Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

High efficiency air stable organic photovoltaics with an aqueous inorganic contact

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Experimental methods

Preparation of the ZnO ink: preperation of the ink followed the procedure previously reported by Bai et al.[1] Initially a stock solution of $Zn(NO_3)_2.6H_2O$ (Fluka) with a concentration of 0.5 M was formed by dissolving the nitrate in de-ionized (D.I.) water. Subsequently 10 mL of 2.5 M NaOH was added drop-wise over a period of 5 min to 15 mL of the above stock solution under rigorous stirring. The resulting hydroxide slurry was centrifuged at 4000 rpm for 5 min and the supernatant removed. The remaining precipitate was then re-suspended in 20 mL of D.I. water and subjected to sonication. The resulting suspension was subjected to centrifugation and re-suspension in D.I. water four additional times to minimise the ionic content in the solution. Following the final centrifugation step, the hydroxide was dissolved in 50 mL of 6.6 M NH_3 solution to form the ink.

Preparation of TiO_x precursor solution: Preparation of the TiO_x precursor solution was carried out using the method described by Kim et al.[2] In brief, 10 ml of titanium (iv) isopropoxide was mixed with 50 ml of 2-methoxyethanol and 5 ml of ethanolamine in a 3 necked flask under a nitrogen background. A two step heating process was carried out where the mixture was initially heated at 80º C for 2 h followed by heating at 120º C for 1 h. The final stock solution was finally diluted to 1:200 in methanol.

Device fabrication and characterization: Photovoltaic devices were fabricated on indium tin oxide (ITO) coated glass substrates (sheet resistance of 15Ω/□) precleaned using acetone and methanol followed by oxygen plasma ashing. For inverted devices with TiO_x, the precursor solution was spincoated in air at 5000 rpm and annealed at at 80ºC for 10 min to remove any residual solvents. For inverted devices with the ZnO interlayer, the precursor was spin coated at 3500 rpm for 45 s. Following this the films were annealed in air either at 80º C for 30 min or at 80º C for 5 min followed by ~140 º C for 25 min. For spin coating multiple layers, the above procedure was reported after the annealing step. For standard devices, PEDOT:PSS (Clevios PVP AI 4083) was spin coated onto ITO and dried at 140º C for 15 min. Following the deposition of the interlayer, the blend of PCDTBT (Solarischem)/ $PC_{70}BM$ (Solenne BV) (35 mg/ml at 1:4 ratio) in a mixed solvent system of dichlorobenzene/chlorobenzene (3:1) was spin coated on top of either ZnO or PEDOT:PSS to form an 80-100 nm thick active layer. This was followed by either thermal evaporation of MoO_3 (~7.5 nm) to form the HTL or spin coating of the TiO_x precursor solution (in air at 5000 rpm) to form the ETL. For TiO_x precursor solution deposited films, the devices were annealed in air at 80ºC for 10 min to remove any residual solvents. The device fabrication was completed by thermal evaporation of the Al cathode. The overlap area between ITO and Al was calculated to be 0.67 cm^2. The photovoltaic device performance of the above devices were characterized in air (without encapsulation) using a 300 W Xe Arc Lamp solar simulator (Abet Technologies) fitted with an Air Mass 1.5G Global (AM 1.5G) filter calibrated to an intensity if 100 $mWcm^{-2}$ and a Keithley 2425 sourcemeter in a four point probe configuration. The incident photon to current conversion efficiency (IPCE) measurements for the devices was carried out using a Bentham PVE300 system. In measuring the device characteristics and the IPCE, an aperture with an area of 28.3 mm^2 was used in order to minimize edge effects and to eliminate an overestimation of short circuit current densities due to shadow effects etc. For lifetime measurements, devices were stored under fluorescent lighting in ambient conditions (relative humidity of ~30-40%, temperature of ~25℃)

Electrical characterization of ZnO thin films: For mobility calculations, ZnO thin films were deposited 300 nm SiO_2 coated p-type Si substrates under conditions similar to those used for OPV device fabrication. Top contacts were deposited through evapouration of Al. A shadow mask with a channel length of 80 μm and a channel width of 1200 μm. For analysis of the electron mobility, the standard equation[3] for the operation of field effect transistors in the saturation regime: $I_{DS} = \frac{1}{2}\left(\frac{W}{L}\right)\mu C_i (V_G - V_T)^2$ was used. Here I_{DS} is the channel current, W and L are the channel width and length (respectively), μ, the charge carrier mobility, C_i the capacitance of the gate dielectric, V_G is the gate voltage and V_T is the threshold voltage.

