

## Supporting Information

### **Kinetics vs thermodynamics: A unique crystal transformation from a uranyl peroxy- nanocluster to a nanoclustered uranyl polyborate †**

Yingjie Zhang,\*<sup>a</sup> Mohan Bhadbhade,<sup>b</sup> Jason R. Price,<sup>c</sup> Inna Karatchevtseva,<sup>a</sup> David Collison,<sup>d</sup> and Gregory R. Lumpkin<sup>a</sup>

<sup>a</sup> Australian Nuclear Science and Technology Organization, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia;

\* E-mail: [yingjie.zhang@ansto.gov.au](mailto:yingjie.zhang@ansto.gov.au).

<sup>b</sup> University of New South Wales, Kensington, NSW 2052, Australia.

<sup>c</sup> Australian Synchrotron, 800 Blackburn Road, Clayton, VIC 3168, Australia.

<sup>d</sup> School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

#### **Experimental Section**

**Na<sub>14</sub>[(UO<sub>2</sub>)(O<sub>2</sub>)<sub>1.5</sub>]<sub>28</sub>·nH<sub>2</sub>O (1) and Na<sub>6</sub>[UO<sub>2</sub>{B<sub>16</sub>O<sub>24</sub>(OH)<sub>8</sub>}]·14H<sub>2</sub>O (2):** One milli-mole of uranyl nitrate hexahydrate was dissolved in 5 mL of deionized (DI) water. 3 mL of 30% H<sub>2</sub>O<sub>2</sub>, 3 mL of 4 M NaOH and 4 mL of DI water were added in a 20 mL glass vial. While stirring and cooling with ice bath, the above uranyl nitrate solution was added to the NaOH/H<sub>2</sub>O<sub>2</sub> aqueous mixture and a clear orange solution was obtained. The solution pH was adjusted to ~8.5 by gradual addition of a saturated boric acid solution. Yellow crystalline product of **1** formed within a few days after slow evaporation. The glass vial was then covered with paraffin film. The crystal transformation process started within a few days with the yellow crystals gradually dissolving and accompanied with simultaneous formation of the new light yellow-green crystals of complex **2**, with over 80% yield based on U content.

**Optical Examination:** An optical microscope (Wild Heerbrugg M400) was used to examine the crystalline products.

**Particle size and distribution measurement:** The particle size and distribution of the initial solution was measured using a Malvern Zetasizer (Nano ZS series) fitted with a 633 nm ‘red’ laser and 173° detection optics.

**SEM-EDS:** Scanning electron microscope -Energy disperse spectroscopy (SEM-EDS) was operating under an accelerating voltage of 20 kV on a Zeiss Ultra Plus SEM (Carl Zeiss NTS GmbH, Oberkochen, Germany). EDS was used to analyse the key elemental ratios.

**Powder XRD:** Powder X-ray diffraction data for complex **2** was collected on a Bruker D8 (Cu K $\alpha$ ) with the specimen rotated during measurement.

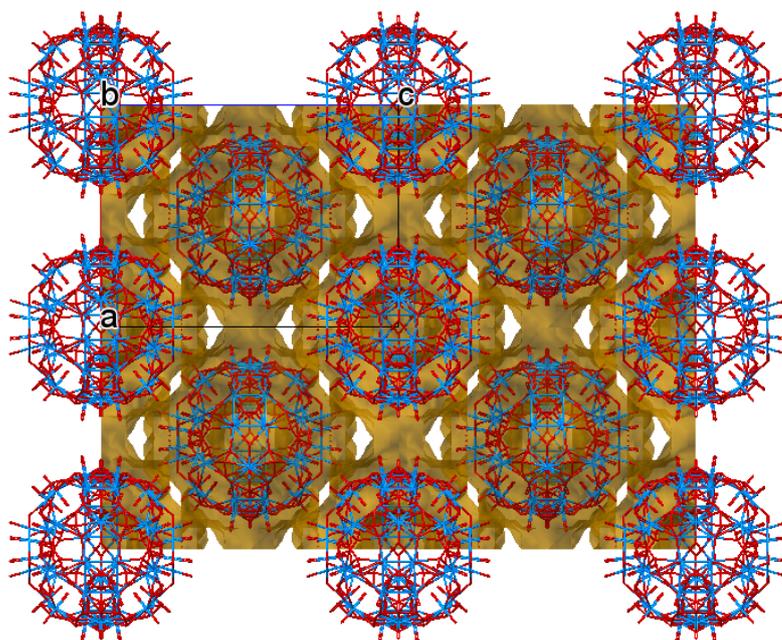
**TG/DTA:** The thermogravimetric and differential thermal analysis for **2** was made on a SEIKO 6300 Thermal Analyzer at a heating rate of 10 °C min<sup>-1</sup> and an air flow rate of 300 cm<sup>3</sup> min<sup>-1</sup>.

