



Lyon 1

La quête de l'aimant à taille moléculaire: *état de l'art et problématique*



Dominique LUNEAU



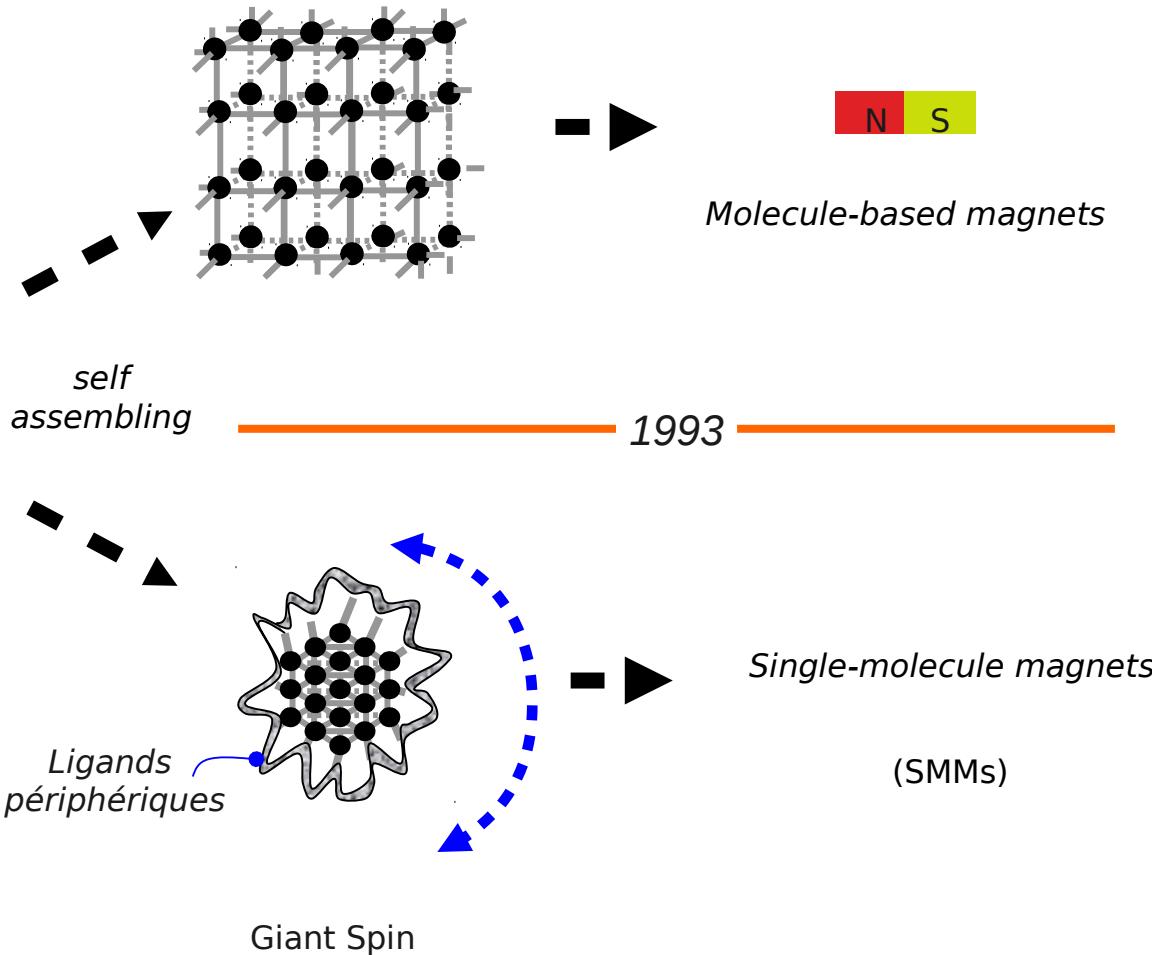
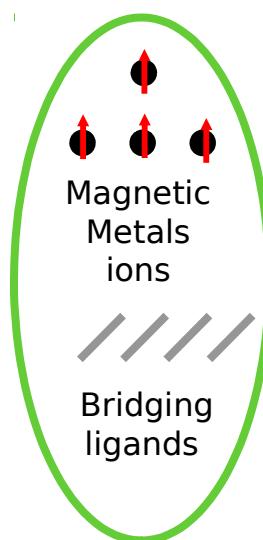
Université Claude Bernard Lyon 1
Laboratoire des Multimatériaux et Interfaces (UMR 5615)

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- **Aimants à base moléculaire**
- **Molécules-aimants**

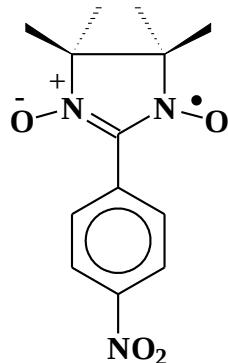
Magnetic Molecular Materials ??

