Electronic Supplementary Information

Layer-structured uranyl-oxide hydroxy-hydrates with Pr(III) and Tb(III) ions: hydroxyl to oxo transition driven by interlayer cations

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Table S1. Calculated BVS at ions and water positions for compounds **U-Pr** and **U-Tb**.

U-Pr					
U1	6.08	O3(O)	1.88	O10(O)	2.22
U2	6.09	O4(O)	2.05	O11(O)	1.79
U3	6.06	O5(O)	1.92	O12(H_2O)	0.56
Pr1	2.37	O6(O)	1.89	O13(H_2O)	0.56
Pr2	2.50	O7(OH)	1.67	O14(H_2O)	0.54
O1(O)	1.88	O8(O)	2.27		
O2(O)	2.11	O9(OH)	1.76		
U-Tb					
U1	5.86	O6(O)	1.64	O18(O)	2.06
U2	6.14	O7(O)	2.10	O19(OH)	1.11
U3	6.00	O8(O)	1.95	O20(O)	1.56
U4	6.08	O9(OH)	1.21	O21(O)	1.99
U5	6.06	O10(O)	1.66	O22(OH)	1.38
U6	5.86	O11(O)	1.94	O1W	0.30
Tb1	2.99	O12(OH)	1.41	O2W	0.28
O1(O)	1.67	O13(O)	2.16	O3W	0.29
O2(O)	1.72	O14(O)	1.52	O4W	0.33
O3(O)	1.96	O15(O)	1.75	O5W	0.31
O4(O)	1.98	O16(O)	1.58		
O5(OH)	1.56	O17(O)	1.56		

Table S2. The average U–O bond lengths (Å) and U–U distances (Å) within the uranyl oxide layers for compounds **U-Pr**, **U-Tb** and schoepite.

Compound	**U-Pr**	**U-Tb**	**Schoepite**
O/OH	1.6	1.0	0.17
U–O_{OXO} (Å)	2.196–2.456	2.175–2.435	2.222–2.238
Average U–O_{OXO} (Å)	2.280	2.271	2.232
U–O_{OH} (Å)	2.218–2.625	2.299–2.658	2.302–2.626
Average U–O_{OH} (Å)	2.367	2.420	2.439
U–U distance (Å)	3.772–3.849	3.706–4.061	3.843–3.976
Average U–U distance (Å)	3.802	3.855	3.900

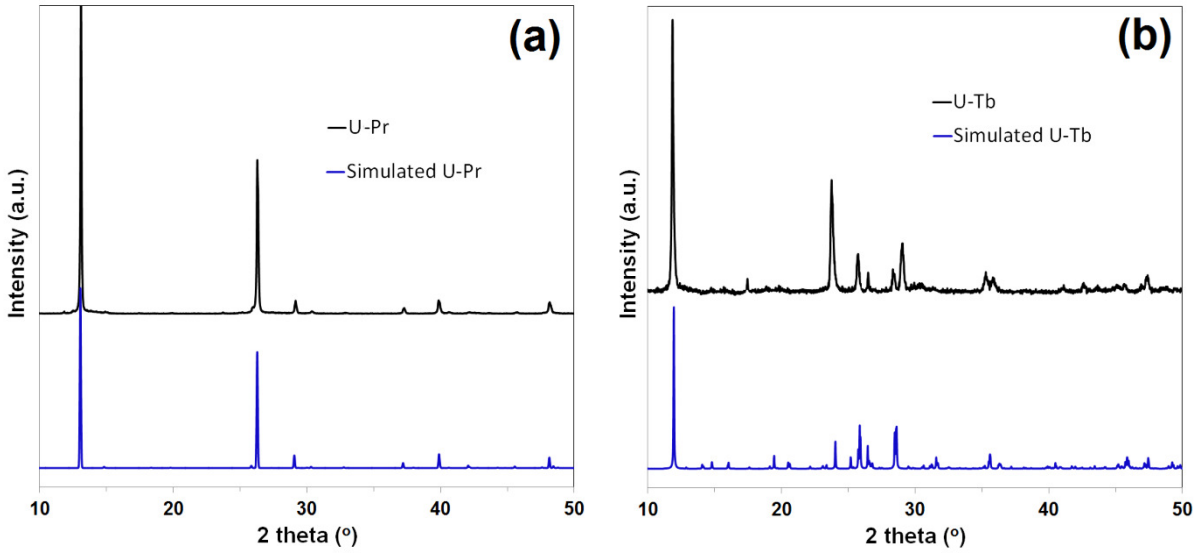

Fig. S1. PXRD patterns of compounds **U-Pr** (a) and **U-Tb** (b) with measured on top of the simulated ones. The simulated pattern for **U-Pr** is in [102] zone axis suggesting a preferred crystal orientation.

