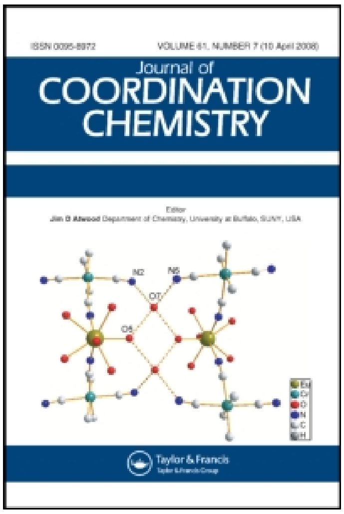

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Synthesis, characterization and fluorescence of lanthanide Schiff-base complexes

Pengfei Yan; Wenbin Sun; Guangming Li[a]; Chunhong Nie; Ting Gao; Zhengyu Yue
[a] School of Chemistry and Materials Science, Heilongjiang University, Harbin, PR China

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Synthesis, characterization and fluorescence of lanthanide Schiff-base complexes

PENGFEI YAN, WENBIN SUN, GUANGMING LI*,
CHUNHONG NIE, TING GAO and ZHENGYU YUE

School of Chemistry and Materials Science, Heilongjiang University,
Harbin 150080, PR China

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Six new lanthanide Schiff-base complexes were synthesized by reactions of hydrated lanthanide nitrates with H_2L ($H_2L = N,N'$-*bis*(salicylidene)-1,2-cyclohexanediamine) and characterized by elemental analysis, DTA–TG, IR, UV and luminescence spectra. The microanalyses and spectroscopic analyses indicate a 1D polymeric structure with the formula of $[Ln(H_2L)(NO_3)_3(MeOH)_2]_n$ [Ln = La (**1**), Ce (**2**), Pr (**3**), Sm (**4**), Gd (**5**) & Dy (**6**)]. The fluorescence spectrum of complex **4** exhibited Sm^{3+} centered, Schiff-base sensitized orange fluorescence, indicating that energy levels of the triplet state of H_2L match closely to the lowest excited state ($^4G_{5/2}$) of Sm^{3+} ion.

Keywords: Synthesis; Characterization; Schiff base; Lanthanide complexes; Fluorescence

1. Introduction

Organo lanthanide complexes attract considerable interest, not only because of their structures, but also potential applications of their luminescent properties [1]. The luminescence of a complex depends not only on the metal ion but also on the coordination environment, e.g., a metal-centered, ligand sensitized luminescence may occur when a suitable ligand efficiently absorbs the excitation energy followed by energy transfer to the metal center. Therefore, finding a suitable ligand to tune the luminescence of a complex is a challenge to chemists. In the past few decades, much effort has been devoted to the choice and design of the ligand. Various lanthanide compounds have been synthesized and their luminescence properties have been investigated [2]. However, the luminescent properties of lanthanide Schiff-base complexes are poorly documented [3]. A Schiff base was used in the synthesis of lanthanide complexes in 1968 [4] and many lanthanide Schiff-base complexes have been synthesized since then [5]. Nevertheless, few were structurally characterized [6] because of difficulty in crystallization. We are interested in the synthesis and photophysical properties of Schiff-base lanthanide complexes. Syntheses and fluorescent properties

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*Corresponding author. Fax: +81-451-86608042. Email: gmli@hlju.edu.cn

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of lanthanide and transition metal Schiff-base H_2L (*N*,*N*′-*bis*(salicylidene)-1,2-cyclohexanediamine) complexes have been seldom reported [7]. In this article, six new lanthanide Schiff-base complexes were synthesized and characterized and their luminescence properties examined.

2. Experimental

2.1. *Materials*

All solvents were analytical grade without purification prior to use. *N*,*N*′-*bis*-(salicylidene)-1,2-cyclohexanediamine (H_2L) was prepared according to the literature method [8]. Hydrated lanthanide(III) nitrate was prepared by reaction of lanthanide-(III) oxide with nitric acid.

2.2. *Apparatus*

Melting points were measured in sealed tubes and were not corrected. IR spectra were determined on a Perkin-Elmer 60000 spectrophotometer and UV spectra (in methanol) were recorded on a Shimadzu UV2240 spectrophotometer. Thermal analyses were conducted on a DTA-1700 with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ in a temperature range from ambient temperature to 900°C. Fluorescence spectra were taken on a LS-55 fluorescence photometer. Microanalyses were performed on a Perkin-Elmer-2400 and the contents of rare earth elements were determined by EDTA titration using xylenol-orange as an indicator.

