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Article

Visible and Near-Infrared Intense Luminescence from Water-Soluble Lanthanide [Tb(III), Eu(III), Sm(III), Dy(III), Pr(III), Ho(III), Yb(III), Nd(III), Er(III)] Complexes

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The synthesis of a new ligand (**1**) containing a single phenanthroline (phen) chromophore and a flexibly connected diethylenetriamine tetracarboxylic acid unit (DTTA) as a lanthanide (Ln) coordination site is reported [**1** is 4-[(9-methyl-1,10-phenantrol-2-yl)methyl]-1,4,7-triazaheptane-1,1,7,7-tetraacetic acid]. From **1**, an extended series of water-soluble Ln·**1** complexes was obtained, where Ln is Eu(III), Tb(III), Gd(III), Sm(III), Dy(III), Pr(III), Ho(III), Yb(III), Nd(III), and Er(III). The stoichiometry for the association was found 1:1, with an association constant $K_A \geq 10^7$ s^{-1} as determined by employing luminescence spectroscopy. The luminescence and photophysical properties of the series of lanthanide complexes were investigated in both H_2O and D_2O solutions. High efficiencies for the sensitized emission, ϕ_{se}, in air-equilibrated water were observed for the Ln·**1** complexes of Eu(III) and Tb(III) in the visible region ($\phi_{se} = 0.24$ and 0.15, respectively) and of Sm(III), Dy(III), Pr(III), Ho(III), Yb(III), Nd(III), and Er(III) in the vis and/or near-infrared region [$\phi_{se} = 2.5 \times 10^{-3}$, 5×10^{-4}, 3×10^{-5}, 2×10^{-5}, 2×10^{-4}, 4×10^{-5}, and (in D_2O) 4×10^{-5}, respectively]. For Eu·**1** and Tb·**1**, luminescence data for water and deuterated water allowed us to estimate that no solvent molecules (q) are bound to the ion centers ($q = 0$). Luminescence quenching by oxygen was investigated in selected cases.

Introduction

Stable complexes of luminescent trivalent lanthanide ions Ln(III)[1−3] are studied because of a wide range of potential uses. A useful way to sensitize the luminescence of lanthanide ions is to employ organic chromophores (L) as antennas for light absorption ($\epsilon \approx 10^4-10^5$ M^{-1} cm^{-1} [4]).[1,2,5−7] The overall efficiency of Ln(III)-sensitized emission (ϕ_{se}) consequent to the light absorption event is regulated by the intersystem-crossing efficiency (ϕ_{isc}), the energy-transfer efficiency (ϕ_{en}), and the intrinsic luminescence quantum yield of the Ln(III) ion (ϕ_{lum}^{MC}), eq 1.

$$\phi_{se} = \phi_{isc}\phi_{en}\phi_{lum}^{MC} \tag{1a}$$

$$\phi_{lum}^{MC} = \frac{k_r}{k_r + k_{nr}} \tag{1b}$$

In water, the 8 and 9 coordination positions of Ln(III) must be conveniently shielded against the intervention of solvent molecules to inhibit nonradiative deactivation (as enhanced by interaction with OH oscillators[1,8]), eq 1b; k_r and k_{nr} are radiative and nonradiative rate constants, respectively.[1,9,10] Strategies for the building up of complexes have relied on

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the use of chelating ligands such as polyaminopolycar-boxylates,[11,12] cryptands,[2] calixarenes,[13,14] podands,[15] and helicates,[16,17] with appended a few chromophoric units both to contribute to coordination and to act as antennas.

We have previously shown that a conceptually simple two-component ligand system L, constituted from a *single* phenanthroline (phen) chromophore flexibly linked via a methylene bridge to a tetraazacyclodedodecane−triacetic acid unit, DO3A, as a highly effective hosting unit for the Ln(III) cation,[18] results in $\phi_{se} = 0.21$ and 0.11 for Eu·L and Tb·L (in air-equilibrated water), respectively.[19,20] Reasons for this behavior are traceable back to the fact that (i) the ISC step for phenanthroline takes place with $\phi_{ISC} \gg 0.85$ (actually, not far from unity) within the complex,[19] (ii) the rate constant for energy transfer step is $k_{en} \approx 10^7$ s^{-1}, which compared to a deactivation rate constant $k_T \sim 3 \times 10^4$ s^{-1} for the T level results in $\phi_{en} \sim$ unity, and (iii) the phen moiety cooperates to fill the coordination sphere around the cation so that no water molecules (q) are directly bound to the Ln(III) center, $q = 0$. It is noticed that a similar approach led to Eu(III)−DO3A systems where the *single* chromophore to act as antenna is acetophenone (however, q was 1).[21]

When the Ln(III) complexes exhibit intense luminescence, a wide range of applications become possible, particularly for near-infrared (NIR) lanthanide emitters such as Sm(III), Dy(III), Pr(III), Ho(III), Yb(III), Nd(III), and Er(III).[22−30] For instance, NIR luminescence from ions such as Pr(III) and Er(III) proves very useful when employed in telecommunication network optical signal amplifiers.[31,32] Regarding Nd(III) species, for long this center has found applications within laser systems.[33,34]

Here we present results concerned with a newly prepared water-soluble two-component system, ligand **1**, Scheme 1 [**1** is 4-[(9-methyl-1,10-phenantrol-2-yl)methyl]-1,4,7-triaza-heptane-1,1,7,7-tetraacetic acid]. **1** features a combination of a single phenanthroline chromophore and a diethylenetri-amine tetracarboxylic unit (DTTA) hosting site, expected to provide highly stable complexes.[35−37] The coordination positions of the Ln(III) center are protected against solvent access, as shown by the comparison of luminescence results obtained in water and deuterated water (vide infra). We provide evidence that, for the 1:1 species obtained with ligand **1** ($K_A > 10^7$ M^{-1}; see below), the luminescence sensitization process in air-equilibrated water is quite effective, resulting in $\phi_{se} = 0.24$ and 0.15 for the visible emitters Eu·**1** and Tb·**1**, respectively; $\phi_{se} = 2.5 \times 10^{-3}$, 5×10^{-4}, 3×10^{-5}, and 2×10^{-5} for the vis and NIR emitters Sm·**1**, Dy·**1**, Pr·**1**, and Ho·**1**, respectively, and $\phi_{se} = 2 \times 10^{-4}$, 4×10^{-5}, and 4×10^{-5} for the exclusively NIR emitters Yb·**1**, Nd·**1**, and (in deuterated water) Er·**1**, respectively.

