*Electronic Supplementary Information (ESI) for*

# Designing stable *closo*-$B_{12}$ dianions *in silico* for Li- and Mg-ion battery applications

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# Contents

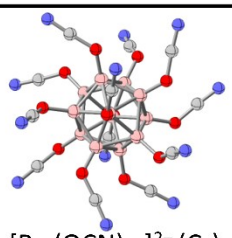
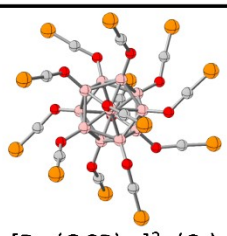
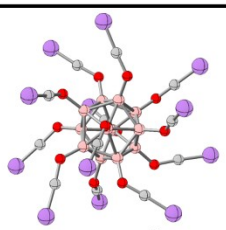
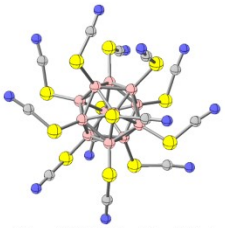
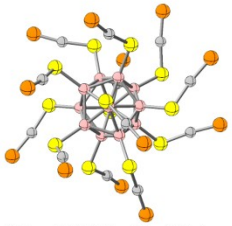
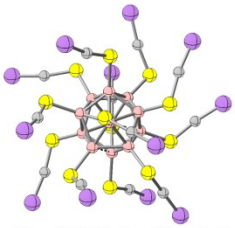
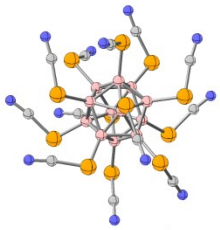
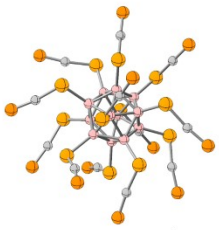
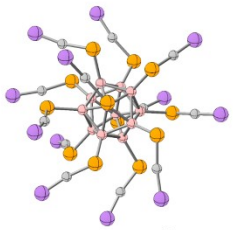
| B (2.04) / C (2.55) | N (3.04) | P (2.19) | As (2.18) |
|---|---|---|---|
| O (3.44) |  $[B_{12}(OCN)_{12}]^{2-}$ ($C_1$)<br>EA1 = 7.86 eV<br>EA2 = 4.89 eV<br>ΔE = 15.66 eV |  $[B_{12}(OCP)_{12}]^{2-}$ ($C_1$)<br>EA1 = 5.50 eV<br>EA2 = 2.99 eV<br>ΔE = 11.94 eV |  $[B_{12}(OCAs)_{12}]^{2-}$ ($C_1$)<br>EA1 = 4.36 eV<br>EA2 = 2.45 eV<br>ΔE = 12.20 eV |
| S (2.58) |  $[B_{12}(SCN)_{12}]^{2-}$ ($C_1$)<br>EA1 = 6.80 eV<br>EA2 = 4.29 eV<br>ΔE = 6.47 eV |  $[B_{12}(SCP)_{12}]^{2-}$ ($C_1$)<br>EA1 = 4.99 eV<br>EA2 = 2.54 eV<br>ΔE = 0.33 eV |  $[B_{12}(SCAs)_{12}]^{2-}$ ($C_1$)<br>EA1 = 4.67 eV<br>EA2 = 2.27 eV<br>ΔE = 0.64 eV |
| Se (2.55) |  $[B_{12}(SeCN)_{12}]^{2-}$ ($C_1$)<br>EA1 = 6.69 eV<br>EA2 = 3.80 eV<br>ΔE = 7.17 eV |  $[B_{12}(SeCP)_{12}]^{2-}$ ($C_1$)<br>EA1 = 4.76 eV<br>EA2 = 2.27 eV<br>ΔE = 0.10 eV |  $[B_{12}(SeCAs)_{12}]^{2-}$ ($C_1$)<br>EA1 = 4.81 eV<br>EA2 = 2.04 eV<br>ΔE = 0.08 eV |

**Fig. S1** Optimized geometries of $[B_{12}(XCE)_{12}]^{2-}$ (X = O, S, and Se; E = N, P, and As) and calculated first (EA1) and second (EA2) electron affinity of their corresponding neutrals. ΔE represents the energy differences between $[B_{12}(XCE)_{12}]^{2-}$ and $[B_{12}(ECX)_{12}]^{2-}$. Values in parentheses are the Pauling electronegativity of each atom and the symmetry of dianions is shown in parentheses under the molecular structures.

