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## Assembly and Luminescence Properties of Two New Metal-Organic Coordination Polymers with *s*-Block Alkaline-Earth Metals and 1,2,4,5-Benzenetetracarboxylate Ligand

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### ABSTRACT

Two metal-organic coordination polymers *e.g.*,  $\text{Ca}_2(\text{BTEC})(\text{DMF})(\text{H}_2\text{O})_3$  (**1**) and  $\text{Ba}_2(\text{BTEC})(\text{H}_2\text{O})$  (**2**) based on BTEC ligands have been solvothermally synthesized and characterized (DMF = *N,N*-dimethylformamide,  $\text{H}_4\text{BTEC}$  = 1,2,4,5-benzene tetracarboxylate). Compound **1** crystallizes in the chiral space group *P*-1 and features an 2D 4, 4-connected square grid constructed by calcium-dimer square secondary building units (SBUs)  $[\text{Ca}_2(\text{C}_2\text{O}_4)_4(\text{CO}_2)_2]$  and 4-connected square BTEC ligand. Compound **2** is a 3D 4, 8-connected framework built from tetrahedron secondary building units  $[\text{Ba}(\text{C}_2\text{O}_4)_4]$  and 8-connected cubic BTEC ligand. Moreover, the influences of the starting reagents and synthesis methods on the structures of these two compounds have been studied. Solid state luminescent properties of the two compounds have also been studied.

### KEYWORDS

1,2,4,5-Benzene tetracarboxylate, Solvothermal synthesis, Luminescence properties, Metal-organic coordination polymers.

### INTRODUCTION

Metal-organic coordination polymers (MOCPs) are porous crystals with structural and functional varieties for their metal-containing cationic units and anionic organic linkers [1,2]. In recent years, the construction of coordination polymers, especially 2D and 3D structures, has attracted extensive interests not only due to their intriguing structure motifs but also their potential applications in optoelectronics, heterogeneous catalysis, chemical sensing, energy storage and drug delivery [3-11]. To date, a great deal of metal-organic coordination polymers with different structures based on aromatic polycarboxylate ligands have been synthesized [12-14]. Especially, metal-organic coordination polymers with ligand 1,2,4,5-benzenetetracarboxylic acid ( $\text{H}_4\text{BTEC}$ ) have been widely studied due to its rich coordination modes with metal ions through partial or complete deprotonation of the carboxyl groups. Till now, metal-organic coordination polymers of various structure types resulting from BTEC and *d*-block metals, such as Co, Ni, Cu, Zn, Cd, Mn, Fe, V have been reported [15-22]. The coordination polymers consisting of *f*-block elements and

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BTEC ligand have also been investigated [23-26]. Compared to the *d* and *f*-block elements, the *s*-block elements that possess variable coordination geometry may be utilized to generate fascinating structures [27]. As far as we know, there are only a few *s*-block metal-organic coordination polymers based BTEC being structurally characterized [28-30]. Recently, our research interest has been focused on a systematic study of coordination polymers based *s*-block alkaline-earth metal ions [31-34] and we have reported the first alkaline earth metal Mg-BTEC MOF [31]. In this paper, we represent the synthesis, structures and luminescent properties of two new Ca and Ba based compounds.

## EXPERIMENTAL

All the starting materials were used as received from commercial sources without further purification. Powder X-ray diffraction data were collected on a Rigaku D/max-2550 diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Fourier transform infrared spectra were recorded within the 4000-400  $\text{cm}^{-1}$  region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Photoluminescence spectra were measured with an Edinburgh Instruments FLS920 spectrophotometer at room temperature.

**Synthesis of [Ca<sub>2</sub>(BTEC)(DMF)(H<sub>2</sub>O)<sub>3</sub>] (1):** Ca(OH)<sub>2</sub> (6 mg, 0.08 mmol), 1,2,4,5-BTEC (10 mg, 0.04 mmol), DMF (1 mL), H<sub>2</sub>O (0.5 mL), HNO<sub>3</sub> (0.2 mL, 2.7 M in DMF) and triazole (0.3 mL, 1 M in DMF) were added to a 20 mL vial, then the solution was heated to 100 °C for 48 h. Colourless strip-shaped crystals of compound **1** were collected, washed thoroughly with DMF and EtOH and dried in air at room temperature. Compound **1** shows the infrared frequencies at 3288(m), 1614(w), 1558(s), 1496(w), 1445(w), 1406(s), 1334(w), 1277(w), 1140(m), 946(w), 928(w), 881(m), 826(m), 682(m), 574(m), 519(w), 447(w).

