

## Luminescence of $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ Complexes of Two Macrobicyclic Ligands Derived from a Tetralactam Ring and a Chromophoric Antenna

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Two macrobicyclic ligands derived from an 18-membered tetralactam ring and 2,2'-bipyridine or 2,6-bis(pyrazol-1-yl)pyridine moieties, **1** and **2**, respectively, form stable complexes with  $\text{Gd}^{\text{III}}$ ,  $\text{Eu}^{\text{III}}$ , and  $\text{Tb}^{\text{III}}$  ions in aqueous solution. The ligand-based luminescence is retained in the  $\text{Gd}^{\text{III}}$  cryptates, whereas this radiative deactivation is quenched in the  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  cryptates by ligand-to-metal energy transfer, resulting in the usual metal-centered emission spectra. Singlet- and triplet-state energies, emission-decay lifetimes, and luminescence yields were measured.  $[\text{Tb} \subset \mathbf{1}]^{3+}$  cryptate shows a long luminescence lifetime ( $\tau = 1.12$  ms) and a very high metal luminescence quantum yield ( $\Phi = 0.25$ ) in comparison with those reported in the literature for  $\text{Tb}^{3+}$  complexes sensitized by a bipyridine chromophore. By comparison to  $[\text{Ln} \subset \mathbf{1}]^{3+}$ ,  $[\text{Ln} \subset \mathbf{2}]^{3+}$  presents markedly lower luminescence properties, due to worse interaction between the 2,6-bis(pyrazol-1-yl)pyridine unit and the metal ion. Moreover, the luminescent metal and the triplet ligand energy levels of  $[\text{Eu} \subset \mathbf{2}]^{3+}$  do not match. The effects of  $\text{H}_2\text{O}$  molecules coordinated to the metal centre and of thermally activated decay processes on nonradiative deactivation to the ground-state are also reported.

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**Introduction.** – The increasing interest in  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  luminescent probes is fully justified by their high sensitivity, especially in biological systems. These ions exhibit relatively efficient long-lived luminescence (ms range) when raised to their excited states, which permits easy temporal resolution from the short-lived (sub- $\mu\text{s}$  range) fluorescence background of biological materials [1].  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions are used as structural and analytical luminescent probes and stains for biomolecular systems [2], and the luminescence of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  organocomplexes is exploited in bioanalytical assays such as immunoassays, nucleic acid hybridizations, enzyme assays, or receptor assays (for recent reviews, see [3]). Lanthanide complexes have also been shown to be excellent donors in luminescence resonance energy transfer (LRET) for homogeneous immunoassays [4] and to measure both static and time-varying distances [5]. In addition, the use of macrocyclic Eu and Tb complexes as luminescent sensors for  $\text{pO}_2$ , pH and other bioactive ions has been recently reported [6].

In attempts to optimize the luminescent properties of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes, a great deal of effort has been devoted to the synthesis of a range of different ligands. Many photoactive ligands, including those based on  $\beta$ -diketones (see, *e.g.*, [7]),

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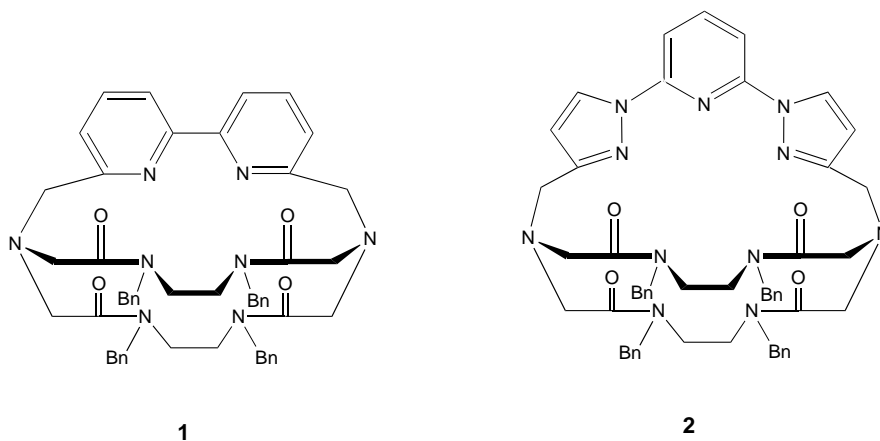
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macrocyclic structures – cryptands or branched macrocycles – (see, *e.g.*, [8]), and a number of polyamino carboxylates (see, *e.g.*, [9]) have been synthesized, and the luminescent behavior of their  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes has been investigated. Among these, particular attention has been focused on cryptands. Indeed, one of the main advantages of lanthanide cryptates may be their high thermodynamic and kinetic stability compared to dissociation at low concentration and to exchange with other ionic species [10]. This is due to the three-dimensional intramolecular cavity of the macrobicyclic ligand, which provides efficient shielding of the bound ion from interaction with solvent or other solute molecules. Such a requirement is of outstanding importance as far as biological applications are concerned. However, a possible drawback of lanthanide cryptates is the compromised approach of the chromophore to the metal ion, compared to complexes of branched macrocyclic ligands, leading to a lesser efficiency of the ligand-to-metal intramolecular energy transfer [11].

For the reported  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes of cryptands, most of the encapsulating ligands developed are based on the trisbipyridyl ligand (tbp) first defined by *Lehn* and co-workers [12], where various heterobiaryl groups substitute one or more of the 2,2'-bipyridine units [13]. Other approaches to the design of lanthanide complexes with cryptands include the use of *p*-(*tert*-butyl)calix[4]arene [14] or a diazatetralactam ring [15] as the macrocyclic platform. In the latter case, the introduction of carboxamide groups in a cryptand structure was expected to stabilize the complexes in hydroxylic solvents and to favor resonant ligand  $\rightarrow$  Ln (Ln = Eu, Tb) energy transfer as described for photoactive lanthanide podates [16]. In previous papers [15], we described the synthesis of  $\text{Eu}^{\text{III}}$  complexes of macrobicyclic cryptands incorporating a tetralactam ring and a sensitizer group (1,10-phenanthroline, dimethyl 2,2'-bipyridine-4,4'-dicarboxylate and its *N*-oxide analogue). These complexes displayed notable luminescent properties in aqueous solution, which may be related to very efficient encapsulation of the metal ion by the tetralactam moiety.

