Supplementary information

Formation of U(VI) peroxide nanoclusters from cascade reactions with a persulfate radical initiator

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Raman spectral features

Table S1. Raman signals summarized for the persulfate ($Na_2S_2O_8$) solution, sodium fumarate ($Na_2C_4H_2O_4$) buffer and reaction mixtures. Solutions are activated with heat and are aged in the dark. The N_2 purged occurred before activation of the $Na_2S_2O_8$ mixture to remove any dissolved oxygen from the system.

$Na_2S_2O_8$	$Na_2C_4H_2O_4$ buffer	Activated solution	$Na_2S_2O_8$ w/ U(VI)	Activated solution w/ U(VI)	Activated solution w/ U(VI) aged 3 weeks	Activated solution w/ U(VI) aged 4 weeks (crystals formed)	N_2 purge Activated solution w/ U(VI)
803	801	807	805	802	800	800	807
			812	819	813	812	
836		837	836	836	837	837	836
					876		
	904	904		903	903 (weak)	904	904
	981	981	981	980	981	982	982
1078		1077	1077	1077			

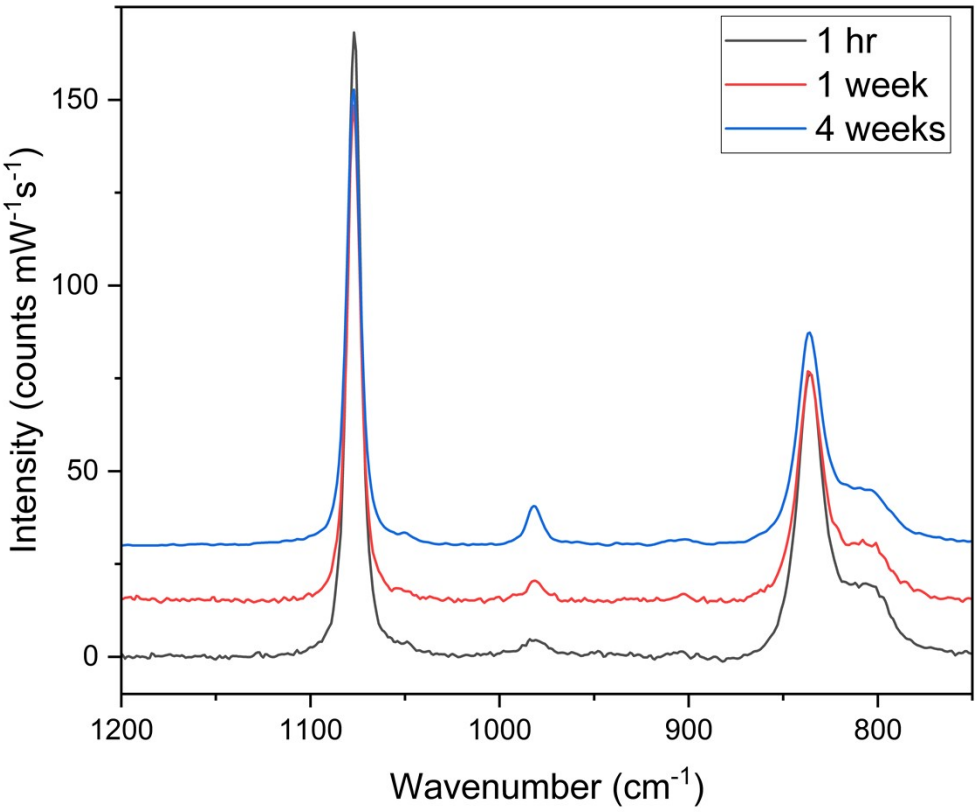

Figure S1. Raman spectrum for the activated persulphate solutions with U(VI) nitrate purged under N_2 gas and aged for 1hr, 1 week, 2 weeks, 3 weeks, and 4 weeks. No evidence of peroxide formation is observed at 860-870 cm^{-1}.

