Hydrogen-Bonds Induced High Performance Quaternary Organic Solar Cells with Efficiency up to 17.48% and Superior Thermal Stability

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1. Experimental Section

Materials: Both the host system materials were purchased from Solarmer Materials Inc. SR197 (also called DIBC) was bought from TCI. In order to ensure that reliable experimental results can be obtained, the same batch of materials was used for experiments. Hole transport materials were purchased from Xi'anp-OLED Technology Corp. Other related materials and solutions were bought from Alfa Chemical Inc. or Sigma-Aldrich Corp and used directly (without extra treatment).

Device fabrication:

All devices in this paper adopted an inverted structure that is Indium Tin Oxide (ITO)/ ZnO/ active layer/ MoO_3/ Ag, in which ZnO is formed by a mixture of 110 mg zinc acetate dihydrate, 31 mg ethanolamine and 1 ml 2-methoxyethanol. The glass substrates covered with ITO were cleaned to remove dust and stains on the surface. Then, ultrasonic process was used for 30 minutes in ethanol, acetone and ethanol in sequence. Next, the substrate was irradiated with an ultraviolet-ozone lamp for 30 minutes to improve the surface environment. Afterward, the prepared ZnO solution was spin coated on ITO substrates with 5000 rpm for 30 s, and then annealed at 200 ℃ for 1 h to promote the formation of ZnO film (30 nm). ZnO-coated substrates were transferred into the glovebox, and an active layer of about 100 nm was formed after spin-coating the active layer solution and annealing at 110 °C for 10 mins. Chloroform (CF) was selected as the solvent to dissolve the active layer material. For PM6:Y6 binary OSCs, the blended ratio of donor and acceptor was 1:1.2. For PM6:Y6:SR197, the ratio was 1:1:0.1, while that of PM6:Y6:$PC_{71}BM$ was 1:1:0.1, and that of PM6:Y6:$PC_{71}BM$:SR197 was 1:1:0.1:0.1, in which the donors concentration is maintained at 7.5 mg/ml with 0.5% CN as addictive. The mixed solution prepared one day in advance was placed in a nitrogen

atmosphere and stirred for more than 10 hours. Ultimately, vacuum vapor deposition was used to deposit 10 nm of MoO_3 and 150 nm of Ag on the active layer as the holes transport layer and anode, respectively.

Measurement Method: Hitachi U-3010 ultraviolet-photoluminescence spectroscopy is used to measure the absorption spectrum of films. Adopting Newport Oriel-Sol3A to simulate AM 1.5G sunlight and processing with Keithley 2400 source meter, the current density versus voltage (J-V) curves are measured. The external quantum efficiency (EQE) is obtained by the QEX10 quantum 16 Efficiency Measurement System. The blended films morphology are conducted though atomic force microscope (AFM, MFP-3D-BIO) and transmission electron microscope (TEM, Hitachi HT7700), respectively. The Grazing-incidence wide-angle X-ray scattering (GIWAXS) is estimated at the BL16B station of the Shanghai Synchrotron Radiation Facility, and 10 keV X-ray is used to irradiate the whole sample at an incident angle of 0.09-0.15°. The mobility of hole (μ_h) and electron (μ_e) for devices are calculated by space charge limiting current (SCLC) method. The structures of ITO/ PEDOT: PSS/ Active layer/ MoO_3/ Au and ITO/ ZnO/ Active layer/ LiF/ AL are adopted to fabricate hole-only and electron-only devices, respectively.

