

## Electronic Supplementary Information

### Perylene Diimide-Containing Acceptor Enables High Fill Factor in Organic Solar Cells

Kui Ding,<sup>a</sup> Tong Shan,<sup>a</sup> Jinqiu Xu,<sup>a</sup> Mengyang Li,<sup>b</sup> Wang Yan,<sup>a</sup> Yi Zhang,<sup>a</sup> Ziyi Xie,<sup>a</sup> Zaifei Ma,<sup>b</sup>  
Feng Liu,<sup>a</sup> Hongliang Zhong<sup>\*a</sup>

<sup>a</sup>School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai, 200240 China, Corresponding to: hlzhong@sjtu.edu.cn (H. Zhong)

<sup>b</sup>Center for Advanced Low-dimension Materials, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, 201620, China.

#### 1. Experimental

##### 1.1 Materials characterization methods

*General.* All reactions were run in oven-dried glassware (100 °C), and monitored by TLC using silica gel pre-coated plates. Anhydrous and oxygen-free solvents were obtained with sodium or calcium hydride reflux. MALDI-TOF MS was measured using a Bruker auto flex Speed TOF analysis. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of intermediates were collected on a Bruker AVANCE III HD 400 and AVANCE III HD 500 Spectrometer at 298 K as solutions in CDCl<sub>3</sub>. The UV-vis absorption spectra were measured from a Lambda 750S spectrophotometer with dilute solutions and solid state films of the acceptors. Cyclic voltammetry (CV) measurements were performed on a CHI604E electrochemical workstation, equipped with a three-electrode cell consisting of a platinum working electrode, Ag/Ag<sup>+</sup> as reference electrode and a platinum sheet counter electrode. CV measurements were carried out in anhydrous dichloromethane containing 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte under an argon atmosphere at a scan rate of 100 mV s<sup>-1</sup> assuming that the vacuum energy level of Fc/Fc<sup>+</sup> was -4.80 eV. The film of sample was tested in 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub>

acetonitrile solution. Density functional theory (DFT) calculations was confirmed by the Gaussian 09 program at the B3LYP/6-31G level. Atomic force microscopy (AFM) measurement was conducted on a Bruker Multimode 8 in tapping mode. Transmission electron microscopy (TEM) measurement was conducted on a Talos L120C G2 from Thermo Fisher Scientific. The characterization of GIWAXS for the blend films was obtained from the Advanced Light Source (Lawrence Berkeley National Laboratory) on beamline 7.3.3. The incident angle and the beam energy were  $0.16^\circ$  and 10 keV, respectively. The samples were spin-coated on the Si/PEDOT:PSS substrates in optimized conditions.

## 1.2 Device fabrication and evaluations

*Device Fabrication.* The patterned indium tin oxide glass (ITO) glass substrates (sheet resistance =  $10 \Omega \text{ sq}^{-1}$ ) were cleaned in detergent, de-ion water, acetone, chloroform, acetone, and isopropanol sequentially by ultra-sonic bath for 15 min each and then dried by  $\text{N}_2$  gas. Further UV-Ozone treatment for 10 min was applied before use. The PEDOT:PSS solution was spin-coated onto the cleaned ITO glass substrate at 3000 rpm of 30 s followed by annealing at  $150^\circ\text{C}$  of 15 min in air. Then the PEDOT-PSS coated substrates were transferred into a nitrogen-filled glove box. PM6:PDFC blends were dissolved in chloroform at  $50^\circ\text{C}$  with total concentration of  $15\text{-}17 \text{ mg ml}^{-1}$  and stirred for 2 h in a nitrogen-filled glove box. The active layers with different thicknesses (110-1100 nm) were obtained by spin-coating the blend solution at room temperature. The film thickness was obtained via AFM measurement. TA was carried out on the thermal platform with optimal temperature of  $140^\circ\text{C}$  for 3 min in a glove box. Then ZnO as the electron transport layer was spin-coated on the active layer at 3000 rpm for 40 s. Finally, the anode, 100 nm Ag was deposited at a speed of  $0.3 \text{ nm/s}$  through a shadow mask by thermal evaporation in a vacuum chamber of under  $2 \times 10^{-6}$  Torr to complete the device fabrication. The active area of each device was defined to  $0.036 \text{ mm}^2$ .

*Device characterization.* The device  $J$ - $V$  characteristics were recorded by a Keithley 2420 SourceMeter unit in forward direction under AM 1.5G 1 sun irradiance ( $100 \text{ mW cm}^{-2}$ ) as generated by a 300 W Xe lamp solar simulator (Enlitech SS-F5-3A)

at room temperature. The effective illuminated area was defined by a shadow mask of 3.2 mm<sup>2</sup>. The light intensity was calibrated using a standard Si diode with KG-5 filter. The EQE spectra were characterized using an Enlitech EQE system (Enlitech QE-M110) with a Si diode as reference cell. Monochromatic light was generated from an Enlitech lamp source with a monochromator.