2.3. *Preparations of 1–6*

To a solution of H_2L (0.339 g, 1.0 mmol) in 10 cm^3 of MeOH/CH_2Cl_2 (3/1) was slowly added $La(NO_3)_3 \cdot 6H_2O$ (0.433 g, 1.0 mmol) in 10 cm^3 of MeOH at room temperature. An initial bright yellow solution turned immediately brown upon addition of $La(NO_3)_3 \cdot 6H_2O$. A solid was collected by filtration and purified by washing with dichloromethane to yield $[La(H_2L)(NO_3)_3(MeOH)_2]_n$ (**1**), 0.52 g, yield 72%. Anal. Calcd for $C_{22}H_{30}LaN_5O_{13}$ (711.40) (%): C, 37.14; H, 4.25; N, 9.84; La, 19.53. Found: C, 36.92; H, 4.17; N, 9.27; La, 19.03. IR (cm^{-1}, KBr disk): 3416 (ν–OH), 1641 (ν–C=N), 1150 (δ–O–H), 1475 (ν_1), 1278 [ν_2, $\nu(C_{ph}$–O) and/or $\nu(NO_3^-)$], 1024 (ν_3), 819 (ν_4), (ν_1–ν_4, bidentate chelating NO_3^- group). UV-vis (MeOH): λ_{max} (ε): 212 (2.73), 244 (0.81), 317 (0.23) nm. Similar procedures were employed for the synthesis of complexes **2**–**6** using corresponding $Ln(NO_3)_3 \cdot 6H_2O$.

$[Ce(H_2L)(NO_3)_3(MeOH)_2]_n$ (2). 0.49 g, yield 70%. Anal. Calcd for $C_{22}H_{30}CeN_5O_{13}$ (712.61) (%): C, 37.08; H, 4.24; N, 9.83; Ce, 19.66. Found: C, 36.89; H, 4.15; N, 9.47; Ce, 19.10. IR (cm^{-1}, KBr disk): 3475 (ν–OH), 1647 (ν–C=N), 1151 (δ–O–H), 1482 (ν_1), 1292 [ν_2, $\nu(C_{ph}$–O) and/or $\nu(NO_3^-)$], 1029 (ν_3), 814 (ν_4), (ν_1–ν_4, bidentate chelating NO_3^- group). UV-vis (MeOH): λ_{max} (ε): 211 (2.50), 243 (0.93), 319 (0.22) nm.

$[Pr(H_2L)(NO_3)_3(MeOH)_2]_n$ (3). 0.53 g, yield 72%. Anal. Calcd for $C_{22}H_{30}PrN_5O_{13}$ (712.40) (%): C, 37.01; H, 4.21; N, 9.81; Pr, 19.75. Found: C, 36.78; H, 4.14; N, 9.12; Pr, 19.21. IR (cm^{-1}, KBr disk): 3456 (ν–OH), 1646 (ν–C=N), 1150 (δ–O–H), 1487 (ν_1), 1291 [ν_2, ν(C_{ph}–O) and/or ν(NO_3^-)], 1067 (ν_3), 812 (ν_4), (ν_1–ν_4, bidentate chelating NO_3^- group). UV-vis (MeOH): λ_{max} (ε): 210 (1.3), 240 (0.79), 342 (0.10) nm.

$[Sm(H_2L)(NO_3)_3(MeOH)_2]_n$ (4). 0.58 g, yield 80%. Anal. Calcd for $C_{22}H_{30}N_5O_{13}Sm$ (722.86) (%): C, 36.55; H, 4.18; N, 9.69; Sm, 20.80. Found: C, 36.34; H, 3.93; N, 9.38; Sm, 20.11. IR (cm^{-1}, KBr disk): ν_{max}: 3461 (ν–OH), 1641 (ν–C=N), 1157 (δ–O–H), 1482 (ν_1), 1277 [ν_2, ν(C_{ph}–O) and/or ν(NO_3^-)], 1030 (ν_3), 808 (ν_4), (ν_1–ν_4, bidentate chelating NO_3^- group). UV-vis (MeOH): λ_{max} (ε): 211 (2.38), 240 (1.32), 327 (0.18) nm.

