Coordination Chemistry in the Structural and Functional Exploration of Actinide-Based Metal-Organic Frameworks

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The coordination chemistry between inorganic and organic species can be optimally exemplified by metal–organic frameworks (MOFs), whose structures and functionalities can be rationally designed from these highly tunable building blocks. The high porosity, stability, and versatile functionalities of MOFs have attracted wide-spread attention from energy-related research and pollution remediation to biomedical applications. A unique and underexplored subset of these materials are MOFs based on actinide nodes; these MOFs have distinguished themselves as a unique platform for investigating the versatile oxidation states, reactivity, and coordination chemistry of actinides. Herein, we will focus on the rational design and synthesis of actinide-based MOFs under the general guidelines of coordination chemistry for their structural and functional explorations. The dimensionality, topology, and structures of actinide-based MOFs can be controlled by selecting pre-designed building blocks of actinide-based nodes and organic linkers with certain desired coordination geometries and functionalities. These unique actinide-based MOFs have shown promise for applications in nuclear waste mitigation, pollution control, and catalysis.

1. Introduction

Coordination chemistry is one of the major thrusts of inorganic chemistry pertaining to compounds bearing coordination bonds between metal centers and ligands. In a coordination compound, the pair of shared electrons that forms the coordination bond is solely provided by the ligand. The concepts of coordination geometry and coordination number, established by Werner in the 1890s, have been ceaselessly guiding the development of this field.¹ In particular, these concepts have been invaluable to the burgeoning field of metal–organic frameworks (MOFs), which lies at the intersection of inorganic coordination chemistry and organic chemistry.² MOFs are porous, crystalline materials composed of inorganic metal ion/cluster-based nodes and organic linkers; the high tunability of both building blocks has offered vast opportunities for structural and functional explorations of MOFs in applications such as gas storage/separation,³ catalysis,⁴ enzyme encapsulation,⁵ and sensors⁶.

Fig. 1 Examples of actinide-based inorganic nodes for the construction of MOFs.

While transition metal coordination chemistry has been extensively investigated, the chemistry of actinide elements, which is essential for mitigating nuclear waste,⁷ has been largely elusive.⁸ The actinides reside in the 5f block of the periodic table; uranium and thorium specifically are the most widely explored of the actinides due to the relatively high abundance of their low radioactivity isotopes.⁹ While actinide coordination chemistry shares some aspects with transition metal coordination chemistry, actinides have certain unique characteristics that have given rise to unusual and intriguing structure, reactivity, and physical properties.¹⁰

The past few decades have witnessed the emergence of MOFs, which marry inorganic chemistry to organic chemistry through the coordination bonds between metal ion/cluster-based nodes and organic linkers. As compared to transition

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Fig. 2 Packing structures of uranyl-based NU-1302 showing structural isomerism in the presence of different guests. Figure reprinted with permission from reference 15. Copyright 2019 American Chemical Society.

metal-based MOFs, the employment of actinide elements as nodes in porous extended frameworks is underexplored.¹¹ The more diffuse 5f orbitals of actinide elements give rise to larger coordination numbers (typically 8–9 coordinated) compared to transition metals (typically 4–6 coordinated). As a result, actinide ions can adopt coordination geometries far different from traditional tetrahedral and octahedral coordination geometries of transition metal ions. Additionally, the wide variety of actinide oxidation states results in unique chemical activity, novel coordination chemistry, and a large range of actinide-based clusters that are distinct from transition metals.¹² Thus, the diverse coordination chemistry of actinides provides an intriguing opportunity of exploring the design and properties of actinide-based MOFs, which is pursued by us and other groups.¹³

In this account, we will synopsise the efforts in our group to design and synthesize actinide-based MOFs, particularly focusing on the coordination chemistry in their structural and functional explorations. Highly intricate extended structures were designed through a rational bottom-up approach from simple, yet versatile building blocks of actinide-based nodes (Fig. 1) and organic linkers.

■ ■ 2. Uranyl-based MOFs

In the past few decades, most efforts in actinide chemistry have been devoted to the structure, bonding, and reactivity of uranium, owing to its role in the nuclear energy cycle. The uranyl (UO_2^{2+}) cation specifically is a ubiquitous unit with short, axial U–O bonds and U in the hexavalent oxidation state. Uranyl can form various coordination motifs with carboxylates, including tetragonal bipyramids (T), pentagonal bipyramids (P) and hexagonal bipyramids (H).¹⁴ Among them,

H type $[\text{UO}_2(\text{RCOO})_3]^-$ is the most prevalent and stable motif for uranium(VI) carboxylate complexes (over 600 compounds to date, according to the Cambridge Structural Database). Thus, a highly common uranium node is the uranyl unit bound to three different carboxylate linkers to form an H-type node (Fig. 1a).

