Thermodynamics and Electronic Properties of Heterometallic Multinuclear Actinide-Containing Metal–Organic Frameworks with “Structural Memory”


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Supporting Information

ABSTRACT: Thermodynamic studies of actinide-containing metal–organic frameworks (An-MOFs), reported herein for the first time, are a step toward addressing challenges related to effective nuclear waste administration. In addition to An-MOF thermochemistry, enthalpies of formation were determined for the organic linkers, 2,2′-dimethylbiphenyl-4,4′-dicarboxylic acid (H₂Me₂BPDC) and biphenyl-4,4′-dicarboxylic acid (H₂BPDC), which are commonly used building blocks for MOF preparation. The electronic structure of the first example of An-MOF with mixed-metal AnAn'-nodes was influenced through coordination of transition metals as shown by the density of states near the Fermi edge, changes in the Tauc plot, conductivity measurements, and theoretical calculations. The “structural memory” effect (i.e., solvent-directed crystalline–amorphous–crystalline structural dynamism) was demonstrated as a function of node coordination degree, which is the number of organic linkers per metal node. Remarkable three-month water stability was reported for Th-containing frameworks herein, and the mechanism is also considered for improvement of the behavior of a U-based framework in water. Mechanistic aspects of capping linker installation were highlighted through crystallographic characterization of the intermediate, and theoretical calculations of free energies of formation (ΔG) for U- and Th-MOFs with 10- and 12-coordinated secondary building units (SBUs) were performed to elucidate experimentally observed transformations during the installation processes. Overall, these results are the first thermochemical, electronic, and mechanistic insights for a relatively young class of actinide-containing frameworks.

INTRODUCTION

The stability of actinide-containing architectures and their chemical interactions with the environment have been increasingly studied over the past decades because of their significance for nuclear waste administration. Due to their modularity, structural versatility, high porosity, and high tunability, metal–organic frameworks (MOFs) have been utilized as a platform for nuclear waste sequestration and actinide immobilization, resulting in the development of materials with a high actinide content and possessing minimal structural density. However, the field of actinide-based MOFs, especially in comparison with non-actinide-containing frameworks, suffers from the fact that fundamental properties including thermodynamics, electronics, or detailed photophysics have not been investigated.

Herein, we report (i) the first thermochemical studies performed for any An-based MOFs including several examples

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of the common organic linkers, (ii) the first example of heterometallic multinuclear An-MOF nodes with a coordinated transition metal and the first electronic structure studies using density of states (DOS) and conductivity measurements, (iii) over three-month water stability of a Th-MOF, (iv) structural “crystalline–amorphous–crystalline” cycling of An-MOFs as a function of metal node geometry, and (v) theoretical studies establishing the dependence of An-MOF stability on the nature of linker connectivity to the secondary building unit (SBU, Scheme 1). In addition, novel actinide-containing frameworks, M-Linker-, (M (Th, U) = a metal in the node, Linker = an organic linker, and n = number of carboxylic groups attached to a metal node) such as Th₆O₄(OH)₄(NO₃)₂(Me₆BPDC)₅ (Th₆-Me₆BPDC-NO₃-10; Me₂BPDC²⁻ = 2,2’-dimethylbiphenyl-4,4’-dicarboxylate), Th₆O₄(OH)₄(Me₆BPDC)₄ (Th₆-Me₆BPDC-8), and U₆O₄(OH)₄(TFA)₂(Me₆BPDC)₃ (U₆-Me₆BPDC-TFA-10, TFA = trifluoroacetate, Figures 1 and S4), were prepared.

The discussion in this paper will be organized in the following order: synthetic details and chemical stability of the An-MOFs, their thermochemical studies including the measurements for organic linkers, analysis of the electronic structure of the heterometallic An-MOFs, “structural memory” effect of An-MOFs (i.e., solvent-directed crystalline–amorphous–crystalline cycling as a function of metal node geometry), and mechanistic insights on the capping linker installation process (i.e., postsynthetic linker coordination to framework metal nodes). The comprehensive analysis of An-MOFs includes single-crystal and powder X-ray diffraction (PXRD), inductively coupled plasma mass spectrometry (ICP-MS), conductivity, solution calorimetric measurements, thermogravimetric analysis, nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopies (XPS), as well as theoretical modeling.

**RESULTS AND DISCUSSION**

**Synthetic Details and Chemical Stability.** Preparation of Th₆O₄(OH)₄(NO₃)₂(Me₆BPDC)₅ (Th₆-Me₆BPDC-NO₃-10), consisting of Th-metal nodes (Figures 1 and S4), has been performed solvothermally by heating Th(NO₃)₄·H₂O and H₂Me₆BPDC in N,N-dimethylformamide (DMF) at 120 °C for 24 h (Figure S4, more experimental details can be found in the Supporting Information (SI) and Experimental Section below). The presence of labile nitrate groups coordinated to the equatorial position of metal nodes allowed us to perform postsynthetic linker installation as described below (Figure 6). The Th₆O₄(OH)₄(BPDC)₈(DMF)₆ MOF (Th₆-BPDC-12; BPDC²⁻ = biphenyl-4,4’-dicarboxylate) was prepared by heating Th(NO₃)₄·H₂O and H₂BPDC in DMF at 120 °C for 72 h.

Modification of the synthetic conditions by increasing the molar ratio of metal salt to linker used for Th₆-Me₆BPDC-NO₃-10 preparation allowed us to reduce the “metal-node-saturation degree” resulting in the synthesis of Th₆-Me₆BPDC-8 with eight linkers per metal node versus ten Me₂BPDC²⁻ observed for Th₆-Me₆BPDC-NO₃-10. Unsaturated nodes (i.e., with a number of linkers <12) can affect framework chemical stability³⁸ as discussed below. We were able to isolate two
different phases of Th$_2$-Me$_2$BPDC-8: Th$_2$-Me$_2$BPDC-8a and Th$_2$-Me$_2$BPDC-8b. The Th$_2$-Me$_2$BPDC-8b MOF crystallizes in the tetragonal P4$_2$/mm space group (a = b = 25.5223(17) Å and c = 14.6275(11) Å), while Th$_2$-Me$_2$BPDC-8a is isostructural to previously reported U$_2$-Me$_2$BPDC-8 (P4$_2$/mm space group) possessing a = b = 24.9768(18) Å and c = 15.9864(12) Å unit cell parameters. A phase transition from Th$_2$-Me$_2$BPDC-8a to Th$_2$-Me$_2$BPDC-8b was observed after soaking of Th$_2$-Me$_2$BPDC-8a in water, and then the reverse transformation from Th$_2$-Me$_2$BPDC-8b to Th$_2$-Me$_2$BPDC-8a was detected through reimmersion of Th$_2$-Me$_2$BPDC-8b into DMF (Figure S5). Since Th$_2$-Me$_2$BPDC-8a was isolated as the major pure phase, it has been chosen for further comprehensive analysis described below, and it will be referred to as “Th$_2$-Me$_2$BPDC-8” (without “a”) in the rest of the manuscript for simplicity.

