Functional Coordination Nanoparticles

Synthesis, magnetic and photomagnetic properties

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Functional Coordination Nanoparticles

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CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

NanoSciences ILE-DE-FRANCE

ANR AGENCE NATIONALE DE LA RECHERCHE

SupNanoMol

MS-MCNP

Objectives

Achieving magnetic bistability at the nanoscale

Investigating the behaviour of one single magnetic object

Integrating bistable objects into devices

Coordination Chemistry at the nanoscale

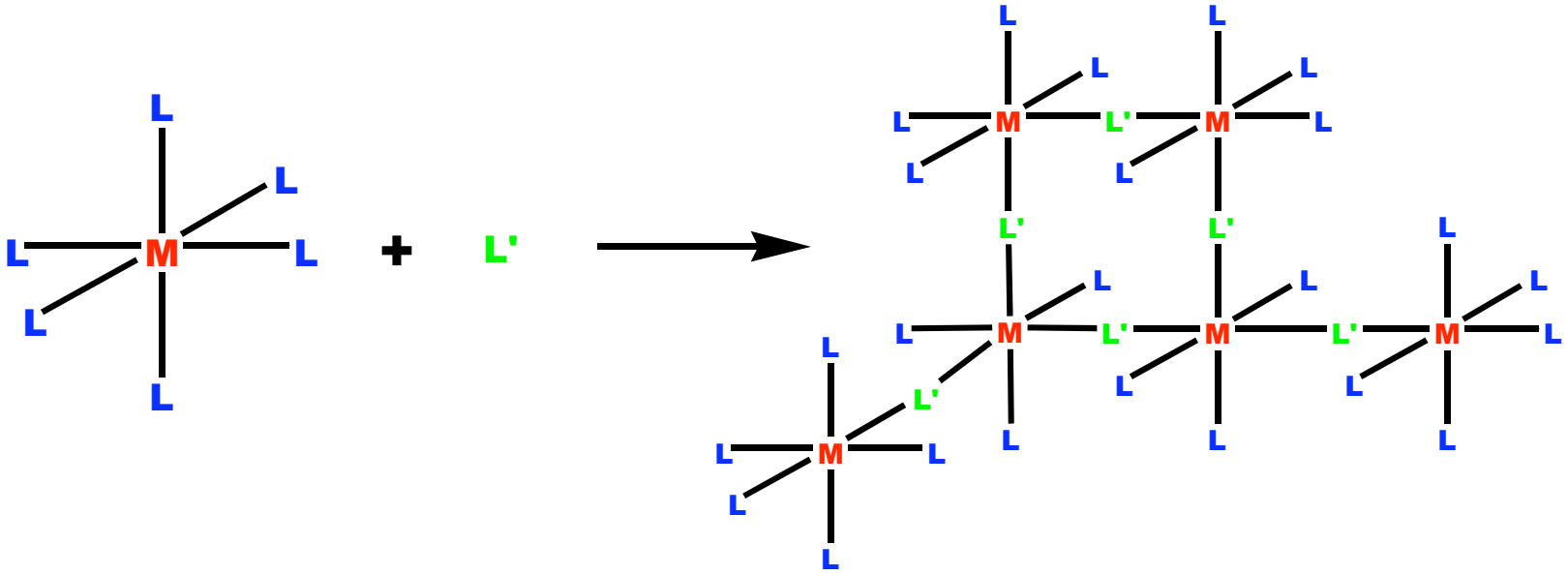
Chemistry at the Nanoscale

Nanoparticles of Coordination Networks
(magnetism, photomagnetism, spin crossover
chirality, porosity, luminescence)

Organizing nanoobjects (molecules…) on surfaces
(behavior of a single molecule)

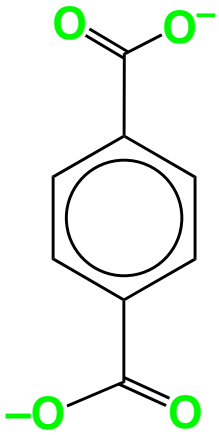
Coordination Nanoparticles

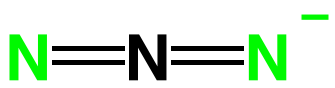
Coordination nanoparticles are obtained by confining the growth of coordination networks that occurs via ligand substitution in the coordination sphere of a metal ion



L' a bridging entity

ligand

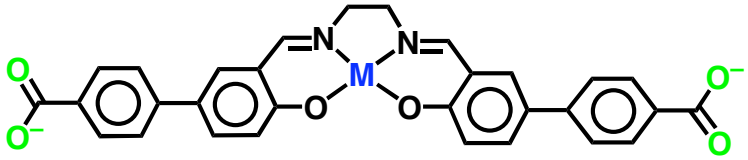


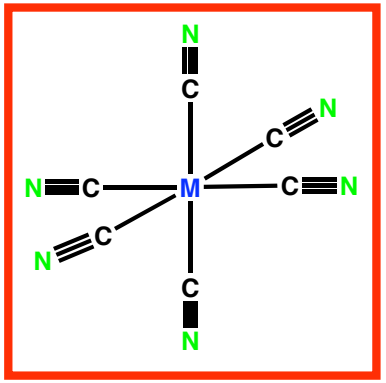


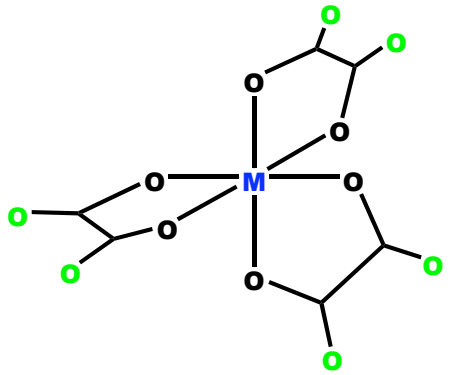
Monometallic objects

or

complex

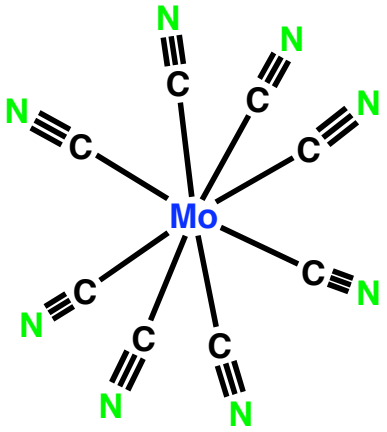


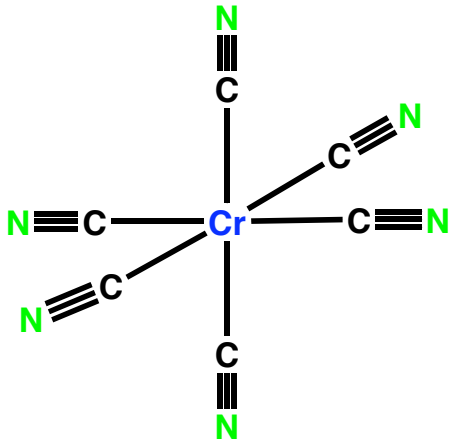


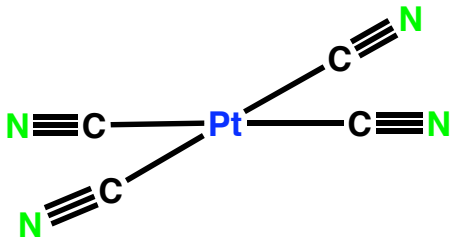


Bimetallic objects

Cyanide Bridging Molecules







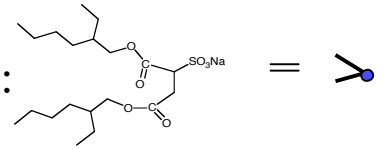
Photomagnetism

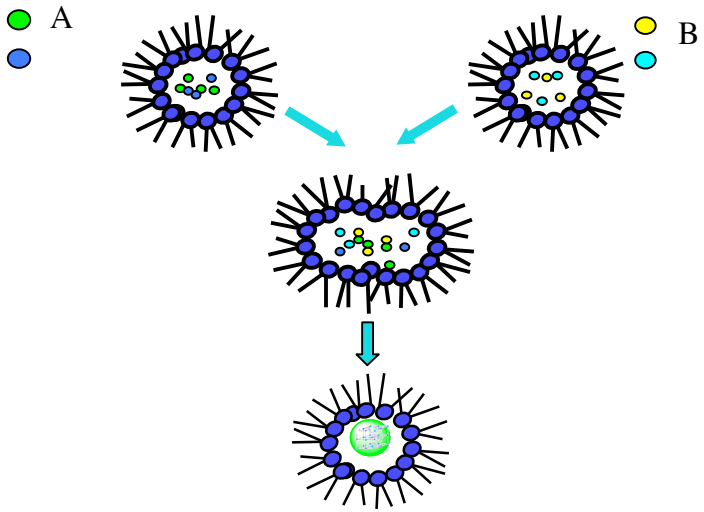
Superparamagnetism

Spin crossover

Synthetic methods

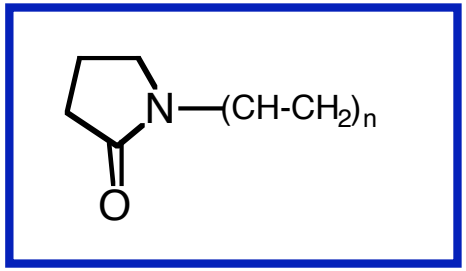
microemulsion

AOT : 

