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Site selective adsorption of the spin crossover complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$ on Au(111)

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Abstract

The iron(II) spin crossover complex $\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2$, dubbed Fe-phen, has been studied with scanning tunneling microscopy, after adsorption on the ‘herringbone’ reconstructed surface of Au(111) for sub-monolayer coverages. The Fe-phen molecules attach, through their NCS-groups, to the Au atoms of the fcc domains of the reconstructed surface only, thereby lifting the herringbone reconstruction. The molecules stack to form 1D chains, which run along the Au[110] directions. Neighboring Fe-phen molecules are separated by approximately 2.65 nm, corresponding to 9 atomic spacings in this direction. The molecular axis, defined by the two phenanthroline groups, is aligned perpendicular to the chain axis, along the Au $[2\bar{2}1]$ direction, thereby bridging over 5 atomic spacings, in this direction. Experimental evidence suggests that the molecular spins are locked in a mixed state in the sub-monolayer regime at temperatures between 100 K and 300 K.

Keywords: molecular magnetism, spin crossover, Fe-phen, Au(111), spin state locking

(Some figures may appear in colour only in the online journal)

1. Introduction

The iron(II) spin crossover complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (phen = 1,10-phenanthroline), dubbed Fe-phen in this paper and shown schematically in figure 1(a), belongs to some of the first known and most extensively studied compounds of iron(II) exhibiting a high-spin state (HS) to low-spin state (LS) transition [1]. The spin crossover (SCO) of Fe-phen is usually induced thermally: crystals of Fe-phen exhibit a steep spin transition within a few degrees around 175 K [1–8], with a hysteresis of <0.5 K in width [2].

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At the origin of this spin state transition is the temperature-dependent entropy contribution to the Gibbs–Helmholtz equation, which is small at low temperatures so that the enthalpically favored low-spin state is observed, and which dominates at higher temperatures favoring the high-spin state. Concomitant with the spin state transition is a change of the bond lengths of the molecular ligands to the Fe(II) and a change of the splitting of the 3d levels t_{2g} and e_g . Typically, at low temperatures, the t_{2g} – e_g splitting is increased to a point where the electronic level occupation does not follow Hund’s rules anymore. The six 3d electrons of Fe(II) then all occupy the t_{2g} level, forming an LS-state with $S = 0$. Above the SCO the t_{2g} – e_g splitting is appropriately reduced so that Hund’s rules are obeyed and the HS state with $S = 2$ is formed. The SCO is, in general and for a broad range of iron(II) SCO complexes, very susceptible to manipulation