$[Gd(H_2L)(NO_3)_3(MeOH)_2]_n$ (5). 0.60 g, yield 82%. Anal. Calcd for $C_{22}H_{30}GdN_5O_{13}$ (729.75) (%): C, 36.21; H, 4.14; N, 9.60; Gd, 21.55. Found: C, 35.95; H, 3.95; N, 9.13; Gd, 20.98. IR (cm^{-1}, KBr disk): ν_{max}: 3436 (ν–OH), 1641 (ν–C=N), 1298 [ν(C_{ph}–O)], 1151 (δ–O–H), 1482 (ν_1), 1284 (ν_2), 1024 (ν_3), 814 (ν_4), (ν_1–ν_4, bidentate chelating NO_3^- group). UV-vis (MeOH): λ_{max} (ε): 210 (2.14), 240 (1.33), 353 (0.22) nm.

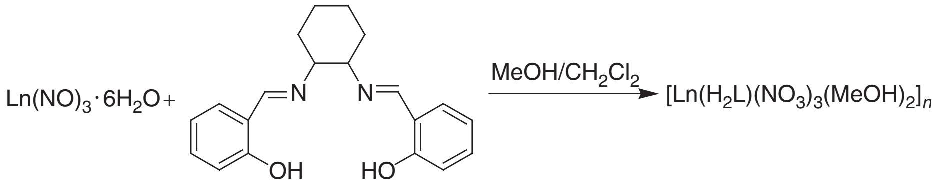
$[Dy(H_2L)(NO_3)_3(MeOH)_2]_n$ (6). 0.57 g, yield 75%. Anal. Calcd for $C_{22}H_{30}DyN_5O_{13}$ (735.00) (%): C, 35.95; H, 4.11; N, 9.53; Dy, 22.11. Found: C, 35.87; H, 3.86; N, 9.09; Dy, 21.65. IR (cm^{-1}, KBr disk): ν_{max}: 3430 (ν–OH), 1640 (ν–C=N), 1292 [ν(C_{ph}–O)], 1284 (δ–O–H), 1482 (ν_1), 1290 (ν_2), 1024 (ν_3), 814 (ν_4), (ν_1–ν_4, bidentate chelating NO_3^- group). UV-vis (MeOH): λ_{max} (ε): 212 (2.70), 239 (1.65), 349 (0.28) nm.

All complexes **1**–**6** began to decompose at 260°C.

3. Results and discussion

3.1. *Synthesis*

Complexes **1**–**6** were synthesized by equimolar reactions of $Ln(NO)_3 \cdot 6H_2O$ and H_2L (equation (1)). Deprotonation of H_2L followed by coordination to Ln(III) in MeOH/CH_2Cl_2 at room temperature gave an orange yellow crystalline solid. The stoichiometry of the as-synthesized complexes was proposed on the basis of the microanalyses and spectroscopic analyses. The ligand exists in a neutral zwitterionic phenolato-iminium form (O^-, NH^+), indicating migration of the protons from the phenolic functions to the imine group to maintain neutrality of the molecule. These complexes are unstable in air and moderately soluble in polar organic solvents such as methanol, ethanol and acetonitrile.



3.2. *Thermal analysis*

Thermal analysis data for **2**, **4**, **5** and **6** are summarized in table 1. The TG–DTA curves of **2**–**6** are similar and consistent with the formula $[Ln(H_2L)(NO_3)_3(MeOH)_2]_n$.

Table 1. Thermal gravimetric data of **2**, **4**, **5** and **6**.

	TGA		
Complex	Temp. range (°C)	Wt. loss (%)[a]	Part removal[b]
2	25–229	8.6 (8.9)	CH_3OH(c)
4	25–252	8.6 (8.9)	CH_3OH(c)
5	25–266	8.2 (8.8)	CH_3OH(c)
6	25–268	8.1 (8.7)	CH_3OH(c)

[a]Found (Calcd). [b]c = coordinated.

