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Pyridine-2,6-dicarboxylic acid for sensitization of europium(III) luminescence with very long lifetimes

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Convenient and mild syntheses of two europium(III) complexes, $Na[Eu(dipic)_2 \cdot 3H_2O].4H_2O$, (dipic=dipicolinate anions), $Na[Eu(dipic)_2 \cdot phen].H_2O$, (phen=1,10-phenanthroline), were reported. These two europium(III) complexes were confirmed by ^1H NMR, FT-IR, UV-Vis spectroscopy, elemental and lifetime analysis. Interestingly, the lifetimes were 2.31 ms and 2.38 ms for $Na[Eu(dipic)_2 \cdot 3H_2O].4H_2O$ in the solid state and in ethanol solution, respectively, though the presence of high-frequency vibrations in the first coordination sphere. Furthermore, the lifetime for $Na[Eu(dipic)_2 \cdot phen].H_2O$ in ethanol solution is 3.23 ms, which was the longest ever reported so far. The $Na[Eu(dipic)_2 \cdot phen].H_2O$ complexes exhibited an interesting quantum yield of 36.1% in ethanol solution, which was longer than that of $Na[Eu(dipic)_2 \cdot 3H_2O].4H_2O$. The value of stimulated emission cross-section (σ_p) for $Na[Eu(dipic)_2 \cdot phen].H_2O$ in ethanol was very close to the values of Nd-glass laser for practical use, which showed promising application as a high-power liquid laser medium.

1. Introduction

The unique luminescence properties of lanthanide(III) ions such as sharp emission, large stokes shift, insensitivity to oxygen and particularly their long excited state lifetime ranging from microseconds (Yb, Nd) to milliseconds (Eu, Tb) triggered the development of optical imaging[1], time-resolved bio-labelling probe[2], luminescent probe[3], OLED[4], lasing systems[5] and so on. The emission originates from 4f-4f intra-atomic electronic and magnetic dipole transitions that are parity-forbidden. As such, the absorption coefficients of the optical transitions for these ions are, however, extremely low which limits their practical application considerably. This drawback can be overcome by the use of highly absorbent chelating ligands, which serve as efficient sensitizers. The luminescent ligands act as antenna chromophores, by analogy to the light harvesting center in photosynthetic systems. Lanthanide(III) ions own large radius and a high affinity for hard donor centers and ligands with oxygen or hybrid oxygen-nitrogen atoms, particularly multicarboxylate ligands. The lanthanide(III) complexes with organic ligands containing carboxylic groups are of durable interest for their usually high thermodynamic stability and peculiar magnetic and luminescent properties. Pyridine-2,6-dicarboxylic acid (H_2dipic), which has a rigid 120°

angle between the central pyridine ring and two carboxylate groups is one of suitable polydentate ligands has attracted much intention in coordination chemistry. The H_2dipic group could potentially provide various coordination motifs to form both discrete and consecutive metal complex under appropriate synthesis condition[6] and sensitize very efficiently the visible emitters europium(III) leading to good luminescence quantum yields in solution and in the solid state.[7,8] The tridentate dipicolinate anions (dipic^{2-}) formed various anionic homoleptic complexes $[Ln(dipic)_3]^{3-}$, which fully satisfied the eight- and nine-coordination requirements of lanthanide(III) and showed a reasonable stability with respect to ligand dissociation even in presence of polar solvents. The $[Eu(dipic)_3]^{3-}$ chelates displayed intense luminescence, thanks to sensitization through the dipic^{2-} triplet state[9] with an efficiency of 61% for the tris complex in solution[7]. These chelates have even been proposed as secondary standards for quantum yield determination[7]. Moreover, several reports dealt with unsaturated lanthanide(III) coordination polymers, which were synthesized through the reaction between H_2dipic and lanthanum(III) nitrate under hydrothermal conditions[10-14]. However, their work concentrated more on the structures of coordination polymers rather than the photophysical properties. Focusing on photophysical properties of europium(III) complexes will be of interest because of its excellent stability, unique red emission and so on.

