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Identifying the Recognition Site for Selective Trapping of $^{99}$TcO$_4^-$ in a Hydrolytically Stable and Radiation Resistant Cationic Metal–Organic Framework

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Supporting Information

ABSTRACT: Effective and selective removal of $^{99}$TcO$_4^-$ from aqueous solution is highly desirable for both waste partitioning and contamination remediation purposes in the modern nuclear fuel cycle, but is of significant challenge. We report here a hydrolytically stable and radiation-resistant cationic metal–organic framework (MOF), SCU-101, exhibiting extremely fast removal kinetics, exceptional distribution coefficient, and high sorption capacity toward TcO$_4^-$. More importantly, this material can selectively remove TcO$_4^-$ in the presence of large excesses of NO$_3^-$ and SO$_4^{2-}$, as even 6000 times of SO$_4^{2-}$ in excess does not significantly affect the sorption of TcO$_4^-$. These superior features endow that SCU-101 is capable of effectively separating TcO$_4^-$ from Hanford low-level waste melter off-gas scrubber stream. The sorption mechanism is directly unraveled by the single crystal structure of TcO$_4^-$-incorporated SCU-101, as the first reported crystal structure to display TcO$_4^-$ trapped in a sorbent material. A recognition site for the accommodation of TcO$_4^-$ is visualized and is consistent with the DFT analysis results, while no such site can be resolved for other anions.

Produced during nuclear fission of $^{235}$U or $^{239}$Pu, $^{99}$Tc is a long-lived ($t_{1/2} = 2.13 \times 10^5$ y) radioisotope and primarily exists in the +7 oxidation state as a TcO$_4^-$ anion under aerobic conditions. The noncomplexing nature, high water solubility, and great stability of TcO$_4^-$ lead to its extremely high mobility in the environment. Tc is volatile during waste vitrification processes and can leach from vitrified glass and greatly interfere with the separation of uranium and plutonium during biphasic solvent extraction, making it one of the most problematic radionuclides in the nuclear fuel cycle. Therefore, it is highly desirable to develop functional materials that can remove TcO$_4^-$ during used fuel reprocessing or remediation of contaminated water systems.

Traditional polymeric anion exchange resins are commercial products that exhibit efficient removal of TcO$_4^-$, but their poor radiation resistances and chemical stabilities under extreme conditions are clear demerits. Furthermore, the sorption kinetics are relatively slow owing to their randomly distributed pores that may hinder efficient transport of targeted anionic species. Crystalline inorganic cationic materials, possessing ordered extended structures with positive net charge, are scarce compared to the neutral and anionic framework materials. Only a handful of such materials including Mg-Al-LDH, Y$_2$(OH)$_5$Cl, Yb$_3$O(OH)$_6$Cl, metal sulfides, and NDTB-1 have been investigated for TcO$_4^-$ removal, but the majority of these exhibit low sorption capacity and poor selectivity toward TcO$_4^-$. The latter property is a critical disadvantage that impedes practical applications, because a large excess of competing anions, such as NO$_3^-$ and SO$_4^{2-}$, often coexist with TcO$_4^-$. Cationic MOFs, a relatively less investigated subgroup of MOFs in general, are emerging candidates for removing anionic pollutants with advantages of high surface area, tunable pores, and facile functionalities. Up to now, very few cationic MOFs have been tested for TcO$_4^-$/ReO$_4^-$ sequestration, and their practical applications are still limited by slow sorption kinetics and poor selectivity.

We recently reported a cationic MOF SCU-100 with open Ag$^+$ sites that can efficiently and selectively capture TcO$_4^-$/ReO$_4^-$ through a structural transformation process. One clear drawback for this material is that large single crystals disintegrate into microcrystalline materials after anion
exchange, making chromatographic extraction inapplicable (Figure S1). Moreover, the incomplete phase transition leads to poor recyclability and limited stability (Figure S2). We document here a solution to all aforementioned demerits, based on a stable cationic MOF, \([\text{Ni}_2(\text{tipm})(\text{C}_2\text{O}_4))(\text{NO}_3)]\cdot2\text{H}_2\text{O}\) (SCU-101, tipm = tetrakis-[4-(1-imidazolyl)phenyl]methane). This compound exhibits fast removal kinetics, high sorption capacity, and unique molecular recognition derived sorption selectivity toward \(\text{TcO}_4^-\).

