Trends in Chemistry

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Opinion

Opportunities of Porous Organic Polymers for Radionuclide Sequestration

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Nuclear power is critical in addressing the growing energy demand required for an improved quality of life. Its sustainable development, however, rests on the accessibility of fuel material and the ability to manage a nuclear fuel cycle safely and efficiently. Recently, porous organic polymers (POPs) have been shown to provide improved radionuclide sequestration performance over traditional porous materials in terms of both uptake capacity and selectivity. These materials also exhibit improved stability and are readily functionalized, rendering them promising materials for a number of emergent applications. This Opinion demonstrates achievements in engineered POPs for nuclear fuel mining and remediation of representative radioactive species, along with discussions of the underlying design strategies and principles. Future research opportunities and implementation barriers are also discussed with the hope of inspiring additional scientists to engage in this emerging area of research.

Highlights

Porous organic polymers (POPs) are an attractive platform for radionuclide sequestration owing to their enhanced stability, large surface area, tunable pore size, lightweight composition, and facile chemical functionalization.

Uptake capacity and binding affinity of radionuclides in POPs is increased through cooperative-binding effects, multisite cooperation, and efficient design of the pore structure and volume. In addition, pore structure partly dictates the accessibility and orientation of binding sites, thereby controlling uptake efficiency and binding affinity toward a target species.

Introduction of assistant groups increases the binding moieties' affinity toward uranyl ions for uranium recovery.

The Sustainable Development of Nuclear Energy

Sustainable energy production has become a major theme underlying many societal challenges, especially with the threat of global climate change and decreasing availability of fossil fuels. While significant progress has been made with renewable energy, nuclear power remains the only near-term scalable, low-carbon energy source capable of replacing fossil fuels [1,2]. To meet the increasing energy demand, nuclear power generation is projected to double by 2040, making uranium availability a matter of energy security [3,4]. The sparsity of uranium ore necessitates the securing of sources other than the conventional terrestrial reserve to safeguard nuclear energy development [5–7]. For this reason, uranium recovery from seawater (the largest uranium reserve) has been identified as one of seven chemical separations that, if improved, would reap global benefits [5]. However, recovering uranium from seawater is a formidable task due to the complexity of seawater, replete with high concentrations of competing ions and an incredibly low concentration of uranium (around 3 ppb). This challenge necessitates the innovation of advanced materials.

In addition, closing of the nuclear fuel cycle by reprocessing and recycling spent fuel helps to exploit the full potential of nuclear power and maximize resource utilization [8–10]. However, the diversity of waste streams, with the elements spanning the entirety of the periodic table (Figure 1; https://whatisnuclear.com/waste.html), poses a grand challenge to effectively recover and reprocess fissile uranium and plutonium together with the conversion of a complex and highly radioactive mixture into waste forms suitable for long-term storage [11–13]. The most important long-lived radionuclides of the fission products include Cs, Sr, Tc, and I, which are the priority pollutants for treatment in terms of both ensuring safe disposal of radioactive waste and assisting in cleanup efforts with legacy waste [13]. These challenges underscore the need for technological innovation. Although significant progress has been made, the development of improved separation technologies continues to attract

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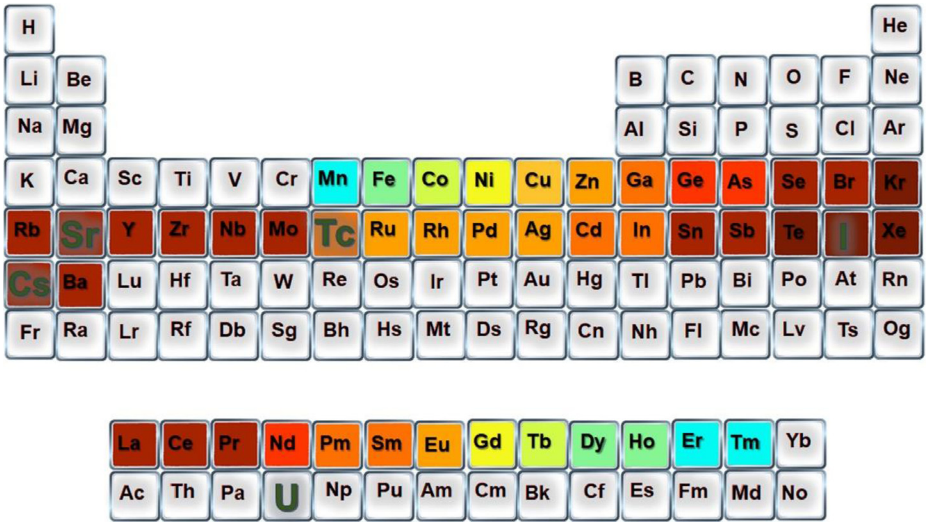

Figure 1. Fission Products Including Radioactive Isotopes. The fission products span a wide variety of elements including alkali metals, transition metals, halogens, and even noble gases. The complex chemistry associated with this diversity is a key challenge in nuclear waste management. The background color is proportional to the log of the instantaneous yield (decreasing from red, orange, yellow, green, and cyan). In this Opinion, we focus on the recent progress with porous organic polymers for target extraction of the elements highlighted in green color.

