

基于一个四羧酸配体构筑的具有(4,8)-连接的镧系金属-有机 框架材料及对小分子的检测试验

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摘要: 以 3,3',5,5'-四-(羧基苯基)联苯为配体(H_4L), 与镧系金属 $Ln(III)$ 盐反应, 自组装形成了 5 个具有三维孔洞结构的镧系金属-有机框架材料: $\{[Ln_3L_2(H_2O)_7] \cdot (OH) \cdot 10DMA\}_n$ ($Ln=Gd$ (**1a**); $Ln=Ho$ (**2a**)), $\{[Ln_3L_2(H_2O)_3] \cdot (OH) \cdot mDMA\}_n$ ($Ln=Er$, $m=10$ (**1b**); $Ln=Yb$, $m=9$ (**2b**); $Ln=Lu$, $m=10$ (**3b**)). 单晶 X 射线衍射分析表明, 这些 MOFs 属于 2 种系列的类质同晶化合物, 分别属于正交晶系 $Ccca$ 空间群和单斜晶系 $C2/c$ 空间群。有机小分子溶剂交换荧光研究发现, **2b** 对小分子二氯甲烷和甲苯荧光有增强效应, 表现出良好的荧光探测功能。

关键词: 3,3',5,5'-四-(羧基苯基)联苯; 金属-有机框架材料; 晶体结构; 荧光性质

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Two Series of (4,8)-Connected Lanthanide-Metal Organic Frameworks Based on a Tetra-carboxylate Ligand for Sensing of Small Molecules

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Abstract: Biphenyl-3,3',5,5'-tetra-(phenyl-4-carboxylic acid) (H_4L) was used to synthesize five microporous three-dimension metal-organic framework with lanthanide metal matrix by intermolecular self-assembly, namely, $\{[Ln_3L_2(H_2O)_7] \cdot (OH) \cdot 10DMA\}_n$ ($Ln=Gd$ (**1a**); $Ln=Ho$ (**2a**)), and $\{[Ln_3L_2(H_2O)_3] \cdot (OH) \cdot mDMA\}_n$ ($Ln=Er$, $m=10$ (**1b**), $Ln=Yb$, $m=9$ (**2b**), $Ln=Lu$, $m=10$ (**3b**)). Single-crystal X-ray diffraction revealed the Ln -MOFs are two series of isomorphous metal-organic frameworks, and belong to orthorhombic $Ccca$ space group and monoclinic $C2/c$ space group, respectively. The luminescence intensity of **2b** can be modulated by organic small molecule solvents, and **2b** exhibited the enhancement of the luminescence intensity when dispersed in CH_2Cl_2 and toluene. CCDC: 1434268, **1a**; 1434269, **2a**; 1434270, **1b**; 1434271, **2b**; 1434272, **3b**.

Keywords: biphenyl-3,3',5,5'-tetra-(phenyl-4-carboxylic acid); metal-organic framework; crystal structure; luminescent property

0 Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are crystalline

solids consisting of metal ions/clusters connected to multidentate organic ligands via coordination bonds. Ever-increasing interest in the design and synthesis of MOFs stems not only from their aesthetic architectures

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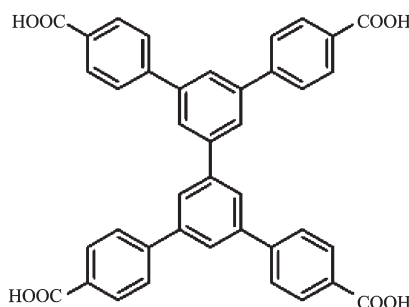
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and topologies^[1-3] but also from their possible potential applications such as gas storage/separation, catalysis, ion conductivity, drug delivery^[4-13]. The lanthanide (Ln) analogues are also highly sought after because Ln ions possess high coordination numbers, flexible coordination geometries, and the effect of Ln contraction that can afford structural diversity. Moreover, Ln-based compounds can show distinct characteristic luminescent emissions^[14-21]. In addition, aromatic carboxylate coordination complexes have been extensively investigated in past decades due to their strong coordination capability, their large conjugated systems, and the possibility of offering new functional materials.

