Supporting Information

Electronic Structure and Characterization of a Uranyl Di-15-Crown-5 Sandwich Complex with an Unprecedented Sandwich Structure

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Computational Methods

The geometry optimizations of the various isomers of $UO_2(15C5)_2^{2+}$ complex were carried out using spin-unrestricted Kohn−Sham density functional theory (DFT). The local density approach (LDA) and generalized gradient approach with PBE exchange-correlation functional were used as implemented in the Amsterdam Density Functional program (ADF2013)[1]. Scalar-relativistic (SR) effects were taken into account using zero-order-regular approximation (ZORA)[2]. The frozen core approximation was applied to the $[1s^2-5d^{10}]$ cores of U, and $[1s^2]$ cores of C and O, with the rest of the electrons explicitly treated variationally. The uncontracted Slater basis sets with triple-ζ plus a polarization function (TZ2P)[3] were used for the valence electrons of UO_2^{2+}, and double-ζ plus polarization basis sets (DZP) were used for C, O, and H atoms in crown ether. All the geometries were fully optimized with proper molecular symmetries and are shown to have all real vibrational frequencies. The vibrational frequencies were computed analytically, and zero-point energy (ZPE) corrections were included in the calculations of relative energies. Energy decomposition analyses (EDA) and extended transition state (ETS) with the natural orbitals for chemical valence (NOCV) theory were performed at the PBE level to assess different orbital contributions to the total bonding energies.

For comparison with the LDA and PBE calculations, geometry optimizations using the hybrid B3LYP, the meta-GGA M06-L, and the meta-hybrid M06 density functionals were carried out using the Gaussian 09 program[4]. The Pople set of valence triple-ζ with polarization functions, 6-311G** for H, C and O atoms

together with the Stuttgart energy-consistent relativistic 32-valence-electron pseudopotential and associated ECP60MWB_SEG valence basis set for uranium were used.[5] The harmonic vibrational frequencies were computed analytically, and the zero point energy (ZPE) corrections were included in the calculations of relative energies in these calculations with Gaussian code. Weinhold's natural bond orbitals (NBO) and natural localized MOs (NLMO) calculations were performed at PBE/6-31G* level on optimized geometries from PBE calculation in NBO 6.0 program.[6]

Structural characterization of the $UO_2(15C5)_2^{2+}$ complex. The gas-phase $UO_2(15C5)_2^{2+}$ complex was produced by electrospray ionization. Computational geometry optimizations and vibrational frequencies analysis were carried out, and the results are summarized in Table S1. Inasmuch as the linear structure of uranyl and the soft-ring structure of 15-crown-5 (15C5) ether are necessarily maintained upon coordination, there are only several possible geometries for two 15C5 ligands to coordinate with uranyl. Using PBE and B3LYP methods we have optimized the following structures, where the four structures listed in Table S1 have no imaginary frequencies, i.e. corresponding to local minima in the potential energy surface.

a) uranyl perpendicular to two parallel 15C5-rings (D_5 symmetry, isomer C in Table S1),
b) uranyl perpendicular to two parallel 15C5-rings, but mainly coordinating to one 15C5 ligand (C_5 symmetry, with an imaginary frequency);
c) uranyl horizontally lying between two parallel 15C5-rings (D_{2h} symmetry, with a few imaginary frequencies);
d) uranyl horizontally lying between two geometrically relaxed parallel 15C5-rings (C_{2h} symmetry, isomer D in Table S1);
e) uranyl$(15C5)_2$ forming slipped sandwich with six coordinating oxygen atoms coplanar (C_i symmetry, the lowest-energy isomer A in Table S1);
f) uranyl$(15C5)_2$ forming slipped sandwich with six non-coplanar coordinating oxygen atoms (C_2 symmetry, isomer B in Table S1).

As far as the conformations of the 15C5 ether rings are concerned, we started from different conformers of 15-crown-5 ring (i.e. different dihedral angles of two neighboring three-atoms entities), and all the geometry optimizations without symmetry constraints led to the alternatively puckered rings of 15C5 ring in all the local-minimum structures. A more comprehensive global minimum search of the conformations of 15C5 rings is not pursued due to the large size of the complex.

Based on optimized relative energies of different isomers and the agreement between the observed and computed IR spectra and intensities (Table S2, Figure S2), the gas-phase complex is assigned as isomer A (Figures 1 and S1). The infrared spectrum of $UO_2(15C5)_2^{2+}$ (Figure 2 and Table S2) show two bands centered at 842 and 976 cm^{-1}. The 842 cm^{-1} band can be attributed to vibrations of the weakly coordinated $U-O_e$ stretching modes. The 976 cm^{-1} band is assigned to the asymmetric $O_{yl}UO_{yl}$ stretching mode of the linear UO_2^{2+} ion core. The calculated vibrational frequencies and intensities from PBE are also in generally good agreement with the experimental values, especially for the antisymmetric $O_{yl}UO_{yl}$ and $U-O_e$ stretching modes. The computed (B3LYP) infrared spectra of the four low-energy $UO_2(15C5)_2^{2+}$ structural isomers (Figure S2) show that two of them (higher-energy isomers C and D) do not whatsoever match the observed IR spectrum.

Although the computed spectra for isomers A and B are generally rather similar, certain features, notably the two closely-spaced peaks at 1279 cm^{-1} and 1291 cm^{-1} are in good accord with the computed peaks at 1308 and 1319 cm^{-1}, which are at 1282 and 1293 cm^{-1} when the scaling factor of 0.98 is applied. Comparison of relative energies and spectral assignments provide convincing evidence that $UO_2(15C5)_2^{2+}$ complexes have a slipped "sandwich" structure (i.e., isomer A), in which uranyl is coordinated by two 15C5 ligands with six-fold coordination in the equatorial plane, rather than a high-symmetry "bis-inclusion structure" (i.e., isomer C), in which uranyl is fully coordinated by two 15C5 ligands with ten-fold coordination in the equatorial plane. It is rather remarkable that the energy of the "bis-inclusion" structure is only 17 kcal/mol higher (B3LYP) than that of the most stable slipped "sandwich" structure, indicating that such structure might exist as meta-stable species in some extreme conditions.

Chemical Bonding Analyses of the $UO_2(15C5)_2^{2+}$complex.

