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RESEARCH ARTICLE

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Synthesis of Eu(III) and Tb(III) complexes with novel pyridine dicarboxylic acid derivatives and their fluorescence properties

Abstract Starting from pyridine-2,6-dicarboxylic acid (DPA), a series of novel pyridine-2,6-dicarboxylic acid derivatives were synthesized. In these compounds, 4-(hydroxymethyl)pyridine-2,6-dicarboxylate (4-HMDPA) and 4-[(bis-carboxymethyl-amino)-methyl]-pyridine-2,6-dicarboxylic acid (4-BMDPA) were used as multifunctional ligands to coordinate with Tb(III) and Eu(III) and the complexes were prepared. The fluorescence properties of the solid complexes and their solutions were investigated in detail. The results indicated that the weak election-withdrawing group 4-hydroxymethyl in 4-position of pyridine in 4-HMDPA could weaken the fluorescence intensity of the lanthanide complexes. The contradistinctive experimental results showed that the fluorescence intensities of these complexes are related to pH values of the aqueous solutions and the dipole moments of solvent molecules: in the neutral aqueous solutions, the fluorescence intensities of these complexes were strongest, while the dipole moments were lower when the fluorescence intensities were stronger. 4-BMDPA is the better sensitizer and may be used as time-resolved fluoroimmunoassay.

Keywords pyridine-2,6-dicarboxylic acid, fluorescence, lanthanide complex

The complexes of rare earth ions have strong luminescence through the energy transfer (sensitizing action) in the lanthanide complexes with some organic ligands. The use of pyridine-2,6-dicarboxylic acid derivatives as sensitizers is better than using others, for example, the salicylate derivatives, 1,10-phenanthroline derivatives and β-dione compounds. It is because the sensitizing actions of pyridine-2, 6-dicarboxylic acid derivatives are better and the lanthanide complexes with pyridine-2,6-dicarboxylic acid are chiral, which is a requirement for circularly polarized luminescence spectra [1]. Pyridine-2, 6-dicarboxylic acid exists largely in biological bodies [2]. Since Richardson [3] used pyridine-2, 6-dicarboxylic acid derivatives to study the kinetics of chiral molecules through luminescence measurements, the lanthanide complexes with pyridine-2, 6-dicarboxylic acid derivatives were studied widely [4]. The substituted pyridine-2, 6-dicarboxylic acid derivatives of Tb(III) and Eu(III) are stabile, luminescence intensities of these complexes are strong, and lifetimes are long. They can be used to tag proteins in time-resolved fluoroimmunoassay. Groves reported that they had used some lanthanide complexes of pyridine-2, 6-dicarboxylic acid derivatives to cut and label DNA [5] and Lamture had done similar works on tag proteins [6]. So pyridine-2, 6-dicarboxylic acid derivatives were studied widely as fluorescence probes in the biochemical analysis [7].

The introduction of bis(carboxymethyl)amino-methyl in 4-position of pyridine conduces to improve the chelation of the ligands, increase the number of chelated atoms, and form the netted structures. In addition, it can affect the stereochemistry of the complexes. Those complexes are chiral.

In this paper, based on the introduction of hydroxymethyl in the 4-position of pyridine-2,6-dicarboxylic, a group of bis(carboxymethyl)amino-methyl was placed at the 4-position of pyridine-2,6-dicarboxylic acid. A series of novel multifunctional pyridine-2, 6-dicarboxylic acid derivatives were synthesized and the fluorescence properties of their complexes of Tb(III) and Eu(III) were analyzed.

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1 Experimental

1.1 Reagents and instruments

Melting points were determined on an XRC-1 apparatus.

Infrared (IR) spectra were recorded on an Avatar-360-FT spectrophotometer with KBr plates. All nuclear magnetic resonance (NMR) spectra were recorded at 297 K with an INOVA-400 MHz apparatus, and gas chromatograph-mass spectra (GC-MS) were performed on a HP5988A gas chromatograph-mass united spectrometer. Fluorescence properties were recorded on anFL-2500 apparatus.

