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**Nanomateriais ópticos e magnéticos contendo matrizes de
 Fe_3O_4 e SiO_2 funcionalizadas com calixareno e complexos de
terras raras**

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**Optical and magnetic nanomaterials containing Fe₃O₄
and SiO₂ matrices functionalized with calixarene and
rare earth complexes**

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“Thou seest not in the creation of the All-merciful any imperfection. Return thy gaze; seest thou any fissure? Then return thy gaze again, and again, and thy gaze comes back to thee dazzled, aweary.”

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ABSTRACT

Khan, L.U. **Optical and magnetic nanomaterials containing Fe₃O₄ and SiO₂ matrices functionalized with calixarene and rare earth complexes.** 2015. 206p. PhD Thesis - Graduate Program in Chemistry. Instituto de Química, Universidade de São Paulo, São Paulo.

The design and fabrication of sophisticated bifunctional luminescent and magnetic nanomaterials based on Fe₃O₄ and RE³⁺ complexes are sought for. Accordingly, novel red-green emitting superparamagnetic Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) nanomaterials were prepared through on-pot method. In this regard, the chemically modified calixarene ligand was used as a surfactant to stabilize the Fe₃O₄ nanoparticles. The calixarene ligand provides colloidal stability and chemically modifiable surface to the magnetite nanoparticles. Thus, this ligand functionalized Fe₃O₄@calix nanoparticles were further coordinated to the RE³⁺ ions *via* one-pot synthesis, using TTA and ACAC ligands as sensitizers (*antenna effect*) to produce highly luminescent nanophosphors. In addition, bifunctional optical and magnetic Fe₃O₄@SiO₂-TTA-Eu(L), L: TTA, TC, AB and AMB as well as Fe₃O₄@SiO₂-TTA-Tb(AB or AMB) nanocomposites were also synthesized through multistep synthetic protocol, utilizing Fe₃O₄ nanoparticles as precursors. They were modified with silica shell, using modified Stöber method and further grafted with RE³⁺ complexes to produce the luminescent and magnetic nanocomposites. The X-ray powder diffraction (XPD), small angle x-ray scattering (SAXS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques were used to determine the structures, morphologies, size distribution and monodispersity of the synthesized materials. These novel Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) as well as Fe₃O₄@SiO₂-TTA-Eu(L) and Fe₃O₄@SiO₂-TTA-Tb(AB or AMB) magnetic luminescent nanomaterials show interesting superparamagnetic and photonic properties. The magnetic properties (M-H and ZFC/FC

measurements) at temperatures of 2, 5 and 300 K were explored in order to investigate the extent of coating and crystallinity effect on the saturation magnetization and blocking temperatures. The influence of the RE³⁺ ions on the magnetization of the optical and magnetic nanomaterials was also studied. Even though magnetite is a strong luminescence quencher, the coating of the Fe₃O₄ nanoparticles with synthetically modified calixarene ligand (calix) and silica shell have overcome this difficulty. Moreover, the intramolecular energy transfer from the T₁ excited triplet states of TTA and ACAC ligands to the emitting levels of Eu³⁺ and Tb³⁺ in the Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) nanomaterials are discussed. The emission quantum efficiencies (η) for the Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@SiO₂-TTA-Eu(L) nanomaterials are also calculated and discussed, as well as the structural features based on the energy levels and experimental intensity parameters, in the case of the Eu³⁺ ion. These novel nanomaterials may act as the emitting layer for the red and green light for magnetic and light converting molecular devices (MLCMDs).

Keywords: Photoluminescence, magnetism, rare earth complexes, magnetite, calixarene, silica.

RESUMO

Khan, L. U. **Nanomateriais ópticos e magnéticos contendo as matrizes Fe_3O_4 e SiO_2 funcionalizadas com calixareno e complexos de terras raras.** 2015. 206p. Tese (Doutorado) - Programa de Pós-Graduação em Química. Instituto de Química, Universidade de São Paulo, São Paulo.

Neste trabalho são investigados o *designer* e a fabricação nanomateriais magnéticos e luminescentes sofisticados bifuncionais baseados em Fe_3O_4 e complexos de RE^{3+} . Portanto, novos nanomateriais $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ e $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ emissores vermelho e verde superparamagnéticos foram preparados pelo método *one-pot*. Neste caso, o ligante calixareno quimicamente modificado como surfactantes para estabilizar as nanopartículas de Fe_3O_4 . O ligante calixareno proporciona uma superfície quimicamente modificada e estabilidade coloidal das nanopartículas magnetitas. Consequentemente, as nanopartículas funcionalizadas ($\text{Fe}_3\text{O}_4@\text{calix}$) foram coordenadas aos íons TR^{3+} por meio da síntese *one-pot*, usando ligantes TTA e ACAC como sensibilizadores (*efeito antena*) para produzir nanofósforos altamente luminescentes. Além do mais, nanocompósitos bifuncionais óptico e magnético $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu}(\text{L})$, L: TTA, TC, AB e AMB bem como $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb}(\text{AB ou AMB})$ foram também preparados por meio de um protocolo de múltiplas etapas, utilizando as nanopartículas Fe_3O_4 como precursoras. Elas foram modificadas com camadas de sílica, usando o método Stöber modificado e ligados com complexos de TR^{3+} para produzir nanocompósitos luminescentes e magnéticos. As técnicas de difração de raios X pelo método do pó (XPD), Espalhamento de Raios-X a baixo ângulo (SAXS), microscopia eletrônica de transmissão (TEM) e microscopia de eletrônica de varredura (MEV) foram utilizadas para determinar as estruturas, morfologias, distribuições de tamanhos e monodispersividade dos materiais sintetizados. Estes novos nanomateriais bifuncionais $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$, $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu}(\text{L})$ e $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb}(\text{AB ou AMB})$

apresentam propriedades fotônicas e superparamagnéticas muito interessantes. As propriedades magnéticas (ZFC/FC e M-H) obtidas nas temperaturas de 2, 5 e 300 K foram investigadas a fim de obter informações sobre o efeito da cristalinidade na magnetização de saturação e das temperaturas de bloqueios. Também foram estudadas a influência dos íons TR^{3+} sobre a magnetização dos nanomateriais. Apesar da magnetita atuar como um forte supressor de luminescência, as camadas do ligante calixareno modificado e da sílica sobre as nanopartículas de Fe_3O_4 compensam esta desvantagem. Do mesmo modo foi considerada a discussão sobre a transferência de energia intramolecular do estado tripleto T_1 dos ligantes TTA e ACAC para os níveis excitados dos íons Eu^{3+} e Tb^{3+} nos nanomateriais $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ e $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$. As eficiências quânticas de emissão (η) dos compostos $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ e $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ foram calculadas e discutidas, bem como suas características estruturais baseadas nos níveis de energia e parâmetros de intensidades experimentais dos sistemas contendo o íon Eu^{3+} . Estes novos nanomateriais podem atuar como camadas emissores vermelha e verde para dispositivos moleculares conversores de luz e magnéticos (MLCMDs).

Palavras-chave: Fotoluminescência, magnetismo, complexos de terras raras, magnetite, calixareno, sílica.

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ABBREVIATIONS AND SYMBOLS

AB: 4-Aminobenzoate
ACAC: Acetylacetonate
AMB: 4-Aminomethylbenzoate
B.M.: Bohr Magneton, $1 \text{ B.M.} = 9.274 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
calix: Calixarene ligand
CPTES: 3-Chloropropyltriethoxysilane
ET: Energy Transfer
emu: electromagnetic unit, 1 erg G^{-1}
H: Magnetic field strength
 H_c : Magnetic Coercivity
RE: Rare Earth
L: Ligands
LCMDs: Light Conversion Molecular Devices
LMCT: Ligand-to-Metal Charge Transfer
M: Magnetization
MLCMDs: Magnetic Light Converting Molecular Devices
 M_s : Saturation magnetization
NMR: Nuclear Magnetic Resonance
Oe: Oersted
SAED: Selected Area Electron Diffraction
SAXS: Small Angle X-ray Scattering
SEM: Scanning Electron Microscopy
TC: Thioglycolate
TEM: Transmission Electron Microscopy
TEOS: Tertaethyl orthosilicate
TTA: Thenoyltrifluoroacetate
XPD: X-ray Powder Diffraction
ZFC/FC: Zero Field Cooling/Field Cooling
 μ : Magnetic moment
 η : Quantum efficiency
 Ω_λ : Experimental intensity parameters
 τ : Emission lifetime

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Chapter 1

INTRODUCTION

1. INTRODUCTION

In nature, smart materials that exhibit significant magnetic and optical properties are very remarkable. For many applications in biotechnology, medicine, and quality inspection, this type of bifunctional materials is sought for [1]. Nanomaterials with unique magnetic and photonic properties have also great potential in biological applications such as MRI contrast agents, drug delivery carriers and biomarkers [2,3]. Several reports have focused on the synthesis and exploration of this type of nanomaterials, such as hybrid [4-6] as well as magnetic and optical core-shell ones [7-9].

Magnetite nanoparticles have been the subject of extensive research in the last decades, owing to their diagnostic and therapeutic applications [10], great importance to biomineralization in natural resources, such as human brain [11], carbonaceous chondrites [12], magnetite production by microorganisms [13] and as a magnetoreceptor in rainbow trout and honeybees [14]. However, due to the high ratio of surface to volume and magnetization, bare magnetite nanoparticles are usually prone to aggregation. This difficulty makes magnetic oxide nanoparticles inadequate candidates for biological applications. Therefore, magnetic oxide nanoparticles are functionalized with carboxylates, amines, diols [15], phosphates, phosphonates and sulfonates [16], in order to ensure the colloidal stability of these nanomaterials in an organic or aqueous medium.

The silica coating is also employed, because it presents not only the encapsulated magnetite nanoparticles a biocompatibility, but also a greater chemical and mechanical stability against variation in pH or temperature. For example, silica coatings retard the oxidation of Fe_3O_4 nanocrystals to $\alpha\text{-Fe}_2\text{O}_3$ at high temperature [17]. In addition, the surface of silica coatings can be further utilized to introduce specific functional groups. Ethylenediaminetetraacetic acid-functionalized Fe_3O_4 nanoparticles can be used for selective uptake of rare earths from aqueous

solution [18]. Besides, Chin and co-workers [19] reported the formation of remarkably stable magnetite ferrofluids by utilizing for first time the “*p*-sulfonato-calix[6&8]arenes and sulfonated *p*-benzylcalix[4,5,6&8]arenes” as surfactants to coat the superparamagnetic Fe₃O₄ nanoparticles.

Calixarenes are macrocyclic molecules made up of *p*-substituted phenolic units linked by methylene bridges *ortho* to the hydroxyl groups. They are known to be useful building blocks for hollow molecular scaffolds with easily functionalisable hydrophilic and hydrophobic lower and upper rims, respectively. Thus, they are well known in supramolecular chemistry for a variety of functions, especially in terms of inclusion complexes [20], molecular scaffolds and molecular recognition for rare earth ions (RE³⁺) [21].

The last two decades have demonstrated the significant growing interest in luminescent materials containing RE³⁺ ions. Their growing photonic applications presently extend from laser physics to materials sciences, agriculture, and medical diagnostics. Selected examples are phosphors for lighting and displays, lasers, optical telecommunications, security inks, anti-counterfeiting tags, probes for luminescent immunoassays, and bioconjugates for photodynamic treatment of cancer [22]. RE³⁺ ions have 4f energy levels that are little affected by the chemical environment due to the effective shielding of the 4f electrons by the filled 5s and 5p external subshells. Therefore, the absorption and emission spectra of the 4f intraconfigurational transitions of the RE³⁺ ions retain more or less their atomic character [23].

The efficient luminescence of the RE³⁺-complexes indicates that the ligands (L) can act as good sensitizers (*antenna effect*) for rare earth ions. Therefore, the promising photonic properties of several RE³⁺ ions have been added a field of research to the coordination chemistry. Among the studied luminescent complexes, the Eu³⁺ and Tb³⁺ complexes exhibit red and green high intensity emissions are the most attractive ones because of their energy level electronic structures and the featuring long emission lifetimes (milliseconds) [23-26].

Generally, to optimize the emission quantum yield of the luminescent RE^{3+} coordination compounds, the ligand should be chosen according to the efficiency of the following processes: *i*) absorption from the ground to the excited singlet states of the ligand ($\text{S}_0 \rightarrow \text{S}_n$); *ii*) non-radiative decay to the triplet state via intersystem crossing ($\text{S}_1 \rightarrow \text{T}_1$) and *iii*) non-radiative intramolecular energy transfer from the T_1 state of the ligand to excited states of the RE^{3+} ion, $\text{T}_1(\text{L}) \rightarrow {}^{2\text{S}+1}\text{L}_J(\text{RE}^{3+})$ [23-26].

In the present work, it was reported the synthesis, characterization as well as optical and magnetic properties of the novel magnetic luminescent nanomaterials based on Fe_3O_4 functionalized with calixarene and rare earth complexes; $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA or ACAC})$, where TTA: thenoyltrifluoroacetate and ACAC: acetylacetonato [27]. In addition, rare earth complexes grafted magnetic core-shell ones; $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE}(\text{L})$, where L: TTA, thioglycolate (TC), 4-aminobenzoate (AB) and 4-(aminomethyl)benzoate (AMB). Based on the magnetic properties at different temperatures, a superparamagnetic model considering interactions was used to better understand the magnetic behavior. Although magnetite acts as a strong luminescence quencher, this difficulty was overcome by functionalizing the Fe_3O_4 nanoparticles with calixarene macrocycle (calix) as well as silica shell in both types of luminescent and magnetic nanomaterials. From the technological point of view, the obtained results are very promising, and present progress on the physical knowledge of superparamagnetic systems with dipolar interactions. Moreover, it was studied the influence of the organic ligands on magnetite and photoluminescence properties of the highly luminescent nanomaterials containing Eu^{3+} and Tb^{3+} ions. The experimental intensity parameters (Ω_2 and Ω_4), radiative and non-radiative rates (A_{rad} and A_{nrad}), for the Eu^{3+} nanophosphors have been calculated. The emission spectral features, the experimental emission quantum efficiency and the emission lifetimes for nanomaterials have been also discussed.

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Chapter 2

RARE EARTHS AND ORGANIC LIGANDS

2. RARE EARTHS AND ORGANIC LIGANDS

The rare earth (RE) elements comprising of lanthanides, ranging from lanthanum to lutetium (Ln: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and scandium (Sc) yttrium (Y). These elements have similar physical and chemical properties. These seventeen RE elements are all electropositive metals with a remarkable uniformity of chemical properties. The similarity of the trivalent lanthanides to each other, especially each to its neighbors as consequence of their general adoption of the +3 oxidation state in aqueous solution, that caused their separation to be an extremely difficult [1,2].

The rare earths are usually occurred in their compounds as RE^{3+} ions other oxidation states are stable only when an empty ($4f^0$), half-filled ($4f^7$), or full ($4f^{14}$) subshell is produced. The predominant oxidation states is trivalent (Ln^{3+} , Sc^{3+} , Y^{3+}), also can be found the divalent (Sm^{2+} , Eu^{2+} , Tm^{2+} , Yb^{2+}) and tetravalent states (Ce^{IV} , Pr^{IV} , Tb^{IV}). The electronic configuration of the RE^{3+} ions is represented by $[\text{Xe}]4f^N$, which shows a gradual increase in the number of electrons N with increasing the atomic numbers of the ions, ranging from $4f^0$ to $4f^{14}$ for the La^{3+} to Lu^{3+} ions [3].

The RE^{3+} ions exhibit a number of features in their chemistry that differentiate them from the d-block metals such as [2,4]: *i)* High coordination numbers (generally between 6 and 12); *ii)* Coordination geometries are determined by ligand steric factors rather than ligand field effects; *iii)* They form labile ‘ionic’ complexes that undergo facile exchange of ligand; *iv)* Small ligand field splitting and very narrow emission and absorption bands in comparison with the d-block metals; *v)* They prefer anionic ligands with donor atoms even of high electronegativity (e.g. N, O, F); *vi)* They readily form hydrated complexes (on account of the high hydration energy of the small Ln^{3+} ion).

Rare earth ions have been widely used in various research fields such as luminescent, steel, alloy, pigment, magnet, laser and catalyst materials, because of their unique properties originating from their 4f intraconfigurational transitions [3]. Rare earth luminescence materials have a special status in photonics due to the unique spectroscopic properties of RE^{n+} ions with respect to light generation and amplification. Following early applications in lighting at the end of the 19th century (Auer mantle, flint stones), the discovery of the bright red emitting phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ at the beginning of the 20th century and the advent of the $\text{YAG}:\text{Nd}^{3+}$ laser in 1964 [5,6].

2.1. Electronic spectroscopy of rare earth ions

The importance of optical spectroscopy of the RE^{3+} ions is mainly associated with their narrow emission bands arising from the intraconfigurational 4f transitions and long lifetimes, which make these ions unique among the luminescent compounds. The 4f-4f energy levels of RE^{3+} ions are only slightly affected by the chemical environment due to the effective shielding of the 4f electrons by the filled 5s and 5p subshells. Therefore, the absorption and emission spectra of the intraconfigurational 4f transitions of the RE^{3+} ions retain more or less their atomic character and similar irrespective of the host matrix. The 4f–4f transitions are parity forbidden, however the Laporte's rule is slightly relaxed for these transitions due to the mixing of opposite parity electronic configurations, produced by the odd components of a non-centrosymmetric ligand field. Moreover, the ligand polarization effects have been shown to be of considerable importance for the 4f-4f transitions [7,8].

The existence of different energy levels of the rare earth ions is a consequence of different interactions operating in the electronic configuration of the ions. Depending on the number, the electrons can distribute in many ways over the $4f^n$ configurations, however some distributions are

energetically more favorable. The selective interactions which split the levels belonging to the $[\text{Xe}]4f^n$ configurations have been schematically shown in Figure 2.1, where the Eu^{3+} ion has taken as an example.

For the systems with more than of two $4f^n$ electrons [9], the electrostatic repulsion (H_{ER}) splits the electronic configuration into spectroscopy terms labeled by “ ^{2S+1}L ” according to the spin multiplicity and the total angular momentum L (Table 2.1) with a separation at around 10^4 cm^{-1} . (Figure 2.1). The spin-orbit interaction (between two magnetic dipoles), H_{SO} , removes the degeneracy of the ^{2S+1}L spectroscopy terms into J levels of the free-ion characterized by L , S , J quantum numbers and labeled by $^{2S+1}L_J$ levels. These levels are relatively higher (10^3 cm^{-1}) because of the heavy rare earth nucleus (Figure 2.1). The energy levels of *free ion* can be described by the $^{2S+1}L_J$ energy levels, where, $2S+1$ represents the total spin multiplicity, L the total orbital angular momentum and J the total angular momentum of the $4f$ electrons.

On placing the RE^{3+} ions in a chemical environment, such as organic ligands or inorganic matrices, the spherical symmetry of free ion is destroyed and each spectroscopic level (J -levels) further splits under the influence of the asymmetric electric field produced by the chemical environment. The ligand field interaction removes to a certain degree the degeneracy of the free-ion levels. The magnitude of the splitting of the $^{2S+1}L_J$ energy levels has been first parametrized in the simplest way assuming a “Point Charge Electrostatic Model (PCEM)” generated by the chemical environment around of the rare earth ions. Usually termed as the ligand field effect (H_{LF}), removing the $(2J+1)$ degeneracy of the J levels, depending exclusively on the point of symmetry about the RE^{3+} ion [5], that is called as Stark levels with splitting at around 10^2 cm^{-1} .

Luminescence originating from the intraconfigurational d transitions is quite different from that of the $4f-4f$ ones. The spectra of d metals are much poorer in the number of observed pure

zero-phonon transitions, since d^n configurations have less microstates by far than the $4f^n$ ones. The vibronic interaction is much stronger than in the case of $4f-4f$ transitions. In addition, for d -transition elements, the ligand field interaction is at least one order of magnitude greater due to the non-screened and more extended d radial distribution. These facts produce very broad $d-d$ transition bands [7].

Figure 2.1. Partial schematic diagram of the splitting of energy levels of Eu^{3+} ion.

Transition metal complexes have usually lower coordination numbers (4 and 6) than the $4f$ elements (from 7 to 9 normally). In the case of four-fold tetrahedral coordination $d-p$ mixing relaxes Laporte's rule allowing the $d-d$ transitions, while in the case of octahedral coordination Laporte's rule is not relaxed, except for the vibronic interaction that instantaneously breaks down

the center of inversion and allows the d–d transitions, with much weaker intensities than in the tetrahedral case [7].

Table 2.1. $4f^n$ electronic configuration, ground state, selective luminescent transitions energy gap of rare earth ions [7].

Element	RE ³⁺ -ground states	RE ³⁺ radius (Å)	Transitions	$\lambda_{\text{emission}}$ (nm)	Energy gap (cm ⁻¹)
²¹ Sc	[Ar]3d ⁰ (¹ S ₀)	0.68	-	-	-
³⁹ Y	[Kr]4d ⁰ (¹ S ₀)	0.88	-	-	-
⁵⁷ La	[Xe]4f ⁰ (¹ S ₀)	1.06	-	-	-
⁵⁸ Ce	[Xe]4f ¹ (² F _{5/2})	1.03	5d→ ² F _{5/2}	-	-
⁵⁹ Pr	[Xe]4f ² (³ H ₄)	1.01	³ P ₀ → ³ H ₆	610	3910
			¹ D ₂ → ³ F ₄	1060	6940
			¹ G ₄ → ³ H ₅	1300	-
⁶⁰ Nd	[Xe]4f ³ (⁴ I _{9/2})	0.99	⁴ F _{3/2} → ⁴ I _{9/2}	1060	5400
⁶¹ Pm	[Xe]4f ⁴ (⁵ I ₄)	0.98	⁵ F ₁ → ⁵ I _J	-	-
⁶² Sm	[Xe]4f ⁵ (⁶ H _{5/2})	0.96	⁴ G _{5/2} → ⁶ H _{9/2}	590	7400
⁶³ Eu	[Xe]4f ⁶ (⁷ F ₀)	0.95	⁵ D ₀ → ⁷ F ₂	615	12300
⁶⁴ Gd	[Xe]4f ⁷ (⁸ S _{7/2})	0.94	⁶ P _{7/2} → ⁸ S _{7/2}	311	32100
⁶⁵ Tb	[Xe]4f ⁸ (⁷ F ₆)	0.92	⁵ D ₄ → ⁷ F ₅	550	14800
⁶⁶ Dy	[Xe]4f ⁹ (⁶ H _{15/2})	0.91	⁴ F _{9/2} → ⁶ H _{13/2}	570	7850
⁶⁷ Ho	[Xe]4f ¹⁰ (⁵ I ₈)	0.89	⁵ F ₅ → ⁵ I _{7,6}	970,1450	3000
			⁵ S ₂ → ⁵ I ₈	550	2200
⁶⁸ Er	[Xe]4f ¹¹ (⁴ I _{15/2})	0.88	⁴ S _{3/2} → ⁴ I _{15/2}	545	3100
			⁴ I _{13/2} → ⁴ I _{15/2}	1500	6500
⁶⁹ Tm	[Xe]4f ¹² (³ H ₆)	0.87	¹ G ₄ → ³ H ₆	480	6250
⁷⁰ Yb	[Xe]4f ¹³ (² F _{7/2})	0.86	³ F _{5/2} → ² F _{7/2}	980	10250
⁷¹ Lu	[Xe]4f ¹⁴ (¹ S ₀)	0.85	-	-	-

2.1.1. Rare earth luminescence

Generally, the luminescence phenomenon is a generic term used for the light emission of different types, for example, *Chemiluminescence* (a result of a chemical reaction); *Bioluminescence* (emission as a consequence of biochemical reaction by a living organism); *Triboluminescence* (emission generated when bonds in a material are broken by applying mechanical stress to crystals or by fracture of crystals); *Electroluminescence* (emission as a result of electric current passed through a substance) and *Photoluminescence* (emission after excitation by irradiation with electromagnetic radiation) and so on [10].

Photoluminescence of the rare earth compounds, involving both *fluorescence* and *phosphorescence* phenomena, usually the fluorescence and phosphorescence are used to describe the light emission by organic molecules. The *fluorescence* is for example singlet-to-singlet transition (spin allowed transition, $\Delta S=0$) with short lifetimes (*e.g.* nanoseconds) and *phosphorescence* is singlet-to-triplet transition (spin forbidden transition, $\Delta S \neq 0$), with long lifetimes (*e.g.* milliseconds...) [10].

