



# Two metal-organic frameworks with different configurations constructed from a flexible tripodal triaromatic acid

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## ABSTRACT

Two metal-organic frameworks  $[\text{Ce}_2(\text{L})_2(\text{DMF})_4]$  (**1**), and  $[\text{Ni}_3(\text{HL}^{2-})_4(\text{bpe})_3(\text{H}_2\text{O})_4] \cdot [\text{H}_2\text{N}(\text{CH}_3)_2]_2(\text{DMF})_6(\text{H}_2\text{O})_8$  (**2**) ( $\text{H}_3\text{L} = 4,4',4''\text{-}[(2,4,6\text{-trimethylbenzene-1,3,5-triyl})\text{tris}(\text{methylene})\text{tris}(\text{oxy})]\text{tribenzoic acid}$ ,  $\text{bpe} = \text{trans-4,4'}$ -bipyridylethylene) have been solvothermally synthesized from a flexible tripodal ligand. Single-crystal X-ray diffraction shows that compound **1** features a 3,6-connected double-layer network which is further connected by weak  $\pi$ - $\pi$  interactions between benzene rings to form a 3D porous network. Compound **2** exhibits an unprecedented (4,5)-connected  $(3^3,4^2,5,6^2,7^2)^2(6,8^4,10)$  topology based on zigzag chains and straight chains. In addition, thermal stabilities and luminescent properties of **1** and **2** were investigated in the solid state.

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## 1. Introduction

Metal-organic frameworks (MOFs) have attracted considerable scientific interest for functional designability and potential applications in magnetism, catalysis, gas separation, drug delivery, chemical sensing and biomedical imaging, etc [1–7]. MOF materials have many structural advantages over inorganic or organic materials for the structural and chemical tailorability, which can be deliberately adjusted via modification of the constituent ligands and metals [8]. The assembly of rigid ligands with certain geometries and lengths with metal ions usually results in MOFs with permanent porosity. On the other hand, flexible organic ligands have less possibility of stabilizing the high porous structures with very large voids or pores due to their configurational freedom [9,10]. The flexibility of the ligand makes it more difficult to control the structures and functions in the self-assembly process and usually results in variable and unpredictable structures and properties [11].  $4,4',4''\text{-}[(2,4,6\text{-trimethylbenzene-1,3,5-triyl})\text{tris}(\text{methylene})\text{tris}(\text{oxy})]\text{tribenzoic acid}$  ( $\text{H}_3\text{L}$ ) is a flexible ligand with a  $-\text{OCH}_2-$  linker between two phenyl rings, which has the probability of adopting diverse configurations according to different coordination environments during the self-assembly process. Only a

few number of complexes have been synthesized based on it [12–19]. Herein, we employed such a flexible tripodal ligand and successfully synthesized two compounds of different structures.

## 2. Experimental

### 2.1. Materials and instrumentation

Ligand  $\text{H}_3\text{L}$  was prepared referring to the literature [12]. All starting chemicals were of analytical grade and used as purchased. Elemental analyses (C, H, and N) were determined with a CHN–O–Rapid analyzer. IR spectrum using KBr pellets was recorded on Nicolet iS50 FT-IR spectrometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Thermogravimetric analysis (TGA) was carried out from  $30\text{ }^\circ\text{C}$  to  $700\text{ }^\circ\text{C}$  using STA 449-F5 in a flow of  $\text{N}_2$  with a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$ . Powder X-ray diffraction (PXRD) analyses were recorded on a Bruker D8 diffractometer with  $\text{Cu K}\alpha$  radiation in the  $2\theta = 4\text{--}30^\circ$  range. Luminescence spectra of the ligands and compounds were measured on FluoroMax-4 spectrofluorometer at room temperature.

