“Multifunctionality and Nanostructuration in Spin Crossover Materials“

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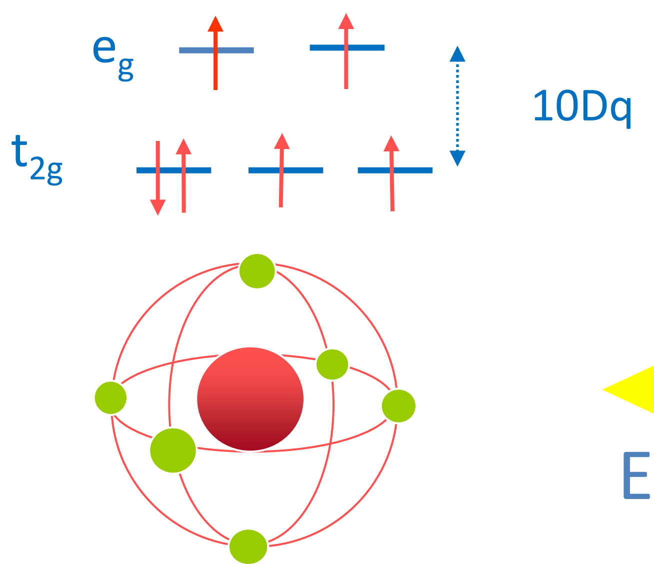
ICMOL, University of Valencia

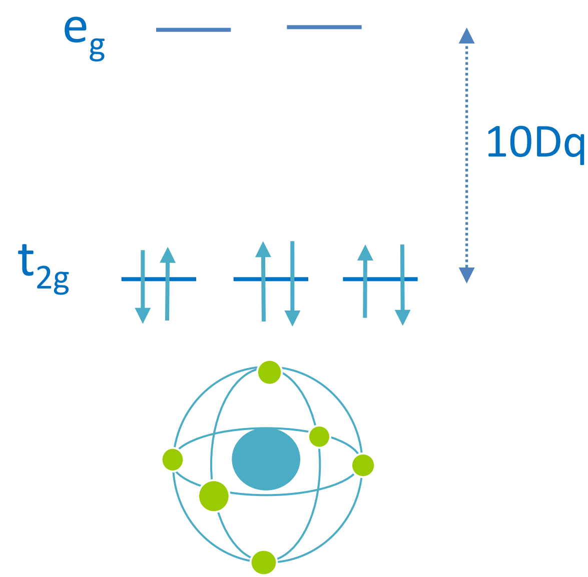
"WS10-ETOLDs", Valencia 2010

Spin Crossover Phenomenon in Fe(II) compounds



T, P, hν

$$E_{HS} - E_{LS} \approx k_B T$$

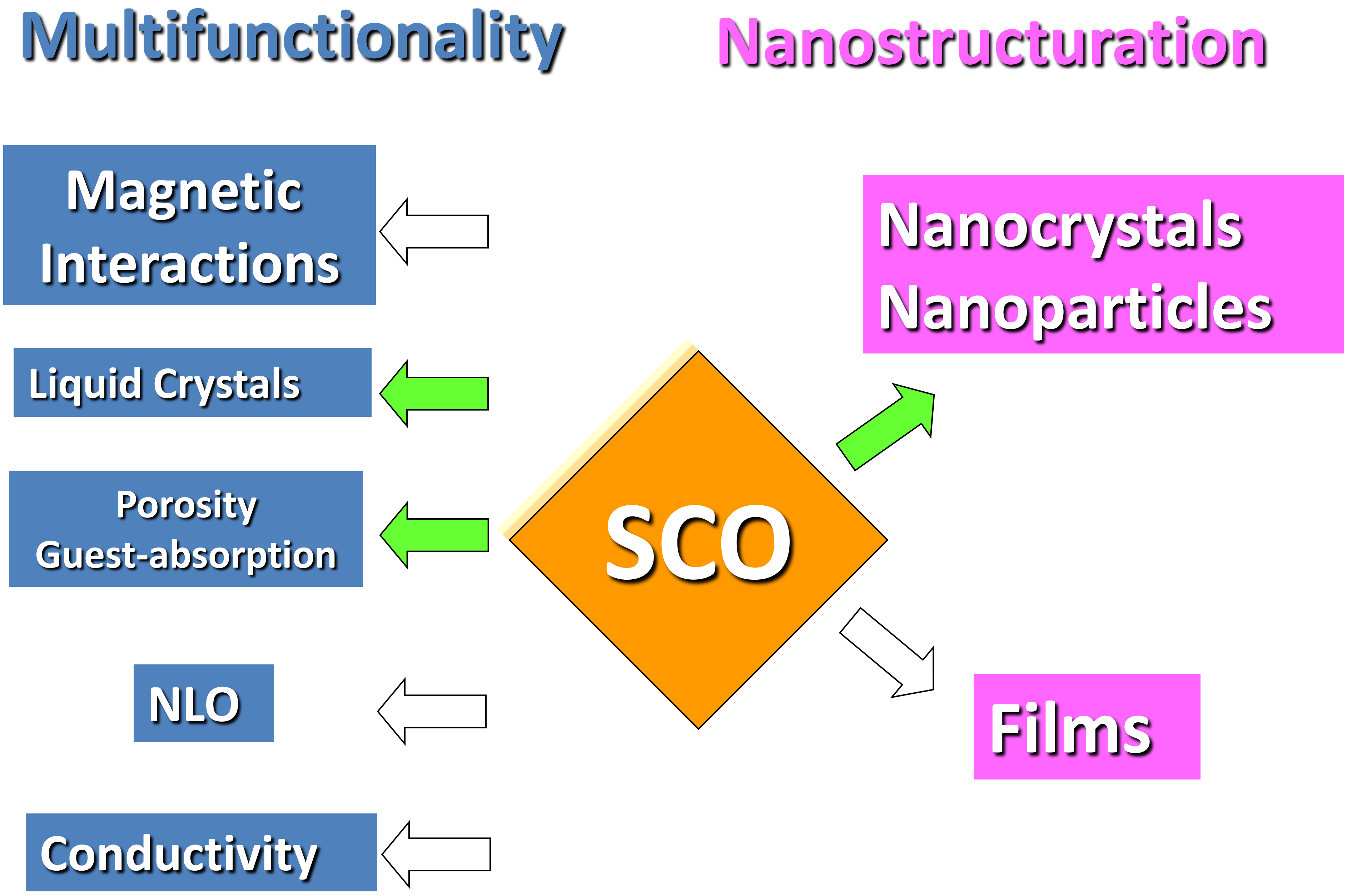


High Spin (HS) $^5T_{2g}$

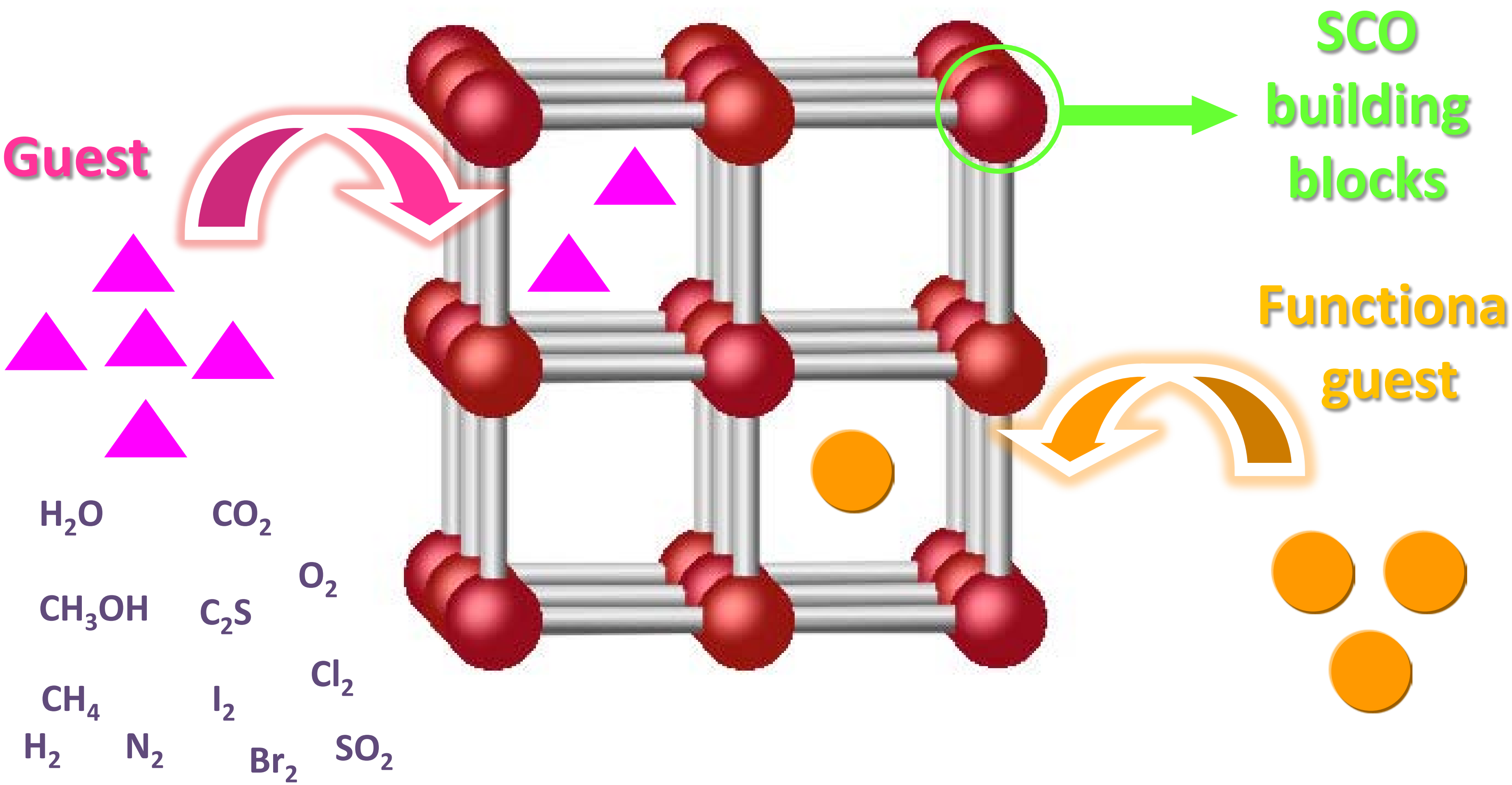
Paramagnetic S = 2

Low spin (LS) $^1A_{1g}$

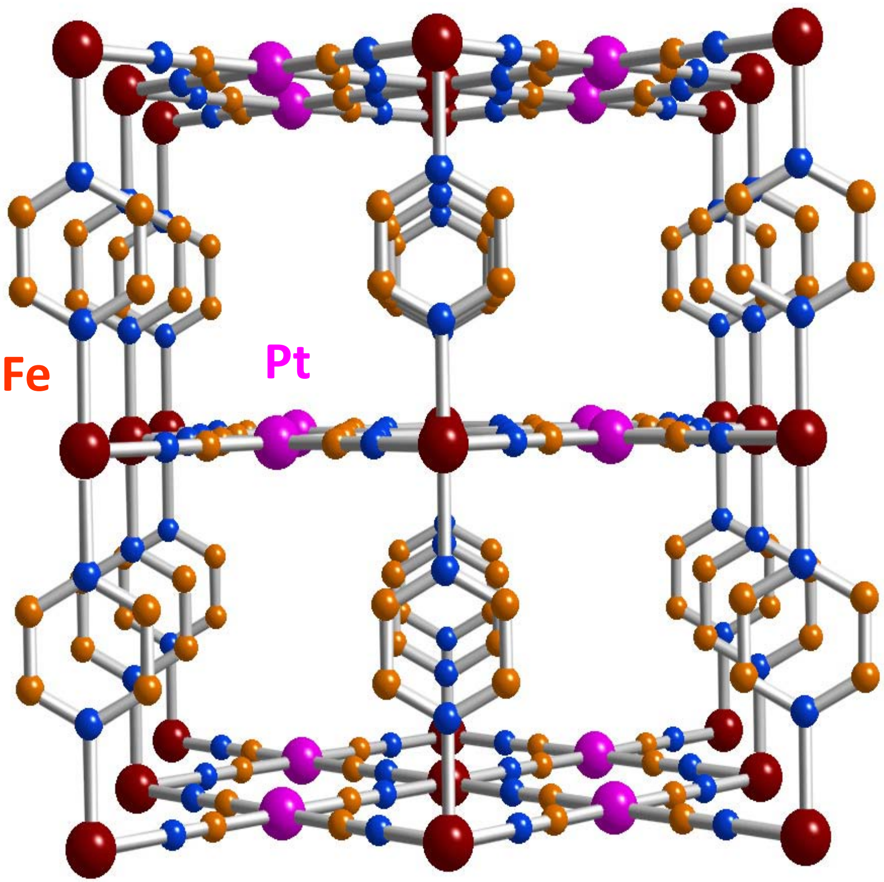
Diamagnetic S = 0

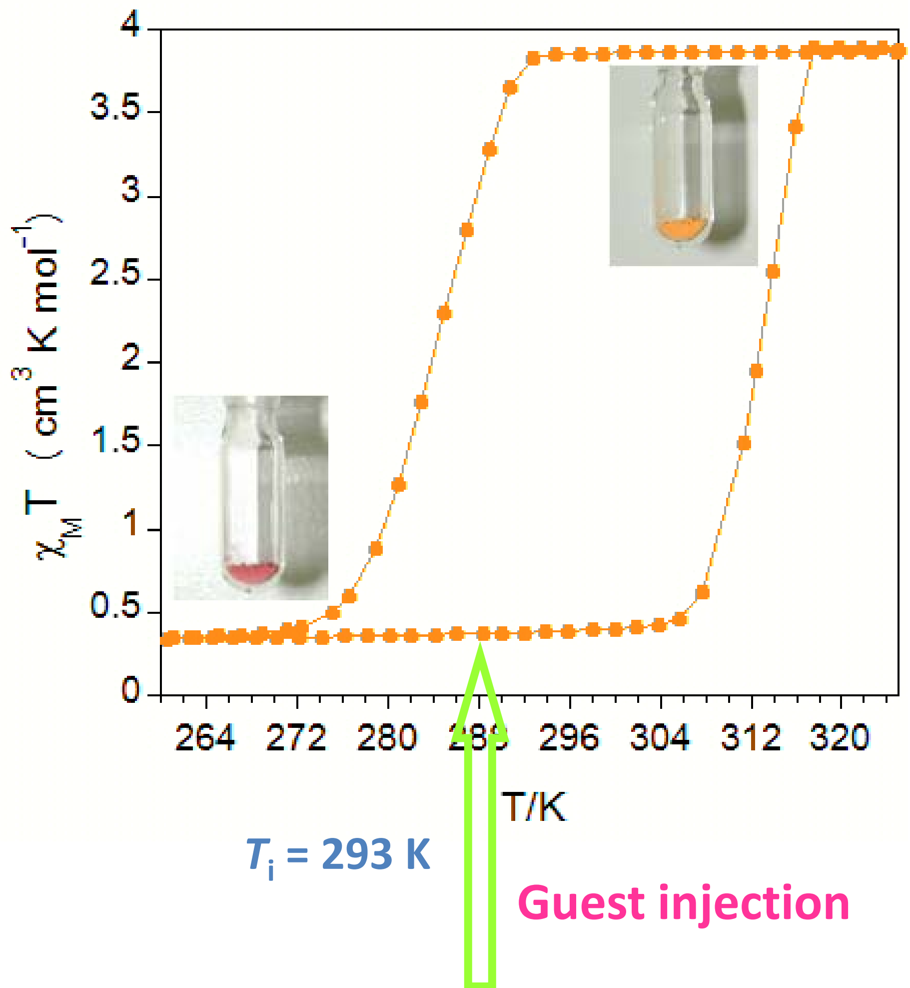

Multifunctionality
Nanostructuration
Magnetic Interactions
Liquid Crystals
Porosity
Guest-absorption
NLO
Conductivity
SCO
Nanocrystals
Nanoparticles
Films

Porous SCO polymers
Host-guest interactions



$[Fe(pz)Pt(CN)_4]$ (pz = pyrazine)





channels gate size [(100) and (010) directions]:

