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Probing the Molecular Orientation of ZnPc on AZO Using Soft X-ray Spectroscopies for Organic Photovoltaic Applications

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The interfacial electronic structure between zinc phthalocyanine (ZnPc) and aluminum-doped zinc oxide (AZO) substrates has been evaluated by ultraviolet photoemission spectroscopy and angle-dependent x-ray absorption spectroscopy to understanding the molecular orientation of a ZnPc layer on the performance of small molecule organic photovoltaics (OPVs). We find that the ZnPc tilt angle improves the π-π interaction on the AZO substrate, thus leading to an improved short-circuit current in OPVs based on phthalocyanine. Furthermore, the molecular orientation-dependent energy level alignment has been analyzed in detail using ultraviolet photoemission spectroscopy. We also obtained complete energy level diagrams of ZnPc/AZO and ZnPc/indium thin oxide.

Keywords : Organic semiconductors, Molecular orientation, ZnPc, AZO

I. Introduction

Organic photovoltaics (OPVs) have received increasing attention over the past few years due to their potential as a renewable, cheap, and economical source of power [1–5]. Despite recent significant advances in device performance, however, current power conversion efficiencies (PCEs) are not enough to make them commercially viable. A general problem in organic electronic devices is the poor transport of charge carriers at the interface between the electrodes and the organic semiconductor. Consequently, recent efforts have been expended in order to improve the charge transport and collection at the electrodes. In particular, the use of transition metal oxides as a transparent electrode has attracted considerable interest. Indium tin oxide (ITO) is widely used as the electrode in OPV fabrication due to its reasonable transparency in the visible region of the spectrum, good conductivity, and easy patterning ability. However, the surface chemistry of ITO is difficult to control [6] and ITO has become approximately ten times more expensive over the past a few years due to diminishing indium resources; [7] the cost of indium is only expected to grow with increasing demand from producers of solar cells on top of the existing flat–panel display industry [8]. Transition metal oxides are believed to prevent unwanted chemical reactions and the optically active organic layer [9,10]. Murdoch et al. reported that Al–doped ZnO (AZO) is an effective ITO alternative for phthalocyanine (Pc)–based OPVs [8]. Even OPV cells fabricated on AZO did not outperform cells fabricated on ITO, OPV cells fabricated on AZO showed a high short circuit current (J_{SC}). However,

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little is known about the origin and the detailed interfacial electronic structures of OPVs containing AZO.

In this respect, we report here a study of the molecular orientation of zinc phthalocyanine (ZnPc) on AZO and ITO using angle-dependent x-ray absorption spectroscopy (XAS). Furthermore, we evaluated the electronic structures and energy level alignments of ZnPc/AZO and ZnPc/ITO. The electronic structure was measured using *in situ* ultraviolet photoemission spectroscopy (UPS).

II. Experimental

Angle-dependent XAS was carried out at the soft x-ray undulator beamline X1B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Multilayer structures were grown in situ in a custom designed ultra-high vacuum (UHV) organic molecular beam deposition (OMBD) chamber (base pressure 2×10^{-9} Torr), attached to a multi technique soft x-ray spectroscopy system, as described below. Clean AZO and ITO surfaces were obtained via Ar^{+} ion sputtering and annealing in UHV. The substrate was held at room temperature during deposition, and the film deposition rate was monitored by a quartz crystal microbalance. After deposition, the samples were transferred without breaking vacuum from the OMBD chamber into the spectrometer chamber (base pressure 2×10^{-10} Torr). Beamline X1B is equipped with a spherical grating monochromator, and the photon beam is focused to an approximate 60×40 μm spot on the sample. C *K*-edge XAS spectra were recorded via the sample drain current to obtain the total electron yield (TEY) and were normalized to the current from a gold-coated mesh positioned in the incident photon beam. The energy scale of the XAS measurements was calibrated using first- and second-order diffraction Ti *L*-edge and O *K*-edge absorption from rutile TiO_2 [11].

In situ UPS measurements were carried out using a PHI 5700 spectrometer and an ultraviolet (He I, 21.22 eV) excitation light source. The base pressure of the analysis chamber was 2×10^{-9} Torr. ZnPc was thermally evaporated on ITO and AZO substrates at a rate of 0.01 nm/s. The total thickness and deposition rate were monitored by a quartz crystal microbalance. The secondary electron cutoff (SEC) positions were measured in normal emission geometry with a sample bias of −10 V.

