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Abstract. A series of tris-dipicolinate europium complexes featuring different complexes has been prepared, and their photophysical study has been performed in the solid state highlighting the crucial role of second sphere water molecules. The non-radiative deactivation constant (k_{nr}) varies significantly with the number of interstitial water molecules and their distance to the europium emitting center. The complex $(NBu_4)_3[Eu(DPA)_3]$, featuring the most lipophilic cation, exhibits excellent solubility and remarkable photophysical properties in aprotic solvents.

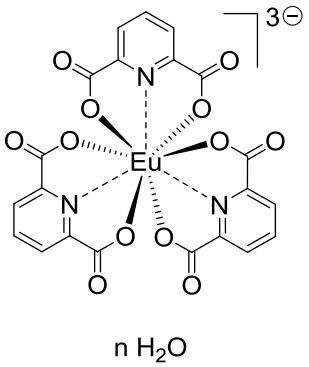
Introduction

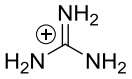
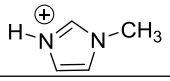
Since their seminal report[1] in the 1960s and their first structural characterization by Albertsson[2] in the early 1970s, lanthanide tris-dipicolinate complexes (dipicolinate = DPA = 2,6-pyridine dicarboxylate) became ubiquitous in the field of *f*-elements coordination chemistry. These tris-anionic complexes, of general formula $[Ln(DPA)_3]^{3-}$ present a threefold D_3 symmetry where the lanthanide ion is coordinated in an almost perfect trigonal tricapped geometry. Over the past 50 years, these tris-anionic complexes have been associated with a large variety of counter-cations such as alkaline (Li^+, Na^+, K^+, Cs^+),[3] alkaline-earth (Mg^{2+}, Ca^{2+}, Ba^{2+}),[4] groups 3 and 13 trications (Sc^{3+}, Al^{3+})[5] but also cationic transition metal complexes[4] or ammoniums.[3a, 6] The nature of the counter-ion generally controls the crystal packing and ensures the structural diversity of the global architecture. More than 380 structures have been deposited in the Cambridge Structural database (November 2021 version). These complexes are mostly soluble in water, and the tris-terdentate character of the dipicolinate chelate induces a propeller-like molecular structure with a helical axis of chirality resulting in the existence of two enantiomers Λ and Δ, in rapid interconversion in solution at room temperature.[7] The large scale synthetic accessibility (multigram scale) enables the preparation of a large diversity of materials such as crystals, co-crystals or core-shell crystals,[8] and metal–organic frameworks materials[9]. These complexes were also used as dopant for ionic-liquid,[10] liquid-crystal[11] or inorganic matrices[12]. This versatility and facile access make these complexes ideal candidates for numerous physicochemical studies in solution or in the solid state.

In this context, the magnetic properties of crystalline materials were thoroughly studied and the intrinsic paramagnetism of *f*-elements was involved in the solution structure determination of proteins[13] or peptides[14] using paramagnetic ^{1}H or DOSY NMR taking advantage of the particular affinity of the tris-dipicolinate complexes for cationic amino-acid residues (arginine, lysine, histidine).[15] In combination with the exceptional anomalous scattering properties of the lanthanide ions, these compounds have also been used as auxiliaries to solve the phase problem in proteins structure determination using X-ray diffraction.[16] However, it is probably the optical properties of these complexes that have attracted most of the attention during the last decades. Indeed, these complexes can be highly luminescent in solution and in the solid state enabling either the study of the crystal field splitting by high resolution spectroscopy or the emission properties of less common emitters (Ce^{3+}, Tm^{3+}, Pr^{3+}, Sm^{3+}, Dy^{3+}…).[6b, 17] The circularly polarized emission properties were also extensively studied upon induction of an enantiomeric excess by addition of supramolecular chiral inducers e.g. amino acids[18] and they have also been used to establish the proof-of-concept of *f*-electron polarization using second order nonlinear optical measurements.[19]

One of the main achievements in this field is the work of Bünzli and co-workers who proposed to use $Cs_3[Ln(DPA)_3]$ (Ln = Eu, Tb) complexes as luminescence standards for quantum yield determination in aqueous solution[20] (ϕ = 24% and 22% for Eu and Tb, respectively) [21] and in the solid state (ϕ = 58% and 30 % for Eu and Tb, respectively) using the absolute method.[22] The high luminescence properties of the europium derivative in particular are explained by the efficient energy transfer from the antenna (n_{sens} = 71% and 85% in solution and in the solid state, respectively) and by the complete saturation of the lanthanide coordination sphere by the surrounding ligands preventing the coordination of water molecules. Since the seminal report of Kropp and Windsor in the 1960's,[23] it is indeed well established that O-H oscillators directly coordinated to the emitting centers are efficient quenchers of luminescence.[24] However, whereas the influence of these quenchers in the first coordination sphere of lanthanide emitters has been widely documented in the literature, including the empirical equations of Horrocks[25] and Parker[26] for the determination of the hydration number *q* by comparison of the emission lifetime in water and deuterated water, the role of water molecules in the second sphere of a complex was comparatively rather neglected (it only appears as a correction term in the above-mentioned phenomenological equation). One can however mention the nice study of May and Richardson showing the effect of interstitial water/deuterated water molecules in $Na_3[Eu(C_4H_4O_5)_3]\bullet 2NaClO_4\bullet 6H_2O(D_2O)$ crystals.[27] The presence of second sphere water molecules may affect significantly the luminescence properties of lanthanide complexes not only in solid state but also in solution as recently suggested by some of us in the case of macrocyclic Eu(III) complexes.[28]

Herein, we explored this effect in detail starting from the well-known $Cs_3[Eu(DPA)_3].8H_2O$ and $Na_3[Eu(DPA)_3].15H_2O$ species (Chart 1). We first tried to replace the water molecules by deuterated water or to remove them by high drying process. Finally, we replaced the hydrophilic alkaline cations by more hydrophobic ammonium cations (Chart 1). For all compounds, a detailed photophysical analysis demonstrates and quantifies the role of second sphere water molecules, illustrating the second sphere water molecules luminescence quenching effect. Finally, the most hydrophobic $[NBu_4]_3[Eu(DPA)_3]$ complex was found to be soluble in dichloromethane enabling to explore the photophysical properties of the tris-dipicolinate family in this unusual aprotic solvent.



