

## An Open Neodymium–Organic Framework with the NbO Structure Type Based on Binuclear SBU Involved In Situ Generated Formate

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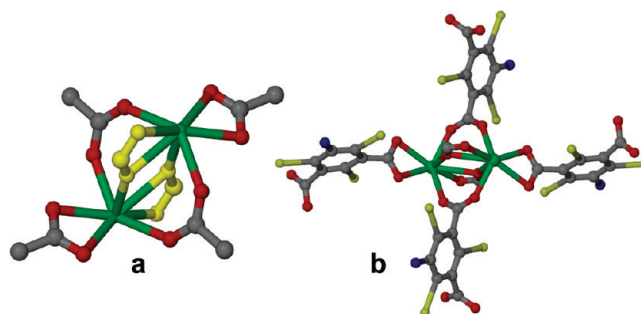
**ABSTRACT:** The solvothermal reaction of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 5-amino-2,4,6-triiodoisophthalic acid ( $\text{H}_2\text{atiip}$ ) in DMF/ethonal/ $\text{H}_2\text{O}$  (5:2:1) in the presence of pyridine gave rise to a new open neodymium–organic framework having the NbO structure type,  $[\text{Nd}(\text{HCOO})(\text{atiip})(\text{DMF})_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**1**). Complex **1** can keep its diffraction pattern even after being heated to 200 °C.

The rational design and synthesis of open metal–organic frameworks (MOFs) received a great deal of attention due to their fascinating structures and intriguing potentials in applications such as in catalysis, separation and gas storage, etc.<sup>1–3</sup> Almost all of the applications are highly determined by the framework stability of the open MOFs. In the past decades, many open MOFs with high stability and porosity have been synthesized and reported.<sup>4</sup> However, most of them are based on transition metal ions, and it is still a great challenge to construct open lanthanide–organic frameworks with high stability.<sup>5</sup>

It is known that lanthanide ions have high affinity for oxygen donor atoms and possess high coordination numbers.<sup>6</sup> In the reported lanthanide–organic frameworks, most of the remaining coordination sites of the lanthanide ions are occupied by coordinated solvates such as  $\text{H}_2\text{O}$ , DMF, etc.<sup>6,7</sup> The coordinated small solvates are easy to be removed from the lanthanide ions, resulting in the formation of unstable low-coordination lanthanide ions and further causing the collapse of the whole framework. Thus, how to decrease the coordinated solvates on the lanthanide ions is the key to construct open lanthanide–organic frameworks with high thermal stability. Recently, the knowledge of the application of in situ generated rigid secondary building unit (SBUs) in the construction of open MOFs has offered an efficient solution for improving the stability of the final framework, especially for lanthanide–organic frameworks. Many lanthanide–organic frameworks based on multinuclear or infinite SBUs with high stability have been constructed. In this communication, we report a new open neodymium–organic framework,  $[\text{Nd}(\text{HCOO})(\text{atiip})(\text{DMF})_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**1**) ( $\text{H}_2\text{atiip}$  = 5-amino-2,4,6-triiodoisophthalic acid), in which the NbO structure type based on binuclear SBU involved *in situ* generated formate.

Solvothermal reaction<sup>8</sup> of  $\text{H}_2\text{atiip}$  and  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in DMF/ethonal/ $\text{H}_2\text{O}$  (5:2:1) in the presence of pyridine resulted in the formation of prismatic crystals of **1**, which was structurally characterized by single-crystal X-ray diffraction.<sup>9</sup> The formula of  $[\text{Nd}(\text{HCOO})(\text{atiip})(\text{DMF})_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  was further confirmed by elemental analysis and TGA.

Single-crystal X-ray diffraction reveals that **1** crystallizes in the rhombohedral  $R\bar{3}$  space group and possesses a three-dimensional open neodymium–organic framework based on a binuclear SBU. The asymmetric unit of **1** consists of one neodymium ion, one *atiip* ligand, one formate group, two coordinated DMF molecules, one uncoordinated DMF molecule, and one uncoordinated water molecule. The neodymium ion is nine-coordinated by four oxygen atoms from three *atiip* ligands, three oxygen atoms from two formate ligands, and two coordinated DMF



