

## Central Units Hetero Di-Halogenation of Acceptors Enable Organic Solar Cells with 19% Efficiency

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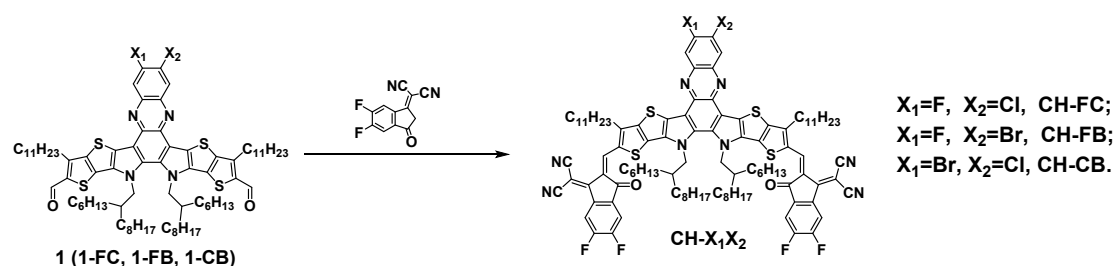
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## 1. Materials and Synthesis

Polymer donor PM6 was purchased from Solarmer Material (Beijing) Inc, Organtec. Compound **1** was synthesized according to our previous reports. All chemicals and other reagents, unless otherwise specified, were purchased from commercial suppliers (such as Alfa Aesar, TCI Chemical Co.) and were directly used without further purification.



**Scheme S1. The synthetic route to CH-FC, CH-FB and CH-CB.** Reagents and conditions: 2-(6,7-difluoro-3-oxo-2,3-dihydro-1H-cyclopenta[b] naphthalen-1-ylidene) malononitrile, pyridine, CHCl<sub>3</sub>, reflux.

Under argon protection, compound 1-FC (450 mg, 0.338 mmol, 1.0 eq.), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (232 mg, 1.00 mmol, 3.0 eq.) and dry chloroform (45 mL) were added to 100 mL of two-necked round bottom flask. Then pyridine (0.5 mL) was dropped into the mixture. The reaction mixture was stirred at 75 °C for 8 h. After cooling to room temperature, the reaction mixture was concentrated to 5 mL and precipitated in 50 mL methanol. The precipitate was purified by column chromatography on silica gel with petroleum ether/ chloroform (v/v=1/1) as eluent to give black compound CH-FC (534 mg, 82%). Compound CH-FB was obtained by a similar method with a yield of 86% as a black solid. Compound CH-CB was obtained by a similar method with a yield of 82% as a black solid.

Data for compound CH-FC:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.05 (s, 1H), 9.04 (s, 1H), 8.50 – 8.39 (m, 2H), 8.265-8.180 (m, 1H), 7.901-7.790 (m, 1H), 7.750-7.654 (m, 2H), 4.85 (d,  $J = 4.5$  Hz, 4H), 3.28-3.095 (m, 4H), 2.29 (s, 2H), 1.932-1.740 (m, 4H), 1.590-1.455 (m, 6H), 1.36 – 0.96 (m, 74H), 0.874-0.784 (m, 6H), 0.760-0.614 (m, 12H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  186.11, 159.01, 158.56, 156.46, 155.74, 155.61, 153.95, 153.14, 153.01, 146.35, 140.76, 140.65, 138.54, 138.42, 137.97, 137.74, 137.68, 136.60, 136.53, 135.96, 135.09, 135.03, 134.50, 134.45, 133.94, 133.69, 133.21, 131.54, 131.46, 129.94, 125.60, 125.38, 119.63, 118.91, 118.68, 114.99, 114.94, 114.78, 114.52, 114.49, 113.19, 112.98, 112.53, 112.35, 68.38, 68.32, 55.92, 39.50, 31.92, 31.85, 31.68, 31.41, 30.76, 29.98, 29.95, 29.73, 29.66, 29.59, 29.45, 29.37, 29.23, 25.87, 22.69, 22.59, 22.52, 14.10, 14.04, 14.02.

Data for compound CH-FB:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.09 (s, 1H), 9.05 (s, 1H), 8.555-8.453 (m, 2H), 8.453-8.348 (m, 1H), 7.93-7.79 (m, 1H), 7.780-7.672 (m, 2H), 4.88 (s, 4H), 3.291-3.132 (m, 4H), 2.402-2.174 (m, 2H), 1.971-1.768 (m, 4H), 1.650-1.466 (m, 6H), 1.460-0.905 (m, 74H), 0.903-0.805 (m, 6H), 0.792-0.616 (m, 12H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  186.12, 159.64, 158.58, 158.51, 157.11, 155.77, 155.62, 153.96, 153.94, 153.17, 153.15, 153.12, 153.03, 153.02, 152.98, 146.39, 146.36, 141.18, 141.06, 138.79, 138.44, 137.86, 137.74, 137.67, 136.58, 135.96, 135.11, 135.01, 134.50, 134.45, 133.93, 133.66, 133.30, 133.21, 131.53, 131.46, 119.66, 119.61, 118.92, 118.65, 115.00, 114.95, 114.93, 114.79, 114.53, 114.48, 113.97, 113.72, 112.85, 112.63, 112.57, 68.39, 68.29, 55.94, 39.53, 31.93, 31.85, 31.69,

31.67, 31.41, 30.78, 30.02, 29.96, 29.90, 29.73, 29.67, 29.61, 29.59, 29.47, 29.45, 29.37, 29.23, 25.91, 22.69, 22.59, 22.53, 14.11, 14.05, 14.03.

Data for compound CH-CB:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.21 (s, 1H), 8.88 (s, 1H), 8.53 (s, 1H), 8.00 (s, 1H), 4.85 (d,  $J=7.6$  Hz, 2H), 3.29 (t,  $J=7.8$  Hz, 2H), 2.25 (s, 1H), 1.93 (s, 2H), 1.46-0.92 (m, 43H), 0.77 (t,  $J=7.2$  Hz, 3H), 0.69 (t,  $J=6.8$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  186.2, 158.4, 154.1, 146.6, 140.0, 140.0, 139.6, 139.3, 138.7, 138.5, 137.7, 136.2, 136.0, 135.6, 133.6, 131.8, 129.3, 126.8, 125.0, 119.7, 118.8, 115.1, 114.5, 68.4, 56.0, 39.6, 31.9, 31.9, 31.7, 31.4, 30.9, 30.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 22.6, 22.5, 14.1, 14.1.

## 2. Single-Crystal Growth

Single crystals of CH-FC, CH-FB and CH-CB were grown by the liquid diffusion method at room temperature. In detail, 1.5 mL of methanol was transferred to 0.15 mL of concentrated chloroform solution of CH-X slowly, and the beautiful cuboid-shape dark purple crystals were formed on the inner glassy tube after about 3 days. The X-ray diffraction signals of single crystal were collected on Rigaku XtalAB PRO MM007 DW. The crystal was kept at 193.0 K during data collection.

