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Supplementary information

Dopant-free hole transport materials based on alkyl-substituted indacenodithiophene for planar perovskite solar cells†

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‡ X. Y. Liu and E. Rezaee have equivalent contribution.

Experimental details

Materials

All materials were used as purchased without further purification unless specified otherwise. Organic solvents were purchased from Sigma Aldrich USA, while spiro-MeOTAD, CH_3NH_3I, and PbI_2 were purchased from TCI. To characterize the materials, their solution and solid thin film UV-Vis spectra were obtained on a PerkinElmer Lambda750S spectrophotometer. Thermogravimetric analysis was performed using a Discovery thermogravimetric analyzer. ^{1}H NMR spectroscopy was performed using a Bruker DPX 400 MHz spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Daltonics flex analysis system. The highest occupied molecular orbital energy level of PTZ-TPA was measured using an ionization energy measurement system (IPS-4) under N_2. Cyclic voltammetry experiments were performed using an Autolab potentiostat (PGSTAT30, Echochimie); for these experiments, a glassy carbon disk, a platinum wire, and a silver wire were used as the working, counter, and reference electrodes, respectively. All measurements were referenced against the ferrocene/ferrocenium redox couple. The crystal data was tested using a Bruker D8 Venture Photon100 CMOS X-Ray diffractometer.

Thin-film characterization

The cross-sections of the perovskite films were investigated using FE-SEM (Mira 3 LMU FEG, Tescan). Steady-state photoluminescence spectra were measured with a FLS980 Spectrometer (Edinburgh Instruments). The samples were excited from the perovskite or $IDTC_4$-TPA/$IDTC_6$-TPA layer with an excitation wavelength of 475 nm. Time resolved photoluminescence spectra was recorded on a PL spectrometer, Edinburgh Instruments, FLS 980 (excitation using a 500-nm-wavelength pulsed laser). The water contact angles were measured using a commercial setup (DSA25, Kruss). The hole mobilities of the HTMs were estimated using the space-charge-limited current method with device structures consisting of ITO/PEDOT:PSS/HTMs/Au. The current density–voltage (*J*–*V*) curves of the devices were recorded using a Keithley 2400 source. Hole mobilities were calculated using the Mott-Gurney law by fitting Equation (1), where ε_0 is the permittivity of free space (8.85×10^{-12} F/m), ε is the relative permittivity of the material (approaching 3 for organic semiconductors), μ is the hole mobility, V is the applied voltage, and d is the thickness of the active layer.

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3} \qquad (1)$$

Synthesis of IDTC$_4$–TPA

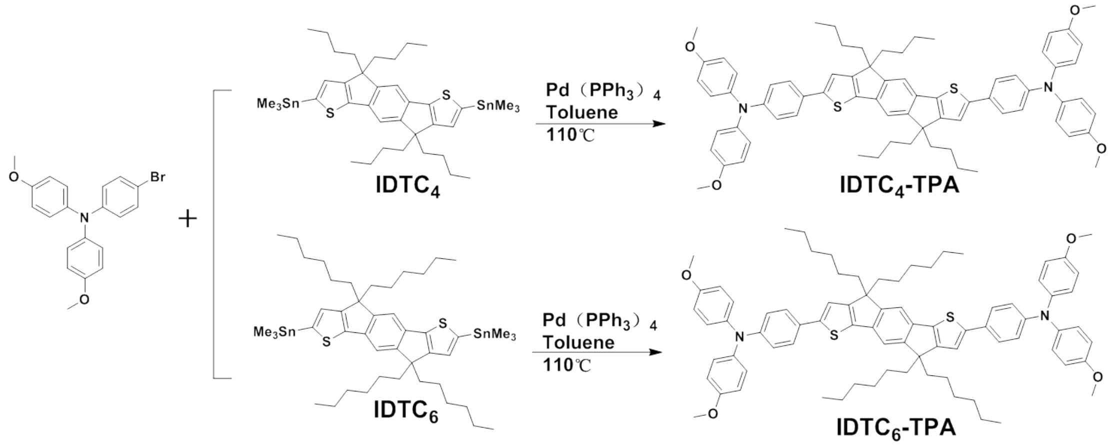
IDTC$_4$-TPA was synthesized using a one-step Stille coupling reaction. IDTC$_4$-bis(trimethylstannane) (327.2 mg, 0.4 mmol) and brominated methoxytriphenylamine (306.4 mg, 0.8 mmol) were dissolved in toluene (60 mL). The mixture was deoxygenated with argon for 15 min. Pd(PPh$_3$)$_4$ (46.2 mg, 0.04 mmol) was added under an argon atmosphere. The mixture was refluxed for 24 h and then cooled down to ambient temperature. Water (60 mL) was added and the mixture was extracted with chloroform (2 × 60 mL). The organic phase was dried over anhydrous MgSO$_4$ and filtered. After the solvent was removed from the filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:3, v/v) as eluent, yielding a yellow solid (302.8 mg, 69%). ^{1}H NMR (400 MHz, CD2Cl2) δ 7.81 – 6.58 (m, 28H), 3.79 (s, 12H), 1.95 (d, J = 44.3 Hz, 8H), 1.30 – 0.97 (m, 8H), 0.76 (dd, J = 32.3, 25.1 Hz, 20H). MS: m/z (M+) 1096.843.

