Supporting Information for

Quantum chemical characterization of single molecule magnets based on uranium

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Table S1: Experimental geometry (Å) for compound **1** ($U(H_2Bpz_2)_3$)[1]

1	U	-0.00294	0.04333	0.04940
2	N	-2.84100	1.08239	1.53726
3	N	1.65371	1.86115	-0.46823
4	N	0.12646	-2.40683	0.52048
5	N	-1.71420	1.28305	-1.42280
6	N	-2.13668	-0.08598	1.43344
7	N	0.83748	-0.78123	-2.19043
8	N	2.58621	0.34698	2.10086
9	N	-0.35260	-3.19865	-0.49005
10	N	-2.53172	2.14021	-0.72421
11	N	1.24091	0.20219	2.26754
12	N	2.93394	1.55389	-0.09803
13	N	0.20857	-1.92650	-2.62427
14	C	-3.94438	-0.43253	2.68004
15	C	-0.24574	-4.48045	-0.12466
16	C	-3.91896	0.85734	2.28074
17	C	0.74247	-2.27730	-3.79834
18	C	1.01393	0.32134	3.56882
19	C	3.04524	3.45665	-1.18684
20	C	1.72423	-1.39623	-4.14375
21	C	3.13857	0.55419	3.30000
22	C	0.52977	-3.24074	1.49279
23	C	-3.27916	2.06972	-2.80048
24	C	1.74364	3.02165	-1.12274
25	C	3.76422	2.50623	-0.53014
26	C	2.17343	0.55779	4.26051
27	C	-3.47205	2.60695	-1.57338
28	C	-2.18097	1.24083	-2.65687
29	C	1.75421	-0.48998	-3.09751
30	C	-2.80520	-0.99030	2.13790
31	C	0.30374	-4.55661	1.12744
32	H	-4.58685	-0.85236	3.20610
33	H	-0.50562	-5.20858	-0.64104
34	H	-4.56306	1.49416	2.49626
35	H	0.48109	-3.01150	-4.30519
36	H	0.17354	0.25338	3.96237
37	H	3.36547	4.22889	-1.59181
38	H	2.77331	-0.49427	0.21085
39	H	4.13461	0.08120	0.74275
40	H	2.25446	-1.40437	-4.90717
41	H	4.04822	0.67698	3.45489
42	H	0.90922	-2.97328	2.29814
43	H	-3.77580	2.22313	-3.57094
44	H	1.01996	3.47764	-1.48547
45	H	4.68485	2.51673	-0.40356

46	H	2.27716	0.69201	5.17511
47	H	-4.14746	3.20562	-1.35040
48	H	-1.82056	0.72269	-3.33957
49	H	2.34060	0.22964	-3.04213
50	H	-2.77775	3.11423	1.09304
51	H	-1.36492	2.43332	0.96809
52	H	-2.54145	-1.87424	2.24972
53	H	0.48409	-5.32381	1.62278
54	H	-1.42516	-3.15489	-2.26917
55	H	-1.52033	-1.79646	-1.48583
56	B	3.17987	0.24901	0.68461
57	B	-2.31164	2.32003	0.78583
58	B	-0.91751	-2.51067	-1.75134

Table S2: DFT/BP86 optimized geometry (Å) for compound **1**.
ADF Bond energy (Relative with repect to the atomic fragments) = -13.65408498 a.u.

1	U	0.03109	-0.01021	0.00000
2	N	0.78541	2.96399	-1.27782
3	N	0.99337	1.66293	-1.64853
4	N	2.15694	-2.22158	-1.27397
5	N	0.94149	-1.70858	-1.63550
6	N	-2.91713	-0.74999	-1.27435
7	N	-1.89378	0.09022	-1.62315
8	N	0.78541	2.96399	1.27782
9	N	0.99337	1.66293	1.64853
10	N	2.15694	-2.22158	1.27397
11	N	0.94149	-1.70858	1.63550
12	N	-2.91713	-0.74999	1.27435
13	N	-1.89378	0.09022	1.62315
14	C	1.75587	1.69108	-2.75903
15	C	1.40702	3.78848	-2.14531
16	C	2.04164	3.01375	-3.11560
17	C	0.53889	-2.38845	-2.72692
18	C	2.50812	-3.20413	-2.12831
19	C	1.49763	-3.34534	-3.07928
20	C	-2.29045	0.74833	-2.73034
21	C	-3.93419	-0.61845	-2.15285
22	C	-3.57416	0.33173	-3.10597
23	C	1.75587	1.69108	2.75903
24	C	1.40702	3.78848	2.14531
25	C	2.04164	3.01375	3.11560
26	C	0.53889	-2.38845	2.72692
27	C	2.50812	-3.20413	2.12831

28	C	1.49763	-3.34534	3.07928
29	C	-2.29045	0.74833	2.73034
30	C	-3.93419	-0.61845	2.15285
31	C	-3.57416	0.33173	3.10597
32	H	-0.96798	2.41748	0.00000
33	H	-0.45481	4.37714	0.00000
34	H	2.04647	0.76358	-3.23914
35	H	1.34753	4.86344	-2.02244
36	H	2.62213	3.36264	-3.96067
37	H	2.60882	-0.43804	0.00000
38	H	4.01460	-1.90184	0.00000
39	H	-0.40867	-2.14701	-3.19548
40	H	3.44957	-3.72734	-2.00966
41	H	1.46782	-4.04015	-3.90953
42	H	-1.57464	-2.00174	0.00000
43	H	-3.52742	-2.53315	0.00000
44	H	-1.63144	1.47447	-3.19275
45	H	-4.83302	-1.21425	-2.04736
46	H	-4.15931	0.66872	-3.95284
47	H	2.04647	0.76358	3.23914
48	H	1.34753	4.86344	2.02244
49	H	2.62213	3.36264	3.96067
50	H	-0.40867	-2.14701	3.19548
51	H	3.44957	-3.72734	2.00966
52	H	1.46782	-4.04015	3.90953
53	H	-1.63144	1.47447	3.19275
54	H	-4.83302	-1.21425	2.04736
55	H	-4.15931	0.66872	3.95284
56	B	-0.05497	3.24102	0.00000
57	B	2.83664	-1.65105	0.00000
58	B	-2.74682	-1.61578	0.00000

