Synthesis and Luminescence Properties of Lanthanide Complexes of a Novel Polyaminopolycarboxylate Ligand

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A novel polyaminopolycarboxylate ligand with many coordination sites, N,N,N^1,N^1,N^2,N^2-[(2,4,6-tri(aminomethyl)-pyridine]hexakis(acetic acid) (TPHA), was designed and synthesized and its lanthanide complexes $Na_6Tb_2(TPHA)Cl_6\cdot14H_2O$, $Na_6Eu_2(TPHA)Cl_6\cdot8H_2O$, $Na_6Gd_2(TPHA)Cl_6\cdot11H_2O$ and $Na_6Sm_2(TPHA)Cl_6\cdot9H_2O$ were successfully prepared. The ligand and the complexes were characterized by elemental analysis, IR, mass, NMR and TG-DTA. The TG-DTA studies indicated that the complexes had a high thermal stability, whose initial decomposition temperature was over 270 °C. The luminescence properties of the complexes in solid state were investigated and the results suggested that Tb^{3+} and Eu^{3+} ions could be sensitized efficiently by the ligand, especially the Tb(III) complex displayed a very strong luminescence intensity (> 10000) and only displayed characteristic metal-centered luminescence. Also, the correlative comparison between the structure of ligand and luminescence properties showed how the number of the coordination atoms of ligand can be a prominent factor in the effectiveness of ligand-to-metal energy transfer.

**Key Words**: Synthesis, Pyridine, Lanthanide complexes, Luminescence

Introduction

Lanthanide trivalent cations have excellent photoluminescent properties usable in a high range of different applications. But the ions' poor ability to absorb light makes it necessary to dress them up with an organic ligand as a skin in the form of a complex.[1] The complexes have become increasingly significant in the last few years due to the wide variety of potential applications in many important areas of chemistry,[2-4] biology,[5-6] medicine[7-8] and imaging.[9-12]

The design of the organic part of such complexes is thus paramount in achieving the required circumstances for the complex to be efficiently luminescent. The ligand needs to incorporate a chromophoric unit (antenna group), for absorbing light and transferring it to the metallic ion, namely, the efficient antenna effect. The usual conditions to be fulfilled are good yields for intersystem crossing and reasonable matching bet-

ween the chromophore first triplet state and the accepting levels of the metal. Another important feature is that the organic ligand must also provide good isolation of the metal from the interaction with water molecules, which would otherwise cause nonradiative deactivation of the excited state.[13] The proton relaxivity of gadolinium complexes is directly correlated to the number of metal-bound water molecules (inner-sphere contribution).[14] In contrast, inner-sphere water molecules contribute to reduce emission lifetime and quantum yield for Tb^{3+} and especially Eu^{3+} luminescence.[15] And it seems that the ligand with more coordination sites can effectively prevent water molecules participating in coordination with metal ion. The achievement of all these requirements is not an easy task and research in this area is very active.

In this article, we have designed and synthesized a novel ligand (Scheme 1), N,N,N^1,N^1,N^2,N^2-[(2,4,6-tri(aminoethyl)-pyridine]hexakis(acetic acid)(TPHA), and studied the lumine-
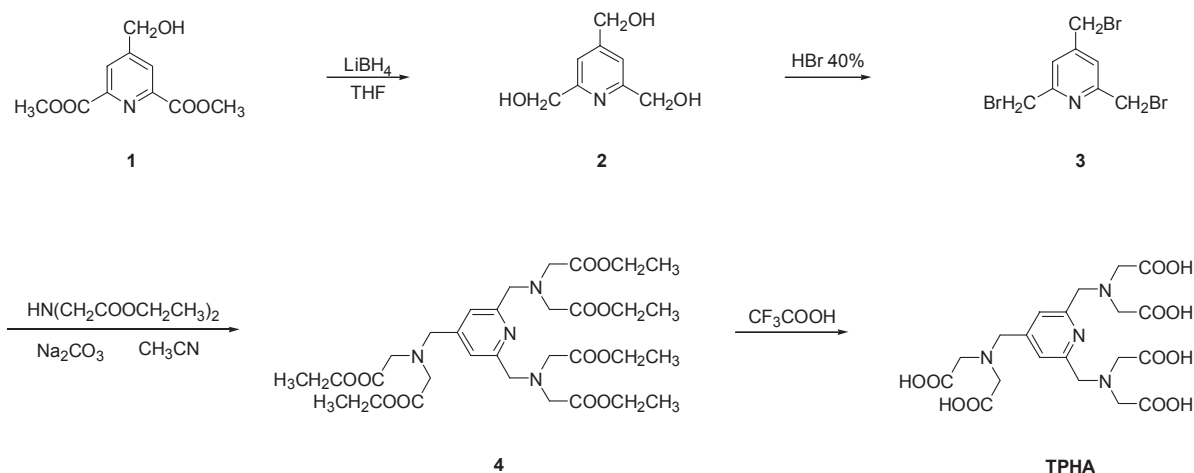
Scheme 1. Synthetic route of TPHA

