Vacuum-Evaporable Spin-Crossover Complexes in Direct Contact with a Solid Surface: Bismuth versus Gold

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ABSTRACT: To investigate the ability for spin-state switching of spin-crossover (SCO) complexes adsorbed to solid substrates, the SCO complex [Fe(H₂B(pz)₂)₂(phenme₄)] (pz = pyrazole, phenme₄ = 3,4,7,8-tetramethyl-1,10-phenanthroline) is prepared. The new complex is investigated by magnetic susceptibility measurements and Mößbauer spectroscopy in the solid state and by temperature-dependent UV/vis spectroscopy in a thin film deposited by physical vapor deposition (PVD) on quartz glass. Thermal- and light-induced SCO is observed in the bulk and the film on glass. Submonolayers of this complex obtained by PVD are studied by temperature-dependent near-edge X-ray absorption fine structure (NEXAFS) on Au(111) as well as Bi(111) and by scanning tunneling microscopy (STM) on Au(111). NEXAFS shows thermal- and light-induced spin-state switching of the complex on Bi(111), however, with a large temperature-independent high-spin fraction (∼50%). On the other hand, combined evidence from NEXAFS and STM indicates that on Au(111) the complex dissociates into [Fe(H₂B(pz)₂)₂] and phenme₄. Similar observations are made with the parent complex [Fe(H₂B(pz)₂)₂(phen)], which on Bi(111) stays intact and exhibits thermal-induced as well as light-induced SCO, but on Au(111) dissociates into [Fe(H₂B(pz)₂)₂] and phen.

INTRODUCTION

Spin-crossover (SCO) compounds of 3d⁴−3d⁷ transition metals can be switched between two spin states and are promising building blocks for applications in spintronics, sensors, and data storage.¹⁻¹⁰ The preparation of high-quality molecular films of these compounds on a surface by physical vapor deposition (PVD) allows the control of thickness and morphology and can be fully integrated into thin-film deposition techniques.¹¹⁻¹⁶ A prominent class of vacuum-evaporable SCO complexes are the compounds [Fe(H₂B-(pz)₂)₂(L)] (pz = pyrazole, L = 2,2’-bipyridine (bipy) or 1,10-phenanthroline (phen)).⁹⁻¹⁴,¹⁷⁻²² Their iron(II) centers are coordinated by two monoanionic H₂B(pz)₂ ligands and a neutral coligand (phen or bipy). The transition from the paramagnetic (S = 2) high-spin (HS) state to the diamagnetic (S = 0) low-spin (LS) state can be induced by temperature, pressure, or light. Thermal- and light-induced spin-state switching in films of SCO complexes has been monitored by ultraviolet photoelectron spectroscopy, inverse photoemission, and X-ray absorption spectroscopy (XAS) as well as scanning tunneling microscopy (STM).⁹⁻³⁰ In the course of these investigations it became evident that in direct contact with a Au(111) surface the complex [Fe(H₂B(pz)₂)₂(phen)] (1) undergoes fragmentation to [Fe(H₂B(pz)₂)₂] and 1,10-phenanthroline.³¹ Keeping the gold substrate at elevated temperatures, however, it was observed that ordered monolayers of intact molecules of 1 are formed which can be spin-switched by electron-induced excited spin-state trapping (ELIESST).³² Nevertheless, in less dense regions of these layers phenanthroline molecules from decomposed 1 were still visible.³¹

Replacing the gold substrate by highly oriented pyrolytic graphite (HOPG), no decomposition of [Fe(H₂B-(pz)₂)₂(phen)] (1) was found and thermal-induced as well as
light-induced spin-state switching of a submonolayer of 1 was detected. This raises the question of whether the decomposition of this complex observed on Au(111) can also be suppressed by deposition on, e.g., bismuth. Possibly this substrate would also enable thermal- or light-induced spin crossover in mono- or submonolayers, which so far has not been achieved for monolayers of 1 and the related complex [Fe(H2B(pz)2)2(bipy)] on Au(111). In fact, the lack of switching of molecules deposited on Au(111) has in some cases been remedied by deposition on Bi(111) or Bi(110). Bismuth is a semimetal with a low density of states at the Fermi level, thus reducing van der Waals interactions with aromatic substrates in direct contact with the surface. With regard to the complex [Fe(H2B(pz)2)2(phen)] (1), this could also reduce the interaction between phenanthroline and the solid surface and thus prevent the decomposition of 1.

