

Supporting Information

**Interaction of perrhenate (ReO_4^-) and pertechnetate (TcO_4^-)
with the uranyl ion (UO_2^{2+}) in acetonitrile solution:
Spectroscopy and theoretical calculations**

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Preparation of NH_4TcO_4

The ammonium pertechnetate stored in our lab is black in color (Figure S1a) and it requires treatment before use. In detail, 0.1246 g black NH_4TcO_4 sample was dissolved in 600 μL concentrated aqueous ammonia, and 150 μL of 30% hydrogen peroxide was added. The solid was gradually dissolved, and the color of the solution changed to dark purple-black. After standing for one week, the color of the solution turned to light brown. After the solvent was evaporated, pink solids were obtained. The solids in pink color were supposed to be the aggregates of TcO_4^- . The solids were redissolved and irradiated with a light source (400-650 nm) for 5 hours. After evaporation, a white product was obtained. The composition was determined to be $\text{NH}_4\text{TcO}_4 \cdot \text{H}_2\text{O}$ based on comparing the weight of the product and the counts by liquid scintillation counting.

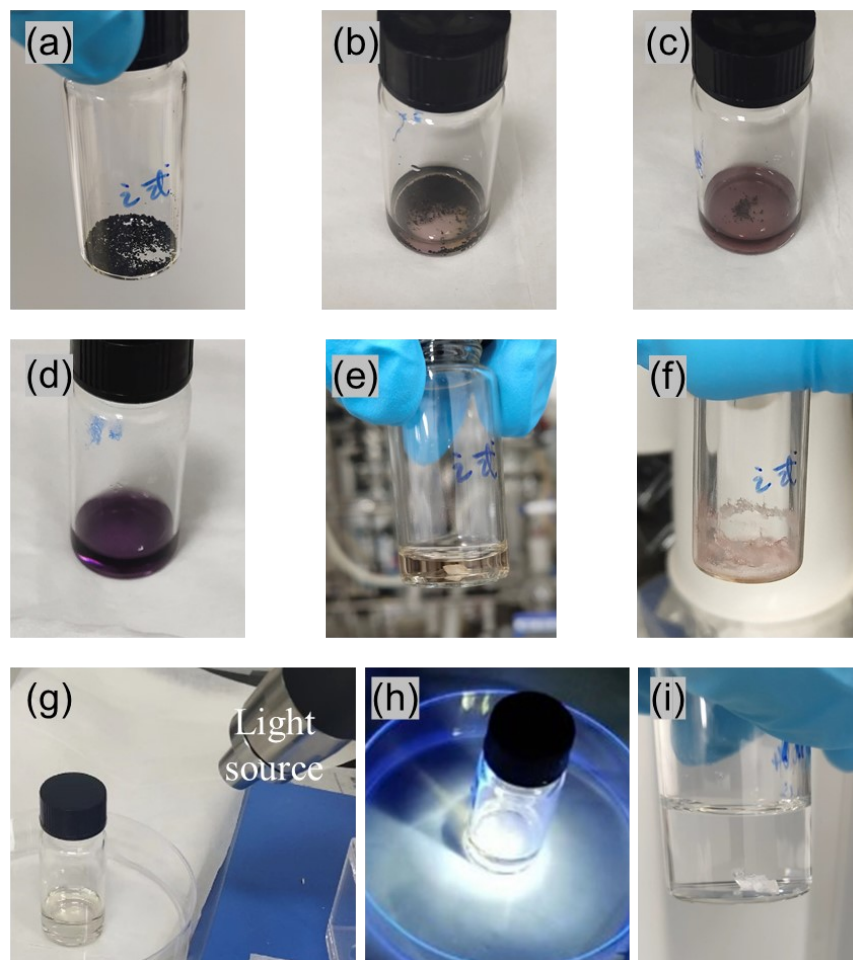


Figure S1. (a) Black sample before treatment; (b) Sample dissolved in concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$; (c) The solution after adding 30% H_2O_2 ; (d) Solid dissolved completely; (e) Solution after standing for one week; (f) Pink solids after evaporation; (g) The light irradiation device; (h) Irradiating the solution for five hours; (i) White solid precipitated during evaporation.

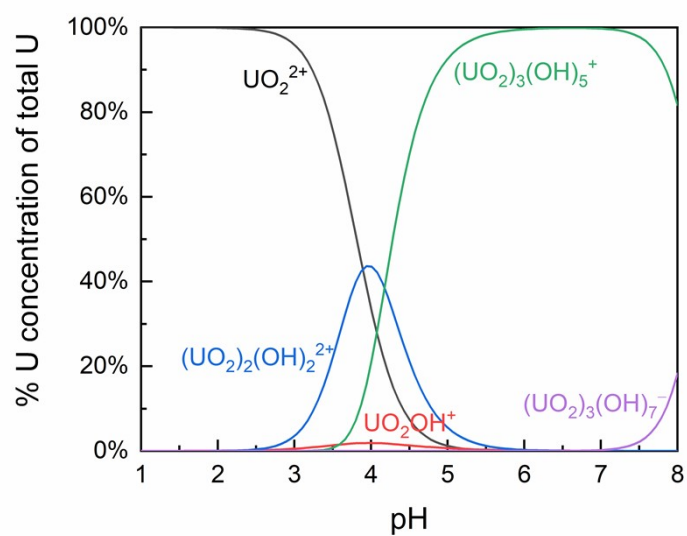


Figure S2. The distribution of U(VI) species as a function of pH in aqueous solution.

