Supporting Information

Relevance of Formation Conditions on the Size, Morphology and Local Structure of Intrinsic Plutonium Colloids

Cyril Micheau,[a] Matthieu Virot,[a*] Sandrine Dourdain,[a] Thomas Dumas,[b] Denis Menut,[c] Pier Lorenzo Solari,[c] Laurent Venault,[b] Olivier Diat,[a] Philippe Moisy,[b] Sergey I. Nikitenko[a]

[a] ICSM, Univ Montpellier, UMR 5257, CEA, CNRS, ENSCM, Marcoule, France.
[b] CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France.
[c] Synchrotron SOLEIL, MARS beamline, l'Ormes des Merisiers, Saint Aubin BP 48, 91192 Gif-sur-Yvette, France.

I. Fitting models

Guinier form factor

$$I(Q) = I_0 exp\left(-\frac{(QR_G)^2}{3}\right)$$

where, R_G is the gyration radius of the particle. I_0 can be expressed with the following equation:

$$I_0 = \phi V \Delta\bar{\rho}^2$$

For a sphere with a radius R

$$R_G = R\sqrt{3/5}$$

Sphere form factor

$$I(Q) = I_0 P(Q)$$

$$I_0 = \phi V_{sphere} \Delta\bar{\rho}^2$$

where, V_{sphere} is the volume of the sphere (cm³) that is equal to $\frac{4}{3}\pi R^3$, $\Delta\bar{\rho}^2$ is the contrast between the sphere and the solvent (cm^{-4}), calculated from the eletronic scattering length density ρ_{sphere} and $\rho_{solvent}$ of the particle and the solvent respectively (cm^{-2}), and ϕ is the volume fraction of the particle.

$$P(Q) = \left(\frac{3(\sin(QR) - QRcos(QR))}{(QR)^3}\right)^2$$

where, Q is the wave vector (nm^{-1}) , R is the radius of the sphere (nm^{-1}),

Core-shell form factor

$$I(Q) = \frac{\phi_{cluster}}{V_{shell}}\left(3\left(V_{shell}(\rho_{shell}-\rho_{solvent})\frac{\sin\left(QR_{shell}\right)-QR_{shell}cos(QR_{shell})}{\left(QR_{shell}\right)^3}\right)+3\left(V_{core}(\right.\right.$$

where, $\phi_{cluster}$ is the volume fraction of the cluster

where, $V_{shell}=\frac{4}{3}\pi {R_{shell}}^3$ the volume of the shell and R_{shell} the radius of the shell, ρ_{shell} the scattering length density of the shell ;

where, $V_{core}=\frac{4}{3}\pi {R_{core}}^3$ the volume of the core and R_{core} the radius of the core, ρ_{shell} the scattering length density of the shell ;

Infinitely large lamella form factor

$$I(Q)=\frac{8\pi\phi\Delta\bar{\rho}^2}{Q^4L}sin^2\left(\frac{QL}{2}\right)$$

where, L is the thickness of the lamella.

Disk form factor ($R_D \gg L$)

$$I(Q)=4\phi V_{disk}\Delta\bar{\rho}^2\int_0^{\pi/2}\left[\frac{sin\left(\frac{1}{2}QLcos\,\alpha\right)J_1\left(\frac{1}{2}QR_Dsin\,\alpha\right)}{\frac{1}{2}QLcos\,\alpha \qquad \frac{1}{2}QR_Dsin\,\alpha}\right]^2 sin\,\alpha\,d\alpha$$

where, V_{disk} the disk volume, L its thickness, R_D its radius, α the angle between the disk and the wave vector $\vec{Q}$ and J_1 the first order *BESSEL* function.

II. ESI Figures

Fig S1 Lab pictures showing the synchrotron SAXS/XAS analytical bench**.**

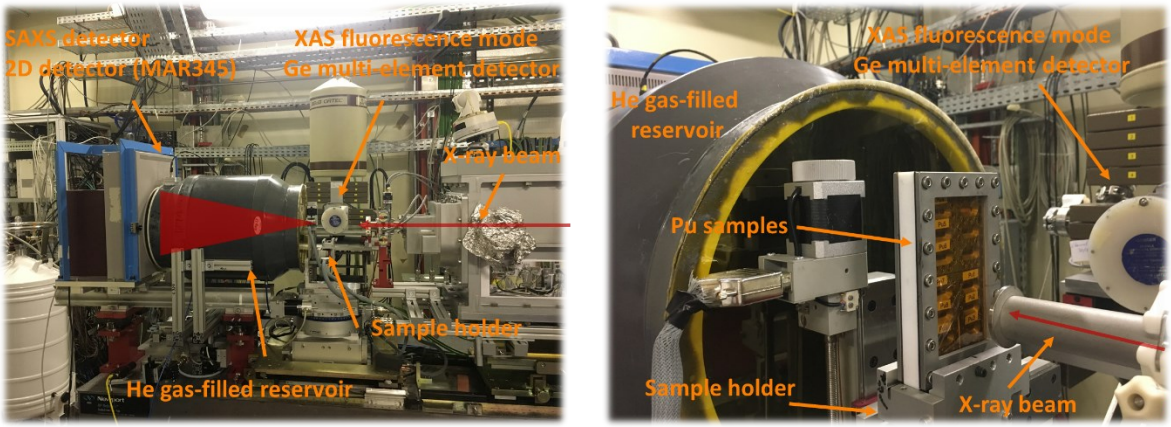


Fig. S2 UV-Vis absorption spectra of stable hydrolytic Pu(IV) colloidal suspensions diluted in milli-Q H_2O at different concentrations: 10 mM (no dilution; black line), 5 mM (blue line) and 1 mM (green line).

