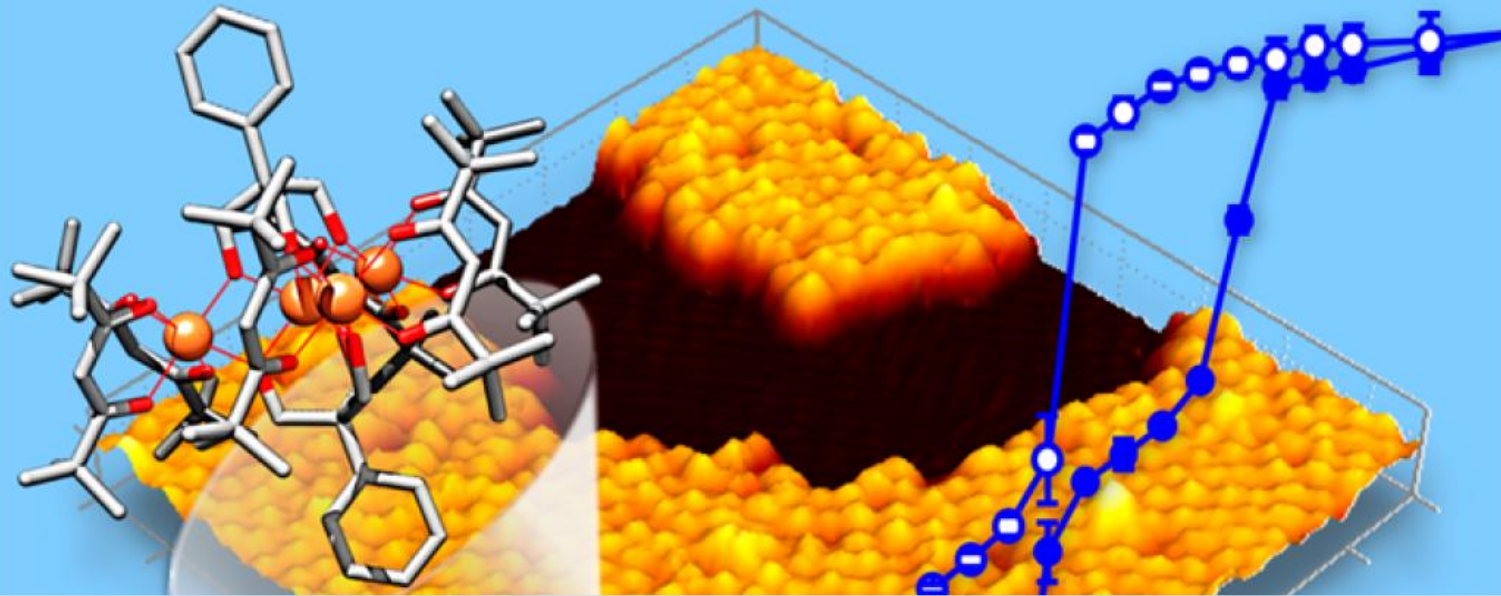


Probing the magnetism of molecular arrays at surfaces



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Acknowledgments

Synthesis & structures

Post-docs, PhD students, & undergraduates

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Magnetic studies, surface science & DFT

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Dept. of Chemistry "U. Schiff" & INSTM, University of Florence, Florence, ITALY

XAS/XMCD

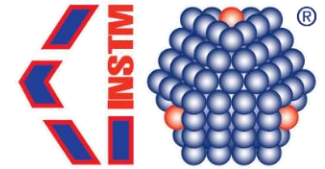
Beamline scientists @synchrotron light sources

Ph. Sainctavit

IMPMC, UMR7590 CNRS, Sorbonne Université, Paris, FRANCE



UNIMORE
UNIVERSITÀ DEGLI STUDI DI
MODENA E REGGIO EMILIA



R. Sessoli



M. Mannini

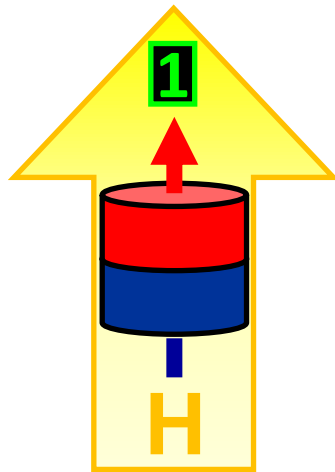


Ph. Sainctavit

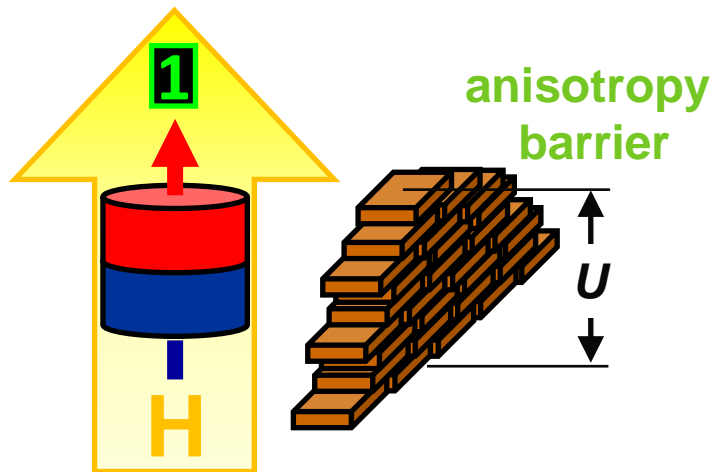


Co-funded by the
European Union

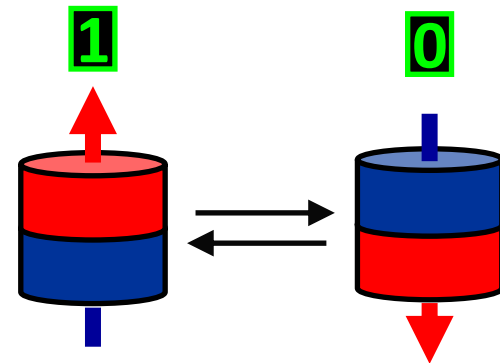
Slow paramagnetic relaxation



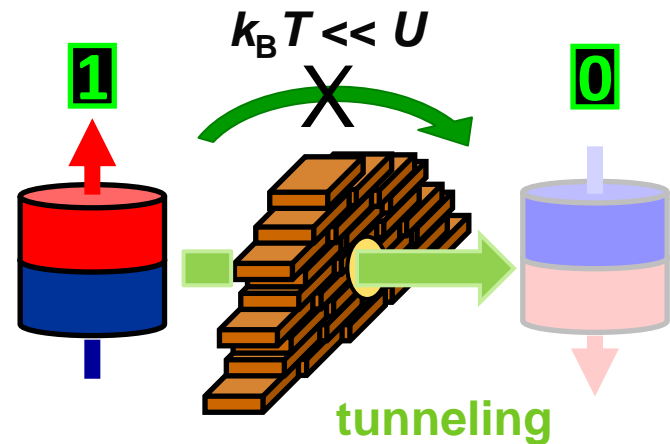
1. Information is written



1. Information is written

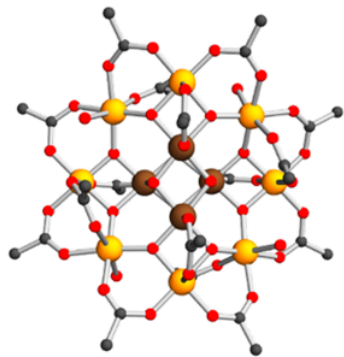


2. Information is **lost**
over $10^{-8} - 10^{-10}$ s

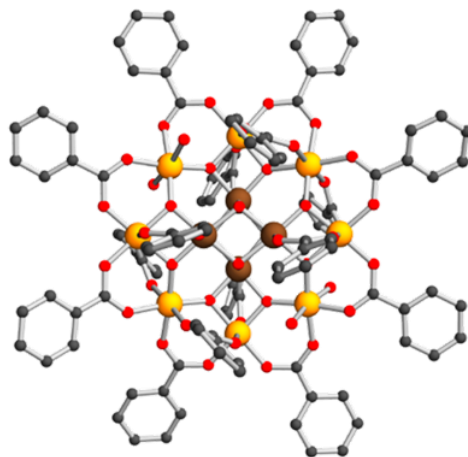


2. Information is **stored**

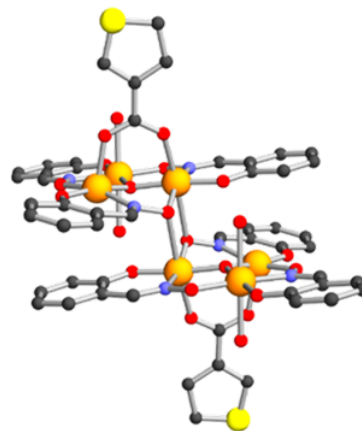
Single-molecule Magnets (SMMs)



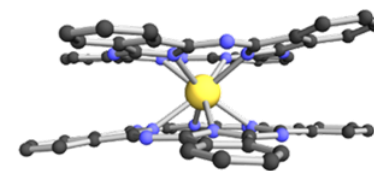
Mn_{12}ac
($S = 10$)



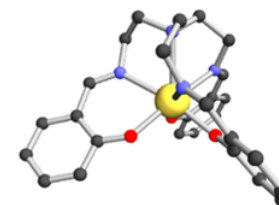
Mn_{12}Ph
($S = 10$)



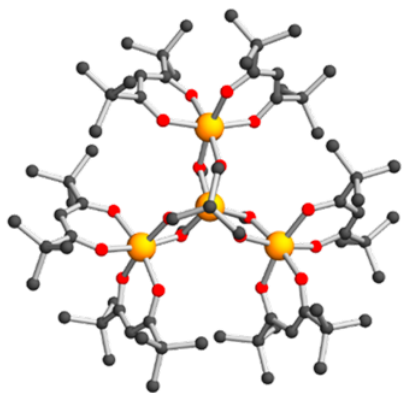
Mn_6th
($S = 4$)



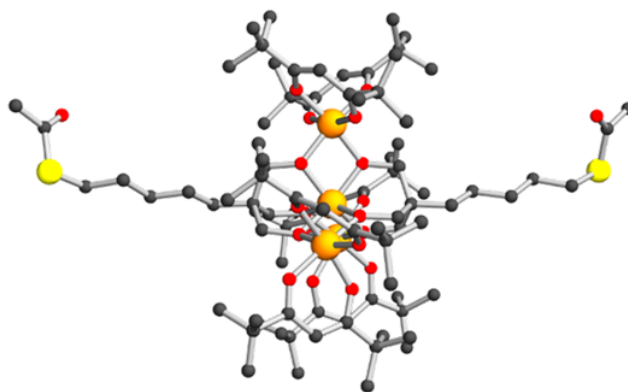
TbPc_2
($J = 6$)



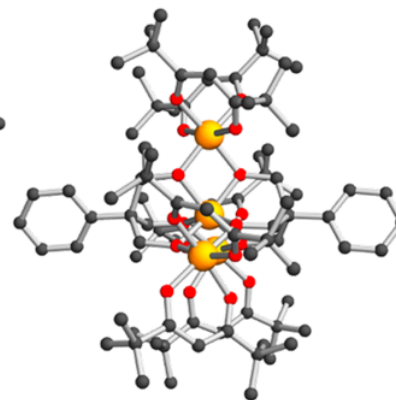
$\text{Er}(\text{trensal})$
($J = 15/2$)



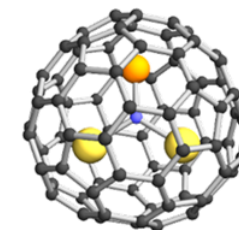
Fe_4H
($S = 5$)



Fe_4C_5
($S = 5$)

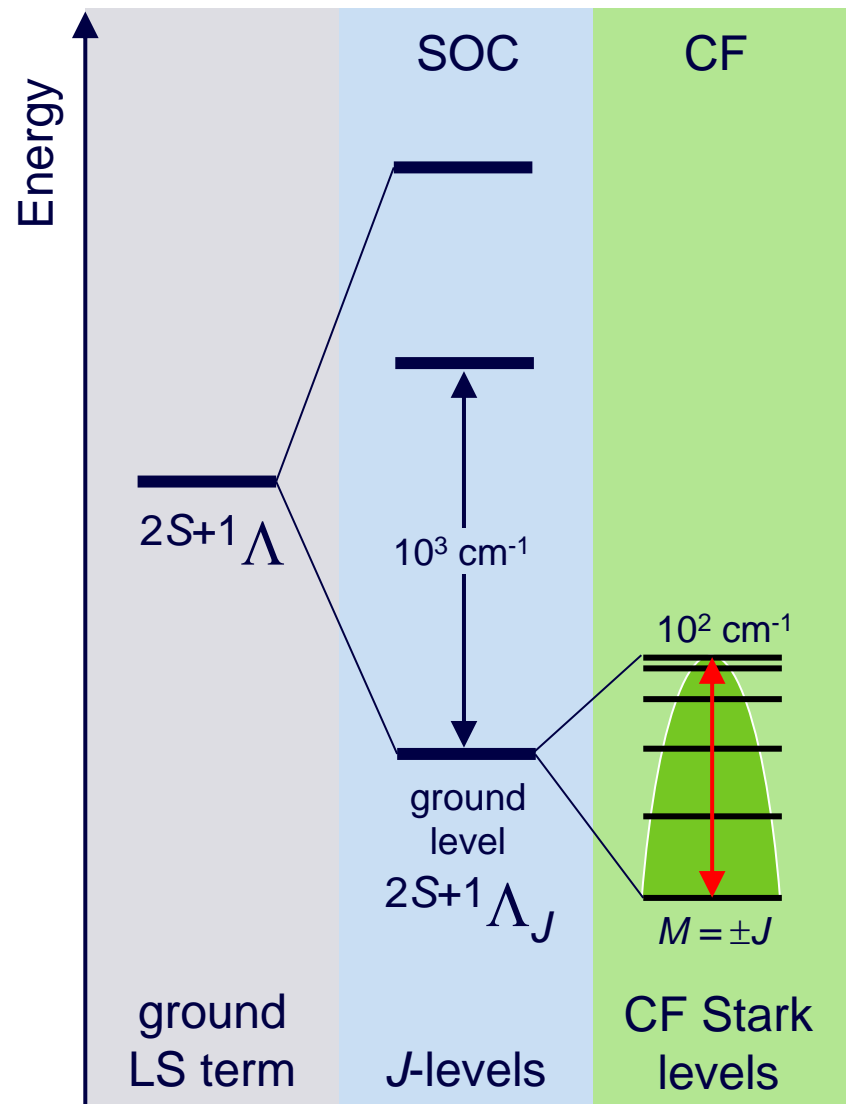
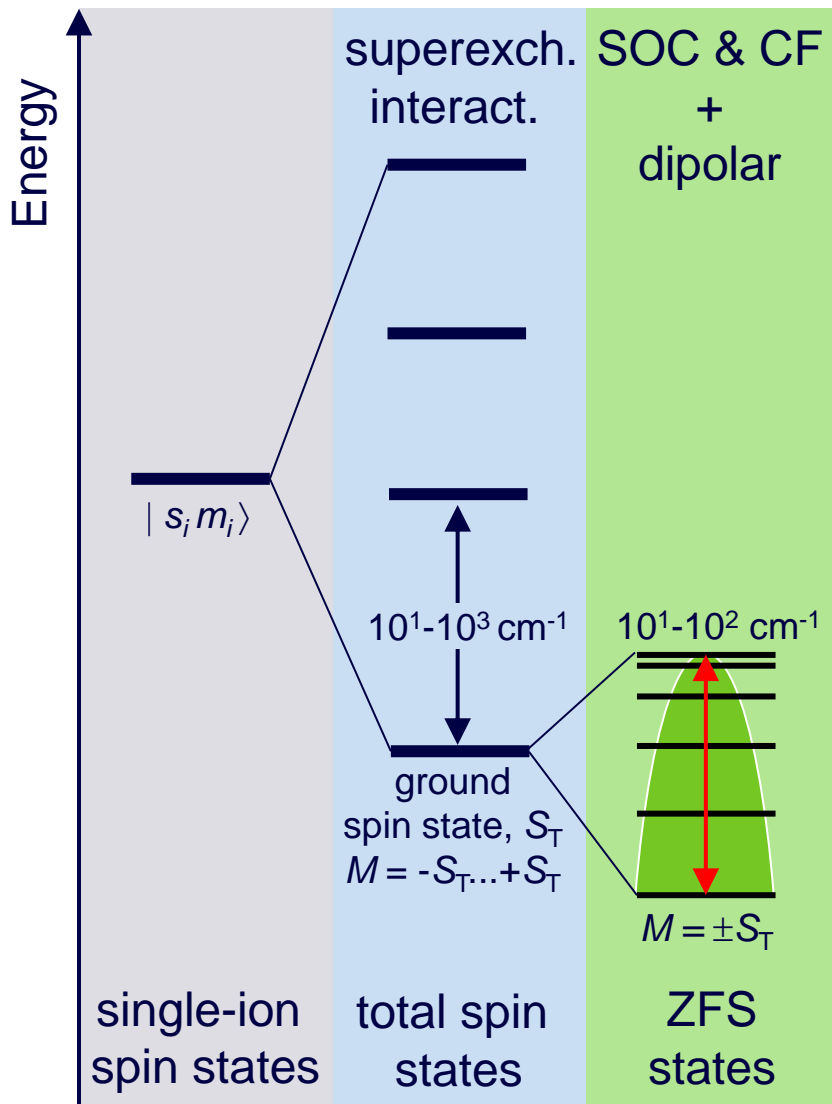


