Influence of Substrate Electronic Properties on the Integrity and Functionality of an Adsorbed Fe(II) Spin-Crossover Compound

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Abstract

The bistability of spin-crossover complexes on surfaces is of great interest for potential applications. Using x-ray absorption spectroscopy, we investigated the properties of $[\text{Fe}(\text{pypyr}(\text{CF}_3)_2)_2(\text{phen})]$ (pypyr = 2-(2'-pyridyl)pyrrolide, phen = 1,10-phenanthroline), a vacuum-evaporable Fe(II) complex, in direct contact to a set of substrates. The electronic properties of these substrates range from metallic to semiconducting. While dissociation is observed on metal surfaces, efficient light-induced switching is realized on semimetallic and semiconducting surfaces. This indicates that the density of states of the substrate at the Fermi level plays a role for the integrity and functionality of the adsorbed compound. In an intermediate case, namely $[\text{Fe}(\text{pypyr}(\text{CF}_3)_2)_2(\text{phen})]$ on graphene/Ni(111), functional and dissociated species are found to coexist. This result indicates that some previous studies may deserve to be reconsidered because the possibility of coexisting intact and fragmented spin-crossover complexes was neglected.

TOC Graphic

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Introduction

The conformation and spin-state bistability of spin-crossover (SCO) compounds make them attractive for applications^{1–6}. In that respect, considerable efforts were made to realize thin films of SCO complexes using physical vapor deposition^{2–4,7–24}. These films usually exhibit decent SCO properties. However, the direct contact to a substrate may change the properties of the SCO complexes. The interaction with metal surfaces can lead to complexes trapped in the high-spin (HS) and/or in low-spin (LS) state^{12,13,17,25–27} or to the fragmentation of the SCO complexes despite their integrity in the gas phase^{28–31}. In contrast, absence of spin-state locking and efficient spin switching was evidenced for SCO complexes on highly ordered pyrolytic graphite (HOPG)^{24,32–35} or for SCO molecules decoupled from the metal surface by a thin insulating layer^{10,25,36}. Considering all these possible outcomes, it appears essential to determine the influence of the substrate properties on the integrity and SCO behavior of the adsorbed SCO complexes, ideally for a single SCO compound.

Here, using x-ray absorption spectroscopy (XAS) spectroscopy, we investigate sub-monolayer coverages of $[\text{Fe}(\text{pypyr}(\text{CF}_3)_2)_2(\text{phen})]$ (pypyr = 2-(2'-pyridyl)pyrrolide, phen = 1,10-phenanthroline) (Fe-pypyr) on Co/Cu(100), Au(111), graphene/Ni(111), HOPG, WSe_2 and HfS_2 . The electronic properties of these substrates range from metallic to semiconducting. While the complexes are found dissociated on metals, (light-induced) spin transitions are observed on semiconducting substrates. An intermediate scenario is found for Fe-pypyr on graphene/Ni(111), where dissociated molecules coexist with fully functional complexes. We demonstrate that this case can easily be misinterpreted as a coexistence of functional and spin-state locked molecules. Furthermore, we show that erroneous conclusions may be drawn if the quality of the sample is not reliably determined by XAS at the Fe $L_{2,3}$ edges.

Experimental Methods

Sample Preparation

Clean and flat Au(111), Ni(111) and Cu(100) surfaces were prepared by several cycles of Ar sputtering (1.2 – 2 keV) and subsequent annealing (500 – 550 °C). For the preparation of graphene/Ni(111), a similar procedure as in Ref. 37 was used. After the last Ar sputtering cycle, the Ni(111) crystal was annealed to 650 °C for 30 s. The temperature was then decreased to 570 °C. After 5 min, a partial pressure of 1×10^{-6} mbar of ethylene gas was introduced in the chamber for 7 min. For the Co/Cu(100) samples, 6 ML Co were deposited by electron bombardment of a Co rod on Cu(100) held at room temperature. $2H\text{-WSe}_2$ and $1T\text{-HfS}_2$ are composed of covalently bonded chalcogen-metal-chalcogen sandwich layers with weak van-der-Waals like forces between these triple layers. Atomically flat and chemi-

cally saturated surfaces were obtained by scotch-tape cleaving the crystals along the basal plane at a pressure below 10^{-7} mbar. The HOPG crystal was cleaved *ex situ* followed by annealing under UHV conditions to 600 °C for one hour³⁸. Fe-pypyr was synthesized as described in Ref. 20. The Fe-pypyr complexes were sublimed in ultrahigh vacuum (base pressure of 10^{-9} mbar) from a Knudsen cell heated to 170 °C onto samples held at room temperature. The determination of the film thickness is described in the Supporting Information ((SI) section 1).

