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Supporting Information

Unusual redox stability of pentavalent uranium with hetero-bifunctional phosphonocarboxylate: Insight into aqueous speciation

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1. Experimental

1.1. Sample Preparation: Phosphonocarboxylate (PC) chelators namely, PFA, PAA and 3-PPA and $NaClO_4$ were procured from Sigma-Aldrich. By dissolving solid U_3O_8 in 1-2 M HNO_3 the stock solution of uranyl nitrate (0.1M) was prepared and standardized through Davies & Gray method. For electrochemical experiments, the Samples were prepared by mixing stock solutions of $UO_2(NO_3)_2$, ligands and $NaClO_4$ to obtain solutions with the required proportion of metal ion, ligand and ionic strength respectively. The pH of the experimental samples was adjusted using a pH meter (Lab India) based on a combination pH electrode (glass membrane electrode and a reference electrode). Aqueous solutions were prepared using milliQ water having resistivity 18MΩ.cm. In the electrochemical experiment, the supporting electrolyte was used as 0.1 M $NaClO_4$. For ESI-MS experiment, the solution containing uranyl ion (1×10^{-4} M) and three PCs (1mM) were prepared in methanol solvent and mixed in the proper ratio to obtain the required concentration of uranyl(VI) and chelators in the complex form.

2. Instrumentation:

2.1. Electrochemistry: The cyclic voltammetry, square wave and chronopotentiometry/amperometry measurements were performed using an AUTOLAB PGSTAT100 electrochemical analyzer with three-electrode systems consisting of SMDE/GC/ITO as working electrode, Ag-AgCl/(sat. KCl) as a reference electrode, and glassy carbon/Pt as an auxiliary electrode. All electrochemical experiment was performed in inert atmosphere with continuous purging of High purity N_2 gas during electrochemical experiments.

Compared to GC and Pt, SMDE as working electrode is more sensitive at low concentration of metal ions, has high over potential for hydrogen evolution which enables to work in more cathodic potentials (beneficial for studying redox speciation process of Uranyl ion and its complexes), broad linear dynamic range, renewability of the electrode surface and high reproducibility (no interference), and its arrangement is practically innocuous in small amounts at room temperature [1-3].

Spectroelectrochemical experiments were carried out by coupling the potentiostat with Ocean optics spectrophotometer with QE 65000 detector. UV-visible absorption Cuvette with the Teflon top was used as a spectroelectrochemical cell. ITO plate was used as the working electrode with Ag/AgCl (sat. KCl) as the reference electrode and Pt wire as the auxiliary electrode.

2.2. ESI-MS: The ESI-MS studies were performed with the electrospray ionization ion source equipped with mass analyzer of Quadruple-Time-of-Flight (model micrOTOFQ-II, Bruker Daltonics GmbH). Bruker Compass Data Analysis software supplied by Bruker Daltonics GmbH was used for the ESI-MS Data analysis. With the help of 100 μL syringe (Hamilton) using a syringe pump (NEMESYS, Cetrol GmbH), the solution was infused into the mass spectrometric system. For the measurement in the positive ion mode and negative ion mode, the capillary voltage of -4500 V and +3800 V were applied, respectively. For both dry gas and nebulizer gas Nitrogen was used at a flow rate of 4 $\mathrm{Lmin^{-1}}$ and the pressure 0.3 bar, respectively.

Proposed theory for disproportionation in Literature:

Scheme S1: Kern and Orlemann [13]. The Potential of the Uranium (V), Uranium (VI) Couple and the Kinetics of Uranium (V) Disproportionation in Perchlorate Media. J. Am. Chem. Soc. 1949, 71, 2102–2106.]

