

A compatible polymer acceptor enables efficient and stable organic solar cells as solid additive

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Materials and Measurements

All solvents and reagents were used as received from commercial sources and used without further purification unless otherwise specified. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a MERCURYVX300 spectrometers. Mass spectra were recorded on a Shimadzu spectrometer. UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-2700 recording spectrophotometer. Cyclic voltammetry (CV) measurements were carried out on a CHI voltammetric analyzer at room temperature. Tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆, 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode with a 2 mm diameter, a platinum wire counter electrode, and

a Ag/AgCl wire reference electrode. Cyclic voltammograms were obtained at a scan rate of 100 mV/s. PL spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. The film morphology was measured using an atomic force microscope (AFM, Bruker-ICON2-SYS) using the tapping mode. The RMS values of the surface AFM images are averaged based on five times testing on different areas for each sample.

Stability tests

The devices for shelf like stability test were stored in simple office table cabinet in Hong Kong University of Science and Technology. The photostability test prepared devices were put under a LED with 150W power illumination outside glovebox. Thermostability tests were carried out upon devices annealed at 150°C hotplate in nitrogen filled glovebox.

Device fabrication and characterization

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/active layers/PNDIT-F3N/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Heraeus Clevios P VP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The blends (1:1.2 weight ratio for donor:acceptor) were dissolved in chloroform (the total concentration of blend solutions was 14 mg mL⁻¹ for all blends), and stirred overnight in a nitrogen-filled glove box. The blend solution was spin-cast at 3000 rpm for 30 s. Subsequently, cast films underwent a 95 °C temperature annealing for 5min. A thin PNDIT-F3N layer was coated on the active layer, followed by the deposition of Ag (100 nm) (evaporated under 5×10⁻⁵ Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 105 nm. The current density-voltage (*J-V*) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm⁻²) using a Newport solar

simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). Optical microscope (Olympus BX51) was used to define the device area (5.9 mm²). 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.

Mobility Measurements

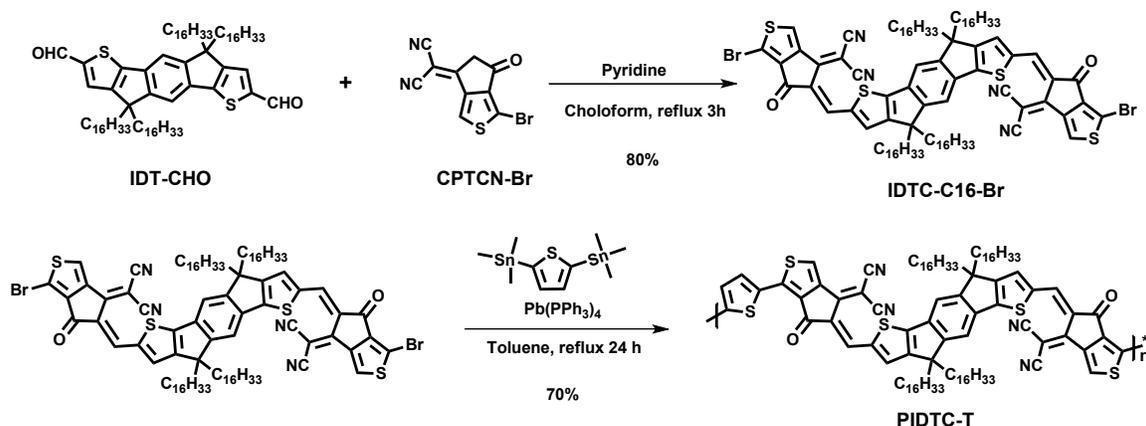
Hole and electron mobility were measured using the space charge limited current (SCLC) method. Device structures are ITO/MoOx/active layer/MoOx/Ag for hole-only devices and ITO/ZnO/active layer/PNDIT-F3N/Ag for electron-only devices. The SCLC mobilities were calculated by MOTT-Gurney equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$. Where J is the current density, ϵ_r is the relative dielectric constant of active layer material usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 3, ϵ_0 is the permittivity of empty space, μ is the mobility of hole or electron and L is the thickness of the active layer, V is the internal voltage in the device, and $V = V_{\text{Applied}} - V_{\text{Built-in}}$ (in the hole-only and the electron-only devices, the V_{bi} values are 0.2 V and 0 V respectively), where V_{Applied} is the voltage applied to the device, and $V_{\text{Built-in}}$ is the built-in voltage resulting from the relative work function difference between the two electrodes.

GIWAXS measurement

GIWAXS measurement were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°. The samples for GIWAXS measurements are fabricated on silicon substrates using the same recipe for the devices.

