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Supporting information

Effect of Methyl thiophene-3-carboxylate Bridge in Indacenodithiophene-based Acceptor-Donor-Acceptor Type Molecule on the Performance of Non-fullerene Polymer Solar Cells

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Instrumentation

^{1}H and ^{13}C NMR spectra were recorded using a Bruker 500 MHz spectrometer (Ascend 500, Bruker) for structural analysis of all synthesized compounds. The absorption spectra of the small molecules and the polymer in chloroform solutions and thin films were recorded using a UV-vis absorption spectrometer (Agilent 8453, photodiode array, λ = 190–1100 nm). The samples in the film state were prepared by spin-coating 0.7 wt% chloroform solution of the compounds on clean glass substrates. The electrochemical properties were characterized by CV (eDAQ EA161) using an 0.1 M electrolyte solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile. Platinum wire and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. DFT calculations were performed by using Spartan 10 at the B3LYP/6-31G(d, p) level, and the long alkyl chain was simplified as methyl.

Grazing-incidence wide-angle X-ray diffraction (GIWAXD) was measured at the 9A (U-SAXS) beamline (energy = 11.055 keV, pixel size = 88.60 μm, λ=1.12148 Å, 2θ = 0–20°) at Pohang

Accelerator Laboratory (PAL). For these measurements, samples were prepared by spin-coating acceptor solutions and mixed solutions of PBDB-T and acceptor on a SiO_2 wafer. We explored the surface morphology of the film using an atomic force microscope (AFM, XE-100, Advanced Scanning Probe Microscope, PSIA) with a silicon cantilever. Samples were prepared as for GIWAXD measurements.

Transmission electron microscope (TEM) imaging was performed using a Tecnai G2F30 transmission electron microscope (FEI Inc., accelerating voltage = 300 kV) to investigate the internal morphology of the thin films made with mixtures of the PBDB-T polymer and low-molecular-weight acceptors. The samples were prepared by coating the mixed solution on a carbon coated copper lattice and drying.

Measurement of Space-charge-limited current (SCLC)

Hole-only devices, with the configuration of ITO/PEDOT:PSS/active layer/Au, and electron-only devices with the configuration of ITO/ZnO/active layer/LiF/Al, were fabricated. The hole and electron carrier mobilities were calculated using the modified Mott-Gurney equation, $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, where J is the current density, μ is the mobility, and V is the applied voltage, and the device thickness, L, is defined. Moreover, ε_0 is the vacuum permittivity and ε_r is the relative permittivity. The mobility was calculated from the slope of $J^{1/2}$-V plots.

PSC Fabrication

Inverted PSCs were fabricated in the form of ITO/ZnO/photoactive layer/MoO_3/Ag. The ITO-coated glass used as the electrode was washed successively with acetone, deionized water, and isopropyl alcohol (10 min each). The ZnO layer was spin-coated for 40 s at 3000 rpm on an ITO glass, which was pretreated for 20 min with UV-ozone, and then the ZnO thin film was annealed at 165 °C for 1 h.

Subsequently, the substrate was transferred to a N_2-protected glove box. Then, the active layer of the PSC was spin-coated on the ZnO layer using a 15 mg mL^{-1} chlorobenzene (CB) solution of PBDB-T:IDT-3MT blends (1:1 w/w). After stirring the combined solution overnight at 60 °C, it was spin-coated on the ITO/ZnO substrate at 3000 rpm for 40 s. Finally, MoO_3 (10 nm) and Ag (100 nm) were deposited on the photoactive layer by thermal evaporation. The *J–V* characteristics were measured using a Keithley 2400 source meter at 100 mW cm^{-2} (Oriel, 1000 W) under an AM 1.5 G illuminometer. The incident light intensity was measured using a calibrated broadband optical power meter (Spectra Physics, model 404). The EQE spectrum was recorded with a K3100 EQX instrument with a K240 XE300 lamp source.

