

## Tailored Porous Organic Polymers for Task-Specific Water Purification

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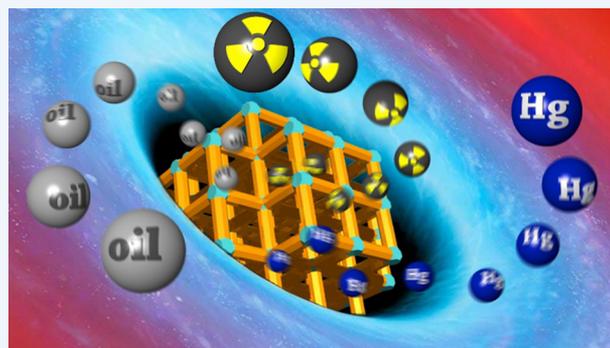
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Supporting Information

**CONSPECTUS:** The Industrial Revolution has resulted in social and economic improvements, but unfortunately, with the development of manufacturing and mining, water sources have been pervaded with contaminants, putting Earth's freshwater supply in peril. Therefore, the segregation of pollutants—such as radionuclides, heavy metals, and oil spills—from water streams, has become a pertinent problem. Attempts have been made to extract these pollutants through chemical precipitation, sorbents, and membranes. The limitations of the current remediation methods, including the generation of a considerable volume of chemical sludge as well as low uptake capacity and/or selectivity, actuate the need for materials innovation. These insufficiencies have provoked our interest in the exploration of porous organic polymers (POPs) for water treatment. This category of porous material has been at the forefront of materials research due to its modular nature, *i.e.*, its tunable functionality and tailorable porosity. Compared to other materials, the practicality of POPs comes from their purely organic composition, which lends to their stability and ease of synthesis. The potential of using POPs as a design platform for solid extractors is closely associated with the ease with which their pore space can be functionalized with high densities of strong adsorption sites, resulting in a material that retains its robustness while providing specified interactions depending on the contaminant of choice.

POPs raise opportunities to improve current or enable new technologies to achieve safer water. In this Account, we describe some of our efforts toward the exploitation of the unique properties of POPs for improving water purification by answering key questions and proposing research opportunities. The design strategies and principles involved for functionalizing POPs include the following: increasing the density and flexibility of the chelator to enhance their cooperation, introducing the secondary sphere modifiers to reinforce the primary binding, and enforcing the orientation of the ligands in the pore channel to increase the accessibility and cooperation of the functionalities. For each strategy, we first describe its chemical basis, followed by presenting examples that convey the underlying concepts, giving rise to functional materials that are beyond the traditional ones, as demonstrated by radionuclide sequestration, heavy metal decontamination, and oil-spill cleanup. Our endeavors to explore the applicability of POPs to deal with these high-priority contaminants are expected to impact personal consumer water purifiers, industrial wastewater management systems, and nuclear waste management. In our view, more exciting will be new applications and new examples of the functionalization strategies made by creatively merging the strategies mentioned above, enabling increasingly selective binding and efficiency and ultimately promoting POPs for practical applications to enhance water security.



### INTRODUCTION

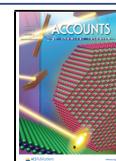
Water pollution has become a pressing global concern, and the sequestration of contaminants present in water has gained significant research attention.<sup>1–5</sup> However, the battle to ameliorate pollution is far from over, given that even well-known cases of contamination are still pending, endangering billions of people. Very recently, the World Health Organization (WHO) estimated that three billion people lack a safe drinking-water supply, demanding effective remediation approaches.<sup>6</sup> Among the developed strategies, adsorption has been regarded as the best available technology for the segregation of trace contaminants from water supplies due to its reasonable cost and effectiveness.<sup>7,8</sup> Given that current adsorbents exceed their limits in meeting more and

more stringent water quality standards, new and innovative technologies are essential for a sustainable future.

Porous organic polymers (POPs) combine the merits of traditional adsorbents with advanced materials such as metal–organic frameworks (MOFs).<sup>9–11</sup> POPs are constructed by purely organic materials via the robust covalent bond and have

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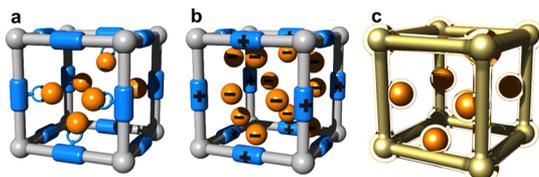


the benefits of tunability, with organic backbones that are ready to functionalize.<sup>12–20</sup> Thus, the resulting material neither dissolves nor decomposes when exposed to a variety of aqueous solutions, contributing to the applicability of POPs for water purification technologies. Depending on the degree of long-range order, POPs can be divided into two subclasses: crystalline and amorphous. By virtue of the flexibility of monomer design and the diversity of chemical reactions, it is possible to dial in any function in principle. Given that the porosity of the POPs facilitates rapid extraction of contaminants and the building blocks encode the target function, POPs are promising candidates for water purification. Moreover, the modularity of POPs enables us to investigate the favorable adsorptive interactions systematically.

Prompted by the vital necessity to diminish contaminants and protect freshwater supplies, this Account will highlight our ongoing research and inspiring progress in the deployment of POPs for radionuclide sequestration, heavy metal decontamination, and oil-spill cleanup. We have achieved successful elimination of such by judicious implantation of specific moieties inside the designed nanospace of POPs, resulting in unparalleled efficiency.

