

Sulfonyl-based Nonfullerene Electron-Acceptor Assisted Grain Boundary Passivation for Efficient and Stable Perovskite Solar Cells

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Materials

ITO substrates (ITO/glass: $R_s \leq 15 \Omega$ per square) were purchased from Shenzhen Nan Bo Group, China. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$), Lead iodide (PbI_2) and 4,7-diphenyl-1,10-Phenanthroline (Bphen) were purchased from Xi'an Polymer Light Technology Corp. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF) and chlorobenzene (CB) were purchased from Sigma-Aldrich. Poly[3-(4-carboxylbutyl)thiophene (P3CT) and PC_{61}BM were purchased from Rieke and ADS, respectively. C_{60} Pyrrolidine Tris-Acid (CPTA) was purchased from Sigma-Aldrich.

Device Fabrication

The ITO substrates ($2 \text{ cm} \times 2 \text{ cm}$) were successively cleaned by a sonication of 15 min in detergent, deionized water, acetone and isopropyl alcohol before being dried in a nitrogen stream. The cleaned ITO substrates were then treated with O_2 plasma for 5 min. Then, the P3CT-N solution^[3] (1 mg mL^{-1} in methanol) was spin-coated onto ITO substrates at 4000 rpm for 20 s and annealed at $100 \text{ }^\circ\text{C}$ for 10 min in the air. The perovskite film was deposited by a typical anti-solvent method in glovebox with the nitrogen atmosphere. The perovskite precursor solution (1.45M in DMF/DMSO cosolvent (DMF:DMSO = 4:1, v/v) with a molar ratio of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 of 1:1) was spin-coated onto ITO/P3CT-N at 4700 rpm for 20 s. During spin-coating, 200 μL IDIC-Th or IDIS-Th chlorobenzene solution with different concentrations (0.025, 0.05, 0.1, 0.2 (for IDIC-Th) and 1.0 mg mL^{-1}) was pipetted onto the spinning film at 8s after the spin-coating began. Subsequently, the film was baked at $60 \text{ }^\circ\text{C}$ for 1 min and $80 \text{ }^\circ\text{C}$ for 2 min to form perovskite film. After cooling to room temperature, the electron

transporting layer (PC₆₁BM 20 mg mL⁻¹ in CB) was spin-coated at 2000 rpm for 60 s. Then, the substrate was annealed at 80 °C for 10 min. Finally, Bphen (2 mg mL⁻¹ in 2,2,2-trifluoroethanol (TFE)) was deposited on the top of PC₆₁BM layer at 4000 rpm for 30 s and an 100 nm Ag electrode was formed by thermal evaporation. The active area, as defined by the overlap of Ag and ITO, was 0.09 cm².

Characterizations and Measurements

¹H and ¹³C NMR spectra were collected at 293 K from a Bruker 400 MHz AVANCE III with tetramethylsilane (TMS) as an internal reference. Mass spectra were recorded on a Finnigan LCQ mass spectrometer. UV-vis absorption measurements were taken on a mapada UV-3300 spectrophotometer. The cyclic voltammetric tests (CV) were carried out on a CHI600D electrochemical workstation with a platinum working electrode of 2 mm diameter and a platinum wire counter electrode at a scan rate of 50 mV/s against a solution (purged with nitrogen for 15 min) of 0.1 mol/L acetonitrile solution containing tetrabutyl ammonium hexafluorophosphate (Bu₄NPF₆). The electrochemical potential was calibrated against ferrocene/ferrocenium redox couple (Fc/Fc⁺).

The current density–voltage characteristics (*J*-*V*) of the photovoltaic devices were recorded using a computer-controlled Keithley 2400 source meter under 1 sun, AM 1.5G simulated solar light (100mWcm⁻²). The *J*-*V* curves were all measured in glovebox at room temperature under forward scan (unless otherwise stated) from 1.2 V to - 0.2 V with dwell time of 50 ms (the delay between measurement points is 50 ms). The EQE measurement was conducted in air using Newport quantum efficiency

measurement system (ORIEL IQE 200TM) combined with a lock-in amplifier and 150W xenon lamp. Fourier transform infrared spectroscopy (FTIR) samples were prepared by scraping the perovskite films off the substrate and then mixed with pre-dried KBr powder. FTIR spectra were recorded in transmittance mode using IR spectrometer instrument (Thermo, Nicolet 6700). The PL spectra were analyzed using a fluorescence spectrophotometer (F-4600, Hitachi Ltd., Tokyo, Japan) with a 150 W Xe lamp as the excitation source at room temperature. Top-view and Cross-section scanning electron microscope (SEM) images were recorded using field emission scanning electron microscope (Hitachi, S-4800).

Table S1 Summary of fitting parameters for time-resolved photoluminescence (TRPL) on the different films.

Sample	MAPbI ₃ /PC61BM	MAPbI ₃ +IDIC-Th/PC61BM	MAPbI ₃ +IDIS-Th/PC61BM
A ₁	0.77	0.77	0.79
τ ₁ (ns)	3.40	3.30	2.91
A ₂	0.23	0.23	0.21
τ ₂ (ns)	23.71	17.28	15.74
τ _{ave} (ns)	17.12	11.82	10.47

Table S2. Summary of the J - V parameters of the PSCs with different C_{IDIC-Th} dissolved in anti-solvent CB.

