

Supporting Information

Impact of Molecular Orientation and Spontaneous Interfacial Mixing on the Performance of Organic Solar Cells

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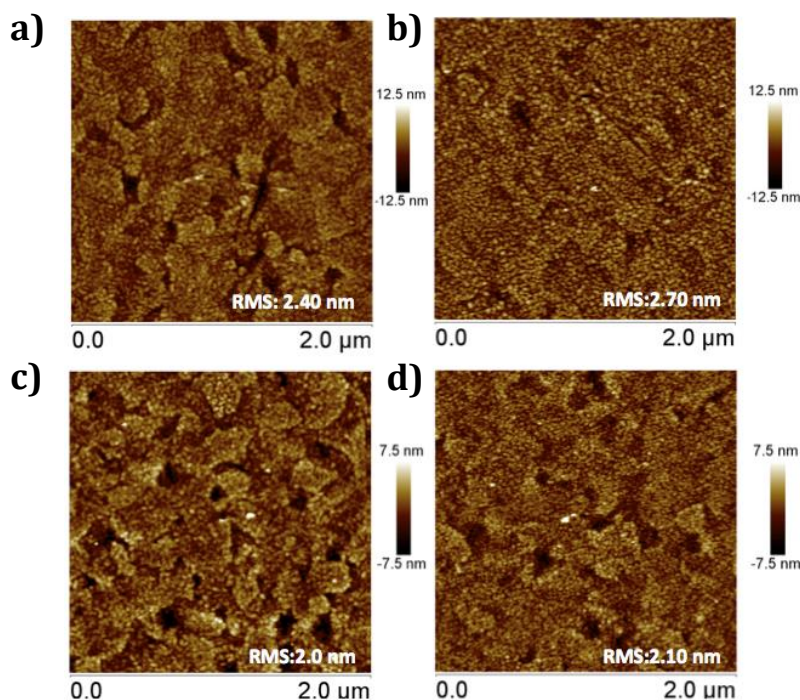


Figure S1: AFM topographic images ($2\mu\text{m} \times 2\mu\text{m}$) of 20 nm-thick ZnPc films evaporated at 0.5 \AA/s on (a) bare ITO and with an additional 3nm- C_{60} layer (c) and on CuI-coated ITO (b) and with an additional 3nm- C_{60} layer (d). Although the films appear to present slightly different morphology, they have a very similar root mean squared roughness both before and after C_{60} deposition ($\sim 2\text{ nm}$) and surface area ($\sim 4.1\mu\text{m}^2$ as measured Gwyddion image analysis software) implying that differences in surface

physical roughness does not account when comparing the number of interfacial charge transfer states. Similarly, the difference in attenuation trends as seen in the photoelectron spectroscopy data is not due to differences in film roughness.

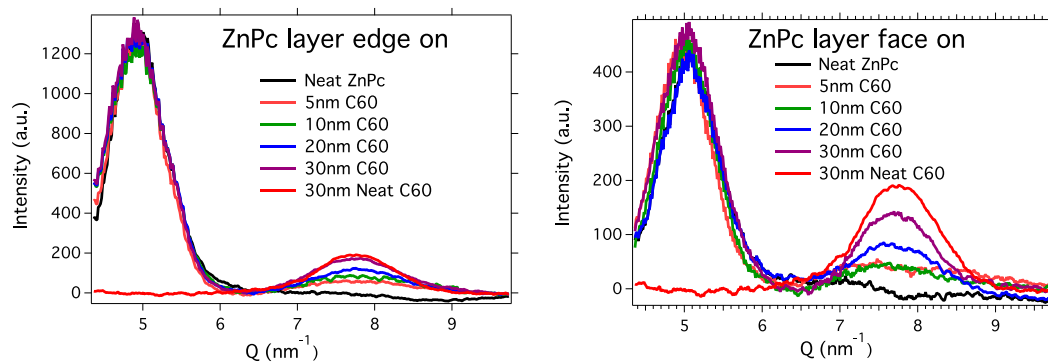


Figure S2: Line cuts showing the integrated scattered signal from the (200) and (002) peaks (at $\sim 4.9 \text{ nm}^{-1}$) for ZnPc and for C₆₀ (at $\sim 7.7 \text{ nm}^{-1}$). Shown on the left is the evolution of the scattering signal on edge-on ZnPc on the right is the similar for face-on ZnPc.