GISAXS characterization. GISAXS was conducted at 19U2 SAXS beamline at Shanghai Synchrotron Radiation Facility, Shanghai, China, using the 0.15° incident angle with 10

keV primary beam.



Scheme S1. Synthesis of PIDTC-T.

Synthesis of IDTC-C16-Br:

Compound **6** (230 mg, 0.2 mmol), CPTCN-Br (222 mg, 0.8 mmol), chloroform (20 mL), and pyridine (1 mL) were added to a two-necked round-bottomed flask. The mixture was deoxygenated with nitrogen for 30 min and then refluxed for 3 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:2) as eluent, yielding a dark blue solid (278 mg, 80%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.92 (s, 2H), 8.31 (s, 2H), 7.71 (s, 2H), 7.60 (s, 2H), 2.11 – 2.00 (m, 4H), 1.98-1.88 (m, 4.4 Hz, 4H), 1.33 – 1.05 (m, 104 H), 0.98 – 0.72 (m, 20H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.21, 157.34, 156.35, 141.85, 140.78, 139.45, 137.59, 127.85, 115.71, 113.71, 76.65, 76.39, 76.07, 53.76, 38.32, 31.29, 29.06, 29.04, 28.69, 23.77 (s), 22.06, 13.49. HR-MS (MALDI-TOF) $[\text{M}+\text{H}]^+$ calcd. for $(\text{C}_{102}\text{H}_{140}\text{Br}_2\text{N}_4\text{O}_2\text{S}_4)$:1738.8226. Found: 1739.8340.

Synthesis of PIDTC-T:

IDTC-Br (348 mg, 0.02 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.082 mg, 0.02 mmol) and dry toluene (10 mL) were added to a 25 mL double-neck round-bottom flask.

The reaction container was purged with argon for 10 min, and then Pd(PPh₃)₄ (8 mg) was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 24 h. The reactant was cooled down to room temperature and poured into MeOH (200 mL), then filtered through a Soxhlet thimble, then the reactant was subjected to Soxhlet extraction with methanol, hexane, and dichloromethane. The polymer PIDTC-T of 234 mg (Yield 70%) was recovered as solid from the chloroform fraction by precipitation from methanol, and was dried under vacuum. Elemental analysis calcd (%) for (C₁₀₆H₁₄₄N₄O₂S₅): C = 76.39%, H = 8.71%. Found: C= 76.18%, H= 8.68%. GPC: Mn = 7878 Da; Mw/Mn = 1.208.

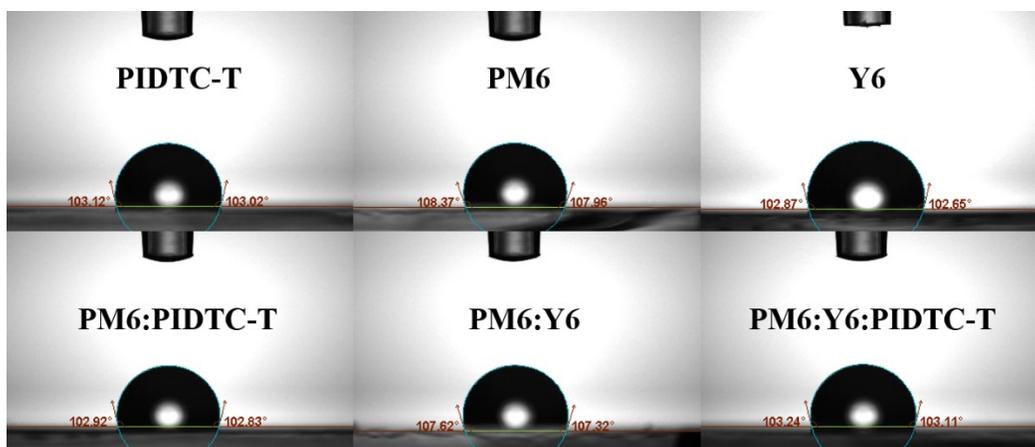


Figure S1. Water contact angles of thin films in this paper.