Among the diverse organic linkers, those containing multicarboxylate groups, including

dicarboxylate, tricarboxylate, tetracarboxylate, hexacarboxylate and octacarboxylate, have been widely employed to synthesize new MOFs because of their preference to stabilize the MOFs through *in situ* formed secondary building units (SBUs)^[22]. A tetracarboxylic acid, biphenyl-3,3',5,5'-tetra-(phenyl-4-carboxylic acid) (H_4L , Scheme 1), was selected specifically as an organic ligand in this work. It is noteworthy that only three MOFs based on this ligand have been reported to date^[23-25]. Using H_4L , we have successfully synthesized two series of new Ln-MOFs under solvothermal condition, $\{[Ln_3L_2(H_2O)_7] \cdot (OH) \cdot 10DMA\}_n$ (Ln=Gd, (**1a**); Ln=Ho, (**2a**)), and $\{[Ln_3L_2(H_2O)_3] \cdot (OH) \cdot mDMA\}_n$ (Ln=Er, $m=10$ (**1b**); Ln=Yb, $m=9$ (**2b**); Ln=Lu, $m=10$ (**3b**)). Here we report their structures and luminescent properties.



Scheme 1 Ligand used to construct the Ln-MOFs

1 Experimental

1.1.1 Materials and general methods

Biphenyl-3,3',5,5'-tetra-(phenyl-4-carboxylic acid) (H_4L) was prepared according to a literature method^[25]. All the other reagents were obtained from commercial sources and used without further purification. The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The infrared spectra were recorded within the 400~4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analyses were performed on a TGA Q500 V20.10 Build 36 thermogravimetric analyzer in the temperature range of 35~700 $^{\circ}C$ under an air flow with a heating rate of 10 $^{\circ}C \cdot min^{-1}$. The luminescence spectra were recorded on a JASCO FP-6500 spectrofluorimeter in solid state at room

temperature.

1.2 Preparation of Ln-MOFs

A mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.032 mmol), H_4L (0.0158 mmol), dimethylacetamide (DMA) (2.0 mL), and pyridine (10 μL) was sealed in a 25 mL Teon-lined stainless steel container, which was heated at 120 $^{\circ}C$ for 72 h, and then cooled down to room temperature at a rate of 5 $^{\circ}C \cdot h^{-1}$. Colorless block single crystals were collected and washed with DMA and dried in air to give the products.

$\{[Gd_3(L)_2(H_2O)_7] \cdot (OH) \cdot 10DMA\}_n$ (**1a**). Yield: *ca.* 66%. Anal. Calcd. for $C_{120}H_{149}Gd_3N_{10}O_{34}$ (%): C, 52.46; H, 5.47; N, 5.10. Found (%): C, 52.78; H, 5.82; N, 5.96. FTIR (KBr, cm^{-1}): 3395, 2919, 1603, 1539, 1231, 1186, 1012, 864, 787, 717, 594, 473.

$\{[Ho_3(L)_2(H_2O)_7] \cdot (OH) \cdot 10DMA\}_n$ (**2a**). Yield: *ca.* 65%. Anal. Calcd. for $C_{120}H_{149}Ho_3N_{10}O_{34}$ (%): C, 52.02;

H, 5.42; N, 5.06. Found (%): C, 52.36; H, 5.78; N, 5.91. FTIR (KBr, cm⁻¹): 3 398, 2 915, 1 609, 1 537, 1 427, 1 184, 860, 784, 717, 586, 472.

{[Er₃(L)₂(H₂O)₃]·(OH)·10DMA}_n (**1b**). Yield: ca. 69%. Anal. Calcd. for C₁₂₀H₁₄₁Er₃N₁₀O₃₀ (%): C, 53.28; H, 5.25; N, 5.18. Found (%): C, 52.58; H, 5.62; N, 6.05. FTIR (KBr, cm⁻¹): 3 397, 2 916, 1 605, 1 534, 1 425, 1 182, 858, 782, 715, 583, 470.

