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Indications of magnetic coupling effects in spin cross-over molecular thin films

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Abstract

Room temperature isothermal reversible spin crossover switching of [Fe(H₂B(pz)₂)₂(bipy)] thin films is demonstrated. The magnetic oxide substrate locks the [Fe(H₂B(pz)₂)₂(bipy)] largely in a low spin state. With an X-ray fluence, excitation to a high spin state occurs, while relaxation back to low spin state is aided by alternating the substrate magnetization.

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Supplementary information following the **References** shows the hysteresis loop and temperature dependent magnetometry.

The spin crossover (SCO) phenomenon, in several classes of 3d transition metal compounds, relates to the temperature-induced transition between a low spin (LS) diamagnetic state of the metal ion to a high-spin (HS) paramagnetic state, usually stable at higher temperature.^{1,2} For molecular devices or memory applications, where non-volatility is required, there is a strong need to identify and control mechanisms to lock, unlock and switch the molecular spin state at a given temperature, ideally around 300 K.^{3,4} For bi-stability at higher temperatures exceeding the SCO transition, it is necessary to “lock” the low temperature LS state into a metastable state. Such a suppression of the spin state transition has been observed for $[\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2]$,⁵ and $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ ($\text{H}_2\text{B}(\text{pz})_2$ = bis(hydrido)bis(1*H*-pyrazol-1-yl)borate, bipy = 2,20-bipyridine),^{4,6–10} molecules or ultra-thin films interacting with a metallic substrate, with a resulting mixed spin state dominated by the LS state at high temperatures.^{4–6,8} This implies a substrate-induced “locking” of the spin state.

The spin state of an ultrathin film can be deliberately manipulated: the Fe(II) spin crossover complex $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$, when locked in the low spin state, by the substrate, can be excited into the high spin state at room temperature by an X-ray fluence and then thermally relaxed backed to the low spin state.⁴ This appears to require an insulating substrate, consistent with the observation of STM tip manipulation of the spin state of $\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2$ on a dielectric substrate like CuN.⁵ Charge displacement is implicated.⁴

The transition of the spin state is critically dependent on the local environment of the Fe ion, which is susceptible to various interactions of the molecule with its surroundings, as well as external stimuli, including voltage. This dependence has been compellingly demonstrated.^{11–17} A transition induced by magnetic field, which could either act on the structure of the molecule, or subtly change the energy levels of the spin-split states, had not been demonstrated. Magneto-electric effects are certainly expected with voltage control of the magnetic anisotropy of $\text{Co}^{\text{II}}(\text{dmphen})_2(\text{NCS})_2$, as predicted by density functional theory.¹⁸ Such magnetoelectric coupling at the molecular level is what is missing for metal–organic molecular materials applications in the field of multiferroics.

Here, we exploit our initial findings,^{4,10} and those of others,⁵ that interactions with a nonconducting substrate can impact the state of SCO molecular films, to achieve the desired room-temperature switching of the spin state.⁴ We extend this concept here by studying the magnetically stimulated relaxation of the optically excited $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ SCO complex (structure schematically shown in Fig. 1). We investigated how magnetic reversal of the magnetic oxide substrate can influence the ligand field of the metal center, and therefore impact the stability of its magnetic state, as summarized in Fig. 1. In this paper, we show that the spin state transition of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, where pz = tris(pyrazol-1-yl)-borohydride and bipy = 2,20-bipyridine, can be influenced through interactions with a magnetic substrates and magnetic interactions are implicated.

The $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, where $\text{H}_2\text{B}(\text{pz})_2$ = bis(hydrido)bis(1*H*-pyrazol-1-yl)borate and bipy = 2,20-bipyridine, as seen in **Fig. 1**, was synthesized according to the literature.^{19,20} The SCO transition temperature measured by magnetometry was found to be about 160 K, in agreement with prior work.^{9,10,19–24}

