# Supporting Information

# Crown Ether Complexes of Actinyls: A Computational Assessment of $AnO_2(15\text{-crown-}5)^{2+}$ (An=U, Np, Pu, Am, Cm)

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**Table S1**. Relative energies (kcal/mol) and binding energy (BE, kcal/mol) of $AnO_2(15C5)^{2+}$ (An = U, Np, Pu) isomers computed at PBE levels of theory.

| | | | Relative E (kcal/mol) | | BDE(kcal/mol) | |
|---|---|---|---|---|---|---|
| Molecule | Isomer | GS | SR | SO | SR | SO |
| $UO_2(15C5)^{2+}$ | Insertion-1 | $^1A$ | 0 | 0 | -233.88 | -235.69 |
| | Insertion-2 | $^1A$ | 0.01 | 0.02 | -233.87 | -235.67 |
| | Insertion-3 | $^1A$ | 2.52 | 2.62 | -231.36 | -233.07 |
| | Side-on | $^1A$ | 15.61 | 15.79 | -218.27 | -219.9 |
| $NpO_2(15C5)^{2+}$ | Insertion-1 | $^2A$ | 0 | 0 | -232.93 | -229.8 |
| | Insertion-2 | $^2A$ | 0.03 | 0.15 | -232.9 | -229.65 |
| | Insertion-3 | $^2A$ | 2.89 | 2.53 | -230.04 | -227.27 |
| | Side-on | $^2A$ | 18.92 | 22.75 | -214.01 | -207.05 |
| $PuO_2(15C5)^{2+}$ | Insertion-1 | $^3A$ | 0 | 0 | -240.23 | -232.87 |
| | Insertion-2 | $^3A$ | 0.02 | 0.84 | -240.21 | -232.00 |
| | Insertion-3 | $^3A$ | 1.98 | 2.56 | -238.25 | -230.28 |
| | Side-on | $^3A$ | 30.86 | 32.87 | -209.37 | -200.00 |

**Table S2**. Selected bond lengths (Å) and bond angles (degree) of the ground state $AnO_2(15C5)^{2+}$ insertion isomers at B3LYP level.

| Species[a] | Insertion | | | | Side-on | | |
|---|---|---|---|---|---|---|---|
| | An-$O_{yl}$[c] (complex) | An-$O_e$[d] | ∠$O_{yl}$-An-$O_e$[d] | ∠$O_{yl}$-An-$O_{yl}$ | An-$O_{yl}$ | An-$O_e$[d] | ∠$O_{yl}$-An-$O_{yl}$ |
| $UO_2(L)^{2+}$ | 1.782<br>1.785 | 2.382, 2.424, 2.422, 2.411, 2.418 (2.411) | 85.3, 90.8, 91.8, 94.6, 96.3 (91.8) | 178.6 | 1.813<br>1.813 | 2.513, 2.529, 2.545, 2.499, 2.587 (2.535) | 102.2 |
| $NpO_2(L)^{2+}$ | 1.763<br>1.765 | 2.362, 2.407, 2.410, 2.416, 2.426 (2.404) | 84.7, 90.7, 91.3, 95.2, 96.0 (91.6) | 179.1 | 1.801<br>1.805 | 2.498, 2.509, 2.509, 2.511, 2.543 (2.514) | 100.7 |
| $PuO_2(L)^{2+}$ | 1.756<br>1.759 | 2.376, 2.403, 2.403, 2.408, 2.417 (2.401) | 94.1, 95.0, 98.9, 88.8, 100.5 (95.5) | 179.2 | 1.803<br>1.808 | 2.490, 2.496, 2.487, 2.505, 2.526 (2.501) | 97.2 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $AmO_2(L)^{2+}$ | 1.750<br>1.751 | 2.380,2.381,2.387,<br>2.413, 2.424 (2.397) | 84.7, 89.8, 90.8,<br>95.6, 95.4 (91.3) | 179.8 | 1.833<br>1.831 | 2.513, 2.478, 2.504,<br>2.453, 2.500 (2.490) | 96.5 |
| $CmO_2(L)^{2+}$ | 1.759<br>1.760 | 2.344, 2.386, 2.388,<br>2.397, 2.399 (2.383) | 85.0, 88.7, 90.0,<br>94.9, 95.1 (90.7) | 179.5 | 1.882<br>1.861 | 2.430, 2.480, 2.552,<br>2.451, 2.475 (2.478) | 86.3 |

[a] L denotes the 15−crown−5 ether. [b] PBE calculated for isolated actinyl. [c] PBE calculated for actinyl complex. [d] Average in parentheses. [e] EXAFS value for $UO_2^{2+}$, $NpO_2^{2+}$, XANES value for $PuO_2^{2+}$ ions with water. [f] XRD values for $UO_2^{2+}$, $NpO_2^{2+}$, and $PuO_2^{2+}$ ions with carbonate.

**Table S3**. Selected bond lengths (Å) and bond angles (degree) of the ground state $AnO_2(15C5)^{2+}$ insertion isomers at B3LYP.

| Species[a] | Insertion | | | Side-on | | |
|---|---|---|---|---|---|---|
| | An-$O_{yl}$[c] (complex) | An-$O_e$[d] | ∠$O_{yl}$-An-$O_{yl}$ | An-$O_{yl}$ | An-$O_e$[d] | ∠$O_{yl}$-An-$O_{yl}$ |
| $UO_2(L)^{2+}$ | 1.753<br>1.754 | 2.396, 2.403, 2.365, 2.410,<br>2.406 (2.396) | 179.1 | 1.783<br>1.783 | 2.494, 2.542, 2.587, 2.498,<br>2.529 (2.530) | 103.5 |
| $NpO_2(L)^{2+}$ | 1.739<br>1.740 | 2.357, 2.397, 2.394, 2.396,<br>2.401 (2.389) | 179.4 | 1.771<br>1.773 | 2.490, 2.500, 2.512, 2.516,<br>2.552 (2.514) | 106.1 |
| $PuO_2(L)^{2+}$ | 1.712<br>1.714 | 2.381, 2.388, 2.353, 2.384,<br>2.396 (2.380) | 179.6 | 1.782<br>1.784 | 2.476, 2.504, 2.489, 2.513,<br>2.484 (2.493) | 97.2 |
| $AmO_2(L)^{2+}$ | 1.714<br>1.715 | 2.391,2.347,2.383, 2.385,<br>2.374 (2.376) | 179.7 | 1.857<br>1.980 | 2.509, 2.422, 2.460, 2.473,<br>2.469 (2.467) | 82.6 |
| $CmO_2(L)^{2+}$ | 1.732<br>1.732 | 2.341, 2.389, 2.382, 2.378,<br>2.392 (2.376) | 179.7 | 2.307<br>2.310 | 2.417, 2.450, 2.437, 2.468,<br>2.472 (2.449) | 57.9 |

**Table S4.** Calculated vibrational frequencies ($cm^{-1}$) and intensities (in parentheses, km/mol) of ground-state $AnO_2(15C5)^{2+}$ (An = U, Np, Pu, Am, Cm) at PBE/TZ2P level.

