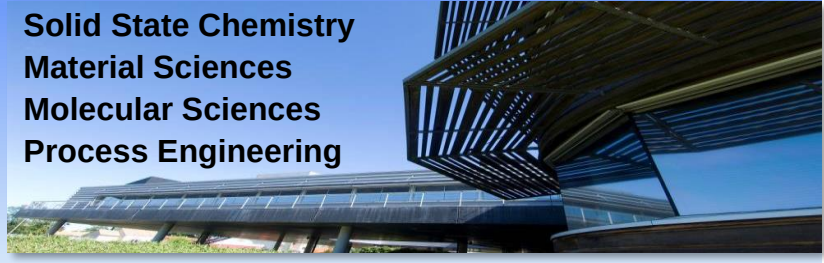


Flavors of Molecular Magnetism

Guillaume CHASTANET

Switchable Molecules and Materials group

icmcb-bordeaux.cnrs.fr

@switchMM2

asso-am2.fr/

@am2_asso

Molecular Magnetism: a definition

Molecular magnetism *deals with the* ***magnetic properties of isolated molecules and assemblies of molecules****.*

These molecules may contain one or more magnetic centers.

Assemblies of molecules are most often found in molecular crystals with very weak interactions between the molecular entities.

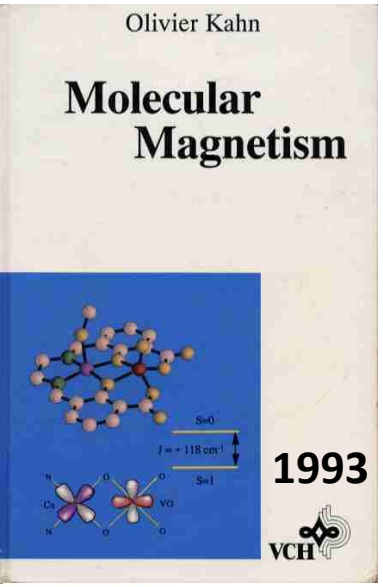
They can be found in extended systems, built from molecular precursors or "bricks", in a way that maximizes the interactions between the bricks and, hopefully, yields bulk magnetic properties.

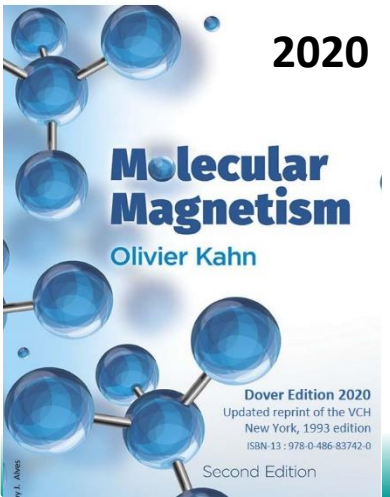
Molecular magnetism *is essentially multidisciplinary.*

First, it involves ***synthetic chemistry****; one of its challenges is to design molecular systems that exhibit predictable properties.*

Second, it uses ideas from ***theoretical chemistry****. To design compounds with expected magnetic behavior, it is necessary to use strategies that derive from an understanding of the underlying mechanism of the phenomena … These approaches actually derive directly from the basic concepts of quantum mechanics.*

Last, molecular magnetism plays an important role in the emerging field of molecular electronics, i.e. the use of molecular systems in electronic circuits and devices.





Molecular magnetism: from chemical design to spin control in molecules, materials and devices

Eugenio Coronado *Nat Rev Mater.* **2020**, *5*, 87

Molecular Magnetism: milestones

1st Spin CrossOver complex

1931

Cambi, L. *et al.*, *Ber. Dtsch. Chem. Ges.* **1931**, 64, 2591

Magnetic exchange in Copper binuclear

1951

Guha, B.C. *Proc. Roy. Soc* **1951**, 206, 353. Bleaney, B. *et al*, *Proc. Roy. Soc* **1952**, 214, 451

1st Molecular magnet

1967

$Fe^{III}(S_2CNEt_2)_2Cl$ (T_C = 2.46 K)
H. Wickman *et al. Phys. Rev.* **1967**, *155*, 563

Olivier Kahn's model of the magnetic exchange

1981

J.J. Girerd, Y. Journaux, O. Kahn, *Chem. Phys. Lett.* **1981**, *82*, 534

1st designed molecule-based ferrimagnet

1988

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

1st organic ferromagnet

1991

M. Tamura *et al. Chem. Phys. Lett.***1991**, *186*, 401

1st room temperature molecule-based magnet

1991

$V(TCNE)_2$
J.M. Manriquez *et al. Science* **1991**, *252*, 1415

1st Single Molecule Magnet

1993

$Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4$ (Mn_{12})
R. Sessoli *et al. Nature* **1993**, *365*, 141

1st paramagnetic superconductor

1995

P. Day *et al. Chem. Commun.* **1995**, 2061

Prussian blue analogs RT magnet

1995

$[V^{II}_{0.42}V^{III}_{0.58}(Cr(CN)_6)_{0.86}]\cdot 2H_2O$
S. Ferlay *et al. Nature* **1995**, *378*, 701

1st photo-induced magnet

1996

O. Sato *et al*, *Science* **1996**, *272*, 704

1st ferromagnetic superconductor

2000

E. Coronado *et al. Nature* **2000,** *408*, 447

Slow dynamics of 1D system

2001

D. Gatteschi *et al. Angew. Chem. Int. Ed.* **2001**, *40*, 1760

1st single chain magnet

2002

R. Clérac *et al. J. Am. Chem. Soc.* **2002**, *124*, 12837

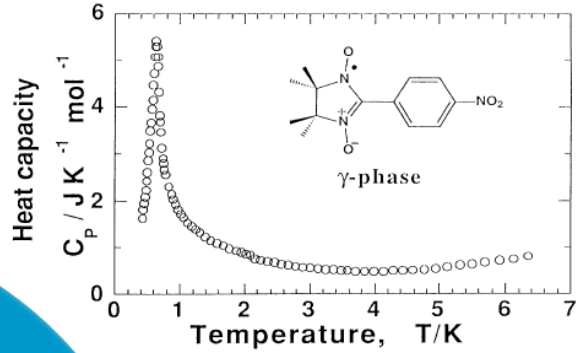
T_c > 500 K molecule-based magnets

2020

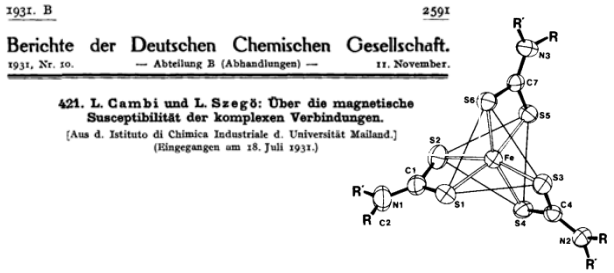
R. Clérac *et al Science*, **2020**, *370*, 587

Molecular Magnetism: what kind of systems?

Molecular magnetism involves architectures based on *p*, *d* and *f* electrons, and their combination



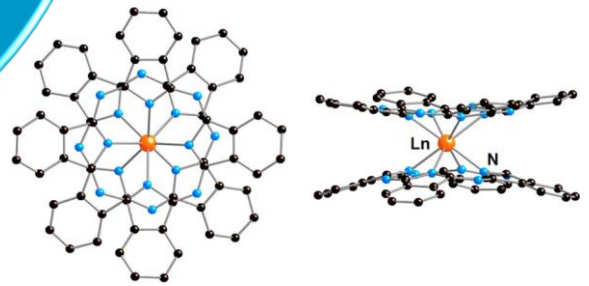
NIT-PhNO$_2$ → **First organic magnet** T_c =0.6 K
Takahashi, M. *et al. Phys. Rev. Lett.* **1991**, *67*, 746-748


1931. B 2591

Berichte der Deutschen Chemischen Gesellschaft.
1931, Nr. 10. — Abteilung B (Abhandlungen) — 11. November.

421. L. Cambi und L. Szegö: Über die magnetische Susceptibilität der komplexen Verbindungen.
[Aus d. Istituto di Chimica Industriale d. Università Mailand.]
(Eingegangen am 18. Juli 1931.)

Fe^{III} Tris(dithiocarbamate)
→ **Spin CrossOver**
Cambi, L. *et al.*, *Ber. Dtsch. Chem. Ges.* **1931**, 64, 2591
Stahl K. *et al.*, *Acta Chem. Scand.* **1983**, A37, 729.



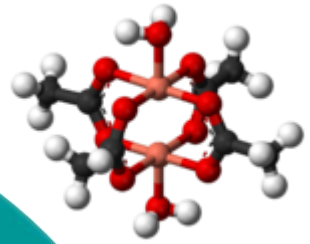
Lanthanide phthalocyanine→ **Ln Single Molecule Magnet (SMM)**
N. Ishikawa., *et al. J. Am. Chem. Soc.* **2003**, 125, 8694

Coordination Chemistry: *p*, *d*, *f*, *p-d*, *p-f*, *d-f*

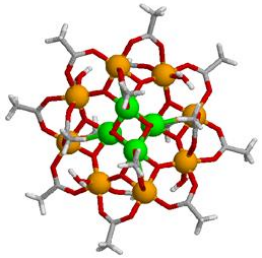
ALL THEIR COMBINATION

Molecular Magnetism: what kind of systems?

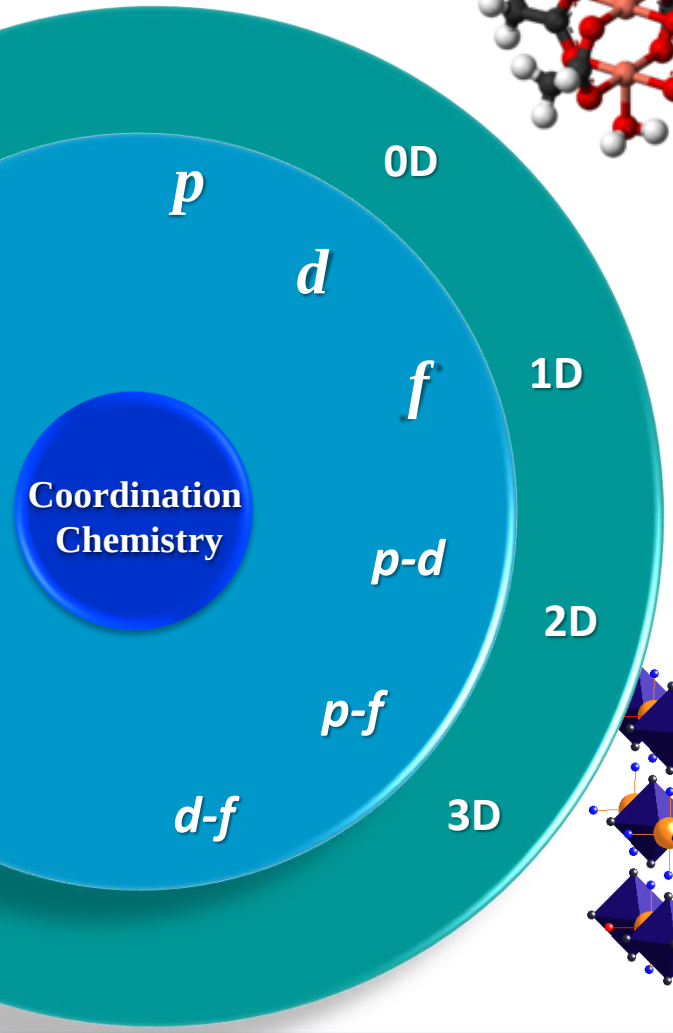
Molecular magnetism gives access to architectures of various dimensionalities

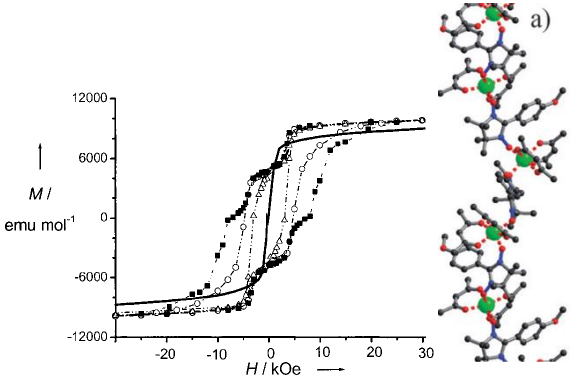


Copper acetate → **Magnetic exchange**
Guha, B.C. Proc. Roy. Soc (London) **1951**, 206, 353.
Bleaney, B. *et al*, Proc. Roy. Soc (London) **1952**, 214, 451

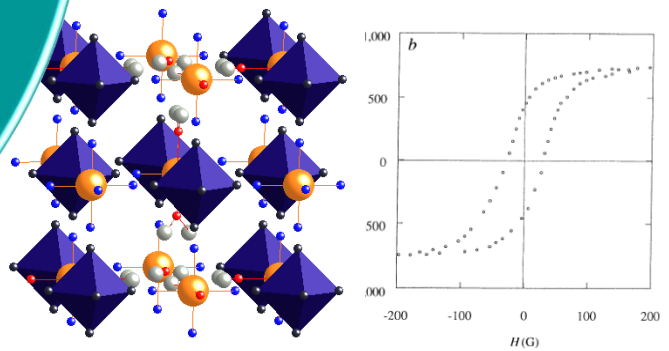


Mn_{12} → **Molecular magnetic bistability**
Sessoli, R. *et al.*, *Nature* **1993**, *365*, 141