### ■ OPPORTUNITIES OF POPs FOR WATER PURIFICATION

With the tunability of the POPs, we can design them for use in coordinative complexation, ion exchange, and host–guest interaction, according to the properties of contaminants (Figure 1). To target the adsorbent materials, the *de novo*



**Figure 1.** POPs as a design platform for task-specific water purification. To effectively extract targeted species, specific functionalities can be introduced, whereby different adsorption mechanisms are involved, mainly including (a) coordinative complexation, (b) ion exchange, and (c) host–guest interaction.

synthetic strategy is ideal as it ensures the degree of grafting, with each monomer unit containing a specific functional group (Figure 2). However, with the ease of functionalization of organic backbones, we can still achieve a very high degree of grafting (Figure 3). This advantage provides selectivity and uptake capacity for a target analyte, which is a foremost improvement from traditional materials that lack such a distinction. Thus, any additional cost is easily counterbalanced



**Figure 2.** Chemical structures of adsorbents mentioned in this Account using *de novo* synthetic strategy by the polymerization of vinyl-functionalized monomers.

by the improved capacity and selectivity. In addition to dialing in a functional group of choice to achieve desired properties, pore structure engineering provides an alternative route to enhance the sorption performance. Two-dimensional (2D) covalent organic frameworks (2D COFs), a type of crystalline POP with an ordered 1D pore channel and a tailorable pore wall, give great promise.<sup>21–26</sup> The channels open a path for the contaminant to travel, and the aligned functional groups in close proximity boost their cooperation. By combining the merits of a designable starting unit and pore structure with the stability of purely organic material, they can be tailored for task-specific water purification.

### ■ RADIONUCLIDE SEQUESTRATION

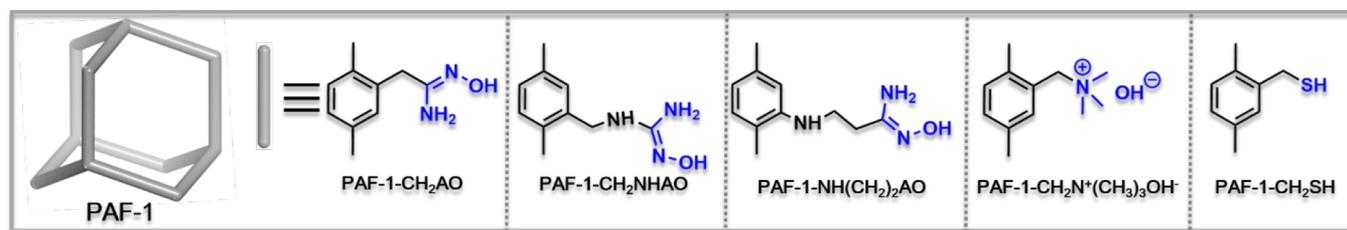
#### Uranium Recovery

Nuclear energy is considered sustainable because the CO<sub>2</sub> emissions are lower than those from solar panels, and it produces virtually no air pollution.<sup>27</sup> As a nuclear fuel, uranium is indispensable, which is contrasted with its extreme chemical toxicity. Therefore, opposition over the security and safety of nuclear reactor materials remains as the scale of these activities has resulted and will continue to result in a significant quantity of radioactive waste, posing an enormous environmental challenge. This horizon of events demands a continuous increase and adaptation in the efforts for the segregation of these species to provide enhanced protection and limit potential risks.<sup>28</sup>

Given the extremely low concentration of uranium and coexistence with an overwhelming amount of competition ions, the fundamental scientific challenges which have to be overcome include increasing the density, accessibility, and binding affinity toward uranium species of chelating groups in the adsorbent materials and, thus, the efficiency and uptake capacity. POPs lend themselves to custom design, allowing their compositions and pore structures to be fine-tuned. To achieve high-performance adsorbent materials, we initiated the project with the aims of (i) understanding the effect of density and flexibility of chelators on the uranium-binding fashions in the adsorbent materials; (ii) understanding how to improve the binding affinity of chelating moieties toward uranium; and (iii) understanding how the pore structures of adsorbents affect the accessibility and cooperativity of chelating groups and, thereby, the uranium capture efficiency. The developed structure–performance relationships are expected to be leveraged to further tailor the outcomes for uranium extraction from contaminated solutions and seawater.

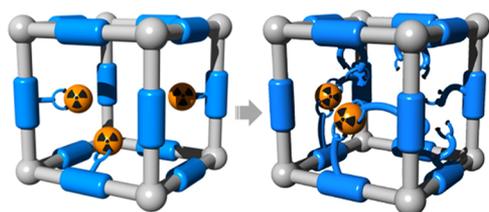
#### i. Increasing the Density and Flexibility of Chelators.

Amidoxime continues to be the center of efforts to design uranium scavengers, as well as the benchmark against which new systems are compared. To show the applicability of POPs



**Figure 3.** Chemical structures with use of PAF-1 as a platform for postsynthetic grafting of varying functionalities mentioned in this Account.

as a decorating platform for uranium extraction, we chose a porous aromatic framework (PAF-1), with the consideration that the ultrahigh surface area (around  $5000 \text{ m}^2 \text{ g}^{-1}$ ) and abundance of phenyl rings can be readily functionalized with a relatively high density and accessible chelators. Amidoxime moieties ( $-\text{C}(\text{NOH})\text{NH}_2$ , AO) were grafted onto PAF-1 through a three-step postsynthetic modification with encouraging results. The resulting material PAF-1- $\text{CH}_2\text{AO}$ , afforded a uranium uptake capacity of over  $300 \text{ mg g}^{-1}$  and managed to lower an aqueous uranium solution of  $4.1 \text{ ppm}$  to less than  $1.0 \text{ ppb}$  within  $90 \text{ min}$ , which surpasses the U.S. Environmental Protection Agency (EPA) limit of  $30 \text{ ppb}$  (see Supporting Information Table S1, a summary of the uranium sorption performance of representative adsorbents).<sup>29</sup> X-ray absorption fine structure (XAFS) analysis revealed that a majority of uranyl ions are bound to one amidoxime group. We reasoned that the rigidity of the incorporated chelator restrains them from cooperative binding (Figure 4, left).