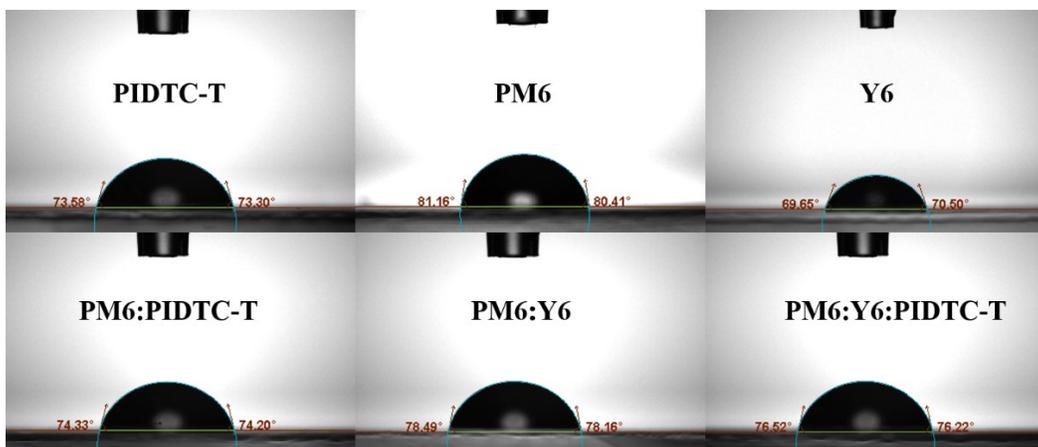


Figure S2. Ethylene glycol contact angles of thin films in this paper.

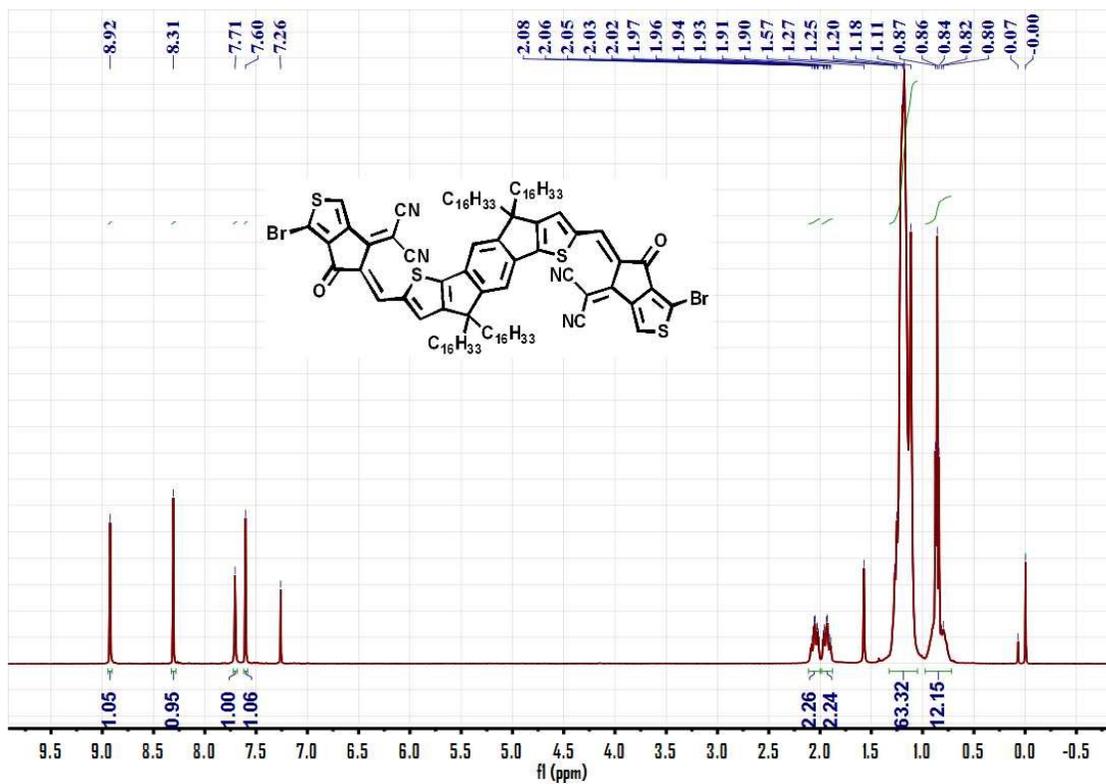


Figure S3. ¹H NMR spectrum of IDTC-C16-Br in CDCl₃.