Experimental Section

Materials and Methods. Solvents were purified by using standard methods and dried if necessary. All commercially available reagents were used as received. TLC was carried out on silica gel Si 60-F$_{254}$. Column chromatography was carried out on silica gel Si 60, mesh size 0.040−0.063 mm (Merck, Darmstadt, Germany). ^{1}H NMR (300 MHz) spectra were recorded with a Bruker AC 300 spectrometer. Elemental analyses were performed by the Departmental Service of Microanalysis (University of Milan). Melting points (uncorrected) were determined with a Buchi SMP-20 capillary melting point apparatus. Scheme 1 provides an outline of the synthetic steps to preparation of ligand **1**.

4-(Benzyl)-1,4,7-triazaheptane-1,1,7,7-tetraacetic Acid Tetrakis(1,1-dimethylethyl) Ester (2). A suspension of benzylamine (0.17 g, 1 mmol), *N*-(2-bromoethyl)imminodiacetic acid bis(1,1-dimethylethyl) ester, and sodium carbonate (0.318 g, 3 mmol) in 20 mL of acetonitrile was refluxed 24 h under magnetic stirring. The mixture was cooled at room temperature and filtered on a fritted glass, and the filtrate was evaporated to afford a residue. This product was dissolved in 50 mL of CH$_2$Cl$_2$ and washed with water (2 × 30 mL). The solvent was removed under reduced pressure and the product purified by column chromatography (silica gel, 95/5 CH$_2$Cl$_2$/MeOH) to afford 0.590 g (90%) of **2** as a light yellow very thick oil. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.25 (5H, m), 3.65 (2H, s), 3.39 (8H, s), 2.87 (4H, m), 2.66 (4H, m), 1.45 (36H, s). MS-FAB+: calcd for C$_{35}$H$_{59}$N$_3$O$_8$, m/z = 649; found, m/z 649 [M].

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Scheme 1. Outline of Synthetic Paths
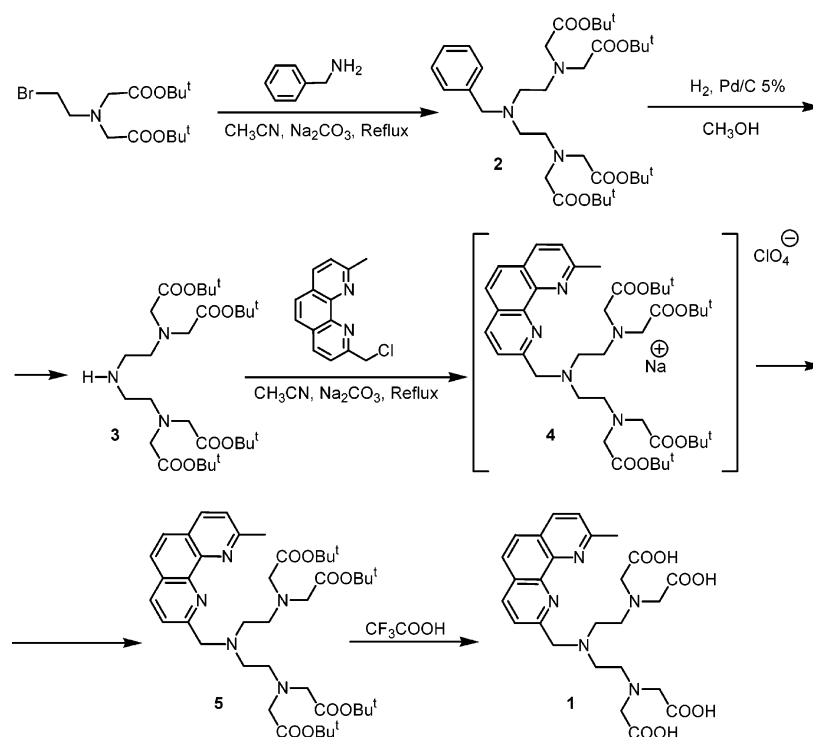
1,4,7-Triazaheptane-1,1,7,7-tetraacetic Acid Tetrakis(1,1-dimethylethyl) Ester (3). A mixture of **2** (0.633 g, 9.8 mmol) in 20 mL of methanol containing 0.22 mL of glacial acetic acid and 5% Pd/C (0.1 g) was hydrogenated at room temperature and ambient pressure. The absorption of hydrogen stopped after 3 h. The reaction mixture was filtered over Celite, the solid washed with methanol (20 mL), and the filtrate evaporated under reduced pressure. The residue was dissolved in 100 mL of CH_2Cl_2 and carefully washed with aqueous 5% $NaHCO_3$ and then with water (2×30 mL). The solvent was evaporated to afford 0.535 g (98%) of a yellow viscous oil. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.42 (8H, s), 2.84 (4H, t. $J = 6.3$ Hz), 2.66 (4H, t. $J = 6.3$ Hz), 1.44 (36H, s).

4-[(9-Methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7-triazaheptane-1,1,7,7-tetraacetic Acid Tetrakis(1,1-dimethylethyl) Ester Sodium Perchlorate Complex (4). A suspension of 9-(chloromethyl)-10-methyl-1,10-phenanthroline (0.153 g, 0.58 mmol), 1,4,7-triazaheptane-1,1,7,7-tetraacetic acid tetrakis(1,1-dimethylethyl) ester (3) (0.324 g, 0.58 mmol), and sodium carbonate (0.254 g. 2.3 mmol) in 20 mL of acetonitrile was refluxed 72 h under magnetic stirring. The mixture was cooled at room temperature and filtered on a fritted glass, and the filtrate was evaporated to afford a residue. This product was dissolved in 100 mL of CH_2Cl_2 and washed with water (2×30 mL) and then with aqueous 30% $NaClO_4$ (3×50 mL). The solvent was removed under reduced pressure and the product purified by column chromatography (silica gel, 95/5 CH_2Cl_2/MeOH) to afford a light brown solid that after trituration with 200 mL of boiling hexane give 0.306 g (69%) of 4 as white solid. Mp: 61.5−63 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.33 (1H, d, $J = 8.4$ Hz), 8.22 (1H, d, $J = 8.4$ Hz), 7.80 (2H, s), 7.68 (1H, d, $J = 8.4$ Hz), 7.58 (1H, d, $J = 8.4$ Hz), 4.14 (2H, s), 3.20 (8H, s), 2.88 (3H, s), 2.86 (4H, m), 2.74 (4H, m), 1.31 (36H, s).