scence properties of its Tb(III), Eu(III), Gd(III) and Sm(III) complexes respectively, in the inner-sphere of which there were none H_2O molecules, proved by IR and TG-DTA studies and in agreement with the expectation. The ligand contain amine and carboxyl functionalities which known for its capability to bind lanthanide ions *via* interaction with C=O oxygen atoms and amine nitrogen atoms.[16] This ligand presents three main advantages: (i) its many donor groups prevent coordination of water molecules; (ii) the pyridine ring may act as an efficient antenna in Ln^{3+} photosensitization; (iii) the tri (iminodiacetate) unit is a very efficient chelating system for Ln^{3+} ions in aqueous solutions.[17] The compounds are stable, water soluble and potentially suited as labels for biological applications.

Experimental Section

Materials and measurements. Rare earth chlorides and 4-(hydroxylmethyl)pyridine-2,6-dicarboxylate **1** were prepared as described in the literatures.[18] Other chemicals were of A.R. grade and used without further purification.

Melting points were determined on a XR-4 apparatus (thermometer uncorrected); elemental analysis was carried out by a PerkinElmer 2400 elemental analyzer; Content of Ln(III) was determined by EDTA titration. Infrared spectra (4000 - 400 cm^{-1}) were recorded with samples as KBr discs using a Nicolet NEXUS 670 FTIR spectrophotometer. UV spectra were recorded on a Varlan UV-vis spectrophotometer. ^{1}H-NMR was measured with a Bruker-500MHz nuclear magnetic resonance spectrometer with $CDCl_3$ or DMSO as solvent and TMS as internal reference. Mass spectrum was measured using a ZAB-HS analyzer. The excitation and emission spectra were recorded on a Hitich F-4500 luminescence spectrophotometer. Thermal gravimetric (TG) and differential thermal analyses (DTA) were performed in the nitrogen atmosphere using a Netzsch TG209 thermogravimetric analyzer at a heating rate of 10 ^{o}C·min^{-1} from 30 to 700 ^{o}C.

Synthesis of 2,4,6-tri(hydroxylmethyl)pyridine (2): To 100 mL of dry THF containing 300 mg $LiBH_4$ was added 1.0 g (4.4 mmol) of **1**. After stirring for 3.5 h at room temperature, 0.6 mL of water, 0.6 mL of 15% NaOH, and 1.5 mL of water were added dropwise to the solution. The solution was filtered to remove precipitate, and the solvent was evaporated. The product was recrystallized with CH_3CN and then dried. A white powder of **2** was obtained (0.66 g, 76.6% yield); mp 116 - 118 ^{o}C. Anal. Calcd for $C_8H_{11}NO_3$ (%): C, 56.80; H, 6.51; N, 8.28. Found: C, 56.72; H, 6.54; N, 8.31. IR (KBr), v/cm^{-1}: 3351, 2927, 2851, 1613, 1568, 1424. ^{1}H NMR (CDCl₃) δ_H 7.92 (2H, s, ArH), 5.29 (4H, s, CH_2), 4.83 (2H, s, CH_2), 4.67 (3H, t, J = 5.8 Hz, OH).

Synthesis of 2,4,6-tri(bromomethyl)pyridine (3): To 8 mL of 40% HBr containing 1 g of **2** (5.92 mmol) was added drop-

wise 15 mL of $(CH_3CO)_2O$, and the solution was refluxed for 24 h with stirring. After the solvent was evaporated, the residue was dissolved in 30 mL of CH_2Cl_2 and then washed with 10% Na_2CO_3. The crude product was then extracted from the aqueous phase with 3×20 mL portions of CH_2Cl_2. The organic phase were combined, dried over $MgSO_4$, and evaporated to dryness in vacuum, affording 1.21 g of pure compound **3** in 57.1% yield; mp 61 - 63 ^{o}C. EI-MS, *m/z* 358 (M$^+$, 6%), 278 ([M - Br]$^+$, 100%), 198 ([M - 2Br]$^+$, 13%), 118 ([M - 3Br]$^+$, 15%). Anal. Calcd for $C_8H_8NBr_3$ (%): C, 26.82; H, 2.23; N, 3.91. Found: C, 26.77; H, 2.26; N, 3.87. IR (KBr), v/cm^{-1}: 3036, 2962, 1601, 1561, 1431, 597. ^{1}H NMR (CDCl₃) δ_H 7.31 (2H, s, ArH), 4.67 (4H, s, CH_2), 4.23 (2H, s, CH_2).