The optical properties of the rare earth ions are fascinating and originate in the special features of the electronic $[\text{Xe}]4f^n$ configurations ($n = 0-14$) as shown in Table 2.1. The more common oxidation states are +3, +2 and +4. However, the +3 oxidation state is characteristic for all rare-earth ions which show a $4f^n$ configuration. These $4f$ configurations generate a rich variety of electronic levels, the number of which is given by $[(4\ell+2)!/(4\ell+2-n)n!]$, yielding to 3003 sublevels for Eu^{3+} and Tb^{3+} ions. As discussed early, they are characterized by three quantum numbers, S , L and J within the frame of Russell-Saunders spin-orbit coupling scheme [7]. The energies of these levels are well defined due to the shielding of the $4f$ by the filled $5s^25p^6$ subshells and they are little sensitive to the chemical environments in which the rare earth ions are placed.

Therefore, in RE^{3+} complexes the ligands in the first and second coordination sphere perturb and splitting the $^{2S+1}\text{L}_J$ energy levels of the RE^{3+} ions only slightly. This shielding is responsible for the specific properties of the rare earth luminescence, more particularly the narrow emission bands and the long lifetimes of the excited states due to forbidden 4f-4f transitions. Moreover, especially the Ce^{3+} ion shows intense broad emission band due to the allowed f-d transitions, the position of the emission maximum strongly depends on the ligand environment of the Ce^{3+} ion [11].

The remarkable feature of RE^{3+} ions is their photoluminescence behavior; some of them show luminescence in the visible or near-infrared spectral regions under UV irradiation lamp. The color of the emitted light depends on the RE^{3+} ion. For instance, Eu^{3+} emits in red, Tb^{3+} green, Sm^{3+} orange and Tm^{3+} blue light. The Yb^{3+} , Nd^{3+} , and Er^{3+} are well known for their near-infrared luminescence. In addition, the Pr^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} and Tm^{3+} ions also show transitions in the near-infrared region as well as Gd^{3+} emits in the UV region (Table 2.1).

The photoluminescence of rare earth ions is an efficient process, nevertheless all the RE^{3+} ions show weak intense absorption bands due to very limited amount of radiation absorbed by direct excitation in the 4f-4f transitions. Therefore, the molar absorption coefficients ε of mostly transitions in the absorption spectra of the trivalent rare earth ions is lower than $10 \text{ L mol}^{-1} \text{ cm}^{-1}$. The luminescence intensity is not only proportional to the luminescence quantum yield but also to the amount of light absorbed, weak light absorption results in weak luminescence. The weak light absorption has been overcome by development of the so-called *antenna effect* (or *sensitization*).

Weissman discovered in 1942 that excitation of RE^{3+} complexes at wavelength corresponds to the absorption band of organic ligand results in intense metal-centered luminescence. Part of the energy absorbed by the organic ligand is transferred to the RE^{3+} excited states, and sharp intense emission bands originating from the metal ion. The phenomenon is termed sensitization of the metal-centered luminescence (also referred to as *antenna effect*) [26].

Besides, the mechanism of the energy transfer from the organic ligand to the lanthanide ion has been investigated in the early 1960s and realized that the RE^{3+} β -diketonate complexes have potential as the active component in chelate lasers; intense research activity has been going on in the field of luminescent materials based on rare earth complexes. The commonly accepted mechanism of energy transfer from the organic ligands to the rare earth ion (intermolecular energy transfer) and subsequent luminescent decay process has shown schematically in Figure 2.2 that is detailed below.

Figure 2.2. Schematic energy level diagram showing the possible energy transfer processes in a RE^{3+} coordination compounds. Dashed arrows indicate energy transfer (ET) and wavy arrows indicate non-radiative decays.

Three pathways have been considered by which the excitation energy can be transferred to the rare earth ion: *i*) The donor $|S_1\rangle$ state transfers energy to a higher excited 4f state $|4\rangle$ which then decays non-radiatively, finally populating the state $|2\rangle$. *ii*) State $|4\rangle$ transfers energy back to a lower ligand triplet state $|T_1\rangle$ which then transfers energy to the lower 4f states $|3\rangle$ or $|2\rangle$. *iii*) State $|S_1\rangle$

decays non-radiatively to the state $|T_I\rangle$, which then transfers energy to the states $|3\rangle$ or $|2\rangle$. In the case of Eu^{3+} and Tb^{3+} ions there is experimental and theoretical evidence that process (iii) is dominant, although in some cases direct energy transfer from singlet state $|S_1\rangle$ (process i) is of importance [8].

When we consider the 4f–4f luminescence of RE^{3+} ions can be divided into four groups depending on their photonic features [7]:

- 1) Sc^{3+} ($3d^0$), Y^{3+} ($4d^0$), La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$) ions exhibit no luminescence because they contain no optically active electrons.
- 2) Gd^{3+} ($4f^7$) ion presents a special case, since there is a large energy gap between the $^8S_{7/2}$ ground state and first $^6P_{7/2}$ excited state ($\sim 32000 \text{ cm}^{-1}$), that can emits in the ultraviolet region. In general, it cannot accept energy from the lower line excited states of the organic ligands *via* intramolecular ligand-to metal energy transfer.
- 3) Sm^{3+} ($4f^5$), Eu^{3+} ($4f^6$), Tb^{3+} ($4f^8$) and Dy^{3+} ($4f^9$) ions have relatively large energy gaps between their excited and ground states. Complexes of these ions generally show strong luminescence because the excited energy levels of the ion lie just below that of the ligand triplet state.
- 4) Ce^{3+} ($4f^1$), Pr^{3+} ($4f^2$), Nd^{3+} ($4f^3$), Ho^{3+} ($4f^{10}$), Er^{3+} ($4f^{11}$), Tm^{3+} ($4f^{12}$) and Yb^{3+} ($4f^{13}$), the complexes of which usually show only weak 4f–4f luminescence, as a consequence of the small energy gap between their emitting and lower energy levels; this increases the probability of non-radiative transitions through coupling with vibrational modes in the ligands

The luminescence properties of RE^{3+} complexes is mostly dependent on the position of the excited electronic states (singlet and triplet) of the ligands. The experimental S states are usually obtained from the electronic absorption spectra of the metal complex in solution. However, the phosphorescence spectra of solid state Gd^{3+} complexes, obtained from the broad intense emission

bands assigned to $T_1 \rightarrow S_0$ transitions, give information about the T_1 state position of the organic ligands. As the ligand phosphorescence is, in general, completely quenched at room temperature, for these coordination compounds, it is necessary to record the spectra at low temperature (77 K), otherwise the T states are deactivated by non-radiative processes. In this case, trivalent gadolinium complexes are generally used due to the intrinsic spectroscopic characteristics of the Gd^{3+} ion [7].

Since there is a large energy gap (*ca* 32000 cm^{-1}) between the $^8S_{7/2}$ ground state and the first $^6P_{7/2}$ excited state of the Gd^{3+} ion, it cannot be widened by energy from the lower laying first excited T_1 state of the β -diketonate ligands *via* intermolecular ligand-to-metal energy transfer. Furthermore, the paramagnetic RE^{3+} ions, and in particular the Gd^{3+} ion that has the $4f_7$ configuration, induce an increase in the intersystem crossing from the singlet state to the triplet state owing to the increase in the S and T mixing (heavy ion effect). Table 2.2 shows the molecular structures and T_1 state energies of some Gd^{3+} β -diketonate and carboxylate complexes. de Sá and coworkers [8] used phosphorescence spectroscopy to obtain the energy values of the T_1 state of several Gd^{3+} β -diketonate compounds, allowing for the test of the accuracy of their theoretically calculated energies.

Table 2.2. Triplet state (T_1) energy of the $[Gd(ACAC)_3(H_2O)_3]$, $[Gd(TTA)_3(H_2O)_2]$ and $[Gd(BTC)(H_2O)_n]$ (BTC = EMA, TLA e TMA) complexes at 77 K [7].

Gd^{3+} complexes	Triplet state (cm^{-1})
$[Gd(ACAC)_3(H_2O)_3]$	25000
$[Gd(TTA)_3(H_2O)_2]$	20492
$[Gd(EMA)(H_2O)_2]$	25694
$[Gd(TLA)(H_2O)_4]$	25523
$[Gd(TMA)(H_2O)_6]$	25100

2.2. Organic ligands

2.2.1. Rare earth β -diketonates complexes

The last three decades the interest in the photophysical properties of rare earth β -diketonates complexes has been grown considerably since several reports in literature (Malta, Bünzli, Binnemans, Thompson, Carlos, Brito [6,7,11-14], *etc.* They proposed that such coordination compounds could be seen as light conversion molecular devices (LCMDs). It is important to mention that the Brazilian' rare earth research groups have been largely contributed for the photoluminescence study of RE^{3+} complexes, mainly Prof. Oscar Malta from Federal University of Pernambuco (UFPE), which includes the theoretical aspects.

Figure 2.3. RE^{3+} β -diketonate complexes forming six membered chelating ring and keto–enol tautomerism.

The energy-transfer process with emission sequence involving distinct absorbing (ligand) and emitting (the rare earth ion) components. While, overcoming the problem of very small absorption coefficients of the RE^{3+} ions, the design of efficient of these complexes has become an important research subject. They have being investigated extensively by the research groups as mentioned above, using different classes of ligands such as β -diketonate, carboxylate, and calixarenes, *etc.* Among the luminescent complexes of the rare earth ions studied, the Eu^{3+} and Tb^{3+} β -diketonate complexes have been found promising for red and green light emitters in visible range.

The β -diketone ligands contain two carbonyl groups that are separated by one carbon atom, designated as α -carbon. In most of the β -diketones, the substituents on the α -carbon are hydrogen, which is activated by adjacent $\text{C}=\text{O}$ groups and a conjugate system is formed containing keto-enol tautomers. Under appropriate conditions the one enolic hydrogen atom of β -diketone can be replaced by a RE^{3+} ion to produce a six membered chelate ring (Figure 2.3) thereby shifting the keto-enol equilibrium favoring the enol form [6].

It is observed that in most β -diketone ligands, the R^3 substituents on the α -carbon are hydrogen atoms. Consequently, only very few examples of luminescent rare-earth α -substituted β -diketonate complexes are known. The β -diketonate anions are good chelating ligands forming highly stable RE^{3+} complexes. In addition, they have also been used as efficient photosensitizers in most of the luminescent rare earth complexes, containing either all similar or different mixed ligands. Rare earth β -diketonate complexes usually are synthesized using the RE^{3+} chloride as starting materials in water or ethanol as solvent. Rare earth chlorides are preferred over nitrate or acetates due to the lower coordination power of chloride anion.

2.2.2. Rare earth complexes with calixarenes

Calixarene compounds act as versatile building blocks in supramolecular and coordination chemistry, since both their lower and upper rims may be derivatized to induce specific functionalities. Structurally calixarenes contain *p*-alkylphenol units linked by methylene groups and are existing in several sizes, depending on the number of the units; the most common ones are from tetramer to octamer as shown in [Figure 2.4](#). Calixarenes are like a vase shape, have upper and lower rims with a characteristic cavity, which can be functionalized at both upper and lower rims with specific ligands to coordinate to certain metal ions.

Figure 2.4. Structure of calixarenes (*p*-*tert*-butylcalix[4]arene).

The calixarenes have been functionalized with various functional groups such as carboxylic acid, phosphonate and amide to coordinate to metal ions (RE^{3+}). The calix[4]arene is a simplest one among all the oligomers which is mostly used as starting material in various synthetic transformations. Several efforts have been made to synthetically modify calix[4]arenes in proper way to be useful sensitizers (*antennae*) for rare earth ions. In this regard, different sensitizer chromospheres (organic moieties) have been synthetically induced at lower rim [\[15\]](#), in order to make them efficient macrocyclic ligands to transfer energy to the RE^{3+} ions ([Figure 2.5](#)). In certain

cases, other ligands such as β -diketonates have been used as external source of photosensitizers to produce highly luminescent macrocyclic systems [16].

Figure 2.5. RE^{3+} complex with calix[4]arene tri-carboxylic acids.

2.2.2.1. Conformational properties of calixarenes

Calixarenes can be obtained in ring sizes ranging from 4 to 8 aromatic residues by base induced condensation of para-substituted phenols and formaldehyde [17]. Temperature dependent ^1H NMR studies of the calix[4]arene and the calix[8]arenes, however, have shown that this is not necessarily the case: the calix[4]arenes and calix[8]arenes show almost identical behavior in nonpolar solvents [18]. On the other hand, calix[5]arenes, calix[6]arenes, and calix[7]arenes, as well as the oxacalixarenes, behave in a more expected fashion and appear to be more flexible molecules.

The smallest members of the series, the calix-[4]arenes, can exist in several conformations. It has been reported that four discrete forms of the calix[4]arenes can exist, which can be designated as the “cone”, “partial-cone”, “1,2-alternate”, and “1,3-alternate” conformations [19], as shown in

Figure 2.6. Several groups have demonstrated the interconvertibility among these conformers by using temperature dependent ^1H NMR measurements [19,20]. The resonance signal arising from the methylene hydrogens (ArCH_2Ar) has been shown greatest importance in these studies; in polar solvent such as chloroform solution it appears as a singlet above room temperature and as a pair of doublets below room temperature.

Figure 2.6. Four fundamental conformations of the calix[4]arene.

It has been reported that the calix[4]arenes prefer the “cone conformation” but the inversion of the cone takes place fairly rapidly at room temperature (ca. 150 s^{-1}), therefore, the doublets (^1H NMR resonance signal of ArCH_2Ar) coalesce to singlets. This spectral behavior is ascribed to the interconversion between two mirror-image cone conformations, which occurs at a rate comparable to that of the NMR time scale (Figure 2.7). X-ray crystallographic studies of the calix[4]arene also provided unequivocal evidence that these compounds exist in the cone

conformation in the solid state. This conformational preference is a consequence of the hydroxyl groups, which make possibly very strong intramolecular hydrogen bonding.

Figure 2.7. Ring inversion between mirror-image cone-cone conformations.

2.2.2.2. Acidity constants of the phenolic OH groups

Calixarenes are macromolecules that contain phenol units, the OH groups in calix[4]arenes form strong intramolecular hydrogen-bonds. Therefore, this affects the acid dissociation properties of these groups. Several research groups have been studied the acid dissociation constants of few calix[4]arenes, such as the *p*-sulphonato-calix[4]arene and *p*-nitrocalix[4]arene at 25 °C, using acid-base titration supported by theoretical calculations and photometric titrations. In addition, it has been used combination of potentiometric and spectrophotometric techniques to evaluate precisely the acidity of corresponding calixarenes. It was observed that the dissociation of the first proton (i.e. pK_{a1}) occurs at unusually low pH values than phenol, whereas pK_{a2} and pK_{a4} either at normal pH values or at higher pH regions than phenol ([Table 2.3](#)).

Table 2.3. pK_a values of OH groups in calix[4]arenes at 25 °C [20,21].

Calix[4]arens	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}
<i>p</i> -sulphonato-calix[4]arene	3.26	11.8	12.8	14
	3.34	11.5	-	-
	3.19	12.1	-	-
<i>p</i> -nitro-calix[4]arene	2.9	10.9	12.3	14

This result has been explained as that the undissociated calix[4]arenes have a neat circular hydrogen-belt composed of four intramolecular hydrogen-bonds (Figure 2.8). This may suppress the dissociation of the first proton. However, the mono dissociated species comprised of one oxide anion and three hydrogen-bonds is more stabilized by the strengthened intermolecular hydrogen-bonds. This causes the remarkable shift of pK_{a1} down to 3.3.

Figure 2.8. Schematic representation for the dissociation of the first proton of calix[4]arene.

2.2.2.3. Inclusion compounds

Calixarene molecules are often associated with their ability to form inclusion complexes with organic or inorganic guests. These coordination compounds are usually formed due to the

guest molecule interaction with the calixarene aromatic cavity and/or substituents attached to it [20]. In fact, the simplest calixarene that is often used as a starting material for a variety of synthetic transformations, *p*-*tert*-butylcalix[4]arene includes a toluene molecule in its structure and is available commercially as a toluene adduct [22]. Inclusion of organic guest molecules in water soluble calixarenes can be occurred because of the action of hydrophobic forces and in a few cases guest selectivity on the basis of the cavity size has been observed. However, guest binding to calixarene cavities takes place non-selectively because of the flexibility and conformational isomerism in calixarenes.

In most cases, the inclusion process leads by the interactions between the guest molecule and the hydrophobic cavity of the calixarene host (Figure 2.9). Since such interactions are weak, the host-guest complexation involving simple neutral molecules is generally observed only in the solid state [23]. Alternatively, the host-guest complexation can be also achieved by functionalizing the upper (aromatic) rim of calixarenes, appropriately with substituents. When a metal particularly a transition metal ions is coordinated to the lower rim oxygen atoms of the calixarene, new possibilities of the host-guest interactions must be taken into account. This kind of interactions increases the partial negative charge on the oxygen atoms of lower rim and the excess of electron density created at the calixarene lower rim, allows the second metal coordination to the corresponding oxygen atoms from the inside of the calixarene cavity (Figure 2.9). Therefore, the second metal ion bearing additional ligands becomes incorporated inside the hydrophobic part of the calixarene ligand because of the first metal coordination on the top of the calixarene lower rim. While included inside the calixarene, the new guests may begin interacting with the cavity [24].

Calix[4]arenes are the lowest oligomers in the series and are readily available, numerous metal complexes have been prepared and structurally authenticated. They are also the species for which $M \cdots \pi$ complexation is most predictable and commonly observed, related to its small ring

size with well-defined cavity for metal ion inclusion. In the unsubstituted form, calix[4]arenes display four distinct structural conformations at room temperature. Normally the cone conformation is favored since it allows maximum intramolecular hydrogen bonding between phenol groups. In the cone conformation the metal ions can bind to the phenolic (or phenolate) oxygen centers either by residing inside or outside of the calixarene cavity, endo and exo, respectively, interacting simultaneously with π -faces of the aromatic groups and phenolic oxygen atoms of calix[4]arene in case of endo inclusion complexation [25], as shown in Figure 2.9.

Figure 2.9. Possible inclusion complexes of calix[4]arenes.

Calix[4]arenes are structurally simple among all the calixarenes, they are prone to synthetic modification; can be easily functionalized at both upper and lower rims with specific ligands for binding to metal ions. As molecular platforms for introducing specific ligating arms in a pre-organized pattern, depending on the nature of the ligating groups and on the dimension of the macrocyclic scaffold. Calixarene ligands are considered the important and selective metal binders, therefore chemically modified calixarene with particular ligands are used as receptors [26], ionic recognition and sensitizer for rare earth ions [27].

2.2.3. Rare earth complexes with carboxylic acids

The carboxylic acids are organic compounds contain a carboxyl group (COOH), the general formula of carboxylic acids are RCOOH, where R is referred to the different small or large organic molecule. They are occurred widely, such as amino acids, acetic acid and different derivatives of benzoic acids, *etc.* The important feature of the carboxylic acids is their relatively higher acidity than the other organic compounds, such as alcohols, phenols *etc.* This fact is attributed to the resonance stabilized structure of the carboxylate anion, when the carboxylic group is deprotonated; its conjugate base forms a carboxylate anion, which is resonance stabilized (Figure 2.10), this increased stability makes carboxylic acids more acidic than alcohols.

Figure 2.10. Resonance stabilization of the carboxylate anion.

Therefore, the carboxylic group of these acids can be easily deprotonated with a base (*e.g.* NaOH, ammonia, *etc.*) and can act as efficient organic ligands for metal ions. In the RE^{3+} carboxylate complexes the cations acts as hard acid and anion as hard base. Therefore, they tend to form complexes with high coordination numbers and flexible coordination geometries, consequently, a wide range of interesting structures and distinct connectivity have been observed [28]. For the RE^{3+} carboxylate complexes, the coordination numbers of the RE^{3+} ions can be exist usually between six and twelve, accomplished by the formation of the dimeric or polymeric structures and with a high degree of solvation, however mononuclear complexes do exist.

The most frequently observed coordination numbers are eight and nine, with square antiprism and tricapped trigonal-prism coordination geometry, respectively. RE^{3+} carboxylates have been found to adopt several coordination modes in the complexes (Figure 2.11), the most common coordination modes for carboxylates are unidentate η^1 , simple chelating η^2 , bridging bidentates μ_2 - $\eta^1\eta^1$ *ZZ*, μ_2 - $\eta^1\eta^1$ *EE*, and μ_2 - $\eta^1\eta^1$ *ZE*, and the chelating tridentate μ^2 - $\eta^2\eta^1$. In mononuclear complexes, carboxylates usually adopt unidentate (a) and the simple chelating (b), while in dimeric or polymeric complexes, the most popular coordination modes for carboxylate are bridging bidentate μ_2 - $\eta^1\eta^1$ *ZZ*, chelating tridentate μ_2 - $\eta^2\eta^1$ and the simple chelating η^2 [29].

Figure 2.11. Coordination modes observed for RE^{3+} carboxylate complexes: a) η^1 , b) η^2 , c) μ_2 - $\eta^1\eta^1$ (O, O), d) μ_2 - $\eta^1\eta^1$ *ZZ*, e) μ_2 - $\eta^1\eta^1$ *EE*, f) μ_2 - $\eta^1\eta^1$ *ZE* and g) μ_2 - $\eta^2\eta^1$.

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Chapter 3

MAGNETIC IRON OXIDE NANOPARTICLES

3. MAGNETIC IRON OXIDE NANOPARTICLES

Nanoscopic magnetic systems contain magnetic particles or agglomerates with at least one dimension of characteristic size in nanometer order. The systems with nanometric particles can exist in solids (also known as granular solids), or liquids (also called magnetic fluids or ferrofluids). In the case of granular solids, the matrix in which the nanoparticles are immersed can be an electric insulator or a conductor, crystalline or amorphous; and can have several phases of different materials [1]. Therefore, physical properties of the nanoparticulated systems can be tailored for specific purposes in academic or technological research. One can easily highlight the use of nanoparticles to obtain enhanced hard and soft magnetic materials with lower energy losses and rapid response at variable magnetic fields and magnetic microsensors. In addition, they can be applied as in medical diagnosis, catalysis, magnetic liquids for drug delivery, pigments for painting and ceramics.

The nanotechnology allows physicists, chemists, material scientists and engineers to synthesize such nanosized systems where the physical laws at the meso scale are different from the counterparts at the nanoscale. As the size of the particle decreases, the surface to volume ratio of the particle increases. This effect yields a large portion of the atoms to be present on the surface as compared to those in the core of the particle. For example, a particle of 1 μm in diameter, nearly contains 0.15% of the surface atoms, while a particle of 6 nm one, approximately 20% of the surface atoms. Therefore, the large surface to volume ratio is the key feature of nanoparticles regarding the novel physical, chemical, and mechanical properties as compared to those of the corresponding bulk material [2].

The magnetic iron oxide particles have been attracted research interest since earlier because of their potential applications in electronic inductors, transformers, electromagnets, computer

memories and magnetic recording as well as medical diagnosis and therapy. The family of iron oxides is formed by 16 compounds, including oxides, mixed oxides (MFe_2O_4), hydroxides and oxyhydroxides. Among the iron oxides, the magnetite (Fe_3O_4) and maghemite ($\gamma-Fe_2O_3$) are preferred in biomedicine because they are biocompatible and potentially non-toxic to humans (FDA approved). In addition, iron oxides are also easily degradable and therefore useful for in vivo applications, they can be quite efficient in most of the biological applications if the sizes of their nanoparticles are smaller than the typical cells and below the critical volume.

Each nanoparticle becomes a single magnetic domain and shows superparamagnetic behavior when the temperature is above the so-called blocking temperature. In addition, during these conditions all the atomic moments on the nanoparticle coherently rotate under the application of magnetic field. The individual nanoparticle can be considered to have a large constant magnetic moment and behave like a giant paramagnetic atom with a fast response to applied magnetic field with negligible remanence (residual magnetism - M_r) and coercivity (the field required to bring the magnetization to zero - H_C) [3]. These features make superparamagnetic iron oxide nanoparticles very attractive for a broad range of biomedical applications, such as the high magnetic moment promote their potential for cancer treatment, drug delivery and magnetic resonance imaging *etc.* Moreover, the risk of forming agglomerates in the case of nonmagnetic mass coated iron oxide nanoparticles is also negligible at room temperature under these specific conditions.

3.1. Special features of magnetic nanoparticles

The magnetic moment per atom and the magnetic anisotropy of magnetic nanoparticles are different than those of the bulk material. The other magnetic properties such as the Curie (T_C) or Néel (T_N) temperatures and the coercivity field (H_C) have been found to be size dependent. The

bulk ferromagnetic materials contain small regions, called magnetic domains, which are resulted from a balance of several energy terms; the exchange energy, magnetocrystalline anisotropy and the magnetostatic (or dipolar) energy [4]. The exchange energy tries to align all the magnetic moments in the same direction; the magnetocrystalline anisotropy orient magnetic moments along specific directions and the magnetostatic energy contributes to the whole magnetization in the magnetic materials.