**Synthesis of [Ba<sub>2</sub>(BTEC)(H<sub>2</sub>O)] (2):** Ba(OH)<sub>2</sub> (13 mg, 0.04 mmol), 1,2,4,5-BTEC (10 mg, 0.04 mmol), DMF (1.5 mL), H<sub>2</sub>O (0.5 mL) and HNO<sub>3</sub> (0.3 mL, 2.7 M in DMF) were placed in a 20 mL vial, the mixture was heated to 100 °C and kept at this temperature for 48 h. The reaction system was cooled slowly to room temperature. Colourless strip shaped crystals of compound **2** were collected, washed thoroughly with DMF and EtOH and dried in air at room temperature. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): Compound **2** 3415(m), 3311(w), 2216(w), 1684(w), 1558(s), 1490(m), 1426(m), 1405(s), 1309(m), 1143(w), 928(w), 881(m), 827(s), 682(w), 574(m), 496(m).

**X-ray crystallography:** Single-crystal X-ray diffraction measurements for compounds **1** and **2** were carried out with a Bruker SMART 1000 CCD diffractometer at 293(2) K. The determinations of unit cell parameters and data collections were performed with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and unit cell dimensions were obtained with least-squares refinements. The program SAINT [35] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using the SADABS program [36]. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [37]. Metal atoms in each compound were located from the E-maps and other non-hydrogen atoms were located in successive difference

Fourier syntheses and refined with anisotropic thermal parameters on F<sup>2</sup>. All the hydrogen atoms attached to carbon atoms were placed geometrically and located based on theoretically riding model. The experimental details for the structural determinations of compounds **1** and **2** are summarized in Table-1, while the selected bond lengths and angles and hydrogen-bonding data are presented in supporting information.

TABLE-1  
CRYSTAL DATA AND STRUCTURE REFINEMENT  
PARAMETERS FOR COMPOUNDS 1 AND 2

	Compound 1	Compound 2
Empirical formula	C <sub>13</sub> H <sub>15</sub> NO <sub>12</sub> Ca <sub>2</sub>	C <sub>10</sub> H <sub>4</sub> O <sub>9</sub> Ba <sub>2</sub>
Formula weight	457.42	542.81
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
a (Å)	9.224(2)	7.813(2)
b (Å)	10.101(1)	17.524(4)
c (Å)	10.474(2)	9.106(2)
$\alpha$ (°)	96.06(3)	90
$\beta$ (°)	99.17(3)	114.39
$\gamma$ (°)	113.14(3)	90
V (Å <sup>3</sup> )	870.5(3)	1135.5(4)
Z	2	2
Calculated density (g/cm <sup>3</sup> )	1.745	3.175
F(000)	472	984
Reflections collected	2889	1425
Independent reflections	2665	1386
Goodness-of-fit on F <sup>2</sup>	1.020	1.070
R <sub>1</sub> <sup>a</sup> /wR <sub>2</sub> <sup>b</sup> [I > 2 $\sigma$ (I)]	0.0312/0.1163	0.0156/0.0423

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

## RESULTS AND DISCUSSION

**Structure of [Ca<sub>2</sub>(BTEC)(DMF)(H<sub>2</sub>O)<sub>3</sub>] (1):** Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the triclinic system with space group P-1 showing a 2D 4,4-connected square grid. The asymmetric unit of **1** consists of two Ca<sup>2+</sup> ions, one BTEC<sup>4-</sup> ligand, one coordinated DMF and three coordinated water molecules. The two Ca<sup>2+</sup> ions can be divided into two groups according to their coordination modes shown in Fig. 1a. Ca1 ion coordinates with eight oxygen atoms, six of which are from three BTEC<sup>4-</sup> anions and the other two from two coordinated water molecules. While Ca2 ion coordinates with eight oxygen atoms, six of which are from three BTEC<sup>4-</sup> anions and the other two from one DMF and one water molecule, respectively. All the Ca-O bond distance are in the range of 2.365(7)-2.658(8) Å, which are closely similar to those reported [38,39]. The two calcium ions can be seen as calcium-dimer square SBUs [Ca<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>]. The BTEC<sup>4-</sup> anion offers all its eight oxygen atoms to chelate with six calcium ions from four calcium-dimer SBUs, which can be seen as a 4-connected square SBU as shown in Fig. 1b. Interestingly, two types of 4-connected square SBUs are arranged in clockwise and anticlock direction with 180° span to generate two helical chains with opposite chirality as seen in Fig. 1c. Furthermore, two types of helical chains are connected to form a 2D 4,4-connected layer structure (Fig. 1d). When it comes to the structural topology of **1**, calcium-dimer

