Supporting Information

Multifunctional PMMA intermediate layer for Sequentially Deposited Organic Photovoltaics

Songtao Wei,[a] Hongxiang Li,*[a] Ruohao Wang,[b] Top Archie Dela Peña,[c, d] Hua Tang,[e] Hailin Yu,[a] Sandra P Gonzalez Lopez,[e] Jiayu Wang,[a] Mingjie Li,[c] Jiaying Wu,[d] Guanghao Lu,[f] Shirong Lu,[g] Dewei Zhao,[b] Cenqi Yan,*[a] Frédéric Laquai,[d] and Pei Cheng*[a]

a. College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China.

E-mail: lihongxiang@scu.edu.cn, yancenqi@scu.edu.cn, chengpei@scu.edu.cn.

b. College of Materials Science and Engineering & Institute of New Energy and Low-Carbon Technology & Engineering Research Center of Alternative Energy Materials and Devices, Ministry of Education, Sichuan University, Chengdu 610065, China

c. Department of Applied Physics, Faculty of Science, The Hong Kong Polytechnic University, Kowloon, Hong Kong 999077, China.

d. Advanced Materials Thrust, Function Hub, The Hong Kong University of Science and Technology, Nansha, Guangzhou 511400, China.

e. KAUST Solar Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia.

f. Frontier Institute of Science and Technology, State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710054, China.

g. Department of Material Science and Technology, Taizhou University, Taizhou 318000, China.

Experimental Section

Materials: PEDOT: PSS (Al4083) was purchased from Heraeus Clevis. PM6, BTP-eC9, PTB7-TH, IEICO-4F, IT-4F, and PFN-Br were purchased from Solarmer Materials (Beijing) Inc. and were used without any further purification. Silver was purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd. PMMA and other chemicals were purchased from Sigma-Aldrich, Inc.

Solar cell fabrication and characterization: Solar cells were fabricated in device configuration of ITO/PEDOT: PSS/Donor/Acceptor/PFN-Br/Ag, ITO/PEDOT: PSS/Donor/ PMMA/Acceptor/PFN-Br/Ag.

The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone, and isopropanol subsequently. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT: PSS (Heraeus Clevios PVP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 20 min in air. For the b-LbL devices, the PM6 solutions (10 mg/mL in chlorobenzene) with 0.3v% of 1,8-diiodooctane were spin-coated on the ITO/PEDOT: PSS substrates at a speed of 1700 rpm for 30 s form a ~60 nm thickness of the polymer donor layer. Then the BTP-eC9 solution (10 mg/mL in xylene with 0.7 v% 1-chloronaphthalene) was spin-coated on top of the polymer donor layer at a speed of 2000 rpm for 30 s to form an acceptor layer with ~40 nm thickness. For the t-LbL devices, the PM6 solutions (10 mg/mL in chlorobenzene) with 0.3v% 1,8-diiodooctane were spin-coated on the ITO/PEDOT: PSS substrates at a speed of 1700 rpm for 30 s to a donor layer with ~60

nm thickness. Then the PMMA solution in acetone of different concentration (0.6mg/mL, 1.2mg/mL, and 1.8mg/mL) was spin-coated on top of the polymer donor layer at a speed of 2650 rpm for 30s. Lastly, the BTP-eC9 solution (10 mg/mL in xylene with 0.7 v% 1-chloronaphthalene) was spin-coated on top of the polymer donor layer at a speed of 2000 rpm for 30 s to form an acceptor layer with a ~40 nm thickness. The PFN-Br (0.5mg/mL in methanol solution) was spin-cast on the active layer at 3000 rpm for 30 s, followed by the deposition of Ag (100 nm) (evaporated under 2×10^{-4} Pa through a shadow mask).

Besides, the other three photovoltaic layers, consisting of three different photovoltaic systems as shown in Figure 2, were dissolved in chlorobenzene/xylene (PM6/L8-BO, PM6/IT-4F, and PTB7-Th/IEICO-4F) with various weight ratios, and spin-coated on top of the PEDOT: PSS layer. For t-LbL devices, the PMMA solution in acetone was spin-coated between the donor and acceptor layer. The PFN-Br (0.5mg/mL in methanol solution) was spin-cast on the active layer at 3000 rpm for 30 s, followed by the deposition of Ag (100 nm) (evaporated under 2×10^{-4} Pa through a shadow mask).

