Electronic Supplementary Material (ESI) for Chemical Science

Water-soluble multi-cage super tetrahedral uranyl peroxide phosphate clusters

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Supporting Information

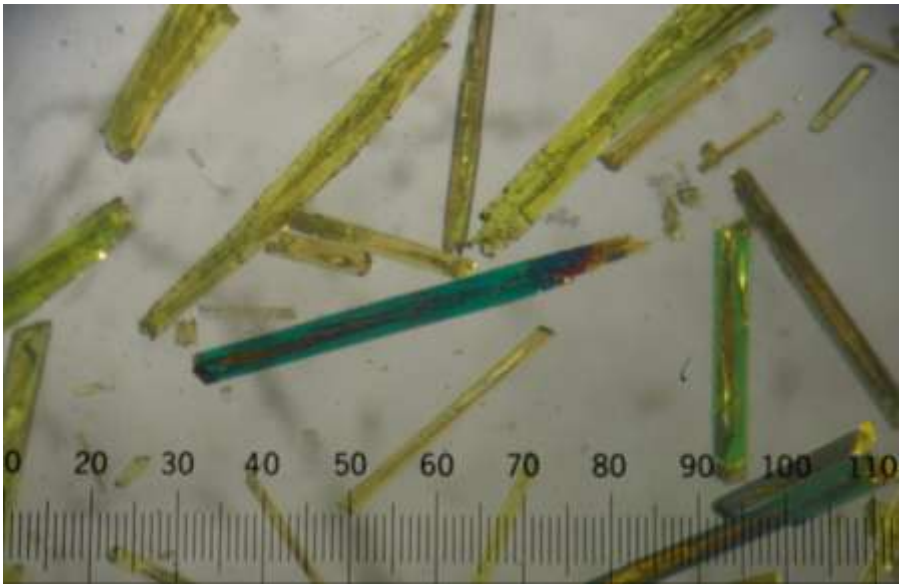

Figure S1. Crystals, shown in plane polarized light, of $U_{124}P_{32}$ after removing the amorphous powder formed in the synthesis. The distance between two small bars is 25 µm.

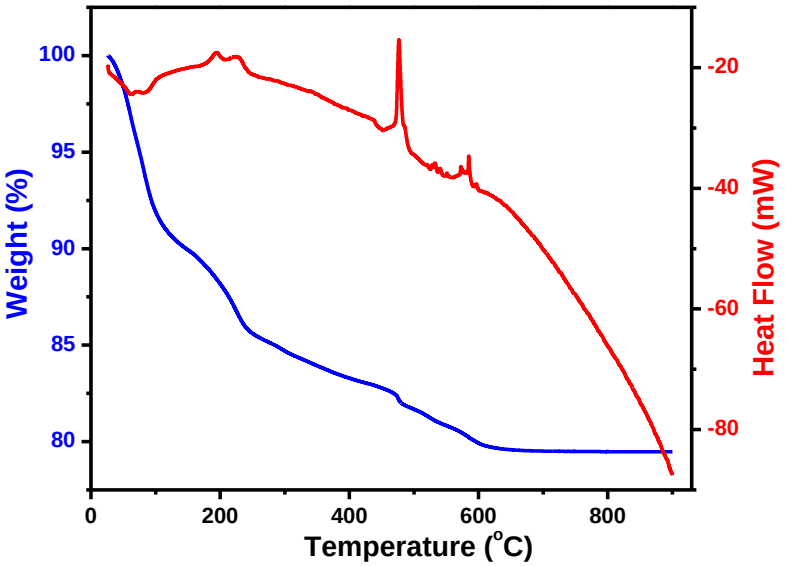

Figure S2. Thermogram of $U_{124}P_{32}$ crystals.