3.92×4.22 Å^2 HS state

3.43×3.94 Å^2 LS state

V. Niel, J. M. Martínez-Agudo, M. C. Muñoz, A. B. Gaspar, J. A. Real, *Inorg. Chem.*, 2001, *40*, 3838

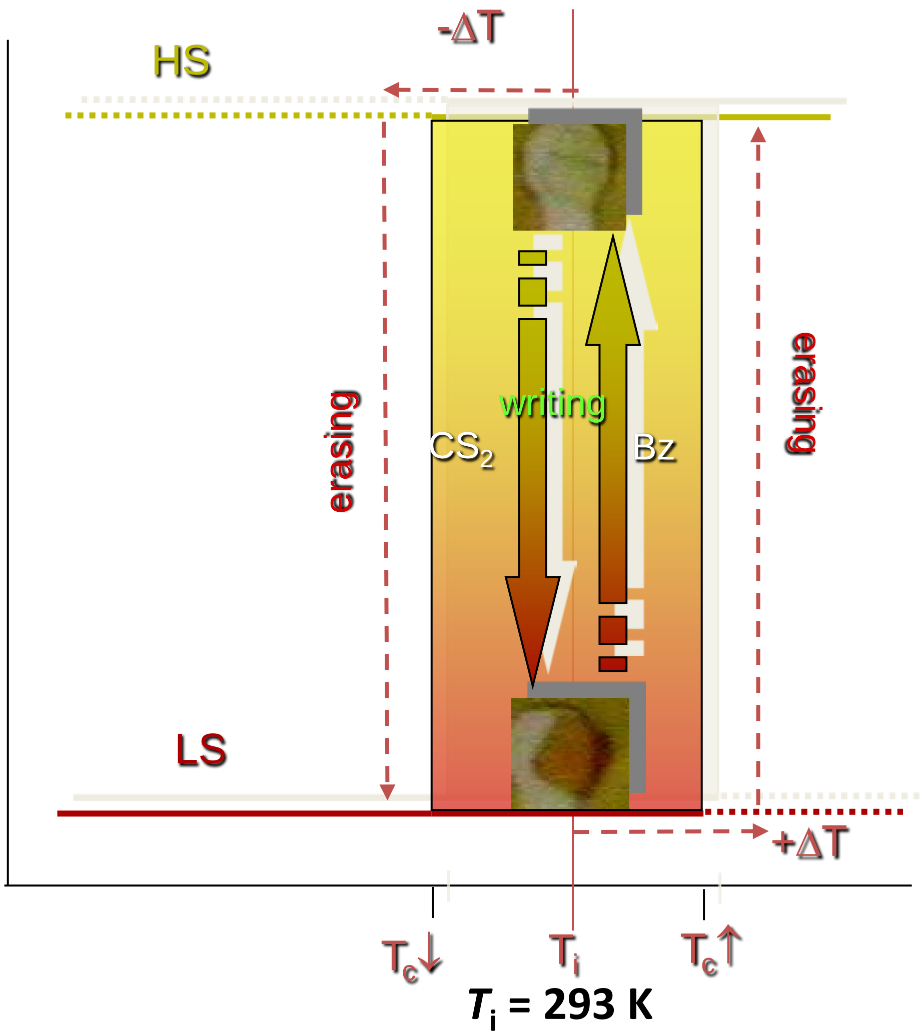
Bidirectional Chemo-switching of Spin State in the Microporous Framework $[Fe(pz)Pt(CN)_4]$

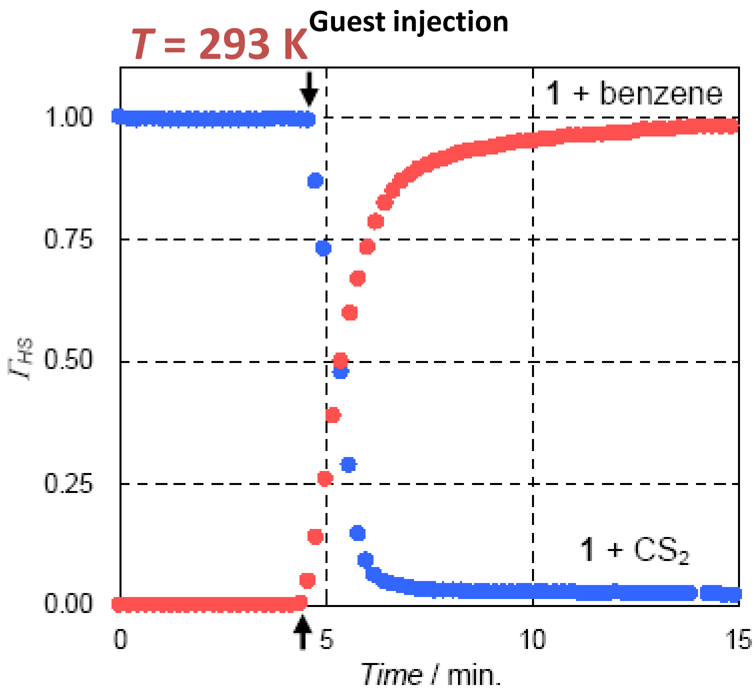
Guest molecule	Class I	Class II	Class III	Class IV
	CO_2	H_2O	benzene	CS_2
	N_2	D_2O	pyrazine	SO_2
	O_2	MeOH	toluene	
	C_2H_2	EtOH	Thiophene*	
		2-PrOH	Pyrrole*	
		acetone	Pyridine*	
			Furan*	
			THF*	
Molecular size	Small	Small/medium	Large	Small/medium
Effect on the spin state	No	High Spin	High Spin	Low Spin

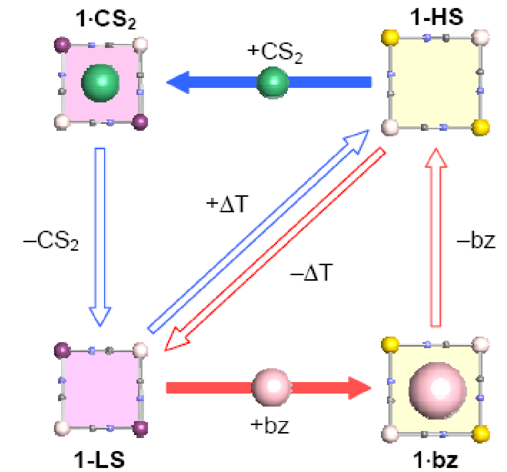
* These clathrates display cooperative spin transitions below 200 K

M. Ohba, K. Yoneda, G. Agusti, M. C. Muñoz, A. B. Gaspar, J. A. Real, M. Yamasaki, H. Ando, Y. Nakao, S. Sakaki, S. Kitagawa, *Angew. Chem. Int. Ed.*, 2009, *48*, 4767

Synergy Between Gas Absorption and Cooperative SCO Properties: Memory in $\{Fe(pz)[Pt(CN)_4]\}$ (1)







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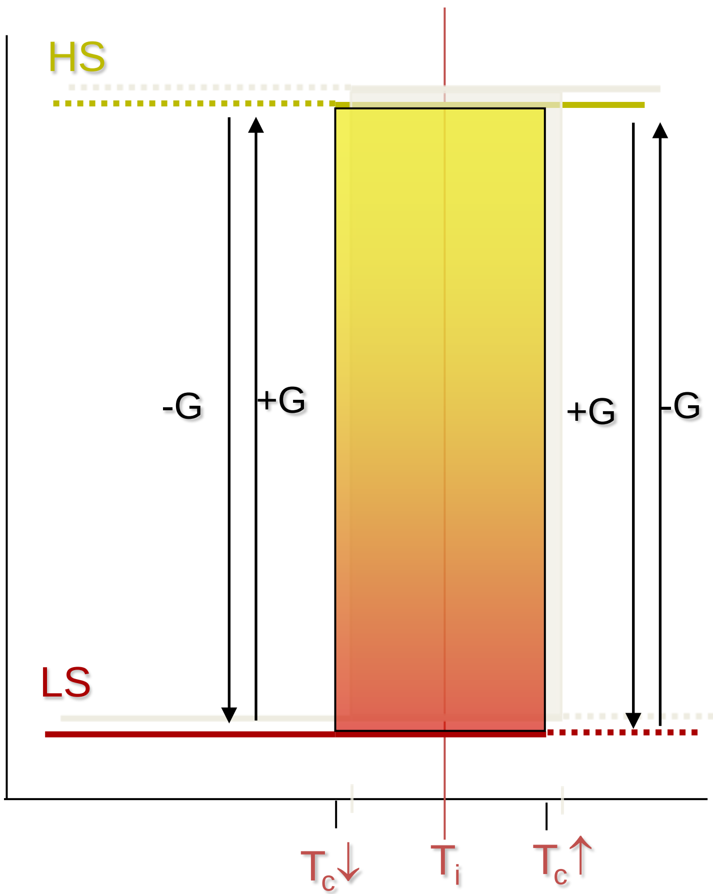
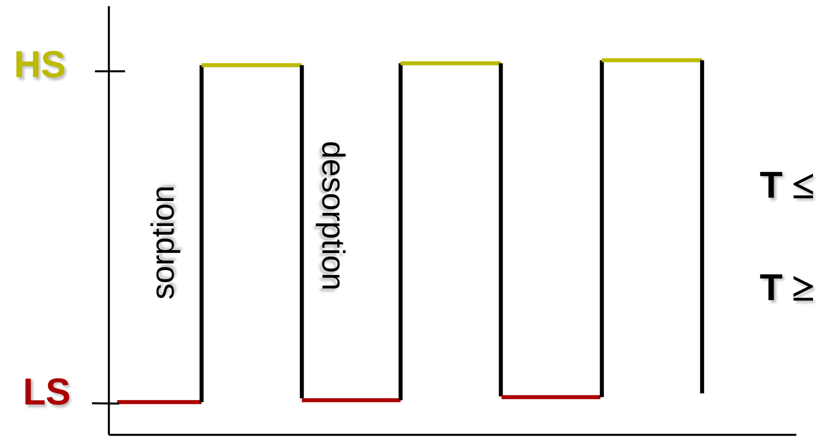
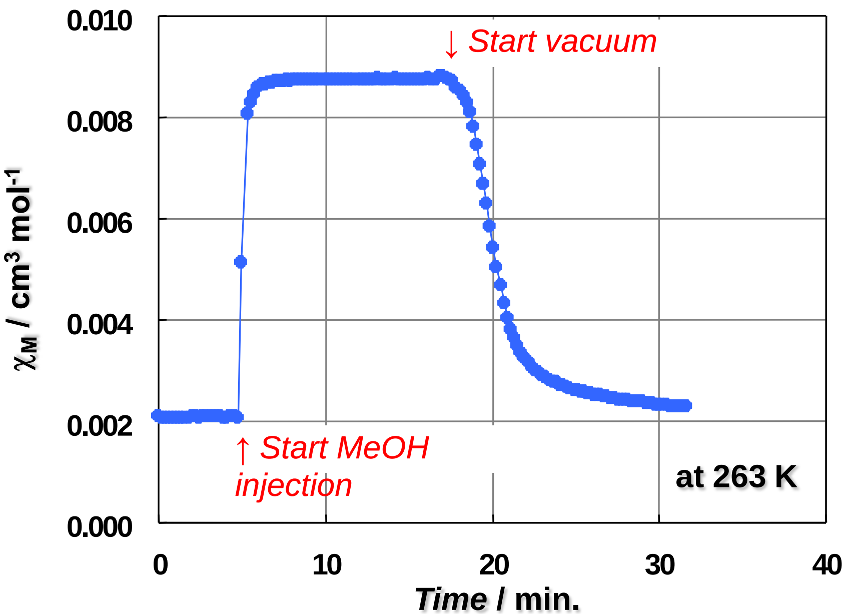
Synergy Between Gas Absorption and Cooperative SCO Properties: Switch in {Fe(pz)[Pt(CN)$_4$]}







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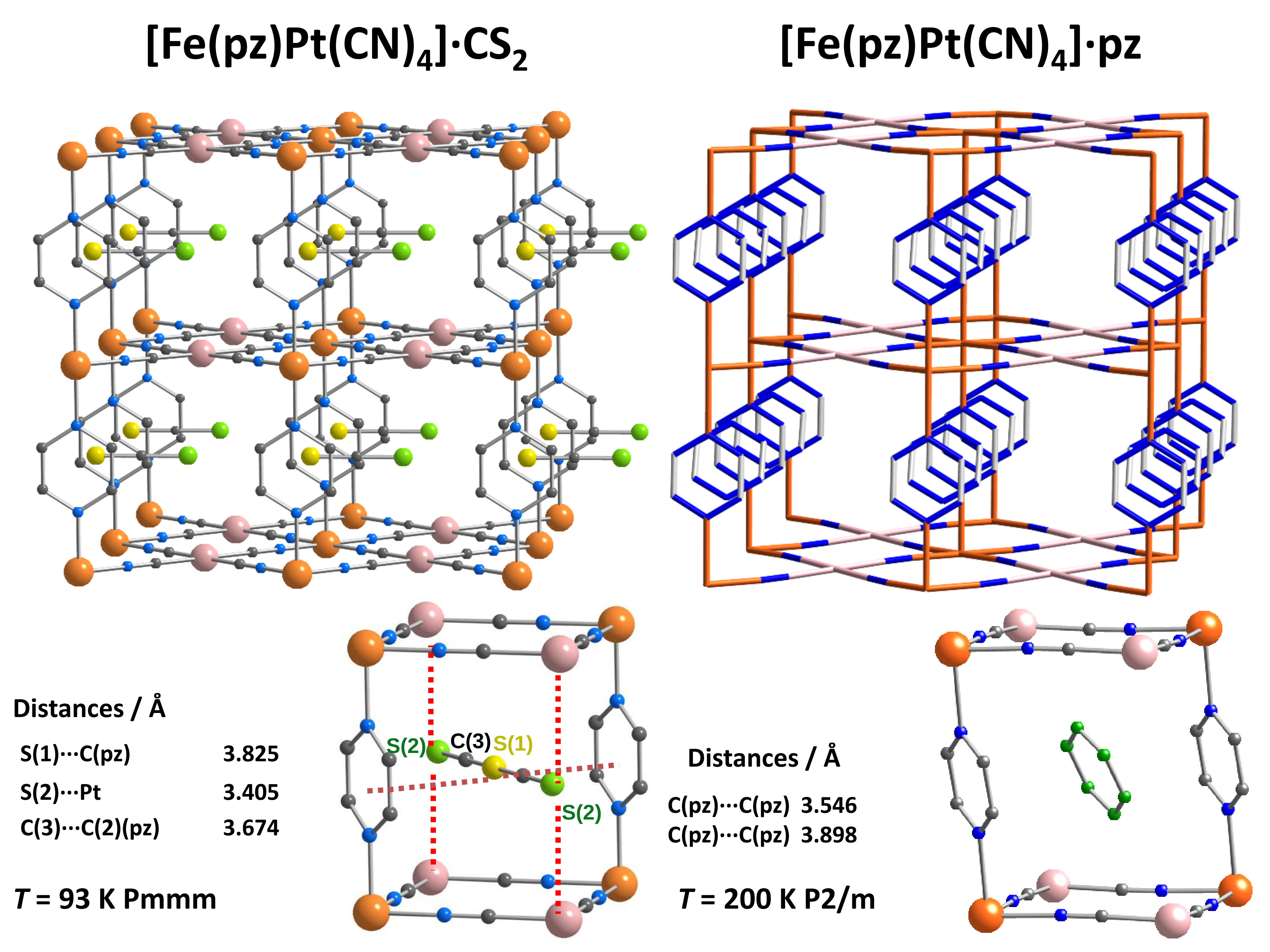


[Fe(pz)Pt(CN)4]·CS2
[Fe(pz)Pt(CN)4]·pz
Distances / Å
S(1)···C(pz) 3.825
S(2)···Pt 3.405
C(3)···C(2)(pz) 3.674
T = 93 K Pmmm
S(2)
C(3)
S(1)
S(2)
Distances / Å
C(pz)···C(pz) 3.546
C(pz)···C(pz) 3.898
T = 200 K P2/m

The structural data of clathrates and the CCSD(T) calculations point to three key factors as the origins of stabilization of the HS and LS states in $\{Fe(pz)[Pt(CN)_4]\}\cdot G$:

