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Supporting information

Introducing Cyclic Alkyl Chain into Small-Molecule Acceptor for Efficient Polymer Solar Cells

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Table of contents

1. General Information……………………………………………………S2
2. Synthesis and Characterization…………………………………………S4
3. Supplementary Figures and Tables………………………………………S8
4. Reference…………………………………………………………………S15
5. ^{1}H and ^{13}C NMR Spectra………………………………………S16

1. General Information

Materials. All reactions were carried out under argon atmosphere. All solvents and reagents were commercially available and used directly without further purification unless otherwise specified. Tetrahydrofuran (THF) was dried from sodium/benzophenone and freshly distilled before to use.

Instruments and Characterizations. NMR spectra were recorded with a 500 MHz NMR spectrometer for ^{1}H NMR and 125 MHz for ^{13}C NMR with tetramethylsilane (TMS) as the internal reference. MALDI-TOF-MS spectra was measured on a BrukerBIFLEXIII mass spectrometer. UV-vis spectra was performed by using a HP 8453 spectrophotometer. Thermogravimetric analyses (TGA) were recorded on a NETZSCH TG 209 at a heating rate of 10 ^{o}C min^{-1} under a nitrogen flow rate of 20 mL min^{-1}. The electrochemical cyclic voltammetry (CV) experiments were carried out on a CHI600D electrochemical workstation equipped with a ITO working electrode, a platinum wire counter electrode, a Ag/AgNO$_3$ reference electrodes and a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammoniumhexafluorophosphate (n-Bu$_4$NPF$_6$) as the supporting electrolyte at a scan rate of 100 mV s^{-1} under a nitrogen atmosphere. The ferrocene/ferrocenium redox couple (Fc/Fc$^+$) was used to calibrate the potential of Ag/AgNO$_3$ reference electrode. The atomic force microscopy (AFM) measurements were carried out on a NanoMan VS microscope with a tapping mode. The geometry of the acceptors were optimized by using Density Functional Theory (DFT) method at a B3LYP/6-31G(d) level to optimize the ground state geometries. All the calculations of the acceptor molecules were performed using the Gaussian 09 package package40, all the straight-chain substituents were replaced with methyl groups and the side-chain substituents were replaced with isopropyl groups for calculations. The transient photocurrent of devices was measured by applying 580 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short circuited devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (SpectraPhysics Spitfire Ace). The photocurrent produced a transient voltage signal on a 50 Ω resistor, which was recorded by an oscilloscope (Tektronix TDS 3052C).

Grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments were carried out on a Xenocs Xeuss 2.0 system with an Excillum MetalJet-D2 X-ray source operated at 70.0 kV, 2.8570 mA, and a wavelength of 1.341 Å. The grazing-incidence angle was set at 0.20°. Scattering pattern was collected with a DECTRIS PILATUS3 R 1M area detector.

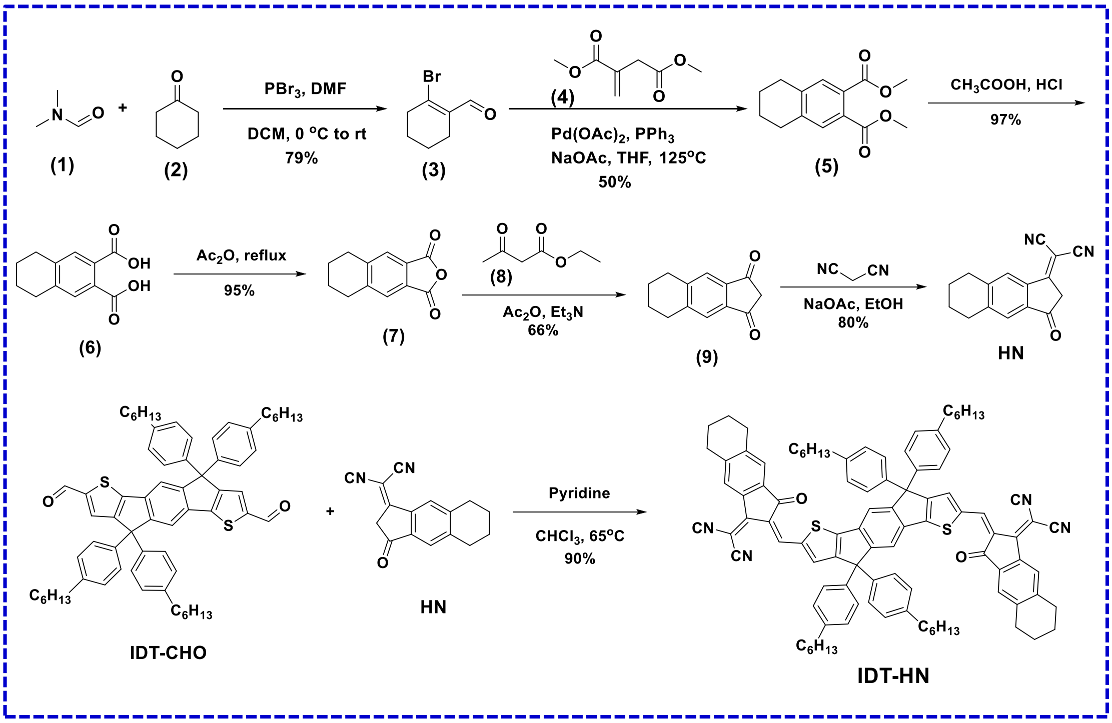
All of the solar cell devices with a conventional configuration of ITO/PEDOT:PSS/active layer/PFN-Br/Ag were fabricated. Firstly, the ITO glass substrates were pre-cleaned sequentially by using detergent, ethanol, acetone, and isopropyl alcohol under sonication, and dried in oven at 70 °C for 10 h before to use. Followed by treating with oxygen plasma for 4 min, the PEDOT:PSS was spin-coated onto the ITO glass at 3000 rpm for 30 s and then annealed at 150 ^{o}C for 10 min in air. Subsequently, the substrates were transferred into a N_2-protected glove box for spin-coating the active layer. The donor polymer **PBDB-T** (Mn = 31.1 kDa) and the small molecule acceptor, **IDT-IC** or **IDT-HN**, were dissolved in CB solution (with variant blend ratios, the total concentration of the donor polymer and the acceptor is 10 mg mL^{-1}). The mixed solution was spin-coated atop the PEDOT:PSS layer at 2000 rpm for 30 s to form the active layer with a film thicknesses approximately 100 nm. Then, the active layers were treated with thermal annealing at 120 ^{o}C for 5 min. Finally, the interface layer (5 nm) of PFN-Br in methanol (0.5mg mL^{-1}) was spin-coated on the blended films, and then the top electrode silver (100 nm) was deposited onto the interlayer PFN-Br by thermal evaporation though a shadow mask in a vacuum chamber with a base pressure of 1×10^{-6} mbar. The active layer area of the device was 0.04 cm^2. The current density-voltage (*J*-*V*) characteristics were recorded using a computer-controlled Keithley 2400 source meter under an AM 1.5G solar simulator (Taiwan, Enlitech SS-F5) at an light intensity of 100 mW cm^{-2}, which was tested by a calibrated silicon solar cell (certified by National Renewable Energy Laboratory) before to test. The PL spectra and EQE spectra were performed on a FLS920 spectro-fluorimeter (Edinburgh Instruments) and a commercial EQE measurement system (Taiwan, Enlitech, QE-R), respectively.

The hole-only and electron-only mobilities of PBDB-T: acceptors blend films and the acceptor neat films were determined from space-charge-limited current (SCLC) devices. The devices were fabricated with the structures of ITO/Al/ blend films (or neat film)/Ca/Al for electron-only mobility and ITO/PEDOT:PSS/blend films (neat film)/MoO_3/Ag for hole-only mobility, respectively. The mobilities were determined by fitting the dark J–V current to the model of a single carrier SCLC which were calculated on the basis of the following equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\,\mu_h\frac{V^2}{d^3}$$

where J is the current, ε_0 and ε_r are the permittivity of free space and relative permittivity of the material, respectively. and μ_h, V and d are the zero-filed mobility, the effective voltage, and the thickness of the organic layer, respectively. The effective voltage can be obtained from the equation $V = V_{appl}-V_{bi}-V_s$, where V_{app}, V_{bi} and V_s are the applied voltage, the offset voltage and the voltage drop, respectively. The electron- and hole-mobility can be calculated from the slope of the $J^{1/2}$–V curves.

2. Synthesis and Characterization



Scheme S1. The synthetic routes of the compound **IDT-HN**.

2-Bromocyclohex-1-ene-1-carbaldehyde (3)

The synthetic route of **(3)** was the same as reported procedure[1] In a dried three-neck 1 L flask. Dimethylformamide (60 mL, 0.78 mol) and 300 mL CH_2Cl_2 were added under an argon atmosphere at 0 °C. Phosphorous tribromide (70.8 mL, 0.71 mol) was slowly added over a period of 1 hour. After stirred for 60 min, a solution of carbonyl compound (25.6 g, 0.26 mol) in CH_2Cl_2 was added drop-wise and the mixture was stirred at room temperature for 20 hours. The resulting red mixture was poured into ice-water and solid sodium bicarbonate was slowly added to neutralize the acids until PH ~ 7. The mixture was extracted several times with CH_2Cl_2. The organic layer was dried with anhydrous Na_2SO_4 and concentrated in *vacuo.* The crude product was purified by flash chromatography (PE:EA = 30 : 1) to get the target product **(3)**. Yield: 79 %. ^1H NMR (500 MHz, $CDCl_3$, δ): 10.00 (s, 1H), 2.74-2.71 (m, 2H), 2.27-2.24 (m, 2H), 1.77-1.71 (m, 2H), 1.69-1.64 (m, 2H); ^{13}C NMR (125 MHz, CDCl3, δ): 192.68, 142.61, 134.24, 37.80, 23.97, 23.23, 20.06.

