Supporting Information

Tuning the Electron-deficient-core of Non-fullerene Acceptor to

Achieve over 17% Efficiency in Single-Junction Organic Solar Cells

Can Zhu,[‡]^a Jun Yuan,[‡]^a Fangfang Cai,[‡]^a Lei Meng,^{*}^b Huotian Zhang,^c Honggang Chen,^a Jing Li,^aBeibei Qiu,^b Hongjian Peng,^a Shanshan Chen,^{d,e} Yunbin Hu,^aChangduk Yang,^dFeng Gao,^cYingping Zou,^{*}^a and Yongfang Li^b

^aCollege of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, P.R. China, E-mail: yingpingzou@csu.edu.cn (Y.Zou).

^bBeijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids,Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China, E-mail:menglei@iccas.ac.cn (L. Meng).

^cDepartment of Physics, Chemistry and Biology (IFM), Linköping University, Linköping 58183, Sweden

^dDepartment of Energy Engineering, School of Energy and Chemical Engineering, Perovtronics Research Center, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea.

^eMoe Key Laboratory of low-grade Energy Utilization Technologies and Systems, CQU-NUS Renewable Energy Materials & Power Engineering, Chongqing University, Chongqing, 400044, China.

Experimental Section

1. Characterizationofmaterials

¹H NMR spectra were recorded using a Bruker AV-400 spectrometer in a deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts are reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under nitrogen. UV-Vis absorption spectra were recorded on the SHIMADZU UV-2600 spectrophotometer. For the solid state measurements, Y18 solutions in chloroform were spin-coated on quartz plates.

The cyclic voltammetry results were obtained with a computer-controlled CHI 660E electrochemical workstation using polymer or non-fullerene acceptor films on platinum electrode (1.0 cm^2) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile, at a scanning rate of 50 mV·s⁻¹. Electrochemical onsets were determined at the position where the current started to rise from the baseline.

2. Fabrication and measurement of devices

All solar cell device structures were constructed in an ITO/ZnO/active layer/MoO₃/Ag configuration. The pre-patterned ITO glass substrates (sheet resistance = $12 \ \Omega \ sq^{-1}$) were ultrasonicated in detergent, deionized water, acetone, isopropanol, and UV-treated in ultraviolet–ozone chamber (Jelight Company, USA) for 20 min. ZnO(Sol-gel) was spin-coated onto the ITO substrate (30 nm) and then the ITO substrates were thermal annealled at 200 °C for 1 h in the air. The polymer PM6:Y18 (D:A = 1:1.5, 16 mg mL⁻¹ in total) were dissolved in chloroform (CF) and 1-chloronaphthalene (CN) (0.8 %, v/v) and spin-cast at 3200 rpm for 30s onto the ZnO(Sol-gel) layer. It was then annealed at 110 °C for 5 minutes. After cooling to room temperature, the sample is transferred to the evaporation chamber. Under the condition of 1×10^{-5} Pa, 10 nm-thick MoO₃ and about 100 nm of Ag were respectively evaporated. The device area was 5.0 mm². The ratio of the PM6:Y18:PC₇₁BM in the ternary system is 1:1.5:0.2, and the rest of the conditions are the same as the binary.

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/cm². The external quantum efficiency (EQE) values were measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

3. Hole mobility and electron mobility measurements

The electron mobility device adopts the ITO/ZnO/active layer/PDINO/Al structure, and the hole mobility device adopts the ITO/PEDOT:PSS/active layer/MoO₃/Ag structure. The hole and electron mobilities are calculated according to the space charge limited current (SCLC) method equation: J = $9\mu\epsilon_r\epsilon_0 V^2/8d^3$, where J is the current density, μ is the hole or electron mobility, V is the internal voltage in the device, ϵ_r is the relative dielectric constant of active layer material, ϵ_0 is the permittivity of empty space, and d is the thickness of the active layer.