^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) 172.5, 159.0, 145.0, 138.3, 137.6, 128.4, 127.6, 126.8, 125.9, 124.7, 123.3, 82.6, 60.7, 56.3, 54.3, 52.6, 28.3. MS-FAB+: calcd for $C_{42}H_{63}N_5O_8 \cdot NaClO_4$, $m/z = 888$; found, $m/z = 788$ ([M −ClO$_4$]$^+$).

4-[(9-Methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7-triazaheptane-1,1,7,7-tetraacetic Acid Tetrakis(1,1-dimethylethyl) Ester (5). Compound **4** (0.270 g, 0.304 mmol) dissolved in methanol (30 mL) was stirred overnight at room temperature in the presence of solid KCl (0.23 g, 3 mmol). The suspension was filtered through Celite, and the solvent was removed under reduced pressure. The residue dissolved in CH_2Cl_2 (50 mL) was washed with water (4×50 mL), and the solvent was evaporated under reduced pressure to afford 0.230 g (99%) of a light yellow viscous oil. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.18 (1H, d, $J = 8.4$ Hz), 8.12 (1H, d, $J = 8.4$ Hz), 7.95 (1H, d, $J = 8.4$ Hz), 7.71 (2H, s), 7.48 (1H, d, $J = 8$. Hz), 4.33 (2H, s), 3.42 (8H, s), 2.90 (11H, m), 1.39 (36 H, s). ^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) 170.5, 159.8, 145.0, 144.8, 136.6, 136.0, 127.5, 126.5, 125.6, 125.2, 123.2, 122.1, 81.3, 61.2, 55.7, 53.0, 51.7, 50.6, 27.8. MS-FAB(+): calcd for $C_{42}H_{63}N_5O_8$, $m/z = 765$; found, $m/z = 766$ ([M + H]$^+$).

4-[(9-Methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7-triazaheptane-1,1,7,7-tetraacetic Acid (1). A solution of **5** (0.38 g, 0.5 mmol) in 10 mL of trifluoroacetic acid was stirred at room temperature for 4 h. The solvent was evaporated, and the crude was triturated with diethyl ether to yield a white solid. The solvent was separated, and the residue, dissolved in 2 mL of water, was adsorbed on a short Amberlite XAD 1600T column which was eluted with water until the pH was neutral and then with 8/2 (v/v) water/acetonitrile to recovery 0.24 g (90%) of product as white solid. ^{1}H NMR (CD$_3$OD, 300 MHz): δ 8.72 (1H, d, $J = 8.4$ Hz), 8.53 (1H, d, $J = 8.2$ Hz); 8.03 (2H, s), 7.95 (1H, d, $J = 8.4$ Hz), 7.91 (1H, d, $J = 8.4$ Hz), 4.70 (2H, s), 3.66 (8H, s), 3.40 (4H, m), 3.30 (4H, m), 3.03 (3H, s).

^{13}C NMR (CD$_3$OD, 75 MHz): δ (ppm) 173.0, 160.0, 156.6, 143.0, 142.2, 141.3, 139.3, 130.3, 129.1, 128.5, 127.3, 126.8, 126.2, 57.3, 52.1, 51.9. MS-FAB(+): calcd for $C_{26}H_{31}N_5O_8$, $m/z = 541$; found, m/z 542 ([M + H]$^+$).

4-[(9-Methyl-1,10-phenanthrol-2-yl)methyl]-1,4,7-triazaheptane-1,1,7,7-tetraacetic Acid (1)−Eu(III) Complex. The complexes for the optical spectroscopic studies were prepared by titration of **1** with Ln(III) cations; see below. A detailed preparation and characterization procedure is reported here only for Eu·**1**. A solution of EuCl$_3$·6H$_2$O (20 mg, 0.055 mmol) in 3 mL of H$_2$O was

slowly added to a solution of ligand **5** (30 mg, 0.055 mmol) in 20 mL of water, maintained at room temperature and under magnetic stirring, controlling the pH at 6.5 by simultaneous addition of diluted aqueous NaOH solution. When the addition was complete, the reaction mixture was heated at reflux for 4 h. The reaction mixture was then concentrated in vacuo at 2 mL, and the product was purified by column chromatography on Amberlite XAD 1600T eluting with water and 9/1 water/acetonitrile to afford 30 mg (78%) of a white solid. MS-FAB(+): calcd for $C_{26}H_{27}N_5O_8Eu$, $m/z = 713$; found, $m/z = 717$ ([M + H]$^+$). Anal. Calcd for $C_{26}H_{27}N_5O_8$-Eu·3H$_2$O: C, 41.0; H, 4.3; N, 9.8. Found: C, 40.3; H, 4.8; N, 10.0. MS-FAB(+): calcd for $C_{26}H_{27}N_5O_8EuNa$, $m/z = 713$; found, $m/z = 714$ ([M + H]$^+$). Anal. Calcd for $C_{26}H_{27}N_5O_8EuNa$·3H$_2$O: C, 40.74; H, 4.34; N, 9.14. Found: C, 40.35; H, 4.53; N, 9.61.

Spectroscopic Measurements. Lanthanide salts were commercially available (Aldrich, Ln(III) chloride hexahydrate, 99.9% purity). The spectroscopic investigations were carried out in triply distilled water from Millipore Milli-RO 15 purification system and D$_2$O (Carlo Erba, 99.8% isotopically pure) solutions. Absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer. For luminescence experiments, the samples were placed in fluorometric 1-cm path cuvettes and, when necessary, purged from oxygen by bubbling with argon. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a peltier-cooled Hamamatsu R928 photomultiplayer tube (185−850 nm). The steady-state NIR luminescence spectra were obtained with an Edinburgh FLS920 spectrometer equipped with Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator with NIR grating blazed at 1000 nm. An Edinburgh Xe900 450 W xenon arc lamp was used as exciting light source. Corrected spectra were obtained via a calibration curve supplied with the instrument. Luminescence quantum yields (ϕ) obtained from spectra on a wavelength scale (nm) were measured for each sample (S) by using eq 2[38]

$$\phi_S = \phi_R \left(\frac{\text{Abs}_R}{\text{Abs}_S}\right)\left(\frac{\eta_S^2}{\eta_R^2}\right)\left(\frac{A_S}{A_R}\right) \quad (2)$$

where Abs is the absorbance value at the excitation wavelength, η the refraction index of the solvent, and A the wavelength-integrated area of the corrected emission spectrum. An aqueous air-equilibrated solution of [Ru(bpy)$_3$]Cl$_2$ ($\phi = 0.028$) was used as reference (R) compound.[39]

