ICG Montpellier

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

UNIVERSITÉ MONTPELLIER 2 SCIENCES ET TECHNIQUES

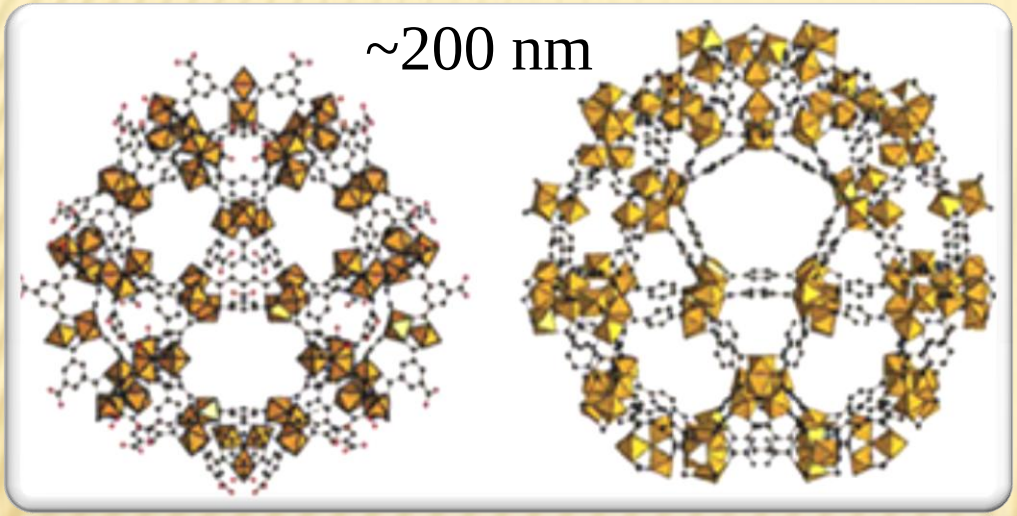
Coordination Polymer Nanoparticles: New Objects and New Trends.

Joulia Larionova

- A new type of inorganic nanoparticles
- Multifunctional magneto-optical nanoparticles
- New contrast agents for MRI and biolabeling

A New type of Inorganic Nanoparticles:
Coordination Polymer Nanoparticles

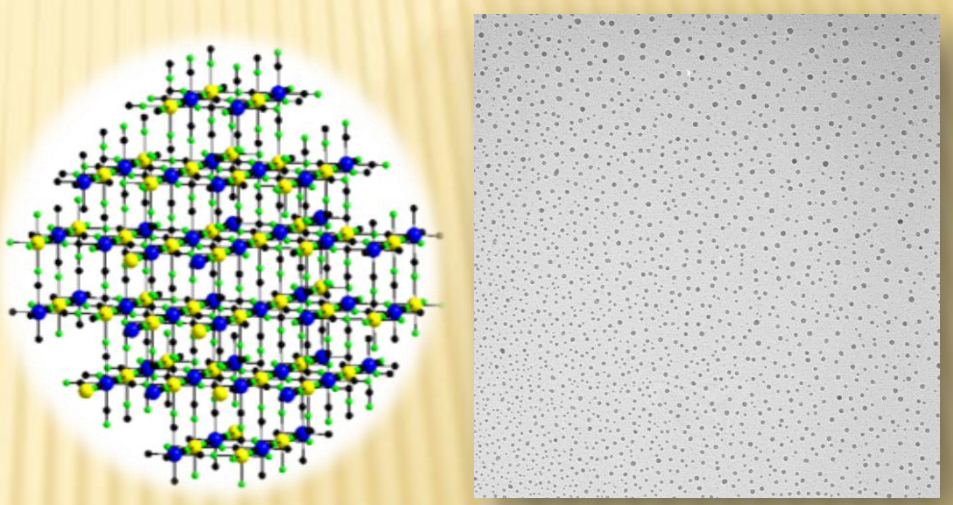
Porous Iron Carboxilates Frameworks Nanoparticles



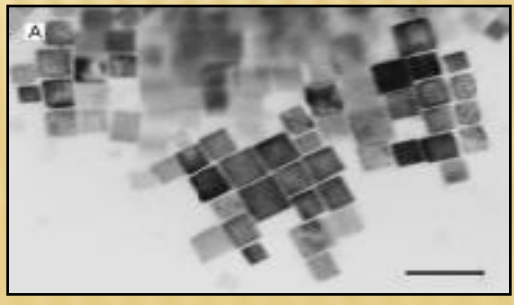
G. Ferey, *Nature Materials* 2010, *9*, 172

Cyano-Bridged Metallic Nanoparticles

1 - 100 nm



Nanocubs of $Fe^{III}_4[Fe^{II}(CN)_6]_3$



S. Mann, *Angew. Chem. Int. Ed.*, 2000, *39*, 1793

Cyano-Bridged Metallic Coordination Polymer Nanoparticles

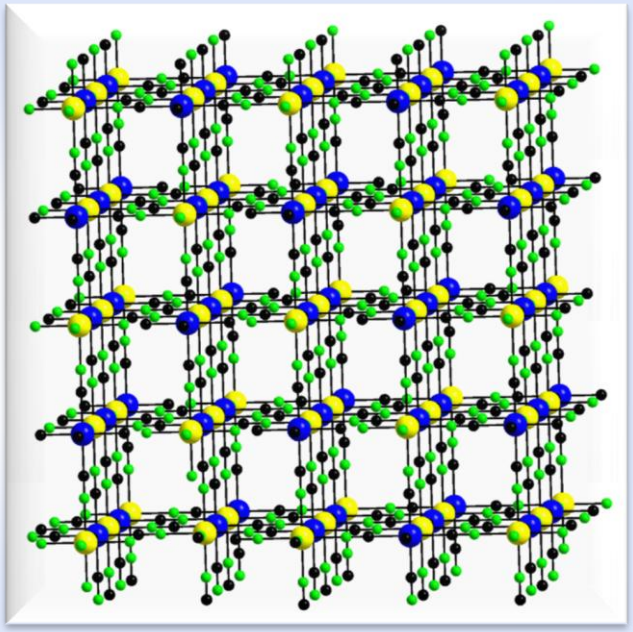
The oldest bulk coordination polymers…

Prussian Blue:

Discovered in1704

$Fe^{III}_4[Fe^{II}(CN)_6]_3$

Johann Conrad Dippel

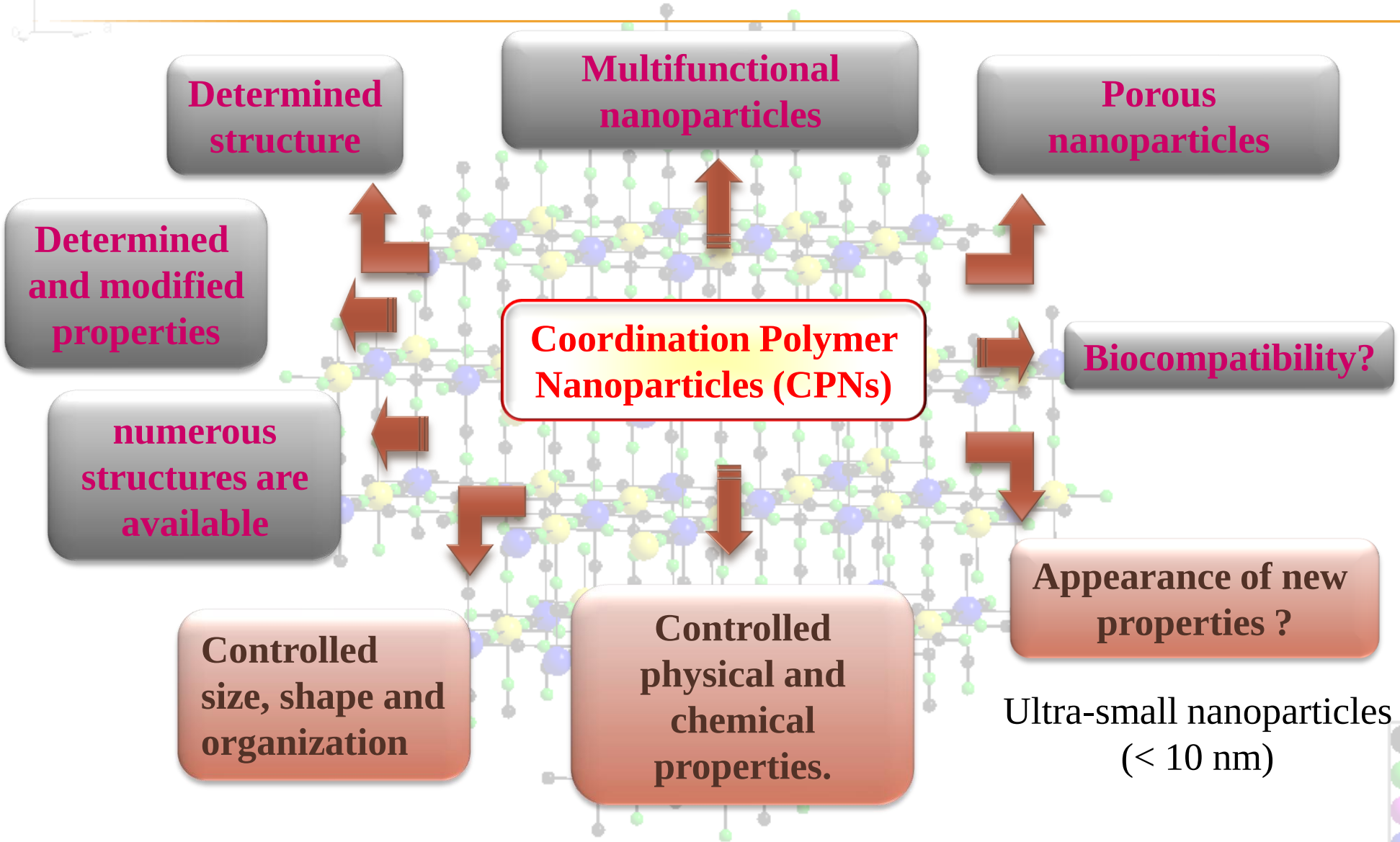


$M_x[M'(CN)_n]_y$

M and M' = transition metal ions or lanthanides

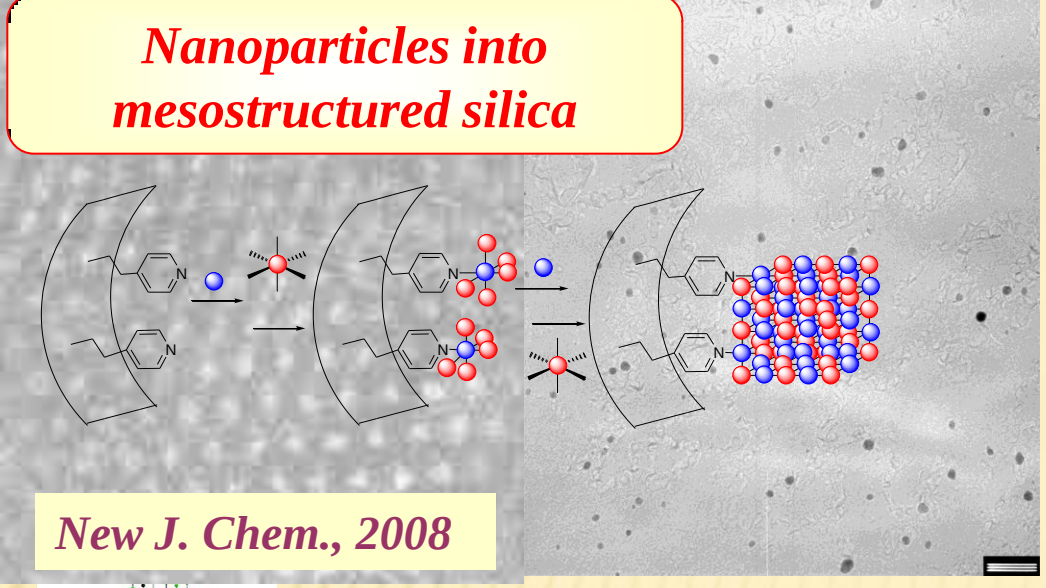
- *a pigment;*
- *magnetic properties: molecular magnets;*
- *photo-magnetic properties;*
- *host-guest properties: molecular sieves;*

Cyano-Bridged Metallic Coordination Polymer Nanoparticles



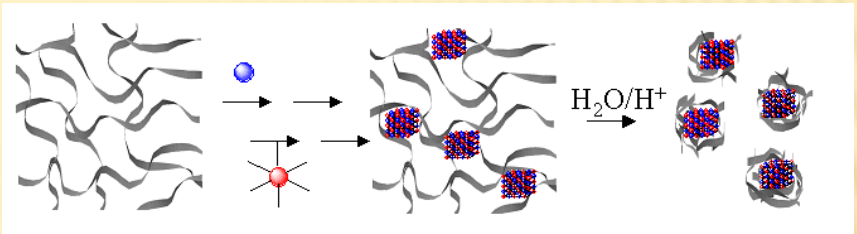
Ultra-small nanoparticles
(< 10 nm)

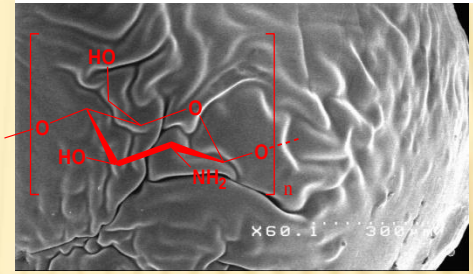
Nanoparticles into mesostructured silica



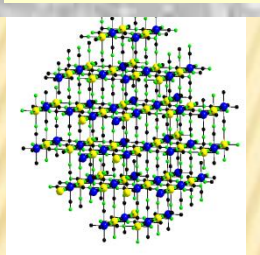
New J. Chem., 2008

Nanoparticles into chitosan



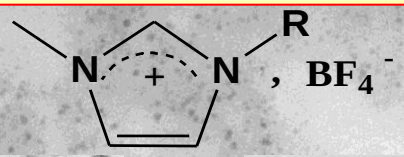


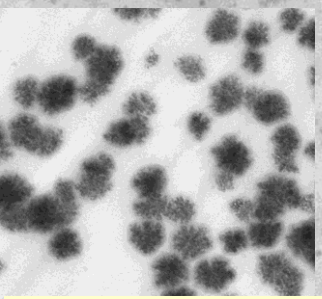
Chem Commun. 2006;
Dalton Trans. 2008
Angew. Chem. 2009

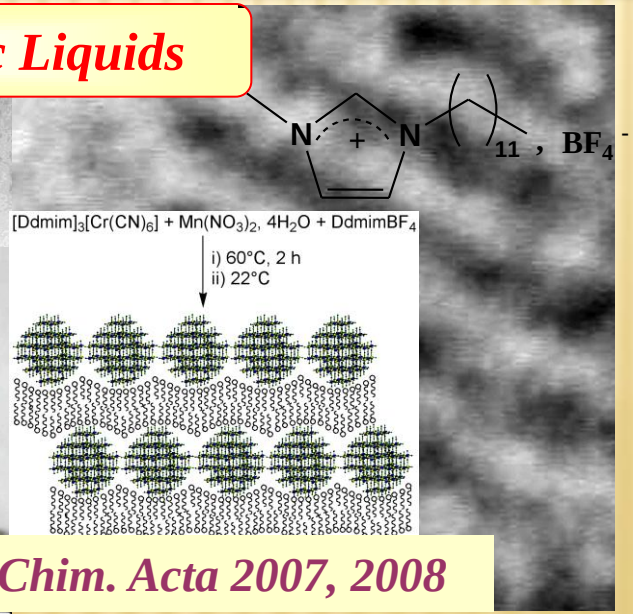


Nanoparticles of cyano-bridged coordination polymers

Nanoparticles into Ionic Liquids

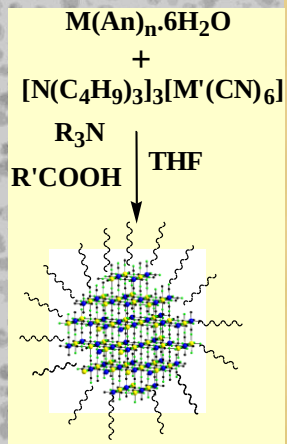






Chem: Eur. J., 2006; Inorg. Chim. Acta 2007, 2008

Nanoparticles with Ligands

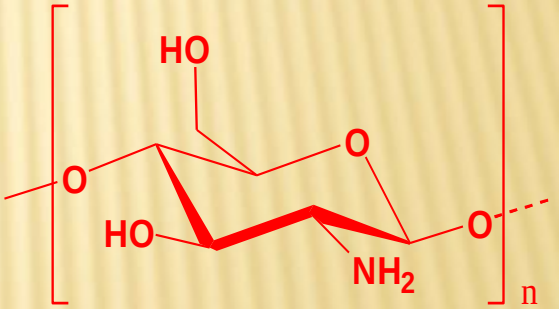


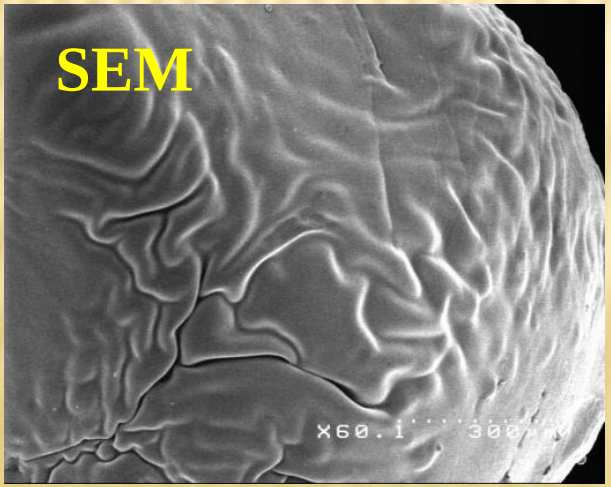
Chem.Mater., 2007

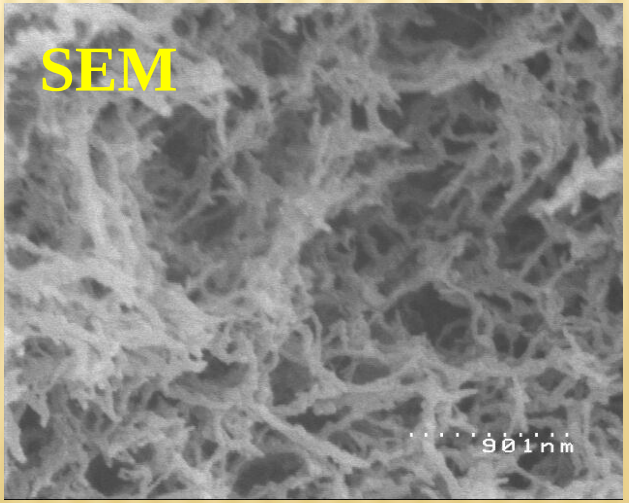
Water Soluble Cyano-Bridged Metallic Nanoparticles enwrapped by biopolymer chitosan

Why we use the chitosan beads?