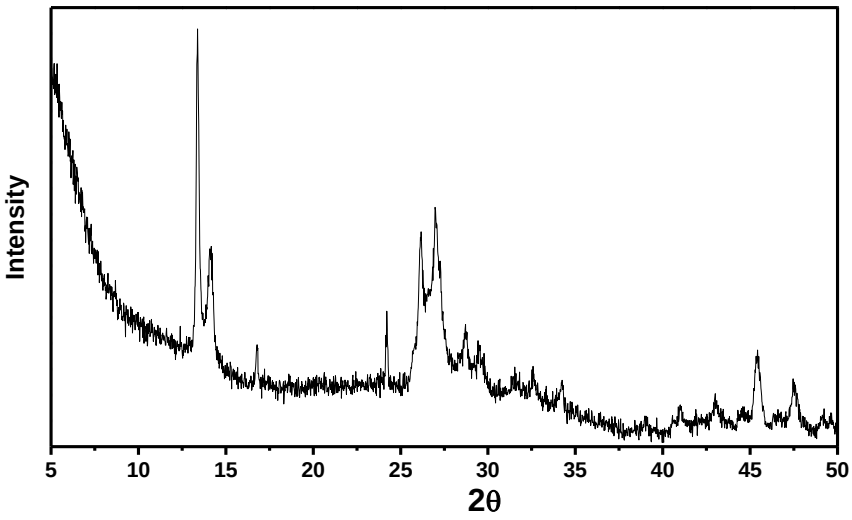

Figure S3. PXRD pattern for the TGA residue of $U_{124}P_{32}$ crystals.

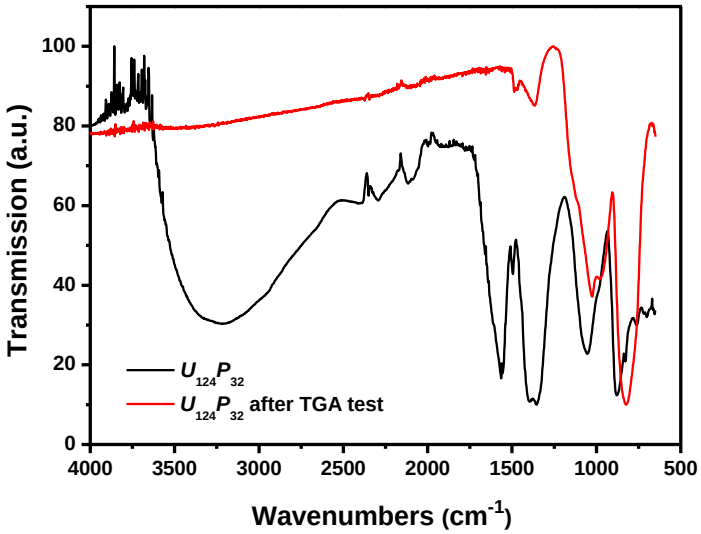

Figure S4. Infrared spectra for $U_{124}P_{32}$ crystals and their TGA residue.

