl_3$.

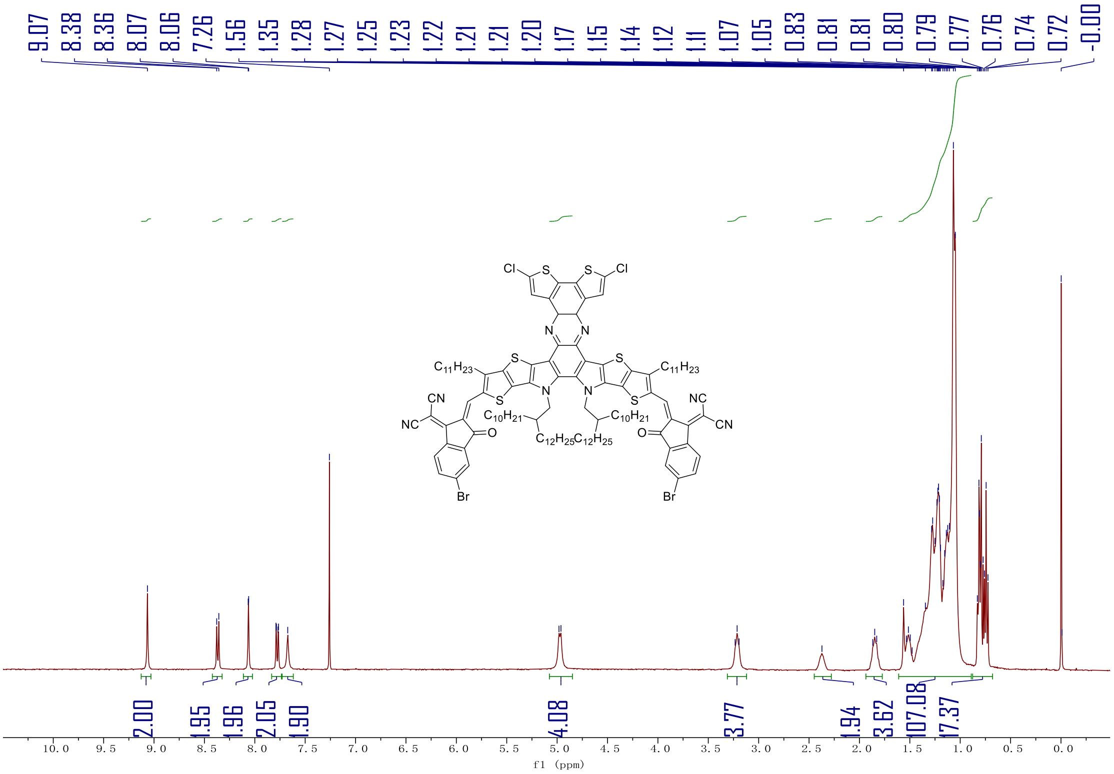


Figure S16. ^{1}H NMR spectra of compound 7 in $CDCl_3$.

