Cyano-bridged coordination polymer nanoparticles

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A survey on the synthesis of cyano-bridged coordination polymer nanoparticles (CPNs) performed in our group and on the study of their related magnetic properties is given. Two synthetic approaches consisting in the one-pot synthesis of soluble CPNs and in the sequential growth of CPNs onto appropriate matrices are reviewed. A special emphasis is placed on the magnetic properties of CPNs and the determination of the magnetic regime in these systems, which strongly depends on various factors. We show that the size of the nanoparticles, the magnetostatic interparticles and/or the NP–matrix interactions provide significant modification of the superparamagnetic relaxation regime.

I. Introduction

For the last thirty years, investigations on inorganic magnetic materials at the nanoscale have been intensively pursued, not only for the fundamental scientific interest in the understanding of new phenomena arising from the size reduction, but also for their potential technological applications. Due to the high surface-to-volume ratio, quantum size effect,[1] and electrodynamic interactions, nano-objects possess unique size-dependent electrical, optical, magnetic and chemical properties that are strikingly different from those of the individual atoms as well as from their bulk counterparts. The chemical and physical properties of nanoparticles (NPs) are mainly governed by their size, shape, composition, crystallinity and structure. For this reason, accurate control of these intrinsic parameters is the most important requirement for many future applications. On the other hand, the NPs behaviour may be strongly influenced by their close environment. Thus, the properties of NP-containing materials will also critically depend on the surface state of the NPs including interactions with ligands, matrices or substrates and/or interactions with other NPs, and consequently on their spatial organization. It is evident that all these phenomena can be differently controlled according to the synthetic methods adopted for the preparation and that the choice for the most suitable method will depend on the desired final application envisaged for the material.

Numerous types of inorganic NPs have been synthesised and investigated. Among the most explored materials we can cite metallic NPs (Au, Ag, Fe, Co, Ni...),[2] metal oxide NPs (TiO_2, Fe_3O_4, Fe_2O_3, Co_3O_4, $CoFe_2O_4$...)[3] and quantum dots (CdSe, CdS, InAs, AnP).[4] These NPs present numerous potential applications in catalysis, biomedicine, data storage, environmental remediation, sensors, photovoltaic devices and

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others. Among inorganic nanomaterials, coordination polymers NPs (CPNs) have been the subject of increasing interest for the last decade. The reason for the present interest in CPNs is due to their specific nature, which is different in comparison to other inorganic nanosized particles. In one hand, these objects present all advantages of bulk coordination polymers such as determined and flexible molecular structures, determined and adjustable physical and chemical properties, porosity, low density, and the possibility to combine several properties in the same multifunctional nano-objects. Furthermore, as their bulk analogues, CPNs may be obtained from molecular precursors by using "soft" chemistry methods by self-assembling reactions. On the other hand, it is possible to design the nano-objects in such a way that they possess controlled size, shape and organisation at the nano-scale level, and thus their physical and chemical properties may be controlled.

The first and the most investigated CPNs belong to the cyano-bridged coordination polymers family. It should be noted that bulk cyano-bridged homo- and hetero-metallic coordination polymers constitute an important family of molecule-based materials presenting interesting magnetic, optic, photo-switchable, catalytic and intercalation properties.[5] These compounds may also be used as molecular sieves, as materials for hydrogen storage, pigments or as radioactive poison antidotes.[6] The oldest bulk coordination polymer, Prussian Blue, $Fe_4[Fe(CN)_6]_3{\cdot}n$Solv, was discovered in 1704 by Dippel and Diesbach. From this date to now, numerous Prussian Blue analogous with two- or three-dimensional structures have been synthesised and extensively studied. These compounds have the general formula $A_xM_y[M'(CN)_n]_z$ where M and M′ are transition metal ions or lanthanides and A is the counter cation. The crystal structure and the properties depend on the nature of the metal ions, on composition and stoichiometry. More recently, a significant part of the research activity was devoted to the synthesis and studies of size- and shape-controlled cyano-bridged coordination polymer materials at the nano-size level. The synthesis of nanocrystals of cyano-bridged coordination polymers was first reported by Moulik *et al.*[7] and by Mann *et al.*[8] a decade ago and since then the number of articles in this field is in constant expansion. The synthesis of cyano-bridged metallic NPs of different size has been performed by using reverse micelles[9] or by means of various matrices such as polymers,[10] biopolymers,[11] alumina,[12] and amorphous silica.[13] In addition, thin films (2D)[14] and ordered porous microstructures (3D)[15] of cyano-bridged coordination polymers have been reported. These methods permit stabilization of coordination polymer NPs into different matrices or as organic or aqueous colloidal solutions.

Within this context, we employ various stabilising agents such as ionic liquids, capping ligands or porous matrices such as the biopolymer chitosan or mesostructured silica in order to obtain NPs in solution or as nanocomposites. In this survey, we will focus on investigations of small size (<10 nm) magnetic cyano-bridged CPNs prepared in recent years in our research group. The chemical methods that we used for the synthesis of these CPNs may be classified in two groups: (i) one-pot synthetic methods in solution which give soluble or well-dispersible NPs and (ii) sequential addition of the molecular building blocks, *i.e.* step-by-step growth syntheses of CPNs by using various matrices which provide nano-composite materials. A special emphasis is also devoted to the magnetic properties of these CPNs. Indeed, the magnetic properties of metallic or metal oxide NPs have been widely investigated and numerous detailed studies and reviews have been published.[16] However, detailed magnetic property studies of CPNs are still rare.[9,17–20] Here, we will try to clarify how the size reduction of the bulk cyano-bridged coordination polymer at the nano-level influences the magnetic properties of these objects and to establish the major factors which determine their magnetic behaviour. To this purpose, we will investigate two different kinds of systems: (i) colloidal solutions containing well dispersed *in situ* obtained NPs with


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Claudio Sangregorio graduated in Chemistry at the University of Florence in 1994 and, in 1997 obtained a PhD in Material Science at the same institution with a thesis on magnetic nanoparticles. After a post-doc at the AMRI institute in New Orleans (USA), in 1999 he moved back to the Univ. of Florence, at the Laboratory for Molecular Magnetism, where at present he has a position as researcher. His research interests are in the field of nanosized magnetic materials, ranging from metal and metal oxide based nanocomposites, to magneto-plasmonic active nano-heterostructures and high spin molecular clusters.


Christian Guérin

Christian Guérin was born in 1946 in Largeasse, France. He received his PhD from the University Montpellier 2 (under the supervision of Professor R. Corriu) in 1978 on stereochemical studies at silicon. After a postdoctoral stay with Professor Sir J. Lewis at the University of Cambridge (UK) on osmium cluster chemistry, he was appointed as an Assistant Professor of Chemistry at the University Montpellier 2 and became a full Professor in 1985, where he served also as the Head of the Department of Chemistry. His current research interests are in the area of main group organometallic chemistry and transition metal complexes and he is presently engaged in the study of their applications as molecular precursors to advanced functional materials.

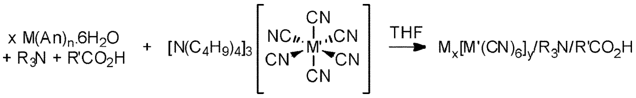
different concentrations and (ii) nanocomposite materials containing dispersed NPs in a porous matrix. These systems offer interesting opportunities to determine the magnetization relaxation dynamics in nano-sized cyano-bridged coordination polymers and to investigate how these are influenced by size, magnetostatic interparticle interactions and NP–matrix interactions.

II. Synthesis of the CPNs

II.1 Soluble CPNs: one-pot synthetic methods

II.1.1 Synthesis of organic-phase soluble CPNs by using stabilising ligands. One of the most common methods for synthesizing inorganic NPs, including CPNs, is based on reactions performed in solution. Typically, CPNs may be synthesised by co-precipitation of soluble building blocks in aqueous or organic solution in the presence of a stabilizer, such as a surfactant, a capping ligand or a soluble polymer or biopolymer. These stabilizers possess a polar group that attaches to the NP surface and a bulky component that provides spatial isolation of the particles from each other and confers solubility property. As a result, the NPs may be prepared as stable colloids or isolated as powdered products which however can be well re-dispersible in appropriate solvents.

