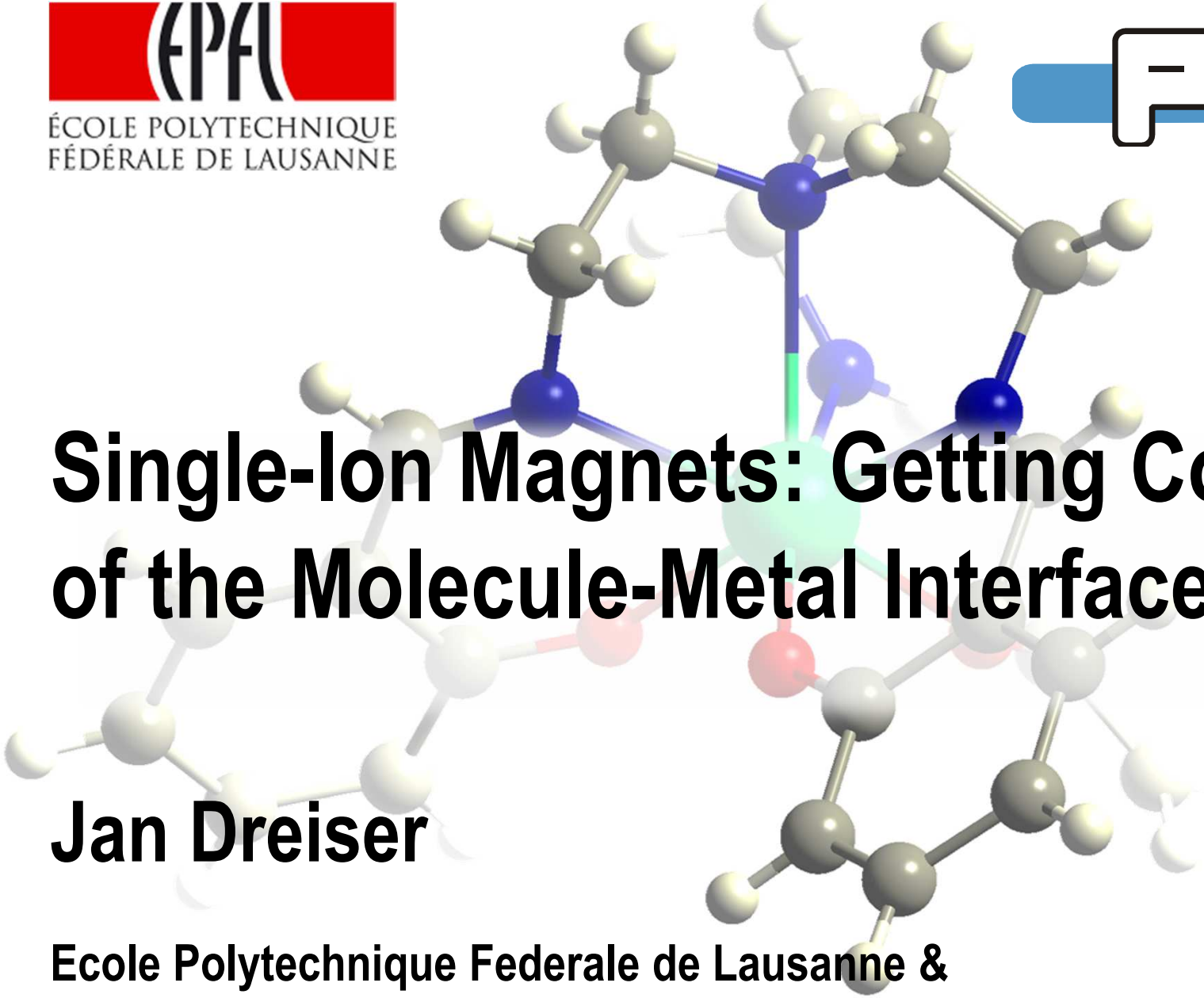
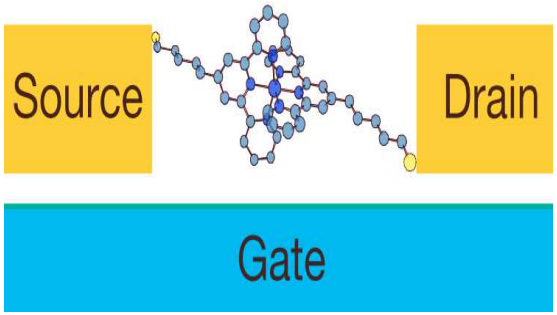


Single-Ion Magnets: Getting Control of the Molecule-Metal Interface

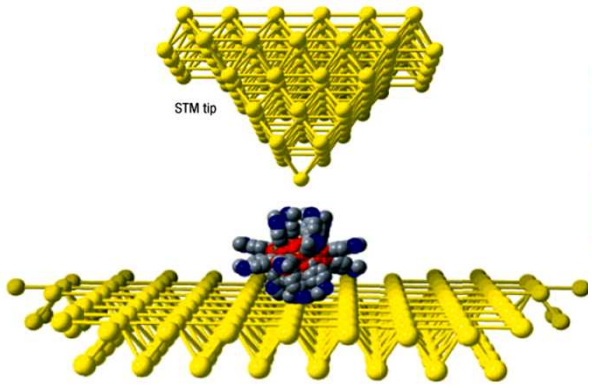
Jan Dreiser

Ecole Polytechnique Federale de Lausanne &
Swiss Light Source, Paul Scherrer Institut, Switzerland