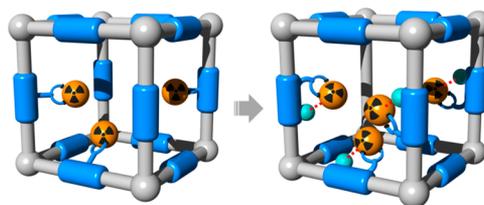
**Figure 4.** Schematic illustration of increasing density and flexibility of chelators for promoting cooperative binding and, thus, the binding affinity.

Given that the amidoxime chelators preferentially bind to uranyl ions in a  $\eta^2$  coordination manner, enhancing their potential cooperation would result in strong binding and high uptakes. With these considerations in mind, we varied the structure of the introduced amidoxime ligand on PAF-1 for targeting cooperative binding, with studies focused on their flexibility and grafting degree.<sup>30</sup> To this end, two adsorbent materials with different content and chain length of amidoxime groups were synthesized, with the resulting materials named as PAF-1- $\text{CH}_2\text{NHAO}$  and PAF-1- $\text{NH}(\text{CH}_2)_2\text{AO}$ . Adsorption results revealed the nonlinear relationship between the uptake capacity and the grafting density in these materials. The grafting density of PAF-1- $\text{CH}_2\text{NHAO}$  with a short amidoxime chain is roughly half that of PAF-1- $\text{NH}(\text{CH}_2)_2\text{AO}$  with a longer amidoxime chain ( $1.64 \text{ mmol g}^{-1}$  vs  $3.37 \text{ mmol g}^{-1}$ ), but the capacities for each differ by a factor of nearly four ( $385 \text{ mg g}^{-1}$  for PAF-1- $\text{NH}(\text{CH}_2)_2\text{AO}$  and  $102 \text{ mg g}^{-1}$  for PAF-1- $\text{CH}_2\text{NHAO}$ ). According to the results of XAFS analysis, the amidoxime ligand in these materials binds to uranyl in a 2:1 ratio, and this would mean that the ligand utilization in PAF-1- $\text{NH}(\text{CH}_2)_2\text{AO}$  is nearly full, corresponding to a value of 96%,

while the ligand utilization for PAF-1- $\text{CH}_2\text{NHAO}$  is only 52%. Given that the configuration of the ligands on the adsorbent material would require both chains to bend toward a common uranyl to bind in the 2:1 fashion, it is then reasonable to assume that the added flexibility and increase in the density of a chelator is preferential, thus leading to higher capacities and better ligand utilization (Figure 4, right). These results highlight the variability of a chelating group and the strategies that can be employed to enhance the practical applicability of adsorbents.

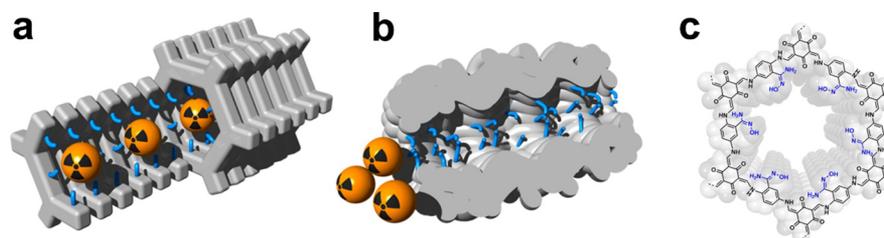
#### ii. Introduction of Secondary Sphere Modifiers.

Intrigued by the cooperative binding effect observed in the materials mentioned above, we further endeavored to design adsorbents with a higher functionality content by constructing the amidoxime moieties into the porous framework directly, for improved cooperative binding. Moreover, the present amidoxime-based sorbents do not yet perform well enough in real-world water samples, such as seawater extraction, as they bind nickel, cobalt, and iron ions present in these systems with higher affinity. With this in mind, to enhance the selectivity of amidoxime to uranyl ions, we were inspired by nature. The affinity of amino acids involved in binding ions can be significantly increased by noncovalent interactions from the surrounding peptides in the protein scaffold and can even achieve femtomolar affinity.<sup>31</sup> We reasoned that the binding affinity of chelating sites toward specific ions could be improved by the integration of an assistant group orientated in a suitable position (Figure 5). To test this hypothesis, amine



**Figure 5.** Schematic illustration of the introduction of secondary sphere modifiers to reinforce the primary binding.

was the functionality of our choice, as it is both an excellent hydrogen bond donor and an electron donor. To guarantee the relative location of the amino substitute and the amidoxime, as well as to enhance the spatial continuity of functional groups in the resultant adsorbents for potential cooperation, a *de novo* synthetic strategy was employed. A set of bioinspired benzamidoxime ligands with varied amino substituent relative positions toward the amidoxime moiety was designed and used to synthesize porous materials. XAFS results indicated a  $\eta^2$ -binding mode for all adsorbents, reinforcing that the increased functionality density in the materials promoted their cooperative binding. Comparative studies revealed that the



**Figure 6.** (a) Schematic illustration of chelators in COF materials. (b) Functionalization of amorphous porous organic polymers, illustrating the blockage of narrow pore channels and bottlenecks. (c) Chemical structure of COF-TpDb-AO.