Pyridine 2,6-dicarboxylic acid was CR, others were AR. Compound (**2**) was prepared as previously described by the procedure in ref. [8]; the yield was 86%. The melting point was 118–121°C (literature [9]: 125–128°C).

1.2 The synthesis of ligands

1.2.1 Preparation of dimethyl 4-(hydroxymethyl) pyridine-2,6-dicarboxylate (**3**)

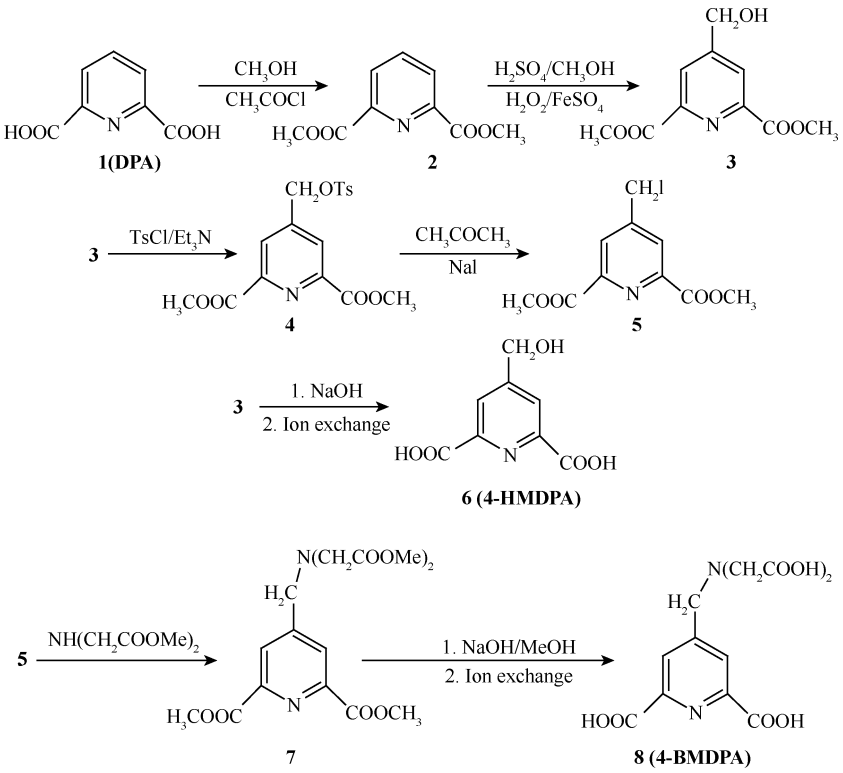
Solutions of $FeSO_4 \cdot 7H_2O$ (700 mmol) and 30% (w/v) H_2O_2 were slowly added through syringe pumps, at the same speed, to the suspension of pyridine 2,6-dicarboxylic acid dimethyl ester (**2**) (100 mmol) in the mixture of methanol (100 mL) and 30% H_2SO_4 (10 mL) while stirring vigorously. . The speed of addition was controlled to maintain the temperature of the reaction mixture at 15–30°C. After completing the addition, the reaction mixture was stirred for an additional 10 min, then K_2CO_3 was added to obtain pH 6–7, and then filtered. The filtrate was extracted by ethyl acetate (20 mL × 5). The extract was dried on Na_2SO_4 and evaporated. The residue was purified by flash chromatography to give dimethyl 4-(hydroxymethyl) pyridine-2, 6-dicarboxylate (**3**)(9.7 g). The yield was 41%. m. p. 154–158°C.

IR(KBr): ν 3485, 3079, 3014, 2959, 1723, 1705, 1609,1453, 1226, 1158, 984 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 2H, Py-3,5-H), 4.91 (s, 2H, CH_2), 4.03 (s, 6H, OCH_3); FAB-MS (*m/z*): 225(M^+).

