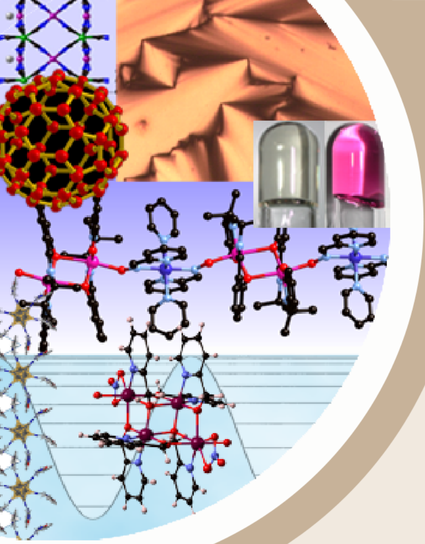

Introduction to Photomagnetism

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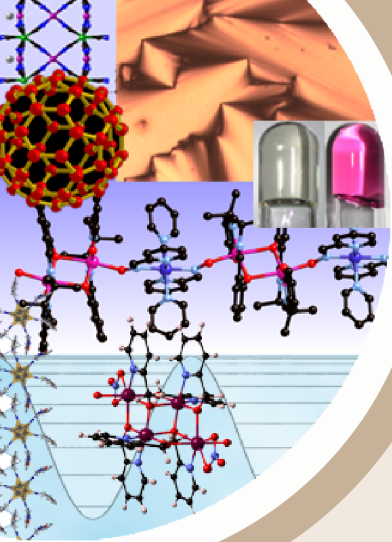


Introduction to Photomagnetism

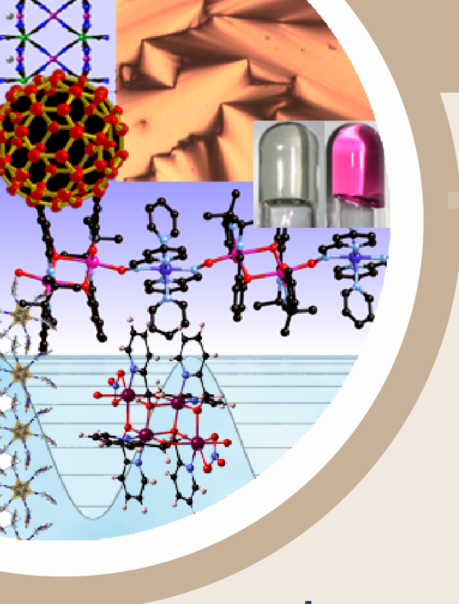
1) The Spin CrossOver (SCO) Phenomenon

1a) Spin Conversion vs. Spin Transition

2) Photomagnetism in coordination compounds

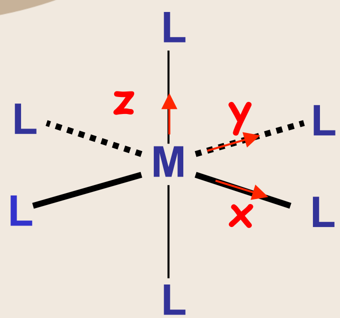
2a) The LIESST effect in SCO Compounds

2b) Photomagnetism in Electron Transfer Compounds



1) The Spin Crossover Phenomenon

The case of Fe(II) : d^6 configuration



$[Fe^{II}(H_2O)_6]^{2+}$

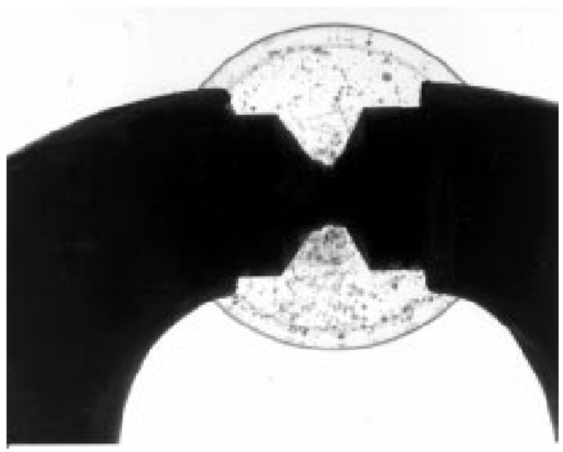


Figure 1. Crystals of $FeSO_4 \cdot 7H_2O$ are paramagnetic and adhere to the poles of a magnet.

$[Fe^{II}(CN)_6]^{4-}$

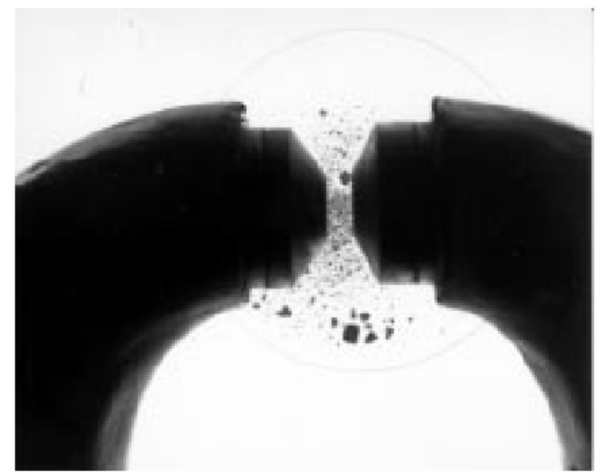
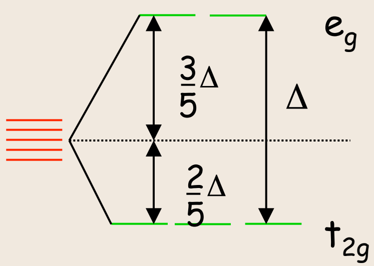
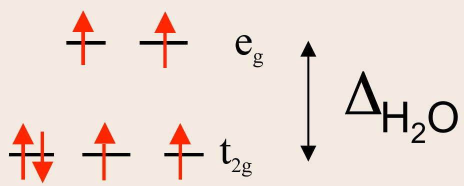


Figure 2. Crystals of $K_4Fe(CN)_6$ are diamagnetic and do not adhere to the poles of a magnet.

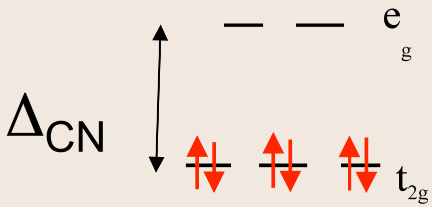
***d* orbitals in O_h symmetry**

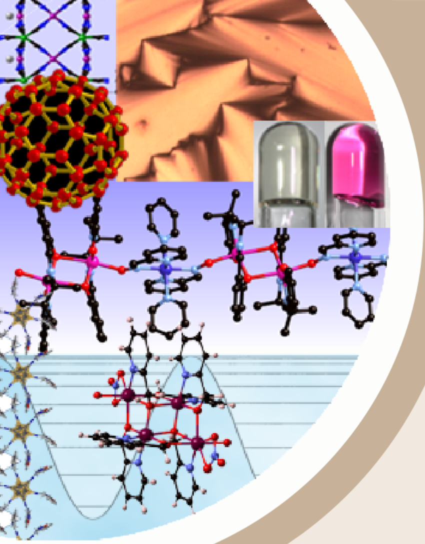


Paramagnetic $\forall T$



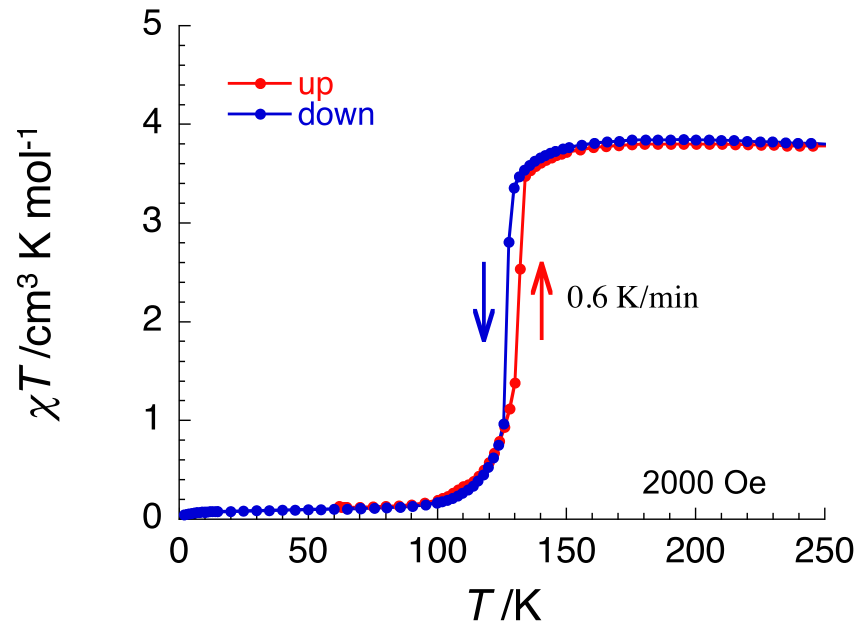
Diamagnetic $\forall T$





1) The Spin Crossover Phenomenon

High Temperature : High Spin configuration $S = 2$

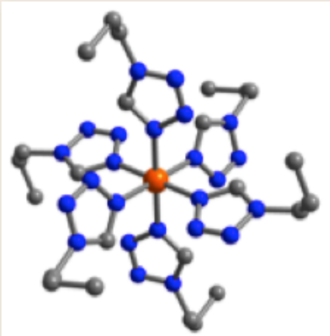


e_g

t_{2g}

χT = 3.9 cm^3 mol^{-1} K
with g = 2.3

$[Fe(ptz)_6]^{2+}$



Orange, Fe; gray, C; blue, N

L = 1-propyl-tetrazole

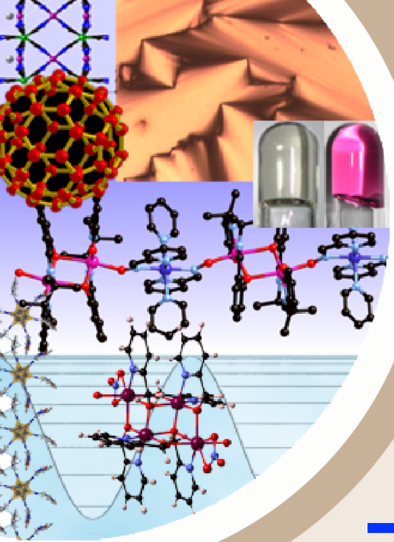
Low Temperature : Low Spin configuration $S = 0$

e_g

t_{2g}

χT = 0 cm^3 mol^{-1} K

S. Decurtins, P. Gütlich, K. M. Hasselbach, A. Hauser, H. Spiering, *Inorg. Chem.* 1985, *24*, 2174; A. Hauser, *Chem. Phys. Lett.* 1986, *124*, 543.

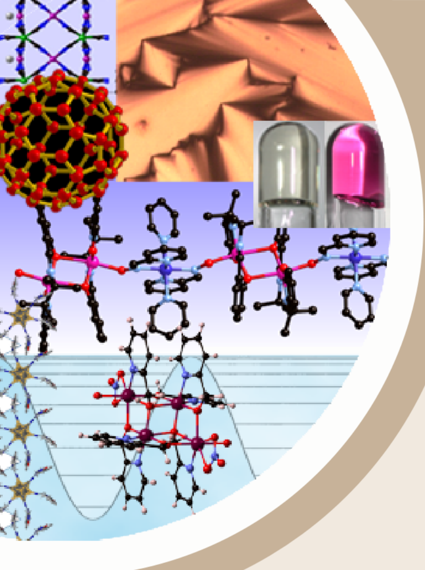


1) The Spin Crossover Phenomenon

The spectrochemical series

Δ →

$Fe^{II}O_6$	$Fe^{II}N_6$	$Fe^{II}C_6$
Weak crystal field		**Strong crystal field**
$[Fe^{II}(H_2O)_6]^{2+}$	$[Fe(ptz)_6]^{2+}$	$[Fe^{II}(CN)_6]^{4-}$
High spin	**High spin** ↑↓ **Low spin**	**Low spin**

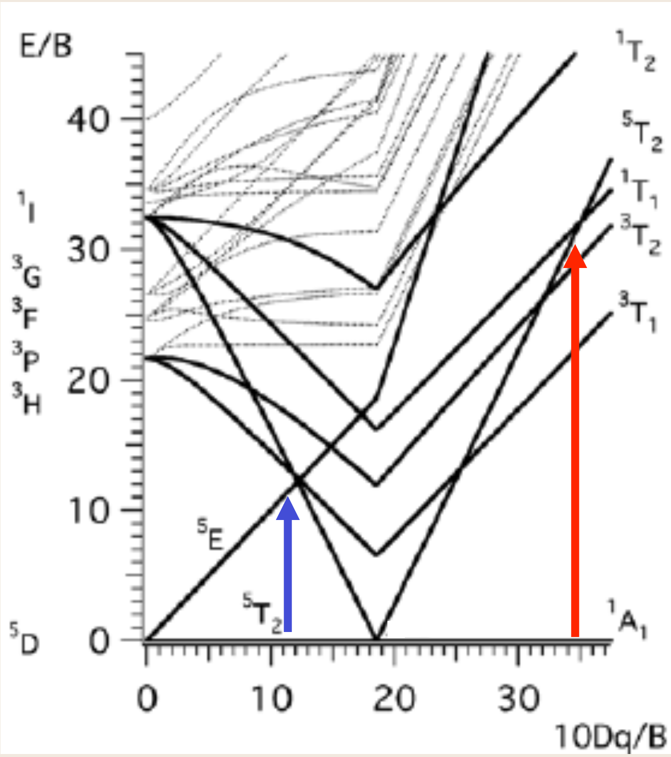


1) The Spin Crossover Phenomenon

Magnetic changes accompanied with optical changes.

A. Hauser, *Top. Curr. Chem.* 2004, *233.*

Ligand field theory



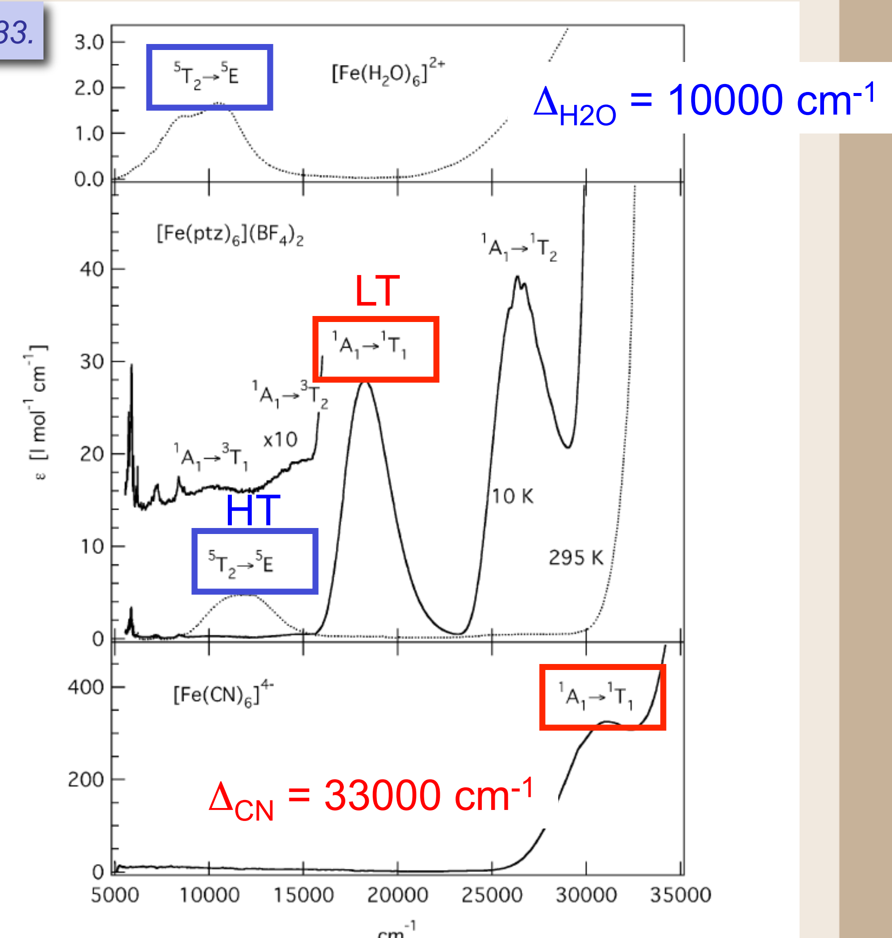
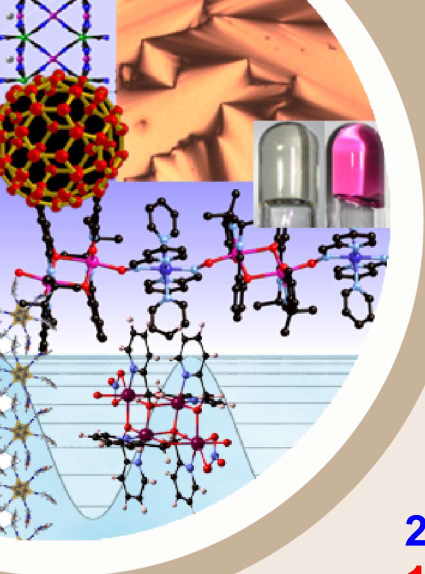
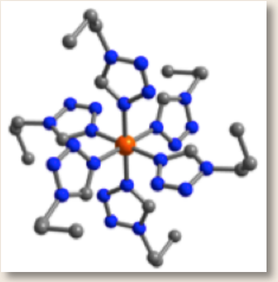


Fig. 3 Absorption spectra of $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ in aqueous solution at 295 K, and single crystal absorption spectra of $[Fe(ptz)_6](BF_4)_2$ at 295 and 10 K