More recently [17], we reported the synthesis of two photoactive tetralactam-based cryptands **1** and **2** and of their  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Tb}^{3+}$  complexes. Ligand **1** contains a 2,2'-bipyridine chromophoric unit, which is usually a good  $\text{Eu}^{3+}$  sensitizer [11], while ligand **2** incorporates a 2,6-bis(pyrazol-1-yl)pyridine heterocycle, which provides a suitable  $\text{Tb}^{3+}$  sensitizer [18]. The lowest metal-centered (MC) excited states of these three central lanthanides lie at different energy levels [19]. Consequently, a combined study of the  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Tb}^{3+}$  complexes of the same ligand can give useful information on the behavior of the ligand-centered (LC) levels, on the efficiency of the ligand-to-metal energy-transfer process, and on the quenching mechanisms involving inner-sphere coordinated molecules or ligand-to- $\text{Ln}^{\text{III}}$  charge transfer. In the present work, we present a photophysical study, in aqueous solution, of the  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Tb}^{3+}$  complexes of ligands **1** and **2** to help us better understand the role played by the various factors that determine the luminescence properties of this cryptate family.

**Results and Discussion.** – The  $\text{Ln}^{3+}$  complexes (Ln = Eu, Tb, Gd) of the ligands **1** and **2** were prepared by ion exchange with  $\text{LnCl}_3$  from  $[\text{Li} \subset \mathbf{1}]\text{Br}$  and  $[\text{Na} \subset \mathbf{2}]\text{Br}$  cryptates as reported in [17]. These lanthanide cryptates are much more soluble in aqueous solution than their parent alkaline counterparts. No change in their absorption



and luminescence spectra in aerated water was observed after several days at room temperature, indicating that these complexes are kinetically inert in this medium. The photo-physical investigations of these complexes were, therefore, carried out in aqueous solution.

The absorption spectra of  $[\text{Li} \subset \mathbf{1}]^+$  and  $[\text{Na} \subset \mathbf{2}]^+$  cryptates showed the bands typical for the 2,2'-bipyridine ( $\lambda_{\text{max}} = 290 \text{ nm}$ ) and 2,6-bis(pyrazol-1-yl)pyridine ( $\lambda_{\text{max}} = 311 \text{ nm}$ ) chromophores. The absorption bands of the Ph moieties are not observed due to their much lower absorption coefficients. The ligand–lanthanide interaction led to red-shifted (*ca.* 20 and *ca.* 5 nm for  $[\text{Ln} \subset \mathbf{1}]^{3+}$  and  $[\text{Ln} \subset \mathbf{2}]^{3+}$ , resp.) and weaker absorptions compared to the parent alkaline counterparts (see *Table 1* and for  $[\text{Tb} \subset \mathbf{2}]^{3+}$ , *Fig. 1*). This may be correlated with the polarization of the chromophore moiety and the variation of the dihedral angle between adjacent azarings during the complexation. The presence of two resolved maxima at 271 and 279 nm in the case of  $[\text{Ln} \subset \mathbf{2}]^{3+}$  complexes indicate slightly different interactions of the two pyrazole rings, leading to distinct  $\pi\text{-}\pi^*$  transitions on each ring [18]. Similar bathochromic shifts and hypochromic effects have been reported for lanthanide complexes with other encapsulating ligands derived from these two azabi(tri)aryl systems [11][18].

Table 1. Ligand-Centered Absorption and Emission Maxima <sup>a)</sup>

Compound	Absorption		Emission		
	Ground state		<sup>1</sup> $\pi\pi^*$ Level <sup>b)</sup>		<sup>3</sup> $\pi\pi^*$ Level <sup>c)</sup>
	$\lambda_{\text{max}}$ [nm]	$\epsilon_{\text{max}}$ [ $\text{M}^{-1} \cdot \text{cm}^{-1}$ ]	$\lambda_{\text{max}}$ [nm]	$\lambda_{\text{max}}$ [nm]	$\tau$ [ms]
$[\text{Li} \subset \mathbf{1}]^+$	290	11000	352	429	900
$[\text{Gd} \subset \mathbf{1}]^{3+}$	311	9250	340	471	3
$[\text{Eu} \subset \mathbf{1}]^{3+}$	309	9100	–	–	–
$[\text{Tb} \subset \mathbf{1}]^{3+}$	309	8700	–	–	–
$[\text{Na} \subset \mathbf{2}]^+$	311	10600	346	414	800
$[\text{Gd} \subset \mathbf{2}]^{3+}$	317	7900	350	428	36
$[\text{Eu} \subset \mathbf{2}]^{3+}$	316	8600	350	–	–
$[\text{Tb} \subset \mathbf{2}]^{3+}$	316	8250	350	–	–

<sup>a)</sup> In aqueous solution at 300 K, unless otherwise noted. <sup>b)</sup> Fluorescence. <sup>c)</sup> Phosphorescence at 77 K.

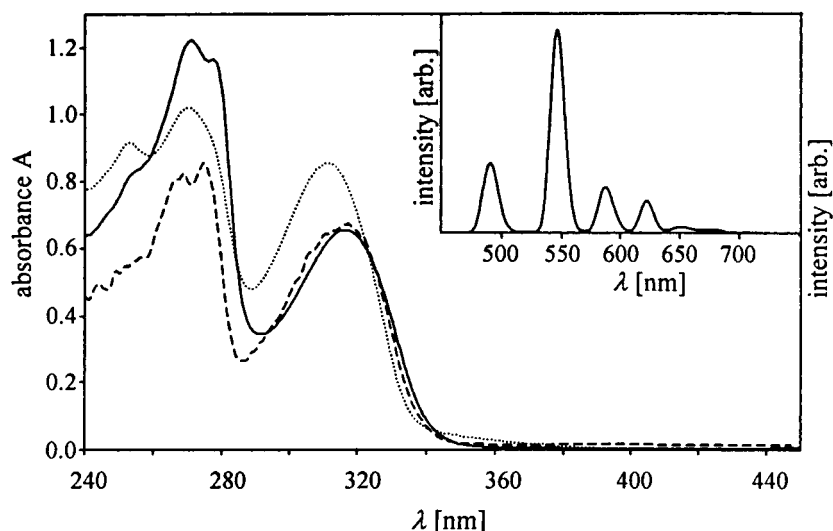


Fig. 1. Absorption spectra of  $[\text{NaC}2]\text{Br}$  ( $\cdots$ ) and  $[\text{TbC}2]\text{Cl}_3$  ( $-$ ), and metal-luminescence excitation spectrum ( $\lambda_{\text{em}} = 545 \text{ nm}$ ) of  $[\text{TbC}2]\text{Cl}_3$  ( $- -$ ) in  $\text{H}_2\text{O}$  ( $c = 8.0 \cdot 10^{-5} \text{ M}$ ). Insert: Corrected emission spectrum of  $[\text{TbC}2]\text{Cl}_3$  in  $\text{H}_2\text{O}$  at room temperature (excitation in the ligand absorption,  $\lambda_{\text{exc}} = 316 \text{ nm}$ ).