To comprehend the relative roles of the U 7s, 7p, 5f, and 6d orbitals and their chemical bonding with crown ether ligands, NLMO analysis[7] of $UO_2(15C5)_2^{2+}$ complexes were carried out (Table S3) and located six $\sigma^2\pi^2$ U−O_e interactions. In the 15C5 ethers, each O_e oxygen atom has two C-O single bonds and two lone-pairs. Upon coordination to uranyl, there are covalent electron donations from the lone pairs to the 5f and 6d orbitals of uranium, with the formation of weak σ and π bonding between O_e atoms and the uranium atom. This is consistent with the calculated bond orders in Table 1. For $UO_2(15C5)_2^{2+}$, the weak "σ-bond" is composed of 1.4 and 96.1% uranium and oxygen character, whereas the π-bond is 6.5 and 91.7% uranium and oxygen character, respectively, with the establishment of a weak U−O_e bonding interaction. For σ-bonding, 5f character dominates the uranium component with 5f: 6d contribution of 1:0.75, and the π-bond mainly has 6d character with a 5f:6d split of 1:0.98.

To assess the bonding interaction between uranyl and the crown ether ligands, energy decomposition analysis (EDA) for $UO_2^{2+} + (15C5)_2 \rightarrow UO_2(15C5)_2^{2+}$ was also performed to evaluate the relative importance of the ionic and covalent bonding effects. EDA results (Table S4) show that the electrostatic interaction and Pauli repulsion are -213.8 and 123.7 kcal/mol, respectively, whereas the orbital interactions are -232.1 kcal/mol. Therefore, both electrostatic interaction and orbital interactions account for major contributions to the total bonding energies, consistent with the character of the U−O_e bonds.

Inspection of the Kohn−Shan orbitals of $UO_2(15C5)_2^{2+}$ complexes (Figure S4) reveals that the orbital interaction of U d_δ, f_δ and f_ϕ with 2p orbitals in U−O_e bonding are of a_u symmetry. Consistent with their molecular orbital analysis (Table S4), bonding interactions are dominated by oxygen 2p orbitals and uranyl bonding orbitals, which indicates substantial covalency of the U−O_e bonds.

To probe the orbital interaction of the uranyl–crown ethers in the $UO_2(15C5)_2^{2+}$ complex, ETS-NOCV analysis were performed, and the calculated results are provided in Figure S4. These five orbitals represent the principal components of the U–O_e bonds, with the first orbital being for the four uncoordinated O_e, lying about 5.44 kcal/mol lower in energy than the second one, which is for the six U–O_e bonding interactions. The key bonding interactions are predominantly 5f orbitals and 6d orbitals, which has been confirmed by additional electron population of uranium primarily on 6d orbitals and 5f orbitals according to Mulliken charge, NPA and NLMO analyses (Tables 1 and S3).

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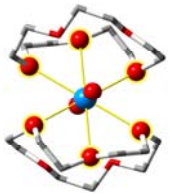
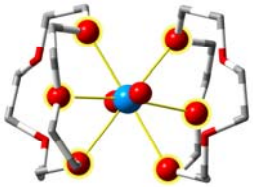
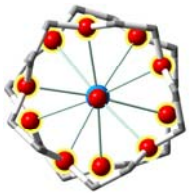
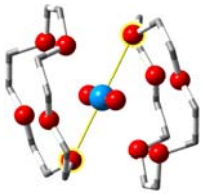
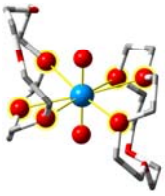
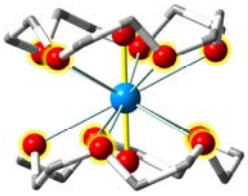
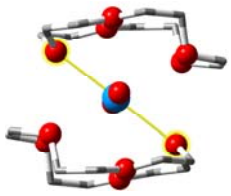
Table S1. Optimized geometrical structures and relative energies of $UO_2(15C5)_2^{2+}$ isomers computed at different levels of theory.[a]

Isomer	**A** (C_i)			**B** (C_2)			**C** (D_5)			**D** (C_{2h})		
Top view												
Side View-a												
	$U\text{-}O_{yl}$ (Å)	$U\text{-}O_e$ (Å)	**Δ**E kcal/mol	$U\text{-}O_{yl}$ (Å)	$U\text{-}O_e$ (Å)	**Δ**E kcal/mol	$U\text{-}O_{yl}$ (Å)	$U\text{-}O_e$ (Å)	**Δ**E kcal/mol	$U\text{-}O_{yl}$ (Å)	$U\text{-}O_e$ (Å)	**Δ**E kcal/mol
LDA	1.767	2.509 2.622 2.786 3.145 3.207	0.0	1.765	2.489 2.531 2.549 3.648 3.903	14.3	1.777	2.718	-9.4	1.755	2.585 2.950 2.899	36.7
PBE	1.772	2.564 2.699 2.822 3.503 3.531	0.0	1.770	2.576 2.619 2.674 3.855 4.017	8.1	1.772	2.812	8.9	1.762	2.643 3.053 3.106	32.4
B3LYP	1.742	2.566 2.658 2.695 3.703 3.823	0.0	1.738	2.565 2.613 2.677 3.855 3.991	8.9	1.741	2.816	17.3	1.727	2.594 3.065 3.132	34.5
M06L	1.744	2.669 2.601 2.888 3.183 3.194	0.0	1.741	2.554 2.650 2.636 3.672 3.868	16.3	1.750	2.775	3.9	1.733	2.643 2.967 3.026	33.7

		2.570			2.546							
		2.619			2.640						2.670	
M06	1.716	2.796	0.0	1.715	2.645	14.1	1.714	2.801	6.7	1.704	2.947	35.1
		3.427			3.804						3.032	
		3.469			3.669							

[a]LDA and PBE calculations were performed using ADF with the TZ2P basis sets for atoms on uranyl, DZP ones for atoms on the crown ether ligands; B3LYP, M06 and M06-L calculations were done with Gaussian code, with ECP60MWB_SEG ECP and basis set for U and 6-311G** for C, H, and O atoms, respectively.

Table S2. Observed and calculated (B3LYP level; unscaled) vibrational frequencies (in cm^{-1}) of $UO_2(15C5)_2^{2+}$.