Synthesis of hexaethyl.

N,N,N^1,N^1,N^2,N^2-[(2,4,6-tri(aminoethyl)-pyridine]hexakis (acetate) (4): To a solution of 20 mL of dry CH_3CN containing 0.286 g of **3** (0.8 mmol), 453 mg of diethyl iminodiacetate (2.4 mmol) and 0.6 g of Na_2CO_3 were added. The mixture was refluxed for 24 h with stirring. After filtering, the solvent was evaporated. The residue was dissolved in 20 mL of $CHCl_3$, and then the solution was washed with 2×20 mL of water. After the organic phase was dried with Mg_2SO_4, the solvent was evaporated. The oily residue was purified by silica gel column chromatography using ethyl acetate as eluent to yield 0.42 g (76.9% yield) of **4**. Anal. Calcd for $C_{32}H_{50}N_4O_{12}$ (%): C, 56.30; H, 7.33; N, 8.21. Found: C, 56.38; H, 7.29; N, 8.23. ESI$^+$MS, *m/z* 683 ([M + H]$^+$, 100%), 705 ([M + Na]$^+$, 26%). IR (KBr), v/cm^{-1}: 2982, 2936, 1737, 1605, 1567, 1446, 1419, 1371, 1194, 1153, 1030. ^{1}H NMR (CDCl₃) δ_H 7.48 (2H, s, ArH), 4.16 (12H, q, J = 7.2 Hz, OCH₂), 4.06 (4H, s, Ar(2,6)CH₂), 3.97 (2H, s, Ar(4) CH₂), 3.62 (8H, s, CH_2), 3.55 (4H, s, CH_2), 1.26 (18H, t, J = 7.2 Hz, CH₃).

Synthesis of N,N,N^1,N^1,N^2,N^2-[(2,4,6-tri(aminoethyl)-pyridine]hexakis(acetic acid) (TPHA): A solution of **4** (457 mg, 0.67 mmol) in CF_3COOH (8 mL) was stirred for 12 h at rt. After evaporation, an oily residue was obtained (344 mg, 100% yield). Anal. Calcd for $C_{20}H_{26}N_4O_{12}$ (%): C, 46.69; H, 5.06; N, 10.89. Found: C, 46.61; H, 4.93; N, 10.96. IR (KBr), v/cm^{-1}: 3475, 2991, 1746, 1672, 1543, 1407, 1211, 1171, 930. ^{1}H NMR (DMSO-d_6) δ_H 7.67 (2H, s, ArH), 3.98 (4H, s, Ar(2,6)CH₂), 3.91 (2H, s, Ar(4)CH₂), 3.56 (8H, s, CH_2), 3.53 (4H, s, CH_2).

Synthesis of the complexes. An solution of $LnCl_3$ (Ln = Tb, Eu, Gd and Sm) (0.4 mmol) in ethanol (6 mL) was added dropwise to a solution of the ligand (0.4 mmol) in ethanol (4 mL) and the mixture stirred at 60 ^{o}C for 8 h. The pH value of the solution was adjusted to 6.0 by dropwise addition of aqueous NaOH (0.01 mol·L^{-1}). The resulting precipitate was collected by filtration, washed three times each with ethanol and chloroform mixture (1:1, v:v) and dried in vacuum to give a flake solid. The results of elemental analysis (see Table 1) indicated

Table 1. Elemental analytical data for the complexes

Complex	Ln (%) found (calc.)	C (%) found (calc.)	H (%) found (calc.)	N (%) found (calc.)
$Na_6Tb_2(TPHA)Cl_6 \cdot 14H_2O$	22.11 (22.16)	16.79 (16.72)	3.74 (3.76)	3.94 (3.90)
$Na_6Eu_2(TPHA)Cl_6 \cdot 8H_2O$	23.18 (23.15)	18.25 (18.28)	3.17 (3.20)	4.30 (4.27)
$Na_6Gd_2(TPHA)Cl_6 \cdot 11H_2O$	22.77 (22.80)	17.48 (17.43)	3.52 (3.49)	4.03 (4.07)
$Na_6Sm_2(TPHA)Cl_6 \cdot 9H_2O$	22.54 (22.61)	18.12 (18.09)	3.29 (3.32)	4.25 (4.22)

