Supporting Information

Dual-Grating-Induced Light Harvesting Enhancement in Organic Solar Cells

Yue-Xing Zhang,[a] Chen Gao,[a] Jing-De Chen,[a] Wei Li,[a] Yan-Qing Li,[a,*] and Jian-Xin Tang[a,b,*]

[a] Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, China

[b] Institute of Organic Optoelectronics (IOO), JITRI, Wujiang, Suzhou, China

* Corresponding authors. E-mail addresses: jxtang@suda.edu.cn (J.X. Tang), yqli@suda.edu.cn (Y.Q. Li)

Table S1. Summary of photovoltaic performance of OSCs based on PTB7:$PC_{71}BM$ system.

Device structures	Voc [V]	Jsc [mA cm^{-2}]	FF [%]	PCE [%]	Refs.
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/PFN/Al	0.76	15.75	70.15	8.37	[1]
ITO/ZnO/[BMIM]BF4/PTB7:$PC_{71}BM$/MoO_3/Ag	0.72	17.23	73.50	9.12	[2]
ITO/PFN/PTB7:$PC_{71}BM$/MoO_3/Al	0.75	17.46	69.99	9.21	[3]
ITO/ZnO/PFN-OX/PTB7:$PC_{71}BM$/MoO_3/Al	0.75	16.63	74.40	9.28	[4]
ITO/ZnO/PEI/PTB7:$PC_{71}BM$/MoO_3/Al	0.73	17.27	70.06	8.90	[5]
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/PDINO/Al	0.75	15.00	73.30	8.24	[6]
ITO/PE0:ZTO/PTB7:$PC_{71}BM$/MoO_3/Ag	0.76	16.14	65.83	8.10	[7]
ITO/ZnO/PBI-H/PTB7:$PC_{71}BM$/MoO_3/Al	0.75	16.84	74.66	9.43	[8]
ITO/PEIE+AgNPs/PTB7:$PC_{71}BM$/MoO_3/Ag	0.76	16.22	67.00	8.26	[9]
ITO/ZnO:PBI-H/PTB7:$PC_{71}BM$/MoO_3/Al	0.76	17.29	70.54	9.09	[10]
ITO/PFN/PTB7:$PC_{71}BM$/MoO_3/Ag	0.76	18.43	69.02	9.61	[11]
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/MSAPBS/Al	0.76	19.25	68.00	10.02	[12]
ITO/PEDOT:PSS/PCDTBT: $PC_{71}BM$/T1-OH/Al	0.76	17.20	71.50	9.30	[13]
ITO/ZnO:FNEZnP-OE /PTB7:$PC_{71}BM$/MoO_3/Al	0.75	17.09	72.13	9.24	[14]
ITO/ PEDOT:PSS/PTB7:$PC_{71}BM$ /PFN/Al	0.75	16.70	73.00	9.11	[15]
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/FNEZnP-OE/Al	0.74	16.38	70.31	8.52	[16]
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/OEABS/Al	0.75	17.80	71.23	9.51	[17]
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/DSAPS/Al	0.77	18.43	71.00	9.79	[18]
ITO/PEDOT:PSS:FOS/PTB7:$PC_{71}BM$/Ca/Al	0.70	16.94	69.30	8.26	[19]
ITO/Tf1/PTB7:$PC_{71}BM$/MoO_3/Al	0.74	16.78	71.72	8.97	[20]
ITO/ZnO/PBI-H/PTB7:PBIC4/PTB7:$PC_{71}BM$/MoO_3/Al	0.76	16.99	73.89	9.47	[21]
ITO/PEDOT:PSS/PTB7:PC71BM/PTB7-NBr/Al	0.75	16.21	65.66	8.00	[22]
ITO/ZnO (flat)/PEIE/PTB7:$PC_{71}BM$/MoO_3/Ag	0.75	16.14	70.99	8.57	this work
ITO/ZnO (imprinted)/PEIE/PTB7:$PC_{71}BM$/MoO_3/Ag	0.76	18.02	72.80	9.92	this work