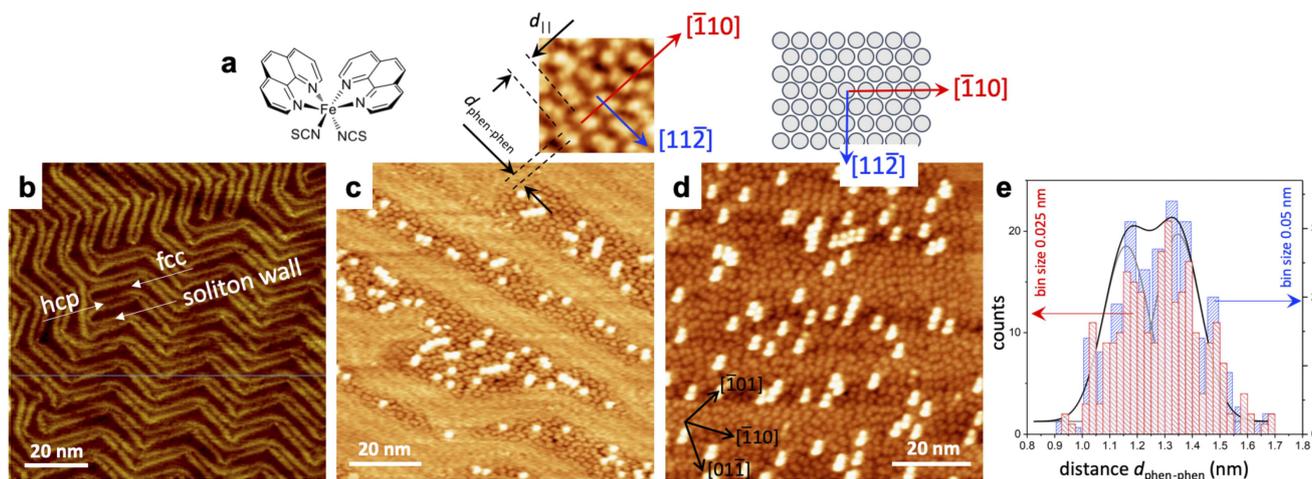


Figure 1. (a) Schematic structure of $\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2$, dubbed Fe-phen. (b) STM image of the Au(111) surface at 300 K. The ‘herringbone’ reconstruction, featuring domains of fcc and hcp stacking which are separated by soliton walls, is clearly visible. (c) Approx. 0.3 ML of Fe-phen on Au(111). Molecules appear as two-lobe structures in the images. The Fe-phen occupy the fcc sites exclusively. (d) Near full-monolayer coverage of Fe-phen. Top: magnified area of a similar sample area, and a structure model of a fcc (111) surface, highlighting molecular rows that are aligned along the $[\bar{1}10]$ direction, with the molecules’ phen groups pointing along the $[11\bar{2}]$ direction. (e) Histogram of $d_{\text{phen-phen}}$ values, defined in (a) and measured in multiple STM images. The histogram suggests a binary distribution for $d_{\text{phen-phen}}$, for two bin sizes, as shown. A double Gaussian peak is shown as a guide to the eye. Scan parameters: 600 pA, 1 V (c) and 500 pA, 1 V (d) and magnified area.

via external parameters, as has been demonstrated in numerous studies [9]. For instance, the SCO temperature can be manipulated with magnetic fields [3], or via dipolar additives such as *p*-benzoquinonemonoimine zwitterions [10, 11].

The recent demonstration of nonvolatile isothermal reversible voltage control of the spin state of $\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{bipy})$, and the accompanying conductance change [12], suggests that device applications are possible, at room temperature. Yet the use of single molecules as switches in high density memory devices, for example, is only possible if the interaction of the molecules with the supporting substrate is appropriately designed. While it is absolutely possible to manipulate the spin state of single molecules with the tip of a scanning tunneling microscope, as was demonstrated by Miyamachi *et al* [13], it appears that the strong molecule–substrate interaction with metallic substrates is generally an impediment; it tends to lock the spin state of the molecules in both the HS state and the LS state at temperatures below and above the transition temperature [13–16].

Several highly promising studies show that clever engineering of the interface between SCO complexes and a supporting substrate can in fact help to manipulate the SCO behavior of such complexes and potentially be exploited as a control parameter. For instance, partial electronic decoupling of the Fe-phen complexes from a Cu(100) substrate by a monolayer thin CuN buffer layer helped unlock the spin state, which made the local manipulation of the spin state possible [13]. Indeed, substrate modification is seen to have an enormous effect of the spin crossover in $\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{bipy})$ [11, 12, 17] and the SCO complex $\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{phenme}_4)$ [18]. In another study, Bernien *et al* have been able to discover that the SCO complex $\text{Fe}(\text{bpz})_2(\text{phen})$ is only weakly interacting with HOPG substrates, which they exploited to

accomplish reversible light-induced switching of the spin state [19].

Although the fragmentation of $\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{phen})$ [20] and $\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{phenme}_4)$ [21] have been observed, the adsorption of spin crossover molecules on the surface of gold remains of considerable interest. Specifically, the $22 \times \sqrt{3}$ —reconstructed Au(111) surface, widely known as ‘herringbone’ reconstruction, appears to be an interesting electronic template to influence the arrangement and the properties of SCO molecular adsorbates. Because of this reconstruction, the layer stacking at the surface of Au results in both hcp and fcc domains, which are separated by soliton walls formed by intermediate stacking, see figure 1(b) [22, 23]. Several studies showed that the hcp and fcc domains also exhibit different electronic properties such as different electron potential [24] and adsorption strength [25, 26]. Adsorbates bind preferentially to the hcp and fcc regions and typically bind very weakly or not at all to the soliton walls [25, 27]. Among the adsorbates that exclusively bind to the fcc-regions at low coverage are 1-nitronaphthalene molecules [28] and pristine sulfur [29]. Sulfur adsorbates at the fcc-like regions exert pressure on the soliton walls, distorting them, until the soliton walls collapse at higher coverage, lifting the reconstruction over extended areas.

