Superatomic molecules MAu_{22} (M = Au, Pd): Targeted syntheses via fusion of superatoms and characterization

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Anisotropic cores of ligand-protected gold clusters can be viewed as quasi molecules composed of superatoms (superatomic molecules). For example, the Au_{23} core of $Au_{38}(SR)_{24}$ (RS = thiolate) corresponds to a di-superatomic molecule of two icosahedral Au_{13} superatoms with 7 electrons.[1] Theoretical calculation suggested that the bonding scheme of the Au_{23} core is analogous to that of F_2.[2] Recently, we developed an efficient synthetic method of $MM'Au_{36}(SR)_{24}$ (M, M' =Pd, Pt) via the hydride-mediated fusion reaction between $HMAu_8(PPh_3)_8^+$ and $M'Au_{24}(SR)_{18}$. The $MM'Au_{21}$ core corresponding to a dimer of icosahedral $M@Au_{12}$(6e) and $M'@Au_{12}$(6e) has different bonding scheme and spin state from those of O_2. Bonding interaction between 1P superatomic orbitals does not generate doubly degenerate SOMOs like O_2, but non-degenerated HOMO and LUMO via tilted interaction.[3] This study aims to reveal electronic structures and bonding schemes of hetero-superatomic molecules of Au_{13}(7e) and $Pd@Au_{12}$(6e).

Mass spectrometry and optical spectroscopy confirmed the formation of $Au_{38}(SR)_{24}$ with a biicosahedral Au_{23} core by the fusion of $HAu_9(PPh_3)_8^{2+}$ and $Au_{25}(SR)_{18}$. In contrast, mass spectrometry revealed the successful isolation of $PdAu_{37}(SR)_{24}$ by the fusion of $HAu_9(PPh_3)_8^{2+}$ and $PdAu_{24}(SR)_{18}$. Single-crystal X-ray diffraction analysis of $PdAu_{37}(SR)_{24}$ demonstrates the formation of the biicosahedral $PdAu_{22}$ core (Fig. 1a). The first absorption peak of $PdAu_{22}$ at ~ 1.0 eV was smaller than that of Pd_2Au_{21}, suggesting LUMO of Pd_2Au_{21} was singly occupied in $PdAu_{22}$ (Fig. 1b). The bonding scheme of $PdAu_{12}$(6e) and Au_{13}(7e) in $PdAu_{22}$ will be discussed based on the comparison of geometric and electronic structure of the cores.

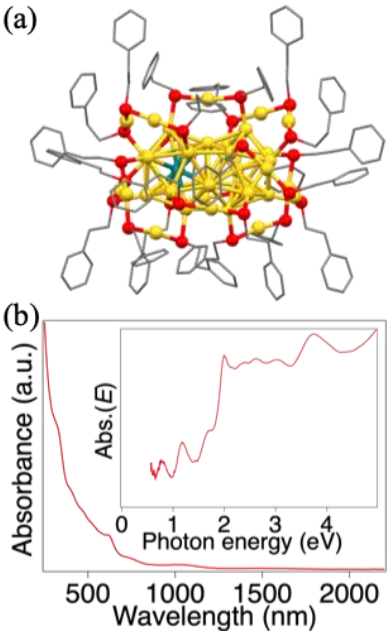

Fig. 1. (a) Crystal structure (Color code: yellow Au; teal Pd; red S; gray C) and (b) Optical spectrum of $PdAu_{37}(SR)_{24}$.

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