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Graphic abstract

Ln-Cd heterometal organic-inorganic hybrid materials based on diverse Ln-Cd oxo-cluster Chains: syntheses, structures and visible Luminescence

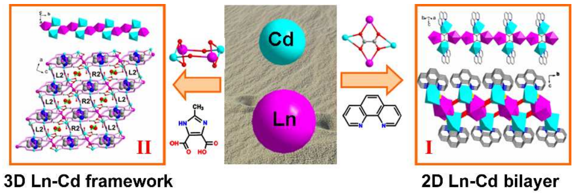
Yan-Qiong Sun,*[a,b] **Qi Liu,**[a] **Liang-Liang Zhou**[a] **and Yi-Ping Chen**[a]

[a] *Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, People's Republic of China.*

[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China.*

Fax: +86-591- 22866340 E-mail: sunyq@fzu.edu.cn

Two types of luminescent Ln-Cd heterometal complexes **I** and **II** based on diverse Ln-Cd oxo-clusters have been synthesized and characterized.



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Ln-Cd heterometal organic-inorganic hybrid materials based on diverse Ln-Cd oxo-cluster Chains: syntheses, structures and visible Luminescence

Yan-Qiong Sun,*[a,b] Qi Liu,[a] Liang-Liang Zhou[a] and Yi-Ping Chen[a]

Three novel Ln-Cd heterometal organic-inorganic hybrid materials, $[LnCd(phen)(ox)_{1.5}(SO_4)(H_2O)_2]\cdot H_2O$ (Type **I**: Ln = Sm **1a**; Eu **1b**; phen = 1, 10-phenanthroline; H_2ox = oxalic acid) and $[EuCd_2(Meimdc)_2(Ac)(H_2O)_2]\cdot H_2O$ (Type **II**: **2**; $H_3Meimdc$ = 2-methyl-imidazole-4,5-dicarboxylic acid; HAc = acetic acid) have been successfully synthesized under hydrothermal conditions. Compounds of type **I** are the first examples of Ln-Cd heterometal organic-inorganic hybrid sulfate-carboxylates with lattice bilayer stuctrure. The extended structure of type **II** consists of EuCd(Meimdc) and Cd_2(Meimdc) helices cross-linked through Ln-Cd oxo-cluster chains, showing 3D microporous architecture with left–/right–handed helical tubes (L1/R1) and channels (L2/R2) along the *b* axis. The luminescence properties reveal that complexes **1b** and **2** exhibit the characteristic emission bands of Eu^{3+} ion. Photoluminescence spectra of **1b** and **2** reveal characteristic line-splitting at room temperature, depending on the site-symmetry of Eu^{3+} ion in the complexes.

Introduction

In recent years, organic-inorganic hybrid materials are attracting great interests because of their extensive applications in gas storage,[1, 2] separation,[2, 3] catalytic,[3] magnetic,[4] biomedicine[5] and chemical sensor.[6] Owing to unique magnetic and luminescent property that derived from the electronic $[Xe]4f^n$ configurations (n=0-14) of lanthanide elements, various of lanthanide-based organic-inorganic hybrid materials with new structures and applications have been synthesized and researched. According to the synthesis methods of lanthanide-based organic-inorganic hybrid materials, the introduction of heterometallic ions, especially *d*-block ions, into these materials are more and more popular. The introduced heterometallic ions not only make the structures plentiful but also make the energy levels of these materials more controllable. To the best of our knowledge, the vast majority of these transition-lanthanide(d-f) heterometal-organic hybrid materials are focused on Ln-M (M=Cu,[4] Co,[5-8] Ni,[5, 7, 9] Fe,[5, 8, 10] Zn,[5, 11, 12] Ag,[5, 13] Mn[14] etc), however, Lanthanide-Cadmium(Ln-Cd) system remain less development.[11, 15, 16] Most of the reported transition-lanthanide(d-f) heterometal-organic hybrid materials are of unique magnetic properties, but some transition-lanthanide(d-f) heterometal-organic hybrid materials are also equipped with excellent luminescent property. And recently, the luminescent application of chemical sensor that quenching and enhancing of luminescence of materials detect small molecule and ions are of significant development. Cd^{2+} with $[Kr]d^{10}$ configuration could be a good structural unit and maybe take part in the luminescence of the materials. Cd^{2+} ion not only itself emits luminescence by ligands-metal interactions, but also acts as a bridge of energy transfer between organic ligands and Ln^{3+} ions. So that Ln-Cd heterometal organic-inorganic hybrid materials could be excellent candidates for the luminescent application of chemical sensor.

