

Electronic Supplementary Information (ESI)

**Prediction of Au<sub>4</sub>S crystal via superatom network model: from cluster  
to solid**

By

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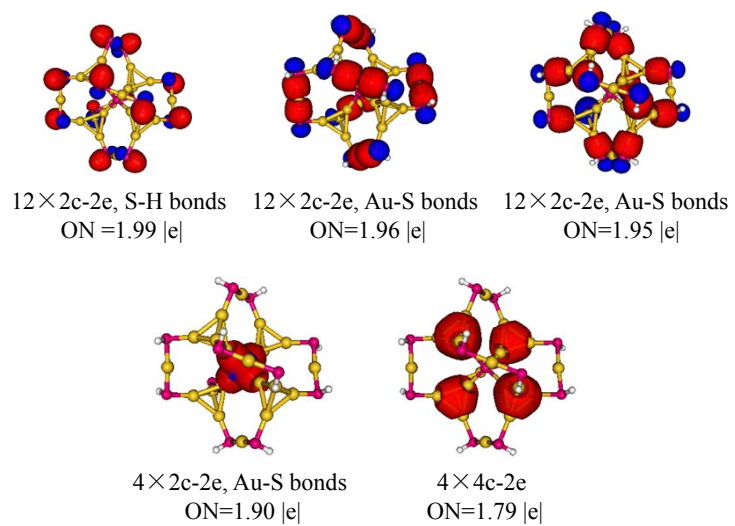
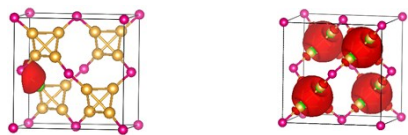
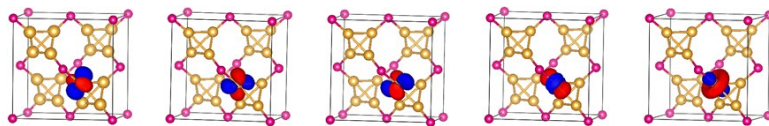


Fig. S1 AdNDP localized natural bonding orbitals of the  $Au_{22}(\mu_4-S)(SH)_{12}$  cluster.



One Au-S  $\sigma$ -bond (ON=1.92 |e|) Four 4c-2e (ON=1.78 |e|)



Five d-type lone pairs on one Au atom (ON=1.93-2.00 |e|)

Fig. S2 SSAdNDP chemical bonding pattern of the  $\text{Au}_4\text{S}$ .

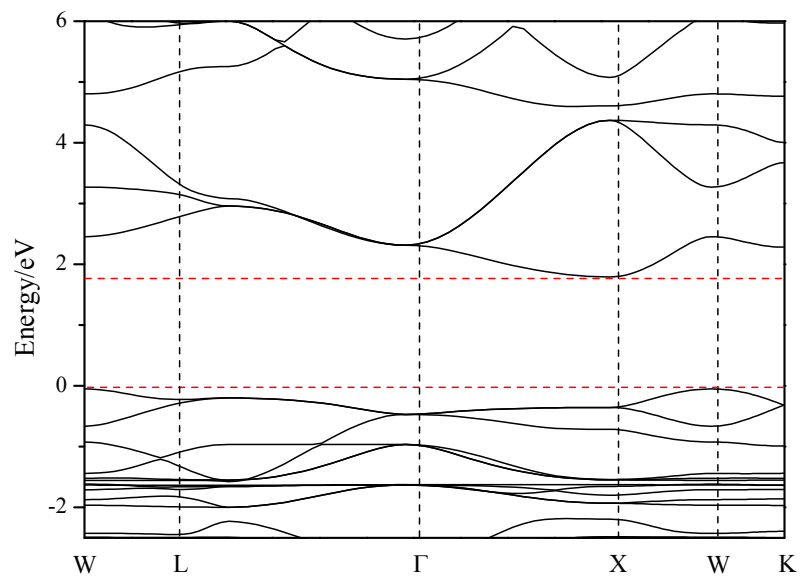


Fig. S3 Electronic band structure of the Au<sub>4</sub>S at the PBE level.