-Size and shape of guest

-G···pz interaction at site A

-G···Pt interaction at site B

Guest of class II and III

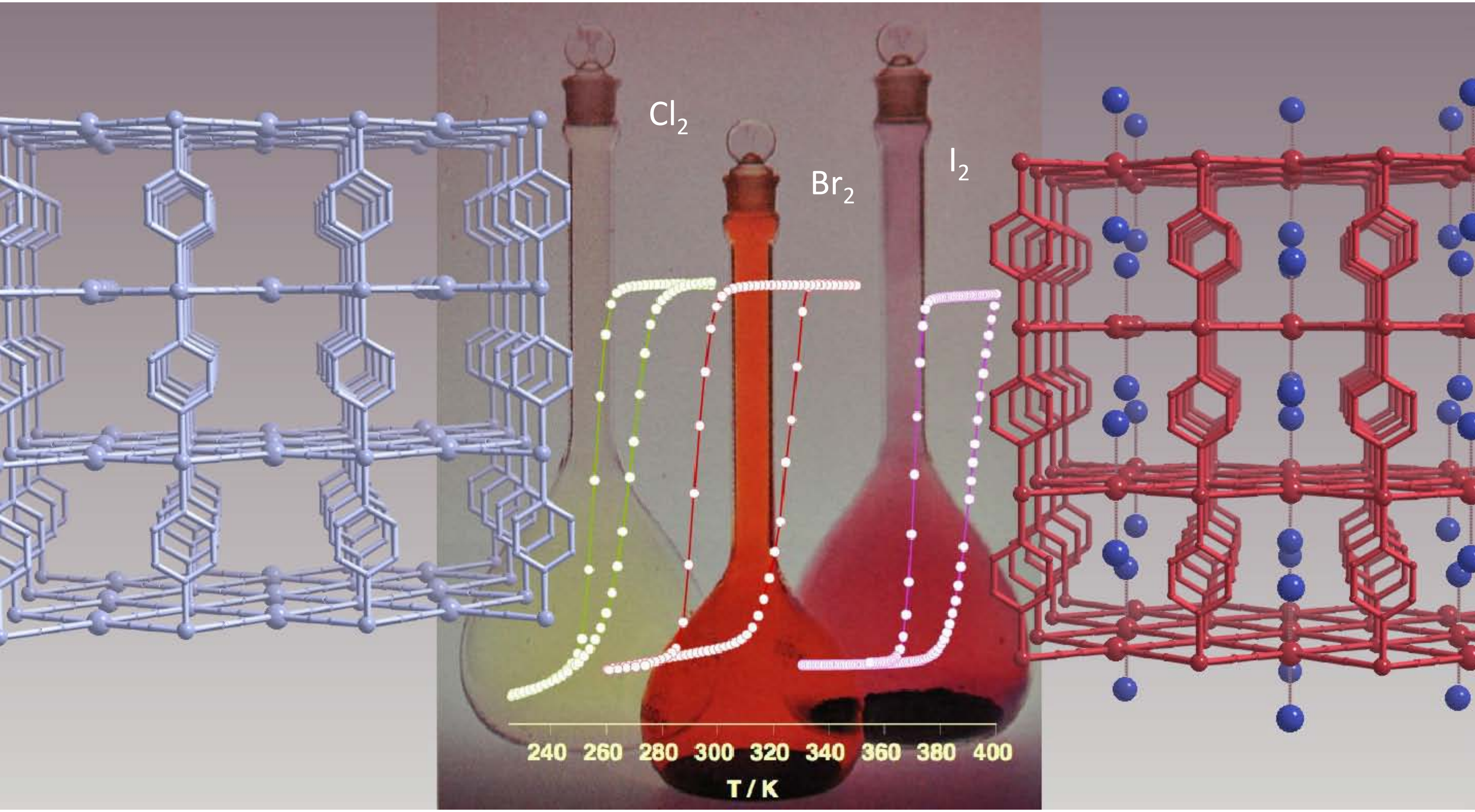
Size and shape of guest

Guest of class IV

-G···pz interaction at site A

-G···Pt interaction at site B

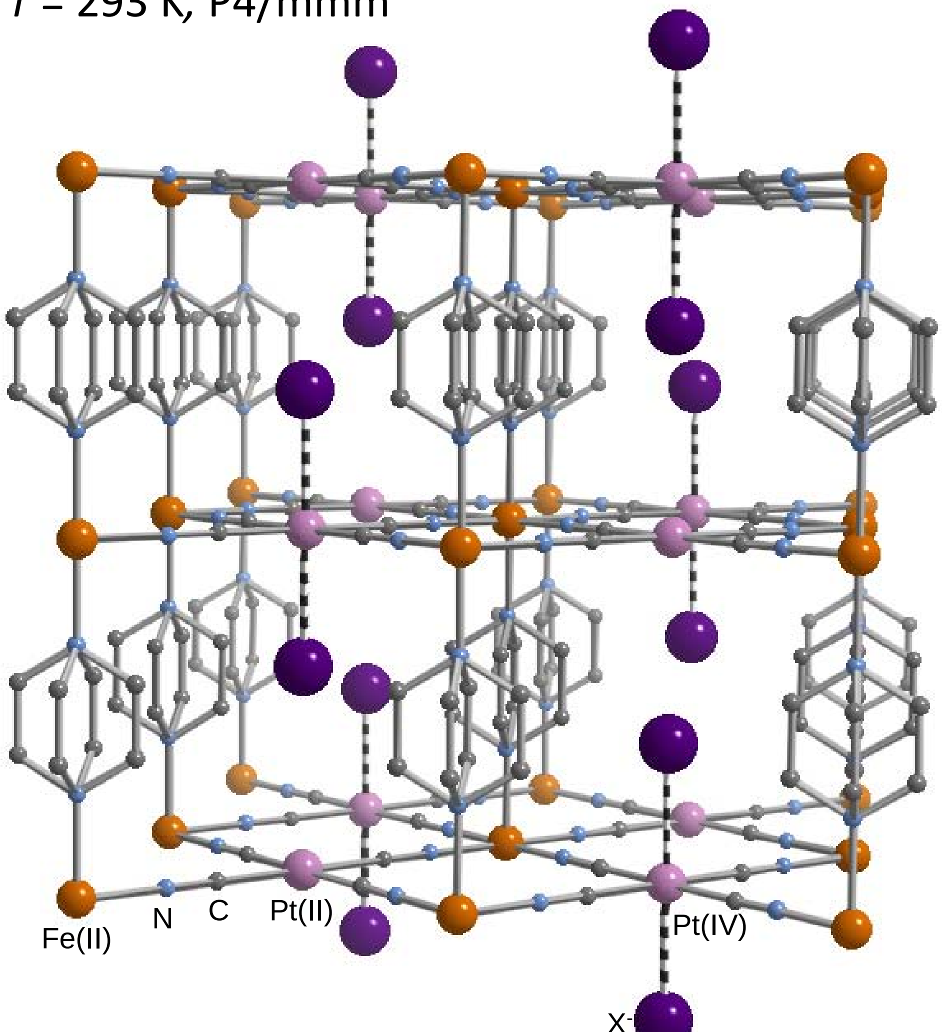
Oxidative Addition of Halogens on Open Metal Sites in the Microporous Framework $[Fe(pz)Pt(CN)_4]$



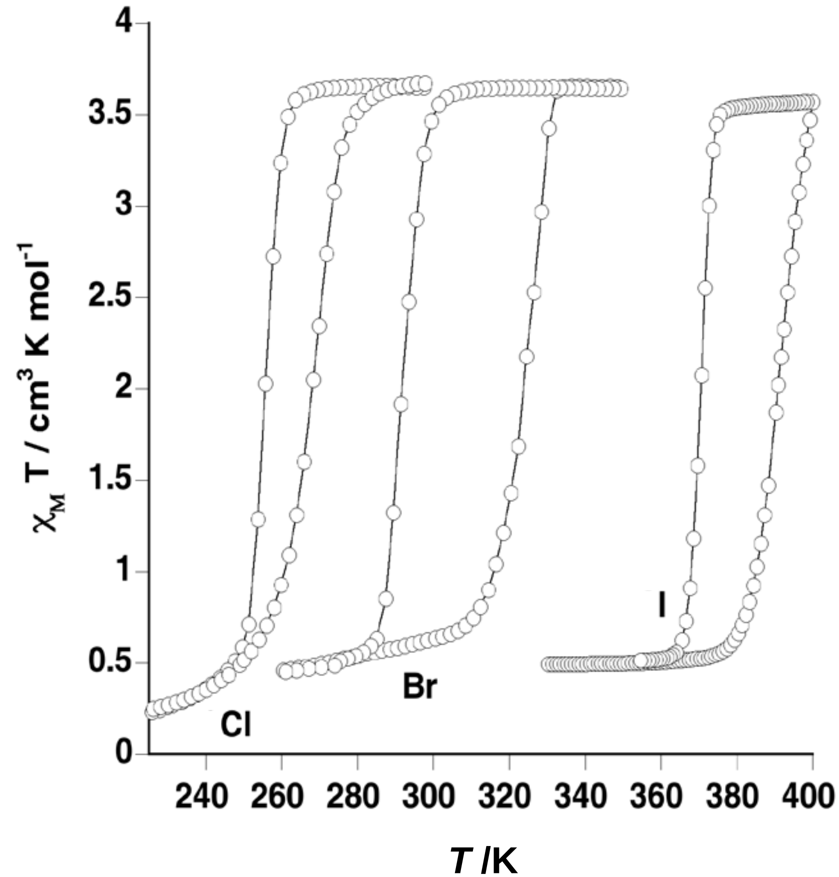
G. Agustí, R. Ohtani, K. Yoneda, A. B. Gaspar, M. Ohba, J. F. Sánchez-Royo, M. C. Muñoz, S. Kitagawa, J. A. Real
Angew. Chem. Int. Ed., 2009, *48*, 8944

Oxidative Addition of Halogens on Open Metal Sites in the Microporous Framework $[Fe(pz)Pt(CN)_4]$

T = 293 K, P4/mmm



$\{Fe(pz)[Pt(CN)_4(X)_p]\}$ [X = Cl^- (p = 1), Br^- (p = 1), I^- (0 ≤ p ≤ 1)]



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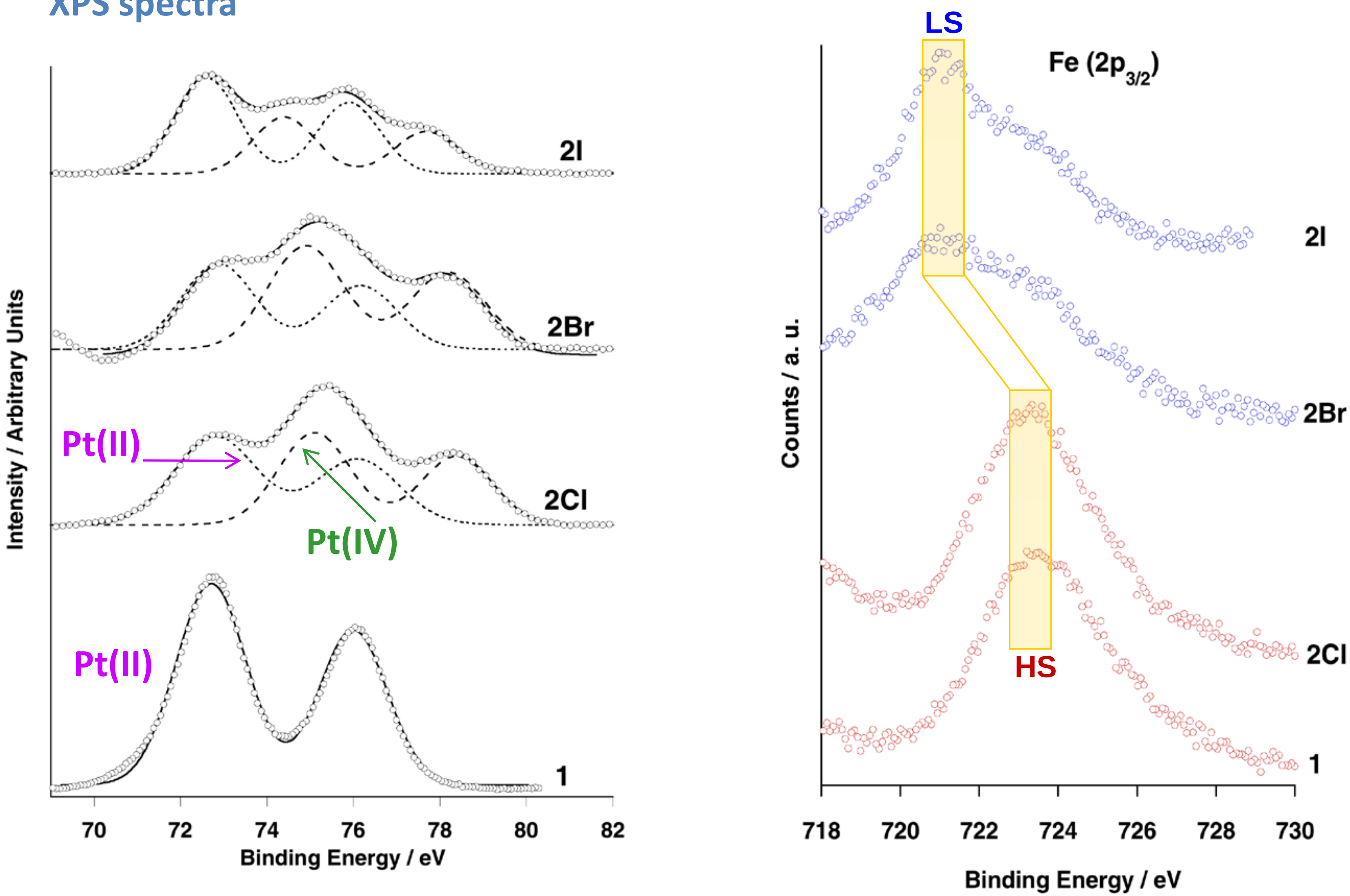
Oxidative Addition of Halogens on Open Metal Sites in the Microporous Framework $[Fe(pz)Pt(CN)_4]$

XPS spectra



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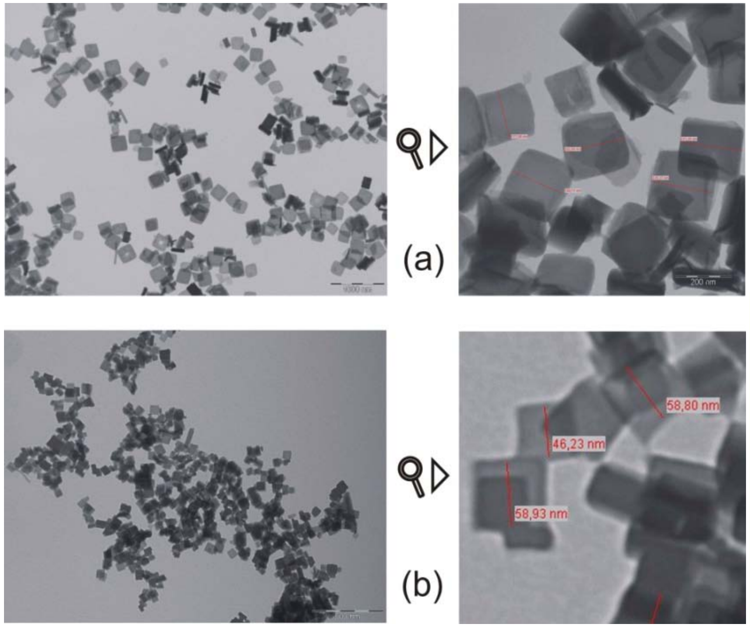
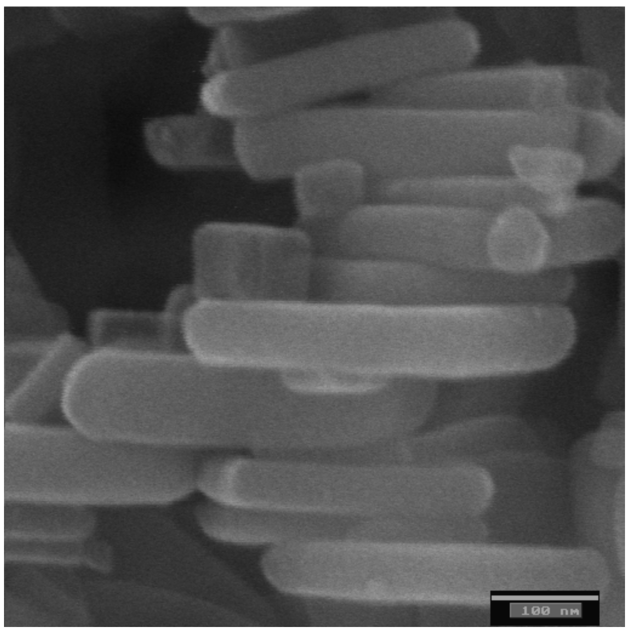
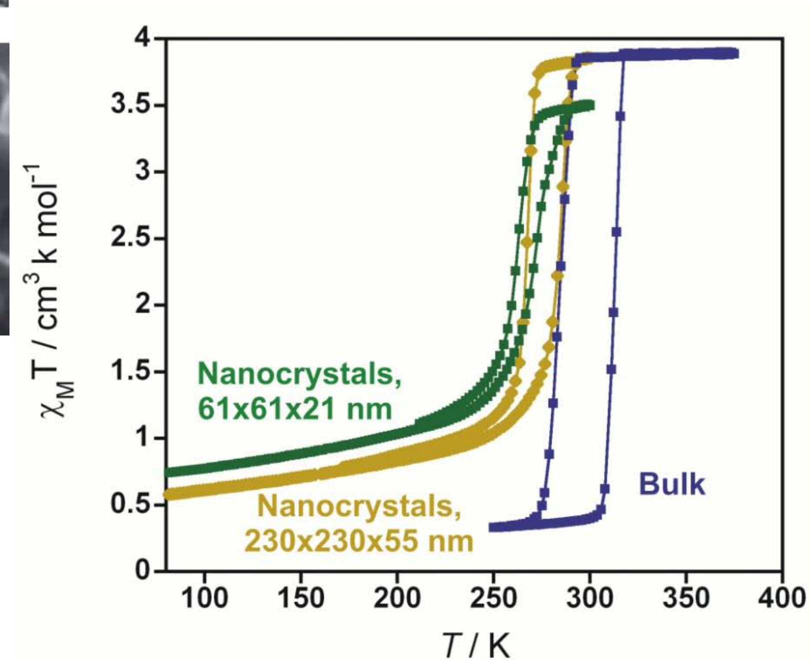
Angew. Chem. Int. Ed., 2009, *48*, 8944