Synthesis of IDTC$_6$-TPA

IDTC$_6$-TPA was synthesized using a one-step Stille coupling reaction. IDTC$_6$-bis(trimethylstannane) (371.4 mg, 0.4 mmol) and brominated methoxytriphenylamine (306.4 mg, 0.8 mol) were dissolved in toluene (60 mL). The mixture was deoxygenated with argon for 15 min. Pd(PPh$_3$)$_4$ (46.2 mg, 0.04 mmol) was added under an argon atmosphere. The mixture was refluxed for 36 h and then cooled down to ambient temperature. Water (60 mL) was added and the mixture was extracted with chloroform (2 × 60 mL). The organic phase was dried over anhydrous MgSO$_4$ and filtered. After the solvent was removed from the filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:3, v/v) as eluent, yielding an orange solid (352.2 mg, 73%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.52 – 6.64 (m, 28H), 3.84 (s, 12H), 1.99 (d, J = 42.0 Hz, 8H), 1.14 (s, 24H), 0.92 (s, 8H), 0.81 (s, 12H). MS: m/z (M+) 1207.587.

Device Fabrication and Characterization

PSCs were fabricated with a FTO/SnO$_2$/PCBM/perovskite/IDTC$_4$-TPA or IDTC$_6$-TPA/Au structure on patterned fluorine doped tin oxide (FTO) glass. The FTO glass substrates (with a sheet resistance of 20 Ω/□, PV Tech, China) were pre-cleaned using an ultrasonic bath of chlorobenzene and acetone followed by treatment in an ultraviolet-ozone chamber (Novascan Company, USA) for 15 min. The SnO_2 electron transport layer was applied following a reported procedure. $SnCl_2\cdot 2H_2O$ in ethanol was used as a precursor solution (0.1 M). The precursor solution was spin-coated onto the substrate at a spin speed of 3000 revolutions per minute (rpm) for 30 s and then the films were annealed in an ambient atmosphere at 180 °C for 1 h. A thin layer of PCBM was prepared on the FTO surface at a spin speed of 2000 rpm and annealed at 100 °C for 10 min. The PCBM solutions were prepared by dissolving 20 mg PCBM in 1 mL chlorobenzene. The perovskite ($CH_3NH_3PbI_3$) films were prepared by fast crystallization-deposition. A solution of $CH_3NH_3PbI_3$ (45 wt%) was spin-coated onto the SnO_2/PCBM film at 4000 rpm. After seven seconds anhydrous chlorobenzene (300 μL) was quickly dropped on the substrate. The film was annealed at 100 °C for 10 min. The hole-transporting materials IDTC$_4$-TPA and IDTC$_6$-TPA were deposited by spin coating at 4000 rpm for 30 s from chlorobenzene solution. Finally, a 100-nm-thick Au film was deposited by thermal evaporation (MB200, MBraun) as the cathode. The active area (0.11 cm^2) of the device was determined by the overlap of FTO and the gold electrode. The *J*–*V* characteristics of the devices were measured with a computer-controlled Keithley 236 source measurement unit (in conjunction with a ss150 Solar Simulator, Zolix, China). The light source was a xenon lamp coupled with AM1.5 solar spectrum filters, yielding an optical power at the sample of 100 mW/cm^2. The IPCE spectra were recorded using a Solar Cell QE/EQE Measurement System (Solar cell scan 100, Zolix) with a model SR830 DSP lock-in amplifier (Stanford Research Systems, USA) coupled with a WDG3 monochromator and 500 W xenon lamp.



Scheme S1 Synthesis routes of IDTC$_4$-TPA and IDTC$_6$-TPA.

