Simultaneous improvement of efficiency and photostability of organic solar cells by modifying ZnO electron-transport layer with curcumin

Yue Liu,[a] Hang Yang,[a] Yue Wu,[a] Hongyu Fan,[a] Xiaoxiao Li,[a] Kewei Hu,[a] Chaohua Cui,*[,a,b] and Yongfang Li[a,b,c]

[a]*Laboratory of Advanced Optoelectronic Materials, Suzhou Key Laboratory of Novel Semiconductor-Optoelectronics Materials and Devices, College of Chemistry Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China*

[b]*Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou 215123, Jiangsu, PR China*

[c]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

E-mail: cuichaohua@suda.edu.cn

1. Materials

All the other chemicals and solvents were purchased from Aladdin Co., Adamas Co., Sigma-Aldrich Co., and Alfa Asear Chemical Co., and used without further purification.

2. Experimental details

Preparation of the ZnO Nanoparticles (ZnO NPs)

0.818 g Zinc acetate was dissolved in 42 mL methanol at 65 °C. To dissolve 0.485 g KOH in 23 mL methanol, then the KOH solution was slowly drop into the zinc acetate solution in 30 minutes. Stop the reaction after 135 minutes and let the reaction bottle stand static overnight. The white precipitate was separated and rinsed with methanol two times to remove the reaction residues. After all, the ZnO NPs were dissolved in the mixed solvent of methanol:chloroform:butanol (1:1:14, v/v/v) with a concentration of 10.0 mg/mL.

3. Instruments and general methods

DFT calculations. Density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d, p) level involved in the Gaussian 09 program.

UPS measurements. The ultraviolet photoelectron spectroscopy was performed on a Kratos Axis Ultra DLD.

AFM measurements. The morphologies of the neat and blend films were investigated by Atomic Force Microscope (AFM) measurements (Bruker, Multimode 8 SPM Systema) in contacting under normal air conditions at room temperature with a 2 μm scanner.

Mobility Measurement. The devices with a structure of glass/ITO/ETL/active layer/PDINN/Ag were fabricated to measure the electron mobilities. The electron mobilities were calculated by using the space-charge-limited current (SCLC) method.

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

where $\varepsilon_r \approx 3$ is the average dielectric constant of the polymer blend, ε_0 is the permittivity of the free space, μ is the charge carrier mobility, V is the applied voltage, and L is the thickness of the film.

Contact angle measurements. The contact angle tests were performed on a Dataphysics OCA40 Micro surface contact angle analyzer.

PL measurements. Photoluminescence (PL) spectroscopy were performed on an Edinburgh Instrumen FLS 980.

ESR measurements. Electron spin resonance (ESR) spectroscopy was carried out with an ESR spectrometer (JES-X320). The samples were prepared by mixing 5 mg ZnO nanoparticles and 1.25 mg E100 power in 400 μL DMPO/water mixed solution (volume ratio: DMPO:H_2O = 0.0056:1). The ESR measurement was performed immediately by JES-X320 after sample preparation illuminated by UV 360 light for 10 mins. Instrument parameters were as follows: microwave power, 1 mW; g value for Center Field: g = 2.000; sweep width, 326±5 mT; modulation width, 0.5 mT; modulation amplitude: 400.

Optical characterizations. UV-vis absorption spectra were recorded on the Cary 5000 UV-Vis-NIR Spectrophotometer. For the solid-state measurements, the solutions were spin-coated on quartz plates.

FTIR measurements. Fourier transform infrared spectrometry (FTIR) spectra were measured with a Bruker VERTEX 70 V.

XPS measurements. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Scientific ESCALab 220 XL electron spectrometer with 300 W Al Kα radiation.

TPV and TPC measurements. TPV and TPC were carried out under a 337 nm 3.5 ns pulse laser (160 μJ per pulse at 10 Hz) and halide lamps (150 W). Voltage and current dynamics were recorded on a digital oscilloscope (Tektronix MDO3102).