Coordination
chemistry



Molecule-based magnets

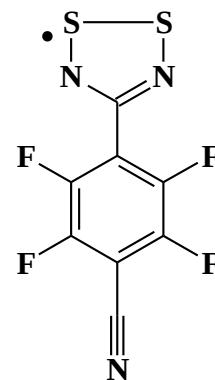
Organic compounds



(a) $T_c = 0.6\text{K}$

M. Kinoshita et al.

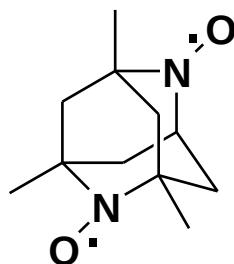
Chem. Lett. **1991**, 1225



(c) $T_c = 35\text{K}$

JM. Rawson et al.

Coord. Chem. Rev. **1999**, 189, 135-68



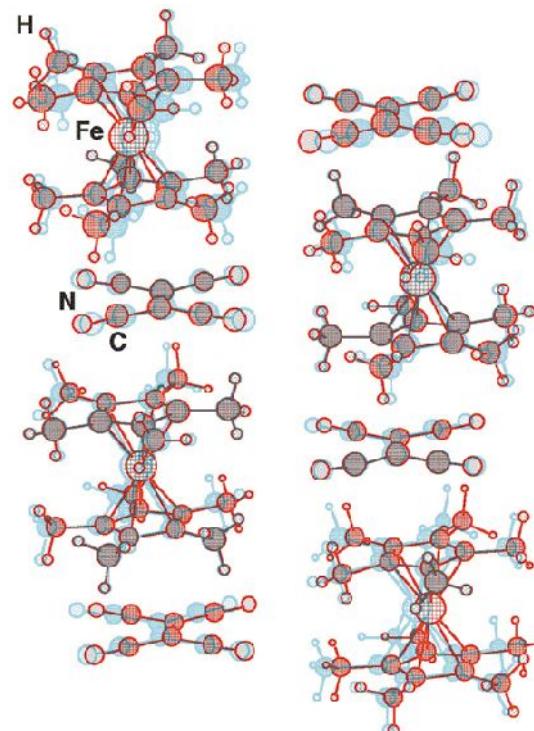
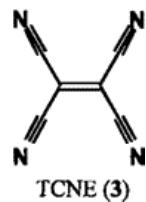
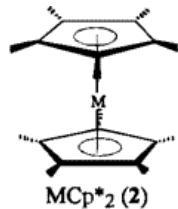
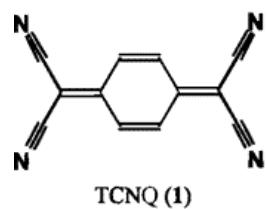
(b) $T_c = 1.48\text{K}$

A. Rassat et al.

Chem. Commun. **1992**, 1081-1082;

