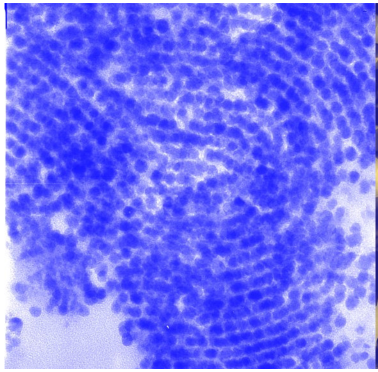
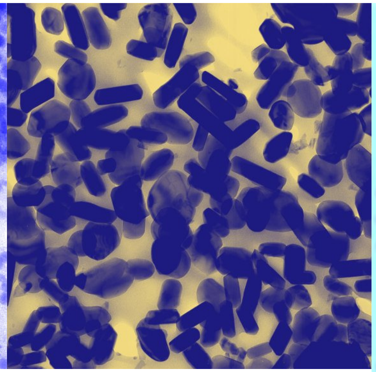
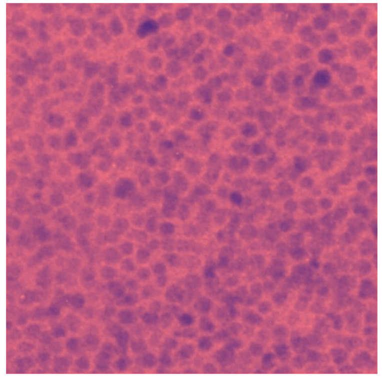
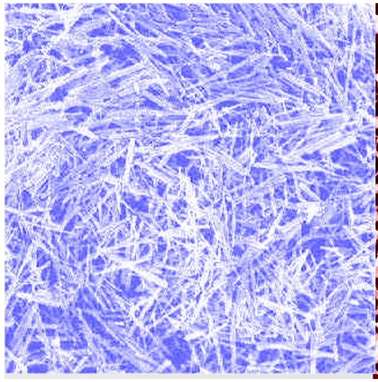
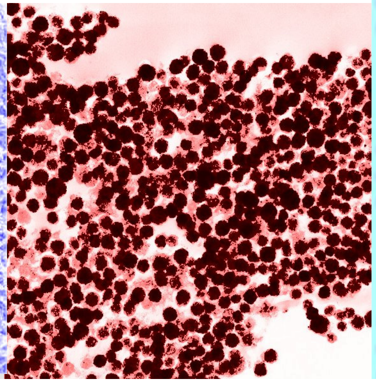




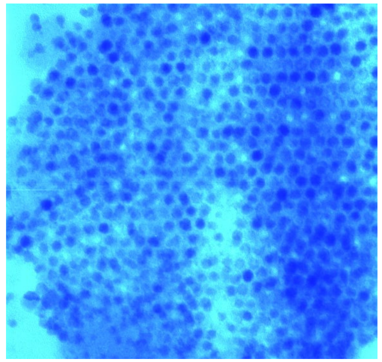
UNIVERSITÉ MONTPELLIER 2
SCIENCES ET TECHNIQUES

CENTRE NATIONAL
DE LA RECHERCHE
SCIENTIFIQUE

Cyano-Bridged Coordination Polymer Nanoparticles.

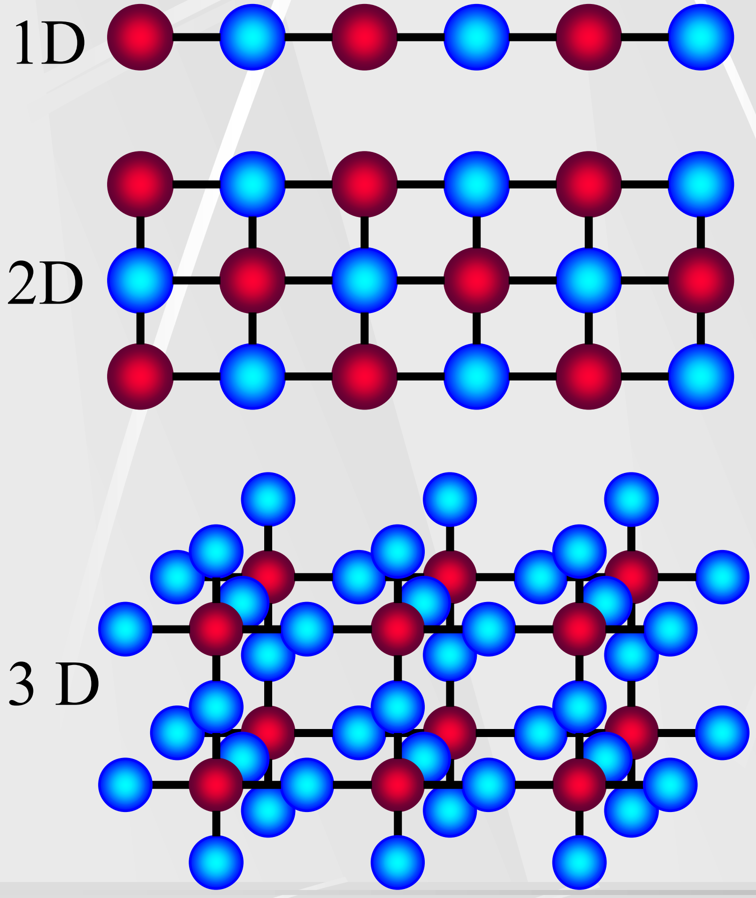



ICG Montpellier
Institut Charles Gerhardt
CMOS



What's Coordination Polymers ?

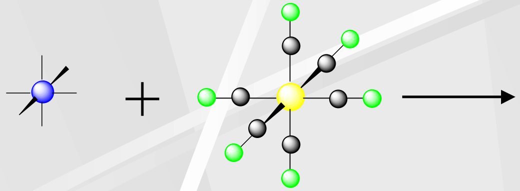
Infinite metal-organic coordination polymers are based on the coordination chemistry of late transition metal ions and polydentate organic building blocks.



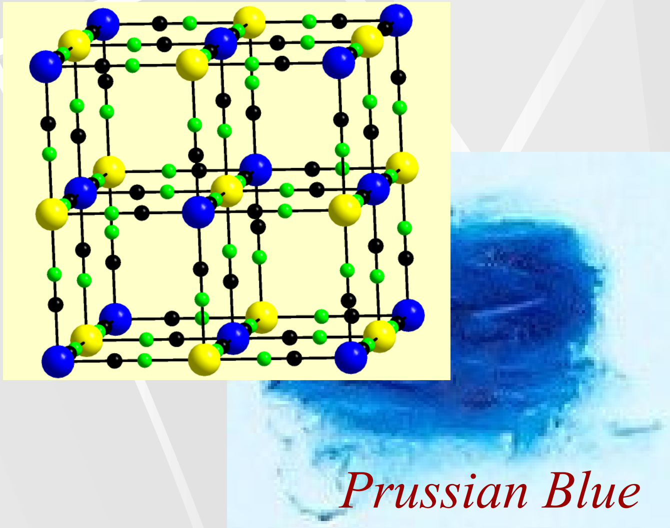
-Pre-determined and flexible molecular structures;
-Physical properties pre-determined by the molecular entities;
-Association of several properties – multifunctional materials;
-Physical properties modulation;
-Low density (ex. 5 – 30 mg/m^3);
-Mechanical flexibility;
-Chimie douce processes;
-High hardness;
-Low environmental contamination;
-Compatibility with organic polymers;
-Biocompatibility;
-Transparency;
-High porosity.

Cyano-bridged Coordination Polymers

A pigment,



Fe^{2+} $[Fe(CN)_6]^{3-}$



its magnetic…

$Fe^{3+}{}_4[Fe^{2+}(CN)_6]_3$, x H_2O

Ordre ferromagnétique

Fe^{3+}-NC-Fe^{2+}-CN-Fe^{3+}

Fe^{3+} S = 5/2 Fe^{2+} S = O

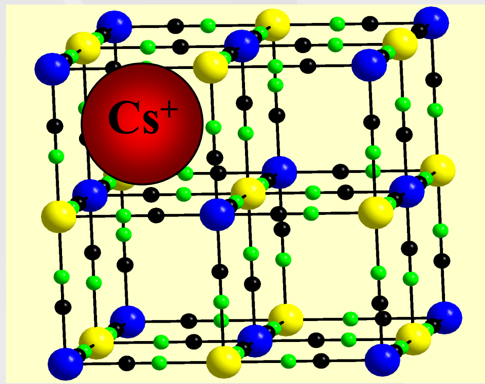
T_c = 5,6 K

$A_x^- C_y^+ V^{II}_{\alpha} V^{III}_{(1-\alpha)} Cr(CN)_6]_z \cdot y$ solvent

…and host-guest properties.

Radiogardase™

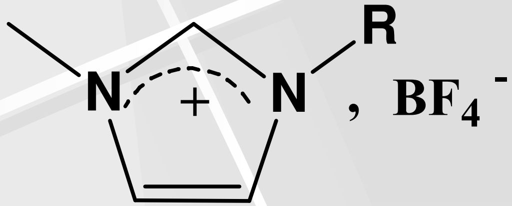
A Cs^+ and Tl^+ poisoning antidote



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

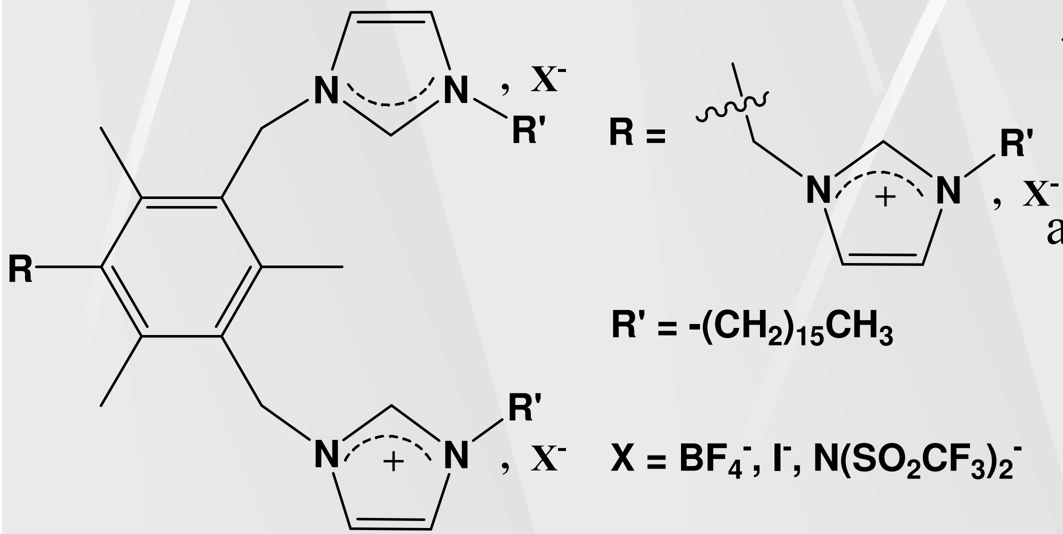
$M_x[M'(CN)_y]_z$ / Ionic Liquid.

$RmimBF_4$ ≡



R = C_4H_9, $C_{10}H_{25}$, $C_{12}H_{25}$, …

Holbrey, J. D. et al. *J. Chem. Soc., Dalton Trans.*, **1999**, 2133



Trilla, M et al. *Langmuir*, **2008**, *24*, 259

Properties of Ionic Liquids

Weak interface tension:
High nucleation rate,
small nanoparticles

Weak interface energy:
Good solvation of molecular species,
« adoptive » structure of ionic liquids

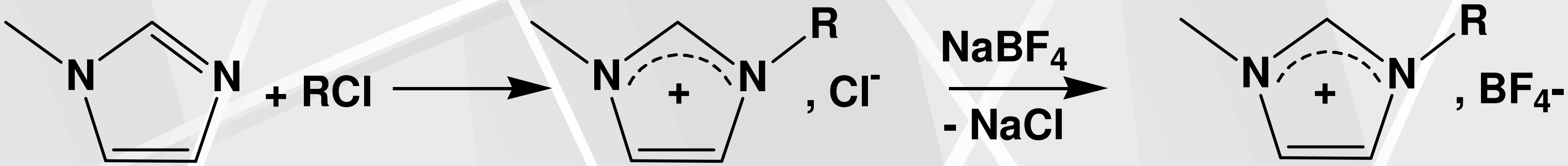
Solubility of polar species:
anhydride or with small water quantity

Structured liquids
by van der Waals bonds.

