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Stabilization of an Unprecedented Hexanuclear Secondary Building Unit in a Thorium-Based Metal–Organic Framework

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S Supporting Information

ABSTRACT: The crystal structures of thorium clusters are important for understanding the formation and transformation mechanisms of actinide species in solution, which can in turns benefit nuclear waste processing and management. However, stabilizing thorium clusters in aqueous solution is quite challenging because of their fast olation and oxolation reactions. Here, we report a thorium-based metal-organic framework, NU-905, with the formula $[Th_6(\mu_3-O)_2(HCOO)_4(H_2O)_6(TCPP)_4]$ [TCPP = tetrakis(4-carboxyphenyl)porphyrin], synthesized by a solvothermal reaction in N,N-dimethylformamide and water at 120 °C. NU-905 contains a hexanuclear secondary building unit (SBU), $[Th_6(\mu_3 O_{2}(HCOO)_{4}(H_{2}O)_{6}]$, which has never been reported previously. The SBUs are capped and bridged by the tetratopic linker TCPP to form a three-dimensional network with scu topology. The activated NU-905 exhibits permanent porosity and shows high catalytic activity for the selective photooxidation of a mustard gas simulant.

s a naturally occurring actinide metal on Earth, thorium has A become a focus of study because of its promising use as a new primary energy source.¹ Thorium fuels breed fissile uranium-233, which can be used in various nuclear reactors. Additionally, thorium-232 can also be implemented as a core part of molten salt reactors.² Because of its tetravalent nature, thorium was often studied as a surrogate of plutonium(IV) to obtain knowledge about the nuclear waste disposal of plutonium(IV).³ Therefore, understanding thorium-based solution and solid-state chemistry is crucial for the processing, management, and disposal of nuclear fuels and radioactive waste. To understand and predict the stabilities and transformation properties of thorium at different conditions, it is essential to characterize the crystal structures of thorium species. However, the rapid and unpredictable multistep olation and oxolation reactions promoted by highly charged tetravalent thorium ions in aqueous solution often lead to the formation of polymeric colloidal poly(oxothorium) species with poorly defined chemical structure.⁴ Although indirect characterization like Raman spectrometry,⁵ mass spectrometry,⁶ and X-ray spectrometry^{7,8} indicates that various polynuclear thorium clusters, including dimers,⁹ trimers,¹⁰ tetramers,¹¹ hexamers,¹² octamers,¹³ and decamers,⁶ may exist under a given pH, the

detailed crystal structures of well-defined polynuclear thorium clusters are rarely reported.¹⁴ On the basis of the Cambridge Crystallographic Data Centre (CCDC),¹⁵ there are only approximately 50 thorium oxide species reported to date. One method to stabilize and capture unstable polynuclear thorium clusters is to incorporate capping ligands or counterions, such as carboxylate,⁸ phosphoate,¹⁶ sulfate,^{17,18} and selenate¹⁹ groups. A wide variety of discrete or polymeric polynuclear thorium clusters have been successfully isolated using this strategy.²⁰ Among the various thorium clusters reported thus far, octahedral hexanuclear Th₆O₄(OH)₄ is the most prevalent and is considered to be a stable building unit.

Recently, actinide-based metal-organic frameworks (MOFs) have received considerable interest.²¹ Stabilizing actinides and their clusters in MOF structures not only facilitates the characterization of various actinide species but also generates novel actinide-based materials with unique chemical and physical properties. A large number of uranyl-based MOFs (U-MOFs) have been prepared and structurally characterized.²² Their diverse topologies,^{23,24} high porosities,²⁵ and novel functionalities, including gas separation,²⁶ adsorption of biomolecules,^{25,27} detection of radiation,^{28–31} and nuclear waste removal,³² have brought great attention to this new family of MOF materials. In comparison with U-MOFs, only a small number of thorium-based MOFs (Th-MOFs) have been reported.^{10,26,33-35} As a pioneer of this field, O'Hare reported a series of three-dimensionally connected Th-MOFs: TOF-1³⁶ and TOF- 2^{37} are constructed from thorium oxyfluoride chains, while TOF-3³⁸ is built from octahedral thorium hexamer clusters consisting of ThO₄F₅ polyhedra. Thierry et al. synthesized the first UiO-66 type Th-MOF containing a hexanuclear $Th_6O_4(OH)_4$ cluster by tuning the ratio of N,Ndimethylformamide (DMF) and water (H_2O) in a solvothermal system.³⁹ On the basis of this finding, a number of Th-MOFs with Th₆O₄(OH)₄ clusters have recently been successfully synthesized by several groups.^{40,41}

