

Supporting information

A 1,1'-vinylene-fused indacenodithiophene-based low bandgap polymer for efficient polymer solar cells

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Experimental Section

Measurements: ¹H NMR and ¹³C NMR spectra were measured in CDCl₃ on Bruker AV 400 MHz FT-NMR spectrometer. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. Gel permeation chromatography (GPC) was performed on Agilent Technologies PL-GPC 220 High Temperature Chromatograph at 160 °C using 1,2,4-trichlorobenzene (TCB) as eluent and polystyrene as the standard. Elemental analysis

was performed on a flash EA1112 analyzer. TGA was performed on a Perkin-Elmer TGA-7. UV-vis absorption spectra were taken on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer, in which the molar concentration of the polymer in *o*-dichlorobenzene (*o*-DCB) was calculated according to the molecular weight of one D-A repeating unit. The electrochemical cyclic voltammetry (CV) was performed on a Zahner Ennium Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. X-ray diffraction (XRD) measurement was performed using a Bruker D8 Advance Instrument at 40 kV voltage and 200 mA current with Cu K α radiation. The bottom-gate/bottom-contact organic field-effect transistors (OFET) were fabricated by evaporating gold source/drain electrodes. The polymer thin films were deposited onto bare SiO₂ by spin-coating method, and then annealing at 280 °C for 10 min.

The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2450. The power conversion efficiencies of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (air mass 1.5 global) (100 mW/cm²) using a SS-F5-3A (Enli Technology CO., Ltd.) solar simulator (AAA grade, 50 mm × 50 mm photo-beam size). 2×2 cm⁻² Monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology CO., Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode with a 5 μm scanner. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, in which the blend films were prepared using a processing technique, as following: first, the blend films were spin-cast on the PEDOT:PSS/ITO substrates; second, the resulting blend film/PEDOT:PSS/ITO substrates were submerged in deionized water to make these blend films float onto the air-water interface; finally, the floated blend films were taken up on unsupported 200 mesh copper grids for a TEM measurement.

Fabrication of polymer solar cells. Polymer solar cell devices with a conventional device structure of ITO/PEDOT:PSS/**PIDTV-ffBT**:PC₇₁BM/PrC₆₀MAIodide Salt/Al were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, a 30 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 °C for 15 min. The active layer was then deposited on top of the PEDOT:PSS layer by spin-coating from a 25 mg/mL *o*-DCB solution of **PIDTV-ffBT**:PC₇₁BM. In the case of the devices using a processing additive, 1,8-diiodooctane (0-2% by volume) was added to the solutions before use. The thickness of the active layer was controlled by changing the spin speed during the spin-coating

process and measured on a KLA Tencor D-100 profilometer. The methanol solution of PrC₆₀MAIodide Salt at a concentration of 0.5 mg/mL was deposited on the active layer at 3000 rpm for 30 s. Finally, 80 nm Al layer were successively deposited in vacuum onto the active layer at a pressure of ca. 4×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 0.04 cm². Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen drybox containing less than 5 ppm oxygen and moisture.

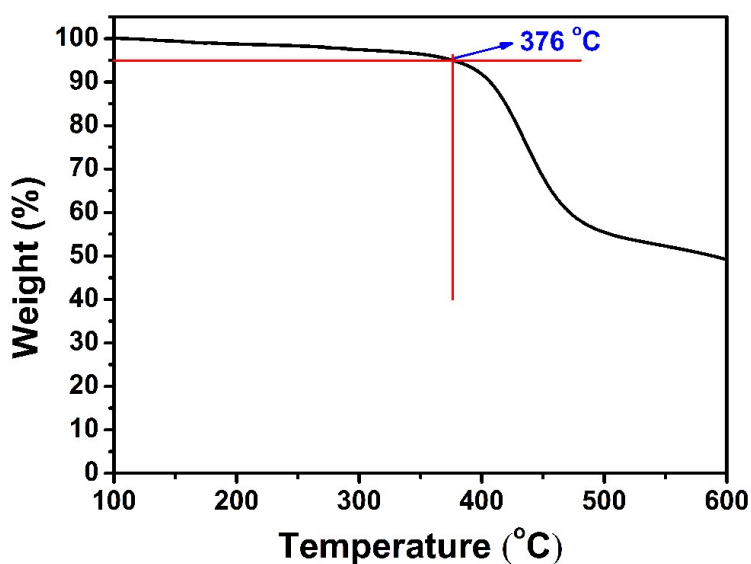


Fig. S1 TGA curve of **PIDTV-ffBT** at a scan rate of 10 °C/min under nitrogen atmosphere.

