



Cite this: *Chem. Commun.*, 2022, **58**, 10961

Received 28th July 2022,  
Accepted 1st September 2022

DOI: 10.1039/d2cc04225h

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Plutonium-based technologies would benefit if chemical hazards for purifying plutonium were reduced. One critical processing step where improvements could be impactful is the adjustment of plutonium oxidation-states during separations. This transformation often requires addition of redox agents. Unfortunately, many of the redox agents used previously cannot be used today because their properties are deemed incompatible with modern day processing facilities and waste stream safety requirements. We demonstrated herein that photochemistry can be used as an alternative to those chemical agents. We observed that (1)  $\text{Pu}^{4+} \rightarrow \text{Pu}^{3+}$  and  $\text{UO}_2^{2+} \rightarrow \text{U}^{4+}$  photoreduction proceeded in  $\text{HCl}_{(\text{aq})}$  and  $\text{HNO}_3_{(\text{aq})}$  and (2) photogenerated  $\text{Pu}^{3+}_{(\text{aq})}$  and  $\text{U}^{4+}_{(\text{aq})}$  could be separated using anion exchange chromatography (high yield, > 90%; good separation factor, 322).

Many important actinide-technologies rely on chemical processing efforts that generate high purity plutonium and uranium. This spans actinide processing for weapons programs<sup>1,2</sup> environmental restoration,<sup>3,4</sup> nuclear forensics,<sup>5,6</sup> and nuclear fuel reprocessing.<sup>7-9</sup> Processing methods that cleanly isolate actinides for these applications often require addition of strong redox agents (oxidants or reductants) that manipulate actinide oxidation states during separations.<sup>10</sup> Unfortunately, many effective redox agents used previously have been reclassified as hazardous and cannot be used today. They are now incompatible with modern day nuclear facilities where large quantities of actinides (like Pu) are processed<sup>11</sup> or are incompatible with actinide processing waste streams and safe long-term storage in geological repositories. The waste drum breach at the Waste Isolation Pilot Plant in 2014 that dispersed plutonium and americium throughout that facility exemplifies validity of those concerns.<sup>12,13</sup> Finding alternative and safe methods to control actinide oxidation states while avoiding addition of harsh chemical agents during processing would have positive impact on actinide-based technologies and waste management activities, alike.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2cc04225h>

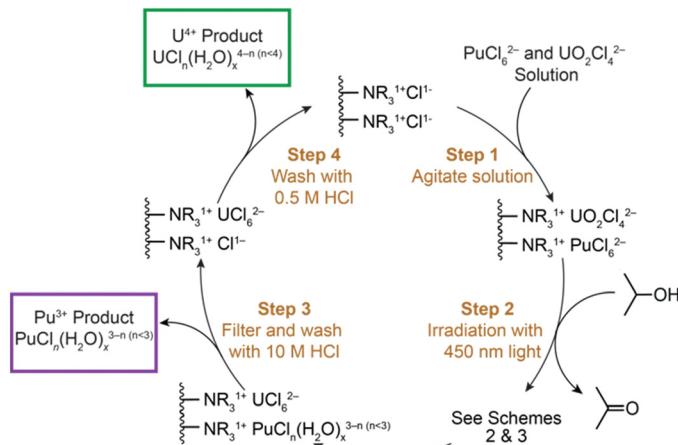
## Photochemical separation of plutonium from uranium†

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Motivated by this charge, we became intimately aware of recent advances in uranium photochemistry.<sup>14</sup> Those studies revealed how uranium oxidation state adjustments could be achieved upon exposure to ultraviolet and visible (UV-vis) light. We were inspired by those discoveries, a limited number of photochemical studies for Pu,<sup>15-17</sup> and reports that describe potential for photochemical separation of actinides.<sup>18,19</sup> Hence, we set out to develop a photochemical method for Pu/U separations. Our approach was distinct in that it used photochemistry and 2-propanol (a sacrificial electron donor) in place of harsh chemical redox agents to reduce  $\text{Pu}^{4+}_{(\text{aq})}$  to  $\text{Pu}^{3+}_{(\text{aq})}$  and  $\text{UO}_2^{2+}_{(\text{aq})}$  to  $\text{U}^{4+}_{(\text{aq})}$  (aq = dissolved in aqueous solutions). This procedure was attractive because it proceeded under aqueous conditions and without oxygen exclusion. It was also rapid (total processing time = 90 min) and could be carried out using commercially available equipment and chemicals (aside from plutonium). Another selling point was that the photoinduced redox events were compatible with ion-exchange chromatography, akin to those used to process large quantities of plutonium from aqueous chloride matrixes, *e.g.* within the Experimental Chloride Extraction Line (EXCEL) at Los Alamos National Laboratory.<sup>20</sup>