Disproportionation is expected to occur through following mechanism under acidic condition

$[U^{VI}O_2]^{2+} + e^- \longrightarrow [U^{V}O_2]^+$ (1)

$[U^{V}O_2]^+ + [H]^+ \longrightarrow [OU^{V}OH]^{2+}$ (2)

$[U^{V}O_2]^+ + [OU^{V}OH]^{2+} \longrightarrow [U^{VI}O_2]^{2+} + [OU^{IV}OH]^+$ (3)

$[OU^{IV}OH]^+ \longrightarrow$ Stable U(IV) species (4)

Rate of reaction: Second order with $[U^{V}O_2]^+$ and pseudo first order with H^+.

Scheme S2: Newton and Baker's Theory [14]: Proposed formation of a complex $U_2O_4^{3+}$ (as given below) and its disproportion rate is much lower than that of UO_2^+.

UO_2^+ [U(V)] + $UO_2^{2+} \longrightarrow U_2O_4^{3+}$ (5)

U(V) + $U_2O_4^{3+} \longrightarrow$ U(IV) + 2U(VI) (6)

Rate of reaction is second-order rate constant for the disproportionation of uncomplexed U(V).

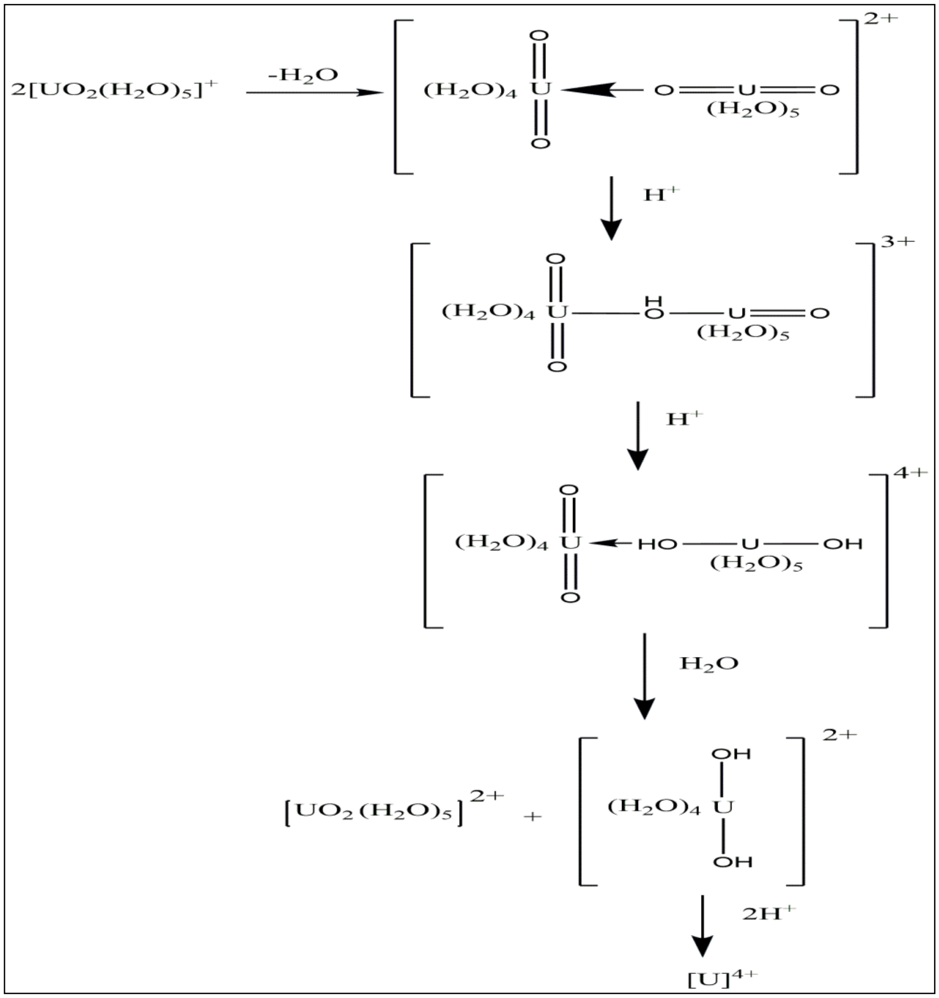
Scheme S3: Ekstorm et al. Theory [15]: Explained the formation of the U^{V}–U^{VI} binuclear complex according to the following equations:

U(V) + U(V) $\longrightarrow U^{V}.U^{VI}$ (7)

$U^{V}.U^{VI}$ + U(V) $\longrightarrow$ U(IV) + 2U(VI) (8)

The rate constant for the disproportionation reaction does not follow a strictly first-order acid dependency of H^+.