III. Results and Discussion

We first measured the molecular orientation of the ZnPc on AZO and ITO. We used a 15 nm-thick ZnPc layer to investigate the organic molecular orientation. Fig. 1 shows the experimental geometry angle-dependent XAS measurements. In order to study the ZnPc molecular orientation depending on a substrate, we measured the angular dependence of the C *K*-edge XAS from ZnPc films grown on AZO and ITO. Fig. 2(a) displays the angular dependence of C *K*-edge XAS from the ZnPc molecule on AZO, which allows the azimuthally averaged tilt of the molecules with respect to the substrate to be determined. A very clear angular dependence of the π^* resonance (photon energy range 283∼292 eV) is observed, with the maximum π^* intensity observed at normal incidence. The π^* intensity (I) in the XAS spectra is related to the tilt angle α of the PTCDA molecular

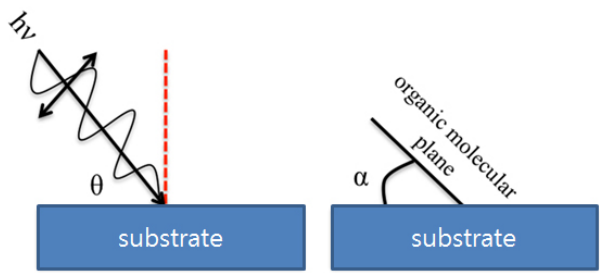

Figure 1. Experimental angle-dependent XAS geometry.

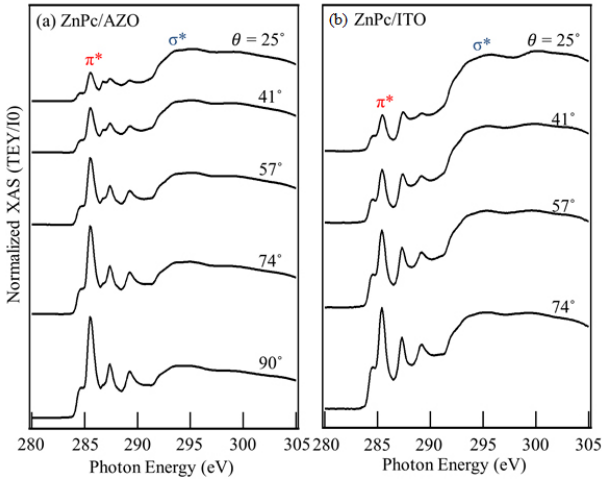

Figure 2. C *K*-edge XAS spectra as a function of the photon angle of incidence. (a) ZnPc on AZO and (b) ZnPc on ITO.

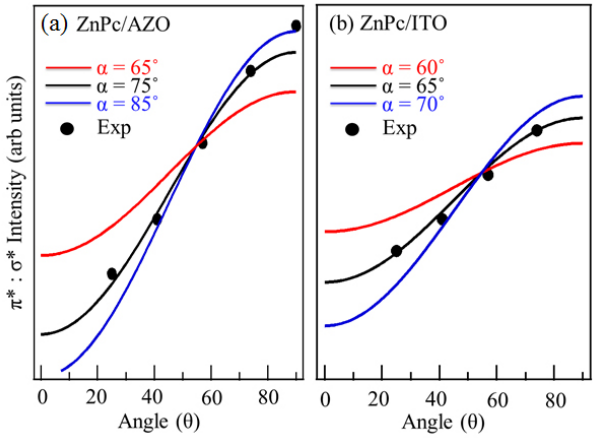

Figure 3. The plotted variation of the experimental $\pi^*:\sigma^*$ peaks intensity (black square) against the calculated variation for a range of planar tilt angles. (a) ZnPc on AZO and (b) ZnPc on ITO.

plane with respect to the substrate plane and the photon incidence angle θ by [12]

$$I(\theta) \propto 1+\frac{1}{2}(3\cos^2\theta-1)(3\cos^2\alpha-1).$$

Fig. 3(a) displays the variation in relative intensity of the $\pi^*:\sigma^*$ peaks in the spectra seen in Fig. 2(a). By comparing the relative peak intensities with the calculated variation for a range of tilt angles, we conclude that the ZnPc molecules have an azimuthally averaged tilt of $75\pm5^{\circ}$ with respect to the AZO substrate. Fig. 2(b) presents the C *K*-edge angle dependent XAS for a ZnPc film grown on ITO. A much less angular dependence is observed compared to that obtained from a film grown on AZO. This indicates that the molecular orientation changes as a result of the different substrate. Fig. 3(b) also displays the variation in relative intensity of the $\pi^*:\sigma^*$ peaks in the spectra seen in Fig. 2(b). The tilt angle α is estimated to be $65\pm5^{\circ}$ for the ZnPc film on ITO. Despite the relatively large error bars in this measurement, this implies that the AZO substrate leads to greater $\pi-\pi$ stacking in the ZnPc. Due to the highly anisotropic nature of optoelectronic properties of π-conjugated molecules, the molecular orientation of organic thin films can significantly affect device performance, such as light absorption and charge-carrier transport [13]. The well-ordered configuration of the conjugated molecules and the resulting increased $\pi-\pi$ overlap thus provides an explanation for the reported improvement in J_{SC} in OPV devices based on this heterojunction [8,14,15].