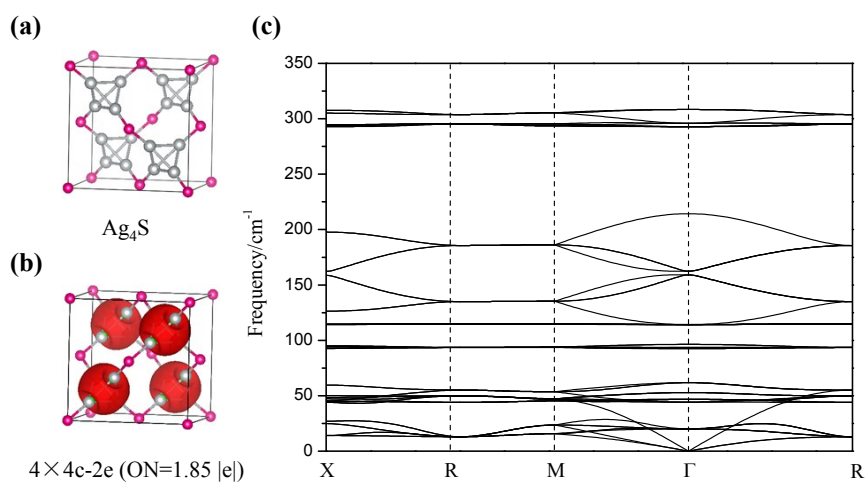


Fig. S4 (a) Optimized structure of the  $\text{Ag}_4\text{S}$  crystal with the unit cell. Gray and red spheres represent Ag and S atoms, respectively. (b) Four  $4c-2e$   $\sigma$  bonding patterns of the  $\text{Ag}_4\text{S}$  using the SSAdNDP method. (c) Calculated phonon dispersion curves along high-symmetry lines in the first Brillouin zone for the  $\text{Ag}_4\text{S}$ .

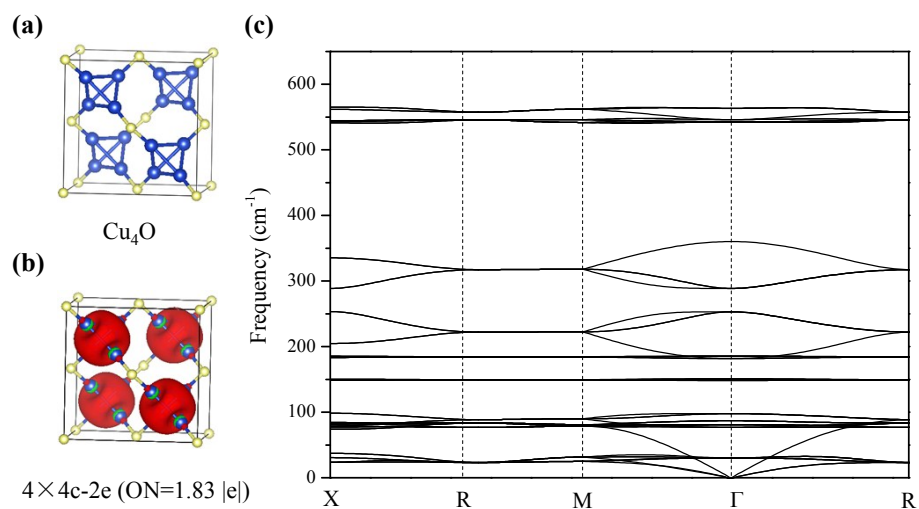


Fig. S5 (a) Optimized structure of the  $\text{Cu}_4\text{O}$  crystal with the unit cell. Green and yellow spheres represent the Cu and O atoms, respectively. (b) Four  $4c-2e$   $\sigma$  bonding patterns of the  $\text{Cu}_4\text{O}$  using the SSAdNDP method. (c) Calculated phonon dispersion curves along high-symmetry lines in the first Brillouin zone for the  $\text{Cu}_4\text{O}$ .