Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information

Tuning molecular geometry and packing mode of non-fullerene acceptors by alternating bridge atoms towards efficient organic solar cells

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General procedure:

All reactions were carried out under argon using solvents and reagents as commercially supplied, unless otherwise stated. 4, 4, 9, 9-tetraoctyl-4, 9-dihydro-s-indaceno[1, 2-b:5, 6-b']dithiophene-2, 7-dicarbaldehyde, (2, 5-dibromo-1, 4-phenylene) bis (4-bromothiene-5, 2-diyl)] bis(trimethylsilane) and dibromo-di-n-octylgermane were synthesized by the reported method.[1, 2] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz) or a Bruker Advanced III (500 MHz) spectrometers, using the residual solvent resonance of $CDCl_3$ or TMS as an internal reference and are given in ppm. UV-Vis absorption spectra were measured by a PerkinElmer Lambda 750S recording spectrophotometer. Cyclic voltammetry (CV) measurements of targeted SMAs thin films were conducted on a CHI660D voltammetric analyzer in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-}Bu_4NPF_6$) as supporting electrolyte at room temperature by using conventional three-electrode configuration consisting of a platinum working electrode, a platinum wire counter electrode and a Ag/AgCl wire reference electrode. Grazing-incidence wide-angle x-ray scattering (GIWAXS) was carried out at beamline 7.3.3 Lawrence Berkeley National Lab (LBNL). The sample was put inside a helium chamber, and Pilatus 2M detector was used to collect the signal.

Device measurement:

OPV device characterization:

The device J-V characteristics were recorded by a Keithley 2420 Source Meter unit in forward direction under AM 1.5G 1 sun irradiance (100 mW cm^{-2}) as generated by a 300W Xe lamp solar simulator (Enlitech SS-F5-3A) at room temperature. The light intensity were calibrated using a standard Si diode with KG-5 filter. The EQE spectra was characterized using an Enlitech EQE system (Enlitech QE-M110) with a Si diode as reference cell. Monochromatic light was generated from an Enlitech lamp source with a monochromator.

Electron and hole mobility measurement.

Hole-only diode configuration: ITO/PEDOT-PSS/blend films/MoO_3/Al. Firstly, PEDOT-PSS was spin-coated onto the ITO-glass substrate. Then the following layer were deposited by the same route as OPV devices. Electron-only diode configuration: ITO/ZnO/blend films/ZnO/Al.

The mobility in blend films were determined by fitting the dark current hole/electron-only diodes to the space-charge limited current (SCLC) model. The mobility was determined by the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3}$$

where J is current density, μ_0 is the hole or electron mobility, ε_0 is the dielectric permittivity of the active layer (generally taken to be about 3 for organic materials), ε_0 is the dielectric permittivity of free space, L is the film thickness, and V is the voltage, which is defined as $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, V_{bi} is the built-in voltage which is related to the difference in the work function of the electrodes.

Synthesis

The synthesis of **2b** was according to the reported literature with similar procedure.[1] A solution of *n*-BuLi (1.06 mL of a 1.6 M solution in hexanes, 1.71 mmol) was added dropwise to a solution of **1b** (0.57 g, 0.57 mmol) in THF (100 mL) at -78 °C, and the reactant was stirred for 1h at that temperature. Then DMF (2.0 mmol) was added dropwise. The cooling bath was removed and the reactant was allowed to warm to RT, followed by stirring for 3h at RT. Water (50 mL) was added, and the mixture extracted (2 x 50 mL dichloromethane). The combined organics were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane/dichloromethane, v: v = 2: 1) to afford a light yellow solid (340mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 2H), 7.79 (s, 2H), 7.77 (s, 2H), 1.50 - 1.44 (m, 8H) 1.33 - 1.14 (m, 48H), 0.84 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.15, 162.96, 146.23, 145.47, 142.56, 142.00, 140.11, 127.54, 32.98, 31.96, 29.33, 29.20, 25.56, 22.77, 14.62, 14.22. MS (MALDI-TOF) *m/z*: Calculated for [M^+] $C_{48}H_{74}Ge_2O_2S_2$ 892.35; found: 892.30.

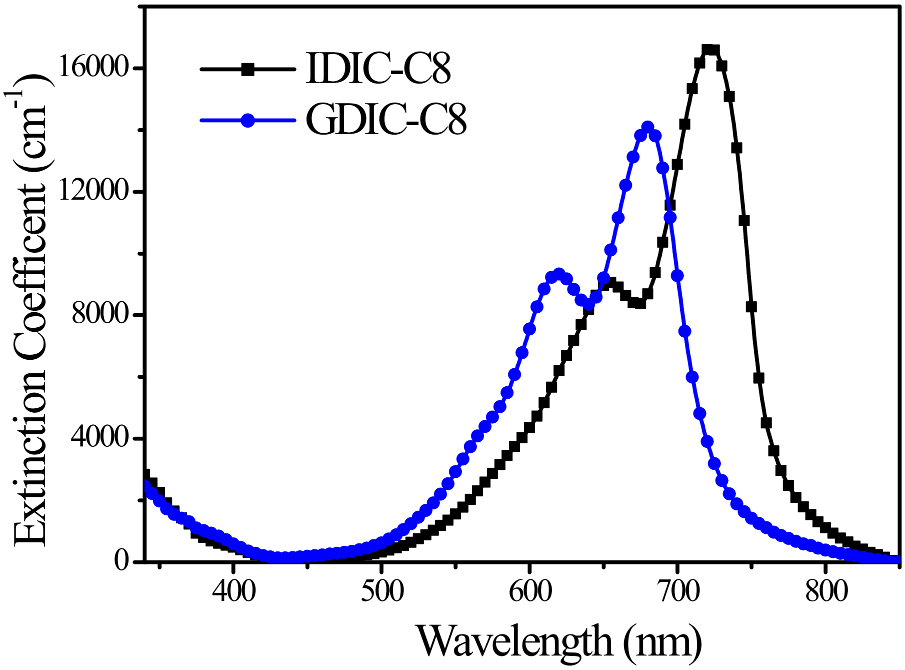

Fig. S1. The absorption spectra of the **IDIC-C8** and **GDIC-C8** in film with extinction coefficient.