Diethyl 5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate (5)

The synthetic route of **(5)** was the same as reported procedure[2] In a 350 mL pressure vessel, 2-bromocyclohex-1-enecarbaldehyde **(3)** (18.9 g, 100 mmol), dimethyl itaconate **(4)** (15.8 g, 100 mmol), $Pd(OAc)_2$ (1.1 g, 5 mmol), PPh_3 (2.6 g, 10 mmol) and NaOAc (24.6 g, 300 mmol) in THF (300 mL) was added. The reaction mixture was flushed with argon and stirred at 125 ^oC for 20 hours. The reaction mixture was passed through a short silica gel column to remove inorganic salts and concentrated in *vacuo*. The crude mixture was purified by flash chromatography to give the target product diethyl 5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate **(5)** (12.4 g, 50%). ^1H NMR (500 MHz, $CDCl_3$, δ): 7.41 (s, 2H), 3.87 (s, 6H), 2.79-2.77 (m, 4H), 1.81-1.78 (m, 4H).

5,6,7,8-Tetrahydronaphthalene-2,3-dicarboxylic acid (6)

The synthetic route was the same as the reported procedure[3]. To a pressure vessel, compound **(5)** (10 g, 40.3 mmol), glacial acetic acid (AcOH) (25 mL) and concentrated hydrochloric acid (HCl) (15 mL) were added. The mixture was deoxygenated with argon and heated at 80 ^oC overnight. After cooling to room temperature, the reaction was poured into ice-water. The resulting precipitate was collected by filtration and washed with water. The crude mixture could be used directly in the next step without further purification. ^1HNMR (500MHz, CD_3OD, δ): 7.43 (s, 2H), 2.82 (t, *J* = 5 Hz, 4H), 1.84-1.82 (m, 4H). ^{13}C NMR (125 MHz, CD_3OD, δ): 170.16, 140.37, 129.71, 129.33, 28.79, 22.46.

5,6,7,8-Tetrahydronaphtho[2,3-c]furan-1,3-dione (7)

The synthetic route was the same as the reported procedure[3]. To a pressure vessel, compound **(6)** (5 g, 22.7 mmol) and acetic anhydride (50 mL) were added. The mixture was deoxygenated with nitrogen for 10 min. The mixture was refluxed for 12 h and then was allowed to cool down to room temperature. The reaction mixture was poured into ice-water, and the resulting precipitate was collected by filtration and washed with water. The crude mixture was used directly in the next step without purification. ^{1}HNMR (500MHz, $CDCl_3$, δ): 7.68 (s, 2H), 2.95 (t, *J* = 7.5 Hz, 4H), 1.89-1.86 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 163.25, 147.14, 128.52, 126.16, 30.36, 22.15.

5,6,7,8-Tetrahydro-1H-cyclopenta[b]naphthalene-1,3(2H)-dione (9)

The synthetic route was similar to the reported procedure.[4] In a dried two-neck 100 mL flask. Compound **(7)** (3 g, 14.9 mmol) was dissolved in acetic anhydride (25 mL), and triethylamine (15 mL) was added under an argon atmosphere. After stirred for a while, ethylacetoacetate (5.8 mL, 44.6 mmol) was quickly added via a syringe and the reaction was stirred at 100 ^{o}C for 12 h. The reaction mixture was cooled to room temperature and poured into HCl (2N) with ice, the resulting yellow precipitate was collected by filtration and washed with water, and then the yellow residual dissolved in HCl (5N) was heated under reflux for 1h. After being cooled to room temperature, the solid crude product was collected by filtration, washed with water and then purified by flash chromatography (CH_2Cl_2). Yield: 66 %. ^{1}HNMR (500MHz, $CDCl_3$, δ): 7.65 (s, 2H), 3.18 (s, 2H), 2.94 (t, *J* = 7.5 Hz, 4H), 1.87-1.84 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 197.66, 146.69, 141.10, 123.35, 45.38, 30.39, 22.37. MS (ESI): calcd for $C_{13}H_{12}O_2$ [M^+], 200.08; found: 200.1

2-(3-Oxo-2,3,5,6,7,8-hexahydro-1H-cyclopenta[b]naphthalen-1-ylidene)malononitrile (HN)

The synthetic route was similar to the reported procedure.[4] In a dried two-neck 100 mL flask. Compound **(9)** (2 g, 10 mmol), malononitrile (2 g, 30 mmol) were dissolved in ethanol (30 mL), and then anhydrous sodium acetate (1.1 g, 13 mmol) was slowly added while stirring.

After stirred 2h, the reaction mixture was poured into ice-water, and acidified to PH 1-2 by addition of hydrochloric acid. The resulting precipitate was collected by filtration and washed with water, the crud product was purified by flash chromatography (CH_2Cl_2) and recrystallized from ethanol to gave the target product **(HN)**. Yield: 80 %. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.30 (s, 1H), 7.66 (s, 1H), 3.66 (s, 2H), 2.77 (d, *J* =5.0 Hz, 4H), 1.89-1.86 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 194.84, 166.62, 147.54, 147.41, 139.90, 138.20, 126.25, 124.83, 112.49, 112.39, 43.53, 30.61, 30.43, 22.22, 22.18. MS (ESI): calcd for $C_{16}H_{12}N_2O$ [M$^+$], 248.09; found: 248.1. Anal. calcd for $C_{16}H_{12}N_2O$: C 77.40, H 4.87, N 11.28; found: C 77.52, H 5.01, N 11.16.

2,2'-((2Z,2'Z)-((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(methanylylidene))bis(3-oxo-2,3,5,6,7,8-hexahydro-1H-cyclopenta[b]naphthalene-2,1-diylidene))dimalononitrile (IDT-HN)

The synthetic route was similar to the reported procedure.[4] IDT-CHO (200 mg, 0.21 mmol), HN (155 mg, 0.63 mmol), chloroform (30 mL), and pyridine (1.0 mL) were added to a two-necked round-bottomed flask, the mixture was deoxygenated with argon for 20 min and then stirred overnight at 65 oC. After cooling to room temperature, the solvent was removed under vacuum. The crud product was purified by column chromatography on a silica gel using dichloromethane as an eluent and then recrystallization from chloroform/methanol to afford IDT-HN as a red solid (266 mg, 90%). ^{1}HNMR (500MHz, $CDCl_3$, δ): 8.82 (s, 2H), 8.35 (s, 2H), 7.70 (s, 2H), 7.69 (s, 2H), 7. 57 (s, 2H), 7.15-7.11 (dd, J = 5.0 Hz, J = 5.0 Hz, 16H), 2.92 (d, J = 5.0 Hz, 8H), 2.58 (t, J =7.5Hz, 8H), 1.84 (s, 8H), 1.63-1.57 (m, 8H), 1.35-1.29 (m, 24H), 0.87 (t, J = 7.5 Hz, 12H). 13C NMR (125 MHz, CDCl3, δ): 188.38, 160.64, 158.01, 157.68, 156.14, 146.27, 145.92, 142.26, 141.40, 140.46, 138.85, 137.66, 137.44, 137.02, 134.72, 128.74, 127.65, 125.95, 124.19, 123.48, 119.82, 114.86, 114.78, 68.10, 67.88, 62.95, 35.56, 31.72, 31.31, 30.72, 30.34, 29.08, 22.59, 22.43, 22.37, 14.11. MS (MALDI-TOF) calcd for C98H94N4O2S2, 1422.6818; found, 1423.5437. Anal. calcd for C98H94N4O2S2: C 82.66, H 6.65, N 3.93, S 4.50; found: C 82.50, H 6.73, N 4.04, S 4.61.

3. Supplementary Figures and Tables

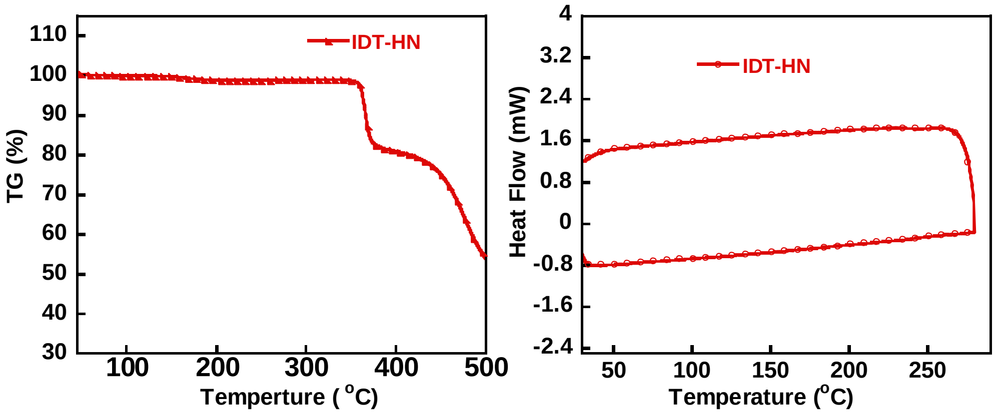


Figure S1. The TG and DSC curves of the acceptor **IDT-HN**.