The hydrolysis constants are obtained from *The Chemistry of Actinide Transactinide Elements*, Morss *et al.*, Springer Dordrecht, 2011, page 2554. At pH < 2.5 ($[H^+] > 0.0032 \text{ mol}\cdot\text{L}^{-1}$), U(VI) in aqueous solution is presented as UO_2^{2+} .

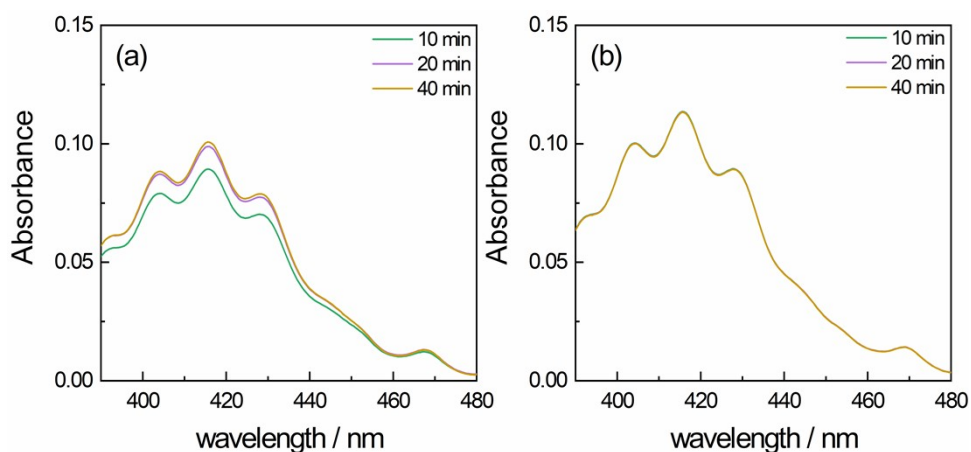


Figure S3. The absorption spectra of UO_2^{2+} in acetonitrile depending on time (a) without adding water and (b) with 0.4 vol% water. The concentrations of UO_2^{2+} are both $20 \text{ mmol}\cdot\text{L}^{-1}$. Both the solutions contain concentrated HClO_4 of $0.01 \text{ mmol}\cdot\text{L}^{-1}$, which would bring a water content of 0.05%. The variation of the absorption spectra of UO_2^{2+} in acetonitrile without adding water is supposed to be due to absorbing moisture from the air.

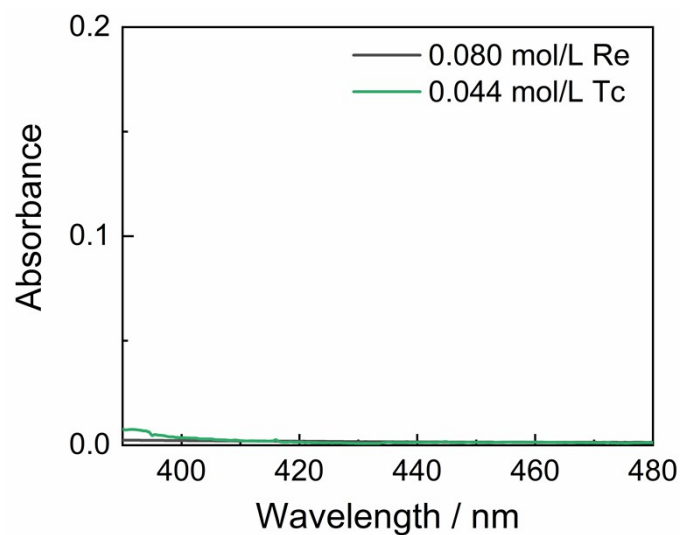


Figure S4. The absorption spectra of ReO_4^- and TcO_4^- in acetonitrile with 0.5% water contents. There is no absorption for ReO_4^- in the range of 390-480 nm, while there is an absorption for TcO_4^- in the range of 390-400 nm. The spectra of TcO_4^- have been considered when processing the titration data with the HypSpec program.

