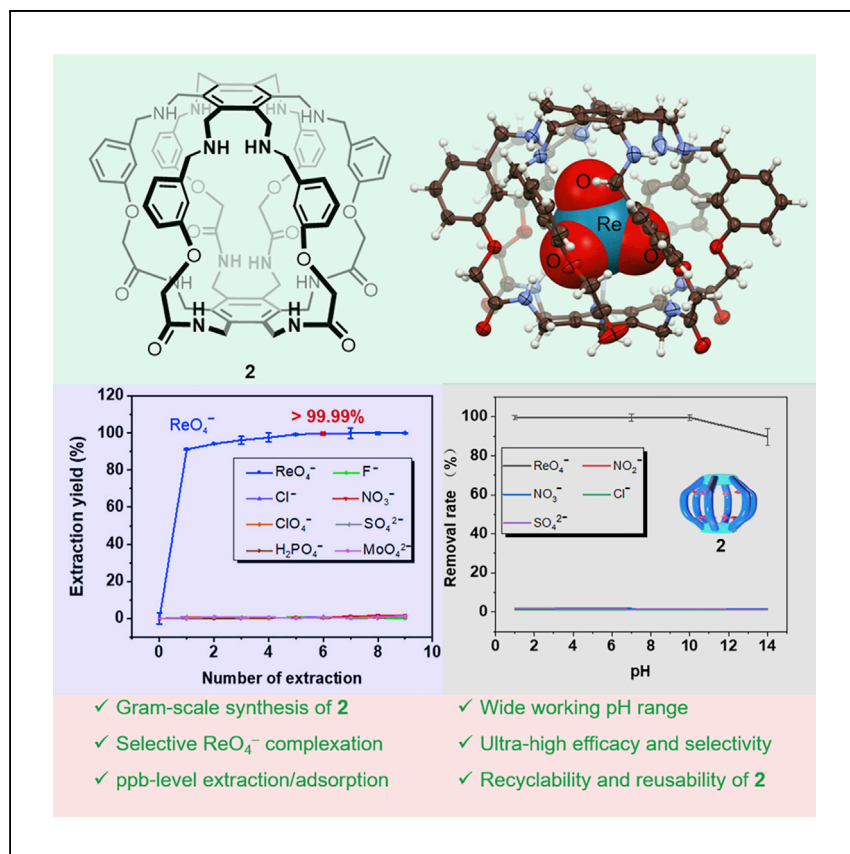


Article

A highly selective superphane for ReO_4^- recognition and extraction



Extraction of low concentrations of rhenium anions from waste streams is important industrially. Zhou et al. present the facile and gram-scale synthesis of a superphane via dynamic imine chemistry coupled with NaBH_4 reduction, which can separate perrhenate from low-content mixtures and simulated Hanford waste streams with exceptionally high efficiency and selectivity, along with good recyclability and reusability.

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Highlights

A superphane for highly selective recognition of ReO_4^- is synthesized in gram scale

Over 99.99% of ReO_4^- can be separated from complex simulated waste streams

Rapid removal of ppb-level ReO_4^- is achieved via extraction or column adsorption

The superphane for ReO_4^- extraction/adsorption can be recycled and reused

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Article

A highly selective superphane for ReO_4^- recognition and extractionWei Zhou,¹ Aimin Li,¹ Philip A. Gale,^{2,3,4,*} and Qing He^{1,*}

SUMMARY

Highly selective anion recognition and extraction is challenging and yet critical for removal of pollutants from the environment and the effective recovery of valuable chemicals from low-content (at sub-ppm or ppb level) sources. In this paper, we detail the gram-scale synthesis of a superphane **2**, an anion receptor that selectively binds ReO_4^- . Superphane **2** can extract perrhenate from solid mixtures containing traces of ReO_4^- anion (as low as 200 ppb) and aqueous media with near 100% selectivity over large excesses of competing anions. Meanwhile, up to 99.99% of ReO_4^- can be separated from complex simulated aqueous waste streams containing ppm-level perrhenate via either liquid-liquid extraction or simple column adsorption. Importantly, after extraction or adsorption, superphane **2** can be recycled and reused by simple treatment with aqueous NaHCO_3 .

INTRODUCTION

Rhenium is a rare metallic element with one of the lowest abundances in the earth's crust.¹ Due to its widespread use in the petrochemical industry, in aviation, as an electrical contact material, and the use of its compounds as catalysts, the demand for rhenium has become an increasingly urgent issue in recent years.^{2–6} To date, no economically viable processing methods exist for producing rhenium as a primary commodity due to the lack of primary rhenium deposits in nature.^{7,8} Instead, rhenium is usually extracted from solid and liquid by-products of molybdenum and copper industries, wherein the rhenium contents are typically found in the range of 200–800 ppm (Mo) and 10–50 ppm (Cu).^{9,10} In addition, the sequestration of radioactive TcO_4^- (ReO_4^- is used as its structural surrogate) is of particular importance in nuclear fuel reprocessing.^{11,12} There is therefore an urgent need to develop new strategies that allow low-content (ppm level) rhenium to be effectively and selectively isolated from rhenium-containing resources, such as the leaching liquors of natural rhenium minerals and rhenium-containing waste streams, in which ReO_4^- is expected to be the dominant rhenium form.^{3,13}

There has been growing interest in developing new approaches to $\text{TcO}_4^-/\text{ReO}_4^-$ removal.^{14–18} For instance, inorganic materials such as metal oxides, layered double hydroxides (LDH), and composite materials have been widely used for investigation of removal of $\text{TcO}_4^-/\text{ReO}_4^-$, usually with a relatively low capacity and selectivity toward $\text{TcO}_4^-/\text{ReO}_4^-$ in the presence of other competing ions.^{19–22} Alternatively, organic exchangers, e.g., organic polymer-based ion-exchange resins, have also been extensively explored to remove $\text{TcO}_4^-/\text{ReO}_4^-$ with high efficiency but unexpected thermal and chemical instability, especially under the intense ionizing radiation fields.^{23–25} Additionally, in recent years, metal-organic frameworks (MOFs) have proven attractive for development of effective materials for scavenging anions

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including $\text{TcO}_4^-/\text{ReO}_4^-$ due to their facile functionalization, tunable pore size, and high surface areas.^{26–29} However, given the instability of MOFs under the highly acidic conditions required for spent nuclear fuel reprocessing, covalent organic frameworks (COFs) containing strong covalent bond linkers with extended structures have found to be effective alternates for separation of $\text{TcO}_4^-/\text{ReO}_4^-$.³⁰ Most, if not all, these materials work by interacting with $\text{TcO}_4^-/\text{ReO}_4^-$ anions via an ion-exchange or a metal-coordination mechanism with ill-defined anion coordination environments, hindering the desired $\text{TcO}_4^-/\text{ReO}_4^-$ removal efficacy or selectivity required for practical applications.

Supramolecular chemistry, in particular host-guest chemistry, provides useful strategies for development of supramolecular hosts as advanced materials for specific species, wherein the size and shape of binding cavities of the hosts could be defined with greater fidelity. More importantly, well-tailored macrocyclic or cage receptors could show stoichiometric recognition and uptake of the guest species of interest. Thus, recognition-based anion separation by supramolecular (and molecular) receptors offers new possibilities for better control of the affinity, efficacy, and selectivity of critical extractants/adsorbents required especially for their uses in the real-world applications.^{31,32} Although many recent advances have been achieved in this area, the chemistry of $\text{ReO}_4^-/\text{TcO}_4^-$ receptors, especially for high-performance $\text{ReO}_4^-/\text{TcO}_4^-$ extraction, is not well developed.^{33–37} Briefly, a series molecular receptors including acyclic organic receptors, transition-metal framework based receptors, macrocyclic receptors (e.g., calixarenes, cyclotrimeratrylenes, and azacryptand) and dendrimers have been found able to capture either pertechnetate or perrhenate, but the $\text{ReO}_4^-/\text{TcO}_4^-$ binding and extraction efficacy and selectivity, *inter alia* in the presence of large excess competing anions, are far from good enough for practical applications.^{34,35,38} In 2018, Nitschke and coworkers reported a self-assembling $\text{Fe}^{\text{II}}_4\text{L}_4$ cage that can extract an equimolar amount of ReO_4^- with decent selectivity.³⁶ Impressive as these recent results are, new systems aimed at more highly effective and selective extraction of $\text{ReO}_4^-/\text{TcO}_4^-$ are urgently needed. The final content of TcO_4^- in radioactive waste before discharge has to reach at least ppb level or lower after the treatment with extractants/adsorbents, notwithstanding the presence of large excess (up to 6,000 times) of competing anions, e.g., NO_3^- and SO_4^{2-} . Up to now, no supramolecular receptors have been reported that can achieve such a goal.

