

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: High Uptake of ReO4– by a Radiation Resistant [Th48Ni6] Nanocage-Based Metal–Organic Framework
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201901786 Angew. Chem. 10.1002/ange.201901786

Link to VoR: http://dx.doi.org/10.1002/anie.201901786 http://dx.doi.org/10.1002/ange.201901786

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High Uptake of ReO₄⁻ by a Radiation Resistant [Th₄₈Ni₆] Nanocage-Based Metal–Organic Framework

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Abstract: Assembled from $[Th_{48}Ni_6]$ nanocages, the first transition-metal (TM)-Th metal-organic framework (MOF, 1) has been synthesized and structurally characterized. 1 exhibits high solvent and acid/base stability, and resistance to 400 kGy β irradiation. Notably, 1 captures ReO₄⁻ (an analog of radioactive ⁹⁹TcO₄⁻, a key species in nuclear wastes) with a maximum capacity of 807 mg/g, falling among the largest values known to date. Furthermore, 1 can enrich methylene blue (MB) and can also serve as an effective and recyclable catalyst for CO₂ fixation with epoxides; there is no significant loss of catalytic activity after 10 cycles. Theoretical studies with nucleus-independent chemical shifts and natural bond orbital analysis reveal that the [Th₆O₈] clusters in 1 have a unique stable electronic structure with (d-p) π aromaticity, partialy rationalising 1's stability.

Radioactive by-products of the fission process used to generate nuclear power are of potential concern regarding their impact on the environment and human beings, and thus much effort has been devoted to nuclear waste disposal.^[1] A key issue is the enrichment and separation of radioactive ⁹⁹TcO₄⁻, because it is highly water-soluble, mobile, and stable, potentially posing a threat to the environment. Furthermore, hundreds of metric tonnes of TcO₄⁻ have accumulated during fission of ²³⁵U or ²³⁹Pu over the past 70 years, increasing the urgency for TcO₄⁻ uptake.^[2,3]

To remove TcO₄⁻, traditional anion exchange resins are widely used.^[4] However they lack strong radiation resistance and chemical stability under extreme conditions.^[5] Therefore, designing and synthesizing novel, stable and porous materials, possessing both strong radiation resistance and high uptake of TcO₄⁻ from contaminated water systems or during fuel reprocessing, is of critical and urgent importance.^[6]

Seeking porous compounds with strong radiation resistance, we focused on the construction of porous metal-organic frameworks (MOFs) built from thorium. We did so because 1) Th is only modestly radioactive and relatively abundant in the earth's

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crust (similar to lead);^[7,8] 2) Th has a relatively low toxicity, no higher than Al³⁺ or Cr^{3+;[9,10]} 3) it is usually found in the +IV oxidation state, and similarly highly charged metal ions (*e.g.* Zr⁴⁺, Hf⁴⁺) have been shown to yield robust MOF frameworks;^[11-13] and 4) flexible coordination of Th⁴⁺ can yield unprecedented frameworks and topologies that cannot be accessed by transition or lanthanide metals.

Since O'Hare *et al.* reported the first Th-MOF in 2003,^[14] other Th-MOFs, especially the stable Th₆-cluster with carboxylate ligands, have also been synthesized in which gas absorption and ion exchange were investigated.^[15-19] However, heterometallic MOFs containing Th and d-block TM ions have not been reported hitherto. In this contribution, we report the synthesis of the first TM-Th MOF, which exhibits radiation resistance, high stability, and a capacity of ReO₄⁻ uptake (as an analog of radioactive TcO₄⁻). This work sheds light on further advanced materials for TcO₄⁻ capture.



