Asian Journal of Chemistry; *Vol. 23, No. 6 (2011), 2411-2416*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Preparation and Fluorescence Properties of Tb(III) Complexes with Pyridine Dicarboxylic Acid Derivatives

GUOLIANG GU* and MING LU

Department of Chemical Engineering, Nanjing University of Science and Technology, Nanjing-210094, P.R. China

*Corresponding author: E-mail: luming@mail.njust.edu.cn; ggliang516@163.com

(*Received*: 27 April 2010; *Accepted*: 4 February 2011) AJC-9580

Two novel ligands containing pyridine-2,6-dicarboxylic acid units, 2,6-*bis*[2-(2,6-dicarboxypyridin-4-yl)vinyl]pyridine (L_1), 4-vinylpyridine-2,6-dicarboxylic acid (L_2) and their complexes with Tb(III) have been designed, synthesized and characterized by elemental analysis, IR spectra and NMR. The fluorescence spectra of Tb(III) complexes in the solid state, in different solvents and at different pH value solutions were investigated. The results exhibit that the ligand with two pyridine-2,6-dicarboxylic acid units is better sensitizer to Tb(III) ion, compared with that with simple pyridine-2,6-dicarboxylic acid unit. The fluorescence intensities of the complexes are strongest in neutral solution and while the less the dipole moment of solvent molecule is, the stronger the fluorescence intensity is. Due to their excellent green-emmiter, they could be used as a candidate material in organic light-emitting devices.

Key Words: Pyridine dicarboxylic acid derivatives, Tb(III) complexes, IR spectra, Fluorescence properties.

INTRODUCTION

Europium(III) and terbium(III) complexes have attracted much attention due to their well-defined luminescence properties, including hypersensitivity to the coordination environment, narrow bandwidth and millisecond luminescence decay times and used as fluorescent probes in biological media, optical amplification in fiber-optic telecommunications systems and photoluminescence devices because of their attractive emission properties such as long lifetime, large stokes shift and line-like emission[1-4]. In the lanthanide complexes, the organic ligands that have π-electrons can efficiently serve as the light absorbing chromophores. For effective excitation of Ln^{3+} ions, organic chromophore, so-called "antenna", is usually attached to Ln complex[5-7]. If the excited state of the antenna organic ligands is energetically high enough and the gathered energy is transferred to the lanthanide metal ions held nearby, the characteristic fluorescence would be emitted. Some rare earth complexes with β-diketone, aromatic carboxylic acid and heterocyclic carboxylic acid group were under development, such as benzoyl acetone[8], benzoyltrifluoroacetone[9], α-thenoyl trifluoroacetone[10] and pyridine-2,6-dicarboxylic acid[11]. Since the lanthanide complexes with pyridine-2,6-dicarboxylic acid derivatives are chiral, they can get more information about structure of biological molecule through measurement circularly polarized luminescence spectra and can be used to tag proteins in time-resolved fluoroimmunoassay (TR-FIA)[12-14].

With an aim to develop novel fluorescence materials and increase the intensity of the lanthanide fluorescence exploiting the antenna effect, we synthesized two novel ligands named 2,6-*bis*[2- (2,6-dicarboxypyridin-4-yl) vinyl]pyridine (L_1) and 4-vinylpyridine-2,6-dicarboxylic acid (L_2) and their Tb(III) complexes. The ligand L_1 has rigid conjugated planar structure, which would be beneficial to the electronic negotiability[15]. Two pyridine-2,6-dicarboxylic units can coordinate with two terbium ions, respectively to form a π-extended conjugated netted structure, which would increase the fluorescence efficiency. The synthetic route of ligands was given in Fig. 1.

EXPERIMENTAL

The purity of Tb(III) oxide exceeds 99.9 %. Pyridine-2,6-dimethanol (compound **1**) and 4-(hydroxymethyl)pridine-2,6-dicarboxylate (compound **4**) were synthesized as described in the literatures[16,17]. Other chemicals were of AR grade and used without further purification.

Melting points were determined on an XRC-1 apparatus (thermometer uncorrected); elemental analysis was carried out by a Perkin-Elmer 2400 elemental analyzer; ^1H NMR was measured with a Bruker-400 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ or DMSO as solvent and TMS as internal reference. Fluorescence properties were recorded on a Hitich F-4500 spectrometer. The infrared spectra were obtained in 4000-400 cm^{-1} region by using a Avator-360-FT spectrophotometer with KBr plates.

