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Supporting Information

Super-electrophiles of Tri- and Tetra-Anions Stabilized by Selected Terminal Groups and Their Role in Binding Noble Gas atoms

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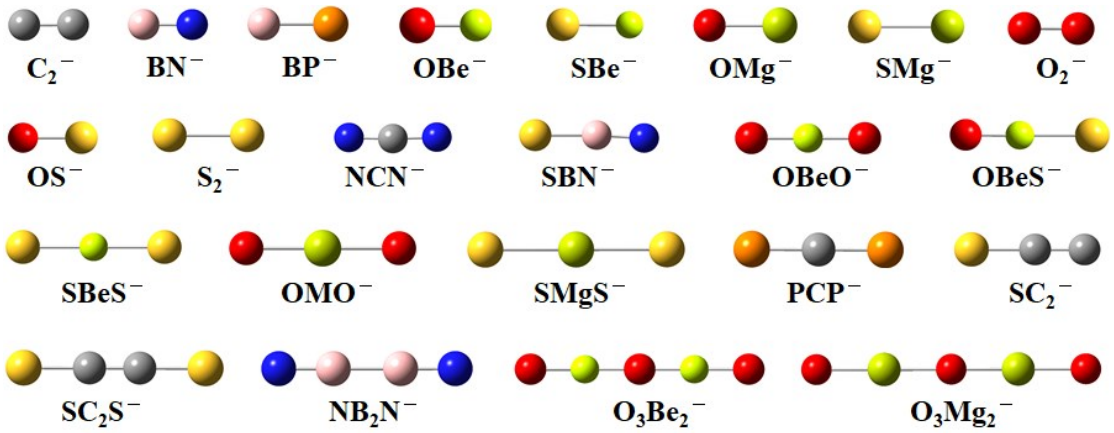


Figure S1 Linear structures of the candidate mono-anions used as terminal groups to stabilize the tri-anions in the gas phase. In each case, the chemical symbol corresponds to the atomic sequence of the cluster.

Table S1. Calculated parameters for the stable monoanions used this study, including the length along the longest dimension (LLD), the molecular volume (MV), the radius (*r*), the multiplicity (M) and the electron affinities (EA) of the clusters. The molecular volume is defined as the volume inside a contour of 0.001 electrons/Bohr^3 density for each cluster. The radius of a cluster is defined as half of its longest dimension plus the ionic radii of the two ending atoms.

Monoanion	LLD	MV (cm^3/mol)	*r*(Å)	M	EA_1 (eV)	EA_2 (eV)
C_2^-	1.27	33.12	0.94	2	4.32	-3.56
BN^-	1.28	43.05	1.12	2	3.86	-3.59
BP^-	1.71	59.99	1.13	2	3.36	-3.24
BeO^-	1.37	44.19	1.50	2	2.28	-3.51
BeS^-	1.82	49.73	1.96	2	2.42	-3.19
MgO^-	1.82	59.12	1.92	2	1.97	-2.79
MgS^-	2.24	44.71	2.37	2	2.17	-2.48
O_2^-	1.35	30.90	2.03	2	2.27	-6.96
SO^-	1.61	40.76	2.40	2	2.50	-4.91
S_2^-	2.05	45.17	2.86	2	2.78	-3.67
NCN^-	2.46	34.25	2.09	2	3.94	-4.52
SBN^-	3.04	56.36	2.87	2	4.30	-2.94
$OBeO^-$	2.87	38.83	2.79	2	4.48	-3.16
$SBeO^-$	3.31	62.05	3.26	2	4.96	-2.21
$SBeS^-$	3.75	72.05	3.71	2	3.71	-1.66
$OMgO^-$	3.70	46.27	3.21	2	4.89	-2.72
$SMgS^-$	4.55	78.19	4.11	2	3.22	-1.28
PCP^-	3.30	49.10	2.09	2	2.77	-3.04
SC_2^-	2.93	40.13	2.53	2	3.54	-3.04
SC_2S^-	4.54	61.46	4.11	2	2.94	-2.61
NB_2N^-	4.19	60.99	2.95	2	5.38	-1.74
$O_3Be_2^-$	5.73	64.25	4.22	2	5.90	-1.17
$S_3Be_2^-$	6.01	94.67	4.84	2	5.00	-0.18
$O_3Mg_2^-$	7.33	94.33	5.02	2	5.34	-1.30
$S_3Mg_2^-$	9.05	84.78	6.36	2	4.87	0.05

