Removal of $^{99}\text{TcO}_4^-$ from legacy defense nuclear tank waste at Savannah River Site is highly desirable for the purpose of nuclear safety and environmental protection, but currently not achievable given the extreme conditions including high alkalinity, high ionic strength, and strong radiation field. Herein, we present a potential solution to this long-term issue by developing a two-dimensional cationic metal organic framework SCU-103, showing ultrahigh stability in alkaline aqueous media and great resistance to both $\beta$ and $\gamma$ radiation. More importantly, it is very effective for $^{99}\text{TcO}_4^-$ separation from aqueous media as demonstrated by fast exchange kinetics, high sorption capacity, and superior selectivity, leading to the successful removal of $^{99}\text{TcO}_4^-$ from actual Savannah River Site high level tank waste for the first time, to the best of our knowledge. In addition, the uptake mechanism is comprehensively elucidated by molecular dynamics simulation and density functional theory calculation, showing a unique chemical recognition of anions with low charge density.
With the development of nuclear power technology, radioactive waste treatment and contamination remediation are great challenges. The Savannah River Site (SRS), located along the Savannah River in western South Carolina (US), was built in the 1950s with the primary mission to produce tritium and plutonium for national defense programs. The main responsibilities of SRS at present are environmental restoration and remediation. Up to date, the vast bulk of legacy nuclear wastes composed of sludge and supernatant liquid that have been generated are stored in underground tanks at SRS awaiting pretreatment and safe disposal. Among these, \( {\text{{}^{99}Tc}} \), a long-lived \( \beta \)-emitting radionuclide, is considered to be one of the most problematic radionuclides. With a high fission yield of 6%, \( \approx 400 \text{ metric tonnes of {\text{{}^{99}Tc}}} \) have been produced since the utilization of \( \text{Tc} \) for nuclear fuel reprocessing. However, these cationic materials exhibit notably poor alkaline stability because the cationic pyridine or imidazolium ring undergoes ring-opening reactions induced by nucleophilic attack from \( \text{OH}^{-} \) in alkaline solutions. Therefore, a qualified \( \text{H}_{2}{\text{{}^{99}TcO}}_{4}^{2-} \) capture material with combined characteristics of excellent alkaline stability, radiation resistance, and excellent selectivity aiming for legacy defense waste partitioning at SRS currently remains elusive.

Metal organic frameworks (MOFs), assembled by organic linkers and inorganic metal ions or clusters, have evolved as an important branch of porous functional materials. Considering the diversity of inorganic and organic components, MOFs exhibit versatile structures and properties, giving them great potential in multiple applications, including gas storage,4,26 adsorption/separation,27 luminescence28, and catalysis29,30. More significantly, MOFs have been proven to be powerful in the field of environmental remediation, especially in the sequestration of toxic pollutants from aqueous solutions via adsorption or ion-exchange processes. As a subclass, cationic MOFs constructed by neutral nitrogen-containing ligands and metal ions have attracted significant research attention as anion-exchange scavengers owing to the presence of substitutable uncoordinated anions residing in the void spaces 32–36. Compared with traditional cationic porous materials, MOFs afford some clear advantages. In particular, the highly tunable structures, achievable by rational selections of inorganic and organic components, or via post-synthetic modification of the surface, contributes greatly to the enhancement of separation selectivity. Furthermore, the crystalline nature allows for precise structure–property correlation, which is greatly beneficial for identifying the separation/exchange mechanism. To date, several types of oxo-anions including \( \text{CrO}_{4}^{2-}, \text{CrO}_{2}^{2-}, \text{MnO}_{4}^{-} \) were reported to be captured by cationic MOFs. A series of cationic MOFs as \( \text{ReO}_{4}^{-–}{\text{{}^{99}TcO}}_{4}^{2-} \) scavengers with high uptake capacity, fast kinetics, excellent sorption selectivity, and good radiation resistance have also been developed recently.

Despite these advantages, the relatively low hydrolytic and chemical stability has stalled the progress of these materials for real-time \( \text{TcO}_{4}^{-} \) separation applications, especially under extremely alkaline conditions.

Therefore, we sought to develop alkaline-resistant cationic MOFs for \( \text{TcO}_{4}^{-} \) segregation in SRS HLW streams. Based upon the soft-hard-acid-base theory, the combination of carboxylate groups and high-valent metal ions such as \( \text{Zr}^{4+}, \text{Hf}^{4+}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+} \), which are characterized as hard Lewis bases and acids, respectively, can facilitate the formation of strong coordination bonds with each other, furnishing frameworks with high stability in neutral aqueous solutions or even in concentrated acids 35–38, whereas these materials usually undergo decomposition in alkaline conditions. The stability of MOFs is closely related to the robustness of the coordination bonds between metal ions and organic ligands and the disintegration of structure was attributed to the competitive coordination to metal ions between organic ligands and other molecular species or anions. For MOFs mentioned above, carboxylate groups coordinated to high-valent metal ions could be easily replaced by \( \text{OH}^{-} \) anions owing to their strong affinity toward high-valent metal ions, thus leading to decomposition in alkaline solutions. Therefore, aiming for decent alkaline stability, metal ions and organic ligands with enhanced softness are highly desirable. With this strategy, the binding interaction between \( \text{OH}^{-} \) anions and metal ions is dramatically weakened and the coordination bonds between metal ions and linkers are robust enough to resist the competition from \( \text{OH}^{-} \) anions. This is particularly true for MOFs built from transition metal ions and nitrogen heterocyclic ligand with high \( pK_{a} \) values. However, the systematic design and development of cationic MOFs with good alkaline resistance is still in its infancy.
Herein, we developed a two-dimensional cationic MOF by employing a neutral tridentate nitrogen ligand tris[4-(1H-imidazol-1-yl)-phenyl]amine (tipa) and Ni^{2+} ions, namely [Ni(tipa)_3(NO_3)_2] (SCU-103). It overcomes the disadvantage of poor alkaline stability of reported cationic MOF materials and exhibits exceptional $^{99}$TcO$_4^-$ capture selectivity, leading to the successful separation of $^{99}$TcO$_4^-$ from actual legacy nuclear waste at SRS.

