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Luminescent and magnetic materials with high content of Eu³⁺-EDTA complexes

Received 00th January 20xx, Accepted 00th January 20xx G.P.Pires,^a I. F.Costa,^a H. F.Brito,^b W. M. Faustino^a and E. E. S. Teotonio^a

> Bifunctional optical magnetic materials with high europium content have been prepared. Chelating groups were introduced on the Fe₃O₄ surface with organosilanes containing ethylenediaminetetraacetic acid (EDTA) derivative, which were previously prepered via reaction between EDTA-dianhydride and aminoalkoxysilanes agents: 3-N-[3(trimethoxysilyl)propyl]ethylenediamine (2N) N¹-(3-(TrimethoxysilyI)propylamine (1N). and trimethoxysilylpropyl)diethylenetriamine) (3N). The first coordination sphere of the Ln-EDTA complexes present on the modified surfaces of Fe₃O₄ particles was completed by addition of β -diketonate ligands (tta: thenoyltrifluoroacetonate, dbm: dibenzoylmetane, bzac: benzoylacetone and acac: acetylacetone) in order to improve their luminescence properties. The materials were characterized by powder X-ray diffraction (XRD), vibrating sample magnetometry (VSM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), wavelength dispersive X-ray fluorescence (WDXRF) and Fourier-transform infrared spectroscopy (FT-IR) as well as by zeta potential measurements and luminescence spectroscopy. The hybrid materials exhibited intense red emission assigned to the 4f-4f transitions of the Eu³⁺ ion, indicating an efficient intramolecular ligand-to-metal energy transfer. The experimental intensity parameters (Ω_2 and Ω_4), lifetimes (τ), as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates of the Eu³⁺ ion were determined and discussed. The stragegies used to obtain these materials may contribute to development of several bifunctional systems for practical applications.

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Dalton Transactions

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Introduction

Bifunctional luminescent magnetic (LM) hybrid materials are remarkable and attractive because they may combine both optical and magnetic properties, which allow easy manipulation and chemical functionalities, playing a key role in different tasks and applications. For instance, LM nanoparticles can be used as probes *in vivo* assay,^{1,2} as reusable catalysts, that might be separated by magnetic manipulation³ and in metal ions⁴ or organic molecules⁵ pre-concentration procedure for quantitative analysis.

Nowadays, special attention has been given to the surface modification in order to adsorb selectively transition metals and trivalent lanthanide ions (Ln³⁺).⁶ For this purpose, magnetite surface has been functionalized with EDTA groups, leading to potential materials for the adsorption and separation of rare-earth ions from aqueous solutions. Moreover, magnetite particles have been combined to the Gd³⁺-imprinted chitosan/carbon nanotubes to prepare a retrievable hybrid materials capable of selective adsorption of the Gd³⁺ion.⁸ In this case, luminescent magnetic microspheres have been prepared by adsorption of pre-encapsulated $Eu^{3+}-\beta$ diketonate complexes to the magnetite surface.⁹ Besides, magnetic mesoporous silica nanospheres have been used as a support for Eu^{3+} tetrakis(β -diketonate) complexes containing ionic liquid compounds as linkers.¹⁰ In different approach, luminescent Eu^{3+} and $Tb^{3+}\beta$ -diketonate complexes have been prepared directly on the magnetite surface functionalized with calixarene through a one-pot method, yielding magnetic and red-green emitting nanomarkers.¹¹

The principal goal of the development of luminescent hybrid materials based on Ln^{3+} complexes is to achieve excellent luminescent properties.¹² Efficient *antennae*, such as carboxylates, heteroaromatics and β -diketonates ligands should be employed to ensure a strong absorption energy by the ligands, leading to the efficient ligand-metal energy transfer. Moreover, some ligands can also protect the emitting ions from interactions with high-energy oscillator groups (*mainly* OH and NH), preventing luminescence quenching. For the hybrid materials, it is also important to consider the content of emitting Ln^{3+} centers in the luminescence intensities.

It is well known that EDTA derivatives are versatile chelating agents. Usually, they act as hexadentate ligands, which allow anchoring covalently metal complexes on different material surfaces, avoiding leaching of the metal ions.¹³⁻¹⁵

Furthermore, the EDTA based silanes participate in the functionalization step in order to obtain different kinds of materials, containing higher number of coordinating groups.¹⁶ These features were explored in our design strategy to prepare new bifunctional luminescent magnetic hybrid materials.