Molecule-based magnets

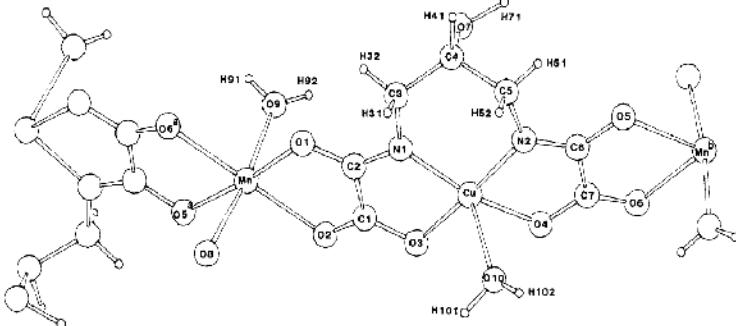
Organometallic compounds



[Fe^{III}Cp*₂].+[TCNE].- $T_c =$
4.8K

Molecule-based magnets

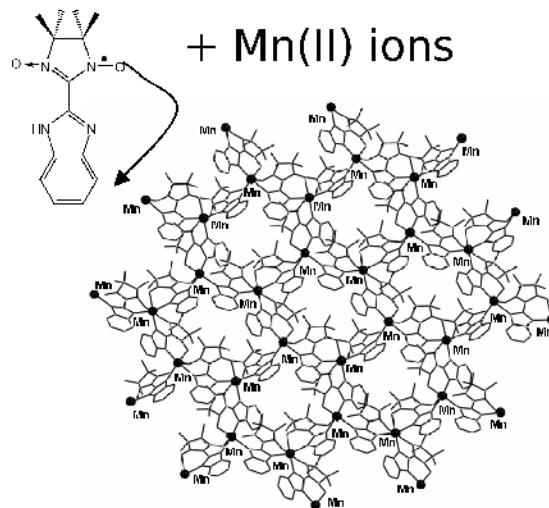
Coordination compounds



T_c ≈ 15 K

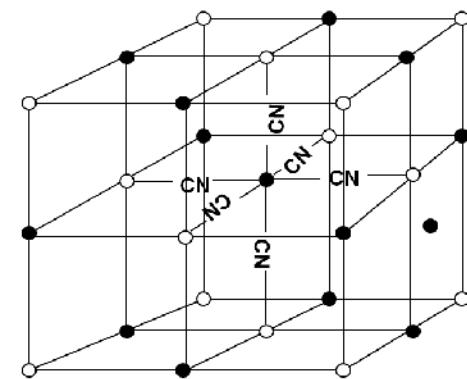
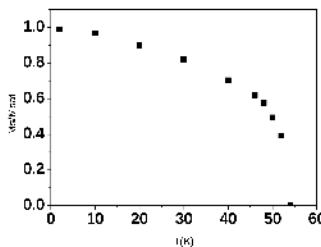
O. Kahn et al. *J. Am. Chem. Soc.* 1988, 110, 782-789

O. Kahn *Molecular Magnetism* (1993) VCH Publishers NY



2D framework
T_c ≈ 50 K
D. Luneau, P. Rey

Coord. Chem. Rev. 2005, 249, 2591-2611



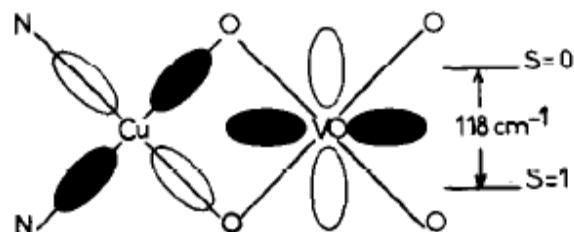
T_c > ambiente

M. Verdaguer et al.
Coord. Chem. Rev. 1999, 190-192, 1023-47

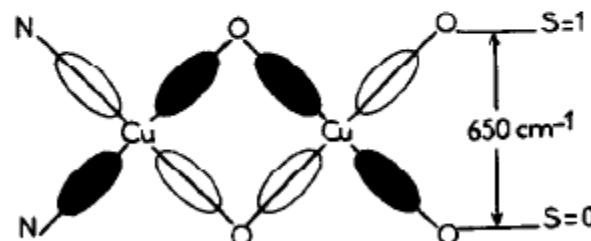
Molecule-based magnets

Magneto-structural relationships

Overlap / orthogonality between magnetic orbitals



Ferro

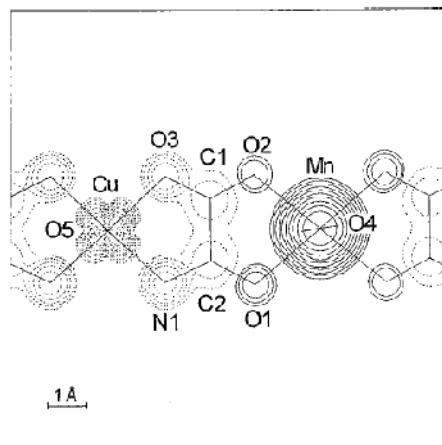
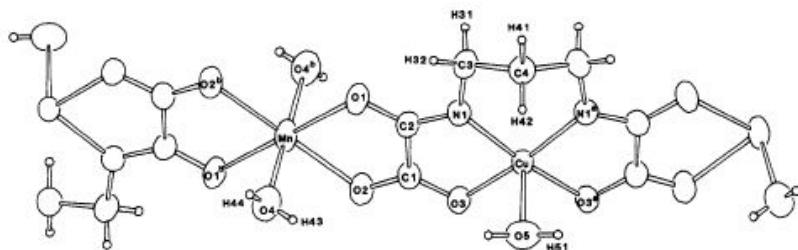