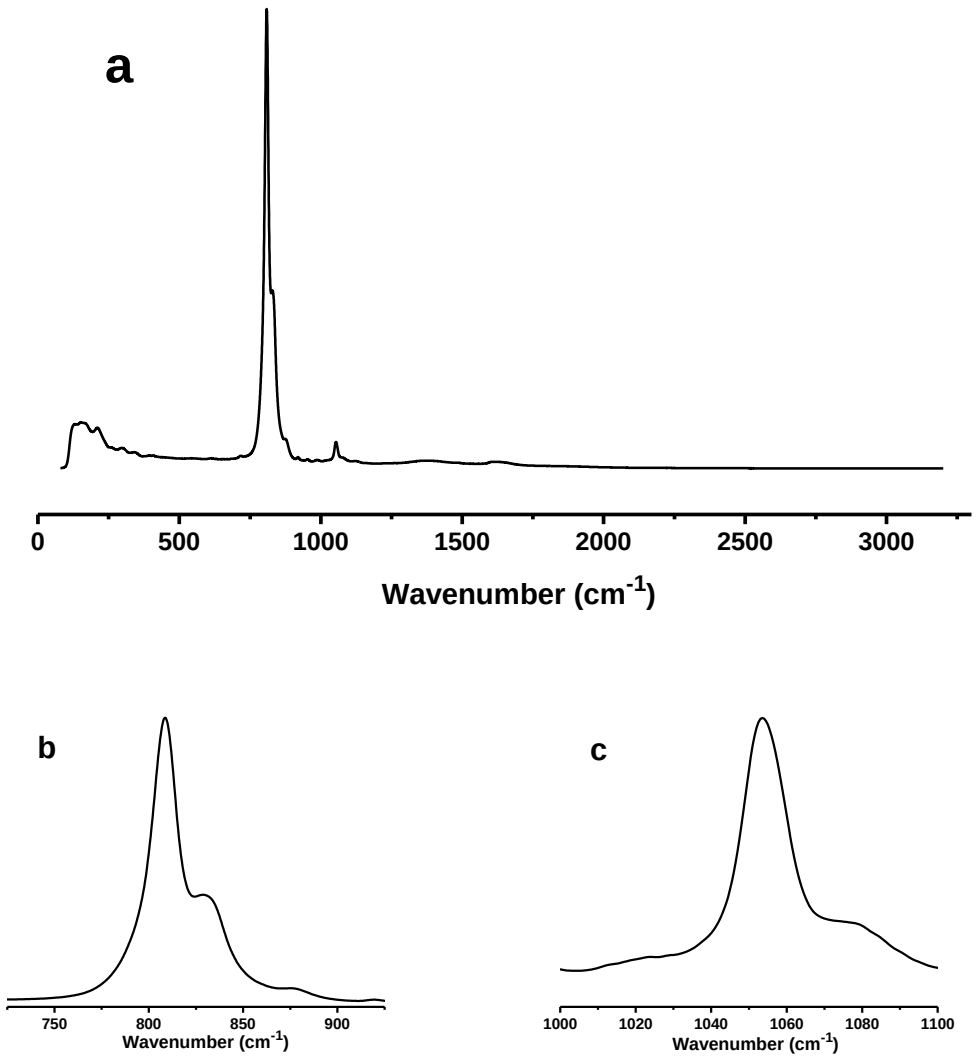

Figure S5. Entire (a), 725-925 cm^{-1} (b) and 1000-1100 cm^{-1} (c) region of the Raman spectrum collected from a single $U_{124}P_{32}$ crystal.

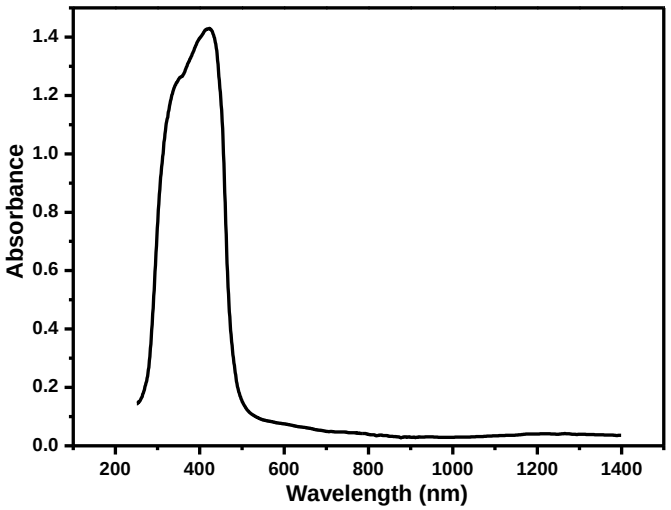

Figure S6. UV-Vis spectrum for a $U_{124}P_{32}$ crystal.

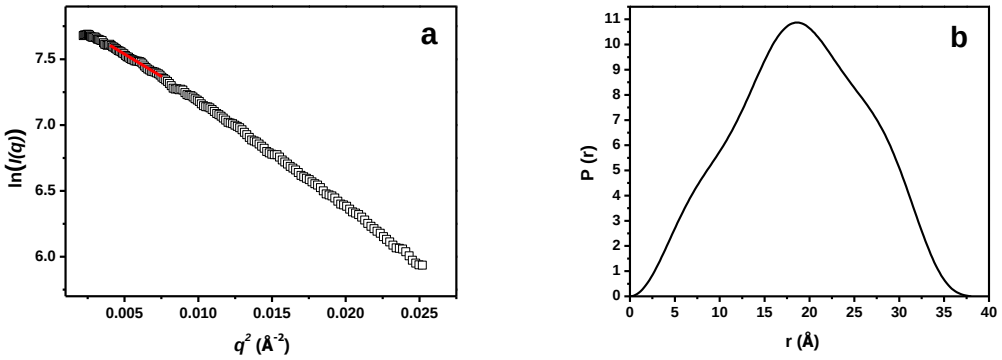

Figure S7. (a): Guinier plot calculated from the experimental SAXS data for a solution created by dissolving crystals of $U_{124}P_{32}$ in ultrapure water.[1] The low-q data was linear fitted (red). (b): Distance pair distribution function (PDF) of the SAXS data. The PDF was obtained by an indirect Fourier transform of the primary experimental SAXS data using the Moore analysis.[2]

