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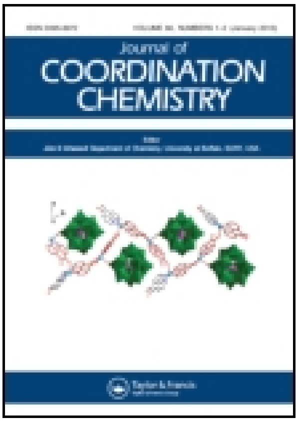

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Synthesis, crystal structures and NIR luminescence of sandwich-like tetradentate salophen phenoxo-bridged heterotrinuclear metal complexes

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Synthesis, crystal structures and NIR luminescence of sandwich-like tetradentate salophen phenoxo-bridged heterotrinuclear metal complexes

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Six phenoxo-bridged tetradentate salophen heterotrinuclear Zn_2Ln complexes, $[Ln(ZnL)_2(NO_3)_3(CH_3OH)_2]\cdot CH_3OH\cdot CH_2Cl_2$ [Ln = Pr (**1**), Nd (**2**)] and $[Ln(ZnL)_2(NO_3)_3(CH_3OH)]\cdot CH_3OH\cdot CH_2Cl_2$ [Ln = Eu (**3**), Ho (**4**), Er (**5**), and Yb (**6**)], have been isolated from reactions of N,N′-bis(salicylidene)-1,2-(phenylene-diamine) with $Ln(NO_3)_36H_2O$ and $Zn(OAc)_22H_2O$. X-ray diffraction analysis reveals that **1**–**6** are isomorphic with phenoxo-bridged, sandwich-like $\{Zn_2Ln\}$ core. Near infrared (NIR) luminescence spectra show that **6** exhibits typical emission of Yb^{3+} upon excitation at the ligand-centered absorption band at 357 nm.

Keywords: Salophen; Heterotrinuclear Zn_2Ln complex; Structure; NIR Luminescence

1. Introduction

Salen metal complexes have been studied for potential applications in homogeneous catalysis, nonlinear optics, magnetics, and biological metalloenzyme mimics [1–10]. Particularly, Salen-type heterometallic complexes have attracted attention due to intriguing properties arising from different metal ions [11–13]. Such complex can be obtained through selection of an appropriate metal ion, Salen-type ligand, bridging group, and counter ion using self-assembly [14–16]. A number of compartmental Salen-type 3d–4f heteronuclear complexes have been addressed with regard to magnetic behavior [17–19] however; photophysical properties have not been addressed systematically. In formation of a series of 3d–4f heterometallic complexes, Salen-type ligands with outer O_2O_2 moieties from RO– groups are apt to bind both 3d and 4f ions [20–25]. Outer RO– groups on Salen-type ligands are not necessary to bind both 3d and 4f ions, because for Salen-type ligands without outer O_2O_2 moieties, two 3d-Salen-type complexes can further coordinate the same 4f ion from their phenolic O, giving a feasible route to 3d–4f heterometallic complexes [26, 27].

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In view of recent reports on structures and luminescent properties of Salen-type heteronuclear metal complexes [28–30] as well as our studies on structures and properties of Salen-type lanthanide complexes [31–35], a series of phenoxo-bridged tetradentate Salophen heterotrinuclear Zn–Ln–Zn complexes **1–6** are synthesized by reactions of Salophen (H_2L) (H_2L = N,N′-bis(salicylidene)-1,2-(phenylene-diamine)) with $Ln(NO_3)_3 \cdot 6H_2O$ and Zn $(OAc)_2 2H_2O$, respectively. The structures of **1–6** are systematically described and near infrared (NIR) luminescence of **6** is investigated and discussed.

