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Electronic Supplementary Information

Automatic Formation of Electron Transport Layer in BHJ Solar Cells using Phenothiazine-based Conjugated Small Molecular Electrolytes

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1. Experimental details

The reagents and starting materials were purchased from commercial suppliers (Aldrich, TCI Korea, or Thermo Fisher Scientific) and used without further purification.^{1}H-NMR and ^{13}C-NMR spectra were measured using a Bruker Ascend 400 MHz spectrometer.

1.1. Synthesis of 10-(6-bromohexyl)-10*H*-phenothiazine (2).

1,6-Dibromohexane (36.6 g, 150.0 mmol) was added to the slurry of sodium hydride (60% in mineral oil, 2.7 g, 67.5 mmol) under an argon atmosphere. To the mixture, *10H*-phenothiazine (10.0 g, 50.2 mmol) dissolved in anhydrous DMF (50.0 mL) was slowly added. After stirring at 40 ^oC overnight, the reaction mixture was poured into water (100.0 mL) and extracted with ethyl aetate (2 × 150.0 mL). The combined organic layer was washed with water (2 × 100.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography, providing 12.5 g (69%) of compound **2** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.17 -7.13 (m, 4H), 6.94-6.84 (m, 4H), 3.86 (t, 2H, *J* = 7.0 Hz), 3.37 (t, 2H, *J* = 6.9 Hz), 1.87-1.78 (m, 4H), 1.49-1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.32, 127.52, 127.22, 125.18, 122.44, 115.48, 47.12, 33.81, 32.64, 27.77, 26.70, 26.06. HRMS (m/z, EI^+) calcd for $C_{18}H_{20}BrNS$, 362.0578, found 362.0577.

1.2. Synthesis of *N,N*-dimethyl-6-(10*H*-phenothiazin-10-yl)hexan-1-amine (PzN1).

Isopropylamine (5.4 mL, 63.0 mmol) was added to the solution of compound **2** (2.3 g, 6.3 mmol) in THF (50.0 mL) under argon atmosphere and the solution was stirred at 40 oC overnight. After concentration under reduced pressure, the residue was extracted with chloroform (2 × 150.0 mL). The combined organic phase was washed with water (2 × 100.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on NH_2-SiO_2, providing 1.05 g (52%) of the PzN1 as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16 -7.11 (m, 4H), 6.90 -6.84 (m, 4H), 3.86-3.82 (m, 2H), 2.19 (s, 6H), 1.83-1.78 (m, 4H), 1.48-1.41 (m, 4H), 1.36-1.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.34, 127.45, 127.19, 124.98, 122.34, 115.42, 59.73, 47.31, 45.48, 27.62, 27.12, 26.90, 26.84. HRMS (m/z, EI$^+$) calcd for $C_{20}H_{26}N_2S$, 327.1895, found 327.1899.

1.3. Synthesis of *N*^{1}-[6-(10*H*-phenothiazin-10-yl)hexyl]ethane-1,2-diamine (PzN2).

Ethylenediamine (4.2 mL, 63.0 mmol) was added to the solution of compound **2** (2.3 g, 6.3 mmol) in THF (50.0 mL) under argon atmosphere. The same reaction condition of compound PzN1 was conducted to obtain 0.95 g (44%) of the PzN2 as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16 -7.11 (m, 4H), 6.92 -6.83 (m, 4H), 3.84 (t, *J* = 7.1 Hz, 2H) , 2.79-2.75 (m, 2H), 2.67-2.60 (m, 2H), 2.57 (t, *J* = 7.1 Hz, 2H),1.87-1.75 (m, 2H), 1.53-1.40 (m, 4H), 1.38-1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.34, 127.45, 127.19, 125.01, 122.35, 115.44, 52.67, 49.76, 47.26, 41.86, 30.14, 26.98, 26.86, 26.84. HRMS (m/z, EI$^+$) calcd for $C_{20}H_{27}N_3S$, 342.2004, found 342.1998.

1.4. Synthesis of *N*^{1}-[6-(10*H*-phenothiazin-10-yl)hexyl]ethane-1,2-diamine (PzN3).

Diethylenetriamine (6.8 mL, 63.0 mmol) was added to the solution of compound 2 (2.3 g, 6.3 mmol) in THF (50.0 mL) under argon atmosphere. The same reaction condition of compound PzN1 was conducted to obtain 0.86g (36%) of the PzN3 as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.18 -7.10 (m, 4H), 6.94 -6.81 (m, 4H), 3.84 (t, *J* = 7.1 Hz, 2H) , 2.79-2.75 (m, 2H), 2.71-2.61(m, 6H), 2.56 (t, *J* = 7.1 Hz, 2H),1.89-1.71 (m, 2H), 1.51-1.40 (m, 4H), 1.39-1.28 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.34, 127.45, 127.19, 125.00, 122.35, 115.43, 52.49, 49.85, 49.55, 49.34, 47.27, 41.79, 30.05, 27.11, 26.99, 26.86. HRMS (m/z, EI$^+$) calcd for $C_{22}H_{32}N_4S$, 385.2426, found 385.2427.

1.5. Synthesis of *N¹*-[6-(10*H*-phenothiazin-10-yl)hexyl]-*N²*-{2-[(2 aminoethyl) amino]ethyl}ethane-1,2-diamine (PzN4).

Triethylenetetramine (9.4 mL, 63.0 mmol) was added to the solution of compound 2 (2.3 g, 6.3 mmol) in THF (50.0 mL) under argon atmosphere. The same reaction condition of compound PzN1 was conducted to obtain 0.92g (34%) of the PzN4 as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15 -7.11 (m, 4H), 6.93 -6.79 (m, 4H), 3.83 (t, *J* = 7.1 Hz, 2H) , 2.81-2.74 (m, 2H),, 2.72-2.64 (m, 4H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.50-2.23 (m,6H), 1.83-1.75 (m, 2H), 1.51-1.39 (m, 4H), 1.35-1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.33, 127.45, 127.18, 124.99, 122.35, 115.42, 61.23, 58.62, 58.03,53.33, 49.97, 47.28, 46.55, 41.81, 38.87, 30.01, 27.23, 26.87. HRMS (m/z, EI$^+$) calcd for $C_{24}H_{37}N_5S$, 428.2848, found 428.2843.