IR Mode[a]	Exptl.[b]	Isomer**A**		Isomer**B**		Isomer**C**	
		Freq.[c]	Inten.[d]	Freq.	Inten.[d]	Freq.	Inten.[d]
C-C rotation	765(w)	782[766]	69	774	57	770	0
		782[766]	0	780	17	770	0
		809[793]	0	800	16	772	0
		811[795]	44	801	23	773	0
		823[807]	55	819	30	799	2
		826[809]	0	820	13	800	2
		831[814]	10	829	4	802	21
		831[814]	0	830	9	803	21
O_eUO_e asym.	842(m)	849[832]	102	848	169	848	232
		855[838]	0	854	0	851	0
		902[[884]	0	907	11	890	0
C-C rotation	910(m)	902[884]	14	907	1	898	0
		921[903]	0	919	2	898	0
C-C rotation	919(m)	924[906]	121	919	69	900	0
		927[908]	0	930	1	900	0
		935[916]	0	931	27	920	2
C-C rotation	931(m)	935[916]	38	933	20	923	0
		939[920]	0	942	50	932	42
		939[930]	82	942	12	932	33
		955[936]	87	953	62	935	132
		955[936]	0	954	38	935	124
$O_{yl}UO_{yl}$ asym.	976(s)	996[976]	98	1004	80	975	250
		1001[981]	0	1011	43	1014	256
		1006[986]	28	1013	23	1016	4

C-O stretching	1006(m)	1022[1002]	108	1023	6	1021	9
		1023[1003]	0	1024	146	1021	9
		1025[1005]	0	1030	39	1026	4
C-O stretching	1020(m)	1027[1006]	204	1033	30	1026	5
		1045[1024]	38	1051	3	1031	92
		1045[1024]	0	1051	56	1035	0
C-O stretching	1030-1060(vs)	1058[1037]	194	1058	47	1057	0
		1058[1037]	0	1059	164	1058	0
C-O stretching	1030-1060(vs)	1065[1044]	160	1064	8	1060	0
		1065[1044]	0	1065	273	1060	0
		1077[1055]	0	1068	14	1064	1
C-O stretching	1030-1060(vs)	1078[1056]	53	1068	1	1064	0
		1099[1077]	0	1100	176	1068	528
C-O stretching	1100(vs)	1099[1077]	163	1101	35	1068	527
		1112[1090]	0	1109	10	1095	0
C-C rotation	1120(vs)	1113[1091]	98	1109	3	1096	0
		1134[1111]	0	1120	20	1097	0
C-C rotation	1115(vs)	1135[1112]	125	1120	37	1098	0
		1140[1117]	10	1131	17	1104	9
		1141[1118]	0	1132	31	1106	0
		1146[1123]	0	1137	1	1121	48
C-O stretching	1131(vs)	1147[1124]	190	1138	191	1121	44
CH_2 rocking	1131(vs)	1156[1133]	64	1159	4	1123	4
		1157[1134]	0	1159	3	1123	2
		1167[1144]	0	1162	0	1149	0
C-O stretching	1142(vs)	1167[1144]	198	1163	180	1149	0
		1174[1151]	0	1168	137	1152	0
CH_2 rocking	1150(vs)	1174[1151]	55	1169	2	1152	0
		1260[1235]	0	1261	4	1268	7
		1260[1235]	3	1261	0	1270	0
		1267[1242]	10	1262	1	1273	14
		1267[1242]	0	1262	9	1273	1
		1271[1246]	0	1275	8	1274	47
CH_2 twisting	1237(m)	1271[1246]	33	1275	19	1275	35
		1277[1251]	23	1278	8	1281	0
		1277[1251]	0	1278	11	1281	0
		1286[1260]	0	1283	21	1282	0

CH_2 twisting	1249(m)	1286[1260]	24	1283	0	1283	0
		1293[1267]	8	1288	6	1312	0
		1294[1268]	0	1289	7	1312	0
		1305[1279]	0	1292	11	1315	0
		1306[1280]	8	1292	9	1315	0
		1308[1282]	0	1313	19	1336	14
CH_2 twisting	1279(m)	1308[1282]	24	1314	13	1336	17
		1317[1291]	10	1316	15	1338	9
		1317[1291]	0	1316	7	1338	12
		1319[1293]	0	1336	8	1343	38
CH_2 twisting	1291(m)	1319[1293]	33	1336	23	1345	3
		1376[1348]	0	1377	1	1388	4
		1376[1348]	4	1377	2	1395	1
CH_2 wagging	1351(m)	1385[1357]	35	1387	7	1397	12
		1385[1357]	0	1388	38	1397	16
		1393[1365]	0	1394	17	1401	6
CH_2 wagging	1351(m)	1393[1365]	50	1395	29	1401	9
		1404[1376]	14	1403	9	1415	0
		1404[1376]	0	1403	6	1416	0
		1412[1384]	0	1407	1	1416	0
		1412[1384]	9	1407	3	1417	0
		1424[1396]	3	1425	1	1432	11
		1425[1397]	0	1425	0	1436	2
		1430[1401]	0	1430	2	1437	1
		1430[1401]	2	1431	0	1437	1
		1442[1413]	0	1435	2	1437	1
		1443[1414]	9	1437	6	1440	4
		1451[1422]	2	1451	6	1441	12
		1452[1423]	0	1452	1	1442	9
		1463[1434]	4	1459	1	1443	1
		1463[1434]	0	1461	0	1444	0
		1486[1456]	3	1482	4	1474	2
		1486[1456]	0	1482	3	1475	3
CH_2 scissoring	1450(m)	1489[1459]	23	1488	22	1476	50
		1489[1459]	0	1489	1	1477	41
		1491[1461]	0	1494	15	1479	1
		1491[1461]	1	1496	2	1479	3

		1497[1467]	0	1498	9	1479	2
CH_2 scissoring	1456(m)	1497[1467]	19	1501	4	1480	2
CH_2 scissoring	1456(m)	1501[1471]	12	1503	5	1480	1
		1501[1471]	0	1504	2	1481	0
CH_2 scissoring	1456(m)	1508[1478]	23	1504	2	1493	0
		1508[1478]	0	1504	13	1494	0
		1510[1480]	0	1512	17	1495	0
		1510[1480]	20	1512	12	1496	0
		1517[1487]	11	1512	1	1500	10
		1517[1487]	0	1513	8	1501	14
		1523[1493]	22	1521	0	1501	5
		1523[1493]	0	1522	23	1502	9
		1530[1499]	17	1528	7	1506	44
		1530[1499]	0	1529	2	1508	8

[a]O_e and O_{yl} denote 15-crown-5 ether oxygen atoms and uranyl oxygen atoms, respectively. [b]Experimental frequency; w, m, s, and vs denote weak, medium, strong and very strong, respectively. [c] B3LYP values for Isomer A scaled by a factor of 0.98 are in brackets. [d]The computed IR intensities are in km/mol.

Table S3. Natural localized molecular orbitals (NLMOs) of 15-crown-5 ether and the $UO_2(15C5)_2^{2+}$ complex.[a]

Molecule	Type	Occ.	NLMO
15C5	LP_{Oe}	2.000	$98.4\%O(sp^{0.89})$
	LP_{Oe}	2.000	96.0%O(p)
$UO_2(15C5)_2^{2+}$	$\sigma_{Oe\text{-}U}$	2.000	$96.1\%O(sp^{4.77}) + 1.4\%U(s^{0.17}p^{0.02}d^{0.75}f)$
	$\pi_{Oe\text{-}U}$	2.000	$91.7\%O(sp^{2.93}) + 6.5\%U(s^{0.19}p^{0.01}d^{0.98}f)$

[a]O_e denotes crown ether oxygen atom; LP denotes lone pair.

