SUPPORTING INFORMATION

Reductive activation of neptunyl and plutonyl oxo species with a hydroxypyridinone chelating ligand

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Supporting Info Section

I. Experimental Details

Caution! ^{237}Np and ^{242}Pu are radionuclides that should be manipulated only in a specifically designated facility in accordance with appropriate safety controls. All measurements were taken either in controlled facilities and/or using multiple containment procedures.

Chemicals

The ligand 3,4,3-LI(1,2-HOPO) was prepared and characterized as previously described,[1] and ligand stock solutions were prepared by direct dissolution in either DMSO (ESI-MS) or methanol (solution-phase Raman). For ESI-MS experiments aqueous stock solutions of $(NMe_4)_2NpO_2Cl_4$ and $PuO_2(HClO_4)_2$ were used, and ^{18}O-labeled neptunyl and plutonyl stock solutions were prepared by dissolution of $(NMe_4)_2NpO_2Cl_4$ or $PuO_2(ClO_4)_2$ in $H_2{}^{18}O$ (Sigma Aldrich, 97% ^{18}O), followed by UV irradiation for four days. ESI mass spectra confirmed partial oxygen exchange to yield appreciable $Np^{16}O^{18}O^{[+/2+]}$ and $Pu^{16}O^{18}O^{+/2+}$ along with substantial unexchanged $Np^{16}O_2{}^{[+/2+]}$ and $Pu^{16}O_2{}^{[+/2+]}$, and some fully exchanged $Np^{18}O_2{}^{[+/2+]}$ and $Pu^{18}O_2{}^{[+/2+]}$. Whereas the charge state of the actinyl cations in solution may be $AnO_2{}^{[2+]}$, the only species observed in the ESI mass spectra were monopositive $AnO_2{}^{[+]}$. For solution-phase Raman studies, Np(V) and Np(VI) stock solutions were prepared by reprocessing from previous synthetic experiments and purifying via cation exchange column containing Dowex-50-X8 resin.

ESI-MS Experiments

The general experimental approach has been described previously.[2-4] Anionic complexes of $NpO_2(L\text{-}H)^-$ and $PuO_2(L\text{-}H)^-$ (L=HOPO) complexes were produced by ESI of a solution of ~100 μM $(NMe_4)_2NpO_2Cl_4$ or $PuO_2(ClO_4)_2$ with ~500 μM HOPO ligand in ethanol (<10% water). Experiments were performed using an Agilent 6340 quadrupole ion mass spectrometer (QIT/MS) with MS^n CID capability located inside a radiological containment glovebox. The gas-phase anion coordination complexes were isolated and subjected to collision induced dissociation (CID)

whereby ions are excited and undergo multiple energetic collisions with helium atoms to induce dissociation. As discussed elsewhere, the background H_2O and O_2 pressures in the ion trap are estimated to be on the order of 10^{-6} Torr, while the helium buffer gas pressure in the trap is constant at $\sim 10^{-4}$ Torr.[3] Anion mass spectra for neptunyl and plutonyl complexes were acquired using the following instrumental parameters: solution flow rate, 60 μL min^{-1}; nebulizer gas pressure,15 psi; capillary voltage, 3500 V; end plate voltage offset, −500 V; dry gas flow rate, 2 L/min; dry gas temperature, 325 °C; capillary exit, −187.5 V; skimmer,−41.9 V; octopole 1 and 2 dc, −10.4 and 0 V; octopole RF amplitude, 300.0 Vpp; lens 1 and 2, 10.3 and 77.5 V; trap drive, 104.5. Cation mass spectra were acquired using the following instrumental parameters: solution flow rate, 60 μL min^{-1}; nebulizer gas pressure,15 psi; capillary voltage, -4500 V; end plate voltage offset, −500 V; dry gas flow rate, 2 L/min; dry gas temperature, 325 °C; capillary exit, 147.3 V; skimmer, 40.0 V; octopole 1 and 2 dc, 12.0 and 3.67 V; octopole RF amplitude, 200.0 Vpp; lens 1 and 2, −5.0 and −60.0 V; trap drive, 180.4. The high-purity nitrogen gas for nebulization and drying in the ion transfer capillary was the boil off from a liquid nitrogen Dewar.

Raman Spectral Analysis

Solution-phase Raman spectra were collected on a SnRI high-resolution Sierra 2.0 Raman spectrometer equipped with 785 nm laser energy and a 2048 pixel TE-cooled CCD. Figures and peak fitting analysis for Raman spectra were done in OriginPro 9.1.0 (OriginLab). Np-HOPO samples used for data collection were prepared as follows.

Np(V)-HOPO: 133 μL of 75 mM $Np(V)O_2$ in 1M HCl and 200 μL of 20 mM HOPO were combined dropwise in a 3mL glass vial.

Np(V)-HOPO/HEPES: 133 μL of 75 mM $Np(V)O_2$ in 1M HCl and 200 μL of 20 mM HOPO buffered in 200 μL of 20mM HEPES/NaOH solution were combined dropwise in a 3mL glass vial.

Np(VI)-HOPO: 158 μL of 63 mM $Np(VI)O_2$ in 1M HNO_3 stock and 200 μL of 20 mM HOPO were combined dropwise in a 3mL glass vial.

Computational Simulations

Density functional theory (DFT) calculations with the B3LYP functional[5] were performed with the open source NWChem software suite version 6.8. Stuttgart small-core relativistic effective core-potentials (ECP) describing the 60 core electrons, and accounting for scalar relativistic effects, plus the associated basis set are used to describe the uranium atom.[6] For C, H, O, and N atoms in the modeled complexes the all-electron DFT optimized valence triple-ζ polarized (TZVP) basis sets were used.[7] In all cases, spherical basis sets were employed, and for the numerical integration of the exchange-correlation an extra fine grid was utilized. NWChem's standard convergence criteria were applied because unrestricted open-shell DFT was used for all molecular complexes. No spin−orbit coupling was included in the calculations. Starting structures for the geometry optimizations were constructed from lanthanide (Eu^{3+}) and actinide (Bk^{4+})-3,4,3-LI(1,2-HOPO) crystal (Eu) and computed (Bk) structures available in the literature.[8, 9] Multiple spin-multiplicities and geometrical configurations were explored with different starting orientations for both the neptunyl and plutonyl cations and different locations of the protons on the hydroxypyridinone units. The optimized structures were used as a starting guess for the subsequent water-loss complexes, where different combinations of proton and oxygen elimination were probed. The geometries of the complexes were optimized and all reported energies include the vibrational zero-point energy correction.

II. Additional Figures

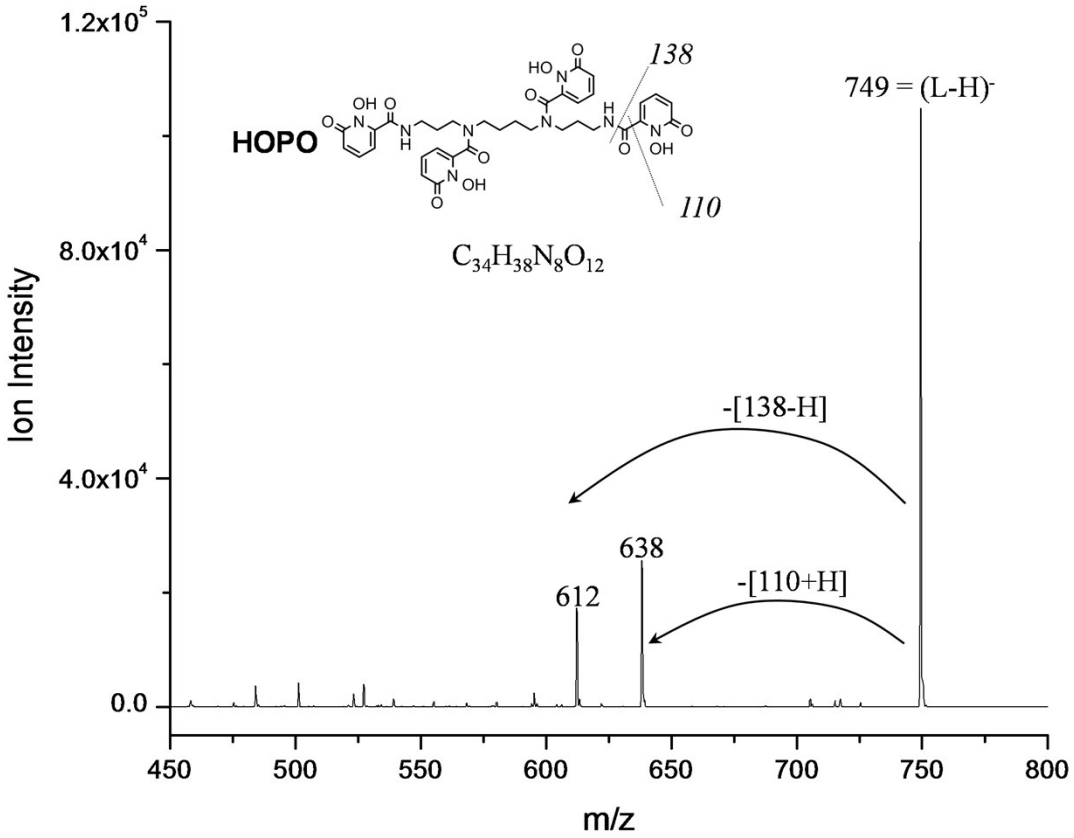

Figure S1 CID mass spectrum of $[HOPO-H]^-$ using a nominal excitation energy of 0.5 V. The dominant pathways correspond to cleavage as indicated in the inset structure, with concomitant transfer of an H atom to the 110 m/z fragment from the 138 m/z fragment.