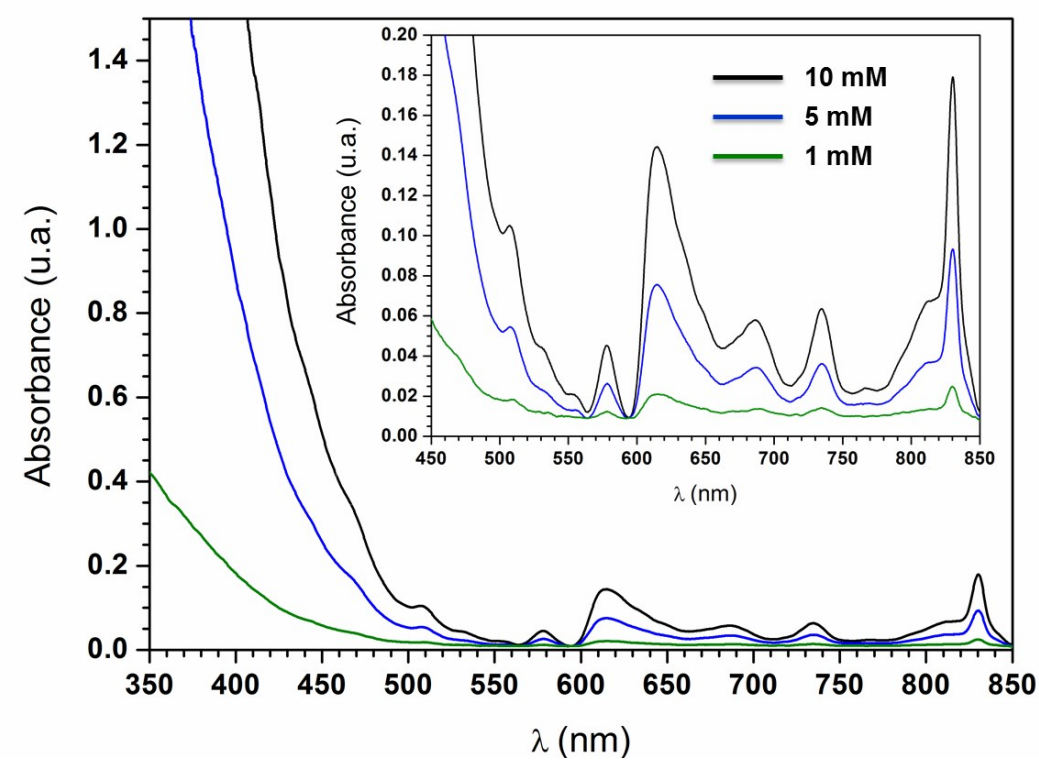


Fig. S3 UV-Vis absorption spectra of stable hydrolytic Pu(IV) colloidal suspensions diluted in HNO_3 42 mM at different concentrations: 10 mM (no dilution; blue line), 5 mM (black line), 1 mM (green line), 0.5 mM (orange line) and 0.1 mM (red line).