Table S4. Energy Decomposition Analysis (EDA, in kcal/mol) for formation of $UO_2(15C5)_2^{2+}$ at the PBE/TZ2P/DZP level.

Species	Steric interaction		Orbital interaction			Total bonding energy
	electrostatic	Pauli	a_u	a_g	sum	
$UO_2(15C5)_2^{2+}$	-213.8	123.7	-121.4	-110.7	-232.1	-322.2

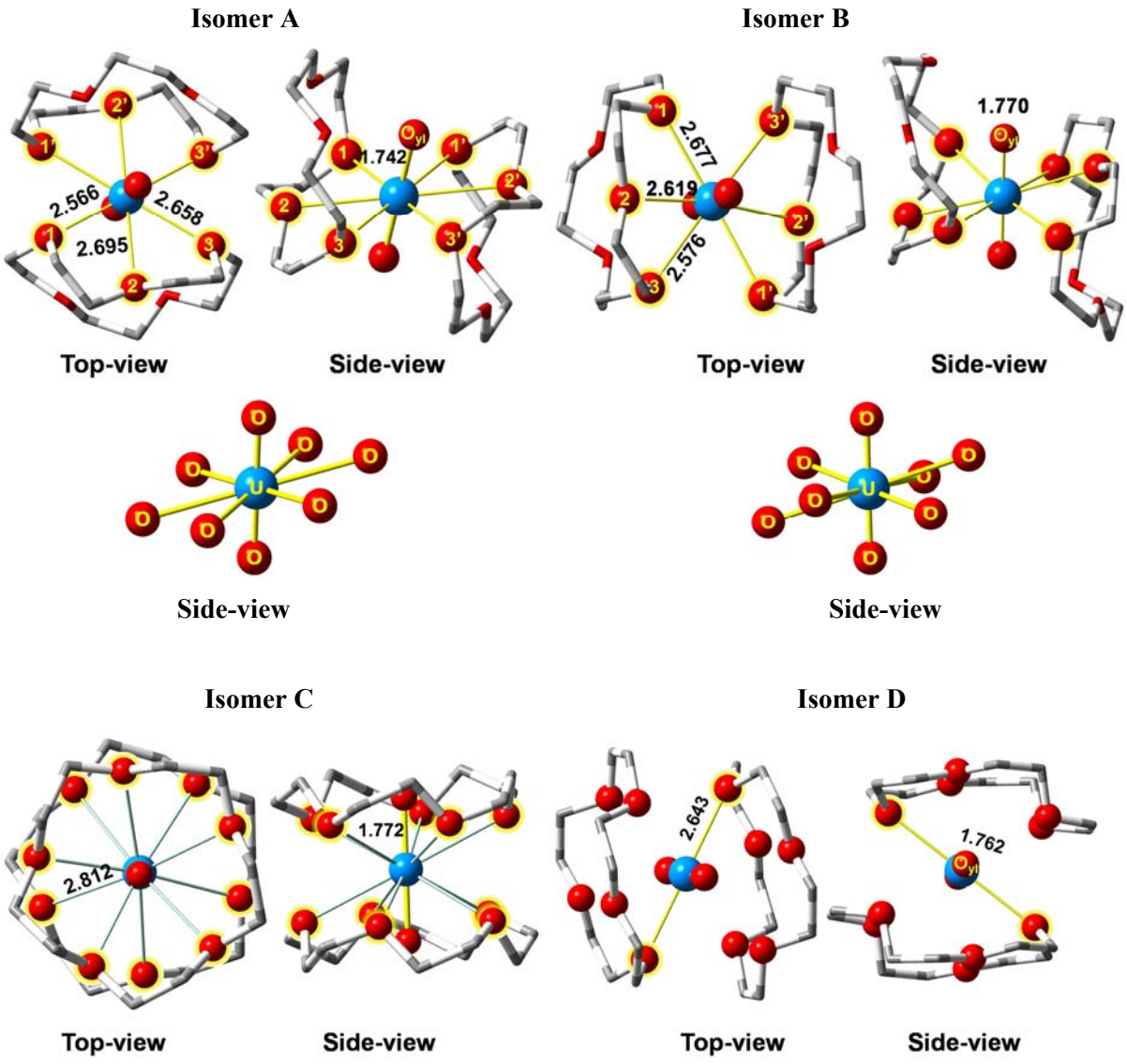
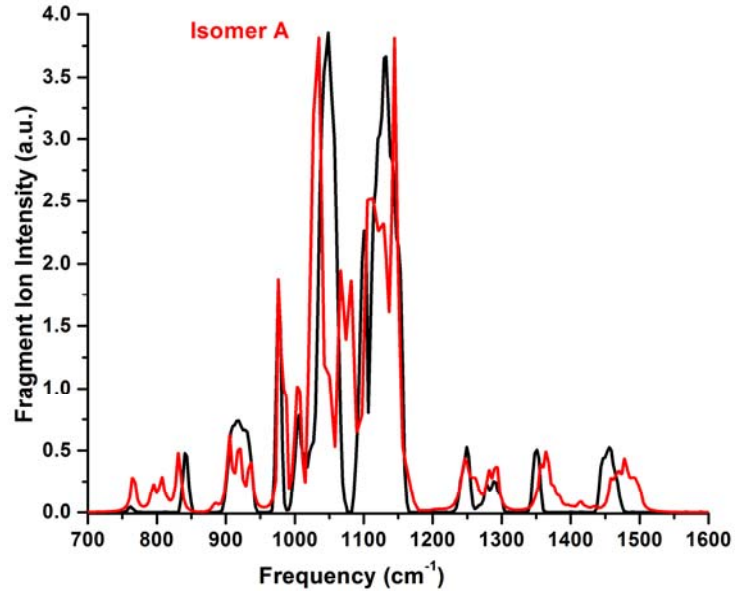
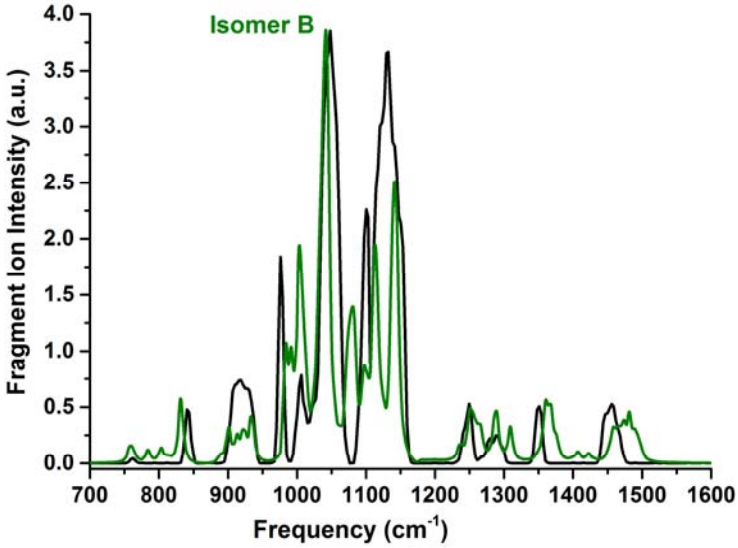
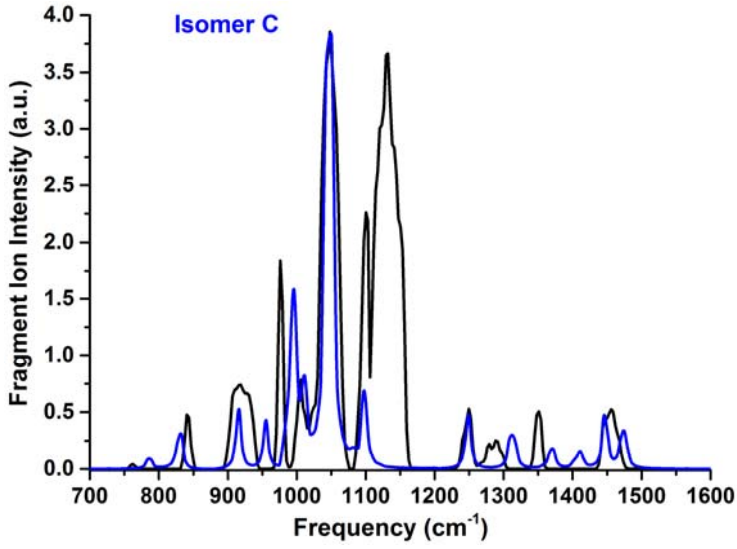


