Synthesis, structures, photo- and electro-luminescent properties of novel oxadiazole-functionlized europium(III) benzamide complexes[†]

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With *N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-benzamide (HL₁) as the first ligand, three new luminescent europium complexes $Eu_2Na_2(L_1)_6(OH)_2 \cdot 2C_2H_5OH \cdot 2CHCl_3$ (1), $Eu(L_1)_3$ (phen) (phen = 1,10-phenanthroline) (2) and $Eu_2Na_2(L_1)_6(L_2)_2(OH)_2 \cdot 8CHCl_3$ [L₂ = 2,5-bis(2-pyridyl)-1,3,4-oxadiazole] (3) have been prepared and structurally characterized. Each ligand L₁ coordinates with a Eu^{3+} ion through a carbonyl oxygen atom and oxadiazol nitrogen atom, the coordination geometry at europium is a distorted square antiprism. Complexes 1 and 3 have centrosymmetric dimeric structural features with OH⁻ as the bridging ligand, while 2 is mononuclear with phen as the neutral ligand. All these complexes show efficient red emissions typical of Eu^{3+} ions at room temperature, the overall quantum yields of complexes 1, 2 and 3 were 0.15, 0.37 and 0.23, respectively. Using $Eu(L_1)_3$ (phen) as the emitting material, an electroluminescent device with the structure ITO/TPD (30 nm)/Eu(L₁)₃(phen): TPD (1 : 3, 50 nm)/AlQ (30 nm)/Mg_{0.9}Ag_{0.1}/Ag was fabricated. The device emits sharp red light originating from europium complex, demonstrating that $Eu(L_1)_3$ (phen) is a promising red emitter with good electron-transporting property.

Introduction

The design of efficient luminescent lanthanide(III) complexes continues to be an active area of research.1 One of the notable recent interests in luminescent lanthanide complexes concerns their application in electroluminescent display.² Among the rare earth complexes studied, europium(III) complexes appear to be the most attractive in view of the high photoluminescent (PL) efficiency and the narrow band red-emission ability, which are widely exploited in full-colour displays.³ There are usually two general approaches for attaining high luminescence. The first involves the addition of an organic ligand capable of efficiently transferring the energy absorbed by chromophores to the rare earth ion. The second approach is to reduce the non-radiation processes of the centre ion's excited state by protecting the ion from O-H oscillators. Much effort has been devoted to designing such ligands, and a great variety of highly photoluminescent europium(III) complexes are now available.4,5 However, high photoluminescence (PL) efficiency of europium(III) complexes does not translate into electroluminescence (EL) efficiency of a comparable magnitude. Several groups have studied using these lanthanide complexes as emitters in electroluminescent devices with limited success.^{6,7} It is generally believed that the poor carrier transporting ability of the lanthanide complexes is a contributing factor.⁸ Wang et al. first reported that EL efficiency of lanthanide(III)

complex could be greatly improved by using oxadiazole-modified β -diketone as the chelating ligand.⁹ This and other work seem to indicate that the photo- and electro-luminescent properties of complexes could be greatly improved by the ligand substituents.^{10,11} Thus, manipulation of oxadiazole and other groups with good electron-transporting ability may represent a promising venue for the development of highly electroluminescent europium(III) complexes.

N-(5-phenyl-1,3,4-oxadiazol-2-yl)-substituted amides have been reported for their synthesis,¹² electrochemical character¹³ and biological activities.14 To our knowledge, however, there are no literatures about their coordination properties with metal ions although this kind of compounds contain two potential coordinating groups: a carbonyl and an oxadiazol. In this paper, we synthesized three new europium complexes, using N-(5-phenyl-1,3,4-oxadiazol-2-yl)-benzamide (HL₁) as the first ligand and 1,10-phenanthroline (phen), 2,5-bis(2-pyridyl)-1,3,4-oxadiazole (L_2) as the second ligand. Compared with other oxadiazole-modified ligands of europium(III) complexes, ligand HL₁ is unique in that the oxadiazole group coordinates directly with the centre ion, and what is more, it is very cheap and convenient to synthesize. The complexes exhibit efficient photoluminescence. Their binding nature was fully characterized by X-ray structure analysis. The electroluminescent property of $Eu(L_1)_3$ (phen) was also investigated.

Results and discussion

X-Ray crystal structures of the complexes $Eu_2Na_2(L_1)_6(OH)_2$ · 2C₂H₅OH·2CHCl₃ (1), $Eu(L_1)_3$ (phen) (2) and $Eu_2Na_2(L_1)_6(L_2)_2(OH)_2$ ·8CHCl₃ (3)

Single crystals of $Eu_2Na_2(L_1)_6(OH)_2 \cdot 2C_2H_5OH \cdot 2CHCl_3$ (1), $Eu(L_1)_3$ (phen) (2) and $Eu_2Na_2(L_1)_6(L_2)_2(OH)_2 \cdot 8CHCl_3$ (3) were

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atoms and three oxadiazol nitrogen atoms of ligand L_1 , two oxygen

complex 1 crystallizes in tetragonal space group $I4_1/a$, featuring a distances are in the range of 2.551(5) to 2.628(4) Å, consisting centrosymmetric dimeric structure. The selected bond lengths and with those reported for β -diketone lanthanide complexes.¹⁵ Each bond angles for complex 1 are listed in Table 2. As shown in Fig. 1, sodium ion is five-coordinated by one ketone oxygen atom from L_1 , each europium atom is eight-coordinated by three carbonyl oxygen one bridging hydroxide anion, one hydroxyl group of ethanol and two oxadiazol nitrogen atoms from L_1 , resulting in a distorted atoms from the bridging hydroxide anions. As shown in Fig. 2, trigonal bipyramidal geometry. The atoms of O(1) and N(9) seem the coordination geometry of europium ion can be described as to occupy the axial sites with angle O(1)-Na(1)-N(9) 150.24(18)°, showing a great deviation from linearity, while O(7) and O(8) distorted square antiprism. The O(1), O(7), N(2), O(7A) and O(3),

2.443(5)

2.564(5)

2.241(4)

2.257(7)