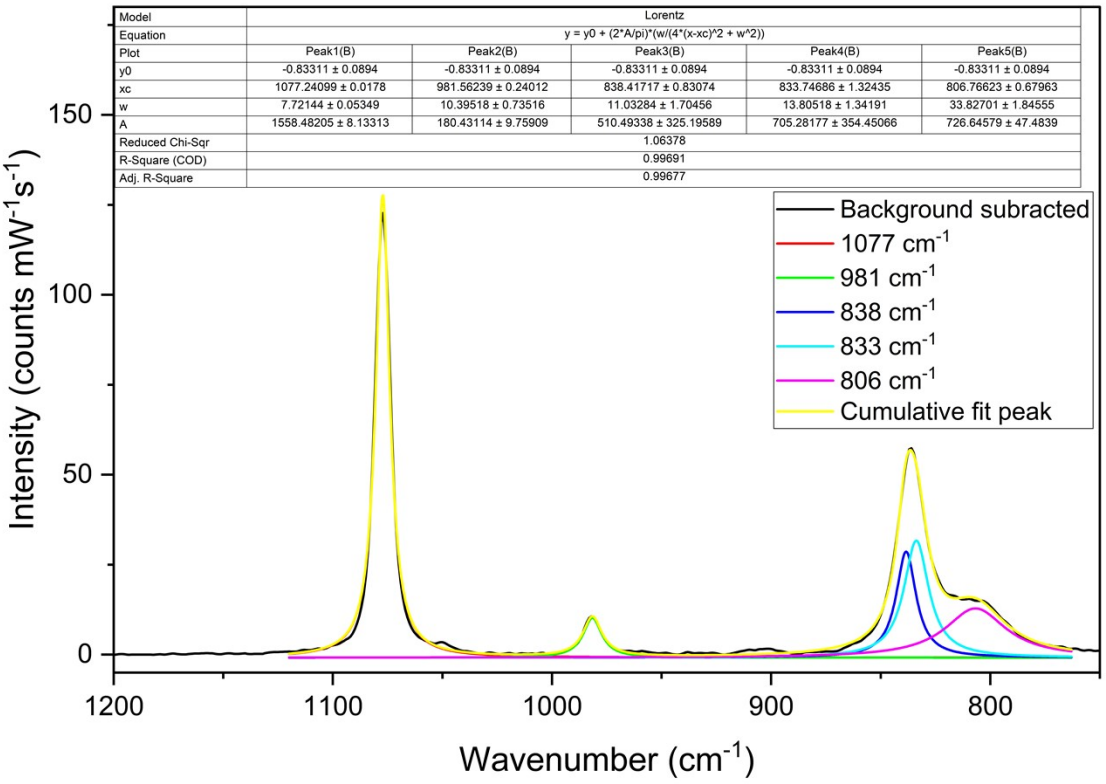

Figure S2. Fitted Raman spectrum for the activated persulphate solutions with U(VI) nitrate purged under N_2 gas and aged for 4 weeks.

Crystallographic Information

Table S2. Select crystallographic data and structure refinement for **NaU24**

Empirical formula	$U_{24}Na_{24}O_{180}H_{136}$
Formula weight (g/mol)	9277.9
Temperature (K)	100.00
Crystal system	tetragonal
Space group	*I*4/*m*
a (Å)	19.7190(5)
b (Å)	19.7190(5)
c (Å)	22.1550(9)
Volume (Å^3)	8614.7(6)
Z	2
ρ_{calc} (g/cm^3)	5.359
μ (mm^{-1})	46.953
F(000)	7824
Crystal size/mm^3	0.05 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection (°)	4.132 to 51.366
Index ranges	$-22 \leq h \leq 23$, $-24 \leq k \leq 21$, $-26 \leq l \leq 26$
Reflections collected	26070
Independent reflections	4182 [R_{int} = 0.0810]
Data/restraints/parameters	4181/0/255
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.0913
Largest diff. peak/hole (e Å^{-3})	1.511/-1.814

Table S3. Selected bond distances (Å) for **NaU24**.

U1-O3	1.791(9)		U3-O7	1.790(7)
U1-O17	1.819(11)		U3-O13	1.813(8)
U1-O8	2.343(8)		U3-O6	2.334(8)
U1-O8	2.343(8)		U3-O8	2.351(8)
U1-O2	2.402(8)		U3-O15	2.398(7)
U1-O2	2.402(8)		U3-O2	2.406(7)
U1-O16	2.406(8)		U3-O14	2.407(7)
U1-O16	2.406(8)		U3-O10	2.466(8)
O2-O8	1.477(10)		O6-O15	1.479(11)
U2-O1	1.788(7)		U4-O4	1.787(10)
U2-O11	1.804(7)		U4-O18	1.801(11)
U2-O9	2.348(8)		U4-O6	2.351(8)
U2-O9	2.348(8)		U4-O6	2.351(8)
U2-O12	2.397(7)		U4-O15	2.408(8)
U2-O12	2.401(7)		U4-O15	2.408(8)
U2-O14	2.401(7)		U4-O16	2.409(8)
U2 O10	2.452(8)		U4-O16	2.409(8)
O9-O12	1.473(10)			
Na1-O4	2.410(11)		Na3-O22	2.36(2)
Na1-O7	2.411(7)		Na3-O18	2.363(13)
Na1-O7	2.411(7)		Na3-O27	2.42(2)
Na1 O3	2.436(11)		Na3-O23	2.43(2)
Na1-O5	2.516(8)		Na3-O26	2.44(2)
Na1-O5	2.516(8)		Na3-O21	2.541(19)
Na1-O5	2.523(8)		O23-O27	1.57(3)
Na1-O5	2.523(8)			
			Na4-O24A	2.34(6)
Na2-O1	2.444(8)		Na4-O24B	2.26(4)
Na2-O1	2.444(8)		Na4-O24A	2.35(6)
Na2-O1	2.444(8)		Na4-O24B	2.32(4)
Na2-O1	2.444(8)		Na4-O27	2.45(3)
Na2-O5	2.512(8)		Na4-O27	2.45(3)
Na2-O5	2.512(8)		Na4-O22	2.49(2)
Na2-O5	2.512(8)		Na4-O22	2.49(2)
Na2-O5	2.512(8)			

