Supporting Information

Inorganic molecule-induced electron transfer complex for highly efficient organic solar cells

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S1. Materials

The polymer donor PBDB-T-2F and the non-fullerene acceptor Y6 and PFN-Br were purchased from Solarmer Materials (Beijing) Inc. The processing solvents used in the device fabrication processes were purchased from Alfa Aesar and were all commercially available anhydrous solvents. Poly(3,4- ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) (AI 4083) and electrode materials were commercially available products without further purification.

S2. Device Fabrication

The spin-coated and blade-coated OSC devices were fabricated and characterized by using a conventional structure of ITO/PEDOT:PSS or PMCs/active layer/PFN-Br/Al, where the PEDOT:PSS and PMCs were all served as the anode interlayers. The ITO substrates were cleaned with detergent water, deionized water, acetone and isopropyl alcohol in an ultrasonic bath sequentially for 20 minutes, and then dried in an oven at 150 ^{o}C for 30 minutes.

Anode interlayers fabrication. After substrates were treated by UV-ozone for 20 min, PEDOT:PSS was coated at 4,000 rpm for 60 s and then annealed for 15 min at 150 ^{o}C in the air. For PMCs as the interlayers, PMCs were dissolved in methanol and then coated on ITO substrates without annealing.

Active layer fabrication. PBDB-T-2F:Y6 (1:1.2, w/w) blend was dissolved in chloroform (CF) solvent at a polymer weight concentration of 7 mg/mL and 0.5% volume 1-chloronaphthalene (CN) was used as the solvent additive. Then 0.5 mg/mL PFN-Br in methanol was spin-coated on the top of active layer at 3,000 rpm for 30 s. Finally, about 100 nm Al were thermally evaporated under a vacuum at a pressure of 3×10^{-4} Pa, giving an area of 0.04 cm^2 and 1.0 cm^2. Except for the spin-coating of PEDOT:PSS, the other the processes were all carried out in an nitrogen-filled glovebox.

S3. Device Characterization

The *J*−*V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5 G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW/cm^2. The EQE spectrum was measured using a QE-R3011 Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan). The film thickness data was obtained via a surface profilometer (Dektak XT, Bruker). UV-vis absorption spectra were measured by Hitachi UH4150 spectrophotometer. XPS was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K_α radiation. UPS was carried out on Thermo Scientific ESCALab 250Xi using a He discharged lamp. AFM height and phase images were recorded on a Nanoscope V AFM microscope (Bruker), where the tapping mode was used. X-ray diffraction (XRD) patterns were collected using a Rigaku D/max 2500 X-ray diffractometer.

S4. Additional Fig.s and Tables

The structural characteristics of these five PMCs are identified using measurements of powder X-ray diffraction (XRD) patterns, as shown in Fig. S1. The Bragg reflection peaks in four ranges of 2θ at 7–10°, 14–22°, 25–30° and 31–35° are the typical characteristic peaks of the Keggin-type structure.[1] The IR spectra of these five PMCs exhibit similar characteristic vibrational features of a typical Keggin structure (Fig. S2): four strong bands are clearly observed at 1079~1064, 982~967, 899~891, and 810~798 cm^{-1}, which are assigned to the symmetric and asymmetric bond stretching modes for P−O, M=O_t, M−O_b−M, and M−O_c−M, respectively, where M denotes the W or Mo atom; O_t denotes the terminal oxygen atom; O_b and O_c denote different bridge oxygen atoms. [2]

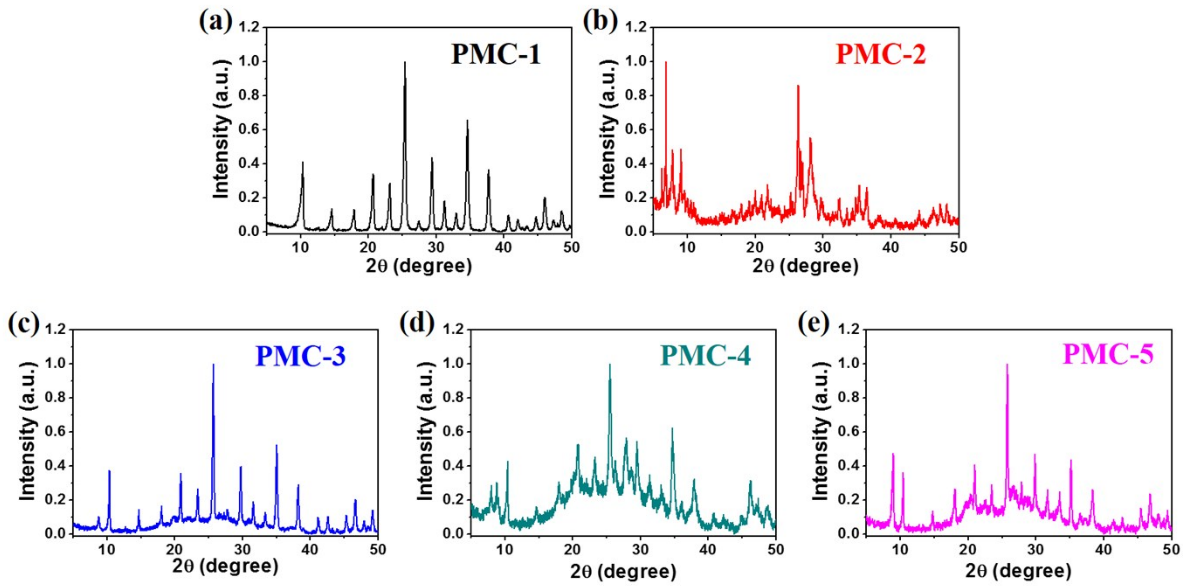

Fig. S1 XRD patterns of (a) PMC-1, (b) PMC-2, (c) PMC-3, (d) PMC-4 and (e) PMC-5.