Figure S1. Optimized geometrical structures at DFT/B3LYP level


Isomer A
Fragment Ion Intensity (a.u.)
Frequency (cm-1)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
700
800
900
1000
1100
1200
1300
1400
1500
1600


Isomer B
Fragment Ion Intensity (a.u.)
Frequency (cm-1)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
700
800
900
1000
1100
1200
1300
1400
1500
1600


Isomer C
Fragment Ion Intensity (a.u.)
Frequency (cm-1)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
700
800
900
1000
1100
1200
1300
1400
1500
1600

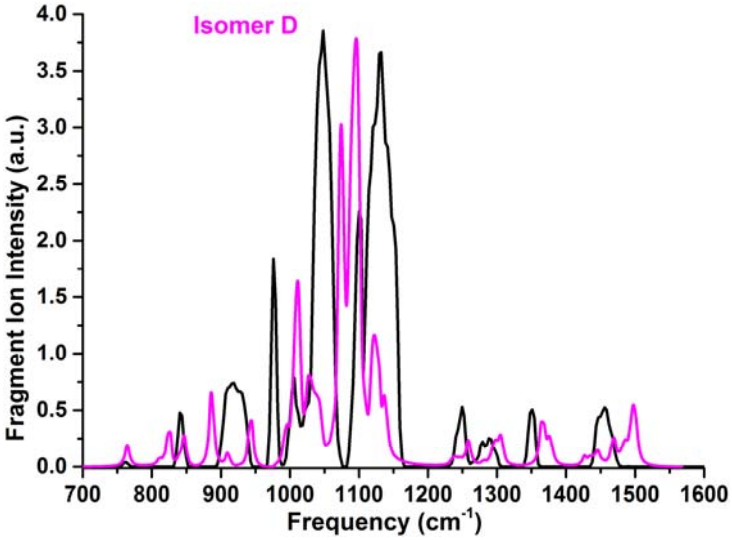


Figure S2. Comparison of B3LYP simulated (in color) and experimental (solid black) IR spectra. A scaling factor of 0.98 has been applied to the computed spectra. The best agreement between experiment and theory is for Isomer A, which is computed to be the most stable structure (B3LYP).

