

Supporting Information

17.25% High Efficiency Ternary Solar Cells with Increased Open-Circuit Voltage by a High HOMO Level Small Molecular Guest Donor in a PM6:Y6 Blend

*Wei Tang,^{‡a,b} Wenhong Peng,^{‡a,c,f} Mengbing Zhu,^a Huanxiang Jiang,^e Wenchao Wang,^a Hao Xia,^a Renqiang Yang,^e Olle Inganäs,^d Hua Tan,^{*a} Qingzhen Bian,^{*d} Ergang Wang,^{*c} and Weiguo Zhu^{*a}*

^a School of Materials Science and Engineering, Jiangsu Collaboration Innovation Center of Photovoltaic Science and Engineering, Jiangsu Engineering Laboratory of Light- Electricity-Heat Energy-Converting Materials and Applications, National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, China.

^b College of Chemistry, Xiangtan University, Xiangtan 411105, China.

^c Department of Chemistry and Chemical Engineering Chalmers University of Technology, Göteborg, SE-412 96, Sweden. E-mail: ergang@chalmers.se

^d Biomolecular and Organic Electronics, Department of Physics Chemistry and Biology (IFM), Linköping University, Linköping, SE-581 83, Sweden.

^e Key Laboratory of Optoelectronic Chemical Materials and Devices (Ministry of Education), School of Chemical and Environmental Engineering, Jiangnan University, Wuhan 430056, China.

^f Hunan Provincial Key Laboratory of Environmental Catalysis & Waste Re-cycling, School of Materials and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China.

**To whom correspondence should be addressed. Email:*

(W. Z.) zhuwg18@126.com

(E. W.) ergang@chalmers.se

Contents

1. Materials.....	1
2. General Measurements.....	1
3. OSC Device Fabrication and Measurement.....	1
4.Characterization of Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS).....	2
5. Steady state photoluminescence of neat materials and their blends	3
6. The progress of the PM6:Y6 based ternary OSCs	3
7. Additional OSC Device Performance Data	4
8. SCLC Measurements	4
9. Low-Temperature Measurement.....	6
10. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) Measurements	6
11. References.....	8

1. Materials

Chloroform (CF) and 1-chloronaphthalene (CN) were purchased from Aldrich and used without further purification. PM6, Y6 and PDINO were purchased from J&K Scientific Co., Ltd. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) (Clevios PVP Al 4083) was obtained from H.C. Starck Germany. Molybdenum oxide (MoO_3) and aluminum (Al) were purchased from Alfa Aesar Co., Ltd. All materials were used without further purification. Particularly, TiC12 was synthesized as reported in our previous work.^[1]

2. General Measurements

UV-vis absorption spectra were obtained using a Shimadzu UV-1800 PC spectrometer. First of all, the blank quartz wafer was used for baseline scanning of the instrument, and then the sample in the spin-coated quartz wafer was scanned. Finally, the ultraviolet absorption spectrum was obtained. The electrochemical cyclic voltammetry (CV) was measured with a CHI630E electrochemical workstation with the working electrode dipped in an acetonitrile solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) under nitrogen at room temperature.

3. OSC Device Fabrication and Measurement

The organic solar cells were fabricated with a conventional configuration of ITO /PEDOT: PSS (30 nm) /active layer (100 nm) /PDINO (5 nm) /Al (100 nm), the area is 0.06 cm². The indium tin oxide (ITO)-glass substrates were sequentially washed by Decon90 dilution solution, deionized water, acetone and isopropyl alcohol using ultrasonic process for each 20 min, respectively, then were treated by UV-ozone for 15 min. The PEDOT:PSS was spin-coated at 4800 rpm for 30 s on the cleaned ITO substrate and annealed at 150 °C for 15 min in air. The substrates were transferred into an N₂-filled glove box for preparing the photoactive layer. The PM6:Y6 blend solutions were prepared using chloroform solvent. The concentration of PM6 in the blend solution is 6 mg mL⁻¹ (donor: acceptor = 1:1.2 by weight), with 0.5% CN by volume as additive, and were stirred for 6 h before use. In the blends, the doping ratio of TiC12 in donor are 0, 5%, 10%, 15%, 30%, 50%, 80%, and 100% by weight. The binary and ternary active