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In this paper, two novel europium(III) complexes, Na[Eu(dipic)$_2$·3(H$_2$O)].4H$_2$O, Na[Eu(dipic)$_2$·phen].H$_2$O have been investigated systematically. Their synthesis, structure and photophysical properties were reported. The lifetimes were 2.31 ms and 2.38 ms for Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O in the solid state and in ethanol solution, respectively, though the presence of high-frequency vibrations in the first coordination sphere. Interestingly, the lifetime for Na[Eu(dipic)$_2$.phen].H$_2$O in ethanol solution is 3.23 ms, which was the longest ever reported so far. The Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O exhibited an interesting quantum yield of 36.1% in ethanol solution. Particular attention was focused on their stimulated emission cross-section (σ_p) values, which were very close to the values of Nd-glass laser for practical use.

2. Experimental

2.1. Materials and synthesis

Europium(III) chloride (99.99%, TCI), Pyridine-2,6-dicarboxylic acid (99%, TCI), 1,10-phenanthroline.H$_2$O (99%, TCI) and other chemicals (analytically pure) were used without further purification.

2.2. Synthesis of Na[Eu(dipic)$_2$·3(H$_2$O)].4H$_2$O

H$_2$dipic (0.334 g, 2 mmol) was added to 20 mL ethanol and its pH value was adjusted to 7 by adding sodium hydroxide (1 M aqueous solution, 4 mL) under stirring. Then EuCl$_3$·6H$_2$O (0.366 g, 1 mmol) was dissolved in another 20 mL ethanol. The precipitation was produced by adding EuCl$_3$·6H$_2$O solution dropwise. Then, the precipitation was filtered and washed with ethanol. Finally, the precipitation was dried and stored in a silica-gel drier. ^{1}H NMR (300 MHz, DMSO-d$_6$, TMS, ppm): 5.36 (s, 2H), 4.77 (s, 4H), Elemental analysis: calculated for Eu$_1$Na$_1$C$_{14}$H$_{20}$O$_{15}$N$_2$: C, 27.07; H, 3.01; N, 5.17%. Found C, 26.64; H, 3.19; N, 4.84%. IR (KBr, cm^{-1}): 1391, 1625 (CO); 482 (OEu); 416 (NEu).

2.3. Synthesis of Na[Eu(dipic)$_2$·phen].H$_2$O

A solution of EuCl$_3$·6H$_2$O (0.366 g, 1 mmol) in deionized water (5 ml) was added to asolution of H$_2$dipic (0.334 g, 2 mmol) in ethanol (10 ml). Then, a solution of phen (0.180 g, 1 mmol) in ethanol (10 ml) was added to the above mixture. The reaction mixture was stirred for 24 h at 60 ℃ and then the solution was filtered to remove any insoluble material. The solution was concentrated and

allowed to stand. Precipitates were filtered and dried. ^{1}H NMR (300 MHz, DMSO-d$_6$, TMS, ppm): 9.10 (m, 2H), 8.50 (d, 2H),8.00 (s, 2H), 7.78 (m, 2H), 5.26 (t, 2H), 4.66 (d, 4H), Elemental analysis: calculated for

Eu$_1$Na$_1$C$_{26}$H$_{16}$O$_9$N$_4$: C, 44.40; H, 2.29; N, 7.97%. Found C, 44.71; H, 2.13; N, 7.82%. IR (KBr,cm^{-1}): 1625 (CO); 502 (OEu); 416 (NEu).

2.4. Characterization

^{1}HNMR spectra were recorded in DMSO-d$_6$ at room temperature on a Bruker Avance 300 spectrometer. Elemental analysis data were obtained from a Vario EL elemental analyzer. Absorption spectra (solution) were recorded on a 6800 double beam Jenway spectrophotometer. FT-IR spectra were carried out using a Nicolet 6700 Fourier Transform Infrared Spectrometer. The photoluminescence (PL) emission, excitation spectra and decay curves were measured on an Fluorolog-3-Tau fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation source.