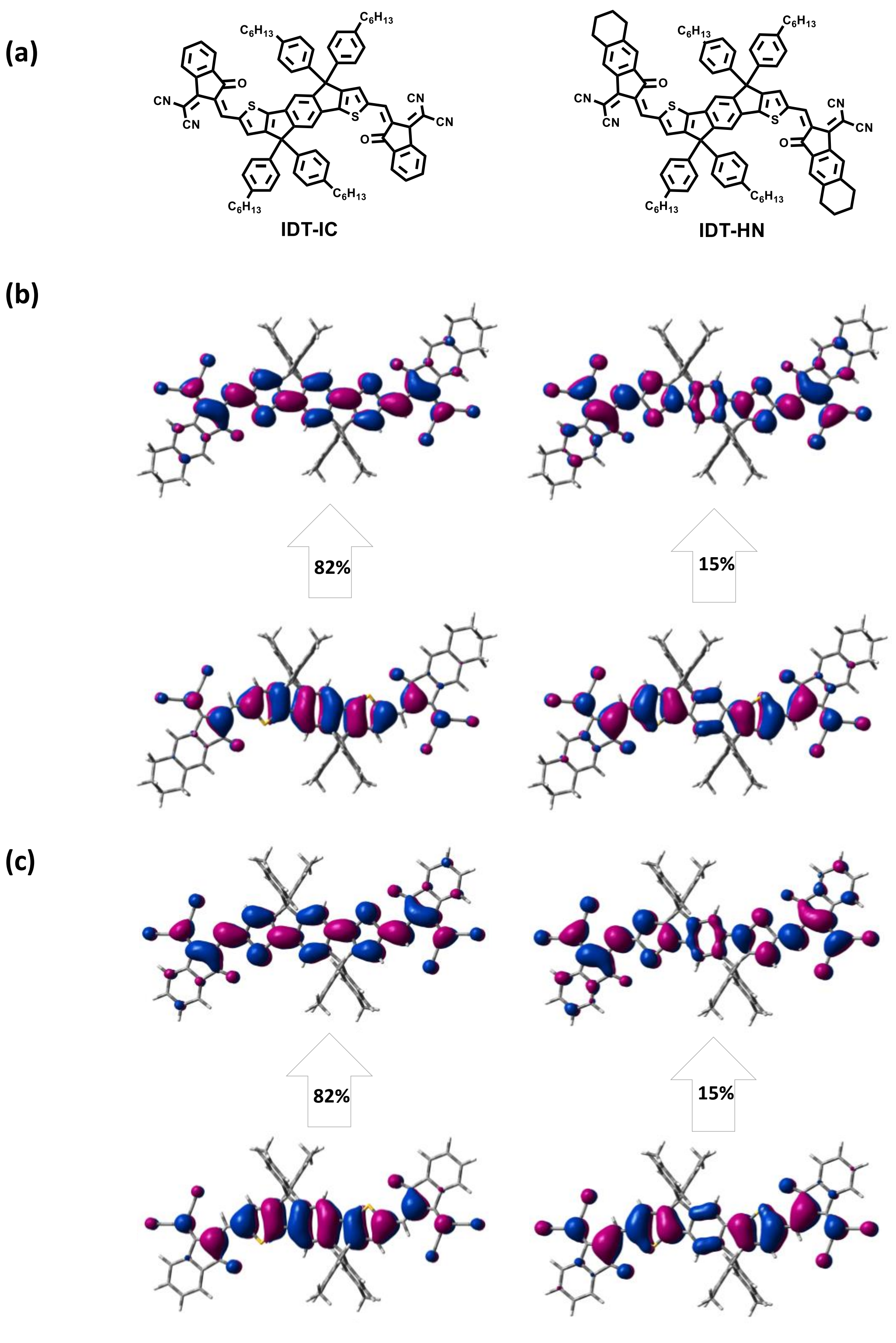


Figure S2. (a) Chemical structure of IDT-IC and IDT-HN; illustration of the major NTOs of S_0–S_1 transition for (b) IDT-HN and (c) IDT-IC based on TD-DFT ωB97X-D/6-31G* calculations. The weights of the particle-hole contribution to the excitation are included.

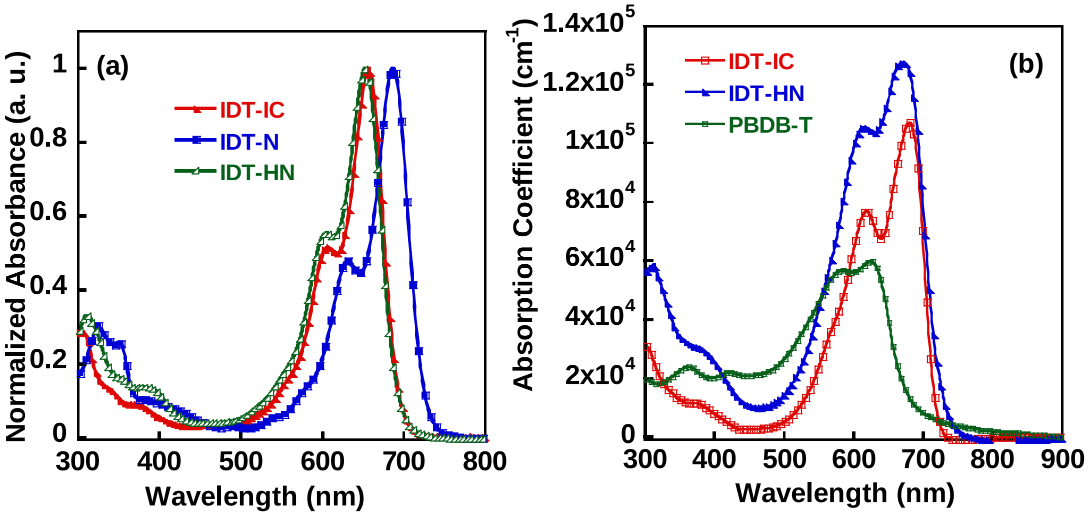


Figure S3. UV–Vis absorption spectra of the acceptors in (a) chloroform solution and (b) the acceptors and donors as films.

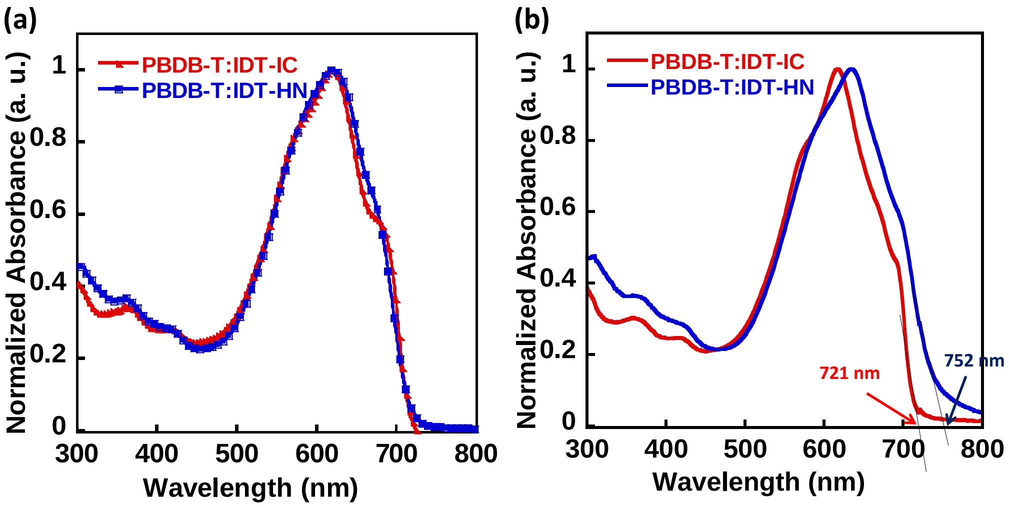


Figure S4. UV–Vis absorption spectra of PBDB-T:IDT-IC and PBDB-T:IDT-HN blend films processed with DIO additive (a) and without DIO additive (b).

Table S1. Optical and electrochemical properties of the two acceptors **IDT-IC** and **IDT-HN**.

	UV-vis in solution		UV-vis as thin films			CV		
Materials	λ_{max}/nm	λ_{onset}/nm	λ_{max}/nm	λ_{onset}/nm	E_g^{opt} /eV	HOMO/eV	LUMO/eV	E_g^{cv} /eV
IDT-IC	657	700	680	740	1.68	-5.84	-3.95	1.89
IDT-HN	653	700	671	740	1.68	-5.92	-3.86	2.06

Table S2. The absorption coefficient of the two acceptors in chloroform solution and in the film state.

