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Abstract. In combined photoemission and inverse photoemission spectroscopy studies, we observe changes in the metal phthalocyanine molecular orbital offsets with respect to the conducting gold substrate Fermi level, with the changing d-electron filling of the metal (II) (Co, Ni, Cu) phthalocyanines. The implication is that the interfacial dipole layer depends upon the choice of metal (Co, Ni, Cu) centers within the metal (II) phthalocyanines adsorbed on Au(111).

For many large molecule adlayers, including a number of organic and metal–organic species, the energy level alignment of the adsorbate with respect to a conducting substrate Fermi level or adjacent layer chemical potential is dependent on the interfacial electronic structure and interfacial dipole layer, as has been demonstrated for a number of molecular species [1–3], including the metal (II) phthalocyanines (MPc) [4, 5]. The metal (II) phthalocyanines offer a family of compounds where the d-electron filling of the metal center atom can be systematically altered, without changing the apparent preferential bonding orientation on Au(111) [6, 7]. This persistent orientation with the molecular plane parallel with the substrate for very thin films of adsorbed MPc species [6, 7] is unlike the case for the macrocyclic metal center tetraazaannulenes (TMTAA) [8]. If the interface dipole formation matters, then metal (II) phthalocyanines adsorbed on Au(111) will be expected to show different molecular orbital alignments with different metal substitutions since metal centers have different 3d orbital configurations (Co^{2+} d^7, Ni^{2+} d^8 and Cu^{2+} d^9). In other words, we expect that the interfacial dipole will alter the placement of the molecular orbitals with respect to the substrate Fermi level in a similar manner that electron filling and depletion alters the placement of the molecular orbitals, but not the ordering, of an organic semiconductor [9].

While there are some indications that the 3d transition metal does affect the molecular orbital alignment from scanning tunneling microscopy (STM) studies [6, 7], no systematic combined photoemission and inverse photoemission studies have been undertaken to experimentally elucidate the molecular band offsets for a family of metal (II) phthalocyanines. Such combined photoemission studies are one of the best methods for identifying the affects of initial state electron filling and depletion on an organic semiconductor molecular orbital placement [9] and distinguishing such effects from final state effects like charging and changes in the electron or hole screening in a final state spectroscopy like photoemission [10, 11]. Model theoretical calculations suggest that most of the molecular orbitals, including the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are dominated by the phthalocyanine (Pc) ligands [12–15]. The exception to this overly general statement would be cobalt phthalocyanine (CoPc) where the cobalt $3d_{z^2}$ weighted molecular orbital (with the z-axis defined here to be along the surface normal) is expected to lie less than 1 eV below the highest occupied molecular orbital (HOMO) of the ligand (i.e. no more than 1 eV greater binding energy relative to the HOMO) [6, 16]. For cobalt phthalocyanine (CoPc) the cobalt $3d_{z^2}$ weighted molecular orbital may be responsible for the appearance of the central "bright spot" in scanning tunneling microscopy (STM) images of CoPc [6, 16].
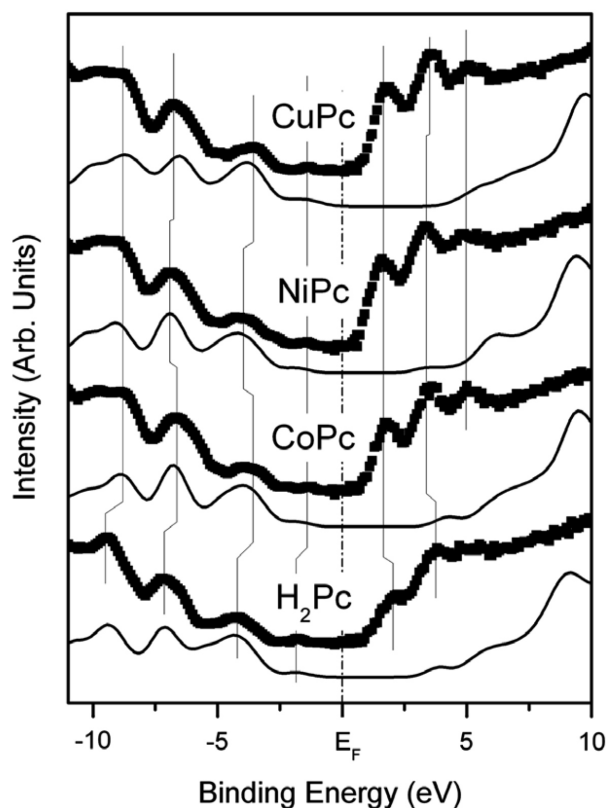
Figure 1. The photoemission and inverse photoemission spectra (thick lines) of molecular multilayer CoPc, NiPc, CuPc and H_2Pc thick films adsorbed on Au(111) substrate at room temperature. Model calculations of the single molecule density of states, using a semi-empirical approach uncorrected for matrix elements and final state effects [3, 5, 8, 9], are shown for comparison as a thin line for each species. Vertical bars roughly indicate the approximate molecular orbital (band) offsets between metal phthalocyanines and H_2Pc.