Collaboration Pr. R. Plexiats

$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

Ionic Liquid Synthesis



Water content = 0.2 wt %
Chloride free

Synthetic strategy

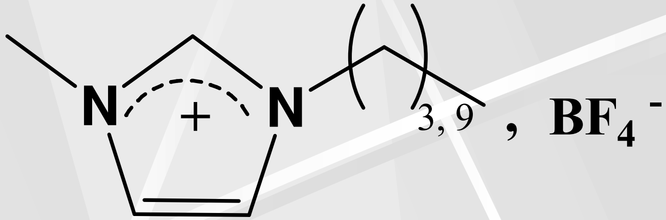
$$K_3[M'(CN)_y] + 3\ RmimBF_4 \xrightarrow[-\ 3\ KBF_4]{MeOH} Rmim_x[M'(CN)_y]$$

$$n\ Rmim_x[M'(CN)_y] + m\ M^{2+} \xrightarrow{RmimBF_4} M_x[M'(CN)_y]_z/RmimBF_4$$

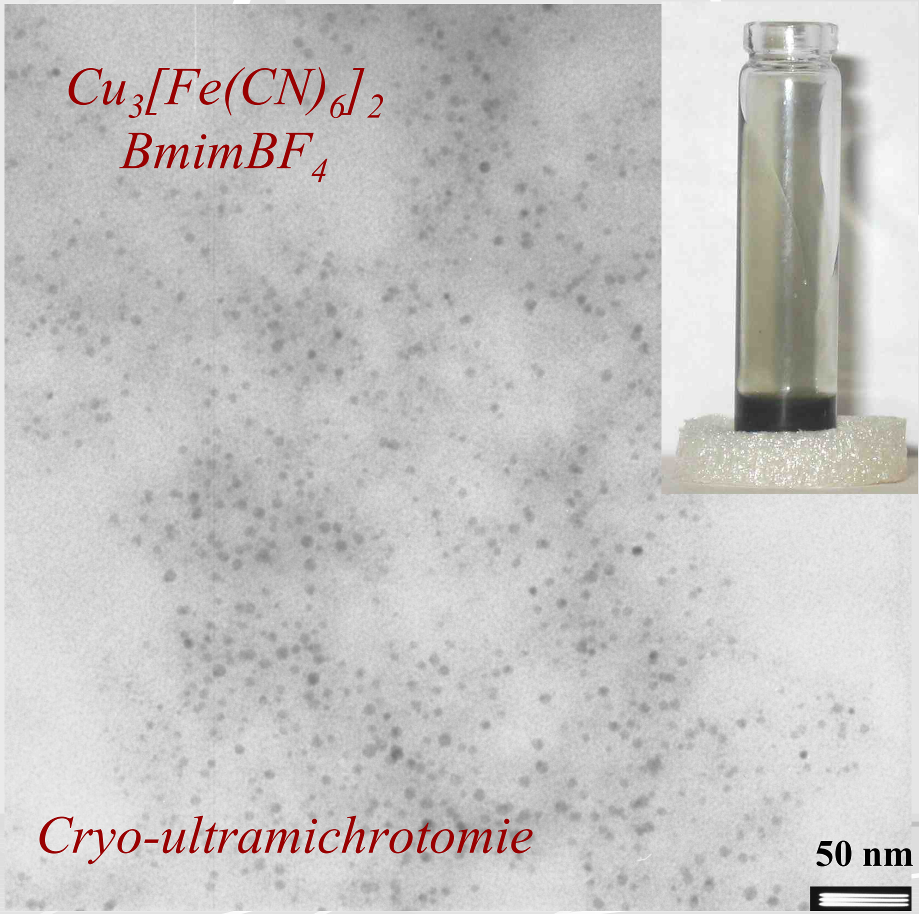
M’ = Fe, Cr (m = 6); Ni, Pt (m = 4); Mo, W (m= 8)
M^{2+} = Fe, Ni, Co; Cu… and also M^{3+} = Gd, Eu, Tb, Yb, …

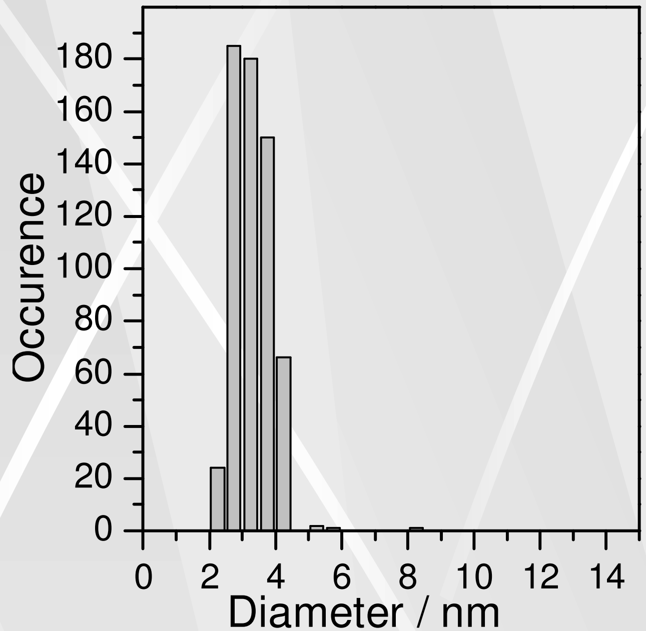
$RmimBF_4$ with R = C_4H_9, $C_{10}H_{25}$ or $C_{12}H_{25}$,

$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.



Spherical nanoparticles with 3d-metal ions/$BMIMBF_4$

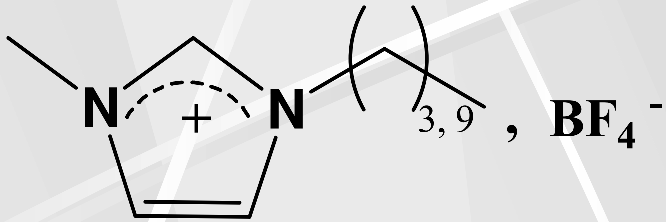




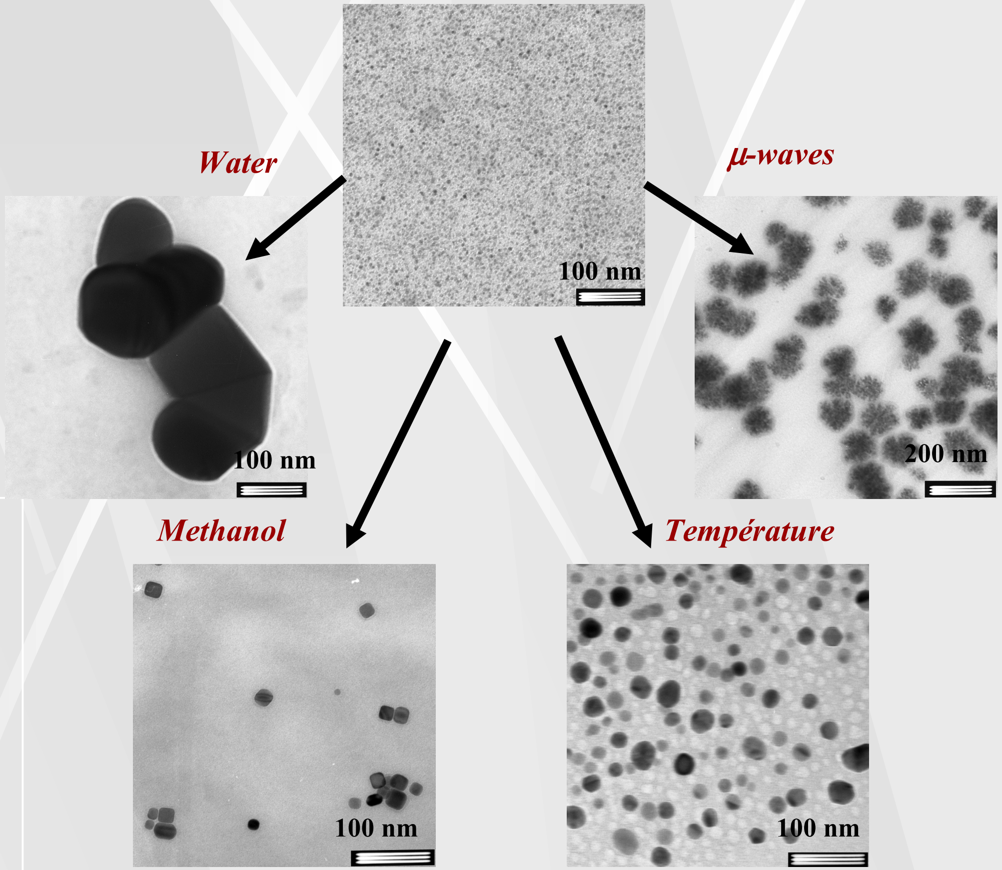
At room temperature:

$Cu_3[Fe(CN)_6]_2$	3.3±0.6 nm
$Ni_3[Fe(CN)_6]_2$	2.7±0.4 nm
$Co_3[Fe(CN)_6]_2$	3.0±0.8 nm
$Fe_4[Fe(CN)_6]_3$	3.0±0.7 nm

$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.



…and many other parameters (water content, co-solvent, microwaves, etc…)



Influence of the temperature…

At 50 °C:

$Cu_3[Fe(CN)_6]_2$	5.1±1.4 nm
$Ni_3[Cr(CN)_6]_2$	6.1±1.5 nm
$Mn_3[Cr(CN)_6]_2$	6.0±1.1 nm
$(VO)_3[Cr(CN)_6]_2$	6.1±1.4 nm

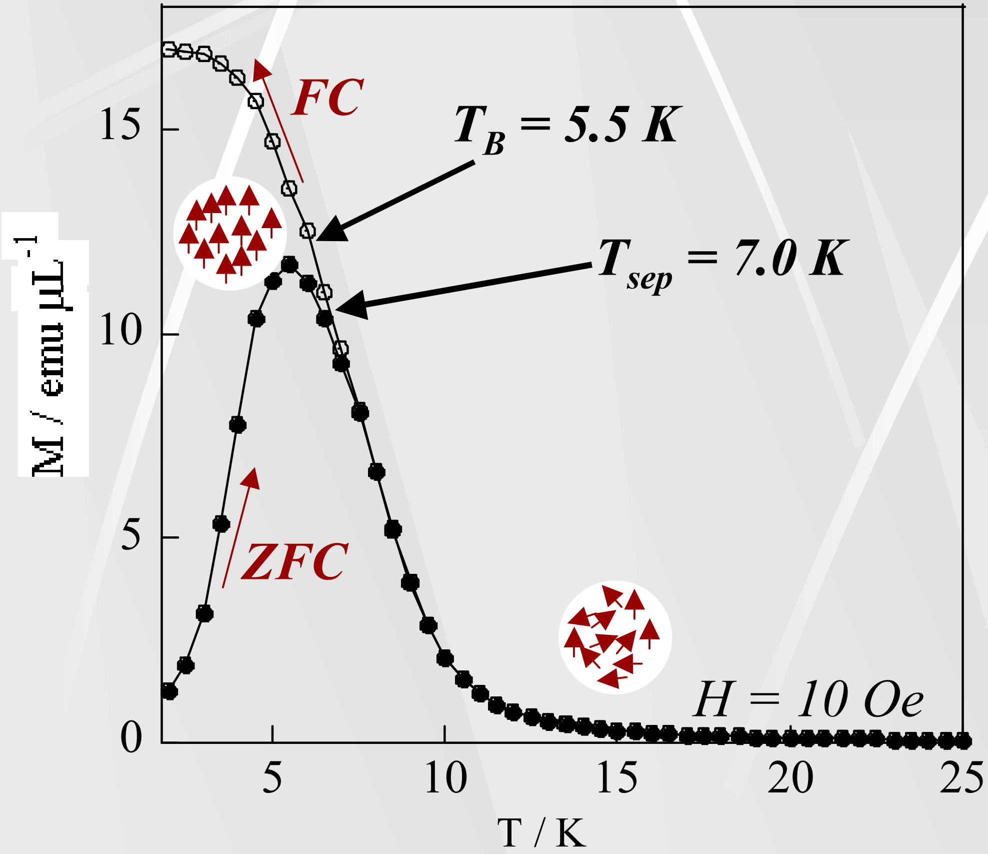
Larionova, J. et al. *Inorg. Chim. Acta*, **2008**, doi:10.1016j.ica.2008.03.038

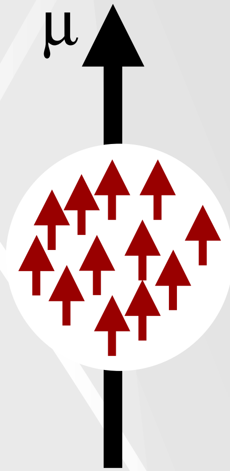
Sayegh, H. et al. *Inorg. Chim. Acta*, **2007**, *360*, 3829.

