

**Supporting Information for:**

## **Construction of a Porous Three Dimensional Rare Earth Metal-Sulfur-Ligand Open Framework**

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## 1. Synthesis of Piperazine-1,4-dicarbodithiolate disodium

Piperazine-1,4-dicarbodithiolate disodium ( $\text{Na}_2\text{pipzdtc}$ ) was synthesized according to the literature procedure.<sup>[1]</sup> Typically, 1.0 g piperazine was dissolved in 5.0 mL methanol, and then 1.020 g NaOH was added. After being stirred at room temperature for 30 minutes, 1.68 mL carbon disulfide was dropwisely added to above reaction system. The reaction was allowed to proceed for 12 hours under ambient condition.  $\text{Na}_2\text{pipzdtc}$  was obtained as a white solid in 80% yield. The solid IR spectra are in agreement with reported data (Figure S1).

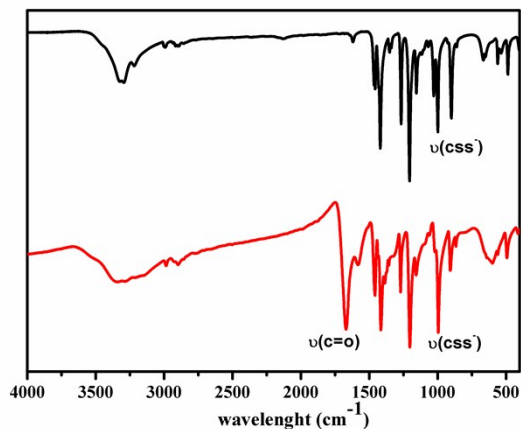
## 2. Characterization

### 2.1 X-ray Single-Crystal Structural Determinations

Single crystal X-ray diffraction data for compound **1** was collected on a Bruker APEX II CCD area detector diffractometer ( $\text{Mo K}\alpha$   $\lambda = 0.71073 \text{ \AA}$ ) at 120 K. The structure of **1** was solved by direct method and refined by full-matrix least-squares techniques using the *SHELXL-2013* programs.<sup>[2]</sup> Anisotropic thermal parameters were assigned to all atoms. It should be noted that the hydrogen atoms of all lattice water molecules in these complexes were not located by difference Fourier map. For disordered carbon atoms of the organic ligands, the hydrogen atoms were not added. In order to eliminate disordered solvent molecules in the framework, the SQUEEZE routine in the PLATON software package was applied.<sup>[3]</sup>

### 2.2 IR spectra of ligand and compound **1**

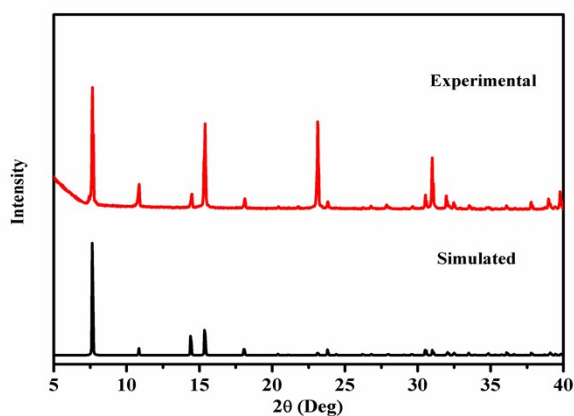
The solid IR spectra of both ligand and compound **1** are shown in Figure S1. The IR spectrum of ligand is in agreement with reported data. The solid IR spectrum exhibit characteristic peaks at 1409 and 997  $\text{cm}^{-1}$  in **1**, which are attributed to the  $\nu(\text{C-N})$  and  $\nu(\text{CSS}^-)$  from pipzdtc ligands. The presence of piperazine moiety is confirmed by the 1200  $\text{cm}^{-1}$  due to the ring vibrations.<sup>[4]</sup> The peaks at 1673  $\text{cm}^{-1}$  are attributed to  $\nu(\text{C=O})$  from formamide in compound **1**. Additionally, the bands in the region of 3000-3500  $\text{cm}^{-1}$  could be ascribed to the character peaks of water and  $\nu(\text{N-H})$ .



**Figure S1.** IR spectra of  $\text{Na}_2\text{pipzdtc}$  (black) and compound **1**(red).

### 2.3 Powder X-ray diffraction

Powder X-ray diffraction data was collected using a Bruker D8 Advance ( $\text{Cu } K_{\alpha 1}$  radiation,  $\lambda=1.5406 \text{ \AA}$ ).

