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Interface versus Bulk Light-Induced Switching in Spin-Crossover Molecular Ultra-Thin Films Adsorbed on a Metallic Surface

Massine Kelaiï,[†] Arthur Tauzin,[‡] Anastasia Railean,[¶] Vincent Repain,[†] Jérôme Lagoute,[†] Yann Girard,[†] Sylvie Rousset,[†] Edwige Otero,[§] Talal Mallah,[‡] Marie-Laure Boillot,[‡] Cristian Enachescu,[¶] and Amandine Bellec^{*,†}

[†]*Université Paris Cité, CNRS, Laboratoire Matériaux et Phénomènes Quantiques,
F-75013, Paris, France*

[‡]*Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris-Saclay, CNRS,
UMR 8182, 91400 Orsay, France*

[¶]*Faculty of Physics, Alexandru Ioan Cuza University of Iasi, Iasi 700506, Romania*

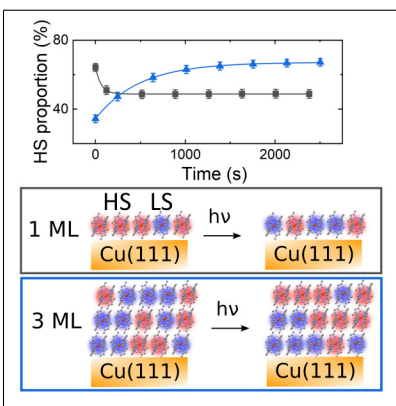
[§]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif sur Yvette, France*

E-mail: amandine.bellec@u-paris.fr

Abstract

Spin-crossover molecules present the unique property to have two spin states that can be controlled by light excitation at low temperature. Here, we report on the photoexcitation of $[\text{Fe}^{\text{II}}((3,5\text{-}(\text{CH}_3)_2\text{Pz})_3\text{BH})_2]$ (Pz= pyrazolyl) ultra-thin films, with thicknesses ranging from 0.9 to 5.3 monolayers, adsorbed on Cu(111) substrate. Using x-ray absorption spectroscopy measurements, we confirm the anomalous light-induced spin-state switching observed for sub-monolayer coverage and demonstrate that it is confined to the first molecular layer in contact with the metallic substrate. For higher coverages, the well-known light-induced excited spin-state trapping effect is recovered. Combining continuous light excitation with thermal cycling, we demonstrate that at low temperature light-induced thermal hysteresis is measured for the thicker films; while, for sub-monolayer coverage, the light enables to extend the thermal conversion over a large temperature range. Mechano-elastic simulations underline that, due to the intermolecular interactions, opposite behaviors are observed in the different layers composing the films.

TOC Graphic



Spin-crossover molecules present the ability to be controllably switched between their two spin-states by external stimuli, such as temperature or light.¹⁻⁵ In the case of Fe^{II}, the molecules present a high spin state (HS, S=2) at high temperature and a low spin state (LS, S=0) at low temperature. In molecular crystals, elastic interactions between the molecules may result in hysteretic transitions.⁶ At low temperature, the low spin state can be switched to the high spin state by visible light excitation known as light-induced excited spin-state trapping (LIESST) effect.^{7,8} In the dark and at low temperature, the photoexcited state is metastable for long times as the HS-to-LS relaxation occurs via a very slow tunneling process. The reverse LIESST effect (HS-to-LS) can be induced by near infra-red excitation.⁹ Combining continuous light-excitation and thermal cycling in the low temperature range, hysteretic behavior, known as light induced thermal hysteresis (LITH), can also be observed in cooperative molecular crystals.¹⁰⁻¹³ The hysteretic behavior is the result of the competition between the photo-excitation to the HS state and the thermal relaxation to the LS state in the case of solids in which cooperative effects are inducing phase separation. In some systems presenting incomplete thermal transition due to specific crystallographic structure, light excitation at low temperature can also enable accessing hidden structural phase for which all molecules are in LS state.¹⁴⁻¹⁶

For spin-crossover molecular crystals, the system size and the surface energy are of critical importance. In parallel to the reduction of the cooperativity and the closing of hysteresis loops that are usually reported in small dimensions, the temperature and the completeness of the transition also decrease.¹⁷⁻²⁰ Going to thin films also enables to exhibit LIESST effect which is absent in powder material.²¹ For films with sub-monolayer coverage directly adsorbed on a substrate, only few examples of full molecular switching under light are reported in the literature.²² And as recently reported by some of us, Fe^{II} molecules in direct contact with metallic substrates can undergo an anomalous light-induced spin-state switching from the high spin state to the low spin state.²³

