



Induced spin polarization of copper spin 1/2 molecular layers

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ABSTRACT

Thin films of the metal organic molecule bis(4-cyano-2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) (or Cu(CNDpm)₂), (C₂₄H₃₆N₂O₄Cu, Cu(II)), deposited on ferromagnetic Co(111) at 40 K, exhibit a finite electron spin polarization. The spin polarization magnitude and sign for Cu(CNDpm)₂ deposited on Co(111) is coverage dependent, but deviates from the mean field expectations for a simple paramagnet on a ferromagnetic substrate. The spin asymmetry is seen to favor select molecular orbitals, consistent with the predicted single molecule density of states. The overlayer polarization observed indicates a strong influence of the ferromagnetic Co(111) substrate and some extra-molecular magnetic coupling.

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1. Introduction

Ferromagnetic substrates can induce magnetic moments in large molecular adsorbates [1–3], as well as small adsorbate species. The induced magnetic ordering in a paramagnetic adsorbate, due to a ferromagnetic substrate, can be roughly described by the Ginzburg–Landau equation [4–6]. This is a mean field “proximity effect”, characterized by an exponential decay of the magnetization with film thickness z as:

$$M(z) = R \bullet \exp(-\kappa z) \quad (1)$$

with a temperature dependent characteristic paramagnetic correlation length κ^{-1} [4–6], related to short range magnetic order. This mean field approximation (Ginzburg–Landau) does not, however, explain the origin of the adsorbate paramagnetic correlation length or the mechanisms (microscopic Hamiltonian) for induced magnetic ordering in molecular adlayers [6]. While there is an increas-

ing body of data that does tend to support ferromagnetic substrate induced magnetic moments for large molecular adsorbates [1–3], the role of magnetic coupling, and the role of the different interfaces remain very open questions.

Unraveling the nature of magnetic coupling in organic layers with induced magnetization, here the organic bis(4-cyano-2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) (or Cu(CNDpm)₂), (C₂₄H₃₆N₂O₄Cu, Cu(II)), is the focus of this Letter. In principle, Cu(CNDpm)₂ is a spin 1/2 system without complications from spin–orbit coupling [7]. The molecule Cu(CNDpm)₂ was shown to have a magnetic moment of $1.05 \pm 0.04 \mu_B$ per molecule and a positive Weiss constant (23 K) was measured indicating weak ferromagnetic exchange between molecules [7]. This occurs in spite of the fact that Cu(CNDpm)₂ molecular films are not metallic, with a relatively large highest occupied to lowest unoccupied molecular orbital gap [7].

Our goal here is to examine, in detail, the spin polarization of the metal organic molecule Cu(CNDpm)₂ deposited on Co(111). Like the metal phthalocyanines adsorbed on ferromagnetic substrates [1,2], thin molecular thin films of Cu(CNDpm)₂ on a ferromagnetic Co(111) substrate will also exhibit spin polarization.

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2. Methods

The synthesis of bis(4-cyano-2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) (or $\text{Cu}(\text{CNDpm})_2$), ($\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_4\text{Cu}$, $\text{Cu}(\text{II})$) was described previously [7,8]. $\text{Cu}(\text{CNDpm})_2$ was isolated as large, blue block crystals (> 1 cm on an edge) that exhibit high thermal stability (> 400 K), reasonable volatilities. For bulk crystals of $\text{Cu}(\text{CNDpm})_2$, the immediate coordination geometry about $\text{Cu}(\text{II})$ is a tetragonally distorted octahedron exhibiting four short Cu–O equatorial bonds and two trans axial Cu–N bonds [7,8]. But this tetragonal structure is not likely adopted with adsorption on $\text{Co}(111)$ [3]. $\text{Cu}(\text{CNDpm})_2$ does adopt a preferential orientation when deposited on the surface of $\text{Cu}(111)$ or $\text{Co}(111)$ that changes as the thickness increases [3].

Molecular thin films of $\text{Cu}(\text{CNDpm})_2$ were adsorbed on epitaxial $\text{Co}(111)$ thin films, freshly grown on $\text{Cu}(111)$. The molecule $\text{Cu}(\text{CNDpm})_2$ was deposited from the vapor as described in prior work [3,7]. The $\text{Cu}(\text{CNDpm})_2$ molecules were deposited on $\text{Co}(111)$ substrates at about 40 K. Adequate $\text{Cu}(\text{CNDpm})_2$ vapor pressure was obtained by subliming the molecule at a temperature of approximately 350 K (80°C). Clean $\text{Cu}(111)$ substrate surfaces were prepared by repeated cycles of Ar^+ ion sputtering and annealing of a Cu single crystal. The epitaxial $\text{Co}(111)$ thin film substrates were grown in situ on a clean $\text{Cu}(111)$ single crystal to a thickness of 20 Å and characterized by low-energy electron diffraction (LEED), photoemission, and spin-polarized photoemission. Typically, epitaxial $\text{Co}(111)$ layers on $\text{Cu}(111)$ possessed 20–40% spin polarization, depending on the incident photon energy and film thickness, consistent with the literature [9–13]. Care was taken to avoid photodecomposition of the molecular film during photoemission experiments, as studied in detail and described elsewhere [14].