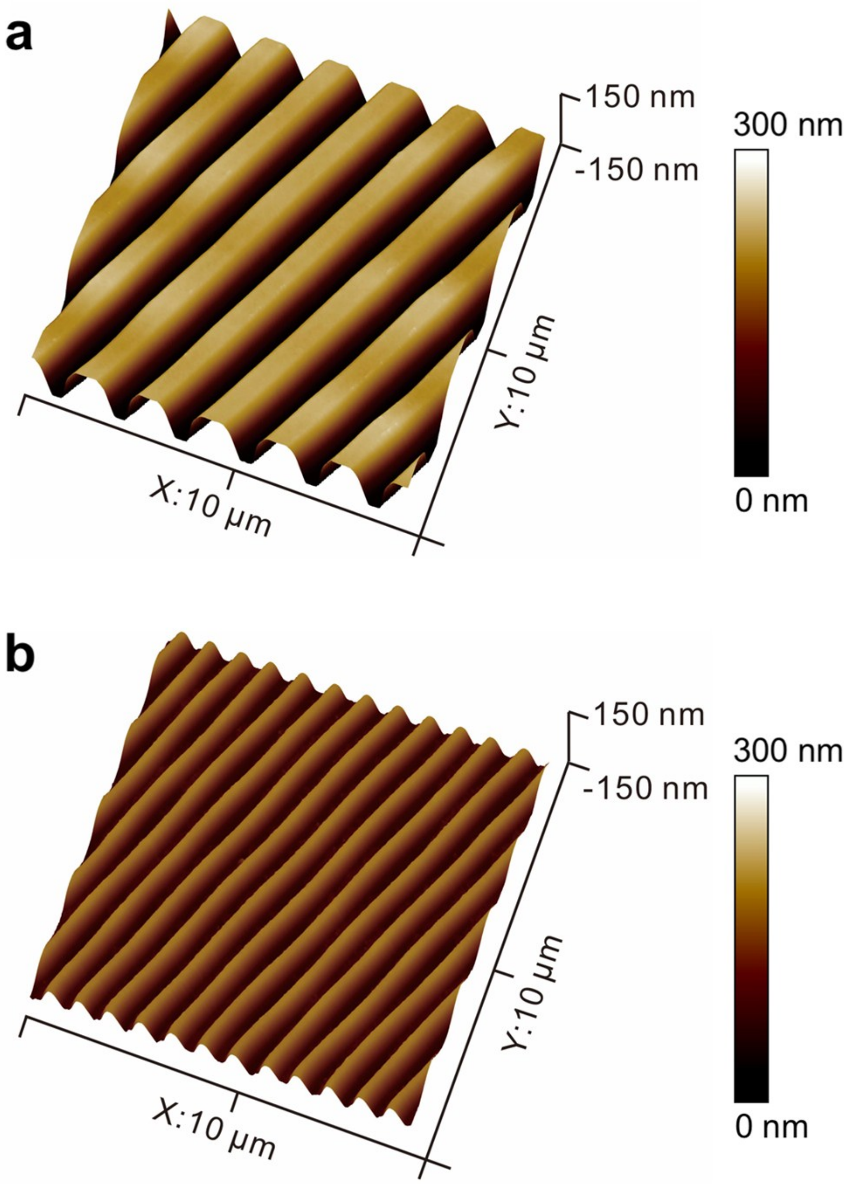

Figure S1. AFM images of (a) CD and (b) DVD disks used in this work.

