

## *Supporting Information*

# **Studies of Aqueous U(IV) Equilibrium and Nanoparticle Formation Kinetics Using Spectrophotometric Reaction Modeling Analysis**

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[Ionic strength correction using SIT formula]

The measured conditional stability constant,  $\log^* \beta_1$  was converted to the standard constants,  $\log^* \beta_1^\circ$  at the standard condition ( $I = 0$ ,  $T = 25^\circ\text{C}$ ) by correcting the effects of  $I$  and adopting activity coefficient terms ( $\log \gamma$ ) as shown in Eq. (S1).

$$^* \beta_1 = \frac{[\text{U}(\text{OH})^{3+}][\text{H}^+]}{[\text{U}^{4+}]}$$

$$\log^* \beta_1 = \log^* \beta_1^\circ + \log \gamma_{\text{U}^{4+}} - \log \gamma_{\text{UOH}^{3+}} - \log \gamma_{\text{H}^+} + \log a_{\text{H}_2\text{O}} \quad (\text{S1})$$

Equilibria involving  $\text{H}_2\text{O}(\text{l})$  as a reactant or product require a correction for the water activity ( $a_{\text{H}_2\text{O}}$ ). The  $\log_{10} a_{\text{H}_2\text{O}}$  were calculated from the  $a_{\text{H}_2\text{O}}$  values at  $25^\circ\text{C}$  provided in NEA-TDB for  $\text{NaClO}_4$  (see Table S1). The SIT formula for activity coefficients is:

$$\log_{10} \gamma_i = -z_i^2 D(I_m) + \sum_j \varepsilon(i, j) m_j \quad (\text{S2})$$

where  $z_i$  is the charge of ion  $i$ .

$$D(I_m) = \frac{A \sqrt{I_m}}{1 + B a_d \sqrt{I_m}} \quad (\text{S3})$$

is a Debye-Hückel term where  $I_m$  is the molal ionic strength;  $A$  and  $B$  are Debye-Hückel constants;  $a_d$  is the size or effective diameter of the ion in angstrom;  $B \cdot a_d$  in Eq. (S3) is considered as a constant ( $= 1.5$ ). In Eq. (S2), the binary ion interaction coefficients ( $\varepsilon$ ) for the pair of species  $i$  and  $j$  are assumed to be equal to zero for neutral species or for ions of the same sign. Thus, for the cations involved in 1:1 U(IV) hydrolysis the summation in Eq. (S1) is restricted to the  $\text{ClO}_4^-$  counter ion ( $= j$ ) that was chosen for ionic strength control in this work. The values of  $a_{\text{H}_2\text{O}}$  and  $A$ ,  $B \cdot a_d$  used in this work are listed in Tables S1 and S2, which were extracted from the literature. For the  $B \cdot a_d$  and  $a_{\text{H}_2\text{O}}$  terms we assume that these values are constant within the temperature range ( $0\text{--}30^\circ\text{C}$ ) in this study, thus the values at RT in Tables S1 and S2 were used for the calculation of  $\log^* \beta_1^\circ$  at other temperatures, i.e.,  $\log^* \beta_1^\circ(T)$ .

[Tables]

**Table S1.** Water activity used in this study (see Eq. (S1)).

$I$ (m)	$a_{\text{H}_2\text{O}}$
0.02	0.9993
0.05	0.9983
0.10	0.9966
0.15	0.9948
0.51	0.9833
1.05	0.9660
2.09	0.9337

Note. Values for  $\text{NaClO}_4$  media are adapted from NEA-TDB (Ref. [3] in the main text). Some values are extrapolated.

**Table S2.** Debye-Hückel constants used in Eq. (S3).

T (°C)	A	$\text{Ba}_d$
0	0.4913	
5	0.4943	
10	0.4976	
15	0.5012	1.5
20	0.5050	
25	0.5091	
30	0.5135	

Note. All values are adapted from Ref.[3] in the main text.

**Table S3.** Comparison of the binary ion interaction coefficient ( $\Delta\varepsilon$ ) obtained in this work and those from literatures.

