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Supporting Information

High-Performance Pseudo-bilayer Ternary Organic Solar Cells with $PC_{71}BM$ as the Third Component

Yujiao Yan, [a] *Xuejiao Zhou,* [a] *Fenghua Zhang,* [a] *Jun Zhou,* [a] *Tao lin,* [a] *Yaohui Zhu,* [a] *Denghui Xu,* [a] *Xiaoling Ma,* *[b] *Ye Zou,* *[c] *Xiong Li,* *[a]

[a]Department of Physics, Beijing Technology and Business University, Beijing 100048, China.

*Corresponding Author: E-mail address: lixiong@btbu.edu.cn (Xiong Li)

[b]Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, Beijing 100091, China.

*Corresponding Author: E-mail address: maxl@bjtu.edu.cn (Xiaoling Ma)

[c]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

*Corresponding Author: E-mail address: zouye@iccas.ac.cn (Ye Zou)

contents

1.Materials

Polymer donor PM6, the host acceptor Y6 and cathode buffer layer PDIN were purchased from Solarmer Material Inc. The guest acceptor $PC_{71}BM$ were purchased from 1-Material Inc. Anode buffer layer PEDOT: PSS was obtained from Heraeus (Clevios P Al4083) and the pre-patterned indium tin oxide (ITO) coated glass substrates were obtained from Huananxiangcheng Technology Co. Solvent chloroform (CF) and additive 2-Chloronaphthalene (CN) were obtained from J&K Scientific Ltd. High-purity argentum (purity>99.99%) was used for the evaporation of electrode. All the materials were used as received without any further treatment.

2. Solution Preparation

PM6 was dissolved in CF at a concentration of 8 mg/ml, and the solution was stirred at 40 °C for 2 h. Small molecule Y6 and $PC_{71}BM$ were dissolved in chloroform (CF) to prepare 8 mg/ml mixed solution, and the weight ratio was kept constant at 0.90:0.10. The cathode buffer layer solvent was prepared by dissolving PDIN in methanol (2 mg/ml) and 0.3 vol% acetic acid was used as auxiliary.

3.Device Fabrication

Patterned ITO electrode was cleaned by sequential sonication in deionized water, acetone, ethyl alcohol each for 20 min, then dried by high-purity nitrogen gas. After 8 min ultraviolet-ozone treatment for the ITO substrate, anode buffer layer was prepared by spin-coating PEDOT:PSS aqueous solution with speed of 3500 rpm and then thermal-annealed at 150 ℃ for 30 min, then the PEDOT: PSS anode buffer layer was obtained with the thickness of about 30 nm. After that, the treated

ITO/PEDOT:PSS films were transferred into a high-purity nitrogen-filled glove box (<0.01 ppm O_2 and H_2O) to fabricate active layers and cathode interlayers. PM6 was spin-coated on top of PEDOT:PSS at speed of 3000 rpm, after the PM6 film drying in Petri dish for 2 hours, the PM6 film with a thickness of about 53 nm was obtained. Then the Y6 and $PC_{71}BM$ blend was spin-coated onto the PM6 layer with a thickness of about 51 nm, and the prepared films were annealed at 85 °C for 5 min. Subsequently, PDIN interlayer was obtained by spin-casting on top of active layers with the thickness of about 10 nm. Finally, Ag of about 100 nm was thermally deposited on the PDIN layer under the vacuum of 2×10^{-4} Pa, and the deposition rate and thickness of Ag was in situ recorded with a quartz crystal oscillator monitor. The effective area of organic solar cells is 0.045 cm^2, which is defined by the overlap of ITO anode and Ag cathode.

4. Instruments and characterization

The UV-vis absorption spectra were conducted with ultraviolet–visible spectrophotometer (Hatachi-U3900H). Current density-voltage (*J-V*) curves for all devices were measured using a Keithley 2400 Source Meter under 100 mW/cm^2 illumination with AM 1.5 solar simulator (San-Ei Electric). AM 1.5 G solar simulator was calibrated by standard silicon solar cells (purchased from Enlitech). The external quantum efficiency (EQE) was conducted with a solar cell QE/IPCE measurement system (Zolix solar cell scan100). Transient photovoltage (TPV), transient photocurrent (TPC) and photo-induced charge extraction linear increasing voltage (Photo-CELIV) were conducted with the Paios system (FLUXiM AG, Switzerland). AFM measurements were performed with a Bruker-Fast scan ultrafast DI AFM with soft tapping mode. The contact angle images were obtained using a surface contact angle tester (Zhongchen, JC2000D1, China). The optimized thickness of the active layer is

~100 nm, which was measured by Bruker Stylus Profile (Dektak XT, Bruker Corporation).