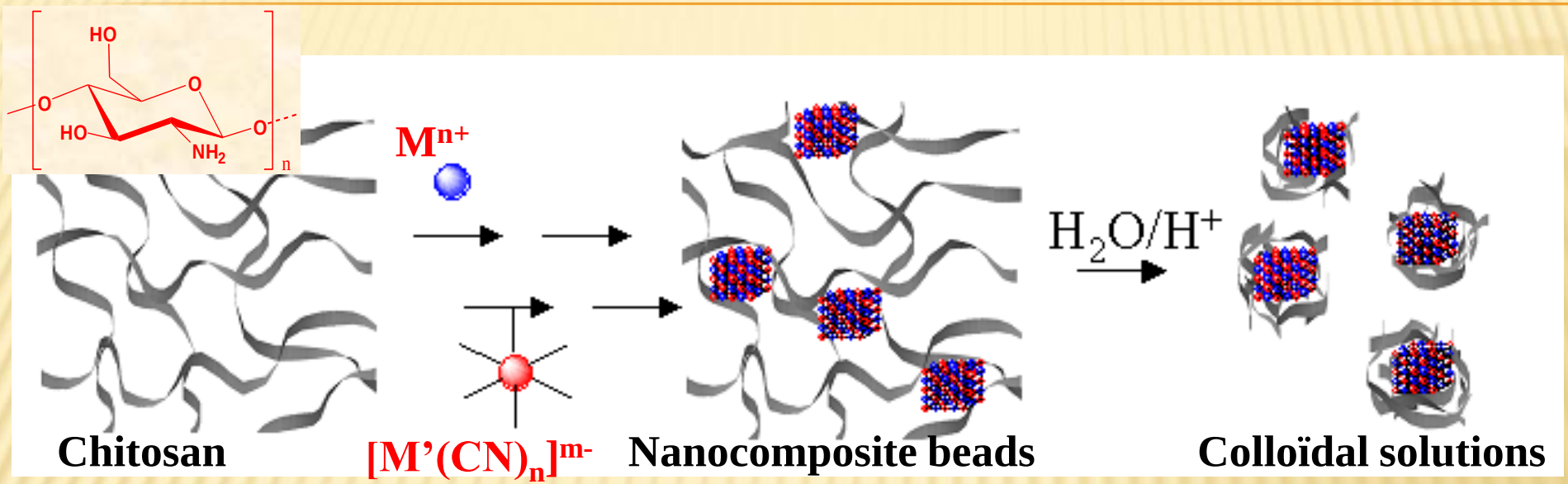
- a porous structure - diffusion of precursors;
- NH_2 groups able to coordinate metal ions -
- high water solubility;
- biocompatibility.







Water Soluble Cyano-Bridged Metallic Nanoparticles enwrapped by biopolymer chitosan



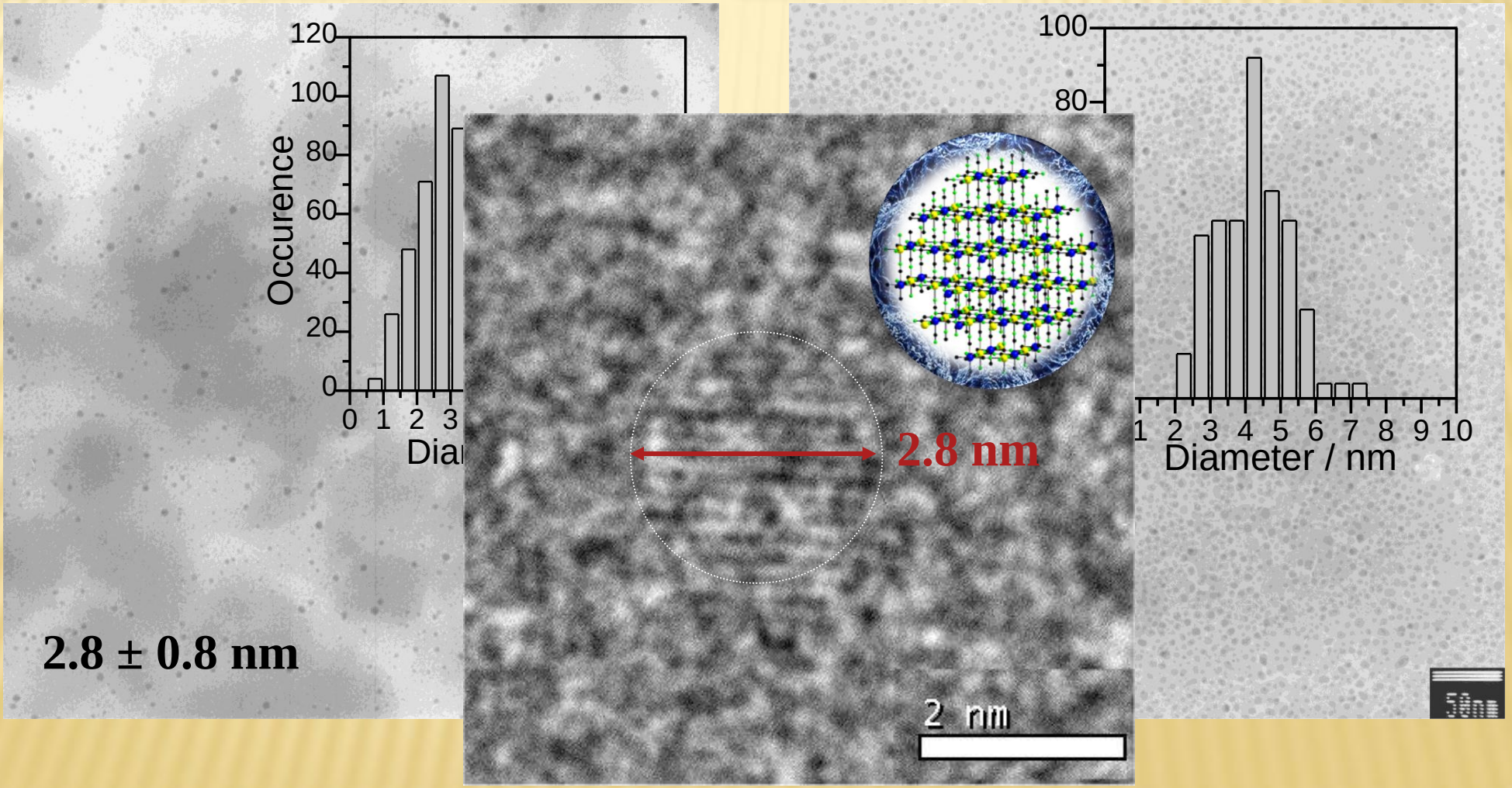
M^{2+} = Fe, Ni, Co, Mn, Cu… and
M^{3+} = Gd, Yb, Eu…
M' = Fe, Cr, Co (n = 6); Ni, Pt (n = 4), Mo (n = 8)