introduction of an amine group relative to the ortho position of the amidoxime (POP-*o*NH<sub>2</sub>-AO) significantly enhanced the uranium adsorption performance.<sup>32</sup> The amino group provides secondary stabilizing interactions to the overall complex, including enriching the electronic density of amidoxime to stabilize the charge and providing hydrogen bonding interaction to enforce the favorable coordination fashion. POP-*o*NH<sub>2</sub>-AO afforded an uptake capacity of 530 mg g<sup>-1</sup> and exhibited rapid kinetics, arriving at equilibrium within 1 h of treatment. It is also capable of eliminating minute concentrations of uranium from 3.6 ppm to less than 0.02 ppb. Such ability is essential for the removal of uranium from wastewater and the extraction of uranyl from seawater, which was shown to give an uptake capacity of 4.36 mg g<sup>-1</sup> from real seawater, 3-fold higher than that of the benchmark material developed by the Japanese scientists.<sup>33</sup> This result is important as the ocean contains 4.5 billion tons of uranium, enough to power the nuclear reactors for the next few centuries.<sup>34</sup> The development of technologies to extract uranium from seawater would thus guarantee the availability of nuclear fuel sources, providing a uranium price ceiling and sustaining nuclear energy for generations.<sup>35–37</sup> These collective results demonstrate a promising strategy to improve the chelator's ability to extract analyte diluted by high concentrations of competitors.

**iii. Regulation of the Pore Structure of Adsorbents.** In addition to increasing the density and flexibility, regulating the orientation of chelators in adsorbents is an alternative strategy for facilitating a coordinative binding and, consequently, the accompanied binding affinity. We postulated that pore structure engineering would provide a promising way to manipulate the orientation of ligands (Figure 6). To fulfill this task, we envisioned that the unique pore structure of 2D COFs could offer an appealing platform. The eclipsed, stacked layered sheets form continuous channels, wherein the chelating groups are aligned into periodic arrays, promoting their cooperation in guest species binding. Additionally, the ordered one-dimensional channel provides a path for the analyte to travel to the chelators on the pore walls, which may be able to offset the shortage of amorphous materials, as buried chelating sites often compromise their performance due to small and irregular pores.

Side-by-side comparisons were made between the COFs and the corresponding amorphous analogs to determine the impact of pore structure on the sorption performance.<sup>38</sup> The COFs decorated with amidoxime groups exceed their amorphous counterparts in all aspects in terms of uptake capacities, kinetics, and removal ability in uranium decontamination. Specifically, COF-TpDb-AO constructed by the condensation of trimethylphloroglucinol with 2,5-diaminobenzonitrile, followed by the amidoximation, afforded a uranium uptake capacity of 408 mg g<sup>-1</sup>, while the corresponding amorphous

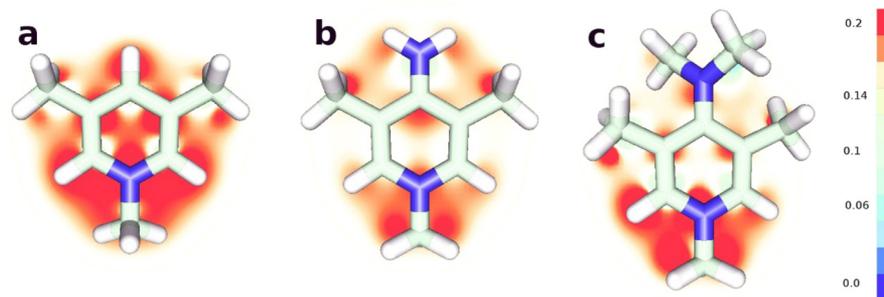
analog (POP-TpDb-AO) gave a value of 355 mg g<sup>-1</sup> (Figure 6c). Further, COF-TpDb-AO was able to reach 95% of its saturated adsorption capacity within 30 minutes; triple that time was needed for POP-TpDb-AO to target a comparable value. Besides the greater accessibility of chelators, COF-TpDb-AO exhibited a higher binding affinity toward uranium by an order of magnitude relative to POP-TpDb-AO. These merits allowed for COF-TpDb-AO to mitigate uranium species from various contaminated water samples, rapidly diminishing the uranium concentration to lower than 0.1 ppb from 5 ppm. COF-TpDb-AO also gave the promise to extract uranium from seawater, affording an uptake capacity of 127 mg g<sup>-1</sup> from a seawater sample spiked with 20 ppm uranium. Furthermore, the adsorption performance can be further engineered by the reticular design of COFs, and larger open channels are beneficial to the enhancement of the mass transfer. These results, therefore, highlight the potential of 2D COFs to be an attractive platform for the sorbent material design.

### Technetium-99 (<sup>99</sup>Tc) Segregation

Technetium-99 (<sup>99</sup>Tc), which is mostly generated as a byproduct of fission of uranium-235, is one of the most hazardous radioisotopes because of its high mobility in groundwater and biological systems and extremely long half-life (213,000 years). <sup>99</sup>Tc predominately occurs as pertechnetate, TcO<sub>4</sub><sup>-</sup>, in both the nuclear fuel cycle and the environment, and this species is highly soluble and non-complexing/weakly complexing, resulting in fast migration. The management of <sup>99</sup>Tc is, therefore, essential with regard to legacy waste site cleanup, as well as abating the off-site migration of the contaminated groundwater to avoid bioaccumulation. Ion exchange has proved to be the most viable method for removing TcO<sub>4</sub><sup>-</sup> from the bulk waste stream.<sup>39</sup> Due to the low hydration energy of TcO<sub>4</sub><sup>-</sup>, there is a natural bias toward exchanging TcO<sub>4</sub><sup>-</sup> preferentially over the other anions such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>. The relatively hydrophobic environment of the polymer could further enhance the ion exchange bias.

