Spectroluminescence measurements of stability constants of $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes in $NaClO_4$ medium and investigation of interaction effects.

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Supporting Information

This supporting information contains four Tables: the liquid junction potentials measured for $NaClO_4$ solutions of different ionic strengths ($0.01\ m \leq I_m \leq 3.5\ m$) using the reconditioned electrode; experimental samples information – pH value, calculated Ringböm coefficients α, $[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$) and deduced F_0; information for samples in Fig. 4; Decay-times of $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ determined at each I_m ; and two Figures: the slope analysis results of $I_m = 3.5\ m$; the predominance plot of the 3.5 *m* experiment.

Table S1. Potential values E_{mes} read on pH-meter for $NaClO_4$ solutions of I_m = 0.01 to 3.5 *m* at pcH = 2 using the reconditioned electrode of 3.5 *m* $NaClO_4$ reference solution: liquid junction potentials ΔE_{mes} calculated to estimate the potential differences between the solutions of a specific $I_m \geqslant 0.1$ *m* and of I_m = 0.01 *m*; ΔE_{mes} then used in the four-point calibration with commercial buffer solution of pH 1.64, 4.01, 6.87, 9.18, assumed as diluted solutions of $I_m \approx 0.01$ *m*; the uncertainties of ± 0.05 pH in text included this non-significant experimental bias.

Solution	Conversion factor (from molarity M to molality *m*)	I_m (mol kg_w^{-1})	E_{mes} (mV)	$\Delta E_{mes} = E_{mes} - E_{mes}$ (I_m = 0.01 *m*)
HCl 0.01 M + $NaClO_4$ 2.99 M	1.1678	3.50	172.2	31.3
HCl 0.01 M + $NaClO_4$ 2.49 M	1.1361	2.84	168	27.1
HCl 0.01 M + $NaClO_4$ 2.19 M	1.1196	2.46	165.5	24.6
HCl 0.01 M + $NaClO_4$ 1.99 M	1.1062	2.21	163.6	22.7
HCl 0.01 M + $NaClO_4$ 1.49 M	1.0780	1.62	158.9	18
HCl 0.01 M + $NaClO_4$ 0.99 M	1.0515	1.05	155.1	14.2
HCl 0.01 M + $NaClO_4$ 0.49 M	1.0265	0.51	150.2	9.3
HCl 0.01 M + $NaClO_4$ 0.19 M	1.0098	0.20	146.6	5.7
HCl 0.01 M + $NaClO_4$ 0.09 M	1.0075	0.10	144.5	3.6
HCl 0.01 M	1.0000	0.01	140.9	0
For the solution of I_m < 0.1 M, the conversion factor taken as 1. The factor values for $I_m \geqslant 0.1$ M taken from Guillaumont et al.[1]				

Table S2. Experimental samples information – pH value, calculated Ringböm coefficients α, $[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$) and deduced F_0; the sample solutions giving the slope of 1 are set in *italics* and those giving the slope of 2 are in ***bold italics*** (*c.f.* Fig. 2 of the main text).