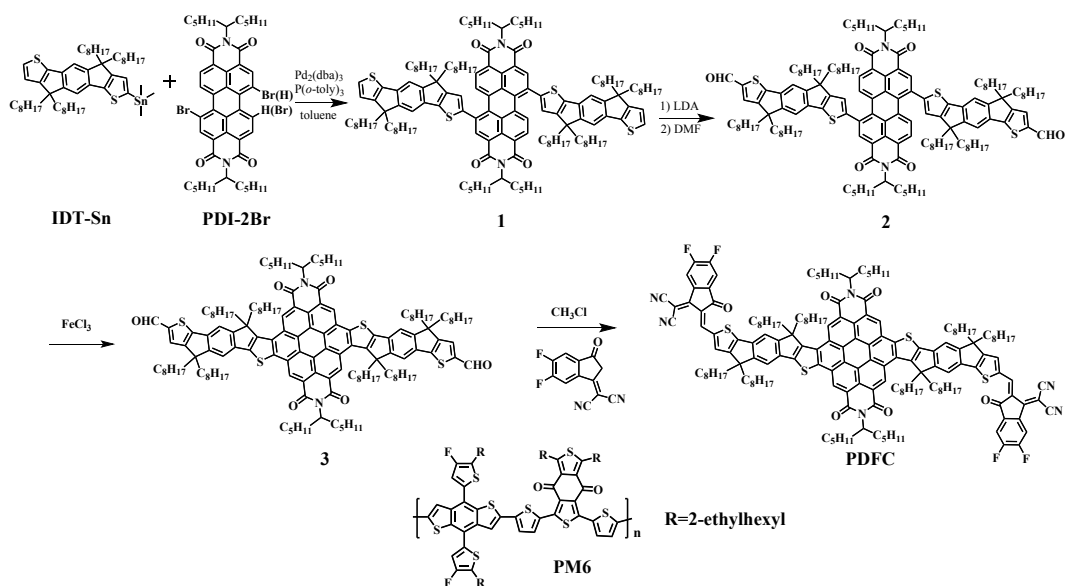
*EL measurement.* EL measurement was conducted by direct-current meter (PW2326, Tectronix) to provide bias voltage for the test device, and the EL spectra were recorded by the fluorescence spectrometer (KYMERA-328I-B2, Andor technology LTD) with cooled silicon array and indium gallium arsenic detector, which was calibrated by standard light source (Ocean Optics).

*EQE<sub>EL</sub> Measurement.* The EQE<sub>EL</sub> was recorded with an in-house-built system comprising a standard silicon photodiode (S1337-1010BR, Hamamatsu Electronics), Keithley 2400 source meter (for supplying voltages and recording injected currents), and Keithley 6482 picoammeter (for measuring the emitted light intensity).

*sEQE Measurement.* A 150 W quartz halogen lamp (LSH-75, Newport) acted as a light source, passing through the monochromator (CS260-RG-3-MC-A, Newport) to provide an adjustable monochromator light source for testing, and then emitted an optical signal at a 173 Hz frequency through the chopper (3502 Optical Chopper, Newport) and focused on the OSC devices. The current generated by the device was amplified by the front-end current amplifier (SR570, Stanford) to reduce the impact of the noise signal. The final signal was collected and analyzed by a Phased-locked Amplifier (SR830 DSP Lock-in Amplifier, Stanford).

### 1.3. Synthesis

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. The compounds **IDT-Sn**, and **PDI-2Br** were prepared according to reported methods in literatures. <sup>[1-3]</sup>



**Scheme S1** The synthetic route of PDFC and chemical structure of PM6.

**Compound 1.** In a 250 mL flask, **PDI-2Br** (2.90 g, 3.38 mmol) and **IDT-Sn** (7.50 g, 8.54 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.10 g), and tri(*o*-tolyl)phosphine (0.11 g) were added with argon protection. After the addition of dry toluene (60 mL), the mixture was heated to 110°C and kept for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM), washed with aqueous NaCl solution, and dried over  $\text{Na}_2\text{SO}_4$ . After the solvent was removed in vacuum, the crude product was purified by silica gel column chromatography with hexane/DCM = 4:1 as the eluent to afford **compound 1** as dark solid (5.85 g, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.76 (br, 2H), 8.42 (br, 2H), 8.15 (br, 2H), 7.40 - 7.28 (m, 4H), 7.25 - 7.20 (m, 4H), 6.99 (br, 2H), 5.16 (m, 2H), 2.20 (br, 4H), 2.09 - 1.67 (m, 20H), 1.20 (m, 72H), 0.82 (m, 36H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 164.96, 164.55, 163.86, 163.47, 156.67, 155.90, 154.01, 153.24, 145.21, 144.93, 141.68, 136.84, 136.45, 135.73, 135.25, 134.20, 133.14, 133.09, 130.10, 129.79, 129.46, 128.42, 126.95, 123.04, 122.89, 122.59, 122.31, 122.12, 113.97, 113.31, 54.91, 54.61, 54.01, 39.54, 39.24, 32.56, 32.07, 32.00, 30.29, 30.25, 29.62, 29.59, 29.49, 26.86, 24.53, 22.90, 22.88, 22.82, 14.34, 14.29. MS (MALDI-TOF)  $m/z$ : Calculated for  $\text{C}_{142}\text{H}_{198}\text{N}_2\text{O}_4\text{S}_4$ , 2123.42; Found, 2123.40.

**Compound 2.** The **compound 1** (1.10 g, 0.52 mmol) was dissolved in 100 mL of

anhydrous THF and cooling to  $-78\text{ }^{\circ}\text{C}$  with argon protection. The fresh made lithium diisopropylamide (1.60 mmol) was added dropwise. Subsequently, the mixture was kept at  $-78\text{ }^{\circ}\text{C}$  for 1 h. The mixture was followed by the addition of dry DMF (1.50 mL, 20.0 mmol). The mixed solution was allowed to slowly return to room temperature and kept stirring overnight. The mixture was quenched with water and extracted with DCM. The organic extraction was dried with  $\text{Na}_2\text{SO}_4$ . After the solvent was removed in vacuum, the crude product was purified by silica gel column chromatography with hexane/DCM = 1:2 as the eluent to afford **compound 2** as dark solid (0.72 g, 64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 9.94 (s, 2H), 8.78 (br, 2H), 8.41 (br, 2H), 8.20 (m, 2H), 7.67 (s, 2H), 7.48 (s, 2H), 7.37 (s, 2H), 7.25 (s, 2H), 5.18 (m, 2H), 2.33 - 2.15 (m, 4H), 2.17 - 1.68 (m, 20H), 1.19 (m, 72H), 0.88 - 0.80 (m, 36H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 183.14, 157.95, 155.66, 155.51, 153.79, 152.45, 146.49, 145.03, 144.36, 138.06, 135.13, 134.92, 133.93, 133.25, 130.86, 129.68, 128.49, 123.16, 122.60, 115.09, 114.05, 54.98, 54.80, 54.40, 39.38, 39.10, 32.52, 32.02, 31.96, 30.17, 29.58, 29.53, 29.44, 26.84, 24.62, 24.54, 22.87, 22.83, 22.78, 14.30, 14.25. MS (MALDI-TOF)  $m/z$ : Calculated for  $\text{C}_{144}\text{H}_{198}\text{N}_2\text{O}_6\text{S}_4$ , 2179.41; Found, 2178.46.

