



# Crystal structures and gas adsorption behavior of new lanthanide-benzene-1,4-dicarboxylate frameworks



Kitt Panyarat<sup>a, b</sup>, Sireenart Surinwong<sup>c</sup>, Timothy J. Prior<sup>d</sup>, Takumi Konno<sup>c</sup>, Apinpus Rujiwatra<sup>a, \*</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200 Thailand

<sup>b</sup> Graduate School, Chiang Mai University, Chiang Mai 50200, Thailand

<sup>c</sup> Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

<sup>d</sup> Chemistry, The University of Hull, Cottingham Road, Hull HU6 7RX, UK

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## ABSTRACT

Six new lanthanide metal organic complexes, i.e.  $[\text{La}_2(\text{NO}_2\text{-BDC})_3(\text{H}_2\text{O})_4]$  (**1**)  $[\text{Ln}(\text{L})_{0.5}(\text{NO}_2\text{-BDC})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$  (Ln = Eu (**2**), Tb (**3**), Dy (**4**) and Ho (**5**); L =  $\text{BDC}^{2-}$  or  $\text{BDC}^{2-}/\text{NO}_2\text{-BDC}^{2-}$ ) and  $[\text{Tm}(\text{NO}_2\text{-BDC})_{1.5}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  (**6**), have been synthesized using mixed ligands of benzene-1,4-dicarboxylic acid ( $\text{H}_2\text{BDC}$ ) and the *in situ* generated 2-nitro-benzene-1,4-dicarboxylic acid ( $\text{NO}_2\text{-BDC}^{2-}$ ). Single crystal structures and topologies of the complexes are presented based on the single crystal X-ray diffraction and spectroscopic data. Whilst the structures of **1** and **6** contain negligible voids, the frameworks of **2–5** are microporous in nature and stable upon the removal of all the water molecules from the structures and thermal treatment to over 400 °C. Based on the study of **2**, significant adsorption capacities for carbon dioxide ( $95 \text{ cm}^3 \cdot \text{g}^{-1}$  or  $4.2 \text{ mmol} \cdot \text{g}^{-1}$ ) and hydrogen ( $79 \text{ cm}^3 \cdot \text{g}^{-1}$  or  $4 \text{ mmol} \cdot \text{g}^{-1}$ ), as well as the remarkable stability of the framework upon the sorption/desorption experiments are revealed.

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## 1. Introduction

Environmental impact caused by the emission of greenhouse gases has become a major global concern which therefore demands technologies to control the emission of such gases especially carbon dioxide which is reported to be the primary culprit for the rising of global temperature [1,2]. Despite extensive research on the capture of carbon dioxide in the last two decades, none of the existing technologies have fulfilled the target performance criteria; for example, large capture capacity, high selectivity, optimal affinity and high stability under capture and regeneration conditions [3–5]. Among the capturing techniques under investigation at the present, solid sorbent materials and metal organic frameworks (MOFs) draw an immense interest as the most promising candidates. This is due to their unprecedentedly high active surface area, remarkably large void volume, structural and chemical robustness, and potential to be tailor-made, up-scaled and made into membranes [4,6–8]. Since the

first report of  $[\text{Zn}(\text{BDC})] \cdot (\text{DMF})(\text{H}_2\text{O})$  (BDC = benzene-1,4-dicarboxylate and DMF = N,N'-dimethylformamide) with promising carbon dioxide capture capacity [9], several series of new MOFs with encouraging performance have been reported. Strategies to enhance the capture capacities and selectivity such as the generation of unsaturated or open metal sites, the fabrication of flexible interpenetrating frameworks, and the installation of desired functionalities on the organic linkers have been proposed [4,10,11]. Regarding the open metal sites, lanthanide metal ions are deemed to be judicious choices as they tend to include small solvent molecules in their coordination sphere which can be removed to generate open metal sites without framework disruption. In addition, there is a tendency for lanthanide metal ions to provide robust frameworks of high dimensionality with adjustable pore characteristics. The study of lanthanide MOFs for carbon dioxide capture has thus far been limited with only few examples reported;  $\text{Tb}_2(\text{BDC})_3$  [12],  $\text{Tb}(\text{BDC})\text{NO}_3$  [13] and  $[\text{Ln}_2(\text{TPO})_2(\text{HCOO})] \cdot (\text{Me}_2\text{NH}_2) \cdot (\text{DMF})_4 \cdot (\text{H}_2\text{O})_6$  (Ln = Y and Eu,  $\text{H}_3\text{TPO}$  = tris-(4-carboxylphenyl)phosphineoxide, DMF = N,N'-dimethylformamide) [14].