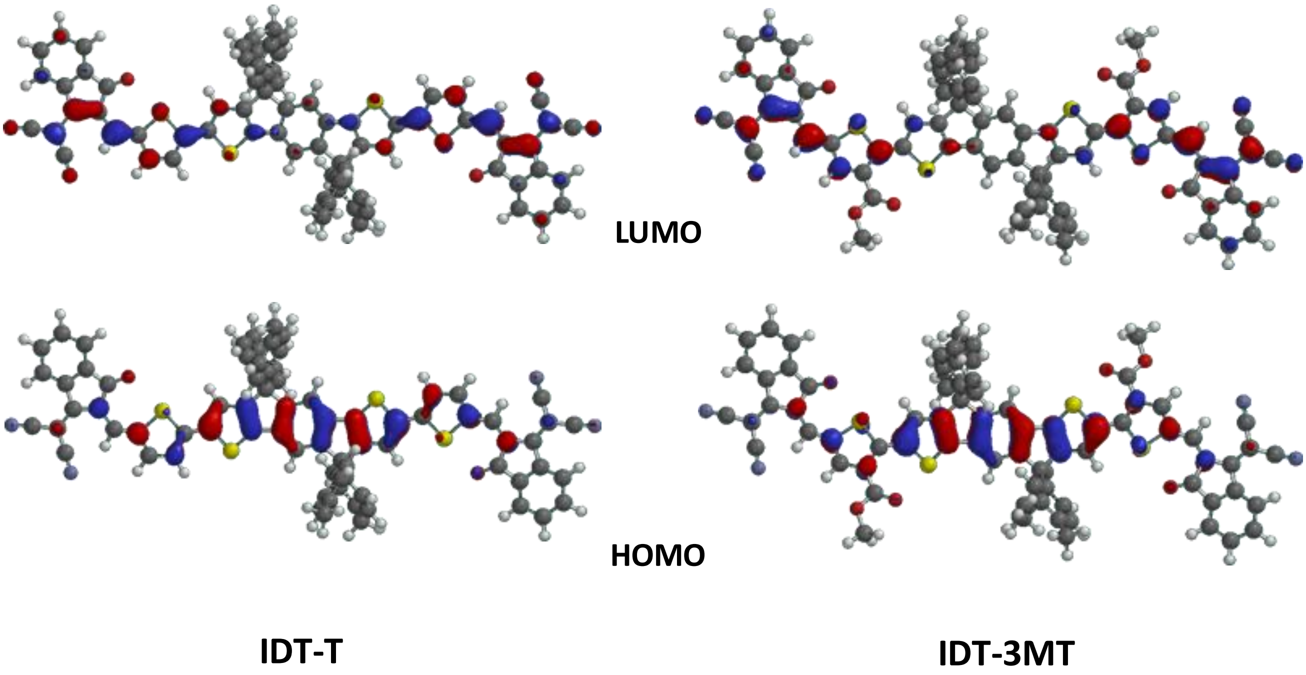

Fig. S1 Optimized molecular geometries and frontier molecular orbitals of **IDT-T** and **IDT-3MT** by DFT calculations.

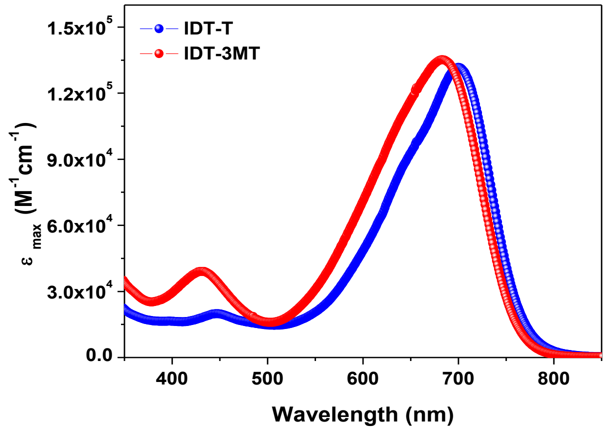

Fig. S2 UV-vis absorption coefficient spectra of the two acceptors in chloroform solutions.