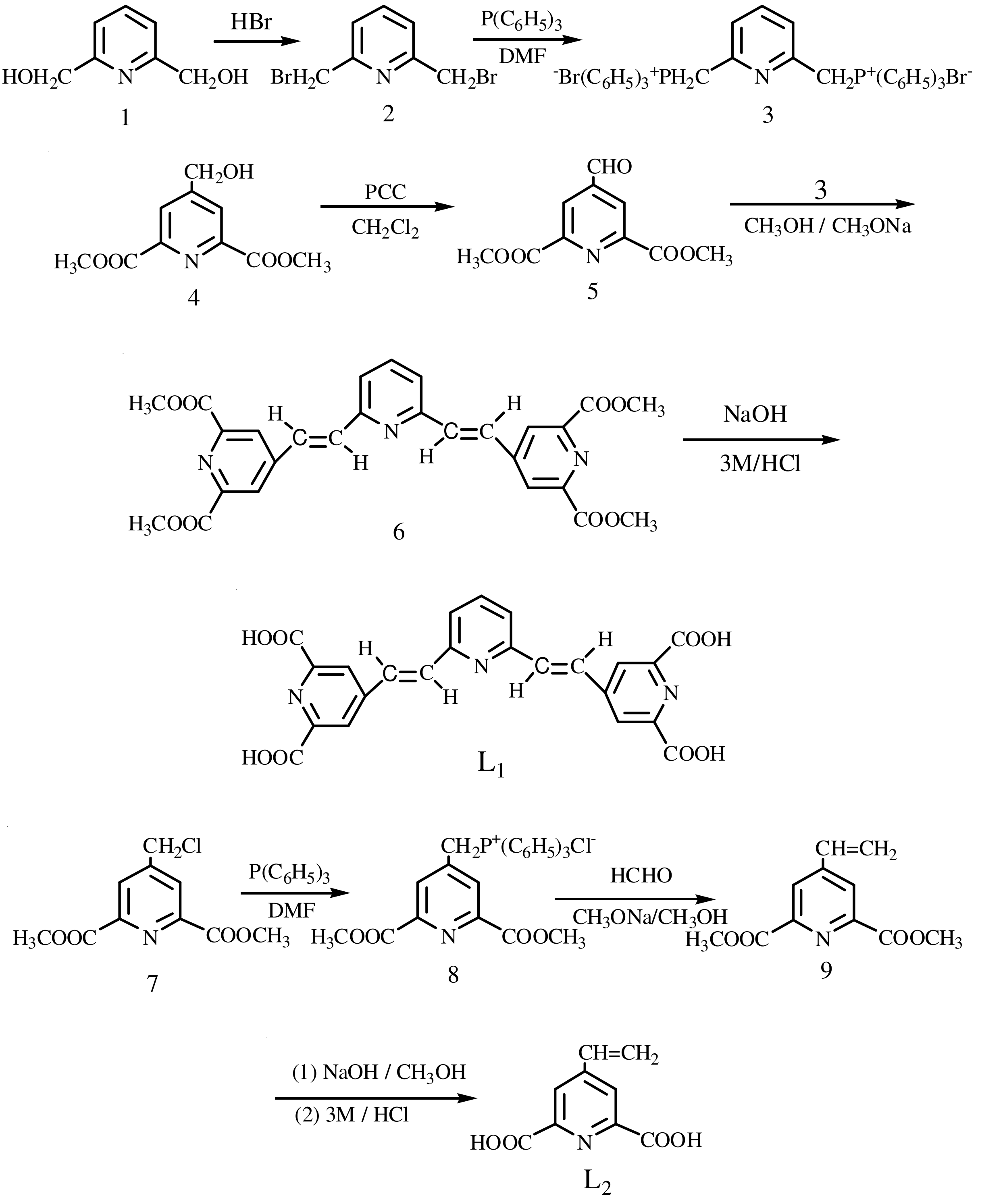

Fig. 1. Synthesis route of ligands (L_1 and L_2)

