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Supporting Information: Relativistic Quantum Calculations to Understand the Contribution of f-type Atomic Orbitals and Chemical Bonding of Actinides with Organic Ligands

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Abstract

The nuclear waste problem is one of the main interests of the rare earth and actinide elements chemistry. Studies of Actinide-containing compounds are at the frontier of the applications of current theoretical methods due to the need to consider relativistic effects and approximations to the Dirac equation in them. Here, we employ four-component relativistic quantum calculations and scalar approximations to understand the contribution of f-orbitals in the chemical bonding of actinides (Ac) to organic ligands. We studied the relativistic quantum structure of an isostructural family made of Plutonium (Pu), Americium (Am), Californium (Cf), and Berkelium (Bk) atoms with the redox-active model ligand; DOPO (2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoxazin-9-olate). Crystallographic structures were available to validate our calculations for all mentioned elements except for Cf. State-of-the-art relativistic calculations were performed at different levels of theory to investigate the relativistic effects and electron correlations: 1) the scalar relativistic zeroth order regular approximation (ZORA) in the hybrid density functional theory (DFT) and 2) the four-component Dirac equation with the Dirac-Hartree-Fock (4c-DHF) and Lévy-Leblond (LL) Hamiltonians. We show that scalar DFT-ZORA could be an efficient first approximation to predict and investigate the geometry and electronic properties of actinides that are difficult to synthesize or characterize, and that the higher level of theory, the 4c-DHF, gives closer results to experiments than scalar DFT-ZORA. We performed spin-free calculations of geometric parameters for the Americium compound and found that they are the same as that of DFT-ZORA. To the best of our knowledge, this is the first time that such kind of large actinide compounds (the largest contains 67 atoms and 421 electrons) are studied with highly accurate four-component methods (all-electron with 6131 basis functions for the largest compound). We show that relativistic effects play a key role in the nature of f-type atomic orbitals contributions to the frontier orbitals of Ac-DOPO compounds.

Table S1: Pu-N and Pu-O bond distances at the ZORA-DFT level w.r.t. experiments.

	Bond Length Å			Difference w.r.t. Experiments Å	
Bonds	Expt.[1]	ZORA-DFT-D3	ZORA-DFT	ZORA-DFT-D3	ZORA-DFT
Pu–N_1	2.412	2.447	2.515	0.035	0.103
Pu–N_2	2.538	2.452	2.515	-0.086	-0.023
Pu–N_3	2.542	2.46	2.538	-0.082	-0.004
Pu–O_1	2.400	2.472	2.482	0.072	0.082
Pu–O_2	2.425	2.483	2.585	0.058	0.160
Pu–O_3	2.289	2.447	2.489	0.158	0.200
Pu–O_4	2.289	2.467	2.481	0.178	0.192
Pu–O_5	2.344	2.457	2.476	0.113	0.132
Pu–O_6	2.387	2.457	2.526	0.07	0.139
RMSD				0.104	0.132

Table S2: The equilibrium first coordination bond distances (C–C, C–N, C–O, excluding the Pu–O and Pu–N bonds) at the ZORA–DFT level compared to experimental values.

Bonds	Expt.[1] Å	ZORA-DFT-D3 Å	Difference Å
C_1–N_1	1.345	1.344	-0.001
C_1–C_2	1.423	1.435	0.012
C_2–O_2	1.316	1.284	-0.032
C_4–O_6	1.425	1.283	-0.142
C_3–C_4	1.323	1.436	0.113
C_3–N_1	1.331	1.340	0.009
N_2–C_5	1.316	1.338	0.022
C_5–C_6	1.454	1.439	-0.015
C_6–O_1	1.272	1.281	0.009
N_2–C_7	1.331	1.344	0.013
C_7–C_8	1.439	1.435	-0.004
C_8–O_3	1.286	1.284	-0.002
C_9–N_3	1.321	1.343	0.022
C_{10}–O_4	1.271	1.284	0.013
C_{11}–O_5	1.273	1.286	0.013
C_{11}–C_{12}	1.439	1.436	-0.003
N_3–C_{12}	1.332	1.343	0.011
RMSD			0.046

Table S3: Pu–O and Pu–N average bond distances of the Pu–DOPO complex at the ZORA–DFT level compared to experimental values.

Bond	Charge	Expt.[1] Å	ZORA-DFT-D3 Å	Diff. w.r.t. Expt. Å	ZORA–DFT Å	Diff. w.r.t. Expt. Å
Pu–N	Pu=+4.0	2.497	2.453	-0.044	2.468	-0.029
Pu–O	Pu=+4.0	2.356	2.464	0.108	2.48	0.124

Table S4: The equilibrium first co-ordination bond distances (C-C. C-N. C-O. excluding the Am-O and Am-N bond distances) at the ZORA-DFT level compared to experimental values.

Bonds	Expt.[1] Å	ZORA-DFT-D3 Å	Diff. Å
C_1–N_1	1.332	1.347	0.015
C_1–C_2	1.462	1.449	-0.013
C_2–O_1	1.265	1.273	0.008
C_4–O_6	1.272	1.272	0.0
C_3–C_4	1.460	1.451	-0.009
C_3–N_1	1.328	1.347	0.019
N_2–C_5	1.334	1.343	0.009
C_5–C_6	1.457	1.450	-0.007
C_6–O_2	1.277	1.273	-0.004
N_2–C_7	1.342	1.343	0.001
C_7–C_8	1.451	1.449	-0.002
C_8–O_3	1.266	1.273	0.007
C_9–N_3	1.321	1.349	0.028
C_{11}–O_5	1.268	1.449	0.181
C_{12}–C_{11}	1.321	1.449	0.128
N_3–C_{12}	1.334	1.349	0.015
C_9–C_{10}	1.457	1.448	-0.009
C_{10}–O_4	1.273	1.273	0.0
RMSD			0.053

Table S5: Am–O and Am–N average bond distances at the three different levels of theory.

Bond	Expt.[1] Å	ZORA-DFT-D3 Å	Diff. w.r.t. Expt. Å	ZORA–DFT Å	Diff. with Expt. Å	4c-DHF Å	Diff. with Expt. Å
Am–N	2.57	2.452	-0.046	2.554	-0.016	2.623	-0.054
Am–O	2.475	2.579	0.105	2.593	0.118	2.541	-0.066

Table S6: The Cf–N and Cf–O bond distance at the ZORA–DFT–D3 compared to experiments.

	Bond Length Å			Difference w.r.t. Expt. Å	
Bonds	Expt.	ZORA-DFT-D3	ZORA-DFT	ZORA-DFT-D3	ZORA-DFT
Cf–N_1	N/A	2.494	2.522	N/A	N/A
Cf–N_2	N/A	2.485	2.511	N/A	N/A
Cf–N_3	N/A	2.492	2.560	N/A	N/A
Cf–O_1	N/A	2.545	2.548	N/A	N/A
Cf–O_2	N/A	2.534	2.544	N/A	N/A
Cf–O_3	N/A	2.567	2.548	N/A	N/A
Cf–O_4	N/A	2.542	2.595	N/A	N/A
Cf–O_5	N/A	2.528	2.562	N/A	N/A
Cf–O_6	N/A	2.567	2.575	N/A	N/A

Table S7: Cf–N, Cf–O, Bk–N, and Bk–O average bond distances of the Cf–DOPO and Bk–DOPO complexes in Å.

Bond	Charge	Expt.	ZORA-DFT-D3	Diff. w.r.t. Expt.	ZORA-DFT	4c-DHF	Diff. w.r.t. Expt.
Cf–N	Cf=+3.0	N/A	2.49	N/A	2.531	N/A	N/A
Cf–O	Cf=+3.0	N/A	2.547	N/A	2.562	N/A	N/A
Bk–N	Bk=+3.0	2.532	2.476	-0.06	N/A	2.585	0.05
Bk–O	Bk=+3.0	2.454	2.539	0.09	N/A	2.515	0.06

Table S8: Contributions of few primitives of Americium atom at the A) 4c-DHF and B) LL level of theory to the complex studied. The contributions of such primitives to the selected OM are $\geq |0.05|$

A. Level of theory: 4c-B3LYP. Am–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Am)			
LUMO+3	-0.019	-0.508	—	—	—	—
LUMO+1	-0.020	-0.550	—	—	—	—
LUMO+2	-0.109	-2.976	—	—	—	—
LUMO	-0.111	-3.008	—	—	—	—
HOMO	-0.196	-5.322	fxzz 0.132	fxxz 0.108	fxyy 0.097	fzzz 0.087
HOMO-1	-0.197	-5.365	fyyz 0.132	fxyz 0.096	fyzz 0.090	fxxz 0.089

HOMO-2	-0.199	-5.415	fxyz 0.131	fxxz 0.077	fxxy 0.068	fxyy 0.062
HOMO-3	-0.206	-5.595	—	—	—	—
HOMO-4	-0.207	-5.620	—	—	—	—
HOMO-5	-0.209	-5.691	—	—	—	—
HOMO-6	-0.210	-5.706	—	—	—	—
A. Level of theory: 4c-DHF. Am–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Am)			
LUMO+3	0.069	1.875	py 0.633	px 0.241	—	—
LUMO+2	0.012	0.338	—	—	—	—
LUMO+1	0.003	0.072	—	—	—	—
LUMO	0.001	0.039	—	—	—	—
HOMO	-0.277	-7.525	—	—	—	—
HOMO-1	-0.277	-7.547	—	—	—	—
HOMO-2	-0.279	-7.587	—	—	—	—
HOMO-3	-0.295	-8.038	—	—	—	—
HOMO-4	-0.296	-8.059	—	—	—	—
HOMO-5	-0.297	-8.091	—	—	—	—
HOMO-6	-0.357	-9.707	fxyy 0.271	fxxy 0.271	fxxx 0.091	—
A. Level of theory: sr-ZORA-B3LYP-D3. Am–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Am)			
LUMO+3	-0.079	-2.142	fxyz 0.377	fzzy 0.241	fxxx 0.162	fyyy 0.110
LUMO+2	-0.142	-3.859	—	—	—	—
LUMO+1	-0.153	-4.152	—	—	—	—
LUMO	-0.154	-4.203	—	—	—	—
HOMO	-0.221	-6.014	fzzz 0.268	fxyz 0.140	fyyy 0.080	fxxx 0.051
HOMO-1	-0.223	-6.059	fxxx 0.411	fxyz 0.139	fzzz 0.200	fzzy 0.085
HOMO-2	-0.225	-6.112	fzzz 0.615	—	—	—