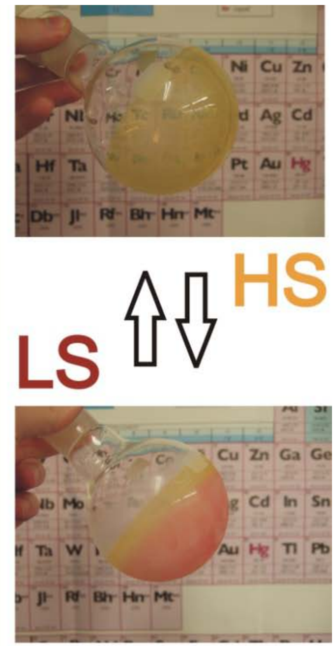
Nanocrystals / Nanoparticles of SCO polymers

Nanocrystals of $[Fe(pz)Pt(CN)_4]$ (reverse micelle)



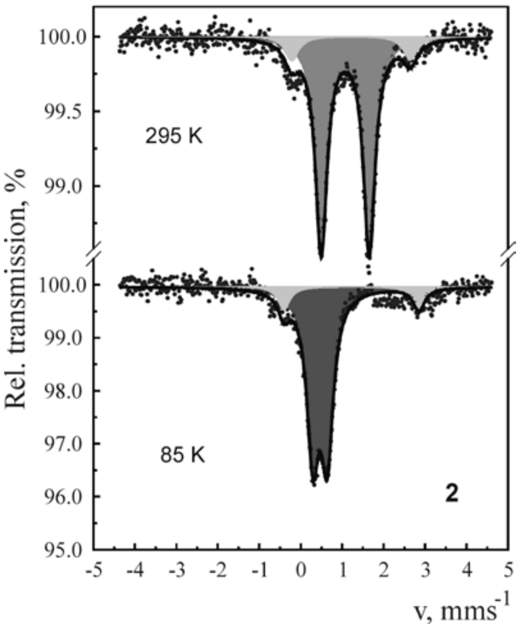


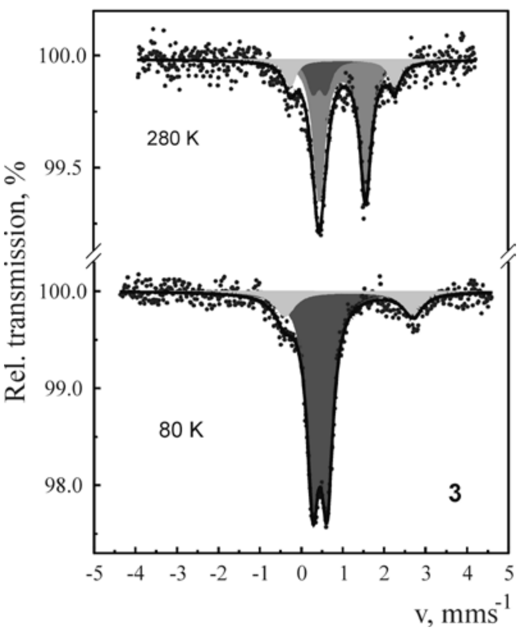


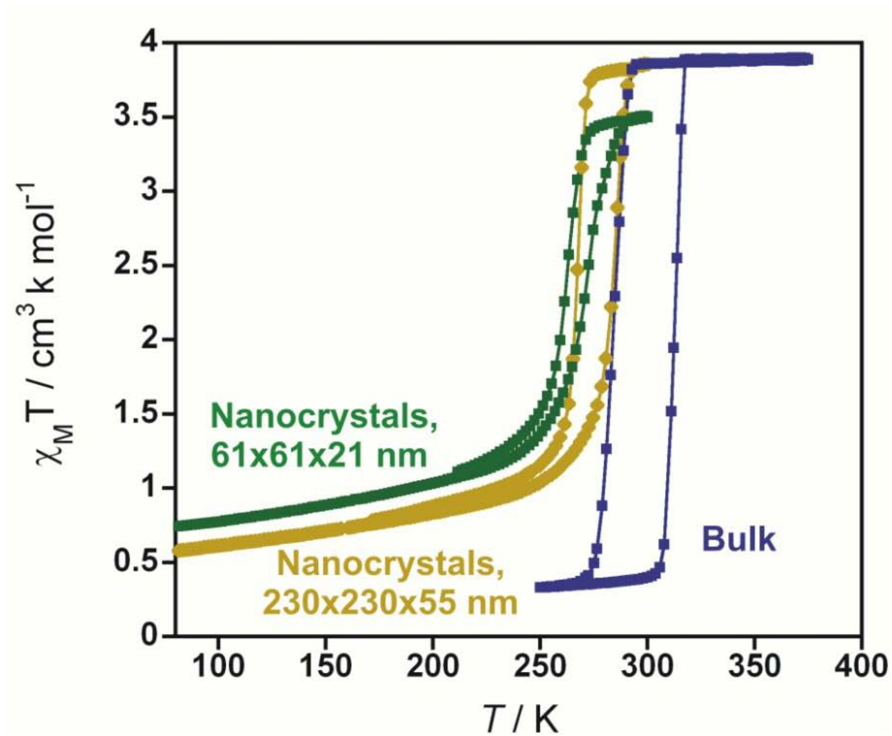


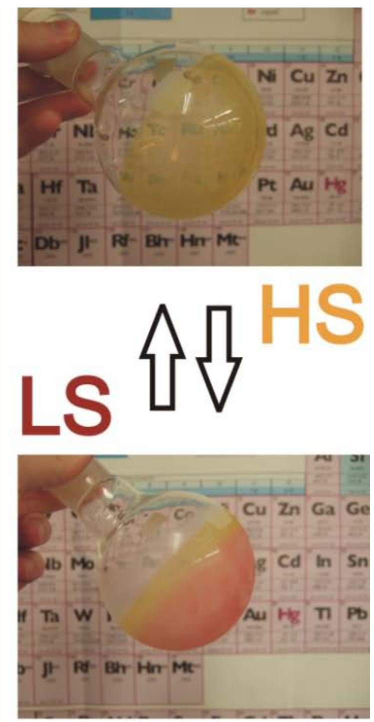
I. Boldog, A. B. Gaspar, V. Martínez, P. Pardo-Ibañez, V. Ksenofontov, A. Bhattacharjee, P. Gütlich, J. A. Real, *Angew. Chem. Int. Ed.*, 2008, *47*, 6433

Nanocrystals of $[Fe(pz)Pt(CN)_4]$ (reverse micelle)









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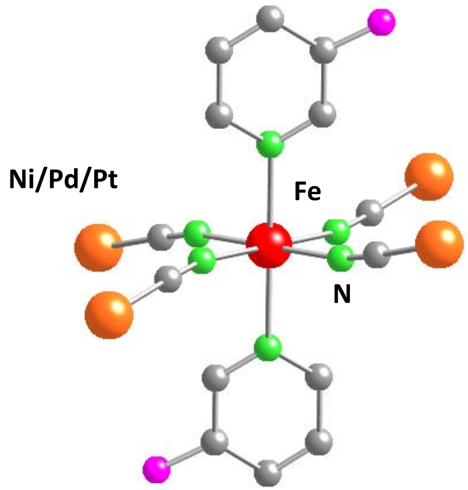
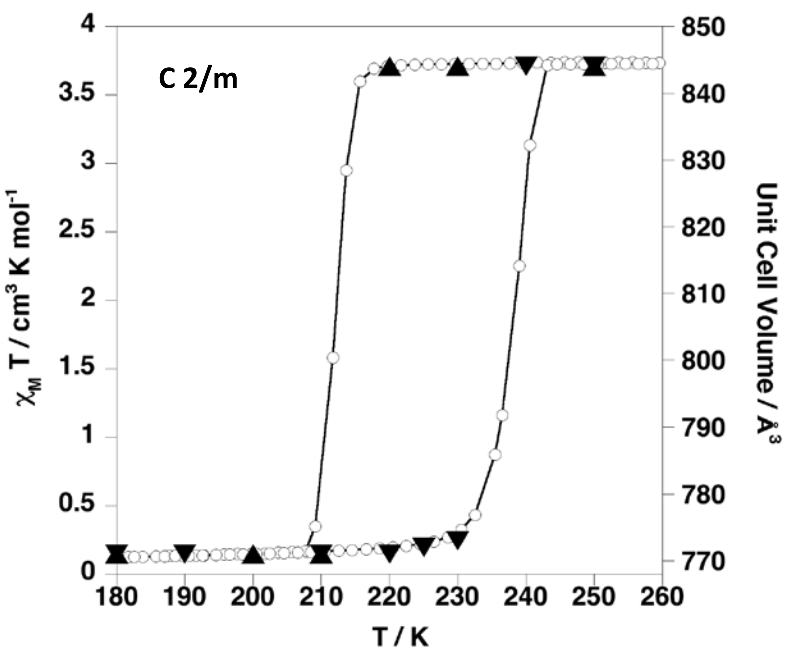
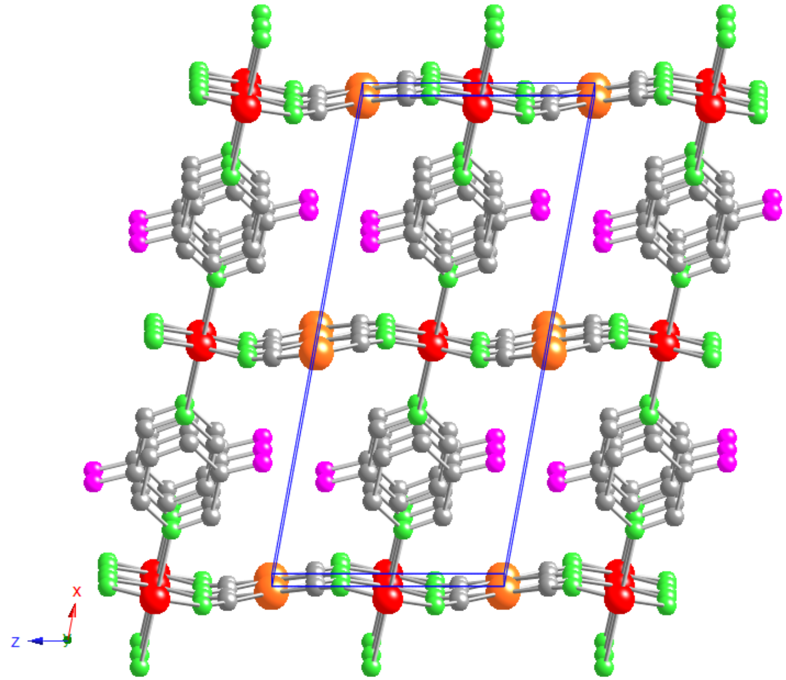
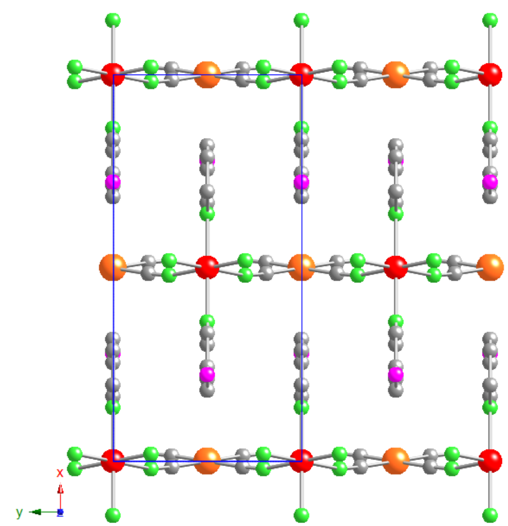
$[Fe(3F\text{-}py)_2M(CN)_4]$ (M(II) = Ni, Pd, Pt and 3F-py = 3-fluoropyridine)