## 3. Device Fabrication, Instruments and Measurements

**Device Fabrication.** The conventional devices were fabricated with the architecture of ITO/PEDOT:PSS/Active layers/PNDIT-F3N/Ag. In detail, ITO coated glass substrates were cleaned in turn with detergent water, deionized water, acetone and isopropyl alcohol in an ultrasonic bath sequentially for 15 mins and dried by nitrogen purge.

Before use, the cleaned ITO substrates were treated with UV exposure for 15 mins in a UV-ozone chamber (Jelight Company). Then a thin layer of poly(3,4-ethylene dioxothiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron PVP Al 4083) was first spin-coated on the ITO substrates with 4500 rpm for 20 s. Note that the PEDOT:PSS solution was pre-filtered through a 0.45 mm poly(tetrafluoroethylene) (PTFE) filter. Subsequently, the PEDOT:PSS films were baked at 150 °C for 20 mins under ambient conditions and transferred to a glove box quickly. Then the PM6:CH-X mixtures (D:A ratio=1:1.2) were fully dissolved in chloroform (CF) with 0.4% 1-chloronaphthalene (CN) as an additive at a total concentration of 13.2 mg mL<sup>-1</sup>. The PM6:D18:CH-X mixtures (D:A ratio=0.7:0.3:1.2) were fully dissolved in CF with 50wt% paradiiodobenzene as a solid additive at a total concentration of 13.5 mg mL<sup>-1</sup>. After spin-coating, the blended films were annealed. The best active layer thickness is about 110 nm. PNDIT-F3N (dissolved in methanol with 0.3% v/v glacial acetic acid at the concentration of 1 mg mL<sup>-1</sup>) layer was spin-coated on the top of the active layers at 3000 rpm for 20 s. Finally, 150 nm Ag was deposited under 2×10<sup>-6</sup> Pa. The active area of the device was 4 mm<sup>2</sup>. The area of the mask was about 2.58 mm<sup>2</sup> in our laboratory.

### **Instruments and Measurements**

**UV-Visible (UV-Vis) Absorption.** The UV-Vis spectra were obtained by a Cary 5000 UV-Vis spectrophotometer.

**Cyclic Voltammetry (CV).** The CV experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer. All measurements were conducted at room temperature with a three-electrode configuration. Among them, a glassy carbon

electrode was employed as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a Pt wire was used as the counter electrode. Tetrabutyl ammonium phosphorus hexafluoride ( $n\text{-Bu}_4\text{NPF}_6$ , 0.1 M) in acetonitrile was employed as the supporting electrolyte, and the scan rate was kept at  $100\text{ mV s}^{-1}$ . Electrochemically reversible ferrocene was employed as internal reference. The HOMO and LUMO energy levels were calculated from the onset oxidation and the onset reduction potentials, respectively, by following the equation  $E_{\text{HOMO}} = -(4.80 + E_{\text{onset ox}})\text{ eV}$ ,  $E_{\text{LUMO}} = -(4.80 + E_{\text{onset re}})\text{ eV}$ .

**Thermogravimetric Analysis (TGA).** The TGA analysis was carried out on a TG209 DSC204 DMA242 TMA202 (NETZSCH) instrument with a heating rate of  $5\text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere.

***J-V* and EQE Measurement.** The *J-V* measurements were performed by using the solar simulator (SS-F5-3A, Enli Technology, xenon lamp, filter model AMFG2.0) along with AM 1.5G spectra ( $100\text{ mW cm}^{-2}$ ), which was calibrated by a standard Si solar cell (made by Enli Technology Co., Ltd., Taiwan, and calibrated report can be traced to NREL). The current-voltage scan speed and dwell time are  $0.02\text{ V/s}$  and  $1\text{ ms}$  respectively. The EQE spectra were measured by using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan).

**Space-Charge-Limited Current (SCLC) Measurement.** The SCLC method was used to measure the hole and electron mobilities, by using a diode configuration of ITO/PEDOT:PSS/active layer/ $\text{MoO}_3$ /Ag for hole and ITO/ $\text{ZnO}$ /active layer/PNDIT-F3N/Ag for electron. The dark current density curves were recorded with a bias voltage

in the range of 0~8 V. The mobilities were estimated by taking current-voltage curves and fitting the results based on the equation listed below:

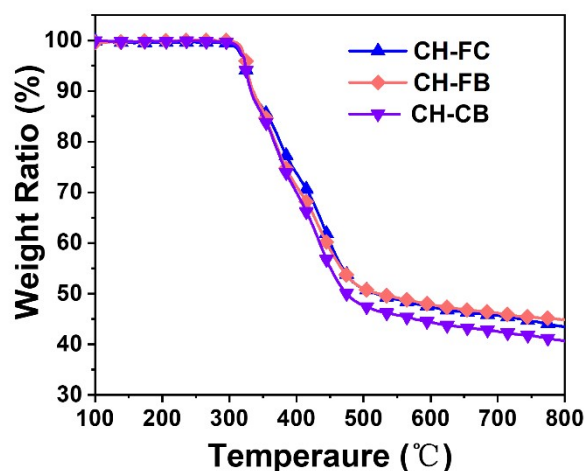
$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

where  $J$  is the current density,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the relative dielectric constant,  $\mu$  is the mobility, and  $L$  is the film thickness.  $V(V_{app}-V_{bi})$  is the internal voltage in the device, where  $V_{app}$  is the applied voltage to the device and  $V_{bi}$  is the built-in voltage due to the relative work function difference between the two electrodes.

**Atomic Force Microscopy (AFM).** The AFM images were performed using in tapping mode on a Bruker Dimension Icon atomic force microscope.

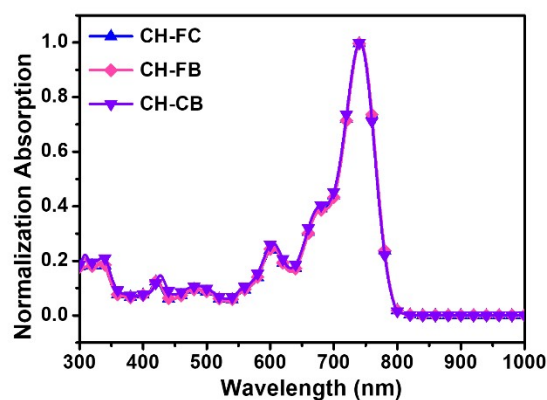
**Grazing Incidence Wide Angle X-ray Scattering (GIWAXS).** The GIWAXS samples were prepared on Si/PEDOT:PSS substrates by use of the same preparation conditions with devices and were carried out at XEUSS SAXS/WAXS equipment.