Table S3: DFT/B3LYP optimized geometry (Å) for compound **1**.
ADF Bond energy (Relative with repect to the atomic fragments) = -15.84010554 a.u.

1	U	-0.00048	-0.01829	0.00000
2	N	0.80262	3.00154	-1.26583
3	N	1.04130	1.70324	-1.58263
4	N	2.18553	-2.24209	-1.26528
5	N	0.94537	-1.78881	-1.58235
6	N	-2.99525	-0.74608	-1.27568
7	N	-1.95751	0.05375	-1.64507
8	N	0.80262	3.00154	1.26583
9	N	1.04130	1.70324	1.58263
10	N	2.18553	-2.24209	1.26528
11	N	0.94537	-1.78881	1.58235

12	N	-2.99525	-0.74608	1.27568
13	N	-1.95751	0.05375	1.64507
14	C	1.82289	1.70418	-2.66597
15	C	1.42656	3.80272	-2.13925
16	C	2.09258	3.01370	-3.06386
17	C	0.55321	-2.45619	-2.67218
18	C	2.55986	-3.18277	-2.14095
19	C	1.54253	-3.35428	-3.06835
20	C	-2.34233	0.71473	-2.73966
21	C	-4.01068	-0.58495	-2.13303
22	C	-3.63793	0.34347	-3.09398
23	C	1.82289	1.70418	2.66597
24	C	1.42656	3.80272	2.13925
25	C	2.09258	3.01370	3.06386
26	C	0.55321	-2.45619	2.67218
27	C	2.55986	-3.18277	2.14095
28	C	1.54253	-3.35428	3.06835
29	C	-2.34233	0.71473	2.73966
30	C	-4.01068	-0.58495	2.13303
31	C	-3.63793	0.34347	3.09398
32	H	-0.97954	2.53346	0.00000
33	H	-0.39188	4.45540	0.00000
34	H	2.14470	0.77408	-3.10206
35	H	1.35398	4.87181	-2.05221
36	H	2.68461	3.34059	-3.89884
37	H	2.68173	-0.46618	0.00000
38	H	4.04326	-1.95022	0.00000
39	H	-0.40776	-2.25545	-3.11320
40	H	3.51923	-3.66176	-2.05545
41	H	1.52599	-4.02771	-3.90566
42	H	-1.71916	-2.06564	0.00000
43	H	-3.68243	-2.48834	0.00000
44	H	-1.67297	1.41382	-3.21111
45	H	-4.92408	-1.14095	-2.01149
46	H	-4.21960	0.69400	-3.92651
47	H	2.14470	0.77408	3.10206
48	H	1.35398	4.87181	2.05221
49	H	2.68461	3.34059	3.89884
50	H	-0.40776	-2.25545	3.11320
51	H	3.51923	-3.66176	2.05545
52	H	1.52599	-4.02771	3.90566
53	H	-1.67297	1.41382	3.21111
54	H	-4.92408	-1.14095	2.01149
55	H	-4.21960	0.69400	3.92651
56	B	-0.04011	3.31086	0.00000
57	B	2.87879	-1.66997	0.00000

58	B	-2.85589	-1.62224	0.00000

Table S4: DFT/M06-L optimized geometry (Å) for compound **1**.
ADF Bond energy (Relative with repect to the atomic fragments) = -14.72730003 a.u.

1	U	0.00411	-0.00881	0.00000
2	N	0.85136	2.99530	-1.26478
3	N	1.10086	1.70045	-1.58577
4	N	2.15107	-2.25503	-1.26687
5	N	0.90851	-1.81376	-1.58910
6	N	-3.00523	-0.76479	-1.26770
7	N	-2.00870	0.09471	-1.60654
8	N	0.85136	2.99530	1.26478
9	N	1.10086	1.70045	1.58577
10	N	2.15107	-2.25503	1.26687
11	N	0.90851	-1.81376	1.58910
12	N	-3.00523	-0.76479	1.26770
13	N	-2.00870	0.09471	1.60654
14	C	1.87488	1.72080	-2.66981
15	C	1.46357	3.79998	-2.14018
16	C	2.12712	3.02524	-3.06183
17	C	0.54974	-2.46250	-2.69637
18	C	2.54977	-3.16094	-2.16453
19	C	1.55642	-3.32191	-3.10204
20	C	-2.42590	0.75122	-2.68798
21	C	-4.01765	-0.63786	-2.13113
22	C	-3.68676	0.31914	-3.06150
23	C	1.87488	1.72080	2.66981
24	C	1.46357	3.79998	2.14018
25	C	2.12712	3.02524	3.06183
26	C	0.54974	-2.46250	2.69637
27	C	2.54977	-3.16094	2.16453
28	C	1.55642	-3.32191	3.10204
29	C	-2.42590	0.75122	2.68798
30	C	-4.01765	-0.63786	2.13113
31	C	-3.68676	0.31914	3.06150
32	H	-0.90388	2.47414	0.00000
33	H	-0.37518	4.41460	0.00000
34	H	2.20374	0.79687	-3.11372
35	H	1.37853	4.86719	-2.04851
36	H	2.71135	3.35999	-3.89816
37	H	2.59900	-0.48023	0.00000
38	H	3.99503	-1.92625	0.00000
39	H	-0.41003	-2.27035	-3.14429
40	H	3.51671	-3.62177	-2.07904