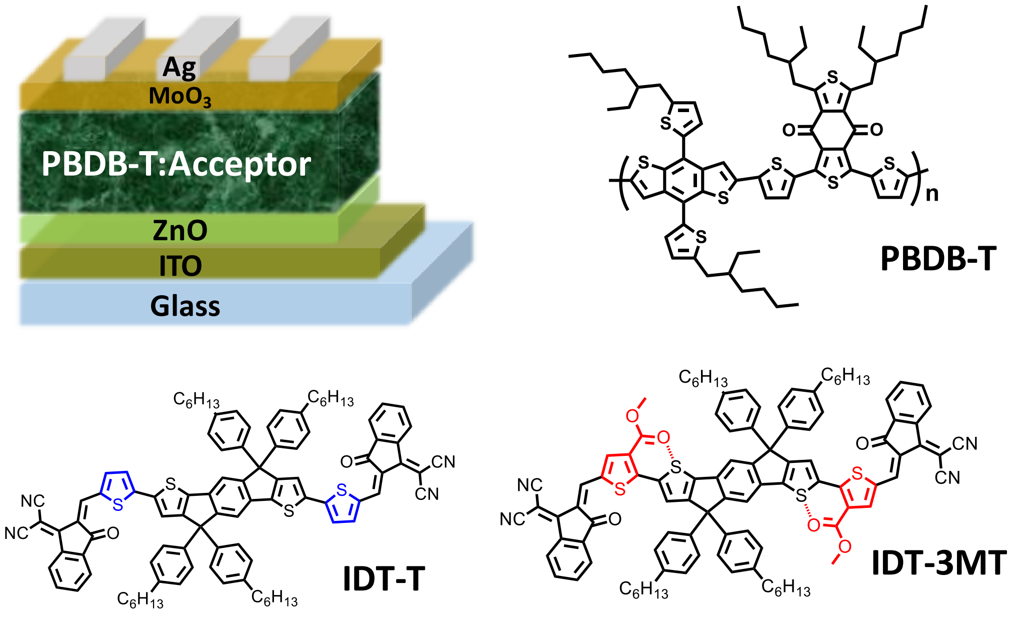

Fig. S3 Chemical structures of the donor polymer and acceptors. Device configuration of the inverted structure PSCs.