Cations
Cs^+
Na^+
 = gua
 = 1-MeIm
$EtNH_3^+$
Me_4N^+; Et_4N^+; Bu_4N^+

Complex	Cations	n(H_2O)
1	3 Cs^+	8
2	3 Na^+	15
3	3 gua^+	3
4	2($EtNH_3^+$), Na^+	6
5	2(1-$MeIm^+$), Na^+	3
6	3($EtNH_3^+$)	3
7	3(1-$MeIm^+$)	4
8	NMe_4^+	5
9	NEt_4^+	5
10	NBu_4^+	1

Chart 1. Compounds discussed in this article.

Results and discussion.

Two reference complexes were prepared from $EuCl_3$,$6H_2O$ and dipicolinic acid (3 eq.) in the presence of Cs_2CO_3 or Na_2CO_3 and purified by three successive recrystallizations in water.[3a] Nice transparent crystals were obtained as tiny diamond-shape plates (Cs^+) or cubes (Na^+), respectively (Figure 1) and the comparison of the XRD cell parameters confirmed that they were identical to those described in the literature (Table S1). These compounds crystallized with 8 and 15 water molecules, respectively, linked either to the Cs^+ (**1**) or Na^+ (**2**) cation or to the $[Eu(DPA)_3]^{3-}$ moieties.[3a],[3d],[29] These water molecules can be replaced by deuterated water by successive cycles of dissolution/recrystallization in hot D_2O. The complete exchange was monitored by FTIR spectroscopy (Figures 2 and S1) indicating the disappearance of the broad O-H stretching vibration band at 3600 cm^{-1} and the appearance of O-D stretches around 2500 cm^{-1}. H_2O/D_2O exchange through recrystallization appeared to be highly efficient even after the first recrystallization, and after 3 cycles it was complete. Transparent crystals with identical shapes and cell parameters were obtained, suggesting an identical formula $Cs_3[Eu(DPA)_3]\bullet 8D_2O$ (**1D**) and $Na_3[Eu(DPA)_3]\bullet 15D_2O$ (**2D**).

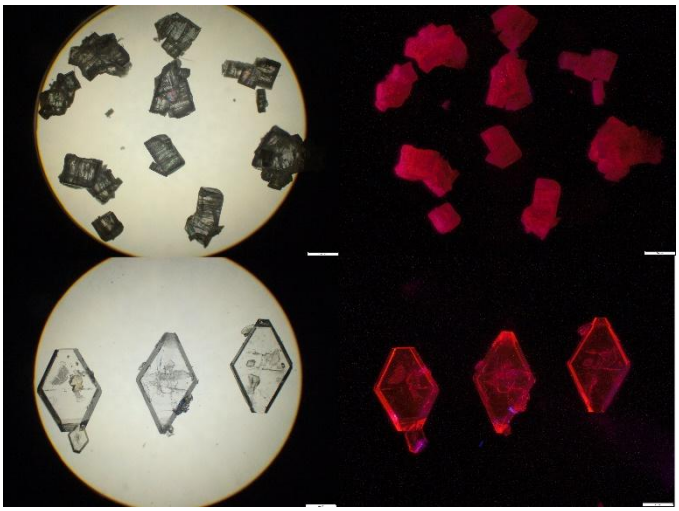


Figure 1. Optical microscopy pictures of crystals of $Cs_3[Eu(DPA)_3]\bullet 8H_2O$ (**1**, bottom) and $Na_3[Eu(DPA)_3]\bullet 15H_2O$ (**2**, top) under white (left) and UV (right) light irradiation.

An alternative way to remove water molecules is to dry the crystalline materials. However reproducible drying procedures are not so easy to perform. The transparent crystals turned to white amorphous powders upon drying under mild conditions (10^{-2} bar, room temperature), indicating the destruction of the crystal lattice upon water evaporation. However, a variable amount of water still remains in the materials as evidenced by luminescence lifetime measurement. Therefore, a thermogravimetric analysis (TGA) of **1** was undertaken (Figure 3). The analysis revealed a first mass loss of 11.6% between 60-150°C, followed by a plateau until 450°C where a second mass loss occurred. The first mass loss can be interpreted as the evaporation of almost all water molecules (7.7 out of 8.0). The drying process was thus conducted at 175°C under high vacuum (10^{-5} bar) during 18 hours and the sample was kept under inert atmosphere for all analyses. The elemental analysis under inert atmosphere of this dried material (Table S2), named $\mathbf{1}^{hd}$ (where *hd* stands for high drying), indicates the presence of 0.5 (+/- 0.5) water molecules in the material which is in perfect agreement with the thermogravimetric analysis. Note that such dried material is very hygroscopic and gets rapidly rehydrated (within ca 10 min) when exposed to air moisture as proved by luminescence lifetime measurements described below.