1.6. Device fabrication

ITO-coated glass substrates were cleaned in an ultrasonic bath with deionized water, acetone, and isopropanol for 15 min and dried in the oven at 80 ^{o}C overnight. After treatment with UV/ozone for 30 min, CSME:BHJ (1:9) or BHJ were spin-coated onto the ITO-coated glass substrate at 800 rpm for the 30s. CSME solutions were diluted in methanol to 0.002 wt%. BHJ solution of PTB7-Th:$PC_{71}BM$ (1:1.5 by weight, total 17.5 mg) solved 1ml chlorobenzene with 1,8-diiodooctane (DIO) additive 3 vol.%.

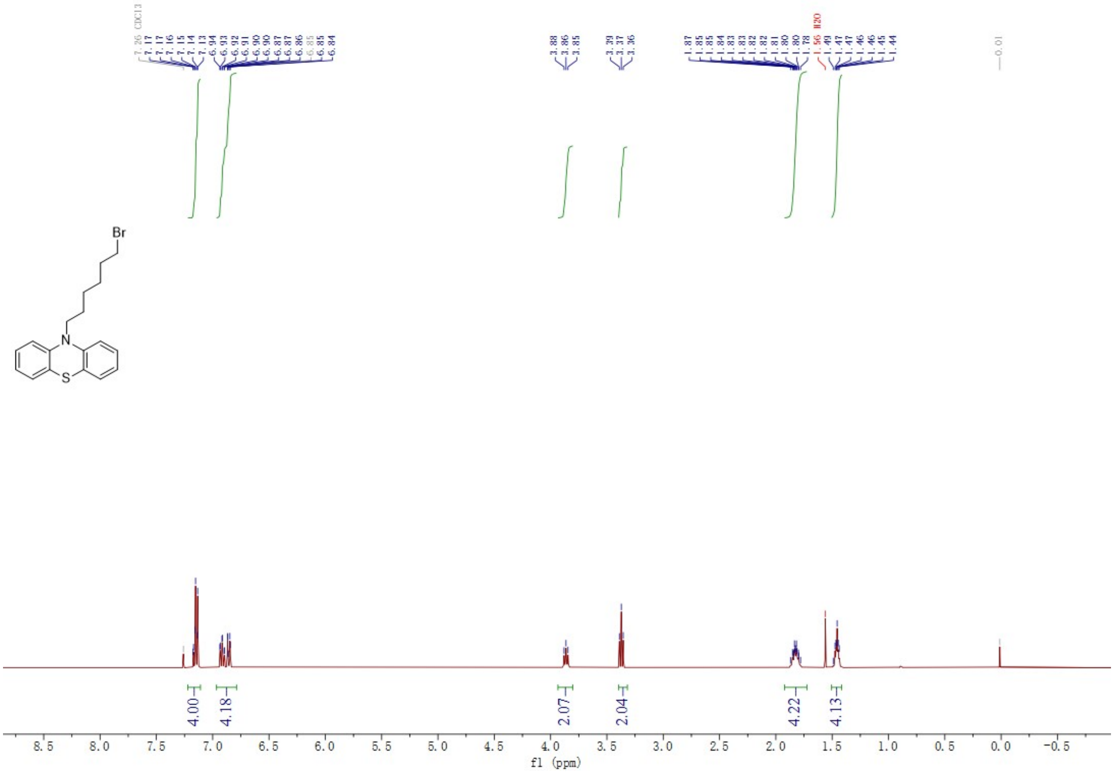
Finally, MoO_x (2 nm) Ag (120 nm) were deposited by thermal evaporation under 5×10^{-7} Torr. The full device was fabricated with the following structures: ITO/CSME:BHJ or BHJ/MoO_x/Ag.

1.7. Characterization

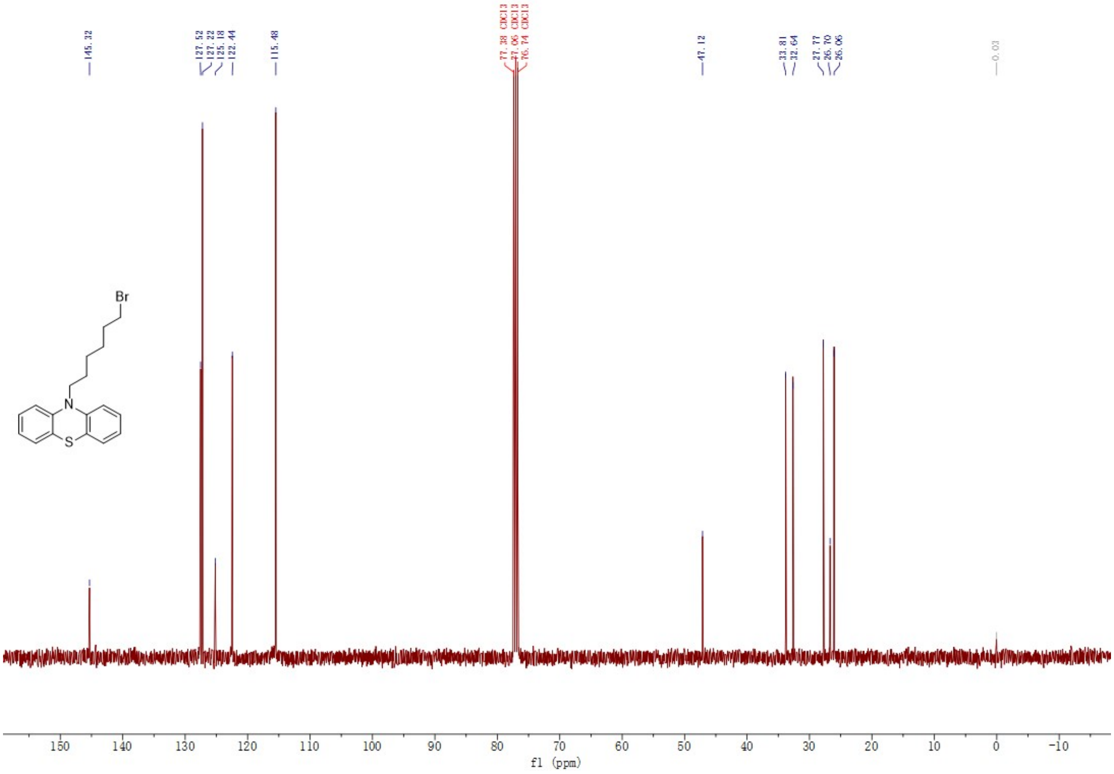
The UV-vis absorption spectra were recorded by Varian 5E UV/VIS/NIR spectrophotometer. Wona-WPG100 was used to obtain the cyclic voltammogram of the target compounds. A three-electrode cell was used at room temperature with scan rate of 80 mV/s. The reference electrode of Ag/$AgNO_3$ was used with Pt counter electrode. The solution of tetrabutylammonium perchlorate with the concentration of 0.1 M in acetonitrile solvent was employed as the electrolyte. The energy level of the Ag/$AgNO_3$ reference electrode (calibrated by the Fc/Fc+ redox system) was 4.4 eV below