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# Quantum Dynamics of a Single Molecule Magnet on Superconducting Pb(111)

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## Abstract

Magnetic materials interfaced with superconductors may reveal new physical phenomena with potential for quantum technologies. The use of molecules as magnetic components has already shown great promise, but the diversity of properties offered by the molecular realm remains largely unexplored. Here we investigate a sub-monolayer of tetrairon(III) propeller-shaped single molecule magnets deposited on a superconducting lead surface. This materials combination reveals a strong influence of the superconductor on the spin dynamics of the single molecule magnet. It is shown that the superconducting transition to the condensate state switches the single molecule magnet from a blocked magnetization state to a resonant quantum tunnelling regime. Our results open perspectives for controlling single molecule magnetism via superconductors and for using single molecule magnets as local probes of the superconducting state.

33 Interfaces between superconducting and ferromagnetic materials are widely investigated for the  
34 richness of the novel physical phenomena they exhibit, which hold great potential in spintronics and  
35 quantum information technologies.<sup>1</sup> Among them, infinite magnetoresistance was observed in spin-  
36 valves embedding superconducting layers between ferromagnetic electrodes.<sup>1</sup> The intercalation of a  
37 ferromagnetic layer in a Josephson junction introduces a tunable phase shift allowing control of  
38 quantum circuits.<sup>1</sup>

39 As far as molecular spins are concerned, scanning tunnelling spectroscopy in the proximity  
40 of flat paramagnetic molecules deposited on ultrathin superconducting layers provided examples of  
41 local quasiparticle excitations within the superconducting gap, giving rise to localized magnetic  
42 states known as Yu–Shiba–Rusinov (YSR) bound states.<sup>2–4</sup> Monolayers of paramagnetic molecules  
43 can also influence the critical temperature of a thin superconducting layer,<sup>3,5,6</sup> and exhibit increased  
44 spin lifetimes on superconducting bulk crystals.<sup>7</sup> However, the use of a superconducting substrate to  
45 manipulate the magnetism of molecular magnets is, to the best of our knowledge, unexplored.

46 Among molecular magnets, molecules showing a directionally bistable magnetic moment  
47 are known as single molecule magnets (SMMs). They combine a large molecular spin with an easy-  
48 axis magnetic anisotropy, which leads to an energy barrier opposing to the reversal of the  
49 magnetization.<sup>8</sup> Moreover, quantum phenomena in the spin dynamics make this class of  
50 nanomagnetic objects very appealing for spintronics and quantum computing.<sup>9</sup> Notably, Grover’s  
51 algorithm has been implemented on a single nuclear spin by embedding a SMM in a nanojunction.<sup>10</sup>

52 SMMs allowing the realization of a well-defined molecule-superconductor hybrid interface  
53 are limited. Tetrairon(III) complexes<sup>11</sup> ( $\text{Fe}_4$ ) with a propeller shape (Figure 1a) constitute one of the  
54 few families of SMMs that have been studied in detail when deposited on a metallic substrate.<sup>12–15</sup>  
55 Hybrid interfaces were obtained from solution,<sup>12,13</sup> as well as via thermal sublimation in ultra high  
56 vacuum (UHV) conditions.<sup>14</sup> In both cases, at variance with other SMM complexes,<sup>16–19</sup> the  
57 magnetic bistability was found to persist at sub-monolayer coverage thanks to the efficient  
58 protection of the magnetic core exerted by the ligand shell.

59 Here we report the investigation of a sub-monolayer of  $\text{Fe}_4$  SMMs on lead, a type I  
60 superconductor. We studied the structural and chemical properties of the  $\text{Fe}_4$  monolayer by  
61 combining scanning tunnelling microscopy (STM) with photoelectron spectroscopies flanked by  
62 density functional theory (DFT) calculations. We employed X-ray magnetic circular dichroism  
63 (XMCD) to observe the magnetic fingerprint of the molecular layer and investigate its magnetic  
64 hysteresis on the superconductive substrate. The results show that the magnetization dynamics of  
65 the SMMs is influenced by the superconductive (SC) transition to the condensate state.

66  **$\text{Fe}_4\text{SMe}$  on  $\text{Pb}(111)$ : surface preparation and characterization**

<<< INSERT FIGURE 1 SINGLE COLUMN AROUND HERE >>>

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68

69 In the structure of Fe<sub>4</sub> SMMs, [Fe<sub>4</sub>(L<sup>R</sup>)<sub>2</sub>(dpm)<sub>6</sub>], the magnetic core is held together by tripodal  
70 ligands (L<sup>R</sup>)<sup>3-</sup> = [RC(CH<sub>2</sub>O)<sub>3</sub>]<sup>3-</sup> located on either side of the molecular plane, whereas  
71 dipivaloylmethanido ligands (dpm<sup>-</sup>) are found at the periphery (Figure 1a).<sup>11</sup> The bridging oxygen  
72 atoms of the tripods promote antiferromagnetic interactions between the  $s = 5/2$  spins of central and  
73 peripheral Fe<sup>3+</sup> ions. The resulting ground state has total spin  $S = 5$  and is well separated (ca. 55-65  
74 K<sup>20</sup>) from the excited  $S = 4$  states. The ground manifold is dominated by a moderate uniaxial  
75 magnetic anisotropy,  $\hat{H}_{an} = D\hat{S}_z^2$ , along the idealized C<sub>3</sub> molecular axis ( $z$ ), which is oriented  
76 normal to the molecular plane. The anisotropy is of the easy-axis type with  $D/k_B \sim -0.6$  K and  
77 creates an energy barrier  $|D/k_B|S^2 \sim 15$  K. Magnetic bistability is thus observable in the hysteresis  
78 loops only at temperatures below 1 K. The loops present the butterfly shape typical of resonant  
79 quantum tunnelling of the magnetization (QTM) in zero field.<sup>8</sup>

80 As a key feature, Fe<sub>4</sub> complexes can be tailored by proper choice of R substituent on tripodal  
81 ligands while only marginally affecting magnetic properties. With R = Ph the molecules sublime  
82 in UHV conditions but the bulky Ph group limits the formation of perfectly ordered monolayers.<sup>14</sup>  
83 On the contrary, Fe<sub>4</sub> SMMs with R = H, deposited using electrospray, adopt a flat adsorption  
84 geometry (*i.e.* with the plane defined by the Fe atoms parallel to the surface) and form an ordered  
85 hexagonal layer.<sup>21-23</sup>

86 After careful screening of alternative substituents, we found that when R = CH<sub>2</sub>SMe (see  
87 tripodal ligand in Figure 1a), the Fe<sub>4</sub> complex is compact enough to warrant the formation of a well  
88 ordered 2D lattice but also presents the necessary thermal stability to allow sublimation. The  
89 synthesis of the new proligand H<sub>3</sub>L<sup>CH<sub>2</sub>SMe</sup> and of its tetrairon(III) complex (Fe<sub>4</sub>SMe hereafter), are  
90 described in the Supplementary Note 1. Structural characterization by X-ray diffraction (see  
91 Supplementary Note 2) revealed the typical pseudo-three-fold symmetry. Characterization of the  
92 magnetic properties by DC and AC methods, flanked by high-frequency electron paramagnetic  
93 resonance (EPR) spectroscopy, confirmed the dominating uniaxial magnetic anisotropy with spin  
94 Hamiltonian parameters in line with other derivatives of the same family (see Supplementary Note  
95 3).

96 A Pb single crystal exposing the (111) face was selected as the substrate for molecular  
97 deposition. Lead behaves as a superconductor below the critical temperature ( $T_C$ ) of 7.2 K and  
98 critical field ( $B_C$ ) of 0.08 T.<sup>24</sup> In this field region, Fe<sub>4</sub> SMMs display enhanced magnetic bistability  
99 because resonant quantum tunnelling is suppressed.

100 Molecules were deposited by thermal sublimation on a clean Pb(111) surface to obtain a  
101 sub-monolayer coverage (see Methods). Different magnifications of STM images of the molecular  
102 film are reported in Figure 2. Islands of Fe<sub>4</sub>SMe molecules partially cover the Pb surface. They  
103 show a highly ordered hexagonal pattern with a periodicity of 1.7(2) nm. A detailed analysis of the  
104 STM height profiles before and after molecular deposition is provided in the Supplementary Note 4.  
105 Different orientations of Fe<sub>4</sub>SMe molecular pattern, specifically addressed in Extended Data Fig.  
106 2a, are observed and locally produce disordered areas at the borders of adjacent islands. The steric  
107 hindrance of the CH<sub>2</sub>SMe group produces a tilted adsorption geometry (similarly to complexes with  
108 R = (CH<sub>2</sub>)<sub>5</sub>SAc and Ph on Au<sup>13,14</sup>). A closer look at the molecular layer (Figure 2b) indicates the  
109 presence of a superstructure of triangles formed by three molecular units. Triangles are packed with  
110 opposite orientation in a double row, or in a single row (Extended Data Fig. 2b).

111 In order to better understand the STM observations, we investigated the Fe<sub>4</sub>SMe/Pb(111)  
112 interface by theoretical methods. One single Fe<sub>4</sub>SMe molecule was optimized at the periodic DFT  
113 level of theory (see Methods). In the relaxed geometry, the idealized three-fold axis (see Figure 1b)  
114 forms an angle  $\Omega \sim 22^\circ$  with the surface normal ( $n$ ). This configuration is driven by van der Waals  
115 interactions of the Pb atoms with the sulphur atom and with the hydrogen atoms of two  
116 dipivaloylmethanido ligands positioned close to the surface. Moreover, DFT foresees a preferred  
117 atop interaction of S with a Pb atom, which is extracted by ca. 0.9 Å from the top layer.  
118 Calculations evidence a low adsorption energy thus suggesting a physisorption process, being the  
119 lysis of the S-Me bond sterically hindered.<sup>25</sup>

120

121 <<< INSERT FIGURE 2 DOUBLE COLUMN AROUND HERE >>>

122

123 The superstructure observed in the STM images can be reproduced through DFT modelling  
124 by taking into account three closely packed molecular units and allowing the structure to relax (see  
125 Methods). Extended Data Fig. 2d shows the minimum energy configuration where molecules retain  
126 their easy axes at 22° with the surface normal, and the easy-axis projections on the surface are  
127 arranged at 120° intervals. The simulated STM image of this structure (Figure 2d) well reproduces  
128 the observed triangular features.

129 A chemical analysis of the Fe<sub>4</sub>SMe/Pb(111) surface performed by X-ray photoelectron  
130 spectroscopy (XPS) confirmed the integrity of the molecular layer after the deposition process (see  
131 Supplementary Note 5). The electronic structure of the molecular film was studied by ultra-violet  
132 photoelectron spectroscopy (UPS), see Supplementary Note 6. The shape of the He(II) spectrum  
133 (see Supplementary Figure 10) is compatible with literature reports on layers of similar Fe<sub>4</sub>

134 complexes.<sup>26</sup> Furthermore, the comparison of the UPS spectrum with the corrected total density of  
135 states (c-TDOS) and with the single-element contributions of the molecules to the TDOS allowed a  
136 careful assignment of each spectral feature. Projected density of states (pDOS) provided more  
137 insights on the molecule/surface interaction. Being the Fermi region of relevance for  
138 superconductivity, we notice that the filled  $3d$  bands (alpha component) of the iron ions extend  
139 from -9 up to -1 eV with respect to the Fermi energy,  $E_f$ , while the empty ones are right above  $E_f$   
140 (see Extended Data Fig. 1b and Supplementary Note 7). Contributions of S, C, and O orbitals are  
141 also present in the range  $E_f \pm 1$  eV (see Extended Data Fig. 1b). To reveal any possible molecule-  
142 substrate hybridization, we computed the electron density difference between  $\text{Fe}_4\text{SMe}/\text{Pb}(111)$  and  
143 its separated components ( $\text{Fe}_4\text{SMe}$  and Pb substrate). Figure 1b shows that the largest difference is  
144 observed for the displaced Pb atom and the  
145  $\text{CH}_2\text{SMe}$  group; this indicates formation of a non-negligible covalent Pb-S interaction, leading to  
146 weak electronic hybridization. However, the spin density computed for the  $\text{Fe}_4\text{SMe}/\text{Pb}(111)$   
147 interface (see Extended Data Fig. 1b) reveals no sizeable spin delocalization on the Pb atoms. This  
148 result indicates that the ligand shell efficiently shelters the Pb surface from the  $\text{Fe}^{3+}$  ions.

