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Electronic structure of the organic semiconductor copper phthalocyanine and K-CuPc studied using photoemission spectroscopy

T. Schwieger,[1] H. Peisert,[1] M. S. Golden,[1,2] M. Knupfer,[1] and J. Fink[1]
[1]*Institute for Solid State and Materials Research Dresden, D-01069 Dresden, Germany*
[2]*Van der Waals-Zeeman Institute, University of Amsterdam, NL-1018 XE Amsterdam, The Netherlands*

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The changes of the electronic structure of copper phthalocyanine (CuPc) caused by the intercalation with potassium are studied using core-level and ultraviolet photoemission spectroscopy. The analysis of the valence-band spectra allows the estimation of the energy gap relevant for transport, which is substantially larger than the energy gap obtained using optical methods, showing that solid CuPc has to be regarded as a correlated material. Furthermore, our experiments indicate that there is structural (polaronic) relaxation of the CuPc molecules upon charging and that the lowest unoccupied molecular orbital of CuPc is more concentrated in the central part of the phthalocyanine molecules.

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I. INTRODUCTION

Recently, there has been growing interest in the properties of organic semiconductors and their potential application in various devices such as organic light-emitting diodes (OLED),[1] organic field effect transistors,[2] or organic solid-state injection lasers.[3] In addition, field effect devices on the basis of organic semiconductors have been used to demonstrate the existence of high-temperature superconductivity or quantum Hall levels in organic molecular crystals.[4,5] The family of the phthalocyanines (PC's) represents one of the most promising candidates for ordered organic thin films, as these systems possess advantageous attributes such as chemical stability and excellent film growth which result in optimized electronic properties.[6] Thus, they can be regarded as model systems for the entire class of low molecular weight, flat, organic molecules. For example, copper Pc (CuPc) has been successfully applied as a buffer layer in organic OLEDs (Ref. 7) and as an active layer in organic field effect transistors.[2] Figure 1 schematically shows the molecular structure of CuPc.

Despite much work on pristine CuPc and on the growth of CuPc thin films on various substrates in recent years,[6] there are only very few investigations on the electronic properties of *p*- and *n*-doped PCs.[8,9] Doped PC's have become increasingly important due to the observation that doping of PC layers with organic molecules enhances their device characteristics in OLED.[10] Detailed knowledge of the electronic structure of the doped molecules provides additional information about both the properties of the doped organic semiconductor itself and about physical phenomena which are associated with charge-carrier transport or injection at interfaces, and is therefore essential for the understanding of device properties. Therefore, in this work we study the electronic structure of CuPc as a function of potassium intercalation using core-level x-ray photoemission spectroscopy (XPS) and valence-band ultraviolet photoemission spectroscopy (UPS). Due to the ionic interaction between the organic molecule and the alkali metal, the intercalation with potassium represents one route to investigate negatively charged CuPc and thus also provides insight into the properties of other *n*-type doped PC's.

II. EXPERIMENT

UPS and XPS studies were carried out using a commercial PHI 5600 system which was equipped with an unmonochromatized He-discharge lamp and a monochromatized Al-$K\alpha$ x-ray source providing photons with 21.2 eV for UPS and 1486.6 eV for XPS, respectively. The UPS spectra were corrected for the contributions from He Iβ and He Iγ radiation. The total-energy resolution of the spectrometer was determined by analyzing the width of a Au Fermi edge to be 100 meV (UPS) and 350 meV (XPS), respectively. The energy scale was aligned by measuring the Fermi edge (0 eV), as well as the $4f_{7/2}$ emission (84.0 eV) of the gold substrate. The error produced by this alignment procedure is smaller than 0.1 eV. All measurements were carried out at room temperature. As a substrate an Au(100) single crystal exhibiting a 5×20 superstructure was used. The gold crystal was cleaned by repeated sputtering and annealing cycles and checked by low-energy electron diffraction and XPS until no

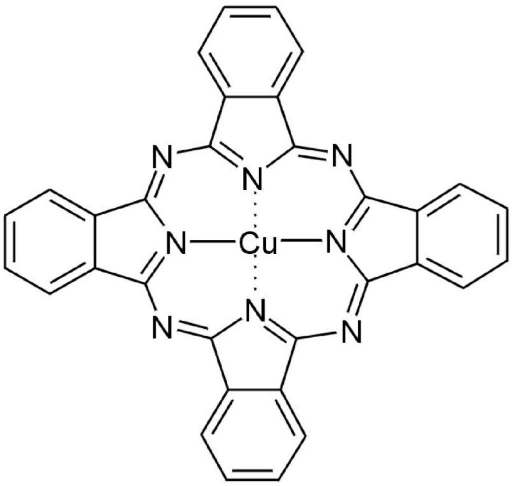

FIG. 1. Schematic representation of the molecular structure of CuPc.