**Compound 3.** The **compound 2** (0.40 g, 0.18 mmol) was dissolved in 100 mL of anhydrous toluene with argon protection. Subsequently, the mixture  $\text{FeCl}_3$  (0.57 g, 3.52 mmol) and  $\text{CH}_3\text{NO}_2$  (4 ml) was added dropwise. The mixture was heated to  $40\text{ }^{\circ}\text{C}$  and kept stirring overnight. The mixture was quenched with water and extracted with DCM. The organic extraction was dried with  $\text{Na}_2\text{SO}_4$ . After the solvent was removed in vacuum, the residual was purified by silica gel column chromatography with DCM as the eluent to afford **compound 3** as red solid (0.34 g, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 10.79 (br, 2H), 10.28 (br, 2H), 9.97 (s, 2H), 7.84 - 7.62 (m, 4H), 7.30 (s, 2H), 5.56 (m, 2H), 3.56 - 3.00 (m, 4H), 2.81 - 2.34 (m, 8H), 2.30 - 1.81 (m, 12H), 1.64 - 0.86 (m, 76H), 0.78 - 0.35 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 183.21, 166.18, 156.12, 155.97, 155.74, 152.05, 150.40, 146.71, 145.65, 143.37, 137.45, 136.55, 134.58, 130.66, 127.82, 126.80, 123.56, 123.21, 122.00, 114.89, 114.25, 58.27, 55.44, 54.62, 39.30, 38.68, 32.87, 32.06, 32.02, 31.77, 30.18, 29.58,

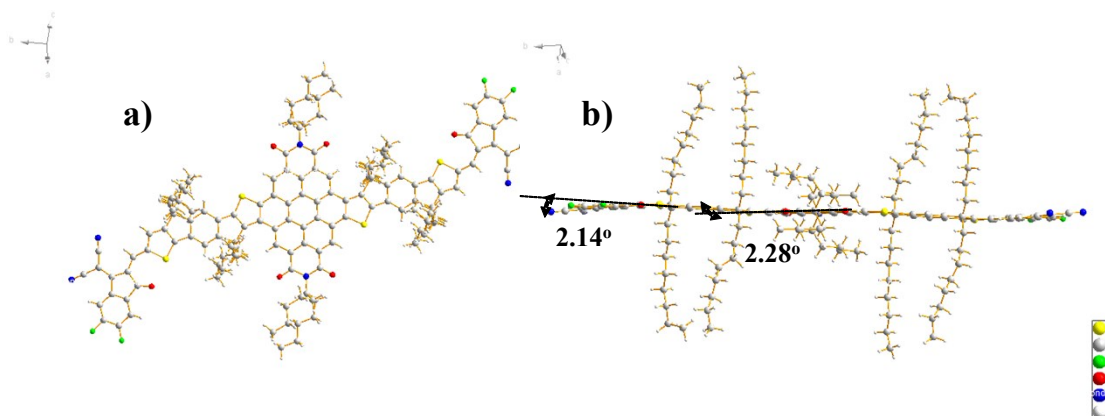
29.44, 29.03, 27.04, 24.64, 24.31, 22.83, 22.56, 14.29, 13.98. MS (MALDI-TOF) m/z: Calculated for C<sub>144</sub>H<sub>194</sub>N<sub>2</sub>O<sub>6</sub>S<sub>4</sub>, 2175.38; Found, 2174.91.

**Compound PDFC.** The **compound 3** (0.30 g, 0.14 mmol) was dissolved in 40 mL of *n*-BuOH and 20 ml CHCl<sub>3</sub> with argon protection. Subsequently, the 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.17 g, 0.74 mmol) was added. The mixture was heated to 100 °C and kept at this temperature for 4 h. After cooling to room temperature, the mixture was quenched with methanol. The precipitate was collected by filtration and washed with methanol. The crude product was purified by silica gel column chromatography with CHCl<sub>3</sub>/ hexane=1:1 as the eluent to afford **compound PDFC** as purple blue solid (0.25 g, 69%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 10.83 (br, 2H), 10.32 (br, 2H), 9.06 (s, 2H), 8.61 (m, 2H), 7.94 (s, 2H), 7.87 - 7.71 (m, 6H), 5.60 (m, 2H), 3.49 - 3.25 (m, 4H), 2.83 - 2.44 (m, 8H), 2.34 - 2.01 (m, 12H), 1.57 - 0.78 (m, 76H), 0.64 - 0.43 (m, 12H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ): -123.47, -124.48. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 186.33, 166.18, 163.00, 158.91, 157.36, 157.30, 156.53, 153.41, 153.27, 151.57, 146.43, 143.99, 140.59, 139.48, 139.08, 138.92, 136.73, 136.36, 134.80, 134.44, 127.78, 126.84, 123.62, 123.41, 123.18, 122.19, 120.62, 115.97, 115.33, 115.12, 114.74, 114.45, 69.10, 58.32, 55.58, 54.77, 39.44, 38.62, 32.88, 32.07, 32.01, 31.77, 30.15, 29.62, 29.57, 29.45, 29.06, 29.02, 27.07, 24.74, 24.40, 22.84, 22.58, 14.29, 14.00. MS (MALDI-TOF) m/z: Calculated for C<sub>168</sub>H<sub>198</sub>F<sub>4</sub>N<sub>6</sub>O<sub>6</sub>S<sub>4</sub>, 2599.42; Found, 2598.63.

