Measuring the Thickness and Potential Profiles of the Space-Charge Layer at Organic/Organic Interfaces under Illumination and in the Dark by Scanning Kelvin Probe Microscopy

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Supporting Information

ABSTRACT: Scanning Kelvin probe microscopy was used to measure band-bending at the model donor/acceptor heterojunction poly(3-hexylthiophene) (P3HT)/fullerene (C60). Specifically, we measured the variation in the surface potential of C60 films with increasing thicknesses grown on P3HT to produce a surface potential profile normal to the substrate both in the dark and under illumination. The results confirm a space-charge carrier region with a thickness of 10 nm, consistent with previous observations. We discuss the possibility that the domain size in bulk heterojunction organic solar cells, which is comparable to the space-charge layer thickness, is actually partly responsible for less than expected electron/hole recombination rates.

KEYWORDS: band bending, charge generation layer, scanning kelvin probe, fullerene, polymer

Carrier generation and recombination (G/R) processes at organic/organic (O/O) interfaces are crucial to the performances of both organic photovoltaics (OPVs) and commercially successful organic light-emitting diodes. Many aspects of organic heterojunctions, in turn, influence G/R including energy band alignment,1 charge mobility,2 and spatial confinement of charge due to nanostructured morphologies [e.g., bulk donor/acceptor (D/A) heterojunctions].3 A particularly important point for G/R is the thickness of the dark-state space-charge layer (SCL) at O/O interfaces.4 As in conventional semiconductor p/n junctions, the space charge at organic interfaces is derived from equilibrium dark-state charge transfer and results in energy-level band bending. The band bending is such that it can promote electron/hole recombination,5 which is undesirable in OPVs, for example. Unlike conventional semiconductors, however, the SCL at organic interfaces is extremely thin, far less than 100 nm, even in most typical cases where there are no added dopants.6–9 The difference between the organic and inorganic systems, of course, is that the donor and acceptor molecules themselves ionize in the region of the interface. Their concentration is high so the SCL is thin. In the end, it is important to understand both the thickness and the potential profile at O/O interfaces because both influence electron/hole recombination rates critical to the device performance.10

There have been a few prior measurements of the SCL thickness and potential profiles by ultraviolet photoelectron spectroscopy (UPS). These studies have shown that in metal/organic (M/O) and O/O systems frontier energy levels can display either a flat-band structure or band bending over a SCL.11,12 The consensus of these studies is that the SCL is often on the order of 10 nm in thickness. The fact that this length scale is comparable to domain sizes in bulk heterojunctions (BHJs) has interesting implications as to whether band bending is ever really important at the critical charge-separating interfaces. That is, overlapping SCLs across a D/A/D heterostructure may effectively lead to flat bands even in the presence of space charge.13

Here we have employed scanning Kelvin probe microscopy (SKPM) as an alternative to UPS to measure the space charge at a model O/O interface, namely, poly(3-hexylthiophene) (P3HT)/fullerene (C60), in the dark and under illumination. Our measurements confirm the small thickness reported for similar interfaces by UPS. The imaging capability of SKPM offers opportunities to extend this work to nanostructured interfaces that can be directly mapped, as has been done for organic/inorganic-based D/A mixtures such as P3HT/TiO2.14,15 Indeed, Ishii et al. have shown that SKPM can reveal important information about the interface charge, D/A charge transfer, and charge trapping at domain boundaries.16 Here we have applied SKPM for the first time to examine charge separation at the benchmark P3HT/C60 interface, which serves as a model D/A interface relevant to solar cells. We find that, by measuring the
surface potential profile as a function of the C_{60} film thickness, we can measure the SCL thickness.

Figure 1a shows a diagram of the experiment. An SKPM probe is moved across the surface, and the difference in the work function between the surface and probe creates an electric field, which is nullified through the application of a direct current (DC) voltage bias. The bias then provides a measurement of the work function difference between the probe and sample, or the contact potential difference (CPD), at any given point. Comparing the CPD between features on the same surface using the same probe then provides a measurement of the work function difference between features. When P3HT, indium/tin oxide (ITO), and C_{60} are brought into contact, the Fermi levels align, and as a result, ΔΦ_{C_{60}/P3HT} represents the difference in the surface potential that the SKPM tip (Figure 1a). Ohmic contact to the sample was established through the application of silver epoxy to the bare ITO surface. The P3HT was grounded through the underlying ITO, while the C_{60} film remained coupled to the electrode only through the P3HT layer. Using a two-pass, constant-height SKPM lift mode, the surface topography and surface potential were mapped both over the lateral length scales required to obtain contrast between C_{60} and P3HT layers (>50 μm) and between local features (<5 μm).