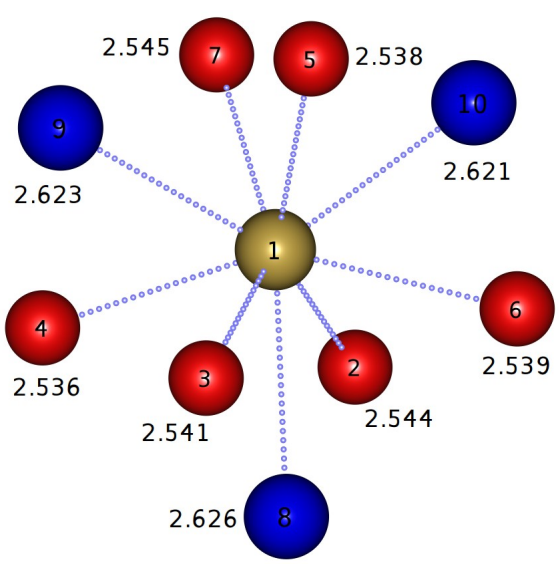
HOMO-3	-0.230	-6.272	—	—	—	—
HOMO-4	-0.232	-6.307	—	—	—	—
HOMO-5	-0.233	-6.327	—	—	—	—
HOMO-6	-0.234	-6.363	—	—	—	—
B. Level of theory: LL. Am–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Am)			
LUMO+3	0.069	1.871	py 0.587	px 0.234	—	—
LUMO+2	0.012	0.322	—	—	—	—
LUMO+1	0.001	0.029	—	—	—	—
LUMO	0.001	0.009	—	—	—	—
HOMO	-0.277	-7.535	—	—	—	—
HOMO-1	-0.278	-7.561	—	—	—	—
HOMO-2	-0.28	-7.611	—	—	—	—
HOMO-3	-0.296	-8.052	—	—	—	—
HOMO-4	-0.297	-8.069	—	—	—	—
HOMO-5	-0.298	-8.097	—	—	—	—
HOMO-6	-0.361	-9.825	—	—	—	—
HOMO-7	-0.361	-9.836	—	—	—	—
HOMO-8	-0.362	-9.858	—	—	—	—

Table S9: Contributions of few primitives of Berkelium atom at the A) 4c-DHF and b) LL level of theory to the complex studied. The contributions of such primitives to the selected OM are $\geq |0.05|$

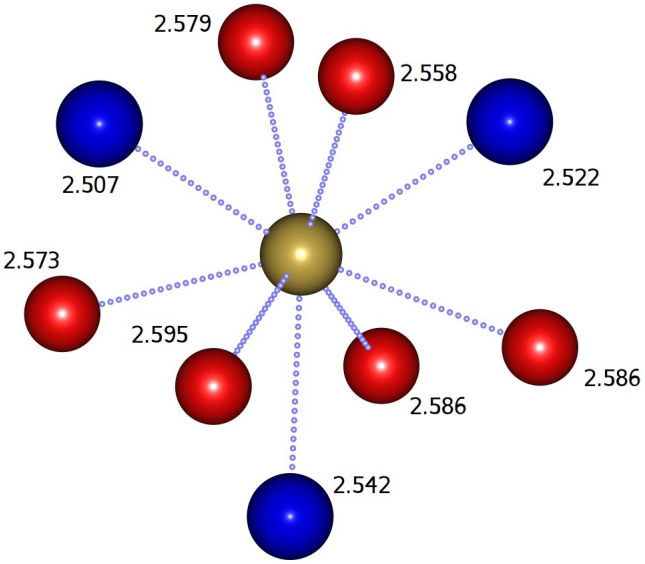
A. Level of theory: 4c-B3LYP. Bk–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Bk)			
LUMO+3	-0.057	-1.558	fxzz 0.168	fxxy 0.106	fxxz 0.184	fxyy 0.152
LUMO+2	-0.102	-2.765	—	—	—	—

LUMO+1	-0.109	-2.977	—	—	—	—
LUMO	-0.112	-3.036	—	—	—	—
HOMO	-0.195	-5.307	fyyz 0.151	fxyy 0.117	fxxz 0.100	fxzz 0.066
HOMO-1	-0.203	-5.530	—	—	—	—
HOMO-2	-0.204	-5.562	—	—	—	—
HOMO-3	-0.207	-5.646	—	—	—	—
HOMO-4	-0.208	-5.663	—	—	—	—
HOMO-5	-0.208	-5.671	—	—	—	—
HOMO-6	-0.211	-5.749	—	—	—	—
A. Level of theory: 4c-DHF. Bk–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Bk)			
LUMO+3	0.072	1.966	py : 0.578	px : 0.268	fxyy : 0.054	—
LUMO+2	0.013	0.364	—	—	—	—
LUMO+1	0.003	0.073	—	—	—	—
LUMO	0.001	0.01	—	—	—	—
HOMO	-0.276	-7.513	—	—	—	—
HOMO-1	-0.279	-7.598	—	—	—	—
HOMO-2	-0.294	-8.009	—	—	—	—
HOMO-3	-0.295	-8.032	—	—	—	—
HOMO-4	-0.298	-8.109	—	—	—	—
HOMO-5	-0.36	-9.787	—	—	—	—
HOMO-6	-0.361	-9.81	—	—	—	—
HOMO-7	-0.362	-9.862	—	—	—	—
HOMO-8	-0.406	-11.039	fxyy : 0.171	fxxy : 0.114	fxxx : 0.063	—
A. Level of theory: sr-ZORA-B3LYP-D3. Bk–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Bk)			
LUMO+3	-0.112	-3.038	fzzz 0.788	fxxx 0.06	—	—

LUMO+2	-0.142	-3.867	—	—	—	—
LUMO+1	-0.151	-4.119	—	—	—	—
LUMO	-0.155	-4.204	—	—	—	—
HOMO	-0.228	-6.204	—	—	—	—
HOMO-1	-0.230	-6.249	—	—	—	—
HOMO-2	-0.231	-6.276	—	—	—	—
HOMO-3	-0.231	-6.292	—	—	—	—
HOMO-4	-0.234	-6.365	—	—	—	—
HOMO-5	-0.235	-6.384	—	—	—	—
HOMO-6	-0.259	-7.040	fzzy 0.352	fyyy 0.087	fzzz 0.063	—
A. Level of theory: LL. Bk–DOPO. Basis set: cv3z (Am. O. N)/3-21G (C. H)						
OM	E [au]	E [eV]	Primitives (Bk)			
LUMO+4	0.065	1.776	px : 0.445	s : 0.351	py : 0.218	—
LUMO+3	0.049	1.331	—	—	—	—
LUMO+2	0.029	0.797	—	—	—	—
LUMO+1	-0.013	-0.345	—	—	—	—
LUMO	-0.132	-3.592	—	—	—	—
HOMO	-0.184	-5.019	fxyy : 0.360	fxxy : 0.134	fyyz : 0.107	—
HOMO-1	-0.223	-6.08	—	—	—	—
HOMO-2	-0.235	-6.394	fxxy : 0.491	fyyy : 0.159	fxxx : 0.093	—
HOMO-3	-0.242	-6.595	—	—	—	—
HOMO-4	-0.25	-6.796	—	—	—	—
HOMO-5	-0.263	-7.17	fxyy : 0.104	fyzz : 0.100	fxyz : 0.093	—
HOMO-6	-0.265	-7.216	fxyz : 0.131	fyzz : 0.119	fxyy : 0.109	—
HOMO-7	-0.31	-8.429	fxxz : 0.363	fyyz : 0.304	fyzz : 0.105	—
HOMO-8	-0.323	-8.789	fyyz : 0.024	—	—	—
HOMO-9	-0.33	-8.967	fzzz : 0.262	fxxz : 0.230	fxzz : 0.090	—



4c-DHF/ dyall.cv3z/ 3-21G level of theory



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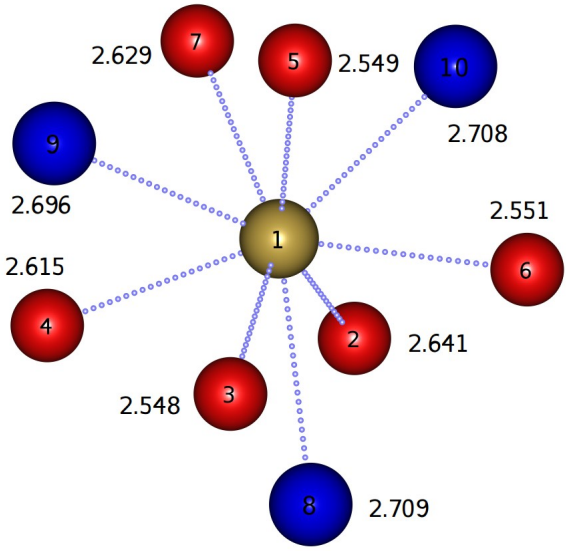
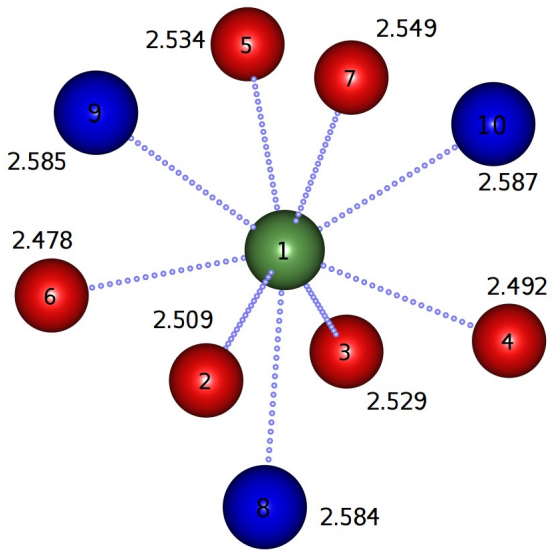
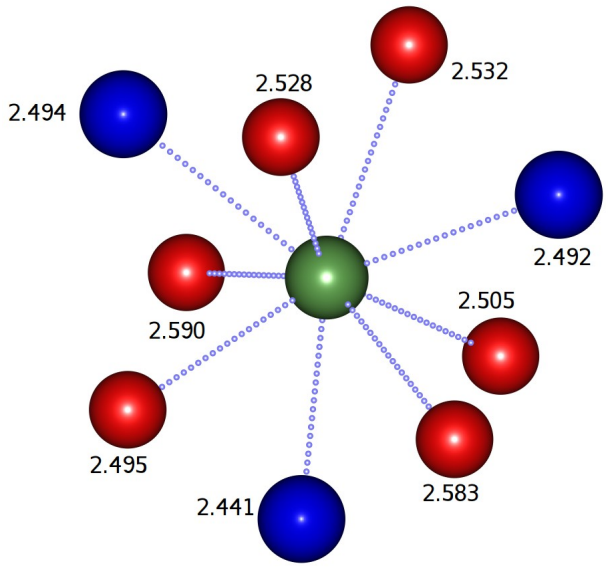


Lévy-Leblond/dyall.cv3z/3-21G level of theory

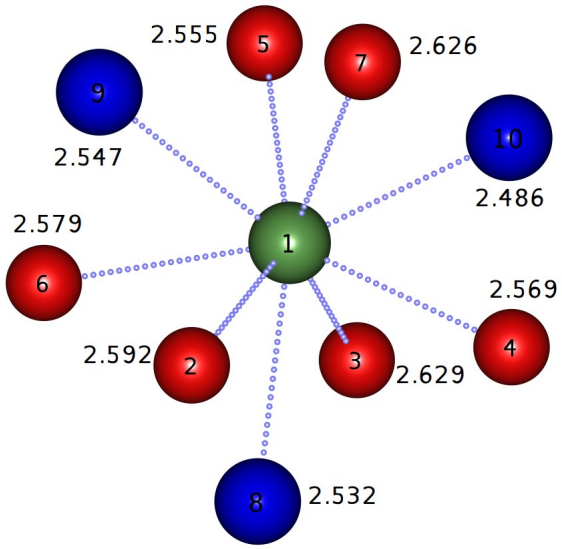
Figure S1: Distances of Am–O and Am–N, d(Am–X; X = O, N), calculated at different levels of theory: 4c-DHF, ZORA, and Lévy-Leblond. In red are the distances from Am to oxygens and in blue the ones to nitrogen. All distances given in Å.