**Raman Spectroscopy:** Raman spectra in the range 2,000-100 cm<sup>-1</sup> were recorded on a Perkin Elmer Raman station 400 with Micro300 Microscope and excitation laser 785 nm. The spectra of **1** and **2** are shown in Figures 5S. The Raman spectrum of **1** shows two prominent bands (Fig. 5S), 803 and 849 cm<sup>-1</sup>. In addition, a very small shoulder centred around 878 cm<sup>-1</sup> could also be seen. The 849 cm<sup>-1</sup> peak has been assigned to the O-O symmetric stretching vibration ( $\nu_{O-O}$ ) of the peroxo ligand which is in direct association with uranyl ions.<sup>1</sup> The lower energy band at 803 cm<sup>-1</sup> has been assigned to the symmetric stretching mode of the uranyl ion ( $\nu_{O-U-O}$ ). The shoulder at 878 cm<sup>-1</sup> is noteworthy as it has been associated with the peroxo ligands ( $\nu_{O-O}$ ) that are not coordinated with metal ions.<sup>1</sup> Finally, two very weak bands in the region 1080-1060 cm<sup>-1</sup> are the vibrational modes of coordinated water molecules. The Raman spectrum of **2** (Fig. 5S) shows very strong and sharp band at 822 cm<sup>-1</sup> due to the symmetric vibration mode of the uranyl ion ( $\nu_{O-U-O}$ ) with corresponding U-O bond length of 1.789(8) Å<sup>2</sup> which is in agreement with the result from the single crystal X-ray diffraction study. Raman bands at 967 and 751 cm<sup>-1</sup> have been assigned respectively to the asymmetric and symmetric stretching modes of B-O in BO<sub>4</sub> tetrahedra. Very weak bands at 1355 and 920 cm<sup>-1</sup> are attributed to the asymmetric and symmetric stretching modes of B-O in BO<sub>3</sub>. Lastly, two broad regions at 1100-1050 cm<sup>-1</sup> and 696 cm<sup>-1</sup> are the vibrational frequencies of coordinated water.

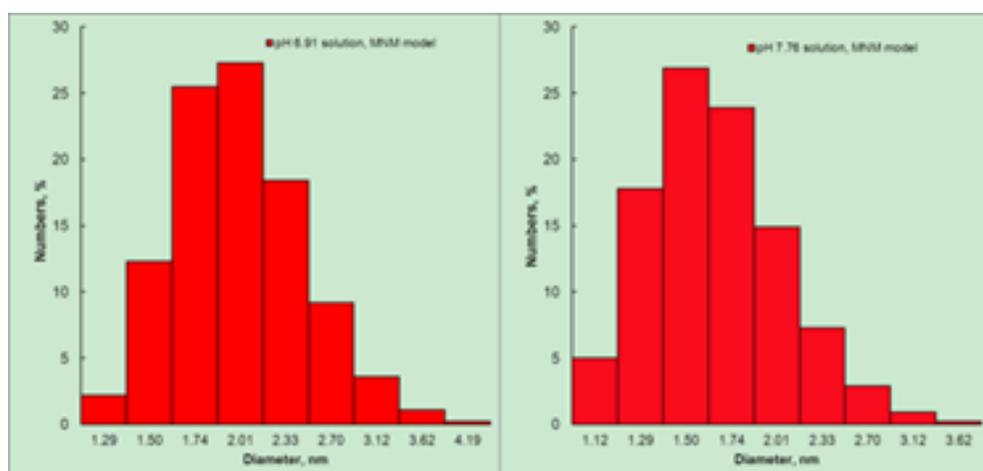
**Single Crystal Structures of 1 and 2:** Single-crystal X-ray data for **1** and **2** were collected at 100 (2) K on MX2 beamline at the Australian Synchrotron with Silicon Double Crystal

radiation ( $\lambda = 0.71073$  and  $0.72930 \text{ \AA}$ ). The longer than normal wavelength ( $0.72930 \text{ \AA}$ ) later on was selected to avoid severe absorption near U L<sub>III</sub> edge. All data were collected using BlueIce software. <sup>3</sup> Cell refinements and data reductions were carried out using XDS software. <sup>4</sup> The structures were solved by direct methods and the full-matrix least-squares refinements were carried out using SHELX suite of programmes. <sup>5</sup>

