Comment

Reply to Comment on "Enhanced Charge Selectivity via Anodic-C$_{60}$ Layer Reduces Nonradiative Losses in Organic Solar Cells"

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We would like to start off by thanking the authors of the comment, Wetzelaer and Blom, for their very helpful and constructive analysis. They present an interesting alternative view on an important and timely research topic. Before discussing the mechanism suggested in their comment, from the viewpoint of our experimental results, we would like to summarize our findings. In our work,[1] we experimentally showed that

- The contact between donor molecules in the active layer of organic solar cells (OSCs) and a molybdenum oxide (MoO$_3$) hole extraction layer (HEL) causes an increase in nonradiative recombination losses, proportional to the extent of contacts.

- We attributed these losses to surface recombination, and we proved that the losses can be suppressed by inserting a thin interfacial fullerene layer at the anode side.

- Analyzing various donor−acceptor mixing ratios, with and without a fullerene-modified HEL, we decoupled and quantified the contribution from surface recombination on the total nonradiative losses occurring in these devices. In the best case, we showed an improvement of 150 meV in V_{OC}, as compared to the reference device. This demonstrates that surface recombination is a considerable contributor to nonradiative voltage losses in these solar cells, which are otherwise commonly occurring through charge-transfer states or energetic trap states because of defects in the bulk. We consider this the main result of our work.

- Measurements by a modified charge extraction by linearly increasing voltage (CELIV) technique provided evidence that the improvement in V_{OC} could be attributed to an enhanced built-in potential (V_{bi}), reducing the presence of minority charge carriers at the respective electrodes.

Although the authors of the comment in general agree with our experimental findings, they argue that the V_{bi} does not play a direct role in suppressing the surface recombination of minority carriers. The introduction of a C$_{60}$ interlayer, they argue, renders the MoO$_3$ contact ohmic.[2] The reduced anodic injection barrier simultaneously increases the V_{bi}, minimizes nonradiative voltage losses upon the extraction of majority carriers (holes), and suppresses minority-carrier (electron) surface recombination, the latter being the result of hole accumulation and associated band bending near the ohmic hole contact. Therefore, the ohmic contact formation suppresses both majority- and minority-carrier surface recombination losses, whereas the built-in voltage per se, they reason, does not play a major role. It is our opinion that the authors of the comment provide a very reasonable alternative explanation for the reduced surface recombination.