4c-DHF/ dyall.cv3z/ 3-21G level of theory



ZORA/TZP/DZP level of theory



Lévy-Leblond/dyall.cv3z/3-21G level of theory

Figure S2: Distances of Bk–O and Bk–N, d(Bk–X; X = O, N), calculated at different levels of theory: 4c-DHF, ZORA, and Lévy-Leblond. In red are the distances from Am to oxygens and in blue the ones to nitrogen. All distances given in Å.

Table S10: Energies of Am(III).3DOPO^{-1}, DOPO^{-1}, and Am(III) in different multiplicities, M, in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYP-D3 with the methodology sr-ZORA.

sr-ZORA-HF / Am: TZP C, N, O, H: DZP								
	Am(III).3DOPO^{-1}		DOPO^{-1}		Am(III)		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
1	-31.835	-83581.53	-10.211	-26807.998	1.229	3226.496	-2.432	-6384.033
3	-31.904	-83762.97	-10.211	-26807.998	1.02	2679.22	-2.292	-6018.197
5	-31.474	-82635.354	-10.211	-26807.998	0.569	1493.357	-1.411	-3704.718
7	-31.033	-81476.366	-10.211	-26807.998	0.241	631.77	-0.641	-1684.142
sr-ZORA-B3LYP / Am: TZP C, N, O, H: DZP								
	Am(III).3DOPO^{-1}		DOPO^{-1}		Am(III)		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
1	-20.814	-54646.313	-6.609	-17351.242	1.457	3825.971	-2.445	-6418.559
3	-20.828	-54683.427	-6.609	-17351.242	1.417	3719.831	-2.418	-6349.533
5	-20.756	-54495.79	-6.609	-17351.242	1.296	3402.346	-2.226	-5844.411
7	-20.593	-54067.417	-6.609	-17351.242	1.096	2876.384	-1.863	-4890.076
sr-ZORA-B3LYP–D3 / Am: TZP C, N, O, H: DZP								
	Am(III).3DOPO^{-1}		DOPO^{-1}		Am(III)		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
1	-21.008	-55156.898	-6.659	-17482.172	1.457	3825.971	-2.49	-6536.353
3	-21.022	-55192.633	-6.659	-17482.172	1.417	3719.831	-2.463	-6465.947
5	-20.951	-55006.375	-6.659	-17482.172	1.296	3402.346	-2.271	-5962.205
7	-20.788	-54578.001	-6.659	-17482.172	1.096	2876.384	-1.907	-5007.868

Table S11: Energies of Am(III).3DOPO^{-1}, DOPO^{-1}, and Am(III) in atomic units, and kj/-mol calculated at different levels theory: HF, B3LYP, and B3LYPD3 with the methodology so-ZORA.

so-ZORA: Am: TZP C, N, O, H: DZP								
	Am(III).3DOPO^{-1}		DOPO^{-1}		Am(III)		Binding Energy	
Methodology	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
HF	-32.023	-84075.888	-10.211	-26808.027	-0.056	-146.343	-1.335	-3505.464
B3LYP	-20.997	-55126.377	-6.609	-17351.274	1.001	2627.985	-2.171	-5700.539
B3LYP–D3	-21.008	-55156.898	-6.659	-17482.205	1.001	2627.985	-2.033	-5338.269

Table S12: Energies of Am.3DOPO, DOPO, and Am in different multiplicities, M, in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYP–D3 with the methodology sr-ZORA.

sr-ZORA-HF / Am: TZP C, N, O, H: DZP									
	Am.3DOPO		DOPO, M: 2		Am			Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	M	E [au]	E [kj/mol]	[au]	[kj/mol]
5	-30.26	-79447.925	-10.164	-26686.341	2	-0.617	-1620.262	0.85	2231.361
7	-29.975	-78699.885	-10.164	-26686.341	4	-0.815	-2138.546	1.332	3497.684
9	-29.788	-78209.281	-10.164	-26686.341	6	-1.087	-2854.842	1.792	4704.585
11	-29.632	-77797.751	-10.164	-26686.341	8	-1.245	-3269.67	2.107	5530.943
sr-ZORA-B3LYP / Am: TZP C, N, O, H: DZP									
	Am.3DOPO		DOPO, M: 2		Am			Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	M	E [au]	E [kj/mol]	[au]	[kj/mol]
5	-19.457	-51084.896	-6.476	-17003.444	2	-0.009	-24.515	-0.019	-50.05
7	-19.183	-50364.286	-6.476	-17003.444	4	-0.315	-827.228	0.561	1473.273
9	-19.103	-50154.448	-6.476	-17003.444	6	-0.33	-866.046	0.656	1721.929
11	-18.965	-49791.398	-6.476	-17003.444	8	-0.45	-1180.207	0.914	2399.14
sr-ZORA-B3LYP-D3 / Am: TZP C, N, O, H: DZP									
	Am.3DOPO		DOPO, M: 2		Am			Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	M	E [au]	E [kj/mol]	[au]	[kj/mol]
5	-19.652	-51595.481	-6.526	-17134.537	2	-0.009	-24.515	-0.064	-167.355
7	-19.377	-50874.868	-6.526	-17134.537	4	-0.315	-827.226	0.516	1355.969
9	-19.297	-50665.033	-6.526	-17134.537	6	-0.33	-866.046	0.611	1604.624
11	-19.159	-50301.983	-6.526	-17134.537	8	-0.45	-1180.207	0.869	2281.835

Table S13: Energies of Am.3DOPO, DOPO, and Am in different multiplicities in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYP–D3 with the methodology so–ZORA.

so-ZORA: Am: TZP C,N,O,H: DZP								
	Am.3DOPO		DOPO		Am		Binding Energy	
Methodology	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
HF	-32.023	-84075.888	-10.102	-26523.032	-1.318	-3460.090	-0.399	-1046.703
B3LYP	-20.997	-55126.377	-6.476	-17003.449	-0.539	-1415.968	-1.028	-2700.063
B3LYPD3	-21.008	-55156.898	-6.526	-17134.542	-0.539	-1415.968	-0.890	-2337.304

Table S14: Energies of Bk(III).3DOPO^{-1}, DOPO^{-1}, and Bk(III) in different multiplicities in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYP–D3 with the methodology sr-ZORA.

sr-ZORA-HF / Bk: TZP C, N, O, H: DZP								
	Bk(III).3DOPO^{-1}		DOPO^{-1}		Bk(III)		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
1	-31.916	-83795.895	-10.211	-26807.998	1.377	3614.375	-2.661	-6986.276
3	-32.146	-84399.863	-10.211	-26807.998	1.25	3282.938	-2.765	-7258.807
5	-31.707	-83246.226	-10.211	-26807.998	0.78	2048.494	-1.855	-4870.727
7	-30.99	-81364.94	-10.211	-26807.998	0.028	73.755	-0.386	-1014.701
sr-ZORA-B3LYP / Bk: TZP C, N, O, H: DZP								
	Bk(III).3DOPO^{-1}		DOPO^{-1}		Bk(III)		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
1	-20.846	-54730.549	-6.609	-17351.242	1.562	4100.801	-2.581	-6777.626
3	-20.857	-54759.707	-6.609	-17351.242	1.519	3987.702	-2.549	-6693.685
5	-20.804	-54620.439	-6.609	-17351.242	1.39	3649.118	-2.367	-6215.832
7	-20.624	-54148.832	-6.609	-17351.242	1.176	3087.214	-1.974	-5182.321
sr-ZORA-B3LYP-D3 / Bk: TZP C, N, O, H: DZP								
	Bk(III).3DOPO^{-1}		DOPO^{-1}		Bk(III)		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
1	-21.04	-55241.017	-6.659	-17482.172	1.562	4100.801	-2.626	-6895.302
3	-21.051	-55270.214	-6.659	-17482.172	1.519	3987.702	-2.594	-6811.4
5	-20.998	-55130.906	-6.659	-17482.172	1.39	3649.118	-2.412	-6333.508
7	-20.818	-54658.427	-6.659	-17482.172	1.176	3087.192	-2.018	-5299.103

Table S15: Energies of Bk(III).3DOPO^{-1}, DOPO^{-1}, and Bk(III) in different multiplicities in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYPD3 with the methodology so-ZORA.

so-ZORA / Bk: TZP C, N, O, H: DZP								
	Bk(III).3DOPO^{-1}		DOPO^{-1}		Bk(III)		Binding Energy	
Methodology	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
HF	-32.172	-84466.498	-10.211	-26808.027	0.310	813.854	-1.850	-4856.272
B3LYP	-21.044	-55250.188	-6.609	-17351.274	1.184	3109.823	-2.402	-6306.188
B3LYPD3	-21.238	-55760.656	-6.659	-17482.205	1.184	3109.823	-2.447	-6423.864

Table S16: Energies of Bk.3DOPO, DOPO, and Bk in different multiplicities in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYP–D3 with the methodology sr–ZORA.