Here, we investigated in detail the influence of the thickness of molecular films on the

light-induced switching of $[\text{Fe}^{\text{II}}((3, 5\text{-}(\text{CH}_3)_2\text{Pz})_3\text{BH})_2]$ (Pz = pyrazolyl) molecules, called FeMPz in the following. We thus studied, by x-ray absorption (XA) spectroscopy, thin films with thicknesses from sub-monolayer to more than five monolayers (ML) of FeMPz molecules adsorbed on Cu(111). By following the dynamics of the conversion under light excitation, we demonstrated that the anomalous light-induced spin-state switching is limited to the molecule/metal interface. We also observed LITH for molecular films larger than 3 ML. Interestingly, for the smaller coverage, the anomalous light-induced thermal effect observed in the low temperature range allows to unlock HS interfacial molecules strained by the substrate and thus to significantly extend the thermal SCO. Mechano-elastic simulations taking into account the photoexcitation with both the HS-to-LS anomalous light-induced switching of the interfacial layer and the LS-to-HS switching (LIESST effect) of the upper layers qualitatively reproduce the experimental results.

FeMPz crystalline powder presents a thermal hysteretic transition centred around 190 K²⁴ and undergo LIESST effect at low temperature.²³ The FeMPz molecules present the advantage to be sublimable under ultra-high vacuum and to self-assemble in dense networks on Cu(111) without any decomposition.²⁵ We thus have grown thin films of FeMPz from 0.9 ± 0.2 ML to 5.3 ± 1.3 ML on Cu(111) single crystal. All the measurements were realised by XA spectroscopy at the Fe $L_{2,3}$ -edges at which the XA spectrum shape is depending on the molecular spin state.

At low temperature (either 4 K or 10 K), XA spectra at the Fe L_3 -edge were recorded for the different molecular thicknesses before and under a continuous light excitation (405 nm). Figure 1.a and 1.b present the spectra measured before light excitation and after saturation of the photoexcited phase for 0.9 ± 0.2 ML and 5.3 ± 1.3 ML molecular coverages. In the spectra, the intense peaks at 707.9 eV and 709.2 eV are characteristic of the HS and LS states, respectively. At low temperature, the thermal transition is partial with a residual high spin state fraction depending on the film thickness.²⁰ This explains the presence of the intense HS peak, compared to the LS one, for the sub-monolayer coverage (figure 1.a), while