X-ray Absorption Spectroscopy

The XAS measurements were performed at the X-Treme beamline³⁹ at the Swiss Light Source (Paul Scherrer Institute, Switzerland) in total electron yield (TEY) mode. The TEY was normalized to the photocurrent of an upstream gold mesh. A defocused beam with a photon flux estimate of 3×10^{10} photons/s (upstream of the gold mesh) and a spot size of $0.3 \times 1.3 \text{ mm}^2$ at the front end was employed. With these parameters and constant beamline conditions, we did not observe any evolution of the XA spectra during hours of measurements on the same sample spot, indicating the absence of photo-induced fragmentation of the Fe-pypyr complex. All XA spectra were recorded at an angle of 60° between the sample normal and the circularly polarized x-rays of both helicities. All spectra, if not otherwise stated, were acquired with a magnetic field of 50 mT in the direction of the beam to increase the signal-to-noise ratio. The spectra are averaged over 2 to 16 single measurements, low-pass filtered and polynomial backgrounds have been removed. Examples of raw data are shown in the SI (section 2). For the LIESST experiments, the spots of five 532 nm, 1 mW lasers were brought to coincidence on the sample.

Results and Discussion

Two electronic configurations of the central Fe^{2+} cation can be realized for SCO complexes, depending on the strength of the octahedral ligand field (Fig. 1a). For a strong ligand field, the six d electrons of the Fe center occupy the t_{2g} set of orbitals leading to a total spin $S = 0$. This state is referred to as the low-spin (LS) state. In contrast, in the high-spin (HS) state, the ligand field is weaker such that both e_g and t_{2g} orbitals are partially filled, combining to a total spin $S = 2$ (Fig. 1a). For the present study, Fe-pypyr (Fig. 1b) is employed. As shown previously²⁰, this compound is suitable for physical vapor deposition. Thin films of this complex on $1T\text{-TiTe}_2$ undergo light-induced spin-state trapping (LIESST) and soft x-ray-induced excited spin-state trapping (SOXIESST) for temperatures below 100 K (Ref. 20). Because the spin-transition temperature of Fe-pypyr is relatively high ($T_{1/2} = 390 \text{ K}$ for powder samples), mostly LS-to-HS transitions induced

by 532 nm laser light for temperatures below 100 K are considered throughout the manuscript.

Figure 1: (a) Simplified electronic configuration of the Fe^{2+} cation of Fe-pypyr. Two configurations leading to two spin states may be realized depending on the strength of the ligand field. (b) Molecular model of Fe-pypyr. (c) XA spectra acquired on 5 ML Fe-pypyr on Au(111) at 3 K under illumination with a 532 nm laser (red curve) and at 120 K (blue curve). These are used as HS and LS reference spectra, respectively. The lower spectrum (black curve) was measured on 0.4 ML Fe-pypyr on Au(111) at 100 K.

XAS at the Fe $L_{3,2}$ absorption edges is particularly suitable to probe the spin state averaged over an ensemble of molecules^{12,16,17,19,20,22–25,30,32–34,40–44}. Indeed, the fine structure and energy of the Fe $L_{3,2}$ edges sensitively depend on the occupation and the ligand field of the Fe d orbitals. This leads to characteristic and distinct x-ray absorption (XA) spectra for the HS and LS states. The fraction of HS molecules in a given sample can be extracted from the corresponding XA spectrum at the Fe $L_{3,2}$ edges using a linear combination of the HS and LS reference spectra (SI section 3) as previously reported^{12,16,17,19,20,22–25,30,32–34,42,44}.

Figure 1c shows XA spectra measured at 3 K under illumination and at 120 K on 5 ML Fe-pypyr on Au(111). These spectra exhibit the characteristic features expected for HS and LS Fe(II), respectively²⁰. In the following, these spectra are used as references for the HS and LS states, and the HS fractions are determined on the basis of these reference spectra. Thereby, it is assumed (as usual; see, *e.g.*, Ref. 33) that the spin transition from LS to HS is complete in the HS reference. Reducing the film thickness to 0.4 ML to reach the sub-ML regime leads to considerable changes (black curve in Fig. 1c). The XA spectrum has a broad L_3

edge centered at 706.7 eV. It is neither similar to the HS nor to the LS reference spectrum. No variation in the XA spectra is observed as the temperature is varied (SI section 4), which is indicative of the absence of SCO behavior. Furthermore, the spectrum is similar to that of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2]$ complex, obtained upon dissociation of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2\text{phen}]$ compound on Au(111) (Ref. 28). Moreover, low-temperature scanning tunneling microscopy measurements of Fe-pypyr deposited on Au(111) reveal phenanthroline ligands on the surface along with fragments compatible with the formula $[\text{Fe}(\text{pypyr}(\text{CF}_3)_2)]^+$ (SI section 5). Therefore, as will be further justified below, the black spectrum in Fig. 1c is representative of that of fragmented Fe-pypyr molecules.

Considering that the molecules withstand the sublimation process, as evident from the measurements on thicker films, the fragmentation process is most probably caused by the interaction between the molecules and the substrate. A similar behavior has been observed for other SCO compounds on Au(111)^{28,30,31} with exceptions^{27,45}. Resorting to less metallic surfaces, on the other hand, has shown to promote the integrity of the molecules along with improved switching properties relative to metallic substrates^{25,30,33,36}. We employed graphene on Ni(111) as a substrate because it can combine two aspects. First, a graphene layer can electronically decouple⁴⁶ the Fe-pypyr molecules from the metallic Ni substrate. Second, the ferromagnetism of the Ni(111) layer can potentially magnetically couple to the moment of the HS Fe-pypyr molecules as observed for different systems^{47–52}, which may be of relevance for molecular spintronics.