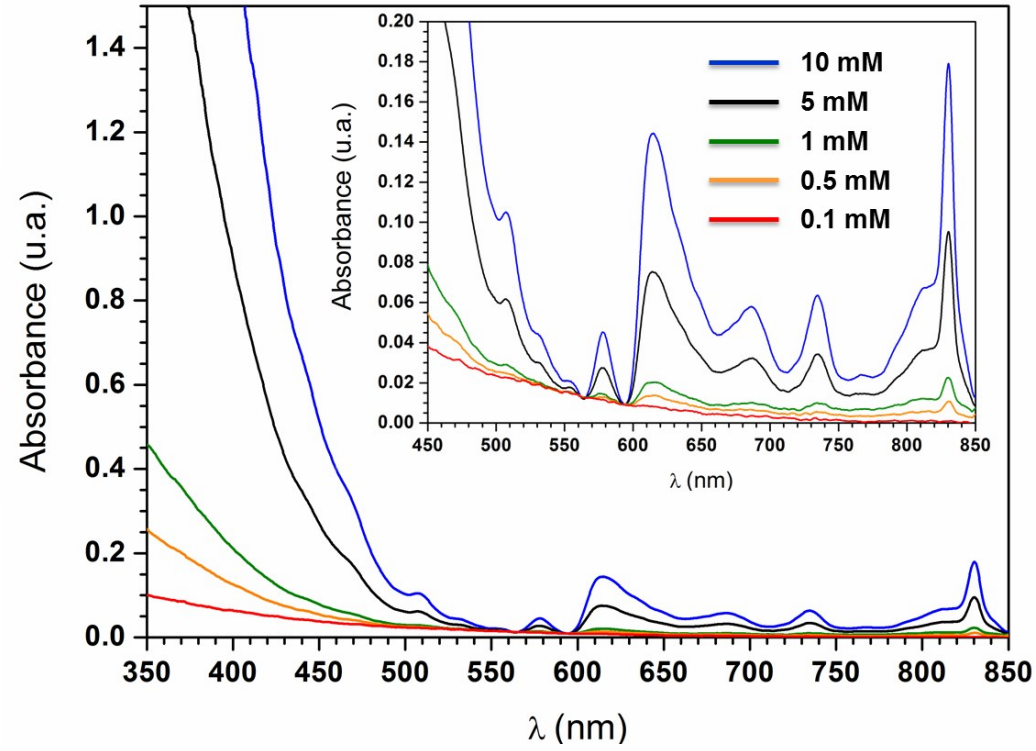


Fig. S4 UV-Vis absorption spectra of stable sonolytic Pu(IV) colloidal suspensions in water at different concentrations: no dilution (0.8 mM, red line) and dilution 10 times in milli-Q water (0.08 mM, black line).

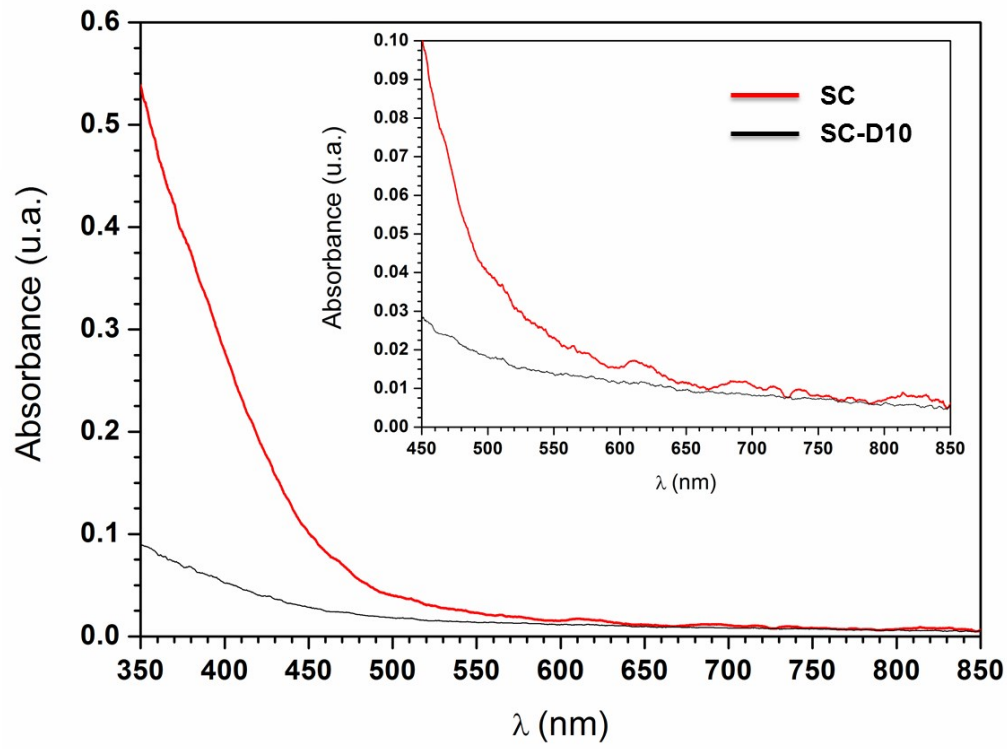


Fig. S5 Fit models applied to SAXS spectra of hydrolytic and sonolytic intrinsic Pu(IV) colloids at different conditions: (i) sonochemical colloid in water diluted 10 times (SC-D10) [disk form factor (red line)], (ii) hydrolytic colloid diluted in HNO_3 42 mM to obtain a final Pu concentration of 10 mM (HC-10-HNO_3), 5 mM (HC-5-HNO_3) and 0.5 mM (HC-0.5-HNO_3) [Guinier model (blue line), sphere form factor (red line), spherical core-shell form factor (green line), sphere form factor with polydispersity (purple line), sphere with SLD gradient (orange line)]; and (iii) hydrolytic colloid diluted in H_2O to obtain a final Pu concentration of 5 mM (HC-5-H_2O) and 1 mM (HC-1-H_2O) [Guinier model (blue line), sphere form factor (red line) and spherical core-shell form factor (green line)]. Insert picture for HC-10-HNO_3 represent the scattering length density profile of each fitting model.

