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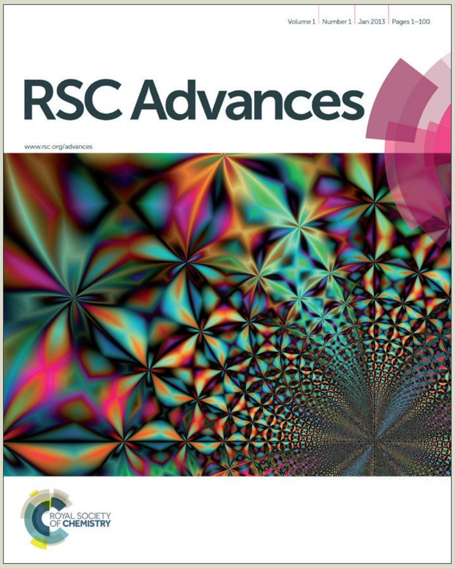

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Photophysical properties of asymmetric and water-soluble dinuclear lanthanide complexes of poly glycol chain functionalized-benzoic acid derivative: experimental and theoretical approaches

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New water-soluble lanthanide complexes with a poly glycol chain (–OEtOEtOEtOMe) functionalized benzoic acid derivative ligand were synthesized and photophysically characterized. The results indicate a formation of an asymmetric dinuclear lanthanide complexes. The $[Eu_2(mee)_6(H_2O)_2]$ complex shows emission in water solution and it was noted that after 48 h part of the ligands are replaced by water molecules resulting on quenching of the emission and decreasing of lifetimes by O-H oscillators from water molecules. The average Judd-Ofelt intensity parameters were determined experimentally from emission spectra of the europium(III) complex. Additionally, the contribution of each asymmetric europium(III) center to the JO intensity parameters were calculated independently using time resolved spectroscopy and the LUMPAC software helping the proposition of the polyhedral coordination sphere determined by the ground state geometry using the Sparkle/PM3 model. The transfer and back energy transfer rates were also calculated. The values obtained for energy transfer rates are lower than previous values obtained for europium(III) complexes with benzoic acid derivative ligands, indicating the role of the poly glycol chain on photophysical properties of the $[Eu_2(mee)_6(H_2O)_2]$ complex.

Introduction

Lanthanide-based materials have unique photophysical properties and therefore a broad range of applications, such as displays, sensors and especially luminescent markers in biological systems. The latter application has drawn the attention of the scientific community, as the long emission lifetimes in the μs – ms range allows the rejection of the short-lived emission from the biological tissues.[1] Strong coordination of the ligand to trivalent lanthanide ions and water solubility of the complexes are important factors for biological applications, and for asymmetric catalysis in organic synthesis.[1,2] Ligands derived from benzoic acid easily coordinate to lanthanide(III) ions. However, the applications of resulting lanthanide complexes are usually in the solid state, due to the low solubility of this class of complexes. Li and co-workers showed that complexes with the benzoic acid nitrogen mustard (banm) ligand are soluble in water with 10 % dimethyl sulfoxide (dmso) and show an inhibitory effect against K_{562} and Vero cell lines.[3] Bünzli and co-workers showed that water solubility of lanthanide(III) complexes can be achieved upon functionalizing the ligand with a glycol chain, –$O(CH_2CH_2O)_nCH_3$.[4,5] The strategy of adding glycol chains into the ligand structure was successfully pursued by Maury and co-workers[6,7] and also by de Bettencourt-Dias and co-workers.[8] Tuck and co-workers reported the addition of carbon chains such as 3,5-bis((*R*)-2,3-dihydroxypropoxy)benzoate and 3,4,5-tris((*R*)-2,3-dihydroxypropoxy)benzoate) to benzoic acid ligand to achieve water solubility of the complexes and demonstrated that these can be used as asymmetric catalysts for epoxide ring opening reactions.[9]

Facing the possibility of increasing the water solubility of lanthanide benzoate complexes, this work reports a facile synthesis of a poly glycol chain (-OEtOEtOEtOMe) benzoic acid derivative ligand (Scheme 1) that can be used in the preparation of luminescent water-soluble lanthanide(III) complexes and their chemical stability in water solution. The benzoic acid derivative ligand was characterized by ^{1}H-NMR and ^{13}C-NMR, FT-IR spectroscopy and mass spectrometry. The lanthanide(III) complexes (Ln = Eu^{III}, Gd^{III} and Tb^{III}) were characterized by high resolution mass spectrometry, TGA, FT-IR and photoluminescence spectroscopies. The photophysical properties were extensively studied in both solid state, in water and acetonitrile solutions. Experimental photophysical parameters were compared to theoretical ones in order to propose a polyhedral coordination sphere and also to give insights about the ligands exchange in water solution.

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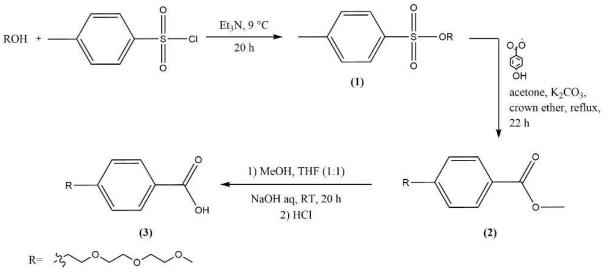
Experimental Section

Synthesis of the ligand and complexes

All solvents and the *p*-toluenesulphonyl chloride were dried and purified, respectively, according to the standard methods. The synthetic route to obtain the ligand 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (Hmee) is represented in the Scheme 1.