increasing interest due to concerns over factors such as efficiency and environmental impacts [14–21], as is true for liquid–liquid extraction, the current state of the art, which generates large volumes of organic waste. Moreover, the equipment required for multistage extraction and stripping increases capital costs. It has been well recognized that the development of advanced sorbent materials provides a promising avenue for increased efficiency. The main properties desired for sorbent materials include: high capacity and selectivity to minimize the volume of the final waste form; the ability to extract the targeted radionuclide from diverse liquid nuclear waste (e.g., varying pH and salinity) or from gaseous waste streams; long-term resistance to both chemical damage and radiation; and an optimized porous structure for high-capacity and efficient extraction.

Opportunities for POPs in Radionuclide Sequestration

Porous materials play vital roles in many fields. The skeleton structure of porous materials has clearly evolved, from the inorganic open frameworks of silicates to metal–organic frameworks (MOFs) to recent organic porous materials. Traditional porous materials, such as zeolites and activated carbons, while extremely robust, cannot be fine-tuned with the myriad reactions available from synthetic organic chemistry to achieve the desired functionality for the demanded binding affinity. The unprecedented modularity and porosity of MOFs make them promising for a number of emergent applications. However, they generally do not possess the hydrolytic stability necessary for long-term application in harsh conditions involving extreme pH environments for radionuclide sequestration. Additionally, the inability of purely inorganic or MOF supports to be completely converted to volatile products by combustion would generate a large volume of secondary radiological waste.

Along with MOFs, POPs comprising predominantly light, nonmetallic elements with rigid covalent bonds show a great combination of structural modularity and stability. POPs can be divided into two subclasses: crystalline and amorphous. A representative example of crystalline POPs are covalent organic frameworks (COFs). Many amorphous POPs have been named separately by individual research groups, such as hyper crosslinked polymers (HCPs), porous aromatic frameworks (PAFs), and porous polymer networks (PPNs). For the sake of simplicity and discussion, we group all of these materials under the umbrella of POPs. POPs are unique because of their combination of properties not found in other materials: (i) amenable synthesis to enable engineering of the uptake performance by varying the composition; (ii) robustness under various chemical conditions (e.g., extreme acidity/basicity and reductive/oxidative environments) allowing long-term stable performance and potential recycling to simplify the workup procedures; (iii) large surface area and tunable pore size to enable high uptake capacity and controlled mass transfer; and (iv) lightweight element composition, with the potential for high gravimetric performance in energy and molecular uptake [22–29]. With these attributes, POPs constitute the newest avenue for high-performance adsorbents, displaying particular innovation and promise as potential 'game-changing' technologies in the field of selective sequestration [30–38].

POPs As a Designer Platform for Radionuclide Sequestration

Given the consensus that adsorbents are likely to play a critical role in sustainable nuclear-energy development, numerous materials have been developed to harvest uranium from seawater and to selectively extract radionuclides from waste streams, focusing primarily on the hazardous and volatile radionuclides (e.g., Tc, Cs, Sr, I). Among these, ion-exchange resins hold great promise as Tc scavengers, ferrocyanide compounds are excellent candidates for Cs entrapment, zeolitic structures readily entrap Sr, and silver-nitrate phases react with iodine species [39]. All of them are efficient for the extraction of the targeted materials; however, the significant challenge for these are low capacity and/or low selectivity in the final form due to the low affinity and/or low accessibility of binding sites. In this section, efforts in the development of POP-based sorbents are exemplified with their potential to address the weaknesses associated with existing adsorbents. The aforementioned intrinsic characteristics of POPs allow us to optimize the chemical environments for target radionuclides with simultaneous high loading and selectivity. There are three main design principles involved; that is, coordinative binding, ion exchange, and host–guest interaction (Figure 2, Key Figure).

POPs for Uranium Recovery

Nuclear fuel cycles are initially based on uranium. Among various natural sources of uranium for use in nuclear reactors, seawater is highly appealing given that the oceans contain about 4.5 billion tons of dissolved uranium, almost 1000 times that estimated for mineral reserves. Mining uranium from seawater has been a topic of active research by various state entities for more than six decades, which can be dated back to 'Project Oyster', initiated in the early 1950s in the UK [40]. Large-scale marine experiments were performed by Japanese organizations from 1999 to 2001 and approximately 1 kg (in the form of yellow cake) was collected, affording an average of 0.5 mg U/g Ads every 30 days [41]. Given the significance, the US Department of Energy established a research program in 2011 with the goal of evaluating and developing the technology. Various sorbent materials have been developed (e.g., inorganic materials, polyolefin fiber-based adsorbents, nanostructured materials, MOFs, genetically engineered proteins) [5] but challenges remain, including increasing the total adsorption capacity, the rate of uranium accumulation, and the reusability of the sorbents [42–46]. POPs represent a new addition to the field of sorbent materials for such an application.