2.1. Uranyl-based 2-D MOFs

The uranyl cation can serve as a trigonal planar secondary building unit (SBU) to form 2-D MOFs with nearly planar, ditopic organic linkers. NU-1302, a uranyl-based MOF published by our group, exemplifies this linker-based dimensionality trend evident in the uranyl-based MOF field.¹⁵ NU-1302 is built from biphenyl-4,4'-dicarboxylic acid and the uranyl unit, which, when crystallized in *N,N*-dimethylformamide (DMF), form two-dimensional sheets (2-DMF). However, guest-dependent single-crystal-to-single-crystal phase transitions were observed when the material was solvent exchanged to ethanol (2-EtOH) and when the solvent was eventually removed *via* supercritical CO_2 activation (2-SA).

All phase transitions resulted in isomers of 2-DMF, where the uranyl unit bound three linkers and crystallized in a hexagonal bipyramid. 2-DMF adopts the honeycomb (**hcb**) topology and $C2/c$ symmetry with one-dimensional, 12 Å channels (Fig. 2A, B). In ethanol, the sheets adopt the same $C2/c$ symmetry and shift to form 2.5 Å channels, and bend in a wave like fashion (Fig. 2C, D). Finally, upon supercritical CO_2 activation, the sheets bend dramatically to the point of docking,¹⁶ and only 3.5 Å pores are observed in this new *P1* space group (Fig. 2E, F).

Table 1. List of actinide-based MOFs in this account.

MOF	Connectivity	Topology	Reference
NU-1302	3-connected (2D)	hcb	15
NU-1300	3,4-connected	tbo	18
NU-1301	3-connected	nun	21
NU-1350	3,6-connected	nuc	22
NU-1351 and NU-1352	3,6-connected	cml-c3	22
NU-1000-U	4,8-connected	csq	25
M-UiO-66 (M = Zr, Hf, Ce, Th)	12-connected	fcu	30a
M-MOF-808 (M = Zr, Hf, Ce, Th)	3,6-connected	spn	30a
M-NU-1008 (M = Zr, Hf, Ce, Th)	4,8-connected	csq	30b
M-NU-1200 (M = Zr, Hf, Ce, Th)	3,8-connected	the	30c
NU-905	4,8-connected	scu	33
Th-NU-1011	4,8-connected	csq	34
NNS- <i>x</i> (<i>x</i> = 1, 2, 3)	4,12-connected	shp	37

A trend of increasing contraction is observed between the three isomers, where **2-DMF** is the most open and eclipsed, **2-EtOH** is an intermediate level of contraction, and **2-SA** is the most contracted structure. The decrease in solvent accessible pore volume as the isomers become more contracted also supports this trend. Furthermore, increasing contraction is also mirrored by increasing distortion from **2-DMF** to **2-EtOH** to **2-SA**; this can be observed by the presence of different linker motifs with larger rotation angles and bending, which generate the warped layers in **2-EtOH** and eventual docking in **2-SA**. Finally, CO₂ physisorption measurements display a step at low pressure, indicative of gate-opening behavior;¹⁷ this suggests that **NU-1302** is not only responsive to solvent guest molecules, but also to guests in the gaseous phase. Here, **NU-1302** acclimates to its environment, while remarkably maintaining its crystallinity and coordination throughout.

2.2. Uranyl-based 3-D MOFs

While the nearly planar ditopic linker in **NU-1302** results in a two-dimensional material, pairing the planar uranyl node with polytopic carboxylic acid linkers, which have a rotation angle between the arms and body of the linker, drives the formation of three-dimensional topologies. We reported a **tbo**-topology MOF (**NU-1300**) designed for this particular challenge.¹⁸ Not only does the **tbo** topology offer large pores, but these pores are also mathematically forbidden to catenate,¹⁹ resulting in open cages large enough to adsorb small organic molecules. Through deliberate selection of the 3-connected, anionic, uranyl carboxylate node [UO₂(RCOO)₃]

and the 4-connected carboxylic acid 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid (H₄TBAPy), we specifically designed **NU-1300** to be comprised of 3-connected and 4-connected building blocks (a requirement of the **tbo** topology). Uranium–carboxylate oxygen bonds are also highly stable; this combination of node and linker thus enhances the water-stability of **NU-1300**. Each linker carboxylate is perpendicular to the pyrene plane; this results in a non-planar linker, which generates the 3-dimensional **tbo** topology when paired with a planar node (Fig 3a).

