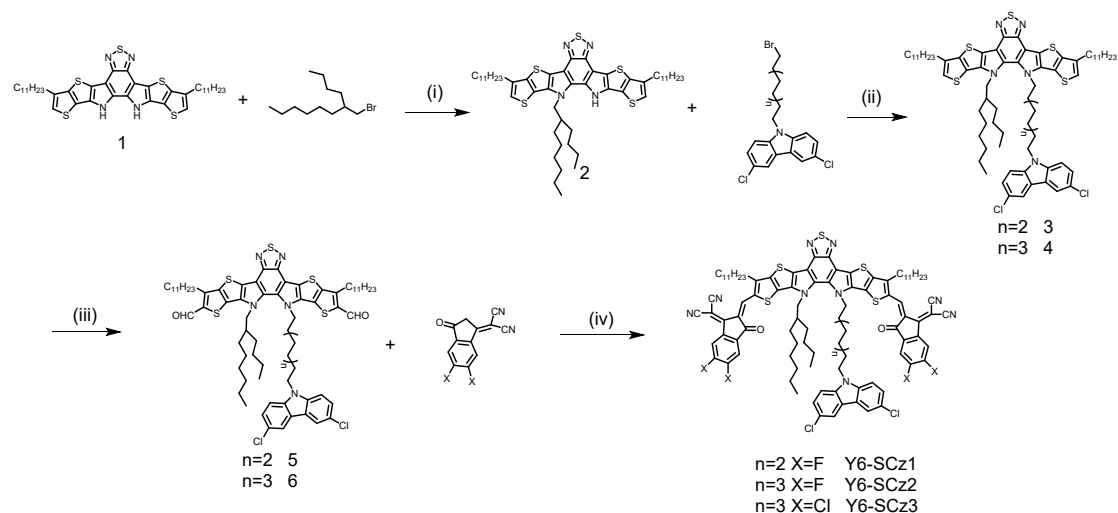


## **Supporting Information**

**Asymmetric non-fullerene acceptors with high photovoltaic performance via the synergistic effect of carbazole-terminated alkyl spacer and halogen substitution**

## 1. Materials and Synthesis

Polymer PM6 was purchased from Organtec Ltd. The other chemicals and solvents were purchased from J&K Scientific Ltd., Bide Pharmatech Co., Ltd., Hyper Inc. and Beijing Tongguang Fine Chemicals Co. without further purification. PDINN was synthesized in our laboratory as reported.



**Scheme S1.** Detailed synthesis route of **Y6-SCz1**, **Y6-SCz2** and **Y6-SCz3**.

### Synthesis of compound 2

Compound 1 (0.97 g, 1.3 mmol),  $K_2CO_3$  (1.44 g, 10.4 mmol) and KI (0.64 g, 3.9 mmol), 1-Bromo-2-ethylhexane (0.25 g, 1.3 mmol) were added to a two-necked flask, with adequate DMF as solvent. The mixture was stirred at 70°C overnight under Ar protection. After cooling to room temperature, the mixture was poured to water and extracted with petroleum ether. The organic layer was dried with  $MgSO_4$  and the solvent was removed under vacuum. Compound 2 was purified by column chromatography in a silica gel column using dichloromethane: petroleum ether: (1: 1, v: v) as eluent yielding an orange solid (0.83 g, 75% yield).

### Synthesis of compound 3

Compound 2 (0.17 g, 0.2 mmol),  $K_2CO_3$  (0.25 g, 1.8 mmol), KI (0.13 g, 0.8 mmol), 9-(8-bromooctyl)-3,6-dichloro-9H-carbazole (0.85 g, 2.0 mmol) were added to a two-necked flask and adequate DMF was used as solvent. The mixture was stirred at 90°C overnight under argon atmosphere. After cooling to room temperature, the mixture was poured to water and extracted with petroleum ether. The organic layer was dried with  $MgSO_4$  and the solvent was removed under vacuum. Compound 3 was obtained by

column chromatography in a silica gel column using dichloromethane: petroleum ether: (1:4, v: v) as eluent yielding an orange solid (0.15 g, 72% yield).

#### **Synthesis of compound 4**

Compound 2 (0.17 g, 0.2 mmol), K<sub>2</sub>CO<sub>3</sub> (0.25 g, 1.8 mmol), KI (0.13 g, 0.8 mmol), 9-(10-bromodecyl)-3,6-dichloro-9H-carbazole (0.91 g, 2.0 mmol) were added to a two-necked flask and adequate DMF was used as solvent. The mixture was stirred at 90°C overnight under argon atmosphere. After cooling to room temperature, the mixture was poured to water and extracted with petroleum ether. The organic layer was dried with MgSO<sub>4</sub> and the solvent was removed under vacuum. Compound 4 was obtained by column chromatography in a silica gel column using dichloromethane: petroleum ether: (1: 4, v: v) as eluent yielding an orange solid (0.16 g, 75% yield).

#### **Synthesis of compound 5**

To DMF (4 ml) in a two-necked flask, phosphorus oxychloride (2 ml) was added by injector, the mixture was stirred at for 30 min 0°C under argon atmosphere. The mixture was then transferred to the solution of compound 3 (0.18 g, 0.2 mmol) and 20 ml dichloroethane in another two-necked flask at 0°C. After stirring for another 5 min at 0°C, the reaction was heated to 80°C and refluxed overnight under argon atmosphere. The mixture was poured into water to quench the reaction and extracted by DCM. The organic layer was washed with saturated aqueous solution of sodium carbonate (200 ml) several times and dried with MgSO<sub>4</sub>. The solvent was removed under vacuum. Compound 5 was obtained by column chromatography in a silica gel column using dichloromethane: petroleum ether: (3: 2, v: v) as eluent yielding an orange solid (0.15 g, 78% yield).

#### **Synthesis of compound 6**

To DMF (4 ml) in a two-necked flask, phosphorus oxychloride (2 ml) was added by injector, the mixture was stirred at for 30 min 0°C under argon atmosphere. The mixture was then transferred to the solution of compound 3 (0.18 g, 0.2 mmol) and 20 ml dichloroethane in another two-necked flask at 0°C. After stirring for another 5 min at 0°C, the reaction was heated to 80°C and refluxed overnight under argon atmosphere. The mixture was poured into water to quench the reaction and extracted by DCM. The organic layer was washed with saturated aqueous solution of sodium carbonate (200

ml) several times and dried with MgSO<sub>4</sub>. The solvent was removed under vacuum. Compound 6 was obtained by column chromatography in a silica gel column using dichloromethane: petroleum ether: (3: 2, v: v) as eluent yielding an orange solid (0.16 g, 80% yield).