Key Figure

Porous Organic Polymers (POPs) As a Designer Platform for Radionuclide Sequestration

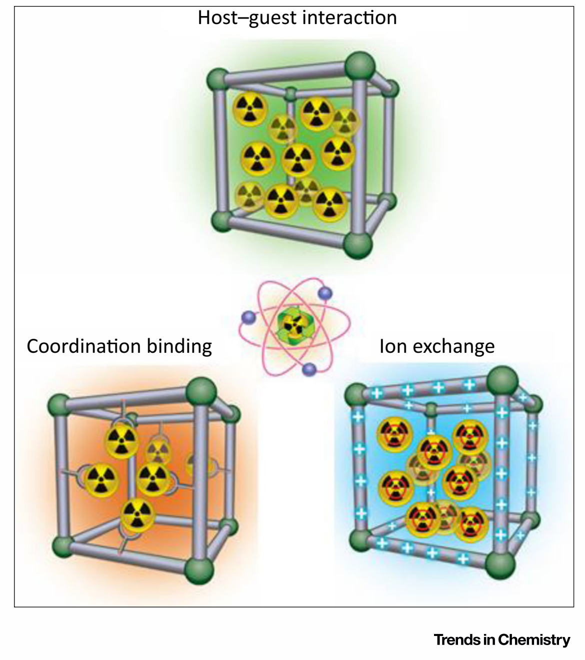

Figure 2. For both amorphous and crystalline POPs, functional groups can be introduced in a *de novo* manner or through post-synthetic modification. Due to the diverse chemistry of radionuclides, to effectively extract targeted species various adsorption mechanisms are involved, mainly coordinative binding, ion exchange, and host–guest interaction. Accordingly, specific functionalities can be incorporated into the materials to achieve selective binding.

Dai and colleagues first reported a mesoporous polymer for the recovery of uranium from seawater [47]. The copolymer supports were formed from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) in the presence of 2,2′-azobisisobutyronitrile (AIBN) by conventional free radical polymerization. The surface area and pore architectures of the poly(DVB:VBC) were tuned as a function of the DVB:VBC ratio. Subsequent atom-transfer radical polymerization (ATRP) of acrylonitrile (AN) was initiated from the chloride in the poly(VBC-co-DVB), which was subsequently converted to amidoxime by treatment with hydroxylamine. The resulting sorbents were screened in a spiked uranyl brine (ca 6 ppm, pH 8), demonstrating a high uptake of 80 mg U/g Ads. When deployed in 5 gallons of real seawater for 27 days, an uptake of ~2 mg U/g Ads was achieved, surpassing the capacity of the irradiation-grafted nonwoven polyethylene fabric (0.75 mg U/g Ads) from the Japan Atomic Energy Agency (JAEA), a benchmark material.

In contrast to the previous work where poly(amidoxime) was grown in the POP cavities, Ma and coworkers reported a POP sorbent (PAF-1-CH_2AO) that was achieved via stepwise post-synthetic modification using PAF-1 as a prototype [48]. Here, amidoxime groups were decorated on the pore wall, providing site accessibility and rapid transport of uranium to the binding sites.

Investigations of uranium adsorption from seawater simulant containing 7 ppm uranium revealed that the material achieved an uptake of 40 mg U/g Ads and reached equilibrium within 24 h, showing promise for seawater uranium mining. Subsequent extended X-ray absorption fine structure (EXAFS) analysis revealed binding of uranium by an average of 1.4 ± 0.3 amidoxime functionalities in an η^2-motif, lower than the thermodynamically stable coordination fashion of 2:1.

The above examples have shown preliminary potential for POPs as a decorating platform for uranium extraction. There is, however, significant room for improvement, especially considering the following: (i) partial or complete blockage of pores during chemical modification as suggested by the drastically decreased surface area; (ii) multistep post-synthetic modification leading to a low overall grafting degree; and (iii) chelating groups being spatially separated in the adsorbent due to (ii), which is unfavorable for cooperative binding, thereby resulting in a low binding affinity.

With these in mind, Ma and colleagues developed a strategy to directly construct the functional moieties into porous adsorbent materials to conserve a sufficiently high density of accessible binding sites [49]. To further optimize the affinity of chelating groups toward uranyl ions, an assistant group was introduced to reinforce the coordinative binding between amidoxime and uranyl, reminiscent of biological systems (Figure 3) [50]. Given the importance of the spatial arrangement of these functionalities for mutual cooperation, the assistant group were introduced *de novo* to better understand resulting structure–function relationships. Accordingly, a family of vinyl-functionalized cyano compounds with different amine locations were designed

