

Sulfate-Centered Sodium-Icosahedron-Templated Uranyl Peroxide Phosphate Cages with Uranyl Bridged by μ - η^1 : η^2 Peroxide

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Supporting Information

Table S1. Crystal data and details of the structure determination for **1** and **2**.

| Compound | 1 | 2 |
|-------------------------------|---|--|
| Formula | Li ₁ Na ₁₈ O ₁₆₅ P ₆ S ₁ U ₂₀ | Li ₆ Na ₁₈ O ₁₈₈ P ₁₂ S ₁ U ₂₀ |
| Formula weight | 7991.24 | 8627.76 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2/c | P2(1)/n |
| a [Å] | 31.882(4) | 17.839(3) |
| b [Å] | 17.584(2) | 18.370(3) |
| c [Å] | 31.647(4) | 27.655(4) |
| α [°] | 90 | 90 |
| β [°] | 111.0014(15) | 91.9724(17) |
| γ [°] | 90 | 90 |
| V [Å ³] | 16563(4) | 9058(2) |
| Z | 4 | 2 |
| D (calc) [g/cm ³] | 3.205 | 3.163 |
| μ (Mo K α) [/mm] | 19.715 | 18.099 |

| | | |
|--------------------------------------|---------------------------|---------------------------|
| F(000) | 13772 | 7512 |
| T [K] | 100(2) | 100(2) |
| λ (Mo K α) [Å] | 0.71073 | 0.71073 |
| 2 θ (min., max.) [°] | 0.684, 27.542 | 1.331, 27.591 |
| Index range (h, k, l) | -41: 41, -22: 22, -41: 41 | -23: 23, -23: 23, -36: 35 |
| Total reflections | 195720 | 107016 |
| N _{ref} , N _{par} | 38027, 982 | 20921, 552 |
| R(int) | 0.1297 | 0.1116 |
| R ₁ ($I > 2\sigma(I)$) | 0.0637 | 0.0481 |
| R ₁ (all data) | 0.0941 | 0.0723 |
| wR ₂ ($I > 2\sigma(I)$) | 0.1576 | 0.1218 |
| wR ₂ (all data) | 0.1797 | 0.1364 |
| S | 0.938 | 0.945 |

Table S2. Bond-valence calculations of O atoms of phosphate groups for U₂₀P₆.

| Atom | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Total Bond valence |
|------|---------|-------------|--------------|---------|-------------|--------------|----------|-------------|--------------|--------------------|
| O59 | P1-O59 | 1.506 | 1.3033 | U1-O59 | 2.3923 | 0.4242 | | | | 1.7274 |
| O10 | P1-O10 | 1.514 | 1.2754 | U2-O10 | 2.3813 | 0.4370 | Na2-O10 | 2.3849 | 0.2058 | 1.9182 |
| O37 | P1-O37 | 1.5249 | 1.2384 | U3-O37 | 2.3677 | 0.4534 | | | | 1.6917 |
| O60 | P1-O60 | 1.5963 | 1.0210 | | | | | | | 1.0210 |
| O93 | P2-O93 | 1.512 | 1.2823 | U16-O93 | 2.4028 | 0.4123 | | | | 1.6946 |
| O42 | P2-O42 | 1.5122 | 1.2816 | U17-O42 | 2.3885 | 0.4286 | Na10-O42 | 2.4066 | 0.1941 | 1.9043 |
| O51 | P2-O51 | 1.52 | 1.2549 | U14-O51 | 2.3602 | 0.4626 | | | | 1.7175 |
| O108 | P2-O108 | 1.6019 | 1.0057 | | | | | | | 1.0057 |
| O56 | P3-O56 | 1.5129 | 1.2792 | U1-O56 | 2.3836 | 0.4343 | | | | 1.7135 |
| O2 | P3-O2 | 1.517 | 1.2651 | U3-O2 | 2.3815 | 0.4368 | | | | 1.7018 |
| O30 | P3-O30 | 1.5258 | 1.2353 | U9-O30 | 2.3779 | 0.4410 | Na5-O30 | 2.4027 | 0.1961 | 1.8725 |
| O44 | P3-O44 | 1.5805 | 1.0656 | | | | | | | 1.0656 |
| O73 | P4-O73 | 1.5002 | 1.3238 | U14-O73 | 2.3787 | 0.4401 | | | | 1.7639 |
| O9 | P4-O9 | 1.5211 | 1.2511 | U6-O9 | 2.3766 | 0.4426 | Na12-O9 | 2.4430 | 0.1759 | 1.8696 |
| O57 | P4-O57 | 1.5307 | 1.2191 | U16-57 | 2.3512 | 0.4740 | | | | 1.6931 |
| O89 | P4-O89 | 1.5696 | 1.0974 | | | | | | | 1.0974 |
| O4 | P5-O4 | 1.5054 | 1.3054 | U10-O4 | 2.4161 | 0.3978 | | | | 1.7031 |