In this work, we report an approach to prepare luminescent magnetic materials with high lanthanide content. Different aminoalkylalkoxysilanes were employed to synthesize the chelating agents and then to functionalize magnetite particles, providing distinct hybrid materials. The high content of Ln³⁺ ions was a consequence of a great number of coordinating sites introduced by functionalization steps. The materials show considerable magnetization, allowing the magnetic manipulation with a regular magnet. Usually, the Fe₃O₄ acts a luminescence quencher. However, this disadvantage was overcome by functionalizing the magnetite with organosilanes containing EDTA derivative and coordinating β -diketonate ligands to the Eu³⁺ ion. The experimental intensity parameters (Ω_{λ}), radiative (A_{rad}) and non-radiative rates (Anrad) for the Eu³⁺ materials were determined. The photonic features such as the experimental emission quantum efficiency (η) and the emission lifetimes (τ) for these hybrid materials are also obtained and discussed.

Experimental

Materials

The following reagents were purchased from Sigma-Aldrich: Iron(III) chloride hexahydrate (FeCl₃·6H₂O, ACS reagent, 97 %) iron(II) chloride tetrahydrate (FeCl₂·4H₂O, Puriss. p.a., \geq 99 %), sodium hydroxide (NaOH, ACS reagent, \geq 97.0%), silver nitrate $(AgNO_3, ACS reagent, \ge 99.0 \%)$, hydrochloric acid (HCl, ACS, 97 30 %), hydrogen peroxide $(H_2O_2,$ %), ethylenediaminetetraacetic acid (EDTA, ACS, 99.4 %), acetic anhydride (Ac₂O, ACS, \geq 98.0 %), polyvinylpyrrolidone (PVP, average molecular weight 40,000), tetraethoxysilane (TEOS, reagent grade, 98 %), pyridine (ACS reagent, ≥ 99.0 %) ammonium hydroxide solution (NH₄OH, ACS reagent, 28.0-30.0 3-(Trimethoxysilyl)propylamine NH₃ basis), (1N. % H₂NCH₂CH₂CH₂Si(OCH₃)_{3.} 97 %), N-[3(trimethoxysilyl)propyl]ethylenediamine (2N, N^{1} -(3-H₂NCH₂CH₂NHCH₂CH₂CH₂Si(OCH₃)₃, 97 %). trimethoxysilylpropyl)diethylenetriamine (3N. H₂NCH₂CH₂HNCH₂CH₂NHCH₂CH₂CH₂Si(OCH₃)₃, technical grade), 2-thenoyltrifluoroacetone (tta, 99 %), benzoylacetone (bzac,

Dalton Transactions Accepted Manuscript

Journal Name

99 %), acetylacetone (acac, > 99 %), dibenzoylmetane (dbm, 98 %), europium (III) oxide (Eu_2O_3 , 99.9 %) and gadolinium (III) oxide (Gd_2O_3 , 99.9 %). Ethanol (P.A.) was obtained from Tedia. All chemicals were used without further purification. Pyridine was stored over 3 Å molecular sieve. Water was deionized to 18 M Ω (Milli-Q, Millipore).

Synthesis of ethylenediaminetetraacetic acid dianhydride (EDTA-DA)

EDTA dianhydride (EDTA-DA) was synthesized according to the method described in references 17 and 18 as following: To a suspension of ethylenediaminetetraacetic acid (EDTA, 36.0 g, 0.12 mol) in pyridine (62 mL) under inert atmosphere (N₂) was added acetic anhydride (48 mL). The resulting mixture was stirred at 65°C for 24 h. Then, it was cooled and filtered under inert atmosphere. The pale yellow solid was washed with acetic anhydride (300 mL) and diethyl ether (300 mL) and dried under reduced pressure (yield 91 %, 27.9 g); mp: 192-194°C; FT-IR stretch from dianhydride carbonyl moiety: $v_{as}(C=O) = 1810 \text{ cm}^{-1}$, s; $v_s(C=O) = 1740 \text{ cm}^{-1}$, s.

Synthesis of LnCl₃.nH₂O compounds

Eu₂O₃ (5 g, 1.42 x 10⁻² mol) or Gd₂O₃ (5g, 1.38 x 10⁻² mol) was suspended in water (100 mL). To this suspension was dropwise added concentrated hydrogen chloride under magnetic stirring until almost total oxide consumption. Then, the resulting solution was filtered (Millipore membrane, 0.22 μ m) and heated in order to obtain a fine white powder.