Scheme 1. Synthetic route to obtain the ligand Hmee.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (1)[10, 11]

6.0 g (31.5 mmol) of *p*-toluenesulphoynl chloride and 5.04 mL (31.5 mmol) of 2-(2-(2-methoxyethoxy)ethoxy)ethanol were dissolved in 81 mL of CH_2Cl_2 followed by the addition of 5.48 mL (39.4 mmol) of triethylamine. The system was kept under stirring at 9 °C for 20 h. The reaction was quenched with sodium bicarbonate solution and extracted with ethyl acetate (3 x 30 mL), dried under Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield a colorless oil that was used in the next step without further purification. Yield: 9.56 g (95 %).^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.79 (m, Ar, 2H), 7.31 (d, Ar, *J* = 8.1 Hz, 2H), 4.16 – 4.09 (m, CH_2, 2H), 3.67 – 3.62 (m, CH_2, 2H), 3.60 – 3.53 (m, CH_2, 2H), 3.51 – 3.46 (m, CH_2, 2H), 3.33 (s, CH_3, 3H), 2.41 (s, CH_3, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.8, 133.0, 129.8, 128.0, 72.5, 71.9, 70.7, 70.5, 69.3, 68.6, 59.0, 21.6 ppm (ESI-Figure S1)

Methyl 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (2)[10]

7.70 g (55.7 mmol) of potassium carbonate, 0.45 g (1.7 mmol) of 18-crown-6 and 1.84 g (10 mmol) of methyl 4-hydroxybenzoate were added to a solution containing 4.56 g (10 mmol) of the freshly prepared **1** in acetone to yield a pale yellow suspension. The system was kept under stirring and nitrogen atmosphere at 55 °C for 22 h. The reaction was quenched with water and the product extracted with ethyl acetate and purified through a silica chromatographic column using ethyl acetate:hexane (1:1) as eluent to yield a colourless oil. Yield: 2.56 g (72 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 – 7.94 (m, CH, 2H), 6.99 – 6.88 (m, CH, 2H), 4.35 (q, *J* = 7.1 Hz, CH_2, 2H), 4.21 – 4.17 (m, CH_2, 2H), 3.91 – 3.86 (m, CH_2, 2H), 3.75 (dd, *J* = 5.9 and 3.5 Hz, CH_2, 2H), 3.72 – 3.64 (m, CH_2, 4H), 3.58 – 3.53 (m, CH_2, 2H), 3.38 (s, CH_3, 3H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C-NMR (100 MHZ, $CDCl_3$): δ 166.3, 162.5, 131.5, 123.1, 114.1, 71.9, 70.9, 70.7, 70.6, 69.6, 67.6, 60.6, 59.0, 14.4 ppm (ESI-Figure S2).

4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (Hmee) (3)

515 mg (1.65 mmol) of **2** was added to a 4.2 mL solution of THF:methanol (1:1, in volume) containing 200 mg (5 mmol) of NaOH and 2.1 mL of water. The system was kept under stirring at RT for 20 h. The aqueous phase was washed with ethyl acetate, and acidified (until pH ~2) with HCl 1 mol L^{-1} aqueous solution and the product extracted with ethyl acetate (3 x 30 mL). The organic phase was dried under Na_2SO_4 filtered and the solvent removed under reduced pressure to yield a white solid. Yield: 374 mg (80 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, Ar, *J* = 8.9 Hz, 2H), 6.97 (d, Ar, *J* = 8.8 Hz, 2H), 4.22 (dd, CH_2, *J* = 4.0 and 5.6 Hz, 2H), 3.91 (dd, CH_2, *J* = 3.9 and 5.6 Hz, 2H), 3.77 (dd, CH_2, *J* = 3.5 and 6.0 Hz, 2H), 3.66 – 3.74 (m, CH_2, 4H), 3.58 (dd, CH_2, *J* = 3.6 and 5.7 Hz, 2H), 3.40 (s, CH_3, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.4, 163.2, 132.3, 121.9, 114.3, 71.92, 70.9, 70.7, 70.6, 69.5, 67.6, 59.0 ppm (Figure S3). ESI-MS: $[M + H]^+$ m/z found (calc.): 285 (285) (Figure S4).

Lanthanides complexes - $[Ln(mee)(H_2O)_x]$ (Ln = Eu^{3+}, Gd^{3+} and Tb^{3+})

The ligand was dissolved in ethanol and a NaOH solution was added in the stoichiometric proportion 1:1 (L:OH^-). $LnCl_3$ was dissolved in a small amount of deionized water and added to the ethanolic solution containing the deprotonated ligand in 1:3 (Ln:L) stoichiometric ratio. The solution was kept under stirring at 25 °C for 5 h. The solvent was removed under reduced pressure, and the precipitate was dissolved in water and filtered off to remove any unreacted ligand. The solvent was again removed under reduced pressure and the solid re-dissolved in chloroform and filtered off to remove any residual salts. The solvent was removed under reduced pressure to yield the product as a pale yellow solid. ESI-MS: $[EuL_3 + H]^+$ *m/Z* found (calc.) 1003.22 (1003.28) (ESI-Figure S5). $[GdL_3 + H]^+$ *m/Z* found (calc.) 1008.25 (1008.29) (ESI-Figure S6). $[TbL_3 + H]^+$ *m/Z* found (calc.) 1009.23 (1009.29) (ESI-Figure S7).