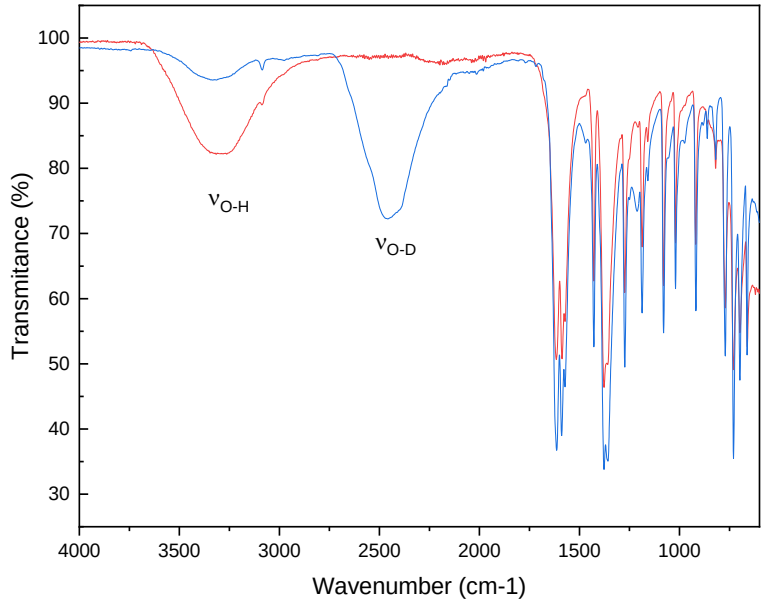


Figure 2. Solid state FTIR spectra of $Cs_3[Eu(DPA)_3]\bullet 8H_2O$ (**1**) (red) and $Cs_3[Eu(DPA)_3]\bullet 8D_2O$ (**1D**) (blue) crystals.

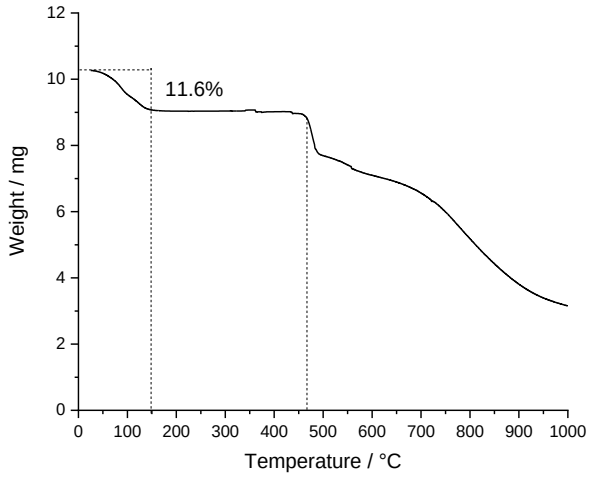
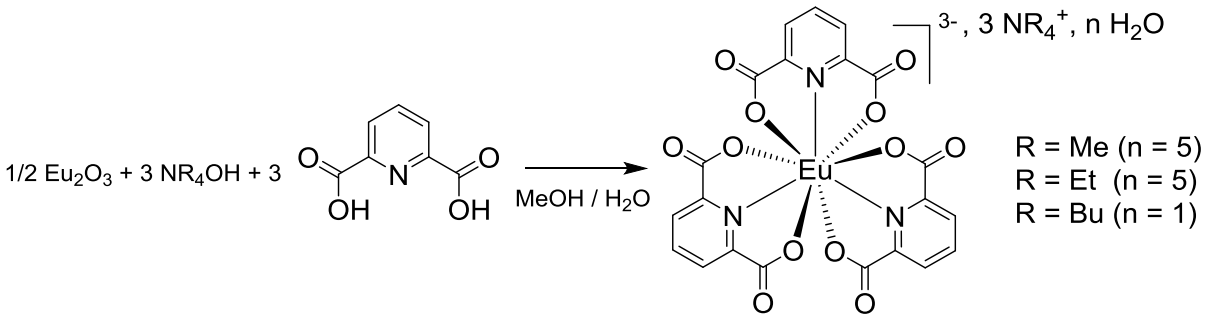


Figure 3. Thermogravimetric analysis under N_2 of $(Cs)_3[Eu(DPA)_3]\bullet 8H_2O$ (**1**).

In order to eliminate the interstitial water molecules, we considered changing the nature of the counter-cation from very hydrophilic alkalines (Na^+ and Cs^+) to organic ammonium cations. In this context, we have previously reported the synthesis and crystallization of $(Gua)_3[Eu(DPA)_3]\bullet 3H_2O$ (**3**, Gua = guanidinium) by a very simple ion-exchange reaction from **1** or **2** with guanidinium chloride in aqueous solution.[30] This cation exchange reaction gave more contrasted results with other ammonium salts. We studied more specifically ethylammonium chloride ($EtNH_3Cl$) as well as 1-methylimidazolium chloride (1-MeImCl) salts. In a typical procedure, **1** or **2** were dissolved in water, the desired ammonium chloride salt was added (3-12 eq.) and the mixture was left to crystallize. The crystals were recovered by filtration and analyzed by NMR spectroscopy (in D_2O solution) and X-ray diffraction. In the case of **1**, no exchange was observed and the starting material was recovered. In contrast, the use of **2** as starting material leads to the formation of monocrystals of respective formula $\{(EtNH_3)_2Na\}$ $[Eu(DPA)_3]\bullet 6H_2O$ (**4**) and $\{(1\text{-MeIm})_2Na\}[Eu(DPA)_3]\bullet 3H_2O$ (**5**) resulting from partial cation exchange reaction (see supporting information for crystal structure description). The ^1H NMR spectra, recorded in deuterated water, unambiguously confirmed the 2:1 ratio between the ammonium cations and the tris-dipicolinate complex. In order to overcome this partial cation exchange reaction, the direct synthesis was undertaken, using 1-MeIm and $EtNH_2$ as a base, generating the ammonium counter ion *in situ*. After recrystallization, transparent colorless crystals of $(EtNH_3)_3[Eu(DPA)_3]\bullet 3H_2O$ (**6**) and $(1\text{-MeIm})_3[Eu(DPA)_3]\bullet 4H_2O$ (**7**) were obtained (see section 2). All these complexes (**3-7**) still feature many -OH or -NH oscillators in the immediate surrounding of the tris-dipicolinate europium moieties, and therefore, more lipophilic tetra-alkylammonium cations were considered (NR_4^+= NMe_4^+, NEt_4^+, NBu_4^+).