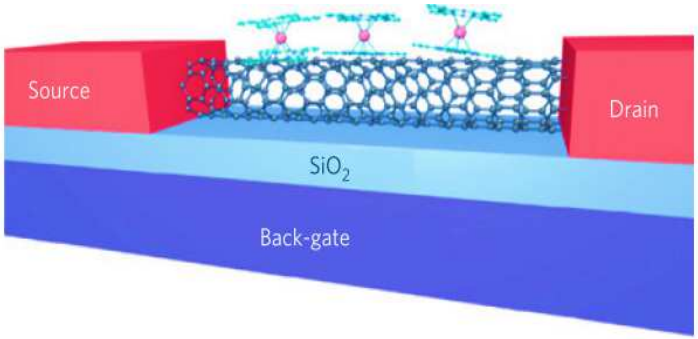
Molecular Spintronics



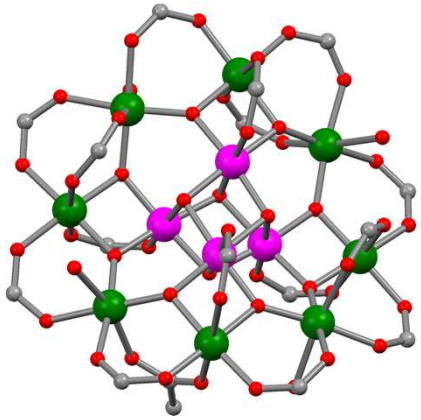
J. Park *et al.*,
Nature 2002



L. Bogani, W. Wernsdorfer,
Nature Materials, 2008



M. Urdampilleta *et al.*,
Nature Materials, 2011

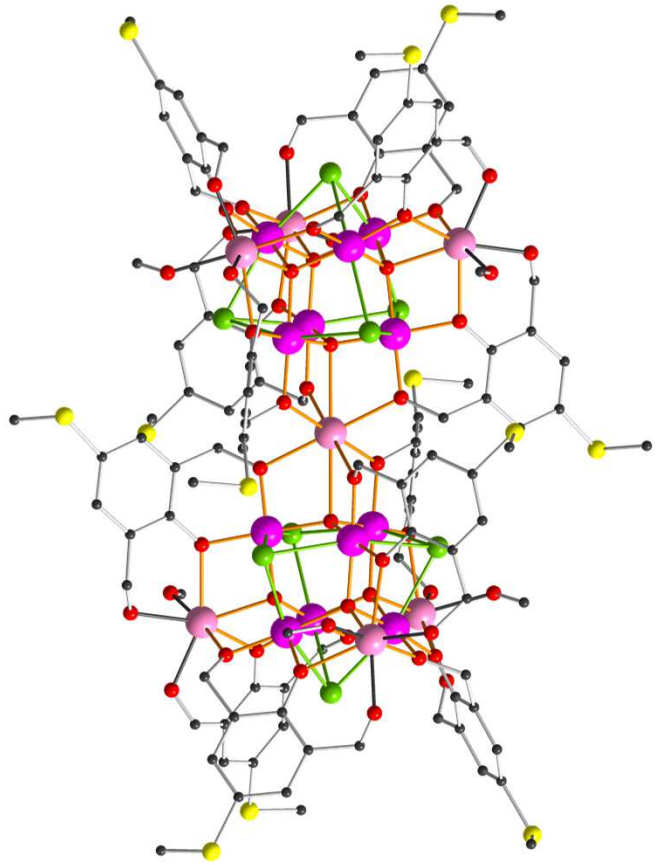


Why Molecules?

- Multifunctional (e.g. spin crossover, optical fluorescence…)
- Chemical engineering possible
- Self assembly on surfaces

Molecule properties can be strongly modified by interaction with the surface.
→ Study bulk and surface-deposited molecules.

The Example of Mn_{19} Coordination Clusters

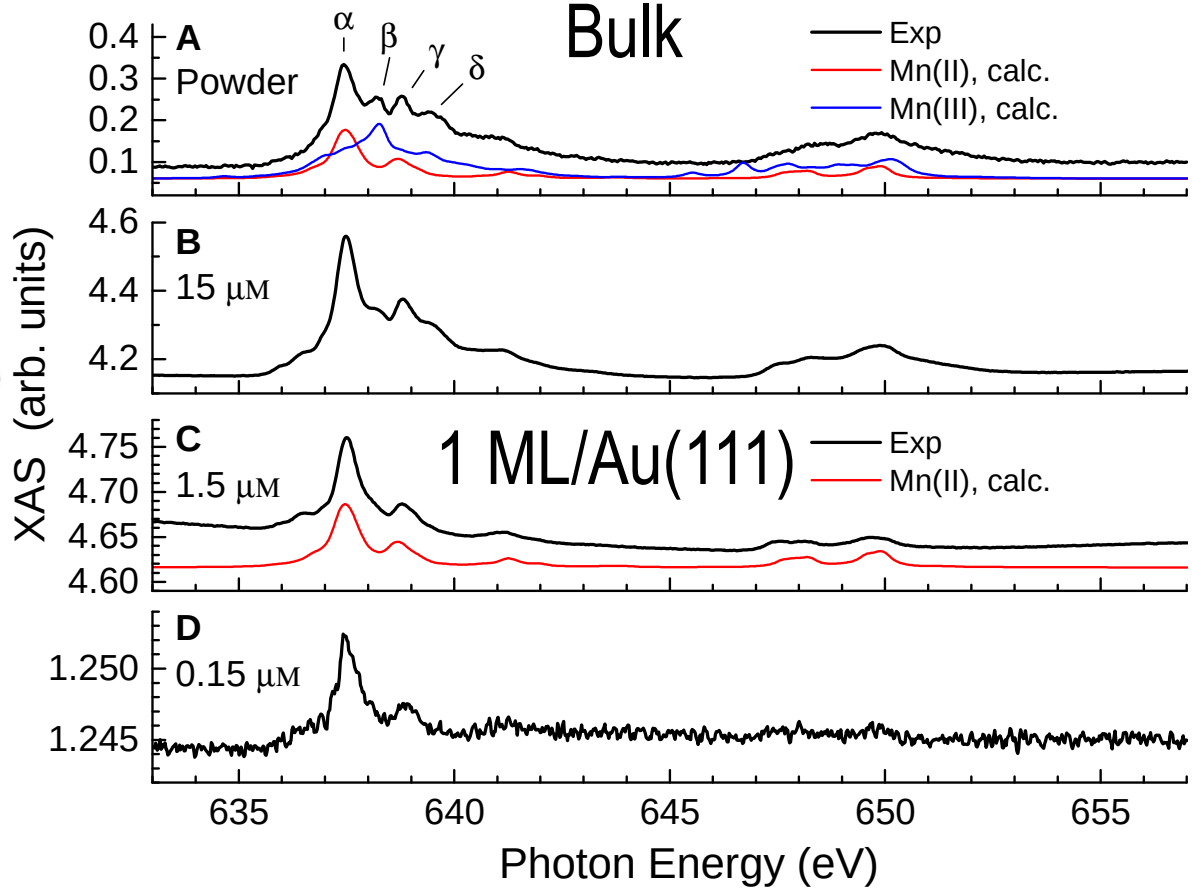


"Mn_{19}(SMe)"

Mn(II)

Mn(III)

JD et al., *J. Phys. Chem. C* 2015



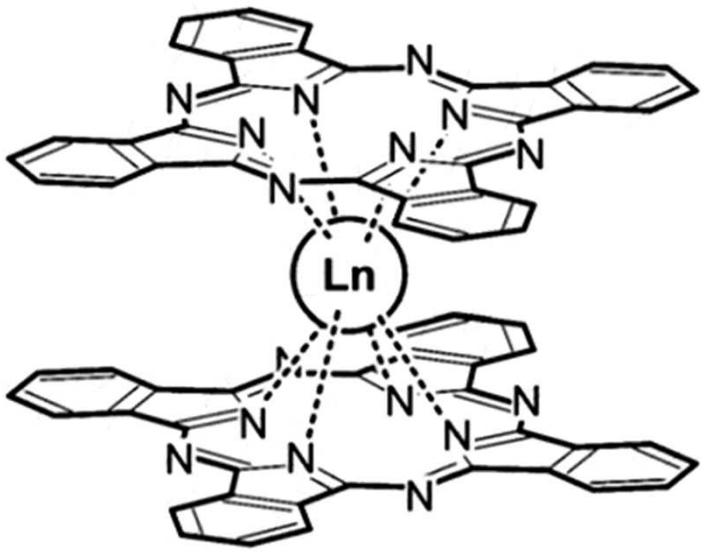
Mn12:
Voss et al., *Phys Rev. B* 2007
Mannini et al., *Chem. Eur. J.* 2008
Saywell et al., *Nanotechnology* 2011

