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The complex nature of phthalocyanine/gold interfaces

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ABSTRACT

We compare the electronic properties of the interface between Au(1 0 0) and cobalt phthalocyanine (CoPc), fluorinated F_{16}CoPc as well as CuPc using X-ray photoemission spectroscopy and valence band ultra-violet photoemission spectroscopy. Our results show that in addition to the formation of an interface dipole at the interfaces of CoPc and F_{16}CoPc to gold, there is a local charge transfer to the central Co ion, which as a result is reduced to Co(I).

1. Introduction

In recent years, the formation of interfaces between organic semiconductors and metals has attracted considerable attention because of aspects of basic science as well as their application in advanced optical and electronic devices. A promising candidate of this material class is the phthalocyanines (Pcs) because of their stability against heat, light, moisture and oxygen. They are used e.g. for organic light-emitting diodes (OLEDs) [1], photovoltaic cells [1–3], organic field-effect transistor (OFETs) [4,5] and organic spintronic devices [6].

Although the electronic properties of the transition metal phthalocyanines have been intensively studied, the explanation of the interaction of some interfaces is still discussed. For well ordered phthalocyanine or porphyrine monolayers on noble metal surfaces (Au, Ag) a charge transfer has been previously reported. In many cases the transition metal center gets the additional charge from the metal substrate. It is thus clear, that the formation of a monolayer on the substrate is connected to a valence change of the transition metal center, which often is Co [7–10,12–15,17–19]. This valence change then must be directly related to a change of the magnetic moment of the corresponding molecule, which represents an important aspect in view of the application of magnetic molecules in molecular or organic spintronic devices or the appearance of the Kondo effect in adsorbed molecules on surfaces [7]. It could also be shown that this ion–substrate bond has an covalent character [19]. A comparison of theoretical and experimental data of CoPc deposited on metal surfaces indicated that this charge transfer is due to the formation of a molecule–metal hybrid state, most likely a local bond between the Co $3d_{z^2}$ and metal states [20,21].

In contrast to cobalt phthalocyanine, copper phthalocyanine shows no evidence of charge transfer [22,23]. In this case copper as central atom is unaffected by the noble metal substrate.

Additionally, phthalocyanines offer the possibility to change the energy position of the (ligand) molecular orbitals via fluorination, i.e. the replacement of hydrogen atom by fluorine. It has been demonstrated that complete fluorination of CuPc and ZnPc to F_{16}CuPc and F_{16}ZnPc results in a shift of the ionization potentials by about 1 eV [24–28] while the energy gap as revealed by optical absorption [26] or a combination of photoemission and inverse photoemission spectroscopy [29] is kept almost the same.

In this contribution we discuss the interface between copper phthalocyanine (CuPc), cobalt phthalocyanine (CoPc) and its fluorinated relative (F_{16}CoPc), and a gold single crystal substrate on the basis of photoemission spectroscopy (XPS, UPS) results, respectively. Our data demonstrate that the interface formation for cobalt phthalocyanine system is determined by two independent and opposite charge transfer processes which involve either the phthalocyanine ligand or the central Co ion.

2. Experimental

The X-ray (XPS) and ultra-violet (UPS) photoelectron spectroscopy experiments have been carried out using an ultrahigh vacuum system, which is equipped with an electron-energy analyzer PHOIBOS-150 (SPECS) and two light sources, respectively. A monochromatized Al Kα source provides photons with an energy of 1486.6 eV for XPS. Photons with an energy of 21.21 eV from a He discharge lamp were used to perform valence band measurements. The UPS measurements were done by applying a sample bias of −5 eV to obtain the correct secondary electron cutoff. The recorded spectra were corrected for the contribution of He satellite radiation. The total energy resolution of the spectrometer was about 0.35 eV (XPS) and 0.06 eV (UPS).

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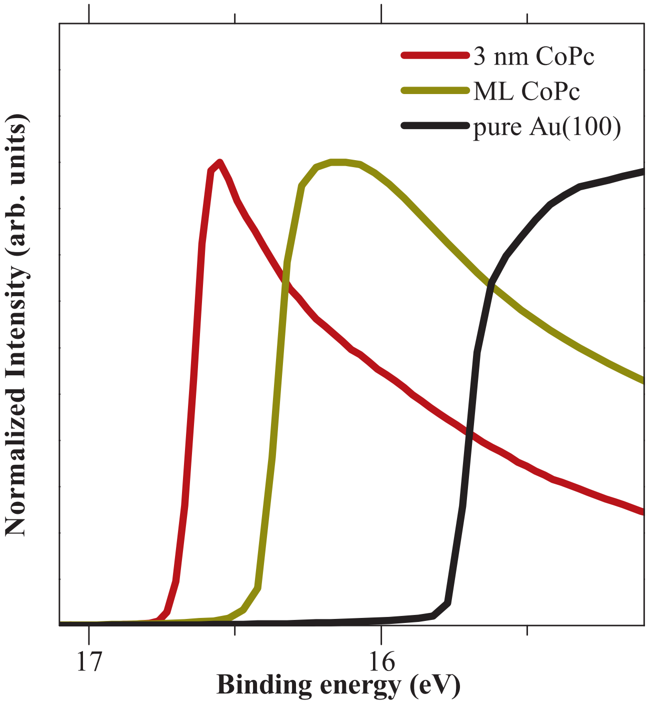

Fig. 1. High binding energy cutoff for 3 nm CoPc, a monolayer (ML) of CoPc and Au(1 0 0).