Device structure	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]
control	1.085 (1.081 ± 0.006)	21.22 (21.08 ± 0.11)	74.9 (73.5 ± 1.56)	17.24 (16.75 ± 0.50)
0.05 mg/mL IDIC-Th	1.077 (1.078 ± 0.002)	21.26 (21.28 ± 0.21)	77.6 (74.8 ± 1.69)	17.78 (17.16 ± 0.42)
0.1 mg/mL IDIC-Th	1.072 (1.069 ± 0.005)	21.72 (21.37 ± 0.39)	78.9 (78.8 ± 0.82)	18.35 (18.00 ± 0.49)
0.2 mg/mL IDIC-Th	1.070 (1.074 ± 0.008)	21.30 (21.34 ± 0.29)	79.8 (77.2 ± 1.95)	18.19 (17.69 ± 0.33)
1.0 mg/mL IDIC-Th	1.064 (1.066 ± 0.006)	21.64 (21.38 ± 0.17)	77.5 (73.6 ± 2.90)	17.84 (16.78 ± 0.78)

Table S3. Summary of the J - V parameters of the PSCs with different C_{IDIS-Th} dissolved in anti-solvent CB.

Device structure	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]
control	1.085 (1.081 ± 0.006)	21.22 (21.08 ± 0.11)	74.9 (73.5 ± 1.56)	17.24 (16.75 ± 0.50)
0.025 mg/mL IDIS-Th	1.087 (1.090 ± 0.002)	21.53 (21.39 ± 0.20)	79.4 (77.9 ± 1.49)	18.58 (18.16 ± 0.30)
0.05 mg/mL IDIS-Th	1.096 (1.088 ± 0.009)	21.70 (21.80 ± 0.16)	81.2 (80.5 ± 1.11)	19.32 (19.09 ± 0.26)
0.1 mg/mL IDIS-Th	1.080 (1.086 ± 0.006)	22.03 (21.43 ± 0.47)	78.8 (78.9 ± 0.98)	18.75 (18.35 ± 0.35)
1.0 mg/mL IDIS-Th	1.084 (1.083 ± 0.003)	21.21 (21.36 ± 0.17)	76.5 (72.9 ± 1.50)	17.58 (17.03 ± 0.40)

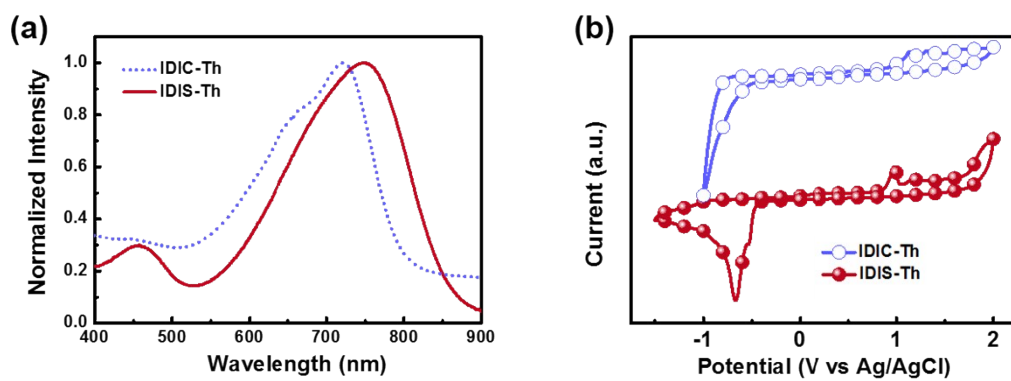


Fig. S1 (a) Normalized film absorption spectra of IDIC-Th and IDIS-Th, (b) CV curves of IDIC-Th and IDIS-Th.

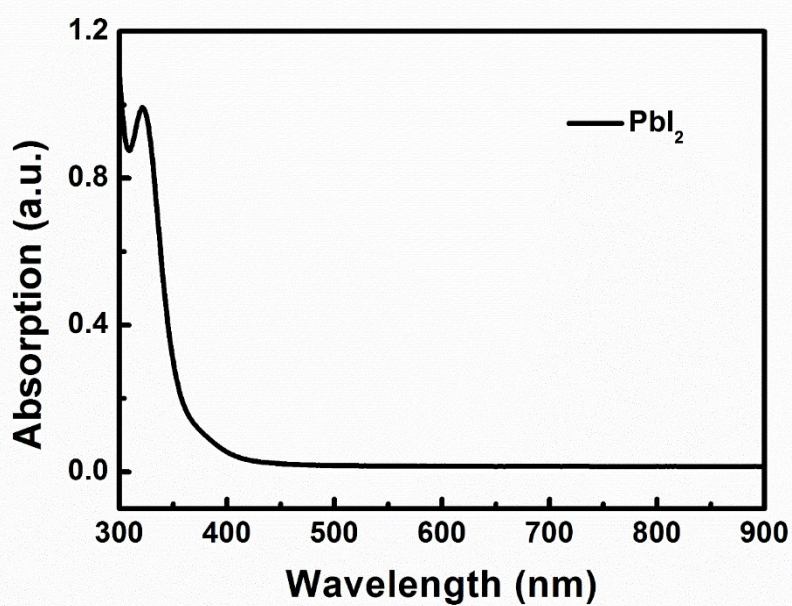


Fig. S2 UV-vis absorption spectra of PbI_2 in DMF solution.

