Structural templating as a route to improved photovoltaic performance in copper phthalocyanine/fullerene (C$_{60}$) heterojunctions

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We have developed a method to improve the short circuit current density in copper phthalocyanine (CuPc)/fullerene (C$_{60}$) organic solar cells by $\sim$60% by modifying the CuPc crystal orientation through use of a molecular interlayer to maximize charge transport in the direction between the two electrodes. Powder x-ray diffraction and electronic absorption spectroscopy show that a thin 3,4,9,10-perylenetetracarboxylic dianhydride interlayer before CuPc growth templates the CuPc film structure, forcing the molecules to lie flat with respect to the substrate surface, although the intrastack orientation is unaffected. This modified stacking configuration facilitates charge transport and improves charge collection. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2821229]

Considerable effort is being directed at the development of small-molecule organic photovoltaic (OPV) devices using materials such as copper phthalocyanine (CuPc) as both the light absorbing and hole-transport layer.[1–3] Fullerene (C$_{60}$) has become the preferred electron acceptor and it has been shown that cell structures containing mixed donor-acceptor layers, fabricated by codeposition of CuPc and C$_{60}$, show significant improvement in device performance over simple bilayer heterojunctions.[4–6] Although CuPc/C$_{60}$ OPV devices have reached power conversion efficiencies (η_p) of $\sim$5%,[5] their performance remains limited by the low exciton diffusion length of CuPc and poor charge transport in the mixed CuPc/C$_{60}$ layers.

The α-polymorph of CuPc, which is formed when films are grown on noninteracting substrates at room temperature, displays strongly anisotropic charge mobility as a result of the formation of one-dimensional (1D) stacks of molecules.[7,8] The molecules in these stacks align with their molecular planes parallel to each other, tilted by approximately 65° to the stacking axis, with the stacks oriented such that a "herringbone" arrangement is adopted by molecules in neighboring columns. The peak charge mobility occurs along the stacking axis due to the strong π-coupling between neighboring molecules, with charge transport between columns limited by a hopping mechanism. The 1D stacks within the polycrystallites are preferentially oriented with the stacking axis parallel to the substrate surface, resulting in a peak charge mobility parallel to the substrate of around 4.13 $\times 10^{-3}$ cm^2/V s.[9] However, in a standard OPV cell, the desired direction of charge transport is perpendicular to the substrate surface and, hence, device performance is limited by the hopping of charges between neighboring stacks. Mobilities around four orders of magnitude lower at 5 $\times 10^{-7}$ cm^2/V s have been reported for this orientation.[10] In order to achieve maximum mobility in CuPc donor layers, it

would be desirable for the 1D stacks to be rotated so that the stacking direction lies parallel to the surface normal.

It is well-known that 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) molecules lie approximately parallel to the substrate surface when deposited onto noninteracting substrates.[11,12] It has also been reported that the initial growth of a thin layer of PTCDA causes a subsequent freebase phthalocyanine (H$_2$Pc) layer to follow the underlying structure rather than adopting its usual herringbone structure,[13–15] an effect referred to as structural templating. This templating effect is caused by an interaction between the π-orbitals of the PTCDA underlayer and the H$_2$Pc molecules, and is long range with no sign of the reappearance of the H$_2$Pc herringbone structure in films as thick as 380 nm.[13,14] In this letter, we show that this templating effect can also be used for CuPc films in an OPV heterojunction cell with significant increase in the short circuit current density (J_{SC}). The results demonstrate the effectiveness of tailoring the structure of the CuPc films for OPV applications.

The structures were fabricated on commercially available indium-tin-oxide (ITO) coated glass substrates (CRL Opto) after initial solvent cleaning. The organic layers were grown by vacuum deposition in a Kurt J. Lesker Spectros system with a base pressure of about 8×10^{-8} mbar. The organic materials used in the devices CuPc (Aldrich 97%), C$_{60}$ (MER Corp. 99.5%), bathocuproine (Aldrich 98%), and PTCDA (Aldrich 97%) were twice purified by thermal gradient sublimation prior to deposition. A deposition rate of 1 Å s^{-1} was used for all organic layers except PTCDA, which was grown at 0.1–0.2 Å s^{-1}. The Al cathodes were deposited *in situ* by evaporation through a shadow mask to a thickness of 1000 Å, giving an active area of 0.16 cm^2. X-ray diffraction (XRD) traces were obtained from a Philips PW1700 series automated powder diffractometer using Cu Kα radiation, whilst electronic absorption spectra were measured using a Perkin Elmer Lambda 2 spectrometer. *J-V* curves were measured with a Keithley 2400 sourcemeter un-