Fig. 2a shows XA spectra acquired on 0.4 ML Fe-pypyr on graphene/Ni(111) at different temperatures. Significant variations of the $L_{3,2}$ edges are observed as the temperature is changed, indicating SCO behavior. Assuming that all molecules are intact, the fraction of molecules in the HS state evolves between 50 and 100 % as the temperature is varied (gray triangles in Fig. 2b). This would imply that 50 % of the molecules are trapped in the HS state.

While locked spin states in sub-ML coverages have been demonstrated by STM measurements^{17,26,27}, an alternative interpretation of the XAS data presented here is possible and actually favored. A better agreement to the XAS data is found when a fraction of the molecules (30 %) is considered as dissociated. Fig. 2c shows XA spectra acquired on 0.4 ML Fe-pypyr/graphene/Ni(111) at 10 K under illumination and at 150 K (green curves). Although the XA spectra can be reasonably well reproduced by a superposition of LS and HS reference spectra (red curves), there are notable deviations, especially at 706.7 eV. In contrast, much less deviation is observed (solid black curves) when a fraction of molecules are considered dissociated. Actually, as significantly better fits are obtained at any temperature when a constant fraction of dissociated molecules is considered (SI section 6), we

conclude that a fraction of complexes are fragmented on graphene/Ni(111). The corrected HS fraction as a function of temperature, evaluated by excluding the contribution from fragmented molecules, ranges from 0 % to 75 % (dark symbols in Fig. 2b). In other words, when taking into account that a fraction of molecules is dissociated, no complex with a locked spin state has to be postulated.

As will be shown below, the evolution of the corrected HS fraction, *i.e.*, the HS fraction of the functional molecules, on graphene/Ni(111) matches that obtained on other substrates for sub-ML coverages of Fe-pypyr. This independently lends support to the claim that some Fe-pypyr molecules are fragmented on graphene/Ni(111). Further independent evidence of dissociation comes from the XMCD data. Indeed, small variations are observed in the fine structure of the XMCD spectra acquired on 0.4 ML Fe-pypyr/graphene/Ni(111) (bottom left gray spectrum in Fig. 2d) compared to that of 5 ML Fe-pypyr/Au(111) (dashed black curve in Fig. 2d) at 10 K under a magnetic field of 6.5 T (Fig. 2d). This suggests that the XMCD spectra measured on 0.4 ML Fe-pypyr/graphene/Ni(111) do not solely originate from HS Fe-pypyr but most probably contain contributions from (magnetic) fragments. We note that LS Fe-pypyr molecules, owing to their zero magnetic moment ($S = 0$), do not contribute to the XMCD signal.

Considering all the points above, we estimate that approximately 30 % of the Fe-pypyr molecules are dissociated on graphene/Ni(111). As it remains uncertain whether the dissociated molecules are in direct contact to the Ni(111) surface or reside on the graphene layer (presumably at defects), further experiments were performed. Magnetic ions in the vicinity of ferromagnetic layers usually magnetically couple to the substrate^{29,48,49,51,52}, such that the XMCD spectra remain non-zero as the magnetic field is reduced to approximately 0 T. This is for instance the case for (fragmented) Fe-pypyr molecules on Co/Cu(100) as shown in the SI (section 7). However, the XMCD signal of 0.4 ML Fe-pypyr on graphene/Ni(111) is essentially zero when the magnetic field is lowered to 0.1 T (bottom right gray spectrum in Fig. 2d). Therefore, the dissociated Fe complexes are magnetically decoupled from the Ni(111) substrate and most probably lie on the graphene layer. We speculate that the fragmentation of Fe-pypyr molecules is induced by defect⁵³ in the graphene layer with increased reactivity. For completeness, we note that the XA spectra of fragmented molecules on different substrates are similar (SI section 8) and can be modeled by multiplet calculations (SI section 5).

So far, the possibility of coexisting intact and fragmented SCO complexes on surfaces has been neglected. In turn, the distinction between complexes trapped in a given spin state and dissociated molecules is not always evident (Fig. 2c), especially when the signal-to-noise ratio of the data is low. Therefore, previous investigations, solely based on XAS data, reporting spin-state

Figure 2: XA data measured on 0.4 ML Fe-pypyr/graphene/Ni(111). (a) XA spectra at 10 K under illumination (red) and 150 K (blue) along with XA spectra measured at intermediate temperatures under illumination with 532 nm laser light. (b) Fraction of HS molecules as a function of temperature evaluated considering all molecules (triangles) or only intact molecules (disks), *i.e.*, evaluated with Eqs. 4 and 5 of the SI, respectively. The uncertainties in the HS fraction inferred from the fits are below 0.5 %. (c) Comparison of fits to the XA spectra acquired at 10 K under illumination (left) and at 150 K (right). While the red curves are bare linear combinations of HS and LS reference spectra, the black curves further include contributions from the dissociated molecules (SI section 6). The dashed black lines show the contribution of fragmented molecules to the spectra. (d) XMCD measurements performed at 6.5 T (left) and at 0.1 T (right). The orange and green curves are XA spectra acquired with different photon helicities. Their difference leads to the XMCD spectra (gray). For comparison, the XMCD spectrum obtained on 5 ML Au(111) is overlaid (dashed black curve).

