Stabilization of Uranyl(V) by Dipicolinic Acid in Aqueous Medium

Rahul Agarwal[a,b]*, Rama Mohana Rao Dumpala[c], Manoj K. Sharma[a,b], Ashok Kumar Yadav[d] and Tamal Kanti Ghosh[e]

[a]Homi Bhabha National Institute, Mumbai 400 094, India

[b]Fuel Chemistry Division, Bhabha Atomic Research Centre (BARC), Trombay, Mumbai 400 085, India

[c]Radio Chemistry Division, Bhabha Atomic Research Centre (BARC), Trombay, Mumbai 400 085, India

[d]Atomic & Molecular Physics Division, Bhabha Atomic Research Centre (BARC), Trombay, Mumbai 400 085, India

[e]The Environmental research group, R&D, Tata Steel, Jamshedpur, Jharkhand, 831001, India

Tel.: +91 22 2559 0642. Fax: +91 22 2550 5151. E-mail: rahulmarru@barc.gov.in or rahulagarwal715@gmail.com

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A. Cyclic Voltammetry:

1. Electrochemistry of UO_2^{2+}-DPA in water:

Table T1. Electrochemical parameters obtained from CVs of UO_2^{2+}-DPA (5 mM U and 37.5 mM DPA) in water (pH 11) on GC electrode at different scan rates.

v/ mV s^{-1}	E_p^c/V	i_p^c/A	E_p^a/V	i_p^a/A	E_0'
50	-0.944	-2.68E-05	-0.240	1.31E-05	-0.592
100	-0.966	-3.40E-05	-0.211	2.06E-05	-0.589
150	-0.974	-3.82E-05	-0.198	2.65E-05	-0.586
200	-0.988	-4.37E-05	-0.186	3.10E-05	-0.587
250	-0.999	-4.86E-05	-0.185	3.51E-05	-0.592

2. Electrochemistry of UO_2^{2+} in Na_2CO_3:

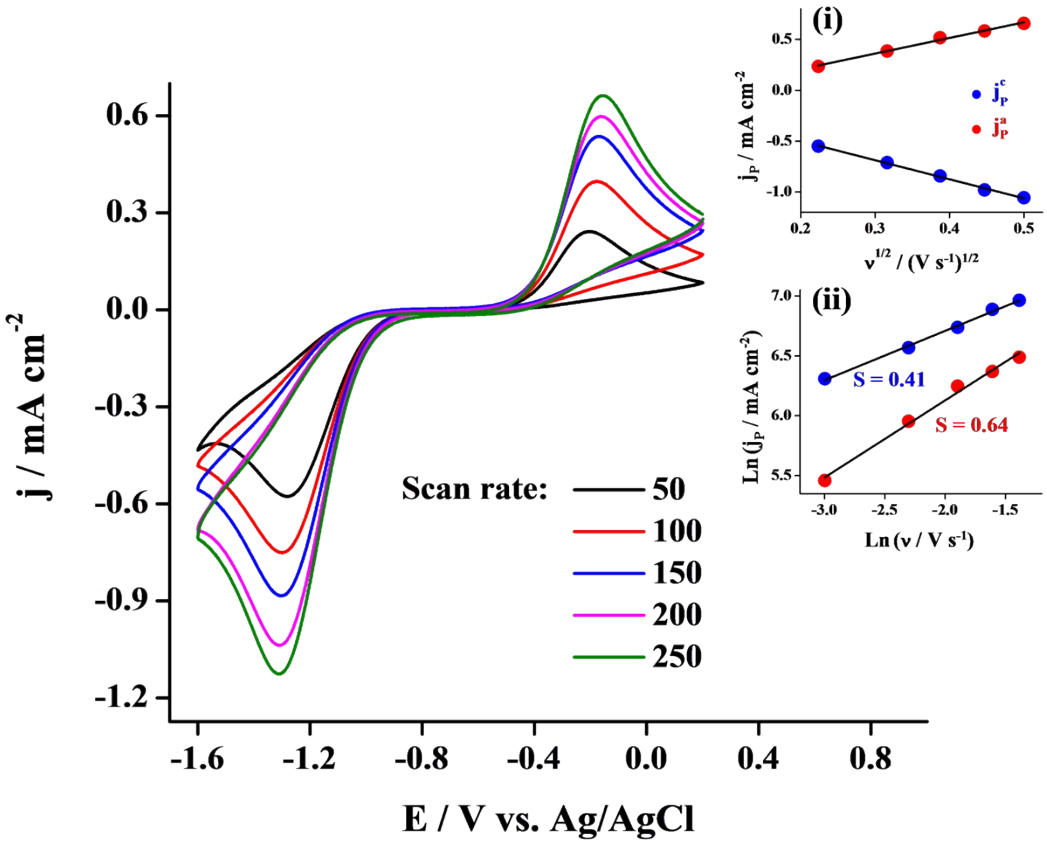


Figure S1. CVs of GC in 10 mM UO_2^{2+} in 1.4 M Na_2CO_3 (pH 11.9) at different scan rates (50, 100, 150, 200 and 250 mV s^{-1}). Inset shows (i) plot of corresponding anodic and cathodic peak current density (j_p) versus square root of scan rate ($v^{0.5}$) and (ii) plot of Ln(j_p) versus Ln(v).

Table T2. Electrochemical parameters obtained from CVs of 10 mM UO_2^{2+} in 1.4 M Na_2CO_3 (pH 11.9) on GC electrode at different scan rates.

v/ mV s^{-1}	**E_p^c/V**	**i_p^c/A**	**E_p^a/V**	**i_p^a/A**	**E_0'**
50	-1.281	-3.88E-05	-0.202	1.66E-05	-0.742
100	-1.302	-5.02E-05	-0.117	2.72E-05	-0.709
150	-1.302	-5.95E-05	-0.170	3.65E-05	-0.736
200	-1.310	-6.92E-05	-0.162	4.12E-05	-0.736
250	-1.308	-7.46E-05	-0.160	4.64E-05	-0.734

Table T3. Comparative table of electrochemical parameters obtained from CVs of different U(VI)/U(V) redox couples on GC electrode at different scan rates.

Medium	**Working electrode**	**E_p^a/V**	**E_p^c/V**	**References**
0.02 M HEPES Buffered water (pH 7)	GC	-0.16 to 0.00 V	-1.56 to -1.65 V	[1]
Na_2CO_3 (pH 12)	GC	0.00 to 0.25 V	-1.5 to -1.7 V	[2]
Water (pH 11)	GC	-0.24 to -0.18 V	-0.94 to -0.99 V	This work

