

Supporting Information

Multifunctional Asymmetrical Molecules for High-Performance Perovskite and Organic Solar Cells

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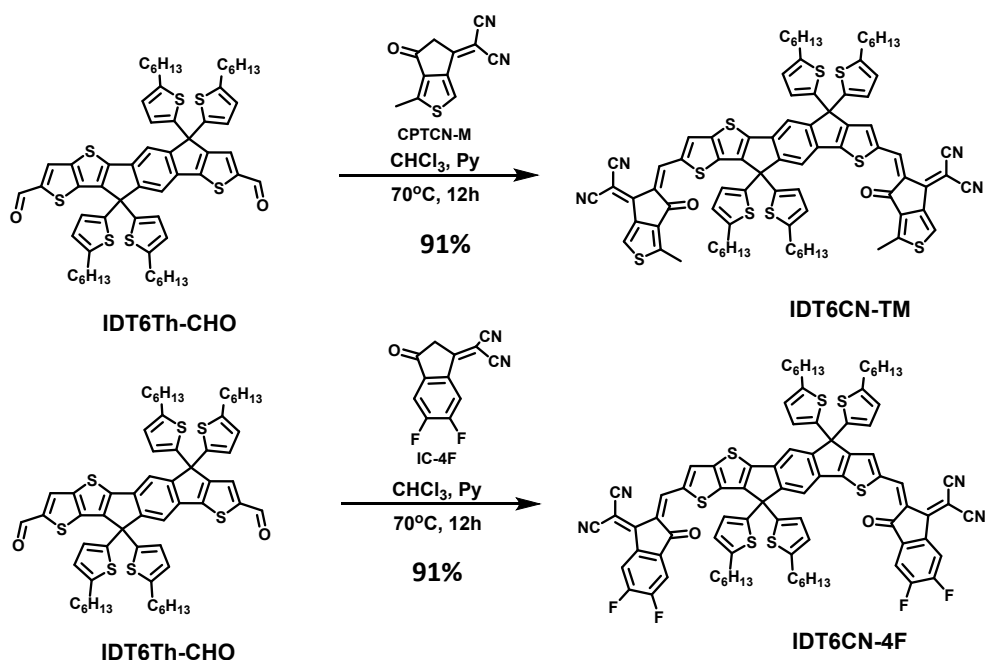
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Materials and synthesis

Compounds IDT6Th-CHO,¹ CPTCN-M² and polymer PM-6³ were synthesized according to the previous work. Other materials were purchased from commercial sources, including IC-4F (Derthon, 98%), P3CT (Rieke Metals), PbI₂ (*p*-OLED, >99.99%), MAI (*p*-OLED, ≥99.5%), PCBM (*p*-OLED, ≥99%), C₆₀ (*p*-OLED), BCP (*p*-OLED), DMF (Sigma-Aldrich, 99.8 %), DMSO (Sigma-Aldrich, 99.8 %) and CB (Sigma-Aldrich, 99.8 %).



Scheme 1. The synthetic routes of IDT6CN-TM and IDT6CN-4F.

Synthesis of compound IDT6CN-TM: To a 100 ml round bottom flask, compound IDT6Th-CHO (104 mg, 0.1 mmol), CPTCN-M (86 mg, 0.4 mmol), chloroform (30 ml) were added under argon protection, and then stirred for a while when pyridine (0.5 ml) was added. The mixture was kept stirring at 70°C for 12 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (130 mg, 91%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.84 (s, 1H), 8.78 (s, 1H), 8.24 (s, 1H), 8.13 (s, 1H), 8.12 (s, 1H), 7.96 (s, 1H), 7.80 (s, 1H), 7.77 (s, 1H), 6.89 (d, *J* = 3.6 Hz, 2H), 6.78 (d, *J* = 3.6 Hz, 2H), 6.62 (d, *J* = 3.6 Hz, 2H), 6.59 (d, *J* = 3.6 Hz, 2H), 2.80 (s, 3H), 2.79 (s, 3H), 2.73 (t, *J* = 8.0 Hz, 8H), 1.61-1.67 (m, 8H), 1.24-1.38 (m, 24H), 0.82-0.88 (m, 12H);

^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 181.43, 180.90, 166.55, 157.45, 155.30, 154.86, 154.61, 154.59, 154.27, 151.02, 145.95, 145.28, 145.14, 144.96, 143.78, 143.68, 142.67, 141.40, 140.90, 140.86, 139.82, 139.64, 138.87, 138.08, 137.70, 137.62, 135.78, 135.71, 135.11, 133.79, 131.17, 129.66, 128.78, 127.94, 127.56, 125.05, 124.22, 124.01, 123.90, 122.38, 122.05, 118.19, 117.05, 113.75, 113.71, 113.20, 113.12, 66.90, 66.23, 65.98, 55.67, 55.56, 30.25, 30.24, 30.13, 30.11, 29.02, 28.99, 27.67, 27.61, 21.29, 12.83; MALDI-TOF-MS m/z : $[\text{M}]$ calcd. for $\text{C}_{82}\text{H}_{74}\text{N}_4\text{O}_2\text{S}_9$, 1434.33, found 1434.51.

