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Supplementary information for:

From Aqueous Speciation to Supramolecular Assembly in Alkaline Earth-Uranyl Polyoxometalates

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Experimental section

Instrumentation

Scanning Electron Microscopy (SEM):

Electron micrographs of the crystalline materials were obtained from a Quanta 600F instrument (FEI) combining a scanning electron microscope and an energy-dispersive X-ray spectrometer (EDS).

Small-Angle X-ray Scattering: SAXS data were collected on an Anton Paar SAXSess instrument utilizing copper radiation (CuKα ; 1.54178 Å) and line collimation. Solutions were measured in 1.5 mm glass capillaries. Pure water was used for the background and the scattering was typically measured for 30 min. The SAXSQUANT software was used for data collection, treatment, and preliminary analysis (normalization, primary beam removal, background subtraction, desmearing, and smoothing). The fits of the scattering data were carried out within IGOR Pro[a] Simulated scattering curves for the uranyl clusters (U_{24}, U_{28}, U_{40}, U_{44}) were calculated from the single-crystal X-ray structures using SolX[b].

[a] J. Ilavsky and P. R. Jemian, Journal of Applied Crystallography 2009, 42, 347-353.

[b] R. Zhang, P. Thiyagarajan and D. M. Tiede, Journal of Applied Crystallography 2000, 33, 565-568.

Raman spectroscopy: Raman spectra were collected on a Thermo Scientific DXR Smart Raman spectrometer with a 780 nm laser source. Solutions and solids in glass vials were placed directly on the sample window for data collection (step size: 1 cm^{-1}, range: 650–950 cm^{-1}).

Powder X-ray diffraction:

Powder X-ray diffraction spectra of crystalline samples were obtained from a Rigaku Ultima IV multipurpose X-ray diffraction system using CuKα radiation (λ =1.54056 Å).

Synthesis: *Caution! Uranium nitrate is a radioactive and chemically toxic reactant, so precautions with suitable care and protection for handling such substances have been followed.*

Crystallization of uranyl-peroxide compounds:

Crystals of **Sr@U$_{24}$** were synthesized by combining the aqueous solution of uranyl nitrate (0.4 mmol), $SrCl_2$ (0.1 mmol), H_2O_2 (30%, 500 µL, ~5 mmol), TMAOH (25%, 500 µL, ~1.7 mmol) and 2 mL of DI water. Uranyl nitrate and $SrCl_2$ was dissolved in 2 mL of DI water. Then hydrogen peroxide is added to the solution under vigorous stirring, involving the formation of yellowish precipitate (studtite; $UO_2(O_2)(H_2O)_2{\cdot}4H_2O$). Then 0.5mL of TMAOH was added to the mixture. At that time, the solution becomes yellow and clear (**Figure SI8**). After 2 months, octahedral crystals (crystals of **Sr@U$_{24}$**) are observed in the bottom of the glass vial (vial closed). The analysis of this solid by powder X-ray diffraction confirms the purity of this phase (**Figure SI12**). Yield:~ 30%

Crystals of **Sr-U-monomer** were synthesized by combining the aqueous solution of uranyl nitrate (0.4 mmol), $SrCl_2$ (0.1 mmol), H_2O_2 (30%, 500 µL, ~5 mmol), and TMAOH (25%, 1 mL, ~3.4 mmol) and 4 mL of DI water. Uranyl nitrate and $SrCl_2$ were dissolved in 2 mL of DI water. Then hydrogen peroxide is added to the solution with vigorous stirring, yielding a yellowish precipitate (studtite; $UO_2(O_2)(H_2O)_2{\cdot}4H_2O$). After several minutes of stirring, 1mL of TMAOH was added to the mixture. The solution becomes reddish and clear. After 24h, large crystals of **Sr-U-monomer** appear (**Figure SI3**). The unit cell determination (single crystal X-ray diffraction, more information below in the SCXRD section), as well as the powder X-ray diffraction (**Figure SI4**) confirm **Sr-U-monomer** is an isotype of the compound $Ca_2[UO_2(O_2)_3]{\cdot}9(H_2O)$ that was reported prior (Burns *et al*, *Inorg. Chem.,* 2007, 46 (9), 3657).