{[Yb₃(L)₂(H₂O)₃]·(OH)·9DMA}_n (**2b**). Yield: ca. 63%. Anal. Calcd. for C₁₁₆H₁₃₂Yb₃N₉O₂₉ (%): C, 52.86; H, 5.05; N, 4.78. Found (%): C, 53.19; H, 5.42; N, 5.96. FTIR (KBr, cm⁻¹): 3 396, 2 913, 5 88, 1 533, 1 429, 1 247, 858, 782, 711, 580, 483.

{[Lu₃(L)₂(H₂O)₃]·(OH)·10DMA}_n (**3b**). Yield: ca. 63%. Anal. Calcd. for C₁₂₀H₁₄₁Lu₃N₁₀O₃₀ (%): C, 52.82; H, 5.21; N, 5.13. Found (%): C, 53.14; H, 5.58; N, 6.00. FTIR (KBr, cm⁻¹): 3 390, 2910, 1 558, 1 529, 1 420, 1 179, 549, 775, 706, 575, 476.

1.3 Crystal structure determination

Data collection of the Ln-MOFs were determined on a Bruker APEX II diffractometer equipped with a graphite-monochromatized Mo K α radiation (λ = 0.071 073 nm) at 296 (2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structures were solved by the direct methods and expanded with the difference Fourier

techniques. The anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2 with SHELXTL-97 program packages [26]. The hydrogen atoms were located by geometrically calculations and assigned with isotropic displacement factors and included in the final refinement cycles. X-ray structure refinements indicated that one of benzene rings in **1b**, **2b** and **3b** disordered over two positions and the site occupancy factors are refined to 0.50:0.50. The solvent molecules are highly disordered, and attempts to locate and refine solvent molecules were unsuccessful. Therefore, the SQUEEZE routine of PLATON [27] was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities, the structures were then refined again using the data. The free solvent molecules were established on the basis of the reactants, single-crystal X-ray diffraction studies, thermogravimetric analysis. The detailed crystallographic and structure refinement data are summarized in Table 1. Selected bond lengths and angles are given in Table 2 and Table 3, respectively.

CCDC: 1434268, **1a**; 1434269, **2a**; 1434270, **1b**; 1434271, **2b**; 1434272, **3b**.

Table 1 Crystal data and structure refinements for the Ln(III)-MOFs

	1a	2a	1b	2b	3b
Empirical formula	C ₁₂₀ H ₁₄₉ Gd ₃ N ₁₀ O ₃₄	C ₁₂₀ H ₁₄₉ Ho ₃ N ₁₀ O ₃₄	C ₁₂₀ H ₁₄₁ Er ₃ N ₁₀ O ₃₀	C ₁₁₆ H ₁₃₂ Yb ₃ N ₉ O ₂₉	C ₁₂₀ H ₁₄₁ Lu ₃ N ₁₀ O ₃₀
Formula weight	2 747.24	2 770.28	2 705.21	2 635.43	2 728.34
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Ccca</i>	<i>Ccca</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / nm	1.650 52(15)	1.632 57(5)	3.231 8(3)	3.248 5(5)	3.230 1(13)
<i>b</i> / nm	5.828 0(6)	5.916 77(13)	2.935 4(3)	2.908 9(4)	2.882 5(10)
<i>c</i> / nm	3.245 5(3)	3.215 08(7)	1.852 32(17)	1.762 9(3)	1.869 2(8)
β / (°)			104.277(2)	104.347(2)	104.24(3)
<i>V</i> / nm ³	31.219(5)	31.056 2(14)	17.030(3)	16.139(4)	16.869(12)
<i>Z</i>	8	8	4	4	4
<i>D_c</i> / (g·cm ⁻³)	1.169	1.185	1.055	1.085	1.074
μ / mm ⁻¹	1.324	1.578	1.521	1.780	1.798
<i>F</i> (000)	11 224	11 296	5 500	3 332	5 536
Reflections collected	128 487	128 487	136 046	56 227	59 053
Unique reflections (<i>R_{int}</i>)	18 161 (0.044 0)	18 161 (0.044 4)	19 083(0.100 5)	18 630(0.059)	17 827(0.079 9)