Preparation of ligands

Preparation of 2,6-*bis*(bromomethyl)pyridine (2): To a mixture of hydrobromic acid and acetic acid (250 mL), 1.20 g (13.0 mmol) of pyridine-2,6-dimethanol **1** was added and refluxed for 48 h, then cooled to 0 ºC. The solution was concentrated under reduced pressure and a whitish solid **2** was obtained. The white precipitate obtained by filtration, then dissolved in CH_2Cl_2 and washed with an aqueous solution of $NaHCO_3$. The organic phases were dried over $MgSO_4$ and evaporated to dryness under vacuum, affording 1.63 g of analytically pure compound in 52 % yield. The product is light sensitive and was stored in a dark brown bottle. ^1H NMR (400 MHz, $CDCl_3$): δ H 4.45 (s, 4H, CH_2), 7.40 (d, 2H, ArH), 7.80 (t, 1H, ArH). EI MS: m/z 265 (M + H^+). EA (calcd. for $C_7H_7NBr_2$): (%) C 32.03 (31.73), H 2.57 (2.66), N 5.23 (5.29).

Preparation of 2,6-*bis*(triphenylphosphonium bromide) pyridine (3): A solution of triphenyl phosphine (6.6 g, 25.0

mmol) and compound **2** (2.7 g, 10.0 mmol) in DMF (8 mL) was refluxed for 6 h, then cooled to the room temperature. To the above solution, the anhydrous benzene (15 mL) was added and refluxed for 1.5 h. The reaction mixture was filtered to obtain the colourless solid **3** (65 g). Yield: 82.7 %.

Preparation of 4-formylpyridine-2,6-dicarboxylate (5): To the solution of compound **4** (22.4 g, 0.10 mol) in dry dichloromethane (100 mL), pyridinium chlorochromate (PCC, 22.5 g, 0.15 mol) was added at room temperature. After stirring for 5 h, 60 % solvent was removed and ethyl acetate (160 mL) was added, then the reaction mixture was washed with water (140 mL), sodium bicarbonate (5 %, 100 mL × 2) and saturated brine (100 mL) sequentially. The organic layer was collected and dried over Na_2SO_4 and then evaporated under reduced pressure. The crude solid product was purified by recrystallization (ethyl acetate/chloroform, 3:1) to give compound **5** as whitish solid (19.5 g). The yield was 87.0 %, m.p. 152-154 ºC.

IR (KBr, ν_{max}, cm^{-1}): 3045, 2971, 2866, 1735, 1702, 1359, 1210, 975, 780. MS m/z: 193. ^1H NMR (400 MHz, $CDCl_3$) δ: 10.05 (s, 1H, CHO), 6.62 (s, 2H, Py-H), 4.10 (s, 6H, OCH_3). EA (calcd. for $C_9H_{10}NO_5$): (%) C 53.62 (53.82), H 4.11 (4.06), N 6.23 (6.28).

Preparation of 2,6-*bis*(2-(2,6-dimethoxycarbonylpyridine-4-yl)vinyl)pyridine (6): To the absolute methanol (60 mL) solution of compound **3** (3.9 g, 5.0 mmol) and compound **5** (2.4 g, 10.0 mmol), the solution of sodium methanolate (0.8 g, 12.0 mmol) in 50 mL absolute methanol was added dropwise and stirred up to 1 h under nitrogen atmosphere at -25 ºC and kept it overnight with stirring at room temperature. The solution was concentrated under reduced pressure and a whitish solid **6** was obtained by flash chromatography eluting from ethyl acetate, petroleum ether and chloroform (1:1:1, v/v). Yield: 81.4 %; m.p. 216-218 ºC. IR (KBr, ν_{max}, cm^{-1}): 3420, 2962, 1728, 1679, 1594, 1433, 1392, 1246, 990, 728. ^1H NMR ($CDCl_3$) δ: 6.97 (d, 2H, =HC-Py-CH=), 7.13 (d, 2H, Py-CH=), 7.76 (s, 1H, Py-H). 7.90 (d, 2H, Py-H), 8.05 (s, 4H, Py-H), 3.98 (s, 6H, OCH_3). EA (calcd. for $C_{27}H_{23}N_3O_8$): (%) C 62.71 (62.67), H 4.59 (4.48), N 8.02 (8.12).

