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Hybrid States and Charge Transfer at a Phthalocyanine Heterojunction: $\mathrm{MnPc}^{\delta+}/\mathrm{F}_{16}\mathrm{CoPc}^{\delta-}$

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Using photoelectron spectroscopy we demonstrate charge transfer at an interface between two well-known transition metal phthalocyanines, MnPc and $\mathrm{F}_{16}\mathrm{CoPc}$, resulting in charged $\mathrm{MnPc}^{\delta+}$ and $\mathrm{F}_{16}\mathrm{CoPc}^{\delta-}$ species. Moreover, the transferred charge is substantially confined to the two transition metal centers. Density functional theory calculations reveal that a hybrid state is formed between the two types of phthalocyanines, which causes this charge transfer. For the hybrid state the Mn $3d_{xz}$ interacts with the Co $3d_{z^2}$ orbital leading to a two-level system. As only the lower of the two hybrid states is occupied, the charge is directly transferred to the Co $3d_{z^2}$ orbital.

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The concept of charge transfer in organic materials has played a very important role in fundamental as well as applied sciences. Prominent examples are organic conductors and superconductors [1–4]. Entire classes of so-called charge transfer salts have been synthesized and demonstrated interesting and often unexpected physical properties ranging from metallicity and superconductivity over complex phase diagrams including charge density and spin density wave phases to highly correlated materials (Mott insulators) [1,3]. Recently, the formation of a two-dimensional metallic layer has been reported as a consequence of charge transfer between the two insulating organic crystals (TTF and TCNQ) [5,6]. In view of more applied aspects, charge transfer has also been investigated and exploited in order to improve or engineer the performance of organic electronic devices. For instance, it has been shown that the inclusion of organic dopants in organic semiconductors can significantly enhance charge carrier injection from electrodes [7], and the modification of electrode surfaces with particular organic layers accompanied by charge transfer allows tuning of hole injection barriers at such junctions [8].

In this contribution, we present a heterojunction made of two structurally very similar transition metal phthalocyanines (TMPc's), MnPc and $\mathrm{F}_{16}\mathrm{CoPc}$, where photoelectron spectroscopy studies and calculations based upon density functional theory (DFT) clearly demonstrate the occurrence of hybridization and charge transfer. Moreover, our results strongly indicate that this charge transfer is very local and essentially affects the transition metal centers only. Interestingly, this kind of interaction could be also possible for other transition metal complexes (e.g., porphyrines, other phthalocyanines and derivatives of those), and it is important to realize that the change of the transition metal charge state (valence) in these molecules is connected to a change of the respective magnetic moment. Thus, the compounds studied here can be seen as fundamental representatives of a peculiar, potentially low-dimensional material class where the interaction is intimately connected to a transfer of magnetic moment or spin, and which could be distinguished by unusual interesting physical properties. Also, organic-organic interfaces demonstrating charge and spin transfer may be used to optimize particular organic electronic or spintronic devices.

The x-ray photoelectron spectroscopy experiments have been carried out using an ultrahigh vacuum system, which is equipped with an electron-energy analyzer PHOIBOS-150 (SPECS). A monochromatized AlK_α source provides photons with an energy of 1486.6 eV for x-ray photoelectron spectroscopy. The total energy resolution of the spectrometer was about 0.35 eV.

As substrates we used the (100) surface of a gold single crystal as well as the (111) surface of silver. These surfaces were prepared by repeated Ar^+ sputtering and annealing cycles, after which a typical 5×20 surface reconstruction for gold and a hexagonal structure for silver were observed using low energy electron diffraction, while no remaining contamination was detected in core level photoemission spectra. MnPc and $\mathrm{F}_{16}\mathrm{CoPc}$ have been deposited by an *in situ* thermal evaporation and with a deposition rate of 1 Å/ min. At the beginning, a 3 nm thick film was deposited on the single crystal at room temperature. This initial film was thick enough to avoid contributions of the metal-organic interface to the spectra. Subsequently, the second phthalocyanine material was deposited. From previous studies it is known that phthalocyanine films grown in this manner result in molecules that are arranged parallel to the substrate surface [9–12]. To estimate the thickness of the Pc films, we monitored the attenuation of the intensity of the Au $4f_{7/2}$ and Ag $3p_{5/2}$ substrate peaks due to the organic film considering the procedure of Seah and Dench [13].

The all electron DFT calculations were carried out using the NRLMOL program package [14]. To include exchange and correlation effects, the generalized gradient functional developed by Perdew, Burke, and Ernzerhof was applied [15]. First we relaxed the structures of the individual MnPc and F_{16}CoPc molecules by performing a geometry optimization. In order to reproduce the relations of the molecules at the interface, the distance and relative shift of the molecules in a dimer consisting of MnPc and F_{16}CoPc was deduced from crystallographic data on the β-MnPc phase obtained from the Cambridge Structural Database. These data clearly show that neighboring molecules arrange such that the metal centers are positioned above nitrogen atoms bridging two isoindolic units of a neighboring molecule. The distance of the nitrogen and the metal is about 3 Å. Using this startup geometry we performed a relaxation of the dimer system.