As a first step to study the thermochemistry and electronic structure of An-MOFs, we explored their chemical stability. For instance, we observed significantly different behavior of Th-MOFs (Th$_2$-Me$_2$BPDC-8 or Th$_2$-Me$_2$BPDC-NO$_3$-10) versus U$_2$-Me$_2$BPDC-8, which could be partially explained by a wide range of accessible oxidation states in the latter case.

Crystals of Th$_2$-Me$_2$BPDC-8 were immersed in water, and changes in crystallinity were monitored by PXRD. We found that Th$_2$-Me$_2$BPDC-8 remained stable in water for three months, the longest time reported for any An-MOFs, rendering Th-MOFs (Th$_2$-Me$_2$BPDC-8, possesses a great degree of structural dynamism) to be one of the most water stable An-MOFs reported to date (Figure 2). Following this result, the stability of U$_2$-Me$_2$BPDC-8 was also explored. Crystals of U$_2$-Me$_2$BPDC-8 were soaked in water for a week under a nitrogen atmosphere. The uranium-based MOF retained its crystallinity under prolonged immersion in water, preserving uranium in the +4 oxidation state, a unique feature which was only achieved due to the fact that the framework was kept under an inert atmosphere. In air, U$^{4+}$ transforms to U$^{6+}$ based on XPS studies leading to framework degradation. In contrast, Th$_2$-Me$_2$BPDC-8 (Th has only one stable oxidation state, +4) does not require this specific precaution, and as expected, Th$^{4+}$ was preserved in air. Under a nitrogen atmosphere, U$_2$-Me$_2$BPDC-8 not only retains its crystallinity, but the single crystals were still suitable for single-crystal X-ray diffraction analysis (Figure 2).

A crystallographic comparison between as-synthesized U$_2$-Me$_2$BPDC-8 and the same sample after immersion in water for 4 days revealed that the framework structure compressed along the c-axis (Δ = 0.87 Å) and exhibited a slight elongation along the a and b axes (Δ = 0.17 Å) resulting in an overall unit cell volume shrinkage (Δ = 417 Å$^3$) from 9972 Å$^3$ to 9555 Å$^3$.

Promoted by the successful water stability experiments with the An-MOF-8, we proceeded to analyze the stability of An-MOFs with 10-coordinated SBUs, specifically Th$_2$-Me$_2$BPDC-NO$_3$-10. The same unexpected result was observed for Th$_2$-Me$_2$BPDC-NO$_3$-10, which was found to be stable in water for 11 days (Figure 2). The FTIR spectroscopic studies of the water-treated An-MOFs (Figures S9 and S10) confirmed the replacement of DMF with water in the MOFs through monitoring the gradual increase of the broad band corresponding to the μ(O–H) (3400 cm$^{-1}$) stretching mode of water, as well as the decrease of stretching modes corresponding to DMF molecules (2927 cm$^{-1}$, 1254 cm$^{-1}$, 1137 cm$^{-1}$, and 1090 cm$^{-1}$). To summarize, we demonstrated that An-MOFs, in particular, Th-containing frameworks can substantially surpass the previously reported limited stability and, in fact, can retain their structural integrity in aqueous environments for significant lengths of time.

The effect of a saturated metal node on An-MOFs was evaluated using a Th-based MOF with 12-coordinated SBUs (Th$_2$-BPDC-12). This MOF, which is analogous to the very stable Zr-based MOF (UiO-67, UiO = University of Oslo), was observed to also be extremely stable in water for at least one month (Figure S28). However, no reversible structural transformations were detected in this system, implying that MOF structural dynamism is a function of a metal-node saturation degree.

After the water stability tests, we investigated the stability of the robust Th$_2$-Me$_2$BPDC-8 in air. The structural degradation and subsequent restoration of the crystallinity of the 8-coordinate Th-MOF in different solution environments were monitored by PXRD. When the Th$_2$-Me$_2$BPDC-8 is exposed to air, we observed significant framework degradation as shown in Figure 3. However, the crystallinity was restored after exposure to DMF for just 1 h, as shown in Figure 3. A similar tendency has previously been observed for Zr frameworks, which underwent significant structural transformations during framework evacuation, while a reverse structural process occurred upon immersion of the Zr-MOF in DMF. Thus, we demonstrated, for the first time, that an actinide-containing MOF, Th$_2$-Me$_2$BPDC-8, possesses a great degree of flexibility by undergoing more drastic reversible phase transformations in comparison with the robust and “more conservative” Zr-MOF.

**Thermochemical Studies.** Intrigued by the exceptional water stability of the An-MOFs, we delved into thermochem-
perform this study, the sample was placed in a controlled atmosphere glovebox (0.2 ppm of O₂ and H₂O) loaded into glass ampoules and subsequently sealed. The ampule was then transferred to a TAM III (TA Instruments) room temperature solution microcalorimeter and immersed in a 2:1 (v:v) 5 M HCl/DMF solvent system while recording changes in temperature offset values.69 Thermocyclic chemical reactions were employed to calculate the reaction dissolution enthalpy, and experimentally measured and related thermodynamic values were used to calculate the enthalpy of formation for Th₆(Me₂)BPDC-8.

Table 1. Enthalpies of Formation of Th₆(Me₂)BPDC-8 Evacuated and Nonevacuated, H₆Me₂BPDC, and H₂BPDC Computed from Experimental Thermodynamic Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔHf (298 K) ± ΔHf (x K)</th>
<th>ΔHf (298 K) ± ΔHf (x K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th₆(Me₂)BPDC-8</td>
<td>−383.73 ± 7.75</td>
<td>−14317.45 ± 8.6</td>
</tr>
<tr>
<td>Th₆(Me₂)BPDC-8 (evacuated)</td>
<td>−312.21 ± 6.53</td>
<td>−3987.08 ± 7.72</td>
</tr>
<tr>
<td>ThO₂ (Thorite)</td>
<td>311.65 ± 1.87</td>
<td>−1226.4 ± 5.35</td>
</tr>
<tr>
<td>H₆Me₂BPDC</td>
<td>4.48 ± 0.06</td>
<td>−715.22</td>
</tr>
<tr>
<td>H₂BPDC</td>
<td>13.25 ± 0.06</td>
<td>−651.00</td>
</tr>
<tr>
<td>DMF</td>
<td>−9.45 ± 0.01</td>
<td>−239.4 ± 1.20</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.07 ± 10</td>
<td>−285.8 ± 0.10</td>
</tr>
</tbody>
</table>

ΔHf (left) and ΔHf (right) are the enthalpies of dissolution and formation, respectively. "Average of the measurements. "The standard error of the average value. "Computed as the square root of the sum of squares of reported errors. "Computed for the solvent (2:1 v:v 5 M HCl/DMF, dissolution at pH = 3.3).