The anion exchange reaction starting from **1** or **2** also failed for all NR_4^+ cations. The direct synthesis was thus considered, starting from dipicolinic acid, europium trichloride and the corresponding tetra-alkylammonium hydroxide (6 eq.) as the base and source of counter-ions. In all cases, the ^1H NMR spectra clearly showed the formation of the tris-dipicolinate europium complex but the amount of NR_4^+ counter-ions was always in excess due to the impossibility to grow mono-crystals no matter the purification technique used (precipitation, extraction with apolar solvents, dialysis or size exclusion chromatography). A careful examination of the literature revealed that tris-dipicolinate complexes are exceedingly difficult to prepare with tetra-alkylammonium cations, and thus rare. This fact is

mainly due to the difficulty to perfectly control the 1-to-3 stoichiometry between the tris-anionic complex and the tetra-alkylammonium cations due to purification issue. As examples, the direct phase extraction with the strongly lipophilic $(NMe_2Oct_2)^+$ cation was described but no characterization is reported.[11] More interestingly, Harrofield[3a] in 1995 and Hopkins twenty years later[18b] reported the direct synthesis of ammonium complexes starting from europium oxide in the presence of NaOH and the intermediate isolation of the hydrated hydroxide intermediate $\{Eu(OH)_3\}_n$. The crystal structure of $[NEt_4]_3[Eu(DPA)_3]\bullet 4H_2O$ was described alongside with its moderate solubility in polar organic solvent.[3b] Inspired by this old synthetic protocol, we developed a direct synthesis of tris-dipicolinate europium complexes with quaternary ammonium counter-cations (NMe_4^+, NEt_4^+ and NBu_4^+) in perfect stoichiometric amount starting from the oxide precursor Eu_2O_3 (Scheme 1). In a typical procedure, europium oxide was reacted with dipicolinic acid (3 eq.) in the presence of the corresponding tetra-alkylammonium hydroxide (3 eq.) in a water/methanol mixture. Since the only side-product is water, the desired complexes were easily isolated after solvent evaporation and drying. ^{1}H NMR characterization indicated the desired ratio between dipicolinate ligands and ammonium counterions (Figure S2-4), and the elemental analyses are in agreement with the formation of the following complexes: $(NMe_4)_3[Eu(DPA)_3]\bullet 5H_2O$ (**8**); $(NEt_4)_3[Eu(DPA)_3]\bullet 5H_2O$ (**9**) and $(NBu_4)_3[Eu(DPA)_3]\bullet 1H_2O$ (**10**) (Table S2). It is worth noting that the hydration number of compound **9** is close to the already described crystal structure.[3b] Interestingly, increasing the length of the alkyl chain profoundly modified the complexes solubility. Whereas **8** and **9** are only soluble in methanol and water, **10** is highly solubile in less polar solvents such as dichloromethane, which is rather uncommon for a tris-dipicolinate complex.



Scheme 1. Synthesis of the tetra-alkylammonium tris-dipicolinate europium (III) complexes.

X-ray diffraction analysis on single crystals revealed the molecular structures of complexes **1**-**7** and most importantly the presence of counter cations and water molecules in their second coordination sphere. The crystal data and refinement parameters are compiled in Table S3. For each compound, the europium coordination environment is very similar, with a typical tricapped trigonal coordination geometry. Selected bond lengths and angles are reported in Table S4. The continuous shape analysis (Table S5) indicates that all coordination polyhedra are close from perfect tricapped trigonal prisms with small dihedral angles between the two bases: 1.8(1)° in $\{(EtNH_3)_2Na\}[Eu(DPA)_3]\bullet 6H_2O$ (**4**); 1.3(1)° in $\{(1\text{-MeImid})_2Na\}[Eu(DPA)_3]\bullet 3H_2O$ (**5**); respectively 1.1(1)° and 5.8(1)° for the two independent complexes in $(EtNH_3)_3[Eu(DPA)_3)]\bullet 3H_2O$ (**6**); 3.4(1)° in $(1\text{-MeIm})[Eu(DPA)_3]\bullet 4H_2O$) (**7**). However, the crystal packing and number of interstitial water molecules are markedly different due to the nature of the different cations.

