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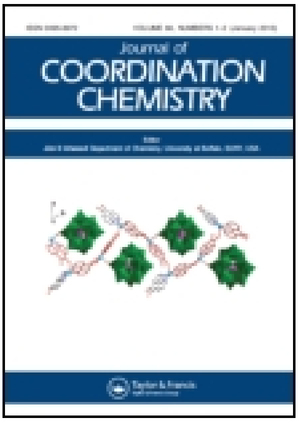

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Syntheses, structures and luminescent properties of a series of ladder-shaped $[Ln_2Sr_3]$ heterometal-organic frameworks

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Syntheses, structures and luminescent properties of a series of ladder-shaped [Ln_2Sr_3] heterometal-organic frameworks

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A series of Ln^{III}–Sr^{II} heterometallic coordination polymers formulated as $[Ln_2Sr_3(pda)_6(H_2O)_{18}]\cdot nH_2O$ (Ln = Pr-**1**, n = 14; Nd-**2**, n = 12; Sm-**3**, n = 11; Eu-**4**, n = 11; Gd-**5**, n = 16; Tb-**6**, n = 13; Dy-**7**, n = 13) were synthesized via assembly of $Ln(NO_3)_3\cdot 6H_2O$, $SrCl_2\cdot 6H_2O$, pyridine-2,6-dicarboxylic acid (H_2pda) and imidazole (im) in H_2O/C_2H_5OH solution. Single crystal X-ray diffraction revealed that they are isostructural. All of these complexes possess ladder-shaped 1-D chain structures. The luminescent properties of Sm-**3**, Eu-**4**, Gd-**5**, Tb-**6** and Dy-**7** have been investigated. The solid-state quantum yields and the lifetimes of Eu-**4** and Tb-**6** are also studied.

Keywords: Heterometallic complexes; Alkaline earth metals; Lanthanide ions; Lifetime; Quantum yield

1. Introduction

Heterometallic complexes have attracted attention due to their applications in magnetism [1–5], molecular adsorption [6–8], catalysis [9, 10], and light conversion devices [11, 12]. We are especially interested in heterometallic complexes containing lanthanide ions, because these complexes often exhibit intense luminescence and have potential applications in lighting devices (television and computer displays, optical fibers, optical amplifiers, and lasers) and biomedical analysis (medical diagnosis and cell imaging) [13–22]. A synthetic challenge involves discovering a good ligand which could simultaneously incorporate many metal ions into a supramolecule. Pyridine-2,6-dicarboxylic acid (H_2pda) is a suitable ligand; it not only can exhibit variable coordination modes, but also can act as the antenna for photosensitization of trivalent Ln^{III} ions [23–30]. H_2pda could coordinate to 4f metals by oxygens of one carboxylic group, and connect to other metals via oxygens of another carboxylic group, generating heterometallic coordination polymers.

In the present work, we have used H_2pda in combination with imidazole for synthesis of some interesting 1-D Ln^{III}–Sr^{II} coordination polymers, $[Ln_2Sr_3(pda)_6(H_2O)_{18}]\cdot nH_2O$

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(Ln = Pr-**1**, *n* = 14; Nd-**2**, *n* = 12; Sm-**3**, *n* = 11; Eu-**4**, *n* = 11; Gd-**5**, *n* = 16; Tb-**6**, *n* = 13; Dy-**7**, *n* = 13). The luminescent properties of Sm-**3**, Eu-**4**, Gd-**5**, Tb-**6** and Dy-**7**, and the solid-state quantum yields and lifetimes of Eu-**4** and Tb-**6** have been studied.

2. Experimental

2.1. *General procedure*

All chemicals were purchased from commercial suppliers and used without purification. C, H and N microanalyses were carried out with a Carlo-Erba EA1110 CHNO-S elemental analyzer. FT-IR spectra were recorded as KBr pellets from 400 to 4000 cm^{-1} on a Nicolet MagNa-IR500 spectrometer. The emissions of samples were collected by two lenses into a monochromator (WDG30), detected by a photomultiplier and processed by a Boxcar Average (EGG model 162) in line with a microcomputer. Reported luminescence lifetimes are averages of at least three independent determinations. Quantum yields were determined by an absolute method using an integrating sphere on FLS920 of Edinburgh Instrument. The luminescence decays were recorded using a pumped dye laser (Lambda Physics model FL2002) as the excitation source.

