

1,2-环己二胺缩邻香兰素单核与四核镱稀土配合物的近红外性质

范仲天¹ 高 博¹ 董艳萍¹ 邹晓艳^{*,1,2} 李光明^{*,1}

(¹黑龙江大学化学化工与材料学院,功能无机材料化学省部共建教育部重点实验室,哈尔滨 150080)

(²《黑龙江大学工程学报》编辑部,哈尔滨 150080)

摘要: 通过配体 1,2-环己二胺缩邻香兰素(H₂L)和不同的镱盐反应,合成了 4 个镱稀土配合物[Yb(H₂L)₂](ClO₄)₃·2CH₃OH·H₂O (**1**), [Yb₄(L)₄(NO₃)₂(H₂O)₂](PF₆)₂·4CH₃CN (**2**), [Yb₄(L)₄(H₂O)₂Cl₂](PF₆)₂·2CH₂Cl₂·2H₂O (**3**)和[Yb₄(L)₄(NO₃)₂(H₂O)₂][Yb(NO₃)₃(H₂O)₂(CH₃OH)](NO₃)₂·4CH₂Cl₂·6CH₃OH (**4**)。X 射线单晶衍射分析表明配合物 **1** 为零维的单核结构,配合物 **2~4** 均为四核结构。研究了 4 个配合物的近红外发光性能。

关键词: 近红外发光; 镱配合物; 结构

中图分类号: O614.346

文献标识码: A

文章编号: 1001-4861(2017)08-1489-08

DOI: 10.11862/CJIC.2017.182

NIR Luminescent *N,N'*-Bis(3-methoxy-salicylidene)cyclohexane-1,2-diamine Mono- and Tetra-nuclear Ytterbium Complexes

FAN Zhong-Tian¹ GAO Bo¹ DONG Yan-Ping¹ ZOU Xiao-Yan^{*,1,2} LI Guang-Ming^{*,1}

(¹Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China)

(²Editorial Board of Journal of Engineering of Heilongjiang University, Harbin 150080, China)

Abstract: A series of four *N,N'*-bis(3-methoxy-salicylidene)cyclohexane-1,2-diamine(H₂L) ytterbium complexes, namely, [Yb(H₂L)₂](ClO₄)₃·2CH₃OH·H₂O (**1**), [Yb₄(L)₄(NO₃)₂(H₂O)₂](PF₆)₂·4CH₃CN (**2**), [Yb₄(L)₄(H₂O)₂Cl₂](PF₆)₂·2CH₂Cl₂·2H₂O (**3**) and [Yb₄(L)₄(NO₃)₂(H₂O)₂][Yb(NO₃)₃(H₂O)₂(CH₃OH)](NO₃)₂·4CH₂Cl₂·6CH₃OH (**4**) have been isolated by reactions of H₂L with various ytterbium salts. X-ray crystallographic analysis reveals that complex **1** is of a discrete mononuclear structure, and complexes **2~4** are of homoleptic tetra-nuclear structure. The NIR luminescence of all complexes were investigated and discussed. CCDC: 916031, **1**; 916032, **2**; 916034, **3**; 916033, **4**.

Keywords: NIR luminescent; ytterbium complexes; structure

0 Introduction

Much recent interest has been focused on the design and preparation of the polynuclear lanthanide complexes, because they could be potentially used in

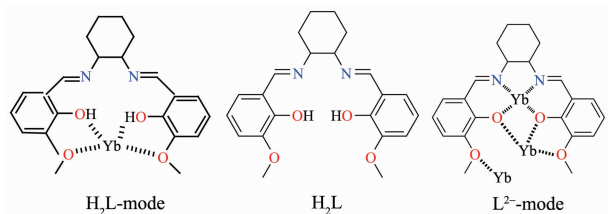
fluorescence^[1-5], magnetism^[6-11]. However, direct excitation of Ln³⁺ ions is difficult because of the weak (Laporte-forbidden) nature of their *f-f* transitions. In order to hurdle it, well-designed organic chromophores have been used to act as antennas^[12-14]. It is well