2. Supplementary Figure Section

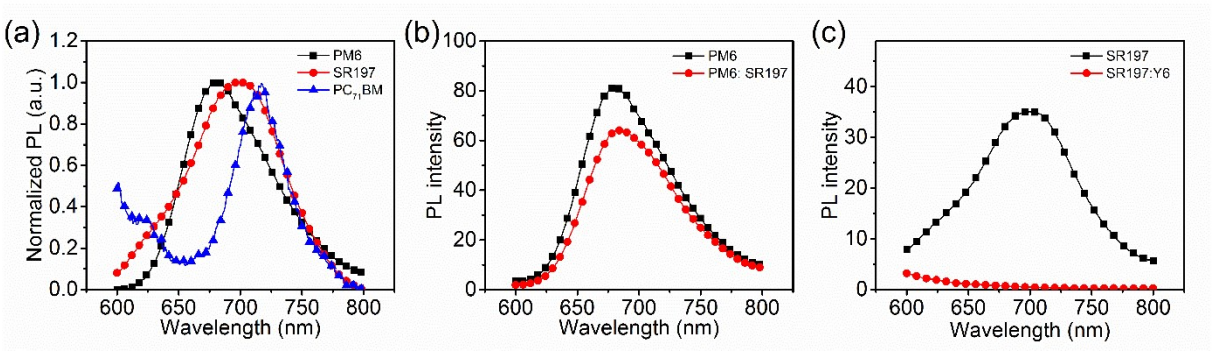

Figure S1. PL spectra of (a) neat PM6, SR197 and $PC_{71}BM$ films and (b) the blended PM6: SR197 film and (c) the blended SR197:Y6 film under 560 nm light excitation.

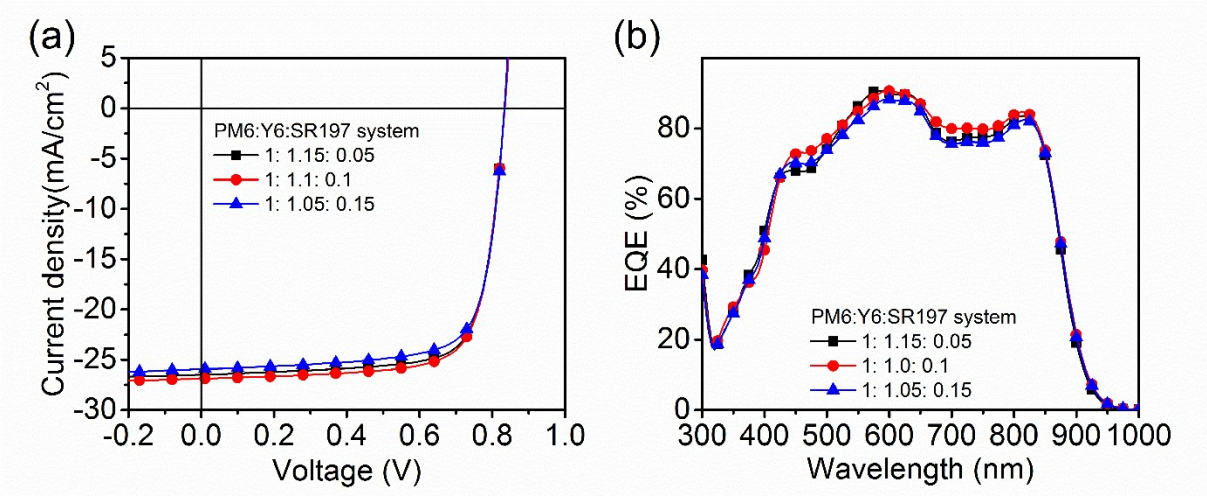

Figure S2. (a) J-V and (b) EQE curves of OSCs based on ternary PM6:Y6:SR197 system.