**Hydrolytic and radiolytic stability.** Except for some preferred orientation, the experimental powder X-ray diffraction (PXRD) pattern is basically consistent with the one simulated from single-crystal X-ray structure analyses, indicating the phase purity of SCU-103 (Supplementary Figure 3). Significantly, SCU-103 possesses great hydrolytic stability as the PXRD patterns after immersion into aqueous solutions with pH values ranging from 3 to 14 match well with those of the pristine compounds (Fig. 2a). Such a unique property is closely related to its structural characterizations. As depicted by the space-filling mode (Supplementary Figure 4), the metal centers are sterically crowded and enclosed within the concave–convex layers by non-planar tipa ligands, thus endowing SCU-103 with strong resistance to H$_2$O and OH$^-$ attack even under basic conditions. PXRD patterns of dried crystals and crystals immersed in water after 100 and 200 kGy of $\beta$ and $\gamma$ radiation remain almost identical to those of the original products (Fig. 2b). In addition, anion-exchange experiments performed after $\beta$ and $\gamma$ irradiation suggest no decrease in adsorption capacity of ReO$_4^-$ as compared with the original samples, further confirming excellent radiation resistance of SCU-103 (Fig. 4d, Supplementary Table 16).
radiation resistance originates from the relatively large conjugated structure of the tipa ligand that can stabilize the radiation induced radicals, similar to several radiation resistant MOFs recently developed\(^{38}\). These results demonstrate that SCU-103 possesses sufficient robustness required for practical applications in high-level nuclear waste streams.

**Sorption kinetics analysis.** The anion-exchange experiment was initially performed by soaking 20 mg of SCU-103 samples in 20 mL of aqueous solution containing 14 ppm of \(^{99}\)TcO\(_4^−\), in which the molar ratio of SCU-103 to \(^{99}\)TcO\(_4^−\) was ~6:1. The effect of contact time of \(^{99}\)TcO\(_4^−\) with SCU-103 was investigated to evaluate the anion-exchange rate and equilibrium time. As shown in Fig. 3a, the concentration of \(^{99}\)TcO\(_4^−\) as a function of contact time was measured by examining the intensity of its characteristic absorption peak at 290 nm in UV–Vis spectra. The relative amount of \(^{99}\)TcO\(_4^−\) removed was ~92% within the first 30 s and increased to >95% after 5 min. Liquid scintillation counting (LSC) measurements further verified that SCU-103 exhibits extremely rapid kinetics with an equilibrium time of ~5 min (Fig. 3b, Supplementary Table 1). The rapid exchange kinetics may derive from the nature of the layered structure, which is beneficial for the rapid delivery of anions. Moreover, high positive charge density and hydrophobicity also increase the affinity of the 2D layers for \(^{99}\)TcO\(_4^−\) anions. Note that SCU-103 exhibits very high anion-exchange efficiency in contrast to typical commercial resins (A532E and A530E)\(^{16,18}\) and other anion exchangers designed for the removal of anionic contaminants including NDTB-1\(^{13,14}\), SLUG-21\(^{39}\), UiO-66-NH\(_2\)\(^{48}\), comparable to those of SCU-100\(^{16}\), SCU-101\(^{42}\), and SCU-102\(^{45}\). The ultrafast sorption kinetics has great application significance and unique advantages as the short contact time between sorbents and radioactive waste solution would effectively reduce the risk of nuclear leakage and lower the damage of sorbents induced by radiation and hydrolysis.

Considering the high total activity of \(^{99}\)Tc sample needed for the anion-exchange isotherm experiment, ReO\(_4^−\) was used as a nonradioactive surrogate for \(^{99}\)TcO\(_4^−\) owing to its similar charge density. In addition, the exchange kinetics for ReO\(_4^−\) under the same conditions are almost identical to \(^{99}\)TcO\(_4^−\) (Fig. 3b, Supplementary Figure 5a and Table 2). Further analysis indicates that the kinetic exchange data for ReO\(_4^−\) was fit well with the pseudo-second-order kinetic model as the plot of \(t/q\) vs \(t\) exhibits a linear relationship with a high correlation coefficient \(R^2\) (>0.99) (Supplementary Figure 5b), indicating that the ReO\(_4^−/^{99}\)TcO\(_4^−\) removal by SCU-103 involves chemical adsorption. The exchange of nitrate anions in SCU-103 by ReO\(_4^−\) anions was also confirmed by energy-dispersive spectroscopy (EDS) (Supplementary Figure 6). Elemental distribution mapping of the exchanged products exhibited the presence of a significant amount of captured Re and its homogeneous distributions in the sample (Supplementary Figure 7). In addition, the new peak at 905 cm\(^−1\) and the decreased intensity of 1332 cm\(^−1\) in the Fourier-transform infrared spectroscopy (FT-IR) spectra of the ReO\(_4^−\)-exchanged SCU-103 material (Supplementary Figure 8) confirm the anion-exchange process.

**Sorption isotherm analysis.** To evaluate the ReO\(_4^−\) uptake capacity of SCU-103, adsorption isotherm experiments at room temperature were executed with the initial concentration of Re ranging from 5 to 400 ppm. As depicted in Fig. 3c, the sorption isotherm curves plotted by the equilibrium concentration against the ion-exchange capacity q (mg/g) are fit well with the Langmuir model and the maximum anion-exchange capacity (\(q_m\)) was calculated to be 318 ± 8 mg/g (Supplementary Tables 3 and 4). This greatly exceeds the capacity of Yb\(_2\)(OH)\(_4\)Cl (48.6 mg/g)\(^{49}\), NDTB-1 (49.4 mg/g)\(^{49}\), UiO-66-NH\(_2\) (159 mg/g)\(^{48}\), NU-1000 (210 mg/g)\(^{47}\), SCP-IHEP-1 (211 mg/g)\(^{46}\), SCU-101 (247 mg/g)\(^{42}\), and SCU-102 (291 mg/g)\(^{45}\), but is lower than those of SCU-CPN-1 (999 mg/g)\(^{21}\), SCU-100 (541 mg/g)\(^{16}\), SLUG-21 (602 mg/g)\(^{39}\), PAF-1-F (420 mg/g)\(^{59}\).