Continued Table 1

Data with $I > 2\sigma(I)$	9 956	9 976	10 203	10 239	8 817
Parameters refined	449	479	489	455	492
R_1, wR_2 $I > 2\sigma(I)$	0.040 9, 0.113 4	0.040 2, 0.108 2	0.050 1, 0.128 5	0.087 5, 0.227 6	0.063 3, 0.160 9
R_1, wR_2 (all data)	0.075 1, 0.119 1	0.075 3, 0.113 9	0.078 2, 0.132 4	0.122 5, 0.242 7	0.108 9, 0.177 3
Goodness-of-fit on F^2	0.996	1.014	1.039	1.028	1.001
$(\Delta\rho)_{\max}, (\Delta\rho)_{\min}$ / (e \cdot nm $^{-3}$)	1 170, -665	1 315, -420	1 510, -457	3 427, -2 660	1 537, -1 619

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for 1a and 2a

	1a	2a		1a	2a
Ln(1)-O(5)	0.222 6(3)	0.220 8(8)	Ln(2)-O(6)#1	0.230 4(3)	0.229 9(7)
Ln(1)-O(8)#2	0.229 8(2)	0.228 0(6)	Ln(2)-O(3)#2	0.238 3(3)	0.236 7(7)
Ln(1)-O(1)#1	0.231 2(2)	0.231 8(5)	Ln(2)-O(3W)	0.241 4(4)	0.240 7(9)
Ln(1)-O(1W)	0.244 0(4)	0.247 5(10)	Ln(2)-O(4W)	0.239 0(5)	0.237 8(12)
Ln(2)-O(2)	0.227 2(3)	0.224 8(7)	Ln(2)-O(4)#2	0.247 0(2)	0.249 5(6)
Ln(2)-O(7)#2	0.225 6(3)	0.227 4(7)	Ln(2)-O(2W)	0.247 4(4)	0.250 2(9)
O(5)-Ln(1)-O(5)#1	165.61(18)	165.3(5)	O(6)#1-Ln(2)-O(4)#2	147.01(16)	147.1(4)
O(5)#1-Ln(1)-O(1)#1	76.22(11)	76.8(3)	O(3)#2-Ln(2)-O(4)#2	52.33(9)	53.0(2)
O(5)-Ln(1)-O(1)#1	115.65(11)	115.4(3)	O(2)-Ln(2)-O(3W)	136.97(15)	135.6(4)
O(1)#1-Ln(1)-O(1)	77.92(13)	76.5(3)	O(7)#2-Ln(2)-O(3W)	146.48(16)	147.1(4)
O(5)#1-Ln(1)-O(8)#2	84.18(10)	91.6(2)	O(6)#1-Ln(2)-O(3W)	77.88(15)	78.6(4)
O(5)-Ln(1)-O(8)#2	91.29(10)	83.7(2)	O(3)#2-Ln(2)-O(3W)	94.28(14)	94.3(3)
O(1)-Ln(1)-O(8)#2	76.36(10)	77.1(2)	O(4)#2-Ln(2)-O(3W)	76.03(12)	74.9(3)
O(1)-Ln(1)-O(8)#3	136.54(10)	136.1(3)	O(2)-Ln(2)-O(4W)	149.66(19)	150.8(4)
O(8)#2-Ln(1)-O(8)#3	143.27(14)	143.0(3)	O(7)#2-Ln(2)-O(4W)	73.10(19)	73.4(5)
O(5)-Ln(1)-O(1W)	82.81(9)	82.7(2)	O(6)#1-Ln(2)-O(4W)	76.9(2)	76.4(5)
O(1)-Ln(1)-O(1W)	141.04(7)	141.75(16)	O(3)#2-Ln(2)-O(4W)	73.27(18)	73.1(5)
O(8)#3-Ln(1)-O(1W)	71.63(7)	71.51(17)	O(4)#2-Ln(2)-O(4W)	113.82(18)	113.7(5)
O(2)-Ln(2)-O(7)#2	76.55(13)	77.4(3)	O(3W)-Ln(2)-O(4W)	73.4(2)	73.7(5)
O(2)-Ln(2)-O(6)#1	105.83(15)	106.7(4)	O(2)-Ln(2)-O(2W)	70.09(14)	69.4(3)
O(7)#2-Ln(2)-O(6)#1	95.00(16)	93.6(4)	O(7)#2-Ln(2)-O(2W)	141.03(16)	141.4(4)
O(2)-Ln(2)-O(3)#2	99.47(13)	99.1(3)	O(6)#1-Ln(2)-O(2W)	75.82(18)	78.2(4)
O(7)#2-Ln(2)-O(3)#2	75.64(12)	76.2(3)	O(3)#2-Ln(2)-O(2W)	128.68(13)	127.2(3)
O(6)#1-Ln(2)-O(3)#2	150.20(18)	149.5(4)	O(4)#2-Ln(2)-O(2W)	76.37(12)	74.2(3)
O(2)-Ln(2)-O(4)#2	80.72(10)	79.9(2)	O(3W)-Ln(2)-O(2W)	69.51(16)	68.8(4)
O(7)#2-Ln(2)-O(4)#2	117.84(11)	119.2(3)	O(4W)-Ln(2)-O(2W)	137.54(19)	137.9(4)