Investigation of the TMAOH/H_2O_2/ UO_2^{2+}/EA^{2+} (EA = Ca, Sr or Ba) system:

Typically, uranyl nitrate (0.04 mmol) and alkaline earth chloride (0.01 mmol) is dissolved in 2 mL of DI water. Hydrogen peroxide (5 mmol) is added to this mixture under vigorous stirring. At that time, a yellowish precipitate (studtite) appears. After few minutes of stirring, TMAOH (1.7mmol) is added to the mixture. Just then, the solution becomes clear and yellow. These were the only reactants, and the final prepared solution has a U:AE:TMAOH ratio of 4:1:17.

Calcium solutions. After approximately 2 days, crystals of $Ca_2[UO_2(O_2)_3]\cdot 9(H_2O)$ crystallizes (**Figure SI5**). This solid then dissolved, followed by precipitation of $Ca(OH)_2$. SAXS analysis of the remaining solution reveals the presence of U_{44} (Figure SI7)

Strontium solutions. After few days, a slight precipitate is observed on the bottom of glass vial. The SEM analysis of this reveals small particles with undefined shape with a molar ratio Sr/U ~ 1/2. The particle size increases with the reaction time. After 2 months, octahedral crystals (crystals of **Sr@U$_{24}$**) are observed in the bottom of the glass vial.

Barium solutions. No precipitation is observed.

Single-crystal X-ray diffraction: Crystals were selected under a polarizing optical microscope. X-ray intensity data were collected at 173±2 K (cryostream system with gaseous nitrogen) on a Bruker DUO-APEX2 CCD area-detector diffractometer using MoKα radiation (λ=0.71073 Å) for **Ca@U$_{24}$** (CSD-433306) and **Sr@U$_{24}$** (CSD-433305). These crystals were suitable for structure determination by single-crystal X-ray diffraction Data reduction was accomplished using SAINT V7.53a[a]. The substantial redundancy in the data allowed a semi-empirical absorption correction SADABS V2.10 [b] to be applied on the basis of multiple measurements of equivalent reflections. The structures were solved by direct methods and refined using the SHELXTL program suite. Heavy atoms (U, Sr, and Ca) were refined anisotropically during final refinements.

[a] SAINT Plus Version 7.53a, Bruker Analytical X-ray Systems, Madison, WI (2008)

[b] Heldrick, G., SADABS, Bruker-Siemens Area Detector Absorption and Other Correction, Version 2008/1 (2008)

Table SI1: Crystal data and structure refinements for the **Sr@U$_{24}$** and **Ca@U$_{24}$**

Compound	**Sr@U$_{24}$**	**Ca@U$_{24}$**
moiety formula	$Sr_{12}[(UO_2)(O_2)(OH)]_{24}\cdot nH_2O$	$Ca_6Li_{12}[(UO_2)(O_2)(OH)]_{24}\cdot nH_2O$
empirical formula	$O_{805}Sr_{48}U_{96}$	$Ca_6Li_8O_{172}U_{24}$
molecular weight [g mol^{-1}]	39936.64	8760.72
crystal system	Cubic	Tetragonal
space group	$Fm\bar{3}c$	$I4/m$
a [Å]	53.688 (7)	18.282 (3)
b [Å]	53.688 (7)	18.282 (3)
c [Å]	53.688 (7)	26.436 (6)
α [Å]	90	90
β [Å]	90	90
γ [Å]	90	90
V [Å^3]	154751 (60)	8836 (4)
Z	8	2
radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	23.41	22.20
crystal size (mm)	0.21 × 0.11 × 0.09	0.25 × 0.2 × 0.2
T_{min}, T_{max}	0.639, 0.745	0.462, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25848, 4589, 2513	30783, 2614, 2169
R_{int}	0.134	0.121
R_1/wR_2 [for $I > 2\sigma(I)$]	0.0757 / 0.1873	0.0644 / 0.1621
R_1/wR_2 [for all data]	0.1599 / 0.2359	0.0811 / 0.1731
GooF	1.066	1.125
largest diff. peak/hole [eÅ^{-3}]	2.88, −4.66	3.14, −2.76