Preparation of 2,6-*bis*[2-(2,6-dicarboxypyridin-4-yl)vinyl]pyridine (L_1): A solution of NaOH (30 %, 10.0 g) was added into **6** (3.1 g, 6.0 mmol) in methanol (50 mL) and the mixture was stirred at room temperature for 36 h. Then the solvent was completely removed under reduced pressure and used the HCl (3 mol/L) to adjust the pH to 4. The whitish solid **6** (1.6 g) was obtained. Yield: 95.7 %; m.p. 289-291 ºC. IR (KBr, ν_{max}, cm^{-1}): 3460, 2921, 1742, 1633, 1590, 1396,1254, 981, 692. ^1H NMR (DMSO-d_6) δ: 6.95 (d, 2H, =HC-Py-CH=), 7.11 (d, 2H, Py-CH=), 7.72 (s, 1H, Py-H). 7.90 (d, 2H, Py-H), 8.21 (s, 4H, Py-H), 12.50 (s, H, COOH).

Preparation of dimethoxy-4-vinylpyridine-2,6-dicarboxylate: Triphenylphosphine (6.6 g, 25.0 mmol) was added into a solution of compound **7** (4.9 g, 20.0 mmol) in DMF (8 mL), the reaction mixture was stirred under reflux for 2 h and filtered. The filtrate was refluxed in dry benzene (15 mL) to obtain the crude product 2,6-dimethoxy-carbonyl-4-triphenylphosphonium-methylpyridine (compound **8**) (8.6 g) as the colourless solid.

18 mL of a 15 % strength solution of sodium methylate in methanol were added to 24 g of 2,6-dimethoxycarbonyl-4-triphenylphosphonium-methylpyridine chloride and 5.5 g of 30 % strength formaldehyde solution in 150 mL mthanol. The mixture was stirred for 1 h at -20 ºC. Kept it stirring at room temperature for 12 h. The solution was concentrated under reduced pressure and a whitish solid **6** was obtained. Yield: 85.3 %; m.p. 166-168 ºC. IR (KBr, ν_{max}, cm^{-1}): 3415, 2958, 1722, 1675, 1590, 1435, 1396, 1251, 992, 729. ^1H NMR (DMSO-d_6) δ: 6.56 (t, H, =HC-Py), 5.46, 5.92 (d, 2H, $C=CH_2$), 3.71 (s, 6H, $-CH_3$), 7.72 (s, 1H, Py-H). 8.89 (s, 2H, Py-H). EA (calcd. for $C_{11}H_{11}NO_4$): (%) C 59.91 (59.73), H 4.92 (5.01), N 6.30 (6.33).

Preparation of 4-vinylpyridine-2,6-dicarboxylic acid (L_2): A solution of NaOH (30 %, 10.0 g) was added into compound **9** (3.1 g, 5.0 mmol) in methanol (50 mL) and the mixture was stirred at room temperature for 36 h. Then the solvent was removed completely under reduced pressure and used the HCl (3 mol/L) to adjust the pH to 4. The whitish solid **6** (1.6 g) was obtained. Yield: 96.5 %; m.p. 239-241 ºC. IR (KBr, ν_{max}, cm^{-1}): 3460, 2948, 1720, 1673, 1594, 1391, 1257, 994, 729. ^1H NMR (DMSO-d_6) δ: 6.56 (t, H, =HC-Py), 5.46, 5.92 (d, 2H, $C=CH_2$), 7.72 (s, 1H, Py-H). 7.72 (s, 1H, Py-H). 8.89 (s, 2H, Py-H), 12.43 (s, 2H, COOH).

Preparation of complexes of Tb(III): The solution of $TbCl_3$ (0.4610 mol/L) was prepared according to the literature method[18]. To a hot solution of L (L = L_1, L_2) in distilled water and ethanol, a two-third molar amount of $TbCl_3$ was added and stirred for 5 h at 60 ºC. The pH value of the solution was adjusted to 7.0 by dropwise addition of aqueous NaOH (0.01 mol/L). The precipitate obtained on concentration was filtered, washed thoroughly with alcohol and chloroform mixture (1:1, v/v) and air-dried.

RESULTS AND DISCUSSION

Properties of the complexes: The results of elemental analysis (Table-1) indicated that the composition of the complexes conforms to $Na_6Tb_2(L_1)_3 \cdot 18H_2O$ and $Na_3Tb(L_2)_3 \cdot 9H_2O$. The complexes are faint yellow coloured and stable. They are soluble in H_2O, DMF, CH_3CN and DMSO, slightly soluble in ethanol and acetone and insoluble in benzene, diethyl ether and tetrahydrofuran.

IR spectra: In the IR spectra of compound **6**, the strong and sharp bands at 975 cm^{-1} is assigned to δ (=C-H) and the medium intensity and wide bands at 1669 cm^{-1} attributed to ν(C=C), which was characterized as *trans*-configuration with double bonds.