The term stabilizing ligand is commonly used for organic molecules that contain a donor group with substituents of varying steric bulk. The main distinction between stabilizing ligands and surfactants lies in the differences of the strength of their binding to metal atoms at the nanocrystal surface, which is greater in the case of capping ligands and has a pronounced covalent character.[21] Generally, colloids containing surfactants have only limited stability, while NPs surrounded by stabilizing ligands are similar to giant metal-cluster complexes that are described as individual substances. Among numerous ligands available, the combination of fatty acids and long-chain amines is a well documented methodology used for the stabilization of metallic and metal oxide NPs.[22] Up to now, only one work has been reported by our group on the direct organic phase synthesis of CPNs which was performed by using a fatty acid as the ligand or a combination of a fatty acid and a long chain alkyl or aryl amine (Scheme 1).[17a] The success of our methodology arises from a sequential two-step addition: first, the self-assembling reaction between the bivalent metal ion and the cyanometallate precursor is performed in the presence of the fatty acid. The latter is known to be a poor ligand, but it can provide sufficient stabilization of the formed NPs. Second, the addition of a long chain alkyl or aryl amine is performed in order to reinforce the stabilizing ligands efficiency allowing thus to obtain CPN-containing solutions which are highly stable over an extended time period. Typically, spherical CPNs of 3–6 nm may be obtained by self-assembling reaction of bivalent metallic salts or lanthanide salts and cyanometallate precursors in THF in the presence of equal quantities of trialkyl- or triaryl-amine and oleic acid at room temperature (Scheme 1). The precipitated NPs obtained by addition of alcohols are well dispersible in less polar or non-polar solvents without further addition of any ligand or surfactant, providing a significant advantage in comparison with the microemulsion method, as it was pointed by other research groups.[23]



Scheme 1 Schematic representation of the organic-phase synthesis of the CPNs from a cyanometallate $[N(C_4H_9)_4]_3[M'(CN)_6]$ and a metal salt $M(An)_n$ with An = NO_3^-, Cl^-; R = $CH_3(CH_2)_4$–, $CH_3(CH_2)_7$–, $CH_3(CH_2)_{11}$–, C_6H_5– and R′ = $C_{17}H_{33}$–.

Transmission electronic microscopy (TEM) measurements are useful in order to observe the presence of CPNs. A typical TEM image of a colloidal solution of $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs obtained by using a trioctylamine–oleic acid mixture in THF and after precipitation and re-dispersion in hexane is shown Fig. 1(a). The NPs are spherical and non-aggregated with an average size of 2.3 ± 0.3 nm. It was shown that the nature of the amine does not influence noticeably the size and the shape of the particles. On the other hand, increasing reaction temperature induces increase of the size of the NPs due to predomination of the growth process over nucleation, as usually observed for inorganic NPs. Indeed, in the case of $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs stabilized by an oleic acid–trioctylamine mixture, the average size increases to 3.5 ± 0.6 nm as the temperature is increased to 70 °C (Fig. 1(b)).

The nature of the metal ions used is also an important parameter for varying the size of the NPs. For instance, NPs obtained with $[Fe(CN)_6]^{3-}$ with different bivalent metal ions, such as Mn^{2+}, Ni^{2+}, Fe^{2+}, and lanthanides such as Tb^{3+}, Eu^{3+} and Sm^{3+} present sizes in the range 2.2–3.5 nm.

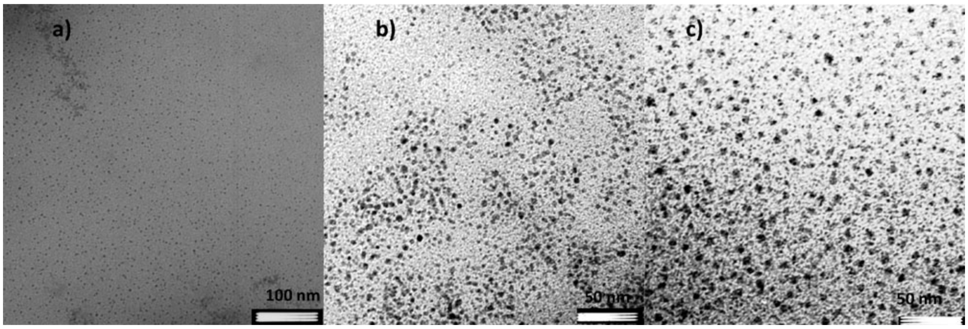


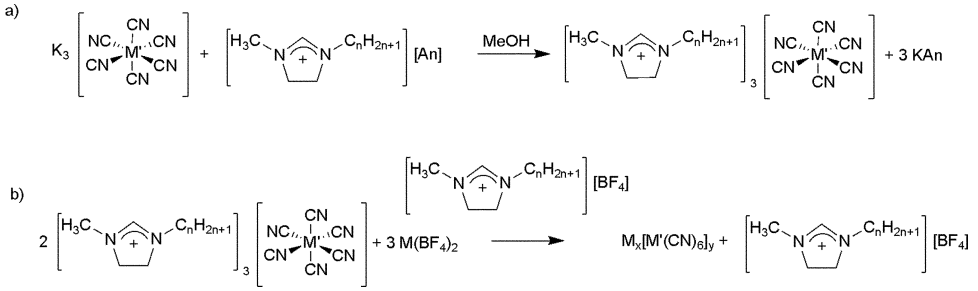
Fig. 1 TEM images of oleic acid–trioctylamine stabilized $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs (a) at room temperature and (b) at 70 °C and (c) $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs at room temperature.

However, using $[Cr(CN)_6]^{3-}$ as precursor leads to the formation of larger NPs with sizes of *ca.* 5 nm. Fig. 1(c) shows TEM images of $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine with size of 5.1 ± 0.9 nm.

II.I.2 Synthesis of CPNs in ionic liquids. Ionic liquids, (ILs), are liquid compounds below 373 K which can be regarded as attractive alternatives to common organic solvents. They are typically composed of organic cations with a variety of substituents such as quaternary ammonium cations, pyrrolidinium, phosphonium, sulfonium and other more exotic cations, along with a variety of inorganic anions.[24] These compounds not only present interesting physico-chemical properties, such as a low melting point, a wide liquid range, negligible vapour pressure, good solubility characteristics, relatively low viscosity, high fluidity, non-flammability, a wide electrochemical window, tolerance to strong acids, and excellent thermal and chemical stability, but they are also excellent media for the synthesis and stabilization of various nano-sized objects.[25] ILs as a "nanosynthetic template" stabilize metal or metal oxide nanoparticles on the basis of a combining effect taking into account the intrinsic high ionic charge, the high polarity plus the steric bulk of these salts. This effect creates electrostatic and steric colloid-type stabilization in the form of a "protective shell", so that no extra stabilizing molecule or organic solvents are needed.[26] In our work, we employ 1-R-3-methylimidazolium salts, $(C_n\text{-MIM})^+$ ($n = 4$–12), as ionic liquids, which act both as stabilizing agent for the NPs and reaction media to synthesise soluble NPs of cyano-bridged coordination polymers $M_x[M'(CN)_6]_y/[C_n\text{-MIM}][An]$ (M^{n+} = Ni, Cu, Co, Mn, Eu, Tb, Gd; M′ = Fe, Cr; n = 4, 10, 12; An = BF_4^-, Cl^-).[18] The typical synthetic procedure consists of two steps (Scheme 2). The first step is the metathesis synthesis of $[C_n\text{-MIM}]_3[M'(CN)_6]$ cyanometallate precursors in which the cationic part of the ionic liquid plays the role of counter cation. Secondly, the self-assembling reaction of bivalent metallic salts or lanthanide salts with these cyanometallate precursors is performed in the appropriate ionic liquid.