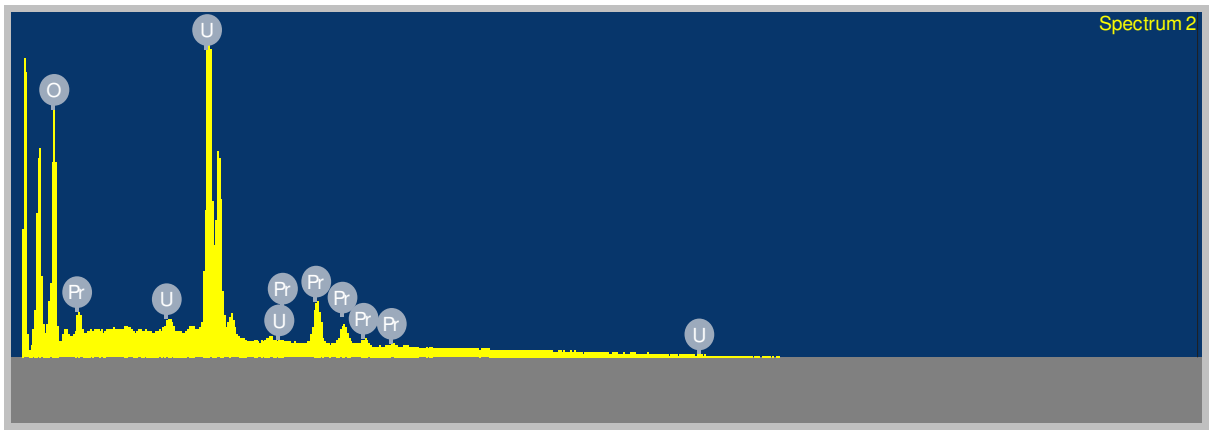

Fig. S2. EDS spectrum of compound **U-Pr** with U : Pr atomic ratio of 2 : 1.

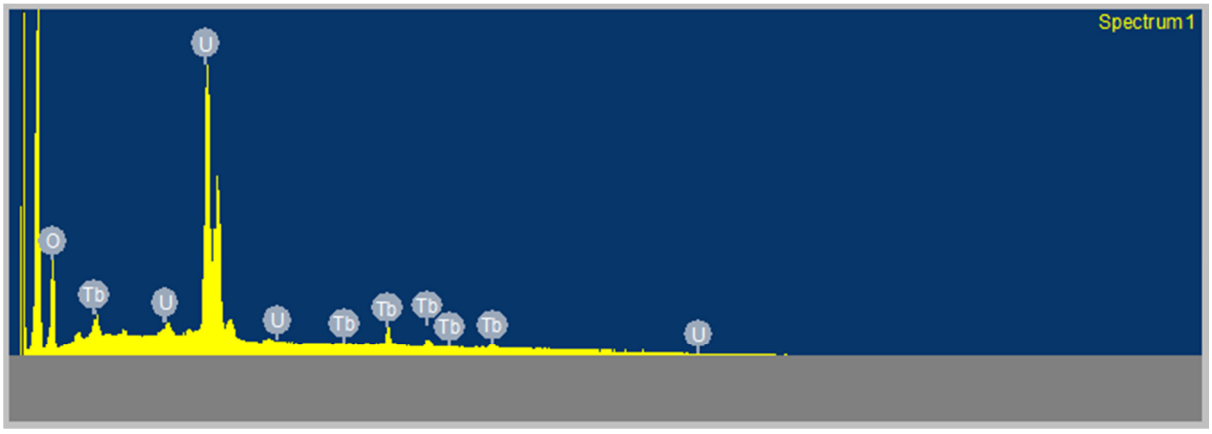

Fig. S3. EDS spectrum of compound **U-Tb** with U : Tb atomic ratio of 6 : 1.

