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Electronic Supplementary Information

Non-fullerene small molecule acceptors with three-dimensional thiophene/selenophene-annulated perylene diimides for efficient organic solar cells

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I. Experimental Section

1. General Information

All reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. Diethyl ether, tetrahydrofuran (THF), and toluene were freshly distilled before use from sodium using benzophenone as indicator. PBDB-T-S was purchase from Zhi-yan. 2,2',6,6'-Tetrabromo-4,4'-spirobi[cyclopenta[2,1-b;3,4-b']dithiophene] (4BrSCPDT)[1] and PDI-S-Br[2] and PDI-Se-Br[3] were synthesized according to the literature procedures.

2. Materials Synthesis

2,2′,6,6′-Tetra(trimethylstannyl)-4,4′-spirobi[cyclopenta[2,1-*b*;3,4-*b′*]dithiophene (4Sn-SCPDT)

Under N_2 atmosphere, 4Br-SCPDT (1.00 g, 1.52 mmol) was dissolved in dry, degassed THF and cooled to −78 °C. n-Butyllithium (n-BuLi; 3.80 mL, 1.6 M) was then added, and the solution was stirred at −78 °C for 90 min before injecting trimethyltin chloride (Me_3SnCl; 7.8 mL, 1 M). The reaction was stirred overnight, quenched with water, and extracted with toluene. The combined organics were washed with water, dried over Na_2SO_4, and filtered. The resulting brown solid was used without further purification. The recovered yield was 1.2 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$ δ): 6.54 (s, 4H), 0.31 (s, 36H).

PDI-S

A mixture of sulfur (2 g, 62.5 mmol) and compound PDI-NO_2 (5 g, 6.25 mmol) were heated in N-methylpyrrolidone (NMP, 120 mL) at 190 °C under an argon atmosphere for 1 h. Next, the cooled mixture was poured into 2 M HCl (1 L) and stirred for 5 min. the resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography (petroleum ether : CH_2Cl_2, 1 : 1) to isolate compound PDI-S as bright yellow solid (4.16 g, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$ δ): 9.30 (d, 2H), 8.91 (s, 4H), 5.32-5.29 (m, 2H), 2.25 (m, 4H), 1.89 (m, 4H), 1.38-

1.22 (m, 32H), 0.85-0.83 (m, 12H).

PDI-Se

Selenium (4.93 g, 62.5 mmol) was dissolved in N-methlpyrrolidone (NMP, 120 mL) and heated to 70 °C for 30 min under argon. Then compound PDI-NO_2 (5 g, 6.25 mmol) was added and the mixture was heated to 190 °C for 3 h with vigorous stirring until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into 2 M HCl (1 L) and stirred for 5 min. the resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography (petroleum ether : CH_2Cl_2, 1 : 1 to 1 : 2, V/V) to give PDI-Se as a yellow-brown solid (4.16 g, 80%). ^1H NMR (300 MHz, $CDCl_3$ δ): 9.32 (d, 2H), 8.90 (s, 4H), 5.32-5.29 (m, 2H), 2.26 (m, 4H), 1.87 (m, 4H), 1.37-1.22 (m, 32H), 0.84-0.82 (m, 12H).

PDI-S-Br

In a closed round-bottom flask, bromine (30.55 g, 0.191 mol) was added in one portion to a solution of Compound (3 g, 3.82 mmol) in 50 mL of dichloromethane with vigorous stirring for 5 h. Then the excess of bromine was quenched with saturated sodium sulfite solution. The organic layer was separated, dried over $MgSO_4$, and purified by silica gel column chromatography (petroleum ether : CH_2Cl_2, 3 : 1, V/V) to give compound PDI-S-Br as an orange solid (3.05 g, 92%). ^1H NMR (300 MHz, $CDCl_3$ δ): 10.32 (d, 1H), 9.34 (s, 2H), 9.13 (s, 1H), 8.94 (s, 1H), 5.36-5.22 (m, 2H), 2.55-2.25 (m, 4H), 2.04-1.98 (m, 4H), 1.68-1.11 (m, 32H), 0.92-0.88 (m, 12H).

