## Supporting information for the manuscript

# Ligand Assisted Cleavage of Uranium Oxo-Clusters

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**General considerations:**

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. The solvents were purchased from Aldrich in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (pyridine, thf, hexane and diisopropylether) or $CaH_2$ (acetonitrile). Depleted uranium turnings were purchased from the "Société Industrielle du Combustible Nucléaire" of Annecy (France). dbmH was purchased from Aldrich and dried under *vacuum*. $[UI_3(thf)_4]$[1] complex **1** and the clusters mixture $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}]^{n-}$ (n=0, 2, 4) were synthesized as previously described.[2]

Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany.

FTIR spectra were recorded with a Perkin Elmer 1600 Series FTIR spectrophometer. UV-Visible measurements were carried out with a Varian Cary 50 Probe spectrophotometer in quartz cells (optical path lengths: 1 mm and 1cm) adapted with Young valves.

$^1H$ NMR spectra were recorded on Varian UNITY 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference.

Static magnetic properties were measured using a Quantum Design SQUID MPMS-XL 5.0 susceptometer. Ultra-Low Field Capability ±0.05 G for the 5 T magnets. Continuous Low Temperature Control/Temperature Sweep Mode (CLTC) - Sweep rate: 0.001 - 10 K/min.

The samples were pressed under argon into an aluminium container which was then sealed in a 5mm Suprasil-Quartz tube. Contribution to the magnetization from the container and tube were measured independently and subtracted from the total measured signal. Diamagnetic corrections were made using Pascal's constants.

## X-Ray crystallography

Synchrotron radiation with λ= 0.69408 Å and MAR345 detector were used for data collection for the structure of **2**•$2CH_3CN$ (SNBL at the ESRF). The structure of **2**•$2CH_3CN$ was solved by direct methods and refined by a full-matrix least-squares technique on $F^2$ using the *SHELXH-97* program.

Crystal data: Crystal data for **2**•$2CH_3CN$: $[U_6O_4(OH)_4(\eta\text{-dbm})_{12}]\cdot 2CH_3CN$ $C_{184}H_{142}N_2O_{32}U_6$, M = 4321.18, Triclinic, space group *P*-1, a = 18.2263(6), b = 18.9950(10), c = 26.5602(7) Å, α = 75.858(3), β = 79.099(2), γ = 64.725(4), V = 8025.3(5) $Å^3$, Z = 2, $\rho_c$ = 1.788 g $cm^{-3}$, $\mu$ = 6.108 $mm^{-1}$, *T* = 100(2) K. Of the 31621 reflections collected, 24813 were unique ($R_{int}$ = 0.0505). $R_1$ = 0.0832, $wR_2$ = 0.2223. Max/min residual density 10.304 and -5.052 $eÅ^{-3}$. Similarity restraints were imposed on the U-factors and bond distances in the acetonitrile molecules. All hydrogen atoms were refined using the riding model. Main peaks of the residual electron density are located in the close vicinity of the uranium atoms. The O-H groups of the hydroxo-ligand are indeed not bonded to electron acceptors. 93% completeness of the data is due to the fact that some reflections stayed on the rotation axis, had no reliable intensity and therefore were not integrated.

Diffraction data for **2·1.5py·0.5thf** were taken using a Bruker SMART CCD area detector three-circle diffractometer $2\Theta_{max}$=46.6° (Mo-Kα radiation, graphite monochromator, $\lambda$ = 0.71073 Å), controlled by the Bruker SMART program. To prevent oxidation and evaporation of co-crystallized solvent molecules, the crystals were coated with light hydrocarbon oil and the data were collected at -50°C. The cell parameters were obtained with intensities detected on three batches of 15 frames with a 10 s exposure time. The crystal-detector distance was 5 cm. For three settings of $\Phi$, 1271 narrow data were collected for 0.3° increments in ω with a 30 s exposure time. At the end of data collection, the first 50 frames were recollected to establish that crystal decay had not taken place during the collection. Unique intensities with $I > 10\sigma(I)$ detected on all frames using the Bruker SAINT program[3] were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the Bruker SADABS program[4]. The structure was solved by direct methods using the Bruker SHELXTL 6.14 package[5] and all non hydrogen atoms, were found by difference Fourier syntheses. All non-hydrogen atoms except, C52 and C8, were anisotropically refined on *F*. Hydrogen atoms were included in calculated positions. The Hydrogens were included in fixed position.