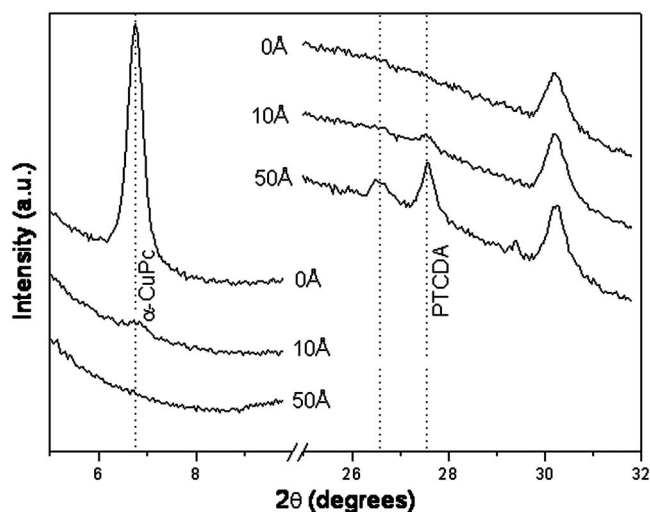a)FAX: +44 (0)24 7652 4112. Electronic mail: t.s.jones@warwick.ac.uk.

FIG. 1. Powder XRD patterns for a 300 Å CuPc layer grown on PTCDA interlayers of thicknesses between 0 and 50 Å. The peak at ~30.2° is due to the ITO coating and is used as a reference for peak position and height, while the sloped background is due to the glass substrate.
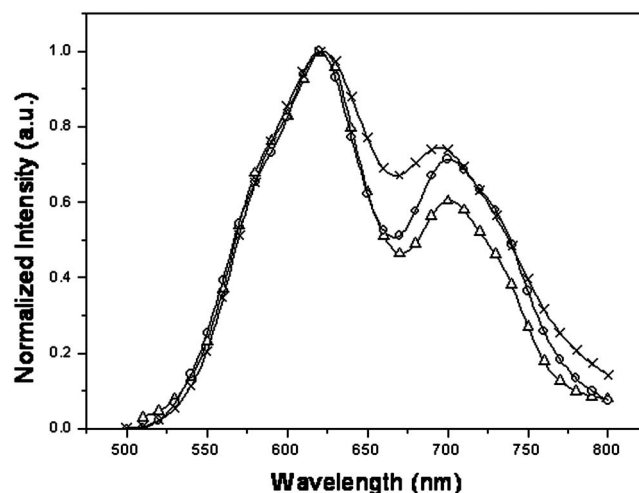

FIG. 2. Electronic absorption spectra of a 300 Å CuPc layer grown directly on ITO (crosses) and on a 20 Å PTCDA interlayer (empty circles), and a 1000 Å CuPc layer grown on a 20 Å PTCDA interlayer (empty triangles).

der AM1.5 solar illumination at 100 mW cm^{-2} (1 sun) from a Sciencetech solar simulator.

Powder XRD traces for 300 Å CuPc layers grown on top of PTCDA interlayers of thicknesses ranging from 0–50 Å on ITO substrates are shown in Fig. 1. With no PTCDA interlayer, the CuPc exhibits a single intense diffraction feature centered at 6.8°, corresponding to diffraction from the (200) plane of α-CuPc, and consistent with the stacking axis lying parallel to the substrate.[16,17] Inclusion of a PTCDA interlayer results in a peak appearing at ~27.6°, corresponding to diffraction from the (102) plane of PTCDA, but is also accompanied by a substantial change in the rest of the diffraction pattern. On increasing the PTCDA layer thickness, the intensity of the α-CuPc peak at 6.8° is severely diminished, until disappearing completely at 50 Å. This suggests that the underlying PTCDA layer has a considerable effect on the structure of the CuPc layer. The disappearance of this peak is accompanied by the gradual emergence of a different peak at ~26.6°, corresponding to an interplanar separation of 3.33 Å, which cannot be explained by the presence of the PTCDA layer or by a reorientation of the bulk CuPc herringbone structure since the peak is not present for α-CuPc in powder form.[18] Instead, it appears that the PTCDA has forced the CuPc layer to adopt a completely different structure.

