Electronic Supplementary Material (ESI) for RSC Advances.

The roles of fused-ring organic semiconductor treatment on SnO_2 in enhancing perovskite solar cell performance

Lu Ren,[a,b,d] Lusheng Liang, [a,d] Zhuangzhuang Zhang, [d] Zilong Zhang, [a,d] Qiu Xiong, [a,b,d] Nan Zhao,[c] Yaming Yu,[c] Rosario Scopelliti,[e] Peng Gao* [a,b,d]

a. L. Ren, L. Liang, Z. Zhang, Z. Zhang, Q. Xiong, Prof. Dr. P. Gao

CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

b. L. Ren, Q. Xiong, Prof. Dr. P. Gao

University of Chinese Academy of Science, Beijing 100049, China

c. Nan Zhao, Prof. Dr. Y. Yu

College of Materials Science and Engineering, Huaqiao University, 361021 Xiamen, China

d. L. Ren, L. Liang, Z. Zhang, Z. Zhang, Q. Xiong, Prof. Dr. P. Gao

Laboratory for Advanced Functional Materials, Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen 361021, China

e. Dr. R. Scopelliti

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

E-mail: peng.gao@fjirsm.ac.cn

Contents

1、Experimental section

1.1、Device fabrication and characterization

Materials: Tin (IV) oxide colloid precursor (SnO_2, 15% in H_2O colloidal dispersion) was purchased from Alfa Aesar. Lead bromide ($PbBr_2$, 99.999%) was purchased from Sigma-Aldrich, and lead iodide (PbI_2, 99.99%) was bought from TCI. Formamidinium iodide (FAI) and methylammonium bromide (MABr) were synthesized by reacting formamidine acetate (FAA, Aladdin) and hydroiodic acid (HI, 55.0-58.0 wt% in H_2O, Aladdin), methylamine (MMA, 30-33 wt% in ethanol, Aladdin) and hydrobromic acid (48 wt% in H_2O, Aladdin), respectively. The particular experimental operations were referred to as previously reported methods[1]. Spiro-OMeTAD was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.

Fabrication of the devices: Chemically etched fluorine-doped tin oxide (FTO) glass substrates (Nippon Sheet Glass) were cleaned by deionized water, acetone, and anhydrous ethanol for 15 min, respectively. Then, after the dry substrates were treated by ultraviolet ozone plasma for 10 minutes, a thin layer of SnO_2 nanoparticle film (SnO_2 colloidal precursor diluted with deionized water in a weight ratio of 1:3) was spin-coated on the cleaned FTO substrates at 3000 rpm for 30 s, and then annealed in ambient air at 150 °C for 30 min. All the following steps are performed in a glove box under a nitrogen atmosphere. The fused ring electron acceptors were dissolved in chlorobenzene (CB, Sigma-Aldrich) at a concentration of 1 mg mL^{-1}, and the solutions were respectively spin-coated on the SnO_2-based substrates at a speed of 3000 rpm for 30 s, and then the substrates were annealed on a hotplate at 60 °C for 5 min. For the perovskite precursor, PbI_2 was dissolved in the mixed solvents of N,N-dimethylformamide (DMF, 99.8%, Sigma-aldrich) and dimethyl sulfoxide (DMSO, 99.8%, Sigma-aldrich) (DMF/DMSO, 95:5, volume ratio). 600mg/mL lead iodide solution was spin-coated at 1500 rpm for 30 s, and then annealed at 60 °C for 1 min. After that, the FAMA precursor solution was prepared with the concentration ratio of FAI / MACl / MABr = 60:6:6 (unit: mg/mL) in anhydrous isopropanol. The solution was spin-coated at 1500 rpm for 30 s, and then annealed at 150 °C for 20 min[2–4]. After the substrates were cooled to room temperature, for the Spiro-OMeTAD solution, 72.3 mg of Spiro-OMeTAD was dissolved in 1 mL of chlorobenzene, 17.5 μL of bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich) solution (520 mg mL^{-1} in acetonitrile) and 28.8 μL of 4-tert-Butylpyridine (tBP, Sigma-Aldrich) were mixed into the solution. The 2,2 ',7,7 '-tetrakis (N,N-dip-methoxyphenylamine)- 9,9′-spirobifluorene (Spiro-OMeTAD) solution as the hole transporting material (HTM), which was spin-coated at 5000 rpm for 30 s. Finally, 60 nm of the gold counter electrode was thermally evaporated under high vacuum.

Device Characterization: The Apreo S LoVac (Czech Republic) instrument was used to collect the field-emission scanning electron microscope (SEM) images. The FLS980 instrument (United Kingdom) with an excitation wavelength of 460 nm from monochromatized Xe lamp was used to record the steady-state photoluminescence (PL) spectra, while the time-resolved PL spectra were carried out with a pulsed diode laser excitation source. X'Pert Pro X-ray diffractometer (Netherlands) was used to measure the XRD patterns with an angle range of 2θ=3° to 50°. UV-vis absorption spectra of SnO_2/perovskite and SnO_2/FROS/perovskite were recorded on an Agilent Cary 5000 spectrophotometer (United States) in the 450-800 nm wavelength range at room temperature. Current density-voltage (J-V) curves and steady-state power conversion efficiencies (PCE) of the PSCs were measured by using a Keithley 2401 source meter under 100 mW cm^{-2} simulated AM 1.5 G irradiation with a SS-F5-3A solar simulator (Taiwan) by reverse (1.2 to -0.1 V) scans or forward (-0.1 to 1.2 V) scans at a scan speed of 200 mV s^{-1} in the glovebox. The active area of devices was defined by a metal shadow mask of 0.1 cm^2. External quantum effciency (EQE) spectra were acquired on a QE-R quantum efficiency measuring instrument (Taiwan), and the measurement scope was 300-900 nm. Electrochemical impedance spectroscopy (EIS) were carried out in the dark under 10 mW cm^{-2} illumination at 0.5 V applied voltages using a Zennium Zahner electrochemical workstation (Germany) with an AC perturbation of 10 mV ranging from 100 mHz to 1 MHz, at room temperature with 40% humidity. EIS were analyzed by using Z-view software.

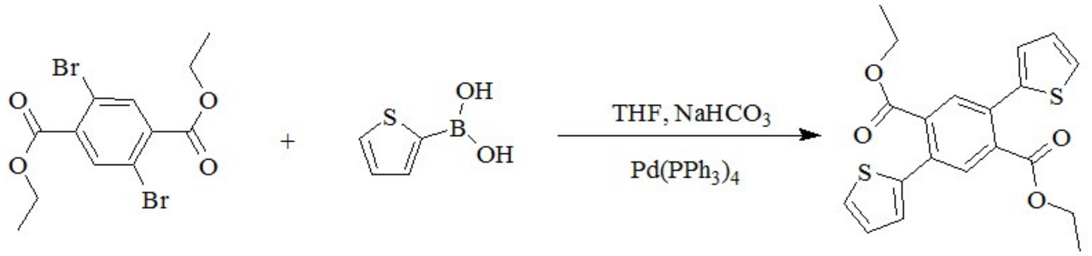
1.2、DFT calculation

Density functional theory (DFT) geometry optimization of all compounds were performed using the B3LYP functional and 6-31g(d) basis set in the Gaussian 09 program package. The optimized structures are stable.

1.3、Synthetic details

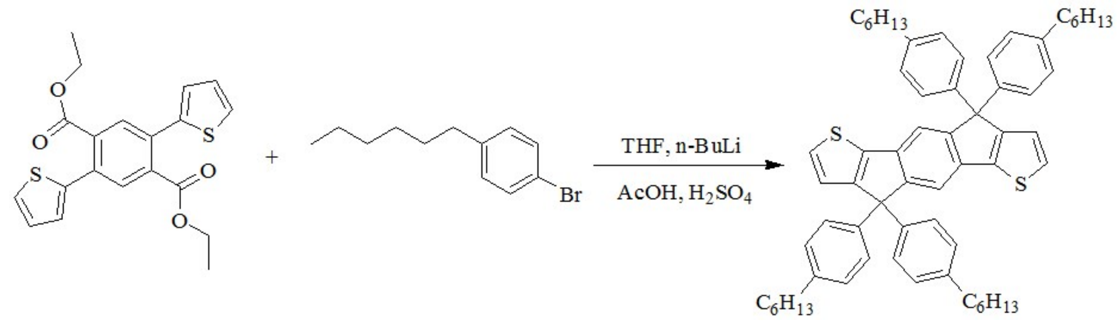
1.3.1、Synthesis of IDT-T

(1) 2,5-Dithien-2-yl-terephthalic Acid Diethyl Ester



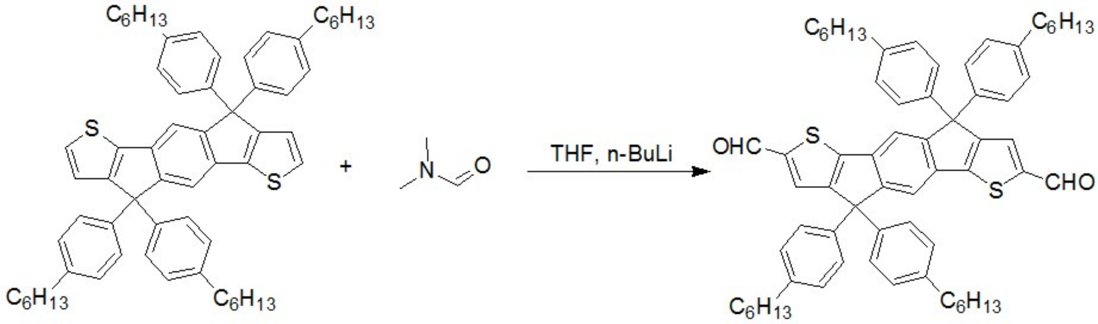
To a mixture of diethyl 2,5-dibromoterephthalate (3.78 g, 10.00 mmol), 2-thiophenylboric acid (2.95 g, 22.73 mmol) in 300 mL tetrahydrofuran (THF) was added sodium bicarbonate ($NaHCO_3$, 4.77 g , 56.82 mmol) and 25 mL H_2O. The solution was flushed with nitrogen for 10 minutes, and then tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, 0.12 g, 0.10 mmol) was added. After flushing with nitrogen for another 20 min, the reactant was heated to reflux for 48 h. After cooled to room temperature, the reaction mixture was poured into saturated ammonium chloride (NH_4Cl) solution. The product was extracted with ethyl acetate (3 * 50 mL). The extracts were combined and washed with saturated brine then dried over anhydrous magnesium sulfate (MgSO4). After filtration, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica and eluted with petroleum ether/ethyl acetate (from 20:0 to 20:1), to obtain 2,5- dithien-2-ylterephthalic acid diethyl ester as white crystal (3.40 g, 88%)[5]. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (s, 2H), 7.39 (d, J = 6.2 Hz, 2H), 7.19 – 7.01 (m, 4H), 4.22 (q, J = 7.1 Hz, 4H), 1.15 (t, J = 7.1 Hz, 6H).