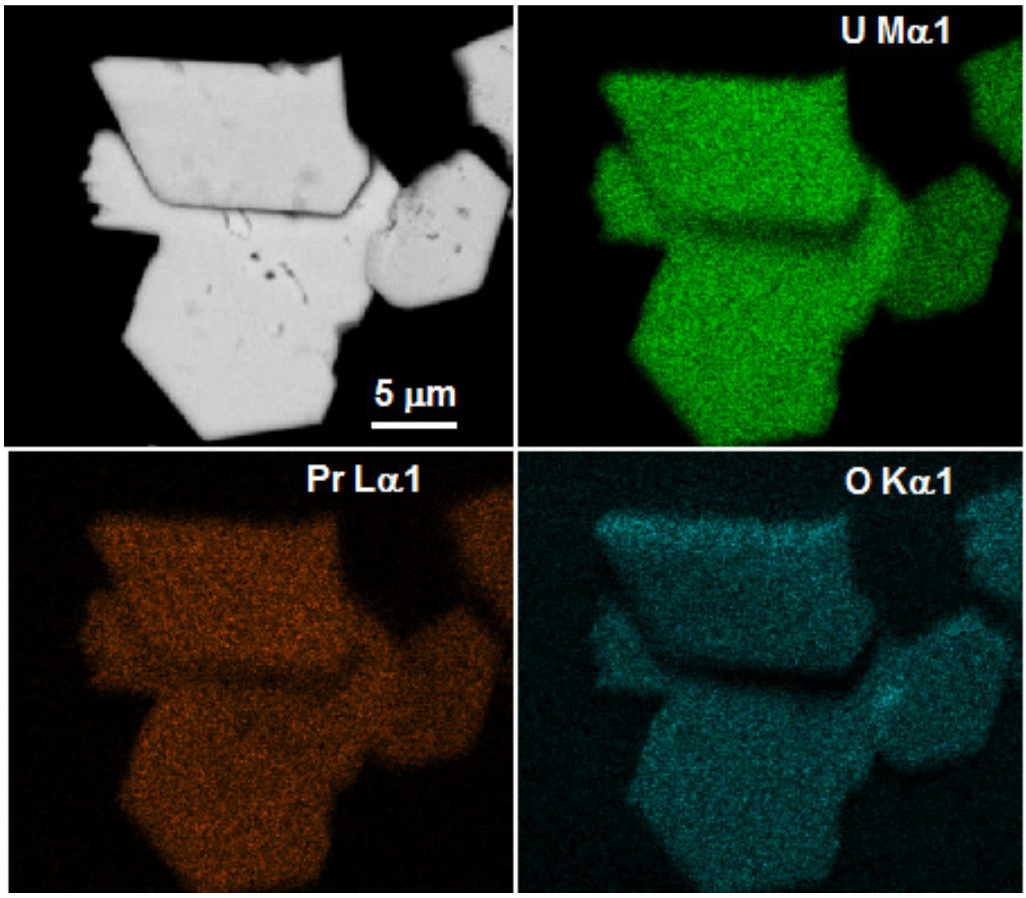

Fig. S4. Backscattered SEM image and EDS mapping of compound **U-Pr**.