Few A alerts remain in the checkcif file which are explained in the following paragraph:

Most remaining alerts deal with the large anisotropic displacement parameters of carbon atoms in the phenyl substituents and they are due to thermal or crystallographic disorder.

The other alert (C202-C203 distance) concerns the pyridine solvent and is caused by the position of the solvent on a symmetry centers rendering the nitrogen atom disordered.

## Syntheses:

**Potassium dibenzoylmethanoate (dbm)K:** A solution of dbmH (200 mg, 0.89 mmol, 1eq) in thf (3 mL) was added to a suspension of KH (39.2 mg, 0.98 mmol, 1.1 eq) in thf (1 mL). The mixture was stirred 1h until the gaseous clearing was complete. After filtration of the excess of KH, 4 mL of diisopropylether was slowly added to the pale yellow filtrate. The precipitate which was formed was filtrated, washed with a small amount of thf and dried. We obtain 208 mg (0.79 mmol, 88 %) of dbmK salt.

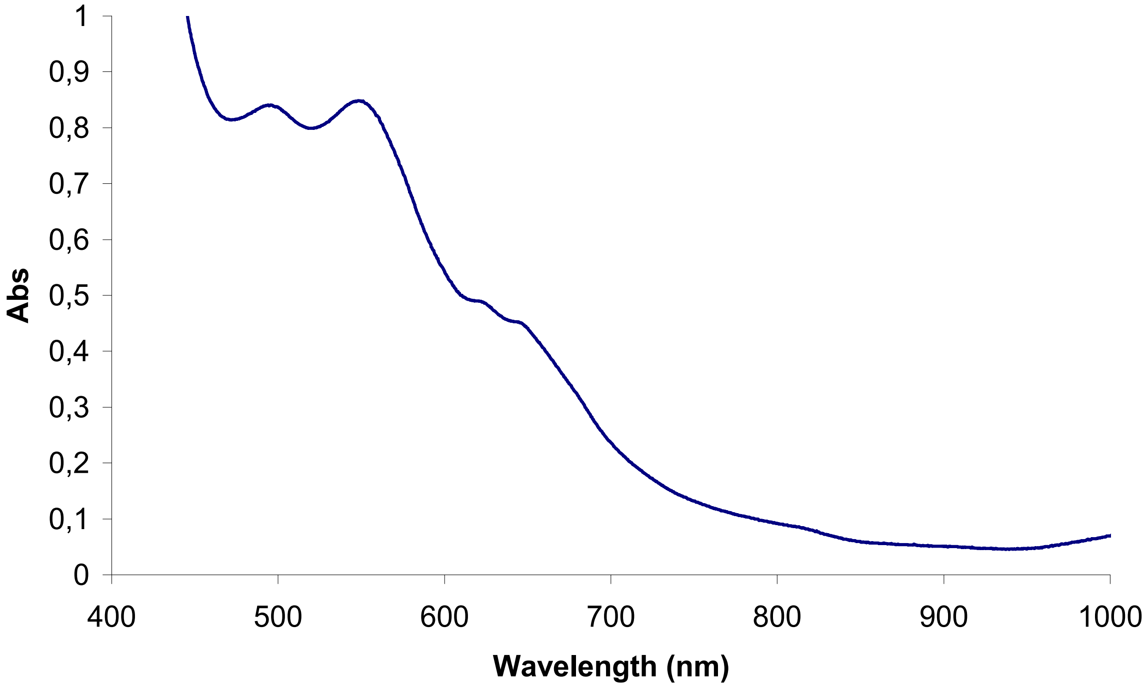
**Synthesis from [$UI_3(thf)_4$]:** An acetonitrile solution (1 mL) of potassium triflate (32.3 mg, 172 µmol, 2 eq.) was added to a solution of $UI_3(thf)_4$ (78 mg, 86 µmol, 1eq.) in anhydrous acetonitrile (1 mL). An acetonitrile solution of water was added via a microsyringe (344 μL, 0.5M in $CH_3CN$, 172 μmol, 2 eq.). The colour of the solution changed immediately from dark green to brown. After stirring for 16 hours at room temperature the brown solution became light emerald green. A dark precipitate formed which was removed by filtration. The resulting green solution was added to an acetonitrile solution (0.5 mL) of dbmK (45.1 mg, 172 μmol, 2eq.). The solution became immediately red and a precipitate formed slowly. The suspension was stirred at room temperature for 2h until the solution became light red and a purple precipitate formed. After filtration, the precipitate was washed with a small amount of acetonitrile and dried to yield 35.3 mg (48%) of a dark powder. A recrystallisation from pyridine and hexane allowed the isolation of X-ray suitable dark crystals. $^1$H NMR (Py-$D_5$, 400MHz, 298K): δ 15.29 (s, br, 12H) ; 6.86 (s, br, 24H) ; 3.87 (s, br, 48H) ; 0.45 (s, br, 48H). $^1$H NMR (thf-$d_8$, 400MHz, 298K): δ 15.08 (s, br, 12H) ; 6.60 (s, br, 24H) ; 3.54 (s, br, 48H) ; 0.11 (s, br, 48H).

