Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Structural and Magnetic Susceptibility Characterizations of Pu(V) Aqua Ion using Sonochemistry as a Facile Synthesis Method

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FIGURE S1

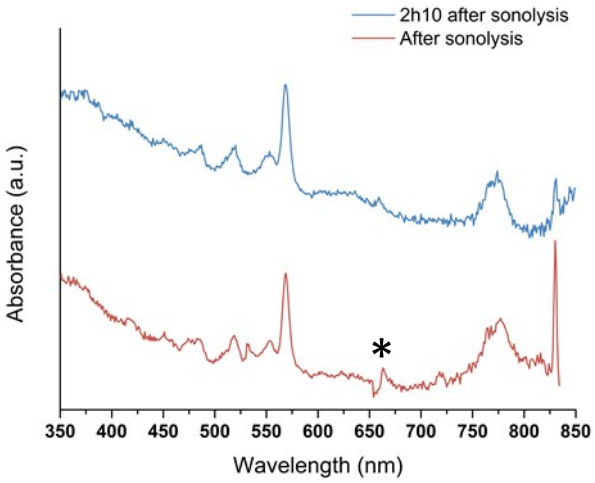


Figure S1: UV-vis spectra of a 1.2 mM Pu(VI) solution sonicated at 21°C under high frequency ultrasound (203 kHz, 0.13 W mL^{-1}, Ar/(20%)O_2). The red spectrum shows the solution composition after 160 min sonication (more than 95% of Pu(VI) is reduced into Pu(V)) while the blue spectrum shows the same solution 2h10 after sonication (<1% of Pu(VI) can be measured in solution). * is an optical artefact due to optic fibers.

FIGURE S2

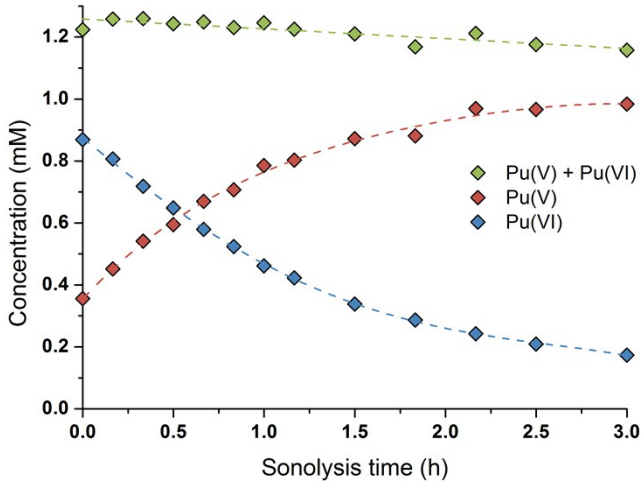
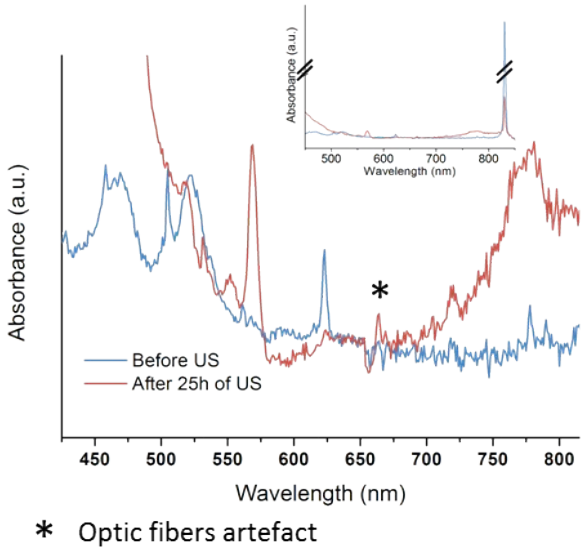


Figure S2: Concentration evolutions of Pu(VI) and Pu(V) under high frequency ultrasound and Ar atmosphere (203 kHz, 21°C, 0.13 W mL^{-1}). The initial solution is a mixture of Pu(VI) and Pu(V) which results from self-irradiation of the mother solution and involved the reduction of a part of the Pu(VI) before the start of the experiments.

FIGURE S3



* Optic fibers artefact

Figure S3: UV-Vis absorption spectra illustrating the behavior of a 1 mM Pu(VI) solution under low frequency ultrasound (20 kHz, 0.34 W mL^{-1}, 21°C, Ar/(20%)O_2) as a function of sonolysis time. The sonication leads to the accumulation of Pu(V) without any other oxidation state for Pu. * is an optical artefact due to optic fibers.