| | | | | | | | | | | |
|------|---------|--------|--------|---------|--------|--------|----------|--------|--------|--------|
| O6 | P5-O6 | 1.5122 | 1.2816 | U8-O6 | 2.3440 | 0.4833 | | | | 1.7649 |
| O38 | P5-O38 | 1.5288 | 1.2254 | U4-O38 | 2.3678 | 0.4532 | Na11-O38 | 2.4777 | 0.1602 | 1.8388 |
| O5 | P5-O5 | 1.5948 | 1.0252 | | | | | | | 1.0252 |
| O58 | P6-O58 | 1.5224 | 1.2468 | U18-O58 | 2.3399 | 0.4887 | Na8-O58 | 2.4713 | 0.1629 | 1.8984 |
| O23 | P6-O23 | 1.5188 | 1.2589 | U8-O23 | 2.3938 | 0.4225 | | | | 1.6814 |
| O3 | P6-O3 | 1.5324 | 1.2135 | U10-O3 | 2.3374 | 0.4920 | | | | 1.7055 |
| O114 | P6-O114 | 1.5704 | 1.0951 | | | | | | | 1.0951 |

Table S3. Bond-valance calculations of O atoms of phosphate groups for U₂₀P₁₂.

| Atom | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Total Bond valence |
|------|--------|-------------|--------------|---------|-------------|--------------|---------|-------------|--------------|--------------------|
| O38 | P1-O38 | 1.5123 | 1.2813 | U8-O38 | 2.3636 | 0.4584 | | | | 1.7397 |
| O4 | P1-O4 | 1.5233 | 1.2437 | U7-O4 | 2.3820 | 0.4362 | Na1-O4 | 2.4013 | 0.1969 | 1.8768 |
| O26 | P1-O26 | 1.5291 | 1.2244 | U2-O26 | 2.3898 | 0.4271 | | | | 1.6514 |
| O50 | P1-O50 | 1.5789 | 1.0702 | | | | | | | 1.0702 |
| O49 | P2-O49 | 1.5103 | 1.2882 | U10-O49 | 2.3374 | 0.4920 | | | | 1.7802 |
| O34 | P2-O34 | 1.5189 | 1.2586 | U1-O34 | 2.3941 | 0.4221 | Na4-O34 | 2.3914 | 0.2022 | 1.8830 |
| O21 | P2-O21 | 1.5344 | 1.2070 | U5-O21 | 2.4215 | 0.3920 | | | | 1.5990 |
| O32 | P2-O32 | 1.597 | 1.0191 | | | | Li3-O32 | 2.4593 | 0.0682 | 1.0873 |
| O48 | 1.5049 | 1.3071 | 1.2980 | U6-O48 | 2.3551 | 0.4691 | | | | 1.7762 |
| O23 | 1.5146 | 1.2733 | 1.2623 | U3-O23 | 2.3823 | 0.4358 | Na2-O23 | 2.4265 | 0.1839 | 1.8930 |