### 2.2. Synthesis of $[\text{Ce}_2\text{L}_2(\text{DMF})_4]$ (**1**)

A solvothermal reaction of  $\text{H}_3\text{L}$  (30 mg, 0.05 mmol),  $\text{bpe}$  (18 mg, 0.1 mmol) and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (38.8 mg, 0.09 mmol) in 5 mL  $\text{DMF}/\text{EtOH}$  (3:2, V:V) was performed in a teflon-lined acid digestion

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bomb at 80 °C for 72 h, the mixture was then cooled to room temperature naturally. Colorless block crystals were collected by filtration with a yield of ca. 43% based on H<sub>3</sub>L. X-ray single structure analysis revealed that **1** does not constitute bpe. An alternate preparation of **1** was thus carried out in the absence of bpe and the same crystals were obtained. Anal. calcd for C<sub>78</sub>H<sub>82</sub>Ce<sub>2</sub>N<sub>4</sub>O<sub>22</sub>: C, 54.86%, H, 4.84%, N, 3.28%; found C, 54.82%, H, 4.87%, N, 3.25%. IR (KBr, cm<sup>-1</sup>): 3414(m), 3069(w), 2928(s), 2535(w), 2362(m), 1670(s), 1608 (s), 1537(m), 1411(s), 1301(m), 1239(s), 1176(s), 1105(s), 1034(w), 995(s), 861(s), 791(s), 704(m), 649(s), 555(w), 413(m).

### 2.3. Synthesis of [Ni<sub>3</sub>(HL<sup>2-</sup>)<sub>4</sub>(bpe)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>][H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(DMF)<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub> (**2**)

A solvothermal reaction of H<sub>3</sub>L (30 mg, 0.05 mmol), bpe (18 mg, 0.1 mmol) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (24 mg, 0.1 mmol) in 6 mL DMF/H<sub>2</sub>O (4:2 vol ratio) was performed in a teflon-lined acid digestion bomb at 80 °C for 72 h, the mixture was then cooled to room temperature naturally. Green strip crystals were collected by filtration with a yield of ca. 48% based on H<sub>3</sub>L. For **2**, no crystals were obtained in the absence of bpe under the same synthetic conditions. Anal. calcd. (%) for C<sub>190</sub>H<sub>224</sub>N<sub>14</sub>Ni<sub>3</sub>O<sub>54</sub>: C, 60.47; H: 5.98; N: 5.19; Found (%): C, 60.38; H, 6.00; N, 5.24. IR (KBr pellet, cm<sup>-1</sup>): 2930(s), 1655(s), 1605(s), 1541(w), 1500(w), 1386(s), 1295(w), 1230(s), 1168(s), 1098(m), 1027(w), 985(s), 857(m), 830(m), 787(s), 647(m), 604(m), 555(s), 506(w), 414(w).

### 2.4. Crystal structure determination

Perfect single crystals of **1** and **2** with suitable dimensions were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at Bruker Apex Smart CCD diffractometer with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and the  $\varphi$ - $\omega$  scan mode. Data reductions and absorption corrections were performed using the SAINT and SADABS programs [20], respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on  $F^2$  using the SHELXL-97 program [21]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The structure was solved by direct methods. The solvent molecules in compound **2** are highly disordered and removed using the SQUEEZE subroutine of the PLATON software. The resulting new files were further refined. Elemental analyses and TGA data reveal that the chemical formula in compound **2** contains six DMF, two [H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations and eight water molecules. Crystal data, collection and refinements data of **1** and **2** are summarized in Table 1.

## 3. Results and discussion

### 3.1. Crystal structure of compound **1**

Single crystal X-ray diffraction studies reveal that both **1** and **2** crystallize in triclinic space group  $P\bar{1}$  (No. 2). In **1**, there are one Ce(III) atom, one L<sup>3-</sup>, and two coordinated DMF molecules in the asymmetric unit. Ce atom is coordinated by nine O atoms to form a polyhedron, seven from five carbonates and two from disordered DMF molecules. The Ce–O bond lengths are from 2.444(3) to 2.853(4) Å, within the range of those usually encountered for lanthanide oxygen coordinations [22]. The two neighboring Ce atoms are connected together by four carboxylate groups and two  $\mu_3$ -O bridging atoms to generate a dinuclear [Ce<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>] unit (Fig. 1a, left). Each Ce atom in the dinuclear unit is further