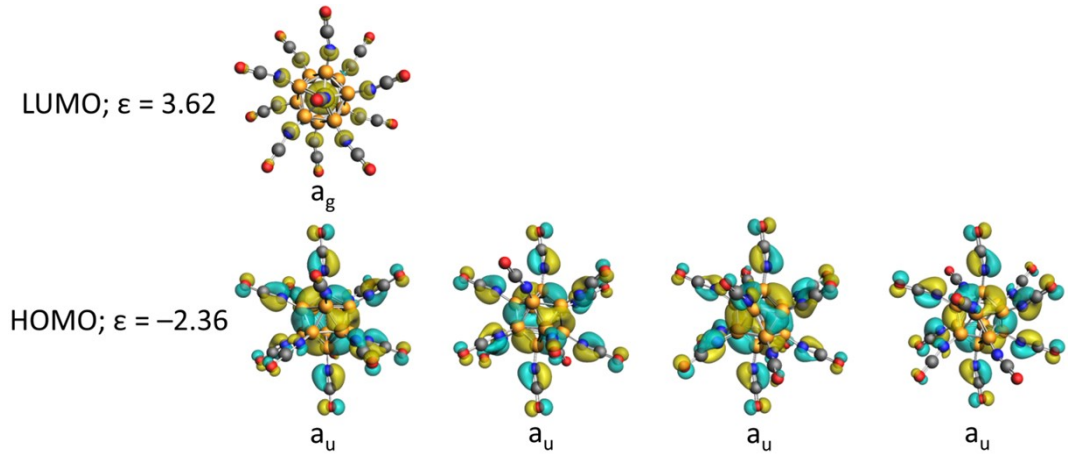



**Fig. S2** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(NCO)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

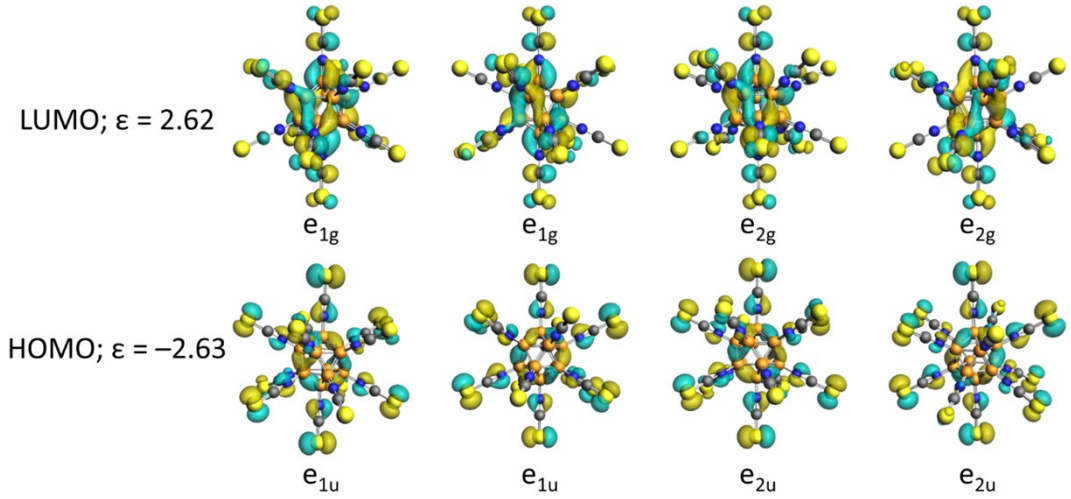



**Fig. S3** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(NCS)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

