

# Structures and Luminescent Properties of Two 2D Coordination Polymers Containing Tb(III) or Dy(III) Ions

Xiaoping An · Hongsheng Wang · Gongchun Li

Received: 4 July 2013 / Accepted: 25 September 2013 / Published online: 5 October 2013  
© Springer Science+Business Media New York 2013

**Abstract** Two 2D rare earth terbium and dysprosium coordination polymers with 2,4-pyridinedicarboxylate and oxalate anions have been synthesized by hydrothermal method, the formula is  $\{[\text{RE}(\text{pda})(\text{ox})_{0.5}(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$  (RE = Tb (**1**) and Dy (**2**);  $\text{H}_2\text{pda}$  = 2,4-pyridinedicarboxylic acid; ox = oxalate anion). The two complexes are isomorphic and crystallized in monoclinic system,  $P2_1/c$  space group. Each pda anion connects two rare earth ions with 2- carboxyl group and the nitrogen atom but the 4- carboxyl group does not coordinate with rare earth ions. Each ox anion connects two rare earth ions by  $\mu_2$ -bridge way. Both the complexes exhibit intense characteristic luminescence of Tb(III) or Dy(III) ion with excitation of UV-rays.

**Keywords** 2,4-pyridinedicarboxylic acid · Photoluminescence · Oxalate · Terbium · Dysprosium

## Introduction

The metal organic coordination polymers synthesized with optically active trivalent rare earth cations such as Sm(III), Eu(III), Tb(III), Dy(III) and aromatic multicarboxylic acids have received much attention due to their unique luminescent properties and potential applications in photoluminescent materials [1–4]. Especially for the Eu(III) and Tb(III) complexes, they have excellent photoluminescent properties in visible

region when the organic ligands are proper. In recent years, the organic multicarboxylic acids containing phenyl group have been widely used as the organic linkers in the synthesis of coordination polymers because they have two or more carboxyl groups and are inclined to forming multidimensional structure [5–8]. The pyridinedi- and tri-carboxylic acids are also important organic ligands for constructing coordination polymers as the nitrogen atom can also coordinate with center metal ions besides the oxygen atoms of carboxyl groups. Much attention has been paid to this field [9–11]. Some complexes synthesized have good luminescent properties and attractive topological structure [12–15].

In this paper, we used the solution of terbium chloride or dysprosium chloride and 2,4-pyridinedicarboxylic acid as the reactants and synthesized two new lanthanide complexes under hydrothermal condition. Parts of the ligands were decomposed and oxalate anions were formed. The oxalate anions also coordinated with rare earth ions. Two complexes of Tb(III) and Dy(III) with two ligands were got accidentally. The photoluminescent properties were studied and the results showed that both the complexes emit strong characteristic fluorescence of Tb(III) or Dy(III) ion in visible region at the excitation of ultraviolet rays.

## Experimental Section

### Synthesis of the Ligand

2,4-pyridinedicarboxylic acid was synthesized by oxidization of 2,4-dimethylpyridine with potassium permanganate. Terbium chloride or dysprosium chloride solution was obtained by reacting hydrochloric acid with  $\text{Tb}_4\text{O}_7$  ( $\geq 99.95\%$ ) or  $\text{Dy}_2\text{O}_3$  ( $\geq 99.99\%$ ) purchased from Grirem Advanced Materials Co. Ltd. Beijing.

X. An  
College of Animal Science, Inner Mongolia Agricultural University,  
Huhhot, Inner Mongolia 010018, People's Republic of China

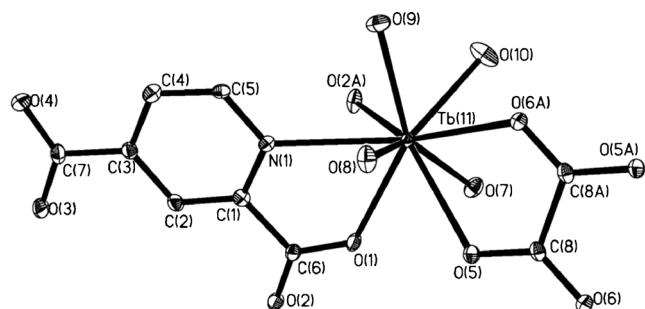
H. Wang (✉) · G. Li  
School of Chemistry and Chemical Engineering, Xuchang  
University, Xuchang, Henan 461000, People's Republic of China  
e-mail: xcuwaller@163.com