the vacuum level. The effective work function was measured by Kelvin probe (KP Technology) on the CSME/ITO substrates and the contact angle was measured using a UNI-CAM(GITSOFTTECH) system. To measure the contact angle, we prepared two types of films consisting of only CSME films and PTB7-Th:PCBM (with or without CSME films). All films were prepared via spin coating at 800 rpm, under the same condition of solar cell devices. And then the water was dropped on bare ITO film or CSME or PTB7-Th:PCBM (with or without CSME) coated ITO film. The XPS analysis was performed using KRATOS Analytical system. For measuring XPS, the CSMEs were diluted in methanol and spin-coated on ITO. The current density- voltage profiles of the devices were acquired using a Keithley 2400 Source Measure Unit. The incident photon-to-current efficiency (IPCE) of the device was measured using a Xenon lamp and calibrated silicon reference cell. Mott-Schottky measurement and electrical impedance spectroscopy (EIS) were performed using an Ivium compactStat.h electrochemical analyzer. Transmission electron microscopy (TEM) and TOF-SIMS were performed using a Hitachi H-7500 and ION TOF-TOF-SIMS 5. The film of BHJ:CSME for TEM measurement was prepared by spin-coating under the same conditions for the solar cell device. After drying, the film was floated off on the water and transferred to Cu-mesh grid.