**Selectivity.** For high-level nuclear waste streams, there is a large excess of competing anions, such as NO\(_3^−\), SO\(_4^{2−}\), CO\(_2^{3−}\), Cl\(^−\), and so on, which generally have large detrimental effects on the selective capture of \(^{99}\)TcO\(_4^−\). Therefore, we investigated the ReO\(_4^−\) ion exchange of SCU-103 in the presence of one equivalent of competing anions with different charge numbers, including NO\(_3^−\), SO\(_4^{2−}\), CO\(_2^{3−}\), PO\(_3^{3−}\), Cl\(^−\), and CIO\(_4^{−}\). Notably, the removal in all cases could achieve 98% (Fig. 3d) with the \(K_d\) values over 10\(^3\) mL/g (Supplementary Table 5), indicating the strong affinity and very high selectivity for ReO\(_4^−\) by SCU-103 against various competing anions. Generally, anions with higher charge densities such as SO\(_4^{2−}\), CO\(_2^{3−}\), PO\(_3^{3−}\) act as strong competitors for ReO\(_4^−\) capture owing to the stronger host–guest electrostatic interactions. For instance, the removal percentages of ReO\(_4^−\) for UiO-66-NH\(_2\) are 15%, 50%, and 20% in the presence of PO\(_3^{3−}\), SO\(_4^{2−}\), and CIO\(_4^{−}\), respectively\(^{48}\) for PAF-1-F, only 21% and 19% of the original concentration could be captured with the presence of PO\(_3^{3−}\) and SO\(_4^{2−}\), respectively\(^{48}\). Although in the present case, SCU-103 still retains a strong preference toward ReO\(_4^−\) despite the presence of PO\(_3^{3−}\) and SO\(_4^{2−}\). For certain types of nuclear waste streams such as Hanford and SRS waste, the competing effects of a huge excess of NO\(_3^−\) and SO\(_4^{2−}\) should be taken into account.
consideration when examining $^{99}$TcO$_4^-$ removal. Therefore, the ReO$_4^-$ uptake selectivity was further checked in the presence of different equivalents of NO$_3^-$ and SO$_4^{2-}$ anions. As depicted in Fig. 3e, the removal percentages remain higher than 97% for the molar ratios of NO$_3^-$ to ReO$_4^-$ ranging from 1:1 to 20:1 and $K_d$ values higher than 7.96 × 10$^3$ mL/g can still be achieved (Supplementary Table 6). Even at a ratio of 100:1, >88% of ReO$_4^-$ ions could be sequestered, comparable to that of SCU-102 45. Impressively, when SO$_4^{2-}$ is present in 6000 fold excess, SCU-103 can still retain high relative amounts of ReO$_4^-$ removal (82%, Fig. 3f) and a high $K_d$ value of 4.66 × 10$^3$ mL/g (Supplementary Table 7). These important results indicate that SCU-103 has high selectivity and strong affinity for ReO$_4^-$/$^{99}$TcO$_4^-$ even in the presence of a large excess of NO$_3^-$ or SO$_4^{2-}$. This remarkable characteristic makes it an extremely viable candidate for selective removal of ReO$_4^-$/$^{99}$TcO$_4^-$ from waste solutions with high ionic strengths.

**pH effect study.** The removal of $^{99}$TcO$_4^-$ anions under extreme conditions, such as in acidic and alkaline conditions is highly desirable. The uptake capability of SCU-103 under different pH values were determined in solutions containing 200 ppm of ReO$_4^-$ at a solid–liquid ratio of 1 mg/mL. As shown in Fig. 4a, the removal percentage remains at a high level (>90%) within a wide pH range of 3–12. Even in 0.1 M and 1 M NaOH (defined as pH 13 and pH 14 for convenience), SCU-103 can still afford ReO$_4^-$ removal efficiency of 61% and 22%, respectively.
Impressively, the removal efficiencies in 1 M NaOH solution can increase to >99% at solid–liquid ratios of 10 mg/mL and above (Fig. 4b, Supplementary Table 9). Such a high removal capability from a highly basic solution is reported for the first time, indicating that SCU-103 is a feasible material for 99Tc separation in alkaline nuclear waste inventory.

Encouraged by the results above, we then evaluated the 99TcO₄⁻ removal capacity by SCU-103 in a simulated SRS HLW waste sample. In contrast to extremely acidic nuclear waste generated in used nuclear fuel reprocessing, the nuclear inventory at SRS is highly alkaline, containing a sufficient excess of OH⁻ (1.3 M), NO₃⁻ (1.82 M), NO₂⁻ (0.489 M), SO₄²⁻ (0.04 M), and CO₃²⁻ (0.48 M) (Supplementary Table 10). The actual waste sample also contained significant quantities of various radionuclides including ¹³⁷Cs, ⁹⁰Sr, ²³⁸Pu, and ⁹⁹Tc, yielding a total gamma activity of 6.3E + 05 pCi/mL, a total beta activity of 8.8E + 05 pCi/mL, and a total alpha activity of 2.1E + 04 pCi/mL. To our best knowledge, this is the first time when an advanced porous material is tested under the real scenario where high alkalinity and ionic strength as well as strong radiation are combined together. As can be seen from the data, the percent removal of ⁹⁹TcO₄⁻ increases as the phase ratio increases. At the highest phase ratio (40 mg/mL) tested, 90% of the ⁹⁹TcO₄⁻ was removed from solution within 3 hrs (Fig. 4c, Supplementary Table 11). A series of batch contact tests were also performed utilizing a sample of actual SRS tank waste with a sufficient excess of OH⁻ (1.88 M), NO₃⁻ (1.82 M), NO₂⁻ (0.489 M), SO₄²⁻ (0.04 M), and CO₃²⁻ (0.48 M) (Supplementary Table 12). The actual waste sample also contained significant quantities of various radionuclides including ¹³⁷Cs, ⁹⁰Sr, ²³⁸Pu, and ⁹⁹Tc, yielding a total gamma activity of 6.3E + 05 pCi/mL, a total beta activity of 8.8E + 05 pCi/mL, and a total alpha activity of 2.1E + 04 pCi/mL. To our best knowledge, this is the first time when an advanced porous material is tested under the real scenario where high alkalinity and ionic strength as well as strong radiation are combined together. As can be seen from the data, the percent removal of ⁹⁹TcO₄⁻ increases as the phase ratio increases. At the highest phase ratio (40 mg/mL) tested, 90% of the ⁹⁹TcO₄⁻ was removed from solution within 3 hrs (Fig. 4c, Supplementary Table 11). A series of batch contact tests were also performed utilizing a sample of actual SRS tank waste with a sufficient excess of OH⁻ (1.3 M), NO₃⁻ (2.6 M), NO₂⁻ (0.1 M), SO₄²⁻ (0.5 M), and CO₃²⁻ (0.03 M), in addition to 8.0 × 10⁻⁵ M TcO₄⁻ (Supplementary Table 10). Up to now, no material has been demonstrated to be functional with sufficient stability under these conditions. More impressively, the removal of ⁹⁹TcO₄⁻ from the simulated HLW by SCU-103 is 52% at a phase ratio of 5 mg/mL and ~90% of ⁹⁹TcO₄⁻ could be extracted at a solid–liquid ratio of 40 mg/mL (Fig. 4c, Supplementary Table 11).
Reusability. We also assessed the reusability of SCU-103 using a neutral solution containing 30 ppm of ReO$_4^{-}$. The ReO$_4^{-}$-exchanged SCU-103 materials could be conveniently eluted by applying 1 M NaNO$_3$ solutions and more than 98% ReO$_4^{-}$ could be dissociated back to the solutions. Even after four cycles of sorption/desorption, the removal efficiency of SCU-103 is not affected (Fig. 4e, Supplementary Table 14). The FT-IR analysis also confirms that the loaded SCU-103 material can transform back to the original material after eluting (Supplementary Figure 8). More impressively, SCU-103 also retains good regeneration properties after removing ReO$_4^{-}$ (Fig. 8). More impressively, SCU-103 also retains good regeneration properties after removing ReO$_4^{-}$ (Fig. 8). More impressively, SCU-103 also retains good regeneration properties after removing ReO$_4^{-}$ (Fig. 8). More impressively, SCU-103 also retains good regeneration properties after removing ReO$_4^{-}$ (Fig. 8). More impressively, SCU-103 also retains good regeneration properties after removing ReO$_4^{-}$ (Fig. 8). More impressively, SCU-103 also retains good regeneration properties after removing ReO$_4^{-}$ (Fig. 8).