trapping may deserve reinterpretation. Furthermore, the purity of the compounds and the preparation conditions, which XAS at the Fe edges is not sensitive to, are of importance for the interpretation of the data. For instance, we show in the SI (section 9) that a different behavior is observed for 0.2 ML Fe-pypyr on Au(111), prepared with insufficient degassing of the crucible. Assuming that all the molecules are intact, the data would suggest that a large fraction (50 %) of the molecules is trapped in the HS state while the other molecules exhibit SCO behavior, in apparent contradiction to the XA spectrum (black curve) shown in Fig. 1c. However, a careful analysis of the spectra (SI section 9) leads to a different interpretation: a fraction of the molecules is in direct contact to Au(111) and dissociated. The remaining molecules are adsorbed on a contaminant layer on Au(111) and are therefore decoupled from the substrate, in turn leading to SCO. In the light of these observations, it appears challenging to prove SCO of molecules in direct contact to metal surfaces with XAS measurements alone when a fraction of the molecules are in a locked spin state and/or fragmented.

Next we employed HOPG as a substrate. Bernien *et al.* demonstrated the complete transition of SCO molecules in direct contact with HOPG³³. To the best of our knowledge, HOPG is the only substrate reported so far where complete SCO is observed for sub-ML coverages of molecules. Fig. 3 shows the evolution of the HS fraction for 0.4 ML Fe-pypyr on HOPG from 0 to 95 %. We speculate that the fraction of switched molecules at low temperatures may reach 100 % at increased 532 nm laser-light irradiance. The fraction of dissociated molecules is estimated to 2 %, much less than the 30 % found for Fe-pypyr on graphene/Ni(111). These measurements indicate that HOPG preserves the integrity and functionality of SCO complexes in direct contact to the substrate, in agreement with previous studies^{24,32–34}. In particular, the SCO properties of Fe-pypyr are better preserved on HOPG than on graphene/Ni(111) or Au(111).

Ossinger *et al.* mentioned that reducing the density of states at the Fermi level of the substrate could reduce the van-der-Waals interaction between the SCO complex and the surface and thus prevent the decomposition of the adsorbed complex³⁰. This suggestion was tested for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phen})]$ (phen = 1,10-phenanthroline) deposited on metallic Au(111) and semimetallic Bi(111) surfaces. While only fragments of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phen})]$ complex were found on the metal, a partial SCO transition was observed on the semimetal³⁰. Here, a similar behavior was monitored for Fe-pypyr on Au(111) (metallic) and HOPG (semimetallic). In the following, we employ WSe₂ and HfS₂ as substrates to further decrease the density of states at the Fermi level. These are semiconducting layered transition-metal dichalcogenide materials with indirect band gaps of 1.2 eV and 2.85 eV, respectively^{54,55}.

The fraction of HS molecules as a function of temperature of 0.4 ML Fe-pypyr on WSe₂ and HfS₂ evolves

Figure 3: Evolution of the fraction of HS molecules as a function of temperature for 0.4 ML Fe-pypyr on different substrates and 5 ML Fe-pypyr on Au(111) as a reference. The samples were constantly illuminated with 532 nm laser light. Some of the corresponding XA spectra are shown in the SI (section 3). Note that contributions from the dissociated molecules have been removed, *i.e.*, the HS fraction is evaluated using Eq. 5 (SI section 6). The uncertainties in the HS fraction inferred from the fits are below 0.6 %.

from 0 to 80 % (blue and red symbols in Fig. 3). Note that approximately 5 % of the Fe-pypyr complexes were found dissociated on these substrates. A quantitative comparison between the different curves in Fig. 3 is not possible, since illumination was performed with several 532 nm lasers, which systematically required a readjustment after sample transfer. The irradiance most probably slightly varies from sample to sample, which in turn may influence the magnitude of the LIESST effect. Thus, the differences observed in the HS fraction of Fe-pypyr on the different substrates (Fig. 3) may either originate from different irradiances or from a (limited) influence of the surface on the LIESST process. Nonetheless, Fig. 3 shows that, within the experimental uncertainties, similar SCO performances are observed for Fe-pypyr on HOPG, WSe₂ and HfS₂. Therefore, this study reveals that WSe₂ and HfS₂ are adequate substrates for efficient SCO, *i.e.*, spin transition without spin-state coexistence, similar to HOPG and Cu₂N substrates.

Conclusion

In conclusion, we investigated sub-ML coverages of Fe-pypyr on different substrates with distinct electronic properties. Efficient light-induced spin switching is observed on semimetallic HOPG and semiconducting substrates (WSe₂ and HfS₂). However, Fe-pypyr dissociates in direct contact to metallic substrates (Au(111) and Co/Cu(100)). This agrees with a previous suggestion³⁰ that reducing the density of states of the substrate at the Fermi level is favorable for the integrity and functionality of deposited SCO compounds. Furthermore, a thorough analysis of an intermediate

case (Fe-pypyr on graphene/Ni(111)) shows that dissociated molecules may easily be confused with complexes trapped in a given spin state. The experimental distinction between the two possibilities is of significant importance for accurate estimation of the robustness and SCO efficiency of complexes on surfaces, which in turn are ingredients for the design of new robust spin-crossover complexes.