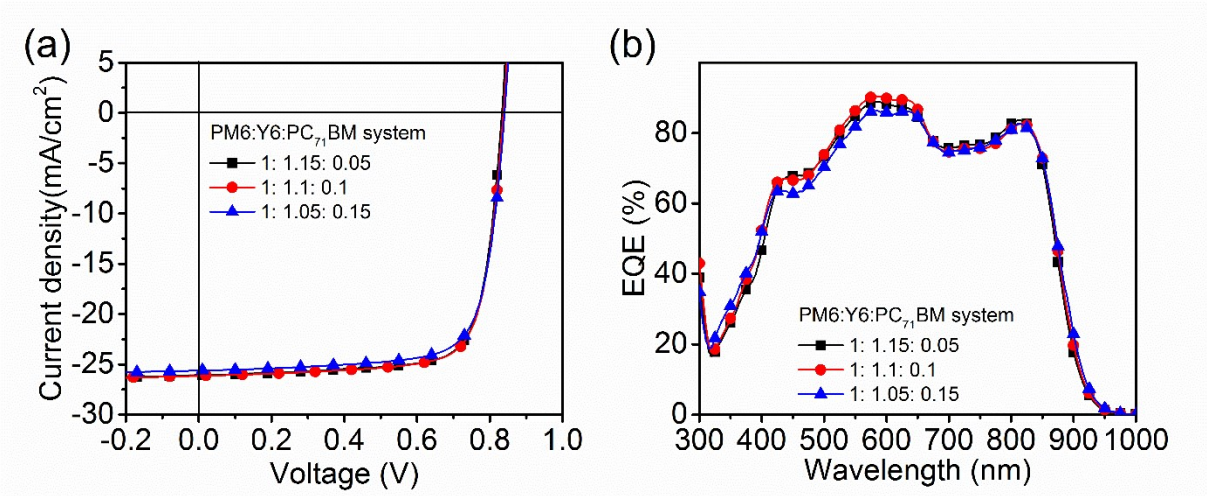

Figure S3. (a) J-V and (b) EQE curves of OSCs based on ternary PM6:Y6:$PC_{71}BM$ system.

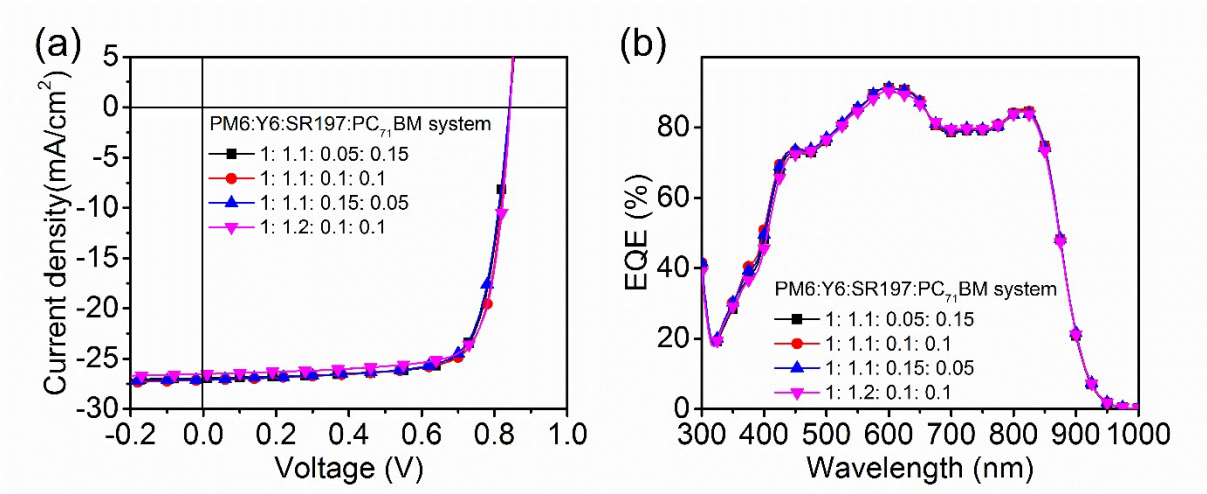

Figure S4. (a) J-V and (b) EQE curves of OSCs based on quaternary PM6:Y6:SR197:$PC_{71}BM$ system.

3. Supplementary Table Section

Table S1. Summary of photovoltaic performance parameters of PM6:Y6:SR197-based ternary OSCs. All data were obtained under AM 1.5G, 100 mWcm^{-2} light source irradiation.