| Molecule | $An-O_{yl}$ | | $An-O_e$ | C−O |
|---|---|---|---|---|
| | asym. | sym. | | |
| $UO_2(15C5)^{2+}$ | 962(144) | 874(0) | 385(35), 378(36), 372(5), 346(2), 336(1) | 982(397), 977(364) |
| $NpO_2(15C5)^{2+}$ | 967(118) | 868(0) | 384(29), 376(35), 367(6), 343(2), 333(1) | 985(391), 981(318) |
| $PuO_2(15C5)^{2+}$ | 961(136) | 844(0) | 378(24), 372(27), 362(1), 347(1), 339(2) | 993(346), 984(360) |
| $AmO_2(15C5)^{2+}$ | 948(113) | 820(0) | 380(21), 369(23), 353(2), 353(2), 344(5) | 991(344), 986(180) |
| $CmO_2(15C5)^{2+}$ | 907(69) | 752(5) | 382(14), 370(17), 359(2), 350(0), 344(1) | 994(396), 968(3) |

**Table S5.** Observed and calculated (PBE level; unscaled) vibrational frequencies (in $cm^{-1}$) of $UO_2(15C5)^{2+}$.

| IR Mode[a] | Exptl.[b] | | Inclusion | | Sleeping | |
|---|---|---|---|---|---|---|
| | | Freq.[c] | Freq.[d] | Inten.[e] | Freq. | Inten.[e] |
| | | 739 | 724 | 16 | 762 | 10 |
| | | 755 | 740 | 10 | 782 | 21 |
| | | 759 | 744 | 26 | 785 | 16 |
| | | 762 | 747 | 38 | 797 | 45 |
| | | 796 | 780 | 1 | 830 | 64 |
| | | 861 | 844 | 14 | 848 | 105 |
| | | 870 | 853 | 0 | 885 | 58 |
| $O_{yl}UO_{yl}$ sym. | | 874 | 857 | 0 | 887 | 29 |
| | | 878 | 860 | 7 | 907 | 6 |
| | | 890 | 872 | 128 | 911 | 43 |
| | | 893 | 875 | 107 | 924 | 118 |
| | | 934 | 915 | 6 | 932 | 114 |
| | | 956 | 937 | 20 | 953 | 1 |
| | | 960 | 941 | 49 | 969 | 5 |
| $O_{yl}UO_{yl}$ asym. | 908(m) | 962 | 943 | 144 | 979 | 15 |
| | | 965 | 946 | 63 | 1012 | 44 |
| C-O stretching | 967(s) | 977 | 957 | 364 | 1017 | 90 |
| | | 982 | 962 | 397 | 1022 | 199 |
| | | 999 | 979 | 24 | 1026 | 204 |
| | | 1005 | 985 | 10 | 1032 | 62 |
| | | 1019 | 999 | 7 | 1036 | 14 |
| C-O stretching | 1002(vs) | 1027 | 1006 | 20 | 1048 | 15 |
| | | 1046 | 1025 | 1 | 1066 | 2 |
| | | 1054 | 1033 | 2 | 1077 | 1 |
| | | 1066 | 1045 | 2 | 1083 | 11 |
| | | 1080 | 1058 | 11 | 1102 | 2 |
| | | 1088 | 1066 | 1 | 1105 | 1 |
| | | 1188 | 1164 | 0 | 1201 | 2 |
| | | 1193 | 1169 | 2 | 1206 | 2 |
| | | 1199 | 1175 | 3 | 1209 | 2 |
| | | 1203 | 1179 | 20 | 1215 | 10 |
| | | 1212 | 1188 | 12 | 1221 | 24 |
| | | 1225 | 1201 | 0 | 1232 | 2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | 1228 | 1203 | 6 | 1237 | 1 |
| | | 1245 | 1220 | 33 | 1257 | 17 |
| | | 1248 | 1223 | 28 | 1258 | 15 |
| | | 1257 | 1232 | 1 | 1269 | 9 |
| | | 1302 | 1276 | 1 | 1312 | 0 |
| | | 1313 | 1287 | 6 | 1324 | 3 |
| | | 1316 | 1290 | 5 | 1325 | 3 |
| | | 1328 | 1301 | 0 | 1344 | 0 |
| | | 1336 | 1309 | 1 | 1349 | 2 |
| | | 1356 | 1329 | 1 | 1364 | 3 |
| | | 1357 | 1330 | 0 | 1374 | 1 |
| | | 1373 | 1346 | 4 | 1390 | 4 |
| | | 1377 | 1349 | 5 | 1403 | 4 |
| | | 1386 | 1358 | 0 | 1413 | 1 |
| | | 1426 | 1397 | 6 | 1431 | 4 |
| | | 1428 | 1399 | 5 | 1433 | 4 |
| | | 1428 | 1399 | 4 | 1435 | 12 |
| | | 1429 | 1400 | 9 | 1436 | 4 |
| | | 1430 | 1401 | 4 | 1438 | 5 |
| | | 1436 | 1407 | 7 | 1443 | 7 |
| | | 1441 | 1412 | 39 | 1446 | 29 |
| | | 1442 | 1413 | 9 | 1450 | 31 |
| | | 1443 | 1414 | 41 | 1452 | 12 |
| | | 1444 | 1415 | 2 | 1454 | 15 |

[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]PBE values of $UO_2(15C5)^{2+}$ without scaled. [d]PBE values scaled by a factor of 0.98.

**Table S6.** Observed and calculated (PBE level; unscaled) vibrational frequencies (in $cm^{-1}$) of $NpO_2(15C5)^{2+}$.

| IR Mode[a] | Inclusion | | Side-on | |
|---|---|---|---|---|
| | Freq.[b] | Inten. | Freq. | Inten. |
| | 738 | 16 | 756 | 16 |
| | 757 | 10 | 782 | 20 |
| | 761 | 35 | 786 | 19 |
| | 764 | 28 | 795 | 42 |
| | 797 | 1 | 822 | 88 |
| | 863 | 15 | 826 | 58 |
| $O_{yl}NpO_{yl}$ sym. | 868 | 0 | 862 | 49 |
| | 875 | 0 | 882 | 3 |
| | 879 | 4 | 903 | 41 |
| | 894 | 118 | 917 | 31 |
| | 896 | 109 | 925 | 91 |
| | 936 | 11 | 934 | 128 |
| | 959 | 11 | 951 | 1 |
| | 961 | 15 | 965 | 22 |
| $O_{yl}NpO_{yl}$ asym. | 967 | 118 | 976 | 5 |
| | 968 | 86 | 1009 | 33 |
| | 981 | 318 | 1017 | 138 |
| C-O stretching | 985 | 391 | 1024 | 203 |
| | 1003 | 38 | 1030 | 59 |
| | 1008 | 5 | 1032 | 89 |
| | 1020 | 6 | 1036 | 31 |
| | 1029 | 19 | 1045 | 10 |
| | 1046 | 1 | 1065 | 0 |
| | 1054 | 2 | 1074 | 28 |
| | 1066 | 1 | 1087 | 2 |
| | 1079 | 10 | 1096 | 12 |
| | 1090 | 1 | 1107 | 2 |
| | 1188 | 0 | 1201 | 0 |
| | 1194 | 1 | 1207 | 2 |
| | 1200 | 2 | 1215 | 0 |
| | 1204 | 20 | 1219 | 3 |
| | 1212 | 13 | 1224 | 34 |
| | 1225 | 0 | 1233 | 2 |

