Unoccupied states in copper phthalocyanine/fullerene blended films determined by inverse photoemission spectroscopy

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A B S T R A C T

Blends of copper phthalocyanine (CuPc) and fullerene (C_{60}) have successfully been used for organic field-effect transistors and photovoltaic cells. In this work we investigate the unoccupied states of CuPc/C_{60} blends by inverse photoemission spectroscopy. The energies of the lowest unoccupied molecular orbitals of CuPc and C_{60} vary linearly with the mixing ratio, which is consistent with the energy shifts of the vacuum level, the highest occupied molecular orbitals and core levels. The observed results can be interpreted as unchanged electron affinities of CuPc and C_{60} in the blended films due to nano-phase separation.

Keywords:
Donor/acceptor blend
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Electronic structure
Organic photovoltaics

1. Introduction

Donor/acceptor (DA) blends have been used for improving the performance of various organic electronic devices so far. For example, DA blended films were introduced in organic photovoltaics (OPVs) as an active layer. Using blends the power conversion efficiency of small molecule-based OPVs has been improved significantly [1–4]. The success in employing DA blends for OPVs is due to an increase in the magnitude of the DA interface and improved efficiency of exciton dissociation, which consequently enhances the photocurrent. DA blended films have also been used in organic field-effect transistors (OFETs) leading to ambipolar character, where balanced mobility can be adjusted by the mixing ratio of the DA blend [5].

For understanding and describing the performance of these devices, knowledge on the electronic structure of the DA blend is important. Previously, Opitz et al. investigated the occupied states of CuPc/C_{60} blends with ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) [6]. It was found that the vacuum level, the highest occupied molecular orbitals (HOMOs) and core levels vary linearly with C_{60} concentration. Recently, the investigation of the electronic structure in occupied states has also been extended to P3HT/PCBM blended films for bulk heterojunction OPVs by Xu et al. [7]. However, the unoccupied states in DA blends have been elusive. So far, the energies of the lowest unoccupied molecular orbitals (LUMOs) in the blended films have only been estimated using the band gaps of neat films of donor and acceptor, which assume that the energy shift of the LUMO is the same as that of the HOMO. However, recently, it was found that the change in the polarization energy leads to the opposite shift of the LUMOs and HOMOs at the planar C_{60}/CuPc interface [8]. These results suggest that the constant band gap is not always a valid assumption at

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an interface, and that the direct measurements of the energies of the LUMOs for donor and acceptor are important to understand the dominant factor which determines the electronic structure.

In this letter, we have investigated the LUMO energies in CuPc/C_{60} blends with various mixing ratios by inverse photoemission spectroscopy (IPES), which can detect the energies of unoccupied states, directly [9]. We found that the LUMOs of CuPc and C_{60} vary linearly with increasing C_{60} concentration. This trend is consistent with the results on the vacuum level, the HOMOs and the core levels. The observed results indicate that electron affinities of CuPc and C_{60} are the same in the blend as in the neat film, which can be attributed to phase separation between CuPc and C_{60} in the blend, as observed by atomic force microscopy and X-ray scattering.

2. Experimental

As substrates we used clean polycrystalline Au films prepared by thermal evaporation on naturally oxidized Si (100) substrate in ultra-high vacuum (base pressure $< 1 \times 10^{-7}$ Pa). The CuPc/C_{60} mixed films were fabricated in situ on the Au substrate by co-evaporation using two glass cells with different evaporation rates to achieve the required mixing ratio. The thickness of the blended films was monitored by a quartz microbalance and adjusted to be 10 nm. IPES measurements were performed in situ in the isochromat mode using a home-made apparatus [10]. The band-pass type detector for photons with an energy of $h\nu = 9.3$ eV consists of a channeltron coated with KCl and is placed behind a SrF_2 window. A low energy electron gun was used to produce a mono-energetic electron beam. The substrate temperature during sample preparation and measurement was kept at room temperature. The morphology of blended films were also analyzed by atomic force microscope (AFM, Seiko Instrument: SPA300) in non-contact mode under ambient atmosphere.