3.1.1 Finite-size effects

The two most studied finite-size effects in nanoparticles are the single domain limit and the superparamagnetic limit (superparamagnetism).

Single domain limit – In large magnetic particles, it is well known that there is a multidomain structure, where regions of uniform magnetization are separated by domain walls. The formation of the domain walls is a process driven by the balance between the magnetostatic energy (ΔE_{MS}), which increases proportionally to the volume of the materials and the domain-wall energy (E_{dw}), which increases proportionally to the interfacial area between domains. If the sample size is reduced, there is a critical volume below which it costs more energy to create a domain wall than to support the external magnetostatic energy (stray field) of the single-domain state [5].

The critical diameter typically lies in the range of a few tens of nanometers and depends on the material nature and also it is influenced by the contribution from various anisotropy energy terms. The critical diameter of a spherical particle (D_C) below which it exists in a single-domain state is reached when $\Delta E_{MS} = E_{dw}$, which implies $D_C \approx 18 \frac{\sqrt{AK_{eff}}}{\mu_0 M^2}$, where A is the stiffness constant, K_{eff} is anisotropy constant, μ_0 is the vacuum permeability, and M is the saturation magnetization.

Typical values of D_C for some important magnetic materials are Fcc Co (7 nm), Hcp Co (15 nm), Fe (15 nm), Ni (55 nm), Fe_3O_4 (128 nm) and SmCo_5 (750 nm) [3]. In a single-domain particle, all the spins can be considered in the same direction, except the surface ones, therefore the particle is considered to be uniformly magnetized (Figure 3.1). There are no domain walls to move, consequently, the magnetization can be reversed through spin rotation rather than through the motion of domain walls.

There are at least two factors, in addition to the freezing of the surface moments, which result in high coercivity of small nanoparticles: *i*) Spin rotation instead of domain wall motion. *ii*) Shape anisotropy: the coercivity is smaller when the particles are spherical, shape anisotropy can also affect the estimation of the critical volume (below which the particle is single-domain). Spherical particles have small critical diameters as compared to those of large shape anisotropy. The second important phenomenon which takes place in nanoscale magnetic particles is the superparamagnetic limit. The superparamagnetism can be discussed in detail as follow.

Figure 3.1. Magnetic behaviors derived from the scale reduction in magnetic materials.

Superparamagnetism – Attempts to produce tiny dispersions of magnetic materials in metals have been done since 1930s. The first modelization of a nanometered-size particle was done by Kittel in 1946. Since the very beginning, the models have been considered that the magnetic moment would follow an Arrhenius law, with a characteristic relaxation time τ . Nevertheless, the determination of τ was only solved by Néel, in 1949 [1]. He supposed that each nanoparticle has been formed by rigidly aligned spins that rotate coherently during magnetization reversal, considering the case of uniaxial anisotropy when the energy barrier is much larger than the thermal energy of the system. The equivalence with a gyroscopic system allowed him to derive an expression for τ , as a function of gyromagnetic ratio, longitudinal magnetostriction constant, Young modulus, energy barrier and thermal energy. He estimated characteristic time relaxation to be of the order of 10^{-10} s, in agreement with available experimental data. When the size of a particle containing magnetic atoms is small enough, the energy necessary to divide itself into magnetic domains is higher than the energy needed to remain as a single magnetic domain, or monodomain.

The magnetic properties of an assembly of monodomain particles are studied within the framework, the so-called superparamagnetic theory, name coined by Bean and Livingston in analogy to paramagnetic systems. The first assumption of the superparamagnetic theory is to consider that all the magnetic moments within the particle rotate coherently, *i.e.*, the net magnetic moment can be represented by an single classical vector, with magnitude $\mu = \mu_{at}N$, where μ_{at} is the atomic magnetic moment and N is the number of magnetic atoms that constitute the corresponding particle [3].

The simplest assumption is to consider an effective uniaxial anisotropy K , which leads to an energy barrier to the magnetization vector which is proportional to KV , where V is the volume of the nanoparticle. However, it is important to mention, that in ultrafine particle systems surface

effects can be very important. In such case the magnetic relaxation does not proceed by coherent rotation of the spins within the particle. The spins in an isolated particle are held in a particular direction (not necessarily parallel to the applied field) by the magnetic anisotropy energy (which is caused by spin-orbital interactions of the electrons and responsible for holding the magnetic moments along a certain direction). If the particles are not isolated, other interactions will be involved. The anisotropy energy per particle is given by Eq. 3.1:

$$E_a(\theta) = K_{eff} V \sin^2 \theta \quad (3.1)$$

(the leading term of the series expansion) where V is the volume of the particle, K_{eff} the effective anisotropy constant, and θ is the angle between the magnetization and the easy magnetization axis of the particle [5]. The maximum energy barrier is $K_{eff} V$, this is the energy which separates the two energetically equivalent easy magnetization directions *i.e.*, the energy barrier to magnetic moment reversal (the size of this energy depends on many factors including magnetocrystalline and shape anisotropies). As the particle size decrease the values of V and E_a also decreases, as a result the $E_{th} = K_B T$, thermal energy, might exceed the E_a , which causes the particle magnetization to rotate freely resulting in the loss of magnetism in the absence of an applied magnetic field.

The temperature at which this spin flipping occurs is called the blocking temperature (T_B). The blocking temperature depends on the particle size and other factors. At $T > T_B$, the isolated (non-interacting) single-domain particle becomes superparamagnetic [6]. In this state, the magnetic moment of the particle behaves as that of a single atom (like a paramagnet) but with much larger magnitude (see Eq. 3.2). The relaxation time of the magnetic moment of a particle, τ_N is given by the Néel expression where the factor $\tau_0 \approx 10^{-12} - 10^{-9} s$ is weakly temperature dependent:

$$\tau_N = \tau_0 \exp\left(\frac{K_{eff} V}{K_B T}\right) \quad (3.2)$$

If the time window of the measurement (τ_m) is longer than the time needed to the particle's magnetic moment to flip, the particle is said to be in a superparamagnetic state. On the other hand, if the experimental time scale is shorter than the moment flipping time, the particle is said to be in the blocked state. The blocking temperature (defined as the mid-point between these two states, where $\tau_N = \tau_m$) depends on several factors: a) The size of the particles, b) The effective anisotropy constant, K_{eff} , c) The applied magnetic field, d) The experimental measurement time e) Dipolar interactions.

The magnetic iron oxide nanoparticles might be composed of a single magnetic domain if its size decreases below a critical limit. It might also display a superparamagnetic behavior as long as the temperature is above a particular temperature which is called the blocking temperature (T_B) [7]. At this regime the thermal energy and anisotropy energy has key role in magnetic instability of single domain magnetic nanoparticles. In the superparamagnetic state and due to thermal energy, the magnetic moments of the nanoparticles fluctuate around the easy axes of magnetization, thus each one of the magnetic nanoparticles will possess a large magnetic moment that continuously changes orientation.

When a magnetic field is applied, the magnetic nanoparticle in the superparamagnetic state display a fast response to the changes of the magnetic field without remanent (residual) magnetization and without coercivity (the magnetic field required to bring the magnetization back to zero). In addition, below the blocking temperature, no sufficient thermal energy is available to overcome the anisotropy energy, thus the fluctuations in the orientations of the magnetic moments of the nanoparticles vanish [1], as a result, all the moments are frozen in random orientations and hysteresis is present on the magnetization cycles.

3.1.2 Surface effects

Nanoparticles are unique physical objects with remarkable magnetic properties which differ greatly from their parent massive ferromagnets or ferrites. The source of this difference, which has numerous and diverse manifestations, is the fact that in fine particles surface effects are not at all negligible in comparison with the bulk ones. As the particles size decreases, the fraction of atoms that lies near or on the surface increases, making the surface effect more and more important. It is estimated that in a 3 nm diameter particle 80% are surface atoms. Surface effects can also be observed not only in small particles, but also in larger particle systems, depending on the chemical composition of the nanoparticles and their crystalline state [5].

The magnetocrystalline anisotropy reflects the symmetry of the neighbors of each atom. The large perturbations to the crystal symmetry at surfaces should lead to magnetocrystalline anisotropy of different magnitude and symmetry for surface sites. In fact, surface anisotropy has a crystal-field nature and it comes from the symmetry breaking at the boundaries of the particle. Accordingly, the surface effects result from the break of symmetry of the lattice at the surface of the particles, which leads to site-specific surface anisotropy of unidirectional character, from the broken exchange bonds [5].

The low coordination number on the particle surface affects the magnetic behavior on the surface and could propagate within the particle. For instance, some experiments and Monte Carlo calculations show that the Curie temperature decreases with decreasing particle size. Therefore, the magnetization near and on the surface is lower than in the core of the nanoparticle. This effect has been indeed reported in magnetization measurements of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. High field magnetization measurements of $\gamma\text{-Fe}_2\text{O}_3$ and Co show an increasing of nonsaturation tendency for small particle sizes [8]. High-field open hysteresis loops have been observed and attributed to the

high surface anisotropy. High-field magnetic relaxation of a sping-glass-like surface state can be observed in Ni-ferrite particles.

Many experiments have been also focused on the effect of surface oxidation on the magnetic properties of ferromagnetic particles. In Fe particles coated by an antiferromagnetic iron oxide with thickness of 1-2 nm, the coercivity shows a large increase when the iron core diameter below 6 nm, reaching to a value of about 2.7 kOe in a particle with core diameter of 2 nm. In materials with a larger core diameter, the coercivity is almost constant (~ 250 Oe).

Néel has been first shown that antiferromagnetic particles can exhibit superparamagnetic behavior if there is an imbalance in the number of spins on the up and down sublattices (uncompensated spins). Experimental work on α -Fe₂O₃ particles in rocks and on Cr₂O₃ particles has been followed the Néel's analysis. More recently, the experimental work has focused on iron oxides, which are used as high-density recording media. The magnetic properties of antiferromagnetic nanoparticles have been investigated by Monte Carlo simulations. These simulations show that the magnetization of a particle arises from the uncompensated spins which could be attributed to the surface of the particle and the temperature variation of the magnetization as well as the coercivity depends on particle size and the number of uncompensated spins [8].

Many of the systems that exhibit surface effects could be described by a core-shell model. This model considers each particle as a nanosystem composed of internal magnetic ordered core (with ferro- or antiferromagnetic ordering) that can be described by the Stoner-Wohlfarth relaxation model; and a disordered shell of spins, that interact among them and the particle core. This model satisfactorily describes the observed features in magnetization measurements of ferromagnetic-like, such as FeNiB and CoNiB nanoparticles as well as antiferromagnetic-like systems such as NiO one.

Ferromagnetic resonance studies performed on the FeNiB, CoNiB and NiO systems also reflect the surface effects. The experimental results show a strong increment of the effective line width at low temperatures due to the surface anisotropy [9]. In addition, the resonance field falls with the increment of the magnetization, owing to the polarization of the core by surface clusters. Thus, the field necessary to get the resonance condition becomes smaller than expected. For small nanoparticles the surface effect must be considered to estimate the size dependence of the effective anisotropy. Usually, it has been considered as an effective anisotropy term given approximately by the following phenomenological expression:

$$K_{eff} = K_V + \frac{6}{\langle D \rangle} K_S \quad (3.3)$$

Eq. 3.3 has been extensively applied in to take into account the effect of the surface on nanostructured systems, with rather good success in most of the cases [1]. In fact, surface effects can be important even when dealing with larger particles, and a careful analysis is necessary to properly separate the effects of structural disorder, interparticle interactions and surface contributions.

3.2. Magnetic iron oxide/organic core-shell

Magnetic iron oxide nanoparticles with organic shell structures have been attracted much research interest because of their greater potential for applications, such as magnetic recording [10], electromagnetic shielding, MRI contrast agents [11], specific drug targeting and magnetic cell separation [12]. Furthermore, novel applications of magnetic nanoparticles have been proposed recently, such as tissue engineering, termed as magnetic force-based tissue engineering (Mag-TE) [13] and magnetic hyperthermia, considering a safe method for cancer therapy, where the

temperature in tumors are increased in the interval of 41 to 46 °C, thereby killing the tumor cells with minimum damage to normal tissue. Therefore, the suspension stability along with high magnetization property of the magnetic nanoparticles under an external applied magnetic field is important for this kind of *in vivo* biological application.

The iron oxide (magnetic core) nanoparticles are usually synthesized by using wet chemical methods, such as co-precipitation, hydrothermal and microemulsion, *etc.*, in order to obtain high crystallinity and magnetization [14]. However, bare iron oxide nanoparticles are usually prone to agglomeration due to high magnetization. Therefore, they are coated with different organic materials, such as hydrophilic polymers and macrocyclic compounds [15]. The stability of the magnetic nanoparticles has been extensively reviewed, using water-soluble biocompatible polymers; poly-(ethylene glycol) (PEG) and amine-terminated poly-(ethylene glycol) (aPEG), where the effects of the concentration of reactants on particle size, crystallinity and magnetic properties have been studied [15].

The magnetite (Fe_3O_4) nanoparticles show strong magnetization among the iron oxide nanoparticles, the crystalline structure and the composition of core Fe_3O_4 can be affected with coating, the Fe_3O_4 particles are partially changed to $\alpha\text{-Fe}_2\text{O}_3$ after coating with a thin outer shell of PEG [16]. In addition, the magnetic properties such as saturation magnetization, coercive field on the blocked state and blocking temperature (T_B) of the Fe_3O_4 nanoparticles also affected with coating [17]. Dextran, a polysaccharide polymer is also widely used as a polymeric shell to coat the magnetic nanoparticles bio-compatibly, to be useful for *in vivo* applications. Ferromagnetic iron dextran particles are also used for labeling red blood cells (RBC) in cell separation studies using high gradient magnetic chromatography (HGMC) [18].

Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) compounds are the only FDA approved magnetic materials that can be used in humans. Magnetite nanoparticles are suitable materials for Magnetic Fluid Hyperthermia (MFH), provided their size be carefully tailored to the applied alternating magnetic field (AMF) frequency [19]. Therefore, the Fe_3O_4 nanoparticles must be highly monodispersed and Ferrofluidic. A remarkably stable magnetite ferrofluids have been reported by utilizing for first time the *p*-sulfonato-calix[6&8]arenes and sulfonated *p*-benzylcalix[4,5,6&8]arenes as surfactants for the superparamagnetic Fe_3O_4 nanoparticles [20]. In addition, the magnetite nanoparticles stabilized with *p*-sulfonato-calix[6]arene macrocycle have been used to held together self-assemble doped LaPO_4 nanorods into three-dimensional ‘ ‘koosh nanoballs’ ’ as a bifunctional luminescent ferrofluidic system (Figure 3.2).

Figure 3.2. Schematic representation of the Koosh nanoball structure of LnPO_4 nanorods ($\text{Ln} = \text{La, Eu, Tb, Ce}$) held together by *p*-sulfonato-calix[6]arene stabilized Fe_3O_4 nanoparticles [21].

3.3. Magnetic iron oxide@silica core shell

Progress in utilizing inorganic nanoparticles for biomedical applications has advanced rapidly due to the extensive amount of work done in the synthesis and modification of the materials [22,23]. These nanosized materials provide a robust framework in which two or more components can be incorporated to give multifunctional capabilities. Iron oxide nanoparticles are a major class of nanoscale materials with the potential to revolutionize current clinical diagnostic and therapeutic techniques [24,25]. Thus, iron oxide nanoparticles are widely studied as magnetically enhanced transfection, magnetically assisted gene therapy, magnetically induced hyperthermia and magnetic-force-based tissue engineering as summarized in the review of Corchero *et al* [26].

The unique physiochemical properties and ability of iron oxide nanoparticles to be useful at the cellular and molecular level of biological interactions, therefore they have been actively investigated as the next generation of targeted drug delivery for more than thirty years [27]. However, due to the high ratio of surface to volume and magnetization, bare nanoparticles are usually prone to agglomeration, to overcome this drawback, coating with mesoporous silica is often promising [28]. In addition to the superparamagnetism and strong magnetic responsiveness, the magnetic nanoparticles used for biological purposes should possess long term colloid stability, favorable water-dispersion, good biocompatibility and tailored surface chemistry for covalent coupling to antigens, antibodies, enzymes, or DNA/RNA hybridization [29,30]. Therefore, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanostructures are more useful because of the combined functionalities of an iron oxide core and silica shell, exhibiting, magnetic responsivity, low cytotoxicity, and chemically modifiable surface. They can be functionalized with specific ligand according to the respective biological applications. In addition, silica offers many advantages as the framework for the multifunctional nanoparticle [31], being able to incorporate other inorganic materials within or

on the surface of the framework [32], and a variety of functional molecules can be attached to the silica surface *via* silane linkers [33].

3.3.1. Silica shell formation on magnetite - $\text{Fe}_3\text{O}_4@\text{SiO}_2$

Two essential methods for the coating of Fe_3O_4 nanoparticles with silica are employed, acidic hydrolysis of silicate in aqueous solution, and modified Stöber method [34]. This involves the basic hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol/water mixture in the presence of Fe_3O_4 nanoparticles. It has been usually observed that coating of silica from silicate solution yields relatively large spherical magnetic particles with a mean size in the range of 80-200 nm [35], that are useful for biomolecule separation or sensing *in vitro*, but cannot be delivered intravenously. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles of mean diameter from 60 to 120 nm can be obtained by the Stöber method, using 5-15 nm size of Fe_3O_4 as precursors if bare magnetite nanoparticles have been pretreated with a small amount of silicate in an aqueous solution [36]. Nevertheless, without pretreatment, direct coating of Fe_3O_4 nanoparticles with TEOS in ethanol and aqueous ammonia mixture produces magnetite clusters embedded in large silica aggregates. The thin silica layer at the magnetite surface reduces the isoelectric point of magnetite and thus maintains the colloidal stability during the second coating. However, the silica pre-coating is not only sufficient to obtain the uniform core-shell nanoparticles. It has been observed that the concentration of pretreated magnetite particles should be less than 12 mg L^{-1} ; otherwise, large aggregates of Fe_3O_4 are possibly formed.

The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles prepared by the Stöber method usually contain about six Fe_3O_4 cores even under optimal conditions as reported in reference [36]. Further detailed studies, of coating the Fe_3O_4 nanoparticles with TEOS have been revealed that this process is highly

sensitive to experimental conditions such as ethanol/water ratio, concentration of ammonia and TEOS, as well as temperature, *etc* [37,38]. In addition, preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, using TEOS as coating agent has been found to be a very slow process: about 12-48 h of mechanical stirring at room temperature is required to obtain uniform silica shell on the surface of magnetite nanoparticles. However, heating of the reaction mixture causes of yielding large size magnetite-silica aggregates with irregular morphology. To improve the homogeneity and morphology of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, as well as to increase the limiting concentration of nanoparticles in reaction medium several efforts [39], have been done to modify Stöber method in reverse microemulsion and sonochemical approach.

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Chapter 4

OBJECTIVES

4. OBJECTIVES

The principle objectives of the work are to design and fabrication of the nanosized materials, which assemble two different photonic and magnetic phenomena into a single entity nanostructure. Moreover, it is to determine the structures of these nanomaterials, utilizing different characterization techniques as well as the study of their photoluminescence and magnetic properties. The detail of the specific objectives is as follow:

- Preparation by one-pot method of optical and magnetic $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA or ACAC})$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanomaterials, RE: Eu^{3+} and Tb^{3+} as well as L: TTA, TC, AB and AMB.
- Characterization of the $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA or ACAC})$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanomaterials, using different instrumental techniques: elemental analysis, nuclear magnetic resonance (NMR), Infrared (IR) absorption spectroscopy, X-ray powder diffraction (XPD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Small angle X-ray scattering (SAXS) analysis.
- Study of the magnetic properties of the prepared optical and magnetic nanomaterials, utilizing hysteretic M - H magnetization as well as Zero Field Cooling and Field Cooling (ZFC/FC) magnetization measurements.
- Study of the photoluminescence properties of the prepared optical and magnetic nanosystems, utilizing excitation and emission spectral data, luminescence decay curves, non-radiative (A_{nrad}) and radiative (A_{rad}) rates, experimental emission quantum efficiencies (η), emission lifetimes (τ) and experimental intensity parameters (Ω_λ).

Chapter 5

EXPERIMENTAL PART

5. EXPERIMENTAL PART

5.1. Reagents and solvents

The commercially available chemical reagents and solvents were used in syntheses of the nanomaterials in entire work and are summarized in [Table 5.1](#). The $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ were synthesized from their respective oxides by treatment with concentrated hydrochloric acid, as described in the literature [1].

Table 5.1. Chemical substances used in experimental part.

Chemical substances	Company
<i>p</i> -tert-butylcalix[4]arene	Fluka
Phenol	Sigma-Aldrich
Formaldehyde solution 37 %	Cinetica quimica ltda.
Dimethylamine 25-30 %	BHD
Thenoyltrifluoroacetone (HTTA)	Sigma-Aldrich
Acetylacetone (HACAC)	Sigma
4-aminobenzoic acid (HABA)	Sigma-Aldrich
4-(aminomethyl)benzoic acid (HAMBA)	Sigma-Aldrich
Thioglycolic acid (HTCA)	Merck
Sulfuric acid	Synth
Hydrochloric acid 37 %	Vetec
Hydrogen peroxide 29 %	Synth
Glacial acetic acid	Vetec
Toluene	Nuclear
Acetonitrile	Vetec
Tetrahydrofuran	Synth
Dimethyl sulfoxide	Merck
Ethyl alcohol	Synth
Sodium hydroxide	Merck
Ammonium hydroxide 29 %	Synth
Iron(II) chloride tetrahydrate	Synth
Iron(III) chloride hexahydrate	Synth
Aluminum chloride	Fluka
(3-chloropropyl)triethoxysilane 95 %	Sigma-Aldrich
Tertaethyl orthosilicate	Sigma-Aldrich
Rare earth oxides 99,99%	Rhodia

5.2. Synthesis of Fe₃O₄/calixarene RE³⁺-complexes core-shell nanomaterials

5.2.1. Synthesis of the calixarene ligand

The preparation of macrocyclic building block: 5,11,17,23-tetrakis(carboxymethyl)calix-4-arene-25,26,27,28-tetrol (calix) was carried out according to the procedure reported in the literature [2-4]. The synthesis of calixarene ligand involves five steps of chemical reactions with crucial step of *Mannich reaction*, for which the conditions were also optimized. The experimental procedure of each step of reaction is described as follow:

25,26,27,28-Tetrahydroxycalix[4]arene (Step 1) – A slurry of 4.0 g (6.0 mmol) of *p*-tert-butylcalix[4]arene, 2.7 g (28.8 mmol) of phenol and 4.2 g (31.4 mmol) of AlCl₃ was stirred in 40 mL of toluene in 100 mL schlenk round bottom flask at room temperature for 1 h, under continuous N₂ flow. After that, the reaction mixture was poured into a beaker containing 80 mL of dilute HCl (0.2 M), the organic phase was separated by separating funnel and the toluene was evaporated with the rotary evaporator. Upon the addition of methanol to the viscous oily reaction mixture a precipitate was formed, which was removed by filtration to give a solid. Recrystallization of the solid product from a mixture of methanol and chloroform was yielded 2.06 g (78%) of colorless crystals.

5,11,17,23-tetrakis(dimethylamino)-methyl-25,26,27,28-tetrahydroxycalix-4-arene: Mannich Reaction (Step 2) – The reaction was carried out by modified procedure [3]. To a solution of 1.80 g (4.23 mmol) of calix[4]arene (step 1) in 65 mL of THF was added 8.3 mL of glacial acetic acid, 9.96 mL (50.89 mmol) of 25-30 % aqueous dimethylamine, and 4.05 mL (50.89 mmol) of 37 % aqueous formaldehyde solution. The reaction mixture was stirred for 60 h at room temperature.

After that, the solvents were removed under reduced pressure with rotary evaporator and the residue was dissolved in 60 mL of water. The aqueous solution was extracted two times with 40 mL of diethyl ether and neutralized with 10 % K_2CO_3 solution. The resulting precipitate was removed by filtration and dried in vacuum desiccator, yielding 2.85 g (99 %) of a white solid.

5,11,17,23-Tetrakis(cyanomethyl)-25,26,27,28-tetrahydroxyca lix[4]arene: p-Quinone Methide

Reactions (Step 3 and 4) – To a solution of 2.0 g (3.06 mmol) of *p*-Tetrakis-dimethylamino-methyl-tetrahydroxycalix[4]arene (step 2) in dimethyl sulfoxide (30 mL) was slowly added 1.16 mL (18.8 mmol) of methyl iodide. After the reaction mixture stirred for 30 minutes at room temperature, 1.86 g (38 mmol) of sodium cyanide was added and the mixture was heated for 2 h at 80 °C, under dynamic N_2 with continuous flow. The reaction mixture was cooled to room temperature then treated with 120 mL of ice water, acidified with dilute HCl (2 M), filtered and air dried. The crude product was recrystallized from CH_3CN to yield 1.48 g (83 %) of a pale yellow solid product.

