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Communication

CdAg(SePh): Non-Noble Metal Doped Silver Nanoclusters

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Cd₁₂Ag₃₂(SePh)₃₆: Non-Noble Metal Doped Silver Nanoclusters

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Supporting Information Placeholder

ABSTRACT: While there are numerous recent reports on doping of a ligand-protected noble metal nanocluster (e.g., Au and Ag) with another noble metal, non-noble metal (e.g., Cd) doping remains challenging. Here, we design a phosphine-assisted synthetic strategy and synthesize a Cd doped Ag nanocluster, Cd₁₂Ag₃₂(SePh)₃₆ (SePh: selenophenolate), which exhibits characteristic UV-vis absorption features and rare near-infrared (NIR) photoluminescence at ~1020 nm. The X-ray single crystal structure reveals an asymmetric two-shell Ag₄@Ag₂₄ metal kernel protected by four nonplanar Cd₃Ag(SePh)₉ metal-ligand frameworks. Furthermore, the electronic structure analysis shows that the cluster is a 20-electron “superatom” and density functional theory predicts that its chiral optical response is comparable to the well-known Au₃₈(SR)₂₄ cluster. Our synthetic approach will pave a new path for introducing other non-noble metals into noble metal nanoclusters for exploring their effect on optical and chemical properties.

Ligand stabilized few-atom (tens to hundreds) nanoclusters (NCs) of metals such as Au, Ag and Cu have gained much attention in recent years for their intriguing properties, including photoluminescence (PL), optical activity, catalysis, and size- and structure-conversion.¹⁻⁴ The NCs (typical size <3 nm) bridge the gap between the metal-ligand complexes and nanoparticles (NPs, size >3 nm). Unlike the classical NPs with large size and composition distributions, the NCs are truly single-sized with precise molecular formulae. Thus, NCs are the potential candidates to gain fundamental insights into the evolution of optical and catalytic properties of materials from discrete atomic to molecular levels.⁵⁻⁸

Since the first report on the X-ray crystal structure of ligated Au₁₀₂ cluster,⁹ several Au, Ag and their heteroatom doped NCs have been synthesized and atomic structures determined.^{1-3, 10} The size, structure and composition are shown to influence the cluster properties significantly. The former two are generally directed by the choice of ligands.^{1-3, 11} The common ligands used to attain different clusters are thiols, selenols, alkynyls, halides, hydrides, phosphines or their combinations,^{1, 2, 12-17} in which selenols are rarely used for stabilizing Ag clusters.^{18, 19}

Another path to modulate the cluster properties is by modifying the metal composition through substitutional doping with heteroatoms.^{20, 21} The doped NCs exhibit enhanced properties compared to undoped ones owing to synergistic effects.^{4, 22, 23} The dopants incorporated into Au and Ag NCs are mostly the noble metals such as Pd and Pt due to their close atomic diameters.^{1, 20} In contrast,

doping a noble metal NC with a non-noble metal such as Cd is challenging largely due to mismatch in their atomic sizes and standard reduction potentials. Recently, several Cd doped Au NCs were synthesized by post-synthetic modification processes,²⁴⁻²⁷ while those of Ag remain unexplored.

Here, we report a novel synthetic method for the non-noble metal doped Ag NCs by a phosphine assisted process. Specifically, by using triphenylphosphine (PPh₃) as an assisting ligand and Cd as dopant, we successfully synthesized a selenophenolate stabilized Ag NC, Cd₁₂Ag₃₂(SePh)₃₆. The details of its synthesis (Figure S1) and purification procedures are provided in the Supporting Information. The single crystals of NCs were grown (Figure S2) by the vapor diffusion of n-pentane into a DCM solution of the cluster.

The single crystal X-ray diffraction (SCXRD) analysis reveals that the final product is a 44 metal atom cluster stabilized by 36 SePh ligands with a molecular formula, Cd₁₂Ag₃₂(SePh)₃₆ (Figure 1). Clearly, the Cd atoms are located on the cluster surface. The cluster crystallizes in a triclinic system of *P-1* space group (Table S1) and its unit cell comprises two NCs (Figure S3). No counterions were identified in the structure, indicating that the cluster is neutral.