PM6:Y6:SR197	V_{OC} [V]	J_{SC} [mAcm^{-2}]	J_{cal} [mAcm^{-2}]	FF [%]	PCE [%]
1:1.15:0.05	0.834	26.46	25.38	75.58	16.68(16.53)
1:1.1:0.1	0.834	26.87	25.88	75.08	16.83(16.64)
1:1.05:0.15	0.833	25.92	25.07	74.77	16.15(16.07)

Table S2. Summary of photovoltaic performance parameters of PM6:Y6:$PC_{71}BM$-based ternary OSCs. All data were obtained under AM 1.5G, 100 mWcm^{-2} light source irradiation.

PM6:Y6:$PC_{71}BM$	V_{OC} [V]	J_{SC} [mAcm^{-2}]	J_{cal} [mAcm^{-2}]	FF [%]	PCE [%]
1:1.15:0.05	0.833	26.04	24.95	76.72	16.64 (16.51)
1:1.1:0.1	0.837	26.12	25.22	76.50	16.72(16.61)
1:1.05:0.15	0.840	25.60	24.75	75.44	16.23 (16.00)

Table S3. Summary of photovoltaic performance parameters of PM6:Y6:SR197:$PC_{71}BM$-based quaternary OSCs. All data were obtained under AM 1.5G, 100 mWcm^{-2} light source irradiation.

PM6:Y6:SR197:$PC_{71}BM$	V_{OC} [V]	J_{SC} [mAcm^{-2}]	J_{cal} [mAcm^{-2}]	FF [%]	PCE [%]
1:1.1:0.05:0.15	0.842	26.90	25.89	76.34	17.29 (17.14)
1:1.1:0.1:0.1	0.841	27.11	26.02	76.62	17.48 (17.38)
1:1.1:0.15:0.05	0.841	27.03	26.00	75.4	17.14 (16.97)
1:1.2:0.1:0.1	0.842	26.49	25.68	77.23	17.25(17.04)

Table S4. Summary of photovoltaic performance parameters of binary OSCs with and without hydrogen bonding inhibitor methanol (inset) and of SR197-doped ternary as well as quaternary OSCs with and without hydrogen bonding inhibitor methanol.

Active Layer	Methanol content [%][a)]	V_{OC} [V]	J_{SC} [mAcm^{-2}]	FF [%]	PCE [%]
PM6:Y6	0	0.830	25.12	74.53	15.56(15.38)
	0.5	0.831	24.86	74.76	15.46(15.43)
PM6:Y6:SR197	0	0.834	26.87	75.08	16.83(16.64)

	0.5	0.835	25.38	74.66	15.84(15.72)
PM6:Y6:SR197:$PC_{71}BM$	0	0.841	27.11	76.62	17.48(17.38)
	0.5	0.837	26.60	74.96	16.69(16.52)

Table S5. Summary of photovoltaic performance parameters of binary OSCs with and without hydrogen bonding inhibitor methanol (inset) and of SR197-doped ternary as well as quaternary OSCs with and without hydrogen bonding inhibitor methanol

Device type	Active Layer	μ_0 ($cm^2 V^{-1} s^{-1}$)	μ ($cm^2 V^{-1} s^{-1}$)
hole-only	PM6:Y6	4.30×10^{-4}	2.90×10^{-4}
	PM6:Y6:SR197	6.17×10^{-4}	3.65×10^{-4}
	PM6:Y6:$PC_{71}BM$	5.75×10^{-4}	3.49×10^{-4}
	PM6:Y6:SR197:$PC_{71}BM$	6.36×10^{-4}	4.01×10^{-4}
electron-only	PM6:Y6	8.02×10^{-5}	6.67×10^{-5}
	PM6:Y6:SR197	1.34×10^{-4}	1.02×10^{-4}
	PM6:Y6:$PC_{71}BM$	1.05×10^{-4}	9.07×10^{-5}
	PM6:Y6:SR197:$PC_{71}BM$	1.55×10^{-4}	1.18×10^{-4}