$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

$Cu_3[Fe(CN)_6]_2$/ $BmimBF_4$

Magnetic properties
FC/ZFC curves





Single domain particles

Magnetic moment
$\{Cu_{84}Fe_{56}\}$
$\mu = 140\ \mu_B$

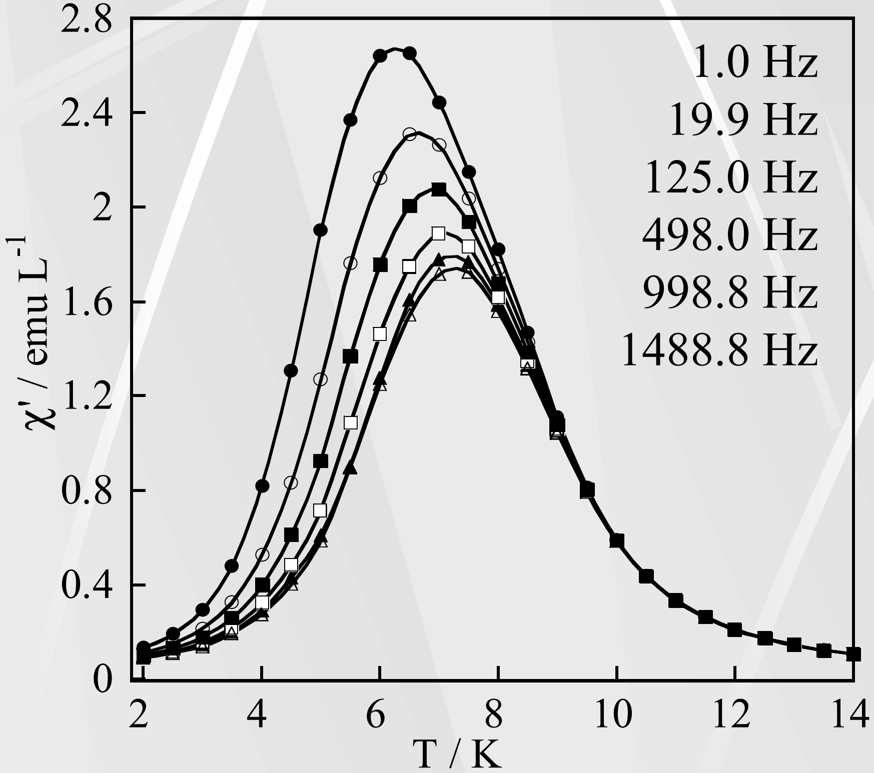
Superparamagnetic behaviour?

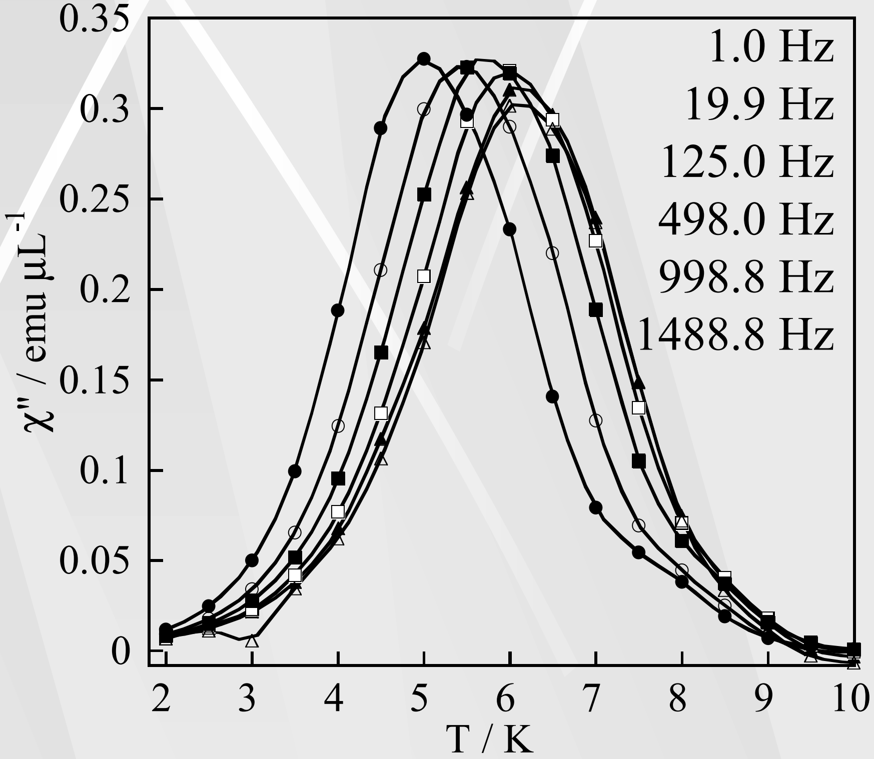
Bulk $Cu_3[Fe(CN)_6]_2$: T_c = 21 K

$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

$Cu_3[Fe(CN)_6]_2$/ $BmimBF_4$

Magnetic properties
ac measurements

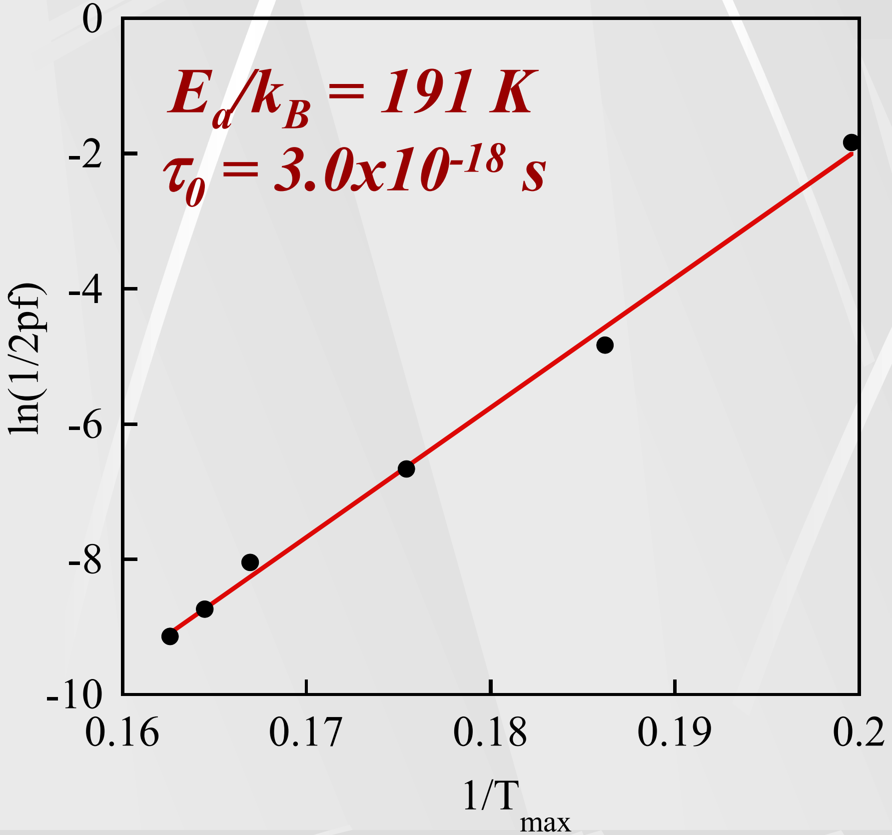


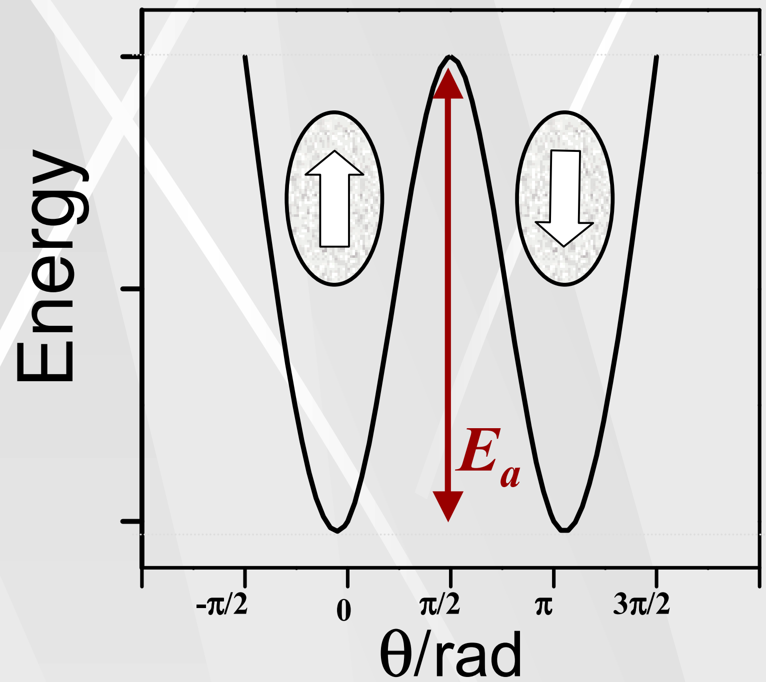


$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

$Cu_3[Fe(CN)_6]_2$/ $BmimBF_4$

Arrhenius law :
$\tau=\tau_0 exp(E_a/k_BT)$

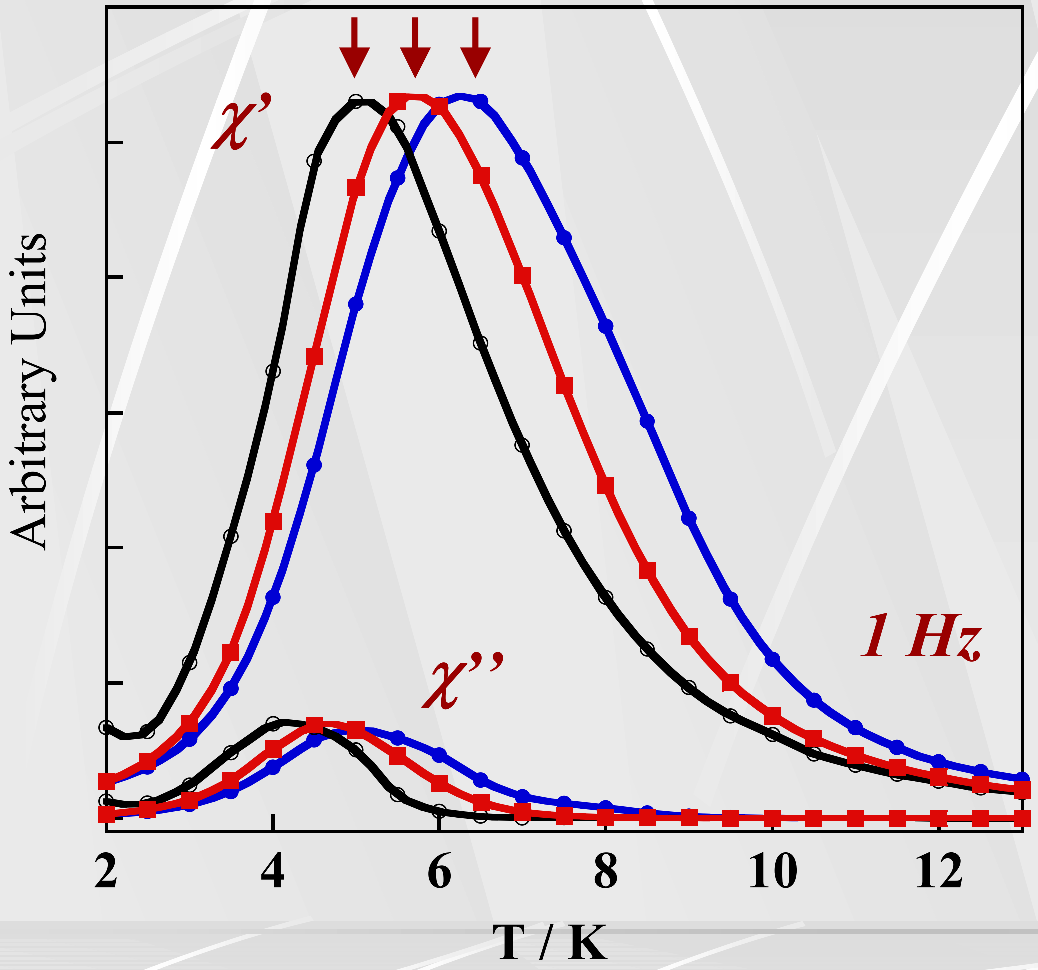




Superparamagnetic systems:
$\tau_0 \approx 10^{-9} - 10^{-12}$ s

$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

T_B decreases as the concentration decreases ⟷ Dilution induces a decrease of interparticle interactions