sign of contamination could be detected. Subsequently, CuPc was evaporated in a preparation chamber (base pressure of 8×10^{-10} mbar) which was directly linked to the spectrometer. Due to the very clean preparation conditions the number of impurities in the deposited CuPc film was very small. Specifically, no oxygen could be detected in the CuPc film. CuPc on Au(100) was grown in a Stranski-Krastanov mode.[11] The thickness of the respective CuPc layer was estimated to be 7 nm by monitoring the attenuation of the intensity of the $4f_{7/2}$ substrate peak before and after the deposition. The mean-free-path length of electrons in the organic overlayer was calculated according to Seah and Dench[12] to be about 29 Å for the kinetic energy of 1402.6 eV (using the Au $4f_{7/2}$ signal from the substrate). The CuPc films were then intercalated using a commercial SAES potassium getter source. The sample was heated to 180 °C during potassium deposition, which resulted in a homogeneous distribution of the potassium in the CuPc layer, within our probing depth. The potassium concentration in the CuPc films was derived from a comparison of the relative intensities of the K $2p$ and the C $1s$ as well as N $1s$ core-level intensities. As sensitivity factors we used 1.3 for K $2p$, 0.296 for C $1s$, and 0.477 for N $1s$.[13] The work function ϕ of the films was extracted from the determination of the high binding-energy cutoff by applying a bias of 5 eV to the sample. In this manner we obtained, for example, $\phi=5.3$ eV for a sputter-cleaned gold foil, in good agreement with the literature.[14] In order to examine the impact of the ordering of the molecules and of the differing molecular orientation on the substrate,[15] we additionally used an Ar ion sputter-cleaned Au foil as a substrate. This led in this case to similar results and these data will not be considered further in this paper.

III. RESULTS AND DISCUSSION

Intercalation with potassium results in a transfer of the outer K $4s$ electron to the CuPc molecules. This results in *n*-type doping of the molecules, which is well known from other π-conjugated molecular systems.[16–18] In the following we will discuss the results of the photoemission experiments on potassium-intercalated CuPc. First, we will turn to the valence-band spectra and subsequently present an analysis of the core-level photoemission results.

A. Valence-band spectra and work function

Figure 2 shows the evolution of the valence-band spectra obtained using UPS as a function of increasing potassium intercalation, up to a concentration of 1.7 potassium atoms per CuPc molecule. The valence band of pristine CuPc well reproduces already published results.[19] The onset of the CuPc valence band, which corresponds to emission from the highest occupied molecular orbital (HOMO) is found at 1.15 eV binding energy. Upon intercalation, the spectra shift to higher binding energy which is typical for an *n*-type doping process, and which results from a shift of the Fermi level towards the lower edge of the conduction band. Furthermore, potassium intercalation leads to the appearance of an intercalation-induced peak in the former band gap, which is caused by the filling of the former lowest unoccupied molecular orbital (LUMO) of CuPc. As the potassium concentration increases, the intensity of this new structure increases with doping. We note that none of the spectra shows emission from the Fermi level, i.e., none of the samples is metallic.

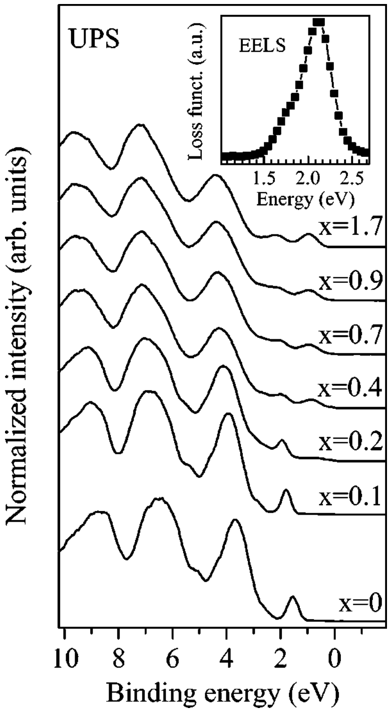

FIG. 2. Valence-band photoemission spectra of CuPc as a function of K intercalation (K_xCuPc). The inset shows the loss function of pristine CuPc measured using electron energy-loss spectroscopy in transmission of pristine CuPc with an excitation onset of about 1.5 eV which represents the optical energy gap.