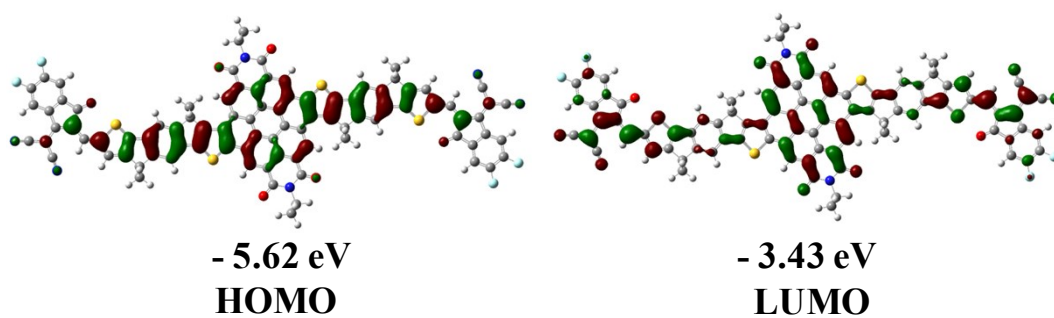
**Table S1** The absorption and energy levels of PDFC and PM6

	$\lambda_{\max}^a$	$\lambda_{\max}^b$	$\lambda_{\text{onset}}^b$	$E_g^{\text{opt } c}$	HOMO <sup>CV</sup>	LUMO <sup>CV</sup>	$E_g^{\text{CV}}$
	nm	nm	nm	(eV)	(eV)	(eV)	(eV)
<b>PDFC</b>	668	691	725	1.71	-5.57	-3.85	1.72
<b>PM6</b>	550	618	679	1.85	-5.54	N/A	N/A

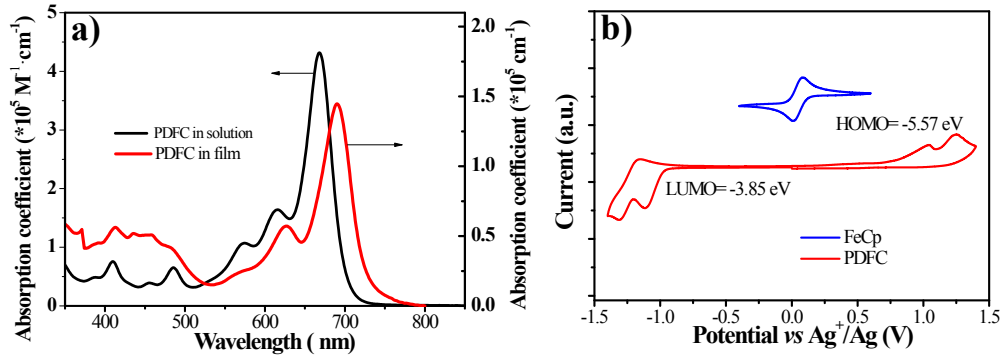
a) In chloroform solution. b) In spun-cast film from chloroform solution. c) Calculated from  $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$ .



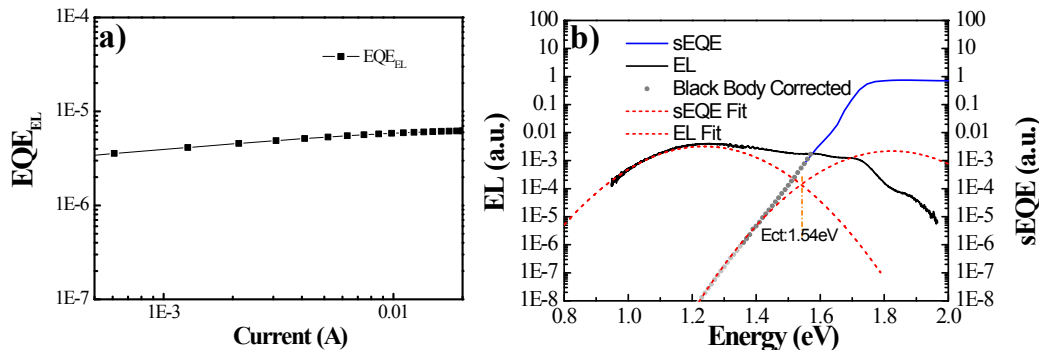
**Fig. S1** The single crystal configuration a) top view and b) side view of PDFC.



**Fig. S2** HOMO and LUMO distributions for the minimum-energy conformations of PDFC calculated by Gaussian 09 at B3LYP/6-31G level.



**Fig. S3** a) UV-vis absorption spectrum extinction coefficient of PDFC in solution and in film. b) Cyclic voltammetry curves of PDFC film.



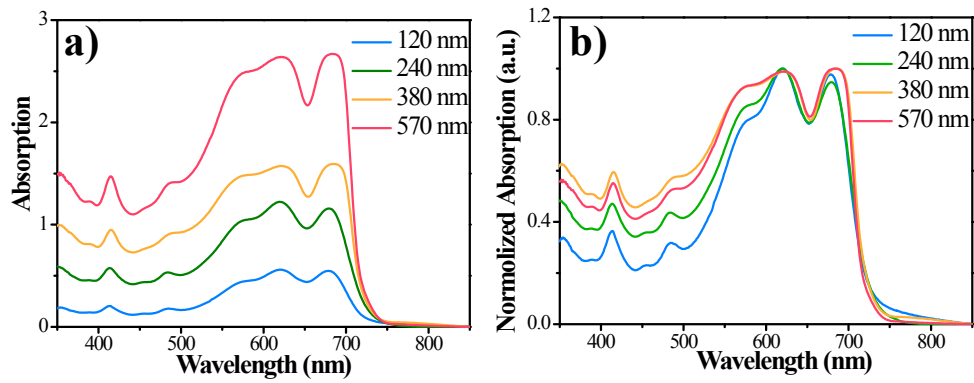
**Fig. S4** (a) External quantum efficiency (EQE) of electroluminescence spectra. (b) Highly sensitive EQE (s-EQE, blue line) and the electroluminescence (EL, black line) of PM6:PDFC device.