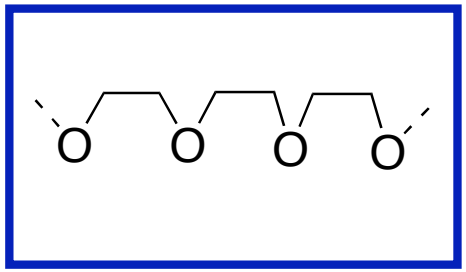


organic polymers

Polyvinylpyrrolidone



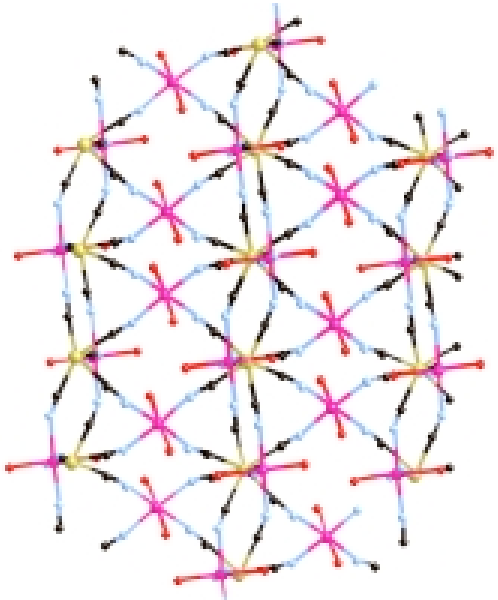
Polyethyleneglycol



Uemura, Kitagawa, JACS, 2003

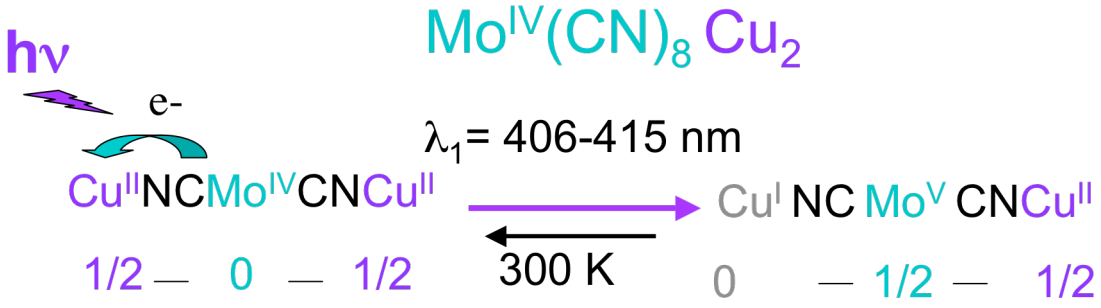
Photomagnetic Nanoparticles

$Mo(CN)_8^{4-} + 2\ Cu^{II}$ ⟶



$M^{IV}(CN)_8M^{II}_2(H_2O)_2$

M = W ou Mo



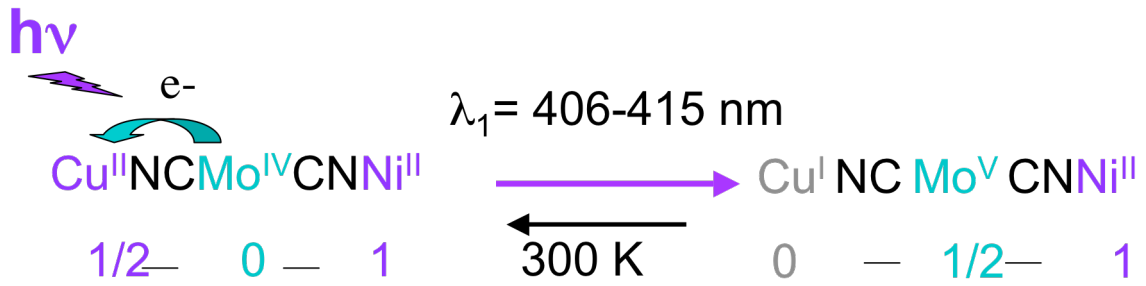
C. Mathonière, O. Kahn et al, Inorg. Chem. 2001
K. Hashimoto et al Syn. Metals, 2001

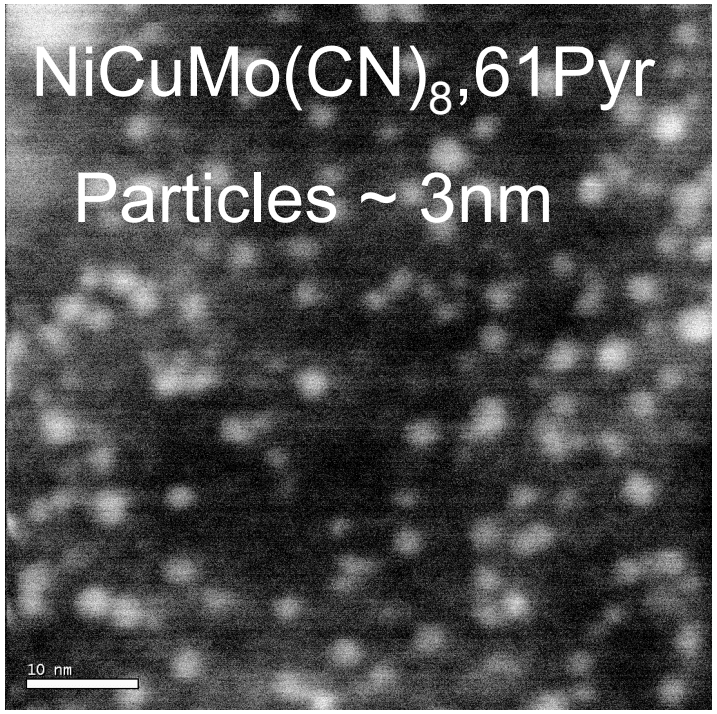
Introducing anisotropy

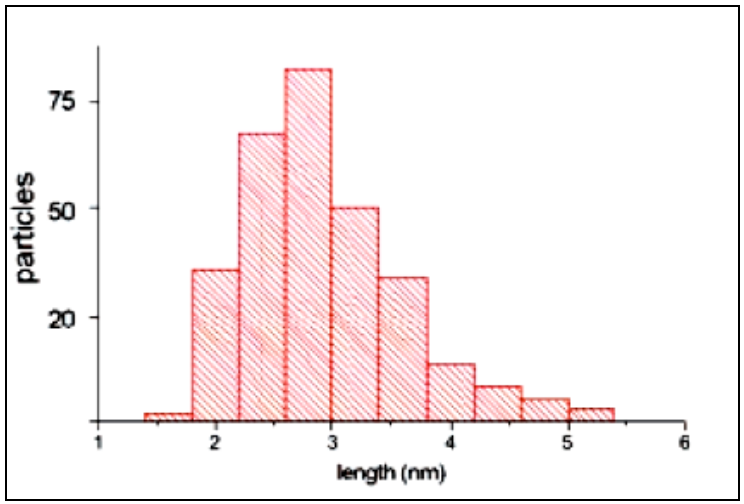
Blocking of the magnetization needs magnetic anisotropy

$$Mo(CN)_8^{4-} + 1\ Cu^{II} + 1\ Ni^{II} \longrightarrow Mo^{IV}(CN)_8\ Cu^{II}Ni^{II}$$

trimetallic 3 nm particles

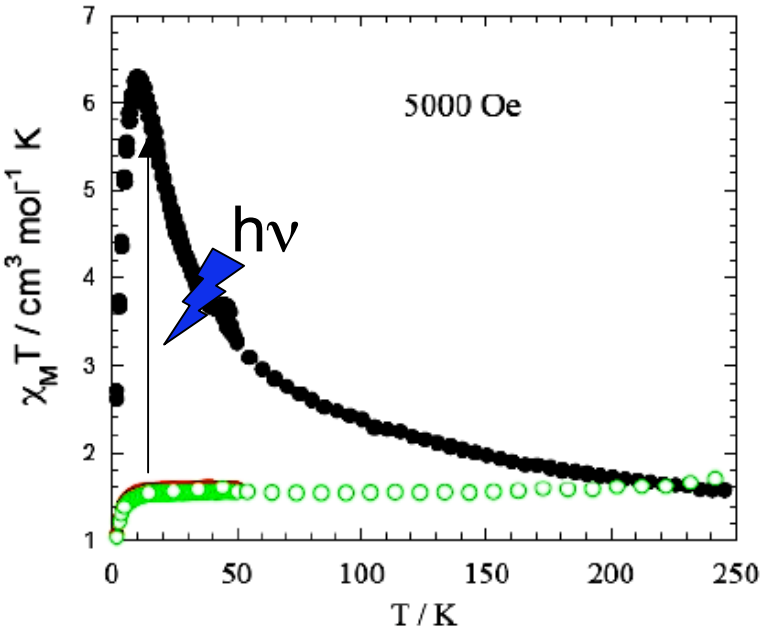




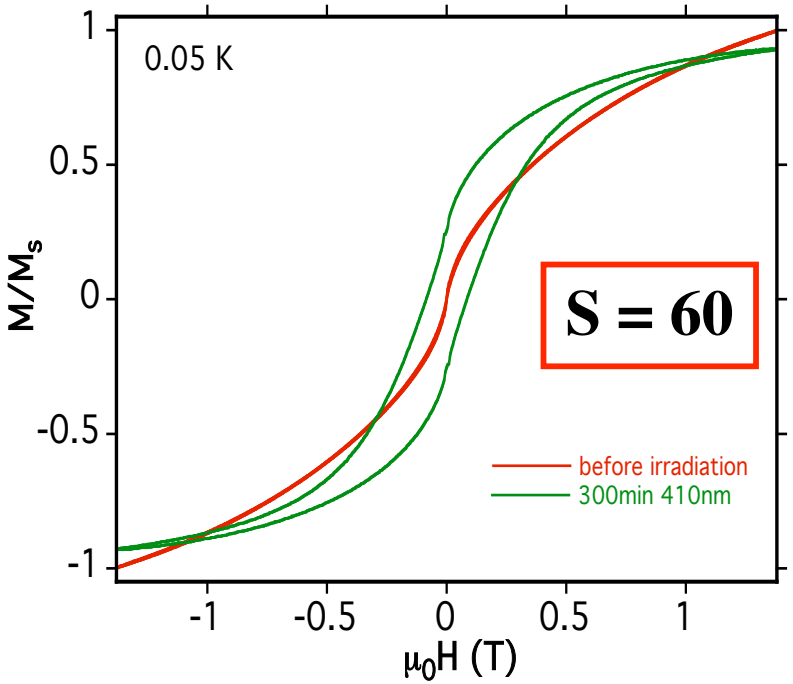


C, **N**, **O**, **Ni** et **Cu** detected by EELS (by A. Gloter, O. Stephan, LPS-Orsay)

light induced blocking of the magnetization



C. Mathonière, ICMCB

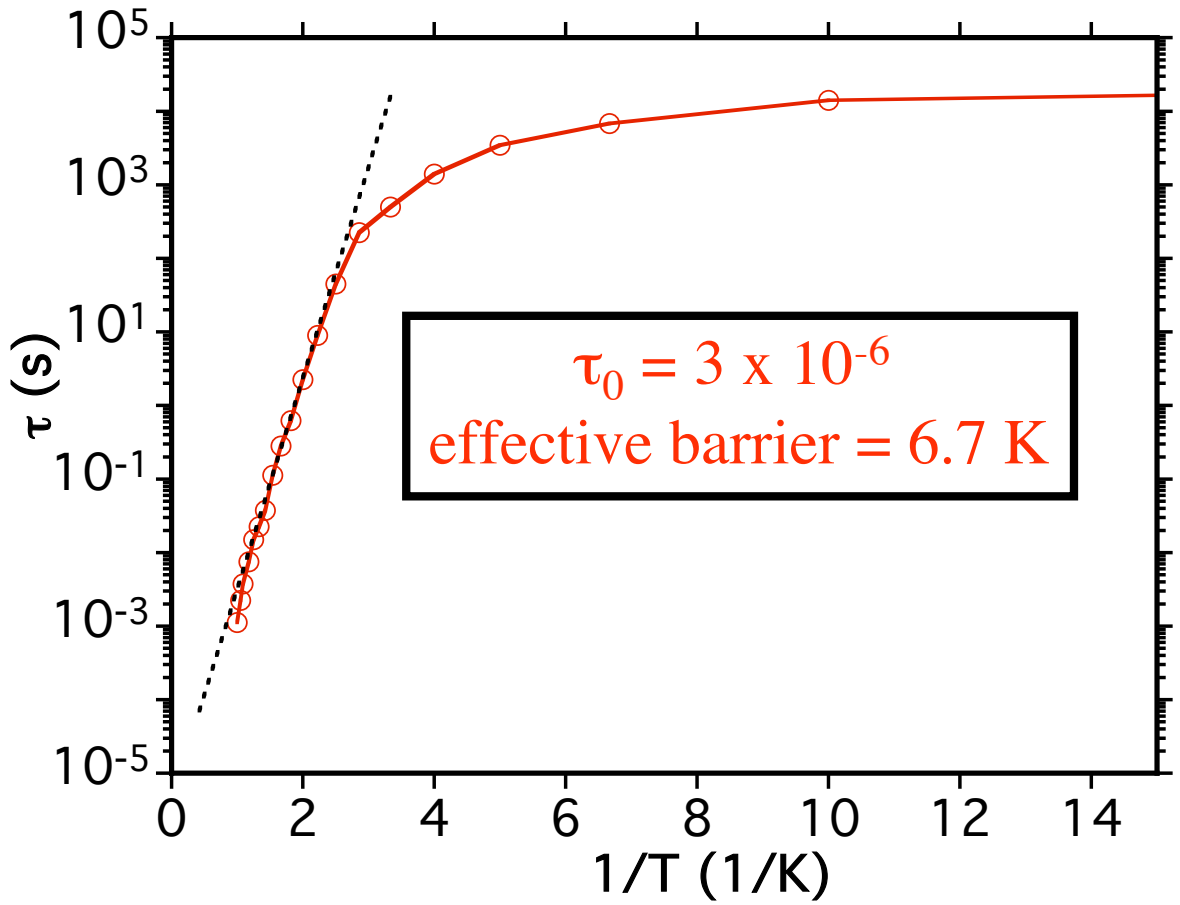


Microsquid experiments on a film of nanoparticles by W. Wernsdorfer, Institut Néel

D. Brinzei, L. Catala, C. Mathonière, W. Wernsdorfer, A. Gloter, O. Stephan, T. Mallah, *J. Am. Chem. Soc.*, **2007**, *129*, 3778.