### Synthesis of Y6-SCz1

Compound 5 (0.10 g, 0.1 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (0.12 g, 0.5mmol) were dissolved in anhydrous chloroform (10 ml) under argon atmosphere. Pyridine (1 ml) was added. After stirring at 60°C overnight, the mixture was poured into methanol (50 ml) and filtered. The residue was purified by column chromatography in a silica gel column using dichloromethane: petroleum ether: (1: 1, v: v) as eluent yielding a dark blue solid (0.09 g, 68% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.04 (s, 1H), 8.95 (s, 1H), 8.59 (s, 1H), 8.43 (s, 1H), 7.87 (s, 2H), 7.68 (s, 1H), 7.41 (s, 1H), 7.23 (d, *J* = 6.7 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.79 (d, *J* = 27.5 Hz, 4H), 4.02 (s, 2H), 3.19 (s, 4H), 2.08-1.29 (m, 62H), 0.98-0.60 (m, 15H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 185.95, 153.80, 153.62, 147.30, 145.17, 145.01, 138.60, 137.21, 133.75, 133.03, 130.65, 126.37, 124.91, 122.60, 120.05, 119.88, 114.79, 114.52, 114.35, 113.45, 109.47, 77.33, 77.21, 77.01, 76.69, 68.89, 51.61, 43.12, 39.31, 31.93, 31.48, 31.04, 30.47, 29.86, 29.67, 29.64, 29.54, 29.46, 29.43, 29.36, 29.32, 28.49, 28.10, 26.74, 26.54, 25.48, 22.77, 22.70, 22.41, 14.13, 13.98, 13.73 (s). HR-MS (MALDI-TOF) *m/z* calcd. for (Y6-SCz1): 1739.58. Found: 1738.94.

### Synthesis of Y6-SCz2

Compound 6 (0.10 g, 0.1 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (0.12 g, 0.5mmol) were dissolved in anhydrous chloroform (10 ml) under argon atmosphere. Pyridine (1 ml) was added. After stirring at 60°C overnight, the mixture was poured into methanol (50 ml) and filtered. The residue was purified by column chromatography in a silica gel column using dichloromethane: petroleum ether: (1: 1, v: v) as eluent yielding a dark blue solid (0.10 g, 72% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.96-8.82 (m, 2H), 8.54-8.42 (m, 2H), 7.91 (d, *J* = 1.9 Hz, 2H), 7.58-7.52 (m, 2H), 7.32 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.16 (d,

$J = 8.7$  Hz, 2H), 4.83-4.71 (m, 4H), 4.11 (t,  $J = 7.3$  Hz, 2H), 3.16-3.10 (m, 4H), 2.20-1.20 (m, 66H), 1.04-0.60 (m, 15H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  185.83, 158.08, 157.55, 153.85, 153.56, 147.30, 147.06, 145.15, 145.02, 138.85, 137.25, 135.20, 134.73, 134.53, 134.19, 133.72, 132.98, 132.73, 132.68, 130.61, 130.40, 126.40, 124.88, 122.78, 120.17, 119.85, 119.47, 114.87, 114.71, 114.61, 114.41, 114.36, 113.47, 113.29, 112.11, 109.65, 77.33, 77.21, 77.01, 76.69, 68.85, 55.34, 51.65, 43.25, 39.33, 31.93, 31.49, 31.20, 31.06, 31.00, 30.47, 29.87, 29.83, 29.66, 29.64, 29.53, 29.45, 29.42, 29.36, 29.33, 29.07, 28.64, 28.07, 27.13, 26.81, 25.48, 22.78, 22.70, 22.41, 14.13, 13.97, 13.75 (s). HR-MS (MALDI-TOF)  $m/z$  calcd. for (Y6-SCz1): 1768.62. Found: 1769.19.

### Synthesis of Y6-SCz3

Compound 6 (0.10 g, 0.1 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (0.13 g, 0.5 mmol) were dissolved in anhydrous chloroform (10 ml) under argon atmosphere. Pyridine (1 ml) was added. After stirring at  $60^\circ\text{C}$  overnight, the mixture was poured into methanol (50 ml) and filtered. The residue was purified by column chromatography in a silica gel column using dichloromethane: petroleum ether: (1: 1,  $v: v$ ) as eluent yielding a dark blue solid (0.11 g, 70% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 64.8$  Hz, 2H), 8.67-8.49 (m, 2H), 7.87 (d,  $J = 1.8$  Hz, 2H), 7.75 (s, 1H), 7.62 (d,  $J = 2.9$  Hz, 1H), 7.30 (d,  $J = 2.0$  Hz, 2H), 7.14 (d,  $J = 8.7$  Hz, 2H), 4.85-4.59 (m, 4H), 4.13 (t,  $J = 7.3$  Hz, 2H), 3.11-2.96 (m, 4H), 2.39-1.24 (m, 66H), 0.88-0.61 (m, 15H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  185.85, 185.69, 157.78, 157.04, 153.94, 153.75, 147.21, 146.88, 145.28, 145.12, 139.36, 139.04, 138.88, 138.80, 138.44, 138.33, 138.11, 137.05, 135.64, 135.29, 135.24, 134.88, 134.65, 134.28, 133.76, 133.25, 132.91, 132.43, 130.98, 130.48, 126.63, 126.52, 126.39, 124.90, 124.51, 123.82, 122.75, 120.18, 119.71, 119.39, 114.80, 114.64, 114.42, 114.36, 113.51, 113.06, 109.61, 77.33, 77.22, 77.01, 76.70, 69.04, 68.98, 55.25, 51.57, 43.21, 39.34, 31.93, 31.52, 31.03, 30.92, 30.46, 29.86, 29.66, 29.64, 29.53, 29.46, 29.43, 29.36, 29.08, 28.64, 28.06, 27.06, 25.62, 22.71, 22.42, 14.13, 14.00, 13.72 (s). HR-MS (MALDI-TOF)  $m/z$  calcd. for (Y6-SCz1): 1834.50. Found: 1835.07.



## 2. Characterization

### Material characterization.

**<sup>1</sup>H NMR.** <sup>1</sup>H NMR spectra were recorded on AVANCE III or AVANCE III HD 400 MHz spectrometer (Bruker Corporation) at room temperature.