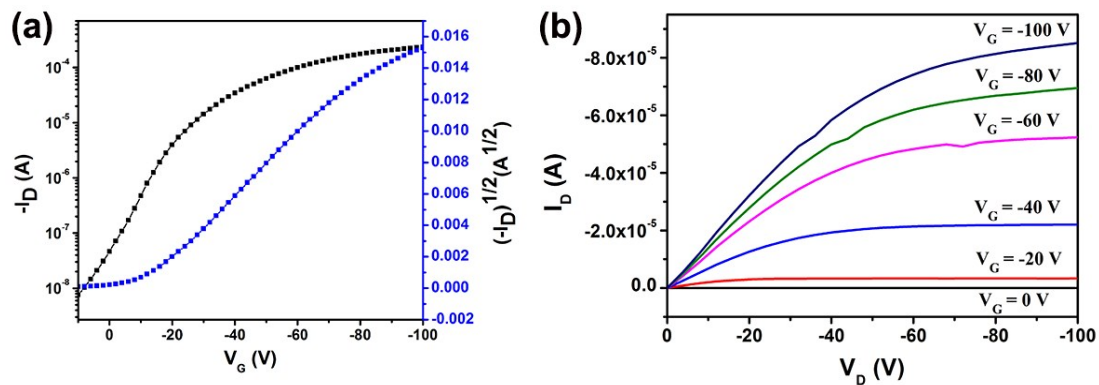


Fig. S2 Transfer (a) and output (b) characteristics of the **PIDTV-ffBT**-based OFETs devices.

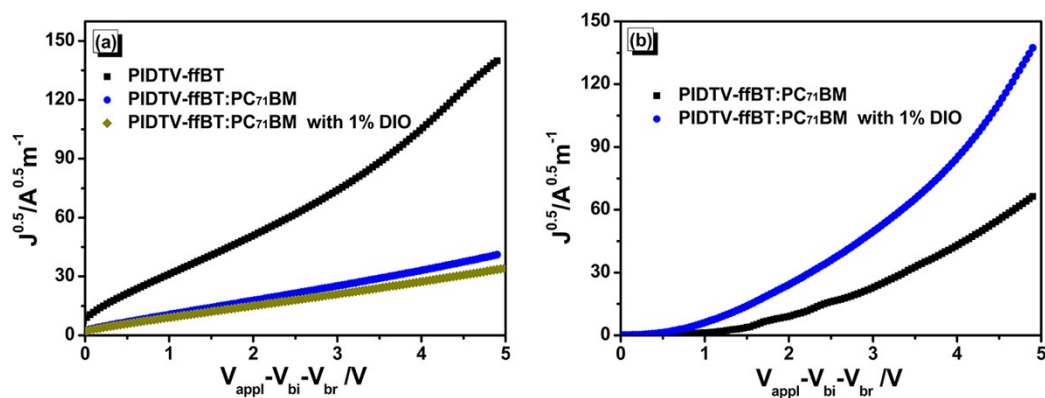


Fig. S3 The J - V curves of (a) the hole-only devices (b) the electron-only devices according to the SCLC model for pure **PIDTV-ffBT** film and **PIDTV-ffBT:PC₇₁BM** blend films with different processed conditions.

Table S1 Charge mobilities of the device active layers measured by SCLC method.

	hole-only devices		electron-only devices	
	mobilities	thickness	mobilities	thickness
	(cm ² /Vs)	(nm)	(cm ² /Vs)	(nm)
polymer	5.04×10^{-3}	220		
blends	1.81×10^{-4}	200	2.16×10^{-4}	170
blends + 1% DIO	4.13×10^{-4}	260	15.7×10^{-4}	200