Spherical NPs of 3–4 nm size are obtained with 3d metal ions at room temperature using a stoichiometric ratio between the molecular precursors. Fig. 2(a) shows a typical TEM image for well-dispersed, non-aggregated spherical $Cu_3[Fe(CN)_6]_2/C_4\text{-MIMBF}_4$ NPs with mean size of 3.3 ± 0.8 nm. This method is highly versatile: the size and the shape of the NPs can be varied from a few nanometers to *ca.* 100 nm by varying the reaction conditions.[27] An increase of the reaction temperature to 50 °C can double the NP size while maintaining their spherical shape and good dispersion property (Fig. 2(b)).[18] However, on increasing the temperature to 80 °C, crystallites of around 100 nm size were obtained (Fig. 2(c)). As microwave treatment results in rapid heating of the reaction mixture, particularly in the sites containing water, the microwave heating of the reaction (10 s, 10 W) leads to the formation of NP superstructures, as can be seen in Fig. 2(d).[24] These "cauliflower" like nano-objects are constituted by small spherical highly aggregated nanoparticles and have a mean size of around 70 nm. It was also shown that the $M^{n+}/[M'(CN)_6]^{3-}$ ratio can affect the aggregation state of the NPs: for instance, increasing of this ratio from 1.5 to 2.5 leads to the formation of dendrites comprised of small NPs (Fig. 2(e)).[28] This effect may be reasonably explained by the formation of positively charged CPNs provided by adding of an excess of the bimetallic ions on the surface of the NPs. Visibly, as in the case of metallic nanoparticles, ILs provide both electrostatic and steric colloid type stabilization of CPNs[18] which is modified as the surface charge of the nanoparticles is changed inducing aggregation of the nanoparticles into dendrites. In the same way, addition of alcohols with 5% of water into the NPs/IL system also leads to destabilization of the system inducing a modification of the shape of the nano-objects: cubic shaped NPs with an increased size of *ca.* 15 nm were obtained by adding methanol or ethanol to $Cu_3[Fe(CN)_6]_2/C_4\text{-MIMBF}_4$ (Fig. 2(f)).

The CPN formation mechanism within ILs may be envisaged considering their possible local structuring. Previously, it was proposed that $[C_n\text{-MIM}]BF_4$ ionic liquids present hydrogen bonding between the imidazolium ring protons and F atoms of the counter-anion.[29] The presence of water molecules at low content replaces the $C(sp^2)$–H···F interactions with hydrogen bonds involving water as an acceptor toward the cation and as a donor toward the $[BF_4]^-$ ion[30] without changing the local structure of the imidazolium entities of the ionic liquid.[31] In other words, at low content, the water molecules are intercalated between BF_4^- and the imidazolium ring in order to form local hydrophilic pockets of variable size depending on the water content (Scheme 3). Consequently, it is reasonable to consider that the hydrophilic building blocks react and form the NPs in these local hydrophilic pockets. Increasing the amount of water produces the increase of the size of the particles, as can be seen for the TEM images of CPNs obtained by adding 0.7, 1.4 and 5 wt% of water (Fig. 2(g), (h) and (i)). However, in those latter cases, the



Scheme 2 Schematic representation of (a) the metathesis reaction to obtain the cyanometallate precursor $[C_n\text{-MIM}]_3[M'(CN)_6]$ and (b) its self-assembling reaction with the second metal ion to form cyano-bridged CPNs $M_x[M'(CN)_6]_y/[C_n\text{-MIM}][BF_4]$ where n = 4, 10, 12.

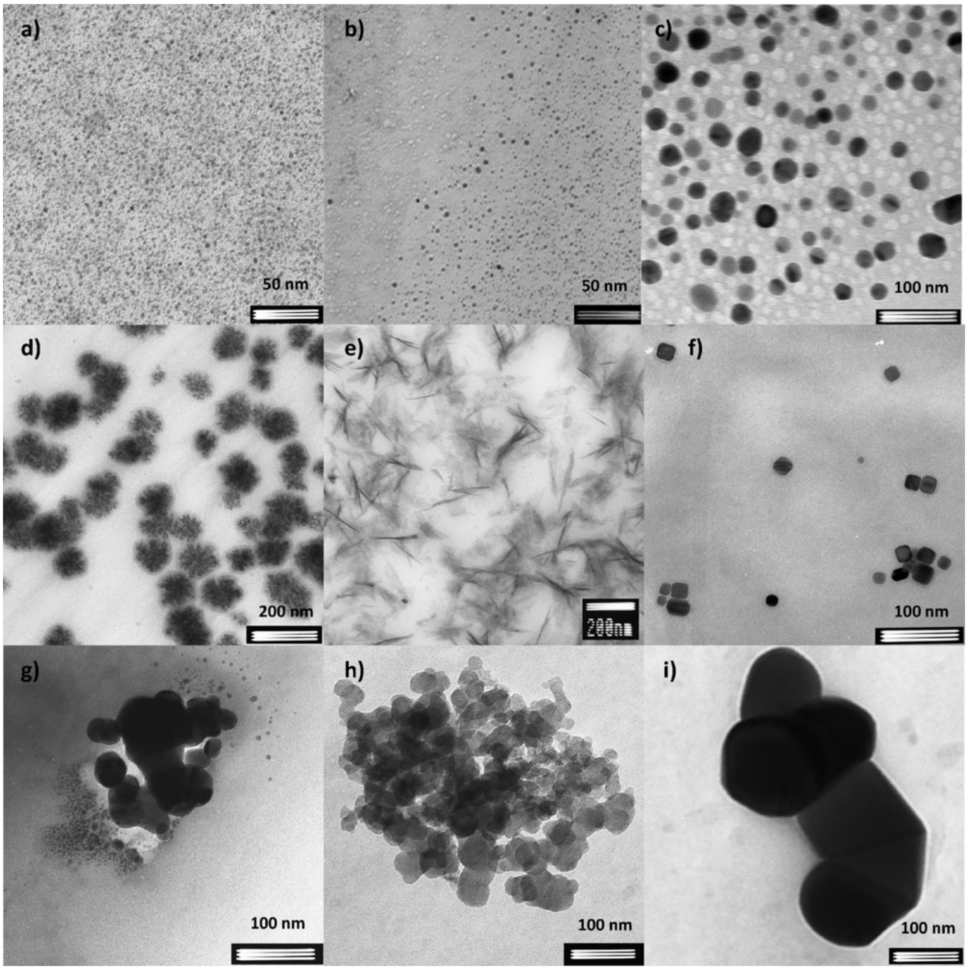
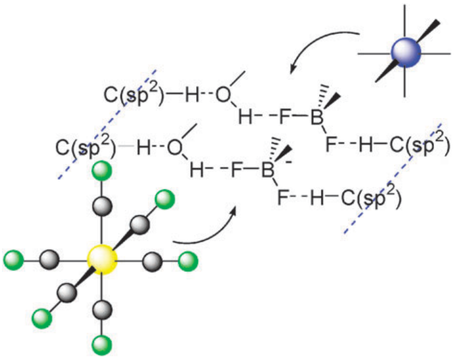


Fig. 2 TEM images of $Cu^{2+}/[Fe(CN)_6]^{3-}$ CPNs synthesized at (a) 20 °C, (b) 50 °C, (c) 80 °C, (d) with microwave treatment, (e) using an excess of $[Fe(CN)_6]^{3-}$, (f) after precipitation with MeOH–H_2O (95 : 5), (g) with 0.7 wt%, (h) 1.4 wt% and (i) 5 wt% water. TEM images (a), (b), (c), (d), (e), (g), (h) and (i) were obtained by using cryo-ultramicrotomy techniques while TEM image (f) was obtained by deposition of a drop of a suspension of the nanoparticles in ethanol.



Scheme 3 Schematic representation of the local hydrophilic channels within ILs where the reaction between the cyanometalate and the metal salt is proposed to take place.

shape and aggregation state of the particles may be attributed to uncontrolled precipitation rather than a controlled growth within hydrophilic pockets.

