Supporting Information

Tuning Complexity by Lithiation: A Family of Intergrowth Structures Using Condensed *Hypho*-Icosahedra in the Li-Doped Ca-Zn System

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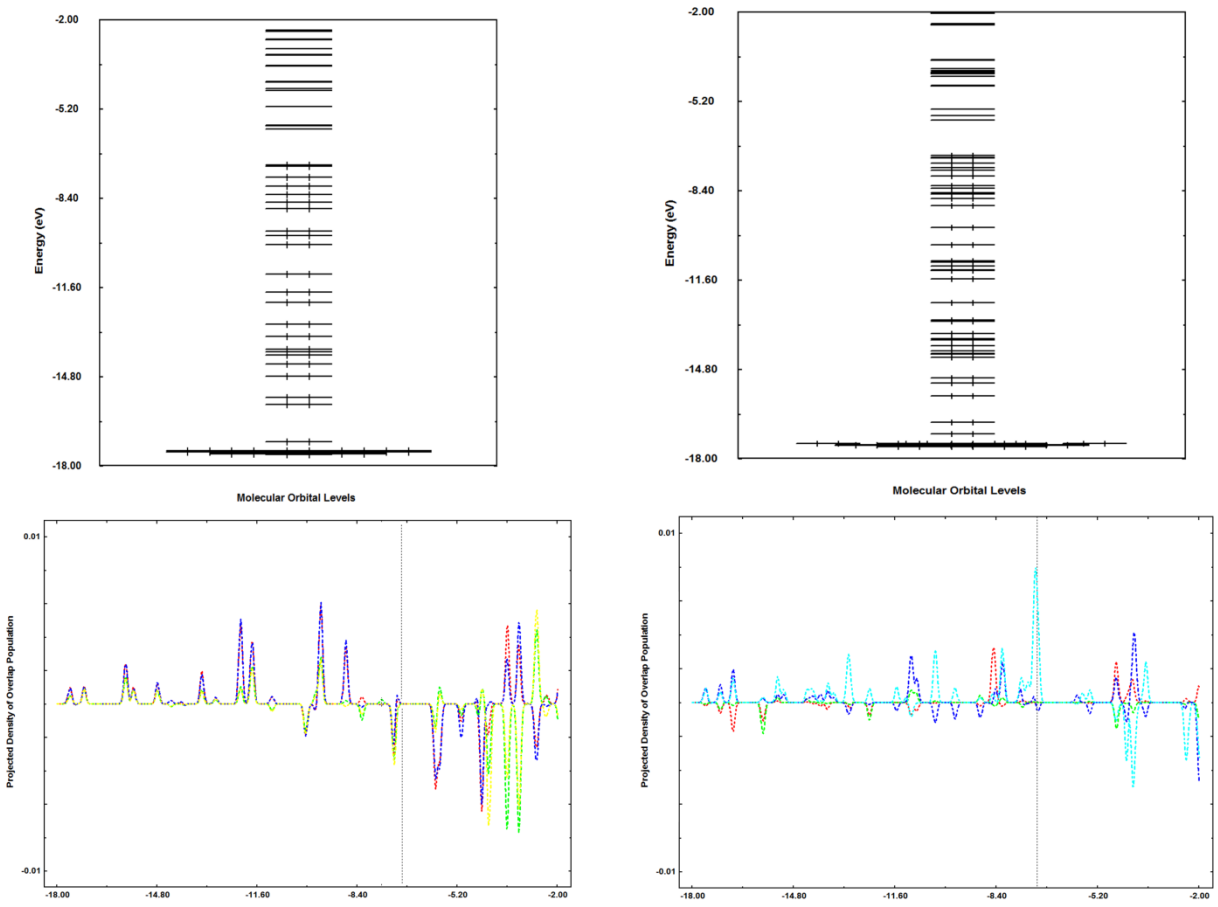

Figure S1. MO and COOP data for isolated $Zn_2@Zn_{15}^{22-}$ and $LiZn_2@Zn_{24}^{31-}$ clusters.

