

An fcu Th-MOF Constructed from In Situ Coupling of Monovalent Ligands

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Abstract: Synthetic efforts targeting highly symmetrical metal–organic frameworks (MOFs) have always been relentless, for the symmetry of a MOF’s pore environment and overall crystal structure are relevant to the MOF’s properties and behavior. Herein, we report a novel Th-based MOF constructed from assembling highly symmetrical Th-oxo clusters via in situ reductive coupling of nitroso groups on the cluster surface. Nitroso groups have long been known to dimerize in a reversible fashion. Putting them on the monovalent ligands that decorate the Th-oxo clusters can facilitate a downstream assembly process that link the said clusters in a controllable and predictable manner, preserving the overall symmetry in the MOF product. Moreover, the assembly can be made permanent by reducing the azodioxo moiety to azo, effectively locking the symmetrical MOF form. We believe this process of assembling pre-formed Th-oxo clusters helps the overall MOF adopt a highly symmetrical topology (face-centered cubic, **fcu**) resembling the well-known UiO series MOFs based on tetravalent Zr/Hf.



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1. Introduction

For more than two decades, metal–organic frameworks (MOFs), as a burgeoning class of versatile materials, have profoundly enriched the knowledge of coordination chemistry and created opportunities in fields like gas storage and separation, catalysis, biomedicine, chemical sensing, and so on [1,2]. Generally, MOFs are synthesized using metal sources (salts etc.) and bridging organic ligands of various geometries that are often relevant to the topology of the final products. One can refer to resources such as the Reticular Chemistry Structure Resource (RCSR) for rational design and outcome predictions for MOFs [3].

Among the 100,000+ MOFs reported in the literature [4], structures with a higher degree of symmetry are particularly appealing from a fundamental viewpoint. Yet it remains challenging to develop straightforward synthetic routes for targeted highly symmetrical MOFs, especially for metals with a broad range of coordination numbers and diverse coordinative reactivities. For example, selective synthesis of MOFs with tetravalent and trivalent metals that are prone to premature hydrolysis and ill-controlled coordination environments are particularly difficult when using conventional synthetic protocols, hence the modulated synthesis (e.g., Zr/Hf- and rare earth-based MOFs) in which the addition of monovalent ligands regulates the specific coordination processes between metal cations and corresponding ligands, slowing down the formation of extended networks [5–9]. Besides coordinative modulation, another potential route to gain better control of the MOF crystallization process is through the introduction of reversible covalent bonding [10–13], as it also slows down the overall formation of extended framework structures. In fact, as the basis of covalent organic frameworks, reversible bonding is required to make the structure periodic and even highly crystalline in some cases [14,15].

Thorium is the most abundant radioactive element found in nature with an extremely long half-life ($t_{1/2} = 1.405 \times 10^{10}$ years) [16]. Th^{4+} is a stable tetravalent cation with one of the richest coordination chemistries (coordination number ranging from 4 to 15) among all metals [17]. Thorium-based MOFs that have been reported so far encompass quite diverse coordinative environments for Th^{4+} [18–20]. Thus, we propose to use a covalent bond-based synthetic protocol to control the formation of MOFs with targeted coordination chemistry for Th^{4+} ; if proven helpful, the method might be seen as versatile and applicable to other metals.

Here, we report a covalently modulated synthesis of a highly symmetrical Th-MOF with **fcu** (face-centered cubic) topology enabled by homologous coupling of nitroso groups that undergo a reductive dimerization process, simultaneously regulating the coordination process and locking the targeted MOF structure. We hypothesize the process takes place in a stepwise manner: (1) formation of highly symmetrical Th-oxo clusters covered with monovalent ligands (i.e., 4-nitrosobenzoate, **L1**); (2) due to the symmetry and stability of said Th_6 cluster, the assembly must also be a selective process that leads to formation of a MOF with high symmetry; (3) nitroso dimers, which are the basis of the assembly, are reduced in situ, effectively locking the MOF product.

