Plasmonic twinned silver nanoparticles with molecular precision

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Determining the structures of nanoparticles at atomic resolution is vital to understand their structure–property correlations. Large metal nanoparticles with core diameter beyond 2 nm have, to date, eluded characterization by single-crystal X-ray analysis. Here we report the chemical syntheses and structures of two giant thiolated Ag nanoparticles containing 136 and 374 Ag atoms (that is, up to 3 nm core diameter). As the largest thiolated metal nanoparticles crystallographically determined so far, these Ag nanoparticles enter the truly metallic regime with the emergence of surface plasmon resonance. As miniatures of fivefold twinned nanostructures, these structures demonstrate a subtle distortion within fivefold twinned nanostructures of face-centred cubic metals. The Ag nanoparticles reported in this work serve as excellent models to understand the detailed structure distortion within twinned metal nanostructures and also how silver nanoparticles can span from the molecular to the metallic regime.
owing to quantum-size and surface effects, nanoparticles frequently exhibit novel physical and chemical properties, which differ from their bulk counterparts in dramatic ways, and they have been gaining increasing attention in the fundamental and applied sciences\textsuperscript{1–7}. Properties of nanoparticles are governed by chemical composition, size, shape and the overall molecular structure\textsuperscript{12–13}. Despite significant progress in the chemical fabrication of uniform functional nanoparticles with well-defined shapes, sizes and compositions over the past two decades\textsuperscript{8–11}, it is still notoriously difficult to manipulate their structures and thus functions with molecular control. Currently, there is the lack of effective tools to characterize the detailed structures (for instance, defects, twinning and surface features) of functional nanoparticles at atomic resolution. Without a detailed molecular structure as a guide, precision synthesis of nanoparticles with targeted functionality is difficult.

During the last several years, two major strategies have been applied in pursuit of detailed structure analysis of metal nanoparticles. One is application of state-of-the-art electron microscopy techniques to probe the atomic-resolution structures of the nanoparticle core\textsuperscript{12–17}. Azubel et al.\textsuperscript{16} have reported the structure determination of a ligand-stabilized Au\textsubscript{68} nanoparticle at atomic resolution by a combination of a low-dose approach and aberration-corrected transmission electron microscopy (TEM). The other avenue is to prepare and crystallize monodisperse metal nanoparticles into single crystals and determine their structures using X-ray diffraction\textsuperscript{18–31}. Such an approach is particularly important to resolve the metal-ligand interfacial features at the metal nanoparticle surface. By this approach, the structures of a few ligand-stabilized (for instance, carbon monoxide and thiolate) metal nanoparticles containing over 100 metal atoms (for instance, Au\textsubscript{102}, Au\textsubscript{133} and Au\textsubscript{130}) have been determined at or near atomic resolution\textsuperscript{18–21,32}. Despite significant progress following both strategies, resolution of the molecular structure of metal nanoparticles containing several hundred metal atoms and having metallic properties remains daunting\textsuperscript{20,33}.

We report here the syntheses and structure determinations of two giant, thiolated Ag nanoparticles containing 136 and 374 Ag atoms. As the largest thiolated metal nanoparticles crystallographically determined so far, these Ag nanoparticles exhibit unprecedented metallic properties with the emergence of surface plasmon resonance (SPR). The nanoparticles are miniatures of two closely related fivefold twinned nanostructures, pentagonal-bipyramidal (that is, decahedral) nanoparticles and twinned nanorods/nanowires derived from decahedral particles by elongation along the fivefold axis. Small distortions from the structure archetype within the fivefold twinned nanostructures are observed. Density functional theory (DFT) studies reveal that the smaller nanoparticle has molecular character with a small but distinct energy gap (band gap) between occupied and unoccupied orbitals (highest occupied molecular orbital–lowest unoccupied molecular orbital gap), whereas the larger one is fully metallic without a band gap. This leads to emergence of the surface plasmon incorporating contributions from the organic ligand layer. These two structurally determined systems represent important exemplars of the cross-over of Ag nanoparticles from the molecular to the metallic regime.