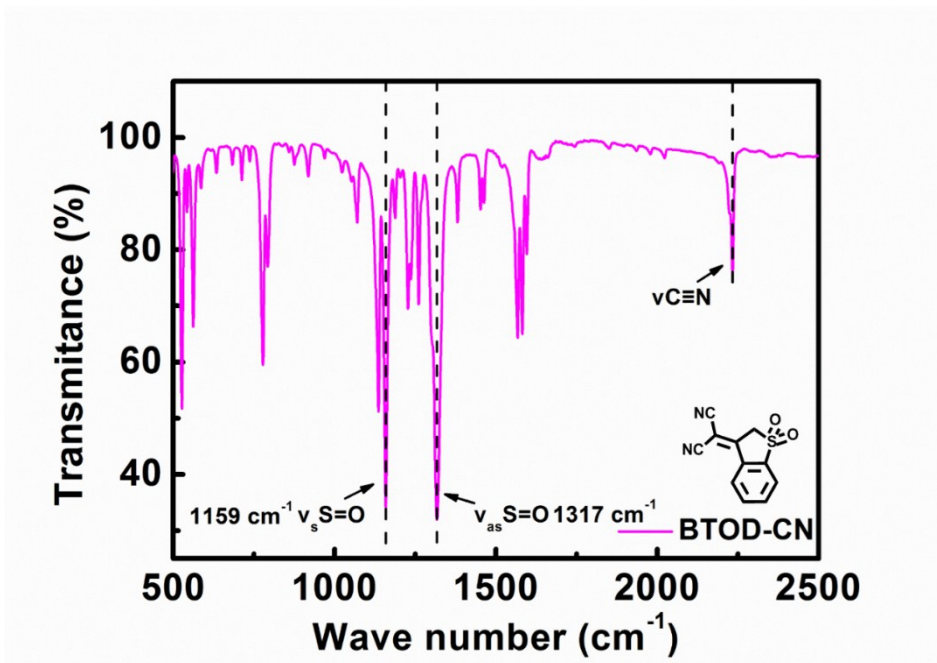


Fig. S3 FTIR spectrum of intermediate BTOD-CN containing sulfonyl group (O=S=O)

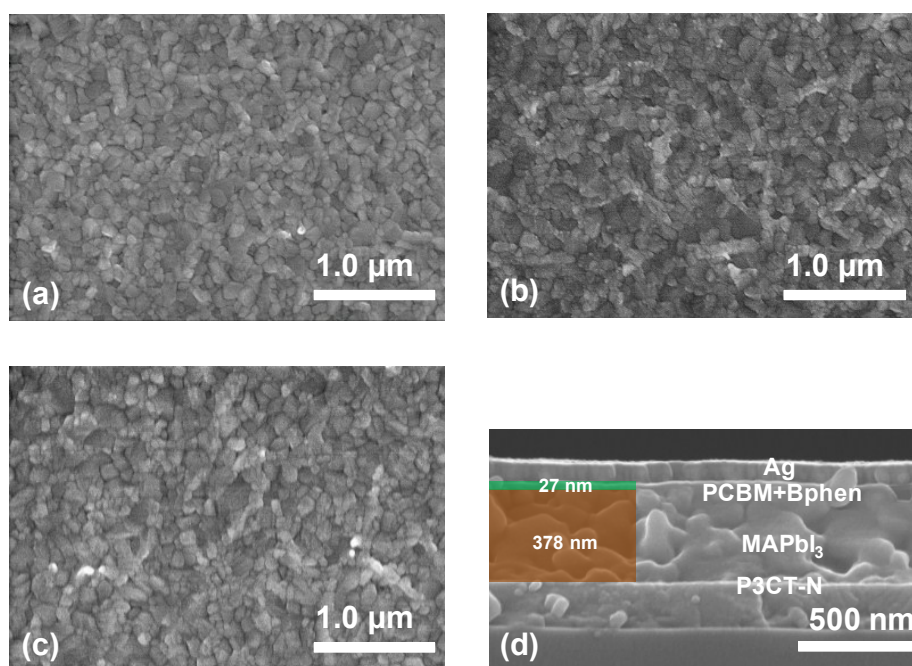


Fig. S4 Plan-view scanning electronic microscopy (SEM) images of the (a) control, (b) IDIC-Th passivated, (c) IDIS-Th passivated films. (d) Cross-sectional SEM image of the complete device

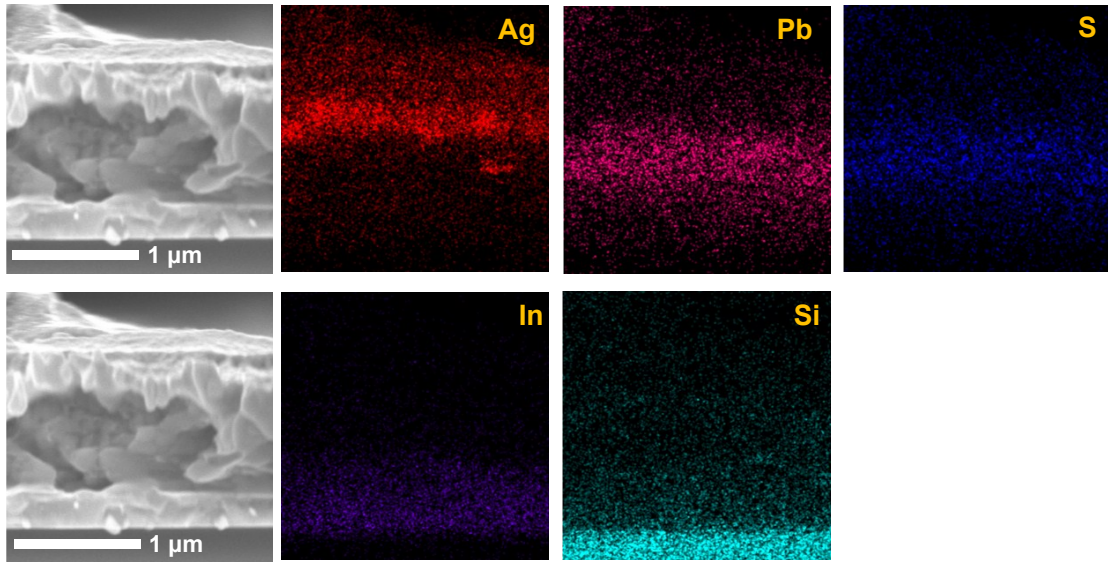


Fig. S5 EDS mapping of complete PSCs with IDIS-Th. In our case, we used S elemental mapping to confirm the existence of sulfur atom of IDIS-Th in the perovskite layer.