Symmetry codes: #1: $-x, y, 1.5-z$; #2: $-0.5+x, y, 1-z$; #3: $0.5-x, y, 0.5+z$ Table 3 Selected bond lengths (nm) and angles ($^\circ$) for 1b~3b

Bond	1b	2b	3b		1b	2b	3b
Ln(1)-O(3)#1	0.220 2(4)	0.216 6(8)	0.217 4(6)	Ln(2)-O(7)#4	0.223 5(3)	0.217 0(6)	0.218 8(5)
Ln(1)-O(2)#3	0.225 6(3)	0.228 1(5)	0.222 1(5)	Ln(2)-O(4)#2	0.229 2(4)	0.226 0(7)	0.224 8(5)
Ln(1)-O(8)#4	0.230 4(3)	0.227 5(6)	0.226 4(6)	Ln(2)-O(2W)	0.234 9(5)	0.228 4(8)	0.223 2(6)
Ln(1)-O(1W)	0.237 6(7)	0.217 8(9)	0.246 1(19)	Ln(2)-O(5)#6	0.236 5(4)	0.232 5(7)	0.237 9(5)

Continued Table 3

Ln(2)-O(1)	0.221 6(4)	0.217 3(8)	0.220 3(7)	Ln(2)-O(6)#6	0.239 2(4)	0.236 7(8)	0.236 6(6)
O(3)#1-Ln(1)-O(3)#2	164.0(2)	162.9(4)	162.7(4)	O(7)#4-Ln(2)-O(4)#2	85.79(14)	85.5(3)	85.13(19)
O(3)#2-Ln(1)-O(2)#3	76.51(15)	76.8(3)	76.7(2)	O(1)-Ln(2)-O(2W)	81.72(15)	83.7(3)	83.4(3)
O(2)#3-Ln(1)-O(2)	78.00(18)	79.4(3)	79.6(3)	O(7)#4-Ln(2)-O(2W)	152.32(15)	153.9(3)	152.3(2)
O(3)#1-Ln(1)-O(8)#4	82.33(14)	81.7(2)	92.3(2)	O(4)#2-Ln(2)-O(2W)	75.26(15)	74.1(4)	74.1(2)
O(2)#3-Ln(1)-O(8)#4	76.29(13)	134.2(2)	134.3(3)	O(1)-Ln(2)-O(5)#6	95.1(2)	95.2(3)	89.4(3)
O(3)#1-Ln(1)-O(8)#5	92.91(14)	93.3(3)	82.9(2)	O(7)#4-Ln(2)-O(5)#6	76.48(14)	75.2(3)	74.1(2)
O(2)#3-Ln(1)-O(8)#5	134.37(15)	75.4(2)	74.4(2)	O(4)#2-Ln(2)-O(5)#6	152.97(17)	152.4(4)	153.9(3)
O(8)#4-Ln(1)-O(8)#5	145.4(2)	146.4(4)	147.5(4)	O(2W)-Ln(2)-O(5)#6	127.84(15)	129.3(3)	130.3(2)
O(3)#2-Ln(1)-O(1W)	81.99(12)	81.4(2)	81.37(18)	O(1)-Ln(2)-O(6)#6	85.61(19)	85.4(3)	85.0(3)
O(2)-Ln(1)-O(1W)	141.00(9)	140.32(15)	140.19(15)	O(7)#4-Ln(2)-O(6)#6	127.01(13)	127.5(3)	126.85(19)
O(8)#5-Ln(1)-O(1W)	72.70(10)	73.19(18)	73.76(18)	O(4)#2-Ln(2)-O(6)#6	147.09(15)	146.8(4)	147.8(2)
O(1)-Ln(2)-O(7)#4	83.15(15)	85.1(3)	84.3(3)	O(2W)-Ln(2)-O(6)#6	74.68(14)	74.9(3)	76.6(2)
O(1)-Ln(2)-O(4)#2	103.01(15)	102.7(3)	104.5(2)	O(5)#6-Ln(2)-O(6)#6	53.21(14)	54.5(3)	53.8(2)

