Enhancing the magnetic anisotropy of maghemite nanoparticles via the surface coordination of molecular complexes

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Superparamagnetic nanoparticles are promising objects for data storage or medical applications. In the smallest—and more attractive—systems, the properties are governed by the magnetic anisotropy. Here we report a molecule-based synthetic strategy to enhance this anisotropy in sub-10-nm nanoparticles. It consists of the fabrication of composite materials where anisotropic molecular complexes are coordinated to the surface of the nanoparticles. Reacting 5 nm γ-Fe2O3 nanoparticles with the [CoII(TPMA)Cl2] complex (TPMA: tris(2-pyridylmethyl)amine) leads to the desired composite materials and the characterization of the functionalized nanoparticles evidences the successful coordination—without nanoparticle aggregation and without complex dissociation—of the molecular complexes to the nanoparticles surface. Magnetic measurements indicate the significant enhancement of the anisotropy in the final objects. Indeed, the functionalized nanoparticles show a threefold increase of the blocking temperature and a coercive field increased by one order of magnitude.
In single-domain superparamagnetic nanoparticles, magnetic anisotropy has a direct impact on the magnetization, its remanence, reversal and relaxation. Magnetic anisotropy is therefore a key parameter in the preparation of magnetic nanocrystals designed for high-density data storage applications or for medical applications. For such applications, achieving a controlled modulation of the magnetic anisotropy for a given size of crystals represents thus one of the most efficient ways to improve and tune their magnetic properties. For example, the optimization of the specific loss power of nanocrystals for magnetic hyperthermia and the comprehension of the interplay between magnetic anisotropy and magnetization is of crucial importance for applications in nanomedicine. On the other hand, the fabrication of small magnetic nanocrystals displaying high blocking temperature while maintaining other hand, the fabrication of small magnetic nanocrystals remains close to the value observed for the bare acidic particles in acidic colloidal solution (sample \( D_0 = 5.1 \text{ nm} \), \( \sigma = 0.12 \); refs 33,34). In a first step, the [Co(TPMA)Cl] \(_2\) complex is added at room temperature to the nanoparticles acidic solution. The number of added complexes has been varied from ~3 to 210 per nanoparticle. At this stage, no ionic-covalent bond between the complexes and the particles surface is expected, albeit supramolecular interactions cannot be ruled out. There are furthermore no sign of increase of the hydrodynamic diameter in dynamic light scattering (DLS). A single peak is detected and it remains close to the value observed for the bare acidic particles \( D_0 = 7.3 \text{ nm} \). In the second step, the condensation of the complexes at the surface of the particles takes place by a brutal aggregation of the particles was occurring in the solution, since it would have led to undesirable magnetic dipolar interactions. Indeed, such inter-particle interactions would have masked the actual impact of the complexes on the nanoparticles magnetic behaviour.

**Synthesis and characterization.** We have used small maghemite nanoparticles in acidic colloidal solution (sample \( D_0 = 5.1 \text{ nm} \), \( \sigma = 0.12 \); refs 33,34). In a first step, the [Co(TPMA)Cl] \(_2\) complex is added at room temperature to the nanoparticles acidic solution. The number of added complexes has been varied from ~3 to 210 per nanoparticle. At this stage, no ionic-covalent bond between the complexes and the particles surface is expected, albeit supramolecular interactions cannot be ruled out. There are furthermore no sign of increase of the hydrodynamic diameter in dynamic light scattering (DLS). A single peak is detected and it remains close to the value observed for the bare acidic particles \( D_0 = 7.3 \text{ nm} \). In the second step, the condensation of the complexes at the surface of the particles takes place by a brutal modification of the pH: from 2.4 to 11 with the addition of a concentrated solution of tetramethylammonium hydroxide (TMAOH), to give the functionalized nanoparticles (Fig. 1c). The very quick crossing of the zero point charge (pH 7–8) allows the conservation of the colloidal stability. An increase of the hydrodynamic diameter is observed after the condensation
reaction, up to $Z_{av} = 10.2$ nm when ~85 complexes were added per nanoparticle in the first step (Supplementary Fig. 1 and Supplementary Table 1). Sample 1, which corresponds to the nanoparticles functionalized by the addition of ca. 60 complexes per particle in the first synthesis step, shows a similar increase. This can be ascribed to the coordination of the complexes and to the presence around the particles of TMA$^+$ counterions, which accompany the modification of the nature of the surface charge (from positively to negatively charged). Indeed, for bare nanoparticles, DLS shows a similar increase of the hydrodynamic diameter (from 7.3 to 9.5 nm) when performing the brutal pH change in the absence of complexes: passing from 0a (pH 2.4) to the basified colloidal solution (sample 0b, pH 11) with the addition of TMAOH. For the functionalized nanoparticles, the absence of any additional peaks in DLS indicates that there are neither aggregation of particles nor side nucleation of cobalt oxide—that could have occurred were the complexes unstable. No evolution of the single peak has been observed over weeks. The addition of 46 complexes per particle induces a dramatic increase of the hydrodynamic diameter, followed by the flocculation of the particles. The latter is probably caused by the loss of the electrostatic repulsion-induced stabilization that should accompany the increase of the grafting rate. In the following we will focus on 0b and 1.