Characterization of ZnO thin films: Atomic force micrographs were obtained using a Veeco Dimension 3000 system in the tapping mode. Samples for AFM were prepared by spin coating the ZnO layer on ITO. Optical transmission of ZnO on ITO was carried out using a Varian Cary UV-Vis spectrophotometer in a single beam mode. Photoluminescence measurements were carried out on a Cary Eclipse spectrometer under 330 nm excitation. Samples were prepared on Si substrates by spin coating ZnO layers under the conditions similar to that used for device fabrication.

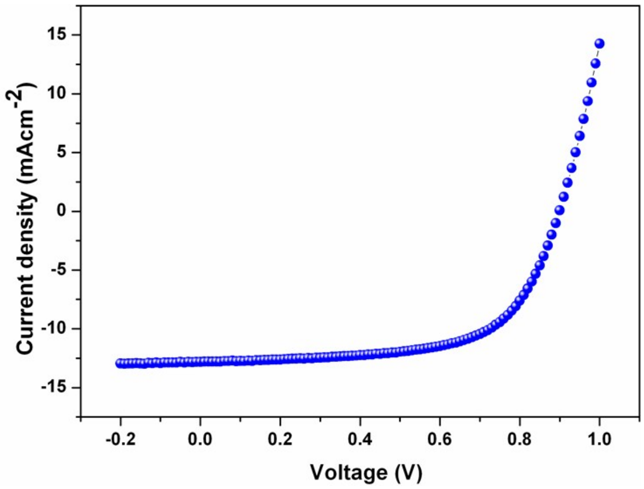

Figure S1 J-V curve of a typical PCDTBT:PC$_{70}$BM device fabricated according to the standard architecture with TiO$_x$ interfacial layer.

Table S1 Performance characteristics of PCDTBT:PC$_{70}$BM devices fabricated according to the standard architecture with TiO$_x$ interfacial layer.

V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE(%)
0.90	12.81	63.58	7.32

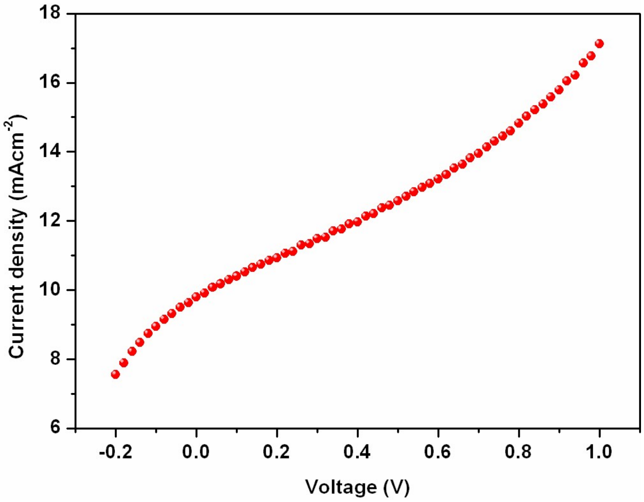

Figure S2 J-V curve of inverted PCDTBT:PC$_{70}$BM device fabricated with TiO$_x$ as the electron transporting interfacial layer.

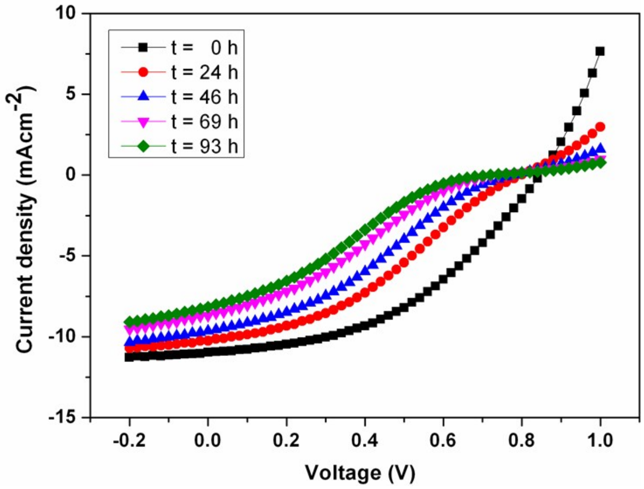

Figure S3 Onset of S-type behaviour for PCDTBT:$PC_{70}BM$ devices fabricated according to the standard architecture with TiO_x interfacial layer, stored in air in the absence of encapsulation.