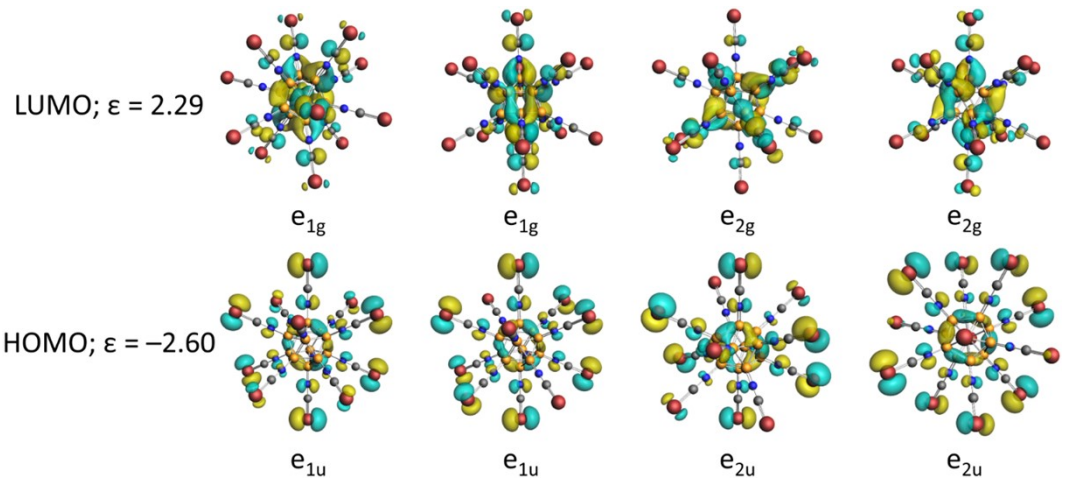



**Fig. S4** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(NCSe)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

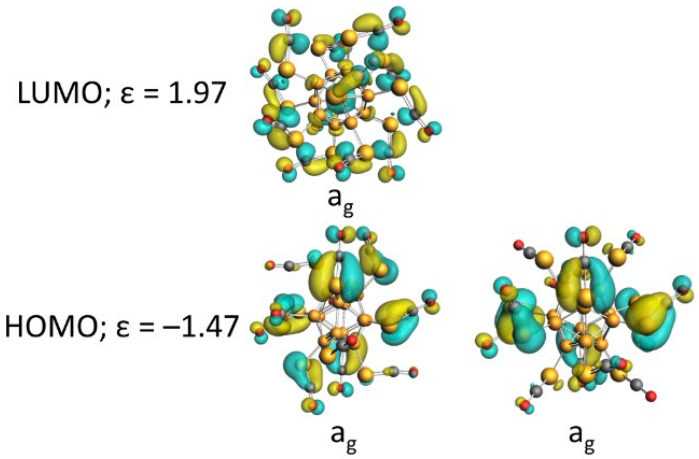



**Fig. S5** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(PCO)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