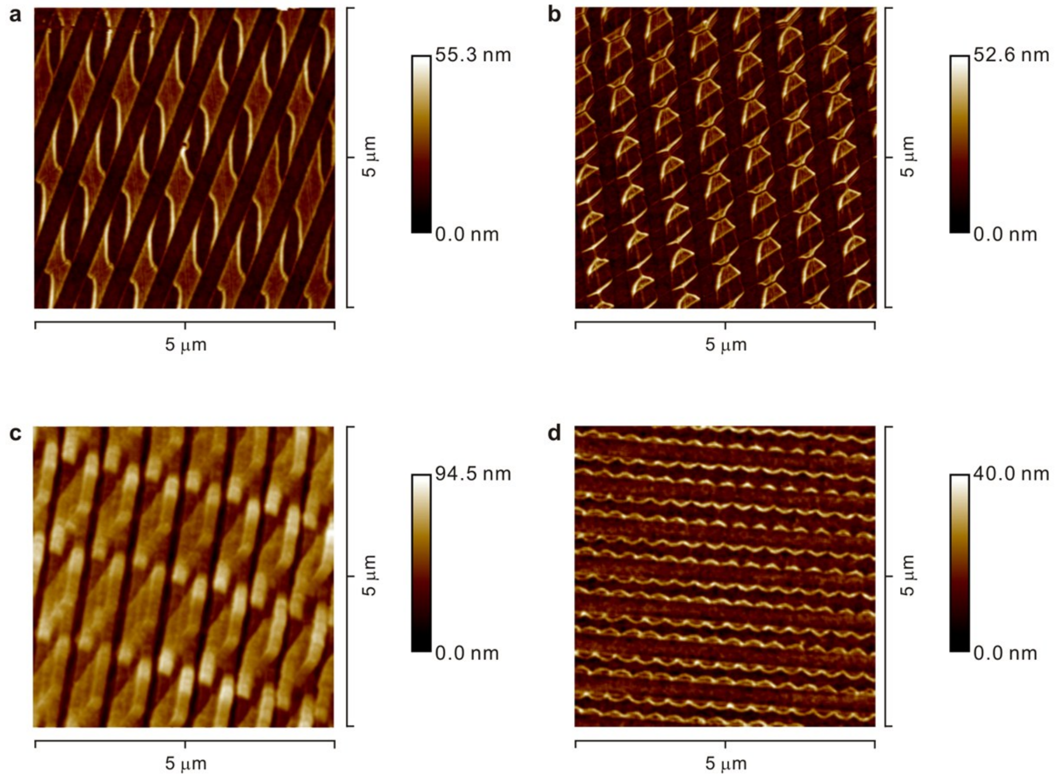

Figure S2. Morphologies of various patterned ZnO layers via two-step soft nanoimprinting technology under different stamping conditions. (a) 1500 nm × 1500 nm (30°), (b) 1500 nm × 1500 nm (60°), (c) 1500 nm × 1500 nm (20°), and (d) 800 × 1500 (90°).

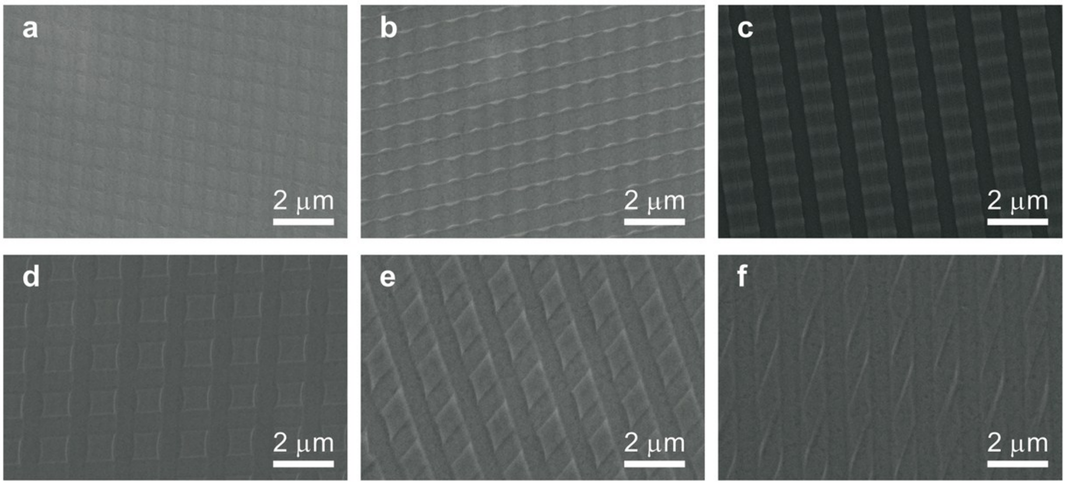

Figure S3. Scan electron microscope (SEM) images of PEIE-coated ZnO layers with various dual-gratings. (a) 800 nm × 800 nm, (b) 800 nm × 1500 nm, (c) 1500 nm × 800 nm, (d) 1500 nm × 1500 nm (90°), (e) 1500 nm × 1500 nm (60°), and (f) 1500 × 1500 (30°).