5.Additional experimental results

Table S1. Recent progress of high performance ternary BHJ OSCs and PPHJ OSCs.

Active layer	V_{OC}(V)	J_{SC}(mA/cm^2)	FF(%)	PCE(%)	Ref.
PM6:Y6:MF1	0.853	25.68	78.61	17:22	1
PM6:Y6:BR1	0.859	26.49	75.7	17:23	2
PM6:Y6:TPD-3F	0.88	25.6	73.4	17.0	3
PM6:Y6:DRTB-T-C4	0.85	24.79	81.3	17.13	4
PM6:Y6:C8-DTC	0.873	26.50	75.61	17.52	5
PM6:Y6:TiC12	0.853	26.80	75.4	17.25	6
PM6:Y6:S3	0.86	25.86	79.17	17.53	7
PM6:Y6:ITCPTC	0.861	25.674	78.8	17.42	8
PM6:Y6:ITIC-M	0.859	26.35	80.10	18.13	9
PM6:N3:$PC_{71}BM$	0.84	26.76	0.78	17.6	10
PM6:Y6:$PC_{71}BM$	0.858	25.2	76	16.4	11
PM6:PM7:Y6:$PC_{71}BM$	0.859	26.55	79.23	18.07	12
PM6:Y6:TF1 PM6/Y6:TF1	0.870 0.870	25.63 25.89	74.79 75.08	16.67 16.91	13
PM6:Y6:BTP-S2 PM6/Y6:BTP-S2	0.880 0.883	26.20 26.45	75.8 76.29	17.43 17.81	14
PM6:BTP-eC9:BPR-SCl	0.856	27.13	77.6	18.02	15
PM6:BTBr-2F:Y6	0.859	27.30	74.11	17.38	16
PM6:BTTzR:Y6	0.87	26.2	77.7	17.7	17
D18-Cl:G19:Y6	0.871	27.36	77.72	18.53	18
PTQ10:m-BTP-PhC6:$PC_{71}BM$	0.869	26.99	80.6	18.89	19
PM6:BO-4Cl:Y6-1O	0.855	27.46	79	18.52	20
PM6:BTP-eC9:L8-BO-F	0.853	27.35	80.0	18.66	21

PBQx-TF:eC9-2Cl:F-BTA3	0.879	26.7	80.9	19.0	22
PTO3/PBDB-TF:BTP-ec9/NDI-i8	0.866	26.6	80.3	18.50	23
PM6/BO-4Cl PM6/BO-4Cl:BTP-S2	0.846 0.861	26.81 27.14	75.40 78.04	17.11 18.16	24
PM6/Y6	0.82	26.3	76.3	16.5	25
PM6/N3:MF1	0.85	25.61	76.95	16.75	26
D18/ BTIC-BO-4Cl	0.86	26.32	77.66	17.6	27
PNTB6-Cl/ N3	0.857	26.58	77.3	17.59	28
D18/N3	0.845	24.95	77.46	17.05	29
PNTB6-Cl/ BTP-4F-12	0.874	26.89	75.79	17.81	30
D18-Cl/N3(DIB)	0.860	27.18	78.8	18.42	31
D18/BS3TSe-4F:Y6-O	0.845	29.41	76.56	19.03	32
D18/L8-BO	0.918	26.86	77.25	19.05	33
PM6:Y6:$PC_{71}BM$ PM6/Y6:$PC_{71}BM$	0.854 0.855	26.79 26.82	74.68 77.73	17.09 17.82	**this work**