Fe_4Ph
($S = 5$)

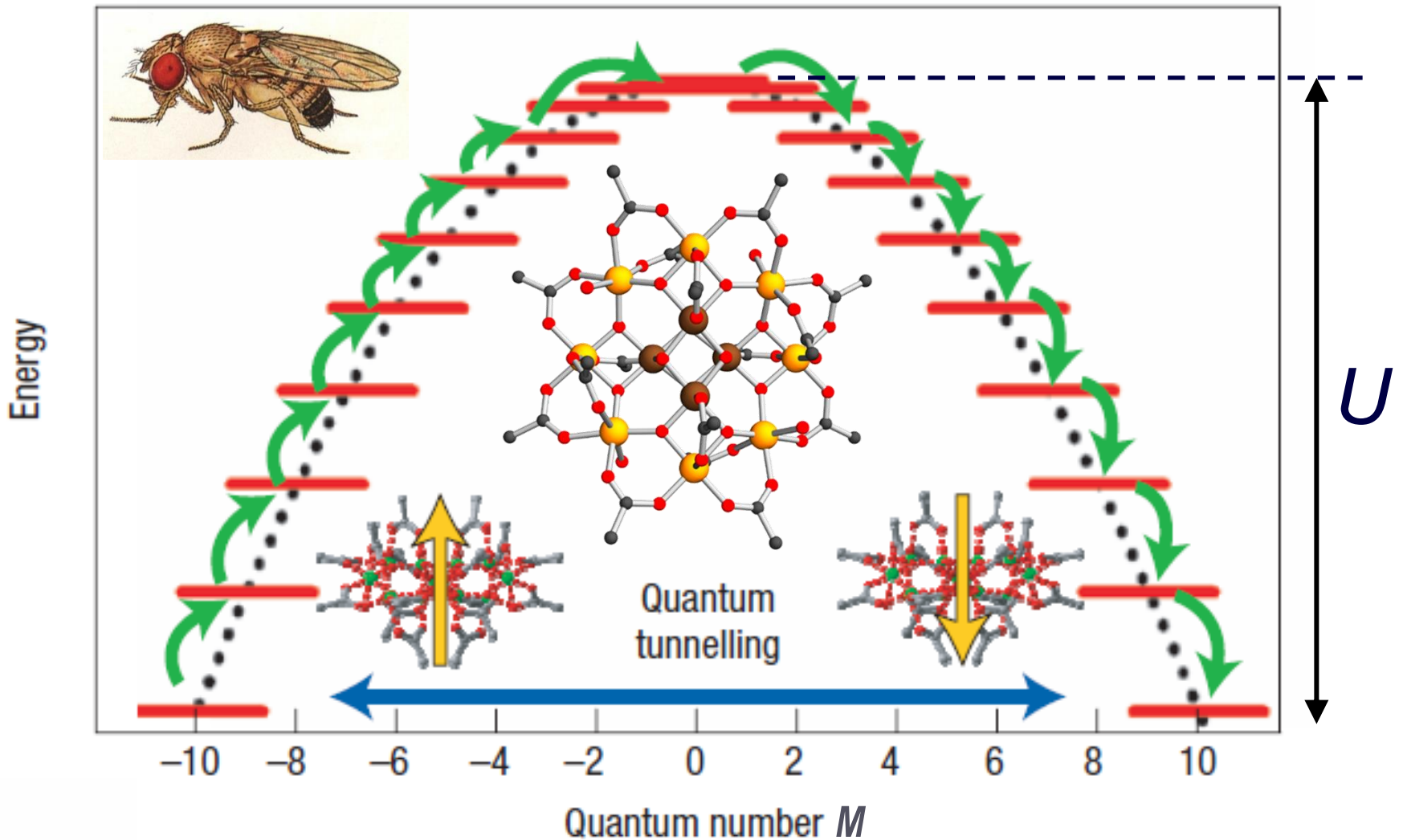


$\text{Dy}_2\text{ScN@C}_{80}$
 $2 \times (J = 15/2)$

The origin of anisotropy barrier: polynuclear 3d- vs mononuclear 4f-metal based SMMs

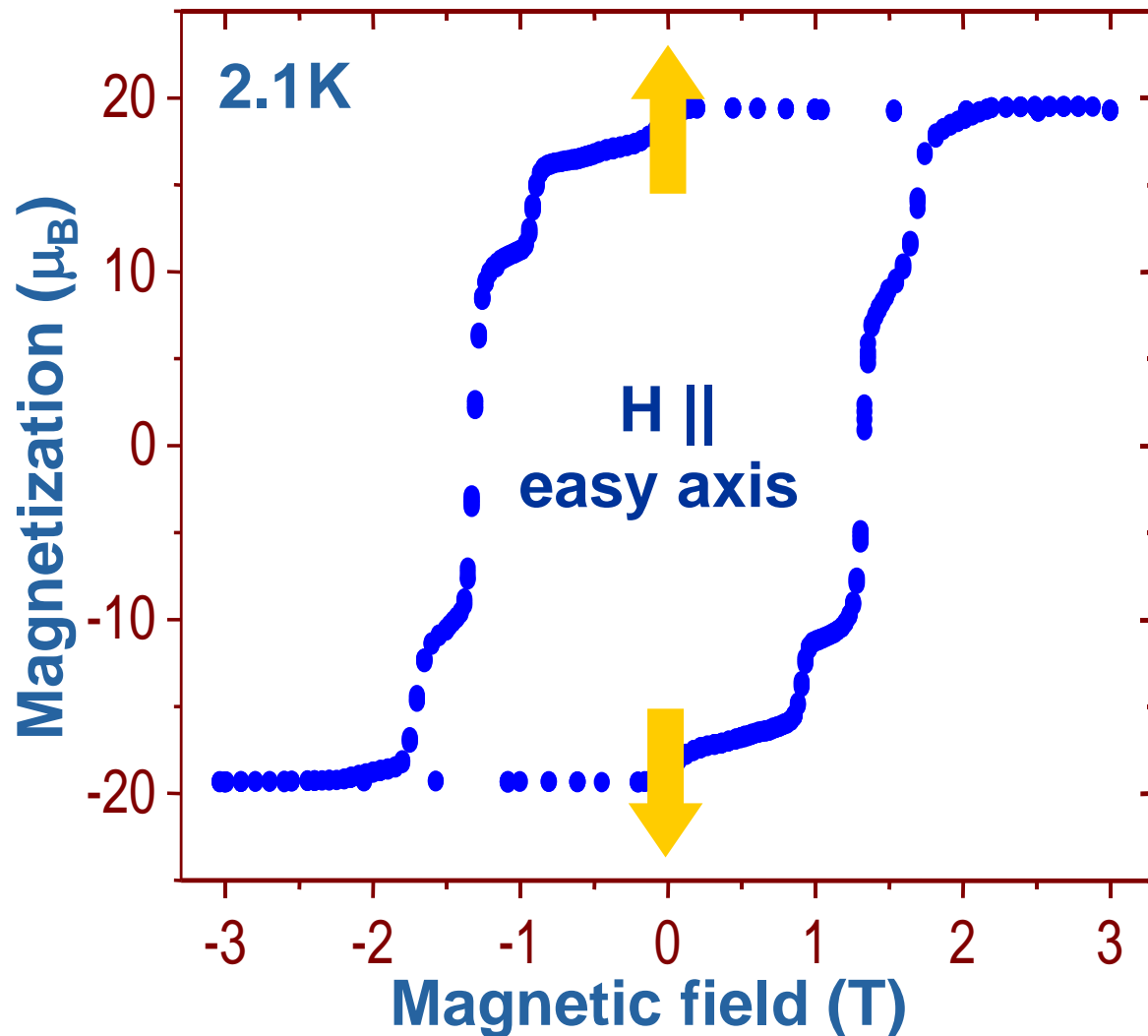


Mn_{12}ac ($S = 10$, $U/k_B = 61$ K) The *Drosophila* of Single-Molecule Magnets



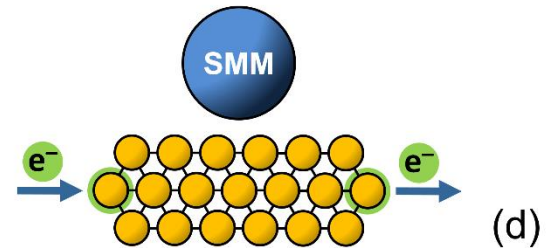
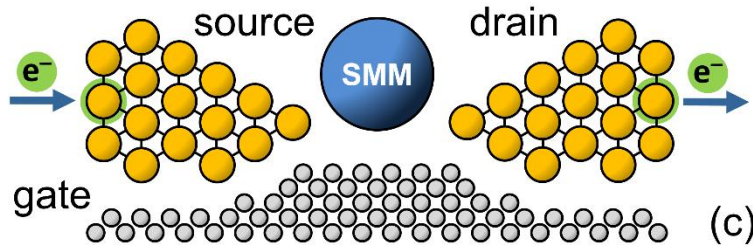
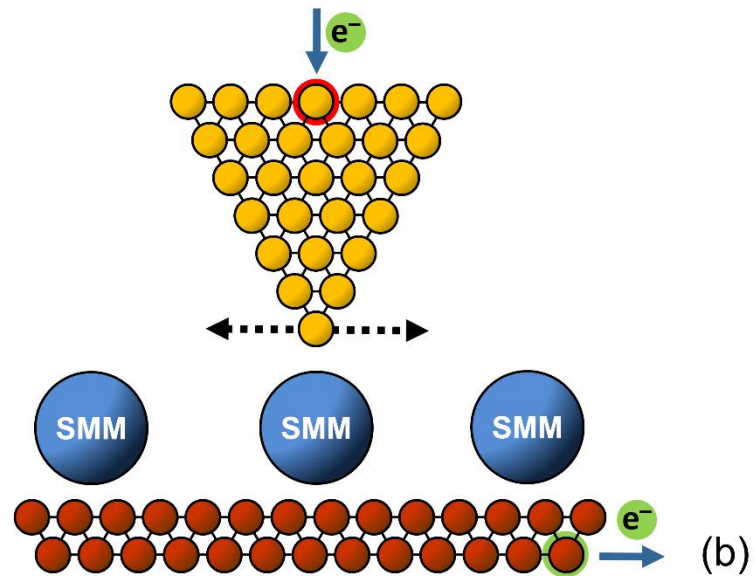
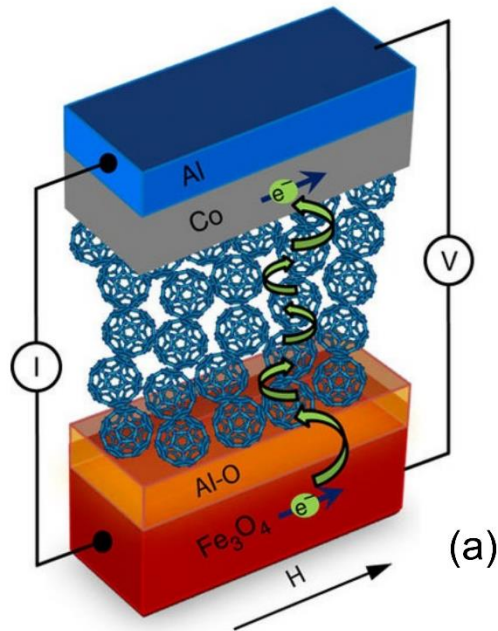
R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* 1993, 365, 141
R. Bagai, G. Christou, *Chem. Soc. Rev.* 2009, 38, 1011

Mn_{12}ac ($S = 10$, $U/k_B = 61$ K)
The *Drosophila* of Single-Molecule Magnets



R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* 1993, 365, 141
R. Bagai, G. Christou, *Chem. Soc. Rev.* 2009, 38, 1011

Towards applications



Does the memory effect persist on surface?

Trivial roles of the surface

- mechanical support
- template
- electrical contact

Non-trivial roles of the surface

- Reactive (e^- rich) environment: fragmentation, rearrangements, hybridization, redox-activity...
- Source of asymmetry: structural distortions

The key-points

- controlling coverage, lateral ordering and orientation on the surface
- controlling electronic and spin-phonon coupling with the surface
- developing «clean» processing protocols for fragile molecules
- measuring composition, structure, and magnetism (including relaxation) of complex molecules at monolayer or submonolayer coverage on surfaces
- are molecules chemically and structurally intact after deposition?
- are magnetic moment and magnetic anisotropy interface dependent?
- how does reduced dimensionality affect magnetic relaxation and memory effect?

Studying molecular assemblies at surfaces



0.1-mg crystal
(MW = 2000)
 $\sim 3 \cdot 10^{16}$ molecules



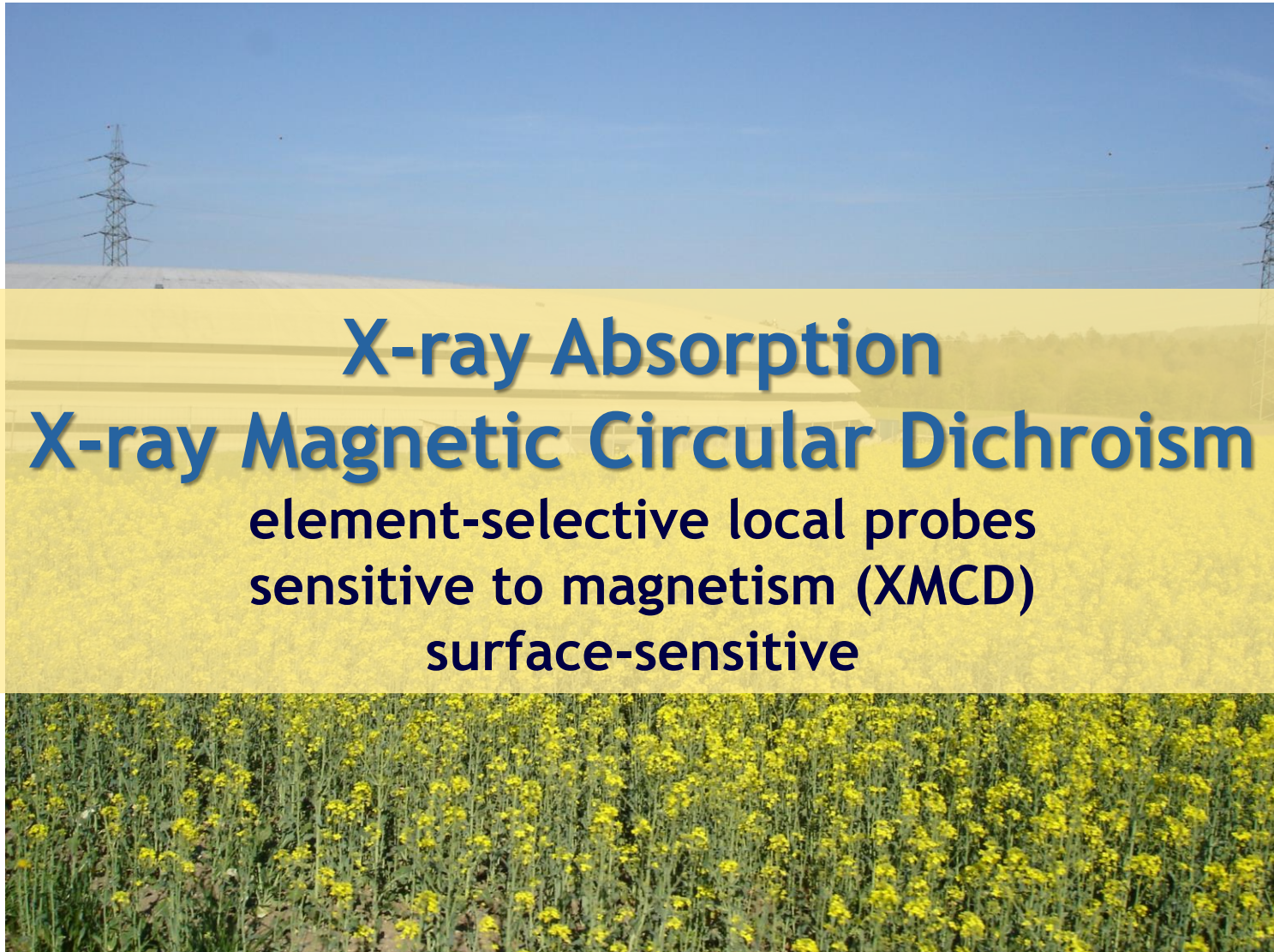
1-cm² surface
(2 nm²/molecule)
 $\sim 5 \cdot 10^{13}$ molecules