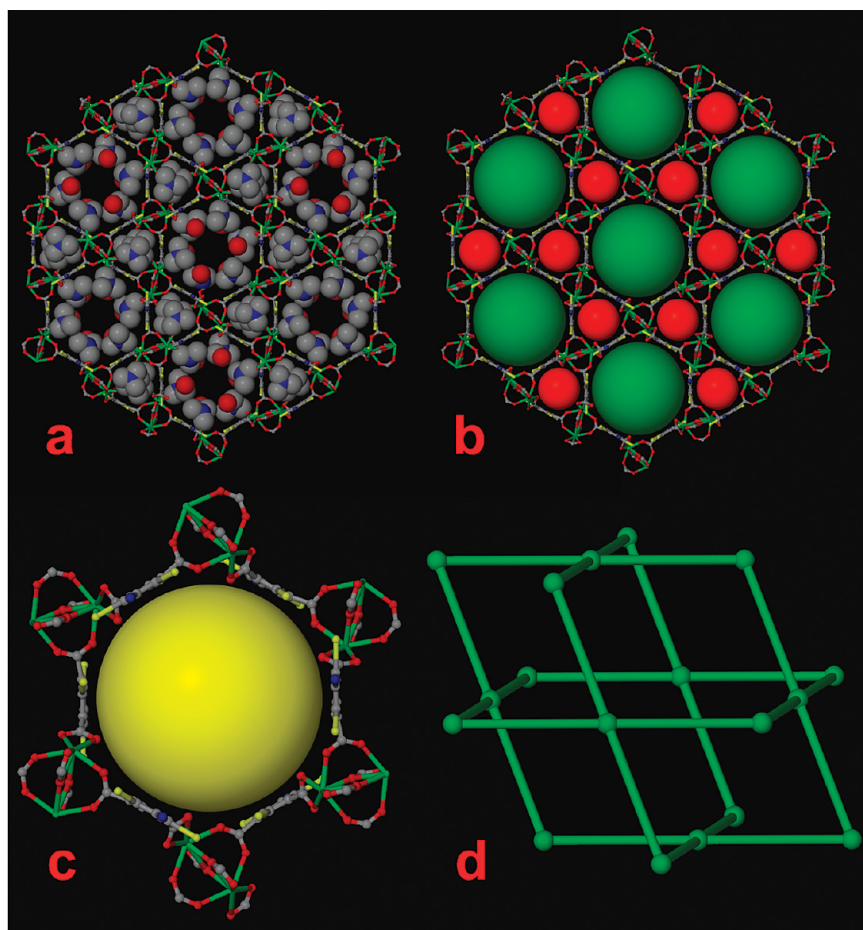
**Figure 1.** (a) The binuclear SBU linked by two formate (yellow color) and two carboxylate groups; (b) the rigid SBU was connected by four *atiip* ligands as a 4-connected node.

molecules, with the average Nd–O distance of 2.510(5) Å. The formate group comes from the hydrolysis of a DMF molecule, which has been widely reported in the literature.<sup>10</sup>

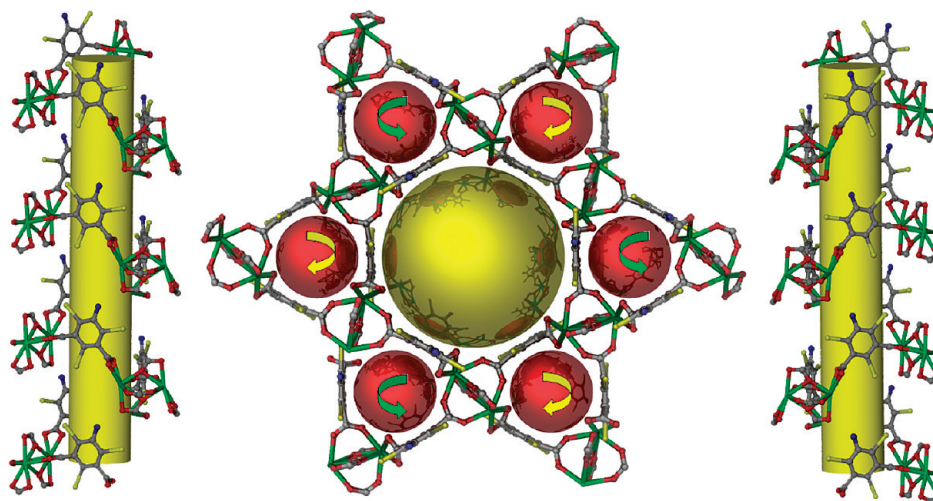
Thus, two neodymium ions are connected by two formate and two carboxylate groups of *atiip* ligands to generate a binuclear SBU (Figure 1a). Each neodymium ion in the SBU is further chelated by one carboxylate group of an *atiip* ligand, and the remaining coordination sites are occupied by coordinated DMF molecules. As found in our previous work,<sup>11</sup> the *atiip* ligand is nonplanar, with the average dihedral angle between the carboxylate groups and the central benzene ring of 87.8°. Both carboxylate groups of *atiip* are deprotonated during the reaction, but each one adopts different coordination modes: one adopts a bidentate bridging mode to connect two neodymium ions in one binuclear SBU, while the other one adopts a chelating mode to link one neodymium ion in another SBU. Thus, every *atiip* ligand connects two binuclear SBUs, and each binuclear SBU attaches to four *atiip* ligands (Figure 1b) to give rise to a three-dimensional open framework containing hexagonal and trigonal channels along the *c* axis (Figure 2a and b), with 54.2% solvent-accessible volume calculated from PLATON. The dimensions of the large hexagonal channel (Figure 2c) are 15.9 Å × 15.9 Å, in which the coordinated DMF and uncoordinated water molecules reside, while the dimensions of the small trigonal channel are 6.3 Å × 6.3 Å, in which only the coordinated DMF molecules reside.

