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# Synthesis, structures and luminescent properties of new heterobimetallic Zn-4f Schiff base complexes

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#### Abstract

A series of new 3d–4f heterobimetallic Schiff base complexes of the general formula  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)_n]$  (Ln = La 1, Nd 2, Gd 3, Er 4 and Yb 5; n = 1 or 2;  $H_2L^2 = N,N'$ -bis(3-methoxy-5-*p*-tolylsalicylidene)ethylene-1,2-diamine) are synthesized and characterized. Complexes 1, 2, 4 and 5 are structurally characterized by X-ray crystallography. The photophysical properties of these complexes are also investigated. At room temperature, complexes 1–5 exhibit similar solution absorption and emission spectra in the UV–Vis region. Furthermore, compounds 2, 4 and 5 exhibit solution emission corresponding to the lanthanide(III) ion in the near-infrared region at room temperature. The triplet state emission of the 3d–4f bimetallic complexes without energy transfer is also determined through the photophysical study of complex 3.

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## 1. Introduction

Lanthanide coordination compounds [1] become an important research topic due to their application as contrast agents for NMR imaging [2,3], catalysts in RNA hydrolysis [4], as active agents in cancer radiotherapy [5], or as luminescent stains for protein labeling and sensitive homogeneous immunoassays [6]. The lanthanide ions are known for their unique optical properties such as line-like emission spectra and long luminescence lifetimes. Although lanthanide ions have intrinsically low absorption cross-sections, their excitation can be done via an antenna chromophore [7–9]. Most of the research attention is placed on the luminescence of terbium

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 $(Tb^{3+})$  and europium  $(Eu^{3+})$  complexes, which emit in the visible region (green for  $Tb^{3+}$  and red for  $Eu^{3+}$ ) and can be used as pure green or red EL devices [10– 13]. Recently, there has been a growing interest in the study of neodymium  $(Nd^{3+})$ , ytterbium  $(Yb^{3+})$  and erbium  $(Er^{3+})$  complexes [7,14–18], which emit in the near-infrared region (NIR). The study of NIR luminescence is of interest because the emission around 900– 1600 nm, which is highly transparent to biological systems and fiber media, is valuable for fluoro-immunoassay and optical telecommunication.

There has been growing interest on dinuclear 3d–4f and 4f–4f' complexes, which exhibit interesting luminescent and magnetic properties [19,20]. Recently, dinuclear 3d–4f Schiff base complexes have been employed as building blocks to form extended structure [21], 2p–3d–4f [22] and 3d–3d'–4f systems [23]. The use of

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transition metal complexes as antenna chromophore for lanthanide ion sensitization has been reported [24]. Zinc(II) Schiff base complexes have been shown to be effective emitters [25]. We are interested in exploring the possibility of using transition metal complexes with Schiff base ligands ( $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ ) as antenna chromophores for lanthanide ion sensitization. We have recently communicated the preparation, structure and luminescent properties of a series of bimetallic Zn-4f Schiff base complexes,  $[Zn(\mu-L^1)Ln(NO_3)_3(H_2O)]$  $[\mathbf{H}_{2}\mathbf{L}^{1} = N, N'$ -bis(3-methoxysalicylidene)ethylene-1,2diamine;  $Ln = Nd^{3+}$ ,  $Er^{3+}$  or  $Yb^{3+}$ ], and shown that the zinc Schiff base could sensitize the emission of lanthanide ions in the NIR region [26]. We are interested in the electronic effect of the substituents of the Schiff base on the photophysical properties of the resulting Zn-4f Schiff base complexes. Herein, we report the synthesis of a new Schiff base ligand, N, N'-bis(3-methoxy-5-p-tolylsalicylidene)ethylene-1,2-diamine ( $H_2L^2$ ), and its Zn-4f heterobimetallic complexes (Scheme 1). The Schiff base and its Zn-4f complexes were fully characterized by elemental analyses, MS and <sup>1</sup>H NMR and their solid-state structures were ascertained by X-ray crystallography. The photophysical properties of these Zn-4f Schiff base complexes were also reported.



#### 2. Experimental

#### 2.1. Chemicals and measurements

Solvents and starting materials were purchased commercially and used without further purification unless otherwise stated. Elemental analyses (C, H and N) were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. Electronic absorption spectra in the UV-Vis region were recorded on a Hewlett-Packard 8453 UV-Visible spectrophotometer, steady-state visible fluorescence and PL excitation spectra on a Photon Technology International (PTI) Alphascan spectrofluorimeter and visible decay spectra on a pico-N<sub>2</sub> laser system (PTI Time Master) with  $\lambda_{exc}$  = 337 nm. Quantum yields of visible emissions were computed according to the literature method [27] using quinine sulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub> as the reference standard ( $\Phi$ =0.55 in air-equilibrated water) [28]. NIR emission was detected by a liquid nitrogen cooled InSb IR detector (EG&G) with a preamplifier and recorded by a lock-in amplifier system. The third harmonics, 355-nm line of a Nd:YAG laser (Quantel Brilliant B), was used as the excitation light source. The emission spectra have been corrected for the spectral response of the instrument. Infrared spectra (KBr pellets) were recorded on a Nicolet Nagna-IR 550 spectrometer and NMR spectra on a JEOL EX270 spectrometer. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to internal deuteriated solvents and then recalculated to SiMe<sub>4</sub> ( $\delta$  0.00). Lowresolution mass spectra (LRMS) were obtained on a Finnigan MAT SSQ-710 spectrometer in the positive FAB mode. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a OSTAR mass spectrometer. Conductivity measurements were carried out with a DDS-11 conductivity bridge for  $10^{-4}$  moldm<sup>-1</sup> solutions either in CH<sub>3</sub>OH or CH<sub>3</sub>CN.



Ln= La, Nd, Gd, Er, Yb

Scheme 1. (a) 4-Methylphenylboronic acid,  $Pd(OAc)_2$ ,  $K_2CO_3$ , D.I. water, 2 days. (b) Ethylenediamine, absolute ethanol, reflux. (c)  $Zn(OAc)_2$ , absolute ethanol, reflux. (d)  $Ln(NO_3)_3 \cdot xH_2O$ ,  $CH_3CN$ , reflux.

