Doping the cage. Re@Au11Pt and Ta@Au11Hg, as novel 18-ve trimetallic superatoms displaying a doped icosahedral golden cage

Muñoz-Castro A.

Expanding the versatility of well defined clusters is a major concern in the design of building blocks towards functional nanostructures. W@Au12 is a prototypical binary bare superatomic cluster involving an icosahedral symmetry, which has been discussed in the literature, precluding the proposal of several endohedral d-block and f-block element structures within a golden cage. Here we pursue the construction of related trimetallic clusters, which has been explored to a lesser extent. Our results expose the great advantages of involving heterocages in the superatom approach, unraveling Re@Au11Pt and Ta@Au11Hg as novel trimetallic candidates. Re@Au11Pt exhibits an electron-deficient element in the cage, and an endohedral atom with an extra electron. In contrast, Ta@Au11Hg is conceived as having an icosahedral cage with an extra electron, and an electron-deficient endohedral element. These new clusters follow the eighteen valence electron principle, with similar characteristics to their W@Au12 parent. This leads to stable clusters with an electronic structure formally described by the 1s21p61d10 closing shell order, showing an interesting approach to design ternary superatoms, where the variation of valence electrons occurs in both cage and endohedral sites. Moreover, the cage doping appears as a useful approach to further evaluate the formation of magnetic superatoms, and also the construction of larger clusters by fusing different icosahedral structures.