Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information of

"Realization of Zn^{3+} oxidation state"

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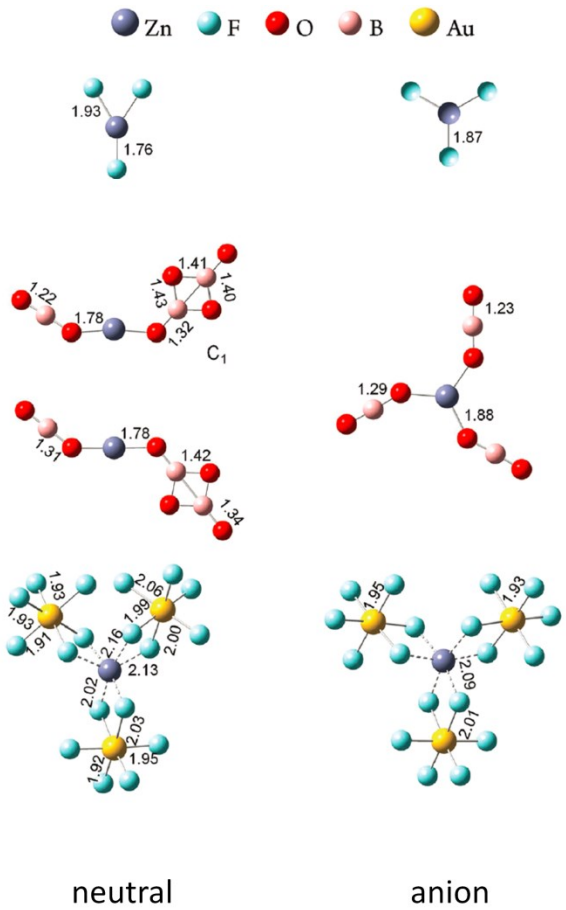

Fig. S1 Optimized structures of the neutral and anionic ZnX_3 (X = F, BO_2, AuF_6) clusters. Bond lengths are in Å.