## 2.2. Preparations of ligands and zinc(II) Schiff bases

## 2.2.1. Synthesis of 5-(4'-methylphenyl)-3-methoxysalicylaldehyde (A)

When a suspension of 5-bromo-3-methoxysalicylaldehyde (3.061 g and 13.25 mmol), 1.3 equiv. of 4-methylphenylboronic acid (2.341 g and 17.23 mmol), 20 mol% palladium(II) acetate (0.595 g and 2.65 mmol) and 10 equiv. of potassium carbonate (18.313 g and 0.13 mol) was stirred in D.I. water (75 ml) for 2 h, the color of the mixture changed from yellow to brown. The reaction mixture was stirred for another 2 days. HCl (6 N) was then added until pH 7. The reaction mixture was then extracted with  $CH_2Cl_2$  (3×50 ml). The organic layer was evaporated to dryness and the crude product was purified by silica-gel column chromatography using a solvent mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> as the eluent to give a yellow solid of A. Yield: 2.56 g (80%). M.p. 93-95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 11.08 (s, 1H, OH), 9.99 (s, 1H, CHO), 7.46 (d, J=8.4 Hz, 2H, CH-6), 7.37 (d, J=2.0 Hz, 1H, CH-8), 7.32 (d, J=2.0 Hz, 1H, CH-9), 7.27 (d, J=8.4 Hz, 2H, CH-4), 3.99 (s, 3H, OCH<sub>3</sub>) and 2.41 (s, 3H, p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 196.4, 150.6, 148.4, 137.2, 136.7, 133.1, 129.5, 126.4, 122.4, 120.7, 116.8, 56.6 and 21.2. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\lambda_{\text{max}}/\text{nm} \left[\log(\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})\right] 366 (3.34), 257 (4.32).$ FAB MS (+ve mode):  $m/z = 243 [M+1]^+$ . IR (KBr): v = 3445m, 2865m, 1664vs, 1488s, 1400s, 1270s, 1234s, 945s, 820s, 742s, 503m cm<sup>-1</sup>. Anal. Calc. for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> (M=242.27): C, 74.36; H, 5.82. Found: C, 74.67; H, 5.43%.

## 2.2.2. Synthesis of $H_2L^2$

To a stirred solution of 1,2-diaminoethane (0.118 g and 1.96 mmol) in absolute ethanol (30 ml), A (0.955 g and 3.94 mmol) was added. The resulting mixture was refluxed overnight. After cooling to room temperature, the yellow crystalline product precipitated out, and the product was washed with cold ethanol and petroleum ether. The crude product was redissolved in CHCl<sub>3</sub> and evaporated to dryness to furnish  $H_2L^2$  as a yellow solid. Yield: 0.913 g (92%). M.p. 149-151 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 13.74$  (s, 2H, OH), 8.37 (s, 2H, HC=N), 7.41 (d, J=8.0 Hz, 4H, CH-8), 7.21 (d, J=8.0 Hz, 4H, CH-9), 7.11 (d, J=2.0 Hz, 2H, CH-6), 7.04 (d, J=2.0 Hz, 2H, CH-4), 3.98 (s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N-), 3.94 (s, 6H, OCH<sub>3</sub>) and 2.38 (s, 6H, p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>13</sup>C NMR  $(CDCl_3): \delta = 166.7, 148.4, 137.6, 136.5, 131.5, 129.6,$ 129.4, 126.5, 121.2, 118.3, 113.1, 59.4, 56.4 and 21.1. UV-Vis  $(CH_2Cl_2,$ °C):  $\lambda_{max}/nm$ 20 [log(e/  $dm^3 mol^{-1} cm^{-1}$ ] 353 (3.58), 262 (4.61). FAB MS (+ve mode):  $m/z = 509 [M+1]^+$ , 531  $[M+Na]^+$ . IR (KBr): v=3430m, 2917m, 1628vs, 1477s, 1389m, 1281s, 1213m, 1104m, 975m, 819s cm<sup>-1</sup>. Anal. Calc. for  $C_{32}H_{32}N_2O_4$  (*M*=508.61): C, 75.57; H, 6.34; N, 5.51. Found: C, 75.78, H, 6.54; N, 5.56%.

# 2.2.3. Synthesis of $ZnL^2$

To a stirred suspension of  $H_2L^2$  (0.508 g and 1.00 mmol) in absolute ethanol (30 ml), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.242 g and 1.10 mmol) was added and the reaction mixture was heated under reflux overnight. The insoluble yellow precipitate was filtered, washed with ethanol and CHCl<sub>3</sub> and dried under vacuum. ZnL<sup>2</sup> was isolated as a yellow solid. Yield: 0.442 g (77%). M.p. >300 °C. <sup>1</sup>H NMR (DMSO-D<sub>6</sub>):  $\delta$  = 8.54 (s, 2H, *H*C=N), 7.51 (d, J=8.0 Hz, 4H, CH-8), 7.20 (d, J=8.0 Hz, 4H, CH-9), 7.12 (d, J=2.0 Hz, 2H, CH-6), 7.09 (d, J=2.0 Hz, 2H, CH-4), 3.83 (s, 6H, OCH<sub>3</sub>), 3.32 (s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N-) and 2.31 (s, 6H, p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). UV-Vis (DMSO, 20 °C):  $\lambda_{max}/nm [log(\epsilon/dm^3 mol^{-1} cm^{-1})] 383$ (3.84), 310 (4.52), 279 (4.66). FAB MS (+ve mode): m/  $z = 593 [M + Na]^+$ . IR (KBr): v = 3415m, 2917m, 1636vs, 1455s, 1395m, 1322m, 1275m, 1203m, 1120m, 975m,  $820m \text{ cm}^{-1}$ .

# 2.3. Synthesis of $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)]$ complexes

Heterobimetallic complexes of the general formula  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)_n]$  (Ln = La 1, Nd 2, Gd 3, Er 4 or Yb 5; *n* = 1 or 2) were prepared by the same method. A typical procedure is given for  $[Zn(\mu-L^2)La(NO_3)_3 (H_2O)_2]$ .