(2) IDT



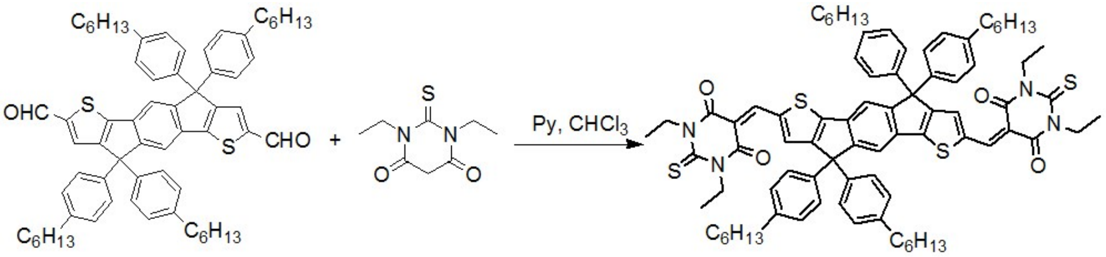
The n-BuLi (5.5 mL, 2.5 M in hexane solution, 13.75 mmol) was added dropwise to a solution of p-hexyl bromobenzene (3.0 g, 12.5 mmol) in THF (25 mL) at -78°C. The resulting solution was stirred for 1 hour, and then quenched with a solution of 2,5-Dithien-2-yl-terephthalic Acid Diethyl Ester (1.0 g, 2.59 mmol) in THF (15 mL). The reaction was kept at -78°C for 1 h, slowly warmed to room temperature and stirred overnight. Water was added to the solution, and the mixture was extracted with ethyl acetate. The combined organic layer was dried with $MgSO_4$, and then the solvent was removed by rotary evaporation. The obtained white solids were added to acetic acid (30 mL). After adding concentrated H_2SO_4 (1 mL), the reaction was refluxed for 5 h and then quenched with water (150 mL). The mixture was extracted with CH_2Cl_2, and the combined organic layer was washed 3 times with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (eluent: n-hexane/dichloromethane (DCM) = 10/1) to obtain a white solid (1.3 g, 67%)[6]. ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (s, 2H), 7.23 (d, J = 4.9 Hz, 2H), 7.15 (d, J = 8.2 Hz, 8H), 7.04 (d, J = 8.2 Hz, 8H), 6.99 (d, J = 4.9 Hz, 2H), 2.63 – 2.49 (m, 8H), 1.66 – 1.49 (m, 12H), 1.36 – 1.21 (m, 26H), 0.87 (t, J = 6.9 Hz, 12H).

(3) IDT-CHO



In a dry round-bottomed flask, the compound IDT (0.245 mg, 0.27 mmol) from the previous step was dissolved in THF (50 mL) and placed under a nitrogen atmosphere. The solution was cooled to -78°C and stirred while 2.4 M n-butyllithium in hexane (0.29 mL, 0.68 mmol) was added dropwise. The mixture was stirred at -78°C for 1 h. Then anhydrous N,N-dimethylformamide (DMF, 79mg, 1.08mmol) was added dropwise. The reactant was warmed to room temperature and stirred overnight. Then, brine was added and extracted with DCM, and dried over $MgSO_4$. The resulting crude compound was Purified by silica gel chromatography using a mixture of n-hexane/DCM as the eluent to give a yellow compound (169 mg, 65%)[7]. ^1H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 2H), 7.66 (s, 2H), 7.59 (s, 2H), 7.13 (d, J = 8.3 Hz, 8H), 7.09 (d, J = 8.3 Hz, 8H), 2.66 – 2.45 (t, 8H), 1.67 – 1.53 (m, 10H), 1.38 – 1.24 (m, 26H), 0.87 (t, J = 6.8 Hz, 12H).

(4) IDT-T

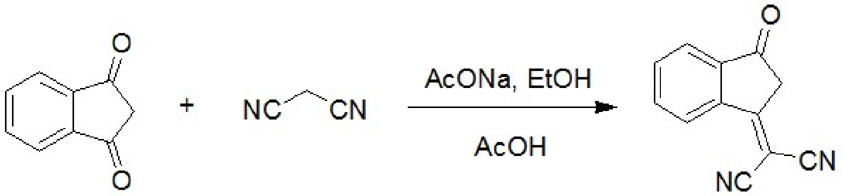


A mixture of IDT-CHO (600 mg, 0.622 mmol), 1,3-Diethyl-2-thiobarbituric acid

(748 mg, 3.74 mmol) and pyridine (1 mL) in chloroform ($CHCl_3$, 30 mL) was refluxed overnight. The solvent was removed by rotary evaporation and the residue was precipitated with methanol. The precipitate was filtered off and further purified by silica gel column with n-hexane/CH_2Cl_2 (1:1) as the eluent to obtain the product IDT-T as copper-green solid (678 mg, 82%)[8]. ^1H NMR (500 MHz, $CDCl_3$): δ 8.67 (s, 2H), 7.78 (s, 2H), 7.74 (s, 2H), 7.12 (d, J = 8.4 Hz, 8H), 7.09 (d, J = 8.4 Hz, 8H), 4.59 (m, J = 21.7, 7.0 Hz, 8H), 2.66 – 2.50 (m, 8H), 1.65 – 1.53 (m, 12H), 1.37 – 1.24 (m, 36H), 0.87 (t, J = 6.7 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.56 , 160.87 , 160.06 , 159.73 , 157.72 , 156.18 , 149.74 , 142.33 , 141.64 , 140.74 , 140.42 , 137.11 , 128.73 , 127.59 , 120.21 , 109.85 , 62.95 , 43.99 , 43.21 , 35.54 , 31.71 , 31.29 , 29.05 , 22.58 , 14.08 , 12.53 , 12.36 .

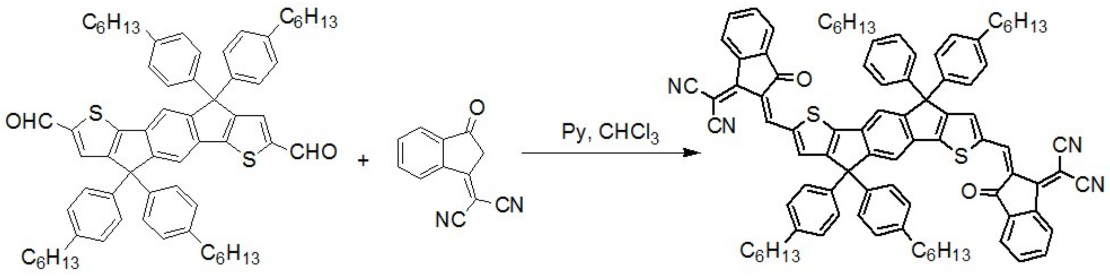
1.3.2、Synthesis of IDT-I

(1) 1,1-dicyromethylene-3-indanone



At room temperature, anhydrous sodium acetate (3.65 g, 44.48 mmol) was added to 1,3-indanedione (5.0 g, 34.21 mmol), malononitrile (4.54 g, 68.77 mmol) and anhydrous ethanol (35 mL) in a stirred mixture. A red color appeared immediately, and the suspended solid slowly dissolved. After 40 minutes, the mixture was diluted with water (60 mL) and acidified to pH 1-2 by adding hydrochloric acid dropwise. After stirring for 10 min, the grey solid was filtered off and washed thoroughly with water. The crude product was recrystallized twice with acetic acid to obtain a reddish solid 1,1-dicyromethylene-3-indanone (4.97 g, 85%)[9,10]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, J = 7.9 Hz, 1H), 8.04 – 7.97 (d, 1H), 7.89 (m, J = 23.7, 7.4, 1.0 Hz, 2H), 3.74 (s, 2H).

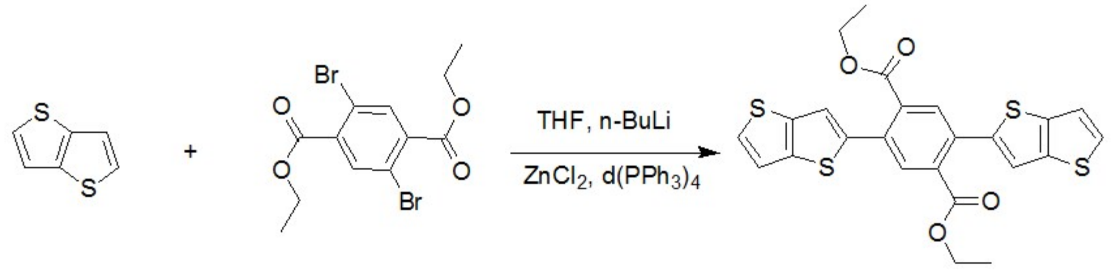
(2) IDT-I



Compounds 1,1-dicyromethylene-3-indanone (1.5 g, 7.66 mmol) and IDT-CHO (1.0 g, 1.04 mmol) were added to a 100 mL two-necked flask, successively. The solvent $CHCl_3$ (100 mL) was added and the two compounds were fully dissolved by stirring for a while. After flushing with a gentle stream of dry nitrogen for 15 min, pyridine (2 mL) was added as the catalyst and the solution was slowly turned into blue-green. The mixture was refluxed at 65°C for 20 h, and most of the solvent was evaporated. The crude product was washed by methanol to remove the excessive 1,1-dicyromethylene-3-indanone, and further purified by column chromatography with n-hexane: CH_2Cl_2 (4:1) as the eluent to obtain the substance IDT-I as the dark purple solid (1.1 g, 81%)[11]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.90 (s, 2H), 8.69 (d, J = 7.8 Hz, 2H), 7.94 – 7.89 (m, 2H), 7.78 – 7.71 (m, 8H), 7.13 (q, J = 8.4 Hz, 16H), 2.63 – 2.55 (m, 8H), 1.68 – 1.56 (m, 15H), 1.38 – 1.26 (m, 26H), 0.87 (t, J = 6.6 Hz, 12H). ^{13}C NMR (126 MHz, CDCl3): δ 188.38 , 160.30, 158.74 , 157.90 , 156.31 , 142.35 , 141.45 , 140.31 , 139.93 , 139.40 , 138.45 , 137.08 , 136.87 , 135.22 , 134.53 , 128.77 , 127.62 , 125.35 , 123.81 , 122.47 , 119.98 , 114.56 , 69.42 , 62.96 , 35.56 , 31.71 , 31.31 , 29.07 , 22.59 , 14.11 .

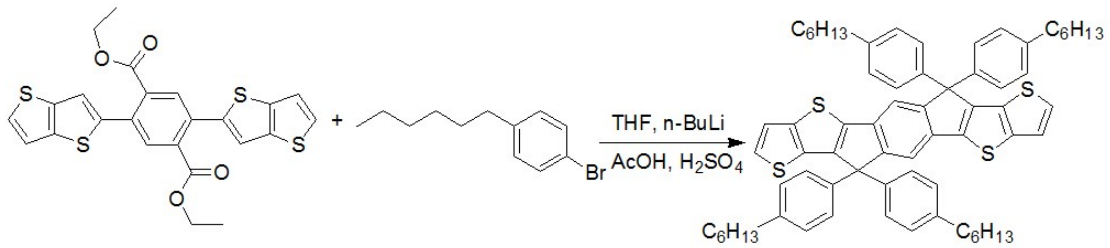
1.3.3、Synthesis of IDDT-T

(1) 2,5-Bis-thieno[3,2-b]thiophen-2-yl-terephthalic acid diethyl ester



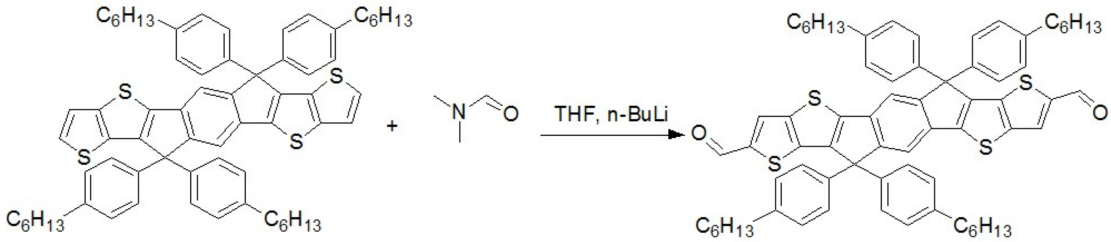
To a stirred solution of thieno[3,2-b]thiophene (1.0 g, 7.13 mmol) in anhydrous THF (25 mL) was added dropwise 2.5 M n-butyllithium in hexane (2.9 mL, 7.13 mmol) at -78°C under nitrogen atmosphere. After being stirred at -78°C for 30 min, the resulting solution was warmed to -35°C and stirred for another 15 min. Then anhydrous zinc chloride (0.97 g, 7.13 mmol) in anhydrous THF (25 mL) was added to the mixture. The mixture was stirred at 0°C for 1 h, and then the cooling bath was removed. Diethyl 2,5-dibromoterephthalate (1.08 g, 2.85 mmol) and $Pd(PPh_3)_4$ (0.16g, 0.14 mmol) were added directly. The reaction mixture was refluxed overnight. After completion, the reaction mixture was filtered, extracted with ethyl acetate and then dried over anhydrous $MgSO_4$. The product was purified by silica gel chromatography to obtain a pale yellow solid (1.18 g, 83%)[12]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.41 (d, J = 5.2 Hz, 2H), 7.30 (s, J = 0.5 Hz, 2H), 7.28 (d, J = 5.3, 0.5 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 1.13 (t, J = 7.1 Hz, 6H).