41	H	1.56372	-3.97105	-3.95719
42	H	-1.67478	-2.02092	0.00000
43	H	-3.61568	-2.53493	0.00000
44	H	-1.79246	1.49329	-3.14281
45	H	-4.89987	-1.24234	-2.02682
46	H	-4.27745	0.65458	-3.89300
47	H	2.20374	0.79687	3.11372
48	H	1.37853	4.86719	2.04851
49	H	2.71135	3.35999	3.89816
50	H	-0.41003	-2.27035	3.14429
51	H	3.51671	-3.62177	2.07904
52	H	1.56372	-3.97105	3.95719
53	H	-1.79246	1.49329	3.14281
54	H	-4.89987	-1.24234	2.02682
55	H	-4.27745	0.65458	3.89300
56	B	0.00405	3.28663	0.00000
57	B	2.83172	-1.67632	0.00000
58	B	-2.83100	-1.64079	0.00000

Table S5: Experimental geometry (Å) for compound **2** ($U(Bp^{Me})_3$).[2]

1	U	0.00000	0.00000	-0.08515
2	N	1.99090	0.05088	1.57098
3	N	2.84101	1.07798	1.25389
4	N	2.94887	0.95935	-1.25924
5	N	2.06542	-0.01273	-1.63954
6	N	-1.03951	1.69873	1.57098
7	N	-2.35407	1.92140	1.25389
8	N	-2.30526	2.07412	-1.25924
9	N	-1.02169	1.79507	-1.63954
10	N	-0.95138	-1.74961	1.57098
11	N	-0.48694	-2.99938	1.25389
12	N	-0.64361	-3.03347	-1.25924
13	N	-1.04373	-1.78235	-1.63954
14	C	1.78586	-1.62638	3.41637
15	C	2.46617	-0.49303	2.71581
16	C	3.61281	0.18590	3.12002
17	C	3.81170	1.16796	2.17371
18	C	4.04812	0.89344	-2.02999
19	C	3.88402	-0.12657	-2.93907
20	C	2.63679	-0.66916	-2.66383
21	C	1.96914	-1.83670	-3.32437
22	C	0.51556	2.35979	3.41637
23	C	-0.80611	2.38228	2.71581

24	C	-1.96740	3.03584	3.12002
25	C	-2.91733	2.71705	2.17371
26	C	-2.79781	3.05906	-2.02999
27	C	-1.83239	3.42695	-2.93907
28	C	-0.73889	2.61810	-2.66383
29	C	0.60606	2.62367	-3.32437
30	C	-2.30142	-0.73341	3.41637
31	C	-1.66006	-1.88925	2.71581
32	C	-1.64541	-3.22173	3.12002
33	C	-0.89437	-3.88501	2.17371
34	C	-1.25032	-3.95250	-2.02999
35	C	-2.05163	-3.30037	-2.93907
36	C	-1.89790	-1.94895	-2.66383
37	C	-2.57520	-0.78697	-3.32437
38	H	0.92896	-1.31659	3.77913
39	H	2.35350	-1.94602	4.14783
40	H	1.62726	-2.35554	2.78055
41	H	4.14649	0.00932	3.88677
42	H	4.51939	1.80261	2.17272
43	H	4.81034	1.45549	-1.95903
44	H	4.49509	-0.40016	-3.61336
45	H	2.10777	-2.64291	-2.78226
46	H	2.35307	-1.97289	-4.21530
47	H	1.00844	-1.65961	-3.40607
48	H	1.53559	2.13017	-0.13528
49	H	3.16717	2.76416	-0.06352
50	H	0.67572	1.46280	3.77913
51	H	0.50856	3.01120	4.14783
52	H	1.22633	2.58701	2.78055
53	H	-2.08132	3.58630	3.88677
54	H	-3.82080	3.01260	2.17272
55	H	-3.66567	3.43813	-1.95903
56	H	-1.90099	4.09294	-3.61336
57	H	1.23494	3.14684	-2.78226
58	H	0.53203	3.02427	-4.21530
59	H	0.93304	1.70314	-3.40607
60	H	-2.61257	0.26477	-0.13528
61	H	-3.97742	1.36077	-0.06352
62	H	-1.60468	-0.14621	3.77913
63	H	-2.86205	-1.06518	4.14783
64	H	-2.85358	-0.23148	2.78055
65	H	-2.06517	-3.59562	3.88677
66	H	-0.69859	-4.81521	2.17272
67	H	-1.14468	-4.89363	-1.95903
68	H	-2.59410	-3.69278	-3.61336
69	H	-3.34271	-0.50393	-2.78226

70	H	-2.88511	-1.05138	-4.21530
71	H	-1.94148	-0.04353	-3.40607
72	H	1.07699	-2.39494	-0.13528
73	H	0.81025	-4.12493	-0.06352
74	B	2.60549	1.85882	-0.05557
75	B	-2.91253	1.32701	-0.05557
76	B	0.30704	-3.18583	-0.05557

