



Water molecule-enhanced CO₂ insertion in lanthanide coordination polymers

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ABSTRACT

Two new lanthanide coordination polymers H₂N(CH₃)₂·[Eu^{III}(L₁)₃(L₂)] (**1**, L₁ = isophthalic acid dianion, L₂ = formic acid anion) and [La^{III}(2,5-PDC)(L₂)](**2**, 2,5-PDC = 2,5-pyridinedicarboxylate dianion) were synthesized under solvothermal conditions. It is of interest that the formic ligand (L₂) is not contained in the starting materials, but arises from the water molecule-enhanced CO₂ insertion during the solvothermal process. Both of the two compounds exhibit complicated three dimensional sandwich-like frameworks.

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1. Introduction

Design and synthesis of coordination polymers have been of great interest, not only due to their intriguing structures but also owing to their applications as functional material in the field of magnetism [1], gas adsorption [2], catalysis [3] and manufacture of light conversion devices [4]. Recent decades, solvothermal technique has been found to be an efficient route for assembling coordination polymers, in spite of the fact that most of the reacting process at high temperature cannot be monitored in real time [5]. In most cases, the reagents used as organic solvents in solvothermal process will act as lattice molecules in the title products or behave as organic ligands coordinated to the central metal cations [6]. However, sometimes the organic solvents or organic ligands will be decomposed or transformed due to the high temperature or catalysis of central metal cations, and the unpredictable title compounds will be achieved [7]. Chen has reported the decarboxylation of pyridine-3,4-dicarboxylate ligands in solvothermal process which was believed to be due to the catalysis of lanthanide cations [7a]. In addition, in our previous work, we have reported the decomposition of DTSA (2,2'-disulfanediyldibenzoic acid) and pyridine-2,5-dicarboxylate ligands which was owing to the hydrothermal oxidation [7b,c]. In this paper, we used lanthanide salts, isophthalic acid, pyridine-2,5-dicarboxylic acid and a mixture of DMF/H₂O (v:v = 1:1) to assemble lanthanide coordination polymers. It is of interest that

the water molecule-enhanced CO₂ insertion was observed and two unpredictable lanthanide coordination polymers H₂N(CH₃)₂·[Eu^{III}(L₁)₃(L₂)] (**1**, L₁ = isophthalic acid dianion, L₂ = formic acid anion) and [La^{III}(2,5-PDC)(L₂)](**2**, 2,5-PDC = 2,5-pyridinedicarboxylate dianion) were obtained.

2. Experimental section

2.1. Materials and methods

All chemicals employed were commercially available and used as received without further purification. The C, H and N microanalysis were carried out with Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm⁻¹ ranges on a Nicolet 5DX spectrometer. Thermal gravimetric (TG) analysis was performed at a rate of 10 °C/min under N₂ using a NETZSCH TG 209 system. The luminescent characterization of compounds **1** and **2** were performed on a FLS920 spectrophotometer at room temperature.

2.2. Hydrothermal synthesis

H₂N(CH₃)₂·[Eu^{III}(L₁)₃(L₂)] (**1**): Eu(NO₃)₃·6H₂O of 0.3 mmol, 0.6 mmol of H₂L₁, 1 mmol of NaOH and 10 mL of H₂O/DMF (v:v = 1:1, DMF = *N,N*-dimethylformamide) solution were sealed in a 23-mL Teflon-lined autoclave. After heating for 72 h at 170 °C and cooled to room temperature at a rate of 5 °C/h, colorless block-like crystals could be isolated in ~60% yield (based on Eu) through

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washing with deionized water. Anal. Calcd. for $C_{27}H_{21}Eu_2NO_{14}$: C, 36.54; H, 2.39; N, 1.58. Found: C, 36.50; H, 2.42; N, 1.64%. IR (KBr, pellet, cm^{-1}): 3618s, 3161s, 1604vs, 1546vs, 1392vs, 744s, 704m, 655m, 542w, 435w.