66.00(14)

80.19(13)

98.22(16)

89.90(13)

66.67(13)

146.70(13)

147.15(14)

145.8(3)

75.47(13)

89.49(16)

N(5), N(6), O(5) form the two facial planes, which being parallel to within 6° and staggered by 40.5°. The distances between Eu centre

and the two faces are 1.355 and 1.380 Å, respectively. The Eu-O

distances are in the range of 2.331(3) to 2.423(4) Å and Eu-N

Na(1)-O(1)#1

O(8)-Na(1)-N(6)

O(8) - Na(1) - N(9)

N(6)-Na(1)-N(9)

O(7)-Na(1)-N(9)

N(6)-Na(1)-O(1)#1

O(7)-Na(1)-O(1)#1

O(8)-Na(1)-O(1)#1

N(9)-Na(1)-O(1)#1

2.738(5)

122.3(3)

107.5(2)

96.16(17)

89.98(15)

78.21(16)

72.74(14)

93.4(3)

150.24(18)

Na(1) - N(6)

Na(1)-N(9)

Na(1) - O(7)

Na(1)-O(8)

O(1)-Eu(1)-N(2)

O(7)-Eu(1)-N(5)

O(5)-Eu(1)-N(5)

O(3)-Eu(1)-N(5)

O(1)-Eu(1)-N(5)

N(2)-Eu(1)-N(5)

O(7)-Eu(1)-N(8)

O(7)-Na(1)-O(8)

O(7)-Na(1)-N(6)

O(7)#1-Eu(1)-N(5)

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(\mathbf{n})	O(7A) = 1O(2)	1 .	1
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Complex	1	2	3	
Empirical formula	$C_{90}H_{62}Eu_2Na_2N_{18}O_{14} \cdot 2C_2H_5OH \cdot 2CHCl_3$	C57H38EuN11O6	$C_{114}H_{78}Eu_2Na_2N_{26}O_{16}\cdot 8CHCl_{10}$	
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	2300.41	1124.94	3372.96	
Space group	$I4_1/a$	$P2_{1}/c$	$P\overline{1}$	
a/Å	38.557(6)	15.7659(12)	15.772(3)	
b/Å	38.557(6)	15.5239(12)	16.611(3)	
c/Å	13.363(3)	19.8423(15)	17.450(4)	
$\alpha /^{\circ}$	90	90	61.65(3)	
β/°	90	94.425(1)	64.05(3)	
$\gamma/^{\circ}$	90	90	72.30(3)	
$V/Å^3$	19 866(6)	4841.9(6)	3590.8(18)	
Ζ	8	4	1	
$ ho_{ m calcd}/ m g~ m cm^{-3}$	1.536	1.543	1.559	
T/K	291(2)	291(2)	291(2)	
λ/Å	0.71073	0.71073	0.71073	
μ/mm^{-1}	1.495	1.362	1.387	
θ range/°	$1.49 < \theta < 25.00$	$2.35 < \theta < 28.41$	$1.42 < \theta < 27.53$	
Reflections collected	24 599	44 719	46 267	
Independent reflections	8215	12 054	16267	
Parameters	623	676	849	
GOF on F^2	1.147	1.020	1.033	
$R_{\rm int}$	0.0612	0.0451	0.0676	
Final $R [I > 2\sigma(I)]^{ab}$	$R_1 = 0.0719, wR_2 = 0.1433$	$R_1 = 0.0370, wR_2 = 0.0741$	$R_1 = 0.0617, wR_2 = 0.1687$	
R (all data)	$R_1 = 0.1355, wR_2 = 0.1623$	$R_1 = 0.0665, wR_2 = 0.0849$	$R_1 = 0.0670, wR_2 = 0.1742$	
${}^{a}R_{1} = \Sigma F_{0} - F_{c} / \Sigma F_{0} $	$ \cdot^{b} \mathbf{w} R_{2} = \{ \Sigma [\mathbf{w} (F_{0}^{2} - F_{c}^{2})^{2}] / \Sigma [\mathbf{w} (F_{0}^{2})^{2}] \}^{1/2}.$			

Table 1 Crystallographic data for complexes 1–3

Table 2 Selected bond lengths (Å) and angles (°) of complex 1

Eu(1) - O(1)

Eu(1)-N(5)

Eu(1)-N(8)

Eu(1)-N(2)

O(7)-Eu(1)-N(2)

O(5)-Eu(1)-N(2)

O(3)-Eu(1)-N(8)

O(1)-Eu(1)-N(8)

N(2)-Eu(1)-N(8)

N(5)-Eu(1)-N(8)

O(5)-Eu(1)-N(8)

O(3)-Eu(1)-N(2)

Symmetry transformations used to generate equivalent atoms: $\#1 - x - \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$.

O(7)#1-Eu(1)-N(8)

O(7)#1-Eu(1)-N(2)

2.423(4)

2.577(4)

2.628(4)

2.551(5)

72.74(14)

91.60(16)

98.77(14)

125.20(14)

126.13(14)

75.52(15)

80.01(14)

66.09(14)

146.94(13)

146.14(14)

2.331(3)

2.339(4)

2.344(4)

2.372(4)

141.11(14)

71.80(14)

146.93(13)

134.20(13)

76.77(15)

77.25(13)

122.94(14)

78.46(16)

77.36(13)

80.45(13)

obtained by slow evaporation of ethanol and chloroform mixed

solution at room temperature, and characterized by single-crystal X-ray crystallography. Details of crystal data and data collection

parameters for complexes 1, 2 and 3 are listed in Table 1. The

Bond lengths/Å

Eu(1) - O(7)

Eu(1)-O(5)

Eu(1)-O(3)

Eu(1)-O(7)#1

Bond angles/° O(7)-Eu(1)-O(5)

O(7)-Eu(1)-O(7)#1

O(5)-Eu(1)-O(7)#1

O(7)#1-Eu(1)-O(3)

O(7)#1-Eu(1)-O(1)

O(7)-Eu(1)-O(3)

O(5)-Eu(1)-O(3)

O(7)-Eu(1)-O(1)

O(5)-Eu(1)-O(1)

O(3)-Eu(1)-O(1)



Fig. 1 A diagram showing the molecular structure of complex 1. Hydrogen atoms and solvent molecules were omitted for clarity.