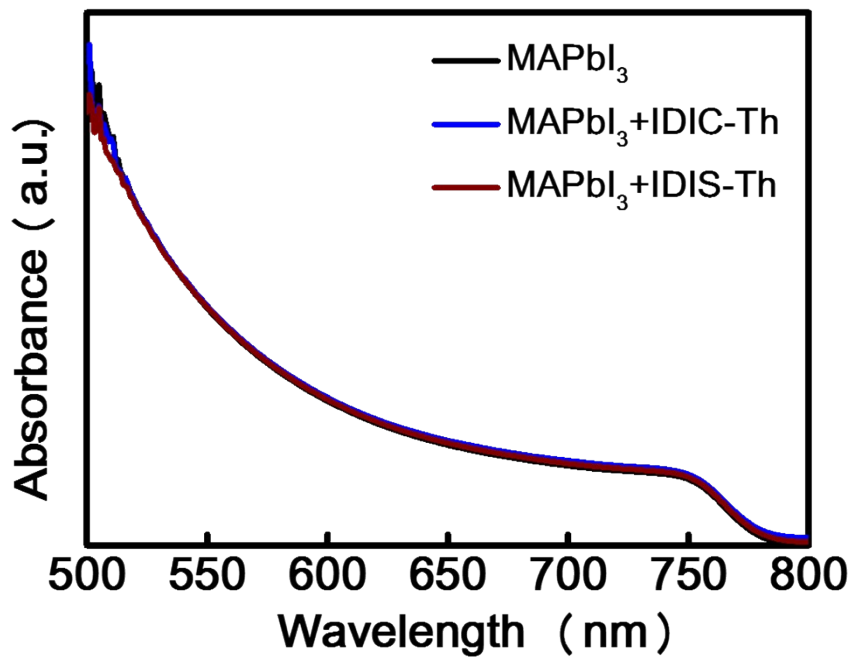


Fig. S6 UV-vis spectra of perovskite films without and with nonfullerene acceptor materials.

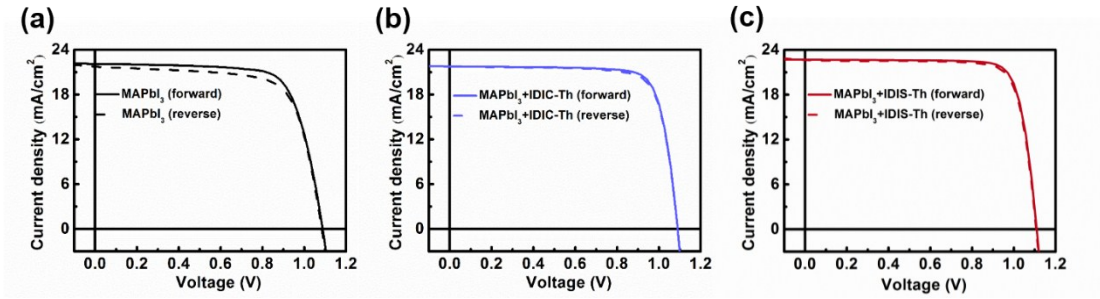


Fig. S7 Forward and reverse scans of the (a) control device, (b) IDIC-Th passivated device and (c) IDIS-Th passivated device displaying suppressed hysteresis when additives are introduced

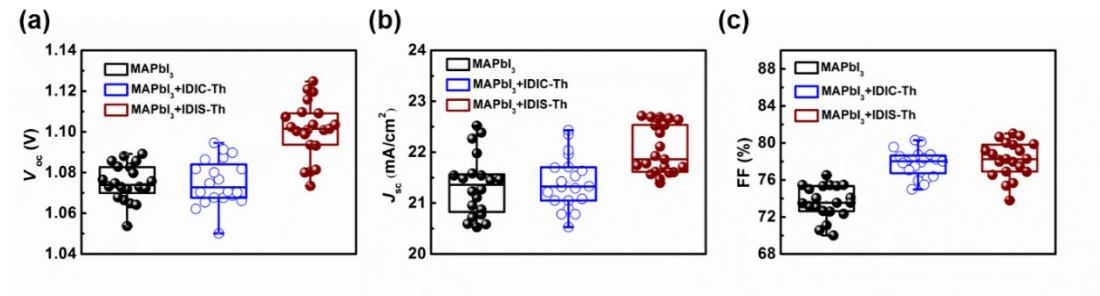


Fig. S8 the statistics of V_{OC} , J_{SC} and FF for 20 separated PSCs based on (a) control devices, (b) IDIC-Th passivated devices and (c) IDIS-Th passivated devices showing performance when additives are introduced.