Characterization

Unless otherwise indicated, all data were collected at a constant temperature of 298 ± 1 K. The ^{1}H and ^{13}C-NMR spectra were obtained in deuterated solvents in a Bruker Avance 400 or 500 MHz. Low resolution electrospray mass spectrum (ESI-MS) of the ligand was obtained in the positive ion mode in a Waters Micromass ZQ quadrupole mass spectrometer. High resolution electrospray mass spectra (ESI-MS) of the lanthanide(III) complexes were obtained in the positive ion mode with methanol as solvent in a Waters Xevo QTOF mass spectrometer. The thermogravimetric analyses (TA instruments SDTQ600) were carried out using a synthetic air flow (100 mL min^{-1}) under a heating rate of 10 °C min^{-1}. Infrared spectroscopy (Cary 630 FTIR) data were obtained in attenuated total reflectance mode. The photoluminescence data were obtained with the samples in the solid state and in aqueous and acetonitrile solutions ($1x10^{-4}$ mol L^{-1}) in a Fluorolog-3 spectrofluorometer (Horiba FL3-22-iHR320), with double-gratings (1200 gr/mm, 330 nm blazed) in the excitation

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monochromator and double-gratings (1200 gr/mm, 500 nm blazed) in the emission monochromator. An ozone-free xenon lamp of 450 W (Ushio) was used as radiation source. The excitation spectra were obtained between 250-550 nm and they were corrected in real time according to the lamp intensity and the optical system of the excitation monochromator using a silicon diode as reference detector. The emission spectra were obtained between 400-720 nm using the front face mode at 22.5° (for solid samples) or right angle (for solutions). The time-resolved emission spectra of europium(III) complexes were obtained with a pulsed 150 W Xenon lamp using a TCSPC system with successive delay increments. All emission spectra were corrected according to the optical system of the emission monochromator and the photomultiplier response (Hamamatsu R928P). The time-resolved phosphorescence emission spectra of the analogous gadolinium(III) complexes were obtained at ~77 K using a TCSPC system with successive delay increments, in order to get only the emissions from the triplet level of the ligand. The energy values of the ligand triplet level were obtained using two approaches: (i) fitting a tangent to the highest energy edge of the emission spectra or (ii) the maximum of the highest energy vibrational-coupled band (0-0 phonon) obtained from the deconvolution of the emission spectra.[12] The emission decay curves were obtained with a pulsed 150 W xenon lamp using a TCSPC system. The Judd-Ofelt (JO) intensity parameters (Ω_2 and Ω_4) and the efficiency parameters (A_{rad}, A_{tot} and η) were calculated using the equations described in the literature.[13] The number of coordinated water molecules (q) was determined using the equation 1, proposed by Horrocks and co-workers, considering that the O-H oscillator is the only quenching route of the emitting level.[14]

$$q = A \cdot \left(\frac{1}{\tau_{H2O}} - \frac{1}{\tau_{D2O}} - \alpha \right) \qquad (1)$$

where $A = 1.1$, $\alpha = 0.31$ and $\tau_{D2O} = \tau_{rad}$ for Eu(III).[15]

The relative quantum yields Φ_x of the samples were determined at $25.0 \pm 0.1\,^{o}$C using the equation (2).

$$\Phi_x = \frac{A_{st} \cdot I_{st} \cdot E_x}{A_x \cdot I_x \cdot E_{st}} \cdot \Phi_{st} \qquad (2)$$

A_{st} and A_x are the absorbance at the excitation wavelength of the standard st and sample x, respectively; I_{st} and I_x are the intensities of the excitation source at the excitation wavelength, E_{st} and E_x are the integrated emission spectra and ϕ_{st} is the quantum yield of the standard. Standards for quantum yield measurements were $Cs_3[Eu(dipic)_3]$ (ϕ~24 %) and $Cs_3[Tb(dipic)_3]$ (ϕ~22 %) in 0.1 mol L^{-1} aqueous TRIS/HCl buffer solution (pH ~7.4).[16,17] The excitation wavelengths were chosen to ensure a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species ($A \leq 0.05$).

Ground state geometries and theoretical calculations

The Sparkle/PM3 model was used to determine the complexes ground state geometries.[18] In this model the lanthanide ion is replaced by a +3e point charge.[19] The RHF wave functions were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) procedure with a convergence criterion of 0.15 kcal mol^{-1} $Å^{-1}$ and the semi empirical PM3 with a convergence criterion of 10^{-6} kcal mol^{-1} for the SCF. In Mopac2016 package[20] the following keywords were used: PM3, SPARKLE, XYZ, SCFCRT=1D-10, GEO-OK, BFGS, CHARGE=X, PRECISE, GNORM=0.25 ALLVEC AUX and T=2D. The theoretical JO intensity parameters were calculated using the adequate equations and adjusting, in the physical acceptable range,[13] the polarizability (α) and the charge factors (g) of the ligands in order to fit the theoretical JO intensity parameters with the experimental ones. The experimental JO intensity parameters obtained without delay correspond to the average value between the two europium(III) sites (Eu_1 and Eu_2) of dinuclear complex. The determination of JO experimental parameters, A_{rad} (radiative emission rate) and A_{nrad} (non-radiative decay rate) of the Eu_2 was done using the time-resolved emission spectra and the experimental parameters of the Eu_2 center were estimated using the equation (3).

$$Eu_2 = \frac{\mathrm{T} - 0.66.\mathrm{Eu}_1}{0.34} \qquad (3)$$

Where Eu_2 refers to the A_{rad} or A_{nrad} or JO intensity parameters of the europium with two coordinated water molecules; T refers to the A_{rad} or A_{nrad} or JO intensity parameters determined from europium(III) stead-state emission spectra and Eu_1 refers to the A_{rad} or A_{nrad} or JO intensity parameters determined from time-resolved europium(III) emission spectra, that eliminates emission from Eu_2 center, that has shorter emission lifetime than Eu_1 center. The 0.66 and 0.34 values are the contribution ratios of the first and second coefficient terms of the bi-exponential function used for fitting the lifetime emission decay curve (ESI-Figure S8).