#### 149 **Magnetic characterization of the molecular film**

150 The magnetic characterization of the  $\text{Fe}_4\text{SMe}$  sub-monolayer on  $\text{Pb}(111)$  was carried out using X-  
151 ray synchrotron light and a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator to access the mK temperature range (see  
152 Methods).<sup>27</sup> X-ray absorption spectra (XAS) were measured at the Fe  $L_{2,3}$  edges with the X-ray  
153 beam directed parallel to the applied magnetic field ( $B$ ) and forming a variable angle  $\theta$  with the  
154 surface normal (see inset in Figure 3d). Spectra were acquired at  $B = 3$  T and  $T = 220$  mK  
155 (nominally the lowest reachable temperature at the sample holder). At normal incidence ( $\theta = 0^\circ$ )  
156 XAS spectra obtained with positive ( $\sigma^+$ , red) and negative ( $\sigma^-$ , blue) circular polarization show the  
157 expected shape for a  $\text{Fe}_4$  complex (Figure 3a).<sup>12-14</sup> The normalized XMCD signal (see Methods)  
158 shows a dominant negative peak at 709.2 eV with an intensity of about 40%. The intensity and line  
159 shape are distinctive of  $\text{Fe}_4$  complexes, being a fingerprint of the antiparallel alignment of nearest-  
160 neighbouring spins in the ground state (Figure 1a).<sup>12-14,28</sup> A slightly lower intensity ( $\sim 37\%$ ) is  
161 observed at  $\theta = 45^\circ$  (Extended Data Fig. 3a), as expected for molecules with the preferential  
162 orientation suggested by STM images and DFT calculations.

163 X-ray natural linear dichroism (XNLD) was used to further assess molecular orientation at  
164 the  $\text{Pb}(111)$  surface. The XNLD spectrum (Figure 3b) is dominated by a dichroic signal at 709.2  
165 eV, whose amplitude (about 6%) is greater than found in other monolayers of  $\text{Fe}_4$  complexes.<sup>13</sup> It  
166 confirms a more pronounced alignment of the molecules, in line with STM and DFT findings.

167 The dynamics of the magnetization of the Fe<sub>4</sub>SMe layer on Pb(111) was studied at normal  
168 incidence ( $\theta = 0^\circ$ ) in the temperature range from 220 mK to 900 mK (Figure 3c) by monitoring the  
169 XMCD signal at its maximum intensity while sweeping the magnetic field in a continuous mode. At  
170 900 mK the hysteresis loop is practically closed; it opens progressively upon cooling and becomes  
171 almost temperature independent below 500 mK. This behaviour is typical of Fe<sub>4</sub> SMMs at the  
172 cross-over from a thermally activated relaxation mechanism to a tunnelling regime.<sup>29</sup>

173

174

<<< INSERT FIGURE 3 DOUBLE COLUMN AROUND HERE >>>

175

176 Magnetic hysteresis was also studied as a function of the incidence angle  $\theta$  at 220 mK  
177 (Figure 3d). The hysteresis curves are characterized by efficient QTM at zero field (“butterfly  
178 shape”), as found in other monolayer deposits of Fe<sub>4</sub> complexes.<sup>13,14</sup> At normal incidence, the  
179 hysteresis closes rather abruptly at about  $\pm 0.45$  T in correspondence to the first field-induced level  
180 crossing, *i.e.* where the  $m_S = \pm 5$  and  $m_S = \mp 4$  levels are degenerate, and QTM is enhanced.<sup>11,30</sup> By  
181 contrast, at  $\theta = 45^\circ$  we observe a gradual change of the magnetization from 0.45 T to 0.70 T.  
182 Geometrical arguments can explain this finding. According to DFT results, molecular easy axes are  
183 tilted by  $\Omega \sim 22^\circ$  from the surface normal and, in first approximation, distributed on the surface of a  
184 cone. While at  $\theta = 0^\circ$  the first level crossing occurs at the same field for all molecules, at  $\theta = 45^\circ$   
185 the angle between the external field and the molecular easy axis spans the interval  $45^\circ \pm \Omega$ , *i.e.* from  
186  $67^\circ$  to  $23^\circ$ . Since level crossing moves to higher fields with increasing angles, the hysteresis closes  
187 over a wider field range.

188

### 189 **Simulation of the hysteresis loops**

190 Simulation of the Fe<sub>4</sub>SMe magnetic hysteresis was performed starting from the spin Hamiltonian of  
191 the ground  $S=5$  state and computing the transition probabilities between the different sublevels.<sup>13</sup>  
192 Thermally-activated processes were treated considering the spin-phonon coupling explicitly, within  
193 the approximations presented in Ref. 8. An additional heuristic term was added to the transition  
194 rates to account for pure tunnelling between almost degenerate levels (see Supplementary Note 8).  
195 The resulting master equation was integrated using the kinetic Monte Carlo method to evaluate the  
196 time-dependent magnetization. The use of (variable-step) kinetic Monte Carlo, based on stochastic  
197 time increments, has the advantage of providing comparable accuracy with less computational  
198 resources compared to previously employed direct integration.<sup>13</sup> The latter, indeed, requires an  
199 appropriate *a priori* choice of the integration (fixed) time step.

200 Hysteresis loops were simulated by placing the molecular easy axes at  $22^\circ$  from the surface  
201 normal and optimizing the spin Hamiltonian parameters to the values reported in the Supplementary  
202 Note 8. The close agreement of the simulated and experimental curves over the whole temperature  
203 range here explored (see Figure 3c) indicates the reliability of this approach. Differences in the  
204 hysteresis loop for different incidence angles (Figure 3d) are also nicely reproduced.

205

### 206 **SMMs dynamics inside the superconducting window of lead**

207 We now focus on the dynamics of the magnetization of  $\text{Fe}_4\text{SMe}$  in the field range in which the  
208 substrate is superconductor ( $|B| < B_C$ ). Figure 4a shows an enlargement of the low field region of the  
209 hysteresis loop at  $\theta = 0^\circ$  and 220 mK (green circles), acquired at a lower field sweep rate (0.0025  
210 T/s) in order to increase the data resolution. Starting from high fields, when the applied field enters  
211 in the SC window ( $B < B_C$ ) the XMCD signal decreases, deviating significantly from the predicted  
212 squared behaviour around zero field (black line) and from the observed response of similar  
213 complexes on non-superconductive substrates<sup>27</sup> (a detailed comparison is available in Extended  
214 Data Fig. 4a). It can be noticed that the noise level in the experimental data increases significantly  
215 when the applied field exits from the SC window. Rapid variations of the magnetic induction  
216 around zero field are known to affect the efficiency of the photoelectrons leaving the sample and  
217 thus to influence the signal detection in the TEY mode (see Methods). Flux noise effects were also  
218 detected in SC circuits and attributed to the presence of  $\text{O}_2$  molecules.<sup>31,32</sup> However, a possible  
219 explanation for the observed asymmetry of the noise is that the magnetic induction of the molecular  
220 film has a mitigating effect on the photoelectrons. When the substrate enters the SC phase, the  
221 molecular layer is fully magnetized, and its magnetization gradually vanishes towards zero field. As  
222 the field is reversed and exits the SC window, the molecular layer is fully demagnetized, leading to  
223 an abrupt change in the local induction felt by the photoelectrons.

224

225 <<< INSERT FIGURE 4 DOUBLE COLUMN AROUND HERE >>>

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227

228 To minimize the noise, the XAS signal was recorded by switching the X-ray polarization at  
229 each sampled magnetic field. The field was ramped back to 1 T before measuring each point of the  
230 hysteresis in order to maintain a sweep rate similar to the continuous mode. The blue circles in  
231 Figure 4a represent the hysteresis data acquired in this “spot” mode. Also in this case, the  $\text{Fe}_4\text{SMe}$

232 magnetization decays below  $B_C$ , clearly evidencing that the SMMs in the monolayer experience the  
233 local field ( $B_{loc}$ ) generated by the superconductor.

234 The approximately linear decrease of the magnetization observed below  $B_C$  is in agreement  
235 with the transition of a type I superconductor to the intermediate state. In this state SC and normal  
236 (N) regions coexist in the metal.<sup>33</sup> In a simplified model, *i.e.* assuming a demagnetization factor  
237 equal to one, the SC fraction ( $f_S$ ) increases linearly by lowering  $|B|$  according to  $f_S \sim 1 - |B|/B_C$ .<sup>33</sup>  
238 Regions of the superconductor entering the complete Meissner state (light grey areas in Figure 4b)  
239 expel the applied magnetic field, pushing the field flux lines in the neighbouring N regions (dark  
240 grey in Figure 4b), where the magnetic field is pinned to the  $B_C$  value.<sup>33</sup> The relative amounts of SC  
241 and N regions vary with the applied magnetic field, as sketched in Figure 4b. Thus, each region of  
242 the superconductor experiences the transition to the Meissner state at different values of the applied  
243 field, ranging from  $B_C$  to zero field.

244 This scenario is expected to represent also our experimental conditions. Magneto-optical  
245 studies, indeed, revealed the presence of the intermediate state in disk-shaped lead crystals with  
246 similar size to ours.<sup>34,35</sup> The topology of the domains depends on the shape of the sample and the  
247 applied magnetic field. Their dimension ranges from micrometric to sub-mm size.<sup>34,35</sup> Being the  
248 size of the X-ray spot about 1 mm in diameter, the XMCD signal averages the response of SMMs  
249 lying on N and SC regions.

250 For  $B < B_C$ , SMMs experience a  $B_{loc}$  generated by the superconductor: those in the proximity  
251 of a normal region feel  $B_{loc} \sim B_C$  until that region enters into the Meissner state,  $B_M$  being the  
252 applied field at which this occurs. At this point, the molecules suddenly feel a local field  $B_{loc} \sim 0$ ,  
253 and magnetic relaxation by QTM becomes possible.

254 To reproduce the hysteresis curve, we simulated a set of hystereses assuming different  $B_M$   
255 values (Figure 4c), so as to describe SMMs that feel an abrupt transition from  $B_C$  to zero field at  
256 different times during the field scan. Taking into account the fractions of the substrate that  
257 experience different  $B_M$  values, and assuming a homogenous distribution of SMMs on the surface,  
258 we obtained the hysteresis curve shown as a red line in Figure 4a. In the SC window, the  
259 demagnetization of the Fe<sub>4</sub>SMe layer is calculated to occur linearly with the field, in good  
260 agreement with the experimental data. It is also interesting to analyse the branch of the hysteresis  
261 measured by increasing the field amplitude but with opposite polarity. Both experimental and  
262 calculated curves are close to zero. Indeed, Fe<sub>4</sub>SMe SMMs cannot be magnetized when the  
263 underlying Pb region exits the Meissner state, and the local field switches back to  $B_C$ . At this field,  
264 resonant quantum tunnelling is suppressed, and the magnetization is practically blocked over the

265 time scale of the hysteresis. The absence of a linear trend in this portion of the hysteresis allows  
266 excluding the presence of species behaving like normal paramagnets.

## 267 **Outlook**

268 The unprecedented combination of two materials, which are archetypes of two very different  
269 classes, *i.e.* superconductors and SMMs, has here provided the proof of principle of a novel  
270 mechanism for SMMs magnetization switching and SC sensing. The formation of the intermediate  
271 state in a type I superconductor induces the transition of Fe<sub>4</sub>SMe SMMs from the blocked  
272 magnetization to the resonant quantum tunnelling regime. Such a transition is promoted by the  
273 external field cancellation associated with the Meissner effect.

274 Fundamental for this achievement were (i) the chemical design of an evaporable Fe<sub>4</sub> SMM forming  
275 an ordered monolayer on the Pb substrate and (ii) the observation of hysteresis curves at sub-kelvin  
276 temperatures by XMCD. It is noteworthy that this surface-sensitive technique has been seldom  
277 employed to investigate superconductivity, as it is unable to detect the diamagnetic state of a SC.  
278 The few available XMCD studies have required the deposition of ferromagnetic overlayers.<sup>36</sup> At  
279 variance with ferromagnets, SMMs have the advantage of a non-cooperative hysteretic behaviour.  
280 Thus, when deposited on SC surfaces, SMMs are a sensitive local tool to monitor magnetic flux  
281 distribution of relevance for more complex domain structures, such as those observed in type II or  
282 2D superconductors. For the latter, we can also expect to have a mutual magnetic influence through  
283 space, *i.e.* the magnetic flux generated by the SMM can locally affect the SC. Particularly relevant  
284 for the scientific community would be the investigation of the SMM/SC interface by scanning  
285 probe techniques with magnetic sensing capabilities and high spatial resolution.