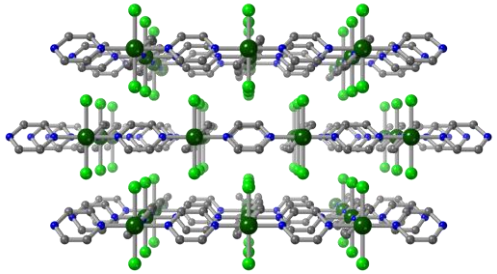
CoPhOMe → **Single-Chain Magnets (SCM)**
Caneschi *et al*, *Angew. Chem.*, **2001**, *40*, *1760*



LETTERS TO NATURE

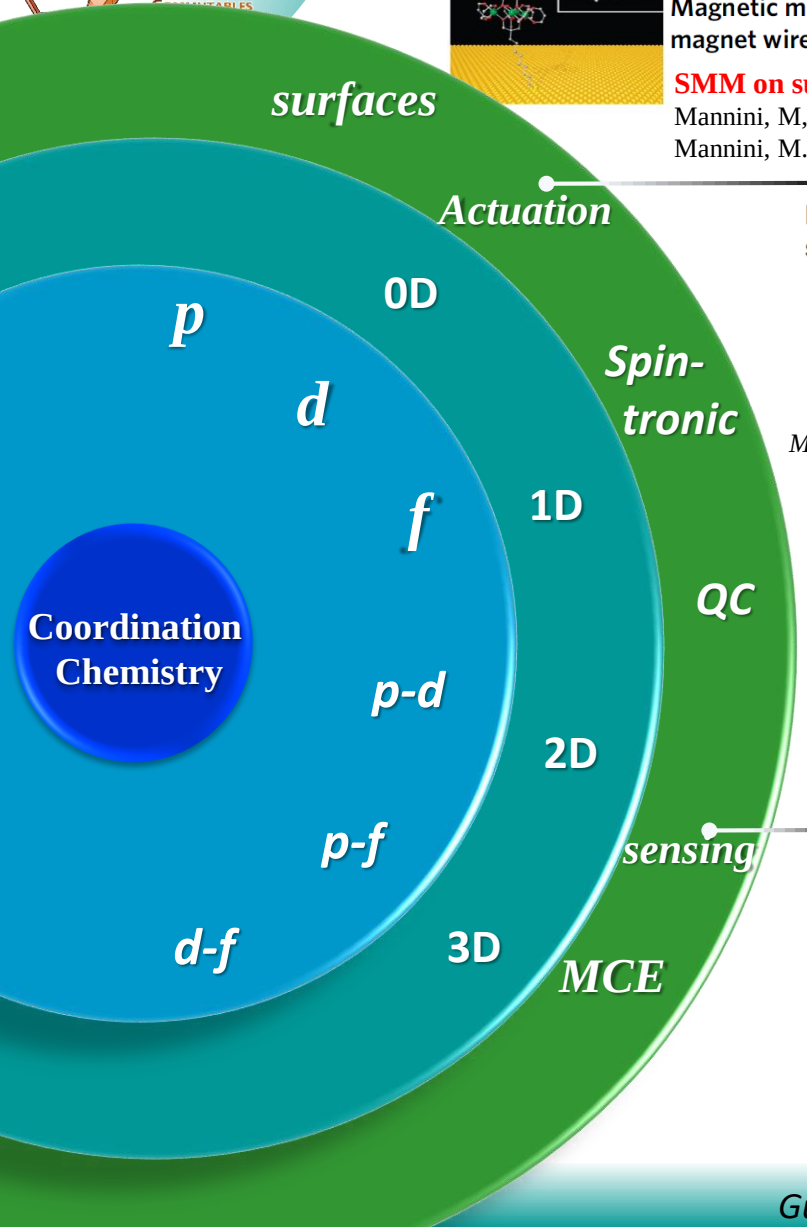
A room-temperature organometallic magnet based on Prussian blue

Prussian Blue Analogs
→ **high Tc permanent magnets**
Ferlay, S. *et al.*, *Nature* **1995**, 378, 701-703.



R. Clérac *et al Science*, **2020**, *370*, 587

Molecular Magnetism: potential applications



LETTERS | PUBLISHED ONLINE: 1 FEBRUARY 2009 | DOI: 10.1038/NMAT2374 | nature materials

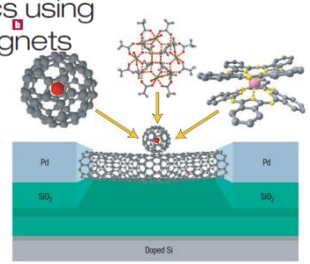
Magnetic memory of a single-molecule quantum magnet wired to a gold surface

SMM on surfaces

Mannini, M, *et al.*, *Nat. Mater.* **2009**, *8*, 194

Mannini, M. *et al*, *Nature* **2010**, *468*, 417

Molecular spintronics using single-molecule magnets

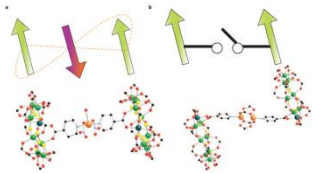


Spintronics

Bogani, L., *et al.*, *Nat. Mater.* **2008**, *7*, 179-186.

nature nanotechnology | ARTICLES | CORRECTED ONLINE: 17 FEBRUARY 2009 | PUBLISHED ONLINE: 1 FEBRUARY 2009 | DOI: 10.1038/NNANO.2008.404

Engineering the coupling between molecular spin qubits by coordination chemistry



Quantum computing

Timco, G. A. *et al.*, *Nat Nano* **2009**, *4*, 173

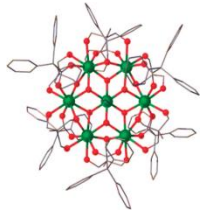
nature COMMUNICATIONS

Sub-Kelvin nano-coolers

ARTICLE | Received 18 Jun 2014 | Accepted 19 Sep 2014 | Published 22 Oct 2014 | DOI: 10.1038/ncomms6321 | OPEN

Quantum signatures of a molecular nanomagnet in direct magnetocaloric measurements

Sharples, J. W. *et al.*, *Nat Commun* **2014**, *5*



nature COMMUNICATIONS

Mechanical actuators

ARTICLE | Received 23 Apr 2013 | Accepted 13 Sep 2013 | Published 24 Oct 2013 | DOI: 10.1038/ncomms3607

Molecular actuators driven by cooperative spin-state switching

H.J. Shepherd. *et al.*, *Nat Comm.* **2013**, *4*, 2607

+ Among others:

- Optical sensing
- MRI
- Molecule-based electronics
- Barocaloric refrigeration
- Pressure sensors
- Liquid crystals
- Light magnets
- …

nature COMMUNICATIONS

Gas sensing MOFs

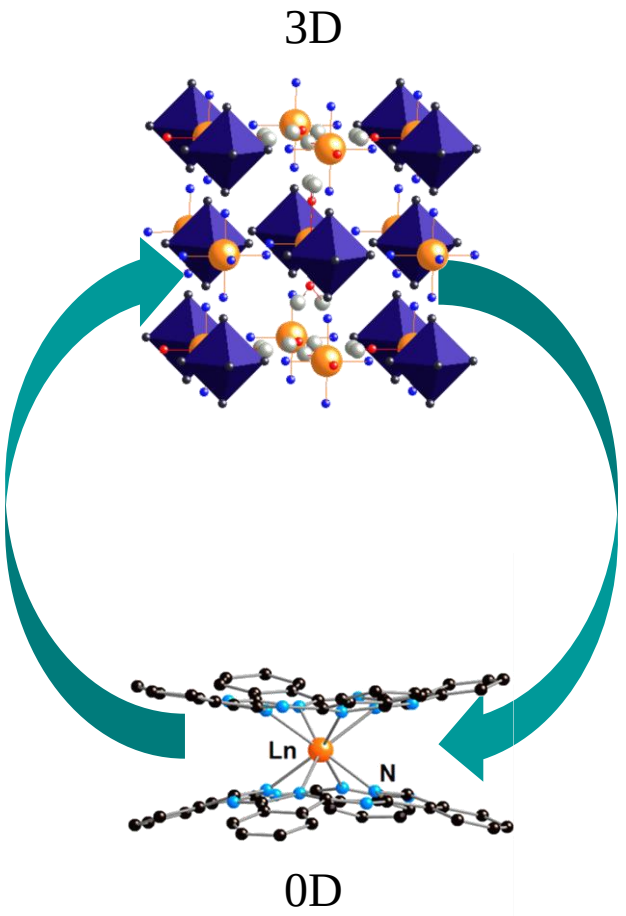
ARTICLE | https://doi.org/10.1038/s41467-022-31274-8 | OPEN

A spin-crossover framework endowed with pore-adjustable behavior by slow structural dynamics

J.-P. Xue *et al.*, *Nat Comm.* **2022**, *13*, 3510

Flavors of Molecular Magnetism: outline

Strength of molecular magnetism: thanks to the molecular design, one can go back and forth from the 3D to the 0D architectures



I. High T_c Molecule-based magnets

II. Towards active molecular units (SMM)

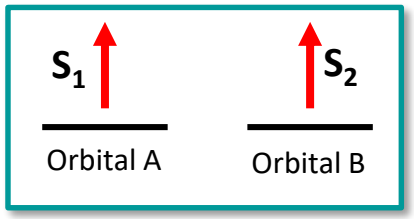
III. Switchable molecules (ET, SCO)

IV. Multifunctionality

Molecular Magnetism: High Tc molecule-based magnets

How to control the magnetic exchange between metallic centers?

→ Interaction model between localised spin



$$\hat{H} = - J \hat{S}_1 \hat{S}_2$$

Heisenberg-Dirac-Van Vleck Hamiltonian

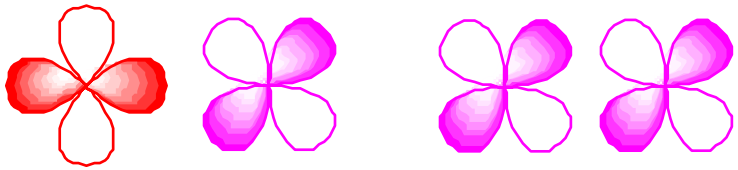
→ Kahn model, a first and useful way of prediction

$$J = 2k + 4\beta S$$

$k > 0$ $\quad$ $4\beta S < 0$

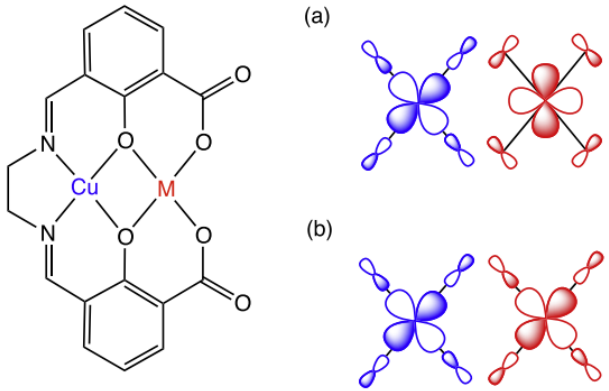
if S = 0
Orthogonality

if S≠0;|ßS|>>k
Overlap



Ferromagnetic exchange

AntiFerromagnetic exchange



Cu^{II} – V^{IV}
no overlap
Ferromagnetic exchange

Cu^{II} – Cu^{II}
Overlap
AntiFerromagnetic exchange

O. Kahn, et al, *J. Am. Chem. Soc.* **1982**, *104*, 2165

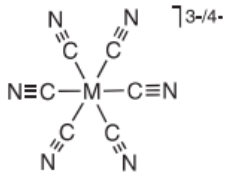
k: bielectronic exchange integral
S: overlap integral
β: transfert integral

J.J. Girerd, Y. Journaux, O. Kahn, *Chem. Phys. Lett.* **1981**, *82*, 534

Molecular Magnetism: High Tc molecule-based magnets

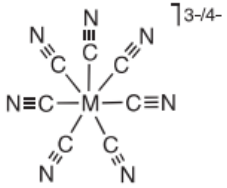
The briging ligand, a tool to spread the exchange interaction

among many others:



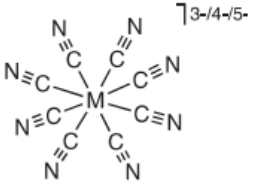
$[M(CN)_6]^{3-/4-}$

M = $Fe^{II/III}$, Co^{II}, Cr^{III}, V^{III}, Mo^{III}, Ru^{III}, Os^{III}



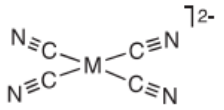
$[M(CN)_7]^{3-/4-}$

M = Mo^{III}, $Re^{III/IV}$



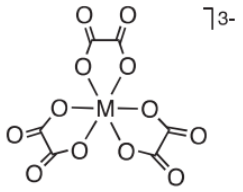
$[M(CN)_8]^{3-/4-/5-}$

M = $Nb^{III/IV}$, $Mo^{IV/V}$, $W^{IV/V}$, Re^{V}

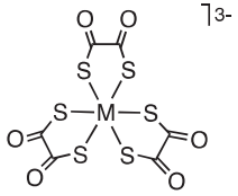


$[M(CN)_4]^{2-}$

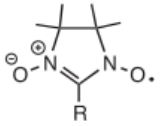
M = Ni^{II}, Pd^{II}, Pt^{II}



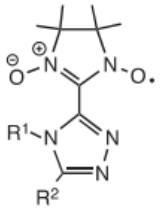
$[M(ox)_3]^{3-}$



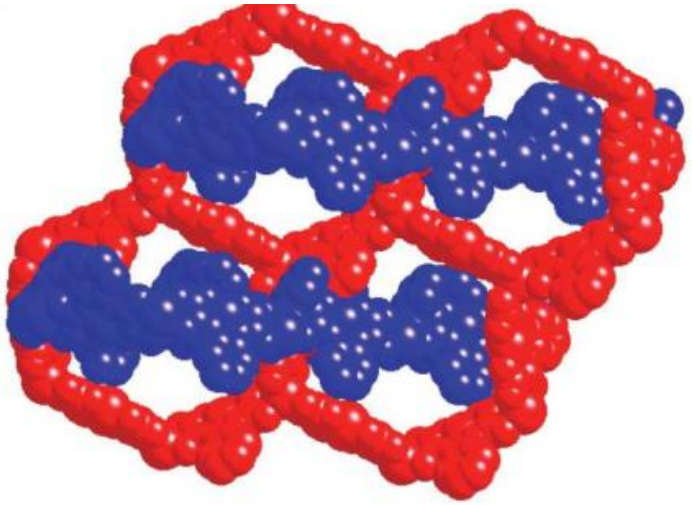
$[M(dtox)_3]^{3-}$



NIT (R = H)
NITEt (R = Et)
NITPr (R = iPr)
NITPh (R = Ph)
NITPhNO$_2$ (R = *p*-PhNO$_2$)
NITPhCO$_2$H (R = *p*-CO$_2$H)