Solvothermal reaction of isonicotinic acid (HIN), Th(NO₃)₄ and Ni(OAc)₂ in N,N-diethylformamide for one day at 120 °C yielded jade-green crystals of **1** ({[Ni₃Th₆(μ_3 -O)₄(μ_3 -OH)₄(IN)₁₂)(H₂O)₁₂]·(OH)₆·5DMF·2H₂O}_{*n*}). Crystallographic analysis of **1** showed that it crystallizes in the cubic system with space group *Pm-3m* (Table S1). The 3D

framework **1** is assembled from cubic [Th₄₈Ni₆] cages with inner diameters of 11.08 Å (Figure 1b), in which each Th₆-cluster occupies one vertex and each face of the cube contains a discrete Ni²⁺ ion (Figure 1b). Additionally, compound **1** belongs to a cationic framework, and free OH⁻ anions exists in the structure for balancing the charge (see detailed analysis in the SI). From the topological point of view, each Th₆-cluster, with an average Th-O bond length of 2.38 Å, coordinates to twelve IN⁻ ligands, forming a 12-connected node. Each Ni²⁺ links four Th₆-clusters, and can be considered as a 4-connected unit. The resulting network can be described as a (4, 12)-connected framework with the *ftw*-type topology, similar to the structure of Cu₃Au alloy.^[20]

The stability of compound 1 was investigated by various ways as below. First, its resistance to radiation was explored. Under a total of 2×10^5 , 4×10^5 Gy β irradiation and 10^5 Gy γ irradiation with a dose rate of 2×10⁴ Gy/hour, 3D frameworks of 1 remain intact, as is evidenced by PXRD of samples before and after irradiation (Figure S3a). It should be noted that humans cannot survive for more than two days under 50 Gy total irradiation, and the radiation dosage from the Hiroshima atomic bomb was about 10 Gy/hour.^[23] Compound 1 clearly possesses radiation resistance. Investigation of iodine adsorption on both un- and irradiated samples showed that the adsorbing capacity is not significantly affected by 200 kGy β irradiation (Figure S4), further supporting the radiation resistance of 1. As far as we know, only a few stable MOFs with radioresistance ability was explored under less than 2×10^5 Gy β irradiation (Table S9),^[1c,21,22,27] whereas the investigations on stability of MOFs under 4×10^5 Gy β irradiation have not been reported so far.

We next explored the solvent stability of **1** by soaking it in different solvents for 20 h; the PXRD patterns show that **1** possesses very good solvent stability (Figure S3b). Finally, the acid/base stability of **1** was also investigated. **1** was immersed in a series of solutions from pH 1 to 14, and the corresponding PXRD patterns show that **1** remains intact from pH 1-13 (Figure S3c). In summary, compound **1** displays radiation resistance and excellent stability to solvent and pH, making it promising for nuclear waste applications.

We performed density functional theory (DFT) studies on several model clusters, including $[Th_6(\mu_3-O)_8(IN)_{12}]^{4-}$, $Th_6(\mu_3-O)_4(\mu_3-OH)_4(IN)_{12}$ and $[Th_6(\mu_3-OH)_8(IN)_{12}]^{4+}$ according to the number of hydroxyl replacing oxygen (n = 0, 4 and 8) for the core cluster of $[Th_6O_8]^{8+}\!.$ As shown in Figure 2, the optimized Th-O (Th-OH) bond lengths are, respectively, shorter and longer than the measured one for n = 0 and 8. For n = 4, however, the average Th-O bond length of 2.395 Å matches well the experimentally determined Th-O bond lengths of 2.38 Å (Table S2). As these three model clusters were studied via constrained geometry optimizations, we additionally performed full geometry optimizations of simplified model clusters $Th_6(\mu_3-O)_8(COOH)_{12}^{4-}$, $Th_6(\mu_3-O)_4(\mu_3-OH)_4(COOH)_{12}$ and $Th_6(\mu_3-OH)_8(COOH)_{12}^{4+}$ by replacing the IN ligand with a formate anion (HCOO-). It is found that these fully optimized R_{Th-O} and R_{Th-OH} bond lengths are almost the same as those from the $[Th_6(\mu_3-O)_8(IN)_{12}]^{4-}$, $Th_6(\mu_3-O)_4(\mu_3-OH)_4(IN)_{12}$ and $[Th_6(\mu_3-OH)_8(IN)_{12}]^{4+}$ clusters, respectively, as shown in Table S2. All these results help to confirm the formula of $Th_6(\mu_3-O)_4(\mu_3-OH)_4(IN)_{12}$. Furthermore, as shown in Figure S5, there is large HOMO-LUMO energy gap of 4.19 eV for $Th_6(\mu_3-O)_4(\mu_3-OH)_4(COOH)_{12}$, indicating the high electronic stability of the cluster core.

