

Ag₁₄ Nanocluster Featuring an Unconventional Non-FCC Metal Skeleton and Its Sensitivity to Oxygen

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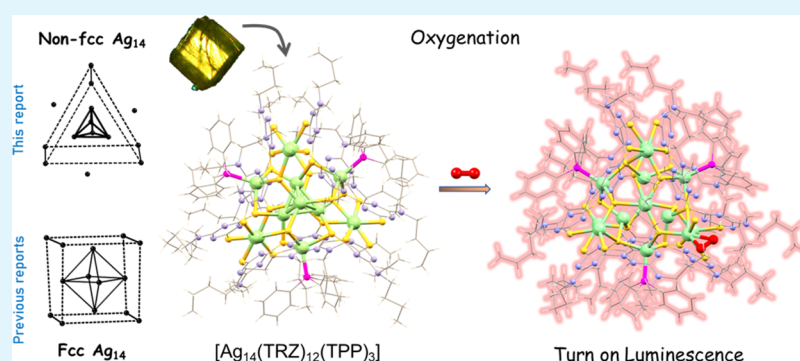
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ABSTRACT: Despite the significant advancements in noble metal-based nanocluster research, challenges remain in making specific metal kernel geometries, especially protected by bulky ligand shells. Here, we synthesized and structurally characterized a neutral silver cluster, $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3]$, where TRZ and TPP refer to 6-(dibutylamino)-1,3,5-triazine-2,4-dithiolate and triphenylphosphine, respectively. The cluster was synthesized under ambient conditions using a TPP-assisted, solvent-mediated structural transformation from the $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ precursor cluster. This non-face-centered cubic (non-fcc) cluster features a central Ag_5 trigonal bipyramidal core surrounded by a distinct $\text{Ag}_{(6+3)}$ tricapped trigonal prismatic (TTP) shell. This type of unconventional metal skeleton differs significantly from the well-known fcc-type Ag_{14} cluster, which typically has an octahedral Ag_6 core and a cubic Ag_8 shell. It is also the first metal cluster to be structurally resolved with TRZ ligands. Quantum chemical calculations indicate that although the non-fcc Ag_{14} skeleton has a lower cohesive energy than the fcc Ag_{14} analogues, bulky TRZ ligands featuring multiple sulfide linkages and n-butyl chains stabilize it. The as-synthesized Ag_{14} cluster is non-emissive, but exposure to oxygen converts it into an orange-emitting species. Density functional theory calculations indicate that the TTP $\text{Ag}_{(6+3)}$ shell prefers binding with oxygen. Emissive lifetime and femto-second transient absorption showed that oxygenation provided greater stabilization of excited states than the parent Ag_{14} cluster. This study presents a new approach for designing metal clusters with unique structural frameworks with unconventional ligand environments and allows for harvesting surface-sensitive electronic properties.

KEYWORDS: silver nanocluster, non-face-centered cubic, luminescence, self-assembly, oxygenation, excited-state electron dynamics

INTRODUCTION

Atomically precise nanoclusters (NCs) protected with ligands are an emerging class of functional materials with core diameters in the range of 1–4 nm, which bridge the gap between isolated atomic complexes and traditional nanoparticles.^{1–3} These nanomaterials exhibit a transition from the molecular to the plasmonic materials as their atomicity is gradually increased.⁴ Because of their ultra-small size and electronic confinement, NCs have distinct, closely spaced electronic energy levels.^{5–7} Electronic transition between these discrete energy levels gives rise to structure-

specific UV–Vis absorption,^{6–8} photoluminescence (PL),^{9,10} electroluminescence,^{11,12} and electrical conductivity.^{13,14} These prop-

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erties make them valuable for the fabrication of optoelectronic devices,^{15,16} nonlinear optics,¹⁷ chemical sensors,¹⁸ and photocatalysts¹⁹ and for the development of contrast agents for bioimaging and radiosensitization.^{20,21} Generally, clusters have an inner metal kernel protected by a layer of ligands, such as thiols,²² phosphines,²³ carbenes,²⁴ alkynes,²⁵ carboxylic acids,²⁶ amido-pyridines,²⁷ deoxyribonucleic acids,²⁸ and polyoxometalates.^{29,30} Significant advancements have occurred in the synthesis and structural elucidation of silver NCs, particularly following the initial structural characterization of Ag₁₄ and Ag₄₄ clusters.^{31,32} It was observed that silver NCs mostly prefer octahedral, cubic, icosahedral, and dodecahedral arrangements of primary inner kernel, followed by a secondary and tertiary layer of metal atoms.^{33,34} A few reports also exist on silver clusters with an inner kernel consisting of distorted metal atoms³⁵ and fusion of cuboidal or icosahedral units.^{36,37} Therefore, developing clusters with new types of metal cores and interfacial motifs is essential, although challenging.