[$La^{III}(2,5-PDC)(L_2)$] (**2**): $La(NO_3)_3 \cdot 6H_2O$ of 0.3 mmol, 0.3 mmol of pyridine-2,5-dicarboxylic acid, 1 mmol of NaOH and 10 mL of $H_2O/DMF(v:v = 1:1)$ solution were sealed in a 23-mL Teflon-lined autoclave. After heating for 72 h at 170 °C and cooled to room temperature at a rate of 5 °C/h, colorless block-like crystals could be isolated in ~85% yield (based on La) through washing with deionized water. Anal. Calcd. for $C_8H_4LaNO_6$: C, 27.53; H, 1.16; N, 4.01. Found: C, 27.55; H, 1.13; N, 4.05%. IR (KBr, pellet, cm^{-1}): 3471s, 1336w, 1325m, 1176w, 1161m, 1061s, 1012s, 931s, 693m, 668m.

2.3. X-ray crystallography

Diffraction data of **1** and **2** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and graphite monochromator using the

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

	1	2
Empirical formula	$C_{27}H_{21}Eu_2NO_{14}$	$C_8H_4LaNO_6$
Formula/mass	887.37	349.03
T (K)	298(2)	298(2)
Wavelength (\AA)	0.71073	0.71073
Cryst. syst.	Triclinic	Orthorhombic
Space group	$P\bar{1}$	Pbca
a (\AA)	8.39360(10)	12.015(3)
b (\AA)	10.53470(10)	7.6586(17)
c (\AA)	17.4093(2)	18.678(4)
α (deg)	99.1740(10)	90
β (deg)	97.1300(10)	90
γ (deg)	100.3480(10)	90
V (\AA^3)	1476.38(3)	1718.7(7)
Z	2	8
D_{calcd} ($g\text{ cm}^{-3}$)	1.996	2.698
μ (mm^{-1})	4.280	4.985
F000	856	1312
Data/restraints/params	6929/2/407	1722/0/149
GOF on F^2	1.025	1.031
$R_1[I > 2\sigma(I)]^a$	0.0240	0.0374
$wR_2[I > 2\sigma(I)]^b$	0.0475	0.0787
Largest diff. peak and hole ($e\text{\AA}^{-3}$)	0.918 and -0.957	1.229 and -1.131

$$^a R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$$

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

Table 2
Selected bond distances (\AA) and angles (deg) for **1**^a and **2**^b.

1		2	
Eu(1)–O(10)	2.267(2)	Eu(2)–O(9)#6	2.337(2)
Eu(1)–O(6)	2.296(2)	Eu(2)–O(8)#7	2.382(2)
Eu(1)–O(7)#1	2.354(2)	Eu(2)–O(12)#2	2.374(2)
Eu(1)–O(11)#3	2.363(2)	Eu(2)–O(14)#6	2.438(3)
Eu(1)–O(3)	2.504(2)	Eu(2)–O(1)	2.485(2)
Eu(1)–O(13)	2.534(3)	Eu(2)–O(5)#6	2.389(2)
Eu(1)–O(4)	2.557(2)	Eu(2)–O(4)#8	2.472(2)
Eu(1)–O(14)	2.557(2)	Eu(2)–O(2)	2.494(2)
O(10)–Eu(1)–O(6)	83.51(9)	O(9)#6–Eu(2)–O(12)#2	84.47(9)
O(10)–Eu(1)–O(7)#1	157.83(10)	O(9)#6–Eu(2)–O(8)#7	157.62(9)
O(7)#Eu(1)–O(11)#3	112.36	O(12)#2–Eu(2)–O(8)#7	106.59(9)
La(1)–O(2)#1	2.456(5)	La(1)–N(1)#4	2.728(6)
La(1)–O(1)	2.474(5)	N(1)–La(1)#4	2.728(6)
La(1)–O(4)#2	2.478(5)	O(2)–La(1)#3	2.456(5)
La(1)–O(5)#3	2.487(5)	O(3)–La(1)#4	2.608(5)
La(1)–O(5)	2.536(5)	O(3)–La(1)#6	2.682(5)
La(1)–O(3)#4	2.608(5)	O(4)–La(1)#7	2.478(5)
La(1)–O(6)	2.612(5)	O(5)–La(1)#1	2.487(5)
La(1)–O(3)#5	2.682(5)		
O(2)#1–La(1)–O(1)	152.15(19)	O(2)#1–La(1)–N(1)#4	131.19(18)
O(2)#1–La(1)–O(4)#2	97.75(17)	O(5)#3–La(1)–N(1)#4	140.61(17)
O(1)–La(1)–O(4)#2	80.94(18)	O(5)–La(1)–O(6)	50.02(17)