Synthesis of compound IDT6CN-4F: To a 100 ml round bottom flask, compound IDT6Th-CHO (104 mg, 0.1 mmol), IC-4F (92 mg, 0.4 mmol), chloroform (30 ml) were added under argon protection, and then stirred for a while when pyridine (0.5 ml) was added. The mixture was kept stirring at 70°C for 12 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (133 mg, 91%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.94 (s, 1H), 8.90 (s, 1H), 8.55-8.57 (m, 2H), 8.26 (s, 1H), 7.98 (s, 1H), 7.88 (s, 1H), 7.79 (s, 1H), 7.69-7.73 (m, 2H), 6.88 (d, $J = 3.6$ Hz, 2H), 6.79 (d, $J = 3.6$ Hz, 2H), 6.62 (d, $J = 3.6$ Hz, 2H), 6.60 (d, $J = 3.6$ Hz, 2H), 2.73 (t, $J = 8.0$ Hz, 8H), 1.61-1.67 (m, 8H), 1.24-1.37 (m, 24H), 0.82-0.91 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 186.15, 185.81, 159.37, 158.19, 156.95, 156.39, 155.95, 155.82, 155.69, 153.37, 153.32, 153.23, 152.98, 147.44, 147.06, 146.53, 146.44,

146.40, 144.12, 142.45, 140.92, 140.90, 140.09, 139.71, 138.79, 138.52, 137.28, 137.24, 136.63, 135.05, 134.55, 126.34, 126.06, 123.63, 123.37, 122.28, 121.63, 119.62, 118.52, 115.18, 114.97, 114.20, 114.16, 114.10, 114.05, 112.89, 112.69, 70.32, 70.10, 56.97, 56.86, 56.48, 31.59, 31.52, 31.50, 31.39, 30.29, 30.25, 28.93, 28.88, 22.55, 14.13, 14.10; MALDI-TOF-MS m/z: [M] calcd. for C₈₄H₇₀F₄N₄O₂S₇, 1466.35, found 1466.48.

Measurements

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advanced II (400 MHz) spectrometer using *d*-chloroform as solvent. The matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) were measured on 5800 MALDI-TOF/TOF mass spectrometry (AB SCIEX, USA) in positive mode. UV-vis spectra were obtained by using a Shimadzu UV-2500 recording spectrophotometer. Cyclic voltammetry (CV) measurements of thin films were conducted on a CHI voltammetric analyzer in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) as supporting electrolyte at room temperature by using a scan rate of 100 mV s⁻¹ and conventional three-electrode. The morphology of perovskite films were characterized by FE-SEM images (JSM-7800F). AFM images were collected in air on a Bruker AFM using a tapping mode. Steady-state PL spectra were recorded on a Hitachi F-4600 FL Spectrophotometer. Time-resolved PL decay curves were measured by a single photon counting spectrometer from Edinburgh Instruments.

PVKSCs device fabrication

The patterned ITO-coated glass were sequentially washed by sonication using detergent, deionized water, ethanol and acetone. On the ITO substrates, a hole transporting layer P3CT-Na⁴ was spin-coated at 4000 rpm for 60 s followed by annealing at 140 °C for 30 min. Then the P3CT-Na-coated substrates were transferred into a N₂-filled glovebox for further use. A CH₃NH₃PbI₃ precursor solution (1.4 M in DMF:DMSO mixed solution with a v/v of 4:1) was spin-coated onto the substrates in a two-step program at 400 and 5000 rpm for 3 and 30 s, respectively. During the second step, 200 μL of chlorobenzene was poured on the spinning substrate at 10 s after the start-up. Next, the as-spun perovskite layer was annealed on a hot plate at 60 °C for 1 min and at 80 °C for 2 min to remove the solvent and form the perovskite phase. Then, PCBM, IDT6CN-TM or IDT6CN-4F solutions in chlorobenzene were spin-coated onto the perovskite layer. To fabricate ITO/P3CT-Na/Perovskite/ETL/BCP/Ag device, subsequently a thin buffer layer BCP and an approximately 100 nm thick Ag counter electrode were evaporated under high vacuum sequentially. To fabricate ITO/P3CT-Na/Perovskite/ETL/C₆₀/BCP/Ag device, C₆₀ (20 nm) and BCP (8 nm) were evaporated under high vacuum on top of the ETL sequentially. Finally, a 100 nm thick Ag electrode was deposited through a shadow mask. The active area of our device is 0.09 cm². The current–voltage (*J-V*) curves were measured under 100 mW cm⁻² (AM 1.5 G) simulated sunlight using Keithley 2400 in conjunction with a Newport solar simulator (94043A). The external quantum

efficiency (EQE) was calculated from the photocurrent measurement under monochromatic illuminations at different wavelengths, using a 150 W xenon lamp and a monochromator.