2. Materials and Methods

The 4-aminobenzoic acid (>99%), Oxone (>99%), dichloromethane (DCM) (>99%), $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ (>99%), HCOOH (FA) (>99%), N, N-dimethylformamide (DMF) (>99%) were purchased from Adamas Co. Ltd. (Shanghai, China) and used without further treatment unless otherwise noted. Ultrapure water was obtained from a Millipak[®] Express 40 system (Merk-Millipore, Darmstadt, Germany). ^1H NMR spectra were collected on a JNM-ECZ400S/L1 (400 MHz) spectrometer (JEOL Ltd., Tokyo, Japan). Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku MiniFlex600 at 40 kV, 40 mA for Cu $\text{K}\alpha$, ($\lambda = 1.54178 \text{ \AA}$) with a scan speed of $10^\circ/\text{min}$ from 3 to 50° at a step size of 0.01° . Single-crystal X-ray diffraction data (SC-XRD) were collected on a Bruker D8 Venture single-crystal X-ray diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). Details of structural determination and refinement are provided in the Supplementary Materials. N_2 sorption measurements were conducted on a BELSORP MAX system (MicrotracBEL, Osaka, Japan) with a relative pressure (P/P_0) range of 0–0.995. Fourier-transform infrared (FT-IR) spectra were collected in the range of $400\text{--}4000 \text{ cm}^{-1}$ on a Spectrum Two Li10014 infrared spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Discovery SDT 650 simultaneous thermal analyzer from room temperature to 900°C at a heating rate of $5^\circ\text{C}/\text{min}$ in a N_2 flow of $100 \text{ mL}/\text{min}$.

Monovalent ligand 4-nitrosobenzoic acid (**L1**) was prepared using a literature protocol, oxidizing 4-aminobenzoic acid with Oxone [21]. MOF crystals were prepared solvothermally by reacting $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ with **L1** in DMF at 120°C (for details, see Supplementary Materials).

3. Results and Discussion

Several framework materials connected by covalent imine bonds formed between reactive groups (i.e., amine and aldehyde) that decorate metal clusters have been reported [10–13,22] in which the imine bonds are reversible to some extent. Here, we hypothesize that using ligands with functional groups that undergo homologous reversible coupling could enable and regulate the growth of MOFs. Nitroso compounds were known to dimerize reversibly to form *cis*- or *trans*- azodioxides and were successfully used to synthesize covalently linked organic framework materials in the form of large single crystals [14]. Hence, we selected a monovalent ligand functionalized with a nitroso group to prepare a Th-oxo complex that served as a structural node in the subsequent construction of a Th-MOF via nitroso dimerization, all in a one-pot approach. We successfully obtained large single crystals of **SUM-5** (SUM = Sichuan University Materials) with high symmetry (face-centered cubic, space group $Fm\bar{3}m$), free of coordinative modulators. We note that

in a recently reported isorecticular series of Th-MOFs with UiO-type structures, Lin et al. employed a typical acid-modulated approach and prepared the MOFs with divalent carboxy ligands with a variety of lengths [23].

To the best of our knowledge, coordinative modulators are essential to successfully synthesize tetravalent Zr/Hf-based MOFs (e.g., UiO-type MOFs). Owing to their strong Lewis acidity, tetravalent metal cations have a high tendency to coordinate with polycarboxylate ligands, often giving rise to bulk polycrystalline or amorphous powders if the coordination process is not properly controlled (modulated). However, in the case of **L1**, which is a monovalent ligand, fast reaction with Th^{4+} only leads to discrete complexes (clusters), and an extended network could only form when the nitroso groups dimerize, bringing neighboring clusters together. Therefore, the reversible dimerization of nitroso groups acts as a self-modulating process, facilitating the formation of large single crystals of **SUM-5**.

