Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Fused Pentacyclic Electron Acceptors with *cis*-Arranged Alkyl Side Chains for Efficient Polymer Solar Cells

Ran Hou,† Miao Li,† Shiyu Feng, Yahui Liu, Liangliang Wu, Zhaozhao Bi, Xinjun Xu,* Wei Ma*, Zhishan Bo*

R. Hou, M. Li, Y. Liu, Z. Zhang, L. Wu, Dr. X. Xu, Prof. Z. Bo

Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China

*E-mail: xuxj@bnu.edu.cn; zsbo@bnu.edu.cn

Z. Z. Bi, Prof. W. Ma

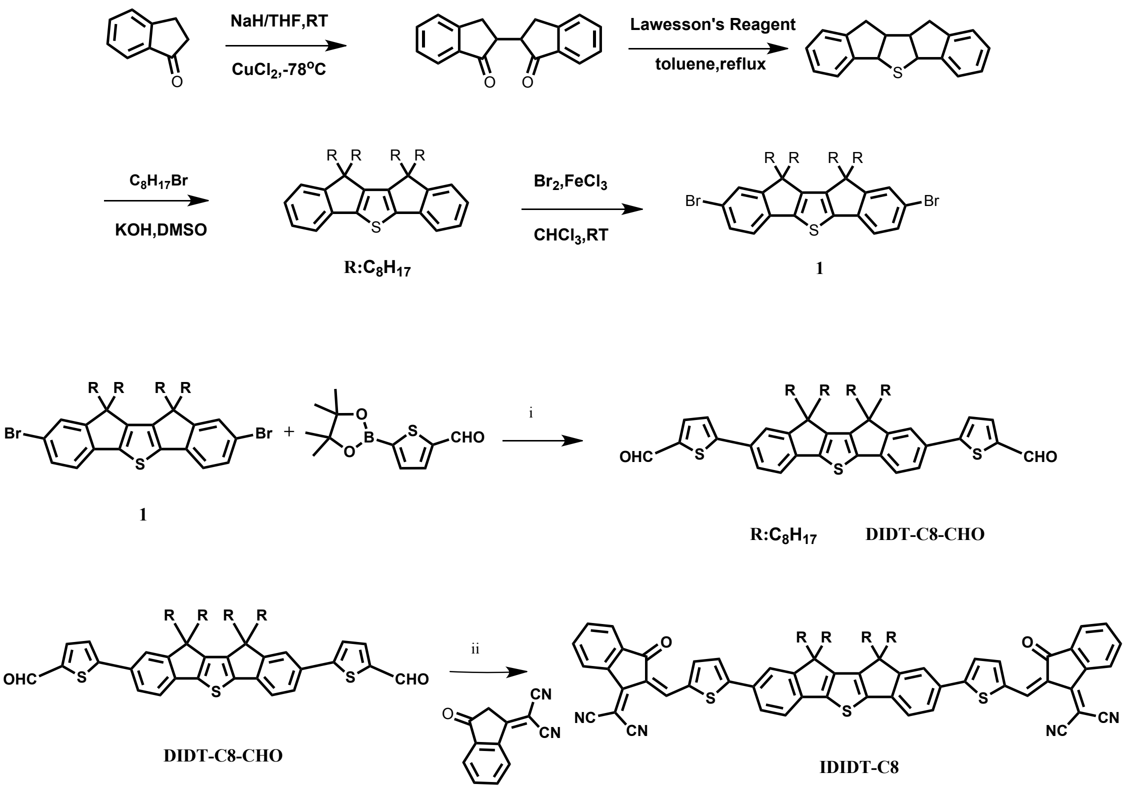
State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, China

*E-mail: msewma@mail.xjtu.edu.cn

1. Experimental section:

Materials and synthesis

The material **1** was synthesized as pervious literature[1]. The other materials were common commercial level and used without further purification



Scheme S1. Synthetic route to **IDIDT-C8**. Reagents and conditions: i) Pd$_2$(dba)$_3$, P-(*o*-tol)$_3$, NaHCO$_3$, THF/H$_2$O, reflux; ii) pyridine, CHCl$_3$, reflux.

