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Enhanced Open-Circuit Voltage in Subphthalocyanine/C_{60} Organic Photovoltaic Cells

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Organic photovoltaic (PV) cells have attracted attention due to their ease of fabrication and potential for low-cost production.[1−4] Since Tang reported the first thin-film organic PV cell based on a single donor−acceptor (D−A) heterojunction,[4] research has been focused on enhancing the efficiency of these cells through use of new materials and device structures. PV cells employing polymer−fullerene heterojunctions have been shown to have power conversion efficiencies (η_P) approaching 5%,[5] obtained through variations in the processing techniques. Recently, Xue et al. reported efficiencies as high as 4% under 4 suns simulated AM1.5G illumination in a double-heterostructure copper phthalocyanine (CuPc)/C_{60} thin-film cell with Ag as the metal cathode.[6] PV cells such as these can be further enhanced by stacking two cells in series, yielding efficiencies exceeding 5.5%.[7]

Efficiency is dependent on the open circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and the fill factor (FF) via[3]

$$\eta_P = (J_{sc}\, V_{oc}\, \mathrm{FF})/P_o \qquad (1)$$

where P_o is the incident optical power. Here, FF depends on the series resistance and is typically between 0.5 and 0.65 for small-molecular-weight organic photovoltaics. J_{sc} is controlled by the overlap between the absorption of the organics and the solar spectrum, as well as the magnitudes of the extinction coefficients and thicknesses of the absorbing layers. However, enhanced spectral overlap must be accomplished without a significant loss in exciton diffusion length or in the charge transport properties of the materials. The typical $V_{oc} \cong 500$ mV at 1 sun for conventional CuPc donor-based PV cells is significantly less than the energy of the absorbed photon (~2 eV). Clearly, an increase in V_{oc} offers a significant opportunity for substantial improvement in η_P. However, it has proven difficult to achieve large increases in the V_{oc} without an accompanying decrease in J_{sc} or FF.[8]

The origin of V_{oc} in organic solar cells is not well understood.[9,10] It has been suggested that this quantity depends on the energy difference between the lowest unoccupied molecular orbital (LUMO) of the acceptor-like material and the highest occupied molecular orbital (HOMO) of the donor-like material at the heterointerface in a bilayer cell (referred to as the interface gap, I_g, Figure 1, inset).[11] In this paper, we report on a double-heterostructure boron subphthalocyanine chloride (SubPc)/C_{60} thin-film cell with $I_g = 1.9$ eV, compared to a CuPc/C_{60} cell with $I_g = 1.5$ eV, resulting in an increase in V_{oc} of approximately the same magnitude, suggesting that V_{oc} is indeed a function of I_g.

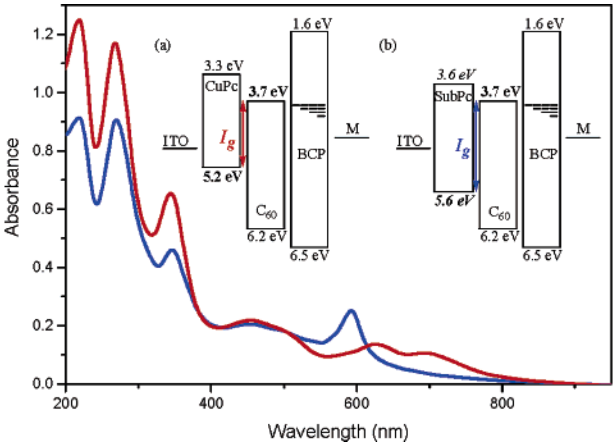

Figure 1. Absorbance spectra (on quartz) of stacked CuPc (200 Å)/C_{60} (400 Å)/BCP (100 Å) (red) and of SubPc (130 Å)/C_{60} (325 Å)/BCP (100 Å) (blue). Inset: Schematic energy level diagram for devices with (a) CuPc or (b) SubPc as the donor layer. HOMO energies are from UPS, and the LUMO energies are from IPES measurements, except for SubPc, where the LUMO[12] and HOMO[13] energies are determined from electrochemistry.

While CuPc is a planar compound with an 18 π-electron phthalocyanine macrocycle, SubPc is composed of three N-fused diiminoisoindole rings centered around a boron core. This 14 π-electron aromatic macrocycle has a nonplanar cone-shaped structure with the tetrahedral boron center out of plane with the aromatic ligand and can pack in different orientations, depending on the deposition conditions.[14,15] With strong absorption in the visible and extinction coefficients similar to CuPc (Figure 1), SubPc is a candidate as an electron donor material. The first oxidation and reduction potentials are 0.69 and −1.40 V vs a ferrocene (Fc/Fc^+) reference.[16] C_{60}, with oxidation and reduction potentials of 1.26 and −1.06 V vs Fc/Fc^+,[17] should therefore be suitable as the acceptor material in a PV cell based on SubPc.[3]

A range of efficiencies have been reported for CuPc/C_{60} device architectures.[3,18−21] To eliminate performance variance due to fabrication conditions, control devices were fabricated simultaneously with the SubPc cells. Conventional PV cell structures fabricated as controls were ITO/CuPc (200 Å)/C_{60} (400 Å)/BCP (100 Å) with a Ag (CuPc1) or Al cathode (CuPc2). The SubPc cells consisted of ITO/SubPc (200 Å)/C_{60} (400 Å)/BCP (100 Å) and a Ag (SubPc1) or Al (SubPc2) cathode.

