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

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Abstract

A critically important question that must be answered to understand how organic solar cells operate and should be improved is how the orientation of the donor and acceptor molecules at the interface influences exciton diffusion, exciton dissociation by electron transfer and recombination. It is exceedingly difficult to probe the orientation in bulk heterojunctions because there are many interfaces and they are arranged with varying angles with respect to the substrate. One of the best ways to study the interface is to make bilayer solar cells with just one donor-acceptor interface. Zinc phthalocyanine is particularly interesting to study because its orientation can be adjusted by using a 2-nm-thick copper iodide seed layer before it is deposited. Previous studies have claimed that solar cells in which fullerene acceptor molecules touch the face of zinc phthalocyanine have more current than ones in which the fullerenes touch the edge of zinc phthalocyanine because of suppressed recombination. We have more thoroughly characterized the system using in situ x-ray photoelectron spectroscopy and x-ray scattering and found that the interfaces are not as sharp as previous studies claimed when formed at room temperature or above. Fullerenes have a much stronger tendency to mix into the face-on films than into the edge-on films. Moreover we show that almost all of the increase in the current with face-on films can be attributed to improved exciton diffusion and to the formation of a spontaneously mixed interface, not suppressed recombination. This work highlights the importance of spontaneous interfacial molecular mixing in organic solar cells, the extent of which depends on molecular orientation of frontier molecules in donor domains.

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Introduction

Organic photovoltaics (OPVs) are emerging as a promising photovoltaic technology because of their potential low cost and ability to be manufactured in a continuous roll-to-roll manner for large-area solar energy harvesting. The power conversion efficiency (PCE) of OPVs has consistently increased over the past 10-15 years, with recent PCEs of 10% for single-junction solar cells and 12% for multi-junction solar cells.^[1-4] These PCE increases have resulted from the development of new active layer materials, new interfacial layers, optimized device architectures, and optimized active layer morphologies. In particular, in both bulk-heterojunction (BHJ) and bilayer OPVs, control over active layer morphology has widely yielded significant increases in PCE. Through understanding the influence of the bulk and interfacial morphologies, further improvements and more rapid material and device development should be possible. The performance of small-molecule OPVs is believed to depend upon a number of morphological factors, including molecular orientation in the thin film bulk with respect to the substrate normal.^[5-11] In small molecule and polymer based OPVs, the exciton diffusion length will depend upon the molecular stacking direction, thus leading to differences in the number of excitons reaching a D-A interface.^[12-15] Additionally, the rate of dissociation of these excitons at the interface between electron donating (D) and electron accepting (A) molecules is believed to depend upon the relative orientation of the donor and acceptor molecules at the D-A interface.^[6,16] However, recent computational studies of small-molecule interfaces indicate that the molecular orientation of D molecules with respect to fullerene A molecules can determine the degree of molecular mixing and disorder at

1 the D-A interface.^[17,18] These studies reveal a greater tendency of molecules to
2 intermix when the π -face of the donor is exposed to the fullerene, i.e. when D
3 molecules are oriented face-on at the D-A interface, than in the edge-on case. The
4 experimental implications of these theoretical predictions have not yet received full
5 attention and a detailed experimental study of the relationship of donor structural
6 order to interfacial mixing is needed. The lack of a precise knowledge of the exact
7 structural configuration at the D-A interface would lead to difficulties in building
8 accurate predictive models and interpretation of device data. Molecular mixing will
9 generally lead to a less crystalline or less aggregated region, which will generally
10 increase the bandgap of the materials in this mixed phase. This mixed interfacial
11 region will then thermodynamically favor exciton dissociation owing to the energetic
12 offsets between the interfacial mixed phase and the pure D and A phases.^[19-21] These
13 observations therefore emphasize the intimate relationships between molecular
14 packing, order and interfacial mixing trends that can exist in organic bilayers and in
15 bulk heterojunction thin films. We take the position that the interdependence of these
16 three factors, namely bulk molecular stacking, interfacial molecular orientation and
17 interfacial mixing, should be observable experimentally in devices based on model
18 systems where all three factors can be controlled independently.

