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Efficient organic photovoltaic devices using a combination of exciton blocking layer and anodic buffer layer

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By using bathophenanthroline (BPhen) as an exciton blocking layer (EBL) at the organic/cathode contact of a standard copper phthalocyanine/C₆₀ organic photovoltaic (OPV) device, power conversion efficiency was substantially increased from 0.86% to 2.64%. The BPhen-based devices showed a 45% increase in power conversion efficiency over that of an equivalent device with an EBL of bathocuproine. The performance improvement was analyzed in terms of the electron energy levels, optical transparencies and electron mobilities of the two EBLs. Based on these results, the roles of and requirements for an effective EBL were discussed. Combining the use of BPhen and a WO₃ anodic buffer layer further increased the power conversion efficiency of the OPV device to 3.33%. © 2006 American Institute of Physics. [DOI: 10.1063/1.2363649]

I. INTRODUCTION

Organic photovoltaic (OPV) devices have received considerable attention because of the potential for low-cost solar energy conversion.^{1–4} Under illumination, excitons are generated in the photoactive layers and some would dissociate into electrons and holes at the donor/acceptor interfaces. These charge carriers are subsequently collected at the respective electrodes, contributing to the photocurrent. At the same time, other excitons may diffuse to the cathode and decay nonradiatively via quenching, which substantially lowers the quantum efficiency.^{5,6} Many approaches have been attempted to improve the device performance, including the introduction of mixed donor-acceptor heterojunctions,^{7–9} multiple heterojunctions,^{2,10,11} triplet photoactive materials,¹² and light-harvesting structures.¹³ In the case of copper phthalocyanine (CuPc)/buckminsterfullerene (C₆₀) bilayer OPV cells, exciton blocking layers (EBLs) between the acceptor and the cathode have been shown to improve the device performance.^{4,7,9,14–16} Peumans and Forrest¹⁴ introduced bathocuproine (BCP) as an EBL, in which a standard CuPc/C₆₀ bilayer OPV cell exhibits a very high power conversion efficiency (η) of 3.6% under 1 sun AM1.5 illumination. With its large ionization potential ($I_p=6.4$ eV) and large energy gap (3.5 eV),¹⁷ BCP acts as an effective EBL which blocks the diffusion of excitons to the cathode. This confinement of excitons increases the chance of exciton dissociation at the donor/acceptor interface and thus leads to efficiency enhancement.

While the approach of using an EBL is important, relatively few studies have been done on other EBL materials.^{18,19} In this letter, we explore the application of bathophenanthroline (BPhen) as an EBL in standard CuPc/C₆₀ OPV devices. BPhen is selected because its highest occupied molecular orbital (HOMO) and lowest unoccu-

piated molecular orbital (LUMO) levels are almost the same as those of BCP.¹⁷ Significantly, the electron transporting ability of BPhen (Ref. 20) is two orders of magnitude higher than that of BCP.¹⁷ By comparing the performance of the BPhen- and BCP-based cells, the roles and influences of the electron mobility and optical transparency of EBL in general are discussed.

Apart from putting an EBL at the cathode side, it has been reported that thin vanadium oxide and molybdenum oxide can be used as buffer layers at the anode side for performance improvement of OPV cell.²¹ In this work, we study the feasibility of using both approaches in the same cell to explore whether cumulative effects can be obtained. We find that when tungsten oxide, a low-cost, nontoxic, and easily evaporable material, was used in combination with a BPhen EBL, an external η of 3.33% was obtained in a standard CuPc/C₆₀ PV cell.