| | | | | | | | | | | |
|-----|--------|--------|--------|---------|--------|--------|----------|--------|--------|--------|
| O28 | 1.53 | 1.2214 | 1.1882 | U9-O28 | 2.3605 | 0.4623 | | | | 1.6837 |
| O61 | 1.6072 | 0.9914 | 0.9903 | | | | | | | 0.9914 |
| O66 | P4-O66 | 1.526 | 1.2347 | U6-O66 | 2.2941 | 0.5531 | | | | 1.7878 |
| O22 | P4-O22 | 1.5269 | 1.2317 | | | | | | | 1.2317 |
| O59 | P4-O59 | 1.5315 | 1.2165 | U9-O59 | 2.3323 | 0.4989 | | | | 1.7153 |
| O46 | P4-O46 | 1.5783 | 1.0719 | | | | | | | 1.0719 |
| O65 | P5-O65 | 1.5035 | 1.3121 | U8-O65 | 2.3006 | 0.5435 | | | | 1.8556 |
| O55 | P5-O55 | 1.5249 | 1.2384 | U2-O55 | 2.3502 | 0.4753 | Na10-O55 | 2.5082 | 0.1475 | 1.8611 |
| O63 | P5-O63 | 1.5354 | 1.2037 | | | | Li1-O63 | 1.9764 | 0.2517 | 1.4554 |
| O68 | P5-O68 | 1.5926 | 1.0313 | | | | Li3-O68 | 2.1965 | 0.1389 | 1.1701 |
| O9 | P6-O9 | 1.494 | 1.3462 | U5-O9 | 2.3982 | 0.4175 | | | | 1.7637 |
| O67 | P6-O67 | 1.4995 | 1.3264 | U10-O67 | 2.3489 | 0.4770 | | | | 1.8033 |
| O52 | P6-O52 | 1.5388 | 1.1927 | | | | | | | 1.1927 |
| O42 | P6-O42 | 1.5783 | 1.0719 | | | | Na7-O42 | 2.4511 | 0.1721 | 1.2440 |

Table S4 Bond-valance calculations of non-bridging O atoms of μ - η^1 : η^2 peroxide groups for $U_{20}P_6$.

| Atom | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Total Bond valence |
|------|---------|-------------|--------------|--------|-------------|--------------|---------|-------------|--------------|--------------------|
| O13 | O13-O19 | 1.4961 | 0.2616 | U3-O13 | 2.2959 | 0.5504 | Na3-O13 | 2.5680 | 0.1255 | 0.9376 |

| | | | | | | | | | | |
|------|---------|--------|--------|---------|--------|--------|----------|--------|--------|--------|
| O45 | O45-O86 | 1.4734 | 0.2782 | U10-O45 | 2.2814 | 0.5724 | Na7-O45 | 2.5627 | 0.1273 | 0.9779 |
| O65 | O20-O65 | 1.4962 | 0.2616 | U1-O65 | 2.2720 | 0.5872 | Na6-O65 | 2.7195 | 0.0833 | 0.9321 |
| O79 | O79-O90 | 1.4714 | 0.2797 | U14-O79 | 2.2793 | 0.5757 | Na4-O79 | 2.6220 | 0.1084 | 0.9638 |
| O96 | O83-O96 | 1.4852 | 0.2695 | U16-O96 | 2.2874 | 0.5632 | Na9-O96 | 2.5972 | 0.1160 | 0.9486 |
| O122 | O7-O122 | 1.4791 | 0.2739 | U8-O122 | 2.2741 | 0.5839 | Na1-O122 | 2.5517 | 0.1311 | 0.9889 |

Table S5. Bond-valance calculations of non-bridging O atoms of $\mu\text{-}\eta^1\text{:}\eta^2$ peroxide groups for $\text{U}_{20}\text{P}_{12}$.

| Atom | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Bond | Bond length | Bond Valence | Total Bond valence |
|------|---------|-------------|--------------|--------|-------------|--------------|---------|-------------|--------------|--------------------|
| O19 | O11-O19 | 1.4734 | 0.2782 | U5-O19 | 2.3035 | 0.5393 | Na6-O19 | 2.4123 | 0.1911 | 1.0086 |
| O30 | O3-O30 | 1.4829 | 0.2711 | U2-O30 | 2.3435 | 0.4840 | Na3-O30 | 2.4168 | 0.1888 | 0.9439 |
| O57 | O16-O57 | 1.4757 | 0.2765 | U9-O57 | 2.4241 | 0.3893 | Na5-O57 | 2.4219 | 0.1862 | 0.8519 |

