Supplementary Information

High Efficiency Tandem Polymer Solar Cells with MoO₃/Ni/ZnO:PEOz Hybrid Interconnection Layers

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Experimental section

Materials. The PIDTT-BT polymer (weight-average molecular weight = 337.0 kDa, polydispersity index = 2.38) was synthesized via a Stille coupling reaction between 3,9-bis(trimethyltin)-5,5,11,11-tetrakis(5-(2-ethylhexyl)thiophene-2-yl)-dithieno[2,3-d:2',3'-d']-s-indaceno [1,2-b:5,6-b']dithiophene) (2Sn-IDTT) and 4,7-dibromobenzo[c][1,2,5]thiadiazole (2Br-BT) using palladium catalysts (see the detailed procedures and characterization results on pages S5 and S9). Zinc acetate dihydrate, ethanolamine, 2-methoxyethanol, and PEOz (weight-average molecular weight = 50 kDa, polydispersity index = ca. 3.5) were supplied from Sigma-Aldrich (USA). PC$_{71}$BM (purity: >99%) was purchased from Nano-C (USA). PBDB-T (number-average molecular weight = 18 kDa, polydispersity index = 2.5) and IT-M were supplied from Solarmer Materials Inc. (China). Precursor solutions of ZnO and ZnO:PEOz (5 wt% PEOz) were prepared by dissolving zinc acetate dihydrate (100 mg) in 2-methoxyethanol (1 ml) in the presence of ethanolamine (28 μl). The sol-gel reaction of precursor solutions was carried out upon stirring at 60 ^{o}C for at least 3 h and maintained at 25 ^{o}C for 24 h. The BHJ solutions for front cells were prepared by blending PIDTT-BT (10 mg) and PC$_{71}$BM (15 mg) in chlorobenzene (solvent) without any additive, followed by stirring at 25 ^{o}C for more than one day. For the preparation of the BHJ solutions used for rear cells, PBDB-T (9.5 mg) and IT-M (9.5 mg) were dissolved in chlorobenzene in the presence of 1,8-diiodooctane (10 μl) as an additive and stirred at 25 ^{o}C for at least one day.

Fabrication of Films and Devices. For the fabrication of tandem polymer solar cells, indium-tin oxide (ITO)-coated glass substrates (sheet resistance = 12 Ω/cm^2) were first patterned by employing standard photolithography/etching processes for making electron-collecting transparent electrodes. The pre-patterned ITO-glass substrates were ultrasonically cleaned in acetone and isopropyl alcohol, followed by drying with a nitrogen flow. The cleaned ITO-glass substrates were subsequently treated inside a ultraviolet-ozone cleaner (AC-6, Ahtech LTS) for

20 min for eliminating any contaminated residues on the ITO surfaces and providing hydrophilic properties on the ITO surfaces. The ZnO precursor solutions were spin-coated on the ITO-glass substrates, followed by thermal annealing at 200 °C for 1 h in air ambient condition, which led to the electron-collecting buffer layers for front cells. Next, the PIDTT-BT:$PC_{71}BM$ layers (thickness = 80 nm) were spun on the ZnO layers inside a nitrogen-filled glove box. These samples were transferred into a vacuum evaporation chamber system inside an argon-filled glove box. When the base pressure of chamber reached ~1 x 10^{-6} torr, molybdenum oxide (MoO_3, 10 nm) were deposited on the PIDTT-BT:$PC_{71}BM$ layers. Then the nickel (Ni) layers (thickness = 2 ~ 10 nm) were thermally deposited on the MoO_3 layers. The Ni layer-coated devices were moved to a nitrogen-filled glove equipped with a spin-coater, followed by spin-coating on the Ni layers using the ZnO:PEOz precursor solutions. These samples were subjected to thermal annealing at 140 °C for 1 h, which led to the completed MoO_3/Ni/ZnO:PEOz interconnection structures. For the stacking the rear cells, the PBDB-T:IT-M layers (thickness = 100 nm) were spin-coated on the ZnO:PEOz layers inside a nitrogen-filled glove box. These stacked samples were transferred into a vacuum evaporation chamber system inside an argon-filled glove box, followed by depositing the 10 nn-thick MoO_3 top buffer layers and 80 nm-thick silver (Ag) electrodes at the base pressure of ~1 x 10^{-6} torr. The final structure of tandem devices was glass/ITO/ZnO/PIDTT-BT:$PC_{71}BM$/MoO_3/Ni/ZnO:PEOz/PBDB-T:IT-M/MoO_3/Ag with the active area of 5.5 mm^2 (see Fig. 1a). The individual devices for front and rear cells (see Fig. 2a) were fabricated by employing the same conditions as used for the tandem devices: (front cell) glass/ITO/ZnO/PIDTT-BT:$PC_{71}BM$/MoO_3/Ag (device thermal treatment at 140 °C), (rear cell) glass/ITO/ZnO:PEOz/PBDB-T:IT-M/MoO_3/Ag (no device thermal treatment). All devices fabricated were stored inside the same glove box.