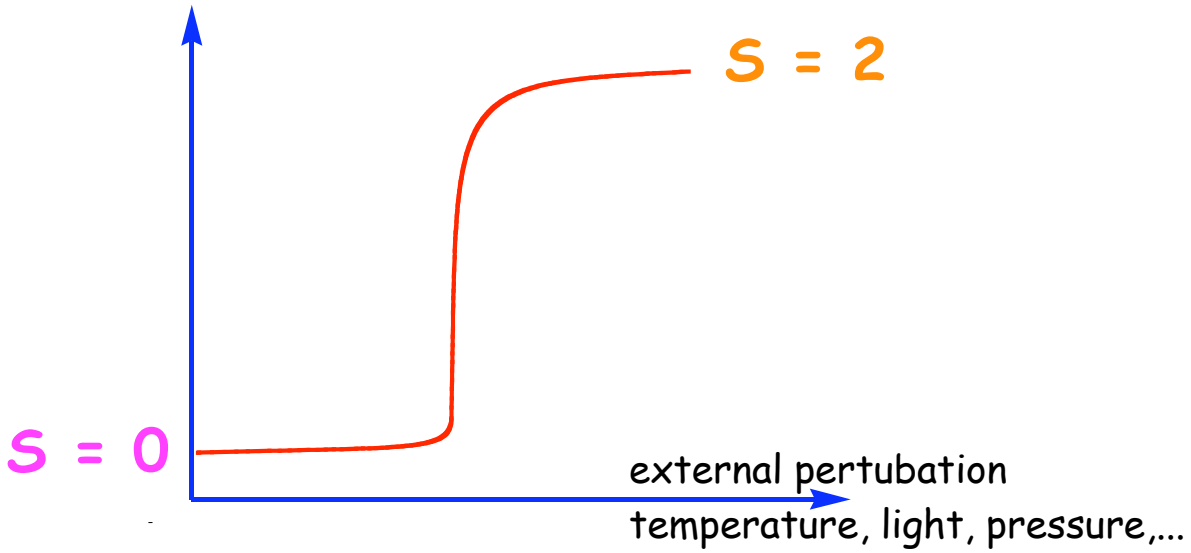
relaxation

3 nm particles spin around 80

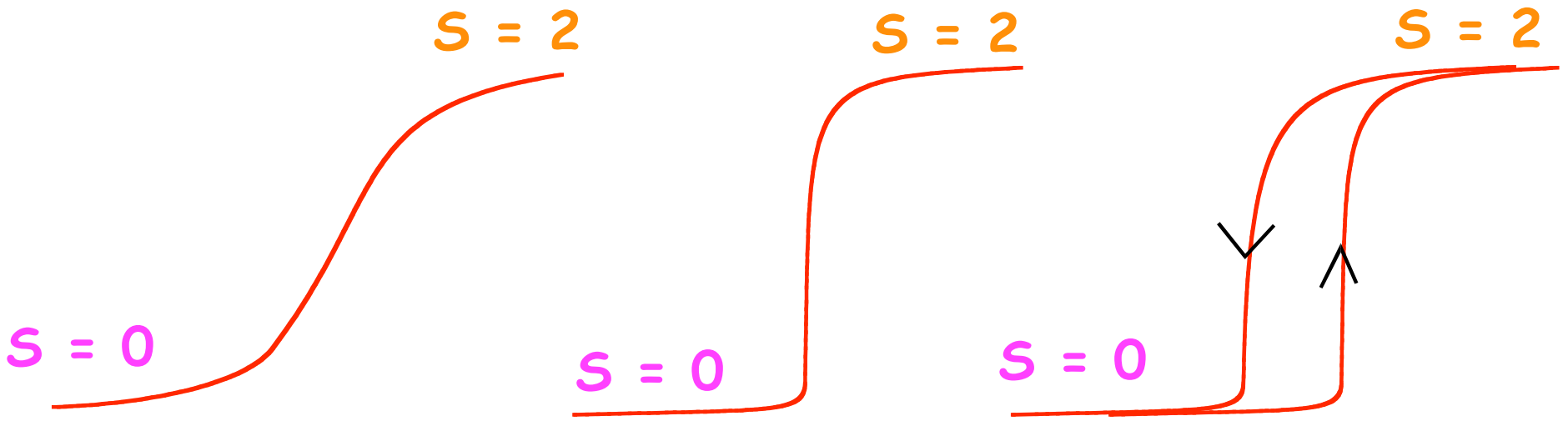


spin crossover nanoparticles

what is spin crossover ??



Bistability in spin crossover systems



smooth conversion

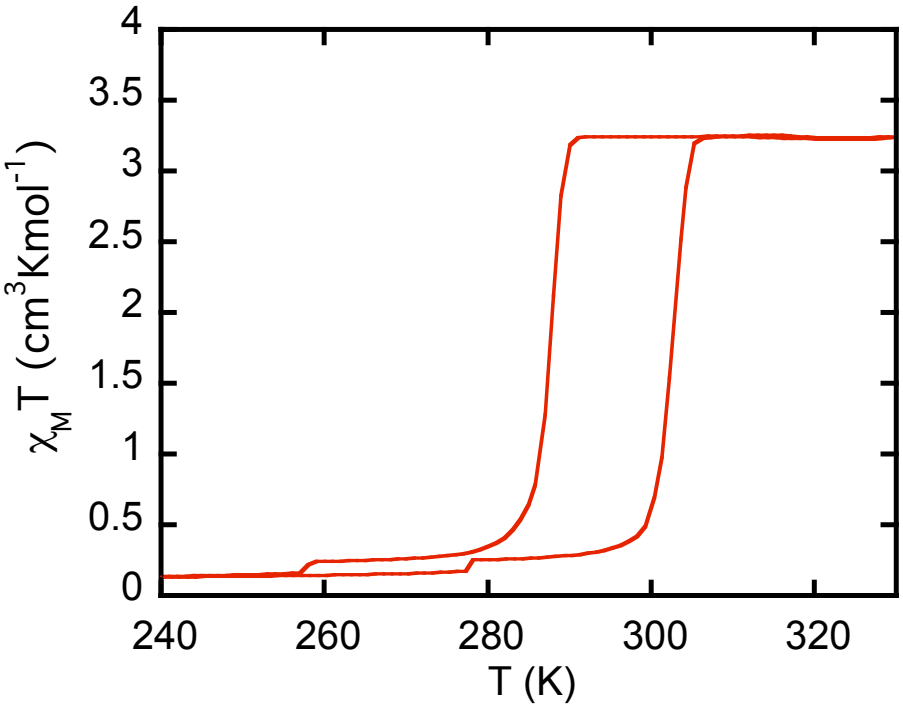
sharp transition

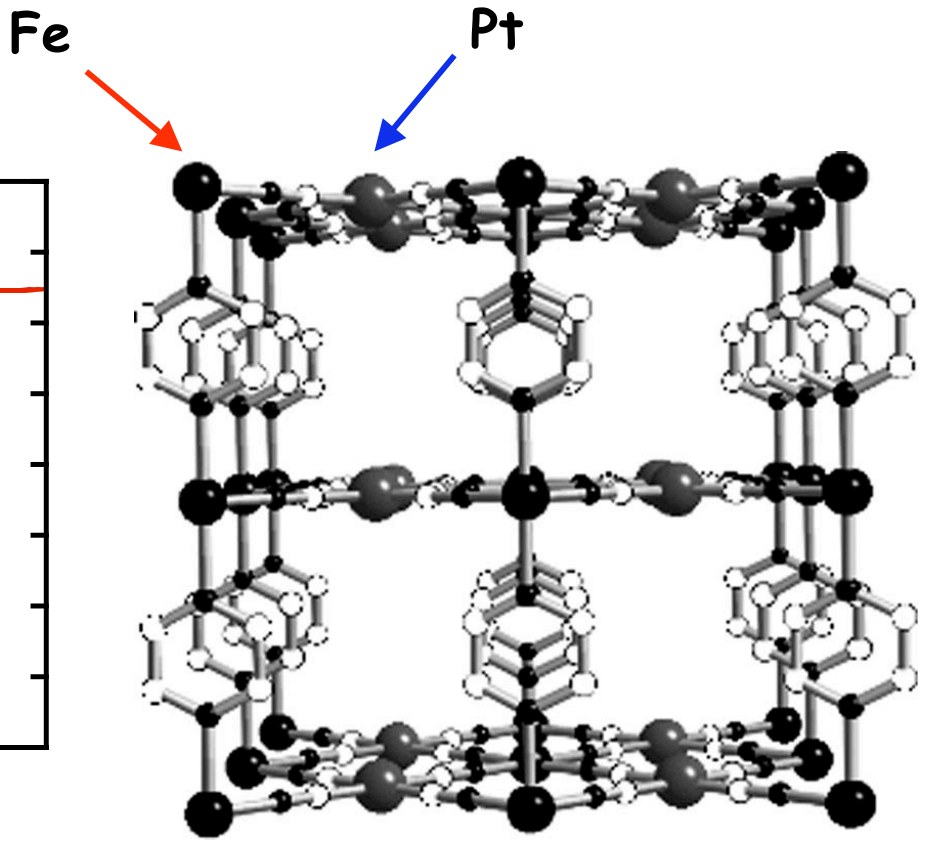
hysteresis loop
and
bistability

Only first order sharp transitions lead to hysteresis and bistability because of long range interactions