2. Results and discussion

2.1. *IR spectra*

Infrared spectra of **1–6** are similar (Supplementary Material). In a typical spectrum of **1**, C=N stretch shifts to higher wavenumbers (by 10–15 cm^{-1} to about 1615 cm^{-1}) in comparison with the same transition in the ligand. This is in accord with $[Ln(H_2L)(NO_3)_3(MeOH)_2]$ (H_2L = N,N′-bis(salicylidene)-1,2-cyclohexanediamine) [36] in which the C=N stretch shifts to higher wavenumbers (by 12–19 cm^{-1} to about 1646 cm^{-1}). Four bands around 1472, 1272, 1167, and 756 cm^{-1} for **1** can be assigned to vibrations of coordinated nitrate, respectively (v_1, v_2, v_3, and v_4). The wavenumber difference of 200 cm^{-1} between v_1 and v_2 is typical for bidentate chelating nitrate (monodentate nitrate groups display much smaller splitting) [37, 38].

2.2. *UV–vis spectra*

UV–vis spectra of the ligand and **1–6** are recorded in MeOH (Supplementary Material). For free ligand, absorptions at 229 and 269 nm are attributed to π–π^* transitions of the aromatic ring and azomethine chromophores. The peak at 332 nm is attributed to n–π^* transition of R band which belongs to azomethine [39–41]. In a typical spectrum of **1**, the absorptions are 242, 294, and 389 nm. UV spectra of **1–6** display similar red shift along with changes in energy levels of the ligand orbitals upon coordination.

2.3. *Structural description*

X-ray crystallographical analysis reveals that **1–6** are isomorphic with a phenoxo-bridged, sandwich-like heterometallic trinuclear core (table 1 and table 2). In a typical structure of **6** (figure 1), the four phenoxo oxygens of the two [ZnL] components coordinate to one Yb^{3+} forming a heterotrinuclear Zn_2Yb core. The Yb^{3+} is eight-coordinate to four bridging phenoxo oxygens and four oxygens from two bidentate NO_3^- adopting a distorted square antiprism geometry. The Yb–O bond lengths are 2.271(3) to 2.426(3) Å in which the bond lengths of Yb–O from phenoxo oxygens (2.271(3) to 2.290(3) Å) are shorter than those from oxygen of NO_3^- (2.382(3) to 2.426(3) Å) (table 3 and table 4). $Zn1^{2+}$ has a five-coordinate environment adopting a distorted square pyramidal geometry, composed of the inner N_2O_2 core from salophen as the basal plane and one methanol attached to $Zn1^{2+}$. $Zn2^{2+}$ has a six-coordinate environment with one nitrate chelated to $Zn2^{2+}$ with one N=O terminal group at the corresponding apical position. The Zn···Yb separations from Zn^{2+} ($Zn1^{2+}$ and $Zn2^{2+}$)

Table 1. Crystal data and structure refinement parameters for **1–3**.

Complexes	**1**	**2**	**3**
CCDC Nos.	853086	853087	853088
Formula	$C_{44}H_{38}Cl_2N_7O_{16}PrZn_2$	$C_{44}H_{38}Cl_2N_7NdO_{16}Zn_2$	$C_{43}H_{38}Cl_2EuN_7O_{15}Zn_2$
FW/g mol^{-1}	1263.41	1266.73	1246.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$	$P\ \bar{1}$
a (Å)	12.297(3)	12.280(3)	11.052(2)
b (Å)	29.245(6)	29.186(6)	12.394(3)
c (Å)	18.129(6)	18.163(6)	19.440(4)
α (°)	90.00	90.00	73.56(3)
β (°)	129.90(2)	130.21(2)	79.36(3)
γ (°)	90.00	90.00	67.93(3)
V (Å^3)	5002(2)	4971(2)	2357.6(8)
F (000)	2528	2531	1244
Z	4	4	2
D_{calc} (g cm^{-3})	1.678	1.692	1.756
μ (mm^{-1})	2.156	2.169	2.513
θ range (°)	3.00−27.46	3.02−27.46	3.09−27.48
R_1, wR_2 (I > 2σ (I))	0.0754, 0.1785	0.0812, 0.2553	0.0439, 0.1253
R_1, wR_2 (all data)	0.1378, 0.2031	0.1151, 0.2730	0.0554, 0.1439
GOF on F^2	1.003	1.075	1.101
$\Delta\rho$ (e Å^{-3})	0.894, –0.818	1.274, –1.075	1.411, –1.113

Table 2. Crystal data and structure refinement parameters for **4–6**.