19 Unfortunately, the complexity of the bulk heterojunction makes it exceedingly
20 difficult to precisely investigate and decouple the effects of molecular packing
21 orientation from intermixing at the D-A interface. Instead, we opt for model bilayer
22 (BL) systems in which molecular packing orientation and interfacial mixing can be
23 controlled during vacuum deposition as desired.^[9,10,22] We first test the premise that
24 face-on molecular packing orientation inherently increases the extent of mixing at the
25 ZnPc/C₆₀ interface in BL devices. Subsequently, we utilize cryogenic deposition of

C_{60} on top of ZnPc to minimize interfacial mixing and compare nominally face-on and edge-on BL devices. We confirm that the extent of molecular mixing is related to the type of molecular orientation present at the D-A interface and that the mixed layer significantly improves the overall device performance by enhancing photocurrent. We go on to show that almost all of the increase in the current with face-on films can be attributed to improved exciton diffusion and to the formation of a spontaneously mixed interface when the donor layer stacking is predominantly face-on.

Experimental section

Materials. Copper iodide and fullerene- C_{60} (sublimed grade) were purchased from Sigma Aldrich. Zinc phthalocyanine (triple sublimed) was purchased from Jilin OLED Materials. The materials were degassed in the warm crucible of an Omicron ultra high vacuum (UHV) MBE chamber in the Amassian lab at KAUST overnight before thin film deposition. When devices were made in the Thompson lab at USC, the materials were instead sublimed in-house before use.

Photoelectron spectroscopies (UPS and XPS). The ZnPc films prepared for UPS and XPS analyses were deposited on ITO-coated glass substrates (Xinyan Technology) in the UHV MBE chamber and characterized in the XPS/UPS chamber connected directly to the MBE in the Amassian lab at KAUST. The base pressure was 1×10^{-10} mbar in the MBE and XPS/UPS chambers. The ZnPc films with thickness of 20 nm were deposited at ~ 0.5 Å/s with the substrate held at room temperature. The fullerene- C_{60} overlayer was deposited stepwise. For low thicknesses (< 2 nm) low rates of 0.01–0.02 Å/s were used whereas a rate of 0.5 Å/s was used for higher thicknesses (> 2 nm). UPS and XPS spectra of the films were measured with He (I)

1 excitation (21.22 eV) and monochromated Al K α excitation (1486.7 eV), respectively.

2 The Omicron SPHERA hemispherical electron energy analyzer was used to generate
3 the spectra with pass energies of 3.0 eV and 20.0 eV for UPS and XPS, respectively.

4 The dwell time of the samples under UV illumination was minimized to minimize
5 material degradation.

6 **Subgap EQE.** The measurements were performed in the McGehee lab at Stanford
7 University and in the Amassian lab at KAUST. The EQE spectra were taken at short
8 circuit condition under focused monochromatic illumination from xenon arc
9 (Amassian lab) or tungsten (McGehee lab) lamps. The light beam was modulated by
10 an optical chopper (275 Hz). The device output current was measured as a function of
11 photon energy using a lock-in amplifier (Stanford Instruments SR 830). The lamp
12 intensity was calibrated with Ge and Si photodiodes.

13 **Device fabrication.** Devices were fabricated both in the Amassian lab at KAUST and
14 in the Thompson lab at USC. The patterned ITO on glass substrates were cleaned with
15 soap, water, acetone and isopropanol in an ultrasonic bath for 15 minutes for each
16 step followed by a 12-minute UV-ozone exposure. For devices made at KAUST, all
17 organic films were deposited in the Omicron UHV MBE system with a base pressure
18 of 10^{-10} mBar on top of precleaned ITO substrates at rates of 0.5 Å/s (ZnPc), 1 Å/s
19 (C_{60}) and 0.5 Å/s (BCP). The CuI layer (0.2 Å/s) and the Al (1 Å/s) electrodes were
20 deposited in a Thermionics vacuum evaporator housed in an Mbraun nitrogen filled
21 glove box. The sample transfer from the UHV to the glove box and back was done via
22 a vacuum suitcase (10^{-7} Torr) to avoid air exposure. For samples designed with
23 minimal interfacial mixing, liquid nitrogen cooling of the sample was performed after
24 ZnPc layer deposition and prior to C_{60} deposition, reducing the substrate temperature
25 to -100 °C according to a thermocouple mounted on the sample plate. For samples

1 requiring a disordered ZnPc layer and minimal interfacial mixing, the entire bilayer
2 stack was grown after cooling the substrate to -100 °C. Deliberate interfacial mixing
3 was made possible by co-deposition of a 3 nm thin mixed ZnPc:C₆₀ layer (1:1 ratio)
4 on top of the ZnPc film. The thicknesses of the ZnPc layer and C₆₀ layer were
5 adjusted to maintain the overall device thickness constant. Devices fabricated in the
6 Thompson lab were prepared at room temperature using a single Angstrom
7 evaporation system for organic and inorganic layers in otherwise similar conditions.