To explore the connection between the molecular adsorption of SCO complexes on metallic substrates further, we investigated here the adsorption of Fe-phen on the reconstructed Au(111) surface at very low coverage. The Fe-phen contains two NCS groups, which are expected to bind to the Au surface with their sulfur atoms and are thus expected to show similar site selectivity as pure sulfur atoms. This study is thus complementary to the work by Gruber *et al* [30] and Miyamachi *et al* [13] in which the spin state of the Fe-phen

molecules in the first and second layer on various metallic substrates was investigated.

2. Experimental details

The $\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2$ complex was synthesized as described previously [31]. Molecular thin films were deposited for this study under ultrahigh vacuum (UHV) using a home-built Knudsen-like molecular evaporator. Single crystal Au(111) substrates were used, which were prepared under UHV following a standard procedure consisting of repeated cycles of Ar^+ ion sputtering and annealing to 650°C . Substrate cleanliness was checked with STM and inferred from the presence of the typical ‘herringbone’ reconstruction, as seen in figure 1(b). Scanning tunneling microscopy (STM) and x-ray photoemission spectroscopy (XPS) measurements were performed *in situ* immediately following the sample growth in UHV. STM measurements were carried out using an Omicron VT-STM at room temperature. XPS measurements were carried out in the same UHV system, using a non-monochromatized $\text{Al K}\alpha$ x-ray source, with a photon energy of 1486.6 eV, and an SPECS PHOIBOS 150 energy analyzer. The core level binding energies were calibrated to a gold reference, with the $\text{Au } 4f_{7/2}$ core level peak placed at 84 eV at room temperature. The CasaXPS software was used to analyze the XPS core level spectra. A Shirley-type background was subtracted to obtain x-ray photoemission core level spectra peak areas [32].

3. Results and discussion

Figure 1 shows STM images of a clean and reconstructed Au(111) surface (b), along with a sub-monolayer coverage of Fe-phen molecules on Au(111) (c) and a nearly full monolayer of Fe-phen on Au(111) (d). Each molecule appears as two bright lobes in the images. It has been argued previously that the Fe-phen attaches with the NCS groups to the Au surface [13] due to the strong affinity of sulfur bonding to Au(111) [29]. Thus, the two phenanthroline (phen) moieties of each molecule point away from the surface, and they appear in STM images as two lobes. From the alignment and the spacing of the molecular phen groups we can therefore infer the alignment and potentially even the spin state of the molecules, as was demonstrated by Miyamachi *et al* [13].

At sub-monolayer coverage of Fe-phen, of the order of 0.1–0.3 ml, figure 1(c), we observe that the molecules condense into solid islands on the fcc sites of the Au(111) surface. Some fraction of the molecules in these islands appears in the second layer on top of first-layer islands, visible as nearly white lobes, but we never observe the condensation of molecules at the hcp-sites or on top of the soliton walls. The herringbone reconstruction has noticeably changed as compared to the reconstruction seen on the clean Au surface in (b). It makes sense to attribute this change in reconstruction to the chemisorption of the NCS-group containing molecules, in analogy to the published results on sulfur adsorption on Au(111) [29].

The crystallographic directions on the Au surface were determined in low energy electron diffraction experiments. We can therefore establish the adsorption geometry of the Fe-phen molecules. Inspection of figures 1(c) and (d), and the magnified area in figure 1(a), shows that often the molecules stack to form 1D chains on the Au surface. These chains run along the $\langle 110 \rangle$ directions of the Au(111) surface, whereas the two molecular phen groups point perpendicular to the chains, along $\langle 112 \rangle$. The spacing between neighboring molecules along the chains, d_{\parallel} , has been determined to be $d_{\parallel} = 2.66 \pm 0.19$ nm. A comparison with the nearest neighbor distance between atoms of Au along $[\bar{1}10]$, $d_{110} = 2.87$ Å, suggests that $d_{\parallel} \sim 9 * d_{110} = 2.58$ nm, or in other words, Fe-phen molecules adsorb approximately every 9 atomic Au spacings of the surface in the $\langle 110 \rangle$ -directions.