Scheme 1 shows the photochemical separation we developed. It started by dissolving  $\text{Pu}^{4+}_{(\text{aq})}$  (0.9 mg) (obtained using previously described methods)<sup>21</sup> and  $\text{UO}_2^{2+}_{(\text{aq})}$  (1.1 mg) in  $\text{HCl}_{(\text{aq})}$  (10 M, 1% 2-propanol, Fig. 1, brown trace) within a quartz cuvette charged with anion exchange resin (1 mL, AG MP-1, 100 mesh). Combining these reagents caused the brown solution to turn colorless, presumably because plutonium and uranium adsorbed quantitatively to the resin. This result was consistent with expectations based on the literature. For instance, the Handbook of Ion Exchange Resins<sup>22</sup> states both  $\text{Pu}^{4+}_{(\text{aq})}$  ( $K_d = > 10^3$ ) and  $\text{UO}_2^{2+}_{(\text{aq})}$  ( $K_d = \sim 10^3$ ) strongly adsorb to anion-exchange resins in  $\text{HCl}_{(\text{aq})}$  (10 M);  $K_d$  is a distribution coefficient, (resin bound analyte/unbound analyte). The next step in the process exposed the colorless mixture to light (22 222.2  $\text{cm}^{-1}$ ; 450 nm). Irradiation at high LED power (100%) rapidly (~15 min) reduced  $\text{Pu}^{4+}_{(\text{aq})}$  to  $\text{Pu}^{3+}_{(\text{aq})}$  and  $\text{UO}_2^{2+}_{(\text{aq})}$  to  $\text{U}^{4+}_{(\text{aq})}$  (*vide infra*). This oxidation-state adjustment imparted different behavior between plutonium and uranium with the anion exchange resin. It is well established that





Scheme 1 Photochemical separation scheme.

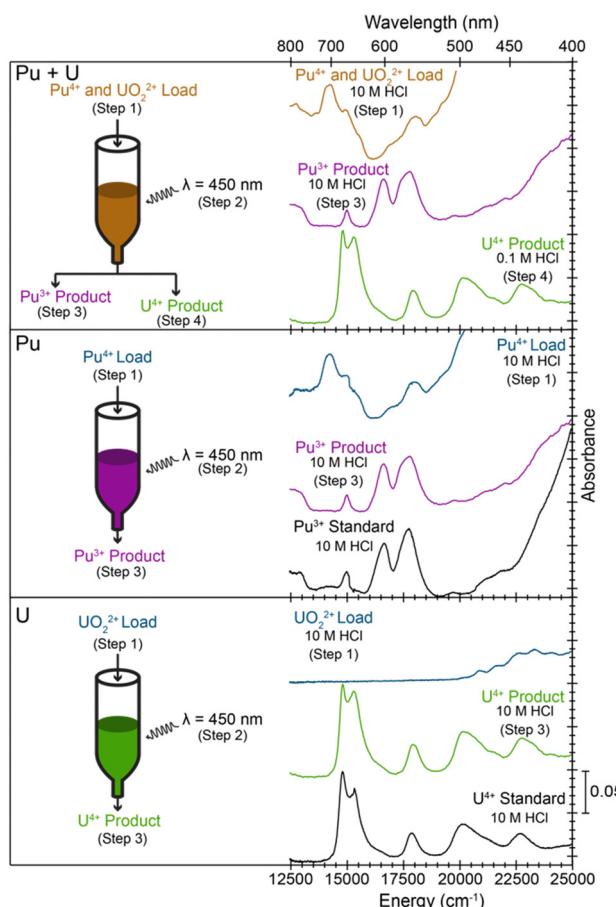


Fig. 1 Left – Comparing photochemical separation of  $\text{Pu}^{4+}_{(\text{aq})}$  and  $\text{UO}_2^{2+}_{(\text{aq})}$  mixtures (top) with pristine  $\text{Pu}^{4+}_{(\text{aq})}$  (middle) and  $\text{UO}_2^{2+}_{(\text{aq})}$  (bottom) solutions. Right – UV-vis spectra from column load solutions, the  $\text{Pu}^{3+}$  (purple traces) and  $\text{U}^{4+}$  (green traces) products, and  $\text{Pu}^{3+}_{(\text{aq})}$  and  $\text{U}^{4+}_{(\text{aq})}$  standards (black traces).