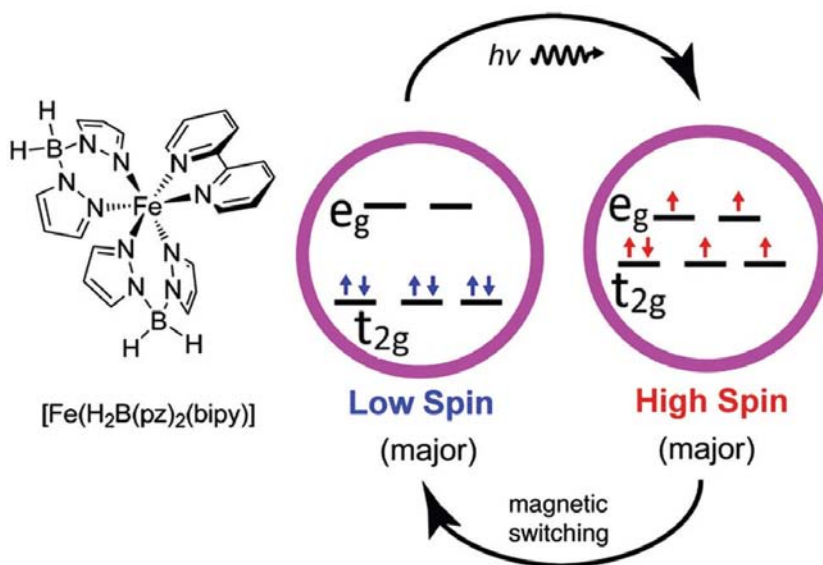


Figure 1. Schematic of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, at the left. On the right, the schematics of reversible control of the spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films, pinned in the majority low spin (LS) state by the substrate at temperatures reaching room temperature (RT). X-ray irradiation switches the state to the majority high spin (HS) state, and repeated magnetization reversal of the magnetic oxide substrate into a majority LS configuration.

This electrically neutral molecule was thermally evaporated on various substrates. We first grew magnetic (B100 nm) thin film $\text{NiCo}_2\text{O}_4(111)$ on $\text{Al}_2\text{O}_3(001)$ substrate by pulsed laser deposition (PLD). The magnetic properties of those films were characterized by magneto-optic Kerr effect (MOKE) and SQUID (Supplemental Information). They have a coercivity of about 200 Oe at room temperature along the out-of-plane direction and a Curie temperature that is about 350 K, which is suitable for our purpose of switching magnetic moment direction around room temperature or even slightly above. The $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ SCO molecule was deposited by thermal evaporation (as done elsewhere^{4,6–10,20,24}), in a UHV growth chamber, on the NiCo_2O_4 surface to a 10 nm thickness.

A 10 nm thick epitaxial film of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3(001)$ (LSMO), using pseudo-cubic notation, grown by off-axis RF magnetron sputtering on a $\text{SrTiO}_3(001)$ substrate,²⁵ was also used as the substrate for a $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film. Because of the formation of a Ruddelston–Popper phase, the stable surface of LSMO is in the paramagnetic insulating phase at room temperature.^{26–28}

The X-ray absorption spectroscopy (XAS) measurements were performed at the bending magnet beamline 6.3.1, at the Advanced Light Source at Lawrence Berkeley National Laboratory. The photon flux is on the order of 10^{11} photons per s per 0.1% BW.²⁹ The temperature was stabilized within ± 1 degree Kelvin. Positive circular polarized X-ray was used. Total electron yield (TEY) mode was used to measure the absorption of the Fe L_3 and L_2 edges, making the measurements relatively surface sensitive. Between measurements, the X-ray beam was blanked or moved to a fresh sample spot when necessary to avoid artifacts through uncontrolled exposure. A 2 Tesla electromagnet supplied the magnetic fields.