Synthesis of the Fe₃O₄ particles

Magnetite nanoparticles were prepared by the chemical coprecipitation method.^{19,20} FeCl₃.6H₂O (11.34 g, 4.20 x 10^{-2} mol) and FeCl₂.4H₂O (4.17 g, 2.10 x 10^{-2} mol) were mixed in degassed water (280 mL). The solution was then brought to a reaction temperature of 70 °C. After that, NaOH solution (2.5 mol L⁻¹) was added dropwise until a pH of 11 was achieved. The solution containing the reactants was stirred for 2 h under dynamic nitrogen atmosphere. The black solid was separated from the mixture using a permanent magnet (Nd₂Fe₁₄B) and washed with water until no more Cl⁻ ions could be qualitatively detected by silver nitrate test. Finally, the product (4.3 g of Fe₃O₄) was washed with 50 mL of ethanol (yield 98 %).

Fe₃O₄ coating by SiO₂

PVP polymer (5.0 g) was dissolved in distilled water (33.3 mL, 1.85 mol), then it was added to the suspension of Fe_3O_4 (4.3 g, 1.86 x 10^{-2} mol in 200 mL of ethanol). Thereafter, the temperature was raised to 60 °C and TEOS (2.67 mL, 1.20 x 10^{-2} mol) was added to the resulting mixture, followed by addition of concentrated NH₄OH aqueous solution (3.67 mL). The mixture was maintained at 60 °C for 8 h, under dynamic nitrogen atmosphere. The magnetic particles were magnetically decanted, washed with water (100 mL) and ethanol (200 mL), and dried under reduced pressure at room temperature.

EDTA functionalization of the silica-coated Fe₃O₄

reaction between EDTA-DA and the The aminoalkylmethoxysilanes was performed as described by Patel¹⁶ with some modification. EDTA-DA (5.06 g, 1.97 x 10^{-2} mol) was dissolved in anhydrous pyridine (60 mL) under inert atmosphere using standard Schlenk line techniques. The aminoalkylmethoxysilane containing one (1N), two (2N) or three (3N) amino groups (3.94 x 10⁻² mol) was added into the EDTA-DA solution. The resulting solution containing the reactants was stirred for 24 h, under dynamic nitrogen atmosphere at room temperature. After that, Fe₃O₄ (2.0 g, 8.65×10^{-3} mol) was added to the reaction mixture, followed by the addition of concentrated aqueous ammonium hydroxide solution (13.85 mL). The mixture was also stirred for 24 h at room temperature. The obtained particles were magnetically decanted and washed with ethanol and deionized water thoroughly to remove non-magnetic products. Finally, the resulting material was dried under reduced pressure.

Ln³⁺ adsorption on functionalized SiO₂ | Fe₃O₄

EDTA-functionalized magnetic particles (1.0 g of Fe₃O₄|SiO₂|xN where x = 1, 2 or 3) were suspended in water (30 mL). To this suspension was added EuCl₃.6H₂O (1.05g, 2.87 x 10⁻³ mol) or GdCl₃.6H₂O (1.06 g, 2.87 x 10⁻³ mol) previously dissolved in 10 mL of water. The mixture was then stirred for 24 h, at room temperature. Thereafter, the material was magnetically decanted and washed with deionized water (200 mL) and ethanol (100 mL). Finally, the material was dried under reduced pressure at room temperature. The resulting products were named as Fe₃O₄|SiO₂|xNEu and Fe₃O₄|SiO₂|xNGd (where x = 1, 2 or 3).

$Ln^{3+}\beta$ -diketonate complexes on the material surfaces

The ethanolic solution of the diketonate ligand $(1.43 \times 10^{-3} \text{ mol})$ tta, bzac, acac or dbm was added to the suspension of the magnetic material containing Eu³⁺ or Gd³⁺ (0.5 g). The reaction was maintained for 6 h under stirring. Finally, the material was washed with ethanol (50 mL) and dried under reduced pressure.