Given the diversity of thorium oxo clusters formed in solution, we envision that Th-MOFs composed of various polynuclear thorium clusters other than $Th_6O_4(OH)_4$ can also be synthesized by judicious choice of reaction conditions. One feasible strategy to achieve this goal is to add a suitable amount



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of H_2O in a solvothermal system to accelerate the olation and oxolation reactions in thorium hydrolysis. Organic linkers and monocarboxylate modulators can also be used to stabilize the clusters formed in situ, generating Th-MOFs containing different types of secondary building units (SBUs). Here, we report the synthesis and characterization of a novel Th-MOF, **N U - 9 0 5**, with the formula [Th₆(μ_3 -O)₂(HCOO)₄(H₂O)₆(TCPP)₄] [TCPP = tetrakis(4-carboxyphenyl)porphyrin], which is built from the SBU, [Th₆(μ_3 -O)₂(HCOO)₄(H₂O)₆]. Importantly, this SBU has never been discovered in any form of thorium species, indicating that MOF materials can uniquely stabilize thorium SBUs, which have not been observed to be stable in other inorganic systems.

After adding a suitable amount of H_2O to the mixture of thorium nitrate and TCPP linkers in a DMF solution, dark-red block-shaped crystals of **NU-905** were obtained at a solvothermal reaction temperature of 120 °C. Single-crystal X-ray diffraction (SCXRD) studies of **NU-905** reveal that it crystallizes in the monoclinic space group C2/m (Table S1). The asymmetric unit of **NU-905** consists of a quarter of the hexanuclear thorium SBU [Th₆(μ_3 -O)₂(HCOO)₄(H₂O)₆] and a TCPP linker (Figures 1a,b and S1). Interestingly, four formic



Figure 1. (a) Hexanuclear SBU composed of three crystallographically independent thorium atoms. A planar rhombic entity formed by Th1 and Th3 is highlighted in purple. (b) Packing diagram of **NU-905** along the *c* axis showing double-layered TCPP linkers with a close $\pi - \pi$ distance. (c) Packing diagram of **NU-905** along the *a* axis showing two types of rhombic windows. (d) *scu-a* topology of a simplified net in **NU-905**.

acid molecules generated from the decomposition of DMF in situ also incorporate into the SBU (Figure S2). However, no other counterions were observed in the crystal structure, indicating that **NU-905** is the neutral framework, $[Th_6(\mu_3-O)_2(HCOO)_4(H_2O)_6(TCPP)_4]$. The complete hexanuclear thorium SBU is composed of three kinds of crystallographically independent thorium atoms (Th1, Th2, and Th3 in Figure 1a),

where two of each kind are observed per SBU. Th1 sits between Th2 and Th3 and is coordinated by nine oxygen atoms, with the Th–O bond lengths ranging from 2.320(16) to 2.743(6) Å. Six of the nine coordinated oxygen atoms are each from a different organic linker. The seventh oxygen atom is a μ_3 -oxo group bridging two adjacent Th3 centers, forming a planar rhombic entity with average Th1–Th3 distances of 4.105 Å. Finally, the remaining two oxygen atoms are from coordinated water and a capping formic acid, respectively. Two Th3 atoms are located in the geometric center of the hexanuclear SBU, and each of them is also coordinated to nine oxygen atoms, with Th-O bond lengths ranging from 2.289(9) to 2.991(17) Å. Four of the nine oxygen atoms are each from a different organic linker, two are from a bridging μ_3 -oxo group, two are from formic acid, and one is coordinated water. The Th3–Th3 distance is 3.691 Å (Table S2). Interestingly, two Th2 atoms are present, one on each side of the SBU, and each is surrounded by eight oxygen atoms, with Th–O bond lengths ranging from 2.279(14) to 2.743(6) Å. Six of the eight oxygen atoms are from four different organic linkers (two chelating carboxylate groups and two monodentate carboxylate groups). The remaining two oxygen atoms are from formic acid and coordinated water, respectively. To the best of our knowledge, this type of thorium SBU has never been reported before.¹⁴ The possible formation mechanism of this unique SBU is the result of in situ hydrolysis of thorium nitrates to form a tetranuclear cluster, which is further bridged by TCPP linkers to form a hexanuclear SBU (Figure S3). In total, each SBU is coordinated by 16 carboxylate groups from organic TCPP linkers, and each TCPP is coordinated to four neighboring thorium SBUs. Two neighboring TCPP linkers align parallel to each other with a close $\pi - \pi$ distance (ca. 3.5 Å; Figure 1b). The packing diagram of NU-905 indicates a rhombic window (14 \times 25 Å diagonal distance) along the *c* axis (Figure 1b) and two rhombic windows $(4 \times 5 \text{ and } 6 \times 8 \text{ Å diagonal})$ distances, respectively) along the *a* axis (Figure 1c). The solventaccessible pore volume is approximately 60%, as calculated by PLATON software. The tetratopic linker TCPP and 16connected thorium SBU assemble into a 4,16-connected network, which can be simplified as a 4,8-connected scu topology (Figure 1d).