Measurements. The PIDTT-BT polymer was characterized using a nuclear magnetic resonance spectrometer (NMR, AVANCE III, Bruker). The weight-average molecular weight

of PIDTT-BT was measured using a gel permeation chromatography (GPC, Alliance e2695, Waters). The film thickness was measured using a high-resolution surface profilometer (DektakXT, Bruker), while an UV-visible-NIR spectrometer (Lambda 750, Perkin Elmer) was used for the measurement of optical absorption and transmittance. The ionization potential of newly synthesized PIDTT-BT was measured using a photoelectron yield spectrometer (AC-2, Hitachi High Tech). The surface morphology of each layer in tandem devices was measured using an atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments). The cross-section parts of devices were measured using a high-resolution scanning transmission electron microscope (HRTEM, Titan G2 ChemiSTEM Cs Probe, FEI Company) after manipulating the samples with a focused ion beam (FIB) system (Versa3D LoVac, FEI Company). The thickness of Ni interlayers was controlled by in-situ monitoring with a quartz crystal microbalance (QCM) sensor system (STM-100/MF, SyCon) equipped inside the vacuum chamber. The exact thickness of the resulting Ni interlayers was cross-checked through the careful measurements with HRTEM (cross-sectional parts of devices) and high-resolution surface profilometer (accuracy: ca. 0.1 nm). The performance of solar cells was measured using a solar cell measurement system equipped with a solar simulator (class A, air mass 1.5 G, 92250A-1000, Newport-Oriel) and a source-measure unit (Keithley 2400, Keithley Instruments). The simulated solar light intensity was controlled to 100 mW/cm^2 (1 sun) by using a standard (calibrated) cell (BS-520, Bunkoukeiki Co., Ltd) accredited by the Advanced Institute of Science and Technology (AIST, Japan). All tandem polymer solar cells were mounted inside a sample holder filled with nitrogen during measurement in order to avoid the influence of oxygen and moisture in the case of measurements in our laboratory. The external quantum efficiency (EQE) spectra were measured by employing a specialized EQE measurement system equipped with a light source (Tungsten-Halogen lamp, 150W, ASBN-W, Spectral Products) and a monochromator (CM110, Spectral Products).

Synthesis of PIDTT-BT

3,9-bis(trimethyltin)-5,5,11,11-tetrakis(5-(2-ethylhexyl)thiophene-2-yl)-dithieno[2,3-d:2',3'-d']-s-indaceno [1,2-b:5,6-b']dithiophene) (2Sn-IDTT, 0.2 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (2Br-BT, 0.21 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 2 mol%), and tri(o-tolyl)phosphine (P(o-tol)$_3$, 8 mol%), were put into a flat bottom three-necked flask inside a nitrogen environment glove box. The flask containing reactants and catalysts was taken out from the glove box and subjected to degassing with argon gas. Next, chlorobenzene (solvent, 20 ml) was added to the mixture and stirred during the coupling reactions at 100 °C for 72 h. To terminate the coupling reaction, the flask was cooled down to room temperature. The solvent in the flask was dried off using a rotary evaporator, leading to a concentrated state solution. After the concentrated solutions were dissolved in chlorobenzene, catalysts were removed by extraction using deionized water. Organic phases in the separation process were filtrated off using a filter paper (pore size = 1 μm), followed by further concentration of the filtrates. The concentrated filtrated solutions were precipitated into methanol (150 ml) and then washed with various organic solvents (methanol, ethanol, isopropyl alcohol, hexane, and toluene) repeatedly in order to remove unreacted starting materials, low molecular weight fractions, and other impurities. Finally, the precipitates were filtered and then dried in vacuum oven at 60 °C for more than 24 h. The characterization results are as follow. ^{1}H-NMR (500 MHz, CDCl$_3$, δ): 8.57 (s, 1H;Ar H), 7.68 (s, 1H;Ar H), 7.18 (s, 1H; Ar H), 6.78 (t, J = 10 Hz, 9H; Ar H), 2.61 (qui, J = 10 Hz, 4H, CH), 1.49-1.17 (m, 24H, CH$_2$), 0.78-0.74 (m, 8H; CH$_3$); ^{13}C-NMR (500 MHz, CDCl$_3$, δ): 154.2, 153.6, 144.3, 149.8, 147.2, 142.1, 137.7, 136.3, 135.5, 134.6, 129. 2, 126.1, 124.0, 61.7, 41.3, 34.4, 32.4, 29.7, 28.9, 25.7, 23.0, 14.1, 10.9, 10.8. The weight-average molecular weight and polydispersity index of PIDTT-BT were 337.0 kDa and 2.38, respectively.