8 **Device Characterization.** At KAUST, the current-voltage characteristics of the
9 bilayer solar cells were recorded in the nitrogen glove box under AM1.5 simulated
10 illumination (ABET technology) with a spectral irradiance of 100 mW/cm². The lamp
11 intensity was calibrated using a reference silicon photodiode. At USC, a Xenon lamp
12 was used instead and the measurements were calibrated to AM 1.5 using the
13 appropriate spectral mismatch.

14 **Grazing Incidence Wide Angle X ray Scattering.** GIWAXS measurements were
15 performed at D-line at the Cornell High Energy Synchrotron Source (CHESS) and at
16 the Advanced Light Source (ALS). At CHESS, a 0.5 mm × 0.1 mm monochromated
17 X-ray beam (double-bounce multilayer monochromator) with 1.15 Å wavelength was
18 used. The diffractograms were recorder using a 50 × 50 mm² charged coupling device
19 (CCD) area detector (Medoptics) with pixel size of 46.9 μm. Experiments were
20 performed at a grazing incidence angle of 0.15° with respect to the substrate plane.
21 The detector was placed at a distance of 92 mm from the sample stage. At ALS,
22 experiments were performed with a monochromated X-ray beam (1.24 Å wavelength)
23 and a fast 2D detector (PILATUS 1M from Dectris) with pixel size of 172 μm. A
24 shallow angle of 0.15° was chosen for the incident x-rays with respect to the sample
25 plane and the detector was placed at a distance of 302.68 mm from the sample stage.

Atomic Force Microscopy. The surface morphology of ZnPc films was examined using tapping mode AFM (Agilent 5400).

UV-Vis Absorption. Absorption spectra were acquired with a Cary 5000 (Varian) spectrophotometer on ZnPc films prepared on ITO-coated glass in the same conditions used for device fabrication.

Results and discussion

Spontaneous interfacial mixing in edge-on and face-on packed ZnPc/C₆₀ bilayer films

We begin by investigating intermixing at the ZnPc-C₆₀ interface and the texture of ZnPc thin films. The molecular packing texture was modified from predominantly edge-on texture on ITO/SiO₂ to face-on texture by pre-coating the substrate with a 2 nm templating layer of copper iodide (CuI).^[6,10] In Figure 1, we present the two-dimensional grazing incidence wide angle x-ray scattering (GIWAXS) data and corresponding integrated intensities in the horizontal (in-plane) and vertical (out-of-plane) directions, which help us confirm the crystalline texture and the stacking orientation of ZnPc in thin films.^[6,10,23] The ZnPc/ITO film exhibits scattering peaks at 4.95 nm⁻¹ in the vertical direction and 5.11 nm⁻¹ and 18.52 nm⁻¹ in the horizontal direction, corresponding respectively to $d_{200}=1.27$ nm, $d_{002}=1.23$ nm and $d_{010}=0.34$ nm of the γ phase of ZnPc with the (002) plane parallel to the substrate, indicative of the edge-on stacking texture. By contrast, the ZnPc/CuI/ITO films exhibit scattering peaks at 4.91 nm⁻¹ and 18.96 nm⁻¹ in the vertical direction and 4.76 nm⁻¹ in the horizontal direction, corresponding respectively to $d_{002}=1.28$ nm, $d_{010}=0.33$ nm and $d_{200}=1.32$ nm of the γ phase of ZnPc with the (010) plane parallel to the substrate,

1 indicative of the face-on stacking texture. The (010) peak corresponds to scattering
2 along the π - π^* stacking direction, and clearly orients itself parallel to the substrate
3 plane in edge-on stacked molecules and perpendicular to the substrate plane in face-
4 on stacked molecules. We found these results to be consistent with what has been
5 reported previously.^[6,23]
6 We utilize photoelectron spectroscopy to monitor the attenuation of the ZnPc signal
7 during stepwise deposition of C₆₀ on top of the pristine ZnPc films. X-ray
8 photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS)
9 are non-invasive and do not induce further intermixing, as sputtering based depth-
10 profiling techniques such as secondary ion mass spectrometry may. In UPS and XPS
11 the escape probability of photoelectrons decreases exponentially with the sampling
12 depth. This feature can be used to probe intermolecular mixing at the interface
13 between two layers. In the case of a non-mixing, discrete interface, the signal from the
14 underlayer follows a rapid exponential decay as it gets buried, with typical inelastic
15 mean free paths of *ca.* 1 nm in UPS and *ca.* 3 nm in XPS.^[24,25] If mixing occurs, the
16 rate of attenuation from the underlayer will decrease as ZnPc mixes with the top C₆₀
17 layer. We perform stepwise deposition of C₆₀ on top of a pristine ZnPc film at room
18 temperature (RT) while monitoring the nitrogen core electron N 1s signal (XPS) or
19 the ZnPc HOMO peak (UPS) area (**Figure 2**). The observed trends in the decay rates
20 reveal a slower decrease in the case of face-on ZnPc as opposed to edge-on ZnPc.
21 These differences in attenuation rates most likely indicate more interfacial molecular
22 mixing taking place in the case of face-on ZnPc on ITO/CuI than in the case of edge-
23 on ZnPc on ITO. Since differences in film morphology and surface coverage would
24 invalidate the *in situ* XPS and UPS conclusions, atomic force microscopy (AFM) was
25 performed on the edge-on and face-on ZnPc films before and after C₆₀ deposition to

