From 8- to 18-Cluster Electrons Superatoms: Evaluation via DFT Calculations of the Ligand-Protected W@Au12(dppm)6 Cluster Displaying Distinctive Electronic and Optical Properties

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Abstract

The iconic W@Au_{12} icosahedral bare cluster reaches the favorable closed-shell superatomic electron configuration $1S^2$ $1P^6$ $1D^{10}$, making it an 18-cluster electron (18-ce) superatom. Here, we pursue the evaluation of a ligand-protected counterpart based on the construction of a fully phosphine-protected [W@Au_{12}(dppm)$_6$] cluster strongly related to the characterized [Au_{13}(dppm)$_6$]$^{5+}$ homometallic counterpart. The later cluster has the same total number of valence electrons as the former but is considered an 8-ce superatom with $1S^2$ $1P^6$ configuration. The fundamental differences between 8- and 18-ce species are investigated. The character of the frontier orbitals varies from 1P/1D in the 8-ce case to a 1D/ligand for 18-ce species, enabling an efficient charge transfer toward the ligands upon irradiation, being interesting for electron injection in optoelectronic devices and black absorbers applications. Excited-state properties are also revisited, showing different geometrical and electronic structure variations between 8- and 18-ce species. Moreover, the continuum between the 8- and 18-ce limits has been explored by varying the nature of the encapsulated dopant between group 6 and group 11. The transition between the 8- and 18-ce counts can be formally situated between Pt (8-ce) and Ir (18-ce). Thus, 18-ce derivatives obtained as doped counterparts of homometallic gold clusters can introduce useful alternatives to achieve different properties in related structural motifs, which can be further explored owing to their extension of the well-established versatility of current gold nanoclusters.