Complexes	**4**	**5**	**6**
CCDC no.	853089	752454	744119
Formula	$C_{43}H_{37}Cl_2HoN_7O_{15}Zn_2$	$C_{43}H_{38}Cl_2ErN_7O_{15}Zn_2$	$C_{43}H_{38}Cl_2N_7O_{15}YbZn_2$
FW/g mol^{-1}	1258.41	1261.70	1267.48
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$
a (Å)	11.033(2)	11.045(2)	11.015(2)
b (Å)	12.388(3)	12.386(3)	12.366(3)
c (Å)	19.409(4)	19.394(4)	19.380(4)
α (°)	73.77(3)	73.88(3)	73.791(9)
β (°)	79.45(3)	79.27(3)	79.657(7)
γ (°)	68.05(3)	67.94(3)	68.121(7)
V (Å^3)	2353.2(9)	2352.2(8)	2343.9(10)
F (0 0 0)	1250	1254	1258
Z	2	2	2
D_{calc} (g cm^{-3})	1.776	1.781	1.796
μ (mm^{-1})	2.866	2.969	3.184
θ range (°)	3.10–27.48	3.10–25.00	3.09–27.46
R_1, wR_2 ($I > 2\sigma(I)$)	0.0397, 0.1113	0.0356, 0.0946	0.0396, 0.1017
R_1, wR_2 (all data)	0.0466, 0.1183	0.0417, 0.0980	0.0439, 0.1039
GOF on F^2	1.067	1.057	1.050
$\Delta\rho$ (e Å^{-3})	1.575, –0.894	1.451, –0.936	1.839, –1.791

with Yb^{3+} ions bridged by four phenoxo oxygens of two salophen are 3.3078(8) and 3.3571 (15) Å, respectively. The dihedral angles of the aromatic ring of salicylaldehyde coordinated to $Zn1^{2+}$ and $Zn2^{2+}$ are 20.185° and 8.132°, respectively. The Zn1–Yb–Zn2 angle of 85.18(2)° is smaller than a right angle.

The trinuclear Zn_2Yb array in **6** is a sandwich-like structure, different than the trinuclear Zn_2Ln complexes from salen-type ligands with outer MeO (hexadentate), which is a

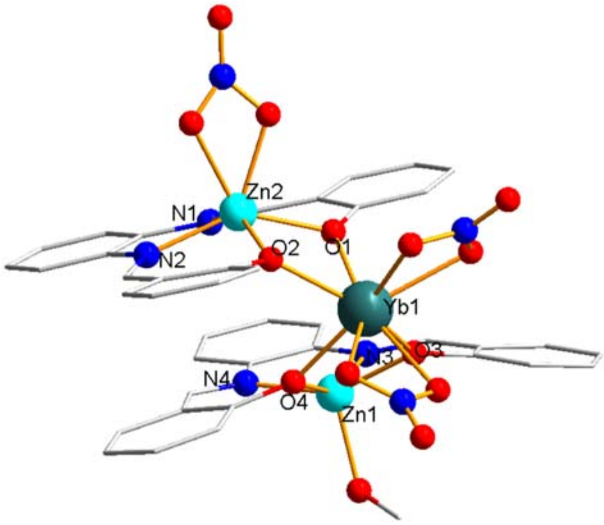

Figure 1. Molecular structure of **6** (hydrogens are omitted for clarity).

Table 3. Selected bond lengths (Å) and angles (°) for **1–3**.