1 compare the roughness of the bare films and surface coverage with C₆₀. The AFM
2 analysis indicates that both ZnPc films are initially equally smooth and become
3 equally smoother after 3 nm C₆₀ deposition (**Figure S1, Supplementary**
4 **Information**). This confirms that the differences in attenuation trends are not
5 primarily influenced by morphological factors and can be assigned to differences in
6 the extent of interfacial mixing. To further validate these observations, we have
7 complimented the surface-sensitive *in situ* XPS and UPS studies with more bulk
8 sensitive measurements relying on a systematic GIWAXS analysis of fullerene-
9 fullerene scattering with increasing thickness of fullerene on face-on and edge-on
10 stacked ZnPc. Above the critical angle of the film, GIWAXS probes the entire sample
11 volume, including the buried fullerene-ZnPc interface. We specifically look for the
12 evolution of fullerene scattering features with increasing deposited thickness, which
13 should behave monotonically if fullerene does not mix with the underlayer, whereas
14 the same signal should decrease if instead fullerene diffuses and mixes with the ZnPc
15 underlayer. While no significant change was detected in the evolution of the ZnPc
16 peak, the C₆₀ peak evolution indicates meaningful differences between edge-on and
17 face-on ZnPc/C₆₀ bilayers (**Figure S2, Supplementary Information**). Fitting the
18 fullerene peak to a Gaussian function and performing appropriate background
19 subtractions, we plot the integrated fullerene signal as a function of the layer
20 thickness (**Figure S3, Supplementary Information**). We observe that the C₆₀ signal
21 increases quasi linearly both on face-on and edge-on ZnPc films with increased
22 fullerene thickness but consistently, the fullerene signal from edge-on samples are
23 higher than that of face-on samples. This shows that in the face-on case, a portion of
24 the C₆₀ layer, and particularly the part deposited initially, scatters less than on edge-on
25 ZnPc. Yet, it is known that the C₆₀ peak has the same characteristics in both cases

1 meaning the crystallite orientation in both cases were isotropic and the d-spacing is
 2 identical within the experimental error. We further remark that, the integrated
 3 scattered intensity of the 30 nm thick fullerene film on edge-on ZnPc is remarkably
 4 close to that of 30 nm C₆₀ on bare ITO while the scattered intensity of the 30 nm thick
 5 film on face-on ZnPc is substantially lower than the control on ITO, indicating that
 6 more C₆₀ was lost through diffusion into the underlayer (**Figure S2, Supplementary**
 7 **Information**). In light of the GIWAXS, XPS and UPS results, we conclude that when
 8 fullerene-C₆₀ is deposited on face-on ZnPc, it mixes to a greater extent than when it is
 9 deposited on edge-on ZnPc, in agreement with computational predictions which have
 10 identified differences in surface energies of face-on and edge-on films as the main
 11 driving force for interfacial mixing.^[17]

12 **Impact of interfacial mixing on the photovoltaic performance**

13 We evaluate the impact of spontaneous interfacial mixing for the above molecular
 14 packing orientations by fabricating a series of devices with different ZnPc molecular
 15 packing orientations at room temperature. The device architectures are based on the
 16 standard device stacks: *ITO/ZnPc (20 nm)/C₆₀ (45 nm)/BCP (12 nm)/Al (100 nm)* for
 17 edge-on ZnPc and *ITO/CuI (2 nm)/ZnPc (20 nm)/C₆₀ (45 nm)/BCP (12 nm)/Al (100*
 18 *nm)* for face-on ZnPc. The J-V curves and associated bilayer cartoons are presented in
 19 **Figure 3**, while device parameters and statistics are summarized in **Table 1**. The
 20 device characteristics of room temperature ZnPc and C₆₀ on ITO and CuI/ITO are
 21 consistent with previously reported data whereby an increase in PCE of ~70% was
 22 observed,^[4] namely from 1.7% to 2.9% in going from a predominantly edge-on to
 23 face-on stacking orientation in the ZnPc layer.