3. Electrochemistry of UO_2^{2+} in water:

In water (pH 7), UO_2^{2+} forms polymeric hydroxide species (monomeric, dimeric, trimeric etc.) according to the eq 3.[3]

$$mUO_2^{2+} + nH_2O = (UO_2)_m(OH)_n^{2m-n} + nH^+ \quad (3)$$

The concentration of the kind of polymer forms depends on the concentration of both UO_2^{2+} and OH^- ions.[3a] Under highly alkaline conditions, it forms insoluble mono and polyuranate salts such as M_2UO_4, $M_2U_2O_7$, etc. (M = Li, Na, K etc.) and precipitates in solution which poses an experimental challenge to study the electrochemistry of UO_2^{2+} in alkaline medium.[3a, 4] It is observed that uranyl nitrate hexahydrate ($UO_2(NO_3)_2.6H_2O$) (5 mM) is completely soluble in alkaline water (0.1 M KCl, pH 11) but precipitates in aged solution. Hence, electrochemistry of UO_2^{2+} in 0.1 M KCl (pH 11) solution was carried out immediately after dissolving $UO_2(NO_3)_2.6H_2O$ salt in solution (0.1 M KCl, pH 11). Figure S2 shows CVs of 5 mM UO_2^{2+} in 0.1 M KCl (pH 11) at a scan rate of 50 mV s^{-1}. The initial scan direction is negative and the hold time at initial potential (0.8 V) is 10s. When the potential is scanned in the negative direction up to -0.4 V, it shows a pair of reduction ($E_P^c = -0.235\ V$) and oxidation wave ($E_P^a = 0.127\ V$) at $E_0^{'}$ = -0.054 V which corresponds to U(VI)/U(V) redox couple. But scanning the potential to -0.8 V results in two reduction waves at -0.235 V and -0.558 V, respectively which represents UO_2^{2+} first reduces into UO_2^{+} which in turn reduces into insoluble UO_2.[5] Since UO_2 is insoluble in water, it deposits at the electrode surface during the negative scan. In the reverse scan, a large and broad peak appeared at 0.103 V which represents direct two-electron oxidation of UO_2 to UO_2^{2+}.[5] In addition to that, two small but sharp oxidation waves are observed at 0.375 and 0.440 V, respectively. The same experiment was repeated many times and these unwanted peaks are repeatedly observed. These peaks may be attributable to oxidation of different U(IV)-hydroxide species at the electrode surface to $[U^{(VI)}O_2]^{2+}$.

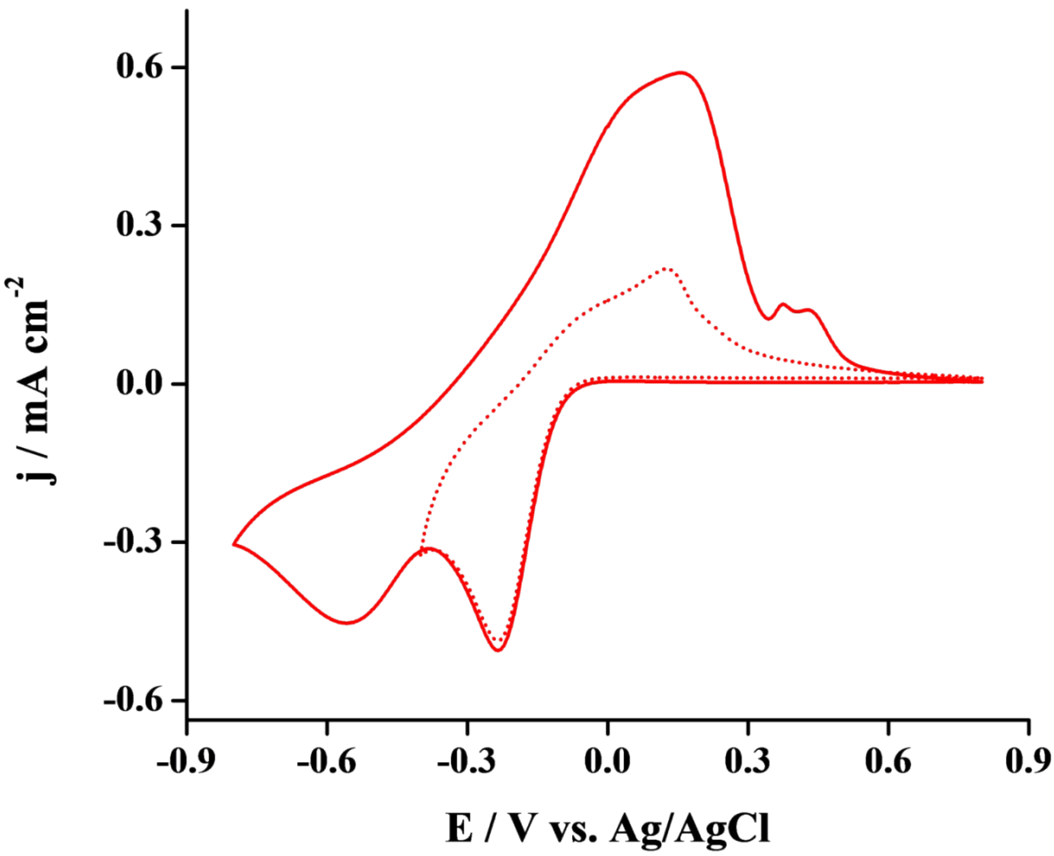


Figure S2. CVs of GC in 5 mM UO_2^{2+} in 0.1 M KCl (pH 11) at a scan rate of 50 mV s^{-1}.

B. EXAFS of U(VI)/U(V)-DPA in water:

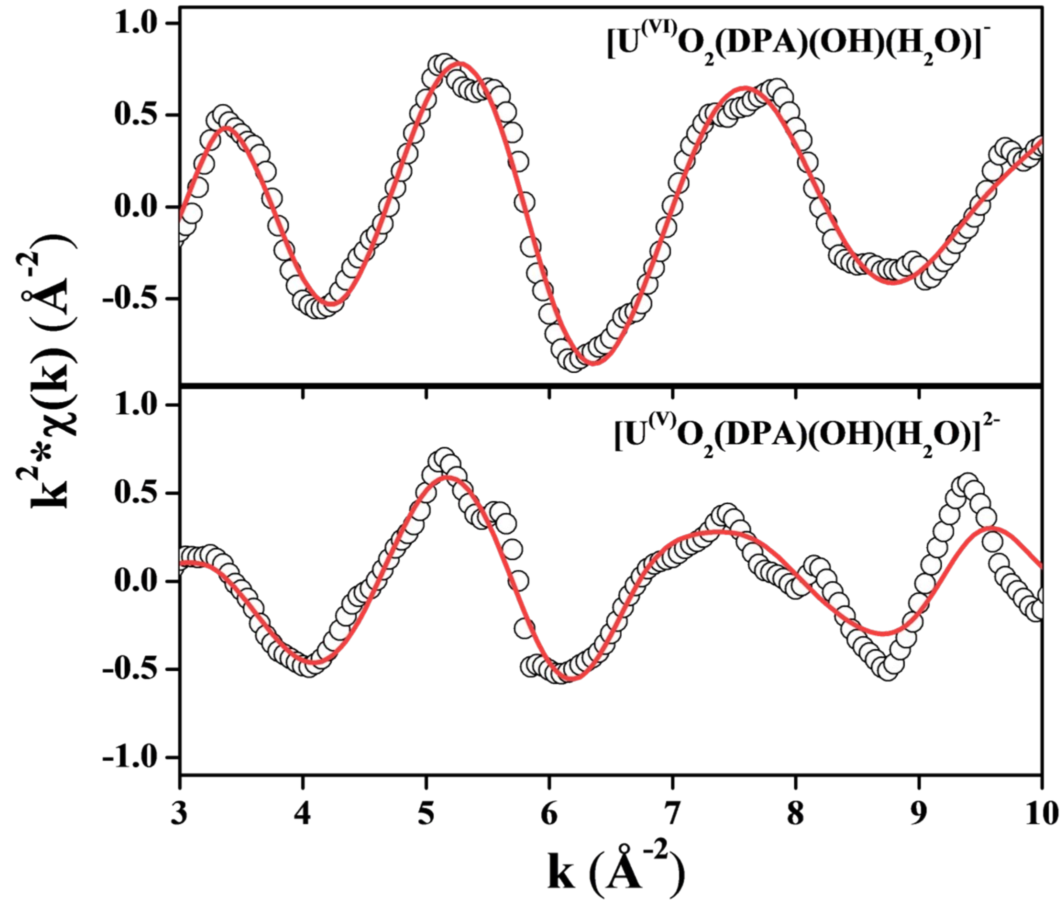


Figure S3. k^2 weighted χ(k) spectra for $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^-$ and $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ in water (pH 11). The experimental data are represented by scatter points, and the theoretical fit is represented by solid line.

