Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

A spectrophotometric study of the impact of pH and metal-to-ligand ratio on the speciation of the Pu(VI)-oxalate system

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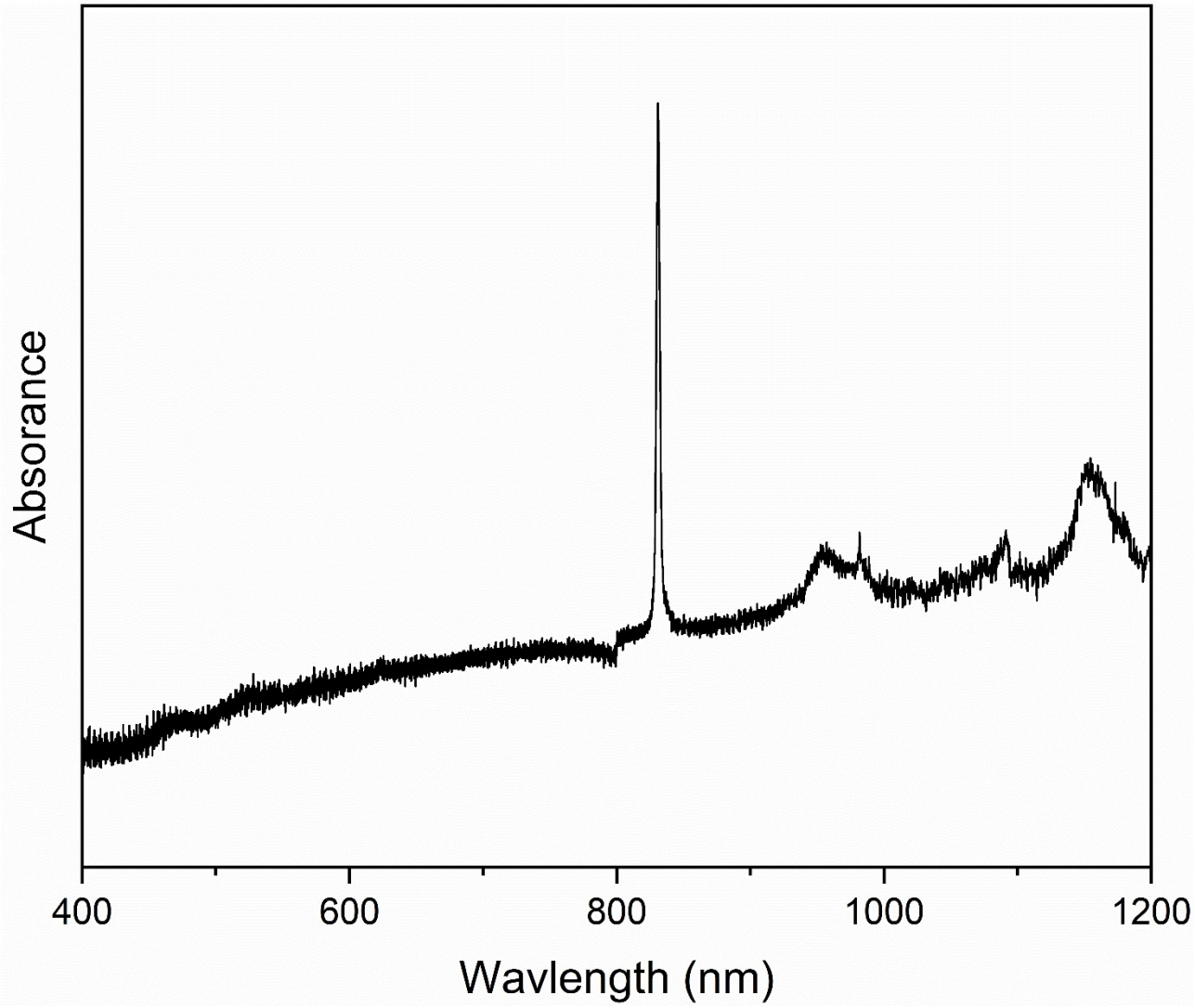

Figure S1: UV-vis-NIR spectrum of Pu(VI) stock diluted to 1 mM in 0.1 M NaCl showing the presence of only Pu(VI) before use in the Pu-oxalate experiments.

