

两个基于 4-(1*H*-1,2,4-三氮唑)苯甲酸的 4*d*-4*f* 异核 配位聚合物的合成、结构及荧光性质

方智利* 熊 珊 李康宇 俞权锋 徐文媛

(华东交通大学理学院, 南昌 330013)

摘要: 以 4-(1*H*-1,2,4-三氮唑)苯甲酸(Htbc)为配体, 采用水热法合成了两种新型 4*d*-4*f* 配位聚合物 $\{[\text{EuAg}(\text{tbc})_3(\text{H}_2\text{O})]\text{ClO}_4 \cdot \text{H}_2\text{O}\}_n$ (**1**) 和 $\{[\text{Eu}_2\text{Ag}_3(\text{tbc})_6(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\}_n$ (**2**)。运用 X 射线单晶衍射法对该配位聚合物进行了结构测定, 并对其进行了元素分析、红外光谱、PXRD 及荧光光谱表征。单晶结构表明, 配位聚合物 **1** 为正交晶系, 空间群 $P2_12_12_1$, 由一维三股螺旋链(其中 2 股右手螺旋和 1 股左手螺旋)通过 Ag 将其连成二维平面。配位聚合物 **2** 属于三斜晶系, 空间群为 $P\bar{1}$, 由内消旋一维两股螺旋链通过 Ag 将其连成二维平面。配位聚合物 **1** 和 **2** 的二维链结构均通过非共价键作用形成三维超分子, 同时也表征了配位聚合物 **1** 和 **2** 的荧光性质。

关键词: 4-(1*H*-1,2,4-三氮唑)苯甲酸; 异核; 晶体结构

中图分类号: O614.122; O614.33*8

文献标识码: A

文章编号: 1001-4861(2016)02-0280-09

DOI: 10.11862/CJIC.2016.046

Two Heterometallic 4*d*-4*f* Coordination Polymers Based on 4-(1*H*-1,2,4-Triazol-1-yl)benzoic Acid: Syntheses, Structures, and Fluorescence Properties

FANG Zhi-Li* XIONG Shan LI Kang-Yu YU Quan-Feng XU Wen-Yuan

(School of Science, East China Jiaotong University, Nanchang 330013, China)

Abstract: Two 2D heterometallic 4*d*-4*f* coordination polymers, $\{[\text{EuAg}(\text{tbc})_3(\text{H}_2\text{O})]\text{ClO}_4 \cdot \text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Eu}_2\text{Ag}_3(\text{tbc})_6(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\}_n$ (**2**) (Htbc=4-(1*H*-1,2,4-triazol-1-yl) benzoic acid) were synthesized under hydrothermal condition using one-step approach and structurally characterized by elemental analysis, FT-IR, powder X-ray diffraction and single-crystal X-ray diffraction. The single-crystal X-ray diffraction analysis reveals that the two complexes present two different types of two dimensional (2D) structures. Complex **1** crystallized in an orthorhombic manner having a $P2_12_12_1$ space group, consisting of 1D triple-stranded helical (PPM) $[\text{Eu}(\mu_3\text{-OCO})_2(\mu_2\text{-OCO})]$ motif as chain which are further linked by the fragments of tbc- ligands and Ag(I). Polymer **2** is crystallized in a triclinic fashion having a $P\bar{1}$ space group, consisting of 1D mesomeric chains $[\text{Eu}(\mu_3\text{-OCO})_2]$ which were further linked by the two different $[\text{N-Ag-N}]$ units to form an interesting 2D 4*d*-4*f* heterometallic coordination polymer in the ab plane. The solid-state luminescent behaviors of compounds **1** and **2** were investigated at room temperature. CCDC: 1018336, **1**; 1024087 **2**.

Keywords: 4-(1*H*-1,2,4-triazol-1-yl) benzoic acid ligand; heterometallic; crystal structure

收稿日期: 2015-06-01。收修改稿日期: 2015-12-04。

国家自然科学基金(No.21365012)资助项目。

*通信联系人。E-mail: fangzhili1972@126.com; 会员登记号:。

0 Introduction

Construction and characterization of metal-organic coordination polymers have attracted intense interest due to their potential applications in enantioselective separation^[1-3], nonlinear optical^[4-5], and magnetic properties^[6-8]. Heterometallic compounds formed from lanthanides and transition-metal ions are of interest not only because of their fascinating structural topology, but also for their potential applications as functional materials in luminescence^[9-11], molecular adsorption^[12], bimetallic catalysis^[13-14] and magnetism^[15-17]. There was also considerable progress to design and fabricate *d-f* heterometallic coordination polymers, from 1D chains, 2D lattices to 3D frameworks^[10,18-20]. Generally, two routes were used to prepare heterometallic coordination polymers: the first route is based on the use of the presynthesized metal complexes which contain uncoordinated donors to combine with the second type of metal ions^[21]; the second route is based on the use of multidentate organic ligands to bind two types of metal ions in a one-pot reaction^[19-20]. Moreover, it is well known that lanthanide ions have a high affinity for binding to hard donors like the O atom, whereas most transition metal ions prefer to coordinate to soft donors like the N atom^[10]. As a consequence, it should be rational to select the polydentate compartmental ligand containing both O and N donors for the construction of new heterometallic coordination polymers. These ligands such as pyrazine carboxylic acid^[22-23], imidazolecarboxylic acid^[21,24] and pyridinecarboxylic acid^[25] have been widely explored for preparing novel *d*-transition and *f*-lanthanide homometallic coordination polymers. Thus, 4-(1*H*-1,2,4-triazol-1-yl) benzoic acid (Htbc), which contains three triazol nitrogen atoms and two carboxylate oxygen atoms, might provide the impetus for the synthesis of novel heterometallic complexes. To the best of our knowledge, there is no report that Htbc ligand is used to construct heterometallic coordination polymers. In the current work, Htbc with both N and O donor atoms was used to fabricate chiral Ln-Ag heterometallic coordination polymers. We herein report the synthesis,

structure and characterization of two 2D heterometallic complexes based on Htbc ligands: one is a chiral 2D heterometallic Eu-Ag coordination polymer $\{[\text{EuAg}(\text{tbc})_3(\text{H}_2\text{O})]\text{ClO}_4 \cdot \text{H}_2\text{O}\}_n$ (**1**), containing triple-stranded helical (PPM) chains with [Eu-OCO] connectivity; the other is a novel achiral 2D heterometallic Eu-Ag coordination polymer $\{[\text{Eu}_2\text{Ag}_3(\text{tbc})_6(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\}_n$ (**2**).