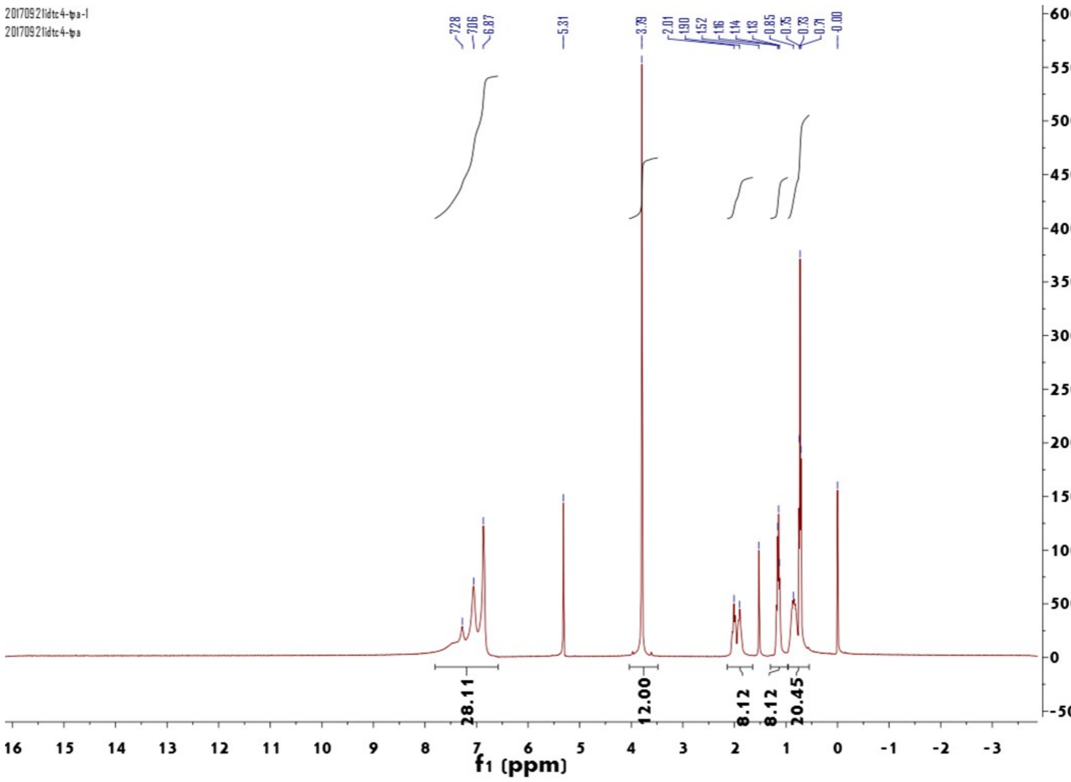


Fig. S1 ^{1}H NMR spectrum of IDTC$_4$-TPA in CD_2Cl_2.

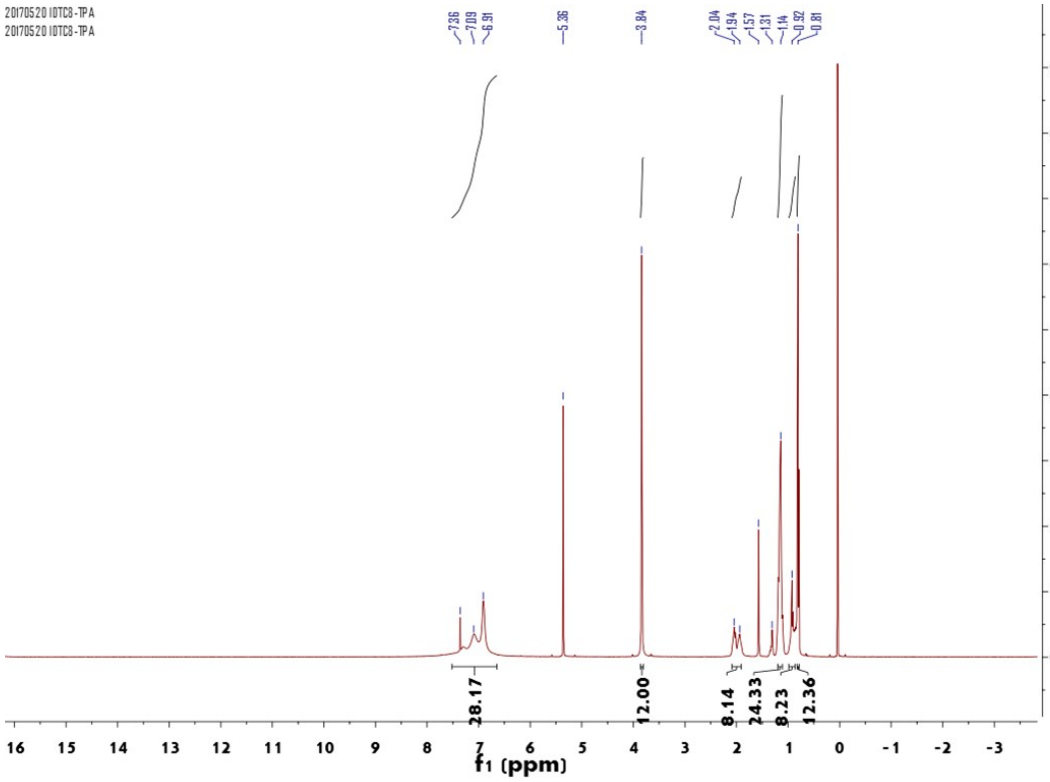


Fig. S2 ^{1}H NMR spectrum of IDTC$_6$-TPA in CD$_2$Cl$_2$.