Lanthanide complex solutions were obtained upon addition of 1 equiv of Ln(Cl)$_6$·6H$_2$O to a water solution of **1** in which were previously added 4 equiv of TBA (tetrabutylammonium hydroxide) to deprotonate the carboxylic groups of the chelating ligand. The stoichiometry of the association between **1** and the lanthanide ions was 1:1, as evaluated by titration experiments in which the metal-centered emission intensity of the forming Ln·**1** complexes was monitored; the experiments were performed for 2×10^{-5} M water solution of ligand **1** by using concentrated solutions ($\approx 10^{-3}$ M) of lanthanide salts. For illustration purposes, insets a and b of Figure 1 show results for the case of Eu·**1**; in the insets, I is luminescence intensity observed at 616 nm (corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition, which appears as the strongest luminescent band[40] when no phototube correction for the fluorometer is taken into account). Inset b provides evidence for the 1:1 association, and the full line
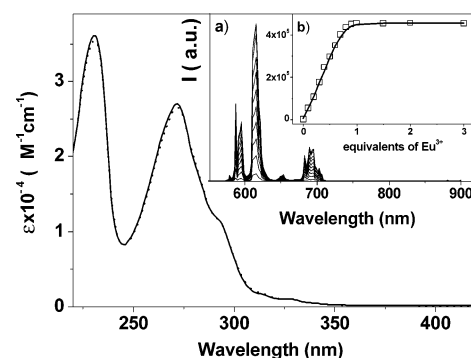
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Figure 1. Absorption spectra of **1** (solid line) and Eu·**1** (dashed line) in H$_2$O solutions. Inset a presents a luminescence titration of **1** in water solution upon addition of aliquots of EuCl$_3$(H$_2$O)$_6$; $\lambda_{exc} = 279$ nm. Inset b presents luminescence intensity changes detected at $\lambda_{em} = 616$ nm. The full line results from the fitting procedure; see text.

results from a fitting procedure in accord with eq 3[41,42]

$$I = I_0 + \frac{\Delta I}{2S_0}[K_{\text{diss}} + X + S_0 - \sqrt{(K_{\text{diss}} + X + S_0)^2 - 4XS_0}] \quad (3)$$

where I_0 and ΔI are the initial luminescence intensity and the its final increase, respectively, as observed at 616 nm, K_{ML} is the association constant, and $K_{\text{diss}} = 1/K_{ML}$; finally, X and S_0 are the titrant and ligand concentrations, respectively. Results of titration experiments always indicated that the 1:1 association takes place with $K_{ML} \geq 10^7$ M^{-1}. Similar results were obtained for other Ln·**1** complexes in the series.

Emission lifetimes on the nanosecond time scale were determined with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the range 2−40 kHz (λ_{exc} = 337 nm, 0.5 ns time resolution); the detector was a red-sensitive (185−850 nm) Hamamatsu R-3237-01 photomultiplier tube. For the emission in the visible region, the luminescence lifetimes in the microsecond−millisecond scales were measured by using a Perkin-Elmer LS-50B spectrofluorometer equipped with a pulsed xenon lamp with variable repetition rate and elaborated with standard software fitting procedures (Origin 6.1). The near-IR emission lifetimes were obtained by using the fourth harmonic (266 nm) of a Nd:YAG laser (JK Lasers) with 20 ns pulse and 1−2 mJ of energy/pulse as source. The detector consisted of liquid-nitrogen-cooled germanium and preamplifier (Northcoast Scientific Corp. model EO-817L). To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz dewar, filled with liquid nitrogen. Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for emission quantum yields, and ±2 and ±5 nm for absorption and emission peaks, respectively.

Results and Discussion

Design and Synthesis of Ligand 1. Bipartite ligand **1**, Scheme 1, features a phenanthroline unit as the light-absorbing chromophore, which is covalently connected through a methylene spacer to a diethylenetriamine tetra-carboxylic acid unit, DTTA, as the lanthanide coordination site. This chromophore was selected because (i) it exhibits good absorbing properties ($\epsilon = 27\,000$ M^{-1} cm^{-1} at 279

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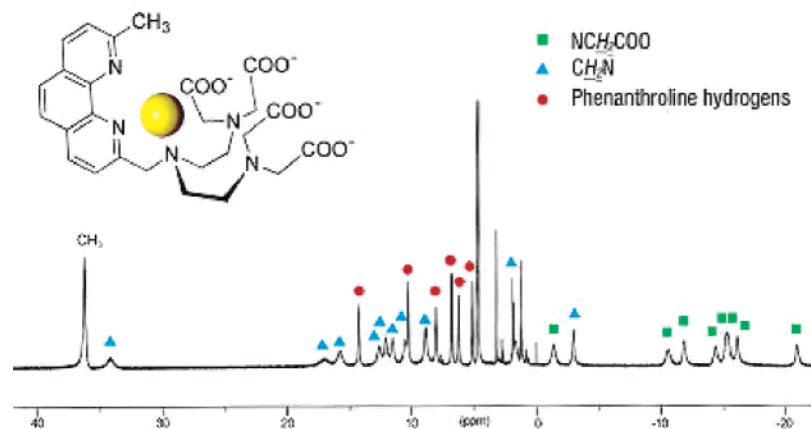
Figure 2. ^{1}H NMR spectrum of Eu·**1** in CD$_3$OD at 293 K.

nm; see Figure 1), (ii) the ISC step takes place with $\phi_{ISC} \gg$ 0.85 (actually, not far from unity within the complex[19]), and (iii) the energy transfer step occurs with $k_{en} \approx 10^7$ s^{-1}, which favorably competes against the triplet deactivation, $k_T \sim 3 \times 10^4$ s^{-1}, resulting in $\phi_{en} \sim$ unity.[19,20] DTTA was selected as a hosting site because of the well-assessed thermodynamic and kinetic stabilities of its lanthanide complexes.[35]