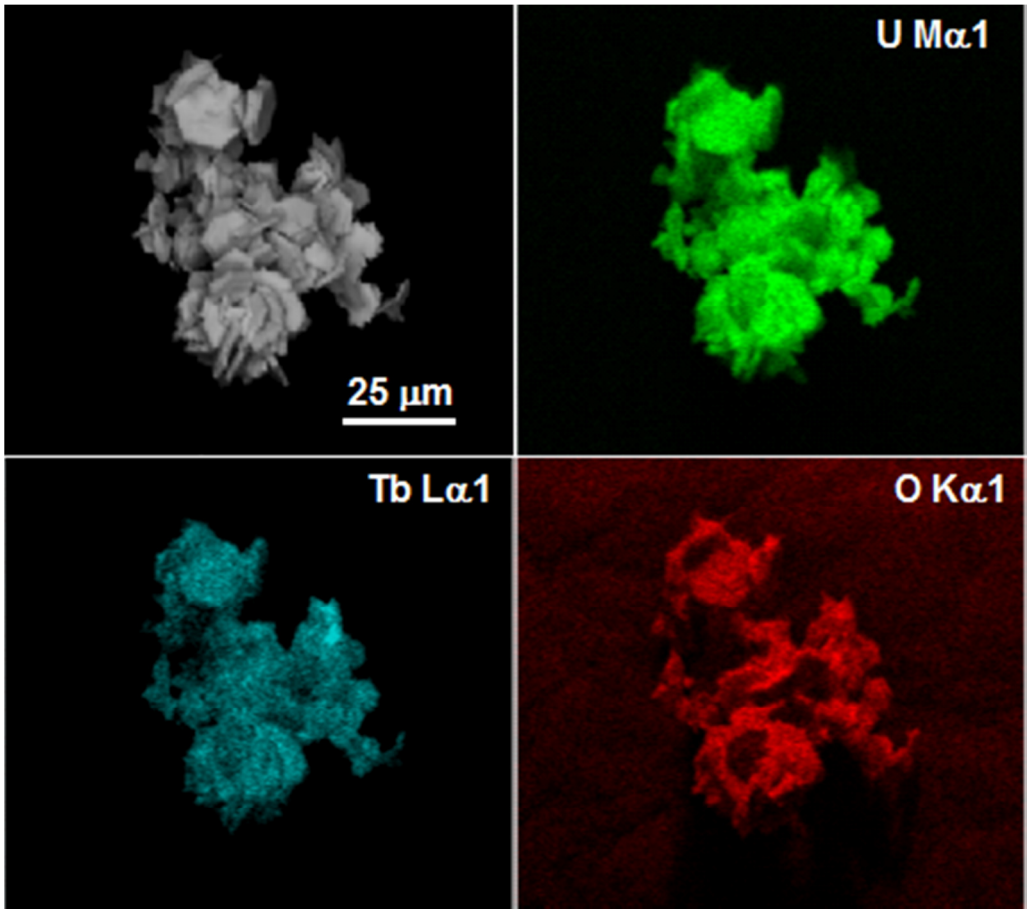

Fig. S5. Backscattered SEM image and EDS mapping of compound **U-Tb**.

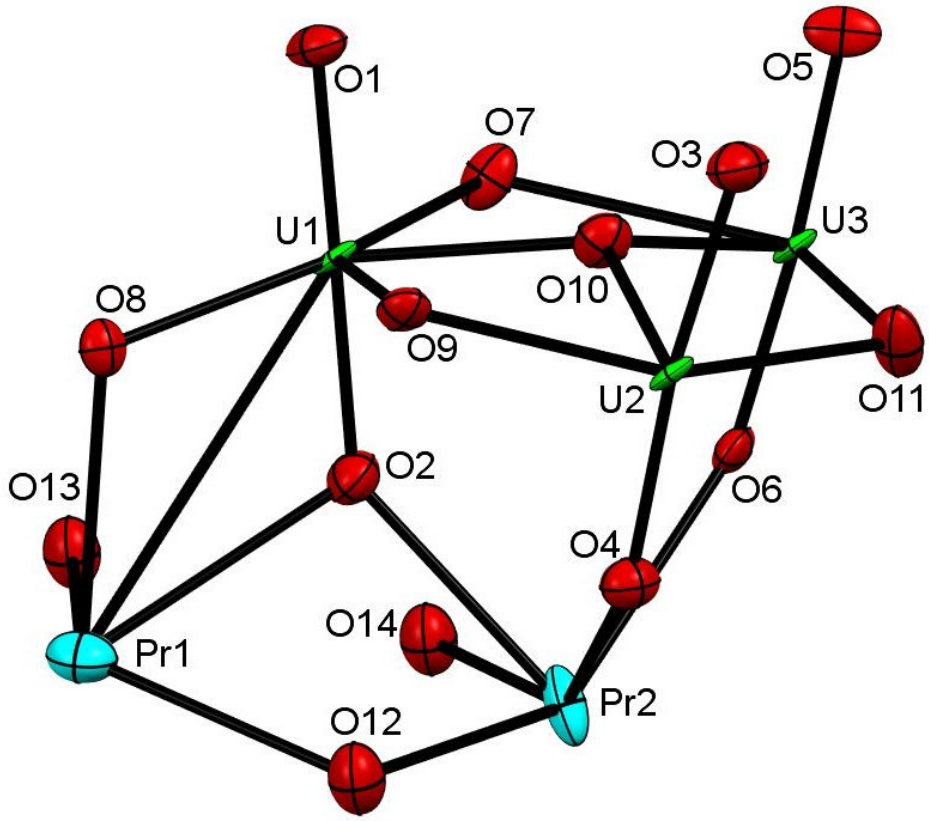

Fig. S6. An ORTEP drawing (50 % ellipsoid) of the asymmetric unit for compound **U-Pr**.