286 Equally relevant is the possibility to locally switch the SMM magnetization dynamics  
287 biasing the magnetic field at the superconductor transition. This effect is highly interesting for  
288 quantum information technologies and is expected to be particularly pronounced for lanthanoid-  
289 based SMMs, whose magnetization relaxation time can be enhanced by several orders of  
290 magnitude<sup>37</sup> in zero field.

## 291 **Data Availability**

292 Experimental data used to draw Fig. 3a-d and Fig.4a are included with the manuscript as source  
293 data. Additional data such as STM images, simulated hysteresis curves and DFT results are  
294 available from the authors on request.

## 295 **Code Availability**

296 The code to compute magnetic hysteresis using the kinetic Monte Carlo method is available from  
297 the ETH Zurich Data Archive: <http://doi.org/10.5905/ethz-XXXXX> (final doi to be inserted in  
298 proofs).

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377

## 378 **Methods**

### 379 **Synthesis and preparation of the hybrid interface**

380 Fe<sub>4</sub>SMe (isolated in crystalline form as the hemidiethylether solvate) was synthesized and  
381 chemically characterized at the University of Modena and Reggio Emilia. A detailed description of  
382 the synthetic procedure and selected characterization data are provided in the Supplementary  
383 Information, Note 1.

384 The Pb(111) crystal (disk-shaped, 4 mm of diameter and 3 mm thickness) was purchased from the  
385 Surface Preparation Laboratory – SPL (Zaandam, NL). Surface preparation and characterization  
386 were performed at the University of Florence. The Pb(111) surface was prepared by cycles of Ar  
387 sputtering (1 keV energy) and annealing at 470 K in Ultra High Vacuum (UHV) and controlled by  
388 XPS and STM measurements. Molecular deposition was performed by thermal sublimation in  
389 UHV. Crystals of Fe<sub>4</sub>SMe were crushed into a powder and inserted in a resistively heated quartz  
390 crucible. The powder was purified by repeated thermal treatment cycles to remove solvent  
391 residuals.

392 The deposition of the Fe<sub>4</sub>SMe sub-monolayer on lead was carried out in controlled atmosphere ( $P <$   
393  $10^{-10}$  mbar) at a temperature of about 490 K measured by a K-thermocouple in direct contact with  
394 the powder. The deposition rate was monitored by a quartz crystal microbalance placed in front of  
395 the crucible.

### 396 **Experimental characterization**

397 The STM characterization was carried out by an Omicron Variable-Temperature STM, where the  
398 sample was cooled down to 30 K by a liquid helium flux. Diffraction pattern images were acquired  
399 by Omicron Spectaleed rear view LEED optics. XPS characterization was performed with a micro-  
400 focused monochromatic Al K-alpha radiation source ( $h\nu = 1486.7$  eV), model SPECS XR-MS  
401 Focus 600, and a multichannel detector electron analyser, model SPECS Phoibos 150 1DL. XPS  
402 spectra were recorded in normal emission with the X-ray source mounted at an angle of  $54.44^\circ$  with  
403 respect to the analyser and using a pass energy of 40 eV. Spectra were calibrated using the  $\text{Pb}4f_{7/2}$   
404 component at 136.9 eV.<sup>38</sup> The spectra were fitted using a linear background and single peak  
405 components were deconvoluted by a mixed Gaussian and Lorentzian function. Spectra were  
406 analysed using the CasaXPS software. UPS characterization was carried out using a He (II) line  
407 (with an energy of 40.8 eV) by non-monochromatized gas discharge lamp (VG Scientific 22-101).  
408 The analyser was the same used for XPS with a pass energy of 10 eV and an entrance and an exit  
409 slit of  $3 \times 20$  mm. A fixed bias of  $-30$  V was applied to the sample to ensure the detection of all the  
410 photoelectrons.

411 XAS, XMCD, and XNLD experiments were carried out at the DEIMOS beamline (SOLEIL  
412 synchrotron, France) using the novel Dichro50 setup working in the mK temperature range.<sup>27</sup>  
413 Samples were prepared in Florence following the above-reported procedures and transferred to the  
414 beamline facilities using a UHV suitcase equipped with a D100 SAES Nextorr Neg - Ion  
415 Combination Pump that guaranteed a pressure  $P < 10^{-10}$  mbar during the transport. All the steps  
416 from sample preparation to synchrotron measurements were accomplished without breaking the  
417 vacuum connection ( $P < 10^{-9}$  mbar). XAS spectra were acquired in Total Electron Yield (TEY)  
418 mode.<sup>39</sup> The XMCD signals, calculated as the difference  $\sigma^- - \sigma^+$ , were normalized with respect to  
419 the  $L_3$  edge-jump of  $(\sigma^+ + \sigma^-)/2$  and expressed in percentage.<sup>15</sup> The XNLD signals were normalized  
420 with respect to the  $L_3$  edge-jump of the isotropic spectrum (*i.e.*  $1/3 \sigma^V + 2/3 \sigma^H$  when  $\theta = 45^\circ$ )<sup>40</sup> and  
421 expressed in percentage.

## 422 **Computational Methods**

423 All the periodic density functional theory calculations (pDFT) were performed with CP2K  
424 quantum chemistry software.<sup>41</sup> Gaussian plane waves formalism (GPW)<sup>42</sup> was employed to  
425 solve the eigenvalue problem. Norm-conserving Goedecker-Tetter Hutter (GTH)  
426 pseudopotentials,<sup>43</sup> along with double zeta basis set with polarization functions (DZVP-  
427 MOLOPT-SR)<sup>43</sup> were employed for all atoms. The cut-off energy for the plane-wave  
428 auxiliary basis set was set to 400 Ry. Meta-GGA RevPBE functional<sup>44,45</sup> with empirical  
429 dispersion correction RVV10<sup>46</sup> was used throughout all the calculations. Constant electronic  
430 smearing of 1500 K was applied to consider the metal character of the slab. The threshold

431 for the atomic forces during the geometry optimization runs was set to 0.003 Hartree/  $a_0$ ,  
432 where  $a_0$  is the Bohr radius ( $1 \text{ Hartree}/a_0 = 8.2387234983(12) \times 10^{-8} \text{ N}$ ). During the single  
433 SCF step the convergence criterion was set to a wavefunction gradient of  $1 \times 10^{-6}$ .  
434 Two different kinds of geometry optimizations were performed: the optimization of a single  
435  $\text{Fe}_4\text{SMe}$  molecule (A) and the optimization of the adduct made by three  $\text{Fe}_4\text{SMe}$  molecules  
436 (B). The dimensions of the periodic cell were set to  $31.5 \times 30.3 \times 60 \text{ \AA}$  for A and to  $45.5 \times$   
437  $42.42 \times 60 \text{ \AA}$  for B, in order to avoid interactions between replicas along both x and y  
438 directions and between slabs along the z direction. The Pb(111) surface was modelled with  
439 three slabs, each one made of  $9 \times 10$  Pb atoms for A and of  $14 \times 13$  for B. The bottom layer  
440 was kept fixed during all geometry optimizations, while the others were left free to relax.  
441 Such Pb(111) surface model was previously validated in Ref. 3, according to Ref. 47.  
442 The starting guess geometry for optimization B was the final geometry obtained from  
443 optimization A. The latter was indeed replicated by a rigid rotation of  $120^\circ$  and  $240^\circ$  along  
444 the normal to the surface.  
445 A total spin value corresponding to a broken symmetry state<sup>48</sup> with  $m_S = 5$  was chosen, with  
446 the central  $\text{Fe}^{3+}$  ion antiferromagnetically coupled with the three peripheral ones.

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470

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474 assistance in using the DEIMOS beamline. The European COST Action CA15128 MOLSPIN, the  
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#### 479 **Author contribution**

480 GS, LP, ALS, GC, and LM performed the synchrotron experiments with the assistance of EO, PS,  
481 and MM. LP, GS, BC, and ALS prepared and characterized the hybrid interface. MB and FT  
482 performed the DFT studies. FP and AC prepared and structurally characterized the Fe<sub>4</sub>SMe SMM.  
483 RS, ALB, and AC performed its bulk phase magnetic characterization. AV developed the kinetic  
484 Monte Carlo method and contributed with GS and RS to the simulation of the XMCD magnetic  
485 data. AC, FT, MM, and RS supervised the activities of the project. All authors contributed to the  
486 discussion and preparation of the manuscript.

487

#### 488 **Competing Interests**

489 The authors declare no competing interests.

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498 **Captions to Figures and Extended Data**

499

500 **Figure 1** (a) Structure of Fe<sub>4</sub>SMe in the crystalline phase (atom colour code: green = Fe, red = O,  
501 yellow = S, brown = C). For clarity, the carbon backbone is drawn using capped sticks. Hydrogen  
502 atoms are not shown. Arrows indicate the arrangement of spin vectors in the ground  $S = 5$  state. The  
503 tripodal ligand with the CH<sub>2</sub>SMe substituent is depicted in the rectangular panel (white capped  
504 sticks = H). (b) Stable structure of Fe<sub>4</sub>SMe on Pb(111) calculated by DFT, showing the deviation of  
505 the magnetic easy axis ( $C_3$ ) from the surface normal ( $n$ ). The computed electron density difference  
506 is also shown (the surfaces are drawn for a value of 0.0025 e bohr<sup>-3</sup>). Cyan and orange colours  
507 correspond to reduced and increased electron densities, respectively, as compared with non-  
508 interacting components (Pb surface and Fe<sub>4</sub>SMe).

509

510

511 **Figure 2** (a-c) STM images ( $V_{bias}=2.6$  V,  $I_{tunnel}=10$  pA) of the Fe<sub>4</sub>SMe sub-monolayer on Pb(111)  
512 at different magnifications. A portion of clean Pb(111) surface is visible in the top-right side of  
513 panel a. The dotted triangle in panel b highlights the molecular superstructure; a single molecular  
514 unit is indicated in shadow. (d) Simulated STM image of three molecules in the layer. Each Fe<sub>4</sub>SMe  
515 molecule appears as two main spots aligned with the projection of the easy axis, which is marked  
516 with a pink line in panels c and d; the brighter and dimmer spots correspond to the CH<sub>2</sub>SMe group  
517 pointing outward and to a tert-butyl group of the topmost dpm<sup>-</sup> ligand, respectively. The second  
518 CH<sub>2</sub>SMe group cannot be directly identified from the experimental images, but it lies just beneath  
519 the latter spot. Additional lateral spots can be attributed to the surrounding envelope of dpm<sup>-</sup>  
520 ligands.

521

522

523 **Figure 3** XMCD (a) and XNLD (b) spectra of Fe<sub>4</sub>SMe on Pb(111) at the Fe L<sub>2,3</sub> edges. XMCD  
524 signal (green) was obtained by recording XAS spectra with positive (red) and negative (blue)  
525 circular light polarization at  $T = 220$  mK,  $B = 3$  T and  $\theta = 0^\circ$ . XNLD signal (cyan) was obtained  
526 from the difference of the XAS spectra recorded with vertical (violet) and horizontal (orange) linear  
527 light polarization at 220 mK, 3 T and  $\theta = 45^\circ$ . Temperature (c) and angular (d) dependence of  
528 experimental (top) and simulated (bottom) hysteresis loops. In the temperature dependence,  
529 experimental data were recorded by monitoring the XMCD signal at 709.2 eV at different

530 temperatures (see legend) and normal incidence while sweeping the field continuously between -  
531 1.5/+1.5 T for right and left circular polarizations with a sweep rate  $v_{sweep} = 0.01$  T/s. In the  
532 angular dependence, experimental curves were recorded at  $\theta = 0^\circ$  (blue) and  $\theta = 45^\circ$  (dark red) at  
533 220 mK. Curves were simulated using the kinetic Monte Carlo approach (see text). In the  
534 simulations, the magnetic easy axes were arranged on the surface of a cone (a magnified version of  
535 the inset in panel d is shown in Extended Data Fig. 3d). Assuming a continuous distribution on the  
536 cone surface or 12 discrete orientations of the easy-axis projection, as suggested by STM analysis  
537 (see Extended Data Fig. 2a), yields virtually identical simulated curves. Thin (thick) lines and  
538 empty (filled) symbols represent upfield (downfield) hysteresis branches. Arrows help to visualize  
539 field scan direction in the simulated curves.