I_m ($mol \cdot kg_w^{-1}$)	0.10				0.51			
Sample	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)
1	9.00	1.00	0	1.49E+08	9.00	1.00	0	2.48E+08
2	8.45	1.02	5.03E-05	1.75E+08	8.13	1.02	3.44E-04	2.10E+08
3	8.41	1.03	9.51E-05	1.55E+08	7.95	1.09	8.46E-04	1.95E+08
4	8.33	1.06	1.35E-04	1.44E+08	7.90	1.17	1.06E-03	1.95E+08
5	8.25	1.12	1.58E-04	2.23E+08	7.87	1.24	1.24E-03	2.10E+08
6	*8.21*	*1.17*	*2.49E-04*	*1.48E+08*	*7.84*	*1.27*	*1.59E-03*	*2.05E+08*
7	*8.17*	*1.19*	*2.88E-04*	*1.41E+08*	*7.81*	*1.38*	*2.00E-03*	*2.23E+08*
8	*8.13*	*1.29*	*4.36E-04*	*1.76E+08*	*7.78*	*1.54*	*2.39E-03*	*2.24E+08*
9	*8.09*	*1.45*	*5.06E-04*	*1.61E+08*	*7.75*	*1.73*	*2.99E-03*	*2.40E+08*
10	*8.01*	*2.03*	*7.77E-04*	*1.77E+08*	*7.72*	*2.00*	*3.86E-03*	*2.36E+08*
11	*7.91*	*3.69*	*1.13E-03*	*2.03E+08*	*7.69*	*2.36*	*4.45E-03*	*2.58E+08*
12	*7.87*	*4.84*	*1.94E-03*	*1.92E+08*	*7.66*	*2.83*	*5.20E-03*	*2.72E+08*
13	***7.80***	***8.04***	***3.08E-03***	***1.98E+08***	*7.64*	*3.21*	*7.61E-03*	*2.79E+08*
14	***7.73***	***13.67***	***5.05E-03***	***2.06E+08***	***7.60***	***4.21***	***9.97E-03***	***2.97E+08***
15	***7.68***	***20.17***	***6.27E-03***	***2.27E+08***	***7.56***	***5.59***	***1.27E-02***	***3.06E+08***
16	***7.62***	***32.36***	***8.69E-03***	***2.33E+08***	***7.52***	***7.54***	***1.56E-02***	***3.41E+08***
17	***756***	***52.16***	***1.00E-02***	***2.30E+08***	***7.48***	***10.22***	***1.69E-02***	***3.63E+08***
18	***7.48***	***98.99***	***1.26E-02***	***2.35E+08***	***7.44***	***13.97***	***2.20E-02***	***3.60E+08***
19	***7.46***	***116.8***	***1.34E-02***	***2.40E+08***				
I_m ($mol \cdot kg_w^{-1}$)	1.05				1.62			
Sample	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)
1	9.00	1.00	0	2.27E+08	9.00	1.00	0	5.45E+08
2	8.13	1.01	8.81E-04	1.71E+08	7.95	1.04	5.53E-04	4.01E+08
3	7.95	1.04	1.46E-03	1.55E+08	7.80	1.09	1.59E-03	3.91E+08
4	7.80	1.08	1.94E-03	1.54E+08	7.78	1.12	2.97E-03	3.75E+08
5	*7.78*	*1.11*	*2.16E-03*	*1.73E+08*	*7.72*	*1.22*	*4.15E-03*	*3.71E+08*
6	*7.72*	*1.20*	*2.70E-03*	*1.69E+08*	*7.68*	*1.36*	*4.61E-03*	*4.19E+08*
7	*7.68*	*1.32*	*3.45E-03*	*1.70E+08*	*7.64*	*1.56*	*5.58E-03*	*4.00E+08*
8	*7.64*	*1.51*	*4.32E-03*	*2.33E+08*	*7.60*	*1.88*	*6.65E-03*	*4.22E+08*
9	*7.60*	*1.80*	*5.57E-03*	*2.15E+08*	*7.56*	*2.33*	*8.82E-03*	*4.42E+08*
10	*7.56*	*2.22*	*7.77E-03*	*2.35E+08*	*7.52*	*2.97*	*1.31E-02*	*4.68E+08*
11	***7.52***	***2.81***	***1.14E-02***	***2.24E+08***	***7.48***	***3.86***	***1.64E-02***	***5.07E+08***
12	***7.48***	***3.64***	***1.33E-02***	***2.57E+08***	***7.45***	***4.79***	***2.25E-02***	***5.05E+08***
13	***7.45***	***4.50***	***1.64E-02***	***2.60E+08***	***7.40***	***6.95***	***2.83E-02***	***5.61E+08***
14	***7.40***	***6.52***	***2.18E-02***	***2.80E+08***	***7.34***	***11.08***	***3.45E-02***	***6.18E+08***
15	***7.34***	***10.36***	***2.53E-02***	***3.53E+08***	***7.32***	***15.00***	***3.73E-02***	***6.13E+08***
I_m ($mol \cdot kg_w^{-1}$)	2.21				2.46			
Sample	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)
1	9.06	1.00	0	3.02E+08	8.80	1.00	0	4.77E+08
2	7.85	1.02	3.72E-03	2.81E+08	8.13	1.00	2.45E-03	4.61E+08
3	*7.82*	*1.05*	*7.07E-03*	*3.14E+08*	7.95	1.01	3.93E-03	4.34E+08
4	*7.79*	*1.05*	*7.80E-03*	*3.37E+08*	7.80	1.02	4.99E-03	4.30E+08
5	*7.73*	*1.07*	*8.77E-03*	*3.53E+08*	*7.58*	*1.17*	*6.20E-03*	*3.96E+08*
6	*7.68*	*1.11*	*9.67E-03*	*3.98E+08*	*7.54*	*1.28*	*7.74E-03*	*3.91E+08*
7	*7.62*	*1.19*	*1.16E-02*	*4.40E+08*	*7.50*	*1.45*	*9.51E-03*	*4.47E+08*
8	*7.58*	*1.24*	*1.51E-02*	*4.42E+08*	*7.46*	*1.69*	*1.13E-02*	*4.17E+08*
9	*7.50*	*1.60*	*1.68E-02*	*4.28E+08*	*7.42*	*2.06*	*1.27E-02*	*4.06E+08*
10	***7.48***	***1.75***	***2.11E-02***	***4.16E+08***	*7.38*	*2.60*	*1.72E-02*	*4.65E+08*
11	***7.42***	***2.38***	***2.89E-02***	***4.41E+08***	*7.34*	*3.34*	*2.01E-02*	*5.22E+08*
12	***7.35***	***3.71***	***3.27E-02***	***4.59E+08***	***7.30***	***4.42***	***2.63E-02***	***5.52E+08***
13	***7.30***	***5.29***	***4.24E-02***	***5.05E+08***	***7.27***	***5.50***	***3.46E-02***	***5.75E+08***
14	***7.22***	***9.62***	***5.54E-02***	***5.56E+08***	***7.22***	***7.97***	***4.13E-02***	***6.82E+08***
					7.18	***10.85***	***5.01E-02***	***7.59E+08***