A second possible strategy of reducing the interaction between complex 1 and a solid surface is the attachment of substituents to the ligand 1,10-phenanthroline. [Fe(H2B(pz)2)2(L)] complexes with methylated 1,10-phenanthroline, annulated 2,2′-bipyridine, diarylethene, or π-radical ligands have been reported. In order to evaluate this approach in the present context, we have prepared the new radical ligands have been reported. In order to evaluate this approach in the present context, we have prepared the new spin-crossover complex [Fe(H2B(pz)2)2(phenme4)] (2) (Figure 1), in which phen is replaced by 3,4,7,8-tetramethyl-1,10-phenanthroline (phenme4). Herein, the spin-crossover behavior of 2 is first determined in the bulk by temperature-dependent susceptibility measurements and Mößbauer spectroscopy. Moreover, thin films of 2 are prepared by physical vapor deposition on glass and studied by optical absorption spectroscopy. Finally, submonolayers of 2 are deposited on the two substrates, Au(111) and Bi(111), and studied by temperature-dependent near-edge X-ray absorption fine structure (NEXAFS) as well as low-temperature STM. The results are compared to similar data obtained with the parent compound 1 deposited on Au(111) and Bi(111) and provide insight into the structural and electronic properties of submonolayers of this class of SCO complexes in direct contact with solid surfaces.

![Figure 1](image1.png)

**Figure 1.** $\chi_M T$ vs $T$ curves of crystalline 2 between 2 and 300 K. The curves resulting from cooling (black symbols) and heating (green symbols) the sample almost coincide. The temperature-induced SCO is fitted by a Boltzmann equation (red line) to obtain $T_{1/2}$. Inset: Molecular structure of 2.

Results and Discussion

The synthesis and the physicochemical properties of the complex [Fe(H2B(pz)2)2(phen)] (1) in the bulk as well as in thin films deposited on Au(111) and HOPG have been reported before. In analogy to the synthesis of 1, a microcrystalline powder of [Fe(H2B(pz)2)2(phenme4)] (2) was obtained with methanol as solvent, starting from iron(II) triflate as precursor. To analyze the thermal spin crossover of 2 in the solid state, magnetic susceptibility measurements were performed (Figure 1).

The new complex shows a gradual spin transition with $X_M T$ values ranging from 3.56 cm$^3$ K mol$^{-1}$ at 300 K to 0.27 cm$^3$ K mol$^{-1}$ at 5 K; the spin transition temperature $T_{1/2}$ is 141 K. This behavior is similar to other analogues of 1.

To obtain further information on the spin state of the iron center, Mößbauer spectra were recorded at 298 and 80 K (Figure 2). At 298 K compound 2 shows a doublet with $\delta_{HS} = 1.00$ mm/s and $\Delta E_Q = 1.74$ mm/s, indicative of high-spin iron(II) centers. At 80 K one doublet at $\delta = 0.51$ mm/s and $\Delta E_Q = 0.43$ mm/s is observed, indicating a low-spin iron(II) species. Mößbauer spectra were also recorded at 141 and 151 K to determine the HS/LS ratio around the spin transition temperature; the results agree with the magnetic susceptibility measurements (see Supporting Information, Figures S1 and S2).

Compound 2 can be evaporated at $T = 175 \degree C$, $p = 3 \times 10^{-2}$ mbar, or at 163 ℃ in an ultrahigh vacuum ($\sim 10^{-8}$ Pa). Differential thermoanalysis along with thermogravimetry (DTA/TG) shows that complex 2 is stable up to about 200 ℃, where decomposition starts to take place (see Supporting Information, Figure S3). The structural integrity of the complex in the vacuum-deposited films is, e.g., evident from the fact that infrared spectra of the film are found to be very similar to those recorded from microcrystalline material. In particular, the symmetric and antisymmetric B–H vibrations are detected both in the bulk material and in the film at $\nu_{sym}(B–H) = 2389$ cm$^{-1}$ and $\nu_{asym}(B–H) = 2285$ cm$^{-1}$, which indicates the integrity of the coordination sphere (Figure 3). Furthermore, elemental analysis of evaporated material shows no major
changes compared to the bulk material, and, most importantly, the thermal spin-crossover properties of the complex are retained.

