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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 towards $TcO_4^-$. More importantly, this materials 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 simulant 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.

$^{99}Tc$ is a long-lived ($t_{1/2} = 2.13\times10^5$ y) radioisotope produced during nuclear fission of $^{235}U$ or $^{239}Pu$ and primarily exists in the +7 oxidation state as $TcO_4^-$ anion under aerobic conditions.[1] The non-complexing nature, high water solubility, and great stability of $TcO_4^-$ lead to its extremely high mobility in the environment.[2] 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.[3] Therefore it is highly desirable to develop functional materials that can remove $TcO_4^-$ during used fuel reprocessing or remediation of contaminated water systems.[4]

Traditional polymeric anion exchange resins are commercial products that exhibit efficient removal of $TcO_4^-$,[5-7] but their poor radiation resistances and chemical stabilities under extreme conditions are clear demerits.[8] 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 and unbound or weakly coordinated anions in the open space ready to exchange, are scarce compared to the neutral and anionic framework materials.[9] Only a handful of such materials including Mg-Al-LDH,[10] $Y_2(OH)_5Cl$,[11] $Yb_3O(OH)_6Cl$,[12] metal sulfides,[13] and NDTB-1[14] have been investigated for $TcO_4^-$ removal, but the majority of these exhibit low sorption capacity and poor selectivity towards $TcO_4^-$.[15] 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.[16] 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.[16a,17]

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.[15a] 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, $[Ni_2(tipm)_2(C_2O_4)](NO_3)_2 \cdot 2H_2O$ (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 towards $TcO_4^-$.

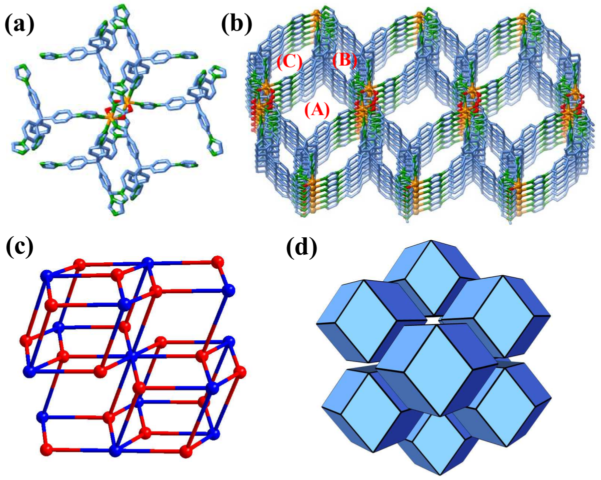

**Figure 1.** Crystal structure of SCU-101. (a) Coordination environment of $Ni^{2+}$ with four tipm ligands and one oxalate group. (b) 3D cationic framework containing three types of channels. Atom colors: Ni=orange; O=red; C=light blue; N=green. (c) Simplified (4,8)-connected binodal *Flu* topology.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

SCU-101 crystallizes in the triclinic space group, $P\bar{1}$, as blue plate crystals (Figure S5 and Table S1). The size of these crystals is ca. 400×100×40 $\mu m^3$, 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 $C_2O_4^{2-}$ anion (Figure S7 and Figure 1a). As shown in Figure 1b, there are three types of channels (A: ~7×9 $Å^2$, B: ~11×5 $Å^2$, and C: ~4×2.5 $Å^2$) 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 $[Ni_2C_2O_4]^{2+}$ 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 dodecahedra (Figure 1d).

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 $^{60}Co$ γ irradiation or 200 kGy β 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.[8]