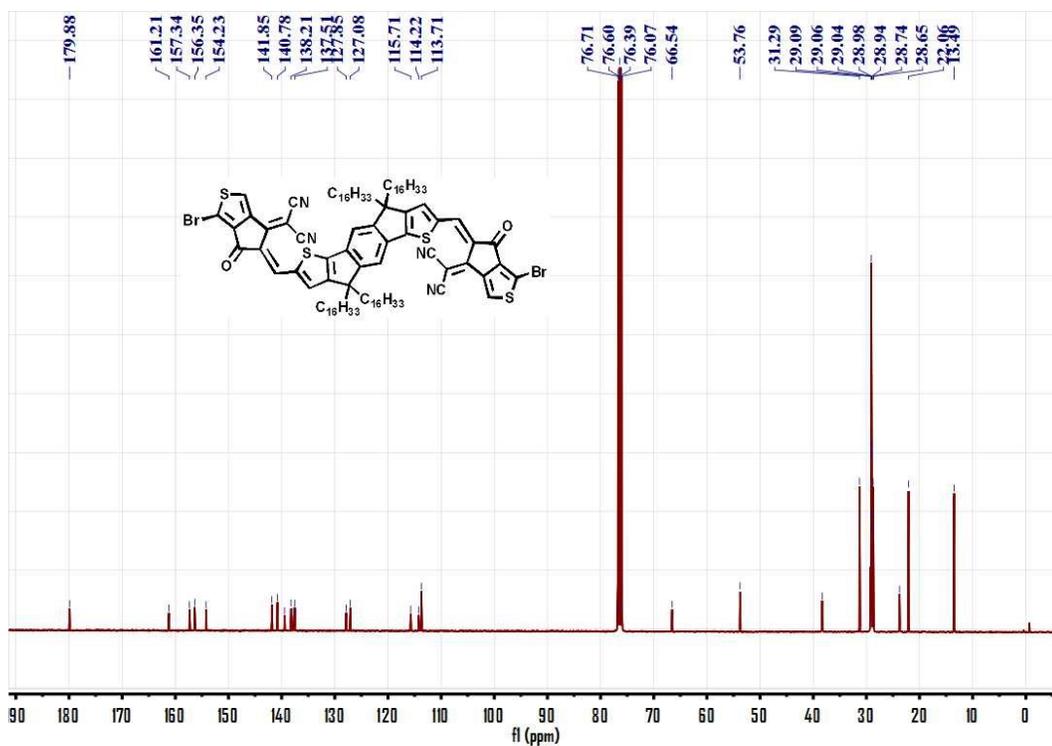


Figure S4. ^{13}C NMR spectrum of IDTC-C16-Br in CDCl_3 .

1 #17 RT: 0.18 AV: 1 NL: 3.34E5
 T: FTMS + p ESI Full ms [500.0000-2000.0000]

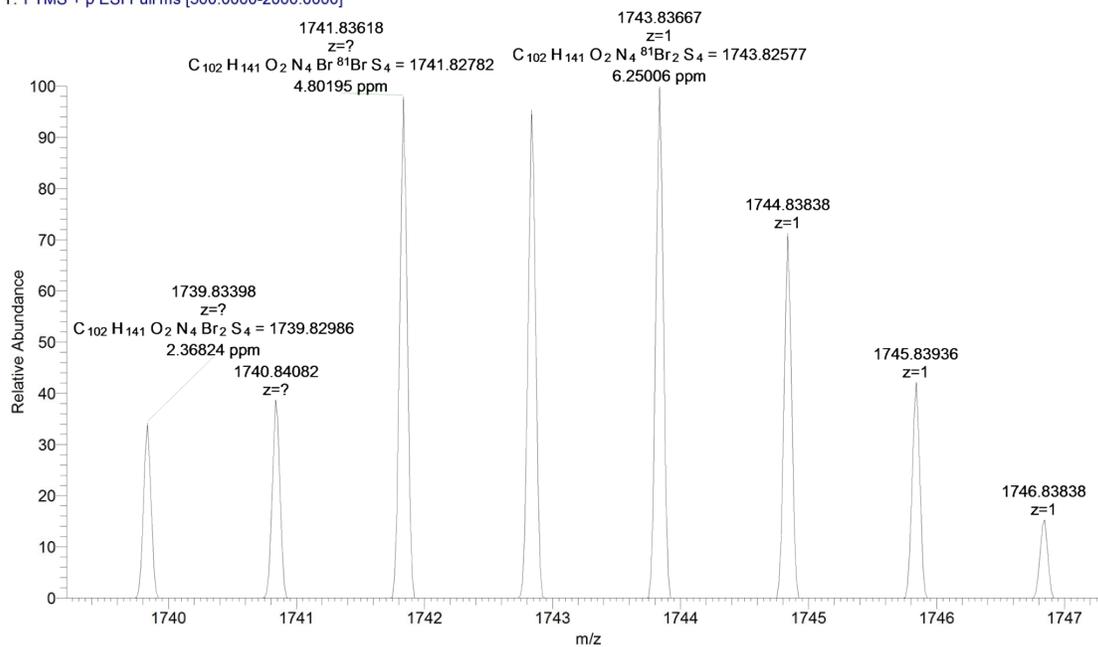


Figure S5. MS spectrum (MALDI-TOF) of IDTC-Br.