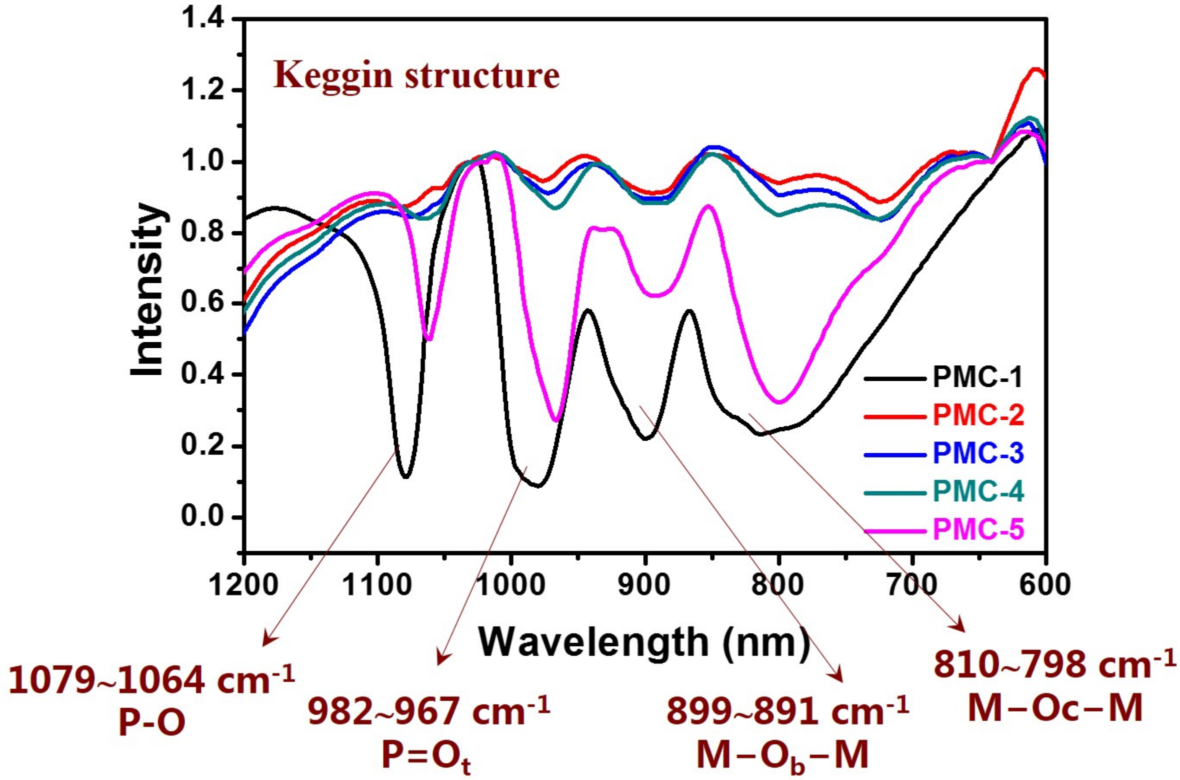

Fig. S2 Infrared (IR) spectra of the PMCs. The IR peaks at 1079~1064, 982~967, 899~891, and 810~798 cm^{-1} indicate the symmetric and asymmetric bond stretching modes for P−O, M=O_t, M−O_b−M, and M−O_c−M.

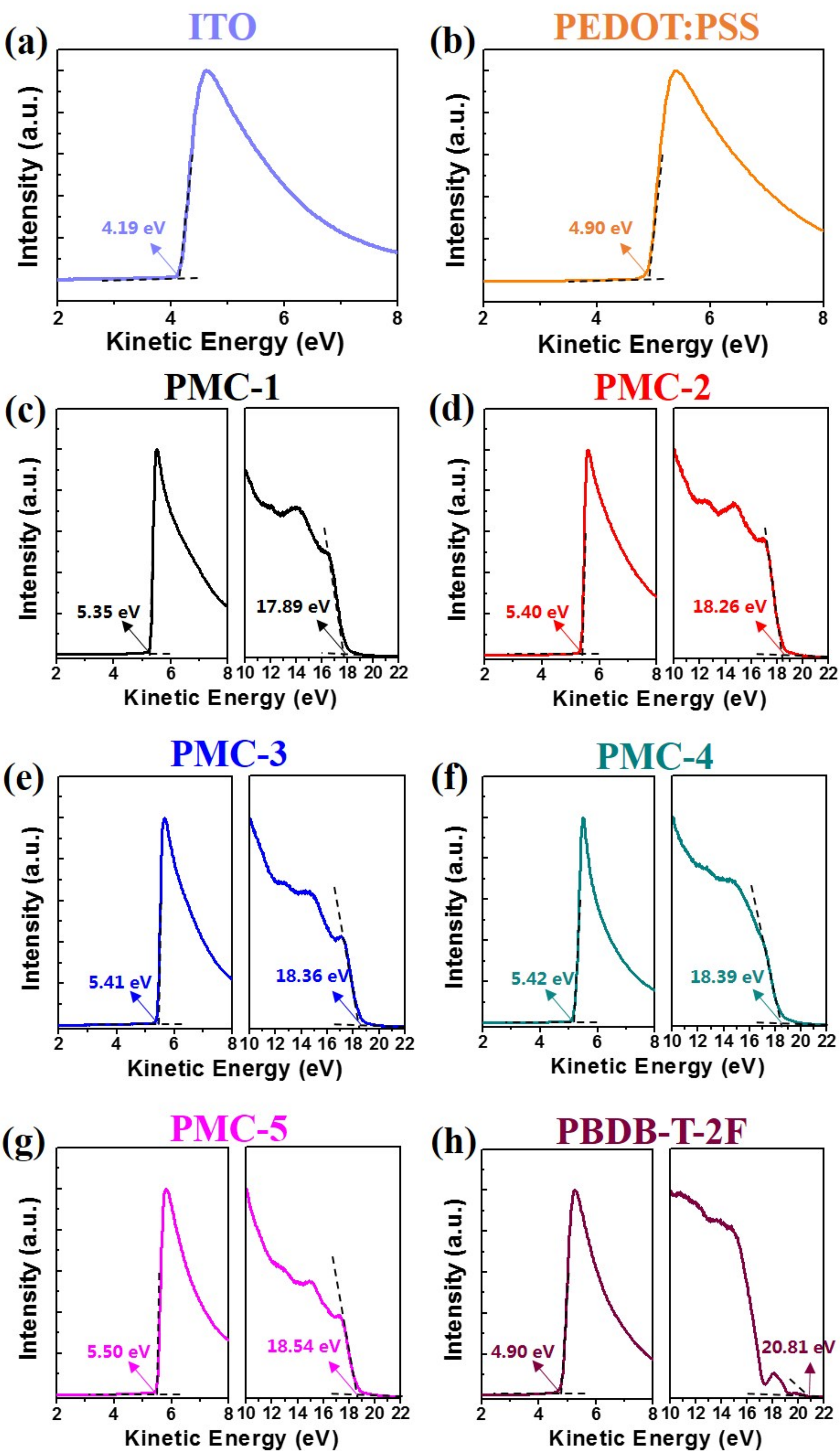

Fig. S3 UPS spectra of (a) bare ITO substrate, ITO covered with (b) PEDOT:PSS, (c) PMC-1, (d) PMC-2, (e) PMC-3, (f) PMC-4 and (g) PMC-5, and (h) the pure PBDB-T-2F film.