that the composition of the complexes conforms to be Na_6Tb_2 $(TPHA)Cl_6 \cdot 14H_2O$, $Na_6Eu_2(TPHA)Cl_6 \cdot 8H_2O$, $Na_6Gd_2(TPHA)$ $Cl_6 \cdot 11H_2O$ and $Na_6Sm_2(TPHA)Cl_6 \cdot 9H_2O$. Generally, polyaminopolycarboxylate ligand should possibly lead to oligomeric typed complexes, however, the ligand synthesized by us has many coordination sites, so it has enough capability to accept two ions. We suspect that the chemical structure of complexes may be like this:
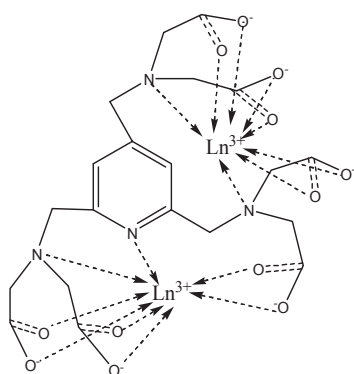
The chemical structure of the complexes.

Results and Discussion

IR spectra of the complexes. The IR spectra of the four complexes are similar (Figure 1-4), indicating that they are structurally alike. Table 2 summarizes the characteristic bands observed for the ligand and its metal complexes. The IR spectra of the free ligand shows bands at 3478, 1748 and 1663 cm^{-1}, which can be assigned as v(C-OH), v(C=O) and v(C=N) of the ligand, respectively. In the complexes, the band for v(C=N) of pyridine ring shows a shift to a lower frequency (1410 - 1435 cm^{-1}) as a result of the coordination through metal-nitrogen bond. The bands v(C=O) at 1748 cm^{-1} in free ligands disappear and new bands appear at 1575 - 1592 cm^{-1} and 1325 - 1364 cm^{-1} assignable to $[v_{as}(COO^-) + v_s(COO^-)]$. In each case, the remarkable shifts suggested that the relevant oxygen and nitrogen atoms of the ligand were involved in coordination to the metal centre and the ligand had a strong capability of coordination. The absorption bands assigned to the v(Ln-O) and v(Ln-N) stretching frequencies of the complex were observed at 427 - 453 cm^{-1} and 556 - 594 cm^{-1} respectively, also confirmed that the oxygen and nitrogen atoms participated in the coordination. The bands v(OH) centered at about 3400 cm^{-1} are always relatively intense and can be attributed to solvated water. The $\rho_\gamma(H_2O)$ and $\rho_\omega(H_2O)$ bands usually at approximately 850 cm^{-1}
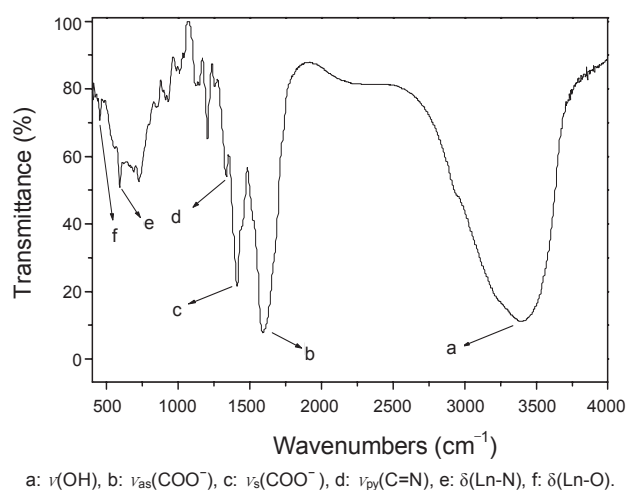
a: v(OH), b: v_{as}(COO$^-$), c: v_s(COO$^-$), d: v_{py}(C=N), e: δ(Ln-N), f: δ(Ln-O).
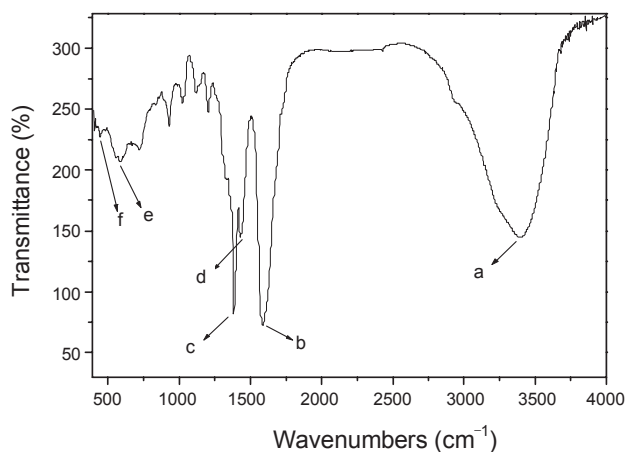
Figure 1. The IR spectrum of Tb (III) complex.