To demonstrate the utility of POPs for ion exchange, trimethylammonium hydroxide moieties were grafted onto PAF-1 (PAF-1-CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>OH<sup>-</sup>). The resulting ion-exchange material demonstrated a high ion-exchange capacity and fast kinetics when evaluated for scavenging MnO<sub>4</sub><sup>-</sup>, a model ion of TcO<sub>4</sub><sup>-</sup>, surpassing the commercial resin of Amberlyst-A26 and other benchmark ion-exchange materials such as clays and MOFs. Advantageously, this ion-exchange process is fully reversible, and the material can be readily regenerated with retained ion-exchange performance.<sup>40,41</sup>

After establishing the intrinsic advantages of POPs to generate high-performing adsorbents for TcO<sub>4</sub><sup>-</sup> remediation, we further manipulated the binding affinity of the ion-exchange site toward TcO<sub>4</sub><sup>-</sup>. Given the overwhelmingly high concen-



**Figure 7.** Distribution of the charge density around the pyridinium is shown by a plot of the electrostatic potential surface just below the molecule. The most favorable binding geometry for a triangular face of an anion has opposite orientations between the cationic building blocks of (a) PQA-Py-Cl, (b) PQA-*p*NH<sub>2</sub>Py-Cl, and (c) PQA-*p*N(Me)<sub>2</sub>Py-Cl (light green, C; blue, N; white, H).

tration of competitors, sorbent materials designed to eliminate TcO<sub>4</sub><sup>−</sup> from real-world water samples and legacy tank waste must possess an exceptionally high selectivity toward TcO<sub>4</sub><sup>−</sup>. The integration of multiple cooperative functionalities in a single material is a practical approach for achieving the requisite affinity. Using pyridinium as a cation-building unit, we described that the affinity of the resulting anion nanotraps toward TcO<sub>4</sub><sup>−</sup> can be improved by engineering the local environment of the cation site. A variety of secondary sphere modifiers were introduced to the para position relative to a pyridinium motif (Figure 7). Density functional theory calculation studies indicate that the implanted electron-donating group of dimethylamino facilitates the formation of kinetically labile complexes and, thus, enables fast ion exchange. Meanwhile, the tertiary amine shows a significant positive partial charge, pulling anionic oxygens toward itself and, consequently, higher efficiency. Encouraged by these results, we constructed this moiety into porous material (PQA-*p*N(Me)<sub>2</sub>Py-Cl). It is worth mentioning that the functional pyridinium is the only monomer used for the adsorbent synthesis, which maximizes the ion-exchange sites in the resulting anion nanotraps, thereby giving rise to the highest sorption capacity reported thus far (1127 mg of ReO<sub>4</sub><sup>−</sup> per gram of the polymer; see also Table S2). Due to the robustness of the resulting frameworks, these materials exhibited outstanding radiation resistance and chemical/hydrolytic stability. This allowed their application in a wide range of conditions, showing unprecedented extraction efficiencies' conditions pertinent to the used fuel reprocessing solution, used nuclear fuel, and legacy nuclear wastes.<sup>42</sup> Specifically, after a single treatment, PQA-*p*N(Me)<sub>2</sub>Py-Cl can extract approximately 70% of ReO<sub>4</sub><sup>−</sup> from the HNO<sub>3</sub> aqueous solution with a NO<sub>3</sub><sup>−</sup>:ReO<sub>4</sub><sup>−</sup> molar ratio of 1875 at a solution to an adsorbent ratio (S/A) of 50 mL g<sup>−1</sup>, and 90% of available ReO<sub>4</sub><sup>−</sup> ions were removed at an S/A of 20 mL g<sup>−1</sup>. In addition, PQA-*p*N(Me)<sub>2</sub>Py-Cl can selectively remove TcO<sub>4</sub><sup>−</sup> from the simulated Hanford LAW melter recycle stream, wherein the concentrations of NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, and Cl<sup>−</sup> are 300 times greater than that of TcO<sub>4</sub><sup>−</sup>. It was found that, at an S/A of 200 mL g<sup>−1</sup>, PQA-*p*N(Me)<sub>2</sub>Py-Cl managed to segregate about 95% of available TcO<sub>4</sub><sup>−</sup>. Encouraged by these results, we further evaluated its efficiency in the elimination of TcO<sub>4</sub><sup>−</sup> at Savannah River Sites, a strongly basic solution of TcO<sub>4</sub><sup>−</sup> in the presence of a large number of other anions with strength over 70000 times that of TcO<sub>4</sub><sup>−</sup>. It was found that, at an S/A of 100 mL g<sup>−1</sup>, approximately 80% of available TcO<sub>4</sub><sup>−</sup> was extracted. Up until now, there have been no materials reported with comparable selectivity, suggesting their practical applic-

ability in nuclear waste remediation. Given that ion exchange often experiences a similar mechanism, we expect that the strategy demonstrated here can be applied to many other sequestration processes. The results above indicate that POP-based nanotraps substantially overcome the long-term challenge of radionuclides extraction under extreme conditions of high ionic strength, superacidity, basicity, and strong irradiation fields.