Table S1: Pu concentrations of UV-vis-NIR samples following Pu spike into oxalic acid in 0.1 M NaCl. Concentrations measured by LSC. Pu blank (M/L = 1:0) sample contained only Pu in 0.1 M NaCl.

Target M/L (Pu:Ox)	[Pu] pH = 1 (mM)	[Pu] pH = 3 (mM)	[Pu] pH = 7 (mM)
1:0	0.7214 ± 0.0018	0.9597 ± 0.0015	0.8130 ± 0.0019
1:10	0.8488 ± 0.0020	0.8429 ± 0.0014	0.8554 ± 0.0020
1:5	0.9180 ± 0.0021	0.7682 ± 0.0014	0.8472 ± 0.0020
1:3	0.9196 ± 0.0021	0.7681 ± 0.0014	0.8591 ± 0.0020
1:2	0.9530 ± 0.0021	0.7665 ± 0.0014	0.9210 ± 0.0021
1:1	0.9064 ± 0.0021	0.7433 ± 0.0015	0.8568 ± 0.0020
3:1	0.9750 ± 0.0021	0.8694 ± 0.0015	0.8957 ± 0.0020
5:1	0.9216 ± 0.0021	0.9179 ± 0.0015	0.8844 ± 0.0020
10:1	0.8672 ± 0.0020	0.8782 ± 0.0015	0.9004 ± 0.0020

Table S2: Experimentally measured pH of UV-vis-NIR samples following Pu spike into oxalic acid in 0.1 M NaCl. Pu blank (M/L = 1:0) sample contained only Pu in 0.1 M NaCl.

Target M:L (Pu:Ox)	Target pH = 1	Target pH = 3	Target pH = 7
1:0	1.02	2.65	7.43
1:10	1.00	2.66	7.47
1:5	0.98	3.48	7.01
1:3	1.01	3.51	6.73
1:2	0.78	3.16	6.68
1:1	1.03	2.89	6.64
3:1	0.99	2.79	6.96
5:1	1.04	2.70	6.85
10:1	1.04	2.67	6.67

