

Electronic Supplementary Information

Interactions Between Uranium(VI) and Phosphopeptide: Experimental and Theoretical Investigations

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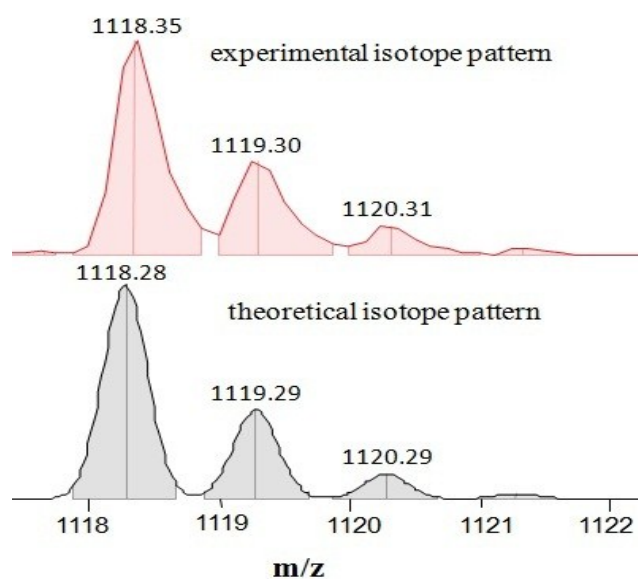


Fig. S1 Experimental and theoretical isotope patterns of 1:1 U(VI)-P¹ ([P¹+UO₂²⁺-H⁺]⁺, m/z = 1118.3) complex, detected by ES⁺-MS.

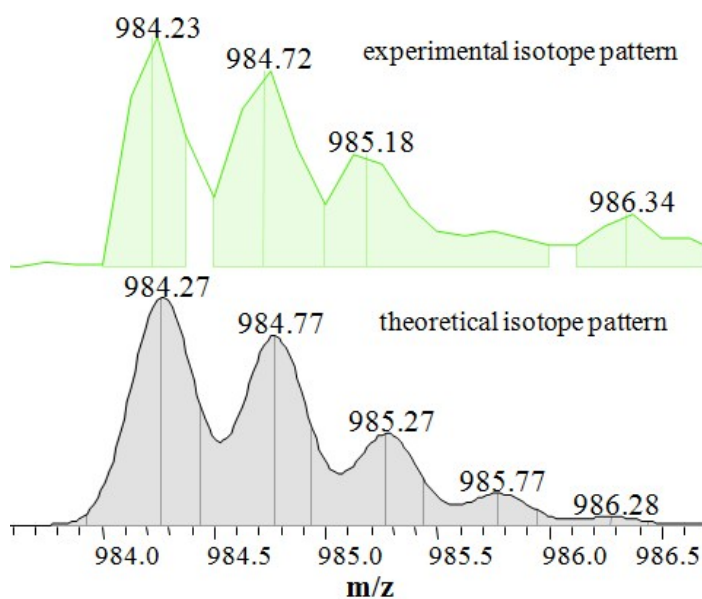


Fig. S2 Experimental and theoretical isotope patterns of 1:2 U(VI)-P¹ ([2P¹+UO₂²⁺]²⁺, m/z = 984.2) complex, detected by ES⁺-MS.

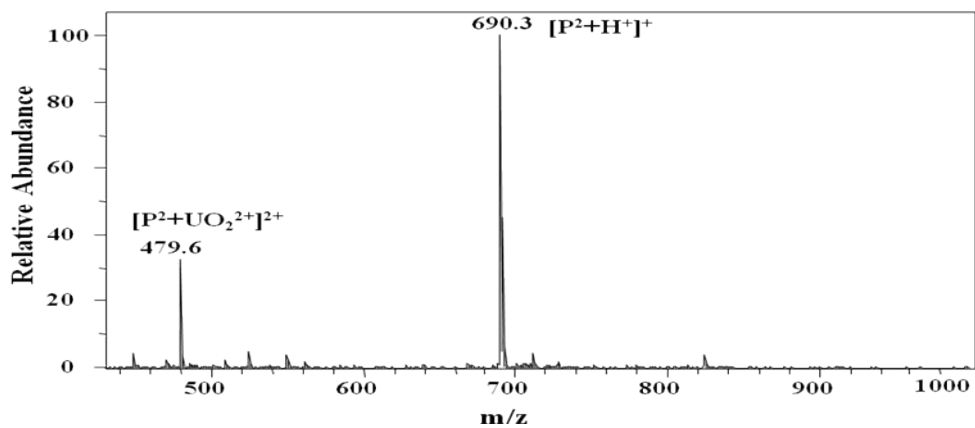


Fig. S3 ESI mass spectrum of the solution containing P^2 ($25 \mu\text{M}$) and 5.0 equiv. $\text{UO}_2(\text{NO}_3)_2$ in AcONH_4 buffer (5 mM, pH 7.0).