Table SI2. Bond Valence Summary for **Ca@U$_{24}$** and **Sr@U$_{24}$**

Ca@U$_{24}$

Element	Bond Valence	Std dev.	R_{ij}	b	ref
U	6.356	0.122	2.042	0.506	1
Ca	2.169	0.053	1.967	0.370	2
μ_3-O,* encapsulated	0.750	N/A	1.967	0.370	2

Sr@U$_{24}$

Element	Bond Valence	Std dev.	R_{ij}	b	ref
U	6.233	0.081	2.042	0.506	1
Sr, encapsulated	2.680	0.183	2.118	0.370	2
Sr, interstitial	2.002	N/A	2.118	0.370	2
μ_3-O, encapsulated*	0.809	0.084	2.118	0.370	2
μ_6-O, encapsulated$^{¥}$	1.314	0.005	2.118	0.370	2

* assigned as water

¥ assigned as oxo, O^{2-}

1. Burns, P., Ewing, R., & Hawthorne, F. (1997). The crystal chemistry of hexavalent uranium; polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *The Canadian Mineralogist, 35*, 1551-1570.

2. Brown, I., & Altermatt, D. (1985). Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica Section B, 41*(4), 244-247.

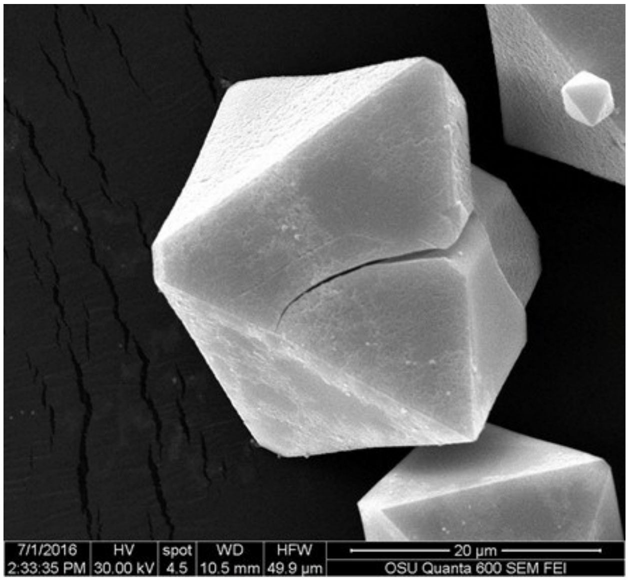

Figure SI1. SEM image of **Sr@U$_{24}$**

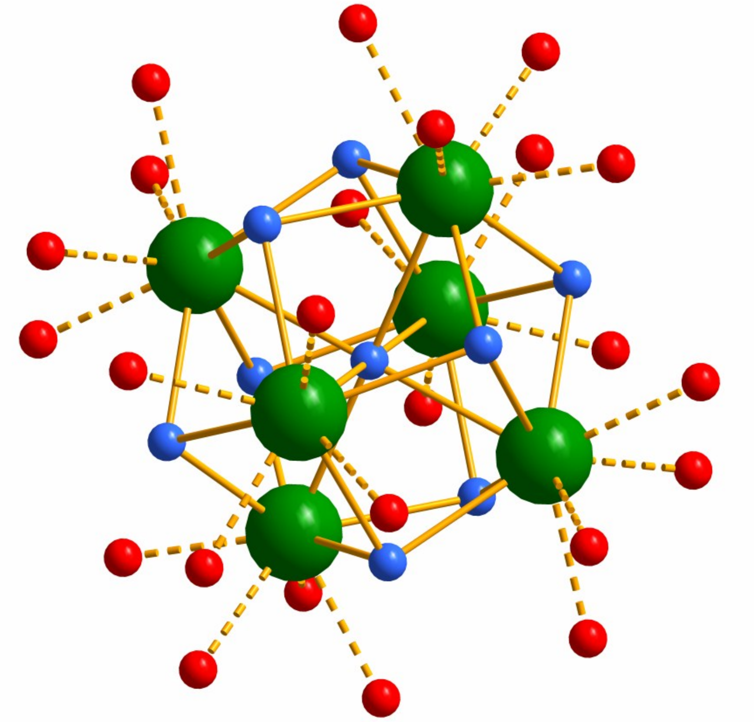

Figure SI2. Illustration of $Sr_6(H_2O)_9{}^{10+}$ polycation that is situated inside **Sr@U$_{24}$**. Green spheres are Sr^{2+}, blue spheres are H_2O, red spheres are O^{2-}. The dashed bonds are to the *yl*-oxos of the U_{24} shell.