Transmission electron microscopy (TEM) indicates that very similar sizes and distributions are observed for 0b and 1 (5.1 nm, $\sigma = 0.12$ and 5.0 nm, $\sigma = 0.09$, respectively; Fig. 1b and Supplementary Fig. 2). Along with the DLS experiments, this supports the absence of aggregation or of higher size particles. It also indicates that the functionalization has a negligible effect on the size of the objects. X-ray powder pattern analysis shows that 0b and 1 both display the cubic structure of the maghemite ($Fd-3m$) while the estimated crystallite sizes are in agreement with TEM imaging (Supplementary Fig. 3 and Supplementary Table 2). High-resolution TEM also confirms the cubic structure for the particles and indicates that no structural evolution has occurred during the functionalization reaction (Supplementary Fig. 4 and Supplementary Table 3). In addition, X-ray photoelectron spectroscopy (XPS) measurement at the Fe 2p edges shows an energy gap between 2p$_{1/2}$ and 2p$_{3/2}$ (13.7 eV), in agreement with the $\gamma$-Fe$_2$O$_3$ structure$^{35}$ (Supplementary Fig. 5).

XPS measurements at the N 1s edge show two peaks at 404 and 399 eV for 1 (Fig. 2). The spectra of the bare nanoparticles 0b and of the complex display only one peak at 403 and 398 eV, respectively. As the presence of nitrogen atoms can originate from the TMA$^+$ counterions in 0b and in 1, and from the TPMA ligand in 1 and in [Co(TPMA)Cl$_2$], the low energy contribution at 399 eV can be assigned to the nitrogen atoms from the TPMA ligand and the high energy peak at 404 eV to the contribution from the TMA$^+$ counterion. The experimental Fe/N$_{lig}$ atomic ratio of the peaks has been found equal to 1.00 for sample 1, which differs from the calculated one (10 accounting for the TPMA ligands only). Nevertheless, the experimental Fe/N$_{lig}$ ratio agrees well with the calculated one if only surface iron ions ($\sim 10\%$) are taken into account. Atomic absorption spectroscopy (AAS) measurements made on a precipitated sample of 1 confirm the presence of cobalt(II) ions. The found $46 \pm 4$ Fe/Co ratio corresponds to 52 complexes per particle (considering 2418 Fe(III) ions for a spherical 5 nm $\gamma$-Fe$_2$O$_3$ nanoparticle, this would indicate an 86% grafting rate corresponding to a surface density of 0.66 complex per nm$^2$.

The presence of complexes coordinated to the nanoparticles surface has been further evidenced by X-ray absorption spectroscopy (XAS) measurements at the $L_{2,3}$ edges of the iron and...
cobalt ions for sample 1 and at the cobalt L\textsubscript{2,3} edges for the [Co(TPMA)Cl\textsubscript{2}] complex. For 1, the spectra at the cobalt edges confirm the presence of octahedral Co(II) and the absence of Co(III) (Supplementary Fig. 6). Moreover, differences are observed between the spectra of 1 and of the ‘ungrafted’ complex [Co(TPMA)Cl\textsubscript{2}]. They can be attributed to a change in the first coordination sphere of the cobalt ion, since we expect the replacement of chloride ions by oxo ligands through the condensation at the nanoparticle surface. Indeed chloride ligands are expected to induce a weaker ligand field than the oxo groups from the particle surface \textsuperscript{36}. This is confirmed by ligand field multiplet calculations of Co L\textsubscript{2,3} edges that indicate a ligand field in 1 stronger than in the [Co(TPMA)Cl\textsubscript{2}] complex (Supplementary Fig. 7 and Supplementary Methods).

In summary, the combination of XPS, AAS and XAS measurements clearly confirms the presence of the \{Co\textsuperscript{II}(TPMA)\}\textsuperscript{2+} complex at the surface of the nanoparticles and the formation of an oxo-bridge between Co(II) and Fe(III) ions.