Figure 1. (a, b) 2D GIWAXS patterns of 20 nm-thick and (c, d) integration plots in horizontal (black) and vertical (red) of the ZnPc films grown on (a, c) ITO/glass and (b, d) on 2nm CuI-coated ITO/glass substrates. Q_{xy} and Q_z refer to the in-plane and out-of-plane components of the scattering vector, respectively.

Figure 2. Attenuation of the nitrogen 1s peak from XPS (a) and ZnPc HOMO peak from UPS (b) of face-on and edge-on ZnPc with increasing C_{60} thickness. Both curves feature a more rapid decay of the photoelectron signal from the ZnPc layer in the edge-on case. In the face-on case the slower decay of the signal suggests more

1 interfacial mixing. The dotted lines are added as visual guides to the eye. The nitrogen
2 1s peak was selected for the analysis because of its larger peak strength as compared
3 to the Zn 2p peak.

5 **Table 1.** Photovoltaic performance characteristics measured under 100 mW/cm²
6 simulated AM1.5 irradiation. J_{sc} is short-circuit current density, FF is fill factor, V_{oc} is
7 the open-circuit voltage and PCE is power conversion efficiency. Standard bilayer
8 refers to the RT devices under investigation.

9

Description	Standard bilayer		“Frozen” C ₆₀ (More abrupt interface)		Standard bilayer with mixed interface		“Frozen” ZnPc and C ₆₀ (Disordered bulk and more abrupt interface)	
ZnPc stacking orientation	Edge-on	Face-on	Edge-on	Face-on	Edge-on	Face-on	Edge-on	Face-on
ZnPc dep. temp. [°C]	25	25	25	25	25	25	-100	-100
C ₆₀ dep. temp. [°C]	25	25	-100	-100	25	25	-100	-100
Mixed interlayer?	No	No	No	No	Yes	Yes	No	No
V _{oc} [V]	0.57±0.02	0.61±0.01	0.56±0.03	0.61±0.02	0.60±0.02	0.60±0.02	0.58±0.02	0.58±0.01
FF[%]	63.30±0.5	70±0.4	59.70±0.5	68.10±0.6	62.40±0.6	69.10±0.3	66.30±0.4	64.00±0.6
J _{sc} [mA/cm ²]	4.70±0.1	6.70±0.1	4.10±0.1	5.60±0.1	5.60±0.1	7.70±0.1	4.40±0.1	5.20±0.1
PCE [%]	1.70±0.06	2.90±0.04	1.40±0.04	2.30±0.05	2.10±0.05	3.20±0.04	1.70±0.05	1.90±0.06

10
11 To make solar cells with minimized interfacial mixing, we cool the substrate to
12 -100 °C after ZnPc deposition at room temperature and subsequently deposit C₆₀ on
13 ZnPc (Table 1: “Frozen” C₆₀, Figure 3a, b). With these cells, a reduction in the device
14 PV performance is observed from 1.7% to 1.4% and from 2.9% to 2.3 % in the edge-
15 on and face-on cases, respectively. This mostly stems from a reduction in
16 photocurrents; ~0.5 mAcm⁻² vs ~1.10 mAcm⁻² drops in the edge-on and face-on cases,
17 respectively. A small decrease in FF is also noted in both cases and could be
18 attributed to the presence of more disorder in the C₆₀ layer deposited in cryogenic
19 conditions. While we do not exclude the possibility of some interfacial mixing
20 occurring once the device returns slowly to room temperature (**Figure S4,**
21 **Supplementary Information**), we expect that molecules diffuse less once the bilayer
22 is formed since molecules in the bulk or at the interface often do not enjoy the same
23 degree of mobility as do molecules at surfaces.^[26-28] The significant reduction in J_{sc}
24 upon minimizing the intermixing suggests that the difference in photocurrents in

devices prepared at room temperature is in part due to differences in the degree of interfacial mixing for face-on and edge-on packed ZnPc films. This more favorably affects the BL device photocurrent in the face-on case since the mixed phase has been shown to induce band gap widening which leads to an energetic cascade that assists excitons dissociation.^[21,33]