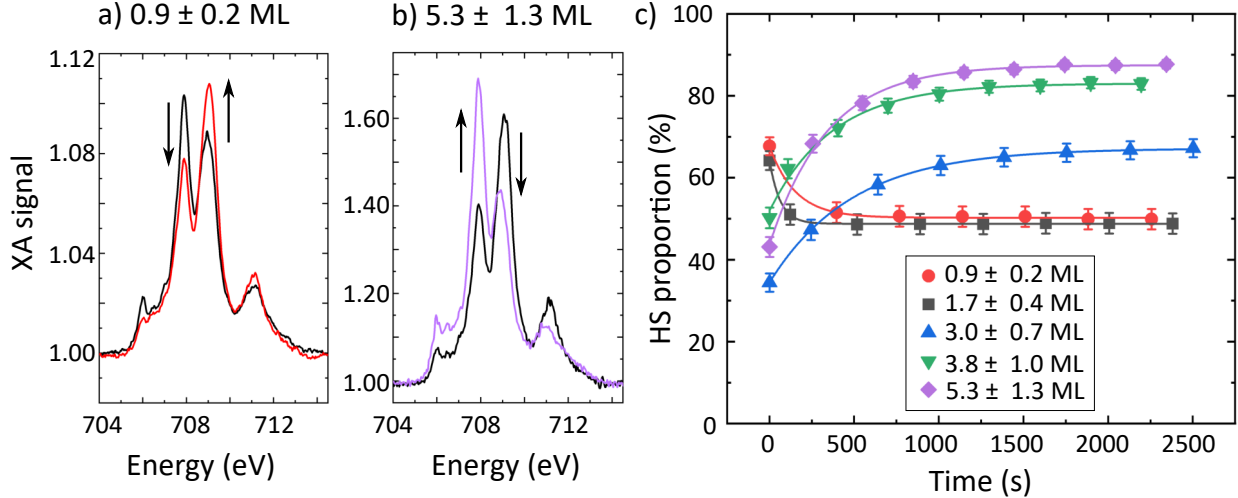


Figure 1: a,b) XA spectra at the Fe L_3 -edge before light illumination (black spectra) and after conversion under blue light (colored spectra) for a coverage of a) 0.9 ± 0.2 ML (at 4 K) and b) 5.3 ± 1.3 ML (at 10 K). The XA signal is normalized to the background so that the signal is directly the ratio of the background signal. The arrows indicate the evolution of the peaks under light excitation. c) Evolution of HS proportion at low temperature (4 K or 10 K) under blue light (405 nm) as a function of time for different thicknesses of FeMPz molecular films. The symbols correspond to the HS proportion measured and the solid lines to exponential fits. Color code: (i) red circles: 0.9 ± 0.2 ML at 4 K, (ii) black squares: 1.7 ± 0.4 ML at 4 K, (iii) blue up triangles: 3.0 ± 0.7 ML at 4 K, (iv) green down triangles: 3.8 ± 1.0 ML at 10 K and (v) purple diamonds: 5.3 ± 1.3 ML at 10 K.

the reverse situation is obtained for the higher coverage (figure 1.b). For the sub-monolayer coverage, the photoexcitation leads to the decrease of the HS peak to the profit of the LS peak thus indicating a partial HS-to-LS conversion (red spectrum in figure 1.a). This behavior is characteristic of the anomalous light-induced spin-state switching demonstrated on different metallic substrates.²³ On the contrary, for higher coverage (5.3 ± 1.3 ML), the standard LIESST effect is observed as visible in figure 1.b in which the spectrum before light (black spectrum) has an intense LS peak that decreases after light excitation to the profit the HS peak. To access the dynamics of the photoinduced conversions, the proportion of molecules in high spin state is extracted from each spectrum by linear combination of reference spectra in high spin and low spin states.²³ The temporal evolution of the HS proportion is presented in figure 1.c. For a molecular coverage of 0.9 ± 0.2 ML, the decrease around 18% of the HS

proportion is observed due to the HS-to-LS transition.²³ For 1.7 ± 0.4 ML, the HS proportion decrease (around 15%) indicates that the molecules also undergo the anomalous HS-to-LS switching. On the contrary, for larger thicknesses (superior or equal to 3.0 ± 0.7 ML), the HS proportion increases under light excitation indicating that LIESST effect is occurring. In addition, the increase of the molecular thickness leads to an increase of the proportion of switching molecules with a conversion of around 30% for 3.0 ± 0.7 ML and up to 45% for the 5.3 ± 1.3 ML.

The light-induced conversion has also been investigated under red light exposure (635 nm), for which similar behaviors are observed (figure S1). For the 0.9 ± 0.2 ML-molecular film, the molecules undergo a small anomalous light-induced spin-state switching, while the LIESST effect is obtained for a thickness of 3.0 ± 0.7 ML. The fact that the kinetic of the LIESST effect for the 3.0 ± 0.7 ML-film is slower and the conversion is weaker than the ones observed with the blue light is fully consistent with the bulk behavior.²³ All these results confirm that the anomalous light-induced spin-state switching is an interfacial phenomenon limited here to the first two layers of molecules in contact with the Cu(111) substrate.