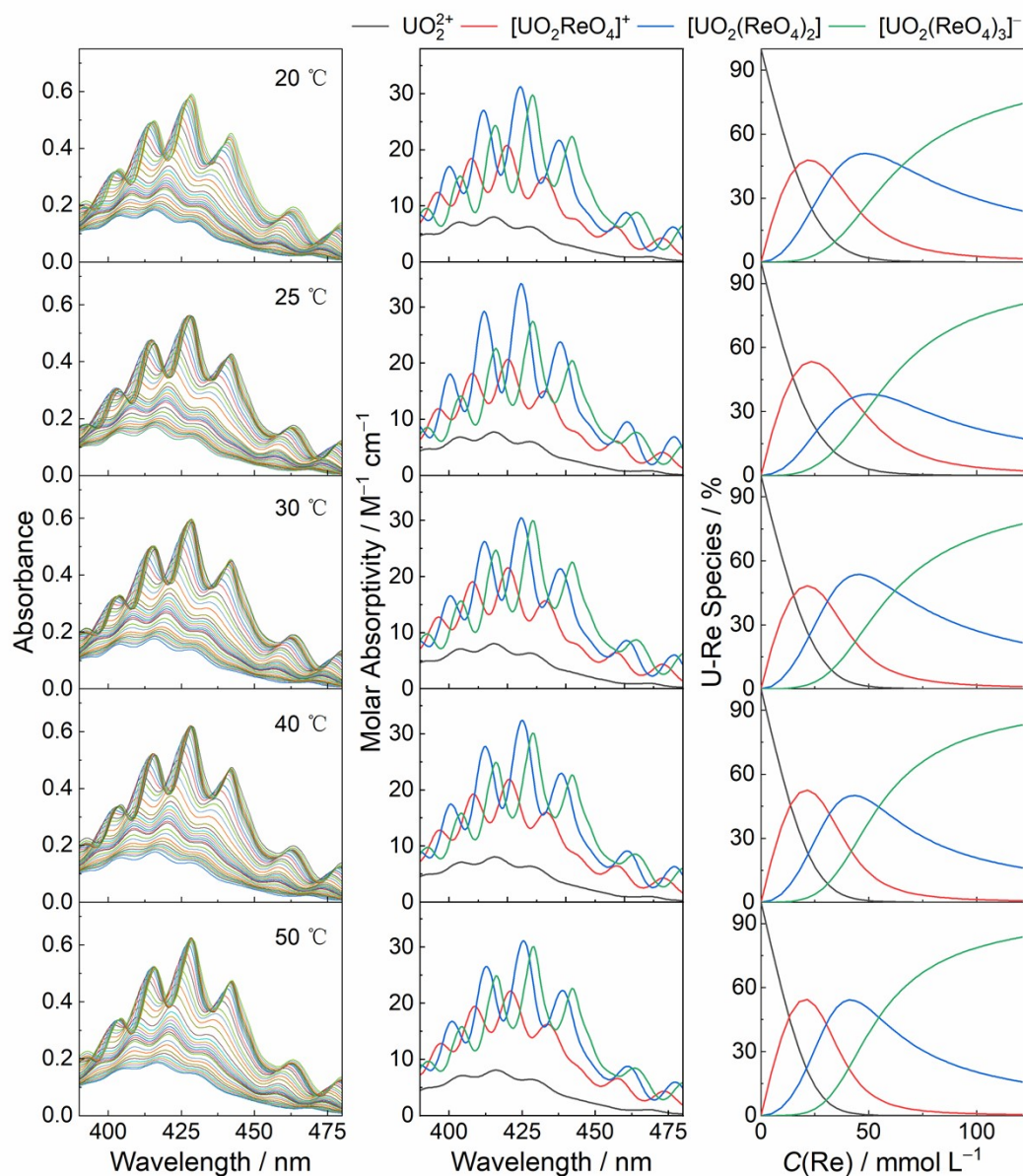


Figure S5. The spectrophotometric titrations of UO_2^{2+} with ReO_4^- at different temperatures. (Left) The normalized absorption spectra were collected in the titrations from 20°C to 50°C. Initial solution: 0.8 mL of 0.02 mol/L $\text{UO}_2(\text{ClO}_4)_2$ / 0.01 mol/L HClO_4 in acetonitrile with 0.5 vol% water; Titrant: 2.5 mL of 0.16 mol/L $[\text{Bu}_4\text{N}][\text{ReO}_4]$ in acetonitrile with 0.5 vol% water. (Middle) The fitted molar absorptivity of UO_2^{2+} - ReO_4^- complexes. (Right) The distribution curves of the complexes in the titrations.