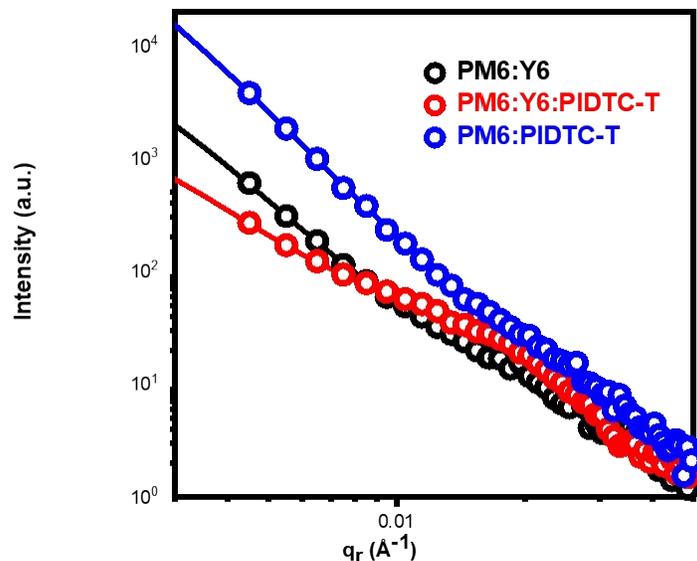


Figure S6. Fitted profiles of GISAXS measurements.

Table S1. Specific value of PCE degradation when devices stored in simple atmosphere.

Active layers	8h ^{a,b}	20h ^{a,b}	47h ^{a,b}	77h ^{a,b}	125h ^{a,b}
PM6:PIDTC-T	99.5±0.6	98.9±0.6	97.2±0.8	94.2±1.5	92.3±1.7
PM6:Y6	97.8±0.5	96.9±0.4	93.4±0.9	89.1±0.9	87.2±1.1
PM6:Y6 (2% PIDTC-T)	99.1±0.4	98.1±0.7	95.5±1.0	93.4±1.1	91.0±0.9

(a) storage time (b) values (%) are derived from 10 devices.

Table S2. Specific value of PCE degradation when devices stored under light soaking.

Active layers	8h ^{a,b}	20h ^{a,b}	47h ^{a,b}	77h ^{a,b}	125h ^{a,b}
PM6:PIDTC-T	98.1±0.7	96.6±0.4	91.3±0.4	88.4±0.8	84.4±1.3
PM6:Y6	97.1±0.9	93.9±0.4	89.4±0.8	86.1±0.4	81.2±1.4
PM6:Y6 (2% PIDTC-T)	97.4±1.0	95.1±0.8	90.5±0.5	87.7±0.7	83.1±1.2

(a) storage time (b) values (%) are derived from 10 devices.

Table S3. Specific value of PCE degradation when devices annealed at 150°C.

Active layers	2h ^{a,b}	7h ^{a,b}	12h ^{a,b}	20h ^{a,b}
PM6:PIDTC-T	94.1±1.7	84.6±3.1	78.3±4.1	69.4±2.9
PM6:Y6	86.1±1.9	70.1±2.8	59.4±3.8	40.5±2.4
PM6:Y6	91.2±1.7	81.3±2.5	73.5±2.5	62.9±3.7

(2% PIDTC-T)

(a) storage time (b) values (%) are derived from 10 devices.

Table S4. Calculated results from $J_{\text{ph}}-V_{\text{eff}}$ curves

Active layers	$J_{\text{sat}}^{\text{c}}$	$J_{\text{ph}}^{\text{ac}}$	$J_{\text{ph}}^{\text{bc}}$	$J_{\text{ph}}^{\text{ac}} / J_{\text{sat}}^{\text{c}}$	$J_{\text{ph}}^{\text{bc}} / J_{\text{sat}}^{\text{c}}$
PM6:PIDTC-T	17.979	16.194	12.640	90.1%	70.3%
PM6:Y6	27.177	25.244	22.635	92.9%	83.3%
PM6:Y6	27.065	25.495	23.565	94.2%	87.0%

(2% PIDTC-T)

J_{ph} values under (a) short-circuit and (b) maximal output condition.

(c) The unit is mA cm⁻²

Table S5. Calculated parameters from GISAXS tests about domain size.

Samples	Intermixing domain size (nm)	Pure phase domain size (nm)
PM6:PIDTC-T	69.2	21.3
PM6:Y6	53.2	26.1
PM6:Y6	42.1	16.6

(2% PIDTC-T)