**Ligand-Centered Luminescence.** Upon excitation through the ligand  $\pi \rightarrow \pi^*$  transition, aqueous solution of  $[\text{LiC}1]^{3+}$  displayed at room temperature a sizeable emission band in the range 300–400 nm with a maximum at 352 nm, assigned to fluorescence from the  $^1\pi\pi^*$  state of the cryptand. In a rigid matrix at 77 K, this short-lived fluorescence was accompanied by a long-lived structured phosphorescence band with a maximum at 429 nm, due to the deactivation of the lowest electronic triplet state. Similar fluorescence and phosphorescence bands were observed for  $[\text{NaC}2]^{3+}$  ( $\lambda_{\text{max}} = 346$  and 414 nm, resp.). As expected, in the Gd cryptates **1** and **2** the ligand-centered (LC) fluorescence and phosphorescence were not quenched, allowing us to investigate the behavior of the LC excited states in a structure analogous to that of other lanthanide complexes. Upon complexation to  $\text{Gd}^{\text{III}}$  the singlet-state emission bands did not shift significantly. The triplet-state emission bands (at 77 K) shifted to lower energies (Fig. 2), and were especially much shorter lived than the alkali cryptate phosphorescence. From the highest-energy-vibration feature of the phosphorescence bands, the value of the zero-zero energy for the  $^3\pi\pi^*$  ligand level was estimated to be 22500 and 24900  $\text{cm}^{-1}$  for  $[\text{GdC}1]^{3+}$  and  $[\text{GdC}2]^{3+}$ , respectively. These values are in accordance with those reported by *Latva et al.* [20] for Gd chelates based on polyamine-poly(acetic acid) ligands containing a 2,2'-bipyridine or 2,6-bis(pyrazol-1-yl)pyridine antenna. We can note that the triplet state of the bipyridine chromophore is much more perturbed by the coordination of the Gd ion than that of the 2,6-bis(pyrazol-1-yl)pyridine unit relative to the parent compounds. In  $[\text{GdC}1]^{3+}$ , the lowest triplet LC excited state of the ligand is reduced by 2450  $\text{cm}^{-1}$ , and the corresponding lifetime is decreased by a factor of 300 as compared to  $[\text{LiC}1]^{3+}$ , when a low-energy shift of 750  $\text{cm}^{-1}$  and a 20-fold decrease of lifetime are noted for  $[\text{GdC}2]^{3+}$  (vs.  $[\text{NaC}2]^{3+}$ ). This indicates a greater perturbation of the electron density of ligand **1**

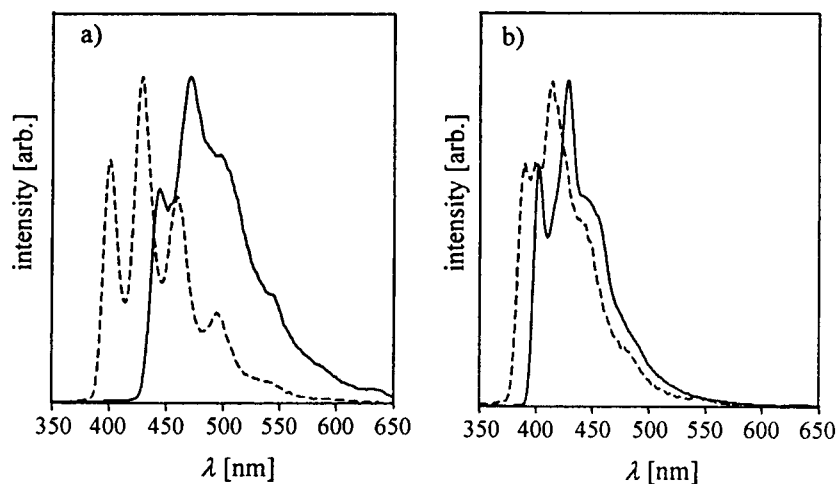


Fig. 2. Time-resolved phosphorescence spectra at 77 K in alcohol of a)  $[LiC1]Br$  (---) and  $[GdC1]Cl_3$  (—); b)  $[NaC2]Br$  (---) and  $[GdC2]Cl_3$  (—)

by the metal ion, and suggests a stronger interaction of Gd ion with ligand **1** than with **2**.