4. Atomic force microscopy (AFM) and Transmission electron microscopy (TEM)

The morphologies of the polymer/acceptor blend films were investigated by AFM (Bruker multimode8 AFM) in contacting under normal air conditions at room temperature with a 5 μ m scanner. Samples for the TEM measurements were prepared as following: The active layer films were spin-casted on ITO/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) substrates, and the substrates with active layers were submerged in deionized water to make the active layers floats onto the air-water interface. Then, the floated films were picked up on an unsupported 200 mesh copper grids for the TEM measurements. TEM experiments were performed on a JEM-2100 transmission electron microscope operated at 200 kV.

4. Materials

Triethylphosphate, 1-bromo-2-ethylhexane andn-butyllithium (n-BuLi) were obtained from Acros Organics were purchased from Sigma-Aldrich.PM6(M_n =49 kDa) were purchased from Solarmer Energy Inc. All other reagents and solvents such as anhydroustetrahydrofuran (THF), pyridine, chloroform, *o*-dichlorobenzene (*o*-DCB), N, N-dimethylformamide (DMF) and methanol were dried and distilled befroe use. 2-(5,6-Difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-malononitrile was purchased from Derthon OPV Co Ltd; 3-hexylthieno[3,2-b]thiopheneand 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]-thiadiazole were synthesized according to previously reported methods.

5. Synthetic Procedures



Scheme S1. Synthetic Route of Y18

Synthesis of 2-(2-ethylhexyl)-4,7-bis(6-hexylthieno[3,2-b]thiophen-2-yl)-5,6-dinitro-2Hbenzo[d][1,2,3]triazole (3)

Tributyl(6-hexylthieno[3,2-b]thiophen-2-yl)stannane(25.68g,50mmol),4,7-dibromo-2-(2-

ethylhexyl)-5,6-dinitro-2H-benzo[d][1,2,3]triazole(10.54g, 22mmol) and Pd(PPh₃)Cl₂ (0.62 g,0.88mmol) were dissolved in 110 mL of dry tetrahydrofuran and stirred at 70 °C overnight. The reaction mixture was allowed to cool to room temperature and was quenched with water. It is then extracted with an aqueous solution containing dilute hydrochloric acid. The crude product was purified on silica gel chromatography using petroleum ether/CH₂Cl₂ (3:1, v/v) to give compound **3** (12.13 g) as a red solid in a yield of 75%.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 2H), 7.14 (s, 2H), 4.77 (d, *J* = 6.7 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 4H), 2.29 – 2.22 (m, 1H), 1.79 (t, *J* = 11.1 Hz, 4H), 1.50 – 1.14 (m, 24H), 0.94 (dt, *J* = 21.4, 6.9 Hz, 12H).

Synthesis of 6,12,13-tris(2-ethylhexyl)-3,9-dihexyl-12,13-dihydro-6H-thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b][1,2,3]triazolo[4,5-e]indole (4)

Compound **3** (7.66 g, 10 mmol) and triethyl phosphate (50 mL) were dissolved in dichlorobenzene (o-DCB, 20 mL) under nitrogen. The reaction was carried out at 180 $^{\circ}$ C for 10 hours, extracted with dichloromethane and water, dried, and then evaporated. The crude product was obtained directly used as the next reaction. The crude product, 1-Bromo-2-ethylhexane (2.90 g, 15 mmol),

potassium carbonate (4.90 g, 35.64 mmol) and DMF (80 mL) was taken in a 250 ml one-neck flask. Stir at 80 ° C overnight under nitrogen. Cool to room temperature and spin dry with dichloromethane and water. Further purification by column chromatography using dichloromethane / petroleum ether (1/10, v / v) as eluent to afford red solid 4 (3.9 g, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.98 (s, 2H), 4.72 (d, *J* = 7.2 Hz, 2H), 4.58 (d, *J* = 7.7 Hz, 4H), 2.82 (t, *J* = 7.6 Hz, 4H), 2.42 – 2.33 (m, 1H), 2.03 – 1.92 (m, 2H), 1.90 – 1.79 (m, 4H), 1.46 – 1.30 (m, 20H), 1.02 – 0.77 (m, 28H), 0.65 – 0.50 (m, 12H).