Acceptors	Solution λ_{max} (nm)	ε (10^5 M^{-1} cm^{-1})	Film λ_{max} (nm)	ε (10^5 cm^{-1})
IDT-IC	657	1.40	680	1.07
IDT-HN	653	1.72	671	1.28

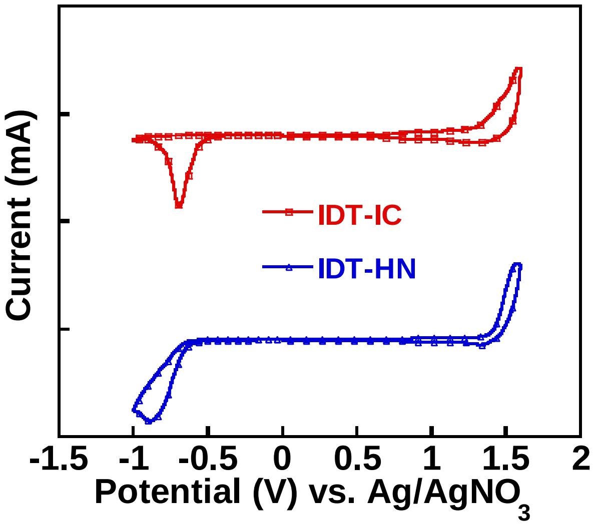


Figure S5. Cyclic voltammetry (CV) curves of the acceptors **IDT-IC** and **IDT-HN**.

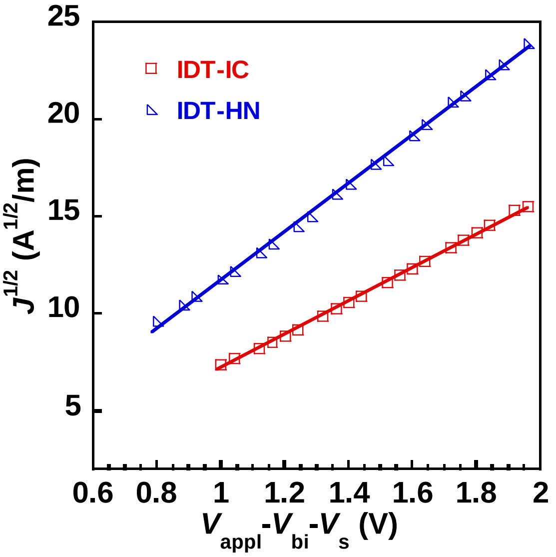


Figure S6. $J^{1/2}$-V characteristics of electron only for IDT-IC and IDT-HN neat films from SCLC.

Table S3. Electron/hole mobility forPBDB-T:acceptor blend films and pristine acceptor films.

Film	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})	μ_h/ μ_e
PBDB-T:IDT-IC	2.42×10^{-4}	9.64×10^{-4}	3.98
PBDB-T:IDT-HN	4.05×10^{-4}	1.04×10^{-3}	2.57
IDT-IC	1.35×10^{-4}		
IDT-HN	2.79×10^{-4}		

Table S4. Photovoltaic properties of the PSCs based on **PBDB-T** as donor and **IDT-HN** as the acceptor under AM 1.5 G at 100 mW cm^{-2}.

D:A (w/w)	DIO (v/v) additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
2:1	w/o	0.94	13.14	67.95	8.36
1.5:1	w/o	0.93	13.35	69.19	8.64
1:1	w/o	0.93	12.98	69.94	8.47
1:1.5	w/o	0.91	11.82	61.82	6.65
1.5:1	0.25 %	0.93	13.64	74.79	9.46
1.5:1	0.5 %	0.93	14.43	76.41	10.22
1.5:1	1 %	0.93	13.46	74.31	9.33

Table S5. The photovoltaic parameters of the PSCs based on **PBDB-T:IDT-HN** with different film thickness under AM 1.5 G at 100 mW cm^{-2}.

Blend	Thickness (nm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PBDB-T:IDT-HN	65±5	0.93	12.84	71.59	8.52
	80±5	0.93	13.24	71.87	8.84
	90±5	0.93	14.18	76.39	10.03
	100±5	0.93	14.43	76.41	10.22
	110±5	0.93	14.32	75.50	10.06
	120±5	0.94	13.94	75.89	9.95
	130±5	0.94	13.69	75.50	9.68
	160±5	0.92	14.14	73.79	9.60
	180±5	0.92	14.01	74.13	9.54
	200±5	0.93	14.88	68.88	9.49
	220±5	0.92	13.80	72.98	9.27
	250±5	0.92	15.70	64.37	9.29

Table S6. Photovoltaic properties of the PSCs based on **PBDB-T** as donor and **IDT-HN** as the acceptor under AM 1.5 G at 100 mW cm^{-2}.

D:A (w/w)	DIO (v/v) additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
2:1	w/o	0.87	9.63	53.89	4.52
1.5:1	w/o	0.88	10.42	54.36	4.93
1:1	w/o	0.87	10.26	55.04	4.90
1:1.5	w/o	0.86	10.00	55.21	4.75
1.5:1	0.25 %	0.88	10.80	56.75	5.42
1.5:1	0.5 %	0.88	11.94	57.90	6.11
1.5:1	1 %	0.89	9.76	53.02	4.63

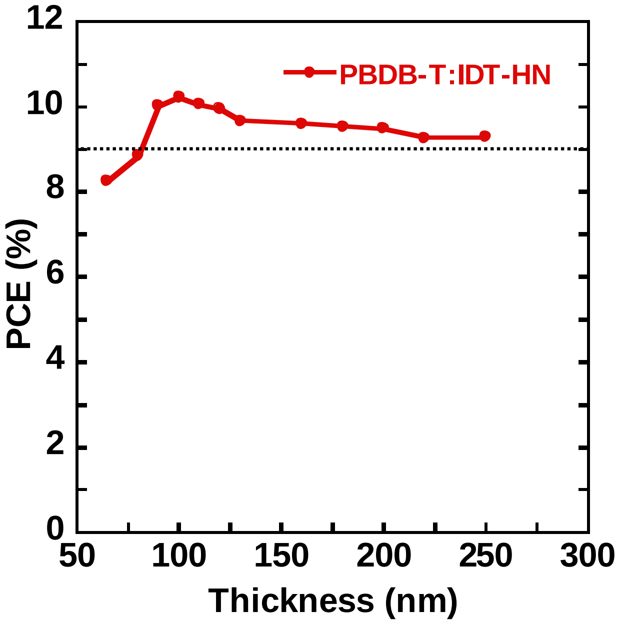


Figure S7. Active layer thickness dependence of the PCE of the device based on PBDB-T:IDT-HN.

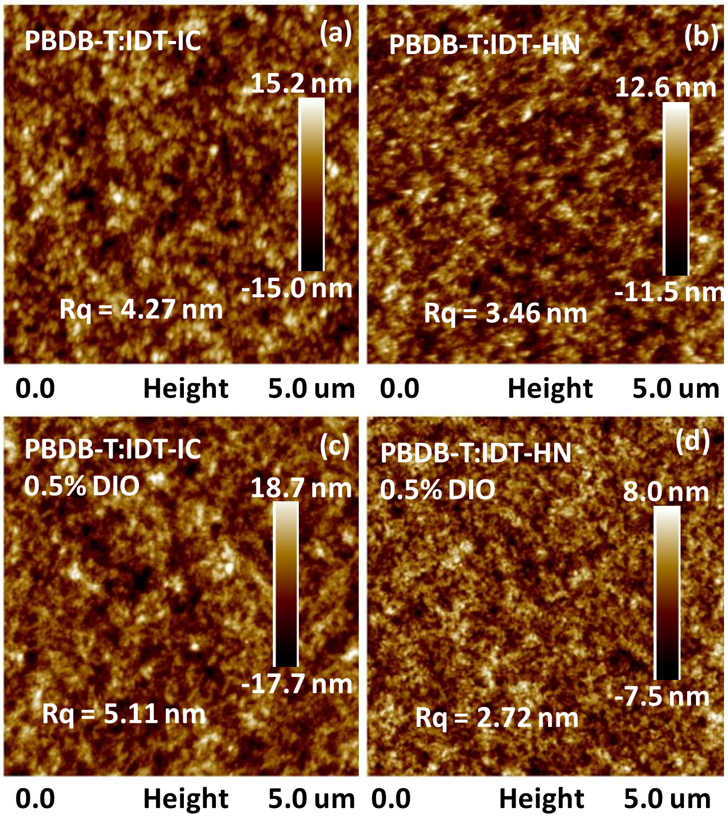


Figure S8. AFM height images (5 × 5 μm) of PBDB-T:IDT-HN and PBDB-T:IDT-IC blend films with and without 0.5% DIO additive.

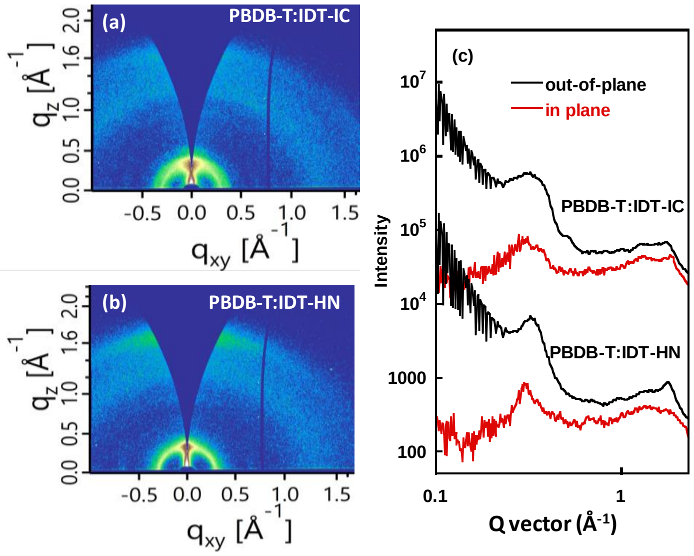


Figure S9. (a,b) 2D-GIWAXS patterns and (c) line-cut profiles of the in-plane (red line) and out-of-plane (black line) direction of PBDB-T:IDT-IC and PBDB-T:IDT-HN blend films.