Table S6: Experimental geometry (Å) for compound **3** ($U(Bc^{Me})_3$).[2]

1	U	0.00000	0.00000	-0.20711
2	N	2.46681	0.53080	2.69955
3	N	2.24507	2.09817	1.24843
4	N	2.53157	2.03443	-1.24790
5	N	2.96767	0.40224	-2.57697
6	N	-1.69309	1.87092	2.69955
7	N	-2.93960	0.89520	1.24843
8	N	-3.02765	1.17519	-1.24790
9	N	-1.83219	2.36896	-2.57697
10	N	-0.77372	-2.40172	2.69955
11	N	0.69453	-2.99337	1.24843
12	N	0.49608	-3.20962	-1.24790
13	N	-1.13548	-2.77120	-2.57697
14	C	1.85255	0.82329	1.51933
15	C	2.35339	-0.73431	3.41011
16	C	3.21902	1.59505	3.14965
17	C	3.07160	2.57638	2.23891
18	C	3.72899	2.31930	-1.88266
19	C	3.99709	1.30743	-2.71802
20	C	2.87640	-0.86866	-3.27606
21	C	2.06098	0.83365	-1.66906
22	C	-1.63926	1.19271	1.51933
23	C	-0.54076	2.40525	3.41011
24	C	-2.99087	1.99023	3.14965
25	C	-3.76701	1.37190	2.23891
26	C	-3.87307	2.06975	-1.88266
27	C	-3.13082	2.80786	-2.71802
28	C	-0.68592	2.92537	-3.27606
29	C	-1.75245	1.36803	-1.66906
30	C	-0.21329	-2.01600	1.51933
31	C	-1.81263	-1.67094	3.41011
32	C	-0.22815	-3.58528	3.14965
33	C	0.69541	-3.94828	2.23891
34	C	0.14408	-4.38906	-1.88266
35	C	-0.86627	-4.11530	-2.71802
36	C	-2.19049	-2.05671	-3.27606

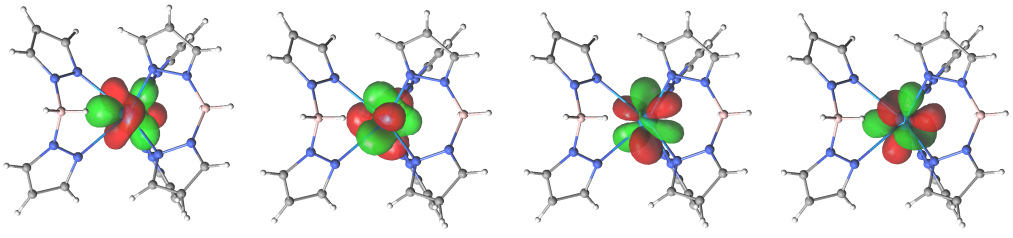
37	C	-0.30852	-2.20168	-1.66906
38	H	3.17900	-0.90311	3.90920
39	H	2.20506	-1.45751	2.76730
40	H	1.59781	-0.69070	4.03219
41	H	3.73828	1.62884	3.94396
42	H	3.46583	3.44009	2.27447
43	H	4.26377	3.09270	-1.75020
44	H	4.74894	1.22889	-3.29347
45	H	2.96059	-0.71767	-4.24160
46	H	2.00932	-1.28498	-3.08622
47	H	3.59568	-1.46149	-2.97315
48	H	0.74401	2.64763	-0.21457
49	H	2.12087	3.84078	-0.08598
50	H	-0.80739	3.20465	3.90920
51	H	0.15971	2.63839	2.76730
52	H	-0.20074	1.72909	4.03219
53	H	-3.27975	2.42303	3.94396
54	H	-4.71212	1.28145	2.27447
55	H	-4.81024	2.14619	-1.75020
56	H	-3.43872	3.49825	-3.29347
57	H	-0.85877	2.92278	-4.24160
58	H	0.10817	2.38261	-3.08622
59	H	-0.53215	3.84470	-2.97315
60	H	-2.66492	-0.67949	-0.21457
61	H	-4.38665	-0.08366	-0.08598
62	H	-2.37162	-2.30154	3.90920
63	H	-2.36477	-1.18089	2.76730
64	H	-1.39706	-1.03839	4.03219
65	H	-0.45852	-4.05186	3.94396
66	H	1.24629	-4.72154	2.27447
67	H	0.54647	-5.23888	-1.75020
68	H	-1.31022	-4.72715	-3.29347
69	H	-2.10182	-2.20511	-4.24160
70	H	-2.11748	-1.09763	-3.08622
71	H	-3.06353	-2.38321	-2.97315
72	H	1.92091	-1.96814	-0.21457
73	H	2.26578	-3.75712	-0.08598
74	B	1.82999	2.78369	-0.08511
75	B	-3.32574	0.19297	-0.08511
76	B	1.49575	-2.97666	-0.08511

Table S7: DFT/BP86 optimized geometry (Å) for compound **4** ($U(Tp)_3$).[3]
ADF Bond energy (Relative with repect to the atomic fragments) = -19.19837915 a.u.