As mentioned above, the binuclear SBU is connected by four *atiip* ligands and can be considered as a square planar 4-connected node. If the bridging ligand of *atiip* can be considered as a linear linker, then the resulting topology of **1** is a NbO structure type (Figure 2d). The Schläfli notation is (6<sup>4</sup>.8<sup>2</sup>) for the Nd<sub>2</sub> node, giving the net the symbol [6(2).6(2).6(2).6(2).8(2).8(2)]. In the past decades, many metal–organic frameworks with the NbO structure type have been synthesized and reported,<sup>12</sup> and most of them

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**Figure 2.** (a) The 3D open framework of **1** with coordinated DMF molecules shown as space-filling; (b) the 3D framework after omitting the coordinated DMF molecules, showing the trigonal and hexagonal channels; (c) highlighting representation of the large hexagonal pore; and (d) the NbO structure type of **1**.



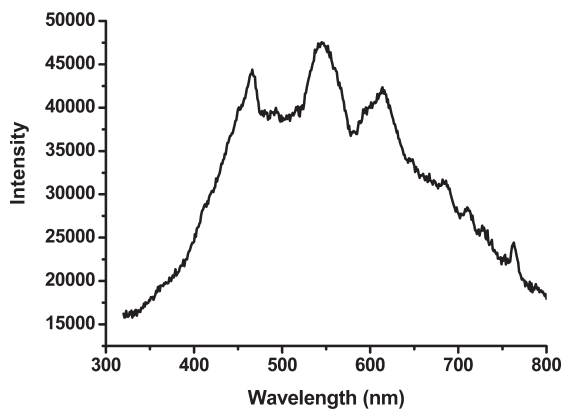
**Figure 3.** Left, the 1D left-handed  $3_1$  helical chain; middle, the large hexagonal channel surrounded by six small trigonal channels that possess left- or right-handed chirality; right, the 1D right-handed  $3_1$  helical chain.

are based on transition metal ions; however, lanthanide–organic frameworks possessing NbO structure type are quite rare.

In the 3D open framework, each trigonal channel is surrounded by three hexagonal channels and each hexagonal channel is surrounded by six trigonal channels. Thus, complex **1** can be considered as formed by infinitely sharing trigonal and hexagonal channels. Indeed, the trigonal channel is made up of a one-dimensional  $3_1$  left- or right-handed helical chain, which is formed

by atip ligands connecting binuclear SBUs, as shown in Figure 3. In the six trigonal channels, there are three left-handed helical chains and three right-handed chains and the left- and right-handed helical chains are alternative (Figure 3, middle). Due to the equality of the left- and right-handed helical chains, the whole structure is achiral.

TGA measurement revealed that **1** can be stable up to 330 °C. The first gradual weight loss of 9.5% from 50 to 240 °C



**Figure 4.** Solid-state emission spectra of compound **1**.

corresponds to the loss of one uncoordinated water molecule and one uncoordinated DMF molecule (calcd: 9.3%). The second rapid weight loss of 12.5% from 240 to 266 °C is in accordance with the loss of two coordinated DMF molecules (calcd: 14.8%). There is no further weight loss before complex **1** starts to decompose at 330 °C.