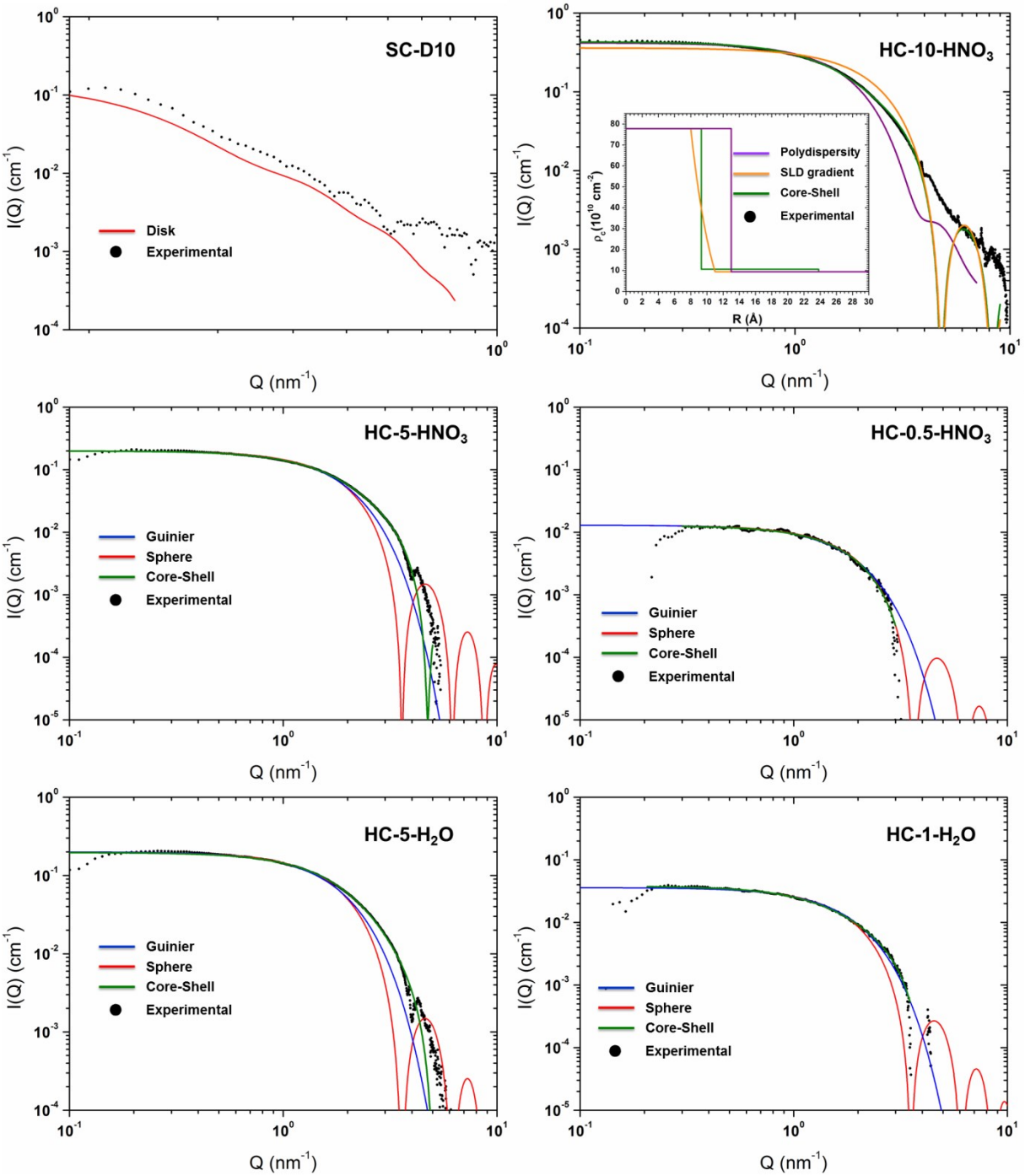


Fig. S6 Scattered SAXS intensity normalized by the theoretical volume fraction (φ_{th}) of 10 mM hydrolytic Pu(IV) colloid (42 mM HNO_3): a) diluted in 42 mM HNO_3 at different concentrations: 10 mM (no dilution; blue squares), 5 mM (black circles) and 0.5 mM (orange triangles); and b) diluted in H_2O at different concentrations: 10 mM (no dilution; blue square), 5 mM (black circle) and 1 mM (green triangle).