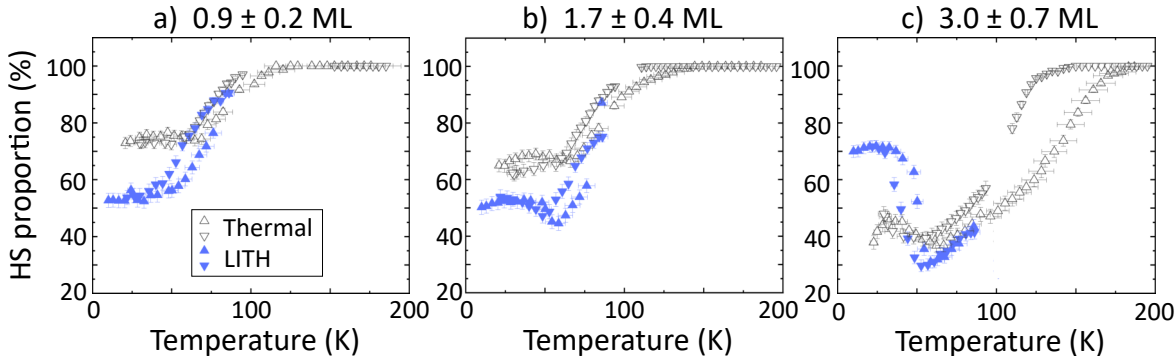


Figure 2: Comparison of the HS proportion evolution as a function of the temperature by ramping the temperature up (up triangles) and down (down triangles) either with (blue symbols) or without (open black symbols) blue light exposure and for different thicknesses. a) 0.9 ± 0.2 ML, b) 1.7 ± 0.4 ML and c) 3.0 ± 0.7 ML.

To better understand the behavior of the system, we combined continuous blue light excitation and thermal cycling ($1 \text{ K}\cdot\text{min}^{-1}$) for the different film thicknesses. Figure 2

presents the evolution of the HS proportion as a function of the temperature compared to the evolution during thermal cycling without any light excitation (see also figure S2 for larger thicknesses). For the larger thicknesses, LITH is observed with a hysteresis width of around 10 K for the 3.0 ± 0.7 ML-thick film (figure 2.c) and up to around 20 K for the thicker films (figure S2). Above 60 K, the evolution of the HS proportion is equivalent with or without the light exposure for the heating ramp.

While ramping up the temperature with the light on for the 0.9 ± 0.2 ML-film, the HS proportion between 4 K and 30 K is not evolving before increasing (figure 2.a). The thermal evolution of the HS proportion under light extends the thermal switching measured in darkness. The observed extension reflects the fact that the thermal transition and the anomalous light-induced switching temperatures are close. Once again, the 1.7 ± 0.4 ML-film presents an intermediate behavior with first a decrease of the HS proportion before showing an increase which extends the thermal switching range.

Experimentally, if for the larger thicknesses, the behavior of the molecular layer resemble the bulk one, for the thinner coverage the behavior is reversed. Indeed, for 0.9 ± 0.2 ML, the molecules in direct contact with the Cu(111) undergo an anomalous light-induced spin-state switching from HS state to the LS state leading to specific behaviors for the photoexcited state relaxation and thermal conversion under light. The 1.7 ± 0.4 ML-film presents an intermediate behavior, as a result of the opposite behaviors of the interfacial layer in direct contact with the substrate that undergoes the anomalous light-induced spin-state switching and the upper ones that resemble the bulk behavior.

The thermal relaxation of the photoexcited state after blue light exposure (at 4 K) while ramping up the temperature with a rate of $1 \text{ K}\cdot\text{min}^{-1}$ also indicates different behaviors between sub-monolayer coverages and the larger ones. Indeed, typical LIESST relaxation,^{3,4} with a LIESST temperature (T_{LIESST}) of 55 ± 4 K, is observed for 3.0 ± 0.7 ML-thick film. On the contrary, for 0.9 ± 0.2 ML film, a slow LS-to-HS relaxation is obtained up to an inflection point at 72 ± 5 K above which the thermal LS-to-HS switching dominates. Once

again, the 1.7 ± 0.4 ML-film presents an intermediate behavior with both a T_{LIESST} at 59 ± 4 K and an inflection point at 72 ± 5 K (figure S3).

Accessing under light excitation at low temperature a state with more molecules in the LS state, compared to the low temperature phase, has been reported in the literature in case of hidden structural phases.^{14–16} Our results are not comparable as (i) we are using visible light and not infra-red to induce this anomalous light effect, (ii) scanning tunneling microscopy measurements never provided evidence for structural phase transition under visible light and (iii) the photoswitching occurs randomly in the molecular network without showing any spin-state organisation.²³ It thus seems unlikely that our system can evolve under light at low temperature to a hidden phase.