Here, a series of six new lanthanide MOFs have been designed and synthesized using  $\text{NO}_2\text{-BDC}^{2-}$  and  $\text{BDC}^{2-}$  as the primary

\* Corresponding author.

E-mail address: [apinpus.rujiwatra@cmu.ac.th](mailto:apinpus.rujiwatra@cmu.ac.th) (A. Rujiwatra).

linkers because of its tendency to generate microporous frameworks which was reported to be suitable for carbon dioxide capture [9,15]. *In situ* nitration was employed to introduce the nitro group to BDC<sup>2-</sup> and therefore to generate the multivariate frameworks comprising both BDC<sup>2-</sup> and NO<sub>2</sub>-BDC<sup>2-</sup> linkers. The inclusion of the nitro group was intended to increase the interaction of the framework and carbon dioxide [16]. Four of the six reported complexes are microporous with accessible voids, extraordinary stability and significant gas capture capacities. The photoluminescence properties of the complexes have also been investigated.

## 2. Experimental

### 2.1. Materials and methods

All chemicals were obtained commercially and used without further purification; La<sub>2</sub>O<sub>3</sub> (99.9%, Merck), Eu<sub>2</sub>O<sub>3</sub> (99.9%, Merck), Tb<sub>2</sub>O<sub>3</sub> (99.9%, Merck), Dy<sub>2</sub>O<sub>3</sub> (99.9%, Fluka), Ho<sub>2</sub>O<sub>3</sub> (99%, Prolabo), Er<sub>2</sub>O<sub>3</sub> (99%, Fluka), Tm<sub>2</sub>O<sub>3</sub> (99%, Merck), HNO<sub>3</sub> (>90%, Sigma-Aldrich), benzene-1,4-dicarboxylic acid (H<sub>2</sub>BDC; C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>, 97%, BDH), and 1,4-diazabicyclo [2.2.2]octane (DABCO; C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>, 98%, Sigma-Aldrich).

Infrared (IR) spectra were recorded using a Bruker Tensor 27 FT-IR instrument and KBr discs (98.5%, BDH). Thermogravimetric analyses were conducted on a Perkin Elmer Pyris Diamond TG/DTA using a heating rate of 10 °C·min<sup>-1</sup> from room temperature to 1000 °C in a nitrogen gas flow. Powder X-ray diffraction (PXRD) experiments were conducted using a Bruker D8 Advance X-ray diffractometer operated with Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å, 48 kV, 30 mA). The gas sorption experiments were performed using a BELSORP-mini II instrument in a range of 0–1 bar pressures. Ultra-pure research grade nitrogen, hydrogen and carbon dioxide gases were used. The samples were heated at 250 °C for 2 h under vacuum before the measurements which were performed at 77 K for the nitrogen and hydrogen and at 195 K for the carbon dioxide. Photoluminescence spectra were collected at room temperature using an Avantes Multichannel

spectrometer with the Ocean Optics LED 255 nm excitation source.

### 2.2. Hydrothermal syntheses of 1–6

To synthesize [La<sub>2</sub>(NO<sub>2</sub>-BDC)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>] (1) [Ln(L)<sub>0.5</sub>(NO<sub>2</sub>-BDC)(H<sub>2</sub>O)]·3H<sub>2</sub>O {Ln = Eu (2), Tb (3), Dy (4) and Ho (5); L = BDC<sup>2-</sup> or BDC<sup>2-</sup>/NO<sub>2</sub>-BDC<sup>2-</sup>} and [Tm(NO<sub>2</sub>-BDC)<sub>1.5</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O (6), the solution of the corresponding Ln<sub>2</sub>O<sub>3</sub> was first prepared by dissolving the Ln<sub>2</sub>O<sub>3</sub> (1.70 mmol) in 1.00 mL of concentrated HNO<sub>3</sub> aqueous solution. Each solution was then mixed with 10.0 mL of an aqueous solution containing H<sub>2</sub>BDC (4.0 mmol) and DABCO (4.0 mmol) with vigorous stirring. The Ln<sub>2</sub>O<sub>3</sub>: HNO<sub>3</sub>: H<sub>2</sub>BDC: DABCO: H<sub>2</sub>O mole ratio of every reaction was 1.70: 5.16: 4.00: 4.00: 556. The reactions were performed using a 23.0 mL Teflon lined hydrothermal autoclave under an autogenous pressure generated at 180 °C for 24 h, and afforded a few crystals as the solid products.