**Metal-Centered Luminescence.** The emission spectra of the Eu and Tb complexes, excited into the lowest energy LC absorption band, showed the well-known structured luminescence of the lanthanide ion, with the highest intensity band around 615 nm for  $Eu^{3+}$  ( $^5D_0 \rightarrow ^7F_2$  transition) and 545 nm for  $Tb^{3+}$  ( $^5D_4 \rightarrow ^7F_5$  transition) (Fig. 1). Although the same transitions  $^5D_0 \rightarrow ^7F_j$  are observed in  $[EuC1]^{3+}$  and  $[EuC2]^{3+}$ , their relative intensities are cryptand-dependent. Since the  $^5D_0 \rightarrow ^7F_1$  emission is magnetic dipolar in character, and its radiative transition probability is not environmentally sensitive, the ratio  $^5D_0 \rightarrow ^7F_j$  ( $j=0, 2$ )/ $^5D_0 \rightarrow ^7F_1$  emission intensity gave us some information about the environment induced by the ligand and solvent around the  $Eu^{III}$  ion [21]. Both complexes displayed a  $^5D_0 \rightarrow ^7F_0$  transition at 581 nm, twofold more intense for  $[EuC1]^{3+}$ , indicating that the symmetry of the metal coordination sphere is not centrosymmetric. The decrease in the 0–2/0–1 intensity ratio from  $[EuC1]^{3+}$  (6.3) to  $[EuC2]^{3+}$  (4.5) is also consistent with a lower symmetry around the  $Eu^{III}$  ion in  $[EuC1]^{3+}$ . The relative intensities of the  $^5D_4 \rightarrow ^7F_j$  transitions were approximately equal in the two  $Tb^{III}$  complexes, since luminescence spectra of  $Tb^{III}$  are not hypersensitive to the detailed nature of the ligand environment [2a]. The excellent agreement between the absorption and excitation spectra (in the case of  $[TbC2]^{3+}$ , see Fig. 1) shows unequivocally that the excitation of the  $Eu^{III}$  and  $Tb^{III}$  ions in **1** and **2** is by an indirect process, *i.e.*, a ligand-to-metal inter-system energy transfer. This process arises principally from the sensitized 2,2'-bipyridine or 2,6-bis(pyrazol-1-yl)pyridine chromophore. The contribution of the Ph groups to this through-space intramolecular energy transfer is certainly not so effective because of the lowest absorption efficiency and the highest distance from the bound ion of these groups with respect to the coordinating azaheterocyclic units. For a given ligand, the  $Eu^{3+}$  and  $Tb^{3+}$  complexes displayed similar excitation spectra with identical excitation maxima, indicating that

the coordination geometries of the organic moiety should be very similar regardless of the metal considered. The ligand-centered fluorescence was completely quenched in  $[\text{Eu} \subset \mathbf{1}]^{3+}$  and  $[\text{Tb} \subset \mathbf{1}]^{3+}$  complexes. A different situation arises from  $[\text{Eu} \subset \mathbf{2}]^{3+}$  and  $[\text{Tb} \subset \mathbf{2}]^{3+}$ , where the LC fluorescence pathway competes with energy transfer to the lanthanide ions. This residual LC fluorescence, although weak, is, however, more intense for  $[\text{Eu} \subset \mathbf{2}]^{3+}$  than for  $[\text{Tb} \subset \mathbf{2}]^{3+}$ .

Measurements of the radiative constants for decay of the excited states of the  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  complexes were performed in aqueous solutions under various experimental conditions, following excitation to the lowest-energy ligand-centered absorption band. In each case, mono-exponential decay curves were observed and the lifetime values obtained are collected in *Table 2*. In  $\text{H}_2\text{O}$  solution and at room temperature, these luminescence lifetimes are in the 0.37–1.12 ms range, with  $[\text{Tb} \subset \mathbf{1}]^{3+}$  having the longest lifetime and  $[\text{Eu} \subset \mathbf{2}]^{3+}$  the shortest. As could be seen for other cryptates [11], the lifetime values of these four complexes are higher in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$ , indicating that nonradiative deactivation of the  $^5\text{D}_0$  or  $^5\text{D}_4$  metal-excited states through the O–H vibrations occurs. Upon solvent deuteration, the lifetime at 300 K for  $[\text{Eu} \subset \mathbf{1}]^{3+}$  is increased by a factor of 1.8 compared to a factor of 2.8 for  $[\text{Eu} \subset \mathbf{2}]^{3+}$ , indicating a smaller number of proximate O–H oscillators in the former complex. The  $\text{Tb}^{\text{III}}$  complexes display smaller variations ( $\tau_{\text{D}}/\tau_{\text{H}} = 1.3$  and 1.7 for ligands **1** and **2**, resp.). This may be rationalized by there being a larger energy gap between the lowest luminescent excited state and the highest ground-state for  $\text{Tb}^{3+}$  ions than for  $\text{Eu}^{3+}$  ions, thus reducing the probability of coupling with O–H vibrations [19]. The number of solvent molecules bound in the inner coordination sphere of the lanthanide ion was determined by the well-established equation of *Horrocks* and *Sudnick* [22]. For  $\text{H}_2\text{O}$ , this relationship is  $q = A (1/\tau_{\text{H}} - 1/\tau_{\text{D}})$ , where  $A = 1.05$  for  $\text{Eu}^{\text{III}}$  and 4.2 for  $\text{Tb}^{\text{III}}$ . It resulted that the apparent hydration state is 0.61 for  $[\text{Eu} \subset \mathbf{1}]^{3+}$  and 1.84 for  $[\text{Eu} \subset \mathbf{2}]^{3+}$ . These fractional  $\text{H}_2\text{O}$  molecules cannot be explained by invoking only the participation of unbound closely diffusing  $\text{H}_2\text{O}$  molecules, which also contribute to the quenching of the  $^5\text{D}_0$  excited state. As a matter of fact, these contributions, whose magnitude depends on the proximity of solvent molecules to the metal center, are generally small. According to the newly published correlations [23], which take into account this  $\text{H}_2\text{O}$  secondary quenching effect, the  $\text{Eu}^{\text{III}}$  complexes of ligands **1** and **2** bind 0.3–0.4 and 1.6–1.8  $\text{H}_2\text{O}$  molecules, respectively. These noninteger values can arise from the presence of two species with different degrees of solvation in exchange faster than the Eu lifetime, or more certainly from the uncertainty of these empirical formulae. Thus, it is likely that the true values of  $q$  are 1 and 2 for  $[\text{Eu} \subset \mathbf{1}]^{3+}$  and  $[\text{Eu} \subset \mathbf{2}]^{3+}$ , respectively. The hydration-state values obtained for  $[\text{Tb} \subset \mathbf{1}]^{3+}$  and  $[\text{Tb} \subset \mathbf{2}]^{3+}$  are analogous to those of the corresponding Eu complexes (see *Table 2*). The presence of one coordinated  $\text{H}_2\text{O}$  molecule in the complexes of **1** is in agreement with an overall coordination number of nine for the lanthanide ion (assuming ligand **1** is eight-coordinated). Although **2** provides an additional donor atom (one heterocyclic N-atom), it allows two  $\text{H}_2\text{O}$  molecules to enter into the first coordination sphere of the metal. Clearly, the expansion of the cavity size of ligand **2** as compared to **1** (two 21-membered vs. 18-membered rings) is an unfavorable factor for the shielding of  $\text{Ln}^{3+}$  ions. Interestingly, the number of coordinated  $\text{H}_2\text{O}$  molecules for  $[\text{Ln} \subset \mathbf{2}]^{3+}$  at 77 K, *ca.* 1, is lower than that obtained at 300 K, while this value remains unchanged for