Sorption mechanism. We studied the selective sorption behavior of $^{99m}$TcO$_4^{-}$ into SCU-103 against various competing anions (including NO$_3^{-}$, SO$_4^{2-}$, and OH$^-$) and elucidated the underlying molecular mechanism using all-atom molecular dynamics (MD) simulations. As shown in Fig. 5a, b, after immersing the solid SCU-103 into the aqueous solution that initially contains various anions (i.e., $^{99m}$TcO$_4^{-}$, NO$_3^{-}$, SO$_4^{2-}$, OH$^-$, and NO$_3^{-}$), ~80% of $^{99m}$TcO$_4^{-}$ in aqueous solution is sorbed into the interior of SCU-103 within a very short period of time (15 ns), whereas 80% of NO$_3^{-}$-originally residing in SCU-103 is released to the bulk water. Impressively, we observed almost no SO$_4^{2-}$ or OH$^-$ anions in the aqueous solution being sorbed into SCU-103 (<3%), which may also account for its alkaline stability (unfavorable binding free energies for SO$_4^{2-}$ (21.1 kJ/mol) and OH$^-$ (16.6 kJ/mol), Supplementary Figure 9). After ~15 ns, the sorption ratios for each type of anions remained constant, suggesting these results from our simulation converge well (Fig. 5b, and also see the Supplementary Movie 1 in Supplementary for a more intuitive demonstration). In another control simulation in pure water (without any competing anions in the external solution environment), ~90% of the residual NO$_3^{-}$ anions are reserved in SCU-103 (Fig. 5b, navy blue curve). These results suggest that SCU-103 exhibits a remarkable sorption selectivity towards $^{99m}$TcO$_4^{-}$ over other competing anions, and the uptake of $^{99m}$TcO$_4^{-}$ is an anion-exchange process. In addition, we also compared the SCU-103-binding sites for the sole NO$_3^{-}/^{99m}$TcO$_4^{-}$ anion pair without any other competing anions (for a better sampling). Clearly, without any interference from other types of competing anions, the preferential binding sites for NO$_3^{-}$ and $^{99m}$TcO$_4^{-}$ are partially similar (Supplementary Figure 10). For instance, a majority of NO$_3^{-}/^{99m}$TcO$_4^{-}$ anions prefer being located near the imidazole rings in the cavity of SCU-103 surface and on the top of the imidazole ring above the surface (Supplementary Figure 10). This is reasonable, as these regions carry the highest positive electrostatic potential (Supplementary Figure 11).

To further probe the driving force for this vigorous anion-exchange (NO$_3^{-}$ replaced by $^{99m}$TcO$_4^{-}$) process, direct interaction energies between $^{99m}$TcO$_4^{-}$/NO$_3^{-}$ and SCU-103, and between $^{99m}$TcO$_4^{-}$ and NO$_3^{-}$ as a function of simulation time were computed and analyzed, and they were also decomposed into the contributions from the van der Waals (vdW) and electrostatic (elec) interactions to illustrate the major driving force. During the main $^{99m}$TcO$_4^{-}$ sorption stage ($t < 15$ ns), the direct interaction between $^{99m}$TcO$_4^{-}$ and SCU-103 drives the sorption of $^{99m}$TcO$_4^{-}$, as witnessed by the sharply lowered (more favorable) interaction energy from 0 to ~1250 kJ/mol (black hollow star in Fig. 5c). The contribution from the electrostatic interaction (~700 kJ/mol) (black hollow triangle in Fig. 5c) is slightly larger than that from the vDW interaction (~550 kJ/mol) (black hollow inverted triangle in Fig. 5c). While, during the same period, the direct interaction energy between NO$_3^{-}$ and SCU-103 is increased by 1000 kJ/mol (from ~1600 kJ/mol to ~600 kJ/mol; red hollow star in Fig. 5c) (less favorable), with the electrostatic interaction contributing ~600 kJ/mol (red hollow triangle in Fig. 5c) and the vDW interaction contributing the other ~400 kJ/mol (red hollow inverted triangle in Fig. 5c). Again, the electrostatic interaction contributes slightly more than van der Waals interaction. Meanwhile, owing to direct electrostatic repulsion, the interaction energy between $^{99m}$TcO$_4^{-}$ and NO$_3^{-}$ is increased from 0 to 50 kJ/mol (repulsive) (purple hollow star in Fig. 5c). These results suggest that direct $^{99m}$TcO$_4^{-}$ anions–SCU-103 non-bonded interactions, with electrostatic interaction contributing slightly more than vdW interaction, has a critical role in the $^{99m}$TcO$_4^{-}$ uptake process.

A representative anion-exchange event was then analyzed, with its most important intermediate state in the process revealed. As shown in Fig. 6a and Supplementary Movie 2 in Supplementary, initially ($t < 1.1$ ns), a NO$_3^{-}$ anion resides very close to an imidazole ring in the interior binding cavity of SCU-103. From ~1.1 ns to ~1.4 ns, a $^{99m}$TcO$_4^{-}$ anion gradually approaches the same binding cavity of the NO$_3^{-}$, and transiently stays on the top of the imidazole ring. From 1.4 ns to ~2.3 ns, the $^{99m}$TcO$_4^{-}$ anion enters the cavity, and is stably anchored to the site close to another adjacent imidazole ring. It is noteworthy that, during the main intruding stage of $^{99m}$TcO$_4^{-}$ into the binding cavity (1.1 ns~2.0 ns), NO$_3^{-}$ oscillates around its original binding site. However, after a very short ~0.1 ns (i.e., $t = ~2.1$ ns), NO$_3^{-}$ is expelled out of its original binding site, and rapidly (from 2.1 ns to 2.3 ns) diffuses into the bulk water, completing the anion-exchange process. Throughout this entire exchange dynamic, clearly, the state when $^{99m}$TcO$_4^{-}$ is bound to its final binding site while NO$_3^{-}$ dwells at its original binding site is the most crucial intermediate state.