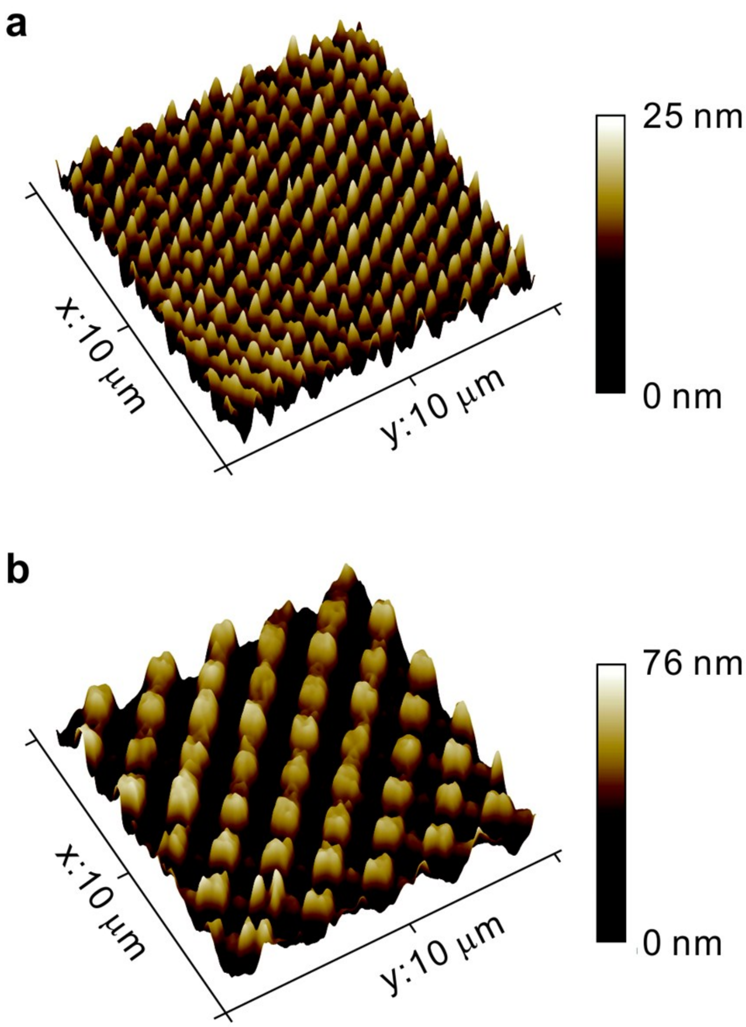

Figure S4. Morphologies of PTB7:$PC_{71}BM$ layers spin-coated on patterned ZnO layers with dual-gratings of (a) 800 nm × 800 nm and (b) 1500 nm × 1500 nm.