Standard enthalpies of formation from the elements, ΔHf (298 K) for the Th-MOF sample were calculated using the appropriate standard enthalpies of formation of the reaction components multiplied by their reaction stoichiometric coefficients and including the dissolution reaction enthalpy of the sample. The data and computed results are reported in Tables 1, S1, and S2 as an average of the experiments with uncertainties reported as the standard error of the experimental average.19–42 The average measured dissolution enthalpy for Th₆(Me₂)BPDC-8 (as synthesized) was found to be −383.73 ± 7.75 kJ/mol per formula unit (see Table 1 and the Supporting Information for more details). The calculated enthalpy from solution components for Th₆(Me₂)BPDC-8 is 2030.47 ± 7.96 kJ/mol of formula, which corresponds to 338.32 ± 1.33 kJ/mol enthalpy per mole of Th (more information on the equations is given in the SI). To shed more light on An-MOFs stability, we further estimated the stabilizing effect of the solvent (DMF) occupying the MOF pores.45 To effectively perform this study, we carried out solution calorimetry on the evacuated sample of Th₆(Me₂)BPDC-8. We found the measured dissolution enthalpy to be −312.21 ± 6.53 kJ/mol of formula unit. The calculated enthalpy from solution components for evacuated Th₆(Me₂)BPDC-8 is 2148.90 ± 7.96 kJ/mol of formula, which corresponds to 360.10 ± 1.13 kJ/mol enthalpy per mole of Th, implying that the DMF solvent stabilizes Th₆(Me₂)BPDC-8 by −21.78 ± 1.33 kJ/mol per mole of Th. These observations show that DMF solvent is more stabilizing in the Th-MOF in comparison with the stabilization effects of solvent reported for MOF-5 (−4.8 kJ/mol of Zn)46 and ZIF-4 (−3.0 kJ/mol of Zn).47 The standard heat of formation of the evacuated Th-MOF from its components in their standard state was also computed to be −9387.08 ± 7.72 kJ/mol (Table 1). The results obtained from our studies show that the solvent molecules contribute to the stabilization of the Th₆(Me₂)BPDC-8 MOF, suggesting a strong interaction of the solvent with the MOF. This solvent–framework interaction is therefore suggested as a key to the observed “structural memory” effect exhibited by the Th-MOF. Following this experiment, the standard heat of formation of the Th-MOF from its components in their standard state was also computed. The obtained value for Th₆(Me₂)BPDC-8 (Table 1) was found to be −14317.45 ± 8.60 kJ/mol. Thus, according to the determined values, MOF formation is a favorable process which is in line with the previous observations made for Cu₃(BTC)₂ (BTC⁻ = benzenetricarboxylate), Zn₃(BTC)₂, and MOF-5.58,43,44

Electronic Structure of Heterometallic An-MOFs. The tunability of the electronic properties of An-MOFs is an unexplored challenge but, at the same time, a fascinating opportunity to compare the effect of f-electrons and unusual oxidation states on the electronic structure of a framework. In this manuscript, we compare the electronic properties of the parent An-MOFs with the properties of heterometallic AnAn’-MOF and AnAn’-M’MOF (M = transition metal).

As a method to synthesize AnAn’-MOFs, we have chosen postsynthetic cation exchange, in which U₆Me₂BPDC-8 crystals were soaked in a solution of ThCl₄, resulting in the formation of U₁₂₃Th₄Me₂BPDC-8. The ratio of uranium to thorium was determined by ICP-MS. As a result of this transformation, the dark green powder converts to an almost white sample. Interestingly, such transmetalation did not occur under a nitrogen atmosphere but only when performed in air. The U₆Me₂BPDC-8 framework remained intact, and reaction
work was heated in a 0.25 M Co(NO₃)₂ solution at 75 °C for 48 h, resulting in U₁₂₃Th₄₋₇₋Me₂BPDC-8. Cobalt was chosen as a transition metal due to the intriguing behavior previously observed for other cobalt-containing heterometallic MOFs. Attempts at incorporation of Co(II) directly into the U₆-Me₂BPDC-8 MOF were unsuccessful due to instability of the U-MOF. Initially, we employed XPS analysis of U₁₂₃Th₄₋₇₋Me₂BPDC-8 and U₁₂₃Th₄₋₇₋Co₋₇₋Me₂BPDC-8 MOFs to monitor changes in the DOS near the Fermi edge (E_F) upon incorporation of the cobalt ion (Figure 3).

Through comparison of the band gap values estimated from Tauc plots (Figure S14), we observed a decrease of the band gap from 3.3 eV (Th₄₋₇₋Me₂BPDC-8) to 2.5 eV (U₁₂₃Th₄₋₇₋Me₂BPDC-8) in the case of An-MOF comprised of both uranium and thorium. The integration of cobalt into U₁₂₃Th₄₋₇₋Me₂BPDC-8 led to further band gap reduction to 1.9 eV.

To rationalize such changes in the electronic structures of heterometallic An-MOFs, we carried out theoretical studies on the truncated model of the U₁₂₃Th₄₋₇₋Me₂BPDC-8 (U/Th-8, Figure 4) and U₁₂₃Th₄₋₇₋Co₋₇₋Me₂BPDC-8 (U/Th-Co-8, Figure 4) MOFs. The density functional theory (DFT) calculations revealed that the Co node extension in U₁₂₃Th₄₋₇₋Me₂BPDC-8 (Figure 4) resulted in changes of the electronic structure near E_F. The band gap values for U₁₂₃Th₄₋₇₋Me₂BPDC-8 and U₁₂₃Th₄₋₇₋Co₋₇₋Me₂BPDC-8 were found to be 3.0 and 1.9 eV, respectively. The partial DOS shown in Figure 4 were obtained by adding the atomic projected DOS over different groups of elements such as C, H, O, Th, U, and Co. Although these plots include contribution from all orbitals, the orbital-projected DOS suggest that DOS of U₁₂₃Th₄₋₇₋Me₂BPDC-8 near E_F originate mainly from the uranium 5f-orbitals, whereas the DOS above E_F (conduction band) are primarily composed of U and Th 5f-orbitals (Figure 4).

When the metal nodes are extended by cobalt, the DOS near E_F are dominated by contributions from the Co 3d-orbitals and oxygen 2p-orbitals (Figure 4), and the band gap is reduced to 1.9 eV. As expected, the decrease of the band gap resulted in changes of the electronic properties of heterometallic MOFs. Indeed, the conductivity (σ) of U₁₂₃Th₄₋₇₋Me₂BPDC-8 was found to be 7.0 × 10⁻¹⁰ S·cm⁻¹, and it was enhanced by 3 orders of magnitude in the case of cobalt incorporation to 1.4 × 10⁻⁷ S·cm⁻¹ (for U₁₂₃Th₄₋₇₋Co₋₇₋Me₂BPDC-8). Our current studies represent the initial steps for achieving improved understanding of the behavior of heterometallic systems containing two or more atoms and can possibly lead to the ability to tune the electronic structure of An-MOFs.