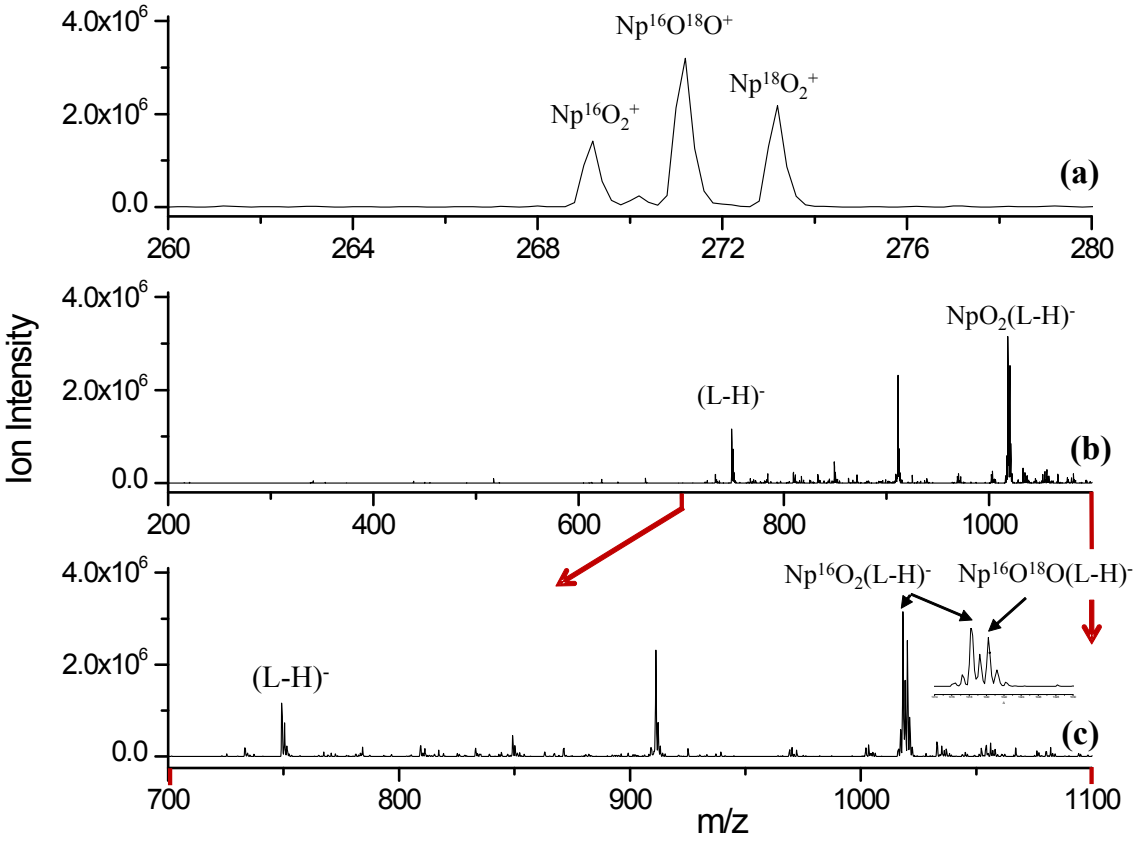

Figure S2 ESI mass spectra of the mixture of HOPO (L) and ^{18}O-labeled neptunyl: (a) positive ion mode; negative ion mode for (b) 200-1100 m/z and (c) 700-1100 m/z. Red arrows in (c) are included to highlight portion of full negative ion mode spectra featuring Np-HOPO peaks of interest.

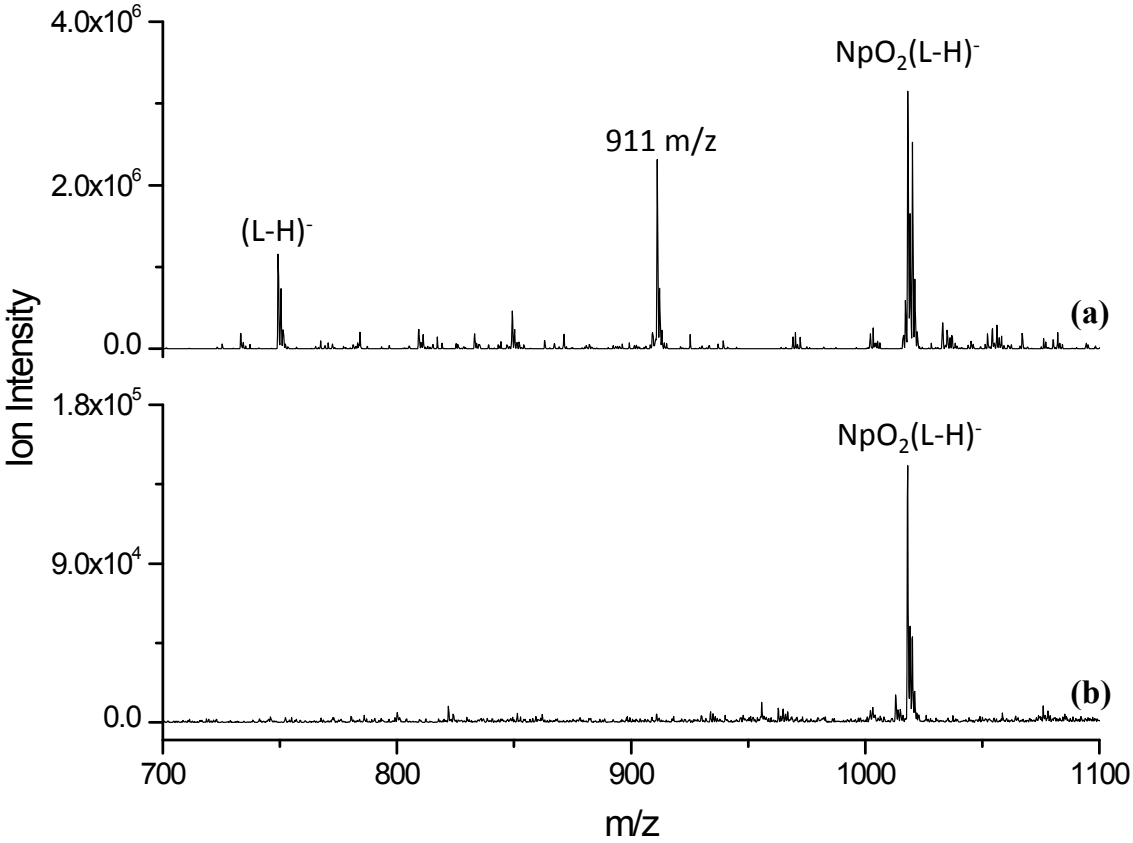

Figure S3 ESI mass spectra for the mixture of HOPO (L) and ^{18}O-labeled neptunyl. (a) is the same as shown in Figure S2; (b) was obtained under nominally the same conditions. The disparity between (a) and (b) illustrates the potential variability in ESI mass spectra. The peak at 911 m/z was not confidently assigned, but it corresponds to $NpO_2(HOPO\text{-}108)^-$ (or $Np(HOPO\text{-}76)^-$).