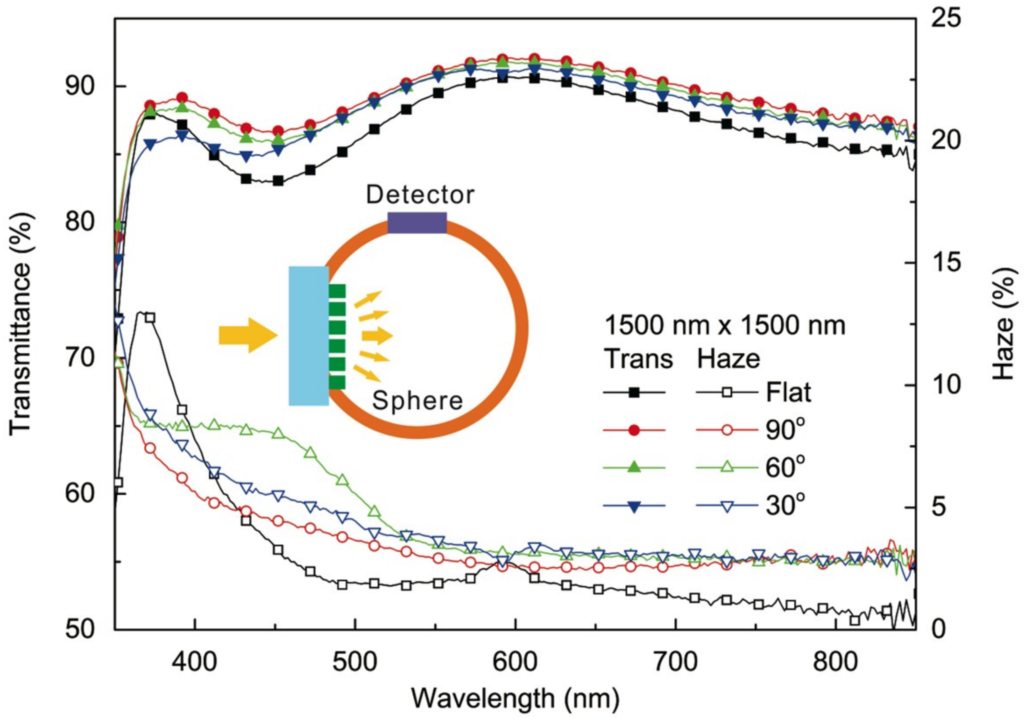

Figure S5. Total transmittance spectra and haze values of ITO glass substrates without and with dual-grating patterned ZnO layers, which were recorded with the incident light from the glass side. Inset depicts the optical measurement configuration using an integrating sphere.

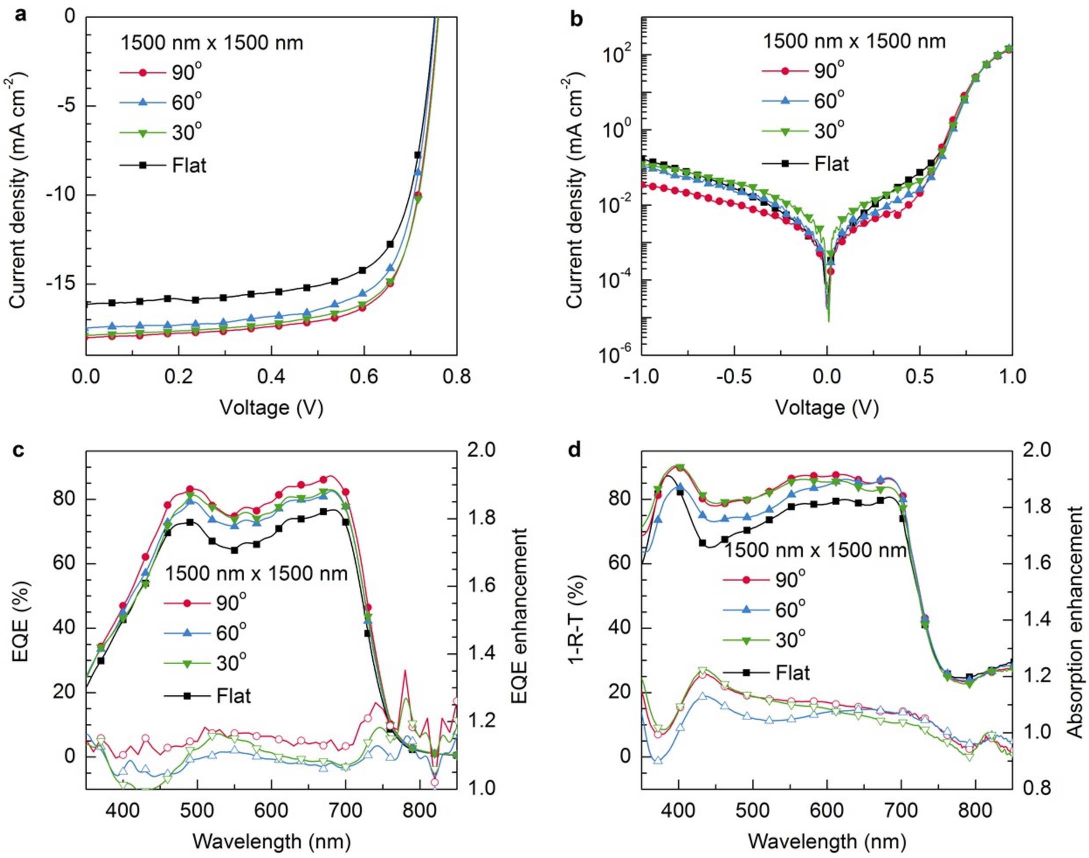

Figure S6. Photovoltaic characteristics of OSCs based on 1500 nm × 1500 nm dual-grating patterned ZnO layers with different angles. (a) J–V characteristics recorded under 100 mW cm^{-2} AM 1.5G simulated solar illumination. (b) The dark J–V curves. (c) External quantum efficiency (EQE) spectra and relative EQE enhancement of patterned devices related to that of the flat one. (d) Absorption spectra and the absorption enhancement.