| | | | | |
|---|---|---|---|---|
| | 1229 | 4 | 1234 | 0 |
| | 1245 | 31 | 1254 | 17 |
| | 1248 | 28 | 1255 | 10 |
| | 1258 | 1 | 1269 | 1 |
| | 1303 | 1 | 1312 | 0 |
| | 1313 | 3 | 1324 | 3 |
| | 1316 | 2 | 1325 | 2 |
| | 1329 | 0 | 1344 | 1 |
| | 1335 | 1 | 1347 | 0 |
| | 1355 | 0 | 1365 | 0 |
| | 1357 | 1 | 1375 | 3 |
| | 1373 | 7 | 1392 | 2 |
| | 1377 | 8 | 1401 | 6 |
| | 1388 | 1 | 1414 | 3 |
| | 1425 | 6 | 1429 | 2 |
| | 1427 | 4 | 1433 | 6 |
| | 1427 | 8 | 1433 | 4 |
| | 1428 | 5 | 1437 | 3 |
| | 1429 | 4 | 1441 | 2 |
| | 1434 | 7 | 1442 | 13 |
| | 1441 | 42 | 1444 | 35 |
| | 1442 | 9 | 1451 | 23 |
| | 1442 | 39 | 1452 | 24 |
| | 1443 | 1 | 1453 | 6 |

[a]$O_e$ and $O_{yl}$ denote 15-crown-5 ether oxygen atoms and uranyl oxygen atoms, respectively. [b]PBE values of $NpO_2(15C5)^{2+}$ without scaled.

**Table S7.** Observed and calculated (PBE level; unscaled) vibrational frequencies (in $cm^{-1}$) of $PuO_2(15C5)^{2+}$.

| IR Mode[a] | Inclusion | | Side-on | |
|---|---|---|---|---|
| | Freq.[b] | Inten. | Freq. | Inten. |
| | 737 | 13 | 759 | 12 |
| | 761 | 9 | 779 | 28 |
| | 765 | 27 | 784 | 37 |
| | 771 | 34 | 787 | 38 |
| | 802 | 2 | 798 | 41 |
| | 844 | 0 | 806 | 88 |
| | 868 | 17 | 840 | 0 |
| | 878 | 0 | 883 | 2 |
| | 883 | 6 | 907 | 34 |
| | 897 | 112 | 919 | 17 |
| | 902 | 88 | 927 | 88 |
| | 941 | 7 | 936 | 120 |
| $O_{yl}PuO_{yl}$ asym. | 961 | 136 | 954 | 1 |
| | 965 | 10 | 966 | 17 |
| | 965 | 15 | 976 | 6 |
| | 970 | 20 | 1010 | 42 |
| C-O stretching | 984 | 360 | 1017 | 114 |
| | 993 | 346 | 1025 | 187 |
| | 1009 | 29 | 1031 | 72 |
| | 1016 | 13 | 1033 | 87 |
| | 1022 | 5 | 1039 | 19 |
| | 1032 | 19 | 1045 | 10 |
| | 1047 | 1 | 1064 | 0 |
| | 1058 | 2 | 1074 | 24 |
| | 1067 | 2 | 1086 | 1 |
| | 1083 | 10 | 1096 | 15 |
| | 1091 | 2 | 1106 | 2 |
| | 1189 | 0 | 1200 | 0 |
| | 1194 | 2 | 1207 | 1 |
| | 1200 | 1 | 1215 | 1 |
| | 1205 | 22 | 1219 | 2 |
| | 1213 | 9 | 1224 | 31 |
| | 1225 | 0 | 1231 | 2 |

| | | | | |
|---|---|---|---|---|
| | 1231 | 7 | 1233 | 0 |
| | 1248 | 32 | 1252 | 17 |
| | 1249 | 20 | 1255 | 10 |
| | 1259 | 1 | 1267 | 1 |
| | 1304 | 0 | 1311 | 0 |
| | 1313 | 2 | 1323 | 1 |
| | 1318 | 3 | 1324 | 1 |
| | 1330 | 0 | 1344 | 1 |
| | 1338 | 1 | 1346 | 0 |
| | 1355 | 1 | 1365 | 0 |
| | 1358 | 1 | 1373 | 2 |
| | 1374 | 8 | 1392 | 3 |
| | 1379 | 10 | 1400 | 10 |
| | 1390 | 1 | 1414 | 3 |
| | 1425 | 4 | 1428 | 2 |
| | 1426 | 6 | 1432 | 6 |
| | 1426 | 6 | 1433 | 4 |
| | 1432 | 9 | 1435 | 2 |
| | 1432 | 7 | 1442 | 10 |
| | 1433 | 1 | 1443 | 26 |
| | 1441 | 16 | 1443 | 17 |
| | 1442 | 42 | 1450 | 34 |
| | 1445 | 15 | 1451 | 15 |
| | 1446 | 17 | 1452 | 6 |

[a]$O_e$ and $O_{yl}$ denote 15-crown-5 ether oxygen atoms and uranyl oxygen atoms, respectively. [b]PBE values of $PuO_2(15C5)^{2+}$ without scaled.

**Table S8.** Observed and calculated (PBE level; unscaled) vibrational frequencies (in $cm^{-1}$) of $AmO_2(15C5)^{2+}$.

| IR Mode[a] | Inclusion | | Side-on | |
|---|---|---|---|---|
| | Freq.[b] | Inten. | Freq. | Inten. |
| | 744 | 10 | 680 | 23 |
| | 753 | 9 | 715 | 48 |
| | 766 | 36 | 749 | 17 |
| | 771 | 21 | 779 | 22 |
| | 799 | 3 | 784 | 17 |
| | 820 | 0 | 796 | 36 |
| | 864 | 15 | 831 | 6 |
| | 879 | 18 | 884 | 1 |
| | 886 | 0 | 898 | 46 |
| | 903 | 71 | 915 | 12 |
| | 905 | 75 | 924 | 76 |
| | 943 | 6 | 932 | 101 |
| $O_{yl}AmO_{yl}$ asym. | 948 | 113 | 949 | 2 |
| | 953 | 47 | 962 | 28 |
| | 968 | 32 | 970 | 6 |
| | 971 | 13 | 1002 | 67 |
| C-O stretching | 986 | 180 | 1011 | 49 |
| | 991 | 344 | 1019 | 144 |
| | 1009 | 77 | 1027 | 80 |
| | 1019 | 7 | 1032 | 68 |
| | 1022 | 11 | 1037 | 20 |
| | 1030 | 14 | 1042 | 40 |
| | 1045 | 2 | 1066 | 1 |
| | 1059 | 1 | 1073 | 21 |
| | 1071 | 2 | 1082 | 3 |
| | 1082 | 26 | 1093 | 10 |
| | 1092 | 2 | 1105 | 4 |
| | 1188 | 1 | 1198 | 0 |
| | 1195 | 1 | 1203 | 1 |
| | 1200 | 1 | 1211 | 1 |
| | 1205 | 18 | 1217 | 2 |
| | 1211 | 12 | 1221 | 30 |
| | 1225 | 0 | 1232 | 2 |

| | | | | |
|---|---|---|---|---|
| | 1233 | 3 | 1234 | 0 |
| | 1247 | 29 | 1252 | 16 |
| | 1250 | 20 | 1255 | 10 |
| | 1259 | 1 | 1268 | 1 |
| | 1302 | 0 | 1310 | 0 |
| | 1313 | 1 | 1321 | 1 |
| | 1315 | 1 | 1323 | 1 |
| | 1327 | 0 | 1343 | 1 |
| | 1336 | 1 | 1344 | 2 |
| | 1353 | 1 | 1361 | 3 |
| | 1355 | 1 | 1371 | 5 |
| | 1373 | 12 | 1386 | 3 |
| | 1375 | 13 | 1399 | 6 |
| | 1392 | 5 | 1412 | 4 |
| | 1421 | 11 | 1423 | 2 |
| | 1423 | 6 | 1429 | 2 |
| | 1428 | 5 | 1434 | 8 |
| | 1430 | 6 | 1435 | 9 |
| | 1431 | 5 | 1437 | 2 |
| | 1439 | 7 | 1438 | 39 |
| | 1442 | 37 | 1439 | 11 |
| | 1443 | 13 | 1445 | 38 |
| | 1445 | 34 | 1452 | 9 |
| | 1446 | 1 | 1453 | 13 |