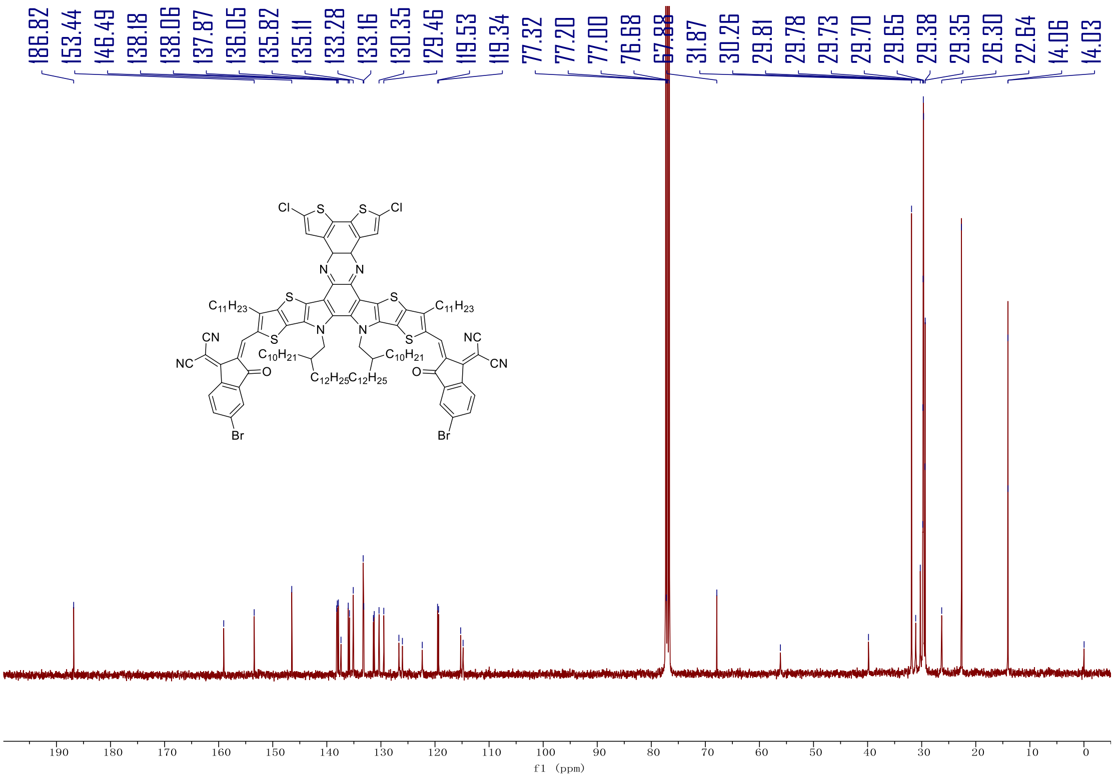


Figure S17. ^{13}C NMR spectra of compound 7 in $CDCl_3$.

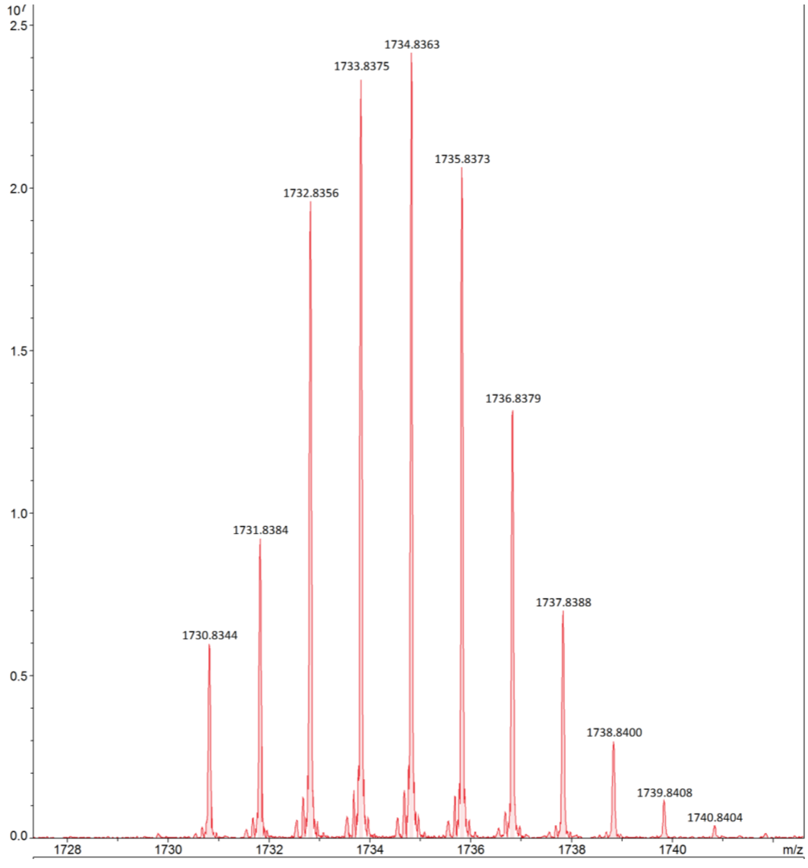


Figure S18. High resolution mass spectra of compound 2.