sr-ZORA-HF / Bk: TZP C, N, O, H: DZP									
	Bk.3DOPO		DOPO, M: 2			Bk		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	M	E [au]	E [kj/mol]	[au]	[kj/mol]
5	-30.759	-80756.931	-10.164	-26686.341	2	-0.031	-81.052	-0.235	-616.855
7	-29.813	-78273.576	-10.164	-26686.341	4	-1.149	-3017.811	1.829	4803.258
9	-29.778	-78181.592	-10.164	-26686.341	6	-1.182	-3103.892	1.897	4981.324
sr-ZORA-B3LYP / Bk: TZP C, N, O, H: DZP									
	Bk.3DOPO		DOPO, M: 2			Bk		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	M	E [au]	E [kj/mol]	[au]	[kj/mol]
5	-19.404	-50944.205	-6.476	-17003.444	2	-0.01	-26.679	0.035	92.805
7	-19.135	-50238.865	-6.476	-17003.444	4	-0.313	-822.664	0.607	1594.13
9	-19.068	-50062.556	-6.476	-17003.444	6	-0.363	-954.04	0.724	1901.816
sr-ZORA-B3LYP–D3 / Bk: TZP C, N, O, H: DZP									
	Bk.3DOPO		DOPO, M: 2			Bk		Binding Energy	
M	E [au]	E [kj/mol]	E [au]	E [kj/mol]	M	E [au]	E [kj/mol]	[au]	[kj/mol]
5	-19.598	-51454.672	-6.526	-17134.537	2	-0.01	-26.679	-0.009	-24.382
7	-19.329	-50749.338	-6.526	-17134.537	4	-0.313	-822.667	0.563	1476.94
9	-19.262	-50573	-6.526	-17134.537	6	-0.363	-954.057	0.68	1784.668

Table S17: Energies of Bk.3DOPO, DOPO, and Bk in different multiplicities in atomic units, and kj/mol calculated at different levels theory: HF, B3LYP, and B3LYP–D3 with the methodology so-ZORA.

so-ZORA: Bk: TZP C, N, O, H: DZP								
	Bk.3DOPO		DOPO		Bk		Binding Energy	
Methodology	E [au]	E [kj/mol]	E [au]	E [kj/mol]	E [au]	E [kj/mol]	[au]	[kj/mol]
HF	-32.172	-84466.498	-10.102	-26523.032	-1.646	-4322.247	-0.219	-575.155
B3LYP	-21.044	-55250.188	-6.476	-17003.449	-0.495	-1299.161	-1.12	-2940.681
B3LYP–D3	-21.238	-55760.656	-6.526	-17134.542	-0.495	-1299.161	-1.165	-3057.868

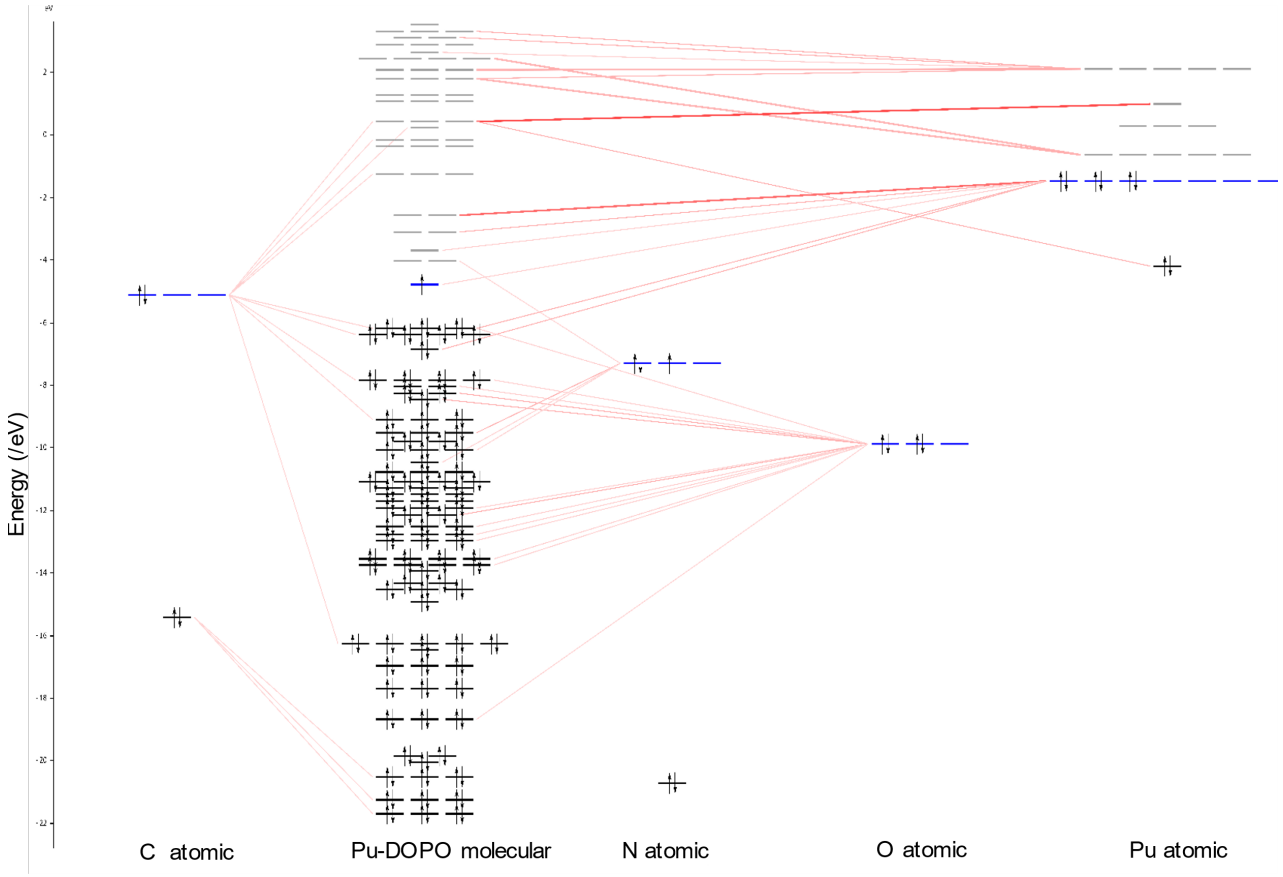


Figure S3: HOMO - LUMO Ligand Field Diagram (LFD) of the Pu-DOPO system for Pu=+4 calculated at the ZORA–DFT–D3 level of theory.

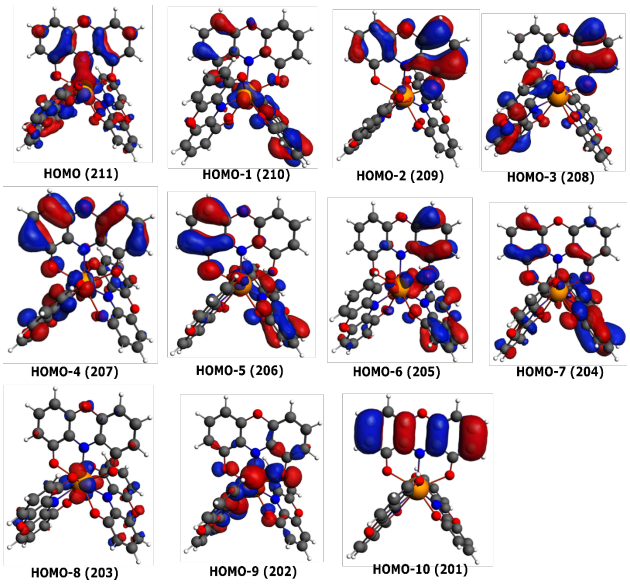


Figure S4: Pu–DOPO, HOMO and HOMO - n, where n = 1 - 10, calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

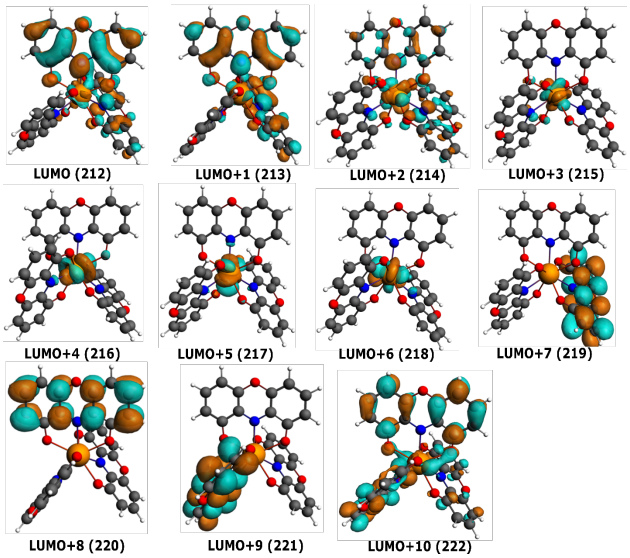


Figure S5: Pu–DOPO, LUMO, and LUMO + n, where n = 1 - 10, calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

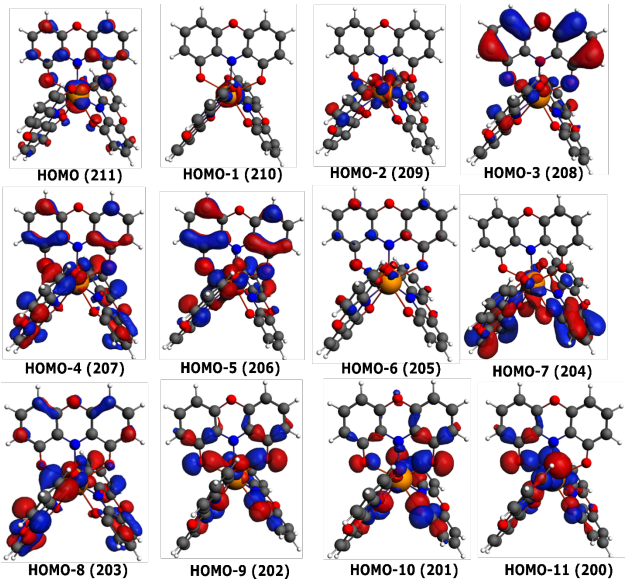


Figure S6: Am–DOPO, HOMO, and HOMO - n, where n = 1 - 11. calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