1) The Spin Crossover Phenomenon

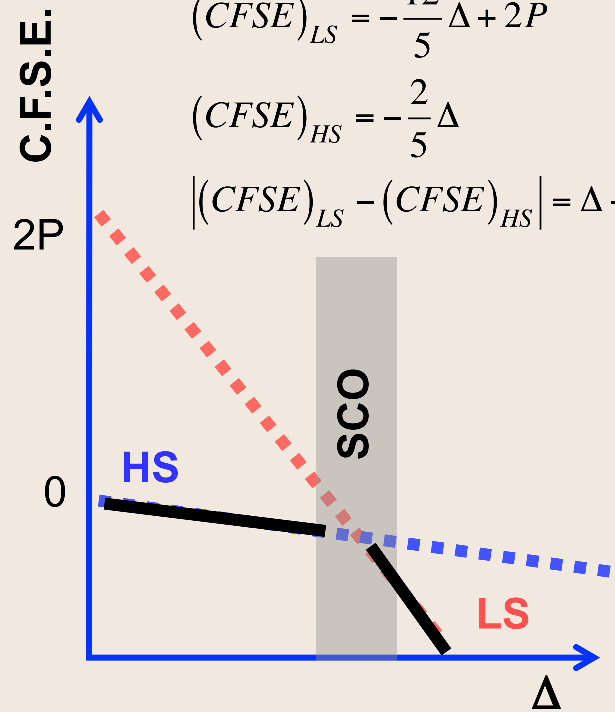


295 K Δ_{HS} = 11800 cm^{-1}
10 K Δ_{LS} = 19410 cm^{-1}
P_{Fe2+} = 17000 cm^{-1}

$$(CFSE)_{LS} = -\frac{12}{5}\Delta + 2P$$

$$(CFSE)_{HS} = -\frac{2}{5}\Delta$$

$$\left|(CFSE)_{LS} - (CFSE)_{HS}\right| = \Delta - P$$



Configuration $t_{2g}^{a}e_{g}^{b}$, P : extra pairing energy

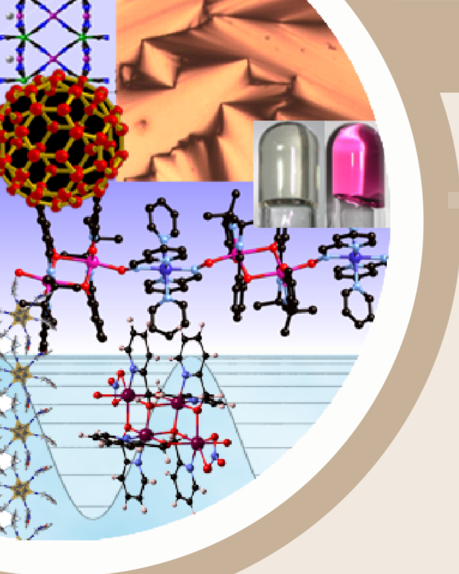
$$(CFSE)_{LS} = a(-\frac{2}{5}\Delta) + b(\frac{3}{5}\Delta) + pP$$

Crystal Field Stabilisation Energy

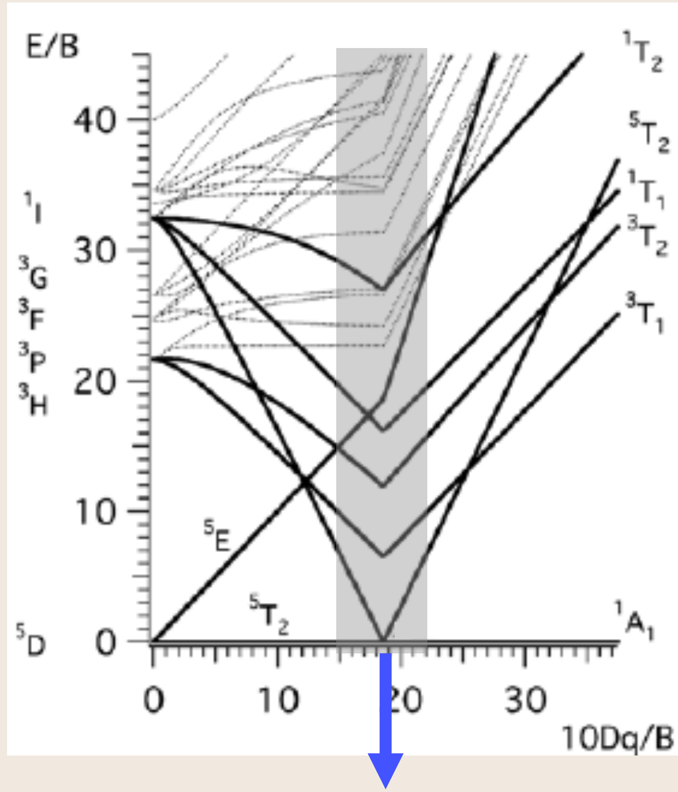
Crystal Field theory

Δ << P	HS
Δ >> P	LS
Δ_{HS} < P < Δ_{LS}	LS ↔ HS

A. Hauser, *Top. Curr. Chem.* 2004, *233.*



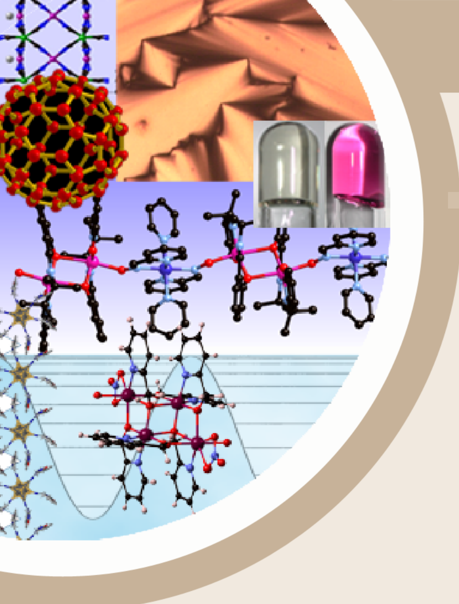
1) The Spin Crossover Phenomenon



10Dq/B ~ 19 or Δ/P ~ (because Δ = 10 Dq then **P ~ 19 B)**

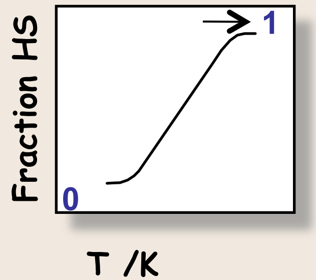
In principle, SCO for d^4, d^5, d^6, d^7 configurations.
Experimentally, rarely observed for d^4 (Mn(III), Cr(II)), d^5 (Mn(II)).
Several examples for d^7 Co(II) and d^5 Fe(III).
Numerous examples for d^6 Fe(II).

Garcia, Y. Top. Curr. Chem. 2004 234.

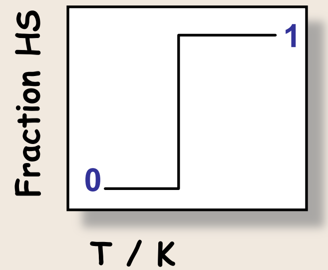


1) The Spin Crossover Phenomenon

Different types of Spin Crossover

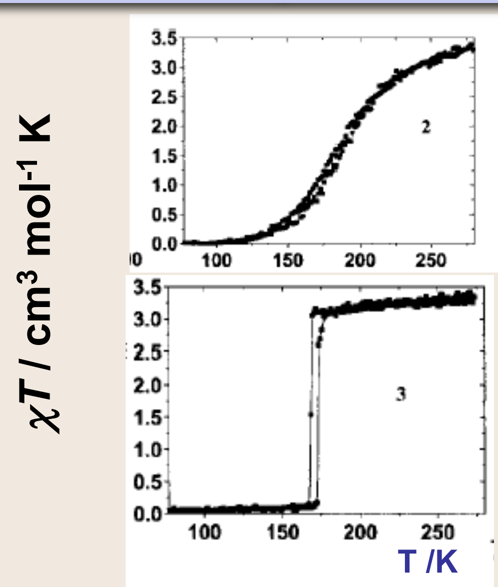


Conversion



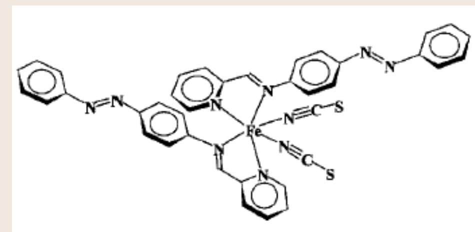
Transition

Létard J.-F. et al. *Inorg. Chem.* 1998, *37,* 4432.



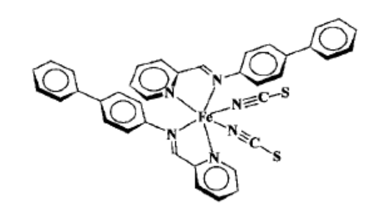
Conversion

Transition
(with Hysteresis)



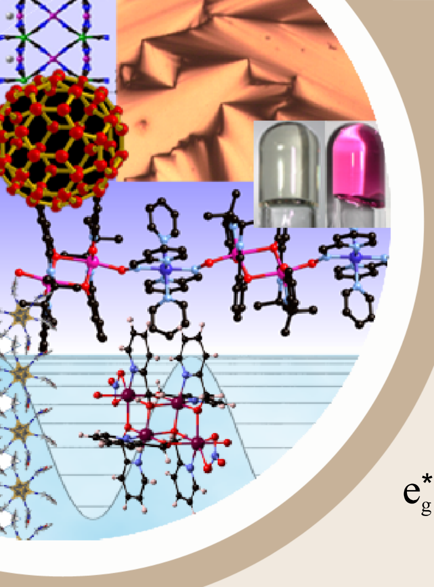
$Fe(PM-AzA)_2(NCS)_2$ 2

$Fe(PM-L)_2(NCS)_2$



$Fe(PM-BiA)_2(NCS)_2$ 3

PM = N-2′-pyridylmethylene and L = aromatic ligand

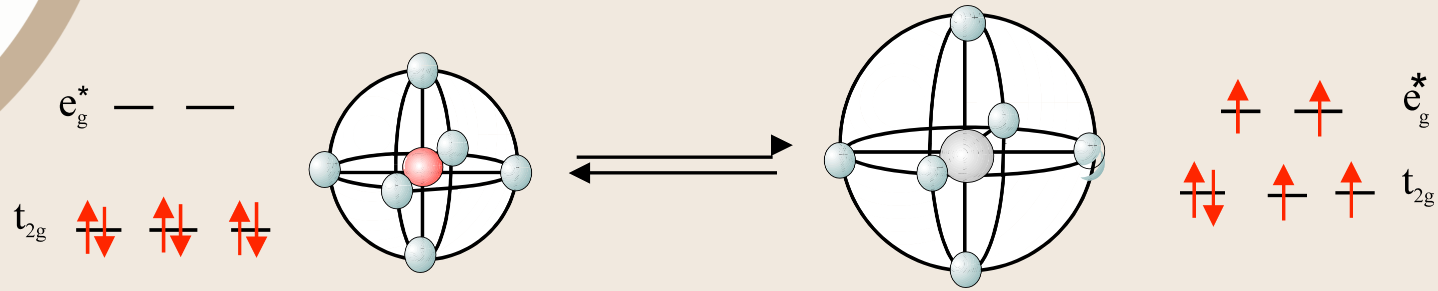


1) The Spin Crossover Phenomenon

Low-Spin
$S = 0$

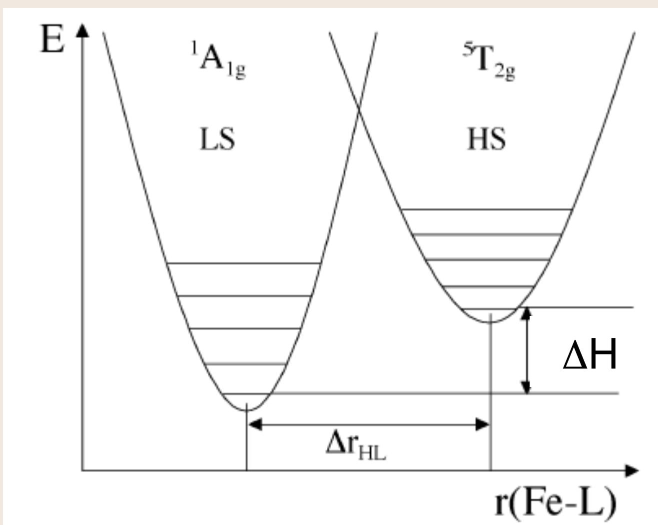
High-Spin
$S = 2$

d^6 Fe(II)



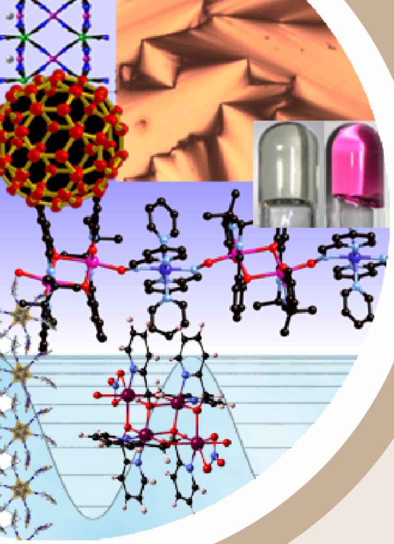
r(Fe-N) ~ 2 Å

r(Fe-N) ~ 2.2 Å

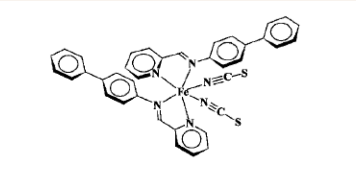


Spin crossover when
ΔH : 0 - 2000 cm^{-1} or 0 - 25 kJ/mol

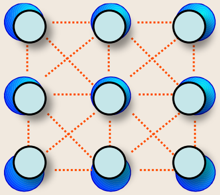
Top. Curr. Chem. 2004, Vol. *233, 234, 235.*

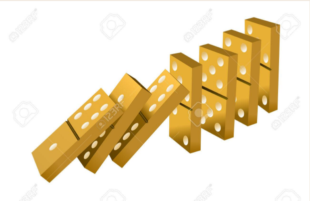


1a) Spin Crossover *vs.* Spin Transition



$Fe(PM\text{-}BiA)_2(NCS)_2$ 3

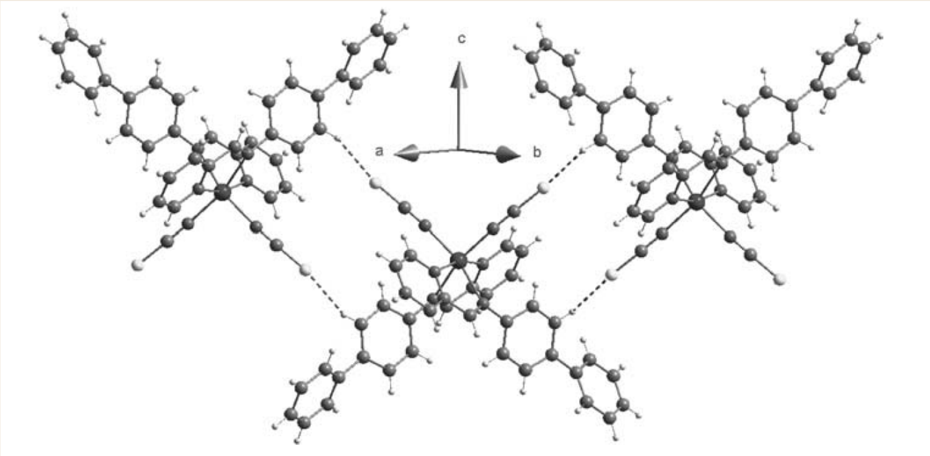




Transition when interactions exist

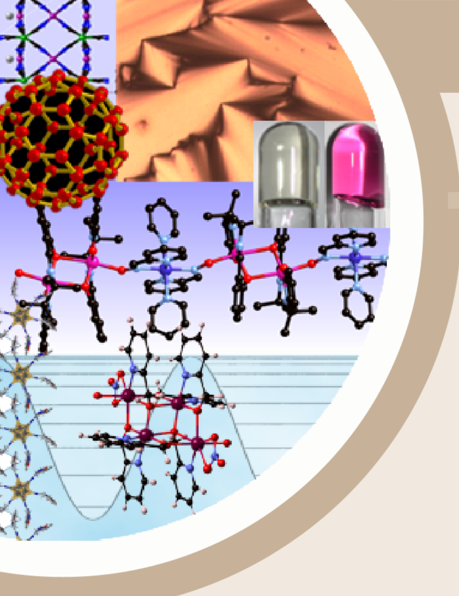
Shortest intermolecular contacts :

S…H**C** : 3.41 Å



(Compared to 3.5 Å for the spin crossover compound)

Guionneau P. et al. *Top. Curr. Chem.* 2004 *234.*



1a) Spin Crossover *vs.* Spin Transition

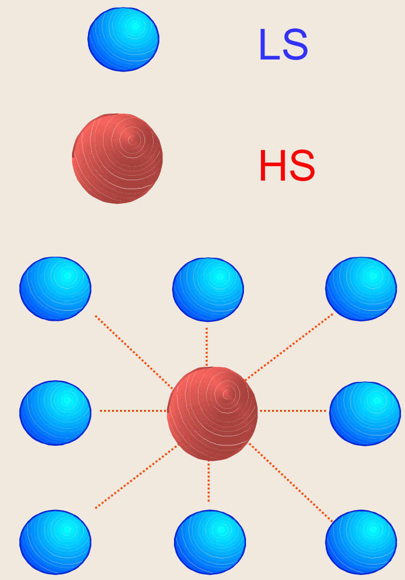
case of *N* molecules : **LS** $\rightleftarrows$ **HS**

$$x_{LS} = 1 - x \qquad x_{HS} = x$$

$$G = x\, G_{HS} + (1-x) G_{LS} - T S_{mix} + \Gamma$$

$$S_{mix} = -R\left[x \ln x + (1-x)\ln(1-x) \right]$$

$\Gamma = W\ x\,(1-x)$ interaction parameter



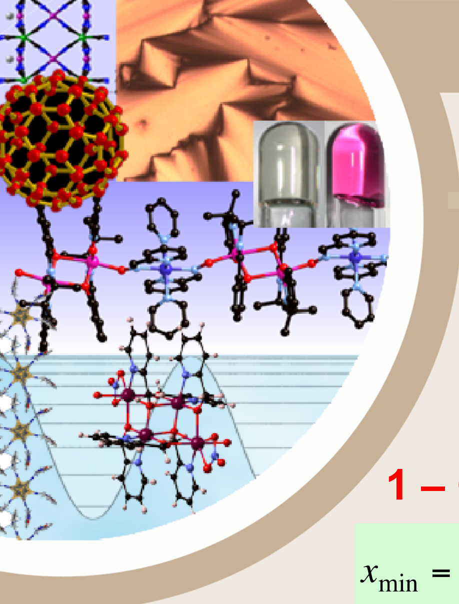
Molecular origin of the interaction parameter :
elastic interactions through weak bonds

$$G = xG_{HS} - (1-x)G_{LS} - RT\left[x \ln x + (1-x)\ln(1-x) \right] + Wx(1-x)$$

$$\frac{\partial G}{\partial x} = G_{HS} - G_{LS} - RT \ln \frac{1-x}{x} + W(1-2x)\ ;\ \text{at equilibrium}\ \frac{\partial G}{\partial x} = 0$$

$$\Rightarrow T = \frac{\Delta H + W(1-2x_{\min})}{R \ln \dfrac{1-x_{\min}}{x_{\min}} + \Delta S} \quad \Rightarrow x_{\min}\ vs.\ T \text{ curves}$$

Atkins P. W. Physical chemistry. 1994 221.
Slichter C. P. J. Chem. Phys. 1972 *56* 2142.