Table S1. Summary of solar cell parameters for the present tandem polymer solar cells with the interconnetion layers (MoO$_3$/Ni/ZnO:PEOz) under illumination with a simulated solar light (air mass 1.5G, 100 mW/cm^2).

Parameters	t_{Ni} (nm)					
	0	2	4	6	8	10
V_{OC} (V)	0.60 ($\pm$0.02)	1.56 ($\pm$0.01)	1.59 ($\pm$0.01)	1.61 ($\pm$0.01)	1.58 ($\pm$0.01)	1.10 ($\pm$0.02)
J_{SC} (mA/cm^2)	7.088 ($\pm$0.85)	5.514 ($\pm$0.26)	6.350 ($\pm$0.09)	12.86 ($\pm$0.18)	11.41 ($\pm$0.15)	9.92 ($\pm$0.52)
FF (%)	29.9 ($\pm$1.20)	42.3 ($\pm$0.40)	42.1 ($\pm$0.30)	68.3 ($\pm$1.20)	73.1 ($\pm$0.40)	69.5 ($\pm$1.80)
PCE (%)	1.257 ($\pm$0.23)	3.640 ($\pm$0.18)	4.220 ($\pm$0.13)	14.05 ($\pm$0.17)	13.19 ($\pm$0.17)	7.59 ($\pm$0.22)
R_S (kΩ cm^2)	1.71 ($\pm$0.55)	0.64 ($\pm$0.06)	0.52 ($\pm$0.06)	0.14 ($\pm$0.01)	0.16 ($\pm$0.01)	0.19 ($\pm$0.08)
R_{SH} (kΩ cm^2)	3.9 ($\pm$0.43)	8.6 ($\pm$0.50)	11.9 ($\pm$0.07)	15.0 ($\pm$1.50)	11.6 ($\pm$1.90)	20.5 ($\pm$1.50)

Table S2. Summary of representative tandem polymer solar cells with the MoO_3-based interconnection layers.

Ref.	Cells	t (nm)[1]	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	Interconnection Layer
	Front	73	1.11	10.23	54.0	6.09	
R1	Rear	99	0.95	14.22	47.0	6.31	MoO_3 / Ag / PFN
	Tandem	73/99	1.97 (2.06)	8.28	52.0	8.48	
	Front	80	1.00	11.9	67.0	8.00	
R2	Rear	100	0.899	16.81	74.2	11.21	MoO_3 / PEDOT:PSS / ZnO nanoparticles
	Tandem	80/100	1.84 (1.899)	9.6	65.0	11.5	
	Front	70	0.98	15.20	68.0	10.13	
R3	Rear	100	0.77	18.71	71.0	10.36	MoO_3 / Ag / ZnO nanoparticles / PFN-Br
	Tandem	70/100	1.69 (1.75)	10.70	73.0	13.20	
	Front	121	0.90	13.88	66.6	8.31	
R4	Rear	95	0.79	15.90	65.8	8.24	MoO_3 / Ag / PFN
	Tandem	121/95	1.68 (1.69)	11.29	61.3	11.62	
	Front	95	0.97	10.56	58.0	6.1	
R5	Rear	100	0.82	11.60	56.0	5.5	MoO_3 / Ag / ZnO nanoparticles
	Tandem	95/100	1.77 (1.79)	7.95	59.0	8.3	
	Front	80	0.89	14.73	47.3	6.13	
This work	Rear	100	0.93	17.29	73.2	11.83	MoO_3 / Ni / ZnO:PEOz
	Tandem	80/100	1.61 (1.82)	12.86	68.3	14.05	

[1] t: thickness of active layers; [2] V_{OC} in red (bracket): V_{OC} sum of front and rear cells.

\<References for Table S2\>

R1. W. Liu, S. Li, J. Huang, S. Yang, J. Chen, L. Zuo, M. Shi, X. Zhan, C.-Z. Li and H. Chen, *Adv. Mater.*, 2016, **28**, 9729-9734.

R2. W. Huang, S.-Y. Chang, P. Cheng, D. Meng, B. Zhu, S. Nuryyeva, C. Zhu, L. Huo. Z. Wang, M. Wang and Y. Yang, *Nano Lett.*, 2018, **18**, 7977-7984.

R3. L. Zuo, X. Shi, S. B. Jo,. Y. Liu, F. Lin and A. K.-Y. Jen, *Adv. Mater.*, 2018, **30**, 1706816.

R4. Z. Zheng, S. Zhang, J. Zhang, Y. Qin, W. Li, R. Yu, Z. Wei and J. Hou, *Adv. Mater.*, 2016, **28**, 5133-5138.

R5. J. Yuan, M. J. Ford, Y. Xu, Y. Zhang, G. C. Bazan and W. Ma, *Adv. Energy Mater.*, 2018, **8**, 1703291.

