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Electronic Supplementary Information

Wide-bandgap polymer based on alkylphenyl-substituted benzo[1,2-*b*:4,5-*b*′]dithiophene unit with high power conversion efficiency of over 11%

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Table S1. Photovoltaic results of high performance (PCE > 8%) devices based on wide-bandgap polymer donors

Polymer	E_g^{opt} (eV)	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)	Reference
PBDT-Se1	1.80	0.86	13.1	74.7	8.3	1
PBDT-T1	1.80	0.96	12.6	70.5	8.4	2
PBT13T	1.80	0.90	15.4	65.9	9.1	3
PM6	1.80	0.98	12.7	74.0	9.2	4
PBDB-T	1.80	0.94	17.4	73.5	12.1	5
PBDB-T-SF	1.80	0.88	20.5	71.9	13.1	6
PBT1-BO	1.81	0.93	13.0	67.5	8.1	7
PBDT-T1	1.81	0.86	13.1	71.8	8.1	8
PTFBDT-BZS	1.81	0.89	12.7	73.0	8.2	9
PTZBIBDT	1.81	0.87	13.5	74.0	8.6	10
PBDT-ST1	1.81	0.91	13.7	74.7	9.0	1
PIT2FBT	1.82	1.00	14.4	62.5	9.0	11
PITFBT	1.82	0.90	15.4	65.9	9.1	12
PBDF-T1	1.83	0.92	13.3	77.4	9.4	8
PBnDT-PyCNTAZ	1.84	0.96	14.1	62.0	8.4	13

PBT1-EH	1.84	0.97	14.2	75.0	10.3	7
PBT1-EH	1.84	0.98	15.7	69.2	10.6	7
PBDT-T1	1.85	0.92	14.1	75.0	9.7	14
PBT1-MP	1.86	0.98	12.9	72.5	8.7	7
PThBDTP	1.86	0.96	12.6	75.5	9.1	15
PBST-Se1	1.93	0.86	13.1	74.7	8.3	16
PSBZ	1.93	0.89	19.0	62.0	10.5	19
PvBDTffBT	1.94	0.94	15.3	58.0	8.3	20
PBFZ-OP	1.94	0.91	18.7	61.8	10.5	21
PBDT(Se)-T1	1.94	0.92	13.1	72.1	8.5	22
PBST-ST1	1.96	0.91	13.7	74.7	9.0	16
PTZ1	2.00	0.92	16.4	76.2	11.5	23
PTZP	2.01	0.90	17.9	73.3	11.8	This work
PvBDTTAZ	2.06	1.08	16.3	64.4	11.6	24

Experimental Section

Synthesis of the polymer PTZP:

(4,8-Bis(4-(2-butyloctyl)phenyl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethyl-stannane) (BDTP) (301 mg, 0.3 mmol), 2,5-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)thiazolo[5,4-*d*]thiazole (TTz) (207 mg, 0.3 mmol) and 10 mL toluene were added in a 50 mL double-neck round bottomed flask. After being purged with argon for 20 min, $Pd(PPh_3)_4$ (17 mg) was added into the flask as the catalyst, and then the reaction mixture was purged with argon for another 30 min. The reaction mixture was stirred and heated to reflux for 24 h under argon atmosphere. When the reaction mixture was cooled down to room temperature, the polymer was precipitated by the addition of 100 mL methanol, collected by filtration and then subjected to Soxhlet extraction with methanol, hexane and chloroform. The polymer was recovered as a solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. As a result, a black-red solid was obtained with the yield of 307 mg (82%). GPC: M_w = 53.15 kDa; M_n = 31.33 kDa; PDI = 1.69. Anal. Calcd for $C_{70}H_{94}N_2S_8$ (%): C, 68.91; H, 7.77; N, 2.30; Found (%): C, 69.85; H, 7.89; N, 2.22.