**Table S2** Detailed  $V_{oc}$  loss of PM6:PDFC device.

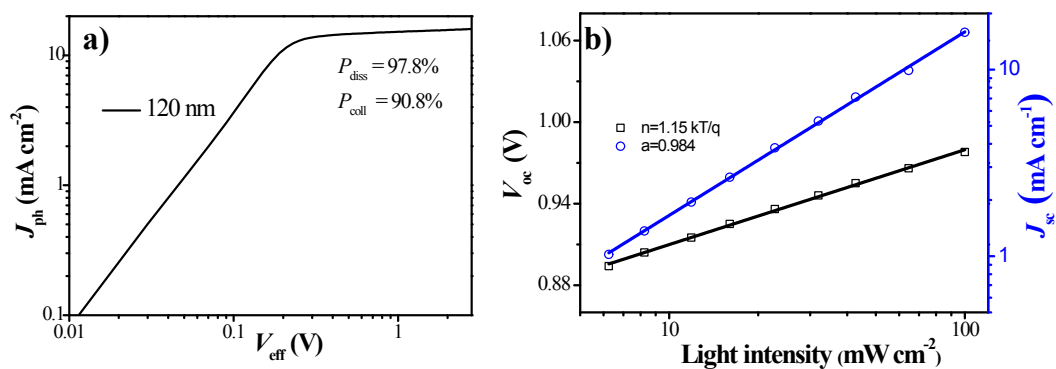
	$V_{oc}$ (V)	$E_g$ (eV) <sup>a</sup>	$E_{loss}$ (eV)	$E_{CT}$ (eV) <sup>b</sup>	$\Delta E_1$ (eV) <sup>c</sup>	$\Delta E_2$ (eV) <sup>d</sup>	$\Delta E_3$ (eV) <sup>e</sup>
PM6:PDFC	0.97	1.72	0.75	1.54	0.18	0.26	0.31

<sup>a</sup> $E_g$  is determined from the derivatives of the EQE curve. <sup>b</sup> $E_{CT}$  is estimated by fitting an expression of the s-EQE and EL spectra based on Marcus theory. <sup>c</sup> $\Delta E_1$  is the voltage loss due to the charge transfer (CT) state, which calculated by  $\Delta E_1 = E_g - E_{CT}$ . <sup>d</sup> $\Delta E_2$  is the voltage loss due to radiative recombination, which is calculated by  $\Delta E_2 = E_{CT} - V_{oc} - \Delta E_3$ . <sup>e</sup> $\Delta E_3$  is the voltage loss due to non-radiative recombination, which is calculated by  $\Delta E_3 = -kT \ln(EQE_{EL})$ .

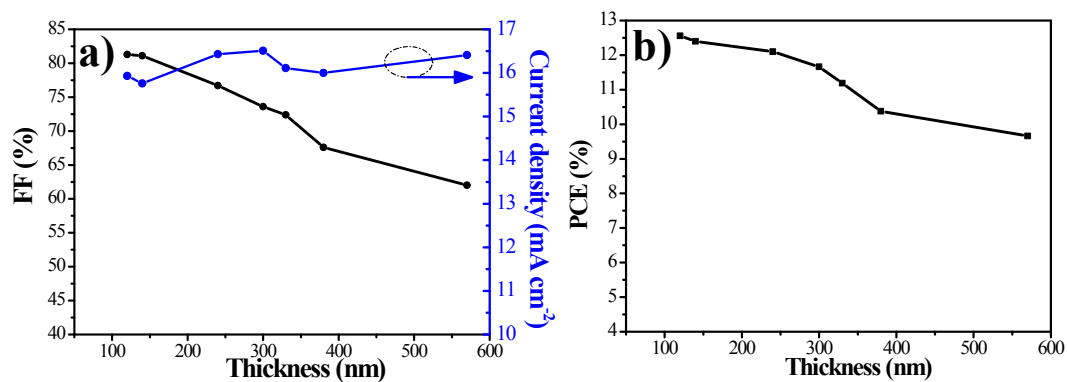




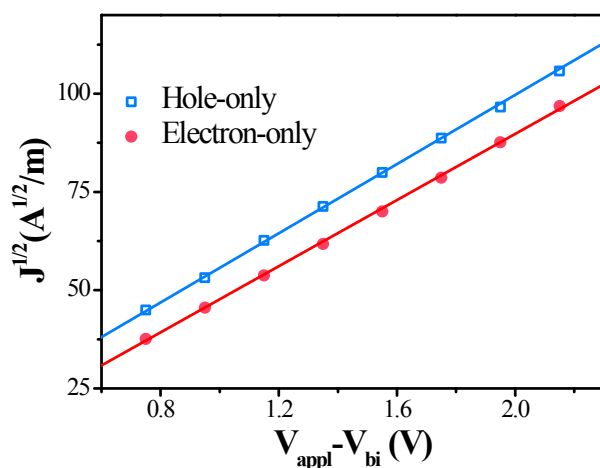
**Fig. S5** a) UV-vis curves of PM6:PDFC blend films at different thicknesses. b) Normalized UV-vis curves of PM6:PDFC blend films at different thicknesses.



**Fig. S6** a) Photocurrent density versus effective voltage of PM6:PDFC with 120 nm. b) Photocurrent density and  $V_{oc}$  versus light intensity of PM6:PDFC with 120 nm.



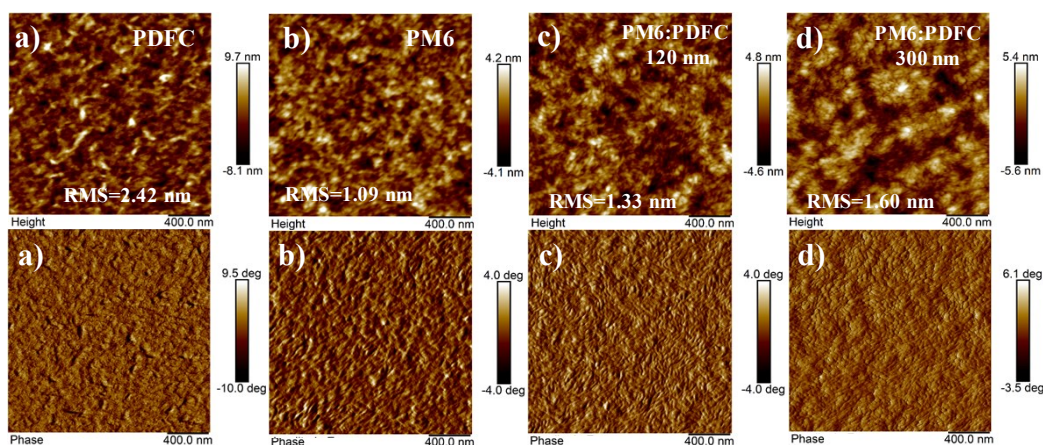
**Fig. S7** Active layer thickness dependence of a)  $J_{sc}$  and FF and b) PCE of the device based on PM6:PDFC.