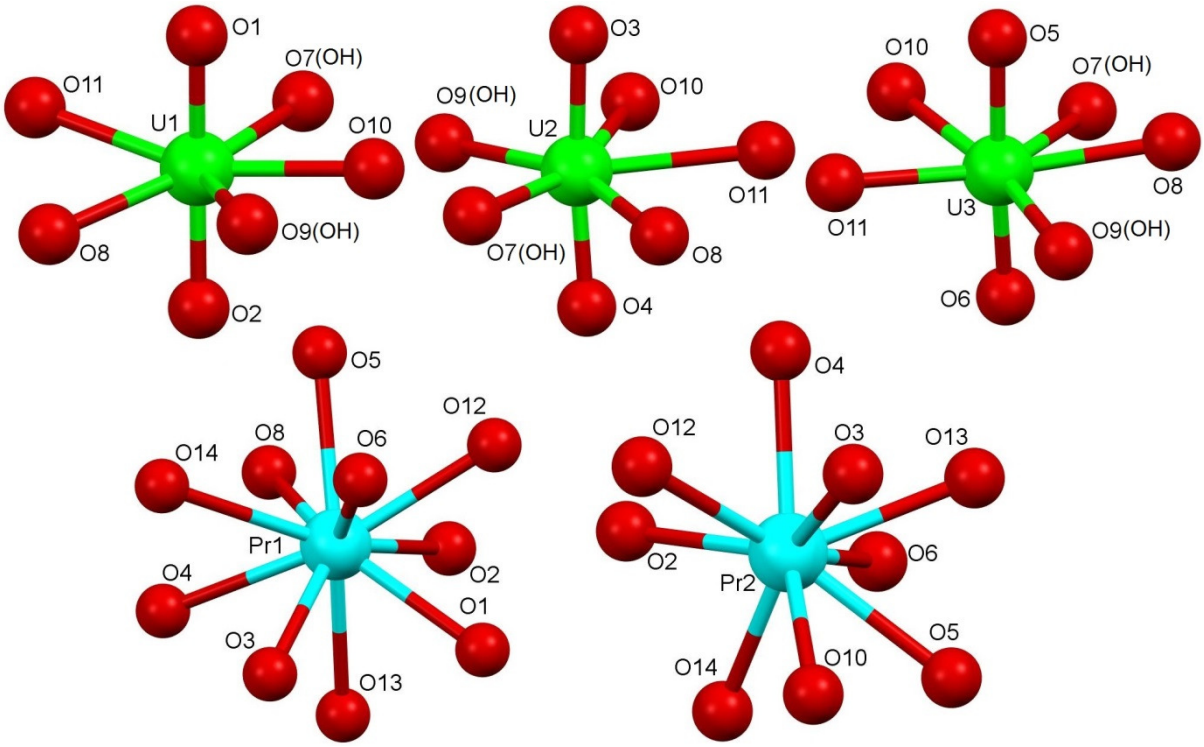

Fig. S7. Metal coordination environments of compound **U-Pr** with hydroxyl (OH) groups marked in brackets.

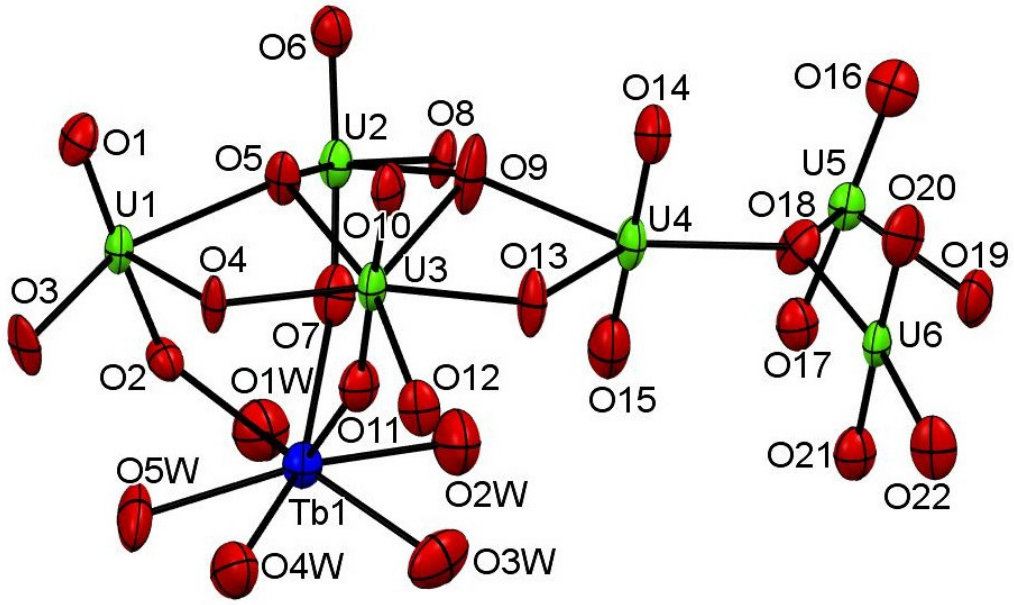

Fig. S8. An ORTEP drawing (50% ellipsoid) of the asymmetric unit for compound **U-Tb**.