Beyond the structural and compositional understanding, attention is given to investigating their surface-sensitive optical properties. These properties depend on surface ligands and the interfacial motifs. Ligand-modulated surface chemistry of clusters resulted in chiral isomers,³⁸ polymorphs,³⁹ cocrystalline solids,⁴⁰ cluster assembled framework solids,⁴¹ and supramolecular nanostructures.⁴² These materials exhibit circularly polarized luminescence, enhanced emission quantum yield, and multiphoton up-conversion.^{38–43} The surface sensitivity of clusters plays a critical role in governing their catalytic activity and self-assembly behavior. Recent progress of electrocatalytic reduction of oxygen⁴⁴ and carbon dioxide⁴⁵ using silver clusters showed the surface-sensitive catalytic nature of these nanomolecules.³⁰ Furthermore, ligand-mediated non-covalent interactions, such as hydrogen bonding,⁴⁶ electrostatic interactions,⁴⁷ π - π stacking,⁴⁸ and van der Waals interactions, resulted in structurally and functionally distinct cluster-assembled nanoaggregates.^{49,50} Morphological evolution of these aggregates upon controlling such interactions through solvents, counter ions, surfactants, and stimulating agents resulted in tunable morphologies. However, the impact of short-contact interactions between clusters and small molecules remains poorly understood.

In view of these effects of ligands, we present a new ligand, 6-(dibutylamino)-1,3,5-triazine-2,4-dithiol with acronym TRZ-H₂, featuring two thiol groups attached to the 2 and 4 positions of triazine, along with di-butyl amino chains linked to the 6 positions. The choice of this ligand is due to enhanced polarity of the ring than its benzene-thiolated analogue. Earlier, we have synthesized gold⁵¹ and silver⁵² clusters utilizing this ligand and characterized them through mass spectrometric studies, although suitable crystals were not formed due to molecular complexity and the challenges associated with crystallization.

Overcoming such challenges, we have successfully utilized the phosphine-induced solvent-mediated structural transformation approach to synthesize a new silver cluster, i.e., [Ag₁₄(TRZ)₁₂(TPP)₃] (denoted as Ag₁₄). Single-crystal X-ray diffraction studies reveal a unique arrangement of the cluster having an Ag₅ trigonal bipyramidal core and an Ag₍₆₊₃₎-trapped trigonal prismatic shell. It may be noted that this is the first metal cluster with a unique geometry, which is structurally resolved using this ligand. This cluster shows oxygen sensitivity, and the oxygenation process turns the non-emitting Ag₁₄ cluster into an orange-emitting one. The excited-state electron

dynamics of the clusters studied using femtosecond transient absorption (TA) reveal an enhancement in lifetime upon oxygenation. Theoretical investigations showed unusual structural stability of the cluster and revealed active sites suitable for the oxygenation processes. Ligand-centered self-assembly of the cluster is also modified upon oxygenation, and distinctly different cluster-assembled superstructures were formed.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Ag₁₄ NC

We have synthesized the Ag₁₄ NC utilizing a mixed solvent-induced conversion method, using TRZ-protected Ag₃₁ as the precursor, as schematically presented in Figure 1a. Ag₃₁ was synthesized following our previous report.⁵² In brief, triphenylphosphine (TPP)-assisted coreduction of silver TRZ-thiolates using sodium borohydride at room temperature (25 °C) yielded the Ag₃₁ cluster. The formation of bluish-violet Ag₃₁ was confirmed by its distinctive UV-Vis absorption features and a mass spectrometric peak at m/z 3024.41 with a 2- charge state (Figure S1). Our previous studies revealed remarkable stability for the Ag₃₁ cluster below 200 °C in the solid state and in dichloromethane (DCM) solution under ambient conditions.⁵² Surprisingly, we observe that the use of a DCM/methanol (1:4 v/v) solvent mixture with TPP resulted in the conversion of Ag₃₁ to Ag₁₄ as only cluster product. After 10–12 days, we have observed the emergence of a greenish-yellow solution, indicating the formation of the Ag₁₄ cluster with a synthetic yield of 30–35% in terms of Ag₃₁ cluster (see the Experimental Section for more details). The insets in Figure 1a show the photographs of the solutions before (Ag₃₁) and after the transformation (Ag₁₄). It is worth noting that various other solvent mixtures, e.g., DCM/acetonitrile, DCM/toluene, DCM/hexane, DCM/acetone, in a 1:4 ratio, did not lead to the formation of the Ag₁₄ cluster.