Synchrotron-based methods



SLS (Villigen, Switzerland)

Synchrotron-based methods

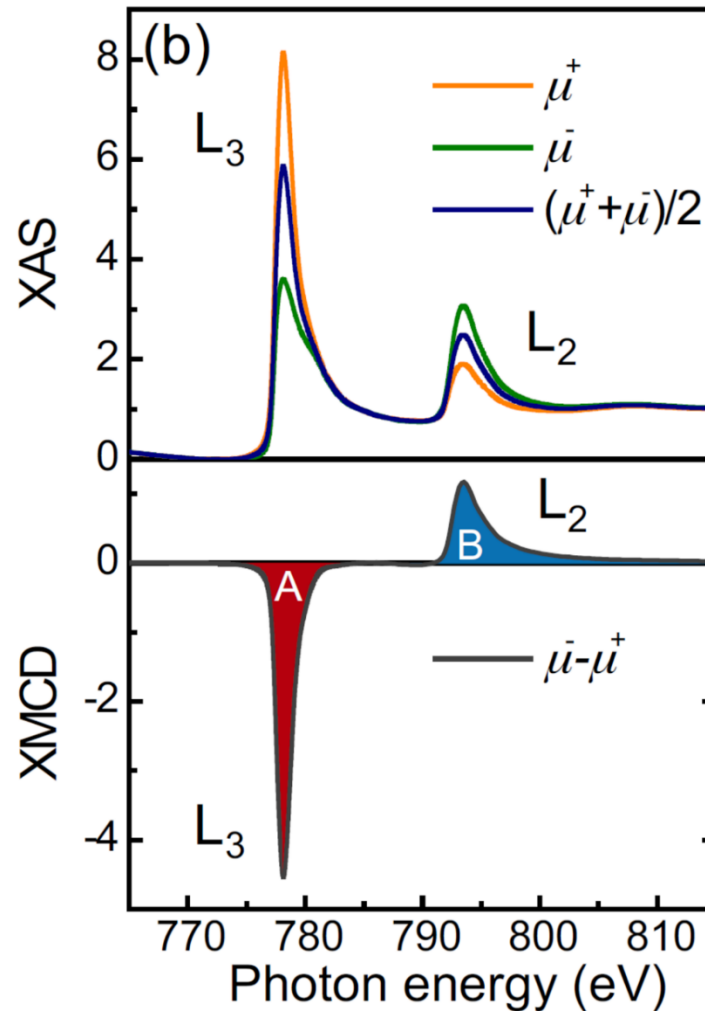
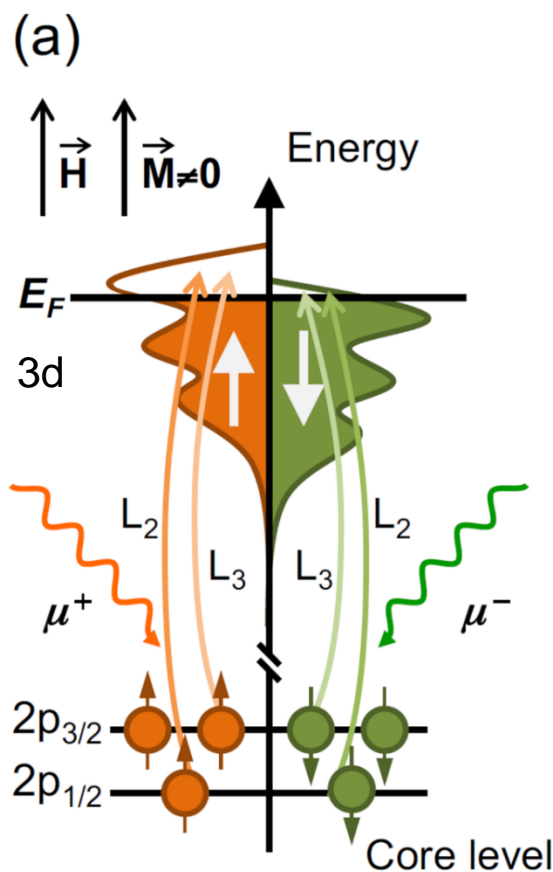


X-ray Absorption

X-ray Magnetic Circular Dichroism

element-selective local probes
sensitive to magnetism (XMCD)
surface-sensitive

XAS and XMCD



enable local, element-selective magnetic measurements with surface sensitivity
(< 0.005 ML)

The difficult early years: redox instability of Mn_{12}ac complexes on Au

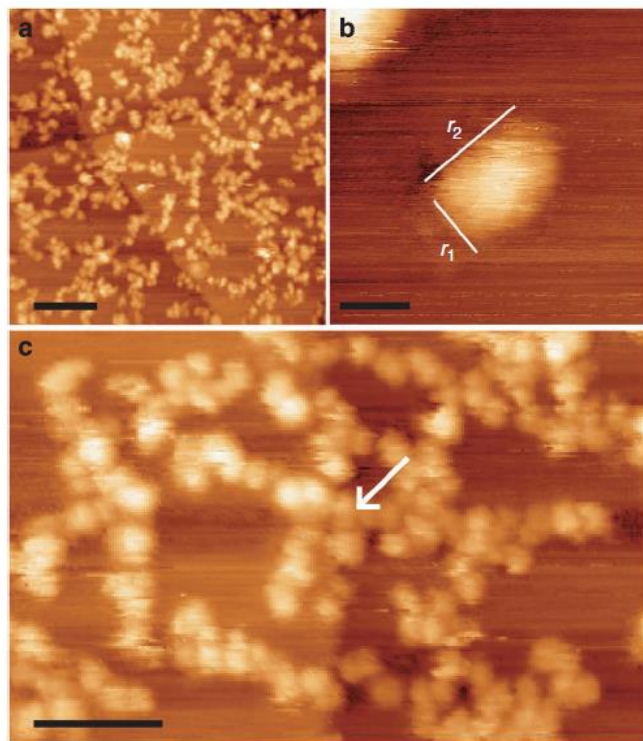
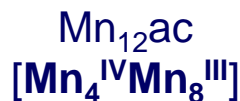
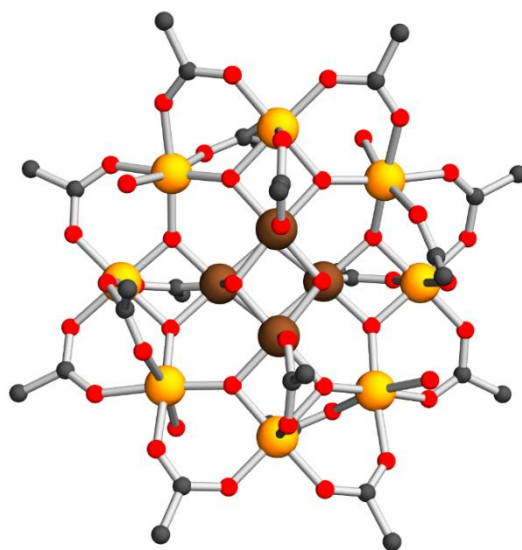


Figure 2 | STM images of $\text{Mn}_{12}(\text{acetate})_{16}$ on Au(111). (a) A large-scale STM image of the Au(111) surface after the UHV-ESD of ~ 0.35 ml of $\text{Mn}_{12}(\text{acetate})_{16}$ ($V_{\text{sample}} = +1.80$ V, $I_{\text{tunnel}} = 0.03$ nA). Filamentary structures are observed to run over the surface and are contiguous at step edges. Scale bar, 20 nm. (b) Closeup STM image of an isolated $\text{Mn}_{12}(\text{acetate})_{16}$ molecule ($V_{\text{sample}} = +2.00$ V, $I_{\text{tunnel}} = 0.03$ nA). The molecule displays an elliptical cross-section ($r_2 > r_1$). Scale bar, 2 nm. (c) STM image showing the internal structure of a molecular aggregate comprised of individual $\text{Mn}_{12}(\text{acetate})_{16}$ molecules ($V_{\text{sample}} = +2.00$ V, $I_{\text{tunnel}} = 0.05$ nA). Arrow indicates the position of the structure relative to a step edge. Scale bar, 10 nm.



Ultrahigh Vacuum
Electrospray Deposition
UHV-ESD

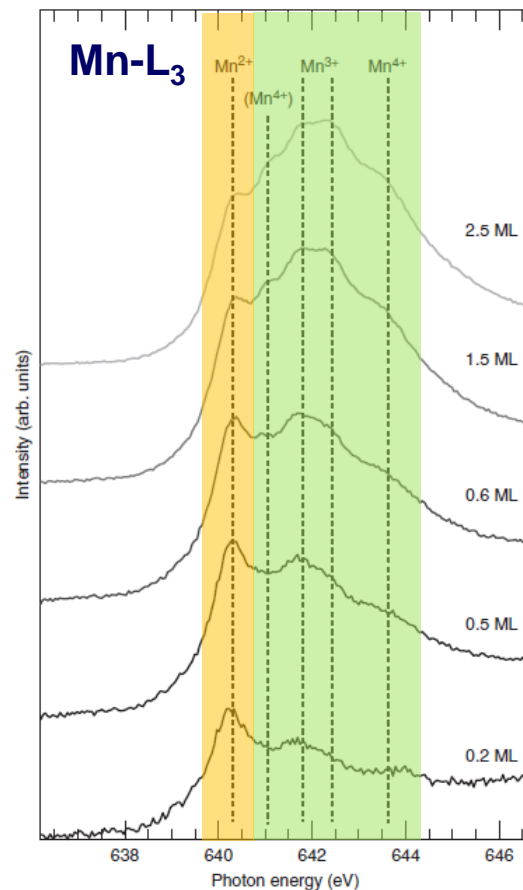


Figure 5 | NEXAFS spectra measured at the Mn 2p adsorption edge (Mn L-edge). Spectra were acquired for a range of coverages (0.2–2.5 ML (monolayer)). Photon energy was calibrated by measuring the energy separation of the Au 4f core-level photoemission peaks excited by first- and second-order X-rays. The positions of the peaks corresponding to the presence of Mn^{2+} , Mn^{3+} and Mn^{4+} are labelled.

The difficult early years: redox instability of Mn₁₂ac complexes on Au

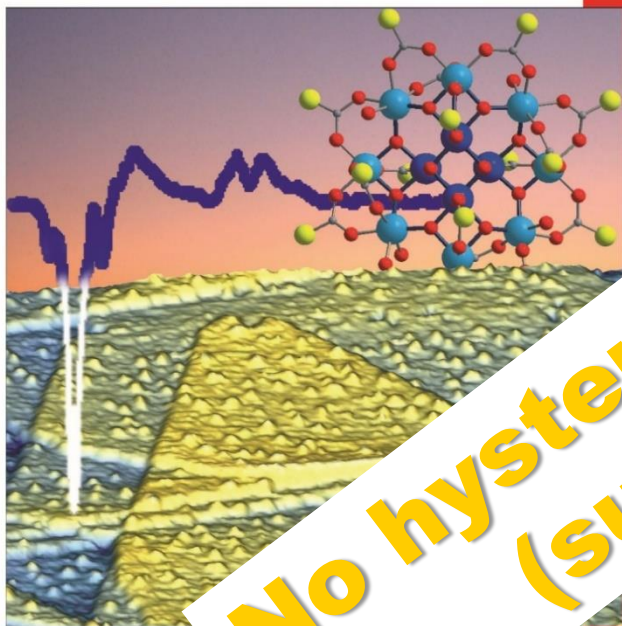
	Naitabdi, A. <i>et al. J. Appl. Phys.</i> 2004 , <i>95</i> , 7345-7347	(Mn ₁₂) (Au)
SQUID	Naitabdi, A. <i>et al. Adv. Mater.</i> 2005 , <i>17</i> , 1612-1616	(Mn ₁₂) (Au)
	Phark, S. <i>et al. Jpn. J. Appl. Phys.</i> 2004 , <i>43</i> , 8273-8277	(Mn ₁₂) (Au)
	Phark, S. <i>et al. J. Magn. Magn. Mater.</i> 2007 , <i>310</i> , e483–e485	(Mn ₁₂) (Au)
	Cornia, A. <i>et al. Angew. Chem. Int. Ed. Engl.</i> 2003 , <i>42</i> , 1645-1648	(Mn ₁₂) (Au)
	Zobbi, L. <i>et al. Chem. Commun.</i> 2005 , 1640-1642	(Mn ₁₂) (Au)
	Pineider, F. <i>et al. Langmuir</i> 2007 , <i>23</i> , 11836-11843	(Mn ₁₂) (Au)
MCD	Bogani, L. <i>et al. Adv. Mater.</i> 2007 , <i>19</i> , 3906–3911	
XMCD	Mannini, M. <i>et al. Chem. Eur. J.</i> 2008 , <i>14</i> , 7530-7535	(Mn ₁₂) (Au)
	Coronado, E. <i>et al., Inorg. Chem.</i> 2005 , <i>44</i> , 7693-7695	(Mn ₁₂) (Au)
	Martinez, R. V. <i>et al. Adv. Mater.</i> 2007 , <i>19</i> , 291-295	(Mn ₁₂) (SiO ₂ /Si)
XMCD	Moro, F. <i>et al. J. Phys. Chem. C</i> 2012 , <i>116</i> , 14936–14942	(Mn ₁₂) (Au)
	Cavallini, M. <i>et al. Nano Lett.</i> 2003 , <i>3</i> , 1527-1530	(Mn ₁₂) (SiO ₂ /Si)
	Gòmez-Segura, J. <i>et al. Chem. Commun.</i> 2005 , 5615-5617	(Mn ₁₂) (HOPG)
XMCD	Grumbach, N. <i>et al. Eur. Phys. J. B</i> 2010 , <i>73</i> , 103-108	(Mn ₁₂) (Si)
XMCD	Donnio, B. <i>et al. Solid State Sci.</i> 2010 , <i>12</i> , 1307-1313	(Mn ₁₂) (Au)
	Voss, S. <i>et al. Phys. Rev. B</i> 2007 , <i>75</i> , 045102	(Mn ₁₂) (Au)
	Voss, S. <i>et al. Appl. Phys. Lett.</i> 2007 , <i>90</i> , 133104	(Mn ₁₂) (Au)
	Burgert, M. <i>et al. J. Am. Chem. Soc.</i> 2007 , <i>129</i> , 14362-14366	(Mn ₁₂) (Au)
	Voss, S. <i>et al. Dalton Trans.</i> 2008 , 499-505	(Mn ₁₂) (Au)
	Voss, S. <i>et al. J. Appl. Phys.</i> 2008 , <i>103</i> , 07B901	(Mn ₁₂) (Au)
	Voss, S. <i>et al. Appl. Phys. A</i> 2009 , <i>94</i> , 491-495	(Mn ₁₂) (Au)
	Condorelli, G. G. <i>et al. Angew. Chem. Int. Ed. Engl.</i> 2004 , <i>43</i> , 4081-4084	(Mn ₁₂) (Si)
	Fleury, B. <i>et al. Chem. Commun.</i> 2005 , 2020-2022	(Mn ₁₂) (Si)
	Steckel, J. S. <i>et al. Nano Lett.</i> 2004 , <i>4</i> , 399-402	(Mn ₁₂) (Au)
	Saywell, A. <i>et al. Nat. Commun.</i> 2010 , <i>1</i> , 75	(Mn ₁₂) (Au)
	Kahle, S. <i>et al. Nano Lett.</i> 2012 , <i>12</i> , 518–521	(Mn ₁₂) (different substrates)

The difficult early years: redox instability of Mn_{12} ac complexes on Au

CHEMISTRY
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14/25

2008



New ISI
Impact Factor
5.330

**No hysteresis observed in
(sub)monolayers**

CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800693

XAS and

Mn

on Gold

Sessoli,^[a]
Arrio,^[a] Marie-Anne Arrio,^[b]

From XAS and XMCD spectra of Mn^{II} and Mn^{III} ions to Mn^{IV} species, respectively. Partial reduction of Mn^{IV} ions to Mn^{III} was clearly observed upon deposition on Au(111) of two different Mn₁₂ derivatives bearing 16-acetylthio-hexadecanoate and 4-(methylthio)benzoate ligands. The average oxidation state, as well as the relative proportions of Mn^{II}, Mn^{III} and Mn^{IV} species, are strongly influenced by the deposition protocol. Furthermore, the local magnetic polarizations are significantly decreased as compared with bulk Mn₁₂ samples. The results highlight an utmost redox instability of Mn₁₂ complexes at gold surfaces, presumably accompanied by structural rearrangements, which cannot be easily revealed by standard surface analysis based on X-ray photoelectron spectroscopy and scanning tunnelling microscopy.

