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

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A slow reaction between Nd³⁺ and piperazine-1,4-dicarbodithiolate disodium (Na₂(pipzdtc)) affords a three dimensional (3D) anionic $[Nd(pipzdtc)_2]_n^n$ framework with dia net. The encapsulated disordered guest molecules could be partially exchanged by Ni²⁺ accompanied with the quench of the typical NIR luminescence of Nd³⁺ ions.

In the past two decades, much attention has been paid on the synthesis, characterization and properties of metal-organic frameworks (MOFs) due to their intriguing structures and potential applications in heterogeneous catalysis, non-linear optics, magnetism, gas storage and so on.¹⁻³ Generally, MOFs are constructed from organic linkers based on oxygen or/and nitrogen donors and metal cations. The substitution of O or N atom by S atom can decrease the lowest unoccupied molecular orbital (LUMO) energy of the ligand and concurrently increase the highest occupied molecular orbital (HOMO) energy because S is less electronegative than oxygen or nitrogen.^{4,5}

Many sulfur-containing ligands such as terephthalic acid (BDC) laced by thiol or thioether groups, tetrathiafulvalenetetrabenzoate (H₄TTFTB) and thiol-containing heterocycles, have been utilized toward this target.⁶ For the former two ligands, their sulphur atoms might not be involved into the final complexation but it did enhance the uptake of noble metal cations by MOFs^{6a,6b} with pendant sulphur atoms or increase the charge mobility through S···S interactions in TTFTB-based MOFs^{6c}. In other cases, the sulphur atom can participate as an auxiliary coordinating atom of O or N atom. ^{6d-6f} Besides these ligands, thiolate and 1,1-dithiolate families have been also pursed to prepare metal coordination polymers, in which the majority are oligomers, onedimensional and two-dimensional structures.^{5c,8-13} Recently, Vaid et al. reported two 3D metal-thiolate frameworks from the reactions between metal acetates and arenepolythiols in refluxing ethylenediamine (en). In one case, a 2D anionic square grid of $[Cd(SC_6H_4S)_2]^{2-}$ accommodating $Cd(en)_3^{2+}$ was converted into a 3D distorted cubic network after exchanging the Cd(en)₃²⁺ with $N(CH_3)_4^+$.^{7a} In another case, the reaction between Pb(AC)₂ and benzene-dithiol, -trathiol or -hexathiol vielded three 3D frameworks, but with marginal porosity.^{7b} The scarcity in constructing 3D structures by these rigid thiolate linkers could be ascribed to their limited metal-S coordination mode. Conversely, 1,1-dithiolate family (dithiocarbamates (dtc), dithiocarboxylates, and xanthates) has afforded much more OD complexes and 1D or 2D coordination polymers when combined with metal cations because the resonance between the two S atoms gives rise to a variety of binding modes.¹⁴⁻¹⁶ So far, the construction of metal-sulfur-ligand MOFs, in which the metal cation connects solely with sulfur donor from the ligand, has been far less investigated.⁷ The only known 3D network, to the best of our knowledge, in which metal-dtc coordination was involved, was exemplified by bridging 1D Cu(I)-Br chains with mononuclear copper(II) units of $Cull(Pyr-dtc)_2$ (Pyr-dtc = pyrrolidine dithiocarbamate).^{5b}

Metal dithiocarbamate complexes have been extensively studied in recent years because of their wide applications in medicine and agriculture industries.¹⁷ Macrocyclic molecules based on the coordination of transition metals by bisdithiocarbamates show unique structures and significant potential in binging charged guest species.¹⁸ Recently, the dithiocarbamate ligands have been also deployed to stabilize noble metal nanoparticles as well as prepare alloyed nanowires and arrays.¹⁹ Inspired by the eight coordination mode of dtc in 0D lanthanide-dtc clusters, e.g. $Ce(\kappa^2-S_2-CNEt_2)_4$,²⁰ and the wide use of robust terephthalate dianions as bridging ligands in constructing MOFs, we chose bis-dithiocarbamate ligand as the organic linker, Nd³⁺ cation as the inorganic motif, to construct a novel Nd-S MOF. This work demonstrates the feasibility of the preparation of metal-S-

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Fig. 1 (a) Two $\operatorname{Nd}^{\operatorname{3+}}$ ions are connected by one disordered $\operatorname{pipzdtc}^{\operatorname{2-}}$ ligand through bidentate chelating S atoms. The pipzdtc2- molecule crosses the mirror (green plane) with ten disordered atoms, only two S(2) atoms sit on the mirror plane. Nd³⁺ connected with four CSS⁻ groups is given in the left and the bond lengths of C-S and Nd-S as well as the distorted dodecahedron is shown in the right (disordered CSS⁻ were deleted for clarity). (b) Scheme of pipzdtc2-.

ligand 3D MOFs and opens a new window in fabricating MOFs using ligands beyond conventional O- and N-donor ligands.