According to the soft-hard acid-base theory, Ln^{3+} ions belong to hard acid which have strong affinity to coordinate to hard bases like O atom, while Cd^{2+} ion is soft and like to bond to soft base S and N atoms. The competitions between Ln^{3+} and Cd^{2+} in the reaction system making it is hard to synthesize Ln-Cd heterometal-organic coordination complexes. Based on what was mentioned above, benzimidazole-5,6-dicarboxylic acid (H_3bidc) and methyl-imidazole-4,5-dicarboxylic acid were used in our synthesis of Ln-Cd heterometal organic-inorganic hybrid materials. These organic ligands have two carboxylate

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[a] *Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, People's Republic of China. Fax: +86-591- 22866340; E-mail sunyq@fzu.edu.cn*
[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China*

† Electronic Supplementary Information (ESI) available: Synthesis,table, supplementary 14 plots including strcutres, luminescent spectra, XPRD ,TG and FT-IR. See DOI: 10.1039/b000000x.

groups of hard base and two coordination N atoms of soft base, making it possible to bond to both Ln^{3+} and Cd^{2+} ions simultaneously in the reaction system.

Recently, polynuclear metal clusters or cluster polymers instead of single metal atoms have been used as connectors to construct MOFs.[17] Compared with single metal cluster, heterometal-cluster-based connectors generally have more structure motifs and are more complicated. Therefore, it should be a rational way to introduce hetero-Ln-TM clusters or cluster polymers to assembly hetero-Ln-TM structures. In a few reported Ln-Cd heterometal-organic hybrid materials, it is found that Ln^{3+} cations and Cd^{2+} ions can be bridged by μ_2-O to form Ln-Cd-O wheel-clusters or cluster chains.[15a,16a] So we can select different organic ligands to obtain distinct types of Ln-Cd-O clusters or cluster polymers and incorporate them into the Ln-Cd frameworks, much more diversity of the structures would be expected. Although many efforts have been focused on the assembly of metal clusters to construct homometallic compounds, the synthesis of hetero-Ln-Cd compounds incorporating Ln-Cd-O clusters, are still rarely reported.[15a,16a] As a continuation of our search for new hetero-Ln-Cd frameworks constructed by Ln-Cd-O clusters, we chose different organic ligands to synthesize two types of Ln-Cd heterometal organic-inorganic hybrid materials, namely $[LnCd(phen)(ox)_{1.5}(SO_4)(H_2O)_2]\cdot H_2O$ (Type **I**: Ln = Sm **1a**; Eu **1b**; phen = 1, 10-phenanthroline; H_2ox = oxalic acid) and $[EuCd_2(Meimdc)_2(Ac)(H_2O)_2]\cdot H_2O$ (Type **II**: **2**; $H_3Meimdc$ = 2-methyl-imidazole-4, 5-dicarboxylic acid; HAc = acetic acid). Single-crystal X-ray diffraction reveals that two types of Ln-Cd frameworks are constructed based upon distinct Ln-Cd-O cluster polymers. The luminescence properties reveal that compounds **1b**, and **2** present characteristic emission bands with the line splitting of Eu^{3+} ions.

Experimental section

Materials and Physical Measurements

Commercially available solvents and chemicals were used without further purification. IR spectra were measured as KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR in the range 400-4000 cm-1. The elemental analyses of C, H and N were carried out on an Elementar Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a X'pert Pro diffractometer (CuKα) at room temperature. Thermogravimetric data were collected on a Mettler Toledo TGA/SDTA 851e analyzer in flowing nitrogen at a heating rate of 10 ºC/min. Luminescence measurements were made with an Edinburgh Instrument FS920 TCSPC luminescence spectrometer on powder crystal material of the compounds.

Synthesis of compounds

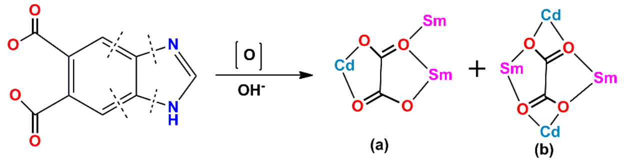
$[LnCd(phen)(ox)_{1.5}(SO_4)(H_2O)_2]\cdot H_2O$ (Ln = Sm 1a; Eu 1b) A mixture of 1,10-Phen (0.1299 g, 0.7 mmol), H_3bidc(0.1054 g, 0.5 mmol), $3CdSO_4\cdot 8H_2O$(0.1538 g, 0.2 mmol), Ln_2O_3(Sm_2O_3 0.1058 g, 0.3 mmol for **1a**, Eu_2O_3 0.1110 g, 0.3 mmol for **1b**), and H_2O(10 mL) was placed in a 23-mL Teflon-lined stainless steel vessel, heated to 160℃ for 7 days, and then cooled to room temperature. Yellow block crystals were obtained. Yield: 0.0200 g (4.5% based on Sm(III)) for **1a**, 0.0300 g (6.5% based on Eu(III)) for **1b**. Anal. Calcd. for $C_{15}H_{14}O_{13}N_2SCdSm$ **1a**: C, 24.85; H, 1.95; N, 3.86. Found: C, 24.79; H, 2.01; N, 3.85. $C_{15}H_{14}O_{13}N_2SCdEu$ **1b**: C, 24.79; H, 1.94; N, 3.85. Found: C, 24.81; H, 1.89; N, 3.84. Selected IR peaks (cm^{-1}): 3483(w), 3353(s), 2920(w), 1620(s), 1433(m), 1307(m), 1117(s), 1073(s), 845(m), 809(m), 714(m), 596(m), 494(w).