#### 4. Supporting Figures and Table

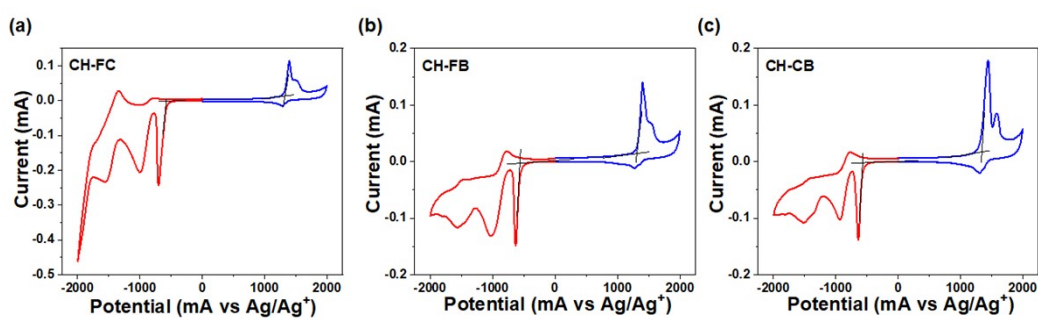


**Fig. S1** Thermogravimetric analysis (TGA) curves of CH-FC, CH-FB and CH-CB. The heating rate is a heating rate of 10 °C/min under nitrogen atmosphere.

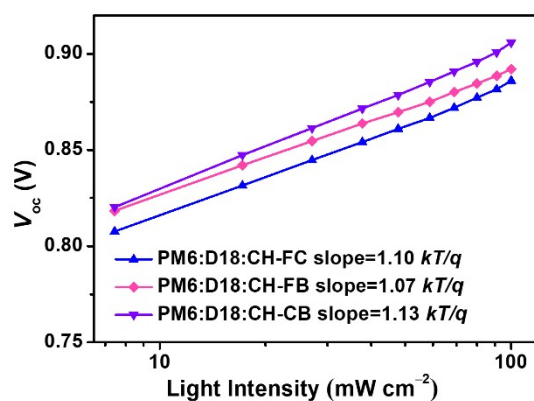




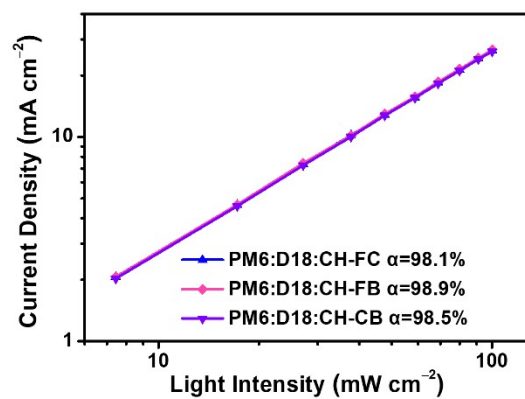
**Fig. S2** Normalized UV-vis absorption spectra of CH-FC, CH-FB and CH-CB in dilute chloroform solutions.



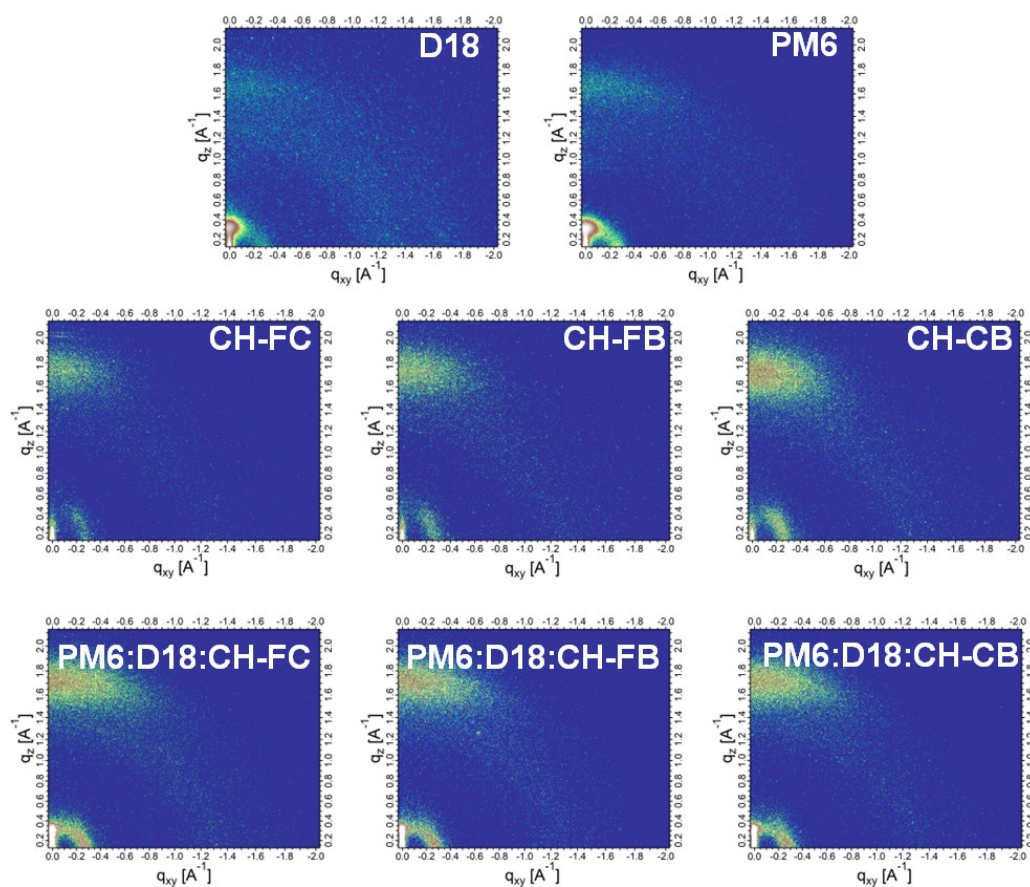
**Fig. S3** Cyclic voltammograms of (a) CH-FC, (b) CH-FB and (c) CH-CB films. Blue line: oxidation cycle, red line: reduction cycle.



**Fig. S4** Dependences of current density  $V_{oc}$  on  $P_{light}$  of optimized OSCs.



**Fig. S5** Dependences of current density  $J_{sc}$  on  $P_{light}$  of optimized OSCs.



**Fig. S6** 2D GIWAXS patterns of D18, PM6, CH-FC, CH-FB and CH-CB-based neat and blended films.

Table S1. The optimal photovoltaic parameters of D18:CH-FC, D18:CH-FB and D18:CH-CB based devices under AM 1.5G Illumination ( $100 \text{ mW cm}^{-2}$ ).<sup>a</sup>

Devices	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	$J_{sc}(\text{EQE}_{cal})^b$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)
D18:CH-FC	0.901 (0.889±0.003)	26.36 (26.32±0.22)	25.43	76.28 (75.98±0.59)	18.12 (18.07±0.21)
D18:CH-FB	0.907 (0.905±0.003)	26.47 (26.35±0.14)	25.26	76.34 (76.02±0.52)	18.33 (18.20±0.26)
D18:CH-CB	0.917 (0.913±0.004)	25.66 (25.45±0.16)	24.91	76.48 (76.51±0.42)	17.99 (17.84±0.15)

<sup>a</sup>The average photovoltaic parameters calculated from 10 independent devices. <sup>b</sup>Current densities calculated from EQE curves.