**Table 1** Crystallographic data for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>8</sub> H <sub>15</sub> NO <sub>12</sub> Tb	C <sub>8</sub> H <sub>15</sub> NO <sub>12</sub> Dy
Formula weight	476.13	479.71
<i>T</i> (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	15.2677(3)	15.23608(16)
<i>b</i> /Å	11.0804(2)	11.04018(10)
<i>c</i> /Å	8.55999(16)	8.55721(9)
$\alpha$ /deg	90.00	90.00
$\beta$ /deg	102.5875(18)	102.5791(10)
$\gamma$ /deg	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	1413.32(5)	1404.85(2)
<i>Z</i>	4	4
<i>D</i> (Mg·m <sup>-3</sup> )	2.238	2.268
$\mu$ (mm <sup>-1</sup> )	5.069	5.384
<i>F</i> (000)	924	928
Crystal size (mm)	0.2×0.2×0.2	0.2×0.2×0.2
$\theta$ Ranges (°)	2.73 to 25.01	2.74 to 25.00
Max. and min. transmission	0.4305 and 0.4305	
<i>h</i> / <i>k</i> / <i>l</i>	-16 ≤ <i>h</i> ≤ 18, -13 ≤ <i>k</i> ≤ 5, -10 ≤ <i>l</i> ≤ 7	-18 ≤ <i>h</i> ≤ 18, -13 ≤ <i>k</i> ≤ 13, -10 ≤ <i>l</i> ≤ 10
Reflections collected/unique	5417/2487 [R(int)=0.0234]	18278/2478 [R(int)=0.0324]
Data/restraints/parameters	2487/16/223	2478/22/238
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
GOF	0.994	1.019
Final R indices [I > 2σ(I)]	R1=0.0207, wR2=0.0450	R1=0.0145, wR2=0.0379
R indices(all data)	R1=0.0271, wR2=0.0467	R1=0.0176, wR2=0.0388
Largest diff. peak and hole (e·Å <sup>-3</sup> )	0.541 and -0.643	0.513 and -0.589

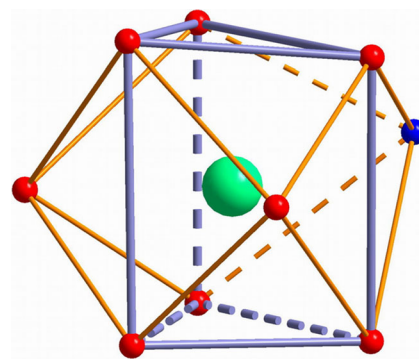
Preparation of {[RE(pda)(ox)<sub>0.5</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O}<sub>n</sub> (RE = Tb (**1**) or Dy (**2**))

A mixture of 2,4-pyridinedicarboxylic acid (0.3 mmol), TbCl<sub>3</sub> or DyCl<sub>3</sub> water solution 5 mL (0.040 mol·L<sup>-1</sup>) and deionized water (10 mL) were placed in a 25 mL Teflon-lined bomb, which were