Scheme S4: Steele and Taylor Theory [16]: The disproportionation of U(V) occurs because of the formation of a dimer (a cation-cation complex) followed by two successive protonations at the axial oxygens of the donor uranyl ion. The protonation of one of the "yl" oxygen atoms of the donor uranyl(V) ion facilitates an immediate inner-sphere electron transfer from the acceptor uranyl(V) to the donor uranyl(V) ion and then one more protonation of the remaining "yl" oxygen atom of the donor uranyl(V) takes place followed by the introduction of a solvent water molecule that decomposes the CC complex into [U(IV)]and $[UO_2]^{2+}$ complexes, as shown below:



Scheme S4. Disproportionation reaction proposed by Steele and Taylor et al.

1. Disproportionation reaction of pentavalent uranium

$$2[UO_2(aq)]^+ + 4H^+ \longrightarrow [UO_2(aq)]^{2+} + U^{4+}(aq) + 2H_2O \quad (S1)$$

2. Sand equation

$i\tau^{1/2}$ for a diffusion-controlled electron transfer process can be quantified using following Sand equation

$$i\tau^{1/2} = \frac{\pi^{1/2}nFAD^{1/2}C}{2} \quad (S2)$$

3. $UO_2^{2+} + 2e^- + 4\ H^+ \longrightarrow U(IV) + 2H_2O$ (S3)

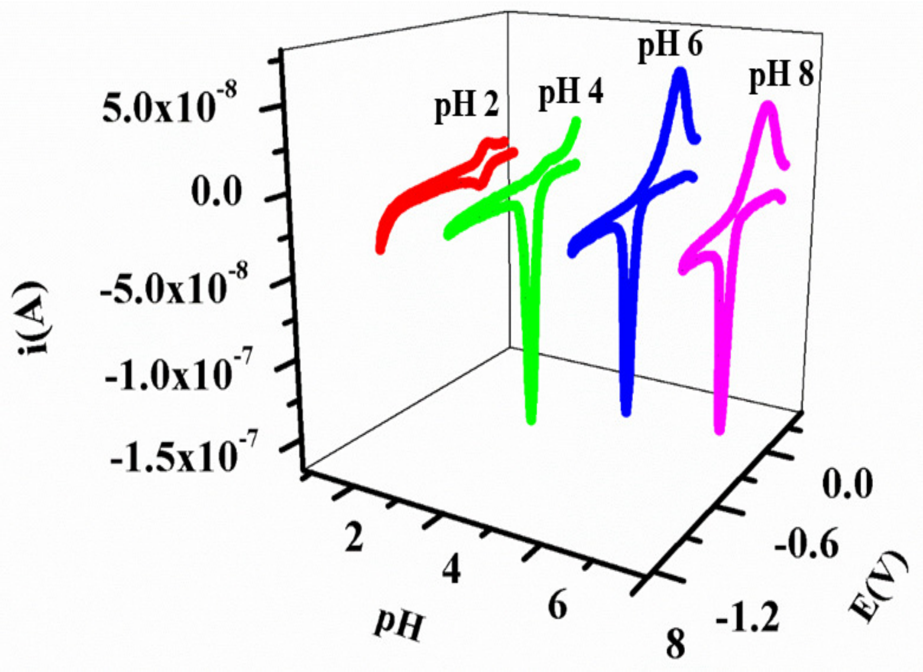


Figure S1. CV plots of U(VI)/U(V) couple with PFA at pH 2, 4, 6 and 8 in 3D.