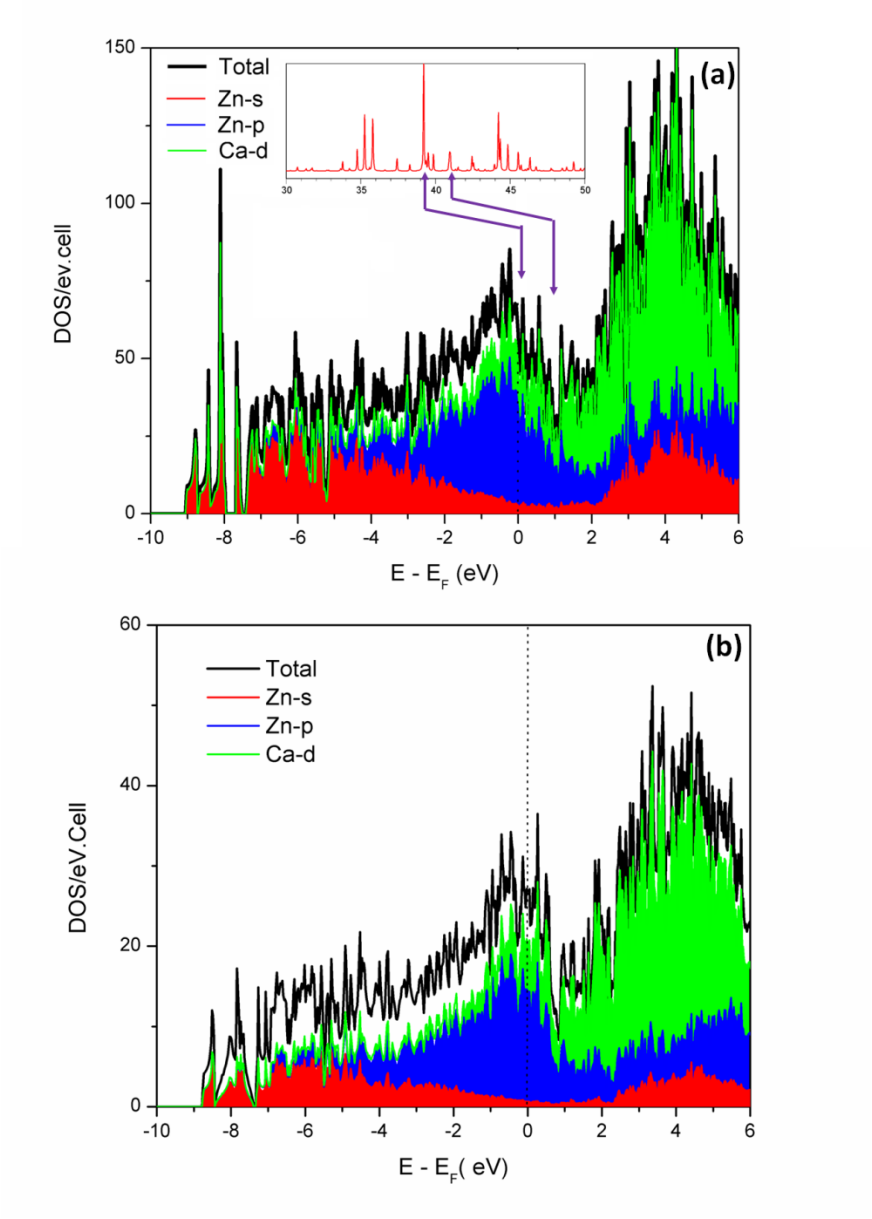

Figure S2. DOS patterns of hypothetical models of (a) "$Ca_{15}Li_{18}Zn_{57}$" for the hexagonal $Ca_{15}Li_xZn_{75-x}$ and (b) "$Ca_{12}Li_{15}Zn_{44}$" for the trigonal $Ca_{12}Li_xZn_{59-x}$ structure. The relationship between X-ray diffraction peaks and pseudogaps around the Fermi energy is also shown for the former model.

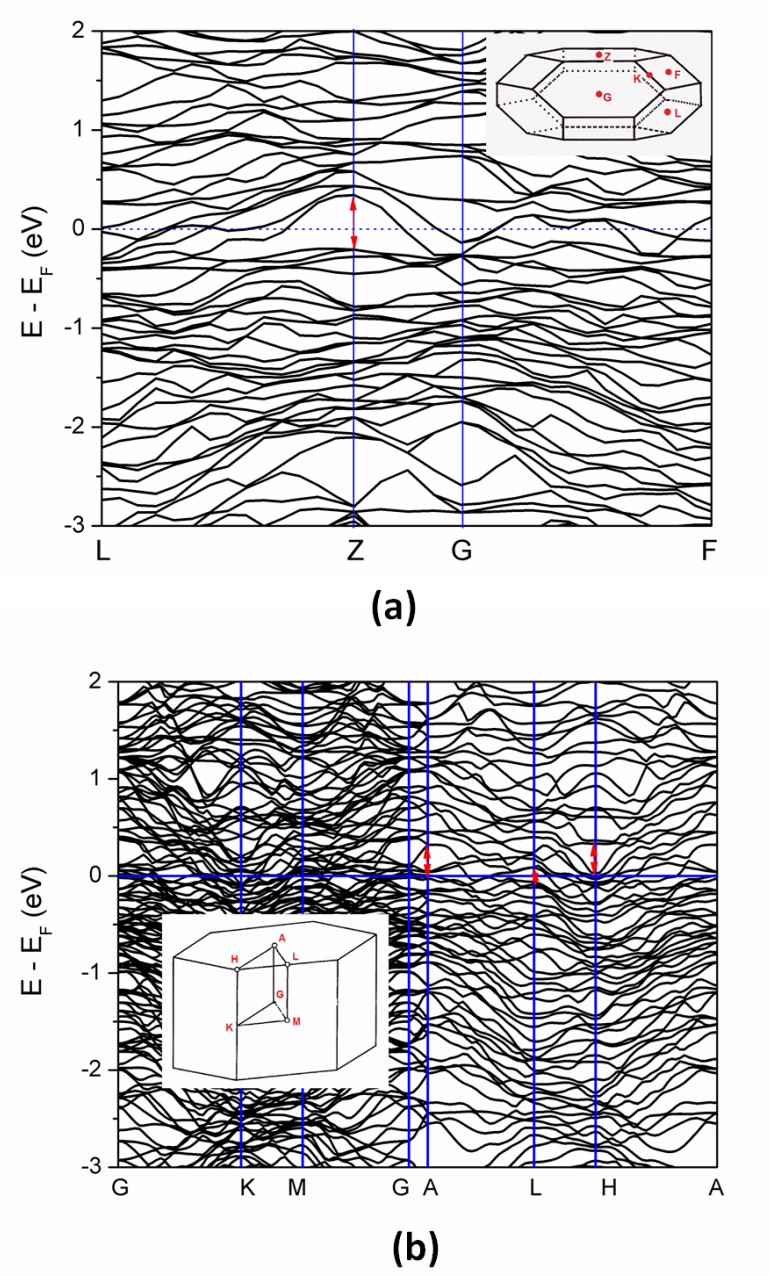

Figure S3. The band structure of (a) hypothetical "$Ca_{12}LiZn_{58}$" (*R*-3*m*) and (b) "$Ca_{15}Li_{18}Zn_{57}$" ($P6_3/mmc$) models. Red marks denote energy gaps around Femi energy along (001) for both structures.