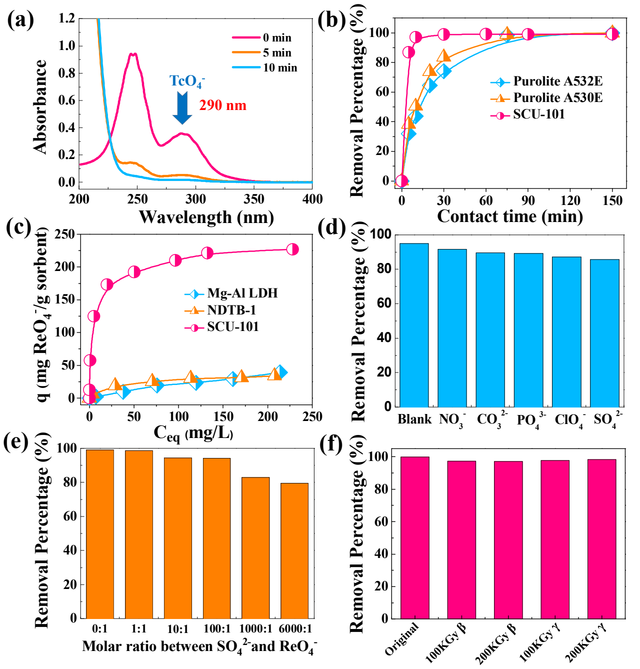

**Figure 2.** (a) UV-vis absorption spectra of $TcO_4^-$ during the anion exchange. (b) Sorption kinetics of $TcO_4^-$ by SCU-101 compared with Purolite A530E and A532E. (c) Sorption isotherms of $ReO_4^-$ by SCU-101, Mg-Al-LDH, and NDTB-1. (d) Effect of competing anions on the removal percentage of $TcO_4^-$ by SCU-101. (e) Effect of $SO_4^{2-}$ on the anion exchange of $ReO_4^-$ by SCU-101. (f) Removal percentage of $ReO_4^-$ after irradiation as compared with the original SCU-101 sample.

Anion exchange of $TcO_4^-$ 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 $TcO_4^-$ 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 $TcO_4^-$ occurs at 85% after 5 min and >95% 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 exchange equilibrium for SLUG-21[16a] and UiO-66-$NH_3^+$ [17] to sequester $TcO_4^-/ReO_4^-$.

To comprehensively study the ion exchange properties of $TcO_4^-$ 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 $TcO_4^-$. The sorption isotherm curve of SCU-101 towards $ReO_4^-$ can be well fitted to the Langmuir model (Figures 2c, 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-

NH$_3^+$,[17] but only lower than PAF-1-F[19] and SCU-100. The distribution coefficient ($K_d$) of SCU-101 towards $ReO_4^-$ reaches 7.5×10$^5$ mL/g, noticeably higher than those of all reported anion sorbent materials (Table S4). The final $ReO_4^-$ 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 $ReO_4^-$ could be exchanged back to the solution using a desorption solution containing 1 M $NaNO_3$, and the material can be fully regenerated for at least four sorption/desorption cycles (Figure S4), representing another advance over SCU-100 (Figure S2). Moreover, SCU-101 can remove $ReO_4^-$ 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 towards $TcO_4^-$/$ReO_4^-$ was first studied by the uptake of $ReO_4^-$ with the presence of one equivalent of competing anions, including $NO_3^-$, $CO_3^{2-}$, $PO_4^{3-}$, $ClO_4^-$ and $SO_4^{2-}$. 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 $ReO_4^-$ by UiO-66-NH$_3^+$ occurs at 15%, 50%, and 20% of the original concentrations in the presence of $PO_4^{3-}$, $SO_4^{2-}$, and $ClO_4^-$, respectively[17]; the removal occurs at 21% and 19% for PAF-1-F in presence of $PO_4^{3-}$ and $SO_4^{2-}$, respectively[19]. Generally, anions with higher charge densities often successfully outcompete with $ReO_4^-$ during the exchange process owing to stronger host-guest electrostatic interactions. Surprisingly, SCU-101 shows much less affinity towards $PO_4^{3-}$ and $SO_4^{2-}$ compared to that of $ReO_4^-$/$TcO_4^-$, 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[16f] and likely originates from the hydrophobic nature of channels constructed by benzene-rich tipm ligands. Considering the extremely high concentration of $NO_3^-$ or $SO_4^{2-}$ in certain types of nuclear waste solutions, we also investigated the uptake of $ReO_4^-$ as a function of their concentrations. As shown in Figure S13, when the molar ratio of $NO_3^-$ and $ReO_4^-$ is 20:1, the uptake of $ReO_4^-$ is still as high as 76%. More impressively, the removal of $ReO_4^-$ is almost unaffected by the concentration of $SO_4^{2-}$. SCU-101 can still remove 80% of $ReO_4^-$ in the presence of 6000 times of $SO_4^{2-}$ in excess (Figure 2e), making it an extremely attractive candidate to selectively remove $TcO_4^-$ 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.[14b] In this type of solution, the concentrations of $NO_3^-$, $NO_2^-$, and $Cl^-$ are all 300 times higher than that of $TcO_4^-$ (Table S7). Notably, SCU-101 can capture 75.2% of $TcO_4^-$ 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 does not change even after the exchange of $TcO_4^-$ (Figure S18), further highlighting the application 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 $TcO_4^-$ 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 $TcO_4^-$ anions in the electron density map with a site occupancy factor (SOF) of ~30%. Note that $NO_3^-$ anions cannot be identified in the original structure. Moreover, we also saturated SCU-101 with a variety of other anions including $Cl^-$, $ClO_4^-$, $SO_4^{2-}$, $CrO_4^{2-}$ and $PO_4^{3-}$ and attempted to locate their positions but all failed. These observations offer hints on the intrinsic driving force for the stabilization of $TcO_4^-$ in the structure of SCU-101 and subsequently the excellent $TcO_4^-$ uptake selectivity.