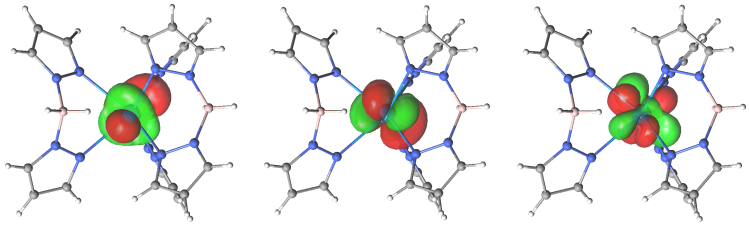
1	U	0.00216	-0.00214	0.00000

2	N	1.49567	1.37637	1.59551
3	N	2.64299	-0.86884	0.00000
4	N	2.72425	1.88838	1.27859
5	N	3.71383	-0.02406	0.00000
6	N	-1.93852	0.60496	1.59405
7	N	-0.56370	2.72166	0.00000
8	N	-2.99383	1.41681	1.27867
9	N	-1.82994	3.22824	0.00000
10	N	0.44974	-1.98837	1.59081
11	N	-2.07453	-1.85107	0.00000
12	N	0.26791	-3.30804	1.27835
13	N	-1.88294	-3.20133	0.00000
14	N	1.49567	1.37637	-1.59551
15	N	2.72425	1.88838	-1.27859
16	N	-1.93852	0.60496	-1.59405
17	N	-2.99383	1.41681	-1.27867
18	N	0.44974	-1.98837	-1.59081
19	N	0.26791	-3.30804	-1.27835
20	C	3.13981	2.72756	2.25777
21	C	2.16194	2.77544	3.24195
22	C	1.15408	1.92072	2.77882
23	C	4.87548	-0.72050	0.00000
24	C	4.56242	-2.07205	0.00000
25	C	3.15970	-2.10911	0.00000
26	C	-3.92660	1.36138	2.25986
27	C	-3.48020	0.48898	3.24369
28	C	-2.23889	0.03816	2.77808
29	C	-1.80629	4.58246	0.00000
30	C	-0.47887	4.98558	0.00000
31	C	0.25317	3.78850	0.00000
32	C	0.77829	-4.08854	2.26133
33	C	1.31524	-3.26644	3.24299
34	C	1.09115	-1.96565	2.77464
35	C	-3.06890	-3.85541	0.00000
36	C	-4.07975	-2.90528	0.00000
37	C	-3.40655	-1.67425	0.00000
38	C	3.13981	2.72756	-2.25777
39	C	2.16194	2.77544	-3.24195
40	C	1.15408	1.92072	-2.77882
41	C	-3.92660	1.36138	-2.25986
42	C	-3.48020	0.48898	-3.24369
43	C	-2.23889	0.03816	-2.77808
44	C	0.77829	-4.08854	-2.26133
45	C	1.31524	-3.26644	-3.24299
46	C	1.09115	-1.96565	-2.77464
47	H	2.51081	-2.97639	0.00000

48	H	5.24835	-2.90994	0.00000
49	H	4.09955	3.22427	2.18434
50	H	5.82946	-0.20704	0.00000
51	H	2.17491	3.35343	4.15739
52	H	0.18726	1.70215	-3.21901
53	H	4.55836	2.06175	0.00000
54	H	1.32841	3.65928	0.00000
55	H	-0.09504	5.99810	0.00000
56	H	-4.83432	1.94879	2.18850
57	H	-2.72743	5.15275	0.00000
58	H	-3.98609	0.21374	4.16050
59	H	-1.56850	-0.69264	-3.21723
60	H	-4.05899	2.92009	0.00000
61	H	-3.83014	-0.67755	0.00000
62	H	-5.14890	-3.07681	0.00000
63	H	0.71773	-5.16798	2.19262
64	H	-3.10453	-4.93821	0.00000
65	H	1.80575	-3.56740	4.16005
66	H	1.39343	-1.01963	-3.21175
67	H	-0.50574	-4.98075	0.00000
68	H	4.09955	3.22427	-2.18434
69	H	2.17491	3.35343	-4.15739
70	H	0.18726	1.70215	3.21901
71	H	-4.83432	1.94879	-2.18850
72	H	-3.98609	0.21374	-4.16050
73	H	-1.56850	-0.69264	3.21723
74	H	0.71773	-5.16798	-2.19262
75	H	1.80575	-3.56740	-4.16005
76	H	1.39343	-1.01963	3.21175
77	B	3.50019	1.48544	0.00000
78	B	-3.03173	2.29030	0.00000
79	B	-0.47089	-3.77628	0.00000

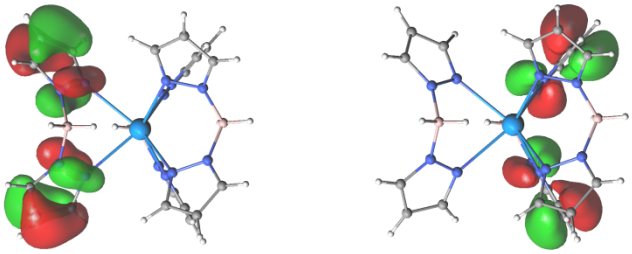


(0.91) (0.84) (0.16) (0.08)



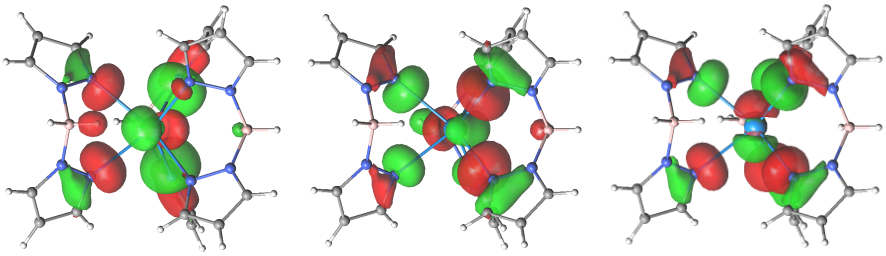
(0.85) (0.13) (0.03)

Figure S1: Molecular orbitals of the CAS(3,7) active space for compound **1**. Occupation numbers of the lowest quartet state.