^a Symmetry codes for **1**: #1 $-x+1, -y, -z$; #2 $-x+1, -y+1, -z+1$; #3 $-x+1, -y, -z+1$; #6 $1+x, 1+y, 1+z$; #7 $1-x, 1-y, -z$; #8 $x, 1+y, z$.

^b Symmetry codes for **2**: #1 $-x+1, y+1/2, -z+3/2$; #2 $x+1/2, -y+3/2, -z+2$; #3 $-x+1, y-1/2, -z+3/2$; #4 $-x+1, -y+2, -z+2$; #5 $x, -y+3/2, z-1/2$; #6 $x, -y+3/2, z-1/2$; #7 $x-1/2, -y+3/2, -z+2$.

ω -scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [8]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. The CCDC reference numbers for compounds **1** and **2** are 696374 and 722720, respectively. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Hydrothermal synthesis

In an attempt to synthesize lanthanide isophthalate coordination polymers, we designed a solvothermal process based on europium nitrates, isophthalic acid and DMF/ H_2O mixed solvent. However, in the final product, the coordinated formic ligand and the dimethylammonium counter cation were found and compound **1** with three dimensional sandwich-like framework was achieved. Because water molecules could enhance the insertion of CO_2 molecules into metal complexes in the form of formic ligands as reported in previous literatures [9], we proposed that the coordinated formic ligand was derived from the CO_2 insertion assisted by H_2O molecules and the dimethylammonium counter cation existed as an impurity of DMF solvent, as well as the CO_2 molecules may arise from the decarboxylation of some isophthalate ligands. With this in mind, we changed the starting materials to lanthanum nitrate, pyridine-2,5-dicarboxylic acid and DMF/ H_2O mixed solvent. It is of interest that there also existed coordinated formic ligands in the component of the product (compound **2**).

3.2. Crystal structure description for compound **1**

As shown in Fig. 1, the asymmetric unit of compound **1** is composed of two Eu^{III} cations, one L_2 , three L_1 anions and one guest dimethylammonium cations. Eu1 is chelated by one L_2 and one L_1 ligands via O13, O14 and O3, O4 atoms, respectively. The dihedral angle between the two chelating circles is $60.62(3)^\circ$ and the coordination polyhedron of Eu1 is further completed by four O atoms from four different L_1 ligands. The Eu–O bond distances fall in the range of 2.268–2.615 \AA , which are comparable with that

reported in literatures [10]. Differently, Eu2 is only chelated by one L_1 ligand through O1 and O2 atoms, and the coordination polyhedron is further completed by five L_1 -O and one L_2 -O atoms with the Eu–O bond distances falling in the range of 2.337–2.494 Å, although the coordination number is eight for