[a]$O_e$ and $O_{yl}$ denote 15-crown-5 ether oxygen atoms and uranyl oxygen atoms, respectively. [b]PBE values of $AmO_2(15C5)^{2+}$ without scaled.

**Table S9.** Observed and calculated (PBE level; unscaled) vibrational frequencies (in $cm^{-1}$) of $CmO_2(15C5)^{2+}$.

| IR Mode[a] | Inclusion | | Side-on | |
|---|---|---|---|---|
| | Freq.[b] | Inten. | Freq. | Inten. |
| | 751 | 3 | 610 | 21 |
| | 752 | 5 | 761 | 3 |
| | 765 | 7 | 774 | 30 |
| | 772 | 37 | 776 | 13 |
| | 774 | 38 | 798 | 41 |
| | 814 | 0 | 830 | 14 |
| | 873 | 4 | 888 | 1 |
| | 878 | 1 | 897 | 37 |
| | 886 | 6 | 907 | 19 |
| | 899 | 101 | 919 | 79 |
| | 905 | 67 | 927 | 72 |
| $O_{yl}CmO_{yl}$ asym. | 907 | 69 | 947 | 0 |
| | 948 | 5 | 962 | 19 |
| | 968 | 3 | 975 | 9 |
| | 968 | 7 | 1003 | 18 |
| | 971 | 31 | 1008 | 146 |
| | 991 | 354 | 1016 | 86 |
| C-O stretching | 994 | 396 | 1026 | 135 |
| | 1012 | 6 | 1032 | 76 |
| | 1017 | 16 | 1037 | 34 |
| | 1026 | 6 | 1050 | 31 |
| | 1030 | 12 | 1063 | 2 |
| | 1051 | 1 | 1072 | 3 |
| | 1058 | 6 | 1079 | 7 |
| | 1069 | 3 | 1097 | 14 |
| | 1082 | 22 | 1102 | 4 |
| | 1090 | 2 | 1195 | 2 |
| | 1191 | 0 | 1200 | 4 |
| | 1197 | 0 | 1205 | 5 |
| | 1202 | 3 | 1211 | 10 |
| | 1206 | 19 | 1217 | 23 |
| | 1212 | 15 | 1232 | 0 |
| | 1226 | 0 | 1235 | 2 |

| | | | | |
|---|---|---|---|---|
| | 1229 | 5 | 1256 | 7 |
| | 1246 | 25 | 1257 | 12 |
| | 1248 | 18 | 1268 | 6 |
| | 1257 | 0 | 1309 | 0 |
| | 1304 | 0 | 1319 | 1 |
| | 1315 | 3 | 1322 | 1 |
| | 1317 | 4 | 1341 | 1 |
| | 1329 | 0 | 1346 | 4 |
| | 1336 | 1 | 1359 | 7 |
| | 1357 | 1 | 1368 | 5 |
| | 1358 | 0 | 1387 | 7 |
| | 1375 | 6 | 1398 | 11 |
| | 1379 | 6 | 1409 | 4 |
| | 1389 | 0 | 1418 | 6 |
| | 1431 | 3 | 1421 | 5 |
| | 1431 | 13 | 1432 | 15 |
| | 1432 | 2 | 1434 | 24 |
| | 1432 | 7 | 1436 | 27 |
| | 1432 | 8 | 1437 | 4 |
| | 1439 | 6 | 1438 | 33 |
| | 1444 | 48 | 1444 | 4 |
| | 1445 | 6 | 1453 | 8 |
| | 1446 | 25 | 1454 | 19 |
| | 1447 | 1 | | |

[a]$O_e$ and $O_{yl}$ denote 15-crown-5 ether oxygen atoms and uranyl oxygen atoms, respectively. [b]PBE values of $CmO_2(15C5)^{2+}$ without scaled.

**Table S10.** The calculated natural localized molecular orbitals (NLMOs) of 15-crown-5 ether and $AnO_2(15C5)^{2+}$ (An = U, Np, Pu) complexes.

| Molecule | | Type | Occ. | NLMO |
|---|---|---|---|---|
| 15C5 | | $LP_{Oe}$ | 5*2.00 | 98.23%O(44%s/55%p) |
| | | $LP_{Oe}$ | 5*2.00 | 95.8%O(100%p) |
| $UO_2(15C5)^{2+}$ | Inclusion | $\sigma_{Oe-U}$ | 5*2.00 | 90.5%O(28%s/72%p) + 7.8%U(14%s/47%d/39%f)<br>90.5%O(29%s/71%p) + 7.9%U(14%s/47%d/39%f)<br>90.6%O(30%s/70%p) + 7.8%U(14%s/48%d/38%f)<br>90.7%O(30%s/70%p) + 7.8%U(15%s/49%d/36%f)<br>91.4%O(42%s/58%p) + 7.6%U(15%s/49%d/36%f) |
| | | $\pi_{Oe-U}$ | 5*2.00 | 96.0%O(21%s/79%p) + 2.1%U(31%d/64%f)<br>95.9%O(19%s/81%p) + 2.1%U(30%d/65%f)<br>95.7%O(17%s/83%p) + 2.2%U(31%d/64%f)<br>95.8%O(17%s/83%p) + 2.2%U(31%d/65%f)<br>93.7%O(96%p/4%d) + 3.6%U(33% d/63%f) |
| | Side-on | $\sigma_{Oe-U}$ | 5*2.00 | 91.8%O(28%s/72%p) + 6.8%U(14%s/52%d/34%f)<br>89.7%O(20%s80%p) + 8.7%U(8%s/29%d/62%f)<br>92.0 %O(29%s/71%p) + 6.7%U(13%s/53%d/34%f)<br>90.1%O(20%s/80%p) + 8.3%U(8%s/36%d/56%f)<br>91.6%O(30%s7/0%p) + 7.1%U(10%s/42%d/47%f) |
| | | $\pi_{Oe-U}$ | 5*2.00 | 95.1%O(16%s/84%p) + 2.7%U(5%s/33%d/61%f)<br>96.5%O(27%s/73%p) + 1.7%U(9%s/42%d/47%f)<br>94.5%O(15%s/85%p) + 3.3%U(8%s/35%d/56%f)<br>96.4%O(26%s/74%p) + 1.7%U(9%s/37%d/52%f)<br>95.0%O(13%s/87%p) + 2.7%U(5%s/34%d/60%f) |
| $NpO_2(15C5)^{2+}$ | Inclusion | $\sigma_{Oe-Np}$ | 5*2.00 | 90.3%O(26%s/74%p) + 7.9%Np(14%s/43%d/43%f)<br>90.9%O(35%s65%p) + 7.9%Np(15%s/46%d/40%f)<br>90.5%O(28%s/72%p) + 7.8%Np(15%s/45%d/40%f)<br>90.3%O(27%s/73%p) + 8.0%Np(14%s/42%d/44%f)<br>90.2%O(25%s75%p) + 8.1%Np(13%s/42%d/45%f) |