1a) Spin Crossover *vs.* Spin Transition

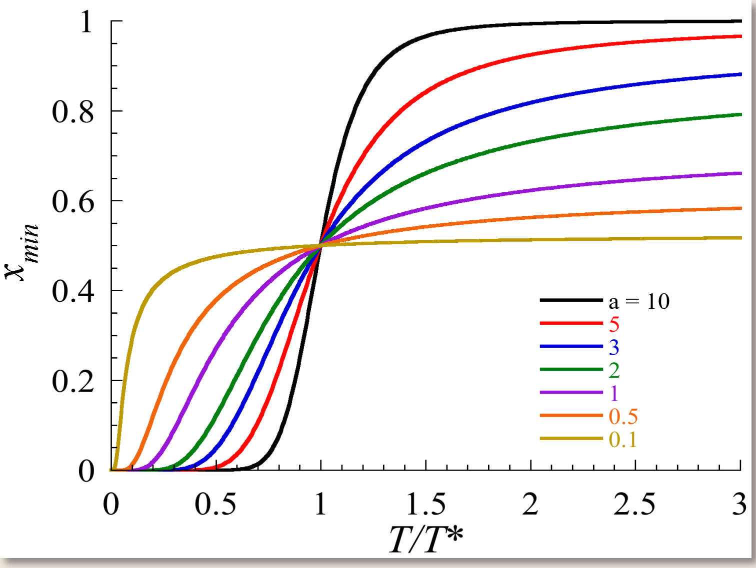
with $T^* = \frac{\Delta H}{\Delta S}$

$$\frac{T}{T^*} = \frac{\frac{\Delta S}{R} + \frac{W}{RT^*}(1-2x_{\min})}{\ln\frac{1-x_{\min}}{x_{\min}} + \frac{\Delta S}{R}} \Rightarrow x_{\min}\ vs.\ T \text{ curves}$$

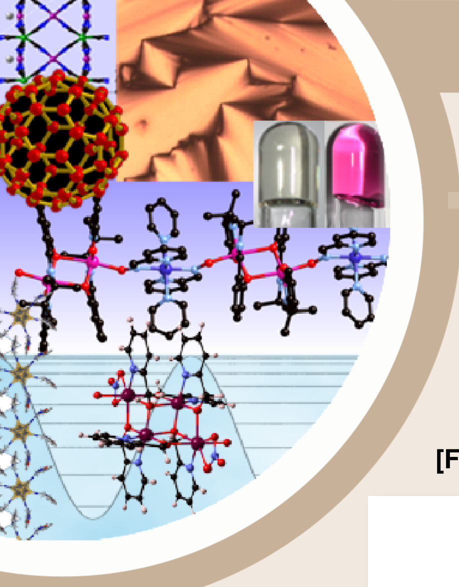
1 – Case *W* = 0 (no interaction) :

$$x_{\min} = \frac{1}{1+\exp\frac{\Delta S}{R}(\frac{T^*}{T}-1)} = \frac{1}{1+\exp a(\frac{T^*}{T}-1)} \quad \text{with} \quad a=\frac{\Delta S}{R} = \ln g$$

- **When T = T* x_{min} = 0.5**
  50 % HS and 50 % LS, T* = $T_{1/2}$
- **One particular case : a = 3**
  (d^6 a = ln 15 = 2.7 only electronic entropy)
  When T = 3T* (≈ HT), x_{min} = 0.85
  HT: 85 % HS and 15 % LS
- **Experimentally, for Fe^{II} SCO compounds,**
  a is comprised between 4 and 10.*
  HT: > 90 % HS and < 10 % LS



* R. Boca, Theoretical foundations of molecular magnetism, in Current Methods in Inorganic Chemistry, Elsevier, Vol 1, 1999



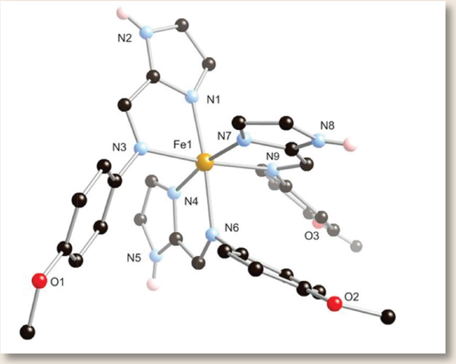
1a) Spin Crossover *vs.* Spin Transition

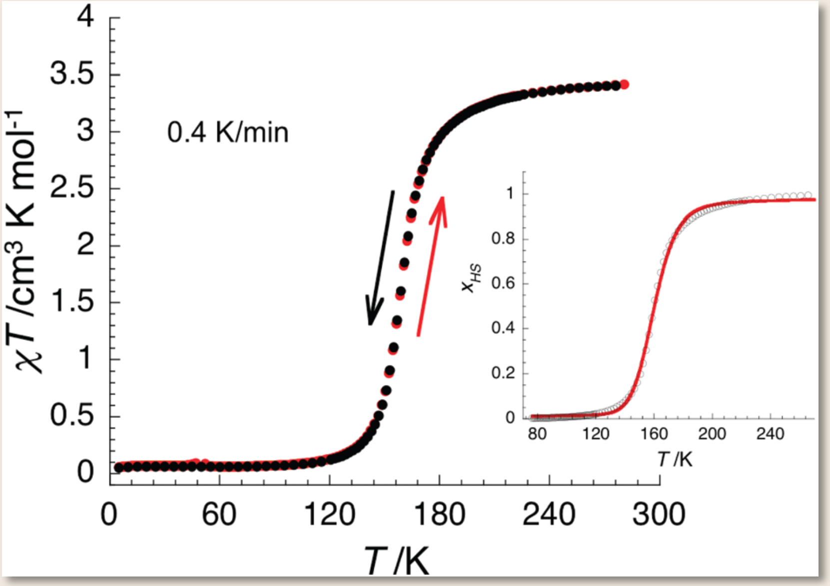
1 – Case *W* = 0 (no interaction) :

Application : **Experiment: $x_{HS} = \chi T/\chi T_{HS}$**

$$\text{Theory}: x_{HS} = \frac{1}{1+\exp\frac{\Delta S}{R}\left(\frac{T^*}{T}-1\right)} \quad \text{with} \quad T^* = \frac{\Delta H}{\Delta S}$$

$[FeL_3](ClO_4)_2$





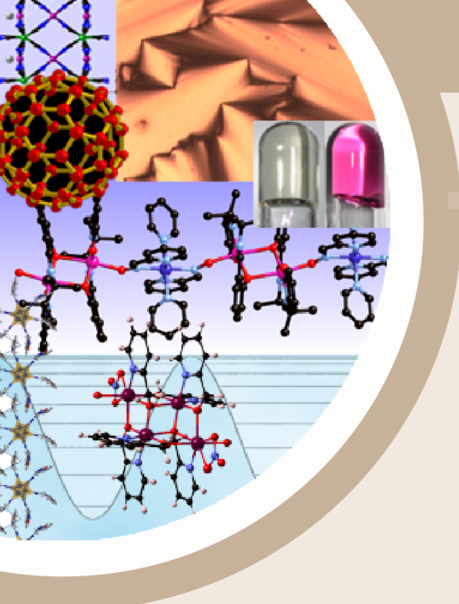
Fit : ΔS = 155 JK^{-1} mol^{-1} T* = 159 K
ΔH = 24.7 kJ mol^{-1}

Comments ΔS > 22.5 JK^{-1} mol^{-1} = ΔS_{elect}

then vibrational contributions in ΔS (intra and inter)

Thomson, J. R., Krueger P., Mathonière C., Clérac R. et al. W. Dalton Trans. 2012, *41* 12720.

L = N-4-methoxyphenyl-(1H-imidazol-2-yl)-methanimine



1a) Spin Crossover *vs.* Spin Transition

2- Case $W \neq 0$ (with interaction) :

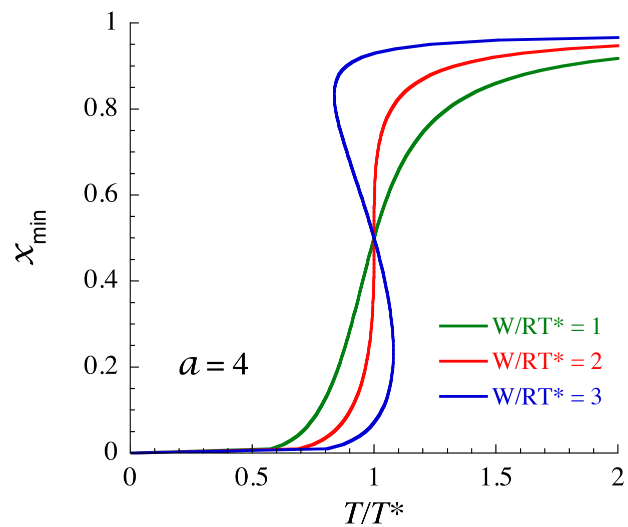
$$\frac{T}{T^*} = \frac{\dfrac{\Delta S}{R} + \dfrac{W}{RT^*}(1 - 2x_{\min})}{\ln\dfrac{1 - x_{\min}}{x_{\min}} + \dfrac{\Delta S}{R}} \Rightarrow x_{\min}\ vs.\ T \text{ curves}$$

with $T^* = \dfrac{\Delta H}{\Delta S}$

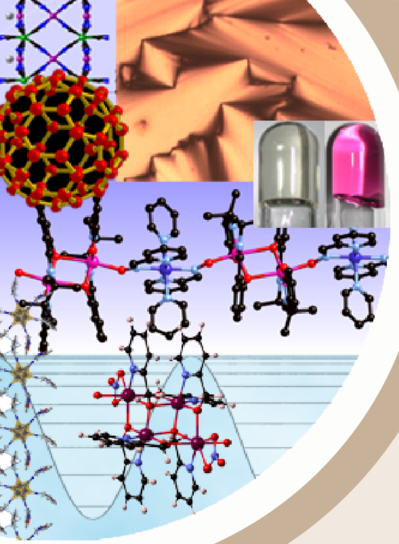
No analytical expression for x_{min} .

$T/T^* = f(x_{min})$ then $x_{min} = f^{-1}(T/T^*)$ for each a

Fixing a at 4 (Fe(II) complexes slide 13)



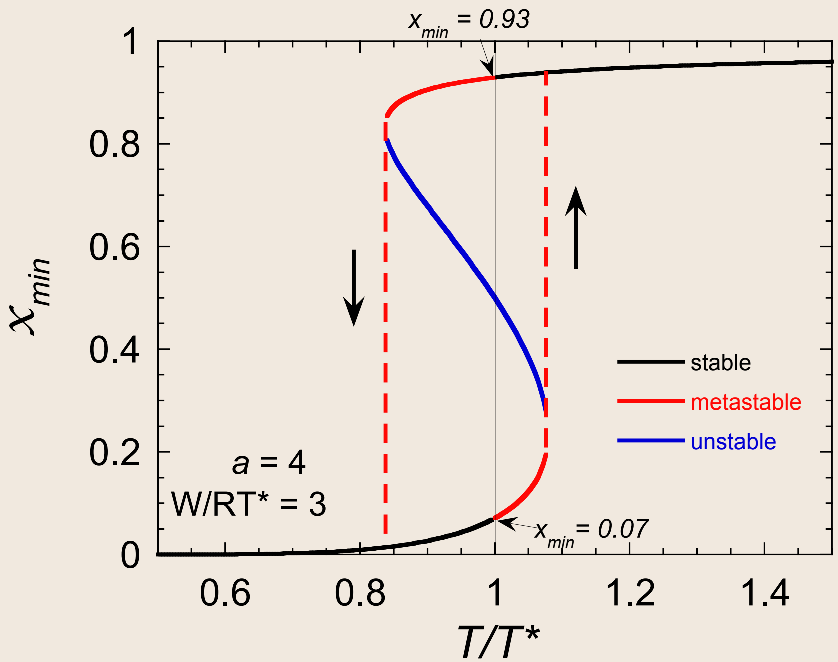
When $W < 2RT^*$, crossover
When $W = 2RT^*$, inflexion point
When $W \geq 2RT^*$, *S*-shape curve



1a) Spin Crossover *vs.* Spin Transition

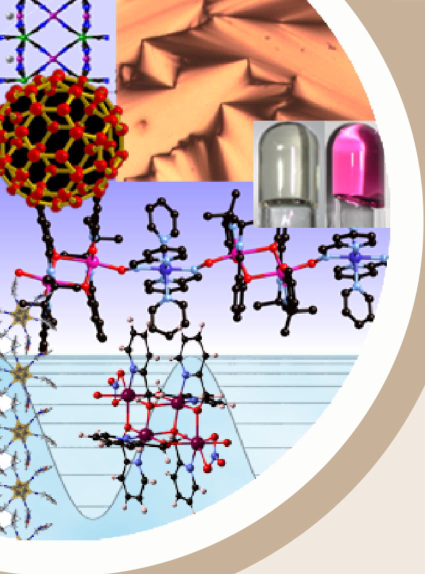
2- Case *W* ≠ 0 (with interaction) :

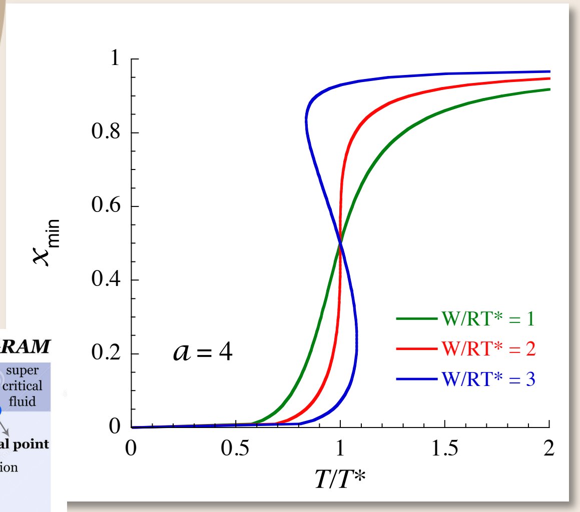
When W ≥ 2RT*, *S*-shape curve
1st order transition with eventually hysteresis

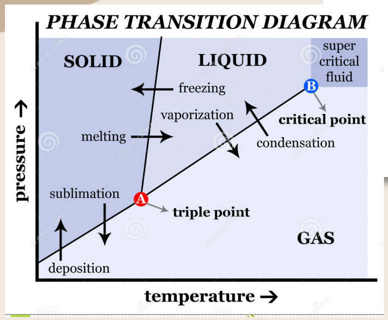


The theory gives the maximum width of the hysteresis.
The experimental hysteresis is sweeping rate dependent.