To understand the effect of molecular orientation on the open circuit voltage (V_{OC}) measured in OPV devices, we also studied the energy level alignment of ZnPc/AZO and ZnPc/ITO. Fig. 4 shows UPS spectra obtained for the deposition of ZnPc on AZO substrate. The spectra shown in Fig. 4(a) were collected in the secondary electron cut-off region. The secondary cut-off position moved noticeably towards a higher binding energy as soon as the ZnPc deposition began on the substrate. The shift of the secondary cut-off position is attributed to the formation of an interface dipole and band bending [16,17]. In these spectra, the total shift of the cut-off position of ZnPc toward higher binding energies was 0.4 eV. Fig. 4(b) shows the evolution of the highest occupied molecular orbital (HOMO) onset during the growth of the ZnPc layer on AZO substrate. In Fig. 4(b), the HOMO onset of ZnPc gradually shifted towards higher binding

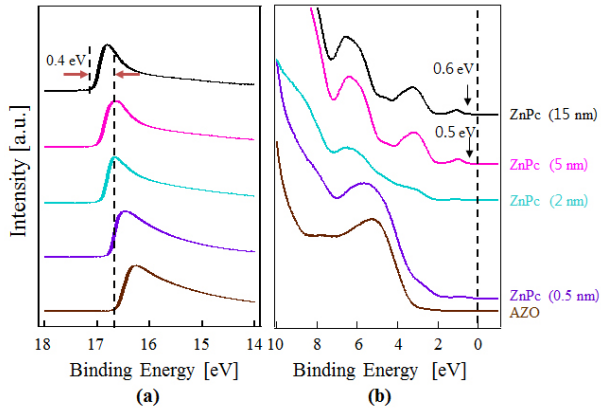

Figure 4. (a) Change in the onset of secondary electron UPS spectra after the deposition of each layer of ClAlPc/AZO. (b) Valence-band UPS spectra recorded near E_F after the deposition of each layer of ClAlPc/AZO.

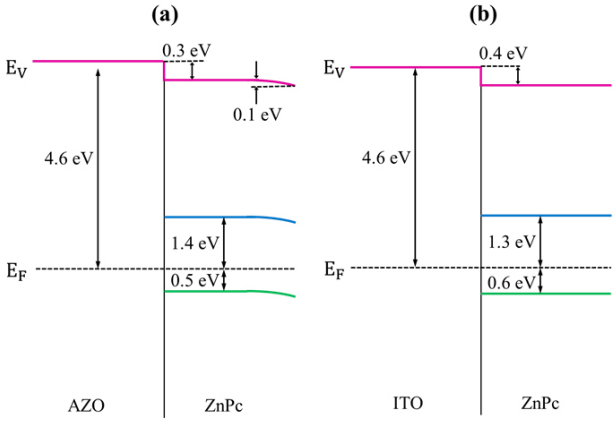

Figure 5. Energy level diagrams of (a) ZnPc/AZO and (b) ZnPc/ITO.

energies from 0.5 eV to 0.6 eV, confirming band bending at the ZnPc/AZO interface.

An energy level diagram was constructed by combining the changes in spectra shown in Fig. 4. Additionally the energy level diagram of ZnPc/ITO from our data (not shown here) was shown for comparison. As shown in Fig. 5, the energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) of ZnPc was about 1.9 eV as previously reported [18,19]. The energy level difference between the HOMO of the donor and the LUMO of the acceptor, $E^{D}_{HOMO}-E^{A}_{LUMO}$, is an important factor in determining the magnitude of the V_{OC} of OPVs, based on a donor-acceptor heterojunction. The measured HOMO onset of ZnPc on AZO and ITO were the same (0.6 eV) regardless of the molecular orientations. This means that the $E^{D}_{HOMO}-E^{A}_{LUMO}$ values would be almost same on AZO and ITO substrates. It agrees with the previous device results.

IV. Conclusions

The interfacial electronic structures of between ZnPc and substrates (AZO and ITO) have been evaluated by UPS and angle-dependent XAS to understanding the molecular orientation of a ZnPc layer on the performance of small molecule OPVs. We find that the ZnPc tilt angle improves the $\pi-\pi$ interaction on the AZO substrate, thus leading to an improved J_{SC} in OPVs based on phthalocyanine. Furthermore, the molecular orientation-dependent energy level alignment has been analyzed in detail using UPS. We also obtained complete energy level diagrams of ZnPc/AZO and ZnPc/ITO.

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