2.2. *Synthesis of complexes*

A mixture of H_2pda (0.0334 g, 0.2 mM), $SrCl_2 \cdot 6H_2O$ (0.0267 g, 0.1 mM), $Ln(NO_3)_3 \cdot 6H_2O$ (0.0217–0.238 g, 0.05 mM), imidazole (0.0136 g, 0.2 mM,) and H_2O/C_2H_5OH (2.5 mL, v/v = 2:1) was sealed in a Pyrex-tube (8 mL). The tube was heated at 120 °C for 4 days and then was gradually cooled to room temperature, giving crystals of the products. The crystals were collected by filtration, washed with H_2O (3 mL) and dried in air.

$[Pr_2Sr_3(pda)_6(H_2O)_{18}] \cdot 14H_2O$ (Pr-1; light-green): Yield: 61% (0.0214 g). Anal. Calcd for $Pr_2Sr_3C_{42}H_{82}N_6O_{56}$ (%): C, 23.89; H, 3.91; N, 3.98. Found: C, 23.70; H, 3.65; N, 4.10. IR (KBr, cm^{-1}): 3423 (m), 1618 (s), 1433 (s), 1389 (s), 1275 (s), 1188 (s), 1082 (s), 1020 (s), 922 (s), 766 (s), 739 (s), 700 (s), 663 (s).

$[Nd_2Sr_3(pda)_6(H_2O)_{18}] \cdot 12H_2O$ (**Nd-2**; light-purple): Yield: 64% (0.0220 g). Anal. Calcd for $Nd_2Sr_3C_{42}H_{78}N_6O_{54}$ (%): C, 24.22; H, 3.78; N, 4.04. Found: C, 24.57; H, 3.50; N, 3.98. IR (KBr, cm^{-1}): 3406 (m), 1617 (s), 1434 (s), 1390 (s), 1275 (s), 1190 (s), 1082 (s), 1019 (s), 922 (s), 768 (s), 732 (s), 702 (s), 660 (s).

$[Sm_2Sr_3(pda)_6(H_2O)_{18}] \cdot 11H_2O$ (Sm-3; colorless): Yield: 51% (0.0173 g). Anal. Calcd for $Sm_2Sr_3C_{42}H_{76}N_6O_{53}$ (%): C, 24.29; H, 3.69; N, 4.05. Found: C, 24.56; H, 3.29; N, 4.07. IR (KBr, cm^{-1}): 3219 (w), 1634 (s), 1434 (s), 1397 (s), 1277 (s), 1192 (s), 1075 (s), 1022 (s), 923 (s), 776 (s), 732 (w), 697 (w), 665 (s).

$[Eu_2Sr_3(pda)_6(H_2O)_{18}] \cdot 11H_2O$ (**Eu-4**; colorless): Yield: 43% (0.0148 g). Anal. Calcd for $Eu_2Sr_3C_{42}H_{76}N_6O_{53}$ (%): Calcd C, 24.25; H, 3.68; N, 4.04. Found: C, 24.89; H, 3.09; N, 4.28. IR (KBr, cm^{-1}): 3415 (m), 1628 (s), 1435 (s), 1394 (s), 1278 (s), 1192 (s), 1076 (s), 1022 (s), 923 (s), 771 (s), 733 (s), 698 (s), 665 (s).

[$Gd_2Sr_3(pda)_6(H_2O)_{18}$]·$16H_2O$ (**Gd-5**; colorless): Yield: 35% (0.0127 g). Anal. Calcd for $Gd_2Sr_3C_{42}H_{86}N_6O_{58}$ (%): C, 24.13; H, 3.98; N, 3.85. Found: C, 24.38; H, 3.41; N, 4.28. IR (KBr, cm^{-1}): 3448 (m), 1623 (s), 1435 (s), 1390 (s), 1278 (s), 1190 (s), 1076 (s), 1022 (s), 920 (s), 769 (s), 732 (s), 697 (s), 663 (s).

[$Tb_2Sr_3(pda)_6(H_2O)_{18}$]·$13H_2O$ (**Tb-6**; colorless): Yield: 46% (0.0163 g). Anal. Calcd for $Tb_2Sr_3C_{42}H_{80}N_6O_{55}$ (%): C, 23.69; H, 3.79; N, 3.95. Found: C, 23.36; H, 3.45; N, 4.53. IR (KBr, cm^{-1}): 3415 (w), 1624 (s), 1435 (s), 1391 (s), 1278 (s), 1191 (s), 1083 (s), 1022 (s), 924 (s), 768 (s), 735 (s), 664 (s).