For a film of compound 2, the metal-to-ligand charge transfer (MLCT) bands at 298 K evolve to a more intense double-band pattern centered at 539 and 600 nm at 78 K (Figure 4).

Similar observations have been made for analogous complexes, indicating thermal spin crossover from HS to LS. Moreover, the vacuum-deposited film of 2 exhibits the light-induced excited spin-state trapping (LIESST) effect; i.e., at 5 K the low-spin state can be converted back to the high-spin state by irradiation at 519 nm for 5 min (Figure 5a). In Figure 5b, the high-spin fraction \( \gamma_{HS} \) derived from the intensity of the MLCT band is displayed versus the temperature. The thermal transition is more gradual than in the bulk (cf. Figure 1), presumably due to weaker cooperative interactions in the vacuum-deposited film. The thermal spin transition temperature \( T_{1/2} \) is 148 K, slightly higher than in the bulk (see above), and the critical temperature for the HS-to-LS relaxation is \( T_c = 54 \) K.

**XA Spectroscopy in Submonolayers.** In order to investigate the physicochemical properties of the new complex 2 in direct contact with a solid surface, it was deposited on Bi(111) and Au(111) with coverages of 0.3 and 0.6 ML, respectively (ML = monolayer). The results are compared to 0.3 ML of the parent complex 1 on Bi(111). To probe the spin states, Fe L\(_3\) edge XA spectra (Figure 6a,b) were recorded at the magic angle between the substrate normal and the electric field vector of the X-rays (at the magic angle, 54.7°, the X-ray absorption is independent of the polarization direction of the beam). On Bi(111), the room-temperature XA spectra at the Fe L\(_3\) edge exhibit two main peaks at 708.1 and 708.8 eV and two broad satellite peaks centered at ~706.5 and ~710.9 eV, as shown in Figure 6a (red line). The spectral shape changes gradually as the temperature is decreased to 60 K, marked by a gradual decrease of the peak intensity at 708.1 eV, the emergence and subsequent intensity increase of a peak at 709.3 eV, and a slight energy shift (accompanied by a relative intensity increase) of the satellite peak from ~710.9 to ~711.5 eV. This is characteristic of SCO complexes undergoing a thermal spin transition. The observed Fe L\(_3\) spectral shape at room temperature (RT) indicates a dominant HS state, and the emergence and gradual intensity increase of the peak at 709.3 eV with decreasing temperature reflect the conversion of the HS to the LS state. Details of the decomposition into HS and LS spectral components are shown in the Supporting Information. Upon further lowering the temperature from 60 K at a rate of 4 K/min, however, the LS species gradually switches back to the HS species, increasing with each successive measurement. This is due to soft X-ray induced excited spin state trapping (SOXIESST). Similar Fe L\(_3\) XA edge spectra are observed for 0.3 ML of the parent complex 1 on the same Bi(111) surface (Figure 6c). The spectrum at 300 K exhibits the characteristic HS shape with the main peaks at 708.1 and 708.8 eV. Upon lowering the temperature, the intensity of the spectrum changes gradually as the temperature is decreased to 60 K, marked by a gradual decrease of the peak intensity at 708.1 eV, the emergence and subsequent intensity increase of a peak at 709.3 eV, and a slight energy shift (accompanied by a relative intensity increase) of the satellite peak from ~710.9 to ~711.5 eV. This is characteristic of SCO complexes undergoing a thermal spin transition. The observed Fe L\(_3\) spectral shape at room temperature (RT) indicates a dominant HS state, and the emergence and gradual intensity increase of the peak at 709.3 eV with decreasing temperature reflect the conversion of the HS to the LS state. 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HS peaks is reduced and the intensity of the peak at 709.3 eV characteristic of the LS state increases. At 5 K, X-ray induced back switching from LS to HS occurs.