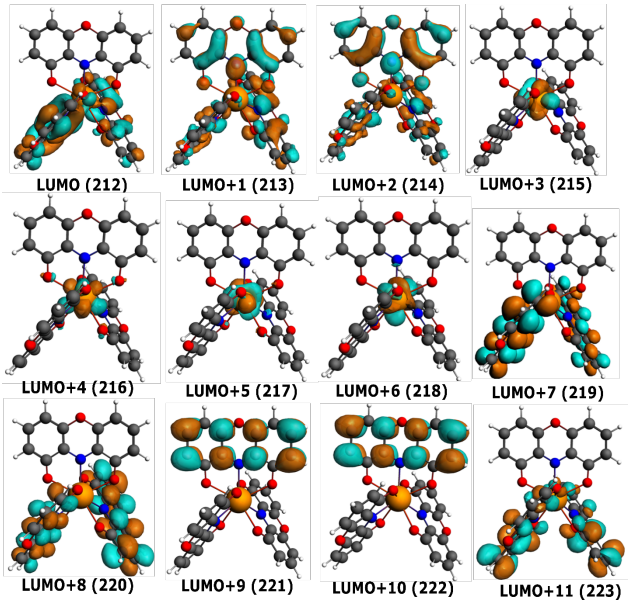


Figure S7: Am–DOPO, LUMO, and LUMO - n, where n = 1 - 11. calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

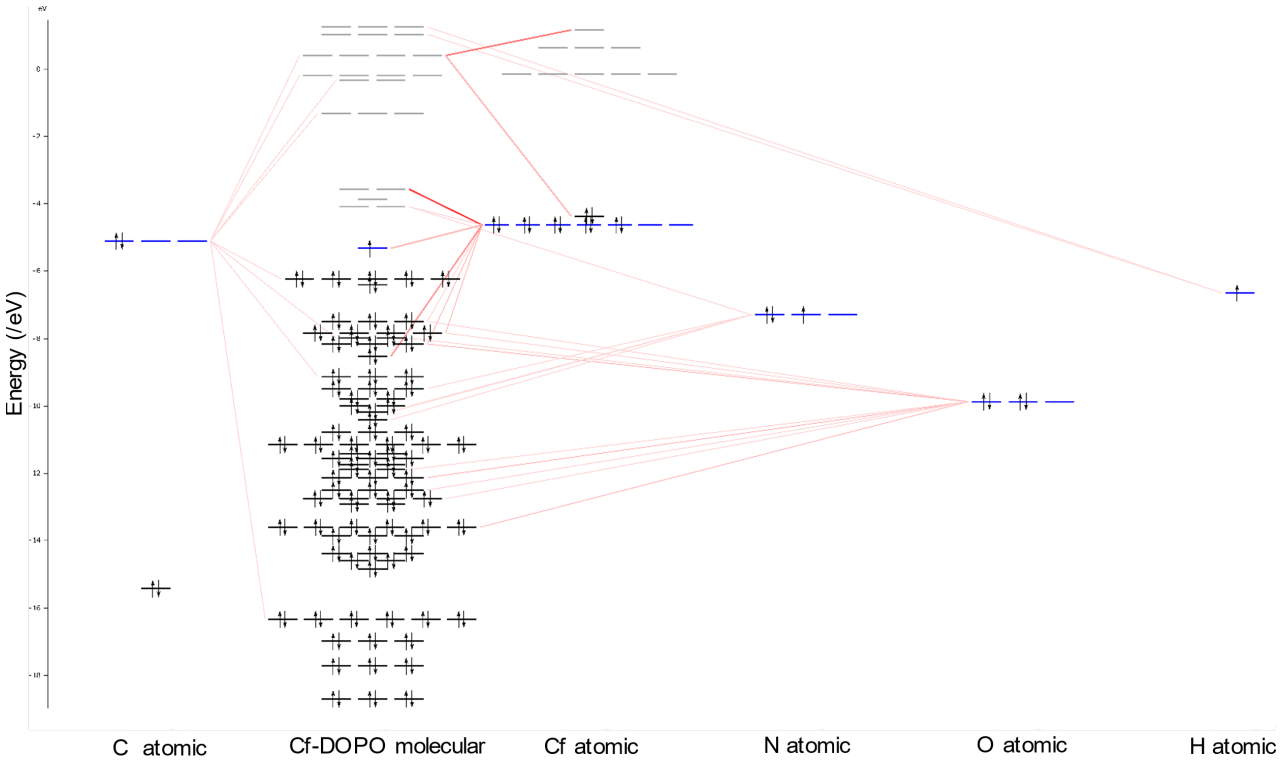


Figure S8: LFD of the Cf–DOPO system calculated at the ZORA–DFT–D3 level of theory.

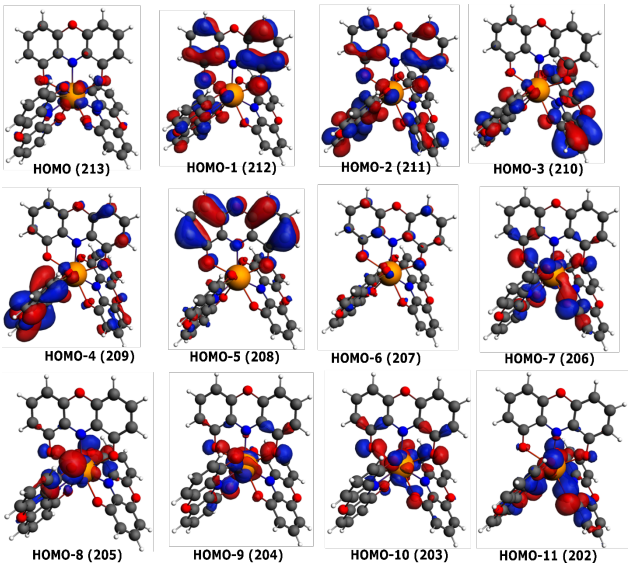


Figure S9: Cf–DOPO, HOMO, and HOMO - n, where n = 1 - 11, calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

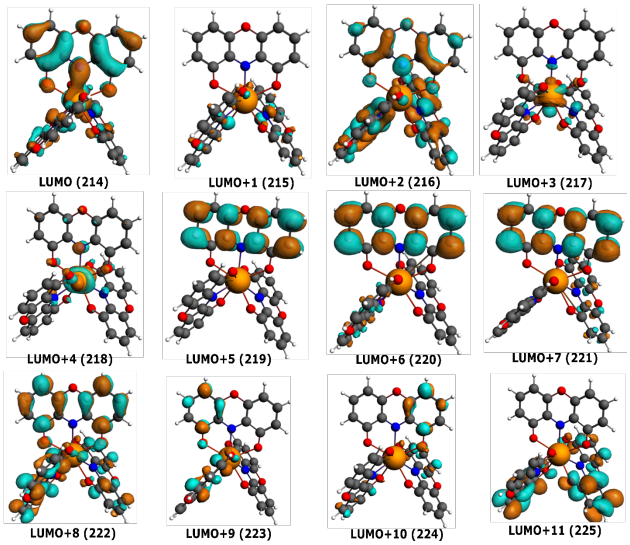


Figure S10: Cf–DOPO, LUMO, and LUMO + n, where n = 1 - 11. calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

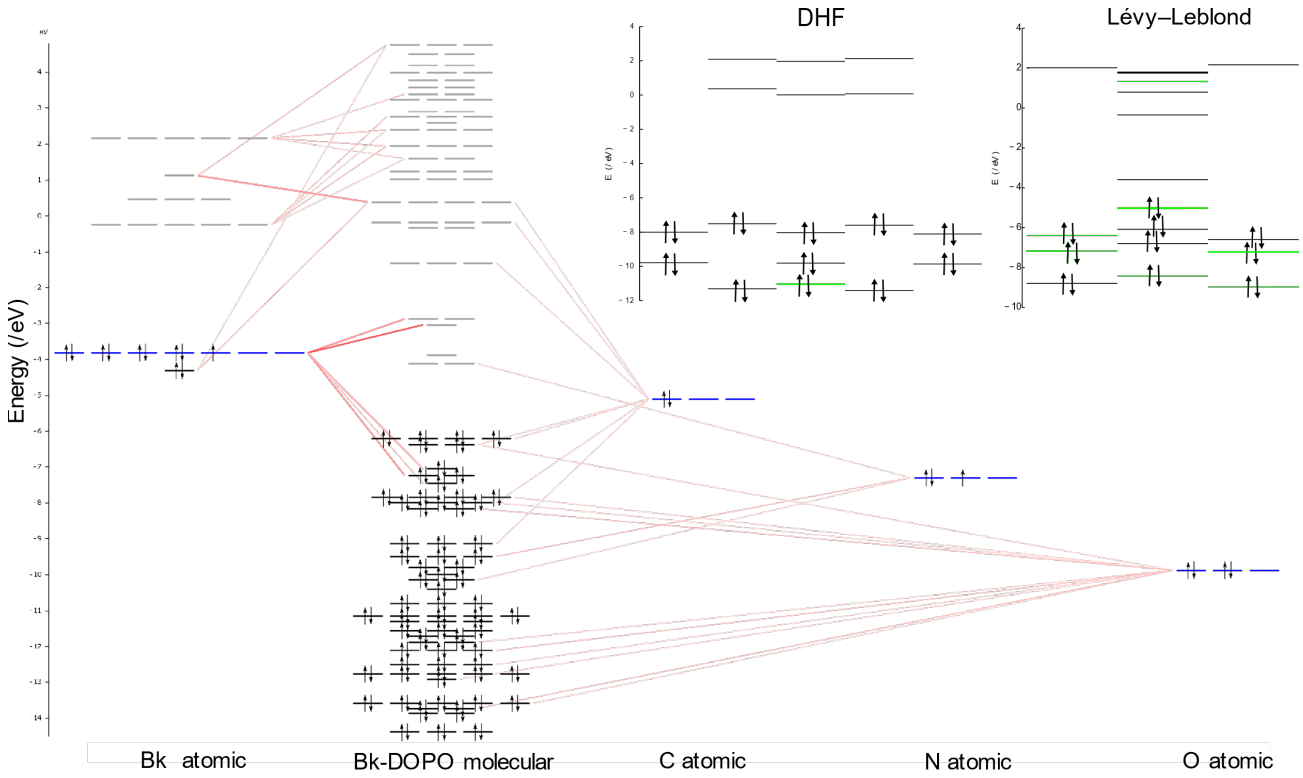


Figure S11: LFD of the Bk–DOPO system calculated at the ZORA–DFT–D3 level of theory. The insets include the energies of frontier orbitals for Bk calculated at the 4c-DHF and LL levels of theory (the line in green represents the OM with f–type primitives of Bk with significant Mulliken magnitudes). The inset with LL orbitals is included for completeness though they are unreliable. They are such that the LUMO and LUMO + 1 orbitals have negative energies.