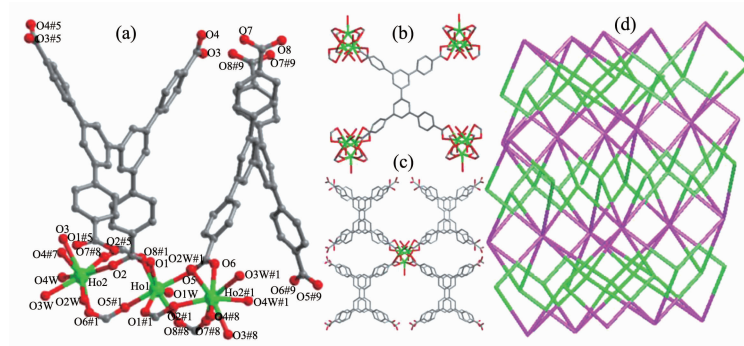
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2 Results and discussion

2.1 Crystal structures of **1a** and **2a**

Single-crystal X-ray diffraction analyses showed that **1a** and **2a** are isostructural and crystallize in orthorhombic *Ccca* space group. Therefore, only the structure of **2a** as representative is described in detail. Besides the guest solvents, the asymmetric unit of **2a** contains one and a half Ho (III) ions, two half- L^4 ligands, three and a half coordinated water molecules. Ho(1) is seven-coordinated with a distorted onecapped trigonal prism coordination geometry by six carboxylate oxygen atoms from six L^4 ligands (Ho(1)-

O 0.220 8(8)~0.231 8(5) nm), one water molecule (Ho(1)-O1W 0.247 5(10) nm). Ho(2) is eight-coordinated with a square antiprism coordination geometry by five carboxylate oxygen atoms from four organic L^4 ligands (Ho(2)-O 0.224 8(7)~0.249 5(6) nm), three water molecules (Ho(2)-O(W) 0.240 7(9)~0.250 2(9) nm). Three Ho(III) ions are connected in the sequence of Ho(2)-Ho(1)-Ho(2) through eight carboxylic groups to form a trinuclear $[Ho_3(COO)_8]$ SBU. The SBUs are further connected by L^4 ligands to construct a 3D framework (Fig.1a). The solvent accessible volume is 64.0% of the volume of the unit cell calculated by PLATON^[27] after removal of the guest molecules.