For 0.6 ML of $\text{Fe(H}_2\text{B(pz)}_2\text{)}_2(\text{phenme}_4)$ on Au(111), in contrast, the Fe L$_3$ edge XA spectrum exhibits no such change in the spectral shape with temperature. Figure 6b shows the Fe L$_3$ edge XA spectra at 300 K (red line) and at 40 K (blue line). Here, the spectra are characterized from 300 K down to low temperature by a single peak at 708.1 eV without an apparent multiplet structure. This is an indication of the loss of SCO behavior, possibly due to fragmentation of the molecule. In fact, N K edge XA spectra and STM measurements show that [Fe($\text{H}_2\text{B(pz)}_2\text{)}_2(\text{phenme}_4)$] (2) dissociates into phenme$_4$ and the tetrahedral complex [Fe($\text{H}_2\text{B(pz)}_2\text{)}_2\text{]}$] (see below). Similar results had been obtained earlier for 0.8 ML of complex 1 deposited on Au(111): the Fe L$_3$ edge XA spectrum is characterized by a single peak at 708.1 eV with no apparent multiplet structure, and the spectral shape is independent of temperature from 300 K down to 5 K. The loss of SCO behavior has been confirmed as being due to the dissociation of 1 into [Fe($\text{H}_2\text{B(pz)}_2\text{)}_2\text{]}$] and phen on Au(111), with SQUID, XAS, and STM measurements. The SQUID measurement of bulk material of [Fe($\text{H}_2\text{B(pz)}_2\text{)}_2\text{]}$] shows that it is in HS state from 300 K down to 25 K, in agreement with its tetrahedral geometry. For 1.3 ML of [Fe($\text{H}_2\text{B(pz)}_2\text{)}_2\text{]}$] on Au(111), the Fe L$_3$ edge XA spectrum consists of a single peak at 708.1 eV at 300 K, similar to that of 0.6 ML of 2 on Au(111), while the distinguishing feature between 0.6 ML of 2 and 1.3 ML of [Fe($\text{H}_2\text{B(pz)}_2\text{)}_2\text{]}$] on Au(111) in the N K edge XA spectrum can be seen in the presence or absence of the $\pi^*$ resonance at 399.1 eV, respectively.

It can thus be concluded that the functionalization of the phenanthroline ligand with four methyl groups does not help to preserve the integrity of the complex on Au(111). On the other hand, both complexes 1 and 2 remain intact on Bi(111), as also indicated by the angle-dependent N K edge XA data (see below). Moreover, both exhibit qualitatively similar thermal SCO behavior, as can be inferred from the temperature-dependent Fe L$_3$ edge XA spectral shape (Figure 6a,c). More quantitative information on this issue is obtained from a determination of the high-spin fraction $\gamma_{\text{HS}}$ as a function of temperature. Owing to the similar temperature-dependent Fe L$_3$ edge XA spectra of 1 and 2, and the data of 1 on HOPG, the latter can be used as a reference for the pure HS and LS spectra (1 exhibits 91(5)% HS at 300 K and 100% LS at 6 K on this substrate). To determine the high-spin fractions $\gamma_{\text{HS}}$ of 1 and 2 on Bi(111) at different temperatures, these reference spectra are linearly combined (see Supporting Information). For the parent complex 1 on Bi(111) (Figure 7a, red dots), the HS fraction at 300 K is estimated as 88(5)% decreasing to 46(5)% at 71 K. At lower temperatures, the HS fraction increases gradually due to the SOXIESST effect, rising to about 60(5)% HS at 5 K (cf. Figure 6c, olive line). The increase in the

Figure 6. (a) Fe L$_3$ edge XA spectra of 0.3 ML of $\text{2 on Bi(111)}$ at 300 K (red line), at 70 K (blue line), and at 37 K (olive line), indicating the SCO behavior, and (b) Fe L$_3$ edge XA spectra of 0.6 ML of $\text{2 on Au(111)}$ at 300 K (red line) and at 40 K (blue line), indicating the loss of SCO behavior. (c) Fe L$_3$ edge XA spectra of 0.3 ML of $\text{1 on Bi(111)}$ at 300 K (red line), at 70 K (blue line), and at 5 K (olive line), indicating the SCO behavior. All spectra are recorded at the magic angle.

Figure 7. Temperature dependence of the high-spin fraction $\gamma_{\text{HS}}$ of (a) 0.3 ML of $\text{1 on Bi(111)}$ (red dots) and (b) 0.3 ML of $\text{2 on Bi(111)}$ (blue dots). The black lines are the fits obtained from the van’t Hoff equation [eq 1].