1		**2**		**3**	
Pr(1)–O(2)	2.432(6)	Nd(1)–O(2)	2.409(7)	Eu(1)–O(3)	2.348(3)
Pr(1)–O(8)	2.445(6)	Nd(1)–O(8)	2.416(7)	Eu(1)–O(4)	2.353(3)
Pr(1)–O(9)	2.428(6)	Nd(1)–O(9)	2.407(7)	Eu(1)–O(5)	2.388(5)
Pr(1)–O(11)	2.495(6)	Nd(1)–O(11)	2.493(8)	Eu(1)–O(6)	2.366(5)
Pr(1)–Zn(2)	3.4616(16)	Nd(1)–Zn(2)	3.4464(18)	Eu(1)–Zn(1)	3.3788(9)
Pr(1)–Zn(3)	3.4918(16)	Nd(1)–Zn(3)	3.4811(18)	Eu(1)–Zn(2)	3.4269(15)
O(8)–Pr(1)–O(2)	68.58(19)	O(8)–Nd(1)–O(2)	69.1(2)	O(3)–Eu(1)–O(6)	140.36(10)
O(8)–Pr(1)–O(9)	133.73(18)	O(8)–Nd(1)–O(9)	134.5(2)	O(3)–Eu(1)–O(4)	69.71(11)
O(11)–Pr(1)–O(9)	66.7(2)	O(11)–Nd(1)–O(9)	67.0(3)	O(5)–Eu(1)–O(6)	69.03(11)
Zn(3)–Pr(1)–Zn(2)	80.34(4)	Zn(3)–Nd(1)–Zn(2)	80.98(4)	Zn(1)–Eu(1)–Zn(2)	84.23(3)

Table 4. Selected bond lengths (Å) and angles (°) for **4–6**.

4		**5**		**6**	
Ho(1)–O(3)	2.319(3)	Er(1)–O(1)	2.295(3)	Yb(1)–O(1)	2.271(3)
Ho(1)–O(4)	2.320(3)	Er(1)–O(2)	2.295(3)	Yb(1)–O(2)	2.275(2)
Ho(1)–O(5)	2.301(3)	Er(1)–O(3)	2.310(3)	Yb(1)–O(3)	2.291(2)
Ho(1)–O(6)	2.302(3)	Er(1)–O(4)	2.307(3)	Yb(1)–O(4)	2.281(2)
Ho(1)–Zn(1)	3.3389(9)	Er(1)–Zn(3)	3.3324(9)	Yb(1)–Zn(1)	3.3081(8)
Ho(1)–Zn(2)	3.3861(15)	Er(1)–Zn(2)	3.3744(15)	Yb(1)–Zn(2)	3.3575(15)
O(3)–Ho(1)–O(6)	141.31(9)	O(1)–Er(1)–O(2)	70.62(11)	O(1)–Yb(1)–O(2)	71.02(9)
O(3)–Ho(1)–O(4)	70.87(10)	O(3)–Er(1)–O(2)	141.65(10)	O(2)–Yb(1)–O(3)	142.20(8)
O(5)–Ho(1)–O(6)	70.32(10)	O(1)–Er(1)–O(3)	70.89(16)	O(3)–Yb(1)–O(4)	71.51(9)
Zn(1)–Ho(1)–Zn(2)	84.68(3)	Zn(3)–Er(1)–Zn(2)	85.12(3)	Zn(1)–Yb(1)–Zn(2)	85.18(2)

propeller-like trinuclear structure [42, 43]. The packing structure of **6** along the *y* axis (figure 2) shows terminal CH_3OH and nitrates play a role in crystal packing of the Zn_2Yb clusters since there are close O···H–O interactions which link adjacent molecules (1.904 and 3.194 Å) forming 1D structures (figure 3). Intermolecular and intramolecular π–π