4. References

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5. ^{1}H and ^{13}C NMR Spectra

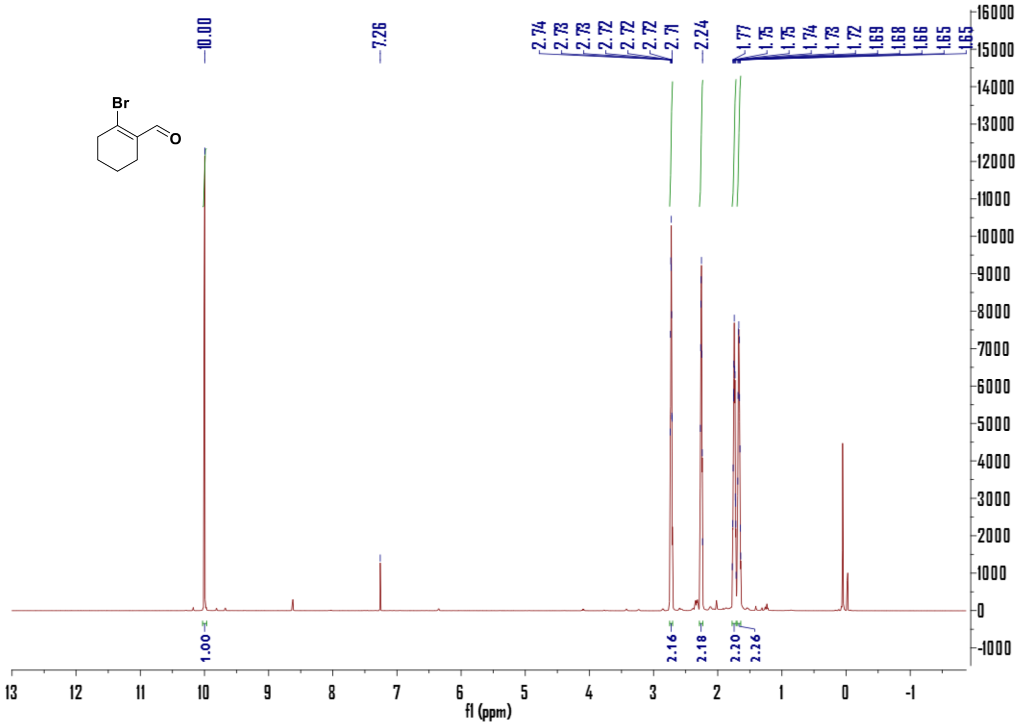

Figure S10. ^{1}H NMR spectrum of **(3)** solution in $CDCl_3$.

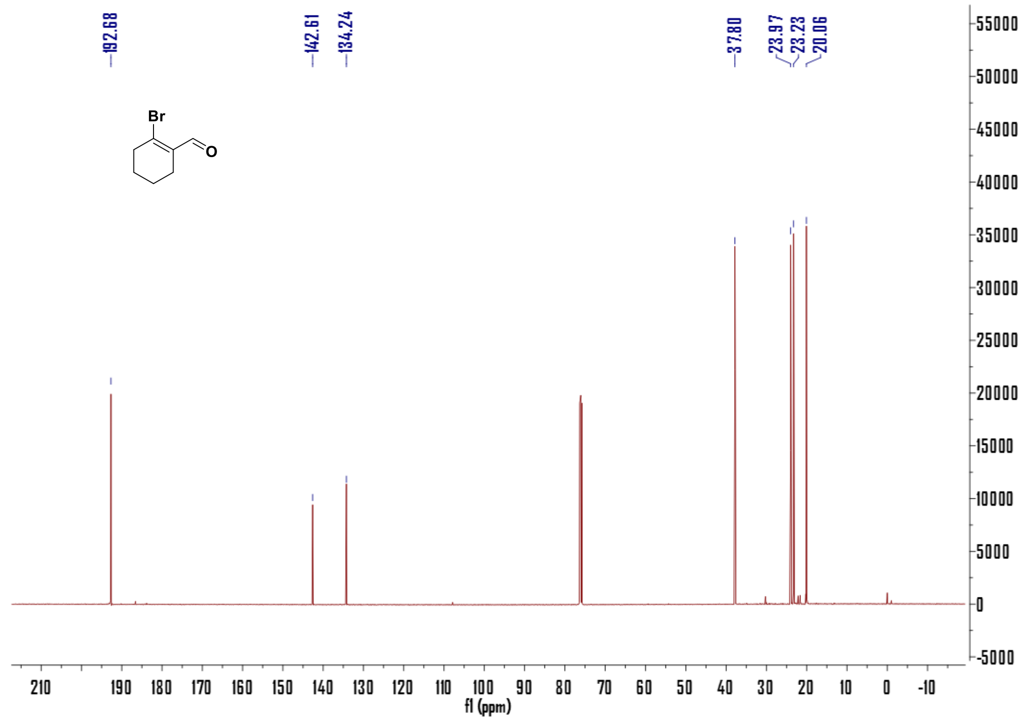

Figure S11. ^{13}C NMR spectrum of **(3)** solution in $CDCl_3$.

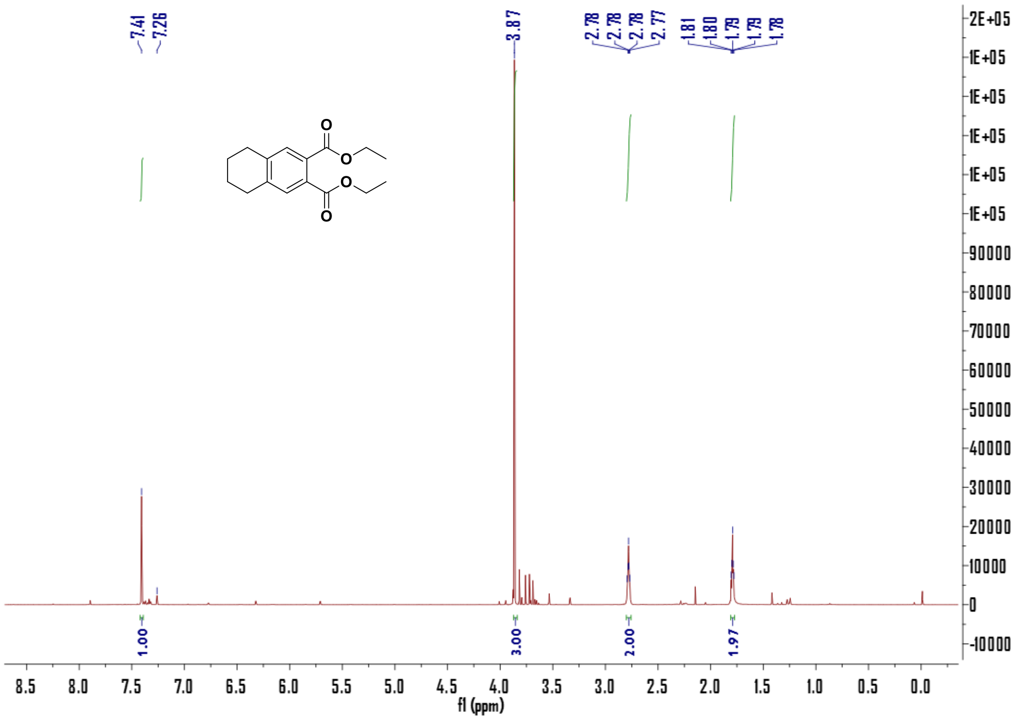

Figure S12. ^{1}H NMR spectrum of **(5)** solution in $CDCl_3$.

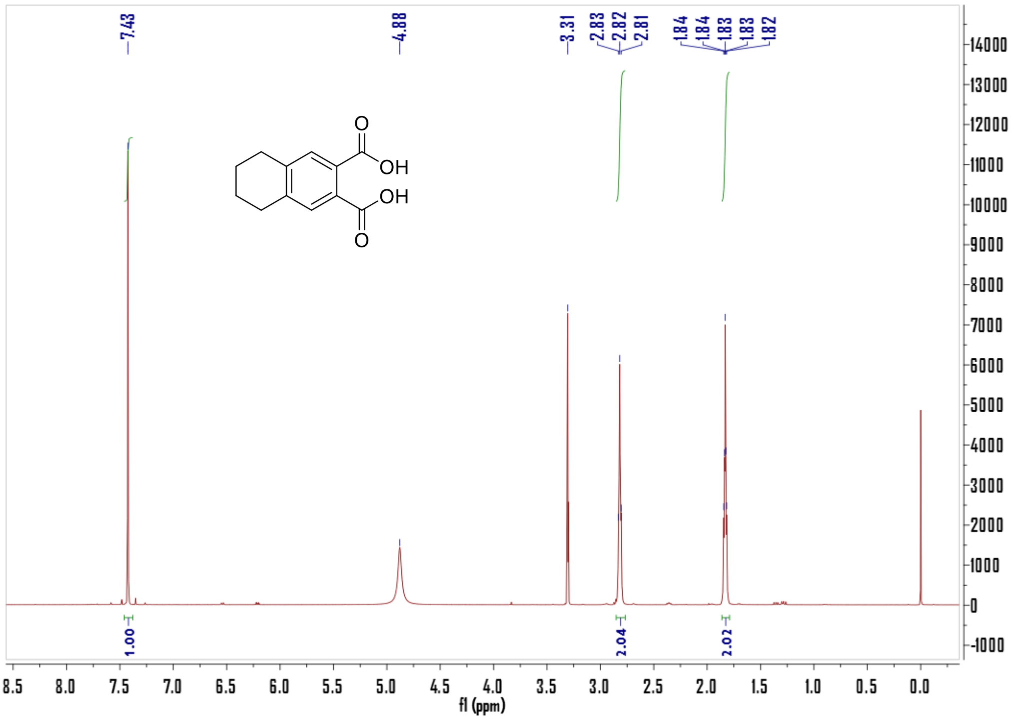

Figure S13. ^{1}H NMR spectrum of **(6)** solution in CD_3OD.

