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## Effect of ligand denticity on the removal of $^{238}\text{Pu}$ from dilute aqueous solutions by hydroxamate-based chelating gels

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Plutonium (Pu) is a chemically and radiologically toxic element, primarily of anthropogenic origin. Reagents that specifically sequester Pu have been developed in the frame of nuclear waste processing and storage. Other potential applications of Pu chelators are *in vivo* decorporation and environmental remediation. Although the medical application has been addressed for a long time by the development of Pu-specific binders, studies concerning the environmental application are scarce. A desferrioxamine-B ( $[(\text{DFO})\text{H}_4]^+$ )-derived tetrahydroxamate chelator, **1H<sub>4</sub>**, which was originally designed for the sequestration of  $\text{Zr}^{4+}$  for  $^{89}\text{Zr}$ -ImmunoPET applications, was grafted on a commercial hydrophilic resin, CM Sephadex C-25<sup>®</sup>. The resin beads were subsequently embedded in an agarose gel, and the resulting material was used for the extraction of  $^{238}\text{Pu}(\text{iv})$  from dilute aqueous solutions at pH 6.5. Comparison of the results with those obtained using the commercial Chelex<sup>®</sup>-100 resin and the H<sub>3</sub>DFO-based CM Sephadex C-25<sup>®</sup> extracting materials showed that Pu was more strongly bound to the **1H<sub>4</sub>**-functionalized resin than to Chelex<sup>®</sup>-100 and the H<sub>3</sub>DFO-based resins, which confirms that the tetrahydroxamate chelator **1**<sup>4-</sup> forms a more stable Pu(iv) complex than the trihydroxamate DFO<sup>3-</sup> siderophore. The fabricated material could be considered in the development of diffusive gradients in thin-films (DGT) devices for the environmental monitoring of Pu.

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## Introduction

Discovered by Seaborg in 1941, plutonium (Pu) is the second transuranic element, after neptunium.<sup>1</sup> Excluding nuclear isomers, it has 21 isotopes spanning from  $^{226}\text{Pu}$  to  $^{247}\text{Pu}$ , all of which are radioactive. This radioelement is produced artificially by neutron irradiation of uranium in nuclear reactors but can also be found naturally in trace amounts in uranium ores.<sup>2</sup> Pu-239 is the most abundant radioisotope of plutonium. It has a radioactive lifetime of 24 100 years and a specific activity of  $2.30 \times 10^9 \text{ Bq g}^{-1}$ . Its main decay route is the emission of  $\alpha$  particles (71% have an energy of 5.157 MeV). Of its descendants, the first and the last are U-235 and Pb-207, respectively.

Pu-239 is fissile; therefore, it is used in nuclear weapons and as a nuclear fuel (MOX or mixed oxides) in nuclear reactors. Like all heavy metals, plutonium is a chemical poison, which is ingested through the respiratory tract. It is deposited mainly in the bones, the bone marrow, the liver, and the lungs.<sup>3</sup>

Plutonium has been widely spread in the environment<sup>4</sup> under three different conditions: (1) nuclear weapons: the fissile material for the Nagasaki bomb was Pu-239. During the following fifty years, several countries including the USA, the USSR, and France have conducted many nuclear weapon tests (NWTs). A moratorium on NWTs was observed after 1998 by all countries except North Korea. (2) Nuclear waste disposal: separations, vitrification of high-activity waste, and storage. (3) Nuclear accidents: these include military airplane and submarine accidents and nuclear power plant accidents, the major ones being Chernobyl in 1986 and Fukushima in 2011.<sup>5</sup> Direct radioactive discharges and fallouts have affected the seas and the oceans all around the globe. The origin of contamination can be traced back by the measure of isotopic ratios of plutonium.<sup>5</sup>

Plutonium encompasses oxidation states ranging from +3 to +7, the most stable one being +4 in the insoluble plutonium oxide  $\text{PuO}_2$ . The most soluble forms of Pu correspond to the

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redox states +5 and +6,<sup>4,6</sup> as in the complex  $[\text{Pu}^{\text{VI}}\text{O}_2(\text{CO}_3)_3]^{4-}$ . Nevertheless, Pu(IV) can be solubilized by complexation with organic compounds naturally present in soil pore waters, such as humic and fulvic acids,<sup>8,9</sup> and siderophores,<sup>10-12</sup> such as desferrioxamine-B ( $[(\text{DFO})\text{H}_4]^+$ ),<sup>13,14</sup> which similarly dissolve highly insoluble iron oxides and oxohydroxides.<sup>15</sup>

Sorption processes have been proposed as an alternative to the widely used PUREX ligand-assisted liquid–liquid extraction for processing nuclear waste.<sup>16</sup> For example, the ion-exchange Reillex<sup>®</sup> HPQ resin, a macroporous polyvinyl pyridine for liquid–solid extraction, has been used successfully to sorb the  $[\text{Pu}(\text{NO}_3)_6]^{2-}$  anions present in concentrated nitric acid.<sup>17</sup> Approaches involving resins modified with grafted metal-binding functions, such as diphosphonic acid groups in the Diphonix<sup>®</sup> resin, have been also proposed.<sup>18</sup> Recently, chelating molecular units rather than functional groups have been grafted onto resins. Such is the case of the benzodioxodiamide-type ligand 2,2'-(1,2-(phenylene)bis(oxy))bis[N,N-(1-methylethyl)]-acetamide (benzoDODA), a highly selective extractant of Pu(IV) from 3.0 M  $\text{HNO}_3$  solutions,<sup>19</sup> which was grafted onto an aminomethyl-functionalized polystyrene resin.<sup>20</sup> The material was robust and could be recycled at least 7 times. Noticeably enough, the simple encapsulation of benzoDODA in polymeric beads afforded a material that outperformed the grafted resin.<sup>21</sup> A weakness of benzodioxodiamide ligands is that, as tetradeinate chelators, they do not fulfill the coordination sphere of  $\text{Pu}^{4+}$ , which requires at least 8 donor atoms. The use of a Pu(IV)-specific ligand, such as those developed by Raymond and coworkers,<sup>12,22</sup> immobilized on a solid support, was recommended long ago (1997), but never achieved to our knowledge.<sup>23</sup>

A few years ago, we successfully designed, prepared, and used a bifunctional octadentate chelator named DFOcyclo\*PhNCS in  $^{89}\text{Zr}$ -immunoPET.<sup>24,25</sup> Moreover, another immunoconjugate of this compound has been recently labelled with  $^{227}\text{Th}$  and tested in internal  $\alpha$ -radiotherapy.<sup>26</sup> DFOcyclo\*PhNCS is an arylisothiocyanate-functionalized tetrahydroxamic acid derived from  $[(\text{DFO})\text{H}_4]^+$  that is coupled to difunctional 1-benzoyloxyperidine-2-one, a benzyl-protected six-membered cyclic hydroxamic acid. In this PIPOBn derivative, the carbon atom (3-C) adjacent to the carbonyl group integrated in the cycle was substituted

with a carboxylic acid function (used for coupling PIPOBn and  $[(\text{DFO})\text{H}_4]^+$ ), and an amine-functionalized (in protected form) pendant group, which had been installed for further bioconjugation (Fig. 1). The precursor of DFOcyclo\*PhNCS is therefore the amine-functionalized tetra hydroxamic acid **1H<sub>4</sub>**.