540

541 **Figure 4** (a) Experimental hysteresis loops acquired close to  $B_c$  (0.08T) at  $\theta = 0^\circ$  and 220 mK:  
542 green circles represent the hysteresis acquired by the continuous method ( $v_{sweep} = 0.0025$  T/s) while  
543 blue circles refer to spot XMCD values (spot method) recorded after magnetizing the sample at 1 T  
544 at each point (detailed explanation is given in the text). Hysteresis loops simulated without  
545 considering the SC substrate (black line) and introducing the effect of the SC substrate in the  
546 intermediate state (red line) are also shown. Thin (thick) lines and empty (filled) symbols represent  
547 upfield (downfield) hysteresis branches. Arrows help to visualize field scan direction in the  
548 simulated curves. (b) Scheme of the interaction of SMMs with the SC substrate during the transition  
549 to the intermediate state ( $|B| < B_c$ ). For  $|B| > B_c$  the molecular spin is aligned along the magnetic  
550 field direction;  $|B| = B_c$  represents the nominal transition of the type I superconductor to the  
551 condensate state. From  $B_c$  to zero field, growing substrate areas enter in the complete Meissner  
552 state (grey) thus excluding the external magnetic field ( $B_{loc} = 0$ ).  $\text{Fe}_4\text{SMe}$  molecules interacting with  
553 these regions feel a magnetic field drop to zero allowing them to bypass the anisotropy barrier via  
554 quantum tunnelling. (c) Simulated magnetization curves (upfield branch of the hysteresis loop) for  
555 molecules experiencing the SC transition of lead at different  $B_M$  and thus at different times in the  
556 hysteresis cycle. Simulated hysteresis loop, red line in panel a, was obtained taking into account a  
557 convolution of these hystereses (see text).

558

559 **Extended Data Fig. 1b.** (a) TDOS for Fe<sub>4</sub>SMe/Pb(111) (purple curve), and pDOS contributions  
560 from Fe<sub>4</sub>SMe (blue curve) and Pb(111) surface (red curve). A full width at half-maximum (FWHM)  
561  $\sigma=0.45$  eV was used. (b) pDOS of atomic contributions in Fe<sub>4</sub>SMe calculated on Fe<sub>4</sub>SMe/Pb(111)  
562 ( $\sigma=0.45$  eV). (c) Computed spin density for Fe<sub>4</sub>SMe on Pb(111). The surfaces are drawn for a value  
563 of 0.001 unpaired e bohr<sup>-3</sup>. Blue and pink colours correspond to spin up and spin down calculated  
564 spin densities, respectively. In the inset, arrows depict the arrangement of the spin vectors in the  $S =$   
565 5 ground state using the same colour code. We notice that a similarly negligible spin delocalization  
566 was observed for VOPc deposited on Pb with the vanadyl moiety pointing up, but the spin density  
567 increased significantly when the molecule was deformed by the STM tip (see Ref. 3). Here, a  
568 similar effect appears very unlikely due to the lack of spin density on atoms close to the Pb surface.  
569

570 **Extended Data Fig. 2a.** (a) Magnification of the STM image of Fe<sub>4</sub>SMe/Pb(111) in Figure 2a  
571 (main text). Orange and pink lines indicate the molecular easy axis projections on the surface. (b)  
572 Scheme of the 12 observed orientations of the C<sub>3</sub> molecular axis projection with respect to the  
573 crystallographic directions of the Pb(111) surface. The projection of the molecular C<sub>3</sub> axis lies  
574 along the main crystallographic directions of Pb(111), orange lines, or at 30° from them, pink lines  
575 (only  $[\bar{1}10]$  is shown in the STM image for convenience). (c) Low Energy Electron Diffraction  
576 (LEED), 60 eV, of the clean Pb(111) crystal used to identify the main crystallographic directions of  
577 the substrate, x axis corresponding to the STM scanning direction.

578

579

580 **Extended Data Fig. 2b.** Magnification of the STM image of Fe<sub>4</sub>SMe/Pb(111) in Figure 2b (main  
581 text). Single row (1) and double (2) arrangements of the triangular molecular Fe<sub>4</sub>SMe  
582 superstructures are highlighted.

583

584

585 **Extended Data Fig. 2d.** Top view of three Fe<sub>4</sub>SMe molecules on Pb(111) calculated by DFT; pink  
586 lines indicate the projections of molecular C<sub>3</sub> axes. This structure allows to explain the  
587 experimental STM topography of Figure 2c.

588

589

590 **Extended Data Fig. 3a.** XAS and XMCD signal measured at the Fe L<sub>2,3</sub> edges on Fe<sub>4</sub>SMe/Pb(111)  
591 at  $\theta=45^\circ$  ( $B=3$  T,  $T=220$  mK).

592

593

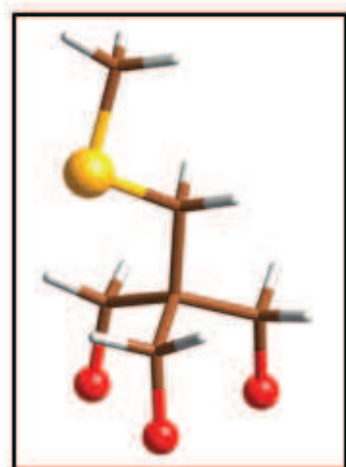
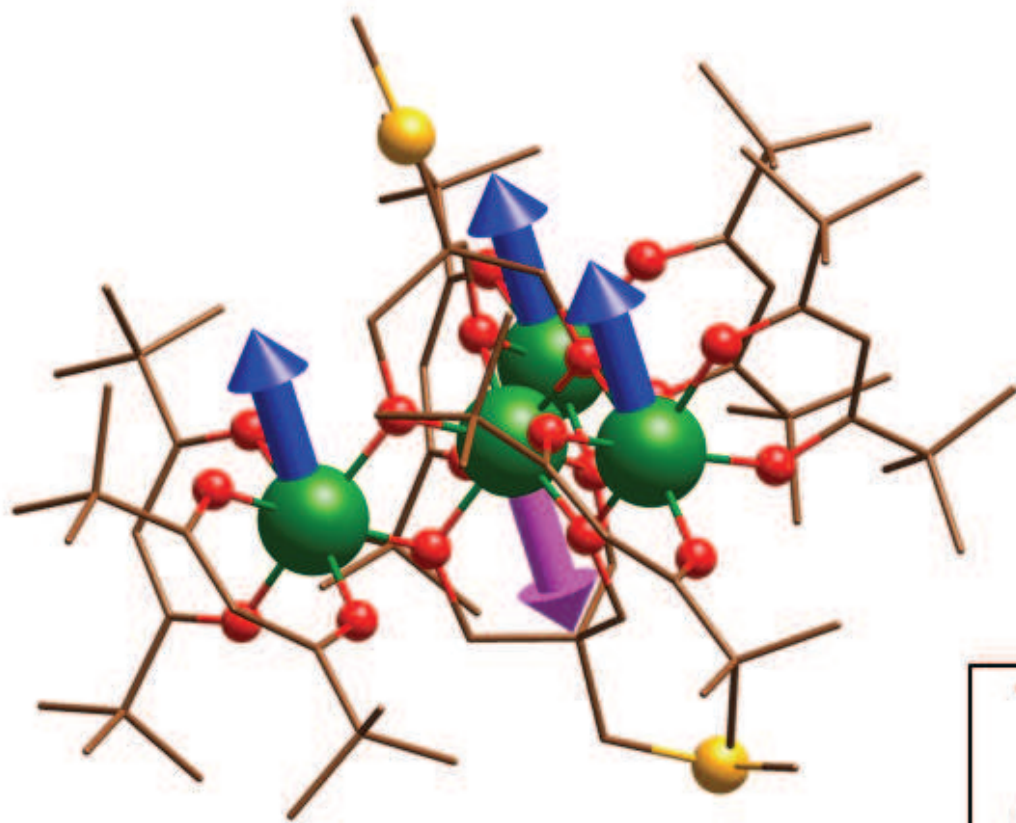
594 **Extended Data Fig. 3d.** Scheme of the distribution of Fe<sub>4</sub>SMe magnetic easy axes on the Pb(111)  
595 surface.

596

597

598 **Extended Data Fig. 4a.** (a) Enlarged version of Figure 4a (main text). (b) Magnetic hysteresis loop  
599 (grey spheres) of a monolayer of a Fe<sub>4</sub> complex on a normal metal (here on a gold substrate, see  
600 Ref. 27) in the same field region as panel a. The dark grey solid line is the hysteresis loop simulated  
601 disregarding the effect of the SC.

(a)

