

Supplementary Materials

**New Perspectives on the Electronic and Geometric Structure of  $\text{Au}_{70}\text{S}_{20}(\text{PPh}_3)_{12}$  Cluster: Superatomic-network Core Protected by Novel  $\text{Au}_{12}(\mu_3\text{-S})_{10}$  Staple Motifs**

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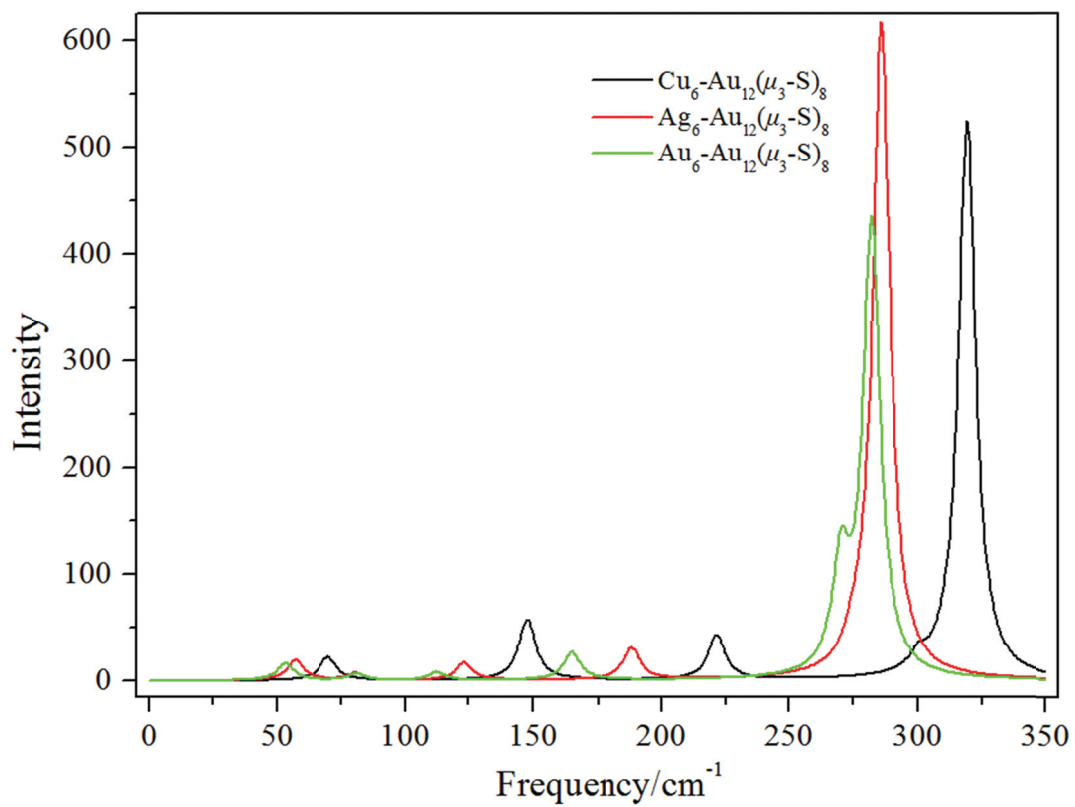
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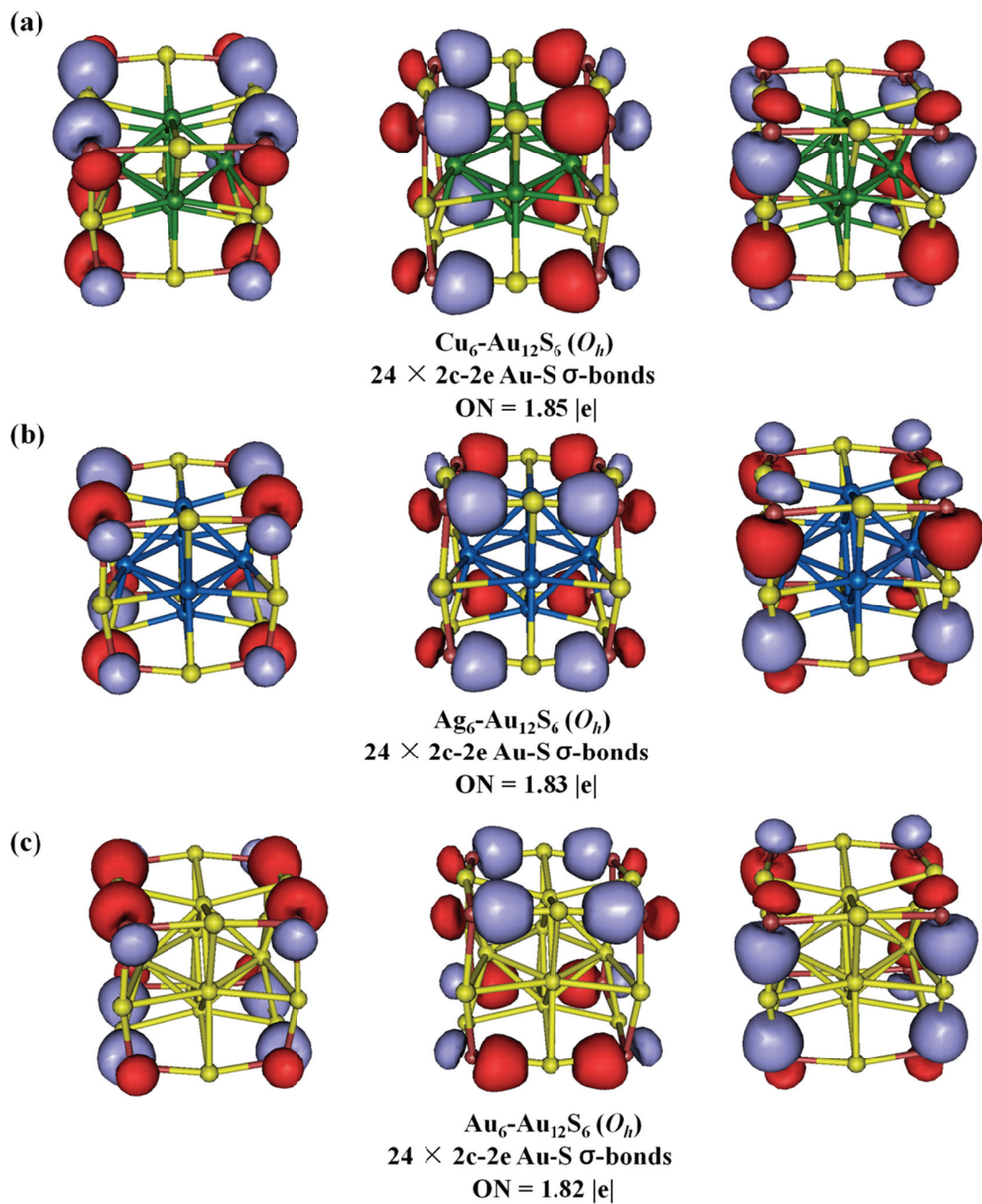
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**Figure S1.** IR spectra of Cu<sub>12</sub>-Au<sub>12</sub>(μ<sub>3</sub>-S)<sub>8</sub>, Ag<sub>6</sub>-Au<sub>12</sub>(μ<sub>3</sub>-S)<sub>8</sub> and Au<sub>6</sub>-Au<sub>12</sub>(μ<sub>3</sub>-S)<sub>8</sub> clusters.



**Figure S2.** Geometries (Cu, green; Ag, blue; Au, yellow) and AdNDP localized natural bonding orbitals of Au-S  $\sigma$ -bonds in (a)  $\text{Cu}_{12}\text{-}(\mu_3\text{-S})_8$ , (b)  $\text{Ag}_6\text{-Au}_{12}\text{-}(\mu_3\text{-S})_8$  and (c)  $\text{Au}_6\text{-Au}_{12}\text{-}(\mu_3\text{-S})_8$  clusters.