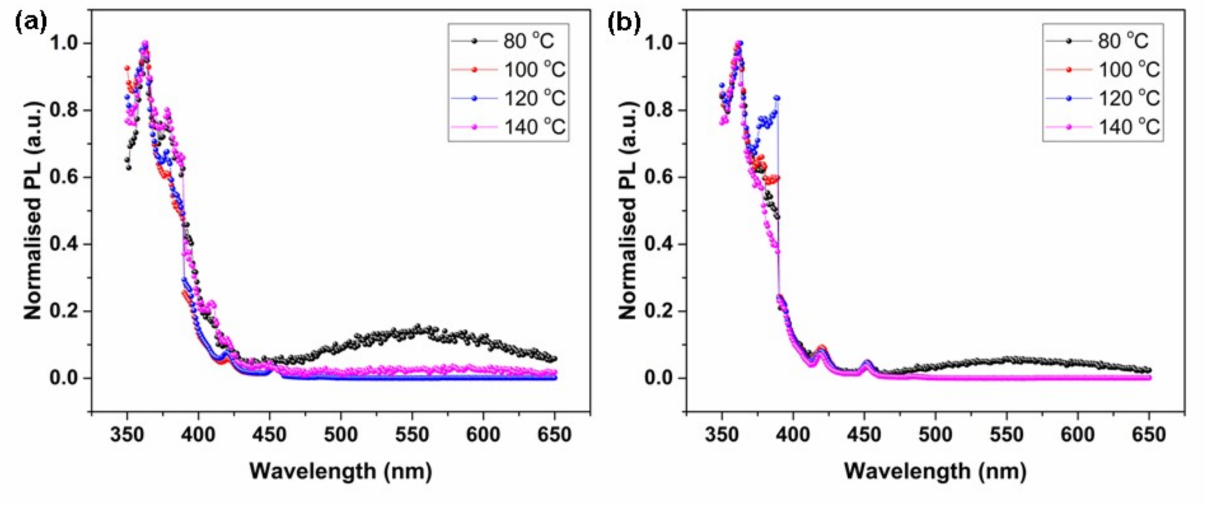

Figure S4 Photoluminescence spectra of ZnO thin films prepared at 80º C and 140º C measured (a) 2-3 hours after deposition and (b) 4 days after deposition.

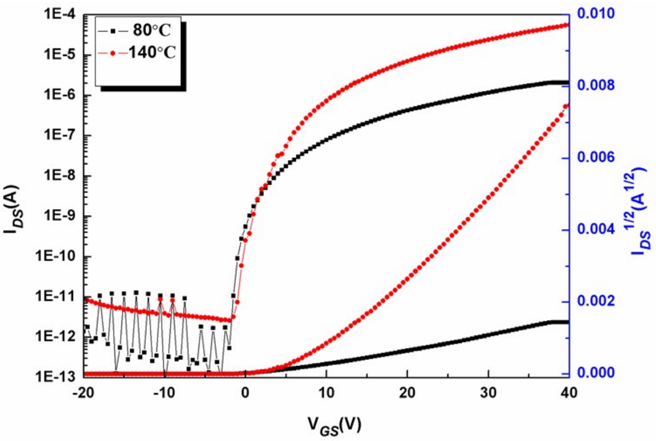

Figure S5 Comparison of transfer characteristics of the ZnO TFTs with different annealing temperatures. (W/L=1200μm/80μm , V_{DS}=40 V, V_{GS} sweep from -20 V to 40 V)

Table S2 Parameter comparison of transfer characteristics of the ZnO TFTs with different annealing temperatures. (W/L=1200 μ m/80 μ m , V_{DS}=40 V, V_{GS} sweep from -20 V to 40 V)