Figure 2. The IR spectrum of Eu(III) complex.

and 650 cm^{-1} respectively were not observed in the spectra of the complexes, indicating that there are none coordinated water molecules in the inner-sphere of the metal, in agreement with the expectation and proved by TG-DTA studies infra.[19]

Thermal analysis. In order to examine the thermal stability of the complexes and confirm the fact that none water molecules participated in the coordination, the two complexes Na_6Tb_2 $(TPHA)Cl_6 \cdot 14H_2O$ and $Na_6Eu_2(TPHA)Cl_6 \cdot 8H_2O$ were selected to perform thermal gravimetric (TG) and differential thermal analyses(DTA). Figure 5 and 6 show the TG-DTA curves of the

Table 2. Characteristic IR bands (cm^{-1}) of the ligand and its complexes

Sample	v(OH)	v(C=O)	v_{as}(COO$^-$)	v_s(COO$^-$)	v_{py}(C=N)	δ(Ln-N)	δ(Ln-O)
TPHA	3478	1748			1663		
$Na_6Tb_2(TPHA)Cl_6 \cdot 14H_2O$	3393		1592	1338	1410	594	453
$Na_6Eu_2(TPHA)Cl_6 \cdot 8H_2O$	3397		1586	1364	1435	587	446
$Na_6Gd_2(TPHA)Cl_6 \cdot 11H_2O$	3411		1591	1325	1414	556	432
$Na_6Sm_2(TPHA)Cl_6 \cdot 9H_2O$	3423		1575	1326	1413	558	427

v_{as}, asymmetric; v_s, symmetric.

Table 3. TG-DTA data of $Na_6Tb_2(TPHA)Cl_6\cdot14H_2O$ and $Na_3Eu_2(TPHA)Cl_3\cdot8H_2O$

Complex	Stage	Temperature range (°C)	DTA peak temperature (°C)	Mass loss rate (%) found (calc.)	Probable lost molecules
$Na_6Tb_2(TPHA)Cl_6\cdot14H_2O$	I	70 - 150	101	16.74 (16.80)	$14H_2O$
	II	310 - 350	370	35.51 (35.57)	TPHA
$Na_6Eu_2(TPHA)Cl_6\cdot8H_2O$	I	65 - 130	81	10.93 (11.02)	$8H_2O$
	II	270 - 550	278	38.76 (38.87)	TPHA
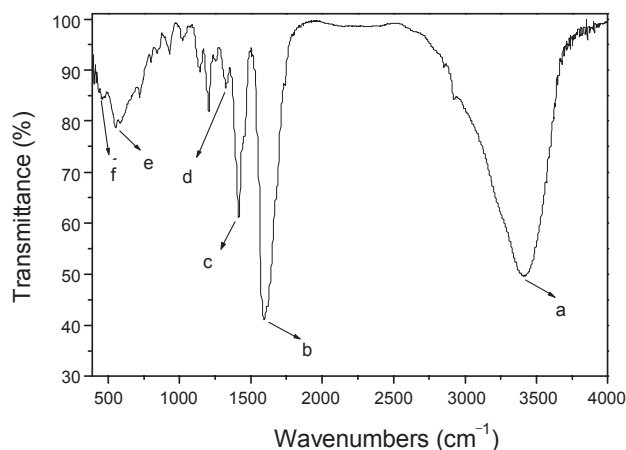
Figure 3. The IR spectrum of Gd(III) complex.
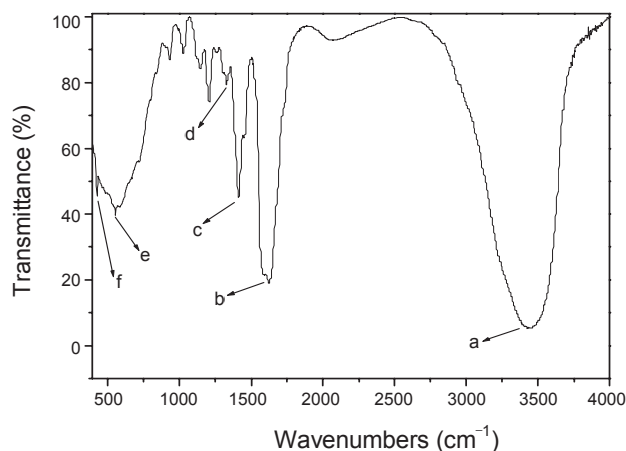
Figure 4. The IR spectrum of Sm(III) complex.