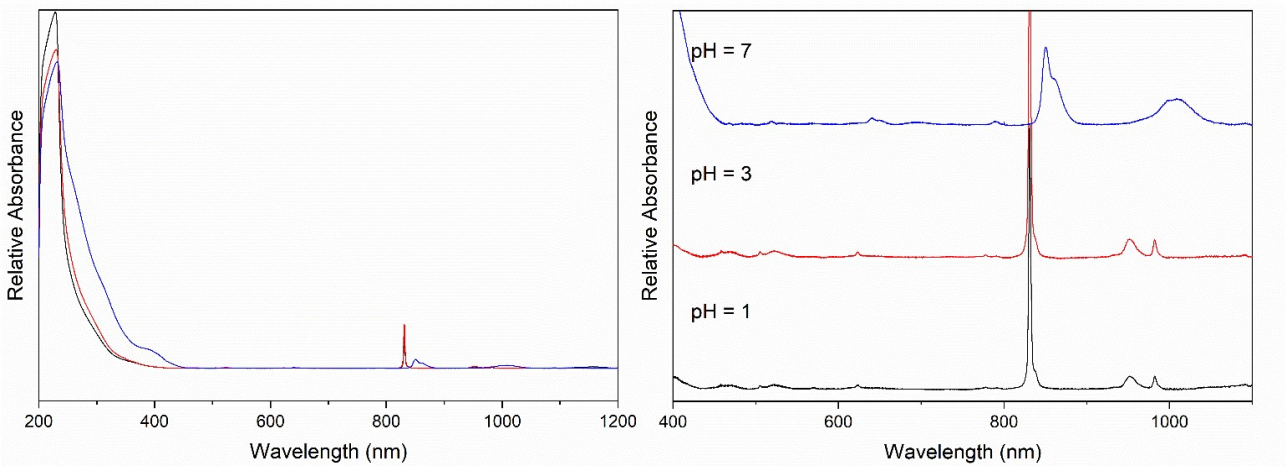

Figure S2: UV-vis-NIR spectra of Pu(VI) controls at pH 1 (black), 3 (red), and 7 (blue) following spike into 0.1 M NaCl. Left: Full spectra showing data from 200–1200 nm. Right: Spectra showing data from 400–1100 nm.