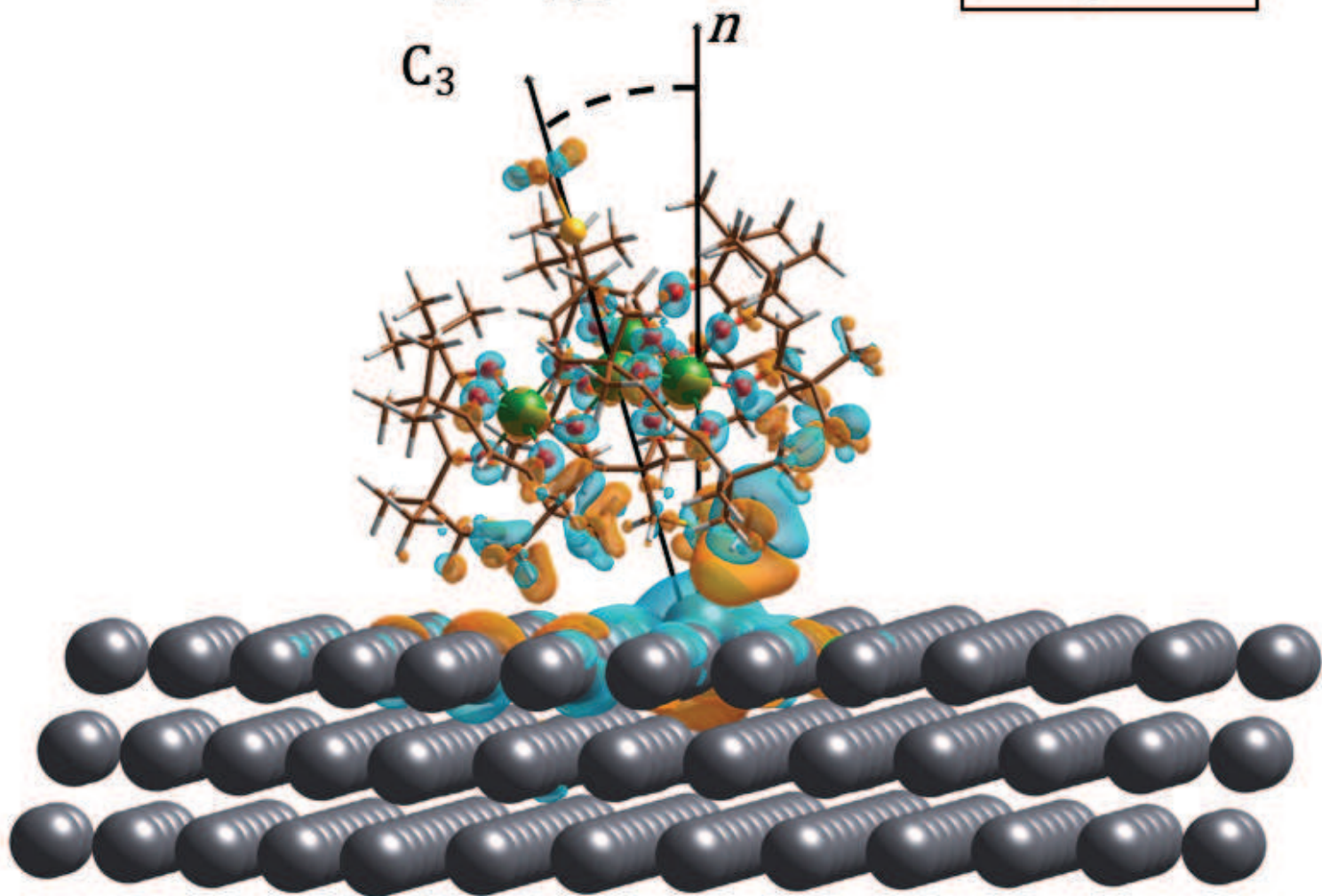


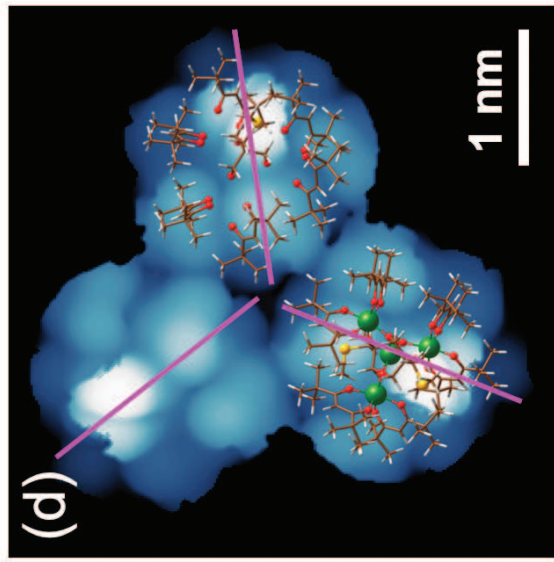
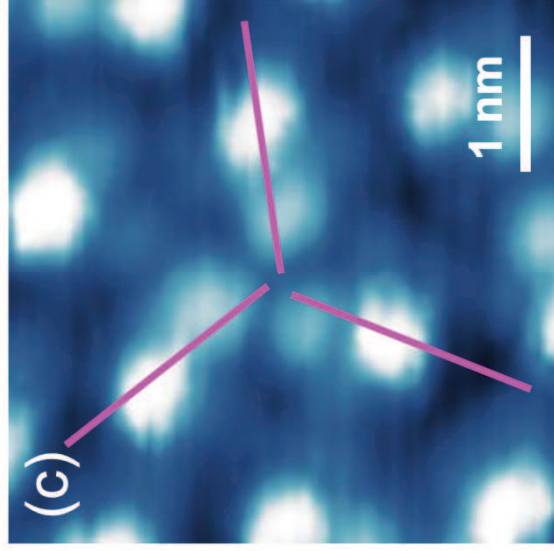
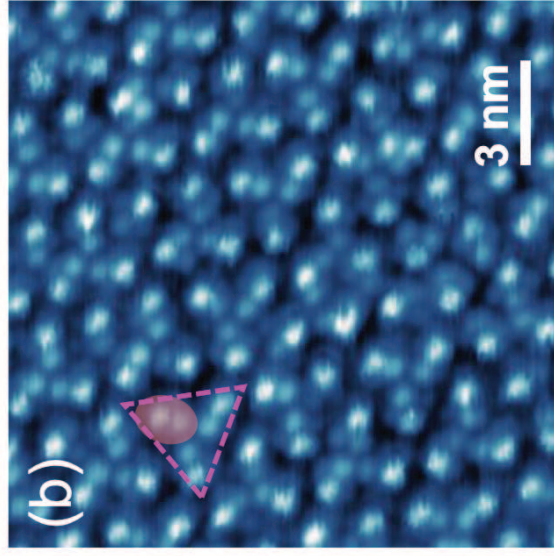
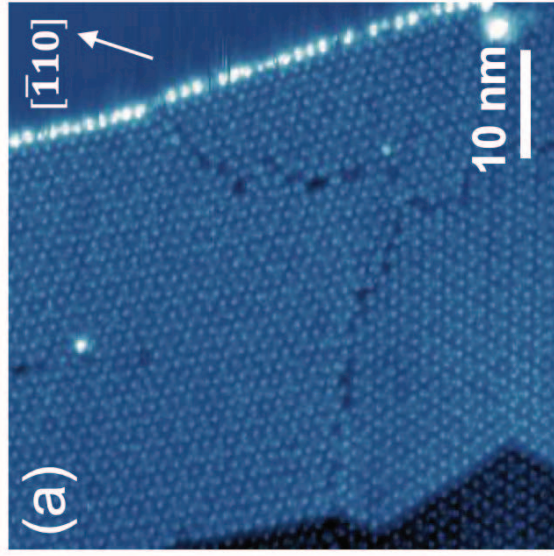
(b)

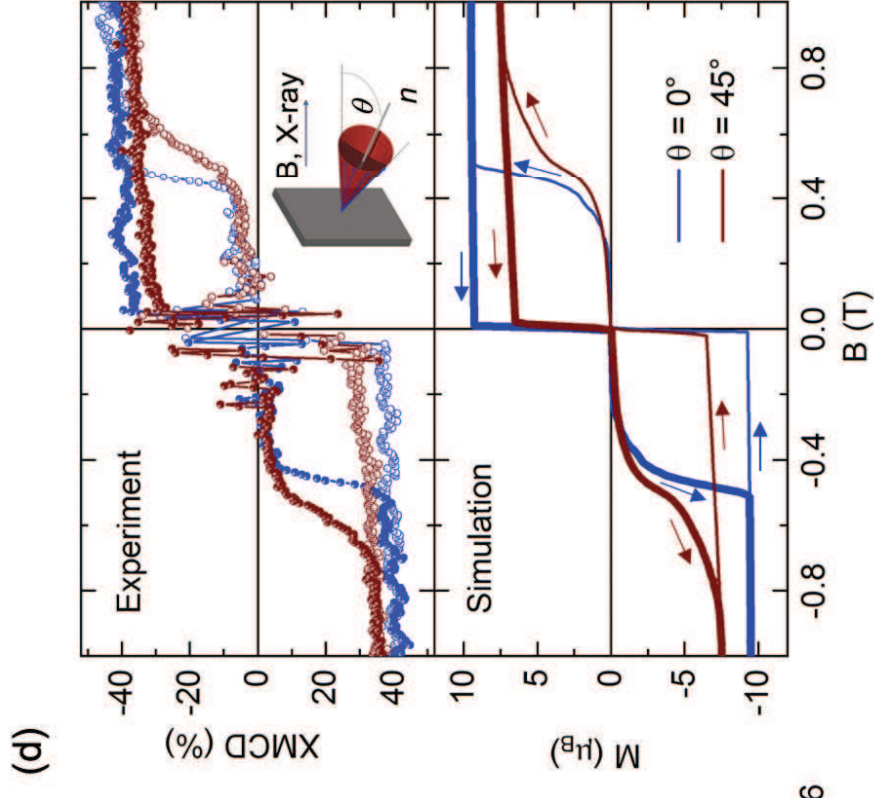
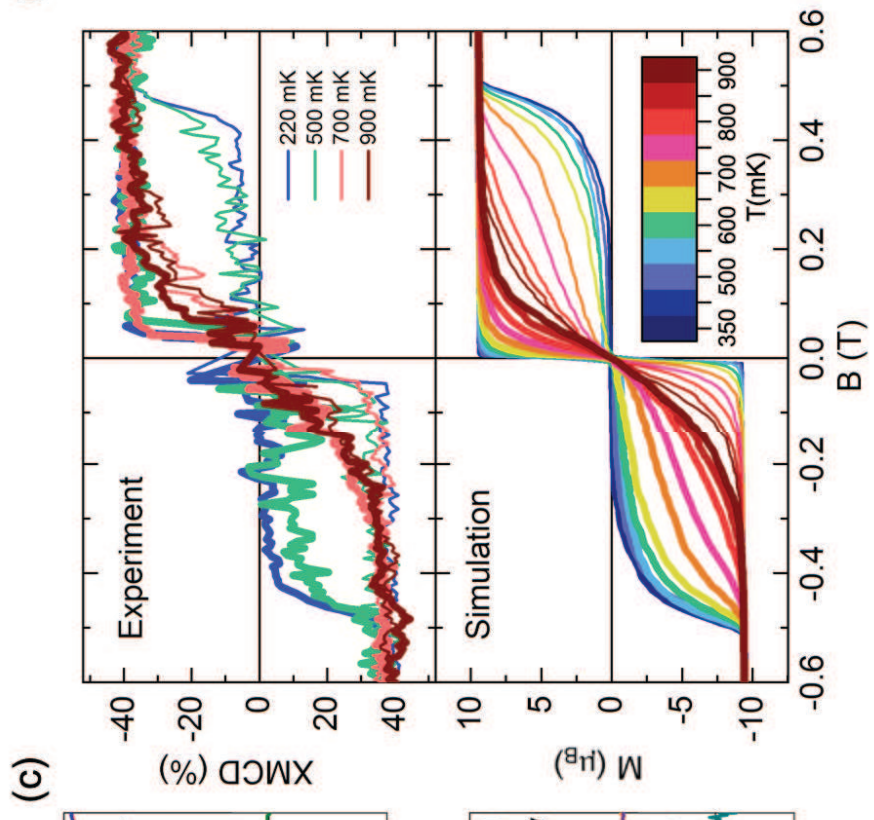
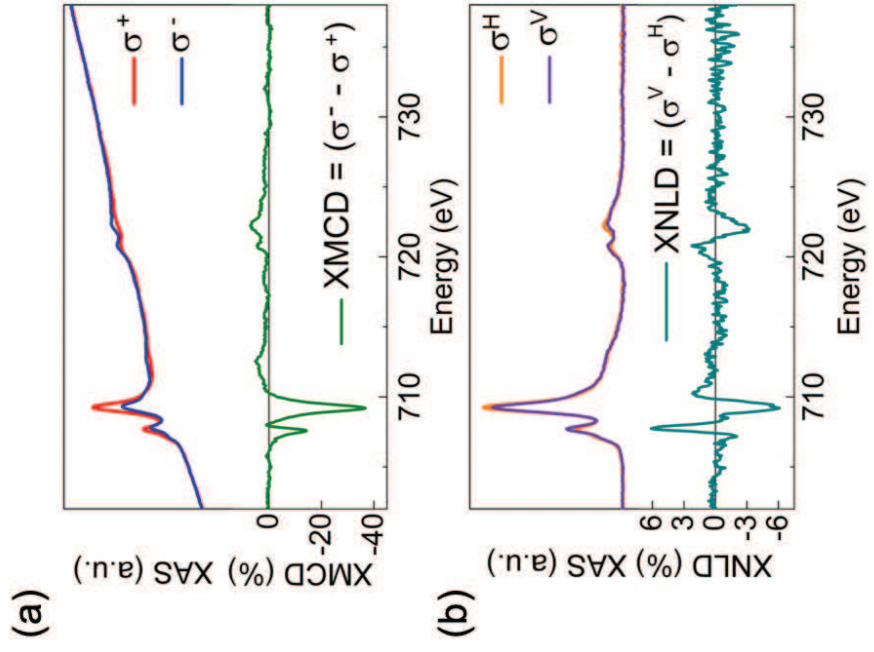
$$\Omega \sim 22^\circ$$