Table S3. Summary of shelf lifetime test results for the present tandem polymer solar cells with the interconnetion layer (MoO$_3$/Ni (6 nm)/ZnO:PEOz) under illumination with a simulated solar light (air mass 1.5G, 100 mW/cm^2) for 100 days.

Parameters	Time (day)					
	0	20	40	60	80	100
V_{OC} (V)	1.61	1.57	1.55	1.53	1.52	1.51
J_{SC} (mA/cm^2)	12.86	12.67	12.525	12.282	11.892	11.697
FF (%)	68.3	65.7	65.6	66.0	65.9	66.1
PCE (%)	14.05	13.07	12.74	12.40	11.91	11.68
R_S (kΩ cm^2)	0.14	0.21	0.27	0.27	0.31	0.37
R_{SH} (kΩ cm^2)	25.9	25.1	24.2	22.5	20.9	19.9
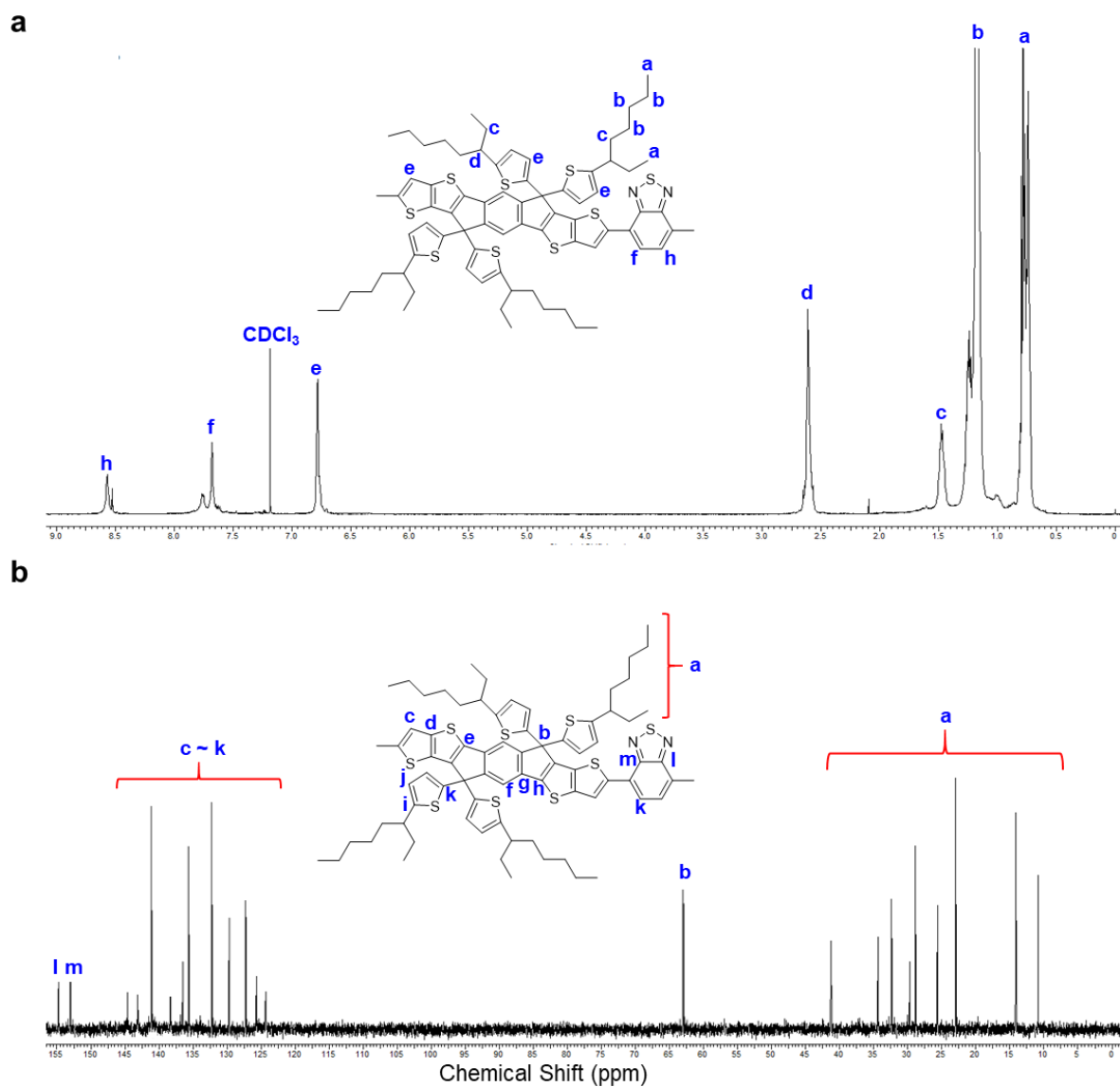
Fig. S1. a, ^{1}H-NMR (500 MHz) and **b,** ^{13}C-NMR (500 MHz) spectra for the PIDTT-BT polymer (solvent: CDCl$_3$) synthesized in this work (see the assigned peaks on the major proton and carbon atoms marked on the molecular structure). Note that the predicted results (chemical shift) are described on the molecular structure (center-top). The detailed interpretation is given in the synthesis section above.