TABLE-1
ELEMENTAL ANALYTICAL DATA FOR THE COMPLEXES

Complex	Tb (%) found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	N (%) found (calcd.)
$Na_6Tb_2(L_1)_3 \cdot 18H_2O$	14.52 (14.78)	38.32 (38.05)	3.87 (3.21)	5.63(5.86)
$Na_3Tb(L_2)_3 \cdot 9H_2O$	16.15 (16.41)	33.29 (33.43)	4.26 (4.02)	3.94(4.33)

TABLE-2
DIAGNOSTIC IR BANDS (cm^{-1}) OF THE LIGAND AND ITS Tb(III) COMPLEXES

Compound	ν(C=O)	ν(OH)	Py'N'	δ(=C-H)	$\nu_{as}(COO^-)$	$\nu_S(COO^-)$
L_1	1742	2921	1590	981	–	–
L_2	1723	2948	1597	974	–	–
$Na_6Tb_2(L_1)_3\cdot18H_2O$	–	–	1426	1017	1614	1447
$Na_3Tb(L_2)_3\cdot9H_2O$	–	–	1422	983	1625	1458

IR spectral bands, useful for mode of coordination of ligands are listed in Table-2. The uncoordinated ligands show the bands of medium intensity at 2921 cm^{-1} (L_1) and 2948 cm^{-1} (L_2) attributed to free νOH of COOH and strong and sharp bands at 1742 cm^{-1} (L_1) and 1723 cm^{-1} (L_2) assignable to C=O. The bands at 1590 cm^{-1} (L_1) and 1597 cm^{-1} (L_2) were assigned to pyridine ring stretching [ν(C=N)][18]. In the complexes, the band for ν(C=N) of pyridine ring shows a shift to a lower frequency about 170 cm^{-1} as a result of the coordination through metal-nitrogen bond. The bands (C=O) in free ligands disappear and the new bands appear at 1614, 1447 cm^{-1} and 1625, 1458 cm^{-1} assignable to $[\nu_{as}(COO^-) + \nu_S(COO^-)]$. The asymmetric stretching vibration frequencies (ν_{as}) of $-COO^-$ in complexes show a shift to a lower frequency about 110 cm^{-1}; mean while the symmetric stretching vibration frequencies (ν_s) of COO^- show a shift to a higher frequency about 45 cm^{-1}, which indicates the ligand coordinates the Tb(III) ions through their carboxyl.

These above suggest that each terbium(III) ion coordinates with three double-chelated pyridine rings which have three nitrogen atoms and six oxygen atoms forming a contorted three coronary triangle prism polyhedral structure[19,20]. So the coordination numbers of Tb(III) is nine. A broad band at 3350-3420 cm^{-1} and a peak between 920 and 935 cm^{-1} in the complexes indicates the presence of lattice water molecules[21]. The non-ligand bands observed in the region about 430 and 525 cm^{-1} are assigned to the ν(Tb-O) and (Tb-N) bands[18,22].

Fluorescence properties of complexes: The fluorescence spectra of the ligands and their Tb(III) complexes was carried out in solid and different solutions at room temperature.

Fluorescence properties of Tb(III) complexes in solid: The emission intensities of Tb(III) complexes along with their assignments in the solid state are showed in the Table-3, Figs. 2 and 3. Fluorescence spectra for the Tb(III) complexes were measured at the drive voltage of 400 V.

TABLE-3
FLUORESCENCE PROPERTIES OF
Tb(III) COMPLEX IN SOLID

Complex	λ_{ex} (nm)	λ_{em} (nm)	RFI*	Assignment
$Na_6Tb_2(L_1)_3\cdot18H_2O$	268	490	3484	$^5D_4 \rightarrow {}^7F_6$
		544	9247	$^5D_4 \rightarrow {}^7F_5$
		583	786	$^5D_4 \rightarrow {}^7F_4$
		620	287	$^5D_4 \rightarrow {}^7F_3$
$Na_3Tb(L_2)_3\cdot9H_2O$	280	491	1843	$^5D_4 \rightarrow {}^7F_6$
		546	3248	$^5D_4 \rightarrow {}^7F_5$
		585	343	$^5D_4 \rightarrow {}^7F_4$
		623	110	$^5D_4 \rightarrow {}^7F_3$

The width of emission slit and excitation slit were 2.5 nm, the voltage of photomultiplier tube was 400 V.