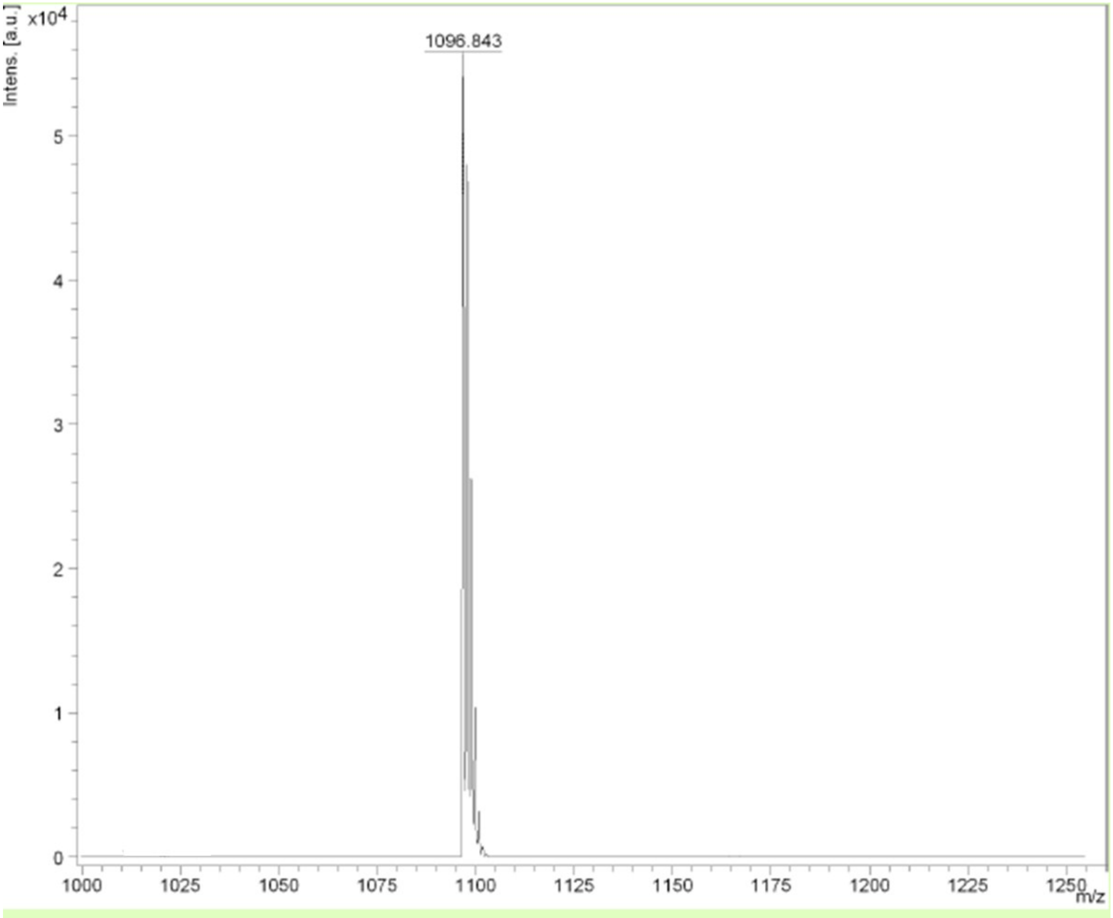


Fig. S3 MALDI-TOF mass spectrum of IDTC$_4$-TPA.