Direct extraction of ReO_4^- from solid mixtures or aqueous solutions into organic phases, e.g., chloroform, with a low concentration of ReO_4^- and abundant competing species such as SO_4^{2-} , NO_3^- , ClO_4^- , H_2PO_4^- , and MoO_4^- remains challenging. To achieve this goal, new receptors for ReO_4^- should be well tailored with exceptional effectiveness and selectivity, which we envisioned might be enhanced if an anion receptor features (1) multiple anionic binding sites, (2) uniform distribution of the binding sites around the 3D cavity, and (3) near-enclosed binding pocket to shield the bound anion from the solvent medium. Such considerations led us to postulate that superphanes, compounds in which the two benzene rings clamp parallel on top of each other by six bridges,^{39–42} could be promising candidates. However, conventional superphanes, e.g., **1**, have no internal voids for binding any guest species (Figure 1A). Recently, our group reported the synthesis and host-guest chemistry of the first ever superphane as the supramolecular receptor based on dynamic imine chemistry.^{43,44} Contemporaneously, the Badjić group independently reported an imine-bearing hexapodal capsule for the recognition of anions, e.g., Cl^- , H_2PO_4^- , and SO_4^{2-} , using a similar templating strategy.⁴⁵

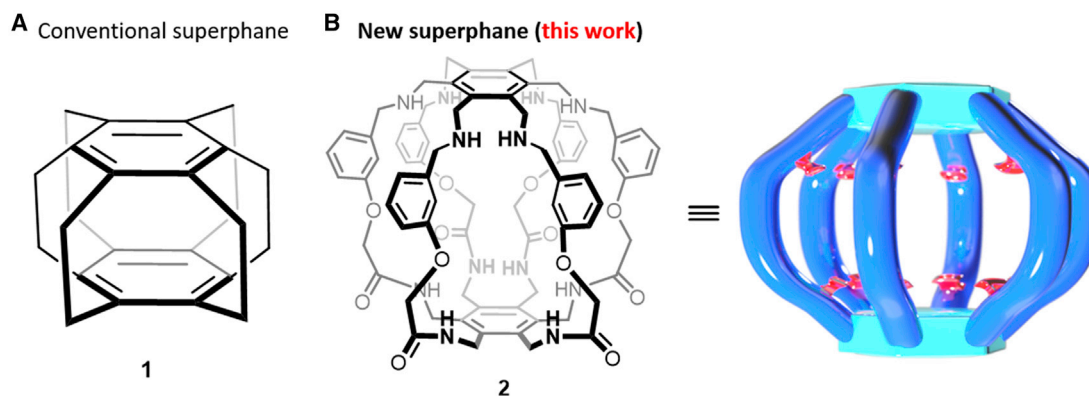


Figure 1. Chemical structures of superphanes 1 and 2

(A) A classical superphane (1) without binding cavity reported in the literature.

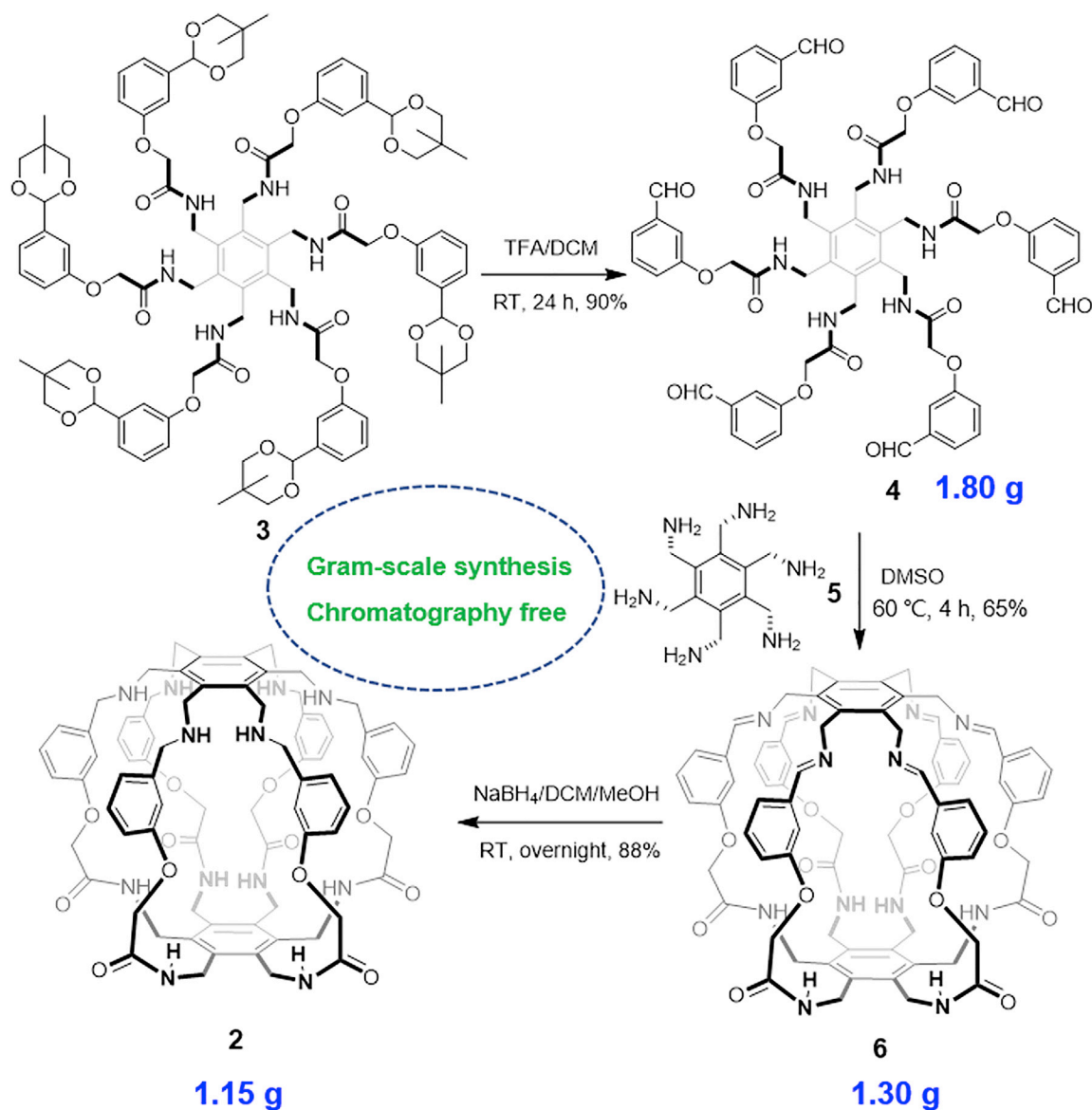
(B) A new superphane (2) with a well-defined binding aperture reported in this work. Cartoon illustration of 2 is also displayed.