We start the presentation and discussion of our results with the evolution of the C 1s core level photoemission signal when F_{16}CoPc is gradually deposited on a 3 nm thick MnPc film on Au(100) as shown in Fig. 1. As a consequence of the high surface sensitivity of such measurements, we observe an increasing contribution of the signal from F_{16}CoPc with respect to that of MnPc. Fortunately, the 2 C 1s emission spectra can be well distinguished due to the presence of fluorine in F_{16}CoPc and the resulting spectral shape with an additional maximum at about 287 eV binding energy in this case [11,16]. Figure 1 also shows the results of a modeling of our data with a simple superposition of the C 1s core level spectra of the two materials with appropriate weights but without any change in relative peak heights, positions or widths.

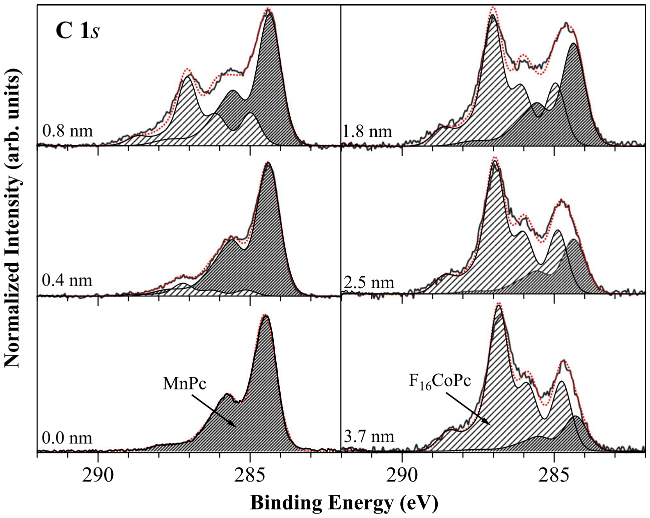

FIG. 1 (color online). Evolution of the C 1s core level photoemission profile upon deposition of F_{16}CoPc on a 3 nm thick layer of MnPc. We additionally show the results of a modeling of the data using an appropriately weighted sum (dashed line) of an otherwise unchanged photoemission profile of the two individual phthalocyanines (filled areas).

The agreement of the measured data and the modeling in Fig. 1 is very good, which clearly shows that the two phthalocyanine ligands are less affected by the neighborhood of the other molecule, respectively, at the heterojunction. In other words, there is no interaction at our F_{16}CoPc/MnPc interface which significantly modifies the Pc ligands, in contrast to, e.g., doping of phthalocyanine films with potassium, where the C 1s photoemission profile is characterized by the appearance of an additional core level feature [17,18]. We note that this conclusion is corroborated by the N 1s core level data (not shown), which do not change as a function of F_{16}CoPc addition, and by the fact that the variation of the relative C1s binding energies of the two species during data modeling is less than 300 meV.

Turning to the Co 2$p_{3/2}$, photoemission spectra at the same interface intriguingly discloses to us an opposite behavior. There is a dramatic change in line shape and binding energy when going from a very thin F_{16}CoPc layer on top of MnPc to a thick layer. This is depicted in Fig. 2, where we also show the Co 2$p_{3/2}$ photoemission spectrum of a monolayer of F_{16}CoPc deposited on Au(100) [19]. The latter data are in almost perfect agreement to a number of studies in the literature where the interaction of Co-phthalocyanines and Co-porphyrines on various metal surfaces has been reported [19–21]. There is a general agreement that the data as shown in Fig. 2 arise from a rather strong interaction of the Co metal center in the molecules and the metal substrate which results in a reduction of this metal center to (at least) Co(I) [19–23], while the Co valence in undisturbed CoPc's and Co porphyrins is Co(II), which gives rise to a Co 2$p_{3/2}$ photoemission line shape and energy as shown in Fig. 2 for the thick F_{16}CoPc film on MnPc. Consequently, there is clear evidence that directly at the F_{16}CoPc/MnPc heterojunction the Co center of the F_{16}CoPc is reduced; i.e., there is substantial interaction accompanied by charge transfer at this interface.