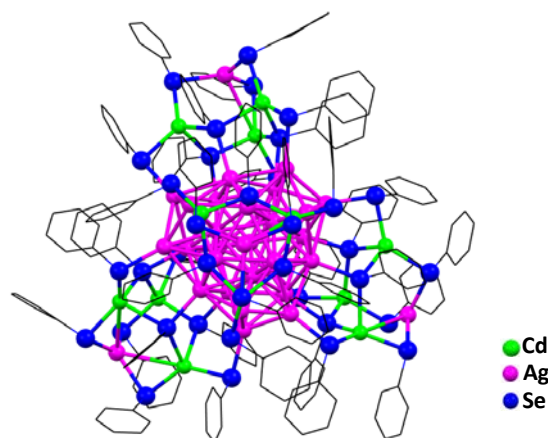


Figure 1. The total structure of Cd₁₂Ag₃₂(SePh)₃₆ cluster. H atoms of SePh ligands are omitted for clarity.

The detailed structural analysis (Figure 2) shows that the NC consists of a Ag₂₈ core stabilized by four Cd₃Ag(SePh)₉ motifs. Further anatomy of the Ag₂₈ core unveils a Ag₄ tetrahedron (Figure 2A) at the center. The average Ag-Ag bond distance of 2.84 Å is close to that of the bulk Ag, indicating the strong Ag-Ag interactions in the NC. Six Ag atoms arrange nearly coplanarly to form a

Ag₆ facet with four triangles (Figure 2B). Such four Ag₆ facets cap the four faces of Ag₄ tetrahedron to form a structure shown in Figure 2C. The interfacet interactions through Ag-Ag bonding produce a Ag₂₄ layer and it completely encapsulates the Ag₄ tetrahedron, forming a two-shell Ag₄@Ag₂₄ core (Figure 2D). Notably, the central Ag₃ triangles of Ag₆ facets (placed exactly on top of the triangular faces of inner Ag₄ core) are significantly elongated from the Ag₄ core compared to other Ag-Ag bonds (Table S2).

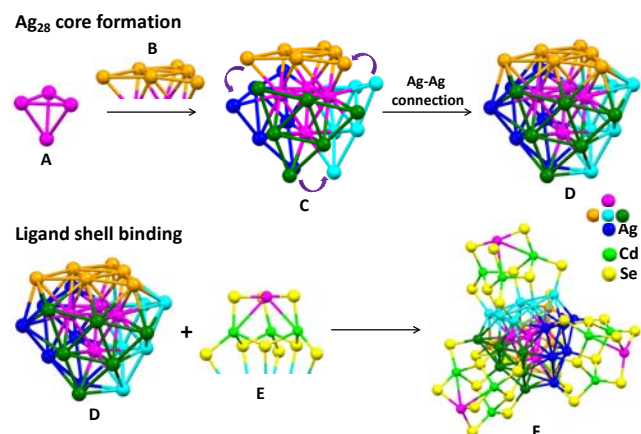


Figure 2. Construction of the structure of Cd₁₂Ag₃₂(SePh)₃₆. (A) Ag₄ inner core and (B) Ag₆ facet. Capping of Ag₄ core with Ag₆ facets and interfacet interactions (purple arrows) result in C and D, respectively. Mounting of Cd₃Ag(SePh)₉ motifs (E) on the Ag₂₈ core (D) gives the total structure of the cluster (F). The phenyl rings of ligands are omitted for clarity.

In Cd₃Ag(SePh)₉ surface motif (Figure 2E), each Cd atom is tetrahedrally coordinated with four Se atoms of four SePh ligands. Totally, three Se atoms from three CdSe₄ tetrahedrons bind with one Ag to form a AgSe₃ cap-like structure, forming the Cd₃Ag(SePh)₉ motif. The capping of four Cd₃Ag(SePh)₉ motifs on four Ag₆ facets of Ag₂₈, through Se atoms that are unbound to motif Ag atoms, produces the total structure of Cd₁₂Ag₃₂(SePh)₃₆ cluster (Figure 2F). Notably, 12 and 24 Se atoms appear in μ -3 and μ -2 bridging modes, respectively. All the four Cd₃Ag(SePh)₉ motifs are mounted over four triangular faces of inner Ag₄ tetrahedron, and therefore, it imparts the tetrahedral shape to the final structure. A similar Ag₂₈ core of our cluster is observed in [Cu₁₂Ag₂₈(SR)₂₄]⁴⁻ cluster,²⁸ however with vividly different metal and ligand composition, electronic charge and the surface structure.