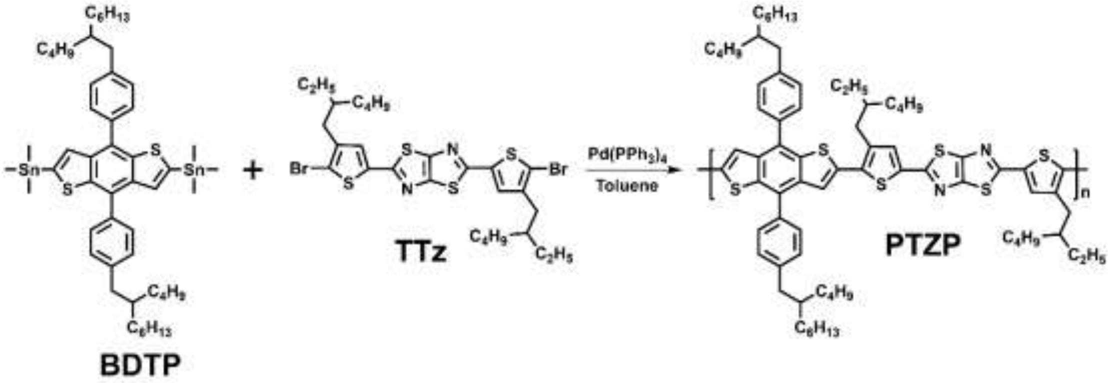

Figure S1. Synthetic route for PTZP

Instruments and measurements: Elemental analysis was carried out on a flash EA1112 analyzer. Gel Permeation Chromatography (GPC) were performed on Agilent Technologies PL-GPC-220 at 160 ºC, where 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was measured on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under a N_2 atmosphere. UV-vis absorption spectra were recorded on Agilent Technologies Cary Series spectrometer. The electrochemical cyclic voltammetry (CV) was taken on Electrochemical Workstation of Zahner Zennium IM6 in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), where glassy carbon disk as the working electrode, Ag/Ag^+ electrode as the reference electrode, and Pt wire as the counter electrode, respectively. Photoluminescence (PL) spectra were obtained using an Edinburgh Instrument FLS 980 spectrometer. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force

Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN instrument at 200 S5 kV accelerating voltage. The Grazing incidence X-ray diffraction (GIXD) measurements were acquired at beamline 7.3.3 at the Advanced Light Source (ALS). Samples were prepared on a Si substrate under the same conditions as those used for device fabrication.

Device Fabrication and Characterization: The PSCs were fabricated with an inverted structure of ITO/PEDOT:PSS/PTZP:IDIC/PFN-Br/Al. In an ultrasonic bath, the ITO-coated glass was cleaned with deionized water, ultrapure water, acetone and isopropanol, successively. The PEDOT:PSS layer was deposited by spin-coating at 5000 rpm on the ITO substrate and then thermal annealing treatment under 150 °C for 15 min. In a nitrogen glove box, the active layers were then deposited atop the PEDOT:PSS layer by spin-coating a chlorobenzene solution of PTZP:IDIC with a blend concentration of 18 mg/mL. Then PFN-Br layer was deposited by spin-coating at 3000 rpm, Finally, 100 nm Al was evaporated on the active layer under vacuum at a pressure of ca. 2×10^{-4} Pa. The PCE values of the PSCs were measured under an illumination of AM 1.5G (100 mW/cm^2) using a SSF5-3A solar simulator (AAA grade, 50×50 mm^2 photobeam size) of Enli Technology CO. Ltd. The 2×2 cm^2 monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO. Ltd. The PCE statistics were obtained using 20 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO. Ltd. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell.

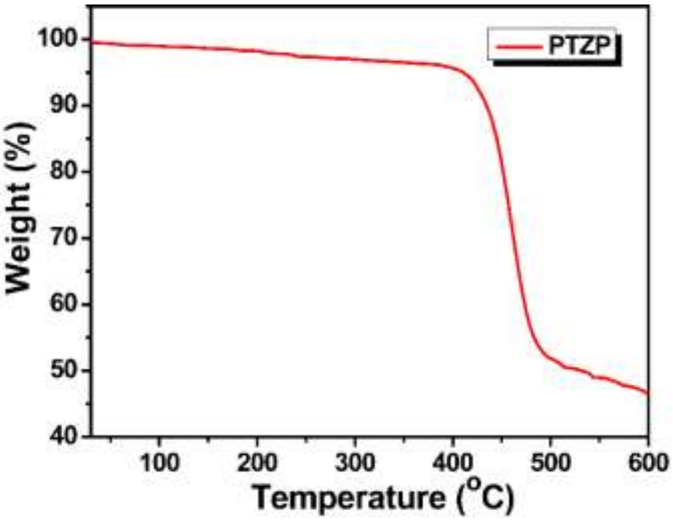

Figure S2. TGA plot of PTZP with a heating rate of 10 °C/min under an inert atmosphere.

