Synthesis and photoluminescent properties of series ternary lanthanide (Eu(III), Sm(III), Nd(III), Er(III), Yb(III)) complexes containing 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedionate and carbazole-functionalized ligand

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A B S T R A C T

A series of new ternary lanthanide complexes Ln(TFNB)$_3$L (where Ln = Eu, Sm, Nd, Er, Yb, TFNB = 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedionate, L = 1-(4-carbazolylphenyl)-2-pyridinyl benzimidazole) have been synthesised. The photoluminescence properties and TGA of them are described in detail. The trifluorinated ligand TFNB displays excellent antenna effect to sensitize the Ln(III) ions to emit characteristic spectra. The carbazole-containing ligand L is testified to be an outstanding synergistic ligand. The luminescence properties investigated and the quantum efficiency measured in dichloromethane solution of Eu(TFNB)$_3$L and Sm(TFNB)$_3$L show that the carbazole moiety is good at absorbing energy to sensitize the metal-centered emitting states and can make the complexes more rigid, provide efficient shielding of the Ln(III) core towards external quenching compared with the reference complexes of Eu(TFNB)$_3$(Pybm) and Sm(TFNB)$_3$(Pybm) (Pybm = 2-(2-pyridine)-benzimidazole) which have no carbazole unit. The quantum efficiency of Eu(TFNB)$_3$L in air-equilibrated CH$_2$Cl$_2$ solution is calculated to be 14.8% by using air-equilibrated aqueous [Ru(bpy)$_3$]$^{2+}$·2Cl$^-$ solution as reference sample (Φ_{std} = 2.8%).

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1. Introduction

In recent years, lanthanide complexes have attracted considerable attention because of their distinguished luminescent properties, especially Eu(III), Tb(III) and Sm(III) complexes which are emissive in the visible region of the spectrum (400–800 nm). Due to the very sharp emission and theoretically quantum efficiency up to 100% [1–5], lanthanide complexes have highly potential value in application in organic light-emitting diodes (OLEDs) [6,7]. At the same time, much efforts have been put in studying the near-infrared (NIR) luminescent lanthanide ions because several lanthanides show luminescence in the telecommunication low-loss NIR-regions of silica and for the best strategies to obtain high-resolution pictures of deep tissues as NIR light diffracts much less than visible light (diffraction is proportional to $1/(\lambda)^{SP}$, SP = scattering power) [8,9]. Among them, Nd(III), Er(III) and Yb(III) are regarded as be more important steming from the following three reasons. First, the basis of the common laser systems is 1064 nm wave, so Nd-containing systems have been taken for the most popular infrared luminescent materials for application

in laser systems. Second, two telecommunication windows for amplification are commonly used for long-distance communication, one at 1.3 μm using Nd emission and the other at 1.5 μm using Er or Ho emission [10–12]. Third, biological tissues and fluids (e.g. blood) are relatively transparent in the NIR region (approximately 1000 nm), the Yb(III) ion emission occurs in this region, thus the development of Yb(III) ion luminescence for various analytical and chemosensor applications is promising.

In order to exploit their luminescence potential, lanthanide ions must be coordinated by a properly selected ligand environment to saturate the coordinating positions of the metal centers as well as to play as a light-harvesting unit (antenna) for the sensitisation of the ion itself [13,14]. β-Diketones are one of the most popular ligands for lanthanide ions [15,16], since they have strong absorption within a large wavelength range and consequently have been targeted to sensitize the lanthanide luminescence. According to the literature reported previously, the C–H bonds vibration in ligands can cause the energy loss, then decrease the emission intensity of the lanthanide ion [17–19] and shorter excited state lifetimes, so replacement of C–H bonds in a β-diketone ligand with lower-energy C–F oscillators is an efficient way to fetch up this deficiency. In addition, the synergistic agent plays an important role in lanthanide complexes, since a vital issue in the design is

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to prevent water molecules from binding to the lanthanide ions. In this work, 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedionate (TFNB) which contains trifluoroalkyl chain was selected as the main sensitizer for synthesizing lanthanide complexes and a new carbazole-containing diimine ligand, 1-(4-carbazolylphenyl)-2-pyridinyl benzimidazole (L), was synthesised as the synergistic ligand. The choice of appending a carbazole moiety has been dictated by its ability to (i) act as light-harvesting unit, (ii) improve the hole-transporting ability in devices, this method can avoid phase separation induced by doping with electron/hole-transporting molecules and is reported by many groups [20–22], (iii) prevent the crystallization of complexes and (iv) increase the solubility in common organic solvents [23].