$[EuCd_2(Meimdc)_2(Ac)(H_2O)_2]\cdot H_2O$ (2) A mixture of $H_2Meimdc$ (0.3445 g, 2.0 mmol), Eu_2O_3 0.1762 g, 0.5 mmol, and H_2O (10 mL) was placed in a 23-mL Teflon-lined stainless steel vessel, heated to 170℃ for 2 days, and then cooled to room temperature, $Cd(Ac)_2\cdot 2H_2O$(0.5332 g, 2.0 mmol) was added, heated to 170℃ for 5 days, and then cooled to room temperature. Yellow block crystals were obtained. Yield: 0.4120 g (50% based on Eu(III)). Anal. Calcd. for $C_{14}H_{15}O_{13}N_4Cd_2Eu$ **2**: C, 20.40; H, 1.83; N, 6.80. Found: C, 20.51; H, 1.92; N, 6.78. Selected IR peaks (cm^{-1}): 3354(m), 3211(m), 1599(s), 1543(s), 1431(s), 1265(m), 1121(m), 831(m), 791(m), 638(m), 498(w).

Table 1. Crystal data and structure refinement for **1** and **2**

Compound	**1a**	**1b**	**2**
Formula	$C_{15}H_{14}O_{13}N_2SCdSm$	$C_{15}H_{14}O_{13}N_2SCdEu$	$C_{14}H_{15}O_{13}N_4Cd_2Eu$
Mr (g. mol^{-1})	725.09	726.70	824.06
Crystal system	triclinic	triclinic	monoclinic
space group	$P\text{-}1$	$P\text{-}1$	$P2_1/n$
a (Å)	8.8213(18)	8.6945(17)	9.6399(19)
b (Å)	9.1383(18)	8.9967(18)	9.924(2)
c (Å)	13.398(3)	13.246(3)	22.078(4)
α (°)	86.62(3)	86.66(3)	90
β (°)	89.74(3)	89.75(3)	91.64(3)
γ (°)	74.37(3)	74.51(3)	90
V ($Å^3$)	1038.2(4)	996.7(3)	2111.3(7)
Z	2	2	4
D_c (g/cm^3)	2.319	2.421	2.593
μ (mm^{-1})	3.998	4.365	5.008
reflns collected/ unique	6929/ 3542	9846/ 4526	19870/ 4790
R_{int}	0.071	0.0571	0.0387
θ range/deg	3.18-24.99	3.08-27.48	3.11-27.48
$F(000)$	696	698	1560
GOOF on F^2	1.10	1.10	1.00
R_1[a]	0.0677	0.0571,	0.0366,
wR_2[b] ($I>2\sigma(I)$)	01845	0.1345	0.0720

[a] $R_1=\sum||F_0|-|F_c||/\sum|F_0|$. [b] $wR_2=\{\sum[w(F_0^2-F_c)^2]/\sum[w(F_0^2)^2]\}^{1/2}$



Scheme. 1 Oxalate anions, formed via the oxidation-hydrolysis of benzimidazole-5,6-dicarboxylic acid

X-ray Crystallography

Suitable single crystals were selected and mounted on a glass fiber. All data of **1a** were collected on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) radiation in the ω scanning mode at room temperature; All data of **1b** and **2** were collected on a Rigaku R-AXIS RAPID diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) radiation in the ω scanning mode at room temperature. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program package.[18] Hydrogen atoms bond N and C were generated geometrically (C-H = 0.93Å, N-H=0.86Å) and refined with fixed isotropic displacement parameters. Crystallographic data for the structures reported have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 969785-969787 for **1a**, **1b** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. The selected crystal parameters, data collection, and refinements are summarized in Table 1**.**

Results and discussion

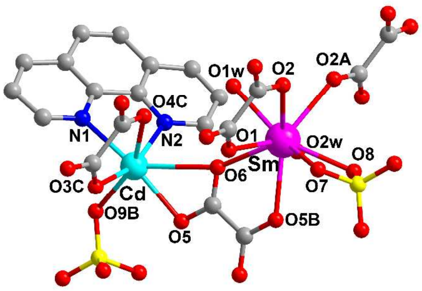


Fig. 1 The coordination environments of Sm^{3+} and Cd^{2+} in **1a**. Atoms having ‘‘A’’, ‘‘B’’ or ‘‘C’’ in their labels are symmetry-generated. A: -x, -y+2, -z+1; B: 1-x, 1-y, -z+1; C:-x, 1-y, 1-z. Hydrogen atoms are omitted for clarity. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow.