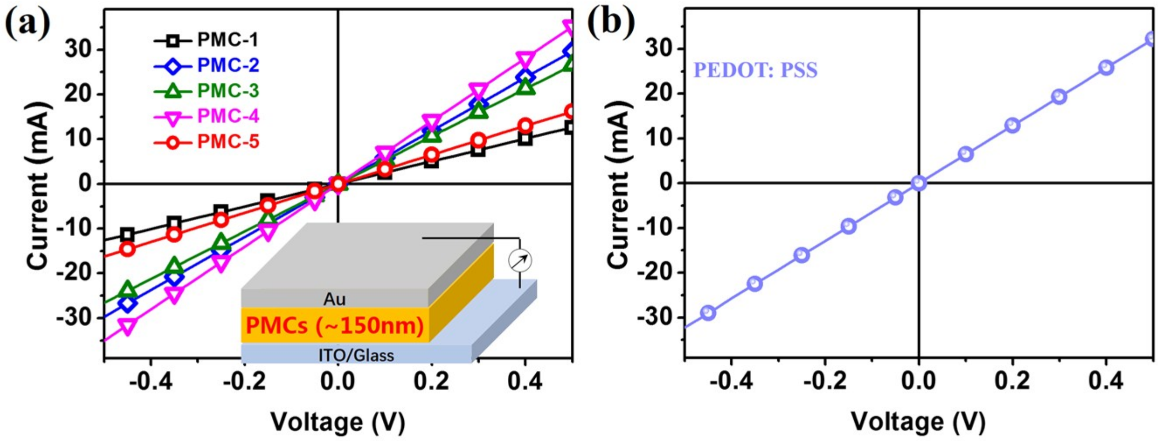

Fig. S4 *I-V* characteristics of longitudinal conductivity measurements for (a) the PMCs and (b) PEDOT:PSS.

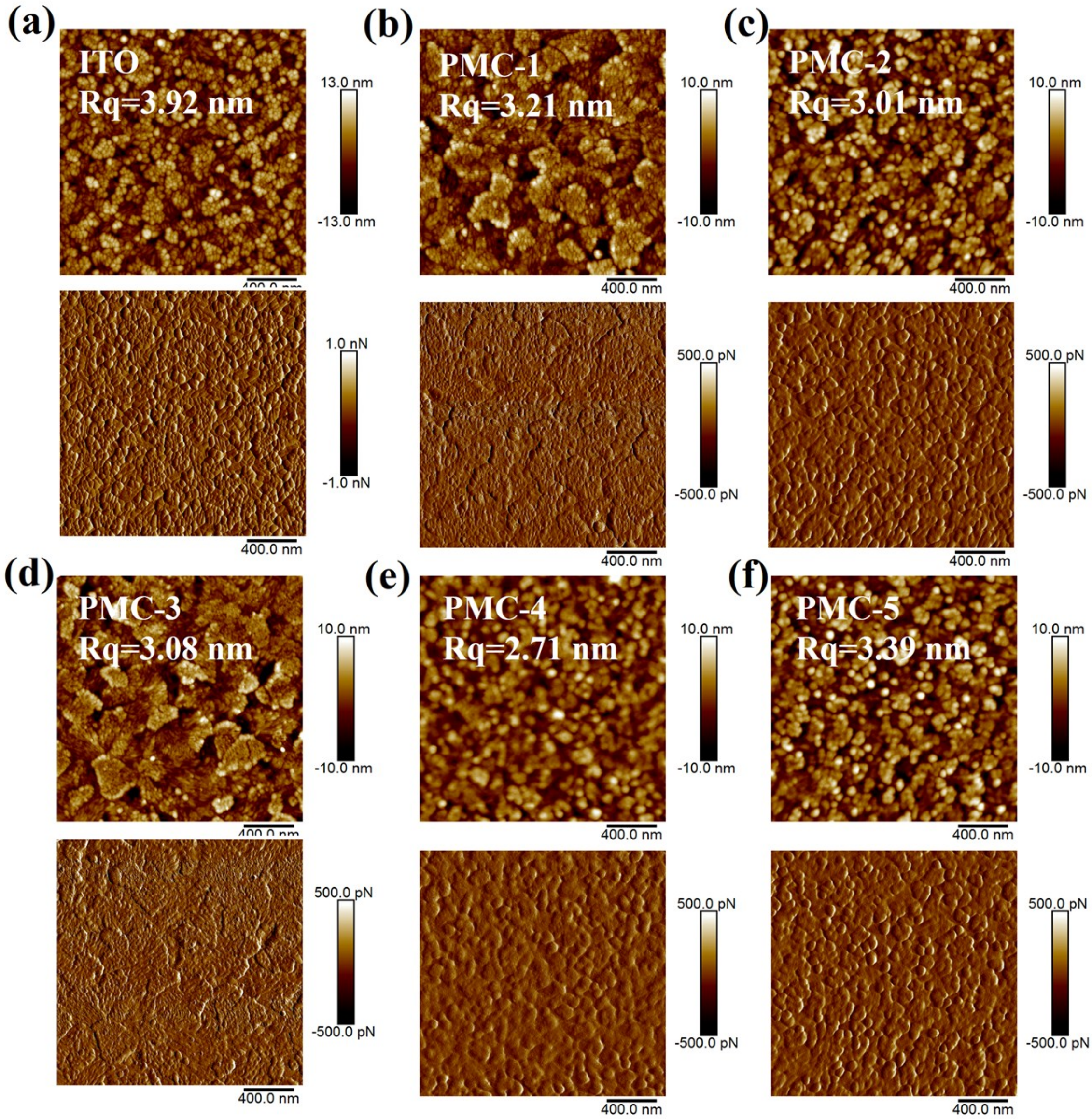

Fig. S5 AFM images of (a) bare ITO substrate and ITO covered with (b) PMC-1, (c) PMC-2, (d) PMC-3, (e) PMC-4 and (f) PMC-5.

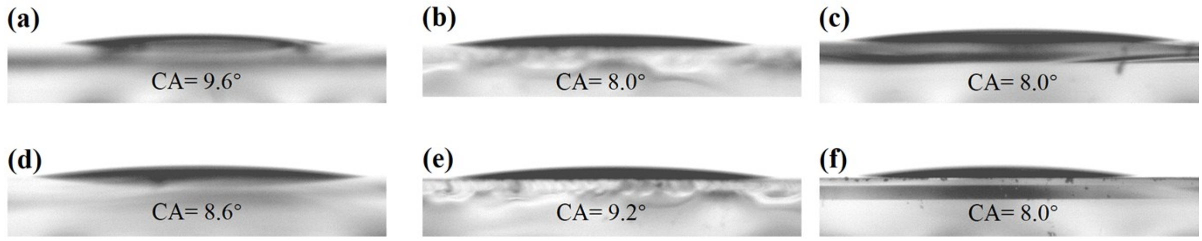

Fig. S6 Contact angle measurements of (a) bare ITO substrate and ITO covered with (b) PMC-1, (c) PMC-2, (d) PMC-3, (e) PMC-4, and (f) PMC-5 using chloroform.