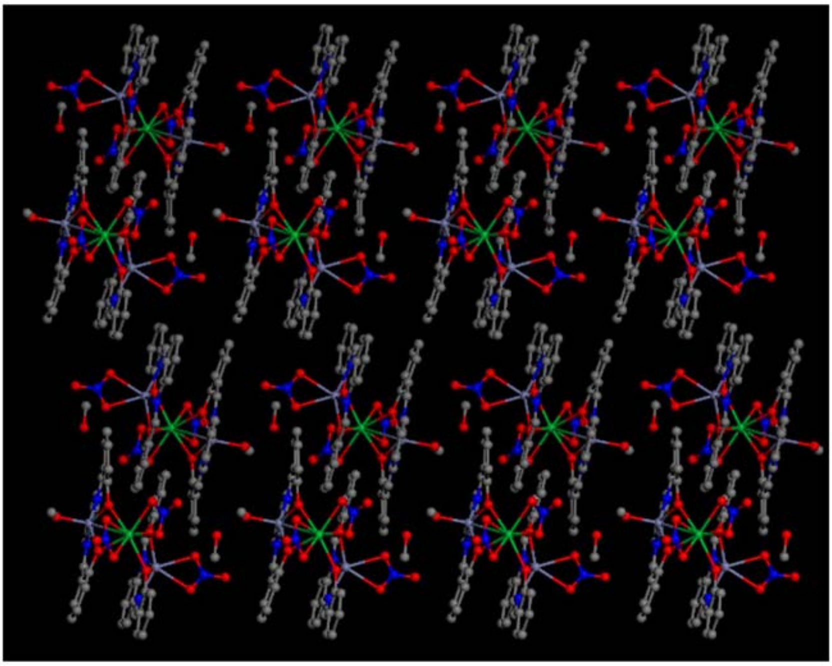

Figure 2. Packing view of **6** along the *y* axis (hydrogens are omitted for clarity).

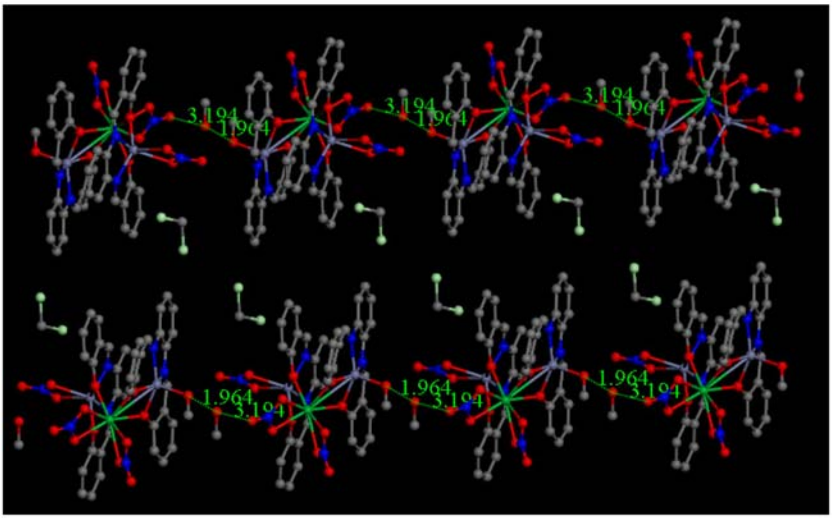

Figure 3. O···H–O hydrogen bonded interactions between nitrate and CH_3OH in **6** (hydrogens are omitted for clarity).