$\text{Pu}^{3+}$  forms cationic (or neutral) aquo and aquo/chloro complexes  $[\text{Pu}^{3+}\text{Cl}_n(\text{H}_2\text{O})_x]^{3-n}$ ;  $n \leq 3$  in  $\text{HCl}_{(\text{aq})}$  (10 M) solutions.<sup>23–25</sup> These species are not retained by the anion-exchanger's cationic

functional groups ( $\text{NR}_3^{1+}$ ). Hence, the resin released  $\text{Pu}^{3+}_{(\text{aq})}$  and the mixture turned blue. Next, the mixture was loaded into an empty Bio-Rad column, which filtered the resin from the supernatant. Under these conditions,  $\text{Pu}^{3+}_{(\text{aq})}$  eluted from the column and the  $\text{Pu}^{3+}$  product was collected. Analysis using UV-vis spectroscopy confirmed presence of  $\text{Pu}^{3+}_{(\text{aq})}$  (Fig. 1, purple trace).<sup>21,26</sup>

During the  $\text{Pu}^{3+}_{(\text{aq})}$  elution,  $\text{U}^{4+}_{(\text{aq})}$  remained retained by the resin. Under these experimental conditions [10 M  $\text{HCl}_{(\text{aq})}$ ],  $\text{U}^{4+}_{(\text{aq})}$  forms anionic coordination complexes. We naively formulated the  $\text{U}^{4+}$  resin-bound species as " $\text{UCl}_6^{2-}$ ." However, lower ( $\text{UCl}_5^{1-}$ ) and higher ( $\text{UCl}_7^{3-}$ ) chloride-containing compounds were possible, as were heteroleptic aquo/chloro compounds  $[\text{UCl}_n(\text{H}_2\text{O})_x]^{4-n}$ ,  $n > 4$  and oligomerization products.<sup>27</sup> Regardless of identity for the resin bound uranium species, the anion-exchanger's cationic quaternary ammonium functional groups ( $\text{NR}_3^{1+}$ ) retained the nominal " $\text{UCl}_6^{2-}$ " anion ( $\text{U}^{4+} K_d \approx 10^2$ )<sup>22</sup> in  $\text{HCl}_{(\text{aq})}$  (10 M). After plutonium removal, dilute  $\text{HCl}_{(\text{aq})}$  (0.5 M) was passed through the resin. This decrease in  $\text{Cl}^{1-}_{(\text{aq})}$  concentration reduced the number of  $\text{Cl}^{1-}$  ligands bound to  $\text{U}^{4+}$  (Scheme 1), lowered the  $\text{U}^{4+} K_d$  value ( $< 10$ ),<sup>22</sup> and enabled the cationic (or neutral) uranium aquo/chloro  $[\text{U}^{IV}\text{Cl}_n(\text{H}_2\text{O})_x]^{4-n}$ ;  $n \leq 4$  species to elute from the column and be cleanly isolated. Analyses using UV-vis spectroscopy confirmed presence of  $\text{U}^{4+}_{(\text{aq})}$  (Fig. 1, green trace).<sup>14,27</sup>

The  $\text{Pu}^{3+}_{(\text{aq})}$  and  $\text{U}^{4+}_{(\text{aq})}$  products were isolated from this procedure in high yield and in chemically pure forms. Analyses of the  $\text{Pu}^{3+}$  product using inductively coupled plasma-mass spectrometry (ICP-MS) and isotope dilution techniques<sup>28</sup> showed a 97.5% plutonium recovery yield, 9.2 uranium decontamination factor ( $\text{U}_{\text{ingoing}}/\text{U}_{\text{Pu Product}}$ ), and 322 plutonium/uranium separation factor ( $\text{SF}_{\text{Pu/U}}$ );  $\text{SF}_{\text{Pu/U}} = (\text{Pu}_{\text{Pu Product}}/\text{Pu}_{\text{U Product}}) \div (\text{U}_{\text{U Product}}/\text{U}_{\text{Pu Product}})$ ). Similarly positive results were obtained for the  $\text{U}^{4+}$  product; 90% uranium yield and 40.6 plutonium decontamination ( $\text{Pu}_{\text{ingoing}}/\text{Pu}_{\text{U Product}}$ ). These metrics were comparable to results obtained when using conventional redox agents under equivalent experimental conditions (1 mg of Pu, 1 mg of U, and 1 ml of resin). Larger separation and decontamination factors were obtained when the amounts of plutonium and uranium were decreased,