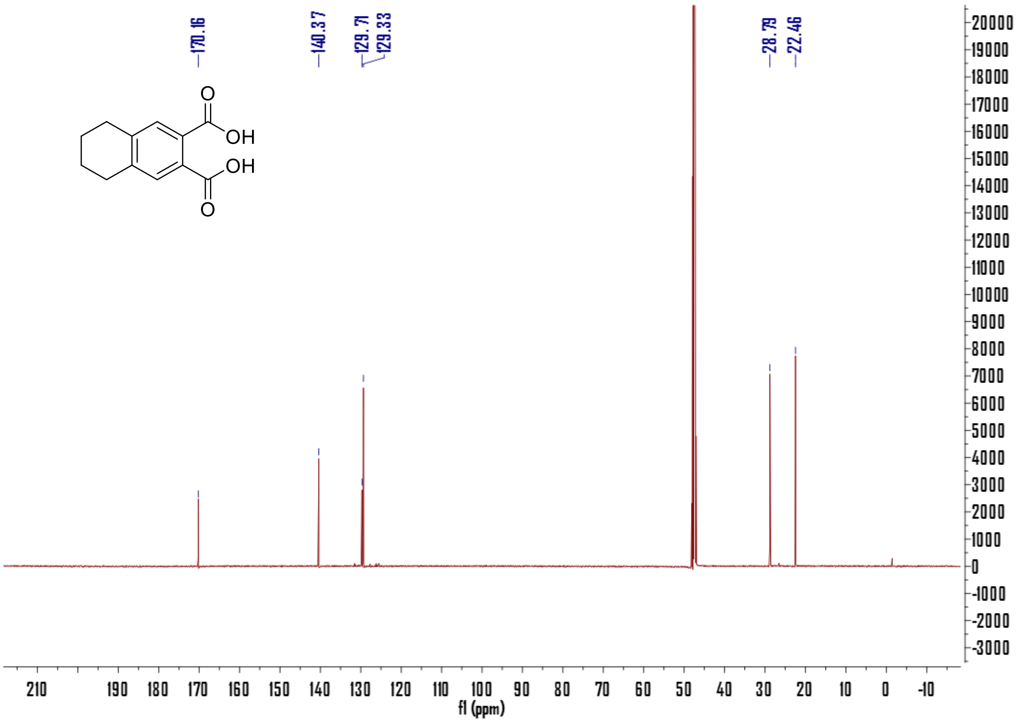

Figure S14. ^{13}C NMR spectrum of **(6)** solution in CD_3OD.

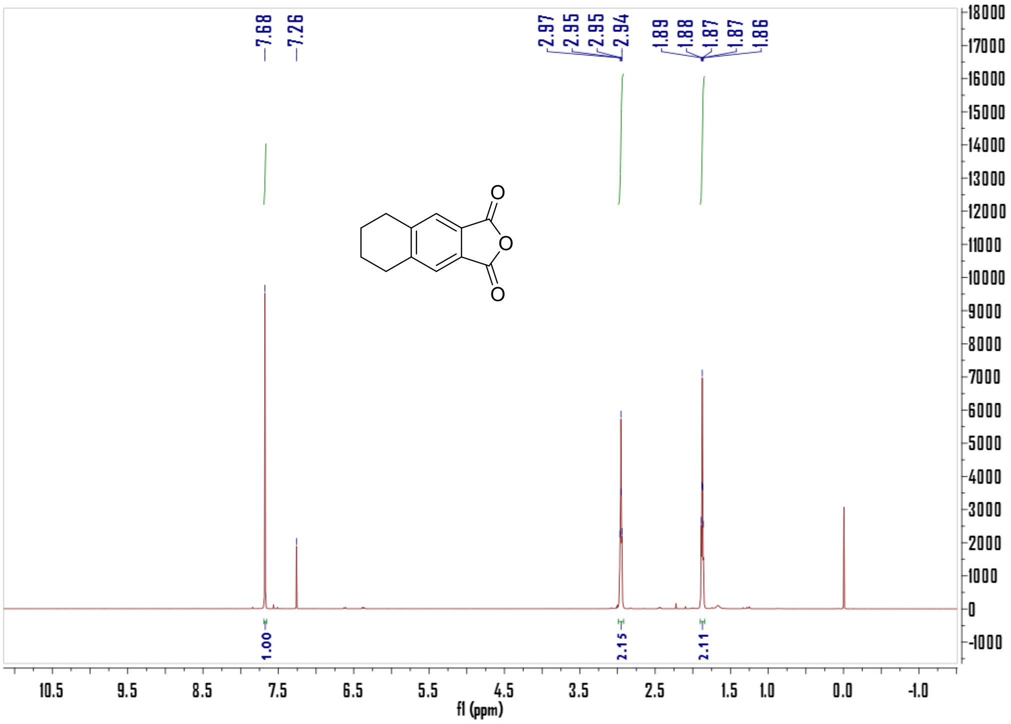

Figure S15. ^{1}H NMR spectrum of **(7)** solution in $CDCl_3$.

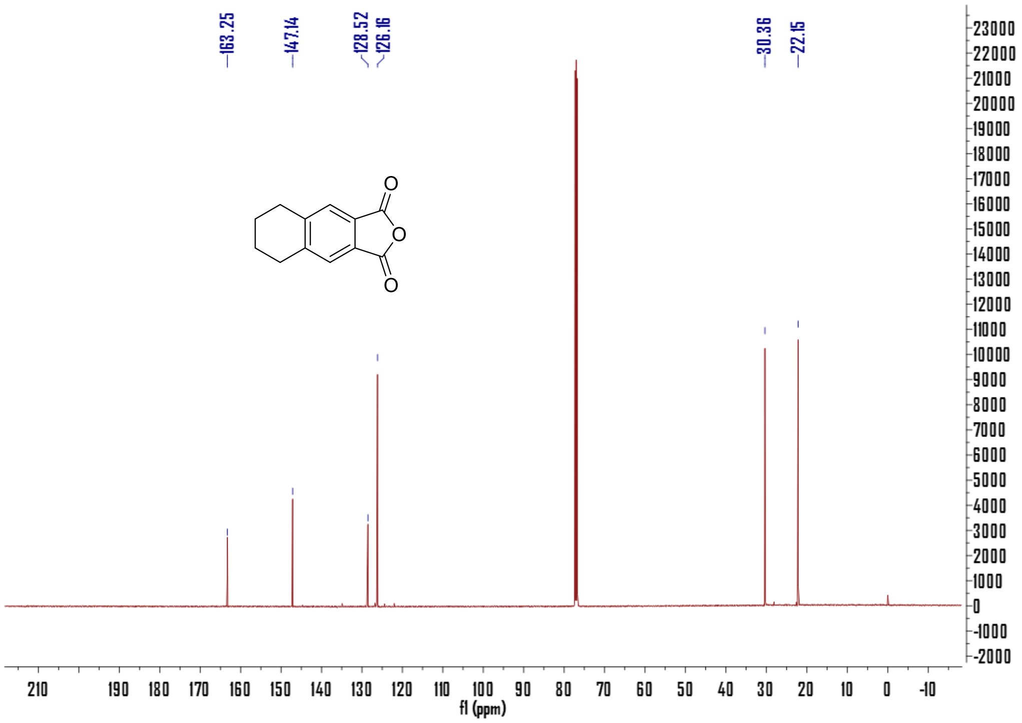

Figure S16. ^{13}C NMR spectrum of **(7)** solution in $CDCl_3$.

