On the ligand role in determining the compact or extended metallic core architecture in gold superatoms. Evaluation of electronic and optical properties from relativistic DFT for $[Au_{11}(dppp)_5]^{3+}$ and $[Au_{11}(dppe)_6]^{3+}$ clusters

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Abstract

The rational synthesis of well-defined clusters requires further understanding of the fundamental aspects related to the stabilization of preferred isomers over other possible species. Atomically-precise gold superatoms offer useful templates to evaluate the role of the characteristics of the ligand shell in the resulting structure. Herein, we explore the the role of different diphenyl ligands in the determining a compact Au_{11} core, or extended Au_9 + 2Au core, provided experimentally by $[Au_{11}(dppp)_5]^{3+}$ and $[Au_{11}(dppe)_6]^{3+}$ clusters, with variable bridging chain length. Our findings highlight the contribution from ligand-ligand and core-ligand interactions, and the core rearrangement, which favors the experimentally characterized compact $[Au_{11}(dppp)_5]^{3+}$ cluster, by 34.4 kcal·mol^{-1} in comparison to the hypothetical $[Au_{11}(dppe)_5]^{3+}$ owing to the decrease in the bridge from -$(CH_2)_3$- to -$(CH_2)_2$-, increasing the steric crowding within the cluster. For the extended Au_9 + 2Au core, the contrary case is found, where the experimentally characterized $[Au_{11}(dppe)_6]^{3+}$ cluster is favored by 49.2 kcal·mol^{-1} in comparison to the hypothetical $[Au_{11}(dppp)_6]^{3+}$ species. The obtained optical characteristics, denotes a similar visible absorption profile for the compact core species, which contrast to the extended Au_9 + 2Au core, which is more sensible to the ligand, as accounted by the calculated optical profile. Thus, the overall structure is determined mainly by the contribution from the ligand shell characteristics and the resulting core-ligand, underlying designing aspects towards tunable clusters for building blocks of nanostructured materials. © 2021 Elsevier Ltd

Author keywords

Clusters; Core; Gold; Phosphine; Superatoms