1 Experimental

1.1 General procedures

Htbc was obtained from Jinan Henghua science and technology Ltd (Jinan, China). The other chemicals were commercially available reagents of analytical grade and used without further purification. Elemental (C, H, N) analyses were performed on Perkin-Elmer 240 element analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000~400 cm^{-1} on a Nicolet 5DX spectrometer. Powder X-ray diffraction (PXRD) patterns of the samples were recorded using an X-ray diffractometer (BRUKER D8 ADVANCE) with Cu $K\alpha$ radiation ($\lambda=0.154\ 18\ \text{nm}$). Fluorescence spectra was recorded with an F-2500 FL Spectrophotometer analyzer.

Caution: Although we have experienced no problem with the compounds reported in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution.

1.2 Preparation of $\{[\text{EuAg}(\text{tbc})_3(\text{H}_2\text{O})]\text{ClO}_4 \cdot \text{H}_2\text{O}\}_n$ (**1**)

A mixture of Eu_2O_3 (0.5 mmol), AgNO_3 (0.5 mmol), Htbc (0.5 mmol), HClO_4 (0.2 mL) and distilled water (10 mL) was sealed in a 20 mL Teflon-lined stainless steel reactor and then heated to 150 $^\circ\text{C}$ for 72 h under autogenous pressure. Then the mixture was slowly cooled to room temperature at a rate of 5 $^\circ\text{C} \cdot \text{h}^{-1}$, and dark red crystals of **1** suitable for X-ray crystal analysis were obtained. Yield: 50%. Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{AgClEuN}_9\text{O}_{12}$ (%): C 33.76, H 2.29, N 13.13; Found (%): C 33.92, H 2.11, N 13.35. IR (KBr, cm^{-1}): 3 456vs, 3 132 m, 2 385 m, 1 606 s, 1 544 s, 1 413 s, 1 282 m, 1 107 m, 1 080 m, 781 m, 501.

2.3 Preparation of $[\{\text{Eu}_2\text{Ag}_3(\text{tbc})_6(\text{NO}_3)_2(\text{H}_2\text{O})_2\} \cdot (\text{ClO}_4)_2 (\text{H}_2\text{O})_2]_n$ (**2**)

A mixture of Eu_2O_3 (0.5 mmol), AgNO_3 (0.5 mmol), Htbc (0.5 mmol), HClO_4 (0.1 mL) and distilled water (10 mL) was sealed in a 20 mL Teflon-lined stainless steel reactor and then heated to 170 °C for 72 h under autogenous pressure. Then the mixture was slowly cooled to room temperature at a rate of 5 °C · h⁻¹, and colorless crystals of **2** suitable for X-ray crystal analysis were obtained. Yield: 10%. Anal. Calcd. for $\text{C}_{54}\text{H}_{45}\text{Ag}_3\text{Cl}_2\text{Eu}_2\text{N}_{20}\text{O}_{30}$ (%): C 30.10, H 2.09, N 13.01; Found(%): C 30.47, H 2.14, N 13.35. IR(KBr, cm⁻¹): 3 128 vs, 2 916 m, 2 788 m, 2 510 m, 1 913 m, 1 691 s, 1 605 s, 1 524 s, 1 445 m, 1 412 s, 1 261m, 1275 s, 1 221m, 1 156 m, 975 s, 861 m, 774 m.

1.3 X-ray crystallographic study

All the diffraction data for complexes **1** and **2** were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) using the ω -scan

technique. Multi-scan absorption corrections were applied with the SADABS program^[26]. The structures were solved by direct methods using the SHELXS-97 program and all the non-hydrogen atoms were refined anisotropically with the full-matrix least-squares on F^2 using the SHELXL-97 program^[27]. The hydrogen atoms of water molecules were located in the difference Fourier maps and the other hydrogen atoms were generated geometrically and refined as riding atoms with isotropic thermal factors. Crystallographic data and structure determination summaries for **1** and **2** are given in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC: 1018336, **1**; 1024087, **2**.

2 Results and discussion

2.1 Description of the crystal structure of **1**

Single-crystal X-ray diffraction analysis of **1** reveals that the complex crystallizes in the orthorhombic chiral space group $P2_12_12_1$ and possesses a 2D

Table 1 Crystal data for compounds **1** and **2**

Compound	1	2
Chemical formula	$\text{C}_{27}\text{H}_{22}\text{AgClEuN}_9\text{O}_{12}$	$\text{C}_{54}\text{H}_{45}\text{Ag}_3\text{Cl}_2\text{Eu}_2\text{N}_{20}\text{O}_{30}$
Formula weight	959.82	2 152.53
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a / nm	0.975 0(2)	0.975 11(5)
b / nm	1.353 9(3)	1.285 31(4)
c / nm	2.369 2(5)	1.428 35(7)
α / (°)		115.031(4)
β / (°)		95.365 (4)
γ / (°)		91.279(3)
V / nm ³	3.127 50(15)	1.611 13(12)
Z	4	1
D_c / (g · cm ⁻³)	2.038	2.219
μ / mm ⁻¹	2.779	3.007
θ range / (°)	2.57~25.01	2.48~25.01
$F(000)$	1 880	1 050
Reflections collected	10 218	12 286
Independent reflections (R_{int})	5 379	5 658 (0.046 7)
Reflections observed [$I > 2\sigma(I)$]	4 881	4 711
GOF on F^2	1.015	1.017
R_1 [$I > 2\sigma(I)$]	0.034 4	0.046 5
wR_2 [$I > 2\sigma(I)$]	0.055 5	0.109 6