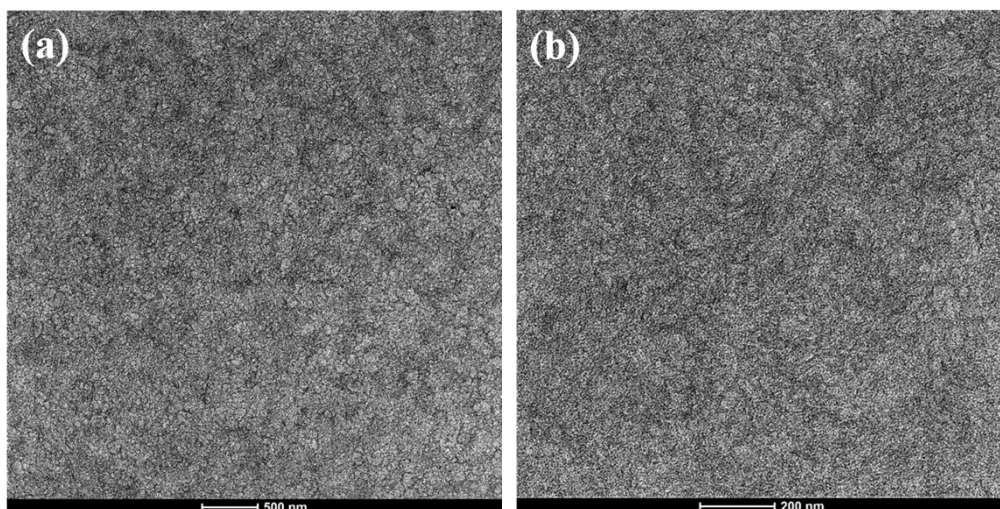
**Fig. S8** Electron mobility and hole mobility for the blend films of PM6:PDFC.

**Table S3** The hole and electron mobility of blend film PM6:PDFC using the SCLC method.

	$\mu_{\text{hole}}$ ( $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	$\mu_{\text{electron}}$ ( $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	$\mu_{\text{electron}}/\mu_{\text{hole}}$
<b>PM6:PDFC</b>	6.89 (6.41 ± 0.25)	7.14 (6.63 ± 0.32)	1.04

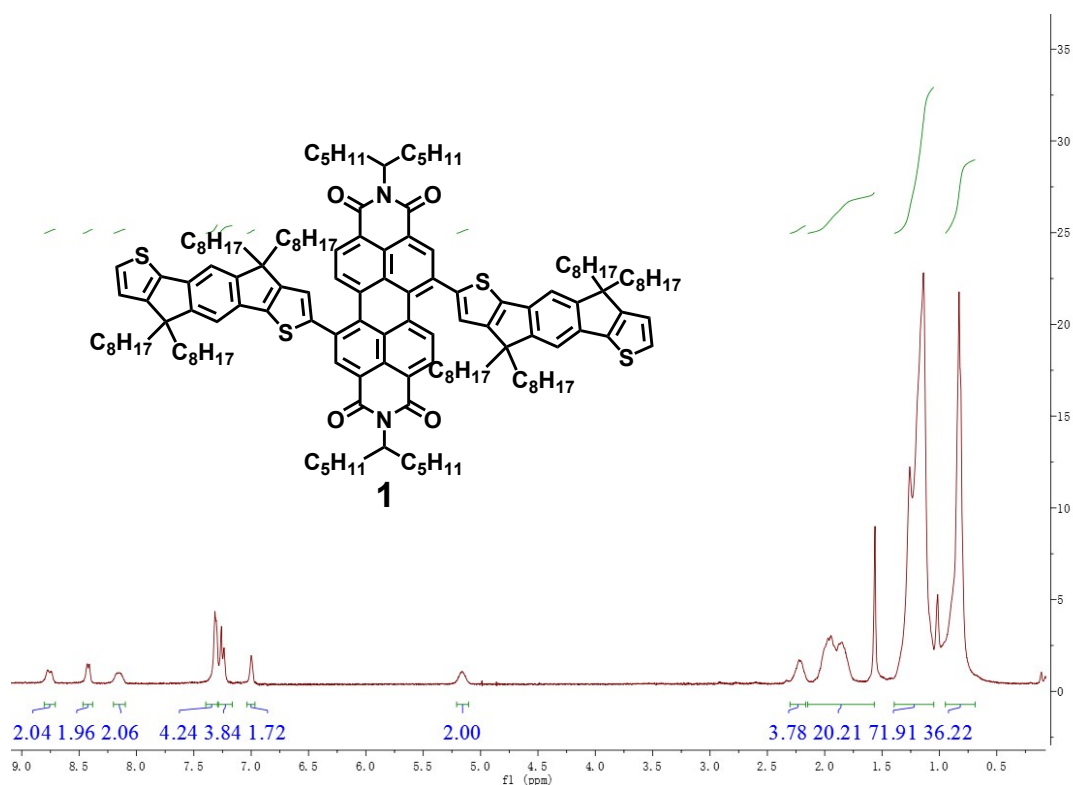


**Fig. S9** AFM height and phase images of a) neat PDFC film, b) neat PM6 film and PM6:PDFC blend film with different thickness c) 120 nm and d) 300 nm. The image size area is  $2 \times 2 \mu\text{m}$ .