## HEAVY METAL DECONTAMINATION

The advances in industrial progress are typically accompanied by environmental pollution, as the development of industry inevitably escalates the emission of toxic species into the environment. Mercury (Hg) is one such species; according to the Agency for Toxic Substances and Disease Registry, it is the third most toxic substance after arsenic and lead. Due to the wide use of mercury in industry and daily life, it is reported that there are over 6000 tons of mercury emitted into the atmosphere per year, warranting new technologies to segregate the mercury found in the environment.<sup>43,44</sup>

To implement the POP as a mercury nanotrap, we first selected PAF-1 for the potential installation of chelators.<sup>45</sup> The material was targeted by two-step postsynthetic modifications: first by a chloromethylation and then by a thiol conversion. PAF-1-SH demonstrated an exceptional mercury saturation uptake capacity of over 1000 mg g<sup>−1</sup>, an extraordinary distribution coefficient *K<sub>d</sub>* value of 5.76 × 10<sup>7</sup> mL g<sup>−1</sup>, and outstanding kinetics (Table S3; see summary of Hg<sup>2+</sup> sorption performance of various sorbent materials). It was able to rapidly reduce the concentration of Hg<sup>2+</sup> from 10 ppm to a very low level, smaller than 0.4 ppb—far below the acceptable limits set by the EPA for drinking-water standards (2 ppb)—within a few minutes. Besides, PAS-1-SH retained the high efficiency for Hg<sup>2+</sup> removal over a wide pH range of 3–11 as well as the system, which was pervaded with high concentrations of background metal ions, including Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>.

We further took the initiative to build and improve upon our initial studies, in order to design a better material with a refined application and to consider its long-term potential for a more economically feasible synthesis for the practical applications. We thus advanced a more *de novo*-type synthesis, incorporating the chloromethyl group into the monomer unit, assuring each monomer is functionalized.<sup>46</sup> Additionally, a more straightforward and more cost-effective free radical polymerization method was employed for polymer synthesis instead of the costly reagents and catalysts (Ni(COD)<sub>2</sub>) to perform the

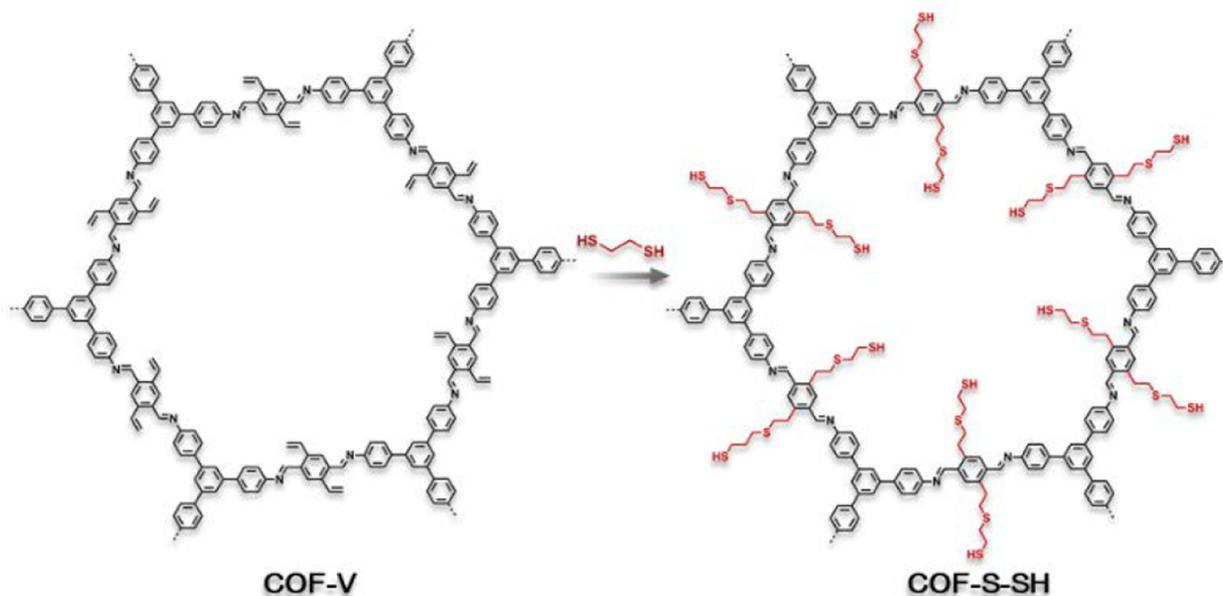


Figure 8. Chemical structures of COF-V and COF-S-SH.