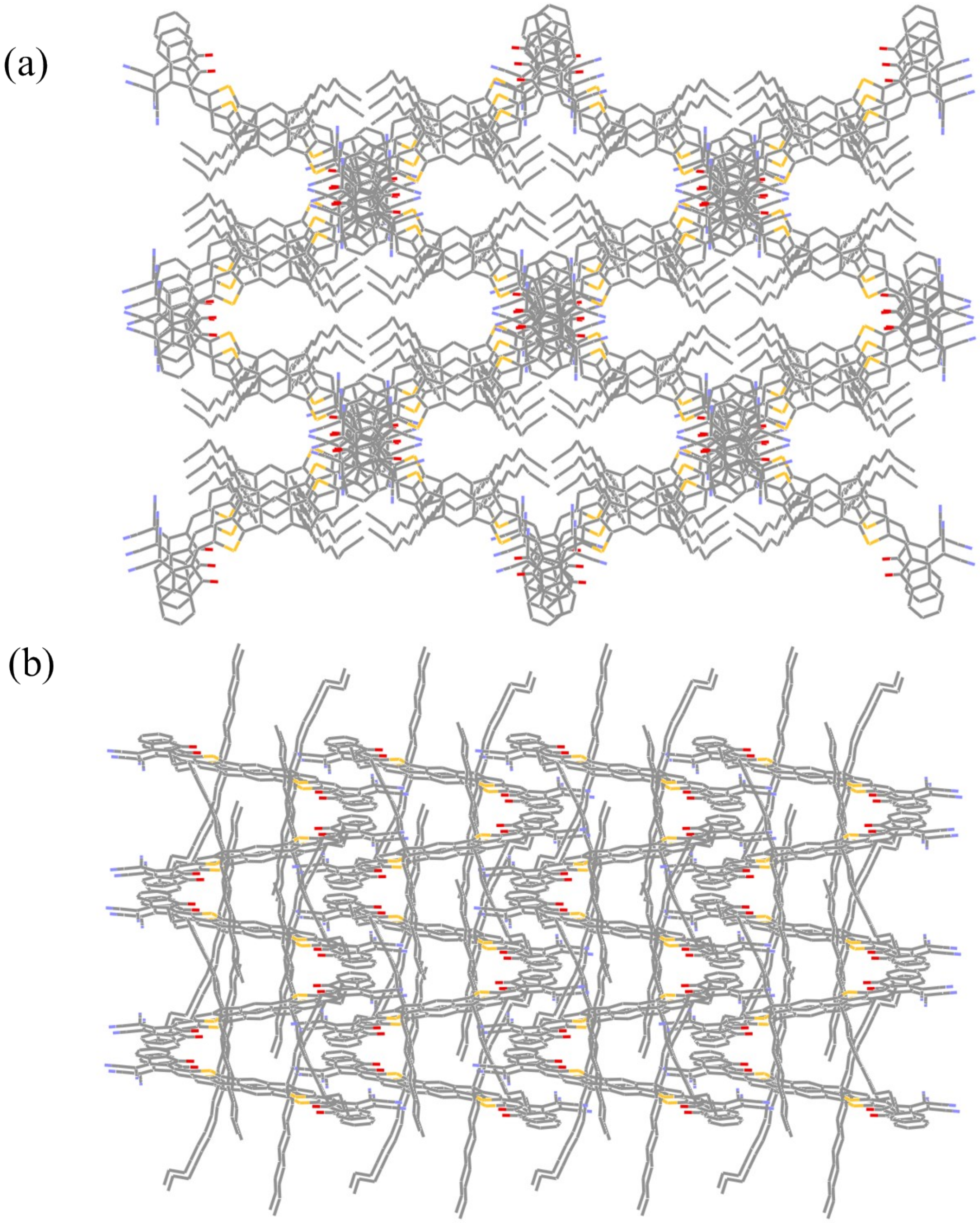

Fig. S2. (a) Top view and (b) side view of crystal packing diagrams for **IDIC-C8**.