Outline

- Lanthanide Single-Ion Magnets
- Magnetic & Spectroscopic Properties of Bulk Er(trensal)
- Molecule-Metal Hybrid Systems
  - Er(trensal) on Au(111)
  - Magnetic Exchange Coupling to Ni/Cu(100)
  - Ordering on Graphene/Ru(0001)
- Conclusions

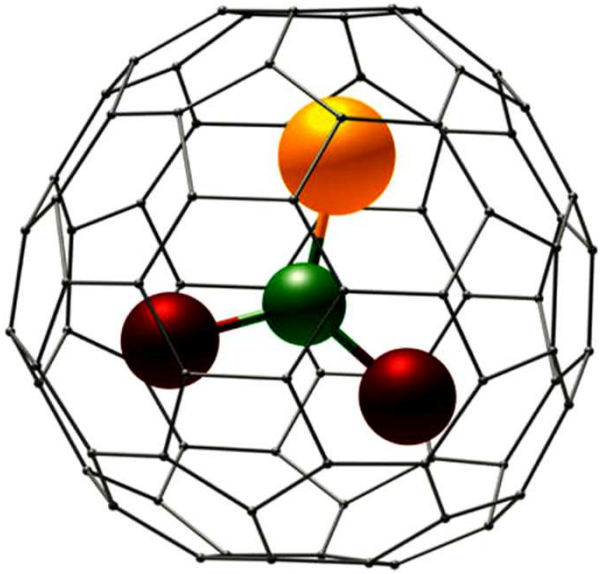
Lanthanide Molecular Single-Ion Magnets

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanum 138.906	Cerium 140.115	Praseodymium 140.908	Neodymium 144.24	Promethium 144.913	Samarium 150.36	Europium 151.966	Gadolinium 157.25	Terbium 158.925	Dysprosium 162.50	Holmium 164.930	Erbium 167.26	Thulium 168.934	Ytterbium 173.04	Lutetium 174.967



Coordination Complex $[LnPc_2]^-$

Ishikawa *et al*., JACS 2003



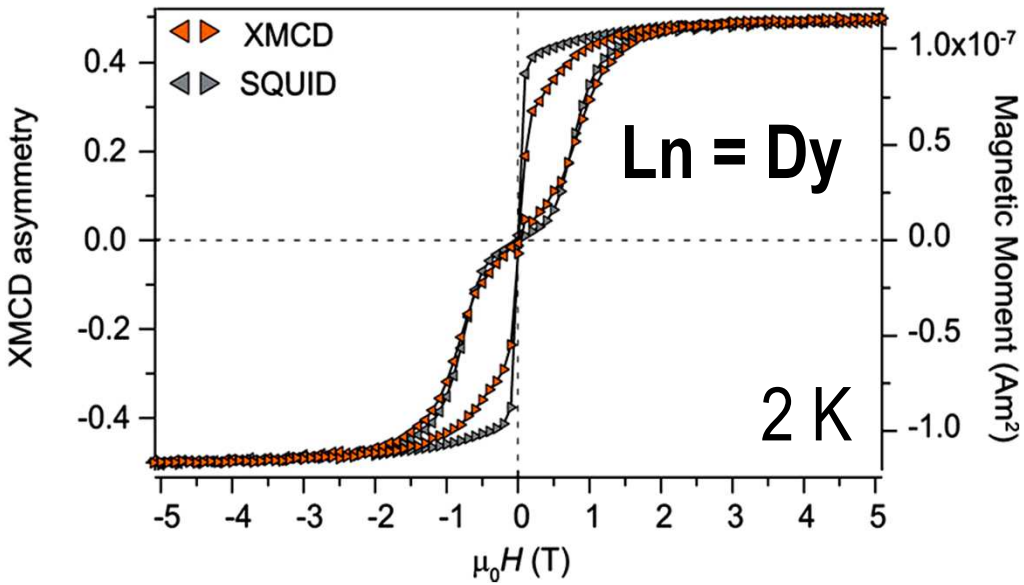
Endohedral Metallofullerene $LnSc_2N@C_{80}$

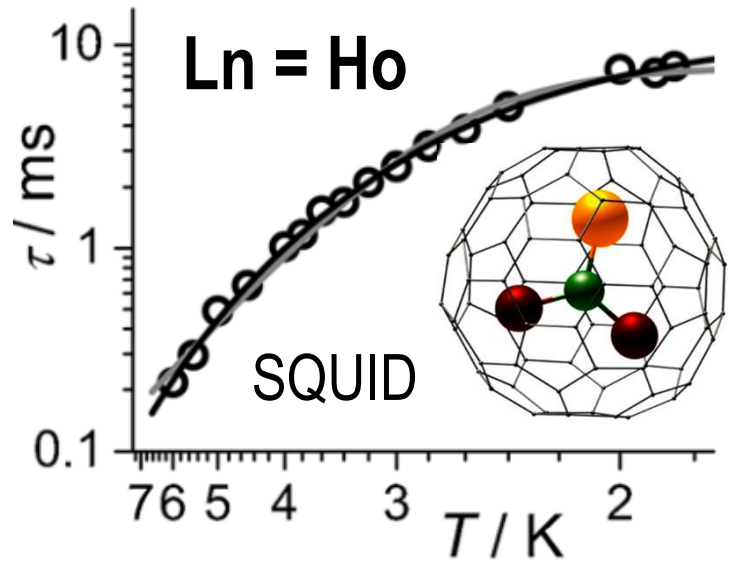
Stevenson *et al*., Nature 1999

- Large magnetic moments
- Large anisotropies
- Single-ion magnets (slow relaxation in a single ion)

