Electronic Supplementary Information

Novel thiophene[3,4-b]thiophene-based polymer acceptors for highperformance all-polymer solar cells

Chentong Liao,^a Hongli, Wang,^b Min Deng,^a Xiaopeng Xu, *^b Qiang Peng *^{ab}

^a College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P. R. China.

E-mail: qiangpeng@scu.edu.cn

^b School of Chemical Engineering and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, P. R. China.

E-mail: xpxu@scu.edu.cn; qiangpeng@scu.edu.cn

1. Materials and Methods

Materials: PM6, M1, M2, and M3 were purchased from Solarmer Materials Inc. PY-IT was purchased from eflexPV. YF-Br was synthesized according to the previous reports.¹ All the other chemicals were purchased from Aladdin, Adamas, Sigma-Aldrich and Alfa Asear Chemical Co., and used without further purifications.



Scheme S1. Synthetic routes of the polymers.

General synthetic procedure of the tin monomer: Compound M1, M2, or M3 (2.32 mmol) was dissolved in 20 mL of dry tetrahydrofuran in a 50 mL three-necked flask. The reaction mixture was cooled to -78 °C and stirred for 1 hour. Then, lithium diisopropylamide (2 M in n-hexane/tetrahydrofuran, 5.80 mmol) was added slowly dropwise. After the addition was complete, the reaction was continued at -78 °C for 1 hour before adding trimethyltin chloride

(6.96 mmol). The mixture was stirred for 30 minutes at this temperature, then allowed to warm to room temperature and react for 12 hours. The reaction mixture was gradually poured into 100 mL of 1.5 M saturated ammonium chloride solution and stirred for another 30 minutes. It was extracted with 100 mL of dichloromethane, then sequentially washed with 100 mL each of saturated potassium fluoride solution, sodium chloride solution, and water. The organic layer was collected in a 250 mL round-bottomed flask, dried over anhydrous magnesium sulfate for 5 hours, and filtered. The filtrate was collected, and most of the solvent was removed by rotary evaporation to give the crude product as a brownish-red solid. Recrystallization of the crude product from isopropanol afforded red crystals S1, S2, or S3.









General synthetic procedure of the polymers: YF-Br (0.1 mmol) and tin monomers of S1, S2, or S3 (0.1 mmol) were dissolved in toluene (8 mL), Pd₂(dba)₃ (5% mmol) and P(*o*-tolyl)₃ (20% mmol) were added to the mixture being flushed with argon for 5 minutes. Then, the reaction mixtures were purged with argon for another 15 minutes. The reactions were stirred at 110 °C for 3 days. After finished, the reaction mixture was cooled down to room temperature and precipitated into methanol (500 mL). The crude polymer was subjected to Soxhlet extractions with methanol, hexane, and acetone to remove the impurities and oligomers. Then the chloroform fraction was concentrated, and the solution was filtered through a silica gel column. The final solution was concentrated and precipitated in methanol to get a dark solid. **PYF-EF:** YF-Br (190.7 mg, 0.1 mmol), S1 (80.6 mg, 0.1 mmol). M_n= 13.65 kDa, D = 2.48. Elemental analysis calcd (%) for PYF-EF (C₁₂₉H₁₅₅F₃N₈O₄S₉): N, 5.03%; C, 69.57%; H,

7.01%; S, 12.96%. Found: N, 4.75%; C, 70.05%; H, 7.31%; S, 12.75%.

PYF-E: YF-Br (190.7 mg, 0.1 mmol), S1 (78.8 mg, 0.1 mmol). M_n= 12.88 kDa, Đ = 1.50.
Elemental analysis calcd (%) for PYF-E (C₁₂₉H₁₅₆F₂N₈O₄S₉): N, 5.07%; C, 70.13%; H, 7.12%;
S, 13.06%. Found: N, 4.88%; C, 70.31%; H, 7.29%; S, 13.21%.

PYF-C: YF-Br (190.7 mg, 0.1 mmol), S1 (75.8 mg, 0.1 mmol). M_n= 11.75 kDa, Đ = 1.51.
Elemental analysis calcd (%) for PYF-E (C₁₂₈H₁₅₄F₂N₈O₃S₉): N, 5.14%; C, 70.55%; H, 7.12%;
S, 13.24%. Found: N, 5.01%; C, 70.78%; H, 7.45%; S, 13.53%.

Methods: Molecular weights of the polymers were determined by waters 1515 gel permeation chromatography at room temperature using chloroform as the eluent. Thermogravimetric analysis (TGA) was conducted on a TA Instrument Model SDT Q500 at a heating rate of 10 °C min⁻¹ and under a N₂ flow rate of 90 mL min⁻¹. UV-vis-NIR spectra were obtained on a Shimadzu UV3600 spectrophotometer. ¹H NMR was record from a JNM-ECZ400S nuclear magnetic resonance spectrometer using CDCl₃ as the solvent. CV measurements were made on a CHI604E potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s⁻¹ with the platinum wire as the counter electrode and the Ag/AgCl as a reference electrode, which was calibrated by the ferrocene/ferrocenium (Fc/Fc+) redox couple to be -4.38 eV. GIWAXS measurements were performed using an X-ray diffractometer (D8 Advance). The instrument is equipped with a stepper motor and optical encoders to achieve high-precision angle control (accuracy of 0.0001°). It is configured with a LynxEye XE array detector, a theta/theta vertical goniometer, and a standard-sized copper target X-ray tube. AFM images were obtained by using a Bruker Inova atomic microscope in tapping mode.