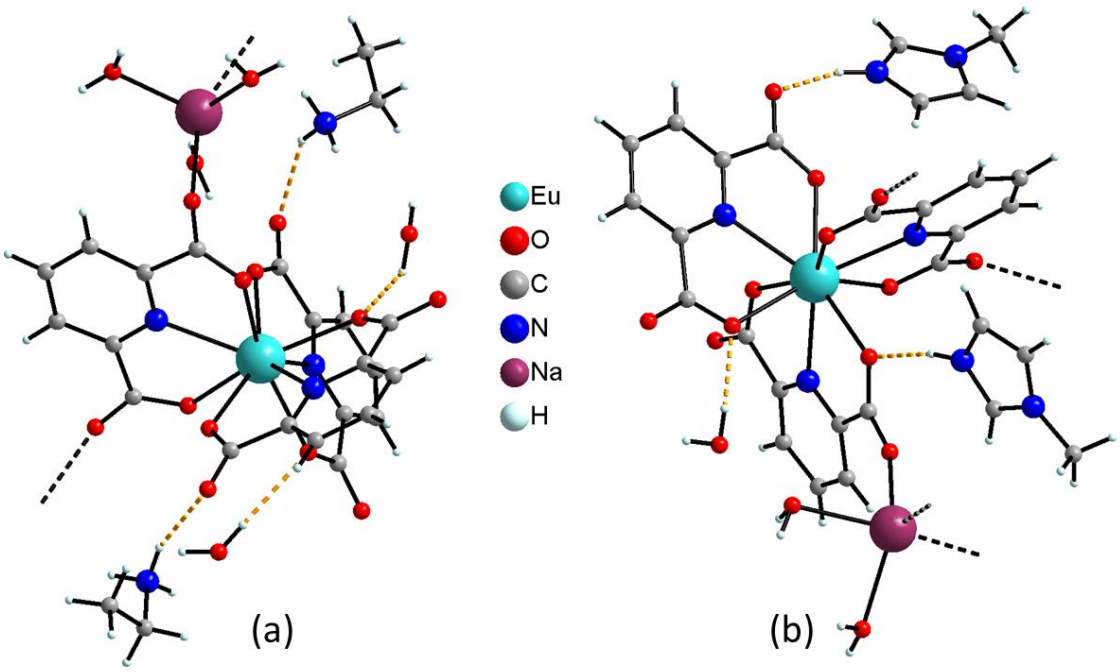


Figure 4. X-ray diffraction structure of complexes $\{(EtNH_3)_2Na\}[Eu(DPA)_3]\bullet 6H_2O$ (**4**, a) and $\{(1\text{-}MeImid)_2Na\}[Eu(DPA)_3]\bullet 3H_2O$ (**5**, b), The main H-bonds are represented in orange dotted lines.

The crystal structure of $(Cs)_3[Eu(DPA)_3]\bullet 8H_2O$ was previously reported by Bünzli and co-workers.[3b] In this compound, eight water molecules are found for each complex, and are either involved in bonding with the Cs^+ cations and/or H-bonding to one another or with DPA oxygens. In the two structures featuring mixed cations, $\{(EtNH_3)_2Na\}[Eu(DPA)_3]\bullet 6H_2O$ (**4**) and $\{(1\text{-}MeImid)_2Na\}[Eu(DPA)_3]\bullet 3H_2O$ (**5**), the sodium cations are 5-coordinated to 5 oxygens belonging to 2 DPA ligands and 3 H_2O molecules in **4** and to 3 DPA ligands and 2 H_2O molecules in **5**, resulting in the formation of coordination polymers networks. Besides H_2O molecules bound to Na^+, three additional H_2O molecules are found in the structure of **4**, forming a H-bonded network between one another and the ammonium cation. One H_2O molecule bonded to the DPA ligand is also found in **5**.

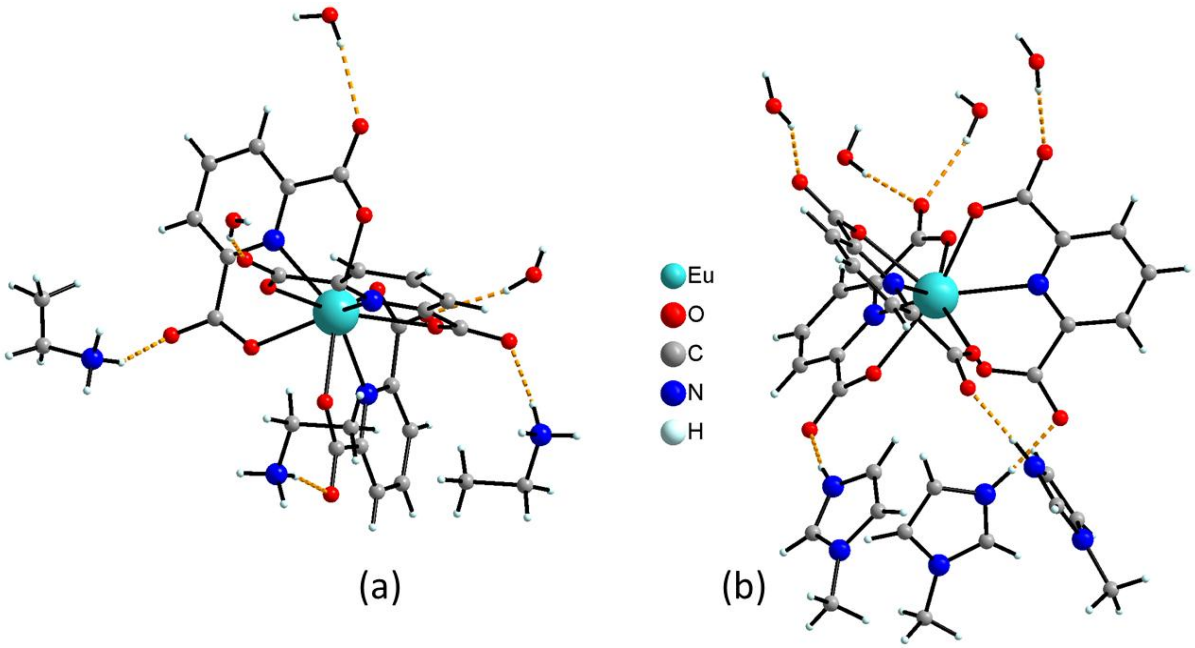


Figure 5. X-ray diffraction structure of complexes $(EtNH_3]_3[Eu(DPA)_3)]\bullet 3H_2O$ (**6**, a) and $(1\text{-}MeIm)_3[Eu(DPA)_3]\bullet 4H_2O$ (**7**, b). The main H-bonds are represented in orange dotted lines.

In compound $(1\text{-}MeIm)_3[Eu(DPA)_3]\bullet 4H_2O$ (**7**), 4 water molecules per complex are found in the crystal forming H-bonds to either the carboxylate moieties of the DPA ligands or to one another. Compound $(EtNH_3)_3[Eu(DPA)_3]\bullet 3H_2O$ (**6**) crystallizes in the triclinic P_{-1} space group, with two independent complexes in the asymmetric unit. 3 water molecules per complex are found in the structure, and form a hydrogen-bonded network with either the surrounding carboxylate groups from the DPA ligands, the ammonium cations and/or other water molecules. Overall, these 5 crystal structures show a large structural diversity, due to multiple complicated intermolecular interactions. These include cation-anion interactions with direct coordination of alkali cations to the DPA oxygens, water coordination to the alkali cations and hydrogen bonding networks of H_2O molecules which can be H-bonded to one another, H-bonded to the dipicolinate oxygens and H-bonded to the ammonium cations. It is thus extremely difficult to predict the exact number of water molecules in the second coordination sphere. Still, the use of non-coordinating ammonium cations seems to reduce the total number of water molecules found in the crystal lattices, but in no case second-sphere H_2O molecules could be avoided. Importantly, these second sphere OH vibrators are located within 4.6-6.8 Å from the Eu sites.