(2) IDDT



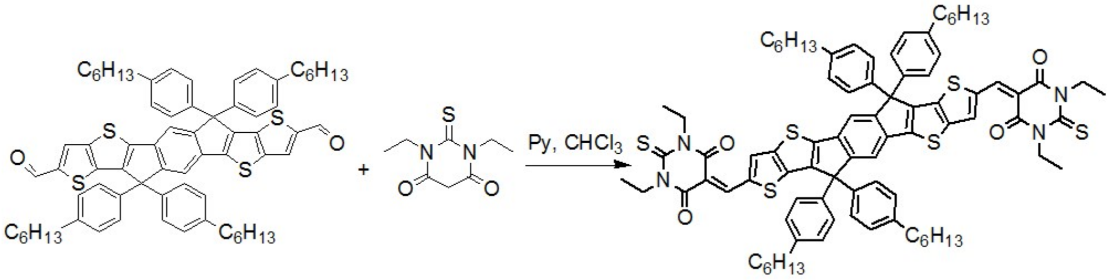
At -78°C, to a solution of 4-hexyl-1-bromobenzene (930 mg, 3.9 mmol) in THF (10 mL) was added dropwise n-BuLi (1.54 mL, 3.9 mmol, 2.5 M in hexane) and the mixture was kept at –78°C for 1 h. Then the previous step compound 2,5-Bis-thieno[3,2-b]thiophen-2-yl-terephthalic acid diethyl ester (400mg, 0.80mmol) was added in THF (10mL) slowly. After this addition, the mixture was stirred at room temperature overnight and then poured into water and extracted twice with ethyl acetate. The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the crude product was charged into three-neck flask. Acetic acid (20 mL) and concentrated H_2SO_4 (0.4 mL) were added, and the mixture was refluxed for 3 h. Then the mixture was poured into water and extracted with ethyl acetate. The obtained crude compound was purified by silica gel column using a mixture of n-hexane/ DCM as the eluent to give a light yellow solid (530 mg, 65%)[12]. ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (s, 2H), 7.27 (d, J = 5.2 Hz, 2H), 7.27 – 7.25 (d, 2H), 7.18 (d, J = 8.3 Hz, 8H), 7.07 (d, J = 8.3 Hz, 8H), 2.57 – 2.52 (t, 8H), 1.61 – 1.53 (m, 8H), 1.33 – 1.25 (m, 27H), 0.86 (t, J = 6.9 Hz, 12H).

(3) IDDT-CHO



In a dry three-necked round-bottomed flask, compound IDDT (1.0 g, 0.98 mmol) was dissolved in anhydrous THF (125 mL). The mixture was deoxygenated with nitrogen for 30 min. At -78°C, a solution of n -butyllithium (2.5 M in hexane, 0.94 mL, 2.36 mmol) was added dropwise. After stirring for 1 hour at -78°C, anhydrous DMF (0.2 mL) was added to this solution. The mixture was warmed to room temperature and stirred overnight. Brine (100 mL) was added and the mixture was extracted with chloroform (2 × 150 mL). The organic phase was dried over anhydrous MgSO$_4$ and filtered. After removing the solvent from the filtrate, the residue was purified by silica gel column chromatography using n-hexane/DCM (1:1) as eluent to obtain a yellow solid (0.98 g, 93%)[13]. ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.88 (s, 2H), 7.94 (s, 2H), 7.61 (s, 2H), 7.14 (d, J = 8.3 Hz, 8H), 7.10 (d, J = 8.4 Hz, 8H), 2.58 – 2.53 (t, 8H), 1.63 – 1.53 (m, 16H), 1.29 (m, J = 8.0, 2.6 Hz, 27H), 0.86 (t, J = 6.9 Hz, 12H).

(4) IDDT-T



The compounds IDDT-CHO (1.0 g, 0.93 mmol) and 1,3-Diethyl-2-thiobarbituric acid (1.37 g, 6.85 mmol) were added in chloroform (100 mL), then pyridine (0.95mL) was added in the solution after the compounds fully dissolved. The mixture was refluxed for 8 h at 80°C. After cooling to room temperature, it was diluted with chloroform and washed with brine, and dried over anhydrous MgSO$_4$. the residue was purified by silica gel column chromatography using n-hexane/DCM (1:1) as eluent to obtain a dark blue solid(1.2 g, 84%)[8]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 2H), 8.16 (s, 2H), 7.62 (s, 2H), 7.22 (d, J = 8.2 Hz, 8H), 7.13 (d, J = 8.3 Hz, 8H), 4.58 (m, J = 10.8, 7.0 Hz, 8H), 2.60 – 2.51 (m, 8H), 1.63 – 1.53 (m, 14H), 1.36 – 1.24 (m, 36H), 0.86 (t, J = 6.7 Hz, 12H). ^{13}C NMR (126 MHz, CDCl3): δ 178.61 , 161.02 , 159.68 , 155.61 , 152.73 , 149.62 , 147.89 , 147.57 , 143.37 , 142.49 , 139.91 , 139.01 , 138.00 , 136.84 , 128.84 , 127.92 , 118.53 , 110.24 , 63.36 , 44.00 , 43.14 , 35.61 , 31.70 , 31.22 , 29.17 , 22.58 , 14.06 , 12.52 ,12.40.

2、Results and Discussion

2.1、^{1}H-NMR, ^{13}C-NMR and MALDI-TOF MS spectra

2.1.1、^{1}H-NMR

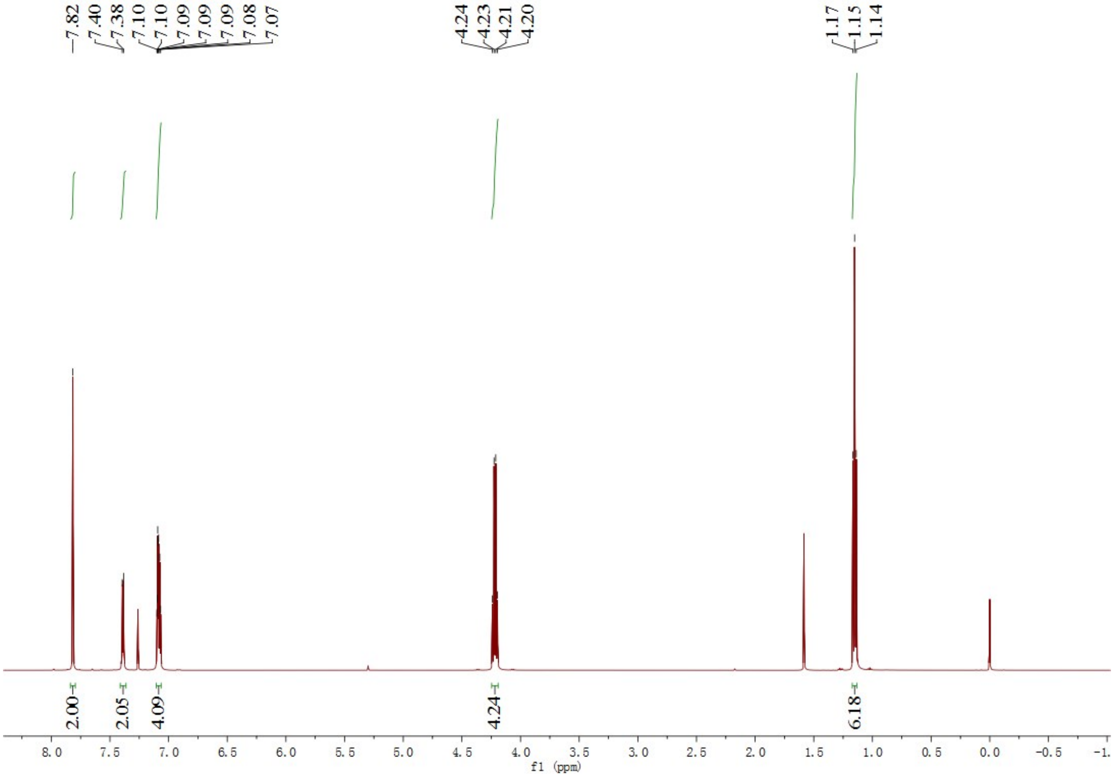


Figure S1. ^{1}H NMR spectrum of 2,5-Dithien-2-yl-terephthalic Acid Diethyl Ester.

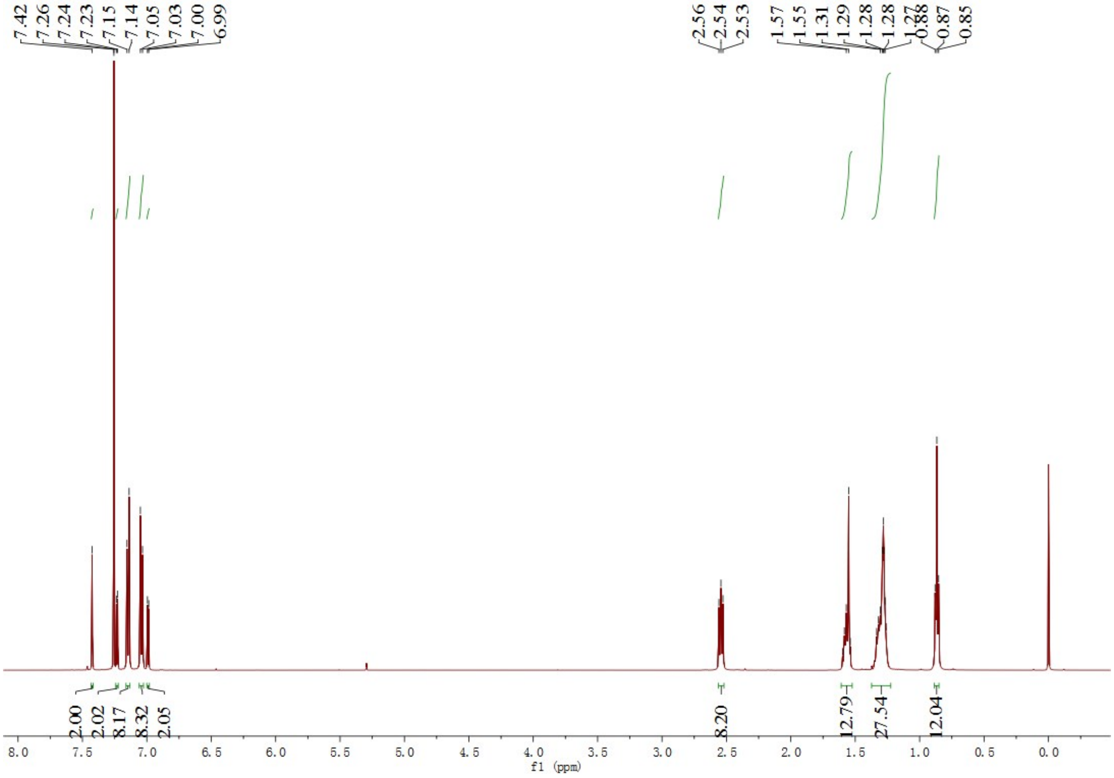


Figure S2. ^{1}H NMR spectrum of IDT.