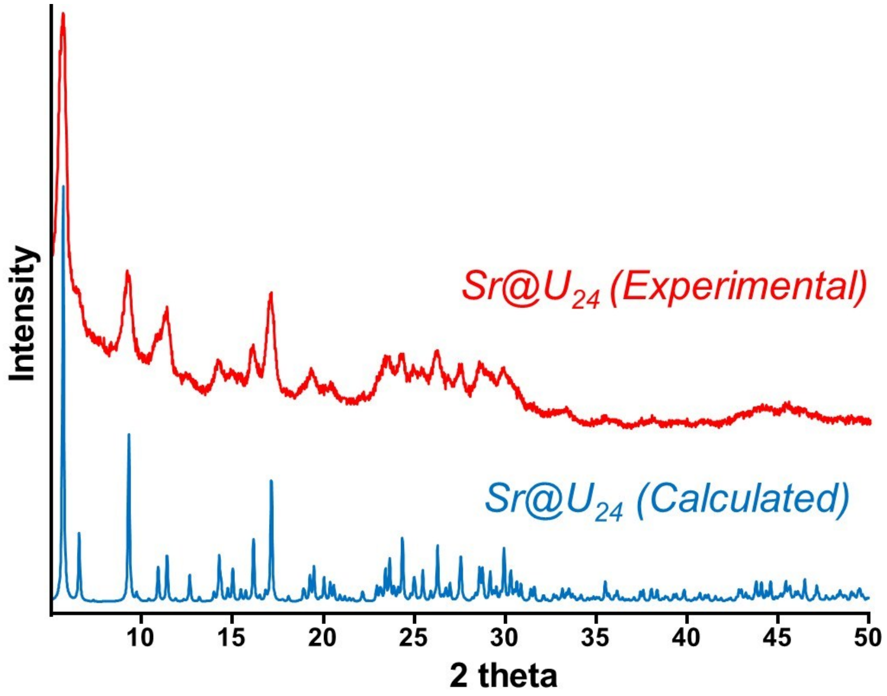

Figure SI3. Comparison of the experimental (red) and simulated (blue) powder XRD patterns of **Sr@U_{24}**. The simulated diagram was calculated from the single-crystal X-ray diffraction model using Mercury 3.6. The broadened experimental peaks is due to dehydration of the lattice waters that reside between the clusters.