1a) Spin Conversion *vs.* Spin Transition

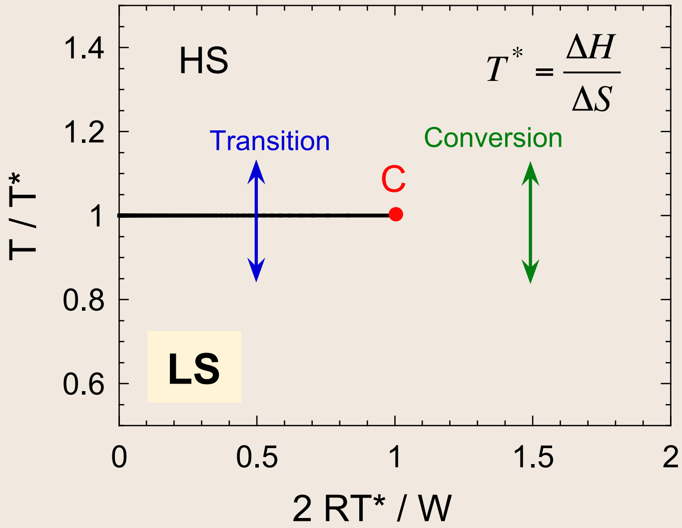






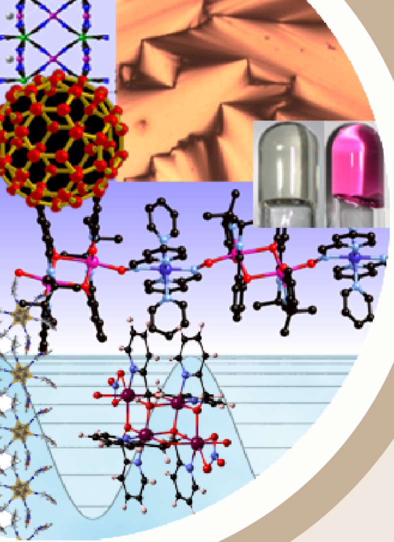
Phase diagram in (T,W) plane

Critical point $W_C = 2\ RT_C$



Spin Conversion (W < 2RT*) : The two spin states are in thermal equilibrium
Isolated molecule behaviour (solution, diluted compound)

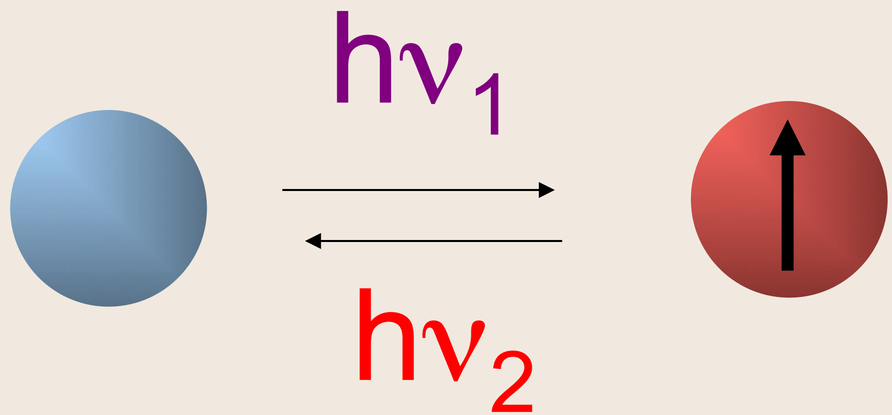
Spin Transition (*W* >= 2RT*) : The two states are coexisting near T* that is a critical temperature
Collective property due to intermolecular interactions
Analogy with the liquid-gas transition (P,T diagram).



2) Photomagnetism in coordination compounds

Photomagnetism Definition :
Control of the magnetic state of a material by light

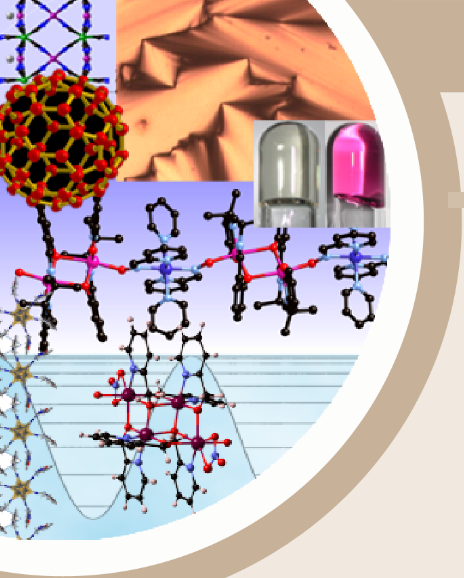
∅< 2±0 nm
monodisperse



Two electronic phenomena :

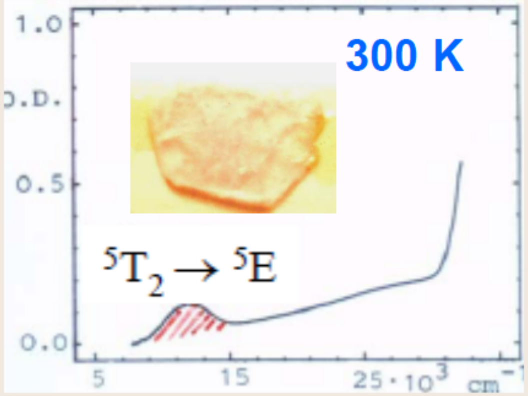
2a - The spin CrossOver phenomena
2b - The photo-induced electron transfer

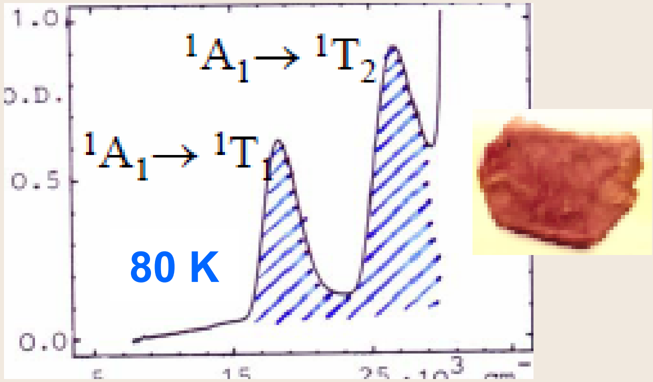
Sato O. Angew. Chem. Int Ed. 2007, *46*, 2152.



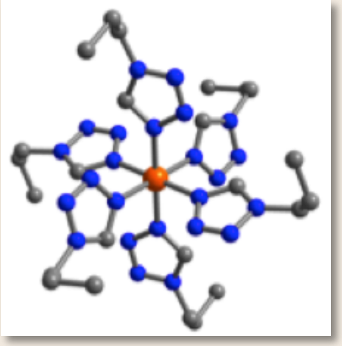
2a) The LIESST effect in SCO Compounds

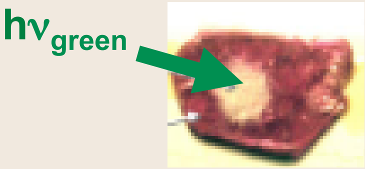
Photo-Induced Spin State Trapping

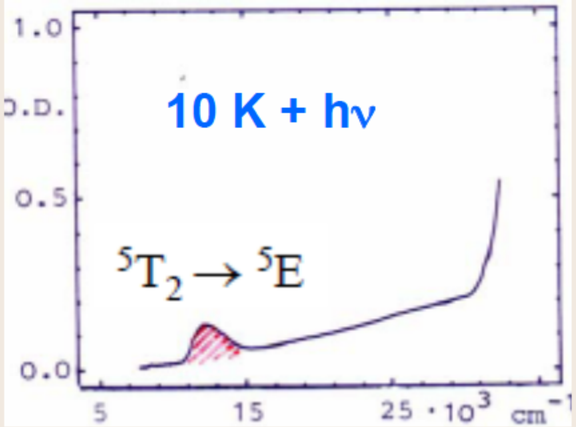




$[Fe(ptz)_6]^{2+}$

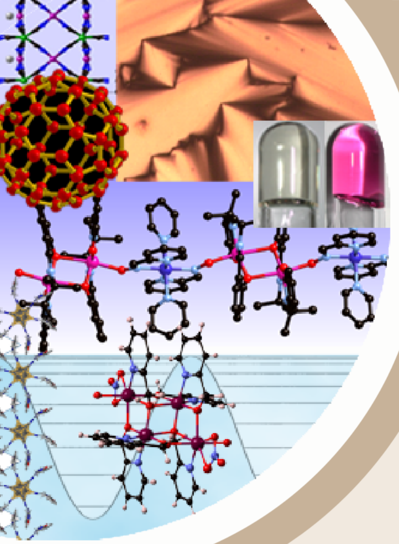






$$\text{LS} \xrightarrow{h\nu} \text{HS}$$

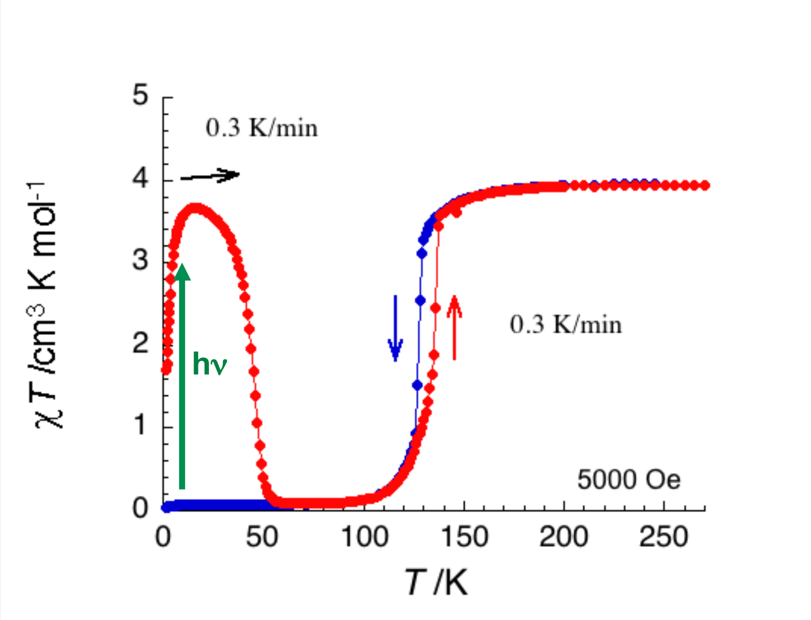
Decurtins S. et al., Chem. Phys. Lett. 1984 *105*, 1. Inorg. Chem. 1985, *24*, 2174.



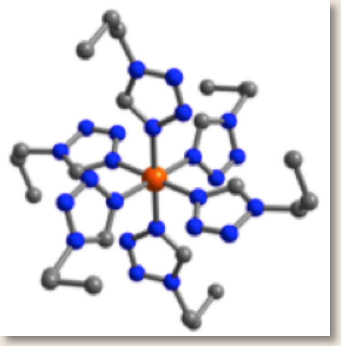
2a) The LIESST effect in SCO Compounds

LIESST : Light Induced Excited Spin State Trapping

Change in magnetic properties induced by light



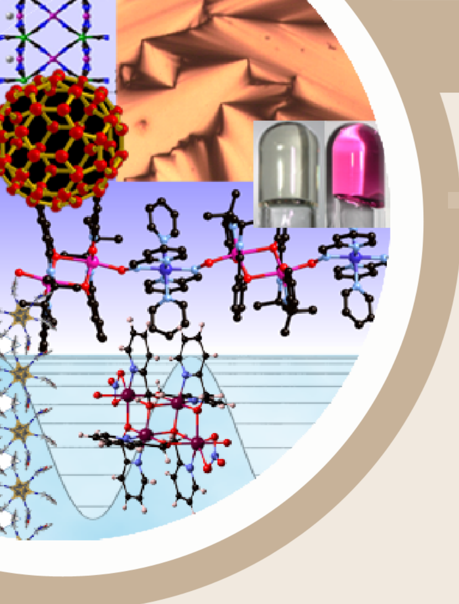
$[Fe(ptz)_6]^{2+}$



LS $\underset{T \searrow}{\overset{h\nu\ ,\ T \nearrow}{\rightleftarrows}}$ HS

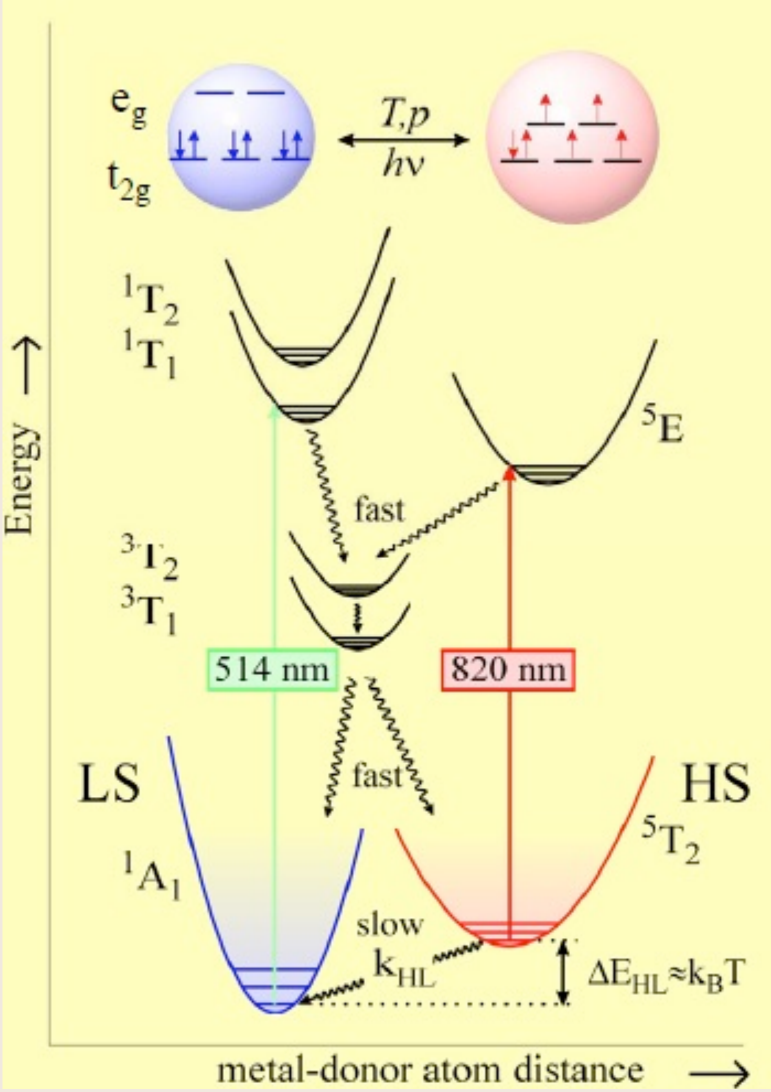
Decurtins S. et al., Chem. Phys. Lett. 1984 *105,* 1.
Gütlich P. Angew. Chem. Int. Ed. 1994, 2024.

2a) The LIESST effect in SCO Compounds

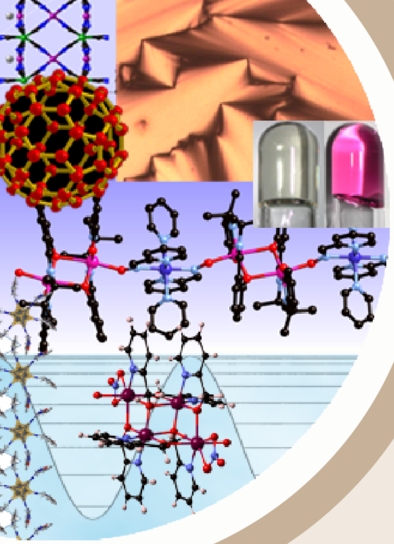


LIESST : 514 nm
Reverse LIESST : 820 nm

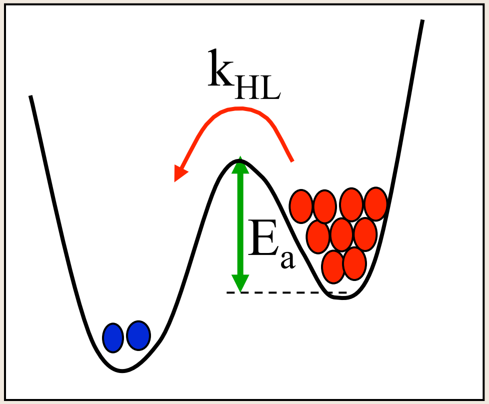
LS $\underset{h\nu_{red}}{\overset{h\nu_{green}}{\rightleftarrows}}$ HS



Gütlich P. Angew. Chem. Int. Ed. 1994, 2024.

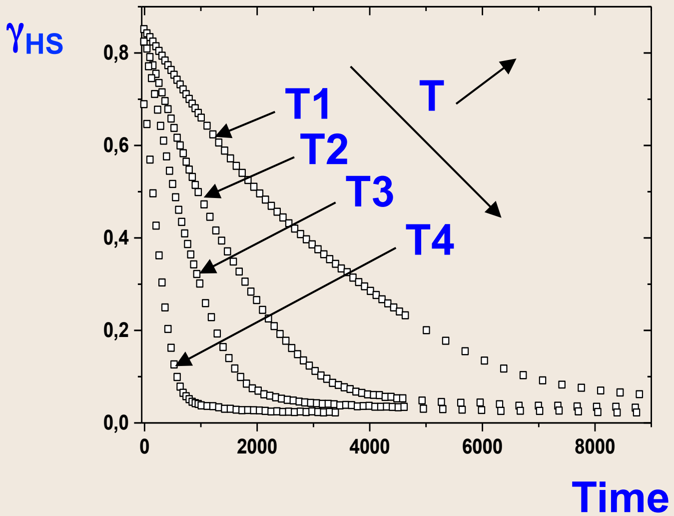


2a) The LIESST effect in SCO Compounds



LS $\xrightarrow{h\nu_{green}}$ HS

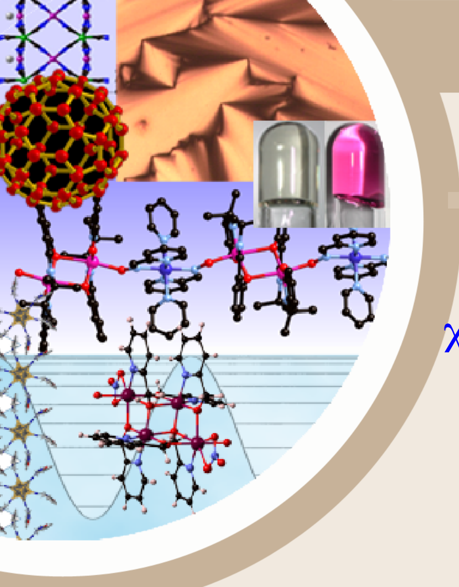
$$\gamma_{HS} = \frac{x_{HS}}{x_{LS} + x_{HS}}$$