Topical Review: JD, *J. Phys: Cond. Mat*. 2015

Endohedral Single-Ion Magnets

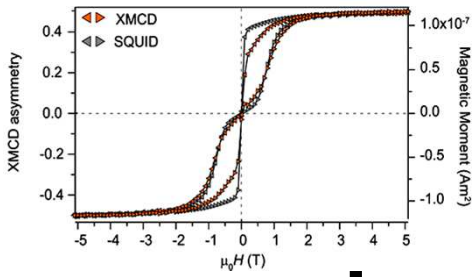


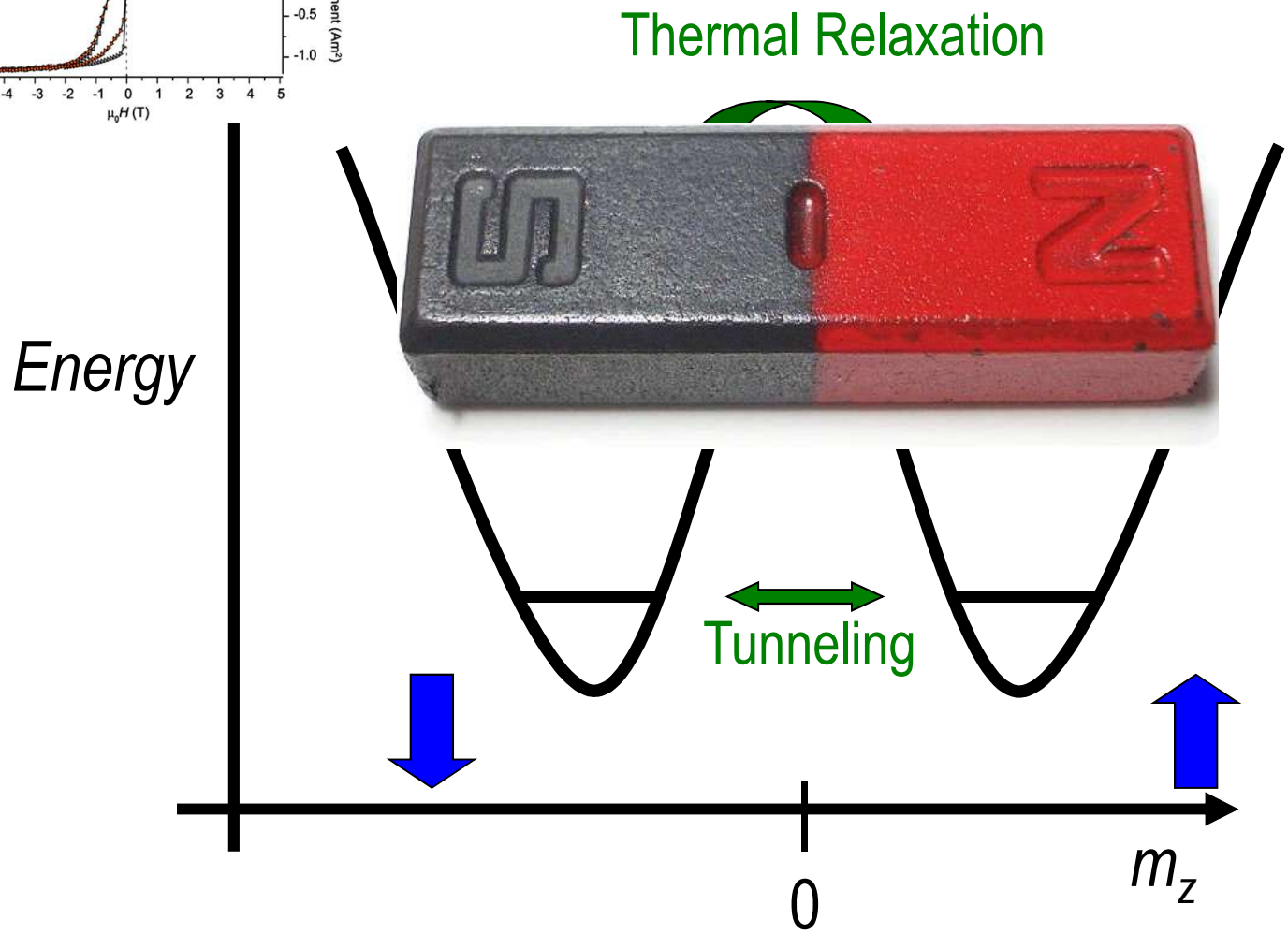


- Strong uniaxial magnetic anisotropy on Dy^{III} and Ho^{III} ions
- Magnetization relaxation times of up to hours at 2 K with Ln = Dy
- Shorter relaxation times with Ln = Ho

Westerström *et al.*, *J. Am. Chem. Soc.* 2012
Westerström *et al.*, *Phys. Rev. B* 2014
Dreiser *et al.*, *Chem. Eur. J.* 2014