The binding free energies (potential of mean force, PMF) of $^{99m}$TcO$_4^{-}$/NO$_3^{-}$ was then calculated for this most important intermediate state. We first investigated the changes in the binding free energy of the two anions to SCU-103 at this critical state, and then compared the values obtained from each of the two anions solely (in the absence of other competing anions) bound to its binding site. The black PMF curves in Fig. 6b, c demonstrate that during the pathway of NO$_3^{-}/^{99m}$TcO$_4^{-}$ alone binding to its final binding site, there are two prominent binding free energy minima. In the case of $^{99m}$TcO$_4^{-}$ (Fig. 6b, black curve), the global minimum is located at the distance of ~0.20 nm (very close to an imidazole ring within the binding cavity), with a $\Delta G$ of ~17.9 kJ/mol. Another local minimum is located at the distance of 0.64 nm (on the top of an imidazole ring above SCU-103), with a $\Delta G$ of ~7.1 kJ/mol. The two minima are separated by a free energy barrier $\sim 2.2$ kJ/mol ($\sim 1$ kBT at room temperature), which can be easily overcome by thermal fluctuation. Similarly, in the case of NO$_3^{-}$ (Fig. 6c, black curve), the global minimum is located at the distance of ~0.21 nm (very near another imidazole ring within the binding cavity), with a $\Delta G$ of ~10.0 kJ/mol, whereas the other local minimum is situated at the distance of ~0.59 nm (on the top of another imidazole ring above the binding cavity), with a $\Delta G$ of ~6.1 kJ/mol. These two minima are also separated by a moderate energy barrier of ~2.1 kJ/mol. This indicates that both anions are energetically favorable to bind to SCU-103. Meanwhile, $^{99m}$TcO$_4^{-}$ shows a notably stronger binding affinity than NO$_3^{-}$, which indicated that the anion-exchange process is thermodynamically feasible. More specifically, the binding free energies for $^{99m}$TcO$_4^{-}$ and NO$_3^{-}$ at their most
energetically favorable binding sites in SCU-103 are −17.9 kJ/mol and −10.0 kJ/mol, respectively. At the crucial intermediate state, the binding of $^{99}\text{TcO}_4^-$ can significantly diminish the global binding free energy minimum of $\text{NO}_3^-$ at the distance of 0.21 nm, and meanwhile, the binding free energy of $\text{NO}_3^-$ at the position is remarkably increased by $\Delta \Delta G = 9.5$ kJ/mol, which eventually reaches −0.5 kJ/mol (nearly comparable to the bulk value) (Fig. 6c, red curve). The data imply that the electrostatic repulsion introduced by $^{99}\text{TcO}_4^-$ can completely offset the binding affinity between $\text{NO}_3^-$ and SCU-103, leading to the diffusion of $\text{NO}_3^-$ from the interior of SCU-103 into the bulk water. At the transition state, the binding affinity of $^{99}\text{TcO}_4^-$ can also be weakened by $\text{NO}_3^-$, e.g., the binding free energy of $^{99}\text{TcO}_4^-$ at the distance of 0.20 nm increases from −17.9 kJ/mol to −13.8 kJ/mol (Fig. 6b, red curve). However, this value is still the global minimum throughout the full $^{99}\text{TcO}_4^-$ adsorption PMF curve (Fig. 6b, red curve), suggesting the moment when $^{99}\text{TcO}_4^-$ is bound close to the imidazole ring within the cavity still represents the most energetically favorable binding state during the whole process.

**Discussion**

The foregoing results demonstrate a rare example of an alkaline-stable cationic MOF with excellent $^{99}\text{TcO}_4^-$ capture capabilities in actual SRS HLW streams, potentially overcoming the long-term challenge in legacy waste partitioning. The unique concave–convex layers containing sterically crowded metal centers in SCU-103 provide suitable recognition sites for the selective incorporation of $^{99}\text{TcO}_4^-$ and sufficient resistance to $\text{H}_2\text{O}$ and $\text{OH}^-$ attack under basic conditions, which is further supported by the combined density functional theory calculation and molecular dynamics simulation. This work not only reports the first example, to the best of our knowledge, of advanced porous materials showing application in a real scenario that combines the extreme conditions of high alkalinity, large excess of competing anions, and strong radiation, but also provides a new design philosophy on solid sorbent materials for the remediation of critical environmental pollutants in the future.

**Methods**

Caution! $^{99}\text{Tc}$ is a $\beta$-emitter ($t_{1/2} = 2.13 \times 10^5$ a) and possesses significant health risks when inhaled or ingested. Standard precautions and procedures for handling...
Fig. 6 Binding free energies of $^{99}$TcO$_4^-$ and NO$_3^-$ to their most energetically favorable sites in SCU-103. a A representative anion-exchange process of NO$_3^-$ by TcO$_4^-$ (left). The red and blue lines with an arrow represent the center of mass motion trajectory of TcO$_4^-$ and NO$_3^-$ from 1.1 ns to 2.3 ns. The most important crucial intermediate state during the anion-exchange process is shown when TcO$_4^-$ binds to its final binding site, while NO$_3^-$ dwells at its original binding site (right). The color gradient of the background demonstrates the binding probability distribution of NO$_3^-$ from lowest probability (0, white) to highest probability (0.110, red). b and c Binding free energies of TcO$_4^-$/NO$_3^-$ alone to its final binding site (black curves), and the binding free energies of the two anions at the crucial intermediate state (red curves). Snapshots highlighted by the black dashed lines represent the typical binding configurations of TcO$_4^-$/NO$_3^-$ anions to SCU-103 corresponding to the energy minima in the free energy curves. The shadows in b and c represent the predictive error of the binding free energy profiles.
deionized water (1.5 mL) was loaded into a 20 mL Teflon-lined stainless steel autoclave. The container was closed, heated at 140 °C for 3 days, and then cooled to room temperature at a cooling rate of 5 °C·h⁻¹. A pure phase of brown hexagonal block-like crystals was collected after washing the product with ethanol three times (Yield: 0.065 g, 60.8% based on tips).

**Single-crystal structure determination.** A single crystal for single-crystal X-ray diffraction was carefully selected under an optical microscope. Data were collected on a Bruker D8 Venture Diffractometer with a Turbo X-ray Source (MoKα radiation (λ = 0.71073 Å) at 296 K. The data frames were collected using the program APEX 3 and processed using the program SAINT routine in APEX 3. The structures were solved by direct methods and refined by full-matrix least-squares on F² using the SHELXL-2016 program package29. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms bonded to C atoms were located at geometrically calculated positions. The disordered NO₃⁻ anions and solvent molecules have been squeezed. The "squeeze" was performed by PLATON using INS or CIF file32. The unit cell was found to contain one void of 2683 Å³, holding 607 electrons, which are contributed by disordered NO₃⁻ anions and solvent molecules.