HS metastable state

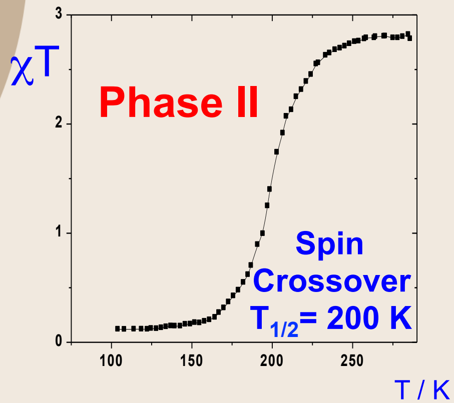
γ_{HS} = f (time) at fixed T

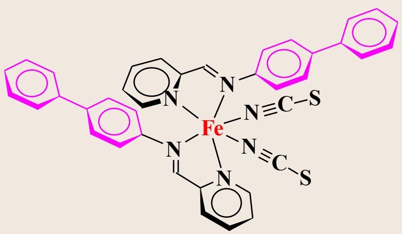
Relaxation thermally activated

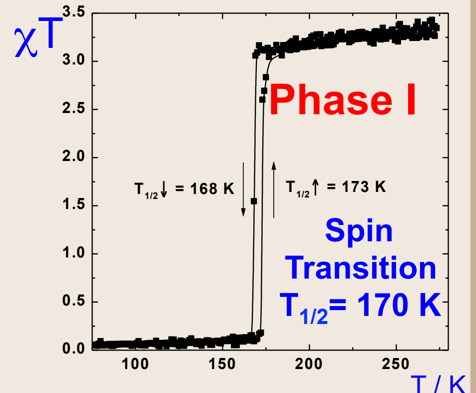


2a) The LIESST effect in SCO Compounds

"Phases I and II of the $[Fe(PM\text{-}Bia)_2(NCX)_2]$"



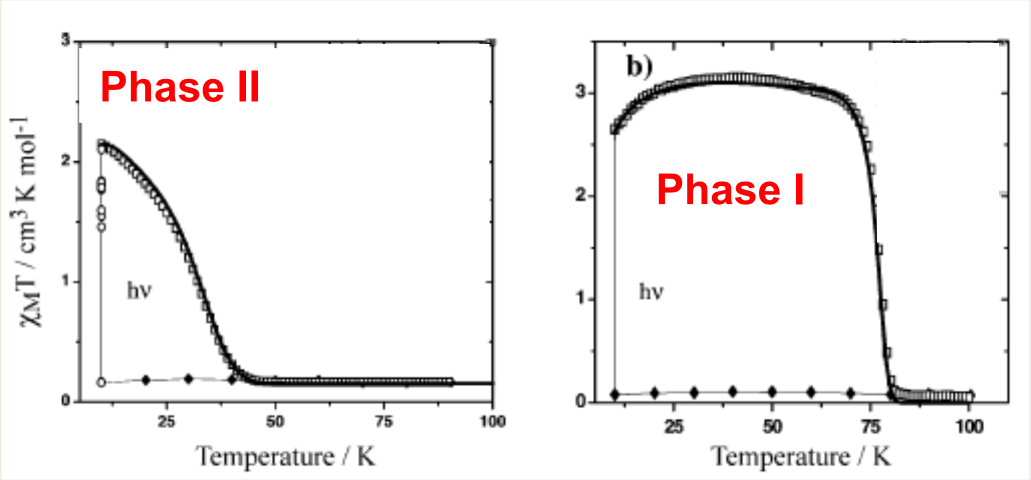




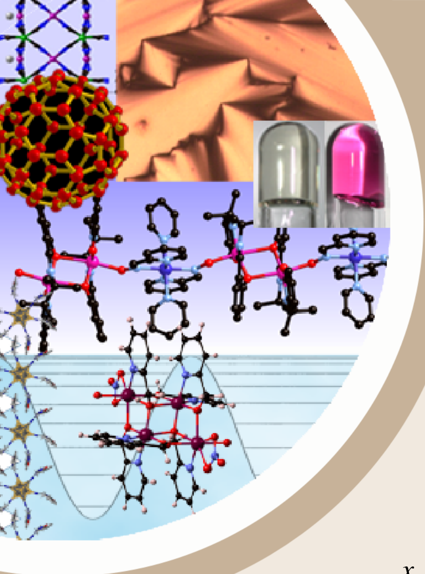
II : X-rays : Pccn, S…HC : 3.54 Å

I : X-rays : $P2_1/c$ S…HC : 3.41 Å (slide 11)

LS $\xrightarrow{h\nu}$ HS

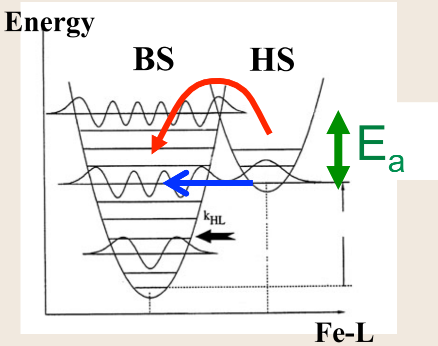


Létard J. F. Monatshefte für Chemie, 2003, *134* 165



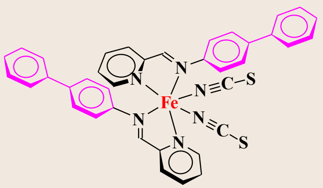
2a) The LIESST effect in SCO Compounds

Létard J. F. Monatshefte für Chemie 2003 , 134 165



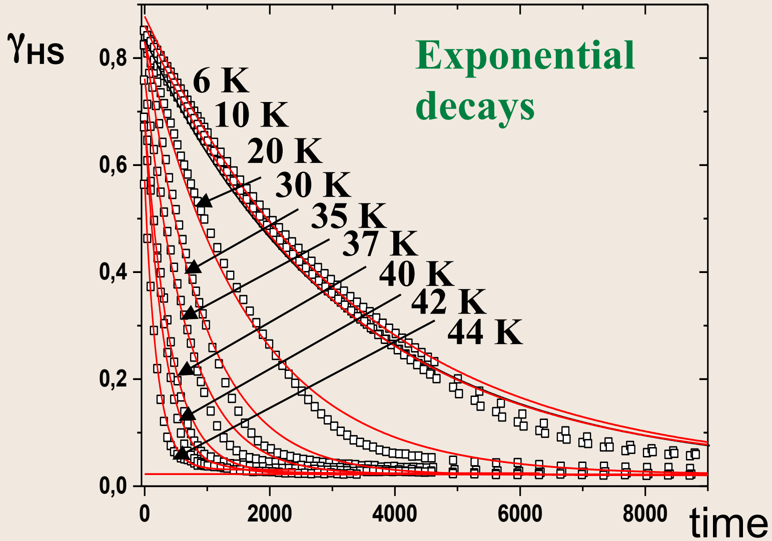
SCO Phase II

$$LS \underset{k_{HL}}{\overset{h\nu}{\rightleftarrows}} HS$$



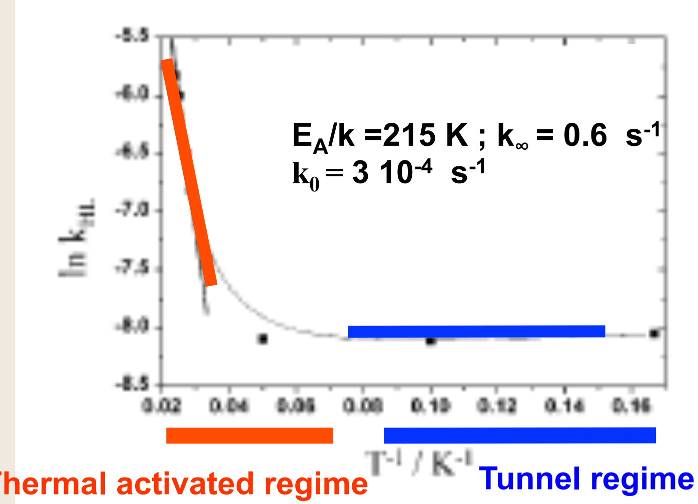
$$\gamma_{HS} = \frac{x_{HS}}{x_{LS} + x_{HS}}$$

$$\gamma_{HS} = \gamma_{HS}^{t=0}(T)\exp(-k_{HL}(T)t)$$



Arrhenius plot ln k_{HL} vs 1/T

$$k_{HL}(T) = k_o + k_\infty.\exp(-\frac{E_a}{kT})$$

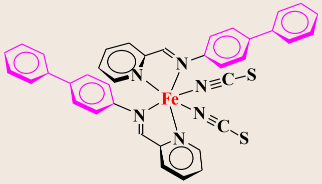


Hauser A. et al., Coord. Chem. Rev., 1990, *97*, 1. Coord. Chem. Rev., 1999, *190-192*, 471.

2a) The LIESST effect in SCO Compounds

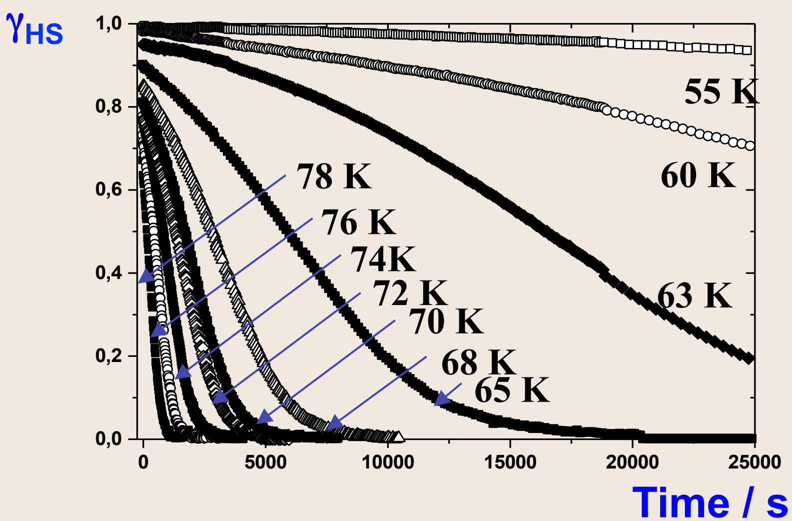
Létard J. F. Monatshefte für Chemie 2003 , 134 165

Spin Transition Phase I
At low T (T < $T_{1/2}$)

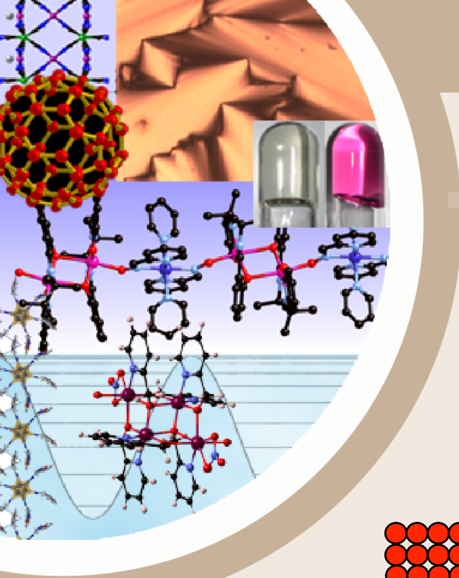


$$LS \underset{k_{HL}}{\overset{h\nu}{\rightleftarrows}} HS$$

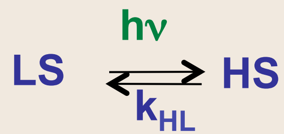
$$\gamma_{HS} = \frac{x_{HS}}{x_{LS} + x_{HS}}$$

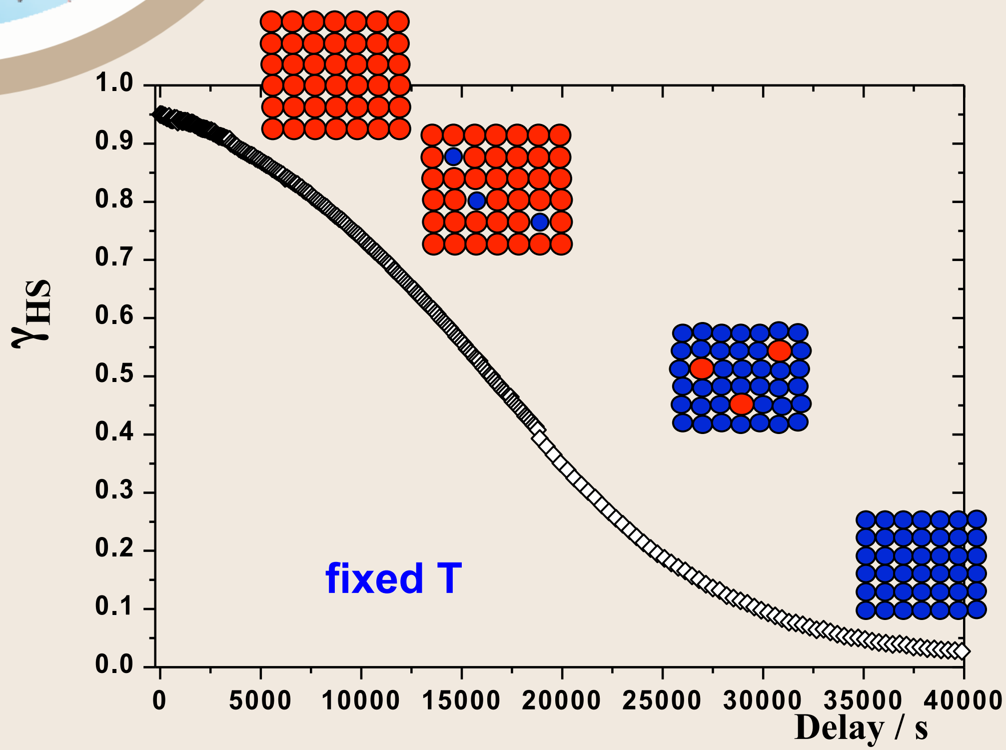


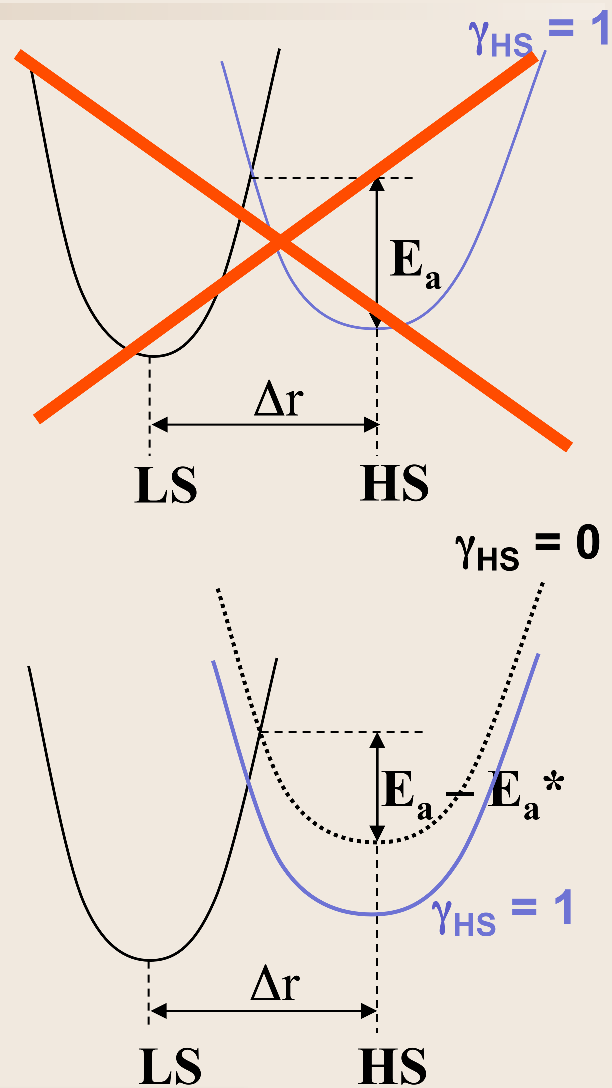
Non-linear effects due to cooperativity
Self-accelerated Decays (Sigmoïdal laws)



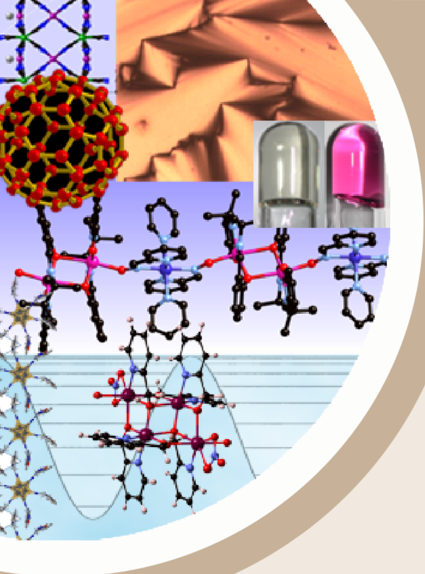
2a) The LIESST effect in SCO Compounds







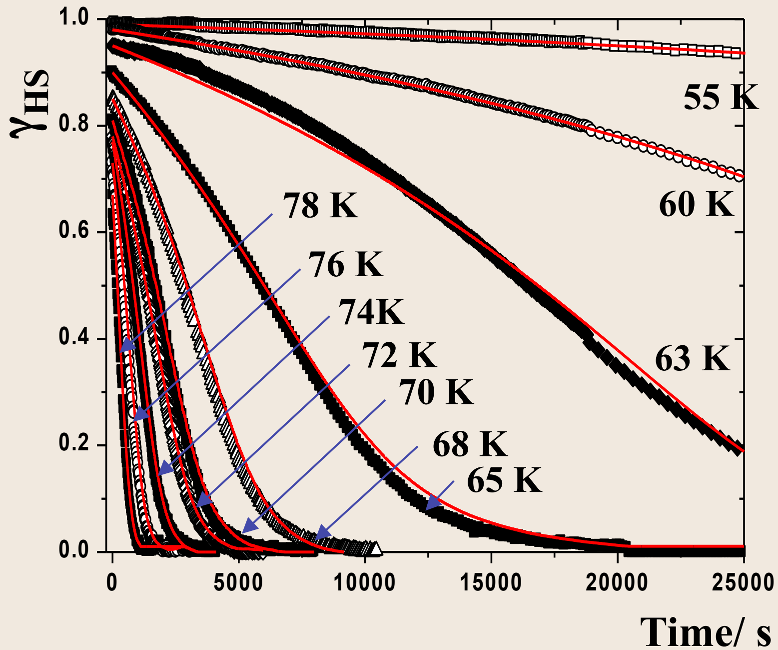
Hauser A. et al., Coord. Chem. Rev., 1990, *97*, 1. Coord. Chem. Rev., 1999, *190-192*, 471.