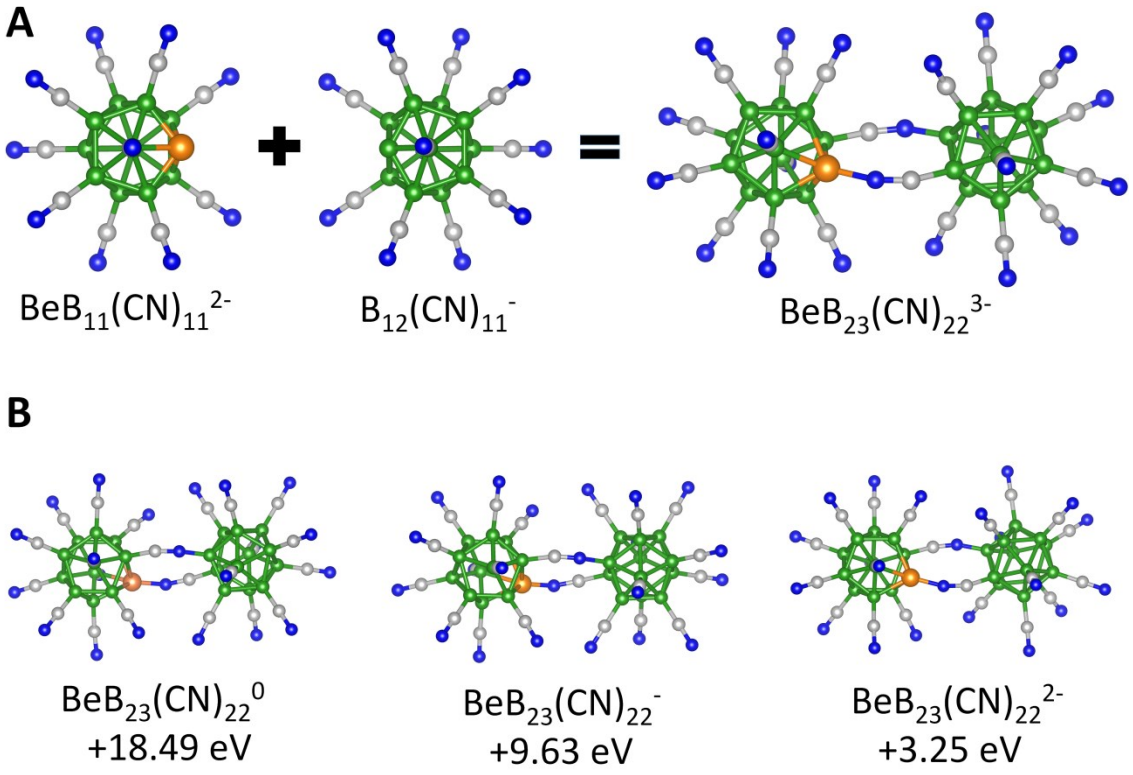

Fig. S2 (**A**) Module assembling of a stable dianion, $BeB_{11}(CN)_{11}^{2-}$, and a stable monoanion, $B_{12}(CN)_{11}^{-}$, to form a stable trianion, $BeB_{23}(CN)_{22}^{3-}$. (**B**) Optimized geometries of the high-energy charge states (0, -1 and -2) of $BeB_{23}(CN)_{22}$. with their relative energies against that of the charge state of -3. The major difference in each case is in the Be-B bond length. The distance decreases from 2.07 to 1.94 Å from charge neutral to -3. Boron atoms are in green, beryllium in orange, carbon in grey and nitrogen in blue.

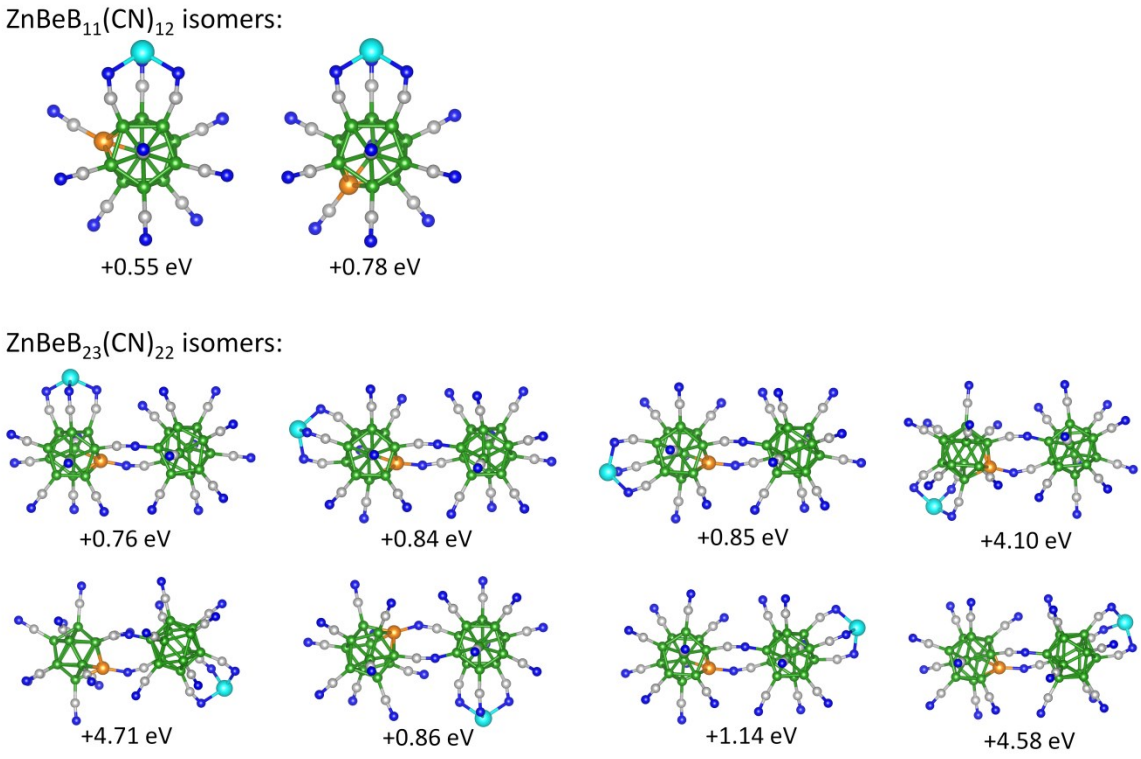

Fig. S3 Optimized structures of high-energy isomers of $ZnBeB_{11}(CN)_{12}$ and $ZnBeB_{23}(CN)_{22}$. Their energies relative to the ground-state energy are shown.