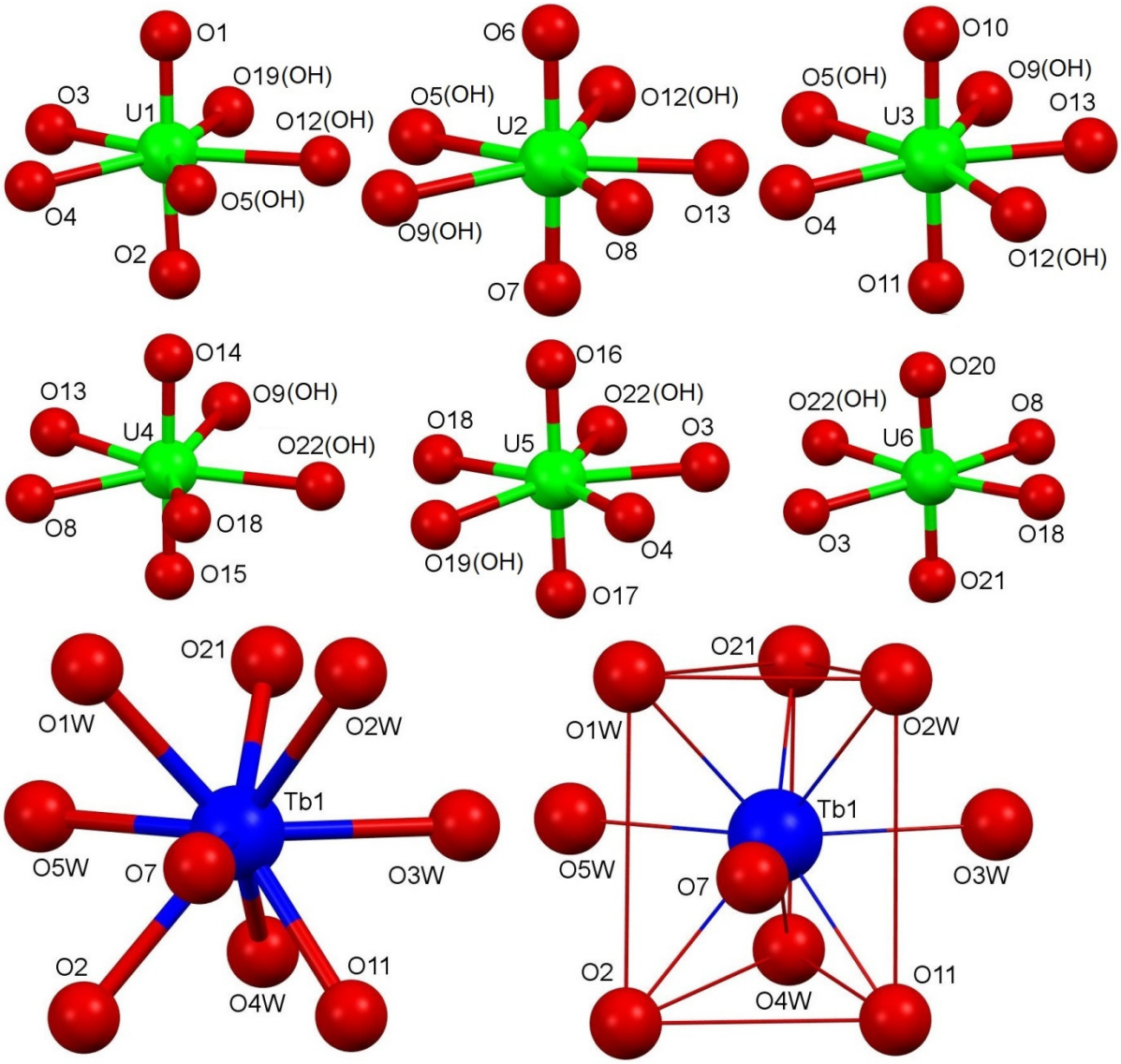

Fig. S9. Metal coordination environments of compound **U-Tb** with hydroxyl (OH) groups marked in brackets.