The photophysical properties of these complexes were studied in the solid state at room temperature and exhibit all the typical $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) emission patterns characteristic of Eu(III) luminescence (Figure 6). The comparison of our experimental data obtained in the case of **1** with that reported earlier by Bünzli's group is excellent[31] and the variation observed falls into the experimental uncertainty. In particular, caution must be taken for the determination of the absolute quantum yield using the integration sphere in order to get reproducible results.[32] Here, upon ligand excitation (280 nm) in an integrating sphere, we measured an overall quantum yield of 54 % which is in good agreement with the previously reported value of 58 ±3%.[31]

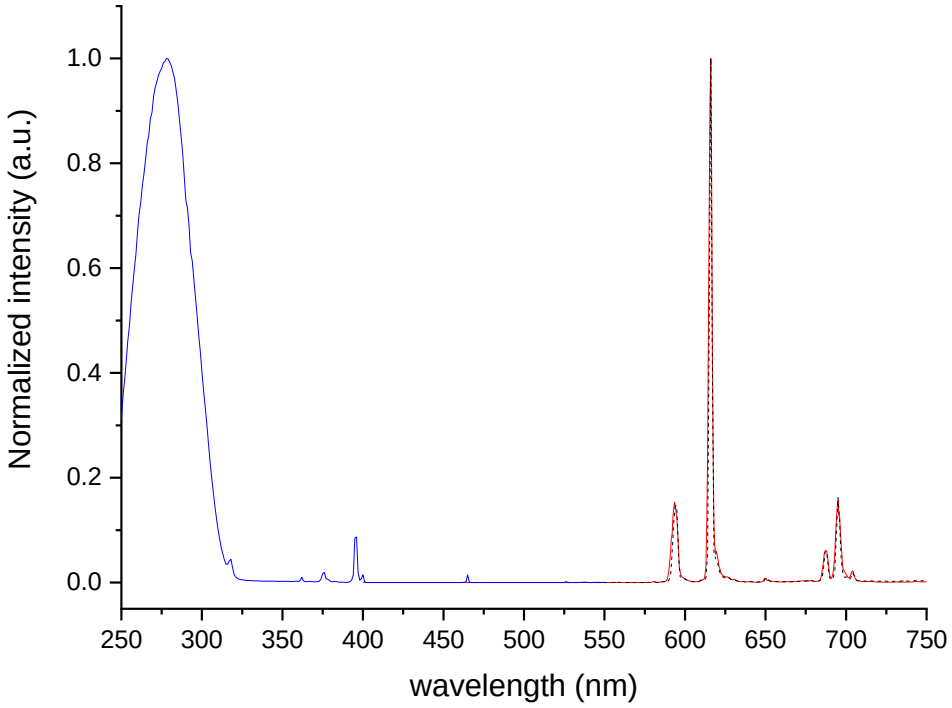


Figure 6. Normalized excitation (blue) and emission spectra of crystals of **1** (λ_{exc} = 290 nm (red), λ_{exc} = 396 nm (dotted black)).

The europium (III) luminescence is known to be particularly sensitive to its surrounding environment making this element very useful as local symmetry probe. Indeed, the emission profile and particularly the branching ratio is extremely sensitive to the symmetry of the first coordination sphere.[24, 33] In the present case, the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition dominates the emission spectra and the nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition is almost absent, which are both characteristic of high symmetry complexes, typically the threefold symmetric tris-dipicolinate species. This branching ratio can be characterized by the $I_{J=1}/I_{tot}$ ratio where $I_{J=1}$ is the emission intensity of the $^5D_0 \rightarrow {}^7F_1$ transition and I_{tot} the total integrated emission.[24] It is worth noting that the J=1 transition presents a pure magnetic dipole character, and is therefore used as a relative internal standard.[34] For all the Eu(III) tris-dipicolinate complexes studied, this ratio is almost constant between 0.14 and 0.18 indicating that the overall symmetry of the complexes is rather insensitive to the nature of the counter-cation or to the amount of interstitial water molecules in the crystal and in the amorphous powder. This result corroborates the crystallographic analysis indicating that the $[Eu(DPA)_3]^{3-}$ moieties are identical in all the studied crystals no matter the associated cations.

The determination of this branching ratio allows to estimate the radiative lifetime, τ_r and the radiative kinetic constant k_r according to the equation (1) proposed by Werts and Verhoven in the 2000's:[17b]

$$k_r = \frac{1}{\tau_r} = A(0,1).n^3.\frac{I_{tot}}{I_{J=1}} \qquad (1)$$

A(0,1) is the spontaneous emission probability considered as a constant equal to 14.65 s^{-1} [35] and *n* is the refraction index of the medium, measured at 1.517 in lanthanide tris-dipicolinate crystals.[31] Then, the non-radiative kinetic constant, k_{nr}, can be calculated from the observed lifetime τ_{obs} measured experimentally by equation (2).