“Structural Memory” Effect of An-MOF. There are a number of studies revealing the unprecedented stability of Zr-based frameworks. For instance, it was reported that the Zr-based MOF (Uio-67) with 12-coordinated SBUs is stable in a wide range of solvents for an extended period of time without detectable structural changes. Indeed, our studies of Zr₆-Me₂BPDC-8 in a range of solvents, including methanol (MeOH), ethanol (EtOH), acetonitrile (ACN), hexanes, dichloromethane (DCM), chloroform, ethyl acetate (EtOAc), and tetrahydrofuran (THF), demonstrated that the structural integrity was preserved, and in addition, there were no or only minimal structural transformations observed as shown in Figures 5 and S26. In contrast, our study of the relatively robust Th₄₋Me₂BPDC-8 framework, possessing the same metal node arrangement as its Zr-analog, revealed structural dynamism (i.e., breaking a long-range structural order resulting in a significant loss of MOF crystallinity and its restoration as a function of exposure to solvent (Figures 5 and S22–26)).

We studied structural dynamism in Th₄₋Me₂BPDC-8 and Th₄₋Me₂BPDC(NO₃)₁₀ MOFs using 11 different solvents (ranging from polar protic and aprotic to nonpolar solvents). Exposure of Th₄₋Me₂BPDC-8 to solvents such as MeOH and ACN resulted in significant loss of crystallinity (Figures 5 and S23). However, MOF crystallinity was fully restored by soaking the relatively amorphous samples in DMF, N,N-diethylformamide, or N,N-dimethylacetamide (Figure S21). In other polar protic solvents such as EtOH or aprotic solvents such as THF, EtOAc, acetone, or ACN, the PXRD revealed similar crystallinity loss except for Th₄₋Me₂BPDC(NO₃)₁₀ in MeOH. This fact allowed us to closely look into the transformation of Th₄₋Me₂BPDC(NO₃)₁₀ in methanol using single-crystal X-ray diffraction since the crystals were preserved upon solvent exchange. Despite the fact that the data collection was performed on Th₄₋Me₂BPDC(NO₃)₁₀ crystals sealed in a capillary under solvent (Figure S19), the structural analysis revealed changes in the unit cell parameters from a = b = 23.7918(8) Å and c = 19.6923(7) Å for pristine Th₄₋Me₂BPDC(NO₃)₁₀ (see the SI) to a = b = 24.0205(8) Å and c = 19.7574(6) Å observed for the Th-MOF immersed in methanol. As shown in a recent comprehensive literature
expected, there was no evidence of structural dynamism, and PCN-700 did not undergo any structural transformations as shown in Figures 5 and S26. It is important to highlight that it is not a “breathing” behavior, a commonly known process for MOFs occurring during their evacuation, but rather a different concept: a “structural memory” effect (i.e., solvent-directed crystalline–amorphous–crystalline cycling as a function of metal node geometry), which is reported for the first time for actinide-containing frameworks.

**Mechanistic Insights on Capping Linker Installation in An-MOFs.** Reports by Yaghi and co-workers, Zhou and co-workers, and a number of other research groups have demonstrated the possibility of the functionalization of MOFs by postsynthetic installation of more than one capping linker.52,54–59 Herein we report not only access to structures through sequential linker installation in Th-based MOFs, which could not be prepared by direct synthesis, but more importantly, through single-crystal X-ray studies, we elucidate a possible mechanism involved in the installation process. As in the case of transition metal coordination (described above), the main requirement for capping linker installation is the presence of unsaturated metal nodes. The Th$_2$Me$_2$BPDC-NO$_3$-10 MOF meets the structural criteria (Figures 1 and S4) through the presence of unsaturated metal nodes, and the pocket B of 15.1 Å size (a distance between the centroids of the oxygen atoms of the terminal nitrate groups, Figure 6) is suitable for capping linker installation. This pocket size is in line with the 15.3 Å length of the linker 2,2”-dimethylterphenyl-4,4”-dicarboxylic acid (H$_2$Me$_2$TPDC, Figure 6). To perform installation, the crystals of Th$_2$Me$_2$BPDC-NO$_3$-10 were heated in a DMF solution of H$_2$Me$_2$TPDC. The single-crystal X-ray diffraction analysis surprisingly revealed that instead of capping linker installation, heating of Th$_2$Me$_2$BPDC-NO$_3$-10 for 24 h in a solution of H$_2$Me$_2$TPDC linker resulted in the formation of Th$_2$Me$_2$BPDC-8, implying the detachment of two equatorial linkers, Me$_2$BPDC$_{5-}^{2-}$, as shown in Figure 6.

In the intermediate with eight-coordinated SBUs, the linker removal resulted in the formation of a second pocket A with a size of 10.7 Å (a distance between the two centroids of the terminal oxygen atoms, Figure 6). Based on this data, it is plausible to suggest that linker installation could result in structural deformation of the MOF with 10-coordinated metal nodes to match the differences of the size of the Me$_2$BPDC linker and pocket A ($\Delta d = 0.4$ Å). For that transformation, the size of the other pocket B should be compressed, which is accompanied by the formation of the intermediate with vacant A and B pockets (Figure 6).

Focusing on the Th-MOF with the 8-coordinated SBUs as a possible intermediate in the installation process, we continued to explore the flexibility of the framework by attempting to reinstall the detached Me$_2$BPDC$_{5-}^{2-}$ linker. For that, the intermediate MOF was heated in a DMF solution of H$_2$Me$_2$BPDC and H$_2$Me$_2$TPDC for 2 days at 75 °C. The single-crystal X-ray data demonstrated installation of both linkers in A and B pockets resulting in the formation of 12-coordinated metal nodes. As shown in Figure 6, the size of pocket B expanded from 15.1 to 15.3 Å in order to accommodate the 15.3 Å-long Me$_2$TPDC$_{5-}^{2-}$ linker. To provide further mechanistic insights on capping linker installation occurring in An-containing frameworks, we explored installation of a linker with one phenyl ring (H$_2$BDC = 1,4-benzenedicarboxylic acid; length ($l$) = 6.9 Å), two phenyl rings.
The installation of the H$_{10}$MOF with the 8-coordinated SBU. The truncated 10 and 12 coordinated SBUs from the truncated model C and O atoms. (coordinated SBUs, respectively, while gray and red spheres represent spheres were chosen for Th atoms for MOFs with 10- and 12-coordinated metal nodes of both MOFs. The teal and purple linker installation using Th$_{10}$MOFs with 10-coordinated and 12-coordinated SBUs were obtained via direct synthesis, highlighting the structural diﬀerence between the adjacent metal nodes of both MOFs. The teal and purple spheres were chosen for Th atoms for MOFs with 10- and 12-coordinated SBUs, respectively, while gray and red spheres represent C and O atoms. (bottom) Table of calculated energy of formation of the truncated 10 and 12 coordinated SBUs from the truncated model with the 8-coordinated SBU.