The current density-voltage (*J-V*) curves of devices were measured using a Keysight B2901A Source Meter in the glove box under AM 1.5G (100 mW cm^{-2}) using an Enlitech solar simulator. The active area of the tested solar cells is 0.04 cm^2, which is determined by mask. The voltage range is -0.2 V to 1.1 V. The step is 0.02 V with a delay time of 0 ms. The scan mode is Normal. The polarity is Normal. The device is tested in the glove box filled with N_2, at room temperature. A 2×2 cm^2 monocrystalline silicon reference cell with a KG5 filter (purchased from Enli Tech. Co., Ltd., Taiwan).

The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard monocrystalline Si photovoltaic cell.

TR-PL measurements: The TR-PL samples were excited with the wavelength-tunable Chameleon Ultra Laser (Coherent, central wavelength 820 nm) at 725 nm. The fundamental of the Chameleon is pumping a Radiantis OPO, from which the generated second harmonic 450 nm (fundamental 900 nm) is used to excite the samples. The repetition rate of the fs pulses was 80 MHz, and typical pulse energies were in the range of 500 nJ. The PL of the samples was collected by an optical telescope (consisting of two plano-convex lenses) and focused on the slit of a spectrograph (PI Spectra Pro SP2300) and detected with a Streak Camera (Hamamatsu C10910) system with a temporal resolution of 1.4 ps. The data was acquired in photon counting mode using the Streak Camera software (HPDTA) and exported to Origin Pro 2020 for further analysis.

GIWAXS and GISAXS measurements: GIWAXS data were obtained at beamline BL02U2 of Shanghai Synchrotron Radiation Facility (SSRF). The monochromatic of the light source was 1.24 Å. The data were recorded by using the two-dimensional image plate detector of Pilatus 2M from Dectris, Switzerland.

GISAXS data of films were obtained at beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF). The monochromatic of the light source was 1.24 Å. The

incidence angle was 0.2°, and the sample-to-detector distance was 2200 mm by calibration for GISAXS. The GISAXS 1D profiles were fitted with a universal model following Equation (1). Data fitting was done using SasView (version 5.01) software.

$$I(q) = \frac{A_1}{[1+(q\xi)^2]^2} + A_2 \langle P(q,R) \rangle \ S(q,R,\eta,D) + B \tag{1}$$

$$S(q) = 1 + \frac{\sin\left[(D-1)\tan^{-1}(q\eta)\right] b \pm \sqrt{b^2 - 4ac}}{(qR)^D} \frac{D\Gamma(D-1)}{\left[1+\dfrac{1}{(q\eta)^2}\right]^{(D-1)/2}} \tag{2}$$