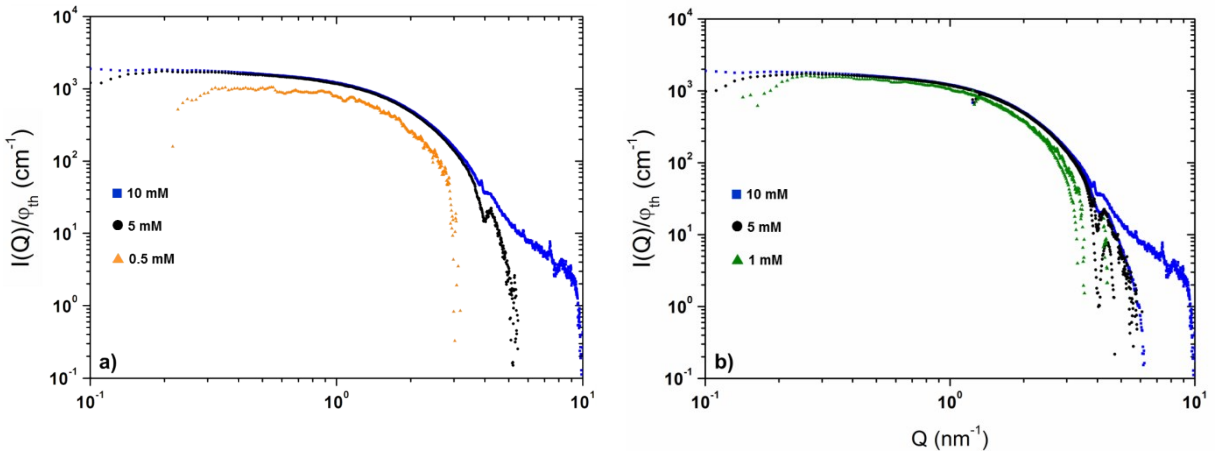


Fig. S7 HR-TEM pictures measured on sonolytic colloids (red) and hydrolytic colloids (blue) with their corresponding electron diffraction patterns. Adapted from Dalodiere et al.[1]

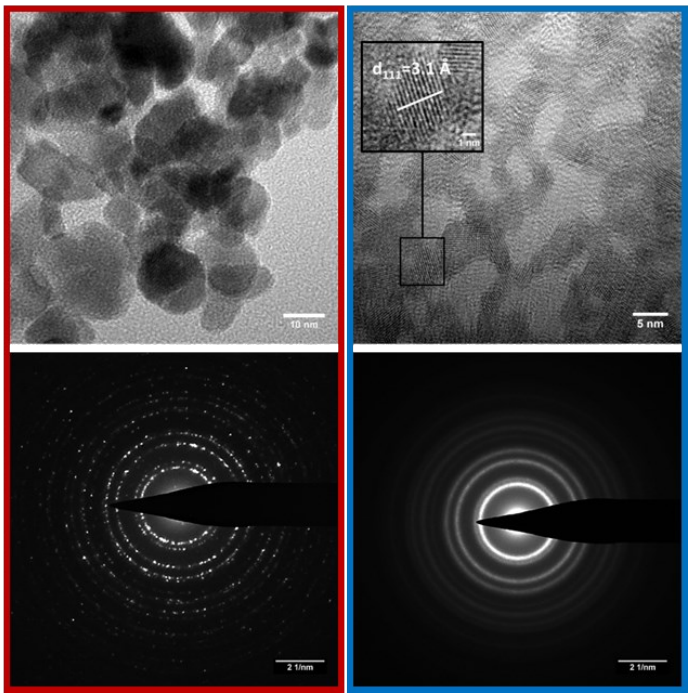


Fig. S8 Normalized Pu L_{III} XANES spectra acquired on a selection of hydrolytic and sonolytic colloids

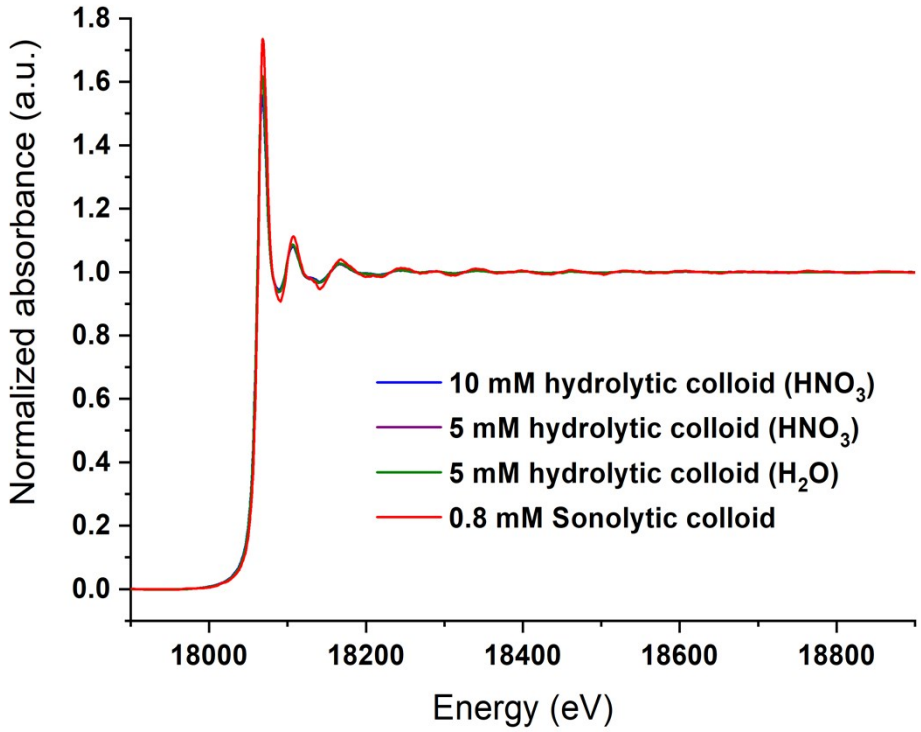


Fig. S9 Pu L_{III} XANES spectra acquired on 10 mM hydrolytic colloid (HNO_3) after several cycles measuring ca. 60 to 90 min per scan. Both figures (a) large view; b) magnification of the area of interest) show the absence of significant variations between the experimental run.