OSCs device fabrication

Non-fullerene polymer solar cells were fabricated with a device structure of ITO/PEDOT:PSS/active layer/ZrAcac/Al. The patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 20 min to improve its work function and clearance. A thin PEDOT: PSS (Heraeus Clevios P VP A 4083) layer with a thickness of about 40 nm was spin-cast onto the ITO substrates at 4000 rpm for 40 s, and then dried at 150 °C for 10 min in air. The PEDOT:PSS coated ITO substrates were fast transferred into a N₂-filled glovebox for further processing. The donor:acceptor blends with weight ratio of 1:1 and total concentration of 14 mg/mL were dissolved in chloroform and 0.25% DIO was added. Then the solution was stirred overnight for intensive mixing in a nitrogen-filled glovebox. The blend solution was spin-cast on the top of PEDOT: PSS layer at 2700 rpm for 40 s. Then it was annealed at 100 °C for 5 min to remove the residual solvent. Subsequently, the active layer coated substrates were quickly transferred to a glovebox integrated thermal evaporator for electrode deposition. A thin ZrAcac layer and Al layer (100 nm) were sequentially evaporated under vacuum of 5×10^{-5} Pa

through a shadow mask. The active area of each device was 5.90 mm² controlled by a shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was about 100 nm. The current-voltage (J - V) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. Photocurrent was measured under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator in an Air. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

SCLC measurements

The electron mobility of IDT6CN-TM and IDT6CN-4F neat films were measured by using the method of space-charge limited current (SCLC). The electron-only SCLC device was a stack of ITO/ZnO/active layer/ZrAcac/Al, The electron-only SCLC devices fabricating methods were same with those for solar cells. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

GIWAXS measurements

GIWAXS measurement was performed at beamline 7.3.3 at the Advanced Light Source of Lawrence Berkeley National Lab (LBNL). The 10 K eV X-ray beam was incident at a grazing angle of 0.12° - 0.16° to obtain optimal signal-to-background ratio. The scattered X-ray signals were detected by using a Dectris Pilatus 2M photon counting detector. The whole experiments were carried out in helium atmosphere.

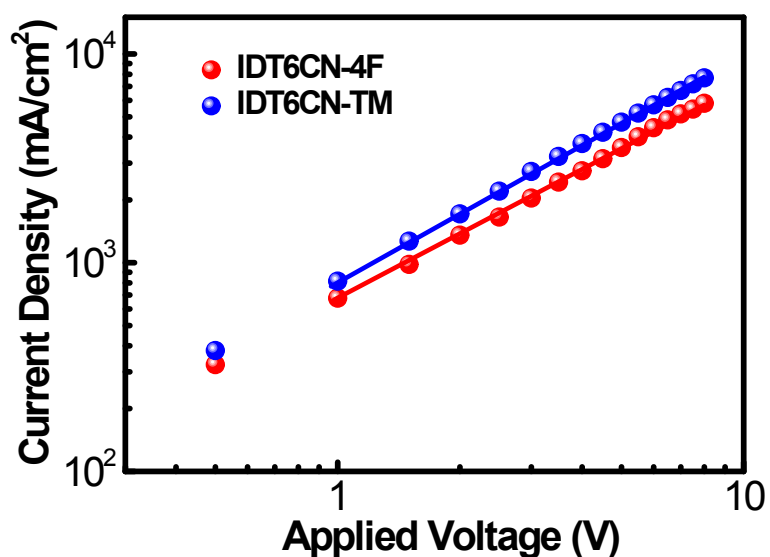


Fig. S1 The J - V characteristics of IDT6CN-TM and IDT6CN-4F pure films in space-charge-limited current (SCLC) devices.