It should be pointed out that complex **1** can keep its diffraction pattern at high temperature. The as-synthesized crystals of **1** were heated at 100, 160, and 200 °C in air for half an hour; single crystal X-ray diffraction on these crystals reveals that there are no changes for the backbone of the framework except that the bond lengths and angles are slightly changed. The careful refinement of the crystal data can give a good *R* value (< 0.10), indicating the crystal lattice can remain unchanged upon heating at high temperature. However, when the crystals were heated to 250 °C, where all the coordinated DMF molecules were lost, the X-ray diffraction pattern of **1** disappeared partly. In the previous reported 3D open frameworks, most of them lost the diffraction pattern upon exposing the crystals to air,<sup>13</sup> especially for the open lanthanide–organic framework. Examples such as **1**, for which the diffraction pattern remains upon heating to high temperature in open MOFs containing large channels, are quite rare.<sup>11,14</sup> Unfortunately, attempts to measure the gas sorption isotherms for the evacuated form of complex **1** failed, which may derive from the negative effect of halogen atoms from ligand<sup>15</sup> or from the generation of detrimental shear forces within the binuclear units when the sample was evacuated.<sup>12b</sup>

Taking into account that the luminescent properties of lanthanide complexes can give useful information regarding their structures,<sup>16</sup> the luminescence of **1** was investigated. Upon excitation at 240 nm, the luminescence of complex **1** consists of three bands at  $\lambda = 465, 544,$  and  $615$  nm (Figure 4), which can be assigned to the  $4F3/2 \rightarrow 4I9/2, 4F3/2 \rightarrow 4I11/2,$  and  $4F3/2 \rightarrow 4I13/2$  transitions, respectively. The strongest emission is observed at the middle band of 544 nm, and the emissions at 465 and 615 nm are weaker, which are in agreement with other reported results.<sup>17</sup>

In conclusion, a three-dimensional open neodymium–organic framework with the NbO structure type has been solvothermally synthesized. The participation of a formate group from the hydrolysis of DMF molecule plays an important role in the formation of the rigid SBU as well as the 3D open framework. Although many transition metal–organic frameworks containing *in situ* generated formate have been widely reported, the examples that the *in situ* generated formates directly coordinate to lanthanide ion to form rigid SBU are quite rare in open lanthanide–organic frameworks. Complex **1** can keep its diffraction pattern even after being heated to 200 °C, which is remarkable in open lanthanide–organic frameworks. Further studies will focus on the synthesis of lanthanide–organic frameworks with

permanent porosity by taking advantage of the hydrolysis of a DMF molecule to generate formate ion.

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**Supporting Information Available:** Description of the method used for crystal structure determination, table of crystallographic data, structural images of **1**, thermogravimetric analysis of **1**, and X-ray diffraction data for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) **Synthesis of 1:** A mixture of Nd(NO<sub>3</sub>)·6H<sub>2</sub>O (15 mg), H<sub>2</sub>atiip (10 mg, 0.02 mmol), and pyridine (1 drop) were dissolved in 10 mL of mixed solvents of DMF, EtOH, and H<sub>2</sub>O (v/v, 5:2:1) at room temperature. After the reaction mixture was stirred for half an hour at room temperature, the mixture was placed in a glass tube and

- heated at 90 °C for 4 days. Beautiful aubergine crystals suitable for X-ray analyses were collected from the walls of the tube (yield: 65%). Elemental analysis. Calcd (%) for **1**: C, 21.99; H, 2.66; N, 5.70. Found: C, 22.40; H, 2.85; N, 5.60%.
- (9) Crystallographic data for **1**:  $C_{15}H_{19}I_3N_3NdO_{8.5}$ ,  $M = 902.27$ , rhombohedral, space group  $R\bar{3}$ ,  $a = b = 36.405(3)$  Å,  $c = 11.6941(17)$  Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $U = 13422(2)$  Å<sup>3</sup>,  $Z = 9$ ,  $D_c = 2.009$  Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 4.883$  mm<sup>-1</sup>,  $T = 298$  K, 26293 reflections collected. Refinement of 6781 reflections (275 parameters) with  $I > 1.5\sigma(I)$  converged at final  $R1 = 0.0377$ ,  $wR2 = 0.1148$ ,  $\text{gof} = 1.057$ .
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