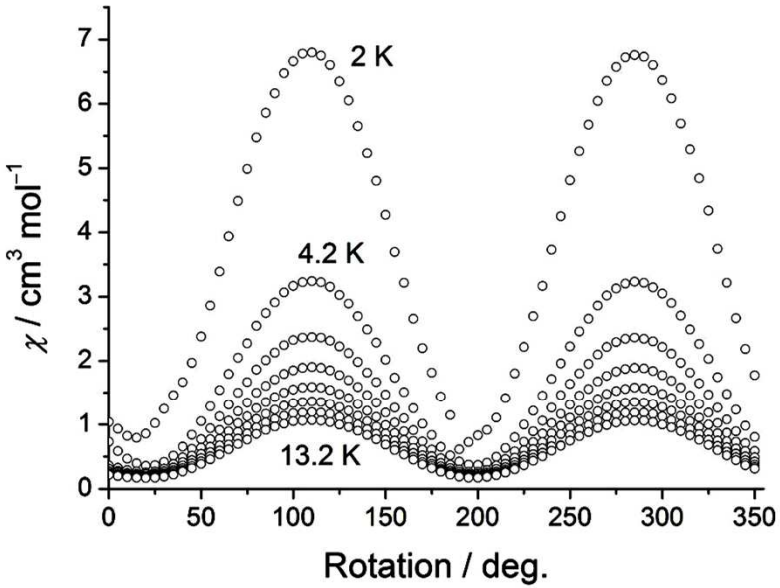
Blocking of Magnetization Relaxation

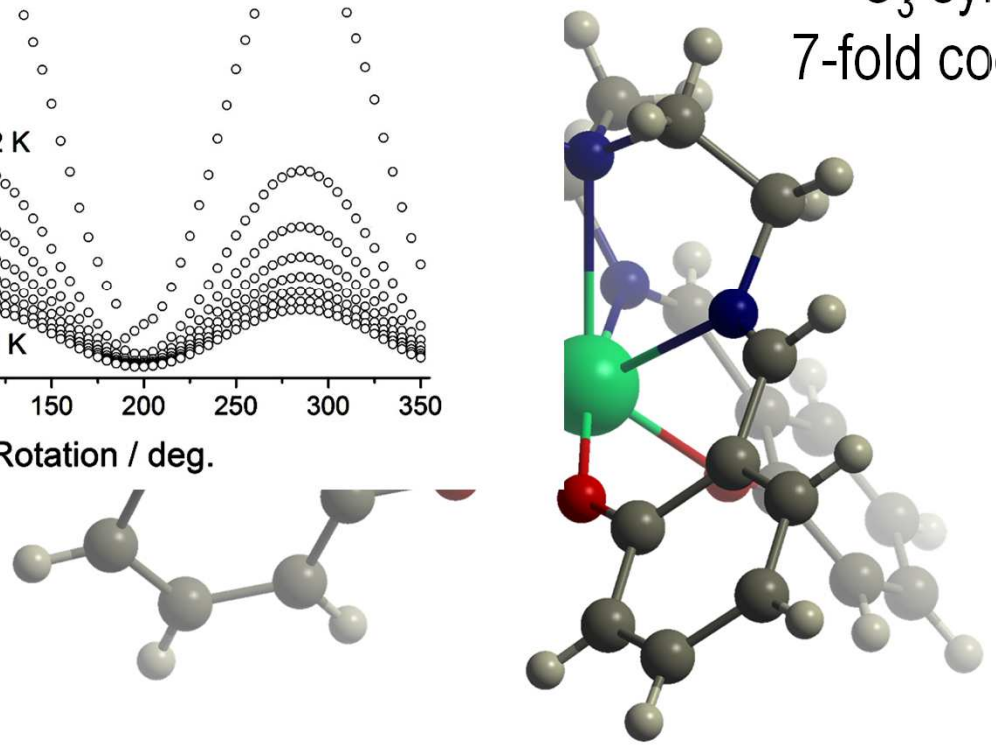




Magnetic Anisotropy

The Er(trensal) Single-Ion Magnet, Bulk Properties





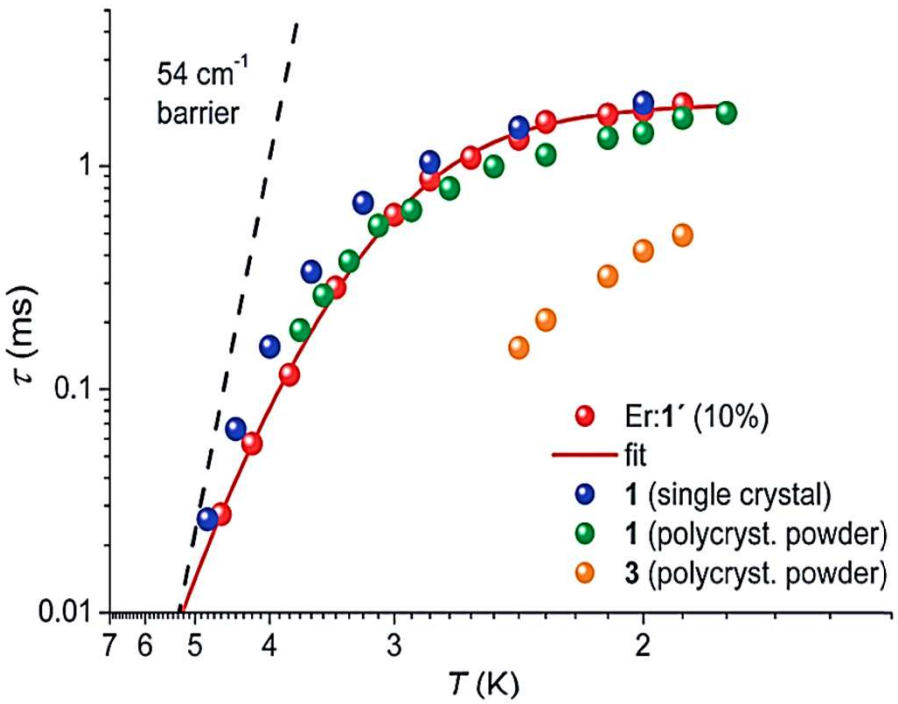
C_3 symmetry
7-fold coordination

Structure from X-ray diffraction

Flanagan et al., *Inorg. Chem.*, 2002
Synthesis and SQUID measurements: K. S. Pedersen, J. Bendix

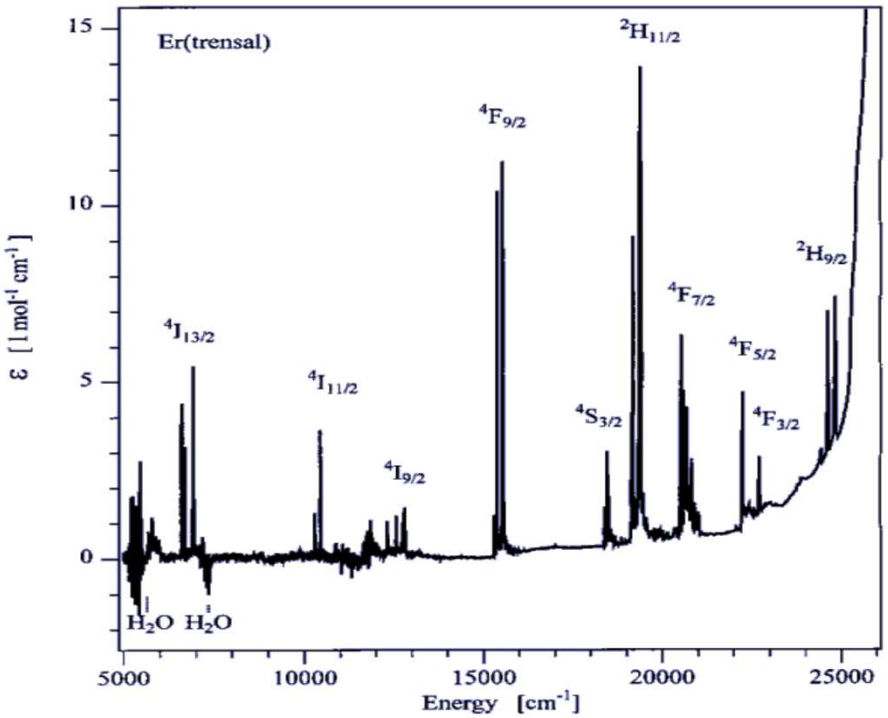
The Er(trensal) Single-Ion Magnet, Bulk Properties