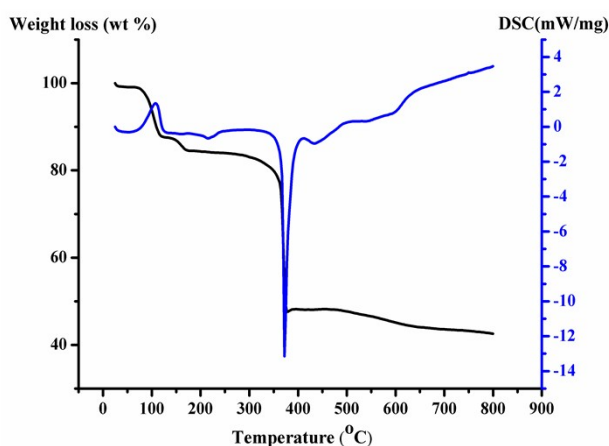


**Figure S2.** Experimental (red) and simulated (black) powder X-ray diffraction patterns for **1**.

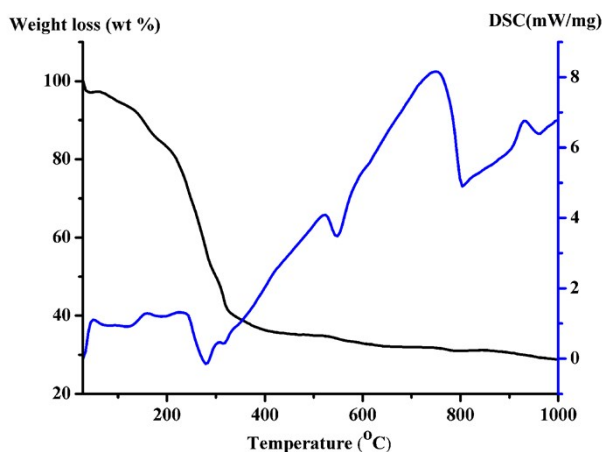
## 2.4 Thermogravimetric analysis

Thermogravimetric (TG) analysis was performed using a Netzsch STA 449 F3 instrument. According to the TG curves of Na<sub>2</sub>pipzdtc (Figure S3), there is about 15% weight loss assigned to partial decomposition of pipzdtc<sup>2-</sup> before 150 °C. So the Na<sub>2</sub>pipzdtc ligand is unstable under the thermal condition. Compound **1** was heated under air in the temperature range of 28–1000 °C at a heating rate of 10 °C min<sup>-1</sup> (Figure S4). The 71.2% weight loss of compound **1** from 28 °C to 1000 °C corresponds to the loss of guest molecules and organic ligands. Powder X-ray diffraction shows that the compound **1** was converted into Nd<sub>2</sub>O<sub>2</sub>(SO<sub>4</sub>) after calcination in air at 1000 °C (Figure S5). Additionally, inductively coupled plasma (ICP) analyses of Nd and elemental analyses of C, H, and N were measured on a Perkin-Elmer Optima 3300DV spectrometer and a Perkin-Elmer 2400 elemental analyzer, respectively. Calcd (%): C, 22.45; H, 3.83; N, 11.73; Found: C, 21.21; H, 3.77; N, 12.76.

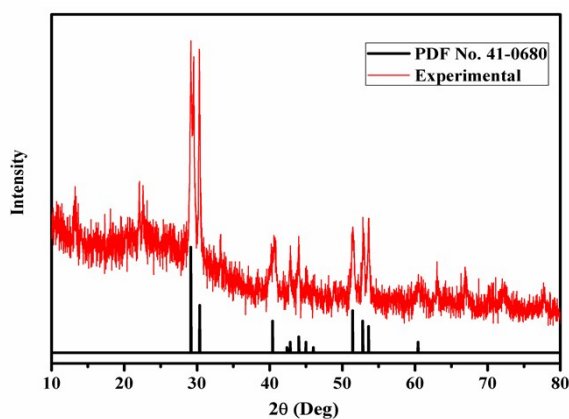
The guest molecules could be derived from the ICP, IR, TG, single crystal structure and elemental analysis. From single crystal analysis, the presence of Nd<sup>3+</sup> heavy metal cations in the channel is unlikely. We presumed that Na<sup>+</sup>, protonated formamide or water might reside in the channel to balance the charge of the framework as well as filling the void space. Firstly, the ICP-MS analysis revealed that there is no Na<sup>+</sup> in our compound. Secondly, the IR peak at 1673 cm<sup>-1</sup> is attributed to  $\nu(\text{C}=\text{O})$  from formamide in the channel. But in the main text, we already point out that our alkaline experimental condition does not favor the protonation of formamide, which could be usually oxygen-protonated under mild acidic condition. Therefore we can only assign protonated water to counteract the negative charge of the framework. The final formula was calculated from the TGA combined with elemental analysis data and gave 2 molecules of protonated water, 3 molecules of free water and 5 molecules of formamide per unit cell. The electron count of the formula (170 e) was different from the SQUEEZE (314 e).



**Figure S3.** TG and DSC curves of Na<sub>2</sub>pipzdtc.



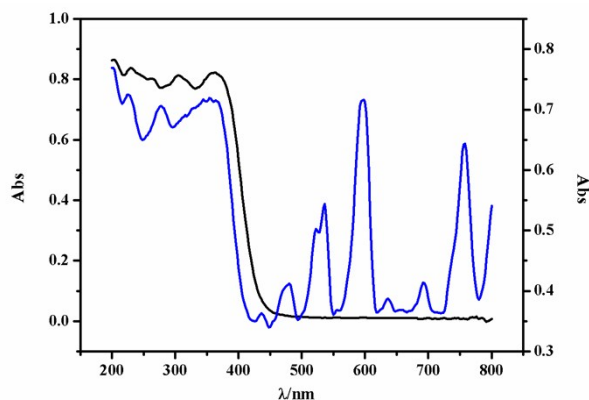
**Figure S4.** TG and DSC curves of compound **1**.