5,11,17,23-Tetrakis(carboxymethyl)calix[4]arene-25,26,27,28-tetrol (Step 5) – To a 250 mL round bottom flask was added 1.3 g (2.24 mmol) of Tetrakis(cyanomethyl)tetrahydroxy calix[4]arene (step 4), followed by glacial acetic acid (25 mL), water (2.5 mL) and concentrated sulfuric acid (3.5 mL) with continuous stirring. The reaction mixture was heated at reflux for 6 h, cooled and poured over crushed ice-cold water in a beaker, which produced a precipitate and was stored during 18 h. The brownish precipitate was removed by filtration (very slow) and washed thoroughly with cold water. The product was dried in open atmosphere and triturated with methanol to furnish whitish powder (Yield: 1.27 g and 86 %).

5.2.2. Synthesis of magnetite nanoparticles

The Fe_3O_4 nanoparticles were synthesized with co-precipitation under dynamic N_2 with a continuous flow (Figure 5.1). In this synthesis, a mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1:2 molar ratio was dissolved in ultra-pure Milli-Q water under constant magnetic stirring [5-7], followed by a dropwise addition of an aqueous NaOH solution (1.0 mol L^{-1}) until a stable black

Figure 5.1. The flow diagram of the synthesis of Fe_3O_4 nanoparticles.

magnetite suspension was formed at around pH 11. The aqueous suspension was stirred further at room temperature maintaining the N_2 flow for 2 h; thereafter the Fe_3O_4 suspension was centrifuged

and the solid material was collected. After that, the black powders were re-dispersed in ultra-pure Milli-Q water and centrifuged again. This process was repeated three times to remove the base and then the magnetite nanoparticles were dried in a vacuum desiccator. The preparation method of magnetite nanoparticles is diagrammatically presented in flow chart (Figure 5.1).

5.2.3. Synthesis of Fe₃O₄@calix-Eu(TTA) red emitting superparamagnetic nanomaterial

These bifunctional magnetic and red emitting nanoparticles were prepared with a new one-pot method (Figure 5.2). The aqueous solution of 2.25 mmol of FeCl₃·6H₂O and 1.15 mmol of FeCl₂·4H₂O in 100 mL ultra-pure Milli-Q water was stirred under a N₂ flow. Then, 0.27 g (0.41 mmol) of *p*-tetrakis(carboxymethyl)calix[4]arene macrocycle (calix) was slowly added to the reaction mixture. 18 mL of a NaOH solution (1.0 mol L⁻¹) was added dropwise until a stable brown colored magnetite suspension was formed maintaining the pH at 11. After 3 h stirring at room temperature, the pH was adjusted to 7 with a dropwise addition of dilute aqueous HCl (1.0 mol L⁻¹). Also, 0.36 g (1.64 mmol) of thenoyltrifluoroacetone (HTTA) in ethanol was added slowly to the reaction mixture. Then, an aqueous solution of 1.64 mmol of EuCl₃·6H₂O in ultra-pure Milli-Q water was added dropwise along with adjustment of pH to ~7 by dropwise addition of the NaOH solution.

The reaction mixture was stirred at room temperature under N₂ for 60 h. The solid Fe₃O₄ material was separated from the aqueous suspension by centrifugation and decantation of the supernatant with applying external magnet. The collected solid material was washed five times with Milli-Q water and chloroform, dried in a vacuum desiccator to get the brown colored

$\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ nanomaterials. The synthesis method of this optical and magnetic nanomaterial is shown in flow chart (Figure 5.2).

Figure 5.2. The diagrammatic presentation of the preparation of $\text{Fe}_3\text{O}_4@\text{calix-RE(TTA or ACAC)}$ nanoparticles through one-pot method.

5.2.4. Synthesis of $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ green emitting superparamagnetic nanomaterial

The bifunctional magnetic and green emitting nanoparticles were prepared by the same procedure as described for the Eu^{3+} system (section 3.2.3), and also lead to a brown powder (Figure 5.2). In this synthesis, 0.5 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.25 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed in 30 mL of ultra-pure Milli-Q water and 0.06 g (0.091 mmol) of *p*-tetrakis(carboxymethyl)calix-4-arene macrocycle was added. Following the procedure, 6-fold excess of acetylacetone (HACAC) and 4-fold excess of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ were utilized to get the $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterial. The preparation method of this green emitting magnetic nanomaterial is shown in flow diagram (Figure 5.2).

5.3. Synthesis of optical and magnetic RE^{3+} complexes grafted $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanomaterials

5.3.1. Magnetite nanoparticles

The Fe_3O_4 nanoparticles were synthesized with chemical co-precipitation according to the reported literature procedure [8,9]. Each 50 mL aqueous solution of FeCl_2 (1 mol L^{-1}) and FeCl_3 (1.75 mol L^{-1}) in Milli-Q water was prepared separately into two different beakers and then transferred together to a 250 mL three-necked flask, stirred under dynamic N_2 with continuous flow. The reaction mixture was heated at 60 °C and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (v/v 28-30 %) was added dropwise until pH adjusted to 11. The suspension was immediately turned black, indicating the formation of magnetite as product, furthermore, the reaction content was heated at 80 °C for 1h. The black color precipitate was isolated from the reaction mixture by decantation of supernatant with applying external magnet, repeatedly washed with Milli-Q water until pH adjusted neutral and dried in

vacuum desiccator under reduced pressure. The synthesis route of Fe_3O_4 nanoparticles is schematically represented in (Figure 5.3).

Figure 5.3. The flow chart of the synthesis of Fe_3O_4 nanoparticles.

5.3.2. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles

The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles were prepared by modified Stöber method [10-13], which involves the hydrolysis of 3-chloropropyl-triethoxysilane (CPTES) and tetraethyl orthosilicate (TEOS) in the presence of Fe_3O_4 nanoparticles. In current synthesis, 2.0 g of the Fe_3O_4

nanoparticles were suspended in 100 mL of distilled water, followed by addition of the mixture of 5.0 mL of CPTES, 15 mL of methanol and 5 mL of aqueous NaF solution (1 %). After stirring the reaction mixture for 5 min, 30 mL of tetraethyl orthosilicate (TEOS) was dropped slowly into the round bottom flask and stirred for 48 h at room temperature. The resultant products were collected by magnetic separation with magnet bar and were thoroughly washed with ethanol and Milli-Q water until neutral, then were dried at room temperature in vacuum desiccator. The preparation route is described in flow diagram (Figure 5.4).

Figure 5.4. The flow diagrams show preparation schemes of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (left) and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ (right) nanostructures.

5.3.3. TTA grafted magnetic core-shell nanostructures ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$)

These nanomaterials were synthesized by chemical modification of the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles and were carried out by the chemical substitution of the Chloro group with thenoyltrifluoroacetate (TTA) on the surface of these nanoparticles (Figure 5.4). In a typical synthesis, a mixture of 0.5 g (2.25 mmol) of HTTA and 0.11 g (4.5 mmol) of NaH in dry DMF/THF (5:15 mL) was stirred at room temperature for 30 min. 1.2 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was added and the reaction mixture was heated at reflux for 96 hours.

After cooling to room temperature, the supernatant was decanted by applying external magnet bar and the resulted nanomaterials were thoroughly washed with ethanol, Milli-Q water and chloroform to remove the excess TTA and then were dried in vacuum desiccator to get brown color $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanomaterials. The preparation route of these nanomaterials is schematically illustrated in flow chart as shown in (Figure 5.4).

5.3.4. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanomaterials

These bifunctional, core shell magnetic and luminescent nanomaterials were synthesized by general procedure, involving the chemical preparation of Eu^{3+} , Tb^{3+} and Gd^{3+} complexes on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructures (Figure 5.5). In a typical procedure, to a suspension of 0.12 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ in 30 mL of ethanol was added 0.36 g of the Ligand (L). After stirring the solution for 10 min few drops of $\text{NH}_3\cdot\text{H}_2\text{O}$ (28-30 v/v %) was added and heated at 50 °C. Thereafter, solution of 0.5 equivalent (relative to Ligand) of the hydrated rare earth chloride in ethanol was added dropwise along with the adjustment of pH to 8 by dropwise addition of $\text{NH}_3\cdot\text{H}_2\text{O}$ (28-30 v/v %). The reaction mixture was continuously stirred at 50 °C, after 4 h the temperature was adjusted to ambient temperature and the reaction mixture was continued to stir for whole night.

The resultant products were collected by magnetic separation with magnet bar and were thoroughly washed with ethanol, methanol, Milli-Q water and chloroform to remove the excess RE^{3+} -complex, then were dried at room temperature in vacuum desiccator. The preparation protocol of these bifunctional nanomaterials is illustrated in flow diagram, as shown in (Figure 5.5).

Figure 5.5. The diagrammatic presentation of the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanocomposites.

5.4. Instrumental

5.4.1. Carbon, hydrogen and nitrogen elemental analysis

The elemental analysis of carbon and hydrogen of the calixarene ligand was carried out using a Perkin-Elmer 2400 CHN Elemental Analyzer of Analytical Center at Institute of Chemistry, University of Sao Paulo (IQ-USP).

5.4.2. Infrared (IR) absorption spectroscopy

The infrared absorption spectra (FTIR) were measured using KBr pellet technique with a Bomem MB100 FTIR from 400 to 4000 cm^{-1} . This FTIR equipment was used in the entire research work, which is present in the Analytical Center of the Institute of Chemistry, University of Sao Paulo (IQ-USP).

5.4.3. Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^1H and ^{13}C NMR spectra of the calixarene macrocycle were recorded by Varian Gemini 200 MHz Fourier-Transform (FT) and DEPT-135 was done by Bruker 500 MHz Fourier-Transform (FT) Nuclear Magnetic Resonance (NMR) equipment of the Analytical Center of Institute of Chemistry, University of Sao Paulo (IQ-USP).

5.4.4. X-Ray Powder Diffraction (XPD)

The term x-ray diffraction (XRD) is a bit generic as there are several forms of XRD, single crystal, powder; thin film, reflexivity, and X-ray rocking curve analysis are some examples of the

types of XRD. Since all the nanomaterials synthesized in current research work are in powder form, Powder XRD must be used with either multicrystalline materials or a material which has been ground to a fine powder. This allows all of the possible crystal orientations to be accessed simultaneously. In the case of nanoparticles there is no need to further powder the nanomaterials, because they are already in a fine power form. Therefore, the X-ray diffraction technique employed to analyze the powder material can be termed as X-ray powder diffraction (XPD).

The X-ray powder diffraction (XPD) data were recorded by a Rigaku Miniflex II diffractometer using $\text{CuK}_{\alpha 1}$ radiation (λ : 1.5406 Å) in the 2θ range of 10 to 80 degrees. This XPD instrument was used in the entire research work and present in the laboratório de nanotecnologia molecular e marcadores integrados, centro de química e meio ambiente (CQMA) at the nuclear and energy research institute (IPEN).

5.4.5. Transmission electron microscopy (TEM)

Transmission electron microscopy images and electron diffraction were measured with a JEOL JEM 2100 LaB6 TEM, Acceleration Voltage: 200 kV. The sample particles were dispersed in Milli-Q water and sonicated for 15 min. Samples were prepared by drying the water-dispersed nanoparticles on a carbon-coated copper grid and images were acquired with the sample on a single-tilt sample holder and a Gatan ES500W TV camera. The TEM images of the whole research work are recorded with this Transmission electron microscope (TEM) of the Brazilian Nanotechnology National Laboratory (LNN_{ANO}), Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Campinas-SP.

5.4.6. Scanning electron microscopy (SEM)

The scanning electron microscopy images were measured with a Jeol, JSM-7401F (FEG) SEM of the Analytical Center, Institute of Chemistry, University of Sao Paulo (IQ-USP). The sample particles were dispersed in isopropanol and sonicated for 15 min. Samples were prepared by drying the isopropanol-dispersed nanoparticles on a cylindrical carbon mount and images were acquired.

5.4.7. Small angle X-ray scattering (SAXS)

Small angle X-ray scattering (SAXS) experiments were recorded at the Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Brazilian Synchrotron Light Laboratory (LNLS) using the beamline SAXS 2, in the energy range from 6.0 to 11.0 keV. The samples were prepared as colloidal solutions in Milli-Q water (v/v 5 %).

5.4.8. Magnetic measurements

DC magnetic properties were studied using a Quantum Design, MPMS XL, SQUID magnetometer. Zero Field Cooling/Field Cooling (ZFC/FC) measurements were done to characterize the static magnetic properties of the nanomaterials. The measurements were carried out as follows: the sample was first cooled down from 300 to 5 K in a zero magnetic field, then a static magnetic field of 50 Oe was applied and the magnetization was measured increasing the temperature up to room temperature (300 K). Subsequently, the samples were cooled down to 5 K under the same applied magnetic field (50 Oe) and the magnetization was measured while warming up the samples from 5 to 300 K. The magnetization as a function of the applied field between -2

and +2 Tesla were measured at selected temperatures from 5 to 300 K. The magnetic measurements (M-H and ZFC/FC measurements) in the whole research work were done with the above magnetometer at the Laboratorio de Materiais de Baixas Temperaturas (LMBT), Instituto de Física Gleb Wataghin (IFGW), UNICAMP, Campinas-SP.

5.4.9. Photoluminescence spectroscopy

The excitation and emission spectra of the Eu^{3+} and Tb^{3+} nanomaterials were recorded with a HORIBA Jobin Yvon Fluorolog-3 and SPEX FL212 Fluorolog-2 spectrofluorometer, using a 450 W Xenon lamp as an excitation source and two 0.22 m double grating SPEX 1680 monochromators for dispersing the radiation. Luminescence decay of the Eu^{3+} nanomaterials were measured using the SPEX 1934D phosphorimeter accessory attached to the 150 W pulsed Xenon lamp. The entire luminescence setup was fully controlled by a DM3000F spectroscopic computer program and the spectral intensities were automatically corrected for the photomultiplier (PMT) response.

5.4.10. Zeta potential and dynamic light scattering (DLS) measurements

The zeta potential and size distribution of the bifunctional luminescent and magnetic nanomaterials were measured with a Malvern Zetasizer Nano ZS90 analyzer of the Analytical Center, Institute of Chemistry, University of Sao Paulo (IQ-USP). The samples were prepared as a colloidal solution in Mill-Q water and sonicated for 20 minutes, then transferred to a clear disposable zeta cell.

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Chapter 6

CHARACTERIZATION

6. CHARACTERIZATION

6.1. Optical and magnetic core-shell nanomaterials

Progress in design and syntheses of bifunctional nanosized materials which assemble two different photonic and magnetic features into a single entity nanostructure are advanced rapidly [1-3] due to their efficient biomedical applications, such as drug delivery carrier [4], cell sorting and tumor cell targeting [5], MRI contrast agent [6,7] as well as magnetic hyperthermia for cancer therapy [8]. Therefore, we reported efficient optical and magnetic nanomaterials containing Fe_3O_4 functionalized with calixarene and rare earth complexes, their preparation is accessible through a facile method, which involves multistep syntheses [9]. The calixarene ligand was prepared by a synthetic protocol comprises of series of chemical reactions as described in the below section 6.1.1.

The syntheses of red and green emitting superparamagnetic, $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomarkers were carried out utilizing the chemically modified calixarene (calix), thenoyltrifluoroacetate (TTA) and acetylacetonate (ACAC) as ligands [9].

The chemically modified calix[4]arene ligand (calix) is a cyclic phenolic oligomer with a hydrophobic cavity, which can form host–guest inclusion complexes [10] and can act as a surfactant to stabilize the Fe_3O_4 nanoparticles. In addition, it also provides biocompatibility [11], colloidal stability and chemically modifiable surface to the magnetite nanoparticles, therefore, the Fe_3O_4 nanoparticles were functionalized with calixarene ligand (calix) and further coordinated to the RE^{3+} ions *via* one-pot method, using TTA and ACAC as sensitizers (*antenna effect*) to produce highly luminescent nanosystems.

According to the literature [12,13], the Fe_3O_4 nanoparticles are stabilized by *p*-sulfonato-calixarenes and sulfonated *p*-benzylcalixarenes. On the basis of studies, the assumed schematic structure of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials, as shown in

Figure 6.1, is consistent with the previous results. The detailed characterizations of the calixarene ligand as well as optical and magnetic $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials are described as follow.

Figure 6.1. Schematic illustration of the structure of the luminescent and magnetic nanoparticles containing Fe_3O_4 functionalized with RE^{3+} complex of β -diketonate and calixarene as ligands $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA or ACAC})$.

6.1.1. Calixarene ligand

The calixarene macrocycles containing carboxyl groups directly attached to the upper rim have been synthesized by several methods. One of them is the preparation of *p*-tetrakis-carboxy-calix[4]arene by lithiation of *p*-tetrabromo-calix[4]arene tetramethyl ether followed by carbonation, which is also applied to synthesize the mono- and dicarboxyl analogs [14,15]. In addition, the direct formylation of calixarenes to *p*-formylcalixarenes with subsequent oxidation to

carboxylic acids have been reported [16]. Similarly, the *p*-Claisen rearrangement route is also employed for the carboxylation of calixarenes at upper rim, which involves the catalyzed rearrangement of 2-propenyl to 1-propenyl groups followed by ozonolysis to the aldehyde and oxidation to the carboxylic acid [17].

The *p*-tetrakis (carboxymethyl)calix-4-arene macrocycle (calix) was synthesized by a synthetic procedure, using the *p*-quinonemethide route and involves five steps of chemical reactions (Scheme 6.1), with overall yield of 55 %, as reported in the literature [18-20]. The whole synthetic route involves a crucial step of the *Mannich reaction* (Scheme 6.1 - step 2), which was carried out by using aqueous dimethylamine (v/v 25-30 %) and aqueous formaldehyde (v/v 37 %) in the presence of glacial acetic acid. The yield of the corresponding reaction was raised from 15 to 99 % by using 12-fold excess of aqueous dimethylamine (v/v 25-30 %) and 12-fold excess of aqueous formaldehyde (v/v 37 %); the reaction time was increased from 24 to 60 h. It is suggested that the yield of the *Mannich reaction* is favored by increase in the concentration of reagents and time of reaction.

The structure of the calixarene macrocycle (calix) (Scheme 6.1 - step 5) was confirmed by using CHN elemental analysis and spectroscopic techniques (FTIR, ¹H-NMR and ¹³C-NMR). The elemental analysis of CHN found (%): C: 61.75, H: 5.38 was very close to the calculated one; C: 60.84, H: 5.39. The result suggests that the calixarene macrocycle has three accommodated water molecules. The spectroscopic and elemental analyses were carried out after drying the macrocycle (5) with a vacuum dryer at 95 °C for 5 h (Scheme 6.1). It is suggested that the hydrophobic cavity of the calixarene moiety contains water molecules when the hydrophobic guest is absent [21]. All of the found FTIR, ¹H-NMR and ¹³C-NMR spectroscopic data are in agreement with those reported in the literature [20].

Scheme 6.1. Systematic preparation route of the *p*-tetrakis (carboxymethyl)calix-4-arene tetrol macrocycle (calix) using different steps of chemical reactions.

6.1.1.1. Infrared absorption spectroscopy of the calixarene ligand

The FTIR absorption spectrum ([Figure 6.2](#)) of the calixarene macrocycle (calix) is dominated by a broad absorption band centered at 3180 cm^{-1} that corresponds to the $\nu_{\text{O-H}}$ stretching of the phenolic unit of calixarene. The strong absorption band observed at 1705 cm^{-1} was assigned to the $\nu_{\text{C=O}}$ stretching of the carboxylic group. The absorption bands observed in the region of $1405\text{--}1480\text{ cm}^{-1}$ correspond to the $\nu_{\text{C=C}}$ stretching in the aromatic ring of the calixarene macrocycle.

Figure 6.2. FTIR absorption spectrum of p-tetrakis (carboxymethyl)calix-4-arene tetrol macrocycle (calix) ligand.

6.1.1.2. ^1H , ^{13}C and DEPT-135 NMR spectra of the calixarene ligand

The ^1H -NMR spectrum of the calixarene ligand (calix) was recorded at room temperature (200 MHz DMSO- d_6) and was closely matched the actual structure of the macrocycle, showing a resonance peak at δ 6.95 for the 8Ar-H of the calixarene (calix-H) (Figure 6.3). In addition, the broad singlet resonance peak at δ 3.82 corresponds to 8H of methylene (ArCH_2Ar). The resonance peak at δ 3.27 represents the 8H of methylene (CH_2COO) in the macrocycle. The ^1H -NMR spectrum also shows one additional peak for water molecules at δ 3.42. This result suggests that the calixarene ligand contain invariable amount of water molecules.

Figure 6.3. ^1H -NMR (200 MHz DMSO-d_6) spectrum of *p*-tetrakis (carboxymethyl)calix-4-arene tetrol macrocycle (calix) ligand.

The ^{13}C -NMR spectrum (Figure 6.4) of the calixarene ligand (calix) was also recorded at room temperature (200 MHz DMSO-d_6) and was closely matched the actual structure of the calixarene macrocycle, showing a resonance peak at δ 172.87 assigned to the CO of the carboxylic group ($-\text{COOH}$). In addition, the resonance peak at δ 148.39 corresponds to the OH bearing lower rim quaternary carbon of the calixarene (C-OH) as well as at δ 129.63, 128.16 and 127.39 correspond to the carbons of the aromatic rings (ArC). The resonance peaks at δ 39.58 represents the carbon of the methylene (CH_2COO) and at δ 30.74 assigns to the carbon of the methylene bridge (ArCH_2Ar) in the calixarene macrocycle.

Figure 6.4. ^{13}C -NMR (200 MHz DMSO- d_6) spectra of *p*-tetrakis (carboxymethyl)calix-4-arene tetrol macrocycle (calix) ligand.

The DEPT-135 NMR spectrum (Figure 6.5) was acquired in order to get information about the total methylene ($-\text{CH}_2$) carbons in the calixarene macrocycle, therefore it was recorded at room temperature (300 MHz NMR and DMSO- d_6 as a solvent). The resonance peaks at δ 39.58 represents the secondary carbon of the methylene group (CH_2COO) and at δ 30.74 assigns to the carbon of the methylene bridge (ArCH_2Ar), confirm the presence of two different types of methylene groups in the calixarene macrocycle. The physical and spectroscopic properties of the calixarene ligand (calix) is shown in Table 6.1.

Figure 6.5. DEPT-135 (300 MHz DMSO- d_6) NMR spectrum of *p*-tetrakis-carboxymethyl-calix[4]arene tetrol macrocycle (calix) ligand.

Table 6.1. Physical and spectroscopic (^1H and ^{13}C NMR) data of the calixarene ligand (calix).

Compound	Yield (%)	Mp ($^{\circ}\text{C}$)	^1H NMR (200 MHz, DMSO- d_6) (δ)	^{13}C NMR (200 MHz, DMSO- d_6) (δ)
Calixarene Ligand (calix)	55	310-312	6.95 (s, 8H, Calix-H), 3.82 (s, 8H, Ar- CH_2 -Ar), 3.27 (s, 8H, CH_2COO)	172.87 (CO), 148.39 (C-OH), 129.63, 128.16, 127.39 (ArC), 40.20 (CH_2COOH), 31.36 (Ar CH_2 Ar)

6.1.2. Preparation of $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials

The nanomaterials with luminescent and magnetic functionalities have been attempted to synthesize in several ways. The nanocomposites containing Fe_3O_4 and $\gamma\text{-Fe}_3\text{O}_4$ nanoparticles integrated with CdTe quantum dots [22], the nanostructures of the Fe_3O_4 core and RE^{3+} doped Y_2O_3 shell [23] and upconversion luminescent and magnetic nanocrystals containing integrated Fe_3O_4 and rare earths [24]. In addition, green light-emitting, superparamagnetic Koosh nanoballs, based on RE^{3+} doped lanthanide phosphate nanorods held together by *p*-sulfonato-calix[6]arene stabilized Fe_3O_4 nanoparticles [13] have been reported.

In present thesis, the red-green emitting superparamagnetic nanomaterials containing Fe_3O_4 functionalized with calixarene and rare earth complexes were prepared by new method. The whole synthetic pathway of the novel $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanoparticles is dominated by two steps of chemical reactions (Scheme 6.2). The one-pot method was designed for the entire synthesis and these bifunctional nanomaterials were then successfully prepared.