PDS-Se-Br

The synthetic route of PDI-Se-Br is similar to the above mentioned methods, expect for using PDI-Se replace PDI-S. The crude product was purified by silica gel column chromatography (petroleum ether : CH_2Cl_2, 1 : 1, V/V) as an eluent to give PDI-Se-Br as a red solid (89% yield). ^1H NMR (300 MHz, $CDCl_3$ δ): 10.32 (d, 1H), 9.34 (s, 2H), 9.13 (s, 1H), 8.94 (s, 1H), 5.31-5.23 (m, 2H), 2.55-2.25 (m, 4H), 2.02-1.88 (m, 4H), 1.37-1.24 (d, 32H), 0.90-0.81 (m, 12H).

SCPDT-PDI_4-S

Under N_2 atmosphere, a mixture of 4Sn-SCPDT (100 mg, 0.1 mmol), PDI-S-Br (388 mg, 0.45 mmol), $Pd(PPh_3)_4$ (24 mg, 0.02 mmol), and toluene (10 mL) were heated to 110 °C for 72 h under N_2. The reaction mixture was then cooled to room temperature and exacted twice with $CHCl_3$. The organic layer was combined, washed with brine, dried over Na_2SO_4, and filtered. The residue was purified by flash column chromatography (*n*-hexane : dichloromethane = 1 : 2) to obtain a black red solid (175 mg, 50% yield) as a product. ^1H NMR (300 MHz, $CDCl_3$ δ): 9.43 (d, 4H), 9.19 (d, 8H), 8.47 (s, 4H), 8.18 (s, 4H), 7.53 (s, 4H), 5.35 (s, 4H), 4.76 (s, 4H), 2.40-1.95 (m, 23H), 1.55-1.10 (m, 138H), 0.81-0.78 (d, 47H). MAIDI-TOF: $C_{217}H_{240}N_8O_{16}S_8$ For $[M+Na]^+$, calcd, 3495.65; found, 3495.13.

SCPDT-PDI_4-Se

The synthetic route of SCPDT-PDI-Se is similar to the above mentioned methods, expect for using PDI-Se-Br replace PDI-S-Br. The crude product was purified by flash column chromatography (*n*-hexane : dichloromethane = 1 : 2) to obtain a black green solid (183 mg, 50% yield) as a product. ^1H NMR (300 MHz, $CDCl_3$ δ): 9.42 (d, 4H), 9.18 (d, 8H), 8.58 (s, 4H), 8.26 (s, 4H), 7.51 (s, 4H), 5.33 (s, 4H), 4.80 (s, 4H), 2.15-1.87 (m, 23H), 1.61-0.92 (m, 138H), 0.82-0.72 (m, 47H). MAIDI-TOF: $C_{217}H_{240}N_8O_{16}S_4Se_4$ For $[M+Na]^+$, calcd, 3684.38; found, 3684.89.

3. Theoretical Calculation

The geometry was optimized by density functional theory (DFT) using the B3LYP hybrid functional with basis set 6-31G(d).[4] Quantum chemical calculation was performed with the Gaussian09 package. All N-hexylheptyl substituents were replaced with methyl groups in the calculations for simplification.

4. Devices Fabrication and Characterization

4.1 OSC Devices Fabrication

The solar cells were fabricated with a conventional structure of ITO/PEDOT:PSS/Active layers/PDIN/Al. The patterned ITO glass was pre-cleaned in an ultrasonic bath of acetone and isopropyl alcohol, then treated in an ultraviolet–ozone chamber (Novascan Company, USA) for 20 min. A thin layer of PEDOT:PSS was deposited through spin-coating on precleaned ITO-coated glass from a PEDOT:PSS aqueous solution ((Baytron P, now Clevios VP AI 4083, from H. C. Starck, Leverkusen, Germany) at 4000 rpm and dried subsequently at 150 °C for 15 min in air. The PBDB-T-S:acceptor blends with 1 : 1 ratio were dissolved in o-DCB (the total of 20 mg/mL^{-1}) was subsequently spin-coated (1600 rpm) on PEDOT:PSS layer. The methanolic solution (0.3% acetic acid) of PDIN (10 nm) at a concentration of 1.5 mg/mL^{-1} was deposited on the active layer at 3000 rpm for 30 s. Finally, an aluminum layer (100 nm) at the vacuum condition of 5×10^{-5} Pa was deposited by thermal evaporation method. The thickness of the photosensitive layer was measured using an Ambios Technology (Santa Cruz, CA) XP-2 profilometer. The J–V curves of the prepared devices were measured on a computer-controlled Keithley (Zolix ss 150 Solar Simulator) 236 source measure unit. A xenon lamp coupled with AM1.5 solar spectrum filters was used as the light source, the optical power at the sample was 100 mW cm^{-2}. The light intensity of the solar simulator was calibrated using a standard silicon solar cell. IPCE spectra were measured by using a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.).