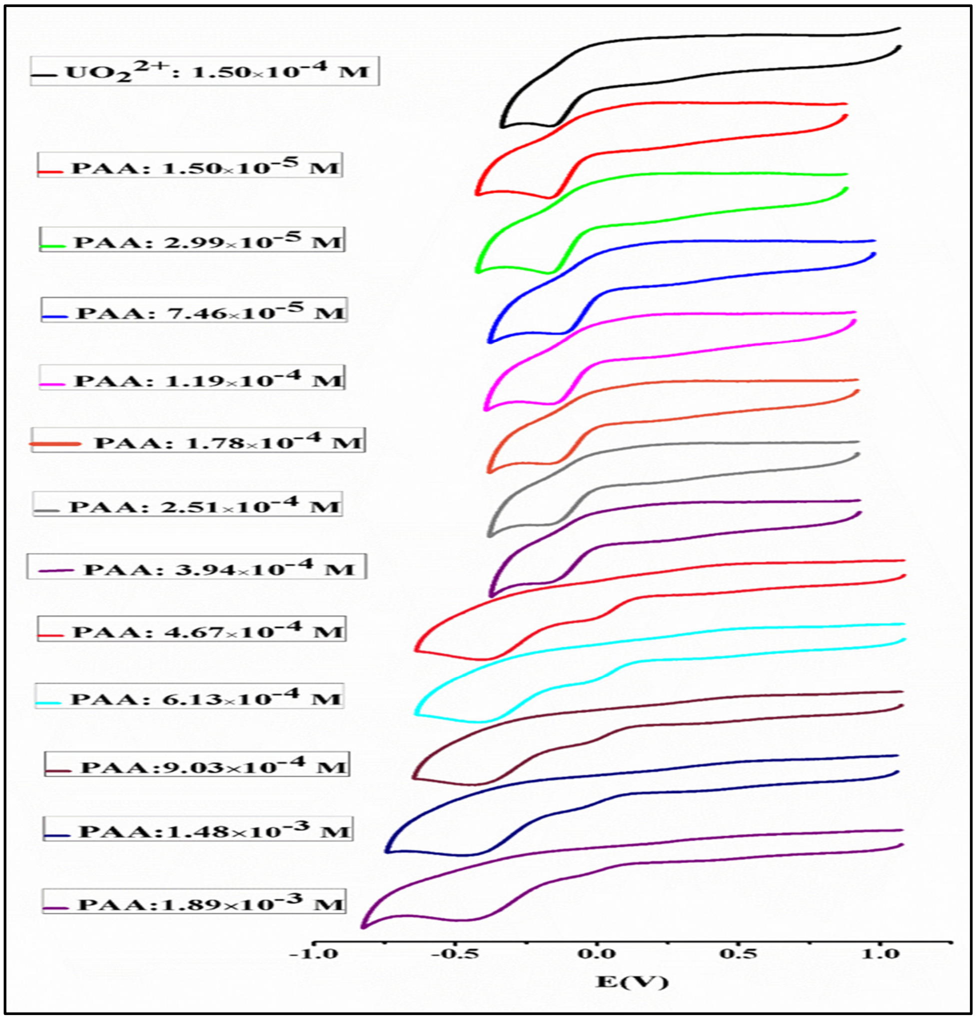
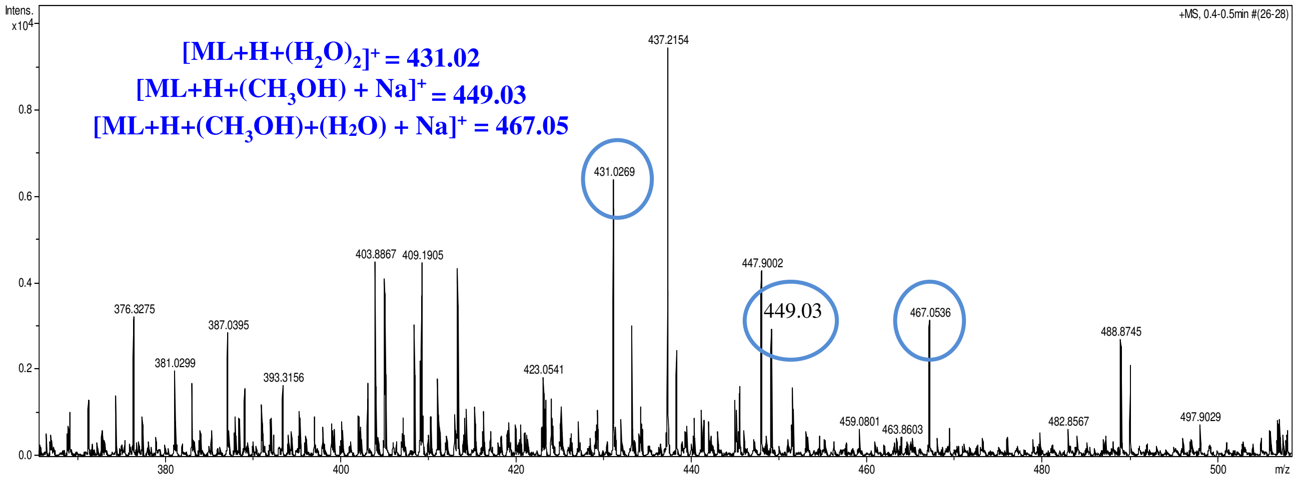