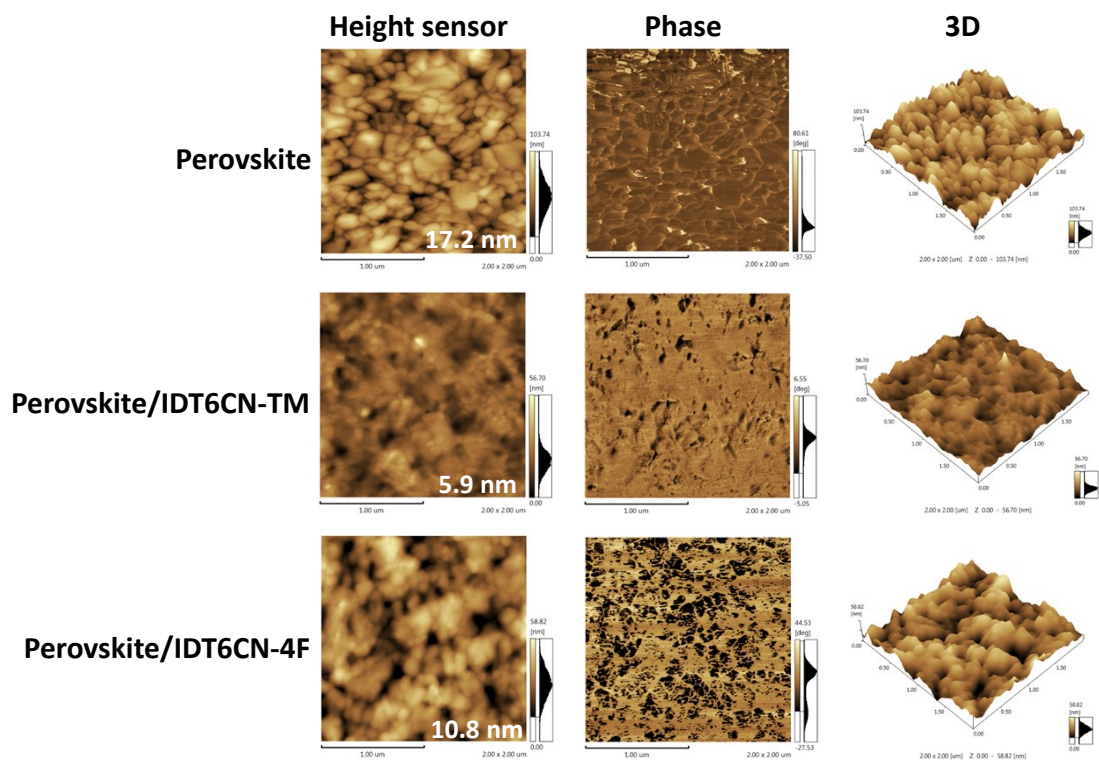


Fig. S2 The AFM height sensor, phase and 3D images of perovskite, perovskite/IDT6CN-TM and perovskite/IDT6CN-4F.

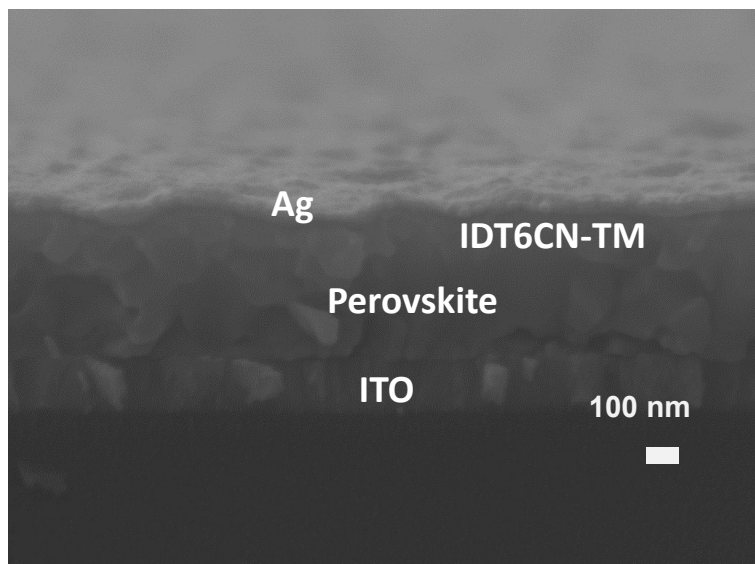


Fig. S3 Cross-sectional SEM images of inverted perovskite solar cells with the device structure of ITO/P3CT-Na/Perovskite/IDT6CN-TM/BCP /Ag.