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HS fraction with increasing exposure time of the sample to the X-ray beam is in part due to the fact that the XA spectra are measured successively at the same spot during the cooling process. For complex 2, on the other hand, the HS fraction at 300 K is estimated as 95(5)%, decreasing to 51(5)% at 68 K before the onset of SOXIESST (Figure 7b, blue dots). The temperature dependence of the high-spin fractions ($\gamma_{\text{HS}}$) of 1 and 2 can be described with a modified van’t Hoff equation, taking the partial nature of the spin switching process into account:

$$\gamma_{\text{HS}}(T) = a + (1 - a)(e^{\Delta H/RT - \Delta S/R} + 1)^{-1}$$

Here, constant $a$ corresponds to the fraction of molecules trapped in the HS state at all temperatures, $\Delta H$ and $\Delta S$ are enthalpy and entropy differences between HS and LS states, respectively, and $R$ is the universal gas constant. From the fit of the experimental data between 300 and 70(60) K, respectively, $\Delta H$ is estimated as 4.6(1) and 5.1(1) kJ mol$^{-1}$, and $\Delta S$ as 26.3(6) and 34.6(8) J K$^{-1}$ mol$^{-1}$, for 1 and 2, respectively. The temperature-independent high-spin fraction $a$ amounts to 46(5)% for 1 and 51(5)% for 2.

Complex 2 exhibits pronounced X-ray and light-induced spin-state switching from the LS to the HS state, as shown for LIESST in Figure 8a (see Figure S2 of the Supporting Information for SOXIESST). Illumination at 17 K for <1 min with a wavelength of 520 nm under a photon flux of 2.5(1) × 10$^{17}$ photons/s/cm$^2$ increases the high-spin fraction of complex 2 from 48(5)% to 94(5)%; upon further illumination the population remains constant. From an exponential fit, the time constant for the light-induced switching process under these conditions is estimated as 2.1(1) s. It should be noted that the spectra were recorded on a virgin position of the sample that had not been exposed to X-rays before in order to start with minimum SOXIESST. There is, however, a contribution to the switching process by X-rays, as is shown in the Supporting Information.

Although no time-dependent measurements have been performed for 1 under illumination, clear evidence for the LIESST effect is obtained for this molecule deposited on Bi(111) as well. Figure 8b shows XA spectra at the Fe L$_3$ edge for the pristine sample at 5 K (red line) and after 7 min illumination (blue line) with a wavelength of 520 nm under a photon flux of 4.0(8) × 10$^{16}$ photons/s/cm$^2$. At 5 K in the pristine state, $\gamma_{\text{HS}}$ is determined as 48(5)%; after 7 min illumination, it increases to 80(5)%.

To obtain information on the adsorption geometries of 1 and 2 on Bi(111) and Au(111) and to estimate molecular orientations of these molecules and their possible decomposition products on the two surfaces, angle-dependent XA spectra at the N K edge were measured at 300 K. Three incidence angles between the electric field vector of the X-rays and the surface normal were employed, i.e., $\theta = 90^\circ$, 54.7° (magic angle), and 25°. The resulting spectra are presented in Figure 9, parts a and b, for complex 2 on Au(111) and Bi(111), respectively, and in Figure 9c for complex 1 on Bi(111). The
\(\pi^*\) resonance at 399.2 eV stems from the two N atoms of the phenme4 ligand, and the shoulder at 400.6 eV and the peak at 401.4 eV are \(\pi^*\) resonances from N atoms of the \(H_2B(pz)_2\) ligands.\(^{31}\) From the XA intensity ratio between spectra taken at 25 and 90° incidence angles, the molecular orientation of the respective orbitals on the surface can be determined.\(^{48}\) Accordingly, the phenme4 ligands are found to lie flat on the Au(111) surface for complex 2 on Au(111) (Figure 9a), indicating a disintegration of this complex. From the peak intensity at 401.4 eV, the delocalized orbitals of the \(H_2B(pz)_2\) ligands are estimated to lie at \(\sim 51(5)^°\) with respect to the substrate normal, which is close to the magic angle of 54.7°. This could also be due to a random orientation of the pyrazole units of the two \(H_2B(pz)_2\) ligands on the surface.