C. **UV-Vis. absorption:**

1. **UV-Vis Titration:**

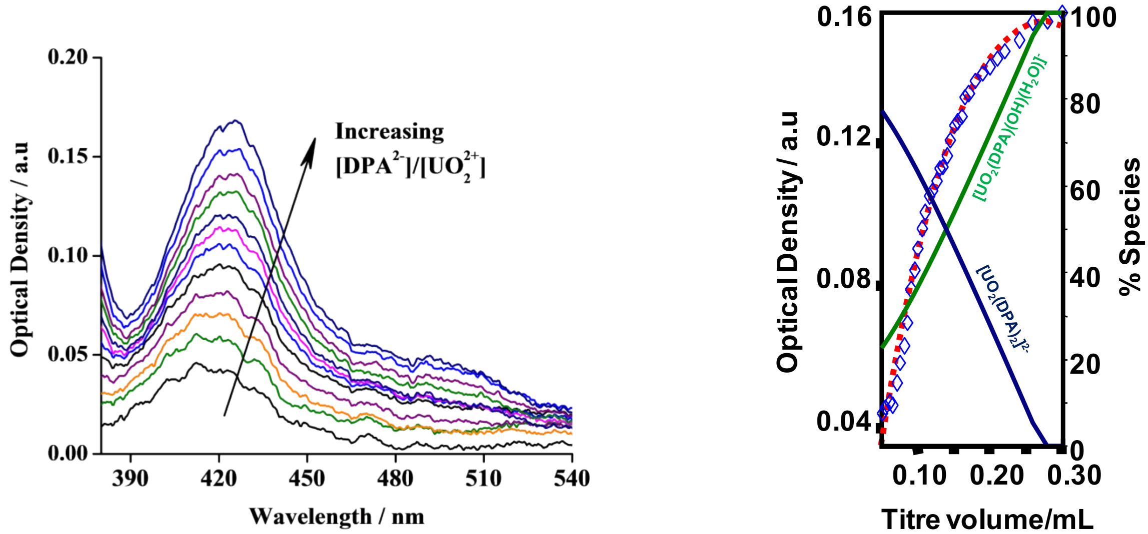


Figure S4. Left: Variation in absorption spectra of $U^{(VI)}O_2^{2+}$ with increase in [DPA^{2-}/UO_2^{2+}] ratio (addition of OH^- leads to more DPA^{2-}). **Right:** Fitted experimental dat with the speciation; Experimental conditions: (in Cuvette - [UO_2^{2+}] = 0.01 M, [DPA] = 0. 05 M; Titre – [NaOH] = 0.08M)

2. **UV-Vis. spectra of U(VI)/U(V)/U(IV)-DPA in water:**

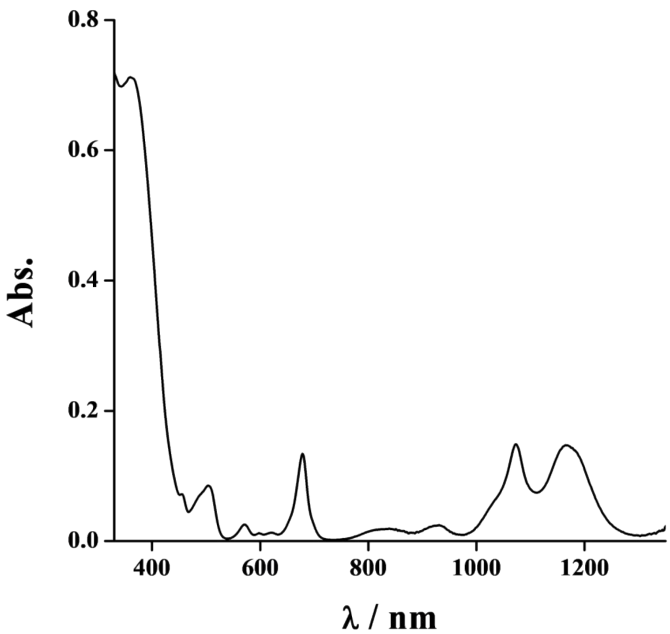


Figure S5. UV-Vis. spectra of 2 mM U(IV) in presence of 4 mM DPA in water (pH 1.7).

3. **Photographs:**

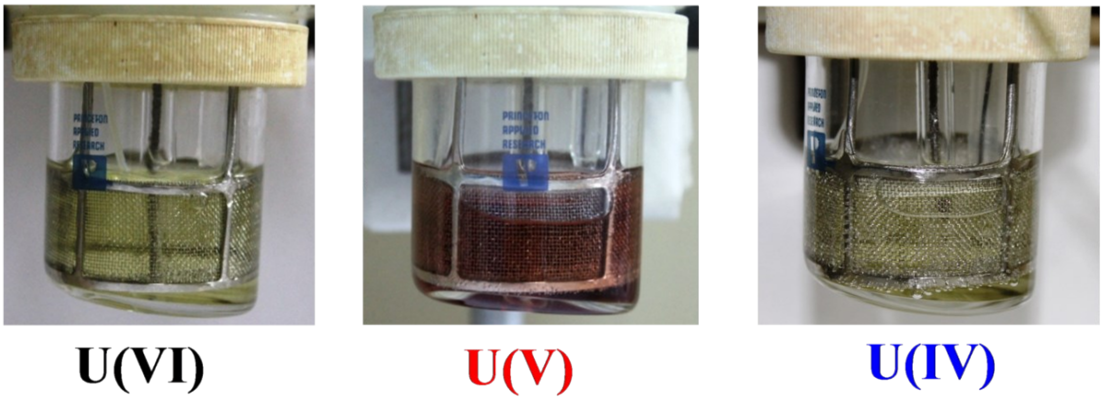


Figure S6. Photographs of [U(VI), U(V) and U(IV)]-DPA in water.

4. **UV-Vis. spectra of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ in water:**