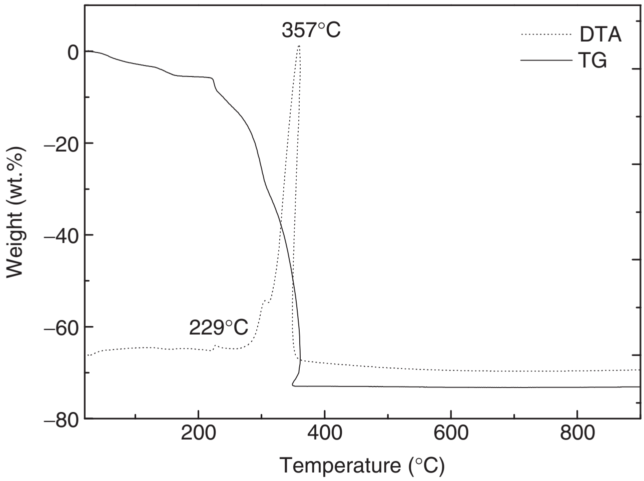


Figure 1. Thermal gravimetric curves of complex **2**.

A representative TG–DTA curve of **2** (figure 1) revealed that the complex has higher thermal stability than H_2L (melting point of H_2L is 109°C). The first weight loss peak of **2** appeared at around 250°C with about 8.6% weight loss corresponding to release of 2 mol MeOH per formula unit (Calcd 8.9%) in agreement with the proposed formula $Ln(H_2L)(NO_3)_3(MeOH)_2$. The thermal stability of different lanthanide complexes increased from La^{3+} to Dy^{3+}, attributed to the significant lanthanide contraction. With smaller Ln^{3+} ions, the interaction between Ln^{3+} ions and H_2L ligand is stronger [5a]. Obviously, the final substance from the thermal decomposition is the corresponding lanthanide oxide. Therefore, the thermal analyses supported the proposed formula of $[Ln(H_2L)(NO_3)_3(MeOH)_2]_n$ (Ln = La, Ce, Pr, Sm, Gd and Dy).

3.3. *IR and UV spectroscopic analysis*

IR spectra of **1**–**6** are similar; representative IR spectra of H_2L, **2** and **6** are shown in figure 2. The C=N stretching vibration shifts to higher wavenumbers (by 12–19 cm^{-1} to about 1646 cm^{-1}) in comparison to the same transition in the Schiff-base ligand. This is in accord with $[Ln(LH)_3(NO_3)_3]$ ($LH = CH_3OC_6H_3(2\text{–}OH)CH{=}NC_4H_9$) [9a] in which the C=N stretching vibration shifts to higher wavenumber (by 30–40 cm^{-1} to

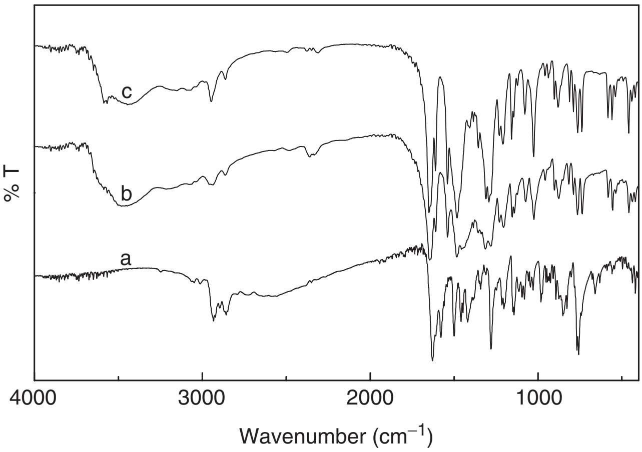


Figure 2. Infrared spectra of H_2L (a), complexes **2** (b) and **6** (c).

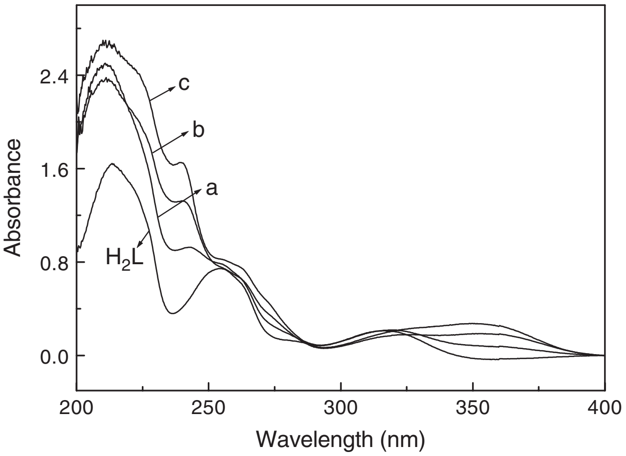


Figure 3. UV spectra of ligand H_2L and complexes **2** (a), **4** (b) & **6** (c).