**Synthesis from the isolated clusters mixture $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}]^{n-}$ (n=0, 2, 4).** 12.4 mg of the turquoise-green solid of the $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}]^{n-}$ (n=0, 2, 4) mixture were dissolved in acetonitrile (0.3 mL) and added in a solution of dbmK (11.6 mg, 44 μmol). The solution turns to red and a precipitated formed. The suspension was stirred 2h at room temperature until the solution became light red and a purple precipitate was formed. After filtration, the powder was washed with a small amount of acetonitrile and it was obtained 8.8 mg of a dark powder (42%). $^1$H NMR (Py-$D_5$, 400MHz, 298K): δ 15.29 (s, br, 12H) ; 6.86 (s, br, 24H) ; 3.87 (s, br, 48H) ; 0.45 (s, br, 48H).

$^1$H NMR (thf-$d_8$, 400MHz, 298K): δ 15.07 (s, br, 12H) ; 6.60 (s, br, 24H) ; 3.54 (s, br, 48H) ; 0.11 (s, br, 48H).

## Solution studies:

**Figure S1:** UV-Visible spectrum (C = 0.37 mM) of **2** in pyridine solution



## Diffusion coefficients:

The translational diffusion coefficient (D) of **2** and of the monomeric [U(dbm)$_4$] complex were determined by NMR experiments (using a Pulsed-Field Gradient STimulated Echo (PFGSTE) sequence). As the compounds are measured under the same conditions the comparison of both values allows calculating the molecular weight of **2** (eq 1). The measured molecular weight is M = 4343 ± 300 gmol$^{-1}$, which is in good agreement with the expected value based on the formula (M = 4239.21 gmol$^{-1}$). This indicates that the cluster is retained in solution.

$$\frac{D_1}{D_2} = \sqrt[3]{\frac{M_2}{M_1}} \qquad (1)$$

**Figure S2:** NMR spectrum of the complex **2** after 5 day in thf (red dots for complex $[U(dbm)_4]$ used as a reference, green dots for cluster **2** and * for impurities and solvents.)