收稿日期: 2017-05-18。收修改稿日期: 2017-06-23。

国家自然科学基金(No.51402092, 21601132)资助项目。

*通信联系人。E-mail: zxy_18889@126.com, gmli_2000@163.com

known that salen type ligands are able to stabilize different metals in various coordination environment^[15-16]. And a series of salen type ligands have been employed in the synthesis of numerous metal complexes, such as a number of salen type homo-polynuclear complexes, some of which exhibit intriguing magnetic^[17-20] and luminescent properties^[21-23]. Previously, Jones and co-workers have reported some salen type ligands to stabilize Ln^{3+} centers and provide the antenna for lanthanide NIR luminescence, *e.g.*, Jones et al. have reported the first salen type sandwich Yb_3 complex which shows NIR luminescence of the Yb^{3+} ion in 2005^[24]. In 2012, they have presented the homoleptic cyclic tetranuclear complexes which exhibit NIR luminescence of the Nd^{3+} ions and Yb^{3+} ions^[25-26]. However, the synthesis and structures are often influenced by a variety of factors, such as the structure of the ligand, the ionic radius of the lanthanide ions and the nature of the counter ions. To the best of our knowledge, few mono-nuclear lanthanide complexes constructed from flexible hexa-dentate salen type ligands with the outer O_2O_2 moiety has been documented. In view of recent emerging significance of homo-polynuclear lanthanide complexes in NIR luminescence and magnetism, based on the hexa-dentate ligand H_2L (*N,N'*-bis(3-methoxy-salicylidene)cyclohexane-1,2-diamine) with the richness of coordination codes (L^{2-} and H_2L modes, Scheme 1). The semi-rigid salen type ligand of H_2L and various ytterbium salts were employed in the experiment to explore the structures and NIR luminescence of the salen type lanthanide complexes. As a result, a series of four mono- and tetra-nuclear ytterbium complexes have been isolated. Their structures have been determined and described as well as their NIR luminescence have been investigated and discussed.



Scheme 1 Molecular structure and bonding modes of the salen type ligand H_2L for mono- and tetra-nuclear ytterbium complexes **1-4**

1 Experimental

1.1 Materials and general methods

All chemicals except $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ and H_2L were obtained from commercial sources and used without further purification. $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ were prepared by the reactions of Ln_2O_3 and hydrochloric acid, nitric acid and perchloric acid in aqueous solution, respectively. H_2L was prepared according to the reported method^[25]. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 analyzer. FT-IR spectra were obtained on a Perkin-Elmer Spectrum 100 spectrophotometer by using KBr disks in the range of $4\,000\sim 500\text{ cm}^{-1}$. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer. Thermal analyses were conducted on a Perkin-Elmer STA 6000 with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in a temperature range from 30 to $800\text{ }^\circ\text{C}$ under atmosphere. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instruments (FLS 920) with a microsecond pulse lamp as the excitation.

1.2 Syntheses of complexes **1-4**

1.2.1 Synthesis of $[\text{Yb}(\text{H}_2\text{L})_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**)

To a stirred solution of H_2L (0.2 mmol, 0.077 g) in absolute CH_2Cl_2 (10 mL), a solution of $\text{Yb}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mmol, 0.063 g) in absolute CH_3OH (10 mL) were added. The resultant mixed solution was allowed to stir for 10 h at room temperature. The solution was filtered and petroleum ether was allowed to diffuse slowly into the filtrate at room temperature and yellow crystals were obtained in a week. For **1**: Yield: 0.083 g, 63%. Anal. Calcd. for $\text{C}_{46}\text{H}_{60}\text{YbCl}_3\text{N}_4\text{O}_{23}$ (%): C, 41.97; H, 4.59; N, 4.26; Found(%): C, 41.92; H, 4.72; N, 4.24. IR (KBr, cm^{-1}): 3 392 (w), 2 952 (w), 1 643 (s), 1 503 (m), 1 451 (m), 1 228 (s), 1 122 (s), 1 093 (s), 745 (w), 627 (w). UV-Vis(CH_3OH , λ_{max} / nm): 226, 274, 361.

1.2.2 Synthesis of $[\text{Yb}_4(\text{L})_4(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{PF}_6)_2 \cdot 4\text{CH}_3\text{CN}$ (**2**)

To a stirred solution of H_2L (0.2 mmol, 0.077 g)

in absolute CH_3CN (10 mL), a solution of $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.093 g) in absolute CH_3OH (10 mL) were added. The mixed solution was allowed to stir for 2 h at room temperature, and then NH_4PF_6 (0.3 mmol, 0.049 g) was added to the solution. The resultant mixture was allowed to stir for 10 h at room temperature. The yellow solution was then filtered and diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and yellow crystals were obtained in a week. For **2**: Yield: 0.072 g, 53%. Anal. Calcd. for $\text{C}_{96}\text{H}_{112}\text{Yb}_4\text{F}_{12}\text{N}_{14}\text{O}_{24}\text{P}_2$ (%): C, 40.77; H, 3.99; N, 6.93; found: C, 39.98; H, 3.91; N, 6.91%. IR (KBr, cm^{-1}): 3 423 (w), 2 937 (m), 2 857 (m), 1 650 (s), 1 619 (m), 1 472 (s), 1 384 (m), 1 290 (m), 1 227 (m), 844 (s), 742 (m), 559 (m). UV-Vis(CH_3OH , λ_{max} / nm): 221, 264, 338.

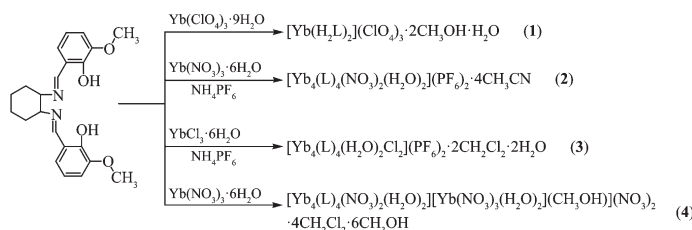
1.2.3 Synthesis of $[\text{Yb}_4(\text{L})_4(\text{H}_2\text{O})_2\text{Cl}_2](\text{PF}_6)_2 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**3**)

The synthesis of **3** is similar to **2** except that $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.078 g) was used instead of $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. For **3**: Yield: 0.067 g, 48%. Anal.