The spin state of 10 nm thick films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on NiCo_2O_4 retains the majority low spin (LS) well above the bulk spin cross transition temperature of 160 K, as has been observed for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on other oxide substrates, notably SiO_2 and Al_2O_3 .⁴ This is evident in the initial X-ray absorption spectra of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ taken at room temperature, as seen in **Fig. 2**. In the LS state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, the 3d electrons occupy the t_{2g} orbitals in pairs leaving the e_g empty.^{4,7,8,10,23,24} This is observable in the $2p_{3/2}$ (Fe L_3) X-ray absorption spectra as a major e_g peak at about 708

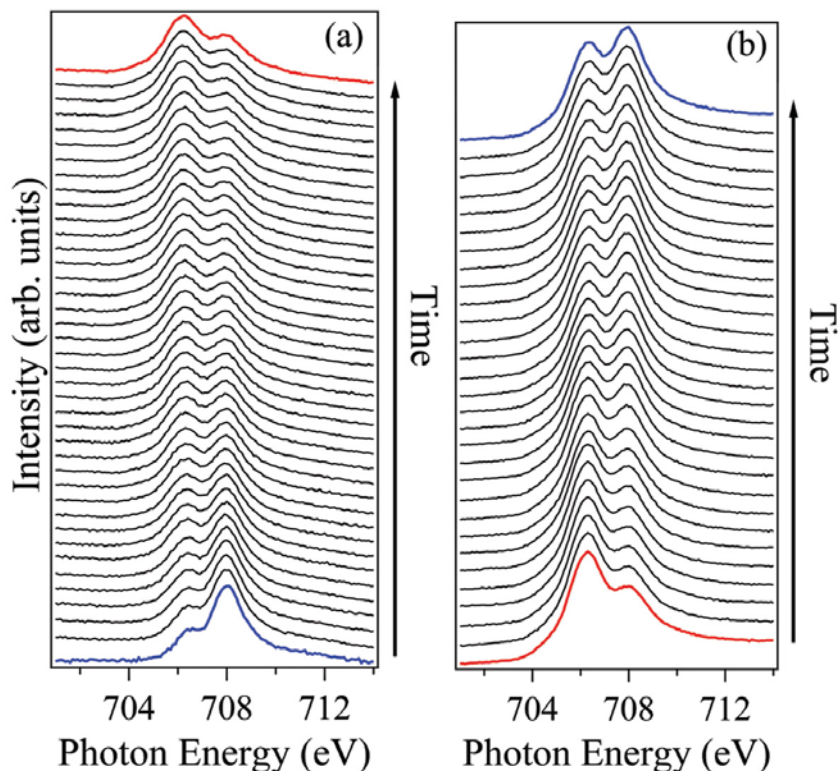


Figure 2. The time evolution of the X-ray absorption spectra of thin films of a 10 nm thin film of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on NiCo_2O_4 in about 23 min (a). From bottom to top, the time is increasing and the spin state changes from the LS state (blue) to the HS state (red). The de-excitation $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ from HS to LS in an alternating magnetic field (b). After each spectrum finished, which is about 1 minute, the external field is switched to opposite direction. The external magnetic field is perpendicular to the sample surface plane.

eV (Fig. 2 and 3). In the HS state, the e_g orbitals are partly populated with the t_{2g} set subsequently partly depopulated, which corresponds in the XAS spectra at the Fe L_3 ($2p_{3/2}$) edge to a decrease of the peak intensity at 708 eV and an increase of the corresponding t_{2g} peak at about 706.5 eV. This locking of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ in largely the low spin state and subsequent X-ray induced transition from a low spin state to a high spin state is observed with increasing exposure to a soft X-ray fluence, as seen in Fig. 2a. This is similar to the observations of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films on SiO_2 and Al_2O_3 , also investigated at room temperature.⁴ The resulting excited HS state, or “unlocked” HS state, is stable for at least one hour at room temperature without X-ray irradiation.