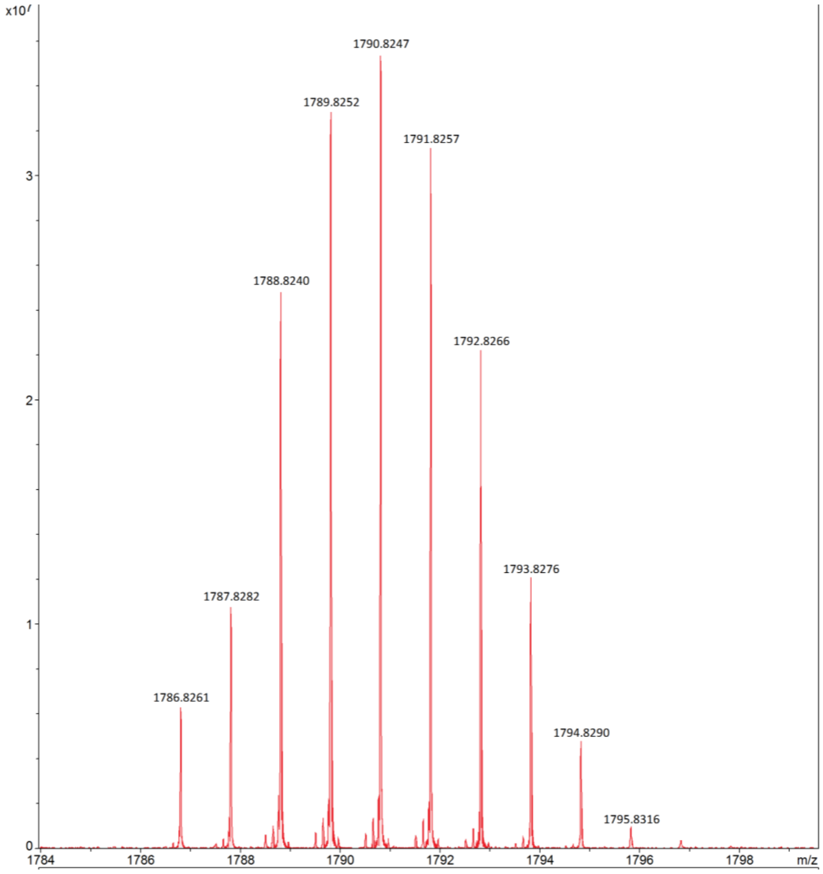


Figure S19. High resolution mass spectra of compound 3.

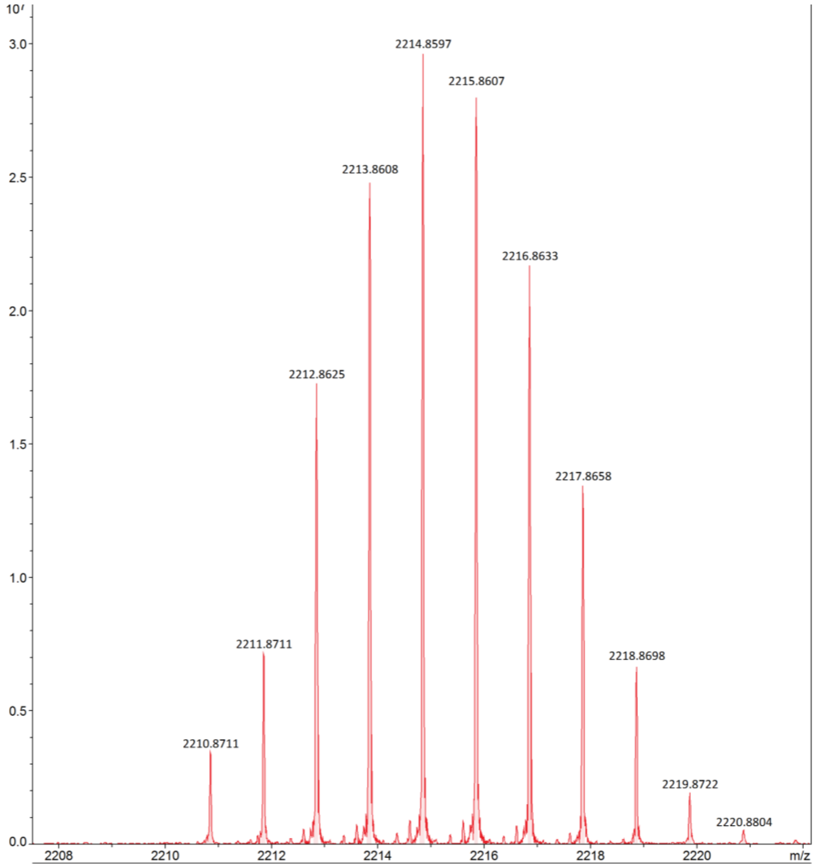


Figure S20. High resolution mass spectra of compound 4.