Figure 3. Current-voltage characteristics under illumination (solid curves) and in the dark (dotted lines) of face-on and edge-on ZnPc/C₆₀ BL solar cells with altered interfacial and bulk molecular packing structures. The black color shows the characteristics of the standard devices for comparison. The inset schematically illustrates the ZnPc molecular conformation and the extent of mixing at the interface. The grey circles illustrate fullerene-C₆₀ in the deliberately mixed layer (a, b): The

1 fullerene-C₆₀ is deposited at -100 °C (referred to as “frozen”) to reduce interfacial
2 mixing in order to achieve a more abrupt interface. **(c, d)**: Devices made with a
3 deliberately mixed co-deposited interfacial layer demonstrating the impact of the
4 mixed layer on PV performance. **(e, f)**: Both the ZnPc and C₆₀ layers are deposited at
5 -100 °C and therefore “frozen” to achieve a more abrupt interface and a disordered
6 ZnPc bulk.

8 To further probe whether interfacial mixing is a key and positive contributor to the
9 performance improvement in face-on vs. edge-on BL solar cells, BL devices with a
10 deliberately 1:1 mixed 3 nm interfacial layer on top of edge-on and face-on ZnPc
11 films (Figure 3c, d) were fabricated. As expected, the presence of the mixed layer
12 improves the edge-on BL device efficiency by ~23% from 1.7% to 2.1%, and by
13 ~10% in the face-on case. The deliberately introduced mixed layer is hence less
14 beneficial for the face-on device, which already had a mixed region spontaneously
15 formed. More importantly the V_{oc} of the face-on device remains unchanged at ~0.6V
16 while an increase in V_{oc}, to practically an identical value to that of the face-on device,
17 is observed for the edge-on device. In the “frozen” ZnPc devices (Table 1) the
18 opposite trend in V_{oc} is observed and vice versa, confirming that the reason for the
19 observed changes in Voc is associated to the degree of interfacial mixing. Although a
20 more focused study of recombination mechanisms is needed to fully understand these
21 changes in V_{oc}, the observations presented herein provide strong indication that the
22 spontaneously formed mixed layer is responsible for the higher V_{oc} observed in the
23 face-on devices. However, this increase in V_{oc} stemming from the mixed phase is *a*
24 *priori* counterintuitive when examined from the point of view of disorder in the mixed
25 interfacial layer, but as will be discussed later and has been shown in the context of
26 polymer:fullerene solar cells, disorder in the mixed interfacial phase favorably
27 impacts interfacial energetics in a manner that favors charge generation.^[21,33] Hence,
28 in light of these results together with the photoelectron spectroscopy data, it appears

1 that more spontaneous interfacial mixing occurs in nominally face-on BL devices than
2 in edge-on ones fabricated at RT, and that this interfacial mixing is in part responsible
3 for the higher photocurrent, V_{oc} and power conversion efficiency in the face-on
4 devices.

5 A direct and inevitable consequence of intermixing should be an increase in the
6 number of ZnPc:C₆₀ bimolecular charge transfer (CT) complexes at the D-A interface.

7 An important characteristic of the CT complex is that it can be photoexcited by direct
8 sub-gap monochromatic illumination and the resulting excited states can generate free
9 charges which can be collected by the electrodes. The generated charges can be
10 detected by a sensitive external quantum efficiency (EQE) measurement performed
11 on a PV device, making it possible to directly investigate interfacial mixing in actual
12 devices. The EQE from the charge transfer state absorption band is modeled by
13 equation 1.

$$EQE = \frac{f}{E\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{CT} + \lambda - E)^2}{4\lambda kT}\right) \quad (1)$$

15 Here, E_{CT} is the energy of the CT state, λ is related to the reorganization energy and
16 energetic disorder,^[29] and f is directly related to the intensity of the CT absorbance
17 band. Specifically, f is the product of the number of interfacial CT complexes, the
18 internal quantum efficiency (IQE) of the CT state, and the square of the electronic
19 coupling matrix element. Therefore, f should be proportional to the film thickness if
20 the CT states are assumed distributed evenly throughout the film. In addition, with f
21 being directly proportional to the number of CT complexes, an increase in f for the
22 same material system can be utilized as a means of determining the relative number of
23 CT complexes. Based on this, we have fabricated a series of BL devices with variable
24 ZnPc thickness and measured the strength of the CT absorbance (**Figure 4a,b**).