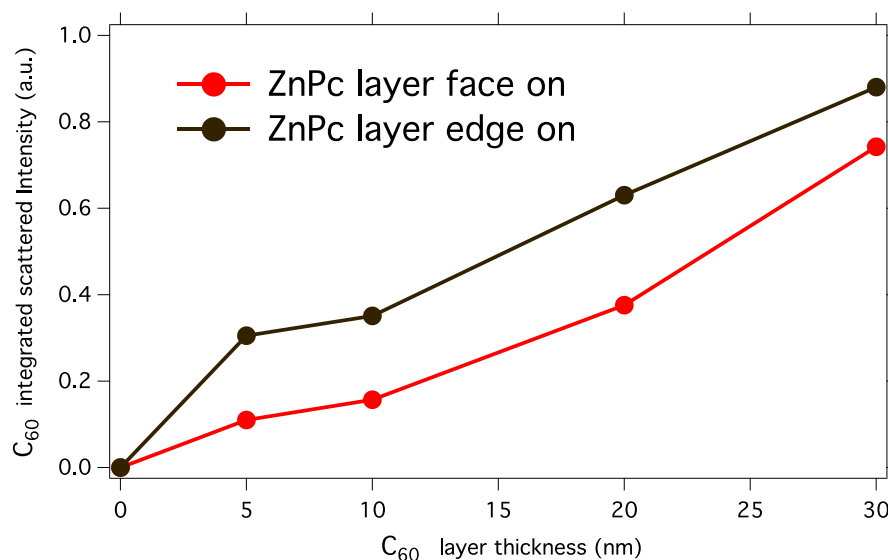


Figure S3: Integrated fullerene signal as a function of the C_{60} layer thickness. The data was obtained by fitting the fullerene peak for each thickness to a Gaussian function from which the peak area was computed and normalized to the area of the fullerene peak from a pure 30 nm neat fullerene film. Background subtraction was applied before the peak area was computed. We observe that on both face-on and edge-on ZnPc, the C_{60} signal increases quasi linearly with increased fullerene thickness but consistently, the fullerene signal from edge-on samples are higher than that of face-on samples indicating that in the face-on case, portion of the C_{60} layer scatters less light compare to the edge-on film. It is to be noted that the integrated scattered intensity of C_{60} for the sample with 30 nm C_{60} was remarkably close to that of 30 nm neat C_{60} on bare ITO as shown in Figure S2. These results further support that when C_{60} is deposited on face-on ZnPc, it mixes to a greater extent than when it is deposited on edge-on ZnPc.

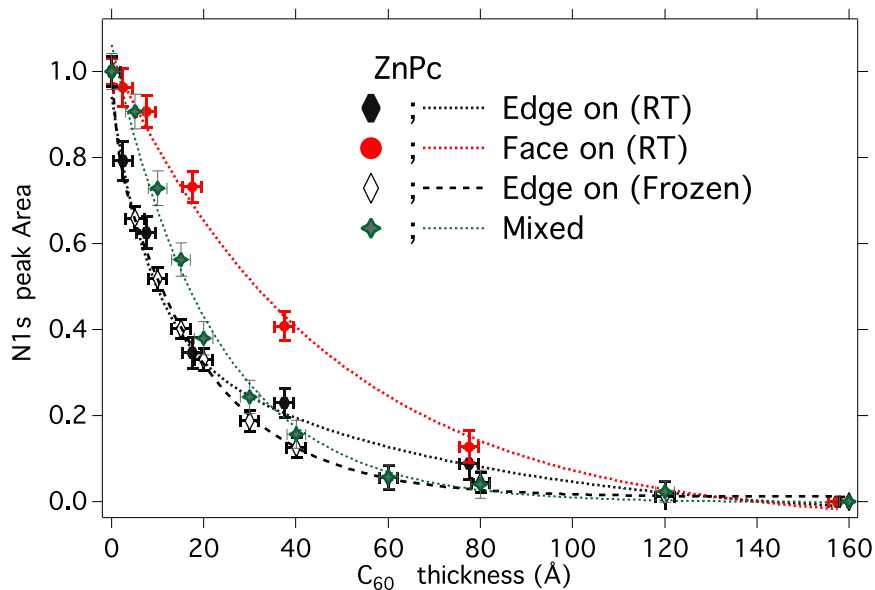


Figure S4: Attenuation of the nitrogen 1s peak from XPS of face-on and edge-on ZnPc for RT and edge-on ZnPc, frozen and with a mixed interface. Introducing a mixed layer results in a faster attenuation, which further supports, our hypothesis that the difference in attenuation for the face-on and edge ZnPc is indeed attributed to the extent of mixing. The attenuation trend for the frozen edge on ZnPc shows the fastest decay. Due to technical limitations we were not able to effectively replicate freezing conditions used during device fabrication.