(2.00) (2.00)

Figure S2: Molecular orbitals added to CAS(3,7) to form CAS(7,9). Occupation numbers of the CASSCF(7,9) ($5f^3$) quartet states in parenthesis.



(2.00) (2.00)

Figure S3: Molecular orbitals added to CAS(3,7) to form CAS(9,10). Occupation numbers of the CASSCF(9,10) ($5f^3$) quartet states in parenthesis.

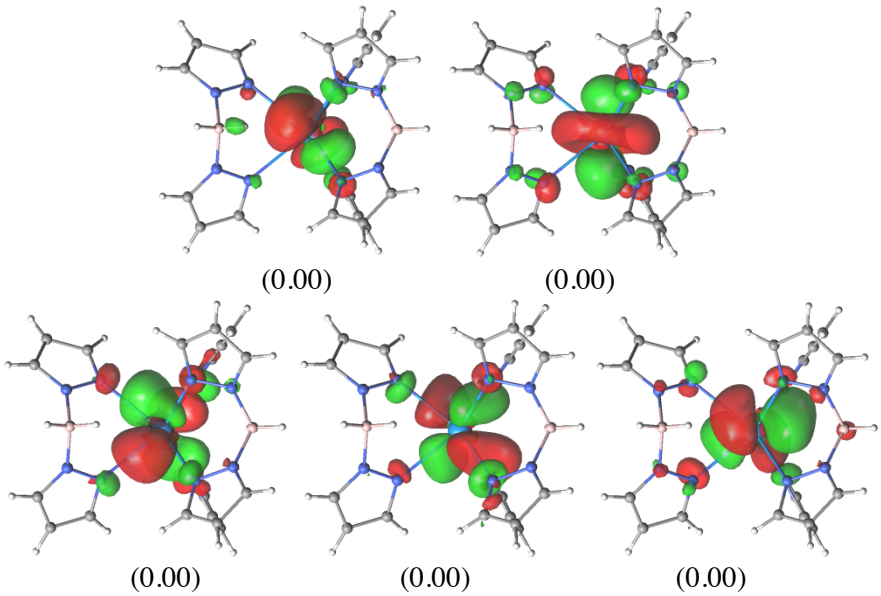


Figure S4: Molecular orbitals added to CAS(3,7) to form RAS(3,12). Occupation numbers of the RASSCF(3,12) ($5f^3$) quartet states in parenthesis.

Table S8: CASSCF(n,m) relative energies (cm^{-1}) for the first 35 quartets of compound **1**. Spin-orbit CASSCF(n,m) relative energies (cm^{-1}) for the first 20 spin-orbit states of compound **1**.

State	CAS (3,7)	CAS (7,9)	RAS (3,12)	SO-CAS(3,7)	SO-CAS(7,9)	SO-RAS(3,12)
1	0.0	0.0	0.0	0.0	0.0	0.0
2	88.8	102.3	88.8	0.0	0.0	0.0
3	122.4	133.1	122.5	98.3	102.1	98.4
4	169.1	189.2	169.1	98.3	102.1	98.4
5	280.2	336.1	280.1	364.4	379.5	364.3
6	384.0	364.1	383.9	364.4	379.5	364.3
7	505.6	548.1	505.6	488.0	520.2	488.0
8	709.6	730.5	709.5	488.0	520.2	488.0
9	742.3	779.0	742.2	598.5	631.5	598.4
10	769.7	807.0	769.7	598.5	631.5	598.4
11	971.8	970.5	971.7	3385.3	3349.1	3385.3
12	1070.8	1139.9	1070.7	3385.3	3349.1	3385.3
13	1163.9	1202.5	1163.7	3411.5	3389.8	3411.6
14	9226.3	7805.0	9226.2	3411.5	3389.8	3411.6
15	9328.0	7951.8	9327.8	3582.9	3571.1	3582.9
16	9439.1	8036.4	9438.8	3582.9	3571.1	3582.9
17	9486.0	8080.4	9485.9	3655.4	3650.3	3655.3
18	9676.1	8400.7	9675.9	3655.4	3650.3	3655.3
19	9796.5	8415.4	9796.2	3674.8	3703.8	3674.8

20	9830.1	8741.1	9829.8	3674.8	3703.8	3674.8
21	10176.6	8875.9	10176.3			
22	14602.9	12883.5	14602.6			
23	14646.6	12923.6	14646.1			
24	14681.6	12990.1	14681.1			
25	14861.4	13145.5	14861.0			
26	14889.0	13279.4	14888.5			
27	15045.1	13412.1	15044.8			
28	15157.8	13528.2	15157.5			
29	15225.8	13638.5	15225.5			
30	15339.3	13722.2	15339.1			
31	23373.4	20499.9	23372.9			
32	23422.5	20555.7	23421.9			
33	24193.6	21301.5	24193.0			
34	24477.2	21728.7	24476.7			
35	24824.0	22069.0	24823.6			

Table S9: CASSCF relative energies (cm^{-1}) without spin-orbit effects for compounds **1** to **4**. The first 35 quartet and doublet states are reported.