NITTrzMe (R^1 = Me, R^2 = H)
NITTrzMe$_2$ (R^1 = R^2 = Me)



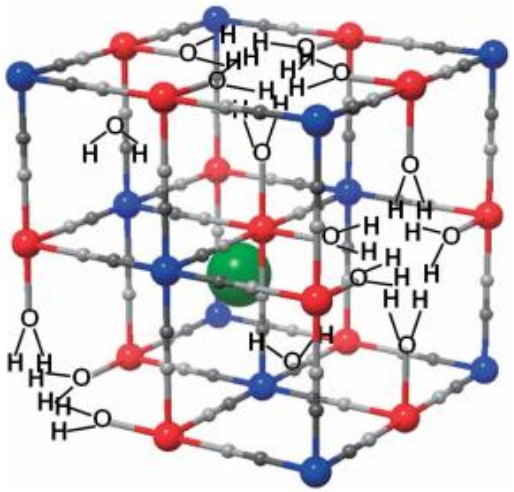
H.O. Stumpf, O. Kahn *et al*, *Science*, **1993**, *261*, 447

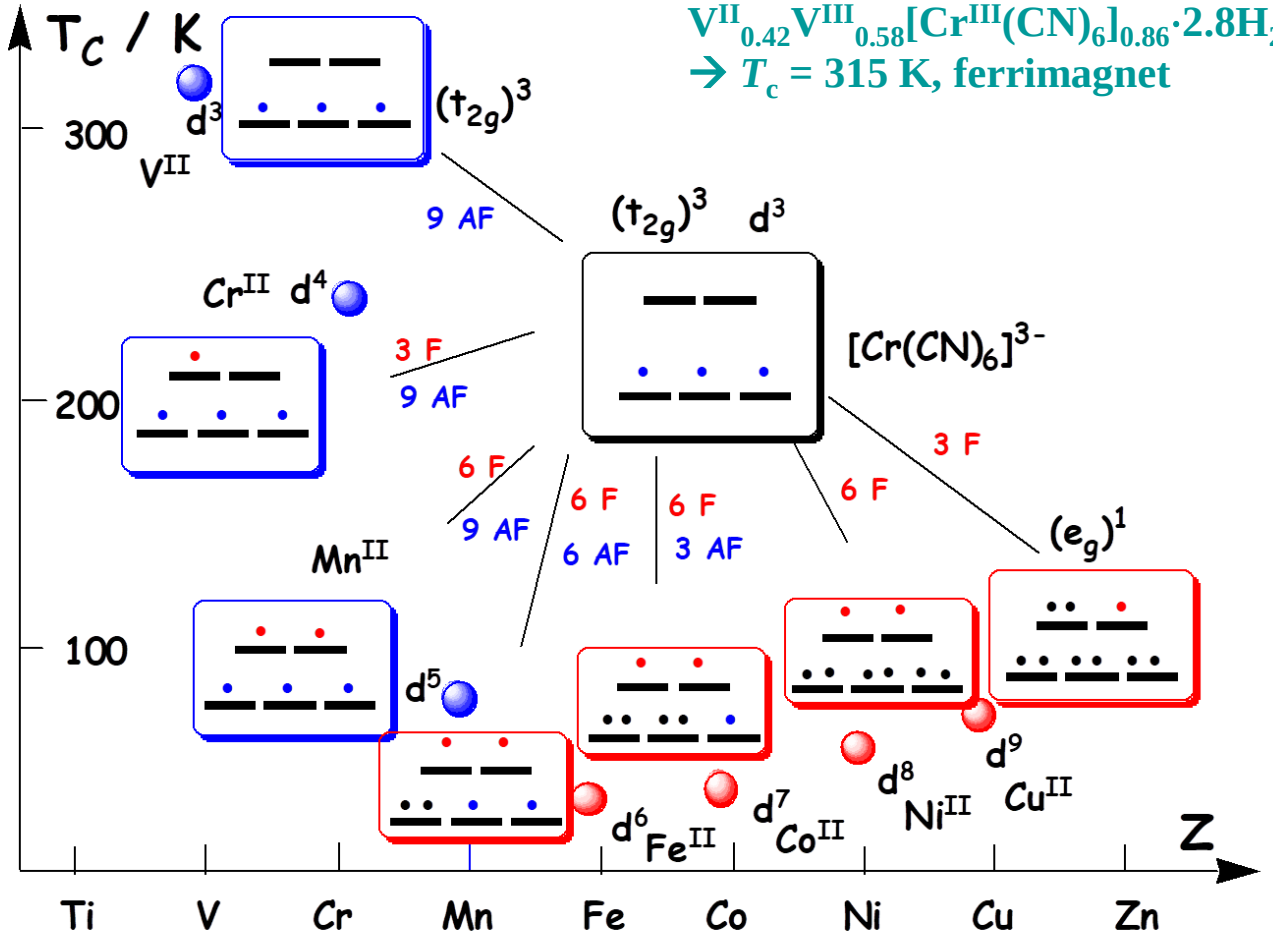
J. Ferrando-Soria *et al*, *Coord. Chem. Rev.* **2017**, *339*, 17
E. Pardo, *et al; Dalton Trans*. **2008**, 2780

Molecular Magnetism: High Tc molecule-based magnets

The orbital overlap and the resulting magnetic exchange can be tuned by an appropriate set of metals and ligands (O, CN, many others)

Prussian blue analogs (PBA):
$A_xM[M'(CN)_6]_{(2+x)/3}.zH_2O$





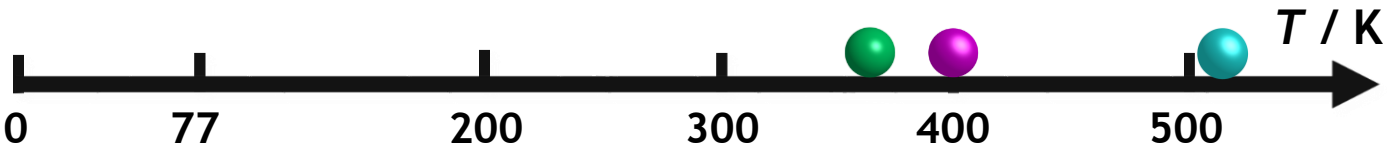
$V^{II}_{0.42}V^{III}_{0.58}[Cr^{III}(CN)_6]_{0.86}\cdot 2.8H_2O$
→ T_c = 315 K, ferrimagnet

Ferlay, S. *et al.*, *Nature* **1995**, 378, 701-703.

10

Molecular Magnetism: High Tc molecule-based magnets

Metal-Organic Magnets with T_C above 300 K:



Prussian Blue analogues (G.S. Girolami, T. Mallah, S.-i. Ohkoshi, M. Verdaguer, J.S. Miller…)

$KV^{II}[Cr^{III}(CN)_6]$, T_c = 376 K

Ferlay, S. *et al.*, *Nature* **1995**, 378, 701-703.
S. Holmes, G. Girolami, *J. Am. Chem. Soc.*, **1999**, *121*, 5593

TCNE and TCNE derivatives-based magnets (J. Miller, G.T. Yee…)

$V^{II}[TCNE]_x$, T_c = 400 K

J. M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, J.S. Miller, *Science*, **1991**, *252*, 1415

$Li_{0.7}[Cr^{II}(pyrazine^{\bullet -})_2]Cl_{0.7}\bullet n$THF: Ferrimagnets with T_C > 500 K

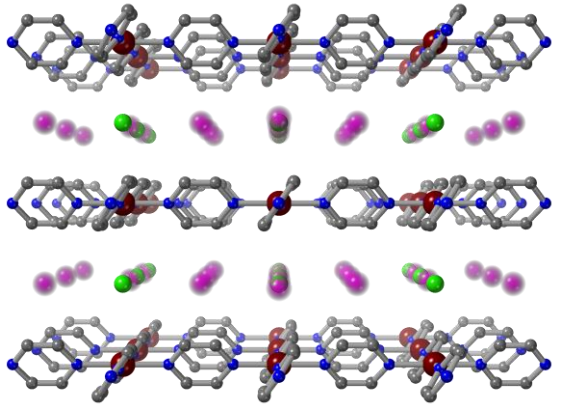
R. Clérac *et al*, *Science*, **2020**, *370*, 587

Molecular Magnetism: High Tc molecule-based magnets

$Li_{0.7}[Cr^{II}(pyrazine^{\bullet-})_2]Cl_{0.7}\bullet THF$

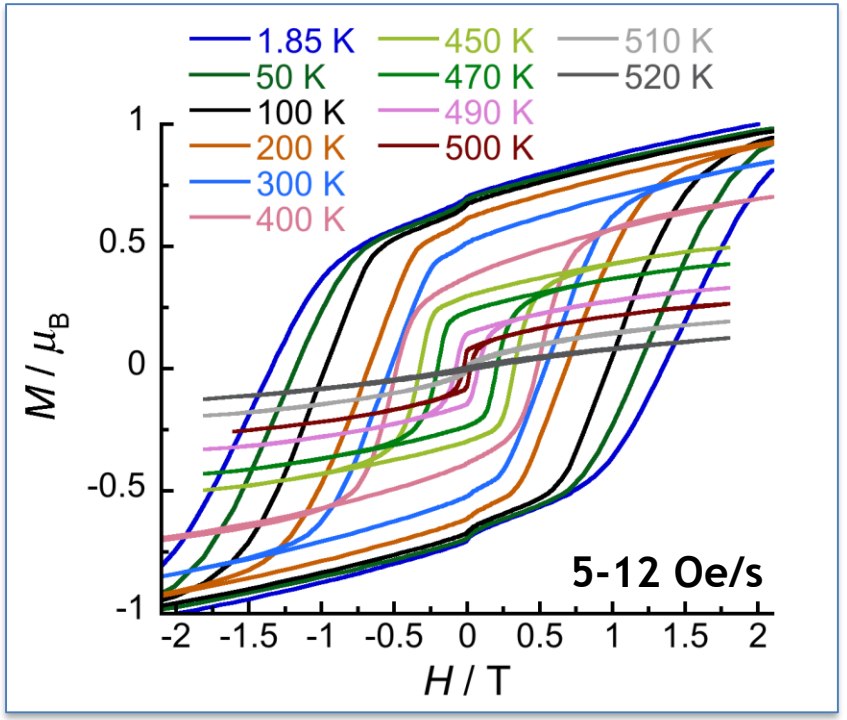
The ligand is also a spin carrier

Magnetically anisotropic ion



A hard magnet at 515 K!

	Compound	T_C (K)	RT H_{coer} (Oe)
Inorganic magnets ~5-9 g/cm³	Hard ferrites	720-735	1100-3100
	$AlNiCo_5$	1130-1175	615-750
	$AlNiCo_8$	1130	1500-1900
	$SmCo_5$	1000	6700-9000
	Sm_2Co_{17}	1070	8000
	$Nd_2Fe_{14}B$	550-590	9300-27000
Molecule-based magnets ~1 g/cm³	$V[TCNE]_x \cdot yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$)	> 350	60
	$V[TCNE]_x$ ($x \sim 2$) thin films	400	~ 4.5
	$V[Cr^{III}(CN)_6]_{0.86} \cdot 2.8H_2O$	315	≤ 25
	$KV^{II}[Cr^{III}(CN)_6] \cdot 2H_2O$	376	~ 4
	TCNQ-linked covalent organic framework	> 400	~ 50
	1,3,5-triazine-linked covalent organic framework	> 400	300
	$Li_{0.7}[Cr^{II}(pyz^{\bullet-})_2]Cl_{0.7} \cdot THF$	~510	~5300
	$Li_{0.7}[Cr^{II}(pyz^{\bullet-})_2]Cl_{0.7} \cdot 0.25THF$	~515	~7500



R. Clérac *et al*, *Science*, **2020**, *370*, 587

Flavors of Molecular Magnetism: outline

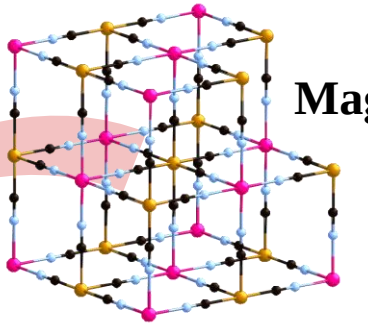
I. **High T_c Molecule-based magnets**

II. **Towards active molecular units (SMM)**

III. **Switchable molecules**

IV. **Multifunctionality**

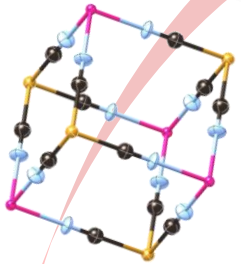
Molecular Magnetism: towards active molecular units