1 Fitting the CT band to the above equation, we extract f and E_{CT} for each device (see
2 **Table S1, Supplementary Information**). The magnitude of the CT absorbance
3 increases with ZnPc thickness (Figure 4b, inset) in the face-on case (~90% increase in
4 f) while remaining virtually unchanged in the edge-on case. It is important to note that
5 the direct excitation (1.5-2.0 eV) of the face-on ZnPc also increases with increased
6 thickness and follows the same trend as the CT band excitation. This could therefore
7 lead to a misinterpretation of the observed increase in f (**Figure 4b,d**). However,
8 looking at the corresponding trends in the edge-on ZnPc whereby the increase in the
9 direct excitation leads to virtually no increase in the CT band excitation (**Figure 4a,c**),
10 we conclude that the opposite trend observed in the face-on case is indeed due to a
11 real increase in CT absorption at the D-A interface and not to any tailing of the
12 absorption of ZnPc. In addition, we rule out the possibility that the difference in CT
13 state absorption may be due to differences in interfacial physical roughness between
14 the edge-on and face-on films on the basis of AFM analysis (**Figure S1,**
15 **Supplementary Information**), which revealed very similar surface roughness for
16 both types of films. Similarly, one might argue that the D/A electronic coupling
17 should be lower in the edge-on orientation, which decreases f , resulting in fewer
18 subgap states being excited upon illumination. However, we believe that even if that
19 were the case, the dependence of the CT absorption on the film thickness for films
20 prepared in identical conditions should still be representative of the variation in the
21 true concentration of CT states that are formed as the film thickness is varied, making
22 such relative comparisons meaningful. Hence, the increase in CT absorbance most
23 likely corresponds to an increase in the number of CT states as a result of increased
24 mixing at the face-on ZnPc/C₆₀ interface. The fact that f increases with film thickness
25 in case of face-on stacked ZnPc films, but not for edge-on stacked films is consistent

1 with no additional intermixing occurring upon deposition of the first monolayer of
2 fullerene in the latter case, whereas in the former case the supply of more fullerene
3 allows the system to undergo further intermixing, resulting in more CT state
4 formation.

5 6 7 **Role of bulk molecular packing and interfacial mixing on the amount of excitons** 8 **reaching a D-A interface**

9 We now have a better handle over the influence that the degree of mixing at the D-
10 A interface can have on the device photocurrent. One should not forget, however, that
11 differences in molecular orientation at the interface stem from stacking differences in
12 the bulk of the donor film. Bulk orientation differences may impact the exciton
13 diffusion length and film absorbance, and therefore affect the device photocurrent.
14 We evaluate the differences in the number of excitons reaching a D-A interface by
15 comparing the EQE of BL devices with different ZnPc thickness, both in
16 predominantly edge-on and face-on orientations (Figure 4c,d). The EQE signal in the
17 case of the edge-on BL devices increases marginally with the ZnPc layer thickness in
18 the key spectral range 1.5-2.2 eV corresponding to the ZnPc Q-band absorption. By
19 contrast, a significant increase of EQE is seen with increasing thickness of face-on
20 ZnPc. These observations indicate that more excitons are reaching the D-A interface
21 for thicker ZnPc films in the presence of predominantly face-on stacking of ZnPc
22 molecules in the donor layer than in the presence of edge-on stacking, likely due to
23 both differences in exciton diffusion length and interfacial mixing in favor of the
24 former.

Figure 4. Top: Spectrally resolved sensitive EQE spectra of ZnPc/C₆₀ BL cells including in the subgap spectral range with varying thickness of predominantly edge-on (a) and face-on (b) stacked ZnPc deposited at room temperature showing the evolution of the CT absorption band. The fits (dotted curves) are performed to extract the electronic coupling term (f), which is directly proportional to the number of interfacial charge transfer states. **Inset of (b):** Evolution of f with ZnPc film thickness for the edge-on and face-on stacked BL devices. The increase observed in the case of face-on stacked ZnPc indicates increased degree of interfacial mixing. **Bottom:** Evolution of the spectral response of the ZnPc/C₆₀ BL solar cells with edge-on (c) and face-on ZnPc donor layer (d) as a function of the ZnPc layer thickness. For the edge-on ZnPc BL devices, the EQE increases only marginally with increasing ZnPc layer thickness. For the face-on ZnPc BL devices, the EQE signal increases more markedly with increasing ZnPc thickness.