To observe the illuminated state, the sample was exposed to a white-light halogen bulb held at a distance of ~4 mm under a variety of precalibrated light intensities while being measured in the SKPM probe station. The resulting ΔΦ_{C_{60}/P3HT} values are shown in the Supporting Information as a function of the incident light intensity. The change with the intensity follows a logarithmic trend consistent with the expected behavior of the open-circuit voltage (V_{OC}) in traditional OPV cells (see the Supporting Information).19,20

Under illumination, the relative work function difference between P3HT and ITO does not show a significant shift (Figure S4). Because under illumination we should be directly observing the occupied energy level of a donor species,19 it appears from the absence of a difference in the surface potential that the highest occupied molecular orbital (HOMO) of C_{60} is pinned near E_F of ITO, placing the HOMO near 4.7 eV based on comparisons to other substrates (Figures S3 and S4) and literature-reported values,21,22 and can be used as a reference for E_F relative to C_{60} (Figure 1b,c).

A map of ΔΦ_{C_{60}/P3HT} in the dark state over a 50 × 30 μm^2 region of a 20-nm-thick C_{60} film deposited over a 40-nm-thick P3HT film (ITO/40 nm P3HT/20 nm C_{60}) is shown in Figure 2a with an average value of ~180 ± 10 mV over the C_{60} layer. The corresponding distribution of ΔΦ_{C_{60}/P3HT} shows a full width at half-maximum (fwhm) of 20 mV (Figure 2c). The map and illumination of the illuminated state (red) with reference to P3HT (0 mV) illustrates the large increase in ΔΦ_{C_{60}/P3HT} upon illumination. The

Figure 2. (a) 50 × 35 μm^2 map of ΔΦ of a 20-nm-thick C_{60} film (right) deposited over a 40-nm-thick P3HT substrate along with (b) a map of ΔΦ under illumination. The inset scale bars are from +100 to −600 mV. (c) Corresponding distributions in ΔΦ_{C_{60}/P3HT} of the dark (black) and illuminated (red) states shown with reference to P3HT (0 mV), illustrating the large increase in ΔΦ_{C_{60}/P3HT} upon illumination. The

corresponding distribution of ΔΦ_{C_{60}/P3HT} shows a full width at half-maximum (fwhm) of 20 mV (Figure 2c). The map and distribution of the illuminated state ΔΦ_{C_{60}/P3HT} under 225 mW/cm^2 illumination (Figure 2b) show an increased value of ~510 ± 10 mV and a uniformity similar to that of the dark state given by a fwhm of 15 mV (Figure 2c). The illuminated-state value of ΔΦ_{C_{60}/P3HT} = ~510 mV closely matches that of V_{OC} measured in typical P3HT/C_{60} solar cells. Therefore, we take the illuminated ΔΦ_{C_{60}/P3HT} value to be a measure of the quasi-Fermi level difference across the junction.23,24

DOI: 10.1021/acsami.6b00367
ACS Appl. Mater. Interfaces 2016, 8, 5772−5776
Figure 3 displays measurements of the dark-state $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}}$ and illuminated-state $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}}$ as a function of the C$_{60}$ film thickness in the regime where the work function is expected to be affected by the space charge. Both the dark-state $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}} (E_{F,\text{C}60} - E_{F,\text{P}3\text{HT}})$ and illuminated-state $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}} (\sim (\text{LUMO} - E_{F,\text{P}3\text{HT}}))$ exhibit asymptotic behavior with increasing thickness, approaching $\sim 200$ mV (dark state) and $\sim 500$ mV (illuminated state) over a range of 10 nm, mirroring the trends seen in other organic thin films.