Calcd. for $\text{C}_{90}\text{H}_{104}\text{Yb}_4\text{Cl}_6\text{F}_{12}\text{N}_8\text{O}_{20}\text{P}_2$ (%): C, 38.43; H, 3.73; N, 3.98; Found(%): C, 38.36; H, 3.90; N, 3.96. IR (KBr, cm^{-1}): 2 936 (m), 2 859 (m), 1 648 (s), 1 618 (m), 1 386 (m), 1 292 (m), 1 226 (m), 844 (s). UV-Vis(CH_3OH , λ_{max} / nm): 224, 271, 342.

1.2.4 Synthesis of $[\text{Yb}_4(\text{L})_4(\text{NO}_3)_2(\text{H}_2\text{O})_2][\text{Yb}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})](\text{NO}_3)_2 \cdot 4\text{CH}_2\text{Cl}_2 \cdot 6\text{CH}_3\text{OH}$ (**4**)

To a stirred solution of H_2L (0.2 mmol, 0.077 g) in absolute CH_2Cl_2 (25 mL), a solution of $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.093 g) in absolute CH_3OH (5 mL) were added. The yellow solution was then filtered and petroleum ether was allowed to diffuse slowly into the filtrate at room temperature and yellow crystals were obtained in a week. For **4**: Yield: 0.078 g, 49%. Anal. Calcd. for $\text{C}_{99}\text{H}_{135}\text{Yb}_5\text{Cl}_8\text{N}_{13}\text{O}_{42}$ (%): C, 35.73; H, 4.09; N, 5.47; Found(%): C, 35.15; H, 3.81; N, 5.59. IR (KBr, cm^{-1}): 3 425 (w), 2 936 (m), 2 860 (m), 1 651 (s), 1 508 (m), 1 470 (m), 1 385 (m), 1 313 (m), 1 227 (m), 742 (m). UV-Vis(CH_3OH , λ_{max} / nm): 223, 274, 353.



Scheme 2 Syntheses of complexes **1~4**

1.3 X-ray crystallography

Suitable single crystals of **1~4** were selected for X-ray diffraction analysis. Single-crystal X-ray data of **1~4** were collected using an Oxford Xcalibur Gemini Ultra diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 293 K. The structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program^[27]. The Yb^{3+} , NO_3^- and Cl^- were easily located, and then non-hydrogen atoms (C, N and O) were placed from the subsequent Fourier-difference maps. All non-hydrogen atoms were refined anisotropically. Crystallographic data and structure refinement parameters for the complexes are presented in Table 1. The SQUEEZE results were consistent

with TG-DSC and elemental analysis. The CH_3CN , CH_2Cl_2 , CH_3OH and H_2O molecules have been included in the formula for the calculation of intensive properties. The SQUEEZE results have been appended to the CIF files.

CCDC: 916031, **1**; 916032, **2**; 916034, **3**; 916033, **4**.

2 Results and discussion

2.1 Synthesis and spectral analysis

As shown in Scheme 2, complex **1** was synthesized by the reaction of H_2L with $\text{Yb}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ with the ligand-to-metal molar ratio of 2:1, while complexes **2~4** were synthesized by the reaction of H_2L with $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and/or NH_4PF_6 with the ligand-to-metal molar ratio of 1:1. In the FT-IR spectra (Fig.