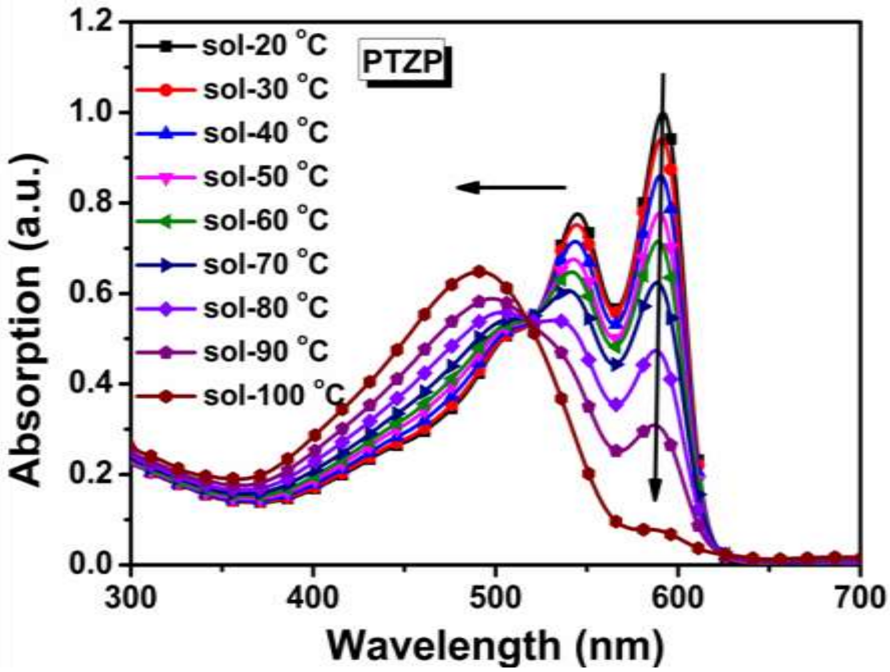

Figure S3. UV-vis absorption spectra of PTZP in CB solutions at different temperatures.

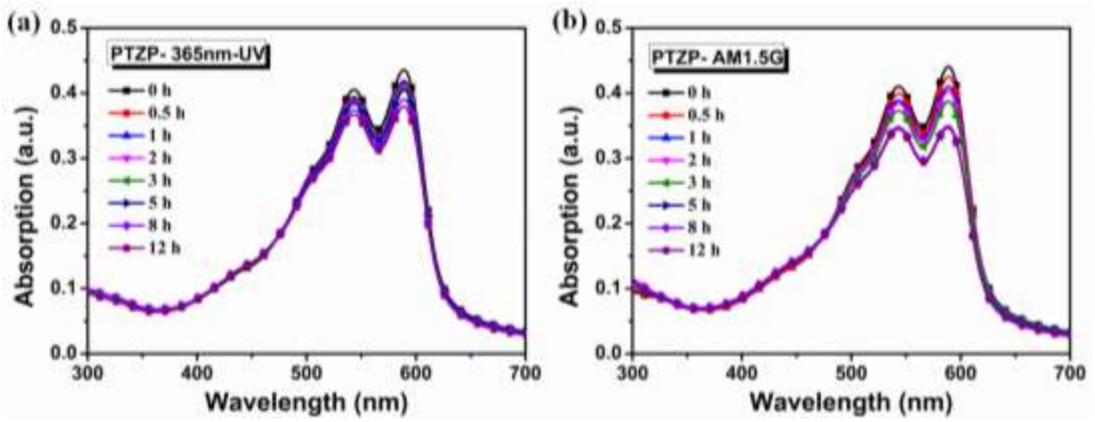

Figure S4. Absorption spectra of PTZP in film (a) under AM1.5 sunlight illumination (b) under the 365 nm UV light with different irradiation time.