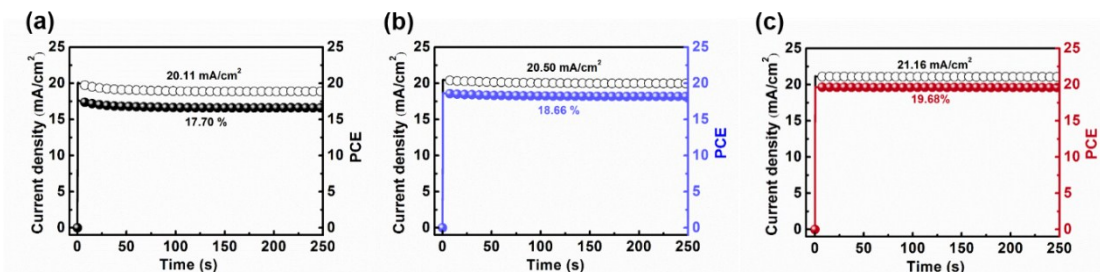


Fig. S9 Steady-state measurement of J_{SC} and PCE of the (a) control device, (b) IDIC-Th passivated device and (c) IDIS-Th passivated device.

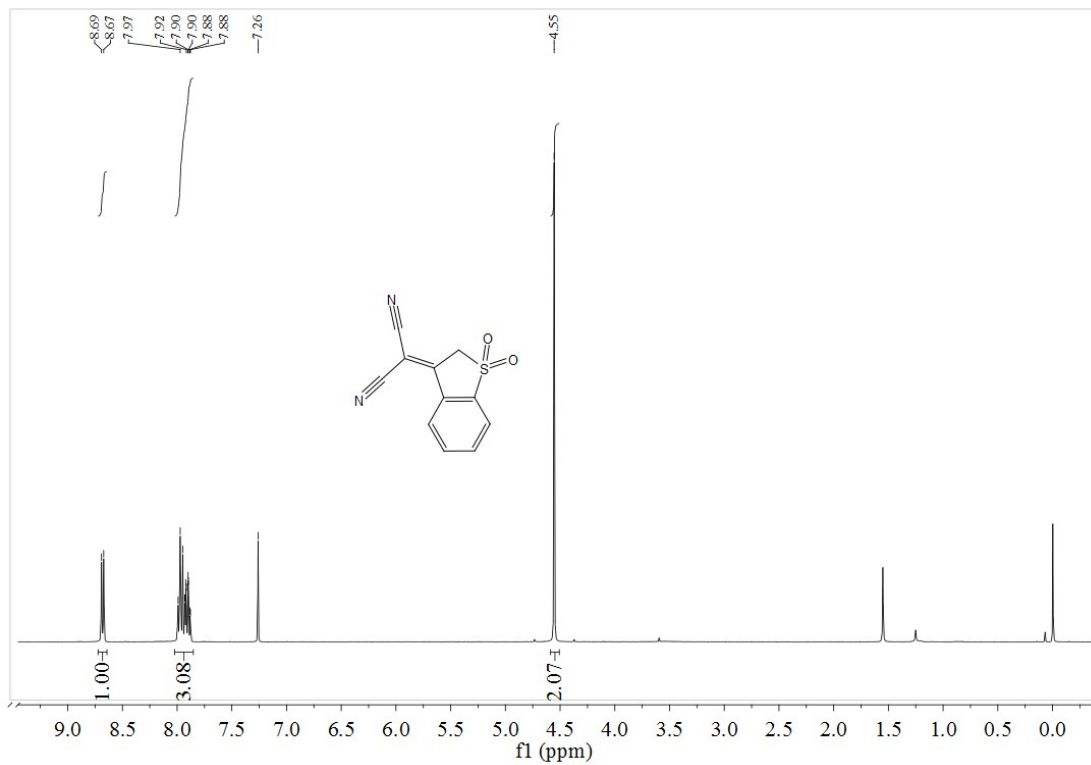


Fig. S10 ^1H NMR of BTOD-CN

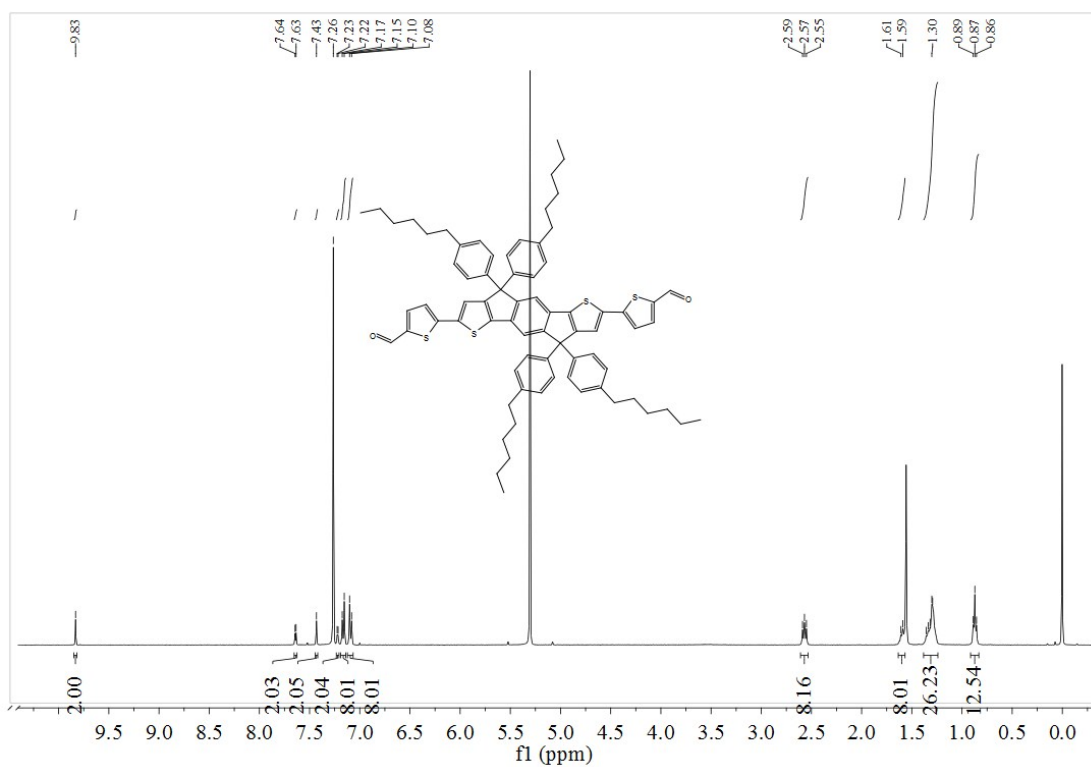


Fig. S11 ^{13}H NMR of ID-CHO

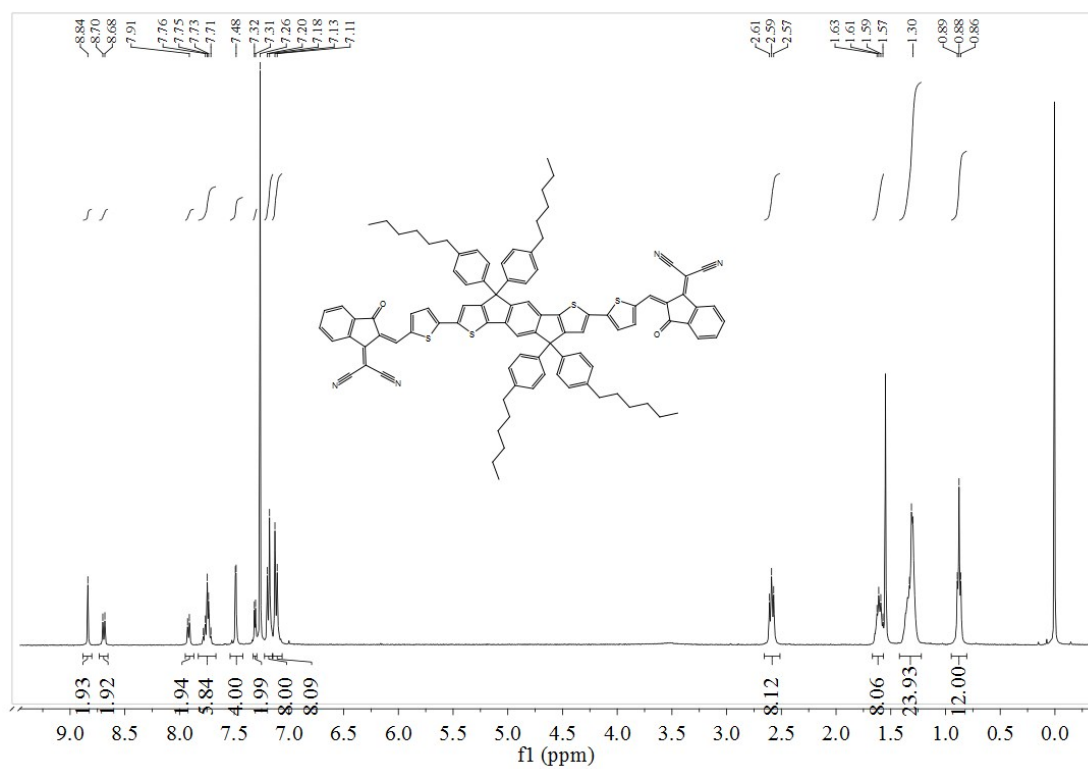


Fig. S12 ^1H NMR of IDIC-Th