$\Delta\varepsilon^a$ (kg/mol)	References
$-(0.14 \pm 0.05)$	Ref. [3]
$-(0.21 \pm 0.04)$	this work <sup>b</sup>
$\Delta\varepsilon_1 = -(0.28 \pm 0.03)$ $\Delta\varepsilon_2 = 0.28 \pm 0.06$	Ref. [4]
$\Delta\varepsilon_1 = -(0.30 \pm 0.05)$ $\Delta\varepsilon_2 = 0.32 \pm 0.08$	this work <sup>c</sup>

<sup>a</sup>  $\Delta\varepsilon$  at  $I = 0$  ( $= \varepsilon(\text{UOH}^{3+}, j) + \varepsilon(\text{H}^+, j) - \varepsilon(\text{U}^{4+}, j), j = \text{ClO}_4^-$ ).

<sup>b</sup>  $\Delta\varepsilon$  was calculated by adding  $\varepsilon(\text{H}^+, \text{ClO}_4^-)$  to  $\Delta\varepsilon'$  presented in Table 1 in the main text.

<sup>c</sup> Based on the two-parameter SIT model in Ref. [4];  $\Delta\varepsilon = \Delta\varepsilon_1 + \Delta\varepsilon_2 \log I$

**Table S4.** Dependence of  $\Delta_r H_m$  and  $\Delta_r S_m$  on  $I$ . Each conditional constant was calculated from the individual van't Hoff plots ( $\log^* \beta_1$  vs.  $1/T$ ) in Fig. 4(b).

Test (pH <sub>c</sub> )	$I$ (mol/kg)	T (°C)	$\Delta_r H_m$ (kJmol <sup>-1</sup> )	$\Delta_r S_m$ (JK <sup>-1</sup> mol <sup>-1</sup> )
C (1.70)	0.02	0 ~ 30	$41.4 \pm 0.5$	$121 \pm 2$
	0.05		$42.8 \pm 0.6$	$124 \pm 2$
	0.10		$41.3 \pm 0.5$	$117 \pm 2$
	0.20		$40.2 \pm 0.6$	$111 \pm 2$
	0.51		$40.1 \pm 0.5$	$109 \pm 2$
	1.05		$38.1 \pm 0.4$	$100 \pm 2$

**Table S5.** Comparison of the reaction enthalpy and entropy data measured in this work and those from literatures for the first hydrolysis of  $U^{4+}$  in aqueous H/NaClO<sub>4</sub> solution.

T (°C)	<i>I</i>	$\Delta_r H_m$ (kJmol <sup>-1</sup> )	$\Delta_r S_m$ (JK <sup>-1</sup> mol <sup>-1</sup> )	References
0 – 30	0	43.4 ± 3.0 <sup>a</sup>	136 ± 11 <sup>a</sup>	this work
	0.15 m	41.6 ± 2.8 <sup>a</sup>	117 ± 10 <sup>a</sup>	
10 – 150	0	46.9 ± 9.0	147 ± 30	Ref. [3]
25 – 150	0	42.9 ± 3.3 <sup>b</sup>	135 ± 10 <sup>b</sup>	Ref. [4]
0 – 150	0	43.3 ± 2.2 <sup>c</sup>	136 ± 7 <sup>c</sup>	this work
15.2 – 24.7	0.19 M	44.3 ± 6	126 ± 20	Ref. [S1], re-estimated in Ref.[5]
10, 43	0.5 M	46.9 ± 3	129 ± 10	Ref. [S2], re-estimated in Ref.[5]
25 – 100	0.5 m	42 ± 7	-	Ref. [S3],
50 – 125	0.99 m	45 ± 7	-	re-estimated in
25 – 150	0	46 ± 4	143 ± 14	Ref.[5]

<sup>a</sup> Data taken from Table 3 in the main text.