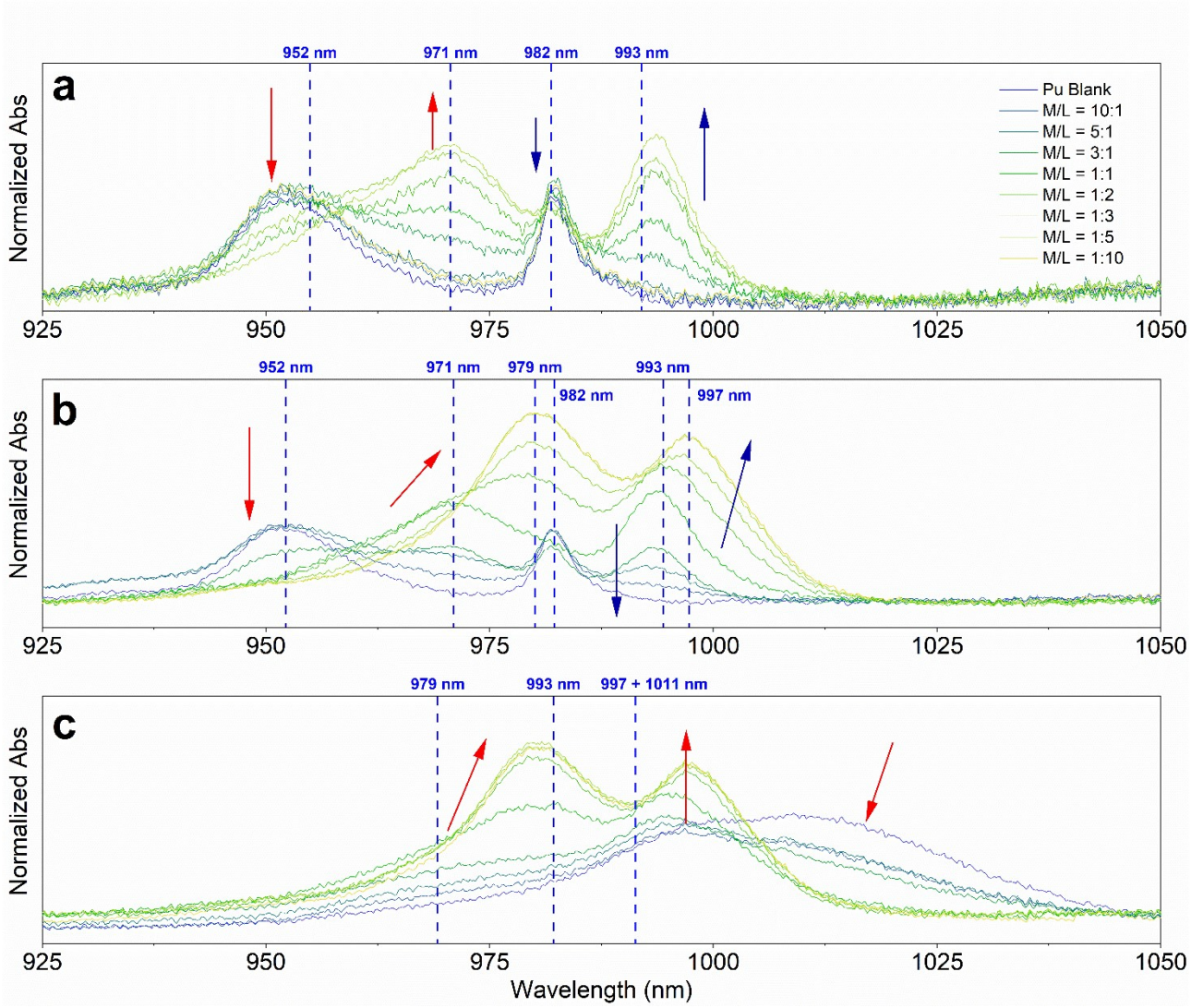

Figure S3: UV-vis-NIR spectra of Pu(VI)-oxalate experiments at (a) pH 1, (b) pH 3, and (c) pH 7 from 925–1050 nm. Red and blue arrows show changes in peak intensity or shifts in peak position with increasing M/L.

Table S3. Selected equilibrium constants (log $K°$ or log $\beta°$) for thermodynamic calculations of Pu(VI)-oxalate formation constants.

Reaction	**log $K°$ or log $\beta°$**	**Reference**
$H^+ + C_2O_4^{2-} \leftrightarrow HC_2O_4^-$	4.250 ± 0.010	[1]
$H^+ + HC_2O_4^- \leftrightarrow H_2C_2O_4(aq)$	1.400 ± 0.030	[1]
$CO_2(aq) \leftrightarrow CO_2(g)$	1.472 ± 0.020	[2]
$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$	-6.354 ± 0.020	[2]
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	-10.329 ± 0.020	[2]
$PuO_2^{2+} + H_2O \leftrightarrow PuO_2(OH)^+ + H^+$	-5.500 ± 0.500	[2]
$PuO_2^{2+} + 2H_2O \leftrightarrow PuO_2(OH)_2(aq) + 2H^+$	-13.200 ± 1.500	[2]
$PuO_2^{2+} + 3H_2O \leftrightarrow PuO_2(OH)_3^- + 3H^+$	-24.000 ± 1.600	[2]
$2PuO_2^{2+} + 2H_2O \leftrightarrow (PuO_2)_2(OH)_2^{2+} + 2H^+$	-7.500 ± 1.000	[2]
$PuO_2^{2+} + Cl^- \leftrightarrow PuO_2Cl^+$	0.230 ± 0.030	[2]
$PuO_2^{2+} + 2Cl^- \leftrightarrow PuO_2Cl_2(aq)$	-1.150 ± 0.300	[2]
$PuO_2^{2+} + CO_3^{2-} \leftrightarrow PuO_2CO_3(aq)$	9.500 ± 0.500	[2]
$PuO_2^{2+} + 2CO_3^{2-} \leftrightarrow PuO_2(CO_3)_2^{2-}$	14.700 ± 0.500	[2]
$PuO_2^{2+} + 3CO_3^{2-} \leftrightarrow PuO_2(CO_3)_3^{4-}$	18.000 ± 0.500	[2]
$3PuO_2^{2+} + 6CO_3^{2-} \leftrightarrow (PuO_2)_3(CO_3)_6^{6-}$	51.000 ± 2.500	[2]
$PuO_2(OH)_2(am,hyd) \leftrightarrow PuO_2^{2+} + 2OH^-$	-22.830 ± 0.650	[2]
$PuO_2CO_3(cr)$ $\leftrightarrow PuO_2^{2+} + CO_3^{2-}$	-14.820 ± 0.120	[2]

Table S4. Ion interaction coefficients ($\varepsilon_{i,j}$) for extrapolation to zero ionic strength using the Specific Ion-interaction Theory (SIT) activity model.[1,3]

i	***j***	**$\varepsilon_{i,j}$ (kg·mol^{-1})**
H^+	Cl^-	0.12
Cl^-	Na^+	0.03
OH^{-+}	Na^+	0.04
CO_3^{2-}	Na^+	-0.08
HCO_3^-	Na^+	0.00
$C_2O_4^{2-}$	Na^+	-0.08
$HC_2O_4^-$	Na^+	-0.07
PuO_2^{2+} (Approx. from UO_2^{2+})	Cl^-	0.21
$PuO_2(C_2O_4)_2^{2-}$ (Approx. from $UO_2(C_2O_4)_2^{2-}$)	Na^+	-0.18