SQUID, ac susceptibility



K. S. Pedersen *et al.*, *Chem. Sci.,* 2014
Lucacchini *et al.*, *Chem. Commun.*, 2014

Optical Absorption UV-vis-NIR



2000 nm 400 nm

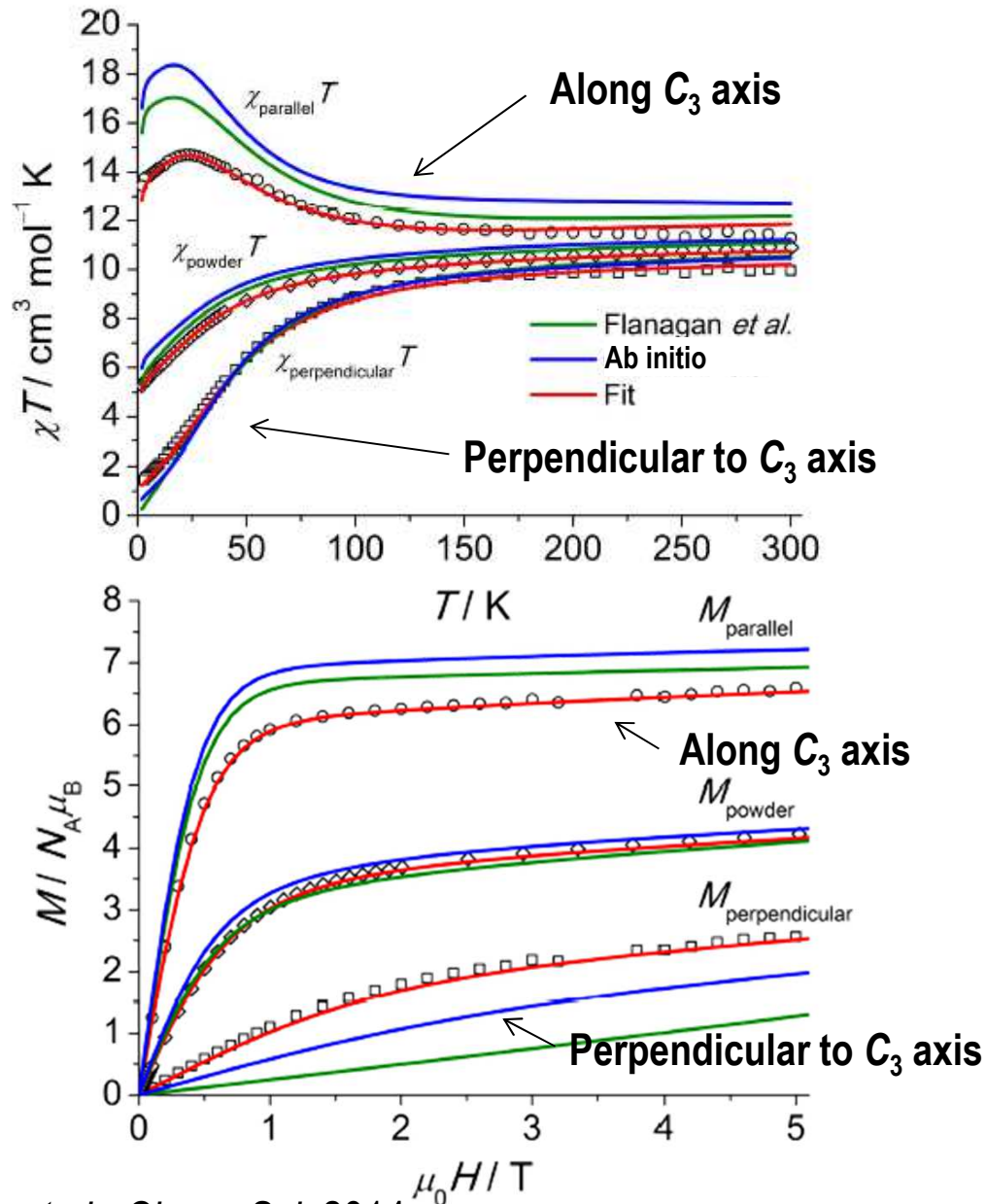
Flanagan *et al.*, *Inorg. Chem.*, 2002

The Er(trensal) Single-Ion Magnet, Bulk Properties

- Strong magnetic anisotropy

$$\hat{H} = \sum_{k,-k\le q\le k} B_k^q \hat{O}_k^q(\mathbf{J}) + \mu_0 \mu_B g_J \mathbf{J}\cdot\mathbf{H}$$

- We know all 9 allowed B_k^q from spectroscopy, $M(H)$ and $\chi(T)$!

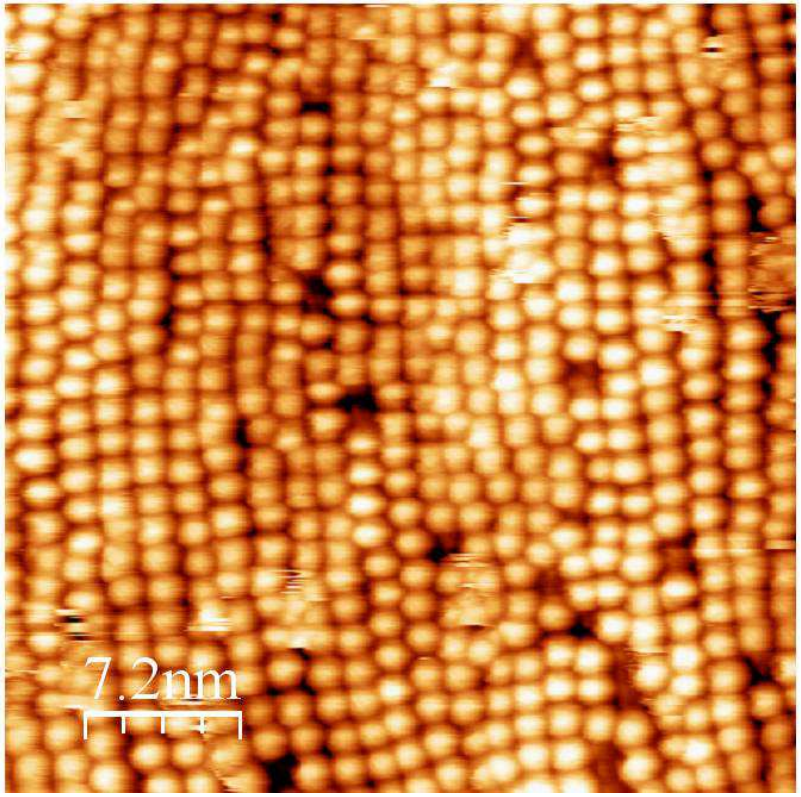


K. S. Pedersen *et al.*, *Chem. Sci.* 2014

Er(trensal) on Au(111)

- Sublime molecules in ultrahigh vacuum
- Deposit onto single-crystalline, clean metal substrates

- Molecules are intact
- At room temperature molecules are mobile
- At low temperatures formation of a quasi-regular pattern



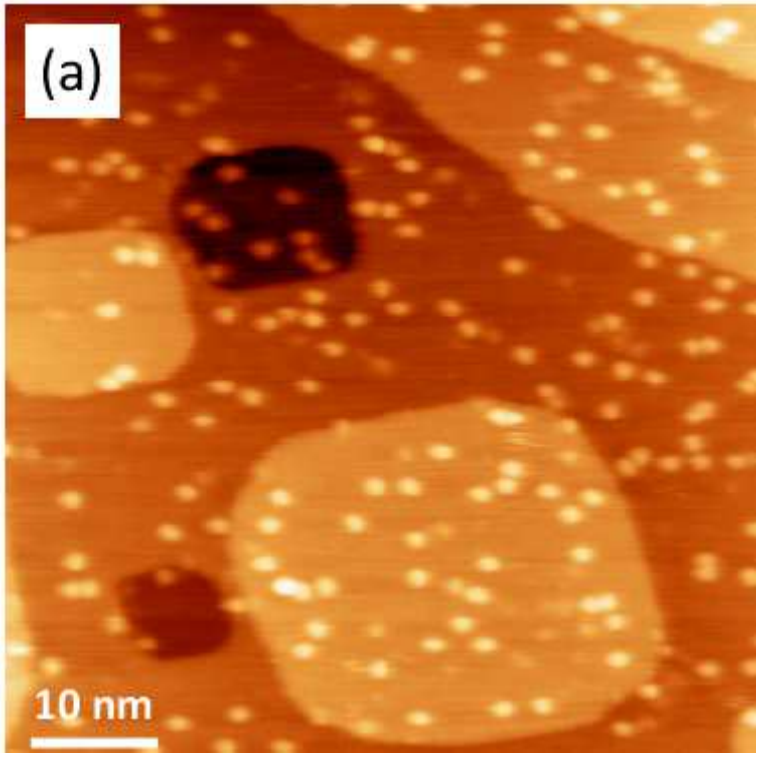
-1.6V, 10pA T = 130 K

STM: C. Wäckerlin

JD *et al., ACS Nano* 2014

Er(trensal) on Ni/Cu(100)

- Molecules are intact
- Molecules are immobile at room temperature
- Random distribution of molecules
- Indicates strong interaction with the Ni surface (chemisorption)