[$Dy_2Sr_3(pda)_6(H_2O)_{18}$]·$13H_2O$ (**Dy-7**; colorless): Yield: 48% (0.0170 g). Anal. Calcd for $Dy_2Sr_3C_{42}H_{80}N_6O_{55}$ (%): C, 23.61; H, 3.77; N, 3.93. Found: C, 23.71; H, 3.44; N, 4.10. IR (KBr, cm^{-1}): 3423 (m), 1630 (s), 1437 (s), 1398 (s), 1280 (s), 1194 (s), 1076 (s), 1023 (s), 926 (s), 774 (s), 732 (w), 698 (w), 665 (s).

2.3. *X-ray crystallography*

Crystal determinations were performed with a Bruker SMART APEX-II CCDC diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 [31] and refined on F^2 using full-matrix least-squares with SHELXL-97 [32]. Crystallographic data together with refinement details for the complexes reported in this work are summarized in table 1. For these complexes, no attempt was made to locate hydrogens of water; other hydrogens were generated geometrically and treated as riding.

3. Results and discussion

3.1. *Structural descriptions of [$Ln_2Sr_3(pda)_6(H_2O)_{16}$]·$nH_2O$*

X-ray crystallography reveals that the seven complexes are isostructural and only have slight difference in the number of lattice waters. Here, Nd-**2** is taken as a representative example to depict the structure in detail. Nd-**2** displays a 1-D chain structure which is constructed by alternatively arrayed $[Nd(pda)_3]^{3-}$ and $[Sr(H_2O)_6]^{2+}$ (figure 1). As shown in figure 1(a), Nd1 is chelated by three pda^{2-} with six oxygens and three nitrogens in a tricapped trigonal prism geometry. Each Nd^{III} is connected to two Sr2 ions and one Sr3 ion by three carboxylic groups (O1–C6–O2, O5–C13–O6 and O11–C21–O12) of three pda^{2-}. The Sr2 ion is eight-coordinate by two O of carboxylic groups (O2 and O12A) and six terminal waters with slightly distorted dodecahedral geometry. The O2–Sr2–O12A angle is 136.88(17)°. Sr3 shows a coordination number of eight, coordinated by two carboxylate oxygens (O6 and O6B) and six terminal waters. The O6–Sr3–O6B angle is 180.0°. Four $[Sr(H_2O)_6]^{2+}$ units and four $[Nd(pda)_3]^{3-}$ anions are connected to form a 32-membered $(–Sr–[Nd(CO_2)_2]_2–Sr–)_2$ ring. The 32-membered rings are arrayed shoulder by shoulder to form a ladder-shaped 1-D chain structure (figure 1(b) and (d)). Two strong intermolecular $\pi\cdots\pi$ stacking interactions with centroid-to-centroid distances of two pyridine rings being 3.657 and 3.566 Å, respectively, generate a three-dimensional supramolecular structure (figure 1(c) and (d)) [33]. Complex **2** features O−H···O intermolecular hydrogen bonds between coordinated waters as hydrogen donors and oxygens from carboxylic (or lattice waters) as hydrogen acceptors. The hydrogen bonds between lattice waters and

Table 1. Crystal data and structure refinements for the compounds.