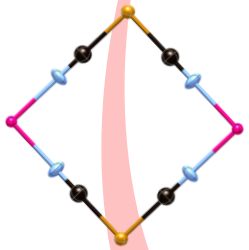
Magnet $\boldsymbol{H} = \boldsymbol{J}S_iS_j + \sum_i S_i\boldsymbol{D}_iS_i$

Magnetic coupling

Magnetic anisotropy



Single Molecule Magnet



Switchable molecules

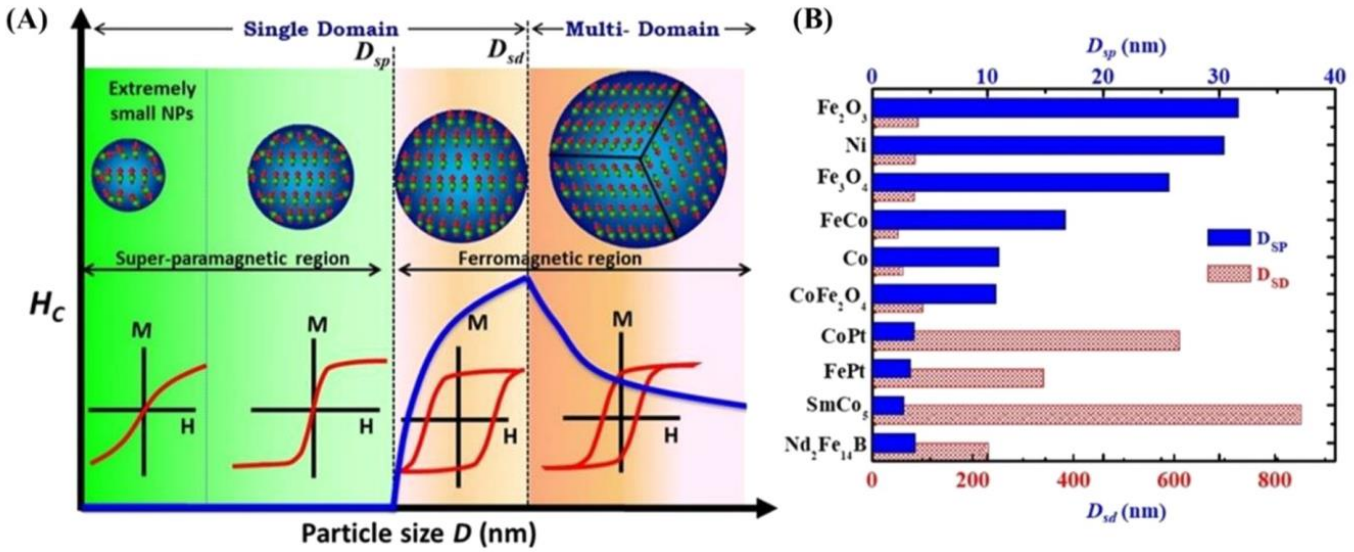
MM: towards active molecular units – Single-Molecule Magnets

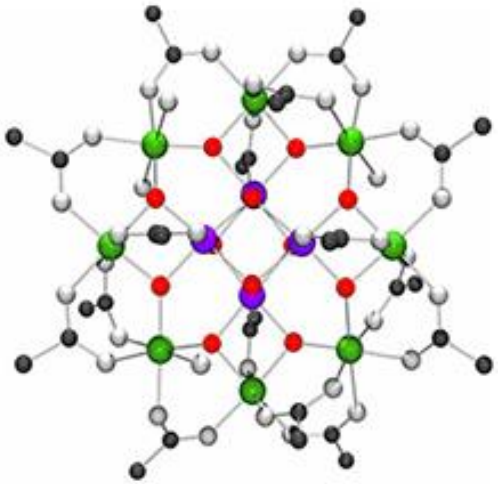
Superparamagnetism: a single domain particle « behaves » as individual spins

- At high temperature, the particles' magnetizations are randomly oriented
- Below the blocking temperature, T_B, these magnetizations are oriented under a magnetic field
- Below T_B, if the magnetic field is removed, a magnetization reversal occurs
- This magnetization reversal dynamics depends on the magnetic anisotropy.

$$\tau = \tau_0 e^{-E_a/k_B T}$$

A molecule can be equivalent to a single domain monodisperse NP and exhibit superparamagnetic behavior

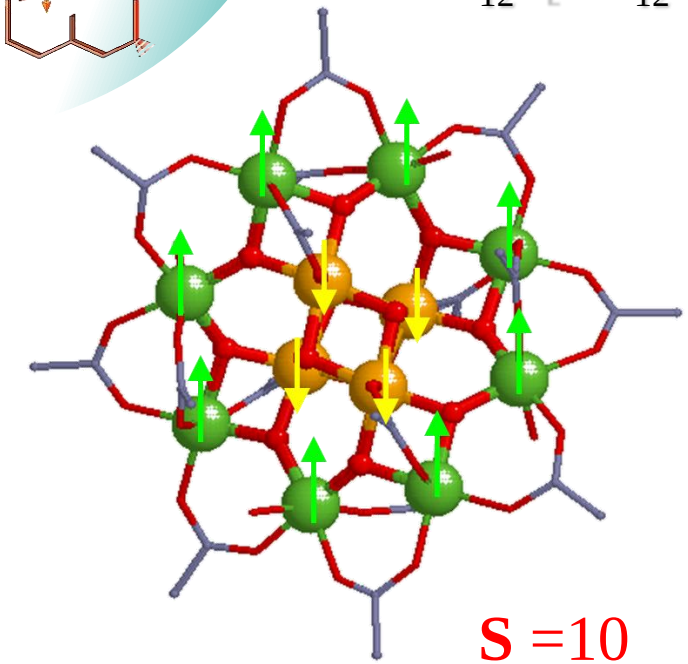




Ma. *et al.*, *Coord. Chem. Rev.* **2003**, 123, 3904.

MM: towards active molecular units – Single-Molecule Magnets

Mn_{12}: $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4].2CH_3COOH.4H_20$



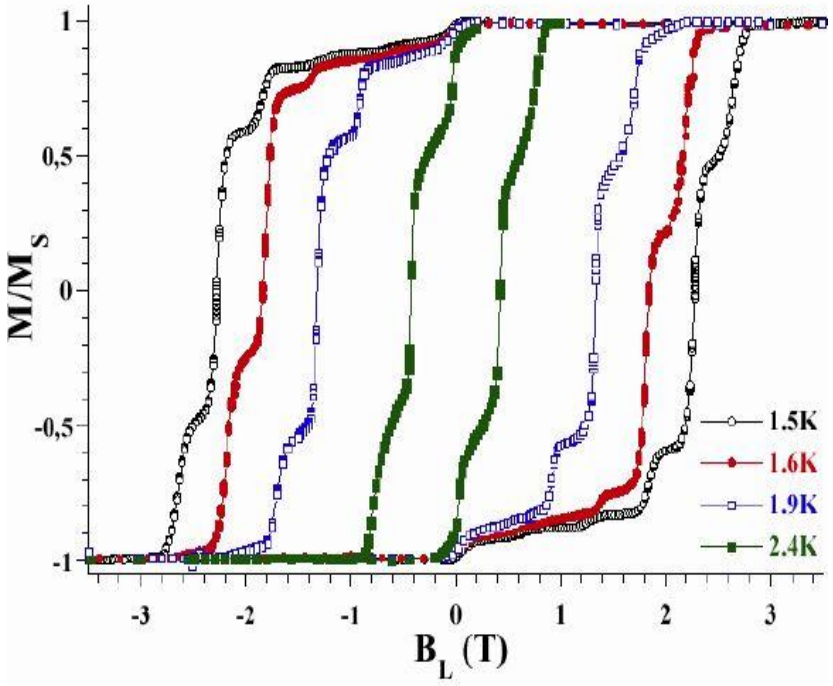
Mn(III) S = 2

Mn(IV) S = 3/2

Oxygene

Carbone

S =10



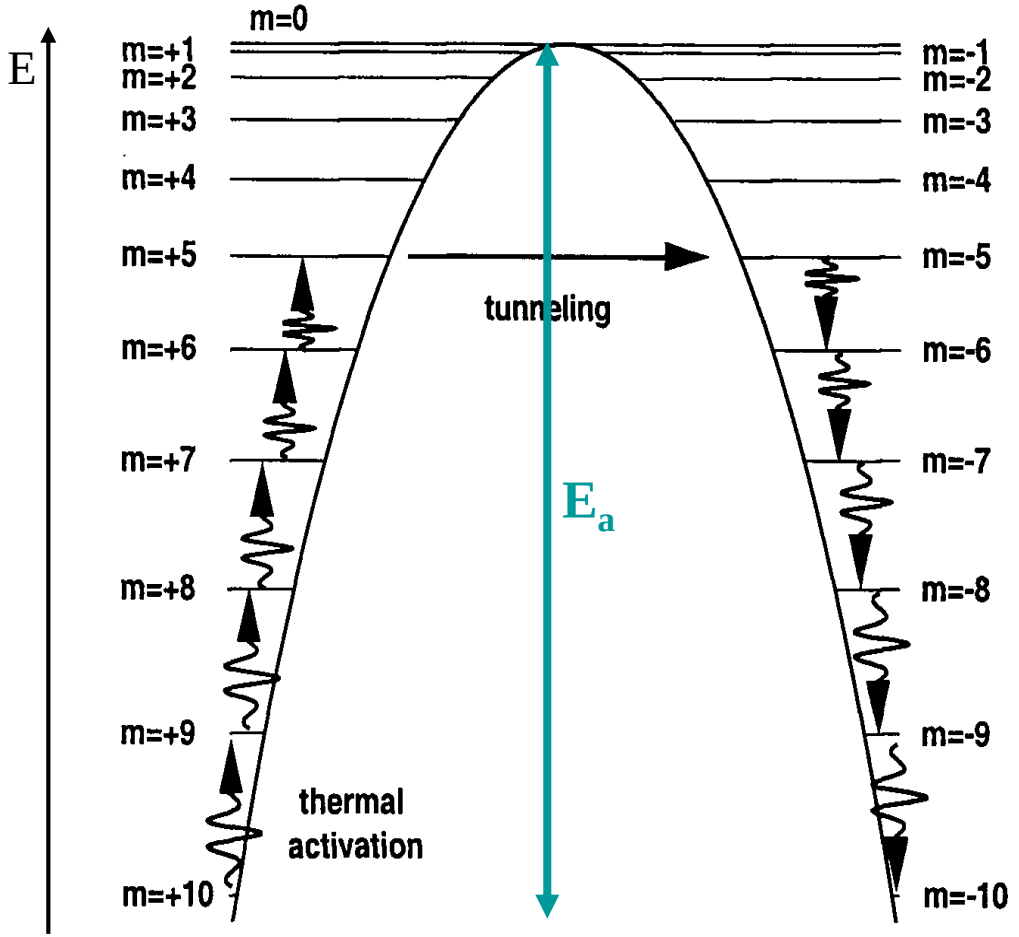
~ fragment of Mn oxyde capped by acetate ligands

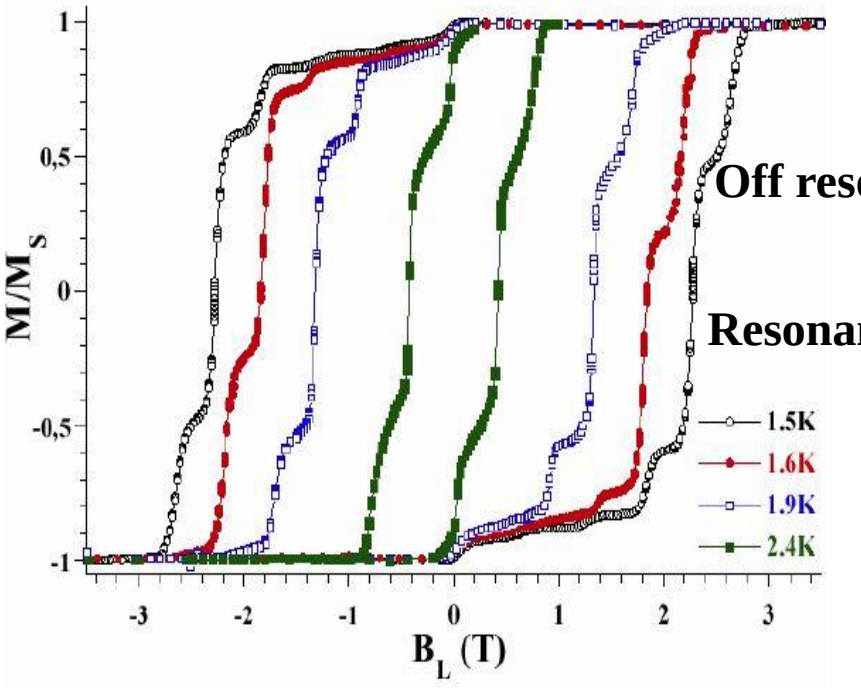
Use the classical magnetic characterizations: ZFC/FC, ac susceptibility, magnetization and hysteresis curves, …

Sessoli, R. *et al.*, *Nature* **1993**, *365*, 141; D. Gatteschi, *et al. Science* **1994**, *265*, 1054; L. Thomas *et al*, *Nature* **1996**, *383*, 145

MM: towards active molecular units – Single-Molecule Magnets

Compare to superparamagnetic NPs, the continuum of levels within the potential wells breaks down and **quantum size effects**, like tunneling, are observed.