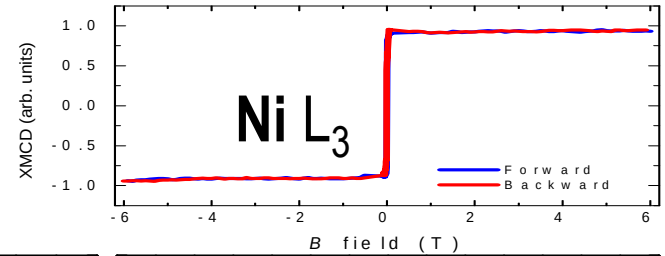
-1.05 V, 80pA T = 300 K

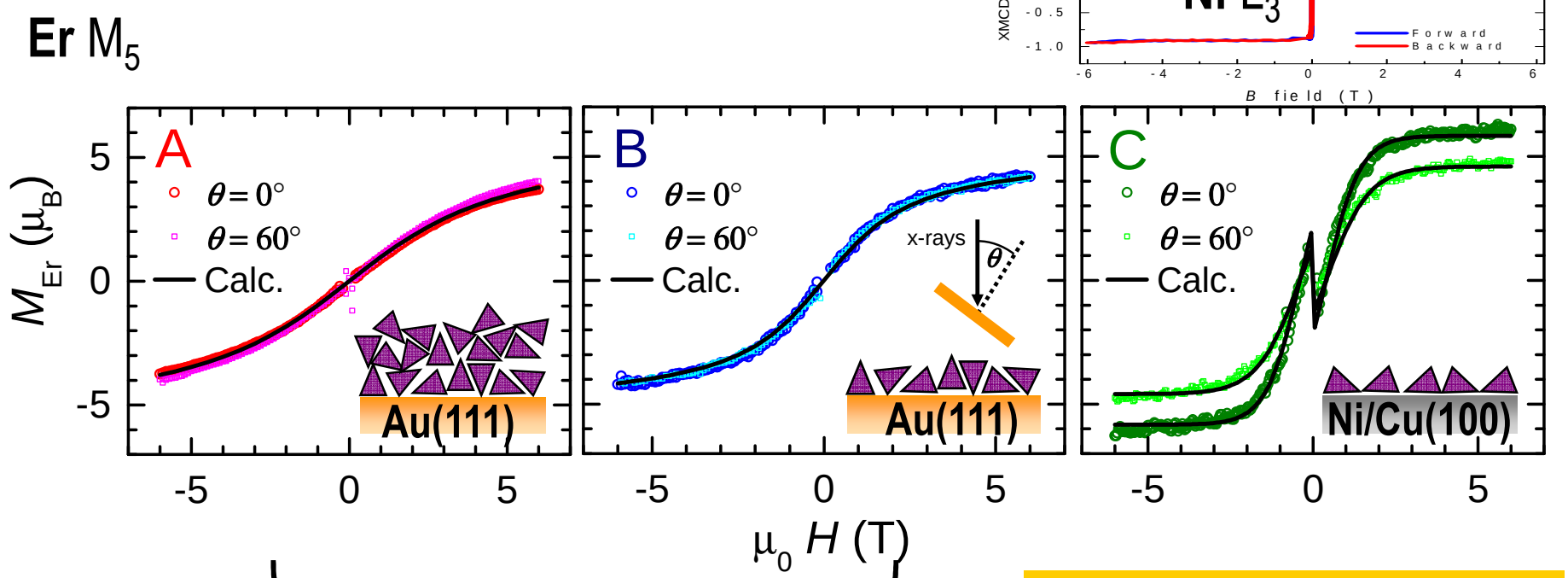
STM: C. Wäckerlin

JD *et al., ACS Nano* 2014

XMCD Reveals Molecule-Surface Exchange Coupling

Data recorded at X-Treme beam line (Swiss Light Source)





$$\hat{H} = \sum_{k,-k\le q\le k} B_k^q \hat{O}_k^q(\mathbf{J}) + \mu_0 \mu_B g_J \mathbf{J}\cdot\mathbf{H}$$

$$\hat{H} = \mu_0 \mu_B \hat{\boldsymbol{\tau}}\cdot\mathbf{g}\cdot(\mathbf{H}+\mathbf{H}_{ex})$$

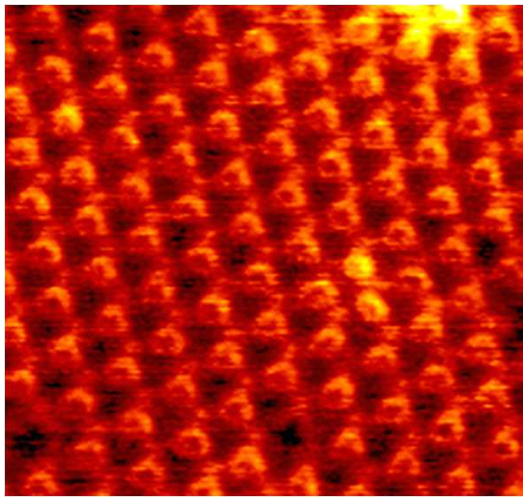
$$\mathbf{H}_{ex} = H_{0,ex}\cdot \mathrm{sgn}(\mathbf{H}\cdot\mathbf{e}_\theta)\cdot\mathbf{e}_\theta$$

- On Au: Bulk mag. anisotropy & random orientation
- On Ni: Different anisotropy & preferred orientation

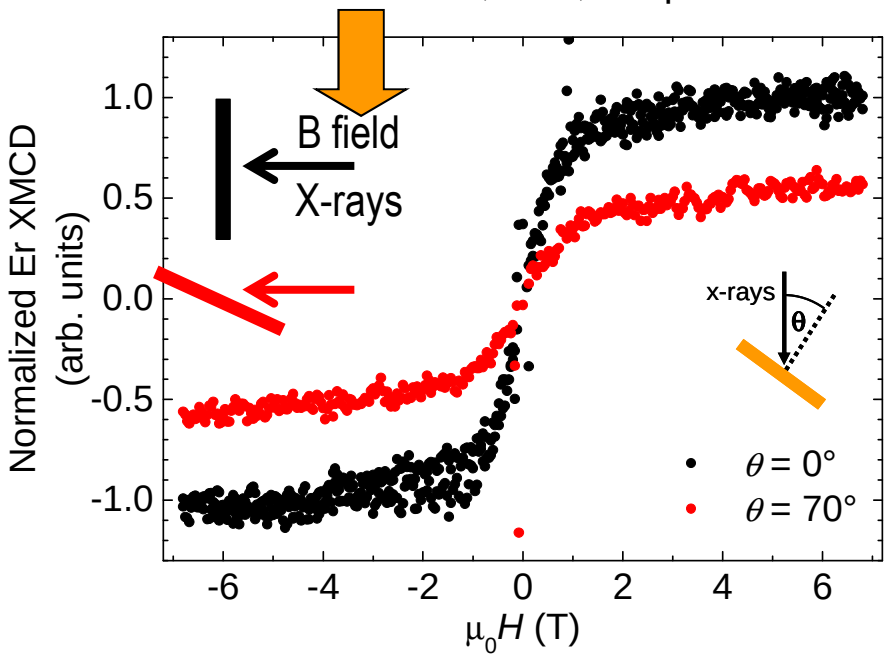
$\mu_0 H_{ex}$ = –0.4(1) T
$g_x = g_y$ = 8(1)
g_z =11.7(8)