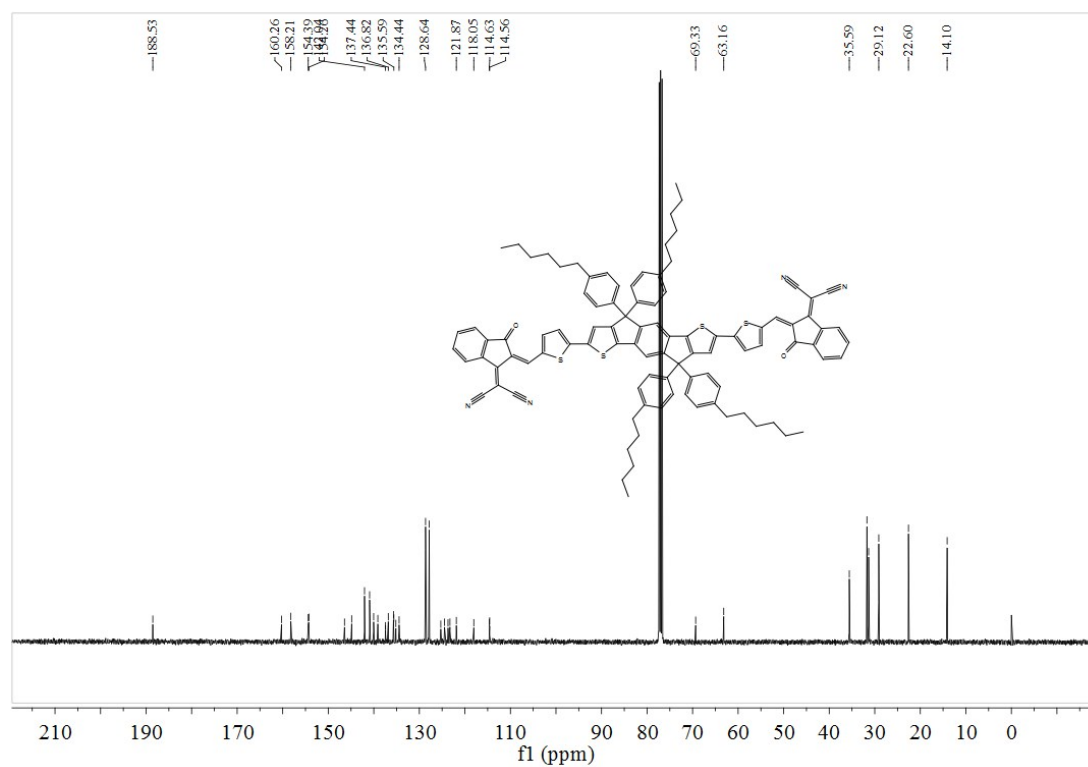


Fig. S13 ^{13}C NMR of IDIC-Th

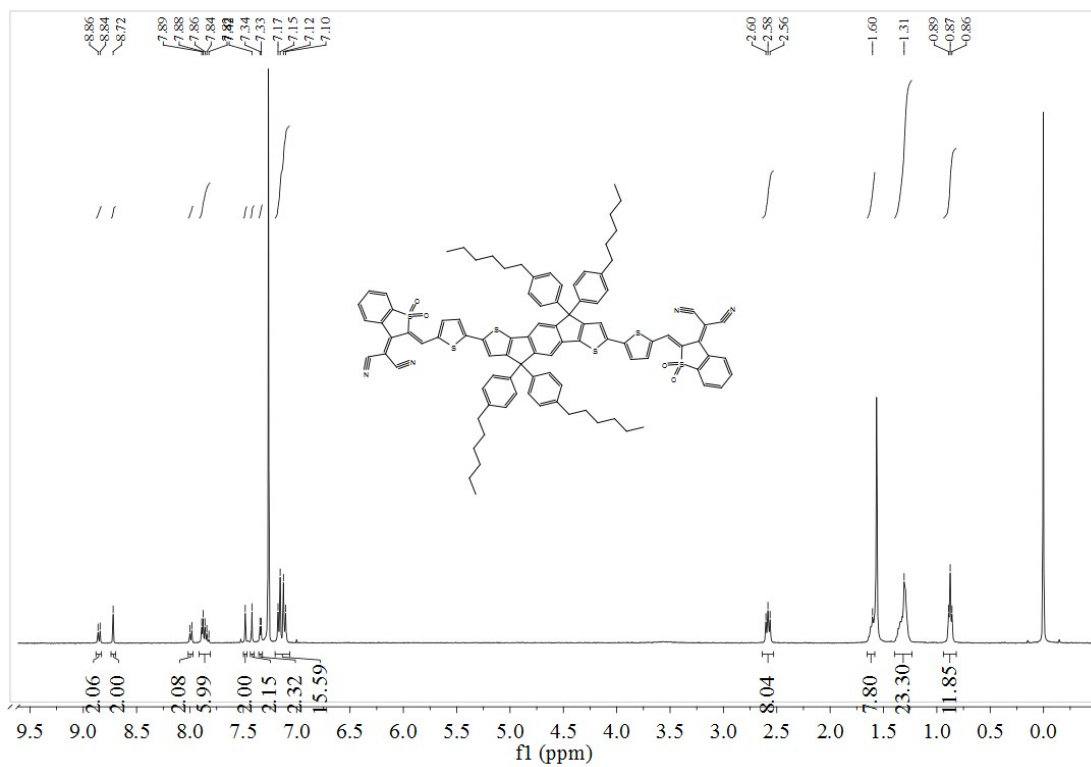


Fig. S14 ^1H NMR of IDIS-Th

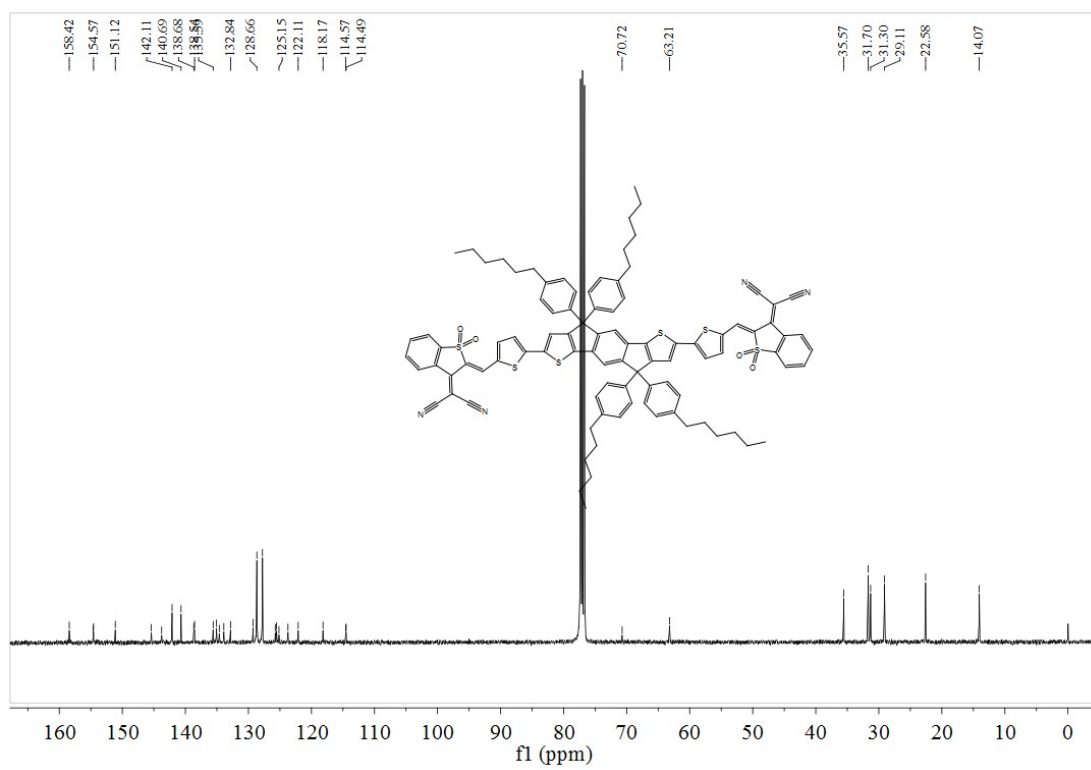