# 2.3.1. Synthesis of $[Zn(\mu-L^2)La(NO_3)_3(H_2O)_2]$ (1)

When  $La(NO_3)_3 \cdot 6H_2O$  (0.055 g and 0.13 mmol) was added to a suspension of  $\mathbf{ZnL}^2$  (0.070 g and 0.12 mmol) in CH<sub>3</sub>CN (30 ml) at refluxing temperature, a clear pale yellow color was observed. The solution was refluxed for 12 h, cooled to room temperature and filtered. The filtrate, when allowed to evaporate slowly at room temperature, gave yellow crystals of 1 in about a week. Yield: 0.067 g (62%). M.p. >300 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta = 8.59$  (s, 2H, HC=N), 7.56 (d, J=8.0 Hz, 4H, CH-8), 7.42 (d, J=2.0 Hz, 2H, CH-6), 7.34 (d, J=2.0 Hz, 2H, CH-4), 7.28 (d, J=8.0 Hz, 4H, CH-9), 4.13 (s, 6H, OCH<sub>3</sub>), 3.96 (s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N-) and 2.37 (s, 6H, p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). UV–Vis (CH<sub>3</sub>CN, 20 °C):  $\lambda_{max}/nm$  $[\log(\epsilon/dm^3 mol^{-1} cm^{-1})]$  362 (3.90), 270 (4.87). Fluorescence (CH<sub>3</sub>CN, 20 °C):  $\lambda_{exc}/nm$  365, 300;  $\lambda_{em}/nm$  480. FAB MS (+ve mode):  $m/z = 832 [Zn(\mu-L)La(NO_3)_2]^+$  for <sup>64</sup>Zn and <sup>138</sup>La. IR (KBr): v = 3424m, 1643s, 1459s, 1384vs, 1264m, 1208m, 1083m, 964m, 820m cm<sup>-1</sup>. Anal. Calc. for  $C_{32}H_{30}N_5O_{13}ZnLa \cdot 2H_2O \cdot CH_3CN$  (M= 973.99): C, 41.92; H, 3.83; N, 8.63. Found: C, 42.32; H, 3.68; N, 8.41%.

# 2.3.2. Synthesis of $[Zn(\mu - L^2)Nd(NO_3)_3(H_2O)_2]$ (2)

Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.053 g and 0.12 mmol) and ZnL<sup>2</sup> (0.062 g and 0.11 mmol) were used. Yellow crystals of **2** were obtained. Yield 0.087 g (88%). M.p. >300 °C. UV– Vis (CH<sub>3</sub>CN, 20 °C):  $\lambda_{max}/nm [log(\epsilon/dm^3 mol^{-1} cm^{-1})]$ 362 (3.83), 271 (4.81). Fluorescence (CH<sub>3</sub>CN, 20 °C):  $λ_{exc}$ /nm 372, 305;  $λ_{em}$ /nm 875, 480. FAB MS (+ve mode): m/z = 838 [Zn(μ-L)Nd(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> for <sup>64</sup>Zn and <sup>144</sup>Nd. IR (KBr): v = 3410m, 2928m, 1680vs, 1461s, 1384vs, 1260s, 1193m, 1104m, 1032m, 959m, 814s, 778m, 509m cm<sup>-1</sup>. *Anal.* Calc. for C<sub>32</sub>H<sub>30</sub>N<sub>5</sub>O<sub>13</sub>ZnN-d·2H<sub>2</sub>O·CH<sub>3</sub>CN (M = 979.32): C, 41.69; H, 3.81; N, 8.58. Found: C, 41.83; H, 3.81; N, 8.39%.

# 2.3.3. Synthesis of $[Zn(\mu - L^2)Gd(NO_3)_3(H_2O)]$ (3)

Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.055 g and 0.12 mmol) and **ZnL<sup>2</sup>** (0.061 g and 0.11 mmol) were used. Yellow crystals of **3** were obtained. Yield: 0.060 g (60%). M.p. >300 °C. UV– Vis (CH<sub>3</sub>CN, 20 °C):  $\lambda_{max}/nm$  [log( $\epsilon/dm^3 mol^{-1}cm^{-1}$ )]: 362 (3.99), 269 (4.91). Fluorescence (CH<sub>3</sub>CN, 20 °C):  $\lambda_{exc}/nm$  365, 295;  $\lambda_{em}/nm$  480. FAB MS (+ve mode): m/z = 851 [Zn( $\mu$ -L)Gd(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> for <sup>64</sup>Zn and <sup>157</sup>Gd. IR (KBr): v = 3425m, 1363m, 1638s, 1462s, 1384vs, 1265s, 1203m, 1088m, 969m, 809m cm<sup>-1</sup>. *Anal.* Calc. for C<sub>32</sub>H<sub>30</sub>N<sub>5</sub>O<sub>13</sub>ZnGd·H<sub>2</sub>O·CH<sub>3</sub>CN (M = 974.31): C, 41.19; H, 3.63; N, 8.62. Found: C, 41.52; H, 3.69; N, 8.53%.

## 2.3.4. Synthesis of $[Zn(\mu - L^2)Er(NO_3)_3(H_2O)]$ (4)

Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.054 g and 0.12 mmol) and ZnL<sup>2</sup> (0.062 g and 0.11 mmol) were used. Yellow crystals of **4** were obtained. Yield: 0.060 g (59%). M.p. >300 °C. UV–Vis (CH<sub>3</sub>CN, 20 °C):  $\lambda_{max}$ /nm [log( $\epsilon/$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)] 360 (3.77), 267 (4.76). Fluorescence (CH<sub>3</sub>CN, 20 °C):  $\lambda_{exc}$ /nm 365, 300;  $\lambda_{em}$ /nm 1515, 480. FAB MS (+ve mode): m/z = 861 [Zn( $\mu$ -L)Er(NO<sub>3</sub>)2]<sup>+</sup> for <sup>64</sup>Zn and <sup>167</sup>Er. IR (KBr): v = 3410m, 2948m, 1633vs,

Table 1

Crystal data and	1 structure	refinement
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1467s, 1384vs, 1301s, 1265s, 1203m, 1187m, 1094m, 959m, 814m, 773m cm<sup>-1</sup>. *Anal.* Calc. for  $C_{32}H_{30}N_5O_{13}Z$ -nEr·H<sub>2</sub>O·CH<sub>3</sub>CN (*M*=984.32): C, 41.48; H, 3.59; N, 8.54. Found: C, 41.88; H, 3.70; N, 8.25%.