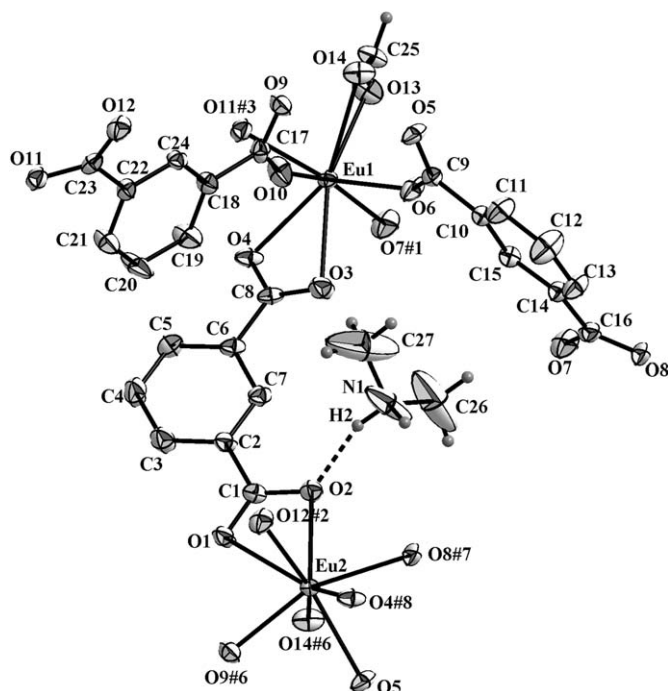


Fig. 1. ORTEP view of the asymmetric unit of **1** with 50% probability displacement ellipsoids (the dashed line represents the hydrogen bond). Symmetry codes: #1 $-x+1, -y, -z$; #2 $-x+1, -y+1, -z+1$; #3 $-x+1, -y, -z+1$; #6 $1+x, 1+y, 1+z$; #7 $1-x, 1-y, -z$; #8 $x, 1+y, z$.

Table 3

Hydrogen bonds with $H\cdots A < r(A)+2.000$ Å and $\angle DHA > 110^\circ$.

D–H	$d(D-H)$	$d(H\cdots A)$	$\angle DHA$	$d(D\cdots A)$	A
N1–H1	0.858	2.061	151.75	2.846	O13 ^{#8}
N1–H1	0.858	2.585	123.19	3.138	O11 ^{#2}
N1–H2	0.865	1.884	161.04	2.716	O2

Symmetry codes: #8 = $x, y+1, z$; #2 = $-x+1, -y+1, -z+1$.

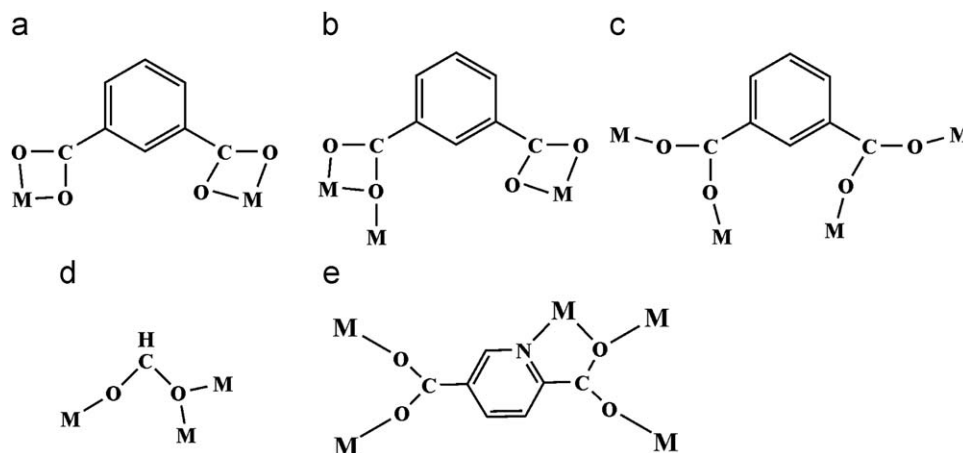
both of Eu1 and Eu2. There exist hydrogen bond interactions between guest dimethylammonium cation and the isophthalate ligand in the form of N1–H2...O2, N1–H1...O11^{#2} and N1–H1...O13^{#8} (#8 = $x, y+1, z$; #2 = $-x+1, -y+1, -z+1$), and the detailed hydrogen bond distances and angles have been listed in Table 3.