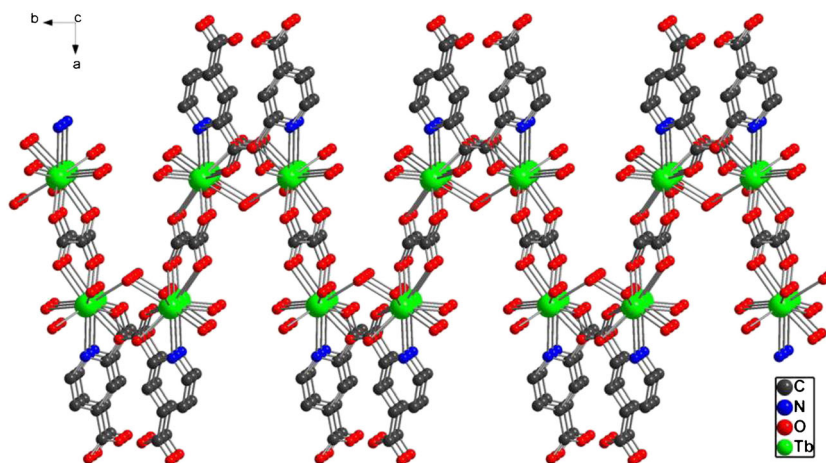
**Fig. 1** The ORTEP representation of **1** showing the coordination environment of Tb(III) ions with 30 % probability of thermal ellipsoids. All the hydrogen atoms were omitted for clarity

heated to 180 °C for 72 h. After the mixture was cooled to room temperature at a rate of 3 °C/h, colorless block crystals were obtained in yields of 43 % for **1** and 48 % for **2**. Elemental Anal. Calcd. for C<sub>8</sub>H<sub>15</sub>NO<sub>12</sub>Tb (%): C, 20.18; H, 3.18; N, 2.94. Found: C, 20.36; H, 3.45; N, 3.19. For C<sub>8</sub>H<sub>15</sub>NO<sub>12</sub>Dy (%): C, 20.03; H, 3.15; N, 2.92. Found: C, 20.09; H, 2.83; N, 3.07.



**Fig. 2** The distorted tricapped trigonal prism formed by the coordination atoms (Oxygen atoms, red; nitrogen atom, blue; Tb(III) ion, green)

**Fig. 3** The two dimensional structure formed with Tb(III) ions and ligands of pda and ox anions



### General Characterization

Elemental analyses were performed in a Perkin-Elmer 240 analyzer. The fluorescence spectrum was tested on a 970CRT fluorescence spectrophotometer at room temperature.

### X-ray Diffraction Analysis

The crystallographic data of the complexes were collected with an Oxford Supernova X-ray single crystal diffractometer. The diffractometer is equipped with a graphite monochromator, and Mo  $K\alpha$  radiation ( $\lambda=0.71073$  Å) was used for experiment. The structure was solved by direct methods with SHELXTL-97 programs [16] and refined by full-matrix least-squares techniques against  $F^2$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms located and refined isotropically. The crystallographic data and structure

refinement parameters for the complex were given in Table 1 and the selected bond lengths and bond angles were listed in Supporting information.

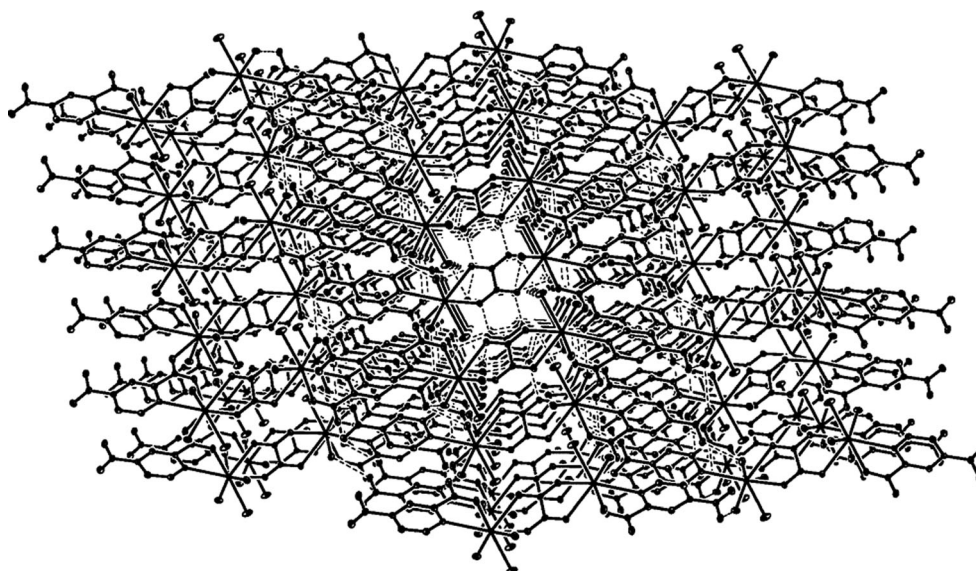
Crystallographic data for the two complexes have been deposited at the Cambridge Crystallographic data centre, CCDC Numbers are 947588 for **1** and 947589 for **2**. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, U. K.; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