the amount of resin increased, and/or the procedure was repeated multiple times.

Studies that generated insight into the redox reactions governing the above plutonium and uranium separations, photochemical reductions, and analyte behaviors with the anion-exchange resin were carried out. These studies utilized pristine stock solutions containing only  $\text{Pu}^{4+}$  (aq) or  $\text{UO}_2^{2+}$  (aq) (vs. the Pu/U mixtures described above) and were carried out within the context of  $\text{UO}_2^{2+}$  photochemistry results published previously in  $\text{HNO}_3$ (aq).<sup>29–35</sup> For example,  $\text{UO}_2^{2+}$  (aq) photoreduction to  $\text{U}^{4+}$  (aq) has been shown to proceed with a variety of reductants, including triethylamine,<sup>36</sup> formate,<sup>35</sup> and 2-propanol.<sup>14</sup> We focused this study on 2-propanol,  $(\text{CH}_3)_2\text{CHOH}$ , as a representative sacrificial electron donor (eqn (1) in Scheme 2). In  $\text{HNO}_3$ (aq), it is proposed that the “photoexcited  $\text{UO}_2^{2+}$ ” ion undergoes electron transfer with sacrificial  $(\text{CH}_3)_2\text{CHOH}$  to generate a  $\text{UO}_2^{2+}$  (aq) radical cation alongside the somewhat long-lived organic radical  $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ .<sup>14</sup> The authors provided evidence that successive reactions between these species generate  $\text{U}^{4+}$  (aq), water ( $\text{H}_2\text{O}$ ), and acetone  $[(\text{CH}_3)_2\text{C}=\text{O}]$ . Armed with this insight, we reproduced the aforementioned reports and showed that pristine solutions of  $\text{UO}_2^{2+}$  (aq) (25 mM) could be photoreduced to  $\text{U}^{4+}$  (aq) using a mixture of  $\text{HNO}_3$ (aq) (1 M; pH = 0), 2-propanol (1% by volume), and a Penn Photoreactor (22 222.2  $\text{cm}^{-1}$ ; 450 nm excitation). We subsequently shifted our focus and demonstrated photoreductions could also occur in  $\text{HCl}$ (aq) (10 M; pH = –1). This was critical for developing our photochemical separations because  $\text{UO}_2^{2+}$  (aq) behaves differently with anion exchange resins in  $\text{HCl}$ (aq) (retained) vs.  $\text{HNO}_3$ (aq) (not retained).<sup>22</sup> We also observed by NMR spectroscopy that photoreduction of  $\text{UO}_2^{2+}$  (aq) to  $\text{U}^{4+}$  (aq) generated  $(\text{CH}_3)_2\text{C}=\text{O}$  (see ESI†). Hence, the reaction pathway described in Scheme 2 may appropriately describe photoreduction of  $\text{UO}_2^{2+}$  (aq) to  $\text{U}^{4+}$  (aq) in  $\text{HCl}$ (aq), as well as in  $\text{HNO}_3$ (aq). Obviously, more data is needed to confirm that proposition.

To provide insight into uranium speciation during the electron transfer process we monitored the photochemical reduction of  $\text{UO}_2^{2+}$  (aq) in  $\text{HCl}$ (aq) *in situ* using UV-vis spectroscopy (Fig. 2). The characteristic manifold of UV-vis absorbances from  $\text{UO}_2^{2+}$  (aq) in  $\text{HCl}$ (aq) (10 M) between 20 000 to 25 000  $\text{cm}^{-1}$  (500 to 400 nm) was unaffected upon addition of 2-propanol (1% by volume). This data suggested  $\text{UO}_2^{2+}$  (aq) had no affinity for alcohol complexation under these conditions. Irradiating this solution at 22 222  $\text{cm}^{-1}$  (450 nm) changed the yellow color to green, wilted the  $\text{UO}_2^{2+}$  (aq) absorbances, and generated peaks characteristic of  $\text{U}^{4+}$  (aq).<sup>37</sup> The spectrum was dominated by a split absorption band between 14 286 and 16 666  $\text{cm}^{-1}$  (700 to 600 nm) with maxima at 14 859 and 15 385  $\text{cm}^{-1}$  (650 and 673 nm) that were followed at higher energy by a series of three lower intensity absorptions (17 929, 20 205, and 22 729  $\text{cm}^{-1}$ ).<sup>27</sup> Comparisons of UV-vis data pre- and