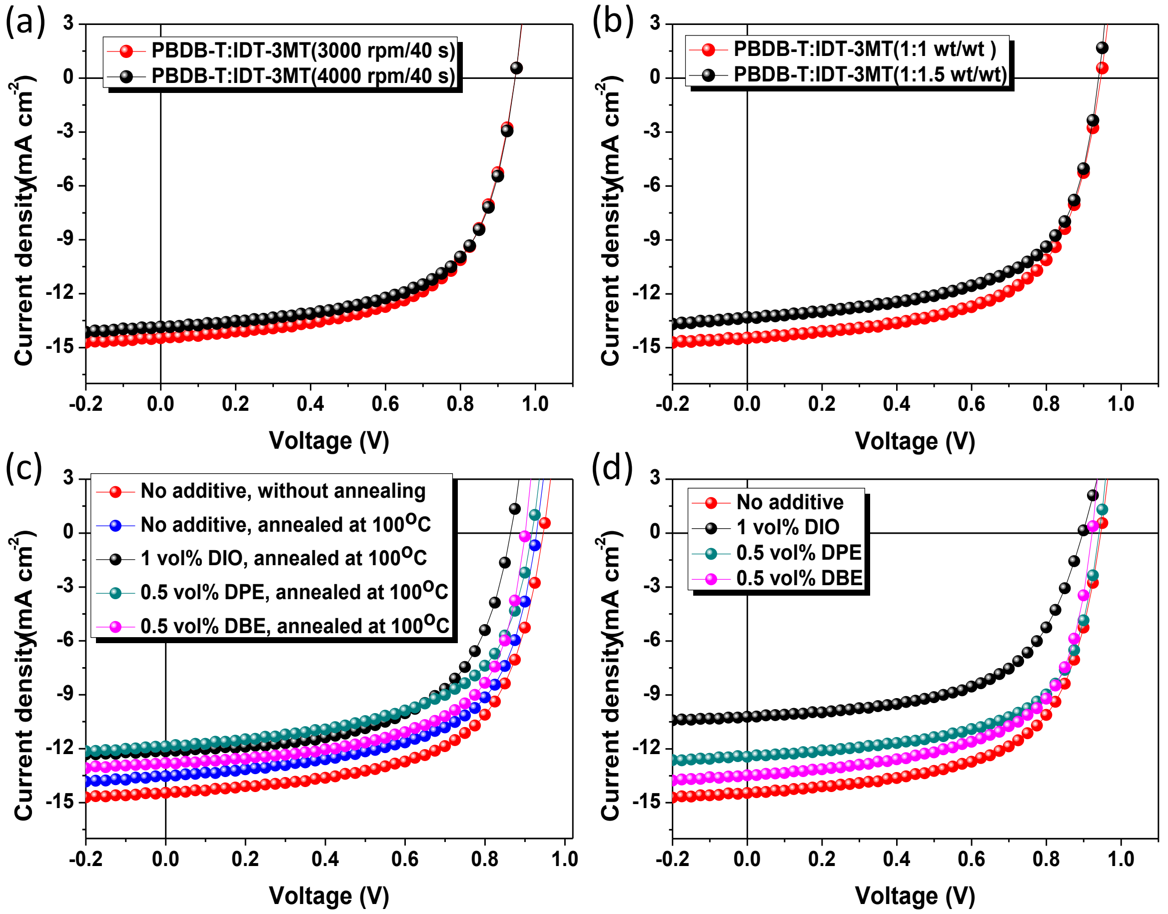

Fig. S4 *J*–*V* characteristics of **IDT-3MT**-based PSC devices under various conditions: (a) effect of thinkness, (b) effect of ratio, (c) effect of solvent additive with annealing and (d) effect of solvent additive without annealing. (DIO : 1,8-diiodooctane, CB : chlorobenzene, DPE : diphenyl ether, DBE : dibenzyl ether).

Table S1 *J–V* characteristics of **IDT-T** and **IDT-3MT** based PSC devices under various conditions.

Polymer:acceptor	Ratio(wt/wt)	Additive	Solvent	Annealing	V_{oc}(V)	J_{sc} (mA cm^{-2})	FF [%]	PCE [%]
PBDB-T:IDT-T	**1:1**	**-**	**CB**	**X**	**0.952**	**11.21**	**59.62**	**6.36**
PBDB-T:IDT-3MT	**1:1**	**-**	**CB**	**X**	**0.950**	**14.43**	**61.32**	**8.40**
PBDB-T:IDT-3MT	**1:1**	**DIO 1.0 vol%**	**CB**	**X**	**0.897**	**10.20**	**57.87**	**5.30**
PBDB-T:IDT-3MT	**1:1**	**DIO 1.0 vol%**	**CB**	**100 ºC**	**0.864**	**12.12**	**58.73**	**6.15**
PBDB-T:IDT-3MT	**1:1.5**	**-**	**CB**	**X**	**0.939**	**13.33**	**61.26**	**7.67**
PBDB-T:IDT-3MT	**1:1**	**DPE 0.5 vol%**	**CB**	**X**	**0.940**	**12.40**	**62.60**	**7.30**
PBDB-T:IDT-3MT	**1:1**	**DPE 0.5 vol%**	**CB**	**100 ºC**	**0.920**	**11.84**	**58.03**	**6.30**
PBDB-T:IDT-3MT	**1:1**	**DBE 0.5 vol%**	**CB**	**X**	**0.920**	**13.46**	**61.22**	**7.60**
PBDB-T:IDT-3MT	**1:1**	**DBE 0.5 vol%**	**CB**	**100 ºC**	**0.901**	**12.81**	**62.01**	**7.16**

*All active layers in PSCs were prepared by spin coating at 3000 rpm for 40 seconds.

Table S2 *J–V* characteristics of **IDT-T** and **IDT-3MT** based PSC devices under thickness conditions

Polymer:acceptor	Rpm	Ratio(wt/wt)	Solvent	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF [%]	PCE [%]	Thickness (nm)
PBDB-T:IDT-3MT	3000rpm/40s	1:1	CB	0.950	14.43	61.32	8.40	90
PBDB-T:IDT-3MT	4000rpm/40s	1:1	CB	0.946	13.85	62.31	8.16	82