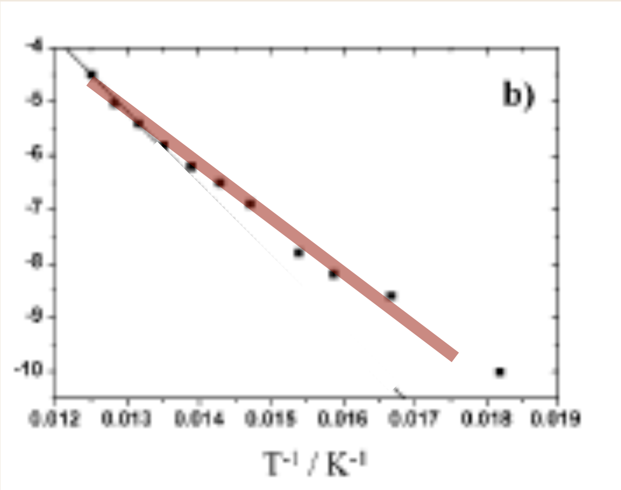
2a) The LIESST effect in SCO Compounds

$$\frac{d\gamma_{HS}}{dt} = -k_{HL}(T,\gamma_{HS})\gamma_{HS}$$

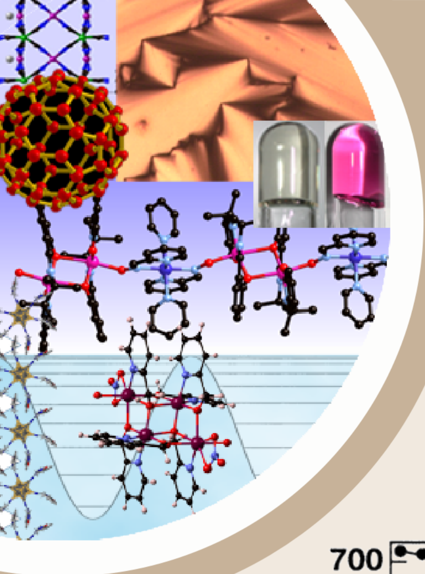
$$k_{HL}(T,\gamma_{HS}) = k_{HL}(T\rightarrow\infty)e^{-\frac{E_a}{k_BT}+\frac{E_a^*}{k_BT}(1-\gamma_{HS})}$$



Arrhenius plot ln k_{HL} vs 1/T



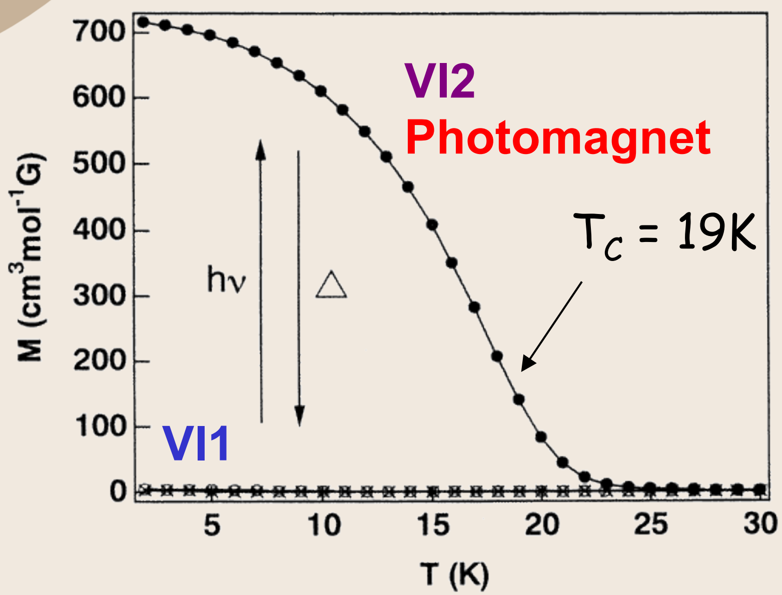
E_A/k =1570 K; E_A^*/k = 171 K, k_∞=2 10^6 s^{-1}

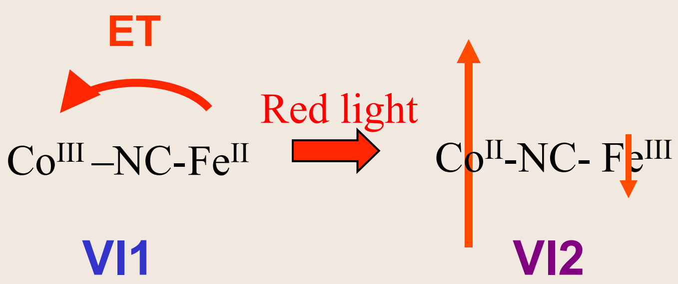


2b) Photomagnetism in Electron Transfer Compounds

Prussian Blue Analogs - 3D Networks

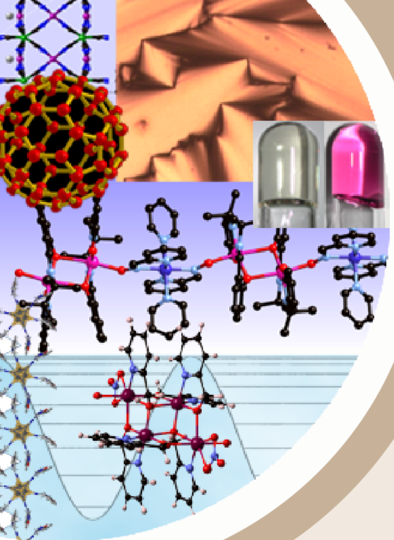
$Rb_{0.54}Co_{1.21}[Fe(CN)_6].17H_2O$





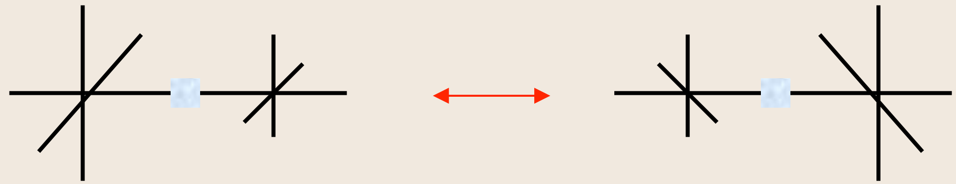
ET Electron Transfer

Sato O et al. *Science* . 1996 *272*, 704. Bleuzen A., et al. J. Am. Chem. Soc. 2000 *122* 6648

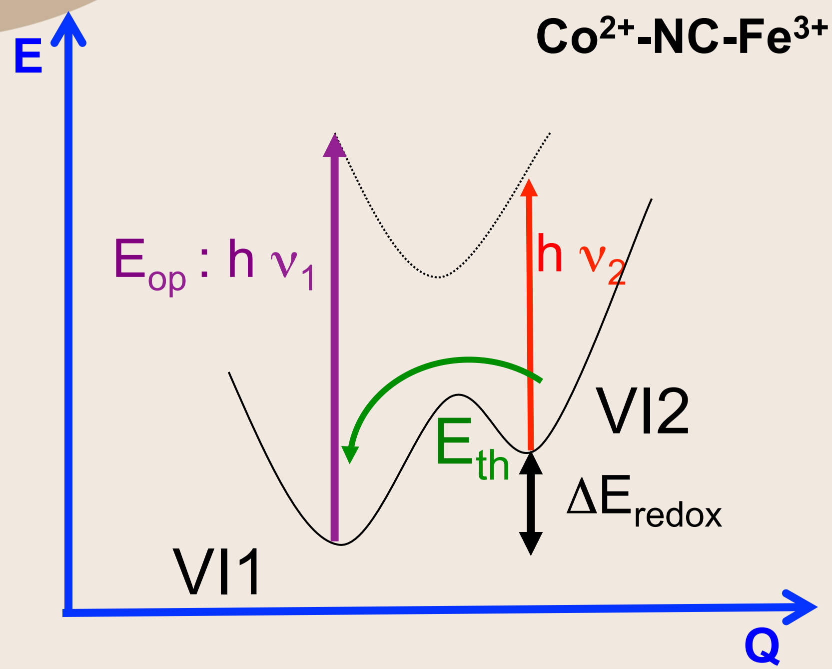


2b) Photomagnetism in Electron Transfer Compounds

The mixed valence compounds : Two valence isomers (VI)
The disymmetrical case



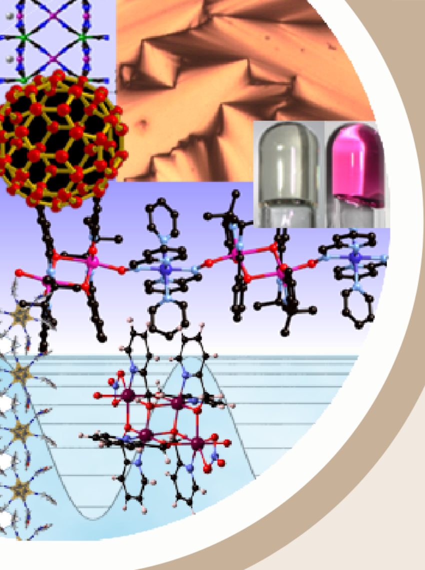
Co^{2+}-NC-Fe^{3+} **Co^{3+} -NC- Fe^{2+}**



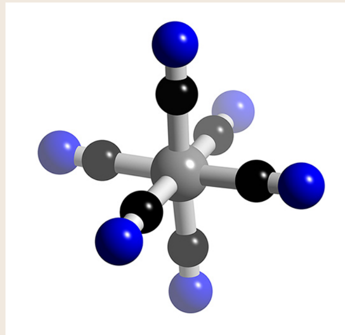
VI1 : stable state
VI2 : metastable state

VI1 $\xrightarrow{h\nu}$ VI2 ?

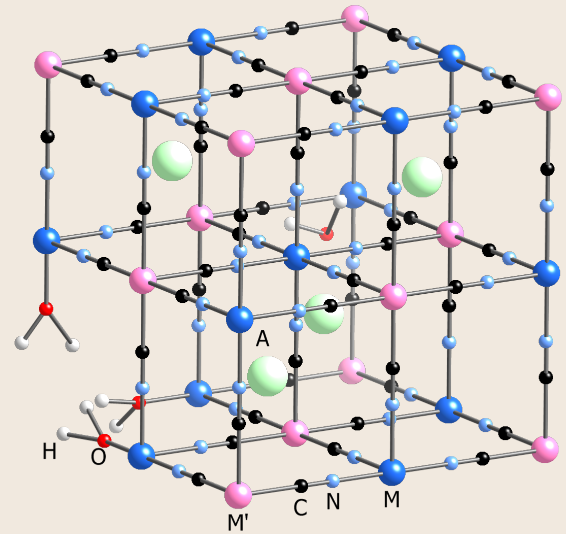
Robin M. Adv. Inorg. Chem. 1967, *10,* 247. Piepho S. B. , JACS, 1978, *100*, 2996.
Kahn O. Molecular Magnetism 1993 VCH.



2b) Photomagnetism in Electron Transfer Compounds



A^{2+} → H_2O $A_k[B(CN)_6]_l \cdot nH_2O$



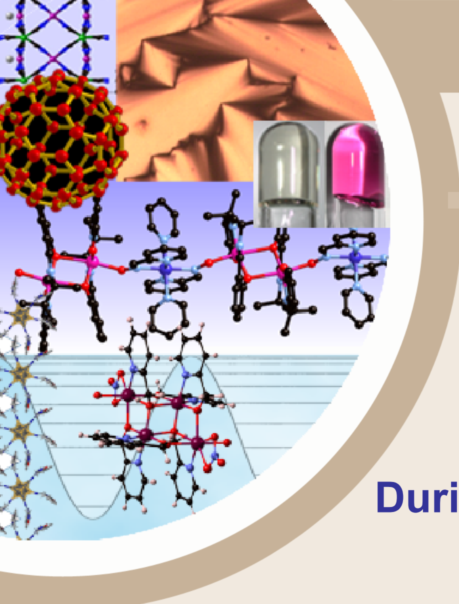
- k = l CFC A : high spin B : low spin
- k > l vacancies of $B(CN)_6$ filled with H_2O
- Phases with alcalii in T_d (A_4 or B_4)

Prussian Blue (PB) is $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$ Magnet F with $T_c = 4.5$ K

Other Prussian Blue analogs:

$Ni^{II}_3[Cr^{III}(CN)_6]_2 \cdot 15H_2O$ Magnet F with $T_c = 53$ K
$CsNi^{II}[Cr^{III}(CN)_6] \cdot 2H_2O$ Magnet F with $T_c = 90$ K
$Mn^{II}_3[Cr^{III}(CN)_6]_2 \cdot 15H_2O$ Magnet F with $T_c = 66$ K
$Ni^{II}_3[Fe^{III}(CN)_6]_2 \cdot 14H_2O$ Magnet F with $T_c = 23$ K
$Co^{II}_3[Fe^{III}(CN)_6]_2 \cdot 14H_2O$ Magnet FI with $T_c = 14$ K

Verdaguer , M. and Girolami
Molecules to materials 2004 VCH



2b) Photomagnetism in Electron Transfer Compounds

Photomagnetic Prussian Blue Analogs - FeCo Networks

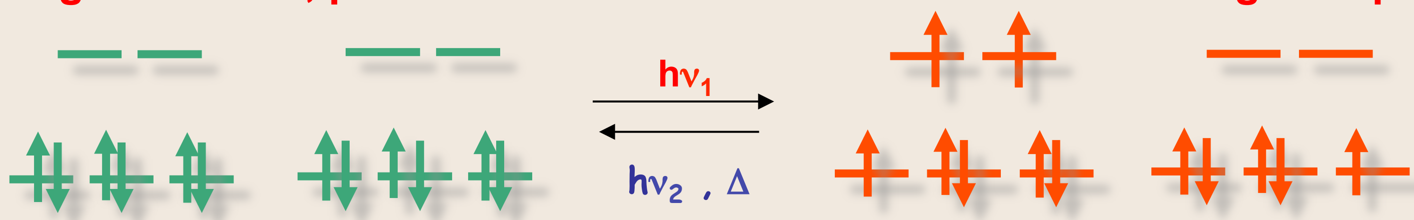
$K_3[Fe^{III}(CN)_6] + Co^{II}Cl_2.xH_2O \xrightarrow{RbNO_3} Rb_{0.54}Co_{1.21}[Fe(CN)_6].17H_2O$

During the synthesis, redox reactions

Initial State **:**

80 % diamagnetic pairs Co^{III}-NC-Fe^{II}
+ some magnetic pairs Co^{II}-NC-Fe^{III}
+ 17 % Fe vacancies

During irradiation, photo-induced electron transfer in the diamagnetic pair

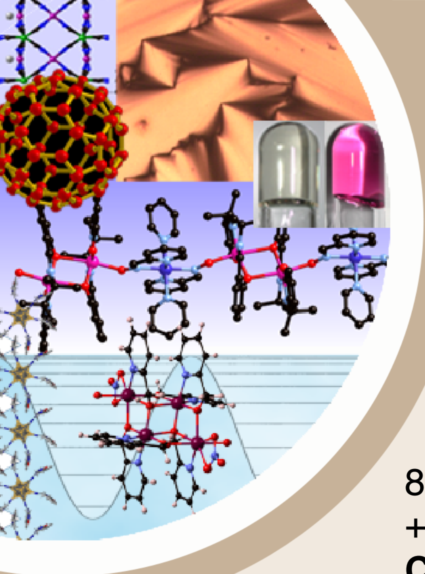


Co^{III} S=0 Strong crystal field	Fe^{II} S=0	Co^{II} S=3/2 Weak crystal field	Fe^{III} S=1/2

CoN_5O
d_{Co-N} = 1.89 Å

CoN_5O
d_{Co-N} = 2.08 Å

Sato O, Hashimoto K. et al. *Science* . 1996 272, 704. Ohkoshi S.-I., Hashimoto K. et al Inorg. Chem. 2002 41 678. Bleuzen A., Verdaguer M. et al. *J. Am. Chem. Soc.* 2000 122 6648; *J. Am. Chem. Soc.* 2000 122 6653. Yamauchi T., Morimoto Y., Ohkoshi S, Phys. Rev. B 2005 72 214425.