4.2 OSC Devices Characterization

4.2.1 Space Charge-Limited Current Method Measurement

The transport properties of the devices were evaluated using the space charge-limited current method on a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo, Japan). The carrier mobility was extracted by fitting the J-V curves in the near-quadratic region according to the modified Mott–Gurney equation

$$J = \frac{9}{8}\varepsilon_0\varepsilon_\mathrm{r}\mu_0\frac{V}{L^3}\left(0.89\beta\sqrt{\frac{V}{L}}\right),$$

where J is the current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity, μ_0 is the zero-field mobility, V is the applied voltage, L is the thickness of the active layer, and β is the field activation factor.

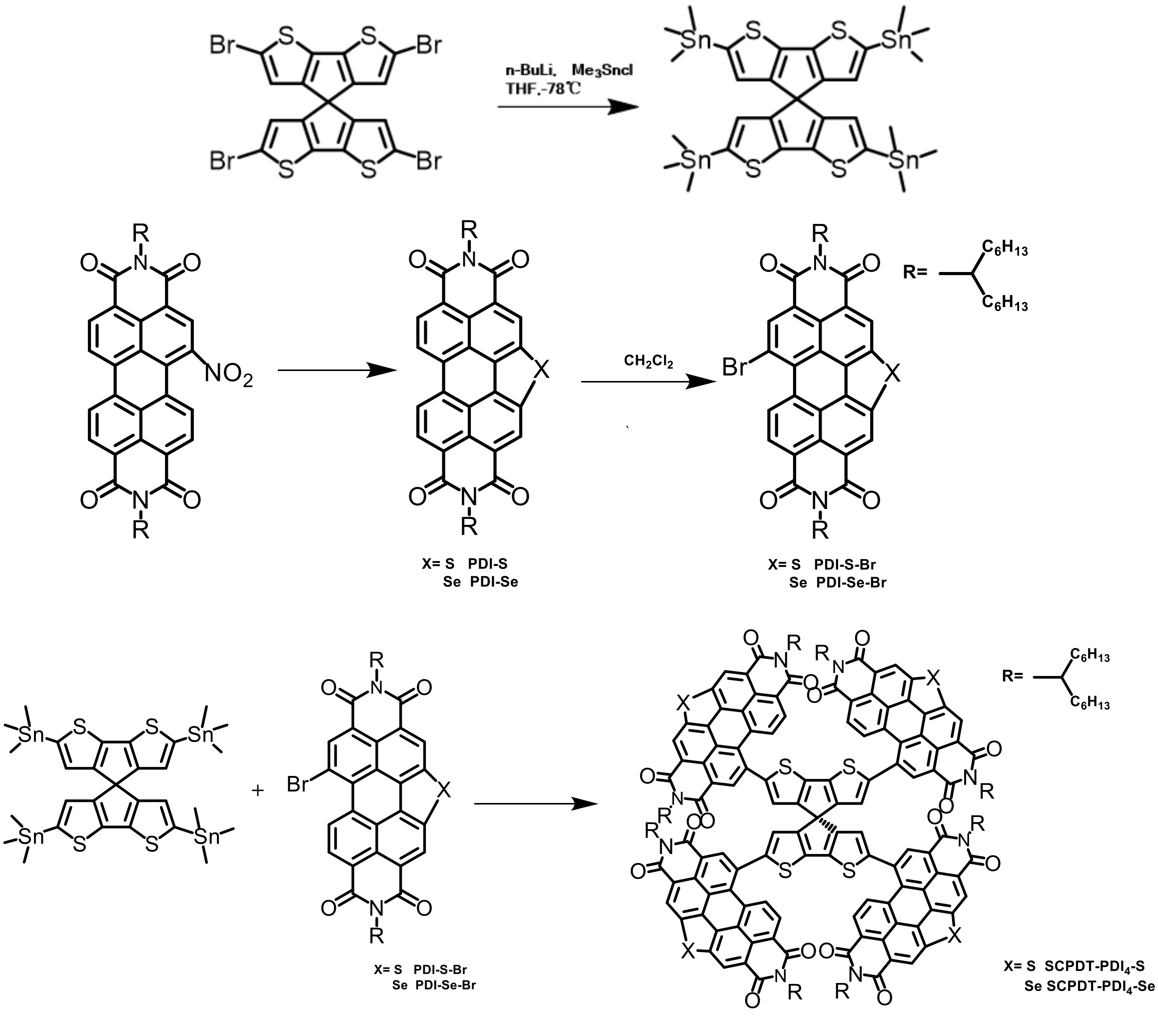
4.2.2 Electrochemical Characterization of the Films