Table S2 (continued).

I_m (mol·kg$_w^{-1}$)	3.50							
Sample	pH value	α	[Ca^{2+}] (mol·kg$_w^{-1}$)	F_0 (counts)				
1	8.94	1.00	0.00001	1.28E+08				
2	8.30	1.01	0.00097	2.39E+08				
3	8.10	1.03	0.00306	3.87E+08				
4	7.90	1.03	0.00719	1.92E+08				
5	7.70	1.06	0.01769	2.28E+08				
6	*7.60*	*1.11*	*0.02156*	*1.86E+08*				
7	*7.50*	*1.29*	*0.02623*	*2.04E+08*				
8	*7.44*	*1.49*	*0.03109*	*2.08E+08*				
9	*7.39*	*1.85*	*0.04189*	*2.18E+08*				
10	*7.33*	*2.58*	*0.05419*	*2.27E+08*				
11	*7.29*	*3.33*	*0.06825*	*2.07E+08*				
12	*7.27*	*3.84*	*0.09060*	*2.48E+08*				
13	*7.25*	*4.44*	*0.14429*	*2.79E+08*				
14	*7.22*	*5.56*	*0.21003*	*3.31E+08*				
15	*7.20*	*6.51*	*0.25634*	*3.57E+08*				
16	*7.17*	*8.23*	*0.32939*	*3.88E+08*				
17	*7.16*	*9.00*	*0.39816*	*4.09E+08*				
18	*7.15*	*9.85*	*0.50482*	*4.05E+08*				

Table S3. Information for samples in Fig. 4 of the main text.

Sample	0.1 m NaCl	0.1 m $NaClO_4$	1 m NaCl	1 m $NaClO_4$
pH value	7.82	7.78	7.43	7.56
$[Ca^{2+}]$ (mol kg_w^{-1})	5.98E-3	5.19E-3	7.80E-2	2.80E-2

Table S4 Decay-times of $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ determined at each I_m.