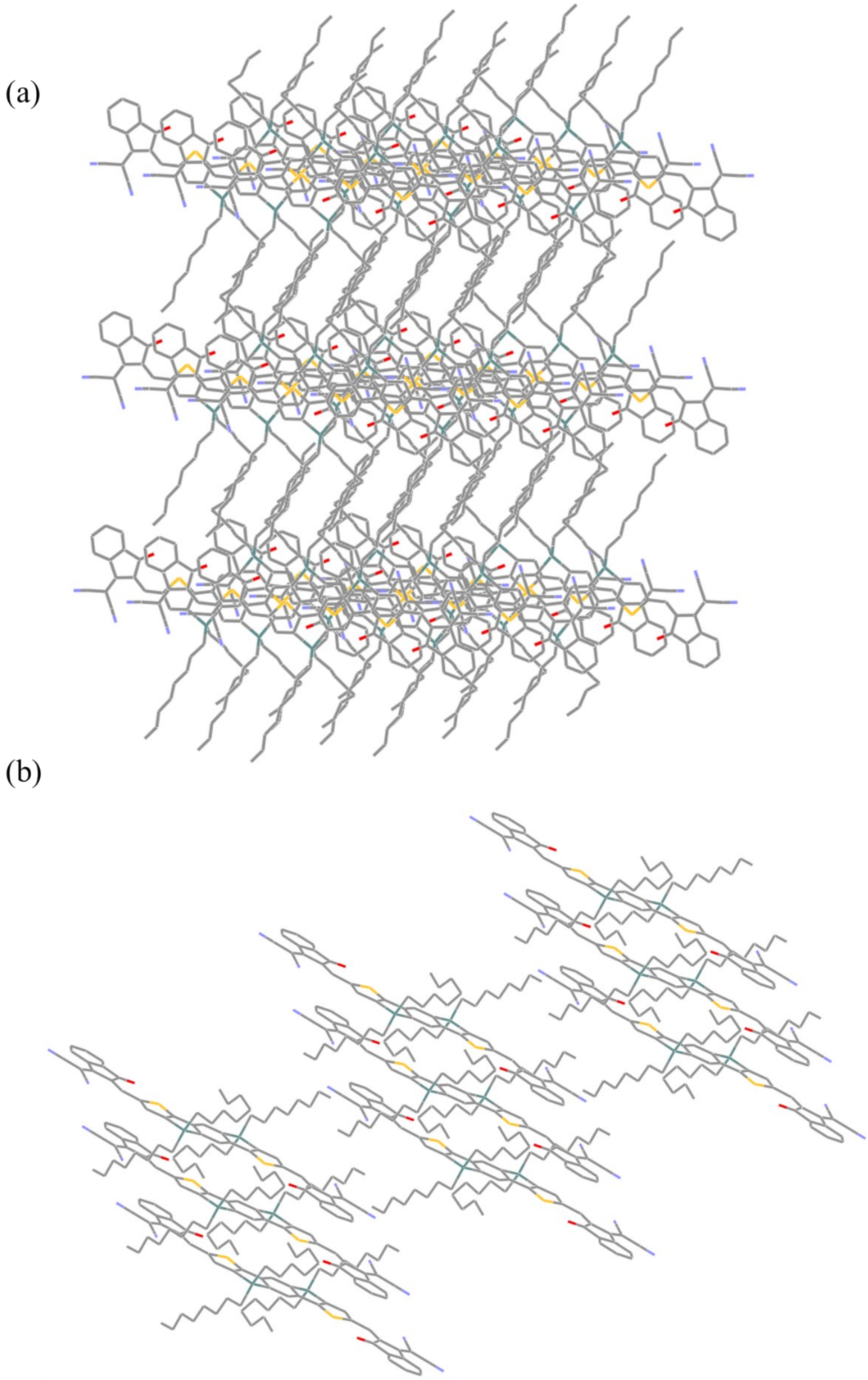

Fig. S3. (a) Top view and (b) side view of crystal packing diagrams for **GDIC-C8**.

Table S1 Photovoltaic parameters of **PM6**:acceptor devices under different fabricated conditions. The devices were in a conventional architecture ITO/PEDOT: PSS/ **PM6**:acceptor /ZnO/Al. The thermal annealing time was 5min.

Active layer	**Solvent**	**Additive**	**Thermal Annealing Temperature (^{o}C)**	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF (%)**	**PCE (%)**
GDIC-C8: PM6	**CF**	**-**	**w/o**	**1.02**	**10.08**	**49.5**	**5.09**
		0.5V%DIO	**w/o**	**1.02**	**9.51**	**44.6**	**4.33**
		0.5V%CN	**w/o**	**1.02**	**10.49**	**53.4**	**5.72**
		1V%CN	**w/o**	**1.03**	**8.32**	**50.0**	**4.28**
	CF	**0.25V%CN**	**w/o**	**1.02**	**11.39**	**58.2**	**6.76**
			80	**1.02**	**10.61**	**54.5**	**5.90**
			100	**1.02**	**10.55**	**54.2**	**5.83**
			120	**1.02**	**10.34**	**54.6**	**5.76**
			140	**1.02**	**9.94**	**54.1**	**5.49**
IDIC-C8: PM6	**CF**	**-**	**-**	**0.98**	**14.67**	**66.6**	**9.57**
		0.25V%CN	**-**	**0.97**	**14.12**	**74.7**	**10.23**
		0.5V%CN	**-**	**0.98**	**14.14**	**69.1**	**9.57**
		0.5V%CN	**120**	**0.97**	**13.48**	**67.5**	**8.83**

Table S2 Photovoltaic parameters of PBDB-T:acceptor devices under different fabricated conditions. The devices were in a conventional architecture ITO/PEDOT: PSS/polymer donors: acceptors/ZnO/Al.

Active layer	Solvent	Additive	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
GDIC-C8: PBDB-T	**CB**	**-**	**0.94**	**9.09**	**61.3**	**5.24**
		0.5V%DIO	**0.93**	**8.58**	**61.1**	**4.87**
		0.75V%CN	**0.93**	**10.97**	**66.9**	**6.83**
IDIC-C8: PBDB-T	**CB**	**-**	**0.83**	**13.36**	**57.0**	**6.32**
		0.5V%DIO	**0.85**	**9.89**	**62.9**	**5.33**
		0.25V%CN	**0.84**	**13.32**	**61.8**	**6.86**

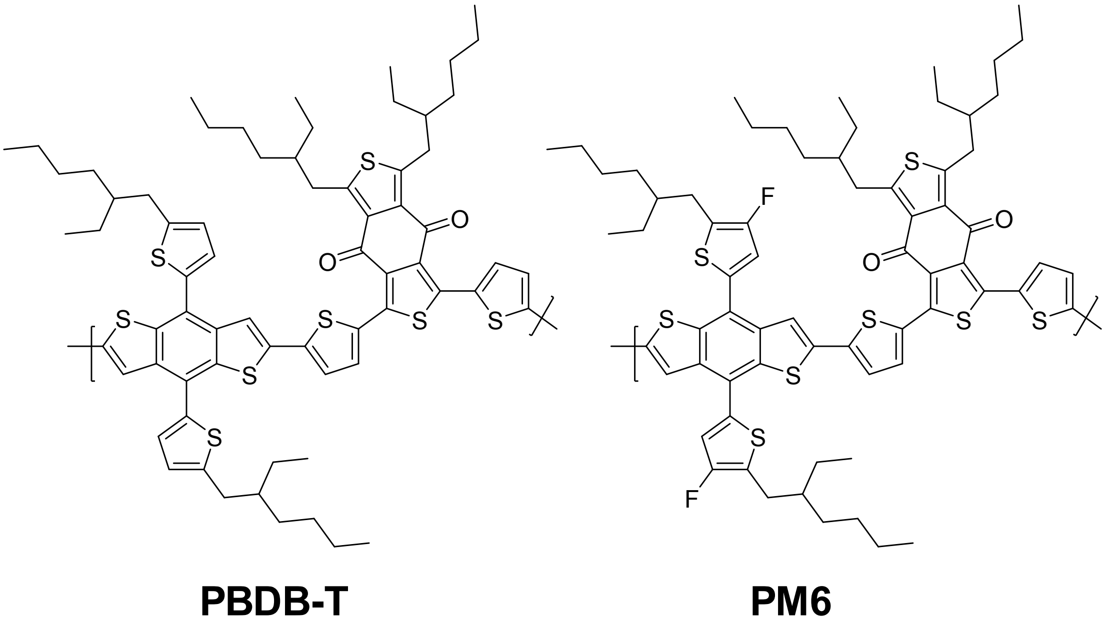

Fig. S4. Chemical structures of **PBDB-T, PM6**.