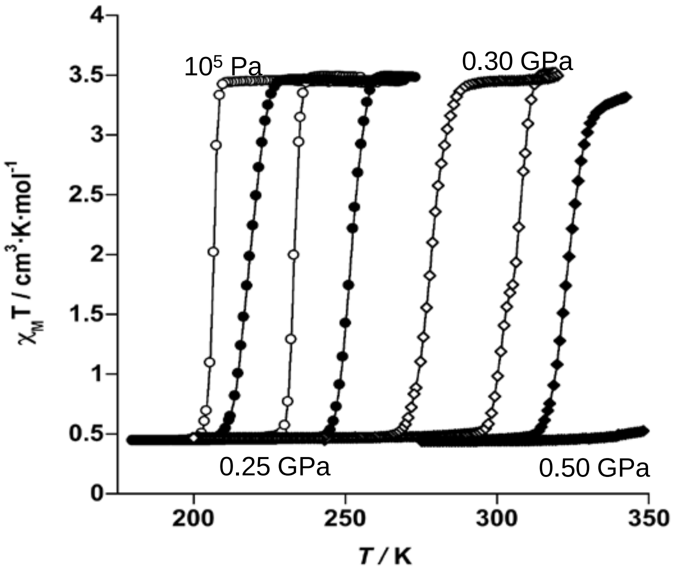




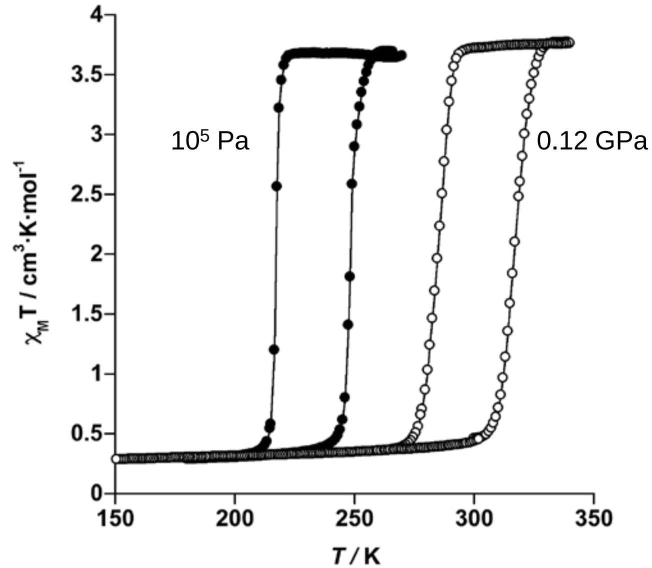


V. García, A. B. Gaspar, M. C. Muñoz, G. Bukin, G. Levchenko, J. A. Real, *Chem. Eur. J.*, 2009, *15*, 10960

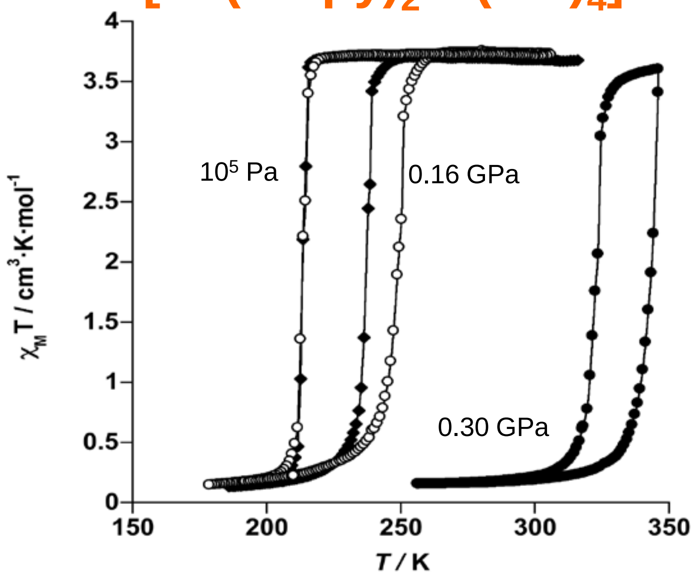
$[Fe(3F\text{-}py)_2Ni(CN)_4]$



$[Fe(3F\text{-}py)_2Pd(CN)_4]$



$[Fe(3F\text{-}py)_2Pt(CN)_4]$



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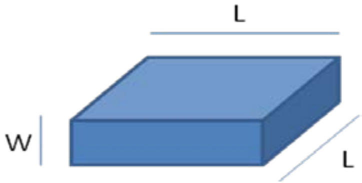
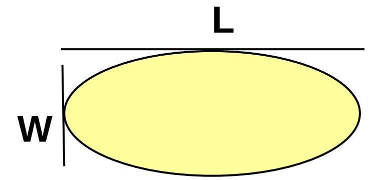
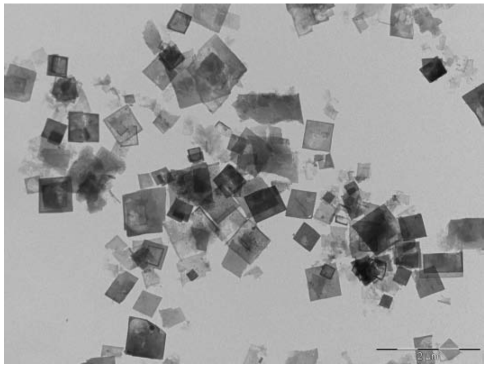
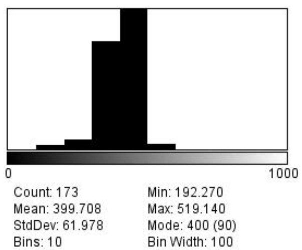


$[Fe(3F\text{-}py)_2Ni(CN)_4]$

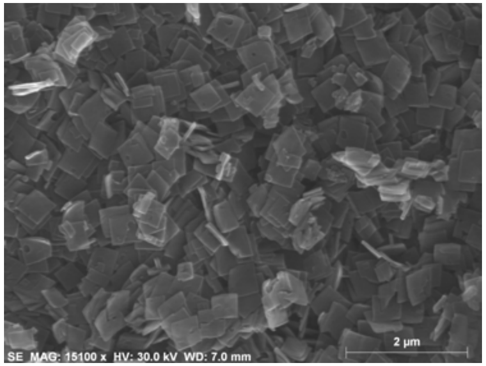


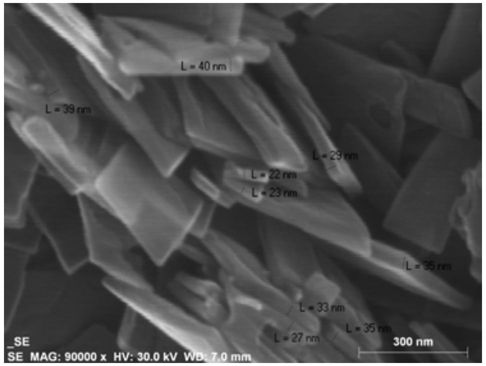
Nanocrystals (reverse micelle)

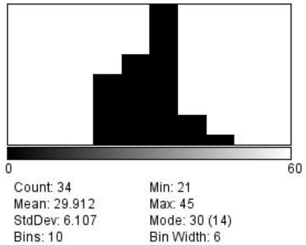




400x400x30 nm

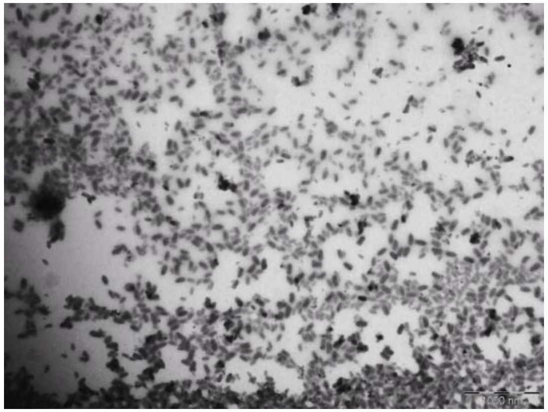


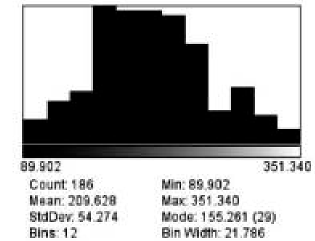


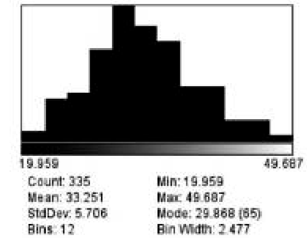


Nanoparticles (PVP coating polymer)

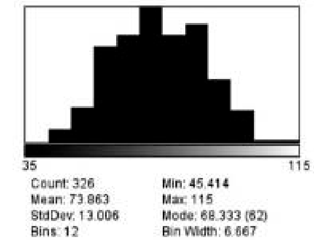
210x140 nm

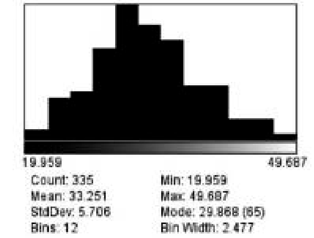






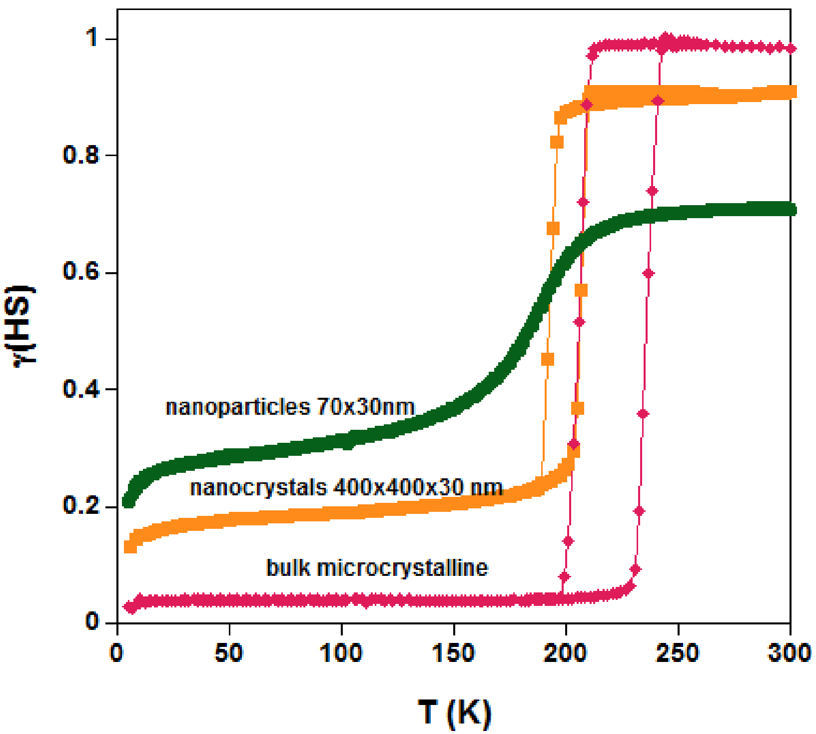
70x30 nm



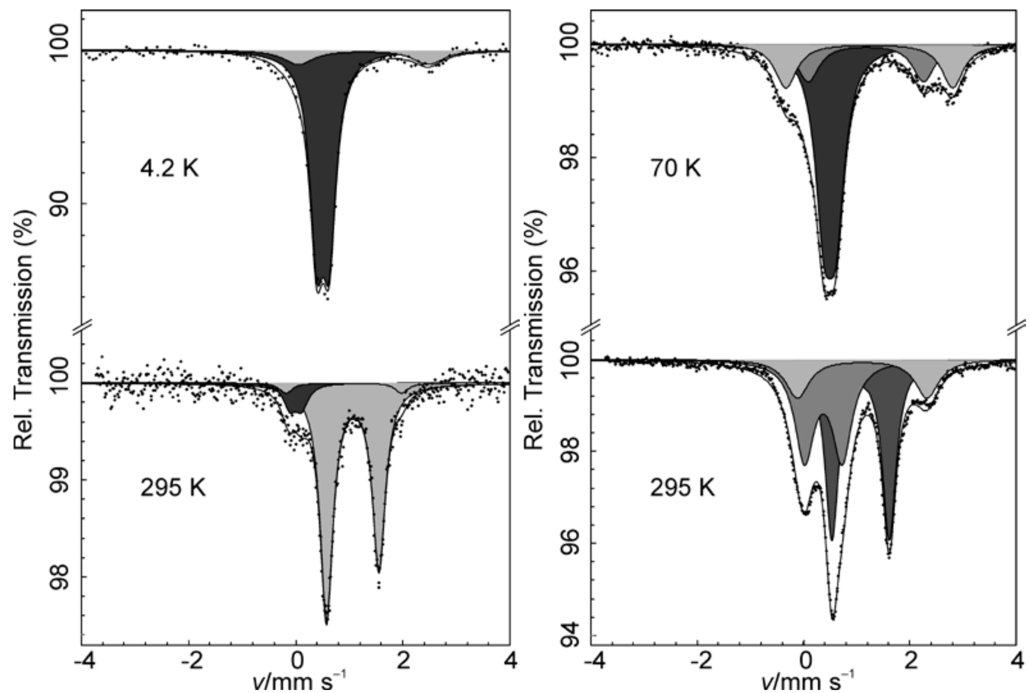


$[Fe(3F\text{-}py)_2Ni(CN)_4]$

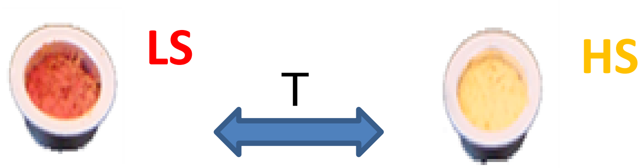
Magnetic properties



Mössbauer spectra



Light grey: HS Dark grey: LS

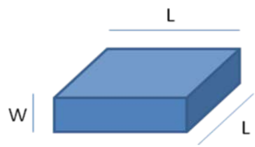


Nanocrystals 400x400x30 nm

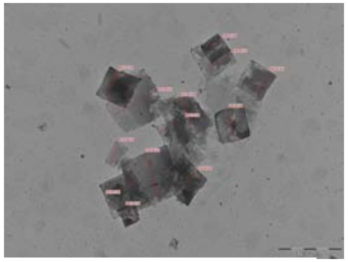
Nanoparticles 70x30 nm

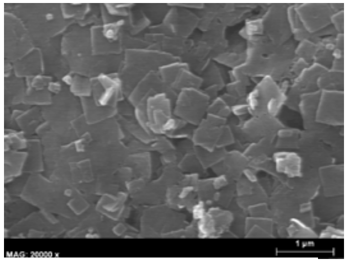
V. Martínez, I. Boldog, A. B. Gaspar, V. Ksenofontov, A. Bhattacharjee, P. Gütlich, J. A. Real, 2010, *submitted.*

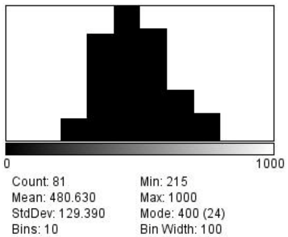
$[Fe(3F\text{-}py)_2Pd(CN)_4]$

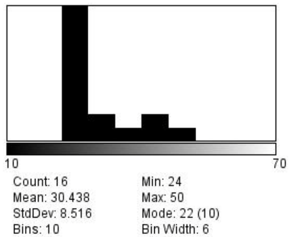


Nanocrystals (reverse micelle)



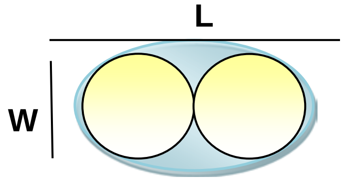


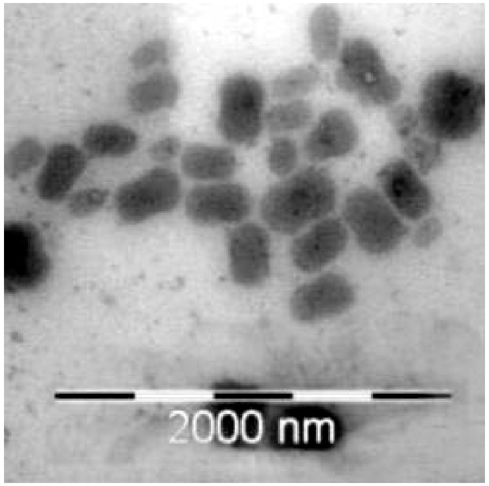


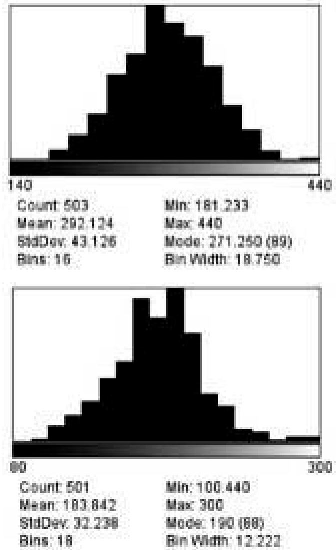


480x480x30 nm

Nanoparticles (PVP coating polymer)



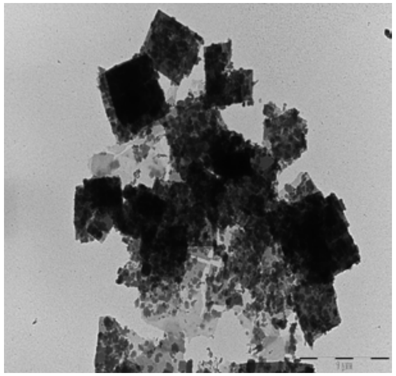


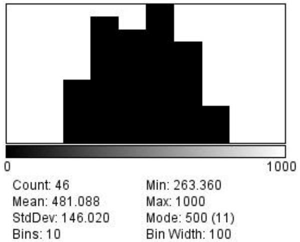


290x180 nm

$[Fe(3F\text{-}py)_2Pt(CN)_4]$

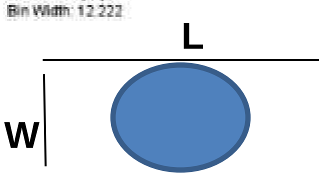
Nanocrystals (reverse micelle)

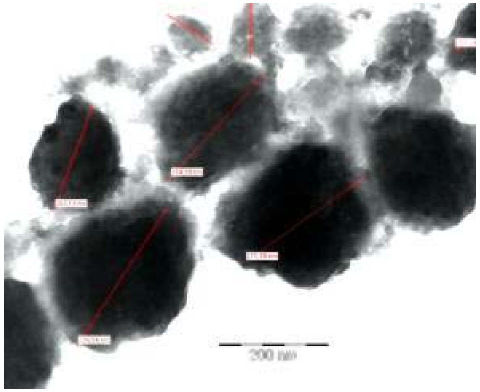


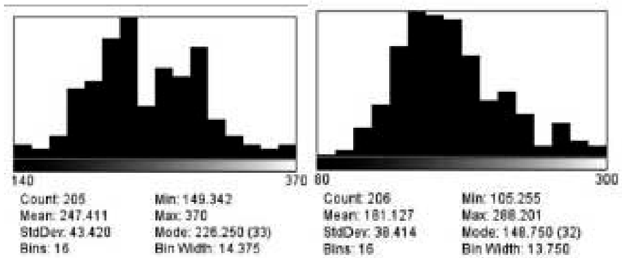


480x480x30 nm

Nanoparticles (PVP coating polymer)