The transition metal  $\text{Zr}^{4+}$  and the actinide  $\text{Th}^{4+}$  are hard 4d and 5f tetravalent cations, respectively. They have a strong affinity for hard oxygen donor ligands, such as those offered by a bidentate hydroxamate ligand. Both  $\text{Zr}^{4+}$  and  $\text{Th}^{4+}$  can pick up four of these ligands.<sup>27</sup> In complexes of  $d^0 \text{Zr}^{4+}$ , the bound oxygen atoms are arranged on the 8 vertices of a distorted square antiprism.<sup>27,28</sup> In the case of the 1-oxy-2-pyridonato ( $\text{OPO}^-$ ) complex of  $\text{Th}^{4+}$ ,  $[\text{Th}(\text{OPO})_4\text{H}_2\text{O}]$ , the metal cation, which is larger than  $\text{Zr}^{4+}$ , is surrounded by 9 oxygen atoms, including one from a water molecule.<sup>29</sup> The coordination polyhedron is a slightly distorted bicapped trigonal prism of  $D_{3h}$  symmetry. The ionic radius of  $\text{Pu}^{4+}$  being smaller than the one of  $\text{Th}^{4+}$ ,  $\text{Pu}^{4+}$  is eight-coordinate in the  $[\text{Pu}(\text{OPO})_4]$  complex, and was shown to display an intermediate geometry between a bicapped trigonal prism and a trigonal dodecahedron.<sup>30</sup> Given the chemical analogies between  $\text{Pu}^{4+}$ ,  $\text{Th}^{4+}$ , and  $\text{Zr}^{4+}$ , and that the  $^{89}\text{Zr}^{4+}$ - and  $^{227}\text{Th}^{4+}$ -radiolabelled bioconjugates of DFOcyclo\*PhNCS proved to be stable complexes in biological media,<sup>24,26</sup> we sought to test the capability of the tetrahydroxamic precursor **1H<sub>4</sub>** to efficiently sequester  $\text{Pu}^{4+}$  and evaluate the effect of ligand denticity by comparing it to trihydroxamic  $[(\text{DFO})\text{H}_3]$ . For this purpose, we investigated the performances of a material incorporating the **1H<sub>4</sub>** chelator to extract  $^{238}\text{Pu}^{4+}$  from slightly acidic solutions buffered at pH 6.5, and the conditions in which the  $\text{Pu}^{4+}$  ions could be released into the solution.

**1H<sub>4</sub>** can be considered as an extended DFO. Materials incorporating DFO are numerous. Therefore, restricting our interest to organic materials, we can mention the use of natural polymers such as cellulose<sup>31,32</sup> and sepharose,<sup>33</sup> and synthetic polymers, such as polyamide 6-6<sup>34</sup> and acrylic polymers.<sup>35-37</sup> We settled on the hydrophilic resin CM Sephadex C-25<sup>®</sup>, a commercial carboxymethyl-modified cross-linked polysaccharide used in gel filtration, which could be functionalized by amide bond formation by reaction with its pendant carboxylic acid functions. The carboxylic acid functions remaining after grafting of the tetrahydroxamic chelator<sup>38</sup> are unlikely to compete with the latter, as, taking acetate ( $\text{AcO}^-$ ) and aceto-hydroxamate ( $\text{AHA}^-$ ) as model functions, respectively,  $\log \beta_1$  for  $[\text{Pu}(\text{OAc})]^{3+}$  is  $\approx 3$  times lower than that for  $[\text{Pu}(\text{AHA})]^{3+}$  (4.9<sup>39,40</sup> vs. 14.2<sup>41</sup>).

In this work, we report (1) the chromatography-free large-scale synthesis of **1H<sub>4</sub>**; (2) the grafting of **1H<sub>4</sub>** and its trihydroxamic acid precursor  $[(\text{DFO})\text{H}_4]^+$  onto CM Sephadex C-25<sup>®</sup>; (3) the incorporation of the modified resins into an agarose (AGE) hydrogel; (4) the use of these materials for the removal of plutonium from buffered solutions; and (5) the study of the recovery of plutonium from the resins. In addition to the modified Sephadex<sup>®</sup> resins, we used the commercial Chelex-100<sup>®</sup> resin, a styrene–divinylbenzene copolymer containing iminodiacetate pendants, which had been already used

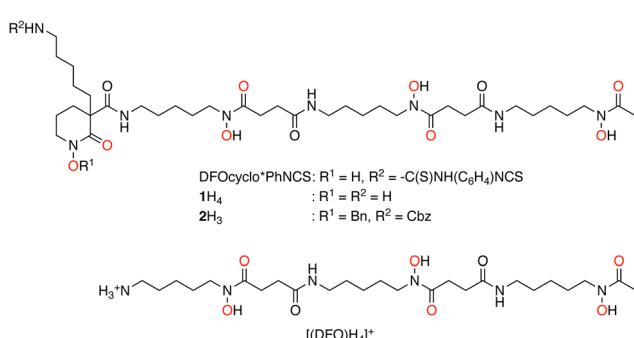


Fig. 1 Chemical structures of the hydroxamic acids mentioned in this study. The metal-binding oxygen atoms are shown in red. The chelators used in this work are  $[(\text{DFO})\text{H}_4]^+$  and **1H<sub>4</sub>**. **2H<sub>3</sub>** and DFOcyclo\*PhNCS are the precursor and derivative of **1H<sub>4</sub>**, respectively.



in diffusive gradients in thin-films (DGT) devices for Pu monitoring.<sup>4,9,42</sup>