Synthesis of 6,12,13-tris(2-ethylhexyl)-3,9-dihexyl-12,13-dihydro-6H-thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b][1,2,3]triazolo[4,5-e]indole-2,10dicarbaldehyde (5)

Add compound **4** (0.74 g, 0.80 mmol) to 25 ml of ultra dry tetrahydrofuran under nitrogen. After stirring at -78 ° C for half an hour, slowly add n-BuLi (1.1 mL, 1.6 M in hexane). Continue After stirring for 2 h, ultra dry DMF (0.19 mL, 5.85 mmol) was quickly added and then taken to room temperature overnight. The reaction mixture was poured into ice water (200 mL) and then extracted with dichloromethane and brine. It was steamed under reduced pressure and dried over MgSO₄. The crude product was purified on silica gel chromatography using petroleum ether/ CH_2Cl_2 (1:1, v/v) to give compound **5** (0.53 g) as a red solid in a yield of 68%.

¹H NMR (400 MHz, CDCl₃) δ 10.13 (s, 2H), 4.73 (d, J = 7.0 Hz, 2H), 4.61 (d, J = 7.8 Hz, 4H), 3.20 (t, J = 7.6 Hz, 4H), 2.40 – 2.34 (m, 1H), 1.99 – 1.86 (m, 6H), 1.51 – 1.20 (m, 21H), 1.04 – 0.73 (m, 28H), 0.59 (dt, J = 16.0, 12.5 Hz, 12H).

Synthesis of 2,2'-((2Z,2'Z)-((6,12,13-tris(2-ethylhexyl)-3,9-dihexyl-12,13-dihydro-6Hthieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-

b][1,2,3]triazolo[4,5-e]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-

dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y18)

Compound **5** (0.15 g, 0.15 mmol) and 1,1-dicyanomethylene-3-indanone (0.20 g, 1.03 mmol) and 30 ml of chloroform were placed in a round bottom flask under nitrogen. After stirring for half an hour, pyridine (1 mL) was added and stirred at 60 °C overnight. After cooling to room temperature, the mixed product was concentrated by rotary evaporation. The crude product was purified on silica

gel chromatography using petroleum ether/ $CHCl_3$ (1:1, v/v) to give compound Y18 (0.13 g) as a dark red solid in a yield of 72%.

¹H NMR (400 MHz, CDCl₃) δ 9.15 (s, 2H), 8.64 – 8.46 (m, 2H), 7.70 (t, *J* = 7.5 Hz, 2H), 4.74 (d, *J* = 7.3 Hz, 6H), 3.23 (t, *J* = 7.8 Hz, 5H), 2.44 – 2.31 (m, 1H), 2.00 (m, 2H), 1.88 (d, 4H), 1.51 – 1.18 (m, 20H), 1.22 – 0.81 (m, 28H), 0.66 (dt, 12H).



Figure S1. ¹H NMR spectrum of 3 in CDCl₃





Figure S3. ¹H NMR spectrum of 5 in CDCl₃



Figure S4. ¹H NMR spectrum of Y18 in CDCl₃



Figure S5. Thermogravimetric analysis curve of Y18 with a heating rate of 10 K min⁻¹.



Figure S6. (a)Molecular structures of the PM6 (left) and the Y6 (right),(b)The GPC chart relates to the molecular weight of PM6.



Figure S7.Normalized absorption spectra of the acceptor Y18



Figure S8.Normalized thin-film absorption of PM6:Y18 blend film.



Figure S9. EQE curves of the OSCs based on PM6:Y6 and PM6:Y18 under the optimized conditions.



Figure S10. Cyclic voltammogram of the Y18 film on a platinum electrode, which was measured in 0.1 mol L^{-1} Bu₄NPF₆ acetonitrile solutions at a scan rate of 50 mV s⁻¹



Figure S11. *J-V* characteristics in the dark for the as-cast and optimized OSCs based on PM6:Y18 blend films.



Figure S12. E_g distribution of PM6:Y18 solar cells before and after post-treatment.



Figure S13. $E_{\rm g}$ distribution of PM6:Y6 solar cells.



Figure S14. (a) The EL spectra and the sensitive EQE curves of the devices based on PM6:Y18 and PM6:Y6 with device optimization. (b) EQE_{EL} of the optimized devices based on PM6:Y18 and PM6:Y6.



