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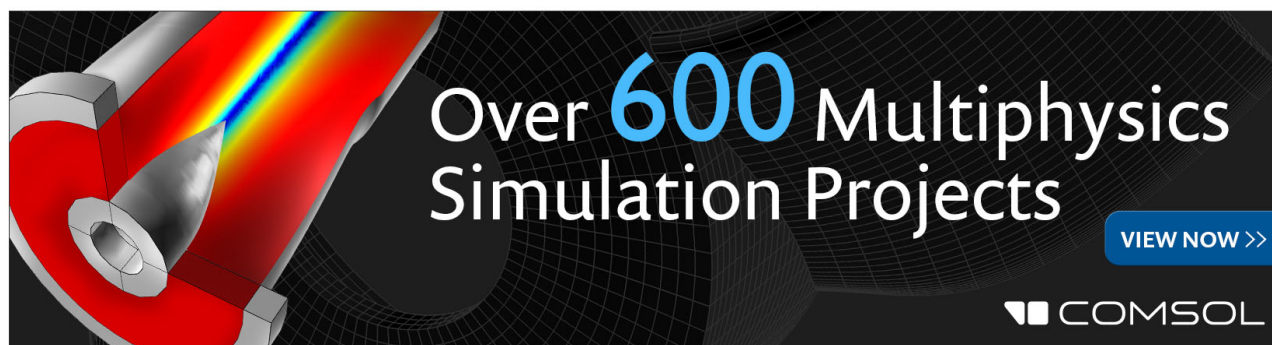
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Influence of chemical doping on the performance of organic photovoltaic cells

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The power conversion efficiency of organic photovoltaic cells can be greatly enhanced by chemical doping to control the conductivity of the organic thin films. We demonstrate a nearly twofold improvement in the efficiency of planar heterojunction copper phthalocyanine/fullerene cells by *n*-doping the electron acceptor layer with decamethylcobaltocene in the vicinity of the fullerene/cathode interface. Doping improves the charge extraction efficiency and decreases the series resistance of the organic films, improving the current density and fill factor, respectively. © 2009 American Institute of Physics. [DOI: 10.1063/1.3138131]

The performance of organic photovoltaic (OPV) devices has been limited by short exciton diffusion lengths,¹ high exciton binding energies,^{2,3} poor exciton dissociation,¹ losses to geminate recombination,⁴ and inefficient carrier extraction.⁵ In recent years, the first three processes have received considerable attention, particularly via the engineering of energy-level offsets and microstructures of bulk heterojunctions.^{6–8} The energy-level offset at the donor-acceptor heterojunction interface provides the driving force for exciton dissociation, whereas bulk interfaces increase interfacial areas while moving active areas closer to regions of exciton generation. As a result, power conversion efficiencies of bulk heterojunction OPVs have improved to $\sim 5 \pm 1\%$.^{9,10} On the other hand, relatively little systematic work has been devoted to reducing geminate recombination and enhancing carrier extraction, which can be improved primarily by increasing the conductivity of organic materials.

Chemical doping has been shown to allow control of the position of the Fermi level in, and to increase the conductivity of, organic films,^{11–15} two phenomena that potentially have significant impact on OPV cell performance. Care must be taken to ensure structural integrity of the device, as some dopants currently used in OPVs have been shown to diffuse appreciably through some organic materials.^{16,17} The molecular dopant cobaltocene was shown to be immobile in tris(thieno)hexaazatriphenylene,¹⁸ up to at least at 60 °C. It is reasonable to assume that the results would be similar in other host matrices, and for the chemically similar, but slightly larger, dopant molecule decamethylcobaltocene CoCp_2^* .

In this letter, the impact of chemical doping and the importance of film conductivity on the performance of OPV devices are presented. To isolate the effects of dopant-induced changes in device performance from the effects of the bulk heterojunction, planar heterojunction OPVs consisting of copper phthalocyanine (CuPc), i.e., the donor, and carbon-60 fullerene (C_{60}), i.e., the acceptor, are employed in

which the C_{60} layer is either undoped or *n*-doped with CoCp_2^* . Devices featuring doped layers exhibit increased short-circuit currents (J_{sc}), open-circuit voltages (V_{oc}), fill factors (FF), and power conversion efficiencies (PCE). These improvements are attributed to an increase in film conductivity that results in decreased series resistance, as well as changes in the electric-field distribution and built-in voltage of the device that assist in carrier extraction.