An additional interest for the use of ionic liquids is that, depending on the chain length of the alkyl substituent on the imidazolium moiety, it is possible to obtain ionic liquids possessing liquid crystal properties. For instance $[C_{12}MIM][BF_4]$ exhibits an isotropic phase above 50 °C, a smectic lamellar phase (SmA) between 50 and 14 °C and a crystalline phase below 14 °C. It is thus possible to perform the *in situ* synthesis of cyano-bridged CPNs in the isotropic phase, at 60 °C, and to obtain their subsequent organization by slowly decreasing the temperature below the clearing point, as we recently demonstrated.[32] Spherical NPs of *ca.* 4 nm in diameter are organized into a two-dimensional array formed by parallel chains of NPs (Fig. 3(a)). The CPN growth mechanism in the isotropic phase of $[C_{12}MIM][BF_4]$ is similar to the above described mechanism proposed for the isotropic ILs. However, upon cooling, $[C_{12}\text{-MIM}]BF_4$ presents a lamellar phase inducing a long-range organization of the NPs at the nanolevel, which is also preserved in the crystalline phase. Such organization may be schematically described as an alternating of hydrophobic layers constituted of alkyl chains of the IL and hydrophilic layers constituted of NPs, water, $[BF_4]^-$ anions, and the imidazolium ring entities (Scheme 4). The interspacing between the NP centres corresponds to the length of a double layer of $[C_{12}\text{-MIM}]BF_4$ plus two half-layers of NPs that could be estimated to be ∼5.2 nm. This value fits

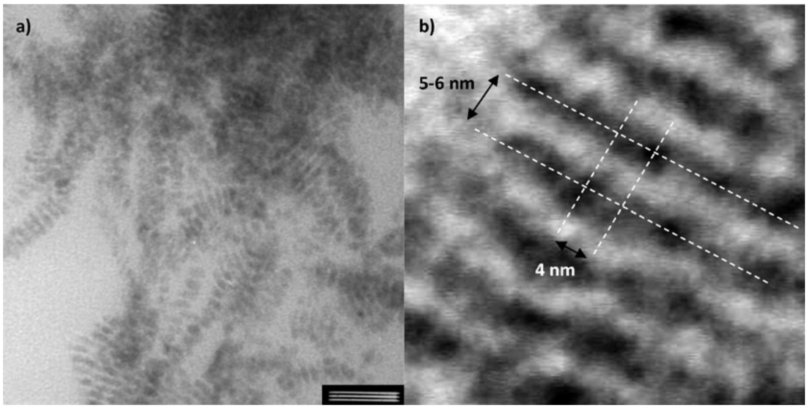
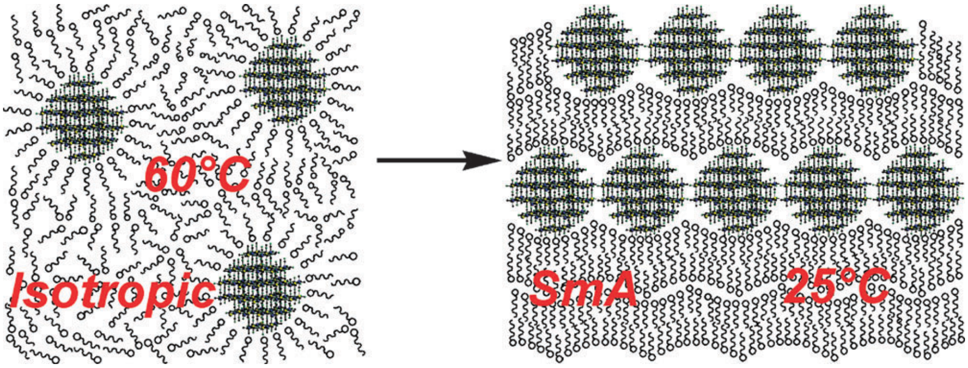


Fig. 3 (a) TEM image of $Mn^{2+}/[Cr(CN)_6]^{3-}$ NPs showing the anisotropic arrangement within $[C_{12}\text{-MIM}]BF_4$ and (b) its magnification. Scale bar = 100 nm.



Scheme 4 Schematic representation of the formation of a lamellar phase inducing a long-range organization of the NPs at the nanolevel upon cooling below the isotropic to smectic lamellar phase (48–49 °C) for $[C_{12}\text{-MIM}][BF_4]$.

well with that obtained from TEM observations, 5–6 nm (Fig. 3(b)).

II.2 Step-by-step growth of CPNs within matrices

The use of a matrix to define the reaction space is an intrinsically attractive approach to the preparation of large amounts of nanocomposite materials which contain confined NPs. A number of matrices have been used for the synthesis of inorganic NPs including gels, silica, alumina and organic polymers.[33] For the synthesis of CPNs, this approach may involve the use of porous matrices such as silica,[34] alumina[35] and organic polymers[36] in which multi-step growth of the coordination polymer network may be achieved. In these systems, the properties of the NPs will be determined by the confinement within the host matrices, which control the size and the shape of the NPs by the size and shape of the host's pores, the internal/external surface properties and others. In comparison to the one-pot synthetic methods of CPNs, this approach consists in the sequential step-by-step coordination of the metal ions and cyanometallates inside the pores of the matrix that provides a good control of the NPs' composition and stoichiometry. The porous matrix provides a nanoscopic or mesoscopic reaction chamber in which the NPs can grow to a given size. Therefore the pore size of the host matrix, the easy diffusion of the precursors inside the pores, the presence of appropriate functionalities able to attach the NPs inside the pores are the fundamental factors for the synthesis of well dispersed NPs with controllable size. Such a step-by-step approach presents a key specificity of the CPN synthesis in comparison with the synthesis of other inorganic NPs in the matrices which are usually obtained by decomposition of organometallic or inorganic precursors incorporated into the matrix.[37]

II.2.1 Synthesis of CPNs in functionalized mesostructured silica. An interesting route to prepare cyano-bridged CPNs-containing silica materials is the employment of hybrid organic–inorganic mesostructured silica as a template for the NPs growth. SBA-15 and MCM-41 type silica are excellent hosts for NP stabilization for the following reasons: (i) they present open pores with hexagonal structuring that permit easy diffusion of precursors and promote the organization of the NPs in relation with the organization of the matrix host; (ii) the pore size may be easily modified without modification of the silica structure; (iii) the silica pores may be functionalized by grafting of appropriate organic groups able to coordinate metal ions and thus able to anchor the CPNs, that provides good dispersion of the NPs into the pores.

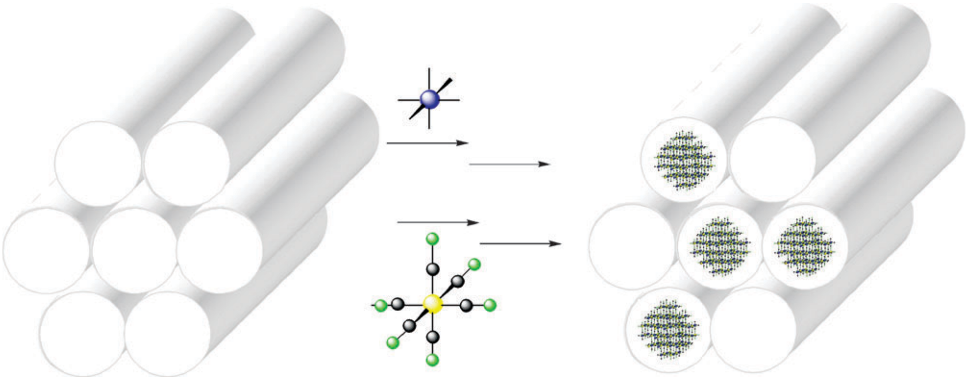
We developed the intrapore growth of a wide range of cyano-bridged networks of general formula $M^{n+}/[M'(CN)_m]^{3-}$ (where $M^{n+} = Ni^{2+}, Fe^{2+}, Co^{2+}, Fe^{3+}$ and $M' = Fe^{3+}, Co^{3+}$ ($m = 6$); Mo^{5+} ($m = 8$)) at specific sites of an hybrid organic–inorganic silica possessing pendant $-(CH_2)_2C_5H_4N$

groups within the pores of a mesostructured silica SBA-15 by the repeated sequential addition of the molecular building blocks.[17b] It should be mentioned that the repeated successive impregnation of the molecular building block is only needed twice to afford the CPNs whatever the pore size of the silica matrix. We have shown that the hybrid silica host with pyridine functionalities allows intrapore controlled growth of molecule-based NPs and provides covalent anchorage in the pores, leading to a uniform dispersion. This methodology which is fairly general, was applied with mesostructured silica material presenting different pore sizes, affording cyano-bridged coordination polymer NPs of various controlled sizes in the nano-domain regime (Scheme 5).[17c] The CPNs can be clearly seen after removal of silica from the nanocomposite material using an HF treatment. For instance, when using hybrid organic–inorganic mesostructured silica with pore sizes of 7.5, 5.3 and 3.4 nm, CPNs of chemical composition $\mathrm{Ni^{2+}/[Fe(CN)_6]^{3-}}$ present narrow size distributions centred at 7.4 ± 1.9, 5.1 ± 1.2 and 2.0 ± 0.2 nm, respectively (Fig. 4). Obviously, the pore size of the silica matrix precludes further growth of the cyano-bridged network and the aggregation of the formed NPs. This evident correlation between the pore size of the silica matrix and the size of CPNs which are grown within such nanoreactors was confirmed for other chemical compositions, demonstrating the generality of the present method for the synthesis of CPNs with a well defined predetermined size.