According to the thermogravimetric analysis, the disordered solvents in one formula unit could be approximately identified as four H₂O and two DMF molecules (Supplementary Figure 13). Therefore, two disordered NO₃⁻ anions, four H₂O, and two DMF molecules contribute 184 electrons in one formula unit. Thus, the voids of one unit cell contain 552 electrons, which are contributed by disordered NO₃⁻ anions and solvent molecules.

**Exchange kinetics studies of SCU-103.** SEM-EDS. Exchange kinetics studies of SCU-103 were done by performing the ion-exchange experiments with various contact times. In all, 20 mg of SCU-103 which had been ground into powder was weighed into a 2 mL solution containing 14 ppm of ReO₄⁻, and the mixtures were kept under magnetic stirring for the desired contact time. The concentrations of ReO₄⁻ in the clear supernatant were determined by ICP-OES. Standard curves with the linear correlation coefficient R² > 0.999 were repeated using 28 ppm of ReO₄⁻. The pH effect study. The solution pH was adjusted by adding negligible volumes of diluted nitric acid or sodium hydroxide. The effect of pH on ReO₄⁻ sorption was carried out by varying pH values from 2 to 14.5 mg of SCU-103 was added to 5 mL of aqueous solution containing 200 ppm of ReO₄⁻. ReO₄⁻ sorption capacity of SCU-103 in the presence of different concentrations of SO₄²⁻ and NO₃⁻ was further conducted by adding 0.15 mM NaNO₃, Na₂SO₄, NaH₂PO₄, NaCl, or NaClO₄ solutions into 0.5 mM ReO₄⁻ solution, respectively. The effect of excessive NO₃⁻ anion was examined by adding 0.15 mM, 0.75 mM, 1.5 mM, 3 mM, or 15 mM NaNO₃ solutions, respectively, into a 0.15 mM ReO₄⁻ solution. The ReO₄⁻ sorption capacity of SCU-103 was found to decrease with the increase of occupied sites. The equation can be expressed by:

\[
q = q_\text{e} \frac{t}{t + t_\text{eq}}
\]  

where \(q\) (mg g⁻¹) is the exchanged amount of the ions at the equilibrium concentration \(C_\text{eq}\) (mg L⁻¹), \(q_\text{e}\) represents the maximum exchange capacity of the exchangers; \(K\) (L/mg) is the Langmuir constant indirectly related to the free energy of the exchange, which characterizes the affinity between ions and absorbers.

The Freundlich model assumes that sorption occurs on the heterogeneous surface, the binding energies differ at adsorption sites, and the binding strengths decrease with the increase of occupied sites. The equation can be expressed by:

\[
K = K_0 C^1/n
\]  

where \(K_0\) and \(n\) are the Freundlich constants related to the sorption capacity and the sorption intensity, respectively. The fitting results of two sorption models are listed in Supplementary Table 4.

**Exchange experiments with SRS HLW stream.** A simulated SRS HLW Stream was prepared according to a reported protocol4 and the molar ratio of each anion to that of 99TcO₄⁻ are provided in Supplementary Table 1. Measured quantities of the simulated SRS HLW Stream were pipetted into sample tubes containing a premeasured quantity of SCU-103 to provide solid/liquid ratios of 1, 5, 10, 20, and 40 g L⁻¹. The sample tubes were placed on an oscillator for 3 h of shaking at ambient temperature. The suspension was separated with a 0.22-μm nylon membrane filter and the filtrate was analyzed by liquid scintillation counting to determine the 99Tc activity. A series of batch contact tests were also performed utilizing a sample of actual SRS tank waste with the composition shown in Supplementary Table 11. The 99Tc activity of this sample was 4.3E+04 pCi/mL. Other key radionuclides in the sample included 137Cs (6.7E+05 pCi/mL), 90Sr (2.9E+04 pCi/mL), and 238Pu (2.5E+04 pCi/mL). A tank downstream of the cesium removal process was selected for working with in the laboratory. Samples of SCU-103 were added to 15 mL conical bottom polystyrene tubes in amounts ranging from 0.004 to 0.16 g. To each tube was then added 4 mL of the SRS tank waste solution to yield experiments with phase ratios ranging from 100 to 10 mg of SCU-103. A tube containing only the SRS tank waste solution (no SCU-103) was also run in parallel as a control sample. The tubes were then mounted on a Thermo Scientific Labogate tube rotator and were tumbled for 3 h. At the end of the 3-hour experiment, the tubes were removed from the rotator. The supernatant from each tube was then decanted and filtered through a 0.1 μm polyvinylidene difluoride syringe filter. The filtrate was analyzed for 99Tc activity.

**Radiation-resistance measurements.** The β-ray was provided by an electron accelerator equipped with an electron beam (10 MeV) and the γ-ray radiation was provided by a 57Co radiation source. Dry crystals of SCU-103 or crystals immersed in 0.5 mL of H₂O were irradiated at two different doses (100 and 200 kGy), respectively. The radiation resistance of SCU-103 was characterized by PXRD measurements and further checked by ReO₄⁻ uptake capacity experiments using the irradiated samples.
Exchange reversibility studies. In order to elute the materials, 50 mg of ReO₄⁻ exchanged products were used in the elution experiments by applying 50 mL of 1 M NaNO₃ aqueous solution under shaking for 12 h on the oscillator at room temperature (~25°C). After this treatment, the solid samples were filtered and washed with deionized water, dried, and analyzed with PXRD and FT-IR measurements. The regenerated products were used for ReO₄⁻ uptake experiments, and the process was repeated for multiple runs.

Computational method. The dynamic trajectories of the selective sorption of ⁹⁹TcO₄⁻ into SCU-103 and the corresponding anion-exchange process were performed using GROMACS 5.1.43 applying the OPLS-AA force field (FF). This FF has been previously used to investigate the hydration properties of ions as well as the interactions between radioactive anions and various porous materials with good compatibility. For a detailed description of the force field parameters and simulation system see the Supporting Information.

Data availability
The data that support the findings of this paper are available in the paper and supplementary information files. The X-ray crystallographic data for the structure reported in this article has been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the number of CCDC 1985724. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Any further relevant data are available from the authors upon reasonable request. Source data are provided with this paper.