Scheme 6.2. Preparation of magnetic and luminescent $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials through one-pot method, using $\text{Fe}_3\text{O}_4@\text{calix}$ and RE^{3+} complexes.

The structures and morphologies of the red and green emitting magnetic Eu^{3+} and Tb^{3+} nanomaterials were characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XPD), Small angle X-ray scattering (SAXS), Transmission electron microscopy (TEM) and Selected area electron diffraction (SAED) techniques. The schematic structure of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials is illustrated as in the [Figure 6.1](#).

6.1.2.1. FTIR spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials

The structures of the magnetite nanoparticles and red-green emitting superparamagnetic $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials were characterized, using Fourier transform infrared (FTIR) spectroscopy. The FTIR absorption spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanoparticles show the broad absorption bands centered at *ca* 3500 cm^{-1} , indicating the presence of the water molecules in the nanomaterials ([Figure 6.6](#)). The broad absorption band appeared at *ca* 595 cm^{-1} in the infrared absorption spectrum of the Fe_3O_4 corresponds to the $\nu_{\text{Fe-O}}$ in the crystal lattice of Fe_3O_4 , is also retained to certain extent in IR spectra of Eu^{3+} and Tb^{3+} nanomaterials.

The high intensity broad absorption band observed for the free ligand at 1705 cm^{-1} corresponds to the $\nu_{\text{C=O}}$ stretching of carboxylic group of the calixarene macrocycle. It was red-shifted in the spectra of all the nanomaterials and appeared in the spectral range from 1450 to 1670 cm^{-1} ([Table 6.2](#)). This result suggests that the carboxylic group of the macrocycle is coordinated to the RE^{3+} ions. Moreover, the absorption bands in the region of 1395 - 1560 cm^{-1} correspond to the $\nu_{\text{C=C}}$ stretching in the aromatic ring of the calixarene macrocycle.

Figure 6.6. FTIR absorption spectra of Fe_3O_4 , calixarene macrocycle coated magnetite ($\text{Fe}_3\text{O}_4@\text{calix}$), $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials.

Table 6.2. FTIR absorption spectroscopy data of calixarene ligand (calix), $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials.

Compounds	The stretching vibration modes of bonds in material (cm^{-1})			
	ν (O-H)	ν (C=O)	ν (C=C)	ν (CH_3)
Calixarene ligand (calix)	3180	1705	1405-1480	-
$\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$	-	1450-1670	1395-1560	-
Eu-TTA	-	1612	-	-
$\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$	-	1450-1670	1395-1560	2961
Tb-ACAC	-	1602	-	2961

In addition, the FTIR absorption spectra of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials show additional absorption bands at 1602 and 1612 cm^{-1} due to the C=O stretching vibrations of ACAC and TTA ligands, respectively (Table 6.2). This result gives support to the carbonyl moiety of both β -diketonate ligands coordinating to the RE^{3+} ions via oxygen atoms.

6.1.2.2. XPD patterns of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials

The structures of the magnetite and red-green emitting magnetic $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanoparticles were characterized by X-ray powder diffraction (XPD) analyses.

Figure 6.7. X-Ray Powder Diffraction patterns of Fe_3O_4 , calixarene macrocycle (calix) coated magnetite ($\text{Fe}_3\text{O}_4@\text{calix}$) nanoparticles, $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials.

As shown in the XPD pattern (Figure 6.7) of the magnetite, the diffraction reflections can be indexed as the face-centered cubic (fcc) lattice of the Fe_3O_4 phase (XPD reference pattern of Fe_3O_4 , ICDD/PDF 19-629). After coating the magnetite (Fe_3O_4) with the calixarene macrocycle and RE^{3+} complexes, Besides, the Fe_3O_4 reflections from the diffraction patterns of the luminescent and magnetic, $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanoparticles also show mainly characteristic reflections of an amorphous phase (Figure 6.7).

6.1.2.3. TEM images and SAED patterns of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials

The transmission electron (TEM) images were recorded in order to know the morphology, size distribution and monodispersity of the as synthesized bifunctional optical and magnetic nanoparticles. The TEM images (Figure 6.8) show that the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanoparticles are probably separated from each other and nonaggregated when compared to the bare magnetite nanoparticles. The similar result can be also observed in the SAXS analysis (section 6.1.2.4). This is probably due to the coating of magnetite nanocrystals with non-crystalline phase (possible organic) as shown in the HRTEM images (Figure 6.9). Moreover, the TEM images also exhibit that the nanoparticles are roughly of spherical or cubic shape, depending on the nanoparticle average size with diameters between 15 and 25 nm. The similar sizes inferred from the XPD patterns and TEM images suggest that the produced magnetic luminescent nanoparticles have single crystals Fe_3O_4 phase, corroborating by HRTEM images.

Figure 6.8. Transmission electron microscopy (TEM) images of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials.

The HRTEM images (Figure 6.9) show that the nanoparticles are faceted single crystals with roughly spherical or cubic shape and with lattice fringes corresponding to the crystallographic planes of the cubic lattice of the spinel structure. This result corresponds to d-spacing such as (in

nm): *i*) 0.294 (220), *ii*) 0.245 (311), *iii*) 0.208 (400) and *iv*) 0.140 (440) as shown in the SAED pattern (Figure 6.10). The Selected area electronic diffraction (SAED) patterns of the magnetic and optical nanomaterial are in agreement with their XPD patterns (Table 6.3); the crystallographic planes (*hkl*) of the magnetic and luminescent nanomaterials are corresponded to the d-spacing, corroborating the cubic lattice of the spinel structure of Fe_3O_4 (reference d-spacing of Fe_3O_4 , ICDD/PDF 19-629) as shown in Table 6.3. Therefore, the SAED data confirm the presence of spinel structure of the Fe_3O_4 phase in luminescent and magnetic Eu^{3+} and Tb^{3+} nanomaterials.

Figure 6.9. High resolution TEM images of (clockwise from top left): Fe_3O_4 , Fe_3O_4 @calix-Eu(TTA) nanoparticles (different magnification), Fe_3O_4 @calix-Tb(ACAC) one (different magnification).

Table 6.3. Crystallographic planes of the cubic lattice of the spinel structure correspond to the d-spacing, as shown in SAED pattern.

$\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$	$\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$	ICDD/PDF 19-629 (Fe_3O_4)	<i>hkl</i>
(nm)	(nm)	(nm)	
0.2943	0.2905	0.2967	220
0.2458	0.2505	0.2532	311
0.2080	0.2050	0.2099	400
0.1408	0.1500	0.1462	440

Figure 6.10. SAED patterns of $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ (left) and $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ (right) nanomaterials.

6.1.2.4. SAXS analyses of $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials

The bifunctional optical and magnetic $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials were characterized by the small angle x-ray scattering (SAXS) measurements, using

synchrotron radiation of Brazilian Synchrotron Light Laboratory (LNLS) as described in [section 5.4.7](#) (Experimental part). The SAXS analyses ([Figure 6.11](#)) show that the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanoparticles are probably separated from each other and nonaggregated when compared to the bare magnetite nanoparticles. TEM images show that the nanoparticles are roughly of spherical or cubic shape ([Figure 6.9](#)), depending on the nanoparticle average size with diameters between 15 and 25 nm. This is in accordance with the SAXS analyses, where the fit was performed on the scattering data, considering a distribution of approximate spherical nanoparticles. The nanoparticles have an average diameter around 26 nm for both $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials.

Figure 6.11. SAXS profile of $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ shows a) scattering intensity as a function of the scattering vector and b) the size distributions obtained from the best fit on SAXS data for the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$.

6.1.2.5. Zeta Potential of the Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) nanomaterials

In an ionic solution, the nanoparticles with a net charge have a layer of ions (of opposite charge) strongly bound to their surface; this is referred to as the Stern layer. A second diffuse outer layer is comprised of loosely associated ions. These two layers are collectively called the electrical double layer. As the particle moves (due to Brownian diffusion or applied force), a distinction is created between ions in the diffuse layer that move with the nanoparticle and ions that remain with the bulk dispersant. The electrostatic potential at this “slipping plane” boundary is called the zeta potential and is related to the surface charge of the nanoparticle.

In zeta potential measurements, an electrical field is applied across the sample and the movement of the nanoparticles (electrophoretic mobility) is measured by laser doppler velocimetry (LDV). The Henry equation is used to calculate the zeta potential, z of the nanoparticles, as shown in Eq. 6.1.

$$U_e = \frac{2\varepsilon z f(Ka)}{3\eta} \quad (6.1)$$

where U_e is the electrophoretic mobility, ε is the dielectric constant, η is the absolute zero-shear viscosity of the medium, $f(Ka)$ is the Henry function, and Ka is a measure of the ratio of the particle radius to the Debye length. Nanoparticles with a zeta potential between -10 and $+10$ mV are considered approximately neutral [25], while nanoparticles with zeta potentials of greater than $+30$ mV or less than -30 mV are considered strongly cationic and anionic, respectively.

The zeta potential (Figure 6.12) of the magnetic and optical, Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) nanoparticles were measured at 25 °C temperature. The water was used as a dispersant medium and were found -6.29 and -28.4 mV for the Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) nanoparticles, respectively. A viscosity of 0.891 centiPoise (cP), a

dielectric constant of 78.5, and refractive index (RI) of 1.330 of the dispersant medium were used for these measurements (Table 6.4).

Figure 6.12. Zeta potential of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ (top) and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ (bottom) nanomaterials, measured in aqueous solution.

Table 6.4. The zeta potential of the materials; temperature, pH, dispersant medium and properties of the medium were used for the zeta potential measurements and calculations.

Material	Temperature (°C)	Dispersant medium	pH	Refractive index	Viscosity η (cP)	Dielectric constant ϵ	Zeta potential Z(mV)
Calixarene ligand (calix)	25	Water	7	1.33	0.887	78.5	0.427
Fe ₃ O ₄ @calix-Eu(TTA)	25	Water	7	1.33	0.887	78.5	-6.29
Fe ₃ O ₄ @calix-Tb(ACAC)	25	Water	7	1.33	0.887	78.5	-28.4

6.2. Preparation of RE³⁺ complexes grafted Fe₃O₄/SiO₂ core-shell nanomaterials

6.2.1 Fe₃O₄@SiO₂-TTA-RE(L) nanocomposites

The bifunctional core-shell luminescent and magnetic nanocomposites were prepared by multi-step syntheses, utilizing Fe₃O₄ nanoparticles as a precursor, which were synthesized with co-precipitation according to the reported procedure [26,27]. The magnetite nanoparticles were further functionalized with silica shell, using tetraethyl orthosilicate (TEOS) and 3-chloropropyltriethoxysilane (CPTES) by modified Stöber method [28-31]. The Fe₃O₄@SiO₂ particles prepared by this process usually contain variable number of Fe₃O₄ cores even under optimal conditions [32,33].

The coating of Fe₃O₄ core nanoparticles with silica using TEOS is a very slow process from 12 to 48 h of mechanical stirring at room temperature in order to obtain a uniform silica shell on the surface of these nanoparticles. In addition, heating of the reaction causes of formation of irregular morphology big magnetite-silica aggregates. [33]. However, Fe₃O₄ acts usually as luminescence quencher [34], the coating of the Fe₃O₄ core with silica shell was overcome this difficulty. In addition, the silica shell also produced a chemically modifiable surface for further

chemical reactions. Therefore, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were further grafted with thenoyltrifluoroacetate (TTA) by chemical substitution of the chloro (Cl) present on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ with TTA.

Subsequently, a series of rare earth complexes were prepared on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TTA nanostructures using different ligands (L), where L= thenoyltrifluoroacetate (TTA), thioglycolate (TC), 4-Aminobenzoate (AB) and 4-Aminomethyl benzoate (AMB), and then optical and magnetic nanocomposites were successfully prepared. The schematic structure and stepwise preparation method of the bifunctional core-shell luminescent and magnetic nanomaterials are illustrated in the [scheme 6.3](#).

Scheme 6.3. Preparation route of core-shell magnetic and luminescent nanocomposites; involving synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, chemical modification with TTA and further syntheses of RE^{3+} complexes on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -TTA nanostructures, using different ligands (L).

6.2.1.1. FTIR absorption spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanocomposites

The FTIR absorption spectra (Figure. 6.13) of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanomaterials are dominated by the broad absorption bands centered at *ca* 3500 cm^{-1} , indicating the presence of the water molecules in the nanomaterials, which is assigned to the O–H stretching of the H_2O molecules. The absorption band centered at 1632 cm^{-1} corresponds to the $\nu_{\text{C=O}}$ of the thenoyltrifluoroacetate (TTA) in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructure. It was red shifted in the spectrum of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$ nanomaterial and appeared at 1619 cm^{-1} (Table 6.5), providing good evidence that the Eu^{3+} ion is coordinated to the TTA ligand through the oxygen atoms.

The results (Figure. 6.13) includes the infrared spectrum of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ shows an absorption band in the region of $1560\text{-}1665\text{ cm}^{-1}$ corresponds to the $\nu_{\text{C=O}}$ of carboxylic group of the thioglycolate (TC) ligand coordinated to the Eu^{3+} ion. In addition, the absorption bands observed at 1627 cm^{-1} and 1637 cm^{-1} correspond to the $\nu_{\text{C=O}}$ of carboxylic group of the 4-Aminobenzoate (AB) and 4-Aminomethyl benzoate (AMB) ligands coordinated to the Eu^{3+} ion in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanocomposites, respectively.

It was also observed the absorption bands in the region of $1412\text{-}1540\text{ cm}^{-1}$ correspond to the $\nu_{\text{C=C}}$ in aromatic ring of the TTA, AB and AMB ligands (Figure. 6.13). In addition, the infrared absorption spectra of all the $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanostructures show a strong absorption band at 1098 cm^{-1} corresponds to the stretching vibration of the framework and terminal Si-O- groups, confirming the coating of Fe_3O_4 nanoparticles with amorphous silica phase. The weak absorption band observed at *ca* 595 cm^{-1} in the infrared absorption spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructures, which corresponds to

the $\nu_{\text{Fe-O}}$ in the crystal lattice of Fe_3O_4 is also retained to certain extent in FTIR absorption spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanocomposites. The infrared absorption spectroscopy data of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanomaterials are shown in Table 6.5.

Figure 6.13. FTIR absorption spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanomaterials.

6.2.1.2. FTIR spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanocomposites

The FTIR absorption spectra (Figure. 6.14) of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanomaterials contain broad absorption band centered at *ca* 3500 cm^{-1} , indicating the presence of the water molecules. In addition, similar to the Eu^{3+} nanocomposites, the absorption bands

observed at 1627 cm^{-1} and 1637 cm^{-1} correspond to the $\nu_{\text{C=O}}$ of carboxylic group of the AB and AMB ligands coordinated to the Tb^{3+} ion in $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ ones, respectively.

Table 6.5. Infrared absorption band data assigned to the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanocomposites.

Materials	The stretching vibration modes of bonds in material (cm^{-1})		
	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{Fe-O})$
Fe_3O_4	-	-	<i>ca</i> 595
$\text{Fe}_3\text{O}_4@\text{SiO}_2$	-	-	<i>ca</i> 595
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$	1632	-	<i>ca</i> 595
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$	1619	1308-1412	<i>ca</i> 595
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$	1560-1665	-	-
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$	1627	1412-1540	-
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$	1637	1412-1540	-
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$	1627	1412-1540	-
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$	1637	1412-1540	-
$\nu(\text{Si-O}) = 1098\text{ cm}^{-1}$			

Thus, similar to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanostructures, it was also observed the strong absorption band at 1098 cm^{-1} in the infrared absorption spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ ones, which corresponds to the stretching vibration of the framework and terminal Si-O- groups, showing the presence of amorphous silica shell around the Fe_3O_4 core nanoparticles. FTIR absorption spectroscopy data of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB or AMB)}$ nanomaterials are shown in [Table 6.5](#).

Figure 6.14. FTIR absorption spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanomaterials.

6.2.1.3. XPD patterns of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanocomposites

The structures of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanomaterials were characterized by X-ray powder diffraction (XPD). As shown in the XPD pattern (Figure 6.15) of magnetite, the diffraction reflections can be indexed as the face-centered cubic (fcc) lattice of the Fe_3O_4 phase (XPD reference pattern of Fe_3O_4 , ICDD/PDF 19-629). Consequently, the XPD patterns of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructures retain

the reflections of the Fe_3O_4 spinel structure. Besides, to the mainly characteristic reflection of an amorphous silica phase, confirming the coating of the magnetite core with silica shell.

However, the intensity of these characteristic reflections decreases due to the further grafting of $\text{Fe}_3\text{O}_4@SiO_2$ with TTA ligand as shown in diffraction pattern of $\text{Fe}_3\text{O}_4@SiO_2$ -TTA. In addition, the diffraction patterns of the $\text{Fe}_3\text{O}_4@SiO_2$ -TTA-Eu(L) nanocomposites show that the characteristic reflections of the magnetite are no longer appeared due to domination by either the diffraction reflections or amorphous phase of the Eu^{3+} complexes. This result suggests that the efficient formation of rare earth complexes on the surface of $\text{Fe}_3\text{O}_4@SiO_2$ -TTA nanostructure.

Figure 6.15. X-Ray Powder Diffraction patterns of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@SiO_2$, $\text{Fe}_3\text{O}_4@SiO_2$ -TTA and $\text{Fe}_3\text{O}_4@SiO_2$ -TTA-Eu(L) nanomaterials.

The mean crystallite size (D) of the precursor Fe_3O_4 was deduced from the full width at half maximum (FWHM, β) of the most intense peak using Scherer's formula: $D = K\lambda/\beta\cos\theta$. Where K is the dimensionless shape factor, λ is the wavelength of the X-ray radiation employed ($\text{CuK}_{\alpha 1}$ radiation, λ : 1.5406 Å), θ is the diffraction angle (Bragg angle) and β is the full width at half maximum of the peak, in radians. The calculated mean crystallite size of the Fe_3O_4 is about at 12 nm.

Figure 6.16. X-Ray Powder Diffraction patterns of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(L)}$ nanomaterials.

6.2.1.4. XPD patterns of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanocomposites

As discussed earlier in [section 6.2.1.3](#), the [Figure 6.16](#) shows XPD patterns of the nanomaterials obtained after coating the magnetite with silica shell (TEOS and CPTES), further grafting with TTA ligand and surface modification with Tb^{3+} complexes using AB and AMB as ligands. The diffraction patterns of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructures show mainly reflection of an amorphous silica phase, in addition to the Fe_3O_4 characteristic reflections, whereas these characteristic reflections are dominated by the diffraction reflections of the Tb^{3+} complexes, suggesting the efficient formation of rare earth complexes on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructure.

6.2.1.5. SEM images and particle size distributions of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanocomposites

The morphology of the optical and magnetic nanocomposites was studied, using a scanning electron microscopy (SEM) technique with an accelerating voltage of 3 and 5 kV. The SEM micrographs ([Figure 6.17](#)) of the bare magnetite nanoparticles show that the particles are aggregated and quite smaller. These nanoparticles are about 12 nm; the average crystallite sizes inferred from the XPD pattern of bare Fe_3O_4 nanoparticles, using the Scherrer formula and were also synthesized by the reported procedure [\[27\]](#).

Generally, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles prepared by the modified Stöber method usually contain variable number of Fe_3O_4 core nanoparticles because of the aggregation of Fe_3O_4 prior to or during the coating process [\[32,33\]](#). Therefore the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanostructures are of irregular morphology and are appeared to be covered with silica spheres as shown in the SEM images. In addition, after grafting with TTA ligand and further modification with RE^{3+} complexes

the morphology of the nanomaterials were changed and the silica spheres were disappeared, representing the grafting of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surface with rare earth complexes as illustrated in the SEM image of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ nanocomposites (Figure 6.17).

Figure 6.17. Scanning electron microscopy (SEM) images (clockwise from top left): of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ nanomaterials.

Consequently, the SEM images show that the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructures as well as the bifunctional Eu^{3+} and Tb^{3+} nanocomposites are morphologically irregular shape and contain aggregation of trapped Fe_3O_4 nanoparticles. This result is corroborated

to the magnetic properties, whereas no blocking temperature (K_B) can be observed in the Zero Field Cooling (ZFC) curves of these nanomaterials when compared to the bare Fe_3O_4 one, as described in [section 8.1.3.2](#) (Chapter 8 magnetic properties). In addition, the sizes of these particles are quite large when compared to the bare Fe_3O_4 one and were found for the Eu^{3+} and Tb^{3+} nanocomposites with the average diameter of 390–500 nm, as shown in the size distribution curves (dynamic light scattering measurements) of the corresponding nanomaterials ([Figure 6.18](#)).

Figure 6.18. The particle size distributions of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ nanocomposites.

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Chapter 7

OPTICAL PROPERTIES OF BIFUNCTIONAL MATERIALS

7. OPTICAL PROPERTIES OF BIFUNCTIONAL MATERIALS

The spectroscopic properties of the luminescent nanomaterials are correlated to the narrow emission bands of the 4f intraconfigurational transitions of the rare earth ions [1-3]. The RE^{3+} ions can emit in the different spectral ranges from visible to near-infrared with relatively long lifetimes and high quantum yields, making the RE^{3+} materials efficient candidates for multidisciplinary photonic applications, extending from laser physics to materials sciences, agriculture, and medical diagnostics [4]. Therefore, the luminescent materials, also called phosphors can be found in a broad range of every-day uses such as cathode ray tubes (CRTs), projection televisions (PTVs), fluorescent tubes and X-ray detectors [5].

As mentioned earlier, the 4f energy levels of RE^{3+} ions are only slightly affected by the chemical environment due to the effective shielding of the 4f electrons by the filled 5s and 5p orbitals. Therefore, the absorption and emission spectra of the 4f intraconfigurational transitions of the RE^{3+} ions retain more or less their atomic character and similar irrespective of the host matrices or their compounds [6].

The Eu^{3+} and Tb^{3+} ions are photonically more studied owing to their intrinsic electronic spectroscopic properties, for example reported in references [4,6-17]. Moreover, the trivalent europium ion provides additional advantages in the interpretation of the spectral data as compared to the Tb^{3+} ion. The Eu^{3+} ion has a great importance since it has a $^5\text{D}_0$ non-degenerate emitting level, contrary to the trivalent terbium ion that has its $^5\text{D}_4$ emitting level can be split in nine components, making the spectroscopic analysis more complicated. Furthermore, the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of the Eu^{3+} ion, when allowed, can split in only one peak (2J+1)-component, giving information about the site symmetry, consequently it acts as a useful luminescent probe for

chemical environment around Eu^{3+} ion. On the other hand, if the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition exhibits more than one emission peak it indicates the existence of at least two different site symmetries.

Besides, the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of the Eu^{3+} ion is not much influenced by the chemical environment (allowed by the magnetic dipole mechanism) and thus it can be used as a reference transition [18-20]. On the other hand, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is hypersensitive to the chemical environment around the Eu^{3+} ion, which can give information about the first coordination sphere [10-14]. Besides, the Eu^{3+} ion presents long luminescence decay time for the $^5\text{D}_0$ level (milliseconds) and exceptionally large Stokes' shift when the emission spectra are obtained through direct excitation of the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition at 394 nm [12,13].

The RE^{3+} ions have particular affinity to coordinate to organic molecules containing fluorine, oxygen, nitrogen or sulfur as donor atoms, with the following binding preference: $\text{F} > \text{O} > \text{N} > \text{S}$. This is due to the character of hard acid assigned to rare earth ions.

The photophysical properties of rare earth materials show that they can be useful as light conversion molecular devices (LCMDs), since introducing the intramolecular energy transfer from the organic ligands to rare earth ions (*antenna effect*) [17] and overcoming the problem of very low molar absorption coefficients ($1.0 \text{ M}^{-1} \text{ cm}^{-1}$) of transitions in 4f levels of these ions. The design of efficient RE^{3+} complexes has become an important research subject, being investigated extensively using different organic ligands as sensitizers [14]. Usually, to optimize the emission quantum efficiency of the luminescent material, the ligand should be chosen according to the efficiency of the following processes such as: a) absorption from the ground singlet to the excited singlet state of the ligand ($\text{S}_0 \rightarrow \text{S}_1$); b) non-radiative decay to the triplet state via the intersystem crossing and c) non-radiative intramolecular energy transfer from the T_1 state of the ligand to the excited states of the RE^{3+} ion, $\text{T}_1(\text{L}) \rightarrow ^{2\text{S}+1}\text{L}_J(\text{RE}^{3+})$, with consequent emission from 4f-4f transitions [12,13].

The remarkable photoluminescence and magnetic behaviors of the bifunctional nanomaterials make them good candidates for the preparation of emitting layers in magnetic and light converting molecular devices (MLCMDs) [2]. These novel synthesized nanomaterials show remarkable photoluminescence properties; they display red and green emissions in visible range as well as show superparamagnetic behavior.