2. ^{1}H NMR spectra

^{1}H NMR



^{13}CNMR



HRMS

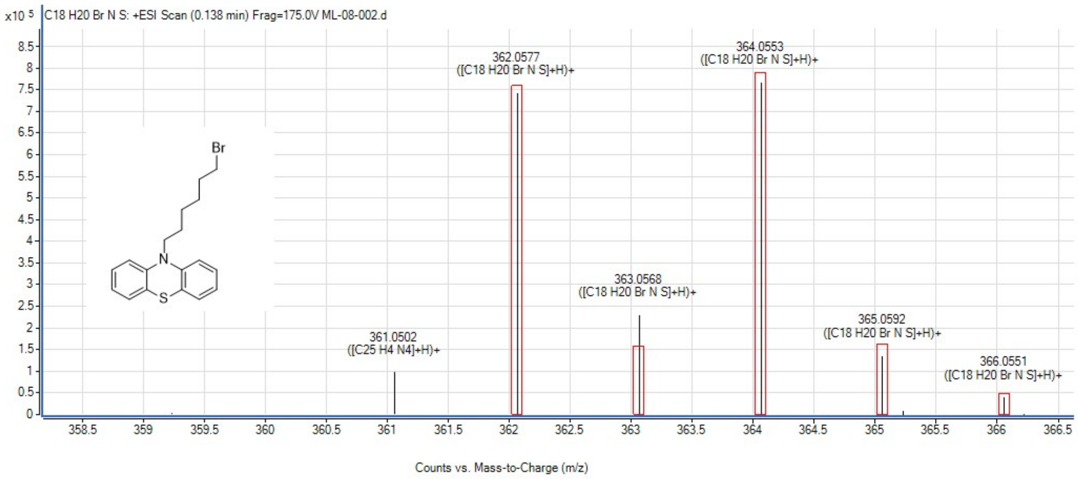
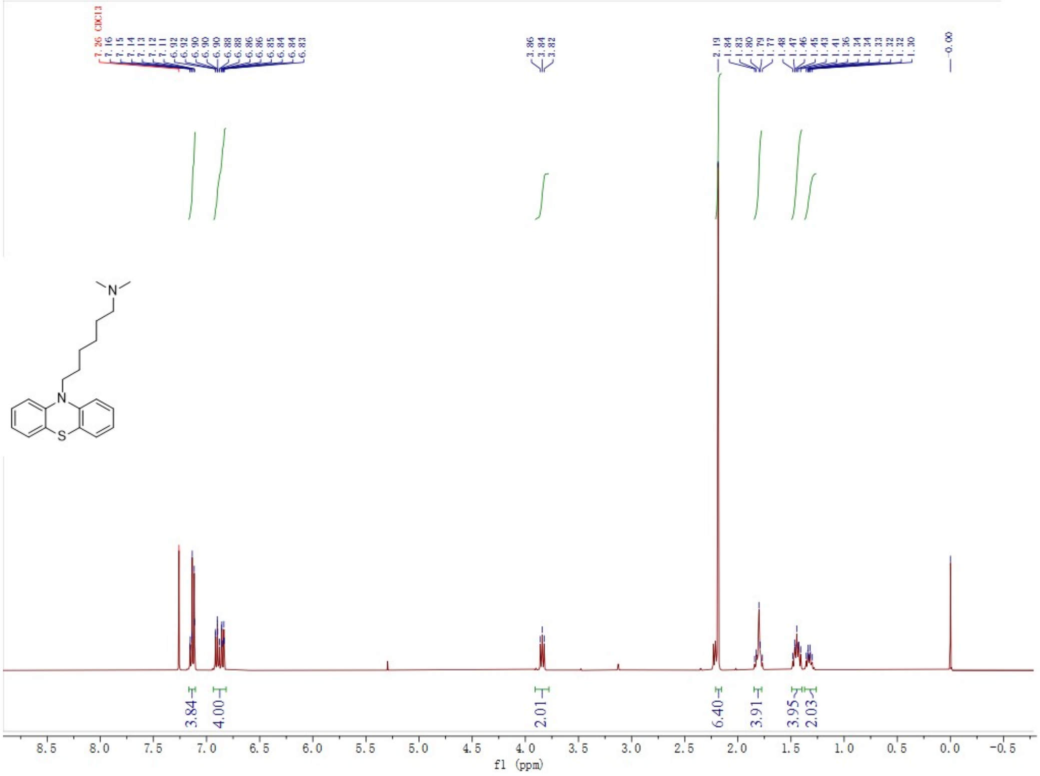
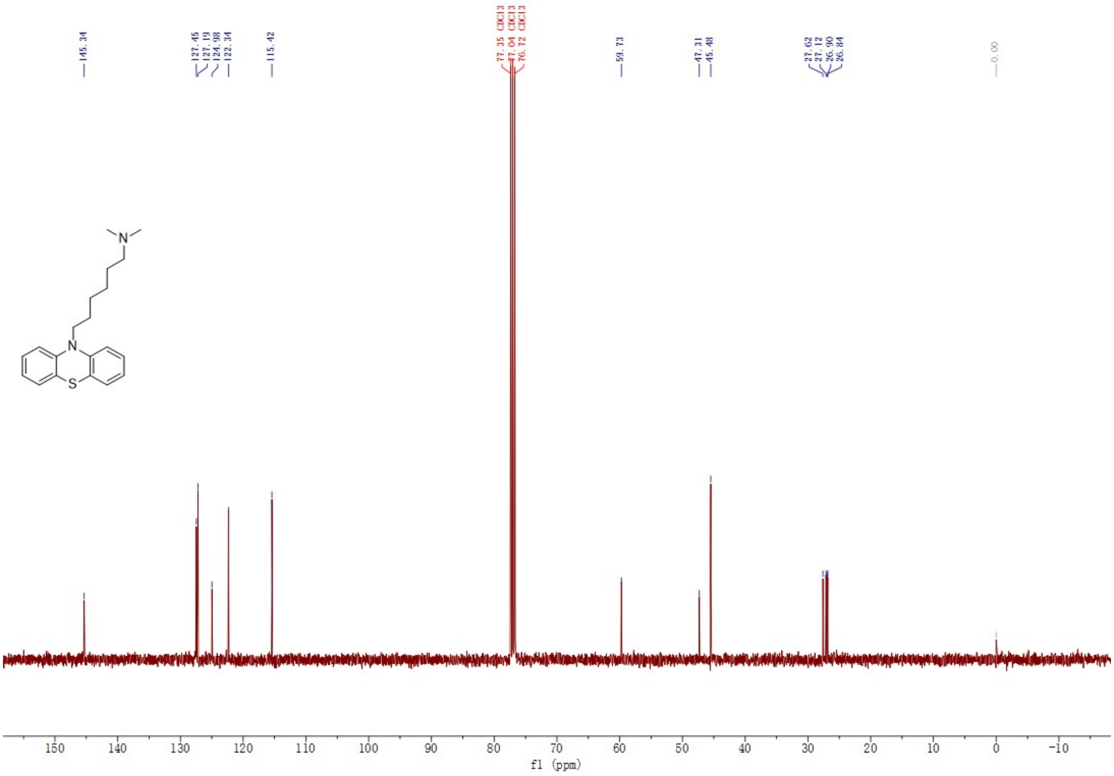