Figure 3 depicts the energy shift of the main valence-band features together with the evolution of the shift of the work function (the actual shift of ϕ has been multiplied by -1) and the shifts of the core levels upon intercalation. First, we

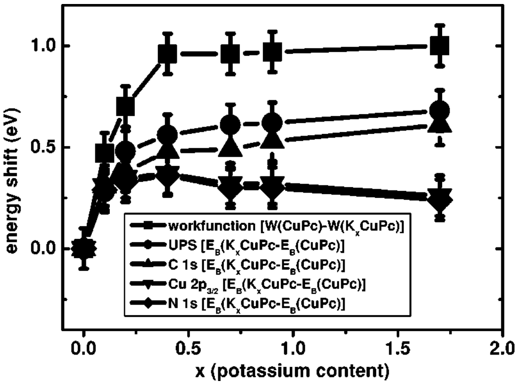

FIG. 3. Energy shift of the C $1s$, N $1s$, and Cu $2p_{3/2}$ core levels; the main features of the valence band (UPS); and the work function upon K intercalation. Since the work function decreases with increasing potassium concentration, we draw the negative shift of the work function to allow a direct comparison of the data.

will discuss the shift of the work function. The work function is defined as the distance between the Fermi and vacuum levels. In pristine CuPc the Fermi level lies in the energy gap of CuPc. Upon increasing potassium intercalation the Fermi level moves closer to the vacuum level and thus lowers the work function of the K-intercalated CuPc layer. Until an intercalation level of 0.4 potassium atoms per CuPc molecule is reached the work function is still changing, but in a region between 0.4 and 1.7 potassium atoms per CuPc molecule the work function stays constant at 3.1 eV.

Within a very simple approach one can neglect any kind of relaxation phenomena at very low intercalation levels. In this case, the Fermi level would be pinned at the bottom of the conduction band, as has been shown recently for Cs-intercalated CuPc,[20] and one can derive the energy gap of pristine CuPc directly from the onset of the valence band in pristine CuPc plus the work-function shift observed at low intercalation. This procedure provides a lower limit of the energy gap in CuPc of about 2.1 eV, a value which is significantly larger than the gap measured using optical or electron energy-loss spectroscopies. These experiments give an optical gap of about 1.5 eV (see inset of Fig. 2). Our results are consistent with recent combined photoemission/inverse-photoemission spectroscopy (UPS/IPES) measurements which reported a band gap of CuPc of about 2.3 eV.[21]

From above it follows that the Fermi energy of CuPc lies in the middle of a HOMO-LUMO gap, which confirms that pure CuPc without any impurities could be regarded as an intrinsic semiconductor. This is in contrast to the common observation of a *p*-type-like behavior of CuPc. This behavior most likely arises from oxygen impurities in the CuPc from the surrounding atmosphere. Even preparation of CuPc films in argon boxes or in high vacuum ($p \approx 10^{-6}$ mbar) introduces these impurities into the material. In CuPc films, which have been prepared in UHV ($p \approx 10^{-10}$ mbar), the number of impurities is small enough to observe an intrinsic behavior of the organic semiconductor in photoemission.[21,22] Further one arrives at a scenario in which the energy gap as derived from photoemission, which is the relevant number for transport processes, exceeds the optical gap. The difference of the two spectroscopic approaches directly points towards an explanation for this observation. While in optical (and related) techniques the number of electrons per molecule is not changed upon excitation, which generates a frenkel exiton on the molecule (N-electron state), photoemission and inverse photoemission probe a final state with one electron less or more ($N-1$ or $N+1$ state), respectively. The change of the number of electrons per molecular unit now affects the energetics of the electronic states due to the mutual Coulomb repulsion of all valence electrons on the molecule. In molecular solids, this Coulomb repulsion energy usually is of the order of the one-particle bandwidth or larger which renders these materials strongly correlated and leads to transport-relevant energy gaps which can be considerably larger than the optical gap. This has already been found for other π-conjugated molecular solids[18,21,23,24] and we consequently ascribe our results to the presence of a relatively strong Coulomb repulsion energy on the CuPc molecules. In addition, our results again demonstrate that the numbers for the energy gap of molecular solids which are measured using optical methods should *not* be used to describe or model charge-carrier transport processes.