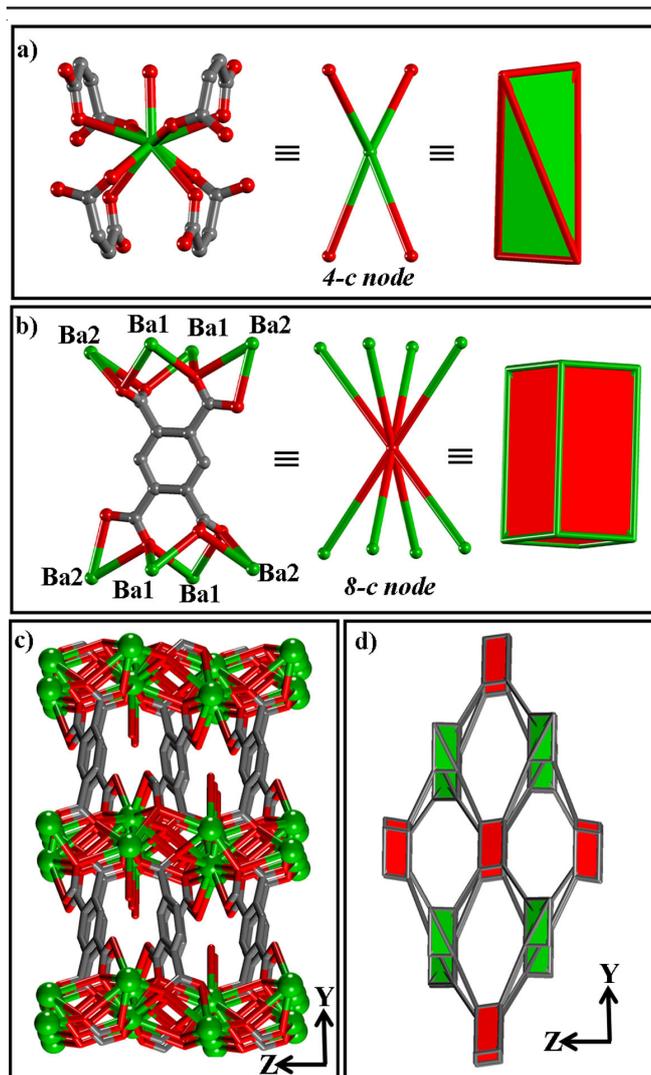


Fig. 1. Structure description for compound 1: a) illustration of the SBU  $[\text{Ba}(\text{C}_2\text{O}_4)_4]$ , viewed as a 4-connected tetrahedron node; b) coordination mode of the ligand  $\text{BTEC}^{4-}$ , viewed as an 8-connected cubic node; c) 3D framework constructed from the SBUs  $[\text{Ba}(\text{C}_2\text{O}_4)_4]$  and  $\text{BTEC}^{4-}$  ligands along the  $[100]$  direction; d) Polyhedral view of the 4,8-connected network along the  $[100]$  direction. Colour scheme: carbon = gray, nitrogen = blue, oxygen = red, barium = green and some of the H atoms were omitted for clarity

SBU and  $\text{BTEC}^{4-}$  ligand can be simplified into 4-connected square nodes, respectively. Therefore, the resulting structure can be interpreted as a 4,4-connected square grid as shown in Fig. 1e.

**Structure of  $[\text{Ba}_2(\text{BTEC})(\text{H}_2\text{O})]$  (2):** Single-crystal X-ray diffraction analysis reveals that compound 2 crystallizes in the monoclinic system with space group  $C2/c$  exhibiting a 3D 4,4-connected framework. The asymmetric unit of 2 consists of two  $\text{Ba}^{2+}$  ions, one  $\text{BTEC}^{4-}$  anion and one coordinated water molecule. Ba1 ion coordinates with nine oxygen atoms, eight of which are from four individual  $\text{BTEC}^{4-}$  anions and one from a water molecule shown in Fig. 2a. Ba2 ion coordinates with eight oxygen atoms from four individual  $\text{BTEC}^{4-}$  anions. The Ba-O bond distances are in the range of 2.657(2)–3.082(2) Å, which are closely similar to those observed in related species [40,41]. The  $\text{BTEC}^{4-}$  anion offers all its eight oxygen atoms to chelate with eight barium ions as shown in Fig. 2b. Therefore,