Table 2. *Metal-Centered Luminescence*

Compound	Lifetime <sup>a) b)</sup> [ms]						$q_{\text{H}_2\text{O}}^{\text{c)}$	
	$\tau_{\text{H}}^{300\text{K}}$	$\tau_{\text{H,F}^-}^{300\text{K}}$	$\tau_{\text{D}}^{300\text{K}}$	$\tau_{\text{D,F}^-}^{300\text{K}}$	$\tau_{\text{H}}^{77\text{K}}$	$\tau_{\text{D}}^{77\text{K}}$	$q^{300\text{K}}$	$q^{77\text{K}}$
[Eu <b>1</b> ] <sup>3+</sup>	0.77	1.65	1.39	2.33	0.87	1.57	0.61	0.54
[Tb <b>1</b> ] <sup>3+</sup>	1.12	1.75	1.42	1.89	1.60	2.09	0.79	0.62
[Eu <b>2</b> ] <sup>3+</sup>	0.37	1.19	1.05	2.39	0.91	2.30	1.84	0.70
[Tb <b>2</b> ] <sup>3+</sup>	1.01	1.87	1.68	2.45	1.66	2.45	1.66	0.82

<sup>a)</sup> In aerated  $1.0 \cdot 10^{-6}$  M H<sub>2</sub>O (H) or D<sub>2</sub>O (D) solutions; in the absence or in the presence of 0.4M KF (F<sup>-</sup>).

<sup>b)</sup> The lifetimes were determined by excitation to the lowest-energy ligand-centered absorption band and recording the intensity of the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> and <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> emissions for Eu<sup>3+</sup> and Tb<sup>3+</sup>, respectively. <sup>c)</sup> Number of coordinated H<sub>2</sub>O molecules, estimated with the *Horrocks* equation [22].

[Ln **1**]<sup>3+</sup>. Modification of the hydration sphere in going from room temperature to low temperature has previously been observed for lanthanide complexes of other cryptands or branched macrocycles exhibiting some flexibility [11][24].

We have also used the greater affinity of F<sup>-</sup> ions (*vs.* H<sub>2</sub>O) for the lanthanides to evidence the presence of directly coordinated H<sub>2</sub>O molecules. As a matter of fact, it has been established that the small anion F<sup>-</sup> can displace the residual H<sub>2</sub>O molecules from the first coordination sphere of Eu<sup>3+</sup> or Tb<sup>3+</sup>, preventing or reducing the H<sub>2</sub>O quenching [25]. This effect has been exploited in sensitized luminescent systems containing Ln<sup>3+</sup> cryptates. For example, in the *TRACE*<sup>®</sup> technology, which is commercially available for time-resolved fluoroimmunoassays, the addition of F<sup>-</sup> ions is used for enhancing the luminescence efficiency of the trisbipyridine europium cryptate [Eu **C TBP**]<sup>3+</sup> [26]. The luminescence lifetimes of the complexes of **1** and **2** are lengthened significantly upon addition of fluoride ion (*Table 2*). This is clearly shown in the case of [Eu **2**]<sup>3+</sup>, where the lifetime in H<sub>2</sub>O is increased by a factor of 3.2 in the presence of  $4 \cdot 10^{-1}$  M F<sup>-</sup>. Comparison of the lifetimes obtained in H<sub>2</sub>O and D<sub>2</sub>O shows that one H<sub>2</sub>O molecule is displaced by F<sup>-</sup> at saturating anion concentration. The incorporation of F<sup>-</sup> ion in the metal coordination sphere is also reflected in the shape of Eu spectra (*Fig. 3*): the twofold decrease in the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>/<sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> ratio, observed upon addition of F<sup>-</sup>, is consistent with a structural change of symmetry around the Eu<sup>3+</sup> ion. We may note that a lengthening of the Eu<sup>3+</sup> and Tb<sup>3+</sup> excited-state lifetimes in the presence of F<sup>-</sup> is also observed in D<sub>2</sub>O. This suggests that the ion-pair formation has an additional effect, apart from H<sub>2</sub>O replacement. Analogous effects were reported by *Sabbatini et al.* for the Eu<sup>3+</sup> or Tb<sup>3+</sup> (2.2.1) cryptate – fluoride systems [25]. In the case of [Eu **C (2.2.1)**]<sup>3+</sup>, these authors have shown that coordination of the F<sup>-</sup> anion to the Eu ion shifts the ligand-to-metal charge-transfer (LMCT) bands of the cryptate to higher energies, thus limiting radiationless decay *via* low-lying charge-transfer levels. For [Eu **1**]<sup>3+</sup> and [Eu **2**]<sup>3+</sup>, this effect may be rationalized by the presence of a C=O-to-Eu<sup>3+</sup> charge-transfer state, which deactivates the excited states of the ligand and the metal-emitting state to the ground state. These LMCT transitions were observed at *ca.* 300 nm for Eu<sup>III</sup> complexes of calix[4]arene tetraamide ligands [27], but could not be located for the investigated Eu complexes derived from **1** and **2**, being hidden under the more-intense ligand transitions.