	Pr-1	**Nd-2**	**Sm-3**	**Eu-4**	**Gd-5**	**Tb-6**	**Dy-7**
Formula [a]	$C_{42}H_{82}N_6O_{56}Pr_2Sr_3$	$C_{42}H_{78}N_6O_{54}Nd_2Sr_3$	$C_{42}H_{76}N_6O_{53}Sm_2Sr_3$	$C_{42}H_{76}N_6O_{53}Eu_2Sr_3$	$C_{42}H_{86}N_6O_{58}Gd_2Sr_3$	$C_{42}H80N_6O_{55}Tb_2Sr_3$	$C_{42}H_{80}N_6O_{55}Dy_2Sr_3$
M/gM^{-1} [a]	2111.82	2082.44	2076.65	2076.65	2180.53	2129.82	2136.98
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*
a/Å	10.004(2)	9.9669(4)	9.9041(10)	9.9898(8)	9.8363(8)	9.7752(8)	9.742(3)
b/Å	12.802(3)	12.6485(5)	12.7814(15)	12.8193(11)	12.7281(11)	12.8487(11)	12.844(4)
c/Å	15.119(3)	15.0369(6)	15.0534(17)	15.2726(14)	15.2451(12)	15.0117(12)	14.996(4)
α/°	84.91(3)	85.948(2)	84.208(6)	83.708(2)	83.349(2)	84.292(2)	84.289(6)
β/°	89.38(3)	88.883(2)	88.836(7)	89.802(2)	89.389(2)	89.162(2)	89.214(5)
γ/°	89.16(3)	88.567(2)	88.796(6)	88.990(2)	88.355(2)	88.054(2)	88.087(5)
V/Å^3	1928.2(7)	1890.02(13)	1895.1(4)	1943.8(3)	1895.0(3)	1874.9(3)	1866.0(9)
Z	1	1	1	1	1	1	1
T/K	173(2)	173(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ/Å [b]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_c/g cm^{-3}	1.819	1.830	1.820	1.777	1.911	1.886	1.902
μ/mm^{-1}	3.416	3.566	3.734	3.744	3.944	4.098	4.225
F (000)	1056	1038	1032	1034	1086	1058	1060
θ Range/°	2.04–25.00	1.36–25.00	1.99–25.00	1.97–25.00	1.98–25.00	1.99–28.38	1.99–28.46
Measd/independent	20,762/6693	26,558/6650	15,735/6589	10,629/6800	28,303/6669	13,242/9270	13,082/9280
R_{int} reflections	0.0551	0.0422	0.0952	0.0244	0.0337	0.0235	0.0372
GOF on F^2	1.056	1.052	1.077	1.075	1.108	1.025	1.023
R_1 [c]	0.0708	0.0467	0.0971	0.0563	0.0543	0.0513	0.0696
wR_2 [d,e]	0.1804	0.1357	0.2762	0.1618	0.1481	0.1366	0.2042
$(\Delta\rho)_{max,\ min}$/e Å^{-3}	2.710, −3.005	1.836, −0.795	4.579, −2.115	3.642, −0.692	3.187, −1.684	1.167, −1.102	2.561, −1.416

[a] Including solvate molecules.

[b] Mo Kα radiation.

[c] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ for observed reflections.

[d] $w = 1/[\sigma^2(F_o^2)+(\alpha P)^2 + bP]$ and $P = [\max(F_o^2,0)+2F_c^2]/3$.

[e] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.