## Results and discussion

### Preparation and characterization of the materials

Three materials were made by the incorporation of a chelating resin (**Rn**) into a gel (**Gn**). The chelating resin was either purchased (**R1**: Chelex-100<sup>®</sup>) or prepared by grafting CM Sephadex C-25<sup>®</sup> with commercially available  $[(DFO)H_4]CH_3SO_3$  or compound **1H<sub>4</sub>**, which afforded the chemically modified resins **R2** ( $(DFO)H_3@Sephadex$ ) and **R3** ( $1H_4@Sephadex$ ), respectively. Grafting a functionalized chelator onto a resin is a low-yield process, and, as relatively large amounts of materials are needed, it is necessary to be able to synthesize and purify the functionalized chelator on a large scale. Compound **1H<sub>4</sub>** was originally synthesized as a precursor of DFOcyclo\*PhNCS.<sup>24,25</sup> It is obtained by hydrogenolysis of **2H<sub>3</sub>** (Fig. 1), in which the cyclic hydroxamic acid function is protected as a benzyl hydroxamate and the pendant amine function with a carboxybenzyl (Cbz) group. As **1H<sub>4</sub>** can usually be isolated in pure form after hydrogenolysis, it is necessary to carefully purify its precursor **2H<sub>3</sub>** prior to the deprotection reaction. Therefore, we developed a simple method for the large-scale purification of **2H<sub>3</sub>**, which allowed us to avoid reverse phase flash column chromatography, a technique that we used for the smaller quantities necessary for biological applications.<sup>26</sup> Accordingly, compound **2H<sub>3</sub>** was purified by fractional precipitation by addition of acetone into a methanol solution at 55 °C. The precipitate, appearing upon cooling, and which could not be isolated by filtration, was separated from the solvent mixture by centrifugation, washed with ice-cold acetone, centrifuged, washed again with acetone several times, and finally, dried in vacuum. The total yield, after repeating the procedure six times (SI, supplementary experimental section and Fig. S1), was 71%.

The grafted resins were prepared as follows. CM Sephadex C-25<sup>®</sup> (chemical structure in Fig. S2) is a hydrophilic resin with an average particle size of 70 µm and a loading of carboxylic acid functions of 4–5 mmol g<sup>-1</sup>, according to the supplier. Examination of the beads by SEM showed that their diameter actually ranged from 40 to 125 µm (Fig. S3). A potentiometric titration of the polymer allowed us to find a value of 4.27 mmol g<sup>-1</sup> for the actual content of carboxylic acid functions (Fig. S4). To our knowledge, CM Sephadex C-25<sup>®</sup> was never used as a support for chelator grafting. However, there are a couple of examples of grafting of PEG chains onto this branched polymer.<sup>43</sup>

The preparation of **R2** and **R3** used classical conditions for the amide bond formation between the pendant carboxylic acid groups of the acidic form of CM Sephadex C-25<sup>®</sup> and the terminal  $[(DFO)H_4]CH_3SO_3$  or pendant (**1H<sub>4</sub>**) primary amine functions of the chelators. The resin was suspended in DMF and reacted with the chelator  $[(DFO)H_4]CH_3SO_3$  or **1H<sub>4</sub>** in the presence of the coupling agents 1-ethyl-(3-dimethylaminopropyl)carbodiimide (EDC) and 1-hydroxybenzotriazole (HOBT),

and the base diisopropylethylamine (DIPEA). We made sure that the resin beads were not damaged in the course of the reaction by homogenizing the reaction mixture either by stirring with vanes or by shaking with a stirrer-shaker apparatus. The reaction was usually run for 4–5 days at 40 °C. After washing with the appropriate sequence of solvents (see the experimental part of the SI), the resin was carefully dried in order to ensure that its nitrogen content originated from the grafted chelator only, not from the residual amine base. The chelator loading could then be evaluated with confidence by elemental analysis of nitrogen (see the SI), and, in the case of **R2**, the quantification of the Fe content (see details below).

For this purpose, the modified resin **R2** was prepared in two steps. First, the dark red  $[Fe(DFO)H]^+$  complex was prepared by mixing stoichiometric amounts of  $[Fe(acac)_3]$  and  $[(DFO)H_4]CH_3SO_3$  in methanol. The complex was then involved in the coupling reaction with the resin, which afforded red beads of  $[Fe(DFO)]$ -functionalized Sephadex<sup>®</sup>, **FeR2**. Different parameters were varied in order to optimize the conditions of this heterogeneous reaction: stirring mode, number of equivalents of iron-complexed chelator, reaction time, and reaction scale (see Table S2). Stirring with a magnetic bar had to be excluded, because it damaged the polymer beads, as shown by electronic microscopy (Fig. S6). Reducing the number of equivalents of amine-functionalized chelators from 0.5 to 0.2 decreased the contents of grafted chelators from 0.333 to 0.217 mmol g<sup>-1</sup> of resin. Increasing the reaction time from 2 to 5 days increased this ratio from 0.428 to 0.531 mmol g<sup>-1</sup>. Finally, scaling up the reaction (mass ranging from 0.100 to 15 g) did not significantly affect the grafting ratio, unless a double envelope reactor was used for a better control of the temperature. The incorporation of iron in the resin allowed us to complement the nitrogen analyses by determining its iron content by different techniques, either directly (the material itself) by ICP-OES and thermogravimetry, or indirectly (supernatant solution) by spectrophotometric and ICP-OES measurements. The results obtained for the iron-loaded **FeR2-2** resin are collected in Table S3.

Demetalation of the **FeR2** resin was carried out by the reaction of a 0.1 M aqueous solution of  $Na_2H_2(EDTA)$  (25 equiv.) during 4 days. The colorless modified resin (Fig. S7) was characterized by scanning electron microscopy (SEM), IR (ATR) spectroscopy, and two-photon emission microscopy. Comparison of the SEM images of the resin beads of **FeR2-7** and **R2-7** (Fig. S8) showed that the demetalation reaction did not affect their morphology. The IR spectra of CM Sephadex C-25<sup>®</sup> and of **R2-2** (Fig. S9) were very similar in the 500–1300 cm<sup>-1</sup> region, but showed noticeable differences in the 1500–1750 cm<sup>-1</sup> region: The intensity of the absorption at 1720 cm<sup>-1</sup> (carbonyl group of the carboxylic acid function) was strongly decreased in the spectrum of **R2-2** by comparison with the spectrum of pristine CM Sephadex C-25<sup>®</sup>. Concomitantly, two new absorption bands were observed at 1541 and 1618 cm<sup>-1</sup>, which are assigned to the carbonyl groups of the amide and the hydroxamic acid functions, respectively.<sup>44</sup> Finally, in order to check that the grafted resin beads were homogeneous, we observed



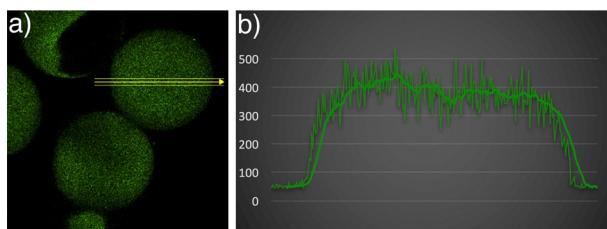


Fig. 2 (a) Two-photon microscopy image and (b) intensity profile of the Tb-emitted light of the resin beads of **TbR2-7**, recorded by moving the microscope stage step-by-step along the yellow arrow shown in the left panel.

them by two-photon emission spectroscopy using an optical microscope after metalation with  $[\text{Tb}(\text{acac})_3]$ , according to a previously reported methodology.<sup>37</sup> As shown in Fig. 2 for **TbR2-7**, upon two-photon excitation at 750 nm, monitoring the green luminescence of the terbium complex in the 500–550 nm range showed the same intensity at the surface of the beads as in their center, which indicated that the distribution of the terbium complex in the beads was homogeneous. From this result, we could infer that the functionalization of the resin by covalent attachment of the  $[\text{Fe}(\text{DFO})]$  complex to the polysaccharide chain of the polymer *via* amide-bond formation proceeded in an homogeneous way.