Keywords: magnetic properties · manganese · monolayers · X-ray diffraction · X-ray magnetic circular dichroism

Introduction

Single-molecule magnets (SMMs) have fuelled an impressive number of studies on quantum magnetism at the nano-

scale. Their unique physical behaviour^[1] can potentially be exploited to realise molecule-based devices for information storage and processing.^[2]

The magnetic addressing of individual SMMs, which is required for many of the above-mentioned applications, is now regarded as a realistic goal given the latest developments of scanning probe microscopies^[3] and nano-gap fabrication.^[4,5] Among the most promising tools for addressing the magnetism of individual molecules are spin-polarized scanning tunnelling microscopy (SP-STM)^[6] and electron spin noise STM (ESN-STM).^[7] For both techniques to be applicable, magnetic molecules need to be organised on conducting surfaces.

So far attention has mainly concentrated on the archetypal SMM, the dodecamanganese acetate cluster [Mn₁₂O₁₂(OAc)₁₆(H₂O)₄] (1) and its derivatives, because of their large anisotropy barrier and very-slow spin dynamics at low temperature.^[8,9] The basic structure of [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄] complexes is sketched in Figure 1. Three main strategies of deposition have been devised to graft Mn₁₂-type complexes on gold substrates:^[10] direct deposition of suitably-functionalised molecules on native metal surfaces,^[11–13] deposition of native clusters on pre-functionalized metals^[15–17] and pre-functionalization of both partners with

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7530



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Turning a nightmare into a vision

news & views

MOLECULAR MAGNETS

How a nightmare turns into a vision

Two independent studies demonstrate how control over magnetic molecules on surfaces may lead to new spintronics applications.

Heiko Wende

Wolfgang Pauli once claimed that God created the volume but the surface was invented by the devil. Maybe for this reason surfaces have a sinister attraction for scientists fascinated by the possibilities of completely new effects and hence functionality at surfaces. But the interactions of molecular adsorbates with surfaces can be complicated and the experimental control of these systems can easily turn into a nightmare. Two papers published in this issue by Matteo Mannini and colleagues¹ (page 194) and Pietro Gambardella and colleagues² (page 189) go through this nightmare of surface physics in order to come closer to realizing the vision of molecular spintronics.

In addition to conventional electronics, where electron charge is used to carry information, the basic idea in spintronics is to exploit the spin, where the use of magnetic systems allows control through, for example, magnetic fields. Magnetic molecules are widely studied as suitable candidates for spintronics applications. Their advantage is their broad flexibility, shown by the fact that complex organic molecules are also nature's preferred systems for realizing highly complex processes. However, molecules must always be seen as part of the environment they are placed in, and to use molecular spintronics for real, a fundamental understanding of the basic interactions of magnetic molecules with surfaces is essential. It is in this context that these two studies move a step closer to the molecular spintronics goal.

In the work by Mannini *et al.*, the focal point is the identification of a magnetic memory effect of a monolayer of single-molecule magnets consisting of Fe₄ complexes wired to a gold surface¹ (Fig. 1). They achieved this by demonstrating that the single molecular magnets show a magnetic hysteresis, meaning that the behaviour of the system depends on its history. Under certain conditions, controlled by temperature and the applied magnetic field, the Fe spins in the individual molecules undergo ordering

due to an exchange interaction within the molecule. Gambardella and colleagues follow a different route to control magnetism². At first they assemble a two-dimensional supramolecular network *in situ* on a copper single crystal. Then they demonstrate that the preferred magnetic orientation of the system, its magnetic anisotropy, can be controlled by the adsorption of oxygen molecules. Without the adsorbed oxygen molecules, the supramolecular assembly consisting of Fe and benzenedicarboxylic acid can be magnetized easily parallel to the surface plane. After oxygen adsorption, this easy direction turns out of the plane. The use of oxygen as an adsorbate is particularly interesting, as in another recent work it is demonstrated that the magnetic coupling of paramagnetic porphyrin molecules to ferromagnetic surfaces can be tailored through oxygen atoms³.

It is helpful to look at the similarities but also the fundamental differences between the two studies published in this

issue: in contrast to the work on the single molecular magnets by Mannini *et al.*, Gambardella *et al.* observe no coupling of the Fe spins in their supramolecular network through, for example, intramolecular exchange interactions. In their case, the Fe spins are ordered only by the applied magnetic field. However, for the single molecular magnets investigated by Mannini *et al.*, the spins within one molecule show ordering phenomena at a temperature of 0.5 K. Still, owing to resonant tunnelling effects in zero field, the remanent magnetization of this single molecular magnets remains pretty small.

As both studies are carried out very low temperatures in the kelvin and even sub-kelvin regime, and the important magnetic effects are determined at sizeable applied magnetic fields ranging from 0.25 T up to 6 T, an immediate realization of a molecular spintronic device is not yet possible. Nevertheless, both works demonstrate the current possibilities and the new frontiers of surface science. An

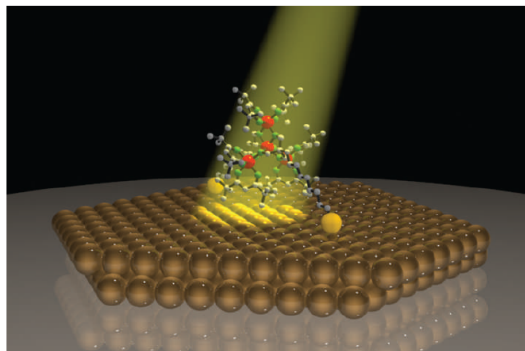


Figure 1 Controlling magnetic molecules on a surface. In the work by Mannini *et al.*¹ single-molecule magnets are bonded to a surface and characterized by the highly sensitive X-ray magnetic circular dichroism technique¹.

news & views

important conclusion of both studies is that the interaction of the magnetic molecules with the surface does not destroy the magnetic behaviour. In particular, in the study by Mannini *et al.* the single molecular magnets were connected to the surface by thiolate-terminated aliphatic chains that allow direct control of the magnetic interaction¹. This bonding was achieved through a wet-chemical synthesis making use of self-assembly effects.

In contrast, the supramolecular network studied by Gambardella and colleagues was constructed using self-assembly by evaporating a molecular precursor layer of terephthalic acid (TPA) followed by deposition of Fe atoms from an electron-beam evaporator under ultrahigh vacuum conditions. Interestingly, both studies

use X-ray absorption spectroscopy at modern third-generation synchrotron radiation facilities to reveal the secrets of their molecules. The X-ray magnetic circular dichroism technique provides the necessary sensitivity to probe the magnetic properties of the molecules in an element-specific manner.

With these techniques it is shown that Fe does indeed connect to the TPA molecules, and thereby the interaction with the Cu substrate is weakened². To support these findings on the electronic structure, the experimental results of Gambardella *et al.* are accompanied by solid density functional calculations and atomic multiplet calculations to model the experimental X-ray absorption spectra². In ref. 1 the experimental spectra reveal that the single molecular behaviour of the

Fe₄ complexes is not destroyed by their connection to the surface, owing to their structural stability and redox robustness. This is a clear advance over well-studied single molecular systems such as Mn₁₂.

In conclusion, both studies demonstrate that the hell that is surface science is not the worst place to be, and that fascinating science can emerge — as long as the place is cooled down sufficiently. □

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2. Gambardella, P. *et al.* *Nature Mater.* 8, 189–193 (2009).
3. Bernein, M. *et al.* *Phys. Rev. Lett.* 102, 047202 (2009).

MATERIAL WITNESS

SHAPING FATE

The promise of stem-cell therapies for tissue regeneration hinges on the fact that, to a first approximation, stem cells can become any other cell type. But therein lies one of the biggest challenges — for how does a stem cell decide its fate? This decision is generally made in the body through complex biochemical pathways involving diffusing signalling molecules. One approach to stem-cell therapeutics is to manipulate these routes using either natural signalling factors or synthetic small molecules that serve the same role.

But there can be another, perhaps more surprising determinant of stem-cell fate. It may be influenced by purely mechanical means such as stretching or stressing cells, for example by altering the stiffness of the matrix in which they grow. Mesenchymal stem cells (MSCs), which are potential progenitors of many cell types including bone-growing osteoblasts, muscle-making myoblasts and tissue-making fibroblasts, will guide differentiation towards myoblasts in a soft matrix that resembles brain tissue, but towards osteoblasts in a hard, bone-mimicking matrix¹. This suggests a role for materials engineering in stem-cell therapy.

It's been long known that cells can sense and respond to deformation, for example via switchable ion

channels in their outer membranes. But more surprising is the fact that they seem responsive to texture and order. MSCs grown on nanopatterned polymer surfaces have been found to become more osteoblast-like when surfaces are embossed with random arrays of nanopits, compared with regular, ordered arrays². That raises the prospect of using nanopatterned matrices to define the distributions of cell types in new tissue seeded from stem cells, for example in bone regeneration.

How does this work? Shu Chien and co-workers at the University of California at San Diego now think they have some clues³. They have found a new guiding factor for MSC differentiation that seems to be purely geometric. They grew human MSCs on substrates of aligned arrays of titanium dioxide nanotubes with varying diameter, from 30 to 100 nm, made electrochemically from thin films of titanium. The behaviour of the cells was strongly dependent on the nanotube size: for 30-nm tubes, they adhered well but didn't really differentiate at all, whereas for 100-nm tubes they became long, thin and osteoblast-like.

Elongation is the key, Chien and colleagues saw that the smaller nanotubes became quickly decorated around their open ends with blobs of



PHILIP BALL

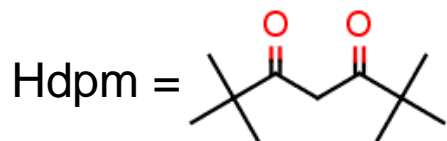
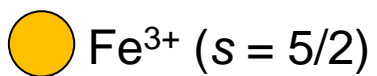
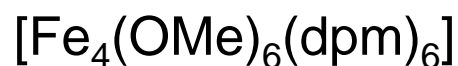
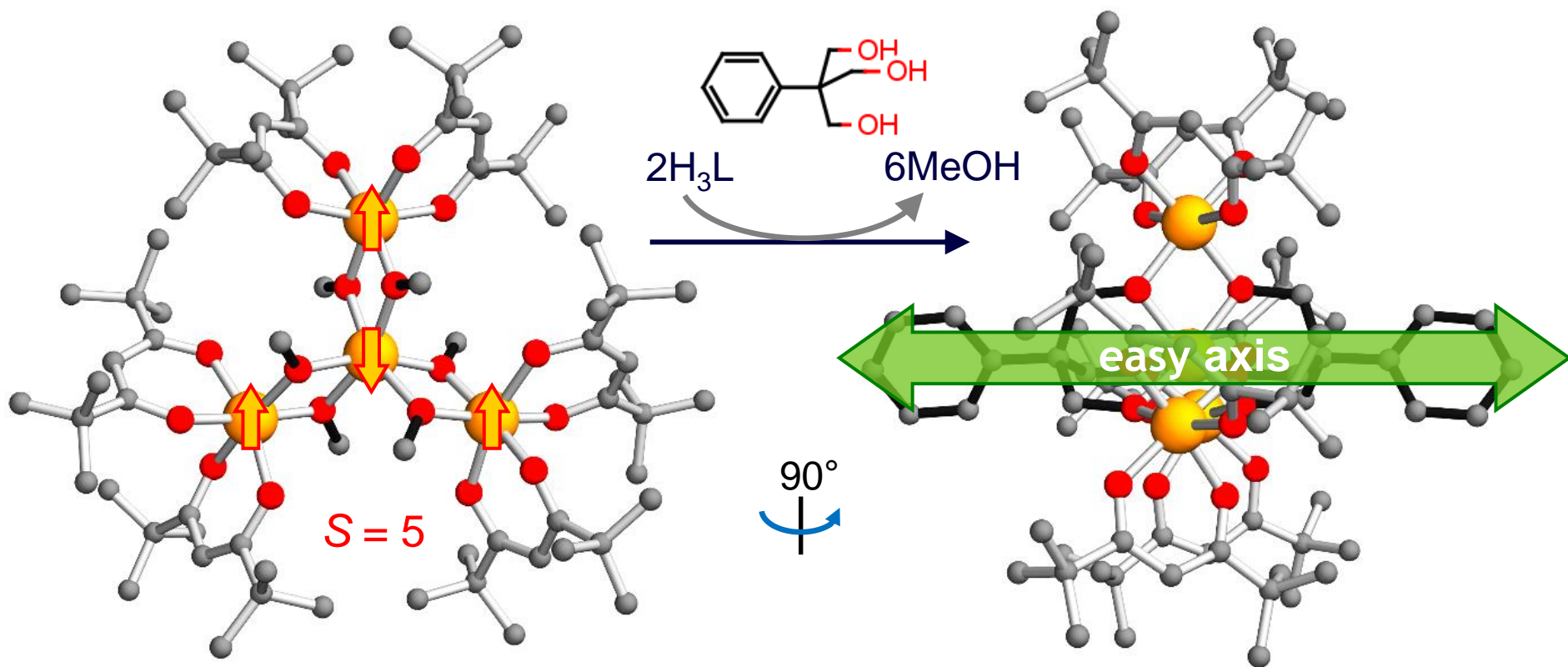
protein: an extracellular matrix deposited by the cells, through which they can adhere to the surface. But these blobs were far less abundant on the wider tubes, simply because there is less space to put them. As a result, cells seeking to anchor themselves have to stretch further in the latter case, and the researchers think that this deformation triggers differentiation to a bone-forming lineage.

That not only suggests a way to guide bone growth by controlling nanostructure: because titanium nanotubes are themselves good candidates for a biocompatible bone-fostering implant material, they can do two jobs at once, providing both support and guidance. □

References

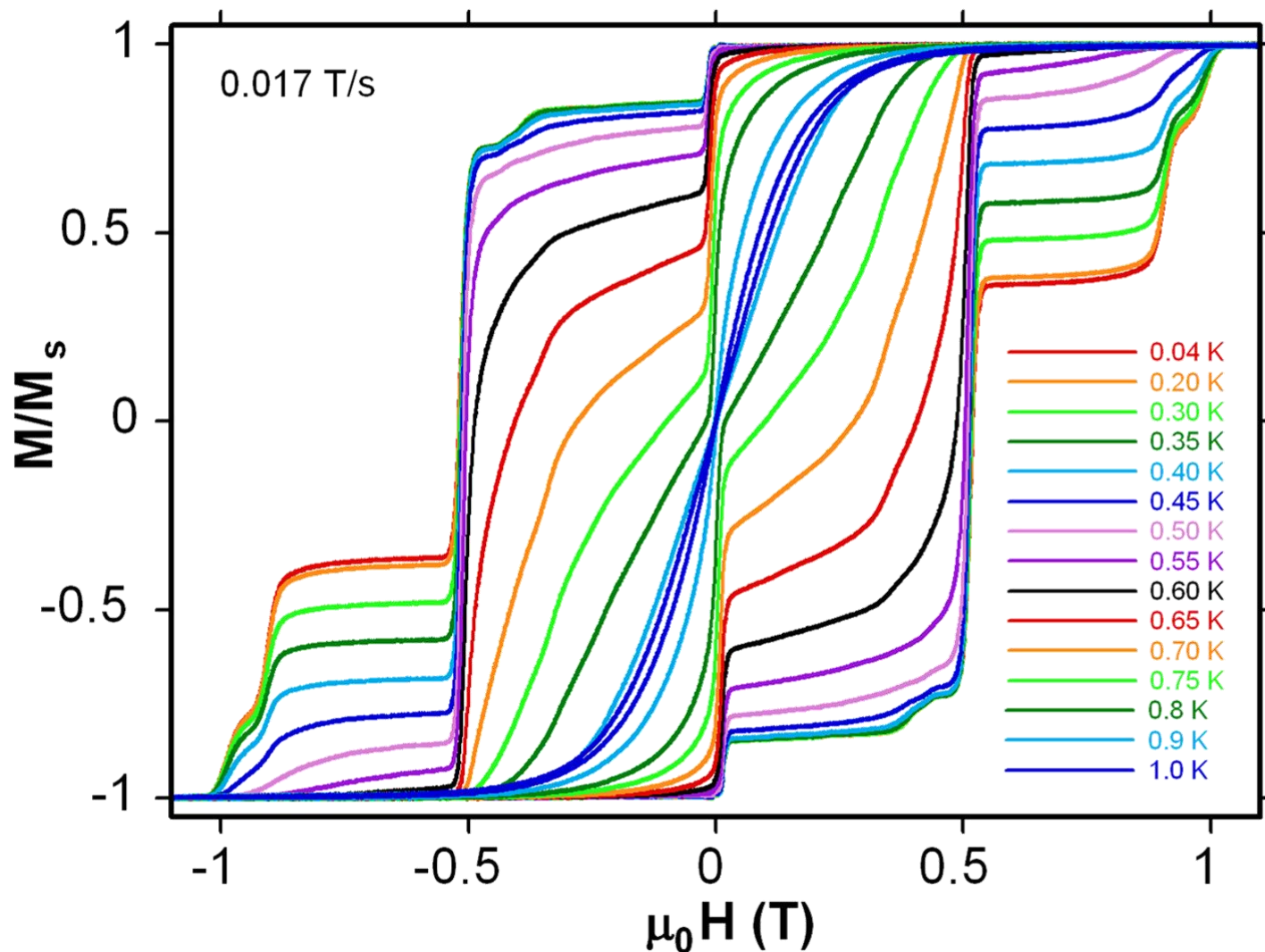
1. Ingber, A. J. *et al.* *Cold Spring Harbor Symp. Quant. Biol.* 72, 677–689 (2007).
2. Dalby, M. J. *et al.* *Nature Mater.* 6, 997–1003 (2007).
3. Oh, S. *et al.* *Proc. Natl. Acad. Sci. USA* doi:10.1073/pnas.0813200106 (2009).