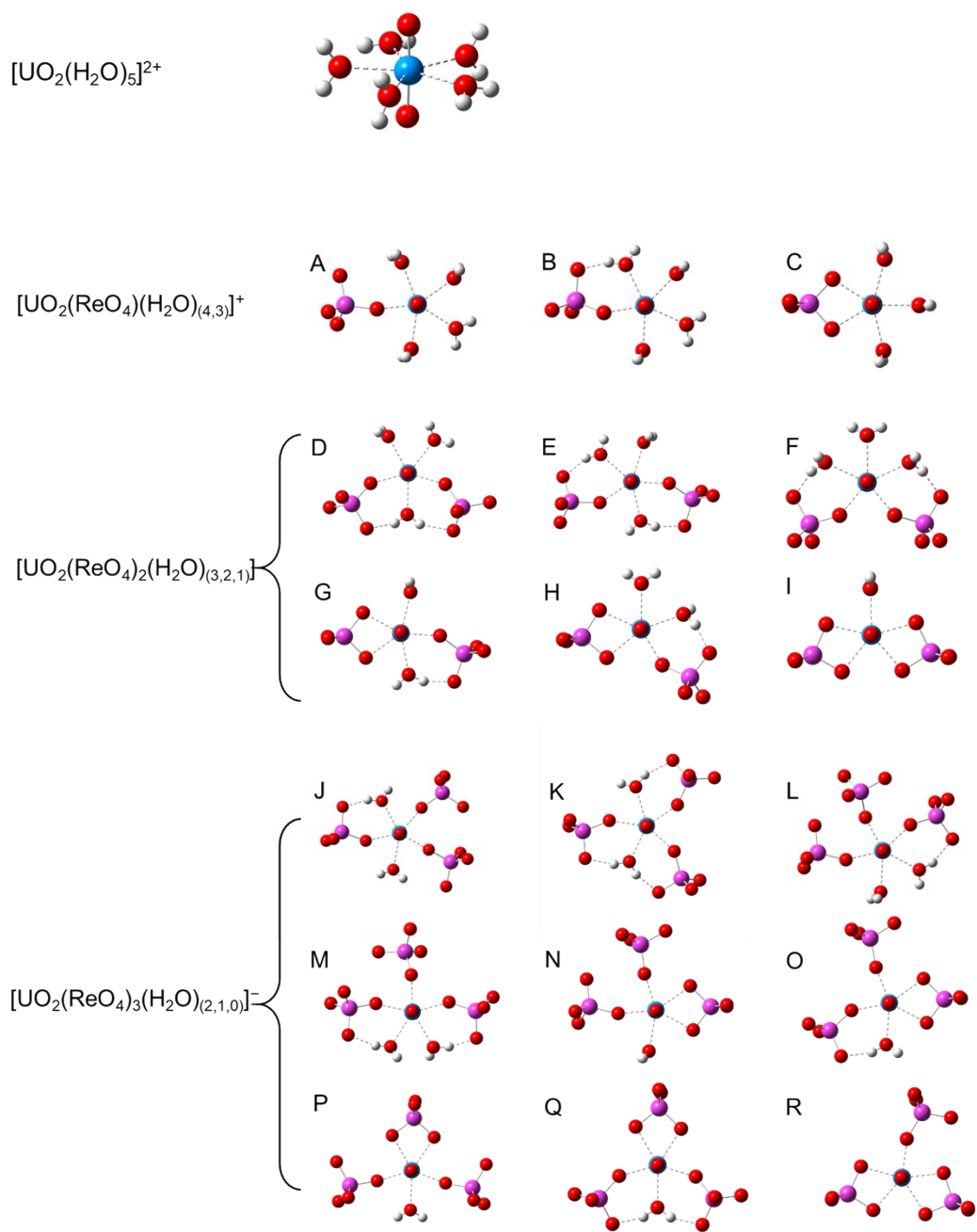


Figure S6. The optimized structures of the hydrated uranyl ion and its monodentate and bidentate coordinated complexes with ReO_4^- . U: blue; O: red; Re: purple; H: white.

Table S1. The calculated total energies for the species in Figure S6.

Species*	Total Energy (a.u.)	Species*	Total Energy (a.u.)
A	-1313.02423	L	-1919.53755
B	-1313.02510	M	-1919.53363
C	-1236.54534	N	-1843.06110
D	-1616.28091	O	-1843.05700
E	-1616.28337	P	-1843.05900
F	-1616.27916	Q	-1843.05570
G	-1539.80532	R	-1766.57568
H	-1539.80256	[UO ₂ (H ₂ O) ₅] ²⁺	-1009.75951
I	-1463.32064	H ₂ O	-76.46836
J	-1919.53854	ReO ₄ ⁻	-379.71105
K	-1919.53621		

*B, E, and J are the most stable monodentate complexes, and C, G, and N are the most stable bidentate complexes.

Table S2. The Gibbs free energies for the construction transform of monodentate complexes (B, E, J) to bidentate complexes (C, G, N).

Reaction		ΔG (kcal/mol)
B to C	$[\text{UO}_2(\text{ReO}_4)(\text{H}_2\text{O})_4]^+ (\text{mono-}) \rightleftharpoons [\text{UO}_2(\text{ReO}_4)(\text{H}_2\text{O})_3]^+ (\text{bi-}) + \text{H}_2\text{O}$	+9.05
E to G	$[\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_3] (\text{mono-}) \rightleftharpoons [\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_2] (\text{bi-}) + \text{H}_2\text{O}$	+7.97
J to N	$[\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})_2]^- (\text{mono-}) \rightleftharpoons [\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})]^- (\text{bi-}) + \text{H}_2\text{O}$	+7.59

Table S3. The averaged bond lengths (Å) of U=O, U–O(Re), U–O(H), Re–O(U), Re=O, and U–Re for the most stable species.