**Magnetic characterization.** To assess the influence of the molecular complex and investigate the magnetic properties of the functionalized nanoparticles we have performed d.c. magnetization measurements, as well as Mössbauer and X-ray magnetic circular dichroism (XMCD) spectrosopies. Where the former gives the macroscopic behaviour of the functionalized nanoparticles, the latter two—as local probes—give element-specific information.

In 1, the presence of the \{Co\textsuperscript{II}(TPMA)\}\textsuperscript{2+} complexes at the nanoparticles surface increases considerably the temperature of the maximum in the zero-field-cooled (ZFC) magnetization curve, reaching 30 K (11 K for 0b, Fig. 3). The fit of the ZFC curves gives—using the same size distribution function—effective anisotropy constants of 26 and 65 kJ m\textsuperscript{-3} for 0b and 1, respectively, attesting thus the anisotropy enhancement (Fig. 3a, see methods for calculation details). This enhancement is also confirmed with the magnetization vs field curves. No break in the hysteresis curve around the remnant magnetization is observed, in agreement with a uniform reversal of the magnetization (Fig. 3b and Supplementary Fig. 8). The presence of the complexes impressively increases the coercive field of the nanoparticles, multiplying the value by 13 (from 62 Oe for 0b to 839 Oe for 1). In an attempt to differentiate the effect of a surface modification due to the coordination of the complexes from that of a magnetic coupling between the Co(II) complexes and the nanoparticle, a Zn(II) analogue of 1 has been prepared and measured (2). The same quantity of the diamagnetic \{Zn\textsuperscript{II}(TPMA)\}\textsuperscript{2+} fragment grafted on the particle surface does not induce a comparable effect on the temperature of the maximum in the zero-field-cooled magnetization curve (from 11 to 14 K; Supplementary Fig. 9). In the magnetization vs field curve, the presence of the \{Zn\textsuperscript{II}(TPMA)\}\textsuperscript{2+} complex has a slight effect on the remnant magnetization but an almost negligible one on the coercive field (from 62 to 73 Oe; Supplementary Fig. 10). These results indicate that the effect of the \{Co\textsuperscript{II}(TPMA)\}\textsuperscript{2+} units on the magnetic properties does not originate from a simple modification of the environment of the iron ions located at the nanoparticles surface. Moreover, since no aggregation of the nano-objects occurs after the condensation of the complexes, the...
observed effect necessarily results from the magnetic interaction of the complexes with the particles, leading to an increase of the magnetic anisotropy. The transmission of the anisotropy from the complexes to the particles is possible only if there is an exchange interaction between the Co(II) and the Fe(III) ions. As the observed enhancement of the magnetic properties is important and effective at relatively high temperature, electrostatic interactions must be ruled out. Only the occurrence of a chemical bond such as an oxo-bridge between the Co(II) and the Fe(III) ions can support the effective anisotropy enhancement, source of the improved properties.

\[ 57\text{Fe Mössbauer spectrometer has been performed at 77 K on frozen solutions of \textbf{0b} and \textbf{1} (Fig. 4 and Supplementary Fig. 11) to discriminate the chemical environment and magnetic properties of the different Fe species, through the analysis of the hyperfine interactions.} ^{37} \]

Indeed, this local probe technique remains a powerful tool for investigating Fe-containing nanoparticles and the influence of the functionalization, thanks to its high sensitivity to electron transfer. \[ ^{38} \] The 77 K spectra result from a minor central quadrupolar doublet and a prevailing broadened lines magnetic sextet: they have exactly the same isomer shift and their proportions are rather independent of the samples. These two contributions are unambiguously assigned to Fe species with fast and weak superparamagnetic relaxation phenomena, due to size distributions in the samples. The lack of resolution does not allow the proportions of iron in tetrahedral and octahedral sites to be estimated but they were accurately estimated from in-8 T field Mössbauer spectra at 12 K (Fe\textsuperscript{III}OH(III)/Fe\textsuperscript{III}Td(III) = 1.70 close to 5/3 as expected for maghemite; Supplementary Fig. 11). The mean values of isomer shift (at 77 K 0.41(2) mm s\textsuperscript{-1}), which probes the electronic density at the 57Fe nuclei, that is the valence state, are consistent with the presence of pure ferric species for both \textbf{0b} and \textbf{1}. This excludes the presence of a ferric impurity and the occurrence of Fe\textsuperscript{2+} species or intermediate valence state. It further evidences that no electron transfer is induced by the presence of the Co(II) complexes. The mean hyperfine field distribution profiles, which correspond to the shape of the magnetic lines, indicate clearly that the grafting of the complexes gives rise to both a shrinkage of the distribution and a shift towards larger hyperfine fields, that is a significant increase of the mean hyperfine field (28.4(5) and 35.1(5) T, respectively). These features distinctly attest a slowdown of the relaxation phenomena of the magnetization in \textbf{1} because the attached Co(II) complexes increase the magnetic anisotropy of the Fe(III) moments, strengthening thus the magnetization of each nanoparticle, in agreement with the ZFC measurements.