Antiferro

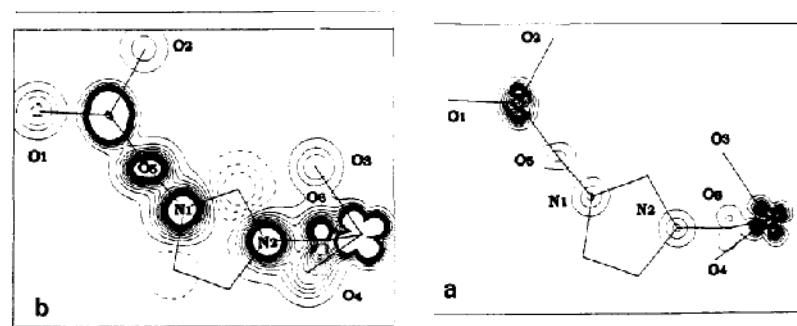
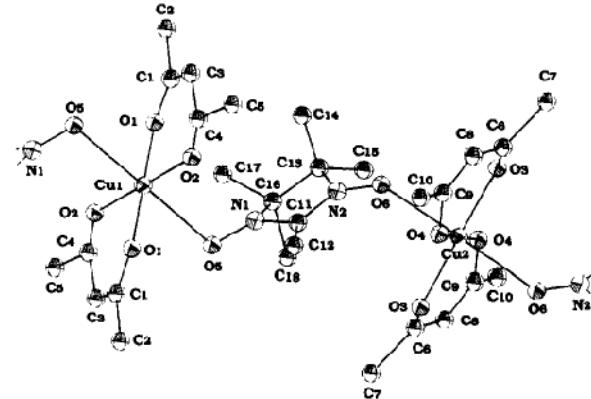
Molecule-based magnets

Magneto-structural relationships

Experimental verification by Polarized Neutron Diffraction (**PND**)



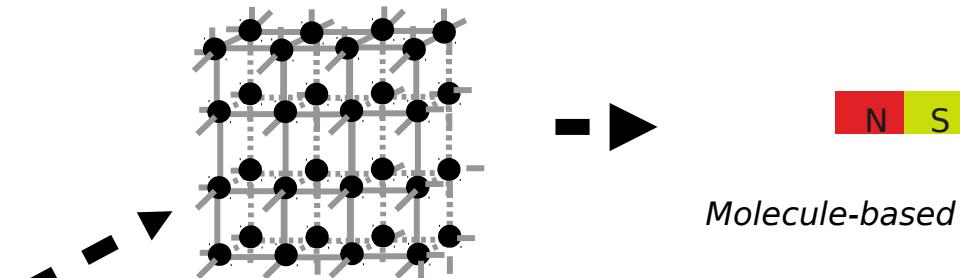
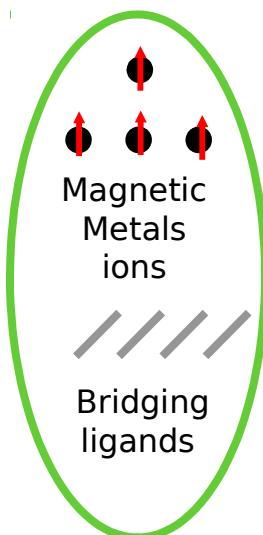
B. Gillon et al.
JACS 1997, 119, 3500-3506



E. Ressouche
JACS 1993, 115, 3610-3617

Magnetic Molecular Materials ??