2. Experimental

2.1. Materials and instrumentation

Lanthanide chloride hexahydrates (LnCl$_3$·6H$_2$O, Ln = Eu, Sm, Nd, Er, Yb) were purchased from Ruike Co. (China). Carbazole was purchased from Yuan Hang Reagent Company (China). TFNB and Pybm (2-(2-pyridine)-benzimidazole) were obtained from Acros Organics Co. (Geel, Belgium). 1,4-Dibromobenzene was brought from J&K Chemical LTD (China). All these reagents and solvents were used directly without further purification. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C analyzer. Fluorescence spectra in visible region were measured with a Hitachi F4600 luminescence spectrophotometer. The photoluminescence lifetime and fluorescence spectra in IR region measurements were measured with an Edinburgh Instruments FLS920P fluorescence spectrometer. Thermogravimetrical analysis (TGA) was performed in N$_2$ atmosphere with a flow rate of 100 ml/min on a simultaneous SDT 2960 thermal analyzer from 20 to 750 °C, with a ramp rate of 10 °C/min.

2.2. Synthesis of 1-(4-carbazolylphenyl)-2-pyridinylbenzimidazole (L)

2.2.1. Synthesis of 1-carbazolyl-4-bromobenzene (Br·carb) [24]
A mixture of carbazole (16.72 g, 0.1 mol), 1,4-dibromobenzene (23.59 g, 0.1 mol), CuI (1.90 g, 0.01 mol), 18-Crown-6 (0.88 g, 0.0033 mol), K$_2$CO$_3$ (27.67 g, 0.2 mol) and DMPU (3 mL) were put into a reactor, and then heat it at 170 °C for 13 h under nitrogen (Scheme 1). After cooling to room temperature, the mixture was quenched with 1 N HCl, and the precipitate was filtered and washed with NH$_3$·H$_2$O and water. The brown solid was purified with column chromatography using hexane as eluant (10.95 g, yield: 34%). M.p.: 152–154 °C. IR (KBr, cm^{-1}): 3056, 1496, 1452, 1230, 751. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.175 (d, 2H, J = 7 Hz), 7.757 (d, 2H, J = 8.5 Hz), 7.495 (d, 2H, J = 8.5 Hz), 7.431 (t, 2H, J = 7 Hz), 7.411 (d, 2H, J = 9 Hz), 7.342 (t, 2H, J = 7.5 Hz). MS(MALDI–TOF): m/z 321.035 [M]$^+$. Anal. Calc. for C$_{18}$H$_{12}$NBr: C, 67.10; H, 3.75; N, 4.35. Found: C, 66.93; H, 3.71; N, 4.31%.

2.2.2. Synthesis of 1-(4-carbazolylphenyl)-2-pyridinyl benzimidazole (L)
The procedure is similar to that of compound Br·carb with the materials of Br·carb (3.22 g, 0.01 mol) and Pybm (1.95 g, 0.01 mol) at the temperature of 230 °C for 13 h, the eluant using in column chromatography was the mixed solvents of ethyl acetate and petroleum ether (V:V = 1:3, 5% triethylamine was added) (2.93 g, yield: 67%). M.p.: 225–228 °C. IR (KBr, cm^{-1}): 3044, 1728, 1593, 1514, 1446, 740. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.489 (d, 2H, J = 4.5 Hz), 8.203 (d, 2H, J = 7.5 Hz), 8.074 (d, 1H, J = 8 Hz), 7.906 (t, 1H, J = 7.5 Hz), 7.762 (d, 2H, J = 8.5 Hz), 7.614 (d, 2H, J = 9 Hz), 7.550 (d, 2H, J = 7.5 Hz), 7.502 (t, 3H, J = 7 Hz), 7.472 (m, 2H),

7.357(t, 3H, J = 7 Hz). MS (MALDI-TOF): m/z 437.130 [M]$^+$. Anal. Calc. for C$_{30}$H$_{20}$N$_4$: C, 82.55; H, 4.62; N, 12.84. Found: C, 82.54; H, 4.69; N, 12.83%.

2.3. Synthesis of the Ln(TFNB)$_3$L Complexes (Ln = Eu, Sm, Nd, Er, Yb, L = 1-(4-carbazolylphenyl)- 2-pyridinylbenzimidazole)

TFNB (0.3 mmol) and L (0.1 mmol) were dissolved in ethanol and acetone mixture solvent (V:V = 1:1), the pH value was adjusted to approximately 8 with appropriate amount of sodium hydroxide solution. After 30 min' stirring, LnCl$_3$·6H$_2$O (0.1 mmol) ethanol solution (about 1 mL), prepared separately, was added dropwise. The solution was refluxed at 70 °C for 5 h, then cooled to room temperature. The solid obtained was recrystallized in ethanol and the crystal collected was washed with water and diethyl ether twice, respectively, to obtain the pure Ln(TFNB)$_3$L complexes (Ln = Eu, Sm, Nd, Er, Yb).

Eu(TFNB)$_3$L (yield: 70.7%) M.p.: 268–270 °C. Anal. Calc. for Eu-C$_{72}$H$_{44}$O$_6$F$_9$N$_4$: C, 62.48; H, 3.20; N, 4.05. Found: C, 62.27; H, 3.40; N, 4.21%.

