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The electronic structures of pristine and Cs-doped CuPc films are investigated using photoemission spectroscopy and inverse photoemission spectroscopy (IPES). The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital can be directly observed by IPES and ultraviolet photoemission spectroscopy simultaneously. We found that the Fermi-level position in organic film can be modified by Cs doping. The observed onset of the LUMO of the CuPc film is shifted by Cs doping to less than 0.2 eV above the Fermi level. The result indicates that the energy alignment and charge injection properties of the organic materials can be modified by a simple doping process. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1426260]

Organic light-emitting diodes (OLEDs) have received considerable attention in recent years because of their scientific and commercial significance.[1–3] There have been intensive efforts in search of materials and device structures for OLED applications. Copper phthalocyanine (CuPc), a material with a cyclic polyconjugated molecular structure that often serves as a model for chemically similar but biologically important porphins,[4] has become an important ingredient in OLEDs for modifying interface properties.[5] CuPc has been found to improve electron injection when doped with alkali metal and inserted as a buffer layer between a metal cathode and tris(8-hydroxyquinoline) aluminum (Alq_3).[3] Commonly considered a *p*-type organic semiconductor, CuPc is traditionally used as a hole injecting material in the OLED.[5] Thus, the use of alkali metal-doped CuPc for electron injection is an unconventional approach. To address the mechanism of this approach, we have used ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) to determine the electronic structure of CuPc and its evolution as Cs is doped into CuPc. The ionization potential, work function, and the highest occupied molecular orbital (HOMO) of CuPc is determined directly by UPS, while the electron affinity and the lowest unoccupied molecular orbital (LUMO) by IPES. Therefore, the electronic structure of CuPc, both occupied and unoccupied, can be observed directly. Photoemission spectroscopy has been extensively applied in studying the interface formation in organic semiconductors.[6–8] In comparison, there have been very few studies using IPES on pristine organic material.[9,10] Little has been done to investigate the metal-doped organic using IPES. In our study of Cs doping of CuPc, we have found that the vacuum level and HOMO position changes rapidly with a low concentration of Cs doping. The change saturates when CuPc is doped heavily as the Cs to CuPc molecular ratio is close to or more than 1. The saturation is characterized as Fermi-level pinning. This is a direct observation of Fermi-level pinning near the LUMO in organic semiconductors.

Two ultra-high-vacuum (UHV) systems were used to collect the data presented in this letter. An ESCA Lab Mark II system was used to follow the evolution of the occupied electronic structure of a Cs-doped CuPc film, and a custom-designed UHV system was used to measure the electronic structure (IPES+UPS) of a similarly prepared Cs-doped CuPc film. In both systems, connected to the spectrometer chamber was an evaporation chamber in which samples could be prepared in ultrahigh vacuum and transferred directly into the spectrometer chamber. Base pressures in the evaporation chamber and spectrometer were, typically 6 $\times 10^{-10}$ and 4×10^{-11} Torr, respectively. The UPS spectra were recorded by using an unfiltered He 1 excitation (21.2 eV) light source with the samples biased at -4.0 V to observe the true, low-energy secondary cutoff. The typical instrumental resolution for UPS measurements ranges from ~ 0.03 to 0.1 eV with photon energy dispersion of less than 20 meV. The IPES spectra were taken with a custom-made spectrometer, composed of a commercial Kimball Physics ELG-2 electron gun and a bandpass photon detector prepared according to an existing design.[11,12] A more detailed description of the photon detector can be found in our previous work.[13] The combined resolution (electron+photon) of the IPES spectrometer was determined to be ~ 0.6 eV from the Fermi edge of an evaporated Au film.

In Fig. 1, the evolution of UPS spectra due to different Cs doping levels is presented. On a Au-coated Si substrate cleaned by Ar^+ sputtering, an 100 Å CuPc film was grown by thermal evaporation followed by sequential Cs evaporation at 1×10^{-10} Torr with UPS and x-ray photoemission spectroscopy [(XPS), not shown] spectra taken at each step in the sequence. The doping concentration, as a Cs atom to CuPc molecule ratio, R_s, is calculated from the XPS data. Figure 1(a) shows the cutoff changes of the UPS spectra, which reflect the vacuum-level change of the sample. It is very impressive that a very low-level Cs doping (as low as $R_s = 0.01$) can significantly change the vacuum level, thus the work function, of the sample. The change slows down and saturates at higher doping concentrations. Figure 1(b) shows the HOMO region of the UPS spectra of the same

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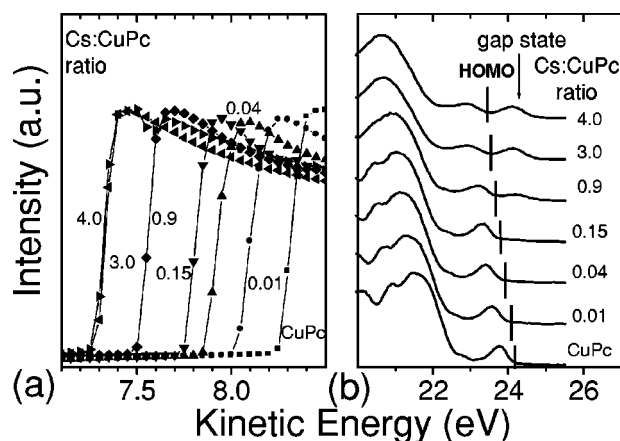[a)]Electronic mail: neilw@pas.rochester.edu