Figure S15. AFM height images of the (a) PM6:Y18 (1:1.5) blend film, (b)PM6:PC₇₁BM (1:1.5) blend film and (c) PM6:Y18:PC₇₁BM (1:1.5:0.2) blend film. (d), (e) and (f) are the corresponding TEM images, respectively.



Figure S16. 2D GIWAXS patterns of (a,b) PM6:Y18:PC₇₁BM and PM6:Y18 optimized blend film.(c,d)Y18 and PM6 neat film.(e) Line cuts of GIWAXS images of neat film and blend film.



Figure S17. 2D GIWAXS patterns of (a) PM6:Y18:PC₇₁BM optimized blend film. (b) PM6:Y18 optimized blend film.(c) Line cuts of GIWAXS images of binary and ternary blend film.



Figure S18. (a and b) GIWAXS images of neat Y6 and Y18.(c and d) GIWAXS image of PM6:Y6 and PM6:Y18 optimized blend films.



Figure S19. The certification report of NREL is shown above.



Figure S20. The device stability about 25 days in the glove box, it still remains a value of 93% of the highest initial efficiency.

values for 15 devices in the brackets), under the illumination of AM 1.5 G, 100 m w cm ² .							
	Active	D:A	V _{oc}	J_{sc}	EQE	FF	PCE
	layer	[w/w]	[V]	[mA cm ⁻²]	[mA cm ⁻²]	[%]	[%]
-	PM6:Y18	1:1	0.85±0.002	25.95±0.28	25.84±0.14	72.2±0.8	15.92(15.71±0.3)
		1:1.2	0.84±0.008	25.44±0.23	25.13±0.18	75.6±0.5	16.15(16.02±0.2)
		1:1.5	0.84±0.004	25.71±0.32	25.33±0.48	76.5±0.6	16.52(16.27±0.3)
		1:1.8	0.83±0.004	24.82±0.42	24.53±0.33	73.8±0.6	15.20(14.92±0.4)

Table S1.Photovoltaic performance of binary devices with different proportions of Y18(the average values for 15 devices in the brackets), under the illumination of AM 1.5 G, 100 mWcm⁻².

Table S2. Photovoltaic performance of theternary devicebased on Y18(the average values for 15 devices in the brackets), under the illumination of AM 1.5 G, 100 mWcm⁻².

A otivo lovor	D:A ₁ :A ₂	V _{oc}	J_{sc}	FF	PCE
	[<i>w/w</i>]	[V]	[mA cm ⁻²]	[%]	[%]
	1:1.5:0.1	0.836±0.017	25.77±0.36	74.6±0.7	16.10(15.95±0.3)
PM6:Y18:PC ₇₁ BM	1:1.5:0.2	0.841±0.001	26.31±0.27	77.4±0.6	17.11(16.88±0.3)
	1:1.5:0.3	0.842±0.015	25.68±0.61	73.2±0.8	15.82(15.72±0.2)

In the brackets), under the multimation of AM 1.5 G, 100 mwcm .							
A ativa lavar	D:A	V_{oc}	J_{sc}	EQE	FF	PCE	
Active layer	[w/w]	[V]	[mA cm ⁻²]	[mA cm ⁻²]	[%]	[%]	
PM6:Y18	1:1.5	0.84±0.004	25.71±0.32	25.33±0.48	76.5±0.6	16.52(16.27±0.3)	
PM6:Y18:PC ₇₁ BM	1:1.3:0.2	0.84±0.003	26.23±0.23	25.87±0.21	76.5±0.8	16.86(16.68±0.4)	
	1:1.5:0.2	0.84±0.001	26.31±0.27	25.91±0.32	77.4±0.6	17.11(16.88±0.3)	
PM6:Y18	1:1.8	0.83±0.004	24.82±0.42	24.53±0.33	73.8±0.6	15.20 (14.92±0.4)	

Table S3.Photovoltaic performance of thedevicebased on Y18(the average values for 15 devices in the brackets), under the illumination of AM 1.5 G, 100 mWcm⁻².