Infrared spectroscopy of solid-state compound

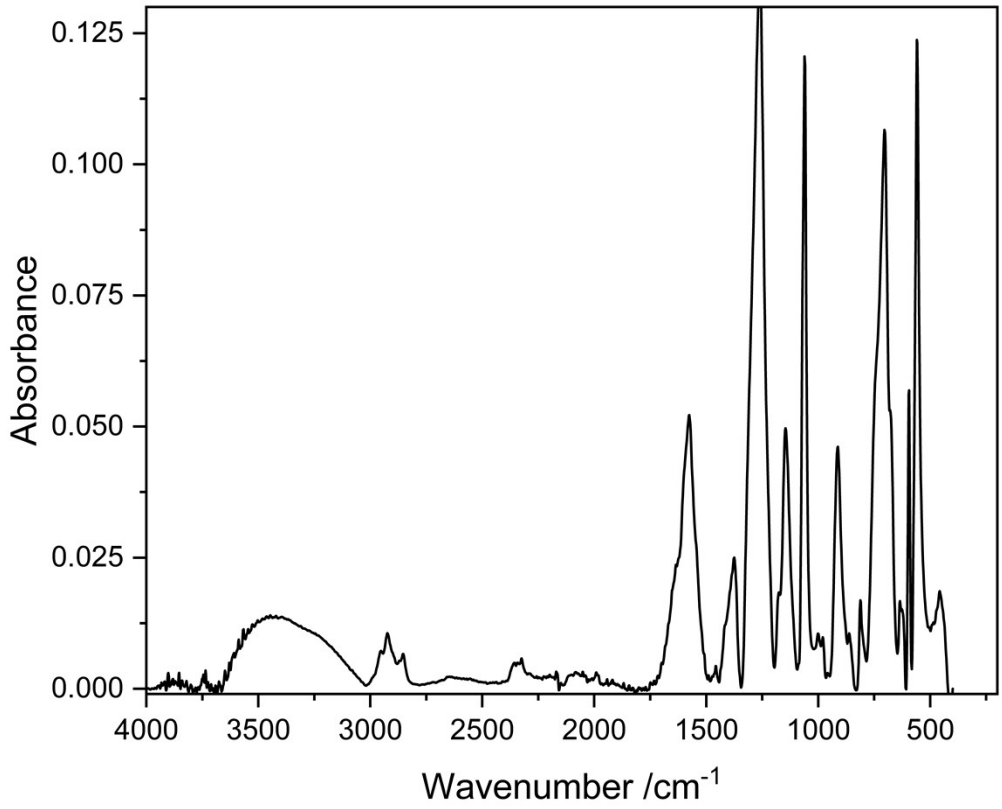

Figure S3. IR spectrum for the solid **NaU_{24}** compound (4000-500 cm^{-1}).