References:

[1] Z. C. He, C. M. Zhong, X. Huang, W. Y. Wong, H. B. Wu, L. W. Chen, S. J. Su, Y. Cao, Simultaneous Enhancement of Open-Circuit Voltage, Short-Circuit Current Density, and Fill Factor in Polymer Solar Cells. *Adv. Mater.* **2011**, *23*, 4636-4643.

[2] W. Yu, L. Huang, D. Yang, P. Fu, L. Zhou, J. Zhang, C. Li, Efficiency Exceeding 10% for Inverted Polymer Solar Cells with a ZnO/Ionic Liquid Combined Cathode Interfacial Layer. *J. Mater. Chem. A* **2015**, *3*, 10660-10665.

[3] Z. C. He, C. M. Zhong, S. J. Su, M. Xu, H. B. Wu, Y. Cao, Enhanced Power-Conversion Efficiency in Polymer Solar Cells Using an Inverted Device Structure. *Nat. Photon*. **2012**, *6*, 591-595.

[4] K. Zhang, C. M. Zhong, S. J. Liu, C. Mu, Z. K. Li, H. Yan, F. Huang, Y. Cao, Highly Efficient Inverted Polymer Solar Cells Based on a Cross-linkable Water-/Alcohol-Soluble Conjugated Polymer Interlayer. ACS Appl. Mater. Interfaces **2014**, *6*, 10429-10435.

[5] S. Woo, W. H. Kim, H. Kim, Y. Yi, H. K. Lyu, Y. Kim, 8.9% Single-Stack Inverted Polymer Solar Cells with Electron-Rich Polymer Nanolayer-Modified Inorganic Electron-Collecting Buffer Layers. *Adv. Energy Mater.* **2014**, *4*, 1301692.

[6] Z. G. Zhang, B. Y. Qi, Z. W. Jin, D. Chi, Z. Qi, Y. Li, J. Z. Wang, Perylene Diimides: A Thickness-Insensitive Cathode Interlayer for High Performance Polymer Solar Cells. *Energy Environ. Sci.* **2014**, *7*, 1966.

[7] M. Thambidurai, J. Y. Kim, Y. Ko, H. J. Song, H. Shin, J. Song, Y. Lee, N. Muthukumarasamy, D. Velauthapillai, C. Lee, High-Efficiency Inverted

Organic Solar Cells with Polyethylene Oxide-Modified Zn-Doped TiO_2 as an Interfacial Electron Transport Layer. *Nanoscale* **2014**, *6*, 8585-8589.

[8] L. Nian, W. Q. Zhang, S. P. Wu, L. Q. Qin, L. L. Liu, Z. Q. Xie, H. B. Wu, Y. G. Ma, Perylene Bisimide as a Promising Zinc Oxide Surface Modifier: Enhanced Interfacial Combination for Highly Efficient Inverted Polymer Solar Cells. ACS *Appl. Mater. Interfaces* **2015**, *7*, 25821-25827.

[9] S. W. Baek, J. H. Kim, J. Kang, H. Lee, J. Y. Park, J.-Y. Lee, Enhancing the Internal Quantum Efficiency and Stability of Organic Solar Cells via Metallic Nanofunnels. *Adv. Energy Mater*. **2015**, *5*, 1501393.

[10] L. Nian, W, Q. Zhang, N. Zhu, L. L. Liu, Z. Q. Xie, H. B. Wu, F. Würthner, Y. G. Ma, Photoconductive Cathode Interlayer for Highly Efficient Inverted Polymer Solar Cells. *J. Am. Chem. Soc.* **2015**, *137*, 6995-6998.

[11] Z. C. He, F. Liu, C. Wang, J. H. Chen, L. L. He, D. Nordlund, H. B. Wu, T. P. Russell, Y. Cao, Simultaneous Spin-Coating and Solvent Annealing: Manipulating the Active Layer Morphology to a Power Conversion Efficiency of 9.6% in Polymer Solar Cells. *Mater. Horizons* **2015**, *2*, 592-597.