Sm(TFNB)$_3$L (yield: 72.5%) M.p.: 256–258 °C. Anal. Calc. for SmC$_{72}$H$_{44}$O$_6$F$_9$N$_4$: C, 62.55; H, 3.21; N, 4.05. Found: C, 62.57; H, 3.24, N, 4.03%.

Nd(TFNB)$_3$L (yield: 52.7%) M.p.: 270–272 °C. Anal. Calc. for NdC$_{72}$H$_{44}$O$_6$F$_9$N$_4$: C, 62.83; H, 3.22; N, 4.07. Found: C, 62.78; H, 3.32; N, 4.09%.

Er(TFNB)$_3$L (yield: 78.0%) M.p.: 269–271 °C. Anal. Calc. for ErC$_{72}$H$_{44}$O$_6$F$_9$N$_4$: C, 61.80; H, 3.17; N, 4.00. Found: C, 61.78; H, 3.14; N, 4.07%.

Yb(TFNB)$_3$L (yield: 69.7%) M.p.: 268–270 °C. Anal. Calc. for Yb-C$_{72}$H$_{44}$O$_6$F$_9$N$_4$: C, 61.54; H, 3.16; N, 3.99. Found: C, 61.51, H, 3.09; N, 3.97%.

Eu(TFNB)$_3$(Pybm) and Sm(TFNB)$_3$(Pybm) which were used as the reference were also synthesised according to the same method. Yb(tta)$_3$phen was synthesised according to a published method [25].

3. Results and discussion

3.1. Photoluminescence properties

The UV–Vis absorption spectra of all the complexes are analogical (Fig. 1) because the absorption spectra of lanthanide complexes are attributed to the organic ligands and the absorption of lanthanide ions is so weak that can be neglected. There are two peaks at 293 and 313–323 nm, respectively. The π–π^* transition of the carbazole moiety in L accounts for the former peak by comparison with Br·carb (Supplementary material Fig. S1) and the later one results from the electronic transitions of the β-diketonate. The main absorption peak of L locates at shorter wavelength than that of TFNB (Fig. 1 inset). From Fig. 1 and Fig. S2, we can find that the carbazole-appended complexes have more intense absorptions than the reference complexes which indicate the light-harvesting function of carbazole unit.

The excitation and emission spectra of each complex were characterized to make a clear understanding of the luminescence properties of these series of lanthanide complexes. As we can see clearly from the absorption spectra of the ligands (TFNB and L, Fig. 1 inset) and the excitation spectra of Ln(TFNB)$_3$L (Ln = Eu, Sm, Nd, Er, Yb) (Figs. 2 and 3) that there are overlaps between the absorption bands of TFNB and L and the excitation band of each lanthanide complex, which suggest the so-called "antenna effect" [26], thus confirms that the Ln(III) ions are surrounded by TFNB and L in the complexes [27,28].
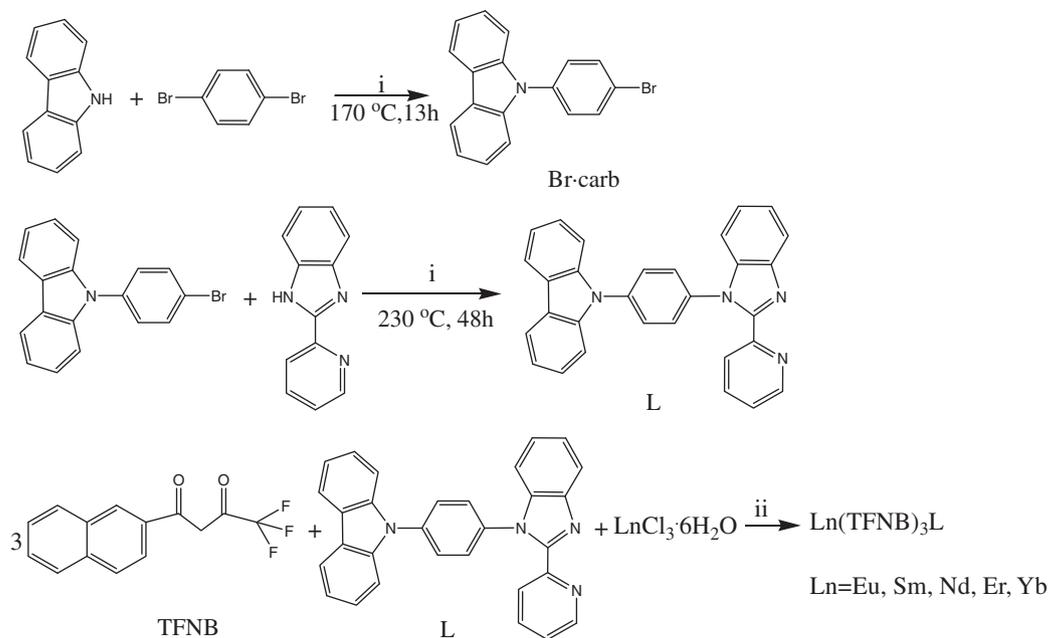
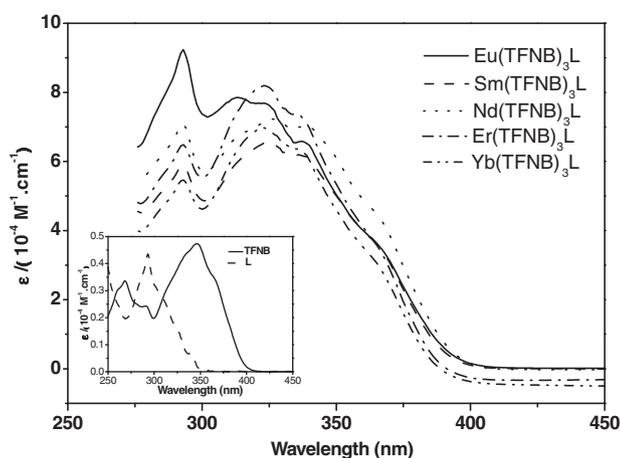**Scheme 1.** Synthetic routes for ligand L and complexes Ln(TFNB)$_3$L (Ln = Eu, Sm, Nd, Er, Yb).