In the crystal structure of compound **1**, isophthalate ligand exhibits three different kinds of coordination modes μ_2 - L_1 (Scheme 1a), μ_3 - L_1 (Scheme 1b) and μ_4 - L_1 (Scheme 1c), while the formic ligand shows the μ_3 - L_2 coordination mode (Scheme 1d). Due to the μ_3 - L_1 and μ_3 - L_2 bridges, the adjacent Eu atoms (Eu...Eu = 4.264, 4.495 Å) are connected and give rise to the formation of one dimensional infinite chains, which are then extended to two dimensional sheets via μ_2 - L_1 bridges (Fig. 2a), and the structure is finally expanded to three dimensional sandwich-like framework based on μ_4 - L_1 bridges (Fig. 2b). It is intriguing that there are two different kinds of channels (A-type (10.749 × 9.911 Å) and B-type (14.632 × 9.932 Å)) in the sandwich-like framework, and only the B-type channels are occupied by guest dimethylammonium cations while there is nothing in the A-type channels.

3.3. Crystal structure description for compound **2**

The asymmetric unit of compound **2** is composed of one La^{III} trication, one 2,5-pyridinedicarboxylate dianion and one formic monoanion. As shown in Fig. 3, La1 is 9-fold coordinated by three L_2 -O atoms, one 2,5-PDC-N atom and five 2,5-PDC-O atoms. In the coordination environment for La1, the chelate circles of La–O–C–O–La and La–O–C–C–N–La are formed based on L_2 and 2,5-PDC ligands, respectively, and the dihedral angle is 75.01(5)°. The La–O/N bond distances fall in the range of 2.456–2.728 Å, which are comparable with that reported in literatures [11]. The O–La–O/N bond angle is in the range of 50.02–152.15°.

In the crystal structure of compound **2**, 2,5-pyridinedicarboxylate ligand exhibits five connected coordination mode μ_5 -2,5-PDC (Scheme 1e) and the formic ligand shows the same μ_3 - L_2 coordination mode as that in compound **1**. Due to the μ_5 -2,5-PDC and μ_3 - L_2 bridges, the adjacent La atoms (La...La = 4.208 Å) are connected and give rise to the formation of one dimensional infinite chains, which are then extended to two dimensional sheets through μ_5 -2,5-PDC bridges (Fig. 4a), and the structure is finally expanded to three dimensional sandwich-like framework via 2,5-PDC spacers (Fig. 4b). Different from the framework of



Scheme 1. The coordination modes of L_1 (a, b, c), L_2 (d) and 2,5-PDC (e).

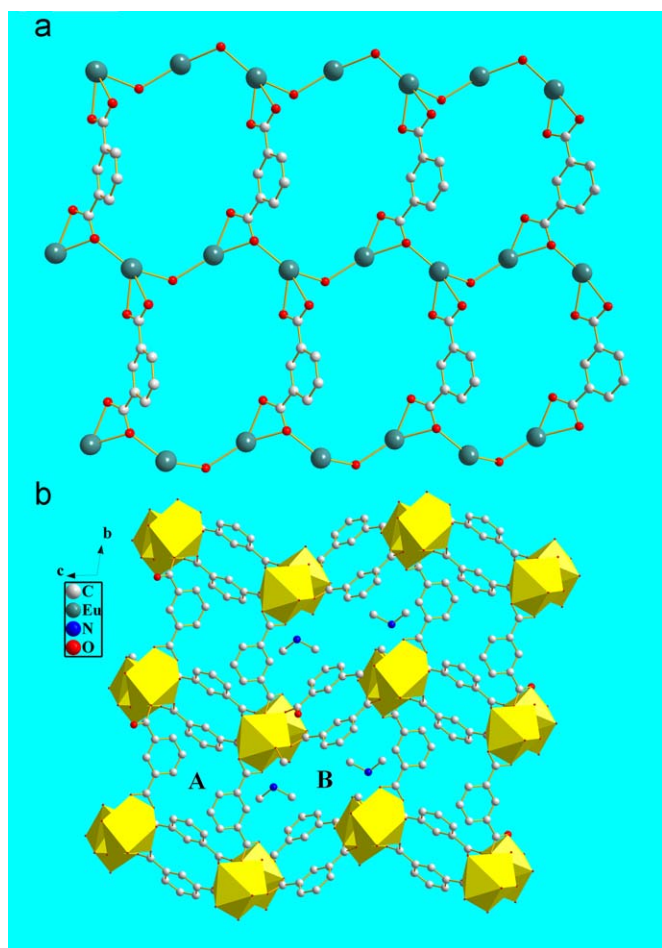


Fig. 2. (a) View of the 2D sheet for **1**; (b) diagram of the 3D sandwich-like framework for **1**. The coordination polyhedrons of Eu atoms are represented. All of the hydrogen atoms have been omitted for clarity.