Two batches of resin **R3** (**R3-1** and **R3-2**) were prepared for the two independent measurement campaigns conducted. The protocol for the preparation of the modified resins being developed for the grafting of the commercially available  $[(\text{DFO})_4]\text{CH}_3\text{SO}_3$  chelator, we used these optimized reaction conditions for the grafting of the homemade chelator **1H<sub>4</sub>**. A mixture of **1H<sub>4</sub>**, CM Sephadex C-25<sup>®</sup>, EDC·HCl, HOBr·H<sub>2</sub>O, and diisopropylethylamine in a ratio of 1/5/5/2.5/6 in DMF (concentration of **1H<sub>4</sub>**: 8.44 mM) at 42 °C was shaken under an Ar flow for 5 days. The crude resin was collected by filtration, washed with aqueous acetic acid, water, and methanol, and dried first in air and then under vacuum at 37 °C until the weight became constant. Under these conditions, the resin contained 0.388 and 0.306 mmol g<sup>-1</sup> of grafted chelator for **R3-1** and **R3-2**, respectively, which corresponded to grafting ratios (GRs) of 0.091 and 0.072, respectively (Table S2). The IR spectrum of **R3-1** (Fig. S10) showed similar features as in the case of **R3-2** in the 1500–1750 cm<sup>-1</sup> region: a weak and a strong absorption band were observed at 1537 and 1621 cm<sup>-1</sup>, for the amide and the hydroxamic acid functions, respectively. Again, nitrogen element analysis of **R3-1** allowed us to calculate the loading of **1H<sub>4</sub>** in the modified resin and the corresponding GR (Table S2).

The next step in the fabrication of the material was the choice of the appropriate hydrogel. To that end, the ability of selected resins to be incorporated into a gel without disruption was tested. Two gels were chosen for these investigations, agarose (AGE) and agarose-polyacrylamide (APA), which is less hydrophilic than the former. The selected resins were pristine CM Sephadex C-25<sup>®</sup> and **R2**. While unmodified Sephadex C-25<sup>®</sup> partially disrupted the AGE gel, and completely the

APA gel, this was not the case for the DFO-modified extracting material **R2**, which was compatible with both hydrogels. Therefore, we selected pure agarose as the structural material for the incorporation of the grafted resins. The following binding gels were prepared according to a published procedure: **G1** from **R1**, **G2** from **R2**, and **G3** from **R3**.<sup>45,46</sup> A picture of the appearance of the gel **G3-1**, which is translucent and homogeneous, is shown in Fig. S11.

### Kinetics of the accumulation of plutonium(IV)

Owing to  $^{238}\text{Pu}$  availability, two measurement campaigns were run. The exposed solutions contained 0.26 nM of  $^{238}\text{Pu}(\text{IV})$ , corresponding to  $39 \times 10^3$  Bq L<sup>-1</sup>. They were buffered at pH 6.5 with a  $10^{-2}$  M solution of 3-morpholino-1-propanesulfonic acid (MOPS) and contained  $10^{-2}$  M of sodium sulfate as the supporting electrolyte. At this very low concentration of Pu, metal adsorption on the walls of the container is not negligible. Therefore, we selected containers made of polycarbonate, because, by contrast with glass,<sup>42</sup> Pu(IV) adsorption was shown to be minimized.

The experimental protocol is summarized in Fig. 3. The gel **Gn** was conditioned in disks of 25 mm diameter and 400 or 480  $\mu\text{m}$  thickness for **G1** and 800  $\mu\text{m}$  thickness for **G2** and **G3**, which were cut out from the gel sheets, as the one shown in Fig. S11.

Each disk, used for a single experiment, was placed in a screw cap vial, into which the  $^{238}\text{Pu}(\text{IV})$  solution was poured. After the required time, the exposure solution was removed for analysis by liquid scintillation. The empty container was treated with a 3 M solution of aqueous nitric acid (flask desorption). The gel disk was placed in a new vial and treated with either 1 M HNO<sub>3</sub> or 1 M HEDPA (1-hydroxyethane-1,1-diphosphonic acid or etidronic acid) for 24 h (resin extraction).

Short-term kinetics of Pu accumulation (over one-hour) was first measured by using the gels **G1**, **G2**, and **G3**. The evolution of the plutonium fractions (expressed as the percentage of the amount of Pu at  $t_0$ ) remaining in the exposure solution and adsorbed on the walls of the vial is shown in Fig. 4a and b. The amount of Pu remaining in the solution after 60 min varied from  $93\% \pm 7\%$  (5 min) to  $69\% \pm 5\%$  and  $54\% \pm 7\%$  for **G1** and

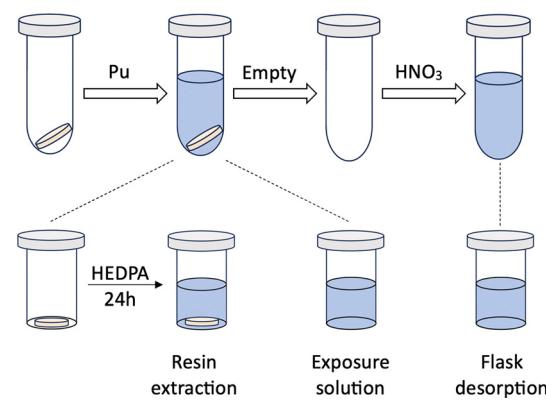


Fig. 3 Experimental protocol for plutonium extraction and desorption (see text for details).