(H$_{2}$Me$_{2}$BPDC; l = 11.1 Å), and four phenyl rings (H$_{2}$QPDc = 1,1′,4,1′,4,1′-quaterphenyl-4,4′-dicarboxylic acid; l = 19.9 Å). The installation of the H$_{2}$BDC linker resulted in a change in the PXRD powder pattern (Figure S31) similar to observations by the Zhou group involving coordination of the same H$_{2}$BDC to a MOF with 8-coordinated Zr-nodes. Figure S31 shows similarity in the PXRD pattern between the Th- and Zr-BDC-installed MOFs, indicative of successful installation of the BDC$^{2-}$ linker into the Th$_{6}$-Me$_{2}$BPDC-NO$_{3}$-10 MOF. $^1$H NMR spectroscopic studies of the digested MOF samples were further used to confirm installation of the BDC$^{2-}$ linker into the MOF (Figure S35). Table S9 summarizes all installation attempts and the degree of capping linker integration. The installation processes of H$_{2}$Me$_{2}$BPDC and H$_{2}$QPDc into Th$_{6}$-Me$_{2}$BPDC-NO$_{3}$-10 were monitored via single-crystal X-ray diffraction and NMR/FTIR spectroscopy. In both cases, our attempts to facilitate the conversion from 10-to-12-coordinated metal nodes were unsuccessful. PXRD and single-crystal X-ray studies did not reveal any structural changes even after several days of heating of the parent framework in a solution of the corresponding linker. It is plausible to suggest that the linker with four phenyl rings (QPDc$^{2-}$) cannot fit due to its size (19.9 Å). However, the length of the Me$_{6}$BPDC$^{2-}$ linker is more likely to fit into pocket B (l = 11.1 Å). To elucidate the possible reason impeding Th$_{6}$-Me$_{2}$BPDC-NO$_{3}$-10 to Th$_{6}$-Me$_{2}$BPDC-12 transformation, we attempted a 10-to-12 transformation using a nonmethylated H$_{2}$BPDC linker. Instead of a 10-to-12 transformation, the BPDC$^{2-}$ replaced Me$_{6}$BPDC$^{2-}$ as confirmed by single-crystal X-ray studies (Figure 7) resulting in a 10-coordinate Th$_{6}$-BPDC-10 MOF, which cannot be synthesized via direct synthesis. Furthermore, we prepared Th$_{6}$-BPDC-12 via direct synthesis. As shown in Figure 6, the orientation of adjacent metal nodes in Th$_{6}$-Me$_{2}$BPDC-10 does not allow for capping linker installation with the H$_{2}$Me$_{2}$BPDC linker (Figure S33) and is drastically different from that in Th$_{6}$-BPDC-12.

To elucidate the theoretically observed flexibility of the An-MOF systems, we carried out theoretical calculations to support the observed transformations during the installation processes. $^6$ Free energies of formation ($\Delta G^{f}$) for the U- and Th-MOFs with 10-coordinated and 12-coordinated SBUs were calculated using their respective MOFs with 8-coordinated SBUs as reference structures. For such calculations, we employed the truncated cluster models, in which two formic acid linkers attached to a M-8 cluster resulting in a M-10 cluster and addition of four linkers results in a M-12 cluster.
(Figure S2). The $\Delta G_f$ values were calculated using eqs (1) and (2) for M-10 and M-12, respectively.

$$\Delta G_f [\text{M-10}] = G_{\text{M-10}} - ([G_{\text{M-10}} + 2G_{\text{HCOOH}}])$$  \(1\)

$$\Delta G_f [\text{M-12}] = G_{\text{M-12}} - ([G_{\text{M-12}} + 4G_{\text{HCOOH}}])$$  \(2\)

We found that $\Delta G_f$ values for both M-10 and M-12 compounds are negative (Figure 6), thus confirming the experimental feasibility of the formation of MOFs with 10-coordinated and 12-coordinated SBUs from their analogs with 8-coordinated metal nodes.

**CONCLUSION**

The first studies of thermochemistry and electronic structure shed light on the properties of monometallic and heterometallic An-containing frameworks including the first examples of actinide-containing MOFs with incorporated transition metals. The thermochemical values reported for frameworks and organic linkers render the presented studies valuable for the future prediction of thermodynamic stability of frameworks. The An-MOFs with mixed-metal nodes allowed us to probe the effect of f-electrons on the electronic structure including the evaluation of the contribution from the transition metal. In combination with theoretical modeling, the electronic properties of An-MOFs were studied spectroscopically (i.e., DOS near the E_F and Tauc plots) and through conductivity measurements. The three-month water stability of An-MOFs provides an opportunity for their detailed studies even in aqueous media. The “structural memory” effect makes the considered framework containing a metal in the +4 oxidation state distinct from the widely used Zr(IV) analogs. We experimentally observed structural flexibility and dynamism of the Th-MOFs involving crystalline-to-amorphous-to-crystalline transformations upon solvent treatments. Through single-crystal X-ray diffraction, we demonstrated that capping linker installation went through a unique intermediate, which has never been detected for any framework to date. In light of the extreme importance of proper radioactive waste administration, we envision that our studies are the first steps in attaining insights for utilizing An-based MOFs as a unique platform where chemical interactions between actinide-containing species can be fundamentally understood and expanded upon.

**EXPERIMENTAL SECTION**

**Caution!** Uranium and thorium salts are radioactive and chemically toxic reactants; suitable precautions, care, and protection for the handling of such substances must be followed.

**Materials.** UCl₄ (>95%, International Bio-Analytical Industries Inc.), ThCl₅ (>95%, International Bio-Analytical Industries Inc.), Th(NO₃)₄·H₂O (99.8%, Strem Chemicals Inc.), ZrCl₄ (99.5%, Alfa Aesar), Co(NO₃)₂·6H₂O (99%, Stem Chemicals Inc.), potassium acetate (lab grade, Ward’s Science), K₂CO₃ (lab grade, Ward’s Science), 1,4-dibromobenzene (98%, Sigma-Aldrich), 4-methoxycarboxylic acid (97%, Oakwood Chemical), methanol (ACS grade, Fischer Scientific), ethanol (200 proof, Decon Laboratories, Inc.), hexanes (ACS grade, VWR Chemicals), dimethyl sulfoxide (ACS grade, Fisher Scientific), acetone (ACS grade, VWR Chemicals), acetonitrile (ACS grade, Fischer Scientific), chloroform (ACS grade, BDH), ethyl acetate (ACS grade, Fisher Scientific), N,N-dimethylacetamide (99%, Alfa Aesar), N,N-diethylformamide (99%, TCI chemicals), N,N-dimethylformamide (ACS grade, BDH), chloroform-d (Cambridge Isotope Laboratories, Inc.), and DMSO-d₆ (Cambridge Isotope Laboratories, Inc.) were used as received.

**Synthesis.** The compounds 1,4-benzedicarboxylic acid (H₂BDC) and 4,4′-biphenyldicarboxylic acid (H₂BPDC) were commercially available while 2,2′-dimethylbiphenyl-4,4′-dicarboxylic acid (H₂Me₂BPDC), 2,2′-dimethylterphenyl-4,4′-dicarboxylic acid (H₂Me₂TPDC), 2,4-quaterphenyl-4,4′-dicarboxylic acid (H₂QPDC), Z₈Me₂BPDC-8, and U₂Me₂BPDC-8 were prepared according to the reported procedures.