Crystal Structure

[LnCd(phen)(ox)$_{1.5}$(SO$_4$)(H$_2$O)$_2$](H$_2$O) (Ln = Sm 1a; Eu 1b)

Compound **1a** and **1b** are isomorphous and the structure of **1a** is described here representatively. The structure of **1a** can be described as the first example 2D Ln-Cd heterometal organic-inorganic hybrid bilayer structure based on 1D heterometallic Ln-Cd oxo-cluster polymer. It is interesting to note that oxidation-hydrolysis occurred and benzimidazole-5,6-dicarboxylic acid was transformed into oxalate under hydrothermal condition in the presence of Ln(III) ions （Scheme 1）. To confirm the formation of oxalate, similar reactions were carried out. When using $H_2C_2O_4.2H_2O$ or $K_2C_2O_4.2H_2O$ or $Na_2C_2O_4$ instead of the benzimidazole-5,6-dicarboxylic acid, the products could not be obtained, indicating a slow release of the oxalate ligand from the benzimidazole-5,6-dicarboxylic acid could reduce the polymerization rate, which may be helpful for the crystallization of the title compound. Other oxidation-hydrolysis reactions catalyzed by Ln(III) have also been reported.[19] As shown in Fig. 1, the asymmetric unit of **1a** consists of one crystallographically independent Cd^{2+} ion, one Sm^{3+} ion, one phen anion, one and a half oxalate anions, one sulfate anion and three H_2O molecules. The coordination geometry of Cd^{2+} ion can be viewed as slightly distorted a distorted pentagonal bipyramid: four O_{COO}- atoms from two oxalate anions, two N atoms from one phen unit and one O atom from one SO_4^{2-} (Supporting Information Fig. S1). The Sm^{3+} ion is nine-coordinated and has a tricapped trigonal prism coordination environment: five O_{COO}- atoms from three oxalates, two O atoms of one SO_4^{2-} as well as two terminal water molecules (Fig. S2). The Cd-O and Cd-N bond lengths are in the range of 2.262(6)-2.873(6) Å and 2.310(7)-2.355(8) Å, respectively. Sm-O bond lengths vary from 2.414(6) to 2.569(6) Å. The oxalate ligands adopt two coordination modes: one coordinates to one Cd centers in a chelating mode and two Sm^{3+} ions through a chelating and bridging coordination (Scheme 1a), while the other adopts an interesting octadentate chelating and bridging coordination mode, which chelates with two Sm^{3+} and two Cd^{2+} ions, forming two five-membered Sm-O-C-C-O rings and two four-membered Cd-O-C-O rings (Scheme 1b). All four carboxylate oxygen atoms of oxalate in mode 1b are bidentate metal linkers. Such a coordination mode was only reported in its sodium-cobalt(II) heterometallic complex[20] and its lanthanum(III) sulfate-oxalate hybrid.[21]

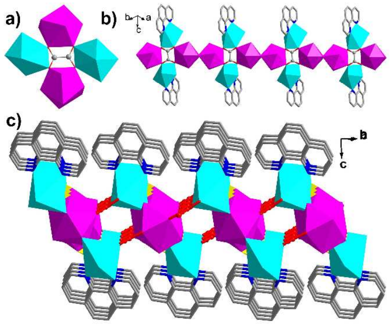


Fig. 2 (a) Polyhedron view of the star-like $Ln_2Cd_2O_4$ tetranuclear cluster with the ox^{2-} anion in the center in **1a**. (b) Polyhedron view of the inorganic centipede-like heterometallic cluster chain running along the [1-10] direction in **1a**. (c) 2-D bilayer structure constructed from heterometallic cluster chains bridged by ox^{2-} anions (red) viewed along the [1-10] direction in **1a**. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow.

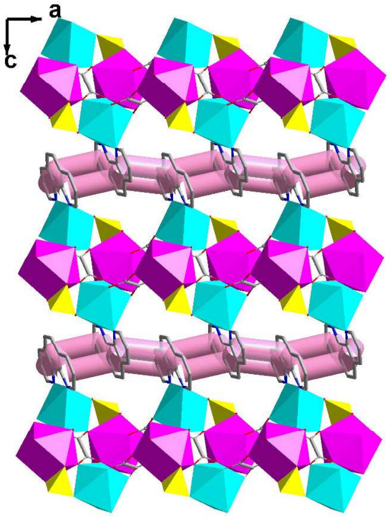
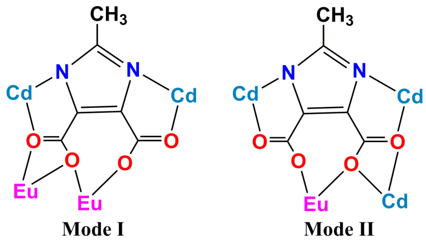


Fig. 3 View of the 3-D supermolecular network through face-to-face π···π stacking interaction in **1a**. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow.