In this paper, we report the facile gram-scale synthesis and host-guest binding properties of superphane 2 (Figure 1B), a receptor that allows ReO_4^- to be encapsulated and extracted efficiently and selectively under both solid-liquid extraction (SLE) and liquid-liquid extraction (LLE) conditions. The ReO_4^- anions in the mixtures could be reduced to ppb level (as low as 6.6 ppb) in the presence of large excesses of competing anions. To the best of our knowledge, system 2 represents the first superphane-based anion receptor for extraction (>99.99% efficiency) of ReO_4^- with high selectivity from a low-content rhenium-bearing source (as low as 200 ppb) in the presence of a large excess (up to 12,000 times) of competing anions to an organic chloroform phase. It is also the first example of a supramolecular receptor to be used for rapid and near-complete removal of ReO_4^- from simulated Hanford waste streams via easy to operate column tests. Last but not least, superphane 2 was found able to extract/adsorb ReO_4^- ions over a wide pH range of 1.0–10.0 with the selectivity nearly unchanged and could be recycled and reused via simple treatment with aqueous NaHCO_3 .

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of compound 2 is shown in Scheme 1. Specifically, intermediate 3 was obtained readily via a simple symmetrical coupling of hexakis(aminomethyl)benzene 5 with functionalized 3-hydroxybenzaldehyde (S3) in the presence of 2-(1H-benzotriazol-1-yl)-1,1,3,3,-tetramethyluronium hexafluorophosphate (HBTU) and *N,N*-diisopropylethylamine (DIPEA) in dimethylformamide (DMF) at 50°C for 24 h (Schemes S1–S3). After deprotection of the acetals of 3 promoted by trifluoroacetic acid (TFA) in dichloromethane (DCM) for 24 h at room temperature, the key hexaaldehyde precursor 4 was afforded in 90% yield via simple filtration. Subsequently, a condensation of hexaaldehyde 4 and hexakis(aminomethyl)benzene 5 in DMSO at 60°C for 4 h gave the expected imine-based superphane 6 in a ratio of 1:1 in a yield of 65%. Notably, in our current case, anionic templates were not necessary for the formation of desired superphane 6, as opposed to the reported synthesis of an imine-based hexapodal capsule, wherein suitable anions, e.g., Cl^- , CO_3^{2-} , HPO_4^{2-} , or SO_4^{2-} , were found to be the *conditio sine qua non*.⁴⁵ To circumvent the instability of imine bonds in 6, a NaBH_4 -mediated reduction strategy was successfully used to transform superphane 6 into its amine version, namely superphane 2, with NaBH_4 in a mixture of DCM and methanol overnight at room temperature in 88% yield. In aggregate, a seven-step synthesis of compound 2 from 3-hydroxybenzaldehyde



Scheme 1. The synthesis of superphane **2** via imine condensation, followed by NaBH₄ reduction

notwithstanding, it is notable that no chromatography is required for the purification of any intermediates involved and the final product. More importantly, both imine-based superphane **6** and secondary amine-based superphane **2** can be successfully prepared on the gram scale under mild conditions with excellent yields, which is remarkable given the complexity of the constructs involved (Scheme 1). Compounds **6** and **2** were fully characterized by standard spectroscopic means, as well as via single-crystal X-ray diffraction analysis (see the supplemental experimental procedures for details, Figures S1–S3). Interestingly, both compounds **6** and **2** were found to be fluorescence emissive in DMSO or CHCl₃ with the emission maxima of 452 (excitation wavelength [ex.] 369 nm) and 442 nm (ex. 368 nm), respectively (see Figures S4 and S5). In the solid state, **6** (quantum yield $\Phi_f = 20.2\%$) and **2** ($\Phi_f = 9.8\%$) also display relatively strong fluorescence with the emission maxima of 462 (e.g., 379 nm) and 403 nm (e.g., 353 nm), respectively (Figures S6 and S7). These observations are in accord with

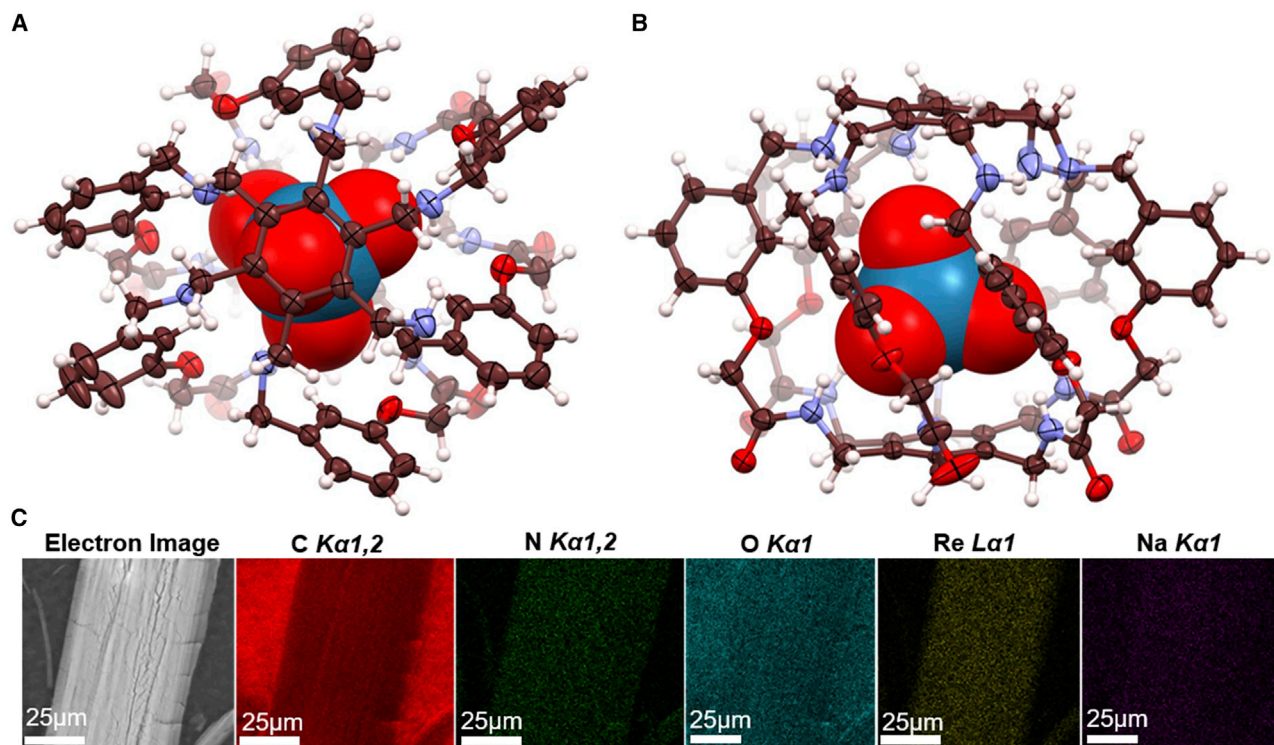


Figure 2. Single crystal structure of $\text{ReO}_4^-@2\text{H}^+$ complex

(A) Top view.

(B) Front view. The host was displayed as ellipsoid model, while the perrhenate anion was shown in the space-filling model. All the solvent molecules outside the cavity were removed for clarity.

