Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

'Record-High Stability and Compactness of Multiply-Charged Clusters Aided by Selected Terminal Groups'

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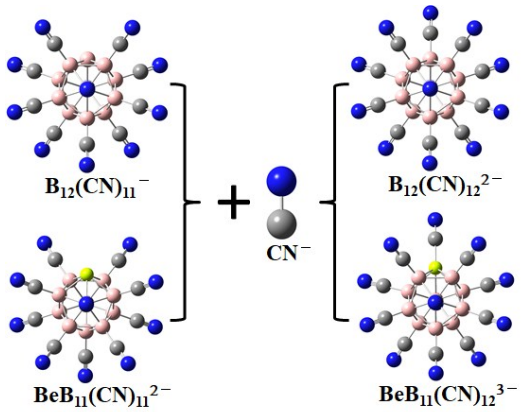

Fig. S1 Structures of the stable gas-phase di-anion $B_{12}(CN)_{12}^{2-}$ and tri-anion $BeB_{11}(CN)_{12}^{3-}$. $B_{12}(CN)_{12}^{2-}$ is a combination of two stable mono-anions $B_{12}(CN)_{11}^-$ and CN^-. $BeB_{11}(CN)_{12}^{3-}$ is a combination of the stable $BeB_{11}(CN)_{11}^{2-}$ di-anion and the CN^- mono-anion.

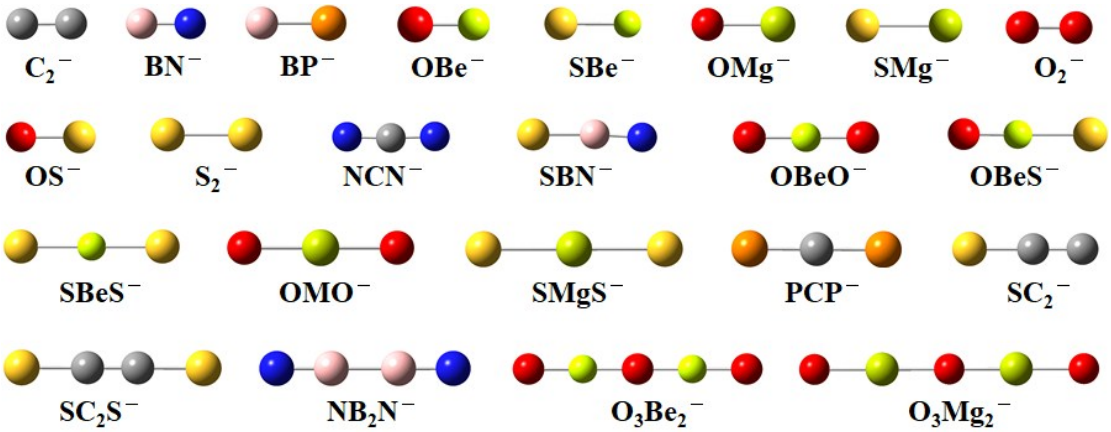

Fig. S2 Linear structures of the candidate mono-anions to be used as terminal groups to stabilize di- and tri-anions in the gas phase. In each case, the chemical symbol corresponds to the atomic sequence of the cluster.

Table S1. Calculated parameters for the stable mono-anions in this study, including the length along the longest dimension (LLD), the molecular volume (MV), the radius (*r*), the multiplicity (M), HOMO-LUMO gap (HLG) and the electron affinities (EA) of the clusters.

Mono-anion	LLD	MV (cm^3/mol)	*r* (Å)	M	HLG (eV)	EA_1 (eV)	EA_2 (eV)
C_2^-	1.27	33.125	0.94	2	2.68	4.32	-3.56
BN^-	1.28	43.050	1.12	2	2.76	3.86	-3.59
BP^-	1.71	59.987	1.13	2	2.52	3.36	-3.24
BeO^-	1.37	44.191	1.50	2	3.38	2.28	-3.51
BeS^-	1.82	49.734	1.96	2	2.52	2.42	-3.19
MgO^-	1.82	59.120	1.92	2	1.83	1.97	-2.79
MgS^-	2.24	44.712	2.37	2	1.77	2.17	-2.48
O_2^-	1.35	30.897	2.03	2	3.22	2.27	-6.96
SO^-	1.61	40.756	2.40	2	2.28	2.50	-4.91
S_2^-	2.05	45.174	2.86	2	1.76	2.78	-3.67
NCN^-	2.46	34.250	2.09	2	2.70	3.94	-4.52
SBN^-	3.04	56.361	2.87	2	2.32	4.30	-2.94
$OBeO^-$	2.87	38.834	2.79	2	2.85	4.48	-3.16
$SBeO^-$	3.31	62.051	3.26	2	2.37	4.96	-2.21
$SBeS^-$	3.75	72.049	3.71	2	1.64	3.71	-1.66
$OMgO^-$	3.70	46.267	3.21	2	2.70	4.89	-2.72
$SMgS^-$	4.55	78.191	4.11	2	1.53	3.22	-1.28
PCP^-	3.30	49.104	2.09	2	1.61	2.77	-3.04
SC_2^-	2.93	40.133	2.53	2	1.90	3.54	-3.04
SC_2S^-	4.54	61.456	4.11	2	1.54	2.94	-2.61
NB_2N^-	4.19	60.992	2.95	2	2.26	5.38	-1.74
$O_3Be_2^-$	5.73	64.249	4.22	2	2.29	5.90	-1.17
$S_3Be_2^-$	6.01	94.666	4.84	2	1.48	5.00	-0.18
$O_3Mg_2^-$	7.33	94.334	5.02	2	2.29	5.34	-1.30
$S_3Mg_2^-$	9.05	84.776	6.36	2	1.30	4.87	0.05