Fig. S1. The ^{1}H NMR, ^{13}C NMR and HRMS of compound 2.

^{1}H NMR



^{13}C NMR



HRMS

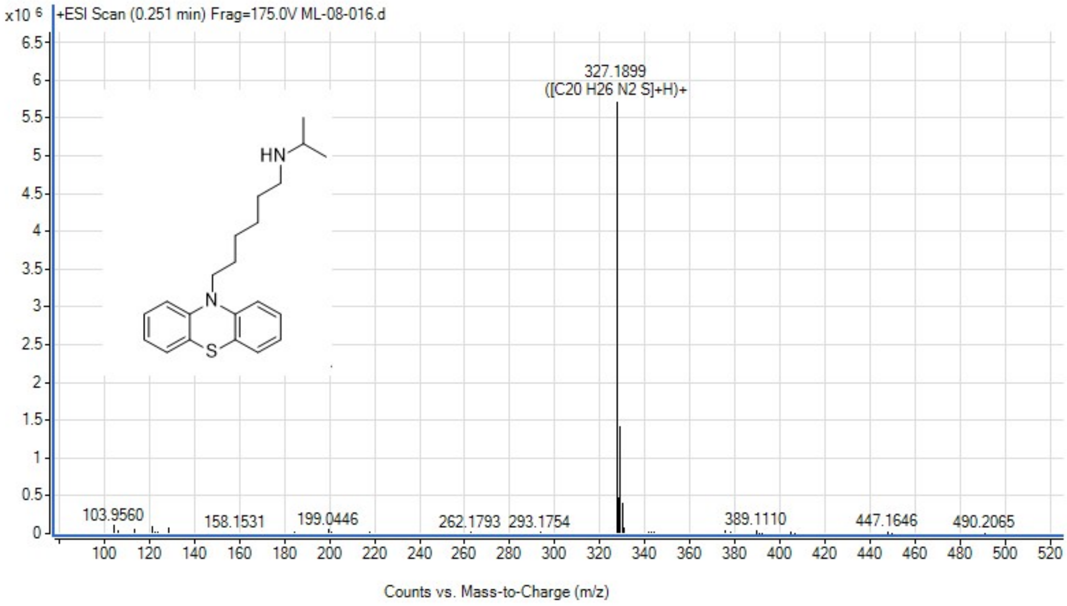
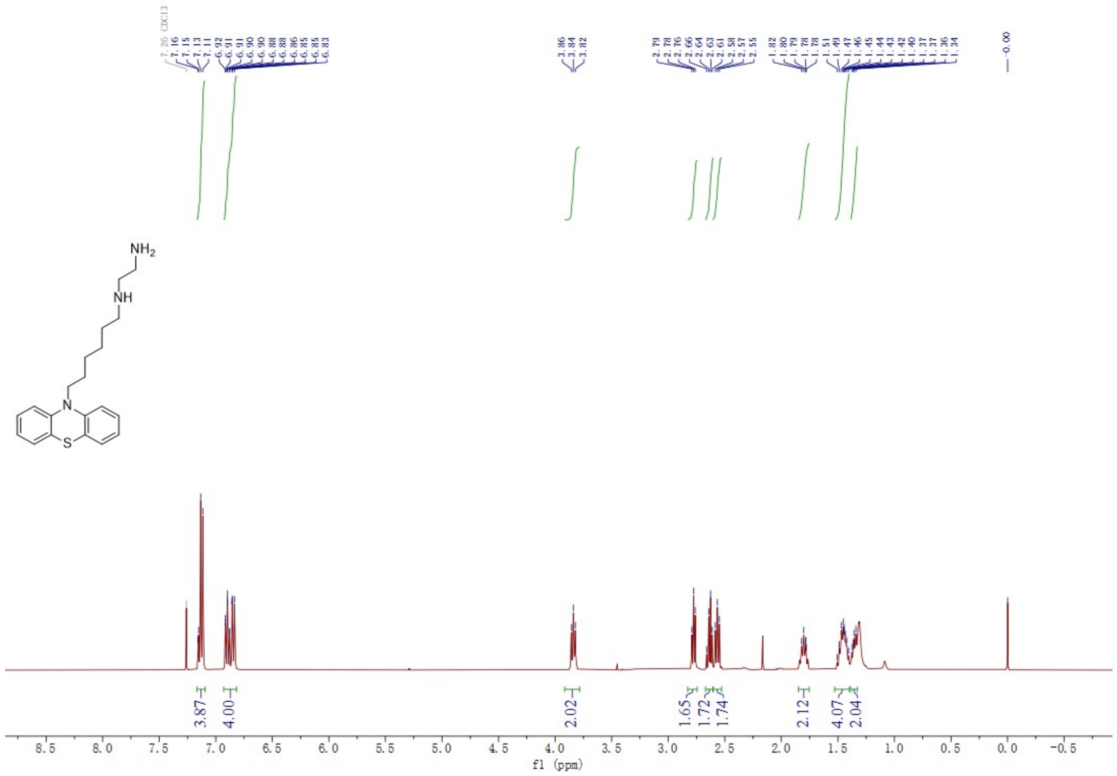
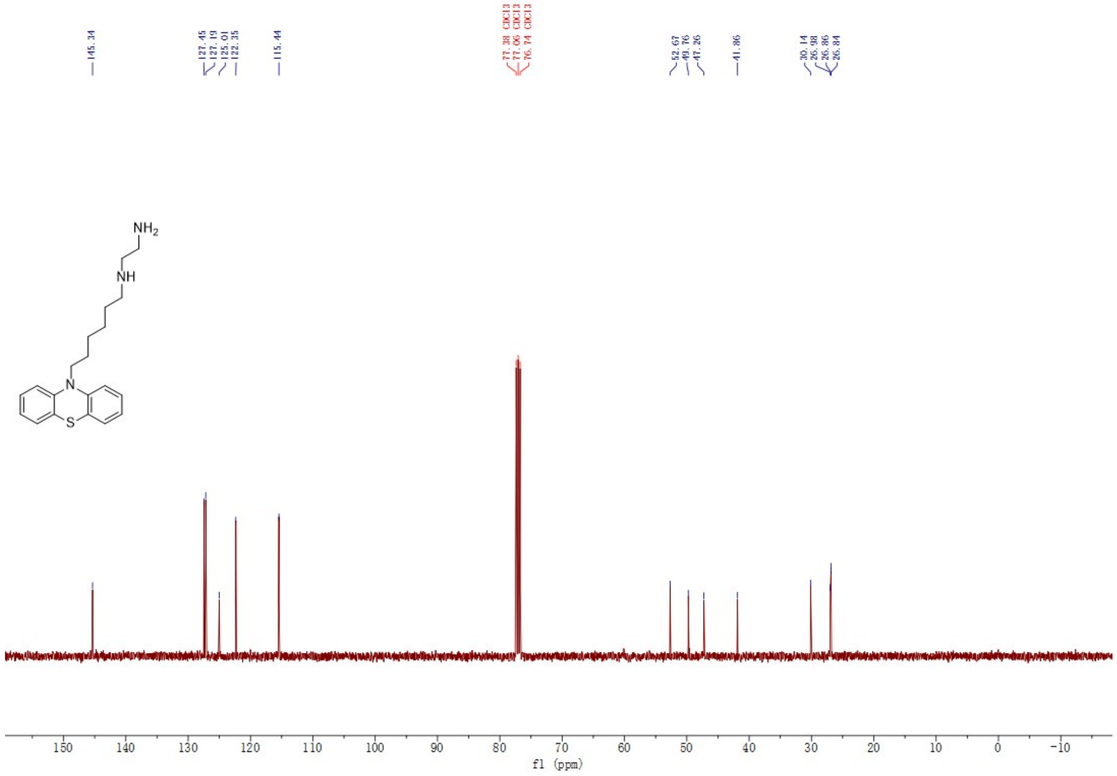


Fig. S2. The ^{1}H NMR, ^{13}C NMR and HRMS of PzN1.