NU-1300 lies in the *Fm* $\bar{3}$ *m* space group with a structure of [(CH₃)₂NH₂]₄[(UO₂)₄(TBAPy)₃]. The uranyl nodes adopt the hexagonal bipyramidal geometry and bind to three unique linkers with typical bond lengths of U–O_{equ} = 2.48 Å and U–O_{ax} = 1.69 Å. Large cages of 17 Å and cavities of 27 Å and 39 Å are observed in **NU-1300** (Fig 3b). The framework also has an impressive apparent Brunauer-Emmett-Teller (BET) area of 2100 m²g^{−1}.

Fig. 3 Schematic representation of the structure of **NU-1300** showing the pore aperture, the tetratopic pyrene-based linker with twisted side arms and the tritopic uranyl nodes. C gray; O red; U teal. Figure reprinted with permission from reference 18. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Since MOFs have shown promise as adsorbents,²⁰ they may also be capable of aqueous-phase separation of small, charged, organic molecules. Because **NU-1300** is negatively charged, it was found to be capable of adsorbing positively charged molecules smaller than its pores. Indeed, competition experiments demonstrated the selective adsorption of cationic organic dyes over anionic dyes *via* UV-vis spectroscopy.

Fig. 4 Schematic representation of the structure of **NU-1301** highlighting the complexity of the structure assembled from simple building blocks. Figure reprinted with permission from reference 21. Copyright 2017 American Association for the Advancement of Science.

Additionally, adsorption of the cationic protein, cytochrome *c*, was observed in the presence of the anionic protein, α -lactalbumin. Finally, **NU-1300** proved to be water-stable by powder X-ray diffraction at pH 1–8. In summary, the anionic, uranium-based MOF, **NU-1300**, was designed and synthesized in the **tbo** topology as a water stable, selective adsorbent for cationic molecules.

In addition to **NU-1300**, our group has utilized this crystal engineering method to synthesize another 3-D uranyl framework, **NU-1301**, with intricate superstructures.^{18,21} Specifically, **NU-1301** contains 10 uranium nodes and seven tricarboxylate ligands. As a result, a 173.3 Å cubic unit cell enclosing 816 uranium nodes and 816 organic linkers was observed in **NU-1301**, making it the largest unit cell for any nonbiological material to date. The key to the structural complexity is *in-situ* generation of cuboctahedron vertices composed of 12 tricarboxylate ligands and 8 $[\text{UO}_2(\text{RCOO})_3]^-$ triangular faces (Fig. 4A). The cuboctahedrons assemble with each other by sharing triangular faces (Fig. 4B) and form two kinds of secondary structures: pentagonal and hexagonal prisms (Fig. 4C). The C_5 symmetric pentagonal prisms and C_6 symmetric hexagonal prisms organize into tetrahedral and diamond quaternary topologies with a high degree of structural complexity. The packing of the structure of **NU-1301** exhibited colossal icosidodecahedral and rectified hexakaidecahedral cavities, which have internal diameters of 5.0 and 6.2 nm, respectively. As a result, **NU-1301** exhibited the lowest density in all MOFs reported to date and the new **nun** topology (Fig. 4D).

We have recently reported our exploration of uranium-based MOFs with hexacarboxylate building units—i.e., **H₆PET-1**, extended **H₆PET-2** and **H₆PET-3**.²² **NU-1350**, which is crystallized from the combination of trigonal planar $[\text{UO}_2(\text{COO})_3]^-$ nodes and 6-connected PET-1 ligands, is based on a chiral 3,6-connected **nuc** net (Fig. 5). Topologically, PET-1 linkers in **NU-1350** are octahedral building units, which are different from the trigonal prisms found in **NU-1500** and **NU-1600**. It is worth noting that the **nuc** net is also known as a theoretical topological type—3,6T22—*via* Topocryst.²³ As suggested by Topocryst, some MOFs²⁴ with metal trimers and tritopic ligands are also based on the **nuc** net, although the augmented net in the original paper^{24a} shows metal trimers have yet to be topologically realized as octahedra. Reactions between trigonal planar uranyl nodes and extended versions of PET ligands (**H₆PET-2** and **H₆PET-3**) led to the formation of two three-fold catenated uranium-based MOFs with 3,6-connected **cml-c3** nets—i.e., **NU-1351** and **NU-1352**, respectively. The slight distortions of linkers when coordinated to inorganic uranyl nodes could be a possible reason for the structural differences between **NU-1350** and **NU-1351/NU-1352**.