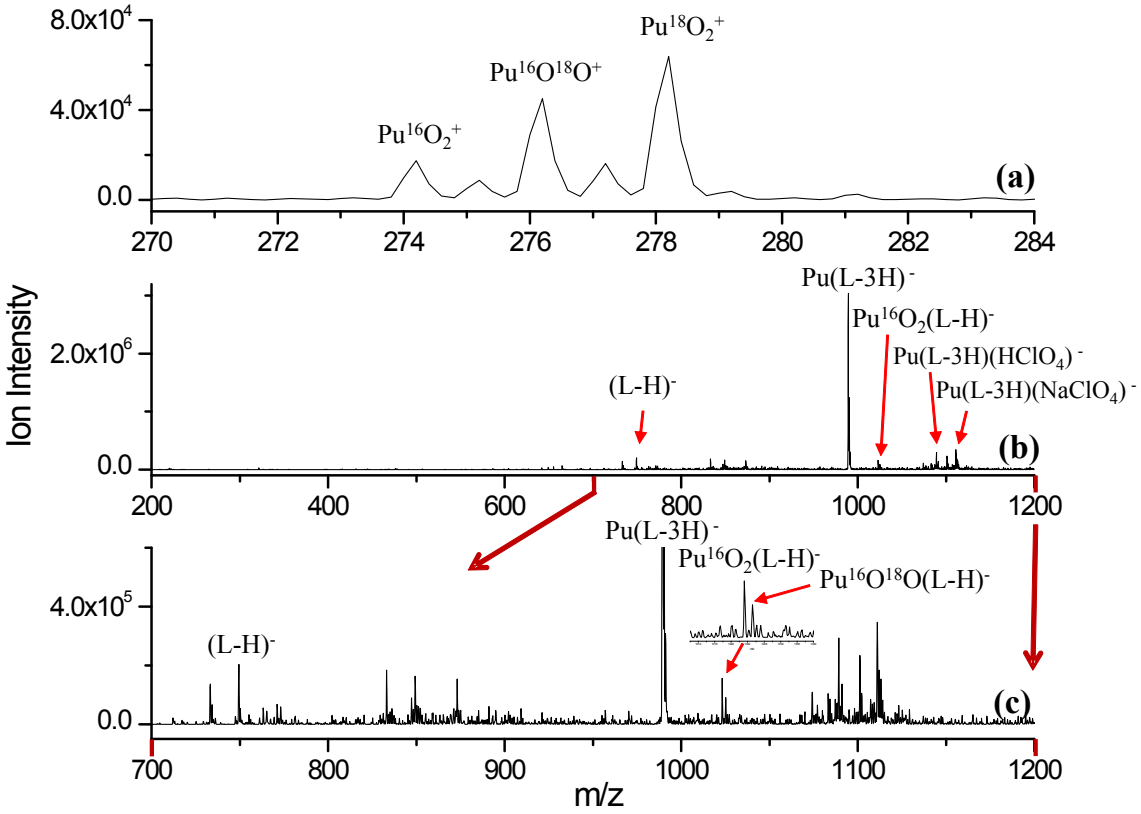

Figure S4 ESI mass spectra of the mixture of HOPO (L) and ^{18}O-labeled plutonyl: (a) positive ion mode; negative ion mode for (b) 200-1100 m/z and (c) 700-1100 m/z. Red arrows in (c) are included to highlight portion of full negative ion mode spectra featuring Pu-HOPO peaks of interest. The intensity scale is expanded for (c) such that the most intense Pu(HOPO-3H)$^-$ peak is off scale. As was observed for neptunyl complexes (Fig. S2), the extent of ^{18}O labeling is apparently greater for PuO_2^+ than for PuO_2(HOPO-H)$^-$, and this disparity suggests more solution exchange prior to, or during, ESI for the anion complexes.

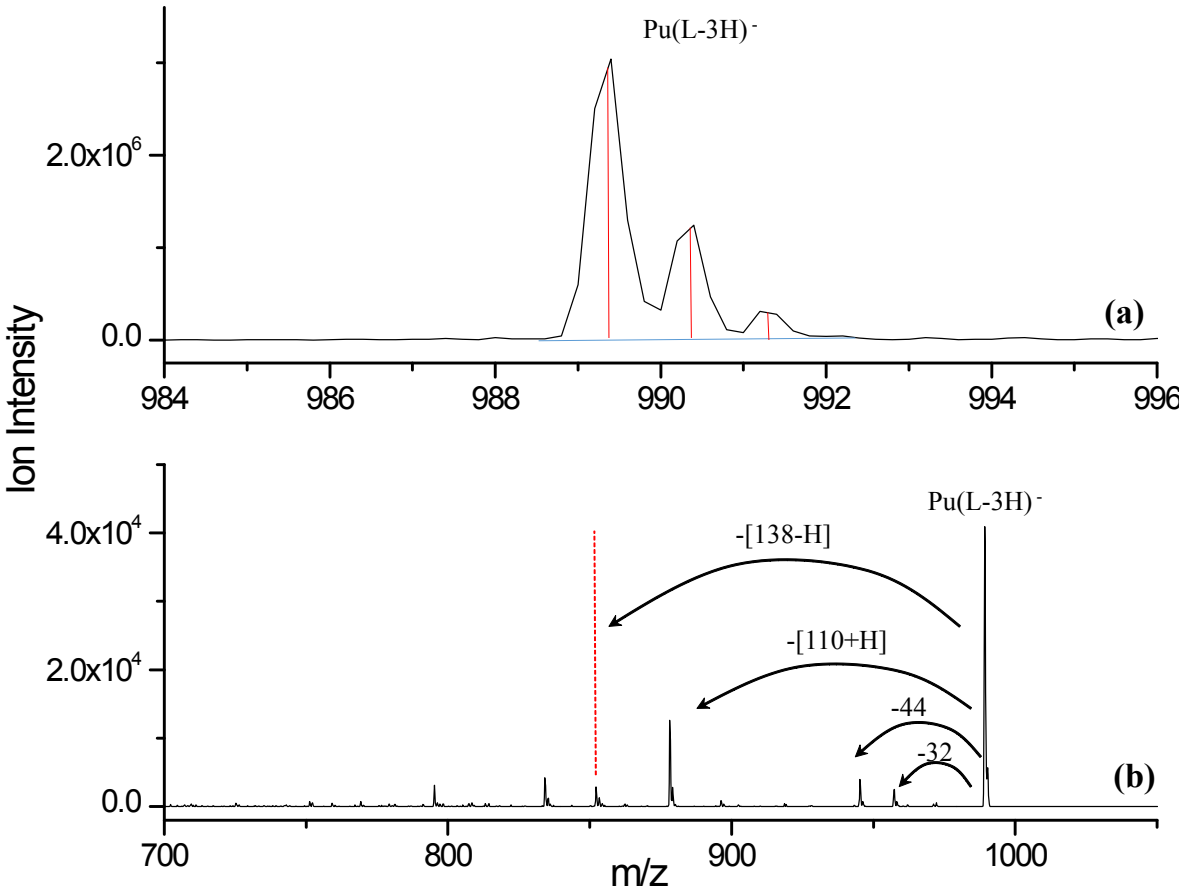

Figure S5 (a) Negative mode ESI mass spectrum from Fig. S4(b) showing experimental (black) and predicted (red) isotopic distribution for $Pu(HOPO\text{-}3H)^-$ (L = HOPO), (b) CID mass spectrum (nominal excitation energy = 0.6 V) of $Pu(HOPO\text{-}3H)^-$ showing a dominant pathway of –[110+H], which is the same as for $(L\text{-}H)^-$ in Figure S1.