Four carboxylate μ_2-O atoms of oxalate in mode 1b alternately connect Sm^{3+} ion and Cd^{2+} ion to form a four-pointed star-like eight-membered tetranuclear $Sm_2Cd_2(\mu_2\text{-}O)_4$ cluster unit(Fig. 2a, S3a). Each $Sm_2Cd_2O_4$ cluster unit is connected with two neighboring such cluster units by edge-sharing linkage of two Sm^{3+} ions, generating an interesting 1D centipede-like heterometallic cluster chain running along the [1-10] direction(Fig. 2b, S3b), which is first observed in Ln-Cd-organic framework. The interconnection of the Sm^{3+} and Cd^{2+} ions from two neighboring cluster chains via oxalate in mode 1a results in a 2-D bilayer in the *ab*-plane with the rectangular cavity (Fig. 2c, S4). The phen rings are attached to the both sides of the bilayer via coordination to Cd^{2+} ions and located in a line along *a* axis. The 2-D bilayers stack in –AAA- mode along the *c* axis. The neighboring phen molecules from the adjacent layers are packed in an offset manner to generat face-to-face π···π stacking interaction between the phen rings with an interplanar separation of 3.470(4) Å, yielding a 3-D supermolecular network. (Fig. 3).



Scheme 2 The coordination modes of the $Meimdc^{3-}$ ligand in **2**.

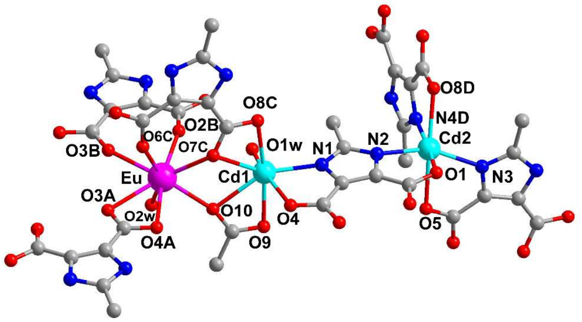


Fig. 4 The coordination environments of Eu^{3+} and Cd^{2+} in **2**. Atoms having ''A'', ''B'' ''C'' or ''D'' in their labels are symmetry-generated. A: 1-x, 1-y, -z; B: x, -1+y, z; C:1+x, -1+y, z; D: -0.5-x, -0.5+y, 0.5-z. Hydrogen atoms are omitted for clarity. Color code: Eu, purple; Cd, cyan; O, red; N, blue; C, grey.

$[EuCd_2(Meimdc)_2(Ac)(H_2O)_2](H_2O)$ (2) The structure **2** is an interesting 3D heterometallic-organic framework based on 1D heterometallic Ln-Cd oxo-cluster chain as pillars with left-/right-handed helical tubes (L1/R1) and channels (L2/R2) along *b* axis. In the asymmetrical units of **2**, there are two crystallographically independent Cd^{3+} ions, one unique Eu^{3+} ion, two $Meimdc^{3-}$ anions, one Ac^- anion and two coordinated water molecules. The coordination geometries of two Cd^{2+} ions are different. The Cd1 is seven-coordinated and is described as a pentagonal bipyramid (Fig. S5**)**: three O_{COO-} atoms and one N_{Im} atoms from two $Meimdc^{3-}$ anions, two O_{COO-} atoms from one Ac^- anion and one coordinated water molecule while Cd2 is six coordinated closed to a octahedron (Fig. S6**)**: three O_{COO-} atoms and three N atoms from three $Meimdc^{3-}$ anions. Eu atom exhibits a dodecahedral coordination environment coordinated by six O_{COO-} from three $Meimdc^{3-}$ anions, one O_{COO-} of one Ac^- anion and one coordinated water molecule (Fig. 4, S7). Two types of $Meimdc^{3-}$ anions both act as μ_8-bridge linking four metal atoms in a tri(bidentate) fashion and the difference lies in the metal atoms: one connects with three Cd and one Eu atoms (Scheme 2 Mode I), while the other links two Cd and two Eu atoms (Scheme 2 Mode II).

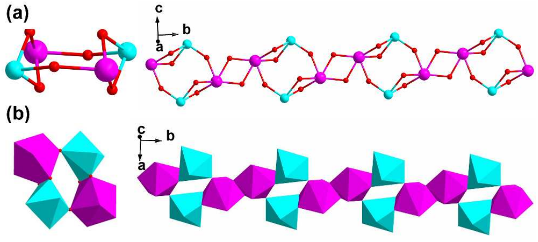


Fig. 5 (a) Ball-stick presentation of cradle-like tetranuclear $[Eu_2Cd_2(\mu_2\text{-}O)_6]$ cluster unit and 1D necklace-like Ln-Cd oxo-cluster ribbon in **2**; (b) polyhedron presentation of tetranuclear $[Eu_2Cd_2(\mu_2\text{-}O)_6]$ cluster and 1D cluster ribbon in **2**. Color code: Eu, purple; Cd, cyan; O, red; N, blue; C, grey.