Characterization of the materials

The X-ray diffraction (XRD) patterns of the materials were recorded with a Lab-X XRD-6000 diffractometer (Shimadzu), using Cu-Ka radiation (λ = 0.154056 nm). Measurements of magnetization curves (at 25 °C) were carried out using a VersaLab Vibrating Sample Magnetometer (VSM, Quantum Design) under a test field range of -10000 to 10000 Oe. Scanning electron microscopy (SEM) images were obtained with a Quanta 450 FEG (FEI) in order to characterize morphological and textural aspects of the materials. The shape and nanostructural features were determined by transmission electron microscopy (TEM) using a JEM-1200(JEOL) operating at 120 kV. Thermogravimetric analysis (TGA) was performed on a DTG-60H thermal analyzer system (Shimadzu) at the heating rate of 10 °C min⁻¹ in a N₂ flow of 50 mL min⁻¹. The quantitative analysis of C, H, and N of the materials were performed by using a Perkin–Elmer model 240 microanalyzer. Europium content was quantitatively determined by

Dalton Transactions Accepted Mar

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Journal Name

ARTICLE

wavelength dispersive X-ray fluorescence using a XRF-1800 spectrometer (Shimadzu), measuring the magnitude of Eu L α spectral line using LiF (200) as analysing crystal, a Rh anode Xray tube (40 kV, 95 mA) and a scintillation counter. For this purpose, analytical curve for Eu was obtained from synthetic standards prepared by adding different amounts of Eu₂O₃ in the Fe₃O₄|SiO₂|1N matrix. Fourier-transform infrared (FT-IR) spectra were recorded on a IR Tracer-100 FT-IR spectrophotometer (Shimadzu) using KBr pellet technique in the range of 400-4000 cm⁻¹. Zeta potentials of the magnetic particles were obtained with a Zetasizer Nano ZSP (Malvern Instruments) and the measurements were performed in water (Milli-Q, Millipore) without addition of buffers at an initial pH of 6.3 \pm 0.1 at 25 °C using a cell drive voltage of 120 V. Photoluminescence spectra of the SiO_2 | Fe_3O_4 | xNLn³⁺ materials were recorded at room and liquid nitrogen temperatures using a Fluorolog-3 spectrofluorometer (Horiba Jobin-Yvon).

Results and discussion

Functionalized magnetite particles

The X-ray diffraction (XRD) patterns of Fe₃O₄ (Fig. 1) show the characteristic narrow diffraction peaks of magnetite relative intensities match well with the standard database peaks of reference pattern (JCPDS file No. 19-0629), confirming the cubic inverse spinel structure of the magnetite. On the other hand, the Fe₃O₄|SiO₂|xN functionalized materials present broad reflections in the 2 θ interval from 20 to 28° assigned to the siloxane lattice on the surface of magnetic particles. In addition, the characteristic diffraction peaks of magnetite were also recognized in diffraction patterns of all materials.



Fig. 1 XRD patterns of Fe $_3O_4$, Fe $_3O_4$ |SiO $_2$ and functionalized materials.

The magnetic properties of the materials were measured using a vibrating sample magnetometer (VSM) at room temperature under an applied field range of -10000 to 10000 Oe. The field-dependent magnetic measurements recorded for Fe_3O_4 , Fe_3O_4 |SiO₂ and functionalized materials (Fig. 2) present nearly zero values of coercivity (H_c) and remanent magnetization (σ_r), suggesting that the materials exhibit superparamagnetic behavior.²¹⁻²³ It is important to report that the coercivity values are consistent with the low magnetocrystalline anisotropy intrinsic of the magnetite. The H_c value of Fe₃O₄ has not varied significantly after coating and functionalization steps (Table S1 in the ESI), indicating that no considerable chemical change has occurred in the magnetic core.²³ Moreover, the low values of σ_r suggest that the materials cannot retain magnetization before and after exposure to an external magnetic field. This behavior contributes to reduce the particle aggregation due to magnetic dipole interaction. The most remarkable difference in the σ_s values of saturation magnetization may be attributed to the layer of nonmagnetic material (i.e., SiO₂ and organic groups). The Fe₃O₄, Fe₃O₄ |SiO₂ and functionalized materials present the

 $\sigma_{\rm s}$ values of 83.6, 55.9 and 15 emu g⁻¹, respectively. This result can be attributed to the success of the particles coating and functionalization steps, resulting in a lower content of magnetite per gram of the hybrid material.



Fig. 2 Variation of magnetization of Fe $_3O_4$, Fe $_3O_4$ |SiO $_2$ and functionalized materials with the applied field at room temperature.

SEM images show no significantly change in the morphological characteristics of the material after silica coating (Fig. S2 in the ESI). The Fe_3O_4 and Fe_3O_4 |SiO₂ materials present a granular structure formed by submicrometer particles. On the other hand, EDTA functionalized materials different morphologies for exhibit all employed aminoalkylalkoxysilanes as compared with non-functionalized systems (Fig. 3). Besides, the SEM micrographs of the Fe₃O₄|SiO₂|1N, Fe₃O₄|SiO₂|2N and Fe₃O₄|SiO₂|3N materials present large agglomerates and different shapes, showing both rough and smooth textures. This morphological alteration is owing to the considerable amount of chelating agents on the magnetic matrix.