about 1662 cm^{-1}). The broad weak O–H stretching vibration of the ligand at 2850 cm^{-1} (on which the CH modes are superimposed) is replaced in the metal complexes by a band at 3440 cm^{-1} (on which an O–H stretching vibration of CH_3OH is overlapped), due to the N–H vibration in $C{=}N^+{-}H$, which differs from some lanthanide and transition metal Schiff base complexes [7, 10]. The broadness of the band shows that this hydrogen atom is involved in intramolecular H-bonding with the phenolic oxygen. The phenolic C–O stretching vibration around 1280 cm^{-1}, observed in the Schiff-base ligand, overlaps in the metal complexes with vibration bands of nitrate. Four bands around 1482, 1284, 1024 and 814 cm^{-1} for the complexes can be assigned to vibrations of coordinated nitrate (respectively, ν_1, ν_2, ν_3 and ν_4). The difference in wavenumber between ν_1 and ν_2 is about 198 cm^{-1}, typical for bidentate chelating nitrate (monodentate nitrate groups display a much smaller splitting) [9].

UV spectra of **2**, **4**, **6** and ligand are shown in figure 3. A new absorption band around 240 nm in **2**, **4** and **6**, was absent for free ligand and $Ln(NO_3)_3 \cdot 6H_2O$, is

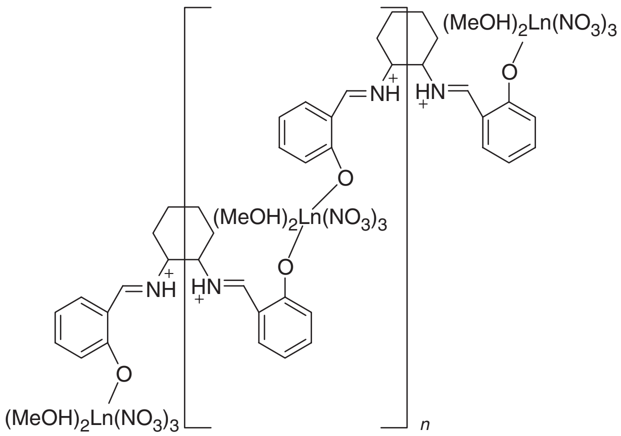


Figure 4. Proposed structure for $[Ln(H_2L)(NO_3)_3(MeOH)_2]_n$ (Ln = La (**1**), Ce (**2**), Pr (**3**), Sm (**4**), Gd (**5**) & Dy (**6**); H_2L = *N*,*N′*-*bis*(salicylidene)-1,2-cyclohexane diamine).

attributed to electron transfer from ligand to metal (LMCT) [6b]. The UV spectrum determined in acetonitrile was identical to that in methanol, though the solubility of the complexes in acetonitrile was considerably lower. The UV spectrum of the complex in DMSO appeared as a simple combination of the corresponding spectra of the free ligand and $Ln(NO_3)_3 \cdot 6H_2O$. These results indicate that the as-synthesized complexes were stable both in methanol and acetonitrile, but dissociated in DMSO.

The microanalyses and spectroscopic analyses of **1**–**6** indicate ten-coordination for lanthanide ions with two oxygen atoms from phenol, two oxygen atoms from methanol and six oxygen atoms from three bidentate nitrates. Two oxygen atoms of each H_2L bridge two lanthanide ions. Thus, a 1D polymeric structure, $[Ln(H_2L)(NO_3)_3(MeOH)_2]_n$, was proposed for complexes **1**–**6** (figure 4). This is in agreement with a previously reported analogue [6a]. Attempt to obtain single crystals to determine their crystal structure is still in progress.

3.4. *Fluorescence spectra*

The solid-state luminescent spectra of **1**–**6** and H_2L were examined at room temperature. The excitation and emission bands and corresponding origins are summarized in table 2.