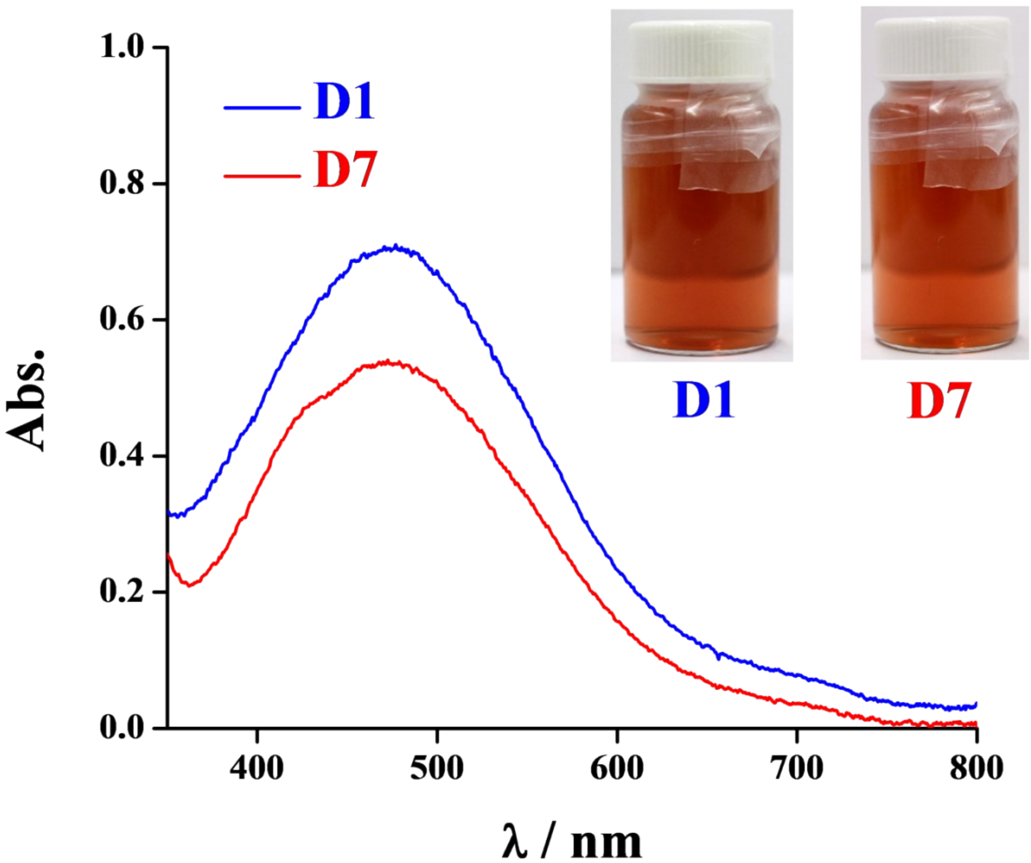


Figure S7. UV-Vis spectra of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ in water (pH 11) on day1 (D1) and day7 (D7). Inset shows the photographs of respective solution kept in scintillation vial.

5. Stability of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ in water (1 – 10 mM):

In open atmosphere, the pink colour of the $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ changes to yellow due to conversion of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ to $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^{-}$. Thus, intensity of the pink colour of the complex can be used to identify the stability of the $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ complex.

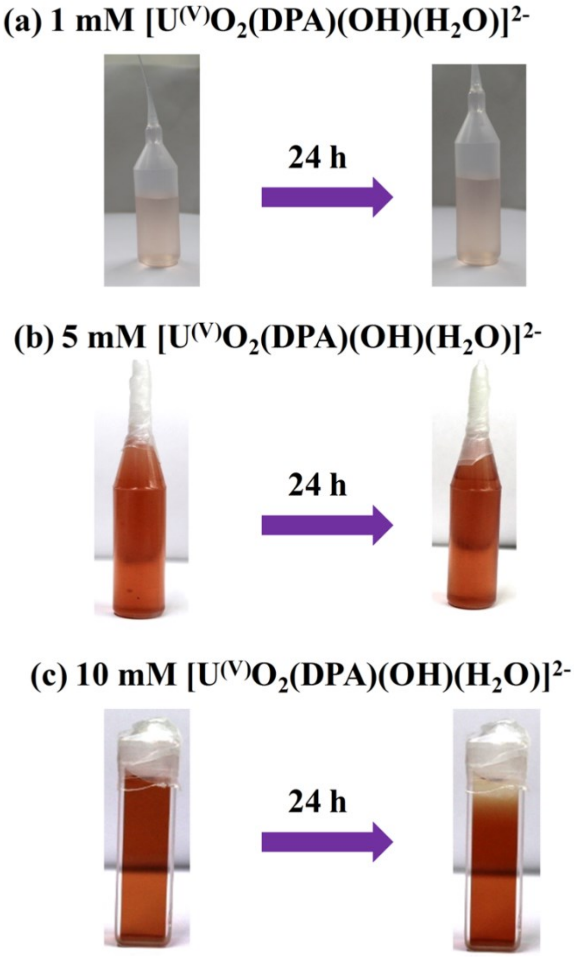


Figure S8: Stability of different concentrations of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ with time.

6. Explanation of CT band in the UV-Vis spectra of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$:

The high-intensity broadband at 471 nm can be explained based on the following two approaches:

Approach 1:

Figure S9a shows UV-Vis spectra of $[U^{(VI)}O_2]^{2+}$-DPA in water (pH 11) (i) before and (ii) after bulk electrolysis at -0.9 V. Initially the solution was yellow (characteristic of $[U^{(VI)}O_2]^{2+}$) and presence of absorption bands at 416 and 478 nm confirms $[U^{(VI)}O_2]^{2+}$ is present (Figure S9a-(i)).[3a, 5b] But after electrolysis, the yellow-coloured solution was turned in to dark pink and shows a broadband at 471 nm (Figure S9a-(ii)). The electron stoichiometry (n) for the reduction of $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^-$ was determined from the charge consumed and is found out to be 0.97 ± 0.05. Therefore, it was confirmed that reduction of $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^-$ in water (pH 11) at -0.9 V results formation of pure U(V) analogue i.e., $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$.[2-6] Thus, the peak at 471 nm should be due to $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$.

<u>Approach 2:</u>

It is also confirmed by recording the UV-Vis. spectra of the same species formed from $[U^{(V)}O_2(CO_3)_3]^{5-}$. Speciation diagram calculation shows the major species present in solution containing 10 mM U(VI) in 0.075 M DPA in 1 M Na_2CO_3 (pH 11.8) is $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^-$ (Figure S10). So at first, 10 mM $[U^{(V)}O_2(CO_3)_3]^{5-}$ is prepared by electrochemical reduction of $[U^{(VI)}O_2(CO_3)_3]^{4-}$ in 1 M Na_2CO_3 at -0.9 V on Pt electrode in Ar atmosphere (Figure S9b-(i)). The colourless $[U^{(V)}O_2(CO_3)_3]^{5-}$ solution shows a weak band at 750 nm in the UV-Vis spectra which confirms the presence of pure $[U^{(V)}O_2(CO_3)_3]^{5-}$.[2b, 6-7] The applied potential was cut off and 0.075 M DPA was added to the pure $[U^{(V)}O_2(CO_3)_3]^{5-}$ solution and the solution pH was maintained above 11.8 by adding required quantity of NaOH. This will result in pink coloured solution which shows a similar broadband at 471 nm (Figure S9b-(ii)). Since, $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ is formed from $[U^{(V)}O_2(CO_3)_3]^{5-}$ by adding DPA (confirmed from speciation diagram, Figure S10), it confirms U(V) is only present. Now, the identical colour and the identical UV-Vis spectra confirm the speciation and oxidation state of U is same in both the cases (Figure S9a & S9b). Hence, we may conclude that the high-intensity broadband at 471 nm is a signature of $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ species and it may be due to L→M charge transfer ($DPA^{2-} \rightarrow [U^{(V)}O_2]^+$) transitions.