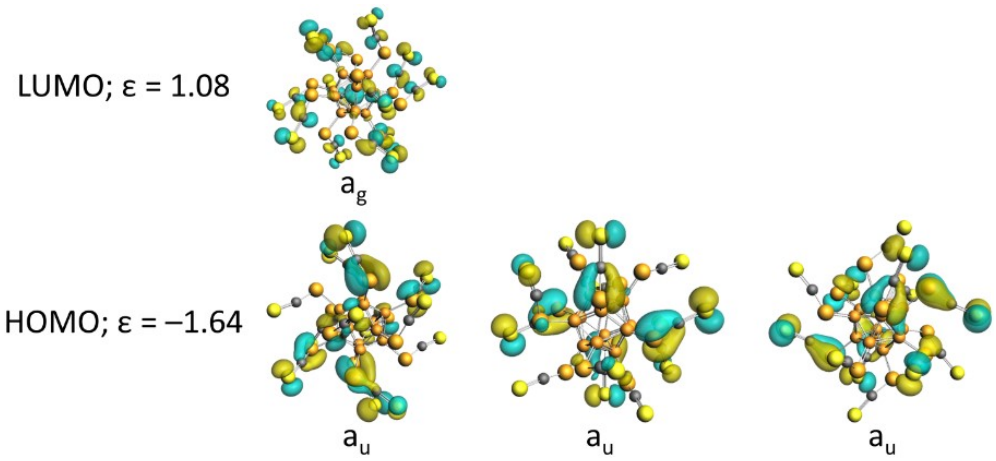



**Fig. S6** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(PCS)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

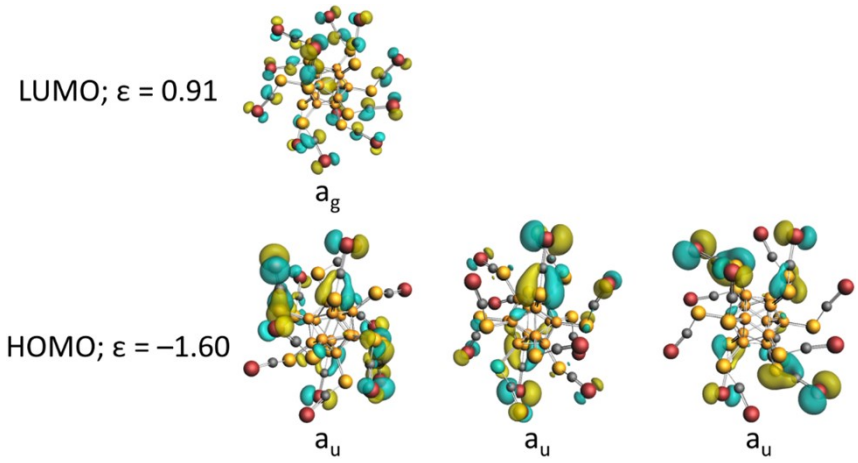



**Fig. S7** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(PCSe)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

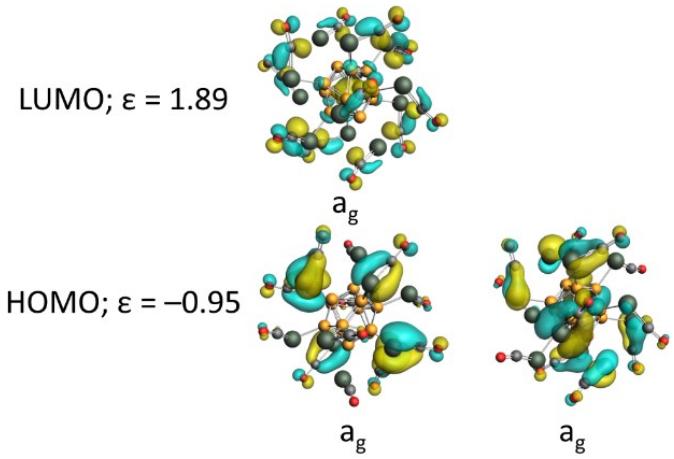



**Fig. S8** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(AsCO)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

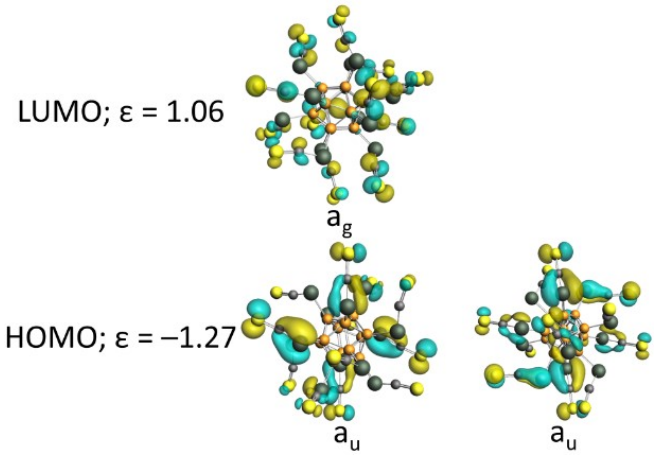



**Fig. S9** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(AsCS)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