**<sup>13</sup>C NMR.** <sup>13</sup>C NMR spectra were recorded on AVANCE III HD 400 MHz spectrometer (Bruker Corporation) at room temperature.

**MALDI-TOF.** The MALDI-TOF mass spectrometry experiments were performed on an Autoflex III instrument (Bruker Daltonics Inc.).

**TGA.** TGA curves were measured on an HTG-1 thermal gravimetric analyzer (Beijing Hengjiu Experiment Equipment Co., Ltd.) with a heating rate of 10 °C min<sup>-1</sup> under a nitrogen flow rate of 50 mL min<sup>-1</sup>.

**DSC.** DSC thermograms were measured on a DSC 1 differential scanning calorimeter (Mettler-Toledo International Inc.) with a heating and cooling rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere.

**UV-vis absorption.** The UV-vis absorption spectra were measured by U-2910 UV-vis spectrophotometer (Hitachi Ltd). In the case of solution absorbance measurements, the dilute solutions of acceptors in chloroform (1×10<sup>-5</sup> M) was prepared. The thin-film samples were prepared by spin-coating (3000 rpm for 20 s) their CF solutions (10 mg mL<sup>-1</sup>) on quartz plates.

**CV.** Cyclic voltammetry was conducted on a Zennium E electrochemical workstation (ZAHNER-elektrik GmbH & Co. KG) using sample film coated on glassy carbon as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution.  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of the acceptors are calculated from the formula  $E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.38)$  eV and  $E_{\text{LUMO}} = -e(E_{\text{red}}^{\text{onset}} + 4.38)$  eV.

**PL.** PL spectra were measured by a FS5 spectrofluorometer (Edinburgh Instruments Ltd.) in an SC-10 front-face sample holder under the excitation at 560 nm with a 650 nm filter.

**AFM.** AFM topographies were measured on a Dimension Icon2-SYS AFM instrument (Bruker Corporation) in the tapping mode. The thin-film samples preparation conditions were consistent with device fabrication of OSCs which can be found in next

part.

### **Device fabrication of OSCs.**

The preparation process is as follows: First, the glass substrate containing ITO is cleaned in an ultrasonic cleaner, then dried by ultraviolet ozone, and then coated with PEDOT:PSS anode modification layer on ITO. Acceptor mixtures (chloroform as solvent, 18mg/ml, 1-chloronaphthalene as additive) were pre-configured to be rotated on the surface of the device. The thickness of the membrane was controlled by the rotation speed during the spinning process. The blending ratio of several different acceptor materials to the donor, the concentration of the blend solution and the spinning speed were all the same in this work, so as to ensure that different acceptor materials were the only variables in the experiment. After the active layer is rotated, the device is heated on the hot table, then transferred to the glove box for thermal annealing. Then, the appropriate thickness of the cathode modification layer PDINN is rotated on the active layer surface. Finally, the silver cathode is steamed on the cathode modification layer by vacuum evaporation. After the device has been prepared, the photovoltaic performance will continue to be characterized in the glove box.

### **Owen Method for calculating the surface energy.**

The Owen's method is often used to calculate the surface energy:

$$\gamma_s = \gamma_s^D + \gamma_s^P, \gamma_l = \gamma_l^D + \gamma_l^P \quad (\text{SI-1})$$

where  $\gamma_s$  is composed of the dispersion force  $\gamma_s^D$  and polarity force  $\gamma_s^P$ .  $\gamma_l$  is surface energy of the liquid and consists of a dispersion force  $\gamma_l^D$  and polarity force  $\gamma_l^P$ .

We can know the surface energies  $\gamma_l^D$  and  $\gamma_l^P$  of the testing liquid and its contact angle on solid film.

And according to the formula:

$$\gamma_l(1 + \cos\theta) = 2(\gamma_s^D \gamma_l^D)^{1/2} + 2(\gamma_s^P \gamma_l^P)^{1/2} \quad (\text{SI-2})$$

We need two known testing liquids to determine  $\gamma_s^D$  and  $\gamma_s^P$ .

$$\gamma_{l1}(1 + \cos\theta) = 2(\gamma_s^D \gamma_{l1}^D)^{1/2} + 2(\gamma_s^P \gamma_{l1}^P)^{1/2} \quad (\text{SI-3})$$

$$\gamma_{l2}(1 + \cos\theta) = 2(\gamma_s^D \gamma_{l2}^D)^{1/2} + 2(\gamma_s^P \gamma_{l2}^P)^{1/2} \quad (\text{SI-4})$$

Finally,  $\gamma_s$  can be determined by  $\gamma_s = \gamma_s^D + \gamma_s^P$ .



### Calculation of Flory-Huggins interaction parameter( $\chi$ ) by DCA

Solubility parameter ( $\delta$ ) can be calculated from the surface tension,

$$\delta = K\sqrt{\gamma} \quad (\text{SI-5})$$

where  $\gamma$  is the surface tension, K is the proportionality constant ( $K = 116 \times 103 \text{ m}^{-1/2}$ ).

And Flory–Huggins interaction parameter ( $\chi_{ij}$ ) can be written as a function of two solubility parameter,

$$\chi_{ij} = \frac{V_0}{RT} (\delta_i - \delta_j)^2 \quad (\text{SI-6})$$

where  $\chi_{ij}$  is the Flory–Huggins interaction parameter between the material i and j,

$V_0$  is the geometric mean of the polymer segment molar volume, R is the gas constant,

T is the absolute temperature, and  $\delta_i$  and  $\delta_j$  are the solubility parameter of material i and j, respectively.

$$\frac{K^2 V_0}{RT}$$

To simplify, we define the parameter  $\kappa = \frac{K^2 V_0}{RT}$ , then the Flory–Huggins

interaction parameter can be written as the formula below,

$$\chi_{ij} = \kappa (\sqrt{\gamma_i} - \sqrt{\gamma_j})^2 \quad (\text{SI-7})$$

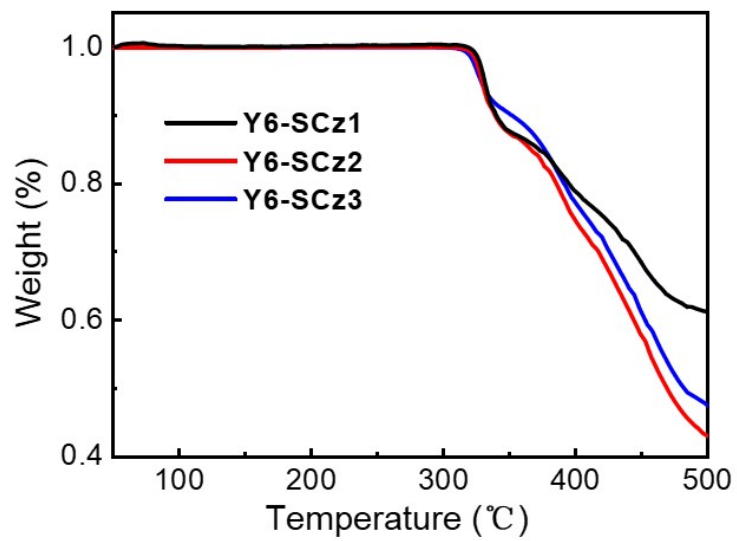
where  $\gamma_i$  and  $\gamma_j$  are the surface tension of material i and j, respectively.