Table S2. Detailed photovoltaic parameters of the PM6:D18:CH-FB based devices processed by the varied ratio of D:A and post-treatment conditions.

D/A (w/w)	Treatment	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)
0.9:0.1:1.2	CS <sub>2</sub> SVA	0.883	26.93	77.35	18.40
	TA 85°C	0.881	26.88	77.38	18.31
	TA 95°C	0.878	26.90	76.76	18.13
0.8:0.2:1.2	CS <sub>2</sub> SVA	0.877	25.49	76.50	17.10
	TA 85°C	0.897	26.75	77.32	18.54
	TA 95°C	0.890	26.80	76.44	18.23
<b>0.7:0.3:1.2</b>	CS <sub>2</sub> SVA	0.882	26.04	76.35	17.54
	<b>TA 85°C</b>	<b>0.890</b>	<b>26.88</b>	<b>77.75</b>	<b>18.60</b>
	TA 95°C	0.882	26.50	77.99	18.22
0.6:0.4:1.2	CS <sub>2</sub> SVA	0.883	26.43	73.51	17.15
	TA 85°C	0.881	26.92	73.81	17.50
	TA 95°C	0.879	26.77	75.11	17.67
0.5:0.5:1.2	CS <sub>2</sub> SVA	0.874	25.13	75.69	16.63
	TA 85°C	0.870	25.13	73.85	16.15
	TA 95°C	0.879	25.83	72.64	16.50

Table S3. Detailed photovoltaic parameters of the PM6:D18:CH-FB based devices processed by the varied ratios of DIB.

D/A (w/w)	DIB (w/w)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0.7:0.3:1.2	10%	0.884	26.32	70.44	16.40
	20%	0.893	26.21	73.60	17.22
	30%	0.885	26.51	75.41	17.68
	40%	0.894	26.65	76.44	18.20
	<b>50%</b>	<b>0.890</b>	<b>26.88</b>	<b>77.75</b>	<b>18.60</b>
	60%	0.892	26.77	76.72	18.32

Table S4. Detailed photovoltaic parameters of the PM6:D18:CH-FB based devices processed by the varied total concentrations.

D/A (w/w)	Concentrations (mg/mL)	$V_{OC}$ (V)	$J_{SC}$ (mAcm <sup>-2</sup> )	FF (%)	PCE (%)
0.7:0.3:1.2	12.0	0.906	25.43	75.69	17.43
	12.5	0.900	25.84	76.39	17.76
	13.0	0.894	26.16	77.55	18.14
	<b>13.5</b>	<b>0.896</b>	<b>26.85</b>	<b>77.62</b>	<b>18.67</b>
	14.0	0.894	26.81	76.56	18.35
	14.5	0.890	27.07	74.75	18.00

Table S5. Detailed photovoltaic parameters of the PM6:D18:CH-FB based devices processed by the detailed varied rotating speeds.

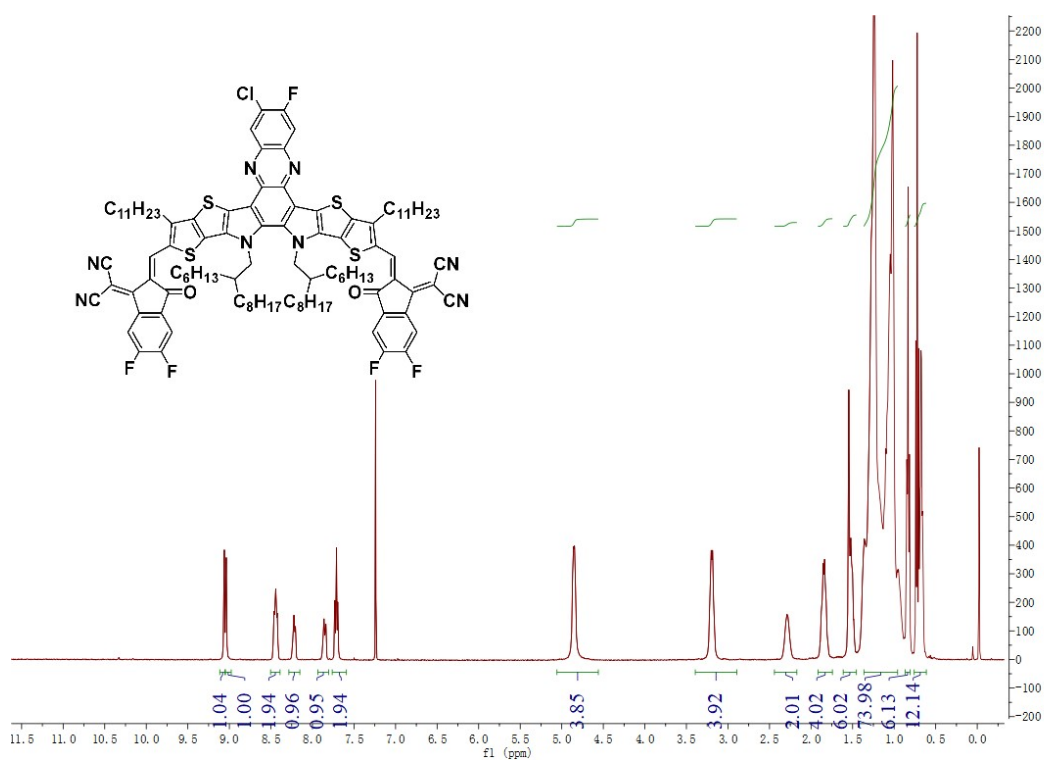
D/A (w/w)	Speeds (r/s)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0.7:0.3:1.2	2100	0.890	26.85	74.51	17.81
	2300	0.888	26.80	76.39	18.19
	2500	0.889	26.82	77.30	18.43
	2700	0.892	26.69	78.27	18.63
	<b>2900</b>	<b>0.888</b>	<b>26.69</b>	<b>80.03</b>	<b>18.97</b>
	3100	0.890	26.66	78.96	18.74

Table S6. The detailed parameters of corresponding 2D GIWAXS.