EIS measurements. Electrochemical impedance spectroscopy (EIS) measurements were performed by an IM6 electrochemical workstation (Zahner Zennium, Germany) in the dark at room temperature with a bias under the respective V_{oc} of the solar cells. Z-view software was used to fit the impedance spectra to obtain the impedance parameters.

Solar cells fabrication. The devices were fabricated with inverted architectures of glass/ITO/ETL/active layer/MoO_3/Al. The pre-cleaned ITO-coated glass was spin-cast from the ZnO at 3000 rpm for 40 s, and then annealed at 150 ℃ for 15 min in glove box. After that, the active layer blend solution was spin-coated onto it, the hole-transport layer of MoO_3 (about 10 nm) and Al (about 100 nm) were deposited in order at a pressure of 3.0×10^{-4} Pa with specific shadow masks.

Fabrication details for ZnO/E100 ETL. E100 was dissolved in methanol at concentrations of 1.0/3.0/5.0/7.0 mg/mL, respectively, and then coated onto ZnO film at 3000 rpm for 40 s. The photovoltaic parameters of the PM6:Y6-based devices processed by various treatments are provided in Table S2.

Fabrication details for the PM6:Y6-based i-OSCs. The PM6:Y6 ratio was kept at 1:1.2 (w/w) with the polymer concentration of 7.5 mg/mL in chloroform. The optimal treatments involved are 0.5% (v/v) CN followed by TA at 100 ℃ for 10 min. Dual additives of 0.5% CN and 1.0/3.0/5.0/7.0 wt% E100 (weight ratio relative to the total

weight of PM6 and Y6) followed by TA at 100 ℃ for 10 min. The optimal thickness of active layer is 95~105 nm. The photovoltaic parameters of the PM6:Y6:E100-based devices processed with different weight ratio of E100 additive are provided in Table S3.

Solar cells characterization. The current density-voltage (*J-V*) measurement of the OSCs were measured under illumination of AM 1.5G (100 mW cm^{-2}) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm^2 photobeam size) of Enli Technology CO., Ltd... Masks were made using laser beam cutting technology and had well-defined areas of 0.056 cm^2 to define the effective areas for accurate measurement. The EQE was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single crystal Si solar cell.

Stability measurements. The i-OSCs were unencapsulated and exposed by continuous UV illumination by a 365 nm UV light lamp (50 mW cm^{-2}, Zhonglian UV lamp) in atmosphere (20 ℃， 30% humidity). After different time of illumination, the PCE of devices were remeasured by Xenon lamp AM 1.5G (100 mW cm^{-2}) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm^2 photobeam size) of Enli Technology.

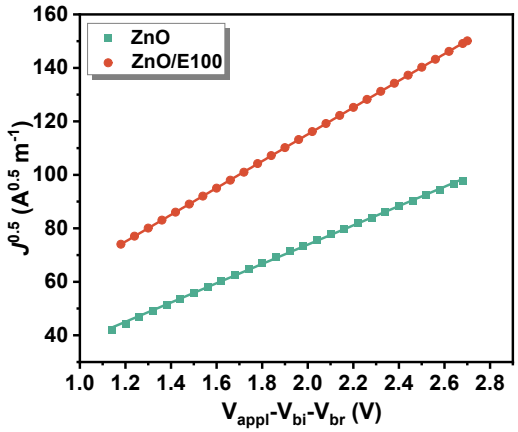

Figure S1. $J^{0.5}$vs (V_{app}-V_{bi}-V_{br}) plots of electron only devices based on PM6:Y6 blend films with ZnO or ZnO/E100 as ETL.