Electronic absorption spectra of a 300 Å CuPc layer grown directly on ITO, and 300 and 1000 Å CuPc layers grown on a 20 Å PTCDA interlayer are shown in Fig. 2. The nontemplated CuPc layer shows a spectrum typical of α-phase CuPc, with the main absorption displaying peaks at 694 and 622 nm as a result of aggregation. It is known that the relative intensity of the peak at 694 nm is indicative of the level of monomer character of the film.[4,19] The only significant change in the absorption features on inclusion of a 20 Å PTCDA interlayer is the relative intensity of the 694 nm peak, suggesting that the dominant electronic interactions between CuPc molecules are unaffected by the structural templating effect imparted by the PTCDA underlayer, and that the 1D stacks remain intact in the modified structure. The 694 nm peak shows a decrease in relative intensity on inclusion of the 20 Å PTCDA interlayer and a further

significant decrease with an increase in the thickness of the templated CuPc layer. This suggests that a higher proportion of the CuPc molecules are able to form aggregate stacks in the templated layers, and is evidence of increased order imparted in the structure by the underlying PTCDA layer. This effect is increasingly apparent at higher CuPc thicknesses, implying that the templating effect is long range.

A structure in which the 1D stacks remain intact (as suggested by electronic absorption spectroscopy), but the parallel plane separation is reduced to around 3.3 Å (as suggested by XRD) is proposed in Fig. 3. Here the initial layer of CuPc molecules are forced to lie flat by the strong π-π interactions with the flat lying PTCDA interlayer, with subsequent layers also forced into the same orientation. The lateral displacement of the subsequent layers remains equal to that in the 1D stacks in the α-phase herringbone structure, resulting in a tilting of the stacking axis by around 26.5° from the surface normal. In this orientation the diffraction plane parallel to the surface has an interplanar separation equal to the perpendicular separation between molecules in a stack, in this case ~3.4 Å, which correlates well to the position of the observed XRD peak. This structure is consistent with that seen for PTCDA/H$_2$Pc.[14] A series of multilayer OPV devices were grown of structure ITO/x Å PTCDA/300 Å CuPc/400 Å C$_{60}$/100 Å BCP/Al, with 0 Å $\leq x \leq$ 50 Å. CuPc and C$_{60}$ layer thicknesses were selected as those optimized previously.[6] Figure 4(a) shows the *J-V* curves for this series of OPV cells, while the inset at Fig. 4(a) displays an energy level diagram for these devices. Fig-
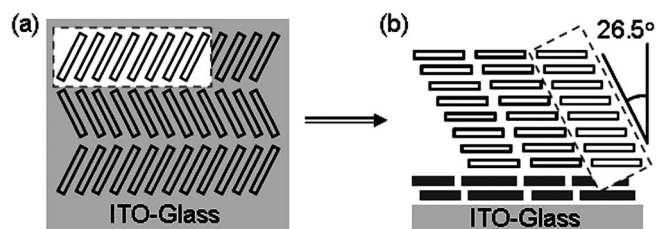