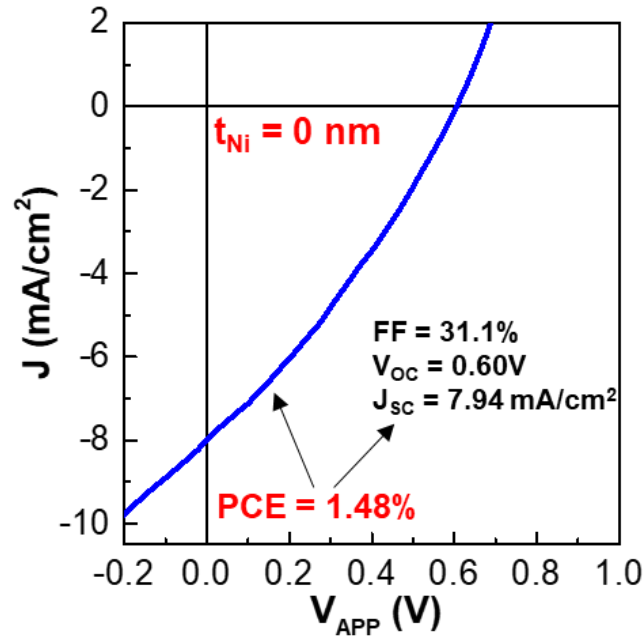
Fig. S2. Light (air mass 1.5G, 100 mW/cm^2) J-V curve for the tandem polymer solar cells without the Ni interlayer (t_{Ni} = 0 nm).
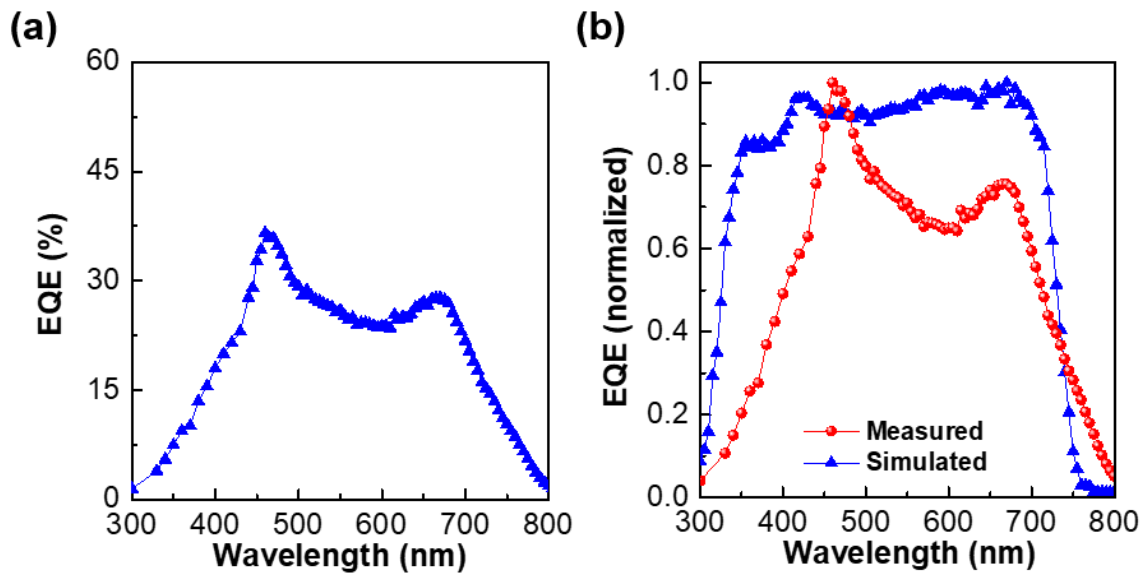
Fig. S3. (a) EQE spectrum measured for the best tandem polymer solar cells (t_{Ni} = 6 nm) by illuminating a monochromatic light (P_{IN} = 484.5 μW/cm^2 at 650 nm), between 300 nm and 800 nm (wavelength), into the glass side of the tandem cells. The calculated J_{SC} value from the measured EQE spectrum was 5.935 mA/cm^2, which is lower than the measured J_{SC} under 1 sun condition owing to the insufficient penetration of the weak monochromatic light into the thick (total 180 nm) active layers of the present tandem cells. (b) Comparison between the measured and simulated EQE spectra after normalization.

