Supporting Information for:

Boosting Highly Efficient Hydrocarbon Solvent Processed All-polymer based Organic Solar Cells by Modulating Thin Film Morphology

Le Jin,[1,8] Ruijie Ma,[3,8] Heng Liu,[4] Wenhan Xu,[5] Zhenghui Luo,[3] Tao Liu,[3]* Wenyan Su,[6] Yuxiang Li,[7] Rui Lu[1],* Xinhui Lu,[4]* He Yan,[3] Ben Zhong Tang,[5] Tao Yang[2]*

[1] Jiangsu Food & Pharmaceutical Science College, Huai'an, Jiangsu, 223003, China
[2]College of New Materials and New Energies, Shenzhen Technology University, Shenzhen, 518118, China.
[3]Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration & Reconstruction, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China.
[4]Department of Physics, Chinese University of Hong Kong, New Territories, Hong Kong, China
[5]Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Department of Chemistry, Institute of Molecular Functional Materials, State Key Laboratory of Neuroscience, Division of Biomedical Engineering, Division of Life Science, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
[6]Guangdong Provincial Key Laboratory of Optical Fiber Sensing and Communications, Siyuan Laboratory, Department of Physics, Jinan University, Guangzhou 510632, China.
[7]School of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, P. R. China
[8]These are co-first authors.

Correspondence Authors

Tao Liu: liutaozhx@ust.hk

Rui Lu: 20191015@jsfpc.edu.cn

Xinhui Lu: xinhui.lu@cuhk.edu.hk

Tao Yang: yangtao@sztu.edu.cn

Solar cell fabrication and characterization

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/active layers/PNDIT-F3N/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Heraeus Clevios P VP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The PM6:PY-IT blends (1:1 weight ratio), were dissolved in chloroform/toluene (the concentration of donor was 7 mg mL^{-1} for all blends), with 1-chloronaphthalene (1% vol) as additive, and stirred overnight in a nitrogen-filled glove box. The chloroform blend solution was spin-cast at 2000 rpm for 30 s onto PEDOT:PSS films followed by a temperature annealing of 95°C for 5 min. The 95°C toluene blend solution was spin-cast at 2000 rpm for 30 s onto 95°C preheated PEDOT:PSS films (to imitate the film formation kinetics of chloroform) followed by a temperature annealing of 95°C for 5 min. A thin PNDIT-F3N layer (0.5mg/mL in methanol, 2000 rpm) was coated on the active layer, followed by the deposition of Ag (evaporated under 3×10^{-4} Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 100 nm. The current density-voltage (*J-V*) curves of all encapsulated devices (by Epoxy) were measured using a Keithley 2400 Source Meter in the air under AM 1.5G (100 mW cm^{-2}) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). An optical microscope (Olympus BX51) was used to define the device area (5.9 mm^2). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

SCLC Measurements

The electron and hole mobilities were measured by using the method of space-charge

limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/PNDIT-F3N/Ag and hole-only devices with the structure of ITO/PEDOT:PSS/active layers/MoO_x/Ag. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the built-in voltage. The carrier mobility is calculated from the slope of the $J^{1/2} \sim V$ curves.

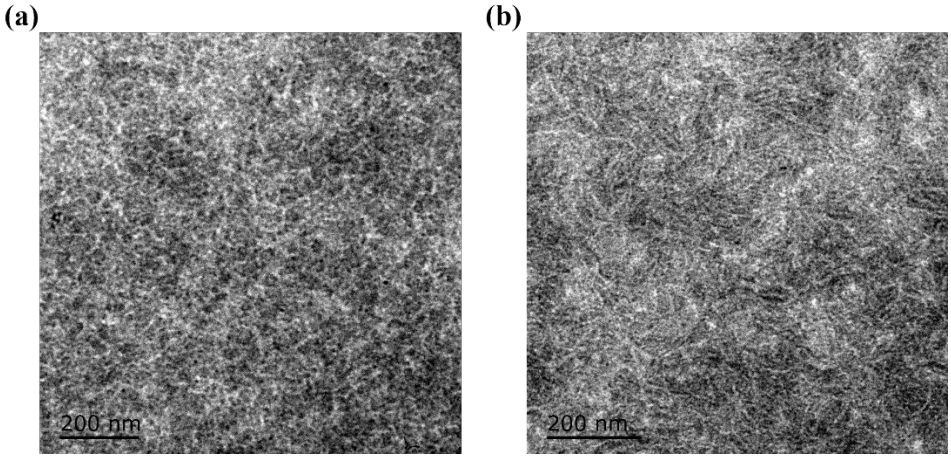

Figure S1. TEM images of PM6:PY-IT films cast from (a) CF and (b) TMB.