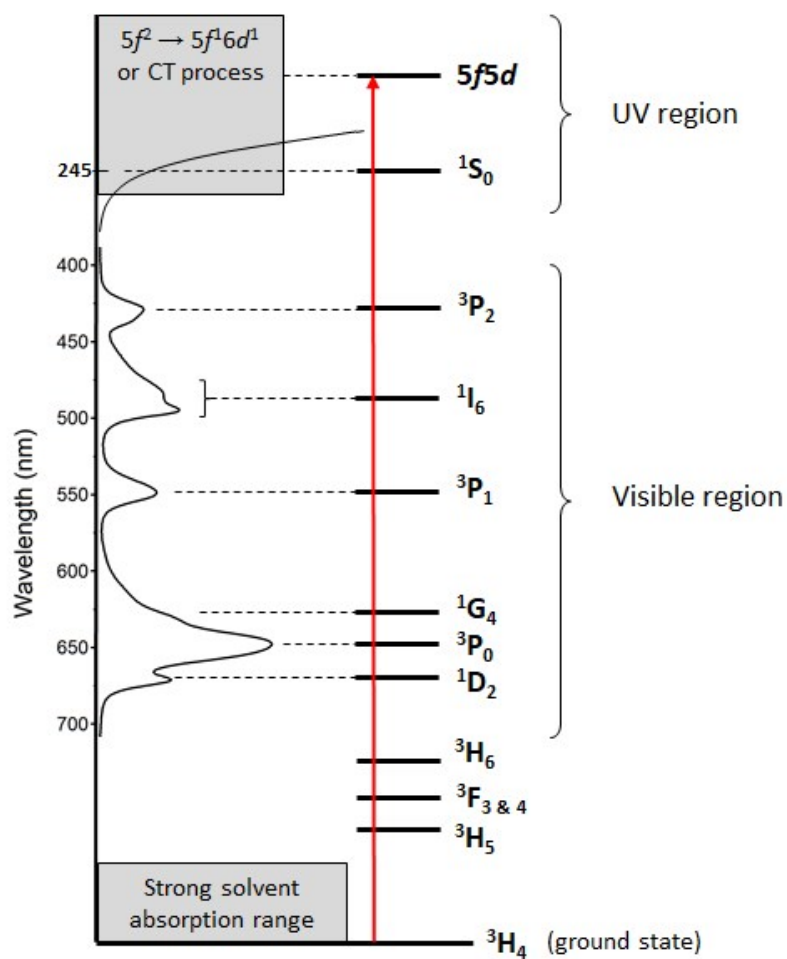
<sup>b</sup> Data calculated from the plot of Fig. S6 using  $\log^* \beta_1^\circ$  values listed in Table 9.6 of Ref. [4].

<sup>c</sup> Reestimated values from the combined data from Table 3 and Ref. [4](see Fig. S6).

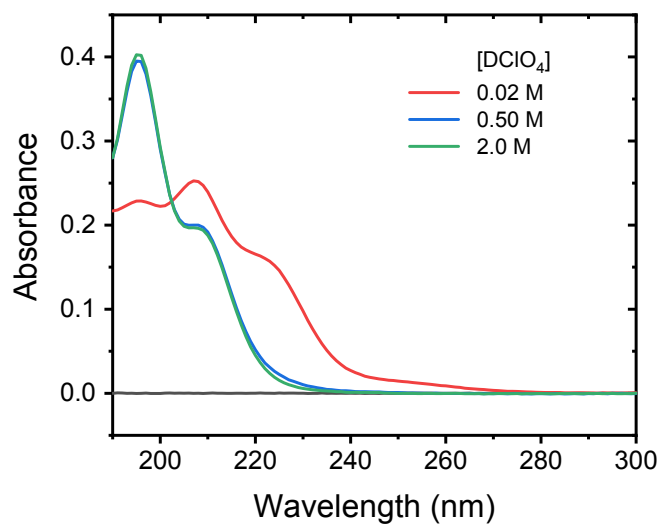
**Table S6.** Stability constants for the first hydrolysis of  $U^{4+}$ , which were used in Fig. S5.