Chem Commun. 2006;
Dalton Trans. 2008,
Angew. Chem. 2009,
PCCP 2010

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

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

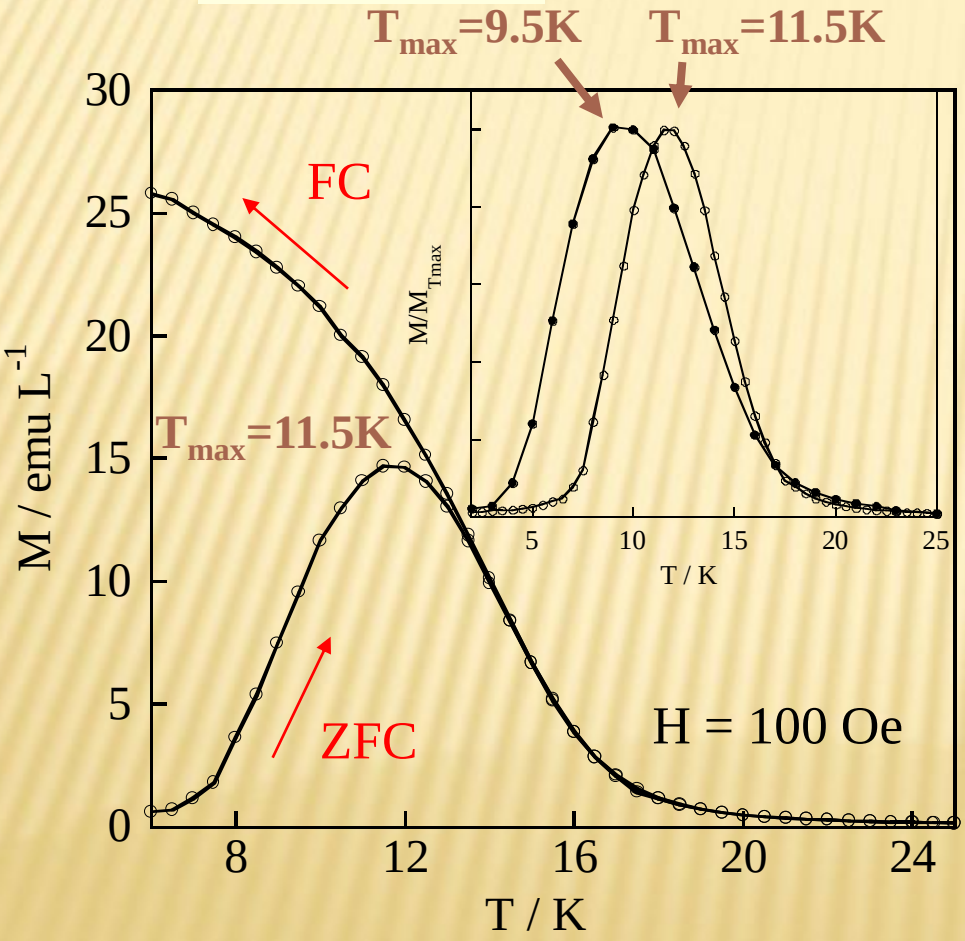
Aqueous colloid of $Ni^{2+}/[Fe(CN)_6]^{3-}$/chitosan



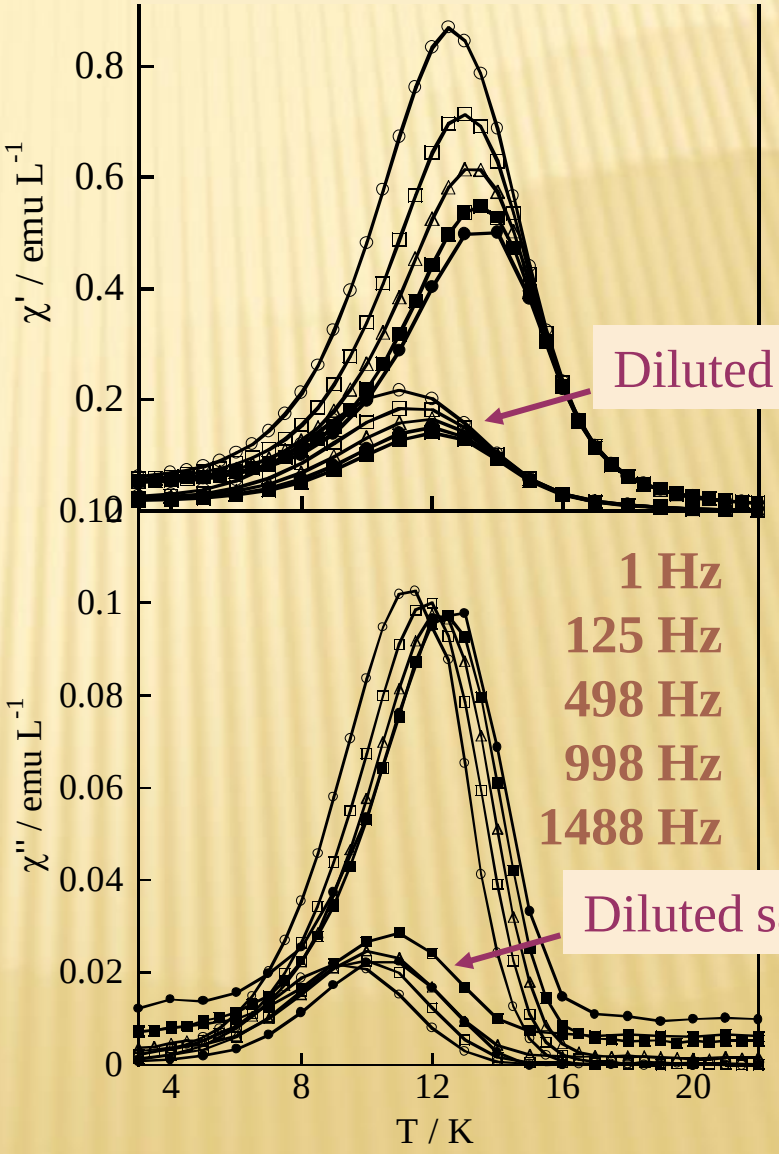
Magnetic Properties as a probe to study nanoparticles behavior

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

Diluted sample:



1 ***Dynamic analysis:***



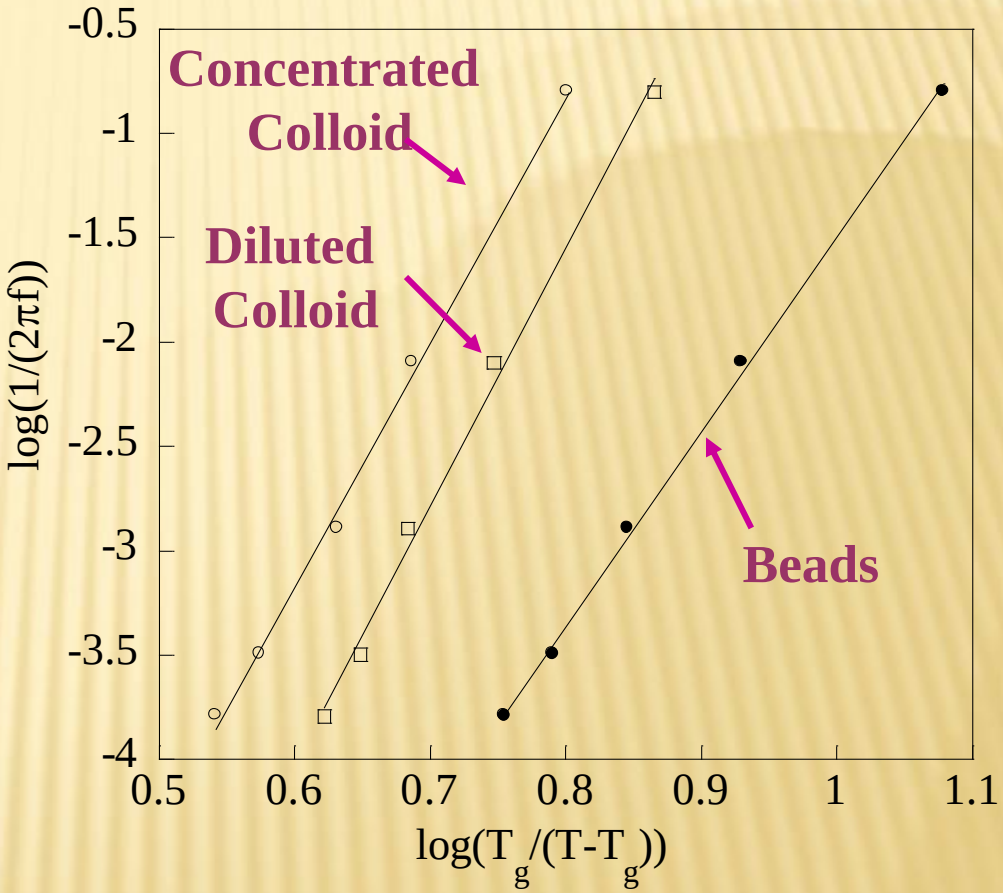
Magnetic Properties as a probe to study nanoparticles behavior

Critical slowing down:

$$\tau = \tau_0 [T_g/(T_{max} - T_g)]^{z\nu}$$

T_g, K	τ_0, s	$z\nu$
Colloids $Ni^{2+}/[Fe(CN)_6]^{3-}$/chitosan		
11.2	$3.56 \cdot 10^{-12}$	12.4
Diluted $Ni^{2+}/[Fe(CN)_6]^{3-}$/chitosan		
9.5	$7.29 \cdot 10^{-11}$	11.7

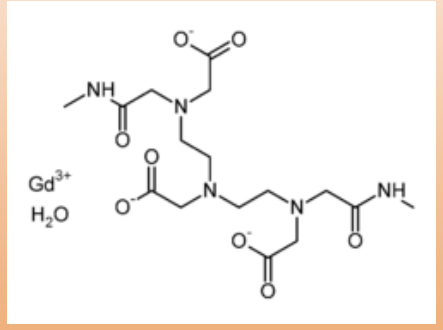
$z\nu = 4 - 12$; $\tau_0 = 10^{-8} - 10^{-13}$ s

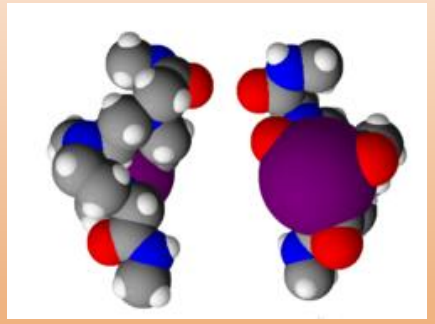


Superspin-glass behavior due to the presence of interparticle interactions and surface spin frustration

Coordination Polymer Nanoparticles as Contrast Agent for Magnetic Resonance Imaging:

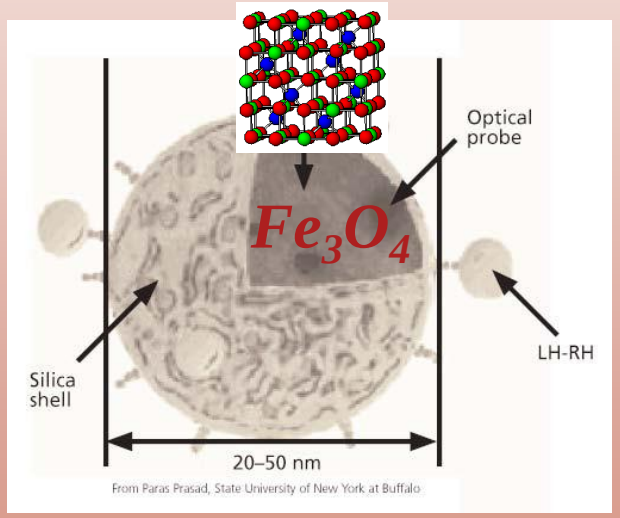
Paramagnetic Gd^{3+} complexes: positives CA





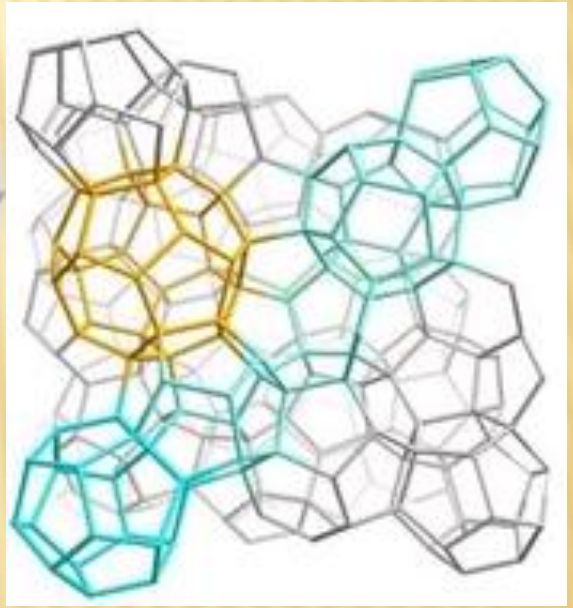
Omniscan®, Gadoteridol®, Dotarem®…

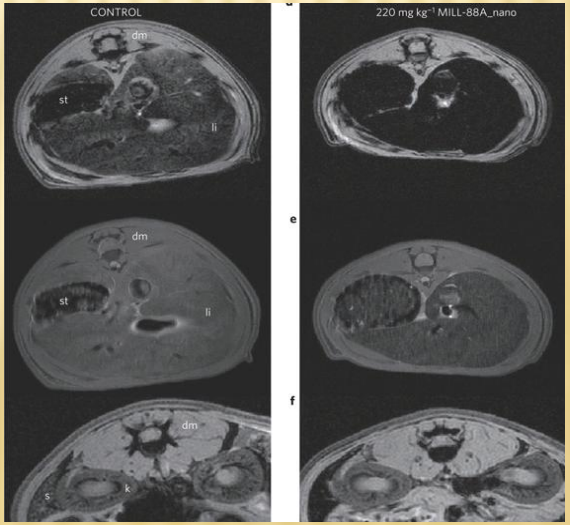
SPIONs: negatives CA



Resovist®, Combidex®, Endorem®…

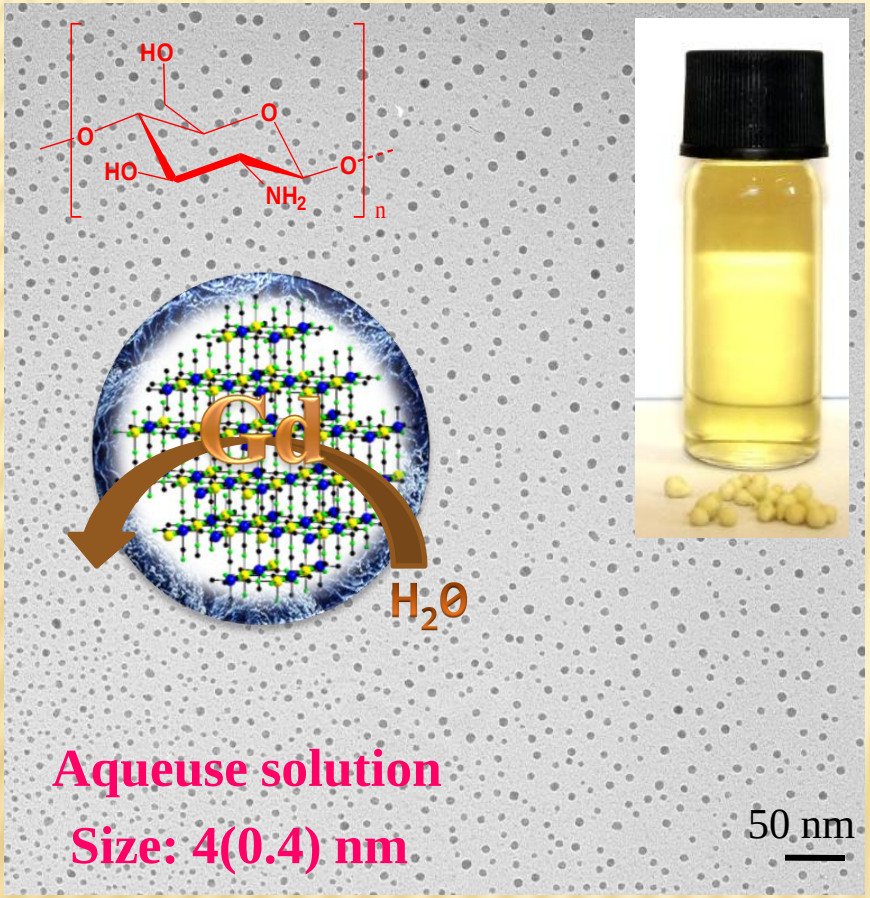
Porous Iron Carboxilates Frameworks Nanoparticles



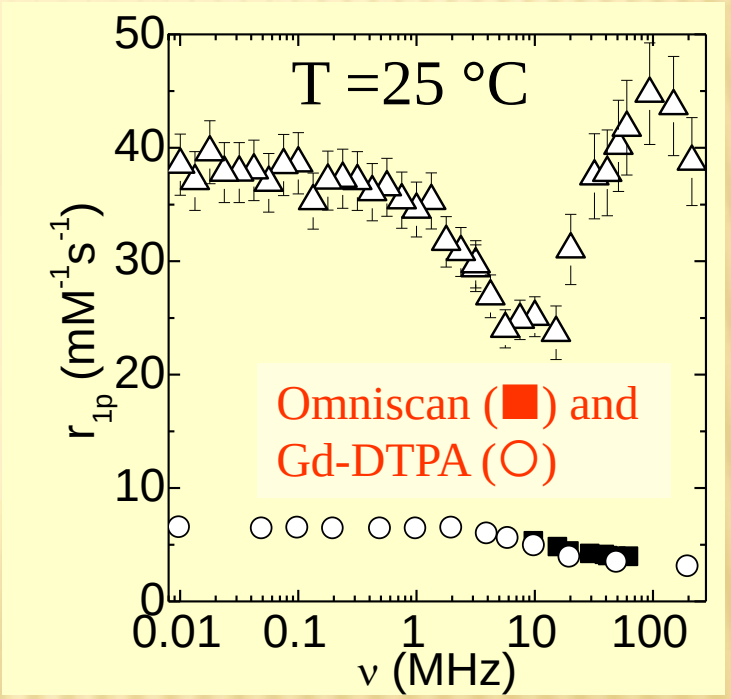


G. Ferey, *Nature Materials* **2010**, *9*, 172

$Gd[Fe(CN)_6]$/chitosan Nanoparticles



Longitudinal relaxivity

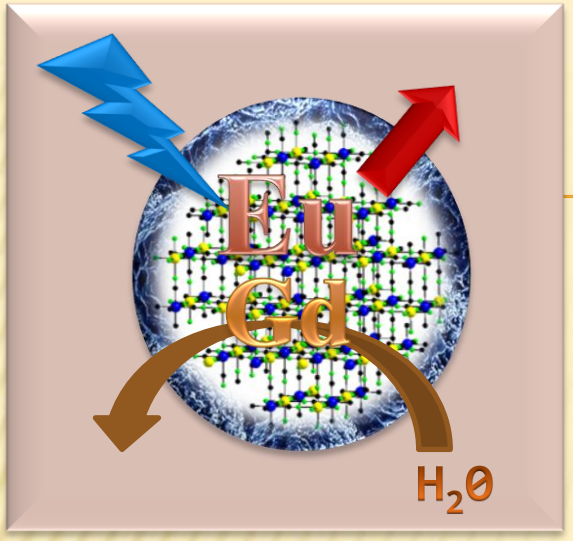


$$r_{ip} = [(1/T_i)_{meas} - (1/T_i)_{dia}]/c \quad i=1,2$$

$(1/T_i)_{meas}$ is the measured value on the sample with concentration c = 4 mmol L^{-1} of Gd^{3+}