S10
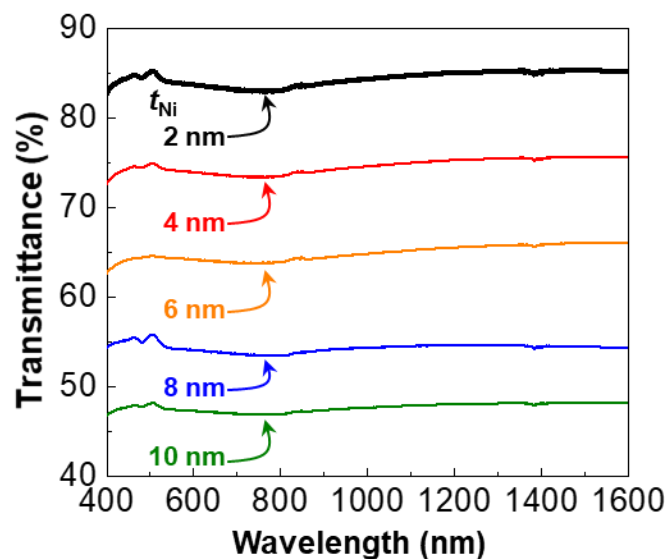
Fig. S4. Optical transmittance spectra (extended wavelength) for the Ni layers, which were coated on quartz substrates, according to the Ni thickness (t_{Ni}).
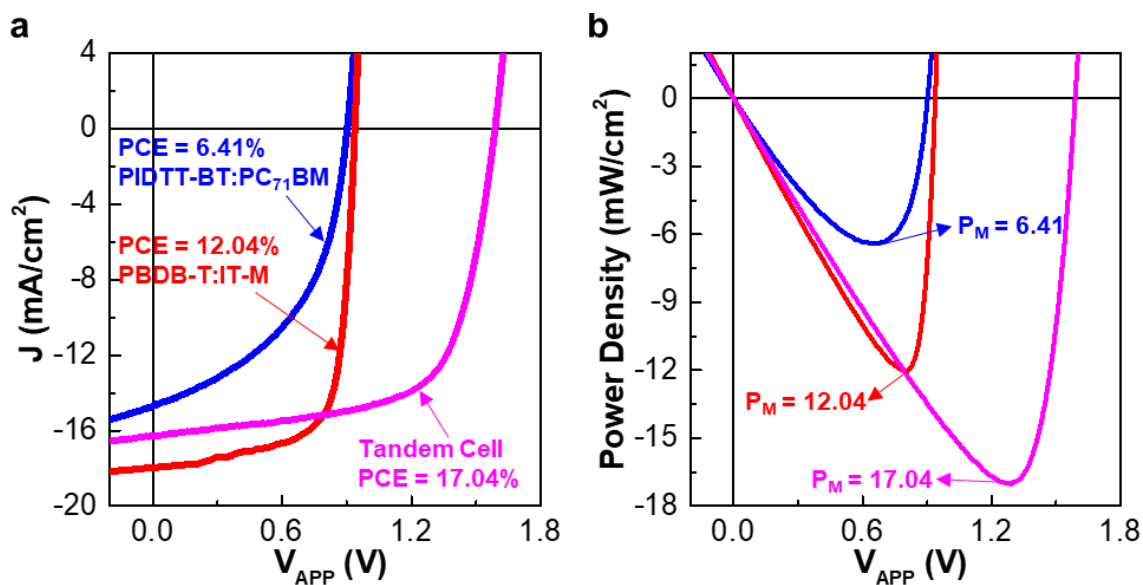

Fig. S5. a, Comparison of light (air mass 1.5G, 100 mW/cm^2) J-V curves for the individual (PIDTT-BT:PC$_{71}$BM and PBDB-T:IT-M) and (optimized) tandem polymer solar cells. **b,** Power density as a function of applied voltage for the individual and tandem polymer solar cells.
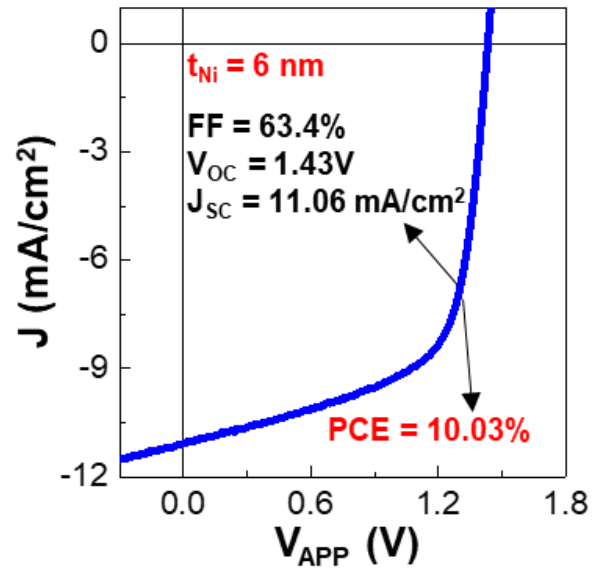
Fig. S6. Light (air mass 1.5G, 100 mW/cm²) J-V curve for the tandem polymer solar cells with the neat ZnO ECBLs without PEOz fabricated at 140 °C and the Ni interlayer (t_{Ni} = 6 nm).