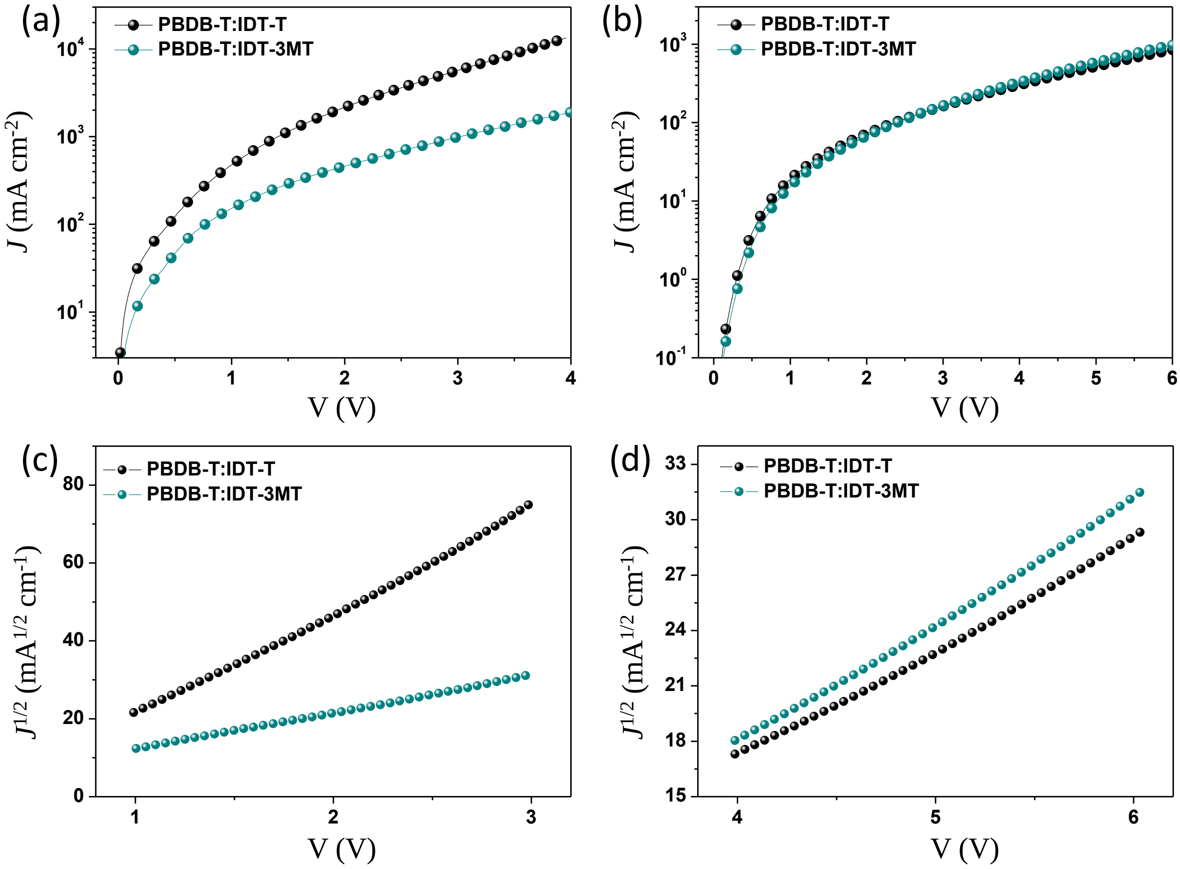

Fig. S5 Space-charge-limited current *J*–*V* characteristics and corresponding $J^{1/2}$-*V* plots of the blend films under dark conditions for (a), (c) hole-only devices and (b), (d) electron-only devices.