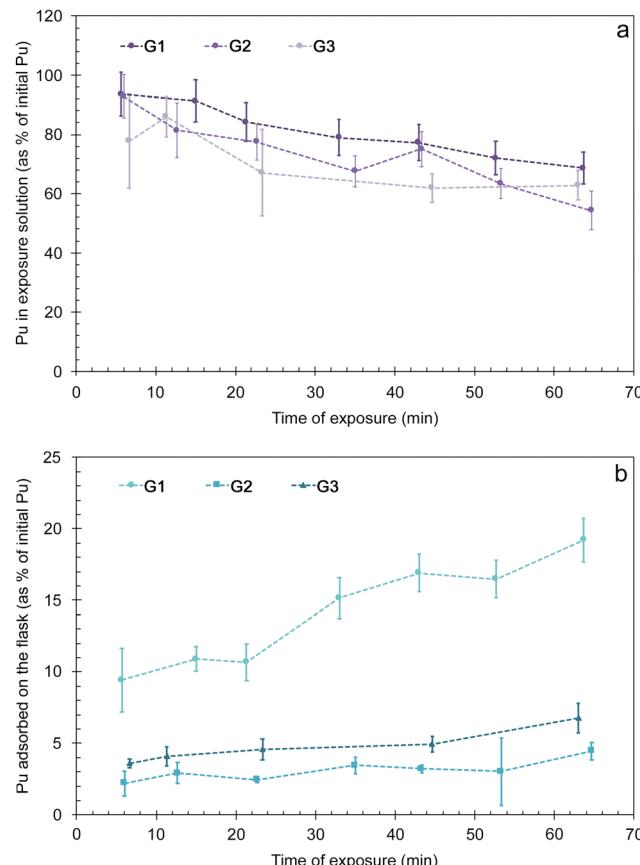


Fig. 4 Time evolution of (a) the Pu content in the exposure solutions and (b) the amount of Pu adsorbed on the walls of the containers of the solutions containing the gels **G1** (dots), **G2** (squares), and **G3** (triangles).

**G2**, respectively, and from  $78\% \pm 16\%$  (5 min) to  $63\% \pm 5\%$  for **G3**. Over the same period, the amount of Pu adsorbed on the walls of the containers increased from  $9\% \pm 2\%$  to  $19\% \pm 2\%$  in the case of **G1**, whereas it increased from  $2.2\% \pm 0.8\%$  to  $4.5\% \pm 0.6\%$  and from  $3.6\% \pm 0.3\%$  to  $7\% \pm 1\%$  in the case of **G2** and **G3**, respectively. The percentage of Pu accumulated by the binding gel is given by the following equation:

$$\%(\text{Pu})_{\text{resin}} = \frac{m_i - m_f - m_{\text{ads}}}{m_i} \times 100, \quad (1)$$

where  $m_i$  and  $m_f$  are the initial and final amounts of Pu measured in the solution and  $m_{\text{ads}}$  the adsorbed amount of Pu.

According to eqn (1), the percentages of Pu accumulation by the gels at 5 and 60 min increased from 0% to 12% (**G1**), 5% to 41% (**G2**), and 18% to 30% (**G3**). At the end of the contact time with the Pu solution, the resins were soaked in a 1 M aqueous solution of nitric acid in order to release Pu. The evolution of the percentage of recovered Pu with nitric acid for each time point is shown in Fig. 5a. After 1 h, it reached 8.4% for **G1**, 7.6% for **G2**, and 0.7% for **G3**, values which should be compared to the percentages that were obtained indirectly from eqn (1). Therefore, the Pu recovery is 70% for **G1**, 19% for **G2**, and 2% for **G3**, which indicates that 1 M nitric acid is not strong enough to desorb  $\text{Pu}^{4+}$  ions from the resins quantitatively,

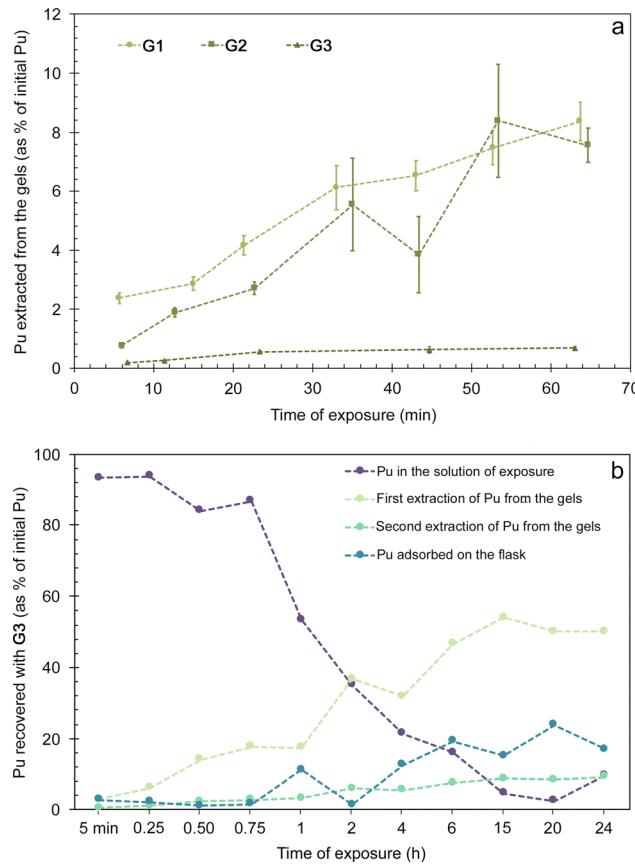


Fig. 5 (a) Time evolution of the amount of Pu extracted from the gels **G1** (dots), **G2** (squares), and **G3** (triangles) by soaking them in an aqueous solution of 1 M nitric acid. (b) Time evolution of the distribution of Pu in the case of the gel **G3**.

especially in the cases of **G2** and **G3**. Therefore, the binding strength of plutonium by the resins decreases in the order of **G3** > **G2** > **G1**. Finally, the mass distribution after 24 h was also measured and gave the results shown in Table 1. The plutonium recovery was satisfactory only in the case of the Chelex-100® resin-based gel (**G1**). In the case of **G2**, about 65% of Pu could not be recovered by the treatment of the resin with a 1 M aqueous solution of nitric acid, whereas in the case of **G3**, the same conditions were practically ineffective at extracting Pu from the resin R3-1. Therefore, this experiment provides an indirect indication that the gel **G3** is the most efficient at sequestering plutonium, which it binds the most tightly. By comparison, the performances of **G2** are significantly lower, whereas those of **G1** are poor.

Commercially available DGT devices, which incorporate Chelex-100®, were tested successfully for the measurement of  $^{238,239}\text{Pu}^{(\text{iv})}$  concentrations in water.<sup>42</sup> However, this first series of experiments suggested that the  $1\text{H}_4$  tetrahydroxamic acid-based resin holds more strongly  $\text{Pu}^{4+}$  ions than the Chelex-100® and the DFO-based materials. Therefore, a second measurement campaign was carried out in order to confirm these preliminary results.