Quartet	**1**	**2**	**3**	**4**	Doublet	**1**	**2**	**3**	**4**
1	0	0	0	0	1	9924	9957	9564	10305
2	89	0	104	95	2	9970	9957	9564	10473
3	122	24	104	149	3	10090	10142	9761	10569
4	169	24	213	592	4	10105	10142	9761	10591
5	280	35	213	640	5	10256	10192	10122	10685
6	384	124	221	669	6	10267	10192	10122	10856
7	506	491	471	1634	7	10289	10284	10351	10885
8	709	811	796	2236	8	10375	10450	10488	11103
9	742	823	796	2252	9	10886	10832	10722	11286
10	770	823	833	2265	10	10915	10832	10722	11417
11	972	1118	1021	2277	11	10954	10868	10859	11494
12	1071	1118	1021	2287	12	12736	12776	12110	13433
13	1164	1256	1118	2387	13	12908	13072	12460	13562
14	9226	9245	8750	8936	14	12958	13115	12589	13795
15	9328	9449	9018	10268	15	12972	13115	12589	13807
16	9439	9449	9018	10283	16	13032	13159	12766	13841
17	9486	9603	9153	10429	17	13234	13439	12946	14060
18	9676	9739	9301	10432	18	13273	13439	12946	14423
19	9796	9898	9596	10467	19	13757	13786	13550	14594
20	9830	9898	9596	10587	20	13784	13786	13550	14881

21	10176	10222	9708	10783	21	14170	14394	14090	15087
22	14603	14685	14141	14923	22	14177	14394	14090	15312
23	14646	14705	14141	14949	23	14410	14724	14284	15322
24	14681	14705	14169	14966	24	14516	14832	14340	15336
25	14861	14921	14249	15215	25	14665	14877	14479	15352
26	14889	14921	14249	15467	26	14669	14877	14479	15416
27	15045	14972	14385	15547	27	14939	14945	14667	15450
28	15157	15236	14385	15844	28	15006	14974	14667	15668
29	15226	15236	14451	16148	29	15046	14974	14699	15755
30	15339	15269	14664	16523	30	15323	15257	14719	16043
31	23373	23780	22625	23807	31	15488	15311	14893	16185
32	23422	23780	22625	23891	32	15555	15389	14981	16286
33	24193	24245	23183	24086	33	15595	15389	14981	16385
34	24477	24245	23183	25060	34	15669	15415	15079	16496
35	24824	24649	23619	25300	35	15738	15415	15079	16731

Table S10: CASSCF(3,7) and MS-CASPT2(3,7) relative energies (cm^{-1}) for the first 21 quartets compound **1**. Set 1 includes only the first thirteen quartets states in the CASPT2 calculation. Set 2 includes the first twenty one quartets and the first eleven doublet states.

State	CASSCF(3,7)	MS-PT2(3,7)-Set 1	MS-PT2(3,7)-Set 2
1	0.0	0.0	0.0
2	88.8	328.7	350.1
3	122.4	504.4	486.1
4	169.1	573.1	566.0
5	280.2	668.6	673.0
6	384.0	772.5	751.4
7	505.6	841.7	812.7
8	709.6	1041.9	1000.1
9	742.3	1070.9	1069.0
10	769.7	1228.7	1226.1
11	971.8	1387.4	1403.0
12	1070.8	1519.5	1516.6
13	1163.9	1929.3	1876.6
14	9226.3	-	6172.6
15	9328.0	-	6287.8
16	9439.1	-	6370.9

17	9486.0	-	6638.5
18	9676.1	-	6692.5
19	9796.5	-	6781.5
20	9830.1	-	7080.7
21	10176.6	-	7317.3

Table S11: Contribution (%) to the 12 twelve lowest spin-orbit states from the CASSCF(3,7) (MS-CASPT2(3,7) in parenthesis) states of compound **1**. Quartet (Q) and doublet (D) states grouped based on the energy gaps.

	1-2	3-4	5-6	7-8	9-10	11-12
Q 1-13	95.8	95.9	95.6	95.5	95.2	98.8
	(95.0)	(95.1)	(94.5)	(93.8)	(93.4)	(98.3)
Q 14-21	0.0	0.0	0.0	0.0	0.0	0.0
	(0.3)	(0.2)	(0.1)	(0.1)	(0.2)	(0.1)
Q 22-35	0.0	0.0	0.0	0.0	0.0	0.0
D 1-11	3.8	3.8	4.2	4.3	4.6	1.1
	(4.8)	(4.8)	(5.37)	(6.08)	(6.45)	(1.6)
D 12-112	0.4	0.3	0.3	0.3	0.2	0.1

Table S12: Boltzmann's population (%) (See Equation 1) of the lowest twelve spin-orbit states of compound **1**. Relative energies (***ε***) used from CASSCF(3,7) with quartets and doublets in the spin-orbit calculation.

States	1-2	3-4	5-6	7-8	9-10	11-12
(Energy)	(0.0)	(108.7)	(352.6)	(467.8)	(565.8)	(3743.7)
T (K)						
5	100.00	0.00	0.00	0.00	0.00	0.00
10	100.00	0.00	0.00	0.00	0.00	0.00
20	99.96	0.04	0.00	0.00	0.00	0.00
30	99.46	0.54	0.00	0.00	0.00	0.00
40	98.03	1.96	0.00	0.00	0.00	0.00
50	95.80	4.20	0.00	0.00	0.00	0.00
100	82.17	17.20	0.51	0.10	0.02	0.00
150	71.32	25.14	2.42	0.80	0.31	0.00
200	62.96	28.80	4.98	2.18	1.08	0.00
250	56.41	30.18	7.41	3.82	2.17	0.00
300	51.27	30.44	9.45	5.44	3.40	0.00

$$Population\ \%\ (i,T) = \frac{100\, e^{-\frac{\varepsilon_i}{kT}}}{\sum_i e^{-\frac{\varepsilon_i}{kT}}} \qquad \text{(Equation 1)}$$

Table S13: DFT/BP86 Optimized geometry for **4'** (carbene isomer of **4**).
ADF Bond energy (Relative with respect to the atomic fragments) = -19.02793771 a.u.