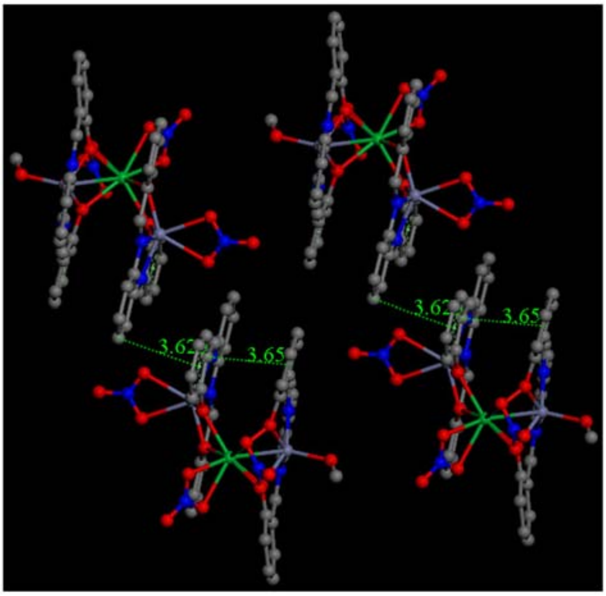

Figure 4. Intermolecular and intramolecular π–π stacking interactions between aryl groups (hydrogens are omitted for clarity).

stacking interactions between phenyl units could be detected. The distances range from 3.625 to 3.655 Å (figure 4). Recently, Jones *et al*. reported the trinuclear Zn_2Ln complexes from salen-type ligands with the outer MeO (hexadentate) in which the Ln^{3+} are sandwiched between two ZnL moieties similar to **6**, however, the Ln^{3+} ions are of different coordination numbers due to two oxygens involved in coordination from the outer MeO groups [44]. Structures of **1–6** are also different from other heterotrinuclear complexes from salen-type ligands without the outer MeO groups. Banu *et al*. have reported a heterotrinuclear copper(II)-praseodymium complex, where praseodymium connected with both copper(II) centers simultaneously through a rare nitrate bridge but does not form a sandwich-like structure [45].

2.4. *Thermal analysis*

TG–DSC curves for **1–6** are similar. In typical TG–DSC curves of **1** (Supplementary Material), the first weight loss of 9.23% is from 20–180 °C, attributed to loss of one uncoordinated MeOH and one Cl_2CH_2 (theoretical loss is 9.26%). Upon further heating, **1** loses coordinated MeOH and then metal-organic framework decomposition begins at 390 °C.

2.5. *Luminescent properties*

NIR photoluminescence of **6** in different solvents is conducted (figure 5). When excited at 357 nm, emissions centered at 977 nm in both CH_3OH and CH_3CN are attributed to $^2F_{5/2}$–$^2F_{7/2}$ transition. However, free Salophen does not exhibit NIR luminescence under the same conditions. The absence of typical Yb^{3+} excitation bands in the excitation spectra and the ligand-centered luminescence in the emission spectra of **6** indicates that the ligand-to-metal energy transfer takes place efficiently. NIR Yb^{3+} luminescence intensity of

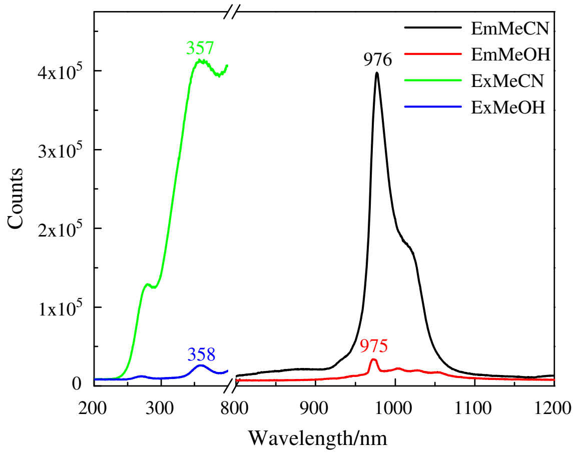

Figure 5. NIR spectra of **6** in CH_3OH and CH_3CN (1×10^{-5} mol/L).

6 in CH_3CN is stronger than that in CH_3OH, attributed to O–H oscillators in CH_3OH, coupling of overtones and the excited state of Yb^{3+}, resulting in nonradiative transition, which also quenches the NIR luminescence [31].