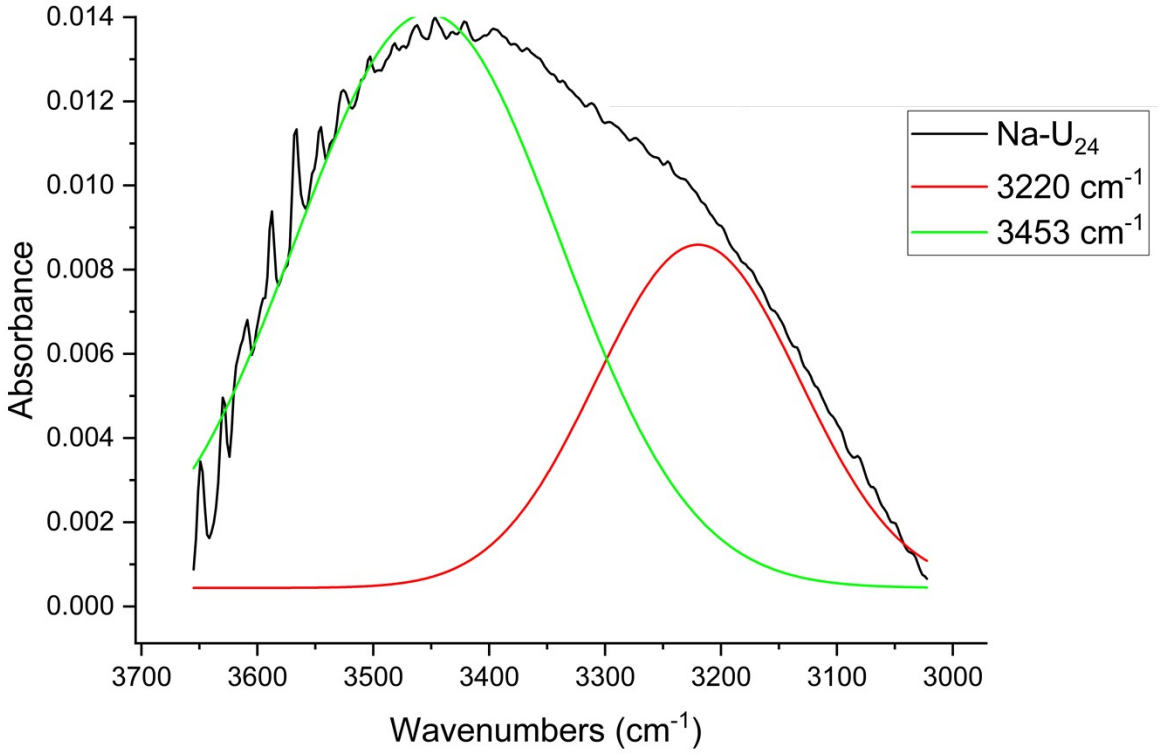

Figure S4. IR spectral features and peak fitting for the solid **NaU_{24}** between 3650-3000 cm^{-1}. R^2 and χ^2 for the fitting are 0.975 and 3.90 x 10^{-7}, respectively.