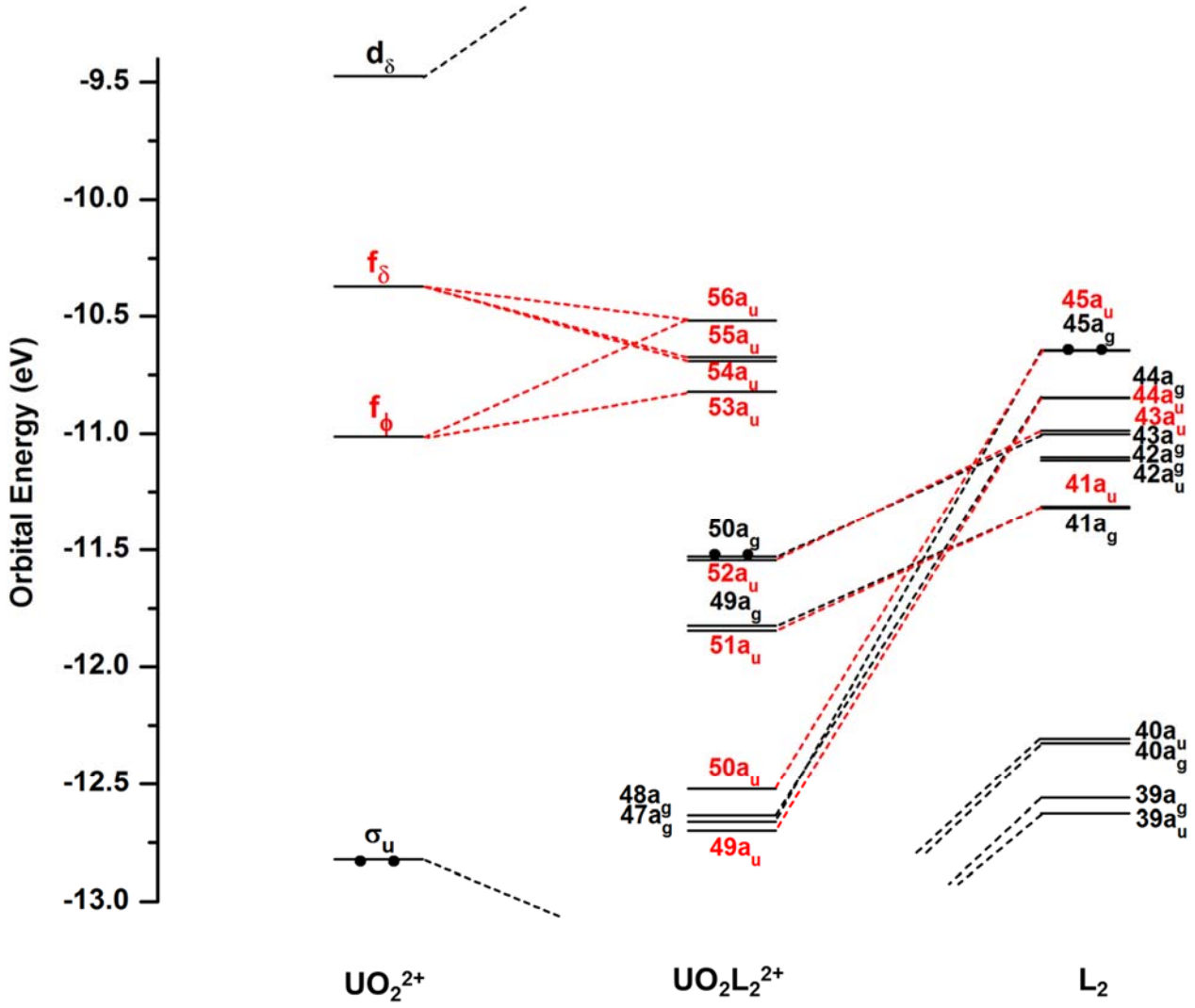


Figure S3. MO energy levels of $U^{VI}O_2(15C5)_2^{2+}$ at SR-PBE/TZ2P/DZP level. Here $50a_g$ orbital from the crown ether is the HOMO, and $53a_u$ orbital from U is the LUMO.

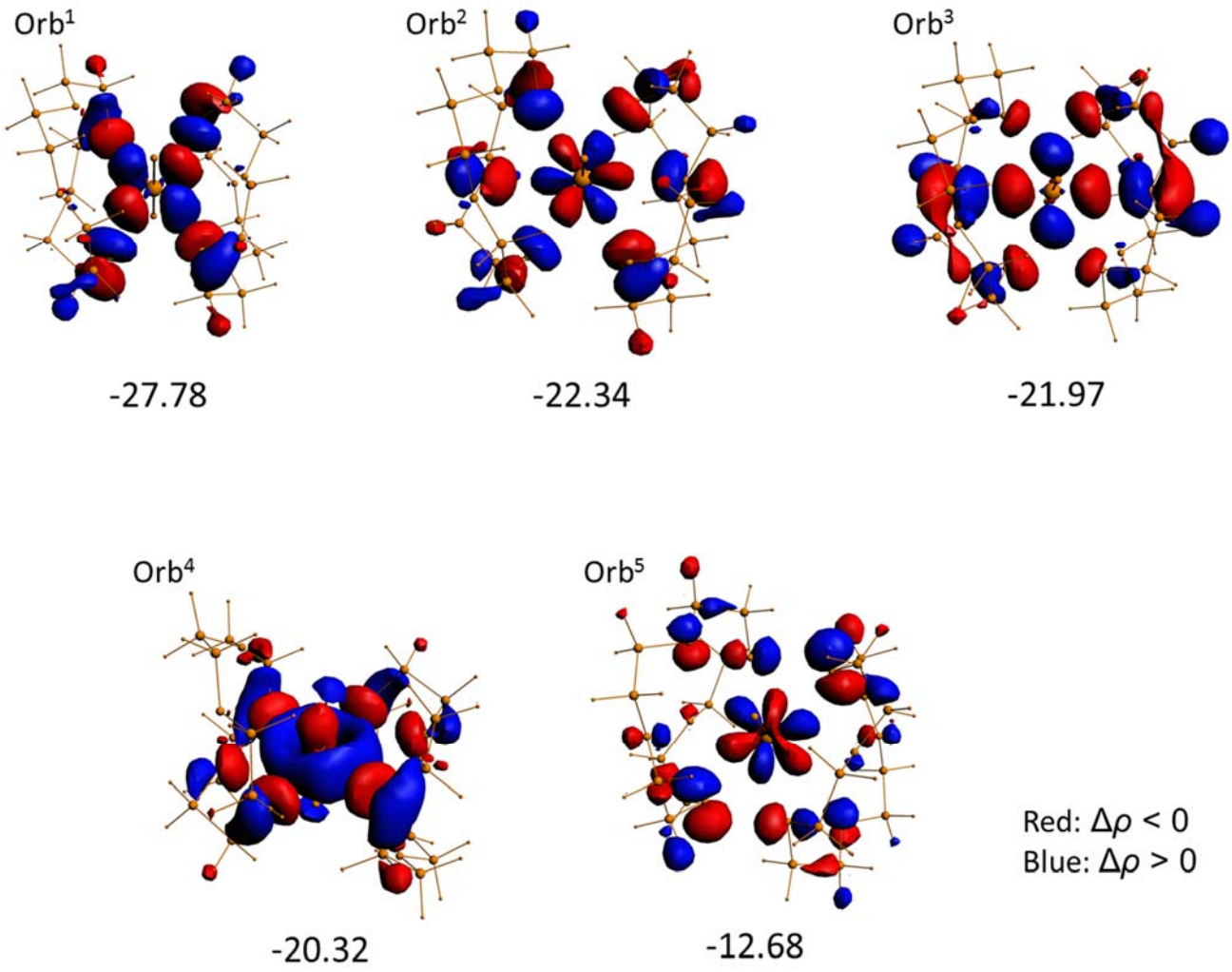


Figure S4. Plot of representative U-O bonding interactions from ETS-NOCV method from a closed-shell PBE calculation (energy unit: kcal/mol, isovalue=0.03).

Cartesian Coordinates (Å) for $UO_2(15C5)2^{2+}$ Calculated at PBE/SR-ZORA/TZ2P/DZP Level of Theory

Table S6. Coordinates and single point energy of Isomer A of $UO_2(15C5)_2^{2+}$ in C_i symmetry.