**GIWAXS.** The GIWAXS data was carried out at Beijing Synchrotron Radiation Facility (BSRF), beamline 1W1A-Diffuse X-ray Scattering.

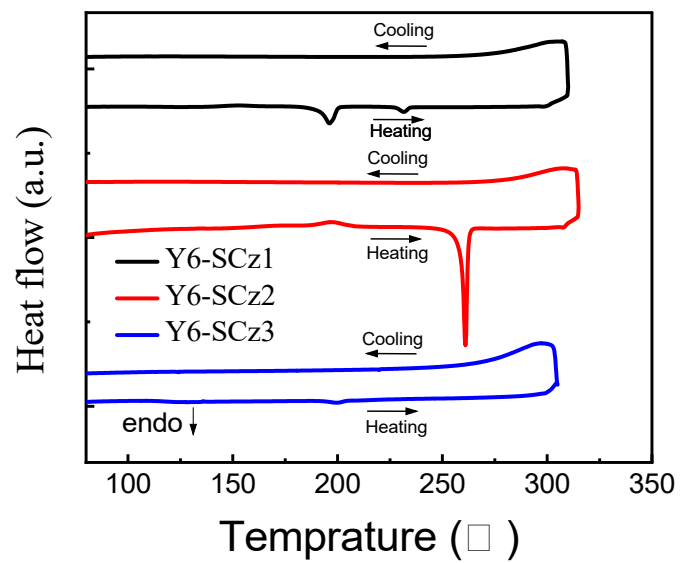
### Calculation of CCL.

The calculation of the coherence length (CCL) CCL was calculated by Scherrer equation:  $\text{CCL} = 2\pi K/\text{FWHM}$ , where K is shape factor (0.9 is used here), FWHM represents the full- width at half-maximum of the peak.

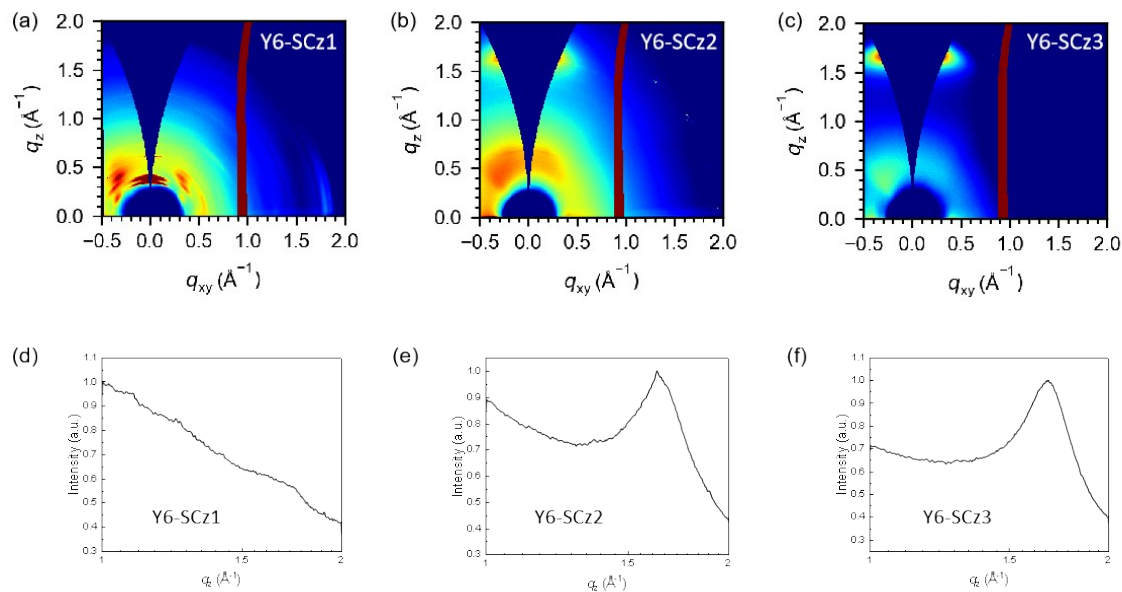
### 3. Supporting Figures



**Figure S1.** TGA curves of Y6-SCz1, Y6-SCz2 and Y6-SCz3.



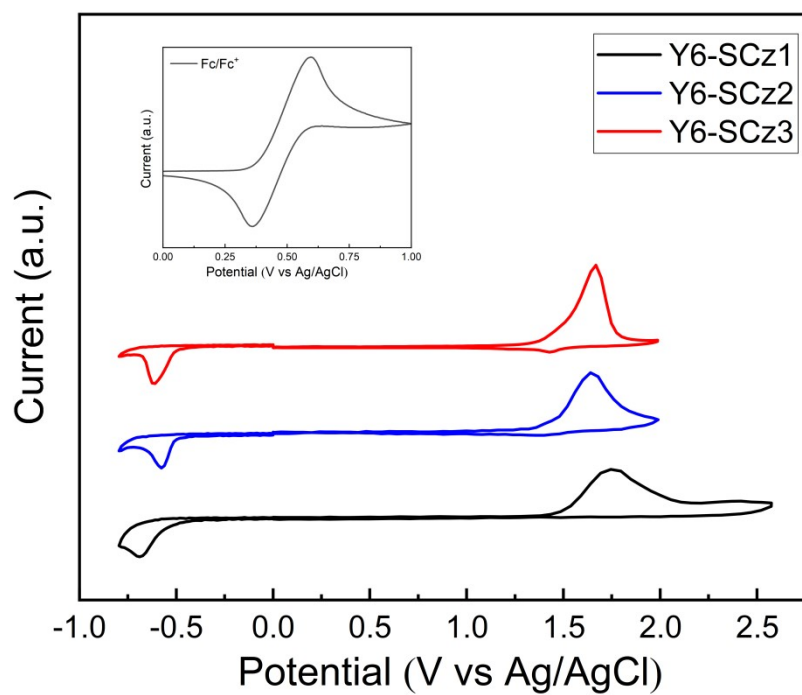
**Figure S2.** DSC measurement of Y6-SCz1, Y6-SCz2 and Y6-SCz3.