Table 4. Luminescence data for the complexes

Complexes	λ_{ex} (nm)	λ_{em} (nm)	LI	Assignment
TPHA	326	438	113	
$Na_6Tb_2(TPHA)Cl_6\cdot14H_2O$	276	489	979	$^5D_4\text{-}^7F_6$
		543	2014	$^5D_4\text{-}^7F_5$
		583	232	$^5D_4\text{-}^7F_4$
		619	84	$^5D_4\text{-}^7F_3$
$Na_6Eu_2(TPHA)Cl_6\cdot8H_2O$	278	590	965	$^5D_0\text{-}^7F_1$
		613	1834	$^5D_0\text{-}^7F_2$
$Na_6Gd_2(TPHA)Cl_6\cdot11H_2O$	325	392	7720	
$Na_6Sm_2(TPHA)Cl_6\cdot9H_2O$	248	396	2161	

two complexes and some thermal analytical data are listed in Table 3. In the TG-DTG curves, there are two main successive mass loss stages. The first mass loss stage of Tb(III) and Eu(III) ion complexes take place between 70 - 150 °C and 65 - 130 °C with mass loss percentage of 16.74% and 10.93% respectively, which corresponds to the release of solvated water content and roughly coincides with the calculated value ($14H_2O$(16.80%) for Tb and $8H_2O$(11.02%) for Eu complex). The relatively low decomposition temperatures indicate that the water in the complexes is solvated water rather than coordinated water, for the coordinated water of similar complexes releases commonly above 200 °C.[20-21] The second stage in region of 310 - 500 °C and 270 - 550 °C is attributed to elimination and/or decomposition of TPHA, with mass loss percentage of 35.51% and 38.76% respectively, also coincided with the calculated value (35.57% and 38.87%). These above suggest that the complexes have the relatively high thermal stability and their composition were reasonable.

Luminescence properties of complexes. The luminescence data for each complex were determined in the solid state at room temperature. The width of emission slit and excitation slit of the Tb(III) complex was 2.5 nm and the others were 5.0 nm, the voltage of photomultiplier tube was 700 V. The maximum excitation wavelengths (λ_{ex}) of the ligand, Tb(III), Eu(III), Gd(III) and Sm(III) complexes were 326, 276, 278, 325 and 248 nm, respectively (see Table 4). The difference between the excitation wavelengths for the ligand and the complexes may be resulted from these: firstly, the states of the ligand (oil) and the complexes (solid) are different; secondly, the ligand was coordinated to the rare earth ions in the complexes, its structure and energy state may be changed due to the affection of the metal ions. Obviously, the CO_2H was converted to CO_2^- in the complexes. While the λ_{ex} of the Tb(III) and Eu(III) complexes of N,N,N^1,N^1-[(2,6-bis(aminoethyl)-pyridine]tetrakis(acetic acid) with only seven donor groups, respectively, were 267 and 265 nm reported by *Veli-Matti Mukkala*,[22] it was not difficult to find that both of the λ_{ex} of Tb(III) and Eu(III) complexes reported by us were shifted to longer wavelength. It can be explained that the increase of the number of the coordination atoms causes the energy transitions from ligand to metal ion to be more effectively, because it shields the lanthanide ion from the interaction with H_2O molecules, which would otherwise cause nonradiative deactivation of the excited state.

Luminescence spectra for the ligand (TPHA) and the complexes were given (Figures 7-11). At 5.0 nm, the luminescence intensity (the maximum peak) observed from the ligand, Eu(III), Gd(III) and Sm(III) complexes were very weak (113, 1834, 7720 and 2161 respectively), while very strong from the Tb(III) com-
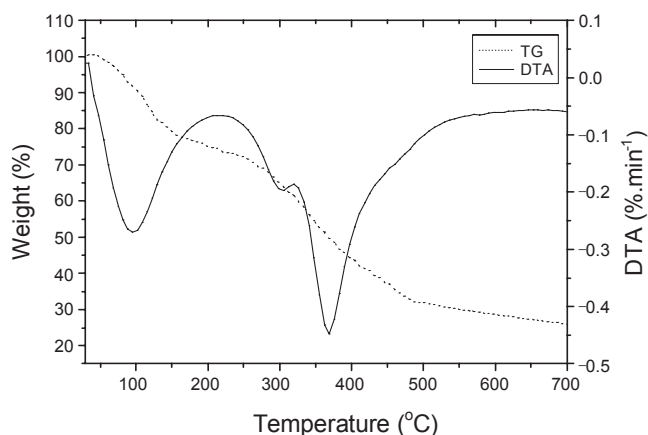
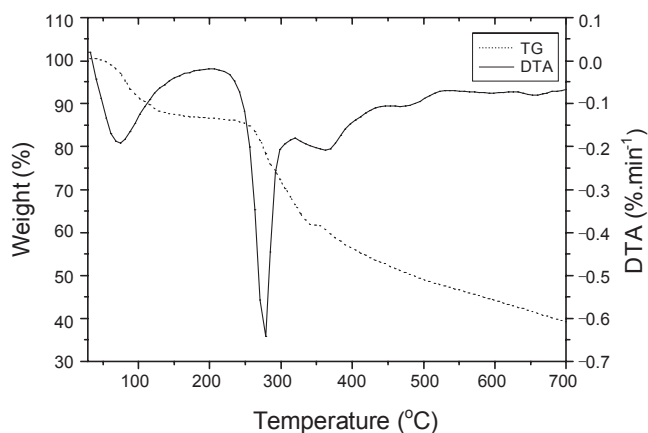**Figure 5.** TG and DTA curves for original Tb(III) complex.