3. Conclusions

Isolation and characterization of **1–6** suggest that salophen (N,N′-bis(salicylidene)-1,2-(phenylene-diamine)) coordinates to Zn^{2+} and Ln^{3+} forming phenoxo-bridged, sandwich-like heterotrinuclear structures independent of radii of lanthanide ions, indicating that tetradentate salophen prefers to form sandwich-like heterotrinuclear structures rather than propeller-like heterotrinuclear structure, although other structures have been isolated depending on the reaction conditions. NIR luminescence shows that N,N′-bis(salicylidene)-1,2-(phenylene-diamine) as the ligand effectively sensitizes the lanthanide-centered NIR luminescence of Yb^{3+} and the solvents affect the NIR luminescence in **6**.

4. Experimental

4.1. *Materials and methods*

All operations were performed in an open atmosphere. H_2L was prepared according to the reported method [46]. $Ln(NO_3)_36H_2O$ (Ln = Pr, Nd, Eu, Ho, Er, and Yb) were prepared by reactions of lanthanide oxides with nitric acid. Other chemicals were commercially available and generally used as supplied. Elemental (C, H and N) analyzes were performed on a Perkin-Elmer 2400 analyzer. FT–IR spectra were obtained on a Perkin-Elmer Spectrum 100 FT–IR spectrometer using KBr disks from 4000–500 cm^{-1}. UV spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer. Thermal analyzes were carried out on a STA-6000 with a heating rate of 10 °C min^{-1} from 20 to 800 °C in N_2. NIR luminescence of **6** was measured with the FLS920 Combined Stead State Fluorescence and Phosphorescence Lifetime Spectrometer.

4.2. *Syntheses*

4.2.1. Synthesis of 1. A mixture of H_2L (0.0632 g, 0.2 mM) in dichloromethane (10 ml) and $Zn(OAc)_2 \cdot 2H_2O$ (0.0440 g, 0.2 mM) in methanol (5 ml) was stirred for 30 min at room temperature. Then, a solution of $Pr(NO_3)_3 \cdot 6H_2O$ (0.0435 g, 0.1 mM) in methanol (10 ml) was added with constant stirring. After 3 h, the resultant solution was filtered and the filtrate was diffused slowly by ether or petroleum ether (60–90 °C). Yellow crystals of **1** were obtained in one week. Yield: 0.0844 g (56%). Elemental analysis (%) Calcd for $C_{44}H_{38}Cl_2N_7O_{16}PrZn_2$ (1263.36): C, 41.83; H, 3.03; N, 7.76. Found: C, 41.81; H, 3.01; N, 7.73. IR (KBr pellet, cm^{-1}) ν_{max}: 3034 (s), 1615 (s), 1585 (m), 1547 (m), 1530 (m), 1472 (m), 1272 (s), 1287 (s), 1167 (s), 756 (s). UV–vis (CH_3OH, 25 °C): λ_{max} (nm) = 242, 294, 389.

4.2.2. Synthesis of 2. The same synthesis process as for **1** was used except Nd $(NO_3)_3 \cdot 6H_2O$ (0.0438 g, 0.1 mM) substitutes for $Pr(NO_3)_3 \cdot 6H_2O$. Yellow crystals of **2** were obtained in one week. Yield: 0.0770 g (51%). Elemental analysis (%) Calcd for $C_{44}H_{38}Cl_2N_7NdO_{16}Zn_2$ (1266.73): C, 41.83; H, 3.03; N, 7.76. Found: C, 41.81; H, 3.01; N, 7.73. IR (KBr pellet, cm^{-1}) ν_{max}: 3445 (s), 1614 (s), 1589 (m), 1544 (m), 1525 (m), 1469 (m), 1278 (s), 1163 (s), 758 (s). UV–vis (CH_3OH, 25 °C): λ_{max} (nm) = 243, 293, 388.