These findings, including the spectral shape of both the N K edge and Fe L\(_2\) edge spectra, are similar to the results of previous studies obtained on 0.8 ML of complex 1 on Au(111).\(^{31}\) Thus, it can be concluded from XA spectroscopy that the addition of four methyl groups to the ligand 1,10-phenanthroline does not prevent fragmentation of \([Fe(H_2B(pz)_2)_2]\) (see XA Spectroscopy in Submonolayers). In our model, the two topographic maxima correspond to protruding pyrazole groups of \([Fe(H_2B(pz)_2)_2]\). The drastic height difference between the upper part of these groups and the rest of the molecule (calculated value by density functional theory (DFT), 0.38 nm) is expected to largely dominate the image contrast. Therefore, a geometric interpretation of the STM topograph is a useful approximation.

The gas-phase structures of the single \([Fe(H_2B(pz)_2)_2]\) and phenme4 molecules as calculated with DFT are shown in Figure 10a. They are arranged to a bimolecular cluster which is overlaid onto the STM image in Figure 10b. We find good agreement of the separation between the maxima in the STM topograph of 0.63 ± 0.02 nm and the calculated distance of the pyrazole groups of 0.64 nm. To further test the model, we performed DREIDING force-field calculations that mimic the interaction between the \([Fe(H_2B(pz)_2)_2]\) and phenme4 molecules in the gas phase (Figure 10b,c). The calculated distance between phenme4 and the more remote \([Fe(H_2B(pz)_2)_2]\) group is 1.15 nm. It is consistent with the measured STM data of 1.17 ± 0.06 nm. According to the calculations, the observed arrangement of \([Fe(H_2B(pz)_2)_2]\) and phenme4 is stabilized by several hydrogen bonds, namely three B–H → N(phen) and two C(pyrazole)–H → N bonds. This may explain the experimental observation that most of the \([Fe(H_2B(pz)_2)_2]\) and phenme4 molecules arrange into bimolecular clusters with a specific geometry on Au(111). The separation of phenme4 and the iron center of \([Fe(H_2B(pz)_2)_2]\) (≈0.86 nm) is significantly larger than expected for a coordinative bond. In fact, we did not observe structures that indicate the presence of the undistorted compound 2.

Figure 10 (a, b) Constant-current topographs of \([Fe(H_2B(pz)_2)_2(phenme4)]\) 2 prepared on Au(111) at ambient temperature. The overview image in (a) shows two typical patterns. The first pattern (example marked by solid circle) consists of two high protrusions and a shallow bean-shaped elevation at one end. It is attributed to tetrahedral \([Fe(H_2B(pz)_2)_2]\) adjacent to a single phenme4. The second pattern (dashed circle) is comprised of two symmetrically arranged bean-shaped features. By analogy with earlier observations,\(^{31}\) we identify it as being due to phenme4 dimers. (c) Top and side views of the calculated structure of \([Fe(H_2B(pz)_2)_2]\) and phenme4, interacting in the gas phase. Two characteristic dimensions are indicated. The calculated structure is superimposed onto the STM image in (b).
The complex \([\text{Fe}(\text{H}_2\text{B(pz)}_2)_2(\text{phen})]\) (1) is known to decay on Au(111) into the four-coordinate complex \([\text{Fe}(\text{H}_2\text{B(pz)}_2)_2]\) and phen. To suppress this reaction, two approaches have been pursued in the present paper. The first one aims at reducing the molecule–substrate interaction by introducing a ligand which presumably is less weakly bound to the metal surface. The second approach involves using Bi(111) as a substrate because Bi is known to lower the strength of the dispersion interaction with aromatic molecules relative to gold. The new complex 2 is found to be suitable for vacuum deposition to obtain molecular layers. Combined evidence from NEXAFS and STM, however, indicates that in a submonolayer deposited on Au(111) at room temperature this molecule dissociates into a four-coordinate complex, \([\text{Fe}(\text{H}_2\text{B(pz)}_2)_2]\), and phen. This finding is similar to the result of previous studies of the parent molecule \([\text{Fe}(\text{H}_2\text{B(pz)}_2)_2(\text{phen})]\) (1).\(^\text{31}\) Apparently the introduction of four methyl groups cannot suppress the decay of this type of SCO complexes on Au(111). In contrast, temperature-dependent NEXAFS measurements of a submonolayer of 2 deposited on Bi(111) indicate thermal-, light-, and X-ray-induced spin-state switching processes. Specifically, we find light-induced spin-state switching at 17 K. Below 60 K, excitation to the high-spin state is further mediated by the SOXIESST effect, which is in agreement with other examples reported.