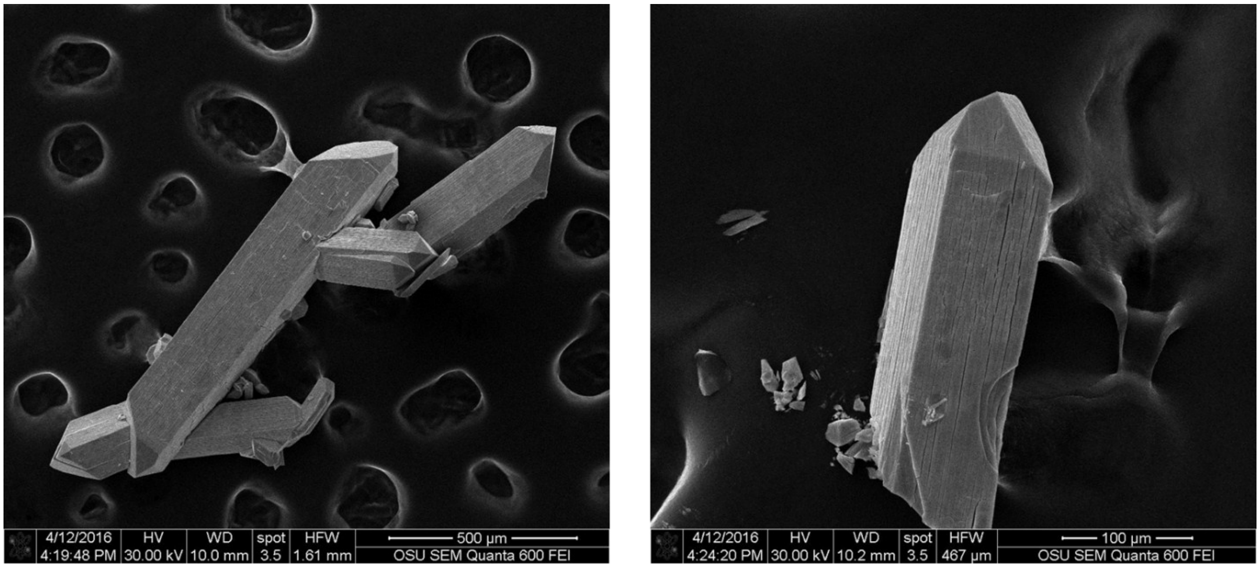

Figure SI4. SEM images of **Sr-U-monomer**

Table SI3. Comparison of the unit cell of $Ca_2[UO_2(O_2)_3]\cdot 9(H_2O)$ and **Sr-U-monomer**.

Compound	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	V(Å^3)	
$Ca_2[UO_2(O_2)_3]\cdot 9(H_2O)$	9.576(3)	12.172(3)	12.314(2)	90	90	90	1435.4(6)	
Sr-U-monomer	9.8052(1)	12.2817(1)	12.5947(1)	90	90	90	1516.71(3)	

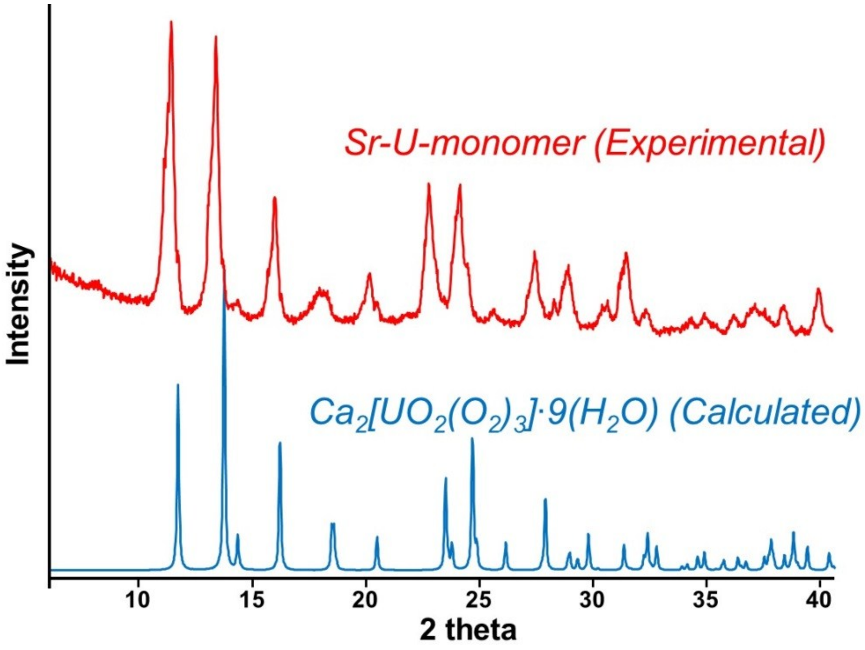

Figure SI5. Comparison of the experimental PXRD of **Sr-U-monomer** (red) with the simulated PXRD patterns of $Ca_2[UO_2(O_2)_3]\cdot 9(H_2O)$ (blue).