(C) SEM image of a selected single crystal and its SEM/EDS mapping for C, N, O, Re, and Na (left to right).

our previous findings where a collection of superphanes were reported to be emissive in solution and the solid state.⁴⁴

Anion recognition ability of superphane 2

Single crystal structures of **2** revealed that either a DMSO molecule or an H_2O -MeOH dimer was fully encapsulated within the inner cavity of **2** (Figures S2 and S3). This led us to suggest that superphane **2** could act as an effective receptor for relatively large guest species, e.g., perrhenate anion (ReO_4^-). Initial evidence for this postulate came from an X-ray diffraction analysis of single crystals obtained by slow evaporation of a chloroform solution of **2** in the presence of excess NaReO_4 . The resulting structure revealed an encapsulated 1:1 complex in the solid state (Figures 2A and 2B). Due to the removal of disordered solvent molecules outside the cavity using SQUEEZE,⁴⁶ the counter-cation, either Na^+ or H^+ , could not be determined by scattering. However, SEM-EDS (scanning electron microscopy and energy-dispersive spectrometry) analysis of a selected single crystal sample revealed that the crystal consists of marked C, N, O, and Re elements but negligible Na (Figures 2C, S8, and S9), indicating the formation of $\text{ReO}_4^-@2\cdot\text{H}^+$ complex. Specifically, superphane **2** adopts a lantern-shaped conformation with one ReO_4^- anion found encapsulated within the deep internal cavity of $2\cdot\text{H}^+$ with all six amide NHs and most of the C_{sp^2} -Hs and secondary amine NHs pointing toward the inside cavity, giving rise to multiple hydrogen bonds between **2** and perrhenate anion (Figures 2A and 2B). Up to 18 hydrogen bonds are involved in the stabilization of the tetrahedral perrhenate ion. This $\text{ReO}_4^-@2\cdot\text{H}^+$ complex in the solid state was also evidenced by a new crystal structure obtained by growing crystals of **2** in

the presence of excess NH_4ReO_4 , wherein very similar unit cell parameters and single crystal structures were seen (Table S1 and Figure S10). Furthermore, the optimized structure of $\text{ReO}_4^-@2\cdot\text{H}^+$, obtained from density functional theory calculations, is consistent with the crystal structures and is characterized by a remarkably favorable binding energy of $-88.5 \text{ kcal mol}^{-1}$ (Figure S11, Data S1). This highly stable complex was further studied using gas-phase molecular dynamics simulations, in which the $2\cdot\text{H}^+$ and ReO_4^- complex maintains its integrity on the simulation timescale (Figure S12). Notably, as shown in the space-filling model (Figure S13), the ReO_4^- anion was fully encapsulated at the center of the 3D cavity of **2**, a finding that might be of importance to SLE and LLE due, in large part, to the energetically favorable complexation of ReO_4^- and the potential protection of the bound ReO_4^- anion from solvation.

The ability of receptor **2** to bind perrhenate anions in solution was probed via ^1H NMR spectroscopy in CDCl_3 . Spectroscopic analysis of compound **2** revealed only one set of resonances in CDCl_3 at room temperature (Figure S14), as would be expected for a relatively flexible system in which different conformations rapidly interconvert. When excess ReO_4^- as its tetrabutylammonium (TBA) salt was added into a 3.0 mM solution of **2** in CDCl_3 , the resonance peaks corresponding to free receptor **2** were observed to disappear slowly, and a new set of peaks corresponding to the perrhenate complex appeared gradually during equilibrium over 9 days (Figures S14 and S15). Specifically, the $C_{\text{sp}^2}\text{-Hs}$ at the 2-positions of the phenyl units on the toroidal bridges slightly shifted to downfield, while three sets of methylene protons located at 4.86 (*i*), 4.16 (*g*), and 3.94 (*a*) ppm underwent shifts to 4.58 (*i'*), 4.07 (*g'*), and 4.01 (*a'*), respectively. These changes are in accord with the conclusion that ReO_4^- is being bound effectively by **2**. Due to the kinetically slow equilibrium between superphane **2** and TBAReO_4 (Figure S16), a mixed solvent system, namely $\text{CDCl}_3/\text{CD}_3\text{OD}$ (1:1, v/v), was used for ^1H NMR spectroscopic titration of **2** with TBAReO_4 . The obtained ^1H NMR data corresponding to the phenyl C-H proton and methylene signals were fitted to a 1:1 binding model, and the resulting binding constant was estimated to be $K_a = (5.62 \pm 0.15) \times 10^3 \text{ M}^{-1}$ (Figures S17 and S18).

There are usually competing anions, e.g., Cl^- , NO_3^- , ClO_4^- , H_2PO_4^- , SO_4^{2-} , *inter alia* the latter four, in the ReO_4^- -bearing resources, such as natural waters and/or nuclear fuel reprocessing streams.^{47–49} To achieve the effective and complete removal of ReO_4^- , its high selectivity over the existing competing anions is critical. We next sought to test whether receptor **2** could bind ReO_4^- selectively in the presence of these competing anions. Initial screening studies were carried out in CDCl_3 using ^1H NMR spectroscopy (Figure S19). It was found that adding 20 equiv of Cl^- , NO_3^- , or ClO_4^- as their TBA salts failed to produce any noticeable changes in the proton NMR spectrum of **2**, a finding consistent with a very weak interaction. In sharp contrast, a similar addition of either H_2PO_4^- or SO_4^{2-} (as their TBA salts) led to downfield shifts in the 2-phenyl proton signals (i.e., from 6.76 to 6.81 and 7.00 ppm, respectively). Meanwhile, the methylene proton signals shifted from 4.86 ppm to 4.52 and 4.50 ppm, respectively. Further detailed ^1H NMR spectroscopic titrations of **2** with TBAH_2PO_4 or TBA_2SO_4 in the same solvent system gave the binding constants of $(2.03 \pm 0.47) \times 10^3$ and $(1.07 \pm 0.13) \times 10^3 \text{ M}^{-1}$ for H_2PO_4^- and SO_4^{2-} , respectively, by fitting the obtained data to a 1:1 binding model (Figures S20–S23). These findings led us to suggest that receptor **2** binds ReO_4^- anion with the selectivity being $\text{ReO}_4^- > \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-} \gg \text{Cl}^-$, NO_3^- , or ClO_4^- .

Highly selective solid-liquid extraction of ReO_4^- by superphane **2**

The above observations led us to consider that superphane **2** would prove effective as a supramolecular extractant for ReO_4^- under both SLE and LLE conditions even in

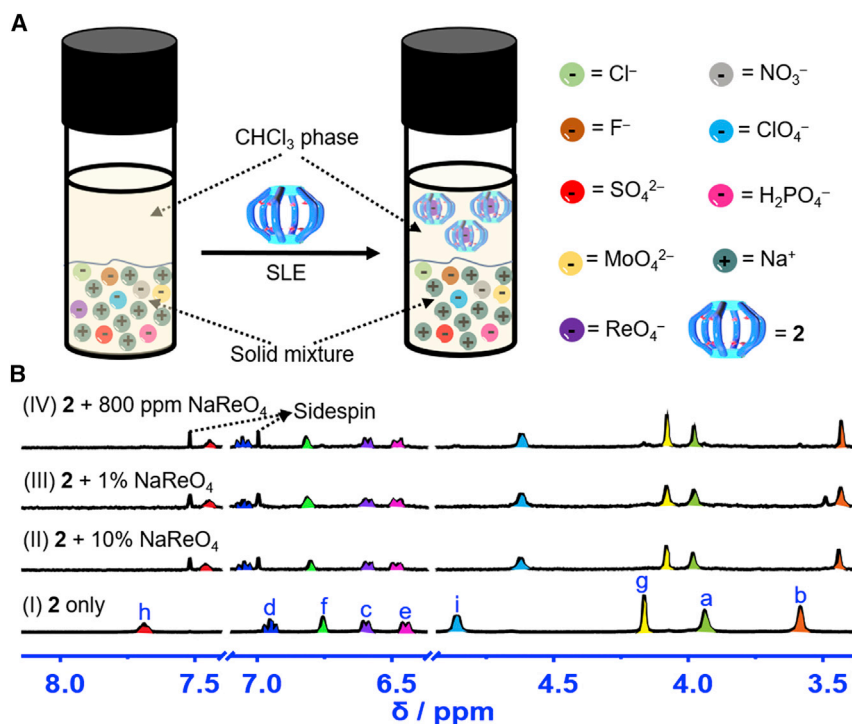


Figure 3. Solid-liquid extraction of ReO_4^- with **2 as the supramolecular extractant**

(A) Cartoon illustration of the selective solid-liquid extraction of ReO_4^- from solid mixtures containing a large excess of competing ions.