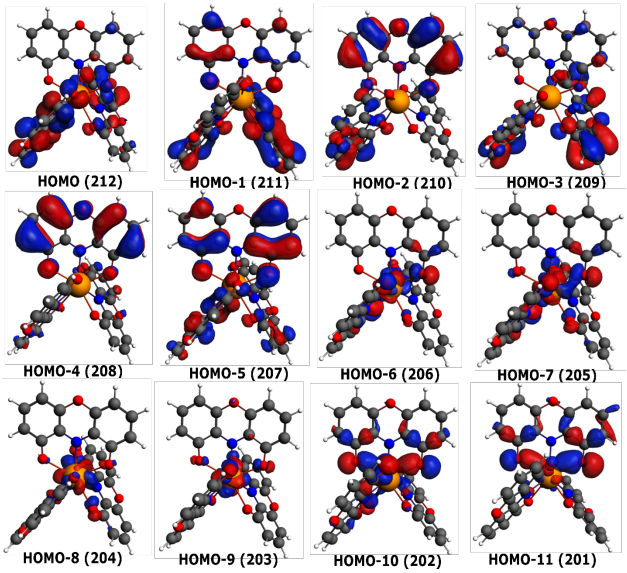


Figure S12: Bk–DOPO, HOMO, and HOMO - n, where n = 1 - 11, calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

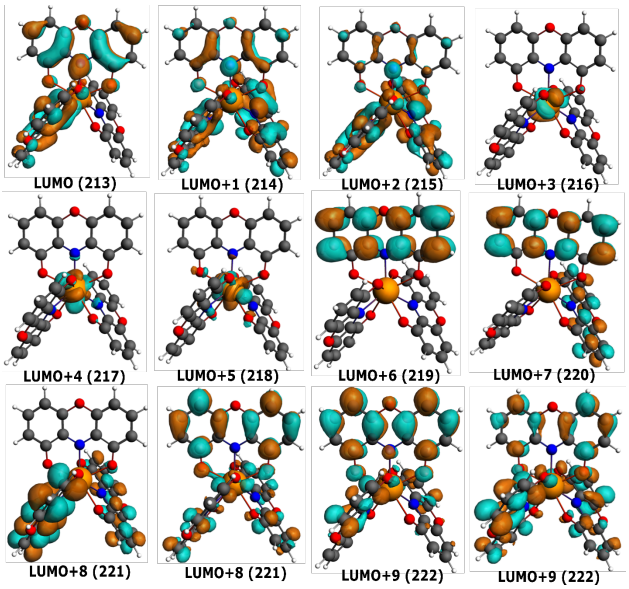


Figure S13: Bk–DOPO, LUMO, and LUMO + n, where n = 1 - 11, calculated at the ZORA–DFT–D3 level of theory. The numbers in parenthesis are the labels to identify the MO number.

Optimized XYZ coordinates of the Actinide Complexes

- Optimized XYZ coordinates of Pu-DOPO (Pu4+) at the ZORA-DFT-D3 level of theory

Pu	-1.853566	-1.082329	6.545622
N	0.231261	-2.352521	6.715363
C	1.304516	-1.824322	7.328421
C	1.110719	-0.520862	7.897333
O	-0.039107	0.036588	7.767367
C	2.228012	0.035993	8.566966
H	2.121633	1.014079	9.01673
C	3.425044	-0.660565	8.635981
H	4.263687	-0.210267	9.154345
C	3.604396	-1.931442	8.06094
H	4.546325	-2.457712	8.12209
C	2.529949	-2.499542	7.40569
O	2.666279	-3.752011	6.822526
C	1.556551	-4.287252	6.185217
C	1.641558	-5.525283	5.582079
H	2.568648	-6.080183	5.603412
C	0.492644	-6.027242	4.940941
H	0.557342	-6.997897	4.463109
C	-0.70786	-5.336927	4.894375
H	-1.572753	-5.746563	4.390054
C	-0.825737	-4.064791	5.509034
O	-1.880832	-3.335566	5.529877
C	0.354951	-3.563283	6.154727
N	-2.795678	-0.986715	4.283594

C	-2.036078	-0.678752	3.225859
C	-0.667567	-0.349775	3.523888
O	-0.290068	-0.38231	4.74738
C	0.149734	-0.022453	2.410578
H	1.185673	0.232226	2.590007
C	-0.373998	-0.040232	1.129205
H	0.272507	0.211172	0.296317
C	-1.713575	-0.376859	0.851264
H	-2.097566	-0.3941	-0.158759
C	-2.5334	-0.697097	1.912687
O	-3.856602	-1.045673	1.683231
C	-4.631921	-1.384014	2.783684
C	-5.948813	-1.759126	2.603934
H	-6.375988	-1.791546	1.611758
C	-6.697778	-2.094604	3.745982
H	-7.731366	-2.391872	3.611378
C	-6.171778	-2.06515	5.028473
H	-6.772921	-2.334133	5.886722
C	-4.823428	-1.688274	5.242057
O	-4.232269	-1.631961	6.381435
C	-4.07372	-1.341121	4.068347
N	-2.867508	0.053286	8.478057
C	-2.975372	-0.57161	9.662095
C	-2.514512	-1.930336	9.681443
O	-2.042087	-2.426868	8.593788
C	-2.620427	-2.602128	10.923506
H	-2.284607	-3.628617	10.984658

C	-3.134027	-1.948154	12.033952
H	-3.197823	-2.485386	12.973197
C	-3.571991	-0.6128	12.002539
H	-3.960955	-0.11888	12.881466
C	-3.485507	0.064807	10.801298
O	-3.903363	1.385639	10.724349
C	-3.763542	2.033114	9.504938
C	-4.140443	3.356945	9.384239
H	-4.541772	3.890922	10.233647
C	-3.981919	3.970983	8.129273
H	-4.278501	5.008584	8.027373
C	-3.462518	3.313024	7.024131
H	-3.349435	3.817387	6.073649
C	-3.061606	1.957556	7.120039
O	-2.558781	1.252134	6.171764
C	-3.243791	1.340019	8.403434

• Optimized XYZ coordinates of Am–DOPO (Am^{3+}) at the ZORA–DFT–D3 level of theory

Am	-1.785561	-1.106167	6.494926
N	0.374772	-2.419388	6.75503
C	1.411583	-1.913264	7.450837
C	1.214226	-0.600231	8.03199
O	0.11128	0.01043	7.852382
C	2.31282	-0.091889	8.785322
H	2.196676	0.882056	9.244168
C	3.48568	-0.816927	8.92953
H	4.297928	-0.395293	9.513314

C	3.665625	-2.084307	8.350556
H	4.582311	-2.646549	8.467359
C	2.615657	-2.61088	7.615109
O	2.775942	-3.865066	7.03607
C	1.698464	-4.384767	6.327534
C	1.829372	-5.638868	5.751908
H	2.753346	-6.191479	5.856286
C	0.731249	-6.146764	5.037938
H	0.822357	-7.126903	4.580069
C	-0.456997	-5.446658	4.898854
H	-1.288926	-5.859891	4.342507
C	-0.629326	-4.155927	5.482021
O	-1.691584	-3.460307	5.406378
C	0.516431	-3.642105	6.207089
N	-2.878656	-0.974112	4.242775
C	-2.178881	-0.61767	3.152734
C	-0.773708	-0.324253	3.356976
O	-0.277842	-0.42411	4.524827
C	-0.046587	0.058955	2.19152
H	1.006021	0.284221	2.309572
C	-0.661929	0.135111	0.952571
H	-0.075951	0.429137	0.08766
C	-2.026102	-0.158824	0.769984
H	-2.499512	-0.10147	-0.200996
C	-2.762791	-0.53344	1.878818
O	-4.112534	-0.833106	1.713505
C	-4.827893	-1.204689	2.848522

C	-6.171264	-1.506398	2.717755
H	-6.646707	-1.452263	1.74753
C	-6.880511	-1.876382	3.875889
H	-7.935362	-2.114264	3.782589
C	-6.280529	-1.943564	5.122895
H	-6.845101	-2.226601	6.002452
C	-4.898795	-1.637974	5.295787
O	-4.279292	-1.670219	6.407409
C	-4.18208	-1.262616	4.093582
N	-2.856736	0.070032	8.451476
C	-2.991547	-0.543848	9.645465
C	-2.497063	-1.903266	9.725971
O	-1.972953	-2.445252	8.699599
C	-2.644356	-2.53568	10.995951
H	-2.282018	-3.551292	11.095108
C	-3.224114	-1.874772	12.067405
H	-3.315809	-2.390138	13.018584
C	-3.697926	-0.55575	11.973498
H	-4.145979	-0.043085	12.813975
C	-3.570336	0.088683	10.753051
O	-4.033456	1.395736	10.644974
C	-3.877213	2.028341	9.416641
C	-4.319916	3.335561	9.285971
H	-4.774231	3.841892	10.126922
C	-4.159703	3.957893	8.036483
H	-4.506468	4.979984	7.919925
C	-3.578052	3.317158	6.954088

H	-3.465416	3.817892	6.000414
C	-3.104223	1.975731	7.055181
O	-2.548678	1.327172	6.111188
C	-3.287886	1.34389	8.34581

• Optimized XYZ coordinate of Cf–DOPO (Cf^{3+}) at the ZORA–DFT–D3 level of theory

Cf	-1.821419	-1.113161	6.479169
N	0.316255	-2.365391	6.763433
C	1.348838	-1.824296	7.426487
C	1.136811	-0.492303	7.957685
O	0.023202	0.08812	7.75693
C	2.227517	0.057204	8.694764
H	2.098289	1.04537	9.118493
C	3.407601	-0.648667	8.865679
H	4.214937	-0.198607	9.434752
C	3.602142	-1.936916	8.33087
H	4.526701	-2.481281	8.47
C	2.562236	-2.504059	7.616836
O	2.731933	-3.77949	7.082177
C	1.651377	-4.335224	6.402264
C	1.778806	-5.605681	5.868819
H	2.705189	-6.152975	5.981972
C	0.674102	-6.144969	5.183039
H	0.766657	-7.13965	4.758497
C	-0.519234	-5.455198	5.03235
H	-1.355319	-5.890491	4.4993
C	-0.687662	-4.147199	5.57381

O	-1.747373	-3.447159	5.487872
C	0.462454	-3.603037	6.266524
N	-2.865718	-1.000196	4.227534
C	-2.153063	-0.6373	3.14417
C	-0.756152	-0.324319	3.375233
O	-0.28098	-0.407458	4.550828
C	-0.014613	0.059788	2.217452
H	1.033545	0.29816	2.349259
C	-0.612711	0.124704	0.969392
H	-0.014664	0.421757	0.113389
C	-1.969056	-0.181542	0.763026
H	-2.428216	-0.130522	-0.215088
C	-2.718978	-0.561056	1.864416
O	-4.061504	-0.874271	1.678455
C	-4.793567	-1.237664	2.80358
C	-6.137746	-1.53895	2.651735
H	-6.597945	-1.489309	1.673984
C	-6.86038	-1.901931	3.801027
H	-7.914256	-2.139994	3.6948
C	-6.279981	-1.964489	5.058432
H	-6.859767	-2.244297	5.92923
C	-4.900392	-1.660304	5.251501
O	-4.295481	-1.687124	6.370878
C	-4.169887	-1.29114	4.056504
N	-2.824831	0.0279	8.453875
C	-2.957259	-0.604837	9.634051
C	-2.511495	-1.983569	9.669205