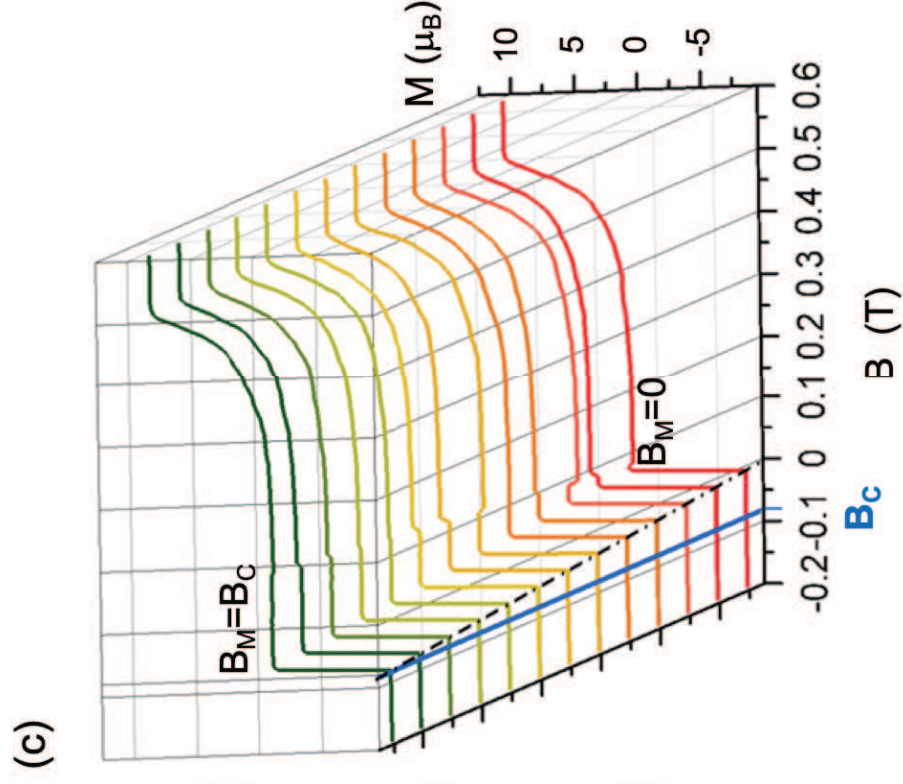
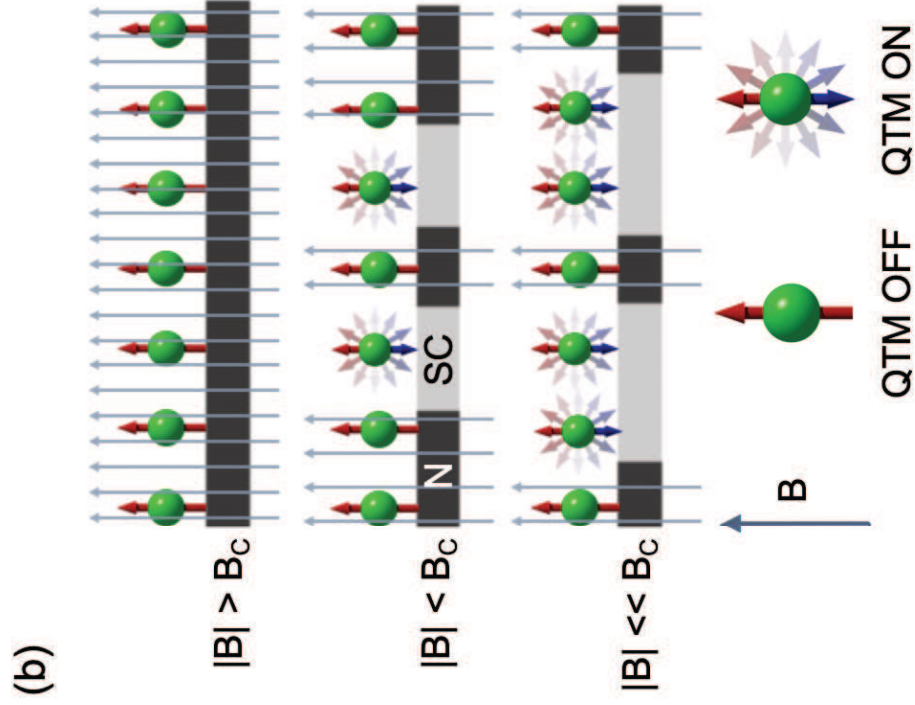
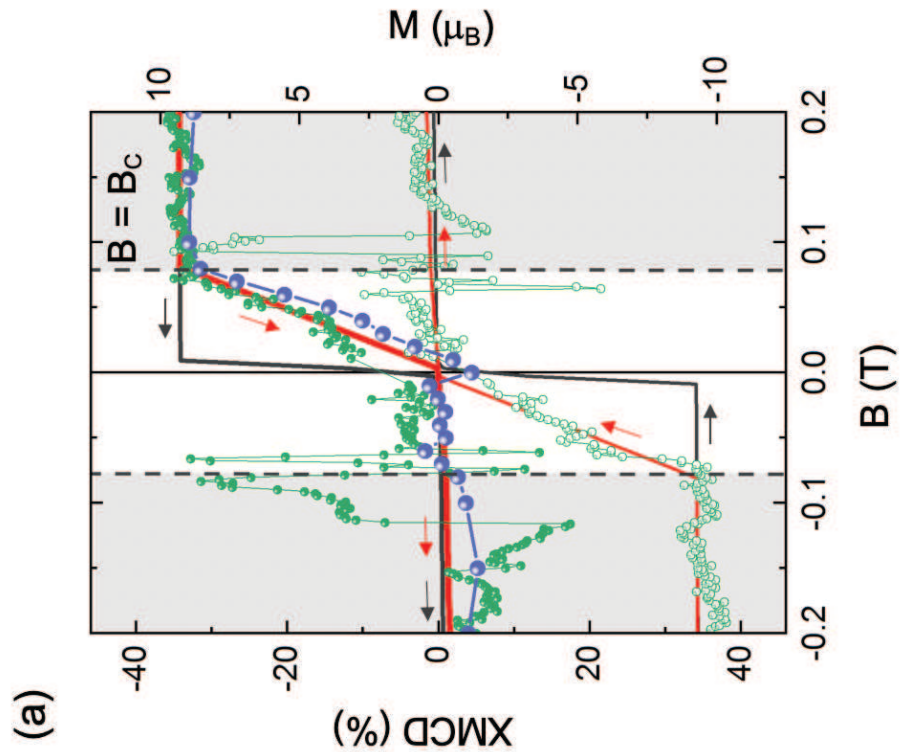
$C_3$

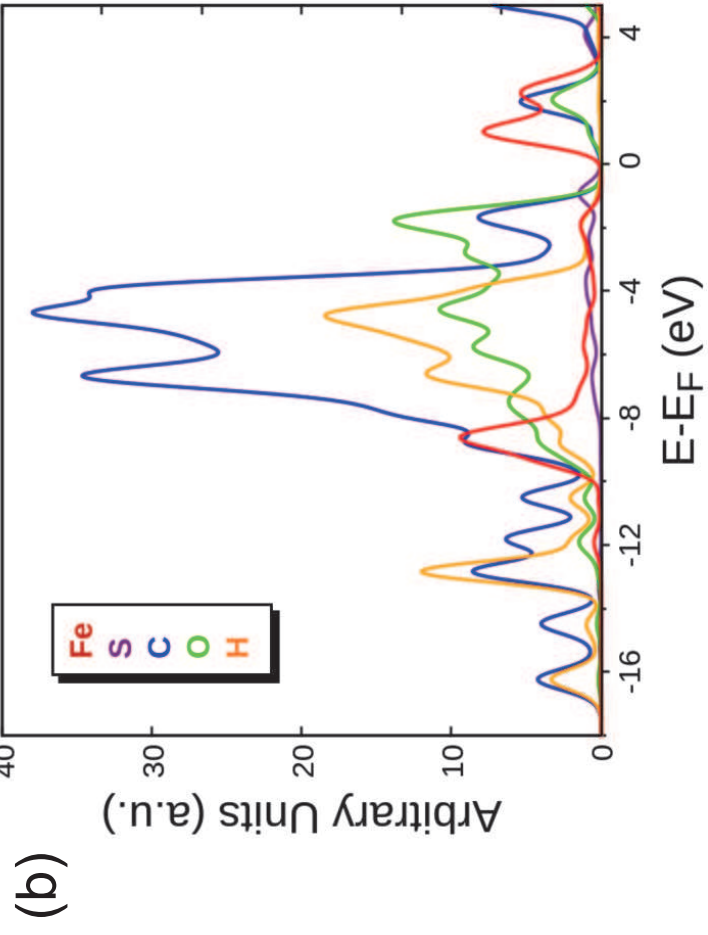
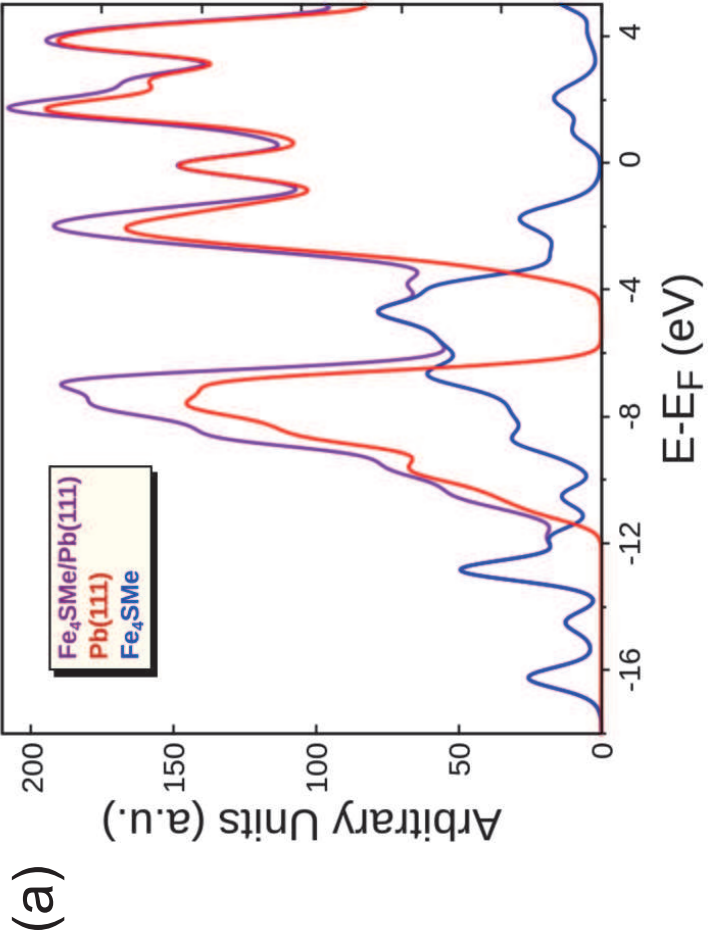
$n$