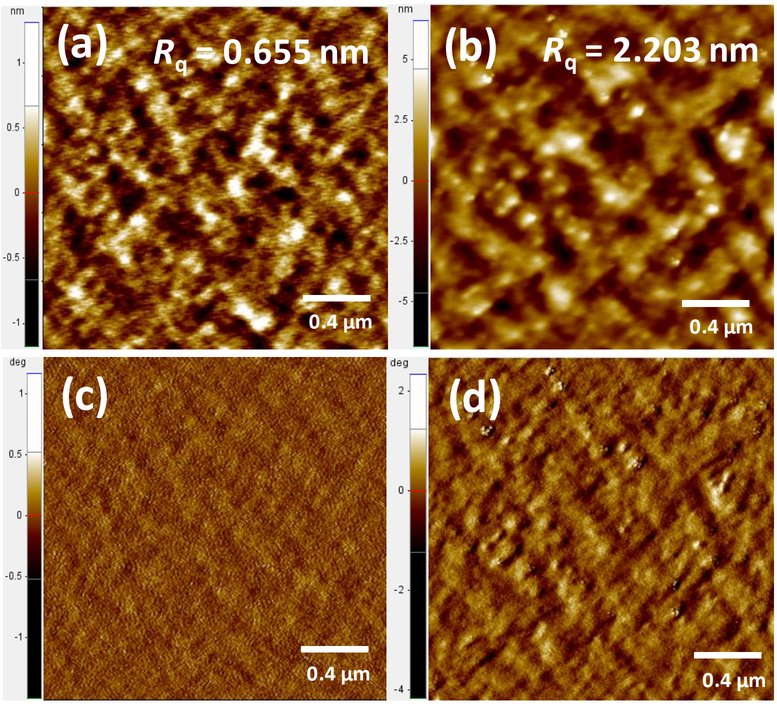

Fig. S6 AFM (a,b) height images and (c,d) phase images (2 µm × 2 µm) of the optimized PBDB-T:**IDT-3MT** blend films (1:1 w/w) prepared in chlorobenzene. (a,c) PBDB-T:**IDT-3MT** without additive and (b,d) PBDB-T:**IDT-3MT** with 1 vol% DIO.

Table S3 lists the structure parameters of the **IDT-T** and **IDT-3MT** in the pristine films and in the blend films with acceptors obtained from the GIWAXD measurements

	Out-of-plane (010)		**In-plane (100)**	
	q **(Å^{-1})**	***d*****-spacing(Å)**	***q*** **(Å^{-1})**	***d*****-spacing(Å)**
PBDB-T	1.67	3.73	0.29	21.78
IDT-T	1.76	3.52	0.32	19.47
IDT-3MT	1.76	3.52	0.33	19.30
PBDB-T:IDT-T	1.74	3.56	0.28	21.96
PBDB-T:IDT-3MT	1.77	3.50	0.29	21.45