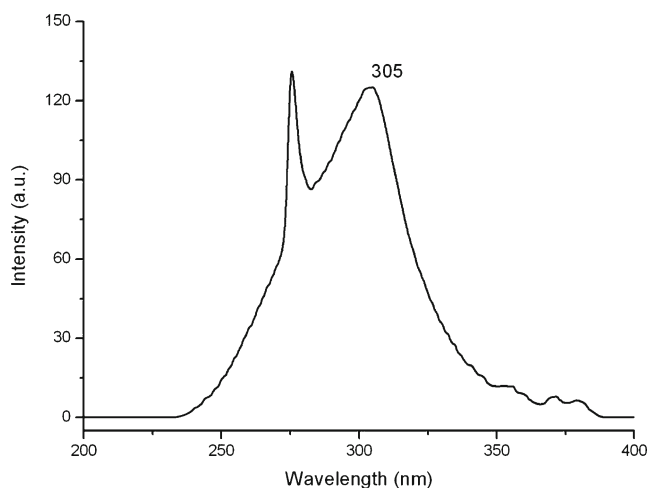
### Results and Discussion

#### Structure Description

Complexes **1** and **2** are isostructural and **1** is taken as an example to describe the structure in detail, as shown in Fig. 1.

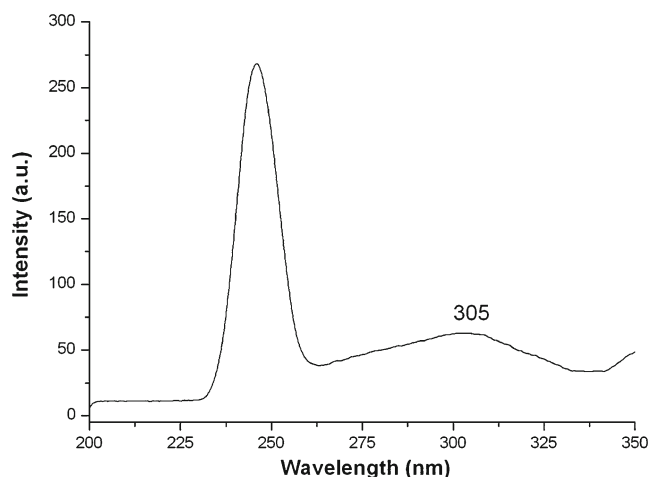
**Fig. 4** The three dimensional structure constructed by hydrogen bonds





**Fig. 5** Excitation spectrum of complex 1

Each Tb(III) ion was coordinated by two pda anions, one ox anion and four water molecules. One pda anion connects to Tb(III) ion with N(1) atom and O(1) atom of 2-carboxyl group by chelating way, the other connects to Tb(III) ion with O(2) atom of 2-carboxyl group by monodentate way. Each ox anion connects two Tb(III) ions with oxygen atoms by chelating way. O(5) and O(6A) atoms chelate one Tb(III) ion and O(6) and O(5A) atoms chelate the other one. The four water molecules coordinated with Tb(III) ion by oxygen atoms of O(7), O(8), O(9) and O(10). The 4-carboxyl group of pda anion does not participate in coordination. There are nine atoms bonded with one Tb(III) ion and they form a distorted tricapped trigonal prism, as shown in Fig. 2. The bond lengths of Tb(11)-O(1), Tb(11)-O(2), Tb(11)-O(5), Tb(11)-O(6A), Tb(11)-O(7A), Tb(11)-O(8), Tb(11)-O(9) and Tb(11)-O(10) are 2.333(2), 2.455(3), 2.531(2), 2.436(2), 2.448(3), 2.384(3), 2.360(3) and 2.435(3) Å, respectively; and the Tb(11)-N(1) bond length is 2.684(3) Å. The bond angles of O-Tb(11)-O