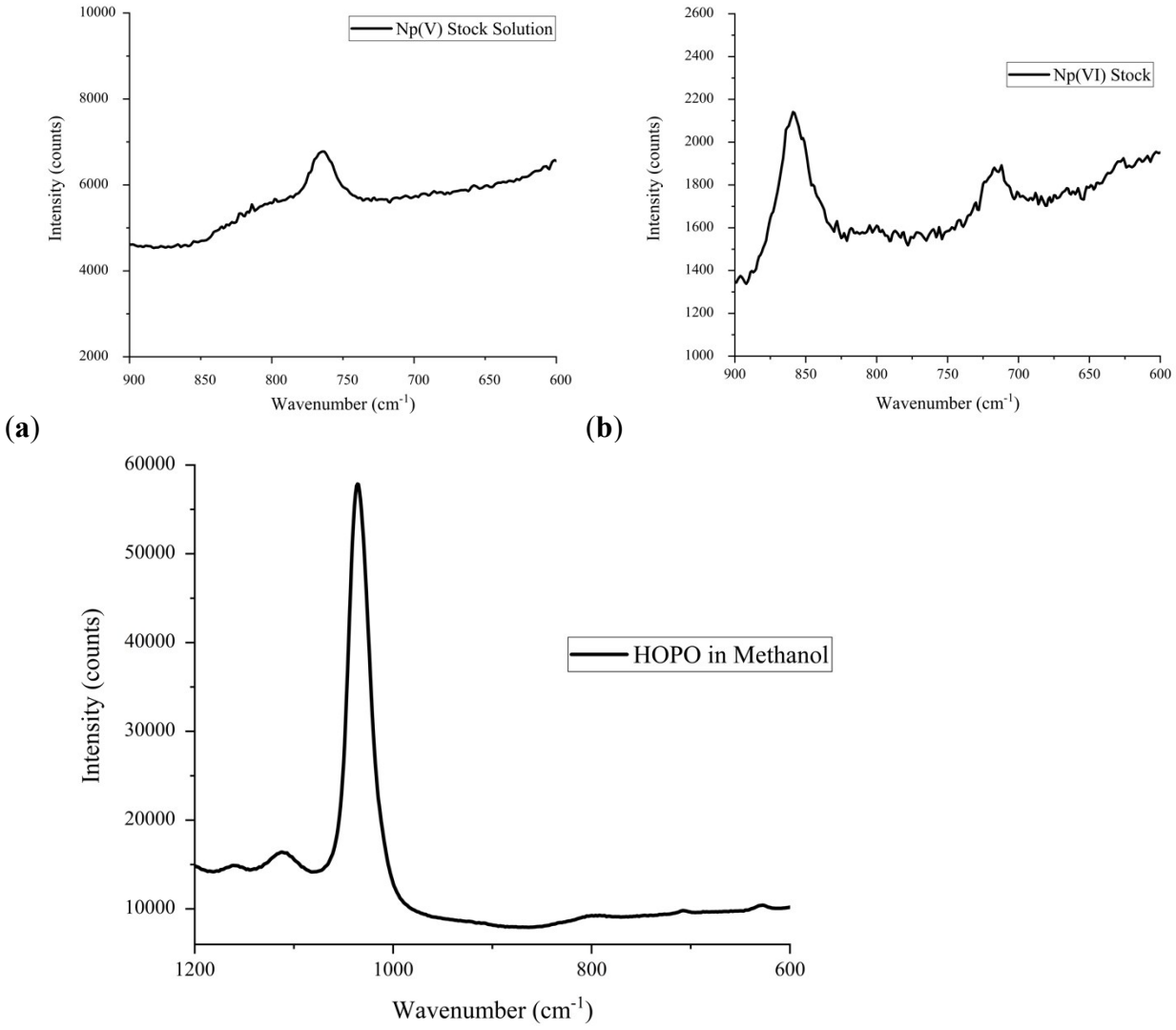

Figure S6 Stock solution Raman of (**a**) $Np(V)O_2^+$ in 1 M HCl (**b**) $Np(VI)O_2^+$ in 1 M HNO_3 (NOTE: Band at 717 cm^{-1} corresponds to $(NO_3)^-$ stretch), (**c**) HOPO ligand in methanol/water solution where the peak at 1035 cm^{-1} is associated with the C-O stretching vibration for methanol.

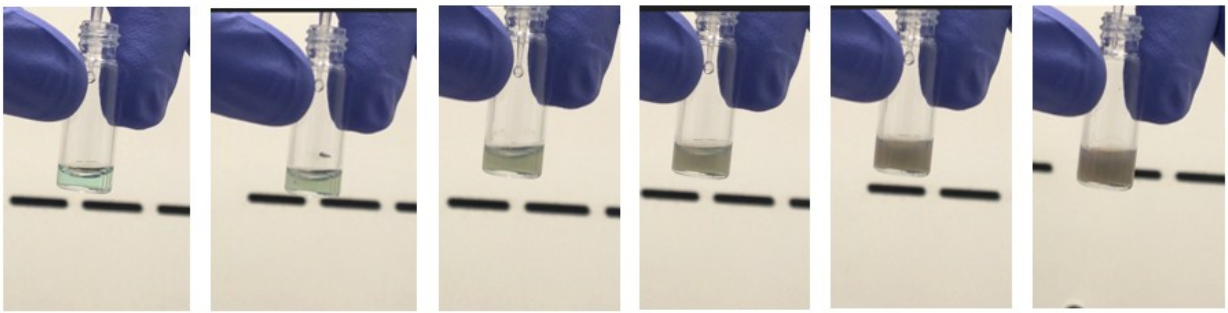

Figure S7 Time lapse photographs (approx. 2 second intervals) of the solution state Np(V)-HOPO colloidal formation in the water/methanol solution.

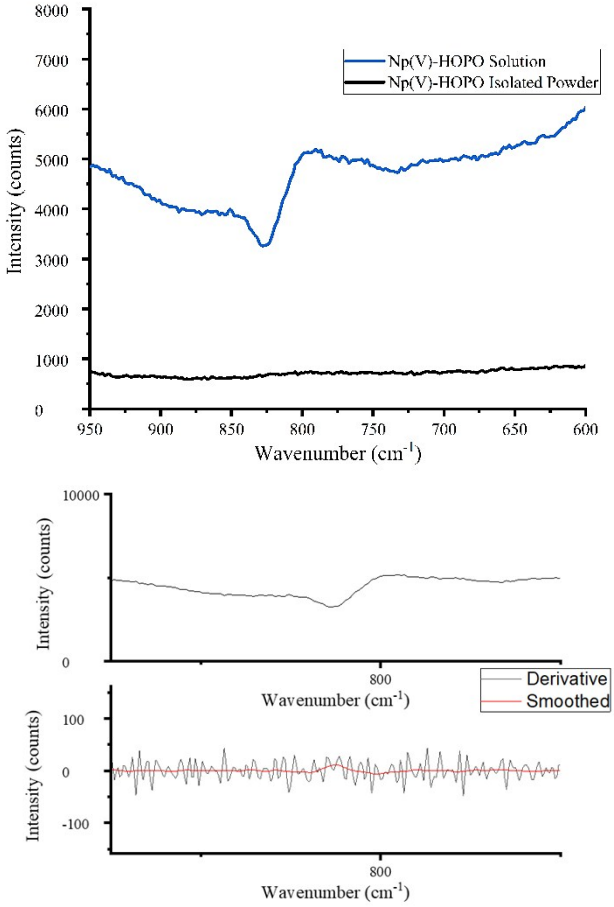

Figure S8 (Left) Raman spectra of Np(V)-HOPO colloidal solution (blue line) and isolated powder (black line). (**Right- Top**) Spectral window between 600-950 wavenumbers for the Np(V)-HOPO colloidal solution (**Right- Bottom**) and the second derivative of the spectrum. Results of the second derivative confirm that there is no peak present in this sample and the variations in the spectra are due to anomalous scattering.

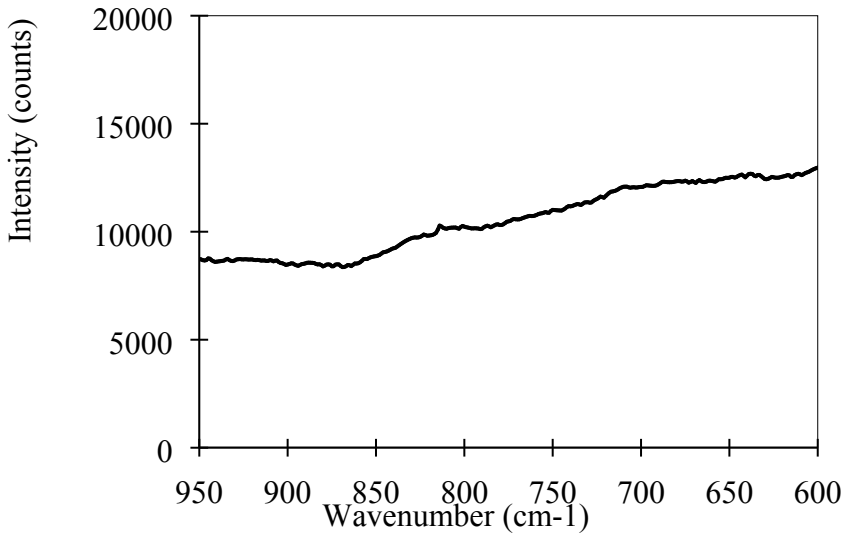

Figure S9 Solution Raman for the spectral window between 600-950 wavenumbers of the Np(V)-HOPO in the HEPES/NaOH buffer.