In an approach toward direct synthesis, we attempted the reduction of silver TRZ-thiolate in the presence of TPP using slow-reducing agents, such as sodium cyanoborohydride and the *tert*-butyl borane-amine complex. However, the reduction reaction resulted in a gray suspension (for sodium cyanoborohydride) and a colorless solution (for the *tert*-butyl borane-amine complex), respectively, devoid of any characteristic absorption feature of the clusters (presented in Figure S2). Time-resolved UV-Vis absorption studies revealed that the three absorption peaks of Ag₃₁, centered at 402, 527, and 598 nm, got transformed into a single absorption band centered at 417 nm with an absorption edge up to 450 nm. This new absorption feature is characteristic of Ag₁₄ (shown in Figure 1b). We note that the absorption spectrum is distinctly different from the reported Ag₁₄ clusters.^{31,53,54} The reproducibility of the synthesis was verified using four distinct sets of experiments, all of which yielded Ag₁₄ after 10 days, exhibiting an identical absorption band at 417 nm, as illustrated in Figure S3.

The chemical composition of the newly synthesized Ag₁₄ was confirmed using high-resolution electrospray ionization (ESI) mass spectrometry (see the Supporting Information for details). The as-prepared NC did not ionize, neither in the positive nor in the negative ion mode of ionization, suggesting a neutral charge state for the cluster. However, upon addition of formic acid (50 μ L of 0.1 M), we observed a sharp peak at m/z