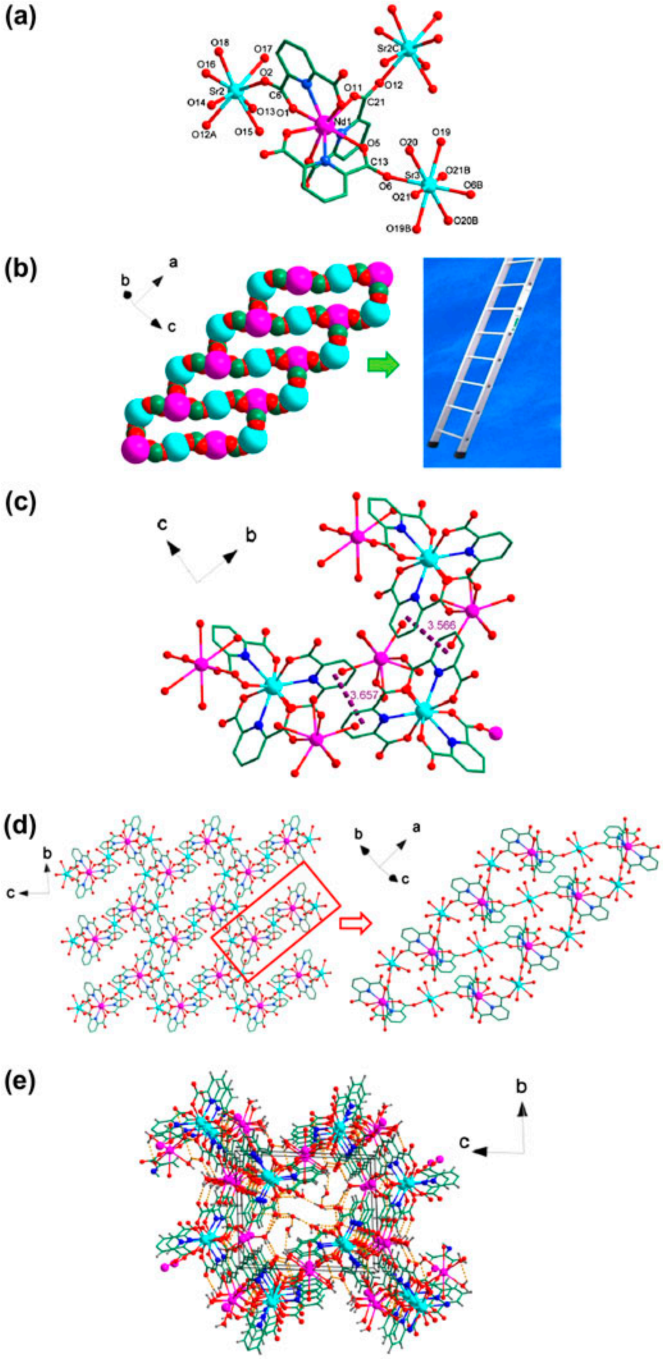

Figure 1. (a) Coordination environments of Sr^{II} and Nd^{III} ions of Nd-**2** (symmetry transformations: A: $x - 1, y, z$; B: $-x + 1, -y, -z + 1$; C: $x + 1, y, z$). (b) The space-filling structure of 32-membered (–Sr–[Nd$(CO_2)_2$]$_2$–Sr–)$_2$ ring in Nd-**2**. (c) The $\pi \cdots \pi$ interactions between the pda^{2-} ligands in Nd-**2**. (d) The structure and packing diagram of Nd-**2** viewed along the *a*-axis; the ladder-shaped configuration of the complex is highlighted. Solvent water molecules and all hydrogens are omitted for clarity. (e) Hydrogen bonding packing diagram of **2**. Color codes: Nd, rose; Sr, light-blue; N, blue; O, red; C, green; H, light-gray (see http://dx.doi.org/10.1080/00958972.2013.855305 for color version).

uncoordinated carboxylate oxygens (or coordinated water) are also found. These hydrogen bonding interactions connect the 1-D chains to form a 3-D supramolecular structure (figure 1(e)). All hydrogen bond distances and angles are summarized in table S8. These hydrogen bonding interactions are similar to those of interactions observed [4, 5, 21, 34–41].

Homometallic coordination complexes of rare earth metals (or alkaline earth metals) are common [42–52], but the heterometallic Ln^{III}–Sr^{II} coordination polymers supported by H_2dpa are very limited [53–55]. To the best of our knowledge, Ln^{III}–Sr^{II} complexes with ladder-shaped structures have not been reported.

3.2. *Luminescent properties*

Solid-state emission spectra of Sm-**3**, Eu-**4**, Tb-**6** and Dy-**7** at room temperature were measured. The low temperature phosphorescence spectrum of Gd-**5** was measured at 77 K. The broad absorption envelope with a peak maximum at ca. 290 nm is attributed to the principal $n \rightarrow \pi^*$ transition of the coordinated pda^{2-} on the basis of previous reports [53]. The spectrum of **3** was measured under excitation at 290 nm. As shown in figure 2(a), Sm-**3** shows four emission bands at 562 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 603 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), 643 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$), 701 and 712 nm ($^4G_{5/2} \rightarrow {}^6H_{11/2}$) [53, 56, 57], respectively.

The emission spectrum of Eu-**4** at room temperature upon excitation at 284 nm (figure 2(b)) originates from the $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4) transitions of 593 nm ($^5D_0 \rightarrow {}^7F_1$),