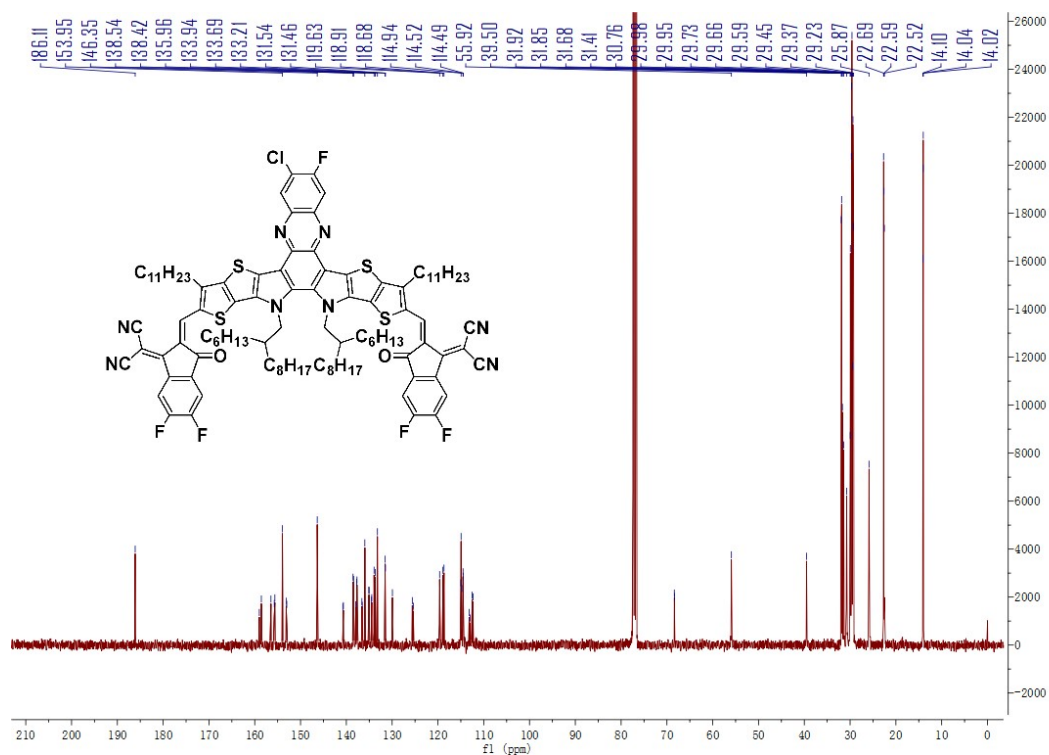
Materials	(010) peak				(100) peak			
	$q$ ( $\text{\AA}^{-1}$ )	$^a d$ ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	$^b \text{CCL}$ ( $\text{\AA}$ )	$q$ ( $\text{\AA}^{-1}$ )	$^a d$ ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	$^b \text{CCL}$ ( $\text{\AA}$ )
<b>CH-FC</b>	1.736	3.619	0.330	17.136	0.282	20.053	0.067	84.401
<b>CH-FB</b>	1.773	3.543	0.275	20.563	0.290	19.450	0.065	86.998
<b>CH-CB</b>	1.762	3.566	0.309	18.301	0.286	21.969	0.062	91.208
<b>PM6:D18:CH-FC</b>	1.730	3.632	0.246	22.987	0.300	20.944	0.060	94.248
<b>PM6:D18:CH-FB</b>	1.742	3.607	0.240	23.562	0.302	20.805	0.059	95.845
<b>PM6:D18:CH-CB</b>	1.734	3.624	0.243	23.271	0.304	20.668	0.057	99.208

<sup>a</sup>Calculated from the equation: d-spacing =  $2\pi/q$ . <sup>b</sup>Obtained from the Scherrer equation:  $\text{CCL} = 2\pi K/\text{FWHM}$ , where FWHM is the full-width at half-maximum and K is a shape factor (K = 0.9 here).