Fig. 2 Coordination environment of europium and sodium ions in the crystal of complex 1.

and the nitrogen atom N(6) reside on the equatorial plane with the bond angles to the axial Na(1)-O(1) or Na(1)-N(9) vectors ranging from 72.74(14) to 107.5(2)°. The Na-O distances are in the range of 2.241(4) to 2.738(5) Å, and the Na-N distances are in the range of 2.443(5) to 2.564(5) Å, the longest contact being to the ketone oxygen atom (O(1)) of L_1 . All the L_1 ligands feature a near co-planar relationship between their oxadiazole and phenyl rings, the dihedral angles between the two phenyl rings being 7, 3, 5° for the O(1), O(3) and O(5) containing ligands, respectively. For ligand L₁, both nitrogen and oxygen atoms in the oxadiazol group have the possibility to chelate with europium ion. However, only nitrogen atom was observed to coordinate with europium ion, although the oxygen atom shows stronger coordination ability than the nitrogen atom, as usually indicated by the shorter Eu-O distances in comparison with Eu-N distances. The steric effect may be responsible for the binding mode.

Compound **2** was designed and synthesized based on the concept of synergistic coordination effect. The coordination of the neutral ligand 1,10-phenanthroline (phen) with the europium ion replaces the chelating water molecules, and as a result a mononuclear complex $Eu(L_1)_3$ (phen) was obtained. Its crystal structure is shown in Fig. 3. The europium ion is chelated with three oxygen atoms and three nitrogen atoms from the ligand L_1 , two nitrogen atoms from the neutral ligand phen, resulting in a eight coordinated geometry of distorted square antiprism. The average Eu–O bond length is 2.326(2) Å. The Eu–N bond lengths involving the nitrogen atoms of ligand L_1 are a little shorter (2.4945(19)–2.5484(18) Å) than those with the nitrogen atoms of phen ligand (2.5750(18)–2.5810(18) Å) (Table 3).



Fig. 3 A diagram showing the molecular structure of complex **2**. Hydrogen atoms were omitted for clarity.

When L_2 was selected as a synergistic ligand and reacted with HL₁ and EuCl₃ in 3: 1:1 (HL₁: L₂: EuCl₃) ratio, a new compound, 3, was obtained. The complex 3 crystallizes in triclinic with space group $P\overline{1}$, also featuring a centrosymmetric dimeric structure (Fig. 4). Each europium ion is chelated by three oxadiazolemodified acylamide ligands and two bridging hydroxide anions. The coordination geometry and the bonding parameters around the europium centre are essentially identical with that of complex 1. However, in complex 3, the neutral ligand L_2 doesn't coordinate with europium ion directly, but links with europium center by chelating with sodium ion, although it has the potential to chelate with rare earth ions as a heterocyclic nitrogen donor, this special binding mode is probably caused by steric effect of L_2 . The overall coordination sphere around each sodium ion consists of one carbonyl oxygen atom of ligand L₁, one bridging hydroxide anion, two oxadiazol nitrogen atoms of L₁ ligands and two nitrogen atoms of L₂ ligands, resulting in a six-coordinated distorted trigonal anti-prismatic geometry (Fig. 5). The Na-O distances range from 2.354(2) to 2.424(3) Å, and the Na-N distances range from 2.514(3) to 2.626(3) Å (Table 4). These data are comparable to those observed in sodium ketoiminate complexes.16

Table 3 Selected bond lengths (Å) and angles (°) of complex 2

Bond lengths/Å								
Eu(1)–O(5) Eu(1)–O(3)	2.3123(14) 2.3255(14)	Eu(1)–O(1) Eu(1)–N(2)	2.3409(15) 2.4945(19)	Eu(1)–N(8) Eu(1)–N(5)	2.5081(17) 2.5484(18)	Eu(1)–N(10) Eu(1)–N(11)	2.5750(18) 2.5810(18)	
Bond angles/°								
O(5)–Eu(1)–O(3)	149.70(5)	O(3)–Eu(1)–N(8)	80.85(5)	O(5)-Eu(1)-N(11)	76.44(6)	N(8)-Eu(1)-N(10)	79.26(6)	
O(5)-Eu(1)-O(1)	83.72(5)	O(1)-Eu(1)-N(8)	134.53(6)	O(3)-Eu(1)-N(11)	125.70(6)	N(5)-Eu(1)-N(10)	81.84(6)	
O(3)-Eu(1)-O(1)	116.59(5)	N(2)-Eu(1)-N(8)	77.15(6)	N(8)-Eu(1)-N(5)	146.33(5)	O(1)-Eu(1)-N(11)	82.96(5)	
O(5)-Eu(1)-N(2)	91.28(6)	O(5)-Eu(1)-N(5)	142.43(5)	O(5)-Eu(1)-N(10)	101.03(6)	N(2)-Eu(1)-N(11)	149.13(6)	
O(3) - Eu(1) - N(2)	77.81(6)	O(3) - Eu(1) - N(5)	67.72(5)	O(3) - Eu(1) - N(10)	76.45(6)	N(8) - Eu(1) - N(11)	122.33(6)	
O(1) - Eu(1) - N(2)	67.43(6)	O(1) - Eu(1) - N(5)	73.53(6)	O(1) - Eu(1) - N(10)	143.40(5)	N(5) = Eu(1) = N(11)	71.50(6)	
O(5) - Eu(1) - N(8)	69.12(5)	N(2)-Eu(1)-N(5)	106.39(6)	N(2)-Eu(1)-N(10)	147.37(6)	N(10)-Eu(1)-N(11)	63.49(5)	