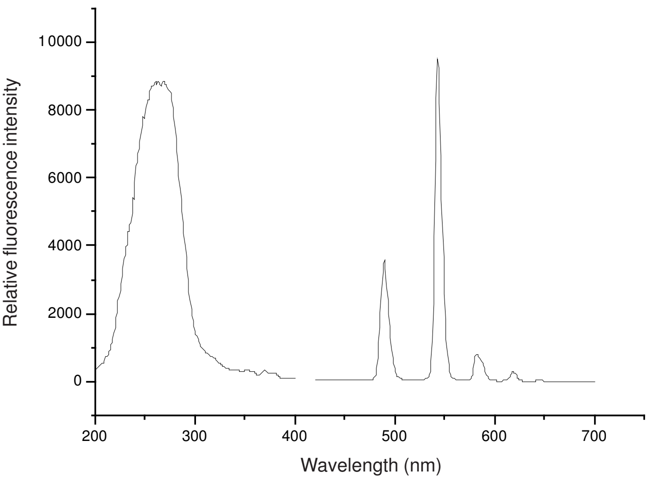

Fig. 2. Excitation (left) and emission (right) spectra of $Na_6Tb_2(L_1)3\cdot18H_2O$

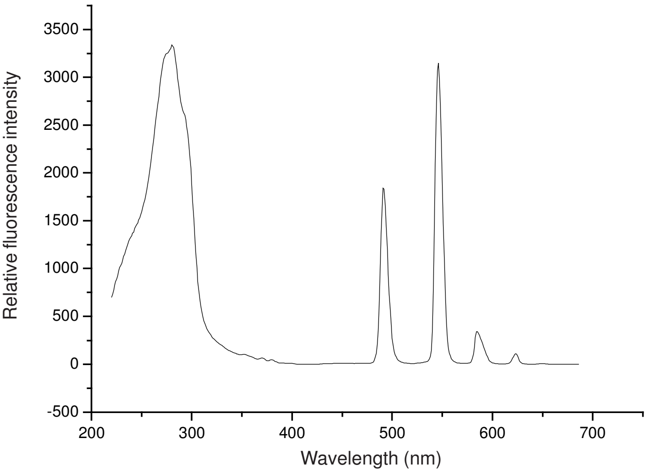

Fig. 3. Excitation (left) and emission (right) spectra of $Na_3Tb(L_2)_3\cdot9H_2O$

In the spectra of Figs. 2 and 3. The maximum excitation wavelengths (λ_{ex}) of the $Na_6Tb_2(L_1)_3\cdot18H_2O$ and $Na_3Tb(L_2)_3\cdot9H_2O$ complexes were 268 and 280 nm, respectively. The wavelengths of emission correspond to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$ transition. The $^5D_4 \rightarrow {}^7F_6$ translation at 490 and 491 nm is moderately strong and is known to be sensitive to ligand environment. It has a strong magnetic dipole character. The $^5D_4 \rightarrow {}^7F_4$ transition at 583 and 585 nm is of moderate intensity. The component at 620 and 623 nm is assigned to the $^5D_4 \rightarrow {}^7F_3$ transition. The strongest is $^5D_4 \rightarrow {}^7F_5$ among them. It is because the lanthanide ions have the $5s^25p^6$ electronic shell, which surrounds the electronic shell of 4f, the affection of ligand field to the 4f electronic energy level is very week, so when the ligand changed, the wavelength of emission almost is unchanged.

The typical narrow emission bands of Tb(III) ions can be detected upon excitation of the ligand-centered absorption band and the ligand-fluorescence is completely suppressed, indicating that the ligand is a comparative good organic chelator to absorb energy and transfer them to Tb(III) ion. It can be explained the giving of energy (ligand) is much more than the accepted (Tb(III)) and the intersystem crossing ($S_1 \rightarrow T_1$) from the first singlet excited state of ligand to the excited triplet state of ligand is increased. The intensity ratio of the two lines ($^5D_4 \rightarrow {}^7F_5$/$^5D_4 \rightarrow {}^7F_6$) is about 2.0, which indicates that the Tb(III) ion is at the center of an asymmetric coordination field[23,24]. The $^5D_4 \rightarrow {}^7F_5$ peak of Tb(III) complexes is sharp and strong, showing higher colour purity and emission intensity[4].