II.2.2 Synthesis of CPNs by using water-soluble chitosan as matrix. Chitosan is a hydrophilic polysaccharide composed mainly of linked glucosamine units. It is a biocompatible polymer that was also considered as a host matrix for the growth of cyano-bridged coordination polymer NPs thanks to several advantages: (i) it may be fabricated as micrometric porous beads with high specific surface by using $\mathrm{CO_2}$ supercritical drying;[38] (ii) the porosity of the chitosan provides easy diffusion of the precursors; (iii) the presence of the functional amino groups offers the possibility to anchor the NPs inside the chitosan; (iv) it is biocompatible; (v) it presents high water solubility in a slightly acidic media. The sequential impregnation of metal ions and cyanometallates was developed in order to grow CPNs of general formula $\mathrm{M^{n+}/[M'(CN)_6]^{3-}}$ (where $\mathrm{M^{n+}} = \mathrm{Ni^{2+}}$, $\mathrm{Fe^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Gd^{3+}}$ and $\mathrm{M'} = \mathrm{Fe^{3+}}$) (Scheme 6).[39] Spherical non-aggregated NPs with sizes of *ca.* 2–3 nm were obtained in all cases showing good size and shape controllability (Fig. 5). In addition, the chitosan spheres containing NPs may be solubilised in slightly acidic water to afford highly stable CPN colloidal solutions (Fig. 6).

III. Magnetic properties of CPNs

In the recent years, magnetic properties of CPNs have attracted considerable interest, however systematic investigations of the relaxation dynamics of the NPs and of the factors which influence it are still rare and only few works have been recently reported.[9,17–20] In this survey, we try to shed some light on (i) how the size reduction of the bulk cyano-bridged coordination polymers to the nano-level modifies their magnetic properties, (ii) which factors are responsible for such



Scheme 5 Schematic representation of CPN growth within a mesostructured hybrid organic–inorganic silica by successive impregnation with a cyanometalate and a metal salt.

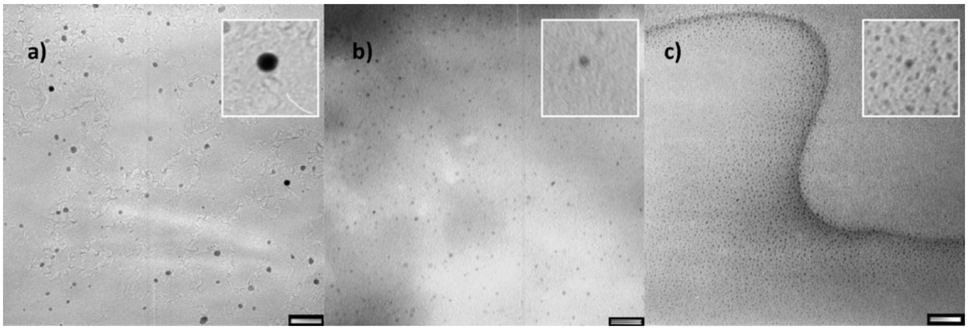
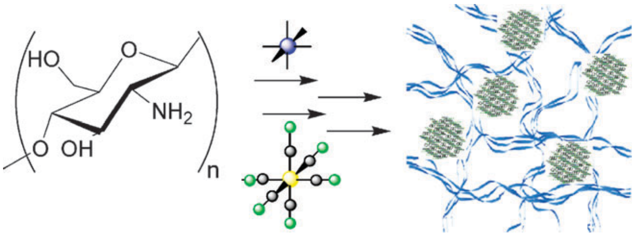


Fig. 4 TEM images of $\mathrm{Ni^{2+}/[Fe(CN)_6]^{3-}}$ with sizes centered at (a) 7.4 ± 1.9 nm, (b) 5.1 ± 1.2 nm and (c) 2.0 ± 0.2 nm. Scale bars = 50 nm.



Scheme 6 Schematic representation of CPN growth within chitosan beads by successive impregnation with a cyanometallate and a metal salt.

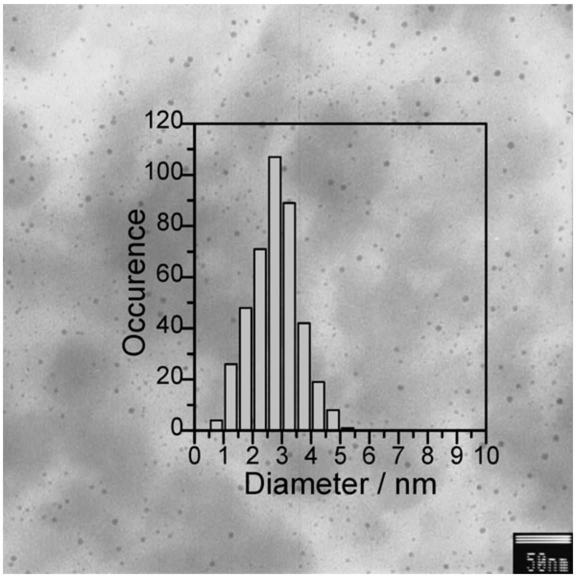


Fig. 5 TEM image of $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs formed within porous chitosan beads.

Fig. 6 Photograph of water colloidal solutions of $Fe^{2+}/[Fe(CN)_6]^{3-}$, $Cu^{2+}/[Fe(CN)_6]^{3-}$, $Ni^{2+}/[Fe(CN)_6]^{3-}$ and $Co^{2+}/[Fe(CN)_6]^{3-}$ NPs and the corresponding chitosan beads (from left to right).

modifications and (iii) how we can determine the magnetic regime of CPNs in different systems.

In bulk cyano-bridged coordination polymers constituted by different paramagnetic metal ions in which the spins interact through the cyano-bridges, the presence of a long-range magnetic ordering is observed. From a thermodynamic point of view, the long-range magnetic ordering requires three major conditions to occur at zero magnetic field: (i) the system should contain non-zero magnetic moments; (ii) strong magnetic interactions compared to the thermal energy should operate through the ligands connecting the paramagnetic centres and align the atomic magnetic moments parallel or antiparallel with respect to each other; (iii) the correlation length, that is the distance between two magnetically correlated spins has to become infinite below a critical temperature. These three conditions are always satisfied in bulk two- and three-dimensional cyano-bridged networks possessing magnetic transition metal ions. Consequently, numerous compounds presenting long-range ferro-, ferri- and antiferromagnetic ordering have been described in which the sign of magnetic interactions and the value of the critical temperature depend on the nature of the metal ions.[5] The size reduction of the bulk coordination polymers to the nano-level prevents the propagation of the magnetic correlation and as a consequence, for CPNs possessing strongly interacting paramagnetic centres, the appearance of important size effects should be expected, the most important being superparamagnetic behaviour. However, in real physical systems the particles are never completely isolated from each other and magnetic interactions (dipole–dipole and/or exchange interactions) will affect the superparamagnetic relaxation. Different relaxation regimes can then be identified, according to the strength of the interactions among the magnetic moments of the particles: (i) superparamagnetic regime of isolated NPs,[40] (ii) superparamagnetic regime modified by weak dipolar interparticle interactions, (iii) spin-glass or cluster-glass like regime arising from strong dipolar interparticle interactions or (iv) spin-glass like regime arising from dominant intraparticle surface spin disorder.