Fig. S15 ^{13}C NMR of IDIS-Th

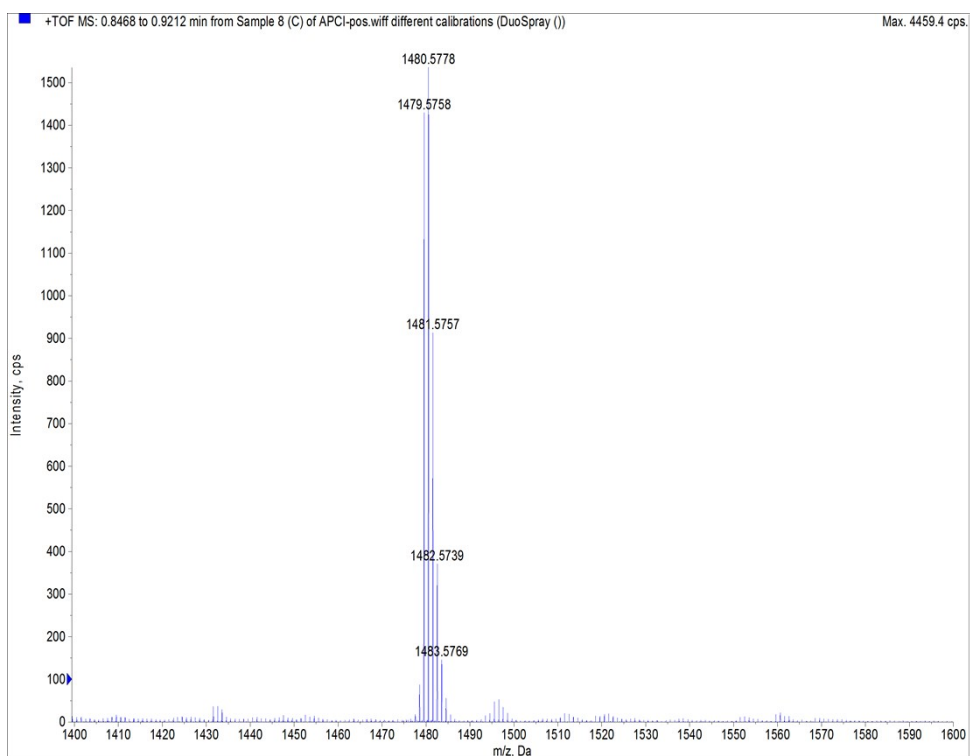


Fig. S16 Mass spectra of **IDIC-Th**

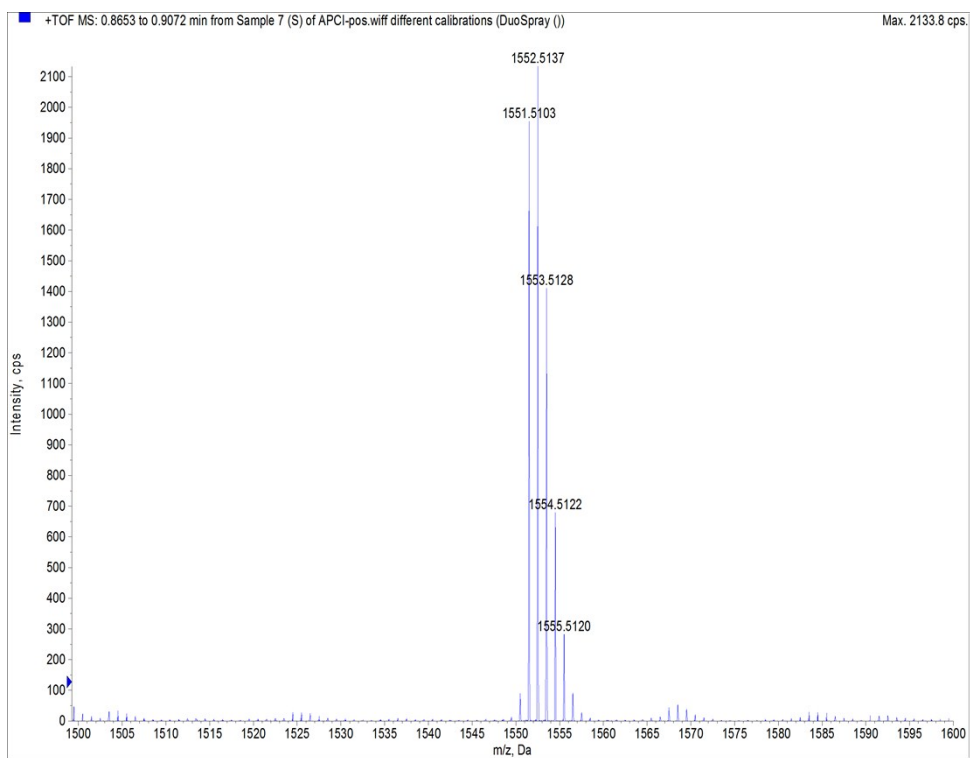


Fig. S17 Mass spectra of **IDIS-Th**