The excited states calculations were performed using ORCA software[21] using the INDO/S-CIS[22] with the lanthanide replaced by a +3e point charge.[13,19] The transfer and back transfer energy rates from the ligand's triplet level to the $^5D_{0,1}$ europium(III) levels as well the theoretical quantum efficiency and quantum yield were calculated using the adequate kinetics equations described by Malta and collaborators[23,24,25] implemented in the LUMPAC software[26] (version 1.2.0).

Results and discussion

New lanthanide complexes (Eu^{III}, Gd^{III} and Tb^{III}) with a benzoic acid derivative ligand, functionalized with the polyglycol chain -OEtOEtOEtOMe at the *para* position were synthetized, isolated and characterized. The stoichiometries of the complexes, as monomer motifs once they were solubilized in methanol containing 0.1 % of formic acid, were confirmed by high resolution ESI-MS (ESI - Figures S5 – S7 and Table S1) and the amounts of coordinated water molecules were determined by TGA (ESI-Figure S9) and by emission lifetime using Horrocks

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equation (1). The coordination mode of the carboxylate moiety was confirmed by the shift to lower wavenumbers of the $\nu_a(COO^-)$, Figure 1. The coordination of the carboxylate ion to the lanthanide(III) can be bidentate bridging, and/or bidentate chelate, and/or monodentate. The value of $\Delta\nu$ [$\Delta\nu = \nu_a(COO^-) - \nu_s(COO^-)$] provides some indication about the possible coordination modes of this group.[27,28] According to the values determined for this series of complexes, Table 1, the ligands may be coordinated to the metal ion through the bidentate bridging mode ($\Delta\nu_{ligand\ salt} \sim \Delta\nu_{complex}$) or chelate bidentated mode ($\Delta\nu_{ligand\ salt} > \Delta\nu_{complex}$). Specifically, for the europium(III) complex, one may note, that both asymmetric and symmetric vibrations mode of carboxylate group are slightly split indicating a possible mixture between the bridging and chelate mode simultaneously, as previously observed.[29]

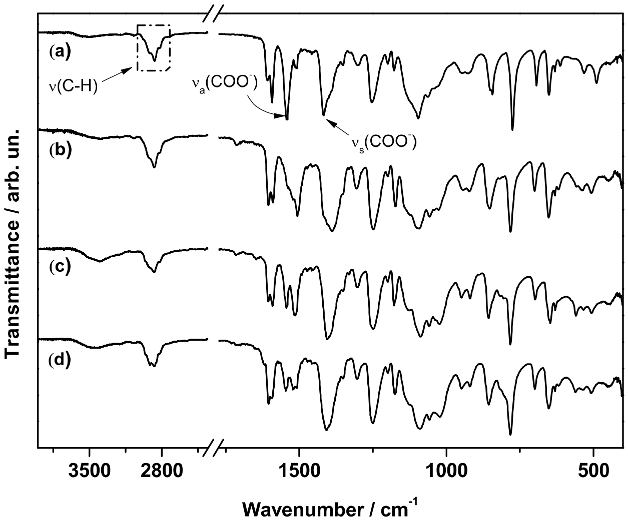

Figure 1. FT-IR spectra of the ligand salt and lanthanide(III) complexes. (a) Na$^+$mee$^-$ (b) europium(III) complex (c) gadolinium(III) complex and (d) terbium(III) complex

Table 1. Values of $\nu_a(COO^-)$, $\nu_s(COO^-)$ and $\Delta\nu(COO^-)$ of the ligand sodium salt and the complexes.

	$\nu_a(COO^-)$/ cm^{-1}	$\nu_s(COO^-)$/ cm^{-1}	$\Delta\nu(COO^-)$/ cm^{-1}	*Coordination Modes*
Na$^+$	1547	1417	130	---
Eu^{III}	1539/1506	1393	146/113	mixed bidentate chelate and bridging
Gd^{III}	1542/1508	1405	137/103	
Tb^{III}	1545/1508	1405	140/103	

In the past years, different coordination modes of the carboxylate ligand toward trivalent lanthanide ions have been identified and consequently a large number of complex geometries have been reported.[30] Recently, Malvestiti and collaborators[31] have published an interesting extended structure with asymmetrical dinuclear units based on 2-(methylthio)benzoic acid derivate. The asymmetric units of the terbium(III) complex obtained from crystallographic data, indicate that the carboxylate group is coordinated basically by bidentate chelate and bridging modes, being one terbium(III) ion coordinated by eight oxygens from carboxylate groups and the other terbium(III) ion is coordinated by four oxygens from carboxylate group plus four oxygens from coordinated water molecules.[31] The benzoic acid-derivate ligand published by Malvestiti and collaborators[31] is structurally similar to the one synthetized in this work. Based on the FT-IR data in addition to the photoluminescence decay curve of the europium(III) complex that was fitted by a bi-exponential decay function indicating at least two emitting centers and two coordinate water molecules in one of the europium centers, it is possible to infer that the structure of the europium(III) complex has two asymmetric units (Figure 2). In the first one the europium(III) ion (Eu$_1$) probably is bonded to eight oxygens from carboxylate groups, where three carboxylate groups (oxygen atoms numbers 9 to 14) are coordinated in a bidentate chelate mode and the other two (6 and 8) are coordinated as a bidentate bridging and chelate mode simultaneously. The other europium center (Eu$_2$) probably is bounded to two oxygen from carboxylate groups (oxygen atoms 3 and 4 - Figure 2) coordinated as bidentate chelate mode, four oxygen (oxygen atoms numbers 5 to 8) from the bidentate bridging and chelate mode from Eu$_1$ and two oxygens (oxygen atoms numbers 1 and 2) from coordinated water molecules. The FT-IR spectra of terbium(III) and gadolinium(III) complexes are comparable to the ones published by Malvestiti and collaborators[31] probably indicating similar structures and coordination modes.