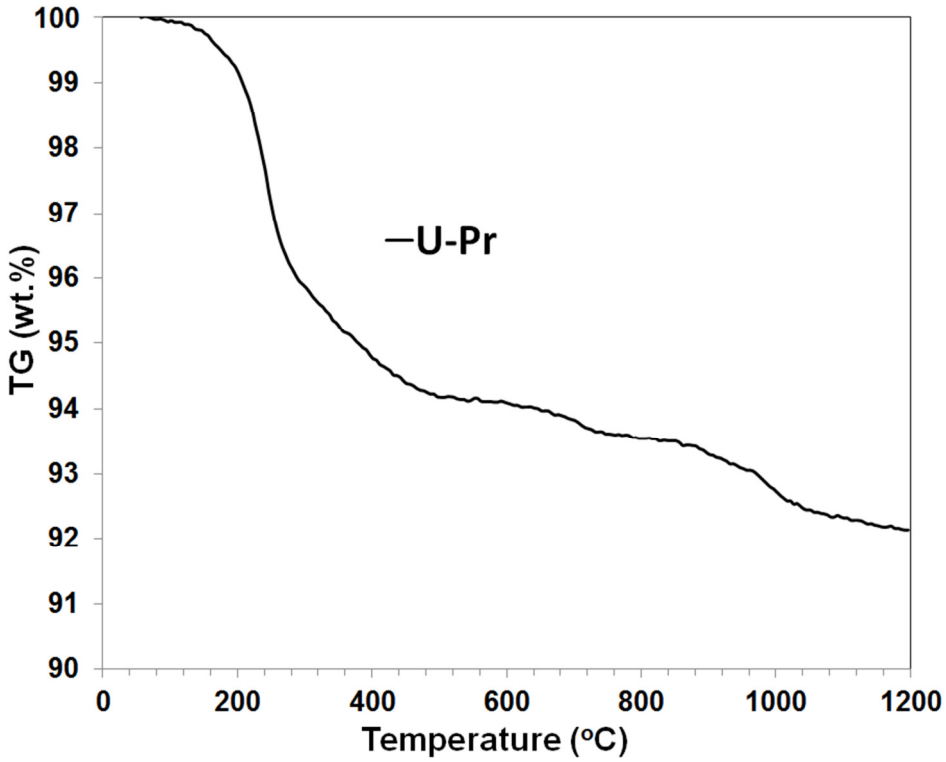

Fig. S10. Thermogravimetric analysis results of compound **U-Pr**.

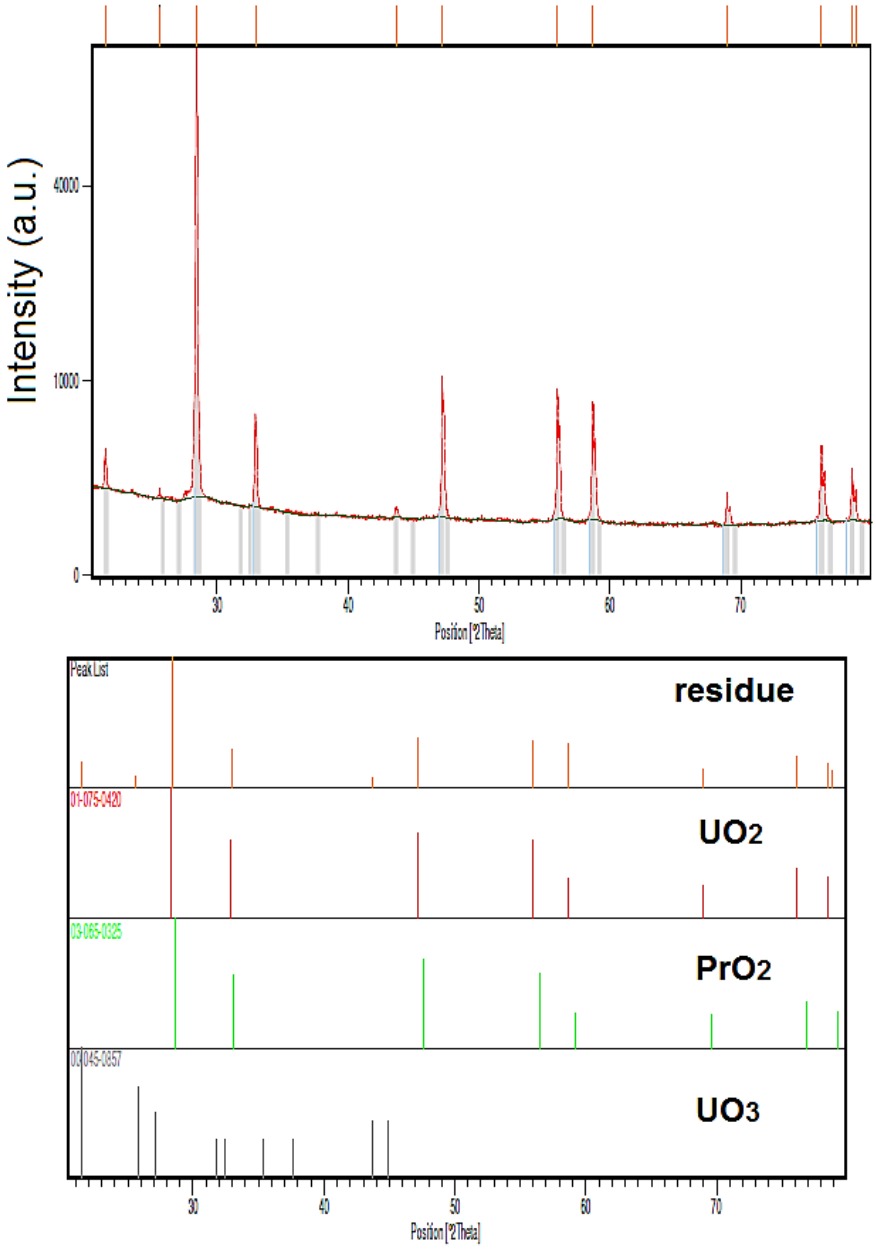

Fig. S11. PXRD pattern (top) and X'pert HighScore phase identification (bottom) of the residue for compound **U-Pr** after TGA measurement.