To analyze the electronic structure of the cluster, we adopt an O_h -symmetry $[Th_6(\mu_3-O)_8]^{8+}$ model cluster as there is similar valence MO-level pattern between $Th_6(\mu_3-O)_4(\mu_3-OH)_4(COOR)_{12}$ and $Th_6(\mu_3-O)_8(COOR)_{12}^{4-}$ (R = H to mimic the bulky phenyl group), as listed in Figure S5. The general MO level pattern is shown in the left side of Figure 3, where the froniter valence-MO group orbitals are seperated with gaps of 10.87 eV and 1.81 eV from the lower and higher groups. This valence group, as shown in the middle of Figure 3, is composed of 102 valence MOs, including mainly three parts: the lowest one is mostly 2p-band with 24 MOs of O8 fragment, the second part is 5f-band with 42 MOs of Th₆ fragment, and the third part is mainly 6d- and 7s-band with 36 MOs of The fragment. The 2p-band is the valent, occupied MOs that is seprated by 3.66 eV from the unoccupied 5f-band. This large metal-ligand energy gap also helps to confirm the stability of this $[Th_6(\mu_3-O)_8]^{8+}$ cluster. Besides, due to metal-ligand $(d-p)\pi$ interaction there is significant mixing of 5fand 6d-orbitals in the 2p-band, as listed in Table S3 where the symmetries, energies, MO compositions and 3D isosurfaces of these frontier MOs are collected. HOMO-9 to HOMO contain 48 electrons and feature the principal 24 2p-band orbitals. Especially notworthy is the eight electrons from four MOs (HOMO-8 & HOMO-5 in Table S3), which provides the net bonding interactions due to the significnat mixing of Th 5f- and 6d-orbitals with O-2p orbitals. These are multi-centre bonds delocalized within $[Th_6(\mu_3-O)_8]^{8+}$ core (Table S3), making this highly symmetric cage potentially aromatic. To further investigate this aromatic stability, nucleus-independent chemical shift (NICS) indices were calculated. Three types of sites were chosen: the centres of the cage, the rhombus face composed of Th-O-Th-O, and at 1 Å above the plane of the rhombus face. All the NICS values at these points are negative (Table 1), indicating that the $[Th_6(\mu_3-O)_8]^{8+}$ cluster posseses aromatic character. In comparision, the prototypical aromatic molecule benzene has a NICS(0) value of -8.0 ppm and a NICS(1) of -10.2 ppm.^[24]





We have also analysed the bonding in $[Th_6O_8]^{8+}$ using the natural bond orbital (NBO) and electron localisation function (ELF) approaches. The NBO results show that the four Th_{μ_3} -oxo linkages are highly oxygen-localised, with composition of 5.7% Th (sp^{0.40}d^{3.50}f^{1.19}) + 94.3% O (sp^{2.10}). Clearly, there is

non-negligible Th particiation, despite the ionic feature. The ionic nature of the Th-O bond is also revealed through ELF analysis. The calculated 3D ELF contour of $[Th_6O_8]^{8+}$ cluster with five different values of the isosurface is shown in Figure S6. The delocalized electron-pair density - evidence for Th-O connection - is shown only at small isosurface values (0.1 and 0.2), while for larger values (0.3, 0.4 and 0.5), only localized closed-shell distributions are present. The ELF diagrams provide evidence that there is non-negligible, albeit weak, covalent and strong ionic interaction in the Th-O bonds, similar to the conclusion from the NBO analysis.