Off resonance

Resonant QT

Clear evidence at the macroscopic level of quantum effects

MM: towards active molecular units – Single-Molecule Magnets

A SMM is a superparamagnetic molecule with a sufficiently slow dynamics of the magnetization reversal to be measured with a given set-up

The observation of hysteresis and magnetization reversal depends on the activation energy

First approximation: Magnetization reversal rate :

$$\tau = \tau_0 e^{-E_a/k_B T}$$

$$E_a \ \alpha \ D S_Z^2 + E(S_x^2 - S_y^2)$$

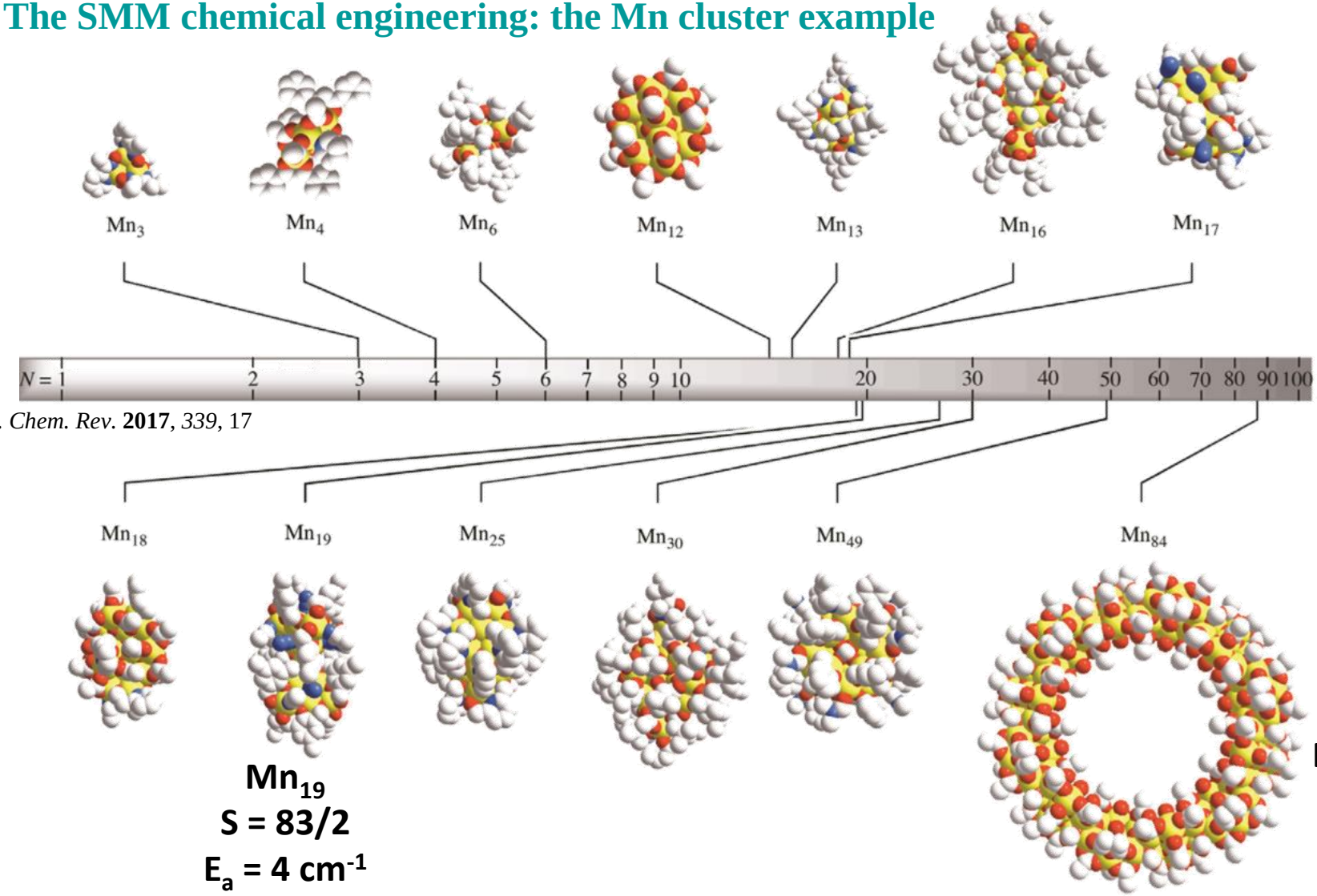
Uniaxial anisotropy

In plane anisotropy favors QT

⇒ Chemical design of thousands of SMMs

MM: towards active molecular units – Single-Molecule Magnets

The SMM chemical engineering: the Mn cluster example



J. Ferrando-Soria *et al*, *Coord. Chem. Rev.* **2017**, *339*, 17

Mn_{19}
S = 83/2
E_a = 4 cm^{-1}

A.K. Powell *et al*, *Angew. Chem. Int. Ed* **2006**, *45*, 4926

Mn_{84}
S = 6
E_a = 12 cm^{-1}

G. Christou *et al*, *Angew. Chem. Int. Ed* **2004**, *43*, 2117

MM: towards active molecular units – Single-Molecule Magnets

A better view of energy barrier:

$$E_a \;\alpha\; D S_Z^2 \;+\; E(S_x^2 - S_y^2)$$

$$D_{kl}^{SOC-(0)} = -\frac{1}{S^2} \sum_{I(S_b=S)} \Delta_b^{-1} \left\langle 0SS \left| \sum_i h_k^{SO}(i) s_{i,z} \right| bSS \right\rangle \times \left\langle bSS \left| \sum_i h_l^{SO}(i) s_{i,z} \right| 0SS \right\rangle$$

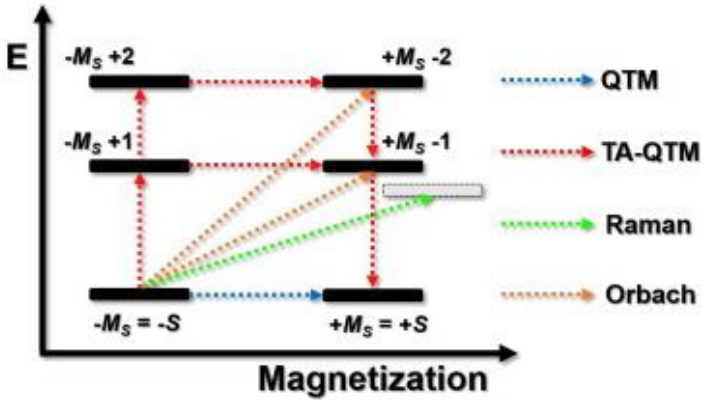
F. Neese *et al*, *Faraday Discussions.* **2011**, *148*, 229

Complete mechanism: Magnetization reversal rate :

$$\frac{1}{\tau} = \frac{1}{\tau_{tunnel}} + \frac{1}{\tau_{Orbach}}$$

$$\frac{1}{\tau} = \frac{C_1}{1+C_2 H^2} + \tau_0^{-1} exp\left(\frac{-\Delta}{k_B T}\right)$$

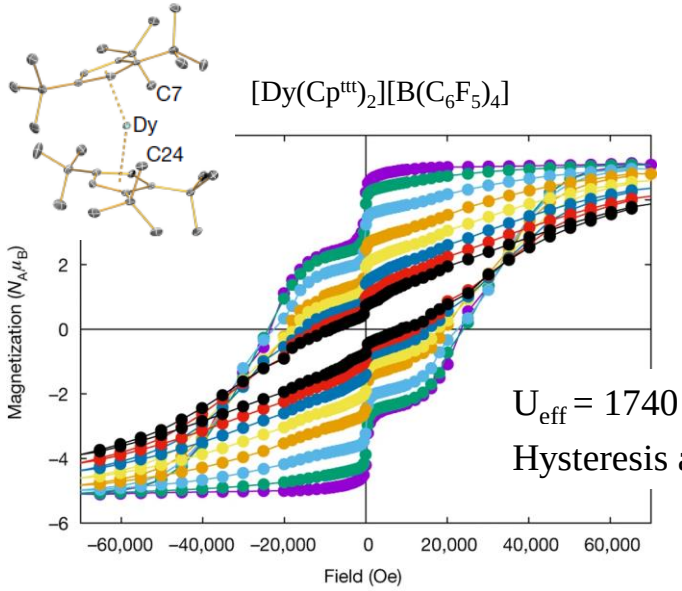
Molecule design



A. Zabala-Lekuona *et al*, *Coord. Chem. Rev.* **2021**, *441*, 213984

MM: towards active molecular units – Single-Molecule Magnets

The combination of theoretical predictions and chemical engineering led to highly performant SMMs

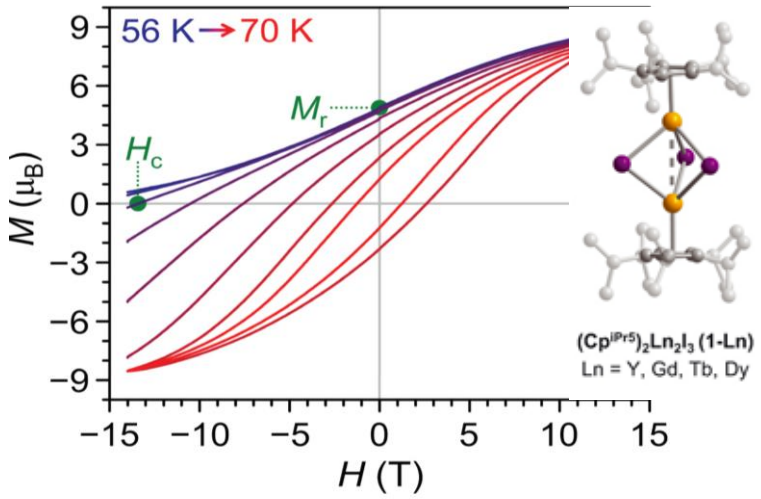


$[Dy(Cp^{ttt})_2][B(C_6F_5)_4]$

U_{eff} = 1740 K

Hysteresis at 60 K

C. Goodwin *et al*. *Nature*, **2017**,548, 439
F.-S. Guo *et al*. *Science,* **2018**, *362*, 1400



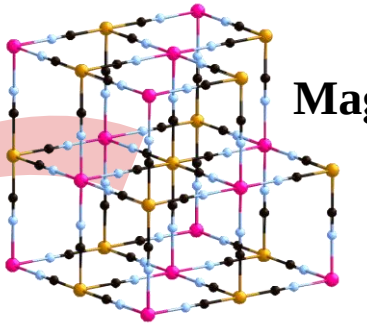
U_{eff} = 2300 K

Hysteresis at 70 K

H_c = 14 T at 60 K

C. A. Gould *et al*. *Science*, **2022,** *375*, 198

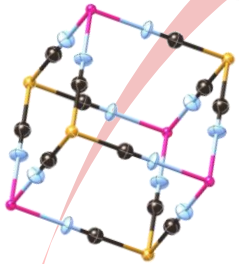
Molecular Magnetism: towards active molecular units



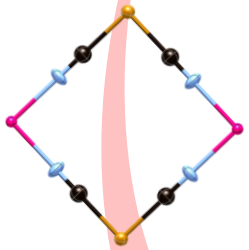
Magnet $H = JS_iS_j + \sum_i S_i D_i S_i$

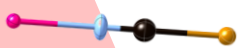
Magnetic coupling

Magnetic anisotropy



Single Molecule Magnet



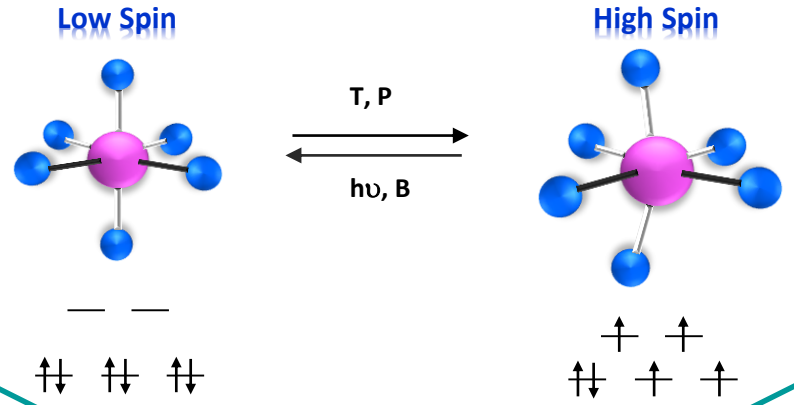


Switchable molecules

MM: Switchable molecules

Spin crossover

Change of electronic configuration on one metallic site

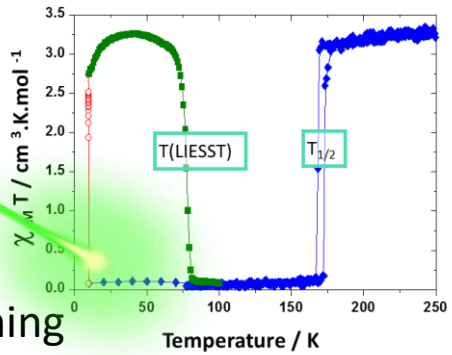


Electron transfer

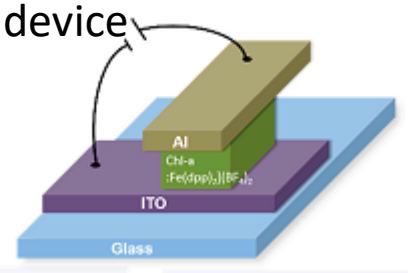
Change of electronic configuration involving two redox active sites