Species	Bond length (Å)					
	U=O	U–O(Re)	U–O(H)	Re–O(U)	Re=O	U–Re
[UO ₂ (H ₂ O) ₅] ²⁺	1.748	-	2.463	-	-	-
B [UO ₂ ReO ₄ (H ₂ O) ₄] ⁺	1.755	2.294	2.490	1.795	1.722	3.873
E [UO ₂ (ReO ₄) ₂ (H ₂ O) ₃]	1.761	2.332	2.508	1.789	1.723	3.931
J [UO ₂ (ReO ₄) ₃ (H ₂ O) ₂] ⁻	1.768	2.335	2.533	1.783	1.723	4.040
C [UO ₂ ReO ₄ (H ₂ O) ₃] ⁺	1.753	2.465	2.454	1.773	1.714	3.285
G [UO ₂ (ReO ₄) ₂ (H ₂ O) ₂]	1.759	2.507	2.469	1.768	1.716	3.307
N [UO ₂ (ReO ₄) ₃ H ₂ O] ⁻	1.766	2.550	2.510	1.763	1.719	3.332
ReO ₄ ⁻	-	-	-	-	1.740	-

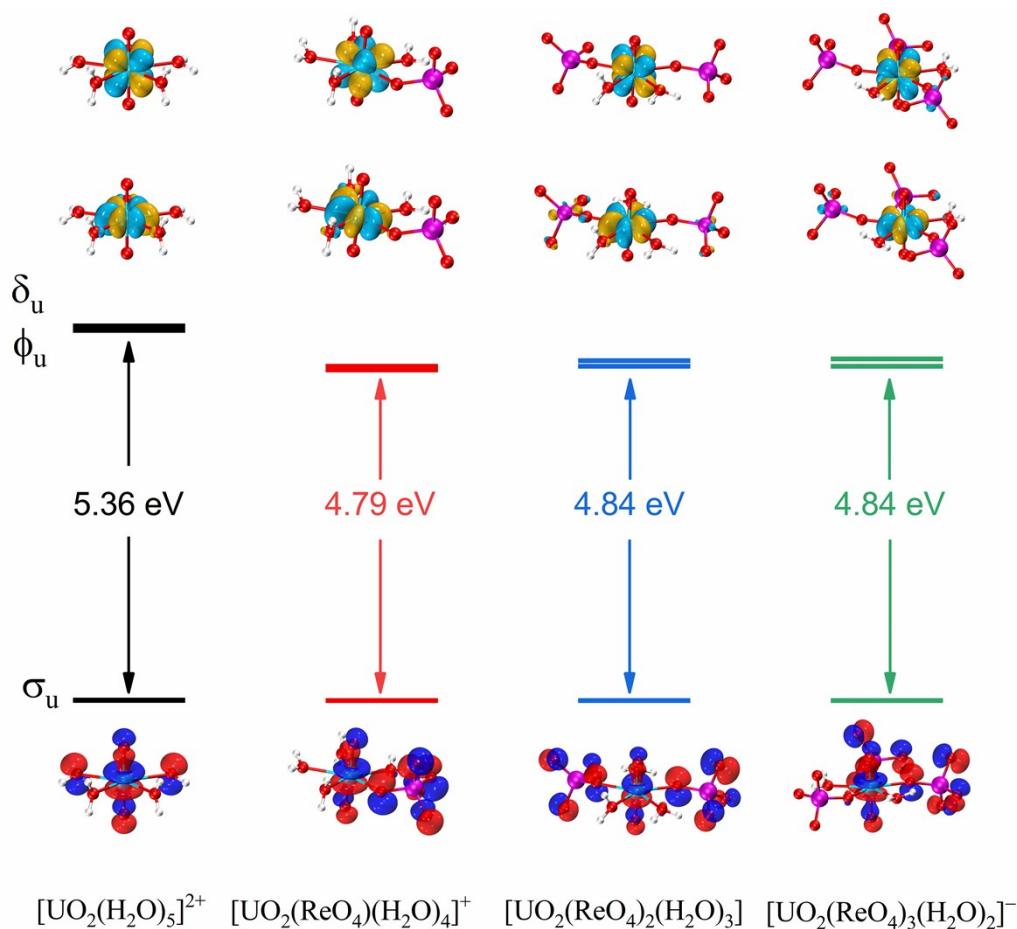


Figure S7. The diagram of the ground-state Kohn-Sham orbital energy levels (Spin Orbit coupling) and the corresponding contours (scalar relativistic, isovalue = 0.04 a.u.) of the HOMO orbital (σ_u character) and two lowest empty orbitals (ϕ_u and δ_u character) for $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, $[\text{UO}_2\text{ReO}_4(\text{H}_2\text{O})_4]^+$, $[\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_3]$, and $[\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})_2]^-$.