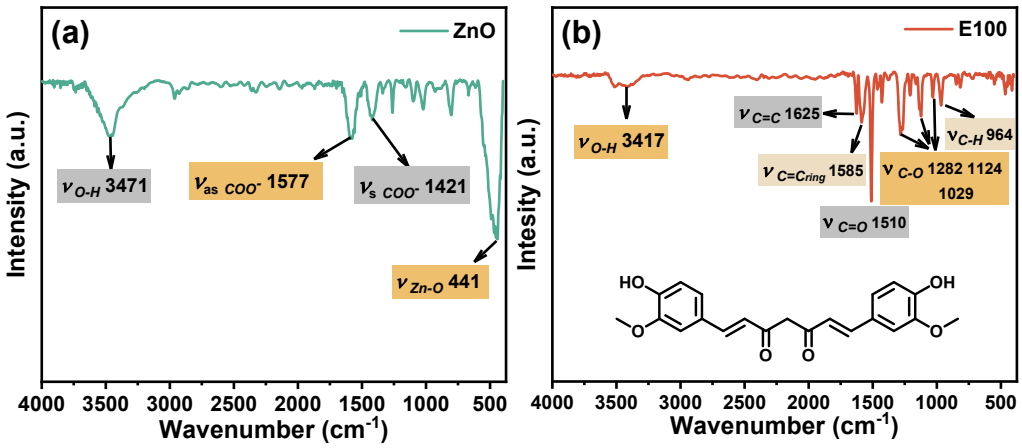

Figure S2. FT-IR spectra of (a) ZnO[1] and (b) E100[2] films.

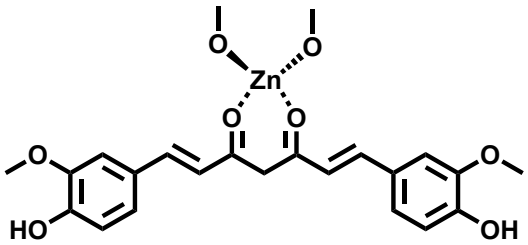

Figure S3. The probable interaction between E100 and ZnO.

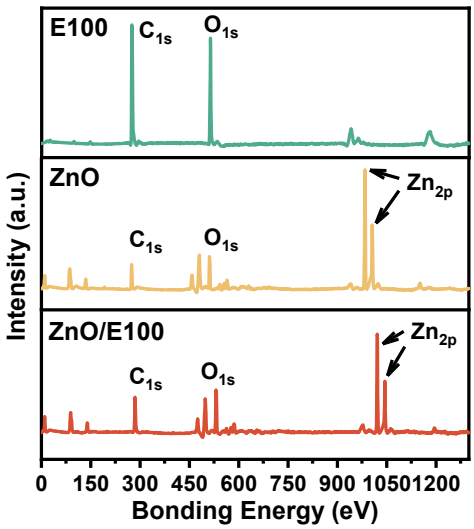

Figure S4. The full scan XPS spectra of ZnO, E100 and ZnO/E100 films.

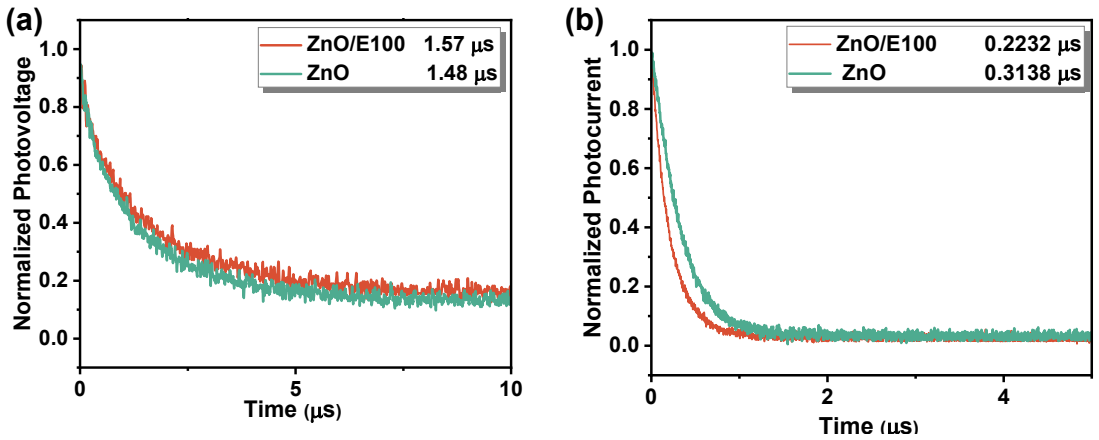

Figure S5. a) transient photovoltage and b) transient photocurrent profiles based on PM6:Y6 blend films with ZnO or ZnO/E100 as ETL.