3. Results and discussion

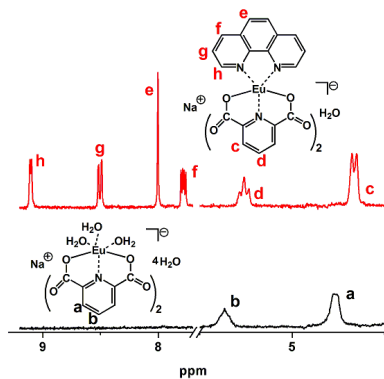### 3.1. Synthesis of europium(III) complexes

Synthetic routes for the europium(III) complexes were outlined in Scheme 1. The synthesis of Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O was rather convenient and time-saving by simply mixing H$_2$dipic ethanol solution after its pH adjustment with EuCl$_3$·6H$_2$O ethanol solution together. Then white precipitates were produced quickly. For Na[Eu(dipic)$_2$·phen].H$_2$O complexes, an aqueous solution of EuCl$_3$·6H$_2$O was added to a ethanol solution of H$_2$dipic. Then, phen ethanol solution was added subsequently. The reaction mixture was stirred for 24 h at 60 ℃. Precipitates emerged when the solution was concentrated and allowed to stand.
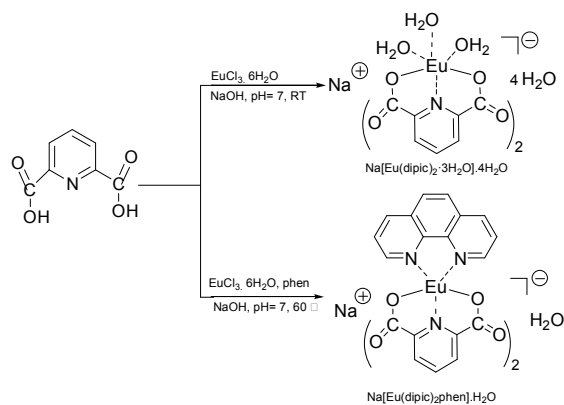
Scheme 1. Synthetic procedures of the europium(III) complexes.

3.2. ^{1}H NMR spectra analysis

The ^{1}H NMR spectra of the Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O and the Na[Eu(dipic)$_2$·phen].H$_2$O complexes were measured in DMSO-d$_6$ (see Fig. 1). Here, we chosen the europium(III) complex of Na[Eu(dipic)$_2$·phen].H$_2$O as an example to discuss the chemical shift in ^{1}H NMR spectrum. The ^{1}H NMR spectrum of Na[Eu(dipic)$_2$·phen].H$_2$O exhibited a doublet at 4.66 ppm, which integrated four protons and were assigned as protons of c position. The peak at 5.26 ppm integrated two protons was attributable to the protons of d position. The h, g, e, and f position protons of phen were observed at 9.10, 8.50, 8.00, and 7.78 ppm, respectively, which integrated 2 protons for each.

Fig. 1. ^{1}H NMR spectra of europium(III) complexes in DMSO-d$_6$

3.3. UV-Vis absorption spectroscopy

The UV-Vis absorption spectra of ligands and europium(III) complexes were recorded in a ethanol solution and depicted in Figure 2. All chromophores exhibited broad, intense, structureless, high-energy absorption transitions in the UV part of the spectra, with λ_{max} between 210 and 300 nm. Careful inspection of the absorption spectra of the ligands revealed the presence of a peak situated at about 220 and 270 nm that coincides with

the π-π* absorption seen for the corresponding complexes, mainly involving orbitals located on the pyridine ring and carbonyl functions. Furthermore, the absorption maximal peaks of europium(III) complexes underwent slight redshifts, which come from the formation of larger conjugated rings when the ligands coordinated to the europium(III) ions[15]
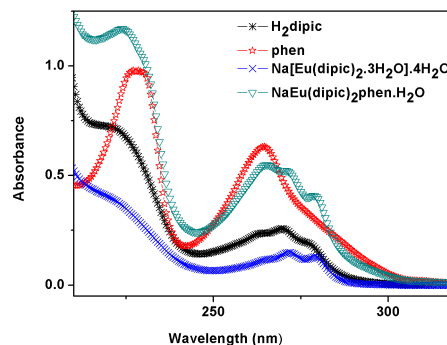
Fig. 2. UV-Vis spectra of ligands and europium(III) complexes in ethanol solution (1×10^{-5} mol.L^{-1}).