The second series of experiments focused on the long-term kinetics of Pu accumulation (over a day) by **G3**, which involved

Table 1 Plutonium distribution (% of the initial amount) after 24 h exposure and elution of the resin with a 1 M aqueous solution of  $\text{HNO}_3$ 

Gel	Pu in the exposure solution	Pu adsorbed by the container	Pu eluted from the resin with 1 M $\text{HNO}_3$	Total Pu	Remaining adsorbed Pu
G1	29 $\pm$ 2	27 $\pm$ 2	31 $\pm$ 3	87 $\pm$ 6	13
G2	2.4 $\pm$ 0.4	15 $\pm$ 8	18 $\pm$ 3	35.5 $\pm$ 5.0	64.5
G3	1.0 $\pm$ 0.6	14 $\pm$ 2	1.3 $\pm$ 0.1	16.3 $\pm$ 1.6	83.7

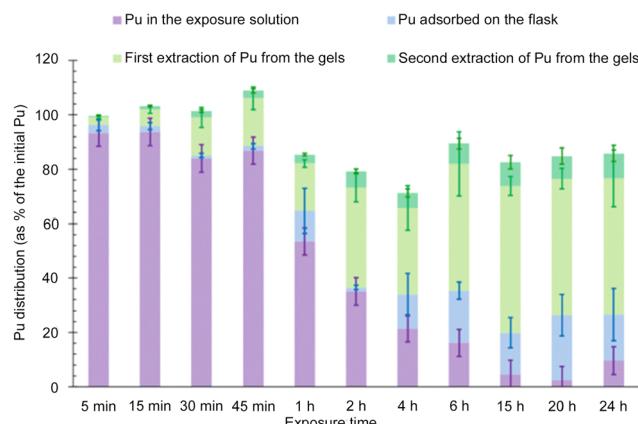


Fig. 6 Evolution of the Pu distribution over time in the case of the gel G3.

control points at 5, 15, 30, and 45 min, and then 1, 2, 4, 6, 15, 20, and 24 h. The amount of Pu remaining in the solution (violet curve in Fig. 5b) decreased from *ca.* 94% to *ca.* 24% within 4 h total contact time. Then, the uptake kinetics of Pu became slower and slower, with about 4% of the initial amount of Pu remaining in the solution after 15 h. The concomitant adsorption of plutonium on the walls of the flask (blue curve in Fig. 5b) started to evolve significantly after 45 min only, stabilizing to a mean value of 20% at 24 h. The rough mirror-image evolution of the contents of Pu on the walls of the flask and in the solution between 2 and 24 h of exposure suggests that adsorbed Pu was in equilibrium with the soluble form of Pu.

The use of a 1 M aqueous solution of HEDPA<sup>47</sup> to extract the plutonium that was sequestered by the chelating resin in this second measurement campaign, instead of the 1 M  $\text{HNO}_3$  solution used in the first campaign, significantly improved the desorption yield. It was nevertheless necessary to conduct this extraction twice, as significant amounts of Pu remained sequestered by the resin after the first treatment. The amounts of Pu released in the course of the first elution are shown in light-green in Fig. 6, and those released in the course of the second elution are shown in green. After 24 h, the total Pu recovery was 90%, with 5% of Pu remaining in solution, 20% being adsorbed on the walls of the flask, and 65% being extracted from the resin, which indicates that only 10% of the initially exposed plutonium remained still sequestered by the gel. The plutonium distribution at different time points upon use of the gel G3 is shown in Fig. 6. Moreover, these results highlight the much higher affinity of the tetrahydroxamate chelator  $1^{4-}$  as compared to the trihydroxamate siderophore DFO<sup>3-</sup> that is naturally present in soils.

### Comparison of the performances of G3 with those of other materials

Unmodified Sephadex, which binds metal cations through carboxylate groups, had been used in the past for the separation of  $^{114}\text{Ce}(\text{m})$ ,  $^{233}\text{U}(\text{vi})$ , and  $^{239}\text{Pu}(\text{iv})$ .<sup>48</sup> The mixtures of the three radioelements were adsorbed on the resin at pH 5.5, and then elution with  $10^{-4}$  M triethylenetetraaminehexamethylene acetic acid (TTHA) selectively removed Pu, Ce, and U at pH 2.5, 4.5, and 7.0, respectively. The relatively gentle conditions of Pu elution from Sephadex by comparison with those used in the case of resin G3 lend support to the fact that the latter sequesters Pu through its hydroxamate groups. The remaining carboxylate functions are likely not involved in Pu coordination by G3, because of the proximity of the four hydroxamate chelate subunits of a grafted  $1^{4-}$  molecule.

Pu sequestration by G3 is quite slower (24 h) than the kinetics reported for a resin obtained by grafting a tetradenate oxygen-based (ether and carbonyl functions) neutral ligand (benzoDODA) onto a styrene–divinylbenzene copolymer matrix.<sup>20</sup> In the latter case, the equilibrium was attained within 60 min. This contrasting behavior can be probably traced back to differing experimental conditions: medium acidity, nature of the chelators and of the materials, and the very low concentrations of analytes. BenzoDODA was operated in 1 M aqueous  $\text{HNO}_3$ , in which Pu(iv) is mainly found in the form of  $[\text{Pu}(\text{NO}_3)_x]^{(4-x)+}$  ( $x \geq 1$ ).<sup>49</sup> The slower Pu<sup>4+</sup> uptake by G3 could be due to the fact that under the pH conditions used herein (6.5), plutonium is likely to be present in the form of colloids rather than discrete species; this could be due to the resin R3 being encapsulated into a gel, in which the Pu species have to diffuse before reaching the sensitive material. The reagents used for the back extraction of Pu<sup>4+</sup> into the solution also differed markedly. In our case, the stripping experiments were conducted with a 1 M HEDPA solution. Repeating the procedure once allowed recovering 90% of the initial amount of Pu<sup>4+</sup> supplied, whereas treating twice the benzoDODA resin with a 1:1 mixture of 0.3 M aqueous hydroxylammonium nitrate and 0.3 M  $\text{HNO}_3$  released 83% of the initial amount of Pu<sup>4+</sup>. In our case, HEDPA is a competitor ligand, whereas in the case of the benzoDODA-based material,  $\text{NH}_3\text{OH}^+$  was used as a reducing agent. As a result, plutonium was extracted as Pu<sup>3+</sup> ions. It is interesting to note that benzoDODA was also simply encapsulated in porous polyether sulfone beads.<sup>21</sup> Kinetic studies of Pu<sup>4+</sup> sorption in a 3 M aqueous nitric acid solution showed that the optimal contact time was about 1.5 h, whereas two consecutive desorption experiments with a mixture of 0.05 M oxalic acid and 0.5 M  $\text{HNO}_3$  afforded nearly 98% of the sorbed Pu<sup>4+</sup>. Interestingly, in spite of the fact that the chelator was not



covalently linked to the polymer, its recyclability was satisfactory, as six consecutive cycles could be performed without loss of sorption capacity.