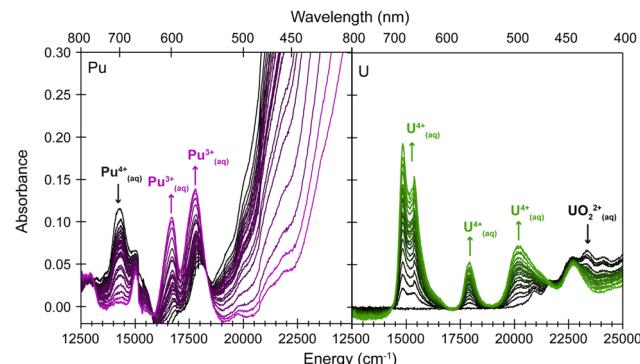
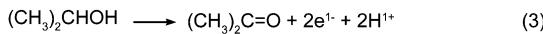
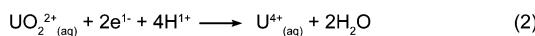
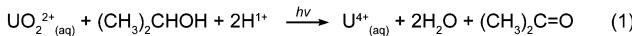


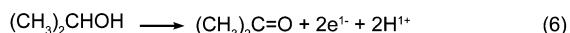
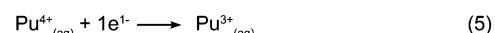
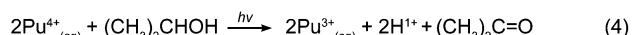
Fig. 2 UV-Vis spectra from photoreduction experiments; left –  $\text{Pu}^{4+}$  (aq) (black) reduced to  $\text{Pu}^{3+}$  (aq) (purple), right –  $\text{UO}_2^{2+}$  (aq) (black) reduced to  $\text{U}^{4+}$  (aq) (green). Reduction occurred in  $\text{HCl}$ (aq) (10 M) and  $(\text{CH}_3)_2\text{CHOH}$  (1% by volume) using a Penn Photoreactor (excitation energy 22 222.2  $\text{cm}^{-1}$ , 450 nm).

post-irradiation suggested quantitative conversion of  $\text{UO}_2^{2+}$  (aq) to  $\text{U}^{4+}$  (aq) occurred in  $\text{HCl}$ (aq) (60 min, LED power = 25%). We also report that  $\text{UO}_2^{2+}$  photoreduction did not occur in the absence of 2-propanol. This reagent was clearly critical.

Although, plutonium photoreduction has been investigated far less than  $\text{UO}_2^{2+}$ , one relevant report came from Toth and coworkers in the 1970s.<sup>18</sup> These researchers observed photochemical reduction of  $\text{Pu}^{4+}$  (aq) to  $\text{Pu}^{3+}$  (aq) in  $\text{HNO}_3$ (aq) (1.2 M) using an irradiation source of 33 333  $\text{cm}^{-1}$  (300 nm) and a variety of sacrificial electron donors (formic acid, ethanol, and hydrazine). Emboldened by those results and the  $\text{UO}_2^{2+}$  (aq) photochemistry described above, we proposed  $\text{Pu}^{4+}$  (aq) would undergo a similar reduction in the presence of  $(\text{CH}_3)_2\text{CHOH}$  in  $\text{HNO}_3$ (aq) and  $\text{HCl}$ (aq) matrixes (see Scheme 3 and ESI†). The UV-vis data we obtained in  $\text{HCl}$ (aq) (10 M, Fig. 2) and  $\text{HNO}_3$ (aq) (1 M, see ESI†) were consistent with that hypothesis. Even though we conducted experiments in  $\text{HNO}_3$ (aq) (see ESI†), our focus was on reduction in  $\text{HCl}$ (aq) because this matrix provided desirable conditions for achieving separations with anion exchange chromatography. Fig. 2 shows the start of the photoreduction (black trace), which represented a solution of  $\text{Pu}^{4+}$  (aq) dissolved in  $\text{HCl}$ (aq) (10 M). This spectrum contained the two  $\text{Pu}^{4+}$  (aq) absorption bands with peak maxima 14 260  $\text{cm}^{-1}$  (701 nm) and 18 005  $\text{cm}^{-1}$  (555 nm). The spectrum was unaffected by addition of 2-propanol, again suggesting that no complexation of 2-propanol by  $\text{Pu}^{4+}$  (aq) occurred under these conditions. Substantial changes were detected, however, when the solution was irradiated (22 222  $\text{cm}^{-1}$ , 450 nm). The  $\text{Pu}^{4+}$  (aq) absorption bands waned amongst emerging peaks from  $\text{Pu}^{3+}$  (aq) (16 639 and 17 857  $\text{cm}^{-1}$ ; 560 and 601 nm). UV-Vis assays showed quantitative conversion of  $\text{Pu}^{4+}$  (aq) to  $\text{Pu}^{3+}$  (aq) within