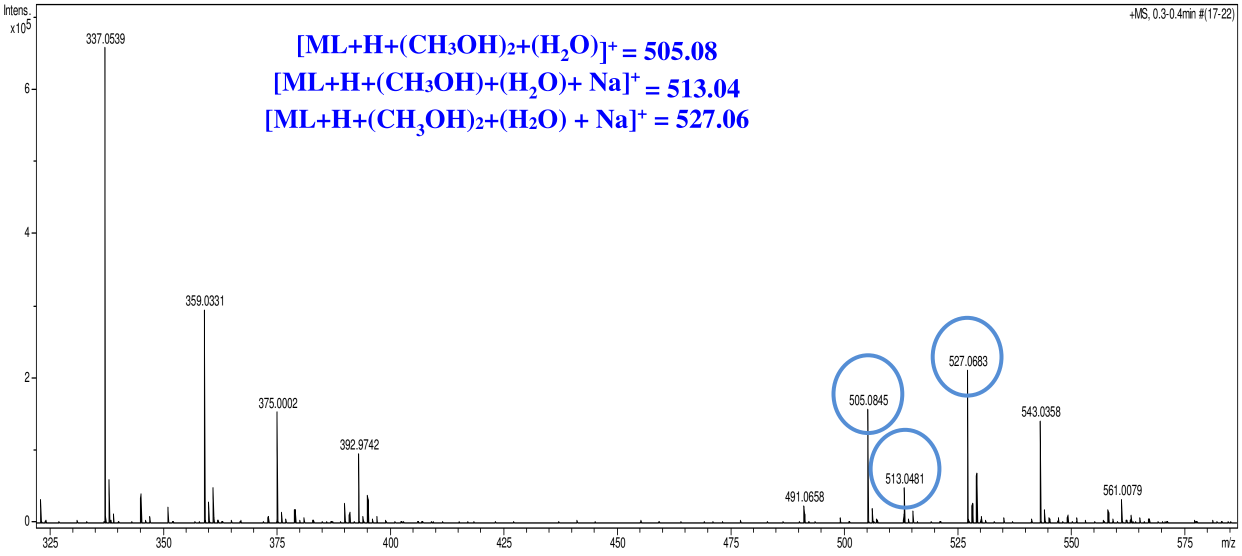