The synthesis of **1** was carried out as outlined in Scheme 1. The bis alkylation of benzylamine with *N*-(2-bromoethyl)-iminodiacetic acid bis(1,1-dimethylethyl) ester[43] was carried out in acetonitrile at reflux and in the presence of Na$_2$CO$_3$ solid as base and afforded 90% yield of **2** after purification by column chromatography. This product was readily hydrogenated in methanol solution at room temperature and pressure with a catalytic amount of 5% Pd/C to afford pure **3**. Alkylation of **3** with 2-(chloromethyl)-9-methyl-1,10-phenanthroline[19] was performed in CH$_3$CN at reflux in the presence of Na$_2$CO$_3$ as base, and subsequent treatment of the crude, dissolved in CH$_2$Cl$_2$, with aqueous NaClO$_4$ afforded the sodium complex **4** isolated in 69% yield after column chromatography. The preparation of **4** is necessary to simplify the chromatographic purification and to allow higher yields of isolated product. Decomplexation of **4** was achieved by continuous extraction of the complex, after Cl$^-$ for ClO$_4^-$ counterion exchange, in H$_2$O/methanol = 9/1 (v/v) with *n*-pentane to give pure **5** as light yellow viscous oil in quantitative yield. Treatment of **5** with CF$_3$-COOH, at room temperature, afforded the desired ligand **1** as a white solid in 90% yield after purification through an Amberlite XAD 1600T column.

Structural Investigation by ^{1}H NMR Spectroscopy. The search for ligands capable of forming lanthanide chelates with high thermodynamic and kinetic stability is a lively (and boundless) area of investigation. Diethylene triamine pentacarboxylic acid, DTPA, behaves as an octadentate ligand and is known to form lanthanide complexes with 1:1 stoichiometry.[35] The three nitrogen atoms and the five carboxylate groups coordinate the metal cation giving a tricapped trigonal prism (TTP) geometry in which the ninth position is occupied by a water molecule. On the basis of the helicity of C−C ethylenic bond with respect to the

N−Ln−N plane, two enantiomeric species $\lambda\lambda$ and $\delta\delta$ can be envisaged, with the interconversion process occurring through a recombination of acetate groups and inversion of diethylenetriamine skeleton. ^{1}H NMR investigations at variable temperature allowed determination of the activation parameters for the interconversion process undergone by Eu·DTPA complex.[44,45] For our complexes, results from ^{1}H NMR spectroscopy are consistent with replacement of an acetate arm of DTPA with a phenanthroline moiety. Figure 2 shows the ^{1}H NMR spectrum of a 0.038 M solution of Eu·**1** in CD$_3$OD at 293 K.

The spectrum is fully resolved and covers a spectral width of about 60 ppm. It is possible to observe 25 distinct signals corresponding to 25 nonequivalent protons of the complex. All the resonances have the same relative intensity with the exception of that at 38 ppm, with relative intensity 3, which is safely attributed to the CH$_3$ of the phenanthroline ligand. The low-field shift of this signal is due to the proximity of the phenanthroline residue to the paramagnetic center, and this represents a strong indication that the two nitrogens atoms are involved in the coordination of the metal cation. It is worth to stress that in the case of Eu·DTPA the ^{1}H NMR spectrum is fully resolved only at 268 K;[44,45] this indicates that the interconversion kinetic for Eu·**1** is slower. In turn, this suggests that replacement of an acetate group of DTPA with a phenanthroline unit gives rise to a stiffer system. Indeed, the calculated T_1 values of the TTA part of Eu·**1** are higher (in the range 50−70 ms) than those reported for Eu·DTPA (in the range 40−60 ms).[44,45] As the temperature is increased, partial coalescence takes place, probably due to exchange processes occurring between the two possible enantiomers of the complex. The EXSY spectrum allowed us to assign all protons, Figure 3. It also indicates that even at room temperature there is an interconversion process between the axial and equatorial hydrogens of the two enantiomeric pairs, in agreement with results for the parent Eu·DTPA.[45]

Absorption Spectra. The absorption spectra of **1** and Eu·**1** in water solution are shown in Figure 1. The spectral shapes of **1** and Eu·**1** remarkably overlap, and the two peaks

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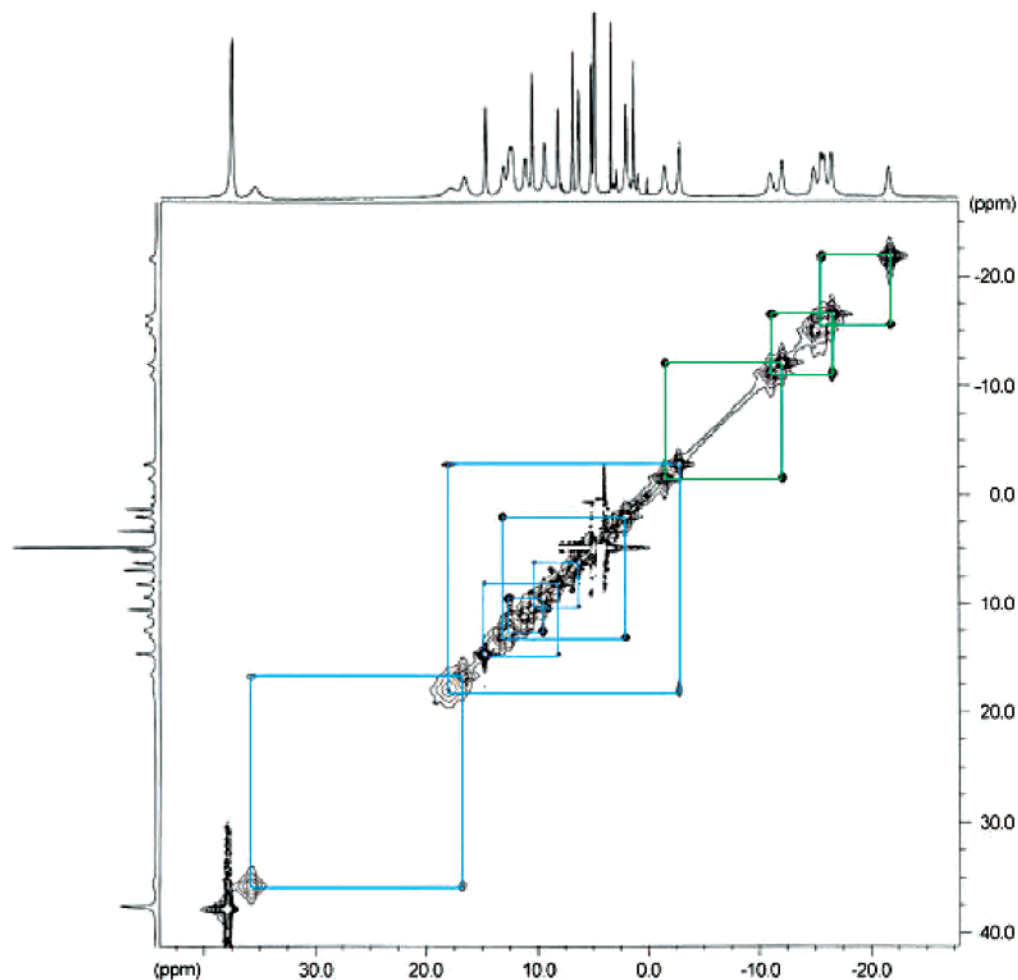(45) Aime, S.; Botta, M. *Inorg. Chim. Acta* **1990**, *177*, 101.