The ground state geometry of the europium(III) complex (Figure 2) was calculated using the Sparkle/PM3 model implemented in the MOPAC2016 software and it will be discussed later.

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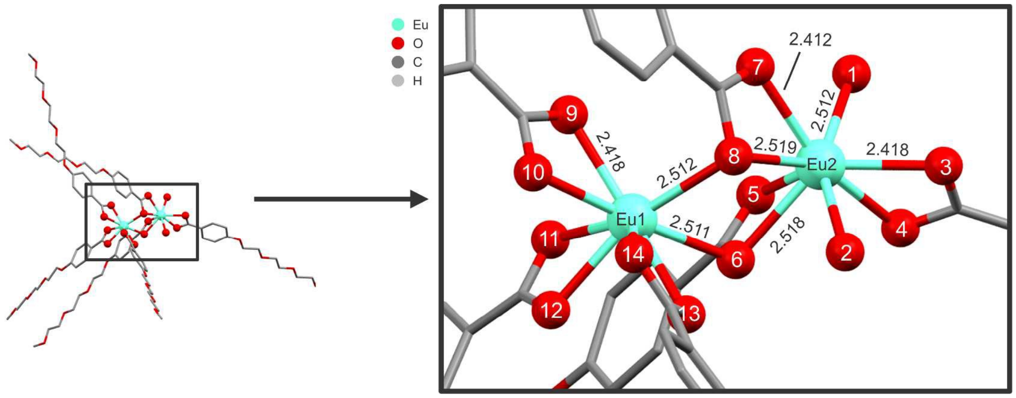
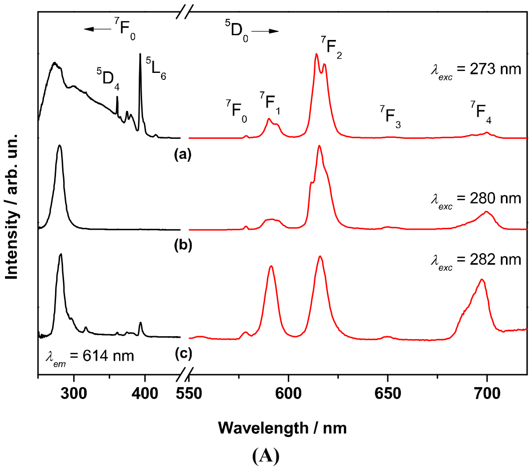


Figure 2. Ground state geometry of the $[Eu_2(mee)_6(H_2O)_2]$ complex obtained using the Sparkle/PM3 model. The theoretical bond distances are in Angstroms.

The triplet energy level (T) of the ligand was determined using the two approaches described in the *Experimental Section*. The time resolved phosphorescence emission spectra of analogous gadolinium(III) complex (ESI-Figure S10.a) and the deconvolution of the phosphorescence bands (ESI-Figure S10.b) are shown in the *Electronic Supporting Information*. The energy values of the triplet energy level obtained by the two approaches were 25,610 cm^{-1} (edge) and 26,130 cm^{-1} (0-0 phonon). These values are comparable to the ones (24,641 cm^{-1} and 23,202 cm^{-1}) obtained for benzoic acid ligand.[32] The excitation and emission spectra of the europium(III) and terbium(III) complexes in the solid state and dissolved in acetonitrile and water are shown in Figures 3A and 3B.



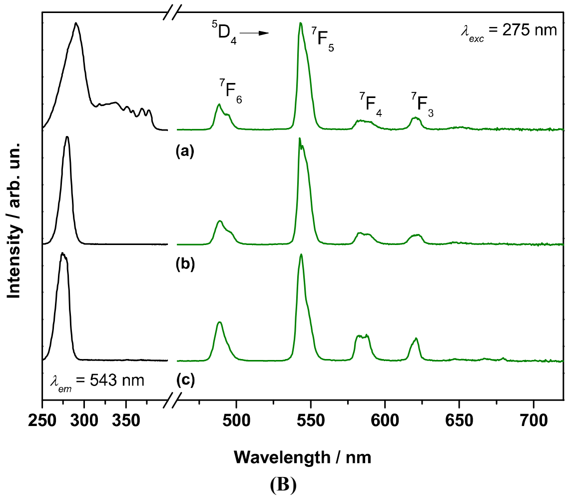


Figure 3. Excitation and emission spectra of the (A) europium(III) and (B) terbium(III) complexes. The spectra were obtained at 298 K in (a) the solid state, (b) acetonitrile and (c) water. The measurements were done after 48 h of the solution preparation.

