Supplementary information

Computational Methodology

The def2-TZPP basis set[1] (obtained from the EMSL Basis Set Exchange[2,3]) was used for all elements except uranium. The def2-TZPP basis set is all electron for F, N, P and As; for Sb, a 28 electron effective core potential (ECP) is used and for Bi a 60 electron ECP. For uranium, the 60-electron quasi-relativistic ECP of the Stuttgart/Cologne Group was used along with the associated atomic natural orbital basis set.[4,5,6] Calculations were performed with Molpro version 2015.1,[7] using the CASSCF program `Multi',[8,9] and the second-order multiconfigurational perturbation theory program 'rs2c'.[10]

Geometry optimisations at the CASSCF level of theory were performed for all molecules NUF_3-$BiUF_3$; geometry optimisations at the CASPT2 level of theory were performed for NUF_3, PUF_3 and $AsUF_3$. Geometry optimisations were first performed in C_s symmetry, but the optimised geometry of NUF_3 was approximately C_{3v}, and was re-optimised in that point group. CASPT2 geometry optimisations and harmonic frequency calculations were numerical, due to the lack of analytical gradients in the rs2c program. A level shift of 0.1 was applied for NUF_3, and 0.3 for PUF_3 and $AsUF_3$ (unless otherwise noted in the SI). Wavefunctions were calculated in C_s symmetry (regardless of the point group of the geometry optimisation) with both space-symmetric and antisymmetric wavefunctions optimised at the singlet, triplet and quintet multiplicities--the effects of spin-orbit coupling were not taken into account.

Quantum Theory of Atoms-in-Molecules (QTAIM)[11] analyses were performed with AIMALL,[12] using .wfx files generated by the Molden2AIM program.[13]

Calculated states of EUF_3 at CASSCF (E = N…Bi) and CASPT2 (E = N, P, As) levels of theory. A [6,16] active space is used in all cases. All states are geometrically optimised. Electronic energy relative to the global minimum, electronic energy, natural orbital occupancies, effective bond orders and E-U bond lengths (in ångstrom) given.

Electronic States

Table S1: **NUF_3 CASSCF**/def2-TZVPP (N, F), SDD (U), optimised geometry

	ΔE_{el} / eV	E_{el} / Ha	σ	π	π^*	σ^*	$f_{(n.b)}$	BO_{eff}	r(N-U) / Å
$^1A'$	0.000	-828.483	1.901	3.805	0.166	0.087	0.000	2.727	1.750
$^3A''$	1.903	-828.413	0.970	3.774	0.194	0.029	0.999	2.260	1.926
$^1A''$	1.953	-828.411	0.976	3.717	0.251	0.020	1.000	2.211	1.962
$^3A'$	2.035	-828.408	1.863	2.849	0.134	0.123	0.993	2.227	1.984
$^5A'$	2.128	-828.405	1.959	1.982	0.000	0.026	1.998	1.957	2.327
$^5A''$	2.576	-828.388	0.991	2.943	0.289	0.000	1.714	1.822	2.221

Table S2: **NUF_3 CASPT2**/def2-TZVPP (N, F), SDD (U), optimised geometry, level shift = 0.1

	ΔE_{el} / eV	E_{el} / Ha	σ	π	π^*	σ^*	$f_{(n.b)}$	BO_{eff}	r(N-U) / Å
$^1A'$	0.000	-829.754	1.903	3.809	0.161	0.086	0.000	2.733	1.753
$^3A''$*	1.602	-829.695	0.970	3.800	0.160	0.030	1.000	2.290	1.886
$^3A'$	1.987	-829.681	1.872	1.862	1.111	0.124	0.992	1.249	1.990
$^1A''$°	2.087	-829.678	0.976	3.752	0.216	0.022	0.998	2.245	1.926
$^5A''$*	2.598	-829.659	1.960	1.985	0.302	0.017	1.699	1.813	2.286
$^5A'$*	2.614	-829.658	1.960	1.985	1.564	0.017	0.437	1.182	2.278

**level shift = 0.2 °level shift = 0.5*

Table S3: **PUF_3 CASSCF**/def2-TZVPP (P, F), SDD (U), optimised geometry

	ΔE_{el} / eV	E_{el} / Ha	σ	π	π^*	σ^*	$f_{(n.b)}$	BO_{eff}	r(P-U) / Å
$^1A'$	0.000	-1114.714	1.932	2.198	1.533	0.017	0.253	1.290	2.855
$^5A''$	0.014	-1114.714	1.931	1.982	1.347	0.018	0.653	1.274	2.883
$^3A'$	0.024	-1114.713	1.932	2.031	1.492	0.017	0.460	1.226	2.879
$^1A''$	0.100	-1114.710	1.931	1.173	1.808	0.017	1.000	0.639	2.873
$^3A''$	0.166	-1114.708	1.940	2.008	0.971	0.021	1.000	1.478	2.860
$^5A'$	0.184	-1114.707	1.942	1.979	1.533	0.018	0.467	1.184	2.865

