Influence of Device Architecture and Interface Morphology on the Power Conversion Efficiency of Small Molecular Photovoltaic Cells

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ABSTRACT

We review several strategies for optimizing the power conversion efficiency of small molecular weight organic PV cells without employing bulk heterojunctions. The limitations of these approaches and future research directions are highlighted.

1. Introduction

The power conversion efficiency, η_P, of organic small molecular weight and polymer photovoltaic (PV) cells has increased steadily in the last decade. This progress is chiefly attributable to the introduction of the donor-acceptor (DA) heterojunction [1-3] which functions as a dissociation site for the strongly bound photogenerated excitons. The external quantum efficiency of a PV cell based exciton dissociation at a DA interface is [4]

$$\eta_{EQE} = \eta_A \cdot \eta_{ED} \cdot \eta_{CC} \quad (1)$$

Here, η_A is the absorption efficiency. The exciton diffusion efficiency, η_{ED}, is the fraction of photogenerated excitons that reaches a DA interface before recombining radiatively or non-radiatively. The carrier collection efficiency, η_{CC}, is the probability that a free carrier, generated at a DA interface by dissociation of an exciton, reaches its electrode. Typically, in bilayer DA PV cells with a total thickness, L, on the order of the optical absorption length, L_A, the absorption efficiency is

$$\eta_A = 1 - exp(-L/L_A) > 50\% \quad (2)$$

if optical interference effects are ignored [4], and $\eta_A \approx$ 100%. However, since the exciton diffusion length (L_D) in organic materials is typically an order of magnitude smaller than L_A, a large fraction of the photogenerated excitons remains unused for photocurrent generation (Fig. 1a), limiting η_{EQE} and hence η_P for this type of cell.

In polymer PV cells, the exciton diffusion bottleneck has been partially removed through the introduction of bulk heterojunctions [5,6] (Fig. 1b). In a bulk heterojunction, the DA interface is highly folded such that photogenerated excitons always find a DA interface within a distance L_D of their generation site. Currently, state-of-the-art bulk heterojunction polymer PV cells have power conversion efficiencies exceeding 3% [7]. The bulk heterojunction is typically built by spin-coating a mixture of soluble versions of the donor and acceptor materials. During spin-coating and solvent evaporation, the donor and acceptor materials phase separate, creating an intricate network. The morphology of the resulting structure is controlled by changing spin conditions, solvents and material concentrations [8]. The challenge of such systems is to balance a high η_{ED}, favouring fine grained morphologies, and a high η_{CC}, favouring coarse grained morphologies, such that the product $\eta_{ED} \cdot \eta_{CC}$ is maximized.

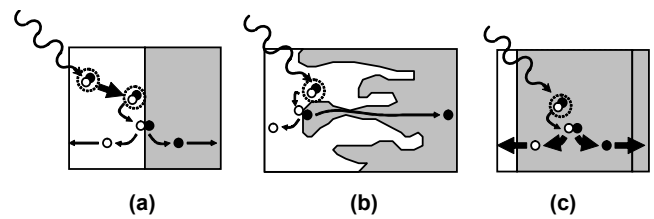

Figure 1. Types of donor-acceptor organic photovoltaic cells. (a) Bilayer cell. (b) Bulk heterojunction cell. (c) Mixed-layer cell.

Realizations of bulk-type heterojunctions in small molecular systems have been largely unsuccessful. Attempts to achieve a bulk heterojunction through co-deposition of the donor and acceptor materials yield devices with power conversion efficiencies falling far short of those achievable in bilayer systems [9]. Strong quenching of the photoluminescence in these systems indicates that $\eta_{ED} \approx$ 100%. Therefore, the low efficiencies are attributed to poor charge transport in the amorphous mixed layer, resulting in a low η_{CC} (Fig. 1c and [9]).

Growth of mixed layers can lead to phase segregation and larger crystalline domains. However, this increase in crystallinity and possibly larger L_D and improved η_{CC} come at the cost of an increased film roughness [10]. The high density of pinholes in such structures makes device fabrication impossible.

In the face of these limits, we discuss several strategies for optimizing the power conversion efficiency of small molecular weight organic PV cells without employing bulk heterojunctions.