3. Results and discussion

Fig. 1 shows the IPES spectra of the CuPc/C_{60} blend films as a function of C_{60} concentration. The abscissa is energy measured from the Fermi level (E_F) of clean Au substrates. Peaks marked with horizontal lines or solid filling are assigned to unoccupied states of CuPc and C_{60}, respectively. The composition of the blended films were determined by fitting each spectra with Voigt functions using the spectral shapes of neat CuPc and C_{60} films. Here, Gaussian width was set to be 0.75 eV including the total energy resolution of IPES measurements at room temperature. Lorentzian widths were properly taken to fit each peak. The spectra of the neat films (0% and 100% C_{60}) are in good agreement with the reported results [11–14]. The spectra of the mixed films in Fig. 1 can be described by a superposition of the spectra for neat CuPc and C_{60} films with proper energy shifts. No additional features are required in the fitting procedure, which indicates that there is no strong interaction between CuPc and C_{60}. From Fig. 1, it was found that

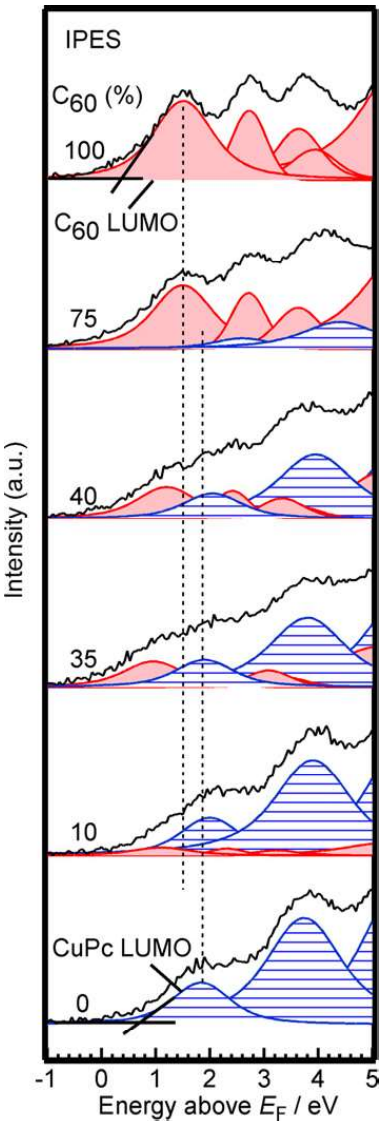

Fig. 1. The IPES spectra of blended films are shown as a function of C_{60} concentration. Peaks marked with striped lines or solid filling are assigned to unoccupied states of CuPc and C_{60}, respectively. Dashed lines are visual aids for recognizing the energy shifts of the LUMOs. The onsets of the LUMO peaks were determined from the cross-point as indicated by solid lines in neat CuPc and C_{60} films (0% and 100% C_{60}).

the LUMO peaks of CuPc and C_{60} move away from E_F with increasing C_{60} concentration.

The energy shifts of the LUMOs are consistent with those of the vacuum level and the HOMOs. Fig. 2 shows the concentration dependence of the observed energies for vacuum level (triangles in Fig. 2(a)), HOMO (squares in Fig. 2(a)) and LUMO (Fig. 2(b)). The upper and lower axes are CuPc and C_{60} concentrations, respectively. The energies of the HOMOs and LUMOs were deduced from the peak onsets. The data of vacuum level and the HOMOs were taken from the UPS spectra that the Augsburg group reported in Ref. [6]. Considering mixed films, the LUMOs of CuPc and C_{60} shift upward by 0.7 and 0.5 eV, respectively, with increasing C_{60} concentration, which is close to the shift of the vacuum level and the HOMOs.

Important to mention are the differences of the two analyses. Whereas the study presented here was carried