FIG. 3. A schematic showing the structure of (a) an α-CuPc film and (b) a templated CuPc film with a PTCDA underlayer. The intrastack geometry, highlighted by the dashed rectangle, remains the same, but the stacking axis is rotated through approximately 90°.
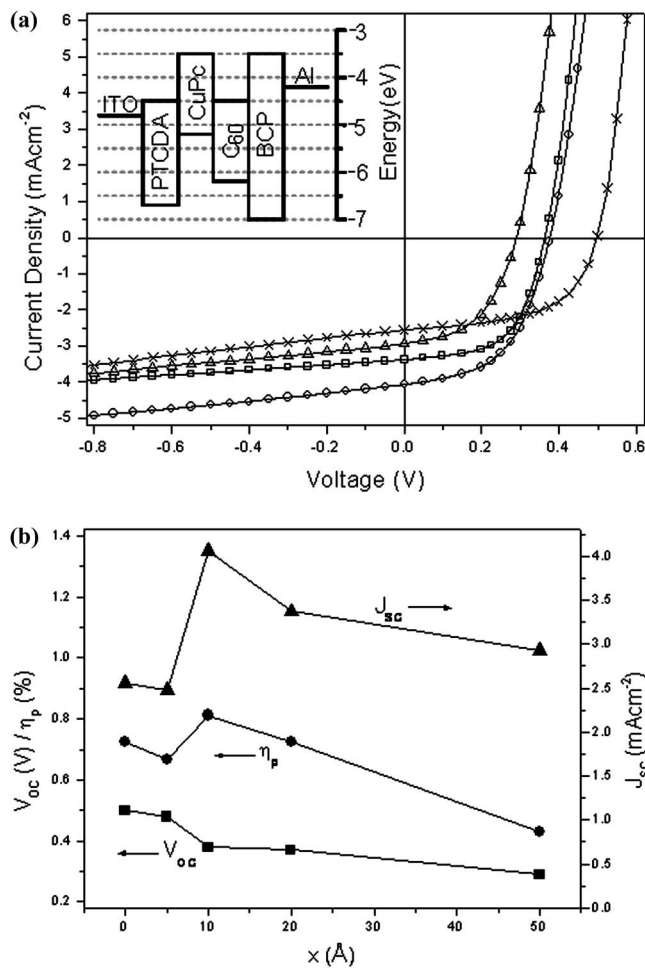
FIG. 4. (a) J-V curves for a series of ITO/x Å PTCDA/300 Å CuPc/400 Å C_{60}/100 Å BCP/Al devices, $x=0$ Å (crosses), 10 Å (circles), 20 Å (squares), and 50 Å (triangles), (a, inset) an energy level diagram for the devices, and (b) device parameters for the series; V_{OC} (squares), J_{SC} (triangles) and η_p (circles).

ure 4(b) shows the trend of short circuit current density (J_{SC}), open circuit voltage (V_{OC}), and power conversion efficiency (η_p) obtained under AM1.5 solar illumination as a function of PTCDA interlayer thickness.

In the absence of the PTCDA interlayer, the standard (nonoptimized) heterojunction CuPc/C_{60} device affords a short circuit current density of $J_{SC}=2.56$ mA cm^{-2} and an open-circuit voltage of $V_{OC}=0.5$ V, leading to an overall power conversion efficiency of $\eta_p=0.73\%$. Inclusion of a 50 Å thick PTCDA layer prior to the CuPc/C_{60} heterostructure gives rise to a significant increase in J_{SC} to 2.93 mA cm^{-2}, which we believe is due to the improved transport in the templated CuPc layer as a consequence of the modified stacking direction. Unfortunately, the improved current density is accompanied by a 40% fall in V_{OC}, consistent with appreciable charge buildup at the PTCDA/CuPc interface, resulting in an overall drop in the power conversion efficiency to $\eta_p=0.43\%$. The offset in highest occupied molecular orbital levels results in a barrier for hole extraction of ~1.5 eV, two orders of magnitude greater than thermal

energy at room temperature. Hole transport across the PTCDA layer would, therefore, only be expected through pinholes and defects in the structure or by tunneling through areas of low film thickness due to the roughness of the layer.

Reduction of the PTCDA layer thickness x results in a gradual increase in J_{SC} and V_{OC} and, hence, η_p, with the optimum PTCDA thickness found to be 10 Å. At this thickness, V_{OC} approaches 0.4 V, still considerably lower than the standard device suggesting that, as expected, charge buildup is still significant even at such low thicknesses due to the difficulty of charges crossing the PTCDA layer. However, J_{SC} reaches 4.06 mA cm^{-2}, an increase of almost 60% over the standard device and sufficient to afford an improvement to $\eta_p=0.81\%$. Further reduction of the PTCDA layer thickness to 5 Å leads to slightly lower J_{SC} and V_{OC} values than the non-templated device suggesting that $x\approx10$ Å is the critical PTCDA thickness to provide the necessary templating effect to the CuPc layer.

The results presented here show how, in principle, charge collection can be improved by aligning the stacking axis of molecular columns with the desired direction of charge transport. While PTCDA is clearly not the ideal surface modification in terms of energy level alignment for hole injection, the effect of templating on charge transport through the CuPc layer is clear to see. A 60% improvement in J_{SC}, despite sufficient charge buildup to cause a 20% reduction in V_{OC}, suggests the potential for a significant increase in OPV performance with a more suitable surface modification layer. Future work using templating layers with more appropriate energy levels will lead to significant improvements in device performance.

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