layers were spin-coated on PEDOT: PSS with the resulting thickness of 130 nm, and then annealed at 100 °C for 10 min. After that, the PDINO (1 mg mL⁻¹ in methanol) was spin-coated on the top of active layers at 3000 rpm for 30 s to form an electron transporting layer. Finally, the Al (100 nm) electrode was thermally deposited with a shadow mask with the device area of 0.06 cm² at the pressure of 10⁻⁴ Pa. The current density-voltage (*J-V*) characteristics of the organic solar cells were performed using a programmable Keithley 2400 source measurement unit under simulated solar light (AM 1.5 G) (DM40S3, SAN-EI ELECTRIC, Japan). The light intensity was determined by the standardized mono-silicon cell (Oriel PN 91150V, Newport, USA). The external quantum efficiency (EQE) spectra were obtained by a photo-modulation spectroscopic setup (Newport monochromator).

Space charge limited current (SCLC) measurement was applied to determine the electron and hole mobilities using the electron-only device with a structure of ITO/ZnO/active layer/PDINO/Al and hole-only device with a structure of ITO/PEDOT:PSS/active layer/MoO₃/Al, respectively. The mobility was determined by the equation:

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{L^3} \quad (1)$$

Where ϵ is the dielectric permittivity of the polymer (generally taken to be about 3), ϵ_0 is the dielectric permittivity of free space, L is the film thickness, and V is the voltage, which is defined as $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, V_{bi} is the built-in voltage which is related to the difference in the work function of the electrodes.

4.Characterization of Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS measurements were performed on a XEUSS SAXS/WAXS system at the South China University of Technology (China, Guangzhou). The samples were initially dissolved in chloroform and then spin coated on the top of silicon wafer at 2000 rpm. The silicon wafers were treated with plasma in advance to optimize the film-forming property.

5. Steady state photoluminescence of neat materials and their blends

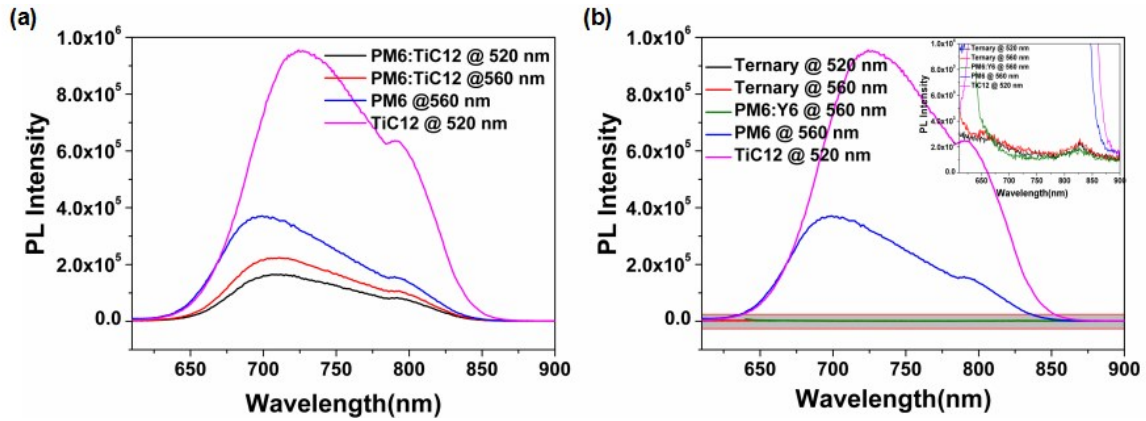


Fig. S1 (a) Photoluminescence spectra of neat PM6, TiC12 film and the PM6:TiC12 blend, with different excitation energy of 560 nm and 520 nm respectively. (b) Photoluminescence spectra of neat PM6, TiC12 film and the PM6:TiC12:Y6 (0.9:0.1:1.2) ternary blend, with different excitation energy of 560 nm and 520 nm respectively.