## Conclusions

In this work, we investigated the possibility of extracting Pu(iv) from solutions simulating slightly acidic environmental conditions (pH 6.5) at variance with industrial conditions (in the frame of nuclear waste processing), which use very acidic solutions. The chelator **1H<sub>4</sub>**, derived from the desferrioxamine B siderophore by extension with a fourth cyclic hydroxamic acid ligand component, was originally designed for the sequestration of Zr<sup>4+</sup>, and used successfully in nuclear medicine based on the  $\beta^+$  emitter <sup>89</sup>Zr<sup>4+</sup> and  $\alpha$  particle emitter <sup>227</sup>Th<sup>4+</sup>. Herein, we showed that this chelator could also sequestrate efficiently <sup>238</sup>Pu<sup>4+</sup> ions by using an agarose gel in which we embedded a **1H<sub>4</sub>**-grafted CM Sephadex C-25<sup>®</sup> resin. Using control resins (Chelex-100<sup>®</sup> and (DFO)H<sub>3</sub>-grafted CM Sephadex C-25<sup>®</sup>), we showed that the Pu<sup>4+</sup> ions were more strongly bound to the **1H<sub>4</sub>**-modified resin than the others, as it could not be removed by soaking the plutonium-loaded material in 1 M HNO<sub>3</sub>, whereas part and all of the plutonium uptaken into the (DFO)H<sub>3</sub> and the Chelex<sup>®</sup>-based resins, respectively, could be released under these conditions. These results confirm the superiority of hydroxamates over carboxylates for Pu(iv) binding and that a hydroxamate chelator with a denticity of 8 outperforms a hydroxamate chelator with a lower denticity of 6. In addition to the promising properties of **1H<sub>4</sub>** as a Pu(iv) sequestering agent, these results lend support to the fact that the material that we have fabricated could be used in the development of passive samplers, such as DGT (diffusion gradients in thin films) devices for the environmental monitoring of plutonium.

## Experimental

### General

Unless otherwise specified, all reagents used in the syntheses were of commercial origin and used as received. The mesylate salt of desferrioxamine B (Desferal<sup>®</sup>, [(DFO)H<sub>4</sub>]CH<sub>3</sub>SO<sub>3</sub>) was obtained from Apollo Scientific Ltd, Manchester, UK. All solutions used for gel fabrication were prepared with deionized water (18.2 M $\Omega$  cm resistivity, Milli-Q water, Millipore). The following chemicals were used: agarose (Bio-rad), 1-hydroxyethane-1,1-diphosphonic acid (HEDPA, 96%, Alfa Aesar), and sodium chloride (suprapur, Merck). The commercial name of Resin **R1** is Chelex-100<sup>®</sup> (BIO-RAD). The precursor of the grafted resins **R2** and **R3** is the commercial resin CM Sephadex C-25<sup>®</sup> (Cytiva), which was conditioned in the acidic form as described in the SI. *N,N*-Dimethylformamide (DMF) was dried by soaking in anhydrous magnesium sulfate, followed by distillation under vacuum and stored over anhydrous magnesium sulfate under argon. Diisopropylethylamine was dried by refluxing over sodium followed by distillation and collection under argon over pellets of potassium hydroxide. <sup>1</sup>H NMR spectra

were recorded using a Bruker Avance III spectrometer operating at 400 MHz. The IR spectra were obtained using a VERTEX 70v FT-IR spectrometer equipped with a RockSolid interferometer and a DLaTGS MIR detector. Inductively coupled plasma optical emission spectrometry analyses were performed using an iCAP 7400 (Thermo Scientific) instrument with axial and radial viewing. C, H, and N elemental analyses were performed using a CHNS/O Thermo Electron Flash EA 1112 Series instrument or a CHNS/O ThermoFisher Scientific Flash 2000 instrument.

### Grafting of [Fe(DFO)] on the acidic form of CM Sephadex C-25<sup>®</sup>: preparation of the resin **FeR2**

A solution of [Fe(acac)<sub>3</sub>] (2.12 g, 6.0 mmol) in methanol (20 mL) was added to a solution of [(DFO)H<sub>4</sub>]CH<sub>3</sub>SO<sub>3</sub> (3.94 g, 6.0 mmol) in methanol (20 mL). The reaction mixture was stirred at 40 °C for one hour. The solvent and acetylacetone were evaporated, to afford the complex [Fe(DFO)H]CH<sub>3</sub>SO<sub>3</sub> as a dark red solid. Next, the following reactants were introduced successively in a round-bottom flask: CM Sephadex C-25<sup>®</sup> (6.00 g, 24 mmol of CO<sub>2</sub>H function), [Fe(DFO)H]CH<sub>3</sub>SO<sub>3</sub> (4.26 g, 6.0 mmol), HOBT (4.60 g, 34 mmol), EDC (3.67 g, 23.6 mmol), DMF (375 mL), and finally, diisopropylethylamine (3.72 g, 28.8 mmol). The mixture was gently stirred for 4 days at 40 °C with a glass blade. The dark red resin obtained was washed several times with water, methanol, water, acetic acid (1 M in water), water, and methanol. After drying by suction, then in vacuum, 7.1 g of resin was recovered. IR (ATR):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) 3307 (br, OH), 2926 (w, CH), 1733 (m, C=O of residual carboxylic acid functions), 1637 (s, C=O of amide and hydroxamate functions), 1571, 1466, 1354, 1259, 1104 (s, C-O of ether functions), 1008, 758, 552. Anal. found (%): C 46.18, H 5.79, N 3.53, which gives 0.420 mmol g<sup>-1</sup> of grafted [Fe(DFO)]. ICP-OES of Fe (mineralization in 4 mL of conc. HNO<sub>3</sub>): 1.84% of bound Fe, which corresponds to an iron and DFO loading of 0.329 mol g<sup>-1</sup>.

### DFO-grafted CM Sephadex C-25<sup>®</sup> resin (**R2**)

**FeR2** (7.1 g) was suspended in a 0.2 M aqueous solution of Na<sub>2</sub>H<sub>2</sub>(EDTA) and the mixture was stirred manually two times a day for four days. The off-white resin **R2** obtained was filtered and washed several times with water and methanol, and finally dried in vacuum. IR (ATR):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) 3290 (br, OH), 2934 (w, CH), 1730 (m, C=O of residual carboxylic acid functions), 1618 (s, C=O of amide and hydroxamate functions), 1551, 1433, 1353, 1218, 1105 (s, C-O of ether functions), 1010, 736, 675, 545. ICP-OES analyses: residual iron content of **R2** (mineralization in 4 mL of conc. HNO<sub>3</sub>): 0.001% of bound Fe<sup>3+</sup>; Fe content of the EDTA filtrate (197 mL): 702.13 mg L<sup>-1</sup>, which corresponds to 138.32 mg of Fe<sup>3+</sup>, to be compared with the 130.6 mg of Fe<sup>3+</sup> found in 7.1 g of **FeR2**; sodium content of **R2** (mineralization in 4 mL of conc. HNO<sub>3</sub>): 1.71% of bound Na<sup>+</sup>, which corresponds to 0.74 mol g<sup>-1</sup> of Na<sup>+</sup>, that is to 17% of carboxylate functions.