Effect of pH on fluorescence properties: H_2O was used to dissolve the ten complexes then solutions of the complexes with concentrations of 0.01 mol/L were obtained. The effect of pH value on the fluorescence intensity of complexes is shown in the Fig. 4.

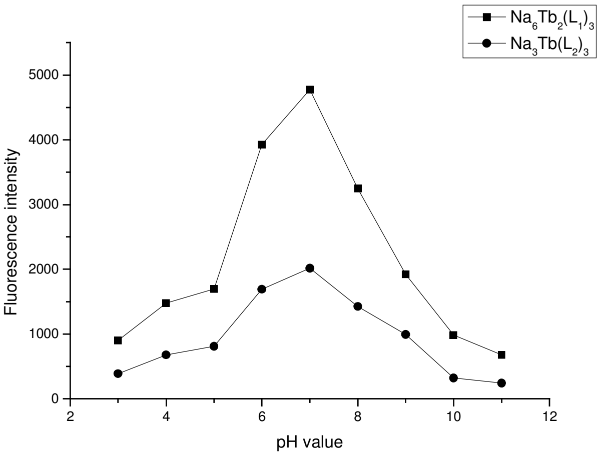

Fig. 4. Changes of fluorescence Intensities of Tb(III) complexes in different pH environment

At pH 7, the fluorescence intensity of the Tb(III) complexes would get to the maximum, which can be explained that carboxylate anions is easy to be protonated in the acidic aqueous solution; while the terbium ions can coordinate with hydroxyl in the alkaline aqueous solution, which lead precipitation to be produced as the pH increases gradually. The result is similar to the literature reported by Xian-Hong Yin[11] about the relationships between the pH and the fluorescence intensity of terbium complexes of other pyridine 2,6-dicarboxylic acid derivatives.

Effect of different solvents on fluorescence properties: The fluorescence intensity of Tb(III) complexes in H_2O, DMF, CH_3CN and DMSO are listed in Table-4. Each solution was diluted to 1.0×10^{-5} mol/L.

TABLE-4
EFFECT OF DIFFERENT SOLVENTS
ON FLUORESCENCE INTENSITY

Complex	Fluorescence intensity			
	H_2O	DMF	CH_3CN	DMSO
10^{20} Dipole moment/C m	1.85	3.82	3.92	3.96
$Na_6Tb_2(L_1)_3 \cdot 18H_2O$	146.86	8.74	6.14	5.85
$Na_3Tb(L_2)_3 \cdot 9H_2O$	86.25	12.51	5.37	4.54

The spectra shows that the fluorescence intensity of the complexes in solution are weaker than that in solid, which can be due to the excited state of the terbium ions is efficiently quenched by interactions with high-energy vibrations groups of the organic solvent[25]. At the same concentration, the fluorescence intensity order of the complexes in different solvents is H_2O > DMF > CH_3CN > DMSO, but the order of solvent dipole moment is contrary. Samy[26] had brought forward a theory to explain the phenomenon: the Franck-Condon excites state exists in the system of fluorescent molecules. The solvent which has lower dipole moment can stabilize the ground state that corresponds to the Franck-Condon excited state. This effect results in that the triplet states of T_2 (π-π^*) exchanges with those of T_1 (π-π^*) in ligand, thus, the transition S (n-π^*) $\rightarrow T_2$ (π-π^*) becomes possible. And the probability of intersystem crossing (Kiso) from the singlet state to the triplet state of ligand increases. The fluorescent mechanism of the ligand-Tb(III) (λ_{em} = 543 nm) is $S_0 \rightarrow S_h \rightarrow S_1 \rightarrow T \rightarrow {}^5D_4 \rightarrow {}^7F_5$ and the increasing of Kiso causes the enhancement of emissive probability $^5D_4 \rightarrow {}^7F_5$ in Tb(III), thus, the less the dipole moment of solvent molecule is, the stronger the fluorescence intensity is[27]. It is similar to the literature reported by Guo-Liang Gu[28] in earlier work.