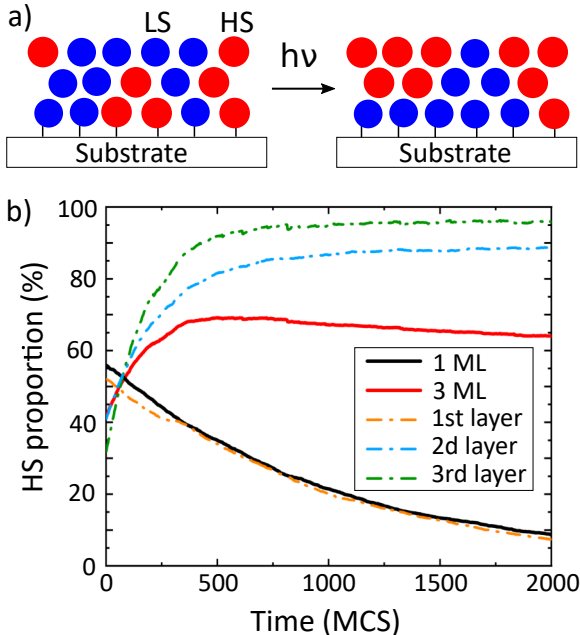


Figure 3: a) Schematics of the mechano-elastic model at low temperature before (left) and after (right) light excitation. The HS and LS molecules are represented as red and blue balls respectively. b) Simulation of the HS proportion as a function of the Monte-Carlo steps (MCS) for 1 ML (black curve) and for 3 ML (red curve) films at 10 K under photoexcitation. The HS proportion is decomposed over the three layers for the 3 ML-film (orange: 1st layer in contact with the substrate, blue: 2^d layer, green: 3rd layer). The simulation parameters are $k_{mol} = 4 \text{ N m}^{-1}$, $k_{sub} = 0.5 \text{ N m}^{-1}$, $I\sigma_1 = 10^{-5}$, $I\sigma_2 = 10^{-4}$.

Simulations using a 3D mechanoelastic model have been carried out to qualitatively

reproduce the experimental results under light excitation (Figure 3.a). The photoexcitation is taken into account via an additional term in the molecular switching probability $I\sigma$ with I the light intensity and σ the absorption coefficient (see methods). So, to reproduce the anomalous light-induced spin-state switching of the molecules in the first layer in contact with the substrate, we introduced an additional HS-to-LS transition probability ($I\sigma_1$). For the molecules in the other layers, an additional LS-to-HS transition probability ($I\sigma_2$) is added to reproduce the LIESST effect. The $I\sigma_1$ probability being the result of the balance between the direct light excitation of the molecules (LS-to-HS conversion) and the dominant anomalous light-induced switching (HS-to-LS), it seems reasonable that its value is smaller than the $I\sigma_2$ value. As in previous work,^{20,26} the intermolecular interactions and the interaction of the molecules to the substrate are modeled by springs with elastic constants called k_{mol} and k_{sub} , respectively. Figure 3.b presents the evolution of the HS proportion under photoexcitation at 10 K for 1 ML- and 3 ML-films. The initial residual HS proportion is due to the trapping of molecules in HS states associated to the partial thermal conversion imposed by the epitaxial constrain to the substrate.^{20,26} For the 1 ML-film, the photoexcitation leads to a decrease of the HS proportion; while for 3 ML-film, the increase of the HS proportion is reproduced. For the 3 ML-film, the HS proportion is decomposed over the three layers. As visible in the figure 3 (snapshots in figure S5.a), the molecules in the first layer in contact with the substrate are undergoing the anomalous light-induced spin-state switching, while molecules in the third layer are undergoing LIESST effect. The second layer shows an intermediate evolution due to the intermolecular interactions and to the opposite behaviors of the first and the third layers. This is even more obvious at 30 K, where the HS proportion for the second layer stays almost constant during the photoexcitation (figures S4 and S5.b). Decreasing the light intensity by a factor of 10 hardly influences the molecules behavior (figure S4). Indeed, under the reduced light excitation, the kinetic of the photo-induced conversion on cooling is too slow to compete with the thermo-induced conversion one.

Figure 4 shows the thermal conversion under continuous light (solid lines) for 1 ML- and

