



## Correlation between energy level alignment and device performance in planar heterojunction organic photovoltaics

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### ABSTRACT

Information on the interfacial electronic structure in organic photovoltaics (OPVs) is essential for fully understanding features of device operation such as the photocurrent generation and relative energy band offsets at the donor/acceptor interface, which directly affect the open circuit voltage ( $V_{oc}$ ). Kelvin probe (KP) measurements fully reveal the energy level alignment in a prototype OPV with a copper phthalocyanine (CuPc)/fullerene ( $C_{60}$ ) planar heterojunction. Energy level pinning at the CuPc/ $C_{60}$  junction fixes the energy band offsets of  $C_{60}$ . A downward energy shift of about 0.9 eV appears at the  $C_{60}$ /bathocuproine junction, which may act as a hole-blocking barrier. A combination of KP and current density–voltage measurements indicates that photocurrent generation depends strongly on the magnitude of the upward energy shift at the CuPc/ $C_{60}$  junction. The dependence of  $V_{oc}$  on the substrate work function is also discussed in terms of the energy level alignment at indium tin oxide/CuPc/ $C_{60}$  junctions.

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### 1. Introduction

The interfacial electronic structure in organic electronic devices is critical for determining the interfacial carrier energetics and device performances. Among organic devices, organic photovoltaics (OPVs) have attracted much attention as next-generation solar cells, owing to their merits of light weight, lower cost, and short pay-back time [1]. Electronic structures at organic/metal and organic/organic interfaces in OPVs have been recognized as critical for optimizing hole/electron extraction toward metal electrodes and for the molecular understanding of charge separation mechanisms at the donor/acceptor (DA) interface [2–4]. The first purpose of this study is revealing the distributions of the internal potentials formed at organic/metal and organic/organic interfaces within a prototype OPV. A band bending-like energy shift and an interfacial dipole at each interface should contribute to the distributions of

built-in potential in OPV devices, which play important roles in carrier transport within the device and the determination of the value of the open circuit voltage ( $V_{oc}$ ) [5]. The electronic properties at the interfaces are sensitive to the work function of the bottom substrate [6–9], deposition sequence of the organic thin films and metal electrode [10–12], and atmosphere used for vacuum-deposition [13]. Thus, an OPV-structured sample prepared under the conditions used for device fabrication can provide more accurate understanding of the interfacial electronic structure in an actual OPV device. One study reported analysis of the double heterojunctions of copper phthalocyanine (CuPc)/fullerene ( $C_{60}$ )/bathocuproine (BCP) with ultraviolet photoelectron spectroscopy (UPS), but the accuracy of the observed energy shift was concerned due to the charging problem which can be caused by photo-hole accumulation on the sample because of the low conductivity of the organic heterojunctions [14].

Unlike UPS, the Kelvin probe (KP) method can be suitable for analyzing the interfacial electronic structure of a device-structured sample, because it is applicable to relatively thick samples with an organic thin film of about 600 nm [15]. The internal potential distributions in poly

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(3-hexyl thiophene) (P3HT):[6,6]-phenyl- $C_{61}$ -butyric acid methyl ester (PCBM) bulk heterojunction photovoltaic cells were recently investigated by Kelvin probe force microscopy, and cathode-interfaced rectification in the devices was found [16]. This study examined the cross-sectional interfaces of a completed device and provided direct information on the interfacial electronic structure in the device. However, layer-by-layer measurement of the interfacial electronic structure is also necessary to understand the origins of the resulting internal electric fields at each interface in OPV cells.

The second purpose of this study is correlating the energy level alignment and device performance in OPVs for providing well-defined guidelines for high-efficiency OPVs. One important factor is the influence of interfacial electronic structures on the energy separation between the highest occupied molecular orbital (HOMO) of donor and lowest unoccupied molecular orbital (LUMO) of acceptor at the DA interface ( $\Delta E_{DA}$ ), because  $\Delta E_{DA}$  is related to the maximum value of  $V_{oc}$  [5].  $\Delta E_{DA}$  depends on the magnitude of the interfacial dipole/band-bending like energy shift at the DA interface, which is modulated by substrate work function and insertion of permanent dipole [6–9,17]. An increase in  $V_{oc}$  in triphenylene ether/benzoperylene cells was examined by the use of the indium tin oxide (ITO) substrates with lower-work function ( $\Phi$ ) [18]. A photoemission spectroscopy study suggested that charge transfer caused by energy level pinning at the DA interface forms the interfacial dipole and is responsible for the enhancement in  $V_{oc}$  [9]. In contrast to Ref. [18], Hong et al. concluded that the OPV performance of CuPc/ $C_{60}$  photovoltaic cells, including  $V_{oc}$ , is unchanged by the surface treatment of ITO substrate [19]. To systematically explain these two different conclusions and deduce a general guideline for control of  $V_{oc}$ , correlating energy level alignment and device operation is necessary.