The shape and intensity of the XMCD signals at the Fe L\textsubscript{2,3} edges for \textbf{1} are similar to those observed for previously reported maghemite nanoparticles\textsuperscript{39}. It bears the signature of antiferromagnetic coupling between Fe(III) ions in tetrahedral sites and Fe(III) ions in octahedral sites (Fig. 5). The magnetic moment for Fe(III) ions in the sub-network of the octahedral Fe(III) is parallel to the external magnetic field. The ratio between the occupation of the tetrahedral and octahedral sites can be determined from the ligand field multiplet analysis of the XMCD shape and a Fe\textsuperscript{III}OH(III)/Fe\textsuperscript{III}Td(III) ratio close to 5/3 is found, as expected for maghemite. Traces of Fe(II) have also been detected. The latter are due to sample preparation (see methods). The XMCD at Co L\textsubscript{2,3} edges in \textbf{1} is mainly negative at the L\textsubscript{1} edge indicating that the Co(II) magnetic moment is, at 6 T, parallel to the octahedral Fe(III) ions and antiparallel to the tetrahedral Fe(III) ions. Element-specific magnetization curves for Fe and Co were also obtained measuring the dependence of the XMCD signal as a function of the applied magnetic field amplitude (see methods). The Co-specific magnetization curve (Fig. 6 and Supplementary Fig. 12) does not show any inversion in the sign of the XMCD when varying the magnetic field, indicating that no inversion of coupling can be expected at low magnetic field. All three curves are superimposed demonstrating that the Co(II) is magnetically coupled to the Fe(III) ions of the maghemite nanoparticle. Moreover, the Co-specific magnetization curve of \textbf{1} differs drastically from the XMCD-detected magnetization curve of the [Co(TPMA)\textsubscript{Cl} \textsubscript{2}] complex. The latter shows a slow increase of the magnetization with no saturation reached at 6.5 T, as expected for a non-interacting paramagnetic Co(II) ion. For \textbf{1}, the magnetization increases abruptly and saturates above 2 T. This behaviour evidences and confirms that the Co(II) ions within the grafted complexes are magnetically coupled to the iron(III) ions at the nanoparticles surface.

**Discussion**

We have presented in this work a synthetic strategy, which, in combining molecular and nano chemistry, offers a way towards control and modulation of the magnetic anisotropy in nanoparticles. Magnetic measurements, Mössbauer spectrometry and XMCD measurements show that [Co\textsuperscript{III}(TPMA)]\textsuperscript{2+} complexes grafted on the surface of maghemite nanoparticles...
massively enhance the magnetic properties of the nano-objects. Our results also indicate that the strong influence of the molecular component on the nanoparticle comes from the covalent linking of the two species through oxo-bridges and the resulting magnetic interaction.

This work may open tremendous prospects in the design of nanomagnets and of multifunctional nano-platforms. Provided that the choice of nanoparticle to functionalize allows the formation of a coordination bridge able to promote magnetic exchange, and that the particle size and the characteristics of the molecule are adequately matched, it should be possible to obtain composite nano-objects with desired blocking temperature leading to sample 1.

**Methods**

**Preparation of 0a**. The solution was prepared according to literature procedures33,34 (5.1 nm, \( \sigma = 0.12 \), \([\text{Fe}] = 0.87 \text{ M}\), \( \%m = 6.96\%\), \( \%v = 1.39\%\), \( pH = 1.8\)).

**Preparation of 0b**. A measure of 250 \( \mu \)l of 0a were diluted 10 times with a \( \text{H}_2\text{O}:\text{MeOH} 50\% \text{v/v} \) mixture. Then, 500 \( \mu \)l of an aqueous TMAOH solution (2.8 M) were brutally added to the solution under strong stirring leading to the sample 0b.

**Preparation of 1**. A measure of 250 \( \mu \)l of 0a were diluted 10 times with a \( \text{H}_2\text{O}:\text{MeOH} 50\% \text{v/v} \) mixture. A volume of 0.550 ml of a \([\text{Co(TPMA)Cl}_2]\) solution (10 mM, \( \text{H}_2\text{O}:\text{MeOH} 50\% \text{v/v} \)) were added dropwise under stirring, followed by the rapid addition of 500 \( \mu \)l of an aqueous TMAOH solution (2.8 M) under strong stirring. Then, the solution was stirred for 4 h at 60 °C and for 24 h at room temperature leading to sample 1.

