Improving the efficiencies of small molecule solar cells by solvent vapor annealing to enhance the J-aggregation

Liangang Xiao[abc], Zhengdong Li[a], Qin Hu[de], Yawei Liu[c], Wenkai Zhong[b], Xueli Mei[f], Thomas P. Russell[de], Yi Liu*[c], Yong Min[a], Xiaobin Peng*[b] and Yong Cao[b]

a. School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China

b. State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China

E-mail: chxbpeng@scut.edu.cn

c. The Molecular Foundry, Lawrence Berkeley National Lab, Berkeley, CA, 94720, United States

E-mail: yliu@lbl.gov

d. Materials Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA, 94720, United States

e. Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, United States

f. College of Chemistry, Chemical Engineering and Material Science of Soochow University, Suzhou, Jiangsu, 215123, China

Experiment Details:

Materials: ZnP2-DPP and PFN-Br were synthesized by our group. All reagents and solvents were purchased from commercial sources (Aldrich and One-material) and used as received.

Device Fabrication: The solution-processed BHJ solar cells were fabricated with a conventional device structure of Indium tin oxide (ITO)/PEDOT:PSS/ ZnP2-

DPP:$PC_{61}BM$/PFN-Br/Al, and the fabrication details are as follows: ITO coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 4 min, 40 nm thick poly(styrene sulfonate)-doped poly(ethylene-dioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-casted on the ITO-coated glass substrates at 3000 rpm for 30 s, the substrates were subsequently dried at 150 ℃ for 10 min in air and then transferred to a N_2-glovebox. The active layers were prepared from ZnP2-DPP:$PC_{61}BM$ in mixed solvent of chlorobenzene/pyridine (100:2 v/v) with an overall concentration of 36 mg/ml. The weight ratio of ZnP2-DPP to $PC_{61}BM$ was kept to 1:1. The blend films were made by spin-coating at the speed of 1000 revolutions per minute for 50 s and the thickness of the films measured by a profilometer were to be 120-130 nm. For solvent vapor annealing treatment, the active layer was put in the petri dish containing 300 microliter solvent for different time. The ultra-thin conjugated poly[(9,9-bis(30-((N,N-dimethyl)-N-ethylammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (PFN-Br) layer was deposited by spin casting from a 0.02% (w/v) solution in methanol (from 2000 rpm for 30 s). Finally, Al (~80 nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 0.16 cm^2.

Measurements and Instruments: UV-vis-NIR spectra of pure and blend films on a quartz substrate were recorded at room temperature (ca. 25°C) using a Cary 5000 UV-Vis-NIR spectrometer. The atomic force microscopy (AFM) measurements of the

surface morphology of blend films were conducted on a NanoScope NS3A system.

PCEs were determined from J-V characteristics measured by a Keithley 2400 source-measurement unit under AM 1.5G spectrum from a solar simulator (Oriel model 91192). Masks made from laser beam cutting technology with a well-defined area of 0.16 cm^2 were attached to define the effective area for accurate measurement. Solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Hamamatsu S1133, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). The tapping mode atomic force microscopy (AFM) measurements of the blends' surface morphology were conducted on a NanoScope NS3A system (Digital Instrument). External quantum efficiency (EQE) values of the encapsulated devices were measured by using an integrated system (Enlitech, Taiwan, China) and a lock-in amplifier with a current preamplifier under short-circuit conditions. The devices were illuminated by monochromatic light from a 75 W xenon lamp. The light intensity was determined by using a calibrated silicon photodiode.

The hole mobility of the blend films were measured under dark by the space charge limited current (SCLC) method with hole-only device structure ITO/PEDOT:PSS/ZnP2-DPP:PC_{61}BM/MoO3/Al. The PEDOT:PSS layer and the active layers were prepared according to the same procedures as the OSCs. Finally, MoO_3 and then Al were thermally evaporated onto the active layers The electric-field dependent SCLC mobility was estimated using the following equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3} exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

Grazing incidence X-ray diffraction (GIXD) characterization of the thin films was performed at beamline 7.3.3 Lawrence Berkeley National Lab. The scattering signal was recorded on a 2-D detector (Pilatus 1M) with a pixel size of 172 μm. The X-ray energy is 10 keV. The samples were ~15 mm long in the direction of the beam path, and the detector was located at a distance of 300 mm from the sample center (distance calibrated using a silver behenet standard). The incidence angle of 0.16° was chosen which gave the optimized signal-to-background ratio. Thin film samples were prepared on PEDOT:PSS covered silicon wafers to match the device conditions. The data was processed and analyzed using Nika software package. RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab (LBNL). A 284.2 eV beamline energy at $PC_{61}BM$ k-edge was chosen to enhance the contrast. Thin films of device thickness was flowed and transferred onto Si_3N_4 substrates, which were then mounted onto sample plate. Transmission electron microscopy (TEM) studies were conducted with a FEI TitanX 60-300 microscope at NCEM LBNL.