We further seek to isolate and validate the contributions to the photocurrent from the bulk molecular packing and interfacial mixing. We have fabricated devices wherein both the ZnPc and the C₆₀ layers are deposited at cryogenic temperatures. This promotes a reduced molecular ordering in the ZnPc bulk (**Figure S5, Supplementary Information**) while also maintaining a minimally mixed interface. The device results (Table 1, “Frozen” ZnPc and C₆₀ and **Figure 3e,f**) show very close

1 PCEs for BL devices on ITO and ITO/CuI, namely 1.7% and 1.9%, respectively,
2 consistent with the fact that both the interface and the bulk are nearly identical in the
3 two device architectures. In comparison to the previous case in which C₆₀ was
4 deposited under cryogenic conditions on ZnPc deposited at room temperature (2.3%),
5 the BL device fabricated fully in cryogenic conditions on CuI/ITO exhibits a further
6 decrease in PCE attributed to all device performance parameters degrading, especially
7 the FF. We find it intriguing and telling that a disordered crystalline ZnPc film should
8 behave just as well as a predominantly edge-on oriented polycrystalline film in terms
9 of device performance. This may be an indication that out-of-plane exciton diffusion
10 in small-molecule donor films exhibiting predominantly in-plane π -stacking is similar
11 to that of a fully disordered layer. Importantly, these results indicate that bulk
12 ordering and stacking direction play important roles alongside interfacial mixing at
13 improving PV performance in small-molecule organic solar cells. The same may not
14 be true in polymer-fullerene solar cells, where intrachain transport is believed to be a
15 dominant contributor to carrier and energy transport.^[30-32] Finally, the mixed
16 interfacial layer in face-on devices is believed to introduce an energetic gradient
17 between the pure fullerene and ZnPc phases that should assist in charge separation
18 and reduce geminate recombination as has been demonstrated by others.^[21,33] This
19 could explain the increase in V_{oc} in the edge-on ZnPc device with deliberate mixing.
20 However a full explanation requires a detailed investigation and is outside the scope
21 of this study.

22 23 **Conclusion**

24 The present study reveals the impact that stacking orientation can have on the
25 donor-acceptor interface in organic solar cells. We have focused our attention on

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1 vacuum-deposited bilayer solar cells where state-of-the-art ultra high vacuum
2 molecular beam deposition techniques allow us to control and ultimately decouple
3 interfacial and bulk molecular stacking effects, with broad implications for either
4 solution and vacuum deposited small-molecule, oligomer and polymer based bilayer
5 and bulk heterojunction solar cells.

6 Through careful experimentation we find that differences in stacking orientation in
7 the bulk and surface of ZnPc films can lead to significant differences in the mixing
8 behavior at the interface with C₆₀. We demonstrate that spontaneous interfacial
9 mixing at room temperature is more favored in face-on terminated ZnPc films than in
10 edge-on terminated ones. The induced mixed layer benefits the bilayer solar cells by
11 increasing the photocurrent and open circuit voltage and its presence at the D-A
12 interface is believed to promote charge separation owing to changes in the energetic
13 landscape that it creates. We have also found that when the molecules pack face-on in
14 the bulk, this contributes to more excitons reaching D-A interfaces, and hence also
15 accounts for the observed improvement in device photocurrent.

16 This study highlights the importance of molecular packing in OPV bilayer devices
17 and its dual impact on both bulk and interfacial PV processes. The ability to precisely
18 control the molecular orientation both in the bulk and at the D-A interface in order to
19 achieve more face-on donor films may play a key role in enabling further
20 improvements in PV performance. This study equally highlights the risks associated
21 to extrapolating interface-related conclusions and interpreting device performances
22 simply on the basis of bulk molecular stacking information in small molecules solar
23 cells either in bilayer or bulk heterojunction device configurations without looking at
24 the state of frontier molecules before and after bilayer formation.

While some of the outcomes of the study, such as the link between bulk molecular stacking and exciton diffusion, may not directly apply beyond bilayer solar cells to modern bulk heterojunction systems, our approach nevertheless offers opportunities to investigate a subset of interfaces within a typical bulk heterojunction solar cell but which, due to their extremely complex combination of morphologies, currently cannot be directly addressed using mean-field spectroscopic techniques. Certainly, the conclusions of this study, with regards to spontaneous interfacial mixing, its link to conformation of frontier molecules and the influence of mixing on free carrier generation and recombination are believed to be widely applicable to bulk heterojunction solar cells. [35-37]

Supporting Information Available

AFM topographic images of pure ZnPc and ZnPc/C₆₀ bilayers films; GIWAXS data for ZnPc/C₆₀ bilayers and grown frozen ZnPc films; XPS attenuation curves for ZnPc/C₆₀ bilayers with cryogenically cooled substrate (abrupt interface) and deliberately mixed interface; EQE spectra for standard, mixed interface, abrupt interface and ZnPc with reduced crystallinity bilayer devices; electronic coupling term and charge transfer state energy values for ZnPc/C₆₀ bilayers.

This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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