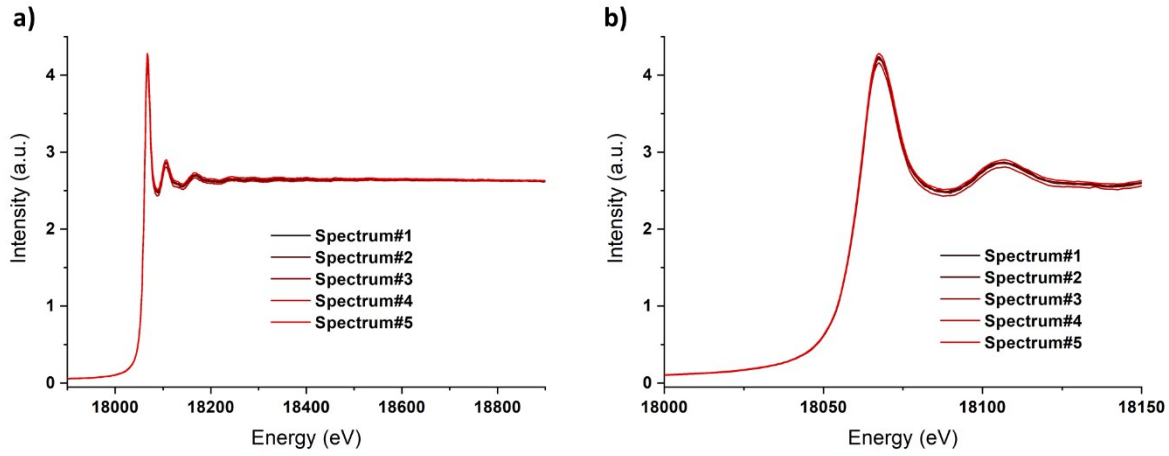


Fig. S10 Derivatives of the normalized Pu L_{III} XANES spectra acquired on a selection of hydrolytic and sonolytic colloids

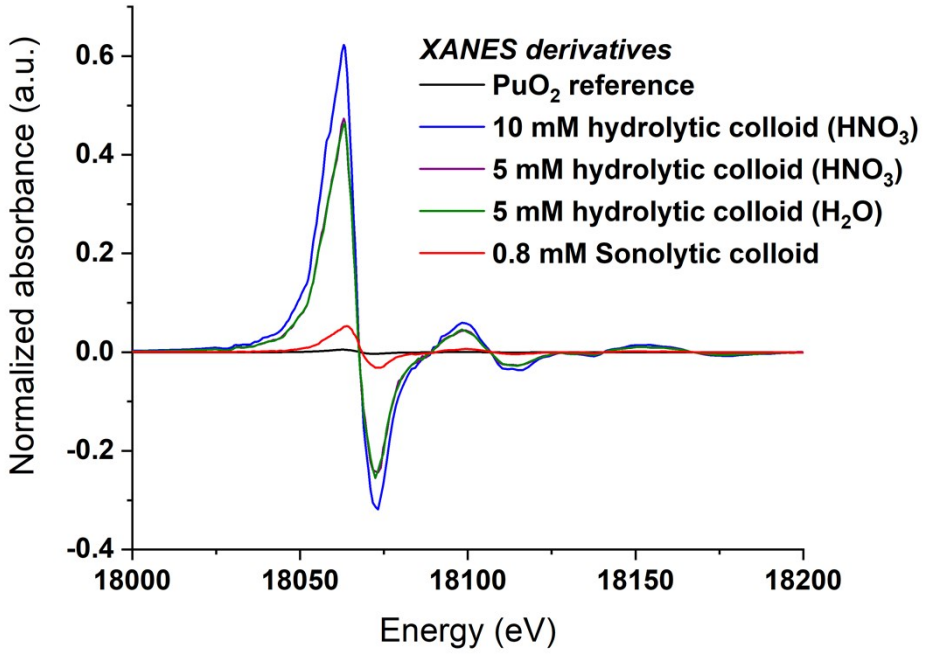


Fig. S11 Normalized Pu L_{III} XANES spectra acquired on a selection of hydrolytic (HC-10-HNO_3) and sonolytic (SC-0.8-H_2O) colloids compared to a) Pu(IV), Pu(III), b) Pu(V) and Pu(VI) references.