where A1, A2, and B are independent fitting parameters and q is the scattering wave vector. The average correlation length ξ of the PM6 domain and the Debye-Andersone-Brumberger (DAB) term make up the first term. The contribution from BTP-eC9 fractal-like aggregations is seen in the second term. Here, R is the mean spherical radius of the primary BTP-eC9 particles, P (q, R) is the form factor of the BTP-eC9, S (q, R, η, D) is the fractal structure factor to explain the primary particles interaction in this fractal-like aggregation system, η is the correlation length of the fractal-like structure, and D is the fractal dimension of the network. Equation 3 was used to calculate the average domain size by the Guinier radius of the fractal-like network R_g.
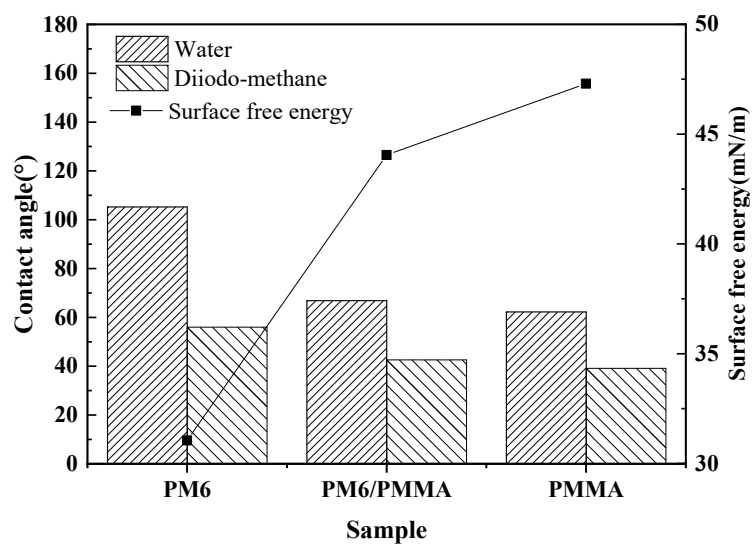
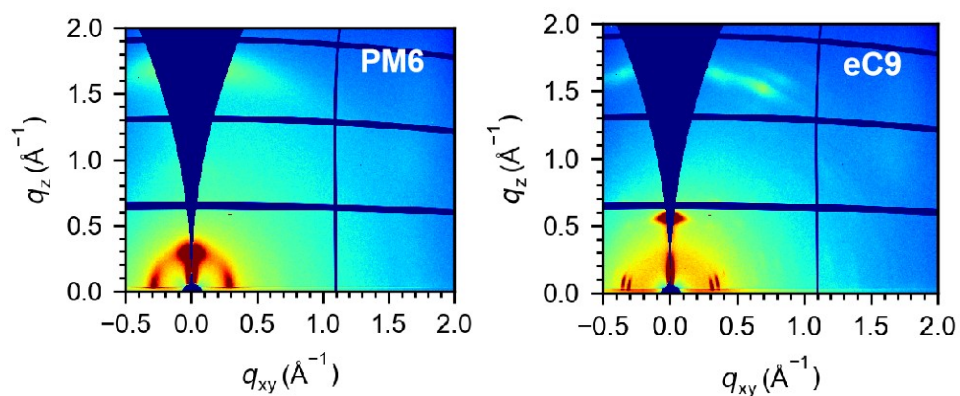$$R_g = \eta \sqrt{\frac{D(D+1)}{2}} \tag{3}$$
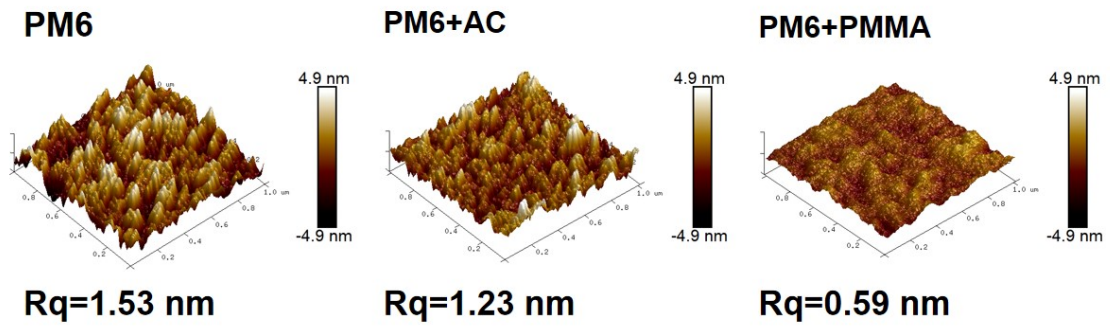
Figure S1. The 3D AFM height diagrams based on PM6, PM6/AC, and PM6/PMMA films.
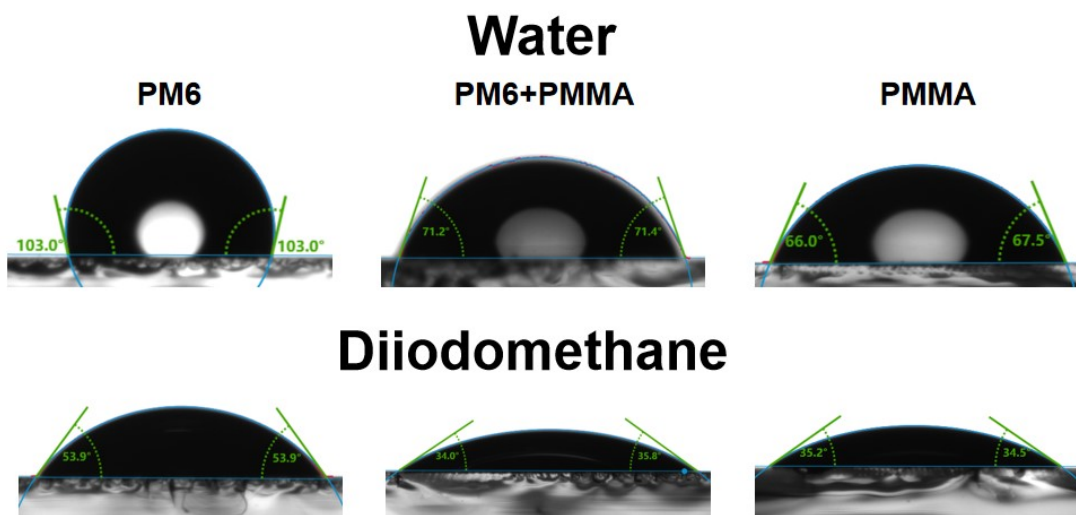
Figure S2. The CA diagrams of PM6, PM6/PMMA, and PMMA films.