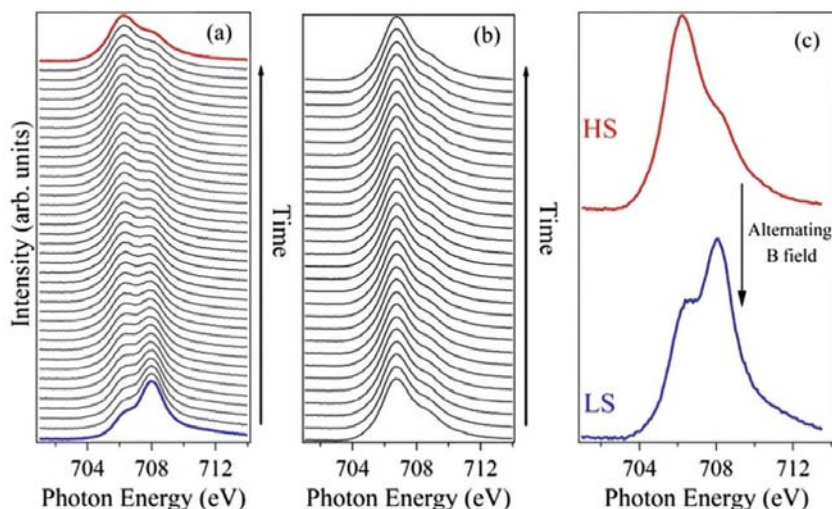


Figure 3. The time evolution of the X-ray absorption spectra of a 10 nm thin film of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on LSMO (a). From bottom to top, the time is increasing and the spin state changes from the LS state (blue) to the HS state (red) in about 28 min. The de-excitation $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ from HS to LS in an alternating magnetic field does not occur, for the duration of 37 min, in the presence of incident X-ray radiation (b), but does in the absence of X-ray radiation (c).

In a similar fashion, the initial spectra of 10 nm thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on LSMO thin films are locked largely in the low spin (LS) state. Again, X-ray induced transition from a low spin state to a high spin state is observed, with increasing exposure to a soft X-ray fluence, as seen in **Fig. 3a**.

We find that retention of the X-ray generated high spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films on NiCo_2O_4 at room temperature (~ 298 K) is suppressed in the presence of an oscillating external magnetic field. The switching of the magnetic field assists in the relaxation of the excited high spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films on NiCo_2O_4 back to a majority low spin state, as seen in Fig. 2b, even with continued X-ray irradiation on the sample. The largely low spin state is restored in about 30 min with around one switch per minute, or roughly with about 20 full cycles of alternating (+/−) magnetic field. We find that the applied magnetic field to change the magnetization needs to be larger than the coercivity of the NiCo_2O_4 thin film. Similar results were observed, nonetheless in the XAS signature of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ spin state, for different amplitudes of applied magnetic field between ± 1.9 T and ± 0.5 T.

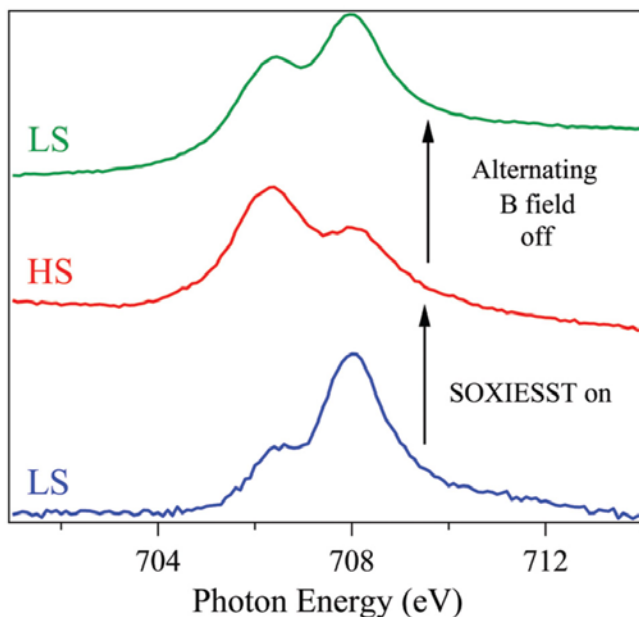


Figure 4. X-ray absorption spectra showing the “unlocking” of a 10 nm thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on NiCo_2O_4 , under soft X-ray fluences (SOXIESST or soft X-ray-induced excited state trapping), towards a HS state within about 23 min at 290 K. This is followed by a reversible return to the locked majority LS phase under an alternating magnetic field, within about 30 minutes, in the absence of X-ray fluence.