Table 4 Selected bond lengths (Å) and angles (°) of complex 3

Bond lengths/Å								
Eu(1)-O(7)#1 Eu(1)-O(1) Eu(1)-O(7) Eu(1)-O(3)	2.3480(19) 2.359(2) 2.358(2) 2.367(2)	Eu(1)–O(5) Eu(1)–N(5) Eu(1)–N(8) Eu(1)–N(2)	2.415(2) 2.574(3) 2.585(3) 2.615(3)	Na(1)-O(7) Na(1)-O(5) Na(1)-N(6)#1 Na(1)-N(3)#1	2.354(2) 2.424(3) 2.514(3) 2.580(3)	Na(1)–N(11) Na(1)–N(10)	2.598(3) 2.626(3)	
Bond angles/°								
$\begin{array}{c} O(7)\#1-Eu(1)-O(1)\\ O(7)\#1-Eu(1)-O(7)\\ O(1)-Eu(1)-O(7)\\ O(7)\#1-Eu(1)-O(3)\\ O(7)-Eu(1)-O(3)\\ O(7)-Eu(1)-O(3)\\ O(7)\#1-Eu(1)-O(5)\\ O(1)-Eu(1)-O(5)\\ O(7)-Eu(1)-O(5)\\ O(3)-Eu(1)-O(5)\\ O(7)\#1-Eu(1)-N(5)\\ \end{array}$	144.31(8) 71.63(8) 84.57(9) 136.91(8) 74.44(9) 148.79(7) 120.55(8) 77.54(8) 77.34(7) 75.77(9) 77.87(8)	$\begin{array}{l} O(1)-Eu(1)-N(5)\\ O(7)-Eu(1)-N(5)\\ O(3)-Eu(1)-N(5)\\ O(5)-Eu(1)-N(5)\\ O(7)\#1-Eu(1)-N(8)\\ O(1)-Eu(1)-N(8)\\ O(3)-Eu(1)-N(8)\\ O(3)-Eu(1)-N(8)\\ O(5)-Eu(1)-N(8)\\ N(5)-Eu(1)-N(8)\\ O(7)\#1-Eu(1)-N(2)\\ \end{array}$	$\begin{array}{c} 112.17(10)\\ 144.70(6)\\ 66.16(8)\\ 135.17(8)\\ 75.05(7)\\ 138.74(7)\\ 106.45(9)\\ 77.00(9)\\ 66.93(8)\\ 81.78(9)\\ 82.94(7)\end{array}$	$\begin{array}{l} O(1)-Eu(1)-N(2)\\ O(7)-Eu(1)-N(2)\\ O(3)-Eu(1)-N(2)\\ O(5)-Eu(1)-N(2)\\ N(5)-Eu(1)-N(2)\\ N(8)-Eu(1)-N(2)\\ O(7)-Na(1)-N(5)\\ O(7)-Na(1)-N(6)\#1\\ O(5)-Na(1)-N(3)\#1\\ O(5)-Na(1)-N(3)\#1\\ \end{array}$	66.66(8) 80.03(9) 111.15(9) 139.04(8) 78.98(9) 153.32(8) 77.22(8) 84.15(9) 158.61(9) 88.33(9) 85.61(10)	$\begin{array}{l} N(6)\#1-Na(1)-N(3)\#1\\ O(7)-Na(1)-N(11)\\ O(5)-Na(1)-N(11)\\ N(6)\#1-Na(1)-N(11)\\ N(3)\#1-Na(1)-N(11)\\ O(7)-Na(1)-N(10)\\ O(5)-Na(1)-N(10)\\ N(6)\#1-Na(1)-N(10)\\ N(3)\#1-Na(1)-N(10)\\ N(11)-Na(1)-N(10) \end{array}$	83.43(10) 155.23(9) 92.49(10) 108.73(12) 113.59(10) 94.07(10) 99.61(11) 92.02(11) 174.62(13) 65.15(10)	

Symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z.

04 N4 N6 N5 N0 02 N1 03 03 N12 - Eur 03 N100 Na1 04 N4 05 N100 Na1 04 N4 05 N100 Na1 05 N1

Fig. 4 A diagram showing the molecular structure of complex 3. Hydrogen atoms and solvent molecules were omitted for clarity.

IR spectra of the free ligand HL_1 and the complex 1

The free ligand HL_1 shows strong C–O stretch vibration at 1713 cm⁻¹. The absence of O–H stretch vibration in the range of 3200–3500 cm⁻¹ indicates that the free ligand mainly exits in



Fig. 5 Coordination environment of europium and sodium ions in the crystal of complex 3.

the ketonic form. In the IR spectrum of the complex 1, the $v_{C=0}$ vibration at 1713 cm⁻¹ disappears, and the $v_{C=N}$ vibration of the heterocyclic ring at 1618 cm⁻¹ moves to 1547 cm⁻¹, showing that the nitrogen of the oxadiazole ring coordinates with Eu(III) ion, which is in accordance with the X-ray analysis results.

Electronic spectroscopy and photoluminescence studies

UV-vis absorption spectra of the ligands (HL₁, L₂, phen) and their Eu(III) complexes measured in methanol are shown in Fig. 6. The broad band at 273 nm for HL₁ can be assigned to $\pi^{-1}\pi^{+1}$ transition, while the shoulder band at 290 nm can be identified as $n-\pi^*$ transition of the free ligand owing to its low absorption intensity. Upon coordinating with europium ion, the absorption at 273 nm shifts to 307 nm, 305 nm and 302 nm for complex 1, 2 and 3, respectively. The hump observed around 272 and 286 nm in complexes 2 and 3, can be attributed to $\pi^{-1}\pi^{+}$ absorptions of the neutral ligands. The spectral shapes of the Eu(III) complexes in methanol are similar to those of the corresponding ligands, indicating that the coordination of the europium ion does not significantly influence the energy of the singlet state of ligands. However, the red shift observed in the absorption maximum of all the complexes is due to the perturbation induced by the Eu(III) coordination.



Fig. 6 UV spectra of ligand HL_1 , L_2 , phen and the complexes 1–3 in methanol solution at room temperature.