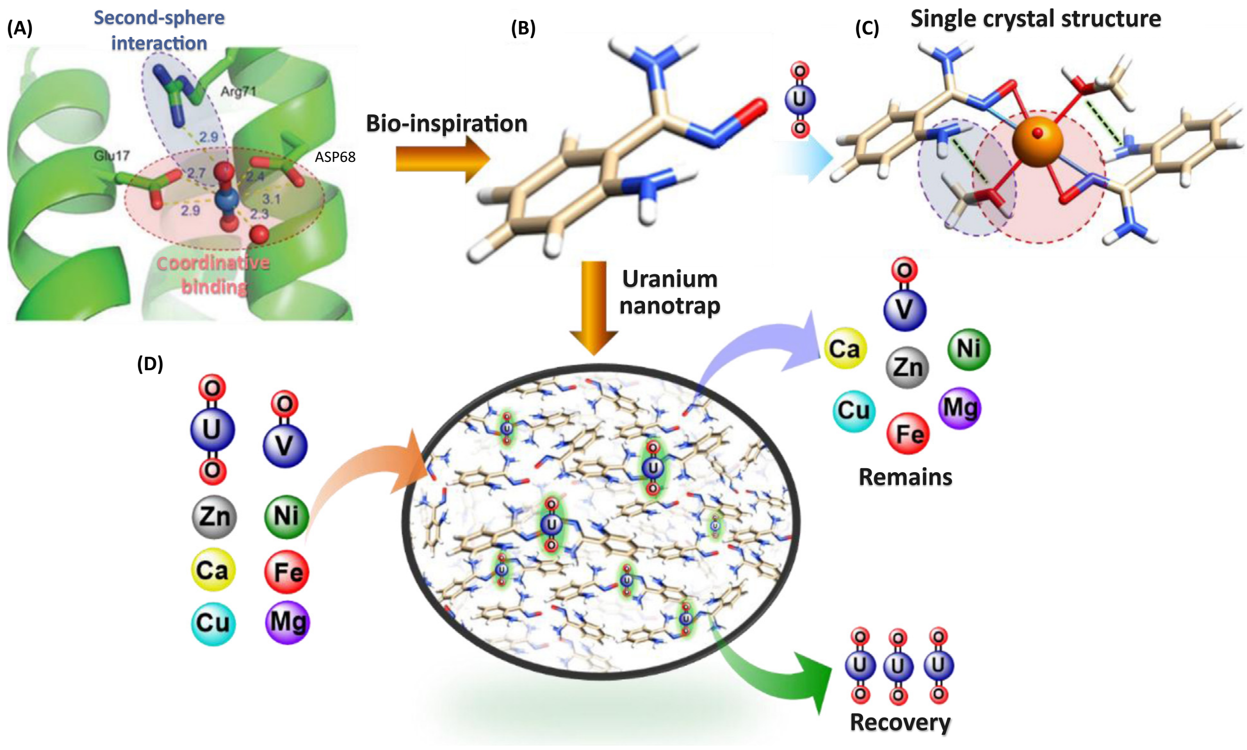

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Figure 3. Uranyl-Binding Pocket Detail of a Protein and Bioinspired Uranium Nanotrap. (A) Uranyl-binding pocket detail of a uranyl-binding protein. (B) The designed structure of a uranyl-binding moiety inspired from (A). (C) Single-crystal structure of the uranyl complex in (B). (D) Construction of a high-affinity and selective uranium nanotrap allows the enrichment of uranium over other metals.

for self-polymerization into highly porous materials followed by conversion of the nitrile to amidoxime with hydroxylamine. Improvements toward uranium adsorption with the resulting amidoxime-based adsorbents are evident with the addition of an amino group together with its relative location. The porous framework bearing 2-aminobenzamidoxime is exceptional in extracting high uranium concentrations with sufficient capacities from simulated seawater with 10.3 ppm of uranium (290 mg/g) and trace quantities of uranium in real seawater (4.36 mg/g), far outperforming those achieved by adsorbents constructed by 4-aminobenzamidoxime (250 and 2.27 mg/g) and benzamidoxime (200 and 1.32 mg/g).

The underlying principles contributing to superior performance were revealed by collaborative techniques, including spectroscopy, crystallography, and density functional theory. It was revealed that the introduction of the amino group neighboring the amidoxime alters the electron density of the complex to lower the overall charge on uranyl and provides an additional hydrogen-bonding site to align uranyl species in a favorable coordination fashion, thereby increasing its affinity toward uranyl. X-ray absorption fine structure (XAFS) spectroscopic studies revealed that each uranyl ion is bound exclusively by two amidoxime groups, further interpreting its excellent affinity. This, in contrast to PAF-1-CH_2AO, indicates that an increase in the density of binding sites benefits both uptake capacity and binding affinity.

The performance of amorphous POPs is often compromised by inaccessible chelating sites due to the small and irregular pores with poorly defined structure, further complicating characterization and rational improvement. With this knowledge, Ma and coworkers first delineated new opportunities using COFs as a platform for the deployment of sorbent materials for uranium extraction due to their unprecedented combination of high crystallinity, outstanding chemical/hydrolytic stability, and amenability to design [51]. Amidoxime-contained moieties were incorporated into 2D COFs linked by irreversible β-ketoenamines. The resultant sorbents extracted uranium from a variety of contaminated solutions, outperforming their amorphous analogs in terms of uptake capacities, kinetics, and binding affinities. These side-by-side comparisons highlighted the effect of the pore structure on the accessibility and orientation of chelating groups (Figure 4). The COF-based sorbent also showed potential for mining uranium from seawater with an uptake capacity of 127 mg U/g Ads from a 20-ppm uranium-spiked seawater sample. These results put forth insights for the design of high-performance sorbent materials.