Arrhenius law fitting of ten times diluted sample :

$E_a/k_B = 86$ K

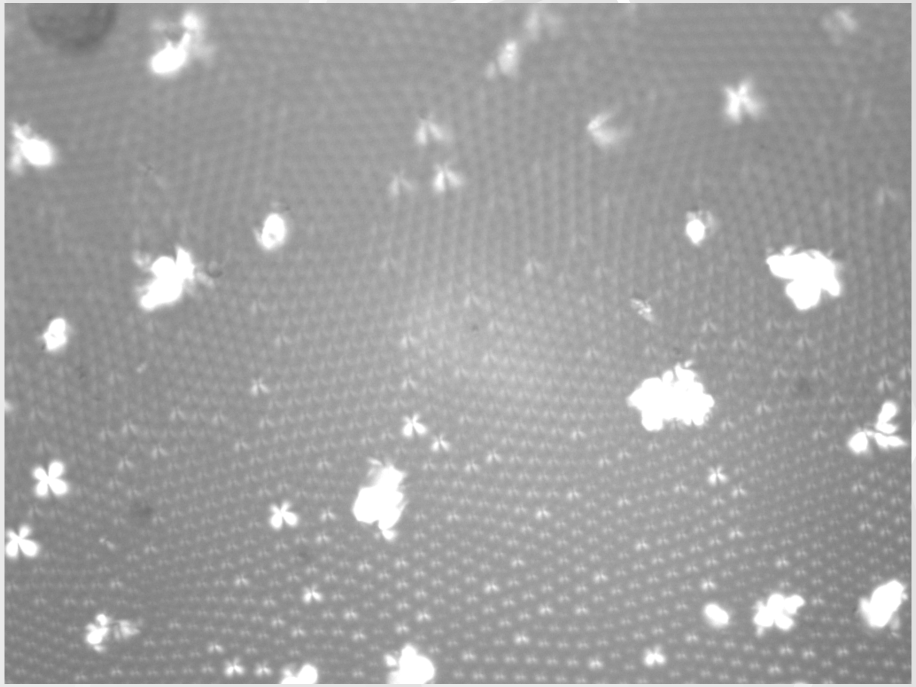
$\tau_0 = 6.7 \times 10^{-12}$ s

Superparamagnetic regime

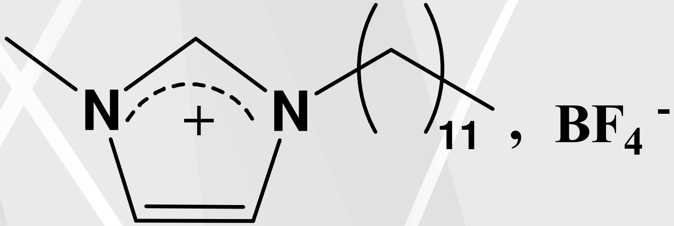
Clavel, G. et al. *Chem. Eur. J.*, **2006**, *12*, 3798

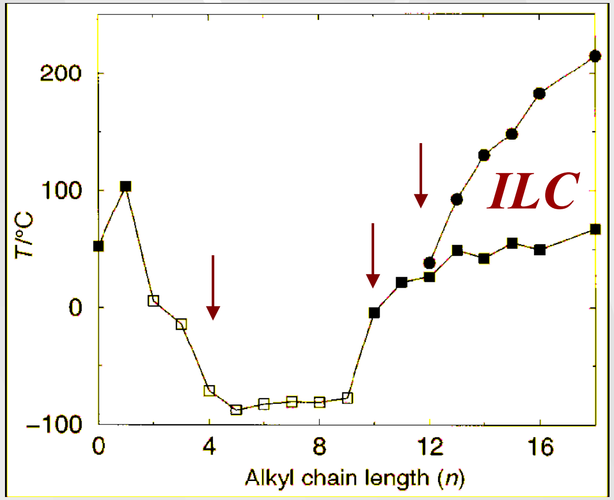
$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

Cross-polarized optical imaging T = 22°C

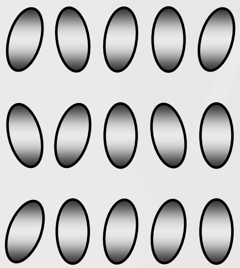


Ionic liquid as structuring media





Ionic Liquid Crystal (Sm A)

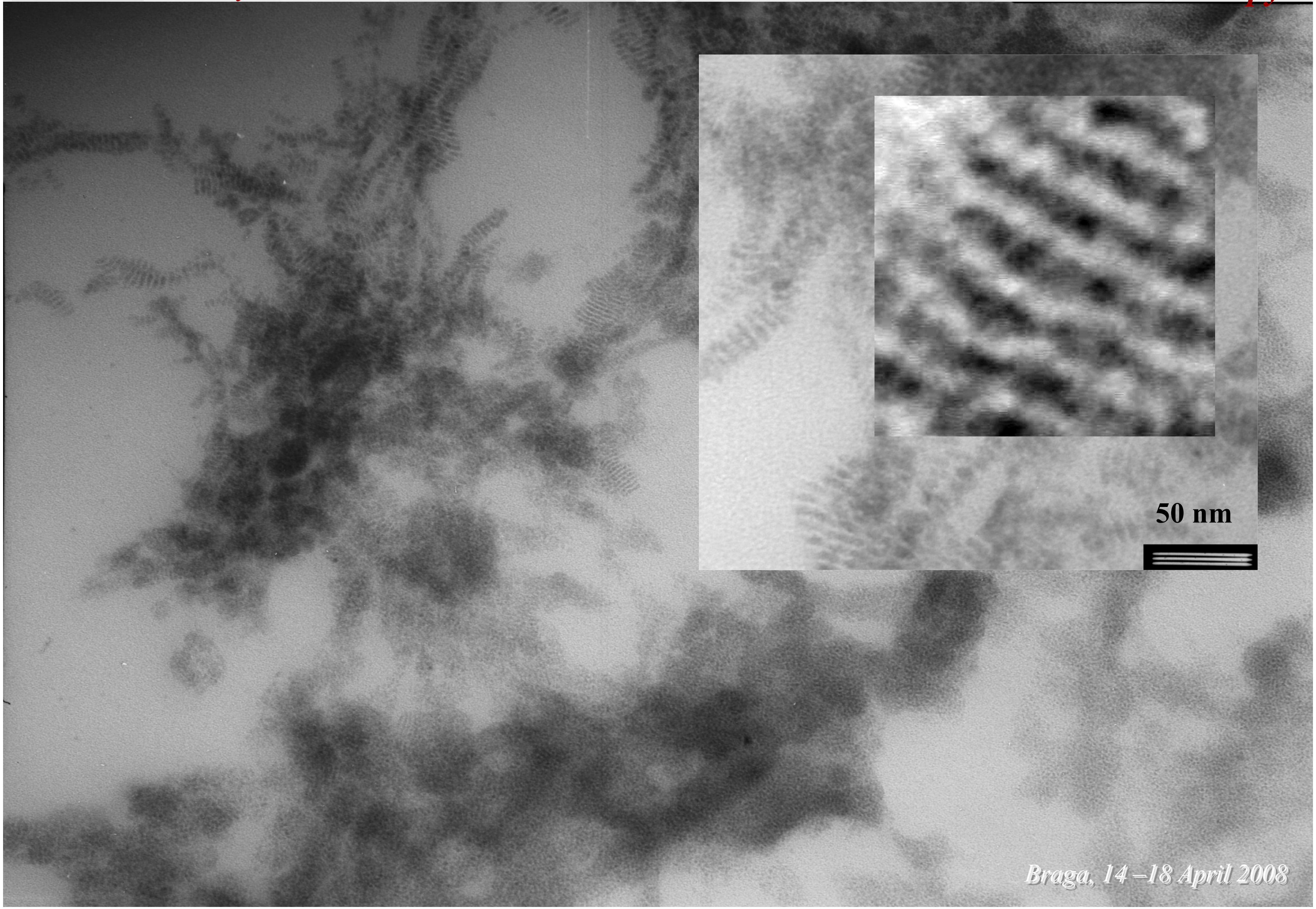


T/°C LC ↔ I = 48-49

Water needed for structural organisation !

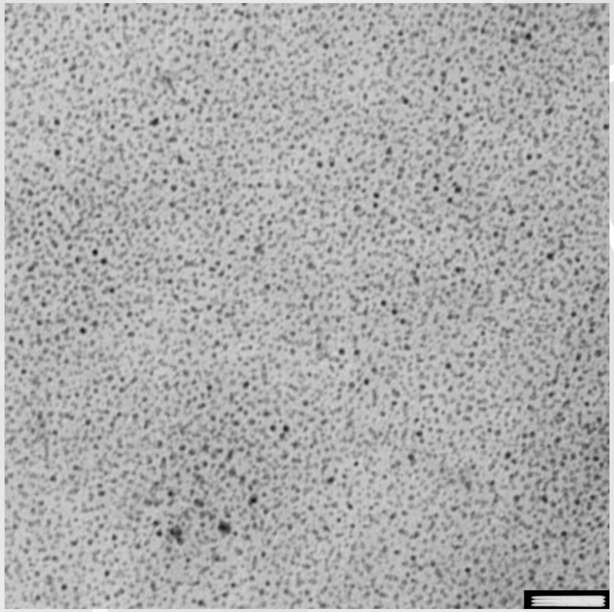
$M_x[M'(CN)_y]_z$ / $RmimBF_4$ colloïdal suspensions.

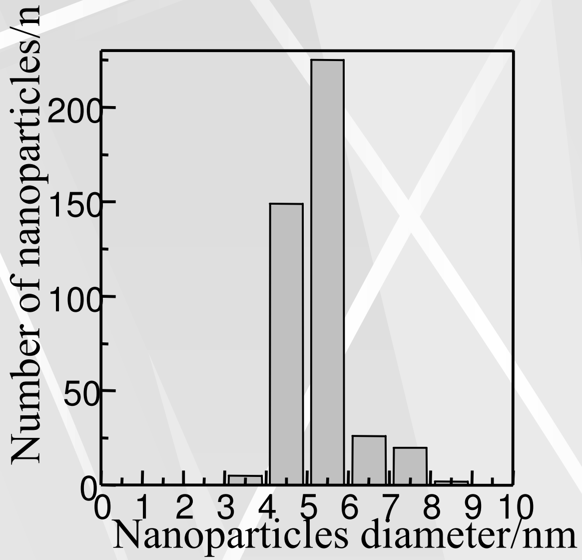
Transmission Electron Microscopy



Ligand-Stabilized $M_x[M'(CN)_y]_z$ nanoparticles

$Mn^{2+}/[Cr(CN)_6]^{3-}$





$M(An)_n.6H_2O$

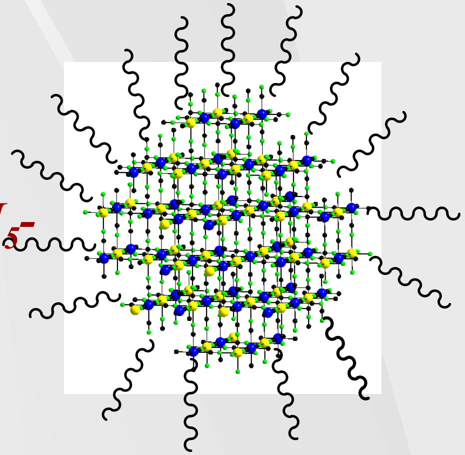
+

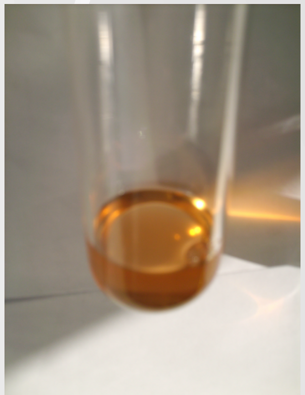
$[N(C_4H_9)_3]_3[M'(CN)_6]$

R_3N

R'COOH

THF





$[M'(CN)_6]^{3-}$; M' = Fe, Cr;

$M^{n+} = Ni^{2+}, Mn^{2+}, Fe^{2+}, Tb^{3+}, Sm^{3+}, Gd^{3+}$;