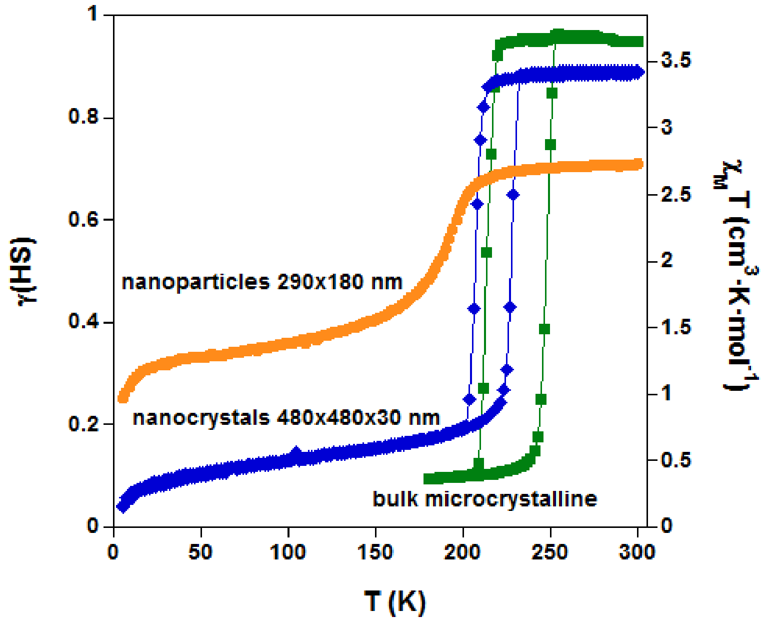




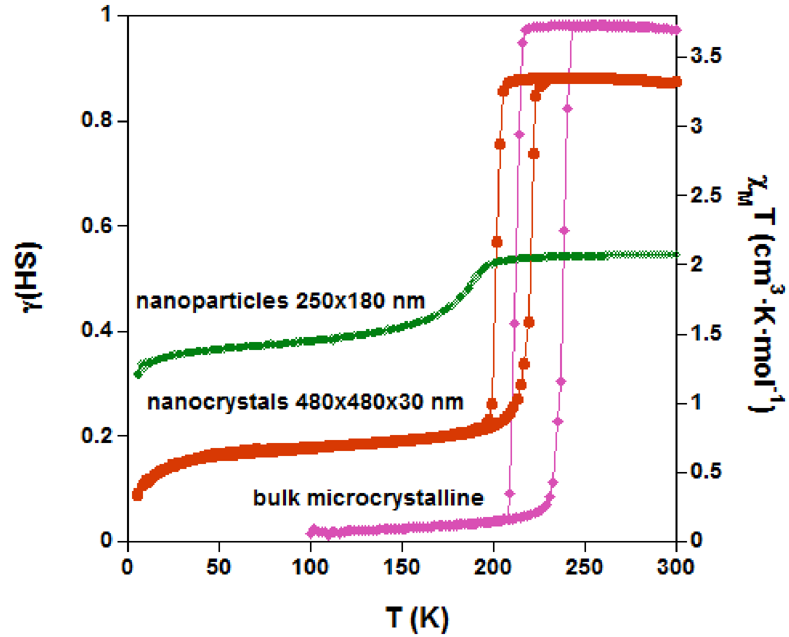


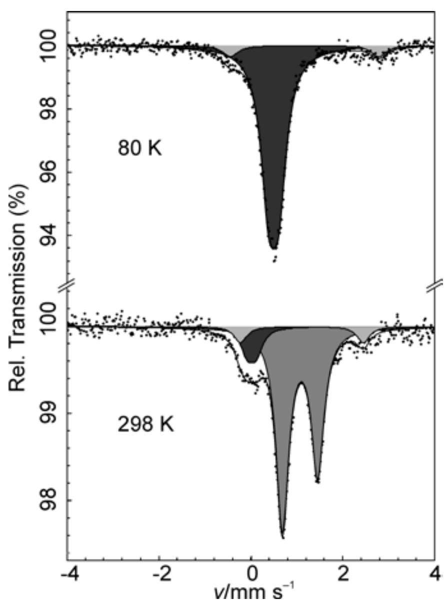
250x180 nm

$[Fe(3F\text{-}py)_2Pd(CN)_4]$

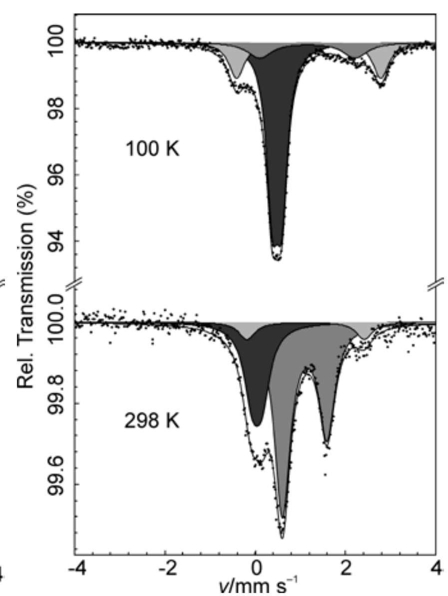


$[Fe(3F\text{-}py)_2Pt(CN)_4]$



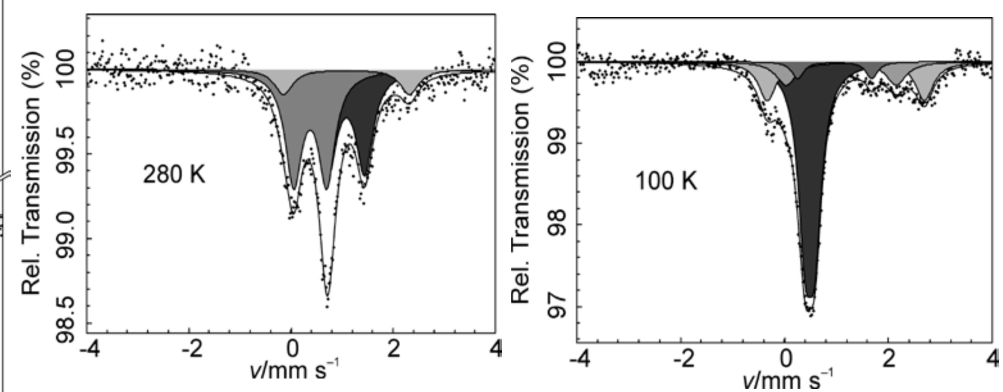


Nanocrystals 480x480x30 nm



Nanoparticles 290x180 nm

Light grey: HS Dark grey: LS

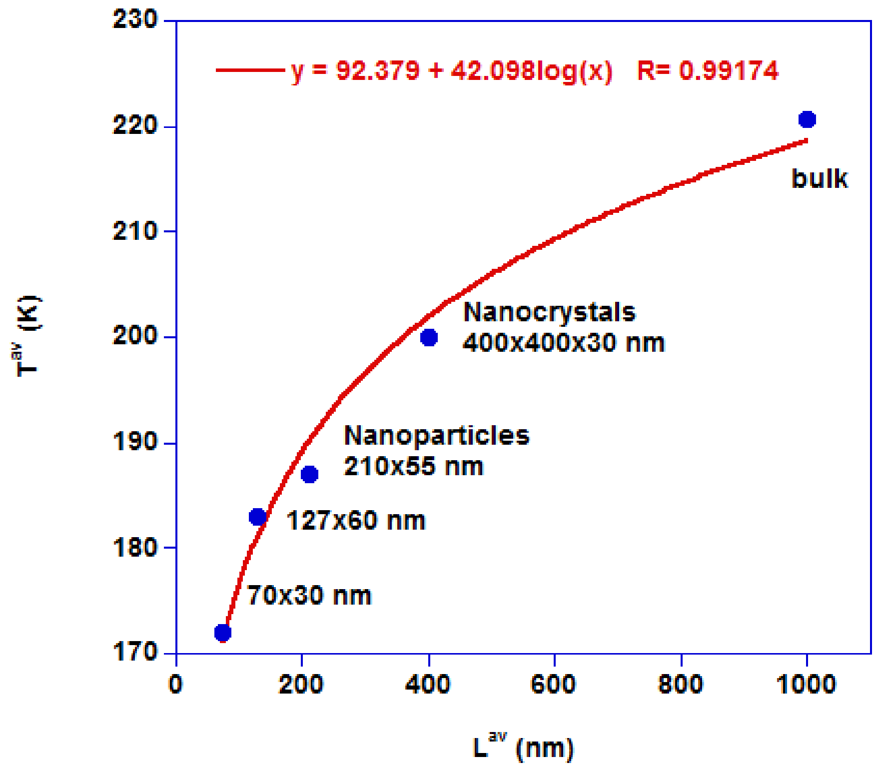


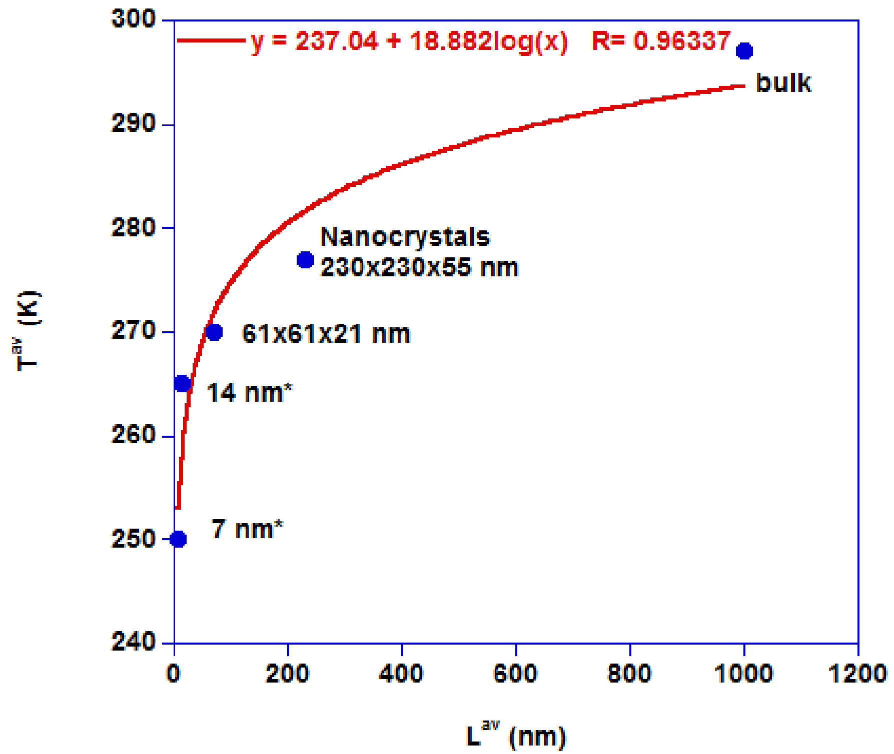
Nanoparticles 250x180 nm

V. Martínez, I. Boldog, A. B. Gaspar, V. Ksenofontov, A. Bhattacharjee, P. Gütlich, J. A. Real, 2010, *submitted.*

2D polymer [$Fe(3F\text{-}py)_2Ni(CN)_4$]

3D polymer [$Fe(pz)Pt(CN)_4$]





* from F. Volatron et al. *Inorg. Chem.* 2008, 47, 6584

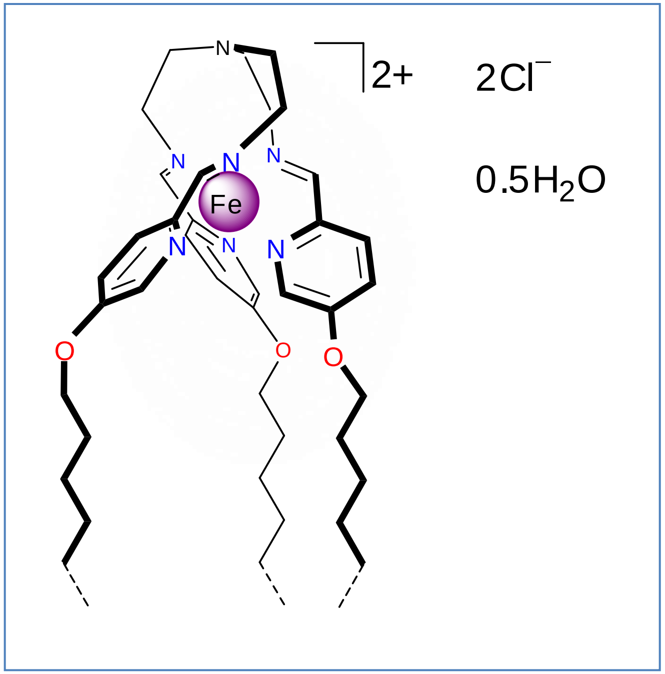
Particle size reduction causes:

-Displacement of Tc's to lower temperatures
-Decrease of hysteresis width
-Appearance of HS and LS residual fractions

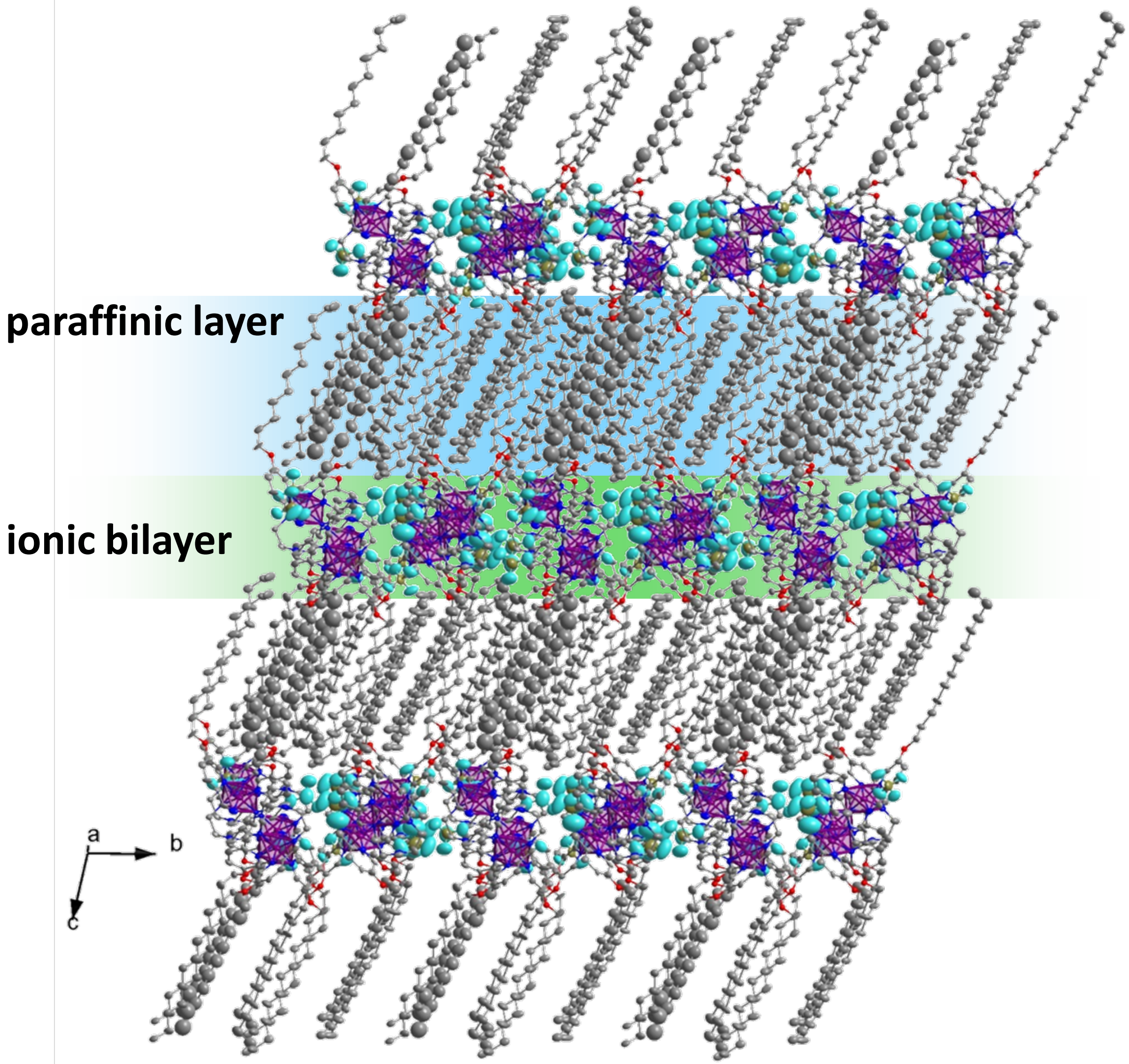
Fe(II) spin crossover metallomesogens
(metal containing liquid crystals)