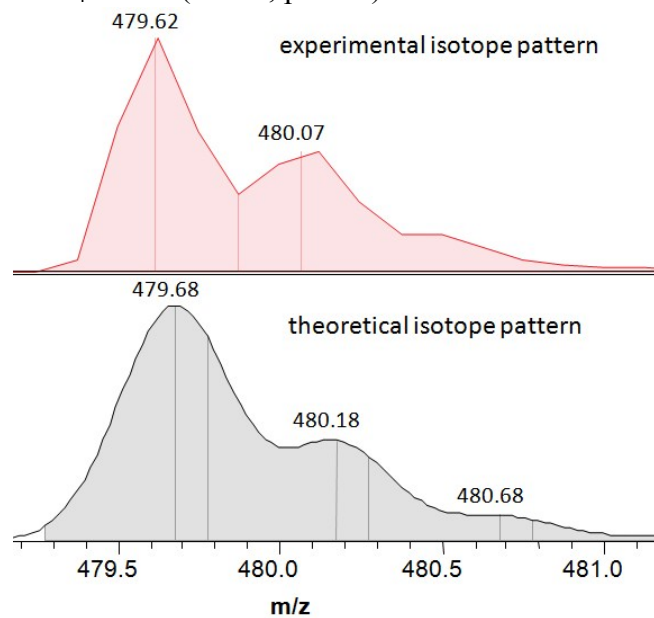


Fig. S4 Experimental and theoretical isotope patterns of U(VI)- P^2 1:1 ($[\text{P}^2+\text{UO}_2^{2+}]^{2+}$, $m/z = 479.6$) complex, detected by ES^+ -MS.

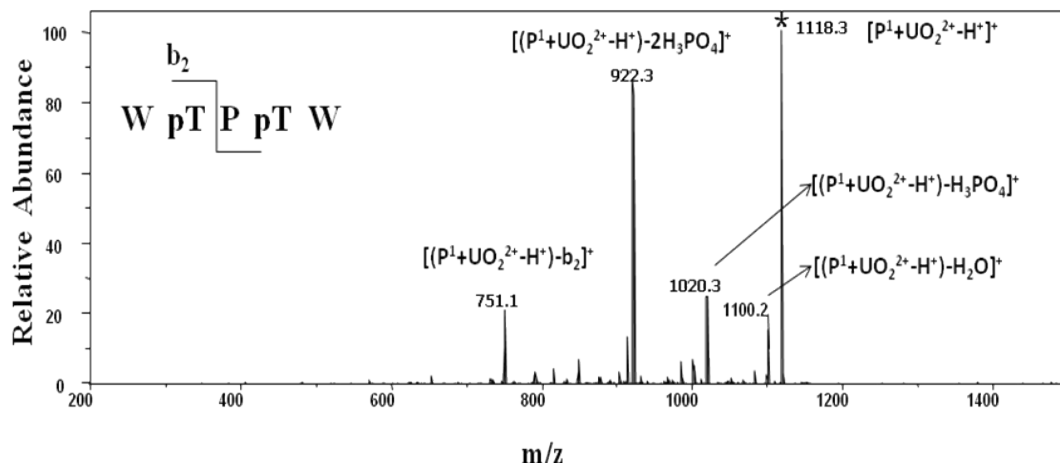


Fig. S5 Collision induced dissociation spectrum of the monocation U(VI)-P¹ 1:1 complex ($[P^1+UO_2^{2+}-H^+]^+$, $m/z = 1118.3$).