Combined photoemission and inverse photoemission spectra were taken from different coverage of metal (Co^{2+}, Ni^{2+}, Cu^{2+}) phthalocyanines on Au(111) substrate, nominally from one monolayer to the thicker multilayer films. In the case of thicker molecular films studied, thicknesses far greater than the mean free path of the photoelectrons emitted from the gold substrate by He I radiation (21.2 eV photon energy) were chosen, but still at a film thickness where the molecular plane of the metal phthalocyanine remained largely parallel with the interface. The MPc films were grown on Au(111) substrates by evaporation of the commercially available CoPc, NiPc and CuPc powders, in a preparation chamber vacuum continuous with the ultra-high vacuum (UHV) chamber equipped with both photoemission and inverse photoemission spectroscopies [5, 9, 17, 18]. The clean gold surface was characterized by photoemission and inverse photoemission spectra, and used to establish the substrate Fermi level which is the reference energy for all spectra reported here. The photoemission spectra were taken with a hemispherical electron energy analyzer using He I radiation of 21.2 eV, with the photoelectrons collected along the surface normal. The inverse photoemission spectra were taken in the same UHV chamber using a Geiger–Müller detector with the electrons incident along the surface normal.

The photoemission spectroscopy studies, as predicted by theory, illustrate the very similar electronic structure of the various MPc adsorbed species for thicker molecular films [19–24]. Indeed, the combined occupied and unoccupied electronic structures of metal (Co, Ni, Cu) phthalocyanine "thick" films on Au(111) (Figure 1) from UPS and IPES provide the expected agreement with prior experimental studies and theory [5, 19–24], although there is an observed decrease, compared to our theoretical expectations, in the single molecule HOMO–LUMO gap due to expected solid state effects. Such expected solid state effects include intermolecular interactions [25] that would tend to lead to a decrease in the HOMO–LUMO gap. In spite of the difference in the HOMO–LUMO gap seen in experiment, from the expectations of model ground state calculations, the qualitative agreement with the combined photoemission and inverse photoemission results tend to confirm that most of the observed photoemission features are from the occupied molecular phthalocyanine (Pc) ligand.

There are a number of complications one needs to consider in comparing the adsorbed metal phthalocyanine films on Au(111). There are indications that for thick MPc films, the plane of the molecule tends to tilt up, adopting molecular orientations that are not coplanar with the substrate surface [21], an undesirable molecular orientation (for the purposes of the comparison discussed herein) that we have made every attempt to avoid in our studies here. Furthermore, the actual molecular film thickness may not always be uniform, as in the case of CoPc which exhibits Stranski–Krastanov growth on some substrates [22]. Fortunately, the interfacial dipoles caused by charge transfer between adsorbed metal phthalocyanines (MPc) and the Au(111) substrate have little influence on the spectra of these thicker MPc films as the interface and the immediate interface molecular layers are buried far below from the topmost surface of the thicker molecular films and are thus at distance larger than the photoelectron mean free path: the Au substrate features are not seen to contribute to any of the spectra of Figure 1. Thus the strong similarities seen in comparing the various metal phthalocyanines, are expected for the thicker molecular films.

The comparison of the combined photoemission and inverse photoemission spectra for the non-metal phthalocyanine and the metal (Co^{2+}, Ni^{2+}, Cu^{2+}) phthalocyanine molecular films (Figure 1) indicates that the 3d orbital contributions of the metal centers to the overall molecular spectra lead to either an additional final state screening channel or an initial state decrease in the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap.