MM: Switchable molecules

(ultrafast) photoswitching

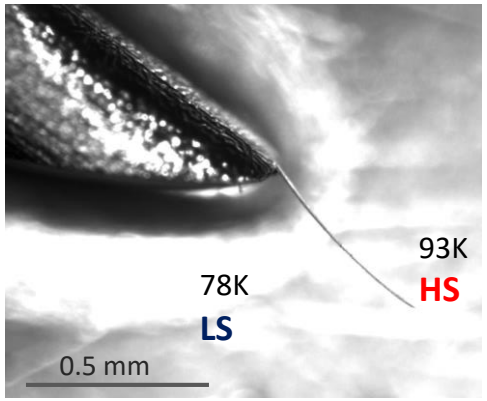


Electronic device



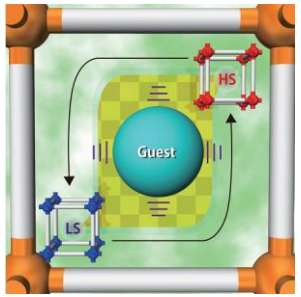
Liquid crystals

Micromechanical devices (actuators, MEMS…)

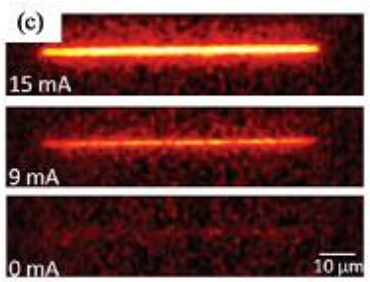


Pressure sensing

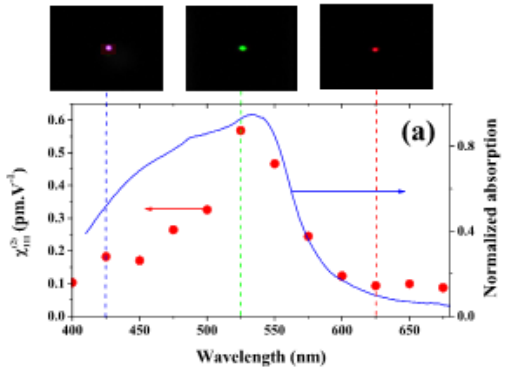
Gas sensing/capture



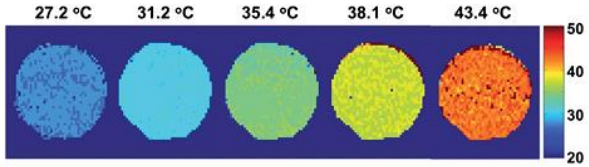
Fluorescence probe



Optics (NLO, plasmonic…)



MRI

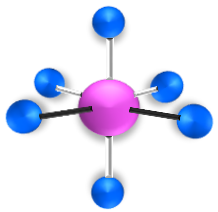


IR sensing

MM: Switchable molecules

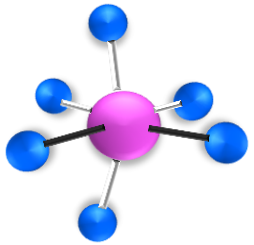
At the molecular level

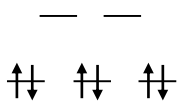
Low Spin — Fe^{2+} (d^6) — **High Spin**



T, P

hυ, B





Anti-bonding MOs
M-L bond disfavored
Volume change

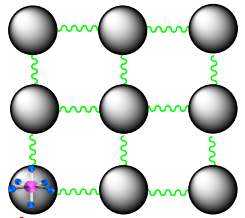
S = 0
diamagnetic

Magnetism change

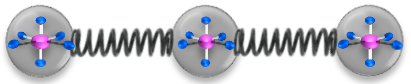
S = 2
paramagnetic

Color change

Dieclectric change

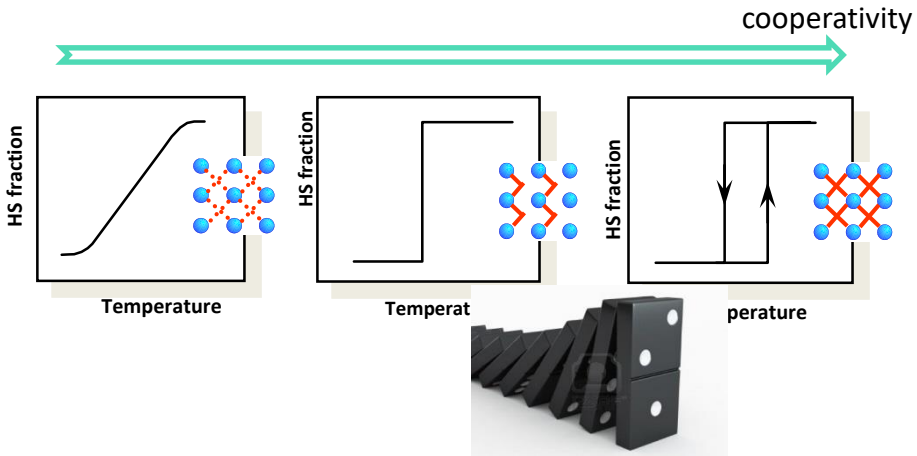


In the solid state molecules are linked by springs



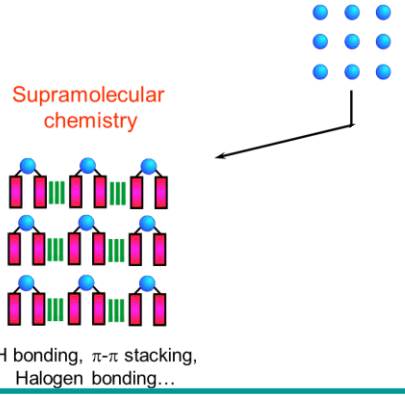
Spring = H bond, π-π stacking, halogen bond, "covalent" bond…

cooperativity = ferro-elastic like behaviour

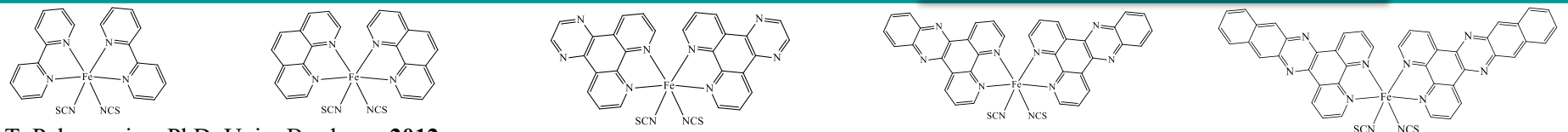


MM: Switchable molecules

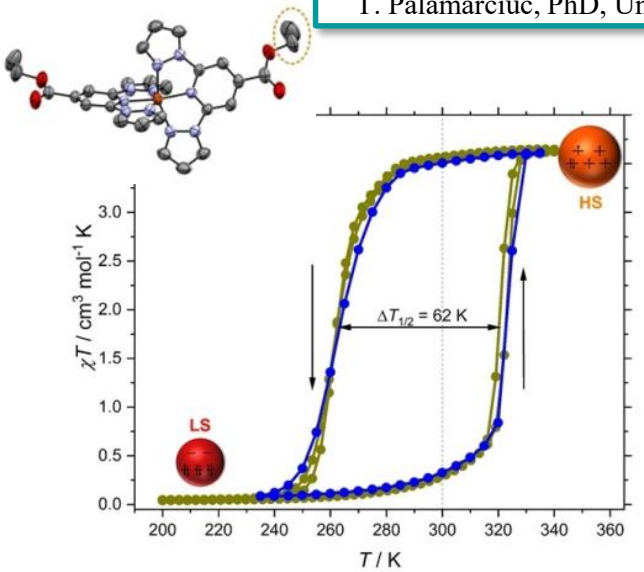
Increase of the ferroelastic interactions: towards RT memories



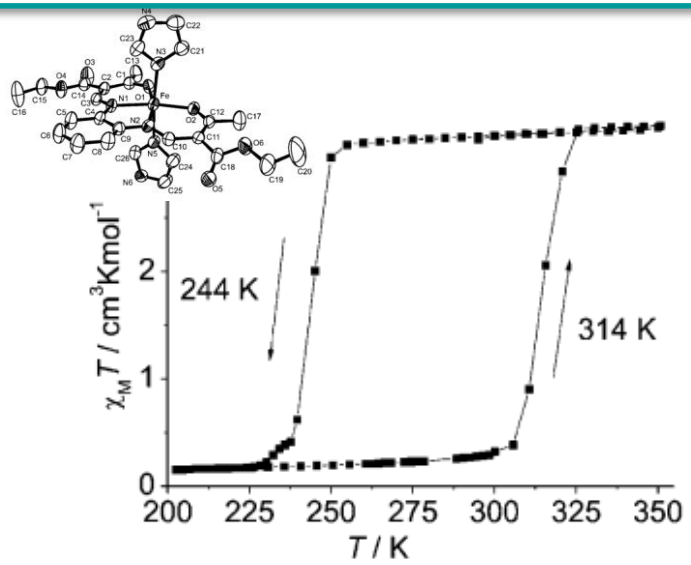
Typical chemical engineering



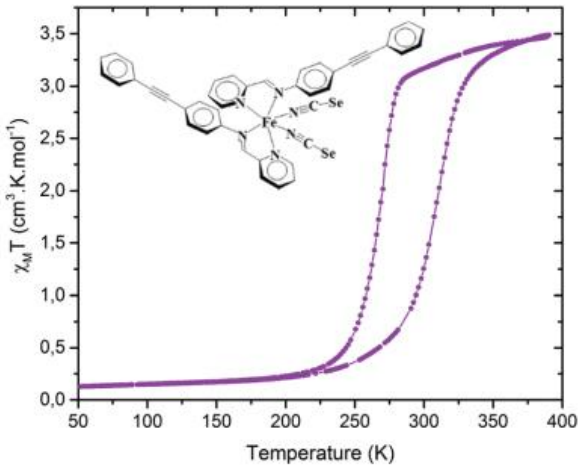
T. Palamarciuc, PhD, Univ. Bordeaux **2012**



N. Suryadevara *et al*. *Chem. Eur. J.*, **2022**, 28, e202103853



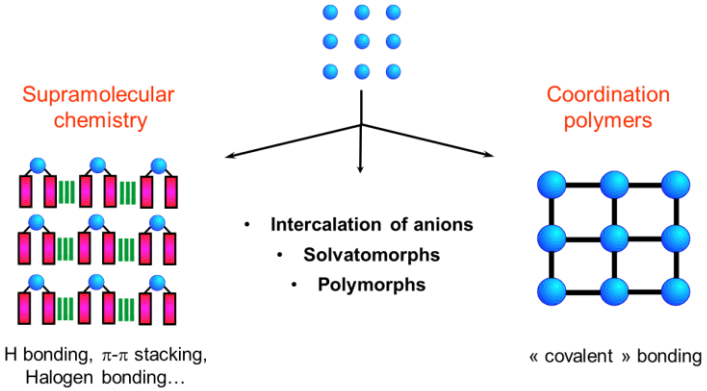
B. Weber *et al*. *Angew. Chem. Int. Ed.*, **2008**, 47, 10098



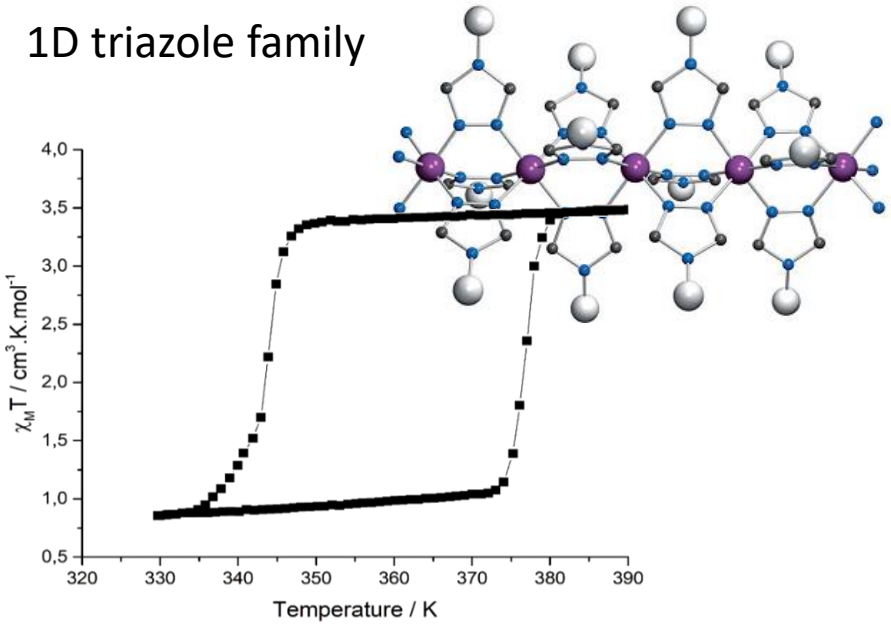
E. Tailleur *et al*. *Chem. Comm.*, **2017**, 53, 4763

MM: Switchable molecules

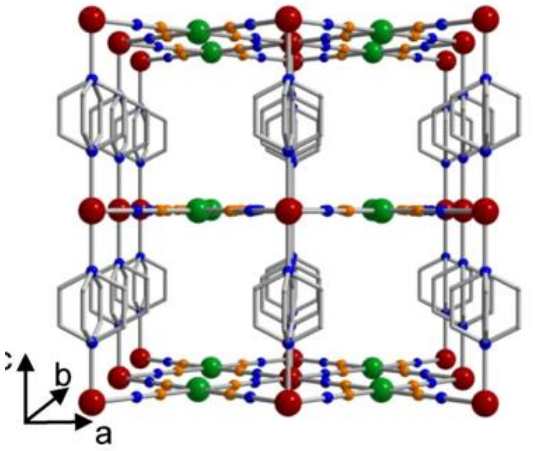
Increase of the ferroelastic interactions: towards RT memories