Single-crystal X-ray diffraction of a suitable crystal revealed that **SUM-5** crystallizes in the cubic space group $Fm\bar{3}m$ (CCDC deposition number 2085727, asymmetric unit shown in Figure S6, for crystallographic refinement details see Table S1). **SUM-5** conforms to the **fcu** topology, connecting $\text{Th}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6$ secondary building units (SBUs) with linear azobenzene dicarboxylate (ABDC) linkers (Figure 1a). There are three types of oxygen atoms bound to Th^{4+} within the SBU: (1) carboxy oxygen atoms with a $\text{Th}\text{--}\text{O}$ bond length of 2.402(5) Å; (2) μ_3 oxygen atoms with a $\text{Th}\text{--}\text{O}$ bond length of 2.448(10) Å; (3) terminal water oxygen atoms with a slightly longer $\text{Th}\text{--}\text{O}$ bond length of 2.65(2) Å. The **SUM-5** MOF is composed of both tetrahedral (Figure S7a) and octahedral cavities (Figure 1b and Figure S7b) with internal pore diameters of ca. 12.2 Å and 15.8 Å, respectively, which are connected by ca. 10.9 Å triangular windows, with van der Waals radii taken into consideration. Phase purity of **SUM-5** was confirmed by comparing the experimental and simulated PXRD patterns (Figure 1c). The crystal structure of **SUM-5** showed that the organic ligand was an azo compound instead of an azodioxide, which is the direct product of nitroso dimerization. The identity of the ligand was also confirmed by the ^1H NMR spectrum of digested **SUM-5** (Figures S2 and S3). The formation of the azo ligand is a result of an in situ reduction of azodioxides, most likely by dimethylamine, decomposition product of DMF, the solvent used. After activation, **SUM-5** exhibited a classic type I isotherm with a maximum N_2 uptake of $338.4\text{ m}^3\cdot\text{g}^{-1}$ at 77 K (Figure 2a), corresponding to a Brunauer–Emmett–Teller (BET) surface area of $1410\text{ m}^2\cdot\text{g}^{-1}$ and a pore volume of $0.5232\text{ cm}^3\cdot\text{g}^{-1}$. Moreover, pore size distribution showed that **SUM-5** has micropores with diameters of 1.26 nm and 1.42 nm, respectively, which are consistent with the crystal structure determined by SC-XRD (Figure 2a inset). As shown in Figure S8, the FT-IR spectrum of **SUM-5** shows peaks at 1590 and 1410 cm^{-1} , which correspond to the asymmetric $\nu_{\text{asym}}(\text{COO})$ and symmetric $\nu_{\text{sym}}(\text{COO})$ vibrations of carboxylates, respectively. The peak centered at 1498 cm^{-1} corresponds to the aromatic $\text{C}=\text{C}$ vibrations [24]. The C-H out-of-plane vibration of the benzene ring was found at 791 cm^{-1} . In addition, **SUM-5** was determined to be thermally stable up to $400\text{ }^\circ\text{C}$, as indicated in the TGA curve (Figure 2b). We note that the physical characteristics of **SUM-5** (BET surface area, etc.) are consistent with the literature [23].