The iron option: tetrairon(III) propellers

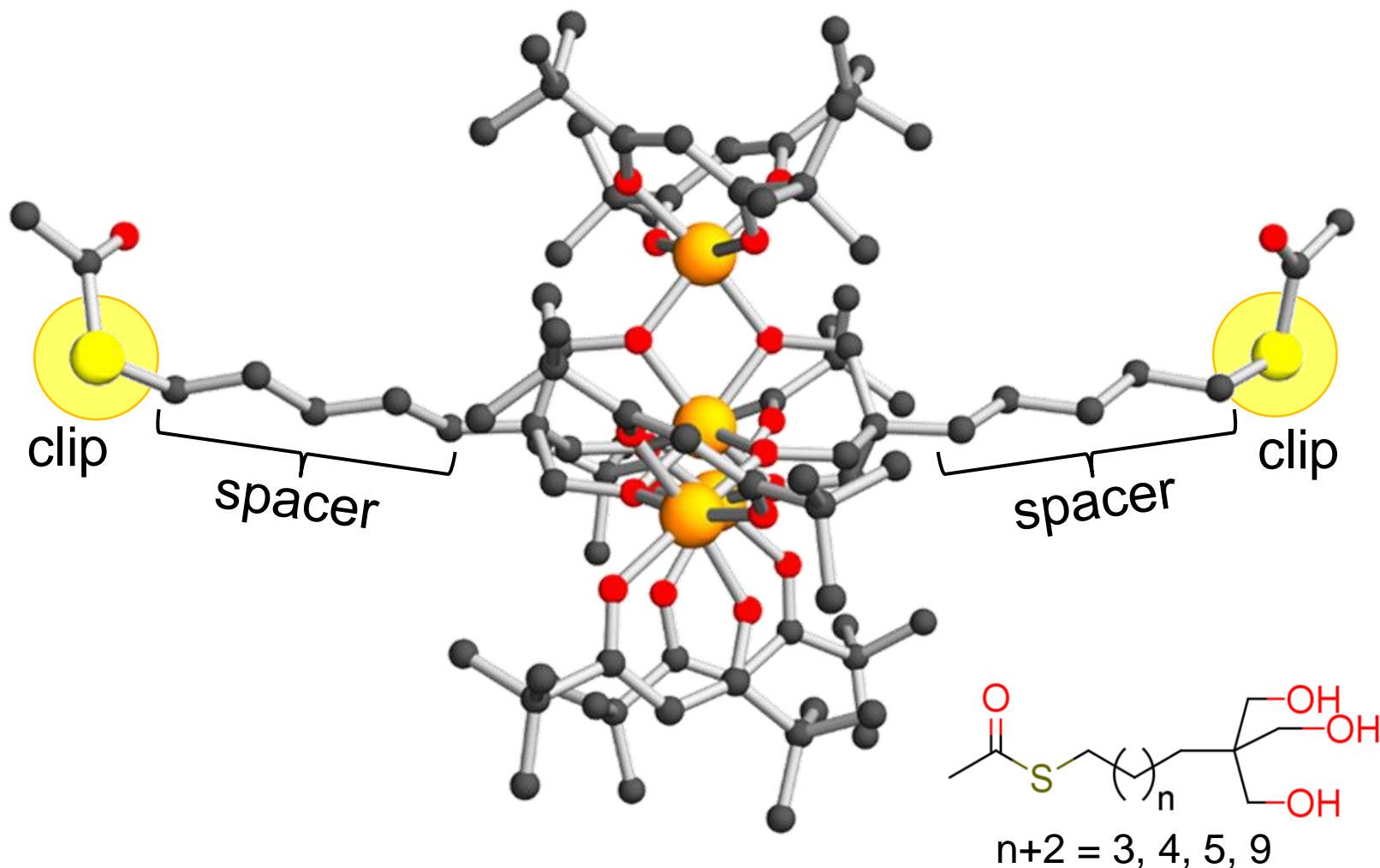


$U/k_B \sim 15\text{-}16 \text{ K}$

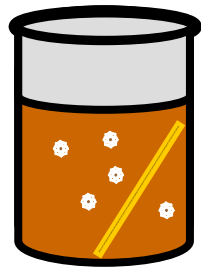
The iron option: tetrairon(II) propellers



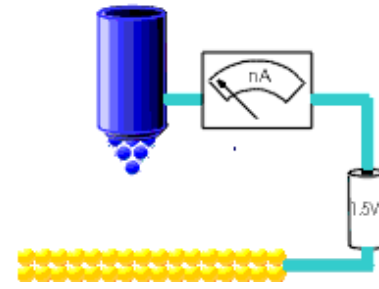
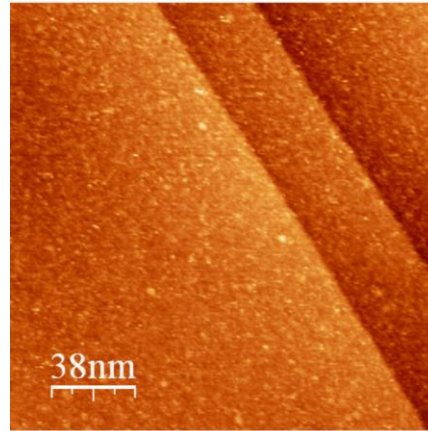
SAc-functionalized Fe₄Cn complexes



Monolayer sample of Fe₄C₉ on Au(111)

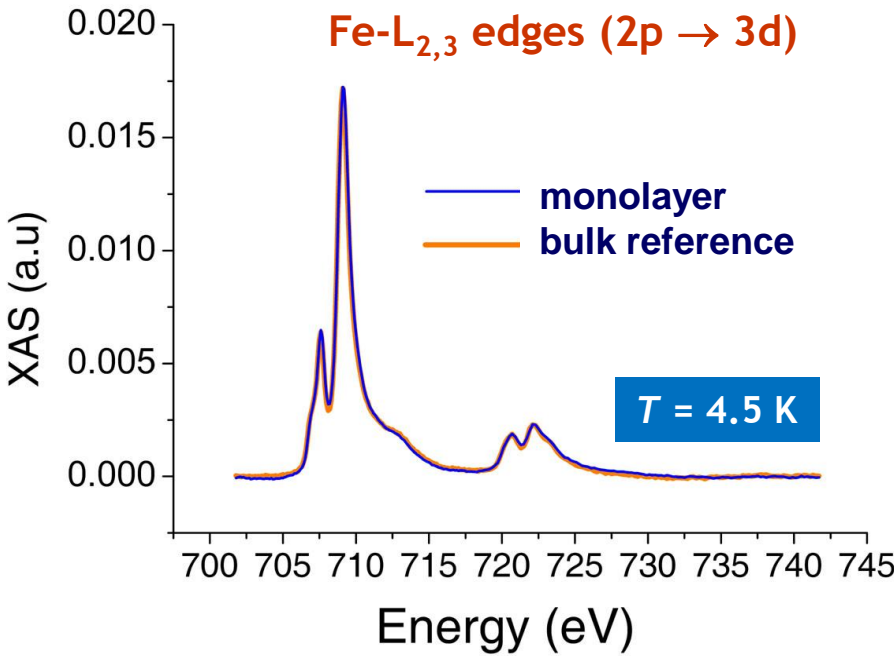
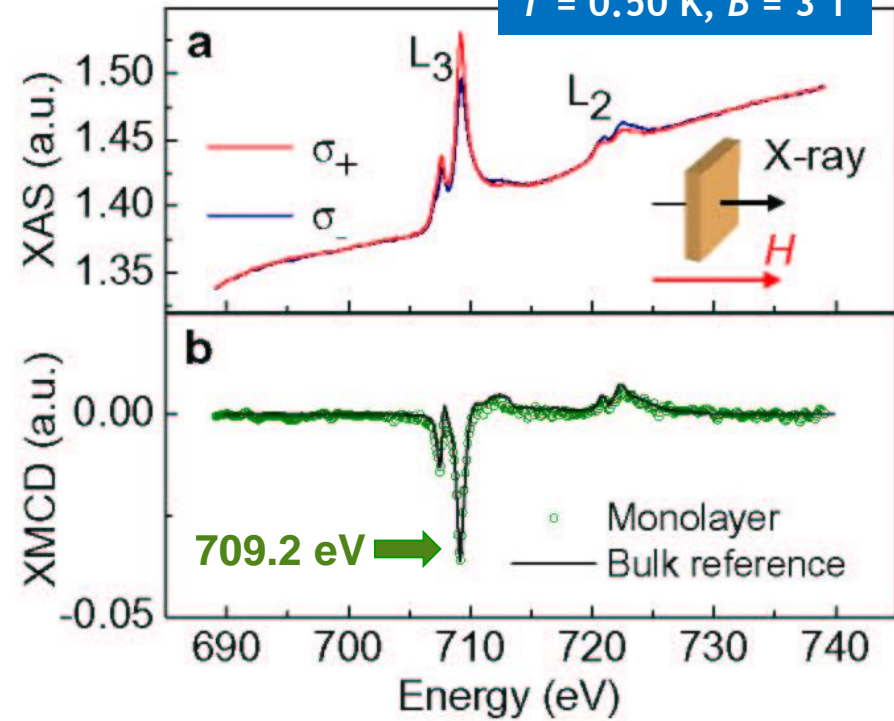


Au(111)
on mica
0.5 mM
in CH₂Cl₂
20 h

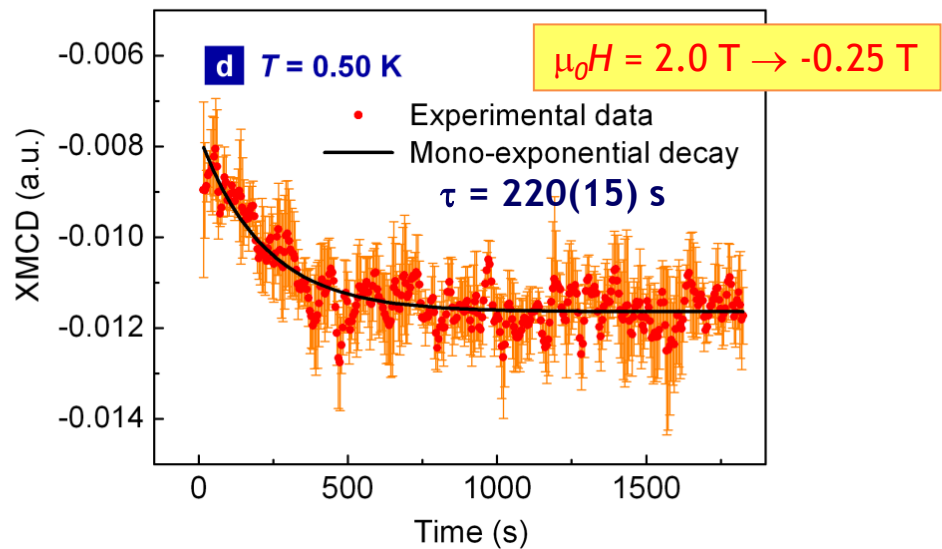
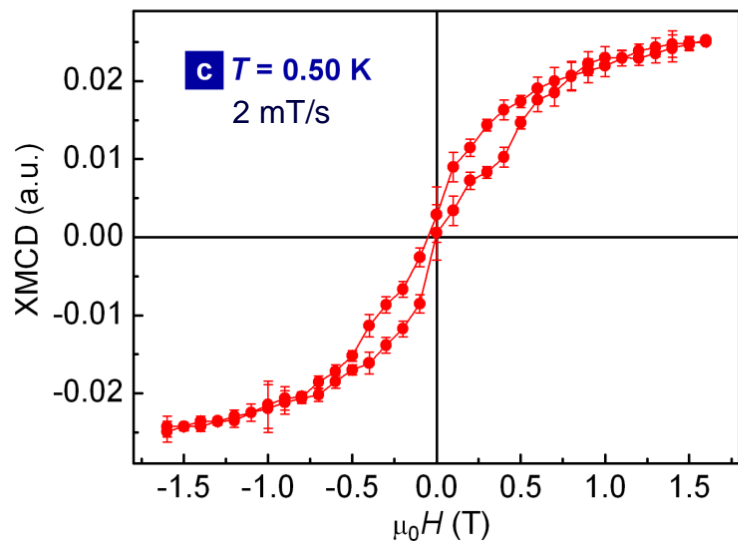
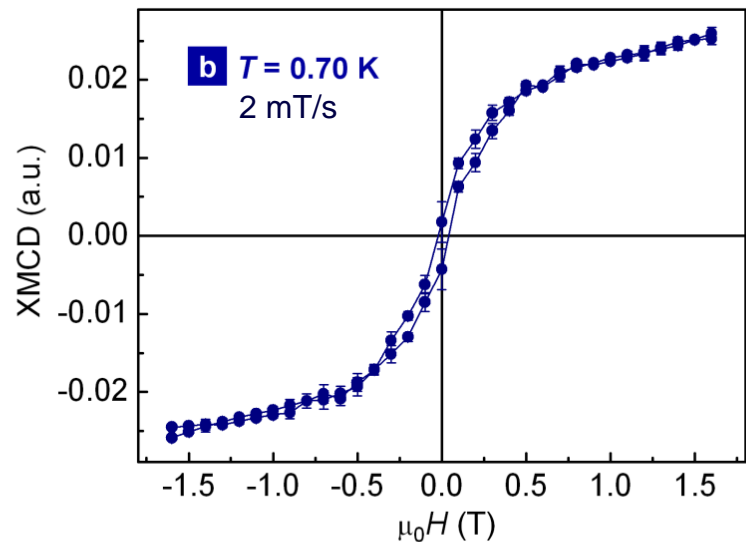
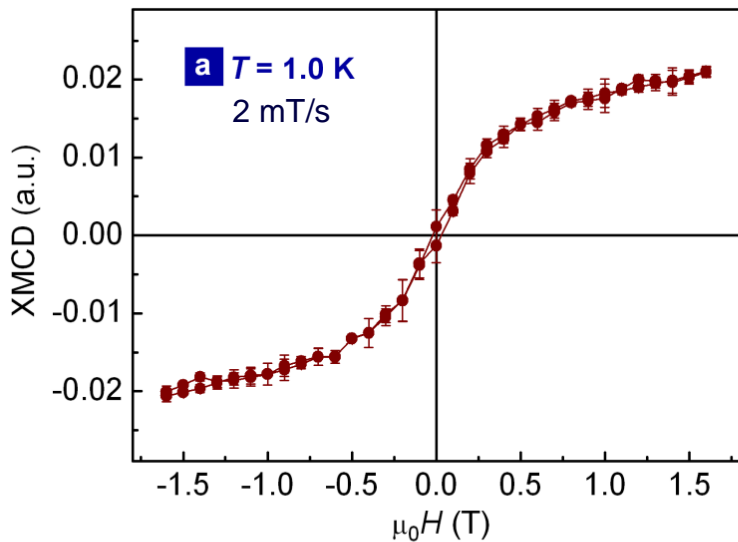


Scanning Tunneling
Microscopy (STM)