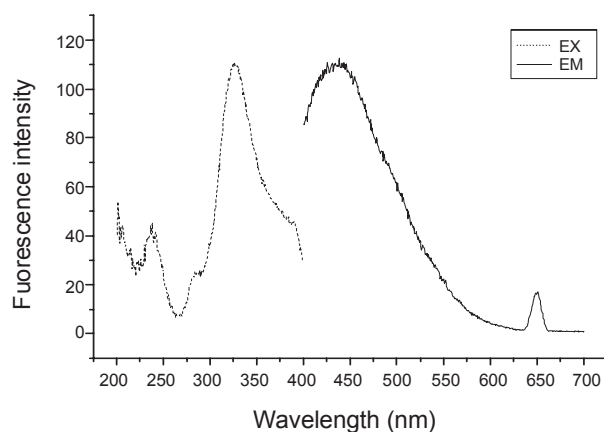**Figure 6.** TG and DTA curves for original Eu(III) complex.

Figure 7. The excitation and emission spectrum of the ligand..

Figure 8. The excitation and emission spectrum of the Tb (III) complex.

Figure 9. The excitation and emission spectrum of the Eu(III) complex.

plex (> 10000) (spectrum not shown) under the same experimental conditions. It appears that the energy-transfer from the organic ligand (HTPA) to the central Tb(III) ions is much more effective compared to the other Ln(III) ions. The luminescence spectrum of the ligand was very broad (400 - 550 nm). On the contrary, the Tb(III) and Eu(III) complexes possessed narrow emission bands and a large difference between the excitation and emission wavelengths, indicating that the ligand is a comparative good organic chelator to absorb energy and transfer it to Tb(III) and Eu(III) ions. However, the Gd(III) and Sm(III) complexes showed broad emission bands (350 - 470 nm and 350 - 550 nm respectively) and the luminescence spectra of them were similar to that of the ligand, indicating that they were attributed to the emission from the ligand, since the luminescence spectra of Ln(III) are very sharp. The $^5D_4$-$^7F_5$ peak of Tb(III) complex is sharp and strong, showing higher color purity and emission intensity.[23] The comparison between the luminescence spectra of the ligand and the Ln(III) complexes indicates that the observed luminescence of Tb(III) and Eu(III) complexes with TPHA is associated with the charge transfer from pyridine to the lanthanide ions. The reasons are: firstly, the excitation energies of the Tb(III) (λ_{exn} = 276 nm), the Eu(III) (λ_{exn} = 278 nm) and the Sm(III) (λ_{exn} = 248 nm) complexes are much higher

than those of the ligand (λ_{exn} = 326 nm) and the Gd(III) complex (λ_{exn} = 325 nm). Figures 7 and 10 illustrate that the 276 and 278 nm excitations cannot produce the emission from the ligand. Therefore, these excitations are unable to afford the energy transfer from the ligand to the Ln(III) ions. Secondly, the observed optical properties of the Gd(III) complex are identical to those