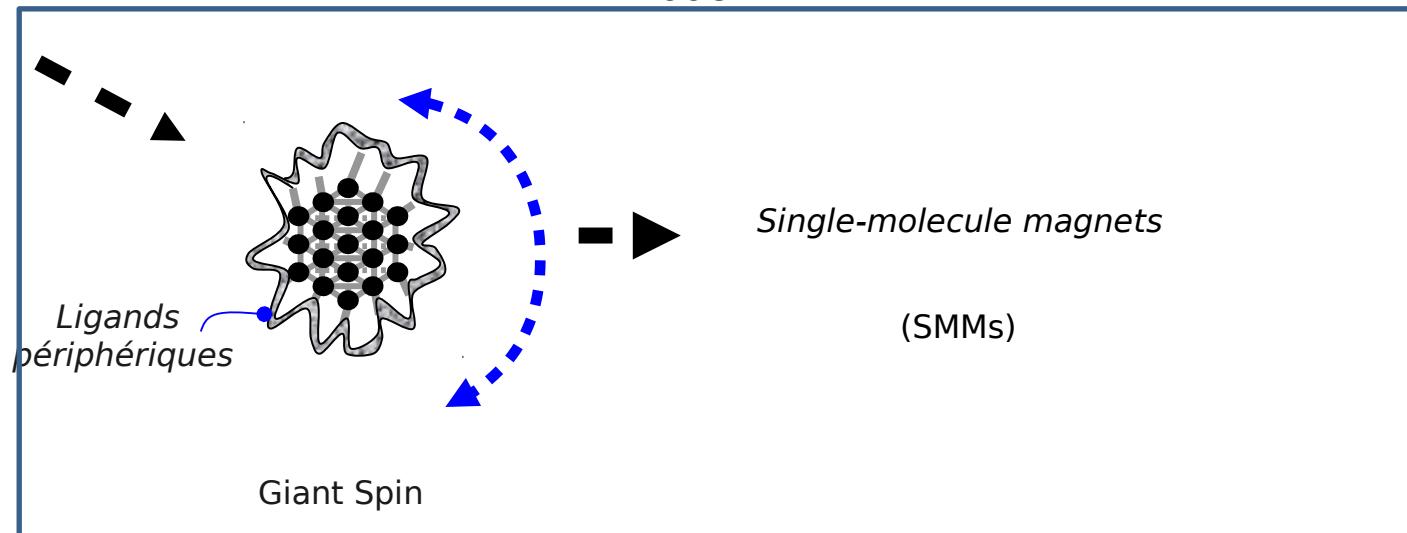
Coordination
chemistry



Molecule-based magnets

*self
assembling*

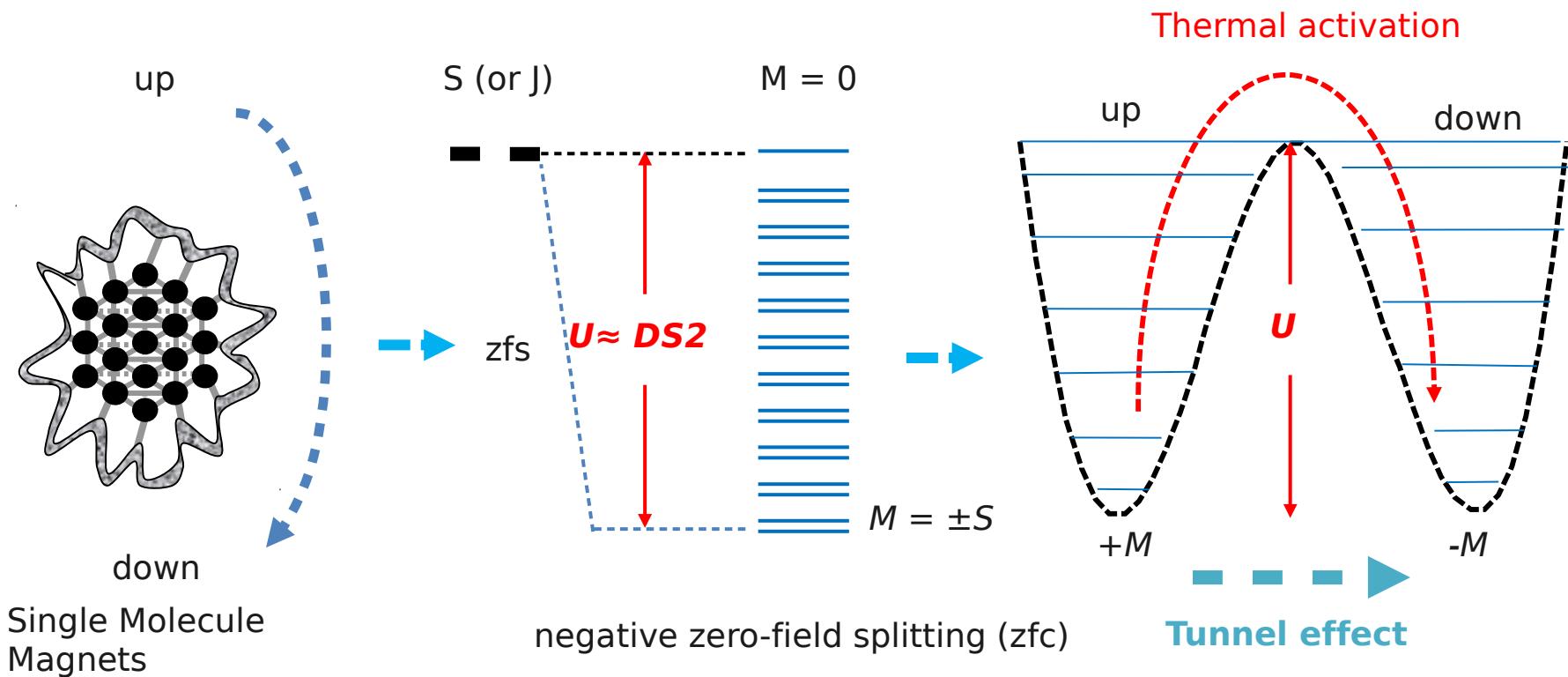
1993



Single Molecule Magnets (SMMs)