TEM micrographs indicate that the magnetite particles were successfully coated with tetraethoxysilane (TEOS) by the sol-gel process (Fig.S2 in the ESI). As can be observed in Fig. 3, TEM micrographs show similar nanostructural characteristics for the $Fe_3O_4|SiO_2|1N$, $Fe_3O_4|SiO_2|2N$ and $Fe_3O_4|SiO_2|3N$ materials. The functionalization process produced a material where magnetite nanoparticles are embedded in the SiO₂ instead of the functional layer follow the shape of the $Fe_3O_4|SiO_2$ particles. For $Fe_3O_4|SiO_2|1N,\ Fe_3O_4|SiO_2|2N$ and Fe₃O₄|SiO₂|3N materials (Scheme 1a-c), the aminoalkylalkoxysilane groups may also bind to another alkoxyde group, increasing the extension of the siloxane network.



Fig. 3 Representative images of $Fe_3O_4|SiO_2|1N$, $Fe_3O_4|SiO_2|2N$ and $Fe_3O_4|SiO_2|3N$ synthesized with aminoalkylalkoxysilane containing one, two or three amino groups, respectively.

The thermal stability of Fe₃O₄, Fe₃O₄|SiO₂ and functionalized materials were evaluated by thermogravimetric analysis (Fig. 4). The TGA curves of the Fe_3O_4 and $Fe_3O_4|SiO_2$ systems show the smallest mass loss due to the nonfunctionalized surface. In the case of Fe₃O₄, it is observed only mass loss that may be attributed to the adsorbed or trapped solvent molecules (water or ethanol), while for Fe₃O₄|SiO₂ it is also possible to observe mass loss owing to the residual ethoxide groups. The TGA curves of the functionalized materials exhibited similar weight loss trend. These materials undergo the first mass loss below 120 °C due to the loss of adsorbed or trapped solvent molecules (water or ethanol). The mass loss of approximately 31 % in the temperature interval from 160 to 550 °C may be related to the decomposition of the organic moieties. The total mass loss of the functionalized materials varied from 60 to 73 %, suggesting similar grafting percentages of aminoalkylalkoxysilane onto Fe₃O₄|SiO₂ surface.

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Fig. 4 Thermogravimetric curves for Fe $_3O_4,\ Fe_3O_4|SiO_2$ and functionalized materials.

FT-IR absorption spectra of the Fe_3O_4 , Fe_3O_4 |SiO₂ and functionalized materials are shown in Fig. S3 (ESI). The strong absorption band centered at 596 $\mbox{cm}^{\mbox{-}1}$ for $\mbox{Fe}_3\mbox{O}_4$ may be attributed to the stretching vibrations v(Fe-O) in both tetrahedral and octahedral sites, while the band at 435 cm⁻¹ is due to the Fe-O stretching in the octahedral Fe site.^{24,25} The absorption band around 1641 cm⁻¹ is assigned to δ (H-O-H) bend mode and the broad band at 3387 cm⁻¹ is due to stretching vibration modes of the hydroxyl ions or water molecules coordinated to Fe ions.²⁶ The absorption spectrum of Fe₃O₄|SiO₂ material shows an absorption band at 1090 cm⁻¹ assigned to the asymmetric stretching of Si-O bonds (v_{as}(Si-O)) from ≡Si-O-Si≡ group. Moreover, it is observed two absorption bands at 1397 and 1643 cm⁻¹ from v_s (C=O) and v_{as} (C=O) stretching of the carboxylate groups, respectively. The bands between 2800 and 3000 cm⁻¹ are assigned to C-H stretching vibrations v(C-H) from $-CH_2$ group. These results also confirm the functionalization of the Fe_3O_4 SiO₂ particles. A schematic representation of the materials is presented in Scheme 1.



Scheme 1 Schematic representation of the materials produced and their functional groups. (a) $Fe_3O_4|SiO_2|1N$, (b) $Fe_3O_4|SiO_2|2N$ and (c) $Fe_3O_4|SiO_2|3N$.