Temp. (°C)	I (mol kg <sup>-1</sup> )	$\log^*\beta$ (accepted)	$\log^*\beta + 6D - \log a(H_2O)$	Reference
25	0.017	-(0.92 ± 0.17)	-0.587	
25	0.033	-(1.07 ± 0.17)	-0.634	
25	0.035	-(1.00 ± 0.17)	-0.553	
25	0.045	-(1.10 ± 0.17)	-0.608	
25	0.063	-(1.14 ± 0.17)	-0.582	
25	0.111	-(1.22 ± 0.10)	-0.540	
25	0.111	-(1.28 ± 0.10)	-0.600	
25	0.121	-(1.23 ± 0.10)	-0.530	Ref. [S4]
25	0.121	-(1.29 ± 0.10)	-0.590	
25	0.274	-(1.35 ± 0.10)	-0.450	
25	0.513	-(1.53 ± 0.10)	-0.468	
25	0.534	-(1.50 ± 0.10)	-0.427	
25	0.534	-(1.49 ± 0.10)	-0.417	
25	0.565	-(1.44 ± 0.10)	-0.353	
25	1.06	-(1.54 ± 0.10)	-0.289	
25	2.21	-(1.59 ± 0.10)	-0.153	Ref. [4]
25	3.5	-(1.88 ± 0.20)	-0.331	Ref. [S5]
25	2.21	-(1.64 ± 0.10)	-0.203	Ref. [S6]
25	3.5	-(1.58 ± 0.10)	-0.031	Ref. [S7]
24.7	0.192	-(1.08 ± 0.10)	-0.270	Ref. [S1]
25	1.05	-(1.61 ± 0.09)	-0.361	Ref. [S8]
25	3.5	-(1.55 ± 0.10)	-0.001	Ref. [S9]
25	0.25	-(1.44 ± 0.20)	-0.564	
25	0.36	-(1.30 ± 0.20)	-0.330	
25	0.48	-(1.39 ± 0.20)	-0.345	
25	0.51	-(1.21 ± 0.20)	-0.149	
25	0.65	-(1.31 ± 0.20)	-0.186	Ref. [S3]
25	0.75	-(1.44 ± 0.20)	-0.278	
25	0.86	-(1.54 ± 0.20)	-0.343	
25	0.99	-(1.68 ± 0.20)	-0.446	
25	1.09	-(1.72 ± 0.20)	-0.461	
26	0.02	-(0.94 ± 0.06)	-0.586	
26	0.05	-(1.05 ± 0.07)	-0.541	
26	0.101	-(1.17 ± 0.06)	-0.506	This work
26	0.202	-(1.25 ± 0.04)	-0.425	(Table 3 of the main text)
26	0.513	-(1.37 ± 0.05)	-0.311	
26	1.051	-(1.48 ± 0.05)	-0.228	
26	2.091	-(1.55 ± 0.03)	-0.131	

[Figures]