1.2.2 Preparation of dimethyl 4-(iodomethyl) pyridine-2, 6-dicarboxylate (**5**)

The solution of *p*-toluenesulphonyl chloride (36.1 mmol in 25 mL of CH_2Cl_2) was added to the suspension of compound (**3**) (25.8 mmol in 40 mL of CH_2Cl_2) at 0°C, while stirring and cooling. After stirring for 20 min, the residue mixture was stirred again for 15 min at 0°C and another 15 min at room temperature. At the end of the reaction, the residue was diluted with a double volume of ethyl acetate, and washed thrice with water and thrice with an aqueous tartaric acid (10%), then dried and evaporated. A whitish solid was obtained. The solid was purified by recrystallization to give dimethyl 4-[(tosyloxy)methyl]pyridine-2, 6-dicarboxylate (**4**) (7.9g). The yield was 81%. m. p.136–137°C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 2H, Py-3,5-H), 7.84-7.81 (d, 2H, J = 8.2 Hz, Ar-H), 7.37-7.34 (d, 2H, J = 8.2 Hz, Ar-H), 5.16 (s, 2H, CH_2), 4.02 (s, 6H, OCH_3), 2.45 (s, 3H, Ar-CH_3).



Compound (**4**) (20 mmol) was added to the solution of NaI (30 mmol in 250 mL of acetone), and the reaction mixture was stirred under reflux for 2.5 h (the reaction was monitored by TLC). The reaction mixture was kept in darkness overnight at room temperature. The next morning the mixture was diluted with 550 mL of ethyl acetate, and washed with water (150 mL × 3), followed by tartaric acid (10%) (120 mL × 3) and a dilute solution of sodium thiosulfate. The reaction mixture was dried with Na_2SO_4 in darkness and evaporated; dimethyl 4-(iodomethyl)pyridine-2, 6-dicarboxylate (**5**) (5.2 g) was obtained with an yield of 78%. M. p. 148–150°C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 2H, Py-3,5-H), 4.45 (s, 2H, CH_2I), 4.04 (s, 6H, OCH_3).

1.2.3 Preparation of 4-(*hydroxymethyl*) *pyridine-2,6-dicarboxylic acid* (**6**)

A quantity of 1.1 mL of NaOH (30%) was added to the solution of 5.5 mmol compound (**3**) in methanol (50 mL), while stirring. After stirring for 24 h at room temperature, the reaction mixture was evaporated and a yellow solid was obtained. The crude product was purified by 732 cation resin column to give 4-(hydroxymethyl) pyridine-2, 6-dicarboxylic acid (**6**) (1.06 g) (indicated as 4-HMDPA). The yield was 98%.

IR (KBr), *v*: 3 485, 3 092, 2 924, 1 707, 1 636, 1 060, 1 441, 1 261, 1 216, 999; ^{1}H-NMR (400 MHz, D_2O): δ8.284 (s, 2H, Py-3,5-H), 4.862 (s, 2H, CH_2); EA (%, calculated for $C_8H_7NO_5$): C 48.59 (48.74), H 3.60 (3.58), N 7.13 (7.10).

1.2.4 Preparation of 4-((*bis*(*carboxymethyl*)*amino*)*methyl*) *pyridine-2,6-dicarboxylic acid* (**8**)

The compound (**5**) (17 mmol) was dissolved in 5 mL of THF and HN(CH_2COOMe) (35 mmol) was added to the solution. The mixture was stirred for 12 h in darkness. At the end of the reaction, the residue was evaporated in vacuum. The oil-like mixture was diluted with 200 mL CH_2Cl_2. The solution was washed thrice with water and 50 mL of 5% $Na_2S_2O_3$, dried, and evaporated. The yellow oil-like mixture was obtained, to which five drops of ethanol was added and filtered to give dimethyl 4-((bis-methoxycarboxylmethyl-amino)-methyl)-pyridine-2, 6-dicarboxylate (**7**) (5.9 g). The yield was 95%. m. p. 95–97°C.