O	2.624422	0.003066	1.037438
O	1.404820	2.135712	-0.193909
O	2.837354	0.618482	-2.008500
O	2.309875	-2.127342	-1.551648
O	1.199715	-2.174563	1.057814
C	2.530366	-0.604803	2.342439
H	3.499315	-0.540074	2.865061
H	1.762778	-0.102048	2.948985
C	2.207971	-2.059794	2.099952

H	1.836697	-2.537915	3.021490
H	3.116348	-2.581396	1.770452
C	1.423353	-3.368539	0.245720
H	1.567422	-4.233754	0.913135
H	0.496668	-3.506754	-0.323131
C	2.593912	-3.222710	-0.700097
H	2.699593	-4.169790	-1.266779
H	3.543255	-3.060807	-0.156403
C	3.448141	-1.672071	-2.289881
H	4.298167	-1.486862	-1.607386
H	3.756749	-2.425710	-3.037891
C	3.063755	-0.400053	-2.997571
H	2.144778	-0.564657	-3.586296
H	3.875415	-0.092291	-3.681009
C	2.121424	1.726782	-2.528807
H	2.669163	2.227932	-3.352287
H	1.143259	1.403418	-2.926361
C	1.959829	2.734341	-1.417885
H	1.281022	3.541456	-1.731454
H	2.936510	3.167806	-1.161310
C	2.239175	2.370168	0.979621
H	2.685393	3.375198	0.924491
H	1.562898	2.330773	1.844003
C	3.284995	1.289937	1.039916
H	3.919713	1.405456	1.932463
H	3.916480	1.304442	0.140530
O	-2.309875	2.127342	1.551648
O	-1.199715	2.174563	-1.057814
O	-2.624422	-0.003066	-1.037438
O	-1.404820	-2.135712	0.193909
O	-2.837354	-0.618482	2.008500
C	-3.448141	1.672071	2.289881
H	-4.298167	1.486862	1.607386
H	-3.756749	2.425710	3.037891
C	-3.063755	0.400053	2.997571
H	-2.144778	0.564657	3.586296
H	-3.875415	0.092291	3.681009
C	-2.121424	-1.726782	2.528807
H	-2.669163	-2.227932	3.352287

H	-1.143259	-1.403418	2.926361
C	-1.959829	-2.734341	1.417885
H	-1.281022	-3.541456	1.731454
H	-2.936510	-3.167806	1.161310
C	-2.239175	-2.370168	-0.979621
H	-2.685393	-3.375198	-0.924491
H	-1.562898	-2.330773	-1.844003
C	-3.284995	-1.289937	-1.039916
H	-3.919713	-1.405456	-1.932463
H	-3.916480	-1.304442	-0.140530
C	-2.530366	0.604803	-2.342439
H	-3.499315	0.540074	-2.865061
H	-1.762778	0.102048	-2.948985
C	-2.207971	2.059794	-2.099952
H	-1.836697	2.537915	-3.021490
H	-3.116348	2.581396	-1.770452
C	-1.423353	3.368539	-0.245720
H	-1.567422	4.233754	-0.913135
H	-0.496668	3.506754	0.323131
C	-2.593912	3.222710	0.700097
H	-2.699593	4.169790	1.266779
H	-3.543255	3.060807	0.156403
U	0.000000	0.000000	0.000000
O	0.096703	-0.450901	-1.710705
O	-0.096703	0.450901	1.710705

PBE Binding Energy = -8908.58 kcal/mol

Table S7. Coordinates and single point energy of Isomer B of $UO_2(15C5)_2^{2+}$ in C_2 symmetry.

O	-2.551655	-1.586995	-2.671557
O	-1.546470	-2.179134	0.234045
O	-2.310654	0.056326	1.234222
O	-1.390249	2.156485	-0.117391
O	-2.910006	1.123480	-2.099813
C	-3.797986	-0.921707	-2.913642
H	-4.450896	-0.954916	-2.023605
H	-4.332418	-1.401913	-3.754661
C	-3.513630	0.519411	-3.252165
H	-2.825707	0.583469	-4.114458

H	-4.463281	1.021518	-3.512691
C	-2.678230	2.514681	-2.230125
H	-3.571040	3.093404	-1.925192
H	-2.447592	2.806695	-3.271828
C	-1.457111	2.874987	-1.391686
H	-0.532682	2.594759	-1.907515
H	-1.438504	3.957911	-1.183120
C	-2.594649	2.327839	0.683196
H	-3.465830	2.099169	0.055080
H	-2.647388	3.364981	1.053449
C	-2.536357	1.356889	1.826478
H	-1.722747	1.578690	2.536393
H	-3.500413	1.367140	2.361400
C	-2.537061	-1.036342	2.159966
H	-3.616973	-1.253099	2.167890
H	-2.218923	-0.754614	3.176730
C	-1.697777	-2.214754	1.673113
H	-0.679463	-2.170635	2.078691
H	-2.151130	-3.169247	1.987285
C	-2.825369	-2.525802	-0.411937
H	-3.547875	-1.719765	-0.215190
H	-3.174782	-3.453580	0.072935
C	-2.685672	-2.767403	-1.899245
H	-1.797769	-3.387047	-2.100470
H	-3.566458	-3.360734	-2.214289
U	-0.001216	-0.009947	0.000604
O	-0.337517	-0.190415	-1.727607
O	0.340838	0.286126	1.711630
O	1.543165	1.992813	-0.490173
O	3.005210	1.460708	1.720444
O	2.456275	-0.940034	3.038819
O	1.378672	-2.262473	0.412783
O	2.294184	-0.467414	-1.175321
C	2.748419	1.840017	-1.293279
H	3.607143	1.737624	-0.616620
H	2.872692	2.721361	-1.943910
C	2.607687	0.589751	-2.111972
H	1.805011	0.657991	-2.864422
H	3.564306	0.376639	-2.617071

C	2.429967	-1.792333	-1.748342
H	3.490950	-2.080869	-1.682618
H	2.122442	-1.789889	-2.806555
C	1.511882	-2.718190	-0.954583
H	0.495328	-2.717368	-1.366911
H	1.890925	-3.753109	-0.978402
C	2.635773	-2.502541	1.144366
H	3.413017	-1.841362	0.733102
H	2.911231	-3.553120	0.948473
C	2.495091	-2.298325	2.637181
H	1.566529	-2.767953	2.997803
H	3.333548	-2.839817	3.117665
C	3.750430	-0.326263	3.093441
H	4.389178	-0.659810	2.256598
H	4.257820	-0.584072	4.041922
C	3.575735	1.168291	3.003477
H	2.903816	1.525903	3.804433
H	4.562295	1.653095	3.119644
C	2.876506	2.844264	1.445944
H	3.805684	3.245455	0.997951
H	2.678865	3.437315	2.358545
C	1.675882	3.038187	0.526755
H	0.739112	2.984919	1.091382
H	1.733901	4.014929	0.017657

PBE Binding Energy = -8900.49 kcal/mol

Table S8. Coordinates and single point energy of Isomer C of $UO_2(15C5)_2^{2+}$ in D_5 symmetry.