The fluorescence spectra of complexes 1, 2 and 3 in solid state were recorded at room temperature. The excitation spectra of complexes 1 and 3, obtained by monitoring ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu(III) ion at 612 nm, were found to be very similar (Fig. 7). They are all dominated by strong bands in the range of 300– 380 nm with the maximum absorptions at 365 nm and 355 nm, respectively. However, the excitation spectrum of complex 2 shows apparent differences from that of complexes 1 and 3. By introducing the second ligand phen, the excitation spectrum of



Fig. 7 Excitation spectra of complexes 1–3 in solid state at room temperature.

Eu(L₁)₃(phen) features a very broad band in the range of 250– 380 nm with intensity dropping slowly toward lower wavelength, the maximum peak is at 337 nm. Furthermore, the relative intensity of the narrow band at 464 nm corresponding to the ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ hypersensitive transition of complex 2 is significantly larger than that of complexes 1 and 3. This result indicates that the asymmetric part of the crystal field is larger in complex 2 compared with complexes 1 and 3, which is in accordance with the X-ray analysis results.

The emission spectra of the three complexes at room temperature show efficient red emission typical of Eu³⁺ ion and no emission bands from organic ligands were observed (Fig. 8), indicating that the energy transfer from the ligands to the Eu(III) centre is very efficient. The assignment of observed bands to appropriate f-f transitions is straightforward, the five sharp peaks at 580, 590, 612, 651 and 701 nm correspond to the ${}^5D_0 \rightarrow {}^7F_0, \, {}^5D_0 \rightarrow {}^7F_1, \, {}^5D_0 \rightarrow {}^7F_2, \, {}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions, respectively. The ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transition is independent of the coordination sphere, while the electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is extremely sensitive to the nature and symmetry of the coordinating environment. The intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions (I_{7F2}/I_{7F1}) is a good measure of the nature and symmetry of the first coordination sphere.^{17,18} In a centrosymmetric environment, the magnetic dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of Eu³⁺ is dominating, whereas distortion of the symmetry around the ion cause an intensity enhancement of the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition.¹⁹ In all those complexes, the domination of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is a typical feature that no inversion centre is occupied by Eu(III) ion in the complexes (Fig. 8). The I_{7F2}/I_{7F1} ratios for complex 1, 2 and 3 are 7.6, 9.5 and 7.9, respectively. The singlet of the ${}^5D_0 \rightarrow {}^7F_0$ transition indicates the presence of only single site symmetry of Eu³⁺ ion, which is in good agreement with the structure analysis results. It is interesting to note that the I_{7F2}/I_{7F1} ratios of these complexes are smaller compared with the reported literature values for tris-(β-diketone) complexes.¹⁹ Judd considered that the polarizability of the coordinating groups play a crucial role in the hypersensitivity of certain lanthanide(III) transitions.²⁰ The nitrogen donor atoms of L₁ are less polarizable than the coordinating carbonyl groups of β -diketonates, resulting in a decrease in the intensity of the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition. As shown in Fig. 8, the complex $Eu(L_1)_3$ (phen) is more strongly luminescent in the



Fig. 8 Emission spectra of 1 ($\lambda_{ex} = 365 \text{ nm}$), 2 ($\lambda_{ex} = 337 \text{ nm}$) and 3 ($\lambda_{ex} = 355 \text{ nm}$) in solid state at room temperature.

red than the other complexes when excited with near–ultraviolet radiation. This result demonstrates that the coordination of the phen can not only erase the H–O vibration quenching from the of water molecules and improve the rigidity of the complex, but also can act as a good light-harvesting group for sensitized Eu³⁺ luminescence.

The photophysical model that explains the sensitization pathway in a luminescent lanthanide complex is well established. The overall quantum yield (Φ_{tot}) of ligand-sensitized lanthanide emission, determined experimentally, is the product of the ligand sensitization efficiency (η_{sens}) and the intrinsic quantum yield (Φ_{Ln}) of the lanthanide luminescence according to:²¹

$$\Phi_{\rm tot} = \eta_{\rm sens} \Phi_{\rm Ln}.$$
 (1)

The energy transfer efficiency (η_{sens}) is the product of the two processes involving intersystem crossing (ISC) from the first excited singlet state of the ligand to the triplet state and energy transfer (LET) to the lanthanide. The intrinsic quantum yield of the lanthanide luminescence step (Φ_{Ln}) can be evaluated on the basis of observed luminescence lifetime (τ_{obs}) and pure radiative lifetime (τ_{R}) of the Eu(III) ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ (J = 0-4) transitions by using:²²

$$\Phi_{\rm Ln} = \tau_{\rm obs} / \tau_{\rm R} \tag{2}$$

$$1/\tau_{\rm R} = A_{\rm MD,0} n^3 (I_{\rm tot}/I_{\rm MD}).$$
 (3)

where $A_{\rm MD,0} = 14.65 \, {\rm s}^{-1}$ is the spontaneous emission probability of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of Eu(III), *n*, the refractive index of the medium, $I_{\rm tot}/I_{\rm MD}$, the ratio of the integrated total area of the corrected Eu(III) emission spectrum to the area of magnetic dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition.

Table 5 presents the radiative lifetimes ($\tau_{\rm R}$), intrinsic quantum yields (Φ_{Ln}), sensitization efficiencies (η_{sens}), the experimentally determined luminescence lifetimes (au_{obs}) and overall quantum yields (Φ_{tot}) of the three Eu(III) complexes. Intrinsic quantum yields (Φ_{Ln}) of complex 1 and complex 3 are similar to each other due to their comparable coordination environments.²³ These values are smaller than that calculated for complex 2. This phenomenon can be attributed to two aspects. Firstly, the presence of O-H oscillators of OH- in the first coordination sphere of Eu(III) centre efficiently quenches the luminescence via vibrational relaxation. Secondly, the energy transfer between Eu³⁺ ions (with the Eu-Eu seperation of 3.78(7) Å) can also be a key factor, which may cause concentration quenching when the distance between Eu^{3+} ions themselves is less than 8.4 Å.²⁴ The efficiencies of energy transfer from the ligands to the Eu³⁺ ion, η_{sens} , are 0.25, 0.53 and 0.38 for complexes 1, 2 and 3, respectively. The differences in sensitization efficiencies of those complexes can be explained