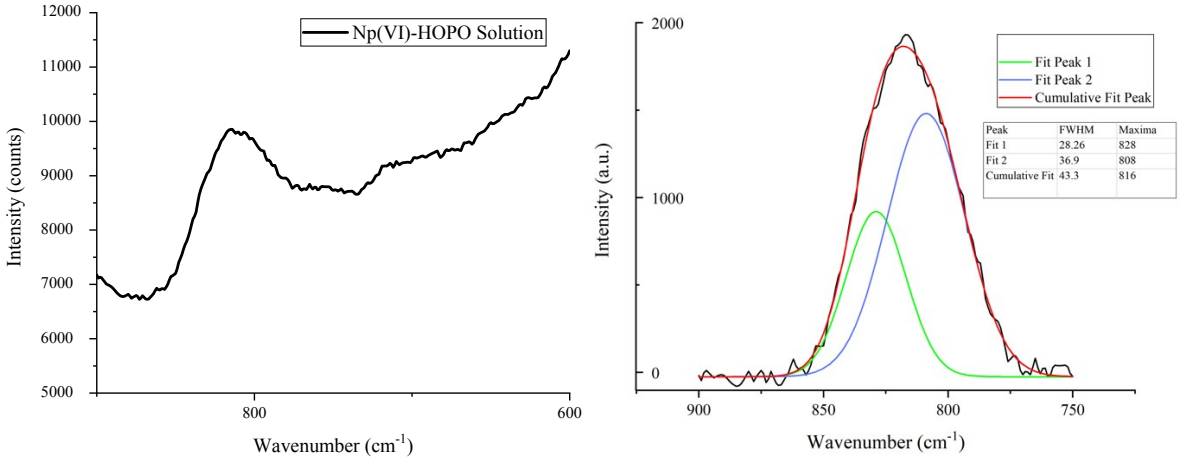

Figure S10 (Left) Raman spectrum of Np(VI)-HOPO solution between 600-950 cm^{-1}. (**Right**) Peak fitting for the $Np(VI)O_2^{2+}$ symmetric stretch (ν_1) associated with the Np(VI) HOPO complex in water/methanol solution.

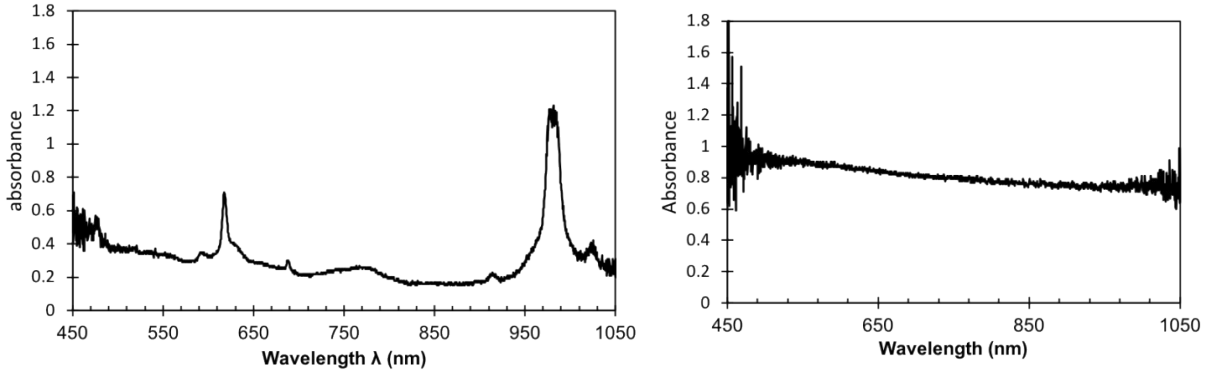

Figure S11 Before and after UV-Vis-NIR spectra of Np(V) solution upon addition of HOPO and subsequent formation of Np-HOPO precipitate. Spectra on left is consistent with Np(V),[10] whereas spectra on right is indicative of formation of solid Np species (confirmed to be Np(IV)-HOPO).

III. DFT Computed Structures and Energies

Table S1 Calculated energies for $[An(OH)_2(HOPO\text{-}3H)]^-$, $[AnO(HOPO\text{-}3H)(H_2O)]^-$, $[An(HOPO\text{-}5H)]^-$ where An=Np, Pu.

Complex	Total energy (Hartree)	Zero-point energy (Hartree)
$[Np(OH)_2(HOPO\text{-}3H)]^-$	-3324.662469	0.715159
$[NpO(HOPO\text{-}3H)(H_2O)]^-$	-3324.650207	0.716382
$[Np(HOPO\text{-}5H)]^-$	-3171.685197	0.663728
$[Pu(OH)_2(HOPO\text{-}3H)]^-$	-3364.114405	0.714536
$[PuO(HOPO\text{-}3H)(H_2O)]^-$	-3364.108405	0.714529
$[Pu(HOPO\text{-}5H)]^-$	-3211.137133	0.663765
H_2O	-76.458867	0.021231

Table S2 Calculated Cartesian coordinates for lowest energy structure of $[Np(OH)_2(HOPO\text{-}3H)]^-$. All units are in Angstroms.

$[Np(OH)_2(HOPO\text{-}3H)]^-$

C	-2.00611001	2.08054652	-3.20934475
C	-1.41939157	2.58370387	-4.35715409
C	-0.60086529	1.74222480	-5.12013049
C	-0.42693103	0.42964662	-4.75527517
C	-1.04976941	-0.14625547	-3.60007201
N	-1.81822063	0.79066239	-2.82153087
H	-0.11497924	2.12572587	-6.01104238
H	-1.63720725	3.60007470	-4.65040635
H	0.18738157	-0.24570070	-5.33652202
O	-2.37235032	0.33444562	-1.68696284

O	-0.96986248	-1.32500993	-3.23975234
C	-2.98727755	2.94991852	-2.46530113
O	-3.94773992	3.41408309	-3.08846454
N	-2.79509140	3.23438673	-1.14498680
C	-1.56150424	2.94937058	-0.40152431
H	-1.84649789	2.71668761	0.62863729
H	-1.11670605	2.03997177	-0.79435678
C	4.39782358	-1.21801726	-1.67736524
C	4.84933790	-1.80402327	-2.84486034
C	4.18076490	-2.90910481	-3.37742251
C	3.06679356	-3.42112248	-2.74905422
C	2.58576892	-2.84142072	-1.55707381
N	3.29645561	-1.74898743	-1.06323312
H	4.53512684	-3.35923735	-4.29715158
H	5.71563918	-1.36244380	-3.31319882
H	2.51202678	-4.26158306	-3.14193248
O	2.81504309	-1.23058719	0.07780744
O	1.57211351	-3.22269672	-0.89089110
C	5.13901940	-0.00063384	-1.15365337
O	6.10235089	0.42452772	-1.80120736
N	4.70370212	0.55195898	-0.00295558
H	3.88406036	0.12080466	0.42682692
C	5.33339346	1.73705560	0.55966389
H	5.28742406	1.65597136	1.64734374
H	6.37993738	1.71818665	0.25721013
C	1.23015500	1.91191811	3.32382740
C	0.46341369	2.60880101	4.23823775
C	-0.71739227	2.03551558	4.71603645
C	-1.11154940	0.78920403	4.27355096
C	-0.33044952	0.07022105	3.34794041
N	0.85791484	0.66788513	2.93018592
H	-1.32920074	2.57352371	5.43014079
H	0.80018065	3.58180651	4.56569519
H	-2.02671437	0.32115451	4.60923372
O	1.64106281	-0.01612404	2.09318991
O	-0.61180083	-1.07547774	2.86003792
C	2.53296580	2.49368547	2.81354370
O	3.45766917	2.62447570	3.61772400
N	2.58053968	2.93738396	1.52590679
C	3.74810988	3.72863139	1.10911558
H	3.38097307	4.66959774	0.68536431
H	4.30035570	3.96699606	2.01698370
C	-4.39636329	-1.49342163	-0.16424363
C	-4.72173973	-2.11452079	-1.34043241
C	-3.89313660	-3.14074061	-1.81825140
C	-2.77045463	-3.51532817	-1.12530606

C	-2.42525836	-2.89359281	0.09646145
N	-3.31240387	-1.92324036	0.53454094
H	-4.11746609	-3.61169550	-2.76715025
H	-5.57445436	-1.76233642	-1.90168510
H	-2.08054049	-4.25756368	-1.49923631
O	-3.12823100	-1.34660983	1.77698711
O	-1.39922090	-3.14672031	0.80056223
C	-5.15514643	-0.31312049	0.40931925
O	-6.16137206	-0.48974170	1.09432087
N	-4.61507262	0.87829291	0.07764975
H	-3.79604682	0.87998734	-0.54357616
C	-5.10027797	2.11124896	0.69379737
H	-4.48263656	2.34558616	1.57175493
H	-6.10024514	1.88948964	1.06621796
C	4.68848625	3.06378714	0.09516392
H	4.18245559	2.89449381	-0.85838741
H	5.47882086	3.79341521	-0.11090563
C	1.45043754	2.84959840	0.58344148
H	1.87681566	2.79024790	-0.42070343
H	0.93085886	1.90445028	0.73164973
C	0.50394400	4.05655442	0.67900654
H	1.09790919	4.97552523	0.63739337
H	0.01906157	4.04711319	1.66071278
C	-0.57178661	4.12632470	-0.41542410
H	-0.10542973	4.18808261	-1.40458730
H	-1.12771435	5.05983923	-0.27891995
C	-3.82785407	4.05063465	-0.49207205
H	-4.02710577	4.93330750	-1.10515390
H	-3.41368398	4.38940949	0.46045534
C	-5.15591286	3.32003736	-0.24557410
H	-5.59223672	3.03042789	-1.20261873
H	-5.83594776	4.05304300	0.20354974
Np	0.69550784	-1.95018183	0.95814637
O	1.50537687	-3.42900829	2.27349445
H	-2.16254302	-1.39065876	2.00237599
O	-0.39852671	-0.54878543	-0.09876340
H	-1.10308869	-0.34111420	-0.77659006
H	2.17976831	-4.09101528	2.08105967

Table S3 Calculated Cartesian coordinates for lowest energy structure of [NpO(HOPO-3H)(H_2O)]$^-$. All units are in Angstroms.