Similar results are obtained for the parent complex \([\text{Fe}(\text{H}_2\text{B(pz)}_2)_2(\text{phen})]\) (1) deposited on Bi(111). These observations thus indicate that complexes 1 and 2 stay intact on Bi(111), rendering this substrate a useful alternative to Au(111) in cases where the strong van der Waals interactions mediated by the Au(111) surface lead to a disintegration of functional molecules. In contrast to the behavior of 1 on HOPG, however, where \(\gamma_{\text{HS}}\) can be switched between 0 and almost 100\%,\(^\text{32}\) only about half of the molecules of 1 and 2 on Bi(111) undergo a spin transition whereas the others remain in the HS state. The suppression of the spin transition may be ascribed to differences in the adsorption geometry leading to a variation in the interaction with the Bi(111) surface. Alternatively, the differences in SCO behavior could be due to lateral interactions between the molecules in the two-dimensional layer which may mediate elastic forces similar to the behavior of SCO complexes observed in some bulk materials.\(^\text{33}\) In fact, a mixture of HS and LS molecules was found for a submonolayer of \([\text{Fe}(3,5-(\text{CH}_3)_2\text{pz})_2\text{BH}_3]\) on Au(111) in which at 4.6 K HS and LS molecules are both present and form an ordered superstructure.\(^\text{15}\) Since we do not have any information about the morphology on Bi(111), we also cannot exclude the possibility that the molecules form clusters or multilayer islands, and that the non-switching fraction is the molecules that are in direct contact with the surface. Understanding the exact conditions for spin-state switching of transition-metal complexes on solid surfaces and elucidating possible factors that influence or limit the switchability of these molecules on surfaces thus remain challenging problems in the area of spintronics.

**EXPERIMENTAL SECTION**

All reactions were carried out in dry solvents and under inert atmosphere. Functionalized 3,4,7,8-tetramethyl-1,10-phenanthroline, iron(II) triflate, and solvents were purchased commercially and used as supplied. Potassium dihydrobis-(pyrazolyl)borate \(\text{K[H}_2\text{B(pz)}_2]\) and complex 1 were prepared according to literature methods.\(^\text{17,51}\)

**Synthesis of [Fe(H\(_2\)B(pz)\(_2\))(3,4,7,8-tetramethyl-1,10-phenanthroline)] (2).** To a solution of Fe(OTf)\(_2\) (354 mg, 1 mmol) in methanol (5 mL) was added a solution of \(\text{K[H}_2\text{B(pz)}_2]\) (372 mg, 2 mmol) in methanol (5 mL); a slightly yellow solution was obtained. A solution of 3,4,7,8-tetramethyl-1,10-phenanthroline (236 mg, 1 mmol) in methanol (10 mL) was added dropwise to the \([\text{Fe}(\text{H}_2\text{B(pz)}_2)_2]\) solution. Immediately, a purple precipitate was formed, filtered off after 1 h, washed with methanol (2 × 5 mL), and dried under reduced pressure. Yield: 429 mg (0.73 mmol, 73\%). Elemental analysis calculated for C, 57.38\%; H, 5.54\%; N, 23.90\%; found: C, 57.19\%; H, 5.49\%; N, 23.87\%. Elemental analysis after physical vapor deposition (T = 175 °C, \(p = 3 \times 10^{-2}\) mbar) calculated for 2: C, 57.38\%; H, 5.54\%; N, 23.90\%; found: C, 57.17\%; H, 5.86\%; N, 23.89\%.

