Electronic Supplementary Information

Enhanced Open-Circuit Voltages and Efficiencies: The Role of Oxidation State of Molybdenum Oxide Buffer Layer in Polymer Solar Cells

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Synthesis of PDTS-DTffBT.

As shown in Figure S1, 4,4′-Bis(2-ethylhexyl)-5,5′-bis(trimethyltin)-dithieno[3,2-*b*:2′,3′-*d*]silole (Monomer 1, 193 mg, 0.259 mmol), 5,6-Dfluoro-4,7-bis(5-bromo-4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (Monomer 2, 172 mg, 0.259 mmol), anhydrous toluene (6mL) and DMF (1mL) were placed in a two-neck round-bottom flask (25 mL) and then the flask was purged with nitrogen for 30 minutes followed by $Pd(PPh_3)_4$ (15 mg) was added to the mixture. The mixture was stirred under nitrogen at 110 ℃ for 28 h. Then the mixture was cooled to room temperature and precipitated in

methanol. The precipitated solid was filtered through a Soxhlet thimble and washed sequentially with methanol, hexane and chloroform in a Soxhlet extractor. The fraction from chloroform was concentrated under reduced pressure, precipitated into methanol, and collected by filtration to yield the final polymer as a black solid (187 mg 78% yield).

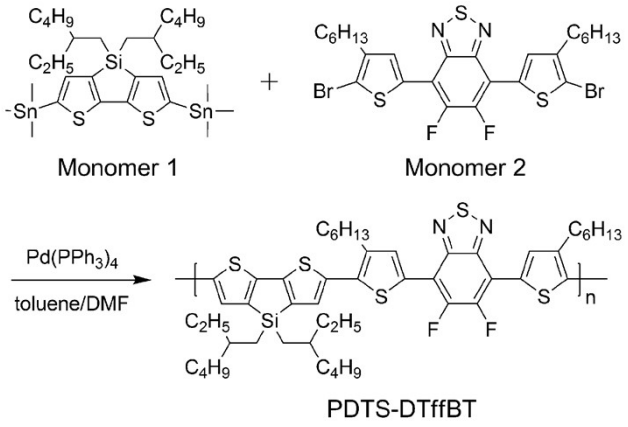

Figure S1. Synthesis of PDTS–DTffBT.

Synthesis of ZnO Nanoparticles.

ZnO Nanoparticles were prepared according to the reference.[1] $Zn(CH_3COO)_2 \cdot 2H_2O$ (2.95 g, 13.4 mmol) was dissolved in methanol (125 mL) at 60 ℃ and KOH (1.48 g, 23 mmol) was dissolved in methanol (65 mL). The KOH solution was dropwise added to the $Zn(CH_3COO)_2 \cdot 2H_2O$ solution in 10 min under vigorous stirring. the solution became translucent and remained translucent after 5 min. The mixture was stirring at 60 ℃ for 2 h and 15 min. Then removed the heater and stirrer and stand for additional 2 h to precipitate. The precipitated ZnO nanoparticles was washed 3 times with methanol (50 mL) and centrifuged for 5 min (4000 rpm). After adding methanol (40

mL) to the ZnO nanoparticles and treating with ultrasonic for 15 min, the ZnO nanoparticles dispersion was obtained as almost transparent blue solution. The ZnO nanoparticles had a diameter of around 5 nm, and the thickness of ZnO film is approximately 30 nm, as our reported before.[2]

Study of the thickness of MoO_x film.

PTB7-Th:$PC_{71}BM$ based solar cells were fabricated with MoO_x film thickness of 3 nm, 6 nm, 9 nm, 12 nm, respectively. Post-air annealing treatment were performed during fabrication. The current density-voltage (*J-V*) curves are shown in Figure S2 and the photovoltaic data are summarized in in Table S1. The devices with MoO_x film thickness of 6 nm exhibit optimal performance with higher J_{SC} and *FF*, and the thickness greater than 12 nm results in V_{OC} degeneration.

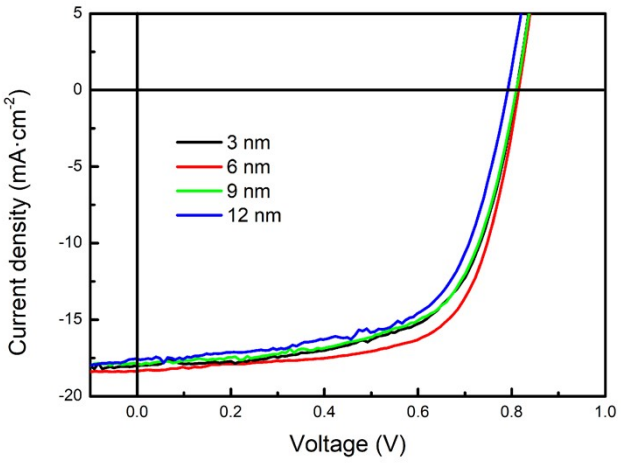

Figure S2. *J-V* curves of PTB7-Th:$PC_{71}BM$ based solar cells with different thickness of MoO_x film

Table S1. Photovoltaic parameters of the post-air annealed solar cells based on PTB7-Th:$PC_{71}BM$ with different thickness of MoO_x film.

thickness of MoO_x film	V_{OC} **(V)**	J_{SC} **(mA/cm^2)**	***FF*** **(%)**	**PCE (%)**	
				Max.	Aver.
3 nm	0.81±0.01	17.62±0.21	62.25±0.42	9.24	8.87
6 nm	0.81±0.01	18.20±0.24	66.78±0.57	10.01	9.84
9 nm	0.81±0.01	17.45±0.22	62.79±0.50	9.19	8.85
12 nm	0.79±0.01	17.24±0.14	62.63±0.35	8.77	8.50

References

[1] W. J. E. Beek, M. M. Wienk, M. Kemerink, X. Yang and R. A. J. Janssen, *J. Phys. Chem. B*, 2005, **109**, 9505-9516.

[2] C. Wang, C. Li, S. Wen, P. Ma, Y. Liu, R. C. I. Mackenzie, W. Tian and S. Ruan, *J. Mater. Chem. A*, 2017, **5**, 3995-4002.