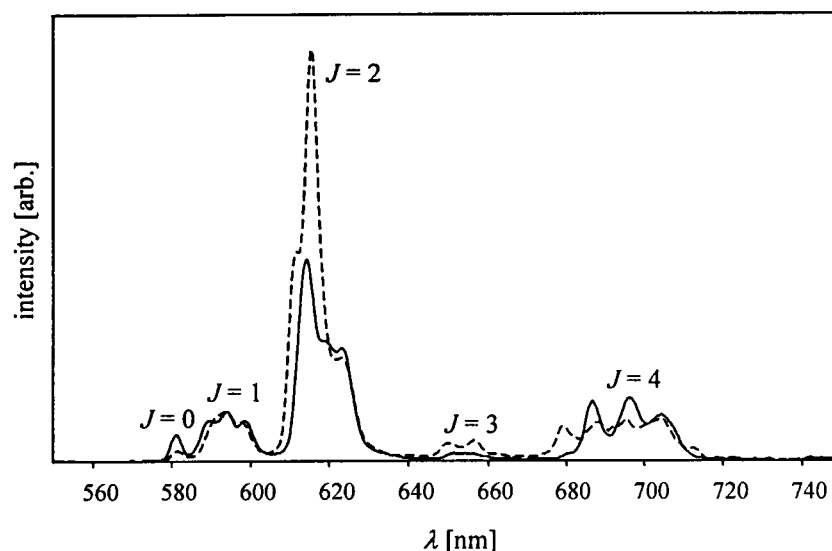


Fig. 3. Corrected emission spectra of  $1.0 \cdot 10^{-6}$  M solutions of  $[\text{Eu} \subset \mathbf{1}]\text{Cl}_3$  in  $\text{H}_2\text{O}$  solution in the absence of  $\text{F}^-$  (---) and in the presence of  $4.0 \cdot 10^{-1}$  M  $\text{F}^-$  (—). The bands arise from the  ${}^3\text{D}_0 \rightarrow {}^7\text{F}_J$  transitions; the  $J$  values are shown on the spectra. The spectra are normalized on the  ${}^3\text{D}_0 \rightarrow {}^7\text{F}_1$   $\text{Eu}^{3+}$  transition.

The quantum yields of the metal-centred emission of the complexes upon ligand excitation are reported in Table 3. It is worthwhile noting that the quantum yield of  $[\text{Tb} \subset \mathbf{1}]^{3+}$  ( $\Phi = 0.25$ ) is the highest value found up to now in aqueous solution for a  $\text{Tb}^{3+}$  complex of a cryptand ligand. Moreover, this value compares very favorably with those reported in the literature for  $\text{Tb}^{3+}$  complexes derived from podands or polyaminocarboxylic ligands containing one [20], two [14b][24][28], or more [8b][11][14b][28b][29] bipyridine chromophores. On the contrary,  $[\text{Eu} \subset \mathbf{2}]^{3+}$  is weakly luminescent, even in  $\text{D}_2\text{O}$  solution, where the ligand-shielding effect towards interaction of the excited state of the europium ion with O–H oscillators does not play any role. This weakening of the luminescence is also evident, albeit less dramatically, for  $[\text{Tb} \subset \mathbf{2}]^{3+}$  ( $\Phi = 0.11$ ) in comparison with  $[\text{Tb} \subset \mathbf{1}]^{3+}$ , while the lifetimes are almost equal in the two cases. The relatively weak luminescence quantum yield of  $[\text{Tb} \subset \mathbf{2}]^{3+}$  was not expected from earlier results concerning a polyacid chelate derived from 2,6-bis(pyrazol-1-yl)pyridine [18]. In fact, this compound is among the most efficient  $\text{Tb}^{\text{III}}$

Table 3. Luminescence Quantum Yields<sup>a)</sup>, Decay Rate Constants, and Energy-Transfer Efficiency

Compound	$\Phi^{300\text{K}} (\cdot 10^2)$	$k$ [ $\text{s}^{-1}$ ]	$k_r$ [ $\text{s}^{-1}$ ]	$k_{\text{nr}}(\text{OH})$ [ $\text{s}^{-1}$ ]	$k_{\text{nr}}(\text{T})$ [ $\text{s}^{-1}$ ]	$\eta_{\text{en.tr.}} (\cdot 10^2)$
$[\text{Eu} \subset \mathbf{1}]^{3+}$	2 (5) <sup>b)</sup>	1300	640	580	80	4
$[\text{Tb} \subset \mathbf{1}]^{3+}$	25	890	480	190	220	46
$[\text{Eu} \subset \mathbf{2}]^{3+}$	0.03 (0.12) <sup>b)</sup>	2700	430	1750	520	0.2
$[\text{Tb} \subset \mathbf{2}]^{3+}$	11	990	410	390	190	27

<sup>a)</sup> In  $\text{H}_2\text{O}$  solution at 300 K unless otherwise noted. <sup>b)</sup> in  $\text{D}_2\text{O}$  solution at 300 K.



emitters in solution reported ( $\Phi = 0.84$  in  $\text{H}_2\text{O}$ ). These data indicate that the difference in luminescence yields between  $[\text{Ln} \subset \mathbf{1}]^{3+}$  and  $[\text{Ln} \subset \mathbf{2}]^{3+}$  cannot be interpreted only on the basis of a better shielding offered in  $\mathbf{1}$  towards deactivating  $\text{H}_2\text{O}$  molecules.

For ligand-sensitized lanthanide luminescence, the quantum yields result from a balance among the ligand to  $\text{Ln}^{\text{III}}$  energy-transfer efficiency ( $\eta_{\text{en.tr.}}$ ), the radiative ( $k_r$ ) and nonradiative ( $k_{\text{nr}}$ ) rate constants of the luminescent  $\text{Ln}^{\text{III}}$  level. The observed quantum yields ( $\Phi$ ) and the overall decay rate constants  $k$  (i.e.,  $1/\tau_{\text{obs}}$ ) can be expressed by *Eqns. 1* and *2*:

$$\Phi = \eta_{\text{en.tr.}} \cdot k_r/k \quad (1)$$

$$k = k_r + k_{\text{nr}}(T) + k_{\text{nr}}(\text{OH}) \quad (2)$$

where  $k_{\text{nr}}(T)$  is the temperature-dependent nonradiative-decay rate constant, and it is assumed that the temperature-independent term receives the most important contribution from the decay through coupling with the high-energy O–H oscillators. Energy-transfer and decay characteristics can be estimated from the experimentally determined luminescence lifetimes and quantum yields (*Tables 2* and *3*) according to the approach described by *Sabbatini et al.* [11]. These data are gathered in *Table 3*.

The photophysical model, yet adequate, that accounts for the sensitization pathway in luminescent lanthanide complexes consists of the absorption of light into the first excited singlet state of the antenna chromophore, subsequent intersystem crossing to the antenna triplet state, and energy transfer to the lanthanide ion. The  $\eta_{\text{en.tr.}}$  term is, therefore, the product of the efficiency of singlet  $\rightarrow$  triplet conversion in the antenna chromophore ( $\eta_{\text{isc}}$ ) and the efficiency of the triplet  $\rightarrow$  metal energy-transfer step ( $\eta_{\text{et}}^3\pi\pi^*$ ).