Table 1 Crystal data and structure refinement for complexes 1~4

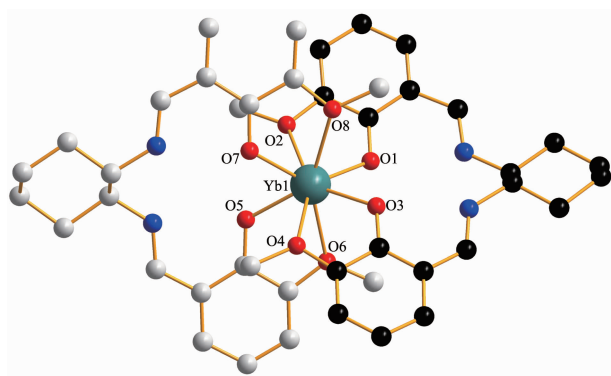
Complex	1	2	3	4
Formula	C ₄₆ H ₆₀ YbCl ₃ N ₄ O ₂₃	C ₉₆ H ₁₁₂ Yb ₄ F ₁₂ N ₁₄ O ₂₄ P ₂	C ₉₀ H ₁₀₄ Yb ₄ Cl ₆ F ₁₂ N ₈ O ₂₀ P ₂	C ₉₉ H ₁₃₅ Yb ₅ Cl ₈ N ₁₃ O ₄₂
Formula weight	1 318.41	2 828.08	2 816.72	3 203.11
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / nm	1.621 6(3)	1.473 7(7)	1.470 2(12)	1.461 6(14)
<i>b</i> / nm	1.503 6(3)	1.475 6(7)	1.470(2)	1.469 6(13)
<i>c</i> / nm	2.288 7(5)	1.509 6(7)	1.477 5(12)	3.004 5(3)
α / (°)	90	111.873(4)	111.720(18)	87.244(2)
β / (°)	106.96(3)	109.822(4)	113.104(12)	79.028(2)
γ / (°)	90	101.275(4)	96.377(17)	73.857 0(10)
<i>V</i> / nm ³	5.338(2)	2.664(2)	2.603(5)	6.085 5(10)
<i>Z</i>	4	1	1	2
<i>D_c</i> / (g·cm ⁻³)	1.553	1.661	1.663	1.526
μ / mm ⁻¹	1.978	3.600	3.727	3.878
<i>F</i> (000)	2 484	1 308	1 276	2 732
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.054 2, 0.145 0	0.034 2, 0.085 3	0.056 1, 0.132 9	0.038 1, 0.087 4
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.091 0, 0.182 6	0.063 8, 0.120 1	0.139 7, 0.184 3	0.074 3, 0.143 2
GOF on <i>F</i> ²	1.038	1.055	0.921	1.030

S1 in Supporting information), the characteristic strong absorptions of the $\nu(\text{C}=\text{N})$ vibration at 1 643~1 651 cm^{-1} for complexes **1**~**4**, are slightly blue-shifted by 17~25 cm^{-1} compared to those for the free ligands (1 626 cm^{-1}) upon coordination of the Ln^{3+} ion. The presence of ClO_4^- in complex **1** as a counter ion was indicated by its IR spectrum, which shows a strong characteristic band at 627 cm^{-1} for ClO_4^- . Four bands around 1 470, 1 385, 1 225 and 742 cm^{-1} for complexes **2** and **4** were observed, which can be assigned to vibrations of coordinated nitrate groups, respectively (ν_1 , ν_2 , ν_3 and ν_4). In addition, the absorption bands at 844 cm^{-1} for complexes **2** and **3** are attributed to the stretching vibrations of the PF_6^- anions. TG-DSC analyses of complexes **1**~**4** (Fig.S2~S5) reveal that complex **1** loses a gradual weight loss of 6.16% in the range of 33~85 °C, which corresponds to the loss of two methanol molecules and one water molecules (Calcd. 6.53%). The loss of four acetonitrile molecules (Obsd. 5.78%, Calcd. 5.81%) is observed for **2** in the range of 33~250 °C. Complex **3** loses two dichloromethane molecules and two water molecules in the temperature range of 33~330 °C (Obsd. 8.90%, Calcd. 7.32%). For **4**, the weight loss between 33 and 180 °C

can be attributed to the loss of four dichloromethane molecules and six methanol molecules (Obsd. 14.90%, Calcd. 15.98%).

2.2 Structural description of complex 1

X-ray crystallographic analysis reveals that complex **1** crystallizes in a monoclinic space group *P*2₁/*c* with an ionic mononuclear structure (Fig.1). Complex **1** is composed of one $[\text{Yb}(\text{H}_2\text{L})_2]^{3+}$ cation, three free ClO_4^- anions, two crystalline CH_3OH and one H_2O molecules. The Yb^{3+} ion is eight-coordinated to eight oxygen atoms from two ligands forming a distorted square antiprism geometry (Fig.1), and shielded in the outer O_2O_2 cavity (two phenol oxygen atoms and two methoxy oxygen atoms) of the ligand, while the nitrogen atoms of imine remain uncoordinated. Notably, the two ligands coordinate to the Yb^{3+} ion in a crossover configuration. The dihedral angle between the coordination planes of two O_2O_2 cavities is 79.793(1)°. The dihedral angles between the two neighboring aromatic rings in different ligands are 28.330(3)° and 36.974(3)°. The Yb-O bond distances from phenol and methoxy groups are in the range of 0.221 4(6) to 0.247 2(6) nm and the average distance is 0.233 6 nm. The three free ClO_4^- ions do not parti-



Hydrogen atoms, free ClO_4^- ions and crystalline molecules are omitted for clarity; Selected bond lengths (nm) and angles ($^\circ$):

Yb(1)-O(1) 0.223 5(6), Yb(1)-O(2) 0.243 8(6),
Yb(1)-O(3) 0.222 4(6), Yb(1)-O(4) 0.247 2(6),
Yb(1)-O(5) 0.221 4(6), Yb(1)-O(6) 0.243 2(6),
Yb(1)-O(7) 0.221 8(6), Yb(1)-O(8) 0.245 3(6);
O(1)-Yb(1)-O(2) 66.9(2), O(3)-Yb(1)-O(4) 66.14(2),
O(5)-Yb(1)-O(6) 66.8(2), O(7)-Yb(1)-O(8) 66.9(2)

