Supplementary Information

Toward Improved Lifetimes of Organic Solar Cells under Thermal Stress: Substrate-Dependent Morphological Stability of PCDTBT:PCBM Films and Devices

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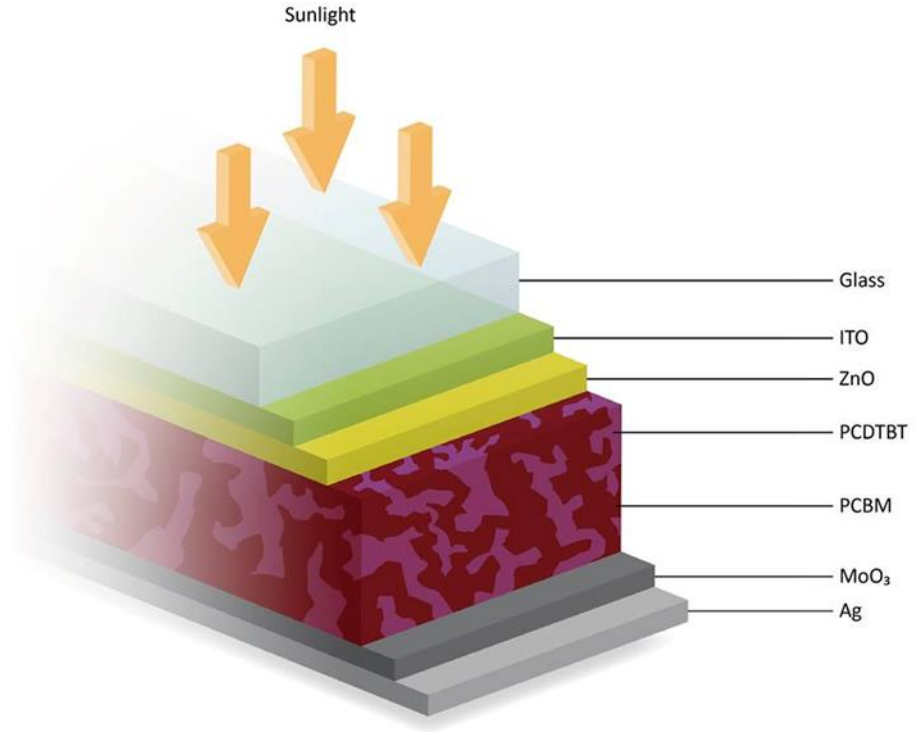

Figure S1. Organic solar cell configuration of inverted ZnO devices.

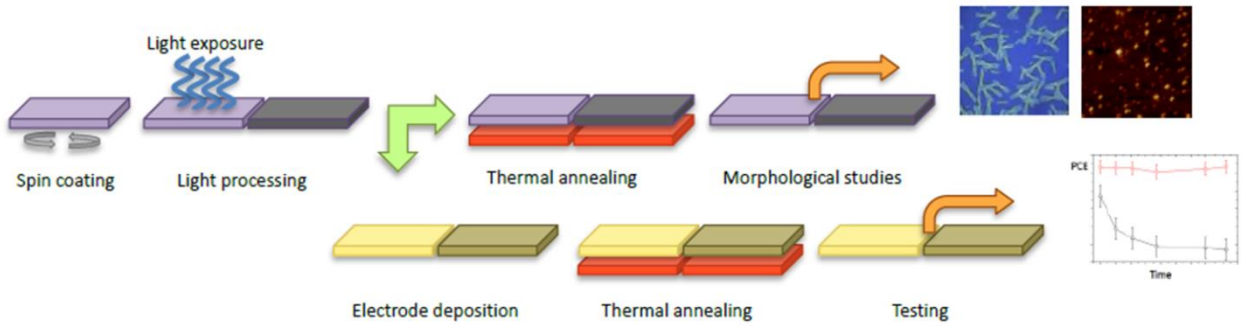

Figure S2. Protocol followed in this work for morphological quantification (top row) and device performance evaluation (bottom row).

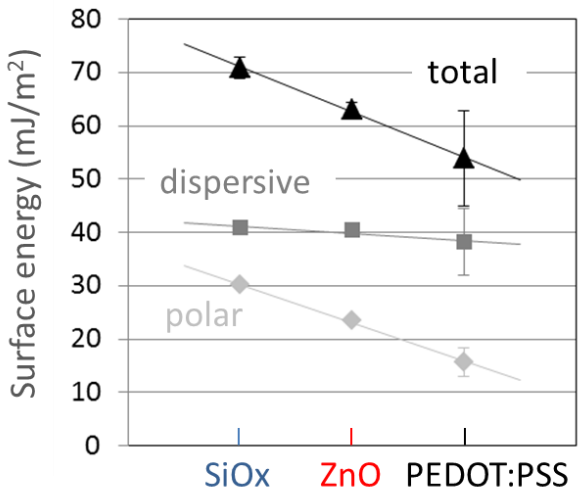

Figure S3. Surface energy of substrates SiOx, ZnO, PEDOT:PSS, including polar and dispersive contributions. The larger uncertainty for PEDOT:PSS likely arises from environmental conditions/ hygroscopy.