$Fe(pyrazine)Pt(CN)_4$ bulk

$Fe(BF_4)_2$ + pyrazine + $K_2Pt(CN)_4$ ⟶ $Fe(pyrazine)Pt(CN)_4$





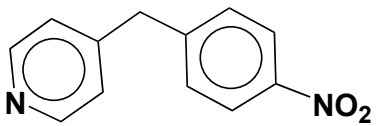
J. A. Real Inorg. Chem 2001

Fe(pyrazine)Pt(CN)$_4$ nanocrystals synthesis

Microemulsion of $Fe(BF_4)_2$ + pyrazine
+
Microemulsion of $K_2Pt(CN)_4$

↓

stable microemulsion and a change of color

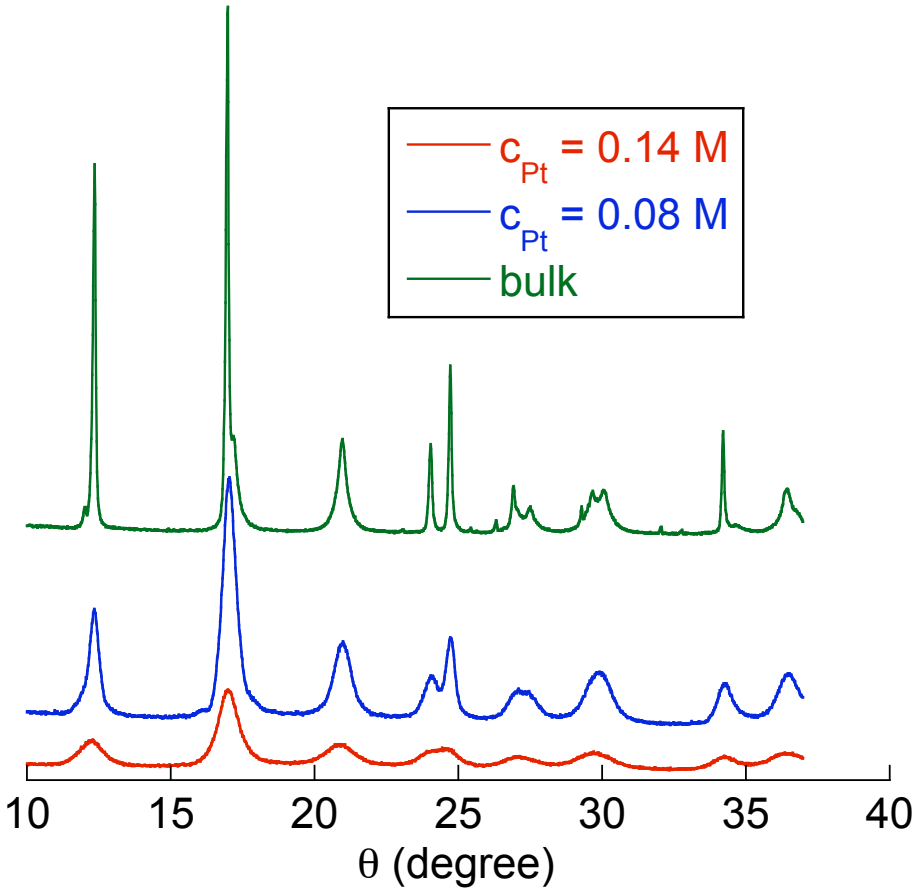


↓ acetone

Orange powder

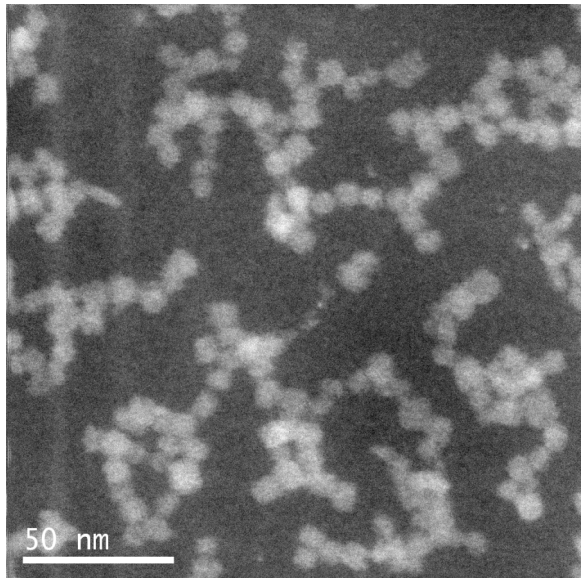
$w = [H_2O]/[AOT] = 10$

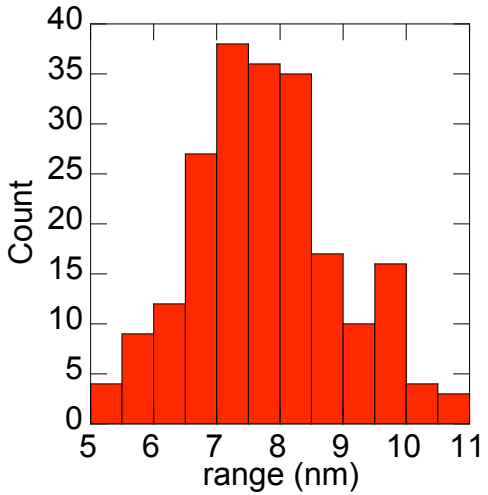
$c_{Pt} = 0.08, 0.14$ M



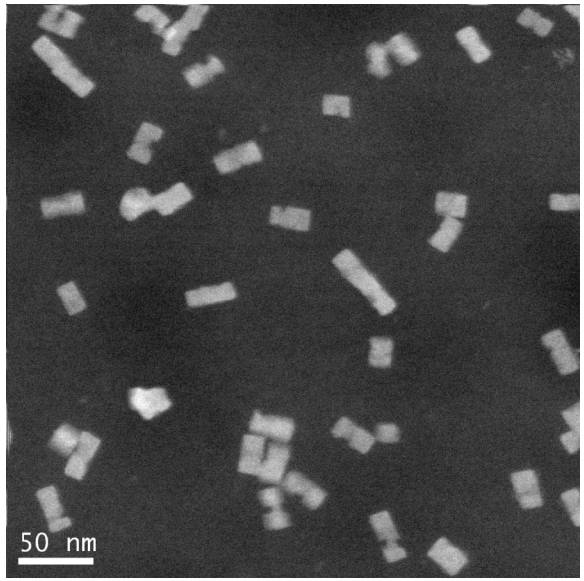