Table S1. Morphology parameters of (100) peaks fitted from GIWAXS data.

PM6:PY-IT	Position ($Å^{-1}$)	d-spacing (Å)	CCL (Å)
Chloroform	0.30	20.9	42.1
Toluene	0.30	20.9	54.3

Table S2. Morphology parameters of (010) peaks fitted from GIWAXS data.

PM6:PY-IT	Position ($Å^{-1}$)	d-spacing (Å)	CCL (Å)
Chloroform	1.67	3.76	24.2
Toluene	1.67	3.76	21.1

Table S3. Photovoltaic performances of all-polymer based OSCs summary

Ref	Solvents	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	PCE (%)
1	chloroform	0.96	20.6	72.1	14.3
2	chloroform	0.891	23.03	73.98	15.17

3	chloroform	0.9	22.3	70	14.4
4	chloroform	0.87	23.96	72.67	15.11
5	chloroform	0.955	22.65	74.3	16.09
6	chloroform	0.896	24.7	71.3	15.8
7	chlorobenzene	0.946	20.65	74	14.45
8	chloroform	0.933	22.3	72.3	15.05
9	chloroform	0.9	22.7	75.3	15.4
10	chloroform	0.936	22.77	73.2	15.62
11	chloroform	0.93	20.71	66.33	13.44
12	chloroform	0.901	23.3	72.4	15.2
13	chloroform	0.91	22	71.53	14.32
14	chloroform	0.899	21.33	65.3	12.53
15	chloroform	0.99	16.48	66.1	10.77
16	chloroform	0.943	15.75	68.2	10.13
17	chloroform	0.947	22.6	74.9	16.04
18	chloroform	0.938	21.5	66.66	13.43
19	chlorobenzene	1	15.2	69	10.5
20	chloroform	0.91	23.2	75	15.8
21	chloroform	0.96	15.27	68	10.3
22	chloroform	0.97	17.96	67	12.06
23	chloroform	0.89	23.41	67.73	14.1
24	chlorobenzene	0.86	18.55	64	10.1
25	chlorobenzene	1.17	13.39	64	10.07
26	chloroform	0.86	22.28	69	13.22
27	2-MeTHF	0.92	22.47	66.7	13.8
28	2-MeTHF	0.88	17.62	75.78	11.76
29	Toluene	0.96	17.1	68.2	11.2
30	CPME	0.85	16.5	77.9	11
31	CPME	0.85	17.2	77.9	11.5
32	o-xylene	0.91	21.22	73.12	14.28
This work	Toluene	0.933	22.52	73.8	15.51

Reference

1. Sun, H.; Yu, H.; Shi, Y.; Yu, J.; Peng, Z.; Zhang, X.; Liu, B.; Wang, J.; Singh, R.; Lee, J.; Li, Y.; Wei, Z.; Liao, Q.; Kan, Z.; Ye, L.; Yan, H.; Gao, F.; Guo, X., A Narrow-Bandgap n-Type Polymer with an Acceptor–Acceptor Backbone Enabling Efficient All-Polymer Solar Cells. *Adv. Mater.* **2020,** *32* (43), 2004183.

2. Wu, Q.; Wang, W.; Wu, Y.; Chen, Z.; Guo, J.; Sun, R.; Guo, J.; Yang, Y.; Min, J., High-Performance All-Polymer Solar Cells with a Pseudo-Bilayer Configuration Enabled by a Stepwise Optimization Strategy. *Advanced Functional Materials* **2021,** *n/a* (n/a), 2010411.

3. Jia, T.; Zhang, J.; Zhong, W.; Liang, Y.; Zhang, K.; Dong, S.; Ying, L.; Liu, F.; Wang, X.; Huang, F.; Cao, Y., 14.4% efficiency all-polymer solar cell with broad absorption and low energy loss enabled by a novel polymer acceptor. *Nano Energy* **2020,** *72*, 104718.