The surface charge was investigated by zeta potential measurement at the equilibrium pH characteristic of each sample suspended in water (Milli Q). The pH of water after suspension of the Fe_3O_4 and $Fe_3O_4|SiO_2$ materials were

observed 6.9 \pm 0.3 and 5.7 \pm 0.4, which presented negative zeta potential values of -32 ± 6 and -35 ± 5 mV, respectively (Fig. 5), indicating negatively charged surfaces. It is noteworthy that the pH values are slightly above their isoelectric point $(6.0-6.8 \text{ for magnetite}^{26} \text{ and } 3.2-3.8 \text{ for silica}^{27})$, which are coherent with the nature of these negatively charged surfaces. For functionalized materials, the equilibrium pH values may be associated with chemical characteristics of the particles surfaces that depend on both the reaction medium and the aminoalkylmethoxysilane compound. used For the Fe₃O₄|SiO₂|1N material without secondary amino groups, the synthesis process (basic pH) produces a predominantly carboxylate (COO⁻) surface, leading to the zeta potential (31.9 mV) and pH (6.9) values. Nevertheless, the Fe₃O₄ |SiO₂ |2N and Fe₃O₄|SiO₂|3N materials present secondary amino groups (NH) that may be protonated, yielding NH_2^+ species due to the slightly acidic pH of the deionized water (pH ~5) used in the washing step. When in contact with water (Milli Q, pH = 6.3±0.1) the protonated secondary amino groups ends up participating in the chemical equilibrium involving carboxylate groups, thereby preventing the increase in the pH observed for samples without secondary amino groups. This behavior reduces the extent of ionization of the carboxylic groups, providing more positive surfaces.



Fig. 5 Zeta potential (ζ) of the materials and pH of water after particle suspension.

Covalently linked lanthanide complexes

All matrices containing Eu^{3+} ions present positive zeta potential (29.4-32.2 mV) and pH values were found in the intervals of 3.5-4.2. In these materials, the Eu^{3+} coordination by carboxylate and residual non-protonated amino groups may contribute to increase the zeta potential values, conferring positive charge to particle surface. The lower pH values can be related to deprotonation of NH_2^+ or due to the moderately acid lanthanide chloride solution used in the adsorption process of the metal ion.

Journal Name

A typical WDXRF spectrum of the final hybrid material shows only some emission lines of the Fe and Eu atoms (Fig. S4 in the ESI). Table 2 shows the values for Eu³⁺ content determined for the functionalized materials. The lanthanide contents are higher to those ones found for other EDTA modified materials.^{28,29} The higher values of Eu content were found in samples based on Fe₃O₄|SiO₂|2N and Fe₃O₄|SiO₂|3N matrices, showing that the absorption process are dependent on the size of chain of the sililant agents. Besides the carboxylate groups, Ln³⁺ ions may be also interact with amino groups arising from aminoalkyl alkoxysilanes. This behavior reflects the ability of the material to provide a large number of possible emitting centers. Although Fe₃O₄|SiO₂|2N and Fe₃O₄|SiO₂|3N materials (Table S2 in the ESI) present different nitrogen contents, but similar Eu³⁺ contents were adsorbed on these systems. These results indicate that the metal ions are coordinated in similar way by aminocarboxylate moieties on both materials surfaces.

Table 1 Europium content of functionalized mater	ials. ^[a]
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Material	Content (% m m ⁻¹)		
$Fe_3O_4 SiO_2 1N$	9.4 ± 0.1		
$Fe_3O_4 SiO_2 2N$	13.4 ± 0.4		
$Fe_3O_4 SiO_2 3N$	13.7 ± 0.8		

[a] Analytical curve and parameters are found in Fig. S5 in ESI.

Luminescence spectroscopy

The luminescence spectra of the (Fe₃O₄|SiO₂|3N) hybrid materials containing Gd^{3+} ion and β -diketonates were recorded at 77 K, under excitation monitored on the singlet-singlet $(S_0 \rightarrow S_1)$ ligand transitions, in order to obtain information about electronic structure of the ligands. The broad emission bands observed in the range of 400 to 650 nm can be attributed to the phosphorescence intraligand $(T_1 \rightarrow S_0)$ transition of the β -diketonate ligands (Fig. 6). These broad bands exhibit a red shift owing to decreasing in triplet state energies in the following order: acac < bzac < dbm < ttaligands.³⁰ It is observed that the $Fe_3O_4|SiO_2|1N$ and Fe₃O₄|SiO₂|2N materials (see Fig. S6 in the ESI) present similar spectral profiles. The broad emission band around 500 nm is assigned to the SiO₂ matrix. According to the literature,^{31,32} the nature of these bands has been attributed to the defect centers or the charge transfer process in the siloxane network, among others.