I_m (mol·kg$_w^{-1}$)	τ ($UO_2(CO_3)_3^{4-}$) (ns)	τ ($CaUO_2(CO_3)_3^{2-}$) (ns)	τ ($Ca_2UO_2(CO_3)_3$(aq)) (ns)
0.10	10.62 ± 0.22	30.41 ± 1.9	51.19 ± 1.85
0.51	8.46 ± 0.17	39.79 ± 2.78	68.53 ± 4.45
1.05	9.51 ± 0.11	37.57 ± 4.77	63.02 ± 4.45
1.62	9.39 ± 0.13	35.52 ± 2.66	65.76 ± 6.35
2.21	11.21 ± 0.40	27.72 ± 1.34	47.54 ± 2.53
2.46	10.61 ± 0.12	38.6 ± 4.33	86.36 ± 10.15
Averaged τ	10.0 ± 1.0 (τ measured from I_m = 0.1 to 2.46 *m*)	34.20 ± 2.24 (τ measured from I_m = 0.1 to 2.21 *m*)	59.21 ± 4.15 (τ measured from I_m = 0.1 to 2.21 *m*)

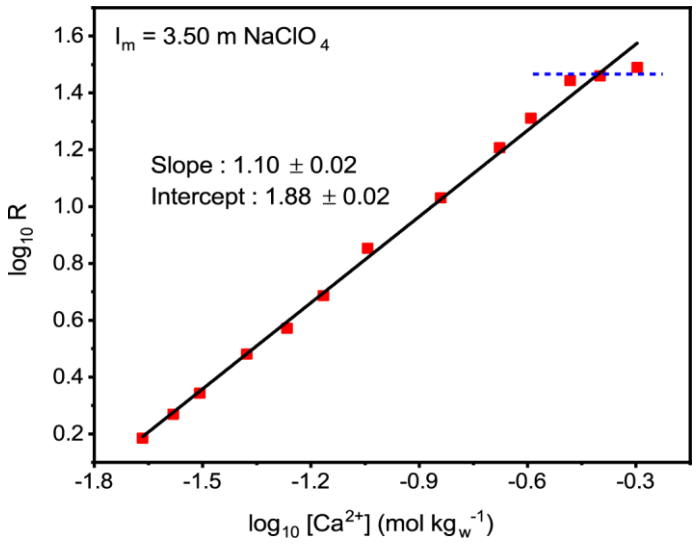

Fig. S1. Plot of logarithmic ratio R as a function of $\log_{10}[Ca^{2+}]$ (mol kg_w^{-1}) at I_m = 3.50 m of $NaClO_4$ medium: $[U]_{total}$ = 50 μmol kg_w^{-1}, $P(CO_2)$ = $10^{-3.5}$ atm.

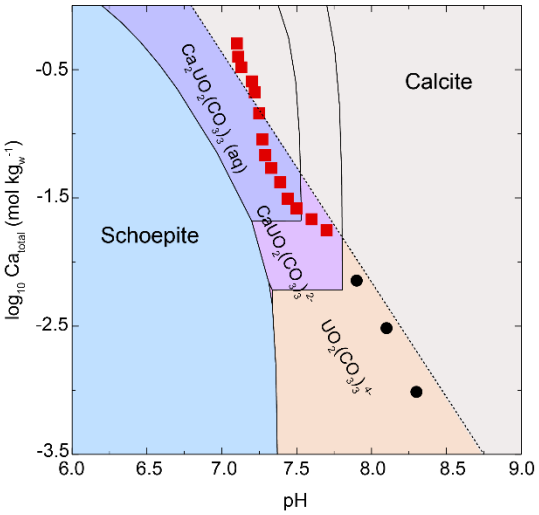

Fig. S2. Predominance plot obtained using PHREEPLOT[2] of Ca-UO_2-CO_3 system at [U(VI)] = 50 μ*m*, $P(CO_2) = 10^{-3.5}$ atm at I_m = 3.50 *m* $NaClO_4$: experimental points giving slopes of one are highlighted with red squares; the black circles represent the beginning of titration where the binary complex dominates; dotted line represent the predominance line between Ca^{2+} and calcite.

References

1. R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D. A. Palmer, I. Grenthe and M. H. Rand, *Update of the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France, 2003.
2. D. G. Kinniburgh and D. M. Cooper, *Creating Graphical Output with PHREEQC*, 2011. http://www.phreeplot.org