

Direct conversion of uranium dioxide UO_2 to uranium tetrafluoride UF_4 , using the fluorinated ionic liquid $[\text{Bmim}][\text{PF}_6]$

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SUPPLEMENTARY MATERIALS

Experimental section

Synthesis.

Caution! Uranium precursors are radioactive and chemically toxic reactants, so precautions with suitable care and protection for handling such substances have been followed.

UO₂ was synthesized in one step from the dehydration at 700°C (H₂@Ar, 2%) of uranium trioxide UO₃.xH₂O provided by Orano. After the thermal treatment, UO₂ is stored in argon atmosphere in a dedicated glovebox (Jacomex GP Campus).

For the synthesis of UF₄, UO₂ (40 mg, 0.15 mmol) was mixed with 2 ml (2.74 g, 9.64 mmol) of [Bumim][PF₆] (Sovionic, 99.5 %) in a 23 ml Teflon cell under Ar atmosphere in a glove box. The closed reactor is then removed from the glove box and placed in a closed stainless steel Parr autoclave (type 4746) and heated at 180°C in a closed oven from 12 h to 96 h. At the end of the reaction, the resulting solid is centrifugated and washed with CH₂Cl₂ (3 x 5 ml) in order to remove traces of ionic liquid. The resulting supernatant and solid are then stored in the glove box before further characterizations.

Techniques

Powder X-ray diffraction. The powder X-ray diffraction patterns were collected at room temperature with a D8 advance A25 Bruker apparatus with Bragg–Brentano geometry (θ - 2θ mode).

Gas sorption. The gas sorption experiments were realized on UF₄ using a Micromeritics ASAP2020 apparatus. Prior to measuring, the solid was degassed at 150 °C for approximately 6 h until the outgas rate was <4 μ mHg. The BET surface was estimated by a krypton sorption isotherm experiment in liquid nitrogen (77 K) from p/p_0 range: 0.02–0.2.

ICP OES. Inductively coupled plasma optical emission spectrometry were realized on an Agilent 5100 dual view, using commercial standards (1g/L) of thorium (Fisher Scientific) and uranium (Inorganic Ventures).

XPS

The XPS spectra were recorded on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatized Al K α X-ray source, operating at 225 W. High-resolution spectra were collected using an analysis area of \approx 300 μ m \times 700 μ m and a 20 eV pass energy. The Kratos charge neutralizer system was used for all analyses. Samples were prepared by placing few drops of the ionic liquid into a cavity on a molybdenum Kratos sample stub. The pressure during the analysis was 2.10⁻⁹ Torr. The binding energies were corrected taking N 1s peak corresponding to the IL imidazolium type bonding at 402.1 eV as a reference.

UV-Vis spectroscopy

UV-Vis spectrum was measured on a Perkin-Elmer Lambda 650 spectrometer.

NMR.

The NMR spectra were recorded on Bruker AVANCEII 400, AVANCEIII 300 and AVANCE NEO 300 spectrometers equipped respectively with a 5 mm BBO, a 5 mm BBO and a 5 mm BBFO probes, respectively.

Half a milliliter of each sample was transferred into standard 5 mm NMR tube. In order to prevent any modification by adding any substance into the samples, a coaxial insert containing D₂O was used to lock and shim each analysed sample.

Mono-dimensional ¹⁹F, ³¹P and ¹³C-DEPT were recorded at 303K.

EXAFS/XANES. XAS experiment was performed at the MARS beamline of Synchrotron SOLEIL, which is dedicated to the study of radioactive samples.^[1] For the optics of the beamline, the monochromator was set with the Si(220) crystals and the mirrors with the Pt strips at 3.1 mrad. The energy of the monochromator was calibrated by measuring the K edge of an Yttrium foil and defining the inflection point at 17038 eV. All the measurements were recorded in fluorescence mode using the HP Ge multi-element detector and were performed in specific 200 μL solutions cells. Data was processed with the ATHENA and ARTEMIS codes.^[2] The k³ EXAFS signal was fitted in R space, considering a U-F contribution obtained by using theoretical phase and amplitude calculated with FEFF6 code^[3] starting from the structure of uranium fluoride (Larson et al.). A Hanning window in the range [2,32 ; 14,06] and a fitting range with R [1,01 ; 2,0] was adopted. Different fits were performed with different fixed coordination numbers. Best fits were in particular obtained with 4, 5 or 6 neighbours, as shown in table S1. The coordination number was fixed to 5. Tests were also performed with 4 or 6 neighbours. The quality of these different fits is unchanged with respectively decreasing values for amplitude S₀². The fit considering 5 neighbours is the one leading to a S₀² closer to the usual value of 0.9 observed for actinides. However the quality was less good.