Table 5 Radiative lifetimes $(\tau_{\rm R})$, intrinsic quantum yields of the lanthanide luminescence step ($\Phi_{\rm Ln}$), sensitization efficiencies ($\eta_{\rm sens}$), the experimentally determined luminescence lifetimes ($\tau_{\rm obs}$) and overall quantum yields ($\Phi_{\rm tot}$) of complexes 1–3

Complex	$\tau_{ m R}/{ m ms}$	$ au_{ m obs}/ m ms$	\varPhi_{Ln} (%)	$\eta_{ m sens}$ (%)	$arPhi_{ ext{tot}}$ (%)
1	1.50	0.87	58	25	15
2	1.42	0.99	70	53	37
3	1.56	0.95	61	38	23

qualitatively in term of the synergistic sensitization effects as well as the antenna-Eu(III) distances. In complex 1, only ligand L₁ acts as energy sensitizer for Eu(III) center. In complexes 2 and 3, both ligand L_1 and neutral ligands (L_2 or Phen) act as energy sensitizers for Eu(III) center. Since the distances between L₁ ligands and europium ions are comparable in complexes 2 and 3, we will focus on the distances between donating neutral ligands and Eu(III) centers. Given the steep distance-dependence of energy transfer mechanisms, even a small change in the distance has a significant effect on η_{sens} .²⁵ In complex 3, the neutral ligand L₂ doesn't coordinate with Eu(III) ion directly, but links with Eu(III) center through chelating with Na+ ion. The relative longer distance between L₂ and Eu(III) center may cause apparent decrease of sensitization efficiency of L_2 . In complex 2, besides the good sensitizing capabilities of ligand L₁ and phen, these antennas also contribute positively to the overall luminescence quantum yield (Φ_{tot}) by increasing the intrinsic quantum yield of Eu(III) ion (Φ_{Ln}).

Energy transfer between ligands and europium(III)

In an effort to demonstrate the energy transfer process, the phosphorescence spectra of the complexes $Gd(L_1)_3(H_2O)_2$ and $Gd(NO_3)_3L_2$ were measured at 77 K for triplet energy level data of the ligand L_1 and L_2 , respectively. Since the lowest excited state 6P7/2 of Gd(III) ion is too high to accept energy from a ligand, the data obtained from the phosphorescence spectra of the complexes actually reveal the triplet energy level of the corresponding ligand.²⁶ The triplet state energy $({}^{3}\pi\pi^{*})$ levels of L₁ and L_2 based on our measurement were found to be 21 270 cm⁻¹ (470 nm) and 20260 cm⁻¹ (496 nm), respectively. The singlet state energy levels of L_1 and L_2 were estimated by referencing their absorbance edges, which were 27 397 cm⁻¹ (365 nm) and 31 056 cm⁻¹ (322 nm), respectively. The singlet and triplet energy $(1\pi\pi^*)$ levels of DBM (28 300 and 20 520 cm⁻¹), bpy (29 900 and 22 900 cm⁻¹) and phen (31 000 and 22 100 cm⁻¹) were taken from the literatures.27,28

Generally, the excited energy of the organic ligand undergoes an intramolecular energy transfer from the triplet state of the ligand to an excited state of Eu(III), and then the emission occurs when the energy transfer from the lowest excited state ${}^{5}D_{0}$ to the ground state ${}^{7}F_{J}$ (J = 0-4) of Eu(III).²⁹ Therefore, matching the energy levels of the triplet state of the ligands to ${}^{5}D_{0}$ of Eu³⁺ is one of the key factors that affect the luminescent properties of the europium complexes.

Based on the above experimental results, the triplet energy levels of L₁ (21 270 cm⁻¹) and L₂ (20 260 cm⁻¹) are obviously higher than the ⁵D₀ level (17 500 cm⁻¹) of Eu³⁺, and their energy gaps $\Delta E({}^{3}\pi\pi^{*}-{}^{5}D_{0})$ between ligand and metal-centered levels are too high to allow an effective back energy transfer. According to Latva's empirical rule, ³⁰ an optimal ligand-to-metal energy transfer process for Eu³⁺ needs $\Delta E({}^{3}\pi\pi^{*}-{}^{5}D_{0}) > 2500$ cm⁻¹ and hence the energy transfer process is effective for complexes **1–3**. We also noticed that the energy gaps between the ${}^{1}\pi\pi^{*}$ and ${}^{3}\pi\pi^{*}$ levels are 6127 and 10 796 cm⁻¹ for L₁ and L₂, respectively. According to Reinhoudt's empirical rule,¹⁶ the intersystem crossing process becomes effective when $\Delta E({}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*})$ is at least 5000 cm⁻¹; thus L₁ and L₂ are effective sensitizers for Eu³⁺ and the intersystem crossing processes in complexes **1–3** are effective.

Electroluminescence property of complex 2

With the aim of developing new bright and efficient red Organic light emitting diodes (OLED). The EL properties of the complexes were also investigated. Of the three complexes studied, only $Eu(L_1)_3$ (phen) is a mononuclear complex and can be used as an emitter in OLED through vacuum deposition. Using $Eu(L_1)_3$ (phen) doped into N,N-bis(3-methylphenyl)-N,N-diphenyl)-benzidine (TPD) as the emitting layer, N,Nbis(3-methylphenyl)-N,N-diphenyl)benzidine (TPD) as the holetransporting layer, tris(8-quinolinolato)aluminium(III) complex (AlQ) as the electron-transporting layer, a three layer device with the structure of ITO/TPD (30 nm)/Eu(L_1)₃(phen): TPD (1:3, 50 nm)/AlQ (30 nm)/Mg_{0.9}Ag_{0.1}/Ag was fabricated. With holetransporting compound TPD as the host in the emitting layer, the oxadiazole-modified europium complex $Eu(L_1)_3$ (phen) is expected to exhibit the combined properties of europium-based complex and electron-transporting property of oxadiazole moiety in the OLED device. Fig. 9 shows the EL spectrum of the resulting device at 12 V. The EL spectrum is dominated by a sharp red emission at 612 nm due to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of the Eu³⁺ ion and no broad emission at 520 nm from the AlQ appears. This result confirms that the complex $Eu(L_1)_3$ (phen) has good electron-transporting ability, and as a result the electron-hole recombination is successfully confined within the $Eu(L_1)_3$ (phen) layer.³¹



Fig. 9 The EL spectrum of the ITO/TPD (30 nm)/Eu(L_1)₃(phen): TPD (1:3, 50 nm)/AlQ (30 nm)/Mg_{0.9}Ag_{0.1}/Ag device.