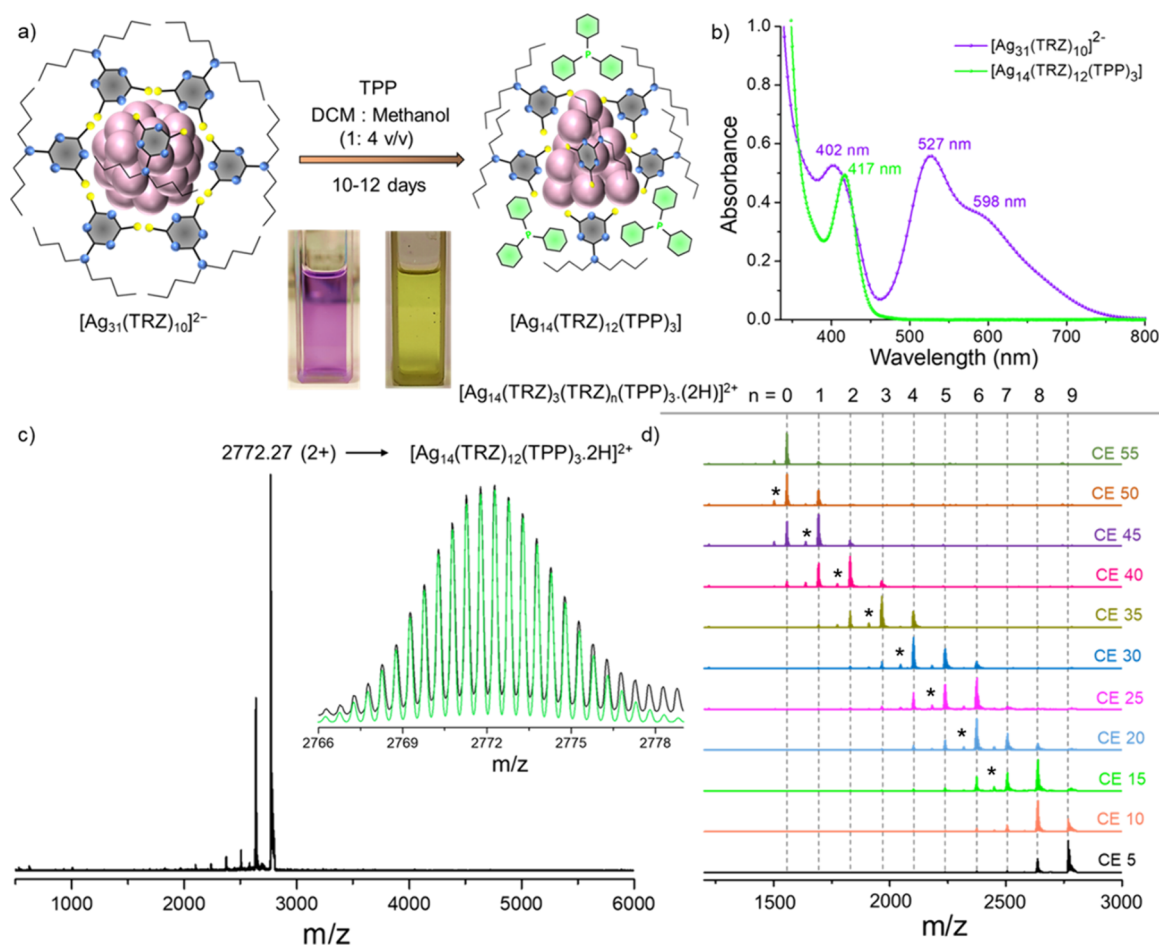


Figure 1. Schematic representation of the mixed solvent-induced conversion of $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ to $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3]$. Inset shows the photographs of DCM solution of the respective clusters. (b) Comparison of the UV-Vis absorption spectra of both the compounds in DCM. (c) Positive ion-mode ESI-mass spectrum of the Ag_{14} cluster. The inset shows an exact match between the isotopic distribution of the experimental spectrum (black trace) and the simulated one (green trace). The second abundant peak is a TRZ loss ion. (d) Collision-energy-dependent MS-MS fragmentation studies of the Ag_{14} cluster, indicating the systematic loss of TRZ and TPP surface ligands. The minor fragmentation series (marked as *) is assigned in Figure S4.

2772.27 in the positive ion mode with a peak-to-peak mass separation of 0.5, indicating a 2+ charge state (Figure 1c). The total mass of the peak, 5544.54, was assigned to the composition, $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3 \cdot 2\text{H}]^{2+}$.

The triazine moieties with tertiary N atoms, present on the surface of the cluster, are likely to be protonated in the presence of formic acid and thus induce ionization. In addition to the primary molecular ion peak at m/z 2772.27, additional peaks appeared in the low-mass range, at m/z 2636.29, 2505.37, 2374.37, and 2238.97 (again with 2+ charge), presumably due to the dissociation of TRZ and TPP ligands from the parent cluster. These peaks are assigned to the compositions $[\text{Ag}_{14}(\text{TRZ})_{11}(\text{TPP})_3]^{2+}$, $[\text{Ag}_{14}(\text{TRZ})_{11}(\text{TPP})_2]^{2+}$, $[\text{Ag}_{14}(\text{TRZ})_{11}(\text{TPP})]^{2+}$, and $[\text{Ag}_{14}(\text{TRZ})_{10}(\text{TPP})]^{2+}$. Notably, no prominent low m/z ions (below m/z 1000) were observed, indicating that the addition of formic acid did not induce further degradation of the cluster. Further structural insight of the cluster was obtained through collision energy-dependent fragmentation studies (shown in Figure 1d). The molecular ion peak at m/z 2772.27 was selected to initiate the fragmentation studies by gradually increasing the collision energy of ions inside the trap cell. Upon raising the collision energy (CE) from CE 5 (in instrumental unit), we observed

sequential losses of ~ 270 mass units from the parent ion peak. These are indicative of the loss of one TRZ ligand (mass of 270.43) in each event.