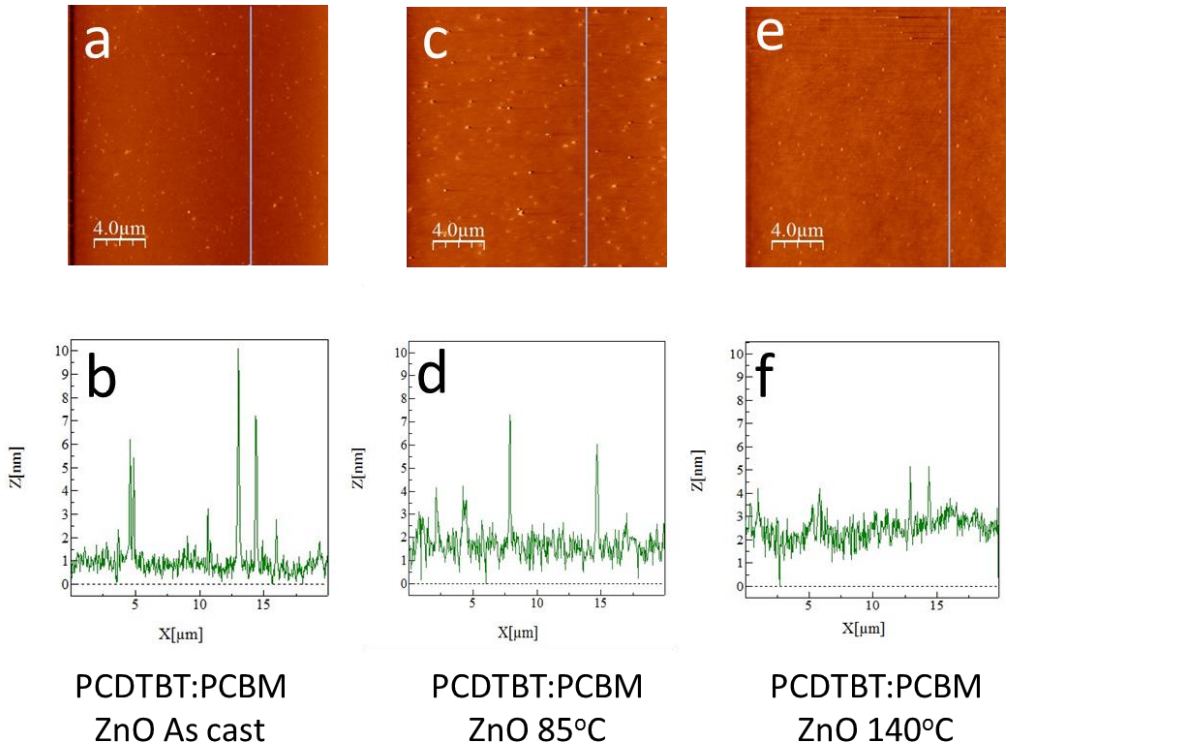

Figure S4. Line scans of AFM images of PCDTBT:PC_{60}BM (1:2) blend films without thermal annealing (a,b), blend films thermally annealed at 85°C (c,d) and 140°C (e,f) on ZnO substrates. The RMS roughness was measured as 2.03nm, 1.06nm and 0.74nm for as cast blend films, blend films thermally annealed at 85°C, and blend films thermally annealed at 140°C respectively.