The presence of Cd, Ag and Se in the cluster was supported by energy dispersive X-ray spectroscopy (Figure S4). The matrix-assisted laser desorption ionization mass spectrometry shows only a single high-mass peak at ~9.6kDa, indicating that the cluster is single-sized. This peak with lower in mass by ~0.7kDa compared to 10.3kDa for Cd₁₂Ag₃₂(SePh)₃₆ may be due to the fragmentation often observed in the Ag clusters¹¹ (Figure S5). The formula of the cluster is further validated by the elemental analysis (Figure S6). The thermogravimetric analysis shows a total weight loss of 54.5%, very close to a theoretical ligand weight of the cluster 54.0% (Figure S7). ¹H nuclear magnetic resonance (NMR) spectrum of the cluster (Figure S8) shows proton signals spread between 6-8 ppm for SePh protection,¹² which is also in agreement with the infrared analysis (Figure S9A). The absence of H and P signals for PPh₃ ligands, which were used during the cluster synthesis, in ¹H and ³¹P NMR spectra is consistent with the SCXRD results.

The “superatom” theory²⁹ calculates a free metal electron count of 20 for Cd₁₂Ag₃₂(SePh)₃₆ cluster i.e., [(12x2)+(32x1)-(36x1)] by considering the *s*-valence of two for Cd and one for Ag as well as

one-electron withdrawing character of the SePh ligand. This electron count predicts that the HOMO state and the molecular orbitals just below HOMO should have 1D-2S symmetries present in a spherical angular momentum analysis, and the LUMO state should have 1F character. This is indeed what we observe by performing symmetry analysis and inspecting visually the frontier orbitals (Figures S10, S11), although the HOMO has a mixed 2S-1F character probably due to the non-spherical symmetry of the metal core. Furthermore, atomic charge analysis (Table S3) shows that the Ag atoms in the Ag₄Ag₂₄ shells are close to neutral, whereas the Ag and Cd atoms in the ligand motifs are clearly positively charged by 0.20 e and 0.66 e, respectively. The SePh ligands are shown as electron-withdrawing with a clear negative total charge by -0.28 e per ligand.

The optical properties and electronic structure of Cd₁₂Ag₃₂(SePh)₃₆ cluster were further studied both experimentally by UV-vis spectroscopy and theoretically by the linear response formulation of the time-dependent density functional theory (LR-TDDFT, see SI for details). The experimental absorption spectrum (Figure 3) displays clear peaks at 451, 534 and 640 nm along with shoulder peaks at 245, 288, 335, and 493 nm. The absorption onset (Figure S9B) at ~900 nm (1.37 eV) is very close to the calculated HOMO-LUMO gap of 1.35 eV, with a slight underestimation of the gap being a typical feature of the used DFT PBE xc-functional. The calculated absorption spectrum for both the experimental (Figure 3) and PBE-relaxed cluster structure show a good agreement with the experiment, with at least six peaks/shoulders identifiable in the computed spectrum (labels a-f).

The absorption features a-f were analyzed by creating the dipole transition contribution maps and by breaking down the contributions by different parts of the cluster to a given transition (Figure S12). The lower energy peaks (a-c) have all similar characters, namely they are superatom-to-superatom transitions concentrated in the Ag core (intraband Ag(sp)→Ag(sp) transitions). It is interesting to note that the energy difference between a and b peaks seems to be a direct measure to the energy splitting of the superatom 1F manifold by the overall tetrahedral symmetry of the cluster (Figure S10). The high-energy features, d-f have increasing contributions also from the metal-ligand interface (mainly from Se(p)) and weakening contributions from the superatom states. We note that the Ag d-band is not actively participating to optical transitions in the analyzed and measured energy range, nor are the Cd atoms (since they are in the formal Cd(II) state).

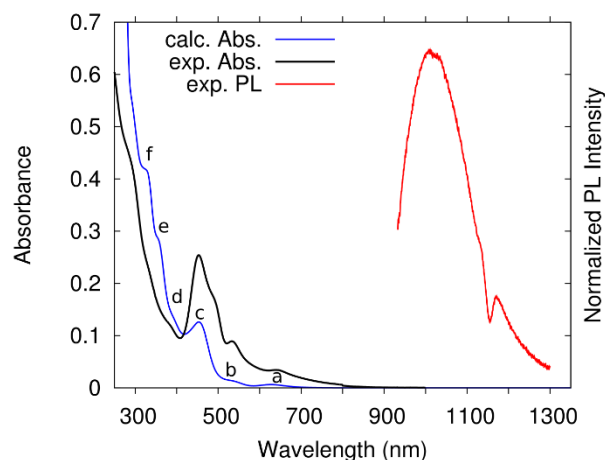


Figure 3. Experimental (black) and calculated (blue) absorption spectra of Cd₁₂Ag₃₂(SePh)₃₆ cluster. For easier comparison, the calculated spectrum is blue-shifted uniformly by 0.3 eV. Red line: experimental PL (excitation: 490 nm).