^{1}H NMR



^{13}C NMR



HRMS

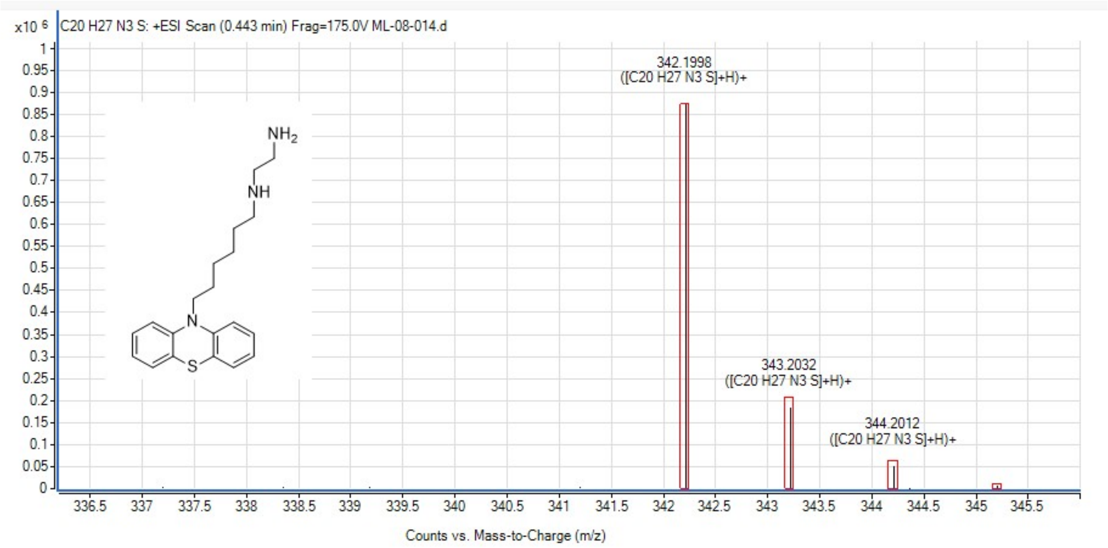
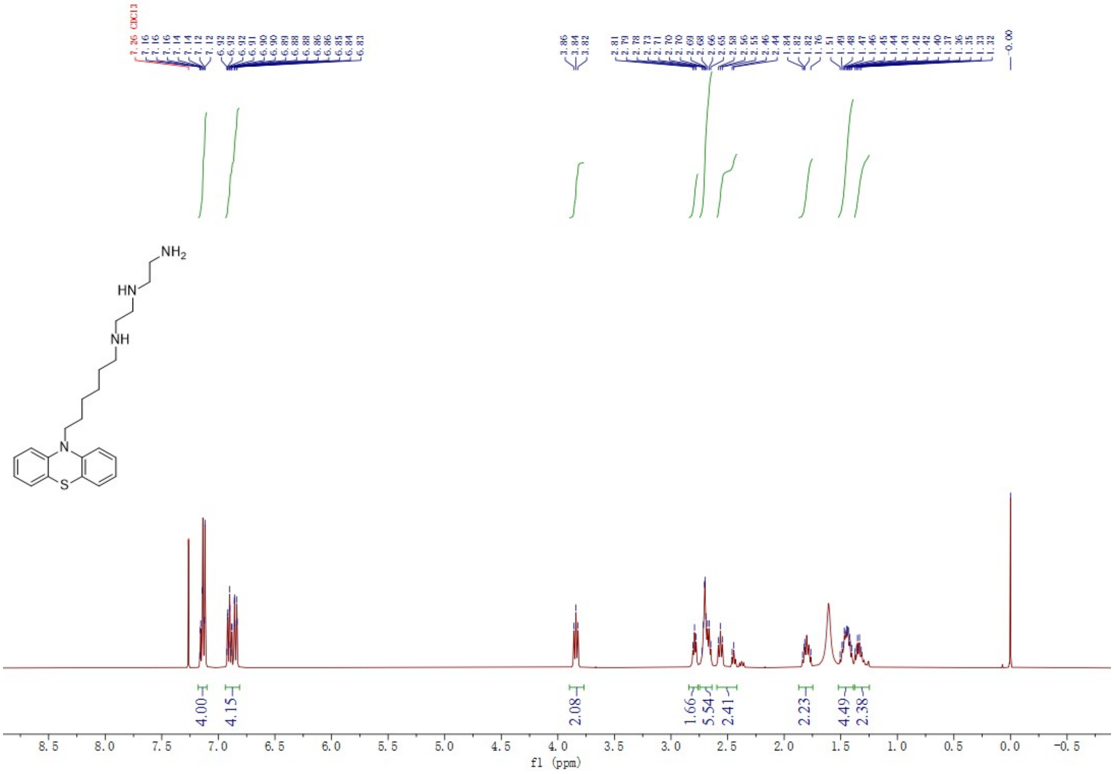
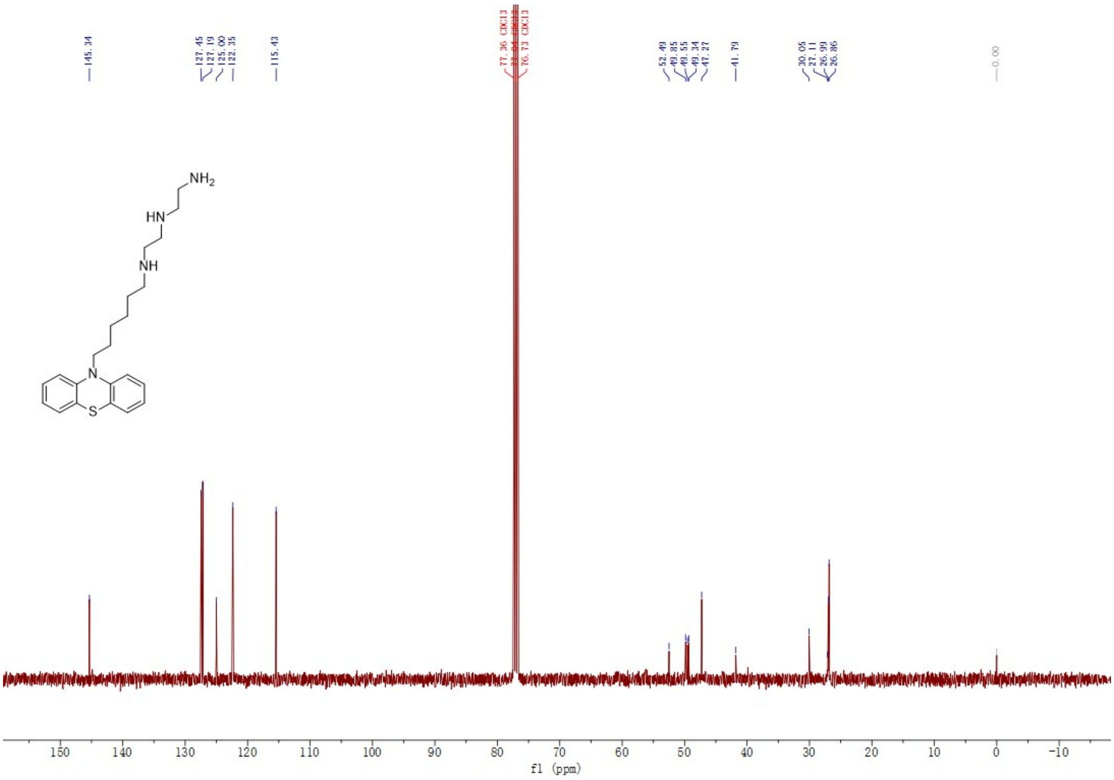


Fig. S3. The ^{1}H NMR, ^{13}C NMR and HRMS of PzN2.