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Supporting Information Available: Additional information is available about molecular coverage estimation, examples of raw data, determination of the HS fraction, additional spectra of Fe-pypyr fragments on Au(111), identification of the Fe-pypyr fragments on Au(111) with low temperature scanning tunneling microscopy and multiplet calculations, distinction between coexistence of dissociated and functional molecules and spin-state coexistence, data of Fe-pypyr on Co/Cu(100), comparison of dissociated molecules on different substrates and peculiar results of 0.2 ML Fe-pypyr on Au(111) prepared under inappropriate conditions. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Supporting Information:

Influence of Substrate Electronic Properties on the Integrity and Functionality of an Adsorbed Fe(II) Spin-Crossover Compound

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S1 Molecular coverage estimation

The coverage estimation is mostly based on the frequency shift of a quartz microbalance, which is calibrated by STM measurements. Integrated Fe $L_{3,2}$ edge-intensities of the x-ray absorption (XA) spectra were used to crosscheck the coverage.

Combined scanning tunneling microscopy (STM) and XA spectroscopy measurements were performed on the same sample, without breaking the ultra-high vacuum conditions. Figure S1a shows a room-temperature constant-current STM topograph recorded upon sublimation of Fe-pypyr complexes on Au(111). Molecular islands are discernible but are more evident in the current channel (Figure S1b). In Figure S1b, the molecular islands occupy 40 % of the surface, which we define as a coverage of 0.4 monolayer (ML). A similar analysis on Figure S1a leads to a coverage estimate of 45 %. In order to evaluate the potential error of the coverage estimation, the topograph shown in Figure S1b is divided in 8 topographs of equal areas. Coverage determinations independently carried out on each subtopograph lead to an average value of $\mu = 0.4$ ML and a standard deviation of $\sigma = 0.2$ ML. We therefore consider a coverage of (0.4 ± 0.2) ML for this sample. The following functions were employed:

$$\mu = \frac{1}{8} \sum_{i=1}^8 C_i, \text{ and } \sigma = \sqrt{\frac{1}{8-1} \sum_{i=1}^8 |C_i - \mu|^2}, \quad (\text{S1})$$

where C_i is the coverage estimate inferred from subtopograph i .

A coverage of 0.4 ML corresponds to a given frequency shift of a quartz microbalance, which we estimated from calibrations before and after the deposition of molecules. All further coverage estimates are primarily based on the frequency shift of the quartz microbalance, which is proportional to the amount of deposited molecules. As similar coverages on the different samples were desired for the present study, the integrated Fe $L_{3,2}$ edge intensity of background-subtracted XA spectra should be constant. Indeed, the total electron yield of an adsorbate layer of thickness Δx and x-ray absorption coefficient μ_A on a semi-infinite substrate with a x-ray absorption coefficient μ_C reads^{1,2}:

Figure S1: (a) Room-temperature constant-current STM topograph (300 nm wide) of a sub-monolayer coverage of Fe-pypyr on Au(111). (b) Overview STM topograph exhibiting molecular islands ($V = 2.5$ V, $I_{\text{set}} = 20$ pA, $1 \mu\text{m}$ wide). For better visibility of the islands, the deviation of the current from the set point is shown. (c) XA spectrum acquired on the same sample at 300 K (background subtracted).

$$Y_{\text{sample}} \sim (1 - e^{-\frac{\Delta x}{\lambda_e}}) \lambda_e \mu_A + e^{-\frac{\Delta x}{\lambda_e}} \lambda_e \mu_C, \quad (\text{S2})$$

where λ_e is the electron escape length. The total electron yield of the Au grid is given by $Y_{\text{grid}} \sim \lambda_e \mu_G$ with μ_G the x-ray absorption coefficient of the grid (Ref. 2). The sample yield divided by the grid yield $Y_{\text{sample/grid}}$ is a quantity independent of the photon flux. $Y_{\text{sample/grid}}$ from different measurements should only be compared when realized on the same beamline and ideally during the same beamtime. This was the case for the present study. The edge jump of spectra solely normalized by the grid current is then given by²:

$$Y_{\text{sample/grid}}^{\text{edge}} - Y_{\text{sample/grid}}^{\text{pre-edge}} \sim (1 - e^{-\frac{\Delta x}{\lambda_e}}) \left(\frac{\mu_A^{\text{edge}} - \mu_A^{\text{pre-edge}}}{\mu_G} \right), \quad (\text{S3})$$

where μ_C is assumed to be constant over the energy range of interest. Equation S3 suggests that, for the same thickness of adsorbate Δx , the edge jump of XA spectra solely normalized to grid current should be constant on different substrates, provided that λ_e stays constant. Different growth modes of the molecules or different magnetic fields on the sample may effectively lead to a change in λ_e . Furthermore, employing Equation S3 to compare thicknesses on different substrates requires the x-ray absorption coefficient of the adsorbate μ_A to be substrate independent. This notably implies that the number of d holes in the adsorbate

should remain constant on the different substrates, *i.e.*, same oxidation state of the metal center for transition-metal complexes.

In the following, we consider the integral of Equation S3 over the energy range of interest. A XA spectrum was measured at the Fe $L_{3,2}$ edges on the very same sample as investigated by STM (Fig. S1c), with an integrated $L_{3,2}$ intensity of 0.097 arbitrary units (gray shaded area). For the samples of 0.4 ML Fe-pypyr on different substrates, variations of the integrated Fe $L_{3,2}$ intensity of less than 35 % were ensured. This indicates that the Fe-pypyr coverage, primarily estimated with the quartz balance, is relatively constant on the different substrates. It is therefore safe to assume sub-monolayer coverages for the investigated samples.