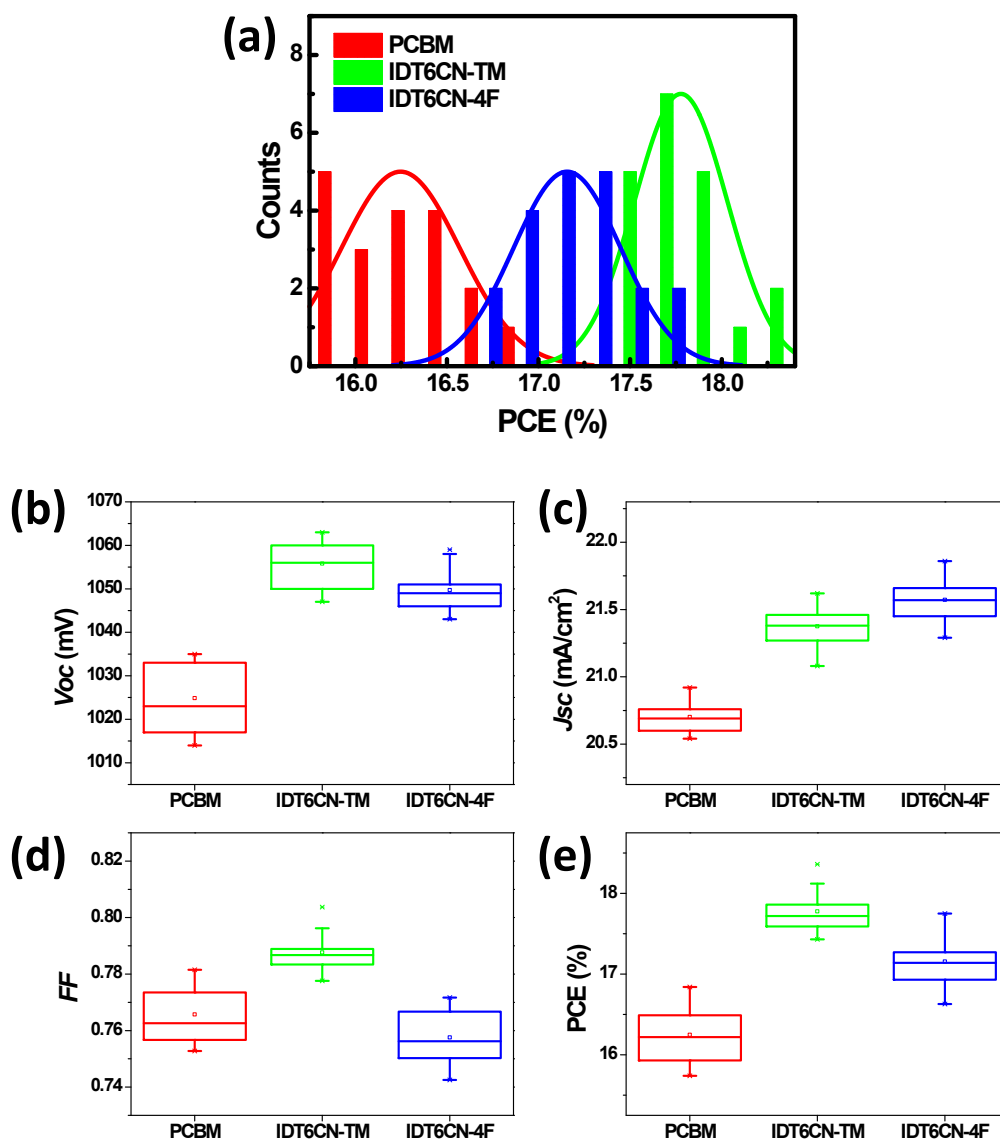


Fig. S4 a) The PCE distributions of perovskite solar cells with PCBM, IDT6CN-TM and IDT6CN-4F as ETMs. b-e) The corresponding photovoltaics parameters statistic.

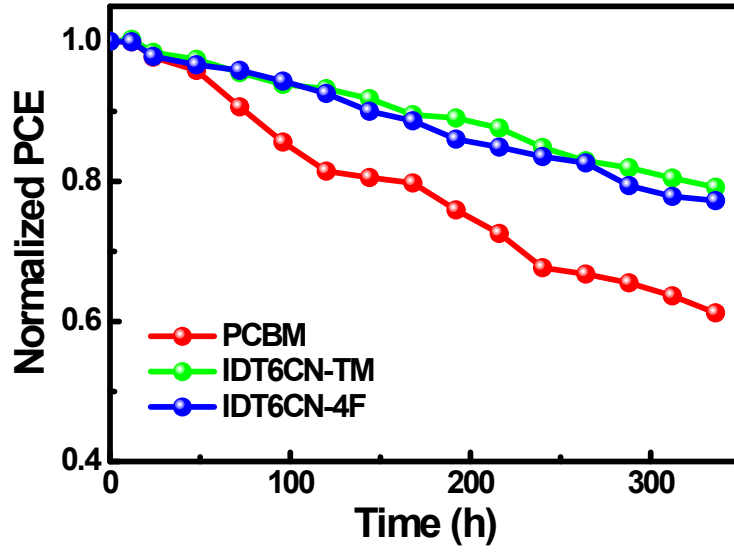


Fig. S5 Stability of the inverted PSCs under ambient conditions with controlled humidity.