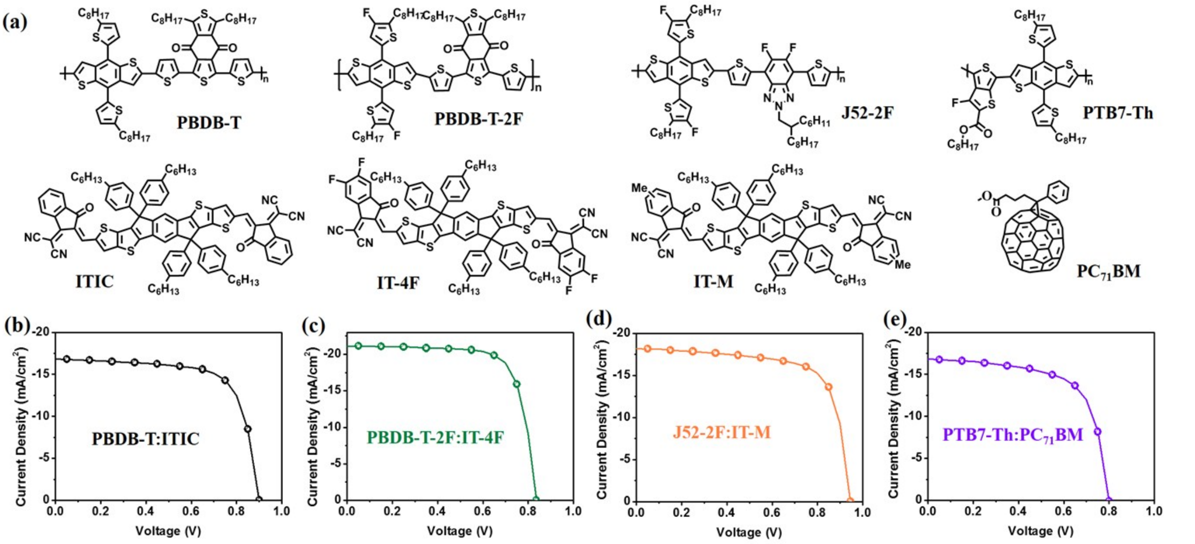

Fig. S7 (a) Chemical structures of PBDB-T, PBDB-T-2F, J52-2F, PTB7-Th, ITIC, IT-4F, IT-M, $PC_{71}BM$. (b)-(e) *J-V* curves of different active layers use PMC-4 as AIL.

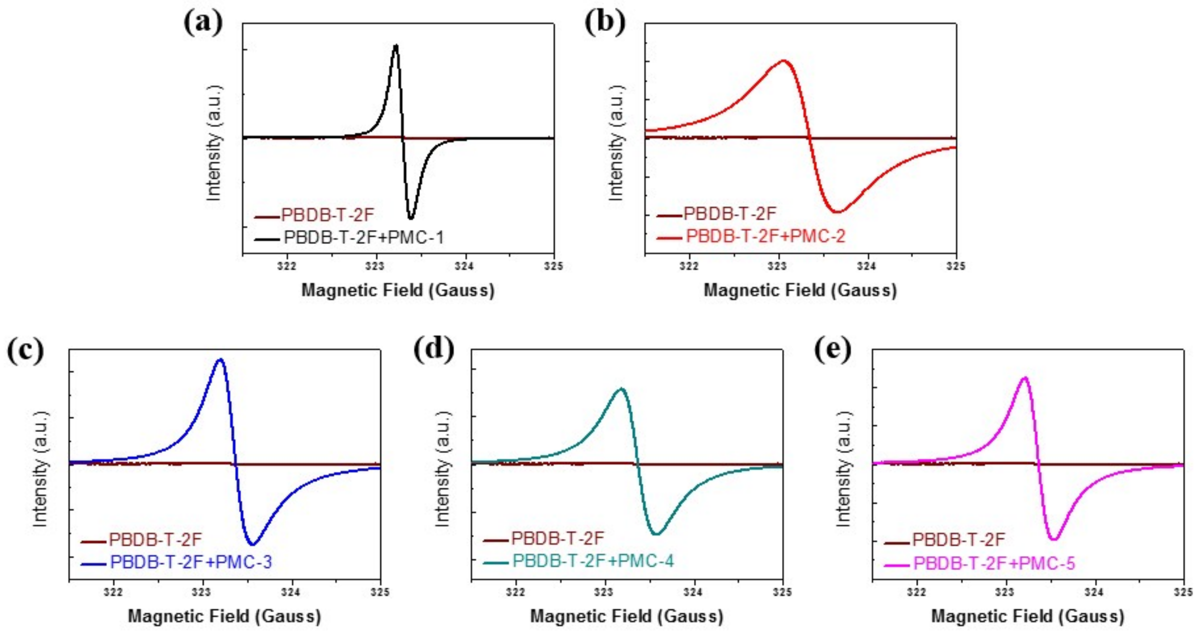

Fig. S8 ESR spectra of pure PBDB-T-2F and solid mixtures of PBDB-T-2F with (a) PMC-1, (b) PMC-2, (c) PMC-3, (d) PMC-4 and (e) PMC-5.

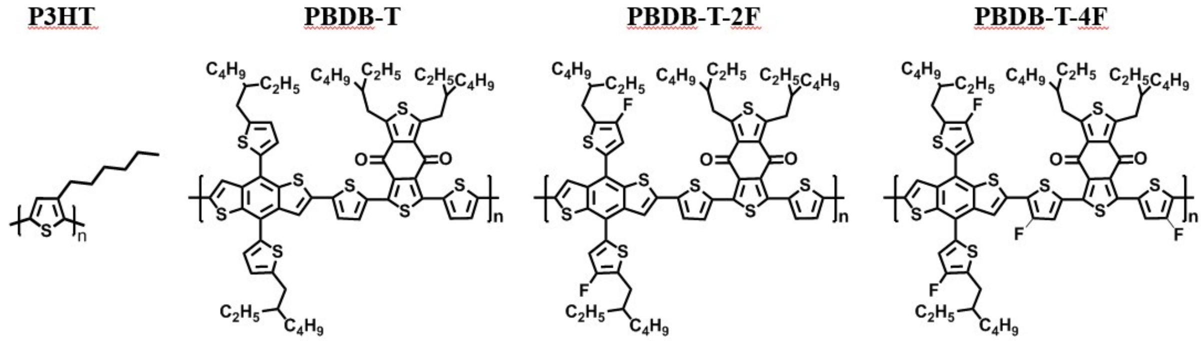

Fig. S9 The chemical structure of P3HT, PBDB-T, PBDB-T-2F and PBDB-T-4F.

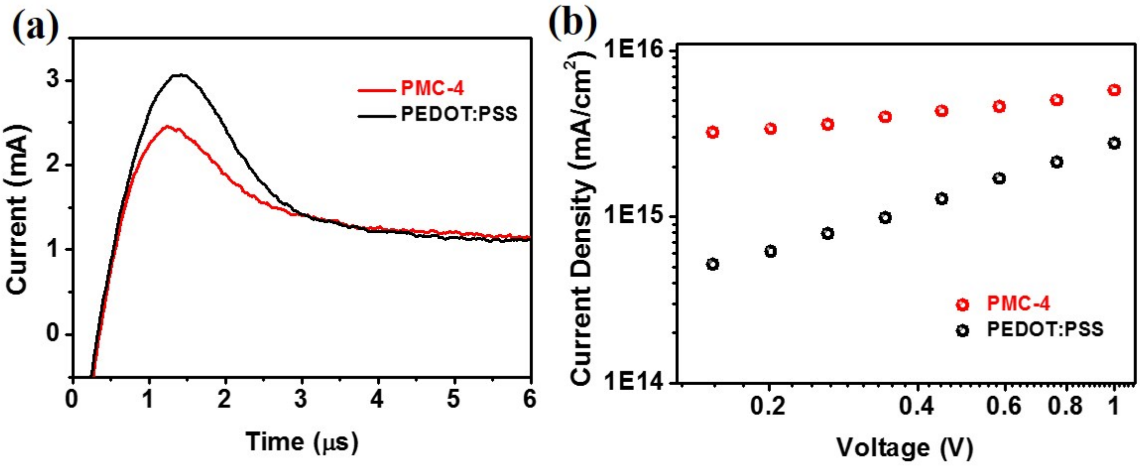

Fig. S10 Photo-CELIV measurement of PMC-4 and PEDOT:PSS devices.