Injection barriers at the contacts are well-known to be detrimental for the performance of OSC as being a major cause of a reduced V_{bi} and increased surface recombination. Injection barriers have been shown to reduce not only the V_{OC} but also the fill factor (FF), sometimes even leading to s-shaped JV curves.[3−5] It has been suggested that, in the case of very large injection barriers, the V_{OC} is given by V_{bi}.[6,7] Although V_{bi} is determined by the difference in the work functions of the contacts, because of Fermi level pinning and the associated band bending, the built-in potential across the active layer, the effective V_{bi}, typically cannot exceed the effective gap of the bulk-heterojunction blend. In other words, the anode Fermi level pins to the highest occupied molecular orbital (HOMO) of the donor, whereas the cathode pins to the lowest unoccupied molecular orbital (LUMO) of the acceptor. In addition, because of disorder, Fermi level pinning typically occurs to discrete gap or tail states, causing additional band bending, which further limits the effective V_{bi}.[8,9] If there is an injection barrier at one contact, an increase or decrease in this barrier is directly reflected in the V_{bi}.[5]
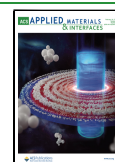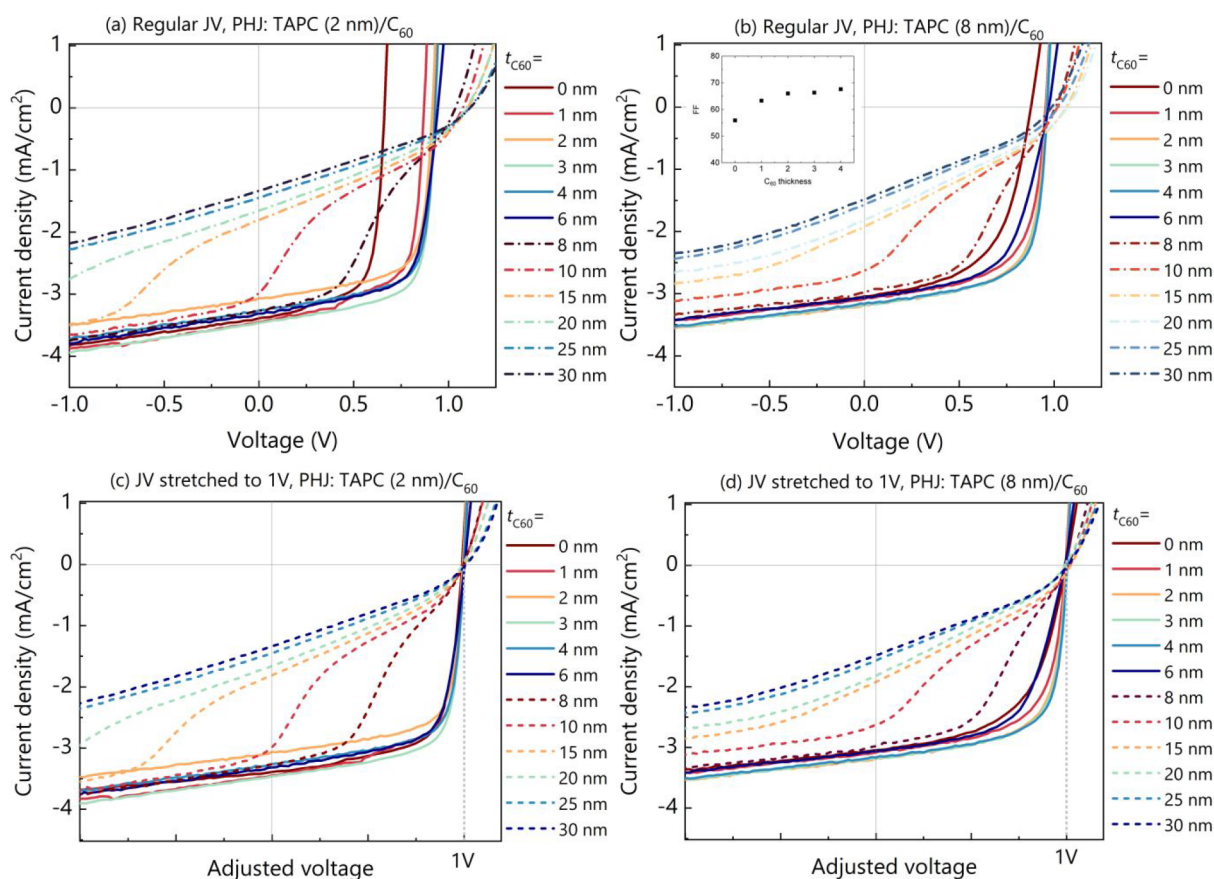
Figure 1. (a, b) Regular and (c, d) stretched JV curves for TAPC/C_{60} PHJ-based devices with 2 and 8 nm donor and for various thickness of anodic C_{60} (t_{C60}). For $t_{C60} < 4$ nm, stretched JV curves exhibit a similar FF, regardless of the anodic C_{60} thickness.
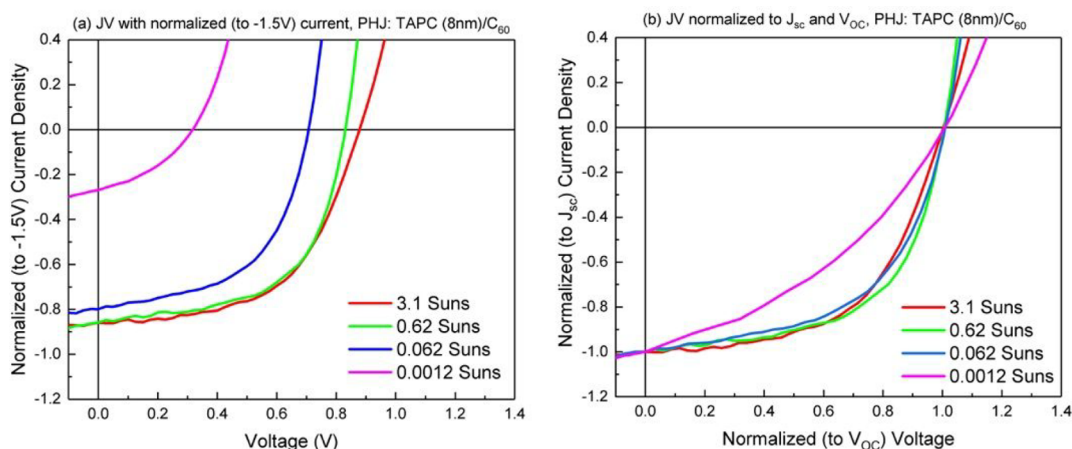
Figure 2. (a) Light intensity dependent JV curves, for the reference device without anodic C_{60}, normalized to the current density at −1.5 V, as outlined in ref 10. (b) Normalized JV curves to J_{sc} and V_{OC} show that there is no significant difference in the shape of the JV curves at any measured light intensity.