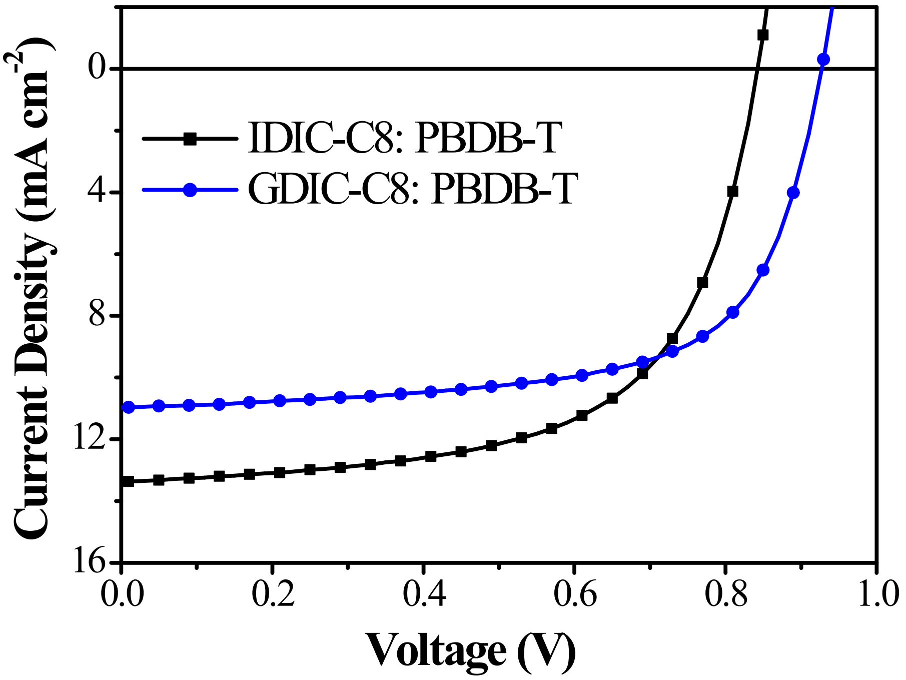

Fig. S5. *J-V* curves for the optimal acceptor: **PBDB-T** devices.

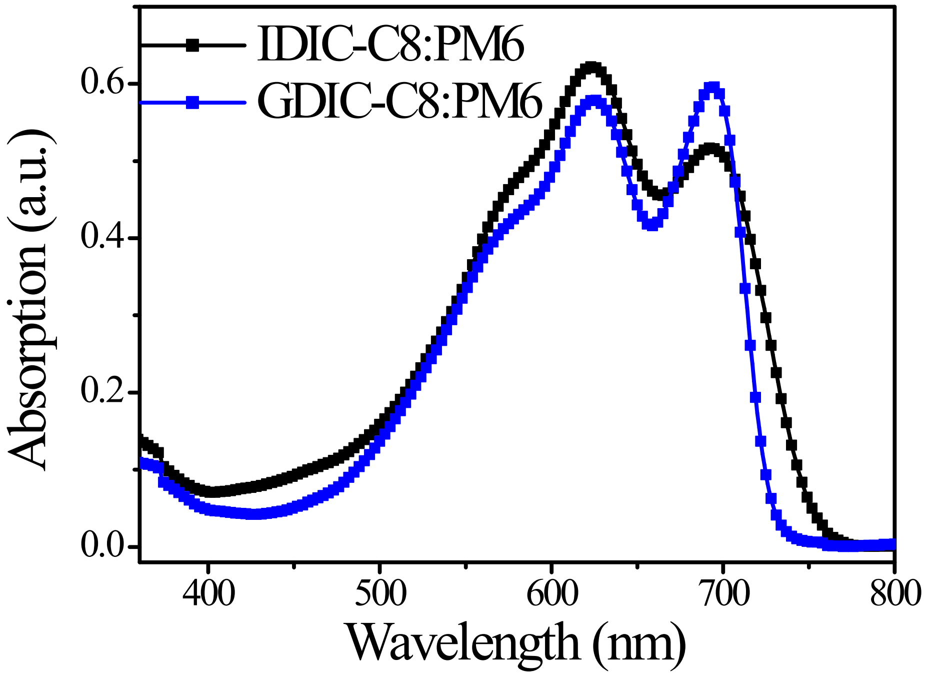

Fig. S6. The absorption spectra of the active layer of the devices based on **IDIC-C8: PM6** and **GDIC-C8: PM6**.