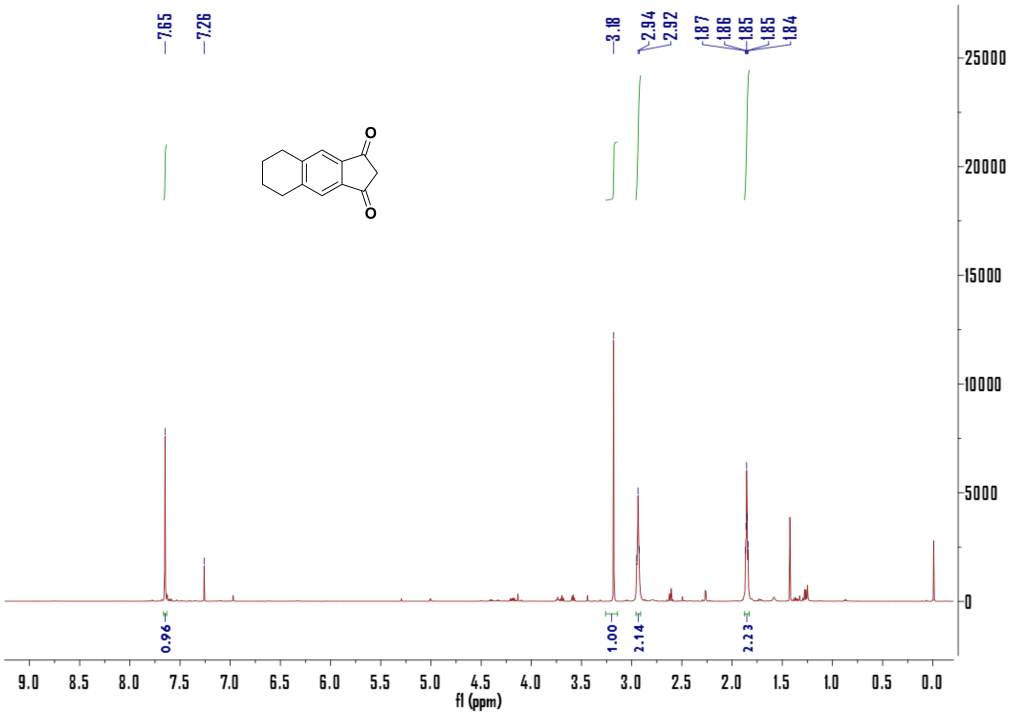

Figure S17. ^{1}H NMR spectrum of **(9)** solution in $CDCl_3$.

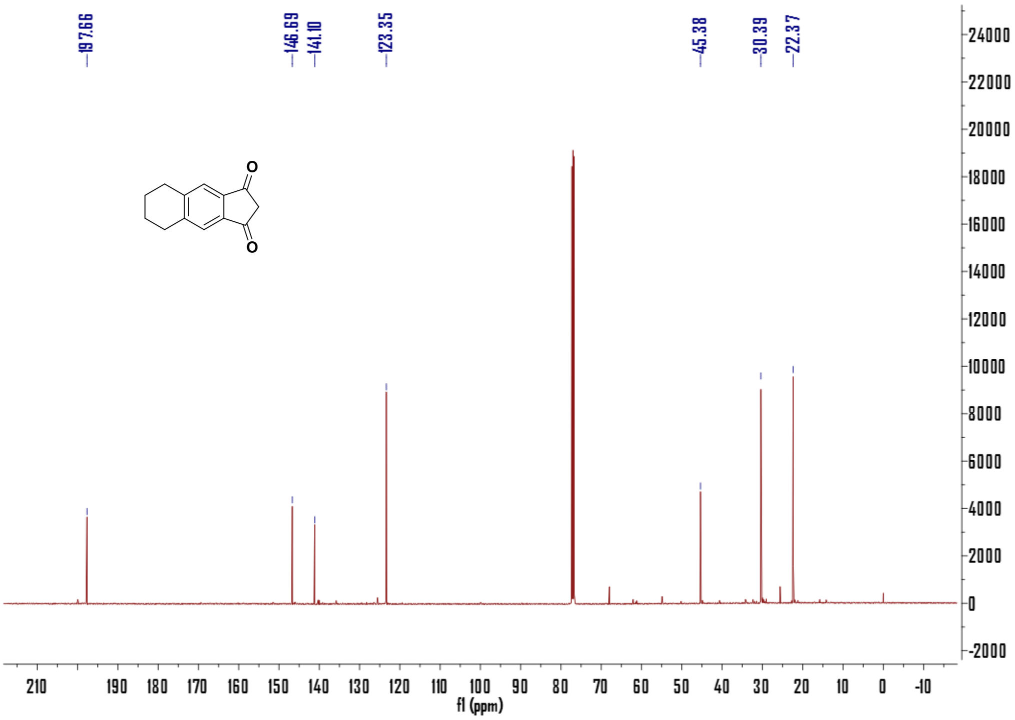

Figure S18. ^{13}C NMR spectrum of **(9)** solution in $CDCl_3$.

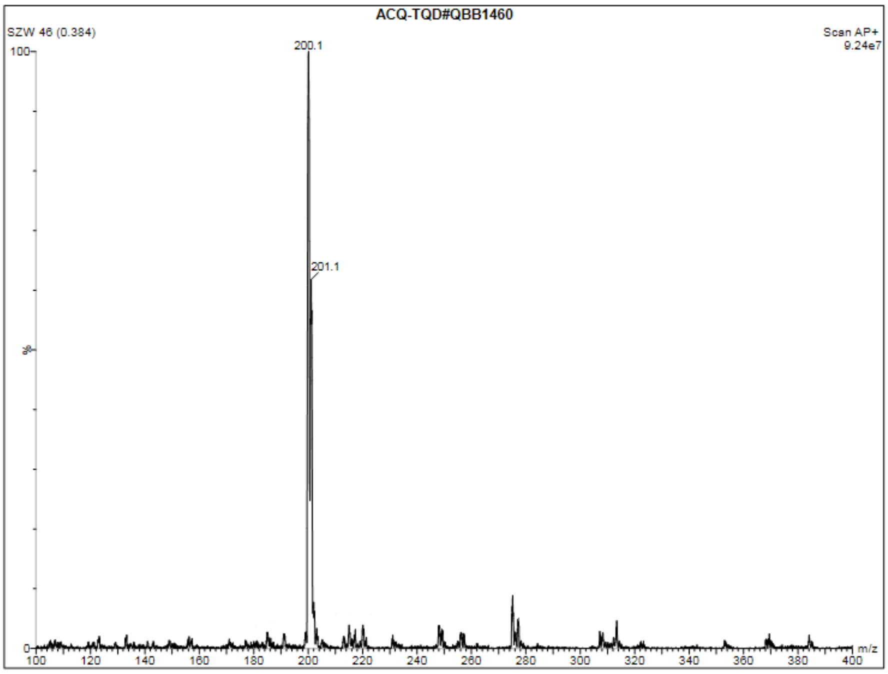

Figure S19. Mass spectrum of compound (9)

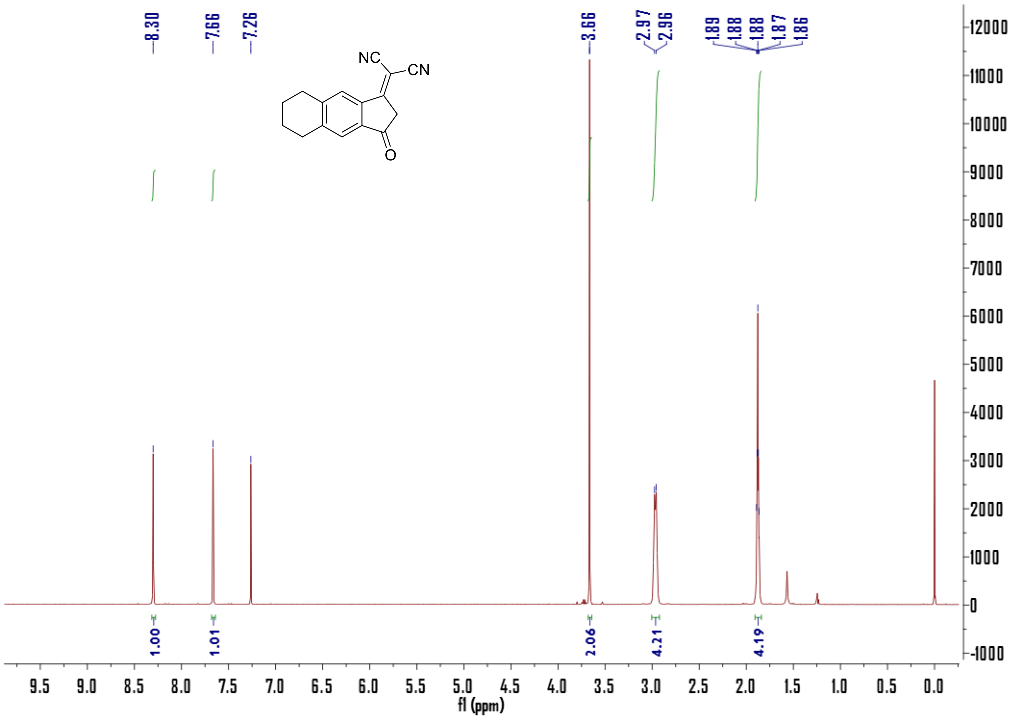

Figure S20. ^{1}H NMR spectrum of **HN** solution in $CDCl_3$.