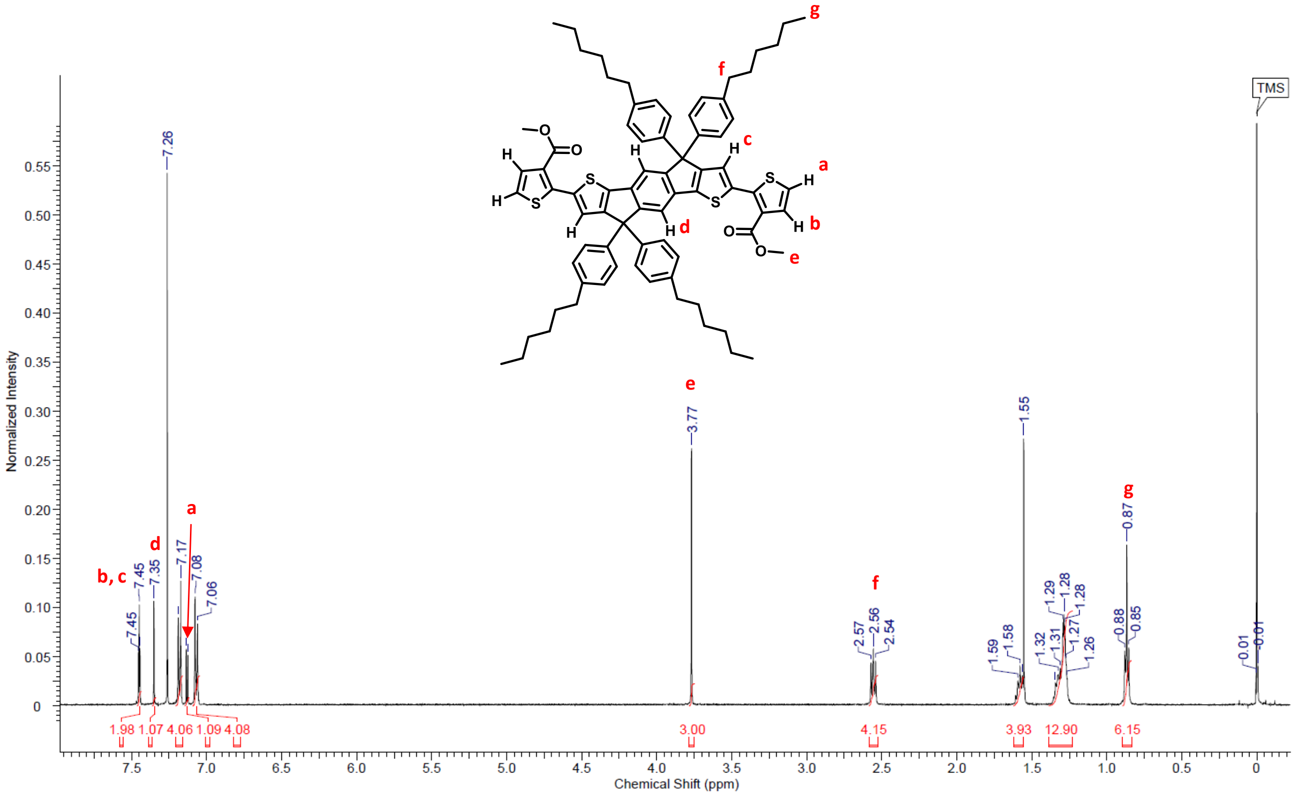

Fig. S7 ^{1}H NMR spectrum of **Compound 3** in $CDCl_3$.

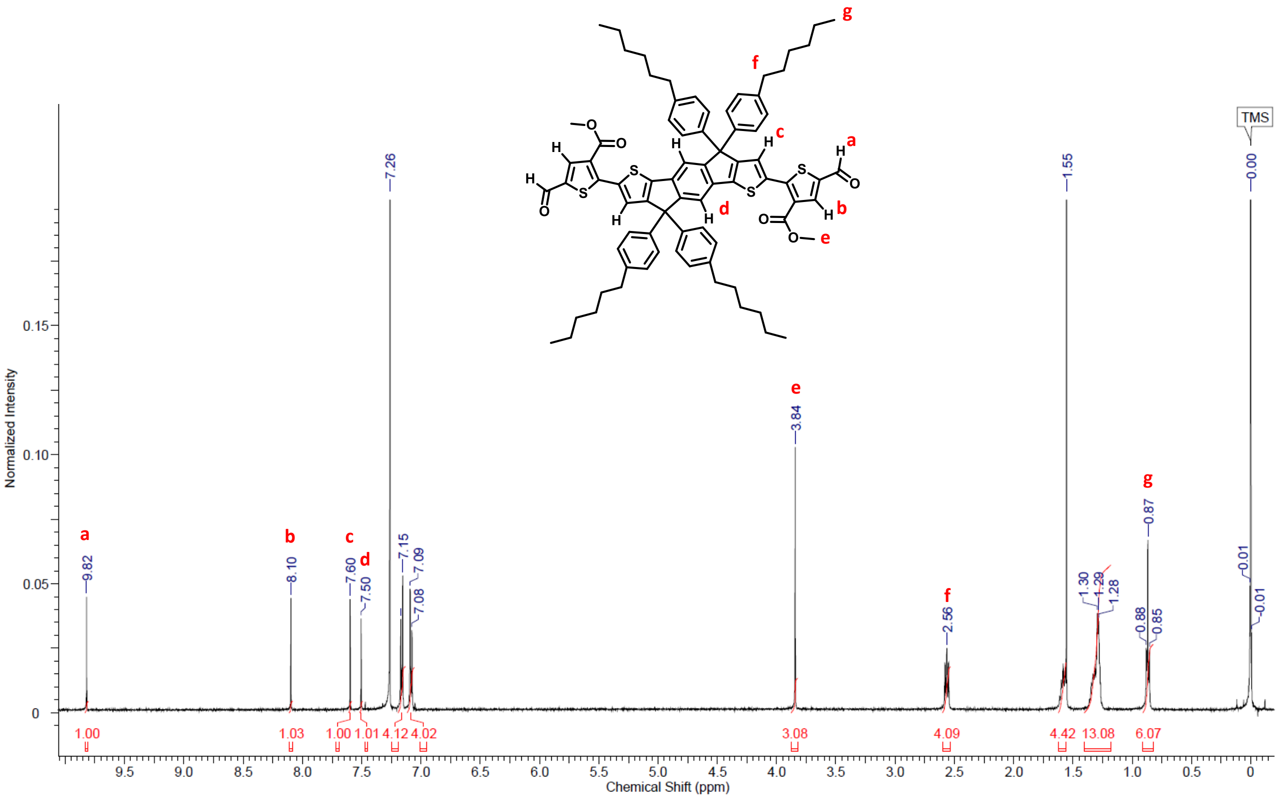

Fig. S8 ^{1}H NMR spectrum of **Compound 4** in $CDCl_3$.

