N-Heterocyclic carbene derivatives to modify gold superatom characteristics. Tailorable electronic and optical properties of $[Au_{11}(PPh_3)_7LCl_2]^+$ as a cluster from relativistic DFT

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Abstract

Atomically precise gold superatoms are useful building blocks whose properties can be tuned by the proper choice of ligands in the protecting ligand layer. Herein, different N-heterocyclic carbene (NHC) derivatives of the prototypical [Au11(PPh3)8Cl2]+ cluster were evaluated by the replacement of a single ligand, which led to isoelectronic [Au11(PPh3)7(NHC)Cl2]+ species, enabling further understanding of the possible changes in the resulting cluster properties. Our results reveal the great variation in the HOMO-LUMO gap and optical features when going from strong to weak σ-donor NHC ligands. The Au11 core retains similar features throughout the series, and the lowest unoccupied orbital (LUMO) is further stabilized, indicating greater π*-NHC character for the weaker σ-donor ligands, which favors directional core-ligand optical charge transfer to a single ligand. The ligand-tailored behavior of the [Au11(PPh3)7LCl2]+ cluster underlies its tunable characteristics, indicating its potential use in novel devices as building blocks of nanostructured materials, which favors further versatility and applications of superatomic clusters.