Enhanced Open-Circuit Voltage in Subphthalocyanine/C₆₀ 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 (ηₚ) 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)/C₆₀ 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 (Vₒc), the short-circuit current density (Jₛc), and the fill factor (FF) via

\[ ηₚ = \left( \frac{Jₛc \cdot Vₒc \cdot FF}{P_i} \right) \]

where Pᵢ is the incident optical power. Here, FF depends on the series resistance and is typically between 0.5 and 0.65 for small-molecule-weight organic photovoltaics. Jₛc 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 Vₒc ≈ 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 Vₒc offers a significant opportunity for substantial improvement in ηₚ. However, it has proven difficult to achieve large increases in Vₒc without an accompanying decrease in Jₛc or FF.⁸

The origin of Vₒc 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, Δg, Figure 1, inset).¹¹ In this paper, we report on a double-heterostructure boron subphthalocyanine chloride (SubPc)/C₆₀ thin-film cell with Δg = 1.9 eV, compared to a CuPc/C₆₀ cell with Δg = 1.5 eV, resulting in an increase in Vₒc of approximately the same magnitude, suggesting that Vₒc is indeed a function of Δg.

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 C₆₀, 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/C₆₀ 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)/C₆₀ (400 Å)/BCP (100 Å)/Ag or Al cathode (CuPc1). The SubPc cells consisted of ITO/SubPc (200 Å)/C₆₀ (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 Vₒc of SubPc1 and SubPc2 is 150 mV higher than for CuPc cells, although both Jₛc and FF are

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are necessary for optimal device performance. Since SubPc absorbs to a high series resistance, which suggests that thinner donor layers 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 C60 thickness to ensure that the SubPc/C60 interface is located in a region where the short-wavelength light intensity is highest. Following this criterion, a device with the following structure was fabricated: ITO/SubPc (130 Å)/C60 (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, Voc of SubPc4 is more than double that of CuPc2, accompanied by a nearly 10% increase in Jsc. 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. Voc 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/C60 device has an \(I_p\) that is 400 meV greater than that for the CuPc/C60 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 \(I_p\), supporting the hypothesis that \(V_{oc}\) is dependent on \(I_p\). \(V_{oc}\) 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 \(I_p\), 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 \(V_{oc}\). However, CuPc1 with an 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/C60-based PV cells have more than twice the \(V_{oc}\) as compared to conventional devices based on CuPc/C60 cells, resulting in a more than doubling of the cell power conversion efficiency. By using a strongly absorbing donor material with a deep HOMO, \(I_p\) and, consequently, \(V_{oc}\) are increased without a concomitant reduction in \(J_{sc}\). This work supports the hypothesis that \(I_p\) 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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**Table 1.** Structure and Photovoltaic Data for Devices Illuminated under 1 Sun AM1.5G Simulated Solar Illumination

<table>
<thead>
<tr>
<th>Cell</th>
<th>(D_{oc} (\text{Å}))</th>
<th>(M^*)</th>
<th>(J_{sc} (\text{mA cm}^{-2}))</th>
<th>(V_{oc} (\text{V}))</th>
<th>FF</th>
<th>(\eta_p)</th>
</tr>
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<tbody>
<tr>
<td>CuPc1</td>
<td>200/1400</td>
<td>Ag</td>
<td>4.13</td>
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<td>0.61</td>
<td>1.2</td>
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<tr>
<td>CuPc2</td>
<td>200/1400</td>
<td>Al</td>
<td>3.07</td>
<td>0.42</td>
<td>0.58</td>
<td>0.9</td>
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<tr>
<td>SubPc1</td>
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<td>Ag</td>
<td>2.05</td>
<td>0.57</td>
<td>0.33</td>
<td>0.4</td>
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<tr>
<td>SubPc2</td>
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<td>Al</td>
<td>1.83</td>
<td>0.58</td>
<td>0.36</td>
<td>0.4</td>
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<tr>
<td>SubPc3</td>
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<td>Ag</td>
<td>3.61</td>
<td>0.98</td>
<td>0.41</td>
<td>1.7</td>
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<tr>
<td>SubPc4</td>
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<td>Al</td>
<td>3.36</td>
<td>0.97</td>
<td>0.57</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* D = CuPc. * D = SubPc. * M is the cathode material.

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**References**