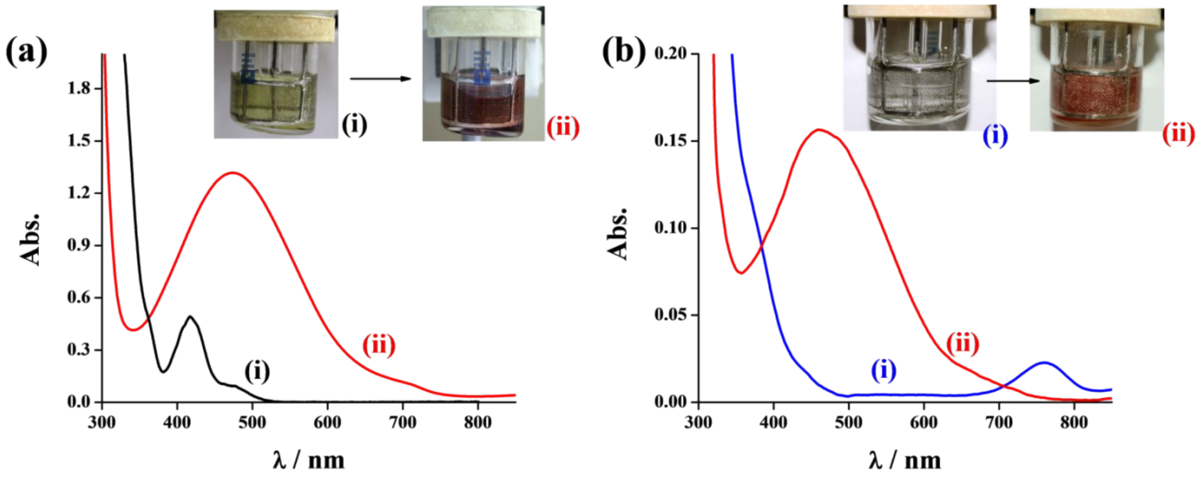
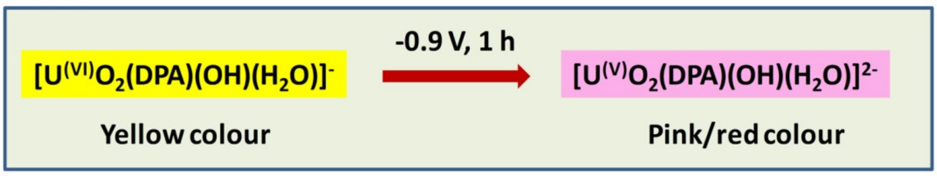


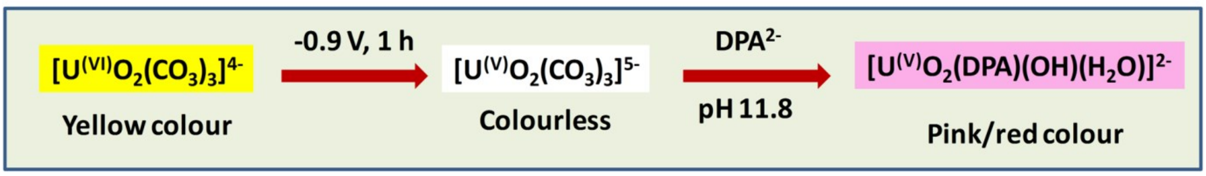
Figure S9. (a) UV-Vis. spectra of $[U^{(VI)}O_2]^{2+}$-DPA in water (pH 11) (i) before and (ii) after bulk electrolysis at -0.9 V. (b) UV-Vis. spectra of (i) 10 mM $[U^{(V)}O_2(CO_3)_3]^{5-}$ in 1 M Na_2CO_3 and (ii) 10 mM $[U^{(V)}O_2(CO_3)_3]^{5-}$ in 1 M Na_2CO_3 with 0.075 M DPA (after 10 times dilution, pH = 12). Inset shows the color of the respective solutions.

For better understanding, it is also represented in the form of schematic representations:

Approach 1



Approach 2



7. Speciation for UO_2-DPA-CO_3-OH system:

We simulated the speciation plot considering all the species including hydroxide and carbonate and found that, in the pH region (>11), $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^-$ as the predominant species (Figure S10) even in presence of carbonate. It is reasonable to assume that U(V) and Np(V) have a similar coordination geometry, as exemplified by the coordination geometry of different Np(V) carbonate complexes in solution and these structures are also very similar to those of the corresponding U(VI) system.[8] The effective charges on NpO_2^+,

UO_2^{2+} are 2.3 and 3.3 respectively.[9] As the thermodynamic data base is not available for U(V) species, the log β values were estimated from the available literature data for U(VI) by multiplying the log β values of U(VI) species by the ratio of their effective charges (2.3/3.3) and the speciation plot thus generated was found to be of similar pattern to U(VI) species showing $[U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$ as the predominant species as in case of U(V) species (Figure S10).

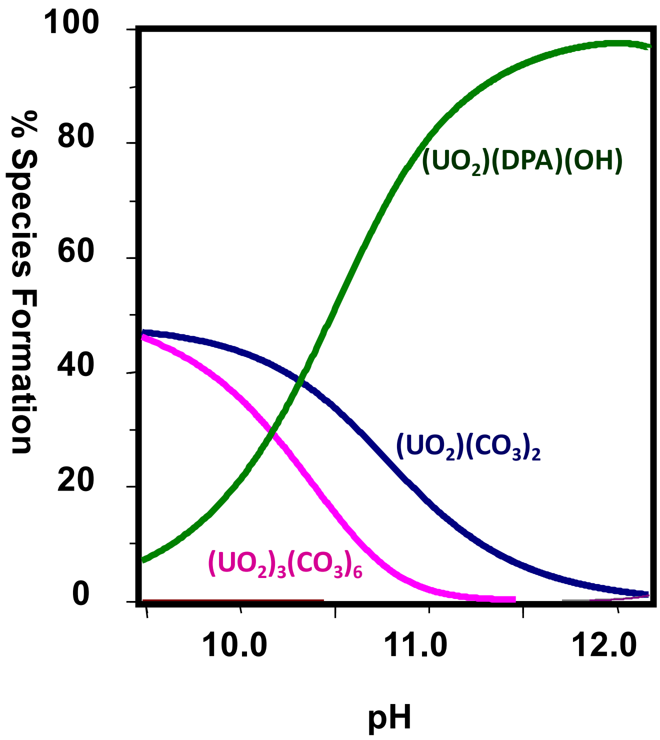


Figure S10. Speciation for UO_2-DPA-CO_3-OH system ($[U^{(VI)}O_2^{2+}$ or $U^{(V)}O_2^{+}]$ = 0.01 M, $[DPA]^{2-}$ = 0.075 M, $[CO_3]^{2-}$ = 1 M, cup Volume = 25 mL, Burette $[OH]^-$ = 0.1 M, anaerobic conditions). The log β values for all the UO_2-CO_3 and UO_2-OH species were taken from literature.[10]