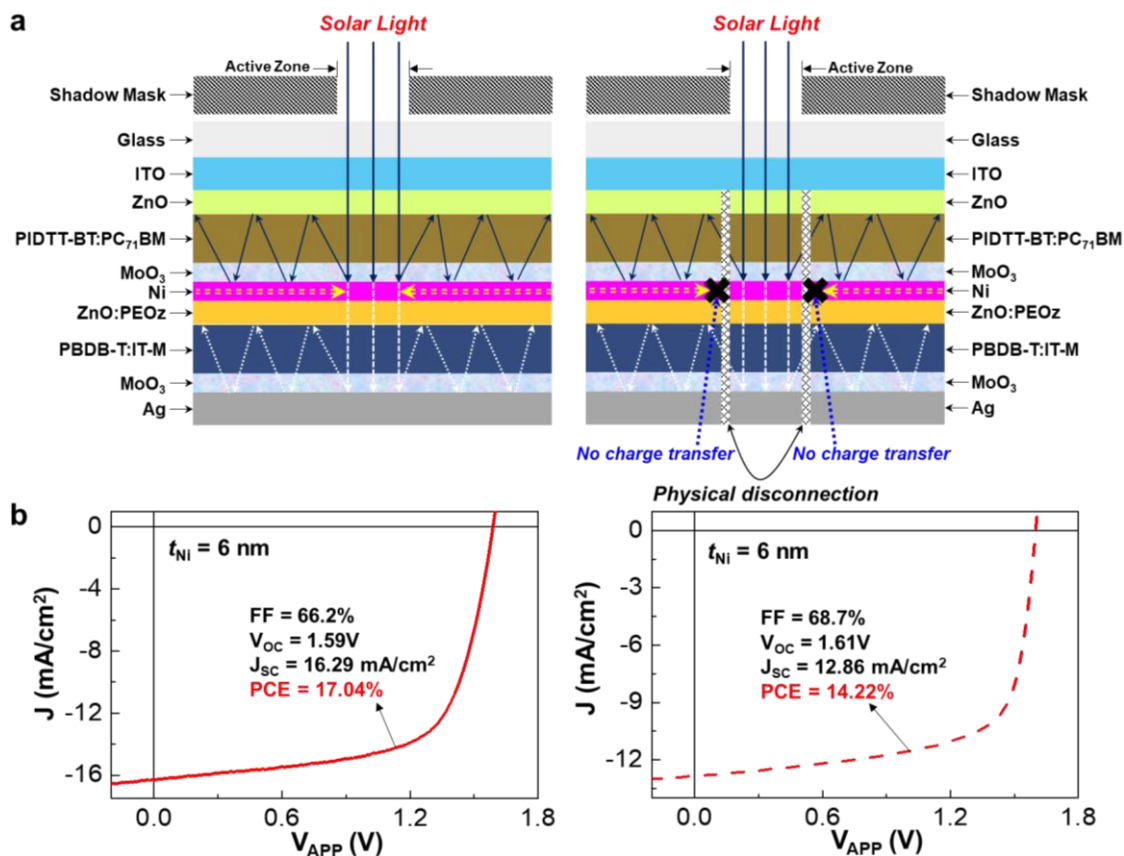**Fig. S7.** Influence of device treatment method on the performance of the present tandem polymer solar cells with the MoO$_3$/Ni(6 nm)/ZnO:PEOz interconnection layers. **a,** Cross-sectional view of devices for the measurement of solar cell performances: (left) placing a shadow mask to *block* incoming solar light except the active zone, (right) placing a shadow mask to *block* incoming solar light except the active zone as well as *isolating* the active zone *electrically* by disconnecting all layers (except ITO) via a physical scribing technique. **b,** Light J-V curves measured under a simulated solar light (air mass 1.5G, 100 mW/cm^2): (left) using the devices treated by the left method in **a**, (right) using the devices treated by the right method in **a**.