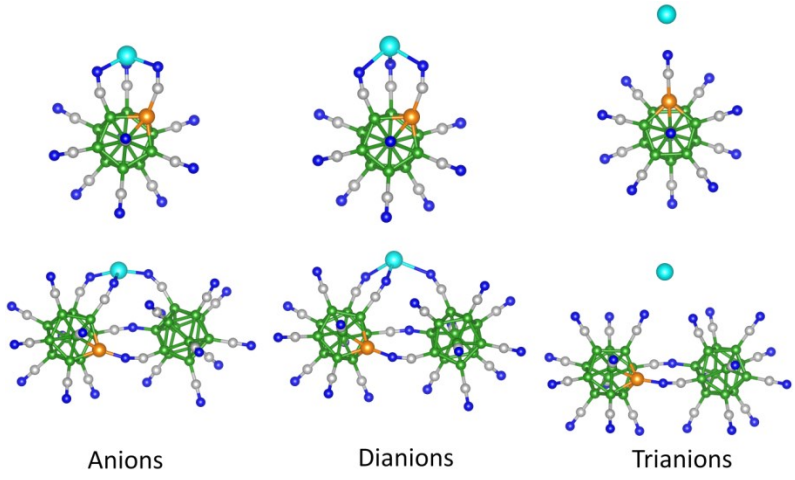

Fig. S4 Optimized structures of the mono-, di- and trianions of $ZnBeB_{11}(CN)_{12}$ as well as $ZnBeB_{23}(CN)_{22}$. Boron atoms are in green, beryllium in orange, carbon in grey, nitrogen in blue and zinc in cyan.

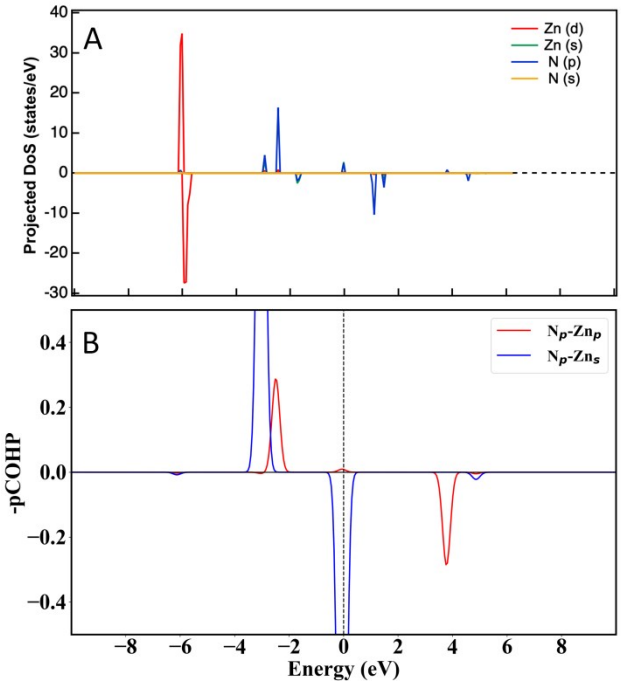

Fig. S5 Calculated (**A**) partial density of states (DoS) and (**B**) crystal Hamiltonian population analysis (–pCOHP) for the ZnN dimer. The overlapping between the 3d orbitals (around -6 eV) and the N orbitals is negligibly small, which is reassured by the negligibly small peak of N_p-Zn_d interaction (around -6 eV) in (–pCOHP) in (**B**).