In current chapter, the photoluminescence properties of the $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA}$ or $\text{ACAC})$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ bifunctional phosphors was also based on the analysis of the emission spectra and luminescence decay curves. The experimental intensity parameters (Ω_λ), lifetimes (τ), as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed. The influence of the chemical structure of the ligand, magnetite and organic moiety on the photoluminescence properties of the Eu^{3+} and Tb^{3+} ions were also studied to produce the highly luminescent nanomaterials.

7.1. $\text{Fe}_3\text{O}_4/\text{calixarene RE}^{3+}$ complexes core-shell nanomaterials photoluminescence

The designed novel sophisticated $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA}$ or $\text{ACAC})$ bifunctional nanomaterials that assemble optical and magnetic features into new single discrete entity nanoparticle and structurally contain Fe_3O_4 functionalized with calixarene and RE^{3+} complexes show interesting photonic properties. They can act as red and green light emitters and display superparamagnetic behaviors.

Qualitatively, the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ nanomaterial emits in red under UV irradiation lamp at 365 nm, while the $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ one displays green emission under the UV

irradiation at 254 nm (Figure 7.1).. Besides, they can be attracted to the external magnet in suspension and solid phase

Figure 7.1. The diagrammatic presentation of the $\text{Fe}_3\text{O}_4@\text{calix-RE}(\text{TTA or ACAC})$ nanomaterials, including the structure and photographs of the nanomaterials (inset) taken with a digital camera displaying the green and red emissions under UV irradiation lamp.

In this section the photoluminescence properties of the optical nanomaterials, including the phosphorescence spectra of the $\text{Fe}_3\text{O}_4@\text{calix-Gd}(\text{TTA or ACAC})$ nanophosphors as well as excitation and emission spectra of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ ones were discussed. In addition, the experimental intensity parameters Ω_λ ($\lambda = 2$ and 4), radiative and non-radiative rates (A_{rad} and A_{nrad}) for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions as well as $^5\text{D}_0$ emission quantum efficiency (η) of Eu^{3+} ion were calculated from the room temperature emission spectral data of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ nanophosphor. The emission life times, intermolecular energy

transfer process and the color coordinates in the CIE chromaticity diagram for both the Eu^{3+} and Tb^{3+} nanomaterials were also discussed.

7.1.1. $\text{Fe}_3\text{O}_4@\text{calix-Gd(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Gd(ACAC)}$ phosphorescence

To design highly luminescent RE^{3+} nanophosphors, the proper energy level positions of the triplet (T_1) electronic state is important to facilitate the efficient intramolecular energy transfer from the ligands to the RE^{3+} ions. Therefore, in order to determine the T_1 state location of the β -diketonate ligands (TTA or ACAC) on the nanoparticle surfaces, the emission spectra of the trivalent gadolinium nanomaterials were recorded with excitation at the $S_0 \rightarrow S_1$ intraligand transition. It is noteworthy to mention that the great advantage of using the Gd^{3+} ion is due to concept that its compounds can simulate structural properties of the Eu^{3+} and Tb^{3+} complexes. In addition, the first $^6P_{7/2}$ excited level of Gd^{3+} ion is located at 32000 cm^{-1} [21], which is usually above the T_1 state of the organic ligands [12,13]. Therefore, the Gd^{3+} ion cannot accept energy from the lower lying excited T_1 state of the TTA and ACAC ligands *via* intramolecular ligand-to-metal energy transfer. As a result, the emission spectra of the gadolinium materials show only the phosphorescence from the excited T_1 states, providing information about the structure of the energy levels of the organic ligands.

The emission spectra of the $\text{Fe}_3\text{O}_4@\text{calix-Gd(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Gd(ACAC)}$ nanomaterials were recorded in the spectral range from 400 to 750 nm at liquid nitrogen temperature, under excitation at 350 and 330 nm, respectively. The T_1 state energy positions of the TTA and ACAC ligands in Eu^{3+} and Tb^{3+} nanomaterials were estimated as energy corresponding to the shortest emission wavelength (0–0 phonon transition), based on the phosphorescence spectra

(Figure 7.2). The energy positions of the T_1 states were found at 20490 and 26520 cm^{-1} for the TTA and ACAC ligands, respectively.

Figure 7.2. Emission spectra of the $\text{Fe}_3\text{O}_4@\text{calix-Gd(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Gd(ACAC)}$ nanomaterials recorded at 77 K, under excitation at 350 and 330 nm, respectively.

7.1.2. $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ red phosphor

The excitation spectrum (Figure 7.3) of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ nanomaterial monitored of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ hypersensitive transition (611 nm) of the Eu^{3+} ion. The distinct broad absorption band centered at 372 nm is assigned to $\text{S}_0 \rightarrow \text{S}_1$ transition of the TTA ligand. The absence of the narrow absorption peaks arising from the $^7\text{F}_{0,1} \rightarrow ^5\text{D}_J$, $^5\text{F}_J$, $^5\text{H}_J$, $^5\text{G}_J$ and $^5\text{L}_J$ transitions of Eu^{3+} ion is consistent with the concept that the luminescence sensitization through intramolecular energy transfer from the TTA ligands to Eu^{3+} ion is very efficient.

The emission spectrum of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ nanomaterial (Figure 7.3) was recorded at low temperature in the range of 400–750 nm, under excitation to the intraligand, $\text{S}_0 \rightarrow \text{S}_1$ transition of the TTA ligand.

This spectrum exhibits groups of characteristic narrow emission bands assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions (where $J = 0, 1, 2, 3$ and 4), dominated by the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ hypersensitive one. The absence of the broad emission band centered at 525 nm, from the triplet state (T_1) of the TTA ligand [6,11] is also consistent with an efficient ligand-to-metal intramolecular energy transfer.

Figure 7.3. Luminescence spectra of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ nanophosphor recorded at low temperature (77 K): excitation (left) spectrum monitoring emission at 611 nm assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and emission (right) spectrum under excitation at 372 nm which corresponds to the $\text{S}_0 \rightarrow \text{S}_1$ transition of the organic ligands.

For the Fe₃O₄@calix-Eu(TTA) phosphor, the broad phosphorescence band of the TTA ligand was not observed, indicating a very operative intramolecular energy transfer from the TTA ligand to the Eu³⁺ ion. In addition, when compare emission spectra of the nanomaterials recorded at room (appendix A1) and low temperatures, showing the same spectral feature, but higher resolution obtained at 77 K (Figure 7.3) .

7.1.2.1. Experimental intensity parameters

The experimental intensity parameters Ω_λ ($\lambda = 2$ and 4) were determined for the Fe₃O₄@calix-Eu(TTA) system from the emission data recorded at room temperature. The Ω_λ , also known as the Judd-Ofelt parameters, are determined by the intensities of the $^5D_0 \rightarrow ^7F_J$ transitions ($J = 2$ and 4) of the Eu³⁺ ion, and the forced electric dipole and dynamic coupling mechanisms are considered simultaneously. Under normal excitation conditions, the emission intensities (I) of the bands may be given by the expression [13,16,22-24]:

$$I_{0 \rightarrow J} = \hbar \omega_{0 \rightarrow J} A_{0 \rightarrow J} N_0 \quad (7.1)$$

where $\hbar \omega_0$ is the energy of the transition (in cm⁻¹), N_0 is the population of the emitting 5D_0 level and $A_{0 \rightarrow J}$ are the coefficients of spontaneous emission. For the experimental determination of the $A_{0 \rightarrow J}$ emission coefficients from the emission spectra, the special character of the magnetic dipole allowed $^5D_0 \rightarrow ^7F_1$ transition was exploited. This 4f-4f transition is formally insensitive to the chemical environment around the Eu³⁺ ion and consequently, can be used as a reference [13]. The values of Ω_λ are obtained from Eq. 7.2 as follow:

$$A_{0 \rightarrow J} = \frac{4e^2 \omega^3}{3\hbar c^3} \frac{1}{2J+1} \chi \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle ^5D_0 \left\| U^{(\lambda)} \right\| ^7F_J \right\rangle^2 \quad (7.2)$$

where $\chi = \frac{n_0(n_0^2 + 2)^2}{9}$ is the Lorentz local field correction and n_0 is the refractive index of the medium (n_0 assumed to be equal to 1.5). The squared reduced matrix elements $\left\langle {}^5D_0 \parallel U^{(\lambda)} \parallel {}^7F_J \right\rangle^2$ have values of 0.0032 and 0.0023 for $J = 2$ and 4, respectively. The coefficients of spontaneous emission ($A_{0 \rightarrow J}$) are then obtained from Eq. 7.3:

$$A_{0 \rightarrow J} = \left(\frac{\sigma_{0 \rightarrow 1}}{S_{0 \rightarrow 1}} \right) \left(\frac{S_{0 \rightarrow J}}{\sigma_{0 \rightarrow J}} \right) A_{0 \rightarrow 1} \quad (7.3)$$

Where the $S_{0 \rightarrow J}$ factors correspond to the integrated area under the curve related to the ${}^5D_0 \rightarrow {}^7F_J$ transition and $\sigma_{0 \rightarrow J}$ are the energy barycenters of the transitions. The emission quantum efficiency (η) of the emitting 5D_0 level is determined according to the Eq. 7.4:[12]

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (7.4)$$

The total decay rate corresponds to $A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{\text{nrad}}$, where $A_{\text{rad}} (= \sum_J A_{0 \rightarrow J})$ and A_{nrad} are the total radiative and non-radiative rates, respectively.

Based on theoretical considerations, the intensity Ω_2 parameter is mostly influenced by small angular changes in the local coordination geometry [2,23]. This effect together with changes in the polarizabilities (α) of ligating atoms has been used to rationalize the hypersensitive character of certain 4f intraconfigurational transitions to changes in the chemical environment. The fact that the Ω_2 and Ω_4 parameters of $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ nanophosphor (Table 7.1) have different values of the $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ complex is an indication of different chemical environment around the Eu^{3+} ion. In addition, the low Ω_2 value for the Eu^{3+} nanomaterial when compared to the corresponding complex indicates hypersensitivity character of the ${}^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ion [12].

The value of the emission quantum efficiency of 5D_0 level for the $Fe_3O_4@calix-Eu(TTA)$ phosphor ($\eta = 14\%$) is lower than for the $[Eu(TTA)_3(H_2O)_2]$ complex ($\eta = 29\%$) (Table 7.1). This result indicates that multiphonon relaxation due to OH groups in calixarene, magnetite and the presence of water molecules in the coordination sphere is more operative in the nanomaterial, leading to a higher non-radiative decay rate ($A_{nr} = 3714\text{ s}^{-1}$). Nevertheless, this phosphor yields considerable luminescence intensity, indicating that the photoluminescent magnetic nanomaterial may be a good candidate for preparation of the emitting layer of magnetic and red light converting molecular devices (MLCMDs) [2].

Table 7.1. The experimental intensity parameters (Ω_λ), lifetimes τ , emission coefficient rates A_{rad} and A_{nr} as well as the emission quantum efficiencies η for the $Fe_3O_4@calix-Eu(TTA)$ nanomaterial.

Materials	Ω_2 (10^{-20} cm^{-2})	Ω_4 (10^{-20} cm^{-2})	A_{rad} (s^{-1})	A_{nr} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$Fe_3O_4@calix-Eu(TTA)$	15	9	633	3714	4348	0.23	14
$[Eu(TTA)_3(H_2O)_2]^a$	33	5	1110	2730	3846	0.26	29

^aReference [12].

7.1.3. $Fe_3O_4@calix-Tb(ACAC)$ green phosphor

The excitation spectrum (Figure 7.4) of the Tb^{3+} nanomaterial was recorded in the range of 200 to 400 nm, monitoring emission at 545 nm assigned to the prominent $^5D_4 \rightarrow ^7F_5$ transition of the Tb^{3+} ion. The spectrum shows a broad absorption band centered at 323 nm and assigned to the $S_0 \rightarrow S_1$ transition of ACAC ligand. Besides, no narrow absorption lines due to $4f^8-4f^8$ transitions of the Tb^{3+} ion can be observed. This spectroscopic result suggested that the $Fe_3O_4@calix-Tb(ACAC)$

nanomaterials can serve as green phosphors due to efficient intramolecular energy transfer from the ACAC ligands to the trivalent terbium ion.

Figure 7.4. Luminescence spectra of the Fe₃O₄@calix-Tb(ACAC) recorded at low temperature (77 K): excitation (left) spectrum, monitoring emission at 545 nm assigned to the $^5D_4 \rightarrow ^7F_5$ transition and emission (right) spectrum under excitation at 323 nm which corresponds to the $S_0 \rightarrow S_1$ transition of the organic ligands.

The emission spectrum of the Fe₃O₄@calix-Tb(ACAC) nanomaterial was recorded in the range of 450 to 700 nm at liquid nitrogen and room temperatures, under excitation at around 323 nm corresponding to the $S_0 \rightarrow S_1$ transition of the ACAC ligand (Figure 7.4). The groups of narrow emission lines were assigned to the $^5D_4 \rightarrow ^7F_J$ transitions ($J = 6-0$) of the Tb³⁺ ion. The emission

data indicates the $^5D_4 \rightarrow ^7F_5$ transition at around 545 nm as the most intense one that results in the green emission color. Similar to the $Fe_3O_4@calix-Eu(TTA)$ phosphor, the broad phosphorescence band of the ligand was not observed, indicating a very operative intramolecular energy transfer from the ACAC ligand to the Tb^{3+} ion.

7.1.4. Intramolecular energy transfer diagram

The photoluminescence properties of the rare earth complexes are dependent mainly on the efficiency of intramolecular energy transfer from the organic ligands to the rare earth ion. The factors affecting this efficiency, among these is the energy gap between the triplet state (T) of the organic ligands and the emitting levels of the RE^{3+} ions is the most important one [12,13]. Thus, from the photoluminescence data, the non-radiative energy transfer pathways from the β -diketonate ligands to Eu^{3+} and Tb^{3+} ions in both phosphors may be described using a theoretical model proposed earlier [13]. Recently, it has been shown [25] that the main luminescence sensitization path in the $[Eu(TTA)_3(H_2O)_2]$ complex occurs through the energy transfer from the first T_1 excited state of the TTA ligand to the 5D_1 excited level of the Eu^{3+} ion (Figure 7.5).

Among the β -diketonate ligands, ACAC has an appropriate triplet state energy (26520 cm^{-1}) for intramolecular energy transfer to the emitting 5D_4 level of the Tb^{3+} ion ($\sim 20400\text{ cm}^{-1}$). Taking into account that the emitting 5D_4 level of the Tb^{3+} ion is higher than the 5D_0 excited level of Eu^{3+} ion, the ACAC ligand is by far a better luminescence sensitizer for the Tb^{3+} ion than the TTA ligand. For the $Fe_3O_4@calix-Tb(ACAC)$ phosphor, the energy gap ΔE ($T_1 - ^5D_4$) is around 6000 cm^{-1} which avoids the possibility of an energy back transfer from the Tb^{3+} ion.

Figure 7.5. Partial energy level diagrams of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ (left) and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ (right) nanophosphors. The dashed arrows represent non-radiative decays, the red and green color arrows correspond to the radiative decays of the Eu^{3+} and Tb^{3+} ions, respectively, most probably intramolecular energy transfer processes from the β -diketonate to rare earth ion.

7.1.5. CIE chromaticity diagram

The Eu^{3+} phosphor shows (x,y) color coordinates ($x = 0.6155$ and $y = 0.3330$) in the red region of the CIE chromaticity diagram (*Commission Internationale de l'Eclairage*) mainly due to the high intensity of the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions at 611 nm of the Eu^{3+} ion (Figure 7.6). On the other hand, the Tb^{3+} nanomaterial displays green yellowish emission color with $(x = 0.4119$ and $y = 0.4691)$ color coordinates due to the $^5\text{D}_4 \rightarrow ^7\text{F}_{6-0}$ transitions of the Tb^{3+} ion. A gradual shift in the (x,y) color coordinates is observed from the green to the yellow spectral region due to the

increased contribution from the emission to the ${}^7F_{4-0}$ energy levels. These superparamagnetic nanomaterials also can act as efficient phosphors for light conversion molecular devices (LCMDs), displaying red and green emission colors arising from Eu^{3+} and Tb^{3+} ions.

Figure 7.6. CIE chromaticity diagram showing the (x,y) emission color coordinates for $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanophosphors irradiated at different wavelengths. The inset figures are photographs of nanomaterials taken with a digital camera displaying the green and red emissions under UV irradiation lamp at 254 and 365 nm, respectively.

7.2. Photoluminescence properties of RE^{3+} complexes grafted $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanocomposites

The synthesized sophisticated bifunctional nanomaterials which contain $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanostructures grafted with Eu^{3+} and Tb^{3+} complexes show interesting photoluminescence

properties. They are red and green light emitters and show superparamagnetic behaviors. The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ nanomaterials emit in red under UV irradiation lamp at 365 nm as well as the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ one at 254 nm. While, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanocomposites display green emissions under the UV irradiation at 254 nm. All of these nanomaterials can be attracted to the external magnet in suspension and solid phase (Figure 7.7).

Figure 7.7. The diagrammatic presentation of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanocomposites, including the structure and photographs of the nanomaterials (inset) taken with a digital camera displaying the green and red emissions under UV irradiation lamp as well as the magnetic separation-redispersion process of the nanomaterial in suspension.

In this section, the photoluminescence data of the bifunctional optical and magnetic nanomaterials are discussed. The phosphorescence spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(L)}$ nanophosphors as well as excitation and emission spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ ($\text{L} = \text{TTA, TC, AB and AMB}$) and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ ones are presented. In addition,

the experimental intensity parameters Ω_λ ($\lambda = 2$ and 4), radiative and non-radiative rates (A_{rad} and A_{nrad}) for the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions as well as emission quantum efficiency (η) were calculated for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanophosphors. The emission life times of the Eu^{3+} and Tb^{3+} nanomaterials were also discussed.

7.2.1. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(L)}$, $L = \text{TTA, TC, AB and AMB}$ Phosphorescence

The properly located triple electronic state (T_1) of the ligands in rare earth complexes are important for the efficient intramolecular energy transfer to the RE^{3+} ions, in order to produce highly luminescent nanomaterials. The main objective of the photoluminescence studies of the Gd^{3+} nanomaterials is to determine the triple state (T_1) positions of the TTA, TC, AB and AMB ligands present on the surfaces of chemically modified core-shell nanostructures.

The emission spectra of the gadolinium nanomaterials were recorded with excitation monitored on the $S_0 \rightarrow S_1$ intraligand transition of the TTA, TC, AB and AMB ligands. As discussed earlier, the advantage of using the Gd^{3+} ion is due to concept that its compounds can simulate structural properties of the Eu^{3+} and Tb^{3+} complexes and also due to the first excited level ($^6P_{7/2}$) of Gd^{3+} ion is located at higher energy (32000 cm^{-1}). Therefore, the Gd^{3+} ion cannot accept energy from the lower lying excited T_1 states of the TTA, TC, AB and AMB ligands *via* intramolecular ligand-to-metal energy transfer. As a result, the emission spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(L)}$ samples show only the phosphorescence from the T_1 states, providing information about the structure of the energy levels of the corresponding ligands.

Figure 7.8. The emission spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(TTA)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(TC)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(AMB)}$ nanomaterials recorded at 77 K, under excitation at 350, 345, 316 and 282 nm, respectively.

The emission spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(L)}$, $L = \text{TTA, TC, AB and AMB}$ nanomaterials were recorded in the spectral range of 350-750 nm at 77 K monitoring the excitation of the intraligand, $S_0 \rightarrow S_1$ transition of the ligands (Figure 7.8). The emission spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(TTA)}$ nanomaterial displays overlapped intense broad bands centered at 525 and 548 nm. The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(TC)}$ nanophosphor also has broad band with maximum centered at 500 nm. Moreover, the emission spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(AB)}$ sample shows strong band with maximum at 463 nm, while the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Gd(AMB)}$ one displays strong band centered at 470 nm. The T_1 state energies of the TTA, TC, AB and AMB

ligands in the Eu^{3+} and Tb^{3+} nanomaterials were estimated as the energy corresponding to the shortest emission wavelengths (0–0 phonon transition) on the basis of the phosphorescence spectra. They were found at 20746, 23041, 23584 and 23364 cm^{-1} for the TTA, TC, AB and AMB ligands, respectively.

7.2.2. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ red phosphors

The excitation spectra of the Eu^{3+} nanophosphors (Figure 7.9) in solid state were recorded at 77 K in spectral range of 240–550 nm under the emission monitored at the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ hypersensitive transition of Eu^{3+} ion. These spectra are dominated by broad absorption bands centered at 372, 360, 364 and 282 nm, which are assigned to the $\text{S}_0 \rightarrow \text{S}_1$ transitions of TTA, TCA, ABA and AMBA ligands, respectively. This result indicates that the luminescence from the Eu^{3+} nanophosphors is a consequence of sensitization of the europium excited state by energy transfer from the corresponding ligands and also due to the operative *antenna effect* of the β -diketonate (TTA moiety) present on the chemically modified surface of core-shell magnetic nanoparticles.

In addition, the narrow absorption bands (Figure 7.9) are also observed that can be assigned to the intraconfigurational-4f transitions arising from the $^7\text{F}_0$ ground state to the following excited states of Eu^{3+} ion: $^5\text{H}_4$ (318 nm), $^5\text{D}_4$ (361 nm), $^5\text{L}_7$ (374 nm), $^5\text{L}_6$ (~394 nm), $^5\text{D}_2$ (~464 nm) and $^5\text{D}_1$ (~525 nm). However, these 4f–4f lines are completely absent or negligibly smaller in the case of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanophosphors, suggesting that the luminescence sensitizations through intramolecular energy transfer from TTA and AMB ligands to Eu^{3+} ion are efficient. Similarly, the intensity of the large broad bands are similar or comparably smaller to those of the 4f–4f lines, as observed in excitation spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ ones (Figure 7.9).

Figure 7.9. Excitation spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanophosphors recorded at low temperature (77 K), monitoring the emission of the ${}^5D_0 \rightarrow {}^7F_2$ hypersensitive transition.

The emission spectra (Figure 7.10) of all the europium nanomaterials were recorded in solid state at 77 K, in the range of 400-800 nm, under excitation monitored at $S_0 \rightarrow S_1$ transition of each TTA, TC, AB and AMB ligands which is centered at 372, 360, 364 and 282 nm respectively. All of these spectra exhibit emission bands assigned to ${}^5D_0 \rightarrow {}^7F_J$ transitions (where $J = 0-4$), with the ${}^5D_0 \rightarrow {}^7F_2$ hypersensitive one, that is centered at 612, 615, 615 and 612 nm for each $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanomaterial, respectively (Figure 7.10).

Figure 7.10. Emission spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanophosphors recorded at low temperature (77 K) under excitation at 372, 360, 364 and 282 nm, which correspond to the $S_0 \rightarrow S_1$ transition of the TTA, TC, AB and AMB ligands, respectively.

It is important to notice that the emission spectra of all the Eu^{3+} nanomaterials no exhibit broad emission band of ligands, indicating an efficient ligand-to-metal intramolecular energy transfer [13]. In addition, the emission intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition indicates that the Eu^{3+} ion is found in chemical environment without the center of inversion, considering that Laporte's rule is slightly relaxed for 4f–4f transitions due to the mixing of opposite parity electronic configurations, produced by the odd components of a non-centrosymmetric ligand field.

It was also observed the broadened emission peaks of the $^5D_0 \rightarrow ^7F_J$ transitions in the emission spectra of the $Fe_3O_4@SiO_2$ -TTA-Eu(TTA), $Fe_3O_4@SiO_2$ -TTA-Eu(TC) and $Fe_3O_4@SiO_2$ -TTA-Eu(AMB) nanomaterials (Figure 7.10), which can be explained by a non-homogeneity of Eu^{3+} sites due to the silica porous nanostructures, consistent with the previous reported result [26]. One of the effects of a distribution of different symmetry sites occupied by the RE^{3+} ion is to produce the inhomogeneous line broadening. Therefore, the Stark levels overlap in such a way that in most cases, even the luminescence line-narrowing technique cannot help to identify a particular site occupied by the rare earth ion [27].

The most appealing result, that deserves to be mentioned here is the two main features observed in the emission spectrum of the $Fe_3O_4@SiO_2$ -TTA-Eu(AMB) nanophosphor. The first one is much lower intensity (practically negligible) of the $^5D_0 \rightarrow ^7F_0$ transition, when it is allowed by symmetry; it “borrows intensity” mainly from the $^5D_0 \rightarrow ^7F_2$ transition through the J -mixing effect. The second one is the abnormally high intensity of the $^5D_0 \rightarrow ^7F_4$ transition, which contrary to the spectral data of other europium nanomaterials is as much intense as $^5D_0 \rightarrow ^7F_2$ transition.