### Grafting of compound **1H<sub>4</sub>** using CM Sephadex C-25<sup>®</sup>: preparation of the resins **R3-1** and **R3-2**

In a single-necked flask, compound **1H<sub>4</sub>**, CM Sephadex C-25<sup>®</sup>, HOBT-H<sub>2</sub>O, and EDC-HCl were successively introduced (Table 2).



Table 2 Amounts of reactants and the obtained grafted resins **R3-1** and **R3-2**

Batch	CM Sephadex C-25 <sup>®</sup>	<b>1H<sub>4</sub></b>	HOBT·H <sub>2</sub> O	EDC·HCl	DIPEA	DMF (mL)	t (d)	<b>R3</b> (g)	<i>n</i> <sub>chelator</sub> <sup>b</sup>	GR <sup>c</sup>
1	1.316 g 5.264 mmol <sup>a</sup>	0.830 g 1.055 mmol	0.405 g 2.638 mmol	1.017 g 5.305 mmol	1.14 mL 6.545 mmol	125	5	1.634	0.388	0.0908
2	2.343 g 9.372 mmol <sup>a</sup>	1.472 g 1.871 mmol	0.714 g 4.651 mmol	1.794 g 9.358 mmol	1.95 mL 11.195 mmol	248	5	2.695	0.305	0.0715

<sup>a</sup> Carboxylic acid functions. <sup>b</sup> *n*<sub>chelator</sub> (mmol g<sup>-1</sup>) = 10*N*%/14*n*<sub>N</sub>, where *N*% is the analytical content of nitrogen by weight of grafted resin, *n*<sub>N</sub> is the number of nitrogen atoms in a molecule of chelator. <sup>c</sup> GR (%) = *n*<sub>chelator</sub>/*n*<sub>CO<sub>2</sub>H</sub> = *n*<sub>chelator</sub>/4.27.

The flask was fitted with swan-neck glassware, connected to the vacuum line and placed under argon. DMF was injected into the flask with a syringe; the flask was fixed to a shaker agitator and immersed into an oil bath. Diisopropyl ethylamine was finally injected into the reaction mixture, which was heated to 42 °C and shaken under these conditions during 5 days (Table 2). The resin was collected by filtration through a sintered glass filter, washed three times successively with DMF, water, then a 6% aqueous solution of acetic acid, water again, and finally four times with methanol. The resin was allowed to dry in air and then under vacuum at 37 °C until a constant weight was obtained. Anal. found (%): C 49.01, H 6.54, N 4.34 for **R3-1** and C 47.17, H 6.39, N 3.42 for **R3-2**.

### Rn binding gel preparation

Resin **R1** (Chelex-100<sup>®</sup>) was purchased from DGT Research Ltd. (Lancaster, UK). First, 0.645 g of wet **Rn** resin beads were mixed with a 1.5% hot agarose aqueous solution (10 mL). The resulting gel precursor was then inserted between two acid-cleaned hot glass plates kept at 45 °C and separated using an 800 µm-thick Teflon<sup>®</sup> plastic spacer. The resulting assembly was left at room temperature for at least 30 min. The **Rn** binding gel plate surface varied between 80 and 90 cm<sup>2</sup>. Once the **Rn** binding gels were completely polymerized, they were separated from the glass plates, rinsed several times to remove unreacted reagents with ultrapure water (24 h) and stored in a 10 mM aqueous solution of sodium chloride. The following gels were fabricated: **G1** (400–480 µm thickness after complete hydration) from resin **R1** (2 g) and the agarose solution (10 mL); **G2** (800 µm thickness) from resin **R2** (1 g) and the agarose solution (7.5 mL); and **G3** (800 µm thickness) from resin **R3** (0.800 g) and the agarose solution (7.5 mL). A picture of a sheet of the gel **G3** is shown in Fig. S11.

### Kinetics of accumulation of Pu

**First campaign of measurements.** Aqueous solutions (20 mL) of [<sup>238</sup>Pu(NO<sub>3</sub>)<sub>4</sub>] (2.61 × 10<sup>-10</sup> M, 39 × 10<sup>3</sup> Bq L<sup>-1</sup>) containing sodium sulfate (10 mM) and buffered at pH 6.5 with MOPS (3-morpholino-1-propanesulfonic acid, Sigma-Aldrich) were prepared in stoppered polycarbonate (PC) centrifugation tubes (Nalgene<sup>®</sup>, Oak Ridge Style). The chelating gel of interest (**Gn**) was introduced into each tube, which was stirred on a rotating shaker (Vertical rotating shaker 360° PTR-60, Grant Instruments Ltd). The accumulation experiment was stopped after the following durations (*t<sub>f</sub>*): 5 min, 10 min, 20 min, 30 min, 40 min, 50 min, 60 min, and 24 h. The Pu content was determined by liquid

scintillation (Wallac Quantulus, DL = 2.5 Bq L<sup>-1</sup>) after acidification of all samples with 2% v/v HNO<sub>3</sub>. The analysis was carried out (1) directly from the exposure solution at *t*<sub>0</sub> and *t<sub>f</sub>* for the Pu remaining in solution, (2) after washing the container with 30 mL of a 10% aqueous solution of nitric acid during 24 h for the Pu adsorbed on the walls of the container, and (3) after soaking the resin in 3 mL of a 1 M aqueous solution of nitric acid during 24 h for the Pu sequestered by the resin.

**Second campaign of measurements.** All materials and methods were the same as for the first campaign, except that (1) **G3-1** was replaced with **G3-2**, (2) the accumulation experiment was stopped after 5 min, 15 min, 30 min, 45 min, 60 min, 2 h, 4 h, 6 h, 15 h, 20 h, and 24 h, and (3) the recovery of Pu from the resin was achieved by soaking the binding gel in 3 mL of a 1 M aqueous solution of HEDPA during 24 h. This procedure was repeated twice.

### Author contributions

Funding acquisition: MM and JCC; conceptualization and methodology: MM, JG, LF, and JCC; investigations: LZ, FM, JCC, OF, SB, and JG; supervision: JCC, LF, and MM; data treatment: LF; writing – original draft: JCC; and writing – review and editing: JCC, MM, LF, and JG.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

Most of the data corresponding to the study reported in this article are available in the main text and in the associated supporting information (SI). Other data can be obtained from either of the corresponding authors: grafting of DFO onto CM Sephadex C-25<sup>®</sup>: development of the reaction conditions and material characterization: Dr Michel Meyer; synthesis and grafting of DFOcyclo\* (compound **1H<sub>4</sub>**) onto CM Sephadex C-25<sup>®</sup>, Dr Jean-Claude Chambron; gel fabrication and experiments of Pu sequestration and desorption: Dr Laureline Février. Supplementary information: large scale preparation of **1H<sub>4</sub>**, optimization of the reaction conditions for the preparation of resins **R2** and **R3**, characterization of the resins CM Sephadex C-25<sup>®</sup>, FeR2, **R2** and **R3**. <https://doi.org/10.1039/d5nj02515j>.



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