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Description	

## Control of open-circuit voltage in organic photovoltaic cells by inserting an ultrathin metal-phthalocyanine layer

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The authors develop organic photovoltaic cells with multicharge separation (MCS) interfaces by inserting a very thin layer of metal phthalocyanine. The devices with MCS interface allow one to control short-circuit current density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ). The power conversion efficiency ( $\eta_p$ ) of the device with MCS interface (Cu-phthalocyanine/ $C_{60}$  and pentacene/ $C_{60}$ ) is enhanced compared with that of the device with single charge separation interface (pentacene/ $C_{60}$ ). The enhancement of  $\eta_p$  is attributable to the increase in  $V_{oc}$  with maintaining the  $J_{sc}$ . By using Zn-phthalocyanine, which possesses longer excited lifetime compared with Cu-phthalocyanine, both  $J_{sc}$  and  $V_{oc}$  have been improved simultaneously and the  $\eta_p$  reaches 2.04%. © 2007 American Institute of Physics. [DOI: 10.1063/1.2775085]

In recent years, attention has been drawn toward solar energy conversion to develop inexpensive renewable energy sources. New concepts and approaches for production of efficient and low-cost organic solar cells have been desired for further development and application. So far, the power conversion efficiency ( $\eta_p$ ) has steadily improved through the use of new materials and device structures.<sup>1-14</sup> In particular, great effort has been made for the enhancement of short-circuit current density ( $J_{sc}$ ). An approach to increase the  $J_{sc}$  is the use of molecules with high carrier mobilities.<sup>4,7</sup> One of the representative materials is pentacene, and the photovoltaic cells using pentacene as the  $p$ -type layer attains high  $\eta_p$  values.<sup>4</sup> The other one is the use of bulk heterojunctions (e.g., the composite of  $p$ -type and  $n$ -type materials) as an active layer in both polymer and small molecule-based solar cells.<sup>8-10,12,13</sup>

In the bulk heterojunction cells, the distance that an exciton must travel from its generation site to charge-separation (CS) interface is reduced by the formation of interpenetrating network of  $p$ -type and  $n$ -type materials. This leads to a higher  $J_{sc}$  owing to the enhanced exciton diffusion length.<sup>13</sup> Thus, the formation of the proper interpenetrating network in an active layer is a key for the improvement of  $J_{sc}$ , which governs the final conversion efficiency  $\eta_p$ . However, in these composite cells, it is quite challenging to precisely control the formation of interpenetrating network by solely fabrication process such as annealing condition. Furthermore, there is no enhancement effect of open-circuit voltage ( $V_{oc}$ ) due to the formation of an interpenetrating network. In other words, for further improvement of  $\eta_p$ , it is essential to enhance  $V_{oc}$ , with maintaining the corresponding  $J_{sc}$ .

Here, we demonstrate photovoltaic cell composed of multicharge-separation (MCS) interfaces in the active layer for the improvement of  $\eta_p$  (Fig. 1). Pentacene and phthalocyanines, Cu-phthalocyanine (CuPc) or Zn-phthalocyanine (ZnPc), are employed as the  $p$ -type molecules to form  $p$ - $n$  junction with  $n$ -type of  $C_{60}$ . The highest occupied molecular orbital (HOMO) levels of those  $p$ -type materials are 5.0 eV

(pentacene)<sup>15</sup> and 5.1 eV (CuPc and ZnPc).<sup>15</sup> By inserting thin layer of phthalocyanines at the CS interface between pentacene/ $C_{60}$ , we obtain enhanced  $\eta_p$  and  $V_{oc}$  in accordance with the increased energy difference between the lowest unoccupied molecular orbital (LUMO) level of the  $n$ -type material and the HOMO level of the  $p$ -type material.<sup>16,17</sup> Importantly, when 2-nm-thick CuPc was replaced with ZnPc,  $J_{sc}$  increase further in addition to the enhancement of  $V_{oc}$ .