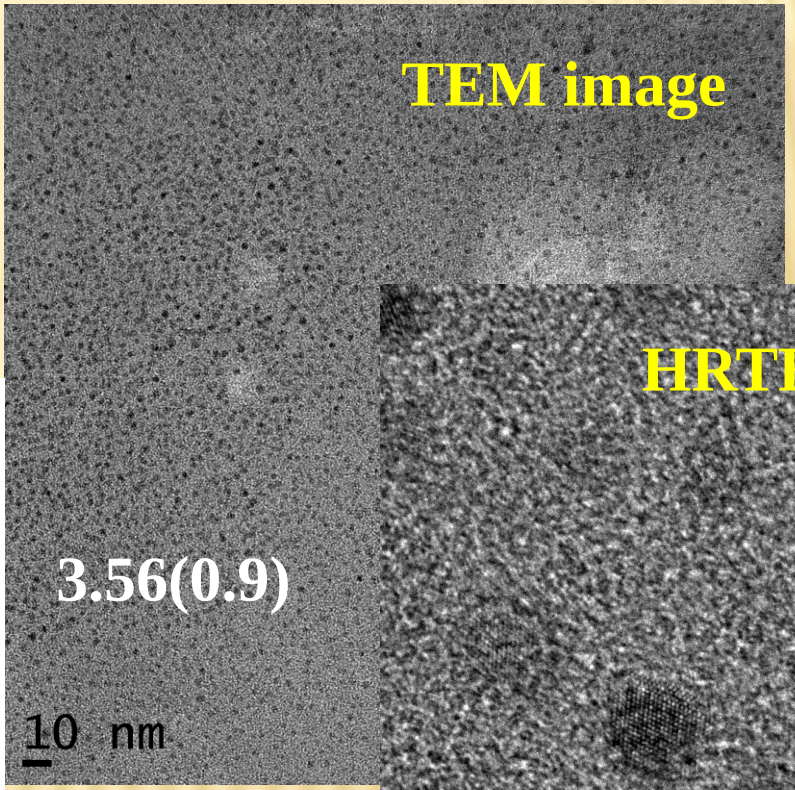
$(1/T_i)_{dia}$ is the nuclear relaxation rate of water

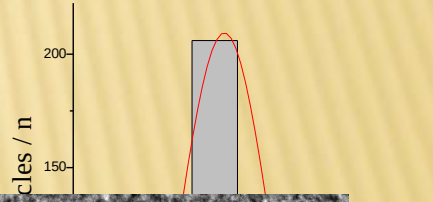
Dalton Trans. 2008.

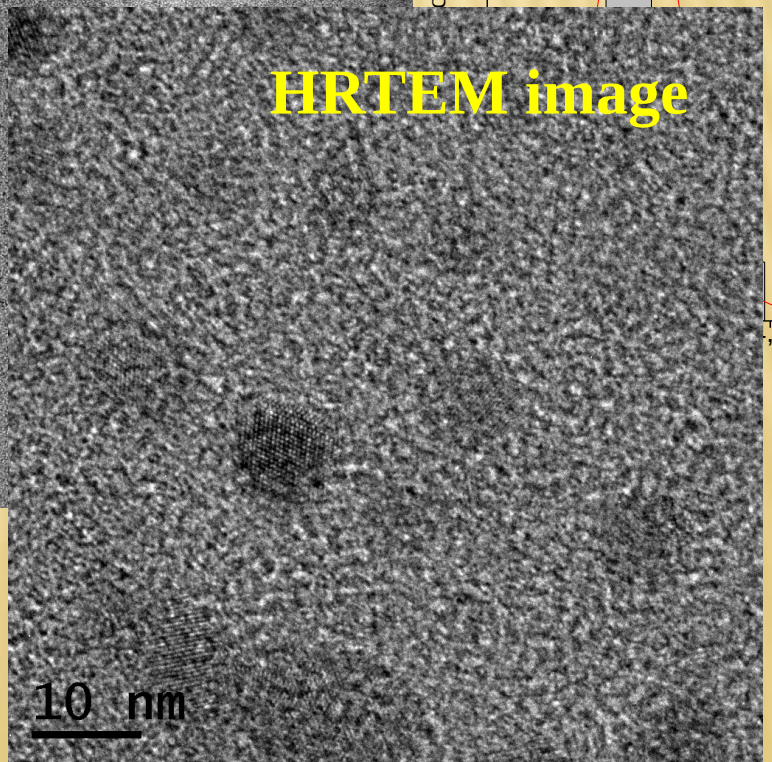


Multifunctional $Gd_{0.5}Ln_{0.5}[Mo(CN)_8]$/chitosan (Ln = Eu, Tb) Nanoparticles

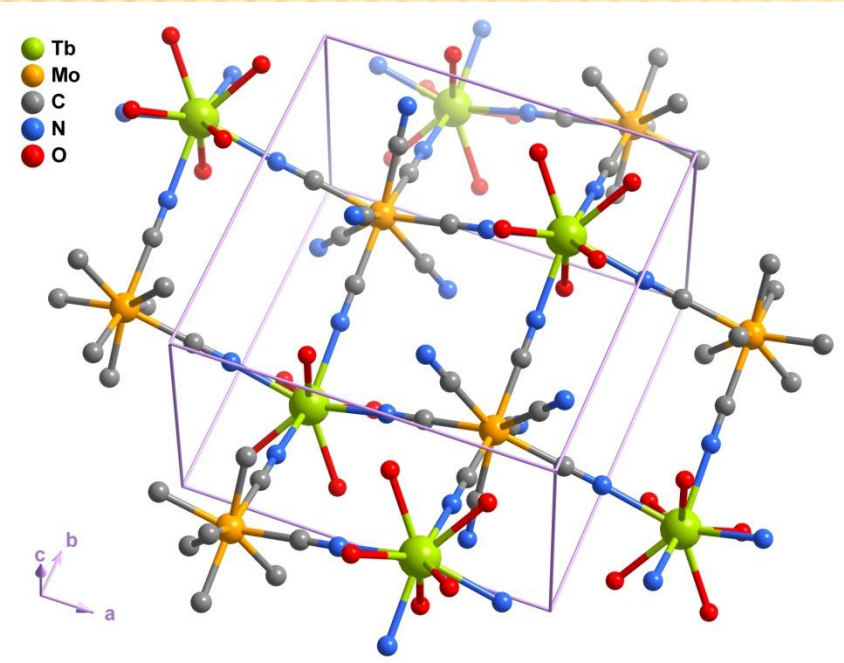
Aqueous colloidal solutions:



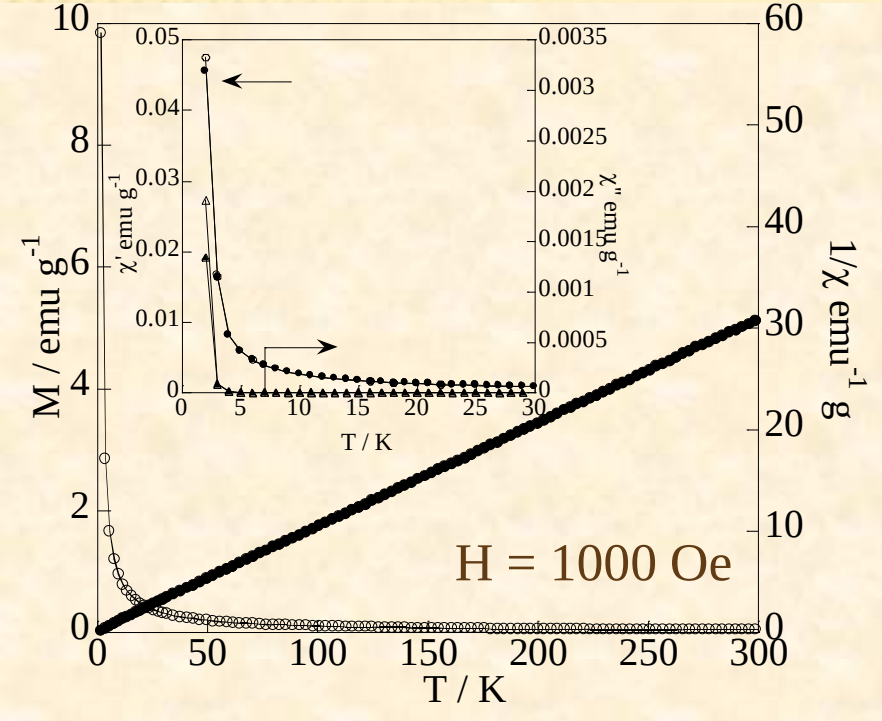




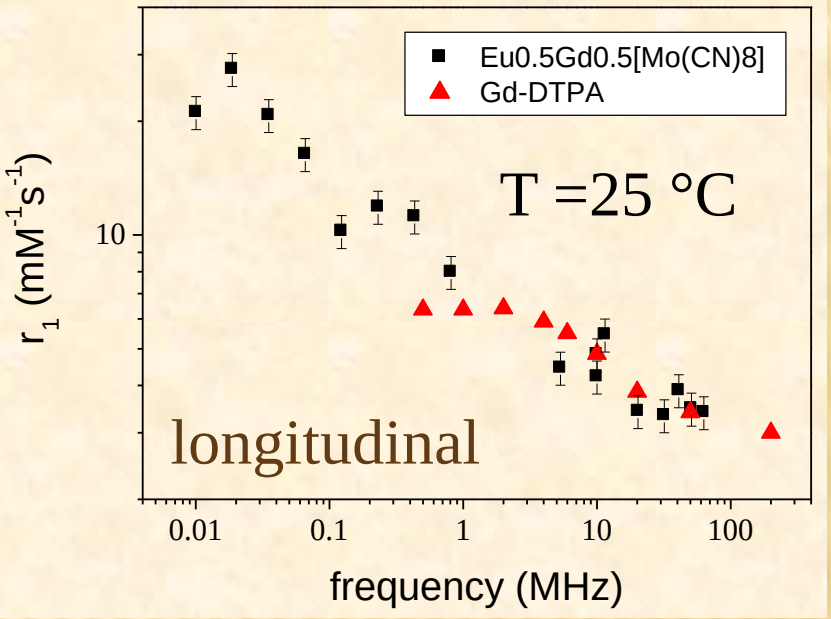
Crystal structure of bulk $Gd_{0.5}Ln_{0.5}[Mo(CN)_8]$