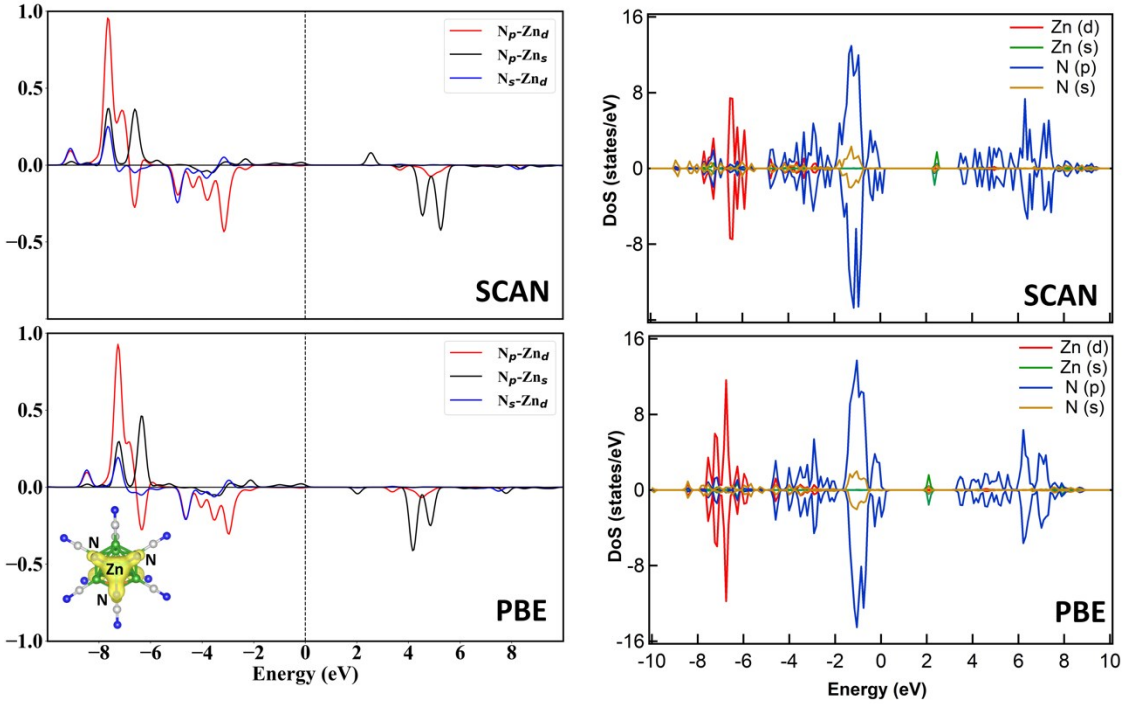

Fig. S6 Crystal Hamiltonian population analysis (–pCOHP) (**Left**) and calculated partial density of states (DoS) for $ZnBeB_{11}(CN)_{12}$ using meta-GGA SCAN functional (see Method in paper) compared to those using the PBE functional. The results are very similar, except that the Zn(d)-N(p) bonding band is shifted to even lower energies with the SCAN functional.

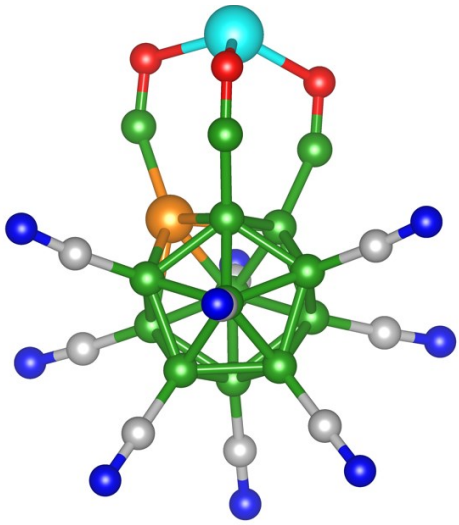

Fig. S7 Optimized geometry of $ZnBeB_{11}(BO)_3(CN)_9$ with three CN ligands attached to Zn in $ZnBeB_{11}(CN)_{12}$ replaced by three BO ligands. Boron atoms are in green, beryllium in orange, carbon in grey, nitrogen in blue, oxygen in red and zinc in cyan. The cluster exhibits even greater binding energy of Zn than that of $ZnBeB_{11}(CN)_{12}$. The three Zn-O bond lengths are 1.94, 1.96 and 1.96 Å.

Table S1. Charges on Zn in $ZnBeB_{11}(CN)_{12}$ and $ZnBeB_{23}(CN)_{22}$ according to the natural bond orbital (NBO) charge analysis. The charges on Zn in dimer ZnN and ZnO are given for comparison.

Method	$ZnBeB_{11}(CN)_{12}$	$ZnBeB_{23}(CN)_{22}$	ZnN	ZnO
NBO	+1.41	+1.43	+0.84	+1.12