The center-to-center separation of the Fe-phen molecules, $d_{\text{phen-phen}}$ in figure 1(a), was measured with STM on a significant number of molecules, and is shown in the histogram in figure 1(e). The histogram is shown for 2 different bin sizes, 0.025 nm (red) and 0.05 nm (blue) to test the shape of the distribution, given the comparatively small number of counts per bin. Since the quantity $d_{\text{phen-phen}}$ is, in principle and with limitations, reflective of the spin state of the molecules [13], we wanted to test whether our experimental data show the presence of Fe-phen molecules in both spin states. Indeed, the histograms with both bin sizes seem to suggest the presence of a double peak distribution, with two mean values for $d_{\text{phen-phen}}$ of 1.15 nm and 1.35 nm. However, we caution that this impression of a double peak could entirely be due to poor statistics. In average, we find a mean value for $d_{\text{phen-phen}} = 1.25$ nm in the $\langle 112 \rangle$ directions, which corresponds to a distance of five atomic spacings in this direction, $5 * d_{112} = 5 * 2.48$ Å = 1.24 nm. The small variations in spacing and the clear symmetry of the imaged molecules allow us to confirm, consistent with prior results [13, 30], that Fe $(1,10\text{-phenanthroline})_2(\text{NCS})_2$ does not fragment on Au(111).

The Fe $2p_{3/2}$ and $2p_{1/2}$ core level photoemission peaks of a full monolayer of Fe-phen on Au(111) show little change at 300 K and at 102 K, i.e. above and below the spin crossover temperature, as shown in figure 2. The Fe $2p_{3/2}$ and $2p_{1/2}$ peaks appear significantly broadened compared to those of pristine Fe, exhibiting a characteristic shoulder on the high energy side. Reasons for this peak broadening have been discussed elsewhere [15, 33–36]. We performed a peak fitting procedure that considers a split $2p_{3/2}$ peak (1, 2) and two shake-up satellite peaks (3, 4), together with a pre-peak (5), as shown on the example of the 300 K data in figure 2. We find for the $2p_{3/2}$ peak splitting, however, that the higher energy peak is of comparatively small intensity. The fits performed on both the RT spectra and the LT spectra in figure 2 are nearly identical.

Splitting is expected for $2p_{3/2}$ XPS core level spectra of Fe species with unpaired spin, i.e. for Fe species in the HS state, and might be absent in the XPS spectra if the Fe species are in the LS state due to paired spins [33, 37–39]. Because of the complications of changing conductance with changes in spin state, as has been seen for Fe $(1,10\text{-phenanthroline})_2(\text{NCS})_2$ [13, 30] and other spin crossover molecular complexes [8, 12,

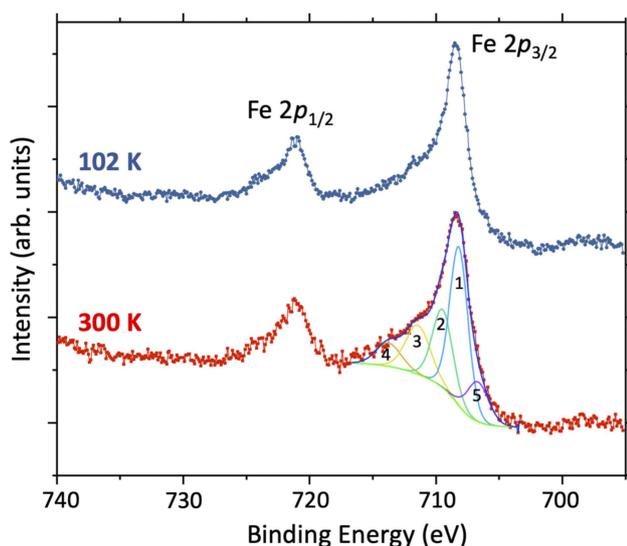


Figure 2. XPS Fe 2p core level spectra of a monolayer of $\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2$ on Au(111) at 102 K (blue) and 300 K (red). See text for a discussion of the multi-peak fit.