Required

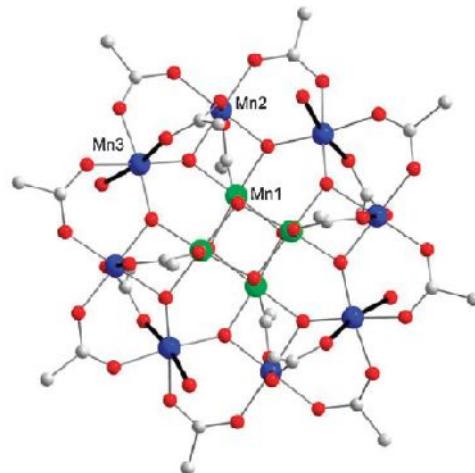
- **High magnetic moment (S)**
- **Strong negative uniaxial magnetic anisotropy ($D < 0$)**



$$[\tau \propto \exp(U/kT)].$$

Single Molecule Magnets (SMMs)

Mn12 : First SMM



D. Gatteschi, G. Christou et al.
JACS 1993, 115, 1804-1816

$S = 10$, $D = -0.5 \text{ cm}^{-1}$, $TB = 3-4 \text{ K}$

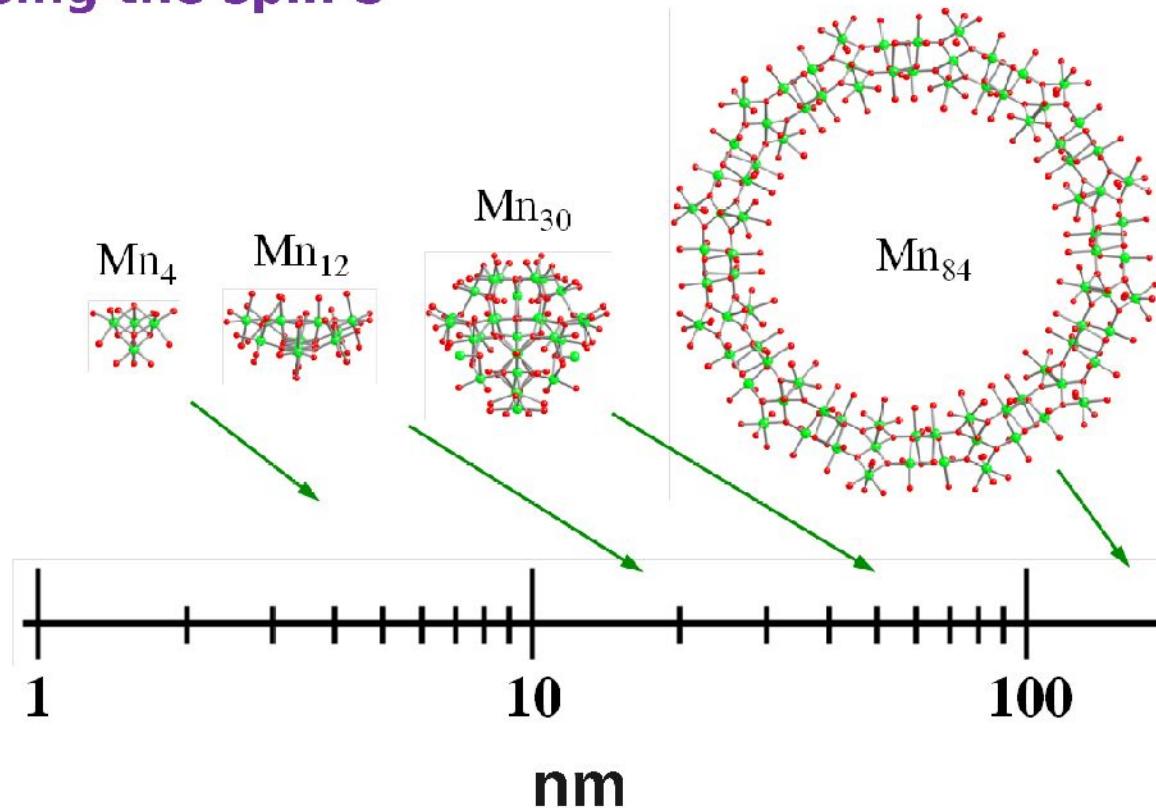
Hysteresis loop for crystals shows step:
Quantum Tunnelling of Magnetisation
(QTM)

Barbara et al, *Nature*, **1996**, 383, 145.