Synthesis of **DIDT-C8-CHO**

A mixture of material 1 (600 mg, 0.69 mmol), 2-(5-bromo-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (280 mg, 1.73 mmol) and $NaHCO_3$ in THF/H_2O (30 mL/1 mL) was degassed before and after $Pd_2(dba)_3$ (19 mg, 0.02 mmol), P-(*o*-tol)$_3$ (12.6 mg, 0.04 mmol) were added. The mixture was refluxed for 3 days under N_2. After cooling to room temperature, the mixture was extracted with DCM and then the combined organic layer dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (silica gel; eluent: petroleum ether:DCM = 1:5) to afford **DIDT-C8-CHO** as an orange-yellow solid. Yield (350 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.90 (s, 2H), 7.76 (d, , 2H), 7.63 (d, 2H), 7.51 (s, 2H), 7.46 (d, 2H), 7.41 (d, 2H), 2.11 (t, 8H), 1.17 -0.60 (m, 60H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 182.65, 155.21, 153.54, 150.36, 145.210, 141.78, 140.35,137.55, 129.98, 125.68, 123.53, 119.68, 118.67, 55.74, 40.21, 31.82, 30.19, 29.60, 29.43, 24.18, 22.61, 14.03. Anal.calcd for $C_{60}H_{80}O_2S_3$(%): C, 77.53; H, 8.68; found: C, 76.88; H, 8.78.

Synthesis of **IDIDT-C8**

A mixture of **DIDT-C8-CHO** (350 mg, 0.38 mmol) and INCN (738 mg, 3.8 mmol) in chloroform was carefully degassed before and after pyridine was added. After refluxed under N_2 overnight, the reaction was cooled to room temperature. The solvent was evaporated out, and the residue was purified on silica gel column with DCM/petroleum ether (1:1, v/v) to give **IDIDT-C8** as a dark blue solid in a yield of 65% (314mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (s, 2H), 8.73 (d, 2H), 7.99 (d, 2H), 7.98 (d, 2H), 7.92-

7.68 (m, 6H), 7.61 (s, 2H) 7.60 (s, 2H), 7.45 (d, 2H), 2.20 (t, 8H), 1.19-0.71 (m, 60H). ^{13}C NMR (100 MHz, CDC_3) δ: 188.50, 161.57, 160.53, 153.79, 150.96, 146.59, 145.96, 141.16, 140.07, 138.02, 136.93, 135.23, 134.56, 130.17, 126.34, 125.38, 124.67, 123.76, 122.16, 119.76, 118.94, 114.62, 114.56, 55.60, 40.24, 31.84, 30.22, 29.70, 29.46, 24.29, 22.62, 14.04. Anal. Calcd for $C_{84}H_{88}N_4S_3$: C 78.71, H 6.92, N 4.37. Found: C 78.30, H 7.09, N 4.32.

Measurements and Instruments.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 ℃/min to record TGA and DSC curves. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. Transmission electron microscopy (TEM) images were obtained with a FEI Technai TF20 (Philip) transmission electron microscopy. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu Kα radiation. The electrochemical behavior of the molecules was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6