IR (KBr): ν 2996, 2958, 1746, 1732, 1720, 1439, 1417, 1214, 1162, 1014, 779, 735cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.03 (s, 2H, Py-3,5-H), 4.11 (s, 2H,CH_2), 4.03 (s, 6H, OCH_3), 3.72 (s, 6H, $OCH_3)_2$), 3.58 (s, 4H, NCH_2). ^{13}C-NMR (400 Hz, $CDCl_3$): 171.13, 165.23, 151.71, 148.55, 127.79, 56.55, 54.54, 53.22, 51.76; MS (*m/z*): 368 (M^+), 337(M-CH_3O), 309 (100%, M-CH_3O-CO); EA (%, calculated for $C_{16}H_{20}N_2O_8$): C 52.32 (52.17), H 5.43 (5.47), N 7.67 (7.61).

A quantity of 20 mL of NaOH (30%) was added to the solution of 15 mmol compound (**7**) in methanol (150 mL), while stirring. After stirring for 24 h at room temperature, the reaction mixture was evaporated and a yellow solid was obtained. The crude product was purified by 732 cation resin column to give 4-[(bis-carboxymethyl-amino)-methyl]-pyridine-2,6-dicarboxylic acid (**8**) (4.6g) (indicated as 4-BMDPA). The yield was 98%.

IR (KBr): 3461, 3131, 1724, 1710, 1637, 1604, 1560, 879, 726 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): 11.50–13.50 (br, 4H, COOH, exchange in D_2O), δ8.29 (s, 2H, Py-3,5-H), 4.04 (s, 2H, CH_2), 3.48 s, 4H, -NCH_2); ^{13}C-NMR (400H, DMSO-d_6): 172.12, 165.45, 152.35, 147.99, 126.88, 56.82, 54.08; EA (%, calculated for $C_{12}H_{12}N_2O_8$): C 46.31 (46.16), H 3.92 (3.87), N 8.94 (8.97).

1.3 Preparation of complexes of Tb(III) and Eu(III) with three ligands

Eu_2O_3 (6.32 mmol) and Tb_4O_7 (3.13 mmol) were dissolved in calculated 3 mol/L HCl solution, respectively. The solutions were heated to remove superfluous HCl, and to obtain pH = 3. The two solutions were diluted with redistilled water to obtain 25 mL accurately. The concentrations of Tb(III) and Eu(III) were ascertained by using 0.01109 mol/L EDTA through titration using the xylenol orange as the indicator.

To three solutions of DPA (1.400 mmol), 4-HMDPA (1.400 mmol), and 4-BMDPA (2.800 mmol) in 25.00 mL of H_2O, triplet 0.4610 mol/L $TbCl_3$ (1 mL) solutions were slowly added while stirring. Then 1mol/L NaOH was added to obtain pH = 6–7 in the above three solutions. The solutions were dried under infrared lamp for 12 h. Many crystalloids were obtained, which were the complexes of Tb(III).

To the solutions of DPA (1.300 mmol), 4-HMDPA (1.300 mmol), and 4-BMDPA (2.600 mmol) in 25.00 mL of H_2O, triplet 0.4401mol/L $EuCl_3$ (1.000 mL) solutions were slowly added while stirring. Then 1mol/L NaOH was added to obtain pH = 6–7 in the above three solutions. The solutions were dried under infrared lamp for 12 h. Many crystalloids were obtained, which were the complexes of Eu(III).

1.4 Preparation of the solutions of Tb^{3+} and Eu^{3+} complexes of three ligands

The solutions of Tb^{3+} and Eu^{3+} and the solutions of DPA, 4-HMDPA, 4-BMDPA all in redistilled water were 0.001 mol/L.

Each of the ligand solutions (1 mL) was mixed with each lanthanide ion solutions (1 mL), then diluted to 0.00001 mol/L. A total of six solutions of complexes were prepared.