Devices were fabricated on a glass substrate coated with an indium-tin-oxide (ITO) electrode. The thickness of ITO was 150 nm and the sheet resistance was 8.2 V/sq. Devices consisted of pentacene as  $p$ -type layer with high hole mobility, CuPc as a  $p$ -type material with large HOMO level,  $C_{60}$  as  $n$ -type layer, and bathocuproine (BCP) as an exciton blocking layer. Pentacene and  $C_{60}$  were purchased from Aldrich and MTR, Ltd., respectively. Pentacene and  $C_{60}$  were sublimed in our laboratory before use. High purity materials of CuPc and BCP were provided by Nippon Steel Chemical Co., Ltd. and were used without further purification. All organic layers were deposited onto the ITO substrate by vacuum evaporation using Knudsen cells under  $10^{-6}$  Torr.

The device structure used in this study is ITO/pentacene (50 nm)/CuPc ( $x$  nm)/ $C_{60}$  (40 nm)/BCP (10 nm)/Ag (100 nm), which is fabricated by vapor deposition method (Fig. 1). The thickness of the CuPc layer is varied from 0 to 10 nm. Figure 1 shows schematic representations of MCS interfaces and the corresponding atomic force microscopy (AFM) images of surface morphologies of CuPc ( $x$  nm)/pentacene (50 nm). In the case of pentacene surface with no CuPc layer [Fig. 1(a)], we observe rough surfaces originated from the crystal growth of pentacene, whereas the image of CuPc (6 nm)/pentacene (50 nm) film becomes relatively flat [Fig. 1(c)], as indicated by root mean square (rms) factors. This may suggest that the surface roughness of pentacene layer on ITO is buried by CuPc layer as increasing the film thickness of CuPc. The increase in the CuPc layer is also confirmed by the absorption spectra. Comparing the absorption spectra of ITO/pentacene (50 nm)/CuPc (0, 2, and 6 nm)/ $C_{60}$  (40 nm)/BCP (10 nm), the absorption intensity of CuPc layer clearly increases (see supplemental information 1).

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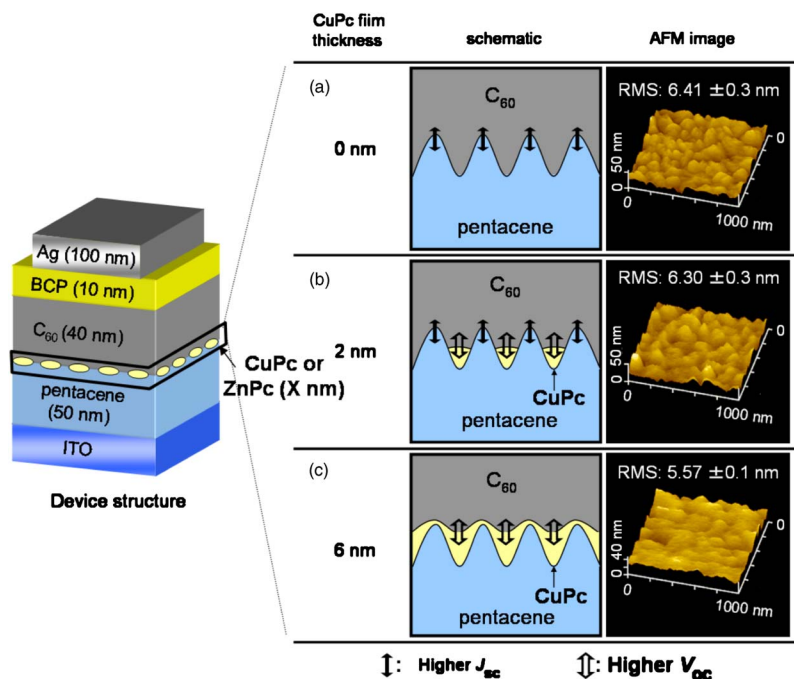


FIG. 1. (Color online) Illustration of the device structure with multicharge separation interface. The model of multicharge separation interface and atomic force microscope (AFM) images of the surface of (a) pentacene (50 nm), (b) CuPc (2 nm)/pentacene (50 nm) and (c) CuPc (6 nm)/pentacene (50 nm) on ITO substrate.