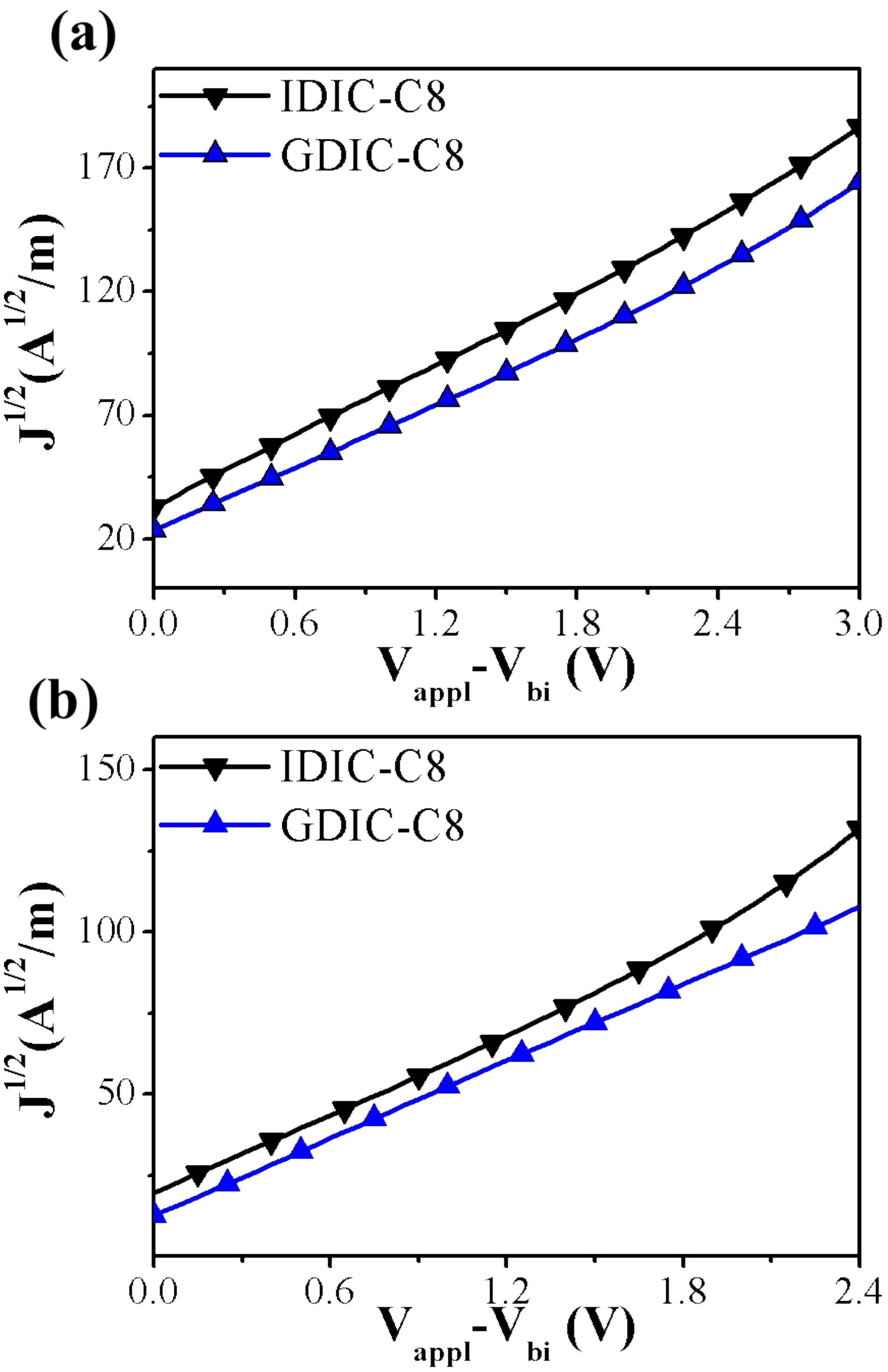

Fig. S7. (a) The $J^{1/2}$-V curves of the hole-only devices; (b) The $J^{1/2}$-V curves of the electron-only devices.

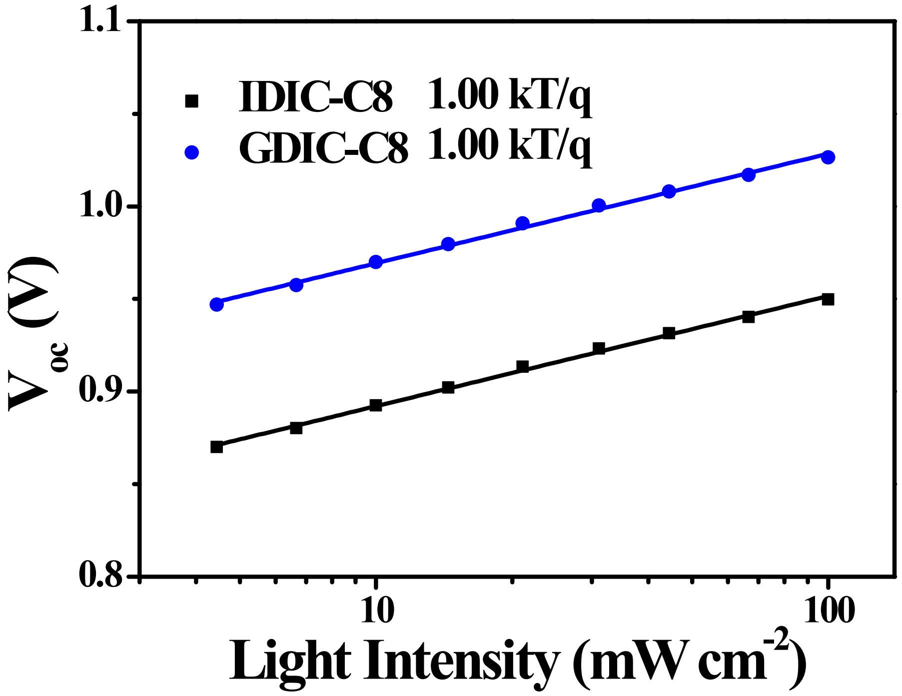

Fig. S8. Light intensity dependence of V_{oc} for the optimal acceptors: **PM6** devices.