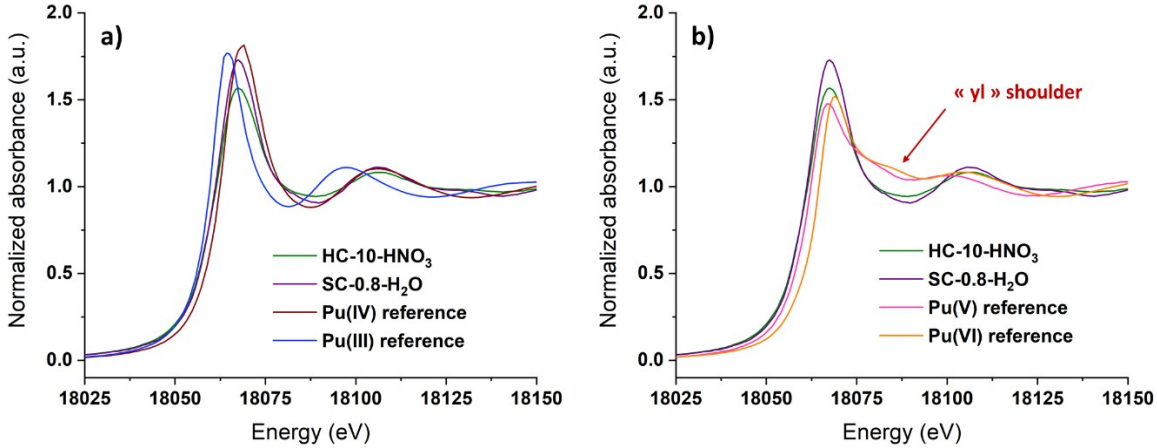


Fig. S12 Modulus (black lines), real (green lines) and imaginary (red lines) parts of the FT for the experimental k^3-weighted EXAFS spectra for a selection of samples.