Table S4: **PUF_3 CASPT2**/def2-TZVPP (P, F), SDD (U), optimised geometry, level shift = 0.3

	ΔE_{el} / *eV*	E_{el} / *Ha*	σ	π	π^*	σ^*	*f (n.b)*	BO_{eff}	*r(P-U) / Å*
$^1A'$	0.000	-1115.949	1.931	2.141	1.333	0.0167	0.510	1.362	2.743
$^3A''$	0.031	-1115.948	1.931	2.012	0.971	0.0171	1.000	1.478	2.770
$^3A'$	0.034	-1115.948	1.931	2.025	0.961	0.0072	0.998	1.494	2.771
$^5A''$	0.063	-1115.947	1.931	1.982	0.312	0.0177	1.688	1.792	2.800
$^5A'$	0.068	-1115.947	1.931	1.982	0.784	0.0177	1.216	1.556	2.796
$^1A''$	0.229	-1115.941	1.931	2.193	0.788	0.017	1.000	1.659	2.771

Table S5: **$AsUF_3$ CASSCF**/def2-TZVPP (As, F), SDD (U), optimised geometry

	ΔE_{el} / *eV*	E_{el} / *Ha*	σ	π	π^*	σ^*	*f (n.b)*	BO_{eff}	*r(As-U) / Å*
$^5A''$	0.000	-3008.183	1.943	1.985	0.327	0.015	1.673	1.793	2.999
$^5A'$	0.002	-3008.183	1.943	1.985	0.505	0.015	1.496	1.704	2.996
$^3A'$	0.007	-3008.183	1.943	2.014	1.440	0.015	0.532	1.251	2.996
$^3A''$	0.014	-3008.182	1.943	2.000	0.986	0.015	1.000	1.471	3.001
$^1A'$	0.080	-3008.180	1.943	2.305	1.674	0.023	0.000	1.275	2.951
$^1A''$	0.296	-3008.172	1.946	1.129	0.861	0.021	1.990	1.096	2.973

Table S6: **$AsUF_3$ CASPT2**/def2-TZVPP (As, F), SDD (U), optimised geometry, level shift = 0.3

	ΔE_{el} / *eV*	E_{el} / *Ha*	σ	π	π^*	σ^*	*f (n.b)*	BO_{eff}	*r(As-U) / Å*
$^1A'$	0.000	-3009.364	1.943	2.085	1.334	0.014	0.567	1.340	2.871
$^3A''$	0.022	-3009.363	1.943	2.009	0.977	0.014	1.000	1.480	2.893
$^3A'$	0.039	-3009.362	1.943	2.020	1.310	0.010	0.655	1.321	2.901
$^5A''$	0.042	-3009.362	1.943	1.985	0.315	0.015	1.686	1.799	2.910
$^5A'$	0.053	-3009.362	1.943	1.985	0.503	0.010	1.498	1.708	2.905
$^1A''$*	0.306	-3009.353	1.943	2.028	0.958	0.014	1.000	1.500	2.890

**level shift = 0.5*

Table S7: **$SbUF_3$ CASSCF**/def2-TZVPP (Sb, F), SDD (U), optimised geometry

	ΔE_{el} / eV	E_{el} / Ha	σ	π	π*	σ*	f (n.b)	BO_{eff}	r(Sb-U) / Å
$^5A''$	0.000	-1013.252	1.943	1.985	1.000	0.016	1.000	1.456	3.220
$^5A'$	0.001	-1013.252	1.943	1.985	1.000	0.016	1.000	1.456	3.219
$^1A'$	0.008	-1013.251	1.943	2.131	1.608	0.015	0.246	1.225	3.208
$^3A'$	0.010	-1013.251	1.943	2.004	1.702	0.015	0.279	1.115	3.221
$^3A''$	0.014	-1013.251	1.943	1.995	1.000	0.015	0.990	1.462	3.225
$^1A''$	0.096	-1013.248	1.942	2.128	0.855	0.016	1.000	1.600	3.220