6. The progress of the PM6:Y6 based ternary OSCs

Table S1. The summary of photovoltaic data of the PM6:Y6 based ternary OSCs.

PM6:X:Y6	D/A ratios	Third component	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	Ref.
PM6:TiC12:Y6	0.9:0.1:1.2	SM_donor	0.853	26.80	75.4	17.25	This work
PM6:TiC12:Y6	0.2:0.8:1.2	SM_donor	0.905	11.97	57.6	6.23	This work
PM6:PC ₇₁ BM:Y6	1:0.2:1.2	Fullerene acceptor	0.861	25.1	77.2	16.7	[2]
PM6:3TP3T4F:Y6	1:0.18:1.02	SM_acceptor	0.86	26.2	75.9	16.7	[3]
PM6:O-DTBR:Y6	1:0.15:0.85	SM_donor	0.85	25.75	76	16.6	[4]
PM6:DRTB-T-C4:Y6	1:0.1:1.2	SM_donor	0.85	24.79	81.3	17.13	[5]
PM6:MF-1:Y6	1:0.1:1.2	SM_acceptor	0.853	25.68	78.61	17.22	[6]
PM6:C8-DTC:Y6	1:0.12:1.08	SM_acceptor	0.873	26.50	75.61	17.52	[7]
PM6:IT-4F:Y6	1:0.2:1.2	SM_acceptor	0.844	25.40	75.9	16.27	[8]
PM6:IDIC:Y6	1:0.2:1	SM_acceptor	0.868	25.39	74.92	16.51	[9]
PM6:PC ₆₁ BM:Y6	1:0.2:1.2	Fullerene acceptor	0.845	25.4	77.0	16.5	[10]

PM6:SM1:Y6	1:0.15:1.2	<i>SM_donor</i>	0.831	25.7	77.5	16.55	[11]
PM6:D18-Cl:Y6	0.7:0.3:1.2	<i>SM_donor</i>	0.871	26.4	76.8	17.61	[12]
PM6:BTzR:Y6	0.8:0.2:1.2	<i>SM_donor</i>	0.87	26.2	77.7	17.7	[13]

7. Additional OSC Device Performance Data

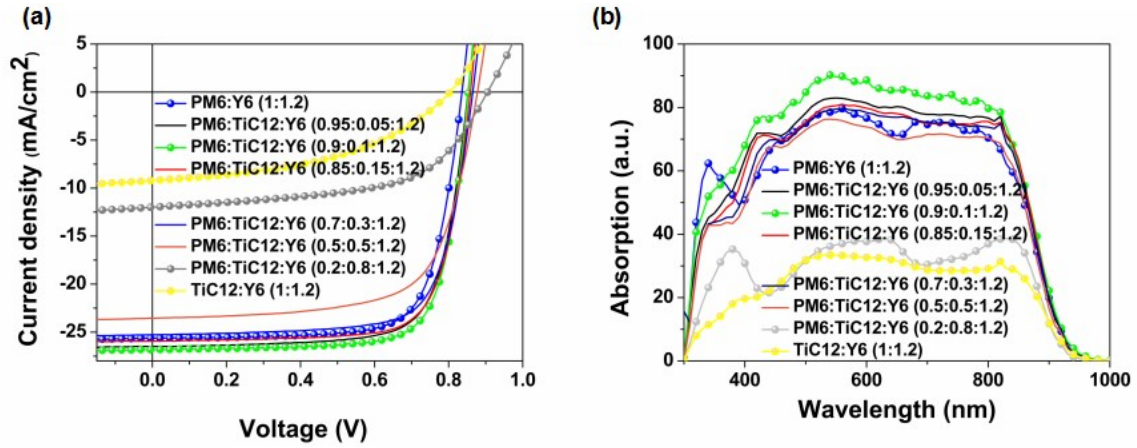


Fig. S2 (a) J - V curves and (b) EQE spectra of binary and ternary OSCs with various contents.