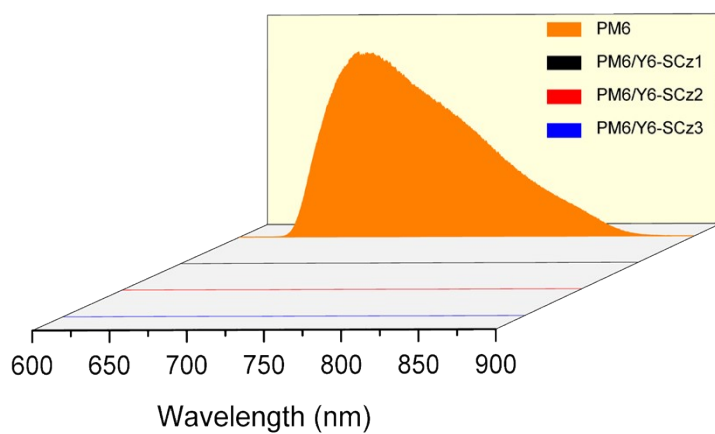
**Figure S3.** 2D-GIWAXS patterns of films: a) Y6-SCz1; b) Y6-SCz2; c) Y6-SCz3; d-f) Corresponding line cuts taken from In-plane (black) and Out-of-plane (red) of GIWAXS profiles.

**Table S1** GIWAXS parameters of Y6-SCz1, Y6-SCz2 and Y6-SCz3 based neat films.

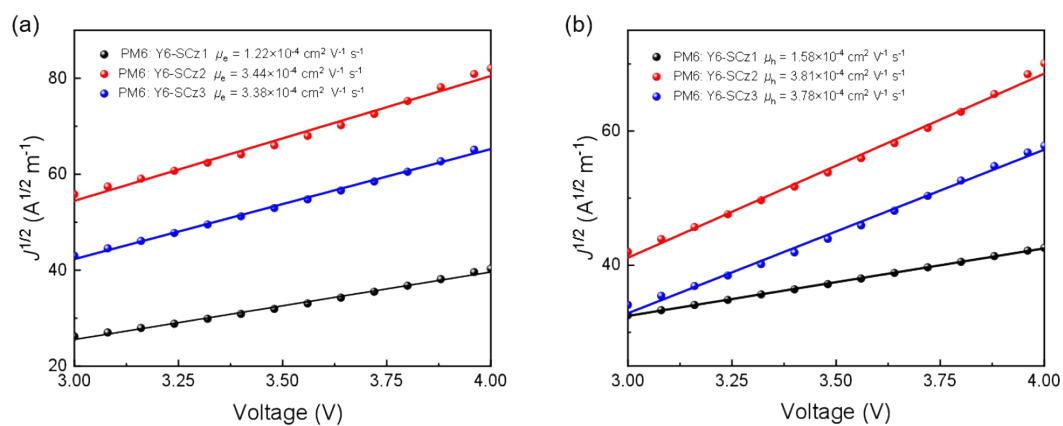
Sample	$q_z$ ( $\text{\AA}^{-1}$ )	$d$ -spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	CCL ( $\text{\AA}$ )
Y6-SCz1	\	\	\	\
Y6-SCz2	1.63	3.85	0.19	30.08
Y6-SCz3	1.67	3.76	0.21	27.19



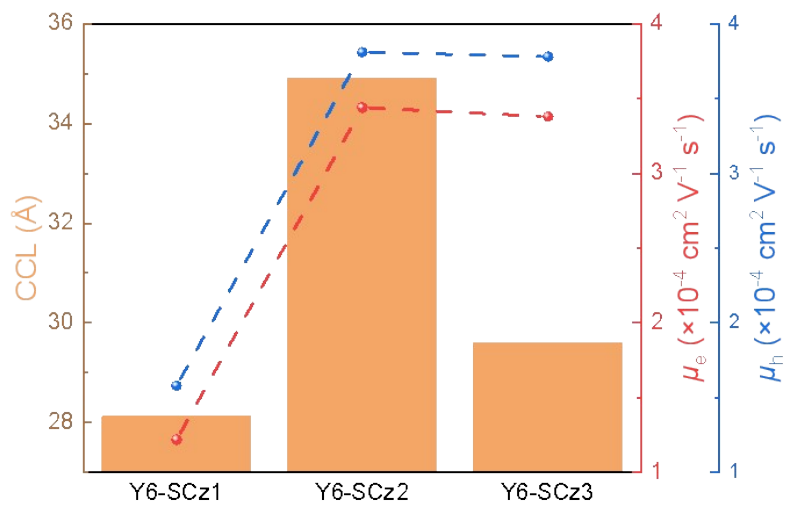
**Figure S4.** CV measurement of Y6-SCz1, Y6-SCz2 and Y6-SCz3.



**Figure S5.** PL spectra of PM6, PM6: Y6-SCz1, PM6: Y6-SCz2 and PM6: Y6-SCz3.



**Figure S6.**  $J^{1/2}$ - $V$  plots of (a) electron-only devices with the structure of ITO/ZnO /blend film/PDINN/Ag and (b) hole-only devices with the structure of ITO/PEDOT: PSS/blend film/MoO<sub>3</sub>/Ag.