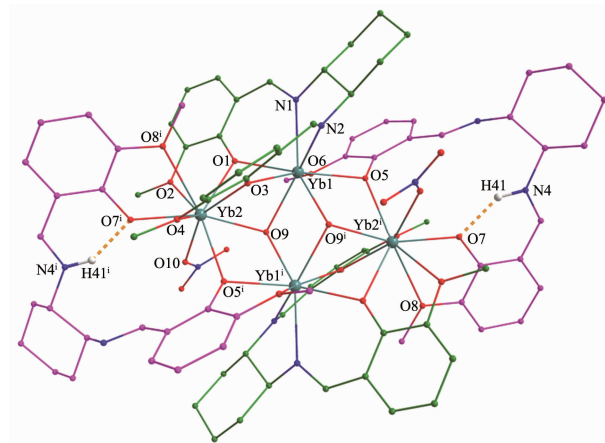
Fig.1 View of the cationic structure in complex 1

participate in the coordination structure but balance the positive charge of the complex. Noticeably, such an ionic crossover mononuclear Yb^{3+} complex is unique with a crossover structure involving pure oxygen atoms coordination. It is similar to the reported mononuclear complex $[\text{Yb}(\text{H}_2\text{L}^1)_2\text{CH}_3\text{OH}](\text{ClO}_4)_3$ ($\text{H}_2\text{L}^1 = \text{N}, \text{N}'$ -bis(2-hydroxy-3-methoxybenzylidene)-1, 3-propanediamine): the Yb^{3+} ion is nine-coordinated to nine-oxygen atoms from two ligands and one methanol^[28]. Previously, two kinds of salen type mononuclear lanthanide complexes have been reported, *e.g.* complexes $[(\text{H}_2\text{L}^2)\text{Nd}(\text{NO}_3)_3]$ ($\text{H}_2\text{L}^2 = \text{N}, \text{N}'$ -bis(3-methoxysalicylidene)propane-1, 2-diamine)^[29], $[\text{Nd}(\text{H}_2\text{L}^3)(\text{NO}_3)_3]$ ($\text{H}_2\text{L}^3 = \text{N}, \text{N}'$ -ethylene-bis(3-methoxysalicylideneimine)^[30], which are of the neutral crab-like structure with a ratio of ligand to lanthanide of 1:1; $[\text{Ce}(\text{salophen})_2]$ (salophen = N, N' -bis(salicylidene)-1,2-(phenylenediamine))^[31] are of crossover structure and distorted sandwich structure with a ratio of ligand to lanthanide of 2:1, in which the Ce ions are +4 oxidation state and the N atoms are coordinated to the $\text{Ce}(\text{IV})$ ions.

2.3 Structural description of complexes 2-4

Single-crystal X-ray diffraction analyses indicate that complexes 2, 3 and 4 are isomorphous, so only structure of complex 2 is described in detail. Complex

2 crystallizes in a triclinic space group of $P\bar{1}$ featuring a discrete ionic structure with a defect-dicubane Yb_4 core. The structural unit is composed of one $[\text{Yb}_4(\text{L})_4(\text{NO}_3)_2(\text{H}_2\text{O})_2]^{2+}$ cation, two free PF_6^- anions, and four solvate acetonitrile molecules (Fig.2). The $[\text{Yb}_4(\text{L})_4(\text{NO}_3)_2(\text{H}_2\text{O})_2]^{2+}$ cation lying about an inversion centre, two equivalent $\text{Yb}_2(\text{L})_2$ moieties are bridged by two μ -O phenoxide atoms (O5 and O5ⁱ) of two salen type ligands with O₄ tetradentate mode (Scheme 1) and two O atoms (O9 and O9ⁱ) of two coordinated μ_3 -OH⁻ groups, resulting in the formation of a homoleptic cyclic tetranuclear $\text{Yb}_4(\text{L})_2(\text{HL})_2$ host structure. In each of two equivalent $\text{Yb}_2(\text{L})(\text{HL})$ moieties, two Yb^{3+} (Yb1 and Yb2) ions with different coordination environments are also linked by two μ -O phenoxide atoms (O1 and O3) of one L^{2-} ligand with N_2O_4 hexa-dentate mode and one O atom (O9) of the coordinated H_2O molecule.