8. SCLC Measurements

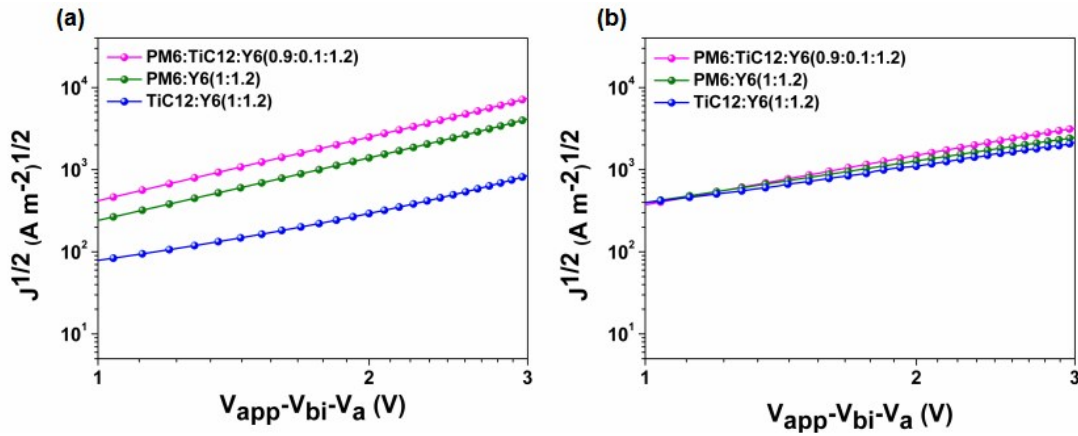


Fig. S3 $J^{1/2}$ - V plots of the electron-only devices (a) and the hole-only devices (b) based on the optimal binary (PM6:Y6 = 1:1.2, TiC12:Y6 = 1:1.2) and ternary (PM6:TiC12:Y6 = 0.9:0.1:1.2) blends.

Table S2. Charge mobilities of the optimal binary (PM6:Y6 = 1:1.2, TiC12:Y6 = 1:1.2) and ternary (PM6:TiC12:Y6 = 0.9:0.1:1.2) OSCs.

Active layers	μ_h [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_e [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_e/μ_h
PM6:TiC12:Y6	1.15×10^{-4}	2.76×10^{-4}	2.40
PM6:Y6	9.07×10^{-5}	1.55×10^{-4}	1.71
TiC12:Y6	8.43×10^{-5}	4.21×10^{-4}	4.99

9. Low-Temperature Measurement

Normal devices and single-carrier devices were mounted in a liquid-nitrogen cryostat for temperature-dependent measurements. The J - V curves were measured using a Keithley 2400 source meter at temperatures ranging from 200 K to 300 K. The temperature was monitored and controlled using a LakeShore 330 Autotuning Temperature Controller.

EQE_{EL} values were obtained from an inhouse-built system including a Hamamatsu silicon photodiode 1010B, a Keithley 2400 SourceMeter to apply the voltage and record the injected current, and a Keithley 485 Picoammeter to measure the emitted light intensity.