II. EXPERIMENT

Patterned indium tin oxide (ITO) glass substrates with a sheet resistance of 30 $\Omega/\square$ were cleaned with Decon 90, rinsed in de-ionized water, then dried in an oven, and finally treated in an ultraviolet-ozone chamber. A 200 Å thick CuPc and a 400 Å thick C₆₀ were used as the electron donor/hole transporter and the electron acceptor/electron transporter, respectively. A layer of 40–200 Å thick BPhen was then deposited as an EBL. All organic materials, CuPc (Aldrich 99%), C₆₀ (ADS 99.95%), and BPhen (Acros 99%), were used as received. An 800 Å thick Al cathode was then deposited by thermal evaporation through a shadow mask, giving an active device area of 0.1 cm². Deposition rates were monitored with a quartz oscillating crystal and controlled to be 1–2 Å/s for both organic and metal layers. Current-voltage characteristics of OPV devices were measured with a programmable Keithley model 237 power source. The photocurrent was measured under illumination from an Oriel

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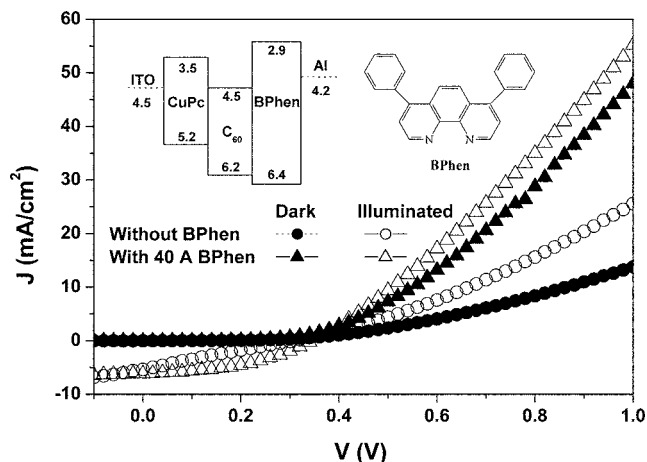


FIG. 1. J - V characteristics of devices without (○) and with (△) 40 Å thick BPhen in the dark and under illumination with an intensity of 45 mW/cm². Inset: energy level diagram of the device structure of ITO/CuPc/C₆₀/BPhen/Al and the chemical structure of BPhen.

150 W solar simulator equipped with AM1.5D (AM: air mass; D: direct) filters, and the light intensity was measured with an Oriel radiant power meter.

III. RESULTS AND DISCUSSION

Figure 1 depicts the current density-voltage (J - V) characteristics of the devices with and without a 40 Å thick BPhen in the dark and under illumination with an intensity of 45 mW/cm². Devices without the BPhen layer show a poor photovoltaic response: short-circuit current density (J_{SC}) = 5.36 mA/cm², open-circuit voltage (V_{OC}) = 0.31 V, and a fill factor (FF) (characterizing the shape of the J - V curve in the power-generating fourth quadrant) of 0.23. The relatively poor performance may be attributed to the cathode-induced exciton quenching.^{6,14} By incorporating BPhen as an EBL, the devices exhibit substantially improved performance; J_{SC} = 6.15 mA/cm², V_{OC} = 0.34 V, and FF = 0.45. These values combine to yield a more-than-twofold increase in power conversion efficiency ($\eta = J_{SC}V_{OC}FF/P_{inc}$, where P_{inc} is the incident optical power density) to 2.10%. In addition, from the dark J - V curves it seems that the EBL also aids in charge injection, in which the introduction of a BPhen layer leads to an increase in the dark current density under forward bias by

TABLE I. Key parameters for photovoltaic devices with different thicknesses of BPhen. All devices were irradiated with AM1.5 direct spectral illumination with power intensity of 45 mW/cm².

BPhen thickness (Å)	J_{SC} (mA/cm²)	V_{OC} (V)	FF	η (%)
0	5.36	0.31	0.23	0.84
40	6.15	0.34	0.45	2.10
50	7.80	0.34	0.45	2.64
80	7.57	0.34	0.43	2.35
100	7.36	0.34	0.30	1.60
150	0.86	0.34	0.21	0.14
200	0.02	0.34	0.22	0.004

a factor of 3.5. This clearly shows that BPhen as an exciton blocking layer can effectively enhance the photovoltaic performance.