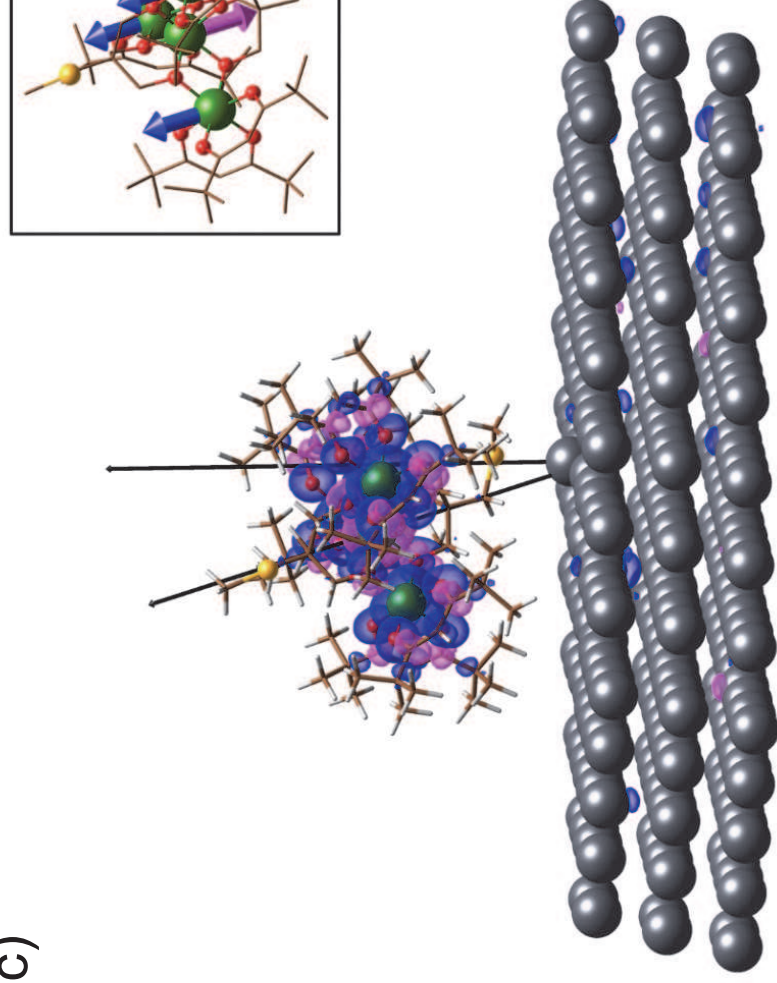


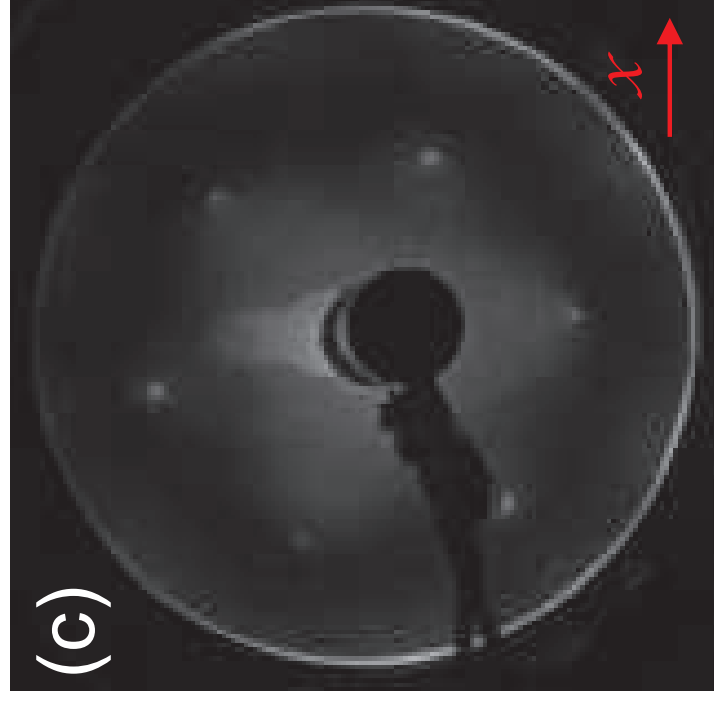
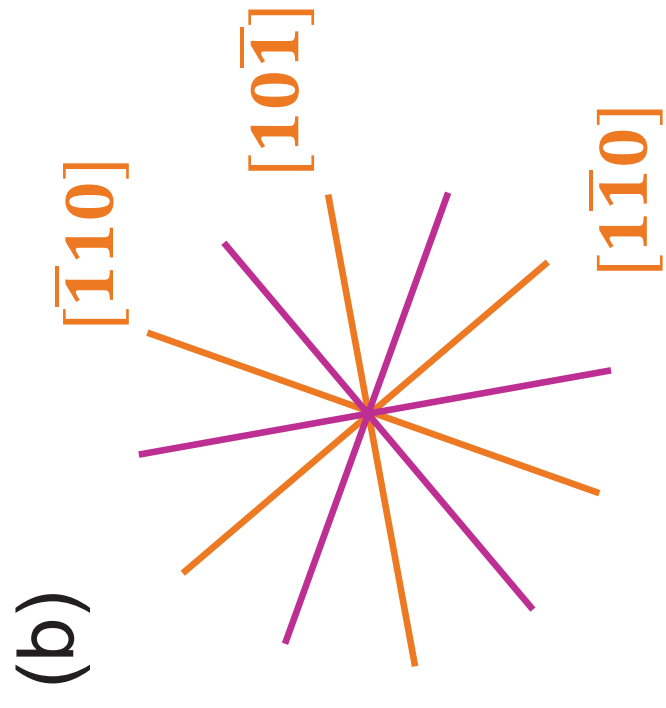
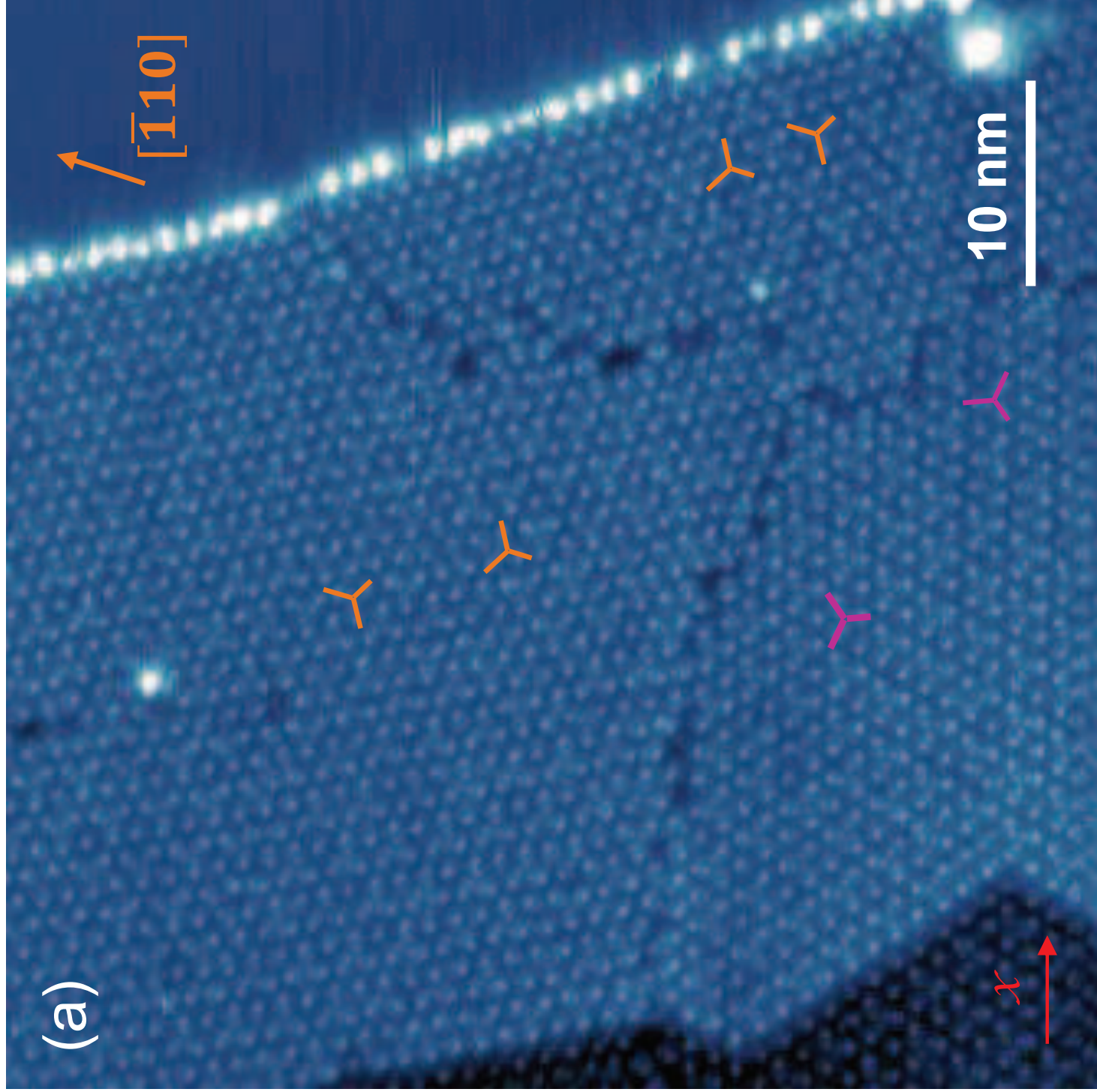