Table 1. NICS values	(ppm)	of [Th ₆ O ₈] ⁸⁺	cluster core.
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Туре	NICS
NICS(0), cubic center	-2.17
NICS(0), rhombus face center	-5.13
NICS(1), 1 Å above rhombus face	-1.51

As the Ni-IN metal-ligand bonding can be a potential weak point in the stability of this MOF, the bonding interaction between a Ni²⁺ center and four IN ligands has been calculated, and the results are shown in Figure S7. Both IN⁻ and HIN ligands are investigated for charge balance consideration. The interaction energies are *ca.* -1189 and -719 kcal/mol, respectively. The former is larger due to stronger electrostatic interaction between cation and anion. This large bonding interaction energy partially aids the stability of this MOF structure.



Figure 3. The energy levels of $[Th_6(\mu_3-O)_8]^{24}$. Left, the general MO energy levels; middle, the frontier MO energy levels including O 2p-, Th 5f- and 6d-,7s-bands; right, the enlarged O 2p-based levels.

Meanwhile, periodic DFT calculations were performed for the MOF structure of ({[Ni₃Th₆(μ_3 -O)₄(μ_3 -OH)₄(IN)₁₂]}(OH)₆)_n) to investigate the interaction between IN⁻ ligand and Th⁴⁺ in the core cluster, as well as between IN⁻ ligand and Ni²⁺ in terms of solid MOF geometry. The partial density of states (DOS) of Th and O from IN⁻ (Figure S8) reveal that at valence states Th ions distribute above fermi level, and only little overlap with O, indicative of that the interactions between Th⁴⁺ and IN⁻ mainly originate from electrostatic interaction. On the other hand, the partial DOS overlap between Ni and N shows more covalent contribution between Ni and N than that of Th and O (Figure S9). These two different interaction types are also further confirmed by charge density difference analysis (Figure S10). The stability

of MOF attributes to both the electrostatic and covalent interactions between $Th^{4+},\,Ni^{2+}$ cations and IN^{-} anions.

Table 2. Su	immary of the	ReO₄ ⁻	adsorbing	capacity o	f MOFs.
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MOFs	Adsorbing Capacity (mg/g)	References
Th-MOF	807	this work
Ag(4,4'-bipyridine)NO3	786	25
SLUG-21	602	26
SCU-100	553	27
SCU-101	217	21
NU-1000	210	28
UiO-66-NH ₂	159	29

The combination of radiation resistance and the large [Th₄₈Ni₆] cage in a stable cationic framework, led us to wonder if 1 can capture and enrich ReO₄⁻. The latter is a non-radioactive analog of 99TcO4- and is often used as a simulation of the radioactive TcO4-. 30 mg samples of 1 were immersed in anhydrous CH₂Cl₂ for seven days, with fresh anhydrous CH₂Cl₂ being added every day during the process. The treated samples were outgassed under dynamic vacuum at 80 °C for 10 h to remove the solvent. Then, the ReO4⁻ adsorption of compound 1 was performed at room temperature. The activated samples were immersed in 0.05 mM ReO4⁻ solution for 10 h, and the corresponding samples were centrifuged and washed by water to remove the attached ReO4⁻. Inductively Coupled Plasma (ICP) was performed to determine the adsorption mass of ReO4; this can reach 807 mg/g, which are falling among the highest values known for MOF (Table 2 and S4).^[21,25-29] Subsequently, in order to explore the selectivity of 1 for capturing ReO₄⁻, 5 mM Cl⁻, OAc⁻ and SO42- were simultaneously mixed with 0.05 mM ReO4solution. ICP showed that under these conditions 1 can still enrich ReO₄⁻ to about 410 mg/g, indicating excellent selectivity for capturing ReO₄. Besides, the exchange capacity of ReO₄was also explored after **1** treated with 4×10^5 Gy β irradiation and 10⁵ Gy γ irradiation, respectively. ICP results suggested that the capacity of capturing ReO₄⁻ exhibited a negligible influence by a dose of 4×10^5 Gy β or 10^5 Gy γ irradiation (Table S4). These results reveal that framework 1 is potentially an attractive candidate for dealing with ⁹⁹TcO4⁻ in nuclear waste disposal.