**Figure S7.** The corresponding crystal coherence lengths and the hole/electron mobilities.



## 5. Spectral Charts of NMR and MS

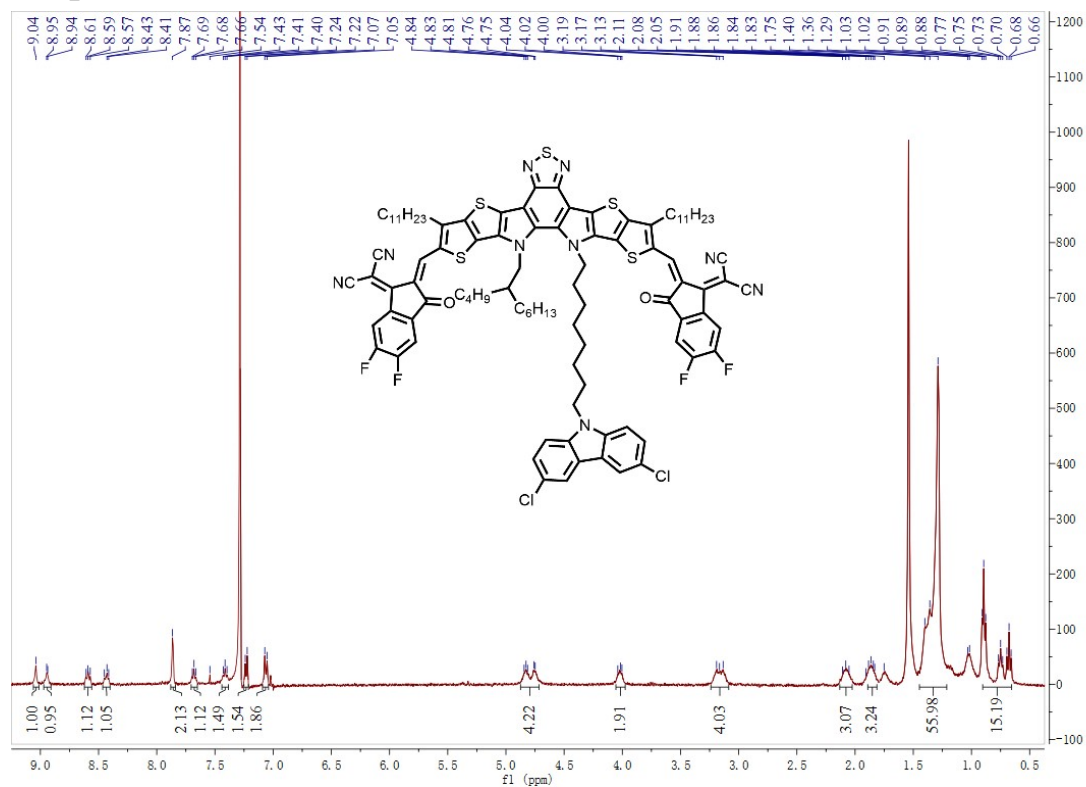
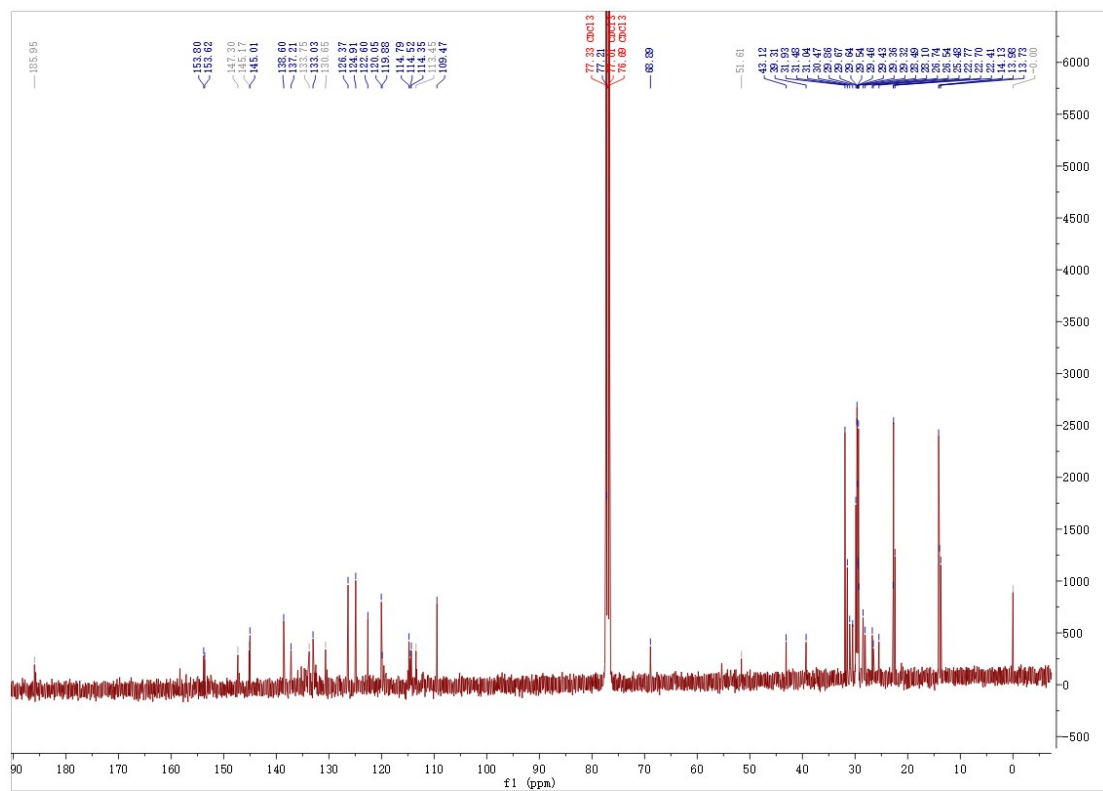
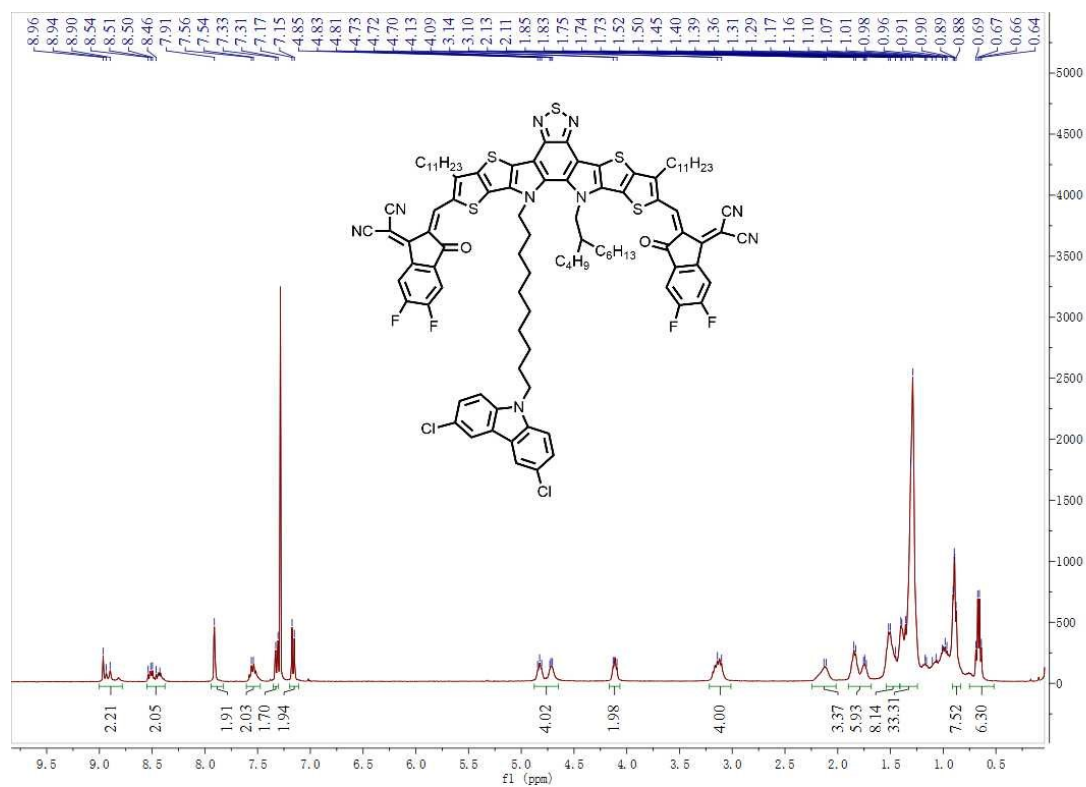