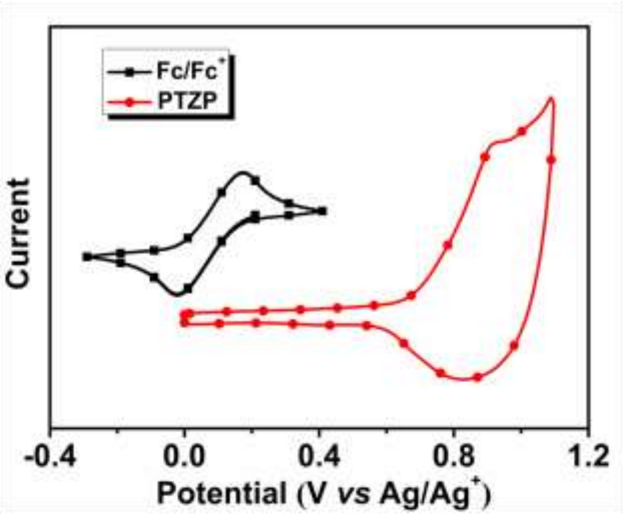

Figure S5. Cyclic voltammogram of PTZP film.

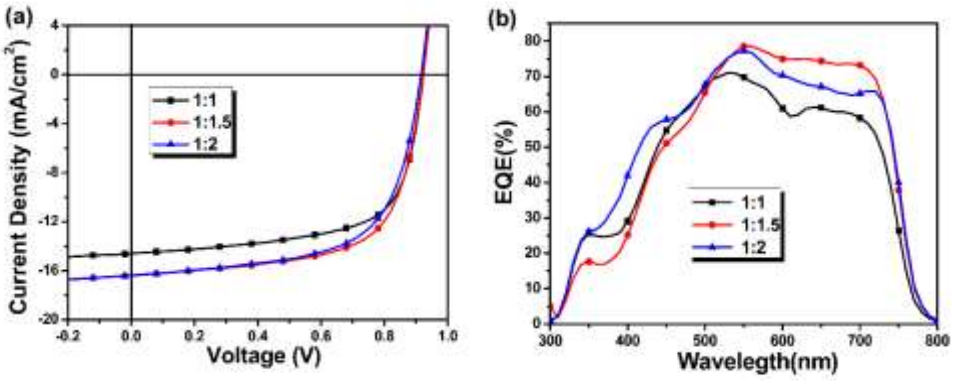

Figure S6. (a) *J*-*V* curves under the illumination of AM 1.5G, 100 mW/cm^2 and (b) EQE spectra of the PSCs based on PTZP:IDIC with different weight ratios.

Table S2. Photovoltaic performances of PSCs based on PTZP:IDIC with different weight ratios under the illumination of AM 1.5G, 100 mW/cm^2.

D/A Ratio	V_{oc} (V)	J_{sc} [J_{sc} $^{a)}$] (mA/cm^2)	FF (%)	PCE [PCE$_{ave}$$^{b)}$] (%)
1:1	0.92	14.6 (13.9)	66.3	9.0 (8.9)
1:1.5	0.92	16.4 (15.8)	65.5	9.9 (9.8)
1:2	0.91	16.4 (15.7)	63.2	9.5 (9.3)

$^{a)}$ The values calculated from EQE. $^{b)}$ The average PCE based on 20 devices are shown in parentheses.

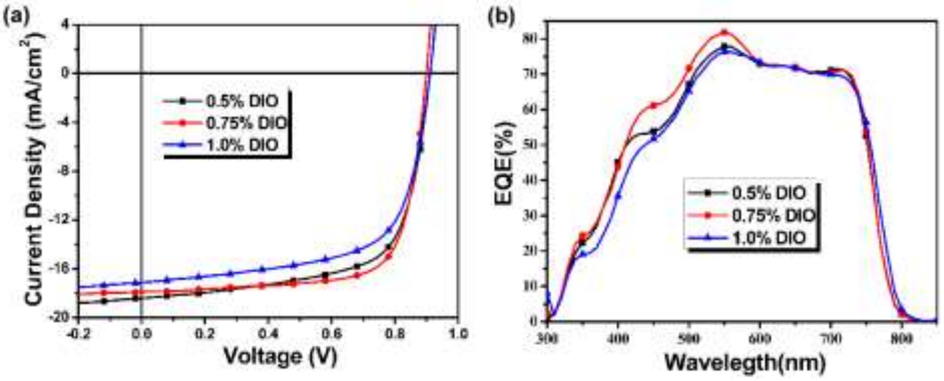

Figure S7. (a) *J-V* characteristics and (b) EQE curves of the PSCs based on PTZP:IDIC with different additive ratios.