Fig. 1. The UV–Vis absorption spectra of Ln(TFNB)$_3$L (Ln = Eu, Sm, Nd, Er, Yb) and the two organic ligands (TFNB and L, inset) in CH$_2$Cl$_2$ solution at room temperature.

In visible region, the photoluminescence spectra of Eu(TFNB)$_3$L and Sm(TFNB)$_3$L were characterized in CH$_2$Cl$_2$ solution at room temperature using identical experimental settings (slit width, voltage, scan speed) (Fig. 2 and Table 1). While in NIR region, the detection conducted in toluene solution, Nd(TFNB)$_3$L and Yb(TFNB)$_3$L were detected under the same conditions, but the solution of Er(TFNB)$_3$L being detected with four times wide slit as former (Fig. 2 and Table 1). Moreover, all the photoluminescence spectra of the five complexes in solid were obtained (Fig. 3 and Table 1).

3.1.1. Europium and Samarium

Being excited at 385 nm, the Eu(TFNB)$_3$L complex shows sharp emission peaks arising from transitions between $^5D_0 \rightarrow {}^7F_J$ components (J = 0, 1, 2, 3, 4), the lack of residual ligand fluorescence suggests an efficient energy transfer between ligands and central mental ion [23]. As expected, the strongest transition $^5D_0 \rightarrow {}^7F_2$ centered at 613 nm accounts for the typical red color that europium complexes emitting, this transition possesses induced
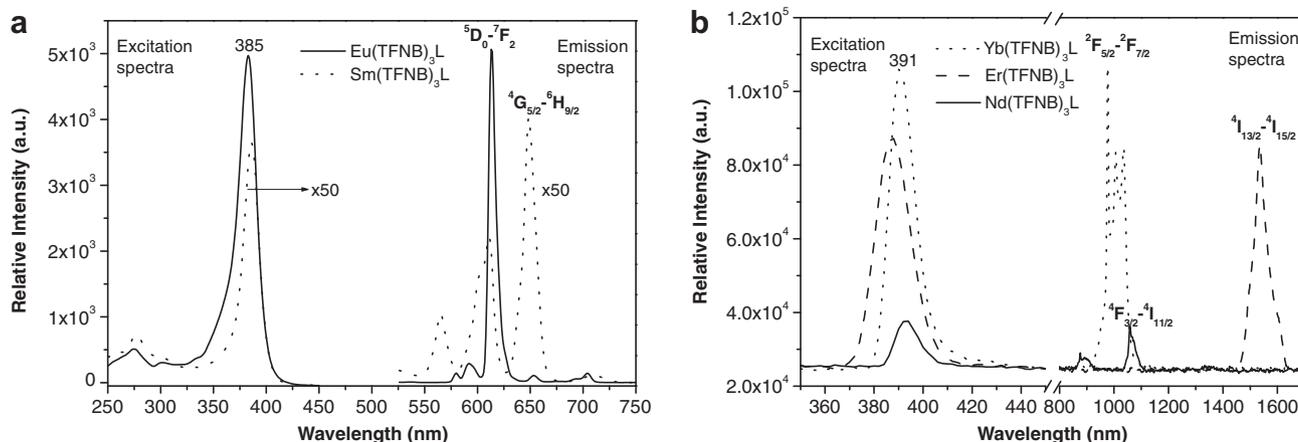

Fig. 2. The excitation and emission spectra of Eu(TFNB)$_3$L, Sm(TFNB)$_3$L (intensity×50) in CH$_2$Cl$_2$ solution (a) and Nd(TFNB)$_3$L, Er(TFNB)$_3$L and Yb(TFNB)$_3$L in toluene solution (b) at room temperature.

electric dipole character and is very sensitive to the coordination environment [29]. The very weak bands at 580, 653, and 704 nm correspond to $^5D_0 \to {}^7F_{0,1,3}$ transition which are forbidden both for magnetic and electric dipole. The intensity of the emission band at 593 nm ($^5D_0 \to {}^7F_1$) is relative strong and independent on the coordination environment due to its magnetic nature.