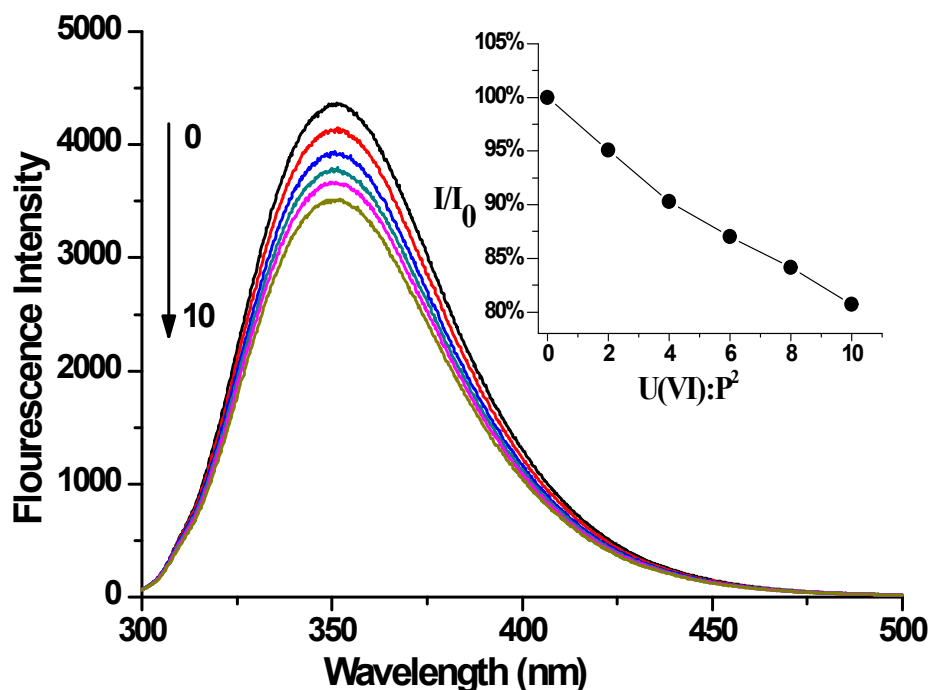


Fig. S6 Fluorescence emission spectra of 20 μM P² in the absence and presence of increasing concentrations of uranyl nitrate (0 to 200 μM). Measured at pH 4.0, HEPES buffer 10 mM, NaClO₄ 0.1 M, 25 °C with $\lambda_{\text{ex}} = 280$ nm. Insert: plots of fluorescence variations at 352 nm expressed as I/I_0 over equivalent U(VI) additions. I_0 is the fluorescence intensity of the P² and I the fluorescence intensities of the resulting U(VI)-P² complex.