Because the model calculations suggest that the 3d orbital contributions of the metal centers to the overall molecular orbitals are far smaller than is in fact observed in Figure 1, we are forced to conclude that 3d orbital contributions to the molecular orbitals affects both the initial and final states in photoemission and inverse photoemission. The transition metal centers of metal phthalocyanines bring an extra 3d orbital interaction with molecular ligand and adjacent adsorbate molecules and provide extra final state screening channels for the photoemission and inverse
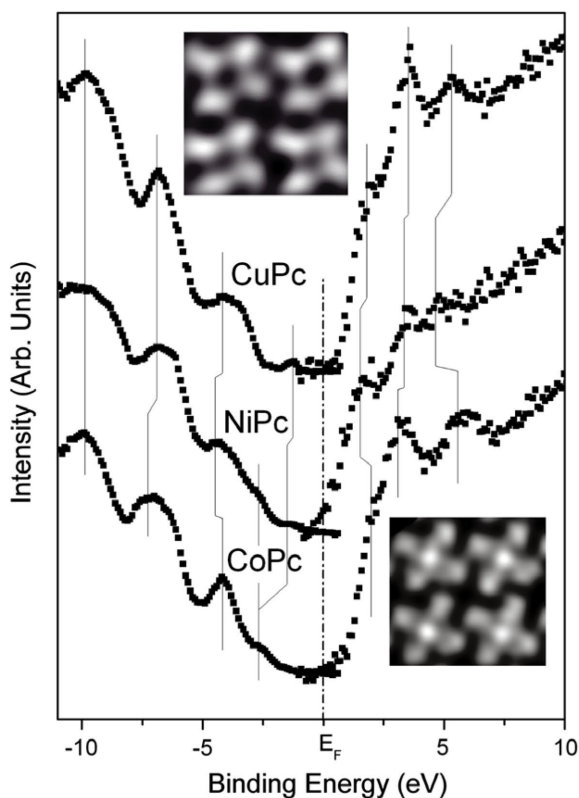
Figure 2. Photoemission and inverse photoemission spectra of CoPc, NiPc and CuPc thin films adsorbed on Au(111) substrate at room temperature. Fermi level is referenced to Au substrate. Molecular orbital offsets among CoPc, NiPc and CuPc are marked by vertical bars. The STM insets for adsorbed CuPc (at top) and CoPc (at bottom) are reproduced from [6], with permission.

Figure 3. A comparison of the molecular chemical potential (HOMO–LUMO gap center) with respect to the Fermi level between the thin and thick MPc films. Filled circles represent the thin films of MPc, empty squares represent thick films.

photoemission processes. The addition of the metal center results in the appearance of a smaller HOMO–LUMO gap for the intra-molecular exited final states [11] than is observed in the photoemission and inverse photoemission from the metal absent center molecule H_2Pc, as seen in Figure 1. A significant displacement of all the molecular orbitals (collectively) for one of the phthalocyanine adsorbate species studied, generally to greater or lesser binding energies, is not observed in these thicker molecular films (Figure 1), so a pure initial state chemical shift is unlikely. Model calculations (both semi-empirical PM3 and DFT) by ourselves (Figure 1) and others indicate that all three species have similar placements of the chemical potential, as prior theoretical calculations also note [12–16]. This is illustrated in Figure 1 where the model single molecule density of states (PM3) for each species has been shifted by some 6.0 eV (a value of about expected work function) to align the calculated orbital energies with photoemission experiments. Thus the similar alignment of molecular orbitals in photoemission and inverse photoemission for the thicker molecular films is as expected.

To study the interfacial electronic structures and interaction between the metal (Co, Ni, Cu) phthalocyanines and the Au(111) substrate, photoemission and inverse photoemission spectra were taken from "thin" molecular films (Figure 2), for a film thickness between 1 and 2 molecular monolayers. For such MPc films, all the molecules lie flat on the Au(111) surface with the molecular ligand copla-
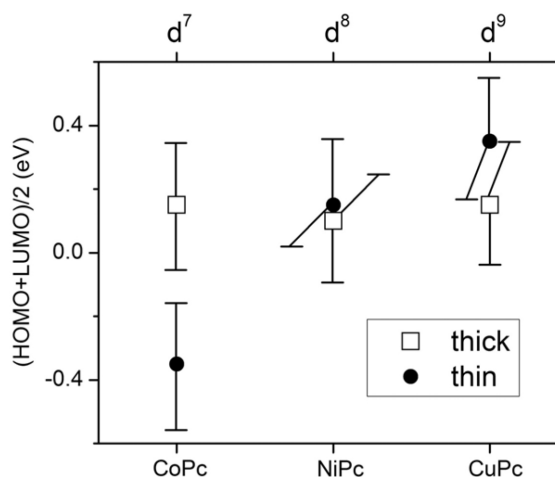
nar with the substrate surface. For these thinner molecular films, the combined photoemission and inverse photoemission spectra generally show different molecular orbital alignments with respect to the substrate Fermi level compared to the thicker films. The molecular orbital alignments with respect to the substrate Fermi level also systematically vary for each metal (Co, Ni, Cu) phthalocyanine according to the 3d metal occupancy. These shifts in the molecular orbital alignments with respect to the substrate Fermi level are indicated by vertical bars in Figure 2. The Fermi level moves towards the lowest partially occupied molecular orbital for CoPc and towards the highest partially occupied molecular orbital for CuPc, while for the thinner NiPc molecular films on Au(111), the molecular orbital features are almost at the same position relative to the substrate Fermi level, as in the spectra of "thicker" NiPc films.