## Results

### Syntheses and TEM characterizations

The syntheses of thiolated Ag nanoparticles were achieved by chemical reduction of a polymeric silver 4-tert-butylbenzenethiolate precursor by NaBH\textsubscript{4} in the presence of PPh\textsubscript{4}Br and triethylamine (see Methods for full details). The resulting Ag nanoparticles were first characterized by TEM as shown in Fig. 1a and Supplementary Fig. 1. The TEM images revealed that these thiolated Ag nanoparticles had a tight particle-size distribution at ~2 nm. Thiolated Ag nanoparticles of larger, likewise uniform size, at ~3 nm (Fig. 1b and Supplementary Fig. 2) were prepared in a similar manner, by increasing the Ag:SR (thiolate) molar ratio to 1.4:1.

Two important features are associated with these thiolated Ag nanoparticles. First, their sizes lie in the region where metallic Ag nanoparticles are said to develop SPR\textsuperscript{34} and thus provide scope to assess the occurrence of SPR from the viewpoint of associated quantum mechanical calculations. Second, the small and large Ag nanoparticles are verified as fivefold twinned nanocrystals as initially revealed by high-resolution TEM analysis (insets in Fig. 1 and Supplementary Figs 3 and 4). Fivefold twinning is a common phenomenon for nanoparticles of face-centred cubic (fcc) metals\textsuperscript{5}. Competing models for the internal structure of fivefold twinned nanoparticles have been debated in the literature\textsuperscript{35,36}. Resolving these atomic scale structures now demonstrates at the molecular level how the lattice mismatches are readily resolved within real fivefold twinned nanoparticles.

### Molecular structures from single-crystal X-ray diffraction

Encouraged by the uniform size of both the small and large thiolated Ag nanoparticles, crystallization of these compounds was undertaken. High-quality black prism crystals of small nanoparticles and block crystals of large nanoparticles that

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**Figure 1 | Electron micrographs of thiolated Ag nanoparticles.** Scanning TEM and high-resolution TEM (inset) images of the as-prepared small (a) and large (b) 4-tert-butylbenzenethiolate-stabilized Ag nanoparticles. Scale bars, 2 nm.
were suitable for X-ray analysis were obtained by diffusion of hexane into their dichloromethane solutions (Supplementary Fig. 5). The fivefold twinned feature of both small and large silver nanoparticles was indeed revealed by detailed single crystal X-ray diffraction studies (for 1.2 Å resolution data in each case; Supplementary Data 1 and 2). Initial structure solutions were acquired by means of SHELXL and model refinements combined techniques of macromolecular crystallography with those more typical of chemical crystallography (Supplementary Methods and Supplementary Tables 1 and 2).

As shown in Fig. 2, the small nanoparticle has a composition modelled as \([\text{Ag}_{136} (\text{SR})_{64} \text{Cl}_3 \text{Ag}_{0.45}]^-\) (denoted as \(\text{Ag}_{136}\)) with the apparent mono-anionic charge balanced by a well-resolved \(\text{PPh}_4^+\) and one entire nanoparticle plus cation pair forming the asymmetric unit. The larger nanoparticle has a composition modelled as \([\text{Ag}_{374} (\text{SR})_{113} \text{Br}_2 \text{Cl}_2]\) (denoted as \(\text{Ag}_{374}\)) with one half molecule lying on a crystallographic twofold axis comprising the asymmetric unit (Supplementary Figs 6 and 7). SR in both cases is 4-tert-butylthiophenolate. The presence of Cl in \(\text{Ag}_{136}\) and both Cl and Br in \(\text{Ag}_{374}\) were confirmed by temperature-programmed decomposition/mass-spectrometric and electrospray ionization mass-spectrometric data (Supplementary Fig. 8). \(\text{Ag}_{136}\) and \(\text{Ag}_{374}\) represent the largest thiolated metal nanoparticles with molecular structures determined by single-crystal X-ray analysis. They bear no structural relationship to a previously reported series of thiolated \(\text{Ag}_n\) particles containing up to 490 Ag atoms, derived from bulk \(\text{Ag}_2\text{S}\) semiconducting materials.