As far as the intersystem crossing yield is concerned, *Steemers et al.* [30] showed that the energy gap between the lowest singlet and triplet states of the antenna sensitizer ( ${}^1E_{00} - {}^3E_{00}$ ) should be at least  $5000 \text{ cm}^{-1}$  to ensure an efficient  $\eta_{\text{isc}}$ . For the studied complexes, this energetic condition is fulfilled, since the singlet-triplet energy-gap value amounts to  $8300$  and  $5200 \text{ cm}^{-1}$  for  $[\text{Gd} \subset \mathbf{1}]^{3+}$  and  $[\text{Gd} \subset \mathbf{2}]^{3+}$ , respectively.

On the other hand, the energy gap between the lowest ligand-centered and metal-centered levels ( ${}^3E_{00} - \text{Ln}^*$ ) may compromise the  $\eta_{\text{et}}^3\pi\pi^*$  efficiency. If this energy gap is too small, thermally activated back-energy transfer can occur from the resonance level of  $\text{Ln}^{\text{III}}$  and the lowest triplet-state energy level of the antenna, which may be subsequently deactivated through the usual pathways.

Thus, the  $\text{Tb}^{\text{III}}$  luminescence quantum yields were observed to decrease when this energy difference is less than  $1850 \text{ cm}^{-1}$  [20]. This quenching mechanism cannot account for the reduced emission quantum yield of  $[\text{Tb} \subset \mathbf{2}]^{3+}$  compared to  $[\text{Tb} \subset \mathbf{1}]^{3+}$ , because the triplet excited state of the ligand  $\mathbf{2}$  lies at higher energy than the triplet excited state of the ligand  $\mathbf{1}$  (ca.  $2400 \text{ cm}^{-1}$  higher, *vide supra*). Moreover, the energy gap ( ${}^3E_{00} - {}^5D_4$ ) measured for the ligand  $\mathbf{1}$  (ca.  $2100 \text{ cm}^{-1}$ ) is above the threshold value of  $1850 \text{ cm}^{-1}$ ; thus, the thermal-energy back transfer seems to be of minor importance in  $[\text{Tb} \subset \mathbf{1}]^{3+}$ , and, consequently, in  $[\text{Tb} \subset \mathbf{2}]^{3+}$ . This is consistent with the relatively weak temperature dependence of the luminescence lifetime reflected in  $k_{\text{nr}}(T)$  ( $< 230 \text{ cm}^{-1}$ ). As a comparison, *Sabbatini et al.* [11] reported a value of  $1300 \text{ s}^{-1}$  for

$k_{\text{nr}}(T)$  for a Tb<sup>III</sup> cryptate including three bipyridine units, in which an equilibrium between the bipyridine donor and Tb acceptor levels occurs at room temperature. However, a significant difference is observed between the  $\eta_{\text{en.tr.}}$  values estimated for [Tb C **1**]<sup>3+</sup> and [Tb C **2**]<sup>3+</sup> (0.46 and 0.27, resp.). A higher donor-acceptor distance due to worse aromatic heterocycles – metal interaction is certainly responsible for the lower  $\eta_{\text{en.tr.}}$  value found for [Tb C **2**]<sup>3+</sup>.

In comparison with the Tb<sup>3+</sup> complexes, a larger difference is observed between the ligand-to-metal energy-transfer efficiencies estimated for [Eu C **1**]<sup>3+</sup> and [Eu C **2**]<sup>3+</sup>. For [Eu C **2**]<sup>3+</sup>,  $\eta_{\text{en.tr.}}$  was by more than one order of magnitude lower. Unlike Tb<sup>III</sup>, a strict correlation between the energies of the lowest triplet-state levels of the ligands and Eu<sup>III</sup> luminescence quantum yields is difficult to establish because Eu<sup>III</sup> can accept energy with all their <sup>5</sup>D<sub>*j*</sub> levels, depending on the triplet-state energy of the ligand. Moreover, when <sup>5</sup>D<sub>1-3</sub> Eu<sup>III</sup> levels act as energy acceptors, they decay non radiatively to the lower-lying <sup>5</sup>D<sub>0</sub> state that is the predominant emitting state and that gives rise to the characteristic lifetime and emission spectrum of the Eu<sup>3+</sup> ion [20]. Looking at the energy of the ligand triplet states in [Gd C **1**]<sup>3+</sup> and [Gd C **2**]<sup>3+</sup>, energy transfer to the metal is feasible to the <sup>5</sup>D<sub>0-2</sub> and <sup>5</sup>D<sub>0-3</sub> levels of Eu<sup>III</sup> in [Eu C **1**]<sup>3+</sup> and [Eu C **2**]<sup>3+</sup>, respectively. On the other hand, from the study of *Latva et al.* [20] on the luminescent properties of 41 different Eu chelates, one may conclude that the best energy-transfer efficiency was obtained for Eu<sup>III</sup>, when the ligand's triplet-state energy lies at *ca.* 21 500–22 500 cm<sup>-1</sup>. In the case of [Eu C **2**]<sup>3+</sup>, The <sup>3</sup>E<sub>00</sub> component of the antenna (24 900 cm<sup>-1</sup>), therefore, does not lie at the most suitable energy, and the appropriate levels being unmatched probably favors alternate mechanisms for energy transfer. Moreover, the strong temperature dependence of the lifetimes observed for this complex ( $k_{\text{nr}}(T) = 520 \text{ s}^{-1}$ ) indicates that an important role of the Eu<sup>3+</sup> emitting state is played by a thermally activated process. Such an effect may be rationalized by the presence of a back energy transfer from the resonant <sup>5</sup>D<sub>3</sub> level of Eu<sup>3+</sup> to the triplet state of the ligand, or (and) by the population of nonemitting LMCT excited states (*vide supra*) from the Eu<sup>3+</sup> emitting state. For [Eu C **1**]<sup>3+</sup>, the thermally activated radiationless decay path is less important than for [Eu C **2**]<sup>3+</sup>. This suggests that, in [Eu C **1**]<sup>3+</sup>, a LMCT level lies at higher energy than in [Eu C **2**]<sup>3+</sup>.