2 Results and discussion

2.1 Synthesis of ligands

Substitution with electrophilic reagents at 4-position of

pyridine is difficult because of nitrogen's polar effect [10]. In the paper, using the nucleophilic substitution of carbon free radical [11], we introduced hydroxymethyl at the 4-position of pyridine-2,6-dicarboxylic acid successfully. Through sulphonylation, replacement by iodine and $HN(CH_2COOMe)_2$, the compound dimethyl 4-((bis-methoxycarboxylmethyl-amino)-methyl)-pyridine-2, 6-dicarboxylate (**7**) was obtained. Finally the ester was hydrolyzed, and 4-((bis-carboxymethyl-amino)-methyl)-pyridine-2,6-dicarboxylic acid (**8**) was prepared. Each reaction had good yield. The synthesis of compound **3**–**8** has never been reported.

2.2 Structures analysis of the complexes

The structures of complexes were confirmed by EA and IR data (Table 1). The EA data indicated that the mol ratio of ligand to lanthanide ion is 3:1 in the 4-HMDPA complex; and the mol ratio of ligand to lanthanide ion is 3:2 in the 4-BMDPA complex. IR data indicated that the ansymmetric stretching vibration frequencies (υ_{as}) of $-COO^-$ in complexes are lower than that of ligands, which is the redshift (74–117 cm^{-1}). Meanwhile the symmetric stretching vibration frequencies (υ_s) of $-COO^-$ are higher than that of ligands, which is the blueshift (6–44 cm^{-1}). From the shifts of IR data, it is concluded that the ligands all matched the lanthanide ion through their carboxyl. The skeleton stretching vibration frequencies of complexes' pyridine ring ($\upsilon_{s,\,C=N}$) are lower than that of ligands (154–194 cm^{-1}). It shows that nitrogen participates in the chelate ring. The new peaks appear near 430 cm^{-1}. It is likely to belong to the stretching vibrations of the bond, which is the coordination bond of the pyridine ring's nitrogen and lanthanide ion.

The structures of Na_3Tb (4-HMDPA)$_3$ and Na_3Eu (4-HMDPA)$_3$ would be similar to the structure of $Na_3Tb(DPA)_3$, which had been reported in ref [12]. Since Tb(Ⅲ), which can only coordinate with nine atoms, is coordinated with one nitrogen of the pyridine group and two carboxyls in each ligand, and interacted with all three ligands in these compounds, the 4-hydroxylmethyl group cannot bond to Tb(Ⅲ). As a result, each lanthanide ion has three double-chelated rings in coordination with three nitrogen atoms and six oxygen atoms, which form a contorted three coronary triangle prism polyhedral structure. Having a different composition, theoretically one 4-BMDPA compound is a six-dentate ligand. However, the limitation of spacial tension forces it to chelate with two lanthanide ions: one lanthanide ion with a nitrogen atom of the pyridine group and two carboxyls and the other with a nitrogen atom and two carboxyls in the 4-positon. This may lead the whole complex into a netted structure.

2.3 Fluorescence properties of solid complexes

The fluorescence properties of solid complexes are shown in the Table 2 and Table 3.

Table 1 Yields, elemental analysis, and IR data of complexes

Complex	Yield (%)	Element analysis (%, Caled.)			IR, cm^{-1}			
		C	H	N	$\upsilon_{as,\,COO^-}$	$\upsilon_{s,\,COO^-}$	$\upsilon_{s,\,C=N}$	$\upsilon_{s,\,N-M}$
$Na_3Tb(DPA)_3•9H_2O$	86	28.30(28.49)	3.08(3.07)	4.79(4.75)	1626	1433	1393	436
$Na_3Tb(4\text{-}HMDPA)_3•24H_2O$	83	23.19(23.30)	5.03(5.06)	3.39(3.37)	1618	1448	1414	431
$Na_6Tb_2(4\text{-}BMDPA)_3•23H_2O$	89	23.99(24.07)	3.89(3.90)	4.70(4.68)	1617	1444	1406	424
$Na_3Eu(DPA)_3•9H_2O$	85	28.59(28.71)	3.12(3.10)	4.77(4.78)	1624	1431	1380	432
$Na_3Eu(4\text{-}HMDPA)_3•24H_2O$	80	23.42(23.27)	5.14(5.13)	3.38(3.39)	1616	1447	1416	435
$Na_6Eu_2(4\text{-}BMDPA)_3•23H_2O$	82	23.93(24.27)	3.99(3.97)	4.71(4.72)	1607	1444	1406	425