40–43], potentially altering the intensities of multiplets and potential two hole bound state photoemission satellite features, and given that there is no Fe^{2+} and Fe^{3+} valence state change across the spin crossover, XPS is not, however, a reliable indicator of a change in spin state.

The absence of change in the XPS, over a wide range of temperature, is, nonetheless, consistent with an absence of molecular fragmentation and a molecular layer whose spin state is frozen. The close proximity of the molecules to the substrate and particularities of the binding geometry can affect the molecular conformation, and thus determine the spin state, typically locking the adlayer spin state [13–16], sometimes into a mixture of high and low spin states, as was discussed above. It is therefore reasonable to conclude that the spin state configuration of our samples does not change noticeably in the temperature range investigated, meaning that the Fe-phen on Au(111) exhibits a locked and mixed spin state for an as-deposited SCO monolayer, just as has been seen for the Fe-phen SCO complex on Cu(100) [13]. We would like to point out that synchrotron-based XPS measurements have been used successfully to determine the spin state of SCO complexes [11], and thus, x-ray absorption spectroscopy (XAS) should be done also for this system to conclusively prove this contention.

4. Conclusion

The adsorption of Fe-phen SCO complexes on the reconstructed Au(111) is highly site-selective as molecules are found to occupy the fcc-domains of the herringbone reconstruction exclusively. The two NCS moieties of the molecules are assumed to bind to Au through the sulfur atoms and this geometry alters, and in fact removes, the herringbone reconstruction. Typically, the molecules arrange themselves in densely packed 1D rows, which are oriented along the $\langle 110 \rangle$

directions of the Au surface. Each molecule straddles over a distance of 5 atomic spacings in the $\langle 112 \rangle$ directions. Experimental data are consistent with a locked molecular spin state in the temperature range between 100 K and 300 K and in the sub-monolayer regime. This study does contribute to our understanding of how interfaces could be leveraged to manipulate the spin state and the spin crossover in SCO complexes and shows an avenue for the structural patterning of functional molecular films. The results also have implications for the use of gold as electrodes in devices built from organic substances.

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References

- [1] Baker W A and Bobonich H M 1964 *Inorg. Chem.* **3** 1184
- [2] Muller E W, Spiering H and Gutlich P 1982 *Chem. Phys. Lett.* **93** 567
- [3] Qi Y, Muller E W, Spiering H and Gutlich P 1983 *Chem. Phys. Lett.* **101** 503
- [4] Lee J J, Sheu H S, Lee C R, Chen J M, Lee J F, Wang C C, Huang C H and Wang Y 2000 *J. Am. Chem. Soc.* **122** 5742
- [5] Ganguli P, Gutlich P, Muller E W and Irlner W 1981 *J. Chem. Soc., Dalton Trans.* 441
- [6] König E and Madeja K 1967 *Inorg. Chem.* **6** 48
- [7] Moulin C C D, Rudolf P, Flank A M and Chen C T 1992 *J. Phys. Chem.* **96** 6196
- [8] Zhang X *et al* 2015 *J. Phys. Chem. C* **119** 16293
- [9] Gutlich P, Garcia Y and Goodwin H A 2000 *Chem. Soc. Rev.* **29** 419
- [10] Costa P, Hao G H, N'Diaye A T, Routaboul L, Braunstein P, Zhang X, Zhang J, Doudin B, Enders A and Dowben P A 2018 *J. Phys.: Condens. Matter.* **30** 305503
- [11] Zhang X *et al* 2017 *Adv. Mater.* **29** 1702257
- [12] Hao G *et al* 2019 *Appl. Phys. Lett.* **114** 032901
- [13] Miyamachi T *et al* 2012 *Nat. Commun.* **3** 938
- [14] Pronschinske A, Chen Y, Lewis G F, Shultz D A, Calzolari A, Nardelli M B and Dougherty D B 2013 *Nano Lett.* **13** 1429
- [15] Beniwal S, Zhang X, Mu S, Naim A, Rosa P, Chastanet G, Letard J F, Liu J, Sterbinsky G E, Arena D A, Dowben P A and Enders A 2016 *J. Phys.: Condens. Matter.* **28** 206002
- [16] Gruber M, Davesne V, Bowen M, Boukari S, Beaurepaire E, Wulfhekel W and Miyamachi T 2014 *Phys. Rev. B* **89** 195415
- [17] Zhang X, Palamarciuc T, Letard J F, Rosa P, Lozada E V, Torres F, Rosa L G, Doudin B and Dowben P A 2014 *Chem. Commun.* **50** 2255
- [18] Ossinger S *et al* 2017 *J. Phys. Chem. C* **121** 1210