[NpO(HOPO-3H)(H_2O)]$^-$

C	-2.10840496	2.41165040	-3.14289552
C	-1.63897097	3.02424576	-4.28898431
C	-0.75673899	2.32626031	-5.11950887

C	-0.39819968	1.03846573	-4.80625018
C	-0.88481319	0.36156869	-3.64840178
N	-1.74744635	1.13785758	-2.81487397
H	-0.36682538	2.79728541	-6.01484461
H	-1.99381710	4.01614961	-4.52695781
H	0.27237082	0.46295311	-5.43051215
O	-2.24038615	0.57636985	-1.69534181
O	-0.60066423	-0.81710810	-3.34951799
C	-3.14982875	3.14029835	-2.33094253
O	-4.16365258	3.53626792	-2.91383342
N	-2.94275825	3.39168886	-1.00766562
C	-1.66701472	3.16932566	-0.31464254
H	-1.90070629	2.99385707	0.73896819
H	-1.23753477	2.24227565	-0.68477785
C	4.50644965	-1.43837146	-1.64120092
C	5.02498931	-2.08991971	-2.74455975
C	4.41116341	-3.25106189	-3.22141431
C	3.28256471	-3.74789984	-2.60823407
C	2.72150604	-3.10083319	-1.48333956
N	3.39664028	-1.95852617	-1.03239728
H	4.82188095	-3.75903691	-4.08625003
H	5.89977397	-1.65748928	-3.20548359
H	2.77509180	-4.63530440	-2.96063046
O	2.85903096	-1.37212201	0.04686939
O	1.67986313	-3.45586663	-0.85775132
C	5.19211628	-0.16414883	-1.17812826
O	6.17723092	0.23864738	-1.80775628
N	4.68341234	0.46422183	-0.09809534
H	3.86199551	0.03207301	0.32818413
C	5.27676660	1.68115737	0.43344618
H	5.19393285	1.64415691	1.52131049
H	6.33383772	1.66234238	0.16979693
C	1.14518807	2.03911470	3.10125251
C	0.39441122	2.74386671	4.02401283
C	-0.81655765	2.20989955	4.46884083
C	-1.25630800	0.99230657	3.98773147
C	-0.48834010	0.26157427	3.06113702
N	0.72938311	0.82077233	2.67022409
H	-1.41420650	2.75235707	5.19156143
H	0.76839032	3.69153098	4.38412071
H	-2.19142094	0.55204446	4.30611727
O	1.48353651	0.13011285	1.81724916
O	-0.79342008	-0.86693531	2.54844540
C	2.47232459	2.58111938	2.60891320
O	3.40184433	2.66190399	3.41231044
N	2.53523833	3.04101635	1.32710427

C	3.74960511	3.74512079	0.88933500
H	3.43861407	4.69272908	0.43657435
H	4.31828282	3.97879689	1.78872465
C	-4.33345218	-1.54244740	-0.25948378
C	-4.57518156	-2.12178754	-1.47544601
C	-3.72556981	-3.15285856	-1.91382264
C	-2.66445250	-3.56415775	-1.15025400
C	-2.38665811	-2.97415508	0.11246925
N	-3.30354981	-1.99828703	0.50603317
H	-3.89323060	-3.60546789	-2.88372459
H	-5.38411572	-1.75011426	-2.08665753
H	-1.97260807	-4.32515253	-1.48274898
O	-3.22557527	-1.47719719	1.78341240
O	-1.41447769	-3.24409878	0.86403296
C	-5.14455898	-0.39942760	0.31907721
O	-6.18625881	-0.62521697	0.92972848
N	-4.60702487	0.82255744	0.09576398
H	-3.77299680	0.88591236	-0.49344169
C	-5.12032334	1.99868183	0.79672416
H	-4.47249550	2.21533109	1.65692514
H	-6.08867015	1.70258121	1.19843300
C	4.63857754	2.98628856	-0.10533685
H	4.08936589	2.75887500	-1.02229588
H	5.43404627	3.68012398	-0.39666136
C	1.38918252	3.02796422	0.40474555
H	1.79133601	2.98290411	-0.61003513
H	0.84283929	2.09699976	0.54078513
C	0.48717001	4.26416093	0.55845141
H	1.10020451	5.16469852	0.44927700
H	0.09002103	4.28296386	1.57814142
C	-0.68147595	4.34224195	-0.43613518
H	-0.30619830	4.38826884	-1.46382938
H	-1.21779742	5.28050535	-0.25934956
C	-4.02217199	4.09498577	-0.29852767
H	-4.29945106	4.98674014	-0.86653598
H	-3.61351530	4.42130032	0.66046590
C	-5.28684848	3.25529886	-0.06491137
H	-5.73022170	2.99250805	-1.02602537
H	-6.00242885	3.91057311	0.44484965
Np	0.83643913	-2.16680226	1.10141545
O	1.46675920	-3.28259346	2.43466869
O	-0.28817847	-0.91598913	-0.73964559
H	-0.17527318	-1.16649666	-1.68982045
H	-1.05958522	-0.29497703	-0.86861952
H	-2.25879629	-1.34924731	2.02168205

Table S4 Calculated Cartesian coordinates for lowest energy structure of $[Np(HOPO-5H)]^-$. All units are in Angstroms.

$[Np(HOPO-5H)]^-$

C	-1.88428689	2.59150324	-2.00652576
C	-1.59312554	3.43090686	-3.06910047
C	-0.49457161	3.15095486	-3.88539865
C	0.28600606	2.03824545	-3.64749547
C	-0.00387037	1.15568581	-2.58054141
N	-1.11962541	1.48794720	-1.78926588
H	-0.25987528	3.80792087	-4.71499160
H	-2.24256533	4.27486026	-3.24835994
H	1.13552618	1.78552449	-4.26747295
O	-1.41531915	0.62775169	-0.81317572
O	0.63405775	0.11235080	-2.27444694
C	-3.11495542	2.87231929	-1.17094990
O	-4.17887083	3.05795160	-1.76844610
N	-3.01117898	2.99130648	0.18152452
C	-1.72384053	3.00006979	0.89534888
H	-1.94323302	2.84202707	1.95254574
H	-1.16472824	2.12580596	0.57172828
C	4.60911356	-2.25879782	-0.42252832
C	5.42947838	-3.11418964	0.29640309
C	4.86235167	-4.00584574	1.20664807
C	3.49290874	-4.04631657	1.37684929
C	2.63982643	-3.19647887	0.64139036
N	3.25748641	-2.31868162	-0.26374868
H	5.49898461	-4.66761211	1.78211180
H	6.49431254	-3.06461053	0.12482235
H	3.01775295	-4.72618499	2.07095418
O	2.45437655	-1.55567418	-1.00355906
O	1.37403329	-3.16035001	0.71867859
C	5.23621289	-1.33327505	-1.42010542
O	6.08722560	-1.77096746	-2.20877726
N	4.97521175	0.01697216	-1.39703129
C	4.22782699	0.81204688	-0.55971252
H	3.57393211	0.32784313	0.14730903
C	1.77169090	1.65153154	2.94468156
C	1.44451501	1.97893282	4.24672804
C	0.36158332	1.33614820	4.85654796
C	-0.36498536	0.38611290	4.16946457
C	-0.03284345	0.02503674	2.83982895
N	1.07865403	0.68383488	2.28900236
H	0.09165710	1.58741216	5.87584111
H	2.03874906	2.72026777	4.76079421
H	-1.20590547	-0.12851687	4.61456665