3.4. FT-IR spectroscopy

The FT-IR spectra for the ligands H$_2$dipic, phen and the corresponding europium(III) complexes were shown in Fig. 3. The spectra of the europium(III) complexes were not similar with the ligands.
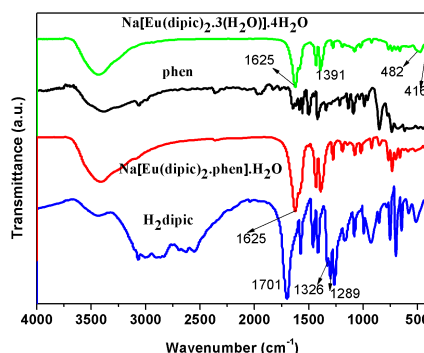
Fig. 3. Infrared spectra of the ligands: phen, H$_2$dipic and complexes: Na[Eu(dipic)$_2$·3(H$_2$O)].4H$_2$O, Na[Eu(dipic)$_2$·phen].H$_2$O.

For the complex Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O, all the bonds involving O-H motions of the carboxylate ground disappeared. For instance, the characteristic carboxyl vibrations in the free H$_2$dipic ligand was found at 1701 cm^{-1} as a strong and broad vibration ($\nu_{C=O}$), and at 1326 and 1289 cm^{-1} was attributed to the ν_{C-O} stretching vibration, which transformed into the asymmetric ν_{sCOO^-} at 1625 cm^{-1}

and symmetric v_{asCOO-} at 1391 cm^{-1} of Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O, indicating that all the carboxylic groups took part in coordination. Meanwhile, two new absorption peaks were observed at about 482 cm^{-1} and 416 cm^{-1}, which were attributed the stretching of O→Eu and N→Eu, respectively. The FT-IR spectrum of Na[Eu(dipic)$_2$·phen].H$_2$O was rather similar to that of Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O except for the presence of the characteristic phen vibrations. The FT-IR results further confirmed the conformation of the europium(III) complexes.

3.5. Excitation and emission spectroscopy

To obtain further information about the interaction between the ligands and the europium(III) ion, excitation spectra were obtained. Fig. 4 showed the excitation spectrum for each of the complexes in the solid state and in ethanol solution, obtained at 615 nm ($^5D_0 \rightarrow ^7F_2$ europium(III) emission). For all the complexes in the solid state, intense peaks were observed at about 260 nm. This can be assigned to the excitation of the π-π* transition centered onto the H$_2$dipic ligand, followed by an energy-transfer process to the europium(III) ion[14]. The excitation spectra showed that europium(III) emission was observed for excitation at short wavelengths in bands that were attributed to ligand absorption. The observed multiple bands centered at 395 nm is attributed to $^7F_0 \rightarrow ^5L_6$, $^5G_2$, $^5L_7$ and $^5G_3$ transition of europium(III)[16]. While the maximal peaks were 283 nm and 275 nm for Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O and Na[Eu(dipic)$_2$·phen].H$_2$O in ethanol solution, respectively. And Fig.4b showed that some of the excitation peaks from europium(III) weakened or even disappeared in ethanol solution, which may attribute to the fluorescence quenching caused by the solvent. A similar phenomenon can be found elsewhere[8]. The excitation spectra for europium(III) complexes in ethanol solution indicated that most of the excitation energy was mainly absorbed by the ligand, and then transferred to the central europium(III) ion, emitting characteristic luminescence. The emission spectrum for each complex was shown in Fig. 4. Each of these was obtained by excitation using the optimum excitation. For each complex, the lines were distributed mainly in the 550-750 nm range, which were associated with the 4f→4f transitions of the $^5D_0$ excited state to the low-lying ^7F_J (J =0, 1, 2, 3 and 4) levels of europium(III) ions. No emission peaks from the ligands were observed under this excitation, confirming that the energy transfer from the ligands to the europium(III) ion center was quite efficient in all europium(III) complexes. From the emission spectra, the transitions of $^5D_0 \rightarrow ^7F_0$ (forbidden in inversion center) and $^5D_0 \rightarrow ^7F_3$ (magnetic and electric dipole transitions) are very weak while those of $^5D_0 \rightarrow ^7F_1$ (magnetic dipole

transition), $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ (electric dipole transition) are strong. A prominent feature noted in these