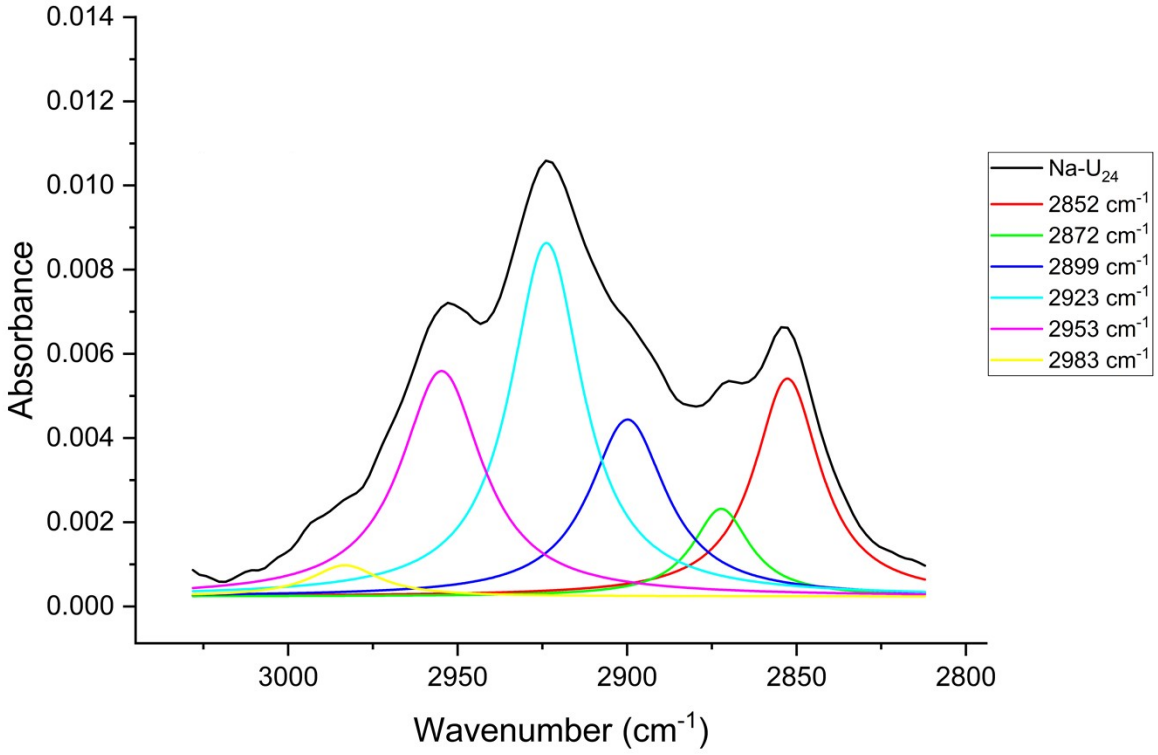

Figure S5. IR spectral features and peak fitting for the solid **NaU_{24}** between 3000-2800 cm^{-1}. R^2 and χ^2 for the fitting are 0.996 and 3.05 x 10^{-8}, respectively.

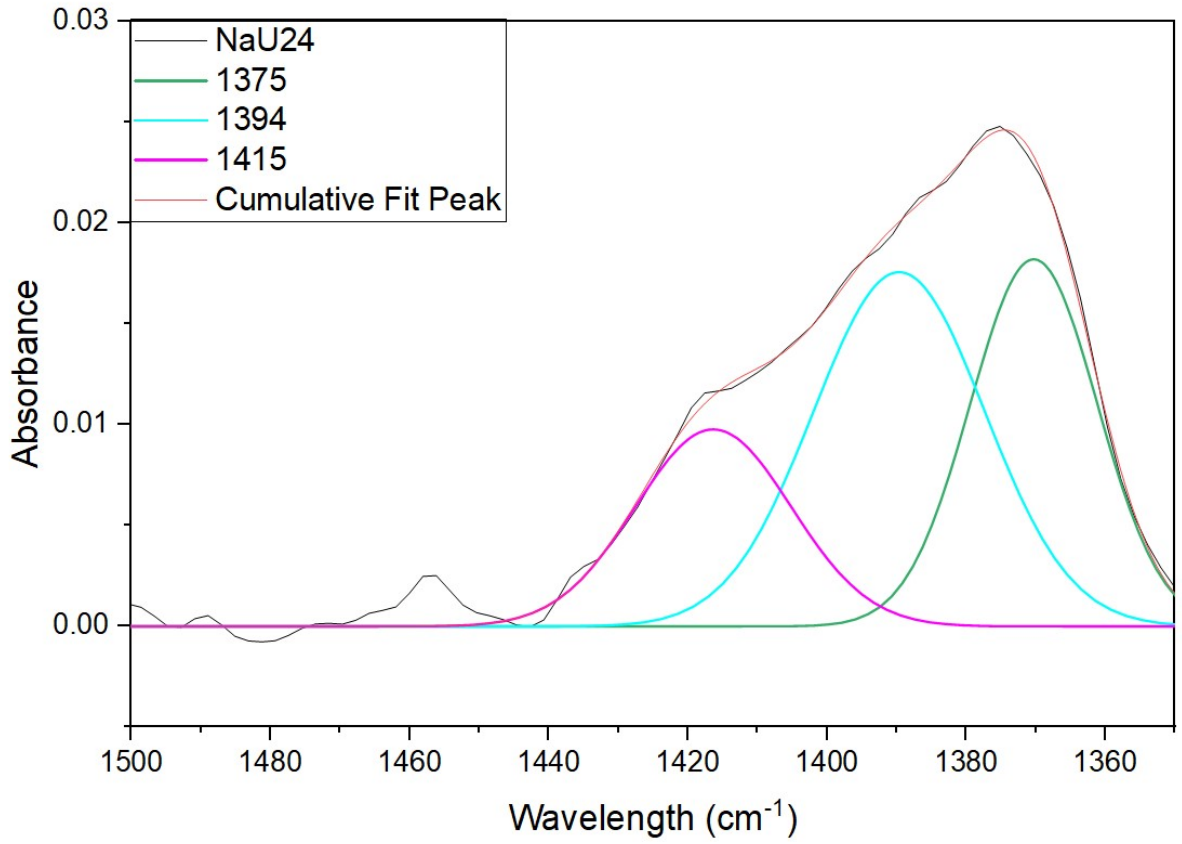

Figure S6. IR spectral features and peak fitting for the solid $\mathbf{NaU_{24}}$ between 1500-1350 cm^{-1}. R^2 and χ^2 for the fitting are 0.995 and 4.25 x 10^{-7}, respectively.