Characterization

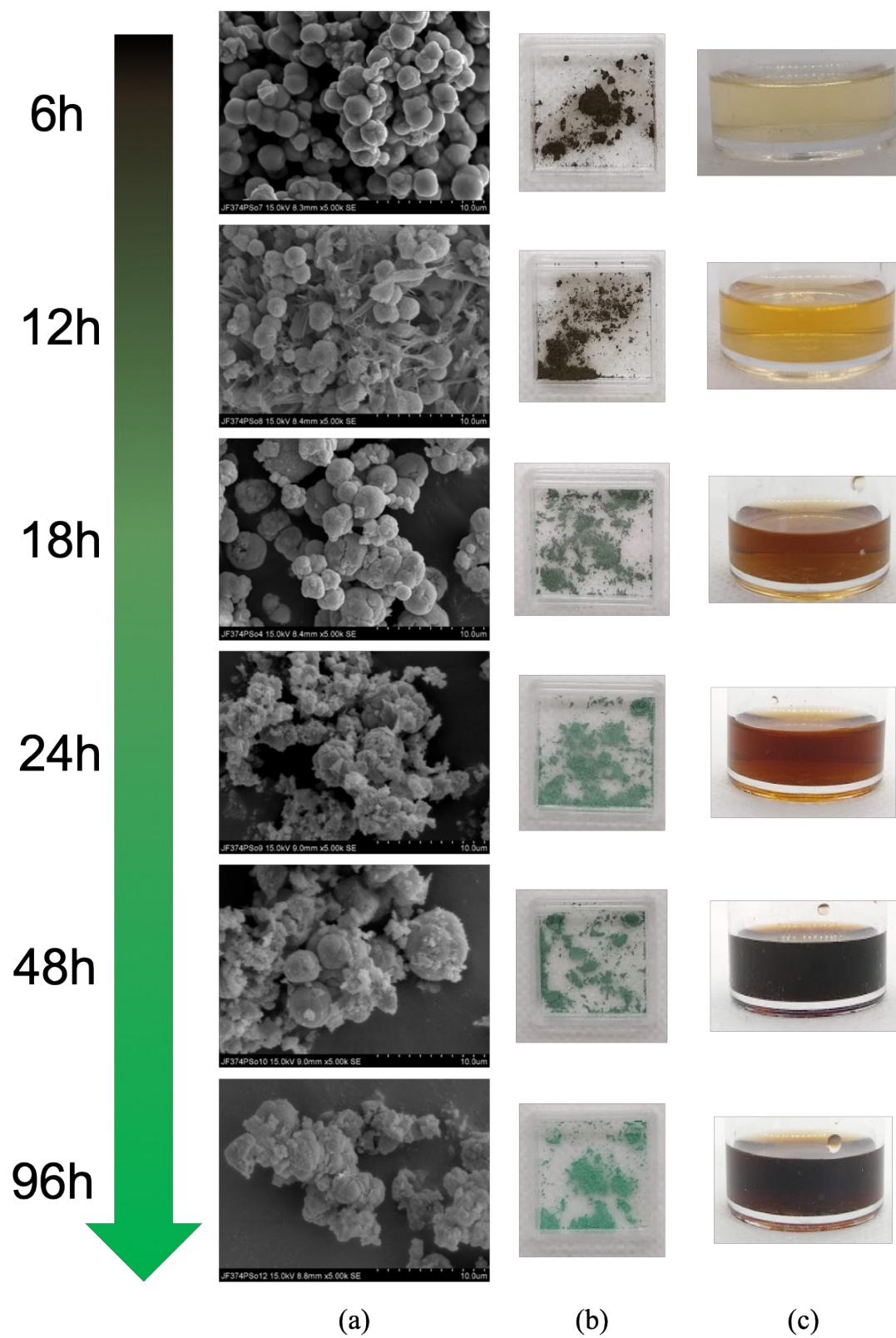


Fig. S1 Pictures of the supernatants and the powders collected after thermal treatments in a conventional oven at 180°C from 6 to 96 h.