### 2.3.5. Synthesis of $[Zn(\mu-L^2)Yb(NO_3)_3(H_2O)]$ (5)

Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.063 g and 0.12 mmol) and ZnL<sup>2</sup> (0.072 g and 0.13 mmol) were used to afford yellow crystals of **5**. Yield: 0.070 g (58%). M.p. >300 °C. UV–Vis (CH<sub>3</sub>CN, 20 °C):  $\lambda_{max}$ /nm [log( $\epsilon$ /dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>)] 366 (3.75), 267 (4.73). Fluorescence (CH<sub>3</sub>CN, 20 °C):  $\lambda_{exc}$ / nm 370, 300;  $\lambda_{em}$ /nm 976, 480. FAB MS (+ve mode): *m*/*z* = 867 [Zn( $\mu$ -L)Yb(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> for <sup>64</sup>Zn and <sup>173</sup>Yb. IR (KBr): *v* = 3430m, 1632s, 1472s, 1384vs, 1306s, 1270s, 1203m, 1198m, 1099m, 1037m, 959m, 814m, 778m cm<sup>-1</sup>. *Anal.* Calc. for C<sub>32</sub>H<sub>30</sub>N<sub>5</sub>O<sub>13</sub>ZnYb·H<sub>2</sub>O·CH<sub>3</sub>CN (*M*=990.10): C, 41.23; H, 3.57; N, 8.49. Found: C, 41.22; H, 3.69; N, 8.33%.

#### 2.4. X-ray crystallography

Pertinent crystallographic data and other experimental details are summarized in Table 1. Crystals of **A** and  $H_2L^2$  suitable for X-ray diffraction studies were grown by slow diffusion of diethylether into a solution of the respective compound in chloroform; whereas crystals of **1**, **2**, **4** and **5** were grown by slow evaporation of a solution of the respective compound in acetonitrile. Intensity data were collected at 293 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =

	Α	$H_2L^2$	1	2	4	5
Empirical formula	C <sub>15</sub> H <sub>14</sub> O <sub>3</sub>	C32H32N2O4	C34H39N6O16ZnLa	C34H37N6O15ZnNd	C <sub>32</sub> H <sub>32</sub> N <sub>5</sub> O <sub>14</sub> ZnEr	C <sub>32</sub> H <sub>32</sub> N <sub>5</sub> O <sub>14</sub> ZnYb
Molecular mass	242.26	508.60	991.99	979.31	943.26	949.04
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	tetragonal	tetragonal
Space group	Pbca	P/n	$P2_1/c$	$P2_1/n$	I4 <sub>1</sub> cd	$I4_1cd$
a (Å)	12.8138(14)	17.4620(12)	8.0586(7)	14.4326(9)	32.649(2)	32.6840(11)
b (Å)	7.3384(8)	7.1051(5)	17.7617(15)	17.2692(12)	32.649(2)	32.6840(11)
c (Å)	26.965(3)	21.5908(14)	28.170(2)	16.1154(11)	14.697(13)	14.6534(10)
α (°)	90	90	90	90	90	90
β (°)	90	95.6590(10)	91.764(2)	99.1480(10)	90	90
γ (°)	90	90	90	90	90	90
$U(\text{\AA}^3)$	2535.6(5)	2665.7(3)	4030.2(6)	3965.5(5)	15666(2)	15653.4(13)
<i>F</i> (000)	1024	1080	2000	1972	7504	7504
Ζ	8	4	4	4	16	16
$D_{\rm calc} ({\rm gcm^{-3}})$	1.269	1.267	1.635	1.640	1.600	1.607
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.088	0.084	1.718	1.975	2.809	3.056
$\theta$ Range (°)	1.51-27.51	1.43-25.01	1.36-28.28	1.74-28.33	1.25-25.01	1. 25-28.31
Reflections collected	13846	12775	23857	23662	30971	45996
Unique reflections	2891	7550	9400	9156	6268	8253
R <sub>int</sub>	0.0370	0.0214	0.0615	0.0666	0.1163	0.0794
Observed reflections	1616	5486	5611	4898	3445	5130
R1, wR2 $(I > 2\sigma(I))^{a}$	0.0573, 0.1389	0.0476, 0.1341	0.0662, 0.1587	0.0482, 0.1017	0.0479, 0.0896	0.0503, 0.1142
R1, wR2 (all data) <sup>a</sup>	0.1045, 0.1675	0.0712, 0.1557	0.1240, 0.1870	0.1207, 0.1254	0.1027, 0.0996	0.1078, 0.1396
Goodness-of-fit on $F^2$	0.971	1.033	1.059	0.988	0.920	1.033

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

0.71073 Å). The collected frames were processed with the software SAINT [29] and an absorption correction was applied (SADABS) [30] to the collected reflections. The structures of all compounds were solved by direct methods (SHELXTL) [31] and refined against  $F^2$  by full matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically for these structures. Hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms.

#### 3. Results and discussion

## 3.1. Synthesis and structural characterization

5-(4'-Methylphenyl)-3-methoxysalicylaldehyde (A) was prepared in good yield (80%) via the modified Suzuki's coupling reaction [32] between 5-bromo-3-methoxysalicylaldehyde and 4-methylphenylboronic acid. The phenyl analog has been synthesized recently via a similar procedure [33]. The <sup>1</sup>H NMR spectrum of A in CDCl<sub>3</sub> exhibited a sharp singlet at  $\delta = 11.08$  for the O-H proton. The chemical shift is typical of the resonance-assisted hydrogen bonded (RAHB) proton of the type  $O-H \cdots O = C$  [34]. This is supported by the solid-state structure of A (Fig. 1), which shows the presence of intramolecular hydrogen bonding between the O-H group and oxygen of the formyl group [2.661(2) Å]. The Schiff base  $H_2L^2$  was synthesized in excellent yield (92%) by the condensation reaction between ethylene diamine and A in a 1:2 mole ratio. The <sup>1</sup>H NMR spectrum of  $H_2L^2$  in CDCl<sub>3</sub> showed a temperature-dependent resonance for the O-H protons. At -50 °C, the O-H protons appear as a sharp singlet at  $\delta = 14.00$ , which is typical for RAHB proton of  $O-H \cdots N = C$  [34,35]. The resonance starts to broaden and shift upfield as the temperature increases. It appears as a broad singlet at  $\delta = 13.74$  ( $v_{1/2} = 21.6$  Hz) and 13.58 ( $v_{1/2} = 43.2$  Hz) at



Fig. 1. Perspective drawing of A with 25% probability thermal ellipsoids.