Fig. 6 Phosphorescence spectra of $Fe_3O_4|SiO_2|3N$ Gd materials containing H_2O and the following β -diketonates as ligands: 2-thenoyltrifluoroacetone (tta), dibenzoylmetane (dbm), benzoylacetone (bzac) andacetylacetone (acac).

It is possible to verify that all hybrid materials containing Eu³⁺ ion exhibit luminescence when exposed to radiation in the spectral range of 290 to 380 nm, as shown in Fig. S1. However, the systems without diketonate ligands display the lowest brightness, suggesting that the β -diketonate play the most important role in the sensitization of the Eu³⁺ ion.

The photoluminescence sensitization process of the Eu³⁺ ion by β-diketonate ligands were investigated by using the excitation spectra recorded at room temperature, under emission monitored on the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 617 nm (Fig. 7 and see Fig. S7 in the ESI). Except for the hydrated materials, all excitation spectra exhibit a high intense broad absorption band in the range of 300 - 420 nm, which is attributed to the absorption of diketonates via $S_0 \rightarrow S_1$ transition followed by intramolecular energy transfer from their T_1 states to the ${}^{5}D_1$ and ${}^{5}D_0$ levels of the Eu $^{3+}$ ion.³³ This result indicates that the β -diketonate ligands act as luminescence sensitizer for the Eu³⁺ ion in the hybrid materials. Additionally, for the materials containing H₂O, acac or bzac as ligands, it is observed narrow absorption bands arising from the intraconfigurational- $4f^6$ transitions of the Eu^{3+} ion: ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ (525 nm), ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ (465 nm), ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ (394 nm), ${}^{7}F_{0} \rightarrow {}^{5}L_{7}$ (379 nm) and ${}^{7}F_{1} \rightarrow {}^{5}D_{1}$ (535 nm).



Fig. 7 Excitation spectra of the Fe₃O₄|SiO₂|3N Eu materials containing H₂O and the following diketonates as ligands: 2thenoyltrifluoroacetone (tta), dibenzoylmetane (dbm), benzoylacetone (bzac) and acetylacetone (acac).

As it can be seen, the relative intensities of intraligand broad absorption bands $(S_0 \rightarrow S_1)$ are higher than those for 4f-4f transitions of the Eu³⁺ ion, confirming that the ligand-to-metal ion energy transfer is operative. In addition, it is observed a shift of the broad absorption bands to lower energy in the following order (aca > bzac > dbm, tta), in agreement with the decreasing energy of the excited singlet state.

Fig. 8 shows the emission spectra of the hybrid materials (Fe₃O₄|SiO₂|3N) containing Eu³⁺ ion and β -diketonate ligands, recorded at room temperature, under excitation on the $S_0 \rightarrow S_1$ transitions. These spectra exhibit narrow emission bands that are assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ transitions (where J = 0, 1, 2, 3, 4) of the Eu^{3+} ion, displaying the hypersensitive ${}^5D_n \rightarrow {}^7F_2$ transition as the most intense one. The emission spectra for all materials (see also Fig. S8 in the ESI) present very similar spectral features, indicating similar symmetries for the chemical environment around the Eu³⁺ ion. In the vicinity of the metal ion, steric hindrance may play an important role in the coordinating abilities of the water and/or β -diketonate molecules. Therefore, it is expected that the first coordination sphere might be saturated with few additional ligand molecules. According to experimental data and selection rules

for the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ transitions, the chemical environment of the Eu^{3+} ion belongs to a symmetry group among C_n , C_{nv} or C_s .³⁴



Fig. 8 Emission spectra of the Fe₃O₄|SiO₂|3N Eu materials containing H₂O and the following diketonates as ligands: 2-thenoyltrifluoroacetone (tta, λ_{exc} = 370 nm), dibenzoylmetane (dbm, λ_{exc} = 350 nm), benzoylacetone (bzac, λ_{exc} = 350 nm) and acetylacetone (acac, λ_{exc} = 315 nm).

Experimental intensity provide parameters can quantitative information about intensity probabilities of 4f6 transitions, nature of the chemical environment and luminescence efficiency may be determined from the optical photoluminescent properties Thus, of the data. Fe₃O₄|SiO₂|1N, Fe₃O₄|SiO₂|2N and Fe₃O₄|SiO₂|3N containing Eu^{3+} ion and β -diketonate ligands were quantified by experimental values of radiative (A_{rad}) and non-radiative (A_{nrad}) rates, Judd–Ofelt parameters Ω_{λ} (λ = 2 and 4) and emission quantum efficiency (η) via methodology described by Sá and

Page 8 of 10

Journal Name

Journal Name

co-workers³⁵ reported in the supporting information. The spectroscopic parameters are shown in Table2 (see Fig. S9 in the ESI). The nature of ligand produces more expressive changes in the experimental intensity parameters than the type of aminoalkylalkoxysilane employed. Although the A_{nrad} values do not exhibit a regular behaviour, it is observed the higher values for systems with water, acac and bzac, while the lower ones are found for hybrid materials containing dbm and tta ligands. However, the A_{nrad} values are still higher as compared with those ones for tris- and tetrakis- β -diketonate coordination compounds, reflecting the heterogeneity of coordinating sites of the hybrid materials.