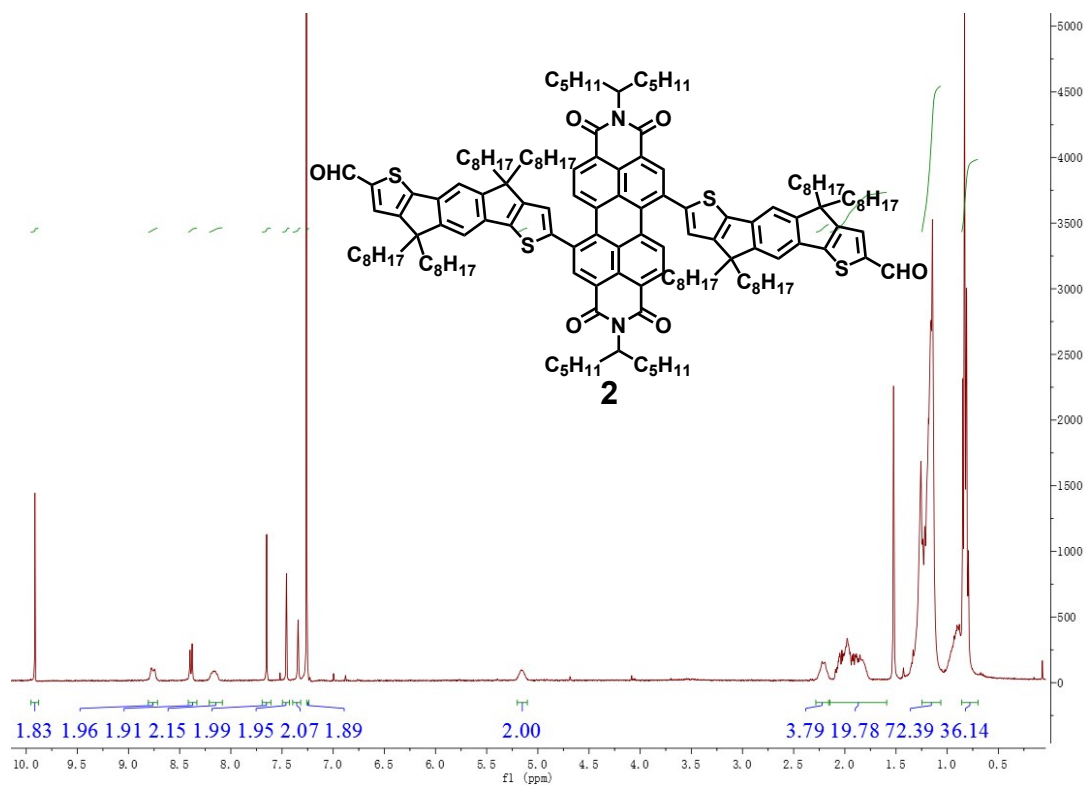


**Fig. S10** TEM images of PM6:PDFC blend film with different magnifications.

## 1.4 Characterizations of the new compounds



**Fig. S11**  $^1\text{H}$  NMR of compound 1 in CDCl<sub>3</sub>.



**Fig. S12**  $^1\text{H}$  NMR of compound 2 in CDCl<sub>3</sub>.

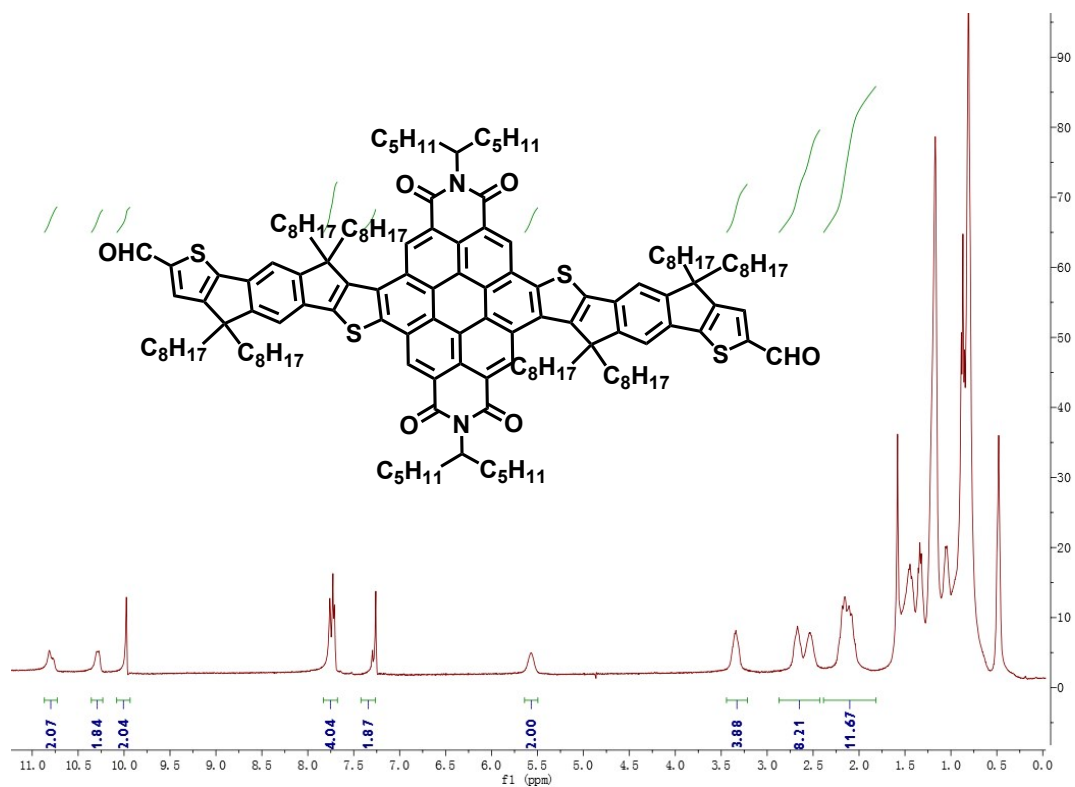


Fig. S13  $^1\text{H}$  NMR of compound 3 in  $\text{CDCl}_3$ .