Furthermore, to illustrate the capacity of the PMCs in modifying the efficient active layer, we evaluated the built-in voltage (V_{bi}) of PMC-modified devices by employing Mott-Schottky analysis.[3] Fig. S11 shows the *C-V* characteristics obtained by applying a low AC perturbation signal with fixed frequency and sweeping the DC bias. The V_{bi} values are determined to be 0.59, 0.60, 0.60, 0.59, 0.59, and 0.57 V for the devices with PMC-1, PMC-2, PMC-3, PMC-4, PMC-5 and PEDOT:PSS, respectively. The V_{bi} values of the PMC-based devices are higher than that of the PEDOT:PSS device, meaning that the ideal internal electric fields can be achieved in the PMC-modified OSCs. Since the V_{bi} is an important parameter to evaluate the upper limit for the V_{oc}, the high V_{bi} may be responsible for the high V_{oc} in the PMC-modified OSCs.

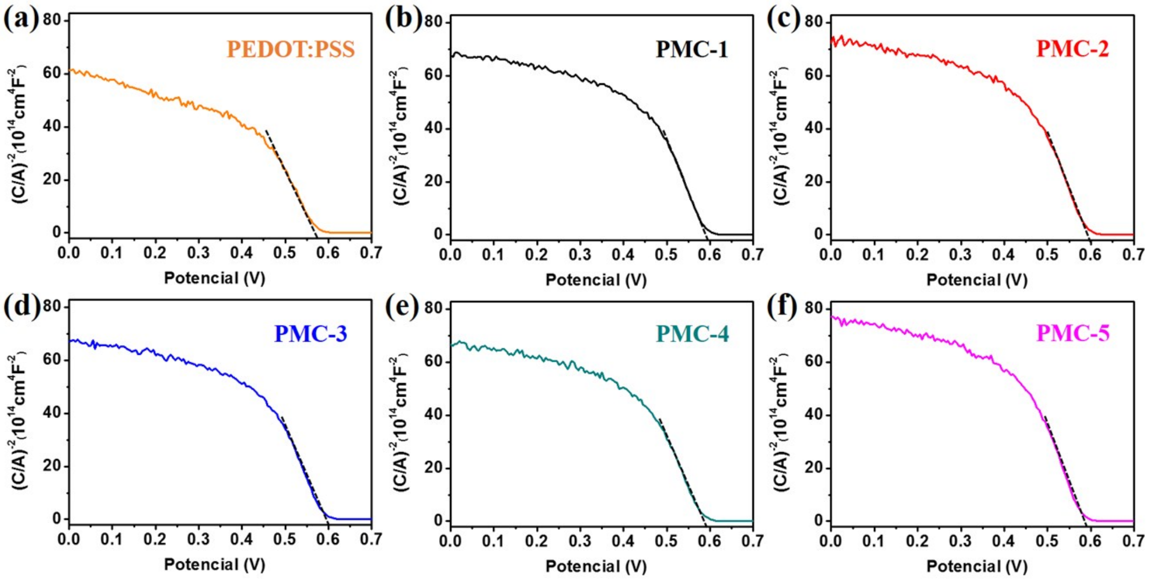

Fig. S11 Mott‑Schottky analysis of devices with PEDOT:PSS and the PMCs.

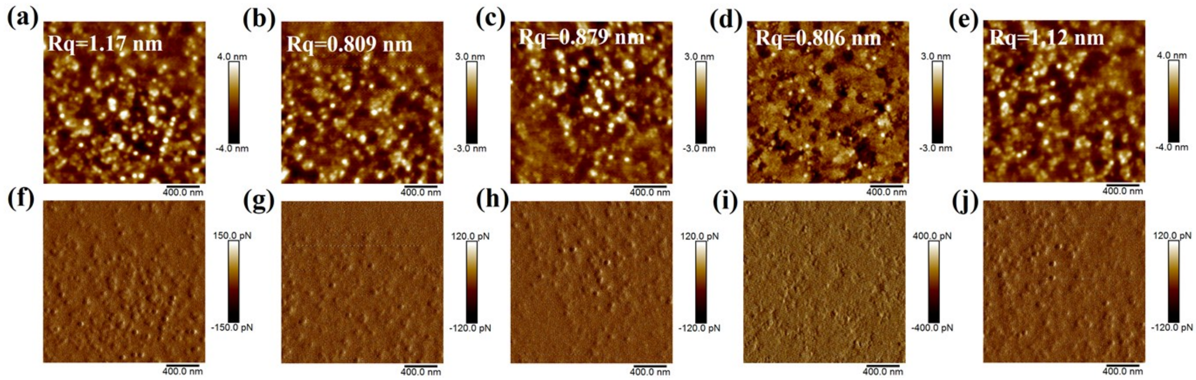

Fig. S12 2 μm × 2 μm AFM images of five different spots collected along the diagonal line of a $1cm^2$ PMC-4 film.

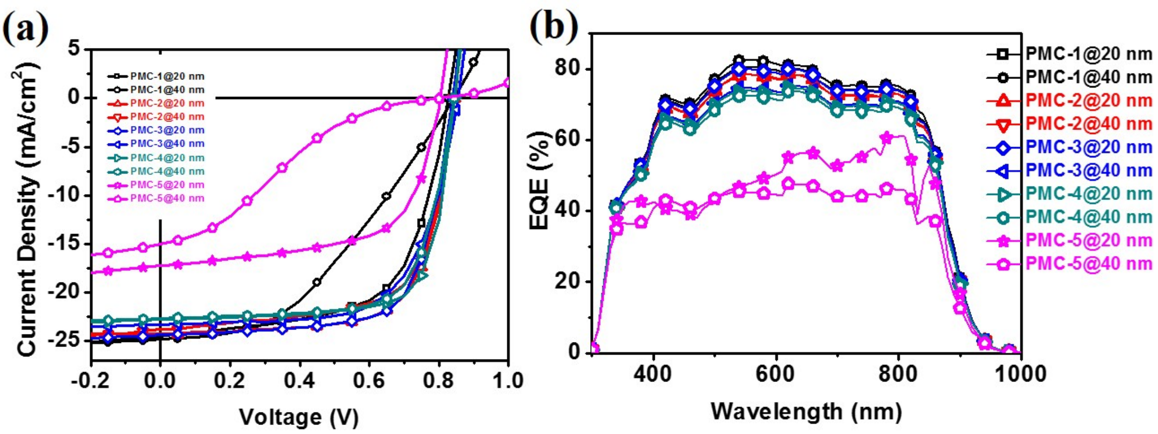

Fig. S13 *J-V* and EQE curves of devices with PMCs thicknesses at 20 and 40 nm.