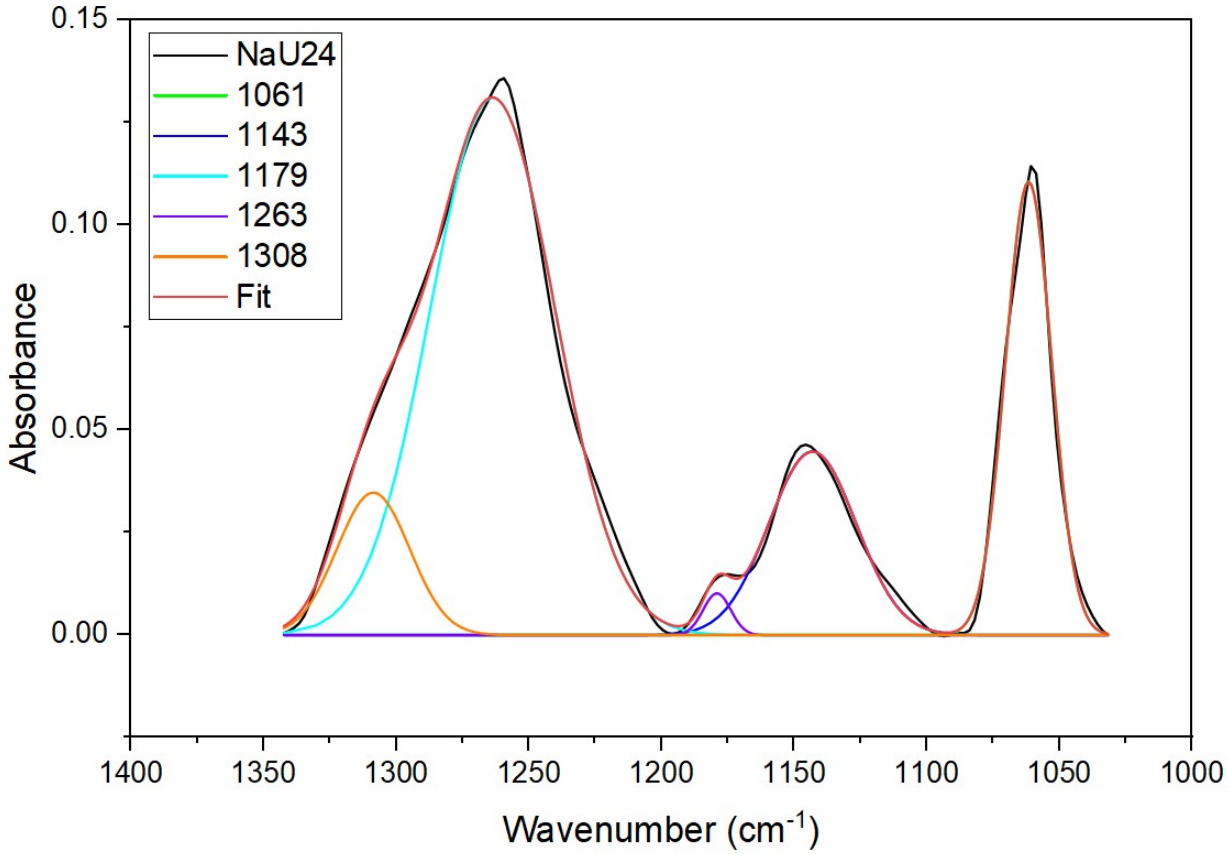

Figure S7. IR spectral features and peak fitting for the solid **NaU_{24}** between 1350-1025 cm^{-1}. R^2 and χ^2 for the fitting are 0.995 and 8.20 x 10^{-6}, respectively.