Figures 2(a) and 2(b) show the current density-voltage ( $J$ - $V$ ) characteristics and values of  $J_{sc}$  and  $V_{oc}$  as a function of the thickness of CuPc layer under the illumination of AM1.5 (100 mW/cm<sup>2</sup>) simulated solar light. We observe increase of  $V_{oc}$  from 0.38 to 0.47 V by inserting thin layer of CuPc. The change of  $V_{oc}$  corresponds to the larger HOMO level of CuPc (5.1 eV) compared with pentacene (5.0 eV) [Fig. 2(c)]. Whereas, the  $J_{sc}$  exhibits plateau in the 0–2 nm range and then it decreased at thicker than 3 nm. Figure 2(d) shows  $\eta_p$  relative to the CuPc layer thickness. The maximum  $\eta_p$  attains 1.97% in ITO/pentacene (50 nm)/CuPc (2 nm)/C<sub>60</sub> (40 nm)/BCP (10 nm)/Ag (100 nm), which is higher than that of the device without CuPc layer.<sup>18</sup> The  $J_{sc}$  decreases in the 3–6 nm range. Both  $V_{oc}$  and  $J_{sc}$  are approximately unchanged in the 6–10 nm range of CuPc layer. At this thickness range, pentacene layer may be completely covered by CuPc layer. The change of  $V_{oc}$  and  $J_{sc}$  as a function of CuPc thickness can be ascribed to the change of charge separation interface from pentacene/C<sub>60</sub> to CuPc/C<sub>60</sub>.

The transition of the dominant charge separation interface was confirmed by the photocurrent action spectra, as shown in Fig. 3(a). The device without CuPc layer exhibits a broad maximum at 440 nm due to the absorption of C<sub>60</sub>, whereas two peaks at 590 and 670 nm are attributed to pentacene. It is obvious that the interface at pentacene/C<sub>60</sub> is responsible to charge separation in this device. By inserting 2–3 nm of CuPc layer, additional increase in external quantum efficiency ( $\eta_{EQE}$ ) was observed in 700–800 nm regions accompanied with the slight decrease of the  $\eta_{EQE}$  at 590 and 670 nm. According to the absorption spectra of CuPc [Fig. 3(b)], the additional response in 700–800 nm is the contribution of CuPc layer. This suggests that charge separation also occurs at CuPc/C<sub>60</sub> and the coexistence of two charge separation interfaces, pentacene/C<sub>60</sub> and CuPc/C<sub>60</sub>. The enhancement of  $V_{oc}$  can be attributed to the enhanced energy difference between HOMO of  $p$ -type material and LUMO of  $n$ -type material.<sup>16,17</sup> Based on these results, the enhancement of  $\eta_p$  is attributed to the MCS interfaces where