Annealing temperature	μ ($cm^2V^{-1}s^{-1}$)	V_{th} (V)	I_{on}/I_{off}	SS ($mVdB^{-1}$)
80	0.021	3.9	1.02×10^6	799.6
140	0.554	6.7	2.16×10^6	652.4

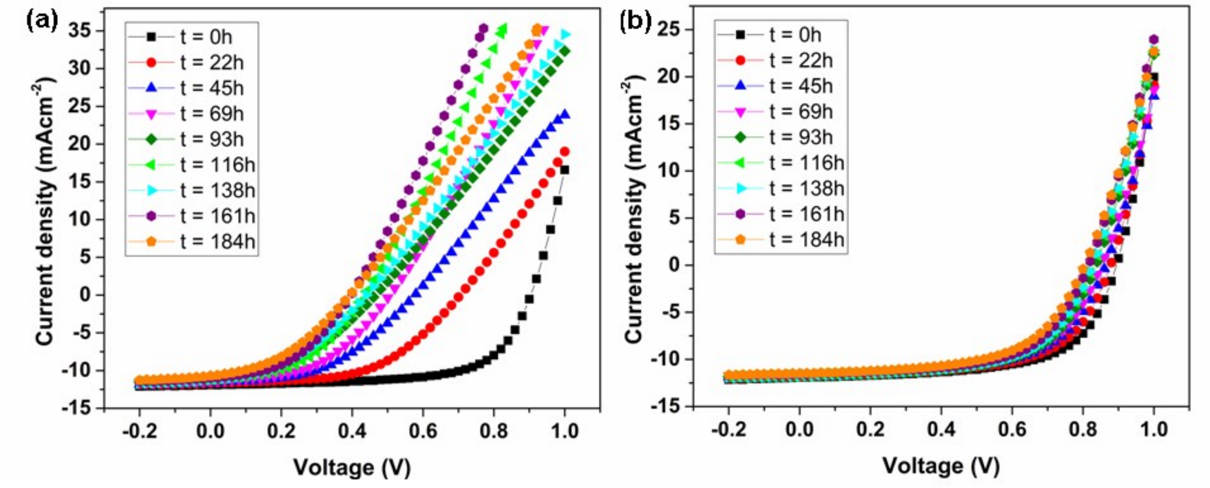

Figure S6 J-V characteristics over time for inverted devices with ZnO layers annealed at (a) 80º C and (b) 140º C.