The magnetic regimes can be described considering different models. In the case of isolated superparamagnetic NPs, the dynamics are described by a thermal activation Arrhenius law for the relaxation time τ of the net magnetization of the particle, $\tau = \tau_0 \exp(E_a/k_BT)$ (where E_a is the average energy barrier for the magnetic moment reversal, τ_0 is the attempt time and k_B is the Boltzmann constant).[41] For non-interacting particles, the pre-exponential factor τ_0 should be in the range 10^{-8}–10^{-12} s. The energy barrier has several origins, including both extrinsic and intrinsic effects such as the magnetocrystalline, shape and surface anisotropy. In the simplest case, owing to the dominant role of surface contribution, it has a uniaxial form and is given by $E_a = KV$, where K is the anisotropy energy density and V is the particle volume. When $\tau \ll \tau_m$ (τ_m is the measurement time) the particle magnetic moment can freely flip between the two energy minima along the easy axis defined by the anisotropy energy. On the contrary, if $\tau \gg \tau_m$, the flipping is slow and quasi-static properties are observed. A blocking temperature, T_B is defined as the mid-point between these two states, where $\tau = \tau_m$. Thus, above T_B the NP moments thermally fluctuate between their easy directions and with decreasing temperature freeze along the easy directions at T_B, when the relaxation time τ becomes equal to the measuring time τ_m.[42]

With the introduction of interparticle magnetic interactions the freezing processes are no longer independent, although their dynamical properties can still be fairly described in the framework of the superparamagnetic relaxation model if the interactions are weak. This case may be alternatively best described by the Vogel–Fulcher law, $\tau = \tau_0 \exp(E_a/k_B(T - T_0))$

with the additional parameter T_0 taking into account the magnetostatic interactions between the NPs.[43] However, when the magnetostatic interactions between NPs become sufficiently strong, it is no longer possible to define a two-well energy for a single particle and a transition to a collective magnetic state can occur. This state, which is characterized by a complex energy structure, is usually described as a spin-glass-like or cluster-glass like regime, whenever the system presents random or frustrated magnetic interactions, as is the case for randomly distributed and oriented nanoparticles.[44] This low-temperature cluster-glass phase is characterized by observation of a critical slowing down and aging effects. The critical scaling law of the spin dynamics, $\tau = \tau_0[T_g/(T_{\max} - T_g)]^{z\nu}$, (where T_g is a glass temperature and $z\nu$ is a critical exponent),[45] and the so-called de Almeida–Thouless (AT) line model, $H \propto (1 - T_{\max}/T_g)^{3/2}$ are commonly used in order to describe spin-glass or cluster-glass like systems.[46]

In the first part of this review, we described several methods permitting the synthesis of small CPNs presenting sizes smaller than 10 nm as colloidal solutions or embedded within matrices. In the former system, the as- obtained NPs are dispersed into an organic phase or in ionic liquids and their concentration can be easily varied. Consequently, these colloidal systems offer an interesting way to investigate the influence of interparticle interactions on the relaxation dynamics of the CPNs. For the latter system, *i.e.* for the NPs stabilized into solid matrices and more specifically for mesostructured silica as the matrix, the NPs size can be well controlled by the size of the silica pores. For this reason, this system offers an interesting opportunity in order to investigate the influence of the NPs size and possible NP interactions on the magnetic regime.

III.1 Superparamagnetic CPNs

Isolated superparamagnetic NPs present non-existent or very weak magnetostatic interactions and the magnetization dynamics can be described by the Arrhenius law. A typical example consists in $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine. These NPs present a narrow size distribution centred at 5.1 nm. The temperature dependences of the zero field cooled (ZFC) and field cooled (FC) magnetizations are shown in Fig. 7. The ZFC curve is obtained by recording of the magnetization when the sample is heated under a small field (100 Oe) after being cooled to the lowest temperature in zero field. The FC data were obtained by cooling the sample under the same magnetic field after the ZFC experiment and recording the change in sample magnetization with temperature. The ZFC/FC curves present irreversibility: the ZFC curve presents a maximum at $T_{\max} = 3.0$ K, while the FC curve at high temperature coincides with ZFC curve, then separates and increases as the temperature decreases and never reaches saturation. Such behaviour is characteristic of the presence of a magnetic moment blocking and $T_{\max}$ is the temperature below which such a process occurs. In the case of superparamagnetic NPs, $T_{\max}$ corresponds, as a first approximation, to the blocking temperature (T_B) of the NPs with mean volume. The temperature at which separation between the ZFC and the FC curves occurs indicates the blocking of the largest particles. The closeness of the blocking temperature and the temperature of the ZFC/FC curves separation evidences the presence of NPs with a narrow size distribution as indeed observed from TEM measurements.[47]

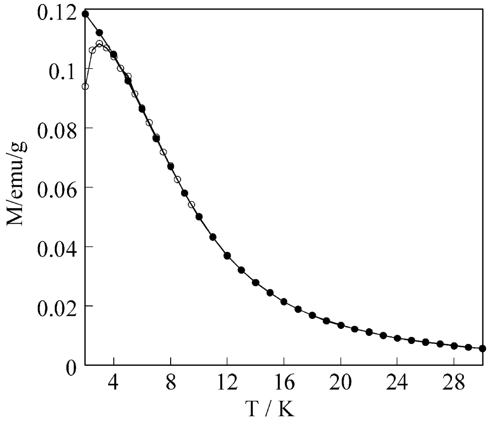


Fig. 7 Zero field-cooled (○) and field-cooled (●) magnetization (ZFC/FC) *vs.* temperature curves for the $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine obtained by applying an external magnetic field of 100 Oe.

In order to determine the magnetic relaxation regime of the NPs, the measurements of the temperature dependence of in-phase, χ' (absorptive), and out-of-phase, χ'' (dispersive), components of the ac susceptibility for different frequencies in zero applied field is the best suited technique. Fig. 8 shows typical thermal dependence of the ac susceptibility for the oleic acid/trioctylamine stabilized $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs. A low-temperature frequency dependent peak, shifting to higher temperature with increasing frequencies, is observed for these nanoparticles. The thermal variation of the relaxation time was obtained by assuming that at the temperature corresponding to the maximum of the out-of-phase component τ matches the working frequency, $\tau = 1/2\pi\varpi$. This can be nicely fitted with the Arrhenius law which gives for the energy barrier, $E_a/k_B = 64(3)$ K and for the pre-exponential factor, $\tau_0 = 1.26 \times 10^{-12}$ s (inset, Fig. 8). These parameters are in the range of the values usually observed for classical superparamagnetic systems containing non-interacting metallic or metal oxide NPs (10^{-8}–10^{-12} s). Considering the average volume obtained from TEM observations, the anisotropy constant was estimated about 1.3×10^4 J m^{-3}.

III.2 Influence of the magnetostatic interparticle interactions in CPN systems

The effects of interparticle interactions on magnetic properties of several inorganic NP systems are available in the literature especially for metallic and metal oxide NPs.[44] In this section, we wish to bring to light the role of interparticle interactions on the relaxation dynamics of CPNs taking as an example $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine with a size of *ca.* 2.2 nm (Fig. 1(a)). To this purpose, three different samples containing the same NPs will be considered: (i) NPs obtained in the solid state by precipitation from THF solution; (ii) a frozen NP colloidal THF solution with concentration of the NPs of 0.5 mmol L^{-1}; (iii) a frozen NP colloidal THF solution diluted 2.5 times having a

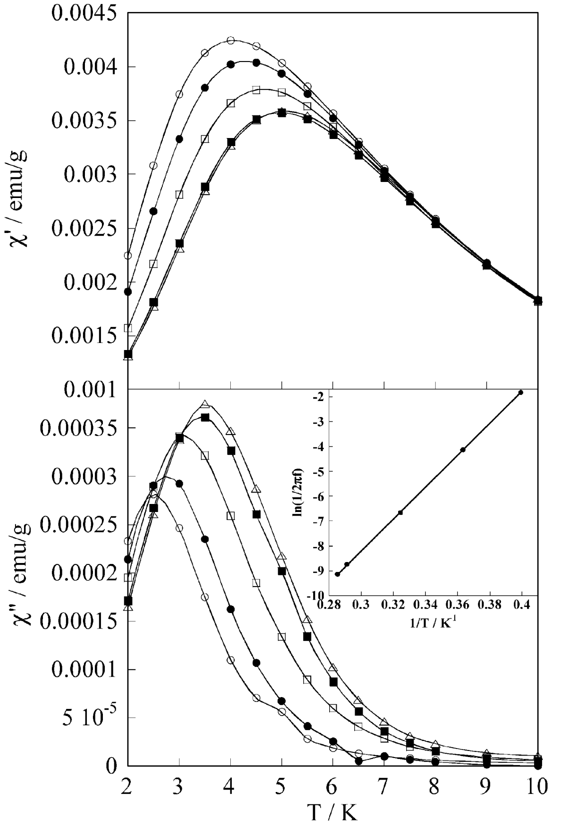


Fig. 8 (Top) Temperature dependence of the in-phase, χ', component of the ac susceptibility of the $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine. (Bottom) Temperature dependence of the out-of-phase, χ'', component of the ac susceptibility of the same NPs; frequencies: 1 Hz (○), 125 Hz (●), 499 Hz (□); 998 Hz (■) and 1498 Hz (△). Inset: Thermal variation of the relaxation time (the solid line represents the fit to the Arrhenius law).