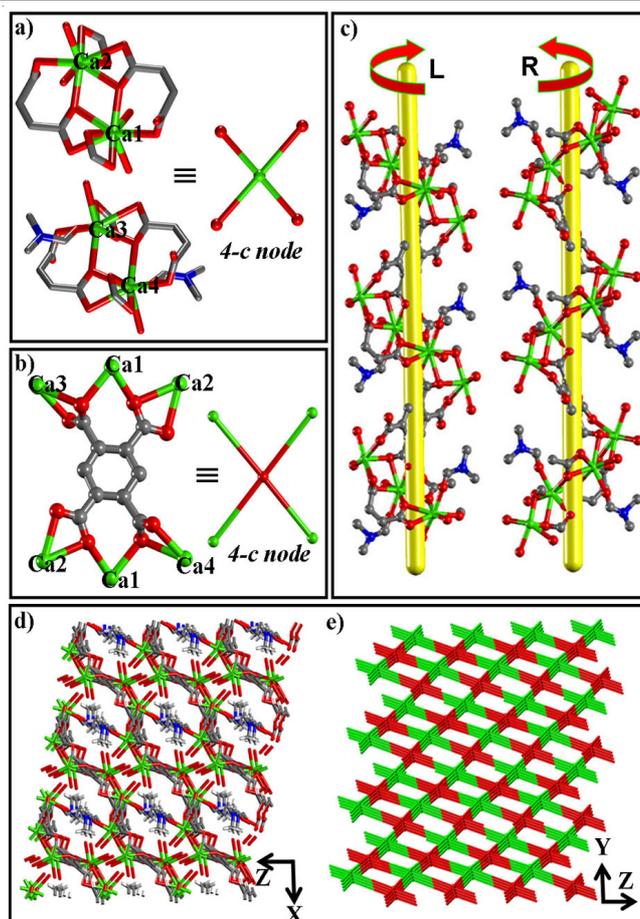


Fig. 2. Structure description for compound 2: a) illustration of calcium-dimer SBU  $[\text{Ca}_2(\text{C}_2\text{O}_4)_2(\text{CO}_2)_2]$ , viewed as a 4-connected square node; b) coordination mode of the ligand  $\text{BTEC}^{4-}$ , viewed as a 4-connected square node; c) ball and stick view of the L- and R-helical chains; d) stick view of the 2D layer constructed from the L- and R-helical chains; e) stick view of the 4,4-connected square grid along the  $[100]$  direction. Colour scheme: carbon = gray, nitrogen = blue, oxygen = red, calcium = green and some of the H atoms were omitted for clarity

each barium ion can be seen as 4-connected tetrahedral SBU and the  $\text{BTEC}^{4-}$  anion can be seen as 8-connected cubic SBU. Consequently, two types of SBUs are connected with each other to construct a 3D framework shown in Fig. 2c. In the view of its topology, the 4-connected SBU and 8-connected SBU can be simplified into 4-connected tetrahedral and 8-connected cubic nodes, respectively. Then, the resulting structure can be simplified as a 4,8-connected network as shown in Fig. 2d, in which there are two T sites with coordinate sequence  $\text{Ba}_{1-10}$ : 4.21.38.137.110.312.218.564.362.892 and  $\text{BTEC}_{1-10}$ : 8.16.76.74.220.162.436.288.724.450. To the best of our knowledge, this type of network has never been reported according to the reticular chemistry structure resource database.

**Powder X-ray diffraction analysis:** In order to check the phase purity of compounds 1 and 2, the powder X-ray diffraction patterns were recorded at room temperature. As shown in Fig. 3, the peak positions simulated and experimental patterns are in good agreement with each other, indicating the phase purity of the product. The differences of intensity are due to the preferred orientation of the crystalline powder samples.