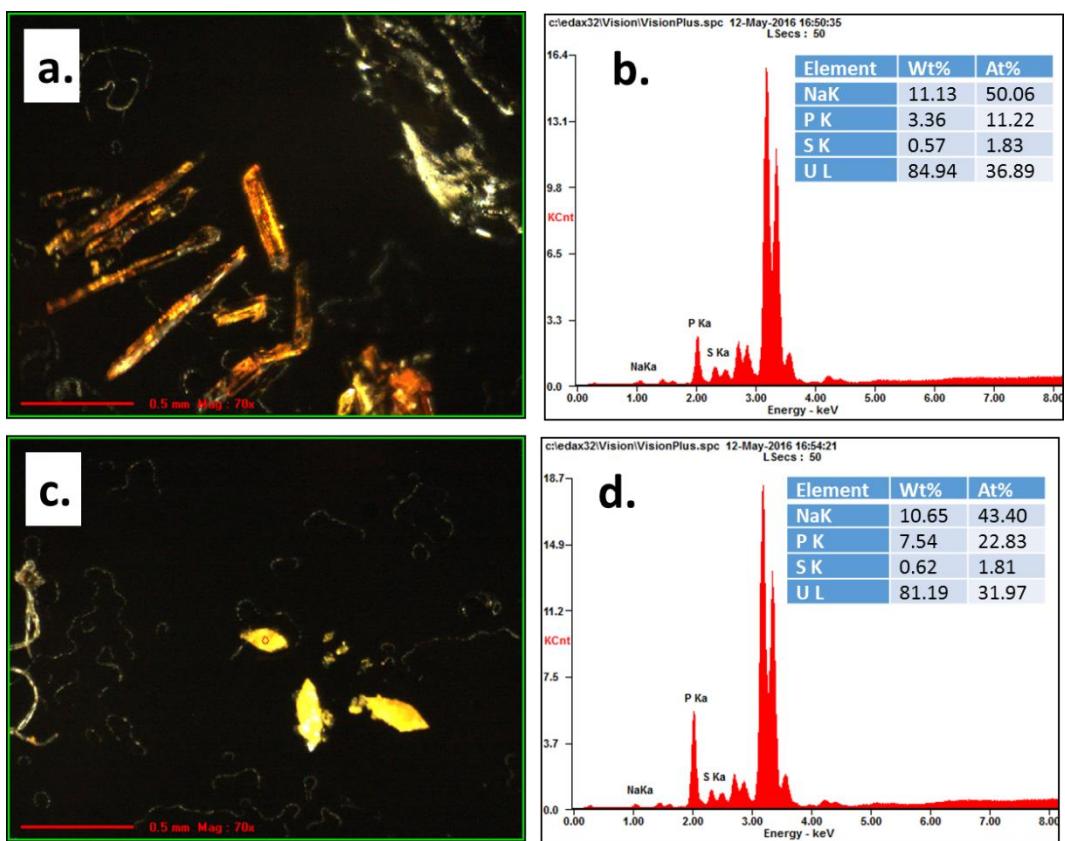


Figure S1. The X-ray fluorescence (XRF) analysis results for compound **1** (a, b) and **2** (c, d).

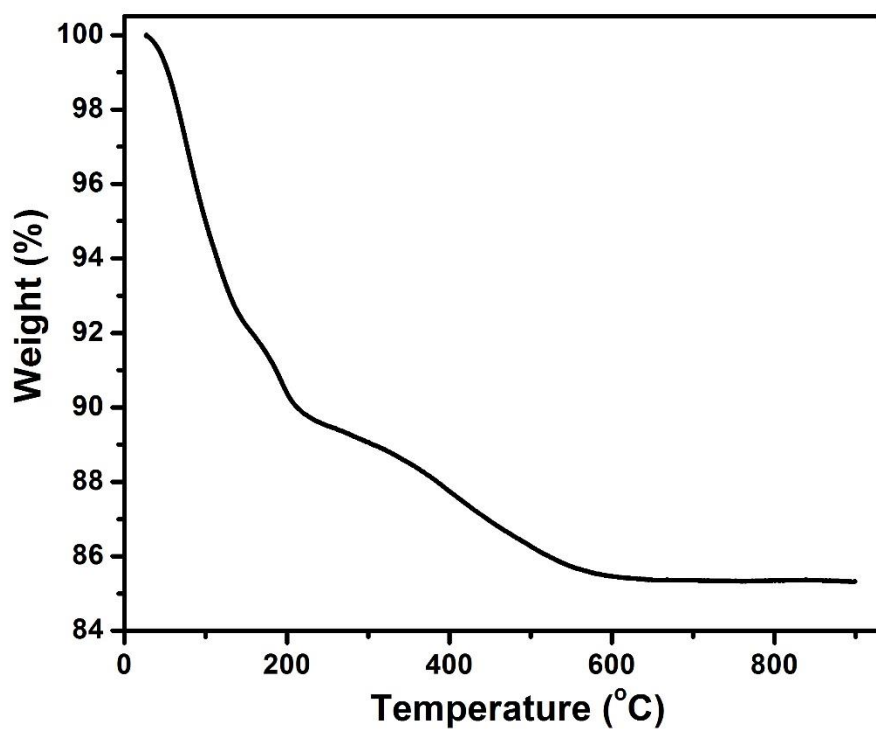


Figure S2. The thermogram of crystals of **1** ($U_{20}P_6$).