JD *et al.*, *ACS Nano* 2014

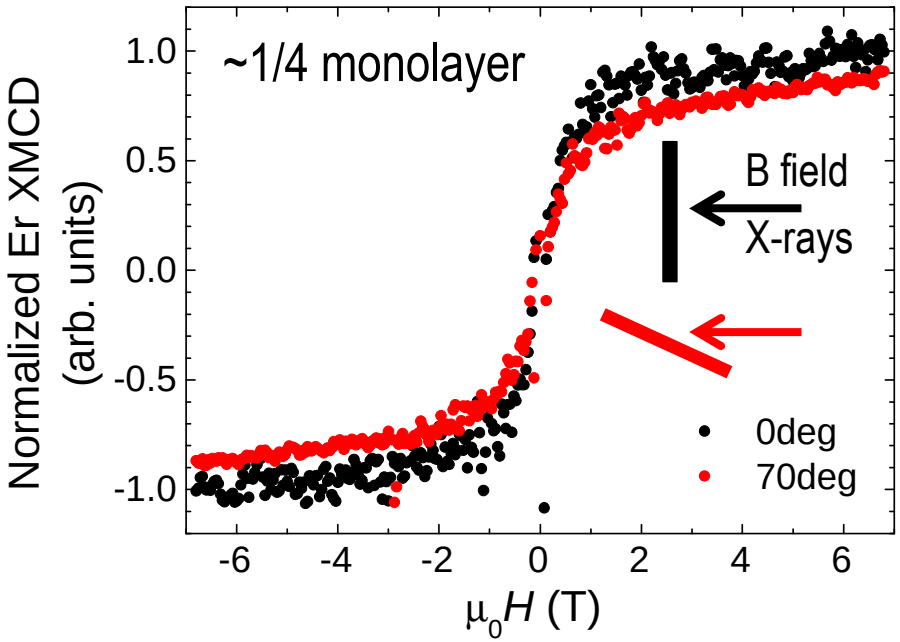
Strong Net Magnetic Anisotropy on Graphene/Ru(0001)



~ 30 x 30 nm^2, 1.0V, 800pA



Er(trensal) on bare Ru(0001)

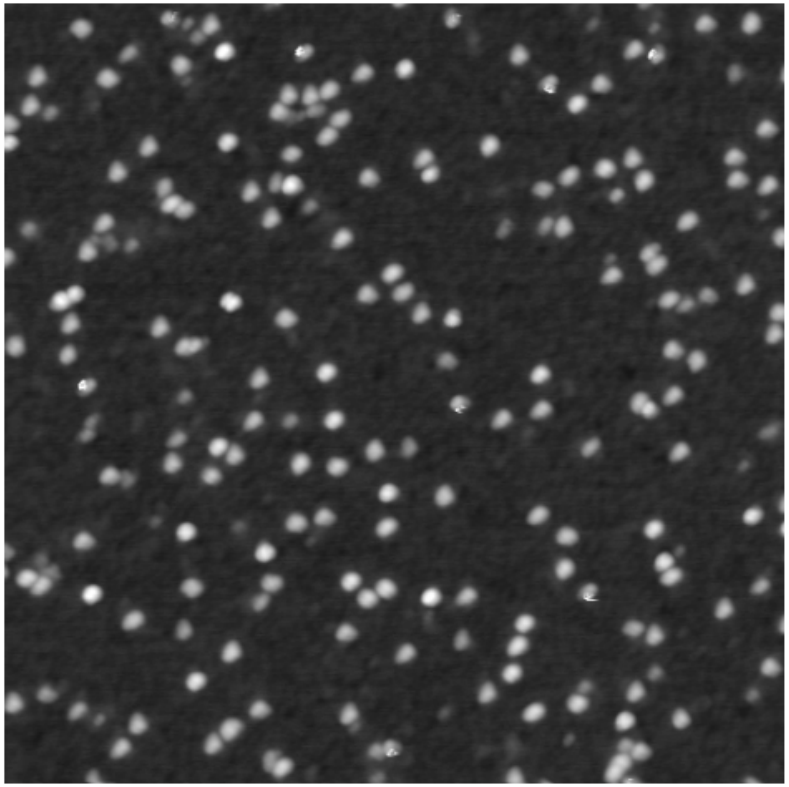


- Ru(0001)
  → Weak orientation
- Graphene/Ru(0001)
  → Strong orientation

2D Crystalline Packing in Er(trensal) Patches

Er(trensal)/Ru(0001)

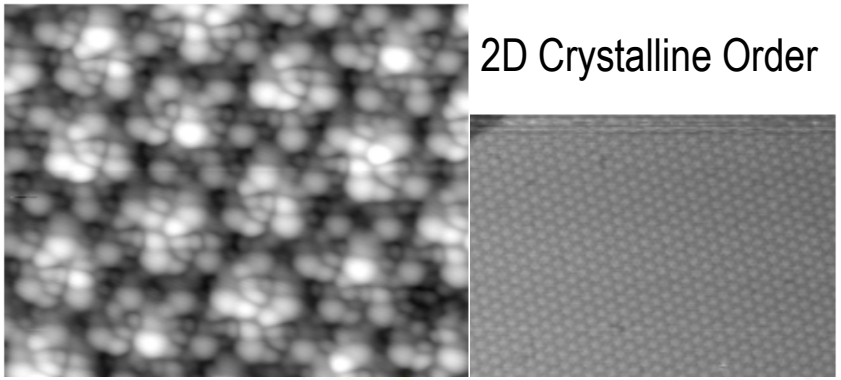
Distribution of adsorption geometries

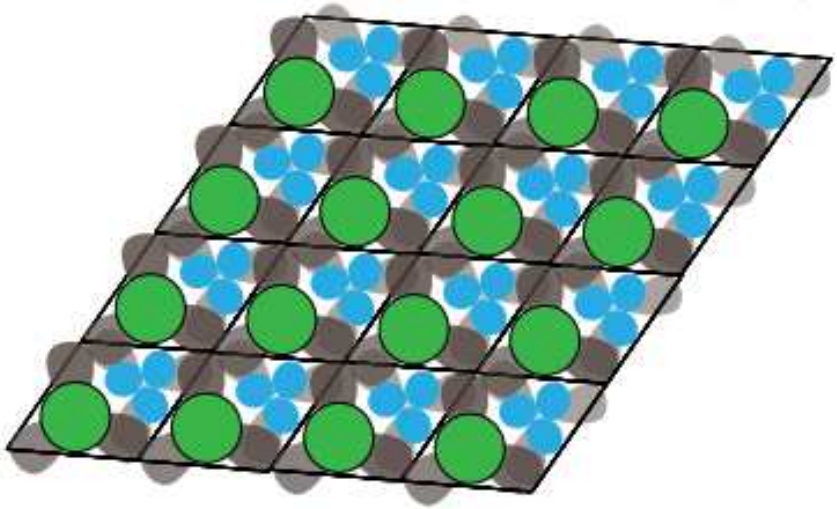


-0.3 V, 50 pA 5 K 10 nm

Er(trensal)/Graphene/Ru(0001)

2D Crystalline Order





-0.7 V, 20 pA 50 K 50 nm

→ Consistent with XMCD results!

M. Pivetta, G. Pacchioni

Conclusions

- Er(trensal) exhibits
  - Random spatial orientation on Au(111)
  - Ferromagnetic coupling to Ni/Cu(100)
  - 2D crystalline order on Graphene/Ru(0001)

→ Properties of surface-deposited single-ion magnets can be engineered by careful choice of substrates.

Acknowledgements / Collaborations

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SNF Ambizione Program

Thank you!