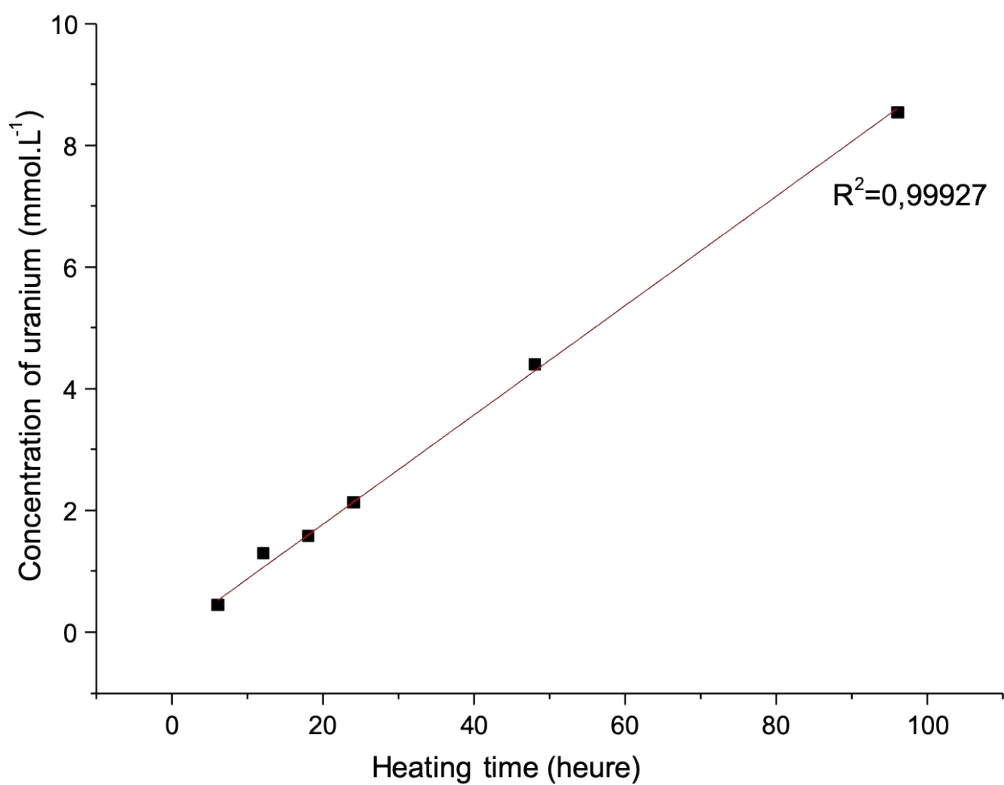


Fig. S2 Concentration of uranium in the supernatant collected during the synthesis at 180°C of UF₄ in [Bmim][PF₆], from 6h to 96h.