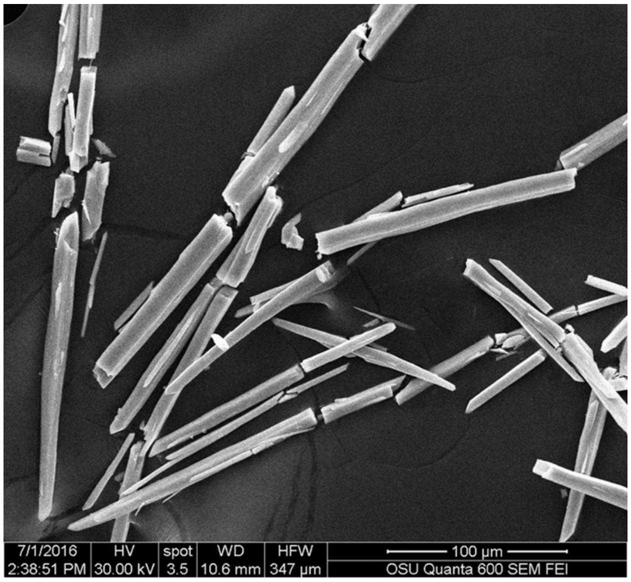

Figure SI6. SEM image of $Ca_2[UO_2(O_2)_3]\cdot9(H_2O)$

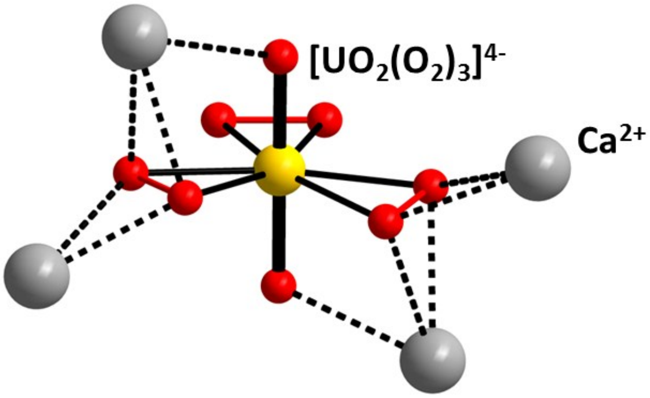

Figure SI7. View of the uranyl trioxide monomer in the crystal structure of $Ca_2[UO_2(O_2)_3]\cdot9(H_2O)$.

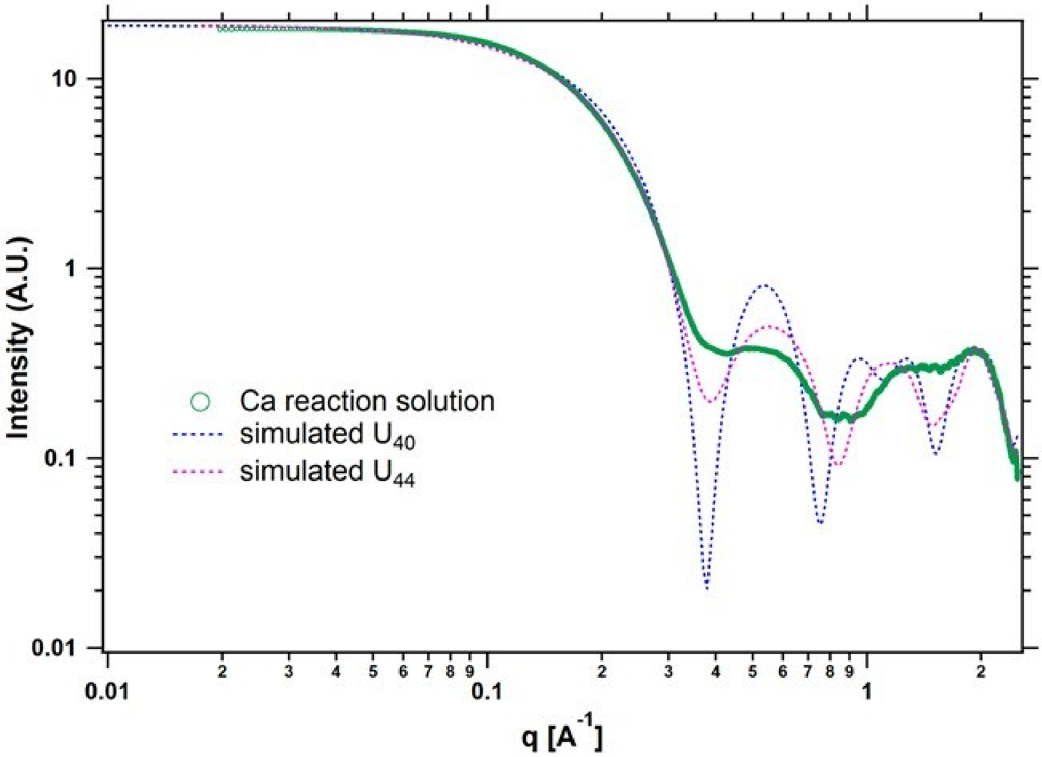

Figure SI8. Experimental scattering data for the reaction solution from which **Ca@U$_{24}$** is obtained, along with simulated U$_{40}$ and U$_{44}$ for comparison. Based on this comparison, we surmise that the initial cluster that forms is U$_{44}$.