4. Peng, F.; An, K.; Zhong, W.; Li, Z.; Ying, L.; Li, N.; Huang, Z.; Zhu, C.; Fan, B.; Huang, F.; Cao, Y., A Universal Fluorinated Polymer Acceptor Enables All-Polymer Solar Cells with >15% Efficiency. *ACS Energy Lett.* **2020,** *5* (12), 3702-3707.

5. Liu, T.; Yang, T.; Ma, R.; Zhan, L.; Luo, Z.; Zhang, G.; Li, Y.; Gao, K.; Xiao, Y.; Yu, J.; Zou, X.; Sun, H.; Zhang, M.; Dela Peña, T. A.; Xing, Z.; Liu, H.; Li, X.; Li, G.; Huang, J.; Duan, C.; Wong, K. S.; Lu, X.; Guo, X.; Gao, F.; Chen, H.; Huang, F.; Li, Y.; Li, Y.; Cao, Y.; Tang, B.; Yan, H., 16% efficiency all-polymer organic solar cells enabled by a finely tuned morphology via the design of ternary blend. *Joule* **2021**.

6. Fu, H.; Li, Y.; Yu, J.; Wu, Z.; Fan, Q.; Lin, F.; Woo, H. Y.; Gao, F.; Zhu, Z.; Jen, A. K. Y., High Efficiency (15.8%) All-Polymer Solar Cells Enabled by a Regioregular Narrow Bandgap Polymer Acceptor. *J Am Chem Soc.* **2021,** *143* (7), 2665-2670.

7. Fan, Q.; An, Q.; Lin, Y.; Xia, Y.; Li, Q.; Zhang, M.; Su, W.; Peng, W.; Zhang, C.; Liu, F.; Hou, L.; Zhu, W.; Yu, D.; Xiao, M.; Moons, E.; Zhang, F.; Anthopoulos, T. D.; Inganäs, O.; Wang, E., Over 14% efficiency all-polymer solar cells enabled by a low bandgap polymer acceptor with low energy loss and efficient charge separation. *Energy Environ. Sci.* **2020,** *13* (12), 5017-5027.

8. Luo, Z.; Liu, T.; Ma, R.; Xiao, Y.; Zhan, L.; Zhang, G.; Sun, H.; Ni, F.; Chai, G.; Wang, J.; Zhong, C.; Zou, Y.; Guo, X.; Lu, X.; Chen, H.; Yan, H.; Yang, C., Precisely Controlling the Position of Bromine on the End Group Enables Well-Regular Polymer Acceptors for All-Polymer Solar Cells with Efficiencies over 15%. *Adv. Mater.* **2020,** *32* (48), 2005942.

9. Zhang, L.; Jia, T.; Pan, L.; Wu, B.; Wang, Z.; Gao, K.; Liu, F.; Duan, C.; Huang, F.; Cao, Y., 15.4% Efficiency all-polymer solar cells. *Sci. China Chem.* **2021,** *64* (3), 408-412.

10. Ma, R.; Zeng, M.; Li, Y.; Liu, T.; Luo, Z.; Xu, Y.; Li, P.; Zheng, N.; Li, J.; Li, Y.; Chen, R.; Hou, J.; Huang, F.; Yan, H., Rational Anode Engineering Enables Progresses for Different Types of Organic Solar Cells. *Adv. Energy. Mater.* **2021,** n/a, 2100492.

11. Wang, W.; Wu, Q.; Sun, R.; Guo, J.; Wu, Y.; Shi, M.; Yang, W.; Li, H.; Min, J., Controlling Molecular Mass of Low-Band-Gap Polymer Acceptors for High-Performance All-Polymer Solar Cells. *Joule* **2020,** *4* (5), 1070-1086.

12. Yu, H.; Pan, M.; Sun, R.; Agunawela, I.; Zhang, J.; Li, Y.; Qi, Z.; Han, H.; Zou, X.; Zhou, W.; Chen, S.; Lai, J. Y. L.; Luo, S.; Luo, Z.; Zhao, D.; Lu, X.; Ade, H.; Huang, F.; Min, J.; Yan, H., Regio-Regular Polymer Acceptors Enabled by Determined Fluorination on End Groups for All-Polymer Solar Cells with 15.2 % Efficiency. *Angew. Chem. Int. Ed.* **2021,** *n/a* (n/a).