| | | | | |
|---|---|---|---|---|
| | | $\pi_{Oe\text{-}Np}$ | 5*2.00 | 96.1%O(23%s/77%p) + 2.0%Np(4%s/33%d/61%f)<br>94.5%O(8%s/92%p) + 3.4%Np(1%s/26%d/72%f)<br>95.9%O(19%s/81%p) + 2.1%Np(4%s/32%d/62%f)<br>96.0%O(19%s/81%p) + 2.0%Np(6%s/36%d/57%f)<br>96.2%O(21%s/79%p) + 1.9%Np(5%s/35%d/58%f) |
| | Side-on | $\sigma_{Oe\text{-}Np}$ | 5*2.00 | 90.1%O(19%s/81%p) + 8.1%Np(8%s/35%d/57%f)<br>90.5%O(25%s75%p) + 8.0%Np(9%s/34%d/57%f)<br>90.5 %O(28%s/72%p) +6.5%Np(14%s/50%d/35%f)<br>89.3%O(19%s/81%p) + 9.0%Np(7%s/25%d/67%f)<br>90.1%O(28%s72%p) + 6.5%Np(14%s/50%d/36%f) |
| | | $\pi_{Oe\text{-}Np}$ | 5*2.00 | 96.6%O(27%s/73%p) + 1.5%Np(9%s/42%d/47%f)<br>96.0%O(18%s/82%p) + 2.0%Np(6%s/40%d/52%f)<br>94.9%O(17%s/83%p) + 2.9%Np(8%s/37%d/54%f)<br>96.7%O(28%s/72%p) + 1.6%Np(11%s/45%d/41%f)<br>95.0 %O(16%s/84%p) + 2.9%Np(8%s/37%d/54%f) |
| $PuO_2(15C5)^{2+}$ | Inclusion | $\sigma_{Oe\text{-}Pu}$ | 5*2.00 | 89.4%O(19%s/81%p) + 8.9%Pu(11%s/34%d/55%f)<br>89.8%O(26%s/74%p) + 8.5%Pu(15%s/43%d/42%f)<br>89.6%O(17%s/83%p) + 8.3%Pu(12%s/38%d/50%f)<br>89.6%O(24%s/76%p) + 8.4%Pu(14%s/42%d/44%f)<br>89.2%O(15%s/85%p) + 8.8%Pu(11%s/35%d/53%f) |
| | | $\pi_{Oe\text{-}Pu}$ | 5*2.00 | 95.5%O(23%s/77%p) + 2.6%Pu(12%s/58%d/30%f)<br>97.1%O(17%s/83%p) + 0.8%Pu(7%s/73%d/17%f)<br>96.0%O(27%s/73%p) + 2.2%Pu(15%s/55%d/30%f)<br>97.2%O(20%s/80%p) + 0.8%Pu(8%s/73%d/16%f)<br>96.0%O(31%s/69%p) + 2.3%Pu(13%s/53%d/33%f) |
| | Side-on | $\sigma_{Oe\text{-}Pu}$ | 5*2.00 | 91.1%O(25%s/75%p) + 7.5%Pu(10%s/35%d/55%f)<br>90.5%O(18%s82%p) +7.7%Pu(8%s/33%d/59%$f^{8.06}$)<br>92.6 %O(31%s/69%p) + 6.1%Pu(16%s/51%d/33%f)<br>89.8%O(17%s/83%p) + 8.4%Pu(8%s/24%d/68%f)<br>92.5%O(30%s70%p) + 6.0%Pu(16%s/50%d/33%f) |

| | | | | |
|---|---|---|---|---|
| | | $\pi_{Oe\text{-}Pu}$ | 5*2.00 | 96.0%O(16%s/84%p) + 1.9%Pu(6%s/45%d/48%f)<br>96.8%O(28%s/72%p) + 1.4%Pu(10%s/47%d/41%f)<br>95.0%O(13%s/87%p) + 2.8%Pu(7%s/38%d/54%f)<br>96.8%O(29%s/71%p) + 1.4%Pu(13%s/51%d/34%f)<br>95.1%O(14%s/86%p) + 2.7%Pu(8%s/38%d/53%f) |
| $AmO_2(15C5)^{2+}$ | Inclusion | $\sigma_{Oe\text{-}Pu}$ | 5*2.00 | 91.3%O(26%s/74%p) +7.1%Am(17%s/47%d/36%f)<br>91.2%O(26%s/74%p) +7.2%Am(16%s/43%d/41%f)<br>90.8%O(21%s/79%p) +7.4%Am(15%s/40%d/45%f)<br>90.8%O(21%s/79%p) +7.4%Am(15%s/40%d/44%f)<br>91.4%O(31%s/69%p) +7.3%Am(16%s/43%d/40%f) |
| | | $\pi_{Oe\text{-}Pu}$ | 5*2.00 | 96.2%O(18%s/82%p) +1.8%Am(6%s/43%d/49%f)<br>96.2%O(18%s/82%p) +1.8%Am(6%s/44%d/48%f)<br>96.6%O(24%s/76%p) +1.6%Am(6%s/45%d/47%f)<br>96.6%O(26%s/74%p) +1.6%Am(6%s/45%d/47%f)<br>95.4%O(11%s/89%p) + 2.5%Am(3%s/36%d/60%f) |
| | Side-on | $\sigma_{Oe\text{-}Pu}$ | 5*2.00 | 91.9%O(21%s/79%p) +6.6%Am(10%s/34%d/56%f)<br>91.8%O(17%s83%p) +6.4%Am(10%s/35%d/55%f)<br>93.0 %O(30%s/70%p)+5.3%Am(18%s/52%d/30%f)<br>90.7%O(16%s/84%p) +7.6%Am(8%s/24%d/68%f)<br>92.8%O(28%s72%p) +5.7%Am(18%s/50%d/32%f) |
| | | $\pi_{Oe\text{-}Pu}$ | 5*2.00 | 96.5%O(21%s/79%p) + 1.6%Am(8%s/53%d/36%f)<br>96.9%O(28%s/72%p) +1.3%Am(12%s/53%d/32%f)<br>95.7%O(14%s/86%p) +2.1%Am(9%s/46%d/44%f)<br>96.8%O(30%s/70%p) +1.6%Am(14%s/55%d/29%f)<br>95.7%O(16%s/84%p) +2.1%Am(10%s/46%d/43%f) |
| $CmO_2(15C5)^{2+}$ | Inclusion | $\sigma_{Oe\text{-}Pu}$ | 5*2.00 | 91.1%O(23%s/77%p) +7.2%Cm(17%s/42%d/41%f)<br>91.2%O(23%s/77%p) +7.1%Cm(16%s/41%d/43%f)<br>91.1%O(22%s/78%p) +7.1%Cm(16%s/41%d/43%f)<br>91.1%O(22%s/78%p) +7.1%Cm(17%s/41%d/42%f)<br>91.2%O(33%s/67%p) +7.2%Cm(17%s/44%d/39%f) |