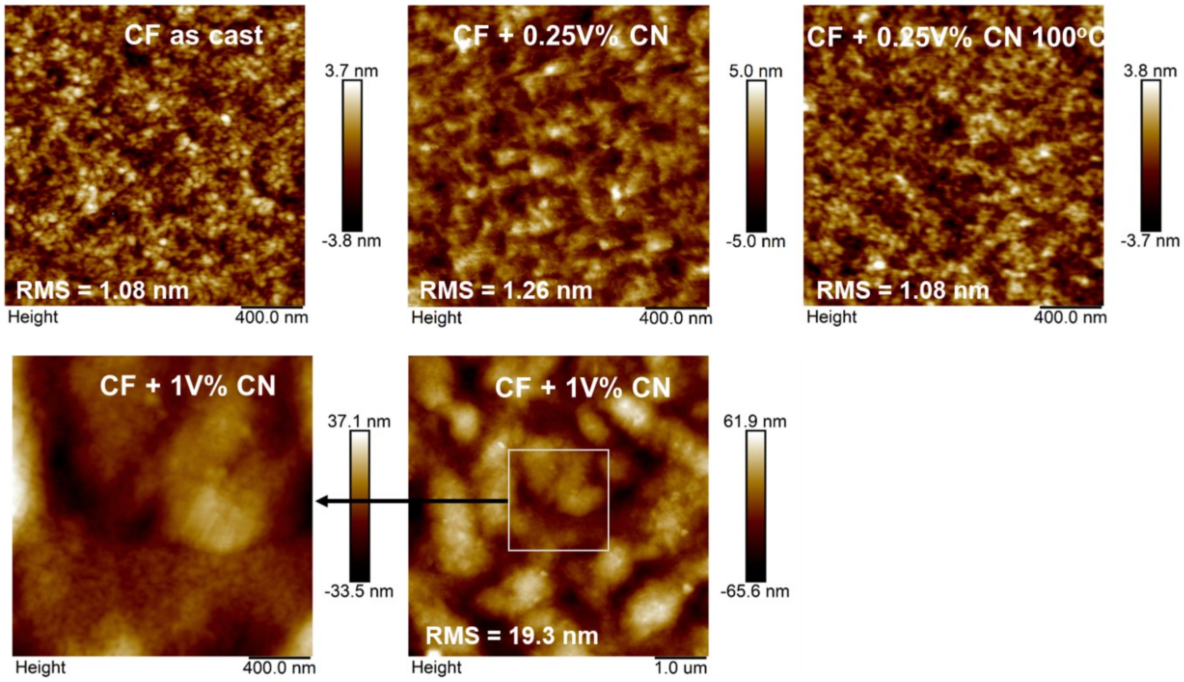

Fig. S9. AFM height images of **GDIC-C8: PM6** blend films fabricated with different conditions.

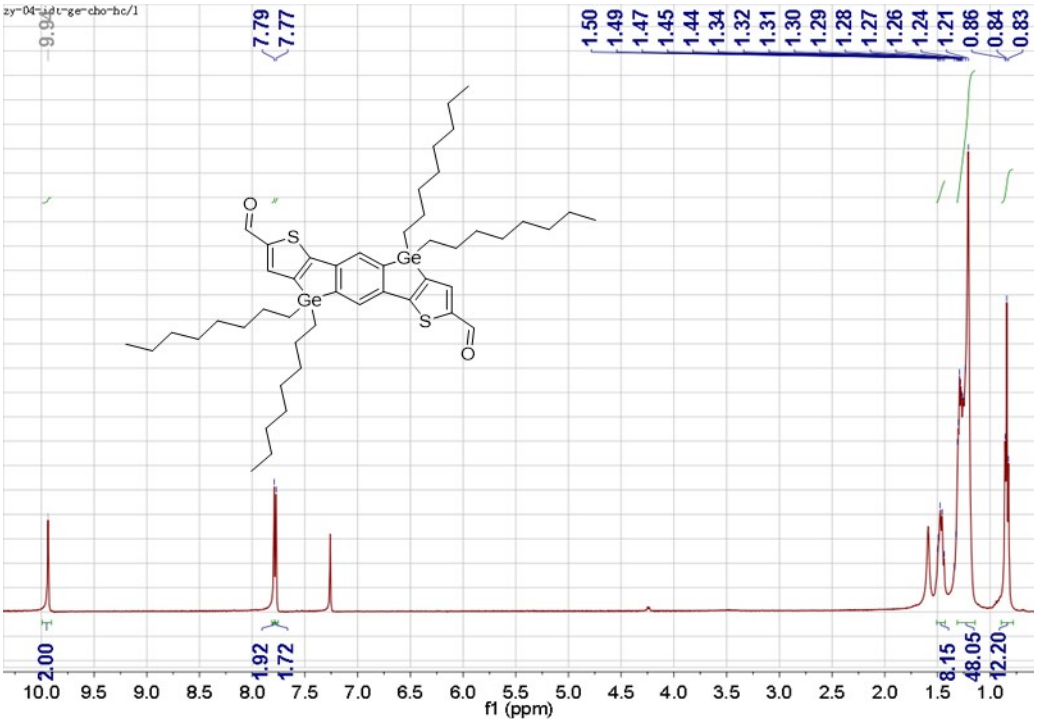

Fig. S10. ^{1}H NMR spectra of 2a.

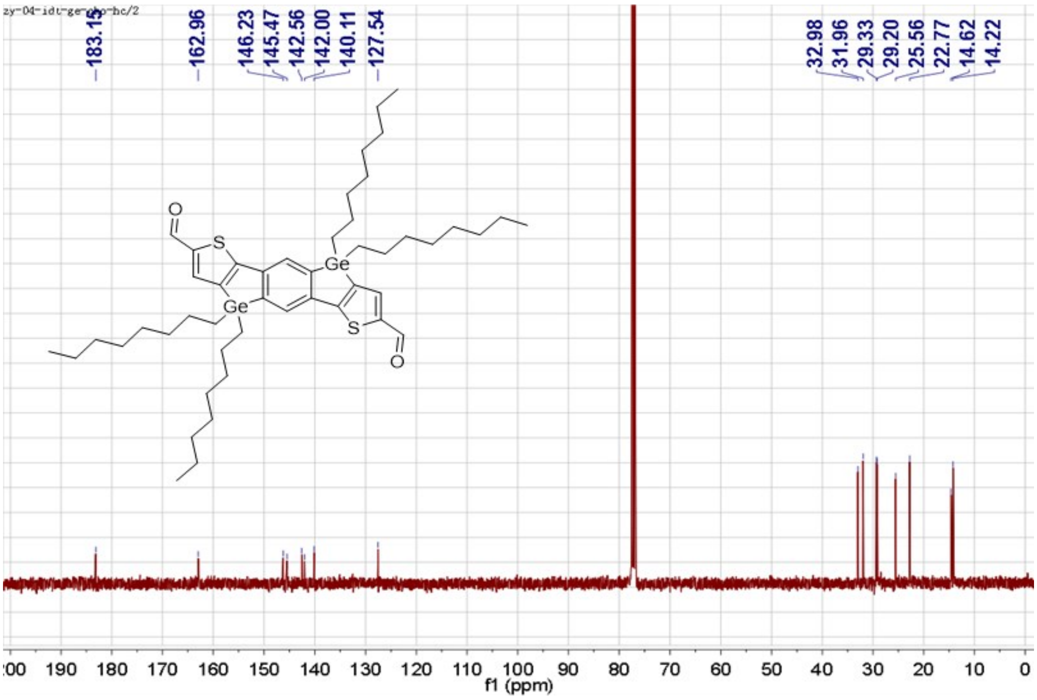

Fig. S11. ^{13}C NMR spectra of 2a.