We finally would like to point out the differences between the determination of the transport gap by combined UPS/IPES measurments and our method described above. Both experiments get the position of the HOMO relative to the Fermi level from the UPS data, whereas the way to derive the LUMO position relative to the Fermi level is different. In the IPES experiment the LUMO position is obtained by adding an electron to the molecule, whereas we determine the position of an unoccupied LUMO which pins the Fermi level at its edge. Even if the experimental approaches are different, the value for the transport gap of 2.1 ± 0.1 eV and 2.3 ± 0.4 eV (Ref. 21) agree within the error bars.

The fact that solid CuPc is a correlated system now also harbors the explanation of the nonmetallic nature of K-intercalated CuPc phases. Although charge carriers are introduced in the latter, their mobility (hopping) between the molecules is substantially reduced by the Coulomb repulsion energy which has to be overcome as a hopping process changes the number of electrons per molecular unit. This reduction most likely is further supported by polaronic effects, i.e., the structural relaxation of the molecules upon charging[25] which can self-trap the charge carriers. In the case of CuPc, the charge-induced structural relaxation might even be stronger than in many other related systems because the LUMO of CuPc is doubly degenerate while the HOMO is not degenerate,[26] which renders the molecule in a negatively charged state susceptible to a Jahn-Teller distortion. The combination of correlation and structural relaxation effects makes the charge transport activated and thus the materials insulating.

We now turn to the energy shift of the valence-band features upon intercalation (Fig. 2). The shift of all valence-band features is 0.3–0.4 eV lower than the negative shift of the work function of CuPc. Thus, the valence band moves closer to the vacuum level with increasing potassium intercalation, meaning that we do not observe a rigid shift of the electronic levels of the valence band. This fact supports our assumption above of a relaxation of the molecular structure and consequently its electronic levels due to the charge transfer to the molecules. Moreover, our results allow an estimation of the polaronic relaxation of the valence levels of 0.3–0.4 eV, in good agreement with the situation in other π-conjugated molecules.[27]

B. Core-level spectroscopy

We additionally have studied the N $1s$, K $2p$, C $1s$, and Cu $2p$ core-level photoemission spectra of CuPc and K-CuPc using XPS. The C $1s$ peak (see Fig. 4) of pristine CuPc consists of three different distinct features, at 284.6 eV (C-1), 286.0 eV (C-2), and 288.0 eV (C-3). According to previous reports, they can be attributed to the aromatic carbon of the benzene rings (C-1), pyrrole carbon linked to nitrogen (C-2), and a π-π^* satellite of the latter.[28,29] However, the ratio of the relative intensities of the C-1 feature compared to the sum of the relative intensities of C-2 and

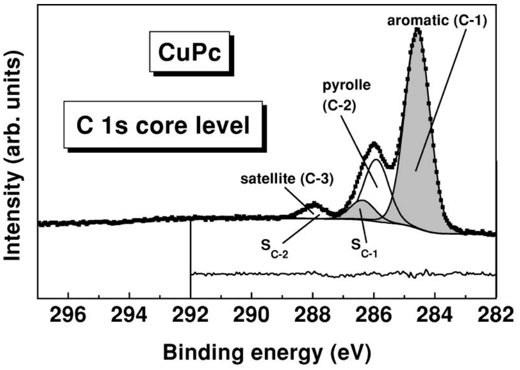

FIG. 4. C 1s core-level spectrum of CuPc in the pristine state. One can distinguish between the aromatic carbon and its satellite (gray) and the carbon linked to the nitrogen and its satellite (white). The graph below the spectrum shows the discrepancy between the fit and the spectrum.