| | | | | |
|---|---|---|---|---|
| | | $\pi_{Oe\text{-}Pu}$ | 5*2.00 | 96.2%O(22%s/78%p) + 1.9%Cm(6%s/43%d/50%f)<br>96.1%O(21%s/79%p) +2.0%Cm(7%s/43%d/49%f)<br>96.2%O(22%s/78%p) +1.9%Cm(6%s/43%d/48%f)<br>96.2%O(24%s/76%p) +1.9%Cm(7%s/43%d/49%f)<br>94.3%O(6%s/94%p) +3.4%Cm(2%s/30%d/68%f) |
| | Side-on | $\sigma_{Oe\text{-}Pu}$ | 5*2.00 | 92.0%O(28%s/72%p) +5.4%Cm(18%s/49%d/33%f)<br>93.2%O(26%s/74%p) +5.1%Cm(18%s/50%d/31%f)<br>91.7%O(17%s/82%p) +6.7%Cm(10%s/27%d/63%f)<br>92.0%O(17%s/83%p) +6.4%Cm(10%s/30%d/59%f)<br>93.0%O(25%s/75%p) +5.2%Cm(15%s/47%d/37%f) |
| | | $\pi_{Oe\text{-}Pu}$ | 5*2.00 | 96.0%O(15%s/85%p) + 1.7%Cm(5%s/46%d/48%f)<br>96.7%O(28%s/72%p) +1.7%Cm(12%s/57%d/29%f)<br>95.5%O(18%s/82%p) +2.5%Cm(12%s/48%d/39%f)<br>96.8%O(28%s/72%p) +1.5%Cm(12%s/56%d/30%f)<br>95.9%O(19%s/81%p) +2.0%Cm(10%s/51%d/38%f) |

$O_e$ denotes crown ether O atom; LP denotes lone pair.

**Table S11.** Energy Decomposition Analyses (EDA, in kcal/mol) for C1 $AnO_2(15C5)^{2+}$ at PBE/TZ2P level. Energy values are in kcal/mol.

| Interacting | $UO_2(L)^{2+}(^1A)$ | $NpO_2(L)^{2+}$ ($^2A$) | | $PuO_2(L)^{2+}$ ($^{-4}A_2$) | | $AmO_2(L)^{2+}$ ($^4A$) | | $CmO_2(L)^{2+}$ ($^3A$) | |
|---|---|---|---|---|---|---|---|---|---|
| Fragments | $UO_2^{2+}$ ($^1\Sigma$) $f^0$ | $NpO_2^{2+}$ ($^2\Phi$) $f\phi^1$ | | $PuO_2^{2+}$ ($^3H$) $f\sigma^1f\phi^1$ | | $AmO_2^{2+}$ ($^4\Delta_u$) $f\phi^2f\delta^1$ | | $CmO_2^{2+}$ ($^5\Sigma$) $f\delta^2f\phi^2$ | |
| | 15C5($^1$A) …$45a^2$ | 15C5 ($^1$A) …$45a^2$ | | 15C5 ($^1$A) …$45a^2$ | | 15C5 ($^1$A) …$45a^2$ | | 15C5 ($^1$A) …$45a^2$ | |
| $\Delta E_{int}$ | -262.94 | -261.24 | | -255.82 | | -255.35 | | -249.17 | |
| $\Delta E_{Pauli}$ | 234.89 | 233.96 | | 221.07 | | 210.81 | | 208.93 | |
| $\Delta E_{elstat}$[a] | -250.31(50.3%) | -247.10 (49.9%) | | -242.30 (50.6%) | | -236.05 (50.6%) | | -237.31 (51.8%) | |
| $\Delta E_{orb}$[a] | -247.52(49.7%) | -248.09 (50.1%) | | -234.59 (49.4%) | | - 230.1 (49.4%) | | -220.78 (48.2%) | |
| | | α | β | α | β | α | β | α | β |
| $\Delta E_1$[b] | -43.51 | -10.33 | -19.48 | -9.78 | -18.91 | -7.08 | -8.83 | -7.08 | -8.83 |
| $\Delta E_2$[b] | -43.77 | -17.25 | -19.56 | -10.02 | -18.80 | -13.59 | -8.88 | -13.59 | -8.88 |
| $\Delta E_3$[b] | -23.18 | -11.81 | -5.72 | -15.66 | -5.33 | -16.04 | -16.75 | -16.04 | -16.75 |
| $\Delta E_4$[b] | -10.9 | -8.86 | -5.27 | -14.98 | -5.19 | -9.43 | -16.66 | -9.43 | -16.66 |
| $\Delta E_5$[b][c] | -9.16 | -11.3 | -5.24 | -11.94 | -9.28 | -12.34 | -5.45 | -12.34 | -5.45 |
| $\Delta E_6$[b][c] | -8.9 | -5 | -11.23 | -5.38 | -7.11 | -3.67 | -11.09 | -3.67 | -11.09 |
| $\Delta E_7$[b][c] | -8.98 | -5.44 | -4.57 | -5.42 | -4.17 | -3.08 | -4.02 | -3.08 | -4.02 |
| $\Delta E_8$[b][c] | -7.88 | -5 | -3.66 | -3.43 | -3.66 | | -2.61 | | -2.61 |
| $\Delta E_9$[b][c] | -7.91 | -3.41 | -3.5 | | -3.39 | | -3.29 | | -3.29 |
| $\Delta E_{10}$[b][c] | -6.98 | -3.12 | -3.36 | | -2.79 | | -3.12 | | -3.12 |
| $\Delta E_{11}$[b][c] | -6.76 | | -3 | | -2.43 | | -3.24 | | -3.24 |
| $\Delta E_{12}$[b][c] | -4.52 | | | | -3.18 | | -3.05 | | -3.05 |
| $\Delta E_{13}$[b][c] | -4.33 | | | | | | | | |
| Sum | -238.76 | -117.28 | -118.77 | -117.92 | -117.03 | -102.02 | -119.25 | -102.02 | -119.25 |

[a] The values in parentheses provide the percentage contribution to the total attractive interactions $\Delta E_{elstat}$ + $\Delta E_{orb}$. [b] The values in parentheses provide the percentage contribution to the total orbital interactions $\Delta E_{orb}$. [c] The $\Delta E$ is the energy change associated with the change in the electronic state of the considered fragments during interacting with each other.