2. Optimizing optical interference effects

The photoresponse of organic PV cells with a well-defined layer structure can be accurately predicted by modeling the optical properties of the multilayer stack while simultaneously solving for exciton diffusion. These calculation procedures are well established and were recently reviewed in Ref. [4].

The importance of optical interference effects in multilayer organic PV cells is illustrated in Fig. 2. The presence of the Al cathode causes strong optical interference effects, increasing the field intensity, and hence absorption, in the CuPc layer by a factor of ~4. It is due to this optimization that we were able to fabricate highly efficient

PV cell structures based on the CuPc/C_{60} material system [12].

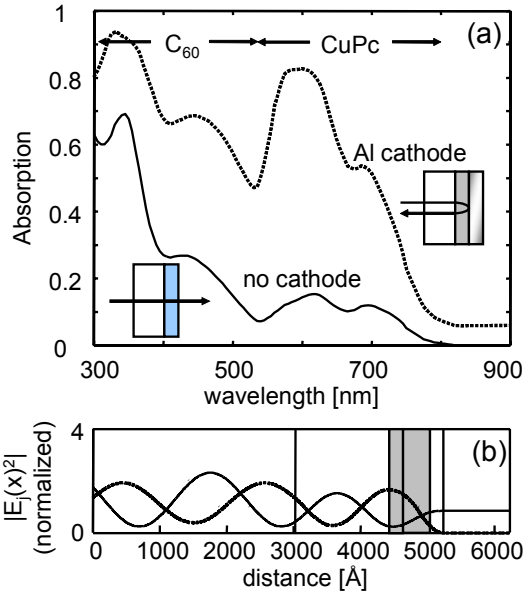

Figure 2. The importance of optical interference effects in organic PV cells. (a) Calculation of the sbsorption of a 140nm ITO/20nm CuPc/40nm C_{60}/20nm BCP multilayer film on quartz measured in the absence (solid line) and presence (dotted line) of an Al cathode. (b) Optical field intensity as a function of position for the same structures.

3. Exciton blocking layer

Applying the same photoresponsivity model to simple "Tang" type bilayer PV cells [1], we learned that cathode induced exciton quenching limits the external quantum efficiency in this architecture [4]. To eliminate this drain on the PV efficiency, we introduced the double heterojunction architecture which incorporates an exciton blocking layer (EBL) [13]. The EBL allows one to grow devices with photoactive layer thicknesses of the order of the diffusion length of the material. Unwanted absorption in regions far away from a DA interface is eliminated.

The use of an EBL is illustrated in Fig. 3, where the internal and external quantum efficiency of a "Tang" type cell with an EBL are shown as a function of the PTCBI layer thickness. In the case without EBL, the quantum efficiency drops drastically for layer thicknesses <200Å.

4. Light trapping in very thin cells

The use of an EBL allows one to grow devices with very thin photoactive layers, leading to maximal internal quantum efficiencies. To translate this into high external quantum and power conversion efficiencies, efficient light traps are required. Using light traps, we were able to increase the power conversion efficiency of a CuPc/PTCBI based cell from 1.0% to 2.4% [13].

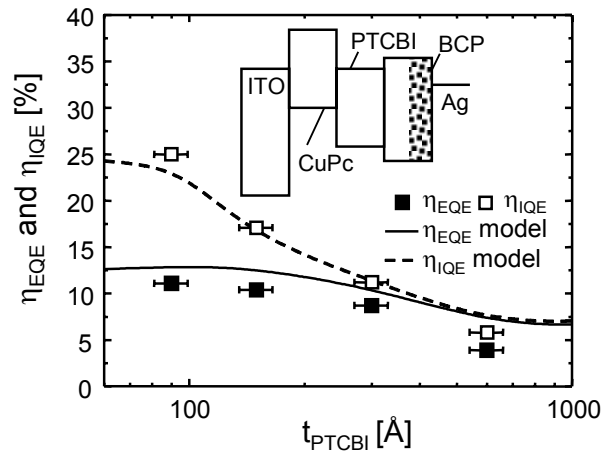

Figure 3. External and internal quantum efficiency of the double heterojunction architecture using the CuPc/PTCBI material system (open and solid squares). Model calculations are shown as well (solid and dashed lines).