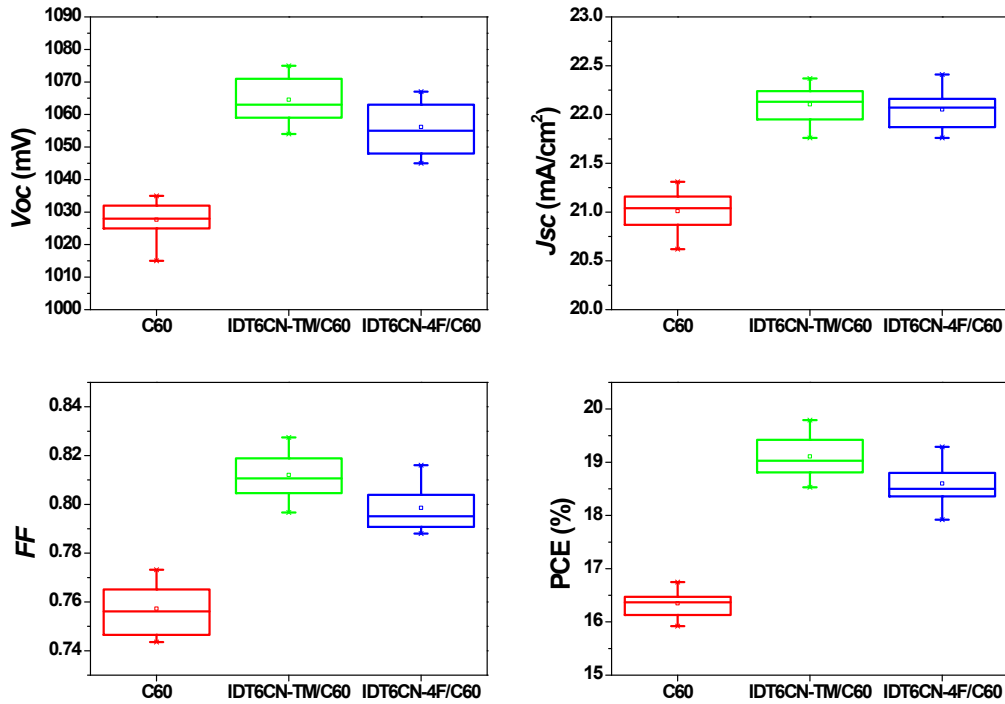


Fig. S6 Photovoltaics parameters statistic for PVKSCs with IDT6CN-TM and IDT6CN-4F as interfacial layers between perovskite and C₆₀ ETL.

Table S1 The photovoltaic performance of PVKSCs with IDT6CN-TM and IDT6CN-4F as ETMs in different thicknesses.

ETL	Thickness (nm)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
IDT6CN-TM	25	1051	21.48	78	17.57
	33	1062	21.51	80	18.36
	41	1038	21.12	81	17.65
	49	1033	20.71	78	16.69
IDT6CN-4F	23	1056	21.65	76	17.44
	37	1058	21.74	77	17.75
	43	1033	21.39	77	16.97
	52	1032	20.78	75	16.04

Table S2. Full comparison of photovoltaic performance between IDT6CN-TM and IDT6CN-4F and other reported molecules.

ETM	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
IDT6CN-TM	1062	21.51	80	18.36	this work
IDT6CN-4F	1058	21.74	77	17.75	this work
PCBM	1030	20.90	75	16.20	5
SFX-PDI4	1080	19.90	71	15.30	6
TPE-PDI4	1013	21.68	74	16.29	7
3	-	-	-	18.00	8
B2F	927	19.05	69.9	12.35	9
HATNASOC7-C _s	1080	20.73	78.6	17.62	10
HATNT	1070	21.83	77.8	18.10	5
ITCPTC-Th	1029	21.77	76	17.11	11
ITCPTC-Se	1030	21.24	74	16.12	11
ILM					
IDT6CN-TM	1072	22.31	83	19.79	this work
IDT6CN-4F	1065	22.23	80	19.29	this work
IDIC	1110	22.96	76.5	19.50	12
INIC-2F	1010	23.10	82.7	19.30	13
ITCPTC-Th	1064	22.54	78	18.75	11
ITCPTC-Se	1053	22.32	79	18.62	11
B2F	1052	20.63	79.15	17.18	9
TPE-PDI4	1052	21.98	81	18.78	7

NF-SMAs					
IDT6CN-TM	953	17.40	74.7	12.40	this work
IDT6CN-4F	859	18.34	69.1	10.88	this work
ITIC-Th	880	16.24	67.1	9.60	14
ITIC-Th1	849	19.33	73.7	12.1	15
ITCPTC-Th	856	17.05	72.7	10.61	16
IDT6CN-Th	810	16.75	76.7	10.41	1
ITIC-Th-S	860	12.3	60.5	6.40	17
ITIC-Th-O	850	12.5	61.2	6.5	17

Table S3. The photovoltaic performance of PVKSCs with PCBM, IDT6CN-TM and IDT6CN-4F as ETMs scanning from forward and reverse directions.

ETL		V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PCBM	forward	1030	20.84	78	16.70
	reverse	1033	20.86	78	16.84
IDT6CN-TM	forward	1060	21.47	80	18.15
	reverse	1062	21.51	80	18.36
IDT6CN-4F	forward	1053	21.75	77	17.55
	reverse	1058	21.74	77	17.75

Table S4. The photovoltaic performance of PVKSCs with IDT6CN-TM and IDT6CN-4F as ILMs scanning from forward and reverse directions.

		V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
IDT6CN-TM/C ₆₀	forward	1068	22.29	82	19.54
	reverse	1072	22.31	83	19.79
IDT6CN-4F/C ₆₀	forward	1060	22.18	81	19.06
	reverse	1065	22.23	81	19.29