[12] X. H. Ouyang, R. X. Peng, L. Ai, X. Y. Zhang, Z. Y. Ge, Efficient Polymer Solar Cells Employing a Non-Conjugated Small-Molecule Electrolyte. *Nat. Photon*. **2015**, *9*, 520-524.

[13] Y. Zou, Z. C. He, B. F. Zhao, Y. Liu, C. L. Yang, H. B. Wu, Y. Cao, Alcohol-soluble Star-shaped Oligofluorenes as Interlayer for High Performance Polymer Solar Cells. *Sci. Rep*. **2015**, *5*, 17329.

[14] C. Liu, L. Zhang, L. G. Xiao, X. B. Peng, Y. Cao, Doping ZnO with Water/Alcohol-Soluble Small Molecules as Electron Transport Layers for

Inverted Polymer Solar Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 28225-28230.

[15] J. X. Chen, L. J. Zhang, X. F. Jiang, K. Gao, F. Liu, X. J. Gong, J. W. Chen, Y. Cao, Using o-Chlorobenzaldehyde as a Fast Removable Solvent Additive during Spin-Coating PTB7-Based Active Layers: High Efficiency Thick-Film Polymer Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1601344.

[16] L. Zhang, C. Liu, T. Q. Lai, H. D. Huang, X. B. Peng, F. Huang, Y. Cao, A Water/Alcohol-Soluble Conjugated Porphyrin Small Molecule as a Cathode Interfacial Layer for Efficient Organic Photovoltaics. *J. Mater. Chem. A* **2016**, *4*, 15156-15161.

[17] L. Ai, X. H. Ouyang, Z. Y. Liu, R. X. Peng, W. G. Jiang, W. Li, L. Zhang, L. Hong, T. Lei, Q. Guan, Z. Y. Ge, Highly Efficient Polymer Solar Cells Using a Non-Conjugated Small-Molecule Zwitterion with Enhancement of Electron Transfer and Collection. *J. Mater. Chem. A* **2016**, *4*, 14944-14948.

[18] Z. Y. Liu, X. H. Ouyang, R. X. Peng, Y. Q. Bai, D. B. Mi, W. G. Jiang, A. Facchetti, Z. Y. Ge, Efficient Polymer Solar Cells Based on the Synergy Effect of a Novel Non-Conjugated Small-Molecule Electrolyte and Polar Solvent. *J. Mater. Chem. A* **2016**, *4*, 2530-2536.

[19] C. T. Howells, K. Marbou, H. Kim, K. J. Lee, B. Heinrich, S. J. Kim, A. Nakao, T. Aoyama, S. Furukawa, J.-H. Kim, E. Kim, F. Mathevet, S. Mery, I. D. W. Samuel, A. A. ghaferi, M. S. Dahlem, M. Uchiyama, S. Y. Kim, J. W. Wu, J.-C. Ribierre, C. Adachi, D.-W. Kim, P. André, Enhanced Organic Solar Cells Efficiency Through Electronic and Electro-Optic Effects Resulting From Charge Transfers in Polymer Hole Transport Blends. *J. Mater. Chem. A* **2016**, *4*, 4252-4263.

[20] Y. Liu, W. J. Zhang, G. H. Xie, X. Zeng, J. F. Fang, C. L. Yang, Triazine-Core-Containing Star-Shaped Compounds as Cathode Interlayers for Efficient Inverted Polymer Solar Cells. *J. Mater. Chem. C* **2016**, *4*, 11278-11283.

[21] N. Zhu, W. Q. Zhang, Q. W. Yin, L. L. Liu, X. F. Jiang, Z. Q. Xie, Y. G. Ma, Layer-by-Layer-Processed Ternary Organic Solar Cells Using Perylene Bisimide as a Morphology-Inducing Component. *ACS Appl. Mater. Interfaces* **2017**, *9*, 17265-17270.

[22] W. Zhang, Y. Li, L. Zhu, X. Liu, C. Song, X. Li, X. Sun, J. Fang, A PTB7-based narrow band-gap conjugated polyelectrolyte as an efficient cathode interlayer in PTB7-based polymer solar cells. *Chem. Commun.* **2017**, *53*, 2005-2008.