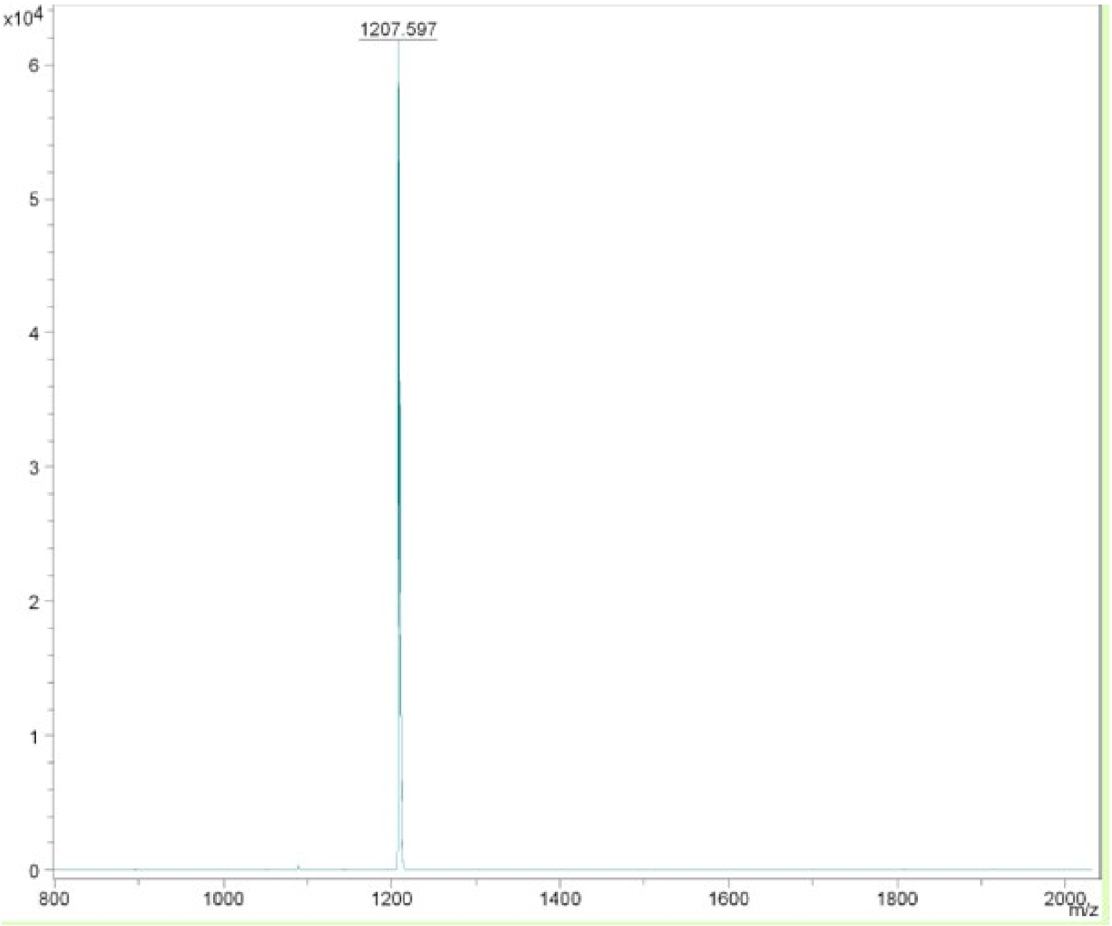


Fig. S4 MALDI-TOF mass spectrum of IDTC$_6$-TPA.

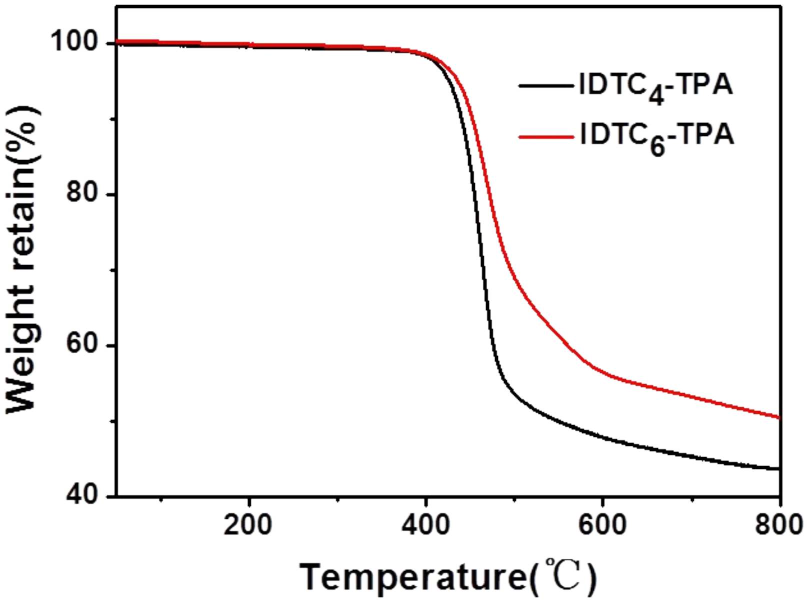


Fig. 5 Thermogravimetric analysis curves of IDTC$_4$-TPA and IDTC$_6$-TPA.

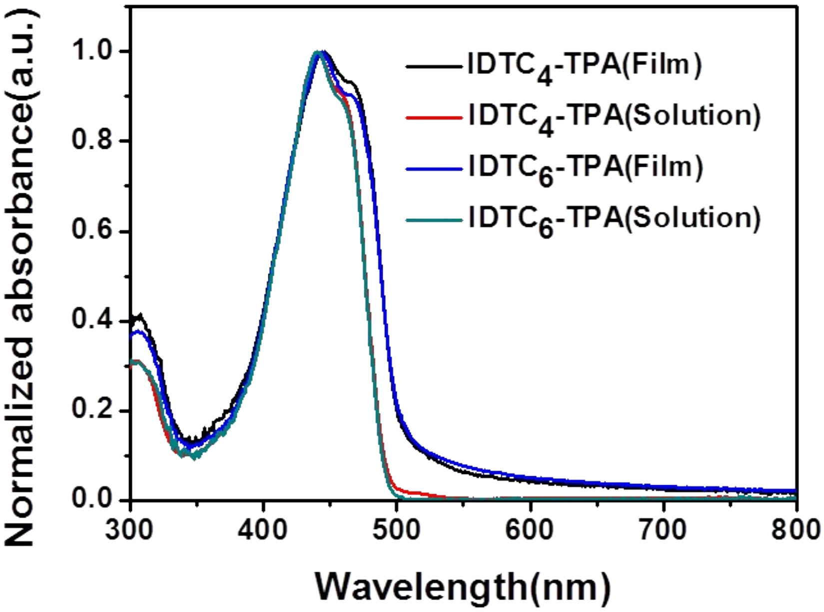


Fig. S6 Absorption spectra of IDTC$_4$-TPA and IDTC$_6$-TPA in dichloromethane solution and as spin-coated thin films.