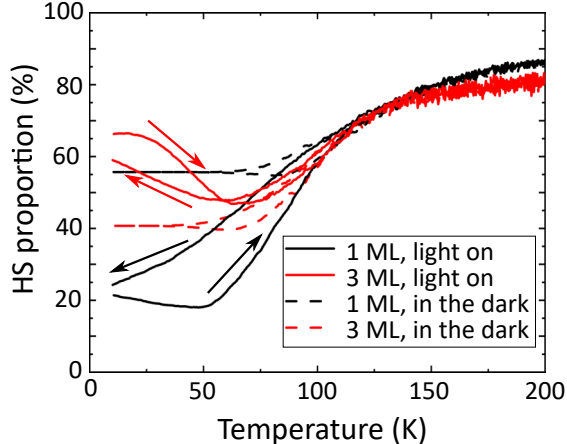


Figure 4: Evolution of the simulated HS proportion as a function of temperature with (solid lines) or without (dashed lines) light for 1 ML- (black) and 3 ML- (red) films. The temperature scanning rate is considered as 2 MCS K^{-1} . The simulation parameters are $k_{mol} = 4 \text{ N m}^{-1}$, $k_{sub} = 0.5 \text{ N m}^{-1}$, $I\sigma_1 = 10^{-5}$, $I\sigma_2 = 10^{-4}$.

3 ML-films compared to the thermal conversion occurring in the dark (dashed lines). For the 3 ML-film, in addition to the thermal hysteresis reproduced with or without light, another hysteresis loop is observed under light below 60 K, which is characteristic of the LITH effect. For the 1 ML-film, the thermal ramping under light excitation results in the broadening of the thermal hysteresis loop and a more complete conversion of the molecules to the LS state. Similarly to the experimental results, the light excitation leads to a significant extend of the thermal switching process. Once again, the three layers of the 3 ML-film show different behaviors. Indeed, the behavior of the layer in contact to the substrate is similar to the one of the 1 ML-film, and the second layer has an intermediate behavior (figure S6). Due to kinetic effects, the light intensity influences the shape of the simulated loop, as for small light intensity larger hysteresis loops are obtained both for the 1 ML- and the 3 ML-films (figure S7). The qualitative agreement between the experimental results and the simulations supports the hypothesis that the anomalous light-induced spin-switching is confined at the interface between the first molecular layer and the metallic substrate. Interestingly, the anomalous light-induced spin-switching enables to partially overcome in the low temperature range the effect of elastic strains imposed by the substrate.

To conclude, experimentally we demonstrated that the anomalous light-induced spin-state switching of the FeMPz molecules is limited to the sub-monolayer coverages on Cu(111), while for higher coverage the well-known LIESST effect is observed. For sub-monolayer coverage, light exposure induces the prolongation of the thermal conversion with a more complete HS-to-LS transition. Increasing the film thickness leads to a slow recovery of the bulk behavior of the FeMPz molecules, i.e. the LS-to-HS transition and LITH under light are observed. As evidenced by the simulation, the intermolecular interactions between the layers leads to intermediate behavior for coverage of a few monolayers. Such light-induced interface effects need to be considered when electronic devices incorporating ultra-thin spin-crossover molecular films operate under light.

Methods

Experimental methods

The molecular films have been grown on a Cu(111) single crystal cleaned under ultra high vacuum (UHV, base pressure of 10^{-10} mbar) by sputtering (Ar^+ ions at 600 eV) and annealing (450°C) cycles. Molecules FeMPz were then sublimated under UHV at a temperature of 85°C from a home-made Knudsen-cell-like evaporator on the Cu crystal kept at room temperature. Thanks to the use of a movable shadow mask during the molecular deposition, films having different thicknesses have been grown on a given Cu crystal. Thus, on one sample, three areas were defined with molecular thicknesses of 0.9 ± 0.2 ML, 1.7 ± 0.4 ML and 3.0 ± 0.7 ML. On a second sample, two areas were defined with molecular thicknesses of 3.8 ± 1.0 ML and 5.3 ± 1.3 ML. Consequently, the same thermal ramps and light fluences were applied on a given sample enabling a direct comparison between the behavior of the different thickness films. The film thicknesses have been determined from the L_3 edge-jump measured at room temperature on each areas and compared a calibrated sample for which the coverage was determined by scanning tunneling microscopy measurement and the L_3 edge-jump by XA spectroscopy measurements.²³ The x-ray absorption spectroscopy measurements have been

realised on DEIMOS beamline at SOLEIL synchrotron. To reduce the soft x-ray induced switching, known as SOXIESST effect,²⁷ we used a low x-ray flux. The total incoming photon flux on the different samples was typically of 10^8 photons.s⁻¹.mm⁻². The proportion of molecules in HS state is extracted from the XA spectra by using a linear combination between reference LS and HS spectra. For the thermal ramp, the HS reference spectrum and the temperature are corrected following the procedure described in Kelai *et al.*²⁰ Light excitation was induced by means of blue laser diode (405 nm) with an estimated fluence on the sample of 3.5 mW.cm⁻² or by means of a red laser diode (635 nm) with an estimated fluence on the sample of 2.2 mW.cm⁻² (in air).