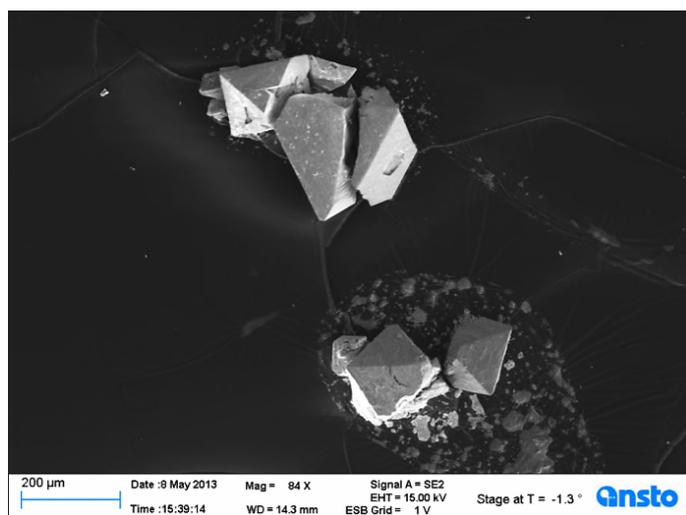
**Structure refinements:** The refinement of **1** was difficult given its nature of orientational disorder which causes sodium ions and water molecules disorder inside the U28 balls leading to voids. In addition, the packing of the U28 balls also leaves large voids in the crystal lattice. These solvent assessable voids would include sodium ions to balance the charges and some water molecules. Although there are peaks of height  $\sim 3\text{-}4 \text{ e\AA}^{-3}$  in the difference Fourier map, it is difficult to distinguish between sodium ions and water molecules and to model them satisfactorily. Therefore, SQUEEZE procedure in PLATON, <sup>6</sup> based on iterative difference Fourier syntheses, <sup>7</sup> was carried out. After five cycles of the SQUEEZE procedure the convergence was reached. The total number of electrons in voids ( $1869 \text{ \AA}^3$  in the unit cell) is  $\sim 116$  electrons, which would account for a few sodium ions and water molecules. The contribution from these to the observed structure factor was removed by the SQUEEZE procedure and final refinement cycles were performed without any of these atoms using program shelXle. <sup>8</sup> For complex **2**, the raw reflections were first corrected for absorption correction using sadabs assuming a strong absorber in a monoclinic lattice and refining the angle of incidence. The absorption correction is necessary to avoid some NPD atoms. The final refinement cycles were performed using program shelXle. <sup>8</sup>



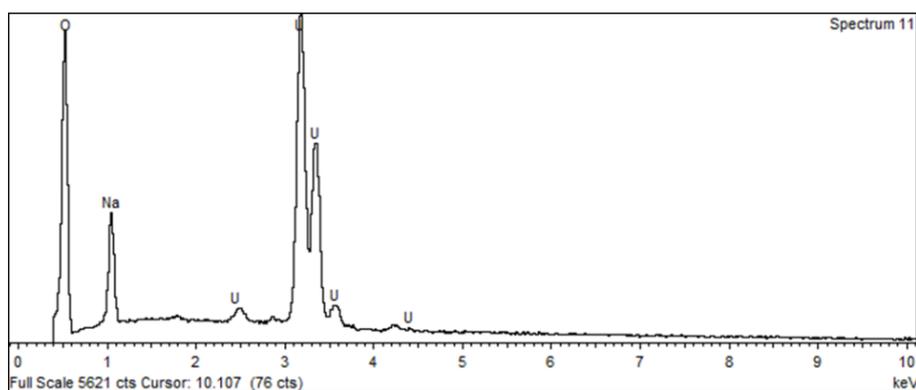
**Fig. 1S** The crystal packing of **1** along the *b*-axis showing large solvent accessible voids both inside and outside the clusters.