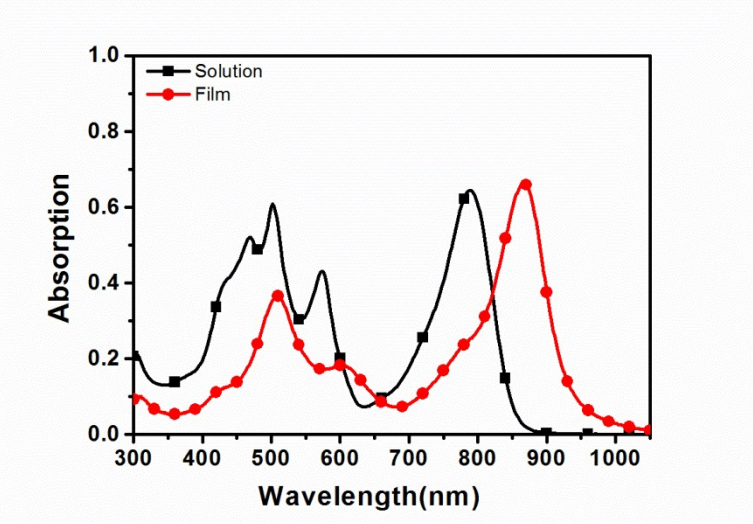

Figure S1 UV-vis-NIR absorption spectra of ZnP2-DPP in solution and film.

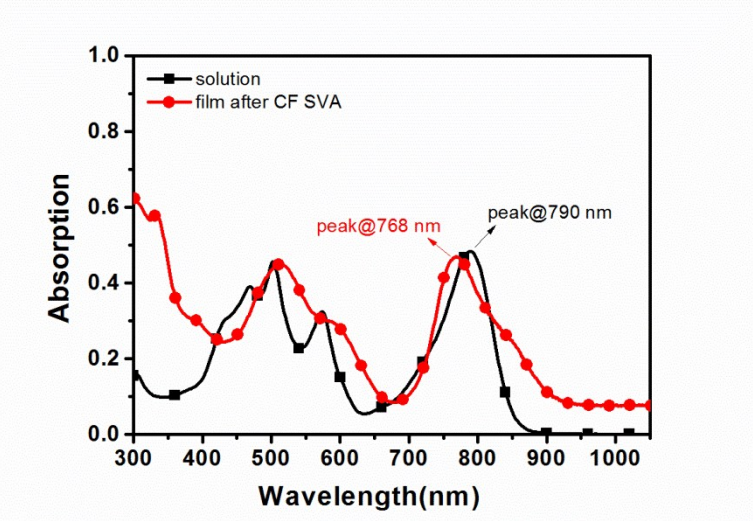

Figure S2 Absorption spectra of ZnP2-DPP in solution and film treated by CF SVA.

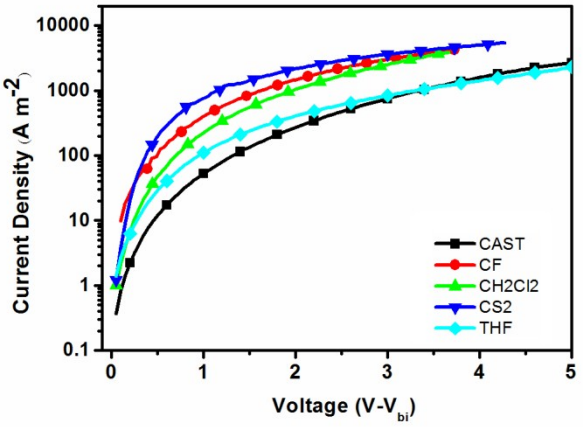

Figure S3 *J-V* characteristics under dark for hole-only devices based on different processing conditions.