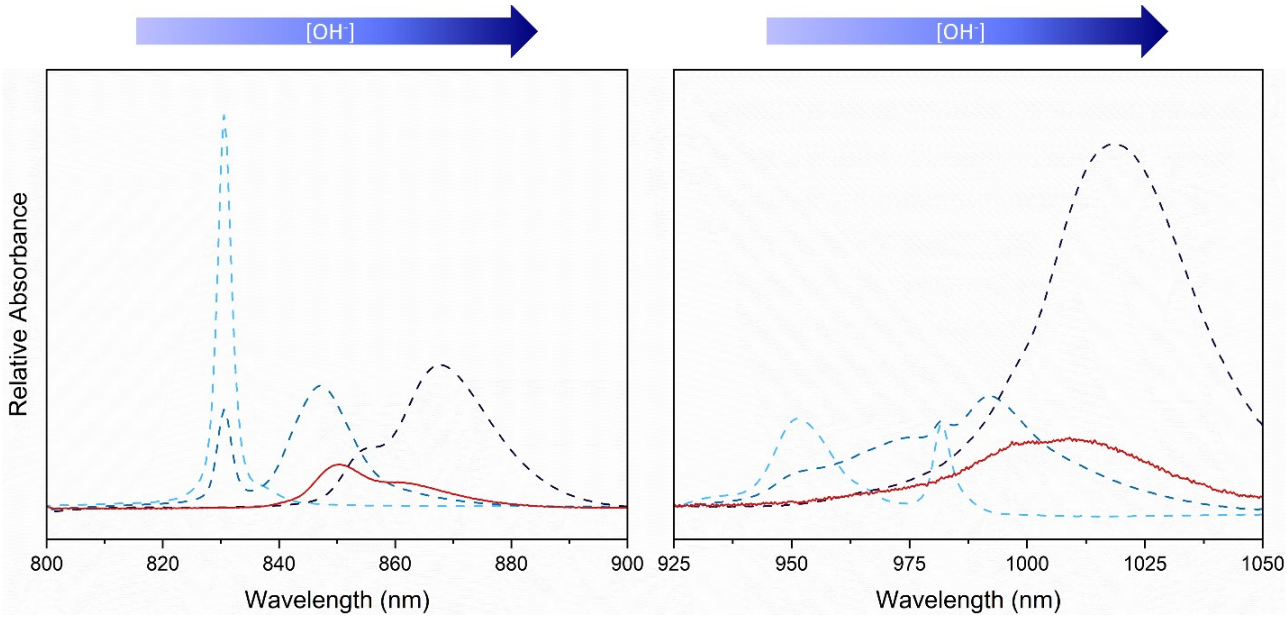

Figure S4: The absorption spectrum of the Pu(VI) control at pH 7 is shown in red. The spectra for the titration of Pu(VI) with increasing [OH^-] is shown as dotted lines in shades of blue, from light blue (lowest [OH^-]) to dark blue (highest [OH^-]).