The current-voltage (I-V) and luminance-voltage (L-V) characteristics of the device are shown in Fig. 10. The EL efficiencies as a function of the voltage are presented in Fig. 11. The turn on voltage is as low as 6 V. Although the brightness of the device increases with increasing current density, the EL spectrum was independent of the bias voltage. The maximum emission intensity of 107 cd m⁻² is observed at 16 V and 74 mA cm⁻². The maximum EL efficiency is 0.16 lm W⁻¹ at 9 V. It is thus concluded that the sublimable complex, $Eu(L_1)_3$ (phen), can be used as a red emitting material with good electron-transporting ability in electroluminescent devices. Comparing with other conventional three-layer devices based on β -diketonates europium complexes, the performance of this device is only moderate.^{7,8} However, $Eu(L_1)_3$ (phen) is the first oxadiazole-modified europium benzamide complex used as the emitter in the EL device, furthermore, neither the configurational nor the compositional structure of



Fig. 10 The current–voltage (I-V) and luminance-voltage (L-V) characteristics of the ITO/TPD (30 nm)/Eu(L₁)₃(phen): TPD (1:3, 50 nm)/AlQ (30 nm)/Mg_{0.9}Ag_{0.1}/Ag device.



Fig. 11 The EL efficiency in lm W^{-1} and cd A^{-1} characteristics of the ITO/TPD (30 nm)/Eu(L₁)₃(phen): TPD (1:3, 50 nm)/AlQ (30 nm)/ Mg_{0.9}Ag_{0.1}/Ag device.

the present device is optimized. More efforts will be taken to develop highly luminescent europium acylamide complexes useful in electroluminescent devices.

Conclusions

Three new luminescent europium complexes $Eu_2Na_2(L_1)_6(OH)_2$. $2C_2H_5OH \cdot 2CHCl_3$ (1), $Eu(L_1)_3$ (phen) (2) and $Eu_2Na_2(L_1)_6$ - $(L_2)_2(OH)_2 \cdot 8CHCl_3$ (3) have been synthesized and structurally characterized. For complexes 1, 2 and 3, the overall quantum yield were 0.15, 0.37 and 0.23, respectively. The decay times of complexes 1, 2 and 3, as measured at room temperature, were 0.87, 0.99 and 0.95 ms, respectively. The lowest triplet state energy levels of the ligands L_1 and L_2 indicate that the triplet state energy levels of the ligands match perfectly to the resonance energy level of Eu(III). All the complexes exhibit strong characteristic emission of Eu^{3+} ion, with $Eu(L_1)_3$ (phen) being the most efficient. Using $Eu(L_1)_3$ (phen) as the emitting material, pure red emission at 612 nm for the ITO/TPD (30 nm)/Eu(L_1)₃(phen): TPD (1:3, 50 nm)/AlQ (30 nm)/Mg_{0.9}Ag_{0.1}/Ag device was observed with the maximum luminance of 107 cd m⁻² and the maximum power efficiency of 0.16 lm W⁻¹. The compound 2 exhibits good electrontransporting property and is a promising red emitter for EL device. Efforts are being taken by our group to develop new kinds of luminescent europium acylamide complexes for EL devices.

Preparation and composition analysis

All the chemicals and solvents were commercial grade, and were purified or dried by standard methods when required. NMR spectra were recorded on Bruker DPX-400MHz spectrometer in DMSO. Chemical shifts (δ) are expressed in ppm relative to Me₄Si for ¹H and ¹³C NMR. IR spectra were recorded as KBr pellets with a Bruker Vector22 FT-IR spectrophotometer. Elemental analysis for carbon, hydrogen and nitrogen were performed with a Carlo-Erba1106 Elemental Analyzer.

Benzaldehyde semicarbazone (I). A solution of benzaldehyde (10 mL, 0.10 mol) in methanol (10 mL) was added slowly to a solution of semicarbazide hydrochloride (12 g, 0.11 mol) in methanol (60 mL) and water (240 mL) with stirring; and a white solid appeared at once. Then the slurry was stirred at 70 °C for 2 h. The white precipitate was collected and dried under vacuum. Crystallization from ethanol aqueous solution gave a white crystalline solid. Yield: 9.78 g, 60%. M.p. 221–223 °C. Anal. calcd for $C_8H_9N_3O$ (%): C 58.88, H 5.56, N 25.75. Found: C 58.42, H 5.63, N 26.03. IR (KBr): 3406, 3289, 1689, 1623, 1595, 1356, 759 cm⁻¹.

2-Amino-5-phenyl-1,3,4-oxadiazole (II). This preparation is based on a published method.³² Yield: 78%. M.p.: 240–242 °C (lit. m.p. 241–243 °C). Anal. calcd for $C_8H_7N_3O$ (%): C 59.62, H 4.38, N 26.07. Found: C 59.54, H 4.42, N 26.13.

N-(5-phenyl-1,3,4-oxadiazol-2-yl)-benzamide (HL₁). Benzoyl chloride (3.68 mL, 0.032 mol) was dropped slowly into the stirred slurry of compound **II** (5.64 g, 0.035 mol) in 50 mL pyridine. Compound **II** dissolved gradually and gave a buff solution. After 2 h, the solution was poured into water; and the white precipitate was collected and dried under vacuum. Pure product was obtained by re-crystallization from ethanol, m.p. 203–205 °C. Yield: 6.28 g, 74%. Anal. calcd for C₁₅H₁₁N₃O₂ (%): C 67.92, H 4.18, N 15.84. Found: C 68.09, H 4.13, N 15.67. ¹H NMR (DMSO, 400 MHz) δ/ppm: 7.55–8.05 (m, 10 H), 12.14 (s, 1 H) ppm. ¹³C NMR (DMSO, 400 MHz): δ/ppm: 165.18, 161.43, 158.14, 133.20, 132.39, 132.00, 129.70, 128.84, 128.45, 126.29, 123.59 ppm. IR (KBr): 1713, 1618, 1582, 1391, 1293, 1245, 1023, 694 cm⁻¹.