Microemulsion dark field STEM images

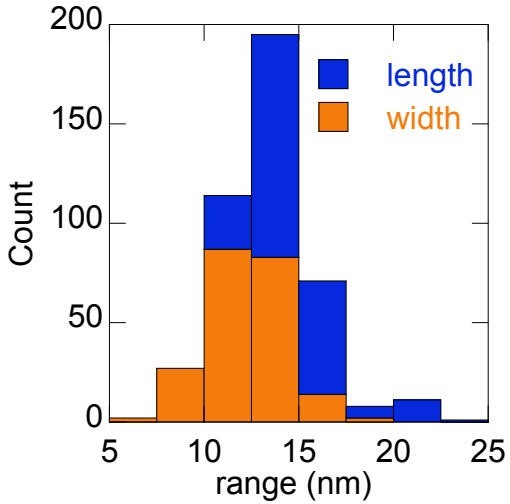
7.7x7.7 nm (σ = 1.1), c_{Pt} = 0.14M





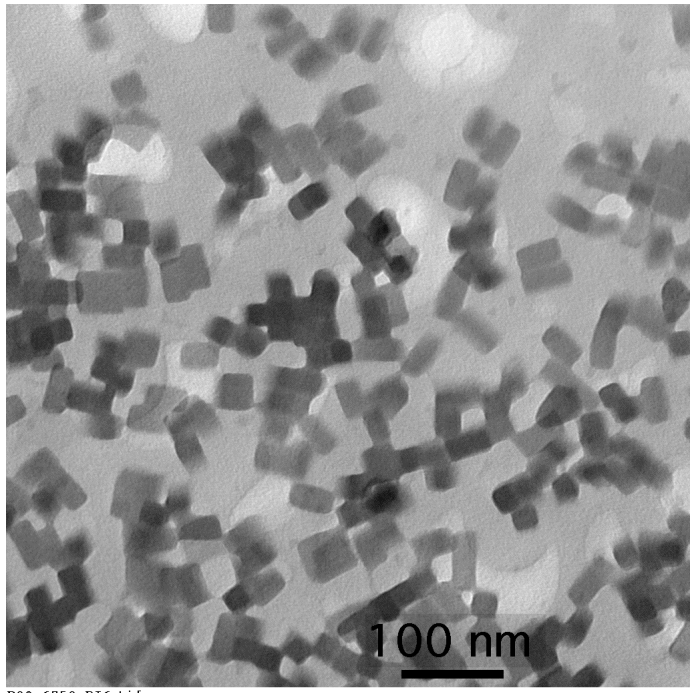
14.7x12.1 nm (σ = 2.1), c_{Pt} = 0.08M



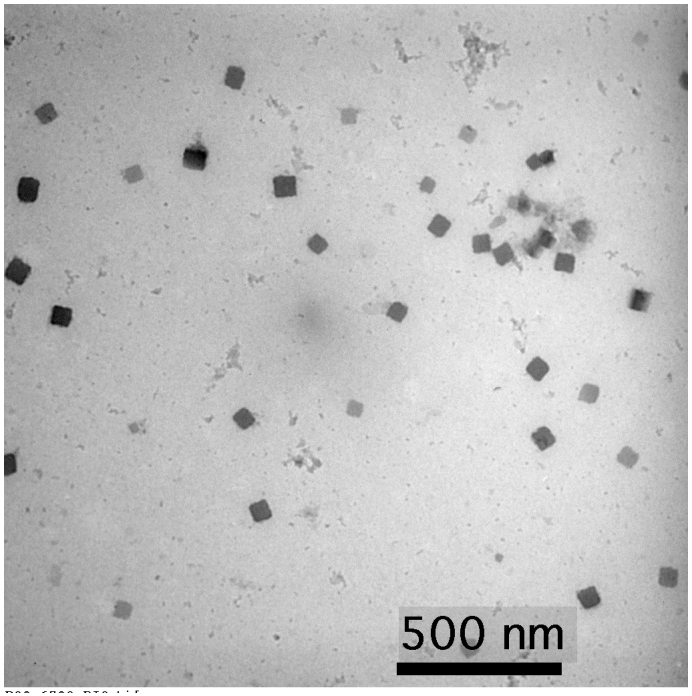


Size control

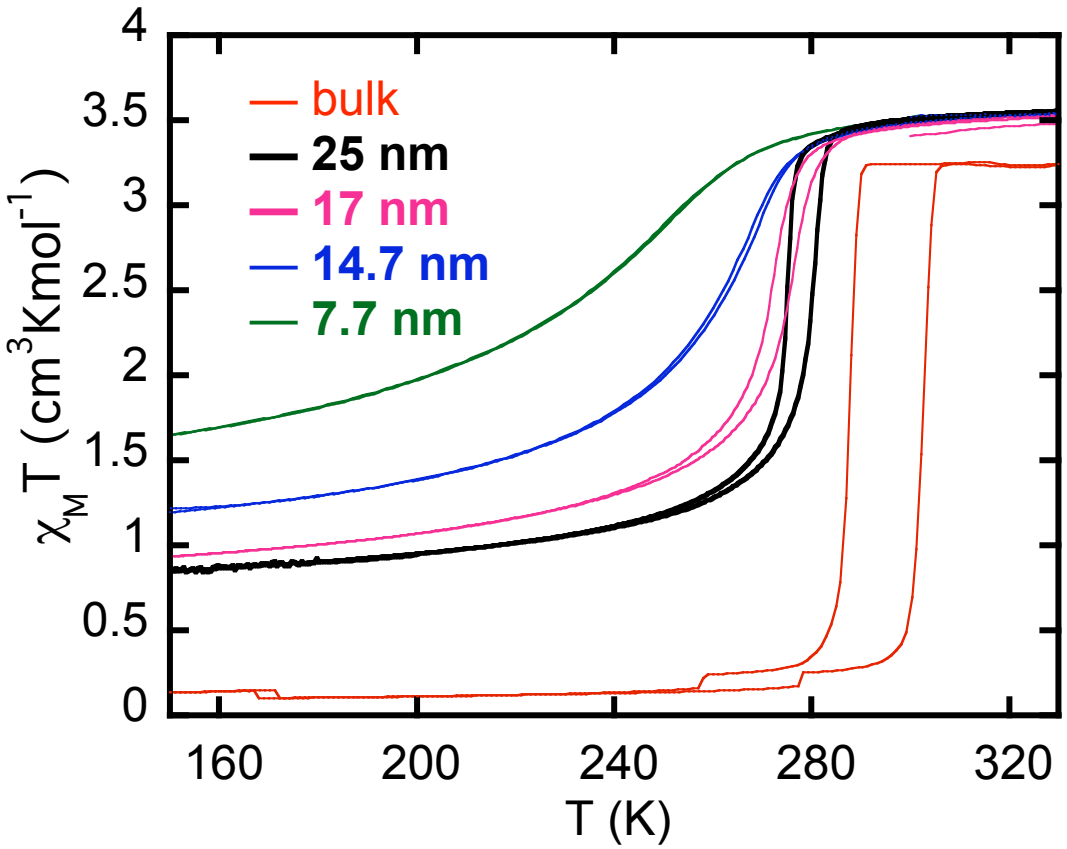
25x25 nm, c_{Pt} = 0.06 M



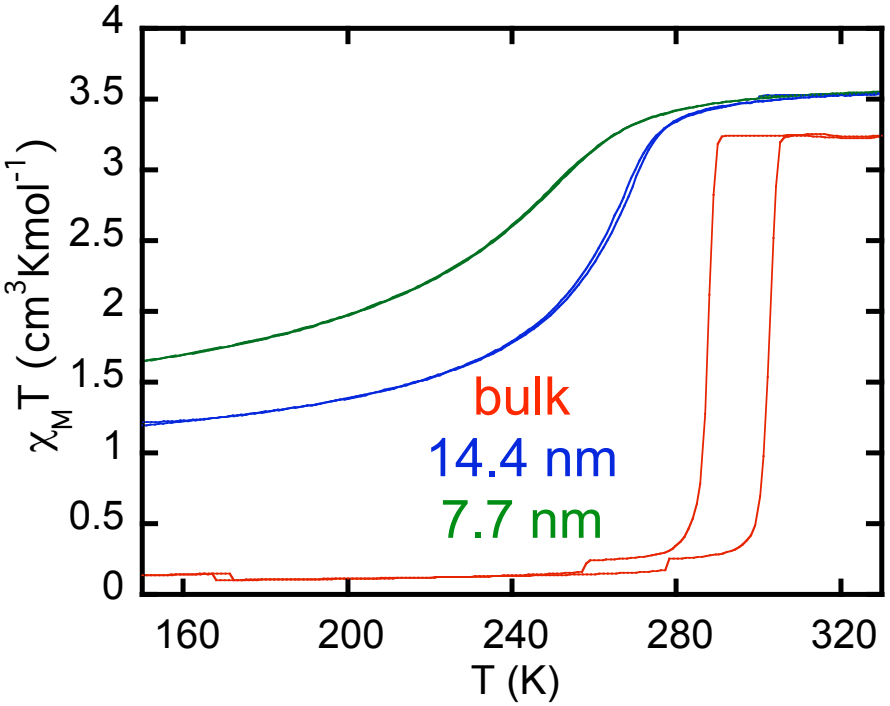
55x55 nm, c_{Pt} = 0.04 M

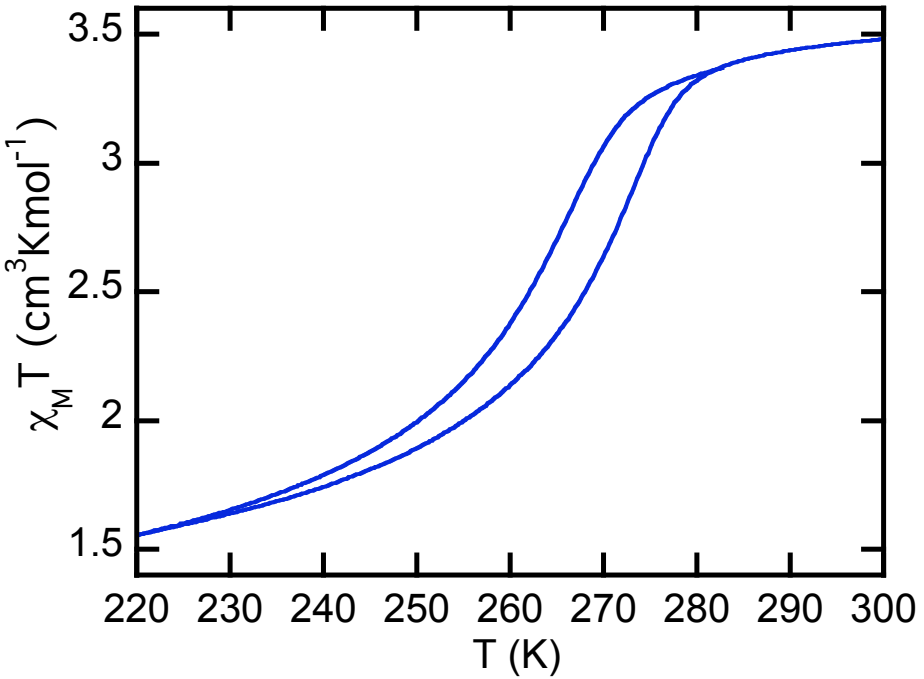


Magnetism/Size Behavior



Magnetic behavior spin crossover nanocrystals

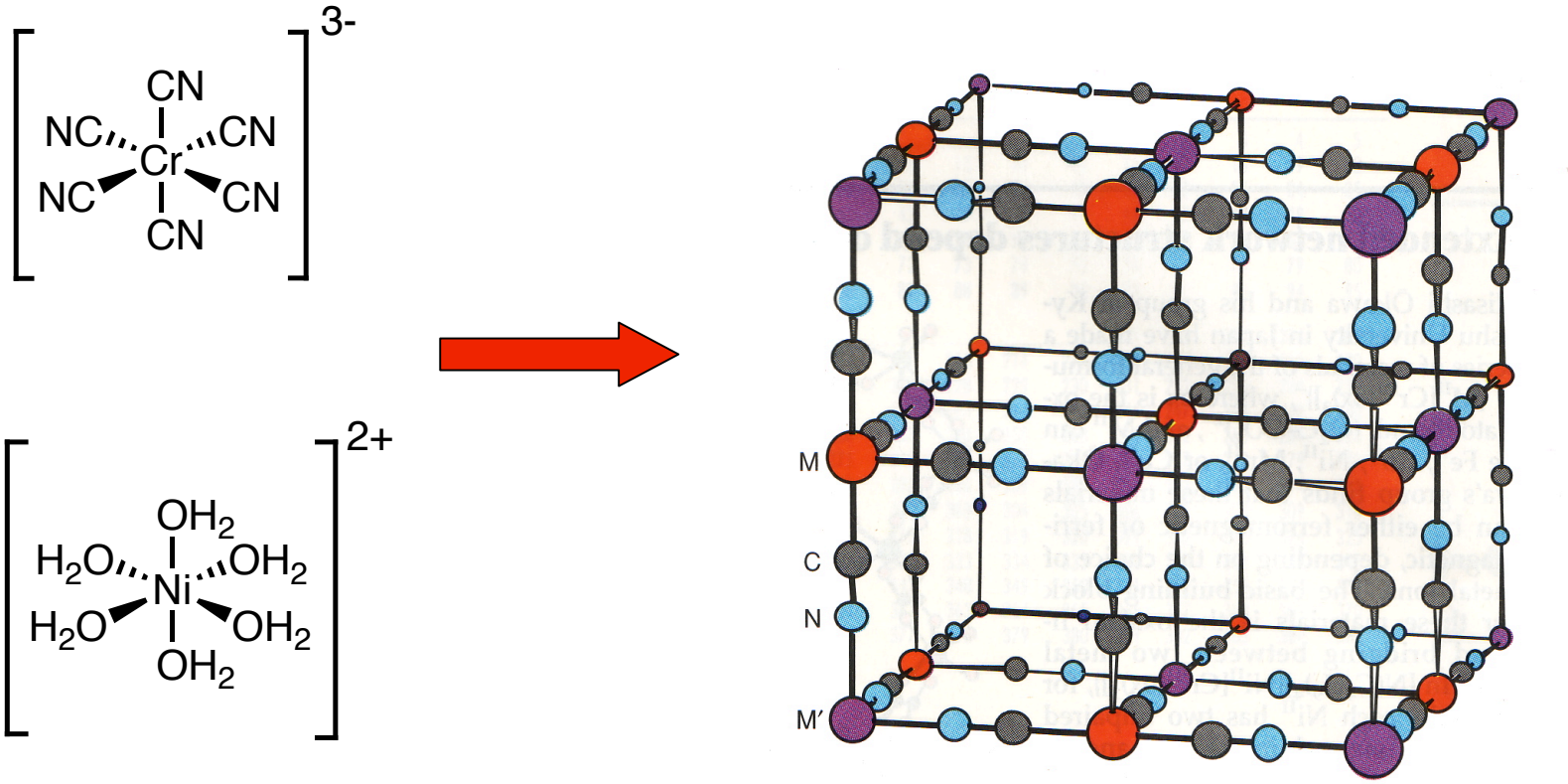




each particle has an abrupt transition ??