Compound 1 (H₃O)[Nd(pipzdtc)₂]·1.5(H₂O)·2.5(CH₃NO) was synthesized by the reaction of a solution (10 mL formamide and 5 mL water) of Nd(NO₃)₃·6H₂O (0.046 g, 0.2 mmol) and an aqueous solution of piperazine-1,4-dicarbodithiolate disodium (Na₂(pipzdtc)) (0.25 M, 5 mL) under room temperature. Na₂(pipzdtc) was prepared according to the reported method and its solution was added to the Nd(NO₃)₃·6H₂O solution using peristaltic pump at a rate of 10 mL h⁻¹. Once the addition of the solution of bis-dithiocarbamate ligand was finished, the reaction solution was kept static for 3-4 hours and light slate grey crystals suitable for single crystal X-ray diffraction analysis were obtained. After decanting the supernatant, crystals of compound 1 were washed with methanol for several times and dried under vacuum at room temperature. Compound 1 was collected in 65.6% yield based on the amount of Nd(NO₃)₃·6H₂O added. Compound **1** was stable in air and insoluble in common organic solvents, such as methanol, formamide, and CH₂Cl₂, but unstable in water.

Single crystal X-ray diffraction analysis under 120 K shows‡ that compound 1 crystallizes in the tetragonal space group $P4_2/nnm$, with cell parameters of a = b = 16.2525(9) Å, c =6.5933(8) Å, $\alpha = \beta = \gamma = 90^{\circ}$, and Z = 2. Its anionic framework, $[Nd(pipzdtc)_2]_n^{n-}$, is constructed from Nd^{3+} and $pipzdtc^{2+}$ ligands. Each Nd³⁺ is coordinated to eight S atoms from four pipzdtc²⁻ anions while each pipzdtc²⁻ ligand, having two dithio groups and acting as a two bidentate chelating ligand, connects two Nd³⁺ ions. Each Nd³⁺ atom locates on a 4-fold inversion axis with a chemical occupancy of 1/8, while the piperazine ring of the pipzdtc²⁻ ligand adopts typical chair conformation. Due to the flexible nature of the chair conformation of the piperazine, each of ligand's ten atoms split into two positions and the resultant two possible chairs mirror a plane as shown in Fig. 1. In this structure, one Nd atom and eight S atoms from 4 ligands form a typical distorted dodecahedron. Such $Nd(\kappa^2-S_2-CNR)_4$ coordination mode possesses the most common binding mode in dithiocarbamate functional group and has been reported in the dithiocarbamate complexes of rare earth ions, actinide elements, and transition metals including Ti, Mo, Nb and so on.²¹ Besides this bidentate chelating mode, the pipzdtc²⁻

(b)

Fig. 2 Interpenetrated dia nets (a) and projection down the c axis showing the 1D open channels (b) in compound 1. Two [001] channels enclosed by L- and R- helices are marked in (b). All hydrogen atoms are omitted for clarity.

ligand was also reported to adopt bridging mode to coordinate

oxygen-protonated under mild acidic condition, it is unlikely

that it can counteract the anion framework in our alkaline

reaction system. ICP-MS analysis (result not shown) also

precluded the incorporation of Na⁺ in the channels. We

presumed that protonated water may help to balance the

charge of the framework. The pore dimension of the channel is

approximately 16 × 10 Å. The solvent accessible volume is

as calculated by using the PLATON program.²⁶ Despite the

structure has 1D channel, it shows no obvious N_2 adsorption

due to the presence of disordered guest molecules.

Additionally, the [001] channels are enclosed by two types of

helices that are consisted of metal cations and organic ligands

in air with the temperature rate of 10 $^{\circ}$ C min⁻¹ (Fig. S4, ESI⁺). Since the boiling point of formamide is above 200 $^{\circ}$ C, the

Thermogravimetric analysis of compound 1 was carried out

with opposite chirality (Fig. 2b).