Figure S3. The CA diagrams and values of PM6, PM6/PMMA, and PMMA films.

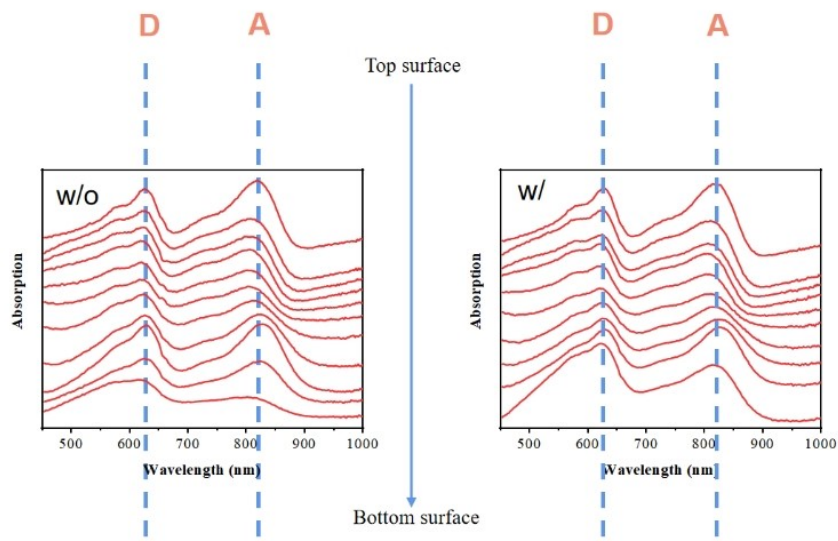**Figure S4.** 2D GIWAXS images of PM6 and BTP-eC9 neat films.

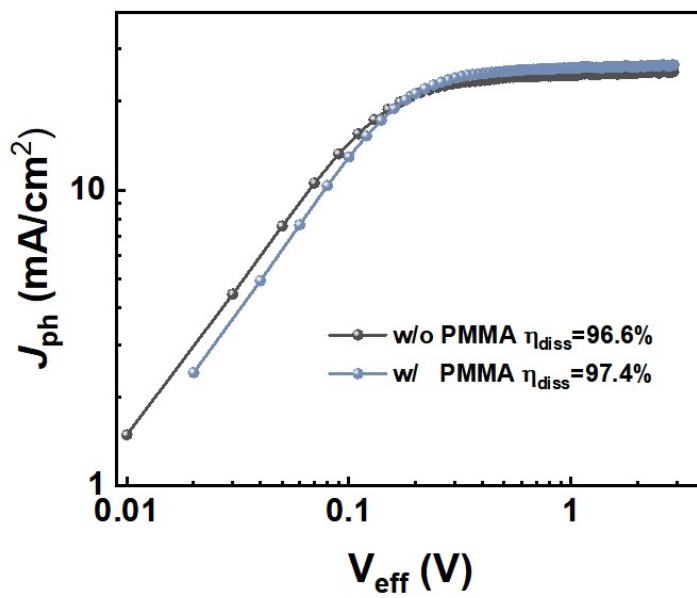**Figure S5.** FLAS of the b-LbL film and the t-LbL film

Figure S6. Plot of J_{ph} versus V_{eff}

Table S1. The CA values of PM6, PM6/PMMA and PMMA

Sample	Value [mN/m]
PM6	31.05
PM6/PMMA	44.05
PMMA	47.3

Table S2. Extracted data of GIWAXS in-plane peaks

Sample	Peak position (Å^{-1})	d-spacing (Å)	CCL (Å)
PM6	0.295	21.30	113.07
PM6/BTP-eC9	0.315	21.30	106.67
w/ 0.6mg/ml PMMA	0.310	19.95	79.88
w/ 1.2mg/ml PMMA	0.303	20.27	77.50
w/ 1.8mg/ml PMMA	0.298	20.77	82.83

Table S3. Extracted data of GIWAXS out-of-plane peaks

Sample	Peak position (Å^{-1})	d-spacing (Å)	CCL (Å)
PM6	1.668	3.77	54.03
PM6/BTP-eC9	1.708	3.68	32.13
w/ 0.6mg/ml PMMA	1.708	3.68	34.68
w/ 1.2mg/ml PMMA	1.708	3.68	33.18
w/ 1.8mg/ml PMMA	1.705	3.68	35.66