The excitation and emission spectra of the europium(III) complex (Figure 3A) in different solvents as well in the solid state provide information about the microsymmetry around the europium(III) ion[33] and the degree of covalence of the Eu–L bonds.[34,35,36] In all cases, Figure 3A, the expected transitions $^5D_0 \rightarrow {}^7F_J$, ($J$ = 0; 1; 2; 3 and 4) are observed. The ratio of the band intensity attributed to the forced electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) and the band intensity attributed to the magnetic dipole one ($^5D_0 \rightarrow {}^7F_1$) correlates with the microenvironment around the europium(III). If the microenvironment around the europium(III) lacks an inversion center, the band attributed to $^5D_0 \rightarrow {}^7F_2$ transition has higher intensity than the $^5D_0 \rightarrow {}^7F_1$ one. Figure 3A shows that the europium(III) lies in a microenvironment without inversion center when in the solid state and dissolved in acetonitrile. However, a decrease in the intensity of the $^5D_0 \rightarrow {}^7F_2$ is observed when the europium(III) complex is dissolved in water (Figure 3A-c) meaning that, in this solvent, the

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microenvironment around the europium(III) ion is more symmetric leading to an increase of the symmetry also illustrated by the intensity of the $^5D_0 \rightarrow ^7F_4$ transition band.

The emission decay curve of the solid state europium(III) complex was fitted using a bi-exponential decay function (ESI-Figure S8) indicating the existence of at least two emitting centers (Table 2). Using the Horrocks equation (equation 1) it was possible to infer that the Eu_2 center has two coordinated water molecules and the Eu_1 has none. The emission lifetime values may be related to emission deactivation of europium(III) ions. In the solid sample, the Eu_1 center has emission lifetime value almost three times higher than Eu_2 center. When the sample is solubilized in acetonitrile the emission lifetime values are higher than the ones in the solid sample, suggesting that, in solid state, the poly glycol chain may entrap water molecules close to the europium(III) ion and/or create other routes for emission quenching. The emission lifetime values are comparable to the ones available in the literature for europium(III) complexes obtained from benzoic acid derivate ligands with no coordinated water molecules[31,37] and with two coordinated water molecules per europium(III) center.[32,38,39,40]

Table 2. Values of the emission lifetime (τ) and relative quantum yield (Φ_L^{Ln}) of the europium(III) and terbium(III) complexes in the solid state or dissolved in acetonitrile or water.

Ln	τ / ms			Φ_L^{Ln} / %		
	Solid	*Acetonitrile*	Water	Solid	*Acetonitrile*	Water
Eu	1.15 ± 0.01 (Eu_1) 0.41 ± 0.01 (Eu_2)	1.60 ± 0.01 (Eu_1) 0.77 ± 0.02 (Eu_2)	0.130 ± 0.001	---*	2.1	< 1
Tb	0.986 ± 0.002	1.451 ± 0.002	0.413 ± 0.001	---*	11.4	1.4

* the absolute Φ_L^{Ln} of the complexes in the solid state were not measured due to limitations of the experimental setup that allows excitations beyond 350 nm.

The excitation and emission spectra of the terbium(III) complex in the solid state or in different solvents (Figure 3B) show the characteristics bands of this ion attributed to the $^5D_4 \rightarrow ^7F_j$ transitions. There are no significant differences of the terbium(III) emission spectra on solid state, in water or acetonitrile solutions. One may see just slight changes on the emission band attributed to $^5D_4 \rightarrow ^7F_6$ in water solution (Figure 3B-c) and a different sensitization of the terbium(III) when the excitation spectra are obtained in solutions (Figure 3B-bc). In all cases, the emission decay curves of terbium(III) complex were fitted using single exponential decay functions (ESI-Figure S12), corroborating with the geometries proposed by Malvestiti and collaborators.[31]

The Judd-Ofelt (JO) intensity parameters Ω_2 and Ω_4 are strongly correlated to the symmetry of the microenvironment around the europium(III) ion. A high value for the Ω_2 intensity parameter means low local symmetry. The decrease of the Ω_2 intensity parameter (Table 3) when the complex is dissolved in water, compared with acetonitrile solutions or the solid state, indicates that the europium complex is not stable in water and possibly undergoes to ligand exchange process. As discussed before, the europium(III) complex has two different chemical environments (centers) and it is possible to determine the theoretical JO intensity parameters for each one. In order to do so, the emission spectra of europium(III) complex were obtained with successive delay increments (ESI-Figure S13) and the minimum necessary delay time to eliminate the emission of the less symmetric Eu_2 ion was calculated from the lifetime emission decay functions. Therefore, the experimental JO intensity parameters of the Eu_1 center were determined using the emission spectra with a delay of 6.5 ms. To evaluate the experimental JO intensity parameters, the optimized ground state geometry of dinuclear complex (Figure 2) was taken and in sequence the JO intensity parameters were calculated considering only the coordinated atoms to Eu_1 center. There is good agreement between the experimental and calculated JO intensity parameters (Table 3) indicating that the proposed overall ground state geometry is acceptable. In order to evaluate the JO intensity parameters of the Eu_2 center, the overall JO intensity parameters ($\boldsymbol{Eu_{total}^{exp}}$) were determined using the europium(III) steady-state emission spectrum, then equation 3 was used to infer the JO values of the Eu_2 center and the experimental values of Ω_2 and Ω_4 of both Eu_1 and Eu_2 were used as a reference for the evaluation of the theoretical ground state geometry (Figure 2). The Ω_2 parameter of the Eu_2 is larger than Eu_1 (Table 3), indicating that the former is situated in a lower symmetric chemical environment than Eu_1 center. One may note that the experimental ($\boldsymbol{Eu_2^{exp}}$) and theoretical ($\boldsymbol{Eu_2^{theo}}$) values of Ω_4 and A_{nrad} are significantly different. That discrepancy probably indicates an important role of the poly glycol chain of the ligands over the photophysical parameters of the Eu_2 center that could not properly be predict because of geometry distortion and/or water molecules entrapped in this chain. These entrapped water molecules may be close enough to Eu_2 center promoting non-radiative routes.