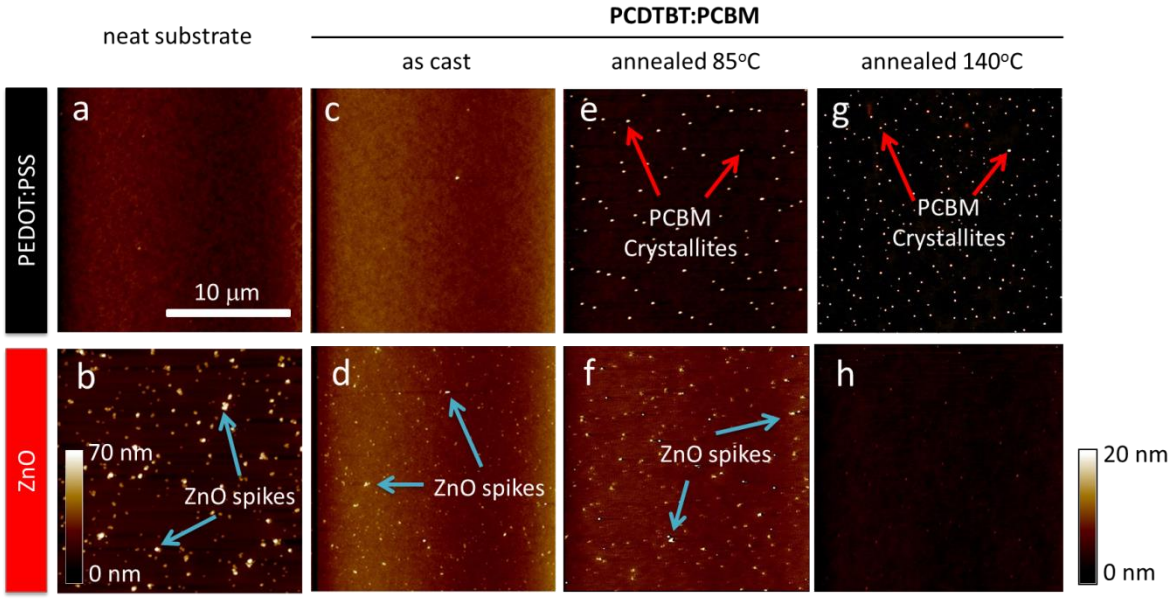

Figure S5. AFM images with arrows distinguishing nanoscale ZnO features and PC_{60}BM crystallites.

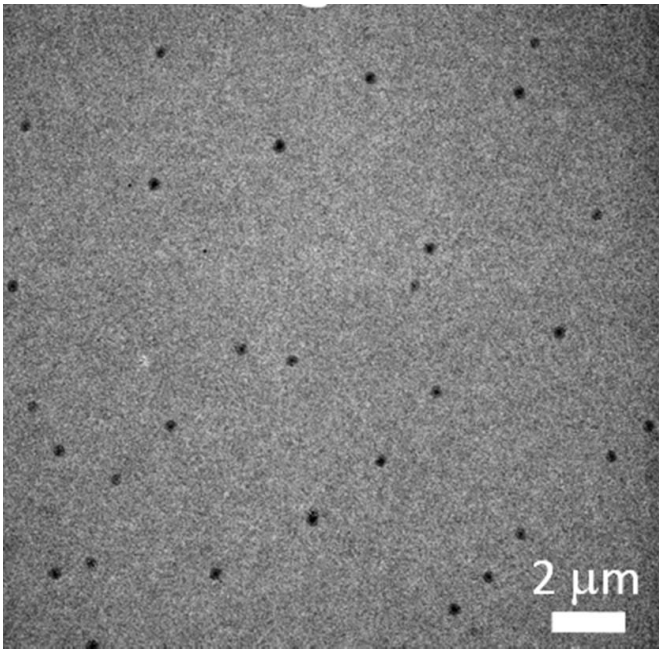

Figure S6. TEM image of thermally annealed PCDTBT:$PC_{60}BM$ blend films on PEDOT:PSS; the greater contrast of the image corresponds to the large mass and electron density expected for PCBM (approx. 1.5 g/cm^3) compared to the polymer.

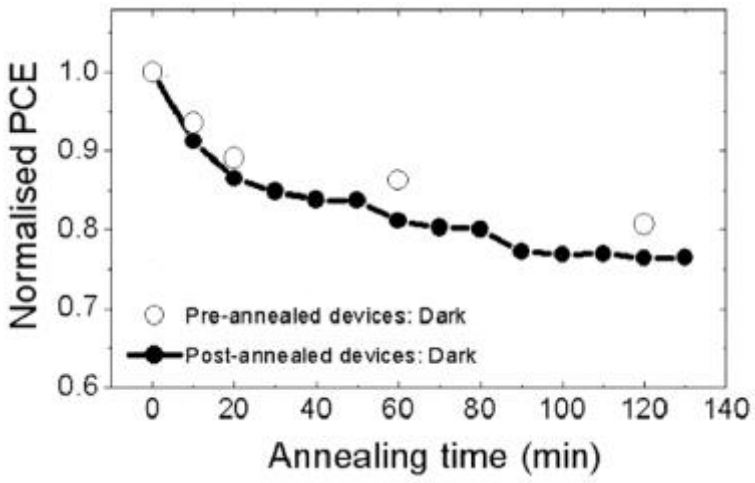

Figure S7. Systematic comparison of thermal ageing of pre- and post-annealed devices to deconvolute the effects of top interface layer/electrode and morphological changes on thermal degradation of OPV devices. This figure shows that both pre- and post-annealed devices show similar thermal stability behavior under thermal stress, inferring that the influence of top electrode on device thermal stability is insignificant, at least for the high T_g PCDTBT based blend system studied herein.