solution in CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/s. A Pt plate working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/ZnO (30 nm)/active layer (100 nm)/MoO_3 (85 Å)/Ag (100 nm). The sheet resistance of ITO is 15 Ω per square. The ITO-coated glass substrates were sequentially cleaned by deionized water, acetone, and isopropanol and then the substrates were dried at 150 °C for 15 minutes. The ZnO precursor was prepared as the pervious literature reported.[2] The ZnO precursor solution was spin-coated on top of a cleaned ITO substrate at 3500 rpm for 40 s and annealed subsequently at 200 °C for 20 min on a hotplate before being transferred into a glove box. A mixture of PBDB-T and **IDIDT-C8** was dissolved in DCB (with or without DIO) with the polymer concentration of 4 mg mL^{-1}. The solution was heated at 110 °C for at least two hours to ensure sufficient dissolution and then the solution was spin-coated at 1200 rmp for 40 s onto the ZnO layer to form the active layer. Finally, 8.5 nm-thick MoO_3 film and 100 nm thick Ag layer were deposited sequentially to complete the fabrication of devices. On one substrate, five cells with an effective area of 0.04 cm^2 for each were fabricated. Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) under an AM 1.5G AAA class solar simulator with an intensity of 100 mW cm^{-2} as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 °C. The EQE measurements of PSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS (30 nm)/active layer/Au and FTO/active layer/Al were fabricated. A solution of PBDB-T and **IDIDT-C8** in 1,2-dichlorobenzene (DCB) was spin-coated onto PEDOT:PSS or FTO to form active layer like PSC devices, and Au (Al) was thermally evaporated at a pressure of 10^{-4} Pa through a shadow mask. Dark *J–V* curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method. Hole and electron mobilities of devices were measured by space charge limited current (SCLC) model and calculated according to equations reported in previous literature. [3-5] Dark *J-V* curves were fitted by using the Mott-Gurney equation: $J = 9\varepsilon_o\varepsilon_r\mu V^2/8d^3$, where J is the space charge limited current, ε_o is the vacuum permittivity (ε_o=8.85×10^{-12} F/m), ε_r is the permittivity of the active layer ($\varepsilon_r = 3$), μ is mobility, and d is the thickness of the active layer.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization

GIWAXS measurements were performed at beamline 7.3.3[6] at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

2. Scheme and Figures

Table S1. Photovoltaic performance of devices fabricated with **PBDB-T** and **IDIDT-C8**.

D:A (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
1:0.8	0.87	12.63	54.28	5.99
1:1	0.88	13.55	53.26	6.43
1:1.5	0.92	14.65	56.56	7.65
1:2	0.93	12.33	50.05	5.95

Table S2. Photovoltaic performance of devices fabricated with **PBDB-T** and **IDIDT-C8** with DIO.

D:A	Additive	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE(%)
1:1.5	0.3%DIO	0.90	13.72	55.19	6.82
1:1.5	0.5%DIO	0.91	15.62	58.10	8.23
1:1.5	0.7%DIO	0.97	15.81	65.88	10.10
1:1.5	0.8%DIO	0.94	15.43	59.87	8.68
1:1.5	0.9%DIO	0.94	15.23	58.32	8.33
1:1.5	1.0%DIO	0.95	14.61	53.93	7.46

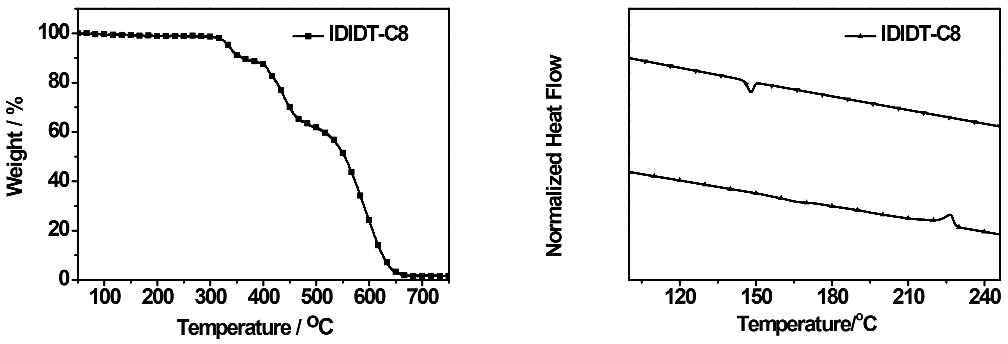


Figure S1. TGA (a) and DSC (b) curves of **IDIDT-C8**.