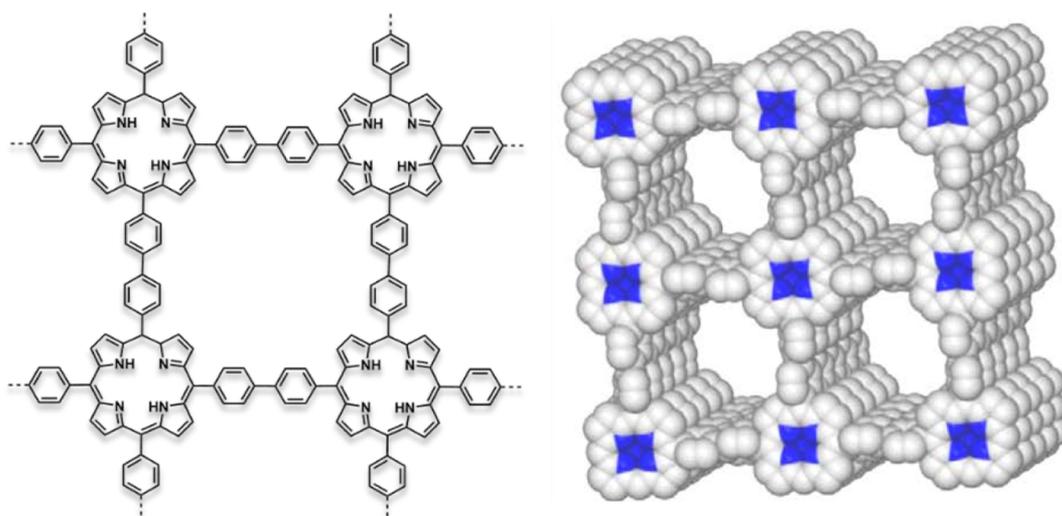
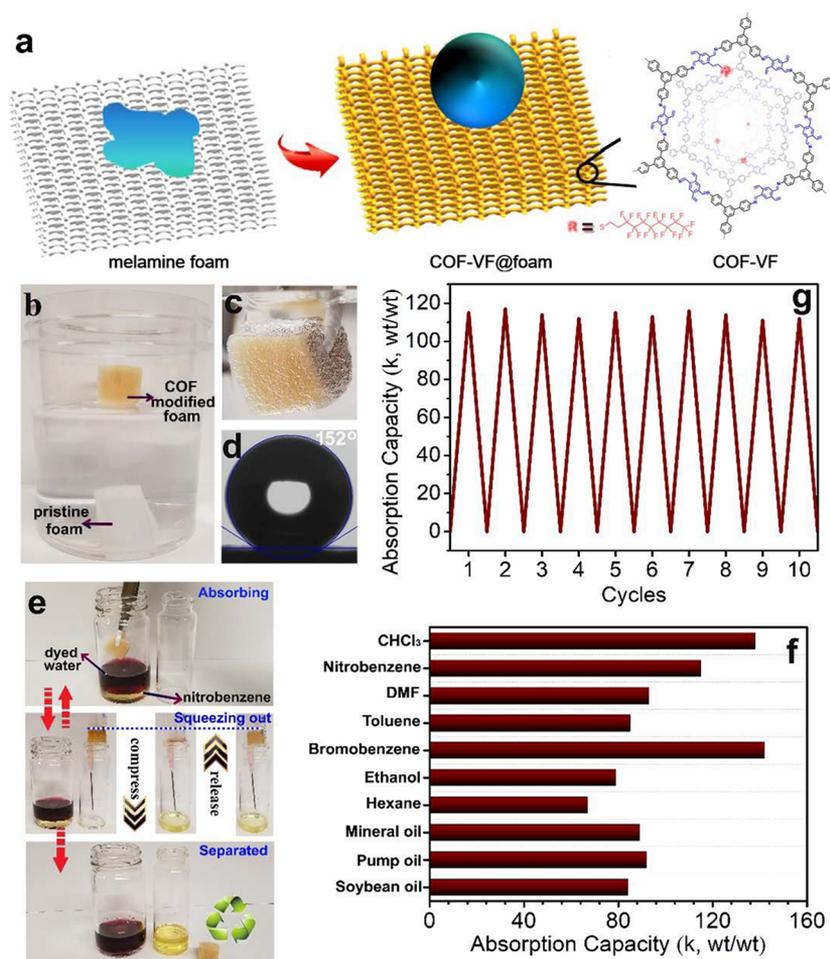


Figure 9. Chemical and simulated crystal structure of PCPF-1.

coupling reaction involved in PAF-1 synthesis. With regard to the performance, the newly developed POP-SH outperforms PAF-1-SH in nearly all aspects. The maximum uptake capacity is  $200 \text{ mg g}^{-1}$  higher, and the  $K_d$  value is a full order of magnitude better than PAF-1-SH. For the kinetic results, PAF-1-SH took a total of 6 h to drop mercury levels to 0.4 ppb, while POP-SH was able to reach 1.0 ppb within 10 min, and after 3 h, the level was below our instrument's detection limit of 0.1 ppb. Moreover, POP-SH was found to be extremely useful for mercury vapor adsorption with an uptake capacity of  $630 \text{ mg g}^{-1}$ . XAFS spectroscopy was performed to understand the exact Hg species coordination environment in POP-SH, which found two distinct Hg–S scattering paths. This result is expected for an amorphous material with a rigid polymeric backbone, obstructing the cooperation of the binding sites.

We speculated that the aforementioned shortcoming could be addressed by using COFs as a decorating platform; the ordered  $\pi$ -columnar structures enforce the anchored chelators that are oriented in the same direction, which facilitates their

cooperation, and consequently, the accompanied binding affinity. To validate this assumption, we designed a vinyl-functionalized 2D mesoporous COF, denoted as COF-V, followed by postsynthetic modification with various thiol and thioether chelating arms via a thiol–ene “click” reaction (Figure 8).<sup>47</sup> The flexibility of chelating arms was proven to have a profound impact on the binding affinity toward the Hg species of the adsorbents. Specifically, the resulting COF material laced with flexible sulfur-based chelating groups is capable of effective removal of  $\text{Hg}^{2+}$  in aqueous solutions and  $\text{Hg}^0$  in the gas phase, with a very high uptake capacity of 1350 and  $863 \text{ mg g}^{-1}$ , respectively. It is able to rapidly diminish the  $\text{Hg}^{2+}$  concentration from 5 ppm to 0.1 ppb even in the presence of numerous competitor. The exceptional performance of COF-S-SH can be readily interpreted by the XAFS spectrum, which shows that each Hg is bound exclusively by two sulfur atoms via intramolecular cooperativity. The synergistic effects stem from the flexible and densely populated chelating groups, allowing for metal ions to adopt a favorable



**Figure 10.** (a) Schematic illustration of the preparation of superhydrophobic COF-VF coated melamine foam (COF-VF@foam). (b) Photograph of COF-VF@foam (yellow color) and melamine foam (white color) after being placed on water. (c) Photograph of COF-VF@foam immersed in water by a force. (d) Water contact angle on the surface of COF-VF@foam. (e) COF-VF@foam can separate under-water oil such as nitrobenzene from water. (f) Absorption capacities of COF-VF@foam for various organic solvents and oils, as indicated by weight gain. (g) Weight gain during nitrobenzene absorption/squeezing cycles. Reproduced with permission from ref 50. Copyright 2018 Elsevier Inc.

form and thus affording the adsorbent with the highest mercury binding affinity reported thus far (Table S3).