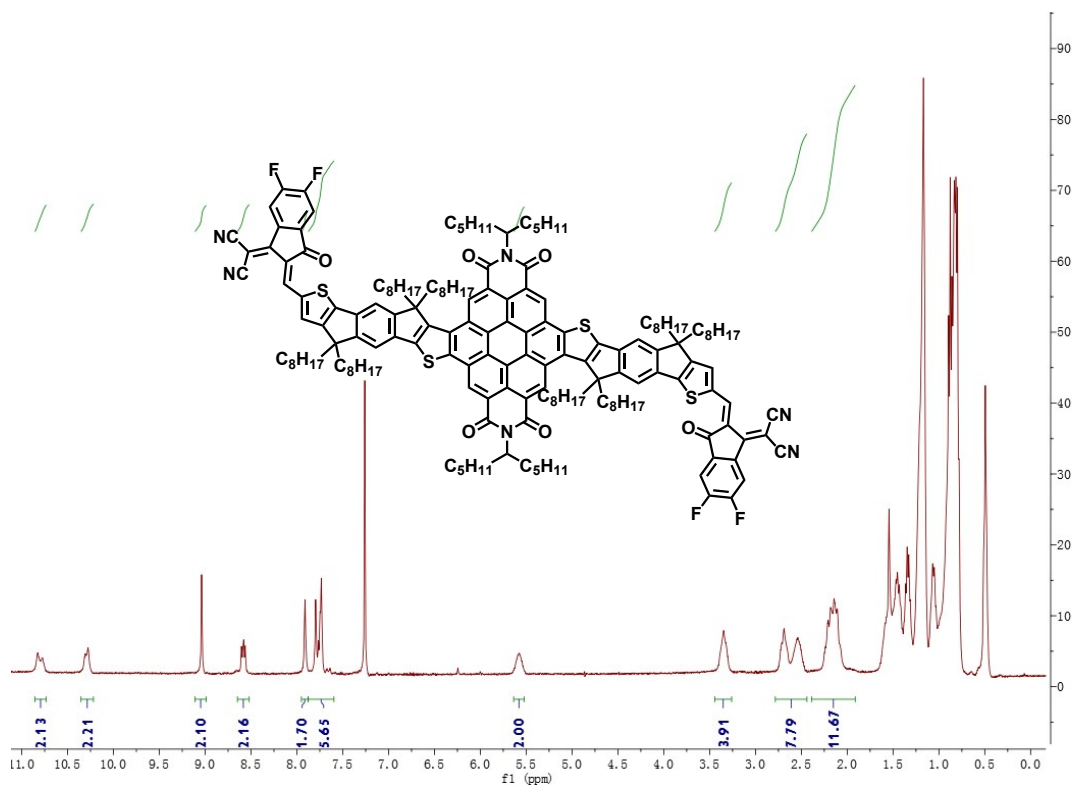
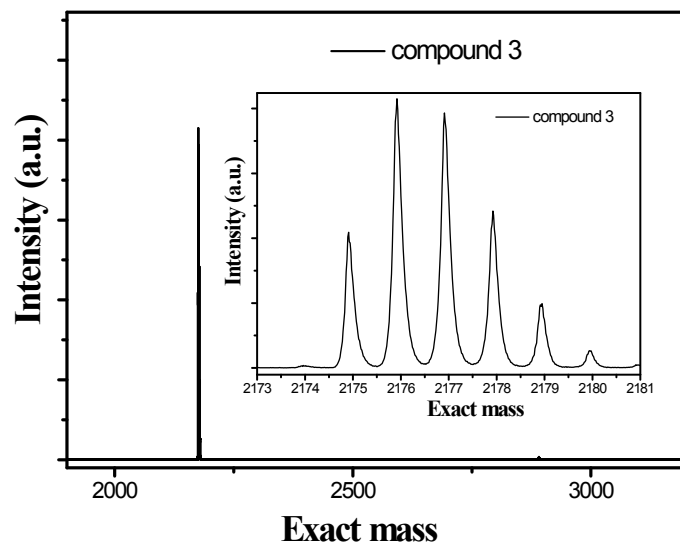
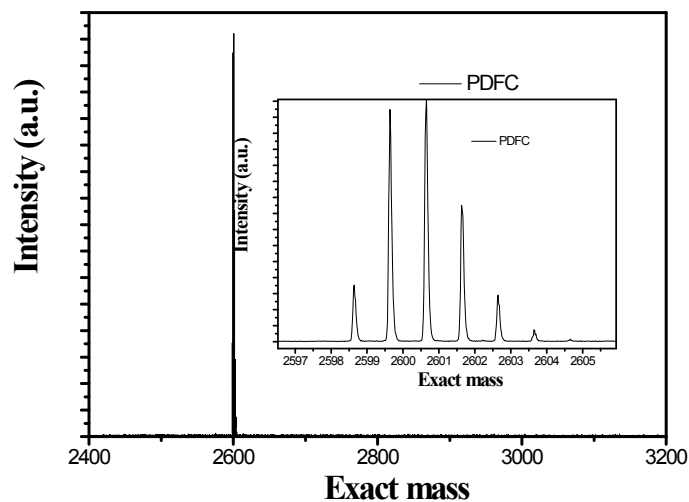


Fig. S14  $^1\text{H}$  NMR of compound PDFC in  $\text{CDCl}_3$ .



**Fig. S15** Mass spectrum (MALDI-TOF) of compound 3.



**Fig. S16** Mass spectrum (MALDI-TOF) of compound PDFC.

- [1] A. H. Endres, M. Schaffroth, F. Paulus, H. Reiss, H. Wadepl, F. Rominger, R. Kramer, U. H. Bunz, *J. Am. Chem. Soc.* **2016**, 138, 1792.
- [2] F. Wurthner, V. Stepanenko, Z. Chen, C. R. Saha-Moller, N. Kocher, D. Stalke, *J. Org. Chem.* **2004**, 69, 7933.
- [3] L. Cai, T. Moehl, S. J. Moon, J. D. Decoppet, R. Humphry-Baker, Z. Xue, L. Bin, S. M. Zakeeruddin, M. Gratzel, *Org. Lett.* **2014**, 16, 106.