POPs for Technetium Removal

Technetium comprises a large portion of the nuclear fission products (841 g/ton), existing primarily as pertechnetate (TcO_4^-) in waste streams. TcO_4^- will coextract with uranium in plutonium-uranium redox extraction (PUREX) processes, potentially contaminating the primary product. As an anion, TcO_4^- is among the most hazardous radiation-derived contaminants because of its long half-life ($t_{½} = 2.13 \times 10^5$ years) and environmental mobility, in essence being able to travel with the solvent front if leaked from an underground storage facility [52–54]. Direct removal of $^{99}TcO_4^-$ from the highly acidic solution of spent nuclear fuel at the first stage (when the used fuel rods are dissolved) is ideal for the subsequent PUREX processes and, more importantly, aids in the elimination of ^{99}Tc discharge into the environment during the vitrification process. This goal requires sorbent materials with high stability in acids, radiation resistance, high TcO_4^- uptake kinetics and capacity, and excellent sorption selectivity.

Given that TcO_4^- is larger and has a lower hydration energy than most other anions encountered in tank waste (e.g., NO_3^-, Cl^-, SO_4^{2-}), there is a natural bias toward preferential exchanging of TcO_4^- over the other present anions. Therefore, ion exchange is considered the most viable method to sequester TcO_4^- from the bulk waste stream [55–60], and different

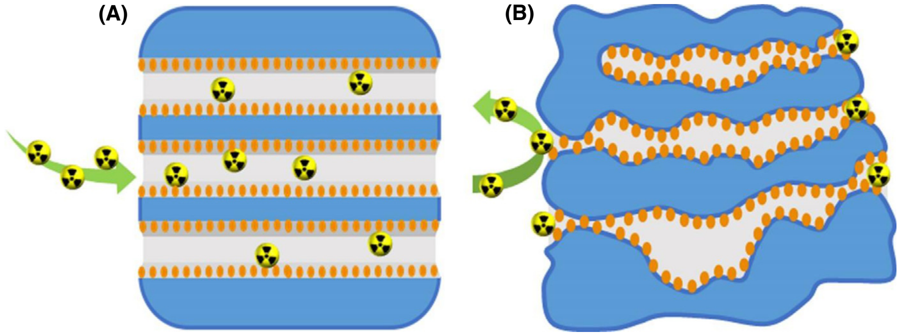

Figure 4. Cross-sectional Schematic of Potential Chelating-Group Distribution in Porous Materials. (A) Schematic illustration of chelating groups in covalent organic framework (COF) materials. The uniform pore morphology of the COFs leads to a functionalized material with unrestricted access of ions to chelating sites. The schematic is not drawn to scale. (B) The functionalization of amorphous porous organic polymers (POPs), illustrating the blockage of narrow pore channels and bottlenecks. Pore blocking is likely to impede access of metal ions to the functional sites in POPs.

types of ion-exchange materials, such as resins and inorganics, have been shown to be successful in capturing TcO_4^- under realistic conditions. However, due to the low density of exchangeable sites and insufficient stability, their uptake capacity and long-term high-performance operation is compromised. Wang and coworkers developed a cationic polymeric network (SCU-CPN-1) from the quaternization reaction between 1,1,2,2-tetrakis-[4-(imidazolyl-4-yl)phenyl]ethane and 1,4-bis(bromomethyl)benzene that exhibited excellent TcO_4^- sorption kinetics and uptake capacity, outperforming all materials reported to date. In addition, due to the robustness of the framework, this material showed excellent radiation resistance and chemical/hydrolytic stability (Figure 5) [61]. This leads to efficient TcO_4^- separation from two different types of simulated nuclear waste solutions: used fuel reprocessing solution in 3-M nitric acid and Hanford Low Activity Waste (LAW) Melter Recycle Stream. Contacted by a 3-M HNO_3 aqueous solution containing 343 ppm of ReO_4^- (NO_3^-:ReO_4^- molar ratio = 2186), SCU-CPN-1 can extract approximately 40% of ReO_4^- at a solid:liquid ratio of 20, and increasing this ratio to 90, 76% of available ReO_4^- was removed. The adsorbent was also tested in a Hanford LAW stream with concentrations of NO_3^-, NO_2^-, and Cl^- far exceeding that of TcO_4^- by more than 300 times. Following 24 h of contact, a removal efficiency of 90% was achieved in a solid:liquid ratio of 5, outperforming other types of materials under similar conditions such as MOFs (SCU-101, 75.2%) [62] and inorganic materials (NDTB-1, 13%) [63].