Both \(\text{Ag}_{136}\) and \(\text{Ag}_{374}\) can be structurally described as a fivefold twinned core enclosed within related structurally distinctive Ag–SR complex shells (Fig. 2). While the fivefold twinned core in \(\text{Ag}_{136}\) is present as a pentagonal bipyramid of 54 Ag atoms, the core in \(\text{Ag}_{374}\) is an elongated pentagonal bipyramid (Ino’s decahedron) consisting of 207 Ag atoms. The \(\text{Ag}_{54}\) core in \(\text{Ag}_{136}\) can be structurally described as five conjoined tetrahedral domains of fcc Ag (Fig. 3a), each of which consists of 20 Ag atoms (Fig. 3b) and having 4 external Ag \{111\} facets. Each tetrahedral subunit is joined to the adjacent tetrahedral subunits by sharing of common triangular faces. In comparison, the \(\text{Ag}_{207}\) core of \(\text{Ag}_{374}\) can be considered as a miniature fivefold twinned nanorod constructed from five conjoined single-crystalline wedge-shaped grains, which are related to the pentagonal-bipyramid by elongation of each constituent tetrahedron to a wedge along the molecular fivefold aspect (Fig. 3c). In each wedge-shaped grain, there are two \{111\} triangular faces at the apices, two \{111\} trapezoids along the fivefold axis and one \{100\} rectangle forming each side (Fig. 3d). Overall, each nanorod has five \{100\} side surfaces parallel to the elongated direction and ten \{111\} surfaces at the apices of the rod. The 207 Ag atoms in the core are distributed about a central Ag atom successively surrounded by three elongated pentagonal bipyramids consisting of 12, 42 and 92 atoms, encircled by a ‘pentagonal cylinder’ of 60 Ag atoms likewise centred about the fivefold axis of the nanorod (Supplementary Fig. 9). The metal distributions in the cores of both \(\text{Ag}_{136}\) and \(\text{Ag}_{374}\) are entirely distinct from that in \(\text{Au}_{133}\) whose structure was reported (after submission of this report) to have a 20-fold twinned icosahedral core. It should be noted that fivefold twinned metal cores have also been previously observed in \(\text{Au}_{102}\) and \(\text{Au}_{130}\) clusters resolved by single-crystal X-ray analysis and \(\text{Au}_{309}\) characterized by aberration-corrected scanning TEM.

**Structural distortions inside fivefold twinned cores.** In regular fcc metals, the idealized angle between two \{111\} faces is 70.53°. When joined together by sharing \{111\} faces along the fivefold axis, without distortion, five ideal single-crystalline grains in a fivefold twinned nanostructure can only subtend an angle of 352.65°, 7.35° short of closure (Supplementary Fig. 10). In a real fivefold twinned nanostructure, this solid-angle deficiency needs to be compensated by sufficiently adjusting the interatomic spacings, introduction of various defects such as dislocations and

![Figure 2](image-url)
stacking faults, or by increased internal vibrations. Structural models with homogeneous or inhomogeneous strain (deviations from idealized values) have been proposed for small metal nanoparticles\cite{35,36}. In the fivefold twinned cores of Ag\textsubscript{136} and Ag\textsubscript{374}, the average Ag–Ag bond lengths are 2.870 and 2.882 Å, respectively, both slightly shorter than the Ag–Ag bond distance (2.889 Å) of bulk silver with Ag\textsubscript{374} only marginally so.