Table S3. Photovoltaic performance of the PSCs based on PTZP:IDIC (1:1.5, w/w) with different additive ratios under the illumination of AM 1.5G, 100 mW/cm^2.

Additive radio	V_{oc} (V)	J_{sc} [J_{sc} $^{a)}$] (mA/cm^2)	FF (%)	PCE [PCE$_{ave}$$^{b)}$] (%)
0.5% DIO	0.90	17.3 (16.5)	68.7	10.7 (10.5)
0.75% DIO	0.90	17.9 (17.0)	73.3	11.8 (11.6)
1.0% DIO	0.91	17.1 (16.4)	65.2	10.4 (10.3)

$^{a)}$ The values calculated from EQE. $^{b)}$ The average PCE based on 20 devices are shown in parentheses.

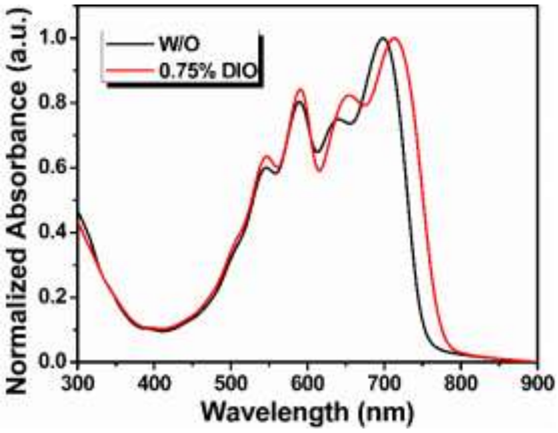

Figure S8. UV-Vis spectrum of the blend films based on PTZP**:**IDIC (1:1.5, w/w) without or with 0.75% DIO.

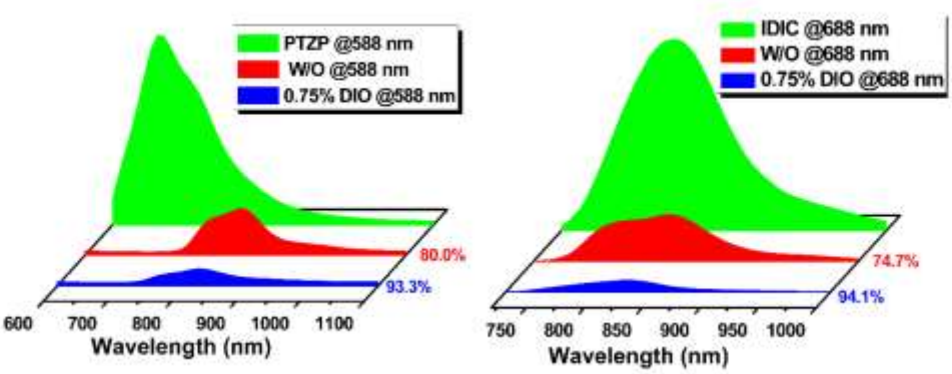

Figure S9. The PL spectra of PTZP (a), IDIC (b) and the related blend films.

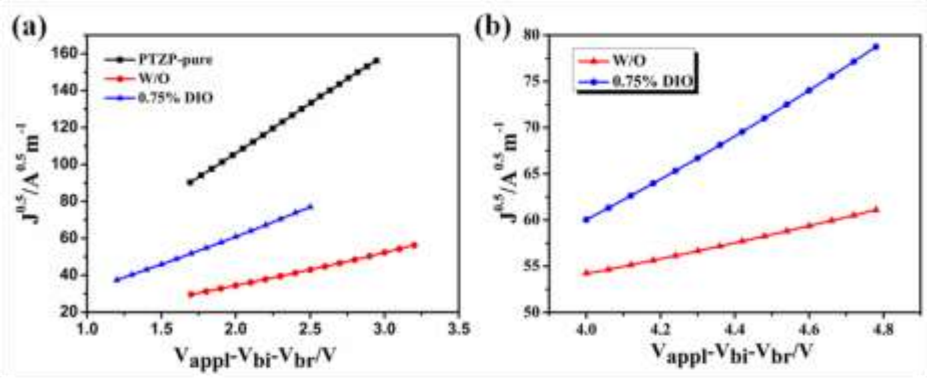

Figure S10. Plots obtained from the (a) hole-only and (b) electron-only devices based on PTZP pure film and PTZP:IDIC blend film without or with 0.75% DIO. The solid line fits the data points.