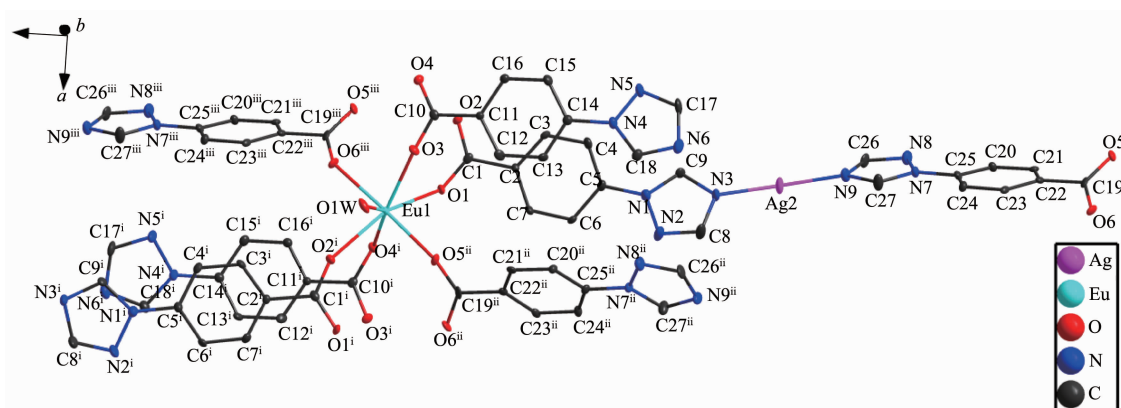
Table 2 Selected bond distances (nm) and angles (°) for **1** and **2**

1					
Eu(1)-O(3)	0.231 4(5)	Eu(1)-O(5) ⁱ	0.231 8(4)	Eu(1)-O(2) ⁱⁱ	0.233 3(4)
Eu(1)-O(6) ⁱⁱⁱ	0.234 3(4)	Eu(1)-O(4) ⁱⁱ	0.235 3(4)	Eu(1)-O(1)	0.235 8(4)
Eu(1)-O(1W)	0.240 6(4)	O(2)-Eu(1) ^{iv}	0.233 3(4)	O(5)-Eu(1) ^v	0.231 8(4)
O(4)-Eu(1) ^{iv}	0.235 3(4)	O(6)-Eu(1) ^{vi}	0.234 3(4)	Ag(2)-N(3)	0.213 5(5)
Ag(2)-N(9)	0.214 8(5)				
O(3)-Eu(1)-O(5) ⁱ	97.09(15)	O(3)-Eu(1)-O(2) ⁱⁱ	136.19(17)	O(5) ⁱ -Eu(1)-O(2) ⁱⁱ	89.72(12)
O(3)-Eu(1)-O(6) ⁱⁱⁱ	83.68(14)	O(5) ⁱ -Eu(1)-O(6) ⁱⁱⁱ	177.11(16)	O(2) ⁱⁱ -Eu(1)-O(6) ⁱⁱⁱ	87.81(14)
O(3)-Eu(1)-O(4) ⁱⁱ	146.03(15)	O(5) ⁱ -Eu(1)-O(4) ⁱⁱ	96.36(16)	O(2) ⁱⁱ -Eu(1)-O(4) ⁱⁱ	74.79(16)
O(6) ⁱⁱⁱ -Eu(1)-O(4) ⁱⁱ	84.45(14)	O(3)-Eu(1)-O(1)	76.03(14)	O(5) ⁱ -Eu(1)-O(1)	85.87(15)
O(2) ⁱⁱ -Eu(1)-O(1)	147.77(16)	O(6) ⁱⁱⁱ -Eu(1)-O(1)	97.02(14)	O(4) ⁱⁱ -Eu(1)-O(1)	74.01(14)
O(3)-Eu(1)-O(1W)	68.77(14)	O(5) ⁱ -Eu(1)-O(1W)	83.22(17)	O(2) ⁱⁱ -Eu(1)-O(1W)	69.20(16)
O(6) ⁱⁱⁱ -Eu(1)-O(1W)	94.49(15)	O(4) ⁱⁱ -Eu(1)-O(1W)	143.99(13)	O(1)-Eu(1)-O(1W)	141.37(14)
N(3)-Ag(2)-N(9)	174.5(2)				
2					
Eu(1)-O(1)	0.234 2(5)	Eu(1)-O(1W)	0.242 4(5)	Eu(1)-O(3)	0.244 1(5)
Eu(1)-O(4) ^{viii}	0.237 6(4)	Eu(1)-O(5)	0.230 4(5)	Eu(1)-O(6) ^{vii}	0.233 1(5)
Eu(1)-O(8)	0.255 3(6)	Eu(1)-N(10)	0.297 7(7)	Eu(1)-O(9)	0.258 6(6)
Ag(1)-N(3)	0.214 3(6)	Ag(1)-N(9) ^{ix}	0.213 2(6)	Ag(2)-N(6)	0.211 3(6)
Ag(2)-N(6) ^x	0.211 3(6)				
O(5)-Eu(1)-O(6) ^{vii}	86.92(17)	O(5)-Eu(1)-O(1)	114.17(17)	O(6) ^{vii} -Eu(1)-O(1)	146.64(19)
O(5)-Eu(1)-O(4) ^{viii}	165.22(18)	O(6) ^{vii} -Eu(1)-O(4) ^{viii}	81.17(16)	O(1)-Eu(1)-O(4) ^{viii}	80.42(17)
O(5)-Eu(1)-O(1W)	89.34(17)	O(6) ^{vii} -Eu(1)-O(1W)	72.52(18)	O(1)-Eu(1)-O(1W)	129.90(17)
O(4) ^{viii} -Eu(1)-O(1W)	78.79(17)	O(5)-Eu(1)-O(3)	78.88(17)	O(6) ^{vii} -Eu(1)-O(3)	140.44(19)
O(1)-Eu(1)-O(3)	71.66(18)	O(4) ^{viii} -Eu(1)-O(3)	104.96(16)	O(1W)-Eu(1)-O(3)	70.60(16)
O(5)-Eu(1)-O(8)	70.02(19)	O(6) ^{vii} -Eu(1)-O(8)	89.65(18)	O(1)-Eu(1)-O(8)	75.14(18)
O(4) ^{viii} -Eu(1)-O(8)	118.34(18)	O(1W)-Eu(1)-O(8)	153.65(18)	O(3)-Eu(1)-O(8)	118.75(16)
O(5)-Eu(1)-O(9)	116.02(18)	O(6) ^{vii} -Eu(1)-O(9)	75.03(19)	O(1)-Eu(1)-O(9)	72.50(18)
O(4) ^{viii} -Eu(1)-O(9)	69.30(18)	O(1W)-Eu(1)-O(9)	137.23(16)	O(3)-Eu(1)-O(9)	144.15(19)
O(8)-Eu(1)-O(9)	49.58(17)	O(5)-Eu(1)-N(10)	93.78(19)	O(6) ^{vii} -Eu(1)-N(10)	83.24(19)
O(1)-Eu(1)-N(10)	70.40(18)	O(4) ^{viii} -Eu(1)-N(10)	93.48(18)	O(1W)-Eu(1)-N(10)	155.37(17)
O(3)-Eu(1)-N(10)	133.96(17)	O(8)-Eu(1)-N(10)	24.94(17)	O(9)-Eu(1)-N(10)	24.75(17)
N(9) ^{ix} -Ag(1)-N(3)	174.1(2)	N(6)-Ag(2)-N(6) ^x	180.0(6)		