2,5-Bis(2-pyridyl)-1,3,4-oxadiazole (L₂). This compound was synthesized according to the reference.³³ Yield: 25%. M.p. 151–153 °C (lit. m.p. 153–154 °C). Anal. calcd for $C_{12}H_8N_4O$ (%): C 64.30, H 3.59, N 24.97. Found: C 64.32, H 3.55, N 24.91.

Complex Eu₂Na₂(L₁)₆(OH)₂·2C₂H₅OH·2CHCl₃ (1). 1 mmol EuCl₃ in ethanol was added to a ethanol solution (30 mL) of 3 mmol HL₁, and neutralized with NaOH aqueous solution (30 mL) under stirring. Then the mixture was stirred at 60 °C for 3 h. The crude product was collected by filtration. The colourless crystals of 1 were obtained in 55% yield by re-crystallization from ethanol and chloroform mixed solution. Anal. calcd for $C_{90}H_{62}Eu_2Na_2N_{18}O_{14}\cdot2C_2H_5OH\cdot2CHCl_3$ (%): C 46.99, H 2.72, N 10.96. Found: C 46.92, H 2.76, N 10.89.

Complex Eu(L₁)₃(phen) (2). An ethanol solution of $EuCl_3$ (1 mmol) was added to a ethanol solution of 3 mmol HL₁ and

1 mmol 1,10-phenanthroline (phen). The mixture was stirred and neutralized with NaOH aqueous solution. The solution was then evaporated to a small volume. The product was obtained by filtration. The pale yellow crystals were obtained in 45% yield by re-crystallization from ethanol/hexane solution. Anal. calcd for $C_{57}H_{38}EuN_{11}O_6$ (%): C 60.86, H 3.40, N 13.70. Found: C 60.79, H 3.41, N 13.68.

Complex Eu₂Na₂(L₁₎₆(L₂)₂(OH)₂·8CHCl₃ (3). 1 mmol EuCl₃ in ethanol was added to a ethanol solution (30 mL) of 3 mmol HL₁ and 1 mmol L₂. The following steps are similar to those of 1 Yield: 28%. Anal. calcd for C₁₁₄H₇₈Eu₂Na₂N₂₆O₁₆·8CHCl₃ (%): C 40.60, H 2.33, N 10.80. Found: C 40.64, H 2.39, N 10.72.

The X-ray crystal structure determination

Single crystals of complexes 1-3 suitable for X-ray diffraction analysis were grown by solvent evaporation of their solutions. Data collections were performed at ambient temperature on a Rigaku Raxis-IV area detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm). In each case the data were corrected for Lorentz and polarization effects. An absorption correction was applied (SADABS)³⁴ to the collected reflections. The structures were solved by direct methods, and the nonhydrogen atoms were refined anisotropically with the full matrix least-squares based on F^2 . Hydrogen atoms were included but not refined. These structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses with the software SHELXTL.35 The crystallographic data and other experimental details are summarized in Table 1. Selected bond lengths and angles of complexes 1-3 are listed in Tables 2-4, respectively.

Spectroscopic measurements

UV absorption spectra were obtained from methanol solutions with a HP-8453 UV-vis spectrophotometer. Excitation and emission spectra were recorded on HORIBA JOBIN YVON FluoroMax-P spectrophotometer and powder samples were used for this purpose. The decay times of complexes 1, 2 and 3 were measured monitoring the main ${}^{7}F_{2}$ Stark component ($\lambda_{ex} = 365$ nm, 337 nm and 355 nm, respectively) by HORIBA JOBIN YVON FluoroMax-P spectrofluorometer system at room temperature. Mono-exponential functions has been used to fit experimental data and the lifetimes were obtained. The luminescence quantum yields were determined at room temperature on a FL3-2-iHR221-NIR-TCSPC transient and steady-state fluorescence spectrometer using a standard integrating sphere, which coated on the inside with PTFE. The aperture ratio of integrating sphere was less than or equal to 3%. Instrument excitation and emission slits were set at 1 and 1.5 nm, respectively.

The overall luminescence quantum yield, defined by:

 $\Phi_{tot} = \frac{number of photons emitted}{number of photons absorbed}$

was measured at room temperature using the technique for powdered samples described by Bril *et al.*,³⁶ through the following formula:

$$\Phi_{\rm tot} = \left(\frac{1 - r_{\rm st}}{1 - r_{\rm x}}\right) \left(\frac{A_{\rm x}}{A_{\rm st}}\right) \Phi_{\rm s}$$

where r_{st} and r_x are the amount of exciting radiation reflected by the standard and by the sample, respectively, and Φ_{st} is the quantum yield of the standard phosphor (sodium salicylate, Merck). The terms A_x and A_{st} represent the areas under the complex and standard emission spectra, respectively. Three measurements were carried out for each sample, so that the presented Φ_{tot} value corresponds to the arithmetic mean value.

Fabrication of electroluminescent device

The EL device with $Eu(L_1)_3$ (phen) as the emitter layer was fabricated on a patterned indium-tin oxide (ITO) substrate with a sheet resistance of 50 Ω m⁻². The ITO glass is cleaned by ultrasonication in detergent solution, pure water, acetone and chloroform in sequence before using it. All the organics layers and the top cathode layer (Mg_{0.9}Ag_{0.1}) were successively vacuum deposited onto an indium tin oxide (ITO) substrate below a pressure of 1×10^{-5} Torr. The layer thickness is controlled *in vacuo* with a quartz crystal monitor. The EL spectra were measured by HORIBA JOBIN YVON FluoroMax-P spectrometer. The luminance of the EL devices was measured with a spectra Pritchard photometer, model 1980 A, at room temperature under ambient atmosphere.

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