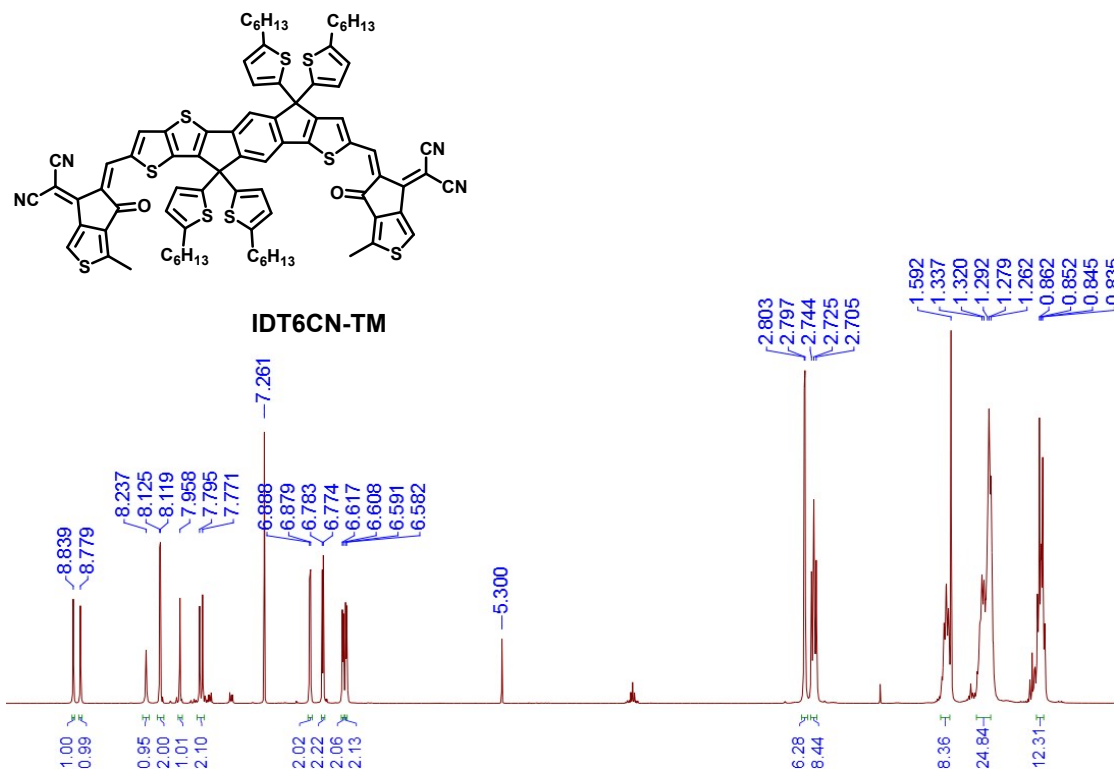


Fig. S7 The ^1H spectrum of IDT6CN-TM in *d*-chloroform.

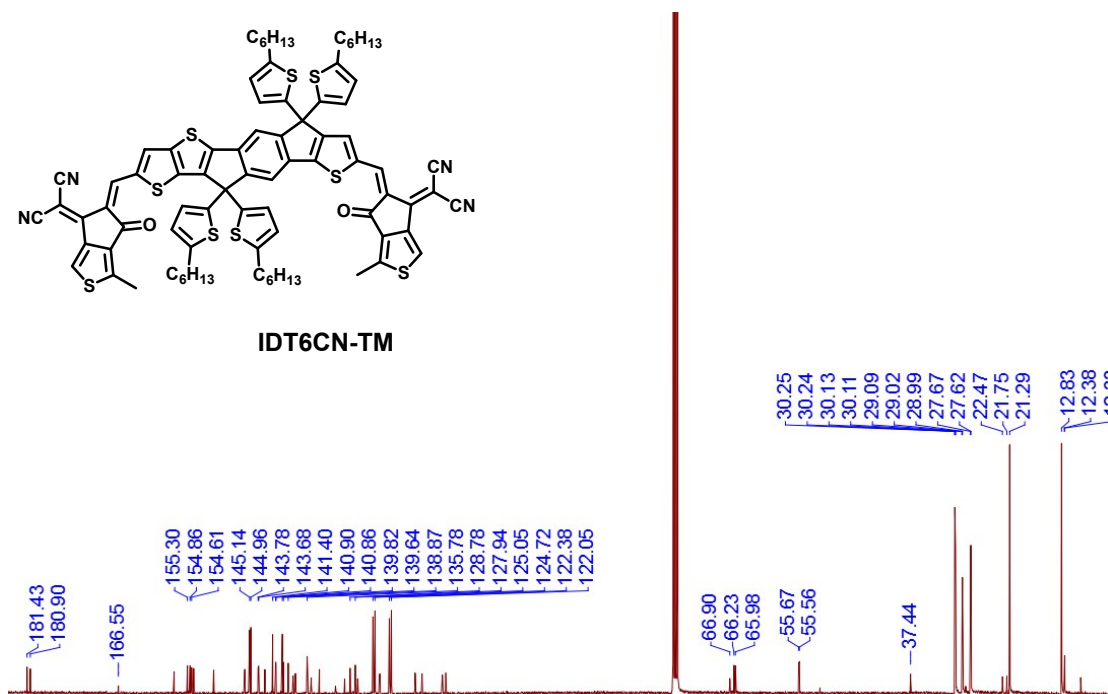


Fig. S8 The ^{13}C spectrum of IDT6CN-TM in *d*-chloroform.