Symmetry codes: ⁱ $x+1/2, -y-5/2, -z+2$; ⁱⁱ $x+1/2, -y+5/2, -z+3$; ⁱⁱⁱ $x, y, z+1$; ^{iv} $x-1/2, -y+5/2, -z+3$; ^v $x-1/2, -y+5/2, -z+2$; ^{vi} $x, y, z-1$ for complex **1**; ^{vii} $-x+2, -y+2, -z+1$; ^{viii} $-x+1, -y+2, -z+1$; ^{ix} $-x+1, -y, -z$; ^x $-x+2, -y, -z$ for complex **2**.

heterometallic coordination framework. The asymmetric unit of **1** contains one perchlorate (ClO_4^-), three tbc anion, one Eu(III) ion, one Ag(I) ion, one coordinated water molecule and one uncoordinated water molecule. As shown in Fig.1, the Eu(III) center is coordinated with seven oxygen atoms, among which six oxygen atoms are derived from six different tbc

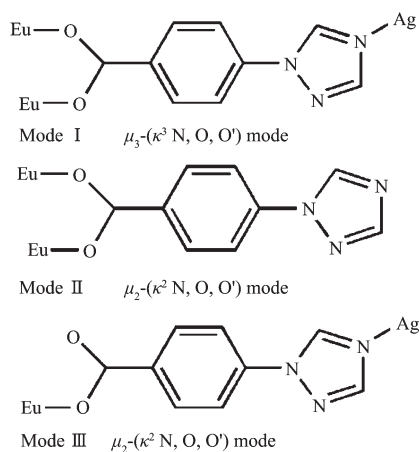
ions and one water molecule completing the coordination sphere of the Eu(III) ion with O_7 donor set. The Eu(III)-O bond lengths (0.231 4(4)~0.240 3(5) nm) are in the normal range^[8]. The bond angles around the central Eu(III) atom vary from $68.76(18)^\circ$ to $177.2(2)^\circ$, similar to those reported for other seven-coordinated Eu(III) coordination polymers with oxygen donor



All hydrogen atoms are omitted for clarity; Symmetry code: ⁱ 0.5+x, 2.5-y, 3-z; ⁱⁱ 0.5+x, 2.5-y, 2-z; ⁱⁱⁱ x, y, 1+z

Fig.1 Coordination environment of the Eu³⁺ and Ag⁺ ions in complex **1** with 30% thermal ellipsoids

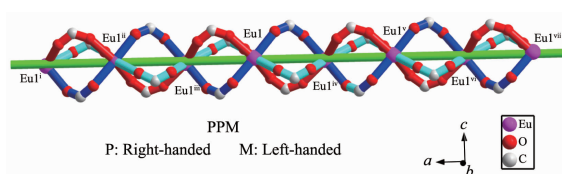
ligands [10]. As far as the Ag(I) ion in the coordination framework is concerned, it exhibits a linear configuration, being coordinated by two N atoms from two bridging tbc ligands. The Ag-N bond lengths are in the range of 0.213 5(6) to 0.214 5(7) nm, and the N-Ag-N bond angle is 174.5(3)°. In complex **1**, the Htbc ligands exhibit two types of distinctly different coordination modes: one acts as a bridging ligand to coordinate one Ag(I) ion and two Eu(III) ions (Scheme 1, Mode I) and the other acts a terminal ligand to coordinate two Eu(III) ions (Scheme 1, Mode II).