behavior of a single particle

Prussian blue analogs



the $Cr(CN)_6$/Ni system

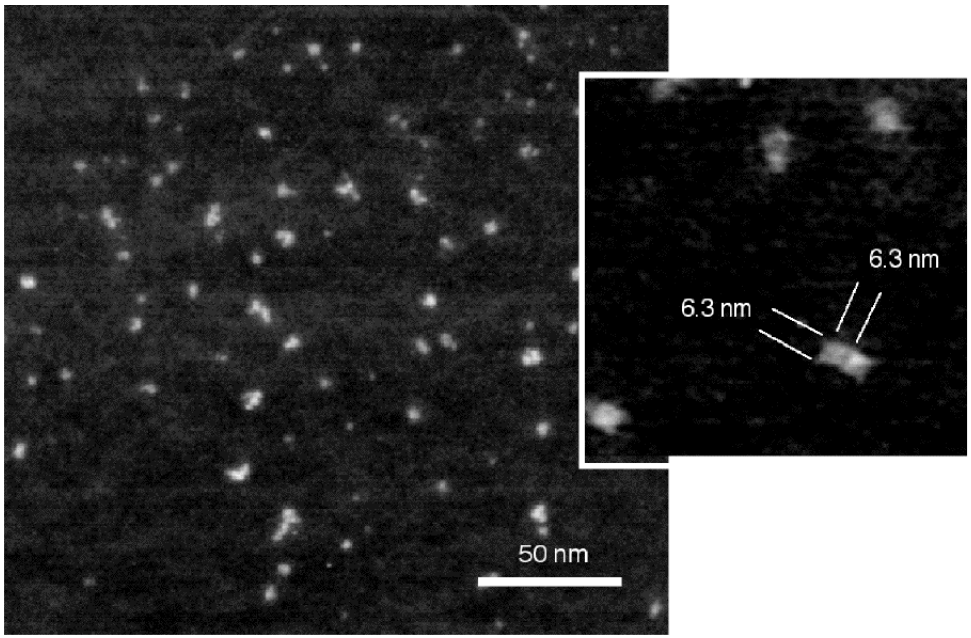
solvent = water
no stabilizing agents

Cs^+	$Ni(H_2O)_6^{2+}$	$Cr(CN)_6^{3-}$	10 mn	20 mn	60 mn
0	1	0,66	50 nm	300 nm	precipitate
0	1	1	10 nm	15 nm	15 nm
2	1	1	6 nm	6 nm	6 nm

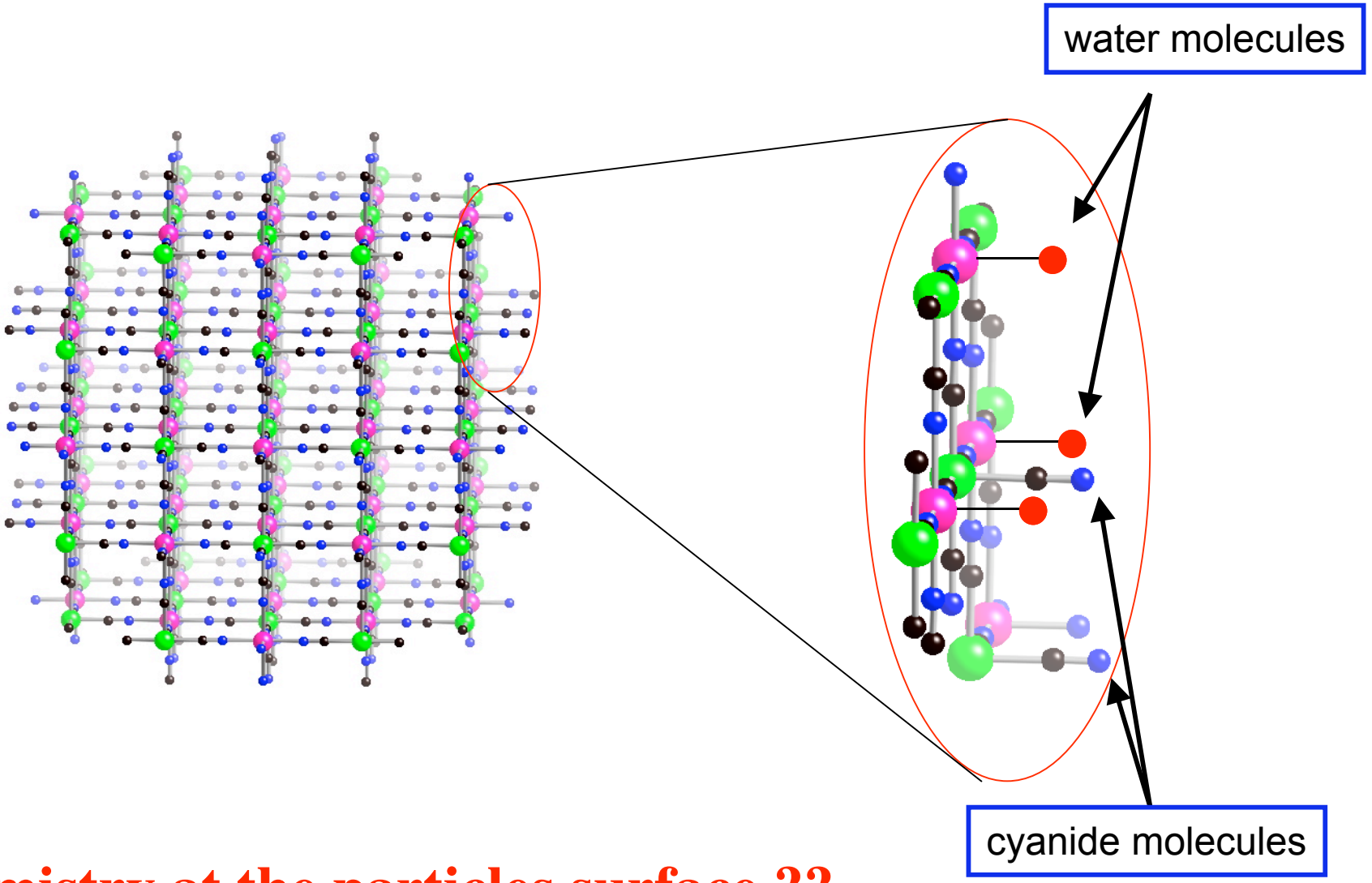
D. Brinzei, L. Catala *et al, J. Mater. Chem.*, 2006, *16*, 2593.

CsNiCr system

$$2CsCl + K_3[Cr(CN)_6] + NiCl_2 \xrightarrow[\text{water}]{} \text{6 nm soluble objects}$$

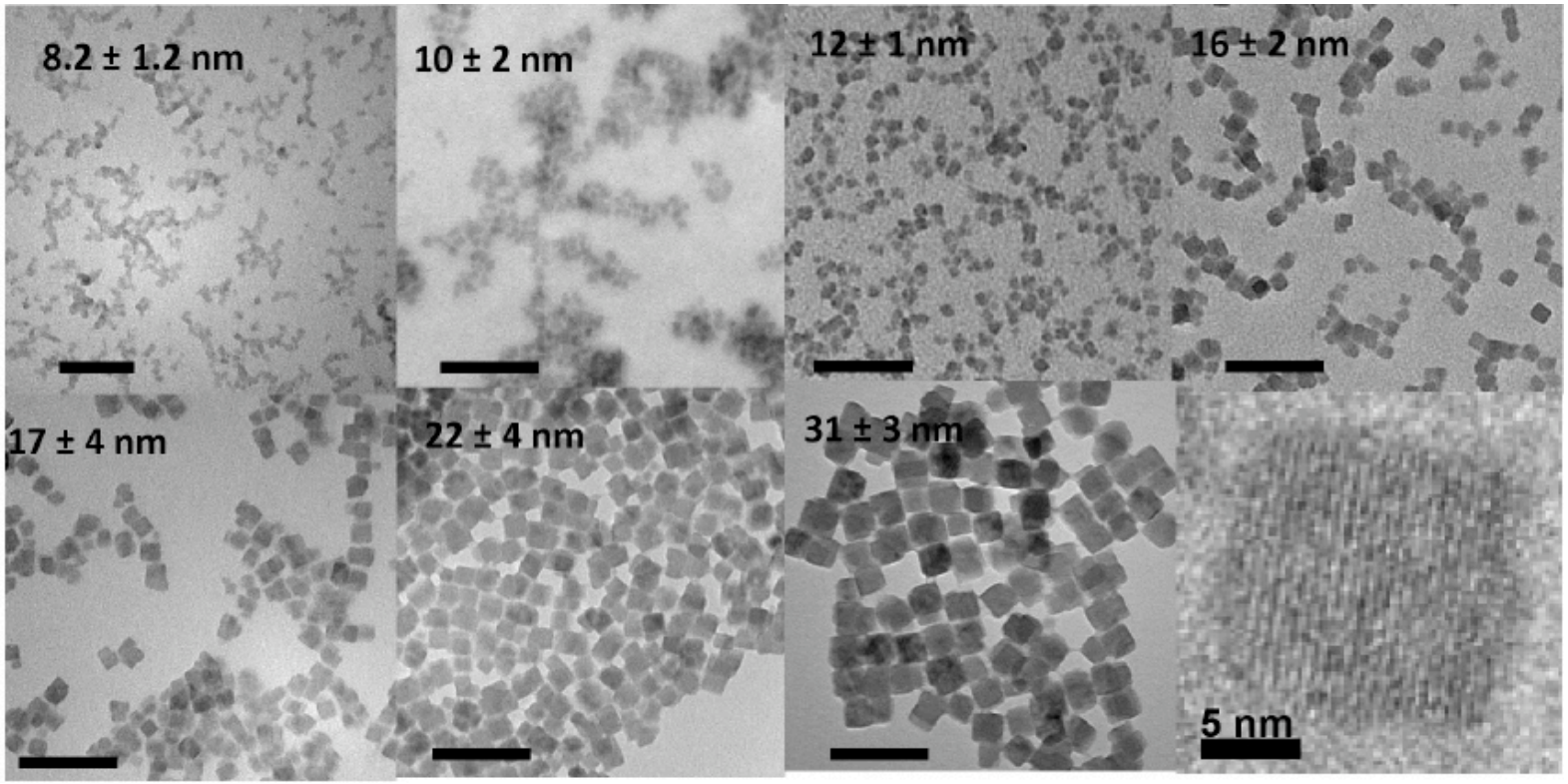


Nature of the particles' surface



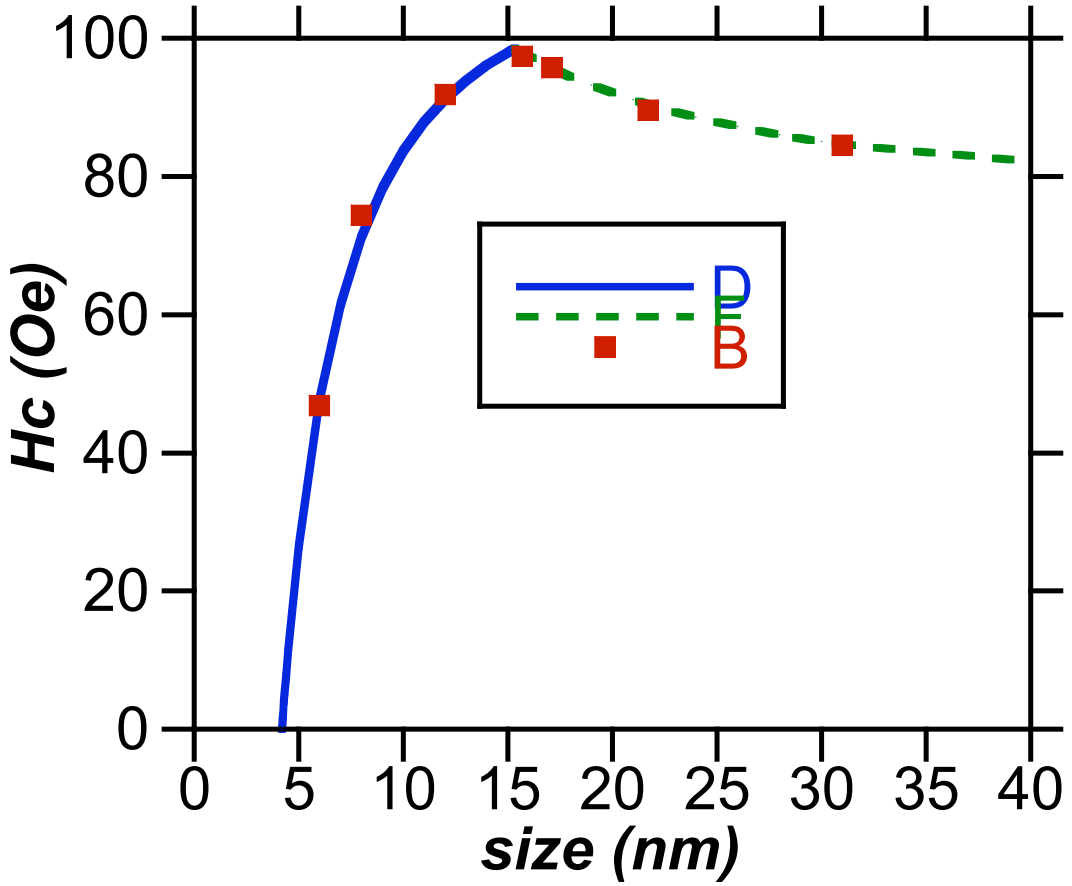
Chemistry at the particles surface ??