Table S8: **$BiUF_3$ CASSCF**/def2-TZVPP (As, F), SDD (U), optimised geometry

	ΔE_{el} / eV	E_{el} / Ha	σ	π	π*	σ*	f (n.b)	BO_{eff}	r(Bi-U) / Å
$^1A'$	0.000	-987.556	1.937	2.164	1.574	0.030	0.242	1.248	3.277
$^1A''$	0.023	-987.555	1.938	2.009	1.232	0.029	0.740	1.343	3.282
$^3A'$	0.027	-987.555	1.939	2.012	1.479	0.027	0.489	1.223	3.261
$^3A''$	0.033	-987.554	1.939	1.995	1.255	0.027	0.730	1.326	3.282
$^5A''$	0.041	-987.554	1.943	1.979	1.372	0.023	0.628	1.263	3.276
$^5A'$	0.042	-987.554	1.943	1.979	1.507	0.024	0.493	1.196	3.274

Frequency Calculations ([6,16] CASPT2)

Table S9: Frequency calculations at the CASPT2 level of theory. Frequency calculations are numerical, and performed without wavefunction symmetry. Frequencies given in cm^{-1}

	U-E stretch a_1 / a′	U-F stretch a_1 / a′	U-F stretch e / a′	U-F stretch e / a″	U-F bend a_1 / a′	U-F bend e / a′	U-F bend e / a″	E-U-F bend e / a′	E-U-F bend e / a″	#imag. freq.
NUF_3 $^1A_1$	928.44	630.44	546.75	546.18	144.48	138.88	138.80	9.52*i*	0.73*i*	2
PUF_3 $^1A'$	260.22	591.61	544.10	530.44	107.69	5.53	100.00	50.09*i*	46.08*i*	2
$AsUF_3$ $^1A'$	193.65	594.34	546.79	528.13	107.85	32.62*i*	91.73	84.11*i*	69.44*i*	3

Optimised Geometries

Z matrix variables of the optimised geometries are given in ångstrom for bond lengths and degrees for angles. Z-matrix all of the form:

U,
E, U, B1,
F1, U, B2, E, A1,
F2, U, B3, E, A2, F1, D1, 0,
F3, U, B3, E, A2, F1, -D1, 0,

Table S10: **NUF_3 CASSCF [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	1.74966363	1.96207590	1.98376709	1.92583599	2.32732023	2.22068830
B2 / Å	2.06247224	2.07064231	2.06034721	2.06169677	2.06327373	2.06528070
B3 / Å	119.26670015	117.53550905	119.97127633	123.22698633	113.12592329	105.03934627
A1 / °	2.06248584	2.07057741	2.07937513	2.07464437	2.06518285	2.06760061
A2 / °	119.31825159	117.68409939	109.11952786	114.19898228	104.62218407	111.79501377
D1 / °	119.98346235	119.99151795	115.59685227	120.33368540	117.22853506	120.44948587

Table S11: **NUF_3 CASPT2 [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	1.75315792	1.92604004	1.99004607	1.88435033	2.27835083	2.28650344
B2 / Å	2.04485854	2.05302879	2.04665842	2.03788217	2.05331815	2.05374786
B3 / Å	2.04485854	2.04921027	2.06635945	2.06054510	2.05942704	2.05624541
A1 / °	122.58314996	99.04872772	121.25316610	141.90245469	103.52253600	109.92919824
A2 / °	122.58314996	127.45327165	107.87668701	107.35099811	106.45590828	104.58243365
D1 / °	119.97200364	113.23606871	114.30883104	124.78557197	116.13020533	122.95979828

Table S12: **PUF_3 CASSCF [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	2.85487233	2.87307254	2.87898686	2.86018471	2.86483680	2.88262101
B2 / Å	2.06330151	2.06754338	2.05713816	2.05488434	2.05870044	2.05577362
B3 / Å	2.06329881	2.05661772	2.06312145	2.06274954	2.06042015	2.06202954
A1 / °	108.08441646	106.12601358	108.25828906	107.67882184	107.50633008	109.81992138
A2 / °	108.07221905	109.18338207	107.83836643	108.02790589	107.50986207	107.03349551
D1 / °	119.98188899	119.91887086	122.26806489	122.39787190	116.46055934	122.65750282

Table S13: **PUF_3 CASPT2 [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	2.74344624	2.77127150	2.78567990	2.76986521	2.79582952	2.79991948
B2 / Å	2.04944358	2.05392432	2.04084123	2.04419397	2.04532166	2.04437239
B3 / Å	2.05246669	2.04555281	2.05383880	2.05142110	2.05020489	2.04899668
A1 / °	105.10446315	103.45650116	105.79445974	105.19041589	108.15012735	109.83601344
A2 / °	104.97744266	109.10153060	104.84078912	106.76007393	105.47665484	105.47531864
D1 / °	111.74179511	119.29915794	125.39655946	123.15852805	123.49864932	123.22404395