Hydrogen atoms, free PF_6^- ions and crystalline molecules are omitted for clarity except H41 and H41ⁱ; Selected bond lengths (nm) and angles ($^\circ$):

Yb(1)-N(1) 0.243 9(6), Yb(1)-N(2) 0.238 6(7),
Yb(1)-O(1) 0.227 2(5), Yb(1)-O(3) 0.231 2(5),
Yb(1)-O(5) 0.229 2(5), Yb(1)-O(6) 0.248 1(5),
Yb(1)-O(9) 0.228 4(5), Yb(1)-O(9ⁱ) 0.227 2(4);
Yb(2)-O(1) 0.233 3(5), Yb(2)-O(2) 0.269 5(5),
Yb(2)-O(3) 0.228 3(5), Yb(2)-O(4) 0.264 3(5),
Yb(2)-O(5ⁱ) 0.239 6(4), Yb(2)-O(7ⁱ) 0.222 2(5),
Yb(2)-O(8ⁱ) 0.254 8(5), Yb(2)-O(9) 0.231 7(4),
Yb(2)-O(10) 0.232 7(6); Yb1...Yb2 0.343 0(4),
Yb1...Yb1ⁱ 0.370 3(6), Yb2...Yb1ⁱ 0.379 1(5);
N(1)-Yb(1)-N(2) 65.8(2), O(1)-Yb(1)-O(3) 69.97(2),
O(1)-Yb(2)-O(3) 69.42(2), O(2)-Yb(2)-O(5ⁱ) 143.16(2),
O(7ⁱ)-Yb(2)-O(8ⁱ) 65.85(18), O(9)-Yb(2)-O(5ⁱ) 67.51(16);
Symmetry codes: ⁱ -x, -y, -z+2

Fig.2 View of the cationic structure of complex 2

The unique inner Yb^{3+} ion (Yb1) is eight-coordinate and bound by the N_2O_2 core of the salen type L^{2-} ligand in addition to two O atom (O5 of MeO group and O6 of μ -O phenoxide atom) from the salen type ligand and two O atoms of two coordinated H_2O molecule. Meanwhile the outer Yb^{3+} ion (Yb2) is nine-coordinated including seven oxygen atoms from two outer O_2O_2 moieties of two salen type ligands, where four O atoms (two of MeO groups and two of phenoxide atoms) are from one salen type ligand and three O atoms (one of MeO groups and two of phenoxide atoms) from another salen type ligand. It completes its coordination environment with one O atom from the monodentate NO_3^- anion and one O atom from the coordinated H_2O molecule. The unique $\text{Yb}\cdots\text{Yb}$ distances are different, with the distances of 0.343 00(4), 0.370 28(6) and 0.379 12(5) nm for $\text{Yb1}\cdots\text{Yb2}$, $\text{Yb1}\cdots\text{Yb1}^i$ and $\text{Yb2}\cdots\text{Yb1}^i$, respectively, in which each of the $\text{Yb1}\cdots\text{Yb2}$ separations in the equivalent Yb_2L_2 moieties is slightly shorter than that ($\text{Yb1}\cdots\text{Yb1}^i$ or $\text{Yb2}\cdots\text{Yb1}^i$ separation) between two equivalent Yb_2L_2 moieties. For the inner Yb^{3+} ion (Yb1 or Yb1^i), the $\text{Yb}-\text{O}$ bond length (0.227 2(4)~0.228 4(5) nm; O atoms from coordinated H_2O molecule) or the $\text{Yb}-\text{N}$ bond lengths (0.238 6(7)~0.243 9(6) nm) are in the range of the $\text{Yb}-\text{O}$ bond lengths (0.227 2(5)~0.231 2(5) nm) with O atoms from the phenoxo groups. For the outer Yb^{3+} ion (Yb2 or Yb2^i), the $\text{Yb}-\text{O}$ bond lengths also depend on the nature of the oxygen atoms, varying from 0.222 2(5) to 0.269 5(5) nm, in which the bond lengths (0.254 8(5)~0.269 5(5) nm) from the oxygen atoms of MeO groups are distinctively longer than those (0.222 2(5)~0.239 6(4) nm, 0.232 7(6) and 0.231 7(4) nm) from the phenoxo oxygen atoms, monodentate NO_3^- anion or coordinated H_2O molecule. It is interesting to note the presence of an ‘apical’ triply bridged H_2O molecule for each of the two central O atoms (O9 and O9ⁱ), which could be shown from the reasonable directionality of the interactions with three Yb^{3+} ions. Furthermore, as to the cation $[\text{Yb}_4(\text{L})_4(\text{NO}_3)_2(\text{H}_2\text{O})_2]^{2+}$, the charge is balanced by the protonation of one (N4 or N4ⁱ) of the imino nitrogen atoms for two of the deprotonated salen type L^{2-} ligands, which endows the

formation of two strong intramolecular H-bond interactions with the short $\text{N4}\cdots\text{O7}$ distance (0.269 8(10) nm) (Fig.2). The PF_6^- is not involved in the coordination to lanthanide ions, and it plays a charge-balancing role.

Notably, although complex **2** is isomorphic to previous reported analog of the salen type homoleptic tetranuclear complexes, *e.g.* $[\text{Yb}_4(\text{L})_2(\text{HL})_2(\text{NO}_3)_2(\text{OH})_2](\text{NO}_3)_2$ ^[25] and $[\text{Yb}_4(\text{L})_2(\text{HL})_2(\mu_3\text{-OH})_2\text{Cl}_2]\text{Cl}_2$ ^[26], the PF_6^- ions instead of NO_3^- or Cl^- ions act as the counter ions balancing the positive charge in **2**. Furthermore, there are obvious differences between the composition of complexes **2**, **3** and **4**, *e.g.* the two coordination NO_3^- anions in **2** are replaced by two Cl^- anions in **3**, while a neutral molecule of $[\text{Yb}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})]$ is crystalline in **4**.