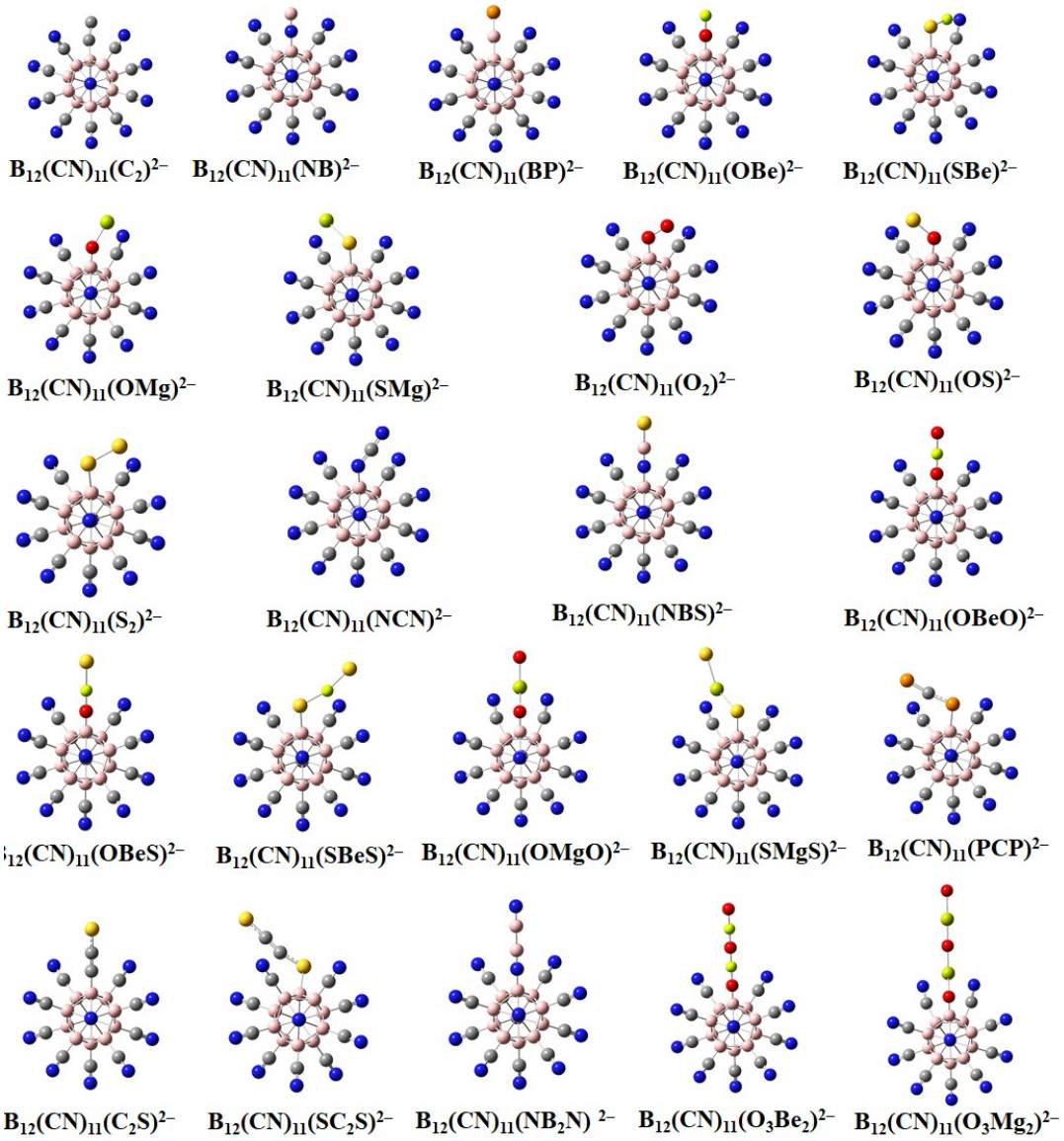

Fig. S3 Structures of stable gas-phase di-anions with the mono-anions in Fig. S2 as the terminal group.