We fully agree with Wetzelaer and Blom that an injection barrier of ∼0.4 eV at the anode as determined using UPS by Kotadiya et al.[2] would limit both V_{bi} and V_{oc}. Removing it (for example, by adding anodic C_{60}) would correlate both with an increased V_{bi} as well as a concomitant increased band bending in the vicinity of the contact. The question is, what is the size of the injection barrier in the devices?

We turn to analyze the FF of our devices with and without anodic C_{60}. As V_{Q}, the onset voltage at which the charge reservoir starts to increase, was determined only in the planar

heterojunction devices, we will limit our discussion to those. Earlier experimental results on vacuum evaporated organic flat heterojunction solar cells with controlled injection barriers showed that even small injection barriers affect the FF negatively.[3] At injection barriers of 0.5 eV, a clear s-shaped JV curve was observed, and even with a barrier as small as 0.1 eV, there was a visible deviation from the ideal case (see Figure 3 in ref 3). If there was an injection barrier in the reference device, which would disappear with the addition of anodic C_{60}, we would expect a concomitant improvement in FF. As can be

seen in Figure 1, there is indeed a small improvement in the FF at anodic C_{60} thicknesses below 4 nm, from ~56 to ~67% (see inset Figure 1b); at larger C_{60} thicknesses, the FF starts to deteriorate. For a fair comparison, in Figure 1c and d, we stretched the voltage axis of all JV curves such that the V_{OC} of every device amounts to 1 V. However, the fact that there is only a minor improvement in the FF suggests the injection barrier cannot be very large. Moreover, by measuring light-intensity-dependent JV curves, as outlined in ref 10, on the reference device without anodic C_{60}, we also see no evidence of a strong injection barrier, see Figure 2. In the case of a planar heterojunction, a V_{OC} higher than V_{bi} is possible, causing an s-kink to the JV curves. As V_{OC} decreases with reduced light intensity, a threshold intensity will be reached where V_{OC} becomes smaller than V_{bi}. Then, the s-kink should vanish. In the measured JV curves, the shape is similar at all measured light intensities, as can be seen more easily in the normalized curves in Figure 2b. On the basis of this analysis of the FFs of our planar heterojunction devices, we can indeed confirm the presence of an injection barrier; however, information in the literature suggests the barrier might be smaller than 0.4 eV.[3,10,11] The discrepancy between the FF results and UPS measurements by Kotadiya et al. (and confirmed by our own UPS measurements) is one we cannot currently resolve. We wish to point out that relating electronic properties of ultrathin surfaces to the properties of complete multilayer devices is not always straightforward. We concede that there seems to be at least a small injection barrier, but we prefer not to speculate on the size of the injection barrier further.