On the other hand, A_{rod} values present a more regular behaviour, exhibiting an opposite trend as compared with A_{nrad} . The higher values obtained for the tta and dbm systems reflect the hypersensitivity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (Table 2). The A_{rod} values are similar to those ones obtained for some highly luminescent Eu³⁺- β -diketonate complexes and higher than those ones for thehybrid luminescent magnetic materials reported in literature.³⁶

It is important to notice that the A_{rad} and η values follow similar trends. In particular, η presents values ranging between 20 and 36%, reaching to the maxima values for materials with tta and dbm ligands. This result indicates that the luminescence efficiency depends on the ligand actuating as antenna. The high contents of Eu-diketonate complexes covalently linked to the material surface lead to strong bright luminescence (Fig. S1).

The Ω_2 and Ω_4 parameters depend on both the local geometry and polarizabilities of the chemical environment of the lanthanide ion, respectively. The higher Ω_2 values were obtained for the materials with tta and dbm ligands, reflecting the higher changes in the chemical environment of the metal ion. On the other hand, it is possible to verify that the Ω_4 parameter is less affected by the type of ligand coordinated to the Eu³⁺ ion. Furthermore, the intensity parameter values are not significantly affected when varying the 1N, 2N and 3N organosilanes.

	Material	(s ⁻¹)	(s ⁻¹)	(10^{-3} s^{-1})	(s ⁻¹)	(10^{-20} cm^2)	(10^{-20} cm^2)	(%)
	Fe ₃ O ₄ SiO ₂	1NEu						
	H ₂ O	438	1787	0.449	2225	7.9	10.2	20
	acac	489	1332	0.549	1821	9.8	10.7	27
	bzac	597	1873	0.405	2470	13.7	9.6	24
	dbm	806	1433	0.447	2239	20.1	10.5	36
	tta	669	1316	0.504	1985	15.6	10.6	34
	Fe ₃ O ₄ SiO ₂	2NEu						
	H ₂ O	420	1671	0.478	2091	7.6	9.9	20
	acac	487	1941	0.412	2428	9.5	10.7	20
	bzac	497	1622	0.472	2119	10.4	9.4	23
	dbm	659	1584	0.446	2243	15.3	10.9	29
	tta	677	1319	0.501	1996	15.9	10.5	34
Fe ₃ O ₄ SiO ₂ 3NEu								
	H ₂ O	454	1384	0.544	1838	8.1	10.9	25
	acac	557	1639	0.455	2196	10.5	10.6	25
	bzac	623	1545	0.461	2168	12.5	10.6	29
	dbm	729	1633	0.423	2362	15.5	11.2	31
	tta	648	1230	0.530	1878	13.5	10.0	35

Table 2 Experimental intensity parameters and average lifetime (τ_{av}) of the hybrid materials based on Fe₃O₄|SiO₂|1N, Fe₃O₄|SiO₂|2N and

 $Fe_3O_4|SiO_2|3N$ matrices, containing Eu^{3+} ion and β -diketonate ligands.

Conclusions

In this study, luminescent magnetic materials with high lanthanide content have been prepared. The high Ln³⁺-EDTA complex content was a direct consequence of the synthesis of EDTA-silane precursors before the functionalization step. Although the field-dependent magnetization was considerably smaller for functionalized materials, the general magnetic behavior of magnetite particles was not substantially altered after their coating with silica and organic moieties. The hybrid magnetic systems containing diketonate ligands exhibited high intense luminescence due to the operative antenna effect, while the matrices play a minor rule on the photoluminescent properties. In addition, a comprehensive characterization of the surface and luminescent aspects have also been presented, showing the bifunctionality of the hybrid materials. The experimental strategies used to prepare luminescent magnetic materials may be applied in order to develop new hybrid systems for applications in different areas such as lanthanide magnetic separation, optical markers, among others.

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Journal Name

ARTICLE

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