Table S14: **PUF_3 CASPT2 [6,6]** optimised geometry

	$^1A'$
B1 / Å	2.44583209
B2 / Å	2.03441332
B3 / Å	2.03441332
A1 / °	120.58416314
A2 / °	120.58416314
D1 / °	120.00000000

Table S15: **$AsUF_3$ CASSCF [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	2.95095386	2.97344563	2.99638316	3.00106915	2.99639075	2.99898403
B2 / Å	2.05856220	2.05443031	2.05806991	2.05269929	2.05760834	2.05360612
B3 / Å	2.05858915	2.06531671	2.05900099	2.06069238	2.05928422	2.05996764
A1 / °	109.10003689	108.87121501	109.31699988	108.62761259	108.18297141	110.03184374
A2 / °	109.07630568	108.75416391	107.07313858	107.88872382	107.19792721	107.34404512
D1 / °	119.96581826	123.88872103	115.85400273	122.63188038	115.93625359	122.65071001

Table S16: **$AsUF_3$ CASPT2 [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	2.87103834	2.89019864	2.90714091	2.89300332	2.90458440	2.91016953
B2 / Å	2.04893379	2.04300197	2.04081681	2.04339804	2.04624629	2.04341232
B3 / Å	2.05169932	2.04990351	2.04656500	2.05069225	2.05130089	2.04884815
A1 / °	105.31355176	105.26257931	110.27643340	105.97650475	104.97318200	110.04834229
A2 / °	105.38649558	107.04913704	105.18514065	106.70908361	105.91751855	105.64739257
D1 / °	112.10479959	123.07590962	115.08441516	123.29710737	113.39243801	123.29995138

Table S17: **$SbUF_3$ CASSCF [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	3.20816964	3.21966056	3.22119937	3.22533659	3.21908393	3.22033463
B2 / Å	2.05773287	2.06274178	2.05507969	2.04979538	2.05488595	2.05060653
B3 / Å	2.05767308	2.05136075	2.05627145	2.05782646	2.05661818	2.05747406
A1 / °	108.63503163	107.45328614	109.48034612	109.06850427	108.55017177	110.18561632
A2 / °	108.58549558	109.17680721	107.38137318	108.19846413	107.59897703	107.78332464
D1 / °	120.05135064	120.23443643	115.69668696	122.61913254	115.82500088	122.64493084

Table S18: **$BiUF_3$ CASSCF [6,16]** optimised geometries

	$^1A'$	$^1A''$	$^3A'$	$^3A''$	$^5A'$	$^5A''$
B1 / Å	3.26067651	3.28187390	3.27730259	3.28142156	3.27416886	3.27630339
B2 / Å	2.06026239	2.05271034	2.05774247	2.05213107	2.05670185	2.05249744
B3 / Å	2.06024022	2.06002321	2.05815706	2.05994190	2.05826193	2.05909817
A1 / °	108.50661518	107.76367729	109.23817717	108.46948235	108.10335375	110.11807776
A2 / °	108.44222008	108.33175721	107.51542263	108.19084219	107.87322869	107.84112289
D1 / °	120.01642730	122.32915801	116.58485815	122.44965955	116.19337716	122.55055062

Table S19: **PUF3 SA-CASSCF [6,16]** pseudo-natural orbital occupancies for each state, electronic energies and relative energies. All states ^{1}A' symmetry, performed at the CASPT2 optimised geometry.

	A′										*A″*								
State	*σ*	*π*	*π**	$5f_U$	$5f_U$	$5f_U$	$3d_P$	$3d_P$	$3d_P$	$3d_P$	*π*	*f*	*π**	$5f_U$	$3d_P$	$3d_P$	$5f_U + \pi^*$	*Eel / Ha*	*ΔE / eV*
1	1.93	1.03	0.55	0.40	0.01	0.00	0.02	0.02	0.01	0.00	1.03	0.51	0.44	0.02	0.01	0.01	1.92	-1114.701	0.00
2	1.93	1.02	0.45	0.51	0.01	0.00	0.02	0.02	0.01	0.00	1.01	0.54	0.41	0.02	0.01	0.01	1.95	-1114.701	0.01
3	1.93	0.99	0.21	0.34	0.31	0.14	0.02	0.02	0.01	0.00	1.02	0.41	0.53	0.04	0.01	0.01	1.98	-1114.694	0.19
4	1.93	1.03	0.22	0.44	0.10	0.19	0.02	0.02	0.01	0.00	1.02	0.13	0.38	0.46	0.01	0.01	1.93	-1114.689	0.33
5	1.93	1.02	0.44	0.04	0.44	0.05	0.02	0.02	0.01	0.00	1.02	0.19	0.31	0.47	0.01	0.01	1.95	-1114.687	0.40
6	1.93	0.98	0.15	0.25	0.26	0.35	0.02	0.01	0.01	0.00	0.98	0.53	0.09	0.40	0.01	0.01	2.02	-1114.685	0.45

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