Mechano-elastic simulations

For the mechano-elastic simulations, spin-crossover molecules are represented as balls arranged inside rectangular layers in a fcc 3D configuration.²⁰ The ball radii code for the molecular spin states by taking a value of 0.22 nm and 0.2 nm for the HS and the LS states, respectively. The distance between two LS molecule centres is 1 nm. In the layer, each molecule is linked to their six first neighbors by springs with an elastic constant k_{mol} . The interlayer interaction is simulated by linking by spring each molecules to three molecules in the adjacent layers (same k_{mol}). The interaction to the substrate is taken into account by linking each molecules of the first layer to three surface sites in a face centred cubic configuration by springs with an elastic constant k_{sub} . The transition probabilities taking into account the photoexcitation can be written as:^{28,29}

$$p_{HS \rightarrow LS}^i = I\sigma_1 + \frac{1}{\tau_1} \exp(-\kappa_1 p_i) + \frac{1}{\tau} \exp\left(\frac{\Delta H - k_B T \ln g}{2k_B T}\right) \exp\left(-\frac{E_a - \kappa p_i}{k_B T}\right) \quad (1)$$

$$p_{LS \rightarrow HS}^i = I\sigma_2 + \frac{1}{\tau} \exp\left(-\frac{\Delta H - k_B T \ln g}{2k_B T}\right) \exp\left(-\frac{E_a + \kappa p_i}{k_B T}\right) \quad (2)$$

where ΔH (here equal to 1698×10^{-23} J) is the HS-LS energy difference and can be regarded as the difference in enthalpy between the two states, g (here equal to 600) is the vibronic degeneracy ratio such that $k_B \ln g$ corresponds to the difference in entropy between the two states of a non-interacting system (equal to 8.86×10^{-23} J K⁻¹). With these chosen values the transition temperature of the FeMPz molecule is reproduced.²⁴ In equations (1) and (2), E_a is the activation energy barrier of the HS-to-LS relaxation (here equal to 850 K), τ is a scaling constant (here equal to 4) chosen so that the above probabilities are well below unity at any temperature and κ is a scaling factor (here equal to $0.2 \cdot 10^{-10}$ m) between the local pressure and the activation energy of the individual molecule.³⁰ p_i is the local pressure acting on molecule i , defined as:

$$p_i = \sum_{\text{neighborsprings}} k \delta x_{ij} \quad (3)$$

with δx_{ij} the elongation and k equals either k_{sub} or k_{mol} . For the present simulations, the k_{mol} value has been taken to fit the thermal hysteresis loop of the bulk system and the k_{sub} value has been determined to reproduce the HS residual fraction measured at low temperature. The expression of the HS-LS probability ($p_{HS \rightarrow LS}^i$, see equation 1) contains a tunneling relaxation term $\frac{1}{\tau_1} \exp(-\kappa_1 p_i)$, according to the theoretical studies of HS-LS relaxation at low temperatures.⁸ However, as discussed in Supplementary Information (see Figure S8), considering this tunneling term does not change qualitatively the simulated curves. Therefore, in order to keep to a minimum the number of parameters used in the model, we neglected it keeping in mind that the $I\sigma_1$ values used are somewhat underevaluated.

The elements of the photoexcitation terms are I the light intensity, σ_1 the absorption coefficient considered only for the first layer, σ_2 the absorption coefficient considered for the second and the third layers. The simulation procedure implies the computation of the switching probabilities, according to equations 1 and 2 for all molecules in the system. After every Monte-Carlo step (MCS), the position of all molecules in the system is updated

by solving a system of differential equations which takes into account the pressure forces determined by the elongations of the springs for every molecules in the system.³¹

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Supporting Information Available

Dynamics under red light, LITH for higher thicknesses, Relaxation of the photoexcited spin-state, Influence of the temperature on the simulated photoexcitation at 10 K and 30 K, Snapshots of the simulated photoexcited state for 3 ML-film, Decomposition of the HS proportion over the different layers for the simulation of the LITH in the 3 ML-film, Influence of the light intensity on the LITH, Influence of the tunneling term in the simulations at 10 K.

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