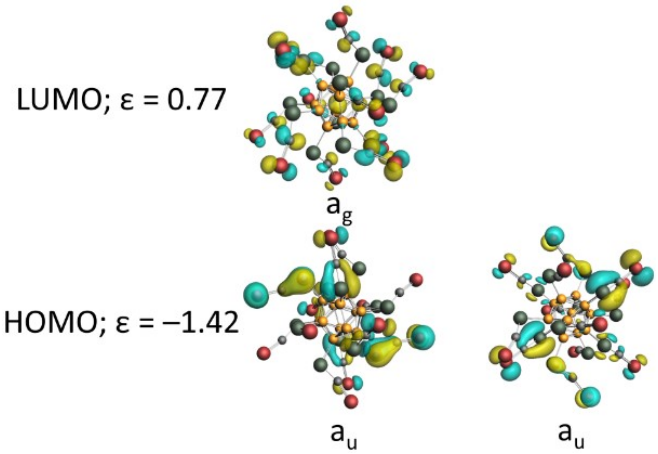



**Fig. S10** Plots of frontier molecular orbitals (isovalue = 0.03) of $[B_{12}(AsCSe)_{12}]^{2-}$ at PBE0/TZ2P. The orbital energy eigenvalues are in eV.

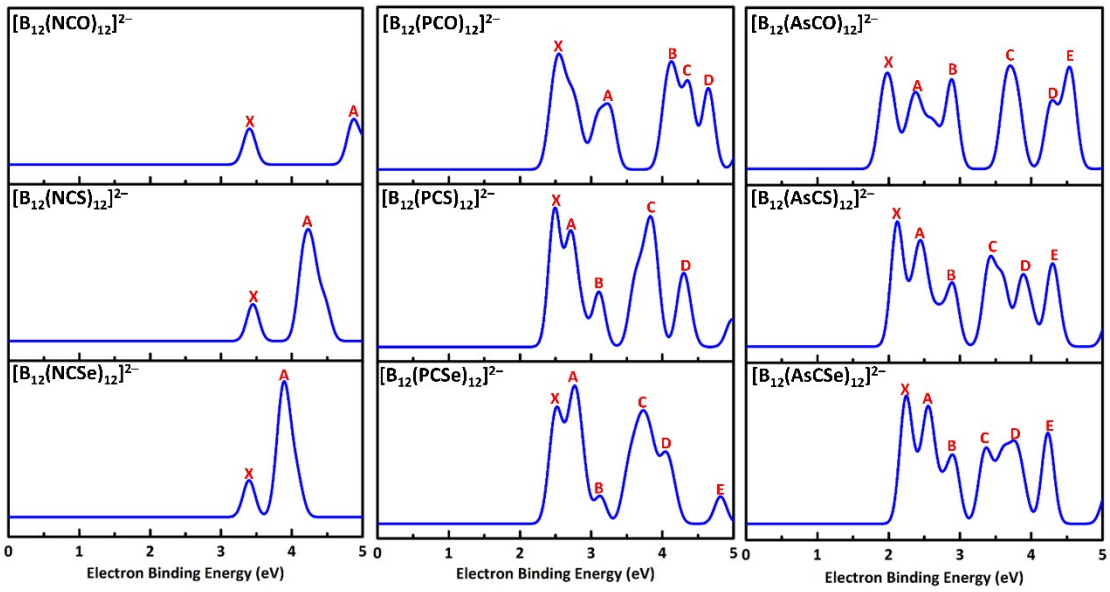



**Fig. S11** Simulated photoelectron spectra