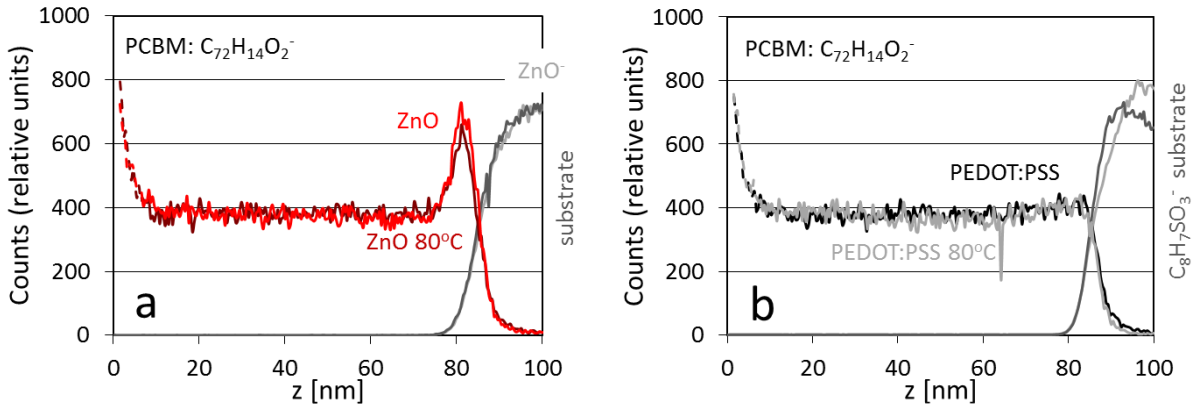

Figure S8. TOF-SIMS results for PCDTBT:PCBM (1:2) films on (a) ZnO and (b) PEDOT:PSS substrates upon thermal annealing at 80°C for 1h. The PCBM content is traced by the $C_{72}H_{14}O_2^-$ signal along the depth [z] of the film. The substrates are located by the ZnO- , SiO2 and $C_8H_7SO_3$- signals for ZnO, SiOx and PEDOT:PSS respectively, and are shown in relative units, commensurate with the $C_{72}H_{14}O_2^-$ trace. No significant changes of PCBM segregation profile as observed on either substrate: (a) PCBM remains segregated to the ZnO interface is observed, and marginally to the PEDOT:PSS interface.

Neutron reflectivity measurements were performed on the D17 reflectometer at Institut Laue-Langevin (ILL), Grenoble, in time-of-flight (TOF) mode using a wavelength range of 2 Å to 20 Å ($\Delta\lambda/\lambda$ ~ 4%) and two incident angles of incidence (0.6 and 2.4 °), obtaining a wavenumber qz window of $0.004 < qz < 0.22$ Å^{-1}. Data analyzed using Parratt32 (v 1.6, HMI Berlin).

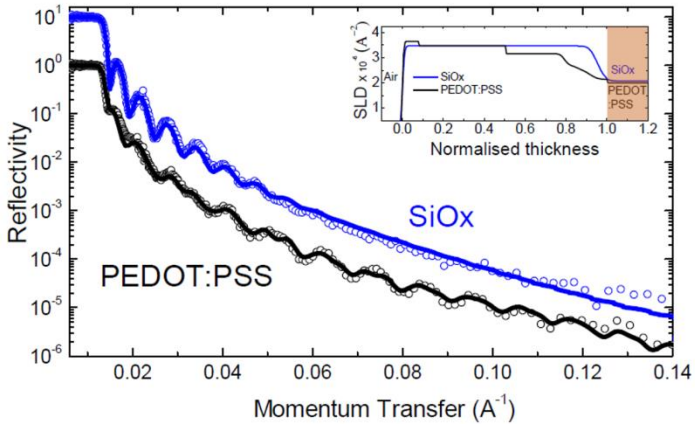

Figure S9. Neutron reflectivity profiles of PCDTBT:$PC_{60}BM$ films spun cast on SiOx and PEDOT:PSS substrates. Inset shows the corresponding scattering length density (SLD) profiles showing a broadly uniform PCBM profile in SiO_x and an asymmetrically segregated profile (towards the air interface) on PEDOT:PSS.