Table S1 Crystallographic data and structure refinement details for IDTC_4-TPA and IDTC_6-TPA

	IDTC4-TPA	IDTC6-TPA
Identification code	er018	er001
Empirical formula	$C_{3.6}H_{3.8}N_{0.1}O_{0.2}S_{0.1}$	$C_{80}H_{92}Cl_{0.16}N_2O_4S_2$
Formula weight	54.87	1209.75
Temperature/K	100.0	150(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	9.3698(7)	11.8347(7)
b/Å	10.9783(8)	11.8480(7)
c/Å	15.2591(10)	15.4459(8)
α/°	87.380(3)	103.656(2)
β/°	76.302(3)	100.909(2)
γ/°	82.659(4)	109.745(2)
Volume/Å^3	1512.28(19)	1893.20(19)
Z	20	25
ρ_{calc}g/cm^3	1.205	1.210
μ/mm^{-1}	1.192	0.261
F(000)	586.0	734.0
Crystal size/mm^3	0.5 × 0.4 × 0.4	0.4 × 0.3 × 0.3
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.12 to 118.44	4.208 to 55.13
Index ranges	$-9 \le h \le 10$, $-12 \le k \le 12$, $-16 \le l \le 16$	$-15 \le h \le 14$, $-15 \le k \le 15$, $-19 \le l \le 20$
Reflections collected	11749	69289
Independent reflections	4315 [R_{int} = 0.0394, R_{sigma} = 0.0463]	8737 [R_{int} = 0.0515, R_{sigma} = 0.0269]

Data/restraints/parameters	4315/0/391	8737/0/438
Goodness-of-fit on F^2	1.045	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0816, wR_2 = 0.2091	R_1 = 0.0407, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.0896, wR_2 = 0.2163	R_1 = 0.0541, wR_2 = 0.1046
Largest diff. peak/hole / e $Å^{-3}$	2.93/-0.30	0.37/-0.53

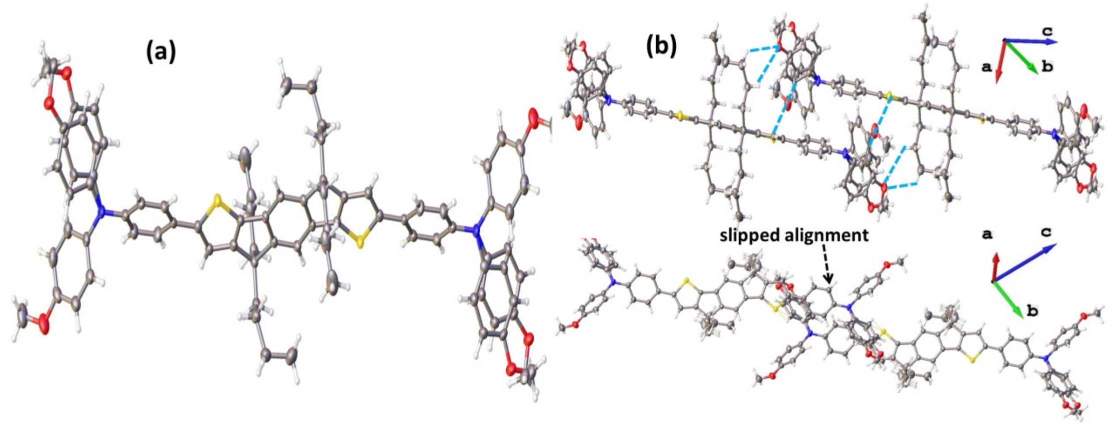


Fig. S7 (a) Oak Ridge thermal-ellipsoid plot program (ORTEP) representation of IDTC$_4$–TPA, and (b) two perspective views showing the packing structures of IDT C$_4$–TPA molecules held by a hydrogen bond (light blue dotted line).