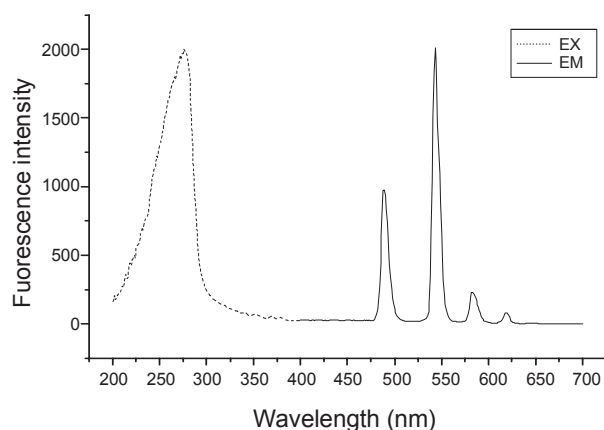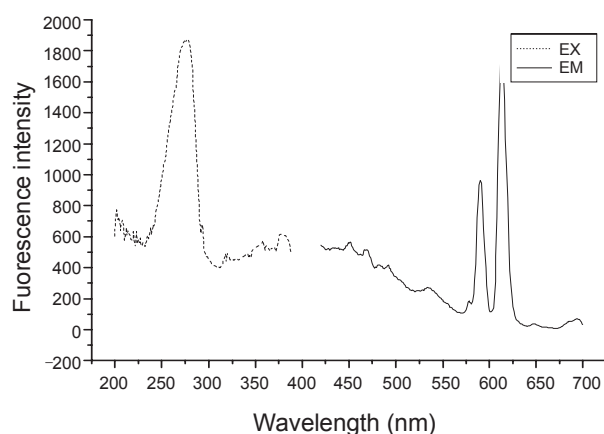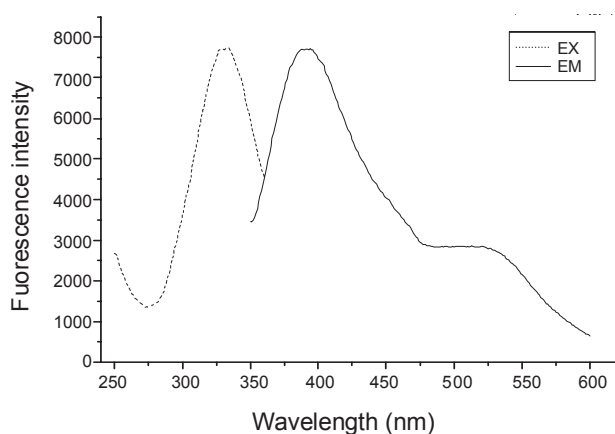**Figure 10.** The excitation and emission spectrum of the Gd (III) complex.

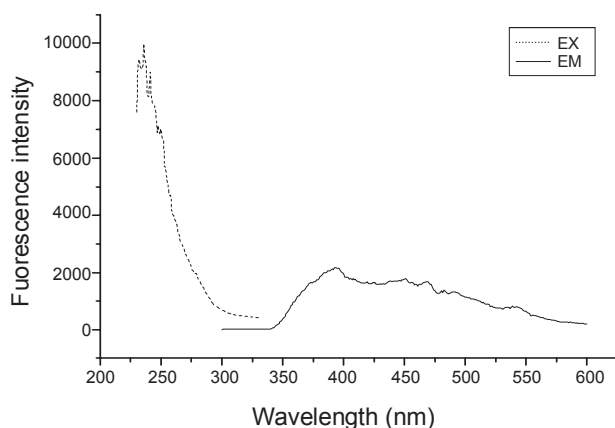**Figure 11.** The excitation and emission spectrum of the Sm(III) complex.

of the ligand. The additional band in the 475 - 600 nm is phosphorescence of the ligand, due to a strong-spin orbit interaction of Gd(III). Finally, the luminescence of the Sm(III) complex corresponds to that of the ligand. The excitation band, peaking at 230 nm, can be found in that of the ligand.

The luminescence of Ln(III) complexes is related to the efficiency of the intra-molecular energy transfer between the triplet energy states of the ligand and the emitting energy states of the metal ions. According to the fact that the observed luminescence intensity of the Tb(III) complex at 543 nm was much stronger than that of the Eu(III), Gd(III) and Sm(III) complexes, it can be inferred qualitatively that the energy difference between the ligand triplet states and the emitting energy state of Tb(III) is more favorable for energy transfer than those of the other three rare earth ions.

Conclusion

A novel fluorescent ligand and its lanthanide [Tb(III), Eu(III),

Gd(III) and Sm(III)] complexes have been synthesized. The TG-DTA and IR spectra of the free ligand and the metal complexes indicated that coordination of each of the four rare earth ions to the ligand was occurring at the nitrogen atoms and the oxygen atoms of the carbonyl. The study of their luminescence properties in solid state shows the Eu(III) and Tb(III) can be sensitized efficiently by the charge transfer from the ligand. Especially, the ligand is a more efficient antenna group for Tb(III) ions, since the Tb(III) complex only displayed characteristic metal-centered luminescence while ligand luminescence disappeared completely.

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