Figure 3. EXSY spectrum of Eu·**1** in CD$_3$OD at 293 K.

in UV region at 230 and 279 nm are ascribed a to ligand-centered transition of the phenanthroline group. Similar results were obtained for the other Ln·**1** complexes investigated. This is an uncommon outcome because the presence of triply charged ions incorporated within a complex is, among others, signaled by a change of the absorption profile of the close chromophore.[15,19] Thus, it seems that coordination of the phenanthroline moiety at Eu(III) ion (see ^{1}H NMR results above) does not actually imply a strong electronic interaction between these two centers. What is relevant, however, is that efficient sensitization of the MC luminescence takes place, as revealed by the intense luminescence observed for Eu·**1** and for the other Ln·**1** complexes studied (vide infra). Thus, the (supposedly) weak electronic interaction between the light-absorbing phen and the light-emitting Ln subunits is however sufficient to promote the occurrence of ligand-to-metal energy transfer. To our knowledge, a similar case is only reported in the literature for a Eu(III)−DO3A system with appended a single acetophenone unit.[21]

Ligand-Centered Emission. The absorption bands of lanthanide complexes are due to ligand-centered [1]LC transitions, and detectable light from lanthanide excited states deactivation originates from intersystem crossing steps (ISC) leading to population of the lowest lying triplet level (E_T) of phenanthroline origin and subsequent ligand-to-metal

intramolecular photoinduced energy transfer processes.[5−7,46] This behavior works for most complexes of lanthanides but not for Gd(III) because its lowest lying excited level ($^6P_{7/2}$ → $^8S_{7/2}$) is located at 32 150 cm^{-1},[47,48] well higher than the E_T levels of most chromophores.[4] On this basis, the luminescence study of Gd·**1** allows one to evaluate the energy levels of the lowest lying singlet (S_1) and triplet (T) excited states in the presence of a heavy and triply charged center. Figure 4 shows luminescence results for Gd·**1** as obtained at room temperature (fluorescence) and at 77 K (phosphorescence), and Table 1 lists luminescence data for the ligand-centered emission at both temperatures.

With regard to the room-temperature results as monitored at the fluorescence band for **1** ($\phi = 3.5 \times 10^{-3}$ and $\tau = 0.9$ ns) and for Gd·**1** ($\phi = 7.4 \times 10^{-4}$ and $\tau < 0.5$ ns), one draws the indication that the metal center causes an improved intersystem crossing within the complex, with respect to what happens for the phen ligand $\phi_{ISC} = 0.85$,[4,19] suggesting that for **1** $\phi_{ISC} \sim 1$. As for the 77 K results, from the highest energy peak of the phosphorescence profile, the E_T level of phenanthroline origin can be estimated to lie at 21 640 cm^{-1}

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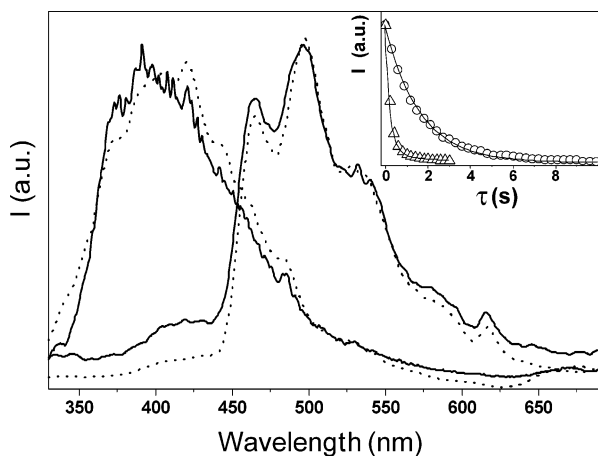
Figure 4. Fluorescence (room temperature, continuous lamp) and phosphorescence (77 K, pulsed lamp, 10 ms delay after flash) spectra of **1** (solid line) and Gd·**1** (dotted line) in water solution. OD = 0.30 at the employed λ_{exc} = 279 nm. Inset: Phosphorescence decay (pulsed lamp, 10 ms delay after flash) of **1** (empty circles) and Gd·**1** (empty triangles) in water solution at 77 K.

Table 1. Ligand-Centered Luminescence Properties in H_2O Solution[a]

	298 K			77 K	
	λ_{max} (nm)	ϕ	τ (ns)	λ_{max} (nm)	τ (s)
1	370	3.5×10^{-3}	0.9	498	1.7
Gd·**1**	380	7.4×10^{-4}	<0.5	498	0.23

[a] Fluorescence at room temperature and phosphorescence at 77 K; excitation at 279 nm.

for both **1** and Gd·**1**. The energy levels for the excited states of Tb·**1**, Eu·**1**, and Gd·**1** are 20 430, 17 000, and 32 150 cm^{-1}, respectively.

Metal-Centered Emission. The normalized luminescence spectra for complexes Eu·**1**, Tb·**1**, Sm·**1**, Dy·**1**, Pr·**1**, Ho·**1**, Yb·**1**, Nd·**1**, and Er·**1** are shown in Figure 5, as arranged according to their predominant emission region, from vis to NIR. Luminescence quantum yields and lifetimes in H_2O and D_2O solutions were obtained and are collected in Table 2. Experiments were also carried out in degassed water solution; only Tb·**1** exhibited oxygen sensitivity. Below we discuss separately a few issues.

Coordination Features. Eu·**1** and Tb·**1** showed a remarkably intense and long-lived luminescence in both H_2O and D_2O solutions, Table 2. Comparison of luminescence results for water and deuterated water provides an assessment of water binding at the Eu(III) and Tb(III) centers. This is done by using the following equations[8,23]

$$q^{Eu} = 1.2(1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.25) \tag{4}$$

$$q^{Tb} = 4.2(1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.06) \tag{5}$$

where q (uncertainty ± 0.5) is the number of coordinated solvent molecules and lifetimes are in ms. For Eu·**1**, use of eq 4 provides q^{Eu} = 0.02. For Tb·**1**, q^{Tb} = 0.01, eq 5.

