

**Electron counting and bonding patterns in assemblies of three, four and more silver-rich
superatoms**

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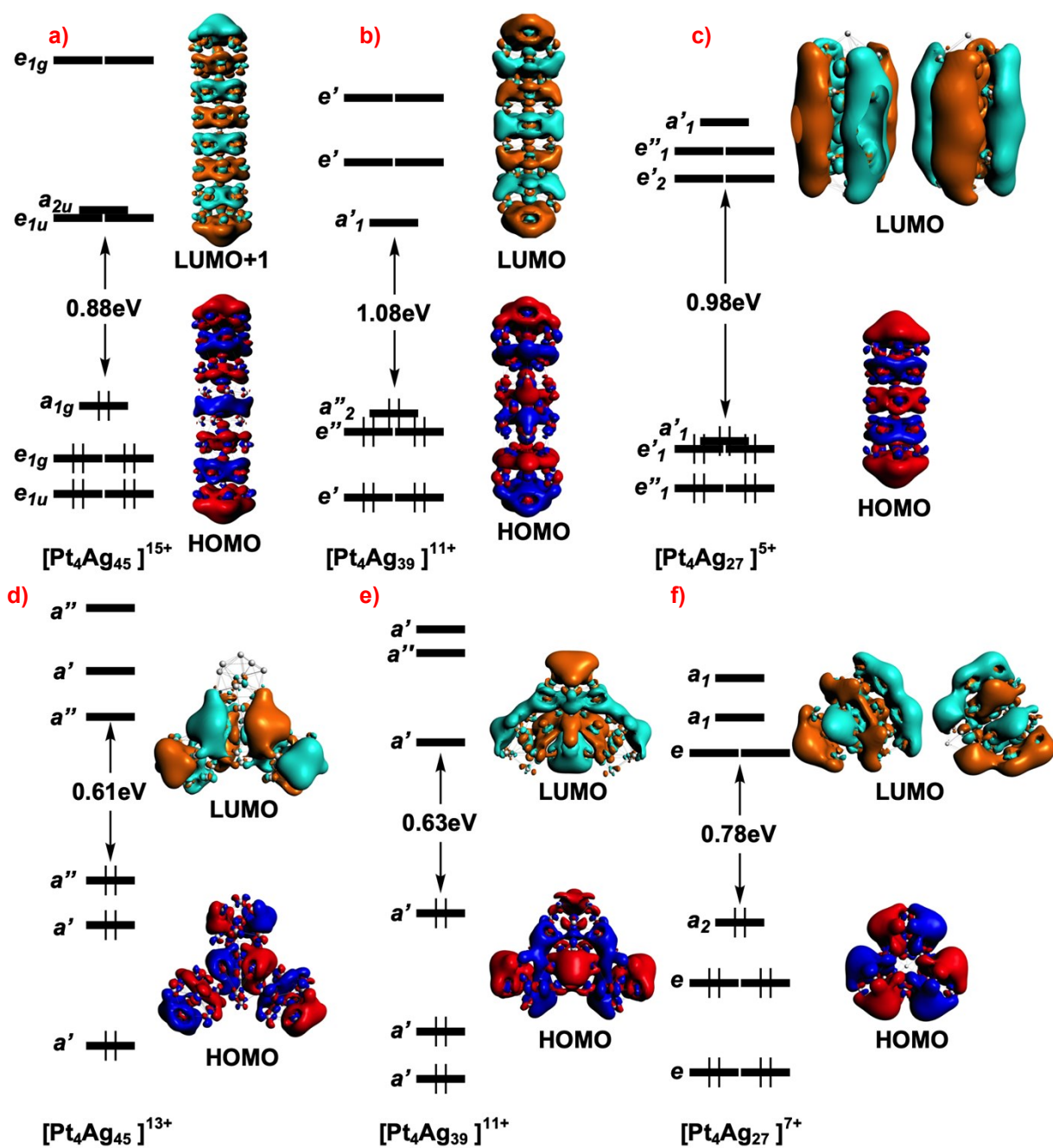


Figure S1. Kohn-Sham orbital diagrams of : (a) The 30-electron $[\text{Pt}_4\text{Ag}_{45}]^{15+}$ (D_{5d}), (b) the 28-electron $[\text{Pt}_4\text{Ag}_{39}]^{11+}$ (D_{3h}), (c) the 22-electron $[\text{Pt}_4\text{Ag}_{27}]^{5+}$ (D_{5h}), (d) the 32-electron $[\text{Pt}_4\text{Ag}_{45}]^{13+}$ (C_s), (e) the 28-electron $[\text{Pt}_4\text{Ag}_{39}]^{11+}$ (C_s), (f) the 20-electron $[\text{Pt}_4\text{Ag}_{27}]^{7+}$ (C_{3v}).

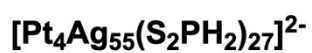
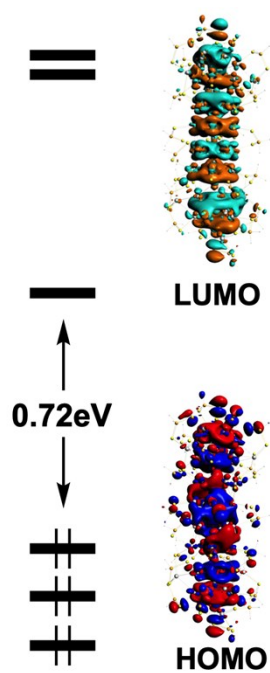


Figure S2. Kohn-Sham orbital diagram of the ligated 30-electron model $[\text{Pt}_4\text{Ag}_{55}(\text{S}_2\text{PH}_2)_{27}]^{2-}$ that contains the $[\text{Pt}_4\text{Ag}_{45}]^{15+}$ core (compare with Figure 1a).