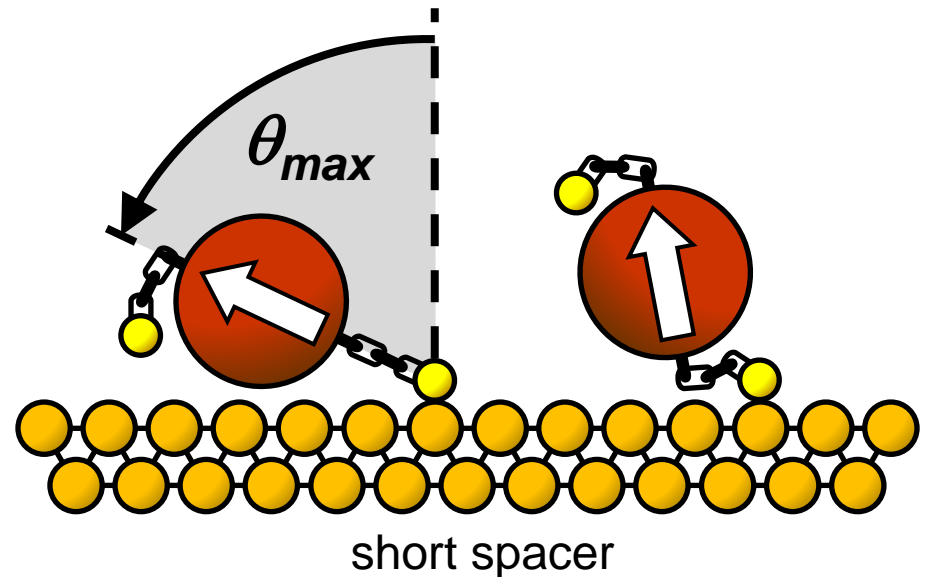
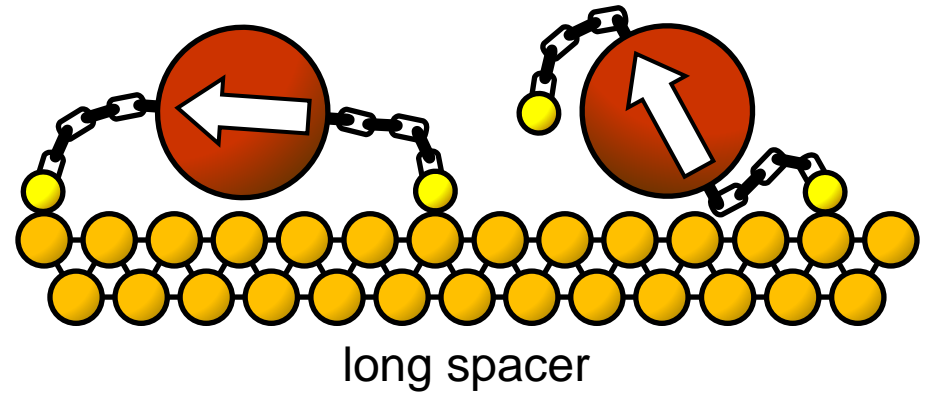
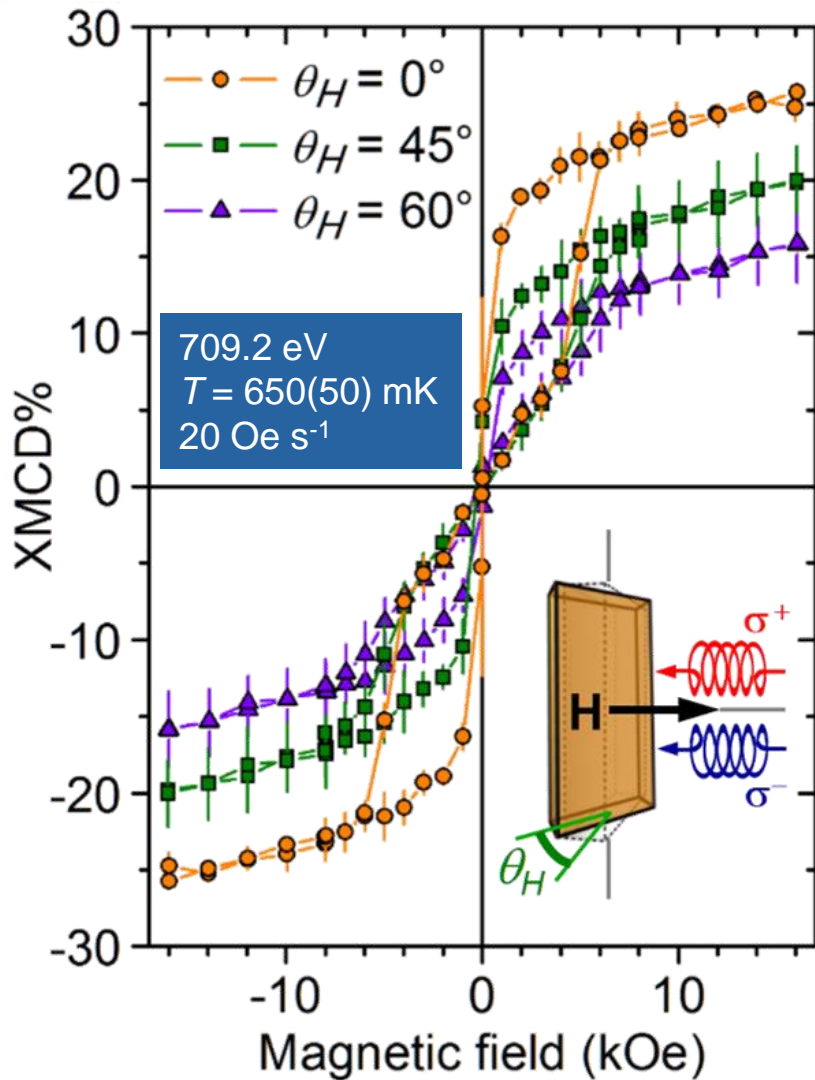
$T = 0.50 \text{ K}, B = 3 \text{ T}$



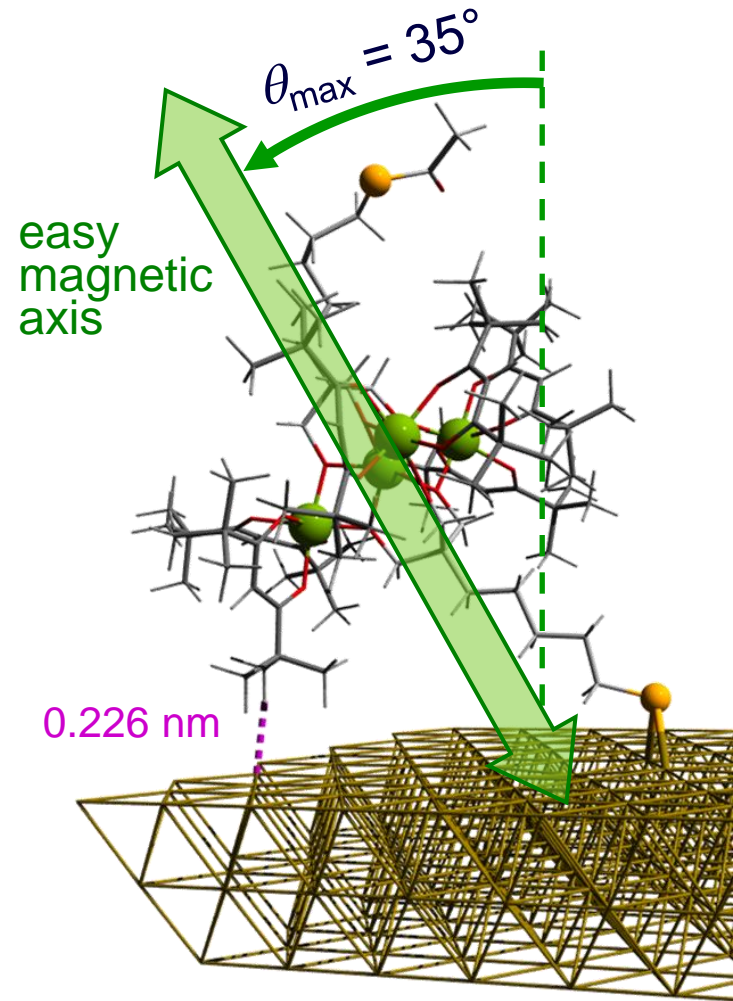
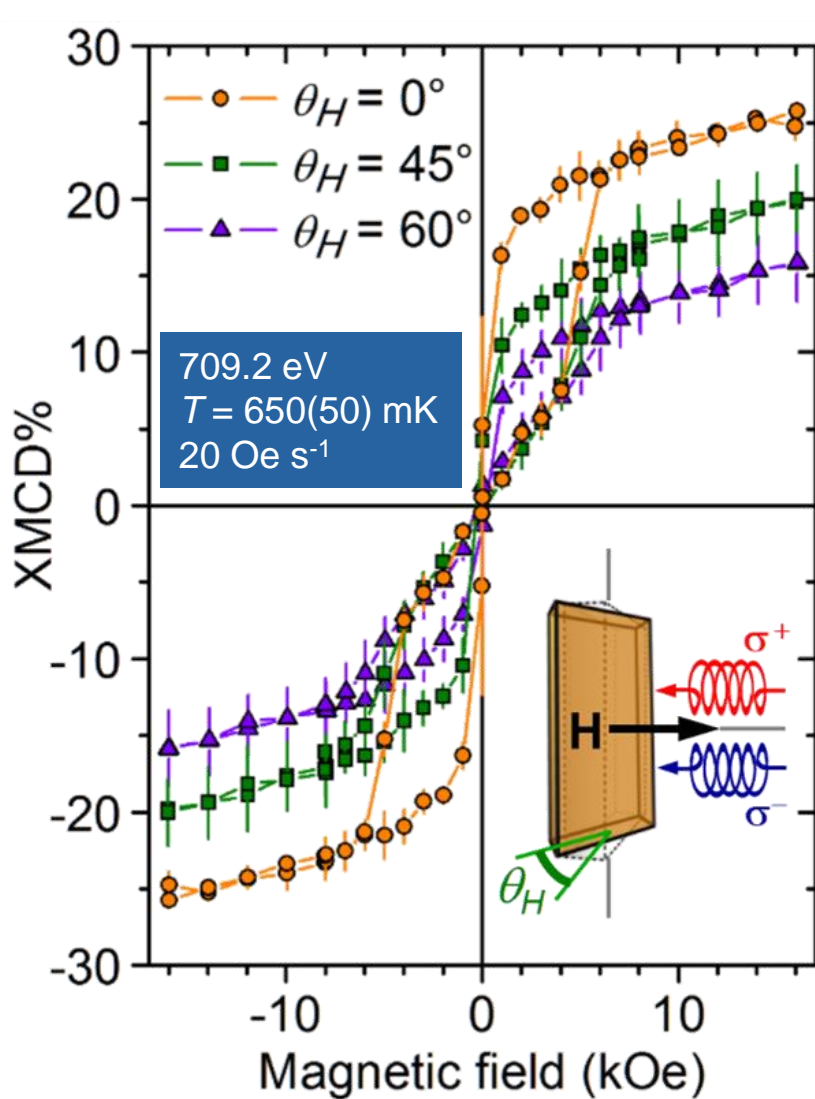
Memory effect of Fe₄C₉ on Au(111)



Memory effect of Fe₄C5 on Au(111)

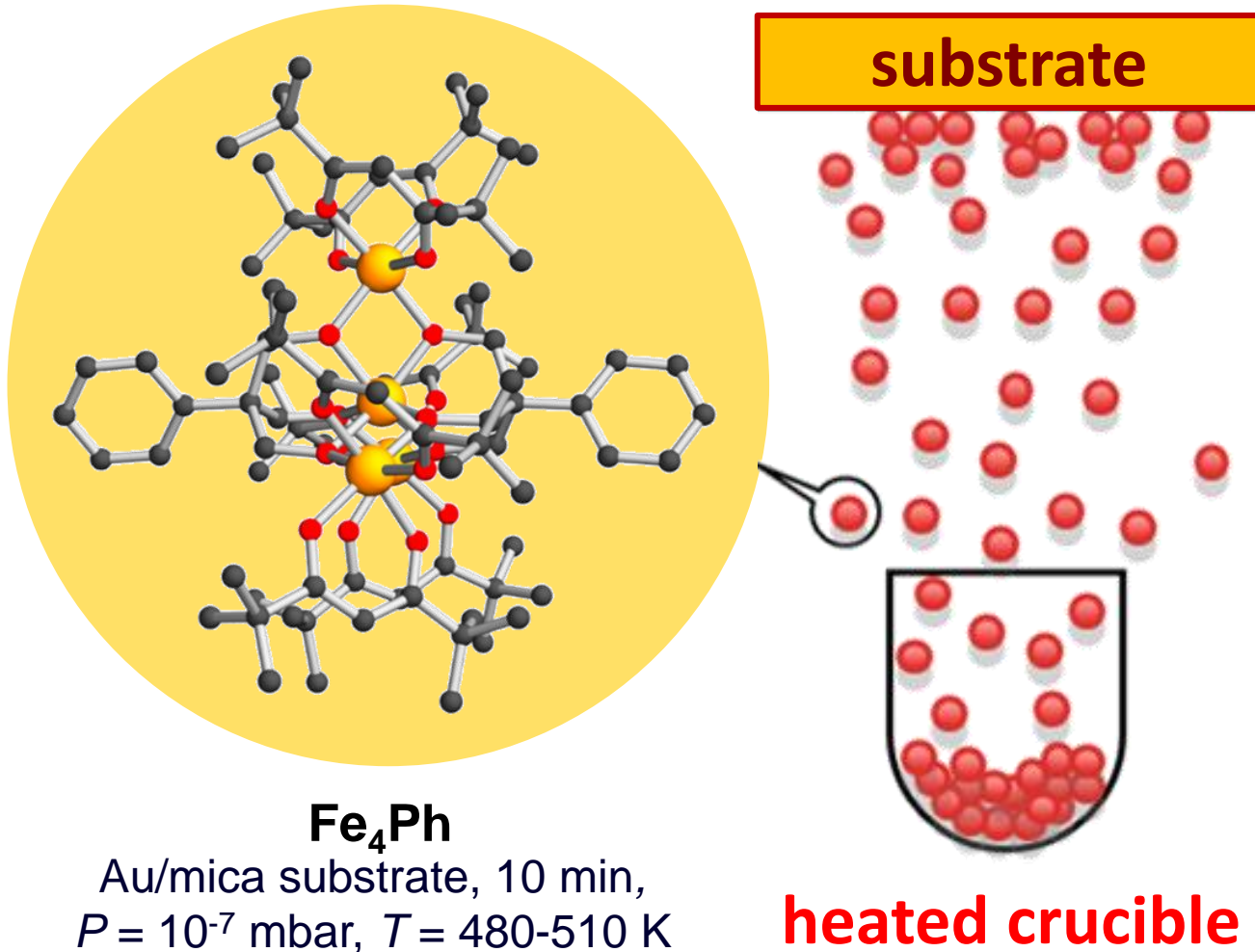


Memory effect of Fe₄C5 on Au(111)



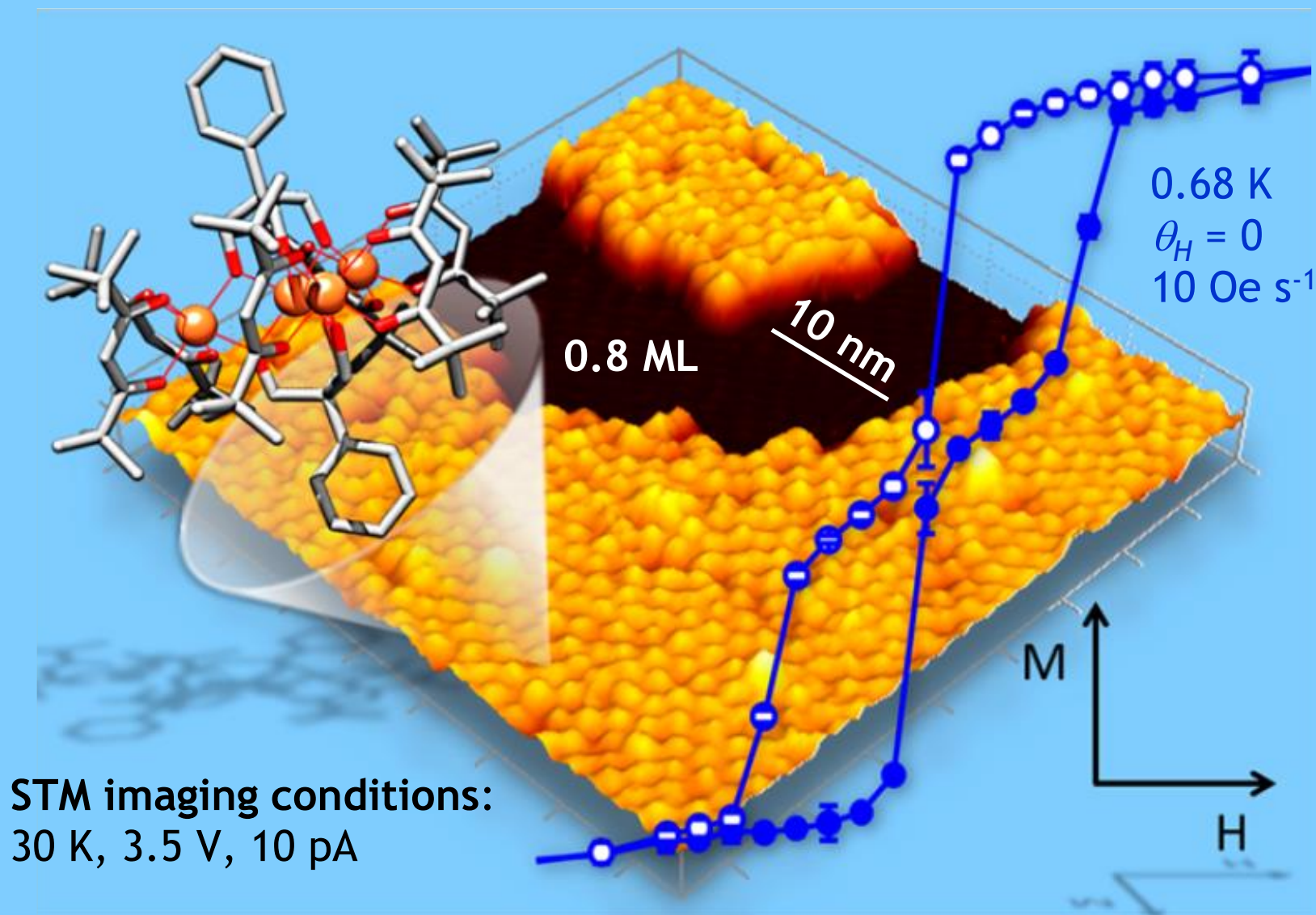
DFT (F. Totti, UniFI)