$R = CH_3(CH_2)_4$-, $CH_3(CH_2)_7$-, $CH_3(CH_2)_{11}$-, C_6H_5-

; $R' = CH_3(CH_2)_7CH{=}CH(CH_2)_7$-;

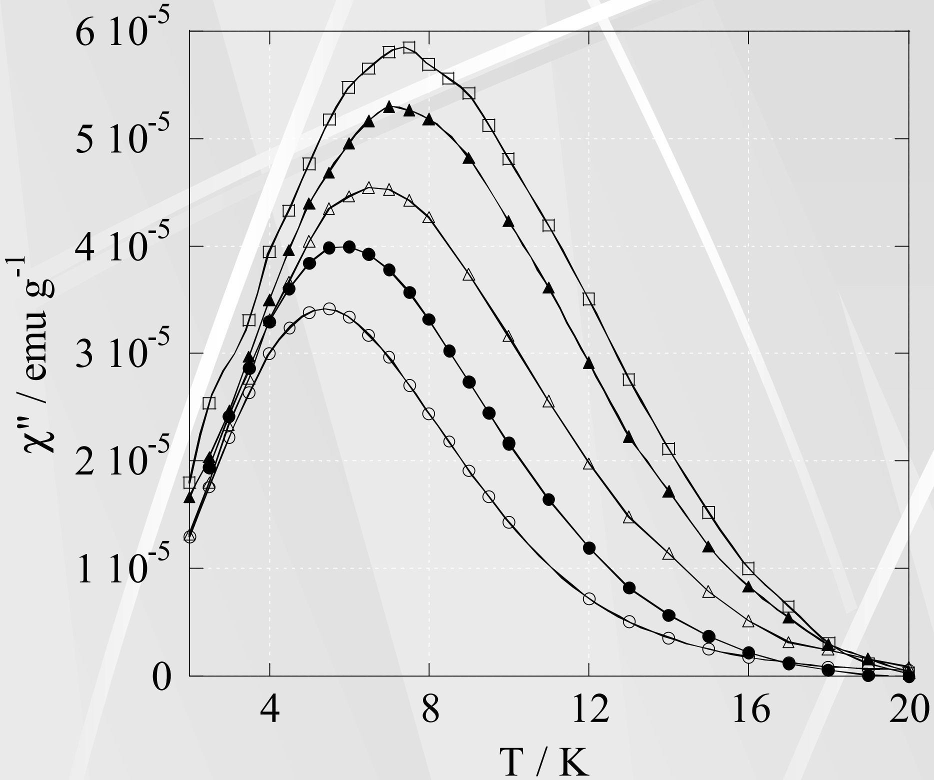
$An = BF_4^-, NO_3^-$

Collaboration Pr. A. A. Trifonov

Chelebaeva, E. et al. *Chem. Mater.*, **2008**, *20*, 1367

Ligand-Stabilized $M_x[M'(CN)_y]_z$ nanoparticles

$Mn^{2+}/[Cr(CN)_6]^{3-}$



T_B = 5.3 K

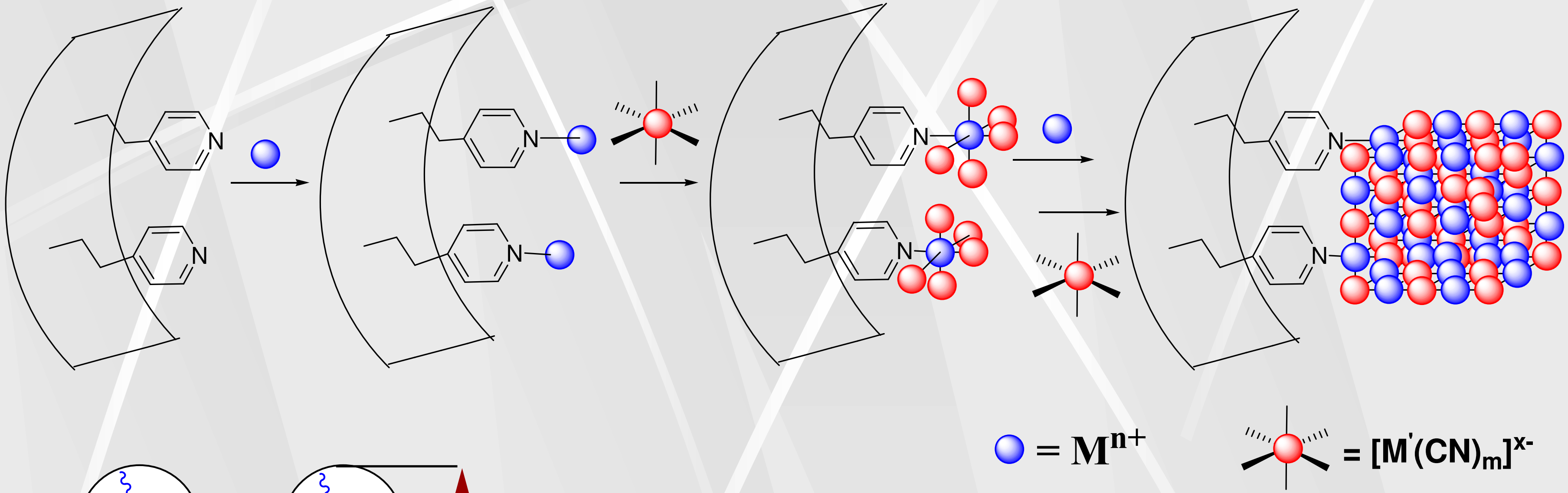
Arrhenius law: $\tau=\tau_0 exp(\Delta E/k_BT)$

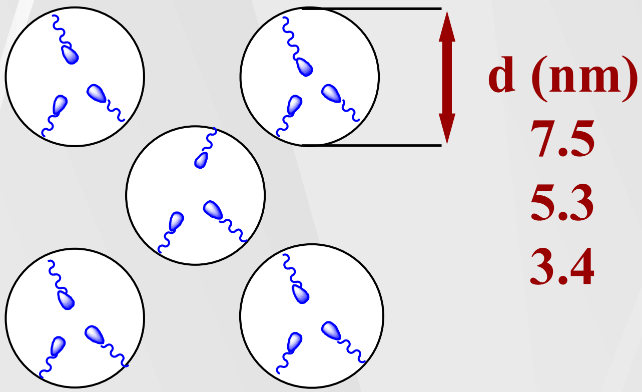
$\Delta E/k_B$=134 K $\tau_0=1.52x10^{-12}$s

Superparamagnetic behavior

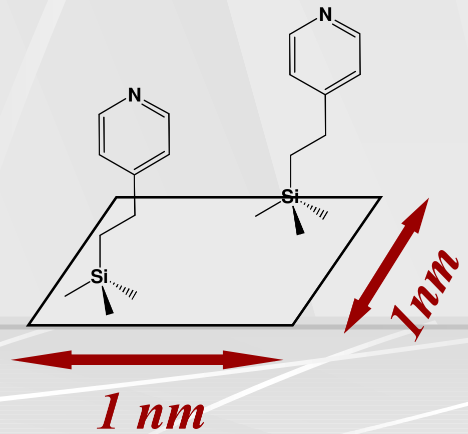
$M_x[M'(CN)_y]_z$ / SiO_2 nanomaterials.

Synthetic strategy



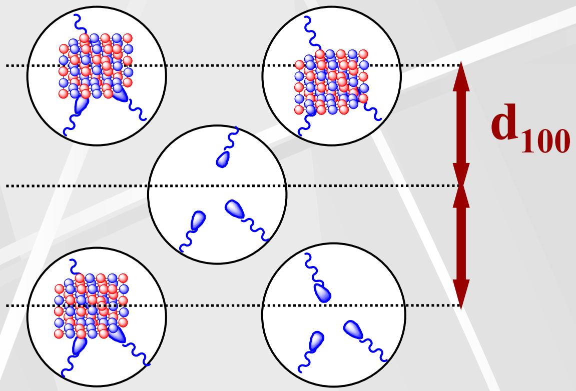


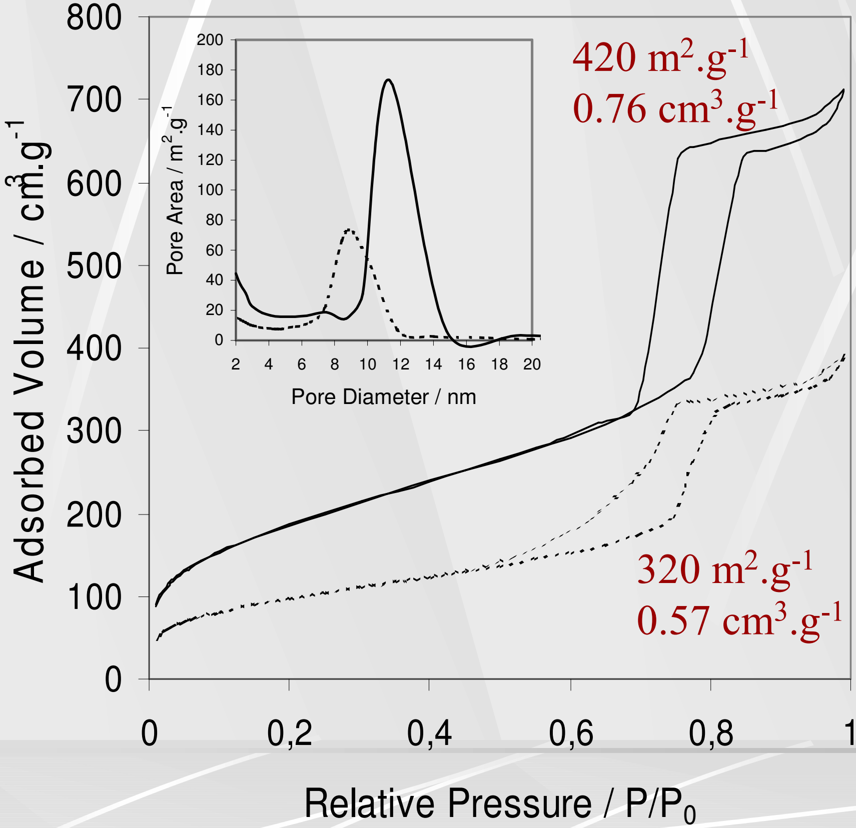
M' = Fe, Co (m = 6); Mo (m= 8)
M^{2+} = Fe, Ni, Co; M^{3+} = Fe



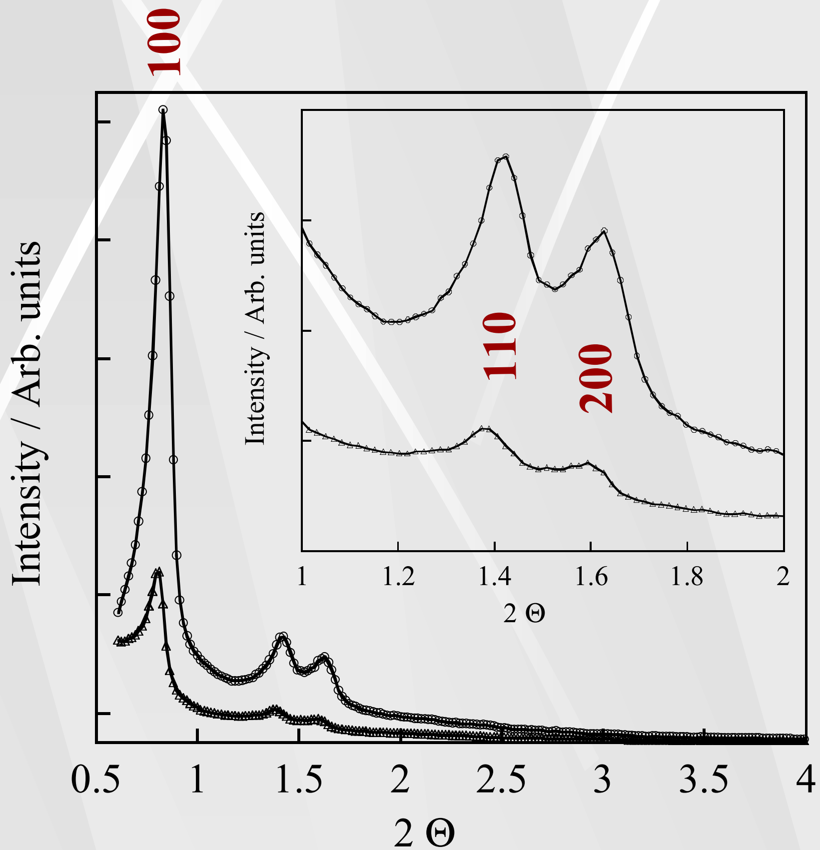
Clavel, G. et al. *New J. Chem.*, **2005**, *29*, 1

$M_x[M'(CN)_y]_z$ / SiO_2 nanomaterials.