Undoped and doped OPV cells (Fig. 1 inset) were fabricated in two parts. Indium-tin-oxide (ITO) substrates were cleaned by mechanical scrubbing with detergent, rinsing in de-ionized water, ultrasonication in methanol, and a 1 min exposure to oxygen plasma at Dalhousie. 20 nm of undoped CuPc and 30 nm of undoped C_{60} were then vacuum deposited ($p_{\text{base}} = 1 \times 10^{-9}$ Torr) at 0.1 nm s^{-1} onto the ITO substrates. The partially completed samples were annealed in a nitrogen atmosphere on a hotplate at 155 °C for 90 min,

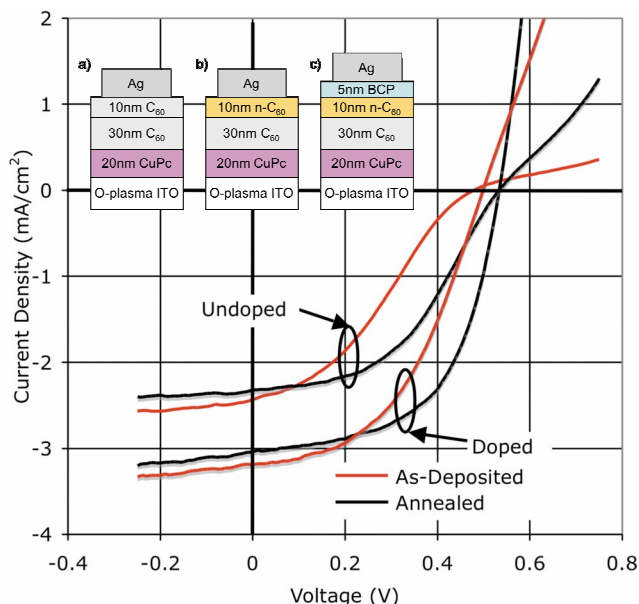


FIG. 1. (Color online) Current density vs voltage (J - V) characteristics of the diodes under 1 sun illumination. Inset illustrates device structures in this study. “Undoped” data correspond to structure (a). “Doped” data are representative of (b) and (c).

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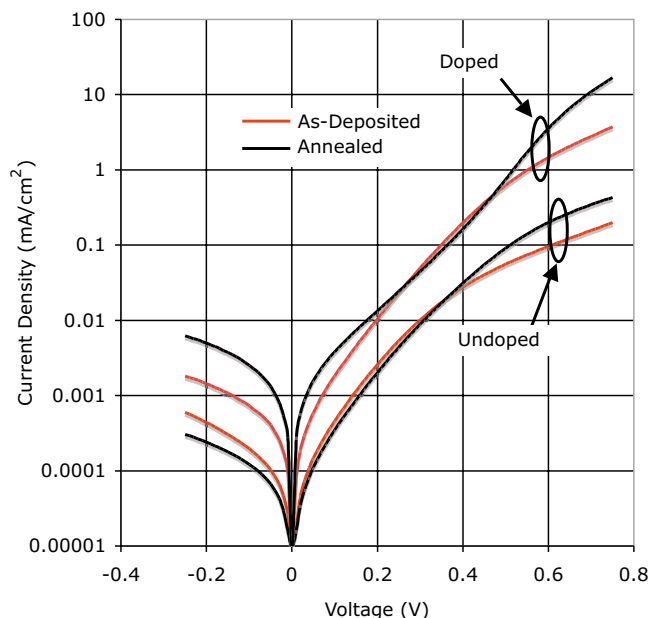


FIG. 2. (Color online) Dark current density vs voltage (J - V) characteristics of the diodes.

packaged in nitrogen, and shipped to Princeton University.