Figure 2(a) illustrates the dependence of J_{SC} and V_{OC} of the photovoltaic devices as a function of BPhen thickness. Under illumination with an intensity of 45 mW/cm², J_{SC} first increases to a maximum of 7.80 mA/cm² as the BPhen thickness increases to 50 Å [Fig. 2(a)], and then decreases as the BPhen layer becomes thicker. On the other hand, V_{OC} is virtually the same for all BPhen-based devices. This is consistent with other works showing that the V_{OC} depends on the energy difference between the HOMO of the donor and the LUMO of the acceptor, and not on the production steps or film qualities.^{22,23} Adding an EBL at the acceptor/metal contact is not expected to significantly alter the V_{OC} . With the optimized BPhen thickness of 50 Å, the devices exhibit the best performance with J_{SC} = 7.80 mA/cm², V_{OC} = 0.34 V, FF = 0.45, and η = 2.64%. The drop-off in J_{SC} in devices with a thicker BPhen layer results in a rapid drop of FF and η from 0.45 and 2.64% to 0.22 and 0.004% for a BPhen thickness of 200 Å. Table I summarizes the key cell parameters as a function of BPhen thickness under illumination. In this article, we concentrate our attention on the dependence of cell parameters on the thickness of EBLs under illumination with the same light intensity. It is worth noting that OPV cell parameters are light intensity dependent, as reported elsewhere.^{2,7,8,14} Here, the comparison of the efficiencies is of particular interest, but not their dependence on light intensity. The reduction in FF and η can be attributed to the higher series resistance of the thicker BPhen layer.²⁴ It has been proposed by Peumans and Forrest that in the EBL, electron transports mainly via defect states induced upon cathode

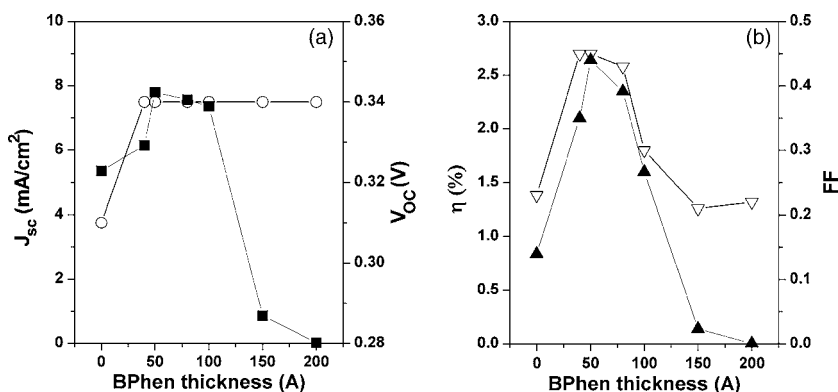


FIG. 2. (a) J_{SC} (■), V_{OC} (○), (b) FF (▽), and η (▲) of photovoltaic devices as a function of BPhen thickness.