**XA Spectroscopy.** The samples, i.e., 0.3 ML of 1 and 2 on Bi(111) and 0.6 ML of 2 on Au(111), were prepared by evaporating the molecular powder from a tantalum Knudsen cell at about 436 K onto the substrate held at RT. The evaporation rate and hence the amount of molecules deposited on the surface were monitored by a quartz microbalance. The molecular coverage was further estimated from the absolute Fe \(L_1\) edge resonance intensity, using the procedure described elsewhere.\(^\text{31}\) One monolayer is defined as having an areal density of 0.82 Fe ion/nm\(^2\), the same as in ref 31. The substrates were cleaned by the standard procedure of repeated sputtering with Ar\(^+\) ions, followed by annealing at 900 K for Au(111) and 300 K for Bi(111) substrates. The XAS measurements were carried out in situ at a base pressure of 5 × 10\(^{-10}\) mbar at the beamline UE56/2-PGM-2 for complex 2, and for complex 1 at the beamline UE46-PGM1 of BESSY II with a base pressure of 5 × 10\(^{-11}\) mbar. The photon flux at the sample position was \(\approx 10^{13}\) photons s\(^{-1}\) cm\(^{-2}\) with the energy resolution at \(\approx 200\) meV for the former, and the photon flux of \(\approx 10^{11}\) photons s\(^{-1}\) cm\(^{-2}\) and the energy resolution at \(\approx 150\) meV for the latter beamline. To probe the thermal SCO behavior and the stability of the molecule, Fe \(L_1\) edge and N K edge XA spectra were recorded at the magic angle of 54.7° as well as at 25 and 90° between the surface normal and the electric field vector of the linearly polarized X-rays. The spectra at 25 and 90° were used for the determination of the molecular orientation. The mode of illuminations used to induce the LIIESST effect has been described elsewhere.\(^\text{31}\) XA was measured by the total electron yield mode, where the sample drain current is recorded as a function of photon energy. The XA spectra were normalized with respect to a gold grid.
upstream to the experiment and to the background signal from clean Au(111) and Bi(111) substrates.

**Scanning Tunneling Measurements.** STM measurements were performed with a homemade STM operated at 4.5 K and in ultrahigh vacuum with a base pressure of 10⁻⁹ Pa. Au(111) surfaces and chemically etched W tips were cleaned by repeated Ar⁺ bombardment and annealing. The apexes of the tips were covered with Au by repeatedly indenting the tip into the Au(111) surface. [Fe(H₂B(pz)₂)₂(phenme₄)] molecules were deposited onto Au(111) at ambient temperature from a heated Ta crucible. The pressure during depositions was 10⁻⁸ Pa. To get submonolayer coverages, the deposition rate was calibrated with the help of a quartz balance and the deposition time was adjusted. The submonolayer coverages were verified by STM images. All images were acquired in the constant-current mode of the STM with the voltage applied to the sample.

**DFT and DREIDING Force Field Calculations.** DFT calculations were performed for isolated phenme₄ with B3LYP/6-311G(d,p) and for [Fe(H₂B(pz)₂)₂] with TPSSH/TZVP as implemented in the Gaussian 09 software package. DREIDING force-field calculations were performed to model the interaction between phenme₄ and [Fe(H₂B(pz)₂)₂] in the gas phase. The DFT geometry of [Fe(H₂B(pz)₂)₂] was kept frozen during the force-field relaxation, because the structure of [Fe(H₂B(pz)₂)₂] is not well described by the DREIDING force fields due to the spin state of the molecule. Furthermore, to model the influence of the surface in the gas phase calculations, the orientation of phenme₄ relative to [Fe(H₂B(pz)₂)₂] was confined parallel to the plane shown in the top view of Figure 10c.

**Other Measurements.** Elemental analyses were performed using a Euro Vector CHNS-O-element analyzer (Euro EA 3000). Samples were burned in sealed tin containers by a stream of oxygen. IR spectra were recorded on a Bruker Alpha-P ATR-IR spectrometer. Magnetic measurements were performed with a temperature circle from 300 K to 2 K to calibrated with the help of a quartz balance and the deposition time was adjusted. The submonolayer coverages were verified by STM images. All images were acquired in the constant-current mode of the STM with the voltage applied to the sample.

K, X-ray-induced spin-state switching plot of 1 on Bi(111) at 5 K, and that of 2 on Bi(111) at 17 K, STM image of 1 for low coverage (PDF)

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