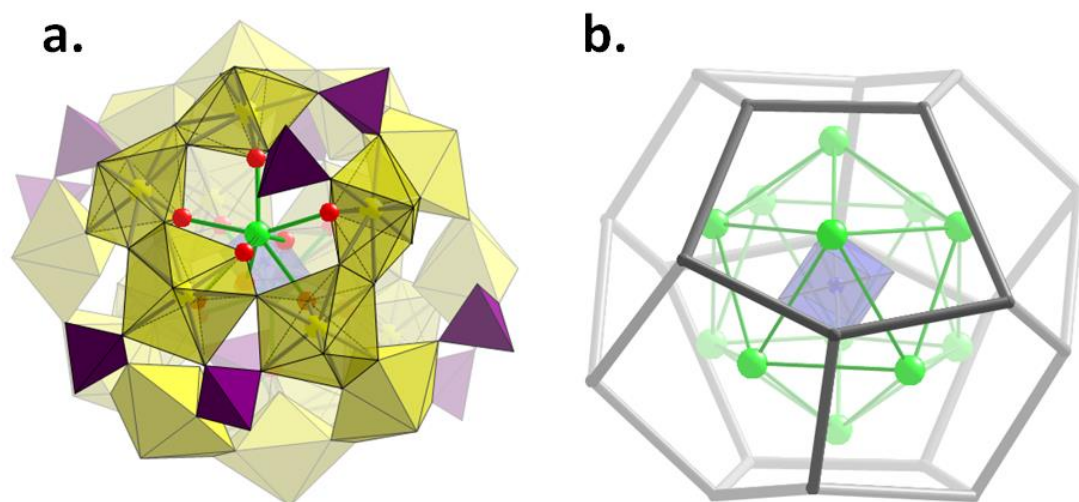


Figure S3. (a) Mixed ball-and-stick and polyhedral representation of $U_{20}P_{12}$ showing the coordination environment of a Na^+ ion. For clarity, only one Na^+ cation is displayed. (b) The sulfate-centered Na isocahedron contained in $U_{20}P_{12}$. For clarity,

$U_{20}P_{12}$ is shown in a graphical representation in which vertices correspond to U^{6+} cations. Color code: U atom and polyhedra are shown in yellow, phosphate tetrahedra in purple, the disordered sulfate polyhedron is in blue, the Na atoms shown as green spheres, and O atoms are shown as red spheres.