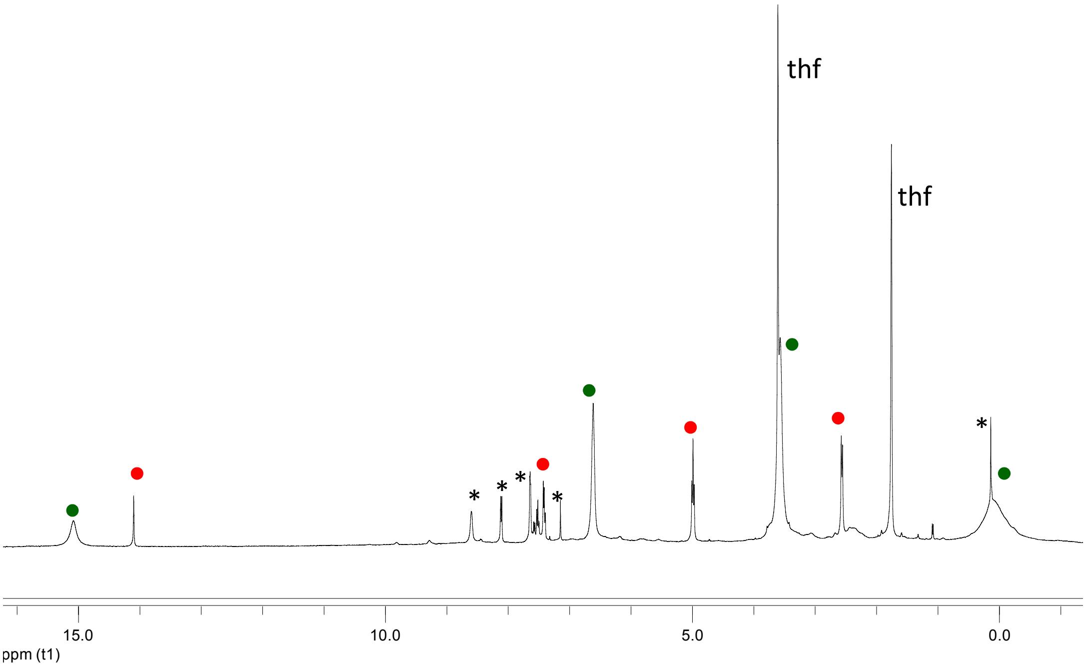
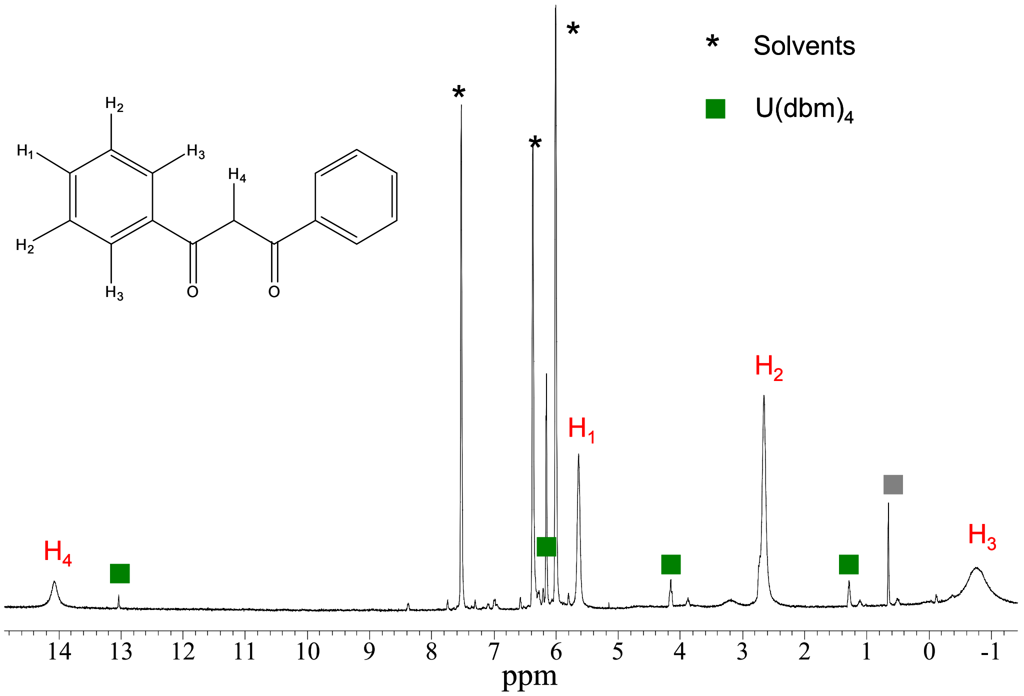