The current density vs voltage ($J-V$) characteristics were measured in the dark and under 1−5 suns AM1.5G simulated illumination, uncorrected for solar mismatch. $J-V$ characteristics at 1 sun are provided in Table 1. The V_{oc} of SubPc1 and SubPc2 is 150 mV higher than for CuPc cells, although both J_{sc} and FF are

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Table 1. Structure and Photovoltaic Data for Devices Illuminated under 1 Sun AM1.5G Simulated Solar Illumination

cell	D/C_{60} (Å)	M^c	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η
CuPc1	$200^a/400$	Ag	4.13	0.43	0.61	1.2
CuPc2	$200^a/400$	Al	3.07	0.42	0.58	0.9
SubPc1	$200^b/400$	Ag	2.05	0.57	0.33	0.4
SubPc2	$200^b/400$	Al	1.83	0.58	0.36	0.4
SubPc3	$130^b/325$	Ag	3.61	0.98	0.41	1.7
SubPc4	$130^b/325$	Al	3.36	0.97	0.57	2.1

[a] D = CuPc. [b] D = SubPc. [c] M is the cathode material.

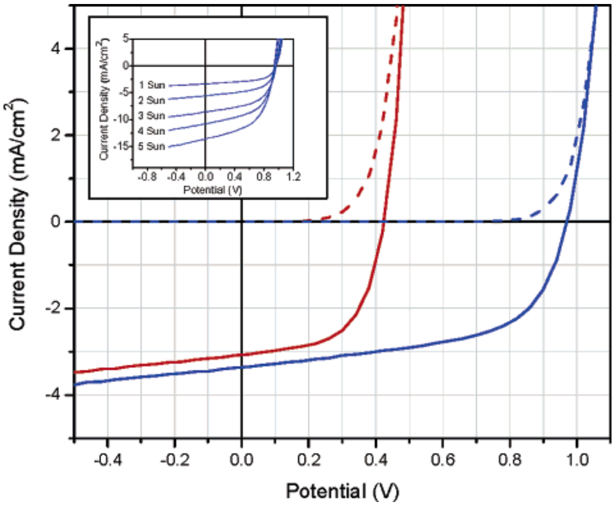

Figure 2. $J-V$ characteristics of CuPc2 (red) and SubPc4 (blue) under 1 sun AM 1.5G simulated illumination (solid) and in the dark (dashed). Inset: Intensity dependence of the SubPc4 device at 1−5 suns.

reduced, resulting in a reduced power efficiency. This is likely due to a high series resistance, which suggests that thinner donor layers are necessary for optimal device performance. Since SubPc absorbs at shorter wavelengths than CuPc, an optimal cell structure requires a corresponding decrease in C_{60} thickness to ensure that the SubPc/C_{60} interface is located in a region where the short-wavelength light intensity is highest.[22] Following this criterion, a device with the following structure was fabricated: ITO/SubPc (130 Å)/C_{60} (325 Å)/BCP (100 Å) with a Ag (SubPc3) or Al (SubPc4) cathode.

The $J-V$ characteristics of SubPc4 and CuPc2 are shown in Figure 2. In this case, V_{oc} of SubPc4 is more than double that of CuPc2, accompanied by a nearly 10% increase in J_{sc}. Although the SubPc absorption is blue-shifted relative to that of CuPc with a decreased absorbance at $\lambda = 700$ nm (Figure 1), this is compensated by the increased absorbance at $\lambda = 590$ nm, which is in a higher intensity region of the solar spectrum. V_{oc} and FF of SubPc4 are nearly independent of light intensity between 1 and 5 suns (Figure 2, inset), while the power conversion efficiency achieves a maximum value of $\eta_P = 2.1 \pm 0.2\%$ at 1 sun.

A proposed energy level diagram for the CuPc and SubPc devices is shown in the Figure 1 inset. The SubPc/C_{60} device has an I_g that is 400 meV greater than that for the CuPc/C_{60} device, correlating to an increase of V_{oc} of approximately the same magnitude (550 mV). We attribute the significant increase in V_{oc} to the smaller HOMO energy of SubPc and the subsequent increase in I_g, supporting the hypothesis that V_{oc} is dependent on I_g. V_{oc} can be increased by series resistance, which may, in turn, depend on the presence of impurities or crystalline disorder (an effect which will be discussed elsewhere). Note that the increase in V_{oc} is approximately 20% higher than that in I_g, suggesting that resistance may be affecting V_{oc}; however, the high FF's indicate that resistance alone cannot account for the increased V_{oc}.

It has been shown that varying the metal cathode has a minimal effect on V_{oc}.[4,11] However, CuPc1 with a Ag cathode shows an increased J_{sc} and FF relative to the analogous device with Al (CuPc2). It is unclear why such an effect on J_{sc} and FF is observed, whereas V_{oc} is the same for both devices. Alternatively for SubPc, FF decreases for the Ag device (SubPc3) compared to the Al device (SubPc4).

In summary, SubPc/C_{60}-based PV cells have more than twice the V_{oc} as compared to conventional devices based on CuPc/C_{60} cells, resulting in a more than doubling of the cell power conversion efficiency. By using a strongly absorbing donor material with a deep HOMO, I_g and, consequently, V_{oc} are increased without a concomitant reduction in J_{sc}. This work supports the hypothesis that I_g is a dominant factor in determining V_{oc} in organic heterojunction cells.

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Supporting Information Available: Experimental conditions for device fabrication, CuPc and SubPc structures (Figure S1), and $J-V$ characteristics for 1−5 suns for SubPc4 (Table S1 and Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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