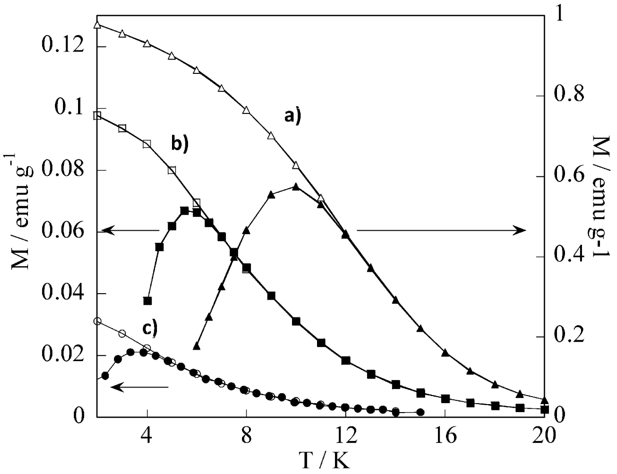


Fig. 9 Field-cooled (open symbols) and zero field-cooled (full symbols) magnetization (FC/ZFC) *vs.* temperature curves for the $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine: (a) in the precipitated state; (b) in concentrated THF solution; (c) in diluted THF solution. All measurements were made with an external magnetic field of 100 Oe.

concentration of 0.2 mmol L^{-1}. In the solid state, the NPs present short interparticle separation defined simply by the organic shell, while in the frozen colloidal solutions the NPs are randomly dispersed in the organic solvent and the interparticle distance increases as the concentration of the NPs decreases. Note that the size of the NPs remains unchanged in solution and in the solid state. Typical ZFC/FC curves obtained for the three samples are shown in Fig. 9. In all cases the shape of the ZFC/FC curves is similar but the temperature of the maximum of the ZFC curve, $T_{\max}$, decreases from *ca.* 10 K to 5.6 and to 3.5 K with decreasing of interparticle distances. This trend is expected when systems with increasing strength of interparticle interactions are compared. According to Dormann *et al.*[40b] the effect of dipole–dipole interactions can be described through an additional term to the energy barrier thus requiring larger temperature for magnetic moment reversal. The temperature dependences of in-phase, χ' (absorptive), and out-of-phase, χ'' (dispersive), components of the ac susceptibility for all the investigated samples show frequency dependent peaks at low temperature. The temperature of the peak decreases as the interparticle distances decrease, in agreement with ZFC/FC curves (Fig. 10). The Arrhenius law fits of the thermal dependence of the relaxation time for these samples give decreasing energy barrier values, E_a/k_B = 403, 182 and 69 K and increasing pre-exponential factors, $\tau_0 = 5.81 \times 10^{-21}$, 3.46×10^{-16} and 5.35×10^{-11} s, as the interparticle distance decreases (Fig. 11(a)).[17a] The parameters observed for the diluted colloidal solution correspond to those expected for classical superparamagnetic behaviour, but for the two other samples (frozen concentrated solution of NPs and solid state NPs), the pre-exponential factors have no physical meaning. However, they can give some indications on the presence of interparticle interactions. In order to take into account the magnetostatic interactions a fit to a Vogel–Fulcher law was performed for these two samples. In the case of the concentrated colloidal solution, the best fit gives E_a/k_B = 89 K and $\tau_0 = 2.88 \times 10^{-12}$ s and the parameter T_0, which by analogy to structural glasses, weights interparticle interactions, equal to 1.8 K,[17a] while in

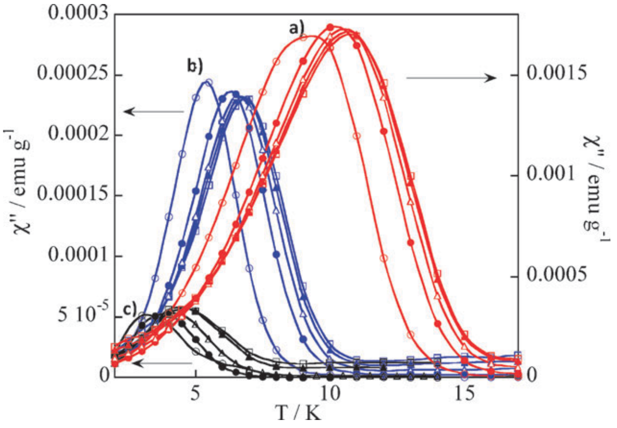


Fig. 10 Temperature dependence of the out-of-phase, χ'', component of the ac susceptibility of the $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine with zero dc magnetic field: (a) in the precipitated state; (b) in concentrated THF solution; (c) in diluted THF solution. Frequencies: 1 Hz (○), 125 Hz (●), 499 Hz (△); 998 Hz (▲) and 1498 Hz (□).

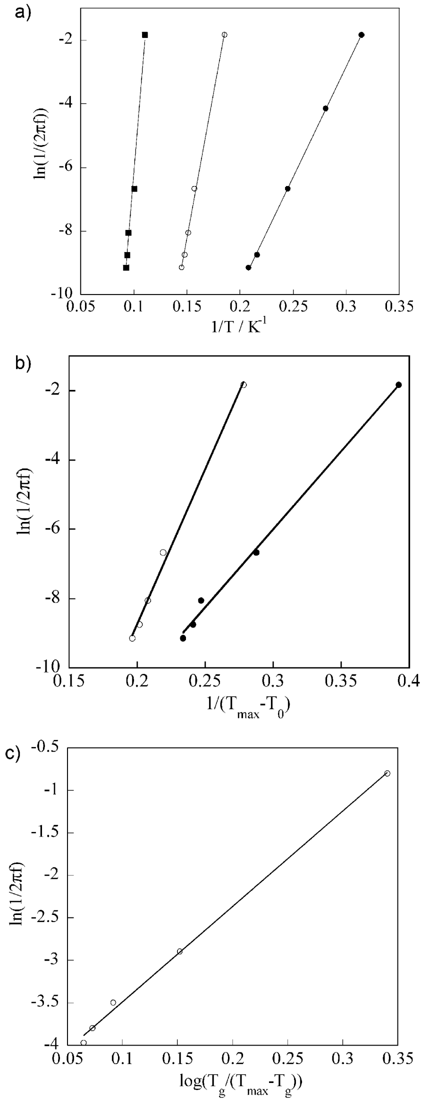


Fig. 11 (a) Thermal variation of the relaxation time according to the Arrhenius law for the $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine in the precipitated state (●); in concentrated THF solution (○); in diluted THF solution (■). (b) Thermal variation of the relaxation time according to the Vogel–Fulcher law for the $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine in concentrated THF solution (○) and in the solid state (●). (c) Thermal variation of the relaxation time according to the critical slowing down law for the $Ni^{2+}/[Cr(CN)_6]^{3-}$ NPs stabilized by oleic acid/trioctylamine in the solid state.

the case of the NPs in the solid state, $E_a/k_B = 45$ K, $\tau_0 = 2.88 \times 10^{-9}$ s and $T_0 = 6.5$ K (Fig. 11(b)). These parameters indicate in both cases the presence of magnetostatic interparticle interactions, which are stronger for the NPs in the solid state, as it was expected.[48]

The relaxation time dependence on frequency of these samples can also be fitted by the conventional critical scaling law of the spin dynamics, $\tau = \tau_0[T_g/(T_{max} - T_g)]^{z\nu}$, used for strongly interacting NPs presenting a cluster-glass like regime.[44] In the case of concentrated NP colloidal solution, the fit gives the following parameters, $T_g = 4.7$ K, $z\nu = 0.08$, $\tau_0 = 2.56$ s, which can be considered as unphysical values,[17a] while in the case of NPs in the solid state, the parameters $T_g = 7.5$ K, $z\nu = 11.2$, $\tau_0 = 2.45 \times 10^{-5}$ s correspond to what are usually observed for the cluster-glass systems (Fig. 11(c)).[45]

To summarize, the oleic acid/trioctylamine stabilized $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs for a diluted solution in THF present a superparamagnetic behaviour for isolated or weakly interacting NPs. When the NPs concentration in solution increases, the interparticle interactions increase but these are still not strong enough to lead to a collective behaviour with appearance of a cluster glass regime. The latter is instead observed only for the solid state where the correlation among the particle magnetic moments introduced by the strong magnetic coupling gives rise to a collective magnetic behaviour. Similar behaviour has been observed for other systems containing CPNs in colloidal solutions such as $CsNiCr(CN)_6$ or $CsNiFe(CN)_6$ nanoparticles stabilized by soluble polyvinyl pyrrolidone (PVP).[17,19]

III.3 CPN size influence on the magnetic properties

The influence of the NPs size in the case of superparamagnetic inorganic NPs is well established. As discussed above, a NP with uniaxial anisotropy has two low energy states, separated by an energy barrier, E_a, corresponding to the parallel or antiparallel alignment of the magnetization of the particle with the easy axis. The blocking temperature, T_B, should increase with increasing particle size because the energy barrier separating the low energy states is, in first approximation, proportional to the volume of the particle.[49] We illustrate the influence of the NP size describing, as an example, the magnetic behaviour of $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs of 7.4 ± 1.9, 5.1 ± 1.2 and 2.0 ± 0.2 nm embedded into mesostructured silica.[17c]

The ZFC/FC curves of these NPs show an irreversibility of ZFC and FC curves with the maximum on the ZFC curves at 4.5, 2.6 and 2.25 K. The observed trend is in agreement with a decrease of the NP size (Fig. 12) but the T_B/V ratio considerably decreases with particle dimensions, suggesting that τ_0 and/or the anisotropy energy density K decrease with increasing sizes.