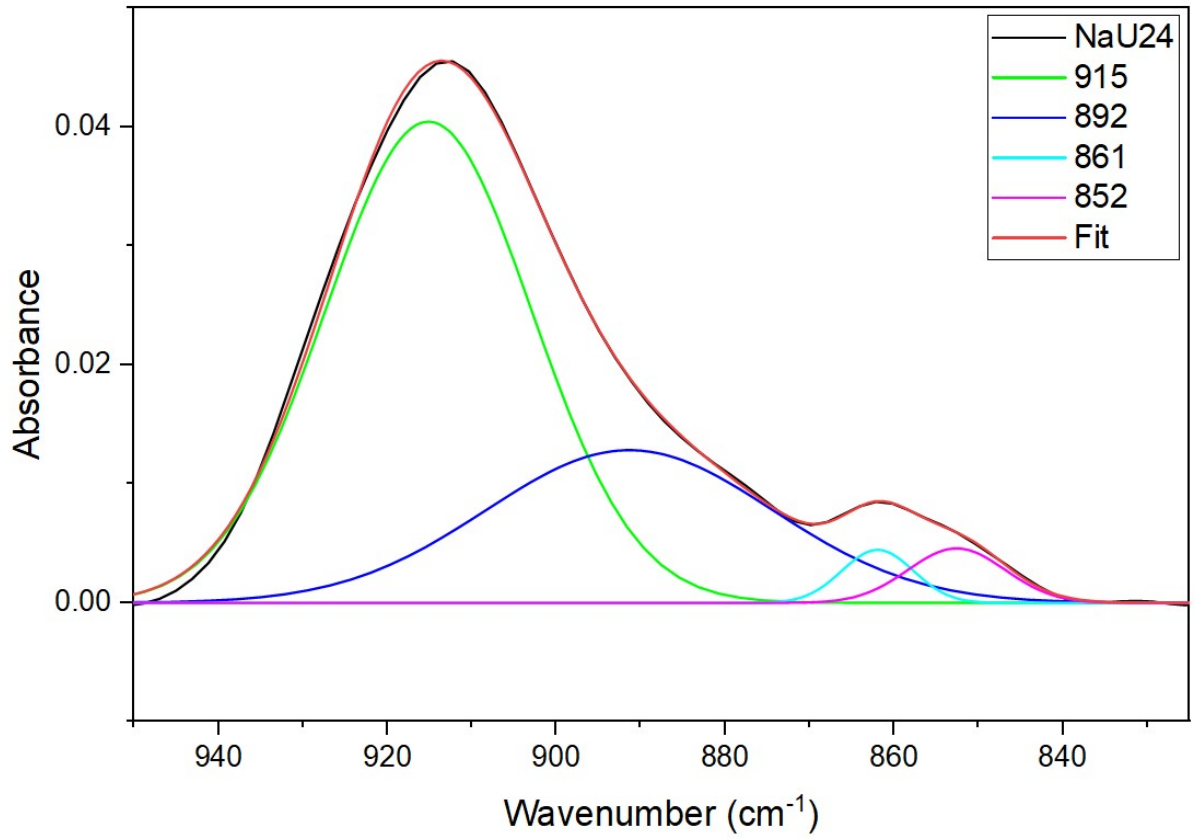

Figure S8. IR spectral features and peak fitting for the solid $\mathbf{NaU_{24}}$ between 950-825 cm^{-1}. R^2 and χ^2 for the fitting are 0.999 and 2.35 x 10^{-7}, respectively.

DFT studies

Table S4. DFT optimized XYZ coordinates of $HO_2^{\cdot}$

O	0.95025	0.24900	0.00000
O	0.02392	1.19836	0.00000
H	0.51523	2.04425	0.00000

Table S5. DFT optimized XYZ coordinates of $HO^{\cdot}$

O	0.49202	-0.04796	0.00000
H	0.16598	0.87296	0.00000

Table S6. DFT optimized XYZ coordinates of $H_2O^{+\cdot}$

O	8.21638	-0.01600	0.00000
H	9.22444	-0.02029	0.00000
H	7.87578	0.93278	0.00000

Table S7. DFT optimized XYZ coordinates of $O_2^{-\cdot}$

O	0.95314	0.22387	0.00000
O	0.03926	1.21453	0.00000

Table S8. DFT optimized XYZ coordinates of $NaO_2^{\cdot}$

O	1.06647	0.62276	0.00000
O	-0.198075	1.09006	0.00000
Na	1.1347058	2.75147	0.00000

Table S9. DFT optimized XYZ coordinates of U-Dimer 1

O	6.0344	13.0459	12.5266
O	6.0903	13.027	13.9894
O	5.9811	15.3158	10.7286
U	6.1027	17.5741	9.8988
U	6.1053	15.1991	13.2918
O	6.2202	19.6763	9.1002
O	6.3024	19.716	10.5483
O	7.978	15.1843	13.145
O	4.2302	15.2939	13.289
O	4.2532	17.6347	9.9276

O	5.9122	16.1221	7.8348
O	7.9337	17.3406	9.7644
O	5.9807	17.3724	7.4155
O	6.1733	17.5067	12.2634
O	6.1962	16.7291	14.9858
O	6.1781	15.3824	15.5602
H	5.8609	18.2306	12.8093
H	6.6716	14.731	10.4064