Table T4. Coordinates of Optimized Geometries

U(V) Species	U(VI) Species
$[UO_2(DPA)(H_2O)_2]^-$	**$[UO_2(DPA)(H_2O)_2]$**
U 1.1486325 0.0182060 0.7795494	U 0.9623488 -0.0259300 -0.2998606
O -0.5910273 -0.1290404 0.1781328	O -0.7325162 -0.4610420 -0.5620098
O 2.8507167 0.3937777 1.3194615	O 2.6234586 0.5690401 -0.0721417
C 1.4852655 -3.2817077 1.4620109	C 1.5734958 -2.9171634 1.3196144
C 1.7764215 -4.6442177 1.3336884	C 1.9143052 -4.2477788 1.5702237
C 2.4166536 -4.2196957 -0.9599765	C 2.3044953 -4.5155530 -0.8036468
C 2.1017606 -2.8730115 -0.7536451	C 1.9528704 -3.1744027 -0.9686345
N 1.6547349 -2.4443085 0.4319566	N 1.6029139 -2.4155262 0.0779896
H 1.6199481 -5.2900547 2.2006407	H 1.8792245 -4.6162059 2.5981062
H 2.7770712 -4.5271473 -1.9442261	H 2.5817645 -5.0995192 -1.6842556
C 2.2242083 -1.8141697 -1.8531893	C 1.9266495 -2.4639814 -2.3143445
O 2.5925410 -2.1510997 -2.9700209	O 2.2195996 -3.0394123 -3.3385063
O 1.1493093 2.4121808 -0.1900314	O 0.2908026 1.7658939 1.4207036
H 0.7347647 2.1617103 -1.0861489	H 1.0011871 2.3776379 1.6873196
H 2.0947509 2.5915789 -0.3365526	O 1.5611256 -1.2106339 -2.1914119
O 1.8884487 -0.6281068 -1.4617164	O 0.9733980 1.3548307 -2.4674408
O 0.0522671 1.2134081 -2.2418552	H 1.0757257 0.5414979 -3.0193809
H -0.5424386 0.7509403 -1.6011444	H 1.7910228 1.8680382 -2.6034095
H 0.7771178 0.5414173 -2.3363628	C 1.1405790 -1.9349176 2.3982934
C 0.9616429 -2.6536053 2.7632707	O 1.0897714 -2.2574212 3.5641180
O 0.7968486 -3.3783920 3.7377662	O 0.8524807 -0.7600289 1.8921596
O 0.7548464 -1.3900452 2.6624938	C 2.2844128 -5.0546402 0.4879528
C 2.2492021 -5.1136134 0.1039927	H 2.5550707 -6.1029018 0.6506746
H 2.4870137 -6.1757036 -0.0268943	H 0.2370140 1.0842196 2.1357875

$[UO_2(DPA)(OH)(H_2O)]^{2-}$	$[UO_2(DPA)(OH)(H_2O)]^{-}$
U 0.7562925 0.0735409 0.1207822	U 1.1703257 0.0687064 0.1256984
O -1.0124614 -0.4086014 -0.0498204	O -0.5372848 -0.3163917 -0.2687776
O 2.5509153 0.6189330 0.1172922	O 2.8960613 0.4435705 0.4311974
C 1.6393088 -3.0862561 1.3554549	C 1.6008043 -3.1112022 1.3606821
C 2.0271918 -4.4279486 1.4651180	C 1.8535112 -4.4824136 1.4743688
C 2.1250014 -4.5193098 -0.9421427	C 2.2758803 -4.5246499 -0.9043663
C 1.7387106 -3.1727603 -0.9672310	C 2.0104659 -3.1520296 -0.9308741
N 1.5038575 -2.4932587 0.1627931	N 1.6862091 -2.4862601 0.1822413
H 2.1237769 -4.8494486 2.4687316	H 1.7714104 -4.9449553 2.4607727
H 2.3007614 -5.0177044 -1.8985774	H 2.5336734 -5.0229720 -1.8416916
C 1.5845473 -2.4036366 -2.2905488	C 2.0568653 -2.3197080 -2.2111457
O 1.8031672 -3.0189876 -3.3412445	O 2.3119113 -2.8623574 -3.2775847
O 0.2129589 2.1057385 0.8902289	O 0.6039060 2.0375475 0.8146304
H 1.0685393 2.5381989 1.0455765	H 1.3374636 2.6069300 1.0971684
O 1.2515278 -1.1849629 -2.1417743	O 1.8001247 -1.0742720 -1.9985337
O 1.6922625 1.4465439 -2.4125230	O 1.1136741 1.3574670 -2.1888536
H 1.5878678 0.5009133 -2.6756020	H 0.1486227 1.4333986 -2.2959365
H 2.2824842 1.3697376 -1.6223181	H 1.3740143 0.4846715 -2.5931429
C 1.3563753 -2.2185783 2.5948034	C 1.2082752 -2.2278606 2.5479206
O 1.4960190 -2.7497945 3.7045337	O 1.1177786 -2.7300892 3.6600137
O 1.0056864 -1.0290461 2.3242905	O 1.0112113 -1.0015006 2.2099231
C 2.2710778 -5.1547909 0.2954279	C 2.1966184 -5.1950921 0.3210957
H 2.5757314 -6.2087213 0.3475492	H 2.4000776 -6.2707371 0.3759941
$[UO_2(DPA)_2]^{3-}$	$[UO_2(DPA)_2]^{2-}$
U 0.2846992 0.2514041 -6.1155090	U 0.2631927 0.2478283 -6.1228367
O -1.4922243 -0.1921656 -6.1695586	O -1.4559992 -0.2146086 -6.1772845
O 2.0638858 0.6899353 -6.0605675	O 1.9854564 0.7038189 -6.0670196

C	1.1052680	-3.0254335	-4.6045272	C	1.1109107	-2.9228968	-4.6175765
C	1.4877912	-4.3623898	-4.4171932	C	1.4918056	-4.2556685	-4.4229917
C	1.6543002	-4.5687453	-6.8088707	C	1.6198305	-4.4805502	-6.8202467
C	1.2608227	-3.2252019	-6.9070164	C	1.2323523	-3.1389472	-6.9180324
N	0.9975060	-2.4865246	-5.8238112	N	0.9883933	-2.3968406	-5.8371005
H	1.5491697	-4.7276161	-3.3885503	H	1.5724730	-4.6215959	-3.3963228
H	1.8537884	-5.1024271	-7.7418359	H	1.8054149	-5.0295759	-7.7467405
C	1.1086062	-2.5248183	-8.2697349	C	1.0561508	-2.4023303	-8.2437116
O	1.3510725	-3.2143100	-9.2815814	O	1.2594712	-3.0208016	-9.2916391
O	0.7494593	-1.3240572	-8.1835987	O	0.7069122	-1.1910907	-8.0789804
C	0.7887560	-2.1003360	-3.4142512	C	0.8108982	-1.9522952	-3.4779918
O	0.8746054	-2.6084611	-2.2769486	O	0.9011394	-2.3617020	-2.3177035
O	0.4804662	-0.9307070	-3.7502359	O	0.4954692	-0.7955787	-3.9002777
C	1.7681861	-5.1455881	-5.5408382	C	1.7505227	-5.0455357	-5.5477044
H	2.0735033	-6.1973107	-5.4290068	H	2.0527246	-6.0948136	-5.4332970
C	-0.2689555	3.8137700	-5.3065192	C	-0.2622106	3.7179389	-5.2959584
C	-0.3374811	5.2129411	-5.3908130	C	-0.3111893	5.1148204	-5.3714822
C	-0.1732773	4.9994173	-7.7825758	C	-0.1063283	4.9083866	-7.7662586
C	-0.1173493	3.6082555	-7.6091844	C	-0.0709194	3.5196977	-7.5942592
N	-0.1595499	3.0467742	-6.3963163	N	-0.1372261	2.9602942	-6.3859018
H	-0.4299958	5.7690243	-4.4541357	H	-0.4170117	5.6764092	-4.4399525
H	-0.1292351	5.3806301	-8.8063269	H	-0.0436468	5.3026027	-8.7837414
C	-0.0111633	2.6449587	-8.8065019	C	0.0214585	2.5200274	-8.7450733
O	-0.0083609	3.1653045	-9.9413924	O	0.0601024	2.9538684	-9.8992601
O	0.0523432	1.4348882	-8.4772843	O	0.0320587	1.3156265	-8.3373450
C	-0.3206403	3.0790828	-3.9542605	C	-0.3652175	2.9307617	-3.9913748
O	-0.4761639	3.7884803	-2.9390095	O	-0.5285879	3.5538073	-2.9391314
O	-0.2022499	1.8321750	-4.0523061	O	-0.2768696	1.6763047	-4.1787338