S2 Examples of raw data

Figure S2 shows examples of averaged raw and processed data acquired on different samples at different temperatures.

The red curves in the left panels of Figure S2 are obtained by averaging 2 to 4 raw spectra and the blue curves represent the linear background associated to the spectra. Subtraction of the linear background from the averaged spectra leads to the spectra shown in red in the right panels of Figure S2. A low-pass filter is then applied to the data (black curves in Figure S2), by taking care that the eventual induced changes in the $L_{3,2}$ edges do not exceed the noise level of the data.

Figure S2: Examples of raw and processed spectra acquired on 0.4 ML Fe-pypyr on (a) Au(111) at 300 K, (b) graphene/Ni(111) at 300 K, (c) HOPG at 3 K with 532 nm laser illumination and (d) WSe₂ at 100 K. The red and blue curves in the left panels represent averages of 2 to 4 raw spectra and an estimate of the linear background, respectively. Background subtracted data before (red curves) and after low-pass filtering (black curves) are shown in the right panels.

S3 Determination of the high-spin fraction

Figure S3: (a) XA spectra of 5 ML Fe-pypr on Au(111) at 3 K under 532 nm laser light irradiation (red) and at 120 K (blue) used as reference for maximum HS and LS state, respectively. (b) XA spectrum of 5 ML Fe-pypr on Au(111) acquired at 42 K compared to the linear combination fit (Equation S4). (c) Exemplary comparison between fits and measured spectra of 0.4 ML Fe-pypr on HOPG, WSe₂ and HfS₂.

The XA spectrum of intact Fe(II) spin-crossover complexes is a linear combination of the characteristic HS and LS spectra. As reference for the characteristic HS and LS spectra, we took the one acquired on 5 ML Fe-pypr/Au(111) at 3 K under illumination and the one at 120 K, respectively (Fig. S3a). We note that the spin transition from LS to HS may be incomplete in the HS reference (red curve in Fig. S3a), for instance because of insufficient laser illumination. The fractions of HS molecules given in the manuscript are relative to these reference spectra. The HS fraction is determined from a fit to the XA spectrum using³:

$$XAS_{\text{mix}} = a [\gamma_{\text{HS}} XAS_{\text{HS}} + (1 - \gamma_{\text{HS}}) XAS_{\text{LS}}], \quad (\text{S4})$$

where a and γ_{HS} are adjustable parameters. The agreement between the fit and the XA spectra is remarkable as shown in Figures S3b–c.

Figure S4: XA spectrum acquired on 5 ML Fe-pypyr on Au(111) at 3 K under illumination with 532 nm laser light (green curve) along with a fit using Equation S4 with HS and LS references from Ref. 3 (black curve). The HS fraction estimate is 92 %.

As stated above, all HS fractions are given relative to references measured on 5 ML Fe-pypyr on Au(111). In the following, we estimate the potential deviation between the relative and absolute HS fractions. In Figure S4, the spectrum used as a HS reference (green curve) in the present manuscript is fitted with the HS and LS references from Ref. 3 using Equation S4. A HS fraction of 92 % is inferred from the fit (black curve in Figure S4). Therefore, the absolute HS fractions are approximately a factor 0.9 lower than the indicated relative values. The main motivations to employ the HS and LS references acquired on Au(111) are: (i) the spectra were measured under the very same conditions as all other spectra shown in the present study and (ii) fits with the references obtained on Au(111) were systematically better than with that from Ref. 3.

S4 Spectra of the Fe-pypyr fragments on Au(111) for different temperatures

The black and blue curves in Figure S5 are XA spectra acquired on 0.4 ML Fe-pypyr on Au(111) at 300 K and 100 K, respectively. These spectra are essentially the same, indicating that the fragmented Fe complex is not affected by a variation of temperature.

Figure S5: XA spectra acquired on 0.4 ML Fe-pypyr on Au(111) at 300 K (black curve) and at 100 K (blue curve).

S5 Identification of the dissociated molecules

To obtain further information about the dissociated complexes on Au(111), scanning tunneling microscopy was carried out at 4 K. Figures S6a,b show typical topographs acquired on Au(111) upon deposition of Fe-pypyr. Structures with an apparent height of approximately 150 pm and a length of 1.2 nm (right ellipses in Figure S6a) match in size and symmetry with phenanthroline (phen) ligands (expected length of approximately 0.9 nm between the outermost hydrogen atoms). Furthermore, this structure is very similar to that of phen ligands on Co/Cu(100) (Ref. 4) and on Au(111) (Ref. 5) and tends to form dimers (left ellipse in Fig. S6a)⁵. We therefore assign these structures to phen ligands, which most probably result from the fragmentation of Fe-pypyr on Au(111).

Other areas of the same sample exhibit dense structures of adsorbates (Fig. S6b). The size and shape of the adsorbates, with an apparent height of approximately 400 pm, are compatible with $[\text{Fe}(\text{pypyr}(\text{CF}_3)_2)]^+$ as indicated by the superimposed scaled molecular models. We note that (i) no information is available about the charge state of the fragments and (ii) there may be other fragments on the surface. Indeed, unidentified structures are observed, *e.g.*, the yellowish structures in Figure S6a.