Table S4. The lowest 16 vertical transition energies (ΔE , eV) and their corresponding oscillator strengths (f) for $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, $[\text{UO}_2\text{ReO}_4(\text{H}_2\text{O})_4]^+$, $[\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_3]$, and $[\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})_2]^-$.

$[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$		$[\text{UO}_2\text{ReO}_4(\text{H}_2\text{O})_4]^+$		$[\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_3]$		$[\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})_2]^-$	
ΔE	f	ΔE	f	ΔE	f	ΔE	f
2.612	1.401×10^{-7}	2.567	6.850×10^{-6}	2.544	3.229×10^{-6}	2.538	2.252×10^{-6}
2.612	2.580×10^{-6}	2.568	8.051×10^{-7}	2.545	2.265×10^{-6}	2.538	3.435×10^{-6}
2.675	2.092×10^{-7}	2.615	4.255×10^{-5}	2.589	1.659×10^{-5}	2.586	3.840×10^{-5}
2.676	1.037×10^{-6}	2.644	1.820×10^{-6}	2.604	3.235×10^{-5}	2.595	1.268×10^{-5}
2.811	1.421×10^{-6}	2.758	1.272×10^{-5}	2.727	9.104×10^{-6}	2.714	6.248×10^{-6}
2.828	6.442×10^{-6}	2.780	5.503×10^{-5}	2.737	1.998×10^{-5}	2.732	2.596×10^{-5}
2.929	1.907×10^{-6}	2.872	4.317×10^{-4}	2.837	2.829×10^{-5}	2.830	4.315×10^{-4}
2.934	8.764×10^{-5}	2.881	2.387×10^{-5}	2.845	4.971×10^{-4}	2.837	9.166×10^{-6}
3.269	2.165×10^{-7}	3.215	6.609×10^{-6}	3.189	3.020×10^{-6}	3.178	1.721×10^{-6}
3.290	8.997×10^{-7}	3.242	1.399×10^{-5}	3.198	8.585×10^{-6}	3.198	8.504×10^{-6}
3.492	4.260×10^{-5}	3.435	3.953×10^{-5}	3.387	1.084×10^{-4}	3.381	8.233×10^{-5}
3.492	2.162×10^{-5}	3.436	1.261×10^{-4}	3.387	1.059×10^{-4}	3.382	9.735×10^{-5}
3.803	2.027×10^{-5}	3.705	1.406×10^{-4}	3.6655	1.160×10^{-4}	3.645	1.482×10^{-4}
3.839	2.094×10^{-6}	3.745	3.709×10^{-4}	3.6812	1.444×10^{-4}	3.674	1.795×10^{-5}
3.916	1.019×10^{-3}	3.780	4.135×10^{-5}	3.7604	9.237×10^{-3}	3.757	6.619×10^{-3}
3.925	2.096×10^{-5}	3.809	1.116×10^{-2}	3.7819	2.695×10^{-4}	3.759	3.348×10^{-3}