O	1.44899657	0.29969529	1.06206718
O	-0.62743753	-0.81535932	2.11561152
C	2.95596980	2.27569067	2.24708902
O	4.06572384	2.15072187	2.76679983
N	2.73868022	2.97339238	1.09103014
C	3.89761570	3.23206402	0.22887060
H	3.81116365	4.24742588	-0.17004109
H	4.78464564	3.18314306	0.85697046
C	-4.38842453	-2.00107732	-0.82739528
C	-5.14717974	-2.59195247	-1.82202592
C	-4.52387972	-3.37299971	-2.79781820
C	-3.15326714	-3.52790922	-2.79786617
C	-2.35360602	-2.91810876	-1.80528450
N	-3.04140602	-2.22904237	-0.79757932
H	-5.11866337	-3.83781946	-3.57564713
H	-6.20910141	-2.39884152	-1.81614019
H	-2.63568126	-4.09595554	-3.55894750
O	-2.28359488	-1.78596587	0.21347453
O	-1.08660764	-2.93930451	-1.74187566
C	-5.07836245	-1.04367863	0.12709537
O	-6.31372218	-1.03141871	0.17697973
N	-4.29078566	-0.18962854	0.81235781
H	-3.28909436	-0.38085162	0.77614228
C	-4.85263262	0.82592426	1.69107838
H	-4.11453970	1.02662021	2.47228526
H	-5.73285511	0.39147039	2.16926659
C	4.02151097	2.23885223	-0.94953142
H	3.12693022	2.32802529	-1.58649955
H	4.86162030	2.58210603	-1.56771943
C	1.40048633	3.21571782	0.51900155
H	1.56378648	3.64287535	-0.47193240
H	0.91156932	2.25658170	0.36030859
C	0.51252200	4.18117824	1.32188745
H	0.98019436	5.17106984	1.33976074
H	0.44653785	3.85140204	2.36164430
C	-0.90508578	4.29407819	0.73004782
H	-0.83613204	4.54299821	-0.33330326
H	-1.43265820	5.12553717	1.20930461
C	-4.25374959	3.27494242	0.91928693
H	-4.74403717	4.13624332	0.45603718
H	-3.95605401	3.56668390	1.92887650
C	-5.28253893	2.13385636	0.99083268
H	-5.64302989	1.90209877	-0.01082115
H	-6.13909168	2.54381277	1.53880236
Np	0.08786559	-1.30724365	-0.27090688
H	5.50800679	0.48396865	-2.12255858

Table S5 Calculated Cartesian coordinates for lowest energy structure of $[Pu(OH)_2(HOPO\text{-}3H)]^-$. All units are in Angstroms.

$[Pu(OH)_2(HOPO\text{-}3H)]^-$

C	-1.99645108	1.97065267	-3.20996170
C	-1.40561788	2.42787513	-4.37469930
C	-0.59169967	1.55447274	-5.10585447
C	-0.42035261	0.25659134	-4.68999249
C	-1.03953883	-0.26936812	-3.51029675
N	-1.81813672	0.69376631	-2.77758343
H	-0.10499674	1.90177507	-6.01098762
H	-1.61532341	3.43489987	-4.70396337
H	0.19465866	-0.44149221	-5.24305363
O	-2.37915324	0.27791242	-1.63159129
O	-0.94868610	-1.42983199	-3.09328771
C	-2.97078895	2.87318578	-2.49615742
O	-3.93131369	3.31729571	-3.13406177
N	-2.77126062	3.20907021	-1.18942484
C	-1.54498664	2.93125698	-0.43021648
H	-1.83958490	2.72499909	0.60267877
H	-1.10238106	2.00988459	-0.79492535
C	4.39226730	-1.12320510	-1.72119608
C	4.83102140	-1.67355959	-2.91159975
C	4.13751374	-2.73997702	-3.48720948
C	3.00796572	-3.24630535	-2.88067037
C	2.54151635	-2.70212844	-1.66768204
N	3.28127083	-1.65399018	-1.12503072
H	4.48220040	-3.16280492	-4.42352674
H	5.70645331	-1.23196669	-3.36273913
H	2.42961928	-4.05349515	-3.30776858
O	2.82040770	-1.17452948	0.03942672
O	1.51253174	-3.08069630	-1.02093060
C	5.15120922	0.06570074	-1.15970956
O	6.11900168	0.49859046	-1.79599957
N	4.72119525	0.59218644	0.00491702
H	3.90103559	0.15437004	0.42692751
C	5.35410302	1.76409480	0.59062771
H	5.30327553	1.66453202	1.67653845
H	6.40162416	1.74713331	0.29118530
C	1.20341556	1.88872525	3.30296587
C	0.40059703	2.58816776	4.18414757
C	-0.78838264	2.00831183	4.63154264
C	-1.15743600	0.75464814	4.18678065
C	-0.34193014	0.03864027	3.29054210
N	0.85839647	0.63587194	2.91355185

H	-1.42768934	2.54706701	5.32056268
H	0.71587510	3.56934814	4.50886972
H	-2.08019442	0.28250815	4.49500814
O	1.67802025	-0.05580792	2.12261017
O	-0.60352403	-1.11117759	2.79497166
C	2.51299034	2.47960521	2.82253108
O	3.41968753	2.61573398	3.64598590
N	2.58240555	2.92750935	1.53691758
C	3.74774072	3.73732413	1.15071609
H	3.37718181	4.67955151	0.73263696
H	4.28074778	3.97009552	2.07142723
C	-4.43423486	-1.47366931	-0.12439546
C	-4.80220129	-2.11716395	-1.27612090
C	-3.98784125	-3.14744703	-1.76866773
C	-2.83255643	-3.49857538	-1.11787916
C	-2.44523574	-2.85325719	0.07785812
N	-3.32503534	-1.89019759	0.54191518
H	-4.24786701	-3.63813101	-2.69840076
H	-5.67787370	-1.77737866	-1.80909971
H	-2.14902044	-4.23738147	-1.50949007
O	-3.10311028	-1.30020755	1.77076941
O	-1.38527690	-3.08240837	0.74183332
C	-5.16951533	-0.27592211	0.44478801
O	-6.17743965	-0.42786016	1.13352697
N	-4.60845884	0.90049977	0.09669083
H	-3.78761441	0.87640597	-0.52282814
C	-5.07213283	2.15336885	0.68824614
H	-4.43978283	2.40336748	1.55120218
H	-6.06937219	1.95184744	1.07894763
C	4.71543471	3.09956854	0.14497571
H	4.23454164	2.95260091	-0.82520851
H	5.50805882	3.83671590	-0.02228988
C	1.47186602	2.83336772	0.57090651
H	1.92005379	2.77425024	-0.42378432
H	0.94943206	1.88749049	0.70697358
C	0.52134946	4.03954201	0.64400102
H	1.11346814	4.95962250	0.59957391
H	0.02601091	4.03799312	1.62061619
C	-0.54401556	4.09785237	-0.46167380
H	-0.06838273	4.13370194	-1.44772933
H	-1.09129544	5.03985267	-0.34964132
C	-3.79859794	4.05243033	-0.56303562
H	-3.99774375	4.91226430	-1.20774709
H	-3.37862378	4.42567573	0.37391765
C	-5.12855904	3.33698485	-0.28336350
H	-5.57477068	3.02269947	-1.22794170

H	-5.80013643	4.08673784	0.15049132
Pu	0.70717108	-1.90895378	0.88371962
O	1.55554563	-3.41428455	2.12196832
H	-2.13444455	-1.37641648	1.99426240
O	-0.29134680	-0.34084350	-0.03933409
H	-1.03210312	-0.28750710	-0.70632196
H	1.56385553	-4.34664496	1.86628267

Table S6 Calculated Cartesian coordinates for lowest energy structure of [PuO(HOPO-3H)(H_2O)]$^-$. All units are in Angstroms.