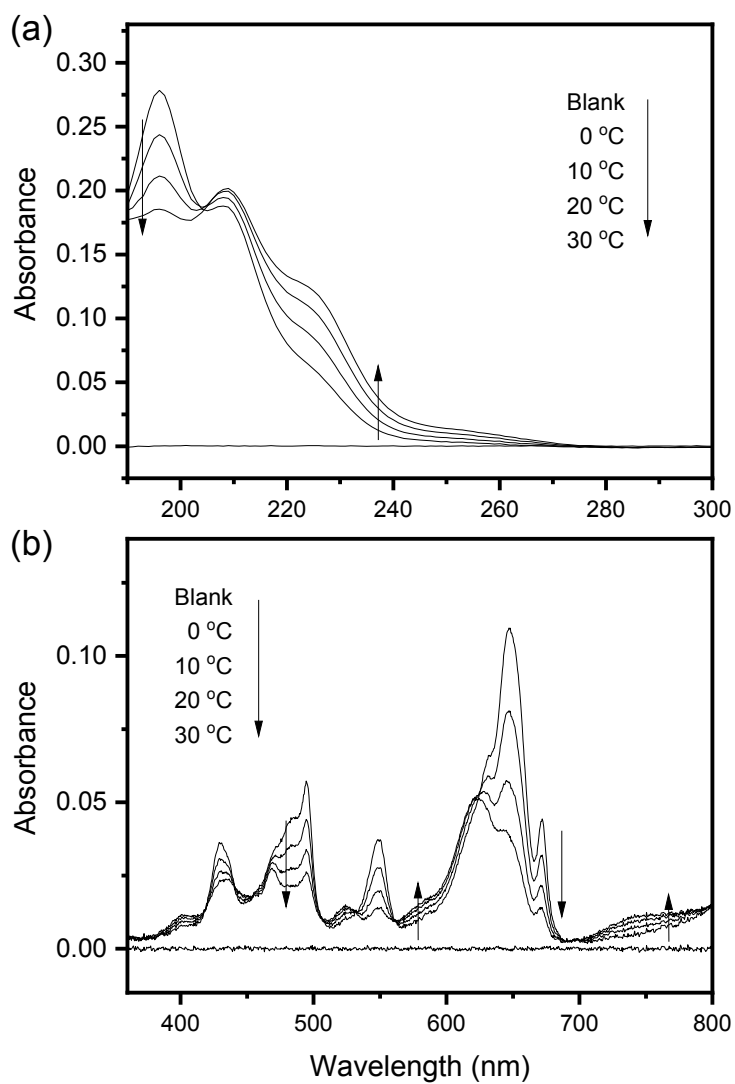


**Fig. S1.** Electronic energy states of  $U^{4+}$  ( $5f^2$ ). The arrow denotes for the transition to the UV region. (adapted from Ref. [23] in the main text)

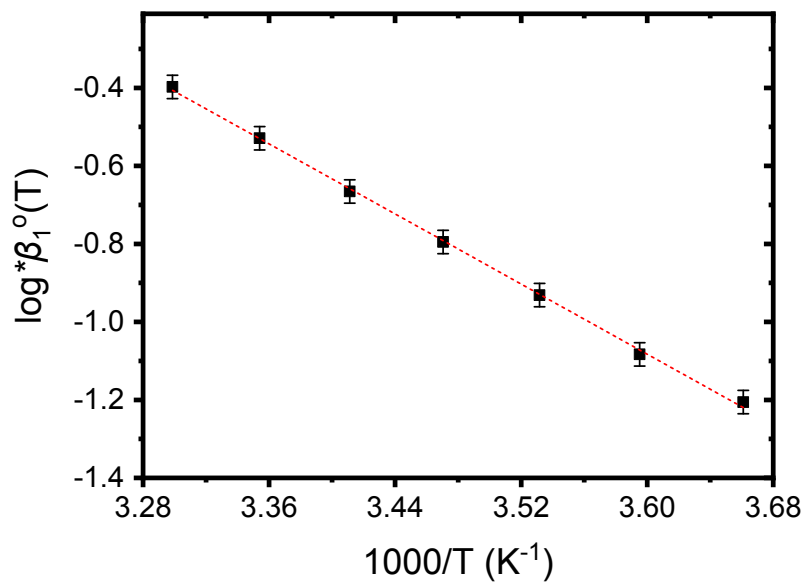


**Fig. S2.** Absorption spectra of D<sub>2</sub>O solutions containing U(IV) (0.7 mM) in the UV region (OPL = 1 mm,  $I \sim [\text{DClO}_4]$ , H/D in solution =  $\sim 0.01$ ). The absorption spectra are nearly identical with those obtained in the HClO<sub>4</sub>/H<sub>2</sub>O solution as shown in Figs. 1 and 2 in the main text.

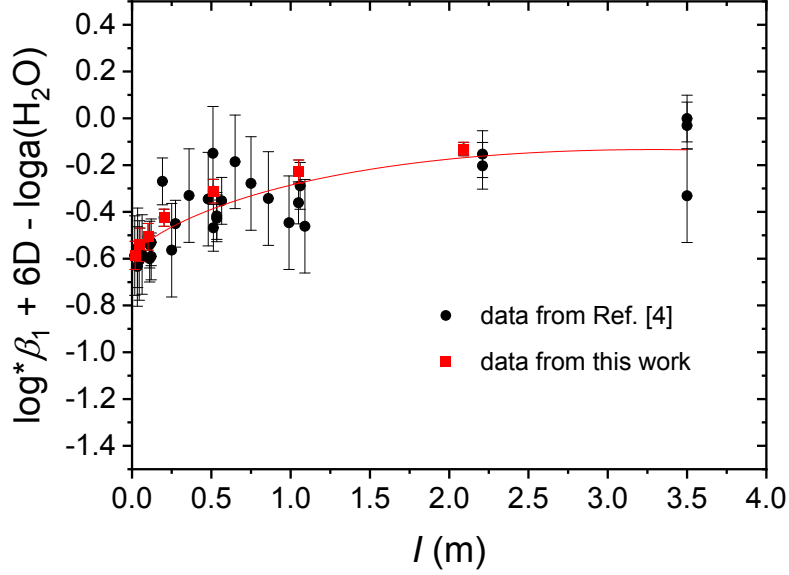




**Fig. S3.** Temperature-dependent changes of the absorption spectrum of aqueous solutions at  $\text{pH}_c = 1.70$  and  $I = 0.15$  m in the (a) UV region and (b) visible regions (OPL = 1 mm and 10 mm;  $[\text{U(IV)}]$ , 0.7 mM and 2.8 mM, respectively).