Our photoemission data of the equivalent interface but prepared in the opposite manner by depositing MnPc on a

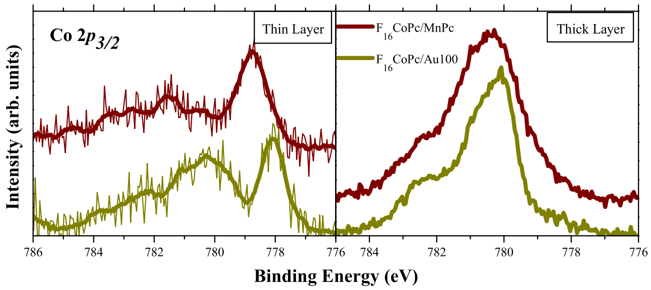

FIG. 2 (color online). Co 2$p_{3/2}$ core level photoemission spectra of a thin and thick F_{16}CoPc layer on top of MnPc. Also shown is the corresponding result for a F_{16}CoPc monolayer on Au(100) [19].

3 nm thick F_{16}CoPc layer complement this surprising result. We note that for this deposition sequence we present data where in a first step F_{16}CoPc is deposited onto a Ag(111) surface. In this way we avoid the contribution of Au $4p_{1/2}$ core level photoemission, which energetically overlaps with that from Mn $2p$ and therefore renders reasonable data analysis impossible.

In Fig. 3 we show both the Co $2p_{3/2}$ and Mn $2p_{3/2}$ core level data as a function of MnPc overlayer thickness on F_{16}CoPc. The Co $2p$ core level data of F_{16}CoPc before MnPc addition are virtually identical to those measured for thick F_{16}CoPc films on various substrates (see also Fig. 2) and thus represent undisturbed F_{16}CoPc. Upon addition of MnPc a low energy structure appears, which is clear evidence for the reduction of cobalt as described above in the context of F_{16}CoPc deposition on MnPc. This arises from the F_{16}CoPc molecules in direct contact with the MnPc layer surface. Note that in this case the Co $2p_{3/2}$ core level spectra always represent a superposition of the reacted upper-most layer (interface) and the other undisturbed layers (bulk) below. For this reason the spectra in Figs. 2 and 3(a) do not have the same line shape. Consequently, the reduction of the central Co atom of F_{16}CoPc in contact with MnPc is independent of the formation sequence of the F_{16}CoPc/MnPc heterostructure.

The question now arises, where does this charge, which is necessary for the reduction of Co atoms, come from? Figure 3 additionally shows the Mn $2p_{3/2}$ spectra for a very thin and a thicker MnPc layer on F_{16}CoPc. These two spectra are clearly different. Both the spectral shape and, in particular, the binding energy change, which signals a variation of the Mn charge state in MnPc, whereas in this case the Mn atoms are oxidized, as seen by the upshift in binding energy.

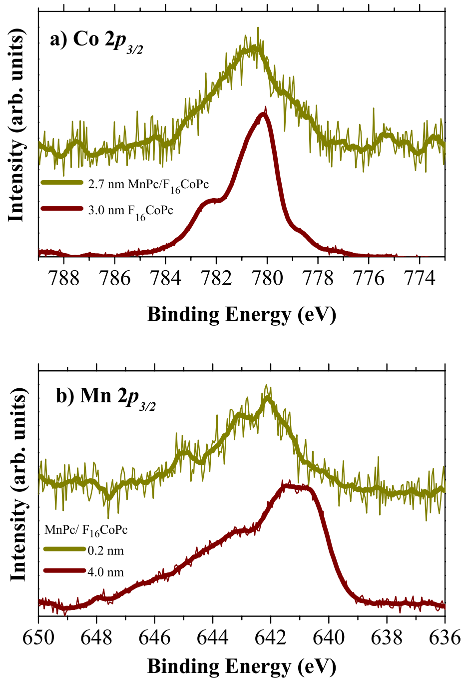

FIG. 3 (color online). (a) Co $2p_{3/2}$ and (b) Mn $2p_{3/2}$ core level photoemission spectra for a MnPc/F_{16}CoPc heterojunction when MnPc is deposited on a 3 nm thick F_{16}CoPc layer.

To summarize the experimental observations, we have presented clear evidence for the formation of a $\text{MnPc}^{\delta+}/F_{16}\text{CoPc}^{\delta-}$ heterojunction, with particular involvement of the two transition metal centers. Our calculations of a dimer made from these two phthalocyanines now give detailed insight into the nature of the interaction at the hetero-interface.

Within the theoretical treatment we first studied the systems F_{16}CoPc and MnPc individually. For F_{16}CoPc one finds that all energy levels as well as the Fermi level is pulled down in energy compared to hydrogenated CoPc due to the strong electronegativity of fluorine. Consequently the electron affinity of F_{16}CoPc is increased by 0.8 eV compared to CoPc (from 2.9 eV to 3.7 eV). Note that these absolute values are for individual free molecules and shielding effects in the bulk will change this quantity. However the energy ordering of the molecular levels near the Fermi level stays the same and also the spin of the system ($S = 1/2$) is preserved. The highest occupied molecular orbital (HOMO) is a purely ligand-derived π state whereas the lowest unoccupied molecular orbital (LUMO) is a Co $3d_{z^2}$ state.