**Synthesis and Characterization of Th₄Me₂BPDC-NO₃-10.** A mixture of Th(NO₃)₄·H₂O (9.6 mg, 20 μmol), H₂Me₂BPDC (4.3 mg, 16 μmol), concentrated nitric acid (35 μL), and DMF (0.79 mL) was put in a 1-dram vial and heated in an isothermal oven at 120 °C for 24 h. After cooling to room temperature, the colorless crystals of Th₄Me₂BPDC-NO₃-10 (7.2 mg, 2.3 μmol, yield: 73%) were collected by filtration and washed three times with DMF. FTIR (neat, cm⁻¹): 3438, 2927, 2864, 1656, 1593, 1537, 1408, 1383, 1255, 1207, 1093, 1062, 1007, 910, 863, 777, and 732 (Figure S5). The obtained crystals were suitable for single-crystal X-ray analysis. A detailed description of the data collection and refinement details is given in the Supporting Information. Table S3 contains the crystallographic refinement details. As shown in Figure S6, the PXRD pattern of as-synthesized Th₄Me₂BPDC-NO₃-10 matches the simulated pattern from the single-crystal X-ray data. PXRD studies were also used to confirm the crystallinity of the bulk material (Figure S6). The thermal stability of Th₄Me₂BPDC-NO₃-10 was studied by thermogravimetric analysis, which demonstrated rapid loss of solvent molecules at the 25–200 °C temperature range (Figure S12). The observed weight loss (∼40 wt %) at this temperature range can be attributed to removal of the noncoordinated solvent mixture of DMF and H₂O.

**Synthesis and Characterization of Th₄Me₂BPDC-8.** A mixture of Th(NO₃)₄·H₂O (31 mg, 64 μmol), H₂Me₂BPDC (4.3 mg, 16 μmol), nitric acid (25 μL), and DMF (0.75 mL) was put in a 1-dram vial and heated in an isothermal oven at 120 °C for 24 h. After cooling to room temperature, the colorless crystals of Th₄Me₂BPDC-8 (8.1 mg, 2.9 μmol, yield: 74%) were collected by filtration and washed three times with DMF. IR (neat, cm⁻¹): 3418, 2930, 2860, 1650, 1587, 1543, 1466, 1408, 1382, 1297, 1254, 1137, 1094, 1062, 1032 1017, 912, 863, 815, 778, 734, and 660 (Figure S7). A prolonged 72 h heating of the mixture resulted in Th₄Me₂BPDC-8b (minor phase) crystals which were suitable for single-crystal X-ray analysis. A detailed description of the data collection and refinement details is given in the Supporting Information. Table S3 contains the crystallographic refinement data. As shown in Figure S7, the PXRD pattern of as-synthesized Th₄Me₂BPDC-8a matches the simulated pattern from the single-crystal X-ray data for U₂Me₂BPDC-8. PXRD studies were also used to confirm the crystallinity of the bulk material (Figure S7). The thermal stability of Th₄Me₂BPDC-8a was studied by thermogravimetric analysis, which demonstrated rapid loss of solvent molecules at the 25–175 °C temperature range (Figure S11). The observed weight loss (∼37 wt %) at this temperature range can be attributed to removal of the noncoordinated solvent mixture of DMF and H₂O.

**Synthesis and Characterization of Th₄BPDC-12.** A mixture of Th(NO₃)₄·H₂O (12 mg, 26 μmol), H₂BPDC (1.6 mg, 6.4 μmol), trifluoroacetic acid (25 μL), and DMF (0.56 mL) was put in a 1-dram vial and heated in an isothermal oven at 120 °C for 72 h. After cooling to room temperature, the colorless crystals of Th₄BPDC-12 (2.5 mg, 0.70 μmol, yield: 69%) were collected by filtration and washed three times with DMF. IR (neat, cm⁻¹): 3339, 2932, 1651, 1591, 1535, 1497, 1388, 1254, 1201, 1178, 1145, 1098, 1062, 1020, 1006, 855, 838, 796, 769, 702, 672, and 662 (Figure S28). The obtained crystals...
were suitable for single-crystal X-ray analysis. The single-crystal structure (Figure S27) and a detailed description of the data collection and refinement details are given in the Supporting Information. As shown in Figure S28, the PXRD pattern of as-synthesized Th$_2$-BPDC-12 matches the simulated pattern from the single-crystal X-ray data. PXRD studies were also used to confirm the crystallinity of the bulk material (Figure S28). The thermal stability of Th$_2$-BPDC-12 was determined via thermogravimetric analysis (Figure S12).

Preparation of U$_2$Me$_2$BPDC-8:H$_2$O-1d and U$_2$Me$_2$BPDC-8:H$_2$O-4d. The green crystals of U$_2$Me$_2$BPDC-8 were washed once with DMF and soaked in water for 1 or 4 days at room temperature under an inert atmosphere. Detailed description of the data collection and refinement details is given in the Supporting Information. Table S4 contains the crystallographic refinement data.

Synthesis and Characterization of U$_2$Th$_{27}$Me$_{77}$BPDC-8. The green crystals of U$_2$Me$_2$BPDC-8 (42 mg) were washed once with DMF and soaked in a 1.0 M solution of ThCl$_4$ in DMF for 72 h at room temperature. After 72 h, the resulting crystals of U$_2$Th$_{27}$Me$_{77}$BPDC-8 (U/Th-8) were collected by centrifugation and washed thoroughly three times with DMF. The PXRD pattern of U$_2$Th$_{27}$Me$_{77}$BPDC-8 matches the simulated pattern. PXRD studies were used to confirm the crystallinity of the bulk material (Figure S14). IR (neat, cm$^{-1}$): 3389, 2930, 1648, 1587, 1543, 1497, 1409, 1383, 1254, 1206, 1140, 1093, 1062, 1007, 916, 863, 838, 777, 731, 659 (Figure S17). The XPS spectra are shown in Figure S3 and S13. The Taue plot is shown in Figure S14b, and the estimated band gap for the prepared heterometallic MOF was found to be 2.5 eV.

Synthesis and Characterization of U$_2$Th$_{27}$Co$_{10}$Me$_{8}$BPDC-8. The prepared U$_2$Th$_{27}$Me$_{77}$BPDC-8 MOF (42.0 mg) was heated in a 0.25 M DMF solution (1.0 mL) of Co(NO$_3$)$_2$·6H$_2$O for 48 h in a preheated oven at 75 °C. As a result of such treatment, the sample changed color from gray to dark yellow-green. After the synthesis of Th$_2$-BPDC-8 intermediate MOF was confirmed (Figure S14). IR (neat, cm$^{-1}$): 3424, 2930, 1649, 1586, 1542, 1482, 1409, 1296, 1253, 1207, 1093, 1062, 1020, 1032, 1007, 912, 863, 815, 778, 734, and 659 (Figure S17). PXRD patterns were measured every 6 h over 48 h to probe changes in unit cell parameters as a function of time, as well as to monitor the incorporation process (Figure S14a). A single peak was observed (6.4°, 20) with a decrease in intensity as the metal-node extension proceeded, while another peak (5.1°, 20) shifted to higher angles. We modeled this change and calculated the diffraction intensity changes as a function of the occupancy of the cobalt ion. Indeed, our simulated diffraction pattern shows a decrease in peak intensity as a function of the amount of cobalt ion incorporated, a result comparable to that obtained experimentally (Figure S14c). To determine that the cobalt ion was incorporated as a metal node extension and not included as a guest in the form of either Co(II) or Co(III) oxides, we performed Raman and XPS measurements. In the Raman spectra, there was no detection of the presence of either Co(II) or Co(III) oxides (Figure S17). Furthermore, XPS data of the Co(II) region agreed with the Raman data (Figure S15). The PXRD studies did not reveal the presence of crystalline cobalt oxides. Conductivity measurements of the heterometallic MOFs were performed in a home-built in situ pressed-pellet device. The metal ratio in the sample, thoroughly washed for 1 week using the Soxhlet washing procedure to ensure removal of any residual metal salts, was determined by ICP-MS analysis technique.