SCU-101 crystallizes in the triclinic space group, \(\text{P}1\text{I}\), as blue plate crystals (Figure S5 and Table S1). The size of these crystals is \(\sim400 \times 100 \times 40\ \mu\text{m}^3\), large enough for chromatographic extraction applications. The overall structure can be best described as a porous 3D cationic nickel-tipm extended framework (Figure S6). Each Ni\(^{2+}\) cation is 6-coordinate and binds to four tipm ligands and one \(\text{C}_2\text{O}_4\)\(^{2-}\) anion (Figures S7 and 1a). As shown in Figure 1b, there are three types of channels (A: \(\sim7 \times 9\ \AA^2\); B: \(\sim11 \times 5\ \AA^2\); and C: \(\sim4 \times 2.5\ \AA^2\)) to accommodate the charge-balancing NO\(^3^-\) anions, confirmed by ion chromatography analysis. However, these anions cannot be located in the electron density map and are completely disordered. Each tipm ligand bridging four Ni\(^{2+}\) cations serves as a 4-connected node, whereas each \([\text{Ni}_2\text{C}_2\text{O}_4]\)\(^{2+}\) cluster acts as a 8-connected node, affording a (4,8)-connected binodal Flu topology (Figure 1c). The structure of SCU-101 can be simplified as a honeycomb consisting of a series of rhombic dodecahedron honeycomb structure.

After immersing SCU-101 crystals into aqueous solutions with different pH values ranging from 2 to 14, the structure remains unchanged (Figure S8). Inductively coupled plasma optical emission spectrometry measurements show that the dissolved Ni\(^{2+}\) concentration is only 0.63 ppm at pH 7, corresponding to 0.9% of the total mass of SCU-101. Such value is much lower than that of cationic MOFs [Ag(bipy)]: NO\(_3\) and SCU-100 (Figure S9).\(^{15a,18}\) Additionally, SCU-101 survives from ionizing radiation fields and maintains its crystallinity even after 200 kGy \(^{60}\)Co \(\gamma\) irradiation or 200 kGy \(\beta\) irradiation (1.2 MeV) (Figure S8). The excellent radiation resistance can be further confirmed by the unaffected anion exchange capacity after irradiation (Figure 2f) and is likely a consequence of the benzene-rich nature, contrasting sharply with state-of-the-art anion exchange resins that lose anion uptake capacities after irradiation.

Figure 1. Crystal structure of SCU-101. (a) Coordination environment of Ni\(^{2+}\) with four tipm ligands and one oxalate group. (b) 3D cationic framework containing three types of channels. Atom colors: Ni = orange; O = red; C = light blue; N = green. (c) Simplified (4,8)-connected binodal Flu topology. (d) Simplified rhombic dodecahedron honeycomb structure.

Anion exchange of \(\text{TcO}_4^-\) was initially investigated by mixing 20 mg of SCU-101 samples with 20 mL of a solution containing 28 ppm \(^{99}\)TcO\(_4^-\). As shown in Figure 2a, the concentration of \(\text{TcO}_4^-\) in aqueous solution as a function of contact time was monitored by its characteristic absorption feature at 290 nm in the UV–vis spectra. The removal of \(\text{TcO}_4^-\) occurs at 85% after 5 min and \(\geq95\%\) at 10 min. It takes approximately 10 min to reach the sorption equilibrium, further verified by liquid scintillation counting measurements (Figure 2b). Note the sorption kinetics of SCU-101 is much faster than those of commercial resins (A532E and A530E). Compared to other cationic MOFs tested for removing anionic contaminants including SCU-100 (Figure S10 and Table S2),\(^{15a,16g}\) SCU-101 also exhibits an advance in the removal rate. For example, it takes more than 24 h to reach the equilibrium for SLUG-21\(^{18}\) and UiO-66-NH\(_3\)\(^{17}\) to sequester \(\text{TcO}_4^-/\text{ReO}_4^-\).