- [19] Bernien M *et al* 2015 *ACS Nano* **9** 8960
- [20] Gopakumar T G *et al* 2013 *Chemistry* **19** 15702
- [21] Naggert H, Rudnik J, Kipgen L, Bernien M, Nickel F, Arruda L M, Kuch W, Nather C and Tucek F 2015 *J. Mater. Chem. C* **3** 7870
- [22] Barth J V, Brune H, Ertl G and Behm R J 1990 *Phys. Rev. B* **42** 9307
- [23] Wöll C, Chiang S, Wilson R J and Lippel P H 1989 *Phys. Rev. B* **39** 7988
- [24] Burgi L, Brune H and Kern K 2002 *Phys. Rev. Lett.* **89** 176801
- [25] Sykes E C H, Mantooth B A, Han P, Donhauser Z J and Weiss P S 2005 *J. Am. Chem. Soc.* **127** 7255
- [26] Bohringer M, Morgenstern K, Schneider W D, Wuhn M, Woll C and Berndt R 2000 *Surf. Sci.* **444** 199
- [27] Baber A E, Jensen S C and Sykes E C 2007 *J. Am. Chem. Soc.* **129** 6368
- [28] Bohringer M, Morgenstern K, Schneider W D and Berndt R 2000 *Surf. Sci.* **457** 37
- [29] Walen H, Liu D J, Oh J, Lim H, Evans J W, Kim Y and Thiel P A 2015 *J. Chem. Phys.* **143** 014704
- [30] Gruber M, Miyamachi T, Davesne V, Bowen M, Boukari S, Wulfhekel W, Alouani M and Beaurepaire E 2017 *J. Chem. Phys.* **146** 092312
- [31] Madeja K and König E 1963 *J. Inorg. Nucl. Chem.* **25** 377
- [32] Shirley D A 1972 *Phys. Rev. B* **5** 4709
- [33] Grosvenor A P, Kobe B A, Biesinger M C and McIntyre N S 2004 *Surf. Interface Anal.* **36** 1564
- [34] Gupta R P and Sen S K 1975 *Phys. Rev. B* **12** 15
- [35] Gupta R P and Sen S K 1974 *Phys. Rev. B* **10** 71
- [36] Cao S, Paudel T R, Sinha K, Jiang X Y, Wang W B, Tsymbal E Y, Xu X S and Dowben P A 2015 *J. Phys.: Condens. Matter.* **27** 175004
- [37] Pronschinske A, Bruce R C, Lewis G, Chen Y, Calzolari A, Buongiorno-Nardelli M, Shultz D A, You W and Dougherty D B 2013 *Chem. Commun.* **49** 10446
- [38] Ellingsworth E C, Turner B and Szulczewski G 2013 *RSC Adv.* **3** 3745
- [39] Matienzo L J, Yin L I, Grim S O and Swartz W E 1973 *Inorg. Chem.* **12** 2762
- [40] Aravena D and Ruiz E 2012 *J. Am. Chem. Soc.* **134** 777
- [41] Gopakumar T G, Matino F, Naggert H, Bannwarth A, Tucek F and Berndt R 2012 *Angew. Chem., Int. Ed. Engl.* **51** 6262
- [42] Mahfoud T, Molnar G, Bonhommeau S, Cobo S, Salmon L, Demont P, Tokoro H, Ohkoshi S, Boukheddaden K and Bousseksou A 2009 *J. Am. Chem. Soc.* **131** 15049
- [43] Rotaru A, Gural'skiy I A, Molnar G, Salmon L, Demont P and Bousseksou A 2012 *Chem. Commun.* **48** 4163