## ■ OIL-SPILL CLEANUP

Pollution by toxic organic solvents, petroleum products, and crude oil is a growing concern, resulting in severe environmental and ecological problems. It costs more than 10 billion dollars for oil-spill cleanups all over the world each year. Adsorbents, such as sand, activated carbons, or zeolites, are widely used. However, the performance of those adsorbents is usually compromised by the water or moisture adsorption, thus necessitating the materials innovation for selectively capturing organic pollutants from water and air.<sup>48</sup> Increasing material hydrophobicity is a general solution to combat the failure associated with water absorptivity.

To design a hydrophobic porous material, we developed a porphyrin-based POP (PCPF-1, Figure 9) by homocoupling of 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (tbpp).<sup>49</sup> The resulting material exhibits a high surface area and strong hydrophobicity, allowing for it to selectively adsorb C5–C8 hydrocarbons from the air and water. Derived from the vapor adsorption isotherms collected at 298 K, the uptake capacities of PCPF-1 for the organic vapor can reach up to 1030 mg g<sup>-1</sup>, exceeding the benchmark materials of hydrophobic MOF

(FMOF-1) and activated carbon material (BPL), which give the adsorption values of 156 and 300 mg g<sup>-1</sup>, respectively. Further, PCF-1 showed a liquid gasoline uptake capacity of 20.5 g g<sup>-1</sup>, outperforming all reported porous organic polymer materials at that time and proving promising in the cleanup of oil spills from water and air (Table S4, summary of oil absorption capacities of various materials). However, PCPF-1 was synthesized as powders, and therefore, its applications in the real world may be affected by their poor processability. Moreover, the limited pore volume of PCPF-1 restricts its adsorption capacities.

To address the concerns mentioned above, we integrated a superhydrophobic COF material (COF-VF) with melamine foams, yielding a superhydrophobic foam (COF-VF@foam, Figure 10),<sup>50</sup> whereby COF-VF was achieved by chemically grafting the pore surface of a 2D COF (COF-V) with perfluoroalkyl groups. Given the superhydrophobicity and superoleophilicity of the resulting foam, it could be practically applied to multiple organic liquids with an uptake capacity of up to 160 times its weight, demonstrating its broad applicability. Advantageously, the foam can be recycled by simply squeezing and fostering the absorption process with minimal loss in absorption capacity for at least ten cycles

(Figure 10). This strategy highlights the opportunity for COFs to design smart materials for oil cleanup.

## OUTLOOK AND FUTURE DIRECTIONS

In this Account, we summarized our recent advances in how sorption performance can be improved for POP-based adsorbent materials. The POPs are tailored specifically for the segregation of radionuclides, heavy metals, and oil spills by deliberately tuning the composition and pore structure. The strategies we advanced include increasing the density and flexibility of chelators, introducing secondary sphere modifiers, and enforcing the orientation of the functionalities to enhance their cooperation. While the POP-based adsorbents discussed in this Account show great potential for providing clean water to meet increasing demands and quality, challenges remain in translating such advanced materials from the laboratory scale to utility-scale plants or applied devices. The following future directions should be pursued to improve the scalability of POP-based adsorbent materials. To add the applicability of bulk POP materials, attention should also be paid to develop POP membranes or integration with substrates. Subsequently, we suggest that future efforts should be paid to advance POP-based technologies for task-specific water purification. (i) *Delineation of structure–property relationships*: the vast majority of the presented computational optimization and design strategies are based upon small molecules; however, the textural parameters of the polymer have a considerable effect on the established binding modes. Therefore, effort should be dedicated to the systematic investigation of these aspects on the performance of the resulting adsorbents and, ultimately, to the rational design of next-generation sorbents. (ii) *Development of scalable and cost-effective POP synthetic methods*: A large number of POPs are notoriously expensive due to the costly catalysts and excessive volumes of organic solvents to perform the coupling reaction during its synthesis. Moreover, some catalysts are air and humidity sensitive, which added difficulties for large-scale synthesis. The development of metal-free polymerization routes, such as free-radical polymerization and acid-catalyzed condensation, are expected to lower the price, a must for any future industrial-scale processes. (iii) *Enhancing POP processability*: To date, POPs exist primarily as powders, challenging their practical implementation. Efforts to integrate these powders with other substrates are crucial to expand their function for practical applications, which may bring about opportunities to further improve their performance. As shown above, the integration of superhydrophobic COF powders with foam can significantly improve the oil uptake capacities by more than 2 orders of magnitude. Mixed-matrix membranes are another promising area as these materials combine POP porosity and functionality with the attractive mechanical properties of polymeric matrices. Although using POPs for environmental remediation is still in its infancy, it would be prudent to start considering the next grand step, given their validated efficiency.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.accounts.0c00007>.

Uranium and Hg<sup>2+</sup> sorption performances, ReO<sub>4</sub><sup>-</sup> uptake capacities, and absorption capacities (PDF)

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### Notes

The authors declare no competing financial interest.

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