C -0.2840062 5.8140894 -6.6515813	C -0.2239068 5.7168947 -6.6308589
H -0.3286766 6.9093614 -6.7526572	H -0.2527240 6.8101441 -6.7277113

Table T5. Vibrational Frequencies of optimized geometries

U(V) Species

1. **$[U^{(V)}O_2(DPA)(H_2O)_2]^-$:**

Mode	Symmetry	Wave Number		Intensity Selection rule	
cm-1	Km/mol	IR	Raman	IR	Raman
1	0	0	-	-	
2	0	0	-	-	
3	0	0	-	-	
4	0	0	-	-	
5	0	0	-	-	
6	0	0	-	-	
7	a	39.4	0.8059	YES	YES
8	a	48.31	1.98313	YES	YES
9	a	60.83	0.31253	YES	YES
10	a	71.41	7.90325	YES	YES
11	a	105.56	1.80497	YES	YES
12	a	129.01	5.54692	YES	YES
13	a	151.2	1.28773	YES	YES
14	a	166.97	5.43777	YES	YES
15	a	179.65	0.47	YES	YES
16	a	185.42	1.35272	YES	YES
17	a	194.05	2.51814	YES	YES
18	a	197.42	1.50729	YES	YES
19	a	218.39	20.6247	YES	YES
20	a	234.8	51.08541	YES	YES

21	a	244.11	2.58277	YES	YES
22	a	248.81	29.88827	YES	YES
23	a	278.96	88.96636	YES	YES
24	a	286.76	31.92694	YES	YES
25	a	316.35	13.07133	YES	YES
26	a	373.89	7.83961	YES	YES
27	a	404.01	24.88139	YES	YES
28	a	461.12	1.17544	YES	YES
29	a	477.19	54.93081	YES	YES
30	a	488.15	239.489	YES	YES
31	a	493.69	2.80319	YES	YES
32	a	513.91	0.39994	YES	YES
33	a	541.45	81.73295	YES	YES
34	a	587.71	2.36485	YES	YES
35	a	678.36	11.38012	YES	YES
36	a	695.5	13.58368	YES	YES
37	a	742.68	62.82152	YES	YES
38	a	779.19	116.7186	YES	YES
39	a	789.05	18.16108	YES	YES
40	a	802.95	110.5333	YES	YES
41	a	813.38	24.02885	YES	YES
42	a	824.43	65.3284	YES	YES
43	a	846.72	48.2651	YES	YES
44	a	861.68	429.6181	YES	YES
45	a	876.66	3.47696	YES	YES
46	a	923.62	65.75993	YES	YES
47	a	964.62	0.03934	YES	YES

48	a	1030.88	0.34568	YES	YES
49	a	1042.82	4.80551	YES	YES

2. [$U^{(V)}O_2(DPA)(OH)(H_2O)]^{2-}$:

Mode	Symmetry	Wave Number		Intensity Selection rule	
cm-1	Km/mol	IR	Raman	IR	Raman
1	0	0	-	-	
2	0	0	-	-	
3	0	0	-	-	
4	0	0	-	-	
5	0	0	-	-	
6	0	0	-	-	
7	a	29.37	9.71504	YES	YES
8	a	40.49	1.81005	YES	YES
9	a	61.29	1.85875	YES	YES
10	a	72.84	9.37792	YES	YES
11	a	99.95	1.23405	YES	YES
12	a	106.96	5.57421	YES	YES
13	a	133.07	1.70894	YES	YES
14	a	148.48	3.63406	YES	YES
15	a	155.86	12.57034	YES	YES
16	a	174.87	2.5999	YES	YES
17	a	178.98	3.51935	YES	YES
18	a	186.27	2.47604	YES	YES
19	a	205.1	16.77549	YES	YES
20	a	211.93	32.42255	YES	YES
21	a	221.27	10.36792	YES	YES
22	a	241.61	17.01013	YES	YES

23	a	266.95	22.51578	YES	YES
24	a	286.69	1.46692	YES	YES
25	a	358.11	0.92244	YES	YES
26	a	401.23	4.48951	YES	YES
27	a	446.1	113.1154	YES	YES
28	a	454.66	136.0922	YES	YES
29	a	461.73	3.3643	YES	YES
30	a	492.06	6.34905	YES	YES
31	a	509.09	57.07843	YES	YES
32	a	513.69	26.57707	YES	YES
33	a	584.69	2.32231	YES	YES
34	a	635.75	231.1737	YES	YES
35	a	662.77	1.44546	YES	YES
36	a	696.28	14.56194	YES	YES
37	a	727.16	75.37118	YES	YES
38	a	739.16	63.9583	YES	YES
39	a	752.2	35.11141	YES	YES
40	a	781.34	18.26786	YES	YES
41	a	815.4	318.7345	YES	YES
42	a	818.56	163.4305	YES	YES
43	a	827.57	19.85982	YES	YES
44	a	864.6	335.2246	YES	YES
45	a	870.98	19.89694	YES	YES
46	a	917.48	50.19244	YES	YES
47	a	953.31	0.00859	YES	YES
48	a	1009.45	0.63389	YES	YES
49	a	1026.67	6.10489	YES	YES

3. $[U^{(V)}O_2(DPA)_2]^{3-}$:

Mode	Symmetry	Wave Number		Intensity Selection rule	
cm-1	Km/mol	IR	Raman	IR	Raman
1	0	0	-	-	
2	0	0	-	-	
3	0	0	-	-	
4	0	0	-	-	
5	0	0	-	-	
6	0	0	-	-	
7	a	14.51	0.70747	YES	YES
8	a	22.15	0.00118	YES	YES
9	a	34.46	0.24902	YES	YES
10	a	54.94	0.58773	YES	YES
11	a	69.33	19.29274	YES	YES
12	a	83.7	0.91352	YES	YES
13	a	87.49	2.24297	YES	YES
14	a	90.47	0.83555	YES	YES
15	a	91.83	57.20379	YES	YES
16	a	100.55	0.30045	YES	YES
17	a	112.03	47.27112	YES	YES
18	a	119.52	5.23358	YES	YES
19	a	152.96	0.20862	YES	YES
20	a	154.79	1.62682	YES	YES
21	a	163.93	11.18904	YES	YES
22	a	169.31	46.38691	YES	YES
23	a	173.79	0.04073	YES	YES
24	a	174	0.04156	YES	YES
25	a	185.5	0.01811	YES	YES

26	a	194.03	0.02104	YES	YES
27	a	212.3	0.02008	YES	YES
28	a	234.83	49.64973	YES	YES
29	a	254.1	32.87506	YES	YES
30	a	287.53	0.09779	YES	YES
31	a	289.3	8.35848	YES	YES
32	a	352.1	1.72469	YES	YES
33	a	355.63	0.04185	YES	YES
34	a	398.89	0.00155	YES	YES
35	a	404.16	11.22169	YES	YES
36	a	459.57	1.93087	YES	YES
37	a	460.17	2.03042	YES	YES
38	a	488.94	0.23135	YES	YES
39	a	489.85	0.03312	YES	YES
40	a	506.99	9.41895	YES	YES
41	a	512.12	0.0239	YES	YES
42	a	582.11	0.14111	YES	YES
43	a	584.43	7.58018	YES	YES
44	a	659.71	0.89744	YES	YES
45	a	660.01	0.45885	YES	YES
46	a	690.73	8.22567	YES	YES
47	a	691.48	25.95057	YES	YES
48	a	733.87	0.01918	YES	YES
49	a	737.62	118.3891	YES	YES