**Fig. 2S** The particle sizes and distributions for the initial solutions.



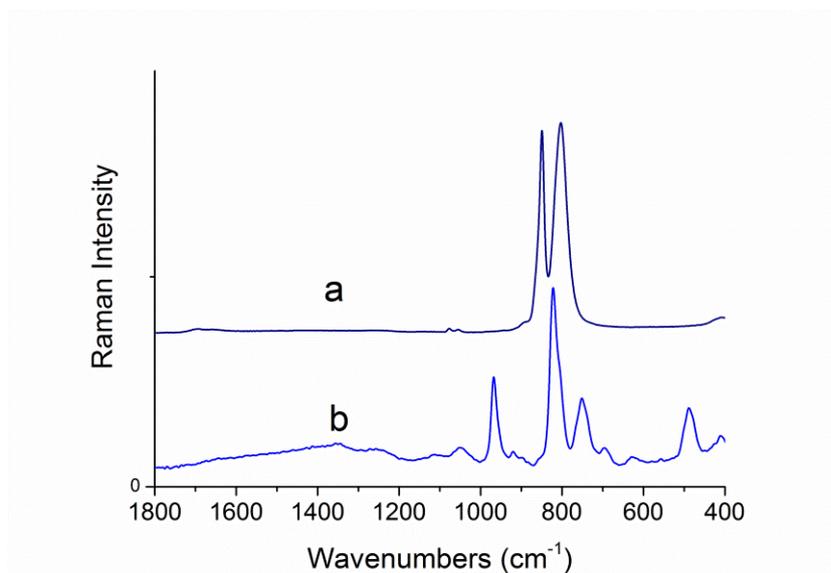
**Fig. 3S** A secondary SEM image of **1**.



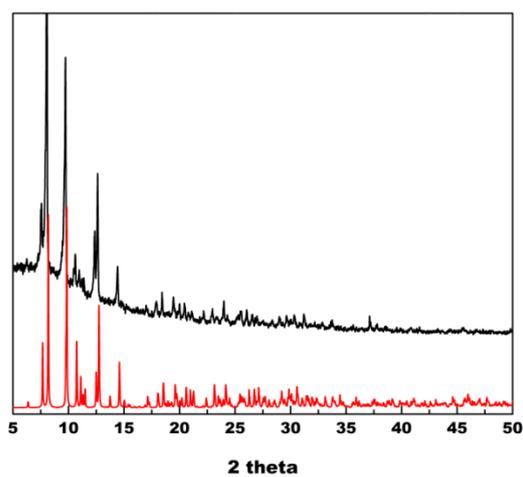
**Fig. 4S** A SEM-EDS spectrum of **1** collected on a relatively flat crystal surface.

**Table 1S.** SEM-EDS analysis results and elemental ratios for **1**.

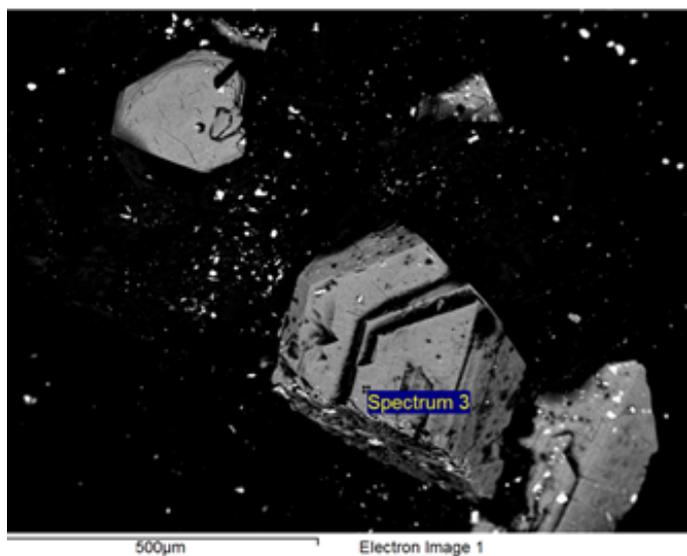
Element	App	Intensity	Weight%	Weight%	Atomic%	Compd%	Formula	Ion ratio
	Conc.	Corrn.		Sigma				
Na <sub>K</sub>	4.66	0.9625	6.59	0.12	16.82	8.88	Na <sub>2</sub> O	1.0
U <sub>M</sub>	50.55	0.9075	75.83	0.26	18.69	91.12	UO <sub>3</sub>	1.0