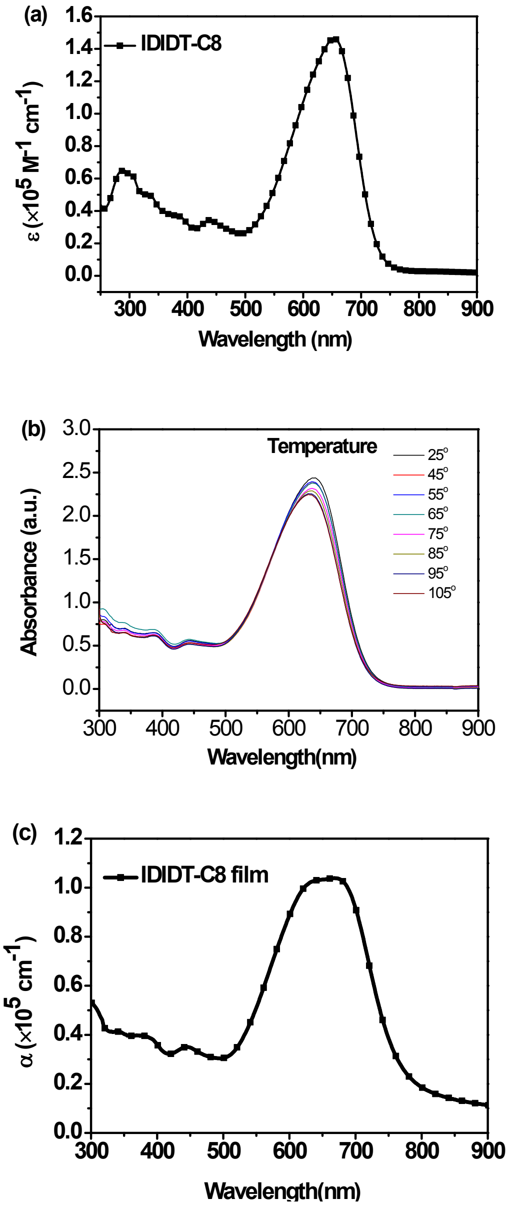


Figure S2. (a)UV-vis curves of **IDIDT-C8** in chloroform solution (10^{-5} M); (b) UV-

Vis absorption spectra of the **IDIDT-C8** solution (0.02 mg mL^{-1} in DCB) at indicated temperatures. (c) Absorption coefficient α of **IDIDT-C8** measured in the neat film spin-coated from chloroform.

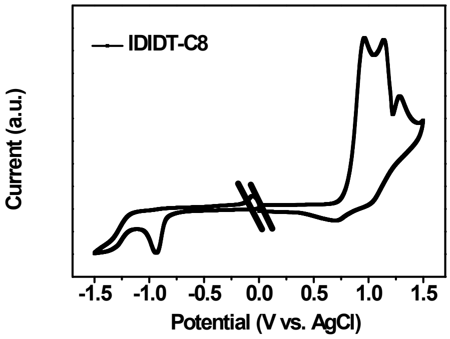


Figure S3. Cyclic voltammograms of **IDIDT-C8** as films on a Pt electrode measured in 0.1 M Bu_4NPF_6 acetonitrile solutions at a scan rate of 100 mV/s.

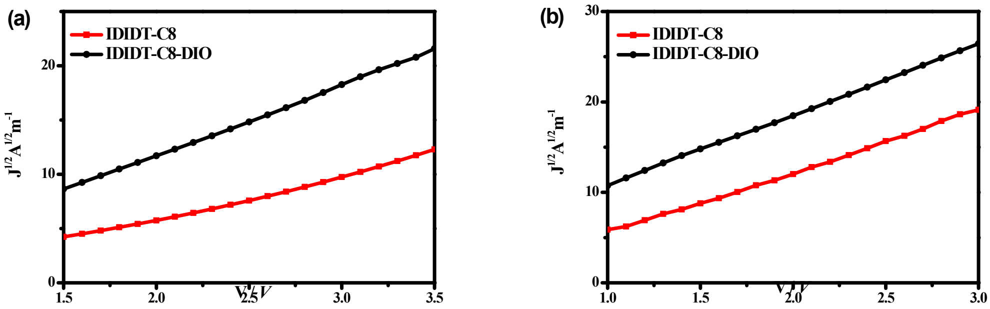


Figure S4. a) The hole mobility and b) electron mobility of blend film based on **IDIDT-C8**.

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