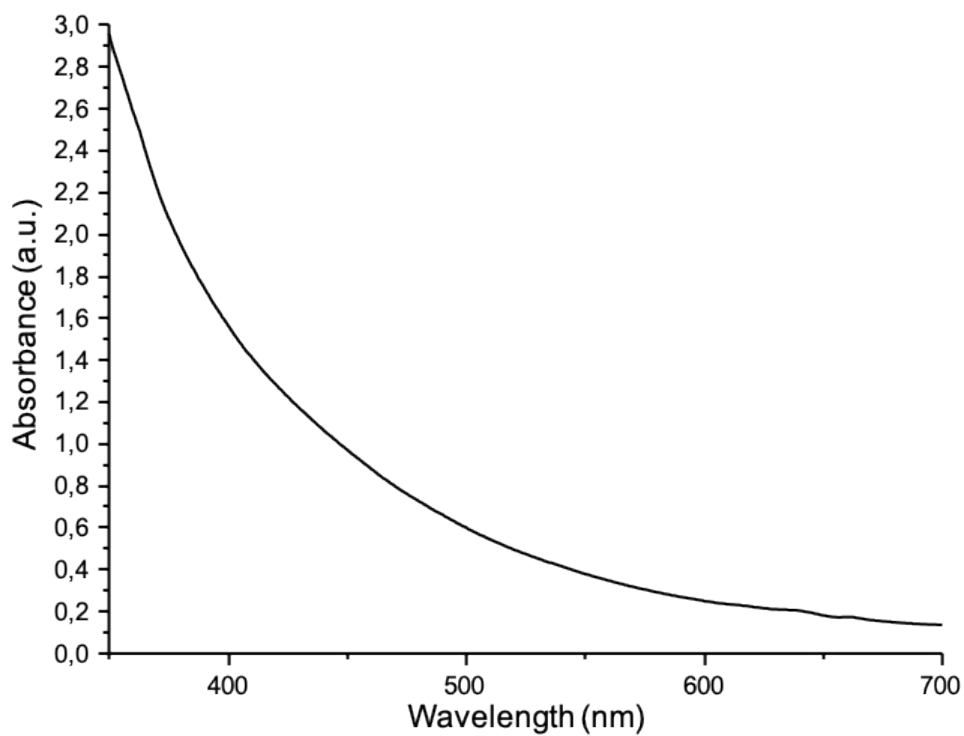


Fig. S3 UV-Vis spectrum of the supernatant collected after the synthesis of UF₄ in [Bmim][PF₆] (96h, 180°C).

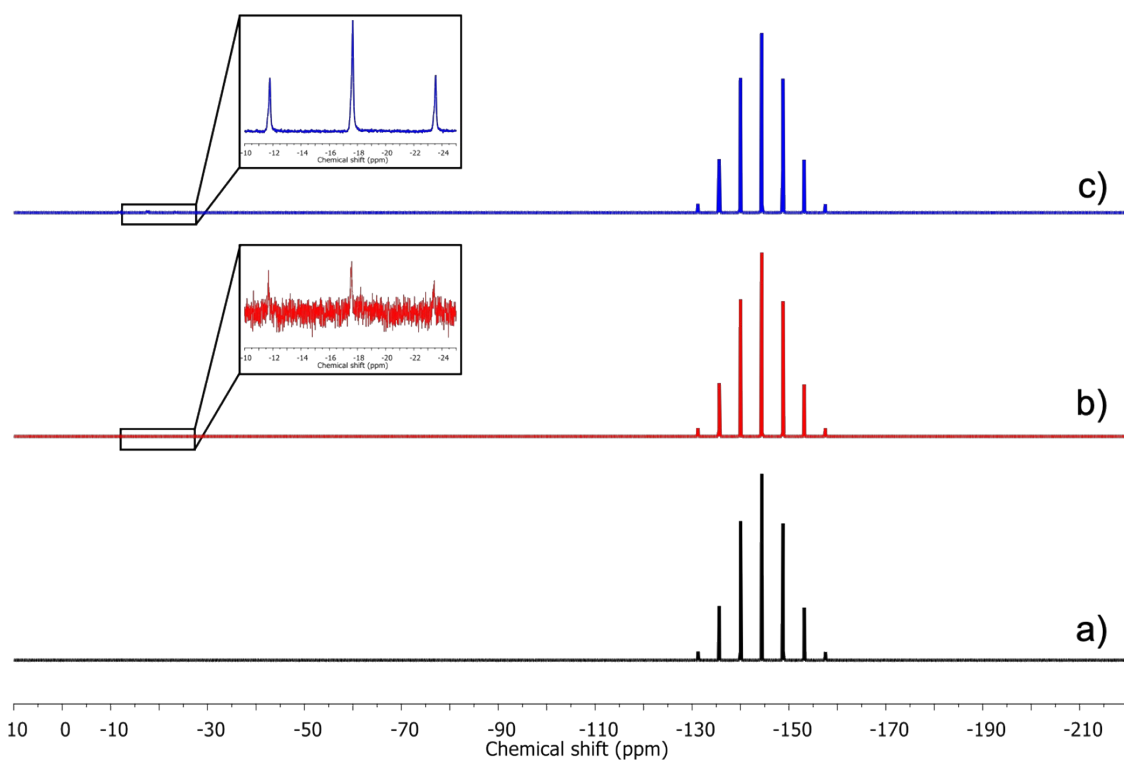


Fig. S4 ^{31}P NMR spectra recorded at 303 K and 7.0 T of neat $[\text{Bmim}][\text{PF}_6]$ (a), $[\text{Bmim}][\text{PF}_6]$ treated at 180°C during 24 h without uranium (b) and the supernatant collected after the precipitation of UF_4 after a reaction at 180°C during 24 h in a conventional oven (c).