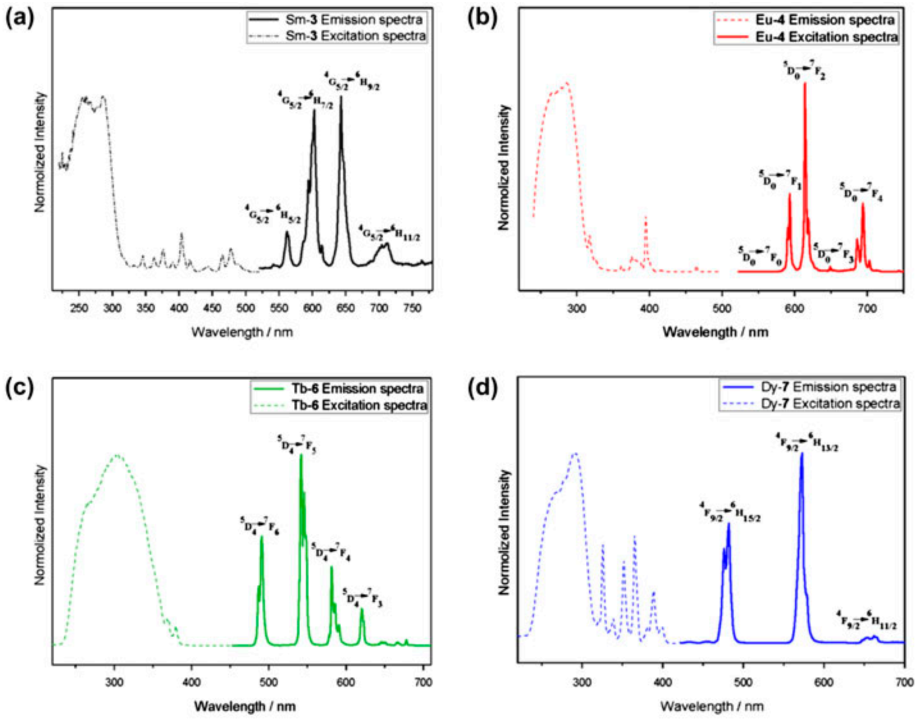

Figure 2. Room-temperature emission spectra for Sm-**3** (a), Eu-**4** (b), Tb-**6** (c) and Dy-**7** (d) in solid state (excitation and emission slits = 1 nm).

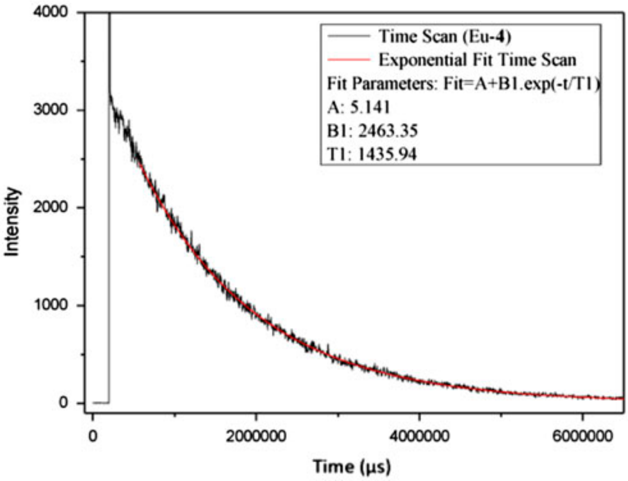

Figure 3. The room-temperature solid-state luminescence lifetime of Eu-**4**.

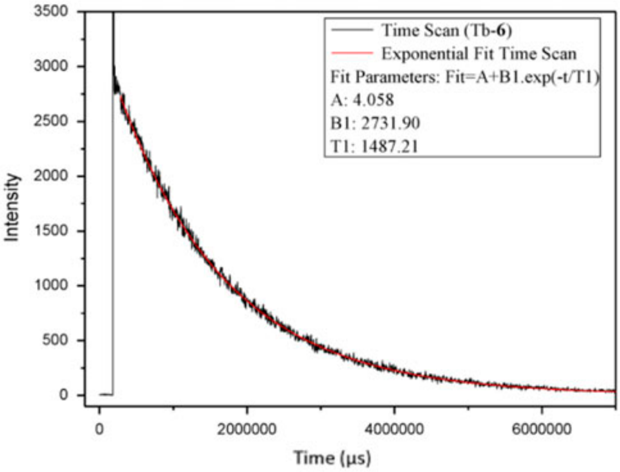

Figure 4. The room-temperature solid-state luminescence lifetime of Tb-**6**.

615 nm ($^5D_0 \rightarrow ^7F_2$), 649 nm ($^5D_0 \rightarrow ^7F_3$), 686 and 694 nm ($^5D_0 \rightarrow ^7F_4$) [53, 57, 58]. The most intense transition is $^5D_0 \rightarrow ^7F_2$, implying red emission of Eu^{III} complexes. The intensity of the $^5D_0 \rightarrow ^7F_2$ transition (electric dipole) is much stronger than that of the $^5D_0 \rightarrow ^7F_1$ transition (magnetic dipole).

Excitation of Tb-**6** at 305 nm displays intense green luminescence and exhibits the characteristic transitions of Tb^{III}. As shown in figure 2(c), the peaks at 487 and 491, 542 and 546, 581 and 586 and 620 nm are attributed to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions [53, 57, 58], respectively. Among these characteristic emission transitions, the $^5D_4 \rightarrow ^7F_5$ (542 and 546) transition shows the strongest green emission.