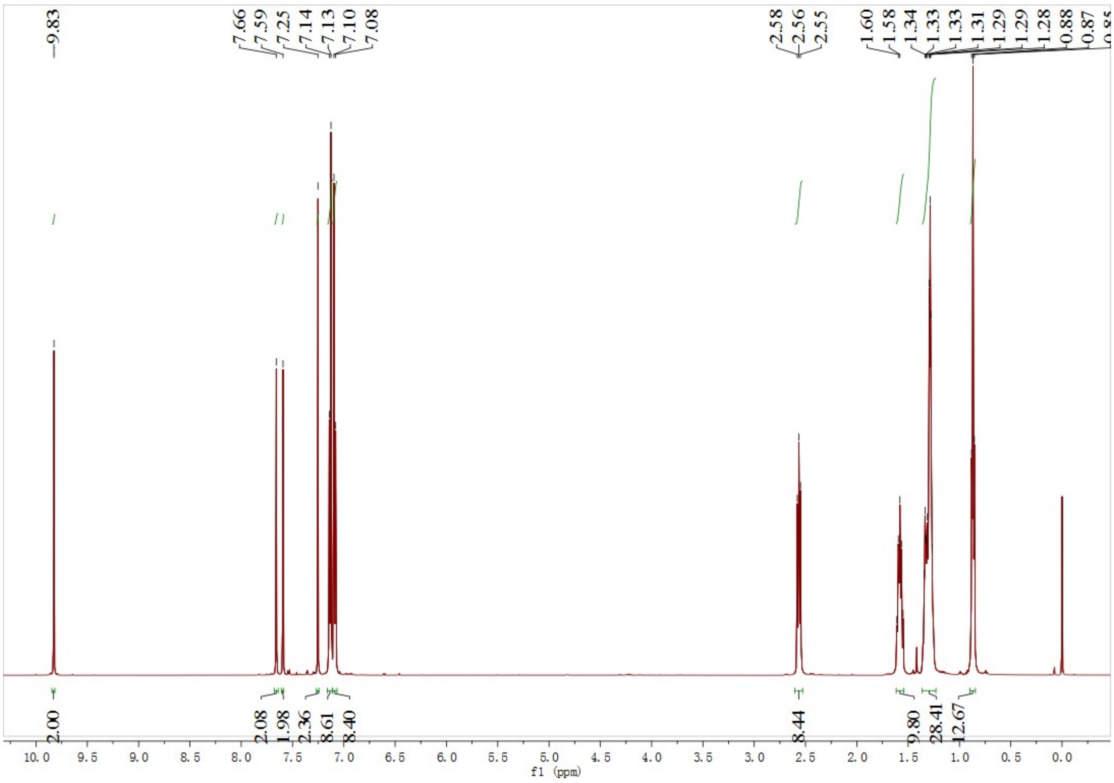


Figure S3. ^{1}H NMR spectrum of IDT-CHO.

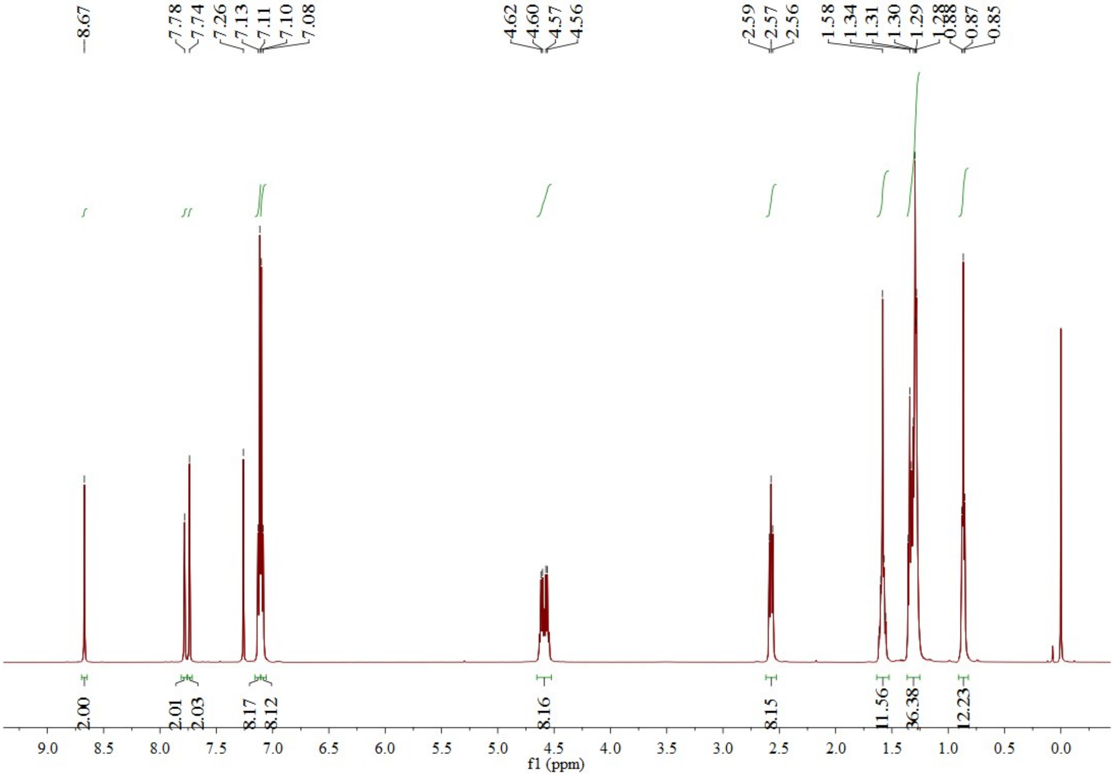


Figure S4. ^{1}H NMR spectrum of IDT-T.

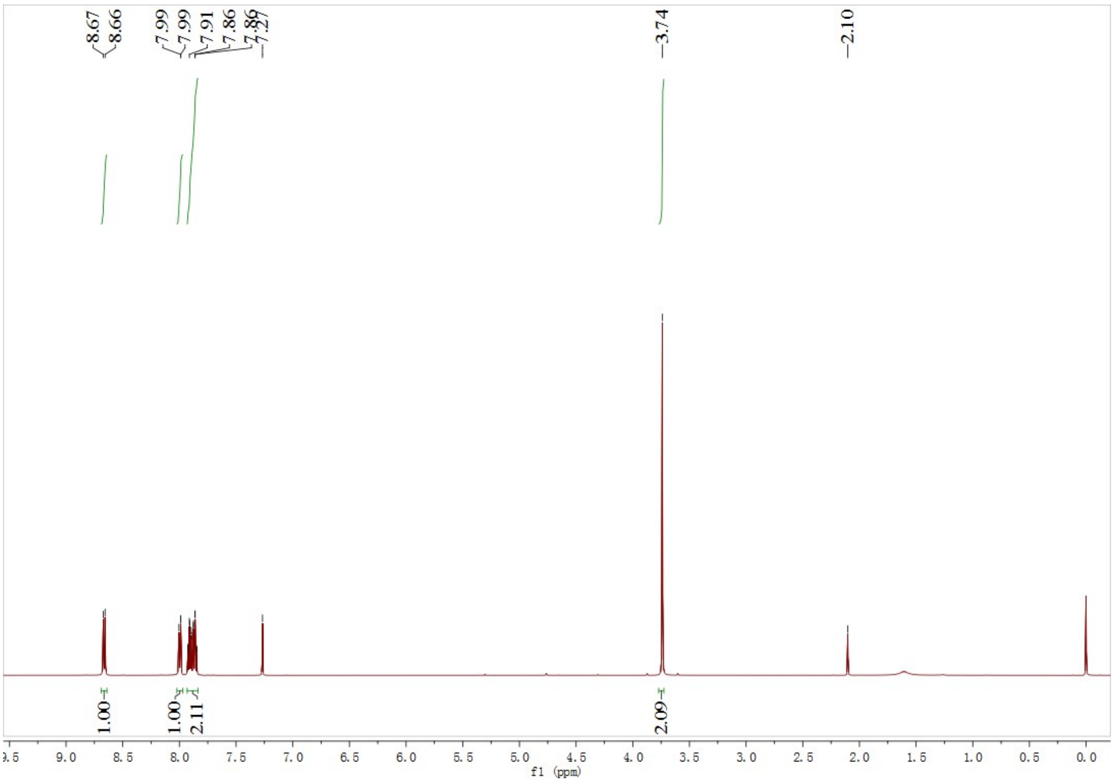


Figure S5. ^{1}H NMR spectrum of 1,1-dicyromethylene-3-indanone.

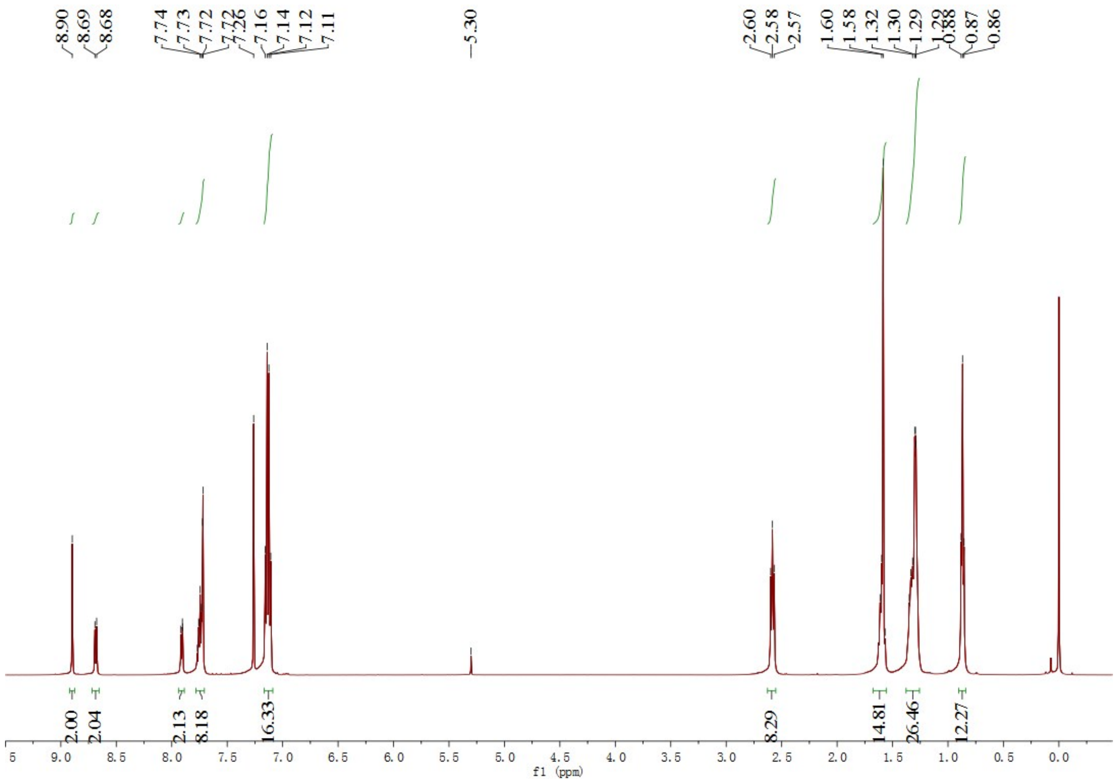


Figure S6. ^{1}H NMR spectrum of IDT-I.