Fe^{II}-trenH-C_n-(Cl)·$0.5H_2O$

tren = tris(2-aminoethyl)amine



C_{16} C_{18} C_{20}

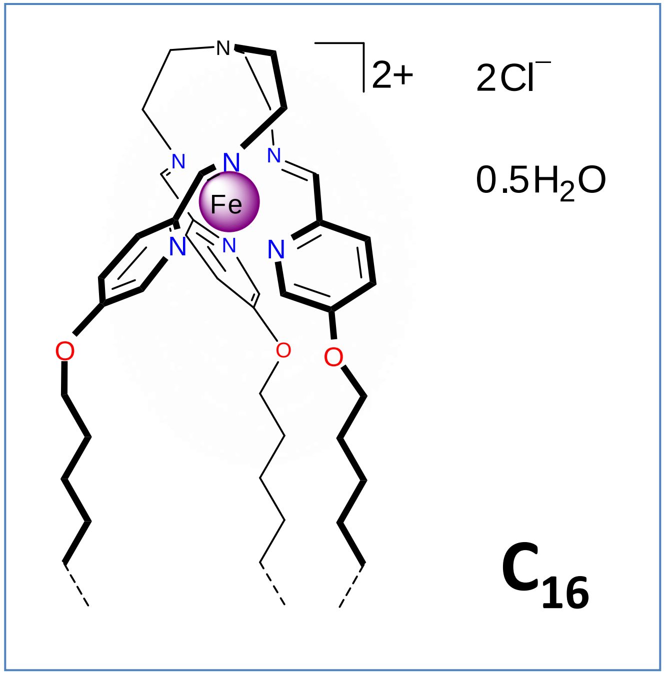


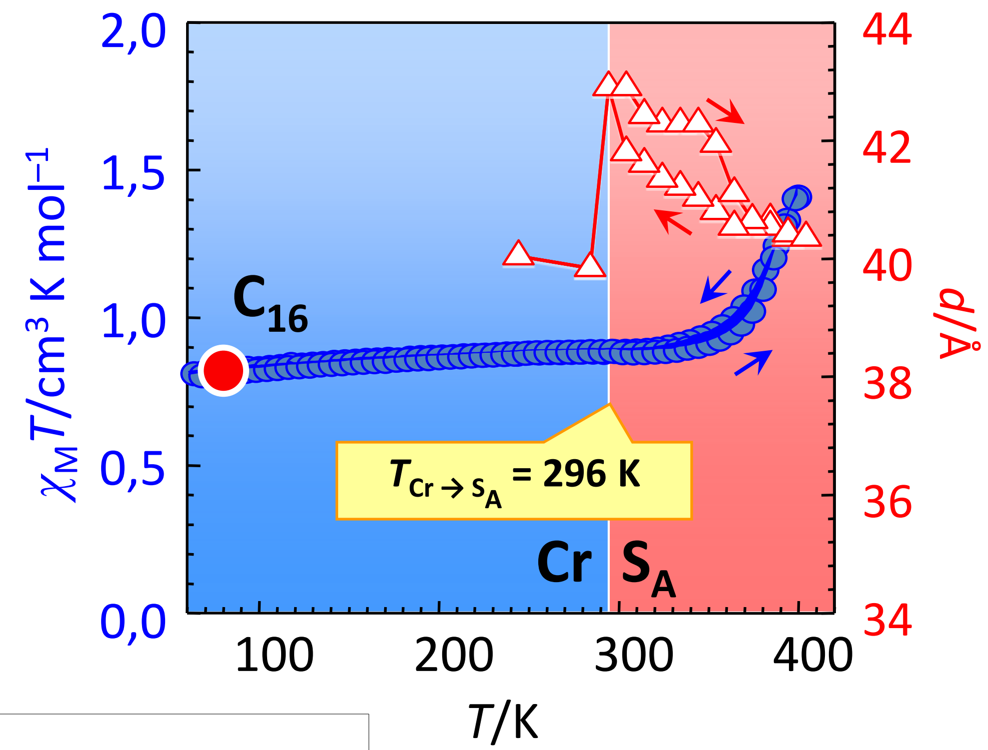
Model compound
Fe^{II}-trenH-C_{12}-(BF_4)

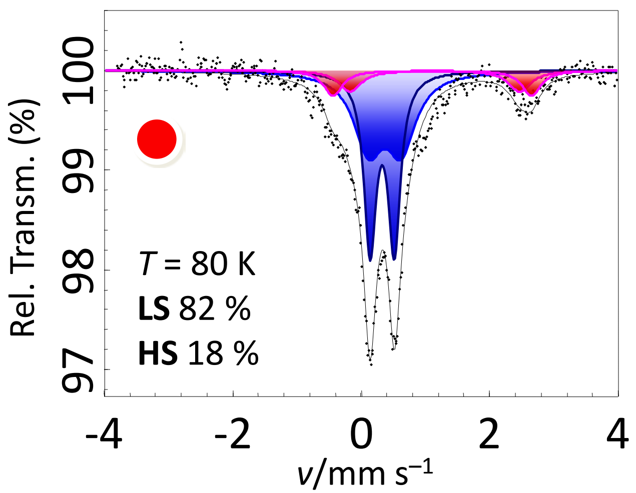
Seredyuk, Gaspar, Ksenofontov, Galyametdinov, Kusz, Gütlich, *J. Am. Chem. Soc.*, 2008, *130*, 1431

Gaspar, Seredyuk, Gütlich, *Coord. Chem. Rev.*, 2009, *253*, 2399

Fe^{II}-trenH-C_{16}-(Cl)·0.5H_2O

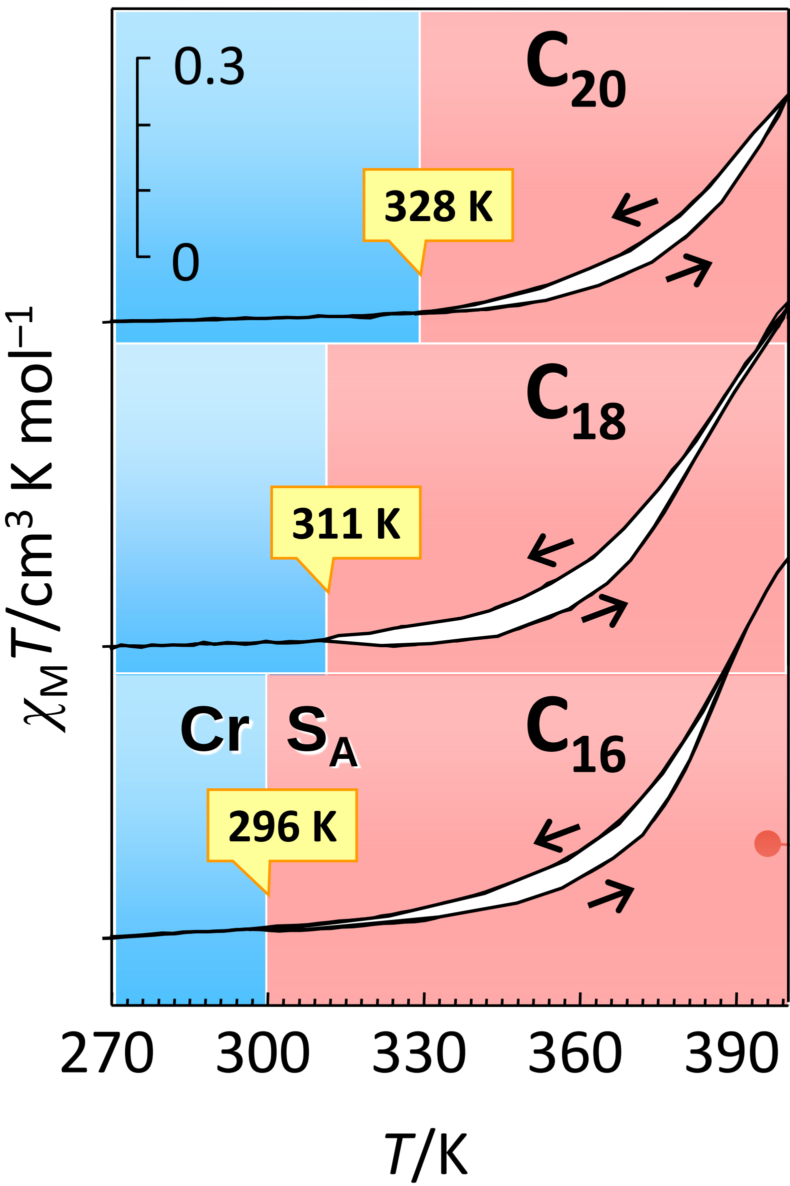






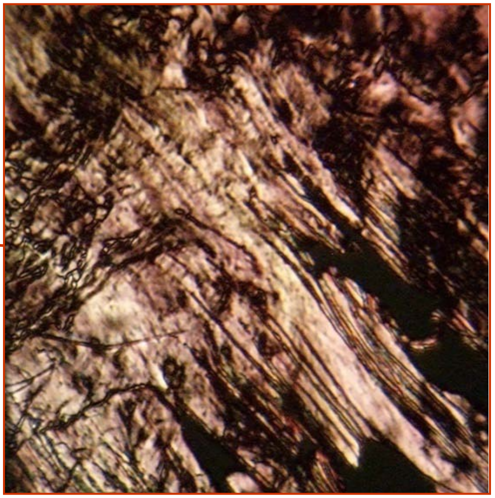
Seredyuk, Gaspar, Ksenofontov, Galyametdinov, Kusz, Gütlich, *J. Am. Chem. Soc.*, 2008, *130*, 1431

Fe^{II}-trenH-C$_n$-(Cl)·0.5H$_2$O, n = 16, 18, 20



Phase transition
Cr → S$_A$
"switches on"
spin-crossover:
Coupled systems

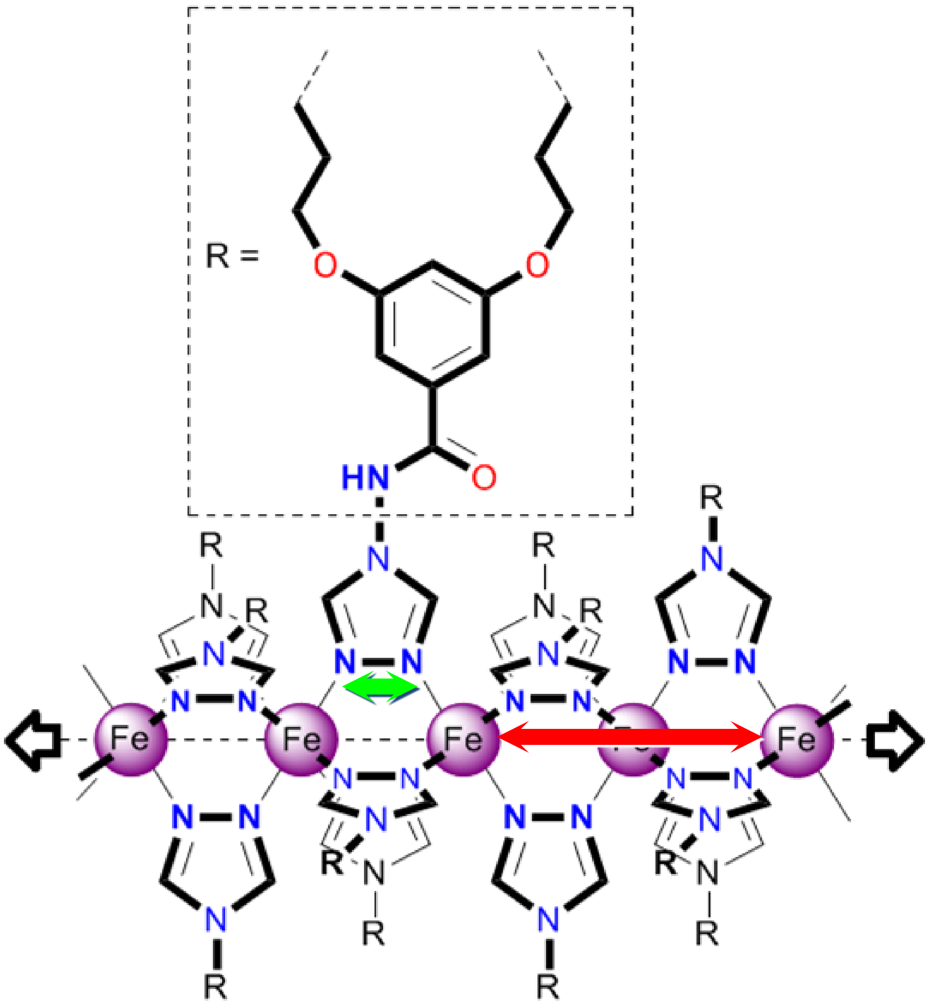
Polarizing optical
microscopy



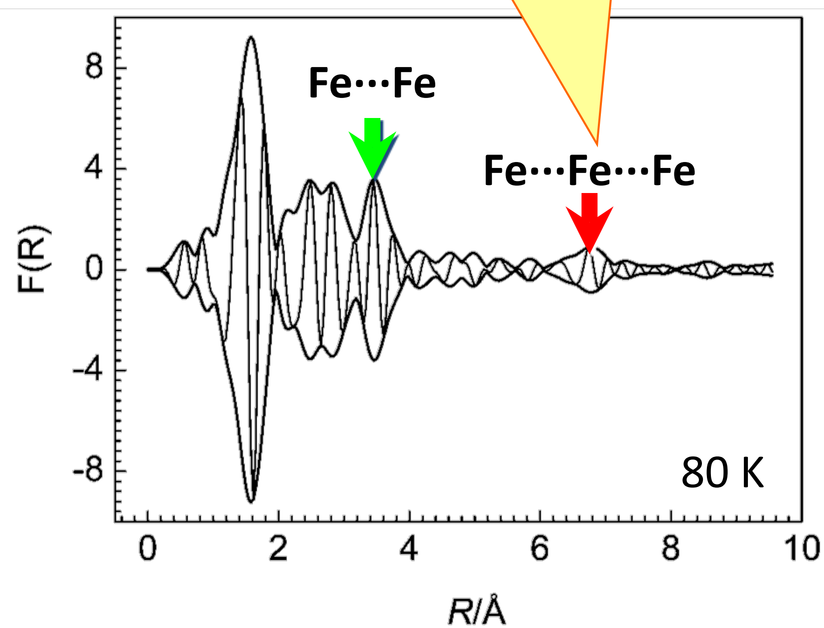
Polymeric one-dimensional metallomesogens of iron(II)

Fe^{II}-tba-C_n-(anion)

C_n-tba = 3,5-bis(alkoxy)-*N*-(4*H*-1,2,4-triazole-4-yl)benzamide



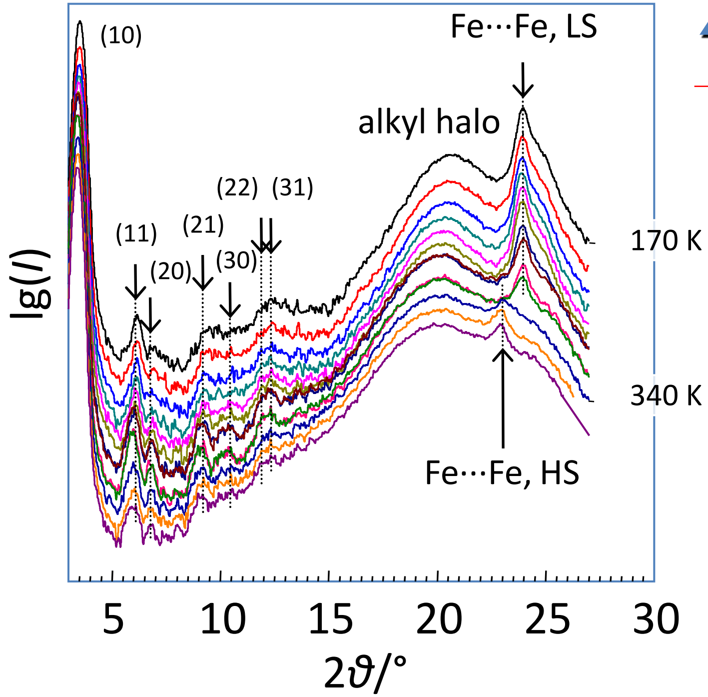
observed when atoms are aligned collinearly