Interestingly, the $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ cluster shows a broad NIR PL (quantum yield: $\sim 0.28\%$) peak at ~ 1020 nm (Figure 3), which is different from the visible PL of Ag NCs.² The similar PL excitation and UV-vis spectra, and the same emission at 1020 nm for different excitations together (Figure S13) indicate that the PL is originated from the cluster. The PL of Cd doped Ag cluster at 1020 nm is clearly different from that of a Cu doped cluster at 900 nm,²⁸ suggesting the successful tuning of NIR PL by the non-noble metal doping (Figure S14). Theoretically estimated PL emissions (see SI for details) at 1134 nm and 1150 nm are in qualitative agreement with the experiment (1020 nm), strongly suggesting that the origin of the high-energy end of broad PL is the de-excitation over the HOMO-LUMO energy gap.³⁰ The low-energy end of PL is likely resulted from the relaxation through an intrinsic $\text{Cd}_3\text{Ag}(\text{SePh})_9$ surface state.

The SCXRD shows that the two clusters in the unit cell are enantiomers (Figure S15) due to asymmetric Ag_{28} core. Since the solution of $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ is racemic, we cannot experimentally measure the chiral optical response, however, it can be straightforwardly calculated for one of the enantiomers. Our calculations predict that the strength of the chiral response in the UV-vis region (Figure 4) is comparable to, e.g., the well-known thiolated chiral $\text{Au}_{38}(\text{SR})_{24}$ cluster.^{31, 32}

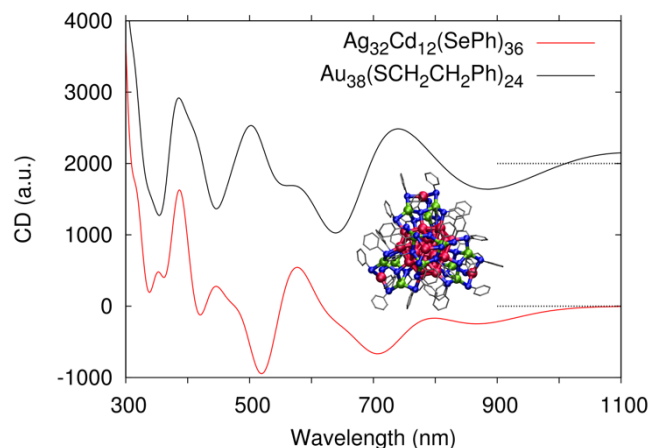


Figure 4. Computed circular dichroism (CD) spectra of one of the enantiomers of $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ (red curve) and $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ (black curve, offset vertically for better visualization) clusters. Inset: the DFT optimized structure of the $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ enantiomer.

We note the absence of PPh_3 in $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ cluster (Figure 1), which could be synthesized only in the presence of PPh_3 and tetraoctylammonium bromide (Figure S16) in our experimental conditions. The absorption spectra (Figure S17) suggest that the formation of $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ proceeds through the intermediate clusters formed after NaBH_4 reduction of metal-ligand complexes. The ^{31}P and ^1H NMR spectra confirm the binding of PPh_3 in the metal-ligand complexes (Figures S18, S19). After NaBH_4 addition, the PPh_3 in the complex transfers the metals to form intermediates and subsequently released into solution, confirming PPh_3 -mediated synthesis of the $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ cluster. This cluster shows moderate and excellent ambient stability in the solution- and solid-state, respectively (Figure S20).

In summary, we designed a phosphine-assisted synthetic strategy to dope an atomically precise Ag nanocluster with a non-noble metal, Cd. By this method, we synthesized a single-sized neutral $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ cluster and elucidated its total structure using X-ray crystallography. The Cd dopant is found to prefer the cluster surface to its core. Our cluster exhibits NIR PL and a chiral core,

resulting optical activity. The absorption spectrum and electronic structure of this cluster are well compared with those from the DFT. Our ligand-assisted synthesis of nanocluster may become a general method to introduce other active metals into noble metal clusters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis, characterization and computational details of the $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ cluster (PDF).

Crystallographic data for the $\text{Cd}_{12}\text{Ag}_{32}(\text{SePh})_{36}$ cluster (CIF).

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Notes

The authors declare no competing financial interests.

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