O	-2.035455	-2.516706	8.617346
C	-2.644344	-2.635684	10.931838
H	-2.317327	-3.665659	11.002085
C	-3.166088	-1.974314	12.032811
H	-3.247382	-2.505549	12.97621
C	-3.591334	-0.635556	11.981485
H	-3.990615	-0.124102	12.84689
C	-3.476252	0.029115	10.770882
O	-3.886825	1.357259	10.699753
C	-3.732911	2.00786	9.479883
C	-4.113377	3.337758	9.380834
H	-4.520074	3.853415	10.240307
C	-3.949025	3.97218	8.138023
H	-4.245851	5.012486	8.046753
C	-3.422021	3.324079	7.03039
H	-3.303124	3.838141	6.084553
C	-3.01258	1.961028	7.100328
O	-2.506959	1.295706	6.138825
C	-3.202245	1.318601	8.383106

• Optimized XYZ coordinate of Bk–DOPO (Bk^{3+}) at the ZORA–DFT–D3 level of theory

Bk	-1.810974	-1.116162	6.468044
N	0.316269	-2.385803	6.741477
C	1.334894	-1.862125	7.444984
C	1.122102	-0.536575	7.988004
O	0.018539	0.06062	7.763284
C	2.19698	-0.002081	8.755293

H	2.064327	0.98277	9.185435
C	3.368482	-0.717742	8.946906
H	4.165303	-0.279229	9.539178
C	3.565133	-2.000381	8.402146
H	4.482009	-2.55382	8.555809
C	2.538532	-2.551229	7.655885
O	2.715257	-3.818622	7.10702
C	1.648043	-4.361052	6.39493
C	1.785125	-5.628419	5.85842
H	2.706754	-6.17864	5.994181
C	0.69691	-6.161648	5.141368
H	0.797275	-7.154555	4.714395
C	-0.488607	-5.467427	4.966069
H	-1.314158	-5.896269	4.411859
C	-0.669273	-4.159319	5.509499
O	-1.729497	-3.467165	5.400495
C	0.466584	-3.61957	6.233483
N	-2.86143	-1.002816	4.267873
C	-2.168831	-0.606491	3.180887
C	-0.787137	-0.266814	3.414248
O	-0.322667	-0.353204	4.602899
C	-0.049314	0.139916	2.267495
H	0.993991	0.397981	2.401169
C	-0.650058	0.204912	1.0176
H	-0.058332	0.521251	0.164212
C	-1.999958	-0.124542	0.810131
H	-2.459552	-0.072162	-0.167878

C	-2.743331	-0.529874	1.90844
O	-4.08304	-0.868922	1.72605
C	-4.796735	-1.262672	2.856538
C	-6.136787	-1.594066	2.720762
H	-6.612863	-1.545629	1.750436
C	-6.834871	-1.987239	3.874709
H	-7.883975	-2.249612	3.780115
C	-6.234243	-2.050068	5.125258
H	-6.795037	-2.352907	6.000831
C	-4.862464	-1.715938	5.295519
O	-4.226372	-1.737771	6.406134
C	-4.161625	-1.319375	4.100585
N	-2.839815	0.05731	8.413545
C	-2.960879	-0.569818	9.600408
C	-2.513979	-1.945373	9.639608
O	-2.041388	-2.480707	8.583566
C	-2.641577	-2.597378	10.900097
H	-2.314986	-3.627406	10.969783
C	-3.156905	-1.933782	12.003365
H	-3.234253	-2.463563	12.947721
C	-3.579991	-0.595184	11.950901
H	-3.974166	-0.081288	12.817211
C	-3.471707	0.067107	10.738079
O	-3.882085	1.393625	10.665208
C	-3.732908	2.042058	9.443066
C	-4.111855	3.371558	9.349616
H	-4.511183	3.885322	10.21361

C	-3.95699	4.008612	8.105808
H	-4.253829	5.049309	8.018882
C	-3.440847	3.362178	6.994604
H	-3.329589	3.876451	6.047962
C	-3.030287	1.995835	7.055579
O	-2.536756	1.340895	6.085558
C	-3.210807	1.34999	8.341711

• Optimized XYZ coordinate of Am–DOPO (Am^{3+}) at the 4c-DHF and Basis sets: cv3z (Am, O, N)/3-21G (C, H)

Am	-1.7885411139	-1.1181810132	6.5105886017
O	0.1008861911	-0.0626910297	7.8471396288
O	2.7900340644	-3.8454037162	7.0416925172
O	-1.617269279	-3.4139735975	5.4358915904
O	-0.3582016293	-0.4802612793	4.5157867879
O	-4.1147635962	-0.8421393349	1.6991081373
O	-4.2690641397	-1.6264368314	6.3374399916
O	-2.0348304957	-2.3903356039	8.6938662172
O	-4.0189893219	1.3937723983	10.6749035503
O	-2.5645859576	1.2849985941	6.1975464459
N	0.4494852506	-2.4627641672	6.7879771286
N	-2.9302960824	-0.9820055415	4.1529305029
N	-2.8901707813	0.1115314702	8.5465370166
C	1.4307869459	-1.9323495606	7.4571669485
C	1.1981830975	-0.6146241381	8.0241738247
C	2.3019766795	-0.0665192437	8.7518878942
C	3.4599142865	-0.7729917991	8.8687172895

C	3.682311307	-2.0650653591	8.3072027405
C	2.6698479739	-2.6286046304	7.6094190579
C	1.7675308484	-4.3865373804	6.348616939
C	1.8674931778	-5.6027865838	5.7654519914
C	0.7321690639	-6.0897508177	5.0525826208
C	-0.4430065854	-5.4163412279	4.9145412276
C	-0.600585786	-4.1233387715	5.5052672736
C	0.5576602115	-3.6356177387	6.2342809809
C	-2.2122656999	-0.6510147778	3.1200955915
C	-0.8066757643	-0.376187277	3.3627000944
C	-0.0545565851	-0.0055893646	2.2039500416
C	-0.6647748805	0.0636021159	0.9893777258
C	-2.0439352436	-0.2141065445	0.7574856615
C	-2.8007638217	-0.5661073093	1.8217702275
C	-4.8482181517	-1.1946146881	2.7739873341
C	-6.165234797	-1.486810443	2.6747702652
C	-6.8561290569	-1.8418363742	3.8705486391
C	-6.2860086506	-1.9047488845	5.1049776682
C	-4.8965796446	-1.6063226266	5.2667234323
C	-4.1983346383	-1.2507687704	4.0438934953
C	-3.0184752128	-0.5234874829	9.6751374442
C	-2.5357565654	-1.8934318521	9.7148851579
C	-2.6946394114	-2.5552416623	10.9735426452
C	-3.258412705	-1.8972990337	12.0229023815
C	-3.7258578194	-0.5508279886	11.9784919278
C	-3.6040542385	0.1182442977	10.8093002104
C	-3.8807330957	2.0439114022	9.5017932899

C	-4.290875013	3.3228654751	9.3436113526
C	-4.1044279677	3.9243630122	8.064175276
C	-3.5427678057	3.303222272	6.9915647354
C	-3.0875443131	1.9516858487	7.1041466681
C	-3.2858365579	1.3434265869	8.4087094043
H	2.1901782651	0.9039064794	9.1879997054
H	4.2718405664	-0.3361016774	9.4178724438
H	4.6178322455	-2.5670414833	8.4326780782
H	2.7633079653	-6.1812148839	5.8373025428
H	0.8228627325	-7.0567166376	4.5967354484
H	-1.2653485483	-5.827798546	4.3675208346
H	0.9857429014	0.2136391938	2.3224505696
H	-0.0761265669	0.3455003762	0.1378076532
H	-2.4625534794	-0.1452342117	-0.2230903466
H	-6.6745624076	-1.4438984243	1.7365381306
H	-7.9006637559	-2.0690557943	3.7790561238
H	-6.8509790108	-2.1794352001	5.9709773823
H	-2.3614440459	-3.5682141636	11.0598340907
H	-3.3649555418	-2.4184018423	12.9550120496
H	-4.1595014165	-0.0897992721	12.8396462802
H	-4.7447346707	3.8633771228	10.1458835298
H	-4.4263121099	4.9419676317	7.9537495028
H	-3.4264598122	3.8012193042	6.0519814064

• Optimized XYZ coordinate of Am–DOPO (Am^{3+}) at the Lévy–Leblond and Basis sets: cv3z (Am, O, N)/3-21G (C, H)

Am	-1.8533614345	-1.216416141	6.5237504911

O	0.1439312513	-0.1160390437	7.8550716779
O	2.8538885039	-3.8901902994	7.0556432785
O	-1.5500085338	-3.5041091367	5.4446528486
O	-0.4207532755	-0.4693998093	4.4670041124
O	-4.1646137187	-0.8393363029	1.6297829881
O	-4.3385121106	-1.7153995218	6.250413859
O	-2.1295649605	-2.3765214609	8.7789318027
O	-3.9913598451	1.4782050709	10.7356267509
O	-2.6113284874	1.2839968546	6.2349833076
N	0.5036227783	-2.5236657112	6.7998002027
N	-2.9868813841	-1.0067858791	4.0864604045
N	-2.9331946692	0.1413181758	8.6032314432
C	1.4723003643	-1.9900776276	7.4722489645
C	1.2321567539	-0.6666785391	8.0432880973
C	2.3306672703	-0.1207435257	8.7881477753
C	3.4862843401	-0.8239284916	8.9119887413
C	3.7189812005	-2.116226366	8.3435636029
C	2.7202034286	-2.6810513146	7.6334087151
C	1.8424467675	-4.4342176276	6.347752253
C	1.966872996	-5.6436604125	5.74730475
C	0.8509291299	-6.1327008757	5.014473691
C	-0.3334422953	-5.4695312567	4.8799977201
C	-0.5150278322	-4.196811987	5.5007960555
C	0.6271582633	-3.7017919306	6.2365572709
C	-2.2732090674	-0.6432761236	3.0682998296
C	-0.8667967869	-0.3479368502	3.3206572079
C	-0.1199053112	0.0683932993	2.16990728