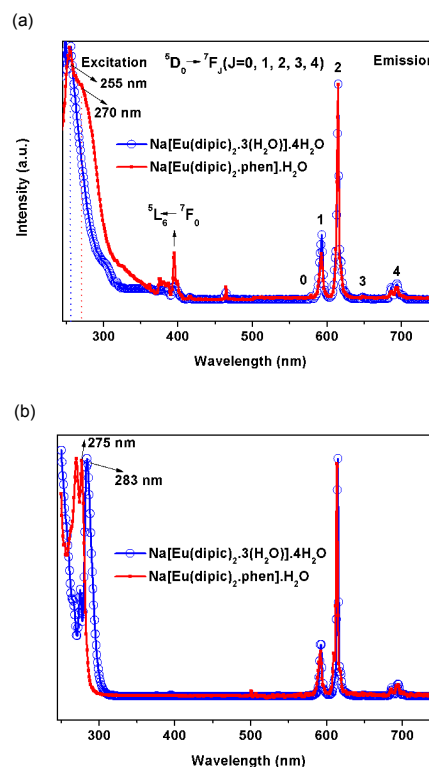

Fig. 4. (a) The PL spectra of europium(III) complexes in the solid state. (Left) Excitation spectra (λ_{em}=615 nm for all complexes). (Right) Emission spectra [λ_{ex}=255 nm for Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O and λ_{ex}=270 nm for Na[Eu(dipic)$_2$·phen].H$_2$O]; (b) the PL spectra of europium(III) complexes in ethanol solution (1 ×10^{-5} molL^{-1}). (Left): Excitation spectra (λ_{em}=615 nm for all complexes). (Right) Emission spectra [λ_{ex}=283 nm for Na[Eu(dipic)$_2$·3H$_2$O].4H$_2$O, 275 nm for Na[Eu(dipic)$_2$·phen].H$_2$O].

spectra is the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition at 615 nm, which is the most intense, pointing to a highly polarizable chemical environment around the europium(III) center. It is known that the nature of the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) is independent of the coordination environment surrounding the metal ion. When the interactions of the lanthanide(III) complex with its local environment were stronger, the complex become more nonsymmetrical, and the intensity of the electric dipole transitions become more intense. We can therefore use the $^5D_0 \rightarrow ^7F_1$ at 590 nm emission to assess the effect of the ligands on the emissions at other wavelengths. The emission line strength of the 615 nm ($^5D_0 \rightarrow ^7F_2$) transition was about 3 times that of the invariant $^5D_0 \rightarrow ^7F_1$ transition for all complexes in the solid state as well as in ethanol solution, which indicated that the significantly low symmetry of the ligand field. The calculated results were showed in Table 1.

The emission spectrum for each complex in solid state and in ethanol solution by excitation using the europium(III) $^5L_6 \leftarrow ^7F_0$ 395 nm transition to allow comparison with emission spectra under ligand excitation

(see Fig.5), and between the complexes. For each complex, three main emission bands were also observed to peak at about 590 nm ($^5D_0 \rightarrow ^7F_1$), 615 nm ($^5D_0 \rightarrow ^7F_2$), and 690 nm ($^5D_0 \rightarrow ^7F_2$). No emission was observed from the ligands in this study or from transitions within the europium(III) ion. Excitation of the complexes at the emission spectra peaks observed in Fig. 5 had no effect on the shape of the emission spectra.
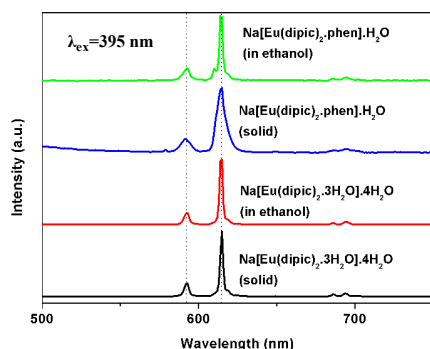

Fig. 5. Emission spectra of europium(III) complexes in solid state and in the ethanol state under direct f-f excitation ($^5L_6 \leftarrow ^7F_0$, 395 nm).