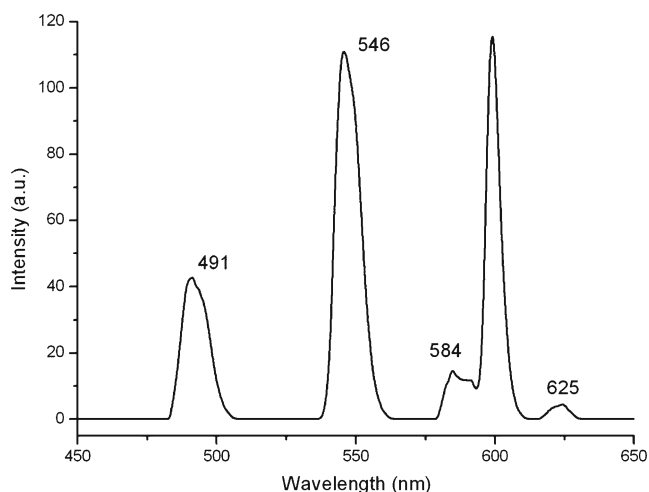


**Fig. 7** Excitation spectrum of complex 2

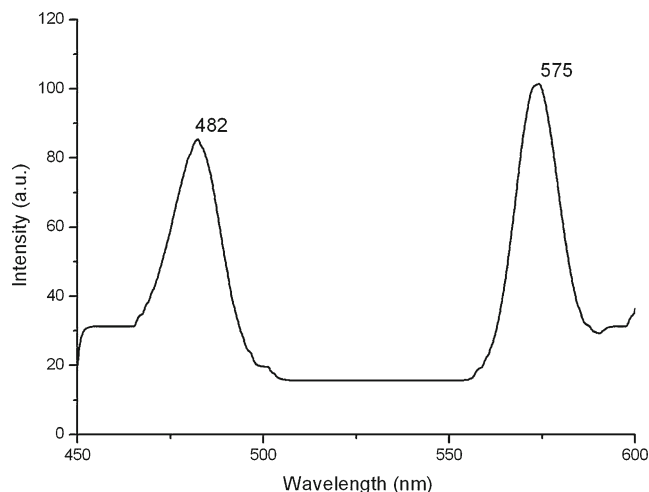
range between  $64.62(8)^\circ$  and  $143.80(9)^\circ$  and that of O-Tb(11)-N range between  $62.22(8)^\circ$  and  $144.30(9)^\circ$ . By the connection of Tb(III) ions, pda and ox anions, 2D layered framework is formed, as shown in Fig. 3. The 2D layers formed 3D network by the connection of hydrogen bonds. These hydrogen bonds are formed between lattice water and coordinating water molecules like O(7)-H(7A)⋯O(11), O(8)-H(8B)⋯O(11), O(10)-H(10A)⋯O(12) and O(12)-H(12A)⋯O(8); lattice water molecules and oxygen atoms of ox anions like O(11)-H(11B)⋯O(6) and O(12)-H(12B)⋯O(5); coordinating water molecules and oxygen atoms of pda anions like O(8)-H(8A)⋯O(3), O(9)-H(9A)⋯O(3) and O(9)-H(9B)⋯O(4), as shown in Fig. 4.