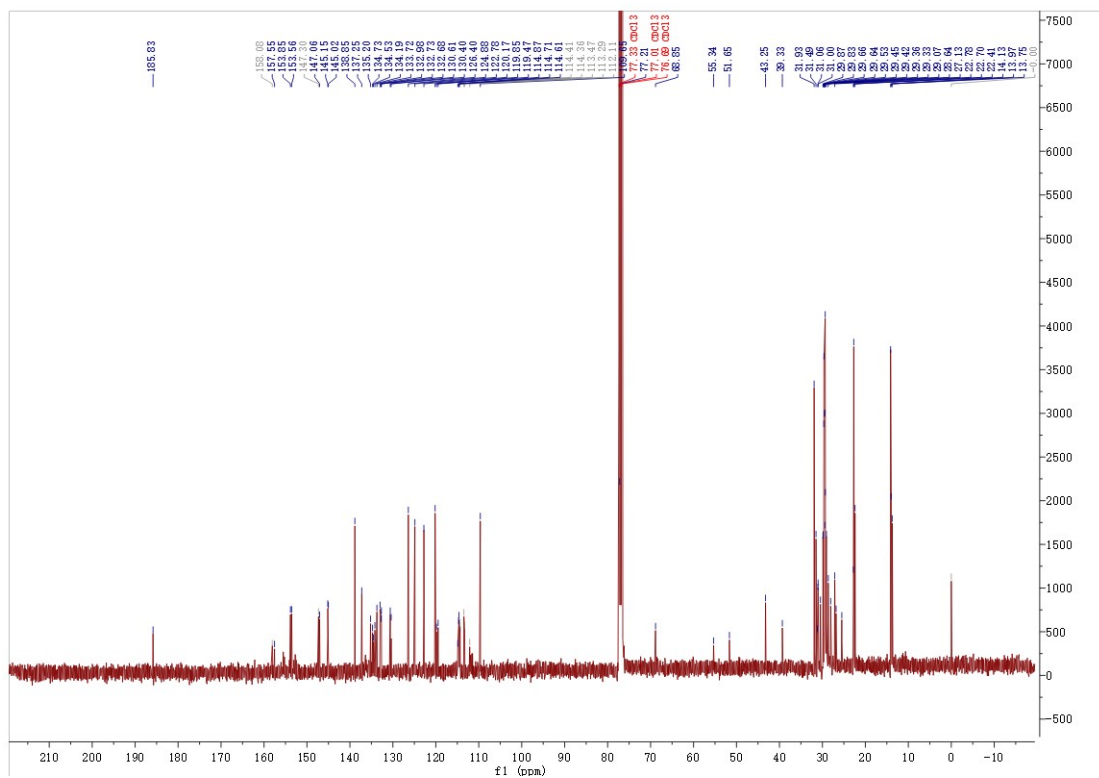
Figure S8.  $^1\text{H}$  NMR spectrum of Y6-SCz1.



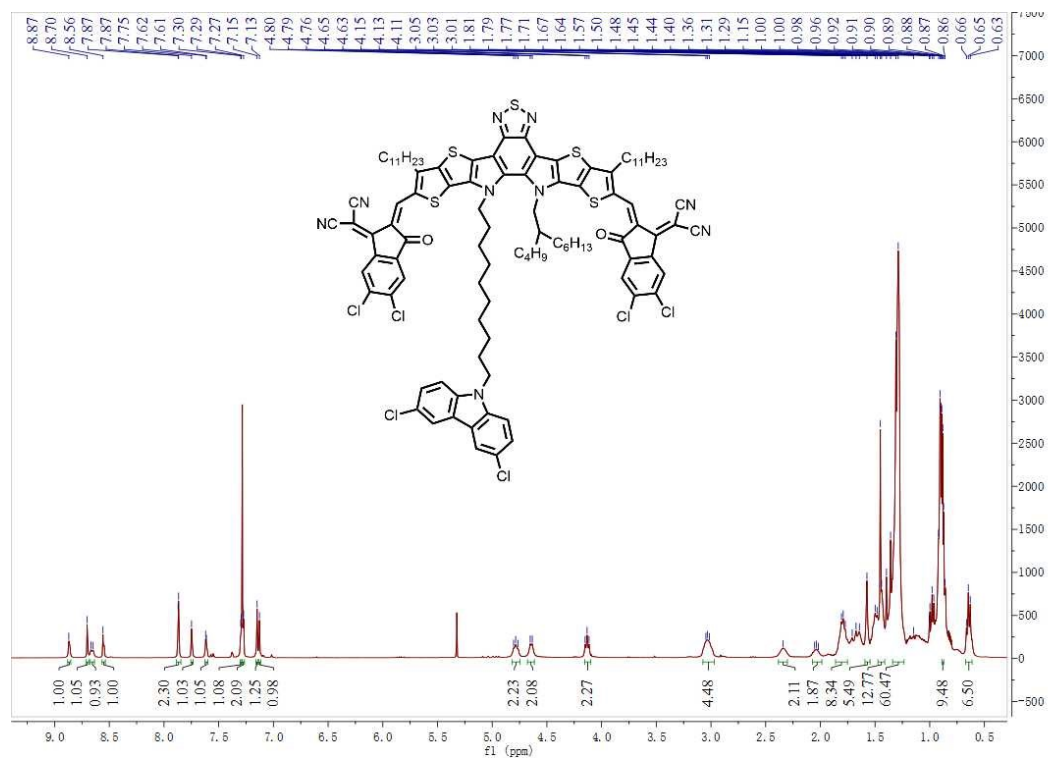
**Figure S9.**  $^{13}\text{C}$  NMR spectrum of Y6-SCz1.