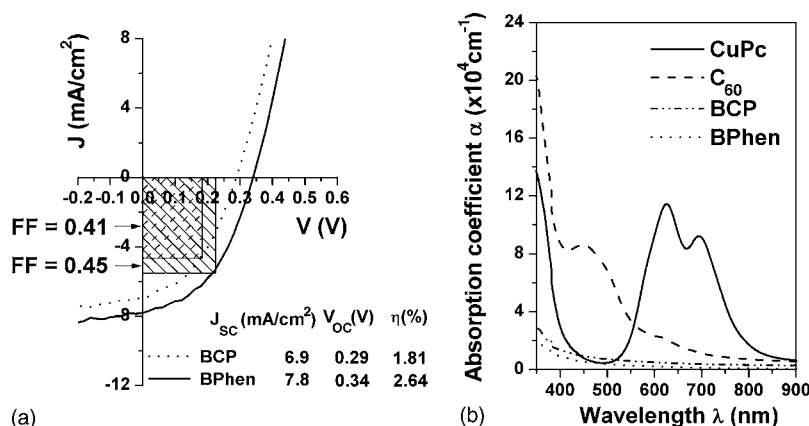


FIG. 3. (a) Illuminated J - V characteristics of devices with either BPhen (solid line) or BCP (dotted line) as EBL and the (b) absorption coefficients of BCP (dashed-dotted line) and BPhen (dotted line) on quartz. Absorption coefficients of CuPc (solid line) and C_{60} (dashed line) are also shown for comparison.

deposition.¹⁴ As the EBL becomes thicker, region far away from the cathode has insufficient defect states for carrier transportation, resulting in a decrease in carrier collection efficiency (defined as the fraction of charges collected at the electrode) at the electrode and hence η .²⁴

It has been recognized that BCP can effectively block excitons from cathode quenching. For comparison, devices of ITO/CuPc (200 Å)/ C_{60} (400 Å)/BCP (50 Å)/Al were fabricated. Figure 3 shows the J - V characteristics of devices with either BPhen or BCP as the EBL. Under an illumination power of 45 mW/cm², all J_{SC} , V_{OC} , and FF increased when BPhen was used instead of BCP. More importantly, η increases to 2.64%, which is considerably higher than that of the BCP-based device (1.81%). The performance enhancement can be explained by the improved transportation of the photogenerated electrons through EBL to the cathode. As shown in Table II, both electron affinity (E_A) and I_P of BPhen (Ref. 25) are identical to those of BCP.^{17,19} Due to the large HOMO-LUMO energy gap, it is reasonable to expect that exciton dissociation is difficult at the C_{60} /BPhen interface, enhancing confinement of excitons at the donor/acceptor junction. Another prerequisite of an efficient EBL is a high optical transparency so that the EBL does not absorb light reflected from metal electrode. Absorption coefficients of BCP and BPhen films on quartz substrates measured with a Perkin Elmer Lambda 2S UV/Vis spectrometer are shown in Fig. 3(b). Clearly, both the BCP and the BPhen films have relatively low absorption coefficients as compared to those of the photoactive CuPc and C_{60} films. While BCP and BPhen have similar optical transparency, and HOMO and LUMO energy levels, electron mobility in BPhen²⁰ at an electric field of 3.6×10^5 V/cm is two orders of magnitude higher than that in BCP.¹⁷ The much higher electron mobility definitely leads to better electron transport through the EBL

TABLE II. Electronic properties of BPhen and BCP, and their electron mobilities at an electric field of 3.6×10^5 V/cm.

EBL	E_A (eV)	I_P (eV)	μ (cm²/V s)	Ref.
BPhen ^a	2.9	6.4	5.0×10^{-4}	20
BCP ^a	2.9	6.4	5.0×10^{-6}	17

^aIt should be noted that mobility values of BPhen and BCP were measured using time-of-flight and transient electroluminescence techniques, respectively. The difference of the two orders of magnitude indicates that BPhen has a much better electron transporting ability as compared to BCP.

and thereby increases the space charge limited current density.²⁴ This is in good agreement with the increase in J_{SC} of the BPhen-based devices over the BCP-based devices.