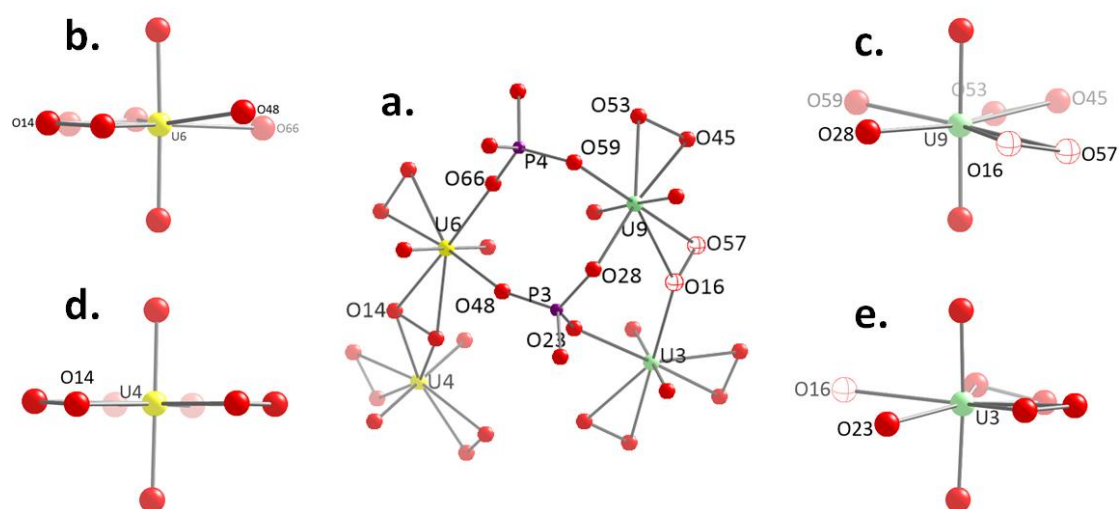


Figure S4. Ball—and-stick representations of a fragment of $U_{20}P_{12}$ containing four uranyl polyhedra labeled in Figure 5a (a) and the corresponding separate uranyl-oxygen coordination polyhedra (b, c, d, and e). These show the four types of coordination environments of uranyl ions in $U_{20}P_{12}$ and distortions of the equatorial planes of the uranyl bipyramids with incorporated phosphate group and peroxide in a $\mu\text{-}\eta^1\text{:}\eta^2$ configuration. U atoms are shown in yellow and pale green, P atoms in purple, and O atoms are in red.

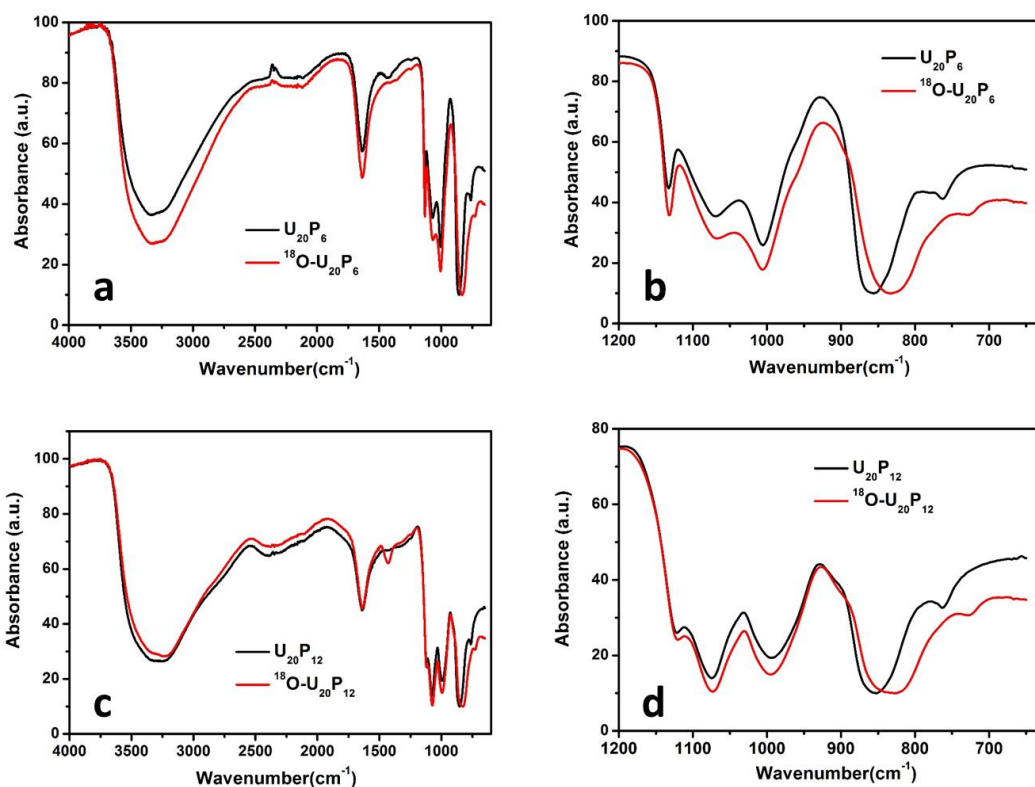


Figure S5. 4000 to 600 cm^{-1} and 1200 to 630 cm^{-1} regions of the IR spectra of crystals of **1** and **2** and their corresponding ^{18}O -uranyl labelled crystals prepared using $\text{U}^{18}\text{O}_2(\text{NO}_3)_2$.

