Reagents

All experiments on transuranium elements were conducted in the Atalante facility (CEA Marcoule, France), in a laboratory dedicated to these highly radioactive elements. All experiments were carried out with approved safety operating procedures in negative pressure glove box. Pu(IV) solution was prepared by dissolving the corresponding oxide, PuO₂, with concentrated HNO₃ in a glove box. It was then purified by fixation on a DOWEX anion exchange resin at 7 mol.L⁻¹ HNO₃ and elution with 0.5 mol.L⁻¹ HNO₃. Oxidation state and concentration of the actinide solutions were checked by Vis-NIR spectrophotometry. DEHBA N,N-dialkyl amides were synthesized by Pharmasynthese (France). DODECANE is purchased from Aldrich.

Sample preparation

The DEHBA samples were prepared by liquid-liquid extraction at 25°C. Nitric acid aqueous phases ([HNO₃] = 3 mol.L⁻¹ and 11 mol.L⁻¹), containing the Pu(IV) were contacted for 15 minutes by means of an automatic vortex shaker with organic solutions (aqueous phase volume over organic phase volume ratio: Vaq/Vorg = 3) containing the ligand. Before the extraction, the organic phase was pre-equilibrated with the targeted nitric acid (Vaq/Vorg = 3) for 30 min at 25°C. The phases were separated after centrifugation. Plutonium concentrations in the organic phase were determined by alpha-spectroscopy. The evolution of Pu(IV) was monitored with Vis-NIR spectrophotometry during several days corresponding to the delay between the samples preparation and their analysis at the Synchrotron.

Table 1. Compositions of DEHBA solutions used in EXAFS and vis-NIR measurements.

<table>
<thead>
<tr>
<th>Pu-DEHBA</th>
<th>Cₐq[NH₃]</th>
<th>Cₐq[HNO₃]</th>
<th>[Ligand]org</th>
<th>[Pu]org</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8M</td>
<td>2.8</td>
<td>0.7</td>
<td>1.2</td>
<td>2.2</td>
<td>vis-NIR</td>
</tr>
<tr>
<td>3.3M</td>
<td>3.3</td>
<td>0.8</td>
<td>1.2</td>
<td>2.2</td>
<td>EXAFS, vis-NIR</td>
</tr>
<tr>
<td>5M</td>
<td>5</td>
<td>1.9</td>
<td>2.7</td>
<td>2.2</td>
<td>vis-NIR</td>
</tr>
<tr>
<td>8M</td>
<td>8</td>
<td>3.4</td>
<td>2.7</td>
<td>2.2</td>
<td>vis-NIR</td>
</tr>
<tr>
<td>11M</td>
<td>11</td>
<td>4.2</td>
<td>2.7</td>
<td>2.2</td>
<td>EXAFS, vis-NIR</td>
</tr>
</tbody>
</table>

a Amide concentration in the organic phase. b HNO₃ concentration in the organic phase estimated values from ref [20] and [24] of the main manuscript. Pu(IV) concentration in the organic phase estimated values from ref [20] and [24] of the main manuscript. Alfa spectroscopy measurements.

EXAFS data acquisition and treatment

EXAFS spectra were recorded at Synchrotron SOLEIL (Saint-Aubin, France) (2.75 GeV at 450 mA), at the MARS beamline. MARS is equipped with a water-cooled Si(220) double crystal horizontal focusing monochromator (DCM). Beam vertical collimation/focusing and rejection of higher-order harmonics were achieved with two Pcoated mirrors before and after the DCM. A 13-element HPGe solid state detector (ORTEC) was used for data collection in fluorescence mode. Monochromator energy calibration was carried out at zirconium K-edge. All measurements were performed at room temperature in 200 µL double-layered cells specifically designed for radioactive samples. All spectra were recorded at the plutonium L₂ edge (18057 eV for Pu). The data represent averages of 4 scans. Data processing was carried out with the Athena code. After energy calibration, the e₀ energy was set at the maximum of the absorption edge. For all the samples, the maximum energy of the absorption edge confirms the redox state +IV for plutonium (18068.2 eV).² The EXAFS signal was extracted by subtracting a linear pre-edge background and a combination of cubic spline functions for atomic absorption background and then normalized by the Lengeler-Eisenberg procedure. Pseudo-radial distribution functions (PRDF) were obtained by Fourier transform in k²χ(k) using the ATHENA code between 1.5 and 12.5 Å⁻¹. For EXAFS data analysis, no fitting procedure is applied. Theoretical scattering phases and amplitudes were calculated by the FEFF9, from computational methods.
Computational details

The geometry and frequency calculations have been performed with Gaussian 09\textsuperscript{6} at the DFT level of theory with the PBE0 functional.\textsuperscript{7} A small core quasi-relativistic effective core potential (RECP – 60 electrons)\textsuperscript{8,9} by the Stuttgart-Cologne group and its corresponding TZ-valence basis set have been used for Pu\textsuperscript{10} and the def-TZVP\textsuperscript{11} basis sets for the other atoms. Solvent effects have been taken into account with a polarizable continuum model (IEFPCM) corresponding to n-dodecane.\textsuperscript{6} The \textit{ab initio} DW factors have been calculated at 300 K for each scattering path from the dynamical matrix extracted from the DFT frequency calculation with the DMDW module of FEFF9.\textsuperscript{4,5} The EXAFS spectra have then been simulated with FEFF9 considering this \textit{ab initio} DW factors, and all multiple-scattering paths up to a half-path length of 6 Å. The scattering potentials were calculated using a self-consistent loop. The amplitude factor $S_0^2$ was fixed to 1. The shift of the photoelectron energy origin $\Delta E_0$ is the only parameter adjusted in the EXAFS simulation and has been taken so that the first amplitudes of the simulated spectra are in phase with the experimental ones.

\begin{enumerate}
  \item Vila, F. D.; Lindahl, V. E.; Rehr, J. J. \textit{Physical Review B} \textbf{2012}, \textit{85}.
  \item Adamo, C.; Barone, V. \textit{Journal of Chemical Physics} \textbf{1999}, \textit{110}, 6158.
\end{enumerate}