Table S2. Calculated parameters for the stable di-anions in this study, including the length along the longest dimension (LLD), the molecular volume (MV), the radius (*r*), the multiplicity (M), HOMO-LUMO gap (HLG), the electron affinities (EA) and the *V* (Eq. 1) values.

Di-anion	LLD (Å)	MV (cm^3/mol)	*r* (Å)	M	HLG (eV)	EA_1 (eV)	EA_2 (eV)	*V* (eV)
$B_{12}(CN)_{11}(C_2)^{2-}$	8.91	334.291	5.04	2	2.45	7.89	5.28	13.17
$B_{12}(CN)_{11}(NB)^{2-}$	8.84	353.326	4.91	2	3.55	9.93	2.28	12.21
$B_{12}(CN)_{11}(BP)^{2-}$	9.54	310.816	5.42	2	2.00	7.31	4.81	12.12
$B_{12}(CN)_{11}(OBe)^{2-}$	8.94	239.752	5.03	2	3.47	7.68	1.08	8.76
$B_{12}(CN)_{11}(SBe)^{2-}$	8.84	320.525	5.28	2	2.52	7.62	1.44	9.06
$B_{12}(CN)_{11}(OMg)^{2-}$	8.88	323.096	4.90	2	2.37	7.19	1.25	8.44
$B_{12}(CN)_{11}(SMg)^{2-}$	9.07	305.660	5.29	2	2.15	6.75	1.00	7.75
$B_{12}(CN)_{11}(O_2)^{2-}$	8.84	320.235	5.28	2	4.18	8.23	4.98	13.21
$B_{12}(CN)_{11}(OS)^{2-}$	8.84	278.224	5.28	2	2.64	7.98	3.84	11.82
$B_{12}(CN)_{11}(S_2)^{2-}$	9.02	369.107	5.86	2	2.60	8.00	3.89	11.89
$B_{12}(CN)_{11}(NCN)^{2-}$	9.67	312.513	5.69	2	2.85	7.73	4.92	12.71
$B_{12}(CN)_{11}(NBS)^{2-}$	10.57	269.701	6.63	2	1.83	7.56	4.80	12.36
$B_{12}(CN)_{11}(OBeO)^{2-}$	10.42	282.310	6.32	2	2.42	7.03	6.03	13.06
$B_{12}(CN)_{11}(OBeS)^{2-}$	10.86	393.660	6.78	2	2.25	7.18	4.96	12.14
$B_{12}(CN)_{11}(SBeS)^{2-}$	10.45	331.158	6.57	2	2.11	6.03	2.32	8.35
$B_{12}(CN)_{11}(OMgO)^{2-}$	10.56	342.256	6.39	2	4.02	6.08	5.76	11.84
$B_{12}(CN)_{11}(SMgS)^{2-}$	11.31	282.352	7.00	2	1.88	8.05	2.33	10.38
$B_{12}(CN)_{11}(PCP)^{2-}$	9.86	384.566	5.58	2	2.31	7.34	3.46	10.80
$B_{12}(CN)_{11}(C_2S)^{2-}$	10.53	353.326	6.61	2	1.89	7.35	4.49	11.84
$B_{12}(CN)_{11}(SC_2S)^{2-}$	11.06	354.555	6.88	2	2.10	7.72	3.60	11.32
$B_{12}(CN)_{11}(NB_2N)^{2-}$	11.76	377.079	6.74	2	1.96	7.47	5.60	13.07
$B_{12}(CN)_{11}(O_3Be_2)^{2-}$	13.27	357.163	7.74	2	1.72	6.61	6.26	12.87
$B_{12}(CN)_{11}(S_3Be_2)^{2-}$	13.00	354.292	7.85	2	1.33	8.50	2.55	11.05
$B_{12}(CN)_{11}(O_3Mg_2)^{2-}$	14.17	310.665	8.19	2	2.36	5.62	5.74	11.38
$B_{12}(CN)_{11}(S_3Mg_2)^{2-}$	12.56	402.572	7.93	2	1.84	4.34	2.54	6.88

Table S3. Calculated relative energy (RE) of the linkage isomers (LI) compared to the ground states (GS).