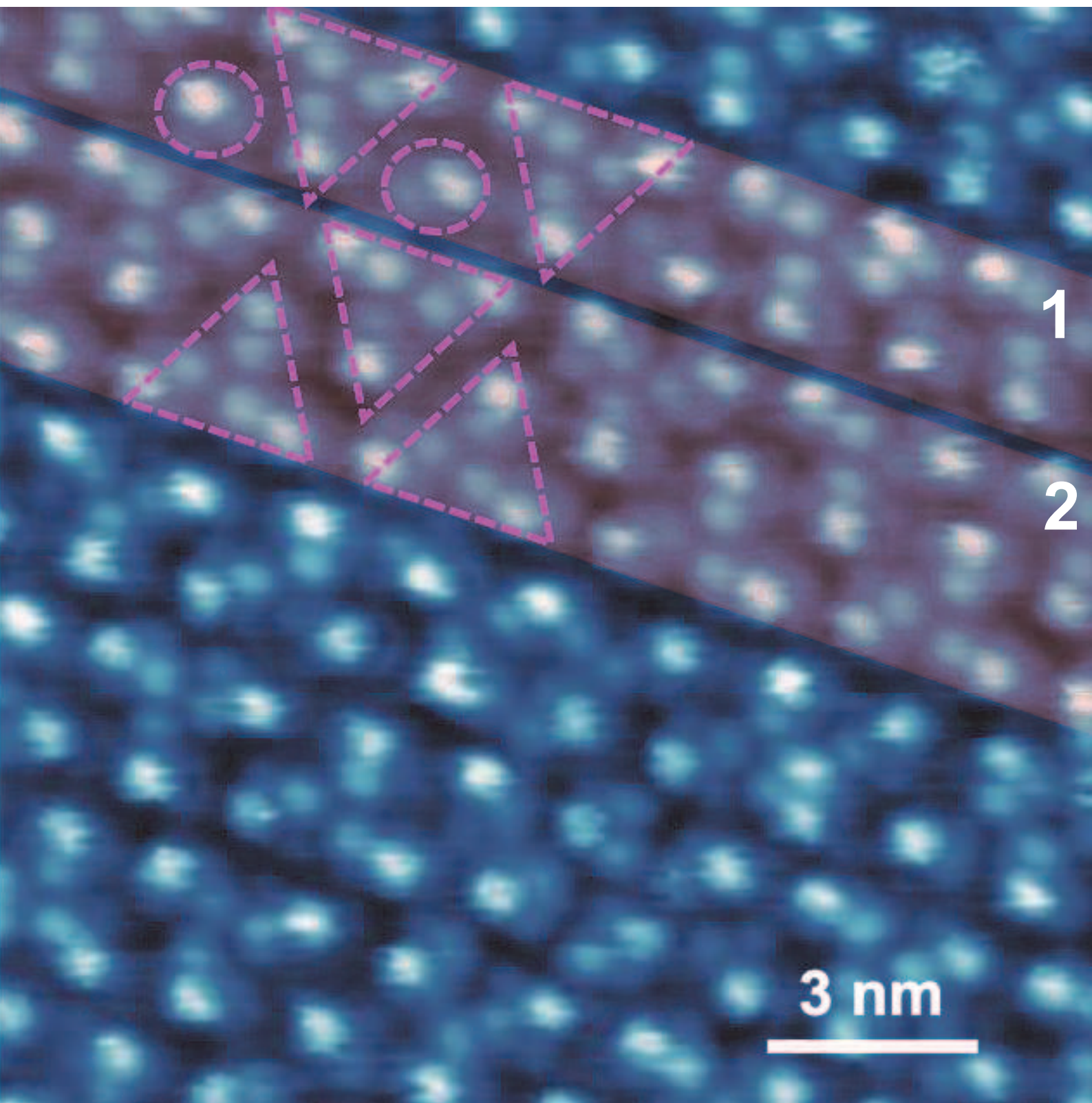


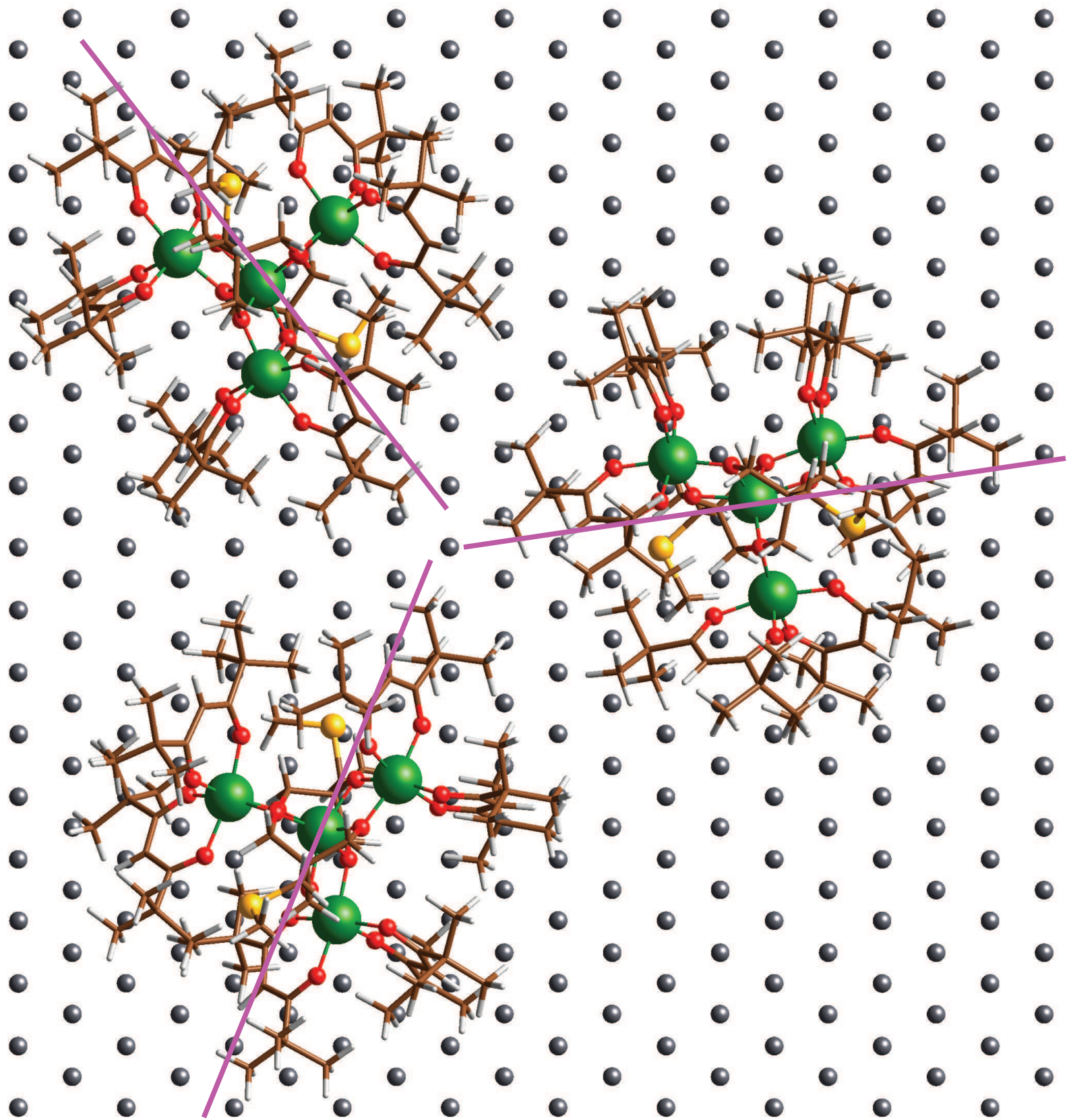


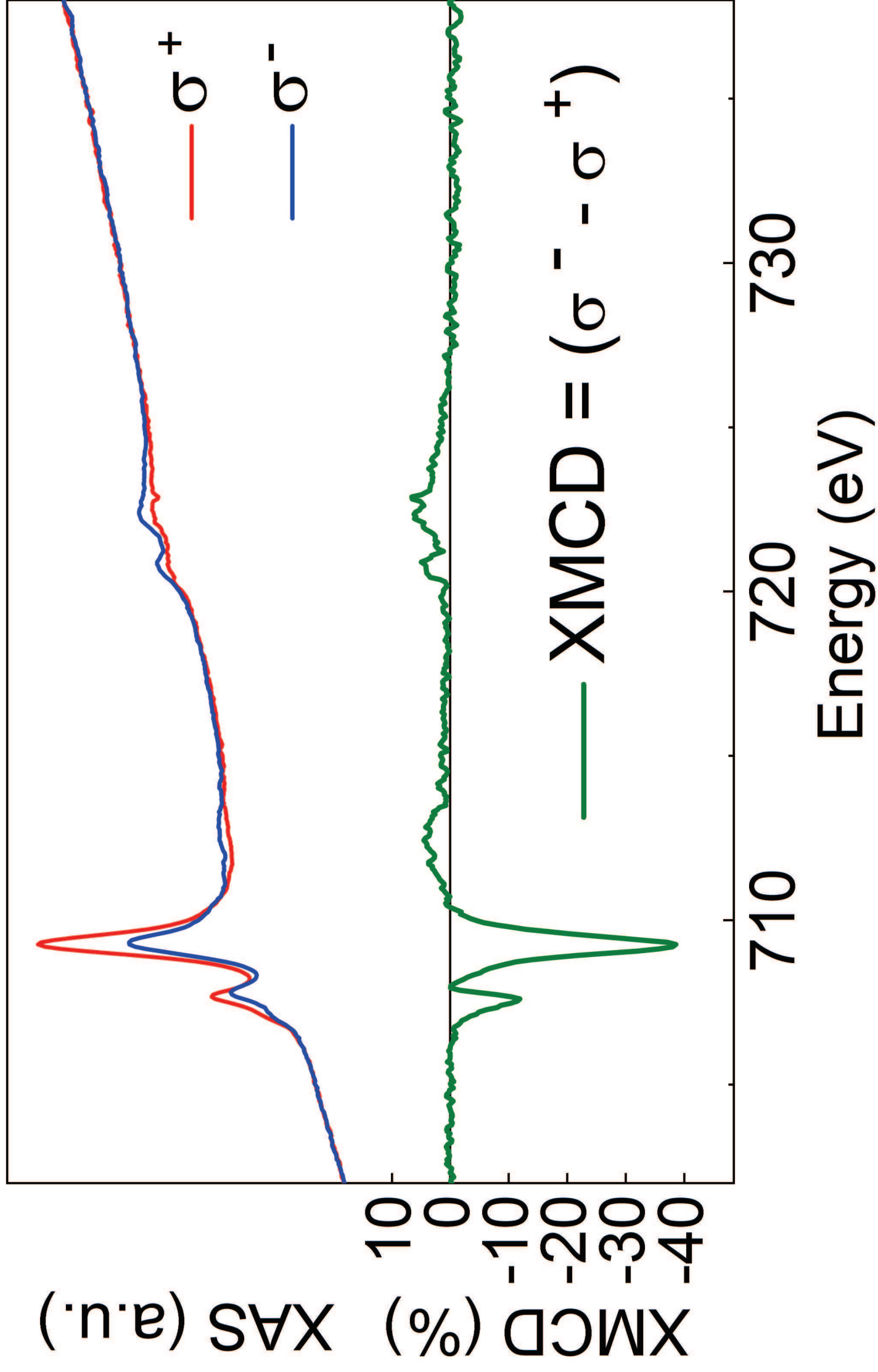
(c)



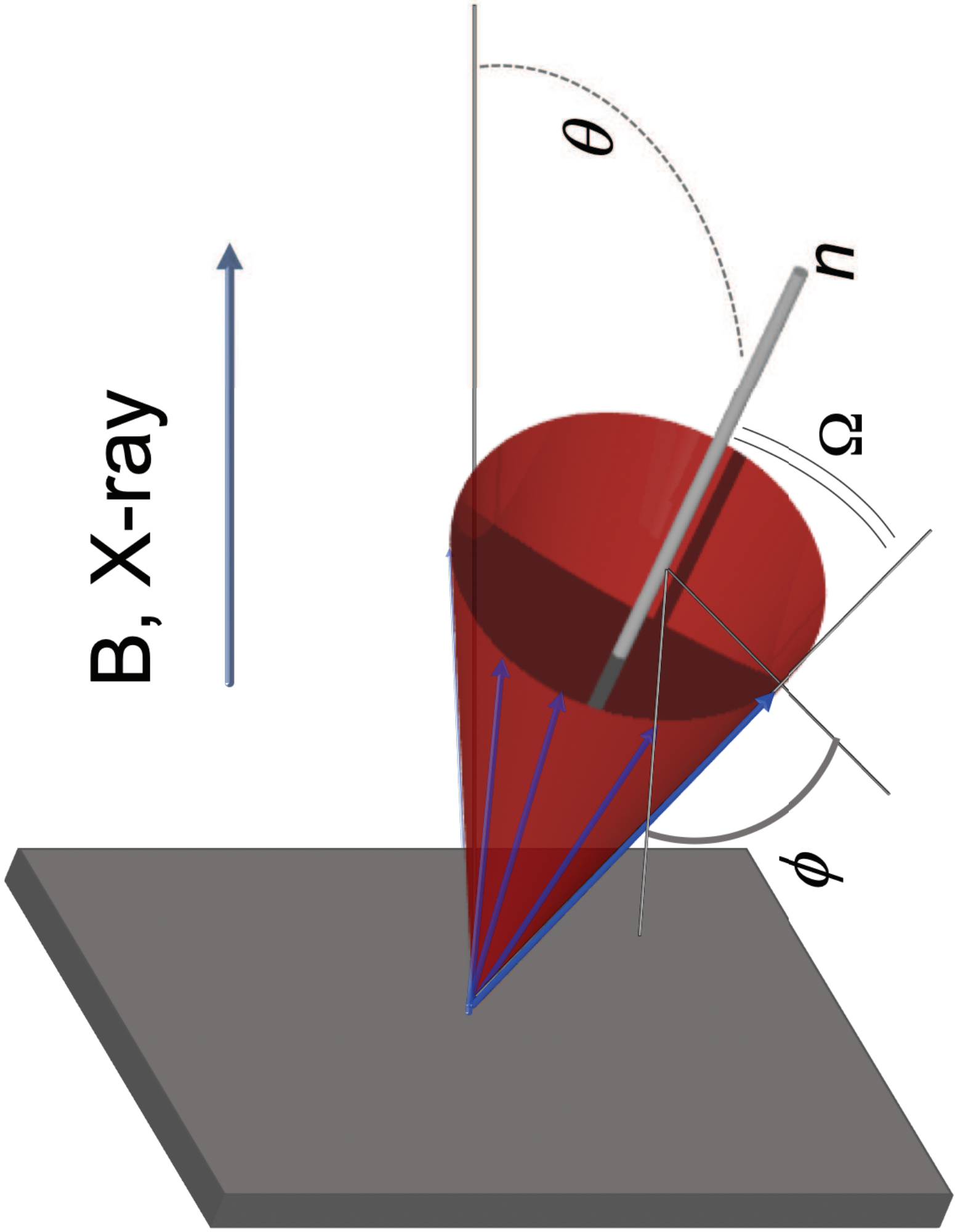




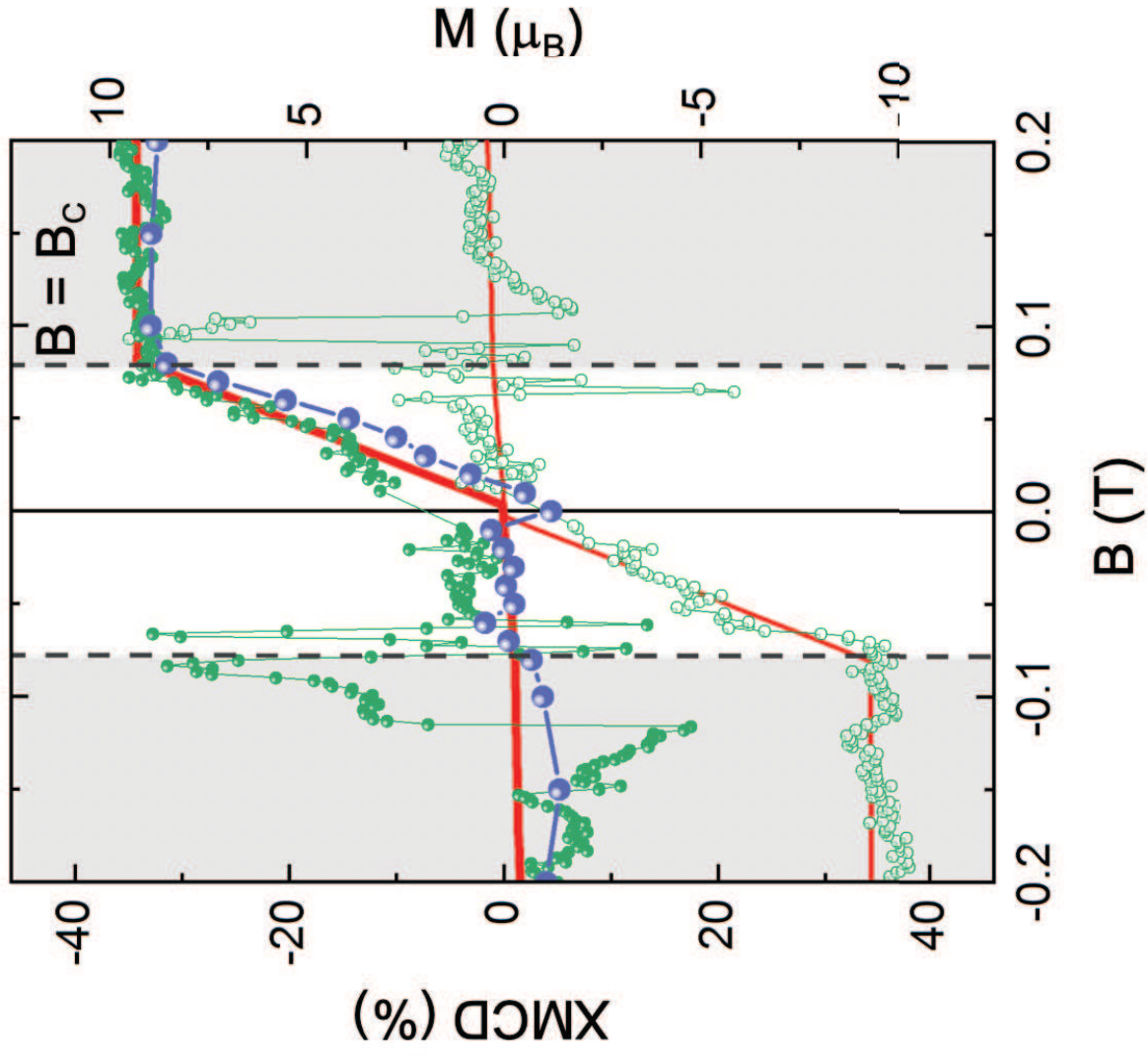




B, X-ray



(a)



(b)