With minimal exposure to air (<1 min), the samples were placed in an ultrahigh vacuum system ($p_{\text{base}} < 10^{-9}$ Torr) where the three devices were completed by depositing either (a) 10 nm of undoped C_{60} , (b) 10 nm of n -doped C_{60} , or (c) 10 nm of n -doped C_{60} followed by 5 nm of bathocuproine (BCP). n -doping was accomplished by evaporating C_{60} in a CoCp_2^* background pressure of 10^{-8} Torr.¹⁵ Because of the favorable energy difference between the highest occupied molecular level of CoCp_2^* (ionization energy of 3.3 eV)¹⁵ and the lowest unoccupied molecular level of C_{60} (electron affinity of 4.0 eV)^{19,20} total dopant incorporation and ionization is expected, resulting in a doping concentration of approximately 3%. Ag top contacts were thermally evaporated through a stencil mask. With minimal exposure to air, the samples were removed from vacuum, packaged in nitrogen, and shipped to Dalhousie University for photovoltaic characterization.

The OPV testing was performed in a nitrogen glove box ($[\text{H}_2\text{O}], [\text{O}_2] < 0.1$ ppm) using a Newport-Oriel 150 W solar simulator under 100 mW cm^{-2} AM1.5D illumination as determined by a thermopile optical power meter. Current-density voltage (J - V) characteristics were obtained using a Keithley 236 SMU, relevant photovoltaic metrics (J_{sc} , V_{oc} , FF, and PCE) were extracted from the J - V curves. After the devices were characterized as-received from Princeton, they were once again annealed in a nitrogen glove box to a temperature of 155°C for 90 min and recharacterized.

Typical illuminated J - V curves for as-deposited and annealed devices are presented in Fig. 1, and dark J - V curves for the same devices in Fig. 2. The data included in both figures are from undoped and doped $\text{C}_{60}/\text{CuPc}$ devices. Doped devices containing a BCP exciton blocking layer were very similar to the doped cells, and are therefore not included in the figures. Figures of merit for typical devices are included in Table I. Both annealing and doping resulted in significantly improved device characteristics. The influence of each will be discussed in the following paragraphs.

For the as-deposited devices, n -doping of the C_{60} layer results in a 30% increase in the short-circuit current density, a 5% increase in the open circuit voltage, a 42% increase in the fill factor, and a 92% increase in power conversion efficiency (Table I). We attribute the improved performance upon doping to two effects. First, the enhanced conductivity of the n -doped region leads to improved electron transport through the acceptor layer, which reduces Ohmic losses and results in higher short-circuit current, improved fill factor, and increased efficiency. Second, doping of the near-contact region reduces the effective distance over which the built-in potential drops, e.g., nominally <50 nm for the doped device as compared to 60 nm for the undoped device. This produces a larger electric field in the region of the donor-acceptor interface, which enhances charge separation, reduces interfacial recombination, and ultimately improves short-circuit current densities and efficiencies.

It is generally accepted that the open circuit voltage (V_{oc}) is limited by the ionization energy of the donor and the electron affinity of the acceptor.²¹ This assumes that the Fermi level at the acceptor-and-donor-electrode interfaces is pinned near the acceptor lowest unoccupied molecular orbital (LUMO) and donor highest occupied molecular orbital levels, respectively. Reduction in V_{oc} may occur if these criteria are not met. Inverse photoemission studies of C_{60}/Ag suggest that the Fermi level is effectively pinned at the LUMO at the Ag/C_{60} interface,²² given the C_{60} electron affinity and the Ag work function, and we therefore do not see an appreciable increase in V_{oc} upon doping of the C_{60} layer.

After annealing, doped devices exhibit $\sim 30\%$ higher short-circuit current densities than undoped devices. The fill factors of both undoped and doped devices improve with annealing (to be discussed below), but those of the doped devices are still 26% larger than those of the undoped devices. As a result of the improved current densities and fill factors, the peak power conversion efficiencies of the doped devices (with and without BCP) are 60% larger than those of the undoped devices. Interestingly, we note that V_{oc} is virtually identical for all three device types following annealing, supporting the hypothesis of a pinned Fermi level just below the C_{60} LUMO at the C_{60}/Ag interface.