Clean, «chemistry-free» deposition

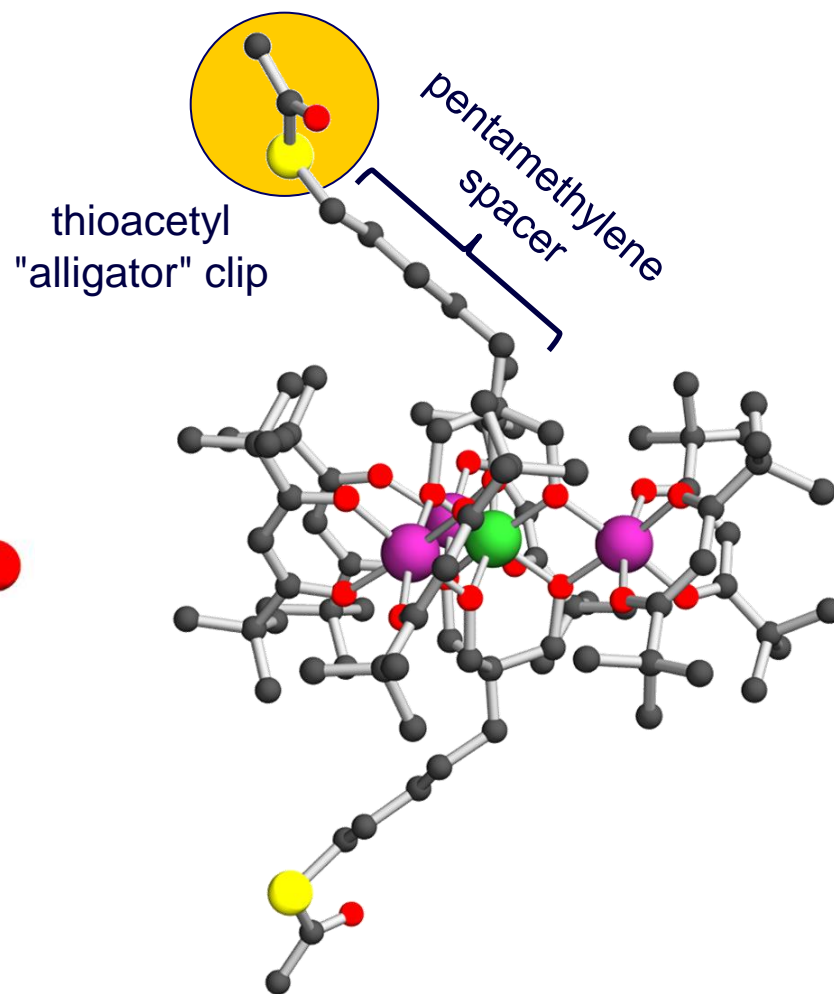
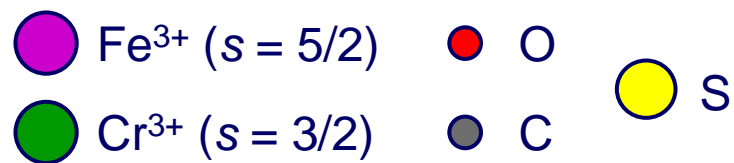
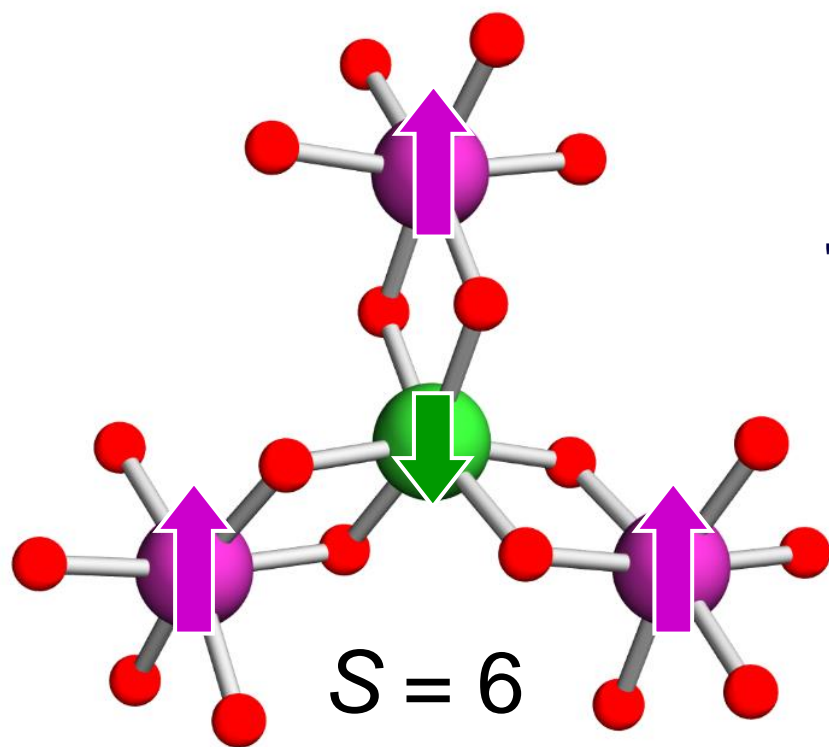


L. Margheriti *et al.*, *Small* 2009, 5, 1460
L. Malavolti *et al.*, *Nano Lett.* 2015, 15, 535

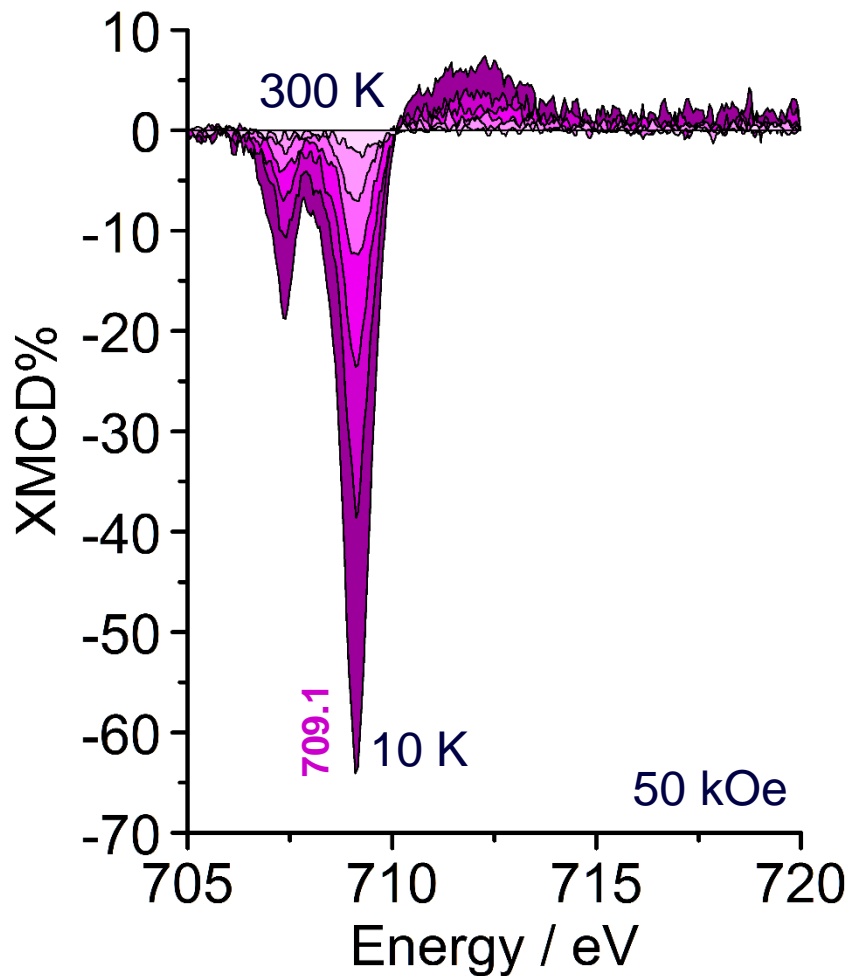
Magnetic hysteresis from a monolayer



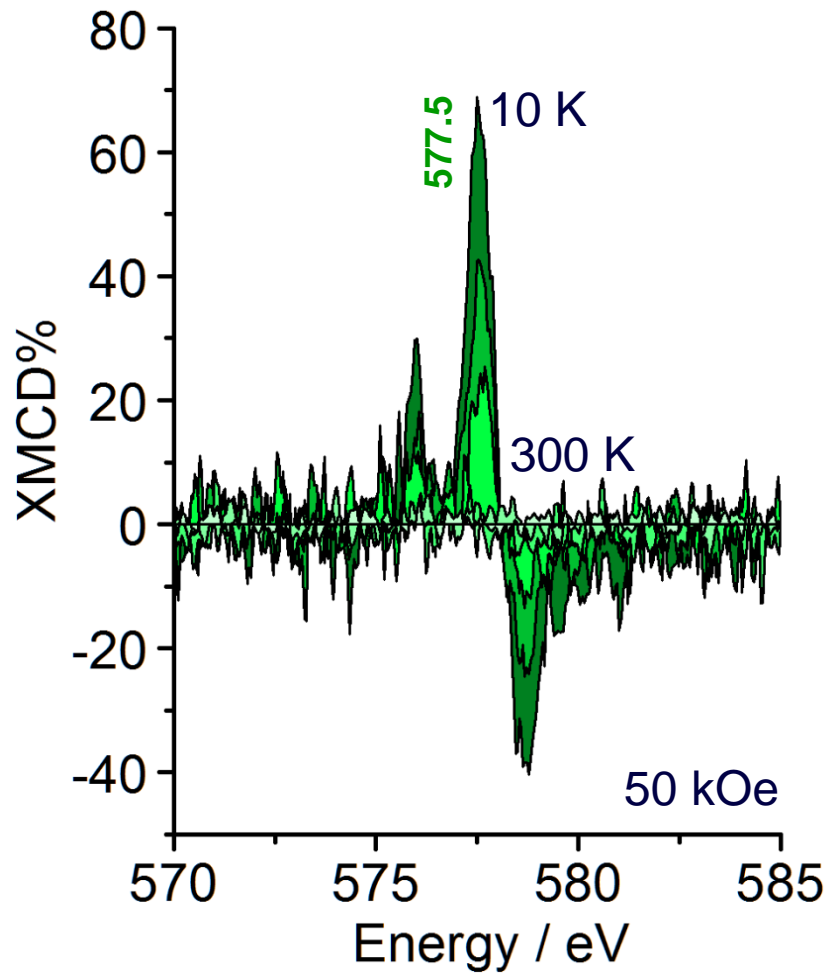
Heterobimetallic propellers: Fe₃CrC₅



Monolayer sample of $\text{Fe}_3\text{CrC5}$ on $\text{Au}(111)$

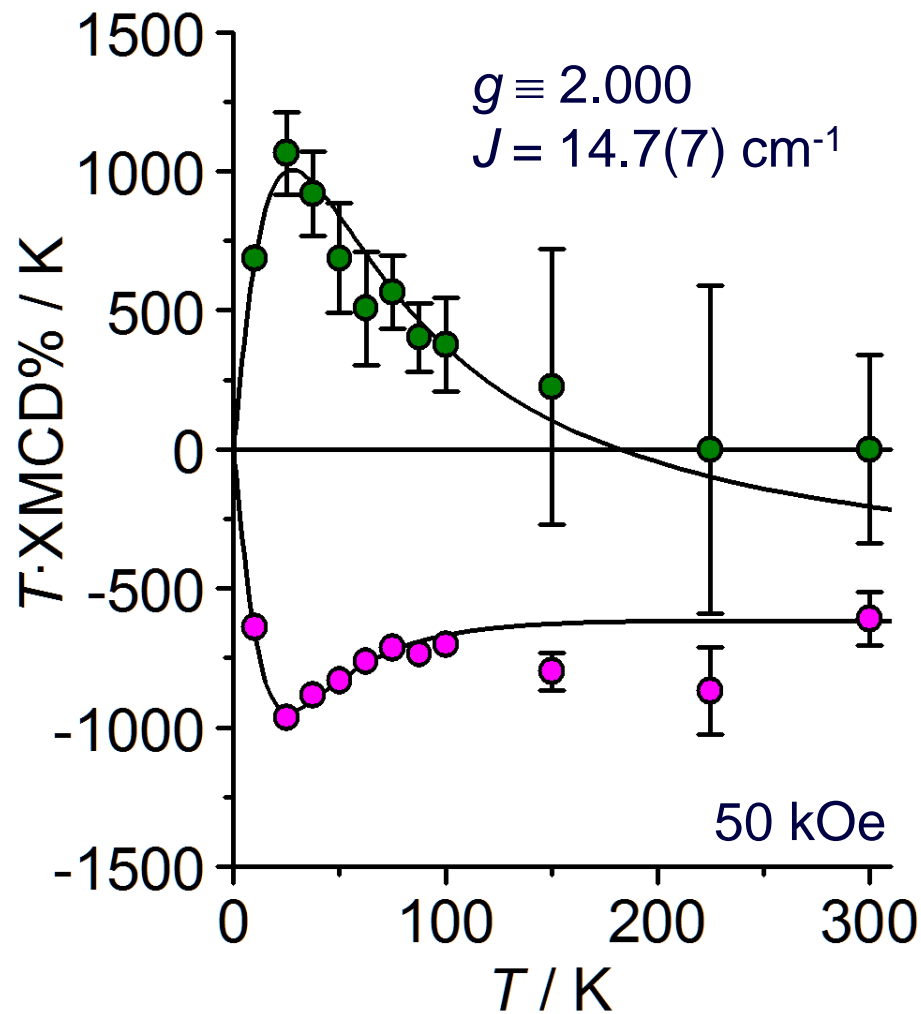
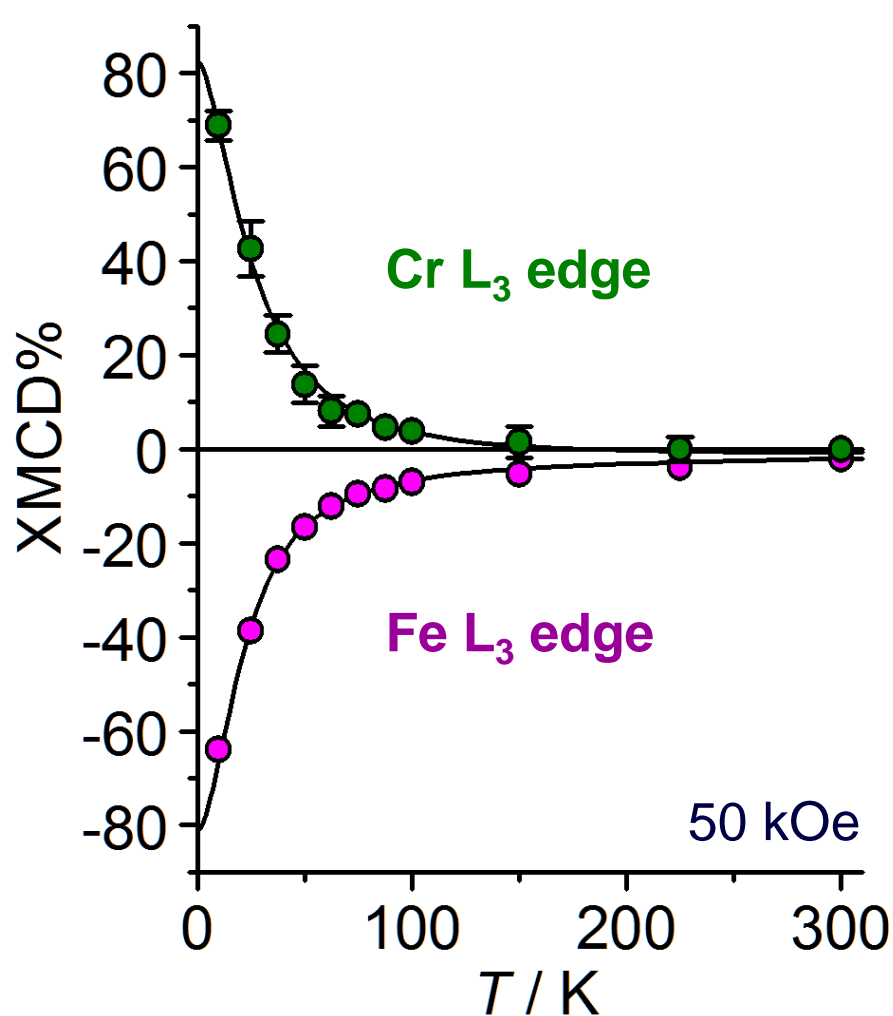