3.6. Emission lifetime and quantum yields (Φ)

To better understand the luminescent properties of the europium(III) complexes in the solid state, in ethanol solution, the room temperature luminescence decay curves of the $^5D_0$ excited state were measured by monitoring the most intense emission lines ($^5D_0 \rightarrow ^7F_2$) of the europium(III) ion center at 615 nm under excitation of a 355 nm Xenon lamp. As shown in Fig. 6, the luminescence decays of the excited states were best fit to the monoexponential decay for all of the complexes. It demonstrated the presence of only one emissive europium(III) ion center in the solid state as well as in ethanol solution, which agreed with the analysis of luminescence spectra of europium(III) complexes. From the monoexponential decays, the luminescent lifetime values (τ_{obs}) of Na[Eu(dipic)$_2$phen].H$_2$O and Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O could be extracted 2.31 ms and 2.38 ms in the solid state, 2.08 ms and 3.23 ms in ethanol solution, respectively. The location of the ligand states at high energy prevents both a mixing of these states with the 4f states and a back-transfer from the excited europium(III) ion to the ligand[17]. Therefore, the lifetimes measured for europium(III) ($^5D_0$) excited level in Na[Eu(dipic)$_2$phen].H$_2$O and Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O were even higher than the values found for the complexes

Na$_3$[Eu(dipic)$_3$].nH$_2$O (τ_{obs}=1.3 ms)[18] and [N(C$_2$H$_5$)$_4$]$_3$[Eu(dipic)$_3$].nH$_2$O (τ_{obs}=2.02ms)[19]. This may reflect differences in the electronic structure and/or different coupling between the electronic structures of the europium(III) ions and ligands compared with other europium(III) complexes mentioned in ref. 18, 19.
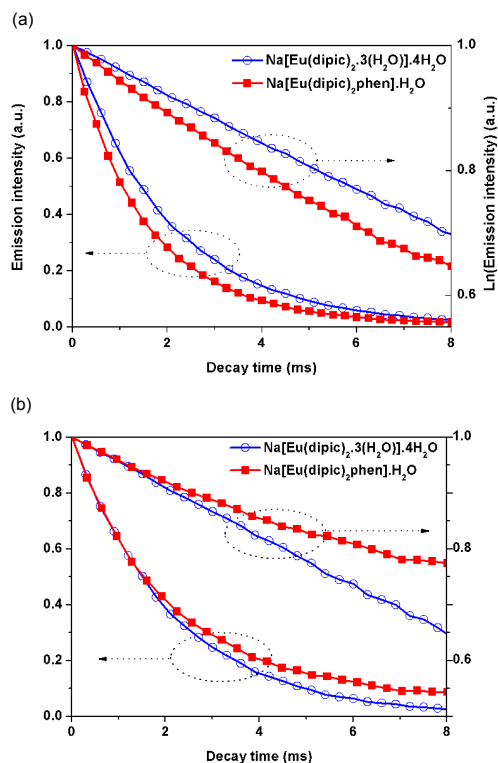
Fig. 6 The room temperature luminescence decay curves of the europium(III) complexes: (a) in the solid state, (b) in ethanol solution (λ_{em} = 615 nm, λ_{ex} = 355 nm).

Furthermore, the lifetime for Na[Eu(dipic)$_2$·phen].H$_2$O in ethanol solution is 3.23 ms, which, to the best of our knowledge, was the longest ever reported so far. The relative long lifetime for Na[Eu(dipic)$_2$phen].H$_2$O in ethanol solution was diagnostic for the absence of high-frequency oscillators in the first coordination sphere. Although there were high-energy C-H, O-H vibrations in the complexes, these were not in the first coordination sphere and thus were less effective in causing radiationless deactivation.