Our group has also recently published work on the post-synthetic grafting of uranyl onto the Zr_6 -based MOF **NU-1000** to better understand uranyl coordination chemistry in MOFs for nuclear waste remediation. The crystal structure of the modified framework **NU-1000-U**, the first MOF containing a grafted actinide, demonstrates bidentate binding of uranyl, as well as slight shrinking of the Zr_6 clusters. Raman spectroscopy clarifies that the uranyl-oxo bond lengths remain unchanged after deposition, thus demonstrating that

Fig. 5 The synthesis of **NU-1350** with the 3,6-connected **nuc** net. The figure was reprinted with permission from reference 22. Copyright 2020, Springer Nature.

the coordination chemistry of uranyl is not strongly affected by anchoring to a framework.²⁵

3. Actinide cluster-based MOFs

3.1. Hexanuclear actinide-based MOFs

Due to the similarity of U(IV) and Th(IV) to tetravalent transition metal and lanthanide ions such as Zr(IV), Hf(IV), and Ce(IV), which form robust hexanuclear oxo-clusters,²⁶ these actinide ions have also been found to form similar hexanuclear clusters.²⁷ Specifically, Zr₆ clusters have been widely studied for the formation of MOFs with the first example being reported in the **UiO-66** series,²⁸ and similar topologies have been reported in U₆ and Th₆ cluster-based MOFs.²⁹

In light of the structural similarity between these tetravalent ion clusters, we have studied several series of isostructural MOFs, which span transition metals, lanthanides, and actinides; these studies allow for the systematic investigation

of the structure-property relationships between d-block and f-block hexanuclear clusters and their potential as Lewis acid catalysts and catalyst supports.³⁰ We have reported the electronic properties of two series of isostructural MOFs, **M-UiO-66** and **M-MOF-808** (M = Zr(IV), Hf(IV), Ce(IV) and Th(IV)). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) demonstrates that bands associated with the non-hydrogen-bonded hydroxyl groups located on the nodes of these two series of isostructural MOFs gradually red-shift with decreasing electronegativity of the metal center. Additionally, this shift also correlates with the binding affinity of H₂O molecules capping the metal atoms on the nodes which are coordinatively unsaturated from either accidental or designed missing-linker defects.³¹

To further probe the labile hydroxyl/water pair and/or the exposed metal center of the hexanuclear clusters, a series of isostructural MOFs (**M-NU-1008**, M = Zr(IV), Hf(IV), Ce(IV) and Th(IV)) were synthesized and investigated for their roles as Lewis acid catalysts in the CO₂ cycloaddition reaction with styrene oxide.^{30b} It was found that the dissociation of terminal water molecules from the M₆ clusters, which allows for higher exposure of the Lewis acidic metal sites, was crucial for increased catalytic activity; more labile water resulted in higher catalytic activity.

These interesting differences in the electronic properties and reactivity of the hexanuclear cluster node-based isostructural MOFs have prompted us to study the effect of these MOFs as catalyst supports, as the electronic properties of supports can influence the catalytic activity of supported catalysts.³²

Fig. 6 Structures of the isostructural **NU-1200** series and the catalytic activities of supported vanadium catalysts on these MOFs. Reprinted with permission from reference 30c. Copyright 2019 American Chemical Society.

Recently, we have synthesized four isostructural **M-NU-1200** ($M = \text{Zr}, \text{Hf}, \text{Ce}, \text{Th}$) MOFs and employed them as supports for vanadium catalysts (Fig. 6).^{30c} Their catalytic activity for 4-methoxybenzyl alcohol oxidation, by using molecular oxygen as the oxidant, showed that the nature of the support is important for the catalysis. For example, activity decreased going down the periodic table (**V-Zr-NU-1200** showed ~20 times higher turnover frequency than **V-Ce-NU-1200**). The catalytic activities are influenced by the electronegativity and the oxidation states of support metals.