The excitation spectrum of Sm(TFNB)$_3$L, obtained by monitoring the $^4G_{5/2} \to {}^6H_{9/2}$ transition at 644 nm, is very similar to that of Eu(TFNB)$_3$L complex in CH_2Cl_2 solution due to the same ligands in the two compounds. All the peaks in emission spectra are characteristic ascribed as follows: $^4G_{5/2} \to {}^6H_{5/2}$ (565 nm), $^4G_{5/2} \to {}^6H_{7/2}$ (611 nm), $^4G_{5/2} \to {}^6H_{9/2}$ (649 nm) and $^4G_{5/2} \to {}^6H_{11/2}$ (705 nm). The intensity (I) sequence of the peaks is I($^4G_{5/2} \to {}^6H_{9/2}$) > I($^4G_{5/2} \to {}^6H_{7/2}$) > I($^4G_{5/2} \to {}^6H_{5/2}$) > I($^4G_{5/2} \to {}^6H_{11/2}$). It is obvious that all

the peaks are greatly weaker than the chief emission band of Eu(TFNB)$_3$L.

By exciting the TFNB ligand at the same concentration and same conditions with Eu(TFNB)$_3$L and Sm(TFNB)$_3$L complexes, the emission intensity of Eu(TFNB)$_3$(Pybm), Sm(TFNB)$_3$(Pybm) (Supplementary material Fig. S3) decrease sharply. It is logically to deduce that the introduction of carbazole group benefits to luminescence. We conclude that the L ligand has higher absorption intensity, the more rigid structure and much better shielding of the Ln(III) core towards external quenching than the Pybm ligand.

3.1.2. Neodymium, erbium and ytterbium

The excitation spectra of NIR complexes (Fig. 2b) in toluene solution were obtained by monitoring the characteristic emission of
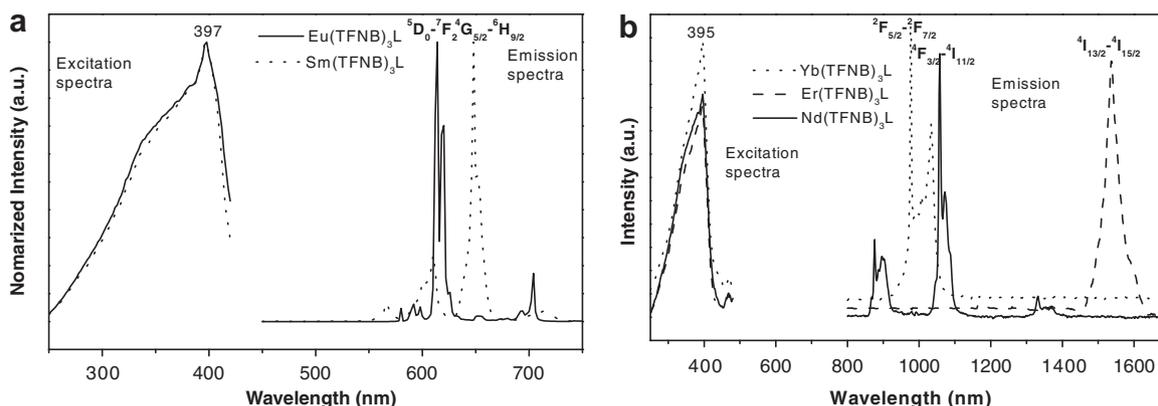

Fig. 3. Excitation and emission spectra of Ln(TFNB)$_3$L (Ln = Eu, Sm (a) and Ln = Nd, Er, Yb (b)) in solid state as powder at room temperature.

Table 1
Photophysical data for all complexes at room temperature in solution and solid state.