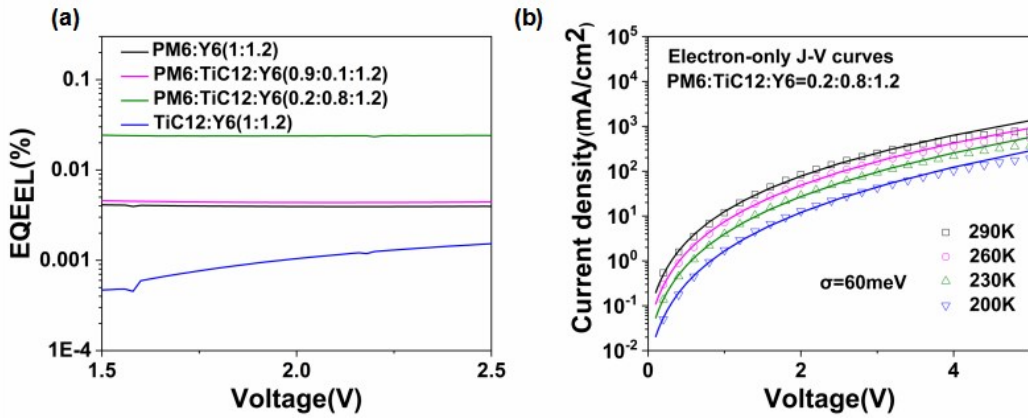


Fig. S4 (a) Electroluminescence quantum yield of the Y6 based devices. (b) Temperature-dependent space-charge-limited current for ternary device. The line are the fitted curves and inset in the calculated disorder

value. The energetic disorder σ can be calculated from $\mu_0(T) = \mu_\infty \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right]$. The k_B is Bozeman constant, T is the temperature and μ is mobility value.

10. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) Measurements

AFM measurements were performed in ambient on a SPID Bruker ICON using a TESPA probe. All the AFM images were flattened and exported from the NanoScope Analysis 1.9 software, the root-mean-square roughness (Rq) values of height images were obtained from the whole scan area ($2 \mu\text{m} \times 2 \mu\text{m}$). Transmission electron microscopy (TEM) images were obtained by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100kV.