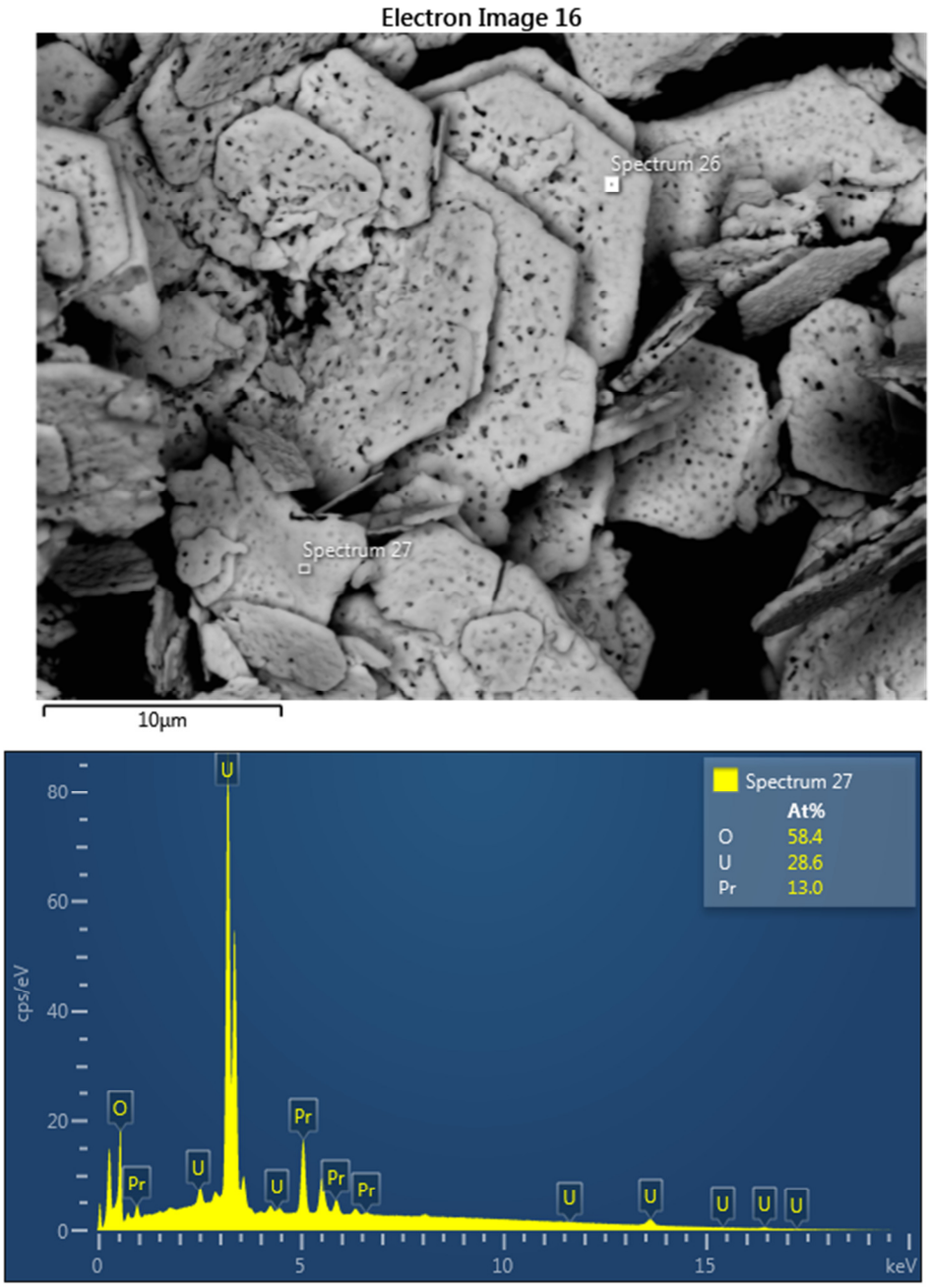

Fig. S12. A backscattered SEM image (top) and an EDS spectrum (bottom) of the residue for compound **U-Pr** after TGA measurement.