771.6 Å³ per unit cell volume and the pore volume ratio is 44.3%

with Au atoms in forming Au₁₆ ring.²²

There are two similar C-S bond lengths (1.712(4) and 1.708(4) Å) as a result of the resonance of the dithio group. Even though, there is a slight difference between the two kinds of Nd-S bond lengths. One is 2.8662(12) Å and the other one is 2.9269(8) Å. Both are close to previously reported values.²³ If each Nd³⁺ and ligand are conceptually viewed as a

pseudo-tetrahedral node and a two bridging linker, respectively, a 3D 4-connected dia net similar to supertetrahedral cluster based metal chalcogenide 3D frameworks²⁴ and zeolites²⁵ could be attained. Due to the difference of two Nd-S bond lengths, the simplified tetrahedron of the $Nd(\kappa^2-S_2-CNR)_4$ unit is dramatically distorted. Consequently, the resultant dia net is elongated. In addition, there are two identical sublattices that interpenetrate each other (Fig. 2a). Compound 1 has 1D channels enclosed by two types of helices with opposite chirality along its [001] direction (Fig. 2b). The channels filled with guest molecules. Similar to the amine templates used in the synthesis of 3D metal chalcogenides, the guest molecules are disordered inside its 1D channels. The v(C=O) centered at 1673 cm⁻¹ in the IR spectrum (Fig. S1, ESI⁺) of compound **1** definitely suggests the presence of formamide as a possible guest molecule. Although theoretical calculation revealed that formamide could be

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Fig. 3 (a) Photos of the compound 1 powders after immersed in Ni²⁺ solutions with various concentrations for 10 mins. (b) The emission spectra of exchanged samples.

weight loss below 100 °C implies that the ligand tends to decompose and volatile CS₂ can be partially released. The total weight loss is about 71.2%. Powder X-ray diffraction shows that the compound **1** was converted into Nd₂O₂(SO₄) after calcination in air at 800 °C (Fig. S5, ESI⁺). Unfortunately, due to the lack of aromatic rings in the ligand, compound **1** shows very poor electrical conductivity (< 10⁻¹² Ω^{-1} cm⁻¹). Its solid-state emission spectrum at room temperature (Fig. 3) exhibits typical NIR emission of Nd³⁺ ions upon excitation at 364 nm. The emission spectrum shows three distinct bands in the NIR spectral range, 903 nm (⁴F_{3/2}→⁴I_{9/2}), 1077 nm ⁽⁴F_{3/2}→⁴I_{11/2}), and 1364 nm (⁴F_{3/2}→⁴I_{13/2}).

The 1D channel of compound 1 and their architectural stability allowed us to carry out ion exchange experiments. We studied the ion exchange behaviour of compound 1 by immersing fresh crystals of compound 1 (0.2 g) in methanol solutions containing soluble metal cations for 10 minutes. Our preliminary investigation reveals that the crystal tends to collapse in most of these solutions or the exchange of guest molecules by most of these metal cations could not be achieved. The only exception occurs in the case of NiCl₂ dissolved in methanol. To have a better understanding of the luminescence response of compound 1 to Ni²⁺ cations, the photoluminescence titration upon the addition of NiCl₂-MeOH solution to compound 1 was further conducted and its emission intensity progressively decreased with the increase of Ni^{2+} concentration from 10^{-6} M to 10^{-1} M (Fig. 3b). Meanwhile, the colour of the crystal changed from light slate grey to olive along with the increase of this concentration as shown in Fig. 3a. All exchanged products show similar powder XRD pattern to that of original product (Fig. S9, ESI⁺), which suggests the stability of compound 1 toward the NiCl₂ methanol solution. Using the traditional Stern–Volmer equation, $I_0/I = 1 + Ksv[Q]$, where Ksv is the quenching constant, [Q] is the quencher concentration, the relation between the luminescence intensity and the concentration of $\mathrm{Ni}^{2\mathrm{+}}$ could be fitted into a nonlinear curve(Fig. S10, ESI⁺). The corresponding exponential equation is $\mathit{I_0/I}$ = $3.27e^{25.96[Ni2+]} + 4.45$ and the quenching