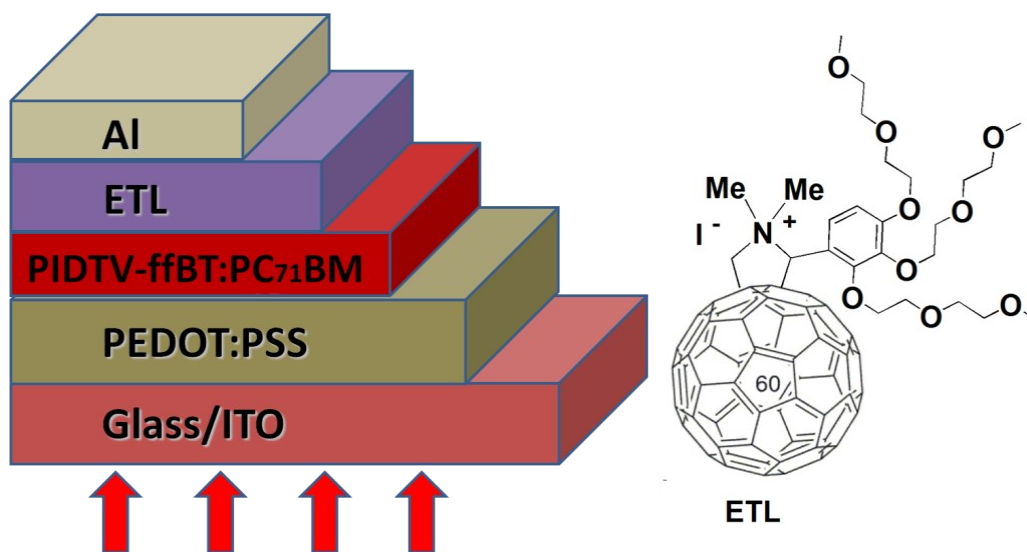


Fig. S4 Device structure of the PSCs and molecular formula of ETL in this study.

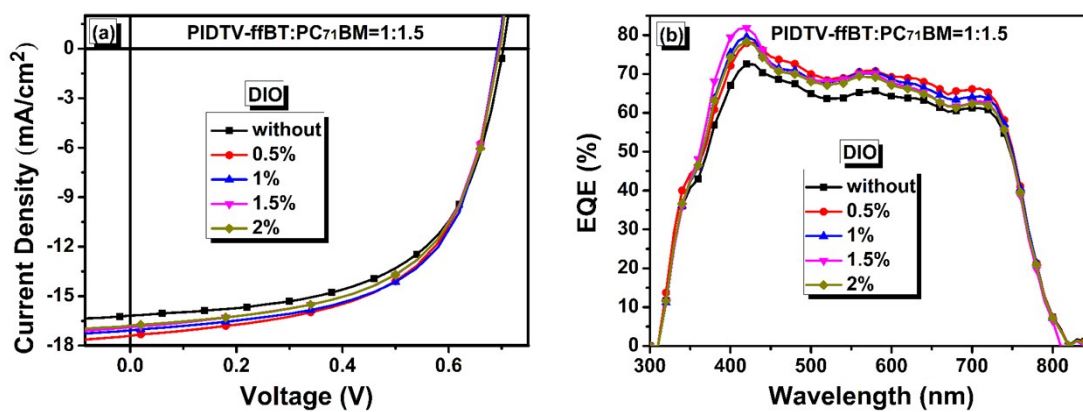


Fig. S5 (a) The J - V curves and (b) EQE curves of the PSCs based on **PIDTV-ffBT:PC₇₁BM** (1:1.5, w/w) with different DIO additive contents under the AM 1.5G illumination (100 mW cm⁻²).

Table S2 Photovoltaic performance parameters of the **PIDTV-ffBT:PC₇₁BM** (1:1.5, w/w)-based PSCs with different DIO additive contents under the AM 1.5G illumination (100 mW cm⁻²).

DIO	V_{oc}	J_{sc}	Calculated J_{sc} ^{a)}	FF	PCE_{max}
[v/v]	[V]	[mA cm ⁻²]	[mA cm ⁻²]	[%]	[%]
0%	0.70	16.2	15.8	59	6.7
	(0.70 ± 0.01)	(15.7 ± 0.3)		(57 ± 1)	(6.3 ± 0.2)
0.5%	0.69	17.4	16.8	59	7.1
	(0.69 ± 0.01)	(16.9 ± 0.2)		(57 ± 1)	(6.7 ± 0.2)
1%	0.70	17.1	16.7	61	7.3
	(0.70 ± 0.01)	(16.7 ± 0.2)		(58 ± 2)	(7.0 ± 0.2)
1.5%	0.69	16.9	16.4	0.59	6.9
	(0.69 ± 0.01)	(16.3 ± 0.3)		(57 ± 1)	(6.4 ± 0.3)
2%	0.70	16.8	16.3	59	6.9
	(0.70 ± 0.01)	(16.3 ± 0.2)		(57 ± 1)	(6.5 ± 0.2)

^{a)} Calculated by EQE. The average values and standard deviations of device parameters based on 15 devices are shown in brackets.