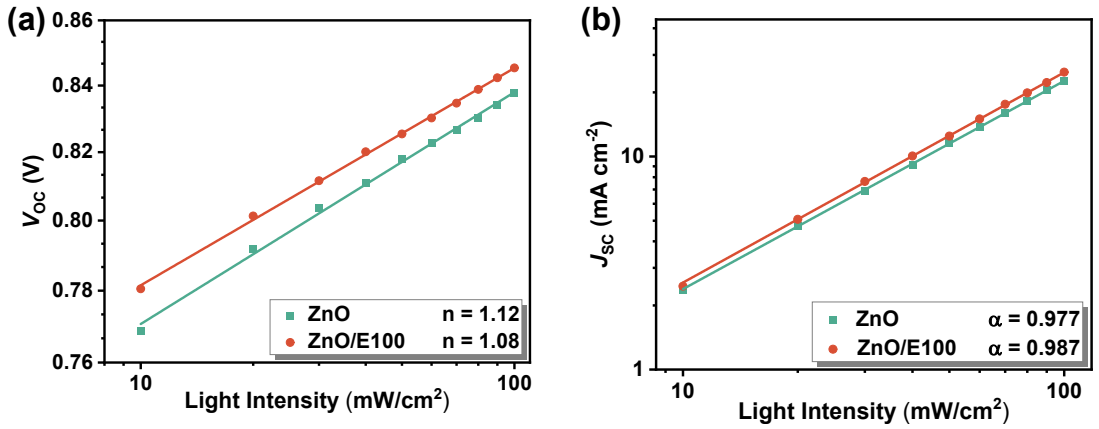

Figure S6. a) V_{OC} and b) J_{SC} versus light intensity plot based on PM6:Y6 blend films with ZnO or ZnO/E100 as ETL.

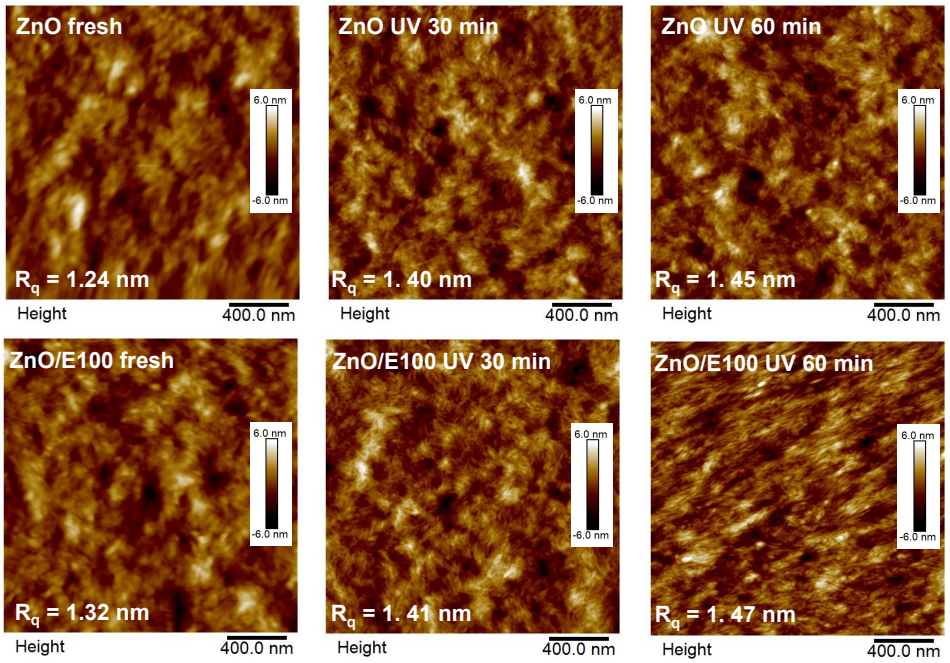

Figure S7. AFM topography images of chloroform processed PM6:Y6 (1:1.2, w/w) blend based on different ETLs before and after UV irradiation.