Figure S2: The CV plots of U(VI)/U(V) couple obtained with increasing concentration of PAA chelator from 0.1 to 10 equivalent.



(a)



(b)

Figure S3. ESI-MS spectrum of uranium with (a) PFA and (b) 3-PPA in positive ion mode.

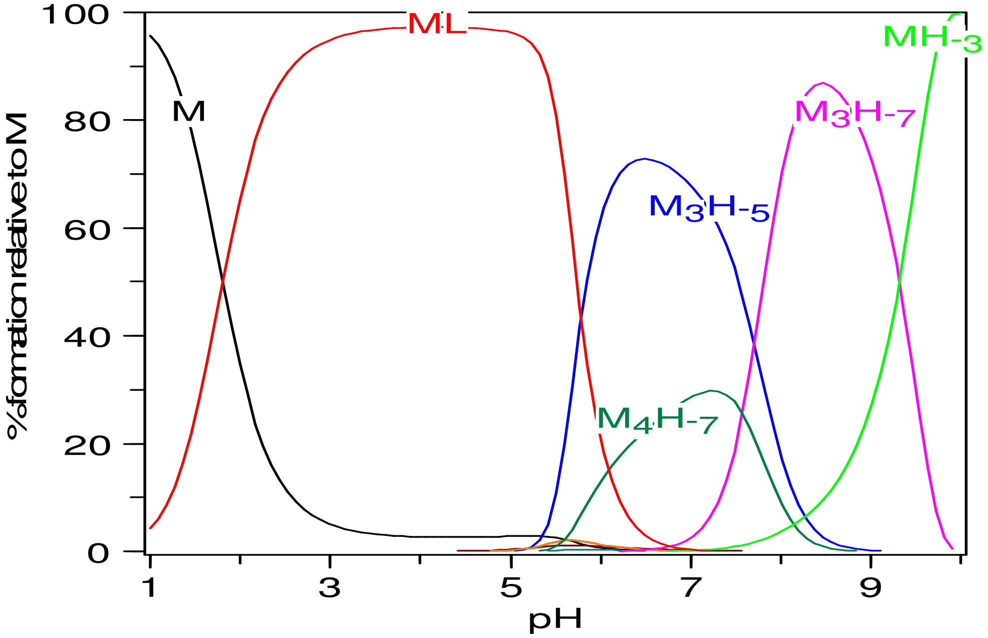


Figure S4. Speciation diagram of uranyl ion [1×10^{-4} M] in presence of PCs [1×10^{-3} M].