Scheme 1 Coordination modes of the tbc anions in compounds **1** and **2**

In the structure of **1**, the chiral unit can be considered as a right-handed helix. A pair of Eu(III) ions are interconnected through three carboxylate groups of three ligands tbc⁻ with modes I and II to give a [Eu(μ₃-OCO)₂(μ₂-OCO)] unit with Eu1 ... Eu1

distance of 0.499 1 nm, which may be viewed as a secondary building unit (SBU) to further extend into 1D triple strand right-right-left-handed helical (PPM) chain along the a axis (Fig.2). Although all the components appearing in the system are achiral, **1** crystallizes in the chiral space group *P*2₁2₁1. A direct vision of the topology of the 1D chain structure is illustrated in Fig.2. As you can see from Fig.2, the net handedness of the chain is right-handed.



Symmetry code: ⁱ 1.5+x, 2.5-y, 3-z; ⁱⁱ 1+x, y, z; ⁱⁱⁱ 0.5+x, 2.5-y, 3-z; ^{iv} -0.5+x, 2.5-y, 3-z; ^v -1+x, y, z; ^{vi} -1.5+x, 2.5-y, 3-z; ^{vii} -2+x, y, z

Fig.2 1D three-strand helical chains [Eu(μ₃-OCO)₂(μ₂-OCO)] (PPM) in compound **1** along the a axis

These parallel right-right-left (PPM)-handed triple stranded helical chains are further linked by the [AgN₂] unit constructed from two triazole nitrogen atoms of the μ₃-(κ³ N, O, O')-tbc⁻ ligands, leading to the formation of a wave-like 2D 4d-4f heterometallic coordination polymer in the ac plane (Fig.3). Furthermore, the adjacent 2D layers are linked through hydrogen bonds (Table 3) involving carboxylate oxygen atoms, coordinated water, uncoordinated water molecules, ClO₄⁻ and triazole nitrogen atoms, thereby producing a 3D supramolecular network (Fig.4).

Table 3 Hydrogen bonding parameters for complex 1 and 2

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
1				
O1W-H1WA...O10 ⁱ	0.090	0.194	0.282 9	172.1
O1W-H1WA...Cl1 ⁱ	0.090	0.281 7	0.365 9	156.2
O1W-H1WB...N6 ⁱ	0.090	0.188 4	0.276 0	165.9
O2W-H2WA...O4 ⁱⁱ	0.090	0.238 0	0.308 2	134.6
O2W-H2WB...O1W ⁱⁱⁱ	0.090	0.254 1	0.338 9	157.3
2				
O1W-H1...O4	0.096	0.203	0.278 5	133.8
O1W-H2...O2 ^{iv}	0.096	0.183	0.265 3	142.0
O2W-H2WA...O4 ^v	0.096	0.233	0.311 6	138.2
O2W-H2WB...O10 ^{vi}	0.096	0.203	0.300 0	170.9
O1W-H2...O1 ^{iv}	0.096	0.250	0.315 5	125.6

Symmetry code: ⁱ -0.5-x, 3-y, 0.5+z; ⁱⁱ -1-x, -0.5+y, 2.5-z; ⁱⁱⁱ -x, -0.5+y, 2.5-z; ^{iv} 1-x, 2-y, 1-z; ^v 1-x, 1-y, 1-z; ^{vi} 1-x, -y, -z.

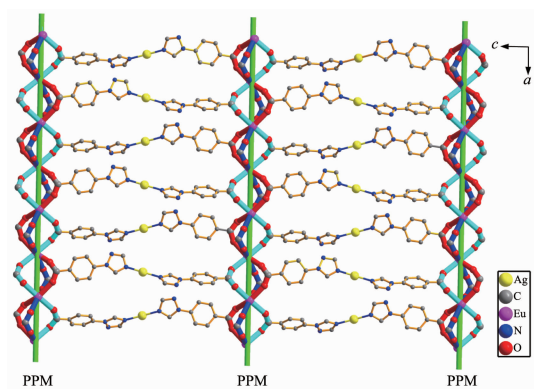


Figure 3 2D chiral heterometallic layer in **1** fabricated by the coordination link of ligand tbc⁻ in mode I between two adjacent right-right-left (PPM)-handed helical chains in the ac plane, in which the ligand tbc⁻ has coordination mode II

Hydrogen atoms, ClO₄⁻ anions, coordinated water and uncoordinated water molecules have been omitted for clarity