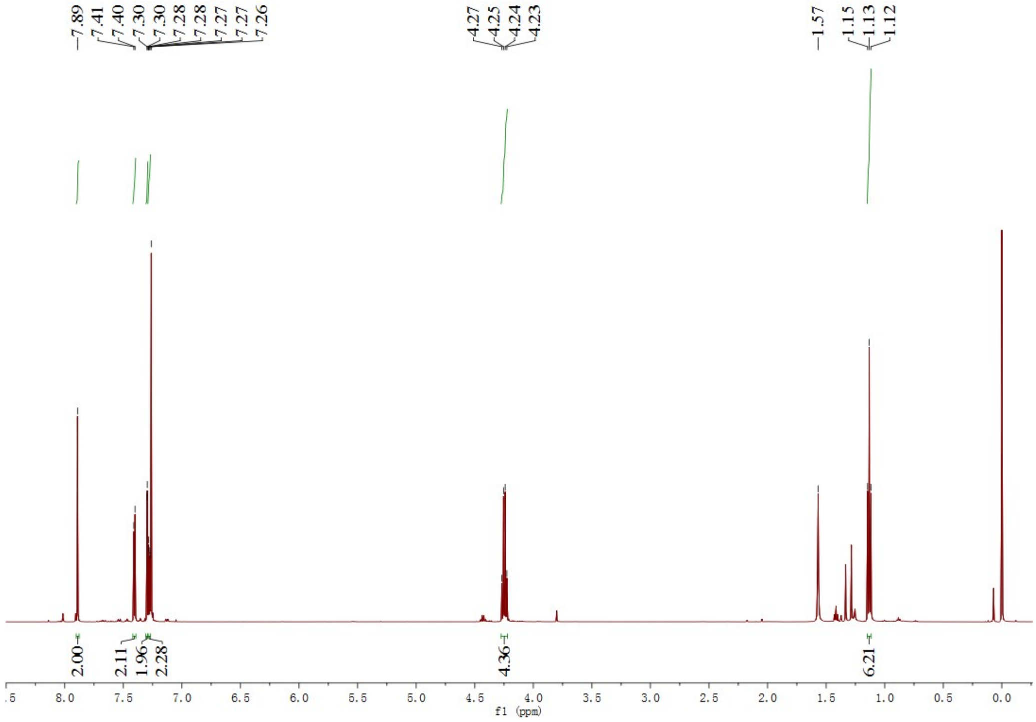


Figure S7. ^{1}H NMR spectrum of 2,5-Bis-thieno[3,2-b]thiophen-2-yl-terephthalic acid diethyl ester.

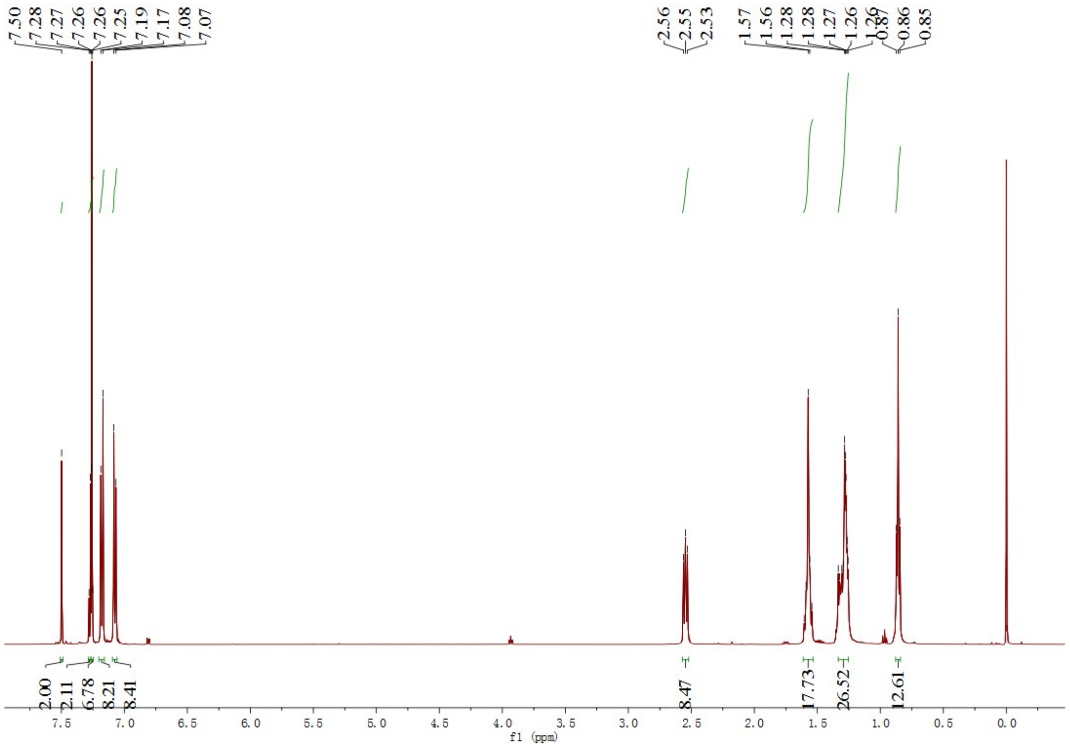


Figure S8. ^{1}H NMR spectrum of IDDT.

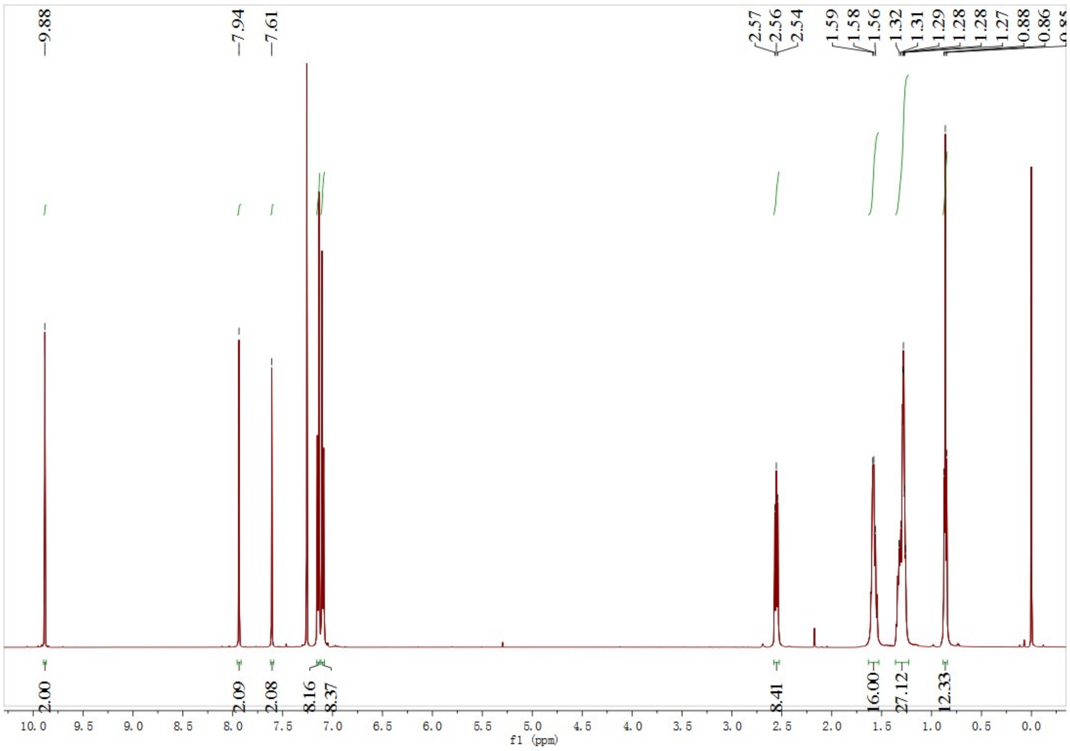
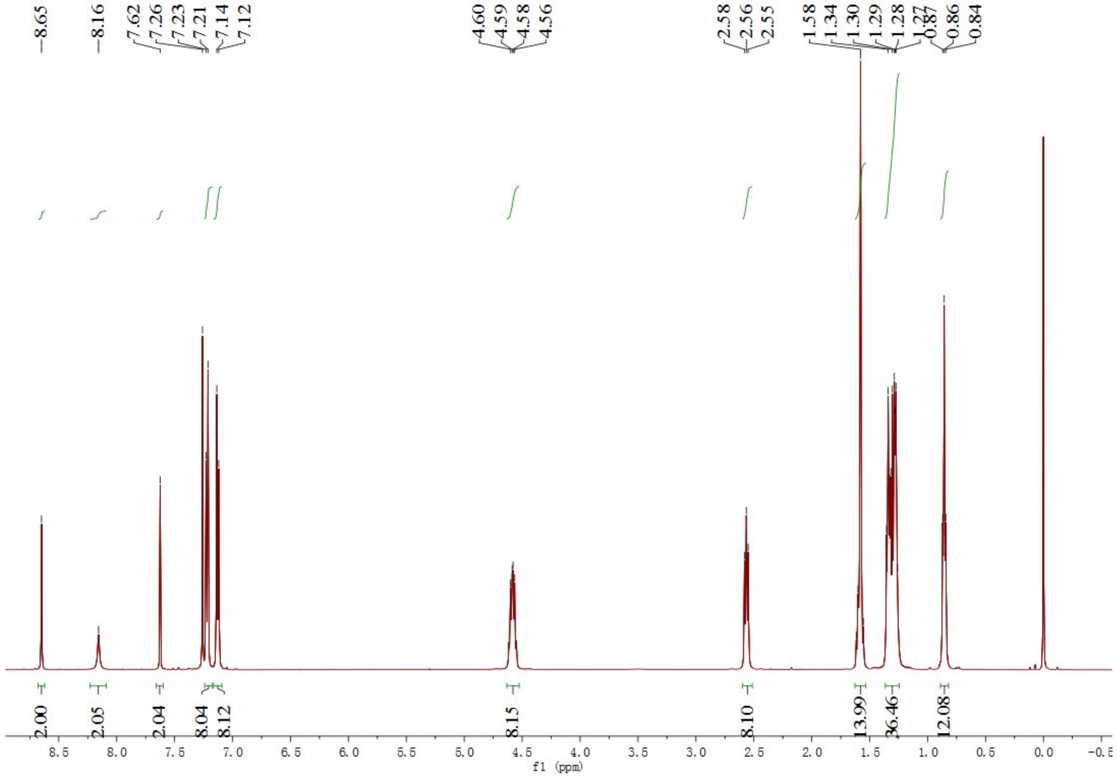


Figure S9. ^{1}H NMR spectrum of IDDT-CHO.



S10. ^{1}H NMR spectrum of IDDT-T.

2.1.2、^{13}C-NMR

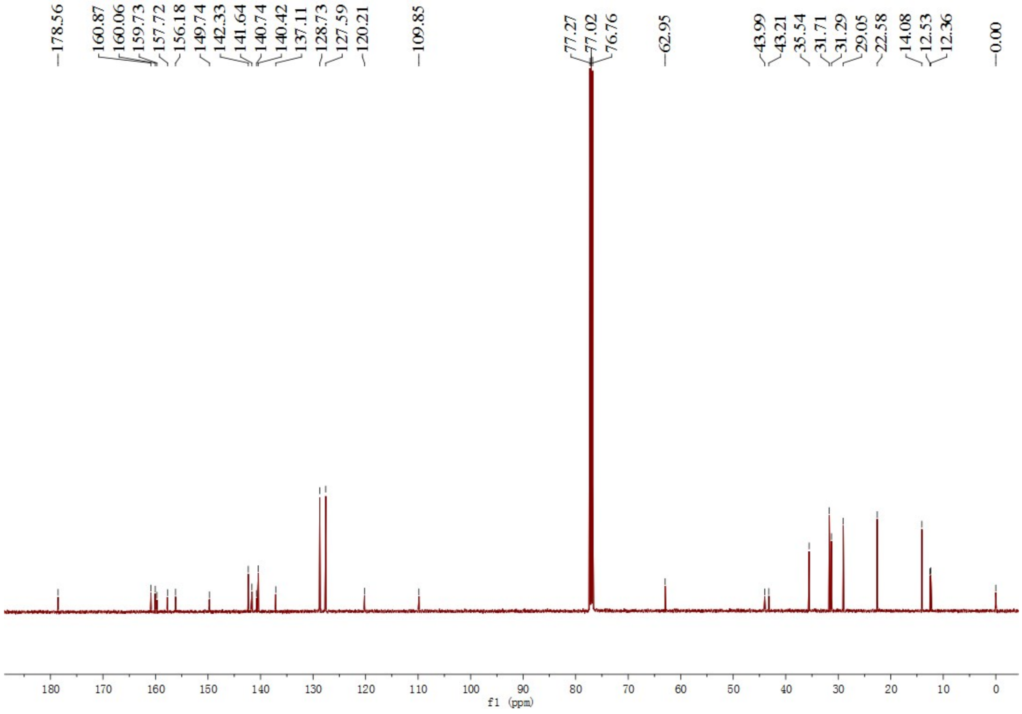


Figure S11. ^{13}C NMR spectrum of IDT-T.