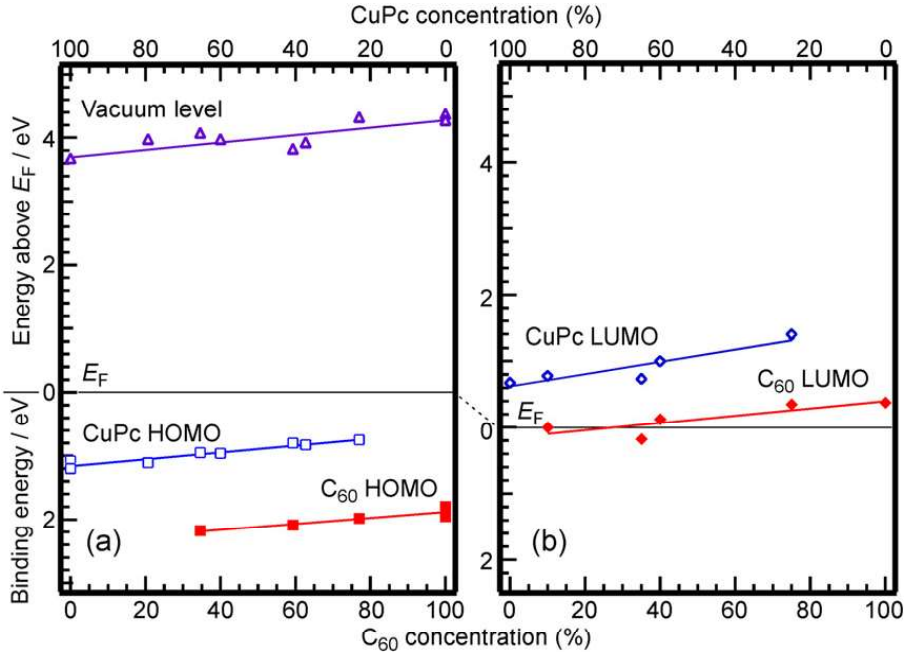

Fig. 2. Dependence of vacuum level and the HOMO (a) and LUMO (b) energies of CuPc and C_{60} on different mixing ratio. The data of vacuum level and HOMOs are deduced from the UPS spectra reported in [6]. Error bars in the LUMO data of CuPc in (b) are derived from an uncertainty of spectral fitting. The lines are linear fits of the corresponding energy levels. The data in (a) and (b) are collected on thin films prepared on contaminated and clean Au substrates, respectively. For a clearance of the difference in work function, *y*-axis in (b) is shifted by 0.35 eV.

out on a clean gold surface (Fig. 2(b)) the substrate of the previous study was contaminated with hydrocarbons (Fig. 2(a) and [6]). After deposition of CuPc and C_{60} on contaminated-Au substrate, the vacuum levels of CuPc and C_{60} films are found at 3.8 and 4.3 eV from E_F, respectively [6]. On the other hand, the vacuum levels of CuPc and C_{60} films prepared on clean Au surfaces are located at 4.21 and 4.63 eV, respectively [15]. Thus a difference in the Fermi levels should be taken into account for the analysis of the energy values of the materials. Assuming a difference of 0.35 eV in the vacuum levels for the semiconducting films, the HOMO–LUMO gap determined from the onset of the peaks is 2.2 eV for CuPc and 2.6 eV for C_{60}, respectively. These values are in between the energy gap derived from peak maxima and onsets which were reported in the literature [11–14]. The differences to the values in the literature are based on the experimental broadening of the peak width which is not accounted here and which is in the range of 0.3–0.4 eV in total for both experiments, UPS and IPES.

Even though different substrates were used for UPS and IPES measurements, similar energy shifts were observed in the vacuum level, HOMO and LUMO. Thus, the difference in substrate work functions can be neglected to discuss nature of electronic properties in the blended films. The similar shift of all levels indicates that the ionization energies and electron affinities of CuPc and C_{60} are constant even in their blended film. The observed constant ionization energies and electron affinities as well as the common vacuum level can be related to nano-phase separation in the mixed film (see below) [16].

In Fig. 3, AFM images of the mixed films with C_{60} concentration of 10%, 35% and 75% are shown. The maximum height increases with increasing C_{60} concentration, which can be attributed to higher roughness of C_{60} films than CuPc films [13]. We also notice that the maximum height exceeds the nominal thickness of the mixed films (10 nm), which also reflects the growth of C_{60} grains. These results can be related to phase separation between CuPc and C_{60} in the blend. Actually, X-ray diffraction (XRD) measurements of a CuPc/C_{60} blend with mixing ratio of 1:1 show the formation of the α-phase of CuPc and the *fcc*-phase of C_{60} even in the blended film [13]. The results of the XRD study indicate that both CuPc and C_{60} crystallites formed in blends are similar to neat films, and that phase separation occurs between the two materials. This can explain the fact that the ionization energies and electron affinities of CuPc and C_{60} in the mixture are similar to those of neat films in the whole range of concentration (Fig. 2). Nevertheless, phase separation occurs only on a length scale of about 10 nm which allows for the preservation of a common vacuum level [6,16–17].

