Supporting Information

Spin Crossover in a Cobalt Complex on Ag(111)

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Experimental details

Synthesis The ligand \((\text{H}_2\text{B}(\text{pz})(\text{pypz}))\) and the Co(II) complex \([\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz})))_2]\) were synthesized according to the procedure reported by Ossinger et al.\(^1\)

Experimental Details The Ag(111) substrate was prepared by cycles of \(\text{Ar}^+\) sputtering (1.5 keV) and annealing to 500°C. \([\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz})))_2]\) molecules were sublimated from a heated crucible (\(\approx 150°C\)) onto the substrate at \(\approx 30°C\). STM tips were electrochemically etched from W wire and annealing in \textit{vacuo}. All measurements were carried out in ultrahigh vacuum with a STM cooled to \(\approx 4.6 \text{ K}\). The XPS setup consist of a regular X-ray source with Al anode source with an x-ray power of 200 W (15 kV) and a hemispherical electron analyser (SPECS PHOIBOS 150). The x-ray source and the analyzer have a fixed angle of 90°. Infrared (IR) spectra were recorded with a Bruker ALPHA-P ATR IR Spectrometer.

Theoretical Details Gas phase calculations were carried out with the ORCA software package.\(^2\)\(^3\) The crystallographic structure of \([\text{Fe}((\text{H}_2\text{B}(\text{pz})(\text{pypz})))_2]\) (polymorph II) was used as a starting point.\(^4\) Geometry optimizations were performed with ORCA at the B3LYP\(^5\)\(^\text{–}\)7/def2SVP\(^8\)\(^\text{–}\)9 level with the D3BJ dispersion correction,\(^10\)\(^11\) the RIJCOSX approximation, fine numerical integration grids (grid4 and gridX4 in ORCA nomenclature), and the CG solver. The orbitals and their energy were calculated with ORCA at the B3LYP/def2-QZVP\(^8\)\(^\text{–}\)9 level with the RIJCOSX approximation.

One-electron process

Figure 1 shows that the switching rate evolves linearly with the magnitude of the tunneling current. This evolution suggests that the switching mechanism involves a single tunneling electron and motivates the definition of a switching yield as the probability of an electron to induce a transition.

![Figure 1: Switching rates from L to H and H to L as a function of the tunneling current at a sample voltage of \(-1.1\text{ V}\) (green crosses). The solid lines are linear fits of the data with slopes of \(a \approx -0.37\) and \(b \approx -0.89 \text{ pA}^{-1}\text{s}^{-1}\). The error margins indicate three standard deviations assuming Poisson statistics.](image)
Switching at $V < 0$

Figure 2 displays proposed mechanisms for the transitions between LS and HS at negative sample voltages. Starting from the high-spin, $S = \frac{3}{2}$ state (upper panel), an $\alpha$-spin electron is first removed from the occupied orbital providing the best coupling to the tip; i.e., $d_{z^2}$. Subsequently a $\beta$-spin electron is added to $L^*$. As a result, the spin of the complex is changed to $S = \frac{1}{2}$. Spin-allowed relaxation to the LS state completes the spin switching process. In the low-spin, $S = \frac{1}{2}$ state at negative sample bias, the $d_{x^2-y^2}$ orbital is not occupied and the occupied $d_{z^2}$ state is ineffective because it is oriented parallel to the surface. Therefore, the electron is most likely withdrawn from the $d_{x^2}$ or $d_{y^2}$ orbitals, generating a $S = 1$ state. Next, an $\alpha$-spin electron is transferred to $L^*$. This generates an excited $S = \frac{3}{2}$ configuration, which relaxes to the HS ground state by a (spin-allowed) transition.

$S = \frac{3}{2}, \text{HS}$

$S = \frac{1}{2}$

$S = \frac{1}{2}, \text{LS}$

$S = 1$

$S = \frac{3}{2}, \text{HS}$

Chemical analysis of sublimated Co complexes

To further ascertain the intactness of the molecules after sublimation, we performed complementary x-ray photoelectron spectroscopy of $\approx 1...3$ monolayers (MLs) of [Co((H$_2$B(pz)(pypz))]$_2$ sublimated onto Ag(111) prepared in situ. Overview spectra acquired at room temperature are shown in Figure 3 for three different thicknesses. The peaks are assigned to their respective core-levels. The relative intensities of the Co $2p_{1/2,3/2}$, N 1s and C 1s peaks are comparable for the three spectra, indicating similar chemical compositions for 1, 2
The atomic fractions of the 3 MLs sample are evaluated with CasaXPS by comparing the weighted spectral areas after a Tougaard-type background subtraction and are compared to the expected atomic fractions of the molecule. The experimentally determined fractions (Figure 3), with associated uncertainties of a few percents, are very close to the ones expected for the Co complex suggesting that the molecules withstand adsorption on the Ag(111) surface.