(B) Partial ^1H NMR spectra of a 1.0 mM solution of (I) **2** only and **2** with solid equal-mass mixtures of NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 containing (II) 10%, (III) 1%, and (IV) 800 ppm of NaReO_4 (mass content). The spectra for (II), (III), and (IV) were recorded after allowing the solid phase and the organic phase to equilibrate for 12, 24, and 72 h, respectively.

the presence of excess competing ions, e.g., Cl^- , NO_3^- , ClO_4^- , H_2PO_4^- , and SO_4^{2-} , as would be present in common ReO_4^- -containing scenarios. Efforts were then made to assess whether superphane **2** was capable of extracting ReO_4^- under SLE conditions. In a first study, exposing a solution of **2** in CDCl_3 to an excess of either powdered NaReO_4 or microcrystalline NH_4ReO_4 over 6 h engendered almost identical distinctive changes in the ^1H NMR spectrum (Figure S24), suggesting that superphane **2** was able to pluck perrhenate anions out of the solids into the organic chloroform phase, presumably, in a 1:1 stoichiometric manner, as reflected in the single crystal structure. In contrast, no appreciable changes were observed in the ^1H NMR spectra of analogous CDCl_3 solutions of cage **2** after exposure to excess solid NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 , respectively, after equilibration for 6 h (Figure S25). We thus conclude that receptor **2** is able to extract perrhenate ions efficiently and potentially selectively under SLE conditions.

Further support for the fact that, under SLE conditions, superphane **2** can act as an effective supramolecular extractant with high selectivity toward ReO_4^- over competing anions, e.g., Cl^- , NO_3^- , ClO_4^- , H_2PO_4^- , SO_4^{2-} , along with F^- and MoO_4^{2-} , came from a series of competition experiments using ^1H NMR spectroscopy and inductively coupled mass spectroscopy (ICP-MS) (Figure 3A). Specifically, solutions of **2** in CDCl_3 were layered over a solid equal-mass mixture of NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 containing either 10% or only 1% of NaReO_4 (by mass) and allowed to stand for 12~24 h. The resulting spectra

gave rise to changes identical to those seen in the presence of solid NaReO_4 alone (Figures 3B, S26, and S27). More strikingly, analogous spectral changes were also seen when a similar mixture of salts containing as low as 800 ppm NaReO_4 was subject to otherwise identical SLE experiments when allowed to equilibrate for 72 h (Figures 3B and S28). Afterward a 1.0 mM solution of **2** in CDCl_3 was placed over a solid mixture as discussed above containing 200 ppm NaReO_4 and equilibrated for 120 h. A new set of discernible peaks was seen in the ^1H NMR spectrum that was readily assigned to $\text{ReO}_4^-@2\cdot\text{H}^+$, along with signals pertaining to free **2** (Figure S29). Such observations are taken as an indication that receptor **2** works as a super selective extractant for perrhenate under SLE conditions wherein chloroform serves as the organic phase.

To test the hypothesis that receptor **2** could also act as an effective supramolecular extractant for selective removal of perrhenate from solid mixtures containing ppb-level ReO_4^- , further SLE experiments were carried out using inductively coupled plasma mass spectrometry (ICP-MS). Specifically, solutions of **2** in CHCl_3 (3.0 mM) were placed over solid equal-mass mixtures of NaCl , NaF , NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 containing 800, 500, and 200 ppb NaReO_4 , respectively, and equilibrated for between 0 and 72 h. As shown in Figure S30, after contact of **2** in CHCl_3 and the solid mixtures for 6 h, the remaining ReO_4^- ions in the solid residues were found to decrease from 800, 500, and 200 ppb to 67, 57, and 42 ppb, respectively. Increasing the exposure time to 72 h led to essentially negligible extraction of more ReO_4^- from the solids to organic phase. The incomplete conversion could be attributed to the ineffective contact of **2** and ReO_4^- because of solid inclusion. Taken in concert, these findings led us to conclude that, under SLE conditions, superphane **2** was capable of extracting perrhenate ions with high selectivity from extremely low-content (as low as 200 ppb) perrhenate sources even in the presence of competing ions. To our knowledge, this is the first example for a host-guest system to complex and effectively extract such small quantities of perrhenate under SLE conditions in the presence of large quantities of competing ions.

Highly selective liquid-liquid extraction of ReO_4^- by superphane **2**

We next sought to explore whether receptor **2** was capable of extracting, *inter alia* extremely low-content, ReO_4^- ions under LLE conditions in neutral aqueous solution. Given the exceptional performance of **2** for extracting perrhenate anions under SLE conditions, we initialized the LLE studies with a relatively low concentration of ReO_4^- in aqueous solution using ICP-MS. Specifically, the first stage extraction was performed by well exposing a 3.0 mM solution of **2** (2 mL) to a solution of NaReO_4 in water at concentration of 820 ppm (2 mL). After careful separation, the aqueous phase was further subject to multiple rounds of extraction with solutions of **2** in chloroform (Figure S31). After each round of extraction, a small amount of the aqueous phase was then separated off and diluted with water for ICP-MS analysis (Figure S32). Pleasingly, the remaining ReO_4^- ions in the aqueous phase were observed to sharply decrease from 820 ppm to 1.2 ppm as the number of extraction cycles increased from 1 to 7. Astonishingly, despite the occurrence of ReO_4^- at ppb level, when the number of extractions increased to 10, the remaining ReO_4^- could be further reduced to < 10 ppb. The extraction yields significantly increased as the number of extractions increased (Figure S33). Eventually, over six consecutive extractions, > 99.99% of the perrhenate ions were found able to be removed from the original aqueous solution. Contrastingly, the concentration of sodium, the counter-cation of ReO_4^- , in the aqueous phase remained almost constant during the consecutive extractions, indicating that perrhenate was probably sequestered from the aqueous phase by **2** in the form of $\text{ReO}_4^-@2\cdot\text{H}^+$, a finding fully in line

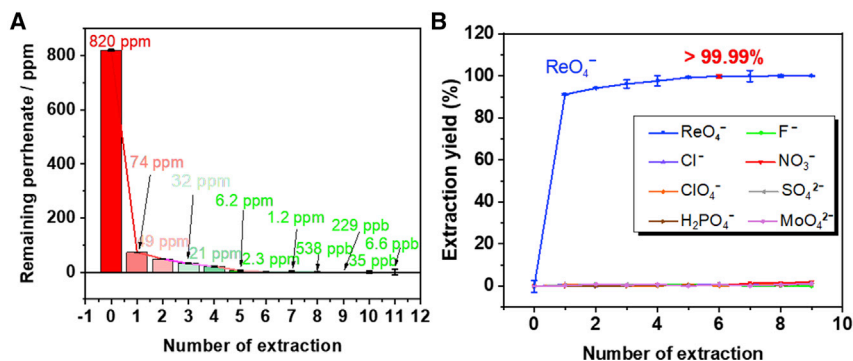


Figure 4. Results of ICP-MS analyses

(A) The remaining ReO_4^- (in ppm) in the simulated aqueous waste streams before and after different numbers of extraction with solutions of **2** in CHCl_3 .

(B) The extraction yields (%) of anions in question after different numbers of extraction. The starting simulated aqueous waste streams consist of equal-molar concentrations (30 mM each) of NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 in water containing 820 ppm of NaReO_4 . Error bars represent SD. $n = 3$ independent experiments.

with what was discussed earlier. These observations allow us to conclude that superphane **2** is capable of virtually complete removal of ReO_4^- , which could lead to practical applications in elimination of TcO_4^- in real waste streams.