To comprehensively study the ion exchange properties of \(\text{TcO}_4^-\) by SCU-101, ReO\(_4^-\) was used as a surrogate to perform batch experiments owing to their almost identical charge densities. Sorption kinetics study of ReO\(_4^-\) under the same condition indeed yields identical anion exchange behavior with that of \(\text{TcO}_4^-\). The sorption isotherm curve of SCU-101 toward ReO\(_4^-\) can be well fitted to the Langmuir model (Figures 2c and S11, and Table S3) and the calculated maximum sorption capacity of SCU-101 is 217 mg ReO\(_4^-\) per
gram of SCU-101, higher than those for LDH, NDTB-1, and UiO-66-NH₂, but only lower than PAF-1-F and SCU-100. The distribution coefficient (Kd) of SCU-101 toward ReO₄⁻ reaches 7.5 x 10⁵ mL/g, noticeably higher than those of all reported anion sorbent materials (Table S4). The final ReO₄⁻ concentration after uptake by SCU-101 is about four times lower than that treated by SCU-100 at similar conditions (Table S5). Additionally, more than 95.7% of ReO₄⁻ could be exchanged back to the solution using a desorption solution of nuclear waste solutions, we also investigated the uptake of ReO₄⁻ in the range from 3 to 12 (Figure S12), which is also a clear advantage compared to the purely inorganic cationic materials.

Moreover, SCU-101 can remove ReO₄⁻ within a wide pH range from 3 to 12 (Figure S12), which is also a clear advantage compared to the purely inorganic cationic materials.

The anion exchange selectivity toward TcO₄⁻/ReO₄⁻ was first studied by the uptake of ReO₄⁻ with the presence of one equivalent of competing anions, including NO₃⁻, CO₃²⁻, PO₄³⁻, Cl⁻, CIOT, and SO₄²⁻. The removal percentage is still as high as ~90% in all cases (Figure 2d). This contrasts with other cationic porous materials reported. Under the same anion exchange condition, the removal of ReO₄⁻ by UiO-66-NH₂ occurs at 15%, 50%, and 20% of the original concentrations in the presence of PO₄³⁻, SO₄²⁻, and CIOT, respectively; the removal occurs at 21% and 19% for PAF-1-F in the presence of PO₄³⁻ and SO₄²⁻, respectively. Generally, anions with higher charge densities often successfully outcompete with ReO₄⁻ during the exchange process owing to stronger host–guest electrostatic interactions. Surprisingly, SCU-101 shows much less affinity toward PO₄³⁻ and SO₄²⁻ compared to that of ReO₄⁻/TcO₄⁻, as the removal of which under the same conditions is only 21.7% and 24.2% (Table S6), respectively. This atypical phenomenon follows the anti-Hofmeister bias and likely originates from the hydrophobic nature of channels constructed by benzene-rich tipm ligands. Considering the extremely high concentration of NO₃⁻ or SO₄²⁻ in certain types of nuclear waste solutions, we also investigated the uptake of ReO₄⁻ as a function of their concentrations. As shown in Figure S13, when the molar ratio of NO₃⁻ and ReO₄⁻ is 20:1, the uptake of ReO₄⁻ is still as high as 76%. More impressively, the removal of ReO₄⁻ is almost unaffected by the concentration of SO₄²⁻. SCU-101 can still remove 80% of ReO₄⁻ in the presence of 6000 times of SO₄²⁻ in excess (Figure 2e), making it an extremely attractive candidate to selectively remove TcO₄⁻ from waste solutions with high ionic strengths.