Scheme 2 Photochemical reduction of  $\text{UO}_2^{2+}$ .



Scheme 3 Photochemical reduction of  $\text{Pu}^{4+}$ .



60 min (LED power = 25%; Fig. 1 and 2, purple trace). The formation of  $(\text{CH}_3)_2\text{C}=\text{O}$  was confirmed by  $^1\text{H}$  NMR spectroscopy, and the transformation is described in eqn (4) and (5). Again, 2-propanol was essential for the photoreduction.

We have demonstrated that  $\text{Pu}^{4+}_{(\text{aq})}$  and  $\text{UO}_2^{2+}_{(\text{aq})}$  undergo photoreduction to  $\text{Pu}^{3+}_{(\text{aq})}$  and  $\text{U}^{4+}_{(\text{aq})}$  in  $\text{HCl}_{(\text{aq})}$  in the presence of 2-propanol. We further showed that this oxidation state adjustment was compatible with ion-exchange chromatography and developed a photochemical separation of plutonium from uranium. Our separation was effective, efficient, and generated chemically pure  $\text{U}^{4+}_{(\text{aq})}$  and  $\text{Pu}^{3+}_{(\text{aq})}$  products in high yield. It could be carried out rapidly using a commercially available photoreactor in aqueous media without exclusion of air. Our usage of photochemistry in place of harsh redox agents during actinide separations was attractive on many other levels. First and foremost, the substitution keeps harsh (*i.e.* hydroxylamine, sodium nitrite, sodium chloride) redox agents out of process waste streams. This reduces threat of waste container failure promoted by unwanted side-reactions and pressurization that can occur during long-term storage. Photoreduction can additionally limit spread of contamination during oxidation-state adjustments. For example, bubbling and splattering (sometime vigorously) can occur when common reducing agents (*e.g.* hydroxylamine hydrochloride) are added to actinide containing acidic solutions.<sup>21</sup> This hazard is avoided by photochemical reduction. The substitution also avoids corrosive redox agents (*e.g.* bromine containing chemicals)<sup>38</sup> known to deteriorate critical hardware in processing facilities (like radiological gloveboxes and hoods). We are excited to implement this photochemical separation method locally when we recover and reprocess small quantities of plutonium for our research campaigns. Potential application also resides outside of our laboratory, within the realm of actinide analytical chemistry (for environmental monitoring and nuclear forensics<sup>1–9</sup>) and for large-scale actinide processing (like EXCEL).<sup>20</sup> From this perspective, data reported herein provides an intriguing “proof-of-principle.” We hope these results inspire others to explore photochemical actinide separations, especially as a tool to improve the safety, efficiency, and effectiveness of actinide processing efforts.

We thank the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Heavy Element Chemistry program (2020LANLE372) and LANL's Laboratory Directed Research and Development program (20190364ER). Postdoctoral support was provided in part by the Los Alamos National Laboratory Named Agnew (DiMucci) and the Glenn T. Seaborg Institute (Root, Jones) Post-Doctoral Fellowships. LANL is an affirmative action/equal opportunity employer managed by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. DOE.

## Conflicts of interest

There are no conflicts of interest to declare.

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