We have proposed [13] a very efficient [4] light trap based on miniaturized non-imaging collectors for this purpose which can be fabricated my molding. This light trap is shown in Fig. 4.

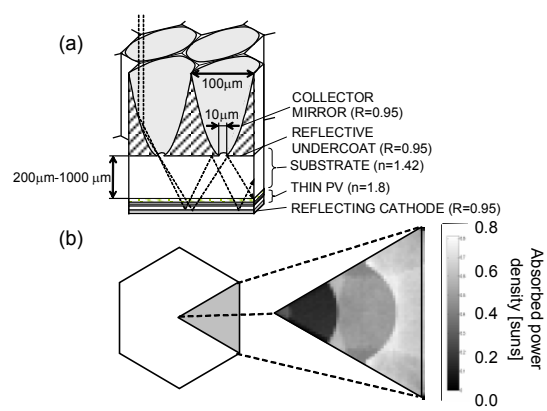

Figure 4. (a) Geometrical configuration of the light trap. (b) Ray-tracing calculation of the optical intensity at the PV cell plane under 1 sun illumination.

5. Stacking thin PV cells

Another means for achieving high power conversion efficiencies is by stacking partially transparent bilayer PV cells with high internal power conversion efficiencies. Ideally, such a configuration yields devices with a short circuit current equal to that of a single cell, but with an open circuit voltage that is *n* times that of a single cell. The challenge in this approach is that ohmic contacts must be placed between the different cells which (a) are highly transparent, and (b) do not negatively influence the efficiency of the thin bilayer cells.

Recently, we have shown that this can be achieved by inserting ultrathin (~0.5nm) layers of Ag between bilayer

cells [14]. The ultrathin layer deposits as nanoscale clusters which are believed to serve as efficient recombination centers.

This approach is illustrated in Fig. 5, where the open circuit voltage of stacks of CuPc/PTCBI bilayer cells is shown as a function of the incident optical power level. The highest power conversion efficiency of 2.4% at 1 sun was achieved in a 2-cell stack (a "tandem" cell), up from ~1% for a single cell device.

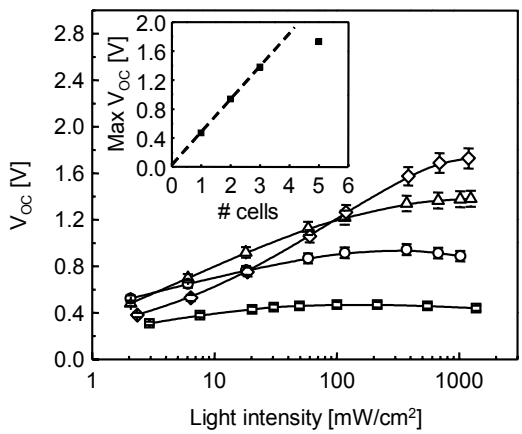

Figure 5. Open circuit voltage of stacked CuPc/PTCBI cells for a single cell (squares), 2-cell (circles), 3-cell (triangles) and 5-cell (diamonds) device. Inset: Maximum open circuit voltage as a function of the number of cells in the stack.

5. Conclusions and future directions

Highly folded DA junctions realized in bulk-type heterojunctions combine the effects of a high exciton diffusion efficiency and high carrier collection efficiency, providing a path towards organic PV cells with external quantum efficiencies approaching 100%. The realization of such devices remains a challenge for small molecular weight material systems. More research is required in this direction.

However, improvements in PV cell efficiency based on increasing η_{EQE} are limited. Assuming η_{EQE} = 100% for λ < 750nm leads to η_P = 7.5%. Further improvements in power conversion efficiency can then be attained by optimizing the open circuit voltage. Indeed, assuming 100% external quantum efficiency across the absorption spectrum of the organic materials and assuming that a band offset of 0.2eV is sufficient for exciton dissociation, an optimal open circuit voltage of V_{OC} = 1.12V is obtained. This leads to an estimate of the maximum obtainable power conversion efficiency of an organic PV cell of η_P = 20%. This requires photoactive materials with an absorption edge extending to 940nm.

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