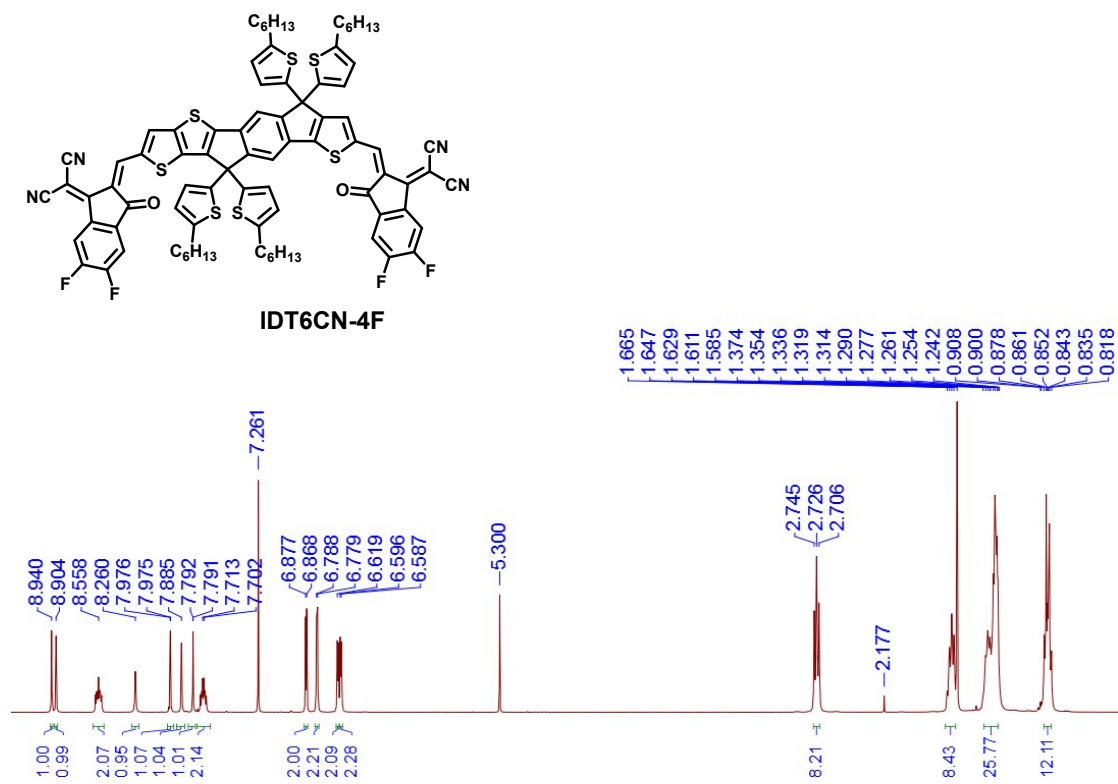


Fig. S9 The ^1H spectrum of IDT6CN-4F in *d*-chloroform.

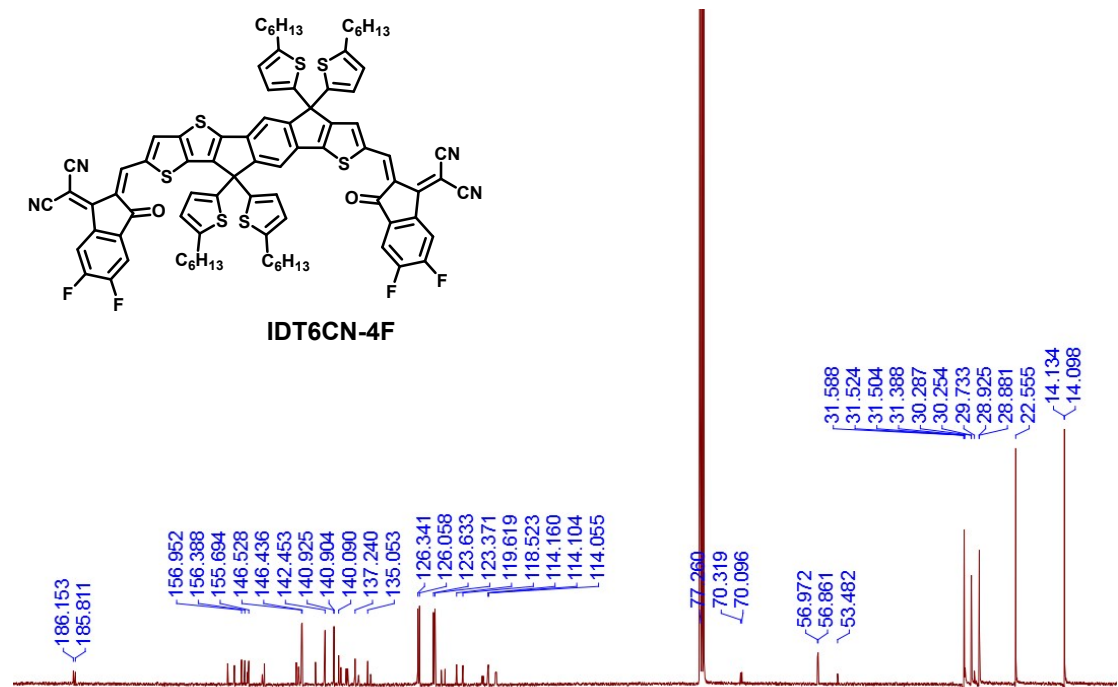


Fig. S10 The ^{13}C spectrum of IDT6CN-4F in *d*-chloroform.

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