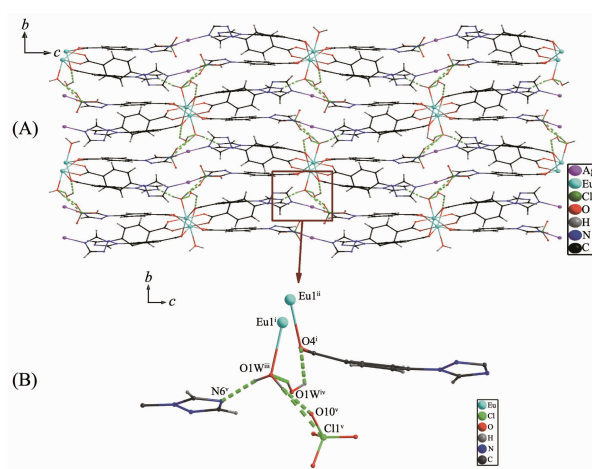


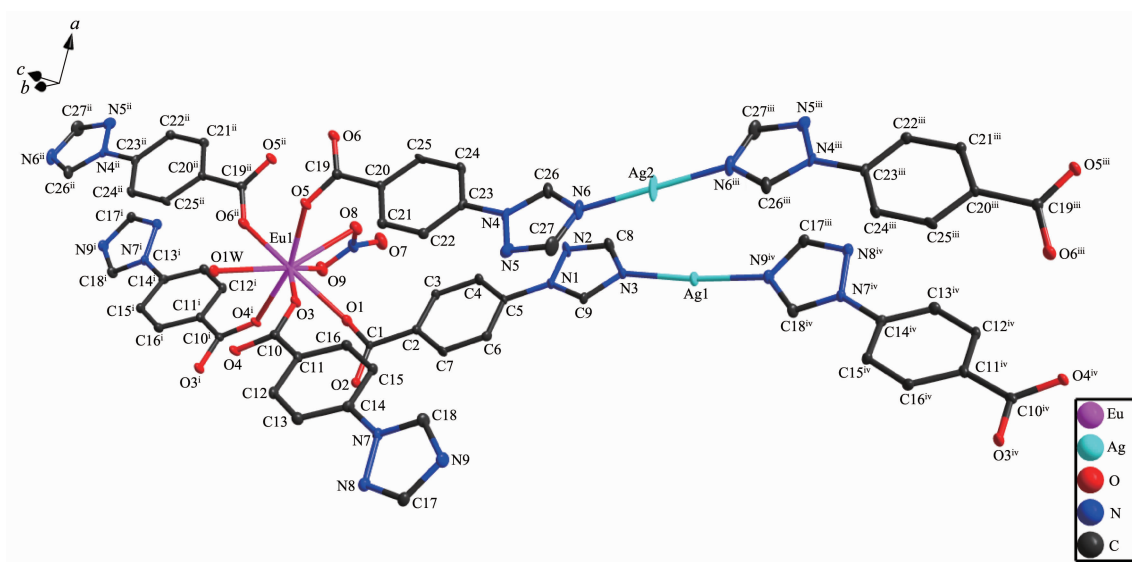
Figure 4 Packing structure constructed through hydrogen bonds (dot line) with an-ABAB-sequence along the *b* axis

Symmetry code: ⁱ 0.5+x, 1.5-y, 2-z; ⁱⁱ 1+x, -1+y, -1+z; ⁱⁱⁱ 0.5+x, 1.5-y, 2-z; ^{iv} 0.5-x, 1-y, -0.5+z; ^v -x, -1.5+y, 1.5-z

2.2 Description of the crystal structures of 2

Single crystal X-ray diffraction analyses reveal that complex **2** crystallizes in the triclinic space group *P* $\bar{1}$ and feature interesting 2D 4*d*-4*f* heterometallic coordination polymers. As depicted in Fig.5, the symmetric unit of **2** consists of one crystallographically independent Eu(III) cation, two Ag(I) cation (The crystallographically occupancy of the two Ag (I) cations is 1 and 0.5 respectively), three unique tbc⁻ anions, one coordinated nitrate ion, one perchlorate (ClO₄⁻), one coordinated water molecule, as well as one lattice water molecule. The coordination

polyhedron around the central Eu (III) atom can be visualized as slightly distorted bicapped trigonal prismatic arrangement with a [EuO₈] coordination sphere: five carboxylate oxygen atoms come from five individual tbc⁻ anions; one oxygen comes from one coordinated water molecule; other two oxygen atoms come from one nitrate anion. The Eu-O bond lengths are 0.230 4(5) and 0.258 6(6) nm. The bond angles around the central Eu(III) atom vary from 24.75(17)° to 165.22(18)°, similar to those reported for other eight-coordinated Eu(III) coordination polymers with oxygen donor ligands^[26]. In complex **2**, the Htbc ligands



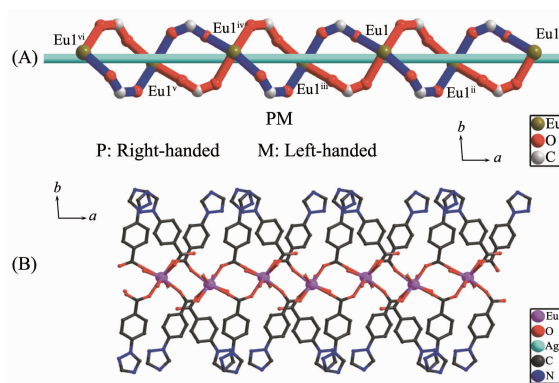
All hydrogen atoms are omitted for clarity; Symmetry code: ⁱ 1-*x*, 2-*y*, 1-*z*; ⁱⁱ 2-*x*, 2-*y*, 1-*z*; ⁱⁱⁱ 2-*x*, -*y*, -*z*; ^{iv} 1-*x*, -*y*, -*z*

Fig.5 Coordination environment of the Eu³⁺ and Ag⁺ ions in complex **2** with 30% thermal ellipsoids

exhibit two bridging modes (Scheme 1, Mode I and III): one acts as a μ_2 bridge between one Eu(III) ion and one Ag(I) ion; the other one acts as a μ_3 bridge between two Eu(III) ions and one Ag(I) ion. Concerning two Ag(I) ions, both Ag1 and Ag2 ions are two coordinated with two nitrogen atoms belonging to two different *tbc*⁻ anions, forming the linear configuration. The Ag-N bond lengths are in the range of 0.211 3(6) to 0.214 3(6) nm, and the N-Ag-N bond angles are 180.0(6)° and 174.1(2)°. The main difference is that Ag1 ion is coordinated by two N atoms from two triazole rings with μ_3 -(κ^3 N, O, O') coordination mode, while Ag2 is coordinated by two N atoms from two triazole groups with μ_3 -(κ^3 N, O, O') and μ_2 -(κ^2 N, O) coordination modes.