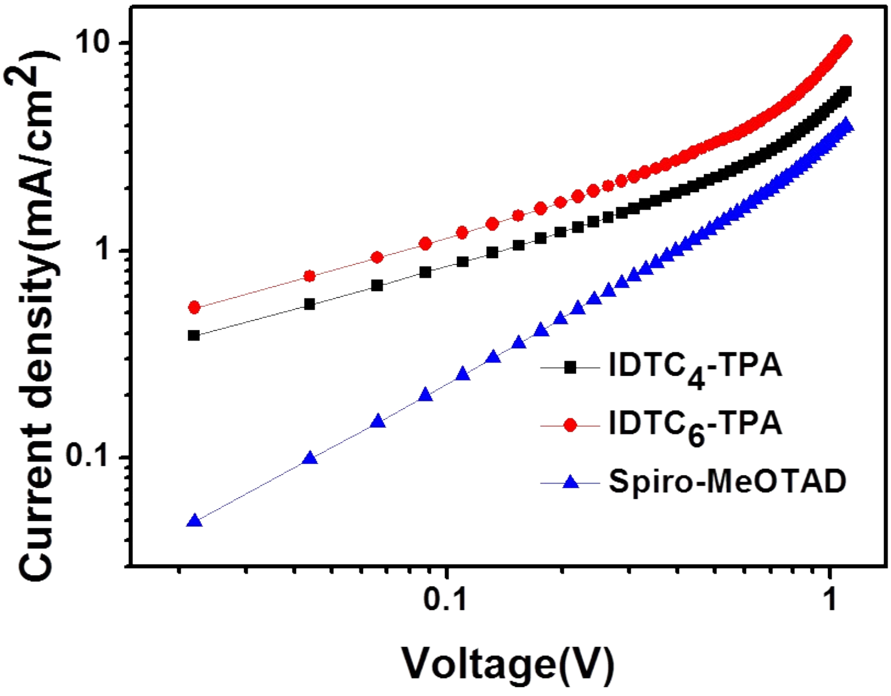


Fig. S8 *J*–*V* characteristics of space-charge-limited current of non-doped HTMs.

Table S2 Summary of the parameters from fitting to the TRPL measurement data.

Sample	τ_1 (ns)	τ_2 (ns)
Perovskite	4.95	18.44

IDTC$_4$-TPA	1.15	6.78
IDTC$_6$-TPA	1.03	5.58
Spiro-MeOTAD(Doped)	1.62	3.81

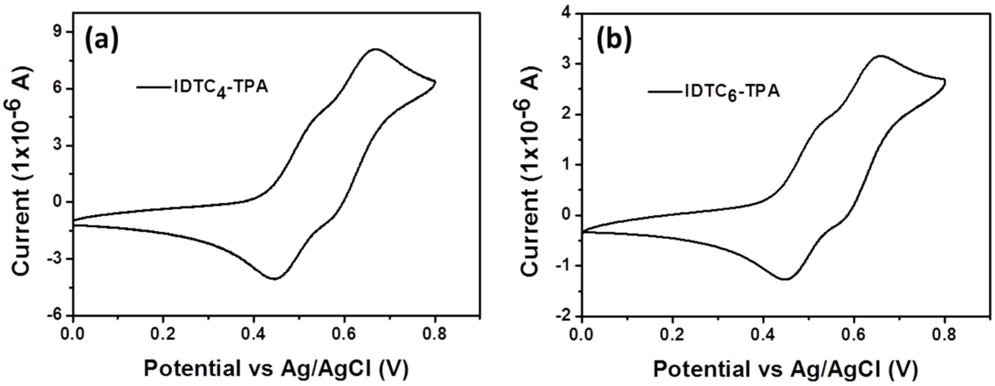


Fig. S9 Cyclic voltammograms of (a) IDTC$_4$-TPA and (b) IDTC$_6$-TPA.

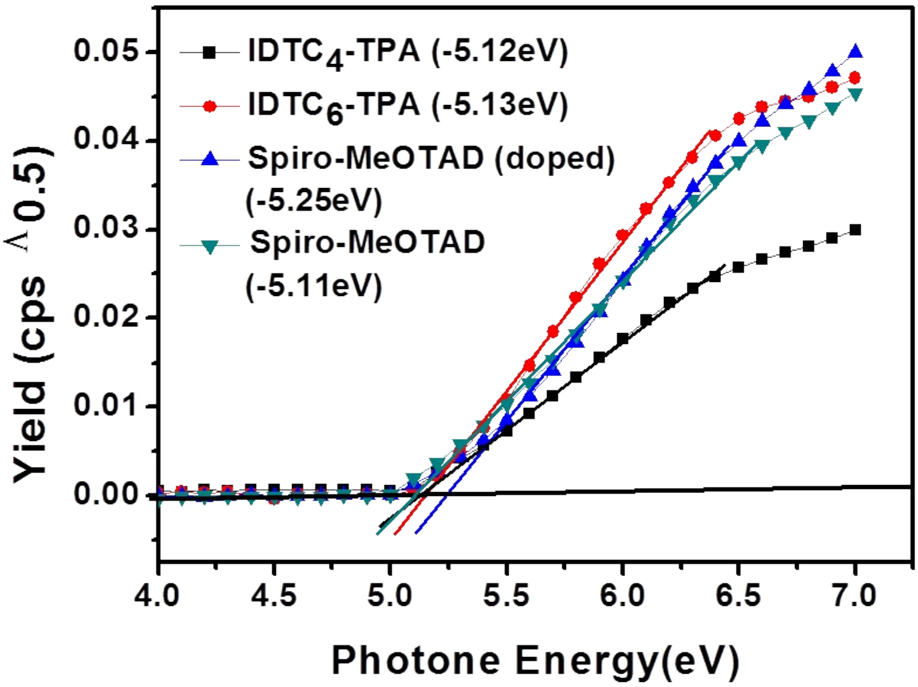


Fig. S10 Highest occupied molecular orbital energy level of IDTC$_4$-TPA, IDTC$_6$-TPA, doped spiro-MeOTAD and pristine spiro-MeOTAD as measured by photoelectron yield spectroscopy (under N$_2$).