1D triazole family

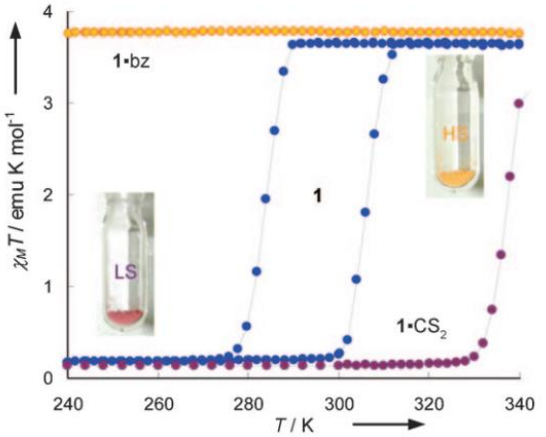


A. Grosjean, *et al Chem. Commun*. **2011**, *47*, 12382
O. Roubeau, *Chem. Eur. J*. **2012**, *18*, 15230



3D Hoffman family

Host-guest interactions

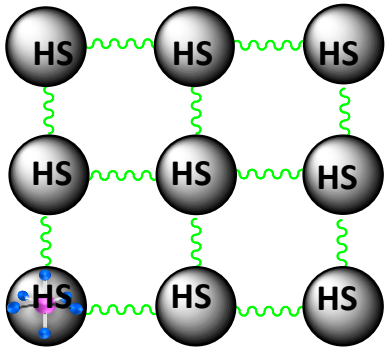


J.A. Real *et al*, *Coord Chem. Rev.*, **2011,** *255*, 2068.
R. Ohtani, S. Hayami, *Chem. Eur. J.,* **2017**, *23*, 2236.
M. Ohba, *et al, Angew. Chem. Int. Ed*. **2009**, *48*, 4767

MM: Switchable molecules

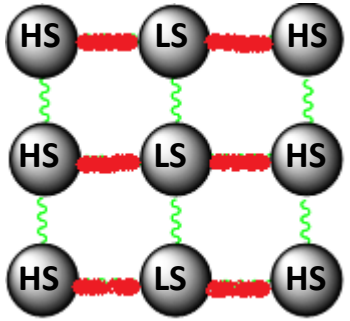
Elastic competition between ferro and antiferro-elastic interactions

Strong ferro-elastic interactions

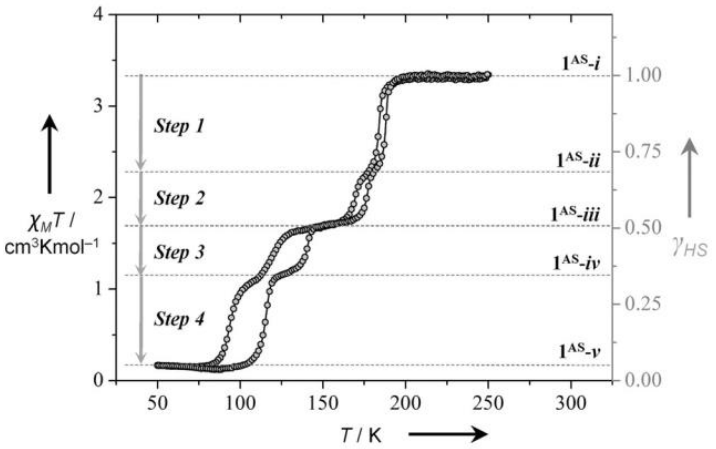


All the metallic sites tend to be in the same spin state

Ferro- AND antiferro-elastic interactions



Symmetry breaking



J.E. Clements *et al Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 15105

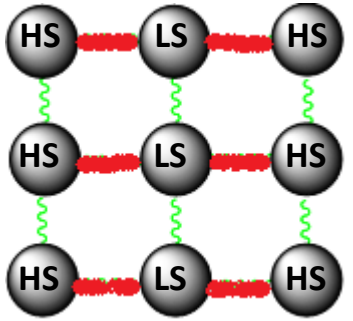
MM: Switchable molecules

Elastic competition between ferro and antiferro-elastic interactions

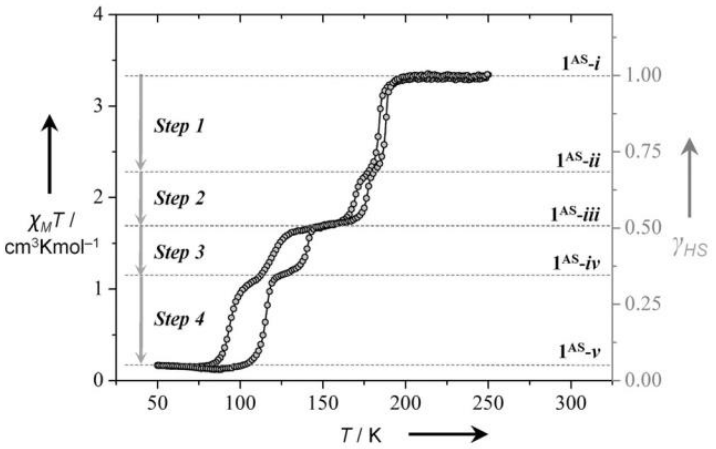
Strong ferro-elastic interactions

E. Trzop et al, *Angew. Chem. Int Ed*. **2016**, *55*, 8675
E. Collet, P. Guionneau, *C. R. Acad. Sci.,* **2018**, *21*, 1133

Ferro- AND antiferro-elastic interactions



Symmetry breaking



J.E. Clements *et al Angew. Chem. Int. Ed. Engl*. **2016**, *55*, 15105

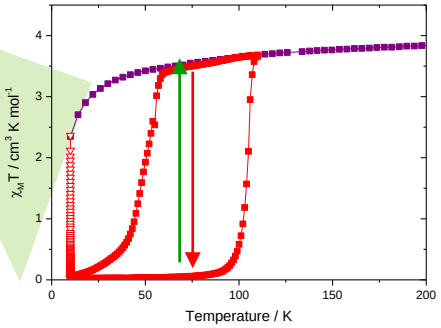
MM: Switchable molecules

Elastic competition between ferro and antiferro-elastic interactions

AntiFerro-elasticity

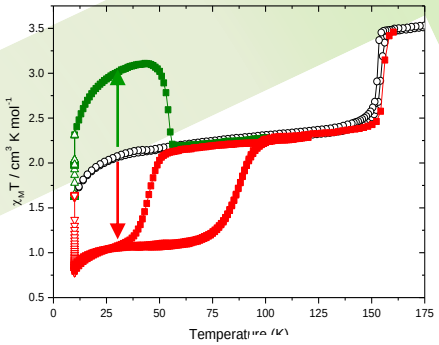
Ferro-elasticity

Elastic competition

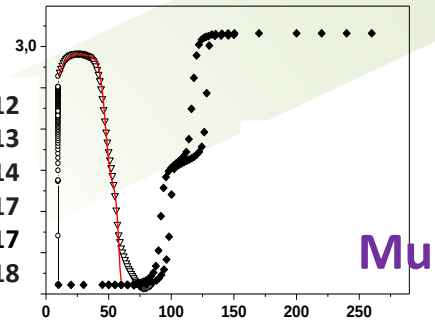


Hidden phases

Eur. J. Inorg. Chem. **2018**
Curr. Inorg. Chem. **2016**



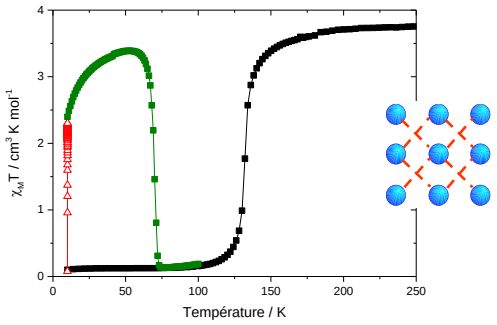
Inorg. Chem. **2016,**
Phys. Chem. Chem. Phys. **2018**
Angew. Chem. ***2019***

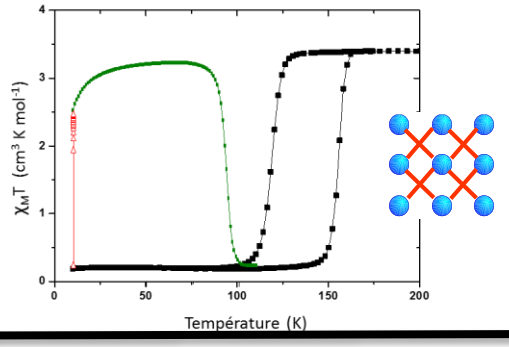


Multistability

Angew. Chem. Int. Ed. **2012**
Eur. J. Inorg. Chem. **2013**
Aust. J. Chem. **2014**
Chem. Commun. **2017**
Chem. Sci. **2017**
Eur. J. Inorg. Chem. **2018**

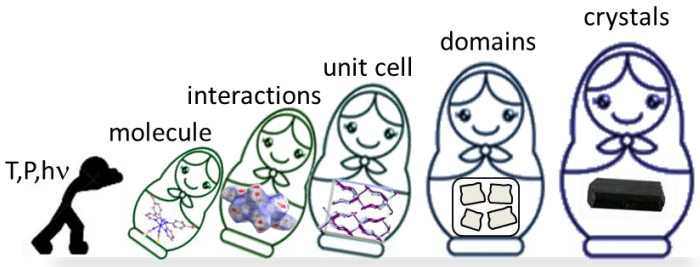
Bidirectional switching

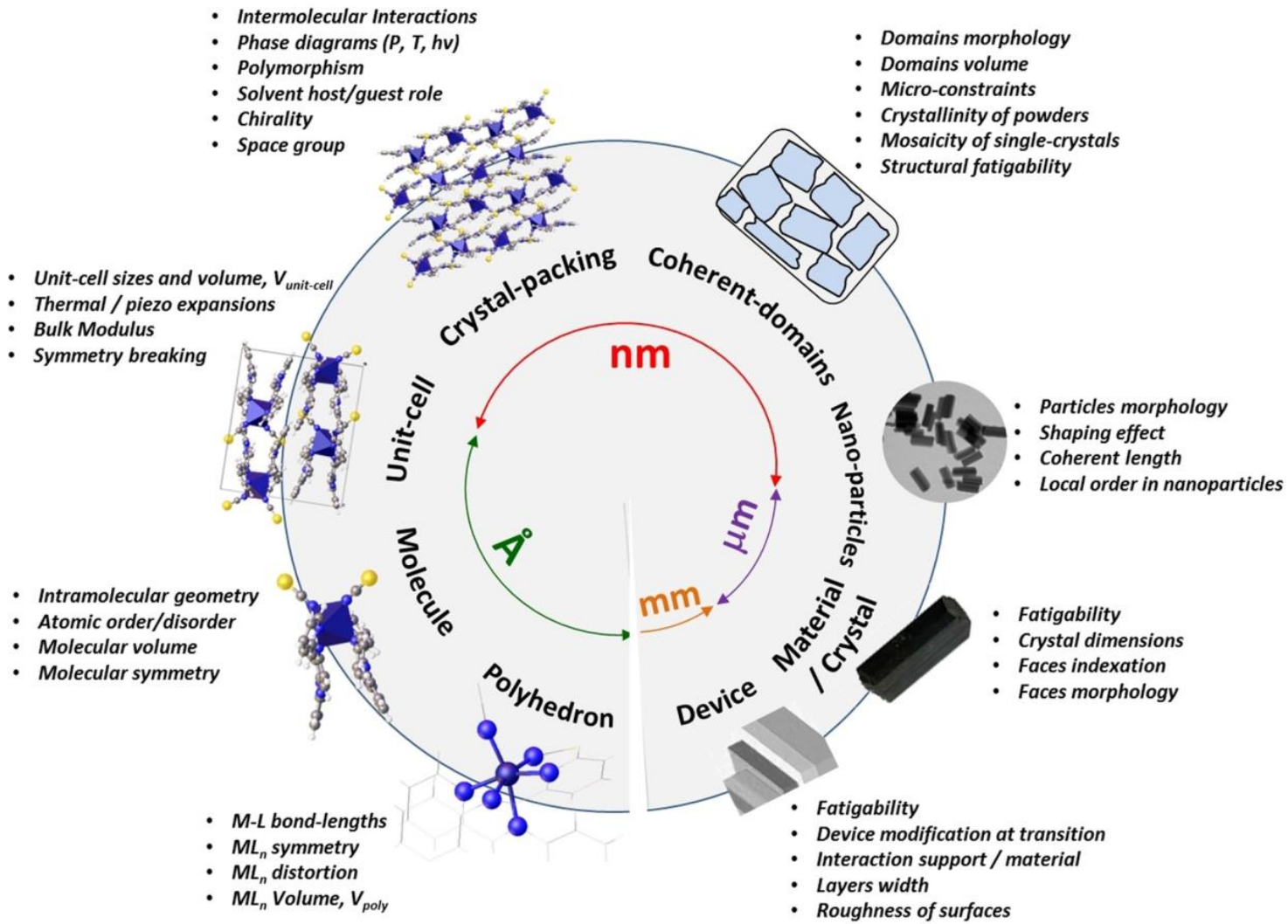




MM: Switchable molecules

Spin crossover a multiscale mechanism

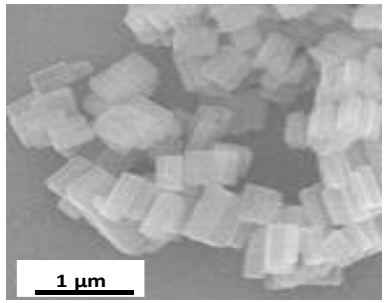




P. Guionneau, *Dalton Trans.*, **2014**, 43, 382-393,
P. Guionneau, M. Marchivie, G. Chastanet, *Chem. Eur. J.* **2021**, 27, 1483 – 1486