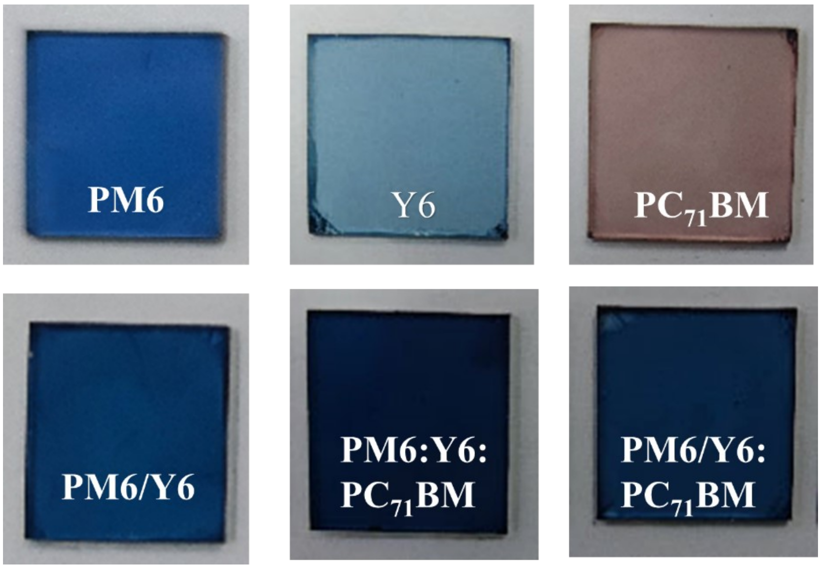

Fig. S1. Photographs of PM6, Y6, $PC_{71}BM$, PM6/Y6, PM6:Y6:$PC_{71}BM$ and PM6/Y6:$PC_{71}BM$ films.

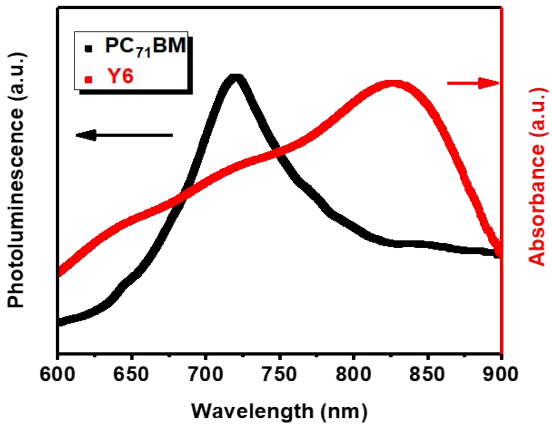

Fig. S2. The $PC_{71}BM$ fluorescence spectrum and Y6 absorption spectrum.

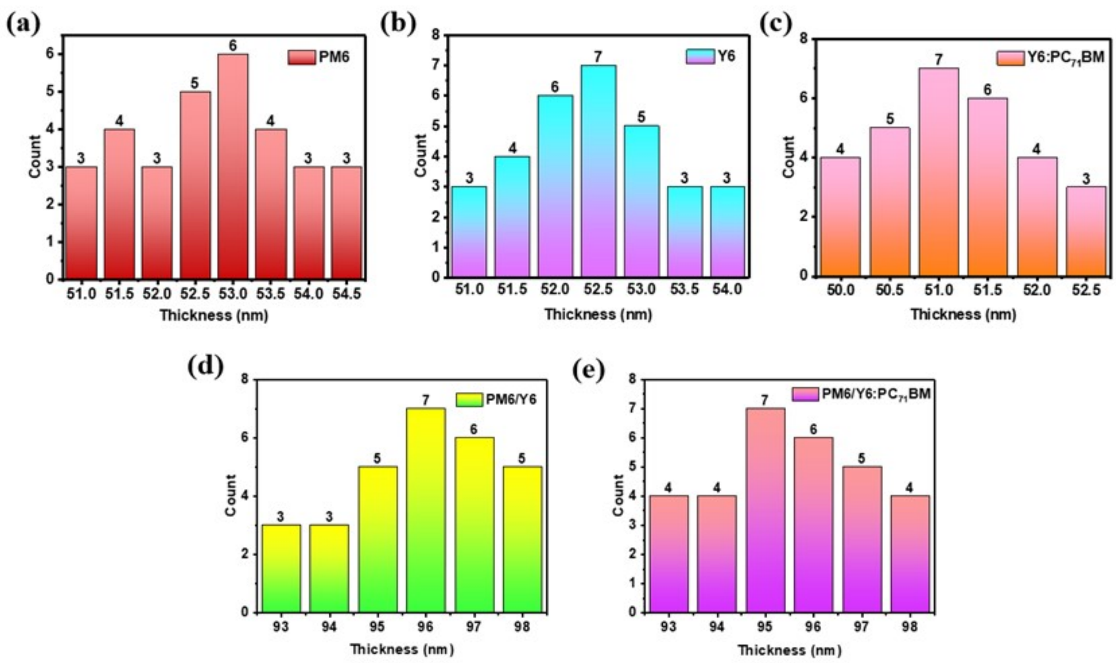

Fig. S3. The statistical data of film thickness of (a) PM6; (b) Y6, (c)Y6: $PC_{71}BM$, (d) PM6/Y6 and (e) PM6/Y6:$PC_{71}BM$ film.