This effect, as summarized in **Fig. 4**, is not observed with $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on LSMO thin films, where relaxation back to the low spin state is not seen to occur in an oscillating magnetic field in the presence of an X-ray fluence. In order to observe magnetically stimulated relaxation, the X-ray beam needs to be blanked during the application of the magnetic field, suggesting that the relaxation, to the low spin state, for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ on LSMO (as seen in Fig. 3c) occurs at a lower rate and can be overwhelmed by re-excitation with X-rays.

Yet it should be emphasized that this soft X-ray-induced transition is also reversible. With mild annealing, only slightly exceeding room temperature, the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ relaxes back to the LS initial state. This reversibility excludes photodecomposition as a possible mechanism, as previously noted.⁴ The fact that the relaxation back to the high spin state is substrate dependent is evidence that the substrate is involved and magnetic coupling with the substrate is implicated.

The significance of this study is to provide evidence that magnetic switching of the substrate influences the relaxation of the photoexcited high spin state occupancy. Since this influence is substrate dependent, it is likely the interaction with the substrate that drives this relaxation, which indicates a magnetic coupling of $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$, and the possible magnetic interaction is mediated either through the ligand field or the spin split band structure. A connection to the ligand field, implies that dipolar effects are at least to some extent key to the reversible manipulation of the molecular spin state. The importance of the coupling of the spin state to the ligand field are suggested by recent studies of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combinations with zwitterions.⁴ Any influence of the magnetic field on the molecular dipole then points to possible magneto-electric coupling in the spin cross complexes. The results here suggest that this is substrate mediated, and does not occur by switching applied field alone. Cooperative effects between adjacent $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ moieties cannot be excluded. This work, nonetheless, adds to the context that the spin state of complexes, like $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$, are highly susceptible to even minor perturbations of the ligand chemistry.^{30,31}

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Conflicts of interest — None.

Contributions — **Xiaoshan Xu** and **Xiaozhe Zhang** are responsible for preparing the NiCo_2O_4 films and the magnetic characterization. **Yuewei Yin** and **Xuanyuan Jiang** are responsible for depositing the $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ films. **Xuegang Chen** and **Xia Hong** prepared the LSMO film. XAS measurements were done by **Xin Zhang** and **Alpha T. N'Diaye** with analysis by **Xiaozhe Zhang** and **Peter A. Dowben**. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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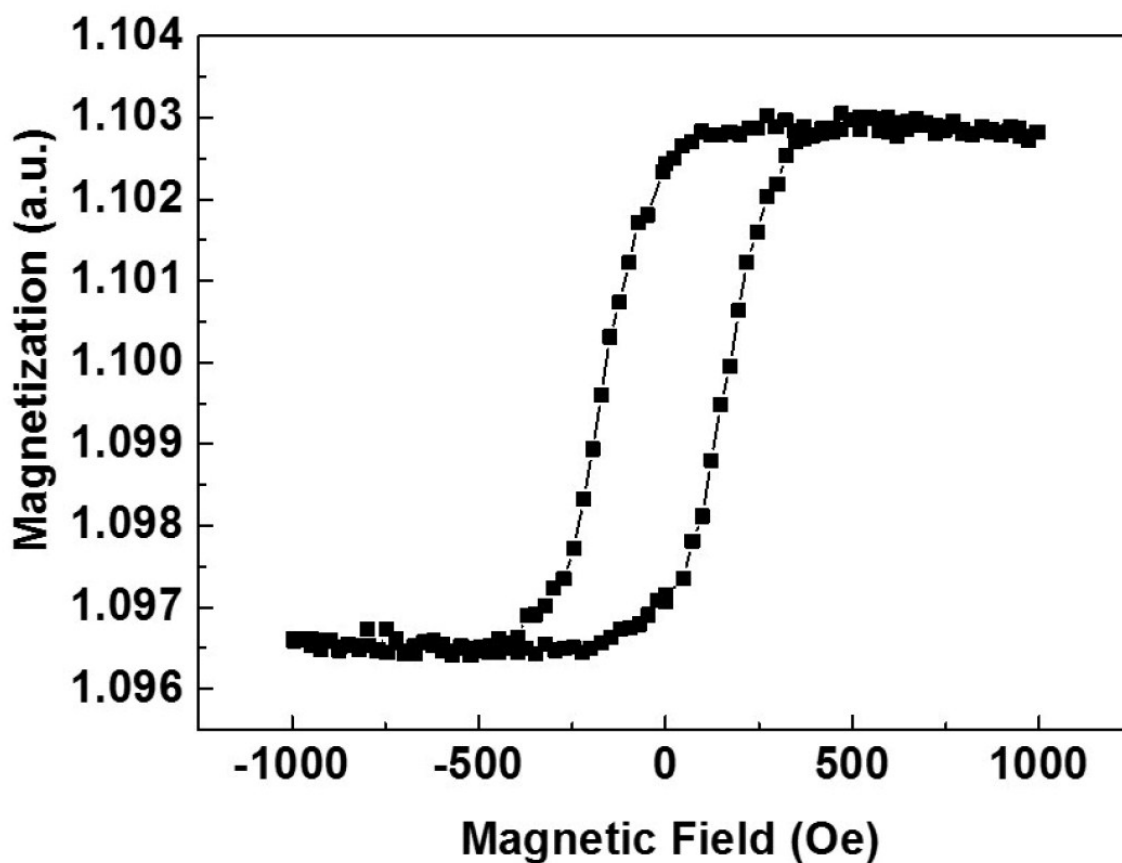
Supplementary Materials to:

Indications of magneto-electric effects in spin cross-over molecular thin films

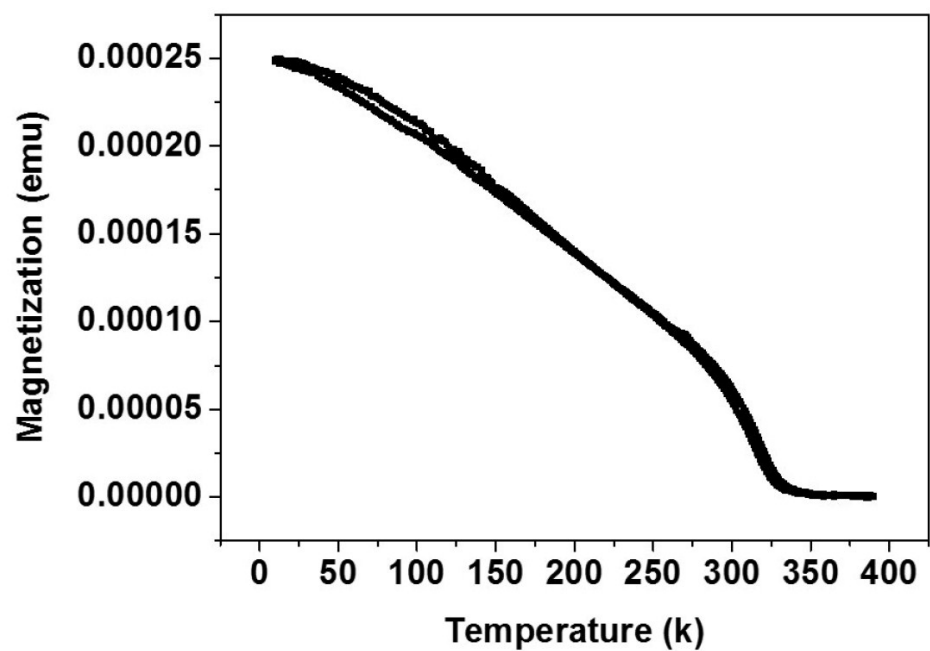
Xin Zhang,^a Alpha T. N'Diaye,^{*d} Xuanyuan Jiang,^a Xiaozhe Zhang,^a Yuewei Yin,^a Xuegang Chen,^a Xia Hong,^a Xiaoshan Xu,^{*a} Peter A. Dowben^{*a}

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S1. The room temperature magneto-optic derived hysteresis loop of a ~100 nm thin film NiCo_2O_4 grown on MgAl_2O_4 . The ferromagnetic coercivity is about 200 Oe out of plane.



S2. Magnetization *versus* temperature curve of a NiCo₂O₄ thin film. The Curie temperature is about 325 K.