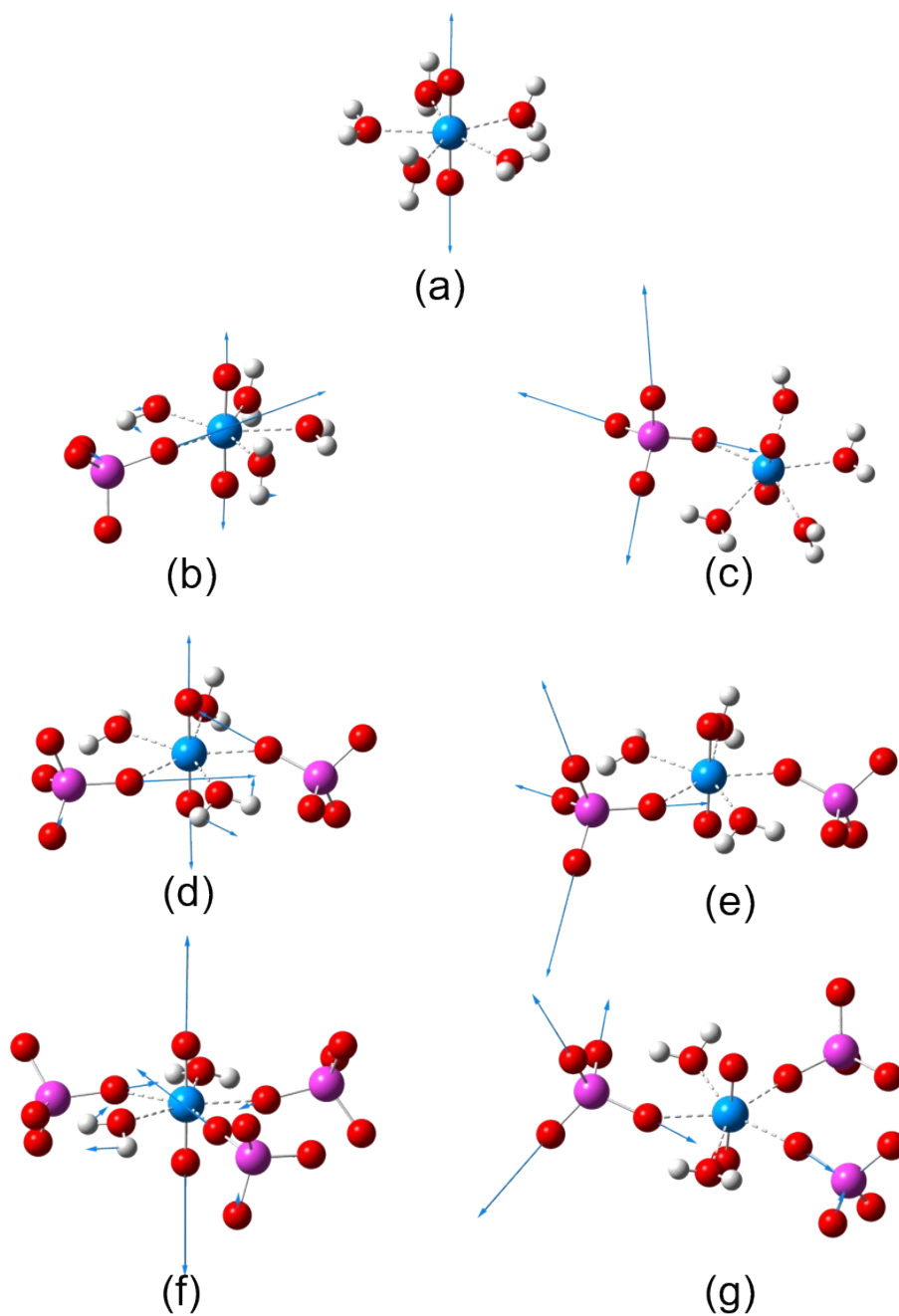


Figure S8. The vibration mode of (a) 926 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, (b) 805 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_4\text{ReO}_4]^+$, (c) 1016 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_4\text{ReO}_4]^+$, (d) 824 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_3(\text{ReO}_4)_2]$, (e) 1018 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_3(\text{ReO}_4)_2]$, (f) 829 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_2(\text{ReO}_4)_3]^-$, and (g) 1023 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_2(\text{ReO}_4)_3]^-$.