constant is calculated to be 84.89 M^{-1} . The nonlinearity of this curve at higher Ni²⁺ concentration suggests the coexistence of both dynamic and static quenching mechanism. The dynamic quenching mechanism was governed by the collisional encounters between the fluorescence moieties of the $pipzdtc^{2-}$ ligands and the electron-deficient Ni²⁺ cations. For the static quenching, it might be due to the formation of ground-state non-fluorescent π -electron-metal complexes between Ni²⁺ cations and the fluorescence moieties and/or coordination of Ni²⁺ cations with the sulfur atoms from pipzdtc²⁻ ligands. The S2p X-ray photoelectron spectroscopy (XPS) studies were carried out on compound **1** and its exchanged compounds. The S2p peak from sulfur atoms coordinated to Nd³⁺ locating at 161.4 eV in compound 1 shifts to 162.5 eV on the addition of Ni²⁺, indicating the interaction between sulfur ligands to Ni²⁺ in Ni@1. This might partially explain the quenching of

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fluorescence of Nd^{3+.27} Efforts have been also made to the synthesis of some main and transition group metal based MOFs, however, no 3D open framework has been achieved yet. Two intrinsic properties of lanthanide cations might be mainly used to interpret this. Firstly, the lanthanide cations are hard acid, which tend to form covalent bonding with soft base sulfur containing ligand used here.²⁸ This provides appropriate reversibilities in forming single crystals in this system. Another one is the large ionic radii of lanthanide cations, which can be coordinated by more bidentate pipzdtc²⁻ anions in comparison with some typical s-, p- and d-block metallic elements. With more coordinated ligands connected to the metallic center, less mechanic strength would be imposed on the framework in forming three-dimensional structures.

In summary, we have successfully prepared a new 3D Nd MOF using sulfur-based ligands under mild conditions. In forming the 3D anionic framework, the pipzdtc²⁻ ligand binds two Nd³⁺ as a two bidentate chelating ligand while each Nd³⁺ is coordinated to eight S atoms, forming a distorted dodecahedron surrounding each Nd³⁺, from four pipzdtc²⁻. A 3D 4-connected dia net could be obtained by viewing the Nd³⁺ and ligand as a pseudo-tetrahedral node and two bridging linker, respectively. Compound 1 has 1D channels enclosed by two types of helices with opposite chirality along its [001] direction. Partial exchange of the disordered guest molecules within its 1D channel by Ni²⁺ could be attained. Due to the interaction of Ni²⁺ with the S atom in the framework, the NIR luminescence of Nd³⁺ was quenched. Our success in preparing compound ${\bf 1}$ and exchanging the disordered guest molecules by Ni²⁺ may shed light on future design and synthesis of porous metal-sulfur-ligand MOFs with appealing optical and electric properties.

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Notes and references

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Crystal data for compound 1 (CCDC 1410415): C_{14.5}H_{29.5}N_{6.5}NdO₅S₈, *M*_r = 775.66, crystal dimensions: 0.40 x 0.20 x 0.20 mm, tetragonal, space group $P4_2/nnm$, a = b = 16.2525(9)Å, c = 6.5933(8) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 1741.6(3) Å³, T = 120(2) K, Z = 2, $\rho_{calcd} = 1.479 \text{ g cm}^{-3}$, $\mu = 2.002 \text{ mm}^{-1} 2\vartheta_{max} = 52.35^{\circ} \text{ GOF} =$ 1.005. A total of 10273 reflections were collected and 923 are unique ($R_{int} = 0.1013$). $R_1(wR_2) = 0.0244$ (0.0570) for 54 parameters and 923 reflections $[l > 2\sigma(l)]$. Crystal data for compound 1 (CCDC 1052054): C_{14.5}H_{29.5}N_{6.5}NdO₅S₈, M_r = 775.66, crystal dimensions: 0.40 x 0.20 x 0.20 mm, tetragonal, space group $P4_2/nnm$, a = b = 16.3046(9) Å, c = 6.6306(7) Å, $\alpha = \beta = \gamma = 16.3046(9)$ 90°, V = 1762.7(3) Å³, T = 296(2) K, Z = 2, ρ_{calcd} = 1.461 g cm⁻³, μ = $1.978 \text{ mm}^{-1} 2\vartheta_{\text{max}} = 52.10^{\circ} \text{ GOF} = 0.941. \text{ A total of } 10075$ reflections were collected and 926 are unique ($R_{int} = 0.1648$). $R_1(wR_2) = 0.0382$ (0.0750) for 54 parameters and 926 reflections $[l > 2\sigma(l)].$

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