2.4 NIR luminescence

The UV-Vis absorption spectra of the ligand H_2L and complexes **1**~**4** were recorded in CH_3OH solution (Fig.3). For free ligand, the typical absorptions at 220 and 261 nm are attributed to the $\pi-\pi^*$ transition of the aromatic ring and azomethine chromophores. The peak at 334 nm is attributed to $n-\pi^*$ transition of R band which belongs to azomethine. For complexes **1**~**4**, the similar ligand-centered solution absorption bands (221~226, 264~274, 338~361 nm) are observed and red-shifted as compared to those (220, 261 and 334 nm) for ligand due to the changes in the energy levels of the ligand orbitals upon the coordination.

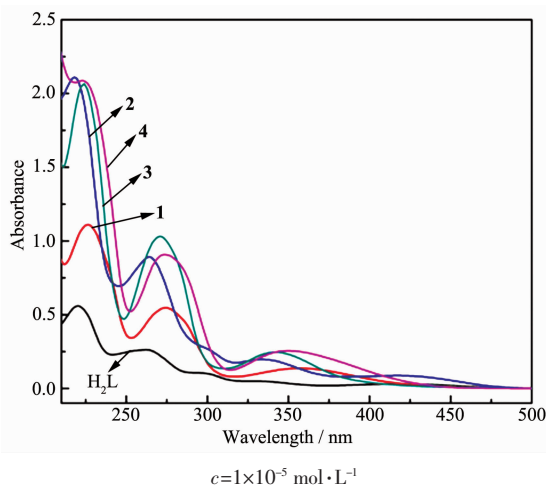


Fig.3 UV-Vis spectra of the ligand H_2L and complexes **1**~**4** in CH_3OH solution

Complexes **2**~**4** show the higher molar absorption coefficients than that for complex **1**, which is attributed to more ligands in complex **1**.

The NIR photoluminescence spectra of complexes **1**~**4** were recorded with the excited wavelength at 370 nm in the isoabsorptive solution at room temperature. NIR photoluminescence spectra of complexes **1**~**4** exhibit that the typical NIR emission bands of Yb^{3+} ion could be observed at 975 nm which is assigned to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition (Fig.4). Notably, the emission of Yb^{3+} ion in complexes **1** and **4** is not a sharp transition that well-split NIR emission peaks are observed, where it appears as a series of bands with two other broad bands centered around 1 024 and 1 056 nm. Similar results have been proposed in previously report which is attributed to the crystal-field or stark splitting^[32]. The absence of the typical Yb^{3+} ion excitation bands in the excitation spectra and the ligand-centered luminescence in the emission spectra of **1**~**4** reveal the occurrence of the ligand-to-metal energy transfer. Obviously, the NIR signal of Yb^{3+} ion for complex **1** is the strongest among the four complexes which can be ascribed to two reasons. Firstly, it might be owing to the existence of the coordinated counter ions, such as NO_3^- anions and Cl^- anions in **2**~**4**, which are believed to quench the NIR fluorescence. Secondly, the Yb^{3+} ion of complex **1** is well enclosed in the crossover structure, which contributes to preventing the NIR luminescence quenching from

solvent molecule effectively. In addition to the steady-state emission, we also perform time-resolved measurements for complexes **1** and **4** in the NIR region by using the time-correlated single photon counting (TCSPC) technique. The decay of the emission band at 975 nm gives a satisfactory fit to a monoexponential decay with lifetimes of 2.90 μs for **1** and 2.59 μs for **4**. The lifetimes of **2** and **3** cannot be obtained due to the weakness of the signal.

3 Conclusions

We have isolated a series of four salen type ytterbium complexes featuring an ionic crossover mononuclear structure for complex **1** and defect-dicubane core structures for complexes **2**~**4** through the self-assembly of the semi-rigged salen type H_2L with various ytterbium salts. It demonstrates that the flexible ligand and the different ytterbium counter ions dominate the structures of salen type ytterbium complexes. All complexes **1**~**4** exhibit the similar typical NIR luminescence of Yb^{3+} ions proposing that the energy transfer from H_2L to Yb^{3+} ions in **1**~**4** takes place effectively and the crossover structure and the defect-dicubane structure can encapsulate the lanthanide ions efficiently prevent the NIR luminescence quenching from solvent molecules.

Acknowledgments: This work is financially supported by the National Natural Science Foundation of China (Grants No. 51402092, 21601132).