General Procedure To Study Structural Dynamism. The Th$_2$-Me$_2$BPDC-N0$_x$-10 and Th$_2$-Me$_2$BPDC-8 MOFs were soaked in 11 different solvents for 72 h during which the solvents were refreshed twice a day. Crystals suitable for single-crystal X-ray studies such as Th$_2$-Me$_2$BPDC-10-MeOH were analyzed. Detailed description of the data collection and refinement details of Th$_2$-Me$_2$BPDC-10-MeOH is given in the Supporting Information. Table S5 contains the crystallographic refinement data of Th$_2$-Me$_2$BPDC-10-MeOH.

PXRD studies were used to monitor sample crystallinity (Figures S19, S22–S26).

General Linker Installation Procedure. Crystals of Th$_2$-Me$_2$BPDC-N0$_x$-10 or Th$_2$-Me$_2$BPDC-8 MOFs were soaked in 0.5 M of the corresponding linker solution in DMF and heated at 75 °C in a preheated isothermal oven. The obtained crystals were collected by filtration and thoroughly washed with DMF using the Soxhlet extraction procedure. The samples were analyzed by single-crystal or powder X-ray diffraction. The linker installation was confirmed by 1H NMR spectroscopy as described below.

Digestion Procedure. To study the linker composition of the synthesized MOFs by 1H NMR spectroscopy, a mixture of 500 μL of DMSO-d$_4$ and 3 μL of concentrated HCl was added to 5 mg of thoroughly washed material (washing was done in DMF using the Soxhlet extraction method), followed by mild heating of the mixture to ensure complete dissolution of sample. The percent of linker installed was calculated based on linker ratios found in the 1H NMR spectra of the digested samples. The amount of linker installed can be calculated from geometrical analysis of the parent MOF structure and length of the corresponding linker as shown by Zhou and coworkers. 42

Synthesis and Characterization of Th$_2$-Me$_2$BPDC(Me$_3$TPDC)-12. Crystals of Th$_2$-Me$_2$BPDC(N0$_x$)-10 (5.0 mg, 1.6 μmol) were heated in 0.5 mL of 15 mM H$_2$Me$_2$TPDC solution in DMF at 75 °C in a preheated isothermal oven for 24 h. This procedure resulted in the Th$_2$-Me$_2$BPDC-8 intermediate MOF as confirmed by single-crystal X-ray crystallography. The crystals of the Th$_2$-Me$_2$BPDC-8 intermediate were then heated for an additional 48 h in the presence of 0.5 mL of a 0.16 M H$_2$Me$_2$BPDC DMF solution. After that, the formed Th$_2$-Me$_2$BPDC(Me$_3$TPDC)-12 crystals were thoroughly washed with DMF to remove any residual linker. The crystals were suitable for single-crystal X-ray studies. Detailed description of the data collection and refinement details is given in the Supporting Information. Table S6 contains the crystallographic refinement data of the Th$_2$-Me$_2$BPDC-8 intermediate and Th$_2$-Me$_2$BPDC(Me$_3$TPDC)-12 crystals. PXRD studies were used to confirm the preserved framework integrity of the MOFs at every stage of the installation process (Figure S31). Based on 1H NMR studies, the percentage of the installed linker is given in Table S9. The 1H NMR spectrum is shown in Figure S34.

Attempts of H$_2$Me$_2$BPDC and H$_2$QPDC Installation into Th$_2$-Me$_2$BPDC-N0$_x$-10. Crystals of Th$_2$-Me$_2$BPDC-N0$_x$-10 (5.0 mg, 1.6 μmol) were heated in 0.5 mL of 15 mM H$_2$QPDC solution in DMF at 75 °C in a preheated isothermal oven for 72 h. After that, crystals were thoroughly washed with DMF to remove any residual linker. Single-crystal X-ray studies of the crystals revealed no structural changes in the Th$_2$-Me$_2$BPDC-N0$_x$-10 structure. Based on the different orientation of adjacent metal nodes, the 12-coordinated MOF cannot be prepared through the installation of the H$_2$Me$_2$BPDC linker in the Th$_2$-Me$_2$BPDC-10 structure. Detailed description of the data collection and refinement details is given in the Supporting Information. Table S7 contains the crystallographic refinement data.

Crystals of Th$_2$-Me$_2$BPDC-N0$_x$-10 (5.0 mg, 1.6 μmol) were heated in 0.5 mL of 15 mM H$_2$QPDC solution in DMF at 75 °C in a preheated isothermal oven for 72 h. After heating, crystals were thoroughly washed with DMF to remove any residual linker. Single-crystal X-ray studies of the crystals revealed no structural changes in the Th$_2$-Me$_2$BPDC-N0$_x$-10 structure. Based on the different orientation of adjacent metal nodes, the 12-coordinated MOF cannot be prepared through the installation of the H$_2$QPDC linker in the Th$_2$-Me$_2$BPDC-10 structure. Detailed description of the data collection and refinement details is given in the Supporting Information. Table S7 contains the crystallographic refinement data.

Synthesis and Characterization of Th$_2$-Me$_2$BPDC(BDCC)-10. Crystals of Th$_2$-Me$_2$BPDC-N0$_x$-10 (5.0 mg, 1.6 μmol) were heated in 0.5 mL of 0.16 M H$_2$BDC solution in DMF at 75 °C in a preheated isothermal oven for 24 h. After the installation process, the MOF was thoroughly washed with DMF to remove any residual linker. Single-crystal X-ray studies of the crystals revealed no structural changes in the Th$_2$-Me$_2$BPDC-N0$_x$-10 structure. Detailed description of the data collection and refinement details is in the Supporting Information. Table S7 contains the crystallographic refinement data.