Electrochemical measurements were performed under nitrogen in deoxygenated 0.1 M solutions of tetra-n-butylammonium hexafluorophosphate in dry dichloromethane using a CHI 660E electrochemical workstation, with a glassy carbon working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. The lowest unoccupied molecular orbital (LUMO) levels were estimated based on the onset reduction potential (E_{red}), and the reduction potential was calibrated using ferrocene ($E_{Fc/Fc+}$) as a reference (energy level = − [E_{red} − $E_{Fc/Fc+}$ + 4.8] eV). Solution and thin film UV-visible absorption spectra were recorded on a Shimadzu UV-1750 UV-Vis spectrophotometer. Fluorescence spectra of the neat and blend films were recorded on a FLS980 spectrometer (Edinburgh Instruments).

4.2.3 Atomic Force Microcopy Analysis of Films

The morphologies of the thin film surfaces were examined using atomic force microscopy (MFP-3D Classic, Oxford Instruments) in the tapping mode.

II. Supplementary Figures and Tables



Scheme S1 Detailed synthesis route of SCPDT-PDI_4-S and SCPDT-PDI_4-Se.

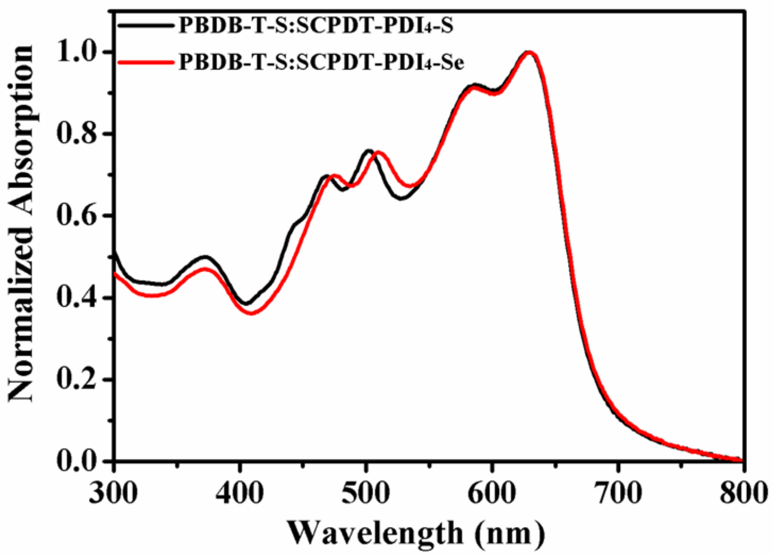


Fig. S1 The normalized absorption spectra of PBDB-T-S:SCPDT-PDI$_4$-S (1 : 1, w/w) and PBDB-T-S:SCPDT-PDI$_4$-Se (1 : 1, w/w) blended films.

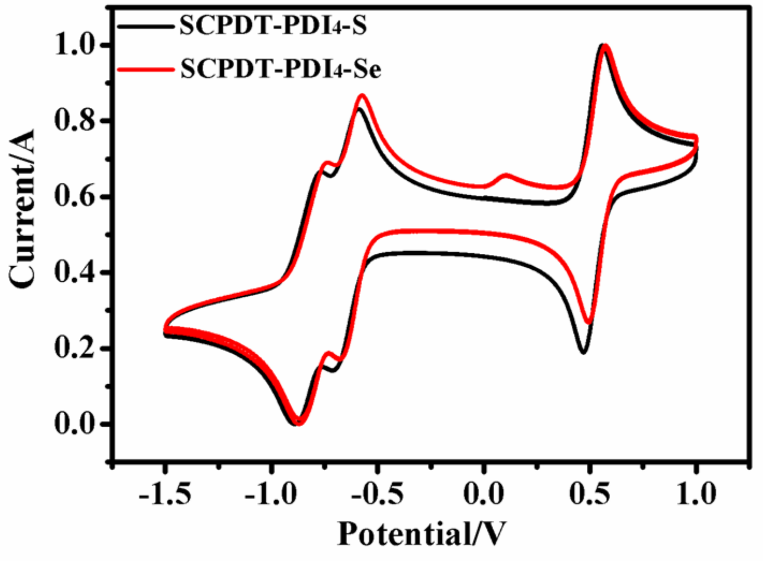


Fig. S2 Cyclic voltammograms of SCPDT-PDI$_4$-S and SCPDT-PDI$_4$-Se with Fc/Fc$^+$ as the reference.