These results indicate that the coordination shell of ligand **1** effectively prevents water from binding at the metal centers. Of course, this is the basic reason for the high luminescence performances of complexes Eu·**1** and Tb·**1** in water, in

agreement with the fact that OH oscillators are kept far from the metal centers and cannot act as quenchers.[8] It is interesting to notice that a potential cause of luminescence attenuation for NIR lanthanide emitters in water could be trivial reabsorption of the emitted light due to the fact that the near-IR emitters exhibit emission profiles that nicely overlap with water absorption regions. For instance, Er(III)-containing complexes (see emission profile in Figure 5 and results in Table 2) undergo complete quenching in water, and their emission can only be detected in deuterated water.[49] On the other hand, complexes whose luminescence does not overlap with the water absorption (i.e., Ho·**L** and Dy·**L**, Figure 5) show practically unchanged emission features in both solvents. Regarding the coordination features of the Sm·**1**, Dy·**1**, Pr·**1**, Ho·**1**, Yb·**1**, Nd·**1**, and Er·**1** complexes, we assume that also in these cases no solvent molecules (q = 0) are present within the first coordination sphere.

Oxygen Effect. Luminescence intensity and lifetime data in air-equilibrated and degassed water solutions of Eu·**1** and Tb·**1** were compared. For Eu·**1**, no relevant changes were noticed. By contrast, a 3-fold increase of both parameters for Tb·**1** in degassed solution was found indicating the occurrence of a quenching by oxygen molecules. As it is known for complexes incorporating the phen chromophore,[19] this effect is due a small energy gap between ligand-centered E_T levels and MC levels, see Scheme 2, so that both forward (ligand-to-metal) and backward (metal-to-ligand) energy transfer processes take place. This allows deactivation of the ligand E_T level through nonradiative quenching pathways by oxygen molecules (Scheme 2). We have modeled the room-temperature equilibrium between the E_T level of phenanthroline origin and the MC luminescent level of Tb(III) by employing the following parameters. (i) The energy gap (ΔE) between the two levels was estimated from the profiles of Figures 4 (77 K case) and 5 and was varied within the 1400 and 1550 cm^{-1} range, depending on the selected energy position (wavenumbers) of the spectral shape (i.e. initial, half or maximum). (ii) The rate constant for the E_T decay was k_P = 1/(35 μs).[4] (iii) The rate constant for diffusional quenching by oxygen was $k_q^{O_2}$ = 2.0 × 10^6 s^{-1}, as evaluated from $k_{diff}[O_2]$, with k_{diff} = 7 × 10^9 M^{-1} s^{-1} and [O_2] = 0.29 × 10^{-3} M.[4] The 3-fold changes of the luminescence features for Tb·**1** could be reproduced for k_{12} (the forward energy transfer rate constant, Scheme 2) ≈ 5$k_q^{O_2}$ [with the backward energy transfer $k_{21} = k_{12} \exp(-\Delta E/RT)$]. Accordingly, the phenanthroline → Tb(III) energy transfer step was evaluated to be k_{en} ≈ 1 × 10^7 s^{-1}.

For the all complexes but Tb·**1**, no changes of luminescence properties were appreciated for air-equilibrated and degassed samples. This behavior can be understood mainly in terms of the energetic factor, i.e., because the energy gap between ligand- and metal-centered levels is $\Delta E \gg 1500$ cm^{-1} (see discussion above for the case of Tb·**1**), too high to allow any effective back energy transfer. A distinctive reason for the lack of oxygen effect is met for the case of Dy·**1**, because the energy level of Dy(III) ($^4F_{9/2} \rightarrow {}^6H_{15/2}$,[48]

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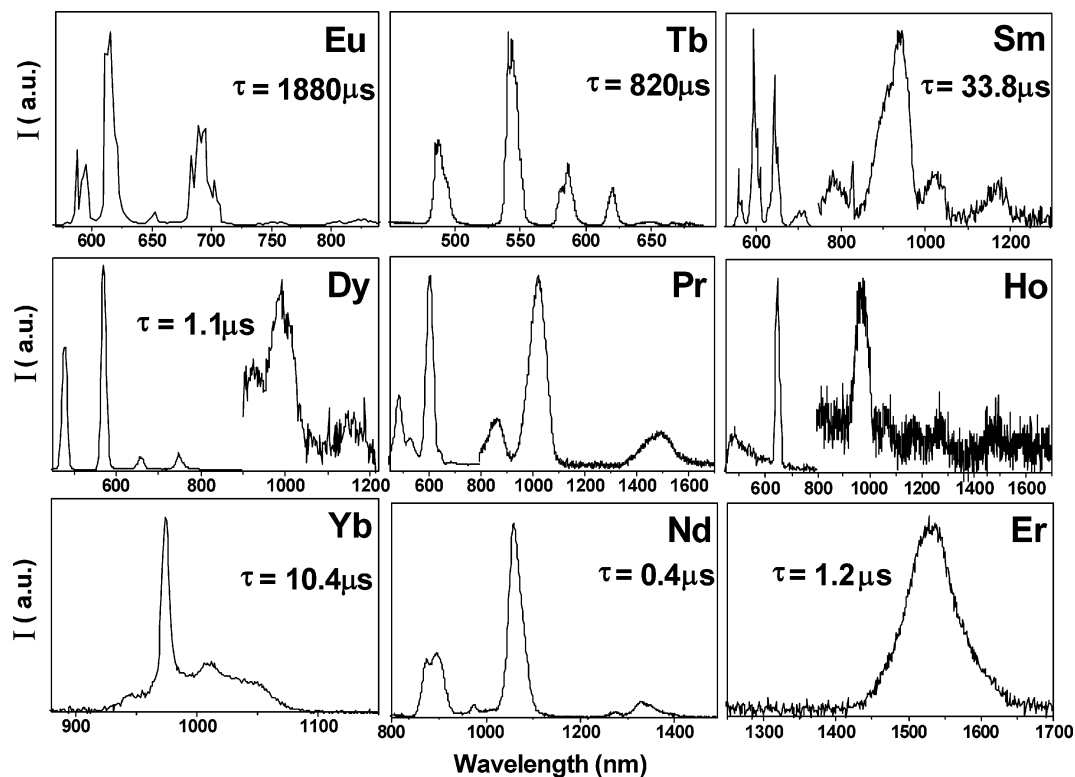
Figure 5. Room-temperature uncorrected emission spectra for the complexes of the indicated lanthanide cations, in air-equilibrated D_2O solvent. OD = 0.20 at the employed λ_{exc} = 279 nm. For each complex, intensities from vis and NIR regions are normalized. Luminescence lifetimes are indicated except for Pr·**1** and Ho·**1**; see text.

