Supporting Information

Manipulation of Optical Field Distribution in ITO-free Micro-cavity Polymer Tandem Solar Cell *via* the Out-of-cell Capping layer for High Photovoltaic Performance

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Single junction device fabrication:

Inverted single junction device (Device A): ITO glass substrates were cleaned by de-ionic water, acetone, isopropanol in ultra-sonic bath. After treated by plasma for 15 min, ZnO precursor solution were spin-coated in glove box and annealing in air at 130 °C for 5 min. Subsequently, C₆₀-SAM was spin-coated on ZnO. PIDTT-DFQT:PC₇₁BM solution (1:4 wt%, o-dichlorobenzene (DCB), 3% 1-chloronaphthalene (CN)) was spin-coated at 800 rpm to form ~100 nm film (calibrated by atomic force microscopy (AFM)), or PCPDT-FBT:PC₇₁BM (1:2.5, wt%, 1,2,4-trichlorobenzene) was spin-coated on top. After annealed at 110 °C for 5 min, the substrates were transferred into the vacuum chamber to deposit 10 nm MoO₃ and 100 nm Ag.

Inverted single junction device (**Device B**): glass substrates were cleaned with the same procedure as ITO glass. After treated in air plasma for 15 min, patterned Ag were deposited. After assembled with mono-layer 11-Mercaptoundecanoic acid (MUA), 20 nm ZnO layer, C_{60} -SAM layer, and the active layer were deposited as previous procedures. After that, the

substrates were transferred into vacuum chamber to deposit 10 nm MoO₃, 10-14 nm Ag and 30-40 nm TeO₂ capping layer to complete the micro-cavity single junction device. *Equations for capping layer dependent micro-cavity behavior:* The reflectance at Ag surface followed the equation below:

$$R = (\frac{n_{Ag} - n_0}{n_{Ag} + n_0})^2 \quad (1)$$

Where, R is reflectivity, n_{Ag} is the refractive index of Ag, n_0 is the refractive index of air. With insertion of capping layer, the surface reflectance change to:

$$R = \frac{r_1^2 + r_2^2 + 2r_1 r_2 \cos \Delta}{1 + r_1^2 + r_2^2 + 2r_1 r_2 \cos \Delta}$$
(2)
$$r_1 = \frac{n_0 - n_{cap}}{n_0 + n_{cap}}$$
(3)
$$r_2 = \frac{n_{cap} - n_{Ag}}{n_{cap} + n_{Ag}}$$
(4)
$$\Delta = \frac{4\pi}{\lambda_0} n_{cap} d$$
(5)

Where, n_{cap} is the refractive index of capping layer, Δ is the phase angle, λ_0 is the incident light wavelength, d is the thickness of the capping layer.



Figure S1. *J-V* characteristic of the active layer thickness dependent organic single junction device with a) PIDTT-DFQT:PC₇₁BM and b) PCPDT-FBT:PC₇₁BM as active layer.



Figure S2. Light intensity distribution in micro-cavity device with different Ag layer thickness: a) 8 nm, b) 14 nm, c) 20 nm. d) simulated EQE spectra of micro-cavity device with different Ag layer thickness.



Figure S3. Light intensity distribution in micro-cavity device with different active layer thickness: a) 50 nm, b) 70 nm, c) 90 nm. d) simulated EQE spectra of micro-cavity device with different active layer thickness.



Figure S4. Light intensity distribution in micro-cavity device with different TeO_2 layer thickness: a) 0 nm, b) 10 nm, c) 30 nm. d) simulated EQE spectra of micro-cavity device with different TeO_2 layer thickness.

TCE	TeO ₂ [nm]	Front cell J _{sc} [mA/cm²]	Back cell J _{SC} [mA/cm²]
ITO		7.59	9.32
Ultra-thin Ag	0	5.52	6.94
	10	6.47	7.73
	20	7.18	8.23
	30	7.33	8.45
	40	6.97	9.09
	50	6.35	9.23
	60	5.74	8.74
	70	5.30	8.09

Table S1. Optical simulation of J_{SC} of ITO based tandem solar cells and micro-cavity tandem solar cells with different capping layer. The active layer thickness is fixed at 100 nm for the front cell and 80 nm for the back cell in all of tandem devices.



Figure S5. Light intensity distribution in micro-cavity tandem solar cells with different thickness of capping TeO_2 layer: a) 0 nm, b)10 nm, c) 30 nm, d) 50 nm.