中国计量科学研究院

测 试 报 告
Test Report

报告编号 GXtc2019-1446
Report No.

客户名称 Client	中国科学院化学研究所 Institute of Chemistry Chinese Academy of Science
样品名称 Sample	有机太阳能电池 Organic Solar Cell
型号/规格 Type/Model	非富勒烯聚合物太阳能电池 Non-fullerene polymer solar cell
出厂编号 Serial No.	2#-NIM MS06-F-02
生产厂商 Manufacturer	中国科学院化学研究所 Institute of Chemistry Chinese Academy of Science
客户地址 Client Address	北京市海淀区中关村北一街2号 No.2 1st North Street Zhongguancun Beijing P.R.China
测试日期 Date of Test	2019-06-06

批准人：
Approved by

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中国计量科学研究院

报告编号 GXtc2019-1446
Certificate No.

中国计量科学研究院（NIM）是国家最高的计量科学研究中心和国家级法定计量技术机构。1999年授权签署了国际计量委员会（CIPM）《国家计量基(标)准和国家计量院签发的校准与测量证书互认协议》（CIPM MRA）。The National Institute of Metrology (NIM) is China's national metrology institute (NMI) and a state-level legal metrology institute. NIM is China's signatory to the Mutual Recognition of National Measurement Standards and of Calibration and Measurement Certificates Issued by National Metrology Institutes (CIPM MRA) which is arranged by the International Committee of Weights and Measures (CIPM).

质量管理体系符合ISO/IEC17025标准，通过中国合格评定国家认可委员会（CNAS）和亚太计量规划组织（APMP）联合评审的校准和测量能力（CMCs）在国际计量局（BIPM）关键比对数据库中公布。NIM's quality management system meets requirements of the ISO/IEC 17025. Its Calibration and Measurement Capabilities (CMCs) that are peer reviewed both by China National Accreditation Service for Conformity Assessment (CNAS) and the Asia Pacific Metrology Programme (APMP) are published in the International Bureau of Weights and Measures (BIPM) Key Comparison Database (KCDB).

2011年，NIM和CNAS就认可领域的技术评价活动签署了谅解备忘录，承认NIM的计量支撑作用和出具的校准/检测结果的溯源效力。NIM and CNAS signed a Memorandum of Understanding (MOU) for Recognition of Technical Assessment in Laboratory Accreditation Field in 2011, in which CNAS recognizing the technical supporting role of NIM in laboratory accreditation and the traceability of NIM's calibration / test results.

测试所依据/参考的技术文件（代号、名称）Reference documents (Code,Name)
参照 Measurement of photovoltaic current-voltage characteristics (IEC60904-1)-2017
依据太阳电池校准规范：光电性能（JJF 1622-2017）(Calibration Specification of Solar Cells: Photoelectric Properties)

测试环境条件及地点 Testing place and environment:
温　度　(24.5±1) ℃　　地　点 Location: 中国计量院光学楼110室
湿　度 Humidity:　(57.8±2) % RH　　其　它 Others: /

测试使用的计量基（标）准装置（含标准物质)/主要仪器
Reference Standards (Including Reference Material) /Instruments used

名 称 Name	测量范围 Measurement Range	不确定度/准确度等级 Uncertainty/Accuracy	证书编号 Certificate No.	证书有效期至 Due Date (YYYY-MM-DD)
标准太阳电池 Reference solar cell	I_{sc}: (0-200) mA	0.9% (k=2)	GXtc2019-0418	2020-03-06
小面积稳态太阳模拟器 Steady solar simulator	(300-1100) nm	AAA 级	GXtc2019-0224	2020-02-13
源表 Sourcemeter	DC-V: 10mV-10V DC-I:100μA-1A	$(5\times10^{-4}$-$10\times10^{-5})$ (k=2) $(10\times10^{-5}$-$40\times10^{-5})$ (k=2)	DLsc2019-0024	2020-01-03

中国计量科学研究院

报告编号 GXtc2019-1446
Report No.

测 试 结 果
Test Results

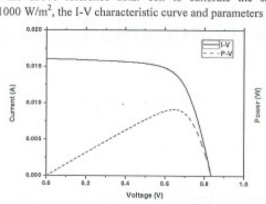
1. 测试条件 Test Conditions:

标准太阳电池：单晶硅（81#）；
Reference Solar Cell: mono-Si（81#）；
太阳模拟器：双光源太阳模拟器，AAA级；
Solar Simulator Classification: double-light source in AAA classification;
温度传感器/控制系统：无；
Teperature Sensor/Control System: None;
扫描方向：正扫
Scan Direction:Forward
电压设置：-0.10V–0.90V；间隔：0.01V
Scan Parameter: From -0.10V to 0.90V with 0.01V interval
光阑 Mask（Y/N）: Y
扫描时间： 31 秒　　扫描点数： 101
Scan Time: 31 s　　Scan Point: 101

2. I-V 特性参数 I-V Characteristic parameters:

以上述标准太阳电池标定太阳模拟器辐照度至 1000 W/m²，校准被测太阳电池的I-V特性曲线和参数如下：

By using the above reference solar cell to calibrate the solar simulator's irradiance to 1000 W/m², the I-V characteristic curve and parameters as follows:



中国计量科学研究院

报告编号 GXtc2019-1446
Report No.