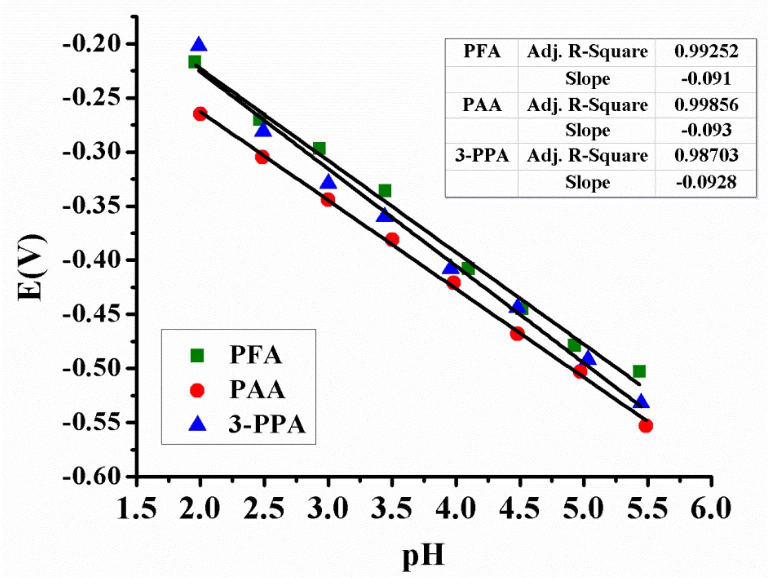
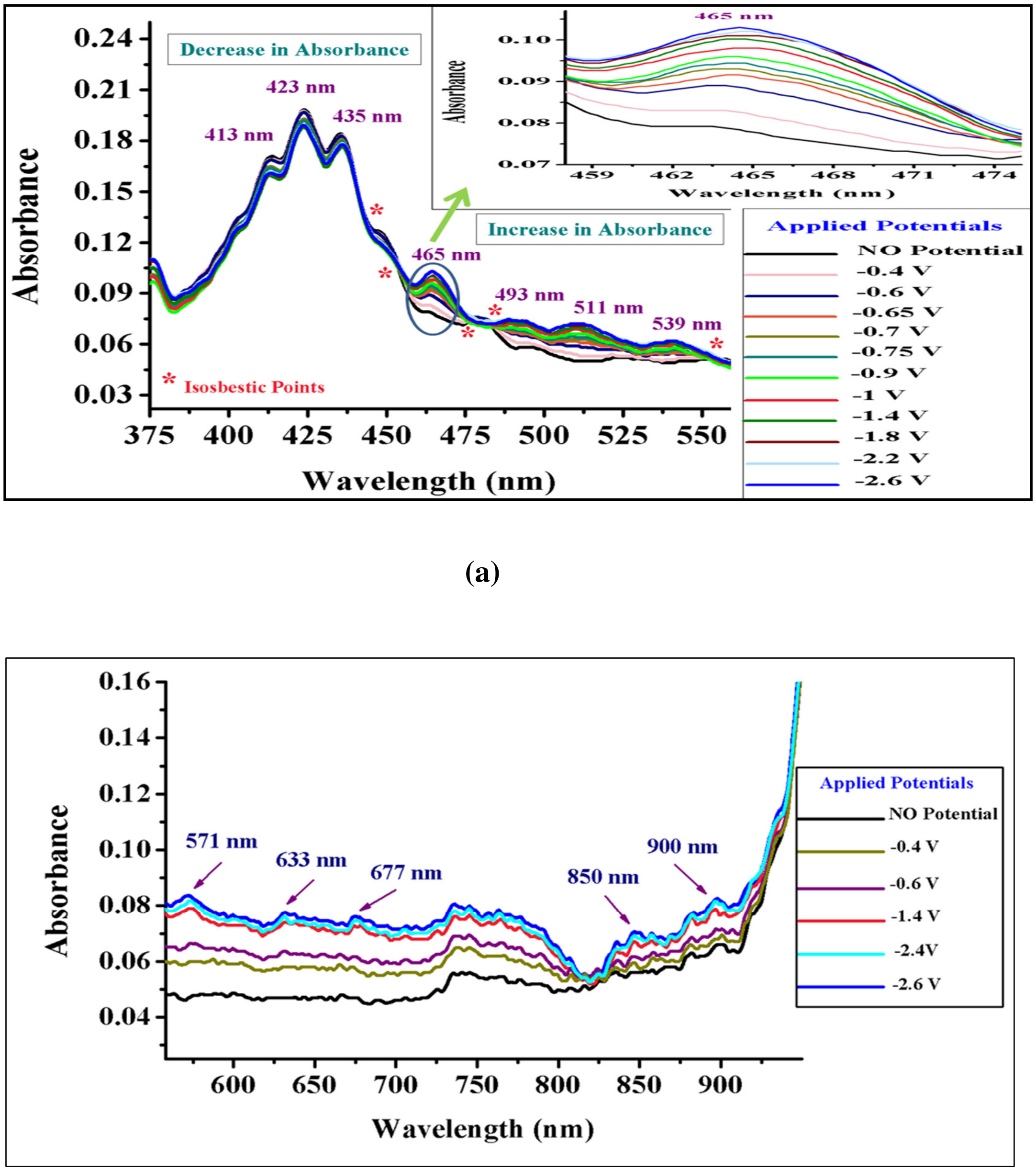