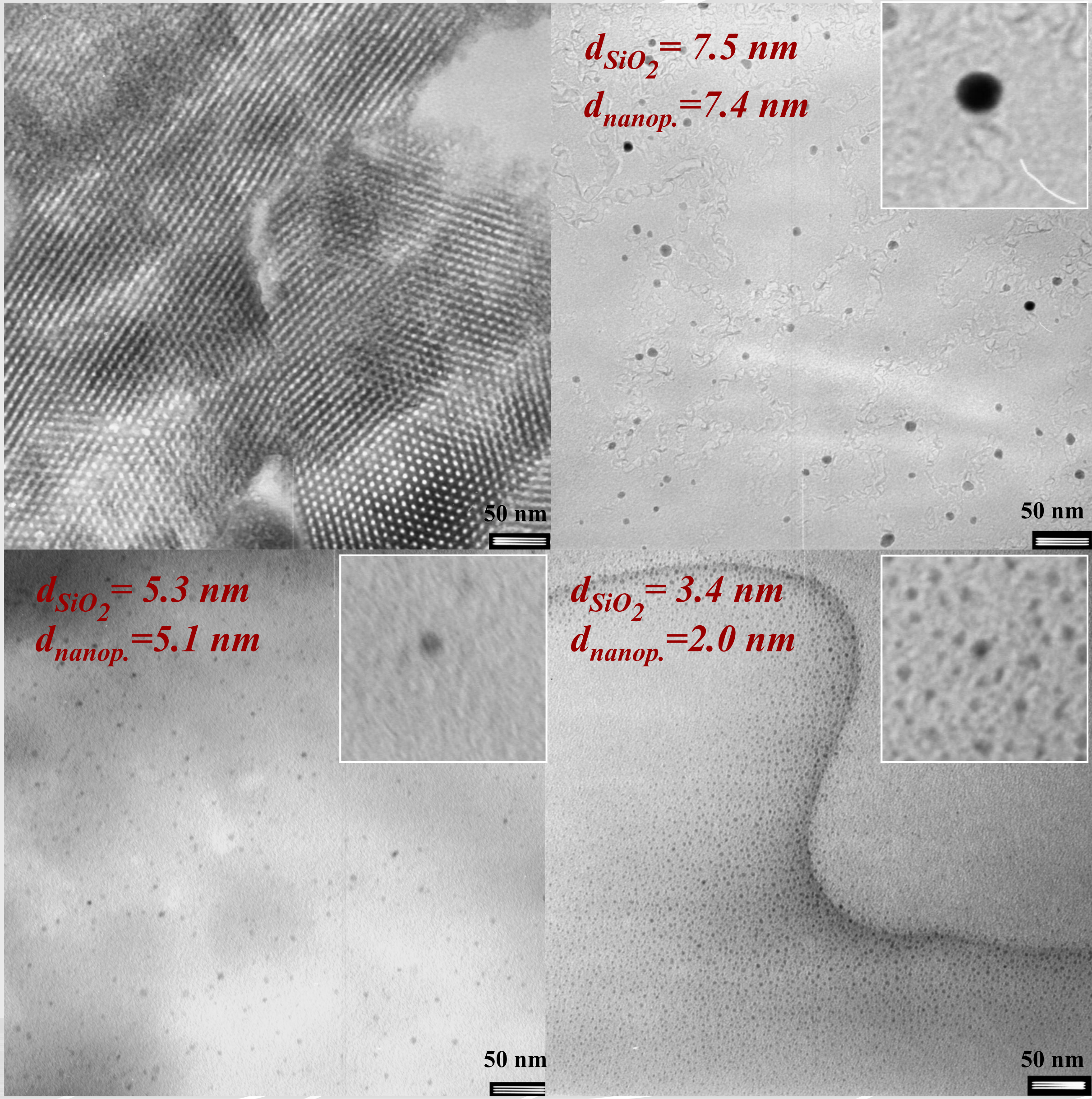


$Ni^{2+}/[Fe(CN)_6]^{3-}/SiO_2$

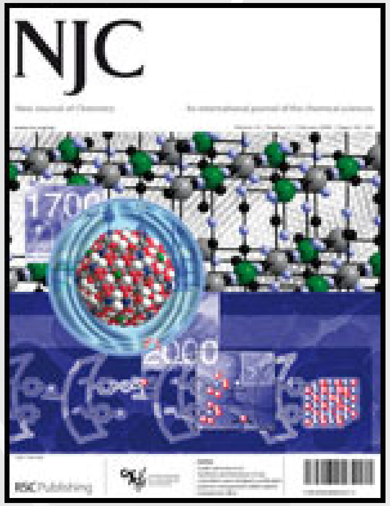


$M_x[M'(CN)_y]_z$ / SiO_2 nanomaterials.

$Ni^{2+}/[Fe(CN)_6]^{3-}/SiO_2$



Extractive replicas

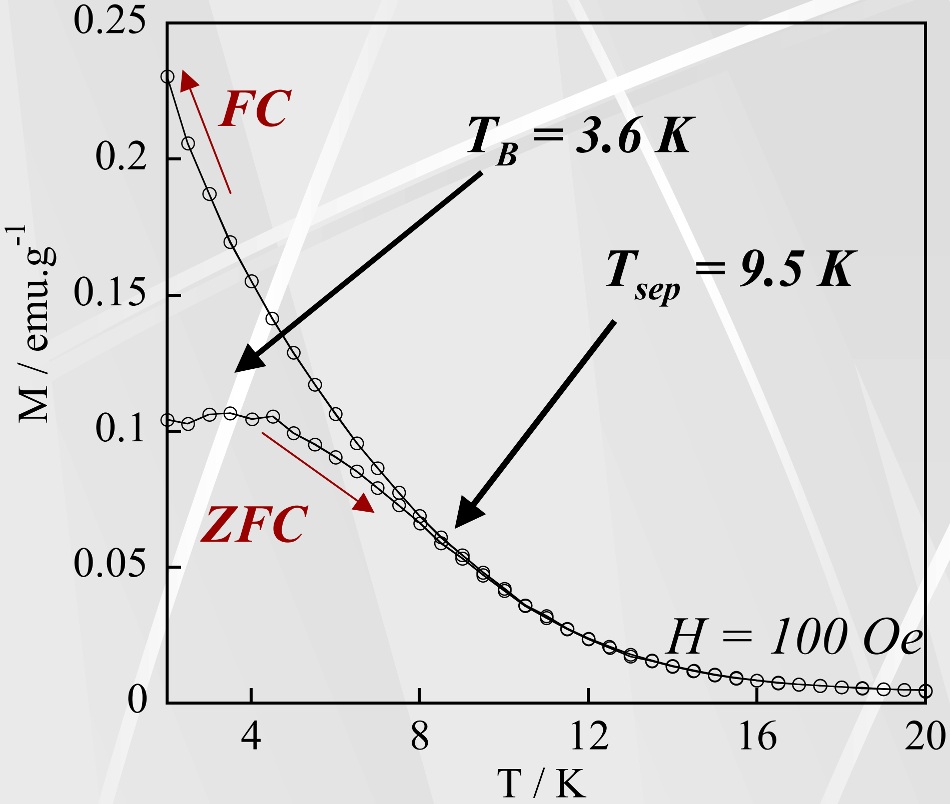


Larionova, J. et al.
New J. Chem., **2008**, *32*, 273

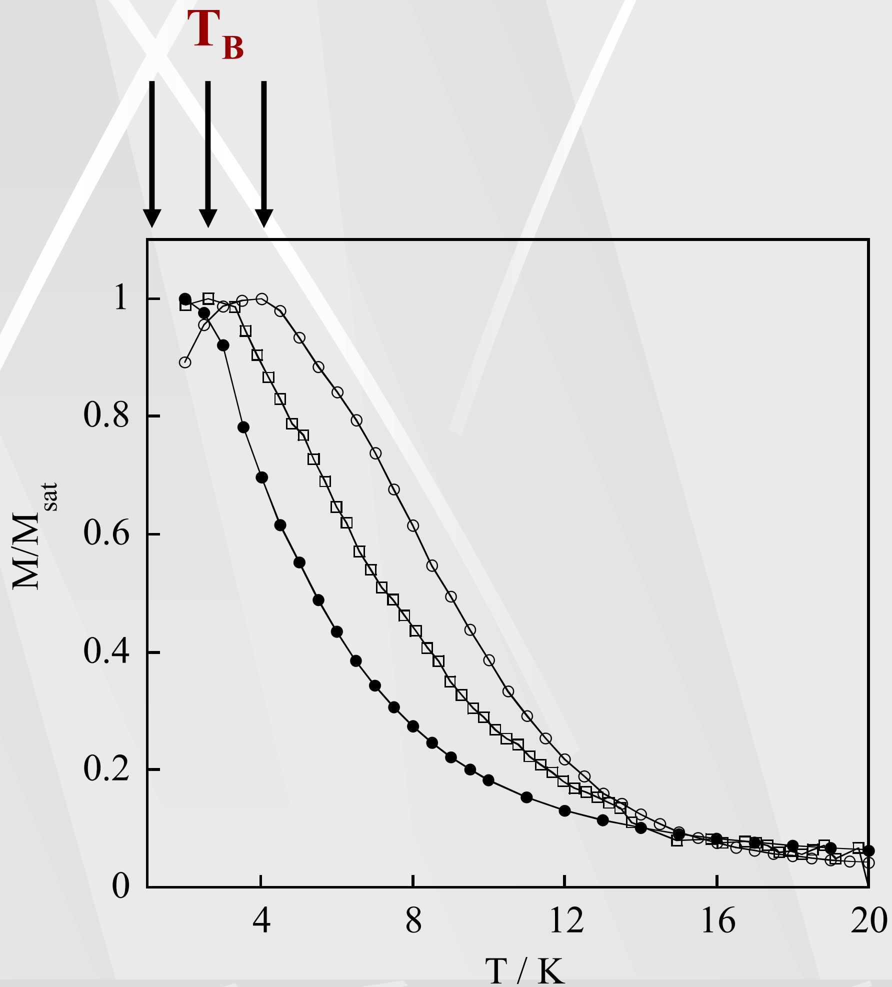
Collaboration
Pr. A. Caneschi
C. Sangregorio

$M_x[M'(CN)_y]_z$ / SiO_2 nanomaterials.

$Ni^{2+}/[Fe(CN)_6]^{3-}/SiO_2$



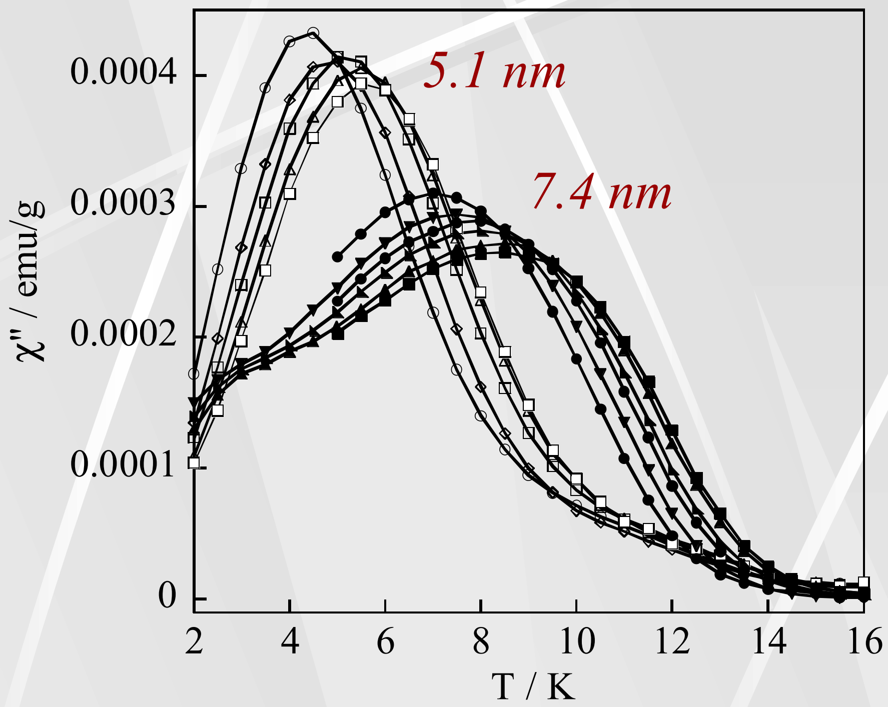
Magnetic properties
FC/ZFC curves



d_{SiO_2}/nm	$d_{nanop.}$/nm	T_B/K
7.5	7.4 ± 1.9	4.5 K
5.3	5.1 ± 1.2	2.6 K
3.4	2.0 ± 0.2	> 1.8 K