Uranyl nitrate (0.4 mmol)
$SrCl_2$ (0.1 mmol)
H_2O_2 (5 mmol)
TMAOH (1.7 mmol)

Uranyl nitrate (0.4 mmol)
$SrCl_2$ (0.1 mmol)
H_2O_2 (5 mmol)
TMAOH (3.4 mmol)

Figure SI9. (Left) Photo of the reaction solution "**Sr@U$_{24}$**" (pH~10). **(Right)** Photo of the reaction solution "**Sr-U-monomer**" (pH~12). While the solution "**Sr@U$_{24}$**" is clear yellow, the similar solution with the excess of TMAOH (solution "**Sr-U-monomer**") is intense orange. This color difference is directly associated to the nature of uranyl species in solution. Typically, uranyl peroxide clusters exhibit a yellow color whereas uranyl trioxide monomers are orange. The comparison of these two pictures underlines clearly the impact of the pH (amount of TMAOH) on cluster formation.

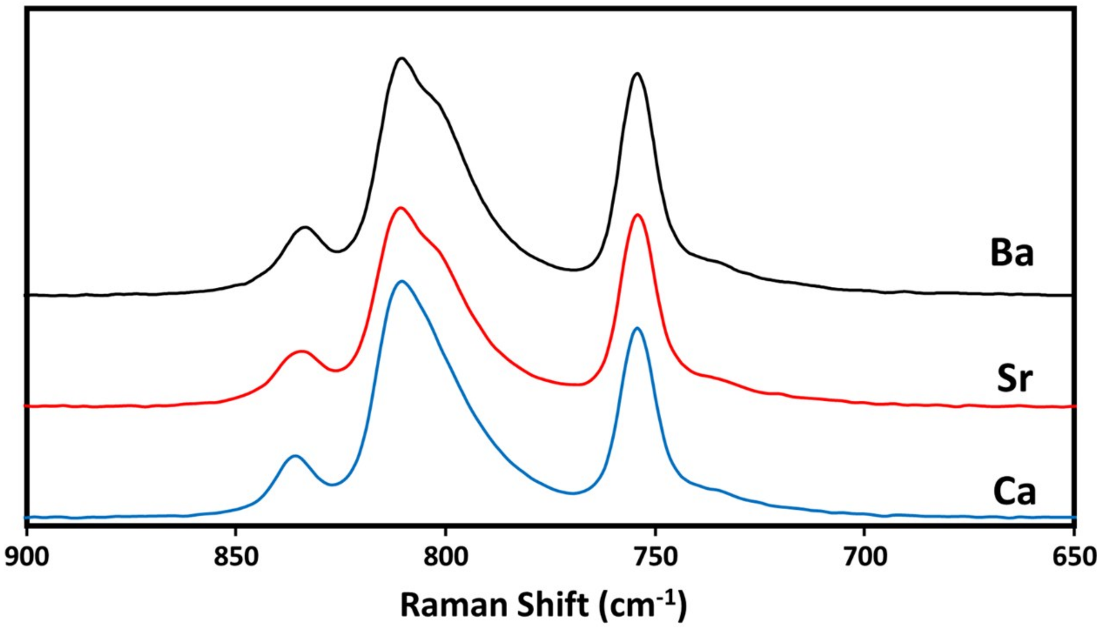

Figure SI10. Comparison of the Raman spectra of reaction solutions (after 4 days) with different alkaline earth cations (AE = Ca^{2+}, Sr^{2+} and Ba^{2+}). These solutions are obtained from a mixture of $UO_2(NO_3)_2$ (0.04 mmol), $AECl_2$ (0.01 mmol), TMAOH (1.7 mmol), H_2O_2 (5 mmol) and 2 ml DI water. Raman spectra of Ba^{2+} and Sr^{2+} are very similar. However, the Raman spectrum of Ca^{2+} is slightly different, especially the shape of the peak located around 810 cm^{-1}. This difference is probably due to the difference of uranyl capsules in solution (for Ba and Sr: U_{28}/U_{24}; for Ca: U_{44}).