POPs for Iodine Capture

In the context of used fuel processing and waste management, iodine is also of concern because it is incompatible with most of the solid materials being considered for high-level waste isolation. Its long half-life (1.57×10^7 years) and bioaccumulation by involvement in human metabolic processes represent substantial hazards that motivate the exploration for efficient iodine sequestration [64–67]. The leading industry technology to remove radioiodine involves the chemical transformation of iodine into AgI using silver-containing zeolites with low practical capacities of 0.10–0.31 I g/g Ads [68].

A convincing case of functional porous polymers for radiological iodine capture was demonstrated by Zhu and coworkers. A series of anionic microporous borate networks (PAF-23, PAF-24, and

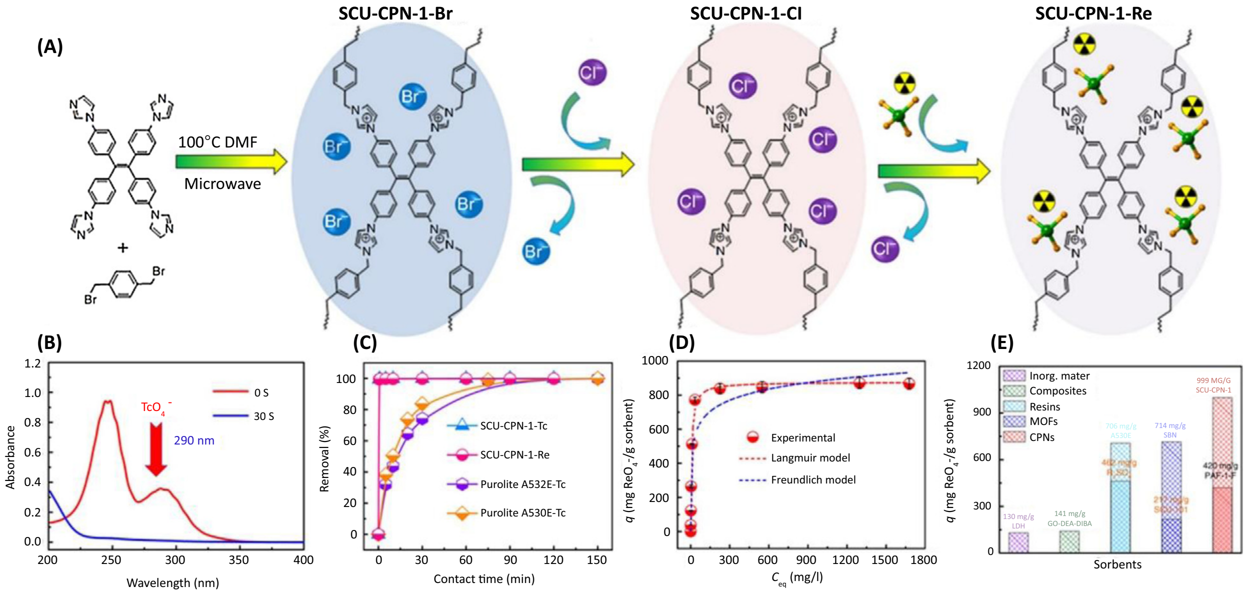

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Figure 5. Preparation and Sorption Performance Evaluation of SCU-CPN-1. (A) Synthetic route of SCU-CPN-1 and its anion-exchange applications. (B) UV–vis absorbance spectrum of a TcO_4^- solution during the anion exchange with SCU-CPN-1. (C) Sorption kinetics of TcO_4^- by SCU-CPN-1 compared with Purolite A530E and Purolite A532E. (D) Sorption isotherm of SCU-CPN-1 for ReO_4^- uptake. (E) ReO_4^- sorption capacity of SCU-CPN-1 compared with other reported anion sorbents. Error bars represent standard deviation of three independent experiments. Adapted, with permission, from [61].

PAF-25) were fabricated from a tetrahedral building unit, lithium tetrakis(4-iodophenyl)-borate (LTIPB), and different alkyne monomers as linkers via a Sonogashira–Hagihara coupling reaction. These networks successfully captured volatile iodine (Figure 6) [69]. The networks featured three effective sorption sites; that is, an ionic site, the phenyl ring, and triple bonds. They exhibited excellent iodine adsorption capability, affording 2.71 g/g, 2.76 g/g, and 2.60 g/g of iodine for PAF-23, PAF-24, and PAF-25, respectively, at 348 K (relevant to nuclear fuel reprocessing conditions). A control experiment was conducted using neutral PAFs with similar topology for I_2 capture under the same conditions, yielding a much lower capacity (1.86 g/g).

To improve the uptake capacity of porous materials for iodine capture, increasing host–guest interaction is a concept widely employed by the design of entangled pores with specific pore environments. However, due to the interpenetrated and/or crosslinked networks that entangle numerous intersections, side pockets, and narrow connecting windows, it has been suggested that only 50% of the materials' pore volume can be occupied by I_2 vapor. With the knowledge that vapor uptake in a porous material is heavily dependent on the in-pore diffusivity (controlled partly by pore topology, size, and connectivity), Jiang and coworkers explored 1D channeled porous materials [70]. This was demonstrated by 2D COFs with uniform 1D open channels that are free of intersections, thereby precluding pore blockage. Iodine vapor capture tests at 350 K under ambient pressure revealed that TPB-DMTP COF with a pore volume of 1.3 cm^3/g gave a saturated iodine uptake capacity of 6.3 g/g, equal to the theoretical value calculated by pore volume multiple solid iodine density, suggesting full occupation of its pores by iodine. Being generally applicable in 2D COFs with various channel shapes (e.g., hexagonal, tetragonal, trigonal) and pore sizes, it thus suggests that 1D channels enable full access to iodine and that pore volume determines the uptake capacity for these materials.