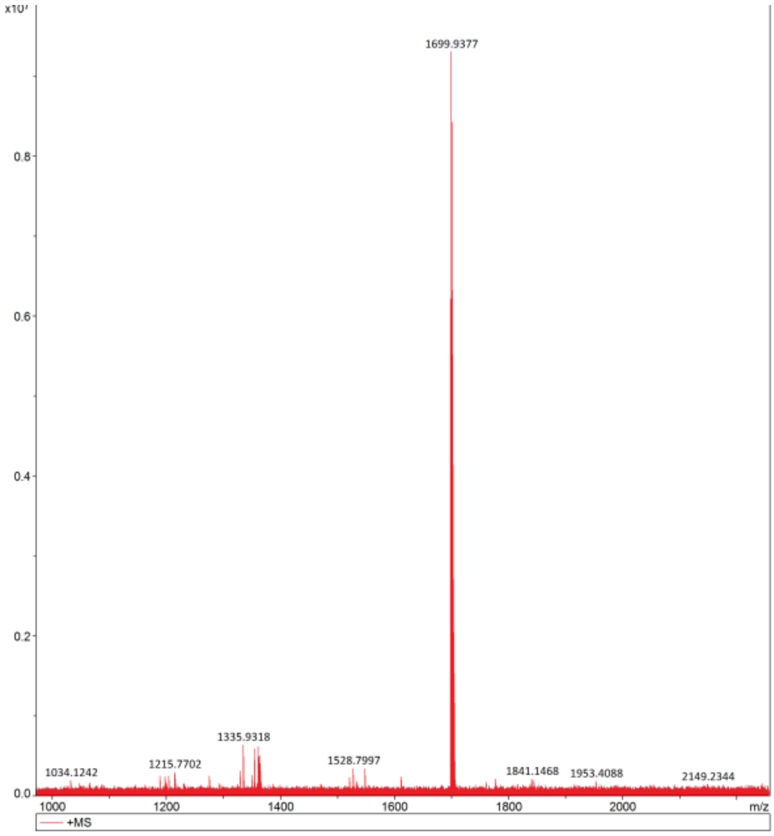


Figure S21. High resolution mass spectra of compound 6.

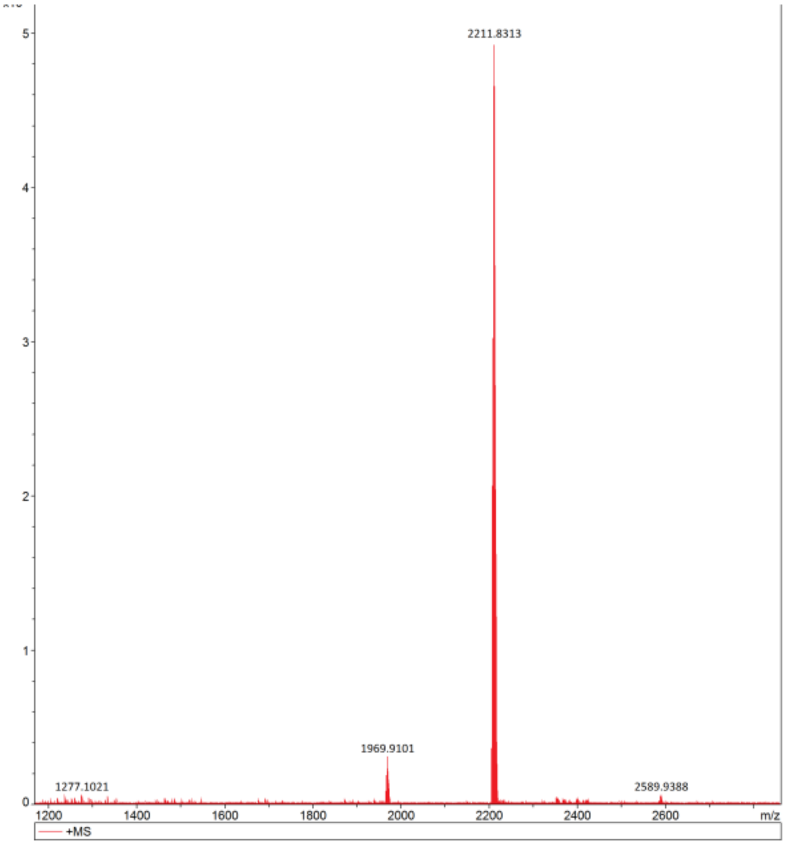


Figure S22. High resolution mass spectra of compound 7.