FIG. 1. UPS spectra evolution of Cs-doped CuPc film: (a) cutoff and (b) HOMO region. A new state in the gap emerges and increases with Cs doping concentration.

film. It can be seen that at low Cs concentrations, the HOMO shift follows the cutoff changes, implying that the CuPc molecule does not undergo significant chemical modification. However, a new state emerges from the gap and its intensity increases with the increase of Cs doping. A more detailed analysis will be given elsewhere.[14] The shift of the energy levels is due to the charge transfer from Cs to CuPc, which saturates when the ratio of Cs atoms to CuPc molecules approaches unity.

When the cutoff shift saturates, the total amount of vacuum level and HOMO shift is about 1.0 eV, noticeably close to the separation of the LUMO position from the Fermi level in pristine CuPc film. This observation suggests a pinning of the LUMO at the Fermi level for heavily doped CuPc. Evidence of such pinning can be obtained by using IPES on doped CuPc. In Fig. 2, comparison of the electronic structure and energy-level alignment of pristine and Cs-doped CuPc is shown. The bottom part is the IPES spectrum of a pristine CuPc film about 1000 Å thick prepared by thermal evaporation. The upper part is another CuPc film doped
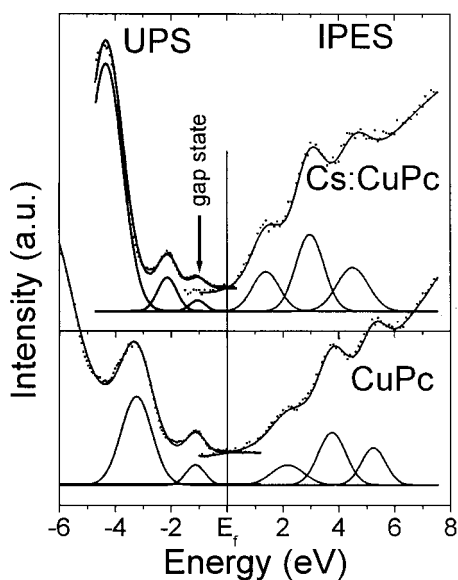
FIG. 2. Comparison of the composite of the UPS and IPES spectra of pristine and Cs-doped CuPc films. After doping, the HOMO and LUMO shift about the same amount and the LUMO is close to the Fermi level.

with Cs. The Cs doping concentration is determined to be about $R_s = 0.85$ by XPS measurement. The spectra of the pristine CuPc are similar to those reported by Hill *et al.*[10] The UPS spectrum was taken first and then the IPES spectrum was recorded on the same film. The origin in Fig. 2 is the Fermi level, which is calibrated by UPS and IPES on the same Au/Si substrate. The peaks next to Fermi level are the HOMO and LUMO in UPS and IPES, respectively. After background subtraction,[10] the IPES spectrum can, therefore, be decomposed into the three Gaussian peaks shown in Fig. 2. The LUMO peak position is at about 2.2 eV with a full width at half maximum (FWHM) of about 1.3 eV. Deconvolution of the LUMO is performed using the IPES resolution of 0.6 eV to eliminate instrument-induced broadening, which reduces the FWHM of the LUMO slightly to ~1.2 eV. Similarly, the UPS spectrum is fitted with Gaussian peaks after removal of background,[15,16] also shown in Fig. 2 with the HOMO peak at about −1.2 eV and FWHM of about 0.5 eV. The effect of instrumental broadening is negligible in UPS. Since the HOMO is closer to the Fermi level than the LUMO, it shows that the CuPc film is a weak *p*-type organic semiconductor, consistent with previous knowledge.[17] As is clearly shown in Fig. 2, with the Cs doping, the LUMO shifts toward the Fermi level and the HOMO shifts away from it. Using the same fitting method and background subtraction described earlier, the IPES can be decomposed to the three peaks again. The LUMO peak is at about 1.3 eV with a FWHM (after deconvolution of instrument broadening) of ~1.1 eV. Similarly, the HOMO peak is at −2.1 eV with a FWHM of ~0.7 eV. We notice a new gap state is found to be about −1.0 eV.