2. Fabrication and characterization of polymer solar cells

2.1 Device fabrication

The patterned indium tin oxide (ITO, sheet resistance = 15 Ω square⁻¹) glass substrates were sequentially ultrasonicated with detergent, deionized water, acetone, and isopropanol. Then, the ITO glasses were treated with UV-ozone for 30 min. Ph-4PACz (0.3 mg/mL) was filtrated through a 0.45 µm nylon filter and then spin-coated on the cleaned ITO substrates at 3000 rpm for 30 s to form a thin layer. For binary device, the PM6:Polymer acceptor solution (1:1.2 by weight and total concentration of 15.0 mg/mL in chloroform with 2% 1-CN) stirred at 50 °C overnight and then spin-coated on the ITO/Ph-4PACz substrates at a speed of 2500 rpm for 30 s to access the active layer with ~100 nm thickness. For ternary device, the PM6:PY-IT:PYF-EF solution (1:1.2 by weight and total concentration of 15.0 mg/mL in chloroform with 2% 1-CN) stirred at 50 °C overnight, and then spin-coated on the ITO/Ph-4PACz substrates at a speed of 2500 rpm for 30 s to access the active layer with ~100 nm thickness. For ternary device, the PM6:PY-IT:PYF-EF solution (1:1.2 by weight and total concentration of 15.0 mg/mL in chloroform with 2% 1-CN) stirred at 50 °C overnight, and then spin-coated on the ITO/Ph-4PACz substrates at a speed of 2500 rpm for 30 s to access the active layer with ~100 nm thickness. For ternary device, the PM6:PY-IT:PYF-EF solution (1:1.2 by weight and total concentration of 15.0 mg/mL in chloroform with 2% 1-CN) stirred at 50 °C overnight, and then spin-coated on the ITO/Ph-4PACz substrates at a speed

of 2500 rpm for 30 s to access the active layer with ~100 nm thickness. Then the substrates were put onto a hot plate and annealed at 90 °C for 5 min. PNDIT-F3N solution (0.5 g/mL in methanol with 5 v% of acetic acid) was spin-coated on the top of the active layer to form a thin cathode interlayer (~10 nm). Finally, argentum electrode (Ag, 100 nm) was deposited under high vacuum (~10⁻⁵ Pa) in an evaporation chamber. The device area was exactly fixed at 4.00 mm².

2.2 Device measurements

The *I-V* characterization was performed on a computer-controlled Keithley 2400 Source under AM1.5G (100 mW cm-2) using a solar simulator (XES-70S1,SAN-EI), which was calibrated by a standard Si solar cell (AK-200, Konica Minolta, Inc.). The EQE values were measured with an EQ-R solar quantum efficiency test system (Enlitech Co., Ltd., Taiwan, China). All fabrication and characterization processes, except for the HTLs preparation and EQE measurements, were conducted in a high purity argon filled glove box.

2.3 Fabrication of hole-only and electron-only devices

Hole-only and electron-only devices for SCLC measurements were fabricated with similar methods in architectures of ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/PNDIT-F3N/Ag, respectively. The ZnO layer was fabricated using a sol-gel method, and gold electrodes were deposited by thermal evaporation in vacuum. All device fabrications were performed in an argon gas filled glove box except for the deposition of PEDOT:PSS and ZnO layers.

2.4 Carrier mobility measurements

Charge carrier mobilities were tested using the space charge limited current (SCLC) method on

hole-only and electron-only devices. The *J*-V curves measured on hole-only and electron-only devices were fitted to $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where *J* is the current density, *L* is the film thickness of the active layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10⁻¹² F m⁻¹), *V* is the internal voltage in the device and $V = V_{appl} - V_{bi} - V_a$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in voltage and V_a is the voltage drop.

6.00 + 37612 4.00-2.00 0.00 13 -2.00 -4.00 -6.00 -8.00 -5.00 10.00 15.00 30.00 35.00 40.00 45.00 50.00 0.00 20.00 25.00 分钟 4 • 保留时间 (分钟) Mw (道尔顿) MP Mv Mz (道尔顿) (道尔顿) Mz+1 (道尔顿) [n]P (dVg) 名称 峰代码 Mn 道尔顿) 多分散性 (道尔顿) 宽分布 24.213 13646 33815 37612 94710 2.477950 108 65692

3. Supplementary Figures



Fig. S1 GPC report of PYF-EF.