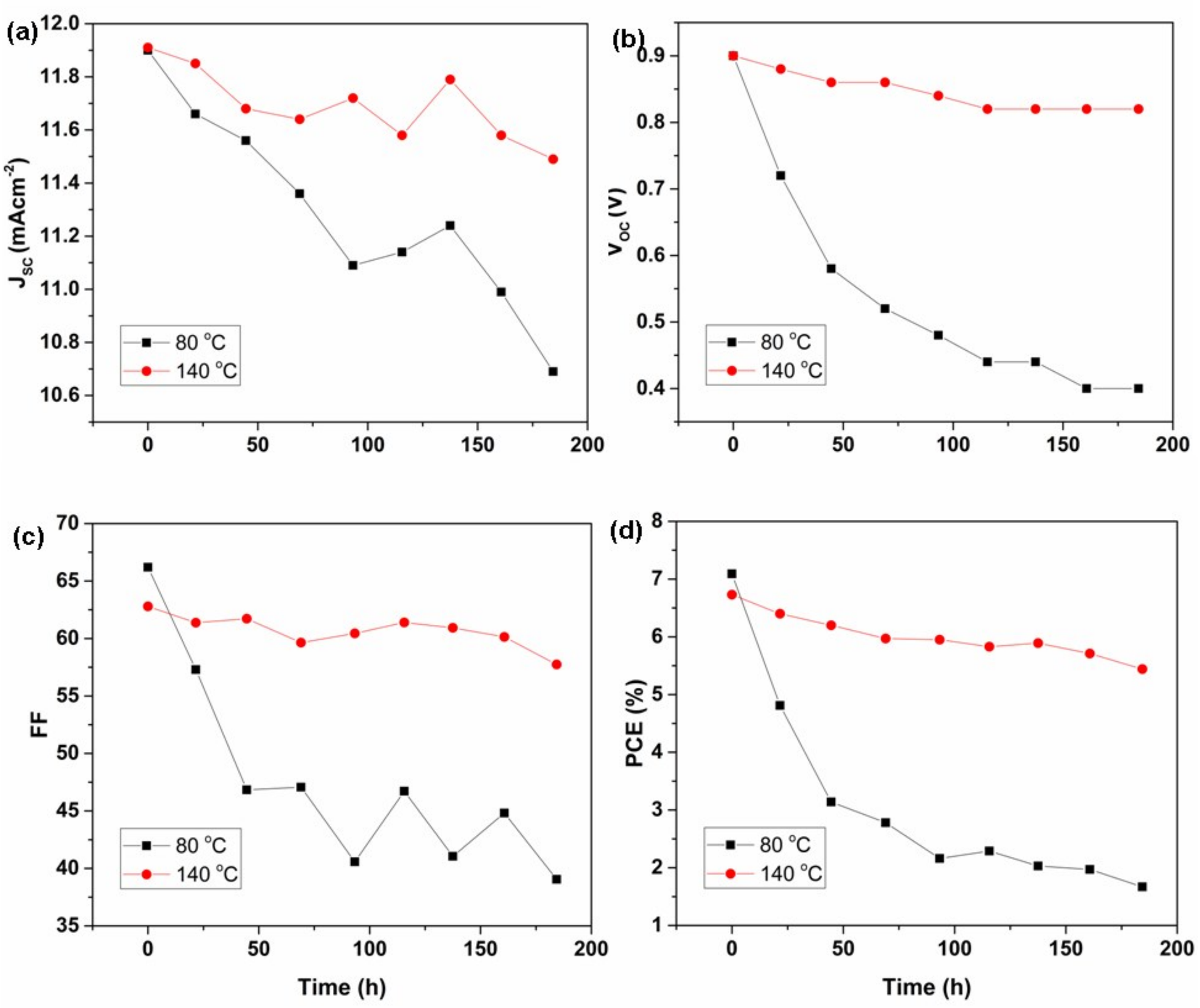

Figure S7 Variation over time in the (a) short circuit current density, (b) open circuit voltage, (c) fill factor and (d) power conversion efficiency of the inverted devices with ZnO interlayers prepared by annealing under 80º C and 140º C.

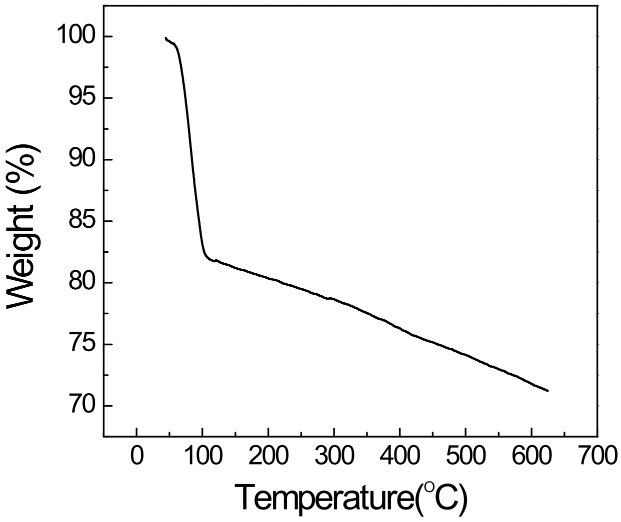

Figure S8 Thermogravimetric analysis of the aqueous ink used for the deposition of ZnO thin film.

References

1. S. Bai, Z. W. Wu, X. L. Xu, Y. Z. Jin, B. Q. Sun, X. J. Guo, S. S. He, X. Wang, Z. Z. Ye, H. X. Wei, X. Y. Han and W. L. Ma, *Appl Phys Lett*, 2012, 100.
2. J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. L. Ma, X. Gong and A. J. Heeger, *Adv Mater*, 2006, 18, 572-576.
3. J. Fan, J. D. Yuen, W. Cui, J. Seifter, A. R. Mohebbi, M. Wang, H. Zhou, A. Heeger and F. Wudl, *Adv Mater*, 2012, 24, 6164-6168.