Supplementary Online Material

Mixed-valence behavior and strong correlation effects of metal-phthalocyanines adsorbed on metals

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SAMPLE PREPARATION

Co-phthalocyanine (CoPc) and Fe-phthalocyanine (FePc) layers were deposited on a clean Au(111) single-crystal in a ultra-high-vacuum (UHV) system with $1 \times 10^{-10}$ mbar base pressure. The Au(111) surface was prepared by repeated cycles of 1 keV Ar$^+$ sputtering and annealing to 650$^\circ$. CoPc and FePc were evaporated at room temperature from a molecular beam source heated to 600 K, after degassing the 99% pure powder material (Sigma Aldrich) for 24 h in UHV. In-situ scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) were used to monitor the growth of the molecular layers. STM measurements were performed in a cross-like geometry over a distance of ±2 mm from the sample center and LEED was performed over the whole sample surface to check the layer homogeneity. The sample was subsequently transferred into the XMCD end-station without breaking UHV and cooled to $T = 8$ K. Figures S1 and S2 show LEED and STM images of the monolayer CoPc and FePc samples prior to transfer. For the monolayer samples, the actual coverage was adjusted to 0.9 ± 0.1 monolayers to avoid the formation of bilayers. Multilayer samples of CoPc were prepared with thicknesses of 4 layers. This was done in order to preserve the planar orientation of the Pc macrocycles, as the molecules tend to

FIG. 1: (a) LEED image of 1 monolayer CoPc/Au(111) at 14 eV electron energy. (b-c) STM images of the same sample showing details of the surface and molecular layer structure at different scales.

FIG. 2: (a) LEED image of 1 monolayer FePc/Au(111) at 21 eV electron energy. (b) STM image of the same sample.
progressively tilt and eventually stack perpendicularly to the surface at higher coverages. The LEED patterns, typical of Pc layers, demonstrate the formation of ordered molecular superlattices. STM images are consistent with LEED observations, further showing that the molecules are homogeneously distributed over different terraces with a 14.5 Å square unit cell. The Au herringbone reconstruction underneath monolayer CoPc and FePc is still visible by STM as no surface reconstruction occurs due to molecular adsorption.

**XAS AND XMCD MEASUREMENTS**

X-ray absorption spectra (XAS) were measured at the $L_{2,3}$ edges of Co and Fe in the total electron yield mode and normalized by the incident photon flux given by the photocurrent of an Au mesh placed between the last optical element of the beamline and the sample. The footprint of the beam at normal incidence was about $1 \times 0.1$ mm$^2$ at full width half maximum. We used both circularly and linearly polarized light with $99 \pm 1\%$ polarization in magnetic fields of up to $B = \pm 5$ T applied parallel to the incident beam direction, as shown in Fig. S3 (b). Spectra were recorded with circularly polarized light with photon helicity parallel ($I^+$) and antiparallel ($I^-$) to $B$. The XMCD signal is defined as $I^- - I^+$. In order to probe the anisotropy of the molecular adlayers, the sample was rotated by an angle $\theta$ comprised between $0^\circ$ (normal incidence) and $70^\circ$ (grazing incidence). Linearly polarized spectra recorded with $E$ in plane and nearly out-of-plane were recorded by switching the polarization from vertical to horizontal at $\theta = 70^\circ$. The equivalent density of the metal ions contained in 1 monolayer MePc is about 6% of the Au atoms in the topmost (111) layer; this made it necessary to average multiple spectra obtained by switching both light polarization and applied magnetic field in order to obtain a satisfactory signal-to-noise ratio at the Co and Fe edges. No evidence of sample degradation was detected due to beam damage or
residual gas contamination during the experiments.

Linear XAS at the $K$ absorption edge of N was used to further confirm the orientation of the molecules. Strong linear dichroism is observed for mono- and multilayer samples, as expected for planar Pc films, whereas no linear polarization dependence is observed for powder samples (Fig. S4). Linearly polarized $L_{2,3}$ edge Fe and Co spectra of monolayer FePc and CoPc on Au(111) are shown in Fig. S5 as a function of temperature. No strong temperature dependence of the XAS lineshape is observed for both molecules between 8 and 300 K, in agreement with our simulations. Note that, due to the intensity tail of the Au $N$ absorption edges, the Fe and Co XAS features are superimposed onto a strong substrate background intensity. As expected from the reduction of the Debye-Waller factor, the background intensity displays strong oscillations at low temperature due to the extended x-ray absorption fine structure (EXAFS) of the substrate.

FIG. 4: (Color online). (a) N-edge XAS spectra of CoPc powder, multilayer, and monolayer samples. (b) N-edge XAS spectra of FePc powder and monolayer samples.
FIG. 5: (Color online). (a) CoPc and (b) FePc spectra recorded with linearly polarized light at 300 K and 8 K for monolayer films on Au(111). The x-ray electric field vector is either fully in-plane or out-of-plane at an angle of 20° with respect to the surface normal.