To test the porosity of **NU-905**, the solvent of the assynthesized MOF sample was exchanged to fresh ethanol and further activated using supercritical CO_2 ,⁴² resulting in **NU-905**-**ScCO**₂. The powder X-ray diffraction (PXRD) pattern for **NU-905-ScCO**₂ indicates that the MOF retains its crystallinity (Figure 2a), and thermogravimetric analysis (TGA) demonstrates that **NU-905-ScCO**₂ can be thermally stable up to 500 °C (Figure S4), which is comparable with that of other reported Th-MOFs.³⁹ The activated **NU-905-ScCO**₂ exhibits permanent porosity, and the Brunauer–Emmett–Teller area calculated from the argon isotherm is approximately 800 m²/g, which is moderate among the reported Th-MOFs.^{33,34} The calculated pore-size distribution shows a broad peak from 4 to 12 Å (Figure 2b), which is consistent with the size of the rhombic pores in the single-crystal structure of **NU-905**.

Previously, our group demonstrated that photosensitizers (such as porphyrin,⁴³ pyrene,⁴⁴ and benzoselenodiazole⁴⁵ chromophores) immobilized in MOFs can be used as stable photocatalysts for the selective aerobic oxidation of a mustard gas simulant, 2-chloroethyl ethyl sulfide (CEES), to the nontoxic product 2-chloroethyl ethyl sulfoxide (CEESO) by light-emitting diode irradiation of the appropriate wavelength. We speculated that **NU-905**, as a porphyrin-containing MOF, could



Figure 2. (a) PXRD patterns of as-synthesized NU-905 (red), NU-905-ScCO₂ (orange), and NU-905 after catalysis (blue). (b) Argon isotherms at 87 K and (inset) pore-size distribution of NU-905.

also demonstrate CEES oxidation under light irradiation. To test the performance of **NU-905** as a photocatalyst, we carried out photocatalysis experiments (see the Supporting Information for details) under our standard conditions.⁴⁶ With 1 mol % catalyst used (based on porphyrin), **NU-905** converted 65% of the starting material in 5 min and 100% in 10 min (Figures 3 and S5



Figure 3. Reaction profiles for the oxidation of CEES with NU-905 as the photocatalyst.

and S6). The selectivity of the catalytic reaction toward the monooxygenated product (CEESO) over toxic dioxygenated 2chloroethyl ethyl sulfone (CEESO₂) was confirmed via NMR of the reaction mixture. The estimated half-life of CEES is 4 min, which is competitive with the best catalysts reported for this reaction.⁴⁶ Additionally, PXRD of **NU-905** after catalysis shows that it is chemically stable under the reaction conditions.

In conclusion, a Th-MOF, **NU-905**, with the formula $[Th_6(\mu_3-O)_2(HCOO)_4(H_2O)_6(TCPP)_4]$ [TCPP = tetrakis(4-carboxyphenyl)porphyrin] was synthesized in a DMF/H₂O mixture under solvothermal reaction conditions. **NU-905**

contains an unprecedented hexanuclear thorium SBU, which is composed of three crystallographically unique thorium atoms. The highly connected thorium SBUs are further stabilized and bridged by TCPP organic linkers to form a three-dimensional framework with *scu* topology. The ScCO₂-activated **NU-905** demonstrates excellent catalytic efficiency and selectivity for the oxidation of CEES. This work may pave the way to construct unexplored Th-MOF materials with novel SBU structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03511.

Crystallographic data table, TGA–differential scanning calorimetry data, and ¹H NMR spectra of CEES oxidation reactions (PDF)

Accession Codes

CCDC 1873150 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval of the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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