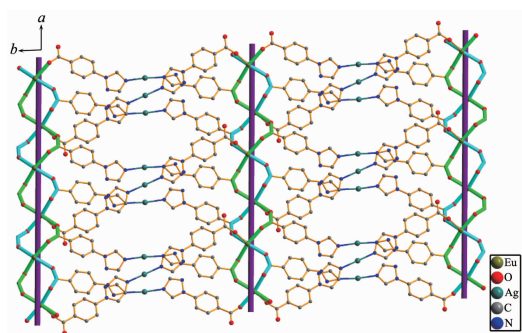
Two of the *tbc*⁻ ligands in complex **2** link to two Eu1 atoms in a μ_3 -(κ^3 N, O, O') mode (Scheme 1a). As illustrated in Fig.6, every two Eu1 ions connect to four μ_3 -*tbc*⁻ ligands and every two μ_3 -*tbc*⁻ ligands link two Eu1 ions, giving rise to an infinite 1D mesomeric chain consisting of a right-left-handed helical (PM) chains along the *a* axis (Fig.6a), where the adjacent two nonbonding Eu(III)···Eu(III) distances are equal to 0.4935 3(6) nm and 0.527 72(6) nm, respectively. These 1D chains are further linked by the [N-Ag1-N] unit from two triazole nitrogen atoms of the μ_3 -*tbc*⁻

ligands and the [N-Ag2-N] unit from two triazole nitrogen atoms of the μ_3 -(κ^3 N, O, O')-*tbc*⁻ and μ_2 -(κ^2 N, O)-*tbc*⁻ ligands, leading to the formation of a n interesting 2D 4d-4f heterometallic coordination polymer in the *ab* plane (Fig.7). Furthermore, the 2D networks are stacked via interdigitation along the *c* axis (Fig.8). The alternate 2D layers are linked by van der Waals interaction and hydrogen bonds (Table 3) involving oxygen atoms of the ligands, perchlorate oxygen atoms and uncoordinated water molecules, thereby producing a 3D supramolecular network (Fig.8).



H atoms of Carbons have been omitted for clarity; Symmetry code: ⁱ 1+*x*, *y*, *z*; ⁱⁱ 1-*x*, 2-*y*, 1-*z*; ⁱⁱⁱ -*x*, 2-*y*, 1-*z*; ^{iv} -1+*x*, *y*, *z*; ^v -1-*x*, 2-*y*, 1-*z*; ^{vi} -2+*x*, *y*, *z*

Fig.6 (a) 1D *meso*-chain [Eu(μ_3 -OCO)₂] (PM) in compound **2** along the *a* axis; (b) A fragment of the 1D *meso*-chain of complex **2**



Hydrogen atoms, ClO_4^- anions, coordinated NO_3^- anions, coordinated water and uncoordinated water molecules have been omitted for clarity

Fig.7 2D heterometallic layer in **2** fabricated by the coordination link of ligand tbc^- in modes I and III between two adjacent *meso*-chains in the *ab* plane

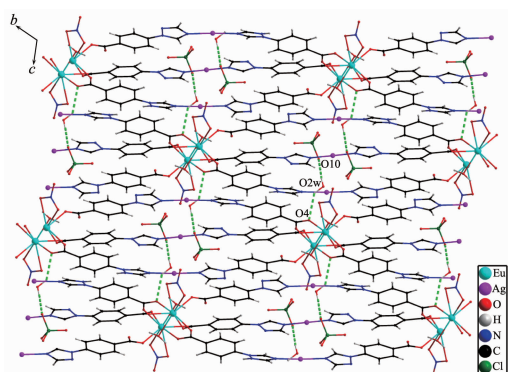


Fig.8 3D supramolecular framework organized by the H-bonding (dot line) in complex **2**

2.3 PXRD pattern and photoluminescent properties

The PXRD pattern of **1** is in good agreement with the ones simulated from single-crystal structural data, which confirmed the purity of the bulk sample (Fig.9).

Because of the excellent luminescent properties

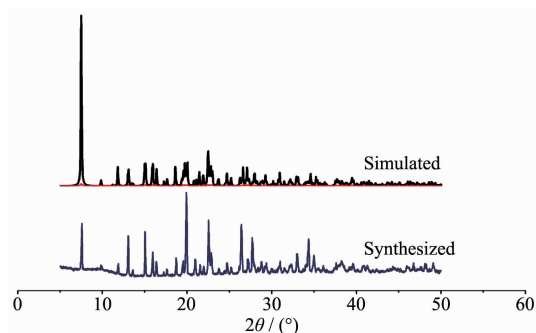


Fig.9 PXRD pattern of **1**

of Eu(III) ions, the luminescences of **1** and **2** were investigated. The emission spectrum of **1** (Fig.10a) at room temperature upon excitation at 395 nm displays red luminescence and exhibits the characteristic transition of $^5D_0 \rightarrow ^7F_J$ ($J=0 \sim 4$) of Eu(III) ions. The emission spectrum is dominated by the characteristic $^5D_0 \rightarrow ^7F_2$ electron dipole transition at 615 nm. In addition, two weak peaks at 651 nm and 705 nm can be attributed to the $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ transition, respectively^[28]. Similarly, complex **2** exhibits the characteristic emission of Eu(III) ions (Fig.10b).