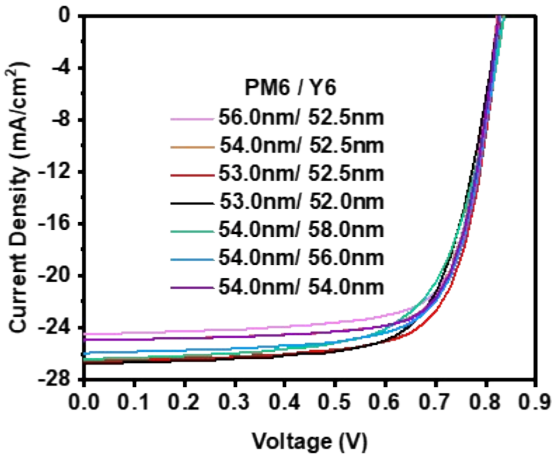

Fig. S4. *J-V* curves of the pseudo-bilayer PM6/Y6 OSCs with different donor layer and acceptor layer thickness.

Table S2. Photovoltaic parameters of the pseudo-bilayer PM6/Y6 OSCs with different donor layer and acceptor layer thickness.

Thickness (nm)	V_{oc}[a] (V)	FF[a] (%)	J_{sc}[a] (mA/cm^2)	PCE (%)
56.0 / 52.5	0.831	73.48	24.52	14.95[a](14.83±0.19)[b]
54.0 / 52.5	0.833	74.17	24.95	15.36[a](15.12±0.17)[b]
53.0 / 52.5	0.835	73.57	26.76	16.44[a](16.21±0.25)[b]
53.0 / 55.0	0.835	70.00	26.79	15.56[a](15.38±0.23)[b]
54.0 / 58.0	0.836	66.89	26.45	14.86[a](14.61±0.26)[b]
54.0 / 56.0	0.835	72.17	25.96	15.55[a](15.36±0.21)[b]
54.0 / 54.0	0.834	74.31	24.98	15.41[a](15.23±0.27)[b]

[a] The maximum values of the devices. [b] The average and deviation values of the PCE obtained from 10 devices.

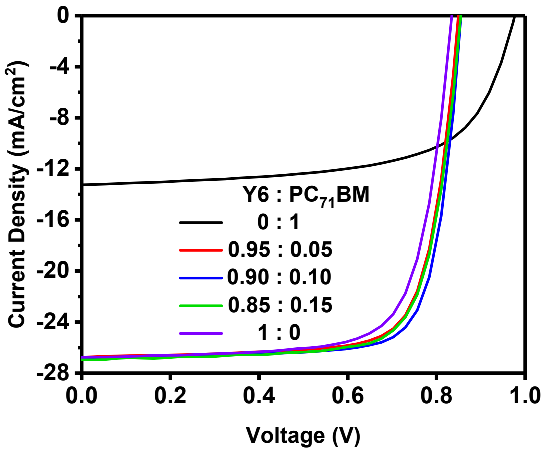

Fig. S5. *J-V* curves of the pseudo-bilayer PM6/Y6: $PC_{71}BM$ devices with different $PC_{71}BM$ contents.

Table S3. Photovoltaic parameters of the pseudo-bilayer PM6/Y6: $PC_{71}BM$ devices with different $PC_{71}BM$ contents.

Y6 : $PC_{71}BM$	V_{oc}[a](V)	FF[a](%)	J_{sc}[a] (mA/cm ^{2})	PCE (%)
0 : 1	0.977	63.72	13.25	8.25[a](7.93±0.21)[b]
0.95 : 0.05	0.854	75.48	26.76	17.25[a](17.09±0.24)[b]
0.90 : 0.10	0.855	77.73	26.82	17.82[a](17.47±0.25)[b]
0.85 : 0.15	0.855	75.17	26.95	17.32[a](17.13±0.22)[b]
1 : 0	0.835	73.57	26.76	16.44[a](16.21±0.23)[b]

[a] The maximum value of the devices. [b] The average and deviation values of the PCE obtained from 10 devices.

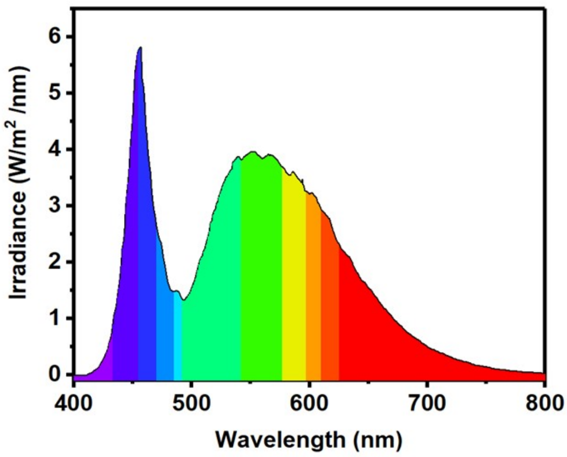

Fig. S6. The illumination spectrum of the white LED.

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