**Fig. S4.** Van't Hoff plot using  $\log^*\beta_1^\circ(T)$  calculated from the ionic strength correction shown in Fig. 4(c) (Test C at  $\text{pH}_c = 1.70$ ,  $0 - 30^\circ\text{C}$ ). Dotted lines indicate linear fit results. The standard state constants,  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$ , were determined to  $43.0 \pm 3.2$   $\text{kJmol}^{-1}$  and  $134 \pm 11$   $\text{JK}^{-1}\text{mol}^{-1}$ , respectively, which are within the uncertainty range of the representative values in this work as shown in Table 3.

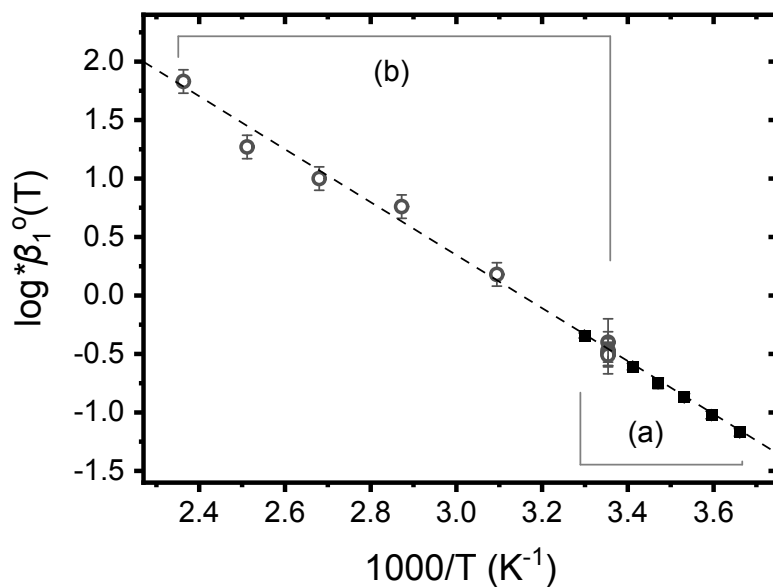


**Fig. S5.** Ionic strength dependence of  $\log^*\beta_1$  for the first hydrolysis of  $U^{4+}$  in perchlorate media. All available stability constants at 25 °C in the literature and those in Table 3 in the main text are combined, which are listed in Table S6. The solid line is the non-linear regression fitting result for the whole data by using the two-parameter SIT model ( $\Delta\varepsilon = \Delta\varepsilon_1 + \Delta\varepsilon_2 \log I$ , see Eq. (S4)) as described in Ref. [4]. As a result two terms of ion-interaction coefficients ( $\Delta\varepsilon_1$  and  $\Delta\varepsilon_2$ ) and  $\log^*\beta_1^\circ$  are derived and summarized in the table below.

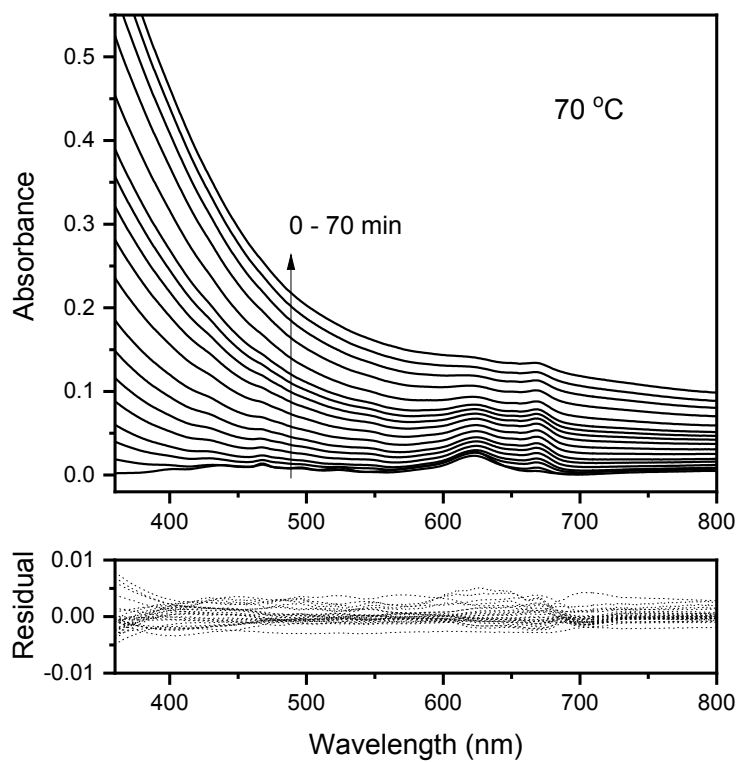
$$Y = \log^*\beta_1 + 6D(I_m) - \log a_{H_2O} = \log^*\beta_1^\circ - I_m (\Delta\varepsilon_1 + \Delta\varepsilon_2 \log I_m) \quad (S4)$$