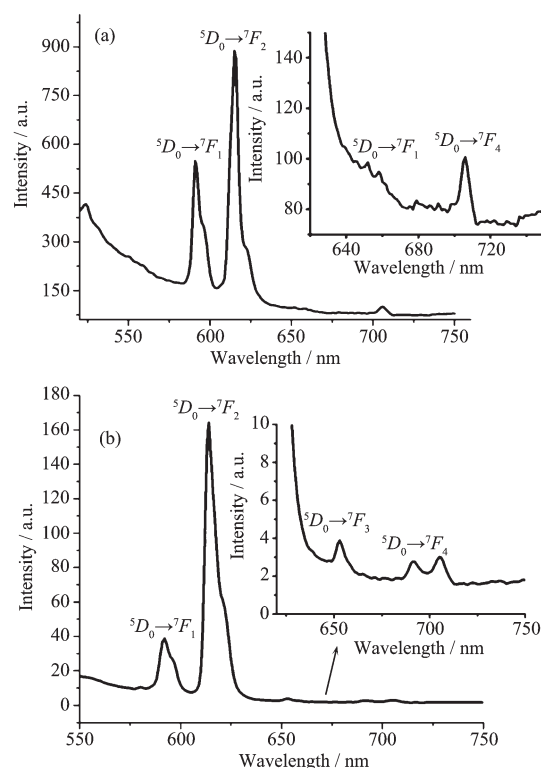


Fig.10 Solid-state emission spectra of complexes **1** (a) and **2** (b)

3 Conclusions

In conclusion, we have successfully synthesized two novel 2D Eu-Ag heterometallic coordination polymers. Compound **1** is chiral and its 2D lattices are constructed from the parallel right-right-left (PPM)-handed triple stranded helical chains $[\text{Eu}(\text{OCO})_3]_n$ which are further linked by Ag(I) and the fragments of tbc^- ligands. In complex **2**, the 1D chains of $[\text{Eu}(\text{OCO})_2]_n$ are linked by the $[\text{N-Ag1-N}]$ unit from two triazole nitrogen atoms of the $\mu_3\text{-tbc}^-$ ligands and

the [N-Ag₂-N] unit from two triazole nitrogen atoms of the μ_3 -(κ^3 N, O, O')-tbc⁻ and μ_2 -(κ^2 N, O)-tbc⁻ ligands, leading to the formation of an 2D 4d-4f heterometallic coordination polymer. The complexes **1** and **2** exhibit characteristic lanthanide luminescence of rare earth ion Eu³⁺. The result obtained here can enrich the structure chemistry of transition-lanthanides with chiral helix Ln-OCO-Ln cluster cores.

References:

- [1] Xie S M, Zhang Z J, Wang Z Y, et al. *J. Am. Chem. Soc.*, **2011**,**133**:11892-11895
- [2] Nuzhdin A L, Dybtsev D N, Bryliakov K P, et al. *J. Am. Chem. Soc.*, **2007**,**129**:12958-12959
- [3] Seo J S, Whang D, Lee H, et al. *Nature*, **2000**,**404**:982-986
- [4] Qu Z R, Zhao H, Wang Y P, et al. *Chem. Eur. J.*, **2004**,**10**: 53-60
- [5] Ye H T, Ren C Y, Hou G F, et al. *Cryst. Growth Des.*, **2014**, **14**:3309-3318
- [6] Train C, Gheorghe R, Krstic V, et al. *Nat. Mater.*, **2008**,**7**: 729-734
- [7] Barron L D. *Nat. Mater.*, **2008**,**7**:691-692
- [8] Zhang W, Xiong R G. *Chem. Rev.*, **2012**,**112**:1163-1195
- [9] YU Gang(禹钢), BIAN Zu-Qiang(卞祖强), LIU Zhi-Wei(刘志伟), et al. *Sci. China Ser. B: Chem.*(中国科学 B:化学), **2014**,**4**(2):267-276
- [10] Gu X, Xue D. *Inorg. Chem.*, **2006**,**45**:9257-9261
- [11] Lestari W W, Lnncke P, Streit H C, et al. *Eur. J. Inorg. Chem.*, **2014**:1775-1782
- [12] Li J R, Tao Y, Yu Q, et al. *Chem. Eur. J.*, **2008**,**14**:2771-2776
- [13] YAO Ke-Min(姚克敏), LI Ning(李宁), HUANG Qiao-Hong(黄巧虹), et al. *Sci. China Ser. B: Chem.*(中国科学 B:化学), **1998**,**28**(6):517-523
- [14] Liu Q Y, Xiong W L, Liu C M, et al. *Inorg. Chem.*, **2013**, **52**:6773-6775
- [15] Tanase S, Andruh M, Müller A, et al. *Chem. Commun.*, **2001**:1084-1085
- [16] GU Jin-Zhong(顾金忠), JIANG Long(姜隆), LU Tong-Bu(鲁统部), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2008**, **24**:1743-1747
- [17] Lampropoulos C, Koo C, Hill S O, et al. *Inorg. Chem.*, **2008**, **47**:11180-11190
- [18] Mukherjee S, Lan Y, Novitchi G, et al. *Polyhedron*, **2009**, **28**:1782-1787
- [19] Li Z Y, Huang H Q, Xu L, et al. *Cryst. Growth Des.*, **2013**, **13**:918-925
- [20] Sun Y G, Wu Y L, Xiong G, et al. *Dalton Trans.*, **2010**,**39**: 11383-11395
- [21] Chen R L, Chen X Y, Zheng S R, et al. *Cryst. Growth Des.*, **2013**,**13**:4428-4434
- [22] Andrews M B, Cahill C L. *CrystEngComm*, **2011**,**13**:7068-7078
- [23] Cai B, Yang P, Dai J W, et al. *CrystEngComm*, **2011**,**13**: 985-991
- [24] Cai S L, Zheng S R, Wen Z Z, et al. *Cryst. Growth. Des.*, **2012**,**12**:2355-2361
- [25] Zhou Y, Li X, Zhang L, et al. *Inorg. Chem.*, **2014**,**53**:3362-3370
- [26] Sheldrick G M. *SADABS, Program for Empirical Absorption Correction*, University of Göttingen, Germany, **1996**.
- [27] Sheldrick G M. *SHELXS-97 and SHELXL-97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [28] Quici S, Cavazzini M, Marzanni G, et al. *Inorg. Chem.*, **2005**,**44**:529-537