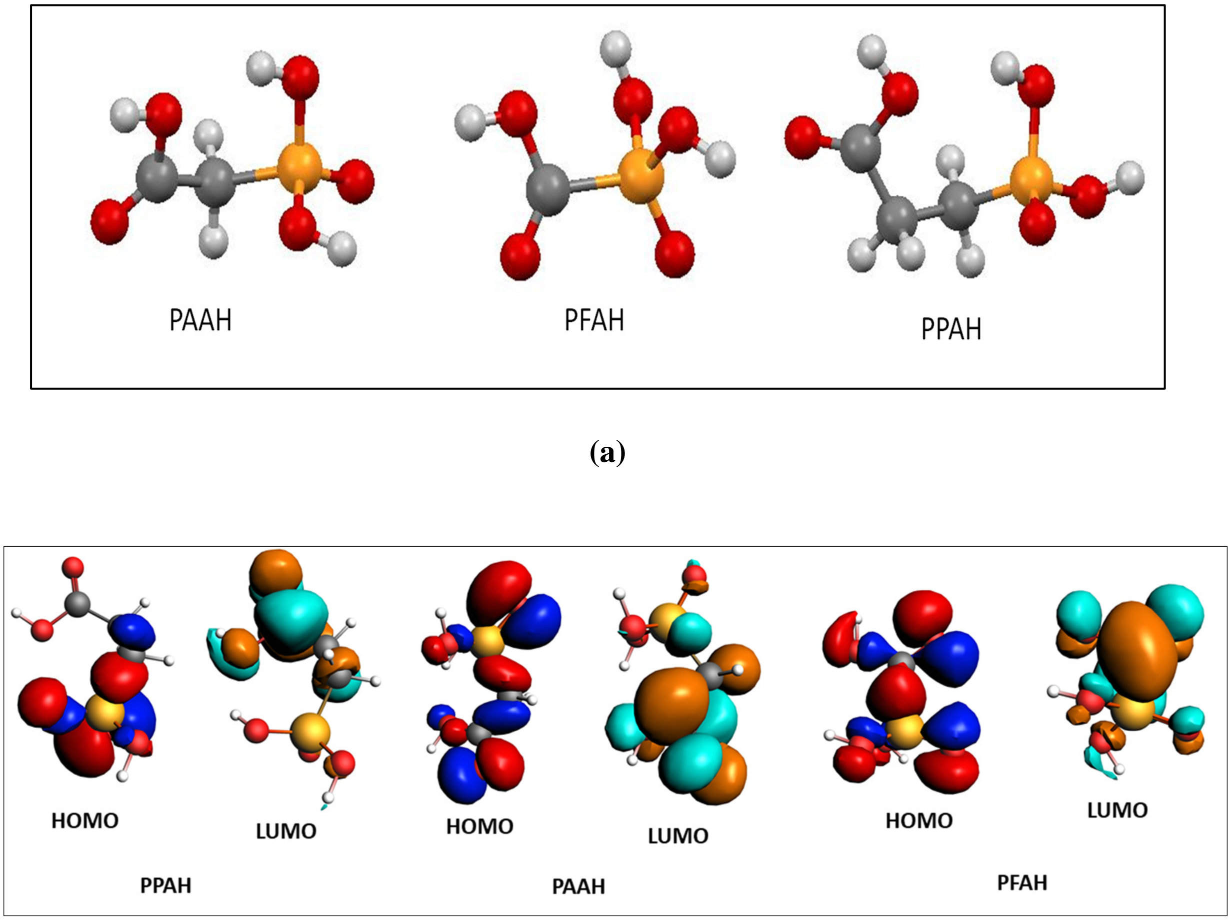
Figure S5: Peak potential (E_p) versus pH plots



(a)

(b)

Figure S6: Spectroelectrochemical evidence for existence of pentavalent uranyl species at pH 8. (a) is the absorption spectra with varying cathodic potentials in the wavelength region 375 nm to 550 nm (b) is the absorption spectra with varying cathodic potentials in the wavelength region 560 nm to 1000 nm.



(a)

(b)

Figure S7. The optimized structures of PC chelators

References

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