0 °C and room temperature, respectively. The resonance disappears completely at 40 °C. This suggests that both resonance forms (Eq. (1)) are significant at room temperature. The crystal structure of  $H_2L^2$  depicted in Fig. 2 revealed the presence of intramolecular hydrogen bonding between the O-H group and the imino N of the Schiff base with the N···O distances of 2.5947(16) and 2.5997(16) Å and are similar to those reported for analogous Schiff bases [36]. The intramolecular H-bonds in salicyl imines (Eq. (2)) have been thoroughly characterized as RAHB protons on the basis of crystal, NMR, IR and computational data [34-36]. For the RAHB protons, the H-bond is strengthened by  $\pi$ -delocalization. The  $N{\cdots}O$ distances in these compounds  $(2.65 > d(N \cdots O) > 2.48 \text{ Å})$  are significantly shorter than those in normal H-bonds. In addition, the <sup>1</sup>H NMR signals of the strongly H-bonded protons are shifted highly downfield (13 <  $\delta_{\rm NH}$  < 18 ppm).



The zinc Schiff base complex,  $\mathbf{ZnL}^2$ , was easily prepared in 77% yield by reacting  $\mathbf{H}_2\mathbf{L}^2$  with  $Zn(OAc)_2$  in a 1:1 mole ratio in refluxing absolute ethanol for 12 h.  $\mathbf{ZnL}^2$  showed very poor solubility in refluxing CH<sub>3</sub>CN, but when  $Ln(NO_3)_3$  was added, it dissolved completely to give a clear solution, which upon work-up, gave heterobimetallic complexes of the general formula  $[Zn(\mu-\mathbf{L}^2)Ln(NO_3)_3(\mathbf{H}_2\mathbf{O})_n]$  (Ln=La 1, Nd 2, Gd 3, Er 4 or Yb 5; *n*=1 or 2) in 58–88% yield (Scheme 1). The complexes were easily crystallized out by slow evaporation of their solutions in acetonitrile. Elemental analyses and FAB MS data also supported the formulation.

The structures of 1, 2, 4 and 5 were ascertained by X-ray crystallography. Selected bond distances of the  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)_n]$  complexes are summarized in Table 2. In all cases, the crystal structures of neutral  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)_n]$  complexes (Ln=La, Nd, Er





Fig. 2. Perspective drawing of  $H_2L^2$  with 25% probability thermal ellipsoids.

Table 2 Selected bond distances (Å) of Zn–Ln complexes

	1 (Ln = La)	<b>2</b> (Ln = Nd)	4 (Ln = Er)	<b>5</b> (Ln=Yb)
Zn–N(1)	2.021(6)	2.020(5)	2.023(10)	2.033(8)
Zn-N(2)	2.009(6)	2.016(4)	2.058(10)	1.987(8)
Average Zn-N	2.015	2.018	2.041	2.010
Zn-O(2)	1.993(4)	2.010(3)	2.055(8)	2.014(7)
Zn-O(4)	2.018(5)	1.989(4)	2.016(8)	2.029(7)
Average Zn-O	2.001	2.000	2.036	2.022
Ln-O(1)	2.726(5)	2.711(4)	2.559(7)	2.499(6)
Ln–O(2)	2.514(5)	2.382(3)	2.284(8)	2.220(7)
Ln-O(3)	2.715(5)	2.721(4)	2.545(7)	2.519(6)
Ln–O(4)	2.471(4)	2.378(3)	2.234(8)	2.249(7)
Average Ln–O	2.607	2.548	2.406	2.372
$Zn\cdots Ln$	3.583	3.543	3.453	3.429

and Yb) revealed that the relatively soft transition metal ion, Zn(II), is located in the inner  $N_2O_2$  cavity and the hard lanthanide(III) ion in the outer O<sub>4</sub> cavity of the Schiff base ligand. The zinc(II) ion is five-coordinate and adopts a distorted square pyramidal geometry, with the imino nitrogen atoms N(1) and N(2), and the phenolic oxygen atoms O(2) and O(3) forming the square base, while the aqua oxygen (Ln=La and Nd) or the monodentate nitrato oxygen (Ln=Er and Yb) occupies the axial position. Depending on the size of the Ln(III) ions, their coordination number varies from 9 (Ln=Er, Yb), 10 (Ln=Nd) to 11 (Ln=La). The Ln(III) ions are surrounded by four O atoms from the Schiff base, two from the bridging phenolic groups and two from the methoxy groups, with the remaining coordination sites by O atoms from aqua and nitrato ligands. For 1, the remaining coordination sites are occupied by seven O atoms, six from three bidentate nitrato ligands and one from the aqua oxygen (Fig. 3); for 2, by six O atoms, four from two bidentate nitrato ligands, one from monodentate nitrato ligand and one from the aqua oxygen (Fig. 4); and for 4 (Fig. 5) and 5 (Fig. 6), by five O atoms, four from two bidenate nitrato ligands and one from the aqua oxygen. The results illustrate that as the ionic size decreases, the lanthanide

ion lowers its coordination number to relieve the congestion by converting one of its bidentate nitrato ligand to a less steric demanding monodentate nitrato ligand. Eventually, the coordination environment of the lanthanide is so congested that it has to transfer the nitrato ligand to the Zn(II) ion. The distance between Zn and Ln ions is 3.429–3.583 Å and is too long for any significant interaction. The average Zn-N and Zn-O bond lengths are in the range of 2.010-2.041 and 2.000-2.036 Å, respectively, which are comparable to those of other similar Zn(II) Schiff base complexes [37,38]. The average Ln–O bond length lies within 2.372–2.607 Å, which is comparable to those of other reported heterobimetallic Zn-4f Schiff base complexes [38]. The decrease in Ln–O distance in the series  $La^{3+}>Nd^{3+}>Er^{3+}>Yb^{3+}$  is in agreement with the lanthanide contraction and reflects a decrease in ionic radii: 1.17>1.12>1.03>1.01 Å [39].