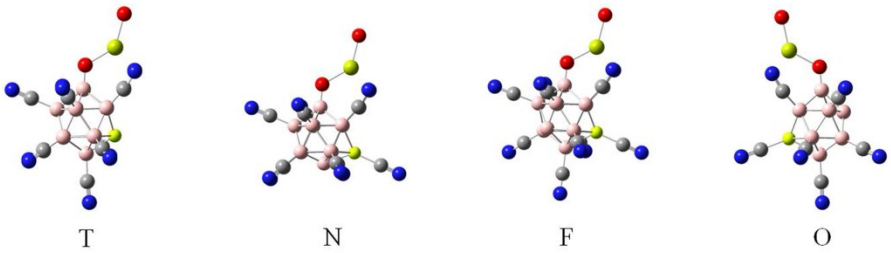
Table S2. The calculated relative energies (eV) of different isomers when one (-CN) ligand in $BeB_{11}(CN)_{12}^{3-}$ is replaced by the linear mono-anions. The ground state isomer in each case is highlighted in red. 'T' means the Be site, 'N' the neighboring B site relative to Be, 'F' the further B site relative to Be, and 'O' the opposite B site relative to Be.

Terminal Ligand	Relative Energy (eV)
C_2 (T)	0.48
C_2 (F)	0.10
C_2 (O)	0.09
C_2 (N)	0.00
BN (F)	0.68
NB (N)	0.10
NB (T)	0.015
NB (O)	0.005
NB (F)	0.00
O_2 (N)	0.34
O_2 (O)	0.31
O_2 (F)	0.28
O_2 (T)	0.00
SO (T)	0.48
OS (N)	0.46
OS (O)	0.43
OS (F)	0.41
OS(T)	0.00
S_2(O)	0.35
S_2(N)	0.34
S_2(F)	0.33
S_2(T)	0.00
NCN (O)	0.36
NCN (F)	0.34
NCN (N)	0.30
NCN(T)	0.00
SBN (N)	2.18
NBS (O)	0.08
NBS (F)	0.08
NBS (T)	0.02
NBS(N)	0.00
OBeO (N)	0.30
OBeO (O)	0.23
OBeO (F)	0.21
OBeO (T)	0.00

SBeO (T)	1.71
OMgO (T)	0.46
OMgO (N)	0.26
OMgO (O)	0.16
OMgO (F)	0.00
SC_2 (N)	2.15
C_2S (O)	0.17
C_2S (F)	0.046
C_2S (T)	0.042
C_2S (N)	0.00
SC_2S (O)	0.55
SC_2S (F)	0.53
SC_2S (N)	0.50
SC_2S (T)	0.00
NB_2N (O)	0.08
NB_2N (F)	0.08
NB_2N (N)	0.04
NB_2N(T)	0.00
O_3Be_2 (O)	1.11
O_3Be_2 (T)	0.90
O_3Be_2 (N)	0.09
O_3Be_2 (F)	0.00

A

	T	N	F	O
Relative energy (eV)	0.00	1.01	1.20	1.30



B

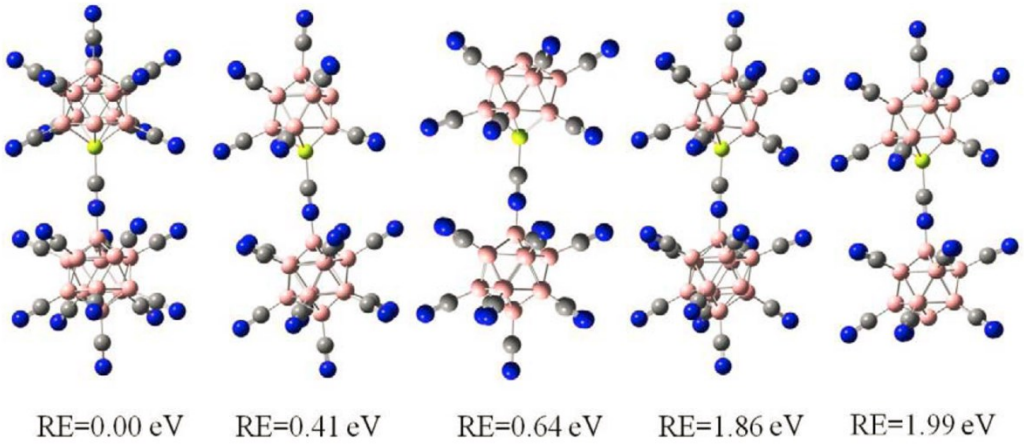


Figure S2 Calculated relative energies of the structural isomers for (**A**) $BeB_{11}(CN)_{10}(OMgO)^{2-}$ and (**B**) $BeB_{23}(CN)_{22}^{3-}$. The ground-state configuration in each case is then used to study the binding with the noble gas atoms.

Table S3. The atomic coordinates of the optimized tri-anion $BeB_{11}(CN)_{11}(OMgO)^{3-}$.