FIGURE S4

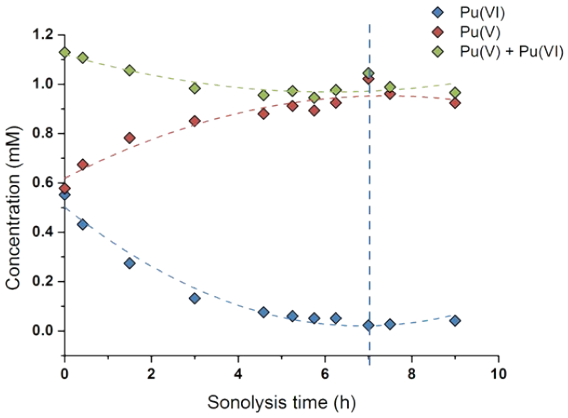


Figure S4: Concentration evolutions of Pu(VI) and Pu(V) under low frequency ultrasound and Ar atmosphere (20 kHz, 0.34 W mL^{-1}). Initial Pu(VI)/Pu(V) ratio is equal to 1 because of self-irradiation of the stock solution which involved the reduction of a part of the Pu(VI) before the start of the experiments.

FIGURE S5

The possible reduction of Pu(VI) by H_2O_2 injections has also been tested in order to confirm the mechanism proposed under ultrasound. Figure S5 (Supporting Information) shows the decrease of Pu(VI) and the increase of Pu(V) concentrations as a function of time after six H_2O_2 injections (0.5 mL at 0.02 M, every 10 minutes). Interestingly, the solution prepared with conventional chemistry exhibits a different Pu(V) aging behavior with the formation of Pu(IV) colloids (see Figure S6, Supporting Information).

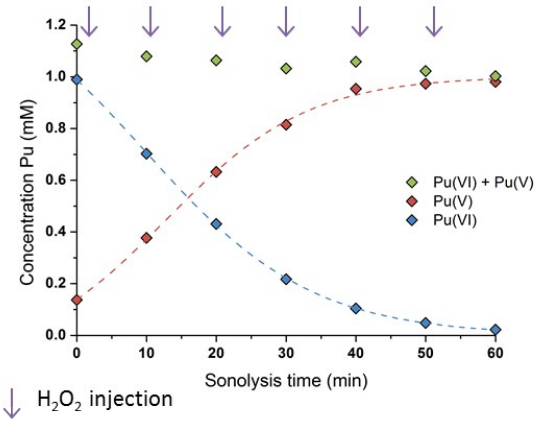


Figure S5: Reduction of a 1 mM Pu(VI) solution at room temperature with the addition of H_2O_2 aliquots (0.02 M, 0.5 mL) represented by the purple arrows.

FIGURE S6

Interestingly the solution prepared with conventional chemistry exhibits a different Pu(V) aging behavior with the observed formation of Pu(IV) colloids. This difference can be related to pH differences and is currently under investigation.

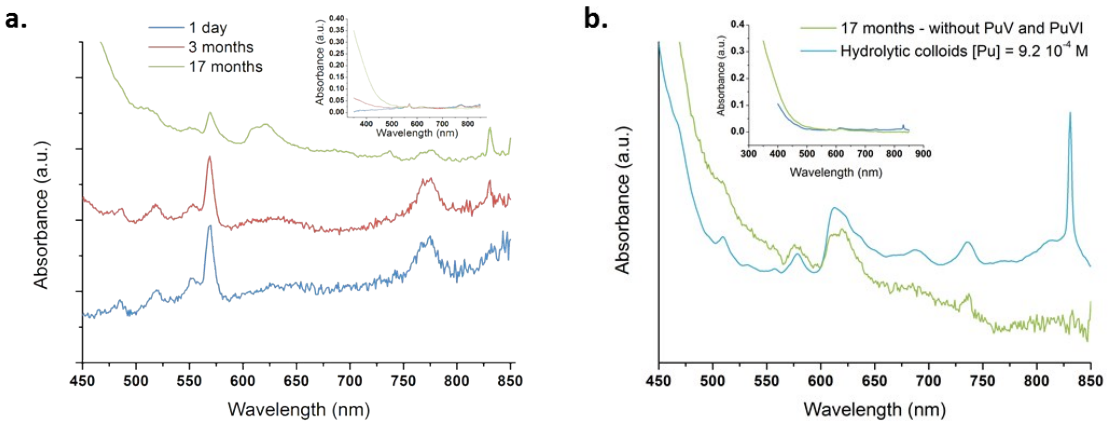


Figure S6: (a) UV-Vis absorption spectra observed after addition of H_2O_2 aliquots to a 1 mM Pu(VI) solution. (b.) UV-Vis absorption spectra obtained for the 1 mM Pu solution after 17 months with the Pu(V) and Pu(VI) contributions mathematically removed. The obtained spectrum exhibit the characteristic peaks from Pu(IV) colloids (blue spectra).