Table 1
Photophysical properties of the europium(III) complexes.

complex		τ_{obs} [ms]	$\Delta\lambda_{eff}$ [nm]	I_{rel}	A_r [s^-]	$\sigma_p\times10^{-20}$ [cm^2]	τ [ms]	Φ_{LN} [%]	Φ [%]
Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O	solid	2.31	2.21	2.56	202	0.77	4.95	46.7	-
	ethanol	2.38	2.50	3.33	177	0.72	5.65	42.1	14.8
	solid	2.08	3.18	3.21	252	0.67	3.97	52.4	-
Na[Eu(dipic)$_2$phen].H$_2$O	ethanol	3.23	2.61	2.75	190	0.75	5.26	61.4	36.1

FWHM of the $^5D_0\rightarrow{}^7F_2$ (615 nm) transition ($\Delta\lambda_{eff}$).

Emission lifetimes (τ_{obs}) of the europium(III) complexes were measured by the excitation at 355 nm.

Quantum yields (Φ) of the europium(III) complexes were measured with excitation at optimal excitation wavelengths ($^5D_0\rightarrow{}^7F_2$) in ethanol solution (1×10^{-5} M).

Einstein coefficient (A_r) was determined using eq 3.

Stimulated emission cross-sections (σ_p) values were determined by eq 4

The effect of the coordination water on the europium(III) emission lifetimes can be clearly seen (Table 1), with the lifetime increasing for all the complexes when the solid state europium(III) complexes were dissolved in ethanol. This arised from the reduction of nonradiative relaxation of the excited europium(III) ion through coupling with OH vibrational modes. When these two complexes were compared, the lifetime of the emission from Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O in ethanol solution was always less than that from Na[Eu(dipic)$_2$phen].H$_2$O. However, for these two complexes in the solid state, the lifetime of Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O was longer than that of Na[Eu(dipic)$_2$phen].H$_2$O ragardless of the unsaturated coordination number in the former. The mechanism was an open question.

The quantum yields for the europium(III) emission of Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O and Na[Eu(dipic)$_2$phen].H$_2$O in ethanol solution were determined using quinine sulfate (dissolved in 0.5 M H$_2$SO$_4$ with a concentration of 10^{-6} M, assuming Φ_{PL} of 0.55) as a standard[20]. The luminescent efficiency was calculated according the following formula:

$$\phi = \phi_r \frac{A_r}{A} \cdot \frac{S}{S_r} \cdot \frac{n^2}{n_r^2} \quad (1)$$

where Φ is the fluorescence quantum yield, S represents the area of the corrected emission fluorescence spectrum, A is the absorbance of the solution at the exciting wavelength, and n is the refractive index of the solvent used. The subscript r denotes the reference substance that its fluorescence quantum yield is already known. The calculated results were shown in Table 1.

The quantum yield of Na[Eu(dipic)$_2$phen].H$_2$O (36.1%) was significantly higher than that of Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O (14.8%). Both of their quantum yields were slightly higher than that of Cs$_3$[Eu(dipic)$_3$] (13.5%) reported as a secondary standard for quantum yield determination [7]. According to energy gap theory, the radiationless transitions are promoted by ligands and solvents with high-frequency vibrational modes. The increase of quantum yield is due to suppression of radiationless transitions caused by vibrational relaxation. However, this comparatively low quantum yield of Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O was not that surprising given the presence of high-frequency vibrations, which is an effective europium(III) excited-state quencher. Although there were high-energy O-H vibrations in the complex Na[Eu(dipic)$_2$phen].H$_2$O, these were not in the first coordination sphere and thus were less effective in causing radiationless deactivation. The exclusion of water from the inner sphere of the Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O complex minimized the nonradiative quenching of the europium(III) emission resulting in a quantum yield that was higher than that of Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O.

3.7. Intrinsic quantum yield (Φ_{LN}), radiative lifetime (τ)

Assuming that non-radiative and radiative processes were essentially involved in the depopulation of $^5D_0$ state, the intrinsic quantum yield Φ_{LN} of the $^5D_0$ emission level in europium(III) complexes at room temperature was obtained based on the luminescence data (emission spectra and emission decay curves).