4.2.3. Synthesis of 3. The same synthesis process as for **1** was used except Eu $(NO_3)_3 \cdot 6H_2O$ (0.0446 g, 0.1 mM) substitutes for $Pr(NO_3)_3 \cdot 6H_2O$. Yellow crystals of **3** were obtained in one week. Yield: 0.0805 g (53%). Elemental analysis (%) Calcd for $C_{43}H_{38}Cl_2EuN_7O_{15}Zn_2$ (1246.44): C, 41.44; H, 3.07; N, 7.87. Found: C, 41.41; H, 3.01; N, 7.80. IR (KBr pellet, cm^{-1}) ν_{max}: 3049 (s), 1613 (s), 1585 (m), 1547 (m), 1530 (m), 1378 (m), 1268 (s), 1186 (s), 754 (s). UV–vis (CH_3OH, 25 °C): λ_{max} (nm) = 241, 293, 383.

4.2.4. Synthesis of 4. The same synthesis as for **1** was used except $Ho(NO_3)_3 \cdot 6H_2O$ (0.0459 g, 0.1 mM) substitutes for $Pr(NO_3)_3 \cdot 6H_2O$. Yellow crystals of **4** were obtained in one week. Yield: 0.0827 g (54%). Elemental analysis (%) Calcd for $C_{43}H_{37}Cl_2HoN_7O_{15}Zn_2$ (1258.41): C, 41.01; H, 3.04; N, 7.79. Found: C, 40.97; H, 3.01; N, 7.76. IR (KBr pellet, cm^{-1}) ν_{max}: 3056 (s), 1612 (s), 1585 (m), 1547 (m), 1480 (m), 1378 (m), 1261 (s), 1159 (s), 756 (s). UV–vis (CH_3OH, 25 °C): λ_{max} (nm) = 241, 292, 389.

4.2.5. Synthesis of 5. The same synthesis as for **1** was used except $Er(NO_3)_3 \cdot 6H_2O$ (0.0461 g, 0.1 mM) substitutes for $Pr(NO_3)_3 \cdot 6H_2O$. Yellow crystals of **5** were obtained in one week. Yield: 0.0859 g (56%). Elemental analysis (%) Calcd for $C_{43}H_{38}Cl_2ErN_7O_{15}Zn_2$ (1261.70): C, 40.93; H, 3.41; N, 7.77. Found: C, 40.95; H, 3.39; N, 7.76. IR (KBr pellet, cm^{-1}) ν_{max}: 3436 (s), 1613 (s), 1586 (m), 1548 (m), 1529 (m), 1280 (s), 1168 (s), 757 (s). UV–vis (CH_3OH, 25 °C): λ_{max} (nm) = 241, 292, 388.

4.2.6. Synthesis of 6. The same synthesis as for **1** was used except $Yb(NO_3)_3 \cdot 6H_2O$ (0.0467 g, 0.1 mM) substitutes for $Pr(NO_3)_3 \cdot 6H_2O$. Yellow crystals of **6** were obtained in one week. Yield: 0.0816 g (53%). Elemental analysis (%) Calcd for $C_{43}H_{38}Cl_2N_7O_{15}YbZn_2$ (1267.48): C, 40.74; H, 3.02; N, 7.74. Found: C, 40.70; H, 3.01; N, 7.71. IR (KBr pellet, cm^{-1}) ν_{max}: 3436 (s), 1613 (s), 1585 (m), 1547 (m), 1530 (m), 1279 (s), 1160 (s), 751 (s). UV–vis (CH_3OH, 25 °C): λ_{max} (nm) = 241, 294, 388.

4.3. *X-ray crystallographic determination*

Suitable single crystals of **1–6** were selected for X-ray diffraction analysis. Structural analyzes were performed on a Siemens SMART charge coupled device diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program [47]. All data were collected at a temperature of 20 ± 2 °C. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program [48]. All nonhydrogen atoms are anisotropically refined.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 853086–853089, 752454, 744119 for **1–6**. Copies of the information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (Fax:+44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with IR and UV spectra can be found in the online version.

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