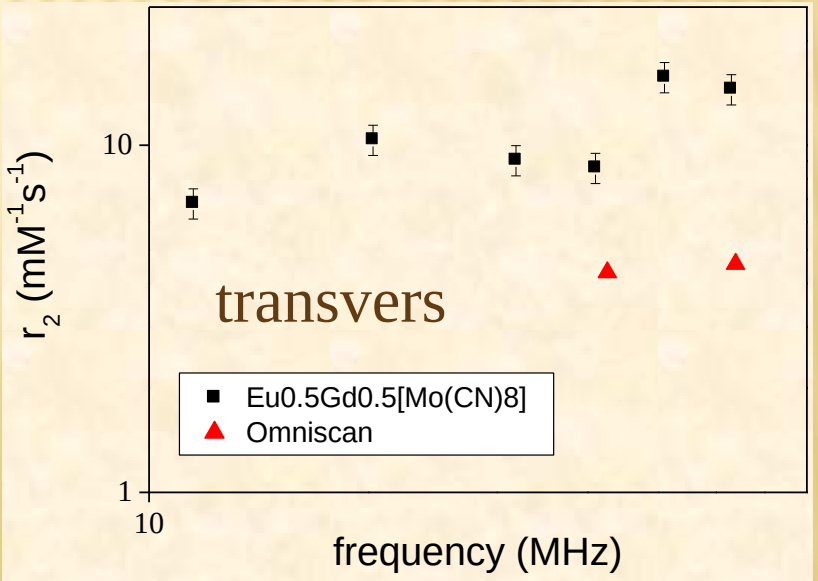


Relaxometry of $Gd_{0.5}Ln_{0.5}[Mo(CN)_8]$/chitosan (Ln = Eu, Tb) Nanoparticles

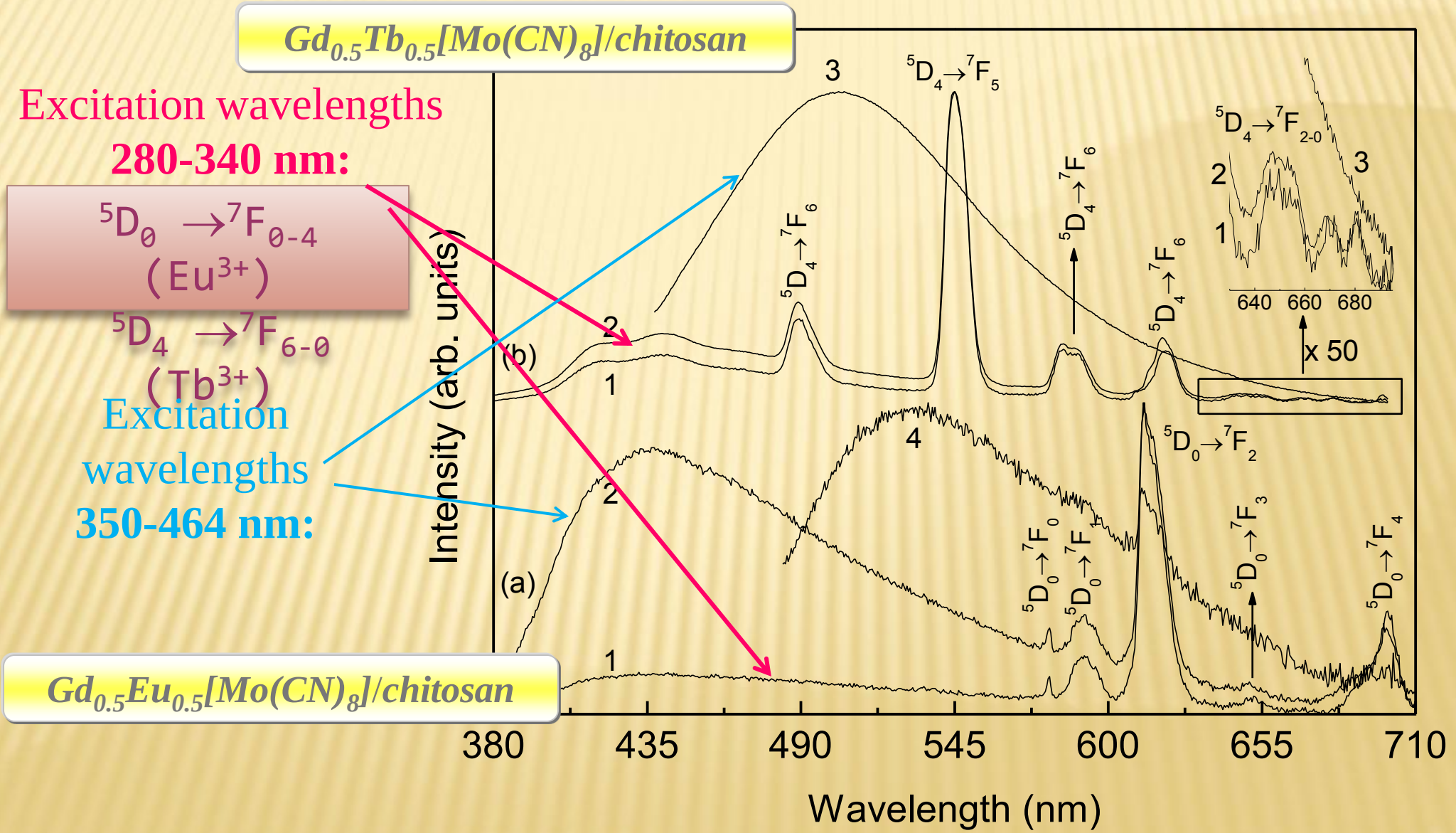


$$r_{ip} = [(1/T_i)_{meas} - (1/T_i)_{dia}]/c \quad i=1,2$$



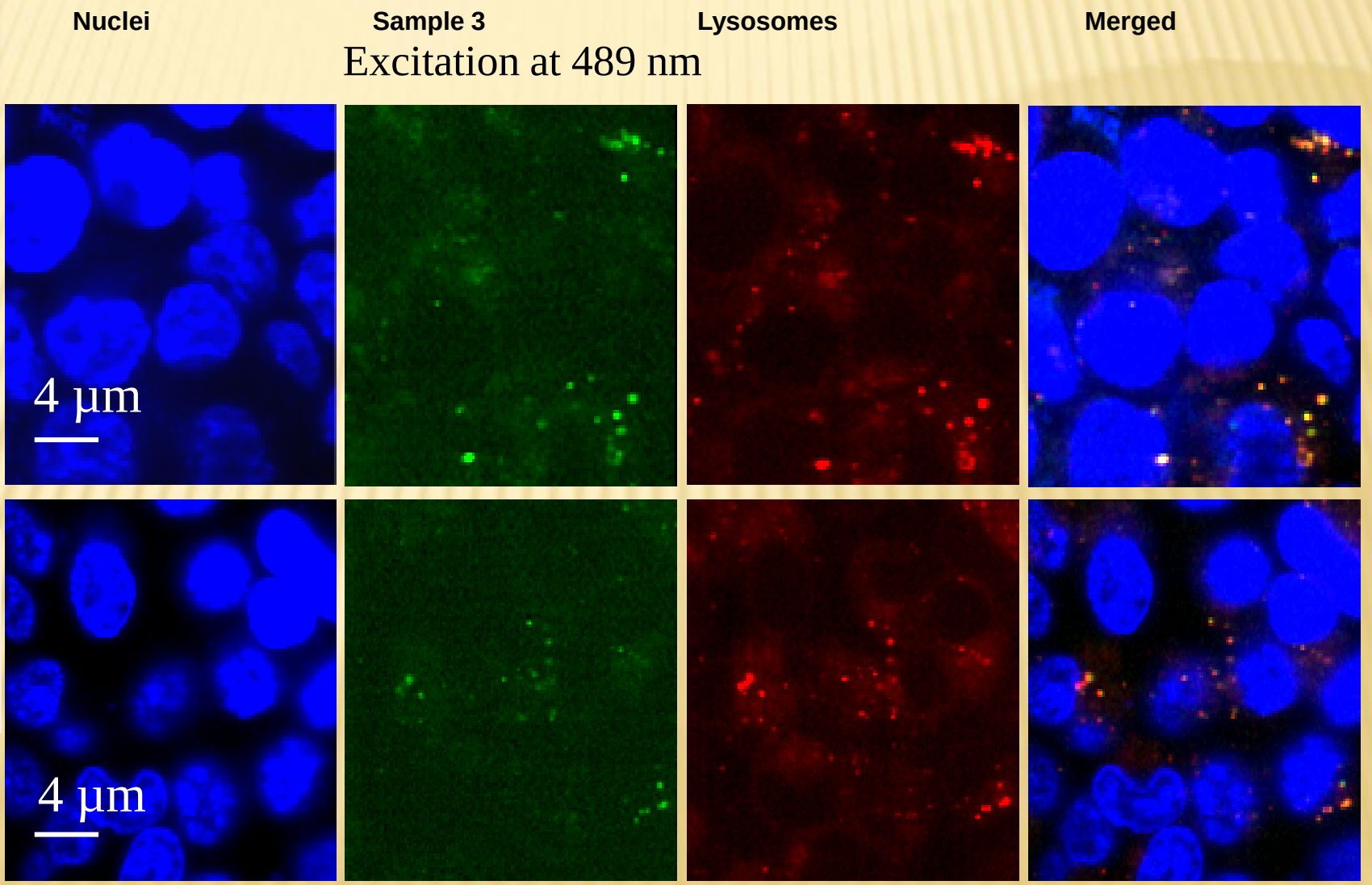


Luminescence of $Gd_{0.5}Ln_{0.5}[Mo(CN)_8]$/chitosan (Ln = Eu, Tb) Nanoparticles



Localization of $Gd_{0.5}Eu_{0.5}[M'(CN)_m]_z$/chitosan in living colon and pancreatic cancer cells by confocal microscopy.

Incubation:
6h at 37 °C
100 ng mL^{-1}

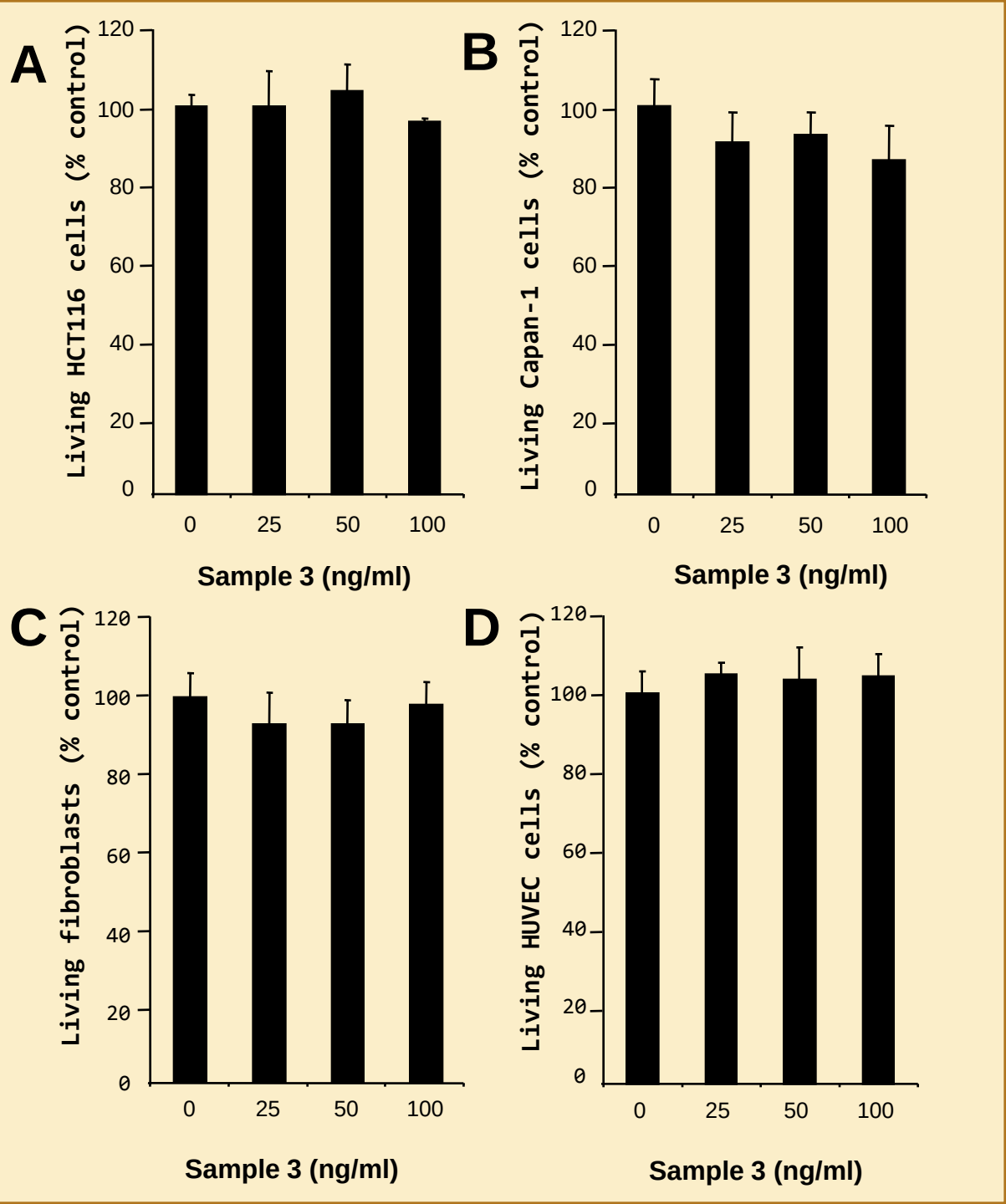


Toxicity Tests

4 days,
Concentration:
(25, 50 and 100 ng mL^{-1})

(A) Human colorectal cancer cells (HCT116),
(B) (B) human pancreatic cancer cells (Capan-1)

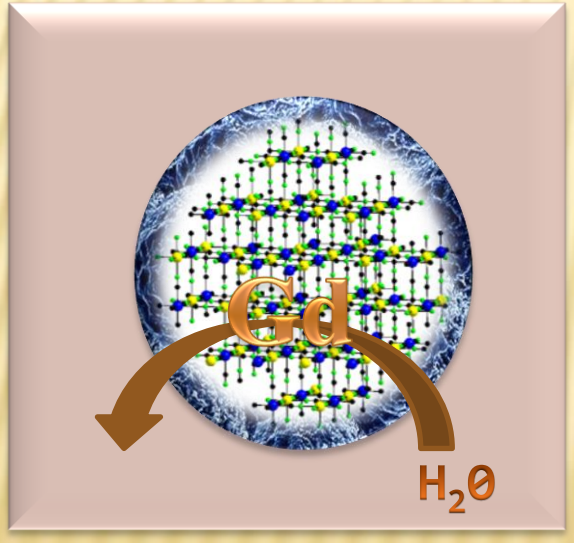
(C) human fibroblasts