Multiplet calculations were performed with the multiX package⁶ to simulate the XA spectra of the fragments. Figure S6c shows the calculated spectra for an Fe^{2+} ion in an octahedral crystal field, where the ligands are considered as point charges. The red and blue

curves are obtained for a crystal-field strength of 0.15 and 0.8 e/Å, respectively (Fig. S6c). These curves are rather similar to the XA spectra of Fe^{II} spin-crossover complexes in the HS and LS states, respectively (see for instance Fig. 1c of the main text for comparison). Indeed, the L_3 edge of the red curve (HS) has a more developed multiplet structure with additional peaks compared to the L_3 edge of the blue curve (LS). Moreover, the energy of the L_3 edge of the red curve (HS) is lower than that of the blue curve (LS). For the sake of generality and comparison with other complexes, the multiplet calculations were realized with a limited set of parameters (crystal-field strength and core-hole broadening). More sophisticated calculations would consider the non-perfect octahedral symmetry of the crystal field and scale the spin-orbit coupling and Coulomb interaction.

In the following, we refer to the coordination number (CN) to distinguish between different Fe^{II}-ligand cages. All the cages were constructed from the CN6 structure, from which point charges have been removed. Therefore, this approximation assumes no relaxation of Fe^{II} cage upon removal of ligands. The XA spectrum of [Fe(pypyr(CF₃)₂)]⁺, the compound presumably observed in the STM experiments (Fig. S6b), is simulated by considering an Fe²⁺ ion with only two points charges (CN2; crystal-field strength of 0.8 e/Å). The calculated spectrum of the CN2 structure (black curve in Fig. S6c) is similar to that of the fragmented complexes on Au(111) (black curve in Fig. 1c of the manuscript). In particular, the adsorption edges of the CN2 structure (black curve) have approximately the same energies as that of the CN6 structure with weak crystal field (red curve). This is in agreement with the experimental evidence that the XA spectrum of fragmented molecules may easily be confused with that of intact SCO complexes in the HS state (section S6). Therefore, the combination of STM data and multiplet calculations suggest that the fragmented complex on Au(111) is [Fe(pypyr(CF₃)₂)]⁺.

For completeness, we show that simulated spectra of the CN2 structure are essentially independent of the crystal-field strength (compare lower green and black curves in Fig. S6d calculated for crystal-field strength of 0.2 and 0.8 e/Å, respectively). Furthermore, similar

spectra are obtained for the CN4 structure (upper green and black curves in Fig. S6d). This implies that, from the XA spectra alone, it is challenging if not impossible to retrieve the composition of the fragments.

Figure S6: (a,b) Low-temperature STM topographs of Fe-pypyr on Au(111). (a) Isolated phen ligands (dashed ellipses) are observed on the Au(111) surface along with unidentified structures (yellowish protrusions). (b) Dense structure of molecular adsorbates with superimposed scaled models of $[\text{Fe}(\text{pypyr}(\text{CF}_3)_2)]^+$. The topograph was acquired on the same sample as for (a). Image sizes: (a) $30 \times 20 \text{ nm}^2$ and (b) $5 \times 2.5 \text{ nm}^2$. (c,d) Multiplet calculations for different Fe-N cages, as depicted in the insets. For every cage, the multiplet calculations were performed for a weak (green and red lines) and for a strong ligand field (black and blue lines). The calculations include a core-hole Lorentzian broadening of 0.5 eV and the energies are shifted by 4.41 eV. The scale parameters for the spin-orbit coupling and the Coulomb interaction were left to their default values.

S6 Distinction between dissociated molecules and complexes trapped in a given spin state

The shape of the Fe $L_{3,2}$ XA spectra of Fe-pypyr on graphene/Ni(111) can, to some extent, be reproduced by linear combination of the reference spectra (red curves in Figs. S7a–b). However, this approach fails to reproduce the correct contribution at some energies, *e.g.*, 706.7 eV. In contrast, the fits are drastically improved when a fraction of the molecules are considered dissociated (with spectral features similar to that of dissociated Fe-pypyr/Au(111)) (black curves in Figs. S7a–b). The spectra are fit by a linear combination of (i) the dissociated-complex spectrum ($XAS_{\text{Diss.}}$) measured on Fe-pypyr/Au(111), (ii) the HS XAS_{HS} and (iii) the LS XAS_{LS} references:

Figure S7: Illustration of the fit quality using Equations S4 (red) and S5 (black) to the spectra acquired at (a) 10 K under illumination and at (b) 150 K on 0.4 ML Fe-pypyr/graphene/Ni(111) (green). (c) Evolution of the HS fraction and (d) the deviation of the data to the fits (χ^2) as a function of temperature by considering all molecules being intact (Equation S4, red) or by assuming that a fraction of molecules are dissociated (Equation S5, black).

$$XAS_{\text{mix}} = a \{ \gamma_{\text{Diss.}} XAS_{\text{Diss.}} + (1 - \gamma_{\text{Diss.}}) [\gamma_{\text{HS}} XAS_{\text{HS}} + (1 - \gamma_{\text{HS}}) XAS_{\text{LS}}] \}, \quad (\text{S5})$$

where $\gamma_{\text{Diss.}}$ and γ_{HS} are the fraction of dissociated molecules and the fraction of HS among the intact complexes, respectively.