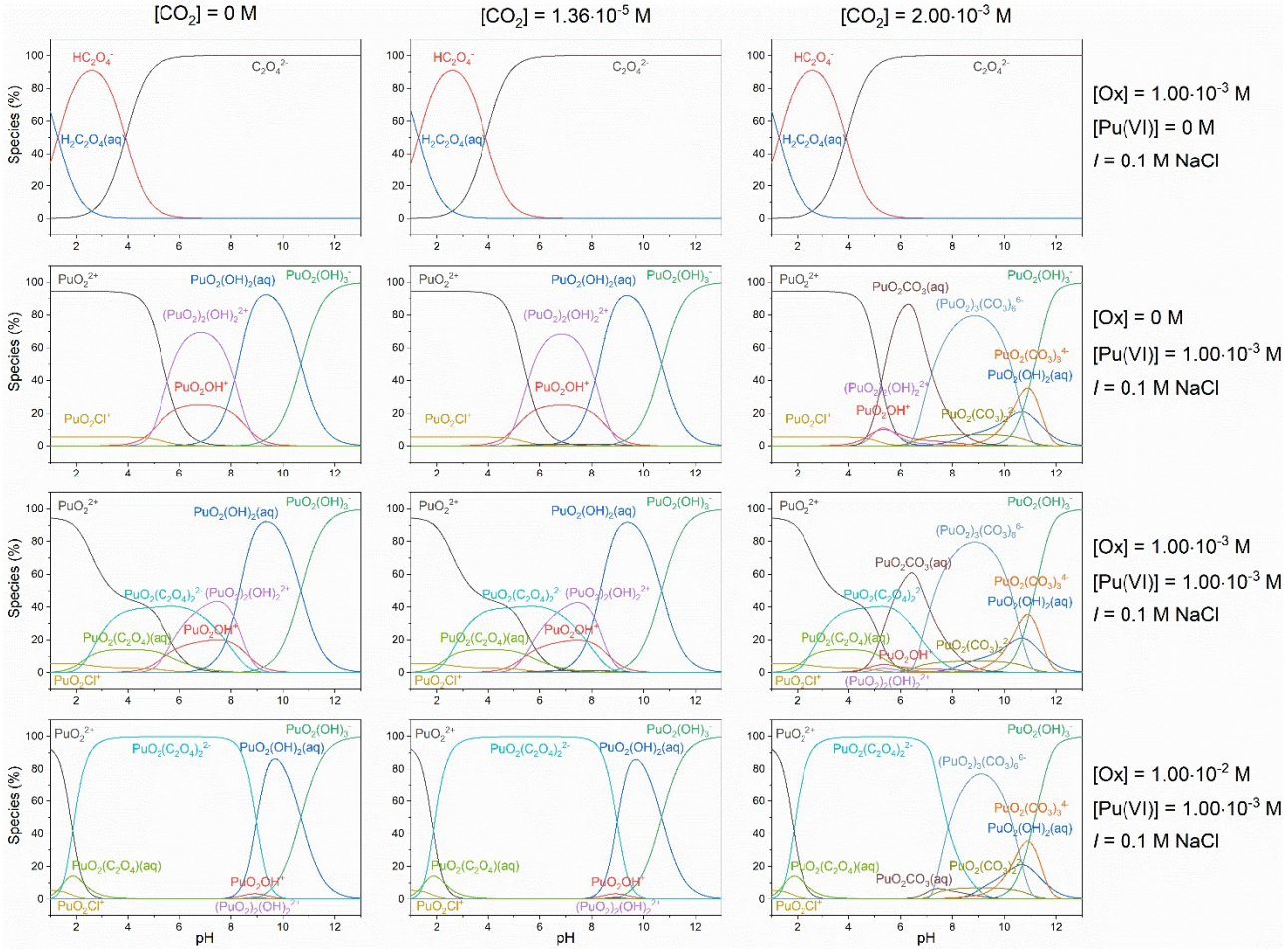

Figure S5: Speciation diagrams as a function of pH for (row 1) oxalate, (row 2) Pu(VI) in the absence of oxalate, (row 3) Pu(VI) in the presence of equimolar oxalate concentrations, and (row 4) Pu(VI) in the presence of a 10x excess of oxalate. Speciation fractions were calculated using thermodynamic values available within the literature or generated within this work. Calculations were conducted with I = 0.1 M NaCl, $[Pu(VI)]_{tot}$ = 1 mM, and either absence of carbonate (column 1), in the presence of $[C]_{tot}$ = $1.36 \cdot 10^{-5}$ M (column 2, calculated to be the dissolved carbon concentration in equilibrium with ~400 ppm atmospheric CO_2), or in the presence of $[C]_{tot}$ = 0.002 M (column 3).

References

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