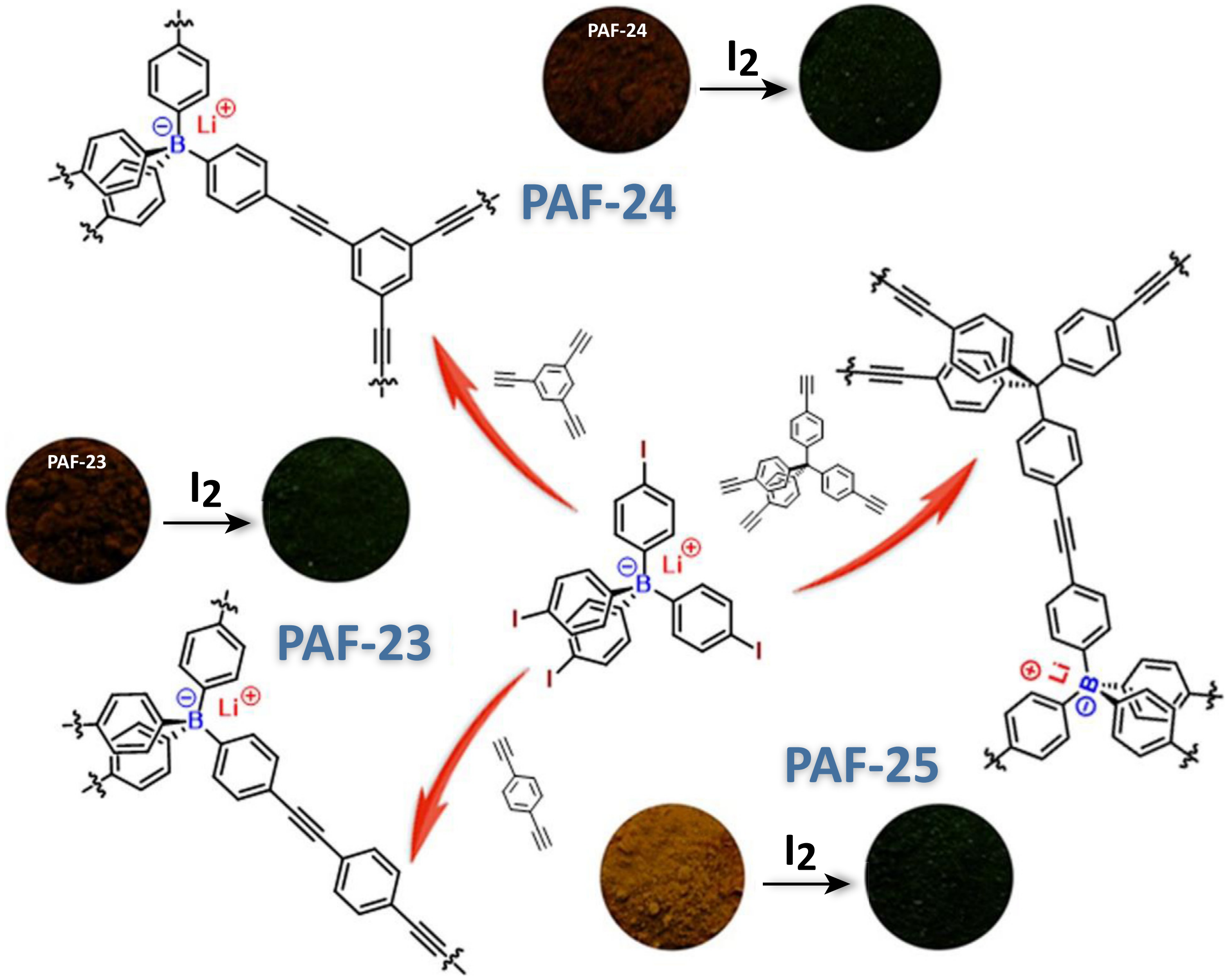

Figure 6. Iodine-Scavenger Design. Synthetic routes for polymers PAF-23, PAF-24, and PAF-25 by Sonogashira–Hagihara coupling reactions. Photographs show the color change before and after iodine capture for polymer networks PAF-23, PAF-24, and PAF-25. Adapted, with permission, from [69].

The work reported by Jiang and colleagues overcomes pore blocking by using 1D-channel COF materials and suggests that iodine capture does not require specific functionalization of the porous skeletons under ideal conditions where there is no competing species. However, to achieve a significant uptake of iodine that is present at vanishingly low concentration in the fission products, adsorptive materials designed for such processes must be engendered with an exceptionally high affinity toward the targeted species. A natural question is whether one can combine the results of the two studies described here and decorate these binding sites on the channels of 2D COFs to achieve significant uptake capacity.

