Symmetry lowering by cage doping in spherical superatoms: Evaluation of electronic and optical properties of 18-electron W@Au 12 Pt n (n = 0-4) superatomic clusters from relativistic DFT calculations

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Attempts to expand the versatility of well defined clusters are a relevant issue in the design of building blocks for functional nanostructures. Here, we investigate the plausible formation of related structures from the emblematic highly symmetrical 18-e [W@Au 12] cluster. The calculated [W@Au 12 Pt n] series, with n = 0, 1, 2, 3, and 4, show cohesion energies, HOMO-LUMO gap, adiabatic electron affinities (AEAs) and adiabatic ionization potentials (AIPs), indicating a relative stability to the parent cluster [W@Au 12] experimentally characterized, where clusters with n = 1 and n = 4 are suggested as the most stable with respect to oxidation. The resulting symmetry lowering away from the high icosahedral symmetry upon adding Pt atoms induces a sizable splitting of the frontiers shells, which in turn effectively modify the properties of the calculated clusters, as observed from calculated optical properties. The estimated absorption spectra show an interesting broadening effect of the absorption peaks, which appears as a useful approach for further design of broad black absorbers, which are able to absorb light in a wider range, with potential capabilities to enhance the efficiency of thin film solar cells and photocatalysis processes, among other applications.

endohedral

gold

heteroatomic

platinum

superatoms

Design for testability

Gold

Ionization potential

Platinum

Semiconductor doping

Solar absorbers

Structural design

Thin film solar cells

Adiabatic electron affinity

Adiabatic ionization potential

Calculated optical properties

Electronic and optical properties

Endohedrals

Functional nanostructures

heteroatomic

Superatoms

Optical properties