**Table S1:**

| Conditions | Compound | D [m².s$^{-1}$] | $r_{sph}$ [Å] | M [g.mol$^{-1}$] |
|---|---|---|---|---|
| THF | $[U_6O_4(OH)_4(dbm)_{12}]$ (**2**) | 5.8(1) $10^{-10}$ | 7.8 | 4343 (calc.) |
| η=0.48 mPa.s @ 298K | $[U(dbm)_4]$ | 9.1(1) $10^{-10}$ | 5.0 | 1131 (ref.) |

**Figure S3:** NMR spectrum of the complex **2** after **1** day in pyridine.



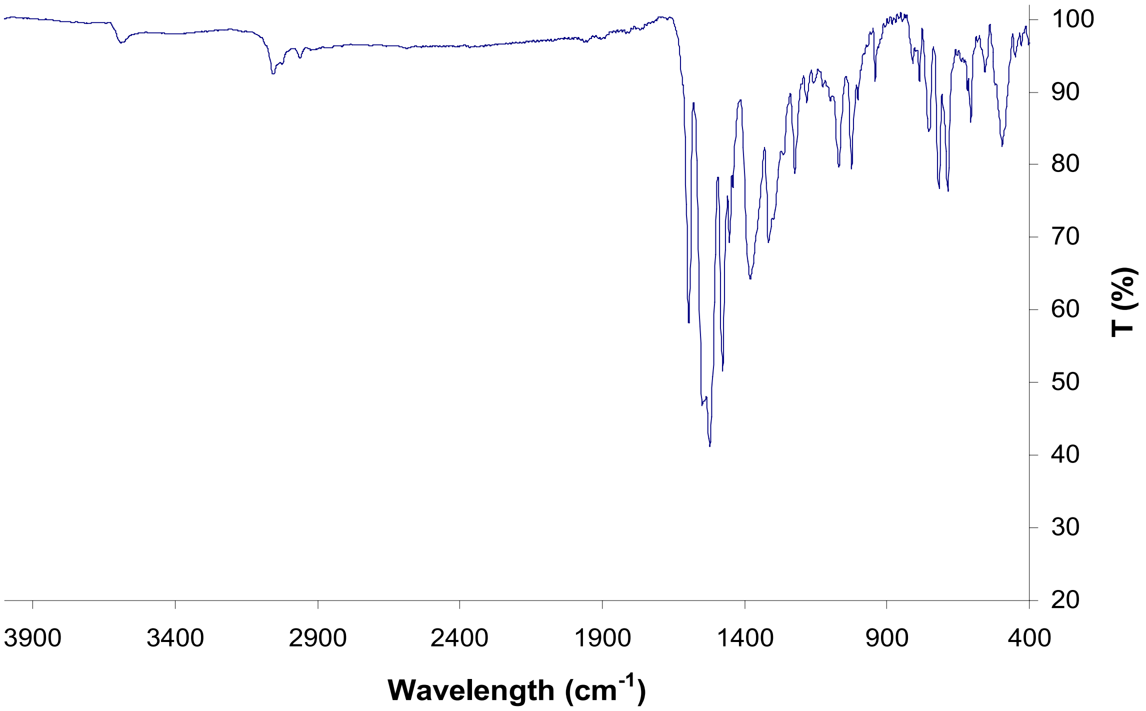
## Stability studies

Just after the dissolution of **2** we estimated the percentage of dissociation to be 8% in pyridine and around 25% in thf. One month after the dissolution of the crystals of **2** in pyridine solution, the amount of remaining cluster was estimated to be around 60% (40% of dissociation) while in thf only traces of the cluster could be observed after the same period of time. Addition of water (1 eq. per uranium) in the pyridine solution did not change the decomposition time.

The addition of an excess of the dbmK ligand (2 additional eq. per uranium) in both thf and pyridine solutions and in acetonitrile suspension leads to an increased dissociation rate toward the formation of the [U(dbm)$_4$] complex (total decomposition after 72 h in pyridine solution, and 24h in thf solution and acetonitrile suspension).

## Solid state studies:

**Figure S4:** FTIR Spectrum of **2** (KBr pellets)



**Magnetic data:**

At 300K we calculated a $\mu_{eff}$ of 3.09 $\mu_B$ ($\chi_{dia}$ = -2.17E-3 emu/mol, m=8.07 mg, M=5558.83 g/mol).

## References

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