The UPS process involves the removal of an electron from the sample. The photoinduced "hole" with surrounding medium in the solid then undergoes different relaxation processes. The electronic (involving the electron distribution around the hole) and vibronic (involving geometric configuration) components are fast processes which contribute to the final energy of the photoelectrons. The observed UPS spectrum is the representation of the filled states of a molecular cation resulting from the photoelectric process modified by the relaxation (polarization). The width of the peaks is presumably due to the inhomogenuity of the film since the organic film is normally amorphous with random disorder.[18] Therefore, the center of the HOMO peak corresponds to the HOMO energy of the most populous molecular cation, with the negative charge (photoelectron) at infinity (beyond the vacuum level). A conceptually similar analysis applies to the IPES spectrum. Induced by injecting electrons, the relaxation (polarization) of the surrounding medium makes the IPES spectrum the representation of the relaxed anion instead of the neutral state of the molecule. Thus, the energy separation of the HOMO–LUMO peaks obtained by UPS and IPES is the energy difference of relaxed positive and negative polarons separated at infinity, sometimes referred to as the energy gap (E_t) of the organic material. However, the charge injection into a solid does not necessarily occur at the most populous or average species. Rather, when the injection is contact limited (usually the case in OLED devices), the charge injects into the molecules with the lowest-energy difference relative to the Fermi level. For example, the hole will
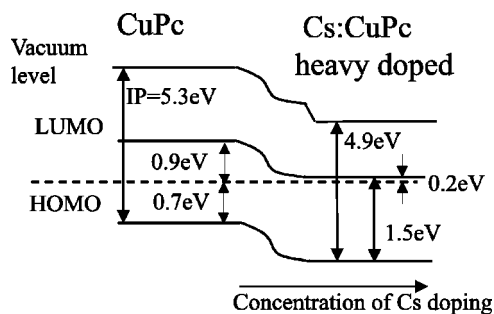
FIG. 3. Energy diagram of Cs-doped CuPc. In heavily doped CuPc, the electron injection barrier is estimated to be only about 0.2 eV. The Fermi-level position in the CuPc energy gap is modified by the Cs doping concentration.

most likely reside on those molecules with a HOMO closest to the Fermi level, resulting in a cation with lowest energy that is represented by the onset of the HOMO peak close to the Fermi Level. We define the "onset" as the extrapolation of the leading edge (closer to the Fermi level) in the spectrum. Similarly, the barrier for the electron injection will be from the Fermi level to the onset of the LUMO. In most organic molecular devices the cathode and anode separation is large enough that the injection of the hole and electron occurs at different molecules and beyond the size of the polarons. Therefore, we define the onset of the HOMO peak as the "HOMO position" of the CuPc film, at -0.7 eV shown in the bottom part of Fig. 2. A similar term is used for the LUMO position, at about 1.0 eV for the pristine CuPc film. The result is an injection energy gap of about 1.7 eV, interestingly very close to the optical band gap of the CuPc E_{opt} (~1.7 eV). E_{opt} is widely used to estimate the LUMO position of organic films from UPS data, which originates from a different mechanism than the formation of a Frenkel exciton with the hole and electron on the same molecule. For the Cs-doped CuPc film, the onset of the LUMO peak is less than 0.2 eV from the Fermi level. Given the width of the LUMO peak, the Fermi level is virtually aligned with the LUMO of CuPc. We can similarly determine that the HOMO position is about -1.5 eV. The experiment gives an injection energy gap of ~1.7 eV, the same as in the pristine film, which is a further confirmation that no chemical reaction occurs when CuPc is doped by Cs.

Previous studies of alkali metals on Alq_3 have shown that charge transfer and Fermi-level pinning do occur.[19–21] However, the pinning of the Fermi level near the LUMO was inferred from the occupied energy-level evolution and the optical band-gap data, since UPS can only directly observe the occupied states. The IPES spectra, therefore, present direct observation of LUMO shifting and pinning of the onset of the LUMO close to the Fermi level.

In Fig. 3, we propose an energy-level diagram showing the Fermi-level pinning. The left part represents the pristine CuPc film. The Fermi level is close to the center of the band gap. The right part represents the heavily doped CuPc, where the LUMO is very close to the Fermi level. The transition between these two phases is represented by a gradual change of energy levels, which reflects changes in Cs doping con-

centration due to diffusion. The Fermi-level position in the electronic gap of CuPc is determined by the concentration of the dopant, and fixed at a position close to the LUMO when the doping concentration increases to where the Cs:CuPc ratio is close to or more than 1. Analogous to the inorganic semiconductor, we name this phenomenon Fermi-level pinning in the organic semiconductor. As a result, Cs-doped CuPc has a very small electron injection barrier and the gradual changes of the doping level may provide a stairway for electron hopping in the CuPc layer. This proposal may be able to explain the successful use of CuPc doped with Cs or other alkali metals as the electron injection layer in OLED devices.

We have shown that the Fermi level in the CuPc can be modified by alkali metal doping. The HOMO of CuPc observed by UPS shifts away from the Fermi level at even very low concentrations of Cs doping (Cs:CuPc ~0.01). When the Cs:CuPc ratio approaches unity, the total energy shift approaches 1.0 eV. The shift of the LUMO can be observed directly by IPES and is equal to the HOMO shift so that the onset of the LUMO of the CuPc film is pinned at the Fermi level. This pinning is attribute to the charge transfer from the Cs atom to the CuPc molecule, resulting in a reduction in the electron energy barrier of Cs-doped CuPc.

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