Encouraged by these results, we further evaluated the selectivity of **2** toward ReO_4^- in the presence of seven other different potentially competing anions, viz., F^- , Cl^- , NO_3^- , ClO_4^- , H_2PO_4^- , SO_4^{2-} , and MoO_4^{2-} , simultaneously in water. These experiments were carried out by consecutive extraction of a simulated aqueous waste stream, consisting of equimolar concentrations (30 mM for each) of NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 in water containing 820 ppm of NaReO_4 . During the consecutive extractions with solutions of **2** in CHCl_3 , the remaining ReO_4^- and other existing potentially competing ions in the aqueous phases were monitored by ICP-MS and ion chromatography, respectively (Figure 4). The remaining ReO_4^- in aqueous phase was found to decrease sharply (from 820 ppm to < 10 ppb) while the extraction yields (%) significantly increased to > 99.99% with increasing the number of extractions (from 1 to 11). In sharp contrast, almost no appreciable changes were observed for all residual competitive anions, viz., F^- , Cl^- , NO_3^- , ClO_4^- , H_2PO_4^- , SO_4^{2-} , and MoO_4^{2-} , in the aqueous phases, even after ten rounds of extraction (Figure S34). These findings revealed an unprecedented LLE efficiency and selectivity of superphane **2** toward ReO_4^- over other competitive anions in question.

The pH effect on selective liquid-liquid extraction by superphane **2**

A wide working pH window proves a *conditio sine qua non* for a promising extractant candidate for practical applications. We next sought to explore if superphane **2** could work efficiently and selectively to extract ReO_4^- over a wide pH range (from 1 to 14). Specifically, these experiments were performed by exposing CHCl_3 solutions of **2** (3.0 mM, 2 mL) to aqueous solutions of NaReO_4 at different pH values (820 ppm, 2 mL). After each extraction, a small amount of the aqueous phase was then separated off and diluted with acidic water solution for ICP-MS analysis, and the extraction yield was plotted as a function of pH (Figure S35). Interestingly, receptor **2** was found able to most efficiently (> 99% extraction yields) extract ReO_4^- from aqueous media to chloroform phase in the pH range 1–3. The extraction yields slightly decreased (from ca. 99% to ca. 80%) as the pH values increased from 3 to

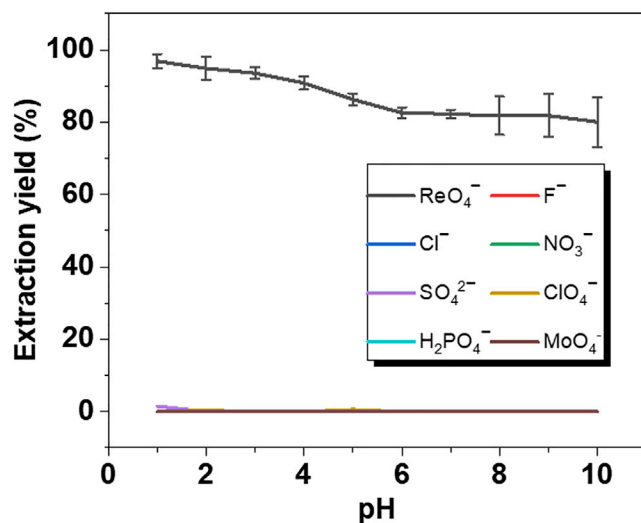
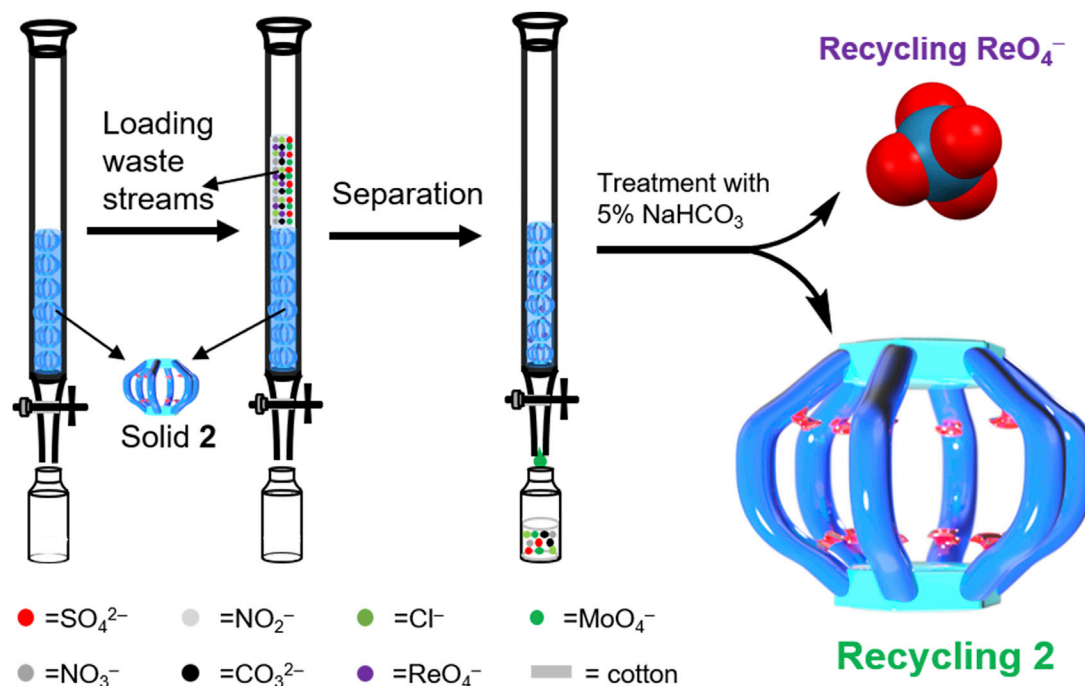


Figure 5. Results of ICP-MS analyses of the liquid-liquid extraction yields (%) versus pH

Each starting simulated aqueous waste stream consists of equal-molar concentrations (30 mM) of NaCl, NaF, NaNO₃, NaClO₄, NaH₂PO₄, Na₂SO₄, and Na₂MoO₄ in water containing 820 ppm of NaReO₄. Error bars represent SD. n = 3 independent experiments.

10. However, increasing the pH to 14 resulted in sharply decreased extraction yields. Receptor 2 works more efficiently in acidic media than in a basic (especially pH > 10) environment, which could be rationalized by the preceding finding that perrhenate ions were captured and extracted in the form of ReO₄⁻@2·H⁺. More importantly, superphane 2 was found very stable during the LLE at the pH values of 1–14, as confirmed by ¹H NMR spectroscopy (carried out in CDCl₃) after its exposure to aqueous solutions at different pH values (Figure S36). These observations allow us to suggest that superphane 2 would be able to work efficiently to extract perrhenate ions at a wide pH range of 1–10, with a low-pH preference.

On this basis, we were encouraged to explore whether superphane 2 could retain its high extraction efficacy and selectivity toward ReO₄⁻ in the presence of competing anions over a wide pH range. These LLE experiments were carried out by subjecting solutions of 2 (3.0 mM, 2 mL) in CHCl₃ to LLE of simulated aqueous waste streams (2 mL) at different pH values (1–10), which consist of equal-molar concentrations (30 mM for each) of NaCl, NaF, NaNO₃, NaClO₄, NaH₂PO₄, Na₂SO₄, and Na₂MoO₄ containing 820 ppm of NaReO₄. As discussed before, after each extraction, a small amount of the aqueous phase was then separated off and diluted with acidic aqueous solution for ICP-MS analysis. Again, the extraction yield was then plotted versus pH (Figure 5). Notwithstanding the presence of a large excess of competing anions, the resulting trend of the extraction efficiency is analogous to what has been seen in the case of LLE of NaReO₄ alone with 2 over the pH range 1–10. Good extraction yields (> 80% with one extraction) can be achieved during the LLE of perrhenate ion using 2 as the supramolecular extractant from simulated aqueous waste streams at pH values ranging from 1 to 10. In sharp contrast, the extraction yields of the other 7 competing anions were unchanged (~0%). Taken together, superphane 2 could serve as an elegant supramolecular extractant for near-complete removal of ReO₄⁻ ions from simulated aqueous waste streams with unprecedentedly high selectivity in a wide pH window (1–10), which could be a promising extractant candidate for practical applications in the real-world scenarios.