Conclusion

We have successfully synthesized two novel ligands (L_1 and L_2) and shown that they can form stable complexes with Tb^{3+} ion. Differences in the IR spectra of the free ligands and the metal complexes indicate that coordination of each of the ligands was occurring at the oxygen atoms of the carbonyl and the nitrogen atoms of the pyridine ring. As expected, the ligand and the complexes have the planar structure, therefore has a suitable conjugated π-electron system to efficiently sensitize Tb(III) ion fluorescence. The complexes each exhibited characteristic fluorescence and the fluorescence intensities of $Na_6Tb_2(L_1)_3 \cdot 18H_2O$ are twice as strong as those of $Na_3Tb(L_2)_3 \cdot 9H_2O$, which indicated the ligand with two pyridine-2,6-dicarboxylic acid units is the excellent sensitizer to lanthanide fluorescence over the ligand with single pyridine-2,6-dicarboxylic acid unit. The fluorescence intensity of the complexes in solid is stronger than that in H_2O, DMF, CH_3CN or DMSO solvents and effect of pH value shows the fluorescence intensity of complexes in neutral solution is stronger than that in acidic or basic solution. The complex with ligand (L_1) is a good green luminescent material that could be used as a candidate material in organic light-emitting devices.

REFERENCES

1. D. Parker, *Chem. Soc. Rev.*, **33**, 156 (2004).
2. J.C.G. Bunzli, *Acc. Chem. Res.*, **39**, 53 (2006).
3. I. Hemmila and V. Laitala, *J. Fluoresc.*, **15**, 529 (2005).
4. H.J. Zhang, R.H. Gou, L. Yan and R.D. Yang, *Spectrochim. Acta*, **66A**, 289 (2007).
5. J. Yuan and K. Matsumoto, *Anal. Chem.*, **70**, 596 (1998).
6. K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano and T. Nagano, *J. Am. Chem. Soc.*, **126**, 12470 (2004).
7. T. Gunnlaugsson and J.P. Leonard, *Chem. Commun.*, 3114 (2005).
8. S.B. Meshkova, *J. Fluoresc.*, **10**, 333 (2000).
9. O.A. Serra, I.L.V. Rosa, C.L. Medeiros and M.E.D. Zaniquelli, *J. Lumin.*, **60**, 112 (1994).
10. K.Z. Yang, R.J. Zhang and H.G. Liu, *Thin Solid Films*, **295**, 228 (1997).

11. X.H. Yin, M.Y. Yang and H.H. Shi, *J. Chin. Rare Earth Soc*., **18**, 211 (2000).
12. J. Sokolnicki, J. Legendziewicz, G. Muller and J.P. Riehl, *Opt. Mater.,* **27**, 1529 (2005).
13. M. Morita, D. Rau and M. Herren, *J. Alloys Compd*., **380**, 260 (2004).
14. R.R. Tang, Z.E. Yan and C.C. Guo, *Chem. J. Chin. Univ*., **27**, 472 (2006).
15. N.W. Paul, *J. Org. Chem*., **66**, 4170 (2001).
16. X.M. Shi, R.R. Tang and G.L. Gu, *Spectrochim. Acta*, **72A**, 198 (2009).
17. R.R. Tang, Y.H. Zheng and Q. Zhao, *Chem. Rea. Eng. Technol.*, **22**, 83 (2006).
18. T. Zafiropoulos, J. Plakatouras and S.P. Perlepes, *Polyhedron*, **10**, 2405 (1991).
19. A.P. Magyar, A.J. Silversmith, K.S. Brewer and D.M. Boye, *J. Lumin*., **108**, 49 (2004).
20. B.S. Panigrahi, *J. Alloys. Compd*., **334**, 228 (2002).
21. W. Paryzek, E. Zankowska and E. Luks, *Polyhedron*, **7**, 439 (1988).
22. J.H. Forsberg, *Coord. Chem. Rev*., **10**, 195 (1973).
23. Q. Su, Rare Earth Chemistry, He Nan Technology Press, Zhenzhou, China, p. 304 (1993).
24. G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz and E.F. da Silva Jr., *Coord. Chem. Rev*., **196**, 165 (2000).
25. Y.L. Zhang, W.W. Qin, W.S. Liu, M.Y. Tan and N. Tang, *Spectrochim. Acta*, **58A**, 2153 (2002).
26. S.A.E. Samy, *Spectrochim. Acta*, **55A**, 143 (1999).
27. L. Te and S.M. Yao, The Modern Molecule Photochemistry, Scientific Press, Beijing, p. 68 (1987).
28. G.L. Gu, R.R. Tang, Y.H. Zheng and X.M. Shi, *Spectrochim. Acta*, **71A**, 209 (2008).