**Table S12**. Selected bond lengths (Å) and bond angles (degree) of the insertion and side-on isomers for $AnO_2(15C5)^+$ at PBE level.

| Species* | Insertion | | | | Side-on | | |
|---|---|---|---|---|---|---|---|
| | An-$O_{yl}$ | An-$O_e$ | ∠$O_{yl}$-An-$O_e$ | ∠$O_{yl}$-An-$O_{yl}$ | An-$O_{yl}$ | An-$O_e$ | ∠$O_{yl}$-An-$O_{yl}$ |
| $UO_2(L)^+$ | 1.843<br>1.834 | 2.500, 2.502, 2.482, 2.493, 2.499 (2.495) | 83.3, 79.2, 93.9, 78.8, 85.8 (84.2) | 177.7 | 1.847<br>1.844 | 2.623, 2.673, 2.762, 2.803, 2.710 (2.714) | 119.9 |
| $NpO_2(L)^+$ | 1.815<br>1.809 | 2.496, 2.487, 2.495, 2.492, 2.474 (2.489) | 85.8, 83.5, 78.8, 92.2, 77.1 (83.5) | 179.1 | 1.796<br>1.790 | 2.646, 2.529, 2.535, 3.706, 4.376 (3.158) | 167.9 |
| $PuO_2(L)^+$ | 1.801<br>1.793 | 2.482, 2.472, 2.479, 2.477, 2.455 (2.473) | 82.2, 96.1, 80.8, 88.8, 87.3(87.0) | 179.4 | 1.771<br>1.759 | 2.466, 2.539, 3.828, 3.826, 4.495 (3.431) | 175.7 |
| $AmO_2(L)^+$ | 1.802<br>1.796 | 2.480, 2.468, 2.473, 2.476, 2.442 (2.468) | 87.3, 81.7, 95.8, 80.4, 89.5(86.9) | 179.8 | 1.774<br>1.776 | 2.608, 2.619, 2.626, 3.992, 4.685 (3.306) | 172.8 |
| $CmO_2(L)^+$ | 1.824<br>1.816 | 2.470, 2.456, 2.457, 2.468, 2.426 (2.455) | 87.0, 82.3, 96.3, 81.2, 89.3 (87.2) | 179.3 | 1.797<br>1.805 | 2.623, 2.528, 3.540, 2.539, 4.097 (3.065) | 165.0 |

* L denotes 15-crown-5 ether.

**Table S13**. Selected bond lengths (Å) and bond angles (degree) of the insertion and side-on isomers for $AnO_2(15C5)^+$ at B3LYP level.

| Species* | Insertion | | | Side-on | | |
|---|---|---|---|---|---|---|
| | An-$O_{yl}$ | An-$O_e$ | ∠$O_{yl}$-An-$O_{yl}$ | An-$O_{yl}$ | An-$O_e$ | ∠$O_{yl}$-An-$O_{yl}$ |
| $UO_2(L)^+$ | 1.804<br>1.815 | 2.479, 2.499, 2.478, 2.460, 2.484 (2.480) | 178.6 | 1.823<br>1.827 | 2.622, 2.656, 2.734; (2.671) 2.794, 2.814 | 123.3 |
| $NpO_2(L)^+$ | 1.787<br>1.796 | 2.464, 2.483, 2.445, 2.476, 2.476 (2.469) | 179.0 | 1.767<br>1.776 | 2.534, 2.542, 2.646; (2.574) 3.709, 4.305 | 167.4 |
| $PuO_2(L)^+$ | 1.767<br>1.776 | 2.467, 2.463, 2.440, 2.475, 2.462 (2.461) | 179.4 | 1.743<br>1.753 | 2.539, 2.553, 2.656; (2.583) 3.710, 4.253 | 171.4 |
| $AmO_2(L)^+$ | 1.771<br>1.777 | 2.462, 2.465, 2.430, 2.468, 2.458 (2.456) | 179.4 | 1.744<br>1.752 | 2.559, 2.565, 2.662; (2.595) 3.688, 4.165 | 172.1 |
| $CmO_2(L)^+$ | 1.805<br>1.815 | 2.467, 2.418, 2.442, 2.452, 2.455 (2.447) | 179.4 | 1.787<br>1.792 | 2.530, 2.534, 2.620; (2.561) 3.590, 4.098 | 164.9 |

* L denotes 15-crown-5 ether.

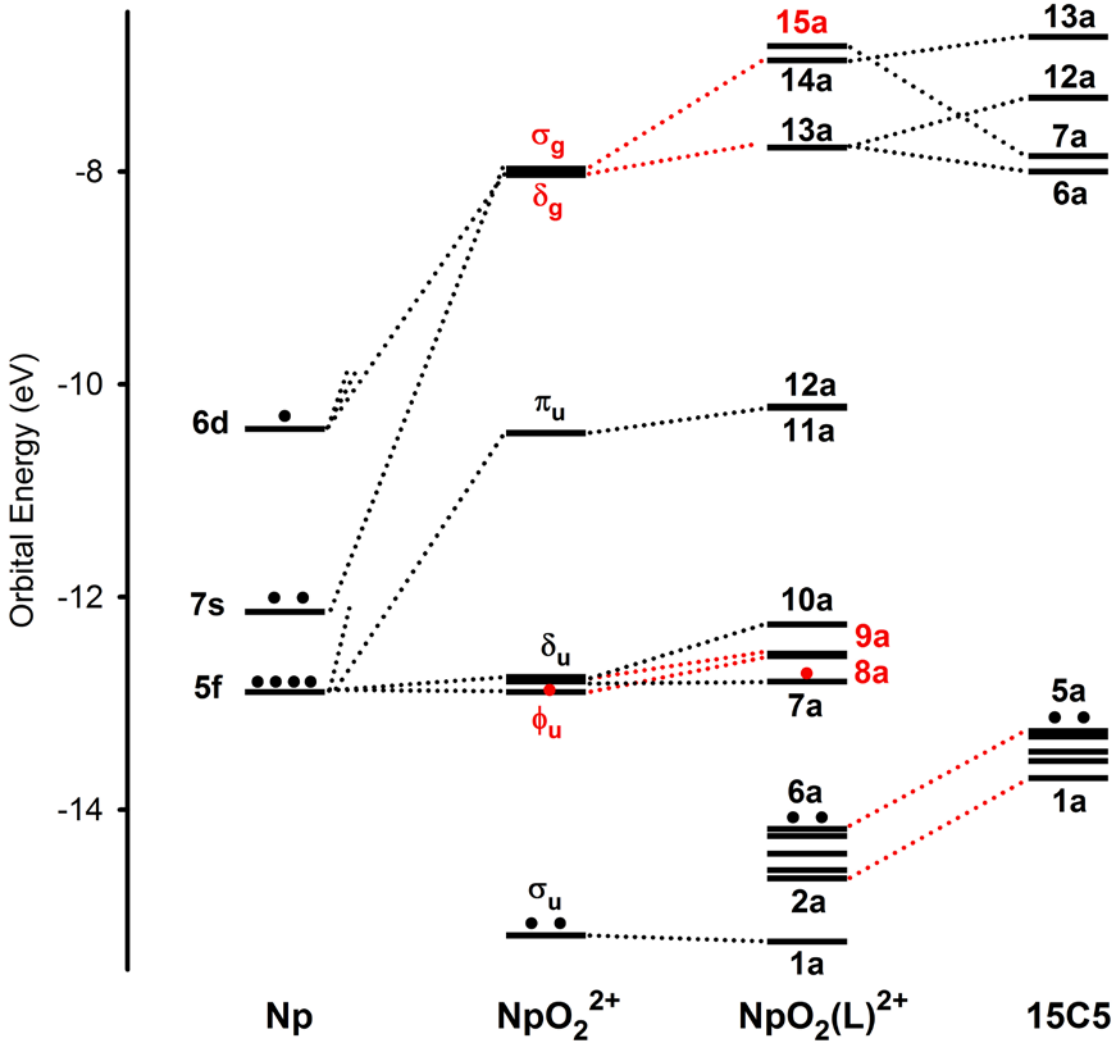


**Figure S1. MO energy levels of $Np^{VI}O_2(15C5)^{2+}$ at SR-PBE/TZ2P level.** 6a orbital is the HOMO, and 7a orbital is the LUMO.