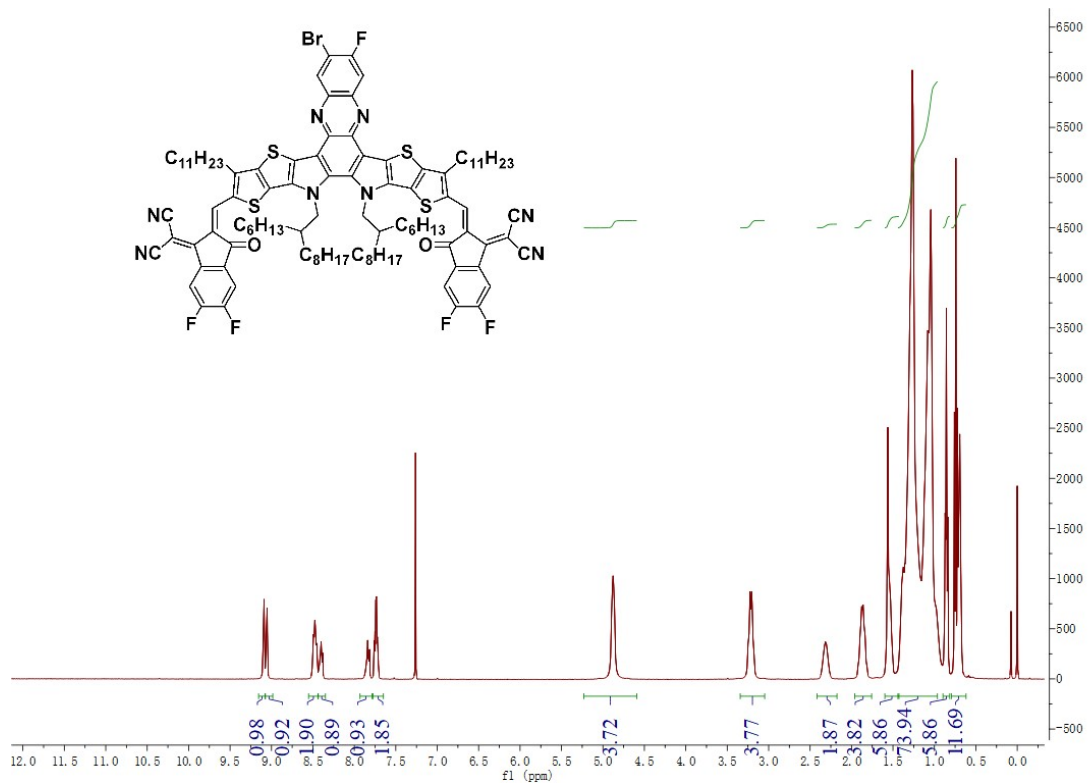
## 5. Spectral Charts of NMR and HRMS



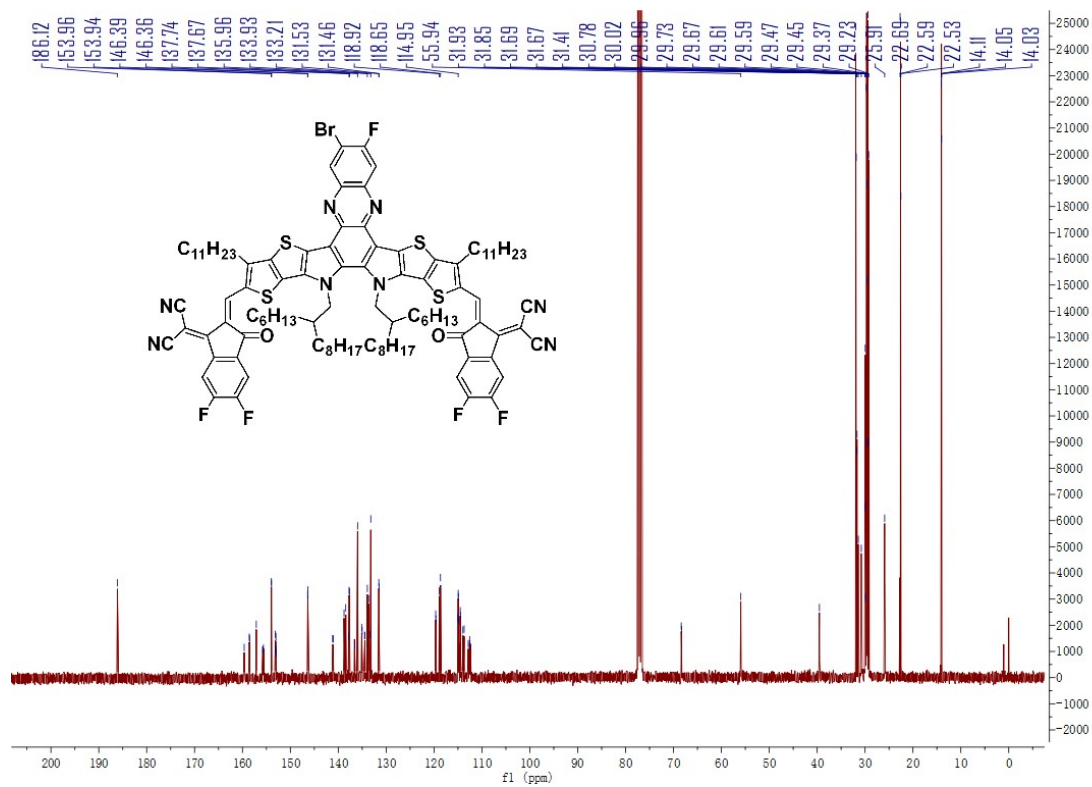
**Fig. S7**  $^1\text{H}$  NMR spectrum of compound CH-FC at 298K in  $\text{CDCl}_3$ .



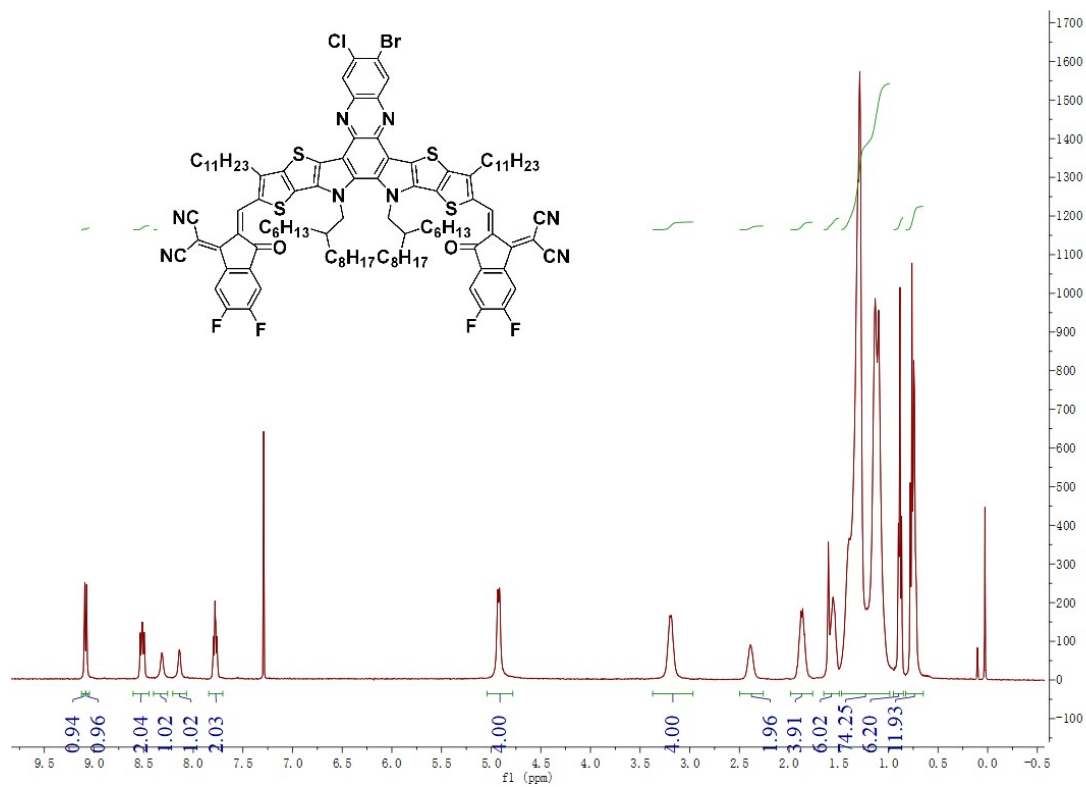
**Fig. S8**  $^{13}\text{C}$  NMR spectrum of compound CH-FC at 298K in  $\text{CDCl}_3$ .