The intrinsic quantum yield of the luminescence step, expressing how well the radiative processes (characterized by the rate constant A_r) compete with non-radiative processes (characterized by the rate constant A_{nr})[21], can be obtained based on the experimental spectroscopic data (emission spectra and emission decay curves)[22].

$$\Phi_{LN} = \frac{A_r}{A_r + A_{nr}} \quad (2)$$

Where, A_r and A_{nr} are radiative and non-radiative transition

rates, respectively. The denominator in Eq. (2) is calculated from the lifetime of the emitting level

$$(\frac{1}{\tau_{obs}} = A_r + A_{nr}).$$

The radiative lifetime (τ), which can be calculated from the simple treatment of its corrected emission spectrum according to eq 3, assuming that the energy of the $^5D_0\rightarrow^7F_1$ transition and its oscillator strength are constant[23], is directly related to the radiative and non-radiative decay rates of the lanthanide ion.

$$A_r = \frac{1}{\tau} = A_{01}n^3(I_{tot}/I_{01}) \qquad (3)$$

where A_{01} (14.65 s^{-1}) is the spontaneous emission probability of the $^5D_0\rightarrow^7F_1$ transition in vacuo, I_{tot}/I_{01} is the ratio of the total area of the corrected europium(III) emission spectrum to the area of the $^5D_0\rightarrow^7F_1$ band, and n is the refractive index of the medium. When n = 1.5 is assumed for solid state metal-organic complexes, the calculated radiative lifetime falls into the narrow range 3.5-5.0 ms for two complexes. Use of eq (3) with n=1.36 for ethanol, yields τ =5.65 ms for Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O and τ =5.25 ms for Na[Eu(dipic)$_2$phen].H$_2$O. From these values, the intrinsic quantum yields Φ_{LN} =40-65% (listed in Table 1) can be calculated.

3.8. The stimulated emission cross-section (σ_p)

To estimate the capability of those europium(III) complexes for being a laser medium, σ_p values were determined. σ_p value is one of the most important factors for laser amplification. With the corresponding emission spectrum, for a Lorentz line, σ_p can be related to the radiative transition rate by

$$\sigma_p(\lambda_p) = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A_r \qquad (4)$$

where c, λ_p, $\Delta\lambda_{eff}$, n and A_r are speed of light, wavelength of oscillation peak, the full width at half maximum (FWHM) of oscillation peak, refractive index of the matrix and Einstein coefficient, respectively[5].

In general, the transition $^5D_0\rightarrow^7F_2$ of the europium(III) ion is interesting for its use in the laser systems. In this work, σ_p values of $^5D_0\rightarrow^7F_2$ fluorescence transition of europium(III) ion were the same order as those shown by

glasses used in solid state laser applications[24]. When factors including the lifetime, quantum yield, stimulated emission cross-section, etc. were taken into consideration, Na[Eu(dipic)$_2$phen].H$_2$O could be more promising than Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O for optical applications such as the high-power laser media. According to the above discussion, the relative emission intensities of $^5D_0\rightarrow^7F_2$ to $^5D_0\rightarrow^7F_1$ transition (I_{rel}), the FWHM of the $^5D_0\rightarrow^7F_2$ transition ($\Delta\lambda_{eff}$), emission lifetimes (τ_{obs}), quantum yields (Φ), radiative rates (A_r), stimulated emission cross-section (σ_p), radiative lifetime (τ), and intrinsic quantum yields (Φ_{LN}) of the europium(III) complexes were summarized in Table 1.

4. Conclusion

Two new europium(III) complexes, Na[Eu(dipic)$_2$phen].H$_2$O, Na[Eu(dipic)$_2$.3H$_2$O].4H$_2$O were synthesized under mild conditions and characterized by various techniques. The photophysical properties in the solid state and in ethanol revealed the presence of a single luminescent site in all europium(III) complexes and efficient ligand-to-metal energy transfer. Europium(III) complexes showed relatively high quantum yields and long lifetimes. The lifetime for Na[Eu(dipic)$_2$·phen].H$_2$O in ethanol solution is 3.23 ms, which was the longest ever reported so far. The stimulated emission cross-section was also determined, which was very close to the values of Nd-glass laser for practical use. Therefore, luminescent europium(III) complex Na[Eu(dipic)$_2$·phen].H$_2$O showed more promising application as a high-power liquid laser medium.

Acknowledgments

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