Table S3 Electrochemical properties of the synthesized HTMs

Compounds	λ_{max}^{sol} (nm)	λ_{max}^{film} (nm)	λ_{onset} (nm)	HOMO [a] (eV)	HOMO [b] (eV)	LUMO (eV)	Band gap (eV)
IDTC$_4$-TPA	440	447	503	-4.95	-5.12	-2.66	2.46
IDTC$_6$-TPA	439	443	505	-4.96	-5.13	-2.67	2.46

[a] Measured in DCM/tetra-n-butylammonium hexafluorophosphate (0.1 M) solution using a glassy carbon disk, a platinum wire, and a silver wire were used as the working, counter, and reference electrodes, respectively. [b] Measured by an ionization energy measurement system with the ionization photoelectron spectrometer model (IPS-4).

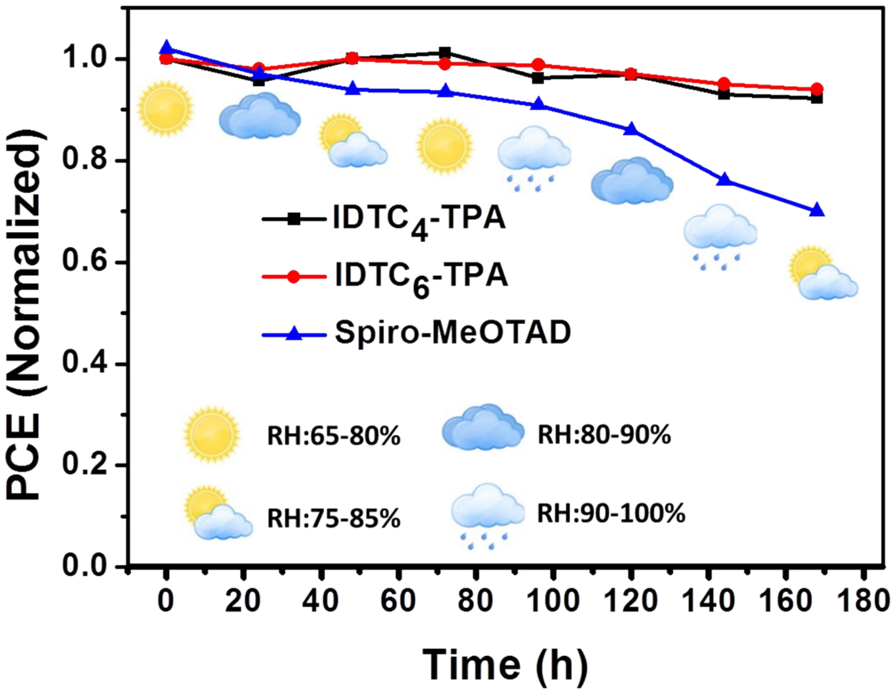


Fig. S11 Normalized PCEs of PSCs as a function of time. After each *J*–*V* measurement the device was removed from the applied light illumination and stored in ambient air without encapsulation. The humidity of the atmosphere was about 65–100%.

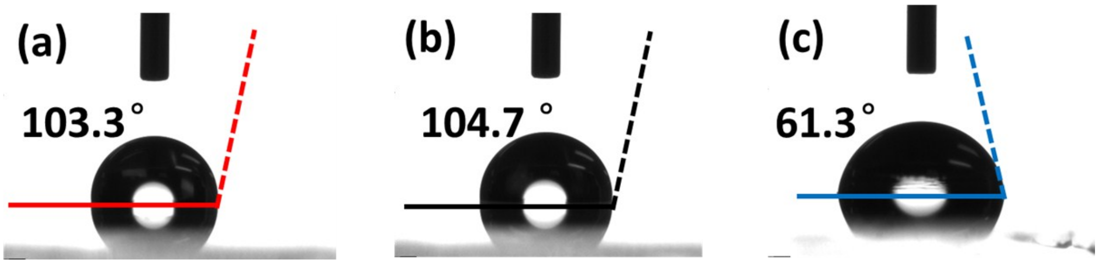


Fig. S12 Droplets of water on films of (a) IDTC$_4$-TPA, (b) IDTC$_6$-TPA, and (c) spiro-MeOTAD