The excitation spectrum of **4** showed that most of the excitation energy was absorbed by the ligand. Some absorbed energy was transferred to the central Sm^{3+} ions, emitting the characteristic fluorescence of the Sm^{3+}. The ligand retains its emission in a shorter wavelength. A dominant luminescent mechanism for complex **4** was proposed from the triplet state of the ligand to the central samarium ion ($L^* \rightarrow M$) [11a] (shown in the Jablonski diagram in figure 5). Schiff base efficiently absorbs excitation energy followed by energy transfer to lanthanide, and finally a metal-centered, sensitized luminescence occurs. Such a process, with light harvested by a strongly absorbing chromophore or sensitizer (H_2L), is usually referred to as the ‘antenna effect’. The energy transfer from chromophore (H_2L) to metal center can take place either from a singlet excited state

Table 2. Fluorescence data for H_2L and **1**–**6**.

Complexes	λ_{ex} (nm)	λ_{em} (nm)	Transition type
H_2L	492	545, 575	π–π^*
1 (La)	347, 395, 470	540	π–π^*
2 (Ce)	394	530	π–π^*
3 (Pr)	394	530	π–π^*
4 (Sm)	400	530, 566, 600, 645	π–π^*, ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$, ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$
5 (Gd)	393, 448	530	π–π^*
6 (Dy)	394, 443	528	π–π^*

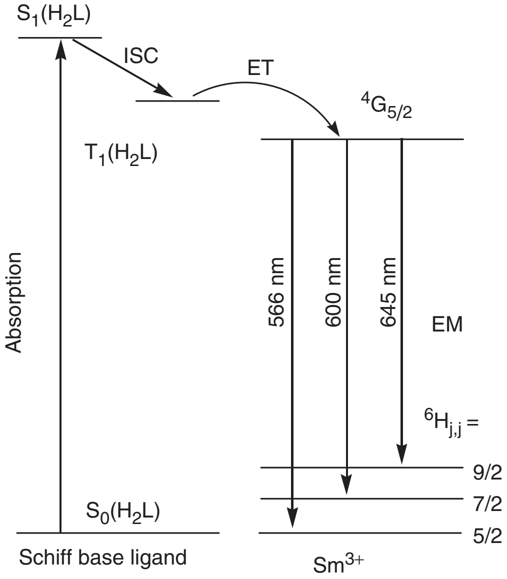


Figure 5. Jablonski diagram illustrating the absorption of incident light on the sensitizing chromophore (H_2L) followed by intersystem crossing (ISC) from the singlet (S_1) to the triplet state (T_1) on the chromophore and energy transfer (ET) to the ${}^4G_{5/2}$ level on the Sm^{3+} center from which deactivation to the ground state ${}^6H_{j,j}$ by emission of light (EM) occurs.

S_1 or from a triplet excited state T_1 after an intersystem crossing. Such an energy transfer in most cases occurs from T_1 rather than from S_1 [1a].

Excitation of **4** (figure 6a) at 394 nm leads to strong orange emission of Sm^{3+} with four emission bands at 530, 566, 600 and 645 nm due to π^*–π transitions of the ligand and ${}^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2, 9/2) transition [11]. The most intense band is the hypersensitive transition ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ at 600 nm, similar to samarium coordination polymers $[Sm_3(C_8H_4O_4)_4(C_{12}N_2H_8)_2(NO_3)]_n$ ($C_8H_4O_4$ = phthalate, $C_{12}N_2H_8$ = 1,10-phenanthroline) [2c] and $[Sm(dpap)_3 \cdot 12H_2O]$ (dpap = 6-diphenylamine carbonyl 2-pyridine carboxylic acid) [11a] in which the dominant band around 600 nm was attributed to the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition. This is different from the previously reported lanthanide *bis*-diketonate complexes in which the hypersensitive band at 647 resulted from ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ [11b]. In comparison with Sm^{3+}, the luminescent intensity of **4** was enhanced. The strong orange fluorescence of complex **4** indicates that the energy level