#### 3.2. Solution behavior

Conductivity measurements showed that complexes 1– 5 behaved as electrolytes in methanol and nonelectrolytes in acetonitrile. This indicates that the



Fig. 3. Perspective drawing of  $[Zn(\mu-L^2)La(NO_3)_3(H_2O)_2]$  (1) with 25% probability thermal ellipsoids.



Fig. 4. Perspective drawing of  $[Zn(\mu-L^2)Nd(NO_3)_3(H_2O)_2]$  (2) with 25% probability thermal ellipsoids.



Fig. 5. Perspective drawing of  $[Zn(\mu-L^2)Er(NO_3)_3(H_2O)]$  (4) with 25% probability thermal ellipsoids.

complexes dissociated one or more of their coordinated nitrates to form cations in methanol but remained neutral and undissociated in acetonitrile. Similar observation has been reported for  $[LnL'(NO_3)_3]$  complexes, where L' is a neutral tripodal ligand bearing benzimidazole and pyridine groups [40]. <sup>1</sup>H NMR study showed that the complexes exist as a mixture of species in methanol solution. For instance, the Zn–La complex 1 exhibited more than one set of proton signals for the Schiff base ligand whose relative intensities vary with temperature. This suggests that there are two or more species present in methanol solution. This is further supported by the electrospray ionization (ESI) mass spectral data. The ESI highresolution mass spectra (positive mode) of complexes 1– **5** in methanol displayed similar patterns and exhibited mass peaks at m/z corresponding to  $[(\mathbf{ZnL}^2)_2 \text{Ln}(\text{NO}_3)_2]^+$ ,  $[(\mathbf{ZnL}^2)\text{Ln}(\text{NO}_3)_2]^+$ ,  $[(\mathbf{ZnL}^2)_2 \text{Ln}(\text{NO}_3)_2]^+$ ,  $[(\mathbf{ZnL}^2)_2 \text{Ln}]^{3+}$ and  $[(\mathbf{ZnL}^2) + \text{H}]^+$ . For instance, complex 1 displayed mass peaks at m/z 1407.1763  $[(\mathbf{ZnL}^2)_2 \text{La}(\text{NO}_3)_2]^+$ , 833.0401  $[(\mathbf{ZnL}^2)\text{La}(\text{NO}_3)_2]^+$ , 672.5905  $[(\mathbf{ZnL}^2)_2 \text{La}(\text{NO}_3)]^{2+}$ , 427.7329  $[(\mathbf{ZnL}^2)_2 \text{La}]^{3+}$  and 571.1547  $[(\mathbf{ZnL}^2) + \text{H}]^+$ , which deviate less than 10 ppm of the theoretical peak values of 1407.1789 (C<sub>64</sub>H<sub>60</sub>N<sub>6</sub>O<sub>14</sub>Zn<sub>2</sub>La), 833.0316 (C<sub>32</sub>H<sub>30</sub>N<sub>4</sub>O<sub>10</sub>ZnLa), 672.5949 (one-half of



Fig. 6. Perspective drawing of  $[Zn(\mu-L^2)Yb(NO_3)_3(H_2O)]$  (5) with 25% probability thermal ellipsoids.

C<sub>64</sub>H<sub>60</sub>N<sub>5</sub>O<sub>11</sub>Zn<sub>2</sub>La), 427.7338 (one-third of C<sub>64</sub>H<sub>60</sub>N<sub>4</sub>O<sub>8</sub>Zn<sub>2</sub>La) and 571.1569 (C<sub>32</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub>Zn), respectively. The observed isotopic distribution patterns of the  $[(ZnL^2)_2La(NO_3)_2]^+$ ,  $[(ZnL^2)_2La(NO_3)_2]^+$ ,  $[(ZnL^2)_2La^3^+$  and  $[(ZnL^2) + H]^+$  peaks match well with the expected theoretical signals. Furthermore, MS–MS studies on the above ions showed that  $[(ZnL^2)_2La(NO_3)]^{2+}$ ,  $[(ZnL^2)_2La]^{3+}$  and  $[(ZnL^2) + H]^+$  exist independently in solution and are not fragmented ions of  $[(ZnL^2)_2La(NO_3)_2]^+$ . This suggests that when dissolved in methanol,  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)_n]$  gave a complex mixture containing cations of  $[(ZnL^2)_2$ 

Ln(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>,  $[(ZnL^2)Ln(NO_3)_2]^+$ ,  $[(ZnL^2)_2Ln(NO_3)]^{2+}$ and  $[(ZnL^2)_2Ln]^{3+}$  (Chart 1) and neutral species of  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)_n]$  and  $ZnL^2$ . The existence of the  $[(ZnL^2)_2Ln(NO_3)_2]^+$  species was further supported by the characterization and X-ray crystal structure of the phenylene bridged Schiff base complex  $[(ZnL^3)_2$ Nd(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][NO<sub>3</sub>], isolated from a methanol solution of  $[Zn(\mu-L^3)Nd(NO_3)_3(EtOH)]$  [41]. For the related  $[Zn(\mu-L^1)Pr(NO_3)_3(H_2O)]$  complex, it dissociated into a mixture containing at least  $[Zn(\mu-L^1)Pr(NO_3)_3(H_2O)]$ and  $ZnL^1$  when dissolved in DMSO and remained undissociated in acetone [20f].



