[Au12(SR)6]2?, As Smaller 8-Electron Gold Nanocluster Retaining an SP3-Core. Evaluation of Bonding and Optical Properties from Relativistic DFT Calculations

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Exploring the versatility of atomically precise clusters is a relevant issue in the design of functional nanostructures. Superatomic clusters offer an ideal framework to gain further understanding of the different distinctive size-dependent physical and chemical properties. Here, we propose [Au12(SR)6]2? as a minimal 8-electron superatom related to the prototypical [Au25(SR)18]? cluster, depicting half of its core-mass (2.3 kDa vs 5.0 kDa). The [Au12(SMe)6]2? cluster fulfills a 1S2 1P6 electronic configuration, with a distorted tetrahedral Au8 core further viewed as an SP3-hybridized superatom. The distinctive optical properties show a blue-shift for the first relevant 1P?1D transition, in comparison to [Au25(SR)18]?. In addition, chiroptical activity is observed, denoting intrinsic core chirality. We expect that our results can shed light into the variation of the molecular properties according to the size-dependent properties, and serve as guidelines for further experimental exploration of minimal or ultrasmall nanoclusters.

computational chemistry

density functional calculations

gold

nanoclusters

superatoms