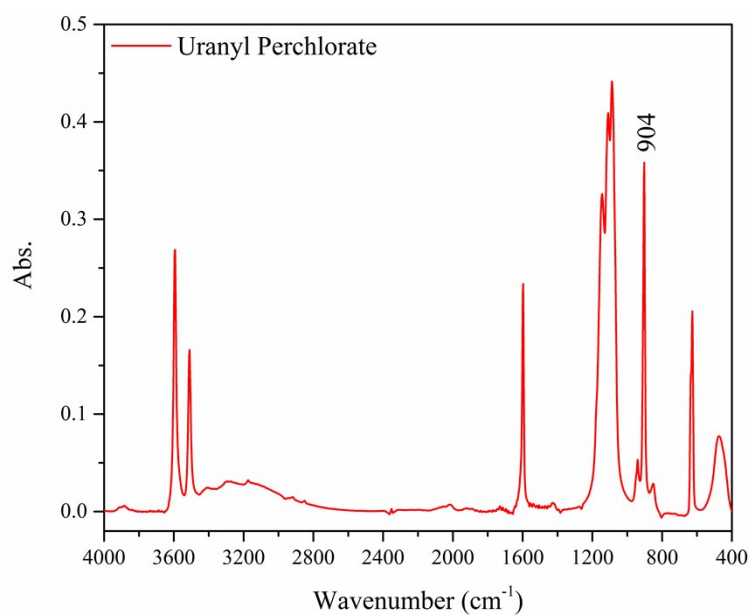


Fig. S7 FT-IR spectra of $\text{UO}_2(\text{ClO}_4)_2$

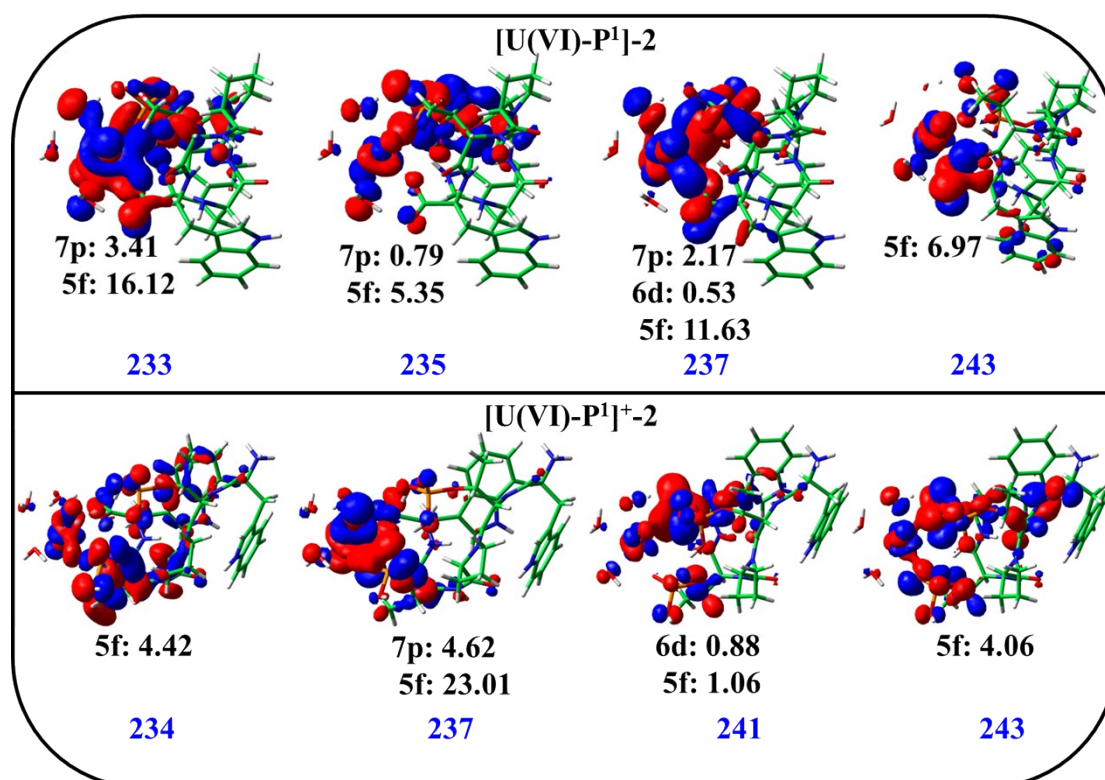


Fig. S8 The MO diagrams relevant to U(VI) ions and P¹ for complexes [U(VI)-P¹]-2 and [U(VI)-P¹]⁺-2. The isosurface value of the MOs is set to be 0.02 au. The uranium atom composition of the corresponding MOs is also provided.

Table S1 The total electronic energy of six U(VI)-P¹ complexes in the gas phase (E_{gas}, au) at the B3LYP/6-31G(d)/RECP level of theory and the aqueous phase (E_{sol}, au) at the B3LYP/6-311+G (d)/RECP/SMD level of theory, respectively.

Complexes	E _{gas}	E _{sol}
[U(VI)-P ¹]-1	-4335.997915	-4337.134684
[U(VI)-P ¹]-2	-4335.992684	-4337.142997
[U(VI)-P ¹]-3	-4335.992555	-4337.137158
[U(VI)-P ¹] ⁺ -1	-4336.412194	-4337.593993
[U(VI)-P ¹] ⁺ -2	-4336.389231	-4337.594933
[U(VI)-P ¹] ⁺ -3	-4336.387694	-4337.572391

Table S2 Calculated NBO populations (s, p, d and f) and natural charges on the uranium atom at the B3LYP/6-31G(d)/RECP level of theory.

Complexes	7s	7p	6d	5f	Q _U
[U(VI)-P ¹]-1	0.19	0.37	1.39	2.56	1.58
[U(VI)-P ¹]-2	0.19	0.38	1.41	2.57	1.55
[U(VI)-P ¹]-3	0.18	0.39	1.42	2.58	1.52
[U(VI)-P ¹] ⁺ -1	0.18	0.37	1.41	2.57	1.59
[U(VI)-P ¹] ⁺ -2	0.18	0.36	1.39	2.57	1.61
[U(VI)-P ¹] ⁺ -3	0.18	0.36	1.38	2.55	1.66