FIGURE S7

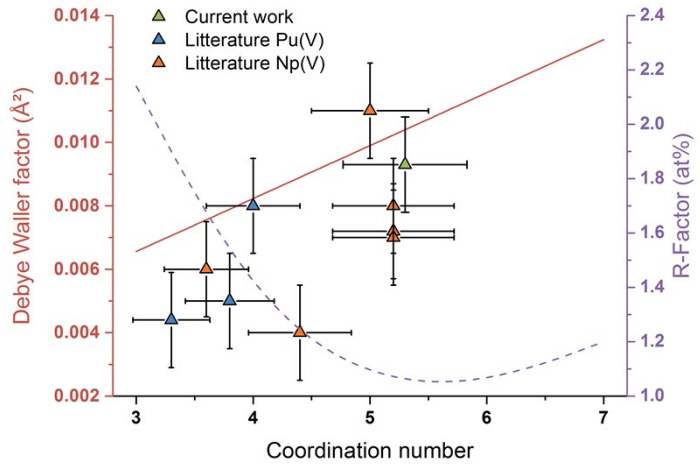


Figure S7: EXAFS fitting parameters obtained for the current work for Pu(V) aqua ion for different $N[O_{eq}(H_2O)]$ interactions and its comparison with Pu(V) and Np(V) literature data

The large error bar in the equatorial oxygen shell coordination number is due to the correlation between the two floating parameters ($N(O_{eq})$ and $\sigma^2(O_{eq})$). Both parameters influence the amplitude of the EXAFS signal. The red line in Figure S7 shows how σ^2 varies with a fixed coordination number and the violet dashed line indicates how the R-factor remains very low for each corresponding $N(O_{eq})$ and $\sigma^2(O_{eq})$ combination. In other words, the best fit from experimental data resulted in a combination of 5.3 water molecules with $\sigma^2(O_{eq})$ equal to 0.009 $Å^{-1}$. However, Figure S7 shows that a combination of 4 water molecules and $\sigma^2(O_{eq})$ equal to 0.007 $Å^{-1}$ (or 6 water molecules with $\sigma^2(O_{eq})$ = 0.012 $Å^{-1}$) would also reproduce very accurately the experimental spectrum (low value of R-factor).

FIGURE S8

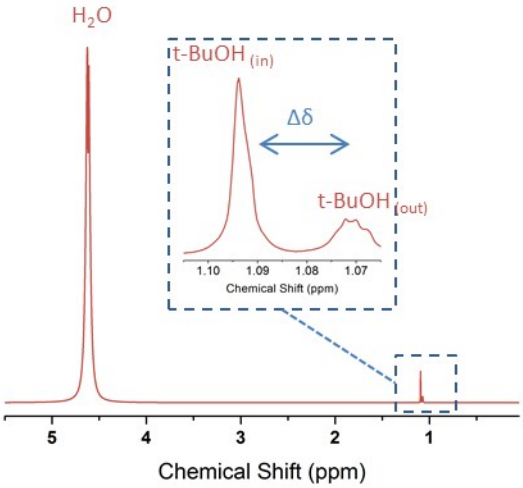


Figure S8: The molar magnetic susceptibility of Pu(V) solutions was calculated by the chemical shift difference Δ*δ* between ^{1}H NMR signal of working (*t*-BuOH in) and reference (*t*-BuOH out) solution using the Evans method. This figure gives a ^{1}H NMR spectrum obtained during the magnetic susceptibility measurement of Pu(V) aqua ion at 25°C.

Note: under our conditions, potential traces of Pu(VI) and H_2O_2 are too small to involve a significant deviation of the magnetic susceptibility thus strengthening the accuracy of our measurements. Some parameters such as radiolysis (with the formation of radical species) or a change of the relative occupancy of the electronic states with the applied temperature could also account for potential data variations but are not plausible in our case. By contrast, considering the relatively weak concentration of Pu(V) and its low magnetic susceptibility, the induced shifts resulting from the Evans method are small and in magnitude order of the digital resolution of the NMR spectra (after Fourier transform) thus explaining small data variations. Bubble formations observed at temperature higher than 50°C led to bad magnetic field homogeneity and therefore precluded magnetic susceptibly measurements but are not responsible for the magnetic susceptibility vagueness at lower temperature.