The mechanism for capturing ReO₄⁻ was further explored. Initially, this was done via X-ray single-crystal analysis, including much effort to produce single crystals of 1 with ReO₄⁻ in order to define the position of ReO_4^- in the pores, but the corresponding diffraction data of the crystals after exchanging ReO4⁻ are too poor to determine the molecular structure. Nevertheless, based on the structure characteristics of [Th₄₈Ni₆] nanocage and the ICP results, we propose that the mechanism is that ReO₄⁻ anions can be captured within the cavities of the nanocages by anion exchange and adsorption. We base this on the following considerations: 1) Samples after exchanging ReO₄- were centrifuged and carefully washed with water many times to remove attached ReO4- on the surface; therefore precipitation outside of the MOF can be excluded; 2) single-crystal structural analyses revealed that each [Th₄₈Ni₆] cage contains six free OHand can exchange six ReO_4^- as the balanced anion; 3) ICP shows that each [Th₄₈Ni₆] cage captures 10.91 ReO₄⁻. This

includes 6 exchanged ReO₄⁻ and 4.91 ReO₄⁻ and K⁺; the amount of K⁺ is very close to 5.01 K⁺ determined by ICP analysis (Table S4); 4) ReO₄⁻ is potentially well stabilized in the cage because the OH⁻ anions in the Th₆-cluster, and Ni-coordinated H₂O, can generate hydrogen bonding network with ReO₄⁻. Additionally, the total volume of 10.91 ReO₄⁻ and 4.91 K⁺ is about 1.98 nm³ (the volume of ReO₄⁻ and K⁺ is 0.143 nm³ and 0.085 nm³, respectively), and the available volume of each [Th₄₈Ni₆] cage is about 2.05 nm³ (after considering the van der Waals radii of each atom in one cage), indicating that these ions can be accommodated in one cage. Finally, PXRD of samples treated with ReO₄⁻ was performed to explore the stability. As shown in Figure S3d, PXRD well matches the simulated one, indicating that the framework keeps intact during the adsorption process.

To confirm the existence of large pores in framework **1**, the adsorption of methylene blue (MB) by **1** was explored. As shown in Figure S11, the dark blue MB solution gradually becomes colourless over 5 h, and **1** changes from light green to bottle green, with the maximum MB adsorbing capacity reaching 266 mg/g. Investigation of CO_2 adsorption was also carried out, and the adsorption CO_2 by activited compound **1** was studied at 198 K, and the result is shown in Figure S12a; **1** can capture CO_2 with an adsorbing capacity of 42.44 cm³/g.

The Th₆-cluster should provide Lewis acidic and defect sites for catalytic reactions. Therefore, porous framework **1** might be expected to be promising for the capture and reaction of CO₂ with epoxides. To explore this hypothesis, a series of reactions were performed with styrene oxide as a model substrate to determine optimal reaction conditions (Table S5). These conditions were then used in a further set of reactions with several typical epoxides; all of the corresponding cyclic carbonates were obtained in excellent yield (89-99%, Table 3) indicating that compound **1** possesses significant catalytic capacity for cycloaddition reactions with CO₂ and various epoxides.

Table 3. Synthesis of various cyclic carbonates from CO_2 and epoxides with catalyst $\mathbf{1}^{[a]}$





O	y of o	89

[a] Reaction conditions: epoxides (240.3 mg, 2.0 mmol), solvent-free, catalyst 1 (40 mg, based on metal center, about 2.5 mol %), TBAB (16.2 mg, 0.05 mmol), CO₂ (0.1 MPa), 12 h. [b] Total yield determined by ¹H NMR using 1.3,5-trimethoxybenzene as an internal standard.

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1 can be straightforwardly isolated from the reaction mixtures through centrifugation, allowing us to evaluate its recycle performance. This was explored as follows: the used compound 1 was separated from the reaction mixture, and the cycloaddition reaction with styrene oxide was repeated using the recovered 1 as catalyst. Pleasingly, the corresponding cyclic carbonate is still produced in excellent yield (99%, Figure S13), suggesting that 1 can serve as a recoverable catalyst for CO₂ conversion with epoxides. To further probe this, the process was repeated up to 10 times, with no obvious loss in catalytic activity (Figure S13). The PXRD of used catalyst 1 was measured (Figure S14), revealing that the framework of 1 is still intact and keeps its crystalline state throughout the cycling. The ICP of the filtered liquor was also tested; no Ni²⁺ ion was detected, indicating only trace amounts of leakage from the robust framework. We therefore conclude that compound 1 is a highly recoverable catalyst for these cycloaddition reactions.