**Table 1**  
Crystal data and structure refinements for compounds **1** and **2**.

Complex	1	2
Formula	C <sub>78</sub> H <sub>82</sub> Ce <sub>2</sub> N <sub>4</sub> O <sub>22</sub>	C <sub>168</sub> H <sub>150</sub> N <sub>6</sub> Ni <sub>3</sub> O <sub>40</sub>
Formula weight	1707.72	3069.07
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> /Å	13.2824(13)	13.709(4)
<i>b</i> /Å	13.9595(14)	17.722(5)
<i>c</i> /Å	16.4130(16)	23.810(6)
$\alpha$	78.475(2)	70.746(4)
$\beta$	74.453(2)	77.493(4)
$\gamma$	88.400(4)	88.400(4)
<i>Z</i>	1	1
<i>V</i> /Å <sup>3</sup>	2871.1(5)	5326(3)
<i>T</i> /K	296(2)	293(2)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	0.988	0.957
<i>F</i> (000)	870	1604
$\mu$ /mm <sup>-1</sup>	0.834	0.322
Total reflections	13138	18475
Unique reflections	10230	11430
<i>R</i> <sub>int</sub>	0.0332	0.0538
GOF on <i>F</i> <sup>2</sup>	1.025	1.004
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0556/0.1609	0.0988/0.2755
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0702/0.1730	0.1253/0.2950

connected by two terminal DMF and one bridging carboxylate via a chelating mode to form an extended network. The L<sup>3-</sup> ligand is in a slightly distorted trigonal coordination geometry, coordinated to five Ce atoms from three dinuclear units via its three carboxylates. The three outer benzoate rings around the central benzene ring in L<sup>3-</sup> adopt *cis*-, *trans*-, *trans*-conformations with two on one side of the center benzene plane and the third on the other side (Fig. 1a, right). The angles between three benzoate arms range from 101.188(44)° to 147.571(49)°.

In **1**, each dinuclear Ce cluster is connected to six carboxylates from six L<sup>3-</sup> while each L<sup>3-</sup> ligand is connected to three dinuclear Ce clusters. This leads to a 3,6-connected square 2D double layer, with the thickness of the single layer about the distance of the dinuclear Ce atoms. The 2D layer is stacked over each other along the (1–11) direction (Fig. 1b). There are weak  $\pi$ - $\pi$  interactions between the central benzene rings in the neighboring layers (Fig. 1c). The centroid-centroid distance is 4.8 Å and the plane-plane angle of 2.0(5)° [23]. As a result, the whole framework of **1** is a van der Waals network constructed from multiple 3,6-connected via  $\pi$ - $\pi$  interactions. As depicted in Fig. 1d, there are round and square pores as viewed along the *a* axis. PLATON calculations indicate that the total solvent-accessible void (1037.01 Å<sup>3</sup> per unit cell) possesses approximately 36.1% of the crystal volume [24].

### 3.2. Crystal structure of compound **2**

The asymmetric unit of **2** consists of one and a half Ni atoms (the occupancies of Ni1, Ni2 are 0.5 and 1 respectively), two HL<sup>2-</sup> ions, one and a half bpe ligands and two coordinated H<sub>2</sub>O molecules. The whole framework is negatively charged, balanced by disordered [H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations located within the channels, which were determined by elemental analyses and TGA data. The Ni1 atom is in an octahedral geometry coordinated by two O atoms from benzoates, two O atoms from H<sub>2</sub>O and two N atoms from pyridine rings. The Ni2 atom is also in an octahedral geometry, coordinated by three O atoms from benzoates, one O atom from H<sub>2</sub>O and two N atoms from pyridine rings. The Ni–O and Ni–N distances are ranging from 2.033(2) Å to 2.147(3) Å. Each Ni1 atom is connected through two N atoms of bpe ligands in the opposite direction to form a straight chain along the *a* axis

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