#### Photoluminescent Property

The fluorescence spectra for the two complexes were determined with solid samples at room temperature. The strongest



**Fig. 6** Emission spectrum of complex 1 with excitation at 300 nm



**Fig. 8** Emission spectrum of complex 2 with excitation at 315 nm

peak was at about 305 nm in the excitation spectrum for **1**, as shown in Fig. 5. The emission spectra was shown in Fig. 6. Complex **1** displayed four emission bands at 491, 546, 584 and 625 nm with excitation of 300 nm, and they were ascribed to  $^5D_4 \rightarrow ^7F_j$  ( $j=6, 5, 4$  and  $3$ ) transition of Tb(III) ion [17–19]. The excitation spectrum of **2** is similar to that of **1** except the intensity of peak, as shown in Fig. 7. Emission spectrum of **2** was determined with excitation of 315 nm, as shown in Fig. 8. Two Emission bands at 482 and 575 nm were assigned to the transition of  $^4F_{9/2} \rightarrow ^6H_{15/2}$  and  $^4F_{9/2} \rightarrow ^6H_{13/2}$  of Dy(III) ion [20–22]. The strong luminescence of the two complexes should be attributed to high effective energy transfer from pda anions to Tb(III) or Dy(III) ions [23, 24]. The energy transfer mechanism for solid lanthanide complexes has been widely discussed to interpret the luminescent properties [25–27]. Efficient energy transfer occurred if the triplet-state energy levels of the ligands matched with the excited states energy levels of lanthanide ions. The results showed the  $^5D_4$  excited state energy level of Tb(III) ion and  $^4F_{9/2}$  excited state energy state level of Dy(III) ion mateded with the triplet-state energy levels of pda anions.

In summary, we have synthesized Tb(III) and Dy(III) coordination compound by using 2,4-pyridinedicarboxylate and oxalate anions as the linker. The two complexes formed two-dimensional layer structure and are isomorphic. They both emit strong characteristic fluorescence of Tb(III) or Dy(III) ions with the excitation of UV-rays.

**Acknowledgment** This work was supported by the Key Scientific and Technological Project of Henan province (Grant 132102210263).