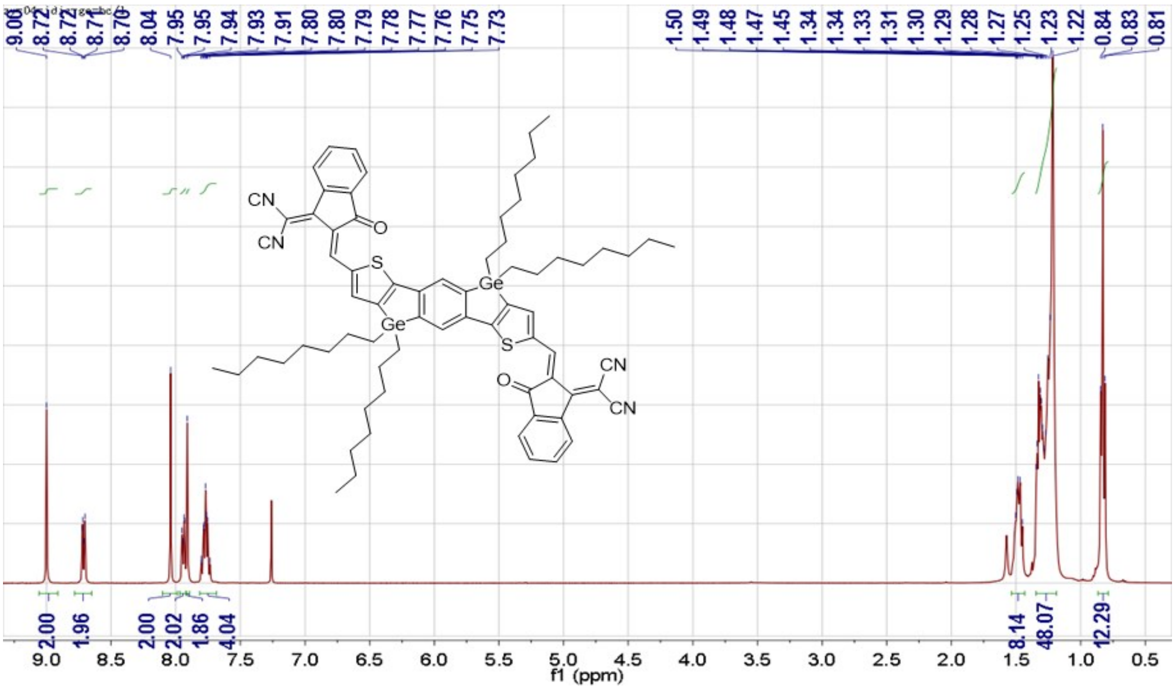

Fig. S12. ^{1}H NMR spectra of **GDIC-C8**.

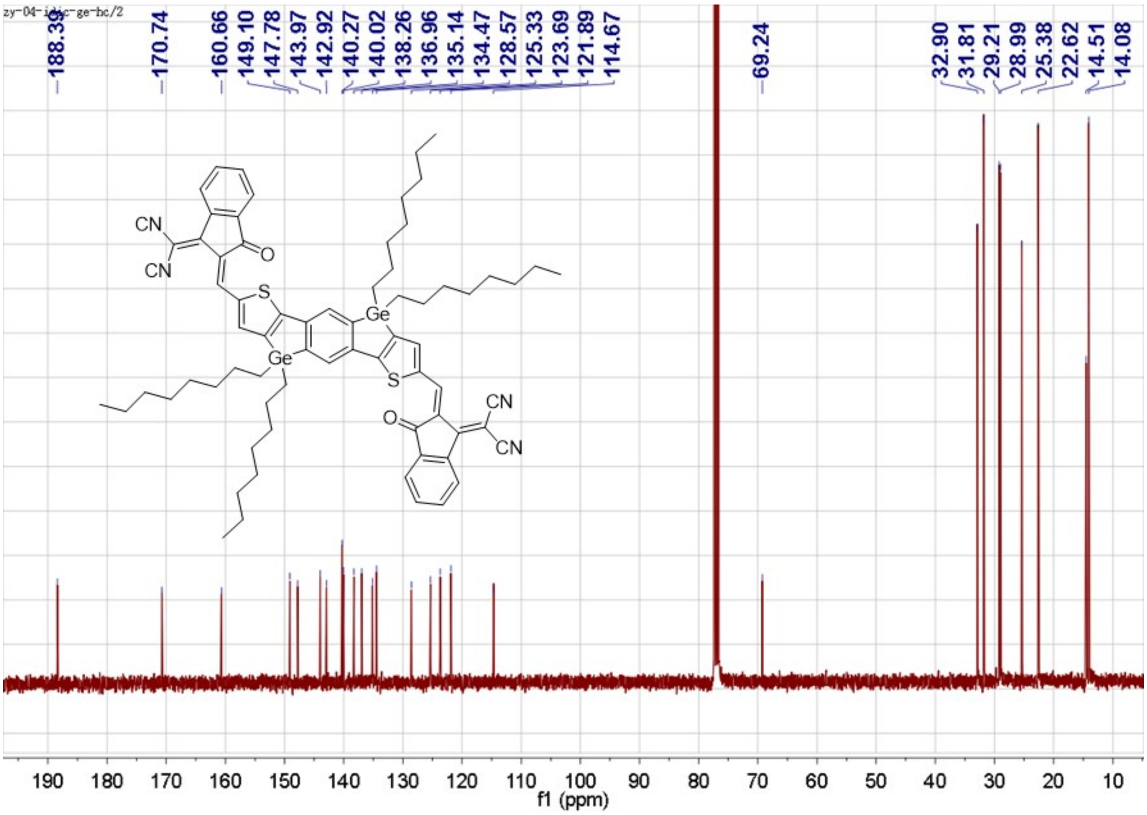

Fig. S13. ^{13}C NMR spectra of **GDIC-C8**.