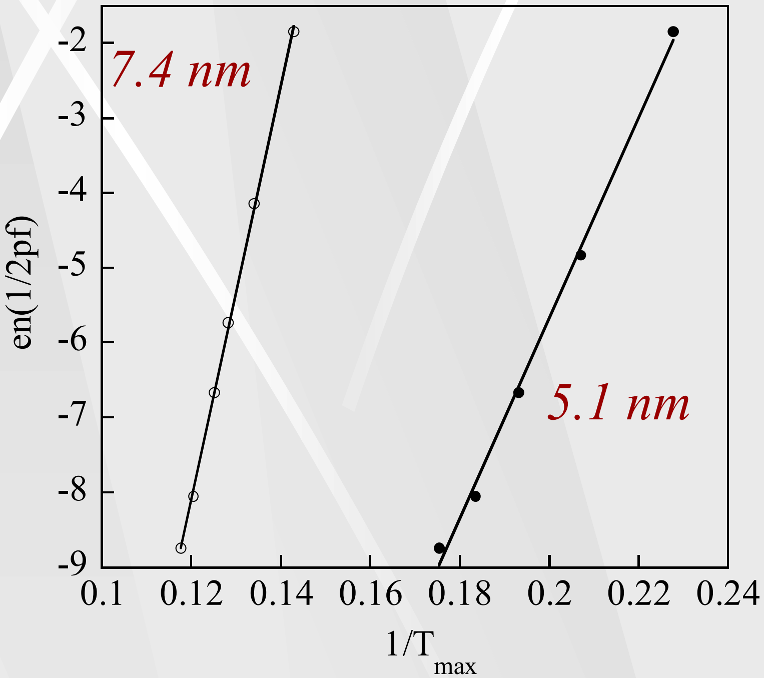
$M_x[M'(CN)_y]_z$ / SiO_2 nanomaterials.

$Ni^{2+}/[Fe(CN)_6]^{3-}/SiO_2$



Arrhenius law :

$\tau=\tau_0 exp(E_a/k_BT)$



Superparamagnetic systems

10^{-9}-10^{-12}

d_{SiO_2}/nm	E_a/k_B/K	τ_0/s
7.5	*276(8)*	*$1.56.10^{-18}$*
5.3	*134(3)*	*$7.75.10^{-15}$*

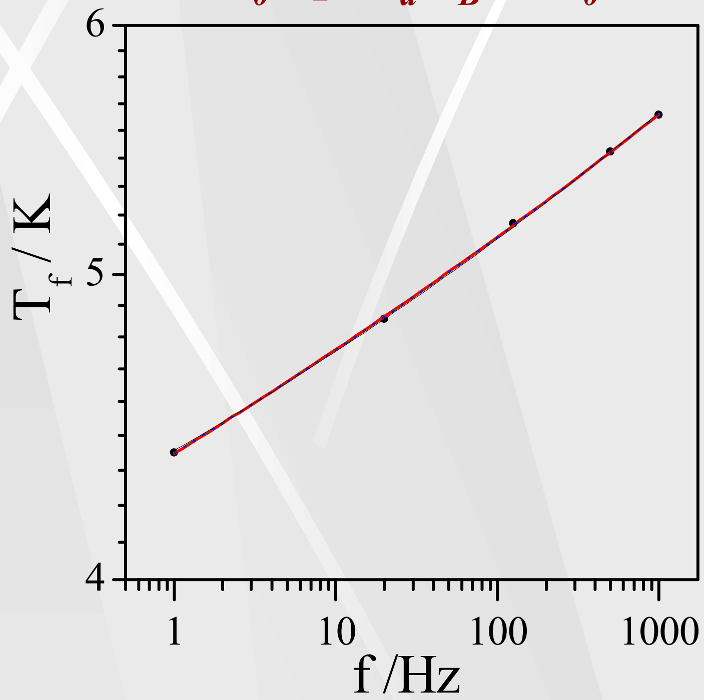
$M_x[M'(CN)_y]_z / SiO_2$ nanomaterials.

$Ni^{2+}/[Fe(CN)_6]^{3-}/SiO_2$

d_{SiO_2}/nm	E_d/k_B/K	τ_0/s	T_0/K
7.5	261(20)	$5.60.10^{-14}$	0.15±0.4
5.3	132(30)	$4.75.10^{-14}$	0.11±0.6

Vogel-Fulcher law

$$\tau = \tau_0 exp(E_d/k_B(T-T_0))$$



Weak magnetically interacting clusters

$$E_{d-d} = \frac{\mu_0}{4\pi} M_S^2 V_m \varepsilon = \frac{\mu_0}{24} M_S^2 d_m^3 \varepsilon$$

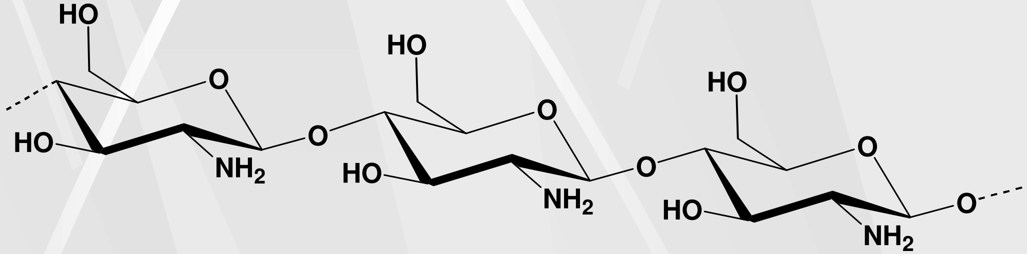
$$E_{d-d}/k_B \approx 1\ K$$

Modified superparamagnetic regime due to the spin-frustration on the surface of nanoparticles.

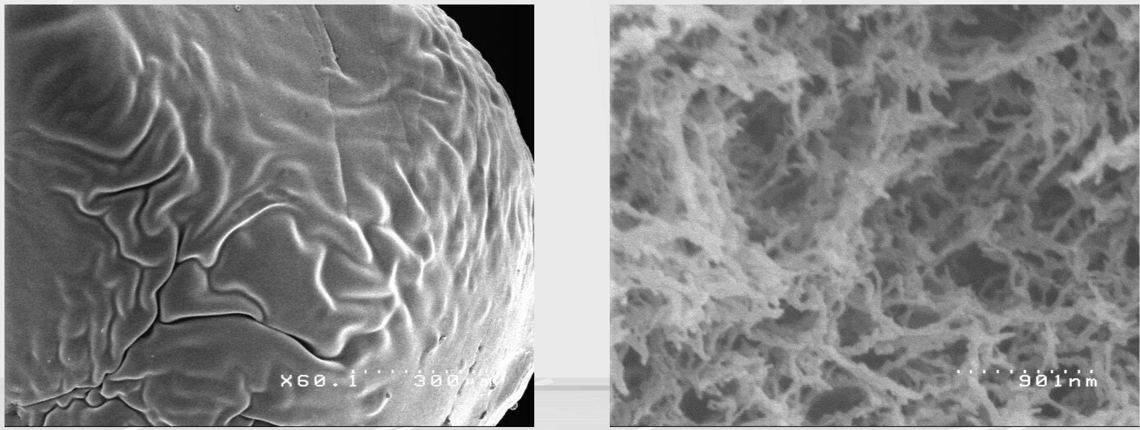
Water soluble coordination polymer nanoparticles

Why we use the chitosan beads?

- a porous structure - easy diffusion of precursors;
- the functional amino groups able to coordinate metal ions - covalent anchoring of the cyano-bridged metallic network;
- high water solubility.



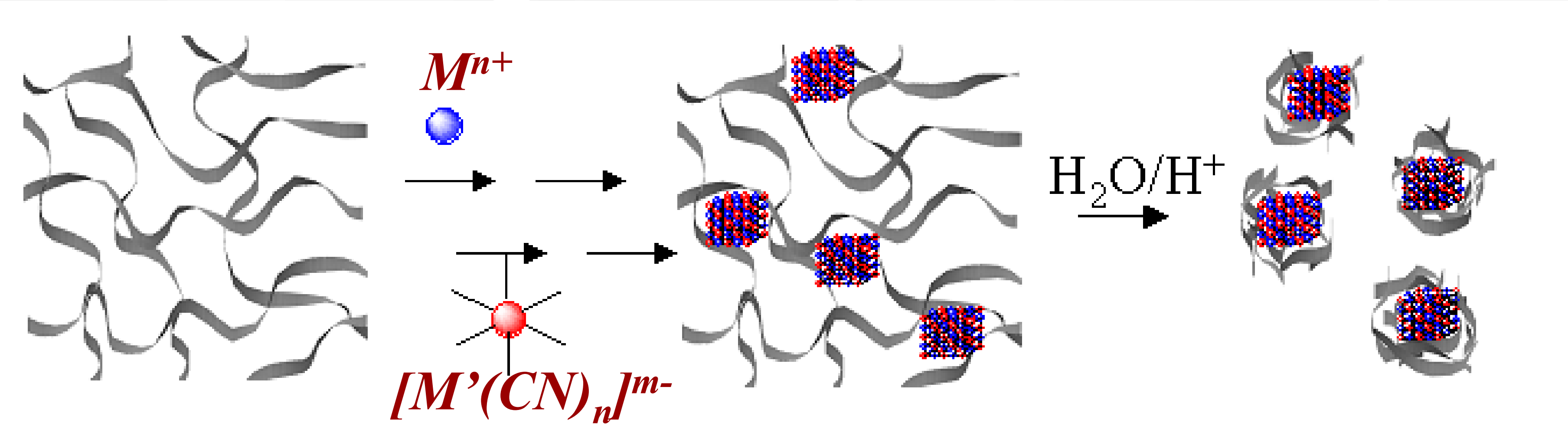
SEM images
of a chitosan bead



Collaboration

Dr. K. Molvinger

Water soluble coordination polymer nanoparticles



Pristine chitosan beads

Nanocomposite beads

Aqueous nanoparticles solution

M^{2+} = Fe, Ni, Co, Mn, Cu… and M^{3+} = Gd, Yb, Eu…
M' = Fe, Cr, Co (n = 6); Ni, Pt (n = 4), Mo (n = 8)

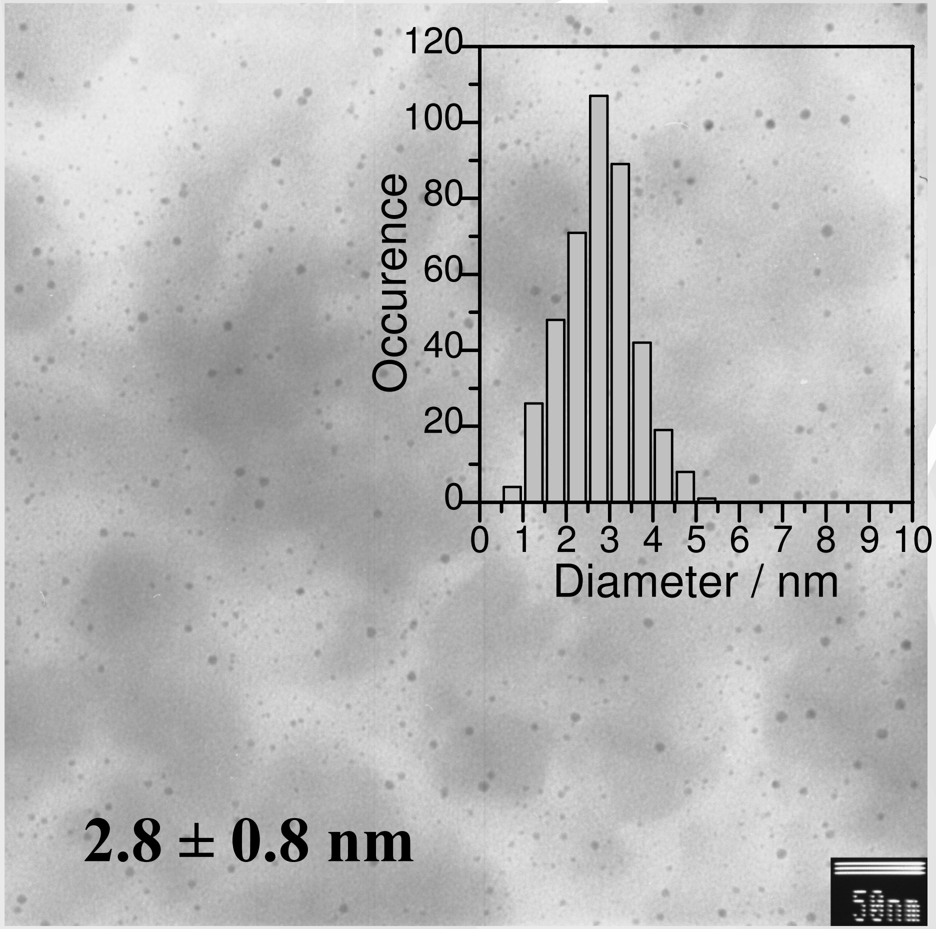
Water soluble coordination polymer nanoparticles