TB = Blocking temperature / temperature at which relaxation (τ) time is 100s
more recent examples: Mn4, Fe8, V4, Fe4, Fe10, Mn10 and Fe19

Single Molecule Magnets: nanoscale magnets

Increasing the spin S



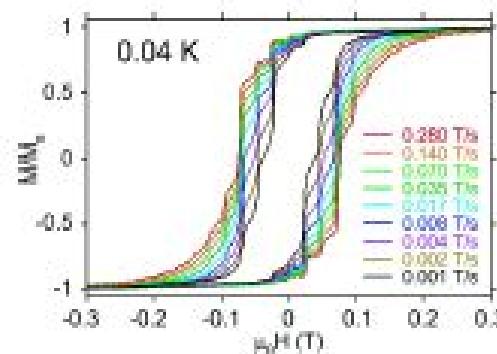
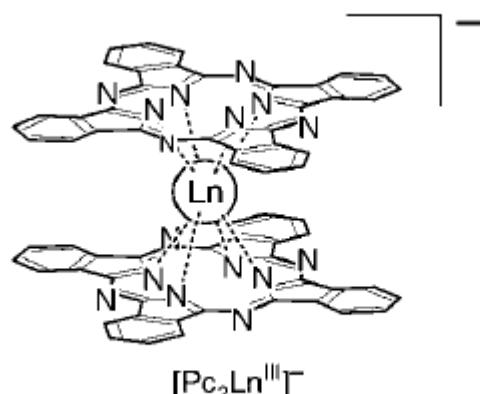
SMMs : anoscale magnets

High Spin but small energy barrier, low blocking temperature...

Single Molecule Magnets (SMMs)

Wanted ! : Magnetic anisotropy

Single-ion magnets



Ln = Tb, Dy , Ho

N. Ishikawa et al. J. AM. CHEM. SOC. 2003, 125, 8694-8695

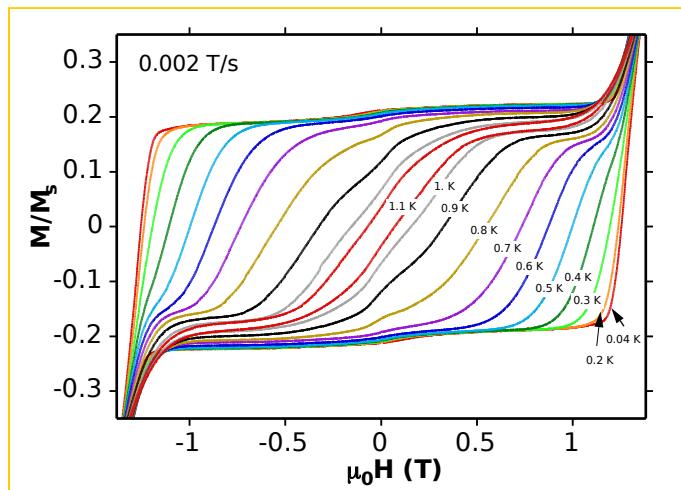
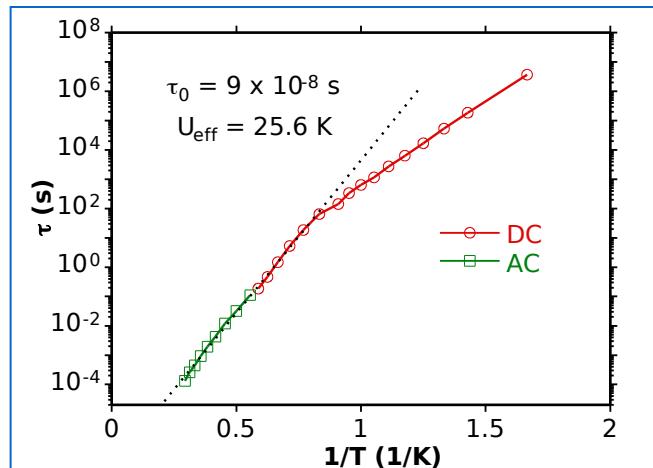
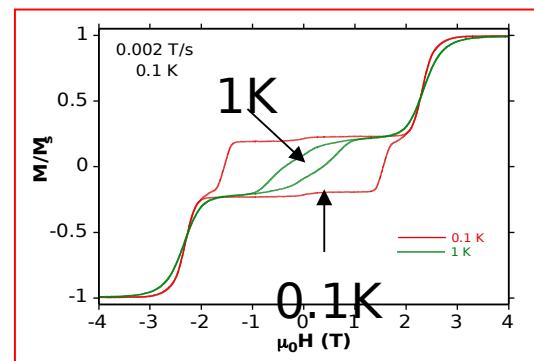
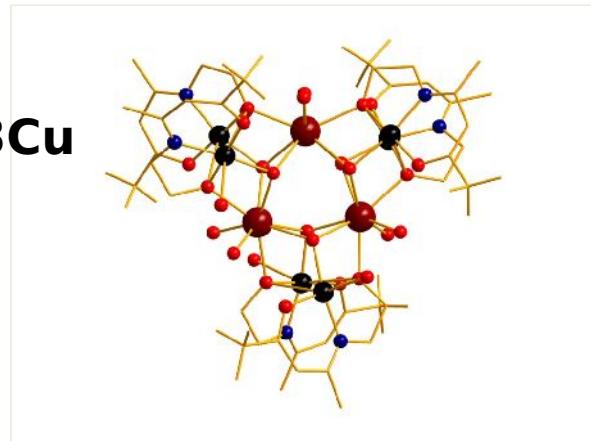
N. Ishikawa, W. Wernsdorfer et al. Angew. Chem. Int. Ed. 2005, 44, 2931 -2935