of $[B_{12}(ECX)_{12}]^{2-}$ (E = N, P, and As; X = O, S, and Se) dianions.

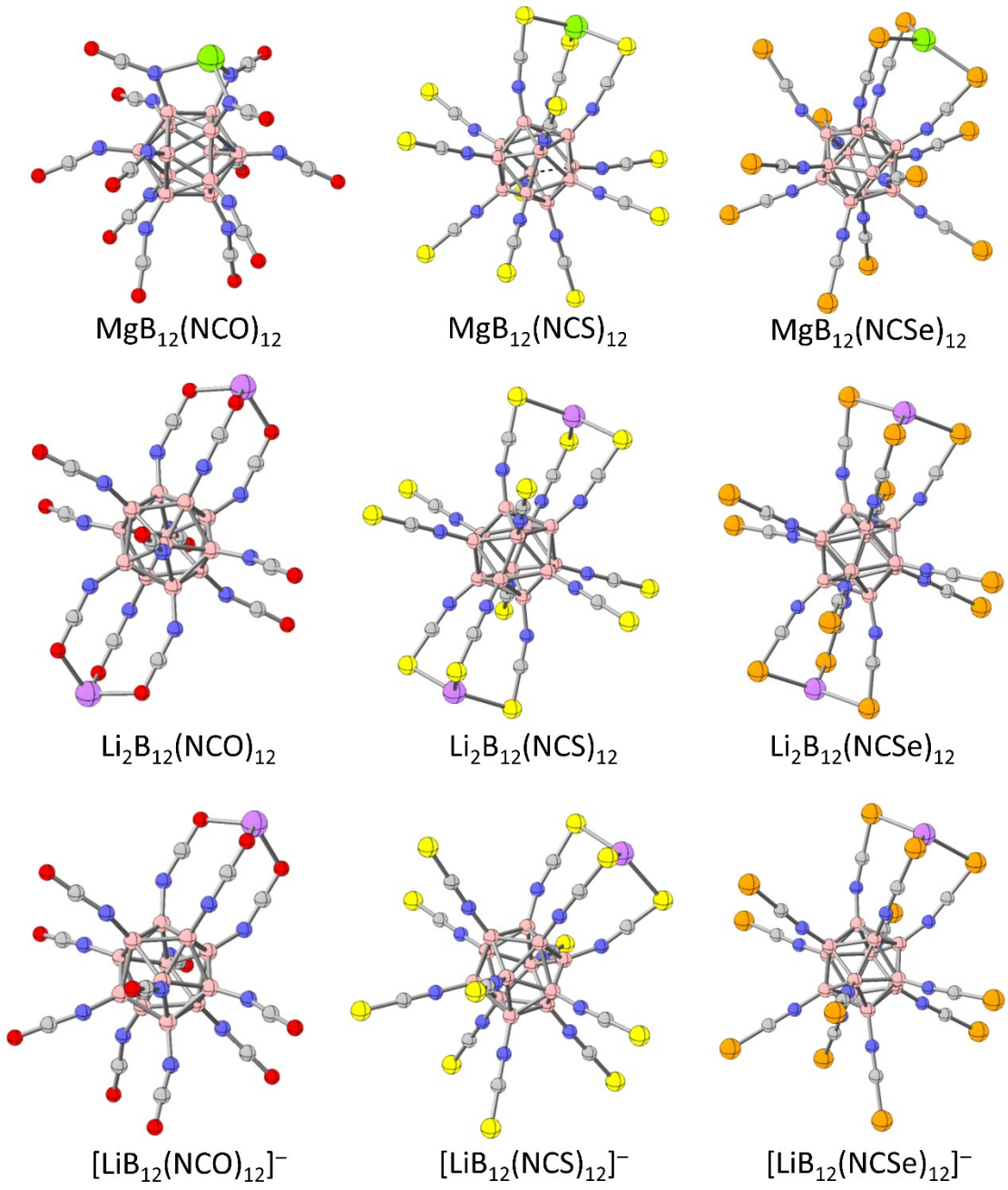



**Fig. S12** Optimized geometries of MY (M = Li or Mg, Y is corresponding *closo*-$B_{12}$ anion) salts.

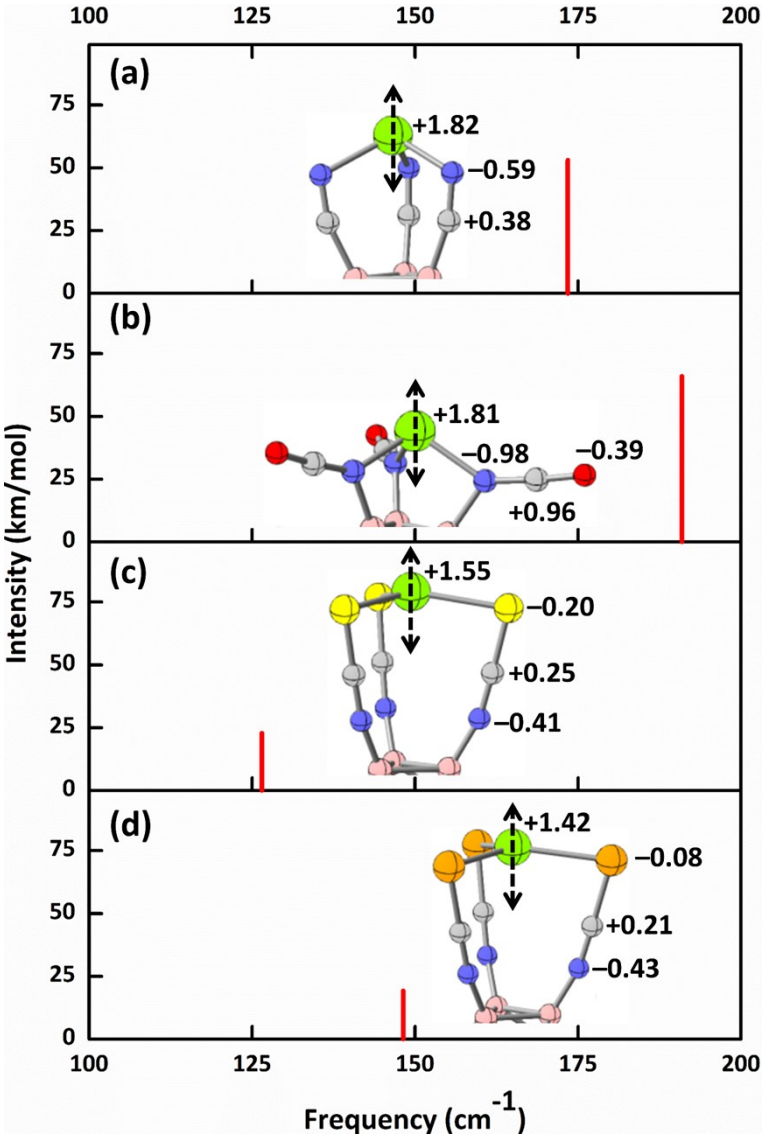



**Fig. S13** Gas-phase infrared vibrations of the metal cation ($Mg^{2+}$) relative to the dianion in (a) $MgB_{12}(CN)_{12}$, (b) $MgB_{12}(NCO)_{12}$, (c) $MgB_{12}(NCS)_{12}$, and (d) $MgB_{12}(NCSe)_{12}$. Arrows signify the direction of vibration while the atomic charge is marked near the atom.