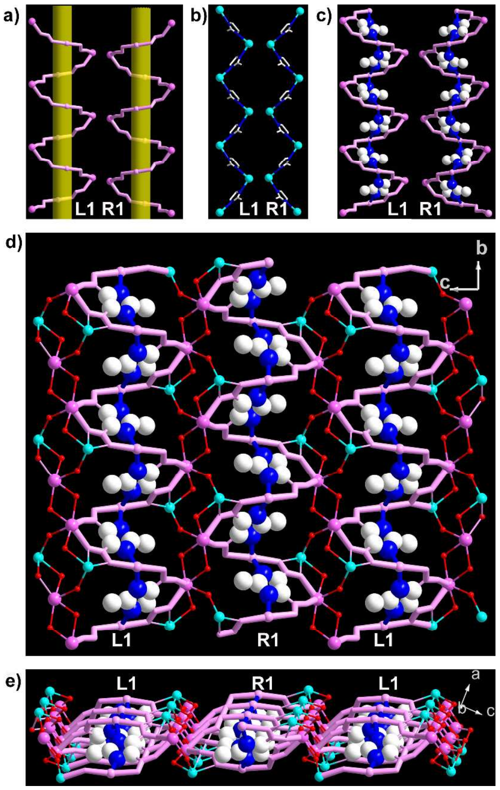


Fig. 6 (a) The walls of the helical tubes made of the helical chains, -Eu–O6–C12–O5–Cd2–O8 –C11–O7–; (b) View of the left-/right-handed –Cd2–Im– helices trapped in the inner of the helical tubes; (c) View of two types of helical tubes in combination with the helical walls and the helical fillers with similar chirality; (d) 2D tubular layer viewed down the *a* axis in **2**; (e) 2D tubular layer viewed down the approximate *b* axis in **2**. Color code: Eu, purple; Cd, cyan; O, red; N, blue; C, white

The most interesting structural feature of **2** is the linkages between Ln-Cd oxo-cluster chain pillars via Meimdc^{3-} to generate an unprecedented 3D framework, arranged alternately left-/right-handed helical tubes(L1/R1), and 1D left-/right-handed helical channels (L2/R2). Two μ_2-O atoms from Meimdc^{2-} and Ac$^-$ ligands bridge one Cd^{2+} and one Eu^{3+}, thus forming an edge-sharing heterometal binuclear [EuCd (μ_2-O)$_2$] unit with Eu…Cd distance of 3.953(7) Å. Two binuclear [EuCd (μ_2-O)$_2$] units are connected each other by μ_2-O from Meimdc^{2-} ligand between Eu^{3+} and Cd^{2+} ions to generate an cradle-like tetranuclear [Eu$_2$Cd$_2$(μ_2-O)$_6$] cluster unit which is first observed in Ln-Cd-organic framework.The [Eu$_2$Cd(1)$_2$(μ_2-O)$_6$] cluster unit is connected with two neighboring such cluster units by edge-sharing linkage of two Eu^{3+} ions to form a beautiful necklace-like Ln-Cd oxo-cluster ribbon (Fig. 5). The ribbons are bridged by Meimdc^{3-} lignds of Mode I to make a 2-D helical tubular layer (Fig. 6). The helical tubes consist of two helices: one as the helical tubular walls, the second one as the fillers. The first kind of helical chains of opposite chirality as tube walls are made of Eu atoms from the Ln-Cd oxo-cluster ribbon and Cd(2) atoms linked by four carboxyls of Meimdc^{3-} lignds in Mode I with a pitch of 9.924(2) Å (Fig. 6a). In the tubes, the adjacent Cd(2) atoms are bridged by the imidazole (im) ring of an Meimdc^{3-} ligand to form a –Cd-im- helices as the fillers trapped in the inner of the helical tubes (Fig. 6b, 6c). The left-/right-helical tubes are alternately arranged, with Ln-Cd oxo-cluster ribbon serving as hinges to generate a 2-D tubular layer in the (-101) plane (Fig. 6d, 6e). Furthermore, adjacent tubular layers are linked together by Meimdc^{3-} lignds of Mode II into a 3-D framework with alternative 1-D small helical channels and 1D large central-symmetric channels (Fig. 7). The left-/right-handed helical channel is constructed by Meimdc^{3-} ligands of Mode II bridged by Cd(1)-O-Cd(2) cluster units with the dimensional of 6.617 Å×4.637Å (Fig. 7a). The free water molecules and Ac$^-$ anion are enclathrated in the large central-symmetric channels.

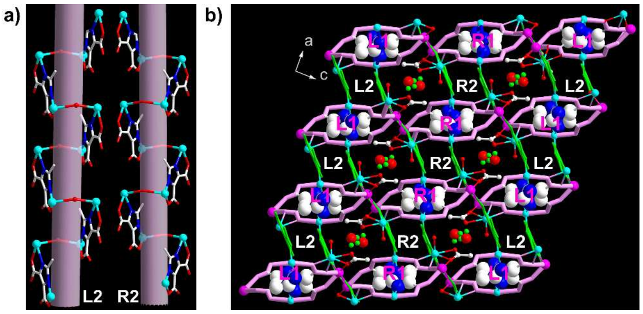


Figure 7. (a) Two types of helical channels constructed by Meimdc^{3-} ligands of Mode II bridged by Cd(1)-O-Cd(2) cluster units in **2**; (b) The 3D framework viewed along b axis showing 1-D small helical channels and 1D large central-symmetric channels.