## References

- Cui Y, Xu H, Yue Y, Guo Z, Yu J, Chen Z, Gao J, Yang Y, Qian G, Chen B (2012) A luminescent mixed-lanthanide metal-organic framework thermometer. *J Am Chem Soc* 134:3979
- Yang X, Jones RA (2005) Anion dependent self-assembly of “Tetra-Decker” and “Triple-Decker” luminescent Tb(III) Salen complexes. *J Am Chem Soc* 127:7686
- Xu J, Ma YF, Liu WS, Tang Y, Tan MY (2011) Preparation, crystal structures and luminescent properties of terbium and europium complexes with a new amino-alkenone type ligand. *J Fluoresc* 21:35
- Wang HS, Zhao B, Zhai B, Shi W, Cheng P, Liao DZ, Yan SP (2007) Syntheses, structures, and photoluminescence of one-dimensional lanthanide coordination polymers with 2,4,6-pyridinetricarboxylic acid. *Cryst Growth Des* 7:1851
- Chen S, Fan RQ, Sun CF, Wang P, Yang YL, Su Q, Mu Y (2012) Lanthanide-based two-dimensional and three-dimensional metal-organic frameworks with 2,4'-biphenyldicarboxylic acid. *Cryst Growth Des* 12:1337
- Hou KL, Bai FY, Xing YH, Wang JL, Shi Z (2011) A novel family of 3D photoluminescent lanthanide-bta-flexible MOFs constructed from 1,2,4,5-benzenetetracarboxylic acid and different spanning of dicarboxylate acid ligands. *CrystEngComm* 13:3884
- Han YF, Fu LS, Mafra L, Shi FN (2012) Hydrothermal synthesis, crystal structures and photoluminescence properties of mixed europium—yttrium organic frameworks. *J Solid State Chem* 186:165
- Chen B, Yang Y, Zapata F, Lin G, Qian G, Lobkovsky EB (2007) Luminescent open metal sites within a metal-organic framework for sensing small molecules. *Adv Mater* 19:1693
- Li CJ, Peng MX, Leng JD, Yang MM, Lin ZJ, Tong ML (2008) Synthesis, structure, photoluminescence and magnetic properties of new 3-D lanthanide-pyridine-2,4,6-tricarboxylate frameworks. *CrystEngComm* 10:1645
- Yang AH, Gao HL, Cui JZ, Zhao B (2011) Syntheses, structures, and photoluminescence of lanthanide coordination polymers with pyridine-2,3,5,6-tetracarboxylic acid. *CrystEngComm* 13:1870
- Zhao XQ, Zuo Y, Gao DL, Zhao B, Shi W, Cheng P (2009) Syntheses, structures, and luminescence properties of a series of LnIII-BaII heterometal-organic frameworks. *Cryst Growth Des* 9:3948
- Li WX, Chai WJ, Sun XJ, Ren T, Shi XY (2010) Synthesis and luminescence properties of two novel lanthanide (III) perchlorate complexes with Bis(benzoylmethyl) sulfoxide and benzoic acid. *J Fluoresc* 20:873
- Song HH, Li YJ (2008) Synthesis, crystal structure and luminescence properties of two novel lanthanide coordination polymers containing double chain. *Inorg Chim Acta* 361:1421
- Zhang HJ, Fan RQ, Zhou GP, Wang P, Yang YL (2012) Syntheses, structures, and luminescent properties of three novel two-dimensional lanthanide coordination polymers with mixed aromatic carboxylate ligands. *Inorg Chem Commun* 16:100
- Cui YJ, Yue YF, Qian GD, Chen BL (2012) Luminescent functional metal-organic frameworks. *Chem Rev* 112:1126
- Sheldrick GM (1997) SHELXL 97, program for the refinement of crystal structures. University of Göttingen, Germany
- Liu SG, Liu W, Zuo JL, Li YZ, You XZ (2005) Synthesis, structure and luminescent properties of lanthanide(III) polymeric complexes constructed by citric acid. *Inorg Chem Commun* 8:328
- de Bettencourt-Dias A (2005) Isophthalato-based 2D coordination polymers of Eu(III), Gd(III), and Tb(III): enhancement of the terbium-centered luminescence through thiophene derivatization. *Inorg Chem* 44:2734
- He Z, Gao EQ, Wang ZM, Yan CH, Kurmoo M (2005) Coordination polymers based on inorganic lanthanide(III)sulfate skeletons and an organic isonicotinate N-oxide connector: segregation into three structural types by the lanthanide contraction effect. *Inorg Chem* 44:862
- Wang HS, Li GC, Chen Y, Zhang ZJ, Liu ML (2010) Structures and luminescent properties of Sm(III) and Dy(III) coordination polymers with 2,4,6-pyridinetricarboxylic acid. *J Coord Chem* 63:4068
- Song XQ, Dong WK, Zhang YJ, Liu WS (2010) Synthesis and luminescence properties of lanthanide complexes with a new tripodal ligands featuring salicylamide arms. *Luminescence* 25:328
- Su Q, Liang H, Li C, He H, Lu Y, Li J, Tao Y (2007) Luminescent materials and spectroscopic properties of Dy<sup>3+</sup> ion. *J Lumin* 122:927
- Dexter DL (1953) A theory of sensitized luminescence in solids. *J Chem Phys* 21:836
- Brown TD, Shepherd TM (1973) Factors affecting the quantum efficiencies of fluorescent terbium(III) chelates in the solid state. *J Chem Soc Dalton Trans* 336
- Supkowski RM, Bolender JP, Smith WD, Reynolds LEL, Horrocks WD (1999) Lanthanide ions as redox probes of long-range electron transfer in proteins. *Coord Chem Rev* 185–186:307
- Beeby A, Faulkner S, Parker D, Williams JAG (2001) Sensitized luminescence from phenanthridine appended lanthanide complexes: analysis of triplet mediated energy transfer processes in terbium, europium and neodymium complexes. *J Chem Soc Perkin Trans* 2:1268
- Zhang ZH, Song Y, Okamura T, Hasegawa Y, Sun WY, Ueyama N (2006) Syntheses, structures, near-infrared and visible luminescence, and magnetic properties of lanthanide-organic frameworks with an imidazole-containing flexible ligand. *Inorg Chem* 45:2896