To estimate the space-charge profile, we employ the one-dimensional formulation of the Poisson equation:

$$\frac{d^2}{dx^2} \Phi(x) = \frac{\rho(x)}{\varepsilon \varepsilon_0}$$

(2)

The charge density $[\rho(x)]$ of the material at any given position is then determined by some depth-dependent excess charge distribution $N(x)$ relative to the bulk charge distribution of the C$_{60}$ layer.

$$\rho(x) = -\varepsilon N(x)$$

(3)

We approximate the potential $\Phi$ at a depth $x$ within a film by the measured surface potential of a given C$_{60}$ film thickness (Figure 3).

Using eq 2, together with a simple empirical fit of $\Phi$, we differentiate the fitted trend to determine $N(x)$ and, taking $\varepsilon = 4.4$, obtain a profile of the charge density (Figure 3b). We see that the charge density is largely confined to a 10 nm region at the interface, being reduced by 95% within this distance. The average charge density over the region is $\sim 5.0 \times 10^{18}$ cm$^{-3}$. This points to the existence of a SCL with a thickness of $\sim 10$ nm at the P3HT/C$_{60}$ boundary, as delineated by the dashed line in Figure 3.

Under illumination, excitons form and separate into free charges across the D/A interface, and the system becomes conducting, with the difference in $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}}$ reflecting the difference in the Fermi levels of P3HT and C$_{60}$ (Figure 1c). That is, there is a negative (positive) charge in the C$_{60}$ (P3HT) film within a thin SCL (Figure 1d). The thickness dependence of $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}}$ under illumination corresponds to this charge. Both the thickness dependence and charge density of the illuminated-state systems are consistent with those previously observed by UPS for comparable polymer/fullerene films and suggest a nonconstant value of LUMO $- E_F$ within the SCL.

These trends are comparable with findings for M/O bilayers by UPS and SKPM as well as O/O bilayers observed through UPS. The width of the SCL in M/O films typically varies over a broad range between 2 and 500 nm, depending on the DOS of the films, the substrate, and the impurity/doping concentration of the material. C$_{60}$/metal layers explored by SKPM have been reported to exhibit two regimes of band bending—one attributed to dipoles between 0.5 and 3 nm and another attributed to space charge between 3 and 500 nm—the magnitude and width of which are related to the purity of the organic material. Here $\Delta \Phi_{\text{C}60/\text{P}3\text{HT}}$ saturates over a thickness regime of the same scale as other O/O and organic/semiconductor heterostructures. Specifically, the region of variation is confined to 10 nm, and the change in $\Phi$ roughly corresponds to UPS measurements of P3HT/C$_{60}$ films measured by Zhang et al.

The narrow SCL observed here is on the same scale as the domain sizes in fullerene/polymer BHJs as well as the exciton diffusion length in many fullerene/polymer blends. If the domain size is $\sim 20$ nm, each fullerene/polymer interface lies within the SCL of the opposing interface (Figure 4). The resulting average potentials reduce the magnitude of the bending. This flattens the HOMO and LUMO bands, which potentially may reduce the electron/hole recombination and make for more efficient devices in ordered polymer/fullerene BHJ blends. That is, small D/A domains may be important for two reasons: (i) maximizing the D/A interfacial area and (ii) reducing recombination processes within the D/A SCL.

In conclusion, using SKPM as a noninvasive probe of energy-level alignment, we have observed thickness-dependent band bending in a prototypical D/A heterojunction in the dark and under illumination. The SCL width of the P3HT/C$_{60}$ bilayers is $\sim 10$ nm, consistent with previous measurements, with a charge density variation of $10^{18} - 10^{19}$ cm$^{-3}$, as determined from the
Poisson equation. The compatible SCL thickness and D/A domain sizes in efficient BHJ organic solar cells may not be a coincidence. Small domains may, in fact, be saturated with carriers, resulting in little to no band bending and thus smaller than anticipated electron/hole recombination rates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b00367.

Experimental details, topography and surface potential maps of 20 and 5 nm films, illumination dependence of the surface potential, work function assignments of gold, aluminum, and ITO and of P3HT in the dark and under illumination (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge financial support from NSF Grant DMR-0706011

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