The complex in acetonitrile solution also has two emission lifetime values, 1.60 ± 0.02 ms (Eu_1) and 0.77 ± 0.02 ms (Eu_2). The Horrocks equation (equation 1) indicates that there are no coordinated water molecules to Eu_2 center and, therefore, probably two acetonitrile molecules are coordinated to Eu_2, as also showed by Kumar and collaborators.[41] As it was done in solid state, the minimum delay time necessary to eliminate the Eu_2 center emission was calculated by adjusting the equations

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from the emission lifetime decay curves (ESI-Figure S8). However, the delay time necessary would be 15.5 ms and using this delay it was not possible to obtain a resolved emission spectrum to proceed with the JO intensity parameters determination for each europium(III) center. Therefore, the steady-state emission spectrum was used to determine the JO parameters and the both europium centers were adjusted to these values showing a good agreement between experimental and theoretical JO intensity parameters in acetonitrile solution.

This result corroborates with that obtained in solid state sample, suggesting again that the proposed overall ground state geometry is reasonable.

Table 3. Experimental and theoretical JO intensity parameters (Ω_2 and Ω_4), radiative emission rate (A_{rad}), of the europium(III) complexes in the solid state or dissolved in acetonitrile or water.

	Solid State					Acetonitrile Solution		
	$\boldsymbol{Eu_{total}^{exp}}$	$\boldsymbol{Eu_1^{exp*}}$	$\boldsymbol{Eu_1^{theo}}$	$\boldsymbol{Eu_2^{exp**}}$	$\boldsymbol{Eu_2^{theo}}$	$\boldsymbol{Eu_{total}^{exp}}$	$\boldsymbol{Eu_1^{theo***}}$	$\boldsymbol{Eu_2^{theo***}}$
Ω_2 x10^{-20} cm²	15.69	12.55	12.55	21.67	23.26	16.12	17.06	16.12
Ω_4 x10^{-20} cm²	5.94	2.61	2.61	12.28	5.76	8.07	4.41	8.07
Ω_6 x10^{-20} cm²	---	---	0.1622	---	0.443	---	0.1630	0.3385
A_{rad}	612.9	466.1	465.5	892.4	834.9	479.5	447.7	467.2
A_{nrad}	1826.1	411.1	411.7	4519.7	1604.1	145.5	177.4	831.5

* The $\boldsymbol{Eu_1^{exp}}$ was determined from time-resolved emission spectra using a delay time of 6.5 ms. ** The values were calculated using equation 3. *** The Eu_1^{theo} and Eu_2^{theo} values were adjusted to $\boldsymbol{Eu_{total}^{exp}}$, that was obtained from steady-state emission spectrum.

When the [$Eu_2(mee)_6(H_2O)_2$] complex is solubilized in water the emission band attributed to $^5D_0 \rightarrow {}^7F_2$ transition has almost the same intensity as the $^5D_0 \rightarrow {}^7F_1$ one and the band attributed to $^5D_0 \rightarrow {}^7F_4$ transition is intensified indicating a modification of the microsymmetry around europium(III) ion. There is also a decrease of the emission lifetime when the europium(III) complex is dissolved in water, compared to solid state or acetonitrile, Table 2. The modification of the microsymmetry and the emission lifetime decrease might be an indication of ligands exchange by water molecules. In order to verify this indication, the emission spectra were obtained in different ratios of water:acetonitrile solution (Figure 4).

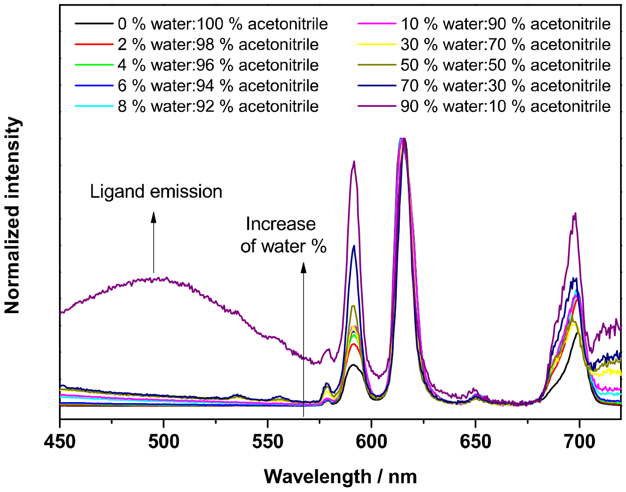

Figure 4. Emission spectra of the europium(III) complex in different water:acetonitrile volume ratios indicated in the figure. The measurements were done after 48 h of the solution preparation.

Another indication of the replacement of the ligand by water molecules is the appearance of the broad emission band between 450 – 575 nm that may attributed to the ligand. If the ligand is non-coordinated or even mono-coordinated to the europium(III), the energy transfer to the europium(III) is reduced and the broad band due to ligand phosphorescence appears. This data agrees with emission lifetime decay curves

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and also with data obtained by ESI-MS (ESI-Figures S5-S7) that indicates a 1Ln:3mee molar ratio. Therefore, the complex dissolution in water probably breaks up the dinuclear unit and subsequently promotes the exchange of part of the ligands by water molecules. A close examination of the theoretical coordination polyhedral (Figure 2) shows that the oxygens from carboxylate group bonded as chelate/bridging modes (Figure 2: oxygens 6 and 8) have long bond distances (2.512 and 2.519 Å) that are similar to the bond distance (2.512 Å) between the water oxygen (Figure 2: oxygen 1) and europium(III) ion. The long distances between these bridging oxygens and the central ion together with the hydrophilic nature of the poly glycol chains may explain the instability of the complex into water solution, being the ligand solvated by water.