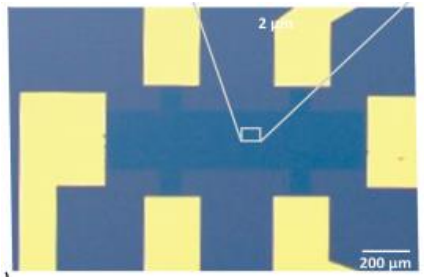
MM: Switchable molecules

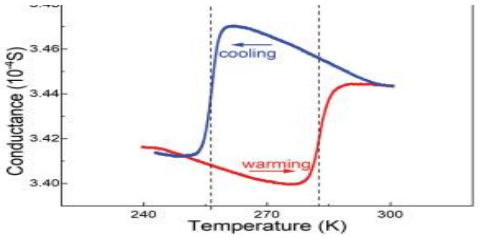
Spin crossover at the nanoscale

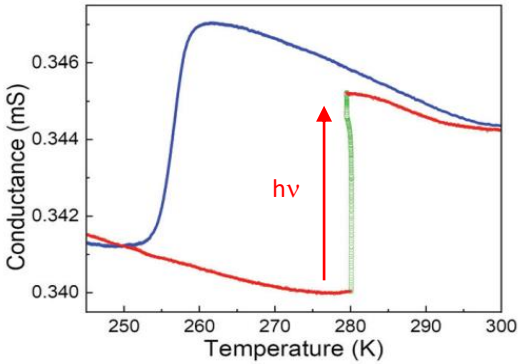


Opto-electronic devices

Graphene
B. Doudin, IPCMS

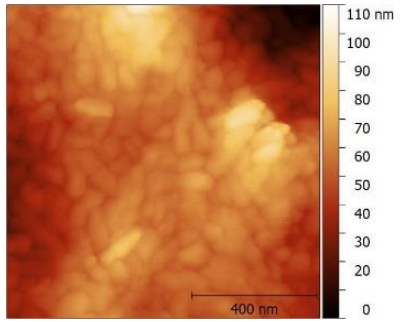




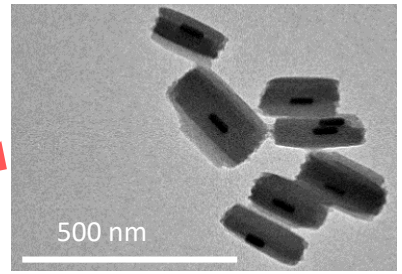


J.-F. Dayen *et al, Material Horizons* **2021,** *8*, 2310

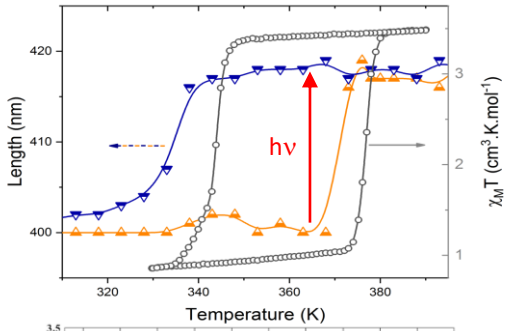
Composite : SCO + PVDF-TrFE

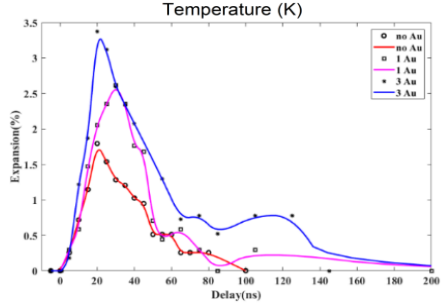


Au@SCO Nanohybrids



G5 (S. Mornet)
E. Freysz, LOMA
F. Banhart, IPCMS





Time-resolved TEM

Photo-thermia
Activated by SPR
on single nanoparticle

M. Palluel *et al*, *Adv. Func. Mater.* **2020,** *30*, 2000447
Y. Hu *et al, Adv. Mater.* **2021,** *33*, 2105586
Y. Hu et al, *Small*, **2023** online

Flavors of Molecular Magnetism: outline

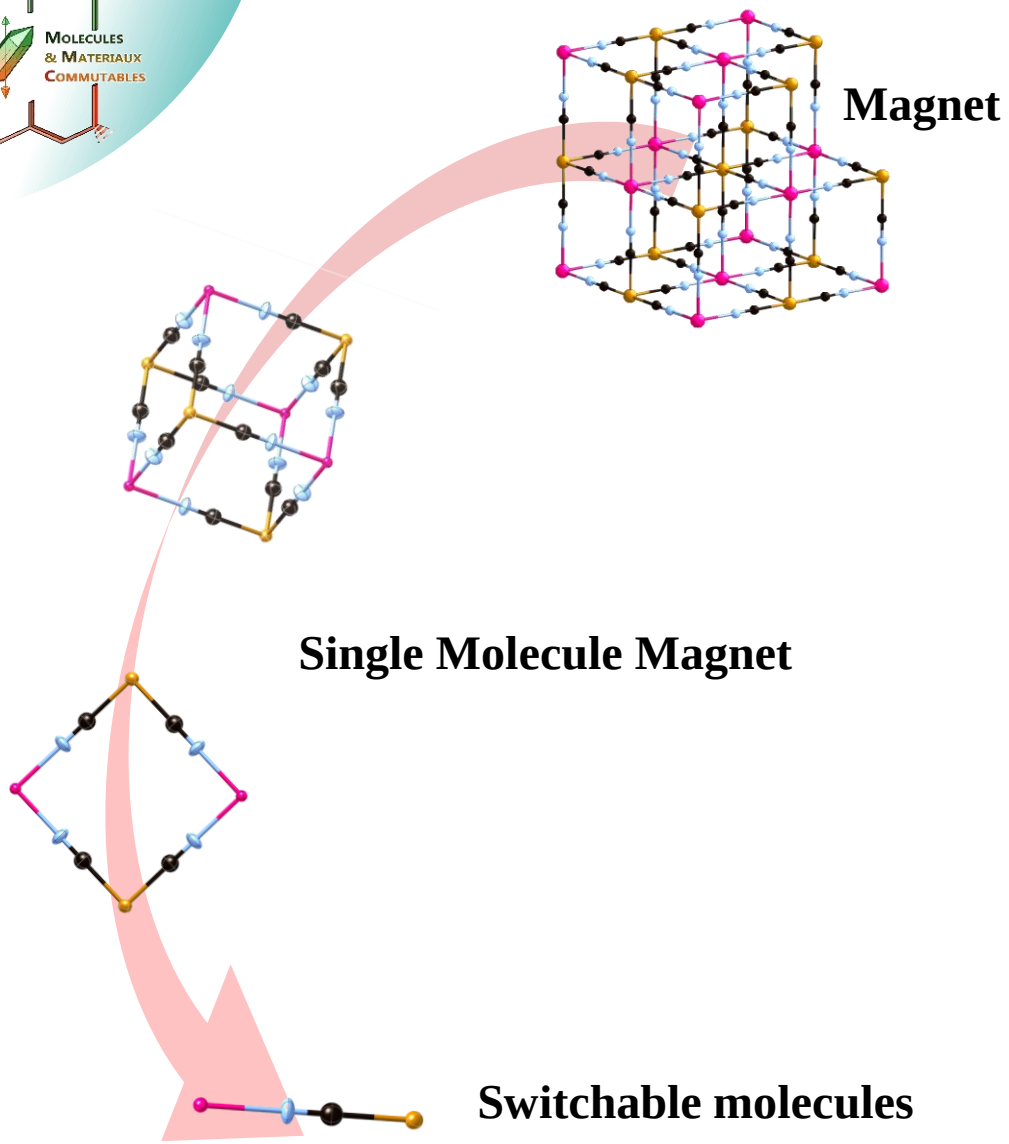
I. **High T_c Molecule-based magnets**

II. **Towards active molecular units (SMM)**

III. **Switchable molecules**

IV. **Multifunctionality**

Molecular Magnetism: towards multifunctionality



Strength of molecular magnetism: thanks to the chemical engineering, one can imagine a create many type of multifunctional systems :

Combination of all these properties in a same molecular material

- SCO + SMM
- Chirality
- Luminescence
- Electronic conduction
- Ferroelectricity

Combination of all these properties in composite materials

- Luminescence
- Electronic conduction
- Spintronic devices
- Ferroelectricity
- Superconductivity
- *and all we can think about…*

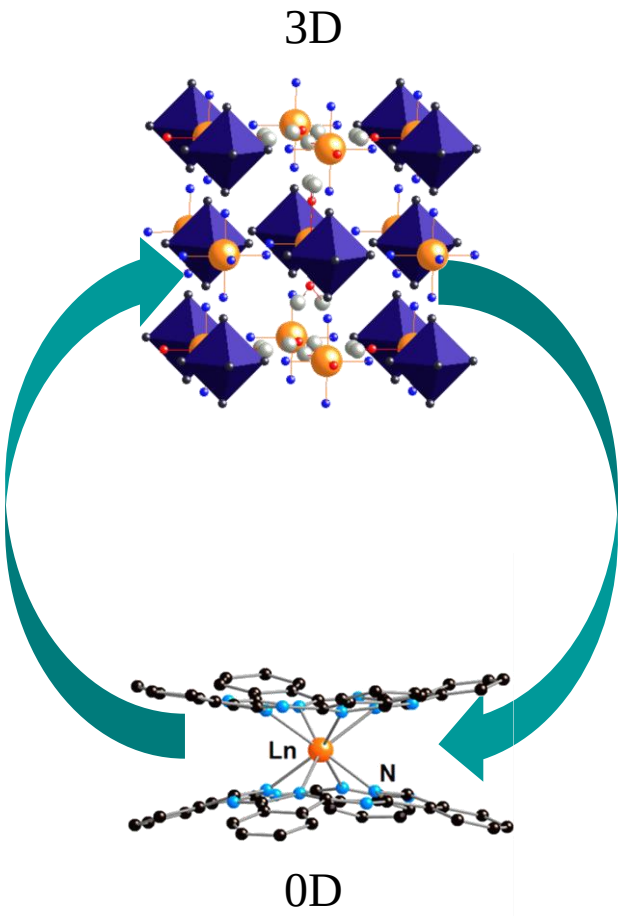
Flavors of Molecular Magnetism: outline

The strength of molecular magnetism:

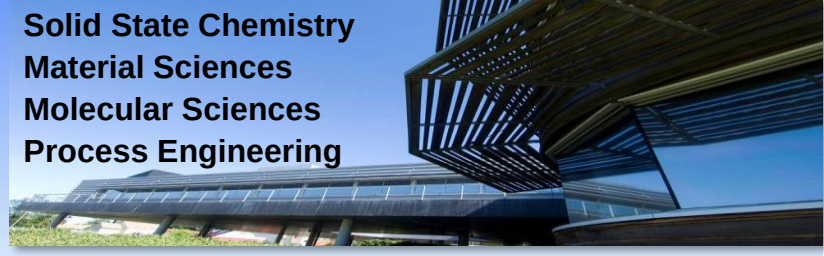
A highly versatile chemical engineering

A strong support from theory

A huge contribution from advanced characterization tools



Aknowledgments



Switchable Molecules and Materials group

Nathalie Daro
Dominique Denux
Cédric Desplanches
Mathieu Gonidec
Philippe Guionneau
Elizabeth Hillard
Mathieu Marchivie
François Riobé
Patrick Rosa
Baptiste Vignolle

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D. Stéphane Mornet (ICMCB, G5)

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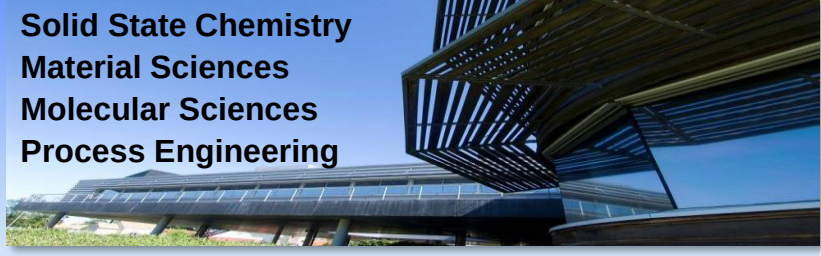
Kévin Bernot (INSA Rennes)

Collaborations

Pr. Eric Collet	IPR Rennes, France
Pr Smail Triki	University of Brest, France
Dr Sébastien Pillet,	CRM2 Nancy, France
Pr Kamel Boukheddaden	GEMaC Versailles, France
Pr Cameron J. Kepert,	University of Sydney, Australia
Dr. Suzanne Neville	University of Sydney, Australia
Pr. Keith Murray	Monash University, Australia
Dr. Julia. Klingele	University of Freiburg, Germany
Dr. Birgit Weber	University of Bayreuth, Germany
Pr. Malcom A. Halcrow	University of Leeds, UK
Pr. David Harding	University of Walailak, Thaïland
Pr. Vasilis Tangoulis	University of Patras, Greece
Dr Kishalay Bahr	Central University of Rajasthan, India
Pr Sin-Ichi Okhoshi	University of Tokyo, Japan
Dr. Paulo, N. Martinho	University of Lisbon, Portugal
Dr I. Ibarra	University of Mexico, Mexico



Merci de votre attention

Guillaume CHASTANET

Switchable Molecules and Materials group

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