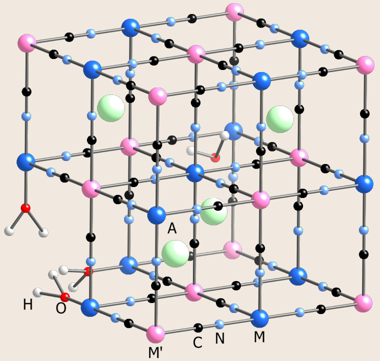


2b) Photomagnetism in Electron Transfer Compounds

Conditions to observe the photomagnetism in FeCo PBA

→ $Rb_{0.54}Co_{1.21}[Fe(CN)_6].17H_2O$ PHOTOMAGNET

80 % diamagnetic pairs Co^{III}-NC-Fe^{II} + paramagnetic pairs Co^{II}-NC-Fe^{III}
+ 17 % vacancies Fe
Co^{III} ion in a mean environment $Co(NC)_5(H_2O)$



→ $CsCo[Fe(CN)_6].3.3H_2O$ NO EFFECT

100 % diamagnetic pairs Co^{III}-NC-Fe^{II}
No vacancies

→ $K_{0.04}Co_{1.48}[Fe(CN)_6].6.8H_2O$ NO EFFECT

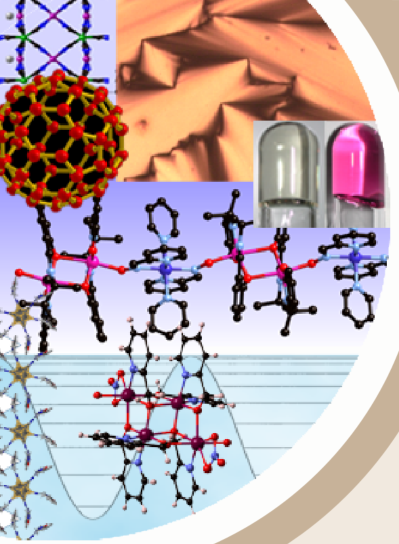
67 % paramagnetic pairs Co^{II}-NC-Fe^{III} + 33 % vacancies Fe
Co^{II} ion in a mean environment $Co(NC)_4(H_2O)_2$

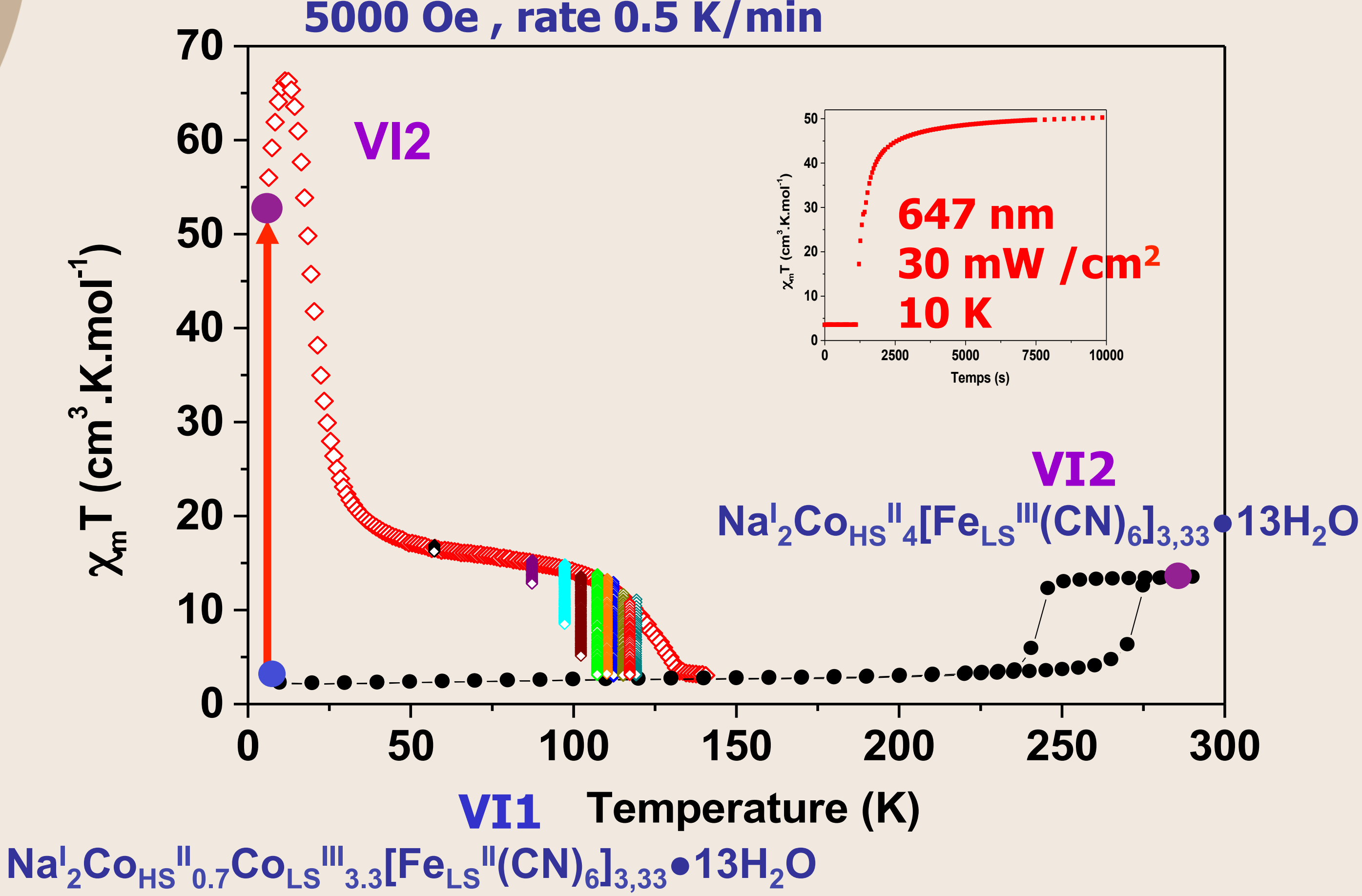
Presence of photosensitive Co^{III}-NC-Fe^{II} pairs but also role of the network….

Bleuzen A., et al. J. Am. Chem. Soc. 2000 *122* 6648; J. Am. Chem. Soc. 2000 *122* 6653.

2b) Photomagnetism in Electron Transfer Compounds

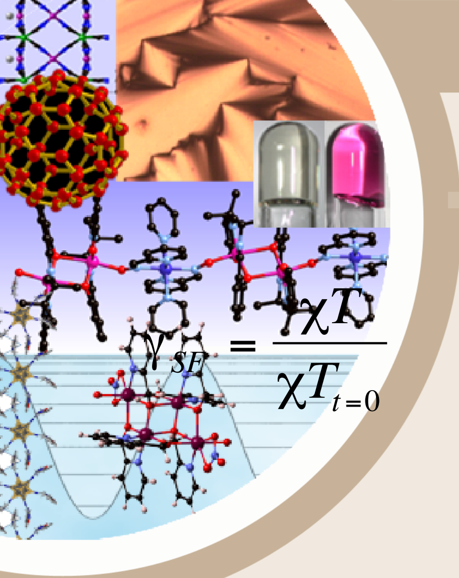
$Na_2Co_4[Fe(CN)_6]_{3.3}.14H_2O$





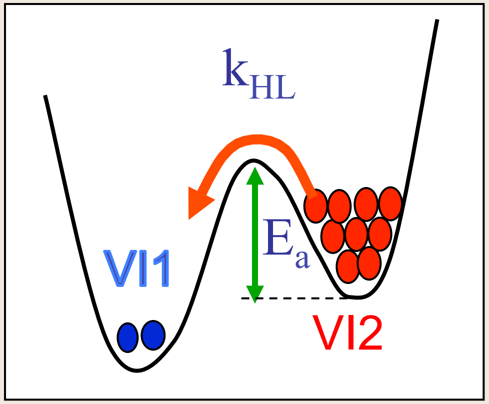
Le Bris R., Cafun J.-D., Mathonière C., Bleuzen A., Létard J.-F. et al. *New J. Chem.*, 2009, *33*, 1255.

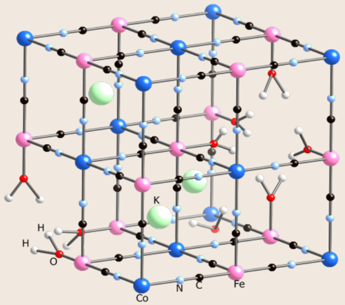
2b) Photomagnetism in Electron Transfer Compounds



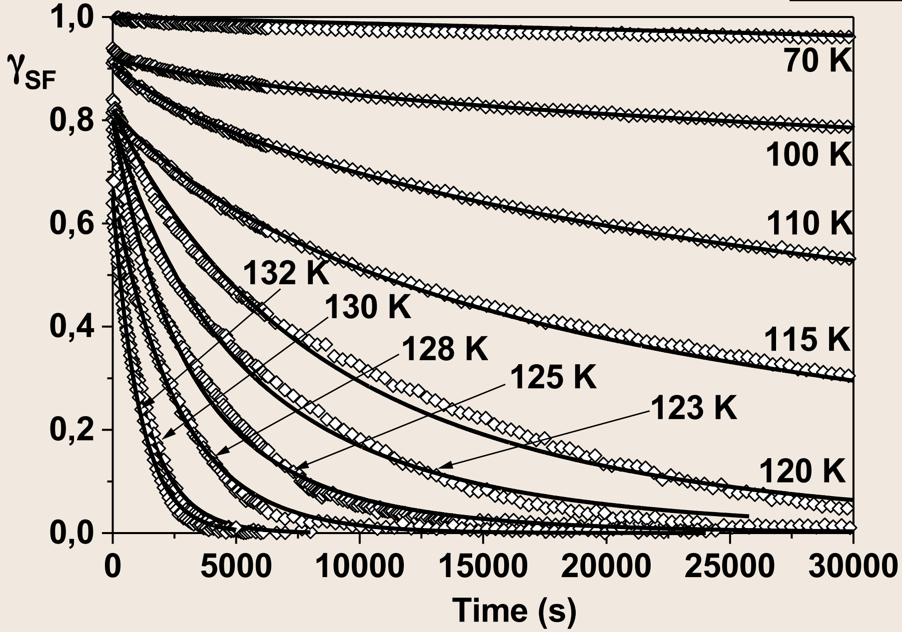
$Na_2Co_4[Fe(CN)_6]_{3.3}.14H_2O$

$$\gamma_{SF} = f(time)$$





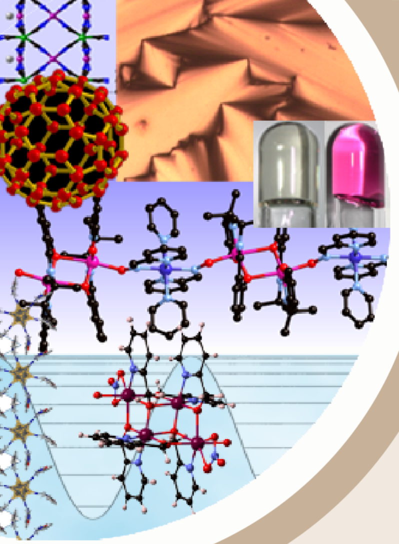
Exponential decays



$$\gamma_{SF} = \exp(-k(T)t)$$
$$= \exp(-t / \tau(T))$$

k : relaxation rate constant

***τ* : relaxation time**



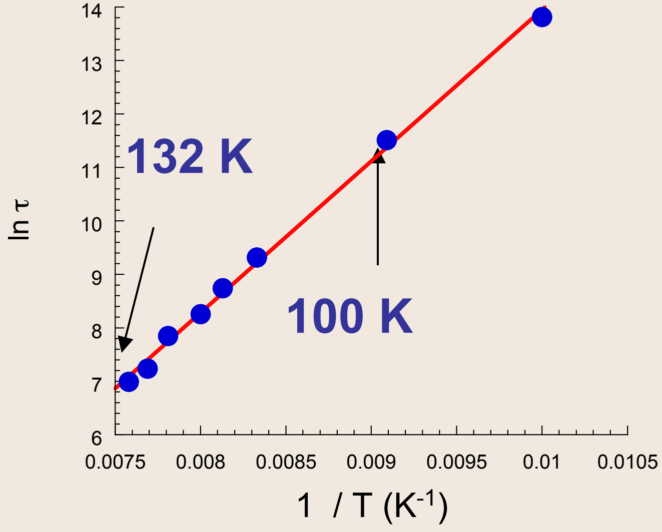
2b) Photomagnetism in Electron Transfer Compounds

$Na_2Co_4[Fe(CN)_6]_{3.3}.14H_2O$

Arrhenius law

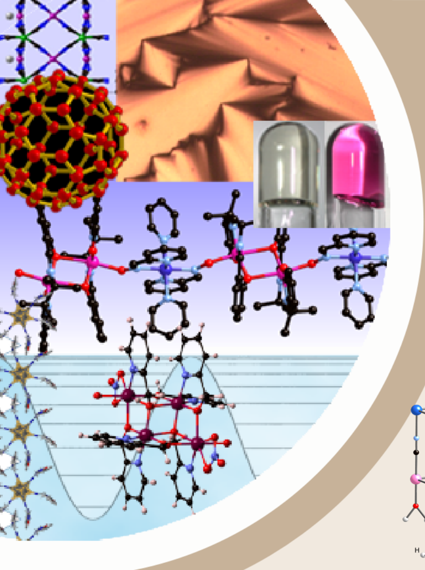
$$k(T) = k_{T\to\infty}.\exp(-\frac{E_a}{k_B T})$$

$$\tau(T) = \tau_{T\to\infty}.\exp(+\frac{E_a}{k_B T})$$



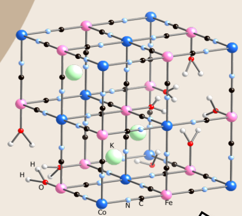
	Na_2
$k_{T\to\infty}$ (s^{-1})	$1.6\ 10^{7}$
$\tau_{T\to\infty}$ (s)	$6.3\ 10^{-8}$
E_a/k_B (K)	3110

Lifetime at 120 K : 3 hours



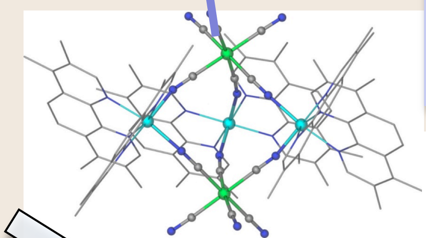
2b) Photomagnetism in Electron Transfer Compounds

Thermal-induced ET : Berlinguette. C. P. et al. *J. Am. Chem.* Soc. **2005**, *127*, 6766.
Light-induced ET : Funck, K. E. *et al. Inorg. Chem.* **2011**, *50*, 2782.



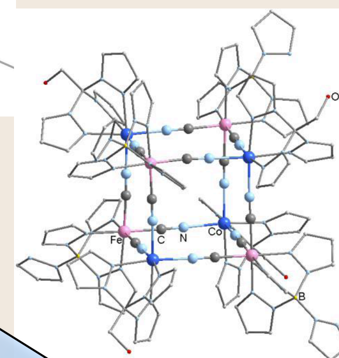
3D networks PBA

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

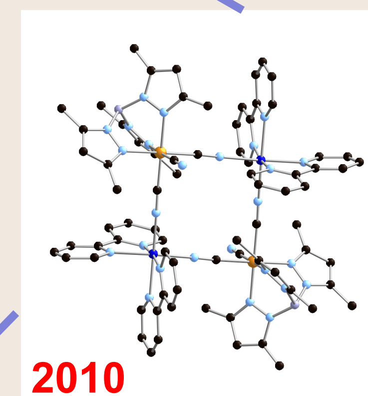


2005

Thermal <u>and</u> photo-induced ET
Li, D. et. al. *J. Am. Chem.* Soc. **2008**, *130*, 252
Zhang, Y. et al. Angew. Chem. Int. Ed. **2010** *49* 3752.

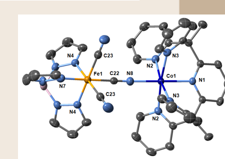


2008

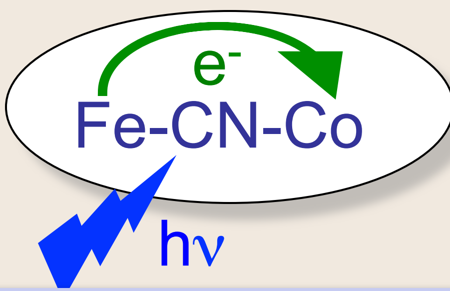


2010

Molecular models of PBA

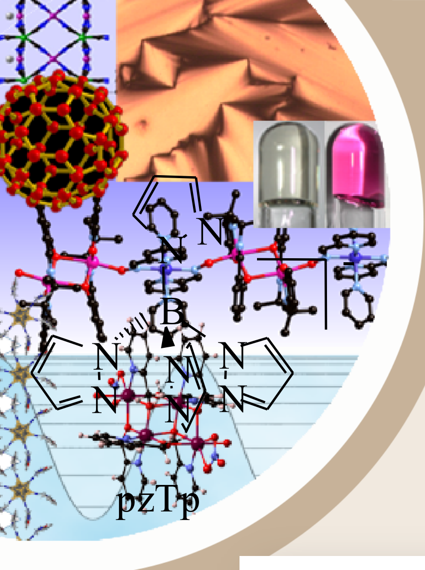


2014



Other photomagnetic squares:
Nihei et al. *Chem Lett*. **2010**, 39, 978; *J. Am. Chem.* Soc. , **2011**, *133*, 3592.
Mercurol Y. et al. *Chem Comm* **2010**, *46*, 8995.

A dinuclear molecule: Koumoousi et *al J. Am. Chem. Soc*. **2014**, *135*, 15461.