Table 2. Metal-Centered Luminescence Properties in H_2O and D_2O Solutions[a]

	H₂O			D₂O		
	λ_{max}[b] (nm)	ϕ_{se}	τ (μs)	λ_{max}[b] (nm)	ϕ_{se}	τ (μs)
Eu·**1**	616	0.24	1250	616	0.30	1880
Tb·**1**	544	0.15	780	544	0.14	820
		0.45[c]	2.3[c]			
Sm·**1**	598	2.5×10^{-3}	13.0	598	2.5×10^{-3}	34.0
Dy·**1**	478	5×10^{-4}	1.2	478	5×10^{-4}	1.1
Pr·**1**	608	3×10^{-5}	d	608	2×10^{-4}	d
Ho·**1**	650	2×10^{-5}	d	650	2×10^{-5}	d
Yb·**1**	980	2×10^{-4}	2.5	980	1×10^{-3}	10.0
Nd·**1**	1064	4×10^{-5}	<0.2	1064	2×10^{-4}	0.4
Er·**1**	1530	d	d	1530	4×10^{-5}	1.2

[a] At room temperature, excitation at 279 nm; the list is arranged according to the predominant vis/NIR emission region. [b] Highest intensity line or band. [c] Degassed solution. [d] Not detected due to weakness of the signal.

Scheme 2. Schematic Energy Levels for the Equilibrium Processes in Tb·**1** and the Effect of Dissolved Oxygen (See Text)
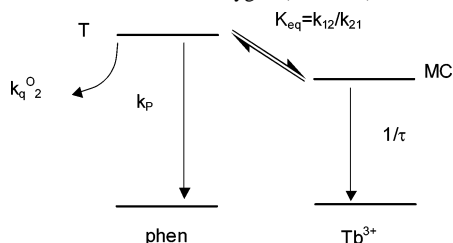
$\sim$21 100 cm^{-1}) is close-lying to that of Tb(III) ($\sim$20 600 cm^{-1}). However the two complexes exhibit opposite performances; see Table 2. In fact, for Dy·**1**, the shorter luminescence decay ($\sim$1 μs) with respect to that of Tb·**1** ($\sim$800 μs) does not allow the establishment of an equilibrium between ligand- (E_T) and Dy(III)-centered levels. For the phen $\rightarrow$ Dy(III) energy transfer step, results of model calculations

are consistent with a forward rate of $k_{12} \approx 1 \times 10^7$ s^{-1}, as for the case of Tb·**1**.

Near-Infrared Emitters and Solvent. As shown in Figure 5, Yb·**1**, Nd·**1**, and Er·**1** are real NIR-emitting lanthanide complexes. Three emission bands were observed for Nd·**1** at 880, 1060, and 1330 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, respectively), one was observed for Yb·**1** at 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$), and one was observed for Er·**1** at 1535 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$).[48,50] Instead, the emission range for Ho·**1**, Dy·**1**, Pr·**1**, and Sm·**1** includes the visible spectral portion. Emissive levels are $^5F_5$, $^4F_{9/2}$, $^3P_0$, $^1D_2$, and $^4G_{5/2}$, respectively.[48] For Yb·**1**, Nd·**1**, and Er·**1**, the emission intensities appear to strongly depend on solvent, likely due to water reabsorption effects (see discussion above). On the contrary, for Ho·**1**,

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Dy·**1**, and Sm·**1** such effects are not registered, which might be explained by the fact that their luminescence profiles fall out of water absorption regions. In the case of Pr·**1**, a relevant emission portion in the NIR region significantly contributes to the total luminescence. This likely explains why, on passing from D_2O to H_2O, a remarkable quenching factor (1 order of magnitude; Table 2) is detected. One can conclude that for the full series of complexes the observed luminescence properties strongly depend on the solvent absorption regions.

Nature of the Energy Transfer Step. As seen above, efficient phen → Ln(III) energy transfer takes place for all investigated complexes; actually on the basis of the observed or derived parameters, $\phi_{ISC}\phi_{en} \approx 1$ can be drawn (from eq 1, oxygen-free case for Tb·**1**). This result is consistent with results from ^1H NMR spectroscopy (see above), indicating that the two nitrogens atoms of phen are involved in the coordination of the metal cation. On the other hand, it is remarkable that the absorption profile for the ligand **1** does not change upon inclusion of the trivalent Ln cations, see Figure 1, as it happens usually.[15,19] A dipole−dipole (Förster-type)[51] mechanism for energy transfer seems unlikely, given that the energy transfer step involves a triplet level for the phen donor (as clearly shown by comparison of results from air-equilibrated and degassed solutions of Tb·**1**; see above). All of these observations could likely be reconciled on the basis of the notion that a very small electronic interaction is enough to permit the occurrence of Dexter-type energy transfer;[52] such a type of interaction might be mediated by the intervening sequence of bonds separating the phen chromophore and the DTTA site hosting the Ln(III) centers.

Conclusions

The preparation and emission properties of an extended series of 1:1 lanthanide complexes ($K_A > 10^7$ M^{-1}, as evaluated with luminescence spectroscopy) of the new water-soluble ligand **1** are reported. The ligand comprises a phenanthroline-like chromophore and a flexibly connected diethylenetriamine tetracarboxylic unit (DTTA) hosting site. ^1H NMR spectroscopy provides evidence for a folded structural arrangement of **1** around the Ln(III) center. The absence of solvent molecules in the first Ln(III) coordination sphere was confirmed by the study of the luminescence lifetimes in water and deuterated water solutions of Eu·**1** and Tb·**1**. Intense emissions were detected in both solvents for the series of examined complexes of **1** with Tb(III), Eu(III), Sm(III), Dy(III), Pr(III), Ho(III), Yb(III), Nd(III), and Er(III) cations consistent with cooperation of the phen and DTTA moieties to fulfill all coordination positions of the Ln(III) centers. Effects from oxygen quenching for the case of Tb·**1** and observations of luminescence attenuation by water reabsorption for cases where emission extended from the visible to the near-IR regions were discussed.

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