### 2.3. X-ray crystallography

Diffraction data of 1 and 6 were collected on a Bruker APEX-II CCD diffractometer and a Stoe IPDS2 image plate diffractometer, respectively, whereas those of 2–5 were collected on a Bruker D8 QUEST CMOS diffractometer. The machines were operated using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298 (2) K for 1–5 and 150 (2) K for 6. Data reduction and an adsorption correction of 1–5 were performed with the SAINT [17] and SADABS [18] software packages, whilst that of 6 was done using the Tompa method [19]. The structures were solved by direct methods implemented within SHELXS-86 [20] and full-matrix least squares refinements were carried out on F<sup>2</sup> for all data with the program SHELXL-97 [20] via either the WinGX [21] or the OLEX2 [22] program interfaces. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms on the organic ligands were located at ideal geometrical positions using a riding model. No hydrogen atoms were assigned on the unbound water molecules. Crystallographic and refinement data are summarized in Table 1.

**Table 1**  
Crystallographic data and structure refinement summary of 1–6.

	1	2	3	4	5	6
CCDC	1517770	1517767	1517771	1517766	1517768	1517769
Chemical formula	La <sub>2</sub> C <sub>24</sub> H <sub>14</sub> N <sub>3</sub> O <sub>22</sub>	EuC <sub>12</sub> H <sub>4.69</sub> N <sub>1.31</sub> O <sub>12.62</sub>	TbC <sub>12</sub> H <sub>4.68</sub> N <sub>1.32</sub> O <sub>12.64</sub>	DyC <sub>12</sub> H <sub>5</sub> NO <sub>12</sub>	HoC <sub>12</sub> H <sub>7</sub> NO <sub>12</sub>	TmC <sub>12</sub> H <sub>4</sub> N <sub>1.5</sub> O <sub>11</sub>
Formula weight	974.20	521.09	528.50	517.67	520.10	514.10
Temperature/K	293 (2)	273.15	273.15	273.15	273.15	150 (2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> /Å	9.7849 (5)	6.8849 (2)	6.8451 (9)	21.6689 (3)	6.7919 (3)	16.5383 (13)
<i>b</i> /Å	10.9160 (6)	21.8286 (7)	21.731 (3)	22.8825 (10)	21.6514 (11)	11.2800 (13)
<i>c</i> /Å	15.6249 (8)	23.0388 (7)	22.936 (3)	6.8125 (11)	22.8375 (10)	15.2694 (15)
$\alpha$ /°	82.299 (2)	90	90	90	90	90
$\beta$ /°	77.197 (2)	90	90	90	90	90.350 (7)
$\gamma$ /°	63.398 (2)	90	90	90	90	90
Volume/Å <sup>3</sup>	1453.99 (13)	3462.45 (18)	3411.7 (9)	3377.9 (6)	3358.3 (3)	2848.5 (5)
<i>Z</i>	2	8	8	8	8	8
$\rho_{\text{calc}}$ /mg/mm <sup>3</sup>	2.225	1.999	2.058	2.036	2.057	2.398
$\mu$ /mm <sup>-1</sup>	3.001	3.685	4.215	4.488	4.777	6.299
<i>F</i> (000)	917.0	1998.0	2016.0	1968.0	1976.0	1948.0
Crystal size/mm <sup>3</sup>	0.08 × 0.06 × 0.05	0.18 × 0.14 × 0.12	0.2 × 0.16 × 0.14	0.4 × 0.2 × 0.2	0.4 × 0.2 × 0.2	0.45 × 0.42 × 0.25
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )
Data/restraints/parameters	9378/7/450	4295/1/244	4780/1/244	5906/0/232	4174/0/232	3127/1/258
Goodness-of-fit	1.087	1.089	1.159	1.120	1.130	0.913
<i>R</i> ( <i>F</i> <sup>2</sup> ), <i>R</i> <sub>w</sub> [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	0.0398, 0.1040	0.0389, 0.0913	0.0377, 0.0882	0.0445, 0.1090	0.0519, 0.1209	0.0254, 0.0577
<i>R</i> ( <i>F</i> <sup>2</sup> ), <i>R</i> <sub>w</sub> (all data)	0.0540, 0.1137	0.0519, 0.0969	0.0438, 0.0908	0.0561, 0.1143	0.0626, 0.1263	0.0355, 0.0589

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