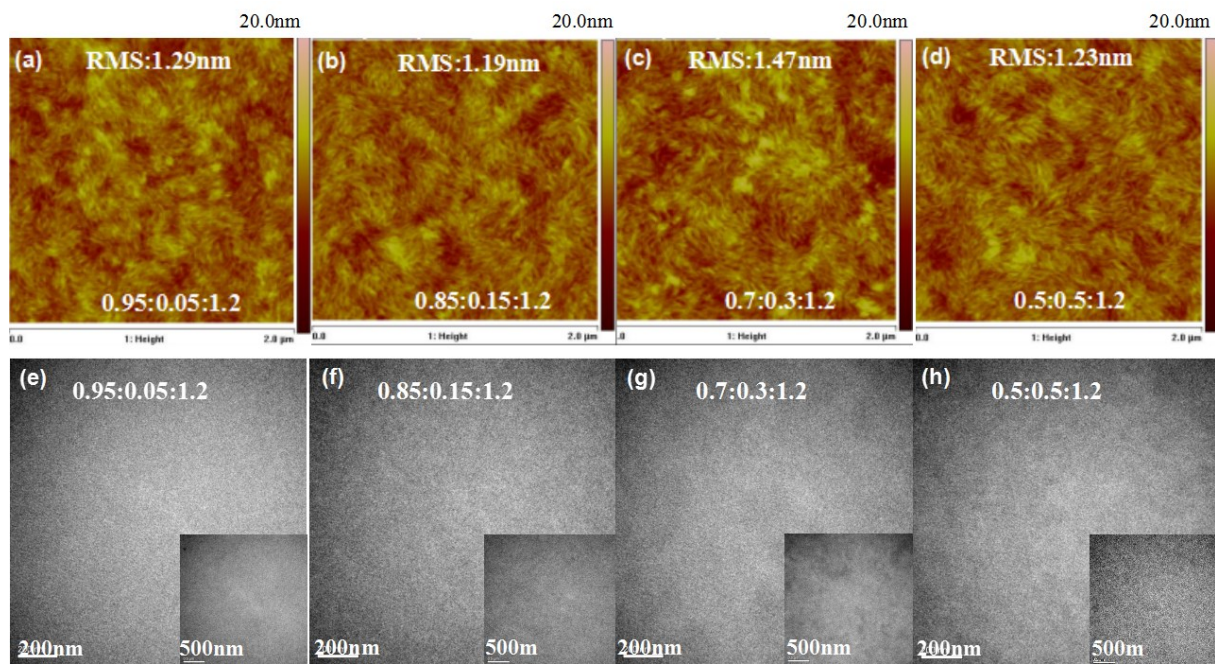


Fig. S5 (a-d) AFM and (e-h) TEM images of (a, e) PM6:TiC12:Y6= 0.95:0.05:1.2, (b, f) PM6:TiC12:Y6= 0.85:0.15:1.2, (c, g) PM6:TiC12:Y6= 0.7:0.3:1.2 and (d, h) PM6:TiC12:Y6= 0.5:0.5:1.2.

11. References

1. W. Wang, G. Zhang, J. Guo, Z. Gu, R. Hao, Z. Lin, Y. Qian, M. Zhu, H. Xia, W. Peng, X. Liu, Q. Peng and W. Zhu, *ACS Appl. Energy Mater.*, 2019, **2**, 4730-4736.
2. M.-A. Pan, T.-K. Lau, Y. Tang, Y.-C. Wu, T. Liu, K. Li, M.-C. Chen, X. Lu, W. Ma and C. Zhan, *J. Mater. Chem. A*, 2019, **7**, 20713-20722.
3. J. Song, C. Li, L. Zhu, J. Guo, J. Xu, X. Zhang, K. Weng, K. Zhang, J. Min, X. Hao, Y. Zhang, F. Liu and Y. Sun, *Adv. Mater.*, 2019, **31**, 1905645.
4. N. Gasparini, S. H. K. Paleti, J. Bertrandie, G. Cai, G. Zhang, A. Wadsworth, X. Lu, H.-L. Yip, I. McCulloch and D. Baran, *ACS Energy Lett*, 2020, **5**, 1371-1379.
5. D. Li, L. Zhu, X. Liu, W. Xiao, J. Yang, R. Ma, L. Ding, F. Liu, C. Duan, M. Fahlman and Q. Bao, *Adv. Mater.*, 2020, **32**, 2002344.
6. Q. An, J. Wang, W. Gao, X. Ma, Z. Hu, J. Gao, C. Xu, M. Hao, X. Zhang, C. Yang and F. Zhang, *Sci. Bull.*, 2020, **65**, 538-545.
7. Q. Ma, Z. Jia, L. Meng, J. Zhang, H. Zhang, W. Huang, J. Yuan, F. Gao, Y. Wan, Z. Zhang and Y. Li, *Nano Energy*, 2020, **78**, 105272.
8. Q. An, X. Ma, J. Gao and F. Zhang, *Sci. Bull.*, 2019, **64**, 504-506.
9. K. Li, Y. Wu, Y. Tang, M. A. Pan, W. Ma, H. Fu, C. Zhan and J. Yao, *Adv. Energy Mater.*, 2019, **9**, 1901728.
10. R. Yu, H. Yao, Y. Cui, L. Hong, C. He and J. Hou, *Adv. Mater.*, 2019, **31**, 1902302.
11. T. Yan, J. Ge, T. Lei, W. Zhang, W. Song, B. Fanady, D. Zhang, S. Chen, R. Peng and Z. Ge, *J. Mater. Chem. A*, 2019, **7**, 25894-25899.
12. C. Xu, X. Ma, Z. Zhao, M. Jiang, Z. Hu, J. Gao, Z. Deng, Z. Zhou, Q. An, J. Zhang and F. Zhang, *Sol. RRL*, 2021, **10**, 2100175.
13. Q. Liu, Y. Wang, J. Fang, H. Liu, L. Zhu, X. Guo, M. Gao, Z. Tang, L. Ye, F. Liu, M. Zhang and Y. Li, *Nano Energy*, 2021, **85**, 105963.