Scheme 2. Cartoon illustration of the rapid selective removal of ReO_4^- from the simulated waste streams of a large excess of competing ions via adsorption column technology

Rapid removal of ReO_4^- by adsorption column technology using superphane 2

Among known separation methods, column adsorption has been considered as one of the most successful techniques in the field of separation technology thanks to its significant advantages, e.g., easy to operate process, no need to use volatile solvent, and high separation efficiencies.⁵⁰ We were thus curious to evaluate the possibility of using solid superphane 2 as adsorbent for direct removal of ReO_4^- ions. To test our hypothesis, we carried out adsorption column experiments with 2. Concretely, 50 mg of solid 2 was filled in a glass pipette as the stationary phase or adsorbent, through which 2 mL of aqueous ReO_4^- solution (820 ppm) passed (3.0 mL/s) (Scheme 2). The eluate was recycled and subject to passing through the same pipette repeatedly. In each cycle of the adsorption column experiment, a small volume of the eluate was collected and diluted with water for further ICP-MS analysis. The resulting removal rate was plotted as a function of adsorption cycles (Figure S37A). Interestingly, the first cycle of the adsorption enabled the perrhenate removal rate to be as high as 96.74%, and remarkably, up to 99.99% removal of ReO_4^- ions could be achieved in two adsorption cycles. Next, the adsorption capacity of superphane 2 for ReO_4^- was preliminarily evaluated by determining equilibrium ReO_4^- concentrations after exposure to aqueous ReO_4^- solutions at initial concentrations from 2.3 to 30,000 ppm. As a result, the adsorption isotherm curve gave saturated adsorption capacity of 267 mg $\text{ReO}_4^- \text{ g}^{-1}$ fitted to the Langmuir model (correlation coefficient 0.99) (Figure S38). The saturated adsorption capacity here is not yet the highest reported. However it is higher than some commercial cationic materials such as LDHs (130 mg g^{-1}), UiO-66- NH_3^+Cl^- (159 mg g^{-1}), and SCU-101 (217 mg g^{-1}).³⁰ Moving forward, upon subjecting a mixed aqueous solution of NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 (30 mM for each), containing 820 ppm of NaReO_4 , to passing through adsorbent 2 in the pipette twice, near 100% removal of ReO_4^- anions was observed as inferred from the ICP-MS analysis results (Figure S37B). More importantly, in the

Table 1. Composition of the simulated Hanford waste streams

Anion	Concentration, mol/L	Anion: ReO_4^- molar ratio
ReO_4^-	1.94×10^{-4}	1.0
NO_3^-	6.07×10^{-2}	314
Cl^-	6.39×10^{-2}	330
NO_2^-	1.69×10^{-1}	873
SO_4^{2-}	6.64×10^{-6}	0.0343
CO_3^{2-}	4.30×10^{-5}	0.222

cases of the simulated waste streams of NaCl, NaF, NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 (30 mM for each) containing 820 ppm of NaReO_4 , a negligible pH effect on ReO_4^- extraction efficiency and selectivity was observed in the pH range 1.0–10.0 (Figure S39). To the best of our knowledge, these findings demonstrate the first supramolecular example where superphane 2 could be used as a highly effective and selective supramolecular adsorbent for rapid and near-complete removal of ReO_4^- ions from complex mixtures containing large excesses of competing anions over a wide pH range (1.0–10.0).

Rapid and near-complete removal of perrhenate anions in simulated waste streams

It is significantly challenging to remediate nuclear waste streams such as that from the Hanford site, due in large part to the high concentration of competing anions that may degrade with the removal performance of $\text{ReO}_4^-/\text{TcO}_4^-$.^{15,26,51} Encouraged by our results, it appeared possible that superphane 2 could be utilized to remediate the Hanford nuclear waste stream. In order to test our hypothesis, a simulated Hanford waste solution was prepared with ReO_4^- and other five competitive anions, viz., NO_3^- , NO_2^- , Cl^- , SO_4^{2-} , and CO_3^{2-} (as listed in Table 1).^{15,26,51} It was worth noting that the starting concentrations of NO_3^- , NO_2^- , and Cl^- were at least 300 times higher than that of ReO_4^- ($1.94 \times 10^{-4} \text{ M}^{-1}$), while the concentrations of SO_4^{2-} and CO_3^{2-} were relatively low. Upon passing a simulated Hanford waste solution at pH 7.0 through solid 2 fixed in a glass pipette twice, near 100% of ReO_4^- ions in the simulated waste stream could be extracted, while the concentration of the competing anions, i.e., NO_3^- , NO_2^- , Cl^- , and SO_4^{2-} , remained constant. To our surprise, the effect of pH ranging from 1.0 to 10.0 on the ReO_4^- removal efficiency and selectivity was not seen at all. Although the ReO_4^- removal efficiency was slightly hampered as the pH values further increased from 10.0 to 14.0, the removal selectivity toward ReO_4^- over other competing anions was not affected (Figure 6A, Table S2). This reflected the excellent performance of superphane 2 on cleaning the “real-world” waste streams with expected efficiency and selectivity.

For certain types of real nuclear waste streams, the concentrations of some competing anions, in particular NO_3^- and SO_4^{2-} , were found to be up to 6,000 times higher than that of targeted $\text{ReO}_4^-/\text{TcO}_4^-$ ions.^{15,26,52} This poses a major challenge to the development of high-performance materials for nuclear waste reprocessing. Subsequently we evaluated the potential selectivity of superphane 2 toward ReO_4^- against NO_3^- and SO_4^{2-} . Pleasingly, when a series of aqueous solutions of NaReO_4 and NaNO_3 , where the concentrations for the latter were set to be 500–12,000 times higher than that of the former, were passed through solid 2 fixed in a glass pipette twice, near 100% of ReO_4^- was found to be removed from the aqueous phase according to ICP-MS analysis (Figure 6B and Table S3). In sharp contrast, notwithstanding the presence of a large excess nitrate (up to 12,000 times), the concentrations of nitrate in the eluates were found to remain essentially

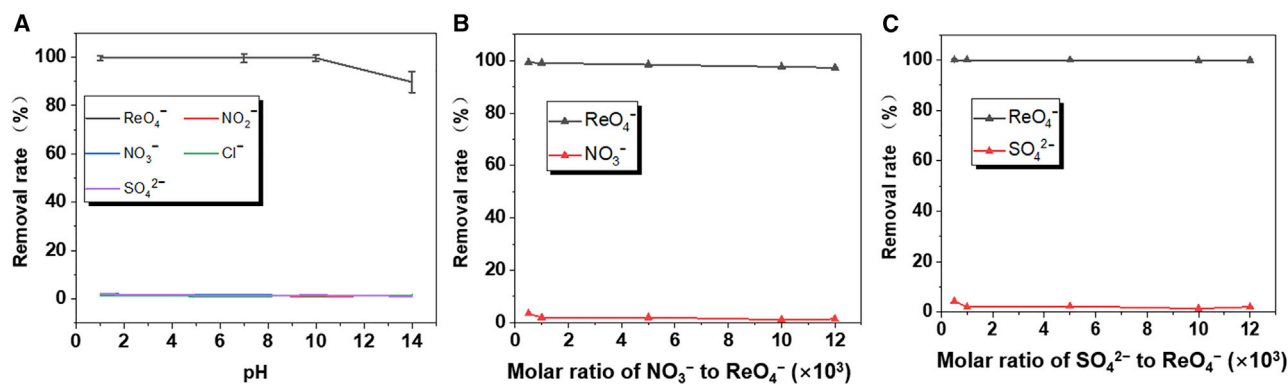


Figure 6. Results of ICP-MS analyses after treatment of the simulated Hanford waste streams with superphane 2 via adsorption column experiments (A) The pH effect (from 1.0 to 14.0) on selective removal of perrhenate against other competing anions. (B) Effect of the ultra-high concentrations of NO_3^- (mole ratio 500–12,000 times) on removal of low-content ReO_4^- (7.32×10^{-5} M) at pH 7.0. (C) Effect of the ultra-high concentrations of SO_4^{2-} (mole ratio 500–12,000 times) on removal of low-content ReO_4^- (7.32×10^{-5} M) at pH 7.0. Error bars represent SD. $n = 3$ independent experiments.

unchanged. In the presence of excess SO_4^{2-} , analogous unprecedentedly high selectivity of 2 for perrhenate anions was observed (Figure 6C and Table S4). These results indicated that superphane 2 proved highly selective to bind and remove ReO_4^- anion, even under the extreme conditions of high-content competing anions.