TABLE I. Summary of figures of merit for solar cells in this study.

	Undoped		Doped C_{60}		Doped C_{60} +BCP	
	As deposited	Annealed	As deposited	Annealed	As deposited	Annealed
V_{oc} (V)	0.48	0.53	0.50	0.53	0.50	0.53
J_{sc} (mA/cm^2)	2.43	2.32	3.18	2.98	3.05	3.04
FF	0.33	0.46	0.47	0.58	0.48	0.57
PCE (%)	0.39	0.57	0.75	0.91	0.74	0.92

Annealing modestly improves the open circuit voltages. The short-circuit current densities decrease slightly for most devices, with the exception of those containing BCP. These decreases are more than compensated by the improved fill factors, and considerably improved power conversion efficiencies are realized by all devices after annealing.

The largest improvement following annealing was observed for undoped devices. The open circuit voltage increased by 10% and the fill factor improved by 40%, while the short-circuit current decreased by 5%, resulting in a net increase in power conversion efficiency of 46%. There are a number of effects that may influence these figures of merit. Molecular ordering may improve during annealing, resulting in higher charge carrier mobilities and reduced Ohmic losses in the films. This would partly explain the improved fill factor and perhaps the increased open circuit voltage. If we assume that the Fermi level is pinned by the tail states in a disorder-broadened LUMO level,²³ the degree of broadening may decrease after annealing, allowing the pinning position to shift slightly (55 meV) toward the LUMO. In the case of undoped devices, the fill factor is clearly influenced by a second effect. The *J-V* curves for as-deposited undoped films contain a region near V_{oc} where the curve becomes concave, as has previously been reported in similar cells.²⁴ This effect is greatly reduced following annealing and results in a significant improvement in the fill factor. Gupta *et al.*²⁵ have discussed concave down *J-V* characteristics in polymer solar cells and demonstrated it to be a contact effect, due to charge accumulation near the electrode. Molecular reordering and improved electron mobility in the contact region following annealing may help reduce charge accumulation and therefore the magnitude of this effect. This effect is absent in the doped devices due to the high conductivity doped region near the contact.

Turning to the *n*-doped devices, annealing was found to enhance the performance of both C_{60} and doped C_{60} /BCP devices. The open circuit voltage of both device types increased by 6%, while the fill factors increased by 23% for C_{60} devices, and 19% for C_{60} /BCP devices. The power conversion efficiencies increased by 21% and 24%, respectively.

We find an increase in PCE between roughly 50% and 100% for all devices, under all annealing conditions, when we compare doped to undoped devices. Doping of the electron acceptor material greatly improves the charge extraction efficiency and decreases the series resistive losses in the cells, as evidenced by the improved short-circuit current densities and fill factors, respectively. We note that these experiments were carried out under nonideal conditions. Shipping the partially completed devices between laboratories definitely had a detrimental effect on the devices. Simple undoped CuPc/ C_{60} /BCP devices fabricated at the Dalhousie laboratory routinely have efficiencies in excess of 1%, compared to $\approx 0.5\%$ reported here, and there are reports in the literature of similar devices having efficiencies as high as 3.6% under 1 sun illumination.²⁶ It is likely that both the doped and undoped devices suffer from similar reductions in efficiency due to the nonideal fabrication conditions. It is even possible that, due to the air sensitivity of the very low ionization energy $CoCp_2^*$ dopant, the doped devices suffer an even greater reduction in efficiency due to shipping be-

tween laboratories. We are therefore confident that our results are representative of the comparative improvement in power conversion efficiencies that can be realized by controlled doping of OPV heterostructures. The results should also hold when extended to mixed heterojunction devices, where the neat films in the contact regions are molecularly doped.

In conclusion, we have demonstrated that improvements in the PCE of organic heterojunction solar cells by nearly a factor of two can be realized by molecular doping to increase the conductivity of the electron acceptor in the region near the acceptor/electrode contact. The improved efficiency is due to increased charge extraction efficiency and decreased series resistance in the acceptor layer. Further improvement would undoubtedly be realized by *p*-doping the donor region to form a *p-i-n* heterostructure device.

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