Fig. S2 GPC report of PYF-E.

1 1		.00					16301	Z	\neg			
		0.00	5.00	10.00	15.00	20.00	25.00 分钟	30.00	35.00	40.00	45.00	50.00
6	名称	保留时间 (分钟)	峰代码	Mn (道尔顿)	Mw (道尔顿)	MP (道尔顿)	Mv (道尔顿)	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性	[n]P k (dVg) (dVg)	alpha
1	宽分布	25.765	108	11749	17794	16301		25937	34589	1.514493		









Fig. S5 Optimized geometries with frontier orbitals of PM6, PBZ-50, and PBZ-100 dimers.







Fig. S7 J-V curves of the ternary all-PSCs with various ratio of PY-IT:PYF-EF.



Fig. S8 Droplet contact angles and corresponding surface energies for donor and acceptor films.







Fig. S10 Electron mobility of the devices.



Fig. S11 Hole mobility of the devices.



Fig. S12 Electron mobility of the devices.



Fig. S13 $J_{\rm ph}$ versus $V_{\rm eff}$ plots of the devices.



Fig. S14 $V_{\rm OC}$ versus $P_{\rm light}$ plots of the devices.



Fig. S15 J_{SC} versus P_{light} plots of the devices.

4. Supplementary Tables

A	$V_{ m oc}$	$J_{ m sc}$	FF	PCE	
Active layer	[V]	[mA cm ⁻²]	[%]	[%]	
	0.923	24.89	70.24	16.15	
PMIO:PYF-E	$0.922{\pm}0.03^{a)}$	24.41±0.35	69.58±0.57	15.66±0.35	
	0.872	24.79	47.33	10.23	
РМ6:РҮГ-С	0.869 ± 0.04	24.21±0.45	46.78±0.46	9.84±0.22	

Table S1. Photovoltaic parameters of the binary blend devices.

^{a)}The average values and standard deviations were obtained from 10 individual devices.

Table S2. Photovoltaic parameters of the ternary blend devices with various ratio of PY-IT:PYF-EF.

A ativa lavar	V _{oc}	$J_{ m sc}$	FF	PCE	
Active layer	[V]	[mA cm ⁻²]	[%]	[%]	
1 1.0 1	0.957	25.63	73.69	18.07	
1.1:0.1	$0.958{\pm}0.02^{a)}$	25.24±0.28	73.28±0.32	17.72±0.21	
1002	0.952	26.08	75.04	18.62	
1.0:0.2	0.951±0.02	25.78±0.43	74.71±0.28	18.32±0.25	

0.0.0.2	0.947	25.37	73.73	17.72
0.9.0.5	0.945±0.03	24.95±0.33	73.36±0.27	17.30±0.36
0.8.0.4	0.939	24.99	72.91	17.12
0.8:0.4	0.938±0.02	24.51±0.40	72.45±0.29	16.66±0.38

^{a)}The average values and standard deviations were obtained from 10 individual devices.

Additive	$\mu_{ m h}$	$\mu_{ m e}$	
Additive	$[cm^2 V^{-1} s^{-1}]$	$[{ m cm}^2~{ m V}^{-1}~{ m s}^{-1}]$	μ_e/μ_e
PM6:PY-IT	7.39×10 ⁻⁴	5.43×10 ⁻⁴	1.36
PM6:PYF-EF	6.31×10 ⁻⁴	4.97×10 ⁻⁴	1.27
PM6:PYF-E	4.36×10 ⁻⁴	2.95×10 ⁻⁴	1.48
PM6:PYF-C	2.14×10 ⁻⁴	1.33×10 ⁻⁴	1.61
Ternary (1:0.2) ^{a)}	9.17×10 ⁻⁴	7.44×10 ⁻⁴	1.23

Table S3. Charge carrier mobilities of the devices

^{a)} PM6:PY-IT:PYF-EF=1:1:0.2.

Table S4. Ordered molecular structure parameters of the neat and blend films.

blend	lamellar stacking					π - π stacking			
-	q	d	FWHM	CCL	q	d	FWHM	CCL	
	(nm ⁻¹)	(nm)	(nm ⁻¹)	(nm)	(nm ⁻¹)	(nm)	(nm ⁻¹)	(nm)	
PM6:PYIT	3.35	1.88	-	-	15.49	0.41	3.21	2.64	
PM6:PYF-EF	3.13	2.01	-	-	15.83	0.40	3.08	2.76	
Ternary	3.25	1.93	-	-	15.53	0.40	3.16	2.69	

References

 H. Yu, M. Pan, R. Sun, I. Agunawela, J. Zhang, Y. Li, Z. Qi, H. Han, X. Zou, W. Zhou, S. Chen, J. Y. L. Lai, S. Luo, Z. Luo, D. Zhao, X. Lu, H. Ade, F. Huang, J. Min and H. Yan, *Angew. Chem., Int. Ed.*, 2021, 60, 10137-10146.