1	U	0.00536	0.02167	0.00000
2	N	-2.77309	1.83782	1.28155
3	N	-1.30139	3.40290	0.00000
4	N	-2.77309	1.83782	-1.28155
5	N	-0.22102	-3.31379	1.27864
6	N	-2.31079	-2.79362	0.00000
7	N	-0.22102	-3.31379	-1.27864
8	N	3.00946	1.45327	1.27223
9	N	3.58734	-0.62040	0.00000
10	N	3.00946	1.45327	-1.27223
11	N	0.82964	3.62371	0.00000
12	N	-3.56634	-1.05747	0.00000
13	N	2.68711	-2.56457	0.00000
14	N	0.80211	-2.21709	2.82186
15	N	0.80211	-2.21709	-2.82186
16	N	-2.29649	0.44605	2.85375
17	N	-2.29649	0.44605	-2.85375
18	N	1.51419	1.82996	2.77849
19	N	1.51419	1.82996	-2.77849
20	C	-3.80251	1.89635	2.21357
21	C	-3.51215	1.01172	3.20953
22	C	-1.03671	4.76529	0.00000
23	C	0.31942	4.91146	0.00000
24	C	-3.80251	1.89635	-2.21357
25	C	-3.51215	1.01172	-3.20953
26	C	0.23933	-4.23929	2.20783
27	C	0.89707	-3.55262	3.18555
28	C	-3.62383	-3.24363	0.00000
29	C	-4.42781	-2.14282	0.00000
30	C	0.23933	-4.23929	-2.20783
31	C	0.89707	-3.55262	-3.18555
32	C	3.58055	2.28950	2.22282
33	C	2.63816	2.54232	3.17536
34	C	4.62147	-1.54528	0.00000
35	C	4.05503	-2.78570	0.00000
36	C	3.58055	2.28950	-2.22282
37	C	2.63816	2.54232	-3.17536
38	C	-1.82048	0.92508	1.66091
39	C	-1.82048	0.92508	-1.66091
40	C	2.36339	-1.23381	0.00000
41	C	1.70586	1.15866	1.59448
42	C	1.70586	1.15866	-1.59448
43	C	-0.14689	2.66393	0.00000

44	C	-2.24842	-1.42484	0.00000
45	C	0.13098	-2.03980	-1.64201
46	C	0.13098	-2.03980	1.64201
47	H	1.81722	3.38934	0.00000
48	H	0.94282	5.79588	0.00000
49	H	-4.64178	2.57097	2.10203
50	H	-1.82293	5.50948	0.00000
51	H	-4.04231	0.76088	4.11846
52	H	-1.86998	-0.34922	-3.31617
53	H	-4.04231	0.76088	-4.11846
54	H	-4.64178	2.57097	-2.10203
55	H	-1.86998	-0.34922	3.31617
56	H	-3.57348	3.53146	0.00000
57	H	-3.85910	-0.08582	0.00000
58	H	-5.50517	-2.04408	0.00000
59	H	0.04858	-5.30016	2.10658
60	H	-3.87471	-4.29655	0.00000
61	H	1.39195	-3.89113	4.08602
62	H	1.30724	-1.45617	-3.26331
63	H	1.39195	-3.89113	-4.08602
64	H	0.04858	-5.30016	-2.10658
65	H	1.30724	-1.45617	3.26331
66	H	-1.31481	-4.83722	0.00000
67	H	1.98415	-3.29587	0.00000
68	H	4.49521	-3.77412	0.00000
69	H	4.60869	2.62151	2.15240
70	H	5.66273	-1.24885	0.00000
71	H	2.67950	3.13449	4.07967
72	H	0.59222	1.92203	-3.19071
73	H	2.67950	3.13449	-4.07967
74	H	4.60869	2.62151	-2.15240
75	H	0.59222	1.92203	3.19071
76	H	4.88099	1.25253	0.00000
77	B	-2.66913	2.72640	0.00000
78	B	-1.05005	-3.65600	0.00000
79	B	3.72004	0.90668	0.00000

Table S14: CASSCF(3,7) and Spin-orbit CASSCF(3,7) relative energies (cm^{-1}) for the first states of **4'**.

CASSCF	Quartet	Doublet	Spin-orbit states	
1	0	8588	1	0.0
2	635	8605	2	0.0
3	689	9011	3	58.8
4	733	9045	4	58.8
5	861	10091	5	528.5
6	950	10160	6	528.5
7	1682	10362	7	711.4
8	1781	10487	8	711.4
9	1810	11010	9	1021.8
10	2023	11141	10	1021.8
11	2163	11158	11	3064.1
12	2202	11317	12	3064.1
13	2470	11551		
14	7731	11764		
15	7975	11797		
16	8095	12153		
17	8349	12216		
18	8496	12416		
19	9379	13134		
20	9459	13636		
21	9795	13677		
22	11917	13742		
23	12062	13802		
24	12245	14150		
25	12337	14380		
26	12640	14479		
27	12786	14552		
28	13101	14576		
29	13997	14594		
30	14031	14791		
31	19640	14945		
32	19748	14975		
33	19841	14977		
34	19922	15039		
35	20462	15453		

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