**Figure S5.** The powder diffraction patterns of the annealed sample.

## 2.5 UV-vis absorption spectra

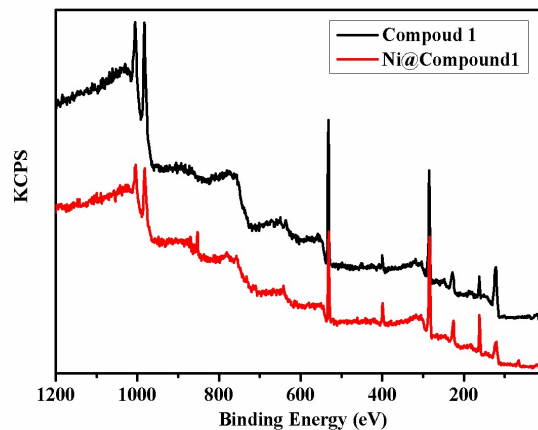
The UV-vis absorption spectra of the ligand and compound **1** are shown in Figure S6. They all exhibit the absorption bands due to the  $\text{pipzdtc}^{2-}$  with a maximum at 364 nm. The compound **1** also exhibits typical parity-forbidden narrow absorption bands from the  $^4I_{9/2}$  ground-state to various excited states of the  $\text{Nd}^{3+}$  ion.



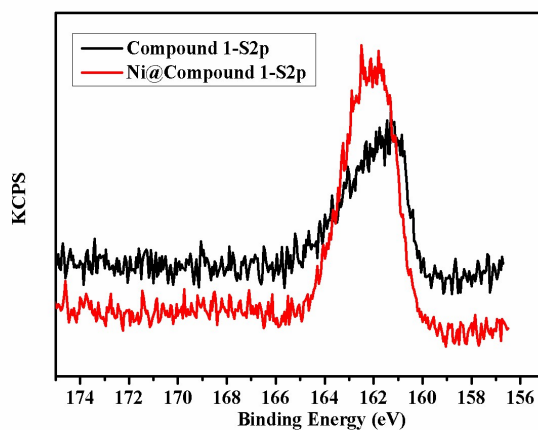
**Figure S6.** UV-vis spectra of the ligand (black) and compound **1** (blue).

## 2.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were taken on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K $\alpha$  X-ray radiation as the X-ray source for excitation.



**Figure S7.** XPS wide scan of compound **1** (black) and Ni<sup>2+</sup> exchanged **1** (red).



**Figure S8.** XPS spectra of compound **1** (black) and Ni<sup>2+</sup> exchanged **1** (red).



## 2.7 Cation exchange

We explored the incorporation in compound **1** of Ni<sup>2+</sup> cations with different concentration. Fresh crystals of **1** (0.2 g) were immersed at room temperature for 10 minutes in six methanol solutions containing 10<sup>-6</sup> M to 10<sup>-1</sup> M nickel salts, respectively. Then, we obtained a series samples after washing crystals several times with methanol, dried under the vacuum. The samples were subjected to PXRD characterization (Figure S9).

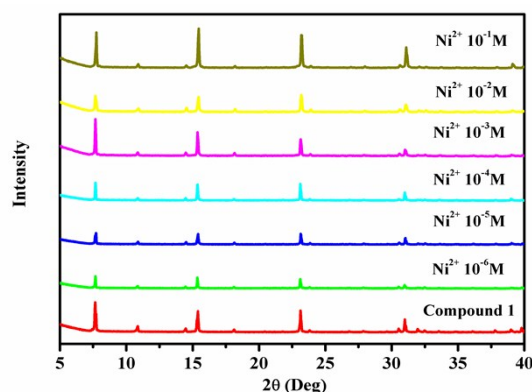


Figure S9. PXRD patterns of exchanged samples.

## 2.8 Stern–Volmer plots

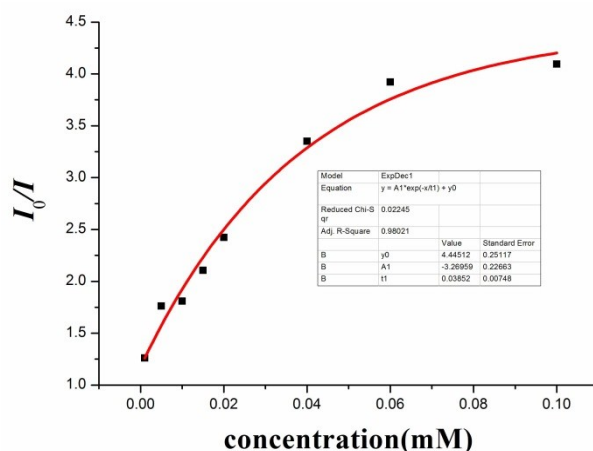


Figure S10. Stern–Volmer plots of  $I_0/I$  versus the Ni<sup>2+</sup> concentration in MeOH.

### Reference:

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3. A. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7
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