N. Ishikawa, W. Wernsdorfer et al. JACS. 2005, 127, 3650-3651

Single Molecule Magnets (SMMs)

Instealing Magnetic anisotropy *Heterometallic systems with d and f elements*

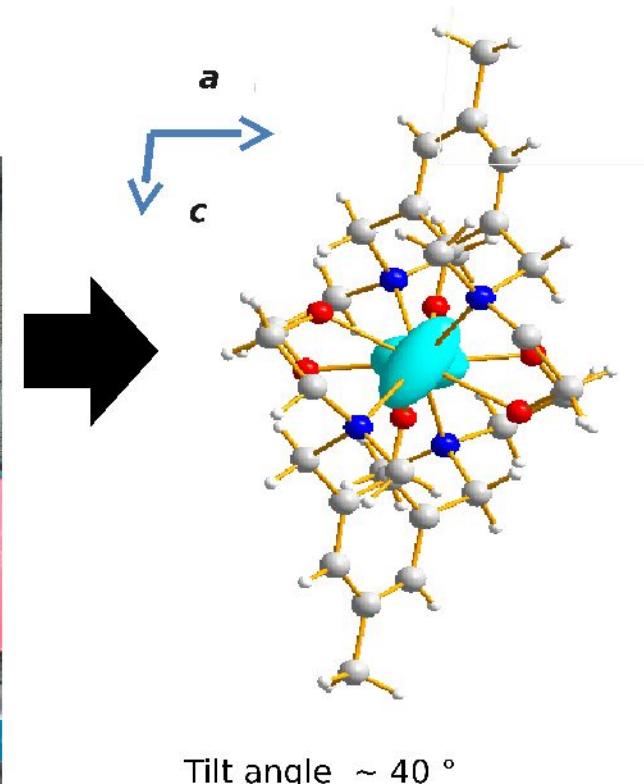
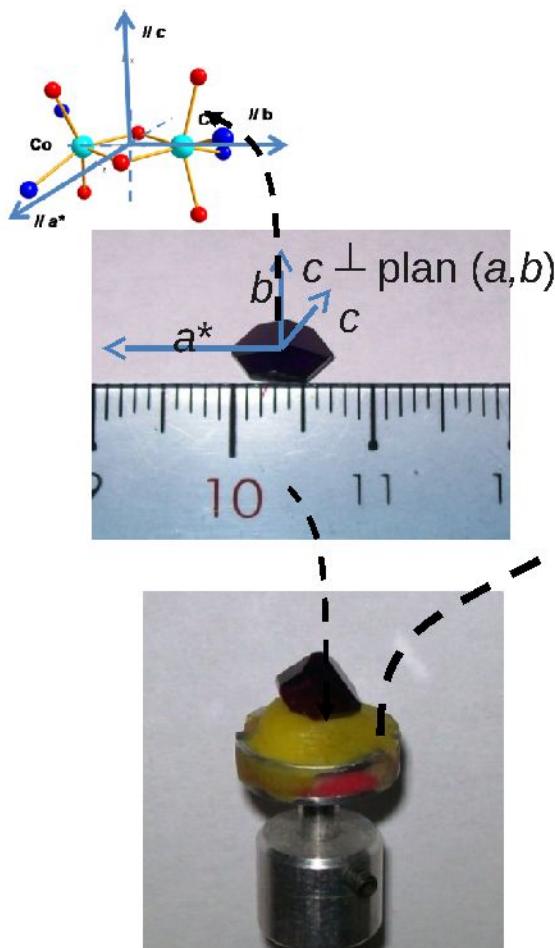
[Dy₃Cu₆]



Single Molecule Magnets

Looking at the magnetic anisotropy

Polarized neutron diffraction at LLB (5C1) collaboration B. Gillon



Acknowledgements

My group

- ▶ A. Lannes
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- ▶ JB Tommasino

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- ▶ C. Paulsen, E. Lhotel, W. Wernsdorfer (IN Grenoble)

---- € € € ---

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