Supporting information is available at <http://www.wjhx.cn>

References:

- [1] Rocha J, Carlos L D, Paz F A A, et al. *Chem. Soc. Rev.*, **2011**,**40**:926-940
- [2] Carlos L D, Ferreira R A S, De Zea B, et al. *Chem. Soc. Rev.*, **2011**,**40**:536-549
- [3] Kieran G, Julia M, Michael A S, et al. *Cryst. Growth Des.*, **2017**,**17**:1524-1538
- [4] Wang G T, Zhang J C, Tang Z Y, et al. *CrystEngComm*, **2016**,**18**:2437-2445
- [5] Elena A M, Anastasiya V Y, Matthias Z, et al. *Dalton Trans.*,

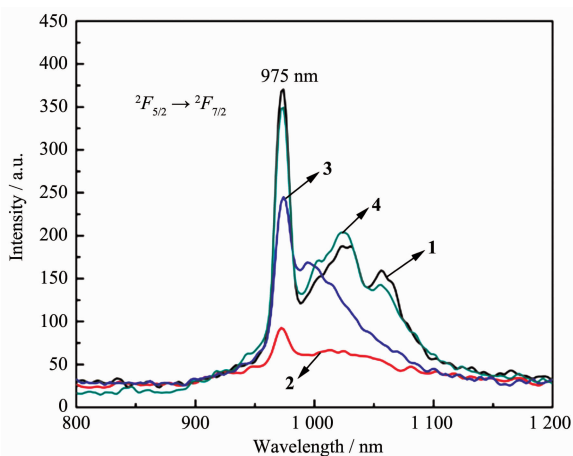


Fig.4 NIR spectra of complexes **1**~**4** in CH_3OH with the excited wavelength at 370 nm in the isoabsorptive solution

- 2017,46**:3457-3469
- [6] Sabdeep K G, Stuart K L, Kamma S, et al. *Inorg. Chem.*, **2017,56**:3946-3960
- [7] Dong Y P, Yan P F, Zou X Y, et al. *Dalton Trans.*, **2016**, 9148-9157
- [8] Mattgew G, Nitholas F C, Ana-Maria A, et al. *Chem. Sci.*, **2016,7**:155-165
- [9] Sunri L, Takuji O. *Chem. Lett.*, **2017,46**:10-18
- [10] Chen Y C, Liu J L, Ungur L, et al. *J. Am. Chem. Soc.*, **2016**, **138**:2829-2837
- [11] Liu J, Chen Y C, Liu J L, et al. *J. Am. Chem. Soc.*, **2016**, **138**:5441-5450
- [12] Akine S, Utsuno F, Taniguchi T, et al. *Eur. J. Inorg. Chem.*, **2010**:3143-3150
- [13] Albrecht M, Osetska O, Bünzli J C G, et al. *Chem. Eur. J.*, **2009,15**:8791-8799
- [14] Chauvin A S, Comby S, Song B, et al. *Chem. Eur. J.*, **2008**, **14**:1726-1735
- [15] Dalla Cort A, De Bernardin P, Forte G, et al. *Chem. Soc. Rev.*, **2010,39**:3863-3874
- [16] ZOU Xiao-Yan(邹晓艳), MA Hui-Yuan(马慧媛), PANG Hai-Jun(庞海军), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2016,32**(9):1647-1652
- [17] Zhu J, Song H F, Yan P F, et al. *CrystEngComm*, **2013,15**: 1747-1752
- [18] Yan P F, Lin P H, Habib F, et al. *Inorg. Chem.*, **2011,50**: 7059-7065
- [19] Zou X Y, Yan P F, Dong Y P, et al. *RSC Adv.*, **2015,5**: 96573-96573
- [20] Dong Y P, Yan P F, Zou X Y, et al. *J. Mater. Chem. C*, **2015,3**:4407-4415
- [21] Yang X, Jones R A, Rivers J H, et al. *Dalton Trans.*, **2009**: 10505-10510
- [22] Yang X, Lam D, Chan C, et al. *Dalton Trans.*, **2011,40**: 9795-9801
- [23] Liu T Q, Yan P F, Luan F, et al. *Inorg. Chem.*, **2015,54**: 221-228
- [24] Yang X, Jones R A. *J. Am. Chem. Soc.*, **2005,127**:7686-7688
- [25] Feng W, Zhang Y, Lü X, et al. *CrystEngComm*, **2012,14**: 3456-3463
- [26] Feng W, Zhang Y, Zhang Z, et al. *Inorg. Chem.*, **2012,51**: 11377-11385
- [27] Sheldrick G M. *Acta Crystallogr. Sect. A*, **2008,A64**:112-122
- [28] Zou X Y, Yan P F, Zhang J W, et al. *Dalton Trans.*, **2013**, **42**:9482-9489
- [29] Sun W B, Yan P F, Li G M, et al. *Inorg. Chim. Acta*, **2009**, **362**:1761-1766
- [30] Gao T, Yan P F, Li G M, et al. *Inorg. Chim. Acta*, **2008**, **361**:2051-2058
- [31] Terzis A, Mentzafos D, Tajmir-Riahi H. *Inorg. Chim. Acta*, **1984,84**:187-193
- [32] Kang T S, Harrison B S, Bouguettaya M, et al. *Adv. Funct. Mater.*, **2003,13**:205-210