Discussion on structural comparison

The present study reports a series of Ln-Cd heterometal-organic hybrid materials based on distinct cluster polymers. Compounds type I and II all contain tetranuclear Ln-Cd-O cluster uints. In the structure of type I, the four-pointed star-like eight-membered tetranuclear Sm$_2$Cd$_2$(μ_2-O)$_4$ cluster unit is formed by the alternative linkage of four carboxylate μ_2-O atoms of oxalate between Sm^{3+} ion and Cd^{2+} ion. In type II compounds, there is a cradle-like tetranuclear [Eu$_2$Cd$_2$(μ_2-O)$_6$] cluster, which is constructed from alternatively connection of Ln^{3+} ions and Cd^{2+} ions via one or two μ_2-O atoms. Such a cradle-like tetranuclear [Eu$_2$Cd$_2$(μ_2-O)$_6$] cluster is first observed in Ln-Cd-organic frameworks. The tetranuclear cluster units are connected with two neighboring such cluster units by edge-sharing linkage of two Ln^{3+} ions to form an interesting 1D centipede-like heterometallic cluster chain in type I and a beautiful necklace-like Ln-Cd oxo-cluster ribbon in type II. These cluster chains are further bridged by different organic ligands to generate Ln-Cd heterometal 2-D bilayer and 3-D tubular structures.

PXRD, IR spectra and thermal Properties

To confirm the phase purity of the compounds, the powder X-ray diffraction (PXRD) patterns have been carried out at room temperature (Fig. S8, S9). The pick positions of experimental and simulated PXRD patterns are in good agreement, which confirm their phase purity.

IR spectra of 1a and 2 exhibit strong bands at 1620, 1433 cm^{-1} for 1a and 1543, 1431, cm^{-1} for 2 associated with ν_{asym}(C=O) and ν_{sym}(C=O), respectively (Fig. S10, S11). Compared with the corresponding ligands they are both shifted to lower wave numbers corresponding to the ν(C=O) of the coordinated carboxylate moieties. According to G. Deacon rules,[22] Compound 1a and 2 with low (Δ(ν_{asym}(COO$^-$)- ν_{sym}(COO$^-$)< 200 cm^{-1}) value has chelating and bridging carboxylate moieties, which are good agreement with the crystal structure. Bands characteristic of the S=O stretching modes of the SO$_4^{2-}$ in 1a are observed at approximately at 1117 and 1073 cm^{-1}.

Thermal gravimetric analyses (TGA) of **1b** were performed in a dry nitrogen atmosphere from 30 ºC to 800 ºC (Fig. S12). The TG curve of **1b** displays the weight loss of 7.47% (calcd: 7.43%) in the temperature range 30-350 ºC, corresponding to the successive release of one free water molecules and two coordinated water molecules per formula unit. The decomposition of H$_2$ox and 1,10-phen is observed from 350 ºC to 800 ºC. The residue might be Eu$_2$O(SO$_4$)$_2$·2CdO (calcd/found: 52.90%/54.20%) for **1b**. In the TGA curve of **2** (Fig. S13), the weight loss of 6.76% (calcd: 6.55%) in the temperature range 40-250 ºC, can be assigned to the successive release of one free water molecules and two coordinated water molecules. The second weight loss of 47.91% is observed from 250 to 841 °C due to the loss of the H$_2$Meimdc and HAc organic species above 558 °C (calc. 41.13%). A small mass loss was observed above 500 ºC in **2** due to the slow evaporation of CdO.[23] The residue might be 1/2Sm$_2$O$_3$·3/2CdO (calcd/found: 44.73%/43.30%).

Luminescent properties

For Ln-Cd heterometal-organic hybrid materials, the most interesting is their luminescent spectra (LS). The luminescent spectra of H_3Meimdc ligand, **1b** and **2** were measured in solid state at room temperature (Fig. S14, 8). All these two compounds show characteristic emissions of Eu^{3+} ion. The bonds at 580, 592, 613, 655, 703 nm correspond to $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_3$, $^5D_0\rightarrow{}^7F_4$, respectively. The intensities of the $^5D_0\rightarrow{}^7F_2$ transition (electric dipole) are stronger than those of the $^5D_0\rightarrow{}^7F_1$ transition (magnetic dipole) of these two compounds, indicating that the Eu^{3+} ions in these two compounds locate at a low-symmetry site without inversion center, in agreement with the crystal structure analysis. In the emission spectrum of **2**, the broad band in the range of 450-550nm is similar with the emission spectrum of H_3Meimdc ligand under the same excitation wavelength, so the the broad band of **2** may be assigned to the ligand-to-ligand charge transfer.