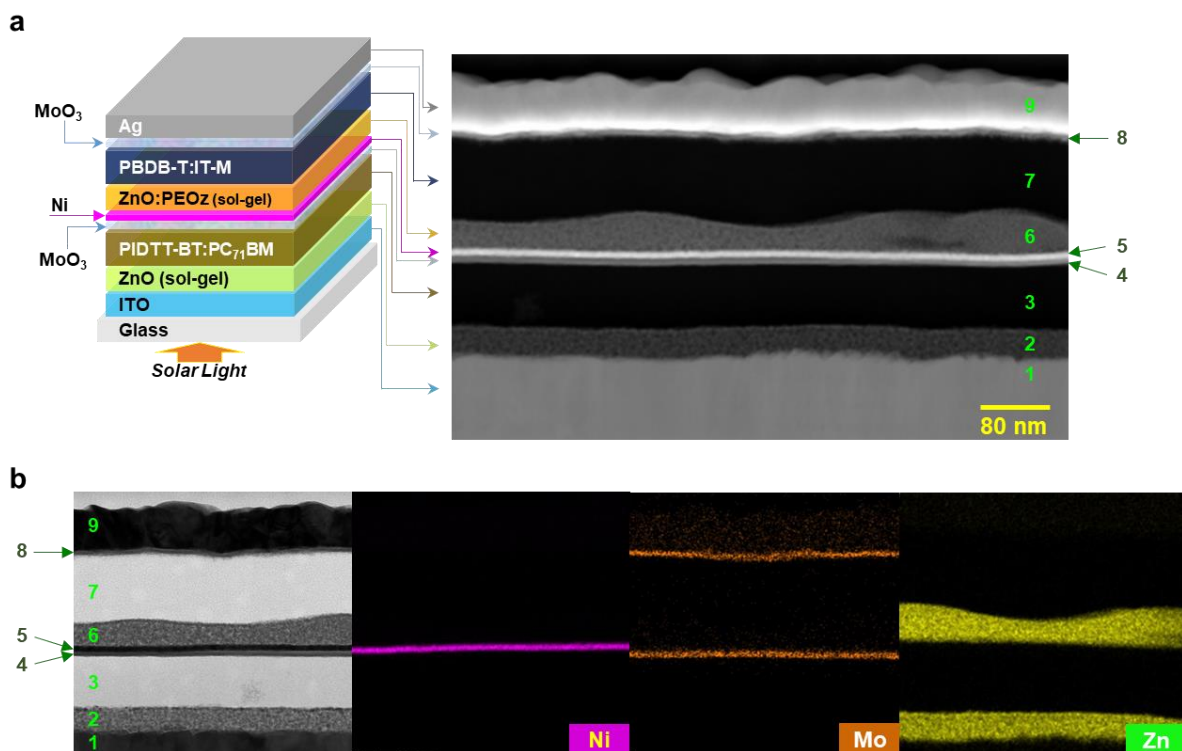
Fig. S8. a, HRTEM image for the cross-sectional part of the tandem polymer solar cells with the interconnetion layer (MoO₃/Ni/ZnO:PEOz). **b,** STEM images to confirm the well-made stacking structure (representative atoms for the interconnection layer: Ni, Mo, and Zn). Note that the device cross-sections were prepared by employing the focused ion beam (FIB) technique.
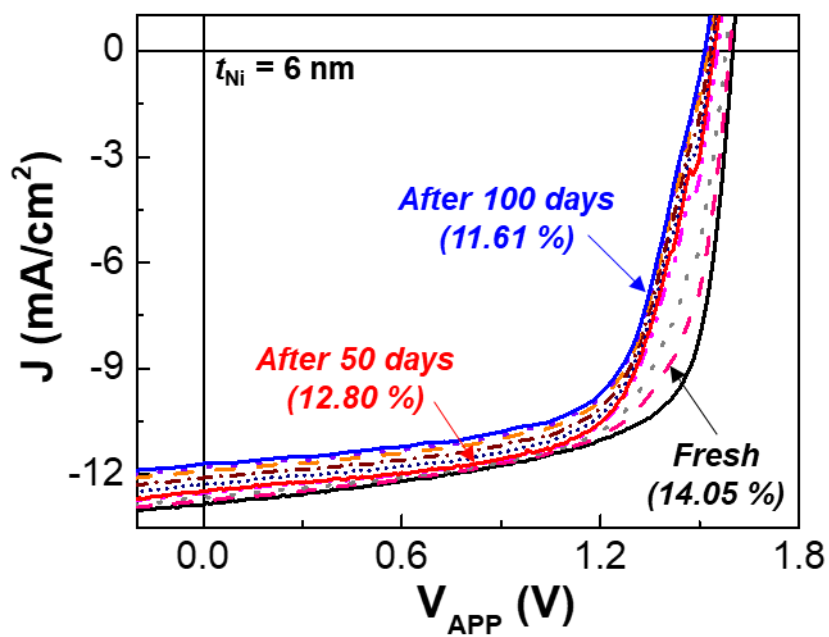
Fig. S9. Shelf lifetime test result (extended data) for the (optimized) tandem polymer solar cells with the interconnetion layer (MoO$_3$/Ni/ZnO:PEOz) (t_{Ni} = 6 nm). The J-V curves of devices, which were stored inside a nitrogen-filled glove box, were measured under simulated solar light (air mass 1.5G, 100 mW/cm^2) for 100 days.