Complex	Transition	Medium	Excitation[a] λ_{max} (nm)	Emission[a,b] λ_{max} (nm)	Lifetime[c] τ (µs)	Efficiency Φ (%)
Eu(TFNB)$_3$L	$^5D_0 \to {}^7F_2$	solid	398	614	339.63 $\chi^2 = 1.000$	[d]
		CH_2Cl_2	385	613	601.12 $\chi^2 = 1.000$	14.8[f]
Sm(TFNB)$_3$L	$^4G_{5/2} \to {}^6H_{9/2}$	solid	397	648	22.40 $\chi^2 = 0.996$	[d]
		CH_2Cl_2	387	649	90.49 $\chi^2 = 1.000$	1.4[f]
Nd(TFNB)$_3$L	$^4F_{3/2} \to {}^4I_{11/2}$	solid	395	1058	1.77 $\chi^2 = 0.987$	[d]
		toluene	392	1058	2.02 $\chi^2 = 0.987$	3.6[g]
Er(TFNB)$_3$L	$^4I_{13/2} \to {}^4I_{15/2}$	solid	394	1537	2.44 $\chi^2 = 0.993$	[d]
		toluene	388	1536	2.67 $\chi^2 = 0.994$	[d]
Yb(TFNB)$_3$L	$^2F_{5/2} \to {}^2F_{7/2}$	solid	395	976	13.57 $\chi^2 = 0.993$	[d]
		toluene	391	976	12.76 $\chi^2 = 0.997$	1.4[g]
Eu(TFNB)$_3$(Pybm)	$^5D_0 \to {}^7F_2$	CH_2Cl_2	383[e]	613[e]	[d]	4.1[f]
Sm(TFNB)$_3$(Pybm)	$^4G_{5/2} \to {}^6H_{9/2}$	CH_2Cl_2	385[e]	650[e]	[d]	0.75[f]

[a] Emission maxima from not corrected spectra.
[b] Excited by the highest excitation peak.
[c] Be detected at the maximal excitation and emission bands of the four lanthanide complexes in solid state.
[d] Not detected.
[e] See Supplementary material Fig. S1.
[f] Calculated by $\Phi_s = \Phi_{std}(I_s A_{std} \eta_s^2)/(I_{std} A_s \eta_{std}^2)$ using air-equilibrated aqueous [Ru(bpy)$_3$]$^{2+}$·2Cl$^-$ solution as a standard sample ($\Phi_{std} = 2.8\%$), the error in this method is estimated to be approximately 10% of the measured value.
[g] Calculated by $\Phi_s = \Phi_{std}(I_s A_{std} \eta_s^2)/(I_{std} A_s \eta_{std}^2)$ using air-equilibrated toluene Yb(tta)$_3$phen solution as a standard sample ($\Phi_{std} = 1.1\%$), the error in this method is estimated to be approximately 10% of the measured value. To estimate the uncertainty of the lifetimes of complexes, the goodness-of-fit parameter χ^2 is very important. In principle a $\chi^2 = 1$ is the best-fit for the given data and error bars.

different lanthanide complexes. All of them have only one peak at −390 nm, mainly come from the electronic transfer in β-diketonate ligand, this is a little different from the former two complexes which have two peaks. Under this effective excitation, the three complexes emit characteristic spectra similar to the reported literatures [30–36] both in the sites and shapes which testify the successful sensitisation of the organic ligands (Fig. 2b and Table 1). For the Nd(TFNB)$_3$L, the intensity of the transition at 1058 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) is the strongest and is potentially applicable for laser emission. The 1335 nm band ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) offers the opportunity to develop new materials suitable for optical amplifiers operating at 1.3 μm [30,31]. For the Er(TFNB)$_3$L complex, a large emission band with the maximal emission locating at 1536 nm (Fig. 2b) attributed to the transition from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) of he Er(III) ion was detected. Only emission from the $^4I_{13/2}$ state is observed, although emission from a number of excited states of the Er(III) ion is feasible, suggesting that an efficient nonradiative decay mechanism exists from these states to the $^4I_{15/2}$ state. The full width at half maximum (FWHM) of the

$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for the Er(TFNB)$_3$L complex is 59 nm, which enable a wide-gain bandwidth for optical amplification [32–34]. The Yb(TFNB)$_3$L complex shows the primary emission band locates at 976 nm which is attributed to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. Human tissue is relatively transparent at approximately 1000 nm indicating that in vivo luminescent probes operating at this wavelength (Yb-based emission) could have diagnostic value [35]. The f–f energy level structure of Yb(III) ion is very simple: besides the $^2F_{7/2}$ ground multiplet, there is only the $^2F_{5/2}$ excited state at around 10,000 cm^{-1}. There is no excited state absorption on reducing the effective laser cross-section, no up-conversion, and no absorption in the visible range. So the intense absorption and intense emission of the Yb complexes make them to be attractive for applications in laser operation [36] and ionic crystals and glasses [37].