In this paper, we used the KP method to investigate the energy level alignment in ITO/CuPc/ $C_{60}$ /BCP/Al cells having the structures shown in Fig. 1a. Two types of ITO substrates, normally cleaned and Al-modified, were used to control the  $\Phi$  value of the substrates and the electronic structure at the CuPc/ $C_{60}$  junction. It was found that energy level pinning occurs at the CuPc/ $C_{60}$  junction, and that the energy levels shift downward and upward by  $\sim 0.9$  eV at the  $C_{60}$ /BCP and BCP/Al junctions, respectively. These findings are independent of the  $\Phi$  value of the ITO substrates. Employing an Al-modified ITO substrate with lower  $\Phi$  enhances the magnitude of the upward energy shift at the CuPc/ $C_{60}$  junction, which strongly suppresses the photocurrent under forward bias condition. This indicates that the magnitude of the upward energy shift at the DA interface is critical for carrier generation. The dependence of  $V_{oc}$  on  $\Phi$  of ITO substrate is also discussed in terms of energy level alignment at the ITO/CuPc/ $C_{60}$  junctions.

## 2. Experimental

CuPc (purity: 99.99%) and BCP (96%) were purchased from Aldrich and used as received.  $C_{60}$  (99.98%) was purchased from Materials Technologies Research and used as

received. For the analysis of pinning levels of CuPc and  $C_{60}$  (see Section 3.1), the following substrates were used: naturally oxidized Al,  $\Phi_{sub} = 3.5$ –4.1 eV; naturally oxidized Si,  $\Phi_{sub} = 4.3$ –4.5 eV; ITO (ultrasonicated in pure water, ethanol, acetone for 10 min each),  $\Phi_{sub} = 4.5$ –4.9 eV; air-exposed Au,  $\Phi_{sub} = 4.9$  eV; ITO covered with poly(3,4-ethylenedioxythiophene):polystyrenesulfonic acid (PEDOT:PSS, Aldrich, spin-coated),  $\Phi_{sub} = 4.9$  eV (air-kept), 5.1–5.5 eV (as-coated).

OPV-structured specimen was prepared on a cleaned ITO substrate ( $\Phi = 4.74$  eV) and Al-modified ITO ( $\Phi = 3.97$  eV). To prepare low- $\Phi$  ITO, 1 nm thick Al was vacuum-deposited on an ITO substrate kept at room temperature in a preparation chamber (base pressure  $< 5 \times 10^{-6}$  Pa). Thin films of CuPc,  $C_{60}$  and BCP were vacuum-deposited at evaporation rate of 0.5–1 Å/s at room temperature. Al cathode was deposited through a shadow mask at 1 Å/s. To confirm the transparency of the Al-modified ITO substrate, the optical absorption spectra were measured with UV-visible spectrometer (JASCO V-670 EX).

Vacuum deposition and measurement of the VL of the organic layers and Al cathode were repeated alternatively to investigate the interfacial electronic structure in ITO/CuPc (30 nm)/ $C_{60}$  (40 nm)/BCP (8 nm)/Al (50 nm) photovoltaic cells. VL was measured with respect to the Fermi level of the substrates by KP method (KP Technology, UHV020) in an analysis chamber (base pressure  $< 1 \times 10^{-7}$  Pa) connected to the preparation chamber. The  $\Phi$  value of reference electrode of KP equipment was determined to be 4.33 eV by correlating contact potentials and  $\Phi$ s of various metal substrates, which were determined by KP method and UPS, respectively. After the KP measurements, the completed OPV-structured specimens were transferred to Ar-filled glove box and their  $J$ - $V$  characteristics were analyzed using a semiconductor device analyzer (Agilent, B1500 A) under AM1.5 simulated solar light irradiation (SAN-EI ELECTRIC, XES-151S). The samples were exposed to air for  $\sim 3$  min during sample transfer. Active area of 0.6 cm<sup>2</sup> was used to perform the KP and  $J$ - $V$  measurements on the same device.

## 3. Results and discussion

### 3.1. Relationship between vacuum levels of CuPc and $C_{60}$ and substrate work functions

First of all, we examined the energy level alignment of CuPc and  $C_{60}$  films on various substrates to know their electronic properties before formation of junctions as used in the OPV. Fig. 1b shows the dependences of the VLs of CuPc and  $C_{60}$  thin films on  $\Phi_{sub}$ . The energies of the VLs were measured with respect to the Fermi level ( $E_F$ ) of the substrate. The thicknesses of CuPc and  $C_{60}$  were fixed at 30 and 40 nm, respectively, which are the thicknesses used in the photovoltaic cells. The VL of CuPc (squares in Fig. 1b) increases linearly up to  $\Phi_{sub} \sim 4.5$  eV which is  $\sim 0.4$  eV lower than the ionization energy of CuPc (4.86 eV). The value of the VL for CuPc is constant above  $\Phi_{sub} \sim 4.5$  eV, which indicates that energy level pinning occurs at higher  $\Phi_{sub}$  range. The cross points (as indicated by arrows in Fig. 1b) of the pinning (dashed lines in Fig. 1b) and

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