The temperature dependence of the χ' and χ'' components of the ac susceptibility for these samples shows a series of frequency dependent peaks in which the temperature of the maximum decreases with the size of the NPs (Fig. 13). The fitting of the thermal variation of the relaxation time with the Arrhenius law gives for the energy barrier 276(8), 134(3) and 109(9) K for the NPs of 7.4 ± 1.9, 5.1 ± 1.2 and 2.0 ± 0.2 nm, respectively, showing a decrease of the energy barrier with decreasing of the NPs size, as expected. However, the values of the pre-exponential factor τ_0 of 1.56×10^{-18}, 7.75×10^{-15} and 2.74×10^{-21} s indicate that no pure superparamagnetic regime is observed in these cases. Consequently, the thermal dependence of the relaxation time was fitted with the Vogel–Fulcher law and the critical scaling down model in order to check the presence of interparticle interactions. The unsatisfactory results for both models used as well as the estimation of a mean interaction energy of 1 K between two neighbouring particles with the formula $E_{d-d} = (\mu_0/4\pi)M_S{}^2V_m\varepsilon$ (where M_S is the saturation magnetization of the NPs, μ_0 is the magnetic permeability ($4\pi \times 10^{-7}$ N A^{-2}), V_m is the median particle

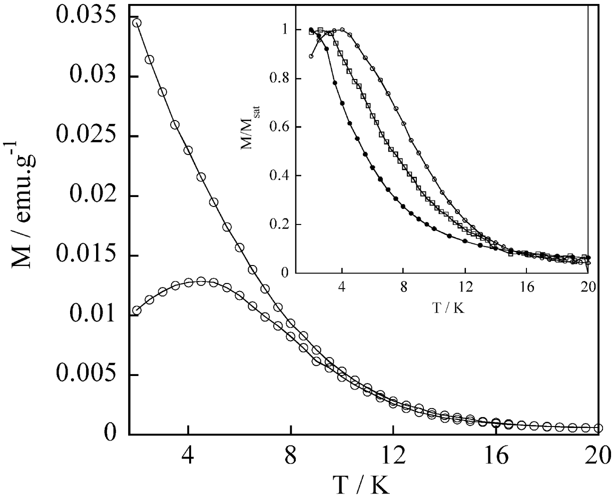


Fig. 12 Field-cooled and zero field-cooled magnetization (FC/ZFC) *vs.* temperature curves for $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs of 7.4 ± 1.9 nm dispersed in a silica matrix. The measuring field is 10 Oe. Inset: Normalized zero field cooled (ZFC) magnetisation curves for $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs with different average size: 7.4 ± 1.9 nm (○), 5.1 ± 1.2 nm (□) and 2.0 ± 0.2 nm (●) dispersed in a silica matrix. The applied magnetic field is 100 Oe.

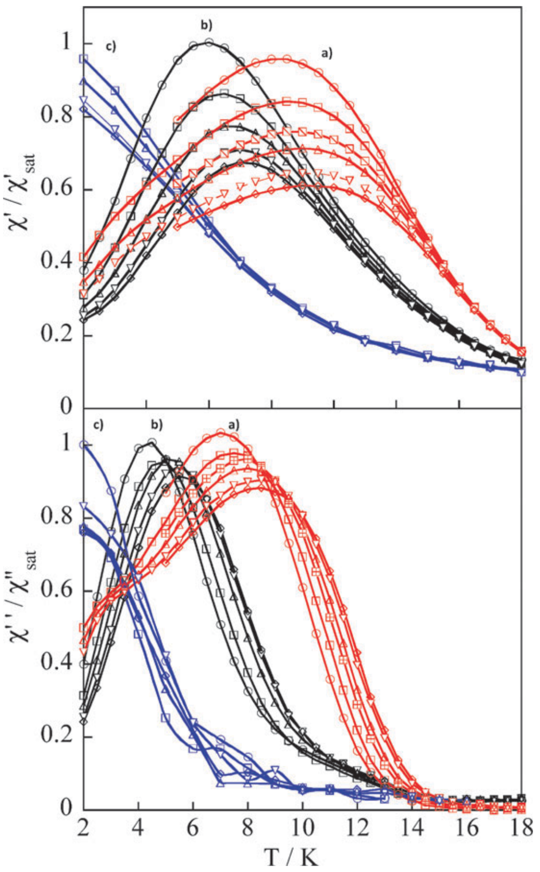


Fig. 13 (Top) Temperature dependence of in-phase, χ', component of the ac susceptibility of the $Ni^{2+}/[Fe(CN)_6]^{3-}$ NPs into mesostructured silica; (Bottom) Temperature dependence of out-of-phase, χ'', component of the ac susceptibility of the same NPs. Frequencies: 1 Hz (○), 10 Hz (□), 125 Hz (☒), 499 Hz (△); 998 Hz (▽) and 1498 Hz (◇). The NPs size is (a) 7.4 ± 1.9 nm, (b) 5.1 ± 1.2 nm and (c) 2.0 ± 0.2 nm.

volume, and ε is the volume concentration of particles), permit to conclude that even if not negligible, no important dipolar interparticle interactions occurred in this system, suggesting that the NPs are relatively isolated from each other in the silica pores.[17c] The deviation from the Arrhenius law can then be attributed to an intraparticle spin-glass like behaviour produced by the surface spin disorder of the NPs.

In summary, the CPNs stabilized into mesostructured silica are isolated from each other and no important interparticle interactions were observed. However, the surface state of these nanoparticles is influenced by NP–matrix interactions providing modification of superparamagnetic regime. The size of the NPs clearly influences the energy barrier and the freezing temperature, which increase as the size of the NPs increase.

IV. Conclusion

In the last decade, there has been growing interest among chemists in the synthesis and investigation of CPNs, especially cyano-bridged CPNs. Such interest in CPN research is stimulated by the diversity of their composition, their size- and shape-dependent properties, and also to their specificity in comparison to other inorganic nanoparticles which consists mainly in easy synthetic methods under mild conditions and the possibility to simply obtain multifunctional nanoparticles. In this survey, we present different approaches to the synthesis of cyano-bridged CPNs that have been performed in our research group, as well as a detailed investigation of their magnetic properties. In particular two synthetic approaches are presented: the first consists in the one-pot synthesis of soluble NPs stabilised by capping ligands or by ILs leading to the formation of soluble cyano-bridged CPNs possessing fine long-term stability, with various concentrations, thus allowing the tuning of interparticle interactions; the second consists in the sequential growth of CPNs into appropriate matrices such as chitosan or mesostructured silica permitting a fine control of the size of the CPNs at the nanoscale and thus allowing the tuning of the energy barrier and blocking temperature of the NPs as well as investigations of CPN–matrix interactions. The CPNs present magnetic properties which strongly depend on various factors such as the size, the magnetostatic interparticle interactions and the CPN–matrix interactions which were shown to provide significant modification of the superparamagnetic relaxation regime. For instance, magnetostatic interparticle interactions were found to introduce a correlation among the particle magnetic moments giving rise, when they are strong enough, to a collective magnetic behaviour. On their own, CPN–matrix interactions were shown to provide an intraparticle spin-glass like behaviour produced by the surface spin disorder of the NPs.

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