^{1}H NMR



^{13}C NMR



HRMS

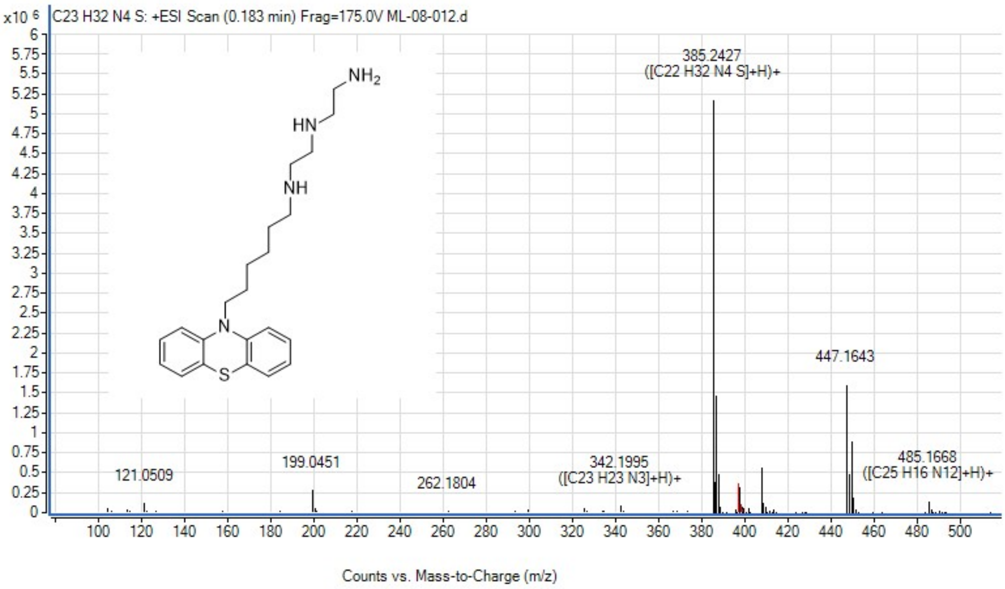
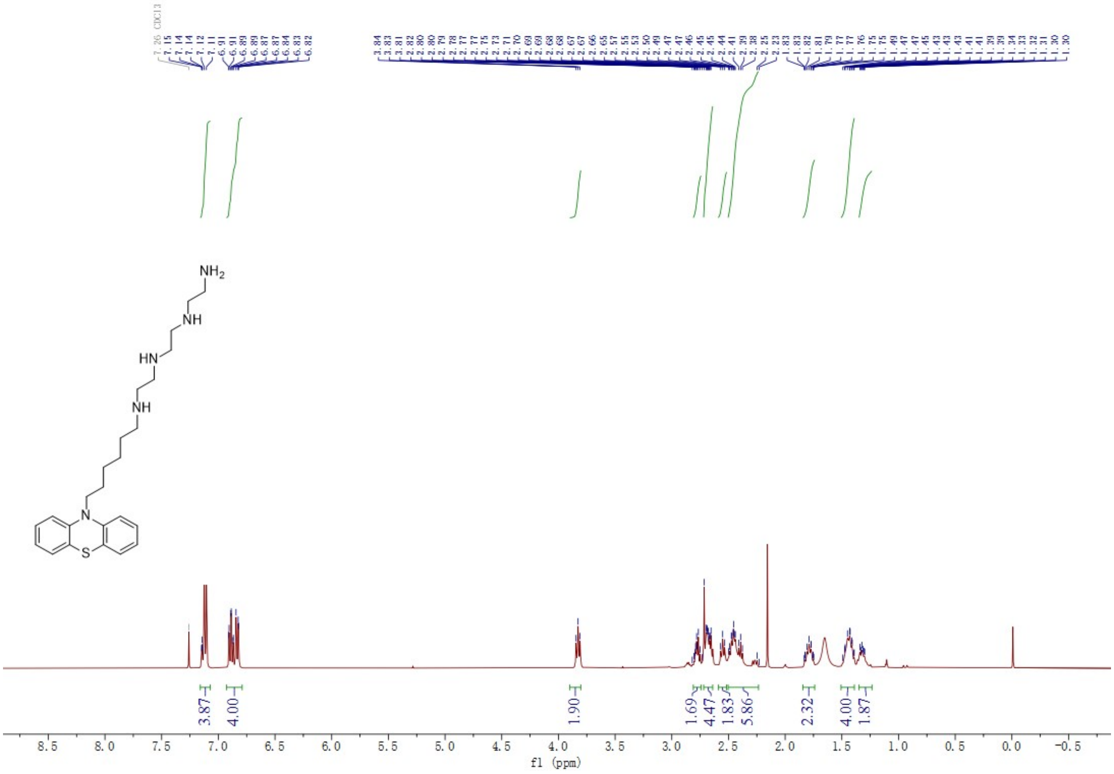
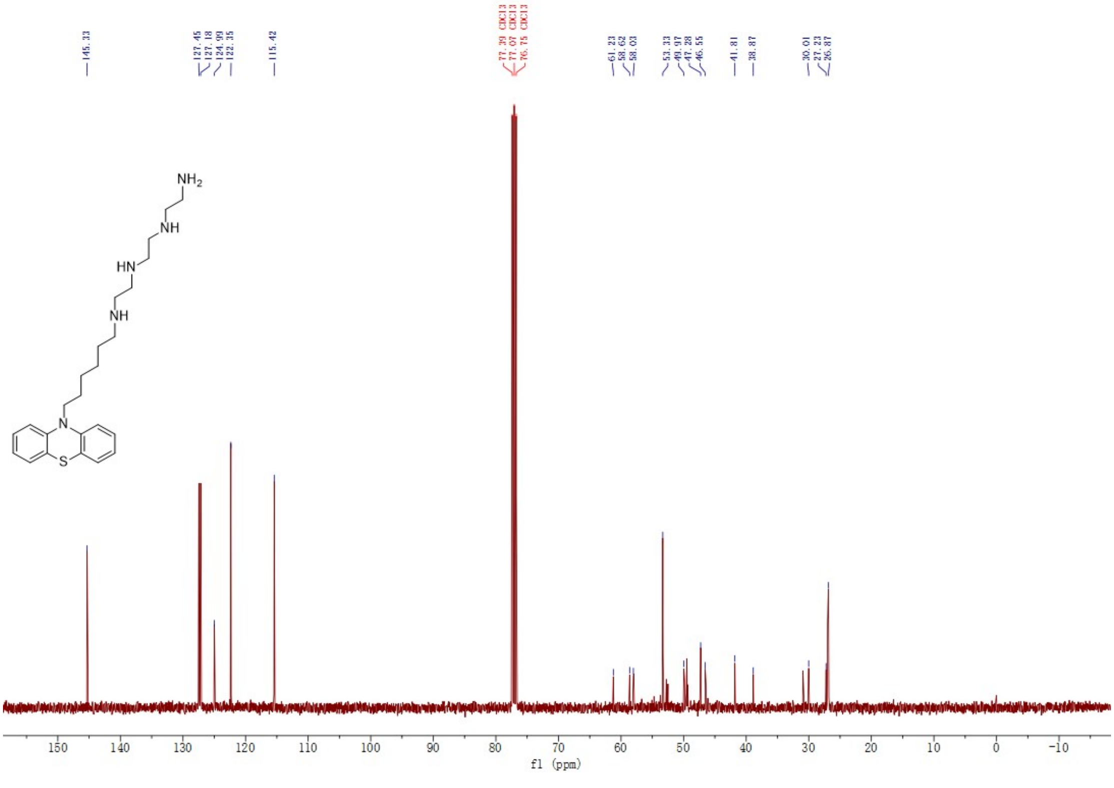


Fig. S4. The ^{1}H NMR, ^{13}C NMR and HRMS of PzN3.