Measurements performed on all the five complexes in solid as power were given (Fig. 3 and Table 1). From the Fig. 3a we can find that all the excitation spectra are almost fully superposed with the strongest excitation peak at −390 nm, compared to the excitation of the samples in solution. The excitation spectra of the NIR lanthanide
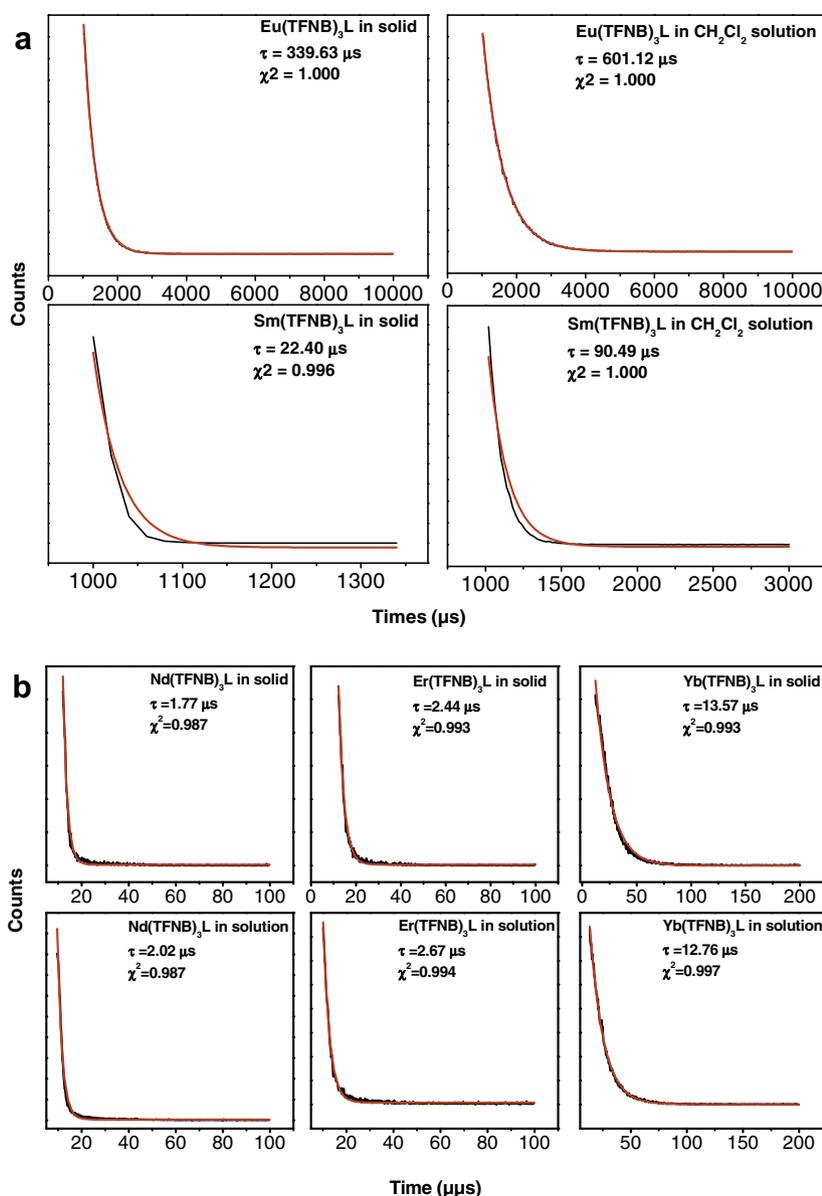

Fig. 4. The emission decay curves of (a): Ln(TFNB)$_3$L (Ln = Eu, Sm) in CH$_2$Cl$_2$ solution and solid state and (b): Ln(TFNB)$_3$L (Ln = Nd, Er, Yb) in toluene solution and solid state, all of them are detected at the maximal excitation and emission wavelength at room temperature.

complexes are similar as Eu(TFNB)$_3$L and Sm(TFNB)$_3$L, so they can be eliminated. The rest figures suggest that all the complexes emit the characteristic emission of Ln(III) ions upon this excitation. A remarkable enhancement in the luminescence intensity relative to that in solution was detected. This shows that the quenching observed in solution, mainly attributable to –OH and –CH vibrations of the solvent molecules, is severely limited in the rigid solid state.

3.2. Calculation of quantum efficiency

The fluorescence quantum yield gives the efficiency of the fluorescence process. It is defined as the ratio of the number of photons emitted to the number of photons absorbed. We used the following equation [38] to calculate the quantum yield of the lanthanide complexes luminescence,

$$\Phi_s = \Phi_{std} \left(\frac{I_s}{I_{std}} \right) \left(\frac{A_{std}}{A_s} \right) \left(\frac{\eta_s}{\eta_{std}} \right)^2$$

where Φ_s is the luminescence quantum yield of the unknown sample, Φ_{std} is the luminescence quantum yield of the standard substance, the η_s and η_{std} terms represent the refractive indices of the corresponding solvents (pure solvents were assumed), I is the wavelength-integrated area of the corrected emission spectrum, and A is the absorbance value at the excitation wavelength. In visible region, we take air-equilibrated aqueous [Ru(bpy)$_3$]$^{2+}$·2Cl$^-$ solution as standard sample (Φ_{std} = 2.8%, η_{std} = 1.3333), lanthanide complexes were dissolved in dichloromethane (η_s = 1.4244). While in NIR region, [Yb(tta)$_3$phen] (tta = thenoyltrifluoroacetonate) in toluene solution was taken as standard [39,40] (Φ_{std} = 1.1% [41], η_{std} = 1.4964), the lanthanide complexes also were dissolved in toluene.