To further validate the potential application of SCU-101 in the partition of nuclear waste, we performed the ion exchange experiments using a simulated Hanford LAW melter recycle stream. In this type of solution, the concentrations of NO₃⁻, NO₂⁻, and Cl⁻ are all 300 times higher than that of TcO₄⁻ (Table S7). Notably, SCU-101 can capture 75.2% of TcO₄⁻ from the stream when adding 100 mg of SCU-101 into 10 mL of the simulated solution.

The anion exchange process was confirmed by energy-dispersive X-ray spectroscopy (Figure S14), Fourier transform infrared spectroscopy spectra (Figure S15), and ion chromatography analysis (Figure S16). The structure of SCU-101 remains intact after anion exchange, verified by powder X-ray diffraction (PXRD) patterns (Figure S17). In addition, the crystal habits of SCU-101 including shape, size, and color do not change even after the exchange of TcO₄⁻ (Figure S18), further highlighting the applicability potential as the chromatographic material. This is very unusual because the single-crystallinity of MOF crystals is often ruined after ion exchange even when the framework structure remains unchanged during the process. We therefore collected single crystal X-ray diffraction data directly on TcO₄⁻ incorporated SCU-101 crystals (SCU-101-Tc). Although the unit cell parameters, space group, and the structure of the main cationic framework are almost identical with the original material, we were able to resolve the position of TcO₄⁻ anions in the electron density map with a site occupancy factor (SOF) of ~30%. Note that NO₃⁻ anions cannot be identified in the original structure. Moreover, we also saturated SCU-101 with a variety of other anions including Cl⁻, ClO₃⁻, SO₄²⁻, CrO₂⁻, and PO₄³⁻ and attempted to locate their positions, but all failed. These observations offer hints on the intrinsic driving force for the stabilization of TcO₄⁻ in the structure of SCU-101 and subsequently the excellent TcO₄⁻ uptake selectivity.

In the structure of SCU-101-Tc, all TcO₄⁻ anions reside only in type A channels, while disordered NO₃⁻ anions are likely trapped in type B and C channels and are not exchangeable, which is responsible for the non-integral SOF of the TcO₄⁻ site (Figures 3a and S19). The bond distances of Tc−O range from 1.691 to 1.776 Å, comparable with other Tc(VII) compounds reported. A close examination of the coordination environment of TcO₄⁻ reveals that TcO₄⁻ is trapped within a very dense hydrogen-bond network with H atoms of phenyl and imidazolyl groups (Figure 3b). Each TcO₄⁻ coordinates to 13 H atoms, forming 17 hydrogen bonds with an average distance of 3.41 Å (Table S8).

We also analyzed the electrostatic potential (ESP) distribution of the SCU-101 framework. As shown in Figures 3c and S20, those spaces close to Ni⁺ centers and oxalate groups offer the most negative ESP, whereas the intersections of the cross-stacked tipm pair provides large areas of positive ESP (red areas in arrow direction) to accommodate the TcO₄⁻ anion. The subsequent DFT geometry optimizations confirm this prediction and show that the binding site of TcO₄⁻ is precisely in the corner constructed by two tipm ligands (Figures 3d and S21), consistent with the experimentally obtained crystal structure (Figure S22). The calculated binding energy between TcO₄⁻ and the framework is −20.42 kcal/mol.
In conclusion, SCU-101 is an attractive sorbent material for $\mathrm{TeO}_3^{2-}$ removal from either nuclear waste solutions with high ionic strengths or contaminated water systems with low $\mathrm{TeO}_3^{2-}$ concentrations. The strong $\mathrm{TeO}_3^{2-}$ uptake capability is elucidated by the single crystal structure of $\mathrm{TeO}_3^{2-}$ incorporated materials and first principle theoretic analysis on electrostatic potential distribution and bonding, which is beneficial to further development of cationic MOF materials with improved sequestration capabilities toward anionic pollutants.

ASSOCIATED CONTENT

Supporting Information
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Notes
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