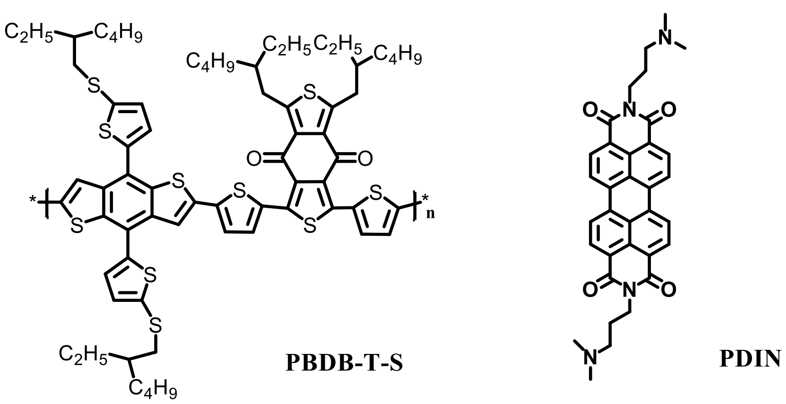


Fig. S3 The molecular structures of PBDB-T-S and PDIN.

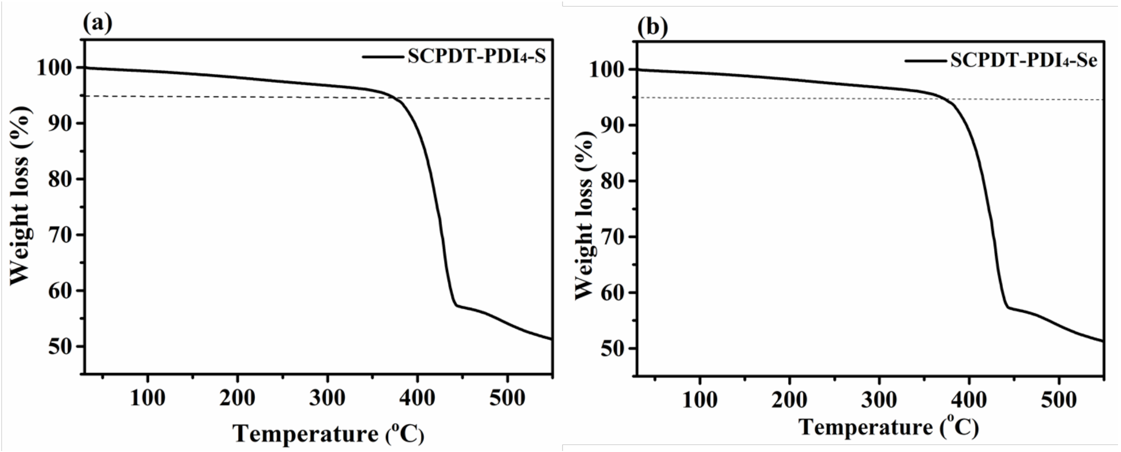


Fig. S4 Thermogram of SCPDT-PDI$_4$-S and SCPDT-PDI$_4$-Se obtained at a heating rate of 10 °C min^{-1} under N_2.