C	-0.7279512992	0.1521323085	0.9574494988
C	-2.1047222674	-0.1469675991	0.7140199215
C	-2.8590722171	-0.5370698715	1.7642043204
C	-4.900452797	-1.2145711159	2.695570783
C	-6.2167069758	-1.5199046578	2.5787094316
C	-6.9092049146	-1.90776081	3.7579351843
C	-6.3427145377	-1.9875303812	4.9953672833
C	-4.9602735809	-1.6770354984	5.1701489246
C	-4.2597092963	-1.2891233793	3.9649908222
C	-3.0549238858	-0.4769755696	9.750847596
C	-2.6063175355	-1.8525911729	9.803824109
C	-2.7528416266	-2.4905474177	11.0723449679
C	-3.2842621495	-1.8050963462	12.124620535
C	-3.7223442308	-0.4526683785	12.0660266881
C	-3.602662238	0.1945918772	10.8815605926
C	-3.8589978005	2.1095444906	9.5535412497
C	-4.2348060009	3.3956261755	9.3855399388
C	-4.0488858046	3.9810932014	8.0944010839
C	-3.5201570109	3.3360183561	7.0210201521
C	-3.1040386994	1.9688734414	7.1378301991
C	-3.2984785948	1.376433819	8.4566653866
H	2.2104857864	0.8454306505	9.2301983007
H	4.290787535	-0.3899178226	9.4718092862
H	4.6545807069	-2.6138784464	8.4772649942
H	2.8717894049	-6.2070299424	5.8177642926
H	0.95962446	-7.0870223258	4.5358976005
H	-1.1439944021	-5.8795337196	4.3156091322

H	0.9150928972	0.3070935158	2.2974137658
H	-0.1439789907	0.4645486231	0.1140332746
H	-2.5195877838	-0.0636499066	-0.266219845
H	-6.715026415	-1.4724536446	1.6348369696
H	-7.9517057049	-2.1499688009	3.6562209925
H	-6.9092542361	-2.2844179474	5.8528990926
H	-2.4399198096	-3.5093617217	11.1676691899
H	-3.3832904474	-2.3101267279	13.0651850255
H	-4.1309673573	0.0336872457	12.9243349579
H	-4.6540641073	3.9606681559	10.1892738958
H	-4.3502038884	5.002757871	7.9781171105
H	-3.39908752	3.8224933064	6.0765411736

• Optimized XYZ coordinate of Bk–DOPO (Bk^{3+}) at the 4c-DHF and Basis sets: cv3z (Bk, O, N)/3-21G (C, H)

Bk	-1.792918281	-1.1195216484	6.4834859669
O	0.0231646034	-0.0068858064	7.8168625246
O	-1.6489519974	-3.4203559101	5.3750046496
O	2.7134203874	-3.8087819839	7.1132277438
O	-0.3306867192	-0.4669100428	4.5681937294
O	-4.0865000525	-0.8382321892	1.7638239782
O	-4.2219637686	-1.6689455377	6.3898148308
O	-3.9103485647	1.3707460135	10.6412195808
O	-1.9925755559	-2.4202886241	8.6138311327
O	-2.5603411724	1.2995135761	6.126921076
N	0.3850693362	-2.4266602102	6.7726577265
N	-2.8372362235	0.0927387372	8.4813193137

N	-2.8921749803	-0.9882568729	4.2131704252
C	1.3529334921	-1.8866376568	7.4588398777
C	1.116730653	-0.5609114873	8.0118537681
C	2.2035313648	-0.014963972	8.7608153598
C	3.3568193213	-0.7239566026	8.9168371968
C	3.5816703774	-2.0199011245	8.376253583
C	2.5825818223	-2.5845027171	7.657241959
C	1.7101773784	-4.3622307036	6.4089715089
C	1.8244347978	-5.5922337694	5.8598440113
C	0.7133097834	-6.0980150829	5.1237291572
C	-0.4538752626	-5.4261478421	4.934172682
C	-0.6363435719	-4.1201435131	5.4926139207
C	0.5044343977	-3.6065826685	6.2469665606
C	-2.1857415529	-0.6367151237	3.180879536
C	-0.7779841084	-0.3506433742	3.4173795678
C	-0.0365163349	0.0405723521	2.2611973846
C	-0.6528507552	0.1186107342	1.0483402103
C	-2.0291695938	-0.1698359755	0.8216324515
C	-2.778777547	-0.5432301368	1.8846144609
C	-4.8124892529	-1.206003927	2.8360766705
C	-6.1283382177	-1.5074350599	2.737134062
C	-6.8136898749	-1.8854554792	3.926301256
C	-6.2372072592	-1.9612337571	5.1587195869
C	-4.8525592482	-1.6524381993	5.3227955931
C	-4.1560288547	-1.2723114158	4.1028092712
C	-2.9536286582	-0.5489808659	9.6112839391
C	-2.483571389	-1.9245889081	9.6421521366

C	-2.6284556539	-2.5860999379	10.8989533977
C	-3.1700367621	-1.9288774375	11.9637333457
C	-3.6219569417	-0.581473982	11.9297902526
C	-3.5080769593	0.0911489817	10.7595187949
C	-3.7820888834	2.0297697967	9.4755283509
C	-4.1707207449	3.3170768418	9.3432820472
C	-4.0005156263	3.936953451	8.0700035434
C	-3.4757282166	3.3200582491	6.9782005906
C	-3.0442367448	1.9556287299	7.0544334316
C	-3.2199908173	1.3248209405	8.3613162908
H	-3.3663533437	3.8296378778	6.0444455298
H	-4.3105919981	4.9591135626	7.9779818789
H	-4.5899009984	3.8497089988	10.1688861382
H	-4.0380455354	-0.1106054472	12.7937554228
H	-3.2657095794	-2.4556822206	12.8926343599
H	-2.3035984197	-3.602157239	10.9745707148
H	-6.7975099586	-2.2512876068	6.0220101302
H	-7.8550499387	-2.1245145688	3.836342627
H	-6.6315040774	-1.4626075293	1.7960196794
H	2.0824361322	0.9582489209	9.1872197218
H	-2.459714083	-0.0944841046	-0.1529246475
H	-0.0686845489	0.415077218	0.1996355136
H	1.0017978936	0.2689618203	2.3780619646
H	-1.2601323554	-5.8494680118	4.3733355107
H	0.8148406377	-7.0749707533	4.6940694493
H	2.7195802903	-6.1628885975	5.9769326049
H	4.5054402372	-2.5343306263	8.5276853528

H	4.1532940778	-0.2837345519	9.4836546138

• Optimized XYZ coordinate of Bk-DOPO (Bk^{3+}) at the Lévy-Leblond and Basis sets: cv3z (Bk, O, N)/3-21G (C, H)

Bk	-1.8106397041	-1.1137940906	6.4711150542
O	0.0739823578	0.0716753047	7.798809894
O	-1.6999294023	-3.5140757289	5.4047003683
O	2.6935115515	-3.8133408619	7.1038580276
O	-0.2994572375	-0.3243391824	4.5499793458
O	-4.0676439571	-0.8716176785	1.7541883242
O	-4.2795984272	-1.7652800036	6.3937872363
O	-3.8787564699	1.3869421361	10.6544901692
O	-2.0478446091	-2.4829664278	8.6442169086
O	-2.5433081138	1.383226823	6.1164377642
N	0.3550510334	-2.3956042435	6.7533582355
N	-2.8573791243	0.0842832492	8.4596815244
N	-2.8807679704	-1.0007015972	4.2297018707
C	1.3253313561	-1.8691857804	7.4313263784
C	1.1180863788	-0.5104944133	7.9876939146
C	2.2338011006	0.004659738	8.7496967075
C	3.3714074546	-0.7135041786	8.9200852771
C	3.5656266803	-2.021537489	8.373181053
C	2.562740206	-2.5728115561	7.6522418556
C	1.6605739169	-4.358750447	6.4105094314
C	1.7750387212	-5.6177085264	5.8779429078
C	0.6754583719	-6.1661823313	5.1586031591
C	-0.4906820266	-5.4948505221	4.9807217933

C	-0.6863980938	-4.1574738657	5.5216773811
C	0.4779848268	-3.6083130484	6.2541414876
C	-2.180579245	-0.6059709205	3.1930401522
C	-0.7843073084	-0.24796224	3.4203460989
C	-0.068026891	0.1734204958	2.2439995069
C	-0.6758499297	0.2325107863	1.0163875596
C	-2.0290871432	-0.112829508	0.8136949214
C	-2.7629532481	-0.5266576635	1.9035458397
C	-4.7905150829	-1.2700119098	2.8335247319
C	-6.1140041815	-1.6114803129	2.6934776343
C	-6.8148164816	-2.0174285264	3.8481341228
C	-6.2380106635	-2.0827956666	5.0922699664
C	-4.8592344826	-1.7384459609	5.3033037127
C	-4.1445454747	-1.3247007092	4.1015035003
C	-2.9666539138	-0.5553628141	9.5965236384
C	-2.5166174629	-1.9561261847	9.6390278861
C	-2.664667747	-2.5999740257	10.92184895
C	-3.1780477568	-1.93706208	11.9923401382
C	-3.6015096083	-0.577839067	11.9402981506
C	-3.4888546028	0.0868475016	10.7581606014
C	-3.7394096623	2.0503278909	9.475810599
C	-4.0966282011	3.3545509047	9.3658161673
C	-3.9259525857	4.0058857824	8.101984405
C	-3.4192216481	3.3875320417	7.0100133959
C	-3.006969188	1.995157248	7.0500085438
C	-3.2009082342	1.3321597766	8.3601671483
H	-3.3008964203	3.8999851539	6.0780229636

H	-4.2165449843	5.0357500124	8.0342913681
H	-4.4939216879	3.8806952698	10.2070301779
H	-3.9976259905	-0.0859675262	12.802602277
H	-3.2717679984	-2.4506039608	12.9293565958
H	-2.3503472752	-3.6206806501	10.9954281243
H	-6.8021870666	-2.3933008048	5.9484040853
H	-7.8488924235	-2.2846613918	3.737288755
H	-6.5891257503	-1.5677126787	1.7365814377
H	2.1197451446	0.9812813333	9.1737827575
H	-2.4801078009	-0.0582196045	-0.1543027852
H	-0.106469546	0.5539912856	0.1651827408
H	0.9615593291	0.4428586238	2.3657712262
H	-1.310124354	-5.9212980192	4.4407540902
H	0.7863516611	-7.1502668338	4.7497071639
H	2.6807391981	-6.1710415868	6.008589574
H	4.4797366146	-2.5531971819	8.5296121321
H	4.1756572742	-0.2943455573	9.4925888755

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