XPS measurements performed at 100 K (3 ML thick sample) shows no evolution of the Co $2p_{1/2,3/2}$ edges (upper-left inset to Figure 3), suggesting the absence of thermal spin transition. Temperature is therefore expected to have no significant direct influence on the spin-crossover properties of the Co tetramers in direct contact with Ag(111).

![XPS spectra](image)

Figure 3: XPS spectra of ≈ 1 (blue), 2 (red) and 3 MLs (gray) $[\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz}))_2)]$ on Ag(111) measured using an Al K$_\alpha$ x-ray source. Two spectra at Co $2p_{1/2,3/2}$ edges of ≈ 3 ML $[\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz}))_2)]$ on Ag(111) taken at room temperature (gray) and 100 K (red) are shown in the upper-left inset. The upper-right inset is a zoom over binding energies ranging from 200 to −5 eV (3 MLs coverage). All spectra are normalized to the intensity of the C 1s peak. Spectra of 1 and 2 MLs were acquired with 1 eV energy steps and a pass energy of 80 eV, while the spectrum of 3 ML was measured with energy steps of 0.25 eV and a pass energy of 44 eV. The thicknesses have been estimated with a quartz microbalance.

**Infrared spectroscopy**

Figure 4 shows IR spectra recorded on $[\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz}))_2)]$ powder and on a film upon sublimation. Both systems exhibit the same vibration modes. The stability of the Co complex during sublimation is confirmed by the combination of XPS and IR data. The former indicate that the elements are present in the correct stoichiometry after sublimation while the latter show that the bonds between the constituents are preserved.
**LS–HS Transitions: Calculated orbital scheme**

In the main text and in the previous paragraph, the current induced transitions between the LS and HS states are discussed using a generic model of the $d$-orbitals. Figures 5 and 6 present more realistic, calculated orbitals of $\left[\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz})))_2\right]$. The molecular $z$-axes in the LS and HS states turn out to be different.

![Figures 5 and 6: Calculated spin-resolved orbitals of $\left[\text{Co}((\text{H}_2\text{B}(\text{pz})(\text{pypz})))_2\right]$ in the HS state. L denotes ligand orbitals displayed in gray. Co $d$-orbitals are shown in black.](image)

In the HS state, the molecular $z$-axis connects the central pyrazole moieties. This axis is also perpendicular to the substrate surface according to the model geometry of the tetramers. Here, both $d_{z^2}$ and $d_{x^2-y^2}$ orbitals along with the three $t_{2g}$ orbitals at lower energy are occupied with $\alpha$-spin electrons while two of the $t_{2g}$ orbitals are occupied with $\beta$-spin-electrons.

In the LS state, the molecular $z$-axis is directed along one of the pyridine-terminal pyrazole axes (Fig-
Irrespective of the re-orientation of the z-axis, the basic features of the model proposed in the main text and in Figure 2 remain valid. Specifically, the highest-energy, unoccupied $d_{x^2-y^2}$ orbital of the LS has a lobe perpendicular to the surface and thus effectively mediates electron transfer between the tip, the complex molecule and the surface, similar to the role of the $d_{z^2}$ orbital of the HS state. Likewise, the $d_{z^2}$ orbital of the LS state has lobes essentially parallel to the surface and thus poorly mediates electron transfer, in analogy to the $d_{x^2-y^2}$ orbital of the HS state. Regarding the $t_{2g}$ orbitals of the LS state, the correspondence to the orbitals of the HS state is obtained using the relations $d_{xy} \rightarrow d_{y'z'}$, $d_{xz} \rightarrow d_{x'z'}$ and $d_{yz} \rightarrow d_{x'y'}$. While the first of these orbitals is parallel to the surface and thus ineffective for electron transport, the latter two can mediate electron transfer, albeit less effectively than $d_{z^2}$ and $d_{x^2-y^2}$ in the HS and LS states, respectively.

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