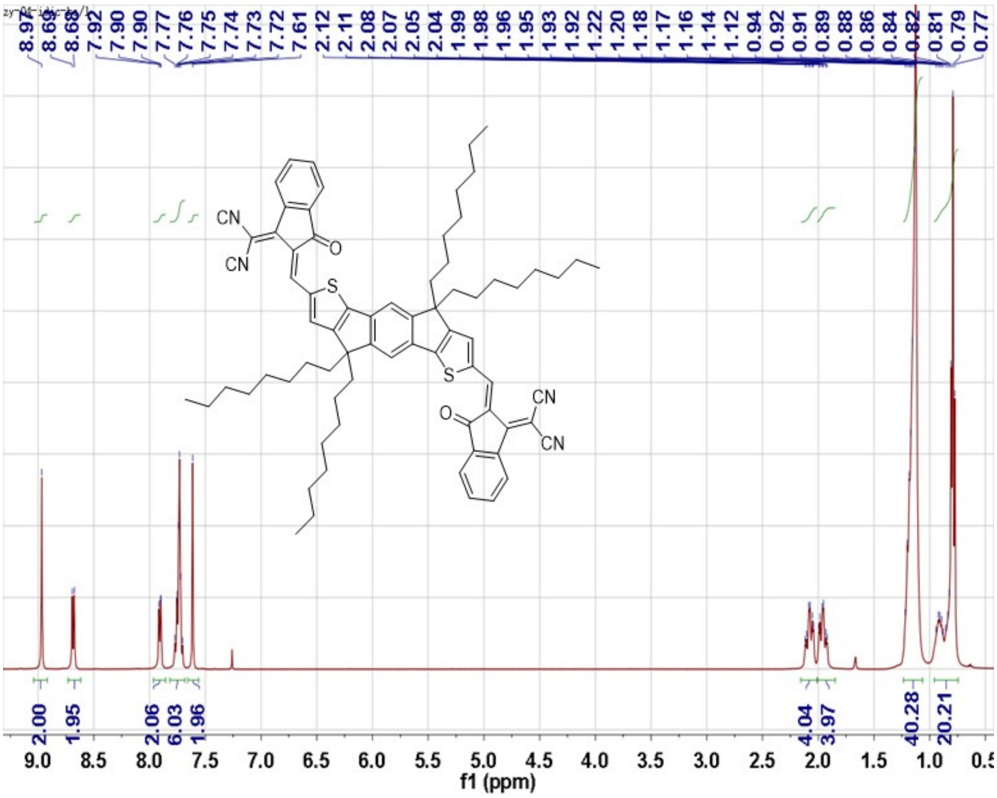

Fig. S14. ^{1}H NMR spectra of **IDIC-C8**.

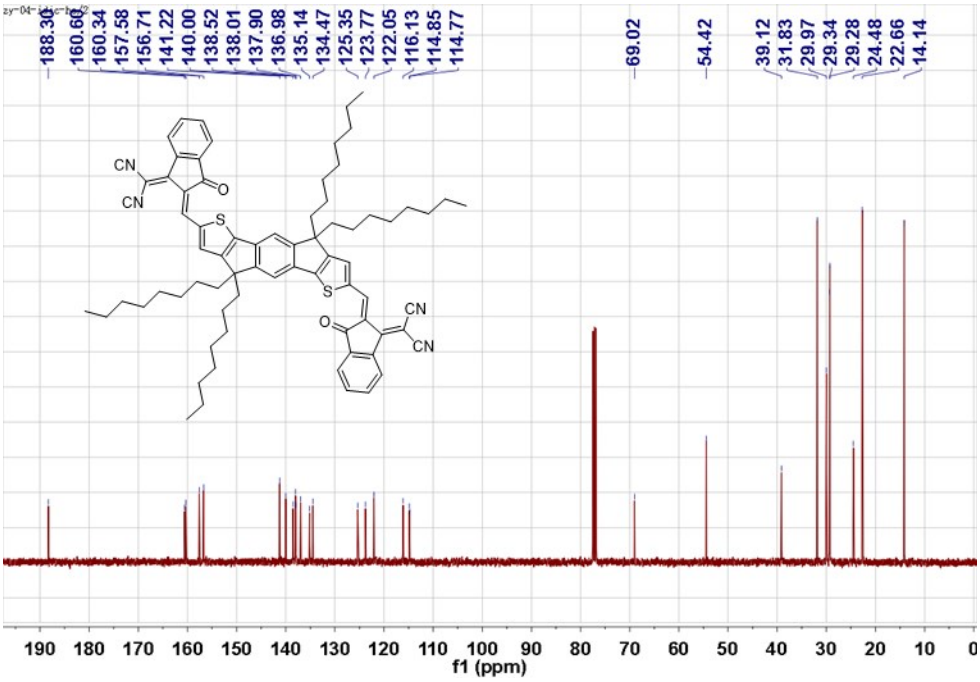

Fig. S15. ^{13}C NMR spectra of **IDIC-C8**.

References:

1. Z. Fei, R. S. Ashraf, Z. Huang, J. Smith, R. J. Kline, P. D'Angelo, T. D. Anthopoulos, J. R. Durrant, I. McCulloch and M. Heeney, Germaindacenodithiophene based low band gap polymers for organic solar cells, *Chem. Commun.*, 2012, **48**, 2955-2957.
2. Q. Fan, Y. Wang, M. Zhang, B. Wu, X. Guo, Y. Jiang, W. Li, B. Guo, C. Ye, W. Su, J. Fang, X. Ou, F. Liu, Z. Wei, T. C. Sum, T. P. Russell and Y. Li, High-Performance As-Cast Nonfullerene Polymer Solar Cells with Thicker Active Layer and Large Area Exceeding 11% Power Conversion Efficiency, *Adv. Mater.*, 2018, **30**, 1704546.