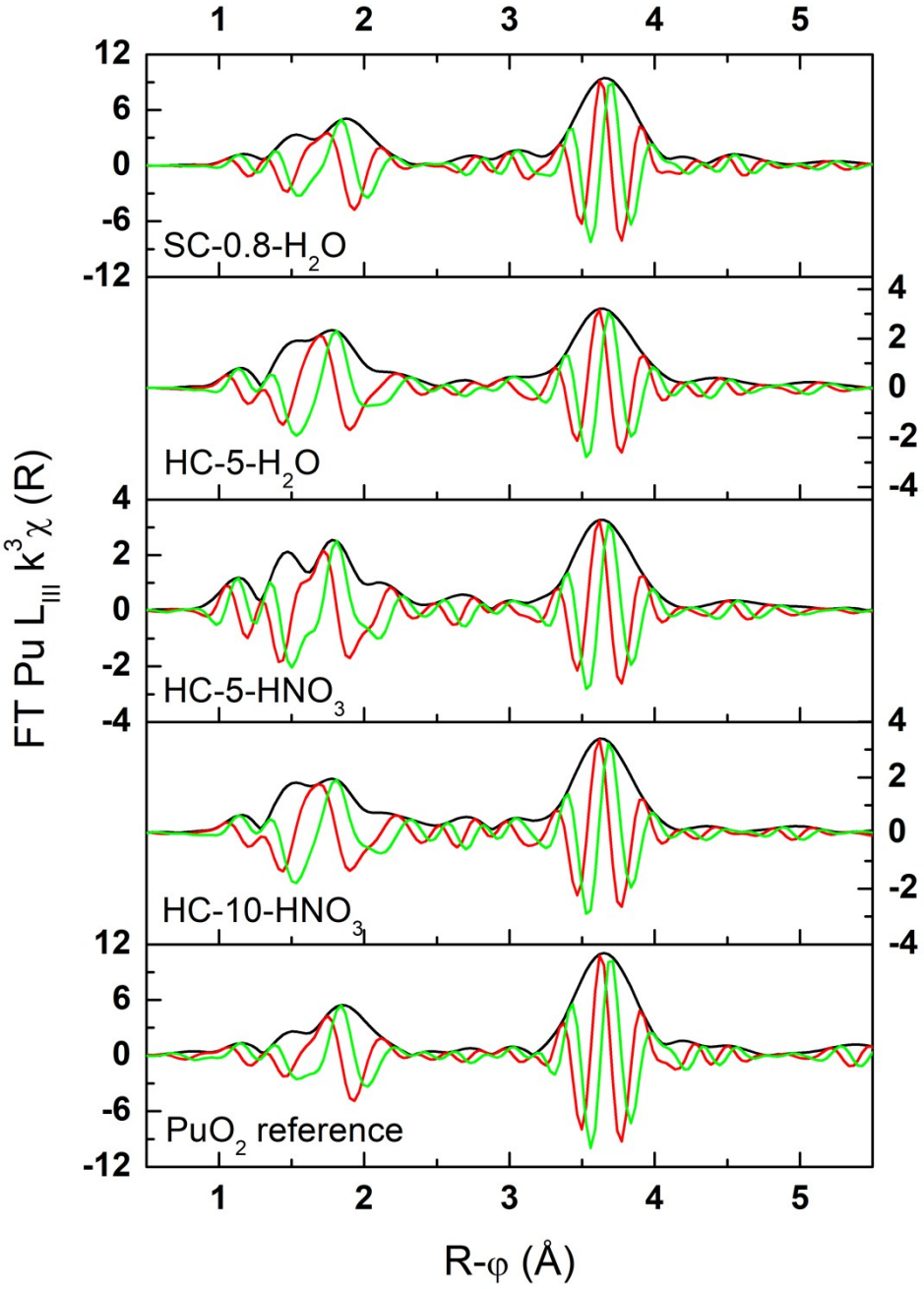
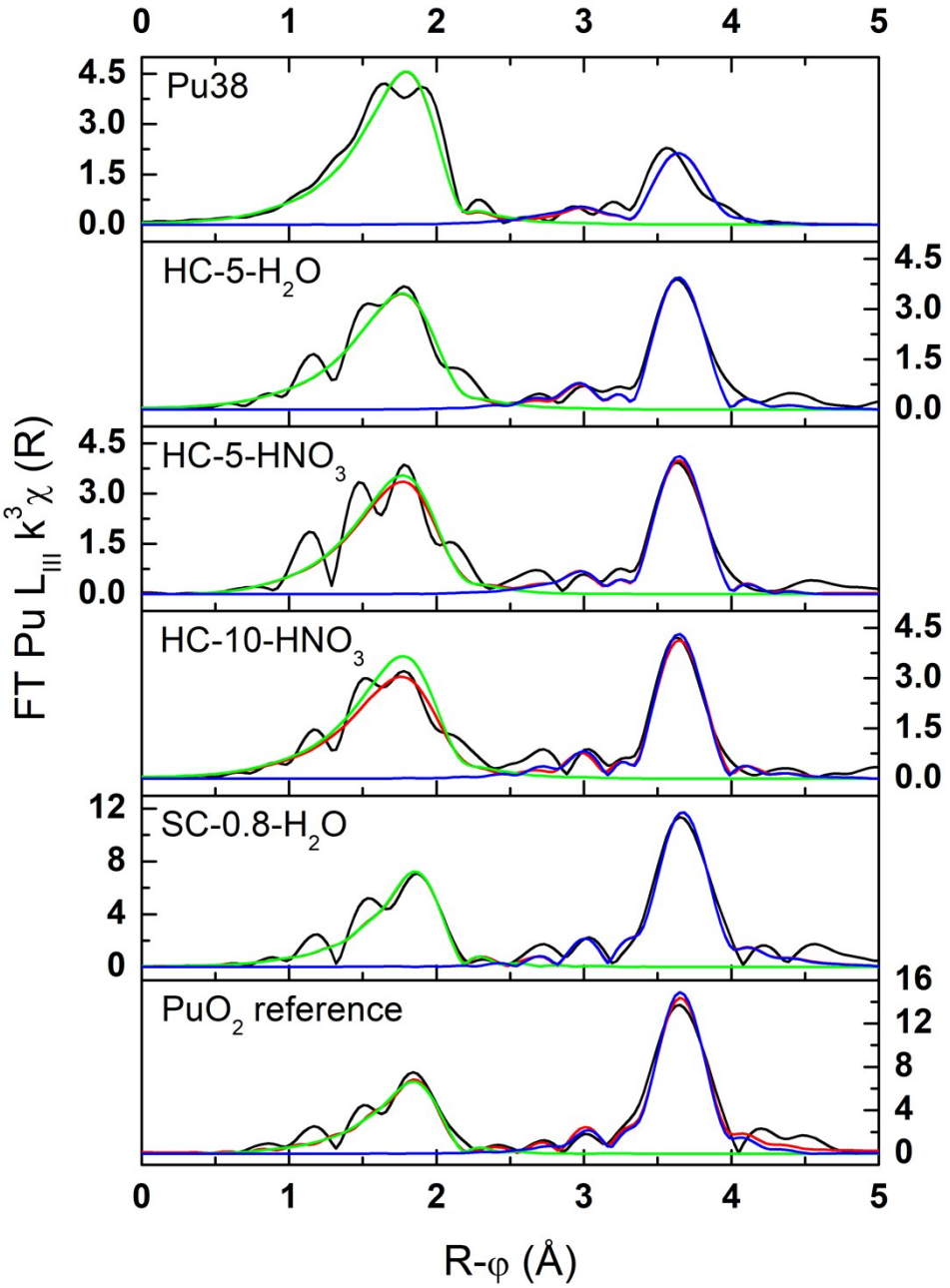


Fig S13. FT of the experimental k^3-weighted EXAFS spectra (black line) superimposed to the best fit results (red line) and the single Pu-O (green line) and Pu-Pu (blue line) scattering paths.



References

1. E. Dalodiere, M. Virot, V. Morosini, T. Chave, T. Dumas, C. Hennig, T. Wiss, O. D. Blanco, D. K. Shuh, T. Tyliszcak, L. Venault, P. Moisy and S. I. Nikitenko, Insights into the sonochemical synthesis and properties of salt-free intrinsic plutonium colloids, *Scientific Reports*, 2017, **7**.