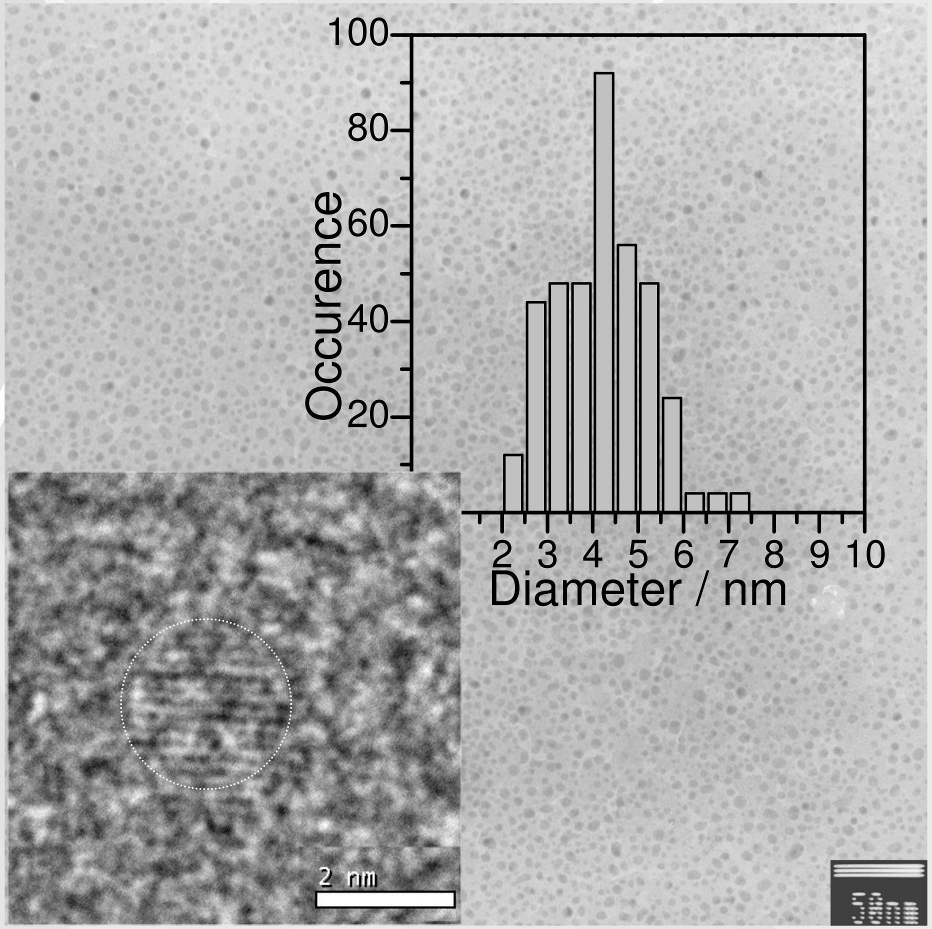
Fe^{2+}/$[Fe(CN)_6]^{3-}$/ chitosan | *Cu^{2+}/$[Fe(CN)_6]^{3-}$/ chitosan* | *Ni^{2+}/$[Fe(CN)_6]^{3-}$/ chitosan* | *Co^{2+}/$[Fe(CN)_6]^{3-}$/ chitosan*

Guari, Y. et al. *Chem. Commun.*, **2006**, 2613.

Water soluble coordination polymer nanoparticles

Ni^{2+}/$[Fe(CN)_6]^{3-}$/chitosan



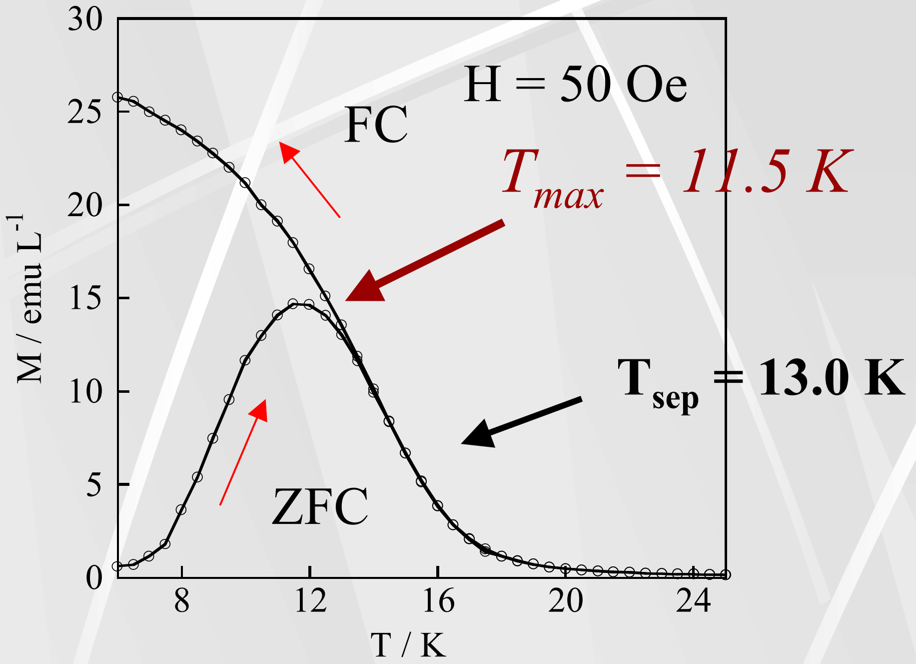


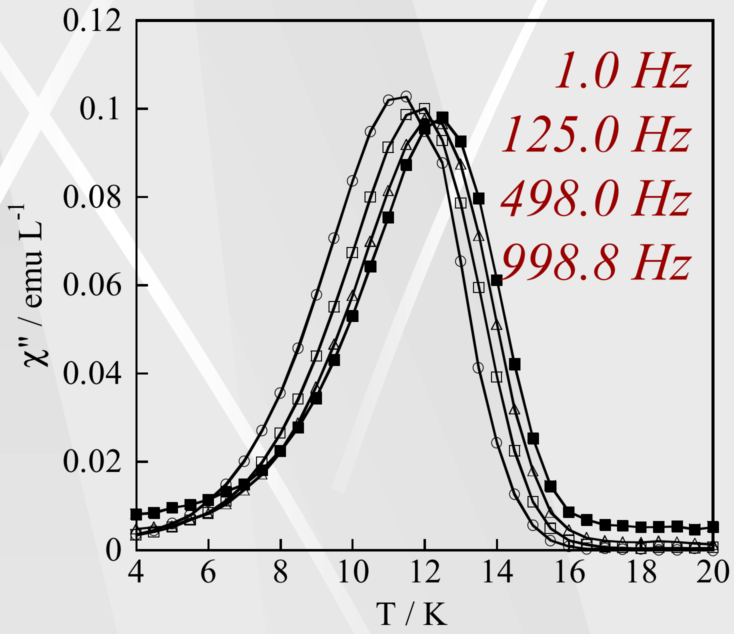
Nanocomposite beads

Aqueous nanoparticles solution

Magnetic Properties

$Ni^{2+}/[Fe(CN)_6]^{3-}$/chitosan





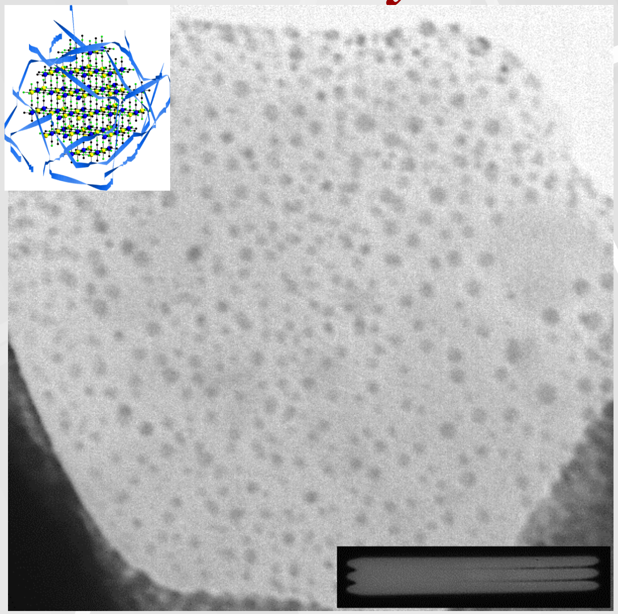
Arrhenius law: $\tau=\tau_0 exp(\Delta/k_B T)$

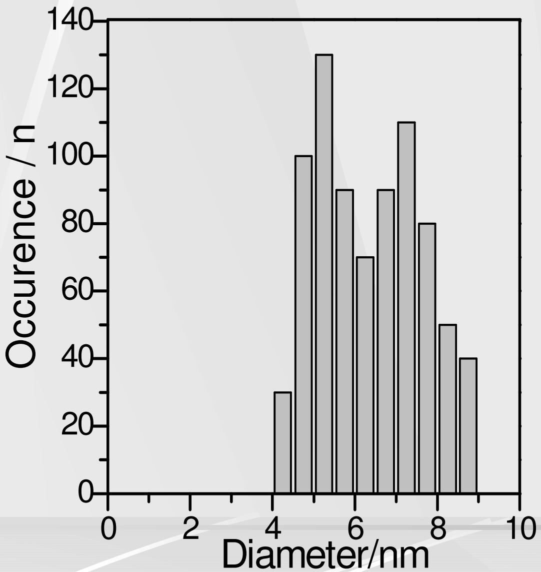
$\Delta E/k_B$=702K τ_0=1.1x10^{-28}s

Spin glass behavior due to the presence of strong interparticle interactions and spin-frustration on the surface.

Almeida-Touless line

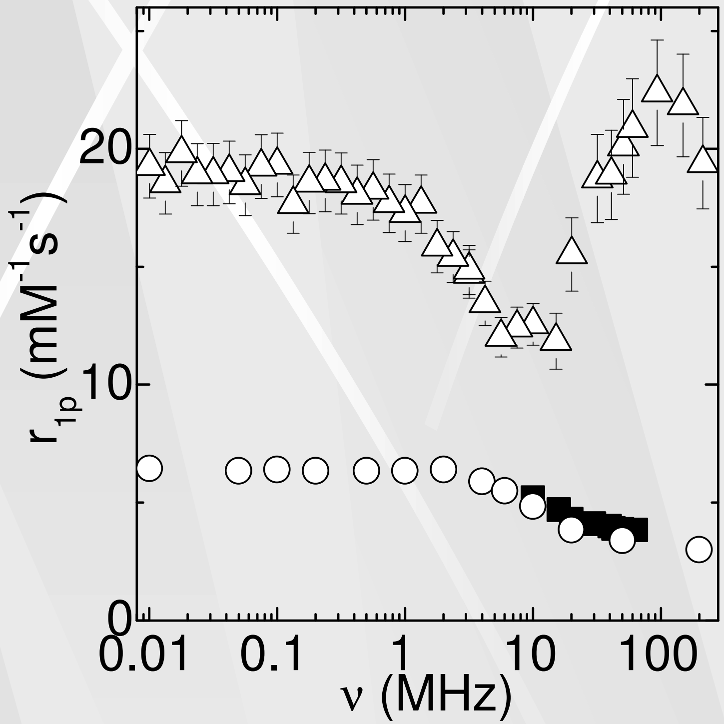
Cyano-Bridged Coordination Polymer Nanoparticles with High Nuclear Relaxivity : Toward New Contrast Agents For MRI.





Guari, Y. et al. *Dalton Trans.*, **2008**.

Longitudinal relaxivity collected at T≈25°C



△ ***$Gd[Fe(CN)_6]$/Chitosan***

○ ***Omniscan***

■ ***Gd(DTPA)***

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