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Synthesis of Novel Silver Nanocluster Protected by Ag_3Cu Planar Complex Units

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Noble metal nanoclusters are attracting intensive attention because of their potential applications in catalysis, biology, and nanotechnology. The compositions, structures and size of nanoclusters influence their distinct properties. In this decade, a large number of gold nanoclusters protected by thiolates or phosphines are synthesized and numerous studies on their properties have been reported. In contrast, the number of silver nanoclusters have been limited due to their intrinsic lability. It has been desired in nanocluster chemistry to develop synthetic routes to silver nanoclusters that can control their structures, sizes and compositions.

Here, we established a synthetic route to novel core-shell type silver nanoclusters $[Ag_{13}X_6(Ag_3Cu)_4(CCTol)_{12}(PPh_3)_{12}]^{3+}$ (X=Cl,Br) (hereinafter called "$Ag_{25}Cu_4$ cluster"). Single crystal structural determination reveals that they have a centered Ag_{13} kernel which are protected by Ag_3Cu planar complex units and halide linker. The general Ag_{13} kernels adopt several geomatric shapes, for example, icosahedron, cuboctahedron and anti-cuboctahedron[1]. However, the present $Ag_{25}Cu_4$ clusters cannot be classified to any of these shapes, they adopt "distorted-cuboctahedron".

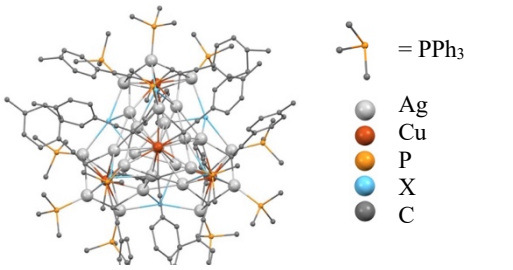

Fig.1 Molecular structure of $[Ag_{13}X_6(Ag_3Cu)_4(CCTol)_{12}(PPh_3)_{12}]^{3+}$(X=Cl,Br)

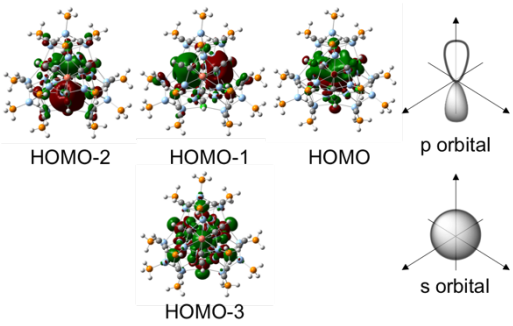

Fig.2 Frontier orbitals of the $Ag_{25}Cu_4$ cluster (X=Cl)

Electronic states of $Ag_{25}Cu_4$ clusters have been investigated. According to the superatom theory[2], the number of free valence s electrons in the Ag_{13} kernel is calclated to be 8, which is a magic number, explaining the formation and stability of the clusters. This result is supported by DFT calculations. The shape of HOMO-3 indicates that the S symmetric molecular orbital localizes at the deep core of the cluster and HOMO, HOMO-1 and HOMO-2 reveal a strong P character over the Ag_{13} kernel, which assigned to superatomic states accomodating 8 electrons.

An UV-vis absorption spectrum shows that $Ag_{25}Cu_4$ clusters have their unique absorption bands in 400-550 nm. These absorptions are originated from Ag_{13} kernel of $Ag_{25}Cu_4$ clusters.

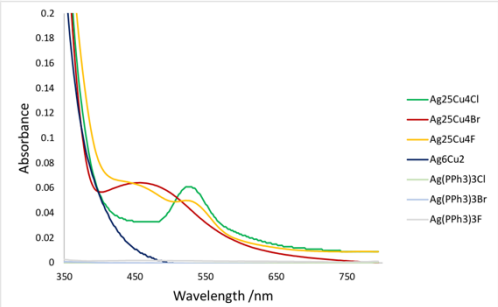

Fig.3 UV-vis absorption spectra of clusters

Reference [1] Shang-Fu Yuan, Pei Li, Qing Tang, Xian-Kai Wan, Zi-Ang Nan, De-en Jiang and Quan-Ming Wang, *Nanoscale*, **2017**, 9, 11405-11409

[2] M. Walter,J.Akola,O. Lopez-Acevedo,P. D. Jadzinsky,G.Calero,C.J.Ac-kerson,R.L.Whetten,H.Grçnbeck,H. Häkkinen,*Proc.Natl.Acad.Sci.USA***2008**,105,9157–9162.