C-3 peaks, leads to a number of 2.3,[30] which is significantly smaller than the ratio expected from the number of different carbon sites (18:6=3.0) in the CuPc molecule. The introduction of an additional satellite for the C-1-peak (see Fig. 4), which is obscured by the C-2 feature, improves the agreement considerably[28,30] and leads to the expected intensity ratio between the aromatic and pyrrole carbon of 3.0. In Fig. 5 the evolution of the C 1s core levels with increasing potassium intercalation is drawn. The K 2p spin-orbit doublet (not shown) appears at binding energies (294.8 eV and 297.6 eV) which are expected for fully oxidized potassium ions in intercalated π-conjugated molecular solids.[16,18,31] This confirms that the outer s electron of the K atoms is transferred to the CuPc molecules. No fine structure of the K 2p doublet could be observed, which confirms that all intercalation sites of the potassium are energetically equivalent. No vertical inhomogeneity in the distribution of the potassium atoms in the CuPc film could be observed upon changing the emission angle of the photoelectrons. With increasing potassium concentration we observe a shift of 0.6 eV of the C 1s structures to higher binding energies which essentially follows that of the valence-band features (see Fig. 3). Moreover, a continuous broadening of the C 1s spectrum is observed with increasing intercalation which leads to a loss of the fine structure of the C 1s photoemission signal. This broadening might be due to a phase separation in the potassium-intercalated CuPc film.

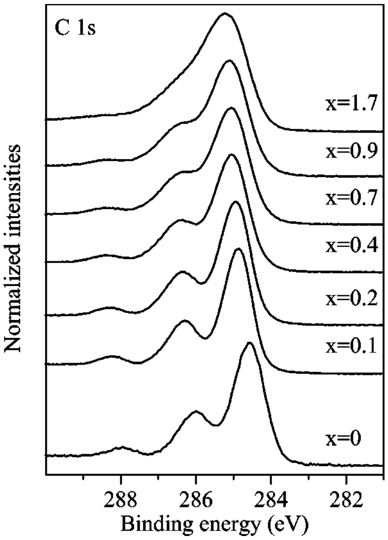

FIG. 5. C 1s core-level spectra of CuPc as a function of K intercalation (K_xCuPc).

The main line of the N 1s core-level spectrum (not shown) in the pristine case appears as a single peak at 399.0-eV binding energy, i.e., the chemical bonding conditions are similar for the two inequivalent types of nitrogen sites in CuPc. The binding energy of the main Cu 2$p_{3/2}$ photoemission signal is 935.4 eV. Upon increasing potassium intercalation one observes a broadening of the spectra and a shift to higher binding energies (see Fig. 3).

In the following we discuss the binding-energy shifts of the different core levels observed for K_xCuPc to obtain further insight into the distribution of the LUMO on the CuPc molecule. Generally, the reasons for binding-energy shifts of core levels in a system such as K_xCuPc can be threefold:

(i) an energetic shift of the Fermi level upon intercalation (see discussion above),

(ii) a change of the Madelung potentials as a consequence of the presence of charged molecules and K ions in the environment, and

(iii) a chemical shift of the core level as a result of a different charge density on the molecules.

Since the first two scenarios affect the molecules as a whole from outside, they would cause the same shift for all core levels, which cannot explain the differences shown in Fig. 3, or [point (ii)] render the different atomic sites of the molecule inequivalent which then would lead to the appearance of a superposition of core-level spectra at noninteger doping levels, which is not the case. Consequently, the distribution of the electrons which occupy the LUMO of CuPc is not homogeneous across the entire molecule. In other words, the LUMO wave function has different probabilities to be found at various atomic sites of the molecules. Since the differences between the core-level shifts of the N 1s and Cu 2$p_{3/2}$ signals are largest as compared to the work function we conclude that the (doubly degenerate) LUMO of CuPc is more concentrated in the central part of the molecule (the N and Cu sites, see Fig. 1). This conclusion corroborates theoretical predictions of the LUMO distribution of CuPc (Refs. 32 and 33) and parallels the situation observed for K_xAlq$_3$ where the distribution of the LUMO on the Alq_3 molecule also has been found to be more concentrated in the nitrogen sites.[16]

IV. SUMMARY

We have presented a photoemission study of potassium-intercalated CuPc thin films. From our experimental results, the estimation of the transport energy gap of pristine CuPc has been possible ($E_g^{transp} \geqslant 2.1$ eV) and it is shown that solid CuPc has to be regarded as a correlated material, similar to other molecular solids. The photoemission spectra additionally provide evidence for a structural relaxation of the CuPc molecules upon charging which can be assigned to the formation of small polarons. Finally, an analysis of the different energy shifts of the photoemission core-level signals demonstrates that the part of the LUMO of CuPc occupied upon electron donation to the molecule is more concentrated in the central part of the phthalocyanine molecules.

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