The increase of the number of coordinated water molecules (*q*) as a function of the percentage of water into acetonitrile solution was calculated using Equation 1. The correlation between the emission lifetime (τ) and the coordinated water molecules (*q*) is shown in Figure 5.

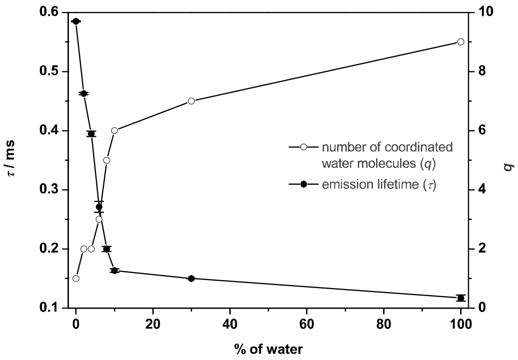

Figure 5. Correlation between the emission lifetime (τ) and the number of coordinated water molecules (*q*) of the $[Eu(mee)_3(H_2O)_n]$ complexes as a function of the amount of the percentage of water into acetonitrile solution.

The data (Figure 5) indicates an increase in the number of coordinated water molecules in the europium(III) complex, explaining the low emission lifetime value in water (Table 2), as the O–H oscillators close to the lanthanide(III) are efficient emission quenchers. The high number of coordinated water molecules obtained for 100% water solution indicate that majority of the ligand molecules were replaced by water. Kumar and co-workers also observed a decrease in the emission lifetimes values for the $[Eu(ba)_3]$ complex (ba = benzoic acid) by increasing water concentration in acetonitrile.[41]

The energy transfer rates (Table 4) from ligand to europium(III) ion, were calculated for the europium(III) complex using the software LUMPAC (version 1.2.0).[26] The energy transfer rates from the ligand to the lanthanide excited levels are higher than the back-transfer ones. However, the combination of the high value of the R_L parameter (from 5.5393 Å to 7.0475 Å) with the high energy of the triplet level (25,606 cm^{-1}) leads to low energy transfer rates ligand → Eu^{III} and, consequently a low relative quantum yields (Table 2). The transfer and back transfer rates calculated for Eu_2 in the solid state or in acetonitrile solution are smaller than that one calculated to Eu_1 center. This can be justified by the higher values of R_L parameter related to Eu_2 than Eu_1 center.

Table 4. Transfer and back energy transfer rates between the ligand triplet level and $^5D_1$ and $^5D_0$ europium(III) levels, calculated from the ground state geometries provided by Sparkle/PM3.

		Solid State		**Acetonitrile Solution**	
	$[Eu(abz)_3(H_2O)_2].3/2H_2O$[32]	**Eu_1**	**Eu_2**	**Eu_1**	**Eu_2**
$T \rightarrow {}^5D_1$ / s^{-1}	$4.8x10^8$	$4.5x10^1$	$1.8x10^1$	$6.8x10^2$	7.8
${}^5D_1 \rightarrow T$ / s^{-1}	$1.2x10^{-5}$	$3.3x10^{-5}$	$1.1x10^{-6}$	$3.3x10^{-5}$	$4.3x10^{-7}$
$T \rightarrow {}^5D_0$ / s^{-1}	$8.3x10^7$	$3.8x10^2$	$1.3x10^1$	$4.3x10^2$	5.6
${}^5D_0 \rightarrow T$ / s^{-1}	$4.6x10^{-10}$	$5.7 x10^{-9}$	$2.0x10^{-10}$	$5.8x10^{-9}$	$7.5x10^{-11}$
R_L / Å	5.5235	5.5782	6.7098	5.5393	7.0475

* reference 31 used the first LUMPAC version.

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Conclusions

In summary, a new series of water-soluble luminescent binuclear lanthanide complexes (Eu^{III}, Gd^{III} and Tb^{III}) were prepared. The ligand coordinates to the lanthanide(III) through the mixed bridging and bidentate chelate mode, as determined by FT-IR and indicated by comparing the experimental and theoretical photophysical parameters determined from ground state geometry, that was calculated using the Sparkle/PM3 model. Both europium(III) and terbium(III) complexes are luminescent in water solution. The decrease of the band intensity attributed to $^5D_0 \rightarrow {}^7F_2$ transition in aqueous solution when compared with the solid, indicates that there is an increase in the microsymmetry around the europium(III) when it is dissolved in water. The decrease of the emission lifetime in aqueous solution and the changes of emission profile in several ratio of acetonitrile:water solutions indicates the replacement of the coordinated ligands by water molecules. The increase of coordinated water molecules (q) was confirmed using the well-established Horrocks equation. The relative quantum yield of sensitized emission is higher in acetonitrile than in water, due to the quenching effect of the O–H oscillators. The transfer and back energy transfer rates were calculated using the LUMPAC software and the values obtained for energy transfer rates are lower than previous values obtained for europium(III) complexes with benzoic acid derivative ligands, indicating the role of the poly glycol chain attached to benzoic acid on photophysical properties of the $[Eu_2(mee)_6(H_2O)_2]$ complex.

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