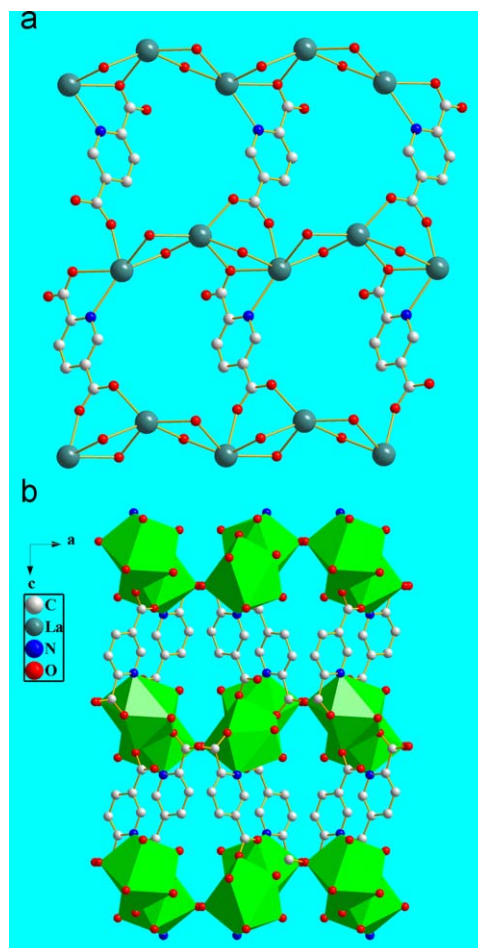


Fig. 4. (a) View of the 2D sheet for **2**; (b) diagram of the 3D sandwich-like framework for **2**. The coordination polyhedrons of La atoms are represented. All of the hydrogen atoms have been omitted for clarity.

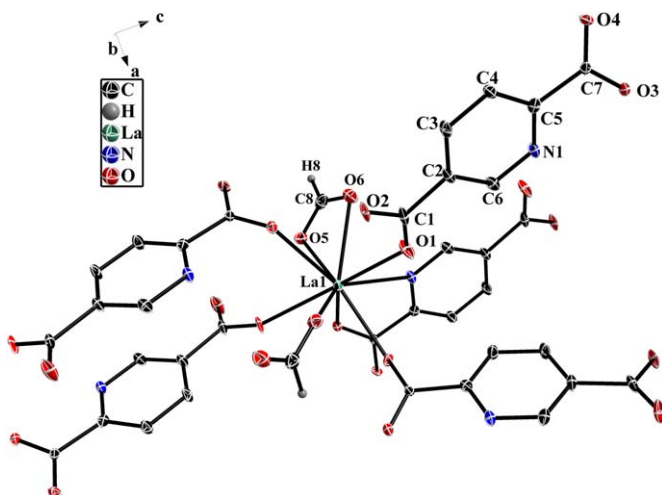


Fig. 3. View of the coordination environment of La1 for **2**. All of the hydrogen atoms except for formic-H atoms have been omitted for clarity.

compound **1**, there is no guest molecule in the skeleton of compound **2**.

XRD powder patterns for compounds **1** and **2** have been collected, and are very similar to the simulated ones, as shown in Fig. 5, which indicates the high purity of the two products.

3.4. Thermal stability

To examine the thermal stability of compounds **1** and **2**, thermal gravimetric analysis was carried out. TG analysis revealed that compound **1** lost its dimethylammonium cation of 5.83% in the range of 180–220 °C (calcd. 5.19%), and begin to collapse at 540 °C, while compound **2** kept thermal stable until 580 °C.