3.2. Novel thorium cluster-based MOFs

As previously mentioned, actinide elements can exhibit unique coordination environments with various cluster-based nodes.^{11b} One notable example from our group is the solvothermal formation of **NU-905** from linear hexanuclear thorium cluster nodes and tetrakis(4-carboxyphenyl) porphyrin linkers (Fig. 7).³³ These linear nodes contain three crystallographically independent thorium atoms: Th1, Th2, and Th3 (Fig. 7a). Th1 and Th3 form a diamond at the center of the cluster and are each coordinated by nine oxygen atoms. Th1 is connected to six linker oxygens, while Th3 is coordinated to 4 linker oxygens. Th2 exists on the edge of the cluster and is eight-coordinated, with six of these oxygens coming from linkers. The high connectivity of each Th atom, combined with strong π - π stacking, renders this unusual

Fig. 7 Schematic representation of the structure of **NU-905**, showing the building blocks, packing and topology. Reprinted with permission from reference 33. Copyright 2019 American Chemical Society.

cluster stable. This coordination geometry has not been observed with any other element in the periodic table, and it thus highlights the truly unique coordination each actinide can achieve. As for a mechanism of formation, the tetramer unit composed of Th1 and Th3 may be subsequently coordinated to an additional, Th2-containing linker on either end during synthesis. The photoactive nature of the linkers motivated us to implement **NU-905** as a catalyst for photooxidation of mustard gas simulants. **NU-905** achieved complete and selective conversion of 2-chloroethyl ethyl sulfide to 2-chloroethyl ethyl sulfoxide within ten minutes under irradiation. It is clear that novel thorium clusters, stabilized through extensive ligand coordination and π - π stacking, may have extremely useful properties dictated by their structure.³³

Assembly of novel thorium polyoxo clusters within MOFs can also be directly controlled through the alteration of reaction conditions. The solvothermal reaction of thorium salts with 4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene

Fig. 8 Schematic representation of the structure of **NU-1008** and **NU-1011**, showing the building blocks and packing structure. Reprinted with permission from reference 34. Copyright 2019 American Chemical Society.

(TCPB-Br₂) linkers produces two distinct MOF phases: **Th-NU-1008** and **Th-NU-1011** (Fig. 8), both (4,8)-connected **csq** MOFs.³⁴ **Th-NU-1008** contains a hexanuclear thorium polyoxo cluster that is structurally analogous to the Zr₆O₈ nodes of previously reported **NU-1008**. The **Th-NU-1011** phase, favored at weakly acidic conditions, contains a previously unreported tetranuclear thorium polyoxo cluster; within this cluster are two crystallographically independent Th atoms connected primarily through the linkers with only two bridging oxygens. The assignment of **Th-NU-1011** and **Th-NU-1008** as kinetic and thermodynamic products, respectively, was confirmed through a single-crystal-to-single-crystal transformation from **Th-NU-1011** to **Th-NU-1008** in benzoic acid. Thus, by simply varying modulator concentrations, different thorium cluster topologies were accessed based on kinetic and thermodynamic favorability.³⁴

3.3. Novel neptunium cluster-based MOFs

Transuranic-element-based materials³⁵ were substantially underexplored in the past but are highly intriguing due to the presence of 5f electrons in bond formation that could lead to materials with unconventional chemical, electronic, and magnetic properties. Compared to other actinides with a pentavalent oxidation state, Np(V) is more stable due to its strong actinyl–actinyl bonding interactions.³⁶ Recently, in a collaboration led by Burns's group, a series of Np(V)-oxide based MOFs, **NNS-*x*** (*x* = 1,2,3), has been synthesized and characterized.³⁷ All these MOF are isostructural and feature an unprecedented 12-connected hexagonal prismatic SBU composed of 18 Np(V) neptunyl ions (Fig. 9A). The SBUs were further extended by tetratopic organic linkers to form the

(4,12)-connected **shp** topology (Fig. 9B, C).³⁸ The strong bond distortions of Np–O in the crystal structures of these MOFs were observed, indicating that this unusual SBU is likely generated *in situ* and stabilized by the bridging linker during the MOF formation process. The novel coordination chemistry in these neptunium MOFs demonstrates that uranium is not a surrogate for neptunium. Thus, a more fundamental study of neptunium is needed to better understand its role in the nuclear fuel cycle.

4. Conclusion

While the general concepts of transition metal coordination chemistry are transferable to the actinide elements, there are certain differences due to the more diffuse 5f orbitals in actinides. The structures of actinide-based MOFs and coordination polymers in general are highly dependent on the oxidation states of the actinide ions, the coordination geometry of the actinide ions/cluster, and the geometry/topicity of the chosen organic linkers. The unusual geometries of actinide ions make it challenging for synthetic chemists to design new structures based on knowledge obtained from the studies of transition-metal-based MOFs. However, the less studied actinide-based MOFs offer opportunities to explore novel and intriguing structures and functionalities with promising applications in nuclear waste mitigation, pollution control, and catalysis.

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Fig. 9 Schematic representation of the structure of **NNS-1**, showing the building blocks, packing and topology. Reprinted with permission from reference 37. Copyright 2019 American Chemical Society.

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