$$\tau_{obs} = \frac{1}{(k_r + k_{nr})} \qquad (2)$$

All these data are compiled in Table 1. The modest variation of the branching ratio results in k_r values varying in a sharp range from 280 to 380 s^{-1}. On the contrary, the variations of the k_{nr} values are more significant and reflect the large variations observed in the measured lifetimes (ranging from 1.35 ms for **2** to 2.25 ms for **10**). Since the structures of the $[Eu(DPA)_3]^{3-}$ moieties are identical, these variations are clearly due second sphere effects. As an example, replacing the 8 interstitial water molecules of **1** by heavy water (compound **1D**) leads to a rigorously identical crystal packings but results in a decrease of the k_{nr} value from 260 to 90 s^{-1}. Similar effect is observed for the ultra-dry sample, $\mathbf{1^{hd}}$, featuring a k_{nr} of about 120 ms^{-1}. This H_2O/D_2O exchange effect is even more pronounced in the case of compound **2** (15 H_2O) with a dramatic k_{nr} decrease from 383 to 116 s^{-1}. Clearly, suppression of second sphere OH oscillators, or their replacement by OD ones, strongly reduces the non-radiative deactivation processes. This effect is strongly dependent on the number of OH oscillators present in the crystal. This quenching process is of course smaller than that observed with a direct coordination of the OH oscillators to the emissive center but is undoubtedly responsible of the 30% variation of the observed lifetime (from 1.35 to 2.25 ms). This sensitivity gave us the opportunity to evaluate the hygroscopic character of $\mathbf{1^{hd}}$. A simple exposure of $\mathbf{1^{hd}}$ to air at room temperature results in a decrease of the observed lifetime from 2.0 to 1.7 ms in 10 minutes (Table S6).[36]

The nature of the counter-cation has an impact on the number of interstitial water molecules and, as a consequence, the lifetime and the k_{nr} values vary accordingly (Table 1). Replacing the hydrophilic alkaline cation by ammonium derivatives (guanidinium (**3**), ethylammonium (**6**)) strongly reduce the number of water molecules present in the crystal structure (3 water molecules for complexes **3** and **6** compared to 8 or even 15 for **1** and **2**, respectively). The k_{nr} values are consequently comparable (235 and 213 s^{-1} for **3** and **6** respectively) and significantly reduced compared to those encountered for **1** (k_{nr}(**1**) = 263 s^{-1}) or **2** (k_{nr}(**2**) = 383 s^{-1}). Still, this interpretation remains qualitative because NH oscillators are also known to act as luminescence quenchers and these guanidinium and ethylammonium cations feature several NH bonds, some of them being in direct H-bonding interaction with the carbonyl moieties of the tris-dipicolinate complexes.

The case of compound **7,** featuring a 1-methylimidazolium counter-ion, is more surprising. The crystal contains 4 water molecules but the solid-state lifetime (2.15 ms) is very high, leading to a very low k_{nr} value of 155 s^{-1}, comparable to that of $\mathbf{1^{hd}}$ or **1D** where the OH oscillators are suppressed or replaced by OD ones. To understand this result, it is important to have a deeper insight into the crystal structure and the quenching mechanism. A generally accepted quenching mechanism proceeds *via* a dipole-dipole exchange process (Förster-like) and therefore its efficiency varies with r^{-6}, where r represents the Eu-O(w) distance (O(w) = oxygen of a second sphere water molecule). Consequently, in addition to the number of second sphere water molecules, it is important to consider their distance to the emitting center. In the XRD structure of **7**, the bulky 1-MeIm counterion are located in the immediate vicinity of the $[Eu(DPA)_3]^{3-}$ complexes increasing the minimal distance of the water molecules to the emitting center. Indeed, the shortest Eu-O(w) distance in **7** is 5.99 Å and much longer than what observed for all other complexes where it ranges between 4.45 Å and 4.72, respectively for **2** and **1** (see section 2). Finally, for complexes **8**, **9** and **10** featuring tetra-

alkylammonium counter cations, X-ray structures are not available but the reduced number of water molecule in **10** and the absence of NH oscillators explain the highest lifetime measured for the complete series (τ_{obs} = 2.25 ms) and consequently a reduced k_{nr} value of 107 s^{-1}.

Table 1. Photophysical data of tris-dipicolinate complexes measured in the solid state.

Compound	τ_{obs} (ms)[a]	$J_{(1)}/J_{tot}$	τ_{rad} (ms)	k_{rad} (s^{-1})	k_{nr} (s^{-1})
1	1.65	0.14	2.8	361	263
1D	2.15	0.14	2.7	373	92
1^{hd}	2.00	0.15	2.6	381	119
2	1.35	0.14	2.8	357	383
2D	2.00	0.13	2.6	381	116
3	1.85	0.16	3.1	319	235
6	1.85	0.16	3.1	328	213
7	2.15	0.16	3.2	312	155
8	2.00	0.18	3.5	287	208
9	2.10	0.17	3.2	309	170
10	2.25	0.15	3.0	337	107

a: precision +/- 0.05 ms

It is worth noting that tris-dipicolinate Eu(III) complexes are mainly studied in solution in aqueous media due to their very low solubility in organic solvents. The preparation of complex **10**, featuring hydrophobic tetra-butylammonium counter-cation, enable us to investigate the photophysical properties in apolar solvents such as dichloromethane (DCM) which is rather unusual for this class of complexes (Figure 7). The compound **10** presents a maximal absorption at λ_{max} = 271 nm (ε = 9600 $mol.L^{-1}.cm^{-1}$) with a shoulder at 280 nm comparable to that observed in water.[19a] Upon excitation in this ligand-centered transition, the bright red emission of europium is observed with the typical $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) emission pattern. The relative branching ratio $I_{J=1}/I_{tot}$ = 0.145 is very similar to that obtained in the solid state indicating that the overall threefold symmetry of the complex is preserved in DCM. This allowed us to calculate the radiative lifetime with eq.(1) τ_r = 3.43 ms in DCM (vs 3.91 ms in water).[31] The most striking differences concern the very high quantum yield Φ = 60% (vs quinine sulfate, see SI for details) and lifetime τ_{obs} = 2.4 ms measured for **10** in DCM compared to **1** in water (Φ = 29% and τ_{obs} = 1.7 ms).[31] These differences can be explained by the lower value of the global non radiative contribution k_{nr}(**10**) = 125 s^{-1} in DCM compared to k_{nr}(**1**) = 332 s^{-1} in water. This difference might be partly due to the suppression of second sphere hydration effects in such hydrophobic solvent, as observed in the solid state, but other contributions such as the Λ/Δ interconversion barrier and ligand lability phenomena could probably play a role.