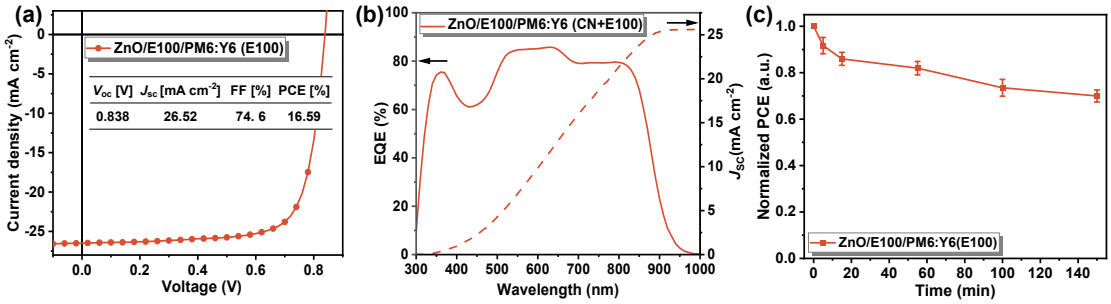

Figure S8. a) *J–V* curve and the corresponding photovoltaic parameters and b) EQE spectrum. c) photostability plots under UV irradiation (365 nm, 50 mW cm^{-2}) in ambient atmosphere of the PM6: Y6: E100-based i-OSCs with ZnO/E100 as ETL (error bars show standard deviation from the arithmetic mean value of 3 devices).

Table S1. Summary of the fitting results of the Nyquist plots and the value of electron mobilities (μ_e) acquired by SCLC method.

ETLs	R_s (Ω)	R_{REC} (Ω)	*CPE* (F)	μ_e ($cm^2\ V^{-1}\ s^{-1}$)
ZnO/E100	18.23	158.6	2.77×10^{-7}	2.95×10^{-4}
ZnO	18.21	68.39	2.15×10^{-7}	1.23×10^{-4}

Table S2. Photovoltaic performance of the i-OSCs based on ZnO/E100 ETL with different concentrations of E100 under the illumination of AM 1.5 G at 100 mW cm $^{-2}$.

Concentration	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0	0.831	25.45	72.3	15.22
1 mg/mL	0.838	25.37	72.1	15.32
3 mg/mL	0.842	25.53	72.4	15.58
5 mg/mL	0.841	26.35	73.9	16.31
7 mg/mL	0.844	26.47	66.5	14.86

Table S3. Photovoltaic performance of the i-OSCs based on ZnO/E100 ETL with different weight ratio of E100 additive (relative to the total weight of PM6 and Y6) under the illumination of AM 1.5 G at 100 mW cm $^{-2}$.

Weigh ratio	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0	0.841	26.35	73.9	16.31
1 wt%	0.842	26.28	72.3	16.01
3 wt%	0.838	26.52	74. 6	16.59
5 wt%	0.828	26.89	70.1	15.60
7 wt%	0.826	27.10	67.6	15.13

Notes and references

1. Y. Han, H. Dong, W. Pan, B. Liu, X. Chen, R. Huang, Z. Li, F. Li, Q. Luo, J. Zhang, Z. Wei and C. Q. Ma, *ACS Appl. Mater. Interfaces*, 2021, **13**, 17869-17881.

2. L. Bechnak, R. El Kurdi and D. Patra, *J Fluoresc*, 2020, **30**, 547-556.