Detailed review of the Ag–Ag bond lengths (Supplementary Fig. 11) demonstrates the presence of a distinctive distortion within the observed pentagonal bipyramidal Ag\textsubscript{54} core, where an obvious anisotropy of these adjustments is clear. Although Ag–Ag distances (18 out of 23) parallel to the fivefold axis are shorter than the average Ag–Ag distance (2.870 Å), most Ag–Ag bonds (47 out of 50) perpendicular to the fivefold axis are longer than 2.870 Å. Such a distribution clearly suggests that the geometric non-ideality in the decahedral core is resolved via a modest compression along the fivefold axis and concomitant relaxation about the directions perpendicular to the fivefold axis. In other words, each tetrahedral grain in the fivefold twinned decahedral nanoparticle is slightly compressed along the molecular fivefold axis.

In Ag\textsubscript{136}, the five relevant angles are 71.5°, 71.7°, 72.1°, 72.3° and 72.5°, slightly expanded from the idealized 70.53° by 1°–2°. These small deviations eliminate the 7.35° deficiency. Geometrically, this slight anisotropy evidently minimizes the total potential energy of the silver core (Supplementary Figs 12–14). In contrast to the anisotropy observed in the Ag\textsubscript{54} core, no obvious trends are seen in the Ag\textsubscript{207} core. However, the crystallographic studies reveal that the thiolate capped outermost Ag atoms deviate from the close-packed archetypes in a significant manner but with a marked congruence of the deviations from close packing observed in the two structures. In Ag\textsubscript{136}, the Ag\textsubscript{54} core comprises two pentagonal pyramids, each of which is surmounted by a bowl-like [Ag\textsubscript{30}(SR)\textsubscript{15}Cl] unit (Fig. 4a). The silver atoms in [Ag\textsubscript{30}(SR)\textsubscript{15}Cl] describe one half of a parabigyrate rhombicosidodecahedron (Johnson solid J73—a circumscribable 60 vertex figure). These 30 silver atoms lie with their fivefold aspect disposed about the same fivefold axis as the Ag\textsubscript{54} core and the opposing Ag\textsubscript{30} unit lies in an eclipsed configuration about the fivefold core aspect. With each apical pentagon surmounted by a Cl\textsuperscript{−} anion, each of the other distorted pentagonal Ag\textsubscript{5} and tetragonal Ag\textsubscript{4} faces is capped by a thiolate ligand. The equatorial pentagon of the Ag\textsubscript{54} core is encircled by a Ag–SR complex ring. Four of the equatorial corners are spanned...
by one of four Ag$_2$(SR)$_5$ units and the remaining corner is spanned by one Ag$_2$(SR)$_4$Cl unit (against which the PPh$_4^+$ counterion rests). Detailed geometric analysis reveals that two significantly larger Ag–SR–Ag bond angles (135.8(4)$^\circ$/C176 and 134.2(8)$^\circ$/C176) occur within these units than in the remainder (107.1(7)$^\circ$, 108.5(3)$^\circ$ and 105.8(5)$^\circ$/C176 for Ag$_2$(SR)$_4$Cl; Supplementary Fig. 16). Each of those with the larger Ag–SR–Ag bond angles is further spanned by Ag$_6$(SR)$_5$ units. These units connect via Ag and S to the units they span and bridge via their Ag termini between the two smaller angle Ag$_2$(SR)$_5$ and Ag$_2$(SR)$_4$Cl completing the outer AgS layer.