However, complexes 1–5 only displayed one set of resonances attributed to the Schiff base ligand in their <sup>1</sup>H NMR spectra when dissolved in CD<sub>3</sub>CN. For instance, complex 1 in CD<sub>3</sub>CN displayed a temperature-independent <sup>1</sup>H NMR spectrum, which only exhibited a set of proton resonances attributed to the Schiff base ligand at  $\delta = 8.58$  (s, 2H, HC=N), 7.56 (d, J=8.0 Hz, 4H, CH-4), 7.42 (d, J=2.0 Hz, 2H, CH-6), 7.34 (d, J=2.0 Hz, 2H, CH-4), 7.28 (d, J=8.0 Hz, 4H, CH-9), 4.13 (s, 6H, OCH<sub>3</sub>), 3.97 (s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N-) and 2.37 (s, 6H, p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). The relative intensity and chemical shifts of the resonances did not change and no other new signal was observed over the temperature range of -40 to 60 °C. This indicates that there is only one species present in acetonitrile solution and the solution structure of the complex in acetonitrile is similar to its solid-state structure. The <sup>1</sup>H NMR data of  $H_2L^2$ ,  $ZnL^2$ , 1, 2, 4 and 5 are given in Table 3. The assignment of the chemical shifts is based on the relative intensity and coupling constants of the signals as well as by comparison with the related  $[Zn(\mu-L^2)Ln(NO_3)_3(H_2O)]$ (Ln = La and Pr) complex [20b]. Attempts to obtain a <sup>1</sup>H NMR spectrum for **3** were unsuccessful.

#### 3.3. Luminescent properties

At room temperature, complexes  $[Zn(\mu-L^2)Ln (NO_3)_3(H_2O)_n]$  exhibited similar solution absorption and emission spectra in the UV–Vis region. Their photo-

physical properties are summarized in Table 4. The absorptions between 267 and 366 nm can be assigned to  $\pi \rightarrow \pi^*$  transitions of the Schiff base ligand. The visible emission of compounds 1–5, with lifetimes  $(\tau)$  ranging from 1.9 to 4.6 ns and quantum yields ( $\Phi_{\rm em}$ ) of 0.38- $2.17 \times 10^{-3}$  for 1 and 3, and  $<10^{-5}$  for 2, 4 and 5, can be assigned to the intra-ligand emission. The absorption, emission and excitation (monitored at 480 nm) spectra of 1 (Fig. 7) are slightly red shifted as compared to the unsubstituted corresponding  $[Zn(\mu-L^1)Ln(NO_3)_3 (H_2O)_n$  complexes [26]. This shows that we can tune the photophysical properties of the Schiff base complexes by changing the electronic properties of the substituents. By extending the conjugation, both the absorption and emission of the complexes are red shifted. The photoluminescence excitation (PLE) spectrum reflects where the maximum contribution of the photoluminescence (PL) comes from. Under steady-state conditions, excited electrons relax from the highest excited states to the lowest excited states before they recombine radiatively or nonradiatively. In this case, the PLE spectrum showed exactly this situation; the maximum PL contribution came from the lowest excited bands with decreasing contribution from the higher energy band. Thus, although the absorption bands coincide with the excitation bands, as they should, the relative intensities of the energy bands by the two techniques can reveal the origin of the physical process measured. The emission spectra and decay time measurements for Gd<sup>3+</sup> complexes

Table 3

<sup>1</sup>H NMR data (chemical shifts in ppm versus SiMe<sub>4</sub>) in CD<sub>3</sub>CN with intensity ratios given in parentheses<sup>a</sup>

	$CH_2$	HC==N	CH-4 <sup>b</sup>	CH-6 <sup>b</sup>	CH-8 <sup>b</sup>	С <i>Н</i> -9 <sup>b</sup>	OCH <sub>3</sub>	$CH_3$	OH
$H_2L^2$	3.98 (4)	8.37 (2)	7.04 (2)	7.11 (2)	7.41 (4)	7.21 (4)	3.94 (6)	2.38 (6)	13.74 (2)
ZnL <sup>2c</sup>	3.32 (4)	8.54 (2)	7.09 (2)	7.12 (4)	7.51 (4)	7.20 (4)	3.83 (6)	2.31 (6)	
1	3.96 (4)	8.59 (2)	7.34 (2)	7.42 (2)	7.56 (4)	7.28 (4)	4.13 (6)	2.37 (6)	
2	7.53 (4)	11.21 (2)	0.38 (2)	7.99 (2)	6.46 (4)	5.93 (4)	-5.28 (6)	1.84 (6)	
4	59.94 (4)	55.32 (2)	6.20 (2)	13.29 (2)	19.79 (4)	13.23 (4)	-10.23 (6)	5.44 (6)	
5	47.91 (4)	45.26 (2)	2.80 (2)	13.15 (2)	17.30 (4)	12.01 (4)	-7.95 (6)	5.43 (6)	

<sup>a</sup> We were unable to obtain a <sup>1</sup>H NMR spectrum for **3**.

<sup>b</sup> Please refer to Scheme 1 for the numbering of the phenyl protons.

<sup>c</sup> The spectrum was recorded in DMSO-D<sub>6</sub>.

Table 4	
Photophysical dat	a of compounds 1–5 in CH <sub>3</sub> CN

	Absorption, $\lambda_{\text{max}}/\text{nm} \left[\log(e/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})\right]$	Excitation, $\lambda_{exc}/nm$	Emission, $\lambda_{\rm em}/\rm{nm}~(\tau/\rm{ns},~\Phi_{\rm em}\times10^3)$
1	362 (3.90), 270 (4.87)	365, 300	480 (1.9, 2.17)
2	362 (3.83), 271 (4.81)	372, 305	480 (4.6) <sup>a</sup> , 875 (1305) <sup>b</sup>
3	362 (3.99), 269 (4.91)	365, 295	480 (1.9, 0.38) <sup>c</sup>
4	360 (3.77), 267 (4.76)	365, 300	480 (4.3) <sup>a</sup> , 1515 <sup>b,d</sup>
5	366 (3.75), 267 (4.73)	370, 300	480 (4.3) <sup>a</sup> , 976 (14590) <sup>b</sup>

<sup>a</sup>  $\Phi_{\rm em} < 10^{-5}$ .

<sup>b</sup> Due to the limitations of our instrument, we were unable to determine the quantum yield of the NIR luminescence of 2, 4 and 5.