[PuO(HOPO-3H)(H_2O)]$^-$

C	-2.12557806	2.48587610	-3.19427828
C	-1.63584168	3.12964367	-4.31443358
C	-0.74028336	2.45372212	-5.14894147
C	-0.38612035	1.15876328	-4.86216580
C	-0.89046642	0.45214927	-3.72976367
N	-1.77477719	1.20241936	-2.89496760
H	-0.33542575	2.94786870	-6.02491306
H	-1.98413305	4.12902515	-4.52950718
H	0.29629697	0.59973115	-5.48846591
O	-2.29877423	0.61057488	-1.80461118
O	-0.60275501	-0.73133293	-3.45410998
C	-3.17145061	3.19879842	-2.37523233
O	-4.18073092	3.61015740	-2.95493188
N	-2.96804727	3.42541599	-1.04649487
C	-1.69519623	3.18582846	-0.35307128
H	-1.93348353	2.97997410	0.69416031
H	-1.25945984	2.27136222	-0.74673178
C	4.47950528	-1.37643945	-1.64538757
C	5.01273408	-2.06713476	-2.71918877
C	4.40890961	-3.24557453	-3.16006732
C	3.27584549	-3.72399823	-2.53713310
C	2.70612952	-3.03706156	-1.44461511
N	3.36121436	-1.87271780	-1.03190748
H	4.82952929	-3.78437431	-4.00095158
H	5.89307653	-1.65003312	-3.18376477
H	2.77565315	-4.62729365	-2.85815482
O	2.80790174	-1.24865093	0.01366920
O	1.65835133	-3.37714898	-0.81183013
C	5.16494668	-0.09364753	-1.21000476
O	6.14731904	0.29867066	-1.85096391
N	4.66403897	0.54772375	-0.13401522
H	3.83860830	0.12321919	0.29562619
C	5.26683228	1.76638782	0.38186086
H	5.20789163	1.73311190	1.47149641

H	6.31758539	1.74773444	0.09446923
C	1.16374154	2.06625739	3.09029130
C	0.44144752	2.74799937	4.05256757
C	-0.76084716	2.20958131	4.51438151
C	-1.22145271	1.00842401	4.01127380
C	-0.48173355	0.30212464	3.04519114
N	0.72858891	0.86217217	2.63810816
H	-1.33508795	2.73527262	5.26771740
H	0.83161931	3.68258412	4.42917755
H	-2.15098566	0.56469268	4.34094263
O	1.44809500	0.19234583	1.74124181
O	-0.80767583	-0.80757509	2.50229018
C	2.47775663	2.62268921	2.58038403
O	3.41506087	2.71370744	3.37401868
N	2.52162621	3.08755533	1.29988535
C	3.72184566	3.81164219	0.85605853
H	3.39271290	4.75547836	0.40817197
H	4.29296339	4.05121910	1.75227794
C	-4.38953454	-1.49208549	-0.29881486
C	-4.64452898	-2.09913508	-1.49848114
C	-3.80289965	-3.14366205	-1.92030626
C	-2.73714366	-3.54169836	-1.15614541
C	-2.44530788	-2.92157311	0.08851384
N	-3.35209419	-1.93149632	0.46625927
H	-3.98171171	-3.61902628	-2.87721797
H	-5.45964900	-1.74079567	-2.10933712
H	-2.05256509	-4.31494858	-1.47497940
O	-3.25728541	-1.37775757	1.72907265
O	-1.46803193	-3.17694519	0.83904925
C	-5.19956609	-0.34341048	0.26812433
O	-6.23783845	-0.56698523	0.88550554
N	-4.66765054	0.87823837	0.03214972
H	-3.83484197	0.94127743	-0.55798667
C	-5.18187363	2.05433982	0.73321963
H	-4.54779247	2.25741544	1.60690046
H	-6.15999547	1.76510518	1.11555262
C	4.61605570	3.06919328	-0.14598158
H	4.06794051	2.84398320	-1.06422361
H	5.40504606	3.77278112	-0.43188824
C	1.36831663	3.06617053	0.38648643
H	1.76490828	3.04885041	-0.63124822
H	0.84377069	2.12071475	0.50881943
C	0.44345866	4.28113161	0.56684322
H	1.04198734	5.19454548	0.48796908
H	0.03724316	4.26565549	1.58305435
C	-0.71596938	4.36762936	-0.43742726

H	-0.33030969	4.43884192	-1.45982290
H	-1.26252512	5.29728034	-0.24708746
C	-4.03896801	4.13788763	-0.33375115
H	-4.29612281	5.04305155	-0.89007469
H	-3.63094701	4.44239728	0.63269214
C	-5.31960122	3.31817041	-0.12084893
H	-5.75619831	3.06988986	-1.08878538
H	-6.03017214	3.98060562	0.38645474
Pu	0.76044769	-2.07550933	1.03139756
O	1.49012877	-3.08649624	2.39058016
O	-0.35238710	-0.88159773	-0.84389691
H	-1.15448682	-0.30217036	-0.99436798
H	-0.17482556	-1.08981287	-1.79361838
H	-2.28796209	-1.27379892	1.96581208

Table S7 Calculated Cartesian coordinates for lowest energy structure of $[Pu(HOPO\text{-}5H)]^-$. All units are in Angstroms.

$[Pu(HOPO\text{-}5H)]^-$

C	-1.92048429	2.70001975	-2.37847916
C	-1.58181681	3.53059211	-3.43328320
C	-0.46189365	3.22816786	-4.21231041
C	0.29617716	2.10790673	-3.94156861
C	-0.03913378	1.23688430	-2.87765178
N	-1.18365869	1.58354425	-2.13703854
H	-0.18994475	3.87670883	-5.03710542
H	-2.20884316	4.38624044	-3.63577516
H	1.16515060	1.84387338	-4.52902489
O	-1.53032738	0.73452968	-1.16709227
O	0.58348528	0.19552844	-2.53394389
C	-3.16490531	3.01030385	-1.57109335
O	-4.21704030	3.19008747	-2.18961704
N	-3.07729412	3.16996888	-0.22162063
C	-1.80189983	3.16319870	0.51164175
H	-2.03779167	3.00227189	1.56511194
H	-1.24632567	2.28520311	0.19468857
C	4.40796939	-1.89316613	-0.02429222
C	5.14549500	-2.77567238	0.74495085
C	4.51383932	-3.86454783	1.36876649
C	3.16893563	-3.97265858	1.20267178
C	2.34815061	-3.11164290	0.47270390
N	3.06864195	-2.10864222	-0.21193723
H	5.08178462	-4.56430223	1.97135503
H	6.20054261	-2.57516310	0.85993673
O	2.35045800	-1.36412953	-1.05683389
O	1.08816435	-3.12513875	0.35094439

C	5.11792127	-0.66457398	-0.55195042
O	6.35295845	-0.65793453	-0.59557800
N	4.36058544	0.41103805	-0.85715237
H	3.36085876	0.24507910	-0.96725701
C	5.00138001	1.63394877	-1.32314249
H	5.86033846	1.83155950	-0.67805809
H	5.40855324	1.46354085	-2.32771412
C	1.74981380	1.75466383	2.58811864
C	1.48796283	2.08268503	3.90572932
C	0.42604446	1.45462832	4.56488865
C	-0.34663908	0.51448137	3.91471067
C	-0.08227031	0.15064770	2.57176109
N	1.00566850	0.80305856	1.96858748
H	0.20969990	1.70787656	5.59638929
H	2.11923889	2.81025005	4.39442327
H	-1.17076679	0.01047256	4.40119359
O	1.30050686	0.42326524	0.72326225
O	-0.71480907	-0.68676180	1.87385761
C	2.91439451	2.37996763	1.85112966
O	4.03732520	2.26608011	2.34433771
N	2.65942235	3.09579196	0.71805217
C	3.79303319	3.60783755	-0.05955499
H	3.57857821	4.65581848	-0.29334493
H	4.66816065	3.58385638	0.58852342
C	-4.57099736	-1.72319728	-1.08358778
C	-5.34249132	-2.27958589	-2.08769524
C	-4.73557205	-3.04403647	-3.08655723
C	-3.36659895	-3.20760150	-3.10155450
C	-2.55625391	-2.62860007	-2.09975144
N	-3.22705648	-1.97208985	-1.06222794
H	-5.34054638	-3.48355224	-3.87114093
H	-6.40087149	-2.06832128	-2.07332842
H	-2.85721336	-3.75718886	-3.88150002
O	-2.46186281	-1.57990504	-0.03493923
O	-1.28811464	-2.65571986	-2.05486468
C	-5.23899999	-0.75822990	-0.12396749
O	-6.47345167	-0.71177106	-0.07752128
N	-4.43148190	0.07753710	0.56080548
H	-3.43509188	-0.13779737	0.53035871
C	-4.97410816	1.14057725	1.39378878
H	-4.23508585	1.36113247	2.16845100
H	-5.86493600	0.74686961	1.88726213
C	4.08326027	2.86106060	-1.38034636
H	3.14759593	2.60636172	-1.88779047
H	4.58744609	3.58102958	-2.03424215
C	1.31066000	3.32478788	0.17431630

H	1.44462018	3.70577768	-0.83961081
H	0.82067735	2.35985716	0.07069664
C	0.44253416	4.32087151	0.96118879
H	0.92694897	5.30299527	0.96499074
H	0.37122897	4.00538580	2.00574068
C	-0.97002055	4.45033870	0.36189090
H	-0.89090859	4.70319290	-0.69993871
H	-1.49437368	5.28399467	0.84081675
C	-4.31561275	3.52807692	0.49053757
H	-4.78149385	4.37039486	-0.02871076
H	-4.01370781	3.87544512	1.48126095
C	-5.37365063	2.42109440	0.62842949
H	-5.74603642	2.14547533	-0.35775849
H	-6.21601805	2.88212025	1.15742022
Pu	-0.08454651	-1.16834760	-0.52956252

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