13. Wang, T.; Sun, R.; Wang, W.; Li, H.; Wu, Y.; Min, J., Highly Efficient and Stable All-Polymer Solar Cells Enabled by Near-Infrared Isomerized Polymer Acceptors. *Chem. Mater.* **2021,** *33* (2), 761-773.

14. Du, J.; Hu, K.; Meng, L.; Angunawela, I.; Zhang, J.; Qin, S.; Liebman-Pelaez, A.; Zhu, C.; Zhang, Z.; Ade, H.; Li, Y., High-Performance All-Polymer Solar Cells: Synthesis of Polymer Acceptor by a Random Ternary Copolymerization Strategy. *Angew. Chem. Int. Ed.* **2020,** *59* (35), 15181-15185.

15. Fan, Q.; Su, W.; Chen, S.; Kim, W.; Chen, X.; Lee, B.; Liu, T.; Méndez-Romero, U. A.; Ma, R.; Yang, T.; Zhuang, W.; Li, Y.; Li, Y.; Kim, T.-S.; Hou, L.; Yang, C.; Yan, H.; Yu, D.; Wang, E., Mechanically Robust All-Polymer Solar Cells from Narrow Band Gap Acceptors with Hetero-Bridging Atoms. *Joule* **2020,** *4* (3), 658-672.

16. Fan, Q.; Ma, R.; Liu, T.; Su, W.; Peng, W.; Zhang, M.; Wang, Z.; Wen, X.; Cong, Z.; Luo, Z.; Hou, L.; Liu, F.; Zhu, W.; Yu, D.; Yan, H.; Wang, E., 10.13% Efficiency All-Polymer Solar Cells

Enabled by Improving the Optical Absorption of Polymer Acceptors. *Solar RRL* **2020,** *4* (6), 2000142.

17. Ma, R.; Yu, J.; Liu, T.; Zhang, G.; Xiao, Y.; Luo, Z.; Chai, G.; Chen, Y.; Fan, Q.; Su, W.; Li, G.; Wang, E.; Lu, X.; Gao, F.; Tang, B.; Yan, H., All-polymer solar cells with over 16% efficiency and enhanced stability enabled by compatible solvent and polymer additives. **Aggregate** *2021*, 00, e58.

18. Wu, Q.; Wang, W.; Wang, T.; Sun, R.; Guo, J.; Wu, Y.; Jiao, X.; Brabec, C. J.; Li, Y.; Min, J., High-performance all-polymer solar cells with only 0.47 eV energy loss. *Sci. China Chem.* **2020,** *63* (10), 1449-1460.

19. Wu, J.; Meng, Y.; Guo, X.; Zhu, L.; Liu, F.; Zhang, M., All-polymer solar cells based on a novel narrow-bandgap polymer acceptor with power conversion efficiency over 10%. *J. Mater. Chem. A* **2019,** *7* (27), 16190-16196.

20. Jia, T.; Zhang, J.; Zhang, K.; Tang, H.; Dong, S.; Tan, C.-H.; Wang, X.; Huang, F., All-polymer solar cells with efficiency approaching 16% enabled using a dithieno[3′,2′:3,4;2″,3″:5,6]benzo[1,2-c][1,2,5]thiadiazole (fDTBT)-based polymer donor. *J. Mater. Chem. A* **2021,** *9* (14), 8975-8983.

21. Yao, H.; Bai, F.; Hu, H.; Arunagiri, L.; Zhang, J.; Chen, Y.; Yu, H.; Chen, S.; Liu, T.; Lai, J. Y. L.; Zou, Y.; Ade, H.; Yan, H., Efficient All-Polymer Solar Cells based on a New Polymer Acceptor Achieving 10.3% Power Conversion Efficiency. *ACS Energy Lett.* **2019,** *4* (2), 417-422.