<sup>c</sup> The lifetime of **3** in CH<sub>3</sub>CN at 77 K was 2.23 ns (monitored at 480 nm), 2.90 ns (fluorescence; monitored at 515 nm) and 6.10 ms (phosphorescence; monitored at 515 nm).

<sup>d</sup> Due to the limitations of our instrument, we were unable to measure the lifetime of the NIR luminescence of 4.



Fig. 7. Absorption (——), excitation ( $\cdots$ , monitored at 480 nm) and emission (–––) spectra of 1 in CH<sub>3</sub>CN at room temperature.

allowed the identification of the lowest ligand triplet state in the complexes [42-45]. This is possible because the metal centered (MC) electronic levels of  $Gd^{3+}$  are known to be located at  $31\,000$  cm<sup>-1</sup>, typically well above the ligand-centered electronic levels of aromatic ligands [46]. Therefore, ligand-to-metal energy transfer and the consequent MC luminescence cannot be observed. Fig. 8 shows the variable temperature emission spectra of 3 in acetonitrile. Time-resolved spectra of 3 showed that the lifetimes at 480 and 515 nm were both 1.9 ns at room temperature, indicating that the emissions came from the same state and corresponded to a ligand-centered (LC) short-lived fluorescence, and at 77 K, on top of the weak LC fluorescence ( $\tau = 2.3$  ns at 480 nm and 2.9 ns at 515 nm), an intense LC long-lived phosphorescence was also observed at 515 nm ( $\tau = 6.10$  ms). This indicates that both LC singlet and triplet states exist at 77 K. The results show that the  ${}^{3}LC$  state is efficiently quenched by thermally activated vibrational modes at



Fig. 8. Absorption (----), excitation (---) and emission spectra at room temperature (---) and at 77 K  $(\cdots)$  of **3** in CH<sub>3</sub>CN.

room temperature, which is minimized at 77 K. The ligand-centered singlet excited state (<sup>1</sup>LC) is estimated to be about 20830 cm<sup>-1</sup> and triplet state (<sup>3</sup>LC) to be 19420 cm<sup>-1</sup>.

Other than the visible emission, compounds 2, 4 and 5 also exhibited emission corresponding to the lanthanide(III) ion in the NIR region (Fig. 9). These NIR emissions are very similar to those reported for Nd<sup>3+</sup>,  $\mathrm{Er}^{3+}$  and  $\mathrm{Yb}^{3+}$  [14,44]. For **2**, the emissions at 875 and 905 nm can be assigned to  ${}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{9/2}$ , 1068 nm to  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$  and 1356 nm to  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$  transitions of Nd<sup>3+</sup>. For **4**, the emission at 1515 nm can be assigned to  ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$  transition of Er<sup>3+</sup> and for **5**, the emission at 976 nm can be assigned to the  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition of Er<sup>3+</sup> and for **5**. sitions of  $Yb^{3+}$ . From Fig. 9, we can observe that the intensity of the  $Ln^{3+}$  emission follows the order: Yb>Nd > Er, typical of other related system [44]. Due to the limitations of our instrument, we were unable to measure the excitation spectrum (monitored at 1515 nm) and the NIR luminescence lifetime of 4. Compounds 2 and 5 show very similar excitation (monitored at the NIR emission peak) and absorption spectra. The excitation spectrum of 2 (Fig. 10) monitored at 875 nm is similar to that monitored at 480 nm. This clearly shows that both visible and NIR emissions are originated from the  $\pi \rightarrow \pi^*$  transitions of the Schiff base ligand. The sensitization process leading to the observable NIR luminescence probably proceeds via excitation of the Schiff base to its singlet state  $(S_1)$  and the energy is then transferred to its triplet state  $(T_1)$  by intersystem crossing, which is, in part, followed by energy transfer to the excited state of the lanthanide ion  $(Ln^{3+})^*$  to produce the final luminescence. The overall NIR luminescence quantum yield ( $\Phi_{tot}$ ) is the product of triplet yield ( $\Phi_{ISC}$ ), energy transfer yield ( $\Phi_{\rm ET}$ ) and intrinsic luminescence quantum yield of the lanthanide ion  $(\Phi_{Ln})$ . Due to the limitations of our instrument, we were unable to



Fig. 9. Room temperature near-infrared luminescence spectra of 2 (----), 4 (···) and 5 (---) in CH<sub>3</sub>CN upon excitation at 355 nm. The concentration of each solution is  $1.1 \times 10^{-4}$  moldm<sup>-3</sup>.



Fig. 10. Absorption (——) and excitation (···; monitored at 870 nm) spectra of 2 in CH<sub>3</sub>CN at room temperature.

measure the overall quantum yields of the NIR luminescence of the complexes directly. However, the intrinsic luminescence quantum yields of lanthanide ions can be estimated from the equation  $\Phi_{Ln} = \tau_{obs}/\tau_0$  [47], in which  $\tau_{obs}$  is the observed emission lifetime and  $\tau_0$  is the radiative or 'natural' lifetime of Ln<sup>3+</sup>, which is 0.25 and 2 ms for Nd<sup>3+</sup> and Yb<sup>3+</sup>, respectively [14]. Thus, the maximum estimated NIR quantum yield is  $5.22 \times 10^{-3}$  for **2** and  $7.30 \times 10^{-3}$  for **5**.

## 4. Conclusion

A series of new heterobimetallic Zn-Ln (Ln = La, Gd, Nd, Yb, Er) Schiff base complexes have been prepared in good yield. Four of these complexes have been structurally characterized. <sup>1</sup>H NMR data of the complexes in CD<sub>3</sub>CN show that their solution structures agree with their solid-state structures. The conductivity measurements revealed that all Zn-Ln compounds are non-conductors in CH<sub>3</sub>CN. The photophysical properties of the Schiff base complexes can be tuned by changing the electronic properties of the substituents. By extending the conjugation, both the absorption and emission of the complexes are red shifted. The triplet state emission of complex 3 was identified at 77 K with a lifetime of 6.10 ms. Energy transfer was observed from the triplet state of the Zn-Ln complex to the excited state of lanthanide metal (Ln=Nd, Er, Yb) which emitted in the NIR region.

#### 5. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. 234508–234513). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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