All the data were listed in Table 1, it is obvious that the quantum efficiency of Eu(TFNB)$_3$L is the highest, which agrees well with the longest emission lifetime about several hundreds microsecond level. For lanthanide complexes in general, the intramolecular energy migration efficiency is the most important factor influencing their luminescence output [39]. We can find that the Φ of carbazole group containing complexes Eu(TFNB)$_3$L and Sm(TFNB)$_3$L are higher than the two reference complexes, which proves the effect of carbazole group from another point of view. It is noted that the Φ of Yb(TFNB)$_3$L is higher than the standard complex Yb(tta)$_3$-phen, the trifluorinated substituent exists in both TFNB and tta, so the ligand L is more useful than phen to improve the emission of Yb(III) ion.

The fluorescence lifetime refers to the average time the molecule stays in its excited state before emitting a photon, which is also an important parameter for practical applications of fluorescence such as fluorescence resonance energy transfer. In this study, the luminescence decay curves of all the complexes were obtained from time-resolved luminescence experiments at the maximal excitation and emission wavelengths (Fig. 4) in solid and in solution, respectively, at room temperature. From the figures we can find that the emission decay curves of the five complexes are best fitted by mono-exponential. In most cases, the emission decay curves of excitation level of lanthanide ions are best fitted by mono-exponential suggesting that all lanthanide ions occupy the same average local environment within each sample [42]. If a decay is not single exponential then that implies there are different sites for the ion and that each site has a different lifetime. If you have well defined systems where there may be two or three well defined sites then it is appropriate to use multiple exponentials. The luminescence lifetimes in our study are in line with or a little higher than other recently published results on Vis/NIR-luminescent lanthanide complexes [40,41,43–46].
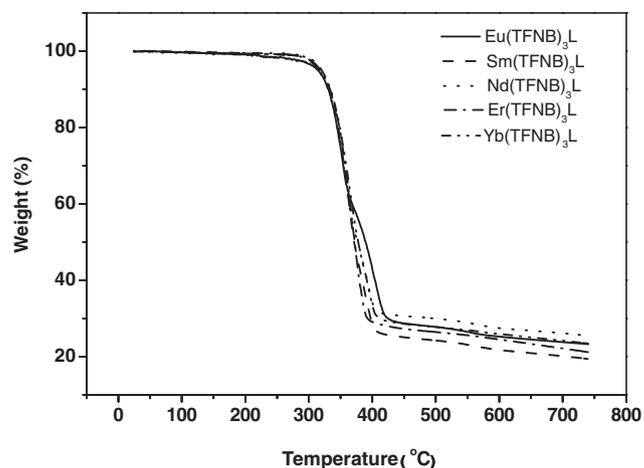

Fig. 5. TGA traces of Ln(TFNB)$_3$L (Ln = Eu, Sm, Nd, Er, Yb) complexes.

3.3. Thermal analysis

In order to investigate the thermal stability of all the lanthanide complexes, TGA was performed on them in a N$_2$ atmosphere, and the traces were described in Fig. 5. The TGA diagrams of all complexes are similar; they begin to decompose at about 280 °C. Specifically, Eu(TFNB)$_3$L starts to lose weight at 294 °C and completed at 430 °C with an overall weight loss of 68.2%, the weight loss of the other four complexes Sm(TFNB)$_3$L, Nd(TFNB)$_3$L, Er(TFNB)$_3$L and Yb(TFNB)$_3$L begin at 284 °C, 282 °C, 294 °C and 294 °C, then finished at 414 °C, 410 °C, 401 °C and 415 °C, with an overall weight loss of 72.0%, 67.3%, 68.8% and 69.5%, respectively. These results indicate that these complexes have good thermal stability and accord with the conclusion reported that a fluorinated substituent in a ligand leads to an improved thermal and oxidative stability and increases the volatility of the complex [47–53]. The improved thermal stability and volatility result in good film-forming ability which facilitates the fabrication of electroluminescent devices.

4. Conclusions

Five lanthanide complexes with β-diketone ligand TFNB and novel synergistic ligand L emit characteristic spectra upon excitation of the ligand absorption bands, this is known as the "antenna effect". The PL properties and quantum efficiency of Eu(TFNB)$_3$L and Sm(TFNB)$_3$L in solution are much better than that of Eu(TFNB)$_3$(Pybm) and Sm(TFNB)$_3$(Pybm) suggesting that the carbazole-containing ligand L can act light-harvesting unit and provide efficient shielding of the Ln(III) core towards external quenching. The fine structure at 1332 nm for the Nd complex and the broadband emission at 1537 nm for the Er complex offer the opportunities to develop new materials suitable for optical amplifiers operating at 1.5 and 1.3 μm and the two telecommunications windows. The emission band near to 1000 nm for Yb complex means that utilization of Yb complex in ionic crystals and glasses is feasible.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.03.067.

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