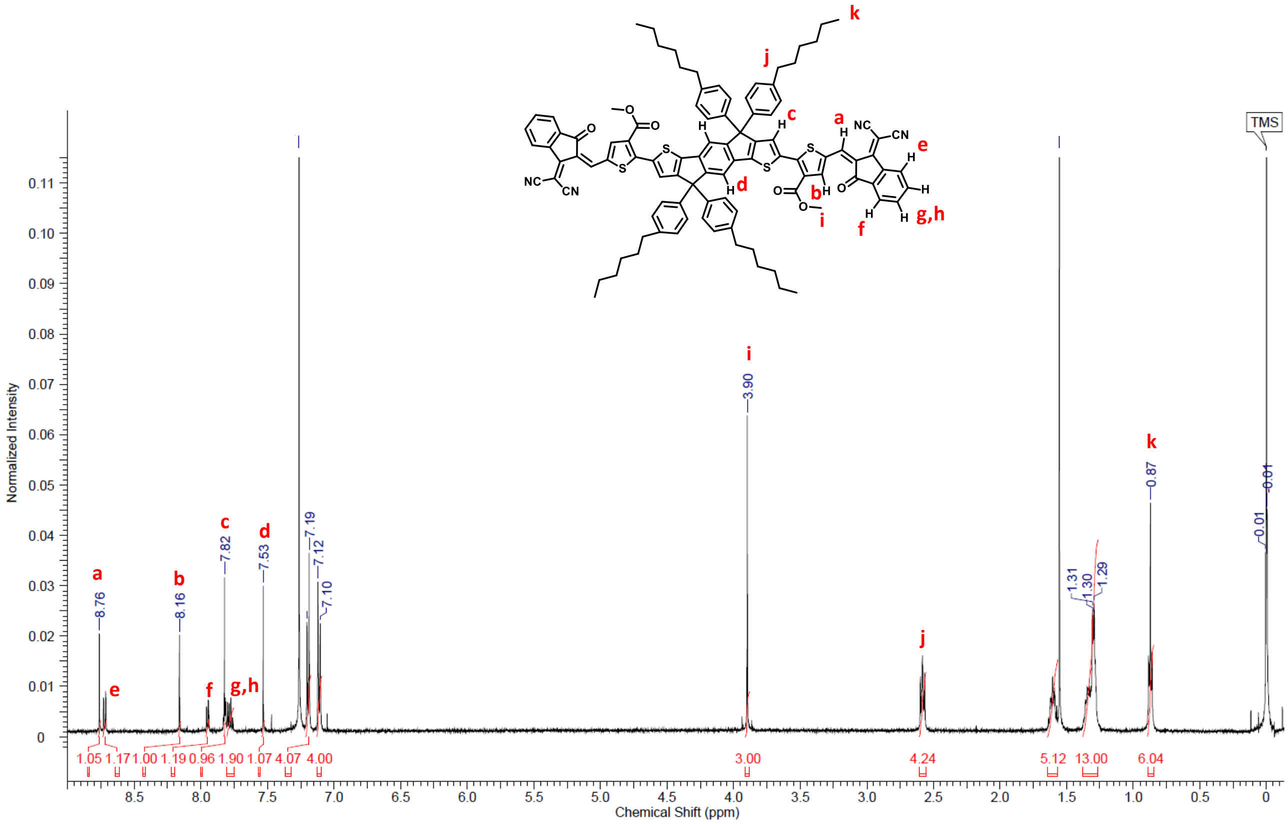

Fig. S9 ^{1}H NMR spectrum of **IDT-3MT** (**Compound 6**) in $CDCl_3$.