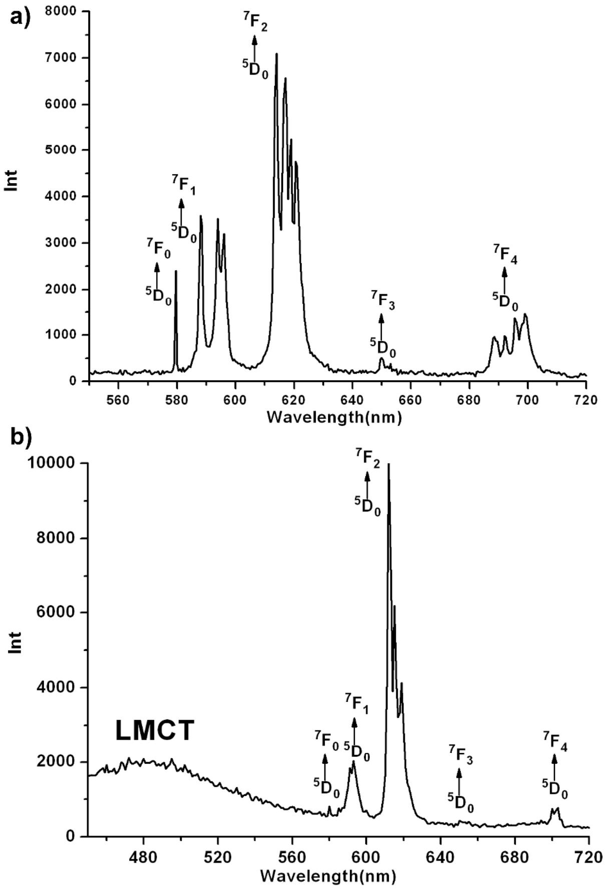


Fig. 8 Emission spectra of **1b** (excitation at 393 nm) (a) and **2** (excitation at 394 nm) (b) in the solid state at room temperature.

The emission spectra of **1b** and **2** exhibit plenty of small splittings, which is useful for confirming the local site symmetry of lanthanide and the effect of the ligand field. As shown in Fig. 8, the splittings for the $^5D_0\rightarrow{}^7F_J$ transition are relatively clear with the exception of the $^5D_0\rightarrow{}^7F_3$ transition. Moreover, it is noted that the $^5D_0\rightarrow{}^7F_0$ transition of Eu^{3+} ions only arises in a limited number of site symmetries (only allowed for the following 10 site symmetries, C_s, C_1, C_2, C_3, C_4, C_6, C_{2v}, C_{3v}, C_{4v}, and C_{6v}).[24] For **1b**, the transitions of $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_4$ produce the well-separated 1, 3, 4, 4 luminescence lines, respectively. For **2**, the one, two, three and two lines splitting were observed for the transitions of $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_4$, respectively. The emission spectra of **1b** and **2** with a few transition lines（$\leqslant 2J+1$) for each $^5D_0\rightarrow{}^7F_J$ (J = 0–4) imply a single Eu^{3+} ion crystallographic site of low symmetry in compounds **1b** and **2**,[25] which is in agreement with the single-crystal X-ray analysis. Because the matching of energy levels of the complex **1b** with phen is better than the complex **2** with Meimdc and complex **1b** shows the well-separated splitting of Eu^{3+} hypersensitive transitions.

As described above, the structures are constructed from the tetranuclear Ln-Cd-O cluster SBUs that lead to 1D inorganic Ln-Cd oxo-cluster chains. Thus the Eu^{3+} ions are encapsulated in a rigid architecture, shielding them from interactions with the environment, especially from interactions with small molecules like water. Radiationless decay pathways associated with the close proximity of high-energy C-H, or O-H oscillators to the lanthanide centers can be eliminated.

Conclusion

In summary, two types of Ln-Cd heterometal-organic frameworks formulated as $[LnCd(phen)(ox)_{1.5}(SO_4)(H_2O)_2](H_2O)$ (Type **I**: Ln = Sm **1a**; Eu **1b**) and $[EuCd_2(Meimdc)_2(Ac)(H_2O)_2]$ (H_2O) (Type II: 2) have been successfully synthesized by hydrothermal conditions. Type **I** presents the first 2D bilayer structure of Ln-Cd heterometal-organic framework based on 1D inorganic heterometallic Ln-Cd oxo-cluster polymer chain. The structure of **2** is built up from left-/right-handed helical tubes (L1/R1), which are pillared by 1D heterometallic Ln-Cd oxo-cluster chain to generate a 3D framework with helical channels. Complexes **1b** and **2** exhibit luminescence in the visible region at room temperature. Formation of inorganic heterometallic Ln-Cd oxo-cluster polymer chain structure plays crucial role in realizing efficient fluorescent emissions of complexes **1b** and **2**. Thus, these complexes could be anticipated as good candidates for luminescent materials and fluorescent probes.

Luminescence

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