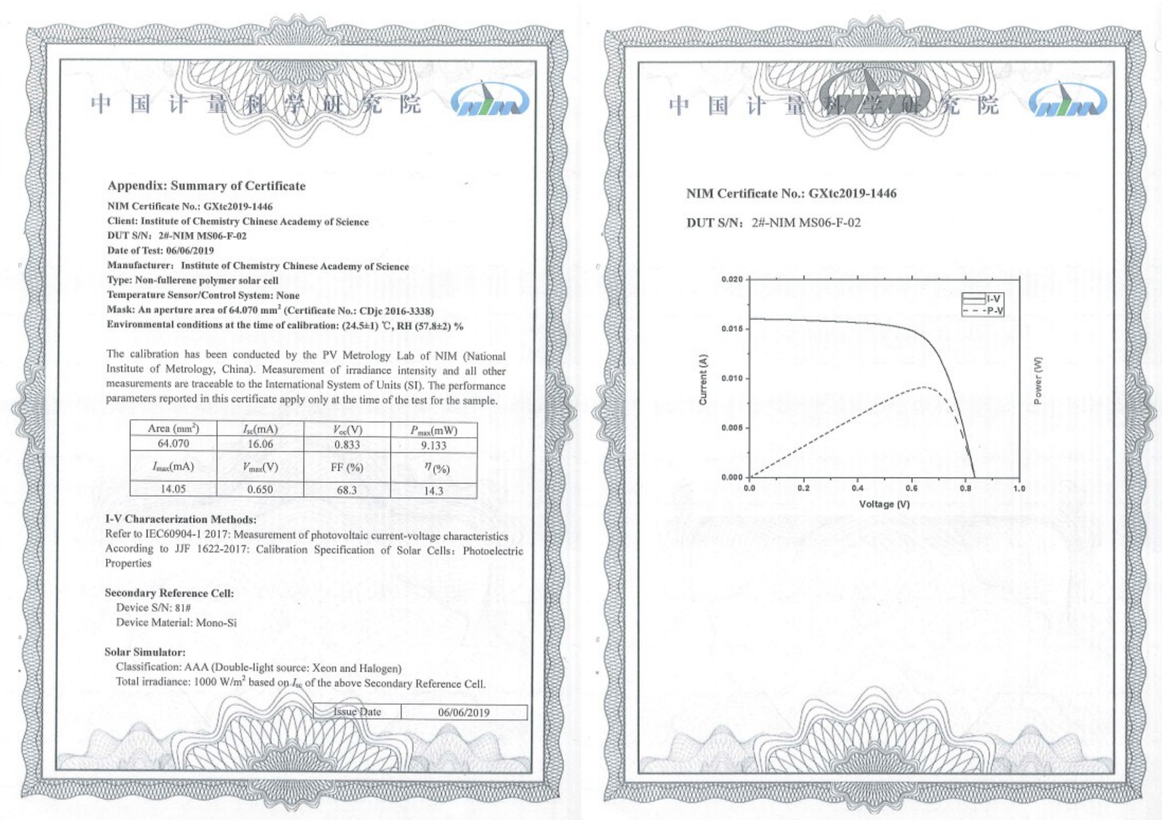
测 试 结 果
Test Results

有效面积 (mm²)	短路电流 I_{sc}(mA)	开路电压 V_{oc}(V)	最大功率 P_{max}(mW)
64.070	16.06	0.833	9.133
最大功率电流 I_{max}(mA)	最大功率电压 V_{max}(V)	填充因子 FF (%)	转换效率(PCE) η (%)
14.05	0.650	68.3	14.3

注 Note:
1. 测试所用 NIM-S06 mask 的面积为 64.070 mm²（证书编号：CDjc2016-3338）。
The mask (NIM-S06) area is 64.070 mm² (Certificate No.: CDjc 2016-3338)
2. 此数据仅对被测样品当时状态有效。
The data apply only at the time of the test for the sample.
（以下空白）

声明 Statement:
1.我院仅对加盖"中国计量科学研究测试专用章"的完整报告负责。
NIM is ONLY responsible for the complete report with the test stamp of NIM.
2.本报告的测试结果仅对所测试的样品有效。
The report is ONLY valid for the tested sample or instrument.
3.本报告用中英文两种语言表达，准确含义以中文为准。
The report is expressed in both English and Chinese, with the Chinese version as standard.

测 试 员：　　　　核 验 员：
Tested by　　　　Checked by



中国计量科学研究院

Appendix: Summary of Certificate

NIM Certificate No.: GXtc2019-1446
Client: Institute of Chemistry Chinese Academy of Science
DUT S/N：2#-NIM MS06-F-02
Date of Test: 06/06/2019
Manufacturer：Institute of Chemistry Chinese Academy of Science
Type: Non-fullerene polymer solar cell
Temperature Sensor/Control System: None
Mask: An aperture area of 64.070 mm^2 (Certificate No.: CDjc 2016-3338)
Environmental conditions at the time of calibration: (24.5±1) ℃, RH (57.8±2) %

The calibration has been conducted by the PV Metrology Lab of NIM (National Institute of Metrology, China). Measurement of irradiance intensity and all other measurements are traceable to the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test for the sample.

Area (mm^2)	I_{sc}(mA)	V_{oc}(V)	P_{max}(mW)
64.070	16.06	0.833	9.133
I_{max}(mA)	V_{max}(V)	FF (%)	η (%)
14.05	0.650	68.3	14.3

I-V Characterization Methods:
Refer to IEC60904-1 2017: Measurement of photovoltaic current-voltage characteristics
According to JJF 1622-2017: Calibration Specification of Solar Cells：Photoelectric Properties

Secondary Reference Cell:
Device S/N: 81#
Device Material: Mono-Si

Solar Simulator:
Classification: AAA (Double-light source: Xeon and Halogen)
Total irradiance: 1000 W/m^2 based on I_{sc} of the above Secondary Reference Cell.

Issue Date	06/06/2019

中国计量科学研究院

NIM Certificate No.: GXtc2019-1446

DUT S/N：2#-NIM MS06-F-02

Fig. S14 Certification report of large-area device (0.8 cm×0.8 cm mask) from National Institute of Metrology (NIM).

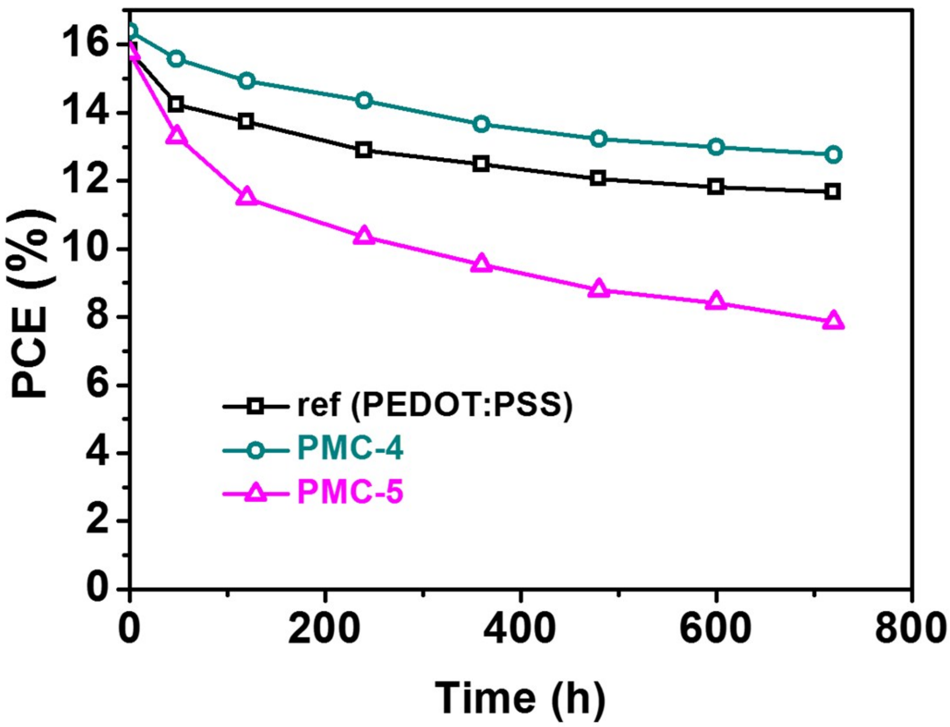


Fig. S15 The PCE for PEDOT:PSS and PMCs-based solar cells as a function of storage time in glove box.