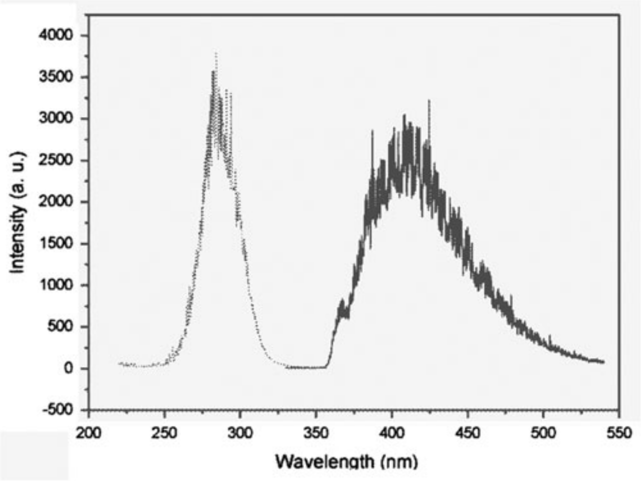

Figure 5. Low-temperature phosphorescence spectrum of Gd-**5** (excitation and emission slits = 1 nm).

Complex Dy-**7** exhibits two apparent emission bands of Dy^{III} (excitation at 285 nm), with the maximum emission wavelengths of 476–482 nm and 573 nm, respectively, which are ascribed to characteristic emissions of $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy^{III}. These bands are in agreement with reported Dy^{III} complexes [53, 56, 57, 59]. The weak intense bands at 655–662 nm are assigned to $^4F_{9/2} \rightarrow ^6H_{11/2}$. As shown in figure 2(d), the intensity of the yellow emission corresponding to $^4F_{9/2} \rightarrow ^6H_{13/2}$ is much stronger than that of the blue ones ($^4F_{9/2} \rightarrow ^6H_{15/2}$).

Solid-state quantum yield measurements were performed to quantify the observed Eu^{III} and Tb^{III} luminescence intensity, using an integrating sphere method. The resulting values for Φ_{total} were 54 ± 10% for Eu-**4** and 73 ± 10% for Tb-**6**. The luminescence lifetimes of solid Eu^{III} and Tb^{III} complexes were also measured, yielding monoexponential decay values of $\tau_{obs} = 1.44 \pm 0.04$ ms for Eu-**4** (figure 3) and $\tau_{obs} = 1.49 \pm 0.04$ ms for Tb-**6** (figure 4).

For a ligand to serve as an effective photosensitizer, the first triplet state should be situated sufficiently above the emitting $^5D_0$ level of Eu^{III} or the $^5D_4$ level of Tb^{III} to permit efficient energy transfer from the triplet state to the higher excited states of the Ln^{III} ions and thereby to prevent quenching by back energy transfer processes. In the present work, the triplet energy levels T_1 of pda^{2-} have been estimated by reference to the lower wavelength emission edges (27,533 cm^{-1}, 363.2 nm for Gd-**5**) of the low-temperature phosphorescence spectrum of the Gd^{III} complex (figure 5). The triplet energy levels of pda^{2-} lie well above the energies of the main emitting levels of $^5D_0$ (17,500 cm^{-1}) for Eu^{III} and $^5D_4$ (20,400 cm^{-1}) for Tb^{III}, thus indicating that pda^{2-} can act as an antenna for photosensitization of trivalent Ln^{III}.

4. Conclusions

A series of Ln^{III}–Sr^{II} heterometallic complexes with ladder-shaped structures have been synthesized and characterized. Their luminescent properties have been investigated; the results show that pda^{2-} can stimulate photosensitization of trivalent Ln^{III} ions.

Supplementary material

Tables S1–S7 give bond lengths and angles for these seven complexes. Figures S1–S7 give the IR spectra for these seven complexes. The special details are described in CIFs. CCDC-773510 (Pr-**1**), -899869 (Nd-**2**), -899483 (Sm-**3**), -899865 (Eu-**4**), -899866 (Gd-**5**), -899494 (Tb-**6**) and -899498 (Dy-**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/conts/retrieving.html. Supplemental data for this article can be accessed http://dx.doi.org/10.1080/00958972.2013.855305.

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