Recyclability and reusability of superphane 2

Finally, to meet the requirements of practical applications, we developed a strategy to recycle and reuse the supramolecular extractant/adsorbent 2. As illustrated in Figure 7, after each extraction, the chloroform layer was separated off, and the organic solvent was evaporated under reduced pressure. The resulting solid $\text{ReO}_4^-@2\cdot\text{H}^+$ complex was then soaked and refluxed in a 5% aqueous solution of NaHCO_3 for 12 h. During this process, the perrhenate ions (in their acidic form) were “back-extracted” into the aqueous phase and neutralized by NaHCO_3 . The solid residues were filtered off and subject to ^1H NMR spectroscopic analysis. The resulting ^1H NMR spectrum proved fully in accord with that of the fresh 2 (Figure S40). This shows that superphane 2 was capable of being recycled during the extraction of perrhenate by a relatively simple and practical operation. Such a recycling method proved able to be extended to the recycling of superphane 2 from the adsorption column experiments (Scheme 2 and Figure S41).

The reusability of superphane 2 was further assessed via illustrative adsorption column experiments using the recycled samples as stated before. Briefly, the recycled superphane 2, confirmed by ^1H NMR spectroscopy (Figure S40), was loaded in a small glass pipette. Then a simulated aqueous waste stream, consisting of equal-molar concentrations (30 mM each) of NaCl , NaF , NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 in water along with 820 ppm of NaReO_4 , was subject to passing through the adsorbent 2 twice. Then the eluate was monitored with ICP-MS. Subsequently, the adsorbent 2 in the pipette was eluted with 5% NaHCO_3 in water and directly reused for separating ReO_4^- from fresh simulated waste stream (as aforementioned). These operations could be repeated 5 times and the performance of superphane 2 on the ReO_4^- removal efficiency and selectivity was found to be not affected at all (Figure 7B). This bodes well for the recyclability and reusability of superphane 2 for rapid and near-complete removal of ReO_4^- with ultra-high efficiency and selectivity in real-world applications.

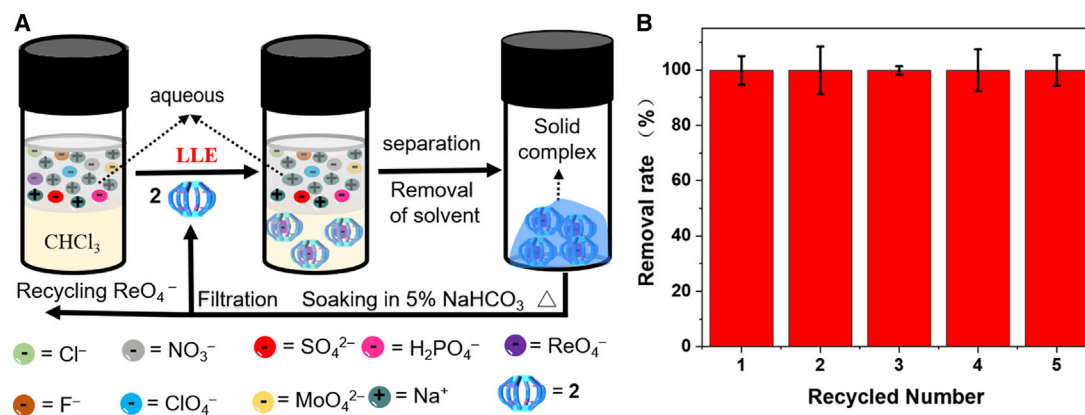


Figure 7. Illustration of the recycling process of superphane 2 and its reusability

(A) Cartoon illustration of the selective liquid-liquid extraction of ReO_4^- from its aqueous mixtures containing a large excess of competing ions and the recycling of superphane 2.

(B) The removal rate of perrhenate with recycled adsorbent 2 during 5 cycles in the adsorption column experiments. Error bars represent SD. $n = 3$ independent experiments.

CONCLUSIONS

A new superphane 2 bearing six amide NH and six secondary NH units was synthesized via a reductive amination strategy. This 6-fold symmetric system 2 featuring both liquid and solid emissive fluorescence was found capable of encapsulating perrhenate (as its acidic form) in a 1:1 ratio with an association constant of $K_a = (5.62 \pm 0.15) \times 10^3 \text{ M}^{-1}$ in a mixture of CDCl_3 and CD_3OD (1:1, v/v). In a series of binding studies, compound 2 displayed high selectivity toward ReO_4^- over other potential competing anions, viz., H_2PO_4^- , SO_4^{2-} , Cl^- , NO_3^- , and ClO_4^- . Interestingly, superphane 2 could separate ReO_4^- from a complex solid mixture of NaCl , NaF , NaNO_3 , NaClO_4 , NaH_2PO_4 , Na_2SO_4 , and Na_2MoO_4 containing extremely low content (as low as 200 ppb) of NaReO_4 with ca. 100% selectivity. When used as a supramolecular extractant for LLE, 2 was also capable of removing ReO_4^- from simulated aqueous waste streams containing only 820 ppm of NaReO_4 in the presence of a large excess of seven competing ions. Notably, this extractant works well for extracting ReO_4^- even at ppb level, and > 99.99% of the ReO_4^- in the complex simulated aqueous waste streams could be removed by consecutive extractions with exceptionally high selectivity. Over a wide pH range (1.0–10.0), superphane 2 was found to extract perrhenate with unaffected efficiency and selectivity. Interestingly, 2 could also act as an adsorbent for rapid and virtually complete removal of perrhenate anions from complex simulated Hanford waste streams with high efficiency and selectivity. Finally, superphane 2 was shown to be easily recycled and reused for effective removal of targeted ReO_4^- ions. To the best of our knowledge, this superphane-based extractant represents the first host-guest system for rapid and complete removal of ReO_4^- under both SLE and LLE conditions, along with column adsorption, with unprecedented efficacy and selectivity. Overall, these studies are expected to advance our understanding of the design criteria for producing ion receptors targeted for the recognition and extraction of species of particular interest with exceptional efficiency and selectivity.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Philip A. Gale (philip.gale@sydney.edu.au).

Materials availability

All unique/stable materials generated in this study are available from the [lead contact](#) with a completed materials transfer agreement.

Data and code availability

All of the data supporting the findings of this study are presented within the article and [supplemental information](#). See [Schemes S1–S3](#) for additional synthetic results, [Figures S1–S13](#) and [Table S1](#) for crystallographic analysis, fluorescent spectra, and theoretical calculations of superphane 2 and its perrhenate complex, [Figures S14–S23](#) for host-guest binding studies, [Figures S24–S30](#) for SLE studies, [Figures S31–S36](#) for LLE, [Figures S37–S39](#) and [Tables S2–S4](#) for column adsorption studies, [Figures S40](#) and [S41](#) for recycling and reusable experiments of 2, [Figure S42–S45](#) and [Tables S5–S8](#) for X-ray experimental details, [Figures S46–S62](#) for high resolution mass spectra (HRMS) and NMR spectra, and [Data S1](#) for Cartesian coordinates and energies of DFT-computed structures. All other data are available from the [lead contact](#) upon reasonable request. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers “CCDC: 2111252, 2111253, 2111254, 2111255.” These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2022.100875>.

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AUTHOR CONTRIBUTIONS

Conceptualization and supervision: Q.H. and P.A.G.; synthesis, characterization, NMR, binding studies, and photophysical experiments: W.Z.; single crystal growing, data collection, and analysis: W.Z. and Q.H.; theoretical calculations: A.L.; writing – original draft: Z.L. and Q.H.; writing – review & editing, Q.H. and P.A.G. All authors proofread, commented on, and approved the final version of this manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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