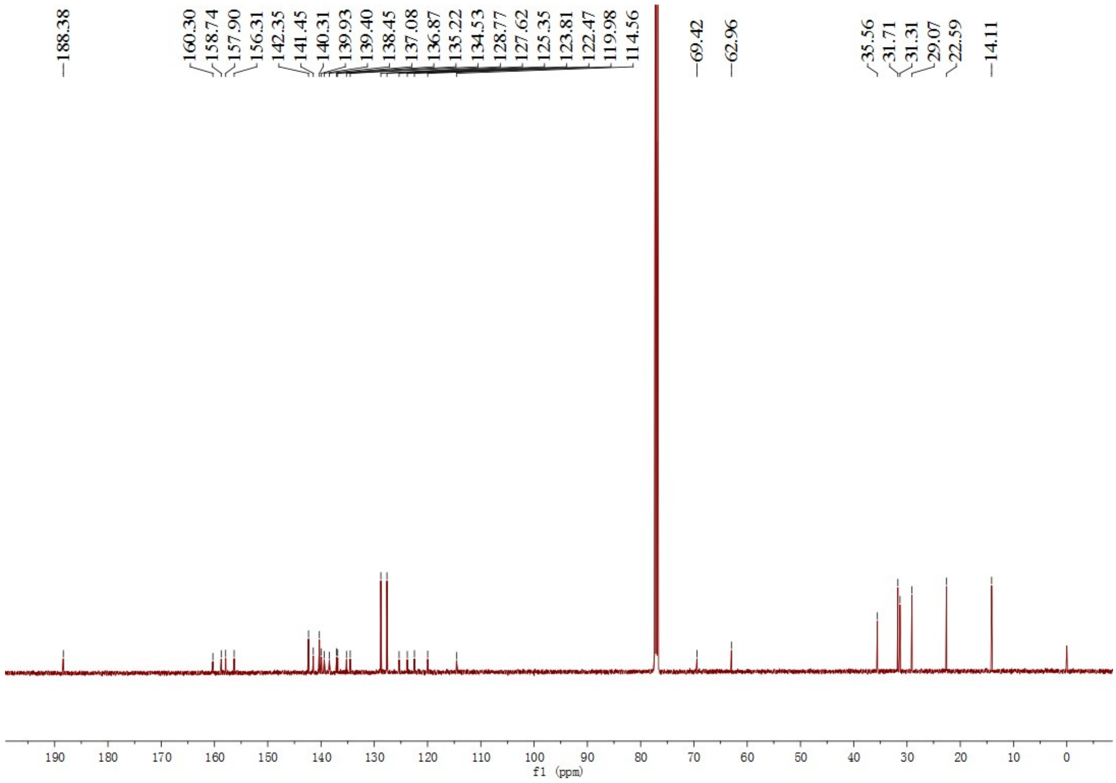


Figure S12. ^{13}C NMR spectrum of IDT-I.

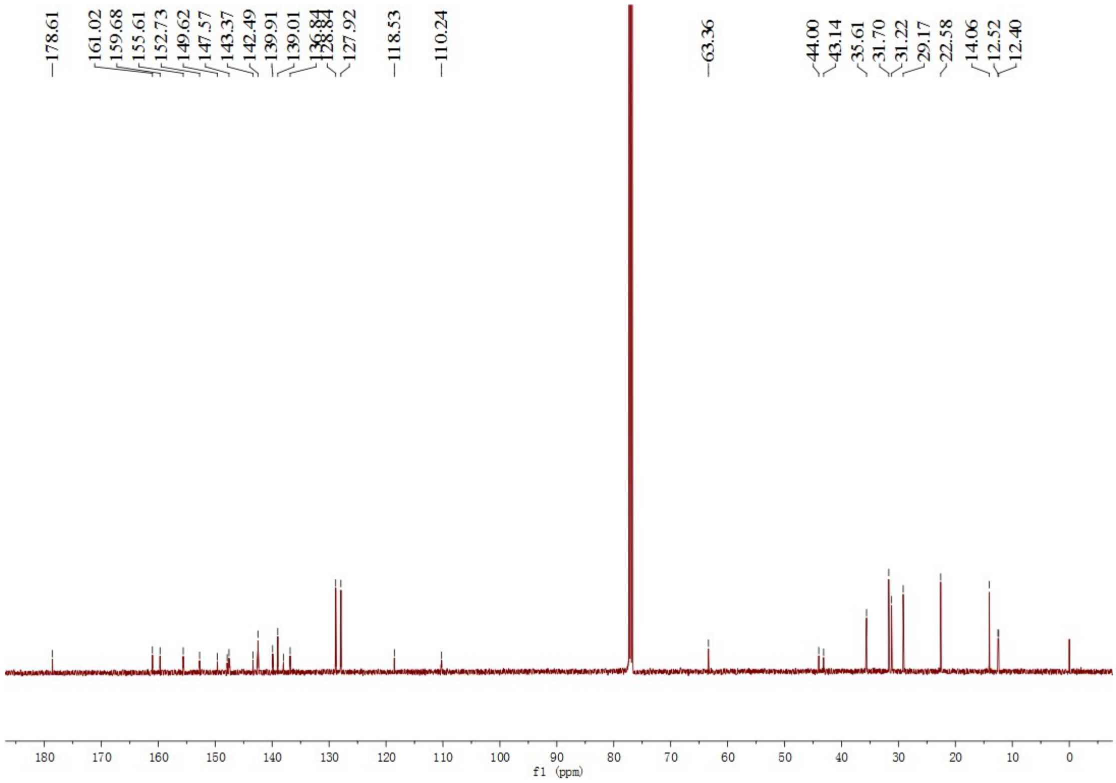


Figure S13. ^{13}C NMR spectrum of IDDT-T.

2.1.3、MALDI-TOF MS spectra

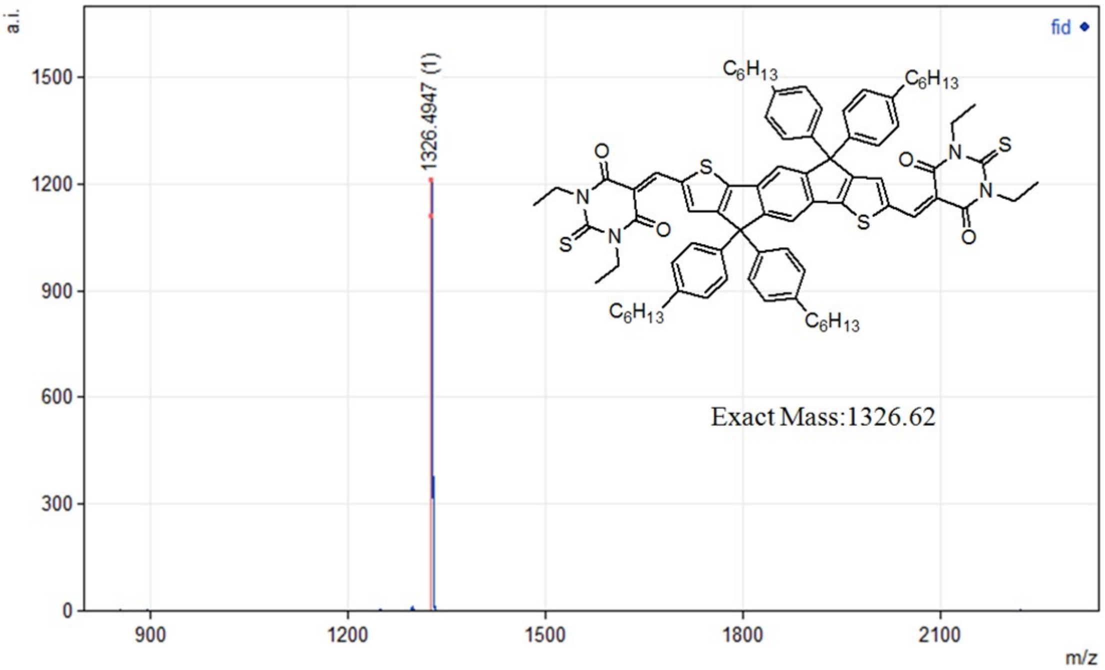


Figure S14. MADLI-TOF mass spectrometry of IDT-T.

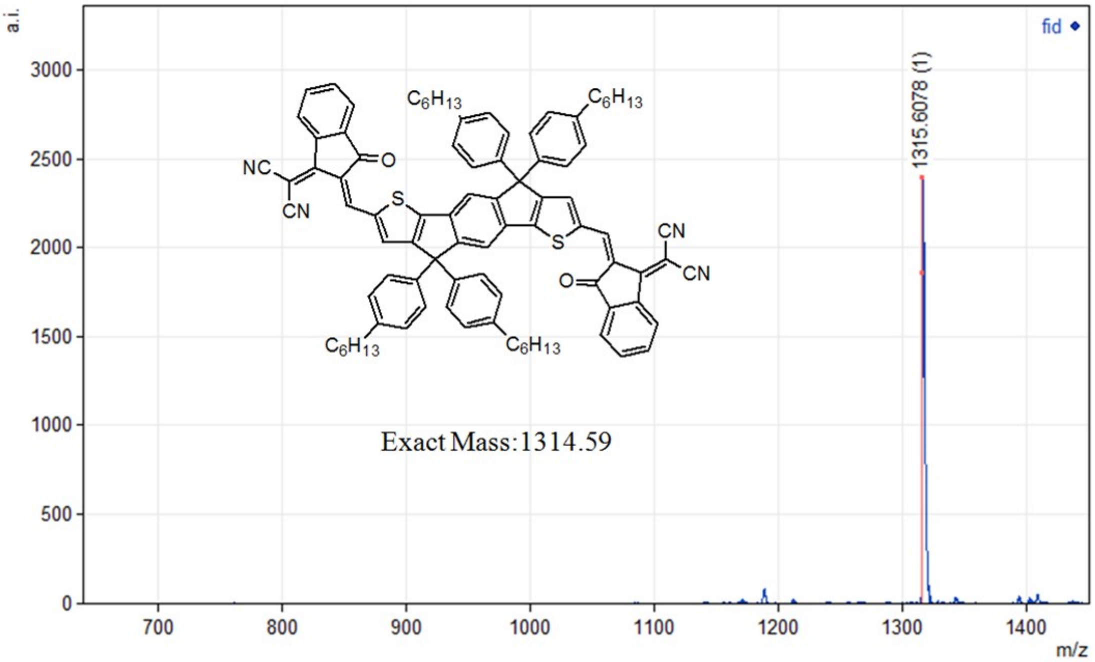


Figure S15. MADLI-TOF mass spectrometry of IDT-I.