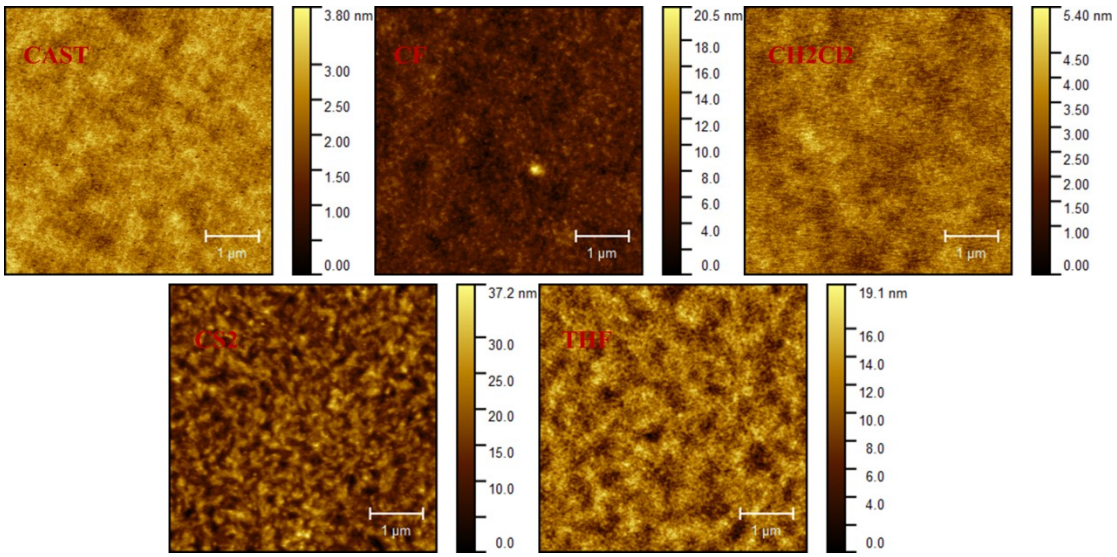

Figure S4 Atomic force microscopy (AFM) height images of ZnP2-DPP:$PC_{61}BM$ based films spin-coated on ITO/PEDOT:PSS substrates under different processing conditions.

Table S1 Photovoltaic parameters of ZnP2-DPP:$PC_{61}BM$-based solar cells with different CF annealing time under illumination of AM 1.5 G, 100 mW cm^{-2}.

SVA time (s)	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF* (%)	*PCE*(%)
0	6.88	0.805	31.02	1.70
80	18.72	0.680	59.36	7.56
100	19.11	0.660	64.28	8.11
120	19.85	0.640	67.04	8.52
140	19.22	0.640	68.12	8.38

Table S2 Photovoltaic parameters of ZnP2-DPP:$PC_{61}BM$-based solar cells with different CH_2Cl_2 annealing time under illumination of AM 1.5 G, 100 mW cm^{-2}.

SVA Time (s)	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF* (%)	*PCE*(%)
0	6.88	0.805	31.02	1.70[b]
100	16.88	0.660	50.23	5.60
120	17.80	0.650	55.60	6.43
140	18.20	0.635	57.36	6.63

160	18.22	0.635	56.22	6.50

Table S3 Photovoltaic parameters of ZnP2-DPP:$PC_{61}BM$-based solar cells with different CS_2 annealing time under illumination of AM 1.5 G, 100 mW cm^{-2}.

SVA time (s)	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF* (%)	*PCE*(%)
0	6.88	0.805	31.02	1.70
120	19.11	0.655	67.21	8.41
140	20.02	0.645	69.01	8.91
160	21.40	0.640	69.14	9.47
180	20.65	0.640	69.52	9.19

Table S4 Photovoltaic parameters of ZnP2-DPP:$PC_{61}BM$-based solar cells with different THF annealing time under illumination of AM 1.5 G, 100 mW cm^{-2}.

SVA time (s)	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF* (%)	*PCE*(%)
CAST	6.88	0.805	31.02	1.70
60	10.50	0.720	55.67	4.21
80	9.47	0.705	66.20	4.42
100	8.11	0.705	66.85	3.82
120	6.23	0.700	67.55	2.95

Table S5 Hole mobility of ZnP2-DPP:$PC_{61}BM$-based devices under different processing condition.

Processing conditions	CAST	CF	CH_2Cl_2	CS_2	THF
Hole mobility(cm^2 V^{-1} s^{-1})	1.65×10^{-5}	1.50×10^{-4}	8.07×10^{-5}	1.76×10^{-4}	3.01×10^{-5}