Table 2 Fluorescence properties of solid complexes of Tb(Ⅲ)*

Complex	λ_{ex}(nm)	Fluorescence intensity (I_{em})			
		491	543	582	620
$Na_3Tb(DPA)_3$	276	5788	6657	617.4	60.72
$Na_3Tb(4\text{-}HMDPA)_3$	273	2125	5441	181.5	15.18
$Na_6Tb_2(4\text{-}BMDPA)_3$	272	4563	9195	562.0	64.26

*The width of emission slit and excitation slit are 2.5 nm, the voltage of photomultiplier tube is 400 V.

Table 3 Fluorescence properties of solid complexes of Eu(Ⅲ)*

Complex	λ_{ex} (nm)	Fluorescence intensity (I_{em})	
		592	614
$Na_3Eu(DPA)_3$	283	1526	2780
$Na_3Eu(4\text{-}HMDPA)_3$	285	725.8	2179
$Na_6Eu_2(4\text{-}BMDPA)_3$	284	1842	4423

*The width of emission slit and excitation slit are 2.5 nm, the voltage of photomultiplier tube is 700 V.

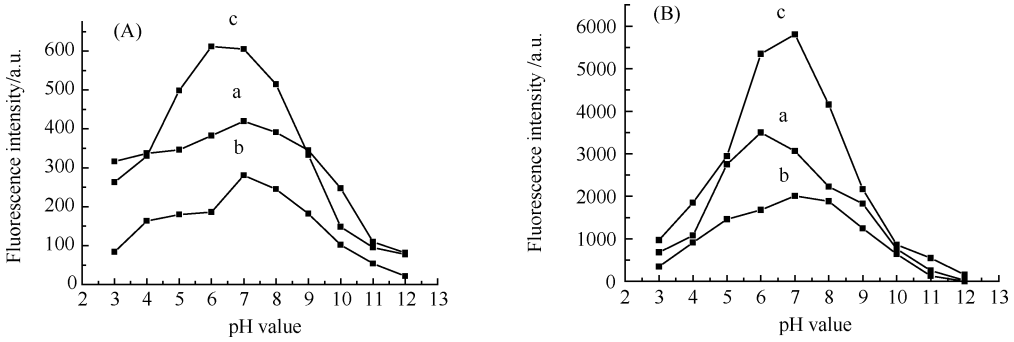


Fig. 1 Changes of fluorescence intensities of Tb(Ⅲ) (A) and Eu(Ⅲ) (B) complexes in different pH environments*

*The width of emission slit and excitation slit are 2.5 nm; (A) the voltage of photomultiplier tube is 400V; a. $Na_3Tb(DPA)_3$, b. $Na_3Tb(4\text{-}HMDPA)_3$, c. $Na_6Tb_3(4\text{-}BMDPA)_3$. (B) the voltage of photomultiplier tube is 700V; a. $Na_3Eu(DPA)_3$, b. $Na_3Eu(4\text{-}HMDPA)_3$, c. $Na_6Eu_3(4\text{-}BMDPA)_3$. The λ_{ex} is the same as in Table 2 and Table 3.

The complexes of Tb(Ⅲ) have the green fluorescence under ultraviolet. The wavelengths of emission: 491, 543, 582, 620 nm correspond to the Tb $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$, respectively. The complexes of Eu(III) have red fluorescence under ultraviolet. The wavelengths of emission: 592, 614 nm correspond to the Eu $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, respectively. It is because the lanthanon ions have the electronic shell of $6s^2$, which surrounds the electronic shell of 4f. The change of ligands cannot affect the electronic shell of 4f. When the ligand is changed the wavelength of emission almost does not change.