The substrate interactions do not simply alter the molecular orbital alignment relative to the substrate Fermi level, but also affect the placement of the molecular orbitals in other ways, as observed in photoemission and inverse photoemission. The highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap increases up a little for all three metal (Co, Ni, Cu) phthalocyanines, when the molecular films are very thin. This effect is quite large for CoPc and indeed for CoPc, both the highest occupied and lowest lying unoccupied molecular orbitals are strongly perturbed in photoemission and inverse photoemission respectively, as indicated in Figure 2. The strong perturbation of the CoPc molecular orbitals, for the thinner CoPc films on Au(111), supports the contention of Lu *et al* [6] that CoPc is more strongly adsorbed on Au(111) than CuPc.

In Figure 3, we have plotted the center of the experimentally determined adsorbate HOMO–LUMO gap, obtained from the combined photoemission and inverse photoemission studies, with respect to the substrate Fermi level for both thin and thick films. As noted above, the molecular orbital alignment is little different for the three metal (Co, Ni, Cu) phthalocyanines, when the molecular films are rather thick.

In the thinner molecular films, the large shifts in the molecular orbital alignment suggest charge transfer between the CuPc and CoPc adsorbate species and the substrate. In the model of orbital filling and depletion [9], the summary plots of the changes in the molecular orbital alignment for the thinner molecular films in Figure 3 indicate that there is electron charge transfer from Au substrate to CoPc. For CuPc on Au(111), the electron charge transfer is in the opposite direction: from the adsorbate to the substrate. For NiPc, the small shift in the molecular orbital alignment suggests little charge transfer could be observed from the photoemission and inverse photoemission spectra and there is little change in the adsorbate molecular orbital charge occupancy, even for the thinner molecular films on Au(111). In general, such electron filling and depletion of the molecular orbitals of the adsorbate species, as observed here at the Au(111) molecular film interface, results in the formation of different interfacial dipoles. Electron filling tends to move the Fermi level position towards the conduction band edge and electron depletion of the molecular orbitals would tend to move the molecular orbital alignment so that the Fermi level is closer to the valence band edge [9]. Band bending at the interface, as occurs with semiconductors, will be unlikely in these systems because of low charge mobility along the surface normal inside the metal (Co, Ni, Cu) phthalocyanine thin film and because of the short extinction length of the molecular orbital wavefunctions outside each individual molecule [26, 27].

Charge depletion from CuPc would tend to deplete the Cu $3d_z^2$ orbital, through the ligand, and lead to an increase of the orbital binding energy, if the ligand to metal bond strength remains largely preserved (again with the *z*-axis defined along the surface normal). Charge depletion from Cu $3d_z^2$ orbital means that the occupied Cu 3d states will be harder to observe in scanning tunneling microscopy. Because the occupied Cu $3d_{xz}$ and $3d_{yz}$ are not fully symmetric states, i.e. they are elements in the E irreducible representation, not the fully symmetric A_1 irreducible representation in C_{4v}, the tunneling matrix elements will be smaller than expected for the Cu $3d_z^2$ orbital [28–33]. Tunneling matrix elements that apply to scanning tunneling microscopy tend to favor the electron states that are fully symmetric: the A_1 irreducible representation in C_{4v} containing states with s, p_z and d_z^2 contributions. While the highest occupied molecular orbitals of CuPc will be placed closer to the Fermi level at the molecule/Au(111) interface than is the case for either NiPc or CoPc, the Cu $3d_z^2$ and s weighted molecular orbitals, with the large tunneling matrix elements values, remain placed well away from the Fermi level, thus a change in the symmetric state occupancy (A_1 irreducible representation in C_{4v}) will have a profound effect on the how well the Cu metal center atom is imaged. The depletion of the Cu $3d_z^2$ orbital occupancy through the ligand, due to interface bonding, means that the Cu center atom will be harder to image for CuPc adsorbed on Au(111) in scanning tunneling microscopy than the metal center of the other phthalocyanine. While there is difficulty in imaging the metal center for CuPc, the ligand for CuPc should be brighter as is indeed observed [6] and illustrated in Figure 2 as an inset. On the other hand, charge donation to the adsorbed CoPc will tend to be through frontier orbitals of the Au(111) substrate: 6s and $5d_z^2$ with spectral weight located near the Fermi level. Such charge contributions will enhance the Co $3d_z^2$ orbitals which means that tunneling at the metal center position for CoPc is highly likely, if substrate contributions are included for low bias voltages (as occurs with alkali metal adsorption on metal surfaces [34]). This increase in tunneling current at the metal center position for CoPc on Au(111) has also been observed [6], and again illustrated in Figure 2 as an inset.

In conclusion, we have demonstrated that molecular orbital filling and depletion of the adsorbed molecular metal (Co, Ni, Cu) phthalocyanines at the Au(111) interface results in different energy level alignments for metal phthalocyanines with different metal centers that scale with the metal d-filling.

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