Size control



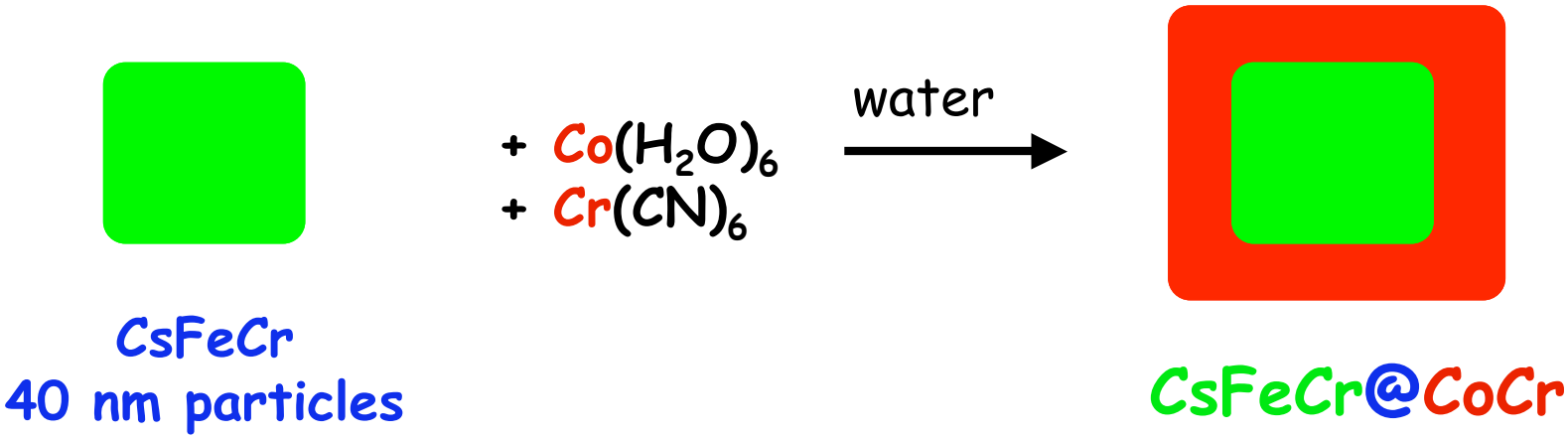
Scale bar = 100 nm

Single domain size-CsNiCr



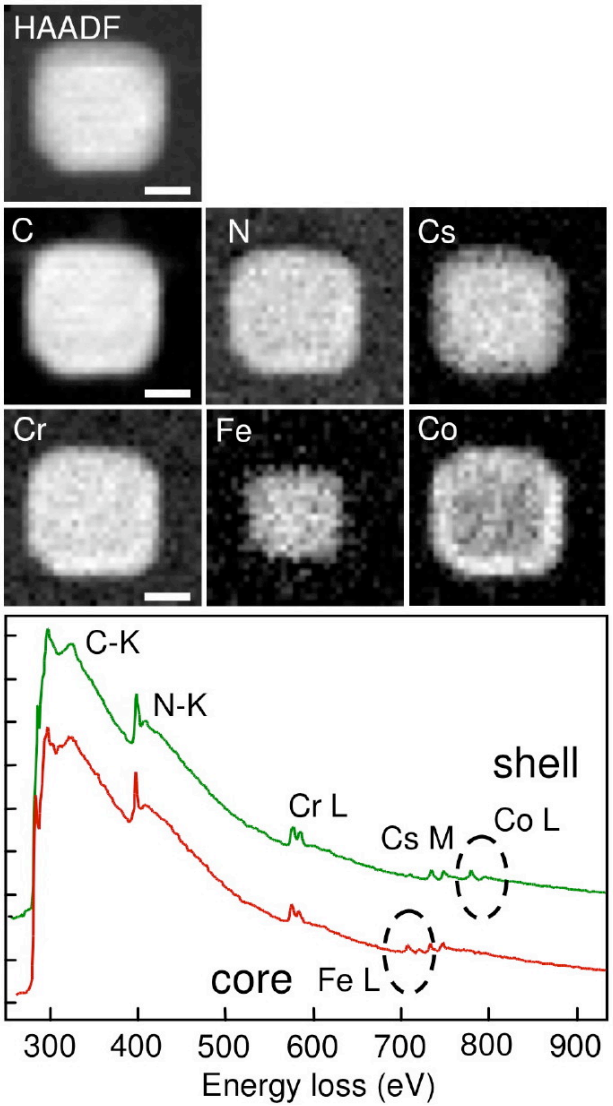
Single domain size = 14-15 nm

CsFeCr@CoCr ??