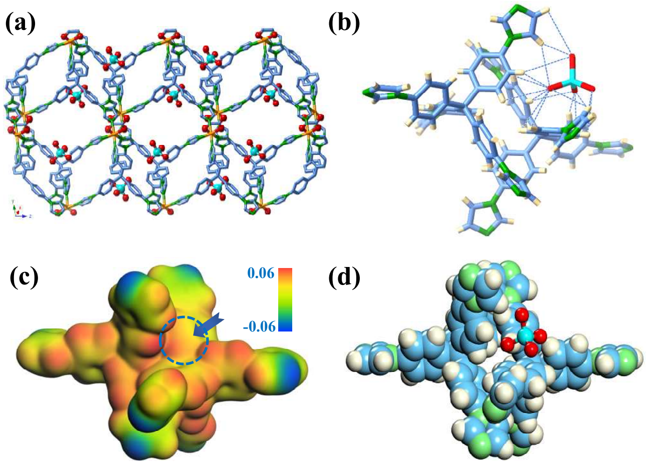

**Figure 3.** (a) $TcO_4^-$ trapped in type A channels. (b) Hydrogen bonds formed between $TcO_4^-$ and SCU-101 framework. (c) Electrostatic potential distribution of the partial framework. (d) Optimized trapping position of $TcO_4^-$ in the framework by theoretical calculations.

In the structure of SCU-101-Tc, all $TcO_4^-$ anions reside only in type A channels while disordered $NO_3^-$ anions are likely trapped in type B and type C channels and are not exchangeable, which is responsible for the non-integral SOF of the $TcO_4^-$ 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.[20] A close examination of the coordination environment of $TcO_4^-$ reveals that $TcO_4^-$ is trapped within a very dense hydrogen bond network with H atoms of phenyl and imidazolyl groups (Figure 3b). Each $TcO_4^-$ 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$^{2+}$ 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 $TcO_4^-$ anion. The subsequent DFT geometry optimizations confirm this prediction and show that the binding site of $TcO_4^-$ is precisely in the corner constructed by two tipm ligands (Figure 3d and Figure S21), consistent with the experimentally obtained crystal structure (Figure S22). The calculated binding energy between $TcO_4^-$ and the framework is -20.42 kcal/mol.

In conclusion, SCU-101 is an attractive sorbent material for $TcO_4^-$ removal from either nuclear waste solutions with high ionic strengths or contaminated water systems with low $TcO_4^-$ concentrations. The strong $TcO_4^-$ uptake capability is elucidated by the single crystal structure of $TcO_4^-$ 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 towards anionic pollutants.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. (PDF)

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§These authors contributed equally.

### Notes

The authors declare no competing financial interests.

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