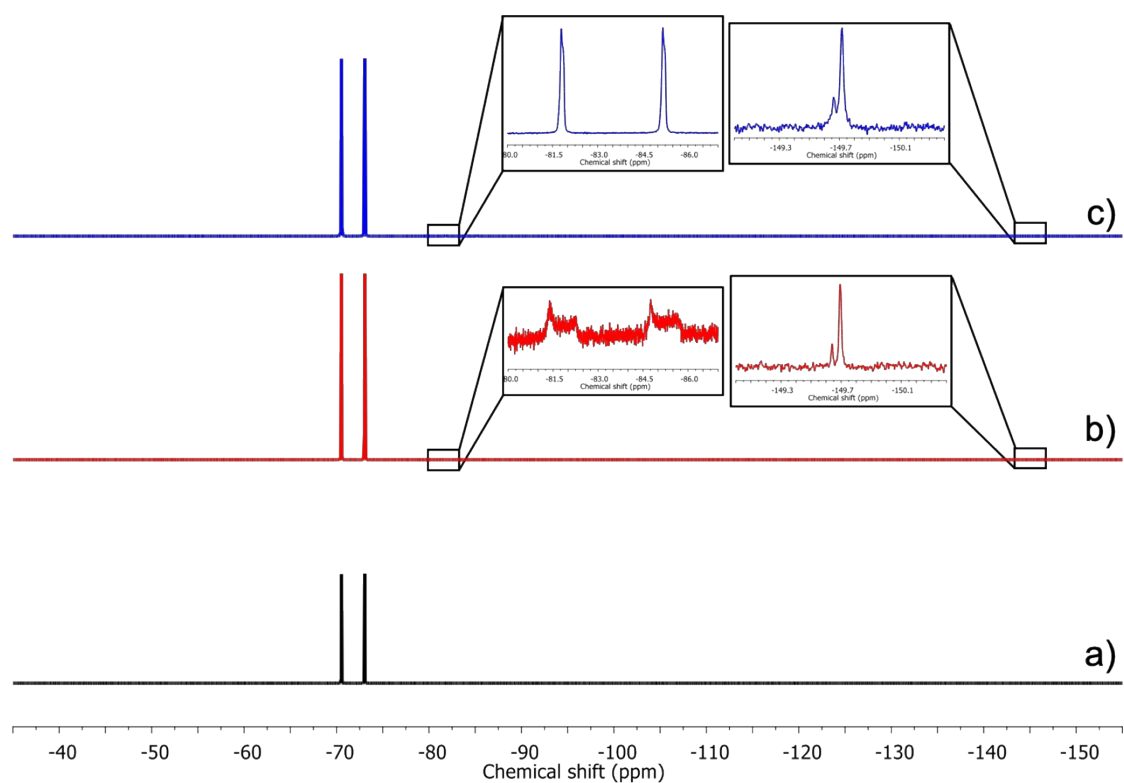


Fig. S5 ^{19}F NMR spectra recorded at 303 K and 7.0 T of neat $[\text{Bmim}][\text{PF}_6]$ (a), $[\text{Bmim}][\text{PF}_6]$ treated at 180°C during 24 h without uranium (b) and the supernatant collected after the precipitation of UF_4 after a reaction at 180°C during 24 h in a conventional oven (c). In (c) the doublet centered at -149.7 ppm is assigned to traces of BF_4^- coming from the reactivity between fluoride and the borosilicate-based NMR tube.^[4]