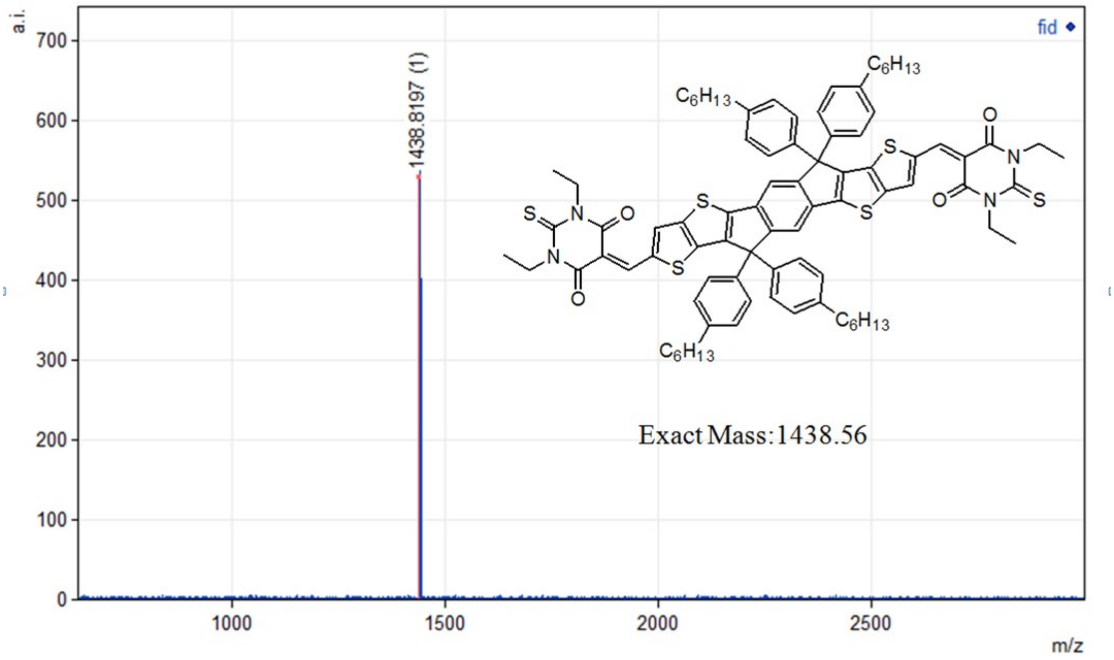


Figure S16. MADLI-TOF mass spectrometry of IDDT-T.

2.2、Elemental analysis

Table S1. Elemental analysis results of IDT-T, IDT-I, and IDDT-T

Compound	C (%)	H (%)	N (%)	S (%)	Measured Formula	Theoretic Formula
IDT-T	74.074	7.050	4.364	9.672	$C_{20.6}H_{23.5}N_{1.0}O_{1.0}S_{1.0}$	$C_{20.5}H_{23.5}NOS$
IDT-I	81.716	6.205	4.698	4.904	$C_{45.3}H_{41.4}N_{2.2}O_{1.0}S_{1.0}$	$C_{45}H_{41}N_2OS$
IDDT-T	72.271	6.558	3.966	13.209	$C_{21.5}H_{23.4}N_{1.0}O_{0.9}S_{1.5}$	$C_{21.5}H_{23.5}NOS_{1.5}$

2.3、Fourier transform infrared (FTIR) spectroscopy

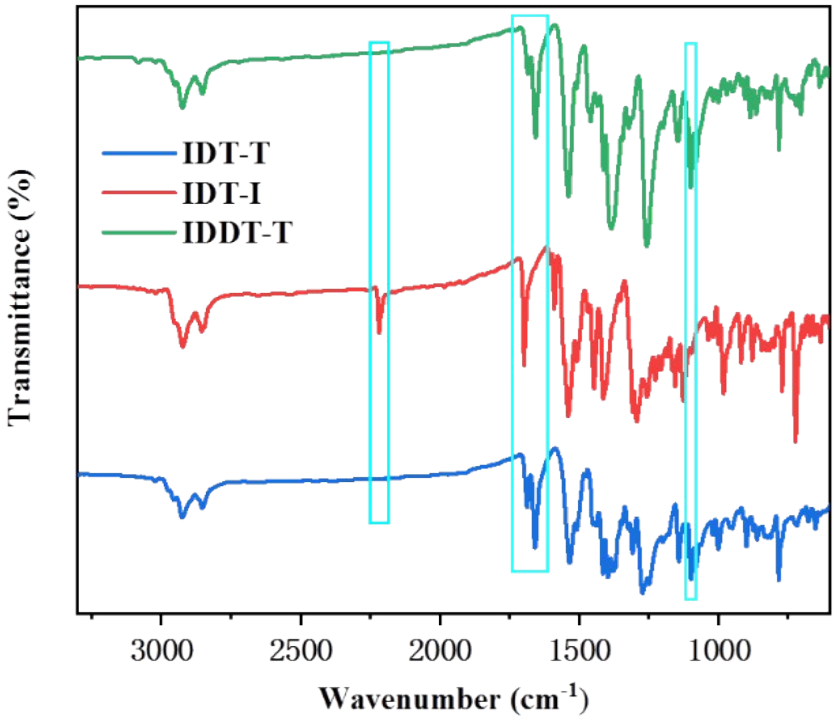


Figure S17. FTIR spectra of IDT-T, IDT-I and IDDT-T.

2.4、Packing structures and crystallographic parameters

2.4.1、Packing structures

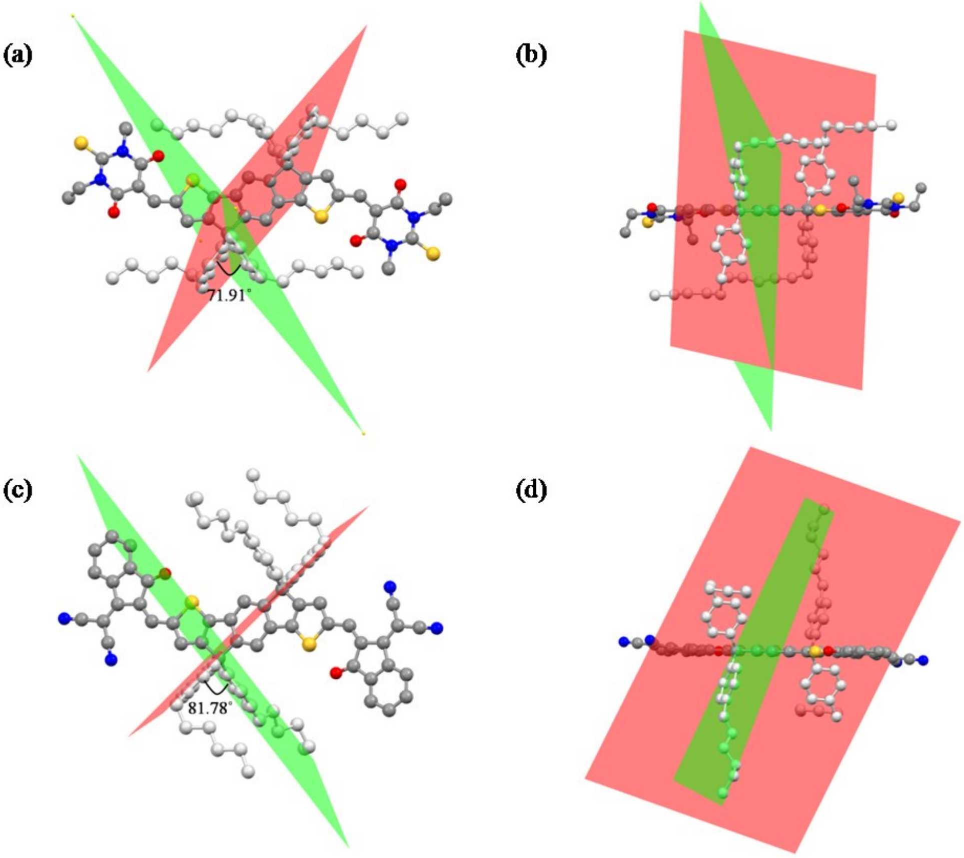


Figure S18. Single crystal X-ray structures of (a,b) IDT-T and (c,d) IDT-I from two perspectives. (a) and (c) are front view, and (b) and (d) are side view. Hydrogen atoms omitted for ease of viewing. Besides, the grey, blue, red, and yellow colored atoms represent C, N,O,and S atoms, respectively. The light grey atom is the C atom of the side chain (p-hexylbenzene). The red and green planes are the planes of adjacent side chains.

2.4.2、Crystallographic parameters

These data can be obtained free of charge from The Cambridge Crystallographic Data

Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystallographic parameters of IDT-T and IDT-I

	IDT-T	**IDT-I**
Empirical formula	$C_{82}H_{94}N_4O_4S_4$	$C_{90}H_{82}N_4O_2S_2$
Formula weight	1327.83	1315.69
Crystal color, habit	Dark purple, needle	Dark blue, plate
Crystal system	tricilinic	tricilinic
a, Å	12.4138 (9)	11.2204(6)
b, Å	13.9061(11)	13.2100(6)
c, Å	14.3368(11)	14.2241(7)
α, deg	65.911(3)	70.006(2)
β, deg	66.250(2)	82.420(3)
γ, deg	69.431(3)	76.769(2)
V, Å^3	2015.6(3)	1925.33(17)
ρ calc, g/cm^3	1.245	1.281
Spcace group	*P* -1	*P* -1
Z value	2	1
Temperature, K	200 (2)	200 (2)
no. of relections measured	6907	8571
no. of variables	455	630
Resiuals: R; wR2	0.0584, 0.1524	0.0631, 0.1457

2.5、Calculated E_{HOMO}/E_{LUMO} energy levels

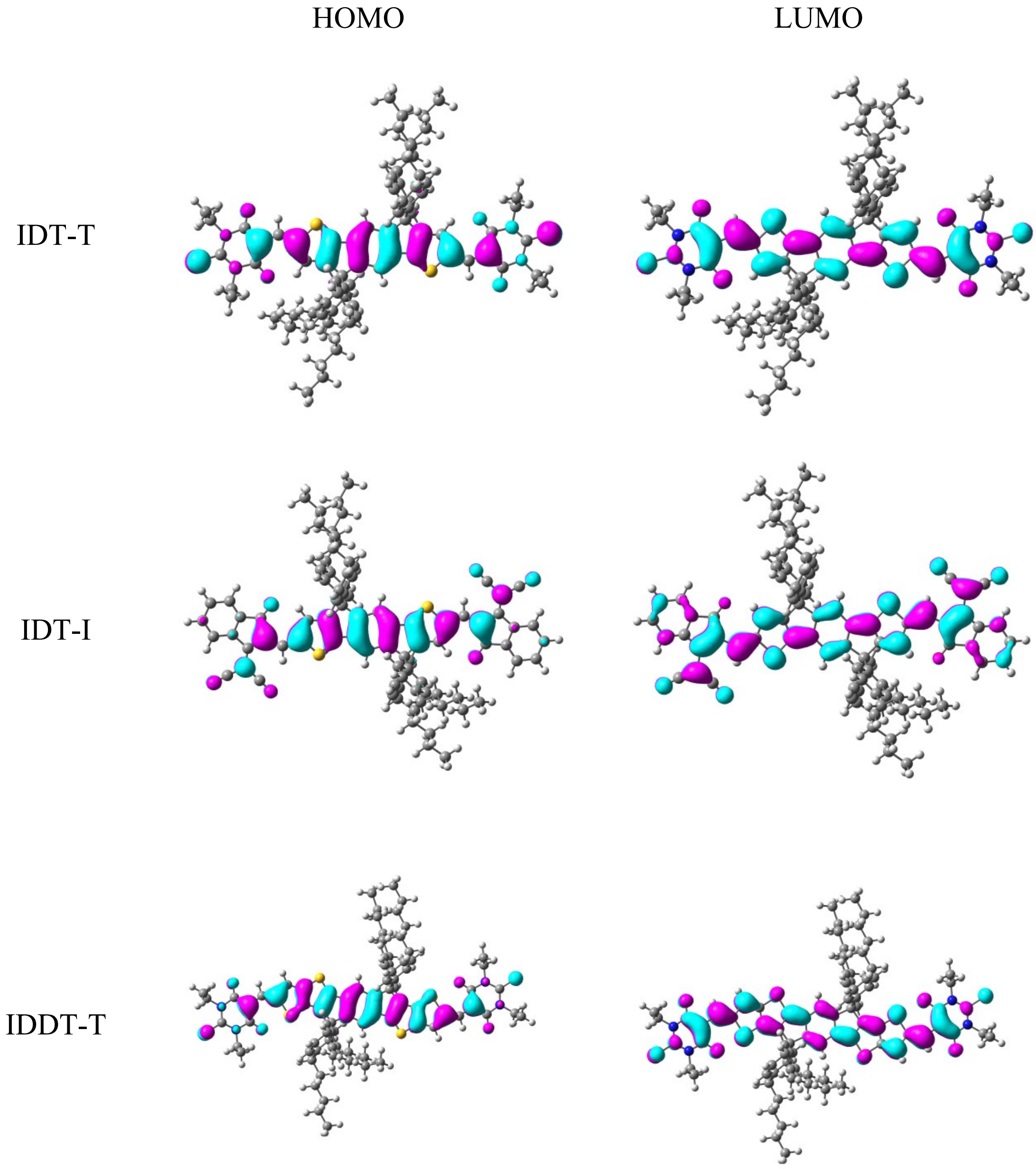


Figure S19. Highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbital (LUMO) of IDT-T, IDT-I and IDDT-T obtained from DFT calculations.