^1H NMR



^{13}C NMR



HRMS

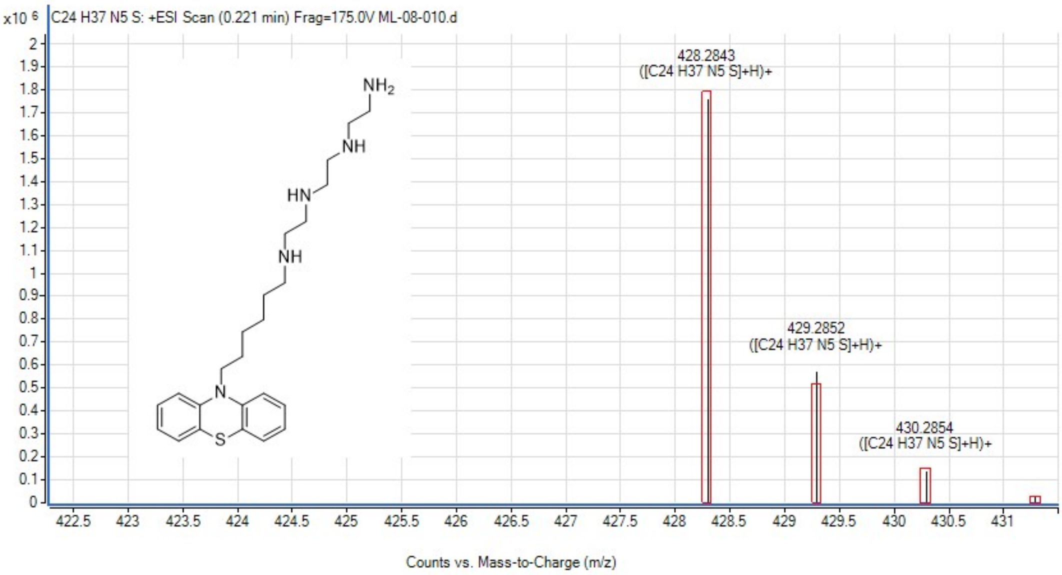


Fig. S5. The ^{1}H NMR, ^{13}C NMR and HRMS of PzN4.

3. UV-visible absorption spectra

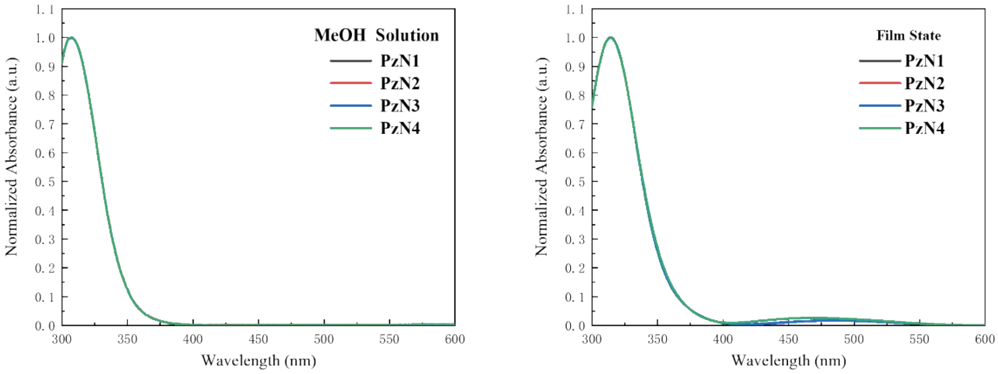


Fig. S6. UV-visible absorption spectra of CSMEs in MeOH solution and film state.

Table S1 Characteristics of UV-vis absorption spectra.

	Sol λ_{max} (nm)	film λ_{max}(nm)	film λ_{oneset} (nm)	Eg^{opt}(eV)
PzN1	307	314	409	3.03
PzN2	307	314	409	3.03
PzN3	307	314	409	3.03
PzN4	307	314	409	3.03

4. Electrochemical properties and Cyclic voltammetry curves

Table S2 Electrochemical properties.

	HOMO[a] (eV)	LUMO[b] (eV)	Eg[elc,c] (V)
PzN1	-7.76	-3.65	4.11
PzN2	-7.74	-3.61	4.13
PzN3	-7.75	-3.56	4.19
PzN4	-7.90	-3.63	4.27

[a] Calculated from oxidation potentials, [b] Calculated from reduction potentials,

[c] Calculated from E_{ox} and E_{red}.

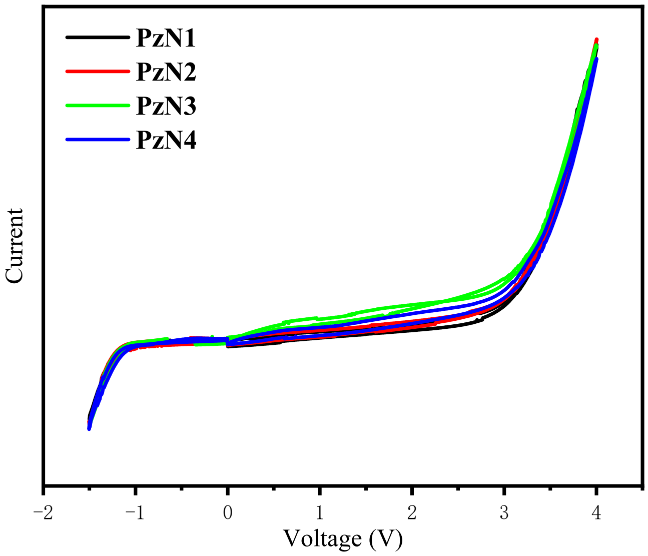


Fig. S7. Cyclic voltammetry curves of the CSMEs in 0.1 M TBAF in acetonitrile solution at a scan rate of 100 mV/s at room temperature (*vs* an Ag quasi-reference electrode).

5. Electrical parameters extracted from the fitting of the Nyquist plots

Table S3 Electrical parameters extracted from the fitting of the Nyquist plots by using the equivalent circuit for solar cell devices with different number of amine groups.

	R1/Ohm	R2/ Ohm
PzN1	31.80	235.8
PzN2	27.49	154.1
PzN3	24.28	201.4
PzN4	24.48	482.4