In a strikingly similar manner, the fivefold twinned Ag$_{207}$ core of Ag$_{374}$ is also fully encapsulated by a complex Ag-thiolate layer. As shown in Fig. 4b, each pentagonal pyramid is analogously capped by a bowl-like [Ag$_{30}$(SR)$_{15}$Br] of similar half J73 configuration with the apical pentagonal sites occupied by bromide. The five side (100) faces of the Ag$_{207}$ core are each covered by five near planar Ag$_{16}$ units. In each Ag$_{16}$ unit, the silver atoms are arranged in somewhat irregular 4/24 patterns (Fig. 4c,d). The atoms in each Ag$_{16}$ unit are face-capped by three SR and two Ag(SR)$_3$ motifs (Supplementary Fig. 17). At the five pentagonal prismatic edges of the Ag$_{207}$ core, the Ag$_{16}$ units are joined together by three Ag$_6$(SR)$_2$, two Ag$_4$(SR)$_2$ motifs and four bridging SR, forming a drum-like layer surrounding the elongated pentagonal prismatic equatorial aspect of the core. This drum-like layer connects the two bowl-like [Ag$_{30}$(SR)$_{15}$Br] units via shared thiolates of the drum and a further two groups of Ag$_6$(SR)$_2$ motifs, and ten bridging SR and one Cl, which completes the closed complex shell having an overall composition of [Ag$_{167}$(SR)$_{113}$Cl$_2$Br$_2$] (Supplementary Fig. 18) surrounding the Ag$_{207}$ core. For both Ag$_{136}$ and Ag$_{374}$, the Ag$_{30}$ half-J73 domes lie with their apical pentagons eclipsed rather than staggered (as occurs in a complete 60 vertex J73 figure).

Electronic structures and optical properties. Both thiolated Ag$_{136}$ and Ag$_{374}$ nanoparticles are readily dissolved in solvents such as chloroform and dichloromethane, to give brown solutions. As shown in Fig. 5a,b, the smaller Ag$_{136}$ nanoparticles display a broad major peak centred around 450 nm (2.75 eV) and a weak shoulder peak at 772 nm, whereas the larger Ag$_{374}$ nanoparticles show only one strong peak at 465 nm (2.67 eV). The Ag$_{374}$ absorption behaviour is distinct from the molecule-like multiband absorption features of previously reported thiolated Ag nanoclusters (for instance, Ag$_{14}$, Ag$_{16}$, Ag$_{25}$, Ag$_{32}$ and Ag$_{44}$) and that of Ag$_{136}$.

The electronic structures of Ag$_{136}$ and Ag$_{374}$ were probed via DFT computations, by using the simplified SPh ligand in place of SPh-$t$Bu for Ag$_{136}$ with a further simplification to SH for Ag$_{374}$. The projected densities of electron states of the clusters are shown in Fig. 5c and Supplementary Fig. 19. The calculated highest occupied molecular orbital–lowest unoccupied molecular orbital band gap for Ag$_{136}$ is 0.37 eV, whereas the band gap is closed for Ag$_{374}$. The calculated band gap and angular momentum characteristics of the frontier orbitals (Supplementary Fig. 20) place Ag$_{136}$ as a molecular system, whereas the Ag$_{374}$ can be characterized as metallic.

The optical absorption of the Ag$_{136}$ cluster was studied by using linear-response (LR) time-dependent DFT calculations. The optical spectrum of the atomistic model for Ag$_{136}$ agrees very well with the experimental data, having an overall similar shape in the ultraviolet–visible region and featuring a broad peak at 425 nm (2.9 eV; Fig. 5a and Supplementary Fig. 21). Analysis of this peak (Fig. 6) shows that it is composed of several contributions including Ag(5s) to ligand, ligand to Ag(5s), ligand to ligand and Ag(4d) to Ag(5s) transitions. The total transition induced density shows a collective dipole oscillation localized across the interface of the metal core with the...
ligand layer. We interpret this as a plasmonic feature where the pi-electron density of the electron-rich ligand layer contributes to the collective oscillation. Based on this information, we interpret the experimental peak of Ag_{374} at 465 nm as of similar origin, where the slight red shift compared with the experimental peak of Ag_{136} is attributed to the much larger size of the system.

**Discussion**

This report demonstrates that it is feasible to deliberately and reproducibly synthesize metal nanoparticles with specific molecular products that readily enter the truly metallic regime with the emergence of SPR. As miniatures of fivefold twinned nanostructures of fcc metals, the success in resolving the total structures of Ag_{136} and Ag_{374} nanoparticles using single-crystal X-ray diffraction provides important models to visualize at the atomic scale the modest distortion from ideality inside fivefold twinned nanostructures of fcc metals and to describe their detailed surface structures. The Ag nanoparticles reported in this work have the lowest size for silver to display surface plasmonic properties reported to date. These structures serve as real models...
to understand how silver nanoparticles can span from the molecular to the metallic regime.