2.6、Thermal properties

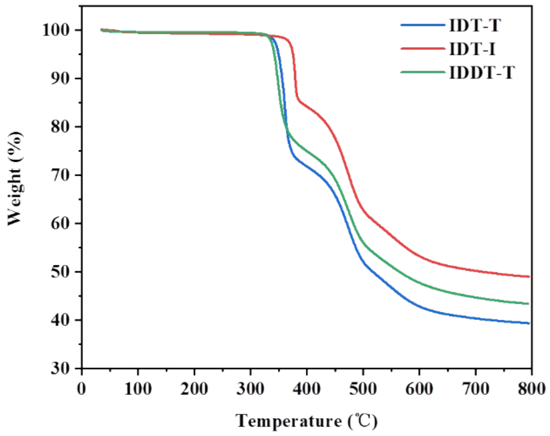


Figure S20. TGA curves of IDT-T, IDT-I and IDDT-T.

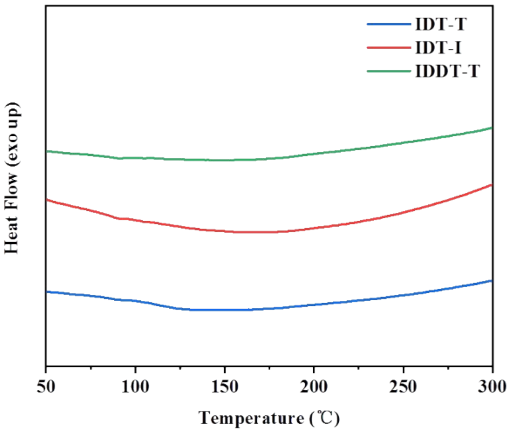


Figure S21. DSC curves of IDT-T, IDT-I and IDDT-T.

2.7、The UV-Vis absorption

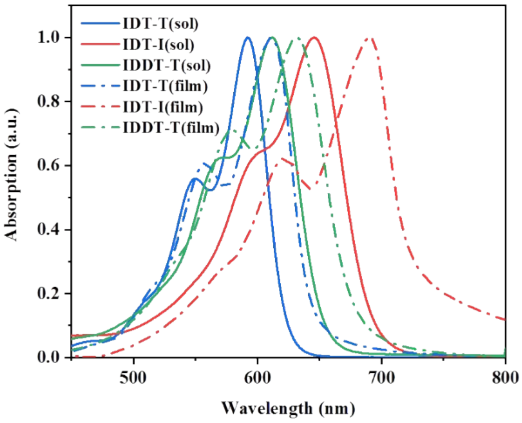


Figure S22. UV-Vis absorption spectrum of FROSs in DCM solution and in film.

2.8、The electron mobility

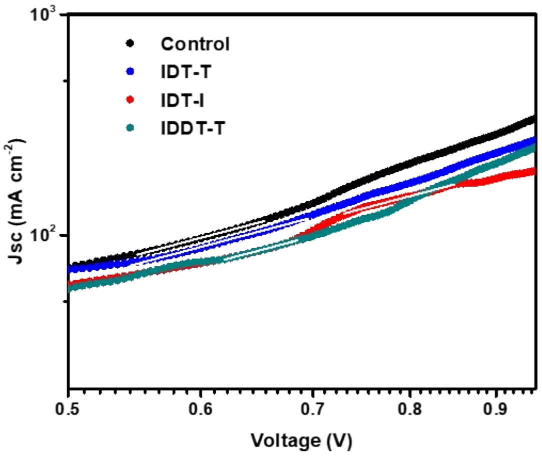


Figure S23. Dark current–voltage curves of electron-only devices: ITO/SnO_2/with or without FROS/Ag, which were fitted by the white lines (n = 2) are the SCLC regions.

Table S3. The electron mobility based on different ETLs

	electron mobility (cm^2/Vs)
Control	1.61×10^{-3}
SnO_2/IDT-T	1.46×10^{-3}
SnO_2/IDT-I	1.40×10^{-3}
SnO_2/IDDT-T	1.21×10^{-3}

2.9、Cross sectional SEM image

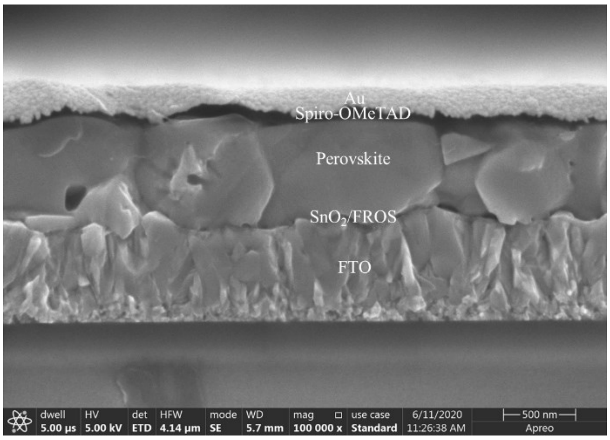


Figure S24. Cross sectional SEM images of the FROS-applied PSCs device.

2.10、Statistical data of TRPL

Table S4. Statistics of all parameters of TRPL

	τ_1(ns)	τ_2(ns)	A_1	A_2	τ_{avg}(ns)
Control	8.74	110.38	0.32	0.62	106.39
SnO_2/IDT-T	3.92	45.00	0.20	0.78	44.10
SnO_2/IDT-I	3.99	62.53	0.29	0.70	61.02
SnO_2/IDDT-T	3.30	53.67	0.17	0.81	53.03

2.11、Average photovoltaic parameters

Table S5. Average photovoltaic parameters for 20 devices with SnO_2 and SnO_2/FROS substrates.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	Efficiency (%)
SnO_2	1.020	23.72	73.62	18.27
SnO_2/IDT-T	1.053	24.02	76.94	18.92
SnO_2/IDT-I	1.068	23.80	77.99	19.22
SnO_2/IDDT-T	1.065	24.00	77.70	19.10

2.12、Photovoltaic parameters of different concentration of IDT-I treatment on SnO_2

Table S6. The photovoltaic parameters for the devices with different concentrations of IDT-I treatment on SnO_2

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	Efficiency (%)
0.5 mg/mL IDT-I	1.066	23.70	75.21	19.00
1 mg/mL IDT-I	1.077	23.64	76.79	19.55
1.5 mg/mL IDT-I	1.072	23.49	74.70	18.81

2.13、Electrical impedance spectroscopy

Table S7. EIS derived series resistance (R_s), transport resistance (R_{ct}) and recombination resistance (R_{rec}) for the different devices at -0.5V under dark conditions.

	R_s (Ω)	R_{ct} (kΩ)	R_{rec}(kΩ)
SnO_2	52.66	6.00	42.90
SnO_2/IDT-T	25.64	12.51	86.48
SnO_2/IDT-I	25.60	22.31	335.97
SnO_2/IDDT-T	22.75	15.64	174.68

2.14、The trap density statistics of perovskite films

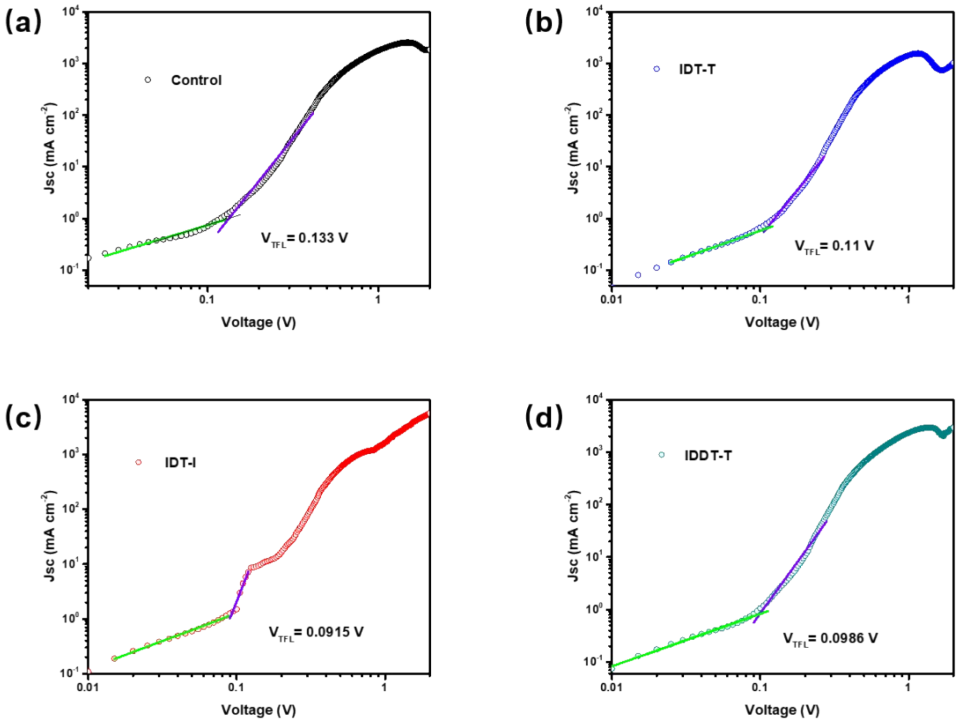


Figure S25. Dark current–voltage curves of electron-only devices: FTO/SnO_2/with or without FROS/perovskite/PCBM/Ag, which were fitted by the green lines (n = 1) are the ohmic regions, fitted by the purple lines (n > 3) are the trap-filled limit regions.

2.15、The stability

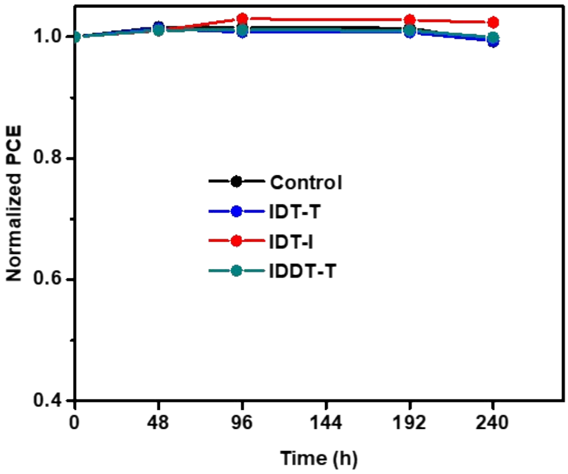


Figure S26. Long-term stability test under 10-20% RH in atmosphere.

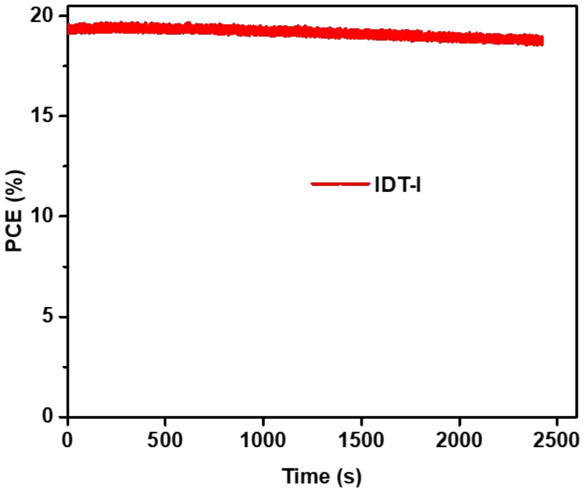


Figure S27. PCE at maximum power output of the device based on SnO_2/IDT-I substrates (at 0.87 V) for 2400 s duration.

3、Supplementary references

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