In principle, both the Th_6 -cluster and Ni^{2+} in 1 can act as catalytic sites in this cycloaddition reaction. To probe this, the isostructural compound 2 was prepared through an approach similar to 1 except that Co(OAc)2•4H2O was used instead of Ni(OAc)₂•4H₂O. The reactions were performed using the same conditions as detailed in Tables S5 and 3, and the corresponding results are recorded in Tables S6 and S7. Generally, Ni²⁺ is a stronger Lewis acid than Co2+ and, as Lewis acidity directly relates to the yield of CO2 cycloaddition reactions, a Ni-based catalyst should show better catalytic performance than a Co-based one, as has been shown previously.^[30] However, **1** and 2 display similar catalytic results, indicating that the different transition metals in the framework do not significantly affect the catalytic efficiency. This suggests that the Th₆ cluster plays the decisive role in the catalytic reaction, especially as Zr⁴⁺ and Hf⁴⁺ show excellent catalytic performance in CO2 conversion with epoxide under mild conditions,[31] whereas such yields always require more rigorous reaction conditions (e.g. higher temperature and pressure) when Ni/Co-based MOFs are used as catalyst.

Taking into account our data and previous reports,^[32] a possible mechanism for this cycloaddition reaction is proposed (Figure S15). First, **1** can capture CO₂ and enrich the substrate in nanocages of [Th₄₈Ni₆]. Second, the coupling reaction occurs between the Th₆-cluster in **1** and the oxygen atom of the epoxide, and the epoxy ring in the epoxide is activated. Third, the nucleophilic Br anion attacks the carbon atom in the epoxy ring, resulting in ring opening. Finally, CO₂ reacts with the oxygen anion in the opened epoxy ring, and the Th₆-cluster stabilizes the resulting alkyl carbonate salt, which is further converted into the corresponding cyclic carbonate through intramolecular ring closure. Hence, the cyclic carbonate is obtained in high yield with **1** as the catalyst.

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In conclusion, a unique framework 1, constructed of $[Th_{48}Ni_6]$ nanocages, has been synthesized and structurally characterized. Notably, 1 exhibits excellent stability in various organic solvents and aqueous environments from pH 1 to 13, and resistance to 400 kGy β irradiation at 20 kGy/hour. DFT-calculated nucleus-independent chemical shifts and natural bond orbitals indicate that the Th₆O₈ clusters in 1 exhibit aromatic character, rationalising the stability of 1. We find that 1 can effectively capture and enrich ReO₄⁻. Additionally, 1 can function as an effective catalyst for CO₂ conversion with epoxides, and the recycle number of this process can reach ten without obvious loss in catalytic activity. Finally, as 1 is the first example of a TM-Th MOF, the work presented here offers a new route into the wider exploration of multifunctional 5f materials.

Acknowledgements

This work was supported by NSFC (21625103, 21571107, 21421001, 21590792, 91426302, and 21433005), the National Programs of the Nano-Ket Project (2017YFA0206700), and 111 Project (B12015). HSH is grateful to the University of Manchester for a post-doctoral research fellowship in the initial stage of this work and for computational resources from the University's Computational Shared Facility. We also thank Tsinghua National Laboratory for Information Science and Technology and the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory for a grant of computer time on the CASCADE facility (Proposal Number 49254).

Keywords: actinide chemistry • metal-organic frameworks • radiation resistance • aromatic electronic structure • enrich nuclear waste

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The stable $[Th_{48}Ni_6]$ nanocage-based metal-organic framework exhibits radiation resistance, effectively enriches $ReO_4^$ and catalytically converts CO_2 into epoxides.



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High Uptake of ReO₄⁻ by a Radiation Resistant [Th₄₈Ni₆] Nanocage-Based Metal-Organic Framework