The observed plasmonic peaks of Ag$_{136}$ and Ag$_{374}$ are below the threshold energy of the well-known Mie plasmon of 3.5 eV for silver (dipolar bulk limit)$^{31}$. In several gas phase, matrix isolation and surface studies in the past, atomic silver clusters from hundreds of atoms down to a few atoms exhibit resonance absorption at energies that are well over the Mie energy$^{34,52}$. The fact that the thiol-stabilized Ag$_{136}$ and Ag$_{374}$ support an even lower bulk limit for the SPR, compared with the classical Mie energy for silver, is a manifestation of the important role played by the interfacial interactions between the thiolate layer and the nanoparticulate metal core. This clearly demonstrates that modifying the interface chemistry by introducing an organic passivating layer that has electronic properties distinct from thiouates could modify the plasmonic behaviour of ligand-stabilized silver nanoparticles. Changes in the interfacial chemistry may provide scope to vary the adjustments in the core and the interfacial structure as well, opening a range of chemical possibilities through which nanoparticle structures and electronic properties can potentially be modified. 

**Methods**

**Synthesis of the Ag-SPhBu complex precursor.** The complex precursor was prepared by following the reported procedure$^{53}$. In a typical synthesis, 4-BuPhSH (0.38 ml, 2.3 mmol) and NEt$_3$ (0.32 ml, 2.3 mmol) were mixed together in 8 ml C$_6$H$_{12}$OH. The mixture was then added dropwise to a solution of AgNO$_3$ (274 mg, 1.6 mmol) in 5 ml CH$_3$CN under stirring. The reaction was sealed in a glove box and left in the dark for 4 h.

**Synthesis and crystallization of Ag$_{136}$ nanoparticles.** Thirty milligrams of the Ag-SPhBu complex precursor (containing 92 μmol Ag and 110 μmol SPhBu$_2$ based on the formula of [(HNEt$_3$)$_2$Ag(SPhBu)$_{82}$]) were added to a mixed solvent of dichloromethane and methanol in a volume ratio of 4:1. The solution was cooled to 0 °C in an ice bath and 12 mg PPh$_4$Br (29 μmol) was added to the solution. After 5 min stirring, 1 ml NaBH$_4$ aqueous solution (45 mg ml$^{-1}$, 1.2 mmol) and 50 μl triethylamine (360 μmol) were added quickly under vigorous stirring. The reaction was aged for 12 h at 0 °C. The aqueous phase was discarded and the organic phase was washed several times with water. The solvent was then evaporated to give a dark solid. Black prism-like crystals were crystallized from CH$_3$Cl/Hexane after 20 days at 4 °C. The synthesis of Ag$_{136}$ with the substitution of Ph$_4$PBr by an equivalent of Ph$_4$PCl also results in Ag$_{136}$ nanoparticles.

**Synthesis and crystallization of Ag$_{374}$ nanoparticles.** Thirty milligrams of the Ag-SPhBu complex precursor were added to a mixed solvent of dichloromethane and methanol. Twelve milligrams of AgBF$_4$ (62 μmol) and 12 mg PPh$_4$Br (29 μmol) were added sequentially. After 5 min stirring, 1 ml NaBH$_4$ aqueous solution (45 mg ml$^{-1}$, 1.2 mmol) and 50 μl triethylamine (360 μmol) were added quickly under vigorous stirring. The reaction was aged for 4 h at room temperature. The aqueous phase was discarded and the organic phase was washed several times with water and evaporated to give a dark solid. Black block-like crystals were crystallized from CH$_3$Cl/Hexane after 2 months at 4 °C.

