The importance of molecular disorder for thin-film solar cells based on disk shaped molecules

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Abstract

In an effort to understand the requirements necessary to make molecular thin-film PV devices more efficient, 2D simulations of I_{sc} for nanoscopic donor/acceptor type hetero-junctions have been performed. The focus is on PV devices with pronounced chemical and photochemical stability and substantial absorption in the visible part of the solar spectrum. Natural choices of donor (D) and acceptor (A) molecules for such purpose are the metallo-phthalocyanines and perylene derivatives, respectively. These disk shaped π-systems have the ability to π-stack with inter-planar separations typically of ~ 0.4 nm, which is often argued to be the optimal condition for an efficient PV device. Consequently, effort has gone into derivatizing metallo-phthalocyanines and perylenes to allow for device processing of photoactive films with large degree of molecular order.
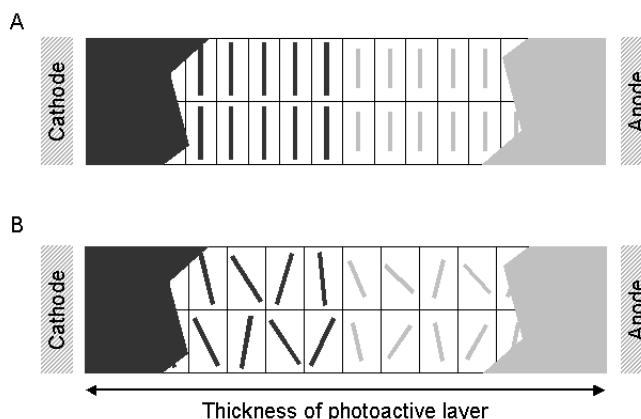
Figure 1: Schematic illustration of a heterojunction PV structure based on disk-shaped donor (dark) and acceptor (grey) molecules. In (A) the molecules are well-ordered in π-stacks, whereas in (B) molecular disorder prevails.

The objective of the presentation is to question to what extent molecular stacking in thin-film PV devices consisting of such π-stacking molecules is important. As naively illustrated in figure 1, the degree of stacking order for such systems is also reflected in the average molecular inter-planar separation. Hence, figure 1A illustrates part of a CuPc|PTCDA thin-film hetero-structure where π-stacking is perfect and the separation between molecular planes is 0.4 nm. In figure 1B, orientational disorder has been introduced to mimic the transition towards a more amorphous film-structure. As a consequence, the average inter-planar distance is increased. In figure 2 preliminary simulations of I_{sc} for these 2D hetero-junction structures are shown as a function of the thickness (d) of the photoactive layer. The simulations were performed with *PhotoSim* 1.13[1], and the underlying methodology of this simulation tool assumes PV action in molecular materials to take place by ionization of localized photo-generated excitons and subsequent hopping transport of electrons and holes. I_{sc} is derived in the limit of no built-in field and thus with charge transport driven exclusively by carrier diffusion gradients. The device temperature is 300 K and a constant light intensity characterized by a

Planckian distribution at 1300 K is assumed throughout the photoactive layer. The CuPc (D) and PTCDA (A) sites are characterized by their HOMO and LUMO energies, the oscillator strengths for the transition between these levels and electron affinities. Rates for the electron transfer (ET) of electrons between identical sites (D or A) are extracted from $^h\mu$ and $^e\mu$ (collectively referred to as μ^{ref} in figure1) as measured for amorphous films of CuPc and PTCDA, respectively. Rates for ET between D and A and for ET between D, A and the electrodes rely on estimates, however.
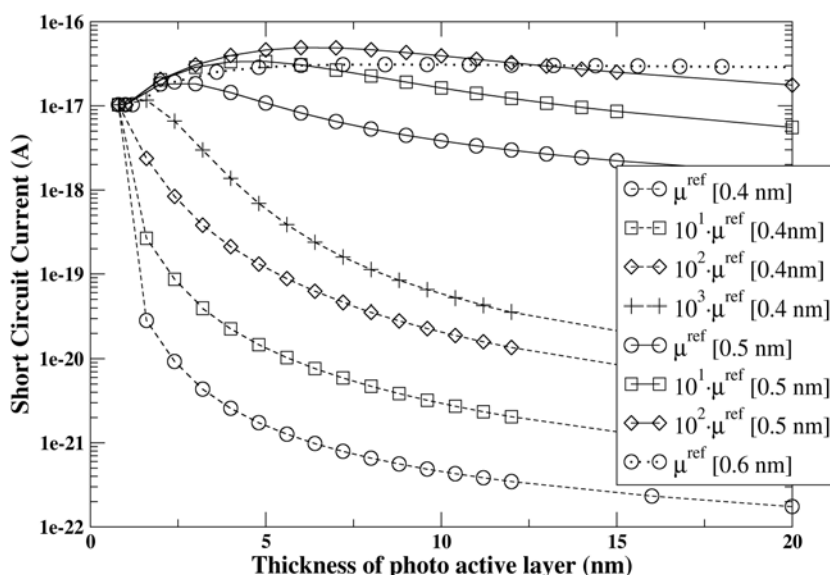

Figure 2: Simulation of I_{sc} versus layer thickness for a CuPc|PTCDA hetero-junction PV device for different π-stacking separations and choices of mobilities.

From the I_{sc}(d) curves in figure 2 as simulated using μ^{ref} for CuPc and PTCDA (curves labeled **O**), a radical decrease in I_{sc} is observed as the inter-planar distance is decreased from 0.6 nm to 0.4 nm. At first glance this appears counter-intuitive as the increased π-π overlap is expected to improve transport of electrons and holes to the electrodes. However, closer analysis of the charge separation energetics for geminate e⁻/h⁺ pairs reveals that as the site distance is diminished, more short-range e⁻/h⁺ pairs are trapped in the deep part of the Coulomb well along the charge separation path. Consequently, as the inter-planar distance is decreased, the charge polarization at the DA interface increases, thus effectively impeding the PV efficiency.

Despite the approximate nature of the simulation model employed, these results indicate that it is the charge separation dynamics of geminate e⁻/h⁺ pairs that governs the PV efficiency in the limit of thin-films and hopping mediated charge transport. To further test this conclusion, in figure 2 also shown are I_{sc}(d) curves as simulated using mobilities up to three orders of magnitude larger than μ^{ref}. Clearly, despite increasing mobilities by 10^3, on decreasing the inter-planar distance from 0.6 nm to 0.4 nm, I_{sc}(d) drops by orders of magnitude as seen by comparing the (+) and upper (**O**) curves in figure 2.

The significance of the simulation results is of conceptual importance mostly as the simplicity of the model tends to exaggerate the sensitivity on D/A topology. The results, however, still question the common perception that tight π-stacking in photoactive films automatically leads to better PV devices. Undoubtedly, tighter molecular stacking leads to increased mobilities within individual and ordered domains, but the increased energetic price of separating geminate e⁻/h⁺ pairs may outweigh this effect.

[1]: *K. O. Sylvester-Hvid and M. A. Ratner: J. Phys Chem. B* **2005***, 109, 200-208*