^{1}H NMR and MALDI-TOF-MS spectra

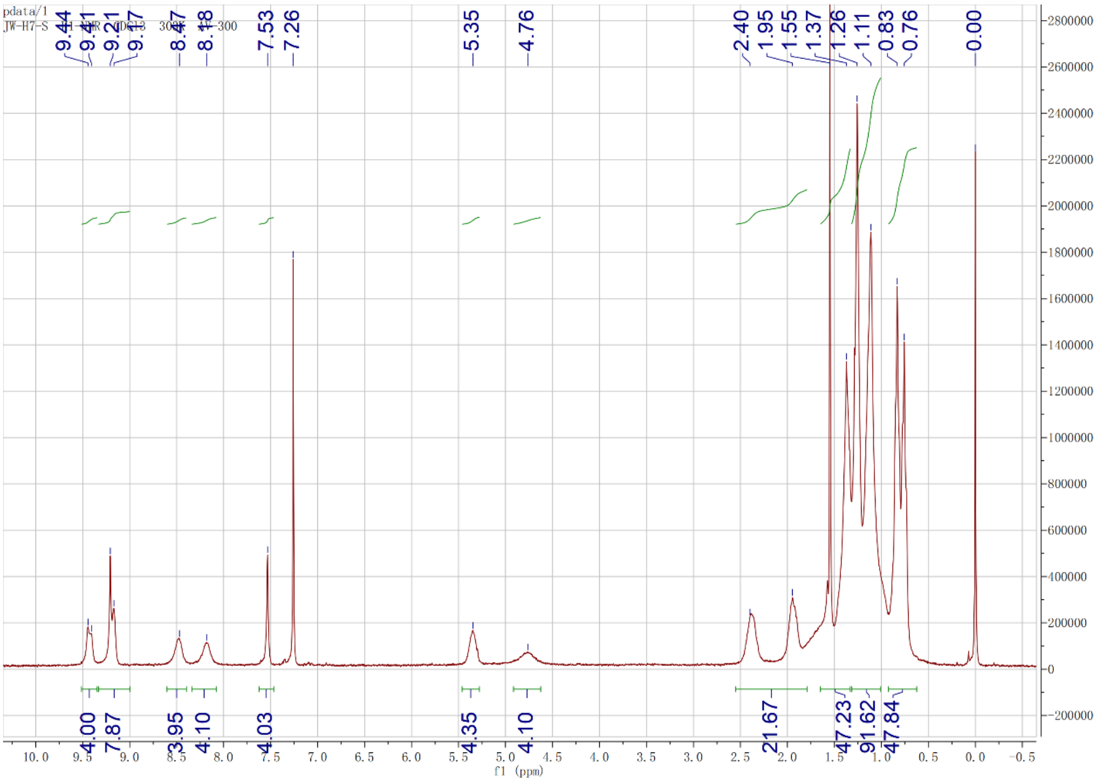


Fig. S5 ^{1}H NMR of SCPDT-PDI$_4$-S.