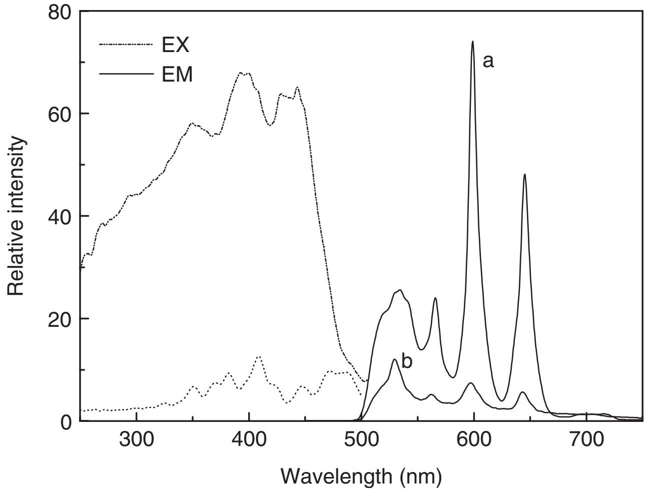


Figure 6. Excitation and emission spectra of **4** (a) and $Sm(NO_3)_3 \cdot 6H_2O$ (b).

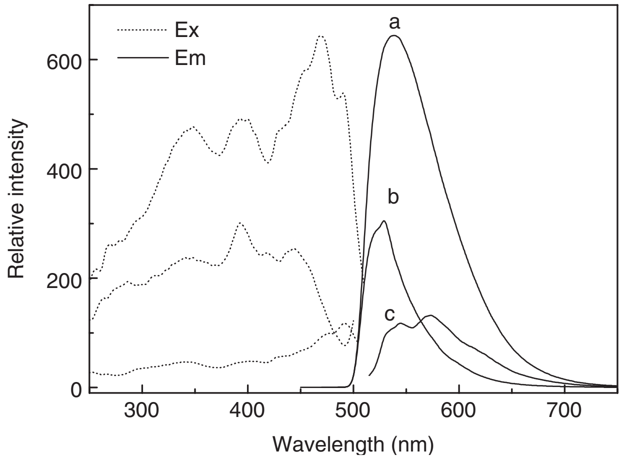


Figure 7. Excitation and emission spectra of **1** (a), **6** (b) and ligand H_2L (c).

of the triplet state of H_2L corresponded to the lowest excited state ($^4G_{5/2}$) level of Sm^{3+} ion. The ligand (H_2L) is a suitable sensitizer for Sm^{3+} luminescence.

The emission spectrum of the ligand (figure 7c) at 492 nm affords two main bands at 545 and 575 nm attributed to π^*-π electron transitions of the ligand. The emission spectra of **1** and **6** (figure 7a and b) at 470 and 394 nm were similar exhibiting one single main band at 540 and 530 nm, respectively, attributed to π^*–π electron transition of the ligand. Therefore, **1** and **6** emit strong green fluorescence characteristic of the ligand (H_2L) and the characteristic band of Dy^{3+} did not appear. On the basis of these results, we conclude that the Schiff base dominates the fluorescent properties of **1** and **6**, and the fluorescence intensity of complexes **1** (La^{3+}) and **6** (Dy^{3+}) was enhanced by lanthanide ions. Thus, La^{3+} and Dy^{3+} showed strong potential to be used in fluorescence probes for the Schiff-base compounds. Finally, two types of lanthanide

Schiff-base compounds with inverse luminescent mechanism from complexes **1**–**6** have been described.

4. Conclusion

Six new 1D lanthanide Schiff base coordination polymers, $[Ln(H_2L)(NO_3)_3(MeOH)_2]_n$ [Ln = La (**1**), Ce (**2**), Pr (**3**), Sm (**4**), Gd (**5**) & Dy (**6**); $H_2L = N,N'$-*bis*(salicylidene)-1,2-cyclohexane diamine], were isolated and characterized by elemental analyses and spectroscopic analyses. Schiff base is a feasible precursor for construction of coordination polymers. Fluorescent spectroscopic analyses indicate that H_2L tunes the luminescent properties of the lanthanide ions. The triplet state energy level of the Schiff base (H_2L) matches well with the lowest excited state ($^4G_{5/2}$) level of Sm^{3+} ion. The lanthanide Schiff-base compounds are promising luminescent materials. Current studies are focused on the design of analogous polymers using various Schiff bases and exploring the accessibility of the Lewis acid lanthanide metal sites in the complexes.

Acknowledgments

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