On theoretical grounds, the intensity parameter Ω_2 is mostly influenced by small angular changes in the local coordination geometry [2,23]. This effect together with changes in the ligating atoms polarizabilities (α) has been used to rationalize the hypersensitive character of certain 4f intraconfigurational transitions to changes in the chemical environment. The fact that the Ω_2 and Ω_4 parameters of $Fe_3O_4@SiO_2$ -TTA-Eu(TTA) nanophosphor (Table 7.2) have different values than the $[Eu(TTA)_3(H_2O)_2]$ complex is an indication of different chemical environment around the Eu^{3+} ion. In addition, the small value of Ω_2 experimental intensity parameter of the corresponding nanomaterial as compared to the $[Eu(TTA)_3(H_2O)_2]$ complex indicates hypersensitivity character of the $^5D_0 \rightarrow ^7F_2$ transition of the Eu^{3+} ion.

Table 7.2. Experimental intensity parameters (Ω_λ), lifetimes τ , emission coefficient rates A_{rad} and A_{nrad} as well as emission quantum efficiencies η for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$ nanocomposites.

Materials	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$	5	12	390	2835	3225	0.31	12
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$	15	13	691	7183	7874	0.127	9
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$	10	8	489	1297	1786	0.56	27
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$	17	10	727	2844	3571	0.28	20
$[\text{Eu(TTA)}_3(\text{H}_2\text{O})_2]^{\text{a}}$	33	5	1110	2730	3846	0.26	29

^aReference [12].

In addition, for the other three nanomaterials the difference among the values of Ω_2 and Ω_4 parameters indicates a different chemical environment around the Eu^{3+} ion for each nanophosphor. Most importantly, the abnormally higher value of Ω_4 ($12 \times 10^{-20} \text{ cm}^2$) parameter as compared to Ω_2 ($5 \times 10^{-20} \text{ cm}^2$) experimental intensity parameter of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanomaterial (Table 7.2) indicates higher sensitive character of the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition of the Eu^{3+} ion. Malta and co-worker [24] has been reported that this result is theoretically interpreted in terms of the Ω_λ intensity parameters. Besides, their dependence on the nature and local symmetry of the chemical environment around the Eu^{3+} ion, leading to the conclusion that the chemical environment is highly polarizable with a local symmetry corresponding to a slightly distorted D_{4d} coordination geometry.

The value of the emission quantum efficiency of $^5\text{D}_0$ level for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$ nanophosphor ($\eta = 20\%$) is smaller than the $[\text{Eu(TTA)}_3(\text{H}_2\text{O})_2]$ complex ($\eta = 29\%$)

(Table 7.2). This result is a consequence of the concept that radiative rates (A_{rad}) is three times higher than radiative contribution (A_{rad}).

The high value of the emission quantum efficiency for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ nanophosphor ($\eta = 27\%$) as compared to the other prepared nanomaterials (Table 7.2) is a consequence of the presence of less water molecules in the coordination sphere. where this fact is reflected by the lower contribution of non-radiative decay rate (A_{nrad}), arising from the OH oscillator of water molecules. On the other hand, the more water molecules in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ nanophosphor contribute to the higher luminescence quenching, consequently lower value of emission quantum efficiency ($\eta = 9\%$). Nevertheless, these nanomaterials present considerable luminescence intensity, indicating that they are good candidates for the preparation of emitting layer of magnetic and red light converting molecular devices (MLCMDs).

7.2.3. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ green phosphors

The excitation spectra (Figure 7.11) of both the terbium samples were recorded in the range of 240 to 500 nm at liquid nitrogen temperature, under emission monitored at the higher intensity $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of the Tb^{3+} ion. The excitation spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ nanophosphor contains intense broad band centered at 305 nm corresponding to the $\text{S}_0 \rightarrow \text{S}_1$ transition of the AB ligand. Similarly spectrum of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ one presents a broad absorption band at 282 nm attributed to the $\text{S}_0 \rightarrow \text{S}_1$ transition of AMB ligand.

The excitation spectra of both the nanomaterials (Figure 7.11) no exhibit the narrow absorption lines due to $4\text{f}^8\text{-}4\text{f}^8$ transitions of the Tb^{3+} ion. As a result, it can be suggested that the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanomaterials act as green

phosphors due to high efficient intramolecular energy transfer from the corresponding AB and AMB ligands to the terbium ion.

Figure 7.11. Excitation spectra of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanophosphors recorded at low temperature (77 K), monitoring emission of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition.

The emission spectra (Figure 7.12) of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanomaterials were recorded in the range of 400 to 750 nm at liquid nitrogen temperature, under excitation at around 305 and 282 nm, assigned to the $\text{S}_0 \rightarrow \text{S}_1$ transitions of the AB and AMB ligands, respectively (Figure 7.12). The emission peaks were assigned to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions ($j = 6, 5, 4, 3, 2, 1$ and 0) of the Tb^{3+} ion. The optical data show the $^5\text{D}_4 \rightarrow ^7\text{F}_5$

transition at around 543 and 542 nm as the most intense one for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanomaterials, respectively.

Figure 7.12. Emission spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanophosphors recorded at low temperature (77 K) under excitation at the 305 and 282 nm which correspond to the $S_0 \rightarrow S_1$ transition of the AB and AMB ligands, respectively.

In addition, the phosphorescence broadened band of the ligands were not observed in emission spectra of both nanomaterials, indicating a very operative intramolecular energy transfers from AB and AMB ligands to the Tb^{3+} ion. As similar to the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanophosphors, same pattern of broadened emission peaks were also maintained in the spectral

features of the Tb^{3+} nanocomposites, corroborating the above mentioned result that produce the inhomogeneous line broadening. In the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ emission spectra line-narrowing technique cannot help to identify a particular site occupied by the trivalent terbium ion.

7.2.4. CIE chromaticity diagram

The chromaticity properties of the red (Eu^{3+}) and green (Tb^{3+}) emitting superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanocomposites were studied using CIE chromaticity diagram (*Commission Internationale de l'Eclairage*). The color coordinates of these nanocomposites were determined by integrating their entire emission spectra, according to the reported procedure [28] and using the SpectraLux program [29].

The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ nanophosphors show similar (x,y) color coordinates in the red region of the CIE chromaticity diagram, mainly due to the high emission intensity contribution of the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J = 1, 2$ and 4) of the Eu^{3+} ion for all these nanomaterials (Figure 7.13). Therefore, the comparable (x,y) color coordinates ($x = 0.6850$ and $y = 0.3082$), ($x = 0.6852$ and $y = 0.3122$), ($x = 0.6902$ and $y = 0.3077$) and ($x = 0.6934$ and $y = 0.3024$) were observed for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TTA)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$ nanophosphors, respectively.

On the other hand, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanomaterial displays green yellowish emission color with ($x = 0.3984$ and $y = 0.5187$) color coordinates when compared to the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ one with ($x = 0.3562$ and $y = 0.5466$) color coordinates due to the $^5\text{D}_4 \rightarrow ^7\text{F}_{6-0}$ transitions of the Tb^{3+} ion (Figure 7.13). Thus, for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanophosphor, a gradual shift in the (x,y) color coordinates is observed from the green to the yellow

spectral region due to the increased emission intensity contribution from the 7F_J energy levels ($J = 6, 5, 4$ and 3) of Tb^{3+} ion. As a result, these luminescent and superparamagnetic nanomaterials also can act as efficient phosphors for light conversion molecular devices (LCMDs), displaying red and green emission colors arising from Eu^{3+} and Tb^{3+} ions.

Figure 7.13. CIE chromaticity diagram showing the (x,y) emission color coordinates for the $Fe_3O_4@SiO_2$ -TTA-Eu(L) and $Fe_3O_4@SiO_2$ -TTA-Tb(AB or AMB) nanophosphors irradiated at different wavelengths.

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Chapter 8

MAGNETIC PROPERTIES OF BIFUNCTIONAL NANOMATERIALS

8. MAGNETIC PROPERTIES OF BIFUNCTIONAL NANOMATERIALS

The bifunctional magnetic luminescent and magnetoplasmonic nanoscale materials have been attracted extensive research interest due to their unique integrating optical and magnetic properties in the single nanoparticles [1,2], making them efficient for the multimodal biomedical applications, such as photothermal destruction of tumor cells [3], multimodal imaging [4] and hyperthermia for cancer therapy [5]. The magnetic behaviors correspond to the presence of magnetic iron oxide core nanoparticles, whereas the contributions of the magnetic moments of rare earth ions to the magnetization of the magnetic luminescent nanosystems are also taking in to account [6].

The magnetite nanoparticles show superparamagnetic behavior when their size is below the critical volume and single magnetic domain as well as the temperature is above the so-called blocking temperature [7]. In addition, during these conditions all the atomic moments on the nanoparticle can be considered to rotate coherently under the application of magnetic field. Hence, in absence of magnetic interaction the individual nanoparticle are assumed to have a large constant magnetic moment and behave like a giant paramagnetic atom with a fast response to applied magnetic field with negligible remanence (residual magnetism) and coercivity (the field required to bring the magnetization to zero) [8].

The rare earth ions are mostly paramagnetic and show well-defined photoluminescence in different spectral ranges from visible to near infrared. The bifunctional magnetic and optical nanosystems can be designed by the direct doping of the rare-earth ions materials with the magnetic ones into a single-component substrate [9]. In addition, another valuable way to achieve these nanomaterials by using the magnetic Fe_3O_4 core nanoparticles and luminescence RE^{3+} complexes integrated in the single nanostructures [6, 10].

The efficient magnetic behavior and characteristic photoluminescence make the bifunctional nanomaterials good candidates for the preparation of emitting layers in magnetic light converting molecular devices (MLCMDs) [6]. In addition they can be useful in development of magnetically controlled electronic and bioelectronics devices, which can examine the effect of external fields on the electrochemical or bio-electrochemical processes with electro-chemoluminescence phenomena [11], for which the efficient magnetism along with optical properties of nanomaterials are important. In this regard, the synthesized novel luminescent and magnetic nanomaterials are remarkable, which display red green emissions in visible range and show superparamagnetic behaviors with efficient capability to attract to external magnet in solid and dispersion phases (Figure 8.1).

Figure 8.1. Photographs of the magnetic separation-redispersion process of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials in the absence and under the UV irradiation lamp, displaying red and green emissions, respectively.

In current chapter, the magnetic properties of the of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ as well as $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$, L: TC, AB and AMB nanomaterials are discussed. Therefore, based on the magnetic properties at different temperatures, a superparamagnetic model considering magnetic interactions was used to better understand the magnetic behavior. From the technological point of view, the results obtained are very promising and show progress on the physical knowledge of superparamagnetic systems with dipolar interactions.

8.1. Origin of magnetic properties

The magnetic properties of the materials are a consequence of *magnetic moments* associated with the individual electrons; the moving electrons in atoms contain both an orbital magnetic moment $\mathbf{m}_l$, corresponded to their orbital angular momentum $\mathbf{l}$, and a spin magnetic moment $\mathbf{m}_s$, proportional to their spin $\mathbf{s}$, as presented in [Eq. 8.1 and 8.2](#):

$$\mathbf{m}_l = g_l \mathbf{l} \text{ (B. M.)} \quad (8.1)$$

$$\mathbf{m}_s = g_s \mu_B \mathbf{s} \text{ (B. M.)} \quad (8.2)$$

where, g_l and g_s : orbital and spin *g-factors*, $\mathbf{s}$: *spin* of the electron, μ_B : *Bohr magneton* ($9.274 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$) and can be defined in term of fundamental constants as : $1\text{B. M.} = \frac{eh}{4\pi mc}$, where e is the electron charge, h Planck constant, m electron mass and c is the speed of light.

The coupling of $\mathbf{m}_l$ and $\mathbf{m}_s$ or the interaction of the electron spin with its motion (orbital angular momentum) gives rise to the *spin-orbit coupling*. That constitutes the origin of the

magnetocrystalline anisotropy, causing of holding the magnetic moment in certain direction, which has discussed in detail in [section 3.1.1](#).

The magnetic moments of atoms, ions and molecules are usually expressed in units called Bohr magneton (B.M.) as explained above. In addition, the magnetic moment of a single electron is given according to the wave mechanics, by the [Eq. 8.3](#):

$$\mu_s(\text{in B. M.}) = g\sqrt{S(S+1)} \quad (8.3)$$

where, S is simply the absolute value of the spin quantum number (total spin of unpaired electrons in atom or ion) and g is the gyromagnetic ratio, more familiarly known as the g -factor, for free electron its value is ~ 2 . This equation is also designated as “spin-only” [\[12\]](#). The magnetic moment μ of the transition elements is due to the presence of unpaired electron, therefore the above [Eq. 8.3](#) can be presented as: $\mu_s = \sqrt{4S(S+1)}$, if only entire spin of the unpaired electrons is taken into account. In addition, it can be also related to the number of unpaired electrons n by the following [Eq. 8.4](#):

$$\mu_s = \sqrt{4S(S+1)} \approx \sqrt{n(n+2)} \quad (8.4)$$

The calculated μ_s and μ_L s as well as observed μ_{obs} magnetic moments of the certain complexes of 3d transition metal ions are listed in [Table 8.1](#).

The orbital angular momentum and hence the orbital moment of the 3d transition metal ions is wholly or partially quenched by the other atoms, ions and molecules surrounding it in compounds as well by ligands in complexes. It is attributed to the interaction of the electronic fields of the other atoms, ions and molecules as well ligands with its 3dⁿ orbitals, restricting the orbital motion of the

electrons. In addition, if the orbital motion makes it fully contribution to the magnetic moments then the magnetic moment can be calculated as by the Eq. 8.5:

$$\mu_{LS} = \sqrt{g^2 S(S+1) + L(L+1)} \quad (8.5)$$

Table 8.1. Magnetic moments of some complexes of 3d transition metal ions (μ in B.M.)

M^{n+}	S	L	μ_{LS}	$\mu_{obs.}$	μ_s
V^{4+}	1/2	2	3.00	1.7-1.8	1.73
V^{3+}	2/2	3	4.47	2.6-2.8	2.83
Cr^{3+}	3/2	3	5.20	~3.8	3.87
Co^{3+}	4/2	2	5.48	~5.4	4.90
Fe^{3+}	5/2	0	5.92	~5.9	5.92

8.1.1. Magnetic properties of trivalent rare earth ions

The rare earth ions are paramagnetic due to the presence of unpaired electrons with the exception of La^{3+} , Lu^{3+} and Y^{3+} ones. Their magnetic properties are determined entirely by the ground state (except for the Sm^{3+} and Eu^{3+} ions), as the excited states are so well separated from the ground state (Figure 8.2) due to the spin-orbit coupling and are thermally inaccessible. The magnetic moment of the RE^{3+} ions is essentially independent of chemical environment and one cannot distinguish between coordination geometries. [13]. Similarly, it is also possible sometime for the transition metal ions, for example octahedral and tetrahedral Co^{2+} complexes.

Therefore, the magnetic moments of the RE^{3+} ions are given by the Eq. 8.6:

$$\mu_{eff} = g_j \sqrt{J(J+1)} \quad (8.6)$$

where the Landé g -factor is defined by: $g_J = \frac{S(S+1)+3J(J+1)-L(L+1)}{2J(J+1)}$.

This equation is quite different from the familiar one: $\mu_{eff} = \sqrt{n(n+2)}$ or $(\sqrt{4S(S+1)})$, spin-only formula), often applicable to the $3d^n$ transition metal ions; as discussed earlier, in the latter case the orbital contribution to the moment is quenched by the interaction of the $3d$ orbitals of metals with the ligands.

Figure 8.3. Experimental, calculated (Spin-only) and van Vleck magnetic moments (μ in B.M.) of RE^{3+} complexes, at 300 K temperature.

The experimental magnetic moments of the rare earth ions in the second half of the series are greater than in the first half one (Table 8.2). For RE^{3+} ion is attributed to the J ground state values, where $J = L - S$ is lower if the electron number is less than half $4f^7$ configuration ($n < 7$), and $J = L + S$ is larger if the electron number is higher than 7 in $4f^n$ configuration ($n > 7$). Thus, the total angular momentum (J) has key role during the calculation of the magnetic moments in the rare earth ions, as a result, the spin-only formula cannot be applicable for the rare earth ions (Figure 8.3).

Table 8.2. Magnetic properties of trivalent rare earth ions (μ in B.M.) [13].

Z	RE^{3+}	Conf ($4f^n$)	Fund. Level	1 st Exc. Level	ΔE (cm^{-1})	g _J	μ_{calc} spin	$\mu_{\text{eff.}}$ J-Hund	$\mu_{\text{eff.}}$ Van Vleck	$\mu_{\text{eff.}}$ Exp.
57	La	$4f^0$	(1S_0)			0	0	0	0	0
58	Ce	$4f^1$	($^2F_{5/2}$)	($^2F_{7/2}$)	2200	0.86	1.73	2.54	2.56	2.3 - 2.5
59	Pr	$4f^2$	(3H_4)	(3H_5)	2100	0.80	2.83	3.58	3.62	3.4 - 3.6
60	Nd	$4f^3$	($^4I_{9/2}$)	($^4I_{11/2}$)	1900	0.73	3.87	3.62	3.68	3.5 - 3-6
61	Pm	$4f^4$	(5I_4)	(5I_5)	1600	0.60	4.90	2.68	2.83	2.7
62	Sm	$4f^5$	($^6H_{5/2}$)	($^6H_{7/2}$)	1000	0.29	5.92	0.84	1.55-1.65	1.5 - 1.6
63	Eu	$4f^6$	(7F_0)	(7F_1)	300	c)	6.93	0	3.40-3.51	3.4 - 3.6
64	Gd	$4f^7$	($^8S_{7/2}$)	($^6P_{1/2}$)	32000	2.00	7.94	7.94	7.94	7.8 - 8.0
65	Tb	$4f^8$	(7F_6)	(7F_5)	2000	1.50	6.93	9.72	9.7	9.4 - 9.6
66	Dy	$4f^9$	($^6H_{15/2}$)	($^6H_{13/2}$)	3300	1.33	5.92	10.60	10.6	10.4 - 0.5
67	Ho	$4f^{10}$	(5I_8)	(5I_7)	5300	1.25	4.90	10.61	10.6	10.3 - 0.5
68	Er	$4f^{11}$	($^4I_{15/2}$)	($^4I_{13/2}$)	6500	1.20	3.87	9.58	9.6	9.4 - 9.6
69	Tm	$4f^{12}$	(3H_6)	(3H_4)	5800	1.17	2.83	7.56	7.6	7.1 - 7.4
70	Yb	$4f^{13}$	($^2F_{7/2}$)	($^2F_{5/2}$)	10000	1.14	1.73	4.54	4.54	4.4 - 4.9
71	Lu	$4f^{14}$	(1S_0)			0	0	0	0	0

The strength of spin–orbit coupling means that the ground state is well separated from excited states except for Sm^{3+} and Eu^{3+} ions, where contributions from low-lying paramagnetic excited states to the magnetic moment is occurred. Therefore, if the magnetic properties of the Eu^{3+} ion were solely determined by the $^7\text{F}_0$ ground state, its compounds would be diamagnetic, whereas contributions from thermally accessible levels such as $^7\text{F}_1$ and $^7\text{F}_2$ [using a Boltzmann factor of $\exp(-\Delta E/kT)$] lead to the observed room-temperature magnetic moment at $3.5 \mu_{\text{B}}$ (Figure 8.2). Similarly, in the case of Sm^{3+} ion, thermal population of the $^6\text{H}_{7/2}$ state leads to moment at around $1.6 \mu_{\text{B}}$, rather than the value of $0.845 \mu_{\text{B}}$ that would be expected if just the $^6\text{H}_{5/2}$ ground state were responsible (Table 8.2).

Herein, the influence of the rare earth ions on the magnetizations of optical and magnetic nanomaterials are discussed in sections 8.2.1, 8.3.1 and 8.3.2. Whereas the effect of the Eu^{3+} and Tb^{3+} ions on the magnetic susceptibilities in the *M-H* and *ZFC/FC* curves of the optical and magnetic nanomaterials can be observed. The magnetic moment of Tb^{3+} ion contributes largely at 2 and 5 K temperatures with abrupt increase of magnetic susceptibility can be observed for Tb^{3+} nanomaterial when compared to the Eu^{3+} ones. This fact could be attributed to the population of $^7\text{F}_0$ ground state of Eu^{3+} ion at low temperature, where $J = 0$ which contributes to its magnetic susceptibility. Besides, the $^7\text{F}_6$ ground stated of the Tb^{3+} ion with $J = 6$, therefore the paramagnetic contribution from the Tb^{3+} ion is high at low temperature.

8.1.2. Magnetic ordering

The paramagnetic materials are characterized by positive magnetic susceptibility due to the presence of unpaired electrons, which are paired in diamagnetic ones, therefore showing negative susceptibility. The magnetic susceptibility of the materials can be represented by a symbol χ_{m} and

can be defined as $M = \chi_m H$ where M is the magnetization of materials and H is applied magnetic field. As discussed earlier in [section 8.1](#), the magnetism in materials is originated from the magnetic moment of the electrons, the orbital magnetic moment relates to its orbital motion around the nucleus and spin magnetic moment stems from its spin, leading to the spin-orbit interaction [\[15\]](#).

The other interactions are also existed between the atoms of the material, which cause of ordering in magnetic materials. The atoms are considered usually multi-electron entities. Therefore, the net spin moment $\mathbf{S}$, arising from the contribution of the entire electron spin moments in atom interacts with the neighboring atom net spin moment. Thus, it extend to the whole lattice of the material, which can be computed using the Heisenberg model, originally formulated for pairs of atoms and can be defined through the Hamiltonian (H) as shown in [Eq. 8.7](#):

$$H = -2 \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (8.7)$$

Where, i and j represent the positions of the atoms within the lattice, J , is the exchange constant if $J > 0$, there is a *ferromagnetic* interaction that couples the spins parallel ($\uparrow \uparrow$); if $J < 0$, then the interaction is *antiferromagnetic* and the spins are coupled anti-parallel ($\uparrow \downarrow$). The first type of interaction is typical in ferromagnets, whereas the second one is found in both ferrimagnetic and antiferromagnetic materials ([Figure 8.4](#)). Briefly, the *exchange interaction* refers to the way in which electrons are coupled, and this coupling is governed by the Pauli's principle restrictions.

The *ferrimagnetic* materials (The term ferrimagnetism is due to Louis Néel after his studies on the magnetism of *ferrites*) could be undistinguishable from their ferromagnetic counterparts, both exhibit a remarkable magnetization in absence of an applied field or spontaneous magnetization and above a certain critical temperature, called *Curie temperature*, their magnetic order vanishes through a paramagnetic transition [\[16\]](#).

Figure 8.4. Types of magnetic order according to the sign of the exchange constant.

The magnitude of the *Curie temperature* varies from material to material; for example, for nickel, magnetite, iron and cobalt these values are 335, 585, 768 and 1120 °C, respectively. Antiferromagnetism is also affected by the temperature and this behavior vanishes above the *Néel temperature* and corresponding materials become paramagnetic.

Magnetite and maghemite – The magnetite and maghemite are ferrimagnetic iron oxide materials. Thus, the magnetite is usually a mixed Fe^{2+} and Fe^{3+} oxide of 1:2 ratio and of an inverse *spinel* structure where oxygen atoms are forming a cubic close packing along the [111] direction. The structural formula of the magnetite can be written as follows, where T_d and O_h represent tetrahedral and octahedral sites respectively:

The stoichiometric ratio of magnetite is $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$, which can be varied relatively to large extent depending on the preparation method and the incorporation of other cations into the spinel structure [16]. Maghemite can be regarded as an oxidized magnetite, as the presence of Fe^{2+} cation in magnetite makes it unstable against the oxidation at ambient oxygen pressure. Therefore,

specific conditions of an inert atmosphere (nitrogen, argon) and coating with coating agents such as polymer, oleic acid and organic macromolecules, *etc* are employed during the preparation before exposition to open air, to prevent the oxidation. This sort of oxidation is mostly favored in small magnetite particles when compared to the bulk one due to the kinetic stability of its bulk phase. The maghemite has magnetite like spinel structure with no Fe^{2+} ion, therefore one-third of the O_h sites are vacant, which tend to compensate the charge imbalance generating a neutral structure:

where, V represents the vacancies. The magnetic properties of the magnetite and maghemite can be explained in similar way due to their common structural characteristics. The structures of both the iron oxides composed of two magnetic sublattices with anti-parallel magnetizations, which do not cancel each other completely due to observing a different effective field, resulting in a net magnetic moment for the overall structure. This reasoning was proposed by Néel to interpret the magnetic behavior of the ferrites [17]. The nanometric scale Fe_3O_4 particles show superparamagnetic behavior. The superparamagnetism was discussed in detail in [section 3.1.1](#).