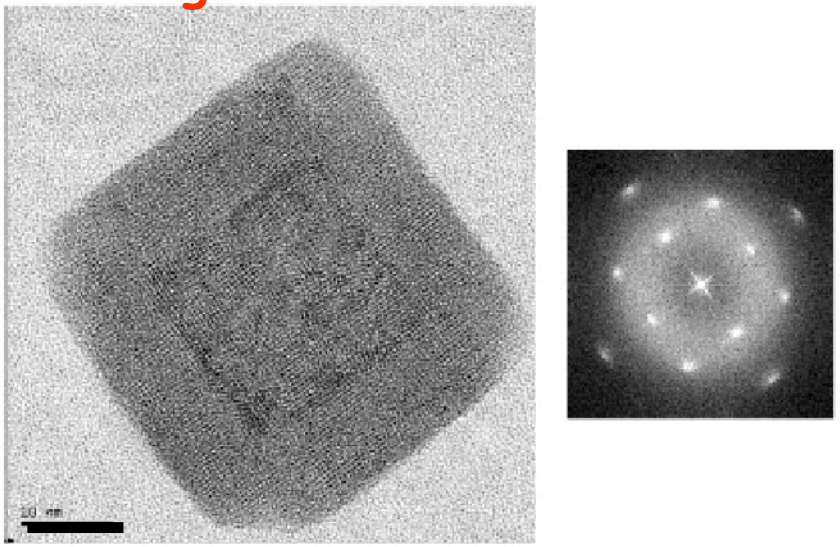


Core-shell CsFeCr@CoCr

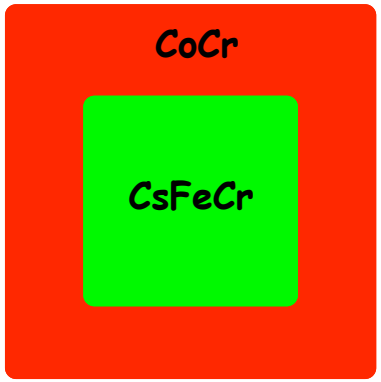
Elemental mapping



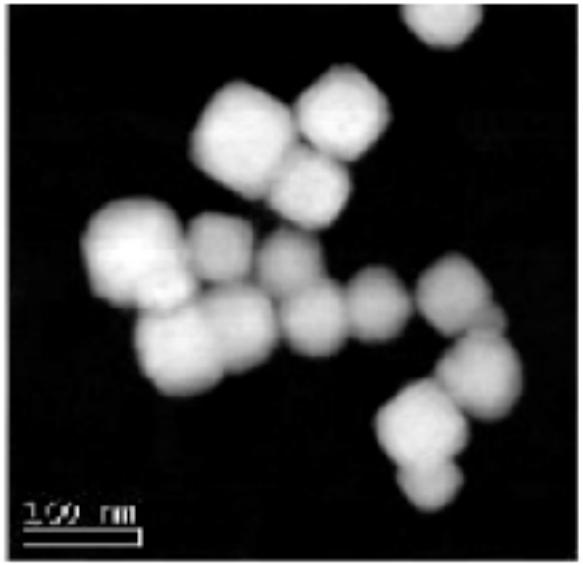
High resolution

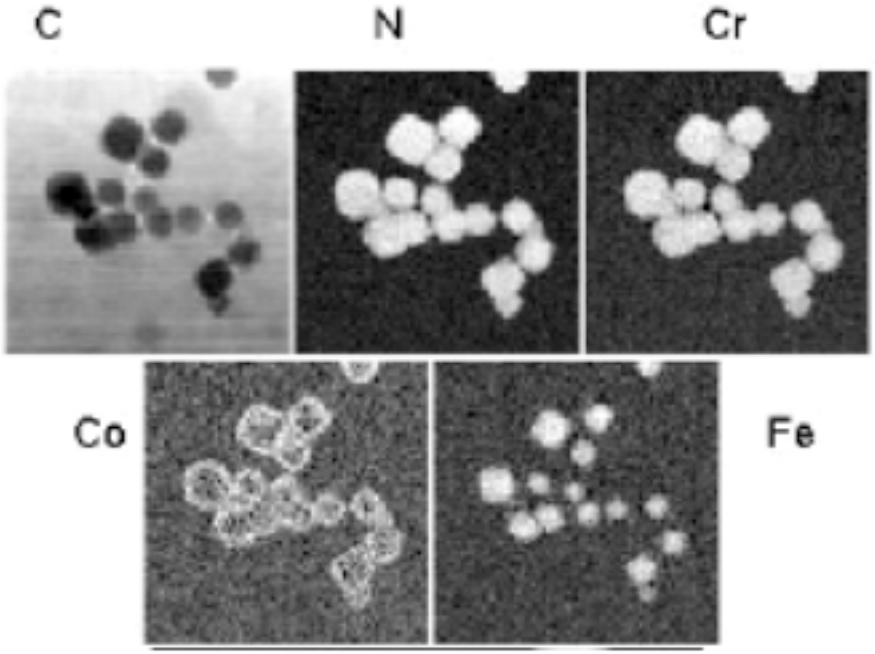


Scale bars 20 nm

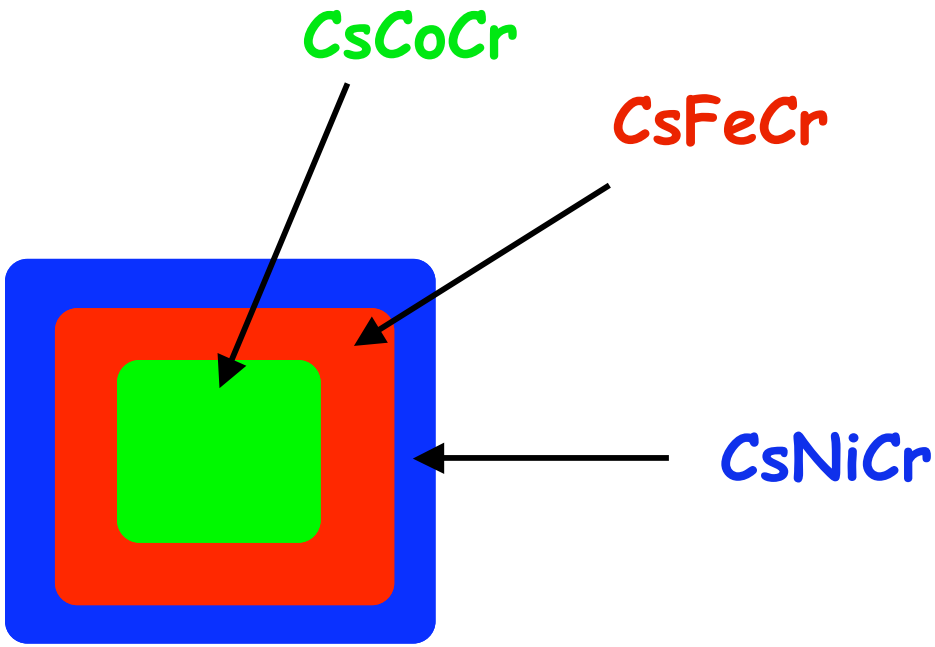


Homogenous core-shell particles

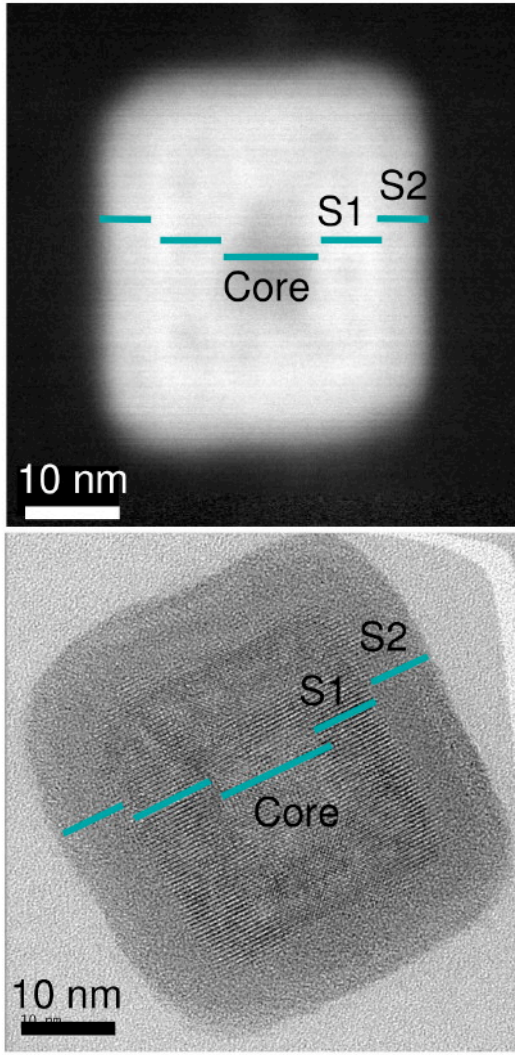


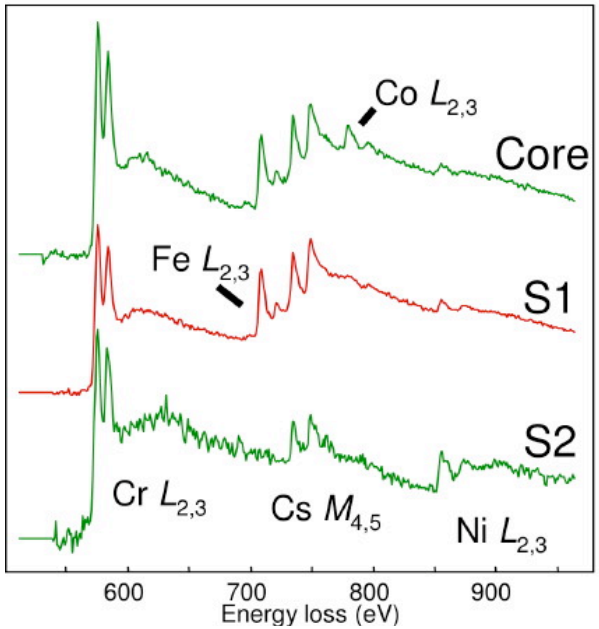


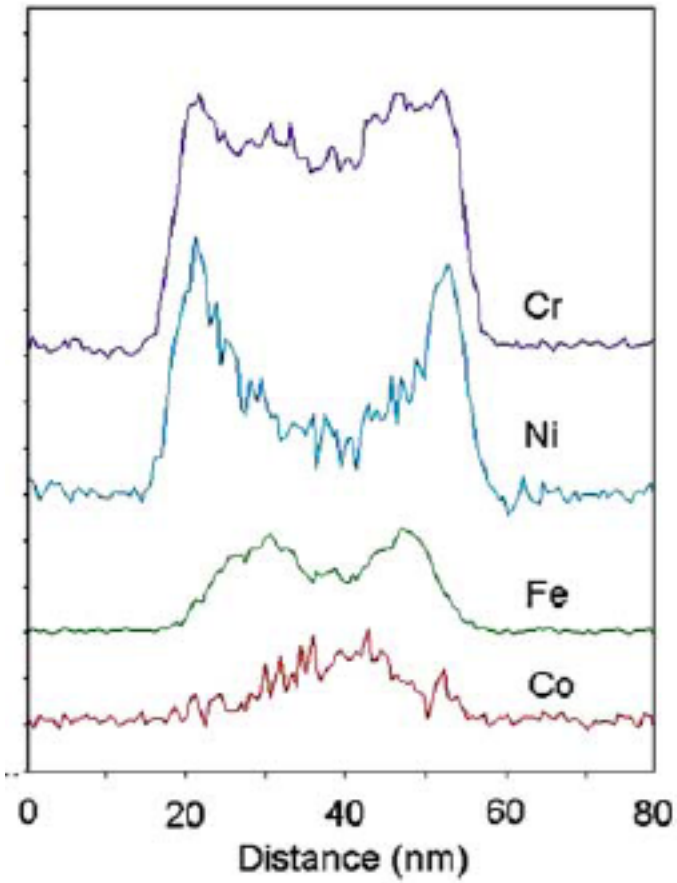
CsCoCr@CsFeCr@CsNiCr



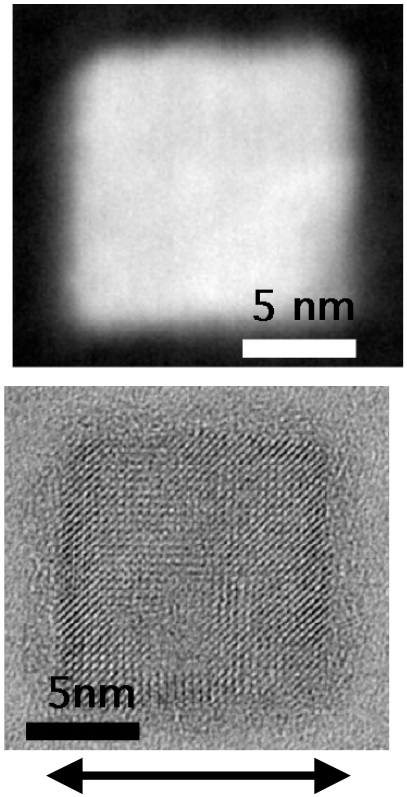
Core multishell CsCoCr@CsFeCr@CsNiCr

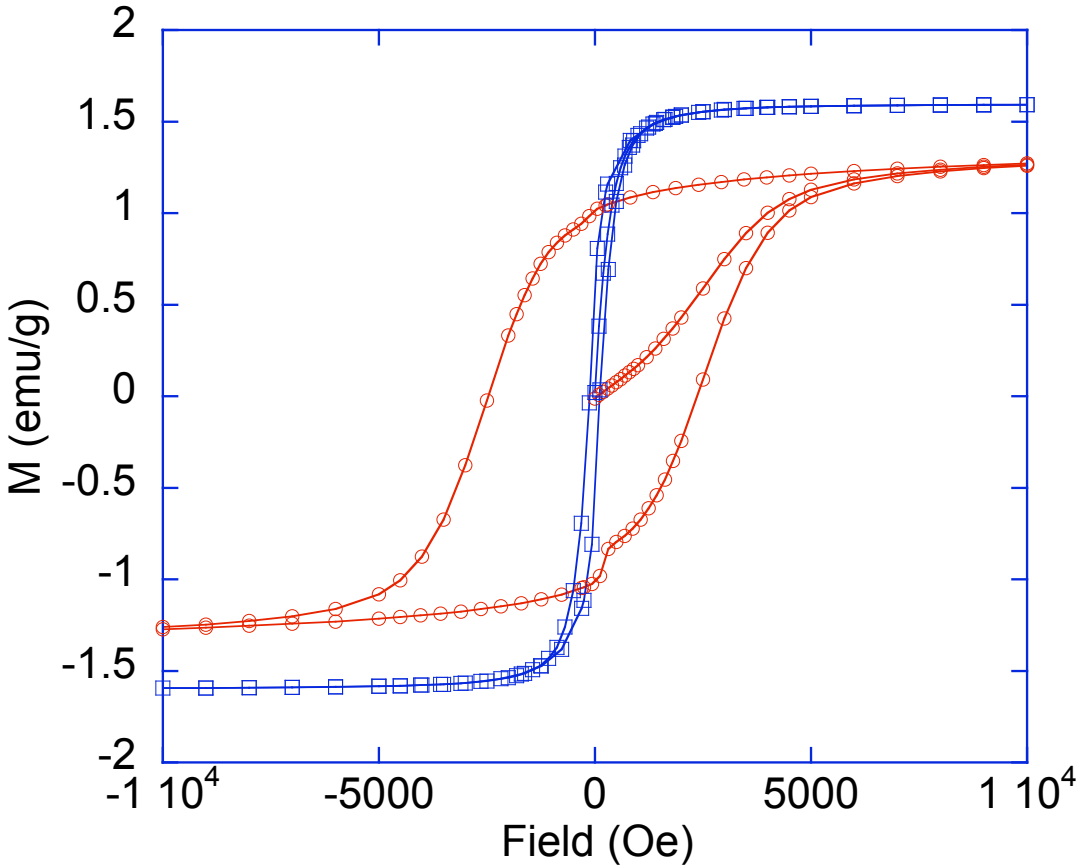






CsNiCr core 9.5 nm and CsCoCr shell of 1.5 nm





Perspectives

Investigating the interplay between magnetism, photomagnetism and transport behaviour of a single object