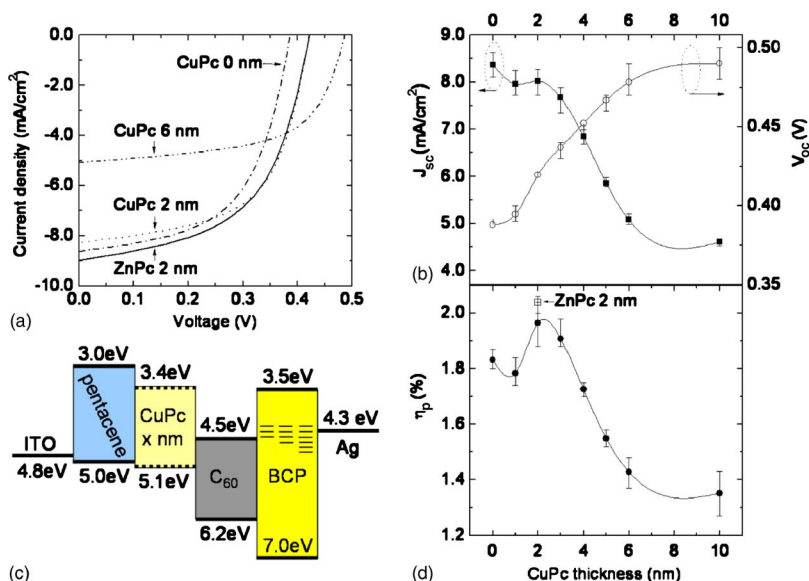


FIG. 2. (Color online) (a)  $J$ - $V$  characteristics of ITO/pentacene (50 nm)/CuPc ( $x$  nm)/C<sub>60</sub> (40 nm)/BCP (10 nm)/Ag (100 nm) under simulated AM1.5 solar illumination, where the thicknesses of CuPc layer are 0, 2, and 6 nm. CuPc layer was replaced with 2-nm-thick ZnPc. (b)  $J_{sc}$  and  $V_{oc}$  as a function of the thickness of CuPc. (c) Energy diagram of the device used in this study. (d)  $\eta_p$  as a function of the film thickness of CuPc. Open square shows  $\eta_p$  of the device with 2-nm-thick ZnPc.

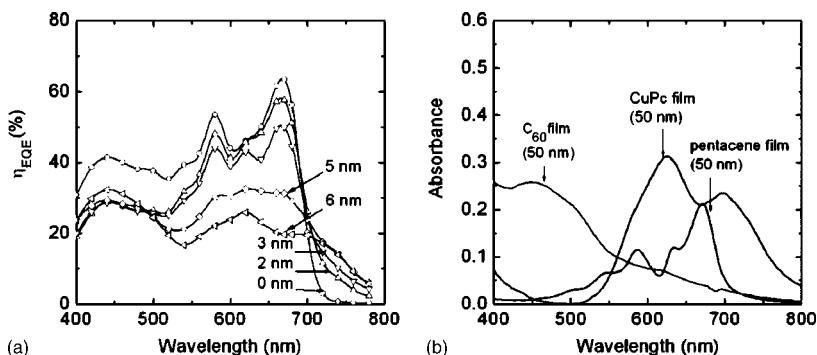


FIG. 3. (a)  $\eta_{\text{EQE}}$  spectra as a function of the thickness of CuPc film. (b) Absorption spectra of the films of pentacene, CuPc and  $\text{C}_{60}$ . The film thickness of all samples are 50 nm.

2-nm-thick phthalocyanine on pentacene layer exclusively increases  $V_{\text{oc}}$  with maintaining the corresponding  $J_{\text{sc}}$ . Increase in CuPc thickness more than 3 nm leads to decrease in the contribution of pentacene/ $\text{C}_{60}$  interface. Finally, the device with 6-nm-thick CuPc layer no longer show the peaks ascribed to pentacene and appears two new peaks at 620 and 700 nm which correspond to the absorption peaks of CuPc. At this thickness, the charge separation interface is dominated by CuPc/ $\text{C}_{60}$  interface.

To get more insights of the MCS interfaces, we have discussed the reason for a decrease in  $J_{\text{sc}}$  by insertion of CuPc layer thicker than 3 nm. Based on the theory for  $pn$  junction solar cells, decrease in  $J_{\text{sc}}$  can be attributed to the increase in  $R_s$ . However, we have confirmed that  $R_s$  remains constant even though the thickness of CuPc is thicker than 3 nm. (see supplemental information 2). Thus, in the device with thicker CuPc layers,  $J_{\text{sc}}$  would be limited by  $\eta_{\text{EQE}}$ , which is the product of the efficiencies of the following four steps: (1) exciton formation by photoabsorption ( $\eta_{\text{A}}$ ), (2) exciton diffusion to the charge separation interface ( $\eta_{\text{ED}}$ ), (3) exciton dissociation by charge transfer at the charge separation interface ( $\eta_{\text{CT}}$ ), and (4) the collection of free carrier at the electrodes ( $\eta_{\text{CC}}$ ). In the present devices, exciton dissociation at charge separation interface  $\eta_{\text{CT}}$ , would be the key parameter for governing  $J_{\text{sc}}$ . Because  $\eta_{\text{A}}$  should be improved rather than decreased as increasing the CuPc thickness,  $\eta_{\text{ED}}$  would be unchanged since the thickness of CuPc layer is always less than the exciton diffusion length of CuPc (10 nm) (Refs. 3 and 6) and  $\eta_{\text{CC}}$  should be always the same since electrode metal is unchanged.