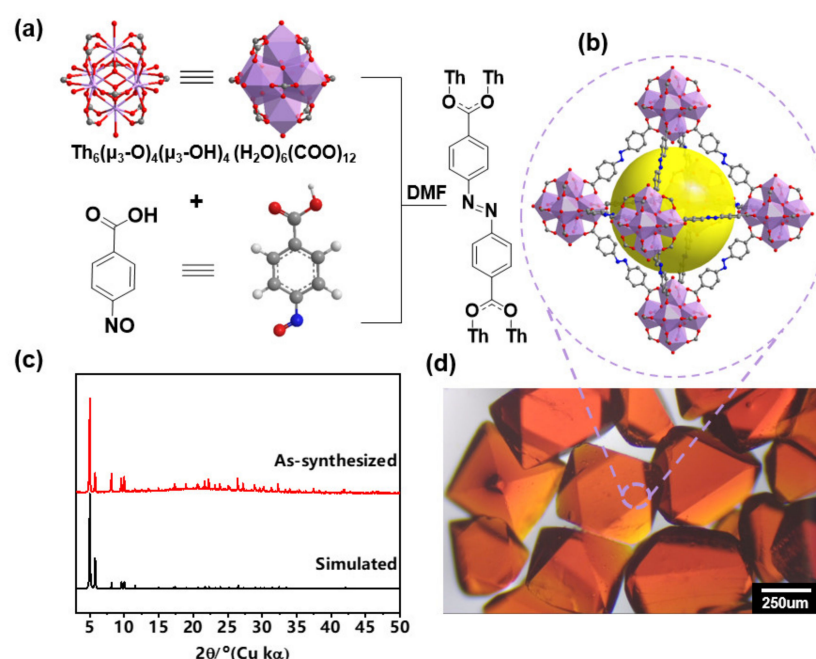


Figure 1. (a) Building units used to construct SUM-5. (b) Single-crystal structure of SUM-5, highlighting the octahedrally shaped cage. The yellow sphere represents the octahedral pore cavity. Atom colors: Th, purple polyhedra; C, grey spheres; N, blue spheres; O, red spheres; H, omitted for clarity. (c) PXRD patterns comparing the experimental (red) and simulated (black). (d) Optical microscopic image of SUM-5.

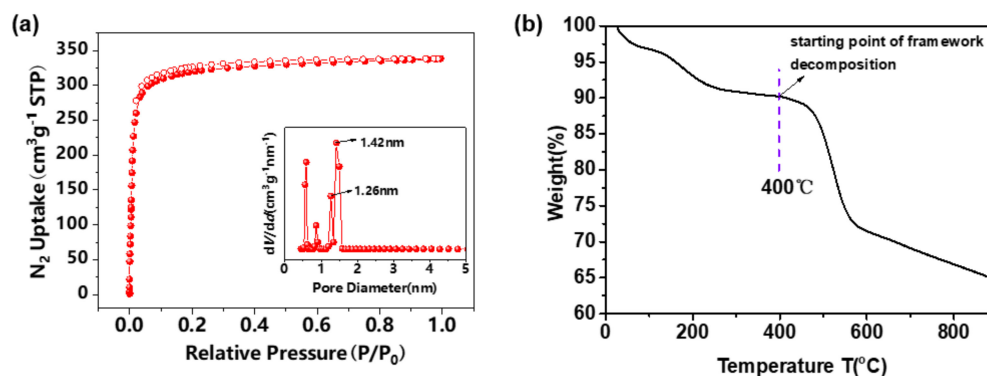


Figure 2. (a) N₂ sorption isotherm of SUM-5 (adsorption: filled circles; desorption: open circles). (b) TGA profile of SUM-5.

4. Conclusions

In conclusion, we have synthesized a Th-based MOF with highly symmetrical **fcu** topology in which the bridging ligands were formed in situ via homo-coupling and reductive dimerization of nitroso groups on discrete Th-oxo clusters. We argue that the use of monovalent ligands circumvents the fast and ill-controlled coordination of tetravalent cations with hard-base bridging polydentate ligands. Instead, the reversible covalent bonding becomes the regulating step, linking the Th-oxo clusters into an extended framework while preserving the symmetry, effectively constituting a self-modulating process that leads to the formation of large single crystals, free of extraneous modulators. Subsequently, the assembly was made permanent by reducing the azodioxy moiety to azo, locking the symmetrical MOF form. The nitroso dimerization-based strategy could be applicable in other systems, linking together various discrete metal clusters. Joining the other Th-MOFs, SUM-5 is potentially applicable as a candidate material for radiation detection, X-ray scintillation, radionuclide storage, etc.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/sym13081332/s1>, supplemental figures, sample preparation protocol, characterization details, etc.

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Conflicts of Interest: The authors declare no conflict of interest.

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