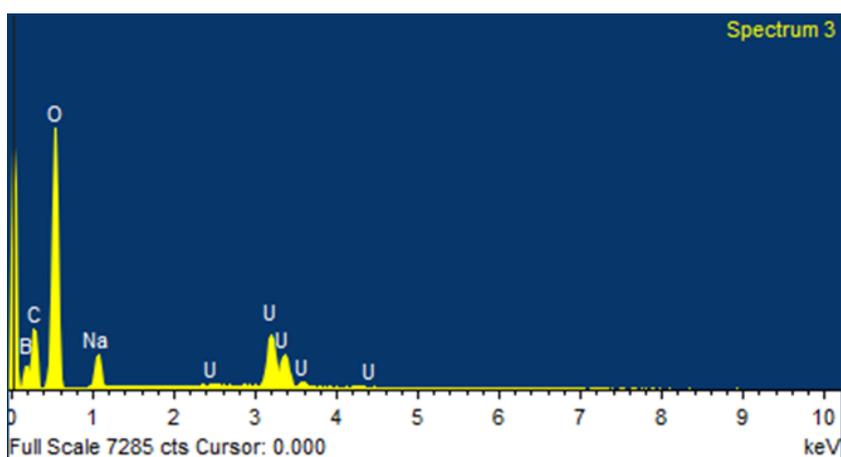
**Fig. 5S** Raman spectra of **1** (a) and **2** (b) in 1,800-400 cm<sup>-1</sup> region.



**Fig. 6S** PXRD patterns of **2** with measured pattern on top of the simulated one from the single crystal data.



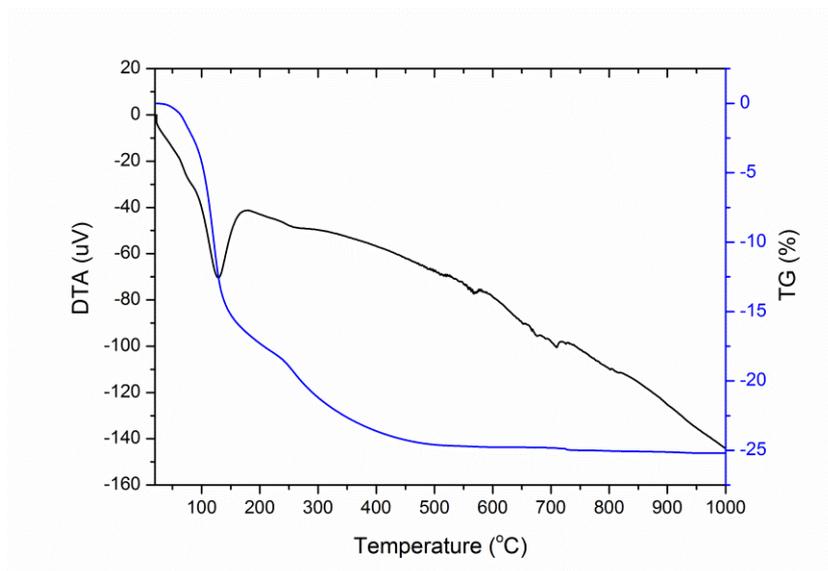
**Fig. 7S** A backscattered SEM image of **2**.



**Fig. 8S** A SEM-EDS spectrum of **2** collected on a relatively flat crystal surface.

**Table 2S.** SEM-EDS analysis results and elemental ratios for **2**.

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%	Compd%	Formula	Number of ions
B <sub>K</sub>	7.55	0.2282	22.95	0.95	35.20	73.89	B <sub>2</sub> O <sub>3</sub>	37
Na <sub>K</sub>	11.37	1.0223	7.72	0.17	5.57	10.40	Na <sub>2</sub> O	6.0
U <sub>M</sub>	13.62	0.7228	13.07	0.32	0.91	15.71	UO <sub>3</sub>	1.0



**Fig. 9S** Thermogravimetric and differential thermal analysis (TG/DTA) results for **2**.

## References

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