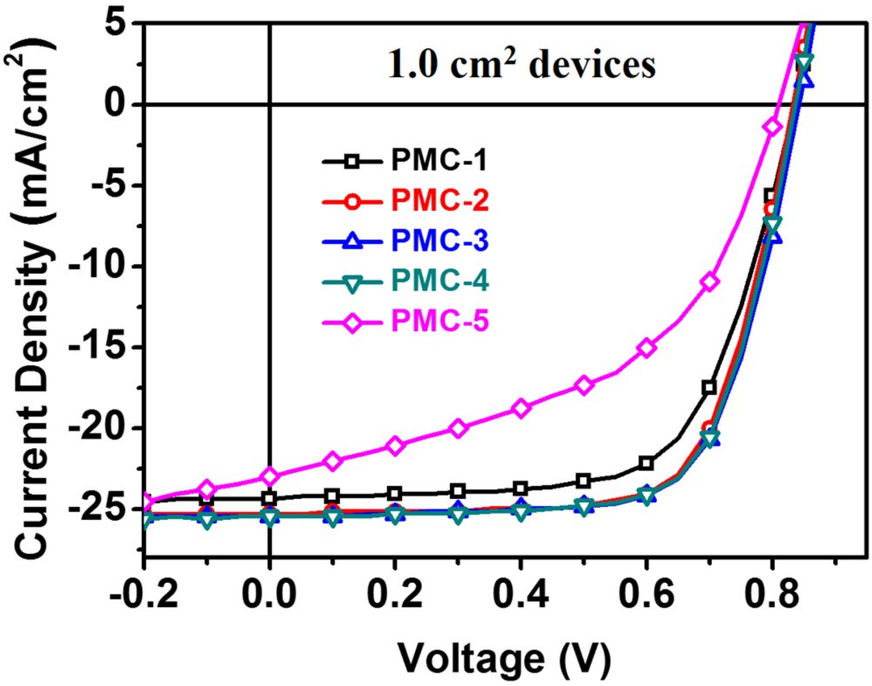


Fig. S16 *J-V* curves of 1cm^2 devices based on PMCs.

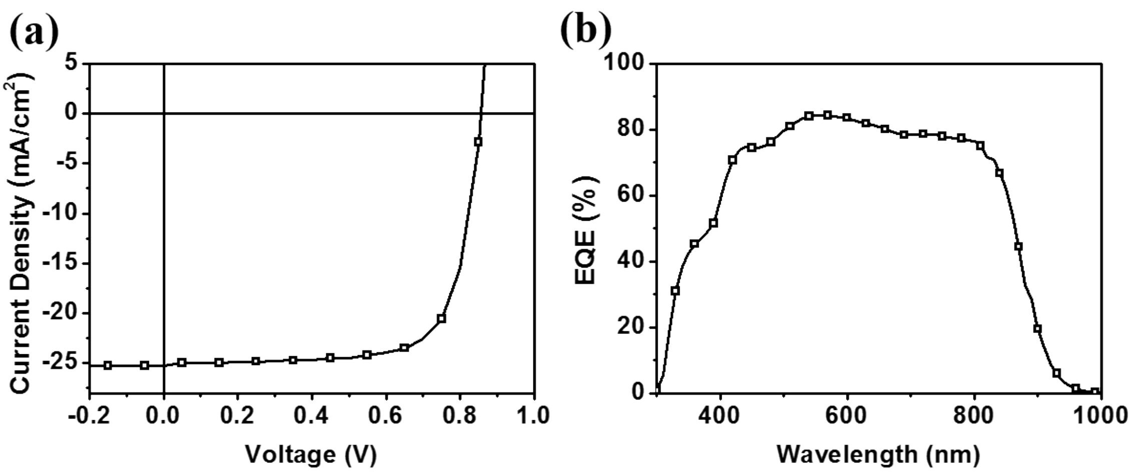


Fig. S17 *J-V* and EQE curves of PEDOT:PSS based devices (0.04cm^2).

Table S1. Photovoltaic parameters of devices based on other different anode interlayers with the same active layer (PBDB-T-2F: IT-4F).

AILs	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
PEDOT:PSS	0.87	20.38	0.77	13.7 [4]
MoO_3	0.81	17.9	0.74	10.8
PCP-3B	0.79	19.7	0.73	11.3
PCP-Na	0.71	20.1	0.65	9.32 [5]

Table S2. Photovoltaic parameters of devices based on PMC-4 films with different active layers.

Active layer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
PBDB-T:ITIC	0.90	16.8	0.71	10.7
PBDB-T-2F:IT-4F	0.84	21.1	0.75	13.2
J52-2F:IT-M	0.95	18.2	0.71	12.2
PTB7-Th:PC$_{71}$BM	0.80	16.8	0.66	8.86

Table S3. Photovoltaic parameters of devices based on PMC films with different thicknesses.

AILs	Thickness	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	J_{cal}^{a} (mA/cm^2)
PMC-1	**20 nm**	0.826	24.52	0.628	12.72	24.18
	40 nm	0.842	24.81	0.409	8.54	24.58
PMC-2	**20 nm**	0.845	24.20	0.697	14.25	23.64
	40 nm	0.841	23.87	0.668	13.41	23.62
PMC-3	**20 nm**	0.839	24.39	0.679	14.25	24.04
	40 nm	0.854	23.31	0.660	13.14	22.73
PMC-4	**20 nm**	0.845	22.82	0.738	14.24	22.54
	40 nm	0.843	22.70	0.704	13.47	22.14
PMC-5	**20 nm**	0.804	17.27	0.625	8.68	16.59
	40 nm	0.797	15.06	0.222	2.67	14.40

^{a}Integrated J_{cal} from the EQE curves.

Table S4. The fitting results of the Nyquist plots of PMC AILs devices.

AILs	Rs (Ω)	Rbulk (Ω)	Cbulk (F)	Rrec (Ω)	Crec (F)
PMC-1	236	54933	4.30E-9	21735	3.87E-9
PMC-2	29.08	111	3.13E-9	30.91	1.49E-8
PMC-3	79.07	82.664	5.37E-9	22.68	2.65E-8
PMC-4	47.51	107.7	4.44E-9	14.71	4.81E-8
PMC-5	320.6	85208	3.34E-9	49940	2.15E-9

Table S5. The PCEs (%) of 30 cells for 1.0 cm^2.

No.1	**No.2**	**No.3**	**No.4**	**No.5**	**No.6**	**No.7**	**No.8**	**No.9**	**No.10**

15.08	15.03	14.83	14.89	14.85	14.71	14.61	14.62	14.54	14.93
No.11 14.81	**No.12** 14.68	**No.13** 14.64	**No.14** 14.60	**No.15** 13.84	**No.16** 13.25	**No.17** 14.85	**No.18** 14.92	**No.19** 14.48	**No.20** 14.49
No.21 14.50	**No.22** 14.55	**No.23** 13.35	**No.24** 14.52	**No.25** 14.77	**No.26** 14.93	**No.27** 14.39	**No.28** 14.77	**No.29** 14.09	**No.30** 14.52

Table S6. Photovoltaic parameters of 1cm^2 devices based on PMCs.

PMCs	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
PMC-1	0.835	24.32	0.662	13.43
PMC-2	0.832	25.32	0.703	14.81
PMC-3	0.843	25.48	0.701	15.05
PMC-4	0.836	25.46	0.707	15.08
PMC-5	0.809	22.97	0.488	9.08

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