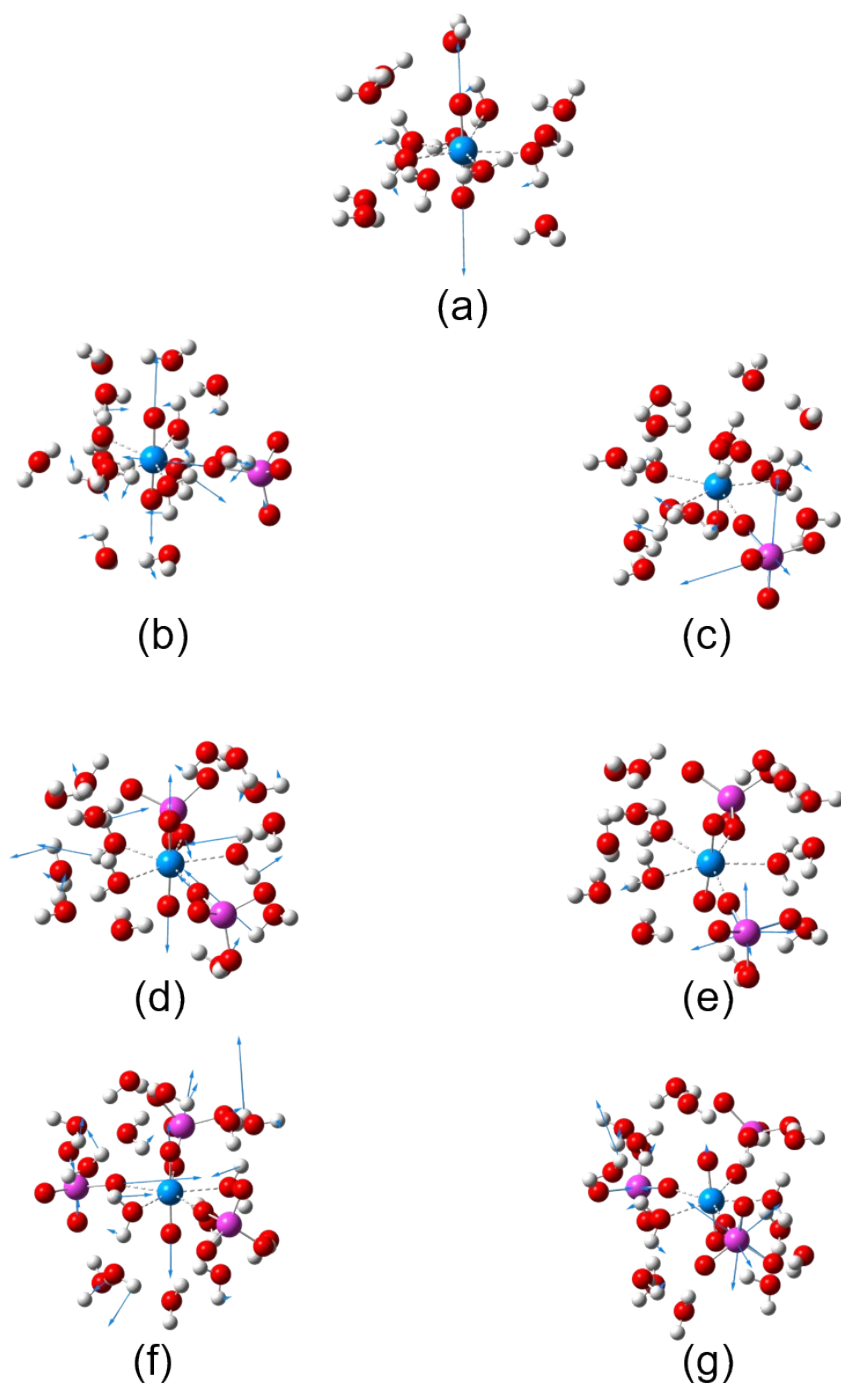


Figure S9. The vibration mode of (a) 883 cm^{-1} of $[\text{UO}_2(\text{H}_2\text{O})_5(\text{H}_2\text{O})_{10}]^{2+}$, (b) 829 cm^{-1} of $[\text{UO}_2\text{ReO}_4(\text{H}_2\text{O})_4(\text{H}_2\text{O})_{11}]^+$, (c) 1023 cm^{-1} of $[\text{UO}_2\text{ReO}_4(\text{H}_2\text{O})_4(\text{H}_2\text{O})_{11}]^+$, (d) 817 cm^{-1} of $[\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_3(\text{H}_2\text{O})_{12}]$, (e) 1018 cm^{-1} of $[\text{UO}_2(\text{ReO}_4)_2(\text{H}_2\text{O})_3(\text{H}_2\text{O})_{12}]$, (f) 838 cm^{-1} of $[\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})_2(\text{H}_2\text{O})_{13}]^-$, and (g) 1023 cm^{-1} of $[\text{UO}_2(\text{ReO}_4)_3(\text{H}_2\text{O})_2(\text{H}_2\text{O})_{13}]^-$.

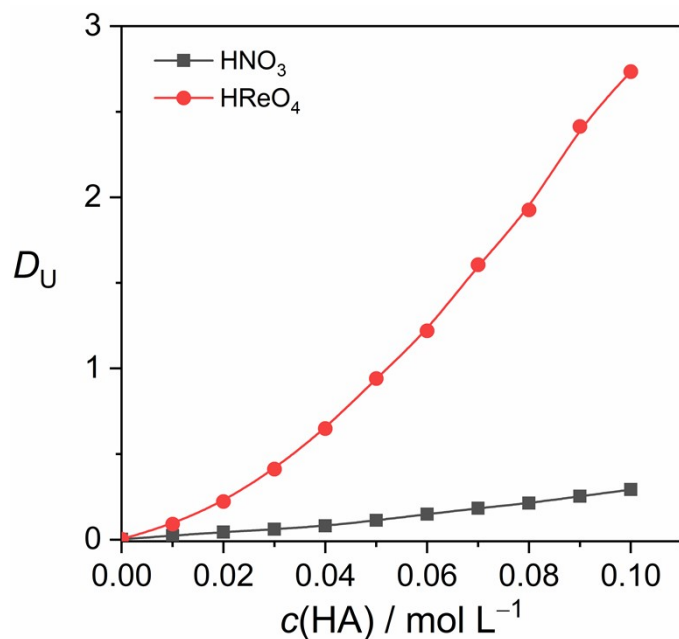


Figure S10. The distribution ratio of U(VI) as a function of the acidity of the aqueous phase. Details of the extraction experiments: HReO₄ or HNO₃ aqueous solutions with 10 mmol·L⁻¹ UO₂(ClO₄)₂ were thoroughly mixed with equal volume of 30% TBP/dodecane organic phase for 15 min. The organic phase was pre-equilibrated with the HReO₄ or HNO₃ solutions for three times. After the extraction, the concentration of uranium in the aqueous were detected by ICP-OES, and the distribution ratio of U were calculated based on $D_U = \frac{c_i - c_f}{c_f}$, where c_i and c_f represent for the concentration of uranium in the aqueous phase before and after extraction, respectively.