The only issue that remains to be clarified is the one of what is the driving force for the improved performance with the addition of anodic C_{60}. As we have seen, the improvement in V_{OC} correlates both with an increased V_{bi} and a decreased injection barrier (and concomitant increased band bending). Because these two parameters are intrinsically linked, it is not possible on the basis of our experimental results to discern which is the most important one in reducing surface recombination. At V_{OC}, the total current is $J = 0$. Taking $x = 0$ to be at the anode contact, $J = J_n(0) + J_p(0) = 0$, i.e., the sum of the minority-carrier (electron) surface recombination current density, $J_n(0)$, and the majority-carrier (hole) current density, $J_p(0)$, is zero at the anode. We then obtain $J_n(0) = -J_p(0)$, meaning that the entire extraction current of majority carriers at the anode is lost because of surface recombination with minority carriers. Therefore, at open circuit, these two processes describe the same loss mechanism, being two sides of the same medal.

Furthermore, it is true that the band bending associated with an ohmic contact will provide a reverse electric field for minority carriers to diffuse against, which by itself reduces surface recombination. However, surface recombination is in general the result of bulk current of minority carriers diffusing against the electric field from across the entire active layer.[12] This means that the reverse electric field in the rest of the active layer is equally important.[13] Because a large band bending near the contact reduces the electric field in the rest of the active layer (relative to what it would have been in the absence of band bending), even though it is harder for carriers to diffuse against the field in a narrow region near the contact, there will be more carriers reaching this region, because of the smaller field in the rest of the layer. We therefore believe that the situation is more complicated and strongly depends on

bimolecular recombination constant in the bulk (β), mobilities, and surface recombination velocities.[4,5,14] To exemplify this, we turn to drift-diffusion simulations, where space charge effects can be artificially turned off, to clarify the effect of band bending on device performance. Because our original paper discusses nonradiative voltage losses at V_{OC}, we here also limit our discussion to V_{OC}; see Figure 3. Here, the injection barriers
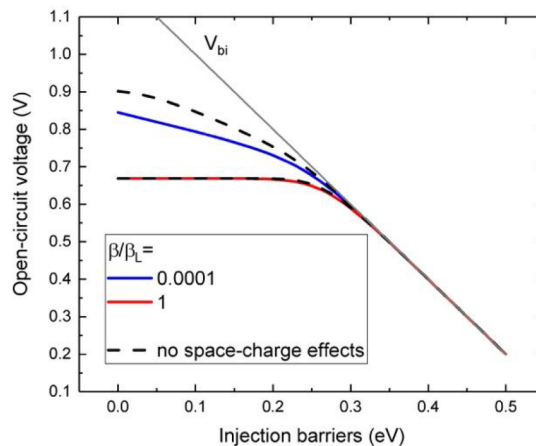
Figure 3. Example of the simulated V_{OC} vs injection barrier, kept the same for the anode and the cathode, at different degrees of bimolecular recombination (β) in the bulk. Here, β is given relative to the Langevin recombination constant β_L. The dashed line corresponds to the case without band bending, where the space-charge effects were turned off in the Poisson equation. A drift-diffusion model[4] was used for the simulations where both contacts are assumed nonselective (large surface recombination velocity), whereas the active layer has a bandgap of 1.2 eV, a thickness of 150 nm, a dielectric constant of 3.5, equal mobilities of 5×10^{-4} cm^2/(V s), effective densities of states of 1×10^{20} cm^{-3}, and a carrier photogeneration rate of 6.24×10^{21} cm^{-3} s^{-1}.

(of majority carriers) at both the anode and cathode are varied equally (both are assumed to be nonselective). As shown, at small barriers and small β, when surface recombination dominates over bulk recombination,[12] the presence of band bending causes a smaller V_{OC} than in the case, where the build-in potential drops continuously over the entire layer thickness. As expected, for predominant bulk recombination ($\beta \cong \beta_L$), there is no difference in the V_{OC} obtained with and without space-charge effects.

Finally, we respectfully argue that from our experimental data it is not possible to draw a final conclusion as to which mechanism gives the best explanation and that further work is needed to clarify to which degree the two mechanisms explain our results.

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Notes

The authors declare no competing financial interest.

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