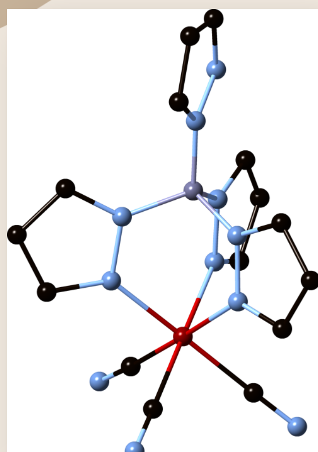


2b) Photomagnetism for Charge Transfer Compounds

Use of the blocking ligands on the Co and Fe sites :

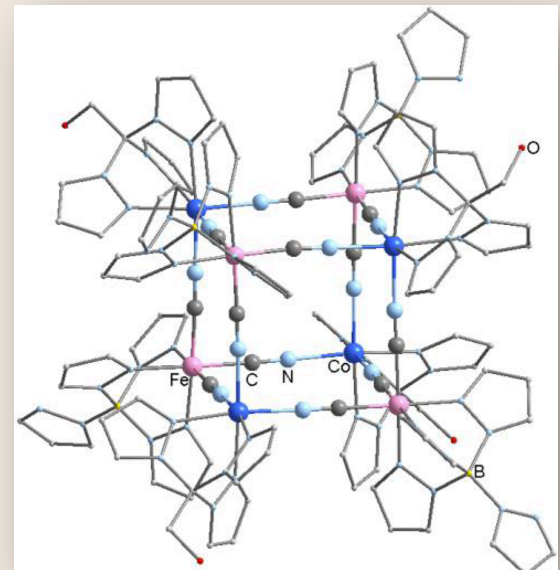
- ✓ Tricyanometalate iron building block
- ✓ Tridentate ligand for the Cobalt site

$[pzTpFe(CN)_3Co(pz)_3CCH_2OH]_4.(ClO_4)_4.13DMF$



1) $Co(ClO_4)_2$
2) L = $(pz)_3CCH_2OH$

→ DMF



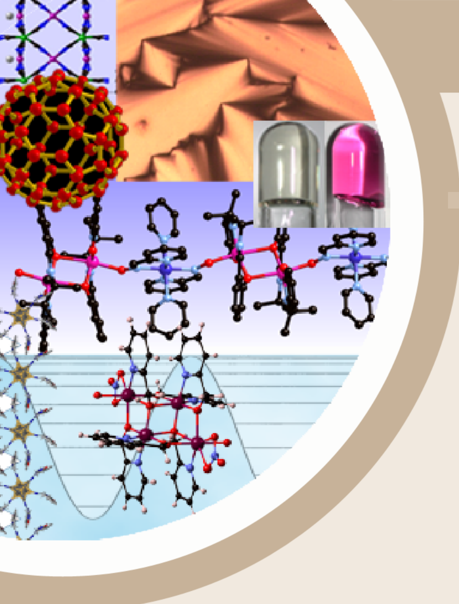
$[NEt_4][(pzTp)Fe^{III}(CN)_3]$*

$\{Fe_4Co_4\}$ box **

$\varnothing \approx 2.2$ nm

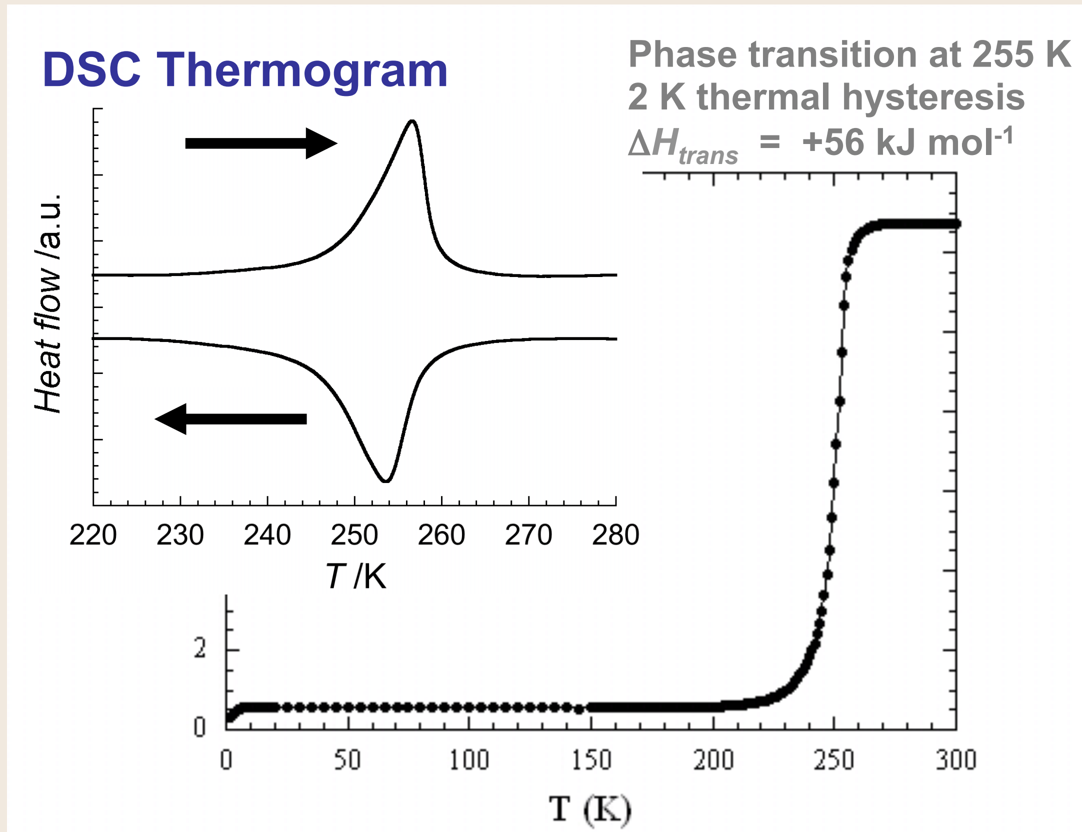
* Li, D.; Parkin, S.; Wang, G.; Yee, G. T.; Prosvirin A. V.; Holmes, S. M. *Inorg. Chem.* **2006**, *45*, 5251.

** Li, D.; Clérac, R.; Roubeau, O.; Harté, E.; Mathonière, C.; Le Bris, R.; Holmes, S. M., *J. Am. Chem. Soc.* **2008**, 130, 252.



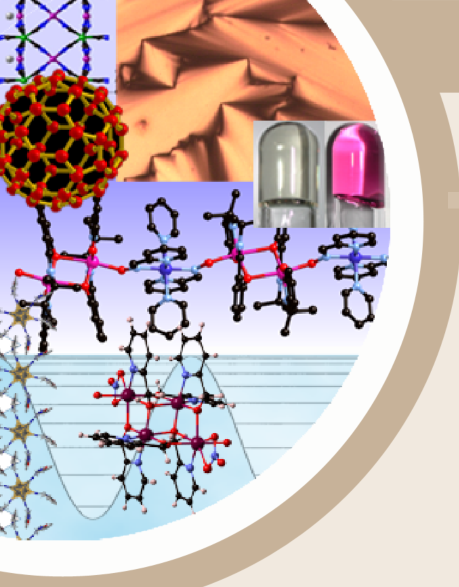
2b) Photomagnetism for Charge Transfer Compounds

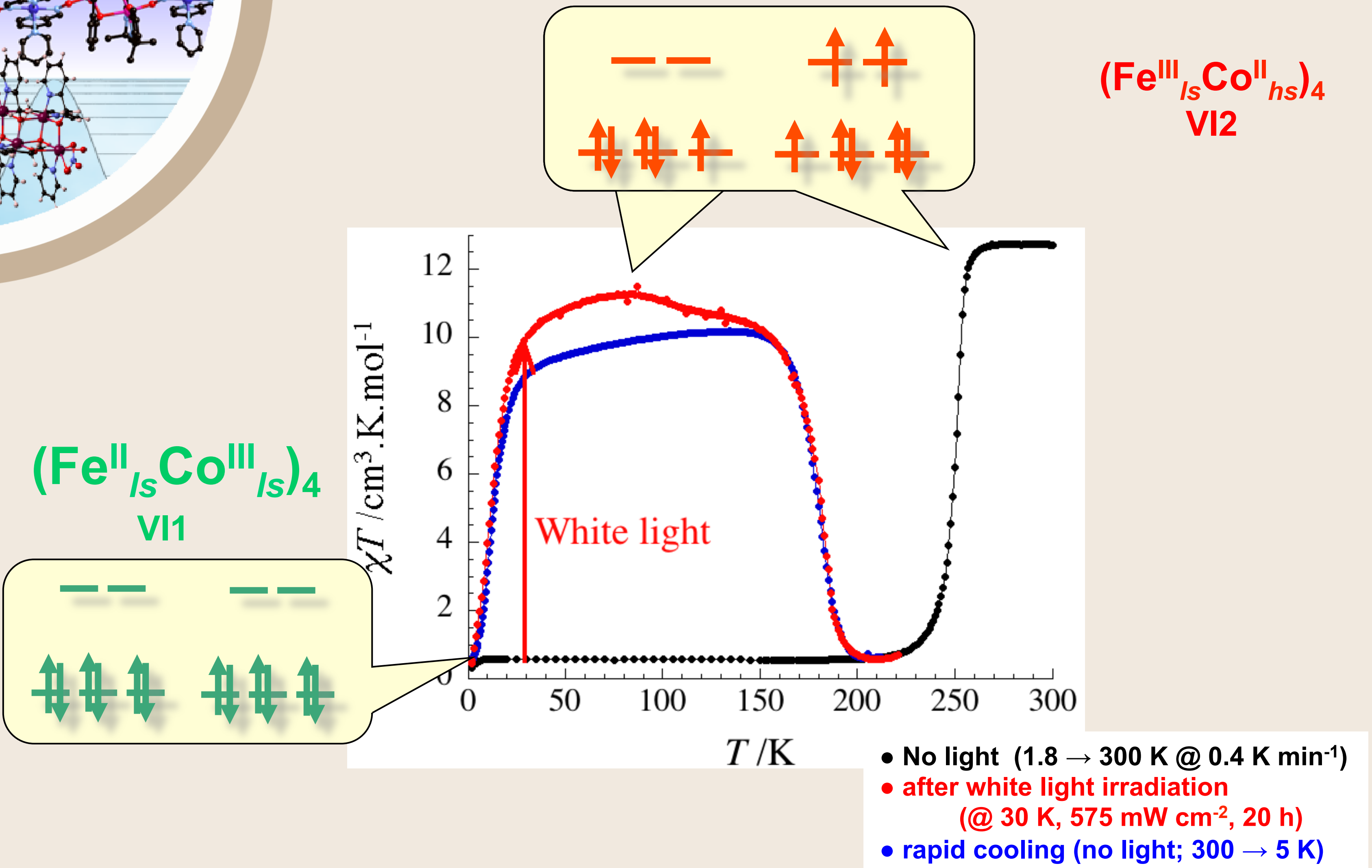
{Fe_4Co_4} box : Magnetic Measurements in the dark

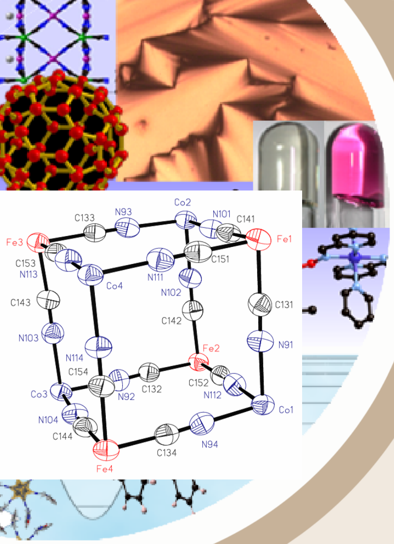


Li, D.; Clérac, R.; Roubeau, O.; Harté, E.; Mathonière, C.; Le Bris, R.; Holmes, S. M., *J. Am. Chem. Soc.* **2008**, 130, 252.

2b) Photomagnetism for Charge Transfer Compounds





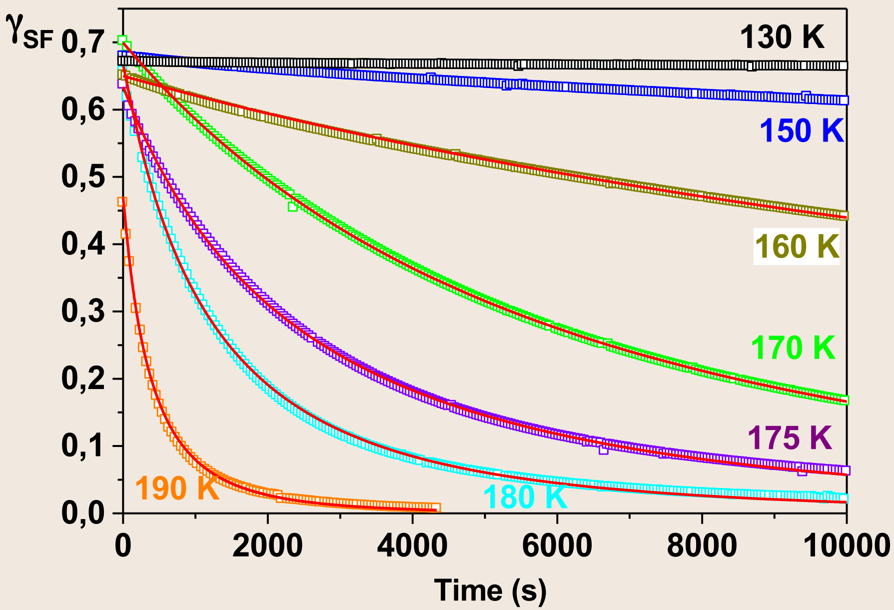


2b) Photomagnetism for Charge Transfer Compounds

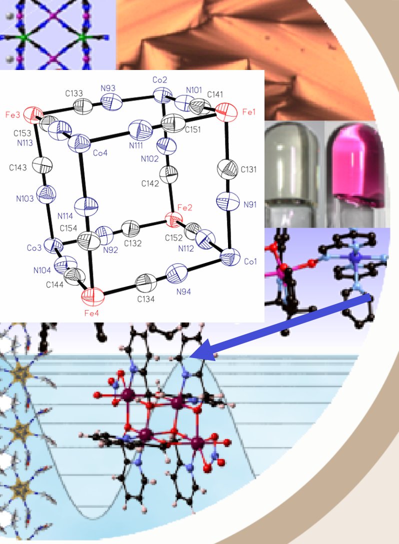
$$\gamma_{SF} = \frac{\chi T_{HT}}{\chi T_{HT} + \chi T_{LT}}$$

Exponential decays

Above 100 K, relaxation of the metastable states



$$\gamma_{HS}(T) = \gamma_{t=0}(T)\exp(-t/\tau(T))$$

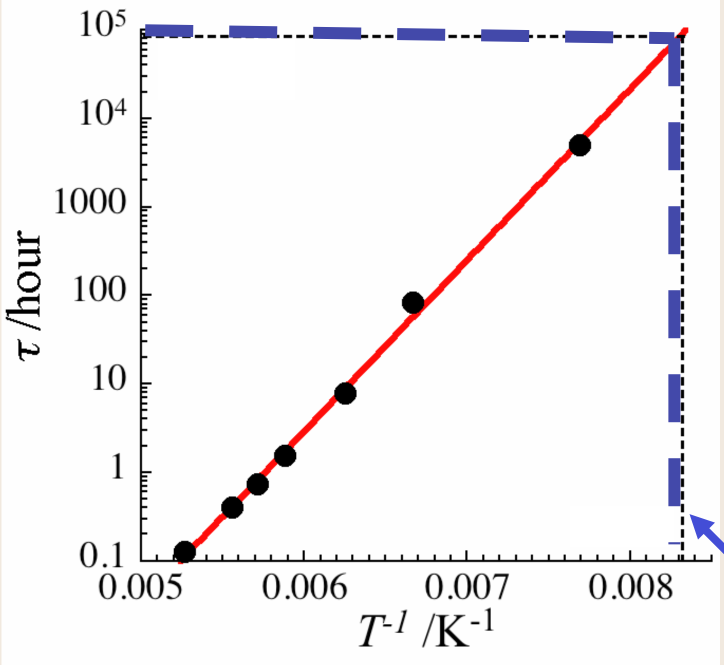


τ

2b) Photomagnetism for Charge Transfer Compounds

Arrhenius law

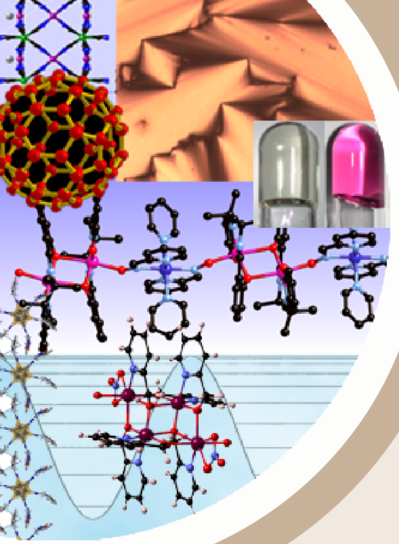
$$\tau(T) = \tau_{T\to\infty}.\exp(+\frac{E_a}{kT})$$



	Molecule	Network
τ_0 (s)	2.6 10^{-8}	6.6 10^{-8}
Δ/k_B (K)	4455	3085

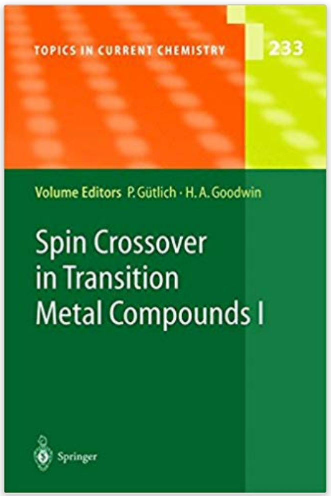
Molecule τ ~ 10 years at 120 K
Network τ ~ 3 hours at 120 K

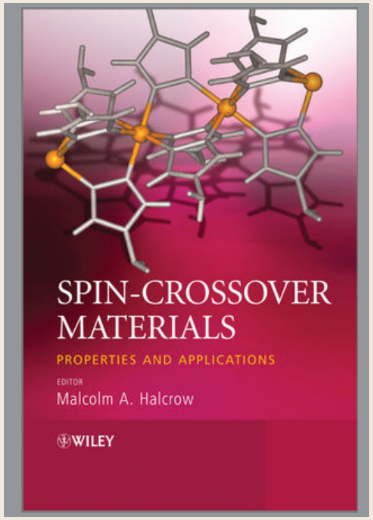
120 K



To go further....

On spin crossover....





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M. Halcrow ed. 2013, John Wiley & Sons Ltd, Oxford, UK.

On charge transfer systems....

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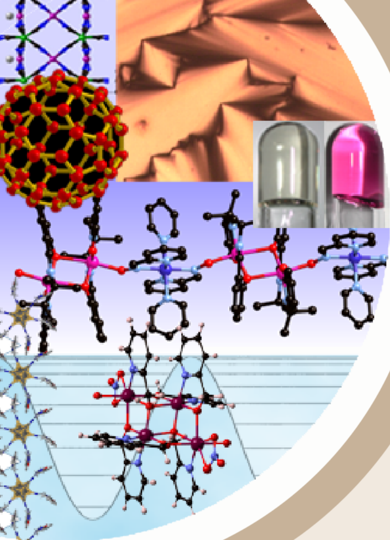
Meng Y.-S., Sato O., Lui T., Angew. Chem. Int. Ed., 2018, 57, 12216.



Acknowledgements

Dr. Chastanet Guillaum — ICMCB, University Bordeaux, France
Dr. Jean-François Létard
Dr. Philippe Guionneau
Dr. Patrick Rosa

Dr Rodolphe Clérac — CRPP, University Bordeaux, France
Prof. Claude Coulon

Dr Dongfeng Li — University of Missouri, USA
Dr Yuan Zhu
Prof. Steve Holmes