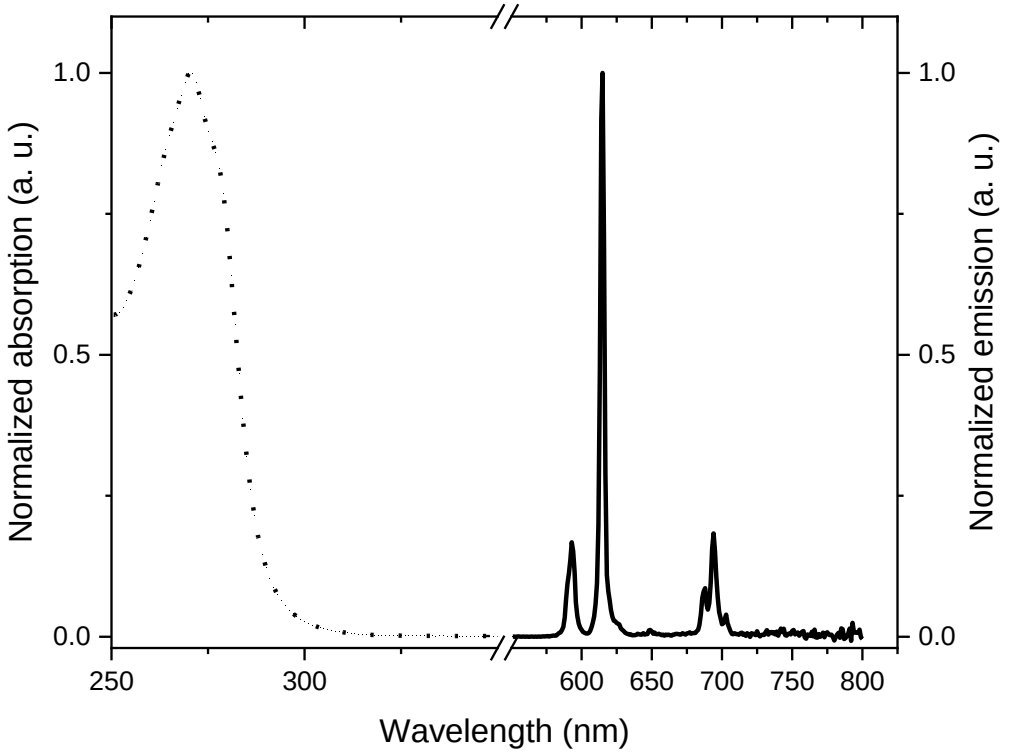


Figure 7. Normalized absorption and emission spectra of **10** in DCM at room temperature (λ_{ex} = 280 nm).

Conclusion.

In this article, we have described the synthesis of tris-dipicolinate europium complexes varying the nature of the ammonium counter-cations. Since the ion-exchange reaction from alkaline precursors failed or was incomplete, we developed a direct synthesis method using Eu_2O_3 as the europium precursor and quaternary ammonium salts. Most of the compounds were characterized by XRD analysis. The photophysical properties of all compounds were thoroughly studied and highlighted the crucial role of second sphere water molecules present in the XRD structure. The non-radiative deactivation constant (k_{nr}) varies significantly with the number of interstitial water molecules and their distance to the europium emitting center. Finally, the complex $(NBu_4)_3[Eu(DPA)_3]$, featuring the most lipophilic cation, exhibits excellent solubility in aprotic solvents such as dichloromethane, alongside with remarkable photophysical properties, in particular very long lifetime and large quantum yield. This last result significantly extends the scope of applications of tris-dipicolinate complexes to non-aqueous media.

Experimental section.

The preparation and characterisation of compounds **1-10** is described in supporting information. Crystallographic details, refinement results for complexes **4-7** are described in the supporting information.

Photophysical measurments. Absorption spectra were recorded on a JASCO V-650 spectrophotometer in diluted solution (ca. 10^{-5} or 10^{-6} mol L^{-1}), using spectrophotometric grade solvents. Emission spectra were measured using Horiba-Jobin–Yvon Fluorolog-3 fluorimeter. The steady-state luminescence was excited by unpolarised light from a 450 W xenon continuous wave (CW) lamp and detected at an angle of 90° for measurements of dilute solutions (10 mm quartz cuvette) by using a Hamamatsu R928. For solids, the sample were studied in quartz EPR tubes capped with young valve for inert atmosphere measurements. All spectra were corrected for both excitation source light-intensity variation and emission spectral responses. Luminescence quantum yields Q were measured in diluted solutions with an absorbance lower than 0.1, by using the following Equation (1):

$$\frac{Qx}{Qr} = \left[\frac{Ar(\lambda)}{Ax(\lambda)}\right] \cdot \left[\frac{n_x^2}{n_r^2}\right] \cdot \left[\frac{Dx}{Dr}\right] \qquad (1)$$

where A(λ) is the absorbance (or optical density) at the excitation wavelength, n the refractive index of the solvent and D the integrated luminescence intensity. “r“ and “x“ stand for reference and sample, respectively. Here, the reference is quinine sulfate in acidic water (Qr = 0.45). Excitations of reference and sample compounds were performed at the same wavelength. For solid a GMP integration sphere was used.

In practical, all emission spectra presented were recorded at room temperature, from 400 to 800 nm, with an increment of 0.5 nm and an integration time of 0.5 ms. The samples were all analysed in solid state, using the right-angle detection mode. All samples were excited either at 280 nm or 300 nm (crystals were also excited at 340 and 360 nm). A GG455 filter ($\lambda_{excitation}$ > 455 nm) was used to cut the 2nd harmonic from excitation source. All luminescence decay measurements were carried out at least 4 times to ensure a constant value for τ_{obs}. Emission intensity was voluntarily maintained under 10 000 counts to avoid photodetector saturation during the measurements. All luminescence spectra and luminescence decays are given in supporting information (figures S5-S23).

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Graphical Abstract.