Table S4. Mobilities of the PTZP:IDIC blend films.

Condition	μ_h (cm^2/Vs)	μ_e (cm^2/Vs)	μ_h/μ_e
PTZP	4.01×10^{-3}	-	-
W/O	2.13×10^{-4}	9.07×10^{-5}	2.35
0.75% DIO	4.51×10^{-4}	3.31×10^{-4}	1.36

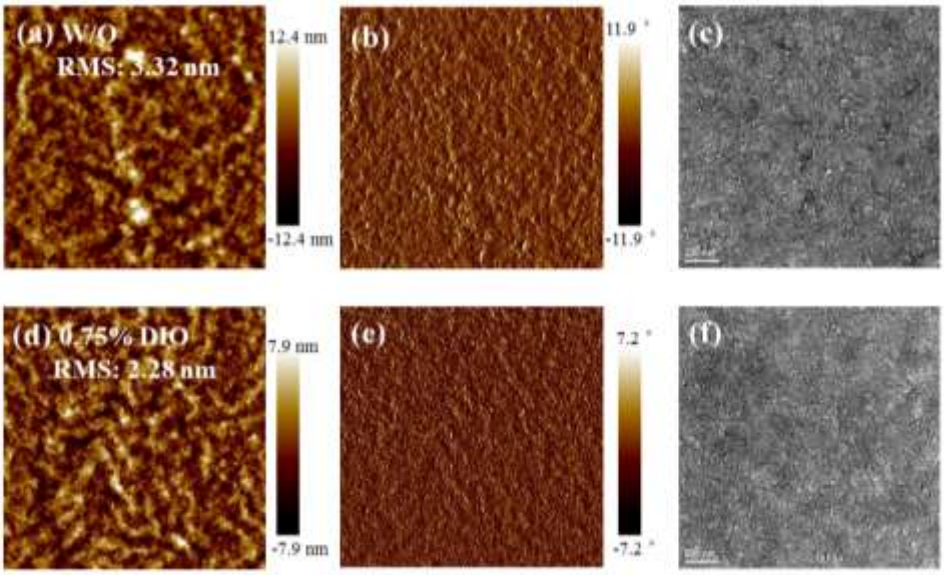

Figure S11. The AFM and TEM images: (a), (b) and (c) for the as-cast blend films; (d), (e) and (f) for the blend films with 0.75% DIO.

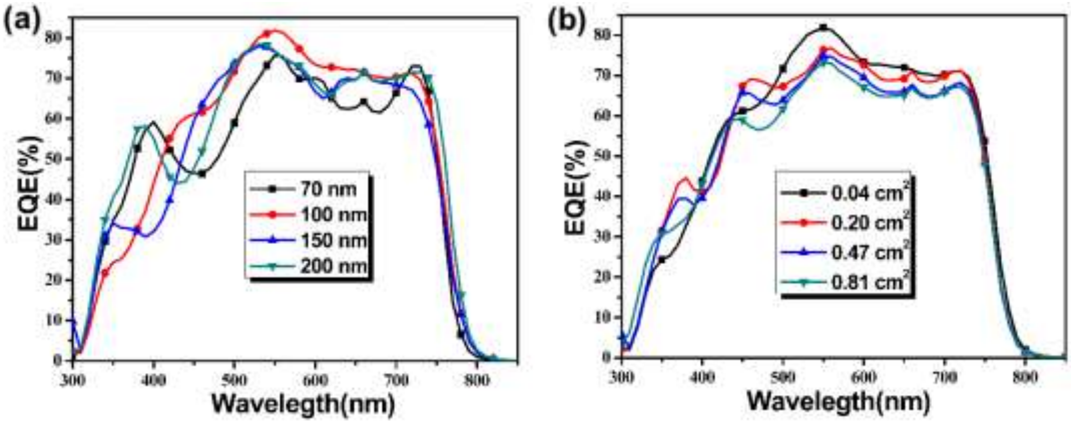

Figure S12. EQE curves of the PSCs based on PTZP:IDIC with different active layer thickness (a) and different active area (b).

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