Based on the discussion regarding  $\eta_{\text{CT}}$  we can interpret the difference of  $J_{\text{sc}}$  by inserting different metal-phthalocyanine. We notice that the lifetime of singlet excited state of CuPc (6 ps) (Ref. 19) is three orders of magnitude shorter than that of pentacene (19 ns).<sup>20</sup> In this situation,  $\eta_{\text{CT}}$  at CuPc/ $\text{C}_{60}$  interface should be reduced compared with the efficiency at pentacene/ $\text{C}_{60}$  interface. On the other hand, if CuPc layer was replaced with ZnPc which possesses the same HOMO level but exhibits longer excited state lifetime (3.3 ns),<sup>21</sup> the  $J_{\text{sc}}$  is expected to enhance in addition to the  $V_{\text{oc}}$ . Indeed, by using ZnPc, we observe the increases in the  $J_{\text{sc}}$  from 8.02 to 8.75  $\text{mA}/\text{cm}^2$  as well as enhancement of  $V_{\text{oc}}$  (0.43 V). By comparing with the device without a thin layer of metal-phthalocyanine, both  $J_{\text{sc}}$  and  $V_{\text{oc}}$  have been improved simultaneously and the resulting  $\eta_{\text{p}}$  reaches 2.04%. Now, we have controlled both  $J_{\text{sc}}$  and  $V_{\text{oc}}$  in photovoltaic cells by taking advantages of the MCS interfaces.

In conclusion, we have proposed organic photovoltaic cells based on MCS interfaces composed of phthalocyanine/ $\text{C}_{60}$  and pentacene/ $\text{C}_{60}$ .

By inserting a very thin layer of phthalocyanine layer ( $\sim 2$  nm), we can increase  $V_{\text{oc}}$  without affecting  $J_{\text{sc}}$ . The maximum  $\eta_{\text{p}}$  attains 2.04% in ITO/pentacene (50 nm)/ZnPc (2 nm)/ $\text{C}_{60}$  (40 nm)/BCP (10 nm)/Ag (100 nm) and the enhancement is largely attributable to the MCS interfaces, where properties of molecules (e.g., lifetime of excited state) directly reflect to device performance. This approach will provide a device architecture for the development of efficient organic solar cells. In addition, since the device structure composed of MCS interfaces allows us to control  $V_{\text{oc}}$ , this device structure would provide a means for systematic investigation of the operation mechanism of organic solar cells.

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<sup>18</sup>We have optimized the structure of CuPc-free device using silver as a cathode, i.e., ITO/pentacene (50 nm)/ $\text{C}_{60}$  (40 nm)/BCP (10 nm)/Ag (100 nm). The device characteristics are  $J_{\text{sc}}=8.37 \text{ mA}/\text{cm}^2$ ,  $V_{\text{oc}}=0.39 \text{ V}$ , fill factor (FF)=0.56, and  $\eta_{\text{p}}=1.83\%$ . When we use aluminum as a cathode,  $J_{\text{sc}}$  decrease to 7.27  $\text{mA}/\text{cm}^2$  and  $\eta_{\text{p}}$  ends up with 1.56%. The  $\eta_{\text{p}}$  value with aluminum electrode agrees well with the reported value in Ref. 4.

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