GS	LI	RE (eV)
--NB	--BN	1.02
--BP	--PB	1.51
--OBe	--BeO	2.24
--SBe	--BeS	0.72
--OMg	--MgO	3.74
--SMg	--MgS	1.22
--OS	--SO	0.27
--NBS	--SBN	2.18
--OBeS	--SBeO	2.10
--C_2S	--SC_2	2.32

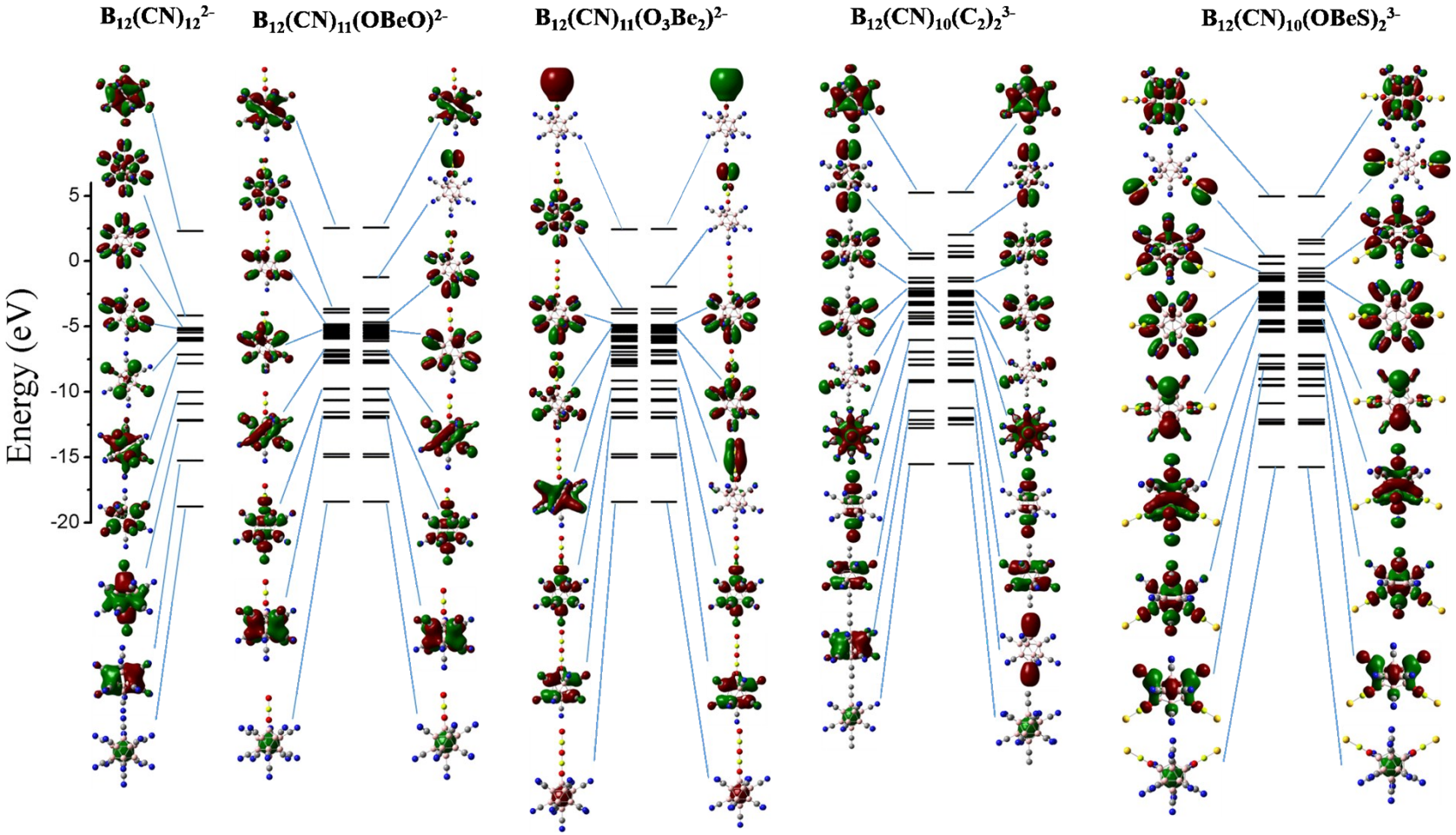

Fig. S4 Calculated molecular orbitals (MOs) for the stable gas-phase di- and tri-anions in the study.