3.5. Luminescent properties

Due to the excellent luminescent property of Eu^{III} cation, the room-temperature solid-state luminescent properties of compound **1** were investigated. As shown in Fig. 6, the emission spectra of compound **1** at room temperature upon excitation at 394 nm shows the characteristic transition: $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4$) of Eu^{III} cations with emission bands: 579, 592, 617, 653 and 702 nm, which may be ascribed to the efficient ligand (L_1) to metal (Eu^{III}) energy transfer (LMCT). The appearance of the symmetry-forbidden emission $^5D_0 \rightarrow ^7F_0$ at 579 nm indicates the low symmetric coordination environment of Eu^{III} cations in compound **1**, which is consistent with the single-crystal-X-ray diffraction analysis. It is well known that the intensity ratio of $^5D_0 \rightarrow ^7F_2$ transition to $^5D_0 \rightarrow ^7F_1$ transition is an efficient subject to characterize the coordination environment and the site symmetry of Eu^{III} cations [12]. The emission band $^5D_0 \rightarrow ^7F_1$ at 592 nm is magnetic dipole transition, which is independent of the

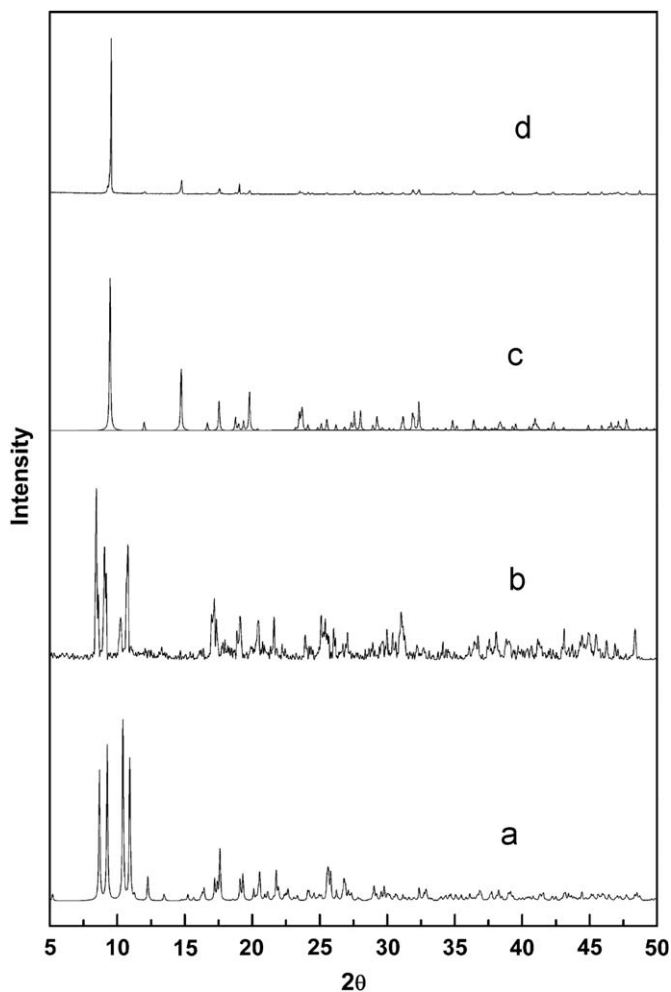


Fig. 5. Experimental X-ray powder diffraction patterns for 1(a)–2(c) and simulated X-ray powder diffraction patterns for 1(b)–2(d).

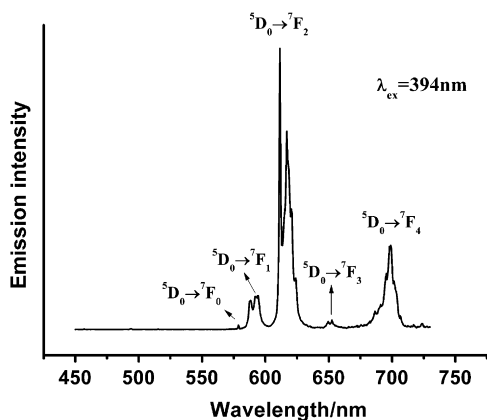


Fig. 6. Photoluminescence spectra of 1 with 394 nm excitation source.