Concerning the radiative rate constants, we can notice that the  $k_{\text{r}}$  values are higher than those reported for the free Eu<sup>3+</sup> and Tb<sup>3+</sup> ions, 190 and 110 s<sup>-1</sup> respectively [2b], reflecting the favorable effect of the organic ligands on the overall radiative decay probability of these ions [31]. These estimated  $k_{\text{r}}$  values are in the range of those reported in recent literature for organocomplexes of Eu<sup>3+</sup> (400 s<sup>-1</sup> <  $k_{\text{r}}$  < 600 s<sup>-1</sup>) and Tb<sup>3+</sup> (250 s<sup>-1</sup> <  $k_{\text{r}}$  < 500 s<sup>-1</sup>) [11][15b] (and refs. cit. therein) [32]. This means that a characteristic quenching of the Eu<sup>3+</sup> and Tb<sup>3+</sup> excited states by CH oscillators does not occur in these cryptates, and that the assumption introduced when  $k_{\text{nr}}$  (other vibrations) is neglected in *Eqn. 2* may be valid.

**Conclusions.** – Cryptands **1** and **2** containing a tetralactam unit and a bis- or trisheterocyclic antenna form Eu<sup>3+</sup> and Tb<sup>3+</sup> complexes that are luminescent upon ligand excitation in aqueous solution at room temperature. Although [Ln C **1**]<sup>3+</sup> and [Ln C **2**]<sup>3+</sup> have similar molar extinction coefficients at  $\lambda_{\text{max}}$ , conversion of absorbed light into emitted light is strongly cryptand-dependent. The Eu<sup>3+</sup> and Tb<sup>3+</sup> complexes of

ligand **1** display a more-intense luminescence than the corresponding complexes of ligand **2**, thanks to a closer proximity of the chromophore to the Eu or Tb ion. This induces better shielding of the metal ion and a more-efficient energy transfer from ligand-to-metal. In addition and in the case of  $[\text{Eu} \subset \mathbf{2}]^{3+}$ , we have observed again the dependence of the energy-transfer efficiency upon the triplet-state energy of the ligand and upon the presence of ligand-to-Eu<sup>III</sup> charge-transfer excited states. Finally, the H<sub>2</sub>O-soluble  $[\text{Tb} \subset \mathbf{1}]^{3+}$  cryptate is characterized by one of the highest values for lanthanide luminescence intensity among the Tb<sup>3+</sup> complexes sensitized by a 2,2'-bipyridine chromophore and is a very promising candidate as long-lived luminescent label for bioaffinity assays. Monofunctionalization of the 2,2'-bipyridine moiety for coupling the complex to biological substrates is under investigation.

### Experimental Part

Distilled, deionized water was used throughout this work, without deaeration. LnCl<sub>3</sub> · 6 H<sub>2</sub>O salts (99.9%) were purchased from *Sigma-Aldrich*. The cryptands **1** and **2** and their complexes were prepared as described in [17].

UV Absorbance spectra were recorded with a *Perkin-Elmer Lambda 17* spectrophotometer. Fluorescence spectra were obtained with a *LS-50B Perkin-Elmer* spectrofluorimeter equipped with a *Hamamatsu R928* photomultiplier tube and operated with *FLDM* software. Quartz cuvettes of pathlength 1 cm were used. The energies of the 0-0 transition of the singlet states were determined by the intercept of the absorption and fluorescence spectra.

The Eu<sup>III</sup> and Tb<sup>III</sup> phosphorescence emission and excitation spectra were acquired with the same instrument operating in time-resolved mode with a delay time of 0.1 ms. The most highly resolved emission spectra were obtained with excitation and emission slit widths of 2.5 nm, following pulsed excitation at 310 ([Ln ⊂ **1**]<sup>3+</sup>) or 316 nm ([Ln ⊂ **2**]<sup>3+</sup>). Emission spectra were corrected from the wavelength dependence of the photomultiplier tube, according to the instrument guidebook. Luminescence excitation spectra were acquired by monitoring emission at 615 nm for Eu<sup>3+</sup> or 545 nm for Tb<sup>3+</sup>, and were automatically corrected. Lifetimes  $\tau$  (uncertainty  $\leq 5\%$ ) are the average values from at least ten separate measurements covering two or more lifetimes. The phosphorescence decay curves were fitted by an equation of the form  $I(t) = I(0) \exp(-t/\tau)$  with a curve-fitting program. High correlation coefficients were observed in each case (higher than 0.999). Liquid N<sub>2</sub> cooling was used to obtain the luminescence and phosphorescence spectra at low temp. (77 K). The phosphorescence spectra of the ligands and of their Gd<sup>III</sup> cryptates were recorded in EtOH/MeOH 4:1. The triplet-state energy levels were determined from the shortest-wavelength phosphorescence bands, which were assumed to be the 0-0 transitions. The luminescence quantum yields (uncertainty  $\pm 15\%$ ) were determined by the method described by *Haas and Stein* [33], with  $[\text{Ru}(\text{bpy})_3]^{2+}$  in aerated H<sub>2</sub>O ( $\Phi = 0.028$  [34]) as standards for the Eu<sup>III</sup> complexes or quinine sulfate in 1N H<sub>2</sub>SO<sub>4</sub> ( $\Phi = 0.546$  [35]) for the Tb<sup>III</sup> complexes, and corrected for the refractive index of the solvent. All samples were prepared with an absorbance between 0.01 and 0.05 at the excitation wavelength, implying an antenna concentration in the range  $1 - 5 \cdot 10^{-6}$  M.

The values of the rate constants for radiative ( $k_r$ ) and nonradiative ( $k_{nr}(\text{OH})$ ,  $k_{nr}(T)$ ) were estimated from the luminescence lifetimes measured in H<sub>2</sub>O and D<sub>2</sub>O soln. at 300 and 77 K according to *Eqns. 3–5*:

$$k_r = 1/\tau_D^{77\text{K}} \quad (3)$$

$$k_{nr}(\text{OH}) = 1/\tau_H^{300\text{K}} - 1/\tau_D^{300\text{K}} \quad (4)$$

$$k_{nr}(T) = 1/\tau_D^{300\text{K}} - 1/\tau_D^{77\text{K}} \quad (5)$$

where  $\tau_H$  and  $\tau_D$  are the lifetimes (in s) of the complexes in H<sub>2</sub>O and D<sub>2</sub>O soln., resp.

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