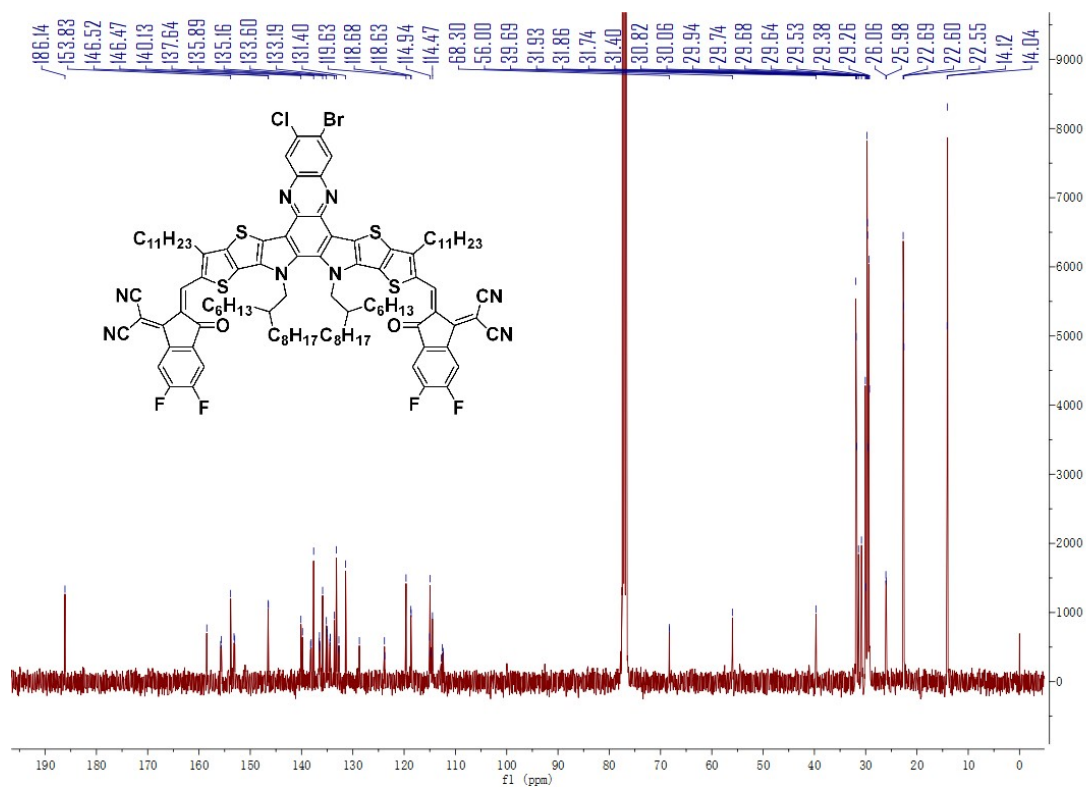
**Fig. S9**  $^1\text{H}$  NMR spectrum of compound CH-FB at 298K in  $\text{CDCl}_3$ .