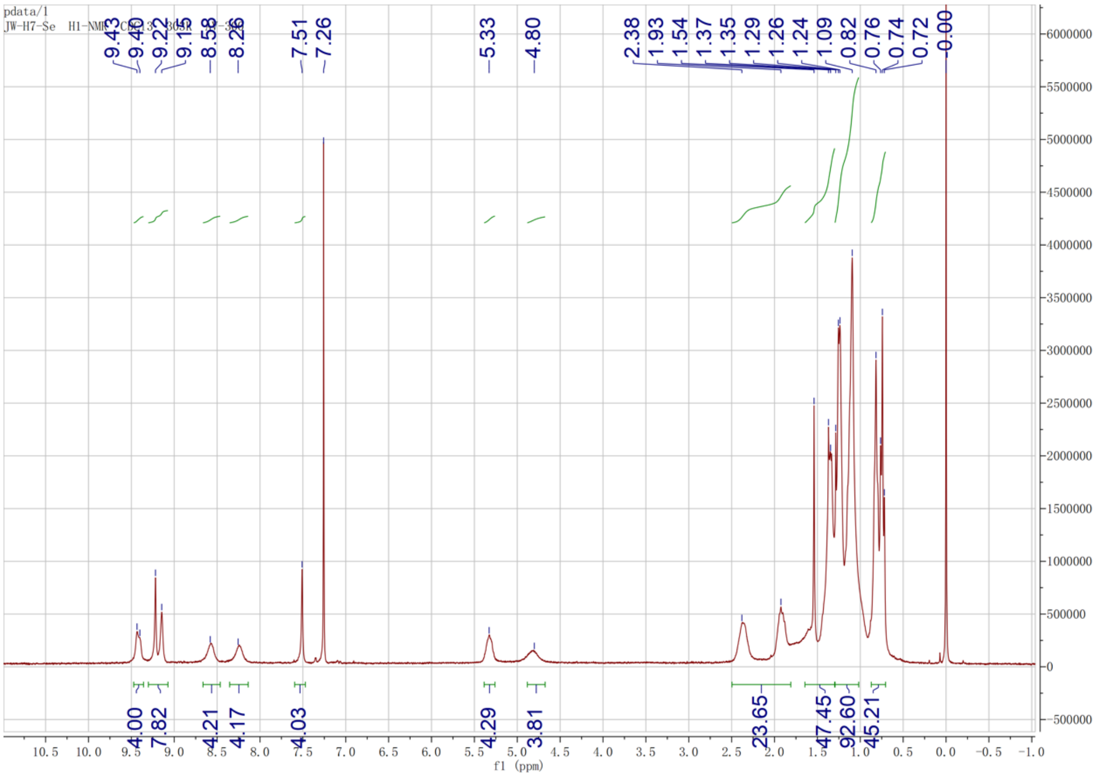


Fig. S6 ^{1}H NMR of SCPDT-PDI$_4$-Se.

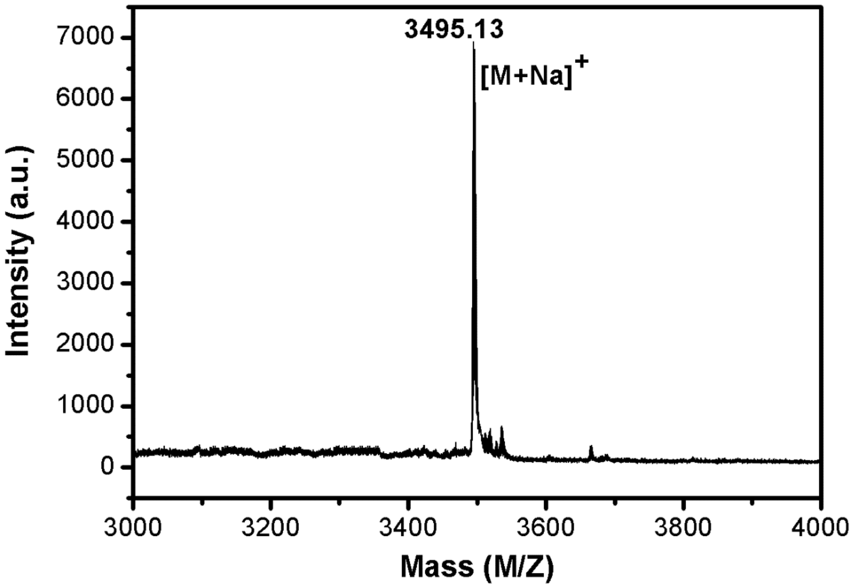


Fig. S7 MALDI-TOF-MS of SCPDT-PDI$_4$-S.

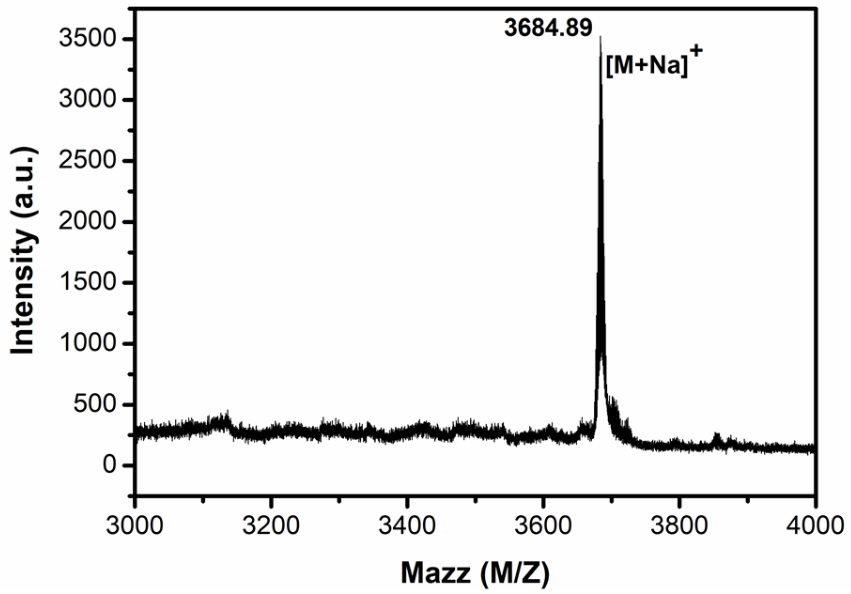


Fig. S8 MALDI-TOF-MS of SCPDT-PDI$_4$-Se.

References

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