22. Yao, H.; Ma, L.-K.; Yu, H.; Yu, J.; Chow, P. C. Y.; Xue, W.; Zou, X.; Chen, Y.; Liang, J.; Arunagiri, L.; Gao, F.; Sun, H.; Zhang, G.; Ma, W.; Yan, H., All-Polymer Solar Cells with over 12% Efficiency and a Small Voltage Loss Enabled by a Polymer Acceptor Based on an Extended Fused Ring Core. *Adv. Energy Mater.* **2020,** *10* (35), 2001408.

23. Yu, H.; Qi, Z.; Yu, J.; Xiao, Y.; Sun, R.; Luo, Z.; Cheung, A. M. H.; Zhang, J.; Sun, H.; Zhou, W.; Chen, S.; Guo, X.; Lu, X.; Gao, F.; Min, J.; Yan, H., Fluorinated End Group Enables High-Performance All-Polymer Solar Cells with Near-Infrared Absorption and Enhanced Device Efficiency over 14%. *Adv. Energy Mater.* **2021,** *11* (4), 2003171.

24. Kolhe, N. B.; Tran, D. K.; Lee, H.; Kuzuhara, D.; Yoshimoto, N.; Koganezawa, T.; Jenekhe, S. A., New Random Copolymer Acceptors Enable Additive-Free Processing of 10.1% Efficient All-Polymer Solar Cells with Near-Unity Internal Quantum Efficiency. *ACS Energy Lett.* **2019,** *4* (5), 1162-1170.

25. Zhao, R.; Wang, N.; Yu, Y.; Liu, J., Organoboron Polymer for 10% Efficiency All-Polymer Solar Cells. *Chem. Mater.* **2020,** *32* (3), 1308-1314.

26. Su, N.; Ma, R.; Li, G.; Liu, T.; Feng, L.-W.; Lin, C.; Chen, J.; Song, J.; Xiao, Y.; Qu, J.; Lu, X.; Sangwan, V. K.; Hersam, M. C.; Yan, H.; Facchetti, A.; Marks, T. J., High-Efficiency All-Polymer Solar Cells with Poly-Small-Molecule Acceptors Having π-Extended Units with Broad Near-IR Absorption. *ACS Energy Lett.* **2021,** *6* (2), 728-738.

27. Zhu, C.; Li, Z.; Zhong, W.; Peng, F.; Zeng, Z.; Ying, L.; Huang, F.; Cao, Y., Constructing a new polymer acceptor enabled non-halogenated solvent-processed all-polymer solar cell with an efficiency of 13.8%. *Chem. Commun.* **2021,** *57* (7), 935-938.

28. Zhu, L.; Zhong, W.; Qiu, C.; Lyu, B.; Zhou, Z.; Zhang, M.; Song, J.; Xu, J.; Wang, J.; Ali, J.; Feng, W.; Shi, Z.; Gu, X.; Ying, L.; Zhang, Y.; Liu, F., Aggregation-Induced Multilength Scaled Morphology Enabling 11.76% Efficiency in All-Polymer Solar Cells Using Printing Fabrication. *Adv. Mater.* **2019,** *31* (41), 1902899.

29. Meng, Y.; Wu, J.; Guo, X.; Su, W.; Zhu, L.; Fang, J.; Zhang, Z.-G.; Liu, F.; Zhang, M.; Russell, T. P.; Li, Y., 11.2% Efficiency all-polymer solar cells with high open-circuit voltage. *Sci. China Chem.* **2019,** *62* (7), 845-850.

30. Li, Z.; Ying, L.; Zhu, P.; Zhong, W.; Li, N.; Liu, F.; Huang, F.; Cao, Y., A generic green solvent concept boosting the power conversion efficiency of all-polymer solar cells to 11%. *Energy Environ. Sci.* **2019,** *12* (1), 157-163.

31. Li, Z.; Zhong, W.; Ying, L.; Liu, F.; Li, N.; Huang, F.; Cao, Y., Morphology optimization via molecular weight tuning of donor polymer enables all-polymer solar cells with simultaneously improved performance and stability. *Nano Energy* **2019,** *64*, 103931.

32. Zhang, J.; Jia, T.; Tan, C.-H.; Zhang, K.; Ren, M.; Dong, S.; Xu, Q.; Huang, F.; Cao, Y., Nonhalogenated-Solvent-Processed High-Performance All-Polymer Solar Cell with Efficiency over 14%. *Solar RRL* **2021,** *n/a* (n/a), 2100076.