O	-2.448767	0.657051	1.245922
O	-0.131818	2.531956	1.245922
O	2.367299	0.907783	1.245922
O	1.594889	-1.970915	1.245922
O	-1.381604	-2.125876	1.245922
C	-3.132649	-0.530228	1.725880
H	-3.871884	-0.242250	2.491971
H	-3.666371	-0.934642	0.856080
C	-2.222292	-1.594100	2.299326
H	-2.853407	-2.411460	2.693072
H	-1.606407	-1.200052	3.122387

C	-0.463766	-3.143176	1.725880
H	-0.966084	-3.757240	2.491971
H	-0.244074	-3.775746	0.856080
C	0.829353	-2.606129	2.299326
H	1.411683	-3.458933	2.693072
H	0.644911	-1.898620	3.122387
C	2.846027	-1.412362	1.725880
H	3.274811	-2.079852	2.491971
H	3.515525	-1.398897	0.856080
C	2.734860	-0.016576	2.299326
H	3.725875	0.273722	2.693072
H	2.004983	0.026641	3.122387
C	2.222707	2.270288	1.725880
H	2.990029	2.471821	2.491971
H	2.416787	2.911180	0.856080
C	0.860883	2.595884	2.299326
H	0.891034	3.628102	2.693072
H	0.594237	1.915085	3.122387
C	-1.472318	2.815477	1.725880
H	-1.426871	3.607521	2.491971
H	-2.021868	3.198105	0.856080
C	-2.202805	1.620921	2.299326
H	-3.175186	1.968569	2.693072
H	-1.637724	1.156947	3.122387
O	-1.381604	2.125876	-1.245922
O	1.594889	1.970915	-1.245922
O	2.367299	-0.907783	-1.245922
O	-0.131818	-2.531956	-1.245922
O	-2.448767	-0.657051	-1.245922
C	-2.222292	1.594100	-2.299326
H	-1.606407	1.200052	-3.122387
H	-2.853407	2.411460	-2.693072
C	-3.132649	0.530228	-1.725880
H	-3.666371	0.934642	-0.856080
H	-3.871884	0.242250	-2.491971
C	-2.202805	-1.620921	-2.299326
H	-1.637724	-1.156947	-3.122387
H	-3.175186	-1.968569	-2.693072
C	-1.472318	-2.815477	-1.725880

H	-2.021868	-3.198105	-0.856080
H	-1.426871	-3.607521	-2.491971
C	0.860883	-2.595884	-2.299326
H	0.594237	-1.915085	-3.122387
H	0.891034	-3.628102	-2.693072
C	2.222707	-2.270288	-1.725880
H	2.416787	-2.911180	-0.856080
H	2.990029	-2.471821	-2.491971
C	2.734860	0.016576	-2.299326
H	2.004983	-0.026641	-3.122387
H	3.725875	-0.273722	-2.693072
C	2.846027	1.412362	-1.725880
H	3.515525	1.398897	-0.856080
H	3.274811	2.079852	-2.491971
C	0.829353	2.606129	-2.299326
H	0.644911	1.898620	-3.122387
H	1.411683	3.458933	-2.693072
C	-0.463766	3.143176	-1.725880
H	-0.244074	3.775746	-0.856080
H	-0.966084	3.757240	-2.491971
U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.774516
O	0.000000	0.000000	-1.774516

PBE Binding Energy = -8899.67 kcal/mol

Table S9. Coordinates and single point energy of Isomer D of $UO_2(15C5)_2^{2+}$ in C_{2h} symmetry.

O	2.547068	0.762551	1.605573
O	1.154300	2.377066	0.000000
O	2.547068	0.762551	-1.605573
O	1.861464	-2.022111	-1.330314
O	1.861464	-2.022111	1.330314
C	2.889797	-0.244717	2.573217
H	3.814011	0.048973	3.102780
H	2.076848	-0.355767	3.310878
C	3.118013	-1.544622	1.862908
H	3.506646	-2.279256	2.589215
H	3.860194	-1.415150	1.057522

C	1.973220	-3.339436	0.777268
H	2.879044	-3.831583	1.162394
H	1.109897	-3.911626	1.144017
C	1.973220	-3.339436	-0.777268
H	1.109897	-3.911626	-1.144017
H	2.879044	-3.831583	-1.162394
C	3.118013	-1.544622	-1.862908
H	3.860194	-1.415150	-1.057522
H	3.506646	-2.279256	-2.589215
C	2.889797	-0.244717	-2.573217
H	2.076848	-0.355767	-3.310878
H	3.814011	0.048973	-3.102780
C	2.012596	1.916615	-2.260241
H	2.740826	2.336344	-2.980031
H	1.099827	1.651213	-2.815448
C	1.756808	2.962247	-1.204918
H	1.098992	3.753104	-1.596695
H	2.711467	3.414115	-0.907571
C	1.756808	2.962247	1.204918
H	2.711467	3.414115	0.907571
H	1.098992	3.753104	1.596695
C	2.012596	1.916615	2.260241
H	1.099827	1.651213	2.815448
H	2.740826	2.336344	2.980031
O	-1.861464	2.022111	1.330314
O	-1.861464	2.022111	-1.330314
O	-2.547068	-0.762551	-1.605573
O	-1.154300	-2.377066	0.000000
O	-2.547068	-0.762551	1.605573
C	-3.118013	1.544622	1.862908
H	-3.860194	1.415150	1.057522
H	-3.506646	2.279256	2.589215
C	-2.889797	0.244717	2.573217
H	-2.076848	0.355767	3.310878
H	-3.814011	-0.048973	3.102780
C	-2.012596	-1.916615	2.260241
H	-2.740826	-2.336344	2.980031
H	-1.099827	-1.651213	2.815448
C	-1.756808	-2.962247	1.204918

H	-1.098992	-3.753104	1.596695
H	-2.711467	-3.414115	0.907571
C	-1.756808	-2.962247	-1.204918
H	-2.711467	-3.414115	-0.907571
H	-1.098992	-3.753104	-1.596695
C	-2.012596	-1.916615	-2.260241
H	-1.099827	-1.651213	-2.815448
H	-2.740826	-2.336344	-2.980031
C	-2.889797	0.244717	-2.573217
H	-3.814011	-0.048973	-3.102780
H	-2.076848	0.355767	-3.310878
C	-3.118013	1.544622	-1.862908
H	-3.506646	2.279256	-2.589215
H	-3.860194	1.415150	-1.057522
C	-1.973220	3.339436	-0.777268
H	-2.879044	3.831583	-1.162394
H	-1.109897	3.911626	-1.144017
C	-1.973220	3.339436	0.777268
H	-1.109897	3.911626	1.144017
H	-2.879044	3.831583	1.162394
U	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.761530
O	0.000000	0.000000	1.761530

PBE Binding Energy = -8876.13 kcal/mol