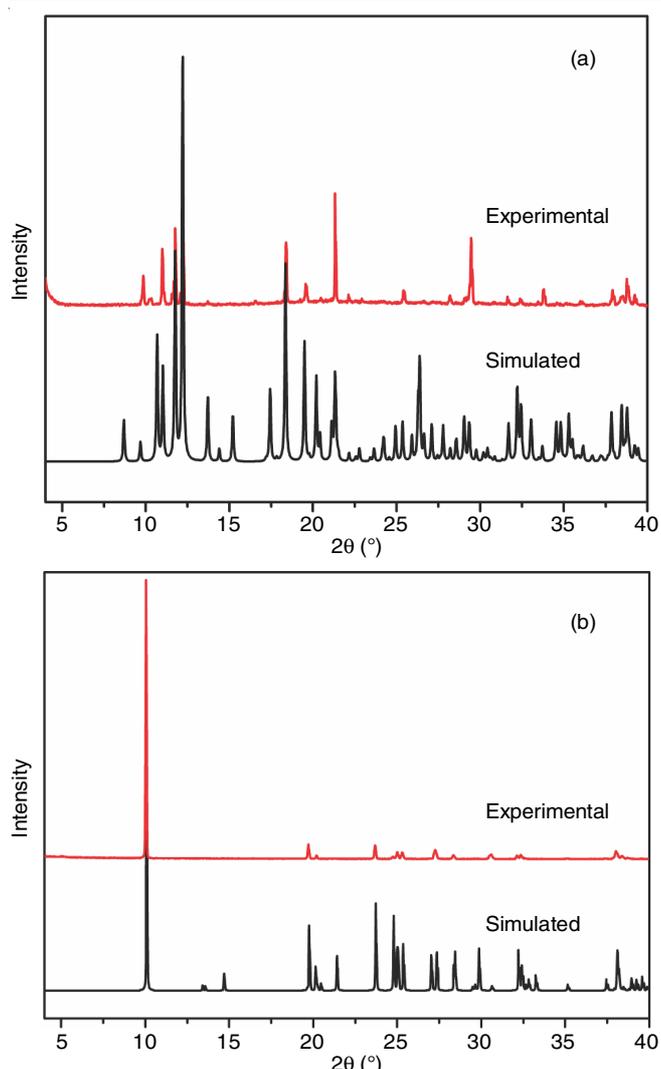


Fig. 3. Experimental and simulated powder X-ray diffraction patterns for compound 1 (a) and compound 2 (b)

**Fluorescent properties:** The luminescent properties of compounds 1, 2 and  $H_4$ BTEC ligand were investigated in the solid state at room temperature (Fig. 4). The free ligand  $H_4$ BTEC emits strong fluorescence centered at 372 nm upon excitation at 316 nm. Its luminescent behaviour was assigned to  $\pi$

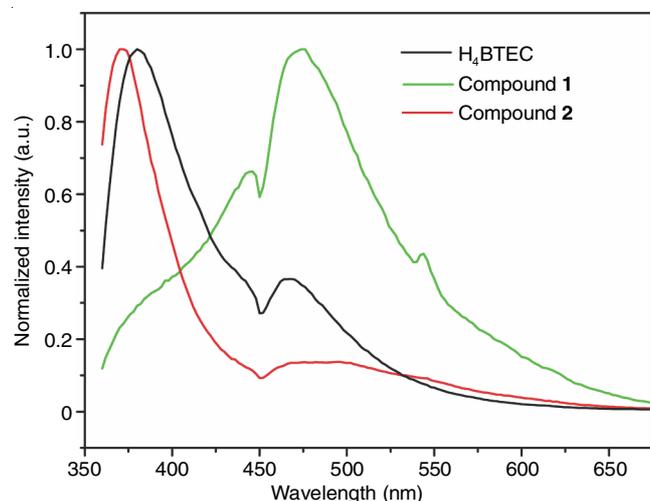


Fig. 4. Luminescent spectra for compounds 1 and 2 at room temperature

or  $n$  to  $\pi^*$  orbital transitions. As shown in Fig. 4, the emission curve of compound 1, measured at  $\lambda_{ex} = 336$  nm, peaks at 474 nm with a long tail into the red. The compound 2 exhibits strong blue luminescence with the max  $\lambda_{em}$  at 380 nm ( $\lambda_{ex} = 340$  nm). It is noteworthy that the emission band of the compound 2 is similar to that of the corresponding free ligand ( $H_4$ BTEC). Therefore, the emission band is neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT) and can probably be assigned to the intra-ligand fluorescent emission. The result suggests that the compound 2 may be an excellent candidate for potential photo-active material.

## Conclusion

Two metal-organic coordination polymers have been synthesized by using  $H_4$ BTEC ligand and alkaline-earth metal  $Ca^{2+}$  or  $Ba^{2+}$  ions. Compound 1 exhibits an 2D 4,4-connected square grid constructed by calcium-dimer square SBUs [ $Ca_2(C_2O_4)_4(CO_2)_2$ ] and 4-connected square BTEC ligand. Compound 2 shows a 3D 4,8-connected framework built from tetrahedron SBUs [ $Ba(C_2O_4)_4$ ] and 8-connected cubic BTEC ligand. Solid state luminescent properties of the two compounds have also been studied. Moreover, compound 2 exhibits intense ligand-centered fluorescence at room temperature and may be a good candidate for photoluminescence materials.

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