**Preparation of 2**. The sample was prepared following the procedure described for 1 using \([\text{Zn(TPMA)Cl}_2]\) instead of \([\text{Co(TPMA)Cl}_2]\).

**Precipitation of the particles**. The addition of three volumes of acetone into the solutions led to the precipitation of the particles. The suspension was placed on a NdFeB magnet to settle the particles and the supernatant was removed. The obtained paste-like solid was washed with an aliquot of ethanol and dried in an oven at 40 °C for 48 h.

**Atomic absorption spectroscopy**. The total iron, cobalt and zinc concentration (mol l\(^{-1}\)) was determined by AAS with a Perkin–Elmer Analyst 100 apparatus after degrading the precipitated particles in HCl (37%).

**Transmission electron microscopy**. Images have been performed on a JEOL 100CX2 microscope with 65 keV incident electrons focused on the specimen. High-resolution TEM has been achieved on a JEOL JEM-2110 microscope with an acceleration voltage of 200 kV and a resolution of 0.18 nm.

**Dynamic light scattering**. The DLS measurements have been performed on a Malvern Zetasizer nanoZS model equipped with a backscattering mode on the solutions containing the particles using the intensity profile. The sizes given in the article correspond to the Z average measurements.

**X-ray powder diffraction**. Patterns were collected on a Philips Xpert Pro diffractometer using Cu-K\(\alpha\)1 monochromatic radiation (\( \lambda = 1.78901 \) Å) and equipped with a Xcelerator linear detector.

**Magnetic measurements**. Magnetic measurements were carried out with Quantum Design MPMS-XL and MPMS-5S magnetometers working in d.c. mode on frozen solutions of the samples. The solution was diluted in a \( \text{H}_2\text{O}:\text{MeOH} 50\% \text{v/v} \) mixture before measurements. The solution volume was 150 \( \mu \)l and the weight concentration 0.4%. The solution is placed in a 0.2 ml epipendorf and inserted in the cryostat of the superconducting quantum interference device.
Anisotropy constants calculations. Following Tamion et al. we have used their semi-analytical model to describe the temperature dependence of the ZFC magnetization and extract an estimate of the magnetic anisotropy energy density $K_{eff}$.

Having defined a switching-field frequency:

$$\nu(T) = \nu_0 \exp\left(-\frac{K_{eff} V_{mag}}{k_B T}\right)$$

with $\nu_0 = 10^8$ Hz the attempt frequency and a characteristic time $\delta(T)$, which depends on the temperature sweeping rate (here 2 K min$^{-1}$), the magnetic moment measured during a ZFC protocol is given by

$$m_{ZFC}(T) = N_H \int_0^{V_{mag}} e^{-\left(\frac{K_{eff} V_{mag}}{k_B T} \right)} \left(1 - e^{-\left(\frac{\nu(T) V_{mag}}{k_B T}\right)}\right) P(D_{mag})dD_{mag}$$

where $m_{ZFC}$ and $m_{mag}$ are the magnetic moment and magnetic susceptibility of the particles. In the equations above, $\nu_0$ and $k_B$ denote the magnetic permeability of vacuum and the Boltzmann constant, $H$ is the magnetic field strength, $m_H$ is the saturation magnetization of the magnetite and $N_H$ is the number of magnetically active clusters.

Using this equation, it is straightforward to calculate an average ZFC curve and optimize the value of $K_{eff}$ in order that make it best match the experimental data.

57Fe Mössbauer spectrometry. 57Fe Mössbauer spectra were performed at 77 K using a conventional constant acceleration transmission spectrometer with a 57Co source (Rh matrix) and a bath cryostat and at 12 K in a 8 T external field. 57Fe Mössbauer spectrometry

The temperature sweeping rate for ZFC/FC measurements was 2 K min$^{-1}$.

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Author contributions

J.F., L.L., V.D. and B.F. conceived and supervised the project. Y.P., J.F., L.L. and B.F. planned and implemented the synthetic and analytical experiments. A.M. and J.F. performed the TEM imaging. N.D. and L.L. performed the powder X-ray diffraction measurements. N.Y. and J.-M.G. analysed the X-ray data. T.G performed and analysed the XPS measurements. Y.P., L.L. and V.D. performed and analysed the SQUID measurements. N.Y. and J.-M.G. performed and analysed the Mössbauer spectrometry measurements. M.-A.A., N.D., C.C.-d.-M., L.L., P.S., F.C., E.O. and P.O. performed and analysed the XAS and XMCD measurements. Y.P. and L.L. wrote the manuscript with the help of all authors.

Additional information

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