Table S10. DFT optimized XYZ coordinates of U-Dimer 2

O	6.1985	13.0485	12.2962
O	5.6623	13.0935	13.6472
O	7.0324	15.1612	10.7841
U	6.1748	15.2109	13.0045
O	7.8888	15.047	13.7049
O	4.4508	15.4607	12.3552
O	4.291	18.835	16.1766
O	6.6656	17.5064	12.4791
O	2.4695	17.6289	18.1297
U	3.9353	16.5791	16.6873
O	5.5908	16.7213	15.0171
O	5.2076	16.6114	18.0159
O	2.8074	14.7008	17.9898
O	5.3756	15.3224	15.3352
O	2.5563	16.4485	15.4781
O	3.6412	14.1417	17.1348
H	6.5213	17.9332	13.3302
H	6.9312	14.2379	10.5325
H	2.8931	17.7952	18.9773
H	4.9943	18.8617	15.5202

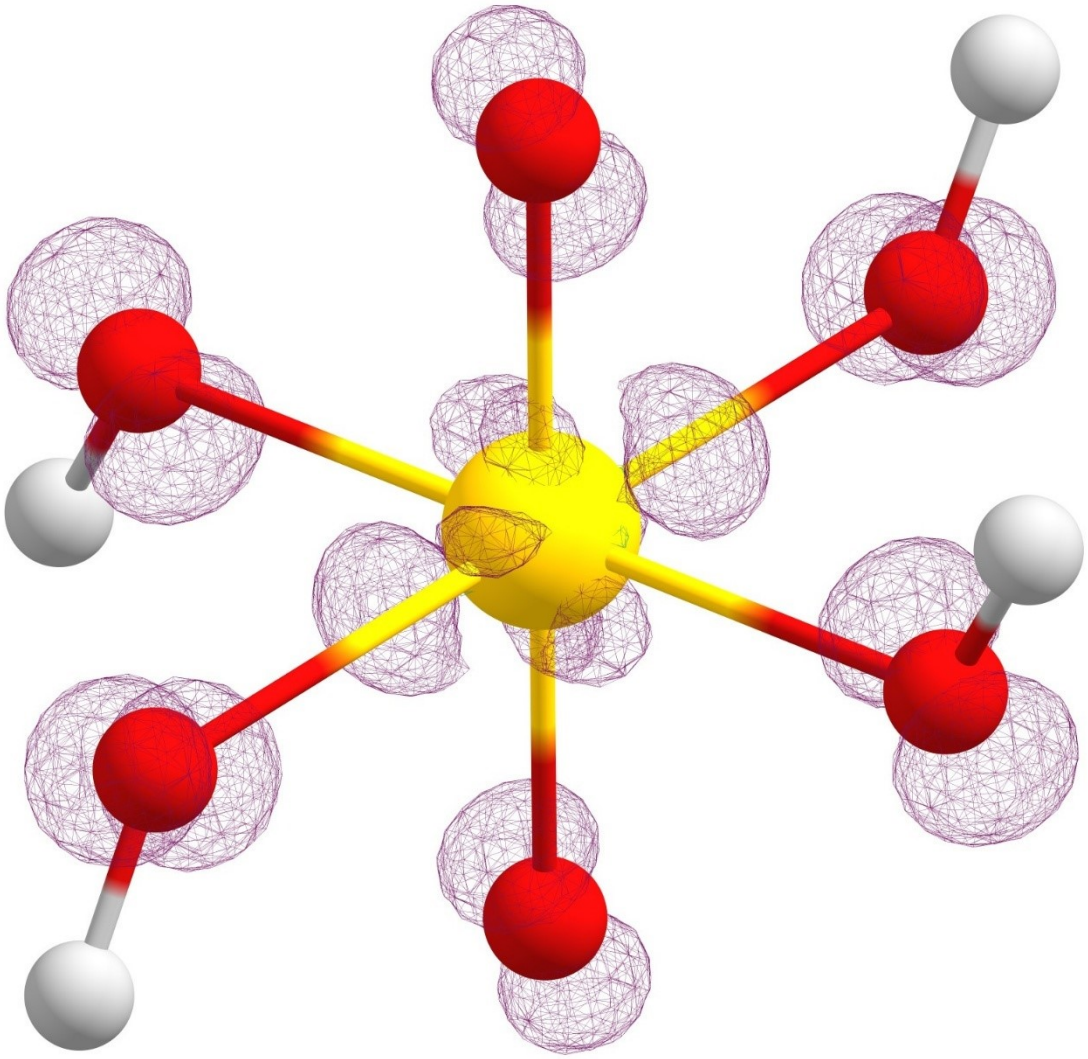

Figure S9. DFT calculated spin density of $[UO_2(OH)_4]^{*-}$ shows the spin density is delocalized across the entire molecule instead of confined to a hydroxo ligand. The iso surface of the spin densities were generated with contour value of 0.015.