**Figure S10.**  $^1\text{H}$  NMR spectrum of Y6-SCz2.

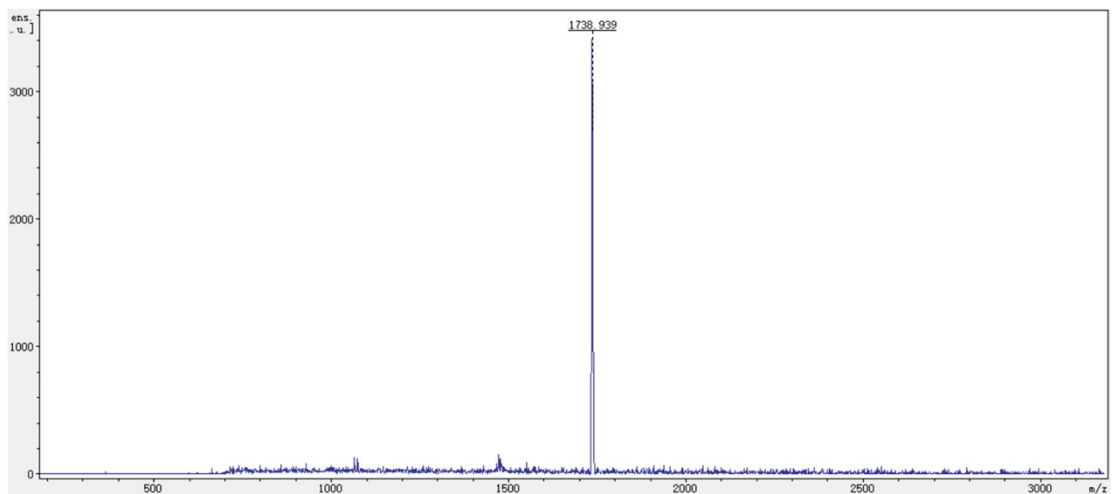


**Figure S11.**  $^{13}\text{C}$  NMR spectrum of Y6-SCz2.

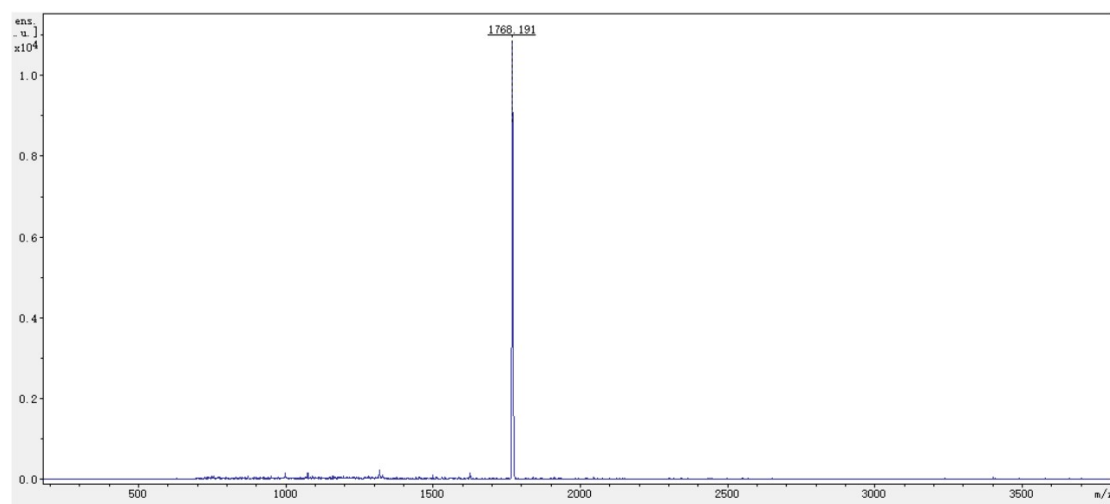


**Figure S12.** <sup>1</sup>H NMR spectrum of Y6-SCz3.



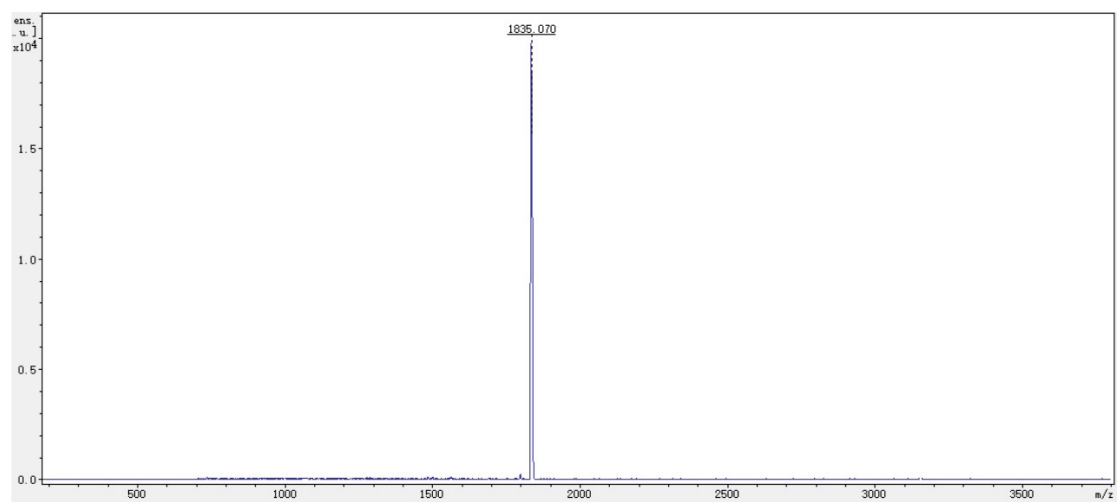


**Figure S14.** MAIDI-TOF-MS spectrum of **Y6-SCz1**.



**Figure S15.** MAIDI-TOF-MS spectrum of **Y6-SCz2**.





**Figure S16.** MAIDI-TOF-MS spectrum of **Y6-SCz3**.