Atoms	x	y	z
B	1.432689	-0.435540	0.872478
B	-1.026806	1.095925	0.846031
B	0.067405	-1.583985	0.755115
B	-1.454079	-0.636594	0.739127
B	-1.478211	0.369865	-0.759721
B	-0.118962	1.485606	-0.630987
B	0.806973	1.302873	0.985214
B	1.005030	-1.176125	-0.732944
B	1.405378	0.536602	-0.615902
B	-0.795344	-1.300665	-0.805668
N	2.682220	-3.010401	-1.833404
N	3.758866	-1.059328	2.126927
N	3.415140	2.267493	-1.022553
N	0.556229	4.049080	-1.046577
N	-2.628565	2.922263	2.059597
N	0.260898	0.330822	-4.804682
N	-3.847078	1.058879	-1.900902
N	-0.202734	-0.259616	4.482502
N	-3.733511	-1.602755	1.855013
N	-2.071835	-3.371109	-2.016735
N	0.186107	-4.045330	1.896352
C	2.754257	-0.801170	1.596451
C	-1.947567	2.128453	1.546367
C	-0.151716	-0.197702	3.320383
C	0.132557	-2.989820	1.407118
C	-2.754741	-1.191121	1.376601
C	-2.841299	0.752719	-1.397077
C	0.170240	0.203289	-3.646349
C	0.090546	2.976472	-0.980347
C	1.957860	-2.237379	-1.346673
C	2.655824	1.378169	-0.956082
C	-1.528020	-2.488964	-1.482688
O	3.325676	5.278690	0.911868
O	1.452344	2.347944	1.531464
Mg	2.312493	3.689349	0.455710
Be	0.059996	0.053527	-1.935191
B	-0.075444	-0.101303	1.776501

Table S4. The atomic coordinates of the optimized tetra-anion $BeB_{23}(CN)_{23}^{4-}$.

Atoms	x	y	z
B	-5.757110	-0.001381	-0.000326
B	-3.279347	-0.332977	-1.500053
B	-4.811017	0.608114	-1.398844
B	-4.812219	1.517936	0.147537
B	-3.279871	1.324497	-0.778403
Be	-2.105499	-0.000437	0.002580
B	-3.281397	-0.614890	1.412400
B	-3.279703	-1.531880	-0.146220
B	-4.810544	-1.143509	-1.011322
B	-4.813375	0.328182	1.490545
B	-4.812450	-1.316635	0.774549
B	-3.281767	1.149990	1.021876
N	-6.100820	0.844974	3.822386
N	-8.469319	-0.003382	-0.002216
N	-6.097435	-3.376652	1.985628
N	-6.093739	-2.933905	-2.595524
N	-2.258682	-0.876923	-3.954848
N	-2.258909	-4.034680	-0.385652
N	-2.264554	-1.617695	3.719715
N	-6.095481	1.560110	-3.590920
N	-2.260244	3.492707	-2.052302
N	-2.263995	3.033981	2.688620
N	-6.099777	3.895333	0.375237
C	-7.305253	-0.002302	-0.001451
C	-2.699170	-0.643650	-2.902382
C	-5.538066	1.153289	-2.653565
C	-5.540973	2.878887	0.278098
C	-2.699945	2.562944	-1.506084
C	-2.703137	-1.187891	2.730241
C	-2.699428	-2.961550	-0.283295
C	-5.537093	-2.168157	-1.918304
C	-5.542145	0.623942	2.825447
C	-5.540055	-2.4957870	1.467703
C	-2.703182	2.226056	1.974118
N	0.837891	0.006363	-0.000632
C	-0.327360	0.003568	0.001398
B	5.743925	-0.002817	-0.000467
B	3.270775	0.636541	-1.398243
B	4.799692	-0.307693	-1.495607
B	4.796318	-1.517479	-0.170404
B	3.266881	-1.129470	-1.035332

B	2.317542	0.005394	-0.001478
B	3.269337	0.312033	1.501055
B	3.272602	1.527912	0.169114
B	4.803716	1.326172	-0.755090
B	4.798140	-0.630556	1.389185
B	4.802042	1.126661	1.027995
B	3.265345	-1.330108	0.756768
N	6.059928	-1.619610	3.570807
N	8.452179	-0.007769	0.000126
N	6.069352	2.893742	2.640923
N	6.072461	3.404571	-1.938590
N	2.209238	1.662272	-3.660868
N	2.211660	3.997616	0.440533
N	2.204281	0.817322	3.931954
N	6.063338	-0.793858	-3.840231
N	2.197949	-2.962369	-2.707486
N	2.195648	-3.485077	1.985693
N	6.056572	-3.899073	-0.434484
C	7.289025	-0.005891	-0.000078
C	2.634538	1.215914	-2.675183
C	5.507988	-0.586234	-2.839694
C	5.502551	-2.882700	-0.322061
C	2.626515	-2.163568	-1.979524
C	2.631443	0.596693	2.873396
C	2.637062	2.922013	0.323030
C	5.515259	2.517499	-1.433406
C	5.505397	-1.197833	2.639580
C	5.512780	2.139259	1.952757
C	2.624288	-2.546515	1.449913