Crystals of Th$_2$-Me$_2$BPDC(BDCC)-10. Crystals of Th$_2$-Me$_2$BPDC-N0$_x$-10 (5.0 mg, 1.6 μmol) were heated in 0.5 mL of 0.16 M H$_2$BDC solution in DMF at 75 °C in a preheated isothermal oven for 24 h. After the installation process, the MOF was thoroughly washed with DMF to remove any residual linker. Single-crystal X-ray studies of the crystals revealed no structural changes in the Th$_2$-Me$_2$BPDC-N0$_x$-10 structure. Detailed description of the data collection and refinement details is in the Supporting Information. Table S7 contains the crystallographic refinement data.
Synthesis and Characterization of Th₆-BPDC-10. Crystals of Th₆-MeBPDC-NO₃-10 (5.0 mg, 1.6 μmol) were heated in 0.5 mL of 16 mM H₂BPDC solution in DMF at 75 °C in a preheated isothermal oven for 72 h. After the installation process, the Th₆-MeBPDC-10 MOF was thoroughly washed with DMF to remove any residual linker. PXRD studies were used to confirm the preserved framework integrity (Figure S32).

Synthesis and Characterization of Th₆-MeBPDC(Me₆TPDC)-10. Th₆-MeBPDC-8 (5.0 mg, 1.8 μmol) was heated in 0.5 mL of 15 mM H₂MeTPDC solution in DMF at 75 °C in a preheated isothermal oven for 72 h. After the installation process, the Th₆-MeBPDC(Me₆TPDC)-10 MOF was thoroughly washed with DMF to remove any residual linker. PXRD studies were used to confirm the preserved framework integrity of the MOFs at every stage of the installation process, as well as ensure the phase purity of the bulk sample (Figure S30). Based on ¹H NMR studies, the percentage of the installed linker is given in Table S9 and the spectrum is shown in Figure S37.

Synthesis and Characterization of Th₆-MeBPDC(Me₆BPDC)-10. Th₆-MeBPDC-8 (5.0 mg, 1.8 μmol) was heated in 0.5 mL of 0.16 M H₂MeBPDC solution in DMF at 75 °C in a preheated isothermal oven for 24 h. After the installation process, the Th₆-MeBPDC(Me₆BPDC)-10 MOF was thoroughly washed with DMF to remove any residual linker. PXRD studies were used to confirm the preserved framework integrity as well as ensure the phase purity of the bulk MOF sample (Figure S31). Based on ¹H NMR studies, the percentage of the installed linker is given in Table S9. The ¹H NMR spectrum is shown in Figure S38.

Attempts of H₂QPDC Installation into Th₆-MeBPDC-8. Th₆-MeBPDC-8 (5.0 mg, 1.8 μmol) was heated in 0.5 mL of 15 mM H₂QPDC solution in DMF at 75 °C in a preheated isothermal oven for 72 h. After the installation process, the MOF was thoroughly washed with DMF to remove any residual linker. PXRD and spectroscopic studies did not indicate successful linker installation (Figure S31).

Physical Measurements. Single-crystal X-ray diffraction data were collected using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). Powder X-ray diffraction patterns were recorded on a Rigaku Miniflex II diffractometer with accelerating voltage and current of 30 kV and 15 mA, respectively. FTIR spectra were obtained on a PerkinElmer Spectrum 100. Raman spectra were measured using a Horiba XploRA PLUS Raman spectrometer with diode laser (638 nm) and solid-state laser (473 nm) using a TE Air cooled CCD detector. NMR spectra were collected on Bruker Avance III-HD 300 and Bruker D8 QUEST diffractometer equipped with a KRATOS XR double focusing magnetic sector. High-resolution core level spectra were measured with a pass energy of 40 eV, and analysis of the data was carried out using XPSPEAK41 software. DR spectra were collected on an Ocean Optics JAZ spectrometer. An Ocean Optics ISP-REF integrating sphere was connected to the spectrometer using a 450 μm SMA fiber optic cable. Samples were loaded in an 8.0 mm quartz sample cell, which was referenced to an Ocean Optics WS-1 Spectralon standard. The conductivity measurements on MOF pressed pellets was performed using a source meter (Keithley Instruments GmbH, Germering, Germany, model 263) and an electrometer (Keithley Instruments GmbH, Germering, Germany, model 617).

Theoretical Calculations Methods. The DFT calculations were performed using the Vienna ab initio simulation package (VASP) and plane wave basis sets. Projector-augmented wave (PAW) pseudopotentials were employed, with the C 2s2p², H 1s, O 2s2p⁴, Th 6s⁷6p⁶6d⁶5f⁵, U 6s⁶7p⁶6d⁶5f⁵, and Co 3d⁴S⁴ treated explicitly. The geometries were optimized using the GGA-PBE exchange correlation functionals. The van der Waals interactions were taken into account using the dispersion correction formula in the PBE-D3 functionals by Grimme et al. with Becke-Johnson damping. In addition, an on-site Coulomb interaction was added to the uranium f-electrons and cobalt d-electrons within the DFT+U formalism to attenuate the electron delocalization due to the self-interaction of electrons. Based on previous studies, a U-J = 4 eV was used for uranium. Although a U-J = 3 eV has been used for cobalt in previous literature, this value underestimates the experimental band gap of Co containing systems in this work. Thus, a U-J = 4 eV was determined for Co to closely predict the conductivity measurements in this work. No DFT+U corrections are needed for Th, based on previous works and also confirmed in this work. The plane-wave energy cutoff was set to 520 eV, and spin-polarized calculations were performed at the Γ-only k-point. Structural optimization was performed with a 25 meV/A as the energy tolerance criteria for the electronic step. Gaussian smearing with a width of 0.05 eV was applied to all optimizations. A conjugate-gradient algorithm was used to relax all the ions. The calculations were performed on SBUs isolated in a cubic box of size 30 Å. The total and partial DOS were calculated by single point calculations following the geometry optimizations.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b04737.

Additional experimental details, X-ray structure refinement data, PXRD patterns, TGA traces, FTIR, XPS, Tauc plots, ¹H NMR spectra and computational details (PDF)

Crystallographic information for Th₆-MeBPDC-NO₃-10, CCDC 1910421 (CIF)

Crystallographic information for Th₆-MeBPDC-8, CCDC 1910422 (CIF)

Crystallographic information for U₆-MeBPDC-TFA-10, CCDC 1910423 (CIF)

Crystallographic information for U₆-MeBPDC-8–4dBPDC NO₃-8, CCDC 1910424 (CIF)

Crystallographic information for U₆-MeBPDC-8–4dBPDC NO₃-8, CCDC 1910425 (CIF)

Crystallographic information for Th₆-MeBPDC-(Me₆TPDC)-12, CCDC 1910426 (CIF)
Crystallographic information for Th$_6$Me$_2$BPDC-8-intermediate, CCDC 1910427 (CIF)
Crystallographic information for Th$_6$Me$_2$BPDC-("QPDC")-10, CCDC 1910428 (CIF)
Crystallographic information for Th$_6$Me$_2$BPDC-("Me$_2$BPDC")-10, CCDC 1910429 (CIF)
Crystallographic information for Th$_6$Me$_2$BPDC10-MeOH, CCDC 1910430 (CIF)
Crystallographic information for Th$_6$BPDC-10, CCDC 1910431 (CIF)
Crystallographic information for Th$_6$BPDC-12, CCDC 1910432 (CIF)

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Notes
The authors declare no competing financial interest.

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■ REFERENCES