Symmetry codes: # 1: -x, y, 1.5-z; #5: -x, 0.5-y, z; #7: -0.5+x, y, 1-z; #8: 0.5-x, y, 0.5+z; #9: 0.5-x, -y, z

Fig.1 (a) View of the coordination environments of Ho(III) ions in **2a**; (b) The organic L^4 viewed as 4-connected node; (c) The trinuclear $[Ho_3(COO)_8]$ SBU viewed as 8-connected node; (d) View of the (4,8)-connected net

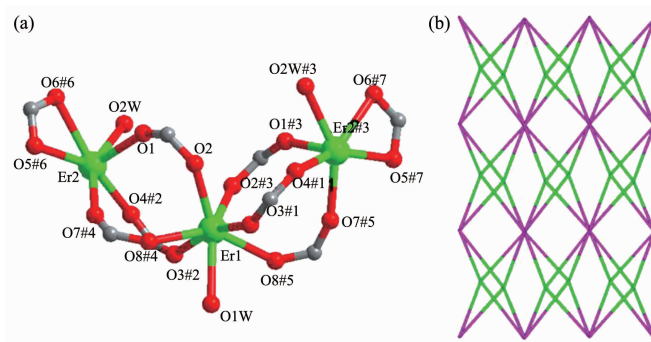
Topologically, each organic L^{4-} ligand links four trinuclear $[Ho_3(COO)_8]$ SBUs and thus can be simplified as 4-connected node (Fig.1b). Each trinuclear $[Ho_3(COO)_8]$ SBU links eight L^{4-} ligands (Fig. 1c) and can be considered as 8-connected node. The resulting network can be described as a (4,8)-connected net with Schläfli symbol of $(4^{11}.6^{14}.8^3)(4^2.6)_2$ (Fig.1d).

2.2 Crystal structures of **1b**, **2b** and **3b**

Single-crystal X-ray diffraction analysis revealed that **1b**~**3b** are isostructural and crystallize in the monoclinic $C2/c$ space group. Therefore, only the structure of **1b** as representative is described in detail. Besides the guest solvents, the asymmetric unit consists of one and a half $Er(III)$ ions, one deprotonated L^{4-} ligand, and one and a half coordinated water molecules. $Er(1)$ is seven-coordinated with a distorted one capped trigonal prism geometry by six carboxylate oxygen atoms from six L^{4-} ligands ($Er(1)-O$ 0.220 2(4)

~0.230 4(3) nm), one water molecule ($Er(1)-O1W$ 0.237 6(7) nm). $Er(2)$ is six-coordinated with pentagonal pyramid by five carboxylate oxygen atoms from four L^{4-} ligands ($Er(2)-O$ 0.221 6(4)~0.239 2(4) nm), one water molecule ($Er(2)-O2W$ 0.234 9(5) nm). Three $Er(III)$ ions are connected by eight carboxylic groups to form a trinuclear $[Er_3(COO)_8]$ SBU. The SBUs are further connected by L^{4-} ligands to construct a 3D framework (Fig.2a). The solvent accessible volume is 68.7% of the volume of the unit cell calculated by PLATON^[27] after removal of the guest molecules.

Topologically, each organic L^{4-} ligand links four trinuclear $[Er_3(COO)_8]$ SBUs and can be simplified as 4-connected node. Each trinuclear $[Er_3(COO)_8]$ SBU links eight L^{4-} ligands and can be considered as 8-connected node. The resulting network can be described as a (4,8)-connected net with Schläfli symbol of $(4^{12}.6^{12}.8^4)(4^6)_2$ (Fig.2b).



Symmetry codes: #1: 0.5-x, 0.5-y, 1-z; #2: -0.5+x, 0.5-y, -0.5+z; #3: -x, y, 0.5-z; #4: 0.5-x, 0.5+y, 0.5-z; # 5: -0.5+x, 0.5+y, z; #6: x, -y, -0.5+z; #7: -x, -y, 1-z

Fig.2 (a)View of the coordination environments of $Er(III)$ ions in **1b**; (b)View of the (4,8)-connected net

2.3 Photoluminescence properties

Considering that the Ln-MOFs are very promising luminescent materials because both the inorganic and organic components constituting MOFs can provide platforms to generate luminescence. The fluorescence properties of **2b** were investigated in the solid state and in different solvent emulsions at room temperature. The free H_4L ligand exhibits a broad luminescence peak centered at 391 nm when excited at 357 nm, which is probably assigned to π or n to π^* transitions^[25]. **2b** shows the characteristic emission

bands of $^2F_{5/2}-^2F_{7/2}$ transition of $Yb(III)$ ion at 980 nm when excited at 325 nm. Furthermore, the excitation energy can be transferred from a LMCT state to the $4f$ levels of the lanthanide ions when the LMCT state lies at high-enough energy^[28-29], indicating that the $Yb(III)$ ion adopt noncentrosymmetric coordination modes, which is in agreement with the crystal structural analysis.