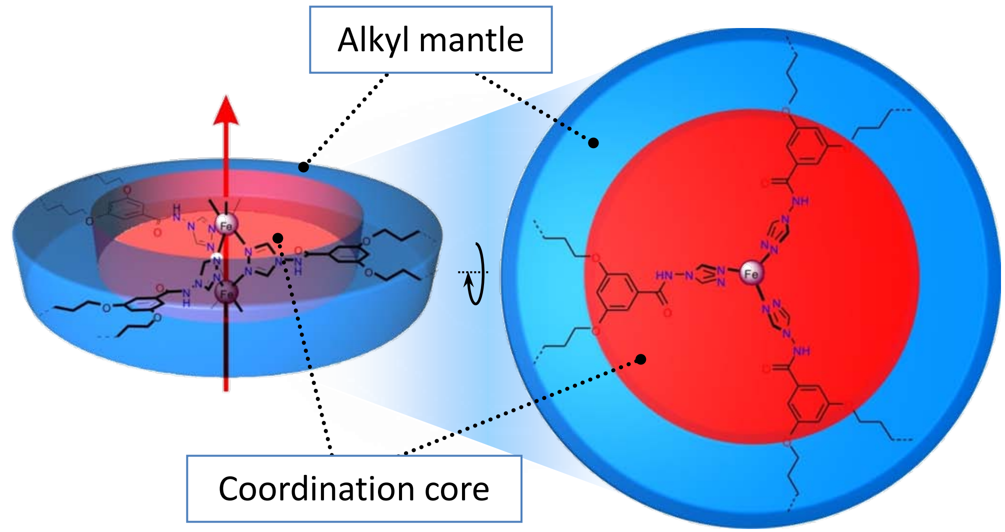


EXAFS data of Fe^{II}-tba-C_{12}-(CF_3SO_3)

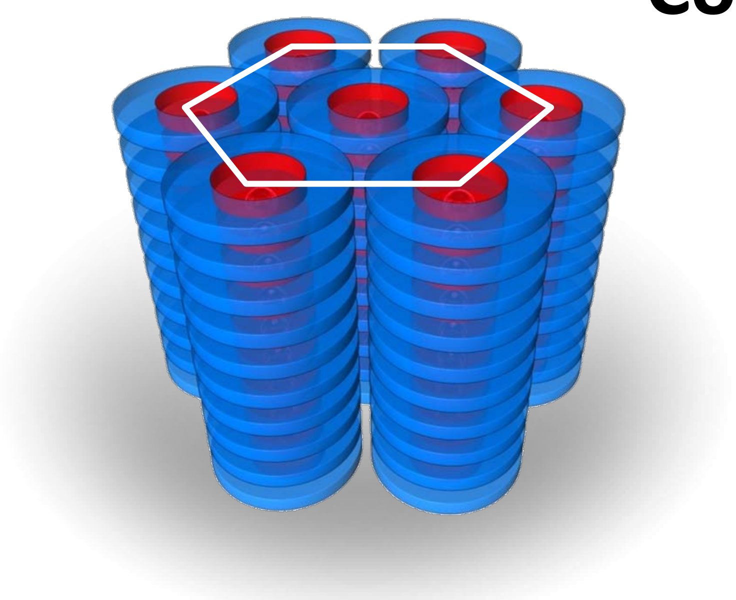
Seredyuk, Gaspar, Ksenofontov, Galyametdinov, Verdaguer, Villain, Gütlich, *Inorg.Chem.* 2008, *47*, 10232

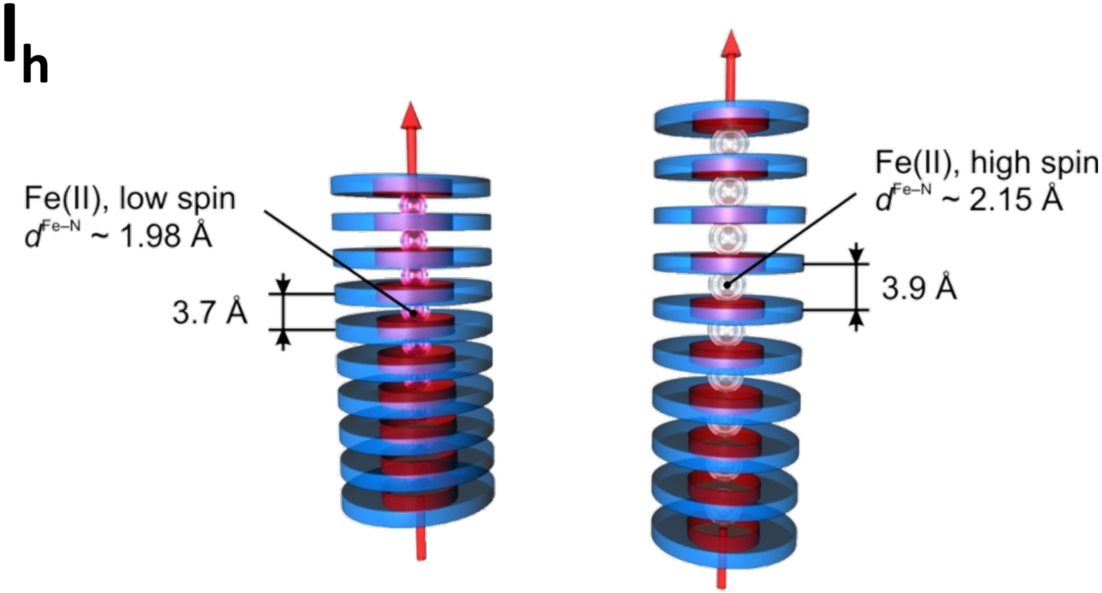
XRD of Fe^{II}-tba-C_{10}-(tosylate)·xH_2O



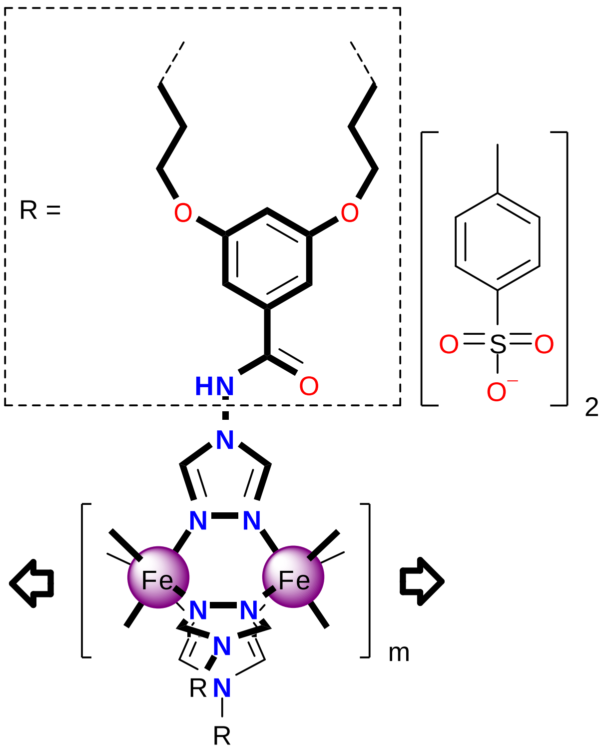


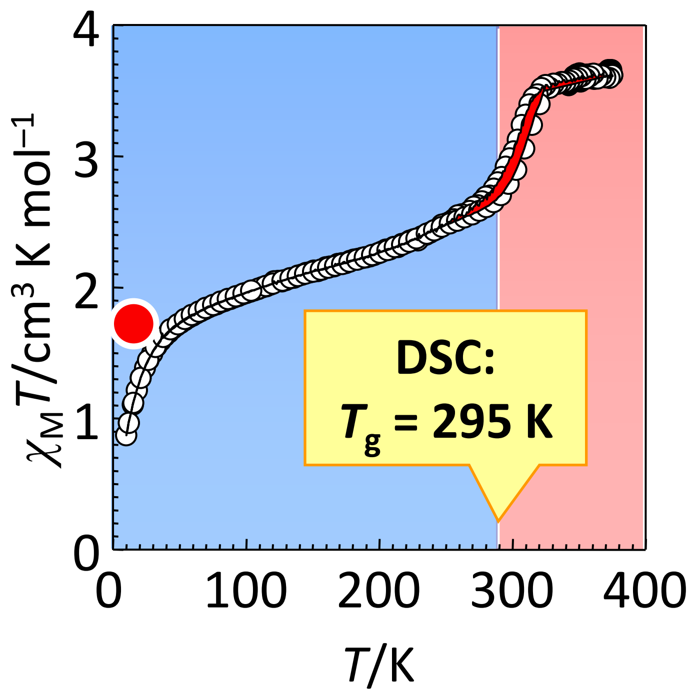
Col$_h$

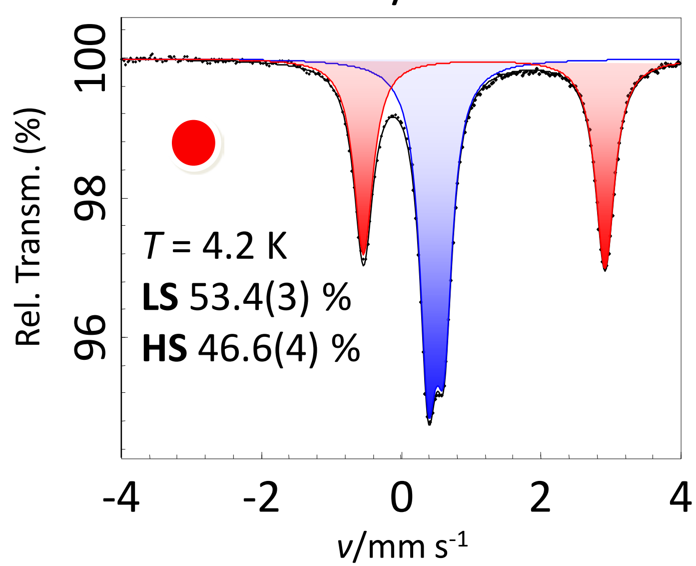




Fe^{II}-tba-C_{10}-(tosylate) (dehydrated)

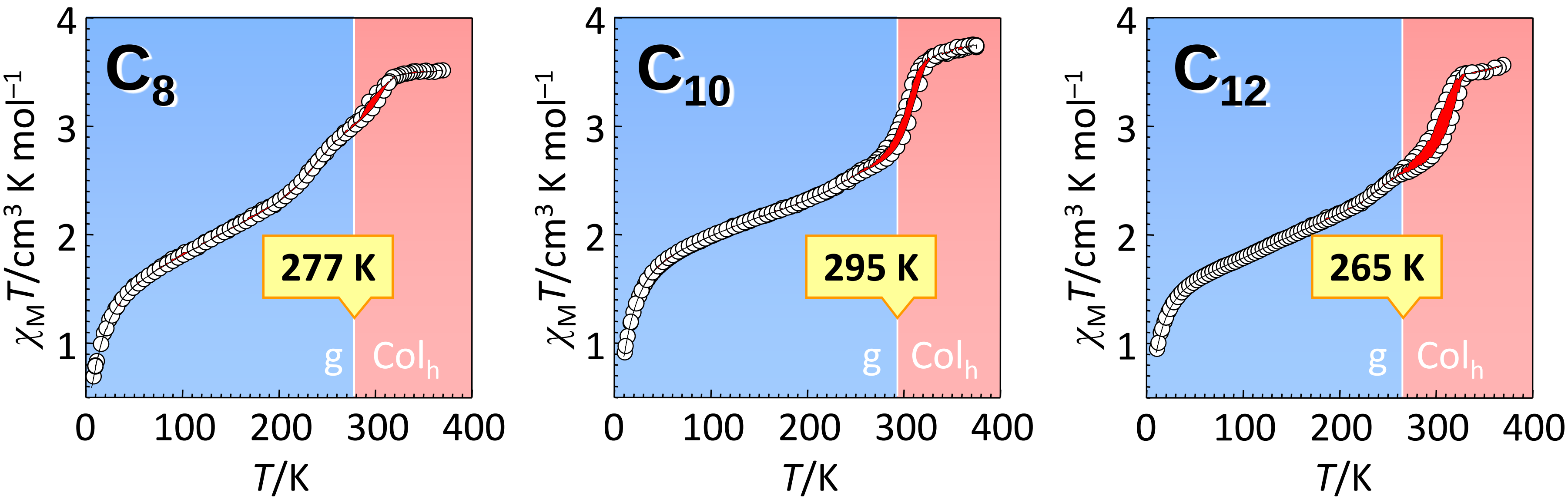






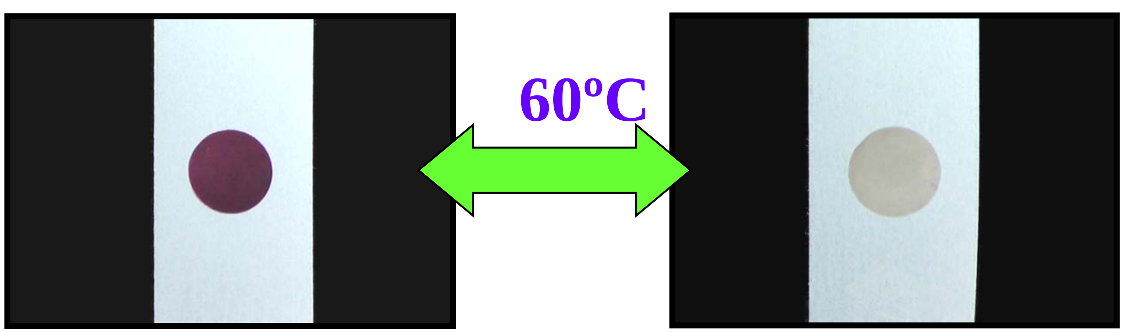
Seredyuk, Gaspar, Ksenofontov, Reiman, Galyametdinov, Haase, Rentschler, Gütlich, ***Chem. Mater.*** **2006, *18*, 2513**

Fe-tba-C_n-(tosylate), n = 8, 10, 12



- Influence of the glass transition;
- Evolution of the hysteresis width in the homologues;
- Similar behavior found for **Fe-tba-C_n-(BF_4), *n* = 8, 10, 12 and Fe-tba-C_n-(CF_3SO_3), *n* = 8, 10, 12**

Coupled transitions



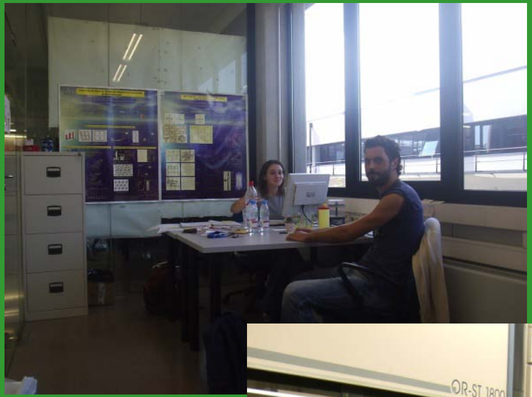
Chem. Mater. 2006, *18*, 2513

Inorg. Chem. 2008, *47*, 10232

Prof. J. A. Real Prof. M. C. Muñoz

Dr. I. Boldog

Dr. V. Martínez



Dr. G. Agustí

F. Muñoz

SMOLMAT, ICMOL Valencia http://www.uv.es/smolmat/

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MICINN, Ministerio de Ciencia e Innovación
GVA, Generalitat Valenciana
DFG, Deutsche Forschungsgemeinschaft
MAGMANET, European Network of Excellence
AvH, Alexander von Humboldt Foundation