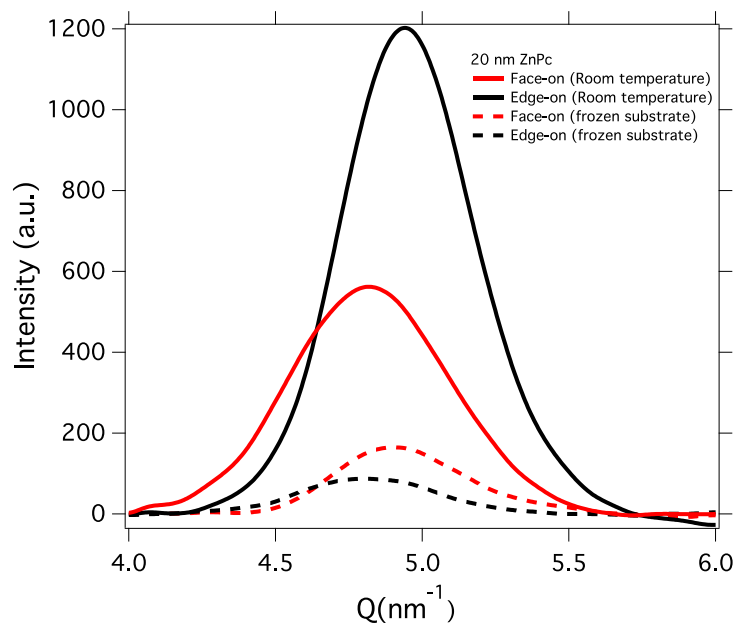


Figure S5: Combined integrated peak intensities for (200) and (002) peaks for edge-on (on ITO) and face-on (on CuI) ZnPc films grown at room temperature and on a frozen substrate (-100 degrees Celcius). The scattering intensity is significantly reduced for the films cast under cryogenic conditions suggesting that most of the film volume is disordered and only a small portion of film remains crystalline or recrystallizes.

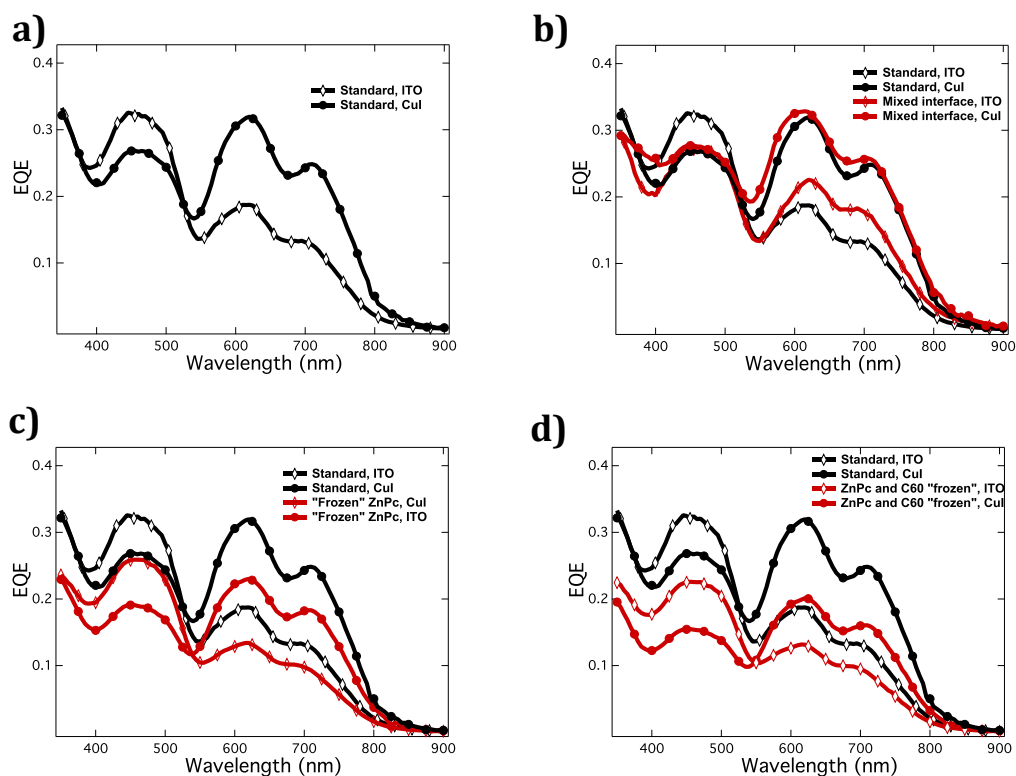


Figure S6: Comparison of EQE responses of the ZnPc:C₆₀ bilayer solar cells. Standard devices only (a); standard devices with devices with a 3 nm deliberately mixed layer (b) with devices with more abrupt interface i.e. “frozen” ZnPc (c) and with devices with disordered ZnPc bulk and more abrupt interface i.e. ZnPc and C₆₀ both “frozen” (d).

Table S1: Electronic coupling term and charge transfer state energy values extracted from fitting the absorption band of the CT state obtained from sensitive EQE measurements on devices with variable ZnPc thickness.

	Edge-on		Face-on	
ZnPc thickness (nm)	$f(\times 10^{-4} \text{ eV}^2)$	$E_{\text{CT}}(\text{eV})$	$f(\times 10^{-4} \text{ eV}^2)$	$E_{\text{CT}}(\text{eV})$
4	1.50	1.16	1.40	1.14
6	1.58	1.13	1.69	1.15
8	1.48	1.10	1.97	1.13
10	1.54	1.14	2.67	1.13