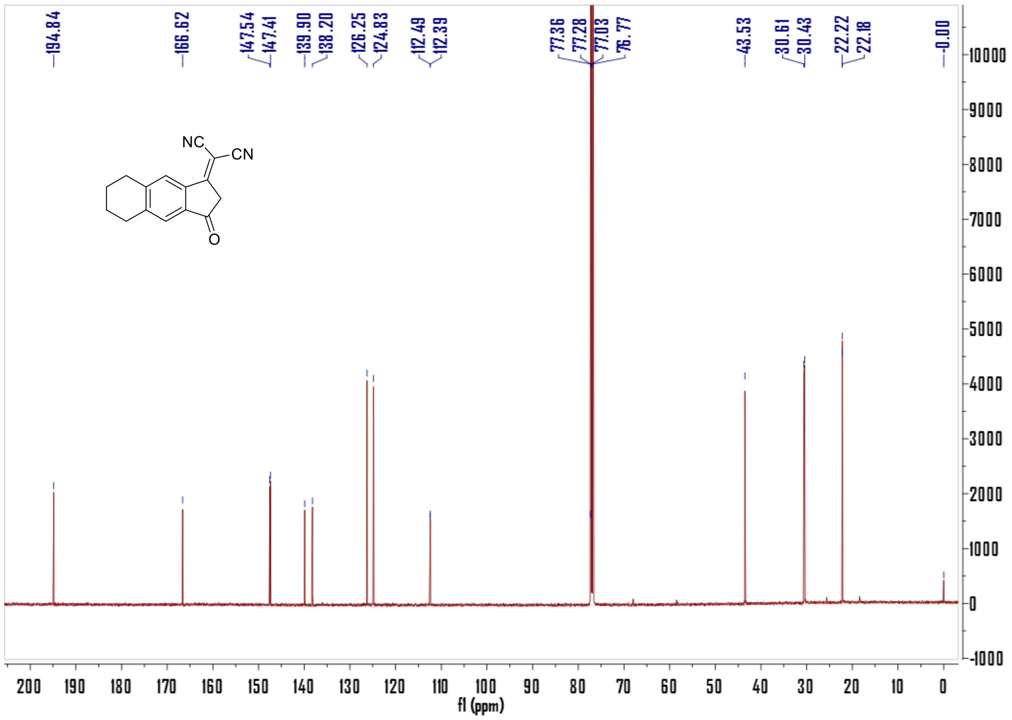

Figure S21. ^{13}C NMR spectrum of **HN** solution in $CDCl_3$.

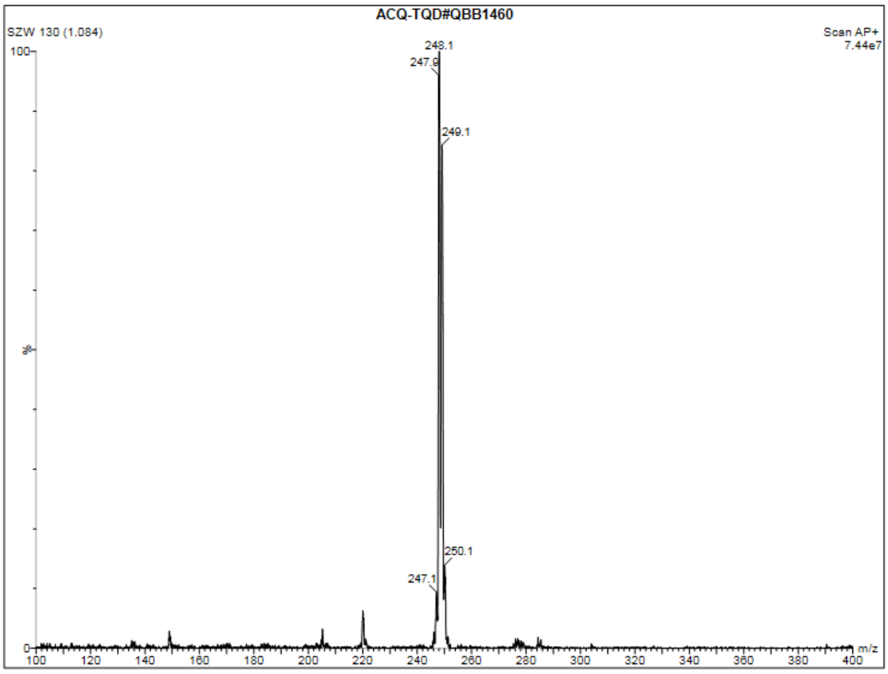

Figure S22. Mass spectrum of compound (HN)

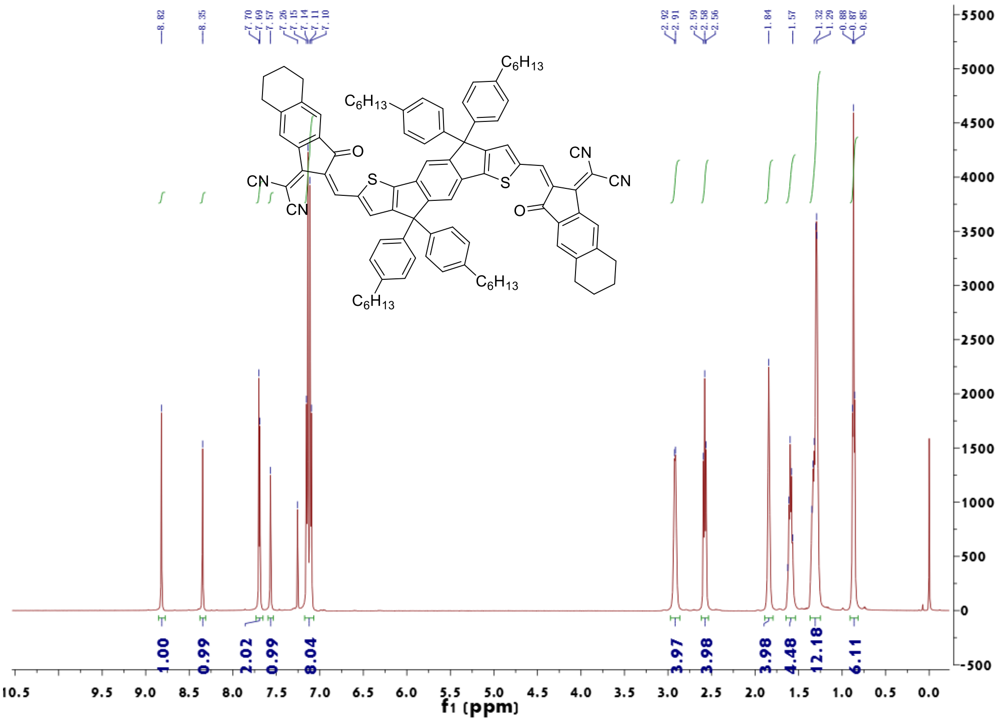

Figure S23. ^{1}H NMR spectrum of **IDT-HN** solution in $CDCl_3$..

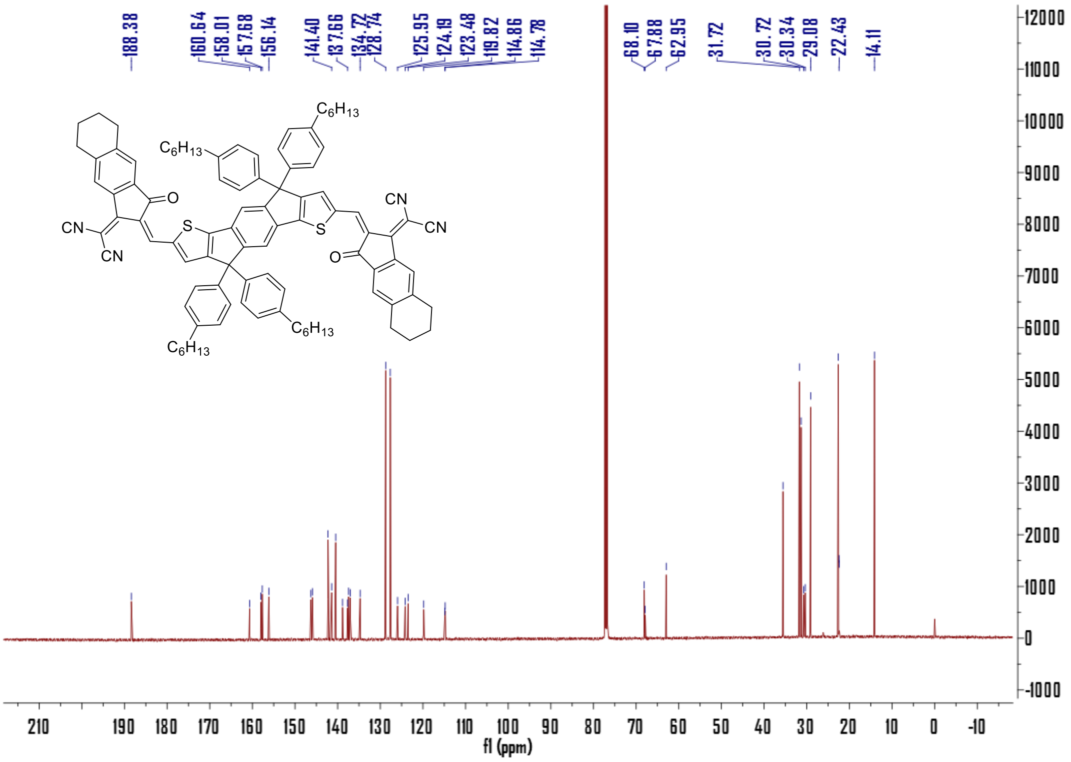

Figure S24. ^{13}C NMR spectrum of **IDT-HN** solution in $CDCl_3$..