U(VI) Species

4. $[U^{(VI)}O_2(DPA)(H_2O)_2]$:

Mode	Symmetry	Wave Number		Intensity Selection rule	

cm-1	Km/mol	IR	Raman	IR	Raman
1	0	0	-	-	
2	0	0	-	-	
3	0	0	-	-	
4	0	0	-	-	
5	0	0	-	-	
6	0	0	-	-	
7	a	46.82	6.55346	YES	YES
8	a	59.89	0.45808	YES	YES
9	a	71.7	4.20305	YES	YES
10	a	90.35	17.57261	YES	YES
11	a	104.12	11.02788	YES	YES
12	a	112.26	1.03749	YES	YES
13	a	116.66	4.7365	YES	YES
14	a	174.31	1.95067	YES	YES
15	a	180.46	0.03089	YES	YES
16	a	188.56	0.32763	YES	YES
17	a	198.23	3.4297	YES	YES
18	a	214.16	1.98976	YES	YES
19	a	230.08	8.90411	YES	YES
20	a	237.66	1.16402	YES	YES
21	a	243.31	33.67044	YES	YES
22	a	255.6	141.6254	YES	YES
23	a	263.65	12.54642	YES	YES
24	a	280.09	0.30257	YES	YES
25	a	283.85	47.86954	YES	YES
26	a	286.16	8.94095	YES	YES

27	a	302.42	82.35988	YES	YES
28	a	394.34	8.73046	YES	YES
29	a	411.85	39.62217	YES	YES
30	a	458.84	2.36291	YES	YES
31	a	491.61	1.98133	YES	YES
32	a	523.77	172.167	YES	YES
33	a	527.54	21.54575	YES	YES
34	a	537.78	202.5862	YES	YES
35	a	595.46	0.43557	YES	YES
36	a	641.99	195.5541	YES	YES
37	a	667.71	582.6286	YES	YES
38	a	680.51	55.27652	YES	YES
39	a	694.09	28.73326	YES	YES
40	a	749.17	89.16381	YES	YES
41	a	791.95	28.81368	YES	YES
42	a	811.76	0.0146	YES	YES
43	a	834.13	0.57035	YES	YES
44	a	879.18	4.4971	YES	YES
45	a	884.41	73.07519	YES	YES
46	a	933.68	65.59487	YES	YES
47	a	971.57	336.8612	YES	YES
48	a	973.88	0.00079	YES	YES
49	a	1043.98	0.42516	YES	YES

5. $[U^{(VI)}O_2(DPA)(OH)(H_2O)]^-$:

Mode	Symmetry	Wave Number		Intensity Selection rule	
cm-1	Km/mol	IR	Raman	IR	Raman
1	0	0	-	-	

2	0	0	-	-	
3	0	0	-	-	
4	0	0	-	-	
5	0	0	-	-	
6	0	0	-	-	
7	a	51	2.58673	YES	YES
8	a	61.02	1.13422	YES	YES
9	a	72.88	7.32084	YES	YES
10	a	96.2	0.11172	YES	YES
11	a	106.21	6.56973	YES	YES
12	a	131.34	2.0175	YES	YES
13	a	156.26	5.50446	YES	YES
14	a	176.62	2.44042	YES	YES
15	a	179.33	3.4003	YES	YES
16	a	184.7	8.97529	YES	YES
17	a	190.52	16.86714	YES	YES
18	a	209.59	6.8222	YES	YES
19	a	234.73	1.97371	YES	YES
20	a	240.6	25.40779	YES	YES
21	a	254	2.60756	YES	YES
22	a	266.69	75.16034	YES	YES
23	a	270.7	62.49298	YES	YES
24	a	290.13	8.11984	YES	YES
25	a	374.63	10.43947	YES	YES
26	a	386.22	58.1312	YES	YES
27	a	412.65	11.59845	YES	YES
28	a	445.5	92.8732	YES	YES

29	a	460.45	2.6143	YES	YES
30	a	492.19	0.0792	YES	YES
31	a	518.2	137.3422	YES	YES
32	a	527.28	88.7512	YES	YES
33	a	539.33	201.2948	YES	YES
34	a	584.46	140.7239	YES	YES
35	a	593.72	4.57468	YES	YES
36	a	674.37	9.3075	YES	YES
37	a	695.85	21.39054	YES	YES
38	a	745.03	69.3891	YES	YES
39	a	787.96	26.49222	YES	YES
40	a	815.15	0.63059	YES	YES
41	a	828.62	11.59955	YES	YES
42	a	847.22	18.08677	YES	YES
43	a	875.83	32.93012	YES	YES
44	a	882.04	401.7875	YES	YES
45	a	929.11	63.30293	YES	YES
46	a	931.52	355.6734	YES	YES
47	a	962.41	0.02431	YES	YES
48	a	1030.24	0.31631	YES	YES
49	a	1039.62	5.12082	YES	YES

6. $[U^{(VI)}O_2(DPA)_2]^{2-}$:

Mode	Symmetry	Wave Number		Intensity Selection rule	
cm-1	Km/mol	IR	Raman	IR	Raman
1	0	0	-	-	
2	0	0	-	-	
3	0	0	-	-	

4	0	0	-	-	
5	0	0	-	-	
6	0	0	-	-	
7	a	10.8	0.21085	YES	YES
8	a	11.52	1.11543	YES	YES
9	a	27.8	0.29953	YES	YES
10	a	69.39	0.31256	YES	YES
11	a	72.78	19.12981	YES	YES
12	a	86.84	0.21618	YES	YES
13	a	91.78	0.64928	YES	YES
14	a	117.35	1.07872	YES	YES
15	a	128.05	63.08912	YES	YES
16	a	132.39	0.75116	YES	YES
17	a	138.07	1.51546	YES	YES
18	a	146.19	3.56777	YES	YES
19	a	156.71	9.91904	YES	YES
20	a	173.43	20.33401	YES	YES
21	a	173.66	10.38786	YES	YES
22	a	173.92	0.23312	YES	YES
23	a	175.73	44.49163	YES	YES
24	a	187.56	103.6883	YES	YES
25	a	204.41	0.2595	YES	YES
26	a	216.4	0.03754	YES	YES
27	a	235.12	0.61734	YES	YES
28	a	265.59	107.2891	YES	YES
29	a	276.77	31.00477	YES	YES
30	a	288.42	0.04764	YES	YES

31	a	292.72	13.45459	YES	YES
32	a	365.34	16.45287	YES	YES
33	a	373.76	0.02665	YES	YES
34	a	410.2	0.00382	YES	YES
35	a	423.79	16.61223	YES	YES
36	a	459.02	4.0769	YES	YES
37	a	459.06	1.0278	YES	YES
38	a	486.79	0.02788	YES	YES
39	a	487.83	0.01035	YES	YES
40	a	523.69	2.43118	YES	YES
41	a	535.77	0.00905	YES	YES
42	a	590.96	0.02107	YES	YES
43	a	595.91	6.75724	YES	YES
44	a	664.6	20.68283	YES	YES
45	a	665.36	1.25294	YES	YES
46	a	689.59	5.00244	YES	YES
47	a	690.35	37.38016	YES	YES
48	a	735.41	0.1993	YES	YES
49	a	742.81	124.1849	YES	YES

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