The behavior of the energy levels in planar and bulk heterojunction solar cells is reported in the literature [18] for layers grown on the device relevant electrode PEDOT:PSS. It was found that the energy gap between the HOMO of CuPc and the LUMO of C_{60} is comparable for blended films and planar heterojunctions in contrast to our previous expectation [6]. This is because the HOMO of CuPc stays constant and the LUMO of C_{60} is also expected to be located at the same energy in the planar heterojunction and blended films [18]. As for CuPc, the hole polaron level of CuPc is pinned to the Fermi level of the electrode material [19] which prevents changes by the variation of the blend ratio. One can therefore expect that the open circuit voltage in planar heterojunction, whose value

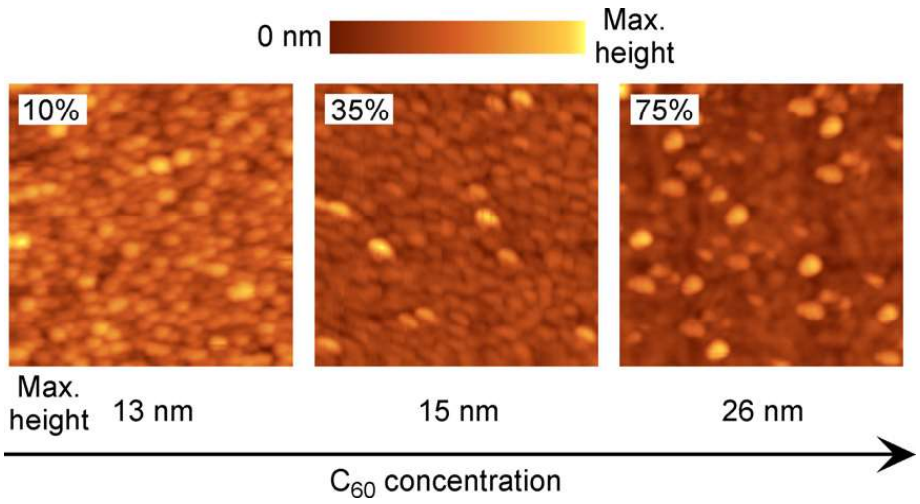

Fig. 3. AFM images for CuPc/C_{60} blends with C_{60} concentration of 10%, 35% and 75%. The maximum heights of each film were deduced from the lowest and highest values in each image. The image size is 1 μm^2.

can be related to the energy gap between the HOMO of the donor and LUMO of the acceptor [20], will be similar to that in blended films. However, this expectation contradicts with the fact that the open circuit voltage in blended films is by 0.2 V smaller than that in planar heterojunction [16–17]. The reduced open circuit voltage in bulk heterojunction solar cells in comparison to planar heterojunction cells are reported to be explained with additional recombination losses [21] or insufficient energy level alignment at contacts [22].

It is also noted that in the case of CuPc/Au interface the Fermi level seems to be near mid-gap of CuPc (Fig. 2(a)), similar to various phthalocyanines/Au substrate interfaces [23], when the work function difference in Au substrates between UPS and IPES studies is considered. However, the pinning of the energy levels is not expected at the present CuPc/Au interface, since Kelvin probe study indicated that the interfacial dipole induced by the push-back effect lowers the energy levels of CuPc on Au substrate and no band bending was observed up to CuPc thickness of 20 nm [24]. On the other hand, for C_{60} films, the energy level pinning occurs at 10–50 nm thickness on Au substrate [25]. This can be attributed to the pinning of the LUMO edge of C_{60} to the Fermi level of Au substrate [26]. Actually, the LUMO edge of C_{60} at C_{60} concentration = 100% is very close to the Fermi level of Au substrate as shown in Fig. 2(b). With increasing C_{60} concentration in CuPc/C_{60} blended films, the energy level alignment gradually changes between CuPc/Au and C_{60}/Au systems.

4. Conclusion

We performed the first investigations on the LUMO energies of CuPc and C_{60} in blends of both materials using inverse photoemission spectroscopy. It was found that the LUMOs of CuPc and C_{60} shift away from E_F by 0.7 and 0.5 eV, respectively, which is similar to the energy shifts of the vacuum level and the HOMO peaks. The coincidence of the energy shifts for the LUMOs with the vacuum level indicates that the electron affinities of CuPc and C_{60} are unchanged in blended films as compared to the neat materials. This can be attributed to nano-phase separation between CuPc and C_{60}, which is indicated by AFM measurements of the blended films. The present results provide information on unoccupied states in DA blends, which will be beneficial for understanding the energetics in DA solar cells.

Acknowledgements

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