coordinated ligands, while the ${}^5D_0 \rightarrow {}^7F_2$ transition is electric dipole transition, and is fairly sensitive to the coordination environment of Eu^{III} cations. In compound 1, the red emission of ${}^5D_0 \rightarrow {}^7F_2$ is the most intense and is always the preferred transition for Eu^{III} containing luminescent materials. The intensity ratio $I({}^5D_0 \rightarrow {}^7F_2)/I({}^5D_0 \rightarrow {}^7F_1)$ is about 5.95, which indicates the noncentro-symmetric coordination environment of Eu^{III} cations in

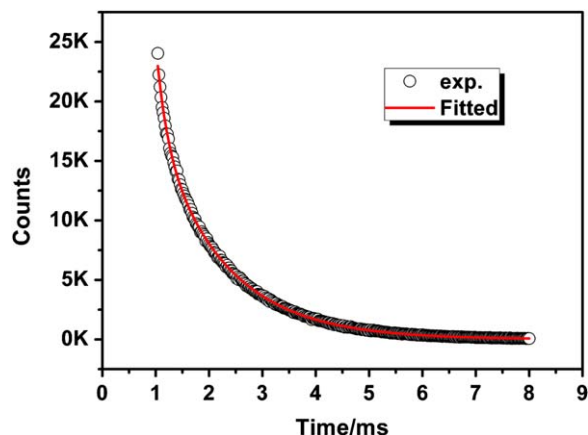


Fig. 7. Fluorescence lifetime decay of 1 (black) and the corresponding biexponential fit function (red) with $\tau_1 = 199.41 \mu\text{s}$, $\tau_2 = 1.27 \text{ ms}$. Condition: Excitation at 394 nm and emission at 617 nm.

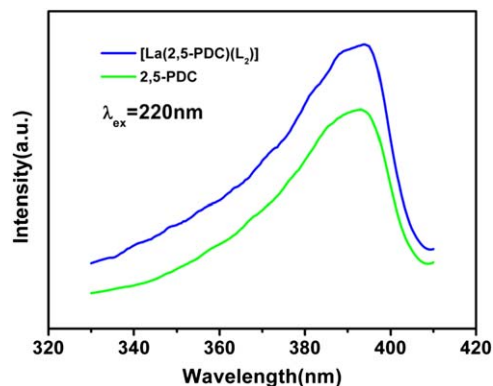


Fig. 8. Photoluminescence spectra of 2 with 220 nm excitation source.

compound 1, which can be proved by the single-crystal-X-ray diffraction analysis. In addition, the luminescent characterization reveals the long fluorescence lifetime for compound 1 with $\tau_1 = 199.41 \mu\text{s}$, $\tau_2 = 1.27 \text{ ms}$ (Fig. 7).

The room-temperature solid-state excitation and emission luminescent spectrum of compound 2 is shown in Fig. 8. As expected, the emission spectra of compound 2 only shows the characteristic pyridine-2,5-dicarboxylic acid emission, and it is of interest that the emission of compound 2 is more intense than that of pure pyridine-2,5-dicarboxylic acid, which may be attributed to the La^{III} to L_2 transfer.

4. Conclusions

In conclusion, we have successfully synthesized two new lanthanide coordination polymers, compounds 1 and 2, under solvothermal conditions, during which the water assisted CO_2 insertion was found, and the interesting process may be due to the high temperature and/or the catalysis of lanthanide ions. Based on effective organic spacers (L_1 in 1, 2,5-PDC in 2), both of the two compounds exhibit three dimensional sandwich-like frameworks. The luminescent characterization reveals that the Eu complex (compound 1) exhibits the characteristic Eu^{III} emission, and has long luminescence lifetime with $\tau_1 = 199.41 \mu\text{s}$ and $\tau_2 = 1.27 \text{ ms}$. All of this may be helpful to the assembly of interesting luminescent materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.06.004.

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