**Fig. S10**  $^{13}\text{C}$  NMR spectrum of compound CH-FB at 298K in  $\text{CDCl}_3$ .

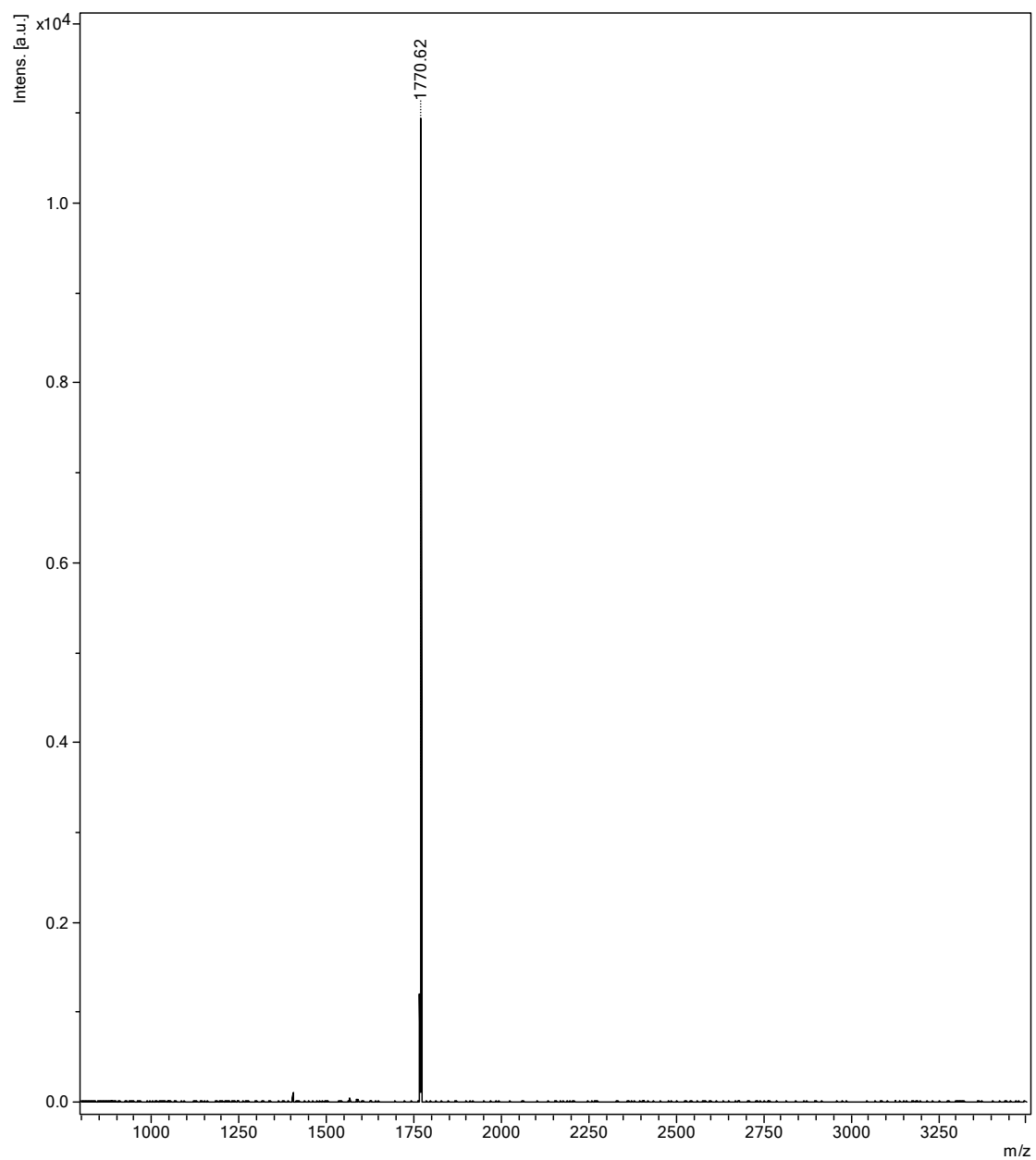


**Fig. S11** <sup>1</sup>H NMR spectrum of compound CH-CB at 298K in CDCl<sub>3</sub>.

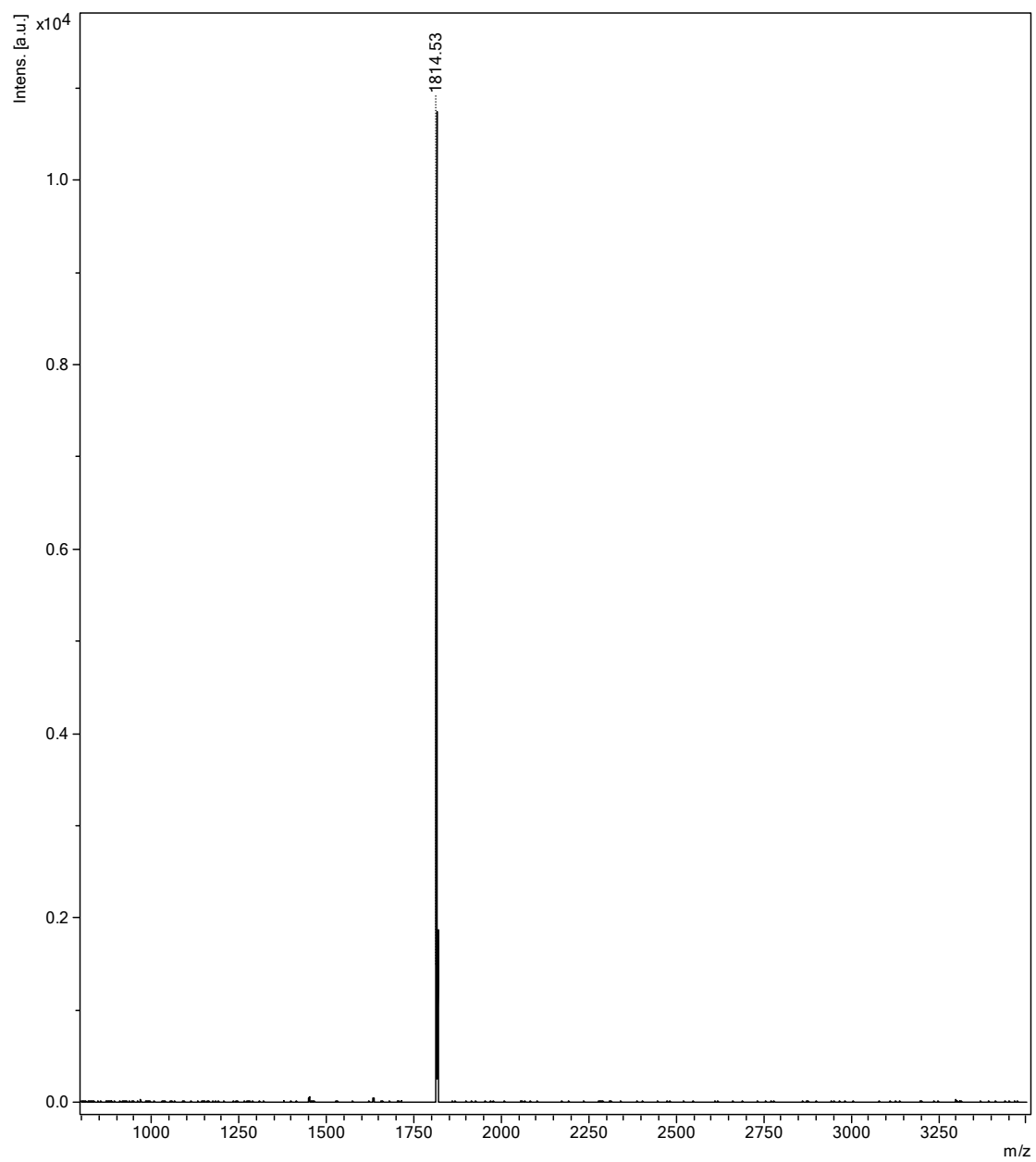


**Fig. S12** <sup>13</sup>C NMR spectrum of compound CH-CB at 298K in CDCl<sub>3</sub>.

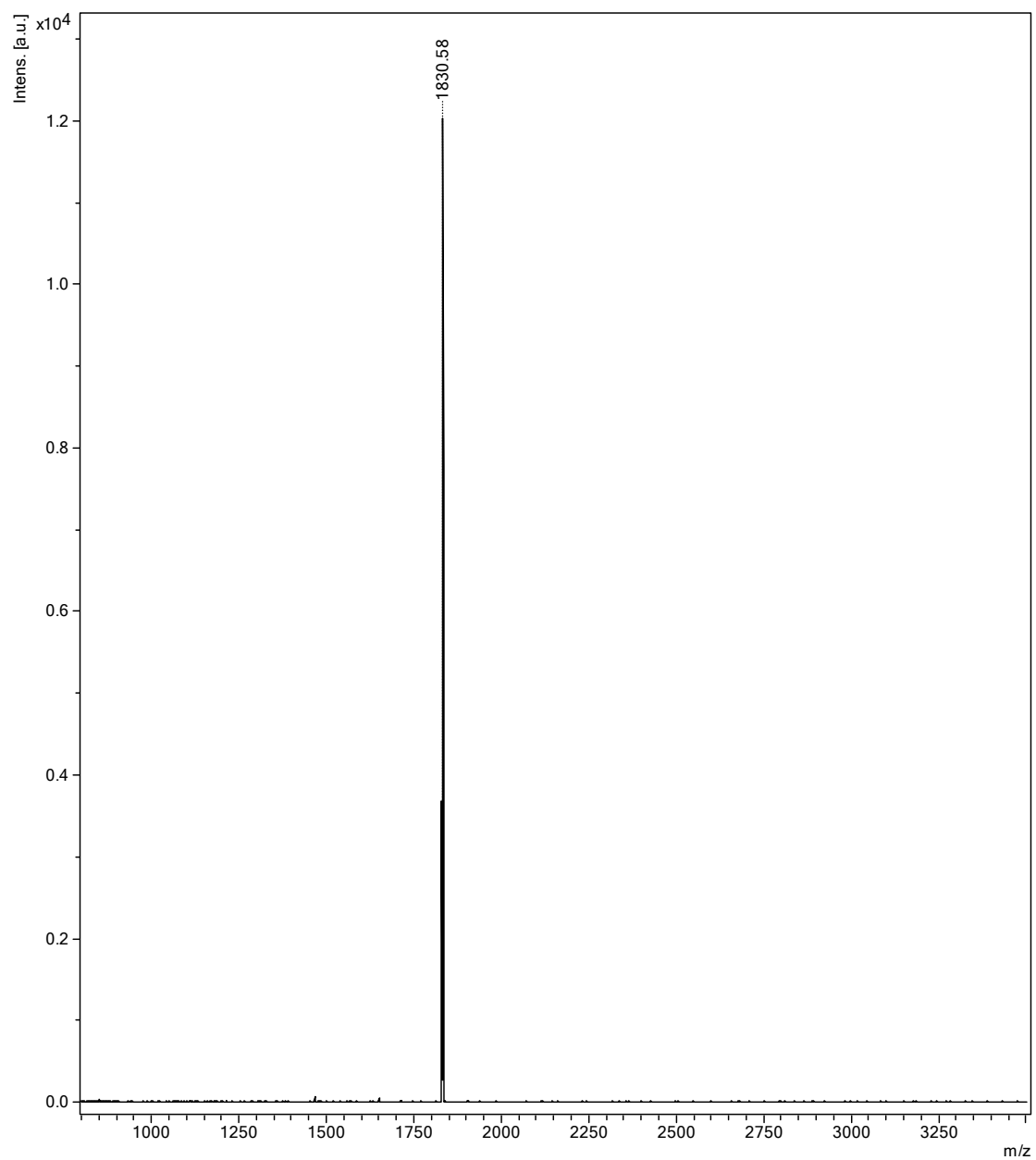




**Fig. S13** High resolution mass spectra (HRMS) of CH-FC.



**Fig. S14** HRMS of CH-FB.



**Fig. S15** HRMS of CH-CB.