Further improvements in device performance can be achieved by inserting a tungsten oxide (WO_3) buffer layer between the ITO and CuPc layers. Devices with a configuration of ITO/ WO_3 /CuPc (200 Å)/ C_{60} (400 Å)/BPhen (50 Å)/Al were fabricated. Figure 4 depicts the J - V characteristics for devices with different thicknesses of WO_3 under an illumination power of 45 mW/cm². The insertion of WO_3 as a buffer layer remarkably increases both the J_{SC} and the V_{OC} . At the optimized thickness of WO_3 (40 Å), the J_{SC} and the V_{OC} increase to 10.1 mA/cm² and 0.42 V, respectively, giving a maximum η of 3.33%. The improved results are primarily a consequence of the high work function of the metal oxide.²¹ Brabec reported that the V_{OC} depends linearly on the anodic work function.²⁶ In our devices, the higher work function of WO_3 (4.8 eV) (Ref. 27) enhances hole collection at the ITO/CuPc contact, resulting in a higher V_{OC} and a better photovoltaic response. It is worthy to mention that the electrode linearity on V_{OC} is only valid for a non-Ohmic contact, such as ITO/CuPc¹⁴ and ITO/poly (3,4-ethylene dioxythiophene).²⁶ For the case of an Ohmic contact, especially at the donor/cathode interface, V_{OC} is given by the HOMO/LUMO levels of the donor/acceptor system.^{23,26}

On the other hand, a thicker metal oxide layer is detrimental to the device performance. As 60 Å thick WO_3 is inserted, both J_{SC} and V_{OC} decrease, hence resulting to a

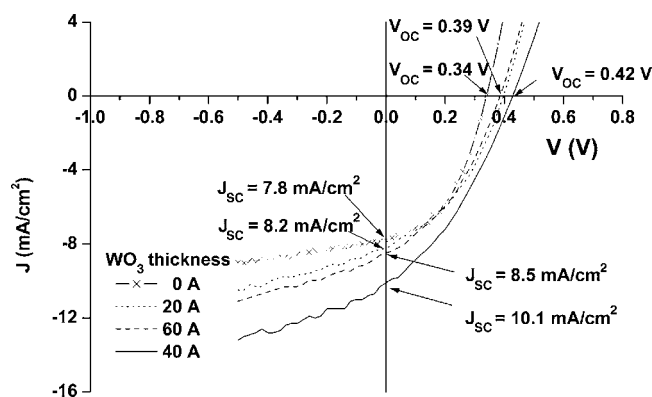


FIG. 4. J - V characteristics for devices with different thicknesses of WO_3 under illumination of 45 mW/cm².

TABLE III. Photovoltaic properties and cell series resistance R_S obtained from dark current density–voltage characteristics of devices with various WO_3 buffer layer thicknesses.

WO_3 thickness ($\text{\AA}$)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	R_S (Ω)
0	7.8	0.34	0.45	2.64	56
20	8.2	0.40	0.38	2.77	75
40	10.1	0.42	0.36	3.33	105
60	8.5	0.39	0.36	2.73	133

lower η . The results can be understood in terms of the cell series resistance R_S . Under illumination, the forward-bias dark current density J_D can be fitted according to the ideal diode equation,²⁸

$$J_D = J_S \left\{ \exp \left[\frac{q(V - J_D R_{SA})}{nkT} \right] - 1 \right\},$$

where J_S is the reverse-bias saturation current density, n is the ideality factor, q is the electron charge, k is the Boltzmann constant, T is the temperature, $R_{SA} = R_S A$ is the specific series resistance, and A is the active area of the devices. Table III lists the key parameters and the calculated R_S obtained from the dark current density of the photovoltaic devices with various WO_3 thicknesses. Clearly, a thicker metal oxide layer results in a higher R_S and, consequently, a lower current density.

IV. CONCLUSIONS

In summary, we have studied the role of BPhen as EBL in double-heterostructured $\text{CuPc}/\text{C}_{60}$ OPV devices. Devices with an optimized thickness of BPhen layer result in substantial improvement in all J_{SC} , V_{OC} , and FF, and a high η of 2.64%. The better electron transport and exciton blocking ability of BPhen are primary contributors to the improved device performance. Introduction of a WO_3 layer as anodic buffer layer further improves η to 3.33%. The results explicitly demonstrate that the combination of an efficient EBL and a high work function anodic buffer layer yields an effective approach for improving the η of OPV cells.

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