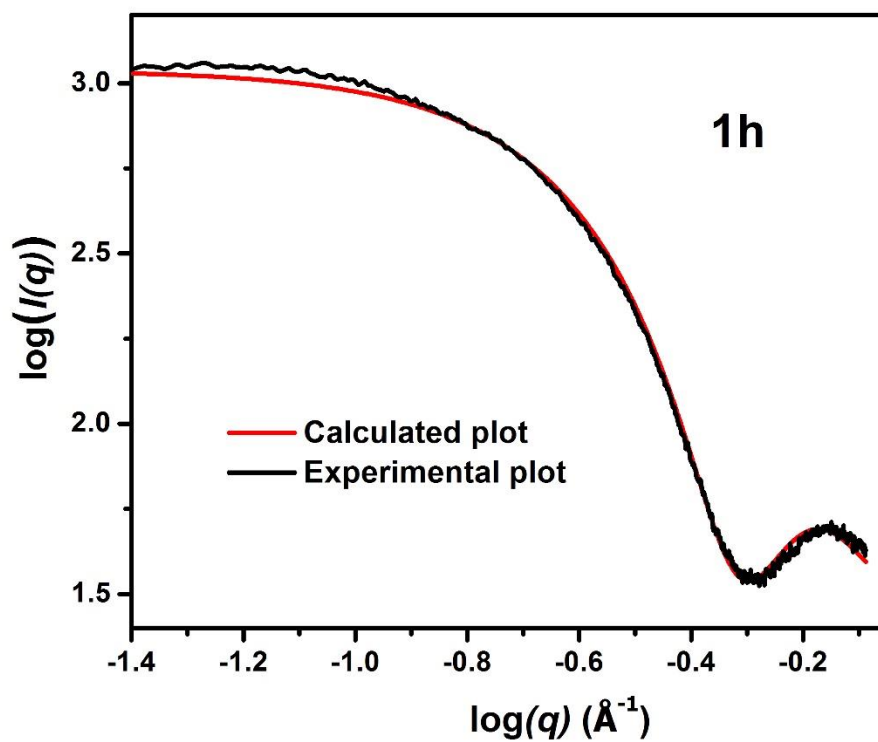


Figure S6. Experimental (black) SAXS plots of a 1h aged parent solution of **1**. As shown in red, the plot was fitted by using a sphere-shell model with a radius of 8.5 \AA , which is comparable to the size measured from the crystal structure and indicates U_{20}P_6 forms in the solution within one hour.

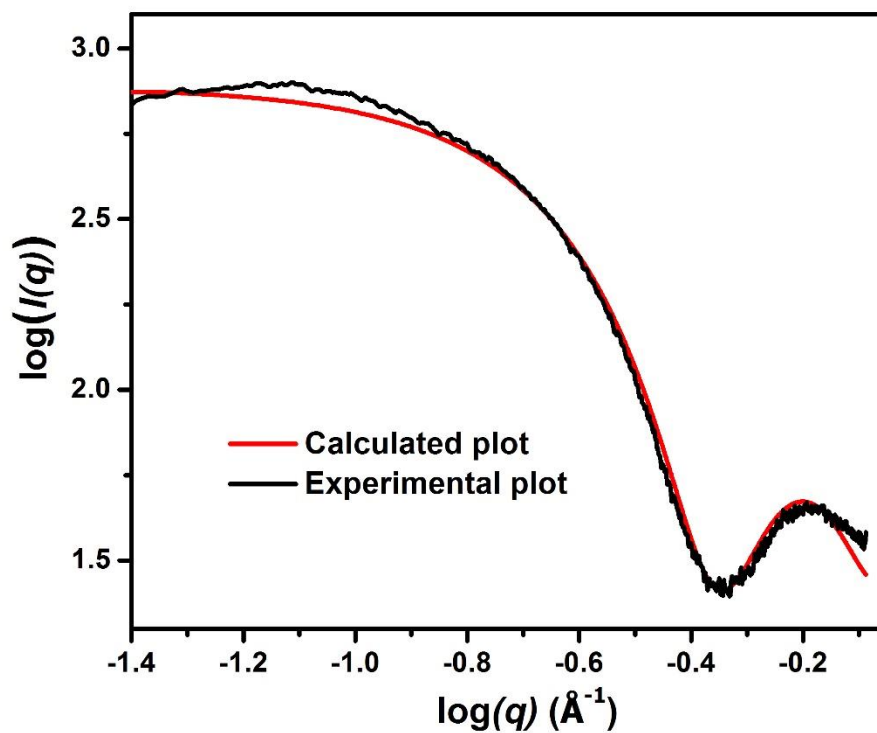


Figure S7. Experimental (black) SAXS plots of the five days aged solution created by dissolving crystals containing U_{20}P_6 in ultrapure water. As shown in red, the plot was fitted by using a sphere-shell model with a radius of 8.7 \AA , which is similar to the size measured from the crystal structure and indicates U_{20}P_6 is stable in the solution.