For MnPc, the orbital alignment around the Fermi level has already recently been published [24]. There the energy levels around the Fermi level are of Mn $3d_{xz}$ and Mn $3d_{yz}$ nature. It is also pointed out that MnPc has an ionization potential of 4.5 eV, which is considerably smaller than the values for all other transition metal phthalocyanines due to the additional levels at the Fermi level. The spin of MnPc is found to be $S = 3/2$.

Because the experimentally revealed charge transfer indicated a strong confinement to the phthalocyanine interface, we performed calculations of a MnPc-F_{16}CoPc dimer system as described before. The results of the DFT calculation show that the level ordering for the molecules is preserved and that the states of the two systems combine to form a new energy level diagram. The crucial finding is that the Mn $3d_{xz}$ and the Co $3d_{z^2}$ state hybridize and form a two-level system as shown qualitatively in Fig. 4. As those two orbitals couple to each other they form one state decreased in energy and one state increased in energy as is the case within the formation of a chemical bond. Since the Mn $3d_{xz}$ state is the HOMO of MnPc and the Co $3d_{z^2}$ state is the LUMO of F_{16}CoPc only the lower one of the two hybrid states is occupied forming the HOMO of the dimer system. As this hybrid state is delocalized over both molecules with the largest contributions at the metal centers, the charge within this orbital is spread out to the dimer system. Hence a charge of approximately 0.2 electrons is transferred from MnPc to F_{16}CoPc. The value of this

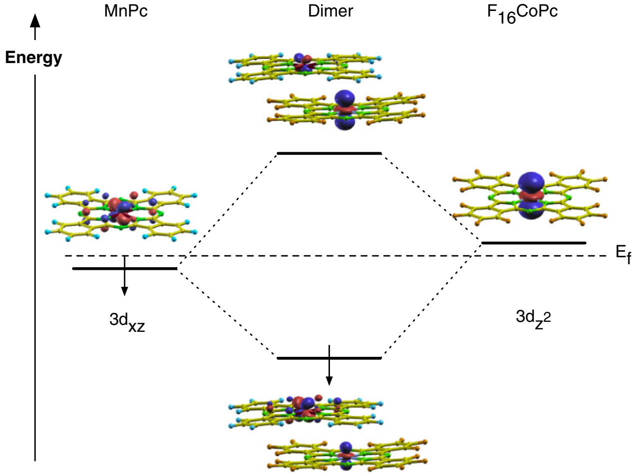

FIG. 4 (color online). Interaction of the MnPc and F_{16}CoPc states in the MnPc-F_{16}CoPc dimer close to the Fermi level. The Mn $3d_{xz}$ and the Co $3d_{z^2}$ orbitals hybridize to form a two-level system.

charge transfer is very sensitive to the actual distance of the molecules at the interface. In addition the systematic underestimation of the band gap within the generalized gradient approximation DFT, which is well known for metal Pcs [25], further complicates an accurate estimation of the transferred charge. However the formation of the hybrid state corresponds quite nicely to the observed experimental data and the charge transfer stated before [26]. The finding can be rationalized by both the low ionization potential of MnPc and the enhanced electron affinity of F_{16}CoPc. As the states of F_{16}CoPc are lowered in energy the LUMO approaches the Mn $3d_{xz}$ HOMO leading to an orbital splitting allowing us to observe the fundamental interaction behind. Hence one can attribute the synthesized phthalocyanine heterojunction as a route to a rational design of interface induced charge transfer systems based on well-known molecules. Further the studied dimer has, based on the theoretical results, a net spin of $S = 2$ which also might make this arrangement attractive for spintronic applications since spin filter effects could be observable.

To summarize, we have demonstrated that the MnPc/F_{16}CoPc organic hetero-interface is characterized by an interface reaction that causes the formation of hybrid states and charge transfer between the two types of molecules right at the interface. The interaction is due to a local hybrid where the Co $3d_{z^2}$ orbital of F_{16}CoPc and the Mn $3d_{xz}$ orbital of MnPc are involved forming a two-level system.

These results are of importance for the application of such interfaces in organic electronic devices since charge transfer considerably affects the energy level alignment and the transport behavior of the respective heterojunction. Moreover, MnPc and F_{16}CoPc may also be able to form a (bulk) charge transfer salt, purely made from phthalocyanines with potentially novel and unexpected physical properties. Since the transfer of charge is also connected to a transfer of spin and the hybrid system has a net spin of $S = 2$, such compounds could also be termed *spintransfer materials* with future applications in the area of spintronics. Finally, since it is reasonable to assume similar interaction for other flat transition metal complexes, the molecule pair studied in this contribution might be an initial representative of a fascinating incipient material class.

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