$\Delta\varepsilon_1$ (kg mol <sup>-1</sup> )	$\Delta\varepsilon_2$ (kg mol <sup>-1</sup> )	$\log^*\beta_1^\circ$
$-(0.30 \pm 0.05)$	$0.32 \pm 0.08$	$-(0.59 \pm 0.08)$

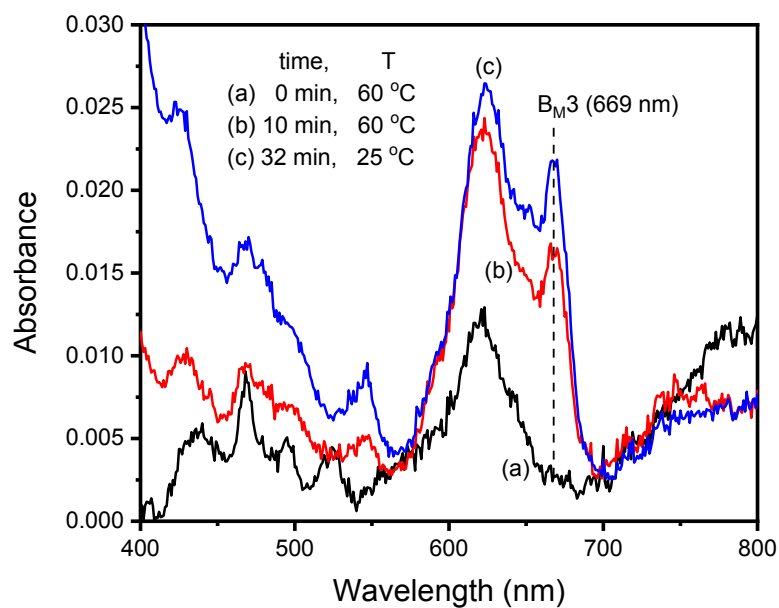
\* Note that non-weighted regression analysis and Levenberg Marquardt iteration algorithm were used.



**Fig. S6.** Van't Hoff plot using the combined  $\log^*\beta_1^\circ(T)$  data from (a) this work (Table 3 in the main text) and (b) Ref. [4] (Table 9.6, 25 – 150 °C). The dotted line indicates a weighted linear fit result. The new standard state constants,  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$ , are determined to  $43.3 \pm 2.2 \text{ kJmol}^{-1}$  and  $136 \pm 7 \text{ JK}^{-1}\text{mol}^{-1}$ , respectively. The constants calculated for the data only from (b) are also shown in Table S5.



**Fig. S7.** Residual plot (bottom) obtained after the kinetic reaction modeling analysis of the spectrophotometric data set of Fig. 6(a) in the main text.



**Fig. S8.** Kinetic spectral data demonstrating the irreversible evolution of the intermediate (M) at 60 °C (OPL = 10 mm; [U(IV)] = 1.0 mM; pH 2.2;  $I = 0.1$  m). The reaction temperature lowered to 25 °C after 10 min when the B<sub>M</sub>3 band of M was evident. In the (c) spectrum the peak of the B<sub>M</sub>3 did not disappear, instead, it increased during the period of temperature change from 60 to 25 °C. This strongly supports that the first step ( $k_1$ ) of the proposed U(IV)-NP formation scheme is kinetically irreversible.

[References]

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