Spin polarized angle resolved photoemission spectra were acquired at the U5UA undulator spherical grating monochromator (SGM) beamline at the National Synchrotron Light Source (NSLS) [15–17]. Linearly polarized light from an undulator source was monochromatized using a spherical grating monochromator (SGM) operating in the range 20 to 150 eV. The ultra-high-vacuum photoemission end station was equipped with a commercial angle-resolved hemispherical electron energy analyzer (EA125, Omicron GmbH) and a post electron energy analyzer Mott detector for spin polarization analysis [15–17]. The spin polarization P for the collected data was determined according to

$$P = \frac{1}{2} \frac{\sqrt{I_L^+ I_R^-} - \sqrt{I_L^- I_R^+}}{\sqrt{I_L^+ I_R^-} + \sqrt{I_L^- I_R^+}} \quad (2)$$

where I_L and I_R represent the number of electrons scattered into the left and right channels of the Mott detector, respectively. Spin minority and spin majority spectra are thus taken simultaneously. To eliminate instrumental asymmetry, it was necessary to measure the sample magnetized “up” (I_L^+ , I_R^+) and the sample magnetized “down” (I_L^- , I_R^-), although the spectra themselves were taken at remanence. Spin polarization was calculated using a Sherman function of $S = 0.15$. The analyzer has a $\pm 2^\circ$ angular resolution, while the combined energy resolution of the analyzer and the light source was approximately 150 meV or less. The photoemission spectra were taken at 45° light incidence angle, with the photoelectrons collected normal to the surface, unless indicated otherwise. Throughout this Letter, all binding energies are referenced to the substrate Fermi level, and angles are defined with respect to the substrate surface normal. In general, the spectra were taken at photon energies in the region of 49–50 eV, so secondary background subtraction from the spectra was not necessary and the spectra shown are as taken.

3. Spin asymmetry

Spin polarized photoemission spectroscopy of adsorbed $\text{Cu}(\text{CNDpm})_2$ molecular thin films deposited on epitaxial $\text{Co}(111)$ at 40 K are shown in Fig. 1 (blue and red lines represent spin majority and minority states, respectively). We found spin asymmetries 40% near the Fermi edge in the 3d band of the clean $\text{Co}(111)$ substrate, as reported for Co [9–13]. The cobalt 3d bands exhibit an exchange splitting near the Fermi edge (Fig. 1(a)) of about 1 eV consistent with the literature [12–16]. $\text{Cu}(\text{CNDpm})_2$ deposited on clean $\text{Co}(111)$ at 40 K leads to a decrease in the observed spin majority polarization near the Fermi edge, in spin polarized photoemission spectroscopy, at one molecular monolayer (ML) coverage (Fig. 1(b)), followed by an increase in the spin minority polarization with increasing molecular film coverages (Fig. 1(c)).

At ten molecular monolayers, there is no spectral density from the $\text{Co}(111)$ substrate in our photoemission spectra (Fig. 1(c)), as noted in more detail elsewhere [3]. Thus the observed spin polarization is the result of induced polarization in the $\text{Cu}(\text{CNDpm})_2$ molecular adlayer. Substrate contributions to the observed spin asymmetry observed in the photoemission from monomolecular films cannot be excluded by any means, and indeed are a likely contribution to the thinner molecular films due to the finite electron mean free path. The increase in the spin minority population, with molecular adsorption occurs at somewhat higher binding energies corresponding to the higher occupied molecular orbitals of $\text{Cu}(\text{CNDpm})_2$, as seen in Fig. 1, and is assigned to the photoemission features resulting from the $\text{Cu}(\text{CNDpm})_2$ molecular orbitals.

Calculations for a single $\text{Cu}(\text{CNDpm})_2$ molecule predict an inherent spin polarization for specific molecular orbitals, as indicated in Fig. 1(d). These model calculations of the density of states are based on a simplistic semi-empirical method for determin-

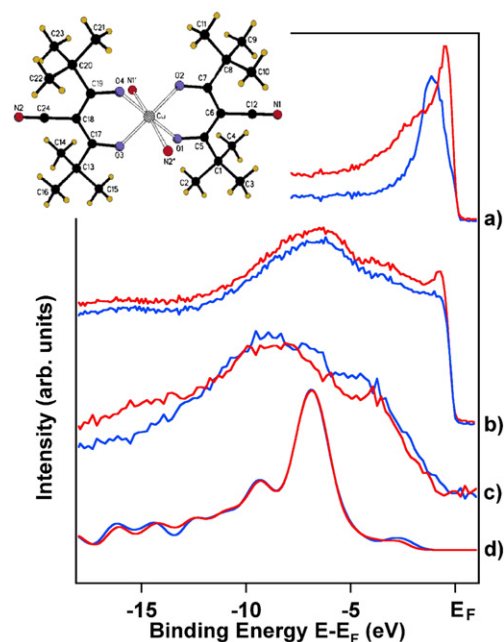


Fig. 1. The spin polarization photoemission spectra of epitaxial $\text{Co}(111)$ and $\text{Cu}(\text{CNDpm})_2$ molecular layers on $\text{Co}(111)$ at 40 K: spin majority is indicated by red, spin minority by blue. The spin polarized photoemission spectrum of 20 Å of epitaxial $\text{Co}(111)$ on $\text{Cu}(111)$, taken at ~ 40 K and a photon energy of 49 eV, is shown (a) to indicate the substrate polarization. One monolayer of molecular $\text{Cu}(\text{CNDpm})_2$ on $\text{Co}(111)$ (b), and 10 monolayers of molecular $\text{Cu}(\text{CNDpm})_2$ on $\text{Co}(111)$ (c) both show differences in the spin polarized photoemission. The photon energy used in spectra (a) and (c) was 49 eV, and the photon energy used in spectrum (b) was 41.5 eV. Photons were incident on the sample at 45° with the photoelectrons collected at normal emission. For comparison, the single molecule model density of states calculations is shown in (d). The inset is a schematic of the $\text{Cu}(\text{CNDpm})_2$ molecule.

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