**Table S1** Bond length (in Å) and bond angle (in degree) of $[B_{12}(ECX)_{12}]^{2-/1-/0}$ (E = N, P, and As; X = O, S, and Se).

| Species | B–B[a] | B–E[a] | E–C[a] | C–X[a] | ∠BEC[a] |
|---|---|---|---|---|---|
| $B_{12}(NCO)_{12}$ | 1.79(1.80)[1.85] | 1.45(1.44)[1.42] | 1.18(1.19)[1.20] | 1.18(1.17)[1.16] | 163°(154°)[149°] |
| $B_{12}(NCS)_{12}$ | 1.80(1.81)[1.83] | 1.44(1.43)[1.42] | 1.18(1.18)[1.18] | 1.59(1.58)[1.57] | 180°(179°)[178°] |
| $B_{12}(NCSe)_{12}$ | 1.80(1.81)[1.82] | 1.44(1.43)[1.42] | 1.17(1.18)[1.18] | 1.73(1.73)[1.72] | 180°(179°)[178°] |
| $B_{12}(PCO)_{12}$ | 1.78(1.79)[1.79] | 1.96(1.96)[1.95] | 1.67(1.67)[1.69] | 1.16(1.15)[1.15] | 103°(101°)[101°] |
| $B_{12}(PCS)_{12}$ | 1.79(1.78)[1.78] | 1.96(1.96)[1.96] | 1.64(1.65)[1.65] | 1.57(1.56)[1.55] | 106°(105°)[105°] |
| $B_{12}(PCSe)_{12}$ | 1.78(1.78)[1.79] | 1.96(1.96)[1.96] | 1.63(1.64)[1.65] | 1.72(1.71)[1.71] | 106°(105°)[102°] |
| $B_{12}(AsCO)_{12}$ | 1.78(1.79)[1.78] | 2.08(2.08)[2.07] | 1.82(1.83)[1.86] | 1.15(1.15)[1.14] | 102°(100°)[99°] |
| $B_{12}(AsCS)_{12}$ | 1.78(1.78)[1.78] | 2.09(2.08)[2.09] | 1.78(1.80)[1.80] | 1.56(1.55)[1.55] | 104°(103°)[102°] |
| $B_{12}(AsCSe)_{12}$ | 1.78(1.78)[1.77] | 2.09(2.08)[2.07] | 1.78(1.78)[1.79] | 1.72(1.71)[1.70] | 104°(103°)[103°] |

[a]Values in parentheses are for monoanions and values in brackets are for neutrals.

**Table S2** Atomic charge distribution and quantum theory of atoms in molecules bond parameter.

| Species | $B_{12}$[a] | ECX[a] | B–X bond | |
|---|---|---|---|---|
| | | | ρ | H/ρ |
| $B_{12}(NCO)_{12}$ | 2.3(2.7)[2.9] | –4.3(–3.7)[–2.9] | 1.177 | –0.893 |
| $B_{12}(NCS)_{12}$ | 2.1(2.2)[2.5] | –4.1(–3.2)[–2.5] | 1.208 | –0.897 |
| $B_{12}(NCSe)_{12}$ | 2.2(2.4)[2.5] | –4.2(–3.4)[–2.5] | 1.212 | –0.900 |
| $B_{12}(PCO)_{12}$ | –3.2(–3.3)[–3.5] | 1.2(2.3)[3.5] | 0.813 | –0.582 |
| $B_{12}(PCS)_{12}$ | –3.2(–3.2)[–3.3] | 1.2(2.2)[3.3] | 0.810 | –0.577 |
| $B_{12}(PCSe)_{12}$ | –3.2(–3.2)[–3.3] | 1.2(2.2)[3.3] | 0.811 | –0.577 |
| $B_{12}(AsCO)_{12}$ | –4.0(–4.2)[–4.3] | 2.0(3.2)[4.3] | 0.699 | –0.477 |
| $B_{12}(AsCS)_{12}$ | –4.0(–4.1)[–4.2] | 2.0(3.1)[4.2] | 0.683 | –0.472 |
| $B_{12}(AsCSe)_{12}$ | –4.1(–4.2)[–4.3] | 2.1(3.2)[4.3] | 0.686 | –0.474 |

[a]Values in parentheses are for monoanions and values in brackets are for neutrals.