The Quantum Design, MPMS XL, SQUID magnetometer was used for DC magnetic measurements of the magnetic and luminescent nanomaterials, which was also discussed in [section 5.4.8](#). (Experimental part). In this chapter, the detailed magnetic properties such as $M-H$ and ZFC/FC measurements of the nanoscale optical and magnetic materials containing integrated Fe_3O_4 and RE^{3+} complexes are discussed.

8.2. Magnetic properties of Fe₃O₄/ calixarene RE³⁺ complexes core-shell materials

The luminescent and magnetic nanomaterials containing Fe₃O₄ functionalized with calixarene and rare earth complexes show interesting superparamagnetic behavior along with red and green emissions in visible region. The superparamagnetic properties are due to the magnetite core nanoparticles, whereas the magnetic susceptibility of the rare earth ions also contributes to the magnetization of the RE³⁺ nanomaterials. In this section, the magnetic properties of the standard Fe₃O₄ as well as Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) red-green emitting nanomaterials are discussed.

8.2.1. Magnetization Curves

The *M-H* measurements were recorded at the 300 and 5 K temperatures with cycling applied magnetic field between +20 and -20 kOe (1 Oe = 79.577 Am⁻¹). The results (Figure 8.5) include the *M-H* hysteretic curves of the Fe₃O₄, Fe₃O₄@calix-Eu(TTA) and Fe₃O₄@calix-Tb(ACAC) nanomaterials, with the saturation magnetization (*M_S*) values of 40, 11 and 4 emu g⁻¹, respectively. The decrease in the *M_S* value of the Eu³⁺ and Tb³⁺ nanomaterials when compared to the standard magnetite nanoparticles can be ascribed to: 1) reduction of crystalline order as indicated by the XPD patterns, 2) surface effect due to the existence of smaller size nanoparticles, as observed in the TEM images, 3) presence of organic coating on the surface of magnetite nanoparticles caused by the functionalization with the calixarene and RE³⁺ β-diketonate compounds and 4) acid damaged magnetite nanoparticles when the calixarenes were introduced in the reaction medium. In this case, the RE³⁺ complexes contribute to a non-magnetic mass in the saturation magnetization calculation. Almost zero coercivity and zero remanence (less than 17 Oe and 0.3 emu g⁻¹, respectively) on the magnetization curves indicate superparamagnetic behavior at room temperature for the magnetite

as well as Eu^{3+} and Tb^{3+} nanomaterials. On the other hand, none of the three nanomaterials no longer presents a superparamagnetic behavior at low temperature (5 K) (Figure 8.5).

Figure 8.5. The M - H hysteresis curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4@calix-Eu(TTA)$ and $\text{Fe}_3\text{O}_4@calix-Tb(ACAC)$ nanomaterials at room temperature (300 K) (left) and low temperature (5 K) (right).

At 5 K, the observed coercivities are of the order of 260, 258 and 190 Oe and remanencies are 14, 4.0 and 1.5 emu g^{-1} for the Fe_3O_4 , $\text{Fe}_3\text{O}_4@calix-Eu(TTA)$ and $\text{Fe}_3\text{O}_4@calix-Tb(ACAC)$ nanomaterials, respectively, signature of the blocked regime. Concerning the saturation magnetization of these nanomaterials, the same trends were observed in behavior both at room and low temperatures. The only difference is that the high field magnetization of the $\text{Fe}_3\text{O}_4@calix-Tb(ACAC)$ nanomaterial is higher than that of the $\text{Fe}_3\text{O}_4@calix-Eu(TTA)$ one. This fact could be attributed to the combination of the higher magnetic moment of Tb^{3+} ion (9.8 Bohr magneton) in comparison to that one of Eu^{3+} ion (3.3 Bohr magneton) with the Curie constant of respective ions. The latter one is much higher in the case of Tb^{3+} ion with the 7F_6 ground state and total angular momentum ($J=6$) than in the Eu^{3+} system, which shows 7F_0 ground state ($J=0$).

Therefore an abrupt increase of magnetic susceptibility was observed at low temperature (5 K) and relatively high magnetic field (higher than 300 Oe) for $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterial. This result indicates that the paramagnetic contributions due to the Tb^{3+} ions cannot be neglected at low temperatures and at magnetic field higher than 300 Oe.

1.2.2. Zero Field Cooling and Field Cooling Curves

The ZFC/FC curves (Figure 8.6) of the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials show the blocking temperatures at 218(2) and 110(2) K, respectively. In addition, suggesting the lower blocking and irreversibility temperatures than for the standard Fe_3O_4 nanoparticles. The value of the blocking temperature obtained for the Eu^{3+} nanomaterial was found smaller or near to the standard magnetite. The behavior of the magnetization as a function of temperature (measured with an applied field of 50 Oe) was found similar for both the Eu^{3+} nanomaterial and the standard Fe_3O_4 , whereas it was completely different for the Tb^{3+} system.

The decrease in the blocking and irreversibility temperature of both Eu^{3+} and Tb^{3+} nanomaterials could be attributed to the existence of smaller magnetic nanoparticles. Moreover, considering SAXS measurements, there is no considerable difference in size distribution between the nanoparticles for both the nanomaterials (Figure 8.6). The observed difference in blocking and irreversibility temperatures may also be due to an increase in the distance between the magnetic nanoparticles generated by the presence of different RE^{3+} ions. This sort of increase in the distance, caused by “external capping” of the rare earth ions generate a reduction in the possible existence of dipolar interaction.

Figure 8.6. The ZFC and FC curves (left) of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$, at 50 Oe applied field. Photo (right): the magnetic separation-redispersion process of $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ nanomaterial.

Based on this hypothesis, it could be expected that the "external capping" of the Tb^{3+} nanomaterial is larger than the Eu^{3+} one. This is consistent with the reduction of magnetization observed in the $M-H$ and ZFC/FC data.

8.3. Magnetic properties of RE^{3+} complexes grafted $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanocomposites

The optical and magnetic nanomaterials containing $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanostructures grafted with europium and terbium complexes show interesting magnetic properties along with red and green emissions in the visible region. The superparamagnetic behaviors are due to the magnetite core nanoparticles, whereas the magnetic susceptibility of the rare earth ions also contributes to the magnetization of these nanocomposites. In this section, the magnetic properties of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles as well as $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ nanostructures and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ red-green emitting nanocomposites are discussed.

8.3.1. Magnetization Curves

The magnetic properties (*M-H curves*) were measured at 300 and 2 K temperatures with the applied magnetic field cycling between +20 and -20 kOe (1 Oe = 79.577 Am⁻¹), respectively. The hysteresis loops of the Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-TTA and Fe₃O₄@SiO₂-TTA-Eu(TC) nanomaterials (Figure 8.7) as well as Fe₃O₄@SiO₂-TTA-Eu(AB), Fe₃O₄@SiO₂-TTA-Eu(AMB), Fe₃O₄@SiO₂-TTA-Tb(AB) and Fe₃O₄@SiO₂-TTA-Tb(AMB) ones (Figure 8.8) show near superparamagnetic behaviors at room temperature (300 K). The saturation magnetization (*M_S*) value of the Fe₃O₄ nanoparticles at *T* = 300 K was 56.3 emu g⁻¹, consequently, coating with silica shell (Fe₃O₄@SiO₂) it was considerably decreased to 9.8 emu g⁻¹, showing large amount of non-magnetic mass contribution from the silica shell. In addition, due to the additional grafting of Fe₃O₄@SiO₂ nanoparticles with TTA organic moiety, the *M_S* value was also largely decreased to near 1.0 emu g⁻¹.

Furthermore the formation of Eu³⁺ and Tb³⁺ complexes on the surface of Fe₃O₄@SiO₂-TTA nanostructure, using different organic ligands results in magnetization with *M_S* values of 0.9, 0.88, 1.59, 3.01 and 3.40 emu g⁻¹ at 300 K temperature for Fe₃O₄@SiO₂-TTA-Eu(TC), Fe₃O₄@SiO₂-TTA-Eu(AB), Fe₃O₄@SiO₂-TTA-Eu(AMB), Fe₃O₄@SiO₂-TTA-Tb(AB) and Fe₃O₄@SiO₂-TTA-Tb(AMB) nanocomposites, respectively (Table 8.3).

The observed decrease in saturation magnetization (*M_S*) values of the Fe₃O₄@SiO₂-TTA, as well as Eu³⁺ and Tb³⁺ nanomaterials, when compared to the Fe₃O₄@SiO₂ nanostructure could be attributed to the aspects, such as reduction of the degree of crystalline order as indicated by XPD patterns or the presence of silica shell and successive organic coating on the surface of Fe₃O₄@SiO₂ nanomaterial caused by chemical modification with TTA organic moiety and rare earth complexes.

Figure 8.7: Magnetization as a function of applied field (clockwise from top left) of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ nanomaterials at room (300 K) and low temperature (2 K) as well as zoom-in of the room (300 K) and low temperature (2 K) M - H curves in low field regions.

In this regard, the silica shell and organic moieties contribute to a non-magnetic mass during the calculation of M_S . In addition, the presence of almost zero coercivity and remanence on the magnetization curves indicate near superparamagnetic behavior at $T = 300$ K for the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ as well as Eu^{3+} and Tb^{3+} nanomaterials. Interestingly, the successive increment of coercive field can be observed on the M - H curves of the magnetite

nanoparticles with silica coating and further grafting with organic compound (TTA), without the nanocomposites containing RE^{3+} ions components.

Figure 8.8. Magnetization as a function of applied field (clockwise from top left) of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB or AMB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanocomposites at room (300 K) and low temperature (2 K) as well as zoom-in of the room (300 K) and low temperature (2 K) M - H curves in low field regions.

The observed magnetic behavior is more prominent at low temperature (2 K) (Figure 8.7) and was also reported by the Gema and co-workers [18]. The increase in coercive field was attributed to the surface effect induced by the silica that generates an extra energy term (possibly due to the surface spin freezing). This surface spin effect is removed during the chemical

preparation of RE^{3+} complex on the surface of silica-coated magnetite, due to the surface spin relaxation caused by temperature during synthesis. On the other hand, the M - H curves (Figure 8.7 and 8.8) of all the nanomaterials show no longer a superparamagnetic behavior at low temperature (2 K). In addition, the coercive fields observed at $T = 2$ K were increased considerably for the silica coated nanoparticles when compared the uncoated Fe_3O_4 ones and then also decreased with introducing further the RE^{3+} ions to form complexes (see Table 8.3).

Table 8.3. Magnetic properties (M_S and H_C values) of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanomaterials.

Material	$M_S^{300\text{ K}}$ (emu g ⁻¹)	$M_S^{2\text{ K}}$ (emu g ⁻¹)	$H_C^{300\text{ K}}$ (Oe)	$H_C^{2\text{ K}}$ (Oe)
Fe_3O_4	56.3	65.7	3	382
$\text{Fe}_3\text{O}_4@\text{SiO}_2$	9.8	12.1	13	463
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$	1	1.31	14	531
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$	0.9	1.4	5	514
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$	0.88	1.36	0	440
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AMB)}$	1.59	1.9	0	460
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$	3.01	34.9	2.6	83
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$	3.39	27	2	213

The M - H curves (Figure 8.8) show similar trend in behavior for the four Eu^{3+} and Tb^{3+} nanomaterials retained at $T = 2$ K as was observed at room temperature, with only slightly increase in M_S value for the Tb^{3+} materials at 2 K. Moreover, at $T = 2$ K the magnetization at high fields is considerably higher for the Tb^{3+} nanomaterials when compared to the Eu^{3+} ones. Considering that the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ nanocomposites have same ligand, this difference on magnetization could be attributed to two possible factors; higher magnetic

moment of Tb^{3+} ion (9.8 Bohr magneton) than that of the Eu^{3+} ion (3.3 Bohr magneton) and the curie constant of respective ions. The latter one is much higher in the case of Tb^{3+} ion which has $^5\text{F}_6$ ground state with total angular momentum ($J=6$) when compared to the Eu^{3+} ion which shows $^5\text{F}_0$ ground state ($J=0$). Therefore, an abrupt increase in magnetic susceptibility of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanomaterials is observed at low temperatures (2 K) and relatively high magnetic field (higher than 300 Oe).

The magnetic susceptibility of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ nanomaterials is increasing thoroughly with decreasing temperature and is more prominent at 2 K (Figure 8.8) with saturation magnetization values of 27 and 34.9 emu g^{-1} for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AMB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB)}$ nanocomposites, respectively (Table 8.3). Accordingly, the Tb^{3+} nanomaterials indicate that the paramagnetic contribution from the Tb^{3+} ion cannot be neglected at low temperatures and high magnetic field (higher than 300 Oe).

8.3.2. Zero Field Cooling and Field Cooling Curves

The temperature dependence magnetization at the zero field cooling (ZFC) and field cooling (FC) modes (Figure 8.9) were measured between 2 and 300 K temperatures for all the samples with an applied field of 50 Oe. From these results, we observed that all the nanoparticles are near the superparamagnetic regime at room temperature with irreversibility near 300 K for all the cases. However, important differences on the ZFC ramp were observed for the different nanomaterials. For the bare magnetite nanoparticles a well-defined maximum can be observed at 230 K, ascribing to the maximum blocking temperature. While all the others nanomaterials (with silica shell as well as Tb^{3+} and Eu^{3+} components) do not show this behavior, which could be related to the dipolar interaction among the Fe_3O_4 nanoparticles.

Figure 8.9. Zero Field Cooling and Field Cooling measurements (clockwise from top left) of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(TC)}$ nanomaterials as well as $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(AB or AMB)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanocomposites at 50 Oe applied field.

This dipolar interaction could be ascribed to the nanoparticles aggregation in the TEOS and CPTES solution during the SiO_2 coating process, as reported in the literature [19]. It is also interesting to notice the magnetization increase on the ZFC and FC curves for the Tb^{3+} nanomaterials at low temperature, as the temperature further decreases. This effect is due the paramagnetic contribution and higher magnetic moment of the Tb^{3+} ion when compared to the

other materials, including the Eu^{3+} ones; confirming the non-negligible effect of Tb^{3+} ion on magnetic properties.

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Chapter 9

CONCLUSION AND PERSPECTIVES

9. CONCLUSION

The bifunctional nanosized materials of the Fe_3O_4 and RE^{3+} complexes, displaying optical and magnetic properties integrated into a single nanostructure, were successfully prepared. The red-green emitting superparamagnetic $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials were synthesized by new method, involving one-pot synthesis. In addition, the bifunctional core-shell luminescent and magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu}(\text{L})$ nanocomposites, where L: TTA, TC, AB and AMB as well as the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb}(\text{AB or AMB})$ ones were prepared by multi-step syntheses. However, the Fe_3O_4 nanoparticles were utilized as a precursor, which were functionalized with silica shell, using tetraethyl orthosilicate (TEOS) and 3-chloropropyl-triethoxysilane (CPTES) by modified Stöber method.

All the synthesized optical and magnetic nanomaterials were characterized with several characterization techniques such as:

- i)* The XPD patterns of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials as well as the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE}(\text{L})$ nanocomposites exhibit mainly characteristic reflections of an amorphous phase, in addition, to the diffraction reflections, representing the face-centered cubic (fcc) lattice of the Fe_3O_4 phase. The XPD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE}(\text{L})$ one also show the reflections for the RE^{3+} complexes. This result suggests the coating of the magnetite with the calixarene macrocycle or silica shell and RE^{3+} complexes.
- ii)* The TEM images of the $\text{Fe}_3\text{O}_4@\text{calix-Eu}(\text{TTA})$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb}(\text{ACAC})$ nanomaterials show that the nanoparticles are roughly of spherical or cubic shape, depending on the nanoparticle average size with diameters between 15 and 25 nm.
- iii)* The SAXS analyses are in accordance with the TEM images, where the fit was performed on the scattering data, considering a distribution of approximate spherical nanoparticles. The

nanoparticles have an average diameter around 26 nm for both $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials.

- iv) SAED data also confirm the presence of spinel structure of the Fe_3O_4 phase in the luminescent and magnetic $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials. Similarly, for the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanocomposites, the 12 nm, average size was inferred from the XPD pattern of the Fe_3O_4 precursor' nanoparticles using Scherer formula.
- v) SEM images of the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-RE(L)}$ nanocomposites were found of irregular morphology and with the average diameter of 390–500 nm, as shown in the size distribution curves (dynamic light scattering measurements).

The photoluminescence data suggest that the TTA and ACAC ligands act as efficient sensitizers for the red (Eu^{3+}) and green (Tb^{3+}) emission in $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ nanomaterials, respectively. Similarly, the AB and AMB ligands present efficient intramolecular energy transfer to Tb^{3+} ion and act as green emitting magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Tb(AB or AMB)}$ nanocomposites. For the $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-TTA-Eu(L)}$ materials, where the TTA and AMB ligands are efficient sensitizer, nevertheless their emission efficiencies are lower than in the complexes. However, the values of the emission quantum efficiency (η) of the europium nanomaterials indicate that they are considerable photonic emitters.

In addition, all of the synthesized nanomaterials also exhibit superparamagnetic behaviors at room temperature, whereas, the M - H hysteretic curves and ZFC/FC measurements were recorded at room and low (2 and 5 K) temperatures. The influence of the nonmagnetic mass (calixarene ligand, silica and RE^{3+} complexes) on the saturation magnetization (M_s) and coercivity (H_c) of all the prepared magnetic nanomaterials were investigated. The efficient contribution of the magnetic

moment of the Tb^{3+} ion to the magnetization of the terbium nanomaterials was also observed, which was more prominent at low temperatures (2 and 5 K), when compared to the Eu^{3+} ones.

As a result, the Eu^{3+} and Tb^{3+} nanomaterials are good candidates for the preparation of red and green emitting phosphors in magnetic and light converting molecular devices (MLCMDs). Moreover, they may be applied as contrast agents in MRI and magnetic luminescent biomarkers, a project that is being launched in the group.

9.1. Perspectives

- ✓ Preparation of novel luminescent and magnetic nanomaterials containing $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanostructures grafted with RE^{3+} complexes of the different organic ligands.
- ✓ The synthesis of bifunctional $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Y}_2\text{O}_3:\text{RE}^{3+}$ nanosystems, exhibiting highly efficient luminescent and superparamagnetic properties.
- ✓ The design and fabrication of the sophisticated nanocomposites containing $\text{MFe}_2\text{O}_4@\text{SiO}_2$ ($\text{M} = \text{Cd}, \text{Co}, \text{Cr}, \text{Fe}, \text{Mn}$ and Zn) nanoparticles incorporated into Y_2O_3 matrix doped with Eu^{3+} ion, for determining the quenching mechanism of the magnetite (Fe_3O_4) and producing highly luminescent and magnetic systems.
- ✓ Preparation of mesoporous multifunctional upconversion luminescent and magnetic nanomaterials based on MFe_2O_4 and rare earth nanocrystals - $\text{MFe}_2\text{O}_4@\text{SiO}_2@ \alpha\text{-NaYF}_4$ or $\text{Y}_2\text{O}_3:\text{RE}^{3+}$.
- ✓ Study of the multimodal biomedical applications of these prepared nanomaterials, such as photothermal destruction of tumor cells, multimodal imaging and hyperthermia for cancer therapy, for which the efficient superparamagnetism along with the luminescence behavior is important.

Appendix

Figure A1. Luminescence spectra of $\text{Fe}_3\text{O}_4@\text{calix-Eu(TTA)}$ nanophosphor at room temperature; excitation (left) spectrum, under emission at 611 nm assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition and emission (right) spectrum under excitation at 372 nm corresponds to the $\text{S}_0 \rightarrow \text{S}_1$ transition of organic ligands.

Figure A2. Luminescence spectra of $\text{Fe}_3\text{O}_4@\text{calix-Tb(ACAC)}$ recorded at room temperature; excitation (left) spectrum, under emission at 545 nm assigned to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition and emission (right) spectrum under excitation at 323 nm corresponds to the $\text{S}_0 \rightarrow \text{S}_1$ transition of organic ligands.

Figure A3. Decay curves of the emitting levels of Eu^{3+} ($^5\text{D}_1$) and Tb^{3+} ($^5\text{D}_4$) with emission life times of 0.23 and 0.82 ms for the $\text{Fe}_3\text{O}_4\text{@calix-Eu(TTA)}$ (left) and $\text{Fe}_3\text{O}_4\text{@calix-Tb(ACAC)}$ nanophosphors (right), respectively.

Annex

Curriculum Summary

CURRICULUM SUMMARY

1. Personal data

- Name: Latif Ullah Khan
- Place of Birth: Lakki Marwat, KPK, Pakistan, 3rd April 1983.

2. Education

- Gomal University Dera Ismail Khan, KPK, Pakistan, 2003.
- Bachelor of Science (BSc)
- University of Peshawar, KPK, Pakistan, 2006.
- Master of Science (MSc)

3. Occupation

- Ph.D. scholarship, CAPES, December 2010 – December 2014.
- Teaching assessment program (PAE) with the Disciplines at the Institute of chemistry, University of Sao Paulo:
- QFL 2342 Reatividade de Compostos Orgânicos I: 1st semester 2012;
- QFL4310 Química Orgânica I: 2nd semester 2012.

4. Publication

- 1) KHAN, L.U.; BRITO, H.F.; HÖLSÄ, J.; PIROTA, K.R.; MURACA, D.; FELINTO, M.C.F.C.; TEOTONIO, E.E.S.; MALTA, O.L. Red-green emitting and superparamagnetic nanomarkers containing Fe₃O₄ functionalized with calixarene and rare earth complexes. *Inorganic Chemistry*, v.53, p.12902–12910, 2014.

5. Summary published in conference proceedings

- 1) KHAN L.U.; BRITO, H.F.; PIROTA, K.R.; MURACA, D.; FELINTO MARIA, C.F.C. Red and green-light emitting superparamagnetic nanomaterials containing Fe₃O₄ core and silica shell grafted with rare earth complexes. In: XIII Brazilian Materials Research Society Meeting (SBPMAT), 2014, JOÃO PESSOA-PB. Brazilian Materials Research Society (B-MRS), 2014.
- 2) RODRIGUES, R.V.; MARINS, A.; ANTONIO A. L.; KHAN, L.U.; CRUZ, P.C.; MATOS, J.R. ; BRITO H.F. ; MACHADO, L.C. Thermodynamic Properties of MTiO₃ [M = Ni] Obtained at Different reaction'n times. In: IX Cbratec - Congresso Brasileiro de Análise Térmica, 2014, Serra Negra - SP. IX CBRATEC - Congresso Brasileiro de Análise Térmica. São Paulo: CBRATEC, 2014. v. 1. p. 1-53.
- 3) RODRIGO R.V.; MATOS, J.R.; BRITO H.F.; HOLSA, J.; CRUZ, P.C.; KHAN, L.U.; MACHADO, L.C.; MARINS, A.; MURI, E. Optical Properties of Tb(DAS)₃.2H₂O Surfactant. In: XIII Brazilian MRS Meeting, 2014, João Pessoa. XIII Encontro da SBPMat 2014. Rio de Janeiro: SBPMAT, 2014. v. 1. p. 1-260.
- 4) KHAN L.U.; BRITO, H.F.; PIROTA, K.R.; MURACA D.; FELINTO MARIA, C.F. C. Red-Green Emitting and Superparamagnetic Nanomarkers Containing Fe₃O₄ Functionalized with Calixarene and Rare Earth Complexes. Symposium VV: Magnetic Nanomaterials and Nanostructures, 2014 MRS Spring meeting & Exhibit - San Francisco, California, USA.

- 5) KHAN L.U.; BRITO, H.F.; PIROTA, K.R.; MURACA D.; FELINTO MARIA, C.F.C. Magnetic-luminescent nanoparticles containing Fe_3O_4 functionalized with rare earth complexes. XII Encontro da SBPMAT - Campos do Jordão - 2013-09-29. XII SBPMAT - Sociedade Brasileira de Materiais p. 18570-18570.
- 6) KHAN L.U.; FELINTO MARIA, C.F. C. BRITO, H.F. Preparation of magneto-optical nanocomposites $[\text{Fe}_3\text{O}_4@\text{Ln}(\text{p-tetrakis-carboxymethyl-calix-4,6,8-arene})]$. In: Brazilian Meeting on Inorganic Chemistry III Latin American Meeting on Biological Inorganic Chemistry, 2012, Florianopolis. Brazilian Meeting on Inorganic Chemistry III Latin American Meeting on Biological Inorganic Chemistry, 2012.