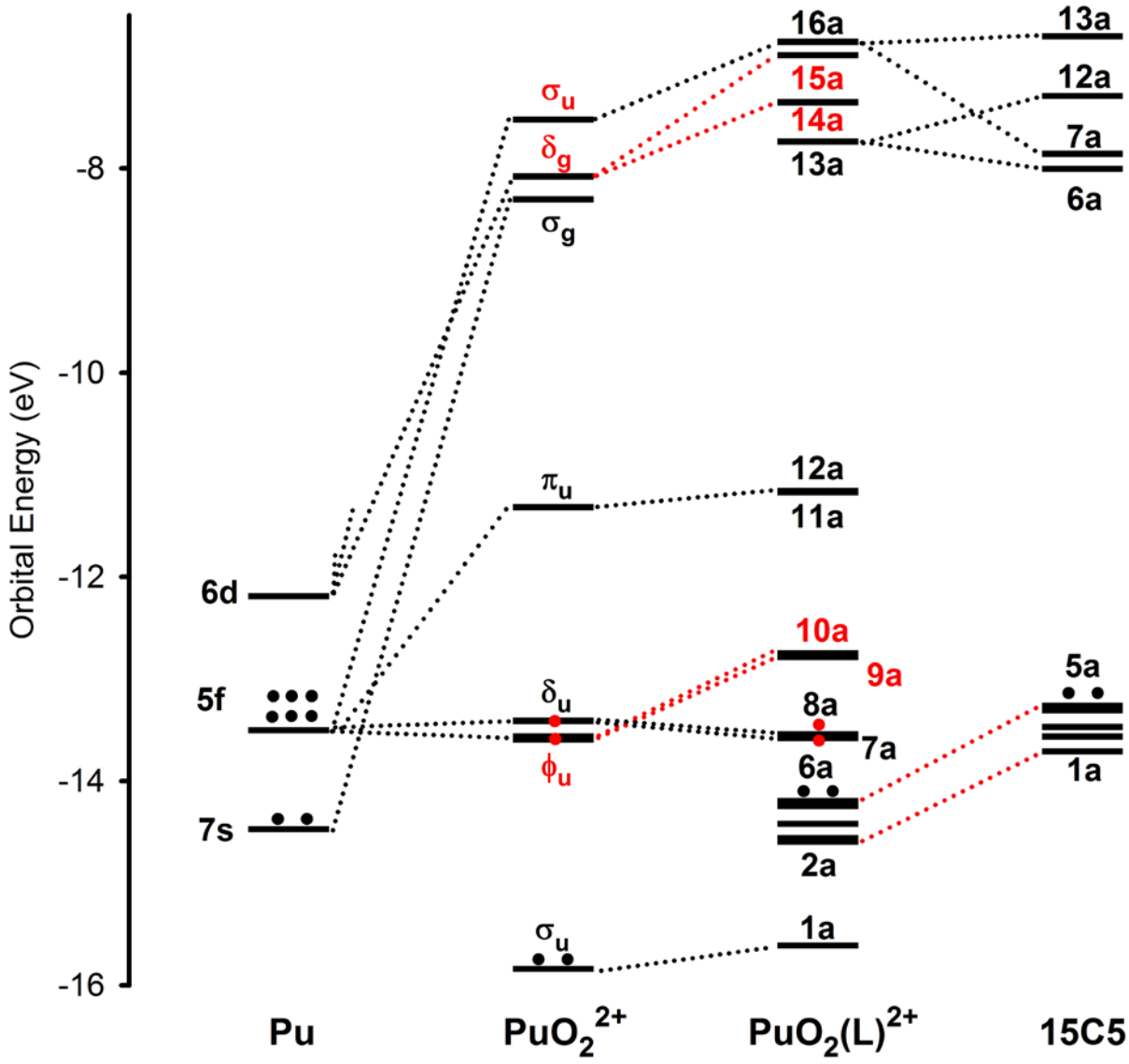


**Figure S2. MO energy levels of $Pu^{VI}O_2(15C5)^{2+}$ at SR-PBE/TZ2P level.** 6a orbital is the HOMO, and 7a orbital is the LUMO.

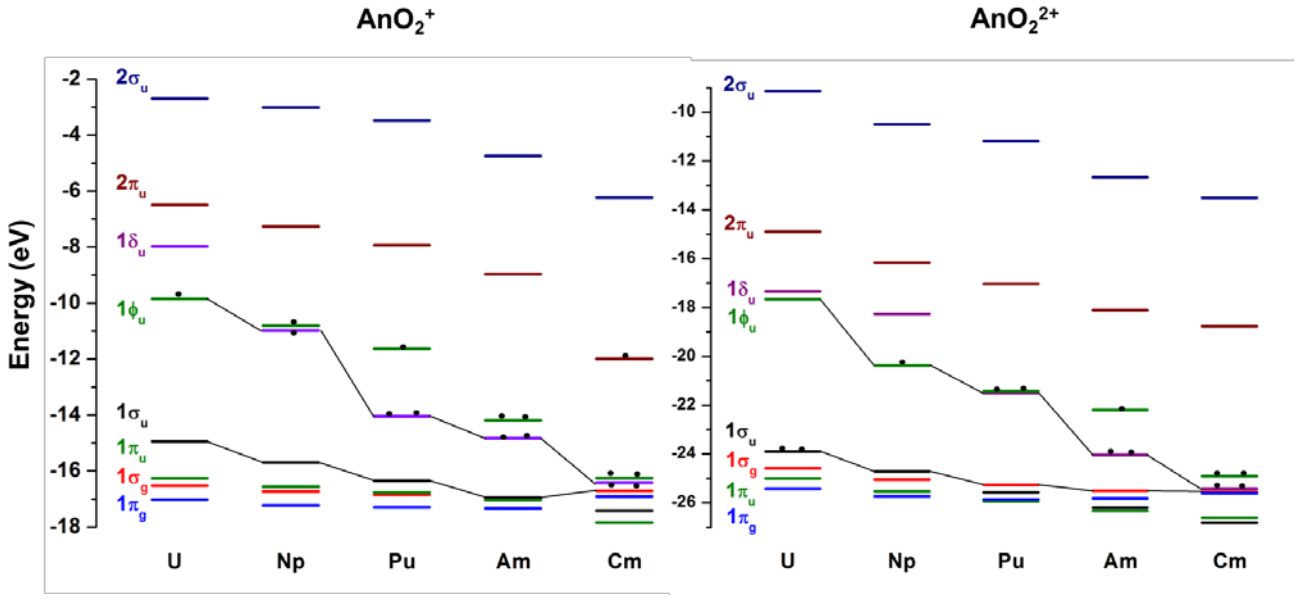


**Figure S3.** Scalar relativistic KS-PBE molecular orbital energy levels of free $AnO_2^+$ and $AnO_2^{2+}$ ions for An = U, Np, Pu, Am, and Cm.