As mentioned above, it is anticipated that the solvent molecules in the larger porous volume could be replaced by other small organic solvents. In this

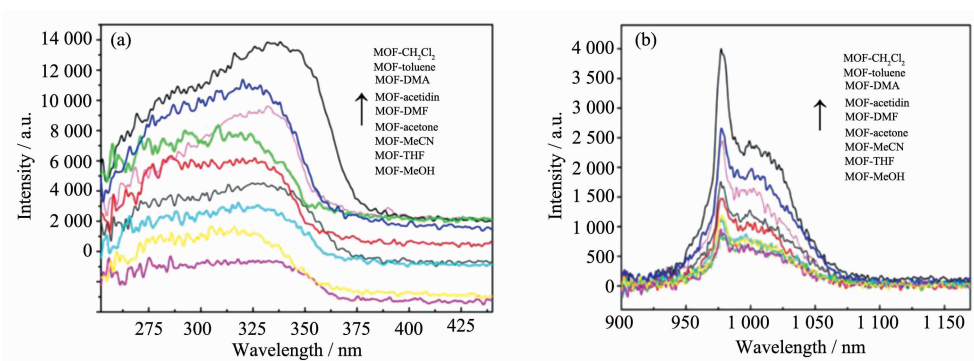


Fig.3 Solid-state photo-luminescent excitation (a) and emission (b) spectra of **2b** in different solvents

regard, to examine the potential sensing of small solvent molecules, grinded crystals of **2b** (3.0 mg) were dispersed in 5 mL organic reagent such as *N,N*-dimethylformamide (DMF), dimethylacetamide (DMA), acetone, dichloromethane (CH_2Cl_2), acetonitrile (MeCN), tetrahydrofuran (THF), acetidin, toluene, methanol (MeOH), sonicated for 30 minutes, and then placed for 24 hours at room temperature in order to form stable suspensions. Interestingly, we found that the **2b** exhibited the enhancement of the luminescence intensity when dispersed in CH_2Cl_2 and toluene, which indicates that **2b** is a potential luminescent sensing material.

2.4 Thermal stability

The TGA diagrams of the MOFs are similar and show two main weight losses in the curves. Therefore, only the TGA curve of **1a** as representative is described in detail (Fig.4). The TGA curve of **1a** shows the first weight loss of 32.65% occurred in the temperature range of 30~205 $^{\circ}\text{C}$, corresponding to the release of solvent molecules and counter ions (Calcd. 32.33%), Above this temperature (205~650 $^{\circ}\text{C}$), the compound starts to decompose gradually. The final residue may be Gd_2O_3 (Obsd. 14.25%, Calcd. 13.20%).

3 Conclusions

In summary, five new (4,8)-connected Ln(III)-MOFs have been successfully synthesized by solvothermal reactions of Ln(III) salts and H_4L . The luminescence of **2b** can be modulated by small organic molecule exchange. It is expected that the compounds can be used as a promising luminescent

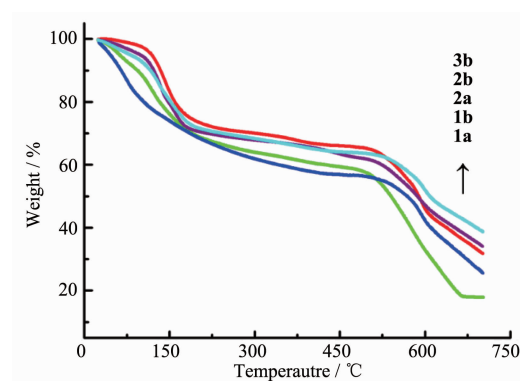


Fig.4 TGA curves for the Ln(III)-MOFs
sensing material in the future.

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