Fe L_3 edge



Cr L_3 edge

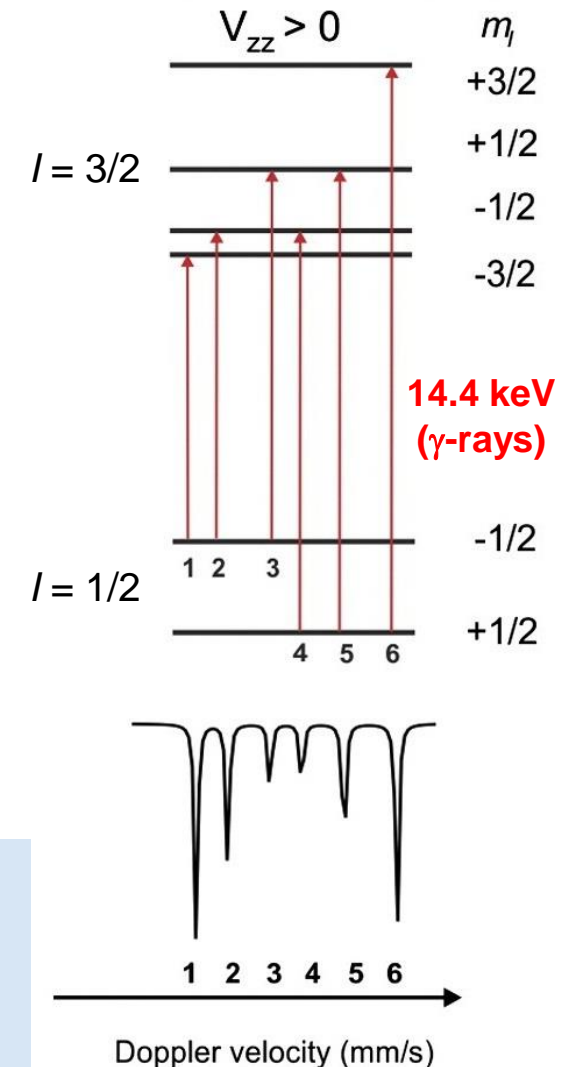
Monolayer sample of $\text{Fe}_3\text{CrC5}$ on $\text{Au}(111)$



Exotics n.1: Mössbauer spectroscopy

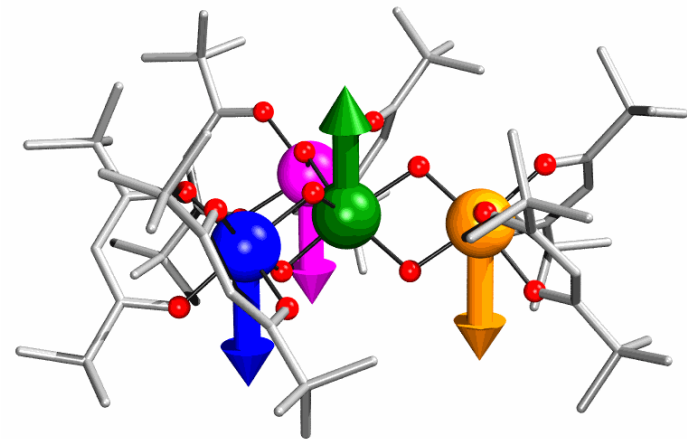
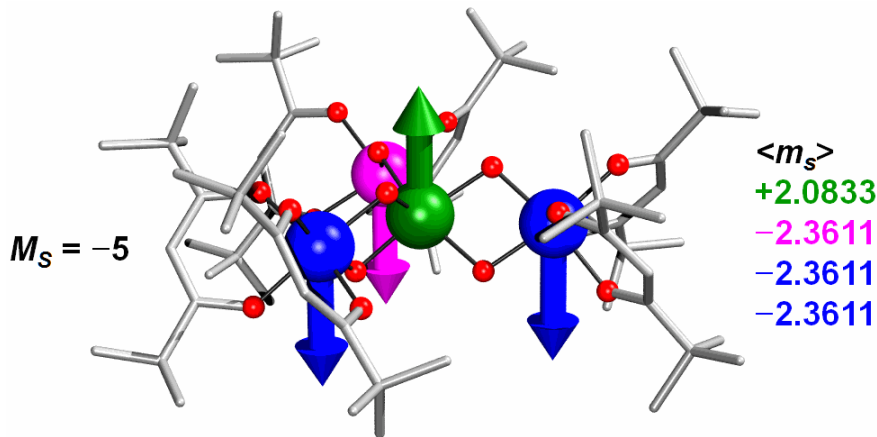
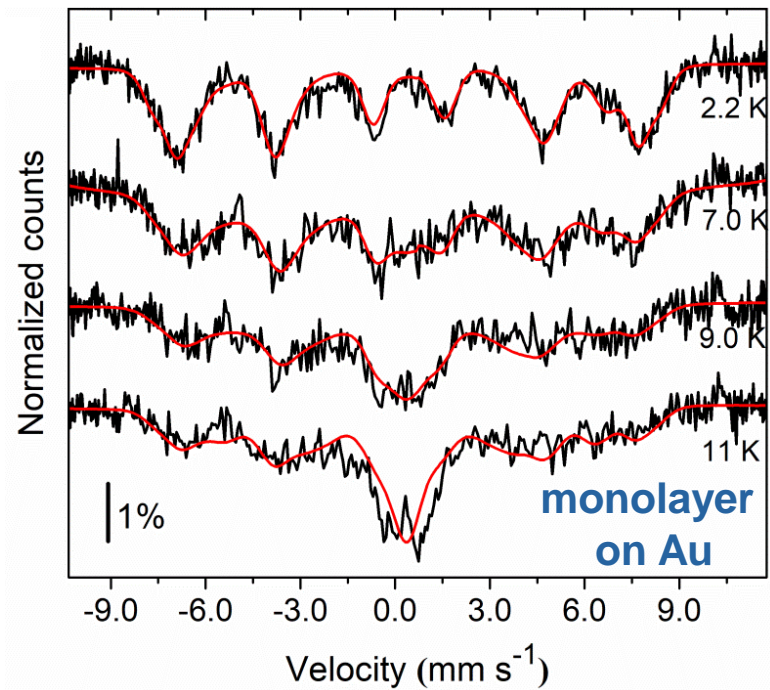
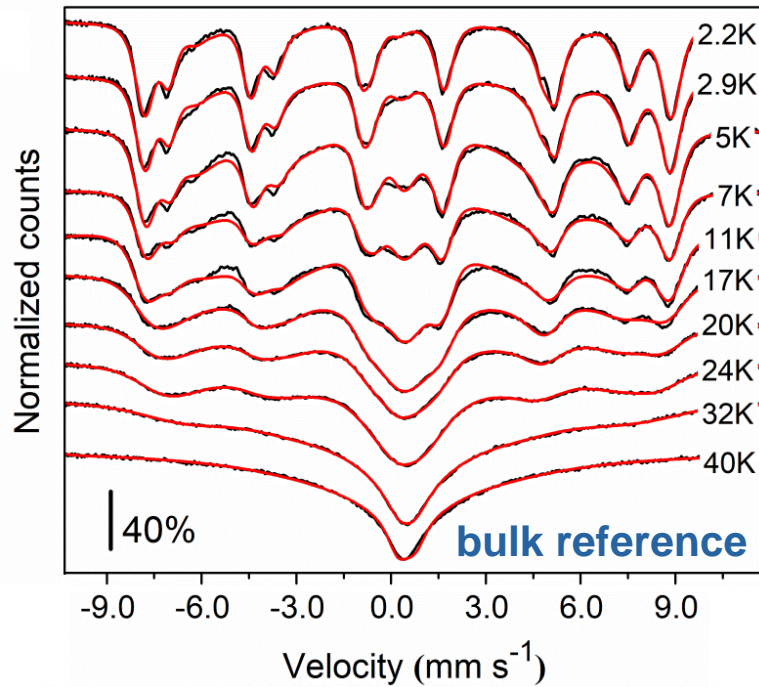
(2.2%)
⁵⁷Fe

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

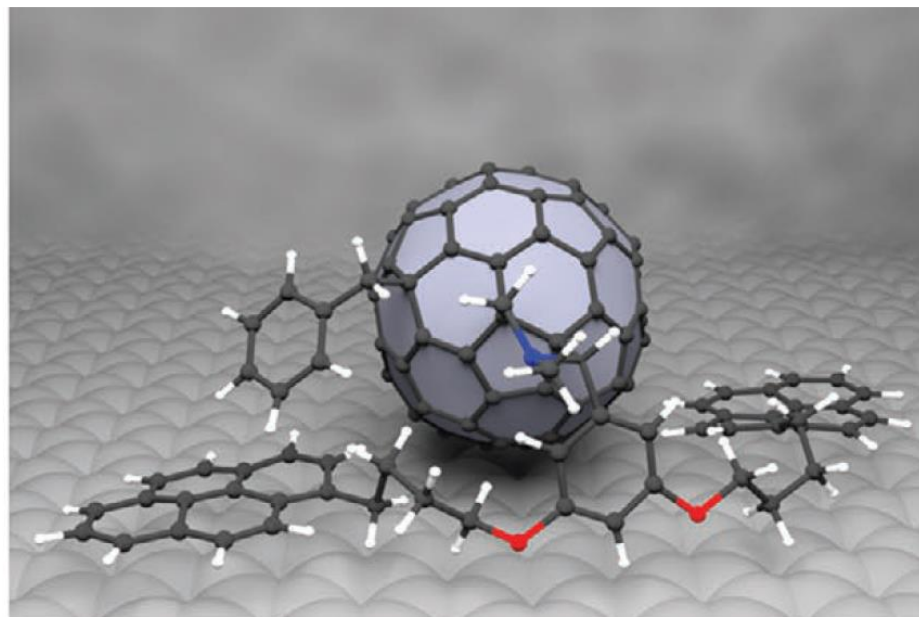
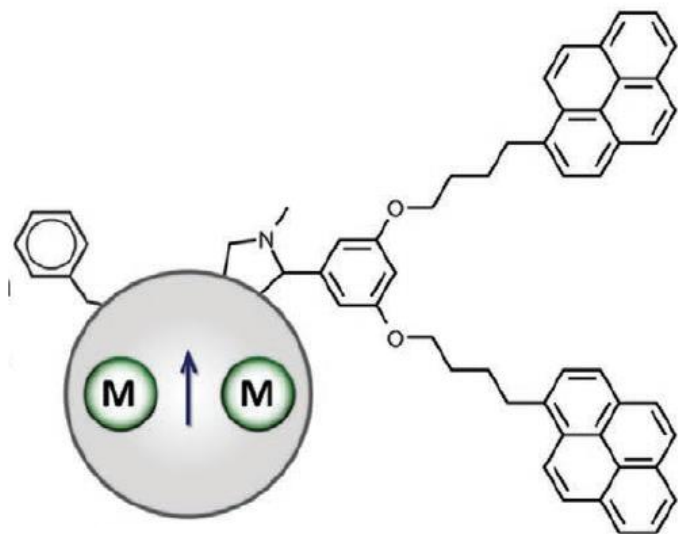


- element-selective local probe, sensitive to oxdn. state, coordination environment, spin state & magnetism
- with conventional equipment, sensitivity is too low for studying molecular monolayers

^{57}Fe -enriched Fe_4C_5 @ESRF



Exotics n.2: endohedral fullerenes



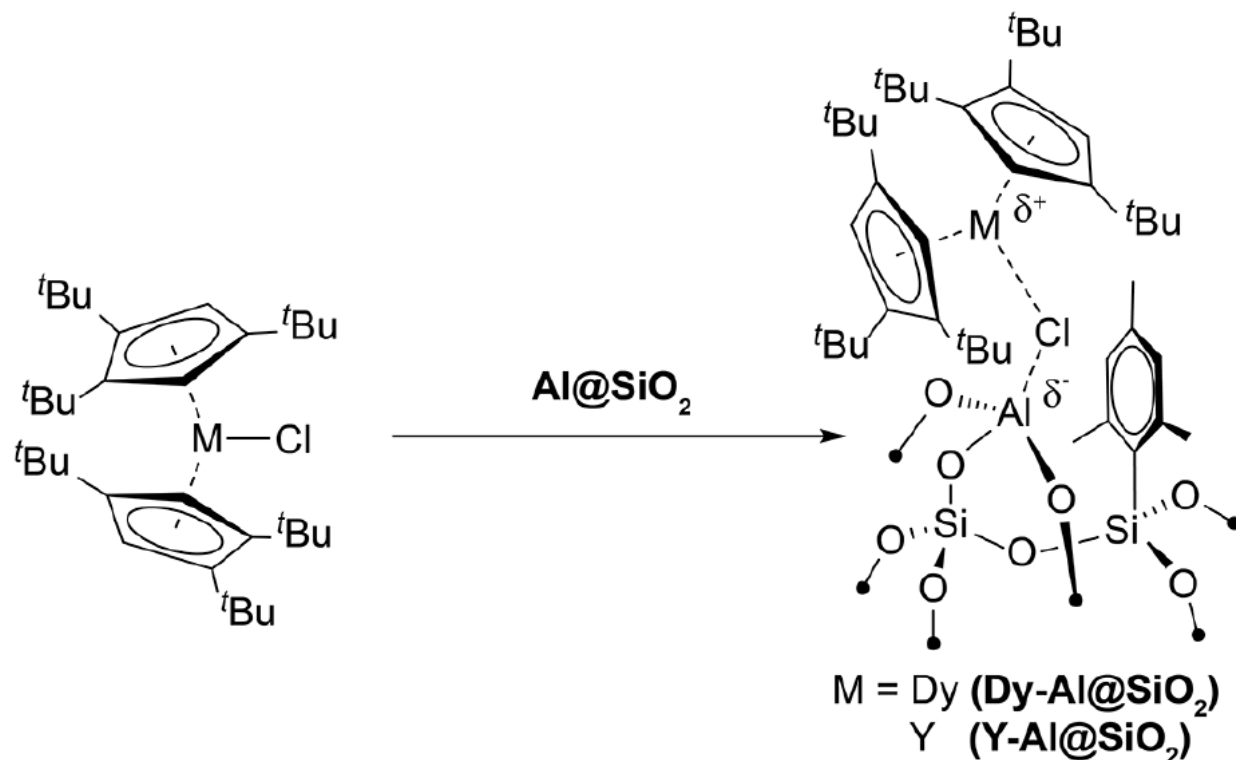
Robust Single Molecule Magnet Monolayers on Graphene and Graphite with Magnetic Hysteresis up to 28 K

Lukas Spree,* Fupin Liu, Volker Neu, Marco Rosenkranz, Georgios Velkos, Yaofeng Wang, Sandra Schiemenz, Jan Dreiser, Pierluigi Gargiani, Manuel Valvidares, Chia-Hsiang Chen, Bernd Büchner, Stanislav M. Avdoshenko,* and Alexey A. Popov*

Exotics n.3: dysprosocenium ions immobilized on silica

Tailored Lewis Acid Sites for High-Temperature Supported Single-Molecule Magnetism

Moritz Bernhardt,[§] Maciej D. Korzyński,[§] Zachariah J. Berkson, Fabrice Pointillart, Boris Le Guennic,^{*} Olivier Cador,^{*} and Christophe Copéret^{*}



- slow magnetic relaxation up to 51 K
- open hysteresis loop up to 8 K

Summary

- for many applications SMMs must be interfaced with a metal surface
- SMM behavior can persist on a metal surface, like Au(111); in rare cases it is enhanced by the surface
- careful selection/development/chemical tailoring of molecules
- development of measurement techniques (XAS/XMCD, synchrotron Mössbauer spectroscopy, scanning probe methods)
- **TO BE DONE:** combining top performances (high T_B values) with processability and chemical stability under ambient conditions; enhancing SMM behavior *via* molecule-substrate interactions;

Further readings

G. Gabarró-Riera, G. Aromí, E. C. Sañudo, Magnetic molecules on surfaces: SMMs and beyond, *Coord. Chem. Rev.* **2023**, *475*, 214858.