(D) human umbilical endothelial HUVEC cells



Summary:

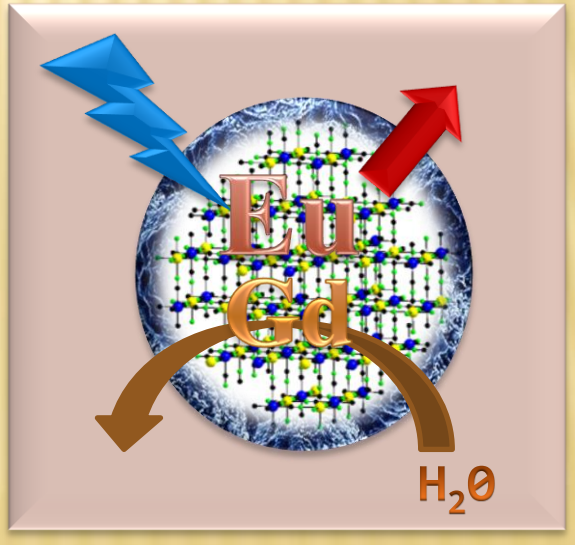
Coordination Polymer Nanoparticles

$Gd[Fe(CN)_6]$/chitosan



Relaxivity

Multifunctional $Gd_{0.5}Ln_{0.5}[Mo(CN)_8]$/chitosan (Ln = Eu, Tb)



Relaxivity, Luminescence

Our group:

ICG-CMOS, Montpellier

PAC-ICG, Montpellier

Pr. Ch. Guérin

Dr. Y. Guari

E. Chelebaeva

Dr. B. Folch

Dr. A. Tokarev

C. Reibel

Our partners:

Dr. A. Caneschi, Dr. C. Sangregorio **INSTM, Florence, Itlay**

Dr. C. Luna **UANL, Mexico**

Dr. A. Lascialfari, K. Tangawel, M. Marione, **IFGCB, Milano, Italy**

Pr. Luis Carlos, Dr. R. Fereira **CICECO, Portugal,**

Dr. N. Baril **LNIA, Marseille, France**

Dr. M. Garcia, Dr. M. Gary-Bobo **IRC, Montpellier, France**

Dr. K. Molvinger**, MACS, ICG, Montpellier**