As substrate we used the (1 0 0) surface of a gold single crystal. The surface was prepared by repeated Ar^+ sputtering and annealing cycles, after which a 5 × 20 surface reconstruction was observed using low energy electron diffraction, while no remaining contamination was detected in core level photoemission spectra. The CoPc and F_{16}CoPc films with a thickness of about 3 nm were prepared by an in situ thermal evaporation and with a deposition rate of 1 Å/min onto the Au(1 0 0) substrate kept at room temperature. From previous studies it is known that CoPc films grown in this manner result in CoPc molecules that are arranged parallel to the substrate surface [30]. To estimate the thickness of the Pc films we monitored the attenuation of the intensity of the Au $4f_{7/2}$ substrate peak due to the organic film considering the procedure of Seah and Dench [31].

A monolayer of each material was produced via a thermal annealing process. Thereby, thicker films are gently annealed at 473 K which results in a desorption of CoPc or F_{16}CoPc molecules except the first monolayer, since the interaction in the first monolayer to the gold substrate is stronger than the interaction between the molecules going to thicker layers [32]. We note that the C 1*s* core level photoemission spectra of these monolayers (not shown) indicate that the molecules are still intact.

3. Results and discussion

In general, interfaces between organic semiconductors and metals are characterized by the occurrence of a short range interface dipole, i.e. a change of the electrostatic potential when crossing the interface [33–36]. Moreover, it has been pointed out that the rationalization of these interface dipoles requires the inclusion of several mechanisms such as a reduction of the metal work function, a (partial or integer) charge transfer between metal and organic material depending upon the strength of the interaction at the interface, screening effects, and the contribution of molecular dipoles. Using photoemission spectroscopy, the presence of an interface dipole is signaled by an energy shift of the so-called secondary electron cutoff (for details see Refs. [35,36]). In Fig. 1 we show the evolution of this cutoff for the interface between CoPc and Au(1 0 0) as a function of CoPc coverage. From this figure it becomes clear that this interface also supports a rather large interface dipole. Analogous data of the interface between CuPc and Au(1 0 0) [22,37] show a very similar behavior.

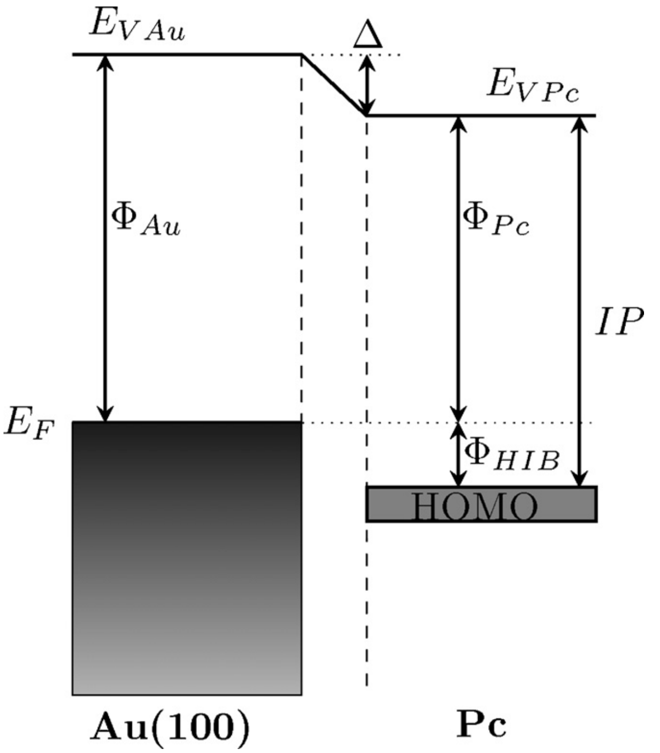

Fig. 2. Schematic energy level alignment for the phthalocyanine gold interfaces as obtained from the photoemission measurements.

Table 1
Interface parameter taken from the photoemission experiments for CoPc and CuPc. The values of CuPc are taken from Ref. [38]. *Note*: All parameters are given in eV.

	Φ_{Au}	Φ_{Pc}	IP	Φ_{HIB}	Δ
CuPc	5.3	4.1	5.0	0.9	−1.2
CoPc	5.4	4.5	5.5	1.0	−0.9

In Fig. 2 and Table 1 we summarize the results of such measurements for the two interfaces CuPc/Au(1 0 0) and CoPc/Au(1 0 0). For both systems, the resulting interface parameters are very similar. CoPc, which is a p-type semiconductor, has an ionization potential (IP) of 5.5 eV, somewhat larger than that of CuPc, and the determined hole injection barriers (Φ_{HIB}) for both phthalocyanines are nearly the same (about 1 eV). Importantly, the observed interfacial dipole (Δ) of −0.9 eV for CoPc and −1.2 eV for CuPc indicates a charge transfer of electrons from the organic semiconductor to the Au substrate, in other words a positive charging of the organic semiconductor. We note that the reduction of the metal work function at these interfaces most likely cannot explain the entire dipoles as observed, which underlines the necessity of a charge transfer in order to understand the full dipole [39].

Furthermore, there is a wealth of information on the CuPc/Au interface, and there is plenty of evidence that the interaction at this interface is rather weak, i.e. apart from the above mentioned charge redistribution to achieve the thermodynamic equilibrium, there is no further hybridization between metal and phthalocyanine orbitals (i.e. no chemical interaction). Such a behavior can be well described within the induced density of interface states (IDIS) model [40,39]. The very similar interface parameters for CoPc/Au suggest that the formation of the interface to gold is independent of