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References
1. Beals, D. M. & Hayes, D. W. Technetium-99, iodine-129 and tritium in the exchanged products were used in the elution experiments by applying 50 mL of 1 M NaNO₃ aqueous solution under shaking for 12 h on the oscillator at room temperature (~25°C). After this treatment, the solid samples were filtered and washed with deionized water, dried, and analyzed with PXRD and FT-IR measurements. The regenerated products were used for ReO₄⁻ uptake experiments, and the process was repeated for multiple runs.

2. Murphy, C. E. & Johnson, T. L. Vegetative uptake of Technetium-99 from buried, solidified, low-level radioactive waste. J. Environ. Qual. 22, 793–799 (1993).
3. Wilmarth, W. R. et al. Review: waste-pretreatment technologies for remediation of legacy defense waste exports. Solvent Extr. Ion Exch. 29, 1–48 (2011).
4. Banerjee, D., Kim, D., Schweiger, M. J., Kruger, A. A. & Thallapally, P. K. Removal of TcO₄⁻ ions from solution: materials and future outlook. Chem. Soc. Rev. 45, 2724–2739 (2016).
5. Xiao, C. L., Khayambashi, A. & Wang, S. A. Separation and remediation of TcO₄⁻ from aqueous solutions. Chem. Mater. 31, 3863–3877 (2019).
6. Diprete, D. P., Diprete, C. C. & Sigg, R. A. Measurement of ⁹⁹Tc in Savannah River Site high activity waste. J. Radioanal. Nucl. Chem. 263, 593–598 (2005).
7. King, W. D., Hassan, N. M., Mccabe, D. J., Hamm, L. L. & Johnson, M. E. Technetium removal from Hanford and Savannah River Site actual tank waste supernates with Superlig® 639 resin. Sep. Sci. Technol. 38, 3093–3114 (2003).
8. Eagles, I. et al. Mobilization of technetium from reduced sediments under seawater inundation and intrusion scenarios. Environ. Sci. Technol. 46, 11798–11803 (2012).
9. Tanaka, K. et al. Adsorption mechanism of ReO₄⁻ on Ni-Zn layered hydroxide salt and its application to removal of ReO₄⁻ as a surrogate of TeO₄⁻. Appl. Clay Sci. 182, 105282 (2019).
10. Wang, Y. F. & Gao, H. Z. Compositional and structural control on anion sorption capability of layered hydroxides (LDHs). J. Colloid Interface Sci. 301, 19–26 (2006).
11. McIntyre, L. J., Jackson, L. K. & Fogg, A. M. Ln₂(OH)₅NO₃·10 H₂O (Ln = Y, Gd-La): a novel family of anion exchange intercalation hosts. Chem. Mater. 20, 335–340 (2008).
12. Gouding, H. V. et al. Yb₂O(OH)₆Cl₂·2H₂O: an anion-exchangeable hydroxide with a cationic inorganic framework structure. J. Am. Chem. Soc. 132, 13618–13620 (2010).
13. Wang, S. A. et al. NDTB-1: a supertetrahedral cationic framework that removes TcO₄⁻ from solution. Angew. Chem. Int. Ed. 49, 1057–1060 (2010).
14. Wang, S. A. et al. Selectivity, kinetics, and efficiency of reversible anion exchange with TcO₄⁻ in a supertetrahedral cationic framework. Adv. Funct. Mater. 22, 2241–2250 (2012).
15. Newey, J. J. et al. Removal of TcO₄⁻ from representative nuclear waste streams with layered potassium metal sulﬁde materials. Chem. Mater. 28, 3976–3983 (2016).
16. Sheng, D. P. et al. Efficient and selective uptake of TcO₄⁻ by a cationic metal-organic framework material with open Ag⁺ sites. Environ. Sci. Technol. 51, 3471–3479 (2017).
17. Bonnesen, P. V. et al. Development of bifunctional anion-exchange resins with improved selectivity and sorptive kinetics for pertechnetate: batch-equilibration experiments. Environ. Sci. Technol. 34, 3761–3766 (2000).
18. Wang, S. A. et al. NDTB-1: a supertetrahedral cationic framework that removes TcO₄⁻ from solution. Angew. Chem. Int. Ed. 49, 1057–1060 (2010).
19. He, L. W. et al. Mechanism unravelling for ultrafast and selective ⁹⁹TcO₄⁻ uptake by a radiation-resistant cationic coherent organic framework: a combined radiological experiment and molecular dynamics simulation study. Chem. Sci. 10, 4293–4305 (2019).
20. Liu, J. et al. ⁹⁹TcO₄⁻ remediation by a cationic polymeric network. Nat. Commun. 9, 3007 (2018).
21. Sun, Q. et al. Optimizing radionuclide sequestration in anion nanotapes with record pertechnetate sorption. Nat. Commun. 10, 1646 (2019).
22. O’Keeffe, M. & Yaghi, O. M. Deconstructing the crystal structures of metal-organic frameworks and related materials into their underlying nets. Chem. Rev. 112, 675–702 (2012).
23. Liu, J. et al. Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. Chem. Sci. 47, 2322–2356 (2018).
24. Desai, A. V., Sharma, S., Let, S. & Ghosh, S. K. N-donor linked based metal-organic frameworks (MOFs): advancement and prospects as functional materials. Coord. Chem. Rev. 395, 146–192 (2019).
25. Karmakar, A., Desai, A. V. & Ghosh, S. K. Ionic metal-organic frameworks (IMOFs): design principles and applications. Coord. Chem. Rev. 307, 313–341 (2016).
26. Wu, H. et al. An unprecedented 2D → 3D metal-organic polyrotaxane framework constructed from cadmium and a flexible star-like ligand. Chem. Commun. 47, 1818–1820 (2011).
27. Desai, A. V., Roy, A., Samanta, P., Manna, B. & Ghosh, S. K. Base-resistant ionic metal-organic framework as a porous ion-exchange sorbent. Science 3, 21–30 (2018).
28. Desai, A. V., Sharma, S., Roy, A. & Ghosh, S. K. Probing the role of anions in influencing the structure, stability, and properties in neutral N-donor linker based metal-organic frameworks. Cryst. Growth Des. 19, 7046–7054 (2019).
29. Desai, A. V., Manna, B., Karmakar, A., Sahu, A. & Ghosh, S. K. A water-stable cationic metal-organic framework as a dual adsorbent of oxoanion pollutants. Angew. Chem. Int. Ed. 55, 7811–7815 (2016).
30. Li, X. R., Xu, H. Y., Kong, F. Z. & Wang, R. H. A cationic metal-organic framework consisting of nanoscale cages: capture, separation, and luminescent probing of Cr₂O₇²⁻ through a single-crystal to single-crystal process. Angew. Chem. Int. Ed. 52, 13769–13773 (2013).
31. Fei, H. H., Bresler, M. R. & Oliver, S. R. J. A new paradigm for anion trapping in high capacity and selective metal-to-crystal transformation of cationic materials. J. Am. Chem. Soc. 133, 11110–11113 (2011).