All the ligands can efficiently sensitize luminescence of Tb(Ⅲ) and Eu(Ⅲ). Since the hydroxymethyl in the 4-position of pyridine is a weak election-withdrawing group, the luminescence intensities of $Na_3Tb(4\text{-}HMDPA)_3$ and $Na_3Eu(4\text{-}HMDPA)_3$ are weaker than that of the others. The fluorescence properties of several lanthanide complexes with multisubstituted pyridine-2, 6-dicarboxylic acid derivatives had been reported in literature [13], and the results are the same. The 4-BMDPA has two coordination centers and forms a binary complex, in which each ligand attaches itself to chelate two lanthanon ions; meanwhile every lanthanon ion has three chelate rings in complexation with three ligands. This reticular structure is propitious to sensitize Tb(Ⅲ) or Eu(Ⅲ). Among the three ligands, 4-BMDPA is the best sensitizer for Tb(Ⅲ) and Eu(Ⅲ).

2.4 Fluorescence properties of complexes in solutions

2.4.1 Effect of pH in aqueous solution of complexes

The effect of pH on the fluorescence intensity of complexes is shown in the Fig. 1.

From the data, it is known that the fluorescence intensity is higher in neutral aqueous solution than in acidic and alkaline aqueous solutions, whether it is Tb(Ⅲ) or Eu(Ⅲ). Obviously, in the acidic aqueous solution, carboxylate anions can be protonized and in the alkaline aqueous solution, the lanthanide ions can be coordinated with hydroxyl. Finally the lanthanide ions are dissociated or formed into hydrates, resulting in depositions. The two weaken the complexing abilities of the three ligands. Therefore, the concentrations of luminescent complexes are decreased.

2.4.2 Solvent effect on fluorescence properties

We used five solvents to dissolve the complexes, and the concentrations of complexes are 0.00001 mol/L. The data of fluorescence intensities in different solutions are shown in Table 4.

Table 4 Solvent effect on fluorescence intensity*

Complexes	λ_{ex}(nm)	Fluorescence intensity/a. u.				
		DMSO	Acetone	H_2O	MeOH	EtOH
10^{20} Dipole moment/C•m		3.96	2.88	1.85	1.70	1.69
$Na_3Tb(DPA)_3$	276	4.247	8.516	115.6	132.1	137.5
$Na_3Tb(4\text{-}HMDPA)_3$	273	4.548	5.841	96.71	124.9	126.5
$Na_6Tb_2(4\text{-}BMDPA)_3$	272	7.368	10.25	100.9	165.5	178.8
$Na_3Eu(DPA)_3$	283	29.87	45.32	225.0	355.3	368.6
$Na_3Eu(4\text{-}HMDPA)_3$	285	5.615	7.415	88.56	109.87	129.5
$Na_6Eu_2(4\text{-}BMDPA)_3$	284	22.31	69.48	297.5	359.6	383.5

*The width of emission slit and excitation slit are 2.5 nm, the voltage of photomultiplier tube is 400 V.

From the data it is shown that the fluorescence intensities are related to the dipole moments of solution molecules. The complexes have stronger fluorescence intensities in the solutions that have lower dipole moments than in the solutions having higher dipole moments. In 1956, E. G. Mcrae had brought forward a theory to explain the phenomenon [14]. The Franck–Condon excited state exists in the system of luminescent molecules. The solvent having lower dipole moment can stabilize the ground state that corresponds to the Franck–Condon excited state. This effect results in that the triplet state of T_2 (π-π^*) exchanges for T_1 (π-π^*) in the ligands. The S(n-π^*)→T_2 (π-π^*) transition becomes possible. The luminescent mechanism of the ligand-Eu(Ⅲ) (λ_{em} = 614 nm) is $S_0 \rightarrow S_h \rightarrow S_1 \rightarrow T \rightarrow {}^5D_0 \rightarrow {}^7F_2$, that of the ligand-Tb(Ⅲ) (λ_{em} = 543nm) is $S_0 \rightarrow S_h \rightarrow S_1 \rightarrow T \rightarrow {}^5D_4 \rightarrow {}^7F_5$, while the ${}^5D_0 \rightarrow {}^7F_2$ or ${}^5D_4 \rightarrow {}^7F_5$ is enhanced in the solvents having lower dipole moments. The fluorescence intensities become stronger [15].

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