**X-ray single-crystal analysis.** Diffraction data of the single crystals grown from the solutions of Ag$_{136}$ and Ag$_{374}$ nanoparticles were collected on an Agilent Technologies SuperNova system X-ray single-crystal diffractometer with Cu K$_\alpha$ radiation (λ = 1.54184 Å) at 100 K to a resolution of 1.2 Å. The data were reduced using CrystalClear$^\text{TM}$. The structures were solved in ShelXS and refined using a combination of ShelXT, Olex2, Shelde and CRYSTALS$^{37-42}$. A customized refinement procedure employing techniques from both chemical crystallographic practice and macromolecular modelling methods (including contoured electron density mapping of all bfu/p groups) was evolved to address the challenges of each structure. For Ag$_{136}$, a silver site of less than half occupancy has been modelled, which may be occupied in some molecules. The associated electron density refines well on this basis and the assignment makes chemical sense, noting that a sulfur atom with a high displacement parameter lies closer to this site than is reasonable. It is proposed that when this additional silver is present, the close sulfur atom lies in a site at the end of the sulfur ellipsoid furthest from the silver site. Significant ‘softer voids’ are noted and it is proposed that these regions are more properly termed ‘frozen solution’ than solid of crystallization in view of the very limited localized electron density features lying in the voids (note CH$_3$Cl is the main solvent). The modest observed residual electron densities lie within the silver nanoparticles. No modifications to the data or refinement were made to account for these void volumes (see Supplementary Discussion and Supplementary Methods for further crystallographic details).

**Computational method.** The electronic structures of Ag$_{136}$ and Ag$_{374}$ were studied by DFT code GPAW, which implements projector-augmented wave method in a real-space grid$^{21}$. The real space had a grid spacing of 0.2 Å. Ag(4s$^2$4p$^3$), S(3s$^2$3p$^3$), Br(4s$^2$4p$^3$) and H(1s$^1$) electrons were regarded as the valence, and the projector-augmented wave setups for Ag included scalar-relativistic corrections. Spin-polarized total energies were evaluated at the gradient-corrected functional of Perdew, Burke and Ernzerhof (PBE) level$^{55}$. It should be pointed out that the configurations for Ag$_{136}$ and Ag$_{374}$ used in the calculations were taken from our preliminary crystallographic model. This Ag$_{136}$ model had a formula of [Ag$_{136}$(SPhBu)$_{82}$Br$_4$] which had 70 metallic free electrons (from the superatom counting rules). The electron number was same as that for the dominant final refined structure [Ag$_{136}$(SPh)$_{64}$Cl$_3$]. The correction to the structural formula for Ag$_{136}$ does not affect our conclusions concerning the electronic structure and optical properties. The preliminary crystallographic model for Ag$_{374}$ had a formula of [Ag$_{374}$(SPhBu)$_{10}$Br$_2$] containing more than 900 sites as that of the final refined structure again. These two sites were ultimately modelled with Cl at the former S site, yielding the same electron count. The organic groups were replaced by SPh$_4$ for Ag$_{374}$, after which the organic layer was relaxed to an energy minimum, while keeping the Ag, S and Br atoms fixed to experimental positions. For Ag$_{374}$, a simplified ligand S = SH was used and the S–H bonds were relaxed, while keeping Ag-S and Br atoms fixed to their experimental positions. Angular momentum analysis of the Kohn–Sham orbitals was done as metal-core projected density of states as described earlier$^{35}$. The optical absorption spectrum of Ag$_{136}$, was calculated with the PBE level using time-dependent DFT formalism in GPAW.$^{21}$ The grid spacing was 0.6 Å. The calculated density and wave functions were calculated by the local density approximation and the PBE functional was used for calculating LR optical absorption spectra. The transitions contributing to selected optical peaks were analysed using a recently developed method based on time-dependent density functional perturbation theory$^{52}$.

**Data availability.** The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition number CCDCC-1496411 (Ag$_{136}$) and 1496412 (Ag$_{374}$). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All other data are available from the authors on reasonable request.

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