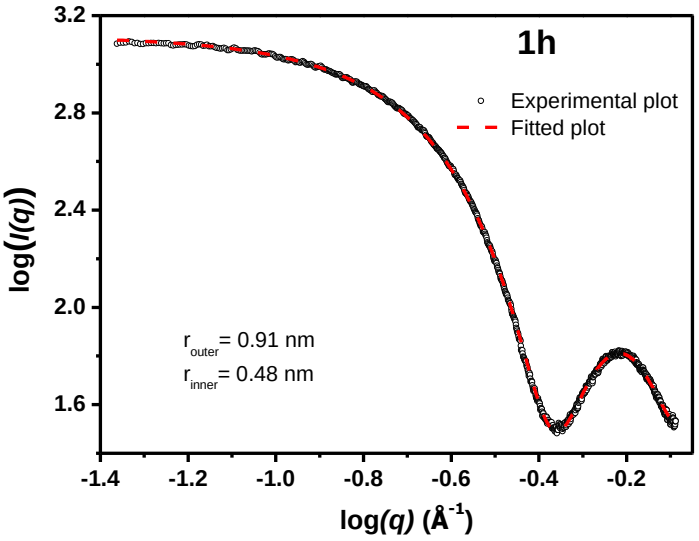

Figure S8. Small-angle X-ray scattering profiles for a solution collected within an hour of mixing the reactants needed to assemble $U_{124}P_{32}$ (black solid line)., and a fit calculated using a sphere-shell model with an outer radius 0.91 nm and inner radius 0.48 nm (red dash).

Table S1 – Counterions, and averages and ranges of U-O-O-U dihedral angles for U-O_2-U and U-$(OH)_2$-U bridges in square, pentagon, and hexgon of uranyl peroxide polyhedra in reported cage clusters[3].

Clusters	Square		Pentagon			Hexagon		
	Cations	U-O_2-U	Cations	U-O_2-U	U-$(OH)_2$-U	Cations	U-O_2-U	U-$(OH)_2$-U
$U_{18}Pp_2PCP_6$	--	--	K^+	142.4 (137.5-148.3)	161.7 (161.7)	--	--	--
U_{20}	--	--	Na^+	140.2 (138.4-142.4)	--	--	--	--
$U_{20}Pp_{6a}$	--	--	K^+*	143.6 (140.5-149.2)	--	--	--	--
$U_{20}Pp_{6b}$	--	--	K^+*	144.1 (138.8-149.5)	--	--	--	--
$U_{20}Pp_{10}$	--	--	K^+	146.4 (145.6-147.0)	--	--	--	--
U_{24}	Li^+*	135.0 (134.4-135.8)	--	--	--	--	135.1 (134.6-135.8)	156.7 (154.9-158.5)
$U_{24}Pp_{12}$	Na^+*	138.3 (136.9-140.4)	--	--	--	--	--	--
$U_{24}PCP_{12}$	--	136.0 (135.3-136.5)	--	--	--	--	--	--
$U_{26}Pp_6$	--	--	K^+*	145.0 (139.5-157.3)	--	--	--	--
$U_{26}Pp_{11}$	--	--	K^+*	146.3	--	--	--	--