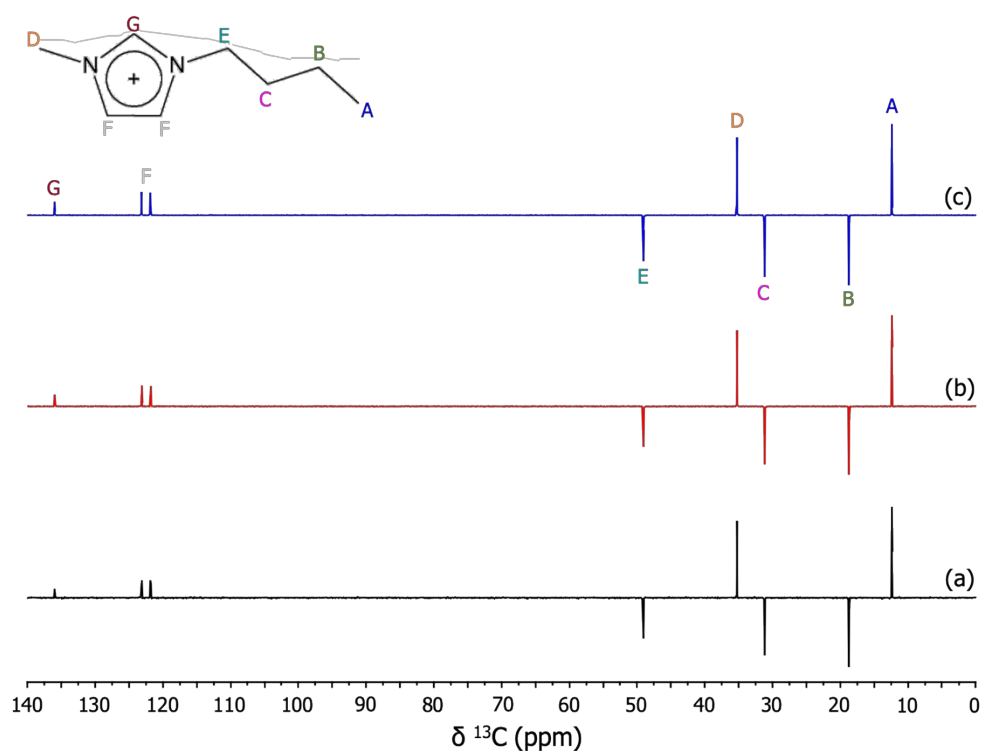


Fig. S6 ¹³C NMR-DEPT35 spectra recorded at 303 K and 7.0 T of neat [Bmim][PF₆] (a), [Bmim][PF₆] treated at 180°C during 24 h without uranium (b) and the supernatant collected after the precipitation of UF₄ after a reaction at 180°C during 24 h in a conventional oven (c)

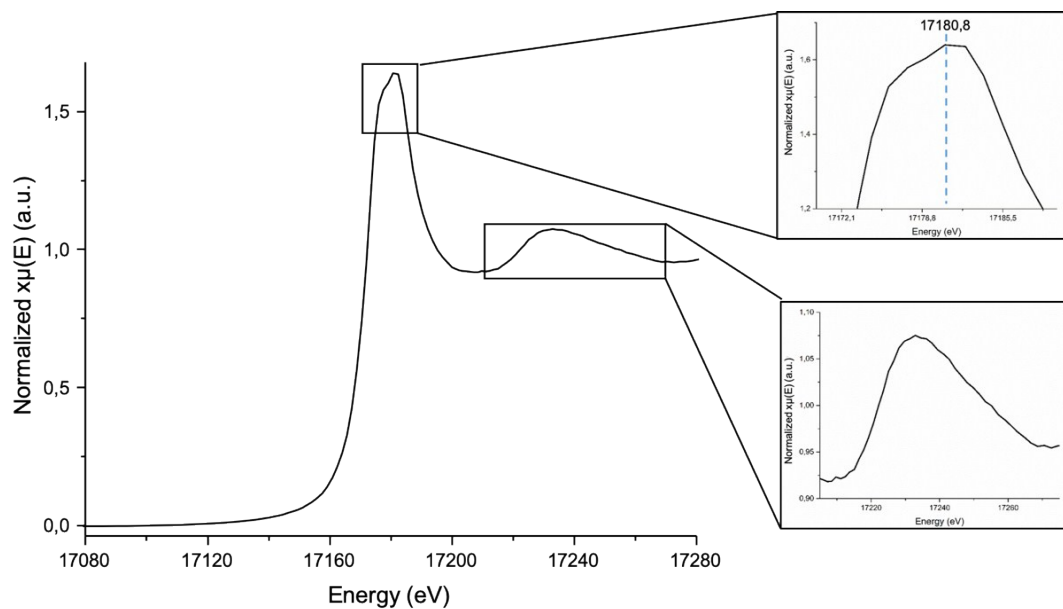


Fig. S7 Normalized U-L₃ XANES spectrum of the supernatant sample (24h, 180°C).

Table S1. EXAFS fitting results obtained for the supernatant sample with U-F contribution and different fixed coordination numbers.

Fit	N*	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	S_0^2	R-factor	χ^2_{red}
1	4	2.060(4)	0.0018(5)	2.2(6)	1.10(5)	0.86%	43.5
2	5	2.060(4)	0.0018(5)	2.2(6)	0.88(4)	0.86%	43.5
3	6	2.060(4)	0.0018(5)	2.2(6)	0.73(3)	0.86%	43.5

*=fixed

References

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- [2] B. Ravel, M. Newville, *J. Synchrotron Rad.* **2005**, *12*, 537-541.
- [3] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, M. J. Eller, *Phys. Rev. B* **1995**, *52*, 2995-3009.
- [4] K. Takao, Y. Ikeda, *Chem. Lett.* **2008**, *37*, 682-683.