32. Fu, H. R. et al. Spatial confinement of a cationic MOF: a SC-SC approach for high capacity Cr(VI)-oxyanion capture in aqueous solution. Chem. Commun. 54, 11645–11648 (2018).
33. Fu, H. R., Xu, X. Z. & Zhang, J. Water-stable metal–organic frameworks for fast and high dichromate trapping via single-crystal-to-single-crystal ion exchange. Chem. Mater. 27, 205–210 (2014).
34. Zhu, L. et al. Identifying the recognition site for selective trapping of ⁹⁹TcO₄⁻ in a hydrodynamically stable and radiation resistant cationic metal-organic framework. J. Am. Chem. Soc. 139, 14873–14876 (2017).
35. Xu, H. et al. High uptake of ReO₄⁻ by a radiation resistant [Th₄Ni₆]²⁺ nanocage-based metal—organic framework. Angew. Chem. Int. Ed. 58, 6022–6027 (2019).
44. Rapti, S. et al. Exceptional $\text{TeO}_3^{2-}$ sorption capacity and highly efficient $\text{ReO}_4^{-}$ luminescence sensing by $\text{Zr}^{4+}$ MOFs. J. Mater. Chem. A 6, 20813–20821 (2018).
45. Sheng, D. P. et al. Successful decontamination of $\text{99TcO}_4^-$ in groundwater at legacy nuclear sites by a cationic metal-organic framework with hydrophobic pockets. Angew. Chem. Int. Ed. 58, 4968–4972 (2019).
46. Mei, L. et al. Anion-adaptive crystalline cationic material for $\text{99TcO}_4^-$ trapping. Nat. Commun. 10, 1532 (2019).
47. Drout, R. J. et al. Efficient capture of perhenate and pertechnetate by a mesoporous Zr metal-organic framework and examination of anion binding motifs. Chem. Mater. 30, 1277–1284 (2018).
48. Banerjee, D. et al. Zirconium-based metal-organic framework for removal of perhenate from water. Inorg. Chem. 55, 8241–8243 (2016).
49. Zhi, L. et al. Exceptional perhenate/pertechnetate uptake and subsequent immobilization by a low-dimensional cationic coordination polymer: overcoming the Hofmeister bias selectivity. Environ. Sci. Technol. Lett. 4, 316–322 (2017).
50. Pearson, R. G. Chemical hardness and density functional theory. J. Chem. Phys. 117, 9645–9657 (2002).
51. Zheng, T. et al. Overcoming the crystallization and designability issues in the ultrastable zirconium phosphate framework system. Nat. Commun. 8, 15369 (2017).
52. Liu, T. F. et al. Topology guided design and syntheses of highly stable mesoporous porphinic zirconium metal-organic frameworks with high surface area. J. Am. Chem. Soc. 137, 413–419 (2015).
53. Wang, K. C. et al. A series of highly stable mesoporous metalloporphyrin Fe-MOFs. J. Am. Chem. Soc. 136, 11983–11986 (2014).
54. Fateeva, A. et al. A water-stable porphyrin-based metal-organic framework active for visible-light photocatalysis. Angew. Chem. Int. Ed. 51, 7440–7444 (2012).
55. Wang, K. C. et al. Pyrazolate-based porphyrinic metal-organic framework with extraordinary base-resistance. J. Am. Chem. Soc. 138, 914–919 (2016).
56. Lv, X. L. et al. A base-resistant metalloporphyrin metal-organic framework for C-H bond halogenation. J. Am. Chem. Soc. 139, 211–217 (2017).
57. Colombo, V. et al. High thermal and chemical stability in pyrazolate-bridged metal-organic frameworks with exposed metal sites. Chem. Sci. 2, 1311–1319 (2011).
58. Wang, Y. L. et al. Umbellate distortions of the uranyl coordination environment result in a stable and porous polycatenated framework that can effectively remove cesium from aqueous solutions. J. Am. Chem. Soc. 137, 6144–6147 (2015).
59. Banerjee, D. et al. Removal of pertechnetate-related oxyanions from solution using functionalized hierarchical porous frameworks. Chem. Eur. J. 22, 17581–17584 (2016).
60. Crawford, C. L. Results for the first quarter calendar year 2019 tank 50 salt solution sample, SRNL-STI-2019-00184, Rev. 0. Savannah River National Laboratory, Aiken, SC 29808 (2019).
61. Sheldrick, G. M. SHELXT-integrated space-group and crystal-structure determination. Acta Crystallogr. A 71, 3–8 (2015).
62. Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. Acta Crystallogr. C 71, 9–18 (2015).
63. Abraham, M. J. et al. GROMACS: high performance molecular simulations through multi-level parallelism from laptops to supercomputers. SoftwareX 1-2, 19–25 (2015).
64. Jorgensen, W. L. & Tiradorives, J. The opls potential functions for proteins-energy minimizations for crystallization of cyclic-peptides and ccrabin. J. Am. Chem. Soc. 110, 1657–1666 (1988).
65. Williams, C. D. & Carbone, P. A classical force field for tetrahedral oxyanions developed using hydration properties: the examples of pertechnetate ($\text{TeO}_4^{2-}$) and sulfate ($\text{SO}_4^{2-}$). J. Chem. Phys. 143, 174502 (2015).
66. Megyes, T. et al. Solution structure of $\text{NaNO}_3$ in water: diffraction and molecular dynamics simulation study. J. Phys. Chem. B 113, 4054–4064 (2009).
67. Li, L. N. et al. A combined experimental and theoretical study on the extraction of uranium by amino-derived metal–organic frameworks through post-synthetic strategy. ACS Appl. Mater. Interfaces 8, 31032–31041 (2016).
68. Nalaparaju, A. & Jiang, J. W. Ion exchange in metal-organic framework for water purification: insight from molecular simulation. J. Phys. Chem. C. 116, 6925–6931 (2012).

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Author contributions
N.S., Z.Y., and S.L. contributed equally to this work. S.W. conceived the project and supervised the research. N.S. and C.X. designed the material and performed the synthesis and characterizations. N.S., C.Y., and J.L. carried out the initial sorption experiments and analyzed the data. N.S. and J.L performed the $\text{99Tc}$ radioactive experiments. Y.Z. performed the SEM-EDS analysis. M.Z. aided in the radiation experiments. S.L., Z.Y., and X.D. carried out the theoretical calculation. K.T-P. and D.L. carried out the actual SRS tank waste experiment. N.S., S.L., C.X., Z.Y., K.T-P., R.Z. and S.W. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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