On a given sample, $\gamma_{\text{Diss.}}$ is first determined and considered as constant. For this purpose, the spectra acquired at 150 K are assumed to be in a pure LS state and fit to Equation S5 imposing $\gamma_{\text{HS}} = 0$. $\gamma_{\text{Diss.}}$ is inferred from the fit and considered constant for the next steps. Then, all spectra, acquired at different temperatures, are fit using Equation S5 with a and γ_{HS} as adjustable parameters.

The complete procedure is illustrated for the sample 0.4 ML Fe-pypyr/graphene/Ni(111). The fit of the spectrum acquired at 150 K to Equation S5 (imposing $\gamma_{\text{HS}} = 0$) leads to $\gamma_{\text{Diss.}} = 0.30$. All spectra are then fit using Equation S5, where $\gamma_{\text{Diss.}}$ is constrained to 0.30 and a and γ_{HS} are adjustable parameters. The obtained fits reproduce the data well as shown in Figures S7a–b (black curves) for two different temperatures. The evolution of the HS fraction (γ_{HS}) as a function of temperature is displayed in Figure S7c (black crosses). It is significantly different from the HS fraction inferred from fits to Equation S4, which assumes that all molecules are intact (red circles in Fig. S7c).

To compare the quality of the fits to Equations S4 and S5, the corresponding sums of the squared difference (χ^2) are calculated. Although both fitting functions have the same number of fit parameters (two in each case), χ^2 is significantly smaller when the spectra are fit to Equation S5 (black symbols in Fig. S7d), indicating that Equation S5 is more appropriate to describe the data.

S7 0.4 ML Fe-pypyr on Co/Cu(100)

The XA spectra at the Fe $L_{3,2}$ edges on 0.4 ML Fe-pypyr on Co/Cu(100) are significantly different from the ones obtained from the HS and LS references, respectively. Instead, they are very similar to that of Fe-pypyr on Au(111) and are therefore indicative of dissociated complexes (Fig. S8). Furthermore, as these dissociated complexes have a non-vanishing XMCD signal (gray spectrum in Fig. S8), they have magnetic moments and their moments are mostly aligned. The alignment of the magnetic moment is realized by a ferromagnetic coupling between the dissociated complexes and the Co layer, as previously observed on other systems^{7–10}.

Figure S8: XA spectra of 0.4 ML Fe-pypyr on Co/Cu(100) acquired at the Fe and Co $L_{3,2}$ edges at 300 K under illumination with circularly polarized left (green) and right (orange) photons. The gray spectrum is the difference (XMCD).

S8 Comparison of dissociated molecules

XA spectra of dissociated Fe-pypyr complexes on Au(111) and on Co/Cu(100) are identical within the noise level (dashed black, solid blue and solid green curves in Fig. S9). In addition, within the noise level, these spectra are indistinguishable from the contributions of dissociated Fe-pypyr complexes on graphene/Ni(111) (red curve in Fig. S9). This suggests that the fragments are the same on the different surfaces.

Figure S9: Comparison of the XA spectra acquired on 0.1 ML Fe-pypyr on Au(111) (blue), 0.4 ML Fe-pypyr on Au(111) (dashed black) and on Co/Cu(100) (green) along with the contributions from dissociated molecules on 0.4 ML Fe-pypyr/graphene/Ni(111) (red). The latter contributions are obtained by removing $(1 - \gamma_{\text{Diss.}})XAS_{LS}$ from the spectrum acquired at 150 K on graphene/Ni(111).

S9 Peculiar results of 0.2 ML Fe-pypyr on Au(111) prepared under inappropriate conditions

Figure S10a shows the evolution of the XA spectra as a function of temperature on 0.2 ML Fe-pypyr/Au(111). A hasty analysis of these data would lead to the following interpretation: Fe-pypyr molecules in direct contact to Au(111) exhibit switching while a fraction of the molecules are locked in the HS state (red circles in Fig. S10b). However, in the light of the detailed analysis performed on other samples and because these results are not reproducible, the conclusion should be significantly different.

Figure S10: (a) XA spectra of 0.2 ML Fe-pypyr on Au(111) acquired at different temperatures after the first evaporation process, *i.e.*, after insufficient degassing of the Knudsen cell. (b) Corresponding HS fraction inferred from fits to Equation S4 (red circles) and Equation S5 (black crosses) of the sample at different temperatures.

First, the presumed fixed fraction of HS molecules actually corresponds to a fraction of dissociated molecules (approximately 30 %). Second, we prepared several samples with sub-ML coverages of Fe-pypyr on Au(111). Only one sample exhibited indication of a fraction of switching molecules. It was the first sample of the series prepared after short degassing of the Knudsen cell. We therefore suggest that the switchable molecules are not in direct contact to the Au(111) but most probably are located on a thin insulating layer of fragments, originating from the degassing of the Knudsen cell. Note that similar results can be obtained when fragments are coevaporated with the complexes. XAS at the Fe edges is insensitive to the eventual Fe-free fragment layer.

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