				(138.1-157.3)				
U_{28a}	Na^+	133.3 (131.0-135.5)	Na^+	139.7 (134.3-146.2)	162.1 (156.4-166.2)	--	138.0 (131.0-146.2)	162.4 (156.4-166.3)
U_{28}	--	--	K^+	144.9 (140.9-151.9)	--	K^+	144.6 (140.9-151.1)	--
RbK-U_{28}	--	--	K^+	143.2 (139.1-150.5)	--	Rb^+	143.4 (141.2-148.2)	--
CsK-U_{28}	--	--	K^+	143.5 (140.7-148.0)	--	Cs^+	144.5 (141.3-146.7)	--
Nb-RbK-U_{28}	--	--	K^+	145.8 (143.2-148.6)	--	Rb^+	148.4 (148.2-148.6)	--
Ta-CsK-U_{28}	--	--	K^+	144.5 (141.7-149.6)	--	Cs^+	145.9 (143.9-149.6)	--
U_{30}	--	135.3 (135.1-135.4)	--	140.8 (136.8-146.1)	--	--	141.1 (135.1-146.1)	158.6 (156.9-161.9)
U_{30a}	Ba^{2+}	133.4 (131.6-137.1)	Rb^+	154.0 (150.0-158.6)	--	--	140.4 (131.6-158.6)	155.4 (152.6-158.5)
$U_{30}Pp_6$	--	--	K^+	147.1 (142.9-159.0)	--	K^+*	145.8 (140.0-150.1)	--
$U_{30}Pp_{10}Ox_5$	--	--	K^+	145.9 (140.8-153.6)	--	--	--	--
$U_{30}Pp_{12}P_1$	--	--	K^+	148.7 (143.6-155.9)	--	--	--	--
U_{32}	--	139.1 (131.1-151.9)	--	142.5 (136.2-165.2)	155.1 (148.8-163.2)	--	142.5 (131.1-165.3)	159.7 (148.8-168.7)
$U_{32}Pp_{16}$	Na^+*	137.8 (132.7-147.6)	--	--	--	--	--	--
U_{36a}	Li^+	133.0	K^+	149.3	--	K^+* or I^-*	142.1	161.4

		(132.1-134.2)		(143.7-159.2)			(132.1-159.2)	(157.3-168.3)
U_{36}	--	--	--	141.0 (137.8-145.3)	--	--	141.1 (137.8-145.3)	176.2 (175.4-176.7)
$U_{36}Ox_6$	--	--	K^+*	141.6 (138.6-144.0)	--	--	142.6 (140.6-144.0)	--
$U_{38}Pp_{10}Nt_4$	--	--	K^+	142.0 (136.2-153.7)	162.0 (157.2-164.4)	--	--	--
U_{40}	Na^+	132.5 (132.1-132.8)	--	141.8 (138.2-145.6)	160.3 (160.1-160.5)	--	140.2 (132.1-146.8)	167.2 (164.6-170.1)
U_{42}	Li^+	133.0 (132.1-133.5)	K^+	147.1 (143.7-150.4)	--	--	143.1 (132.1-150.4)	163.0 (156.8-167.2)
$U_{42}Pp_3$	--	134.5 (132.7-135.3)	K^+	146.6 (142.7-149.0)	--	--	142.8 (135.3-148.1)	172.9 (169.2-175.1)
U_{44}	--	--	Na^+ or K^+	143.2 (141.5-145.6)	--	--	142.0 (139.5-144.8)	--
U_{44a}	Li^+	133.5 (131.1-137.3)	--	--	--	--	135.7 (131.1-140.9)	159.8 (154.4-163.1)
$U_{45}Pp_{23}$	Na^+	137.0 (133.3-140.5)	--	143.4 (136.3-152.4)	--	--	--	--
U_{50}	--	--	--	141.2 (133.1-153.5)	157.4 (153.3-161.9)	--	141.0 (133.1-153.5)	172.4 (157.7-179.9)
$U_{50}Ox_{20}$	--	--	K^+	140.2 (137.2-144.0)	149.8 (149.8)	--	--	--
U_{60}	--	--	K^+	144.8 (143.2-146.7)	--	--	144.1 (143.0-146.7)	174.2 (174.0-175.0)
$U_{60}Ox_{30}$	--	--	K^+	144.0 (140.4-146.4)	--	--	--	--

*: It means that only several polygons of uranyl peroxide polyhedra are templated by cations.

(1) Feigin, L. A.; Svergun, D. I. *Structure Analysis by Small-Angle X-Ray and Neutron Scattering*; Plenum Press: New York 1987.
(2) Moore, P. B. *J. Appl. Crystallogr.* **1980**, *13*, 168.
(3) Qiu, J.; Burns, P. C. *Chem. Rev.* **2013**, *113*, 1097.