POPs for Caesium and Strontium Extraction

The extraction of the long-lived isotope of caesium (^{137}Cs, 1230 g/ton), one of the major contaminants in the fission products of nuclear waste, is crucial for public health and the continuous operation of nuclear power plants due to the specific mobility of these radionuclides from nuclear disposals. However, as the largest of the unreactive alkali metal cations, Cs^+ is weakly hydrated and resistant to the formation of coordination complexes, making its selective removal from nuclear waste a challenge that has been met with limited success. With respect to strontium, besides its radiation, Sr^{2+} generates significant heat as it decays, complicating the matter of containing and storing the waste. With Sr^{2+} removed, the remaining waste can be stored more densely and require less space. By virtue of the relative softness of Cs^+ and Sr^{2+} compared with smaller alkali or alkaline earth ions, various sorbents, such as zeolitic chalcogenide, layered metal sulfide, and sulfur-loaded zeolites, for Cs^+ and Sr^{2+} removal have been acknowledged. However, these materials suffer from slow kinetics and decreased selectivity with high salt concentrations [71–74]. So far, no POP-based material has been reported on either application. We believe that by appropriate functionalization, these materials can exhibit substantial adsorption of Cs^+ and Sr^{2+} from aqueous solutions. For example, size-recognition phenomena have proved to be a viable means of manipulating the speciation of Cs^+ for successful sequestration. Separation procedures have been developed around the use of crown ether or calixarene compounds, typically large polyether species with molecular cavities designed to accept large cations of low charge [75–77].

Concluding Remarks and Future Perspectives

The recent progress in using POPs for radionuclide sequestration illustrated in this Opinion shows the high potential impact of these materials for mining uranium from seawater and decontamination of radioactive pollutants. The unparalleled versatility of these materials allows many different aspects to be designed on demand to rationally enhance their selectivity and uptake capacity, thereby lending credence to their prospect as next-generation adsorbent materials. Waste minimization is one of the most pressing environmental issues currently facing society [78–87] and POP-based adsorbents with the merits of rapid sorption kinetics, high capacity, and exceptional selectivity could play a significant role in meeting this challenge. It was shown that POPs outperform reference materials, such as resins and inorganic materials, in radionuclide adsorption. Despite progress in research on POPs, this class of materials remains largely unexplored, with few nuclear waste relevant species investigated. Given the feasible synthesis, moving forward a wealth of research opportunities thus exist for POPs, and further progress in the understanding of these materials is anticipated in the next few years.

Following this overview, we now briefly address the questions of what remains to be learned and where the field will bring us, thereby identifying the main upcoming challenges of the field. The first question raised is that most of the presented design strategies and computational optimization are based on molecular-level understanding; however, polymer morphology potentially has a profound effect on the established binding modes. Thus, direct validation of the metal-binding behavior on adsorbents is indispensable to achieve optimal performance. In addition, a number of the proposed POP-based adsorbents have been studied under laboratory conditions, but convincing demonstrations of their utility for practical applications are lacking. To be applicable under practical conditions, there are several challenges that must be first tackled for such materials (see Outstanding Questions). Focused efforts to integrate unprocessable POP powders with other substrates to expand their application has significantly progressed and brought to fruition several demonstrations of their importance for practical applications [88–92]. One exciting avenue is the use of POP nanoparticles as the building blocks in mixed-matrix membranes. For instance, incorporating functionalized POP nanoparticles into membranes could maximize their potential separation capabilities, taking advantage of the extremely high external surface areas of POPs and the attractive mechanical properties (e.g., stretchability, elasticity, toughness) of polymeric matrices. Such combinations will inevitably lead to a rich spectrum of material properties and functionalities, in part due to their tunable chemistry.

Outstanding Questions

How can the POP-based sorbent materials fit with the current industrial systems? Almost all POPs have been evaluated for their sorption properties using the batch method. Many industrial and wastewater treatment processes, however, rely on the use of continuous bed flow columns or membranes.

How can the processability of POPs be improved to satisfy the requirements for industrial applications? Most POPs share the drawbacks of other porous materials with regard to shaping, morphology control, and processing. As predominantly highly crosslinked polymers, these materials are not meltable or soluble in any solvent. The generation of thin films, membranes, or molds presents a formidable challenge.

Can we set up an evaluation system to ensure valid comparisons for screening the most suitable system for industrial applications? Large-scale availability at low cost, physical resilience, ease of deployment, rapid binding kinetics, high loading capacity, and facile elution are listed as essential requirements to merit further investigation.

Which kind of material can meet the challenge of improved selectivity and uptake capacity while allowing cost-effective and large-scale synthesis? Fundamental scientific challenges that must be overcome include enhancing the coordinative moieties' binding affinity toward a given radionuclide species and increasing the density and accessibility of chelating groups to increase both selectivity and uptake capacity.

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