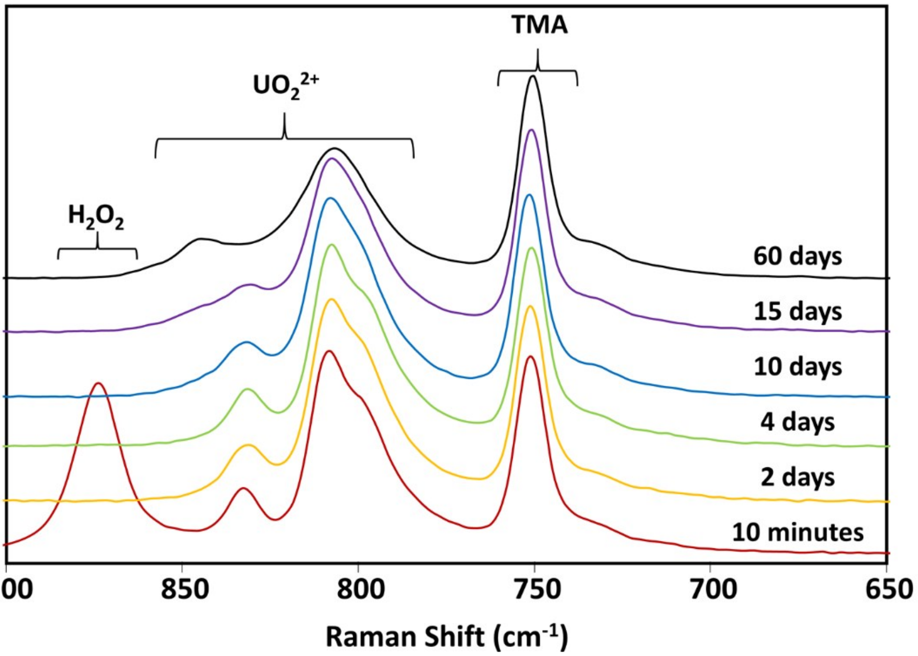

Figure SI11. Raman kinetic study of the reaction solution ”**Sr@U$_{24}$**“ from 10 minutes to 60 days. This reactant solution corresponds to a mixture of $UO_2(NO_3)_2$ (0.04 mmol), $SrCl_2$ (0.01 mmol), TMAOH (1.7mmol), H_2O_2 (5mmol) and 2ml DI water.

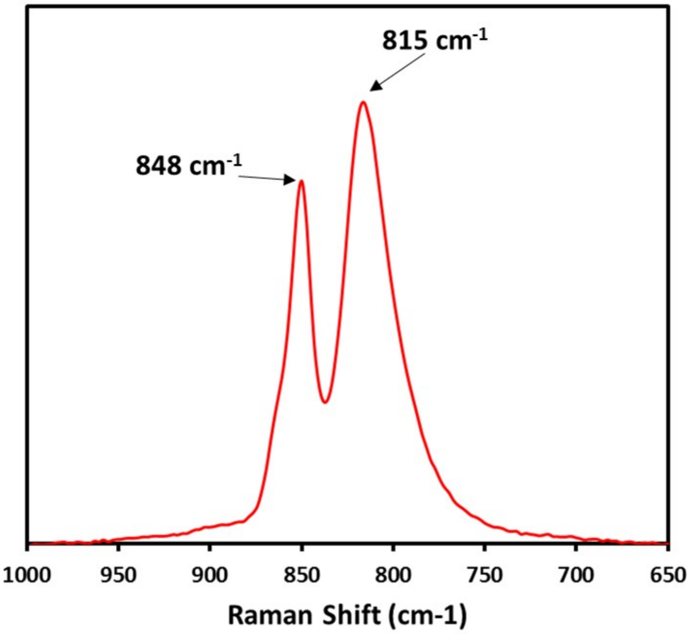

Figure SI12. Raman spectrum of the solid **Sr@U$_{24}$**