By continuous increase of the CE up to 55, we observed nine successive TRZ losses, verifying the presence of TRZ on the outer surface of the cluster. However, further increasing the CE beyond 55 significantly reduced the ion intensities, which limited additional fragmentation studies. Another fragmentation series is also found in MS-MS spectra, labeled as * in Figure 1d, and the respective assignment is shown in Figure S4. The initial peak appeared at m/z 2451.42 (at a CE of 15) is due to the loss of the $\{\text{Ag-TRZ-TPP-2H}\}$ fragment from the parent cluster, and this peak is assigned with the composition, $[\text{Ag}_{13}(\text{TRZ})_{11}(\text{TPP})_2]^{2+}$. Upon further increasing the CE, additional loss of two TPP ligands (mass of 262.29) and subsequent detachment of five TRZ ligands (mass of 270.43) were observed (see Figure S4). Altogether, MS-MS fragmentation studies confirm the presence of TRZ and TPP in the cluster. A similar type of fragmentation of surface ligands was reported for other silver clusters.^{54,55}

The ^1H NMR spectrum of a solution of Ag_{14} displayed broad resonance signals at δ 0.84, 1.26, 1.48, and 3.49 ppm, arising

from the *n*-butyl chains of the TRZ ligands and multiplets between 7.16 and 7.66 ppm attributed to the protons from phenyl groups of the TPP ligands (Figure S5). The proton-decoupled ^{13}C NMR spectrum showed multiple resonance peaks at δ 128–135 ppm, indicating the presence of TPP ligands; signals at δ 13.98, 20.04, 29.93, and 46.81 ppm are due to the *n*-butyl chains of the TRZ ligands (Figure S6). The ^{31}P NMR spectrum showed a broad peak at 6.05 ppm (Figure S7) due to TPP binding to the cluster. A similar type of spectral broadening was observed in the literature for other phosphine-protected silver clusters.^{55,56}

The FT-IR spectroscopic studies further verified the binding of TRZ ligands (shown in Figure S8). The C–H stretching vibrational modes at 2930 and 2955 cm^{-1} corresponding to *n*-butyl chains of the TRZ ligand on the Ag_{14} cluster match well with the spectral features of the TRZ- H_2 ligand. The C=N and C–N stretching vibrational modes related to the heterocyclic $\{\text{C}_3\text{N}_3\}$ triazine moiety appeared at 1572, 1530, and 1127 cm^{-1} . The reduction of peak intensity is due to the binding of the ligands to the electron-rich Ag atoms. The X-ray photoelectron spectroscopy (XPS) survey spectrum indicates the presence of elements Ag, S, P, N, and C (shown in Figure S9). Selected area scans showed the characteristic features. Peaks at 367.8 and 373.6 eV, corresponding to $3\text{d}_{5/2}$ and $3\text{d}_{3/2}$, respectively, are due to silver atoms exhibiting mixed oxidation states of 0 and 1+. Spectral fitting of the C 1s region shows peaks at 284.8, 285.4, and 287.1 eV due to C–C, C–N,

and C=N bonds of the TRZ and TPP ligands. Two peaks at 398 and 399.3 eV of the N 1s region are due to C–N and C=N bonds of TRZ, respectively. The peaks at 131.3 and 132.2 eV correspond to P $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$, respectively, of TPP attached to the cluster.

Molecular Structure of the Ag_{14} Cluster

The molecular structure of Ag_{14} was determined using single-crystal X-ray diffraction studies. The single crystal was obtained using vapor diffusion of methanol into the DCM solution, which resulted in yellowish cuboidal single crystals (see Figure S10). This cluster crystallizes in the monoclinic crystal system, with the space group $P2_1/n$ (Table S1), with four molecules per unit cell ($Z = 4$). The Ag_{14} cluster features a unique molecular structure with an inner Ag_5 core in a trigonal bipyramidal (TBP) arrangement (shown in Figure 2a) with Ag–Ag distances ranging from 2.80 to 2.85 Å (shown in Figure S11), suggesting argentophilic interactions stabilizing the inner kernel. This inner structure of the Ag_{14} cluster is distinctly different than the previous reports of fcc Ag_{14} clusters based on octahedral Ag_6 cores.^{31,53,54,57–60} To the best of our knowledge, we are hereby reporting the smallest core structure for Ag_{14} clusters. In addition to the unprecedented cluster core, the Ag_{14} cluster also exhibits a unique Ag shell structure composed of a trigonal prismatic Ag_6 shell (Ag⋯Ag distances at 7.51–7.97 Å) with three Ag atoms capping each rectangular face of the prism. Figures 2a and S12 illustrate the structural anatomy and

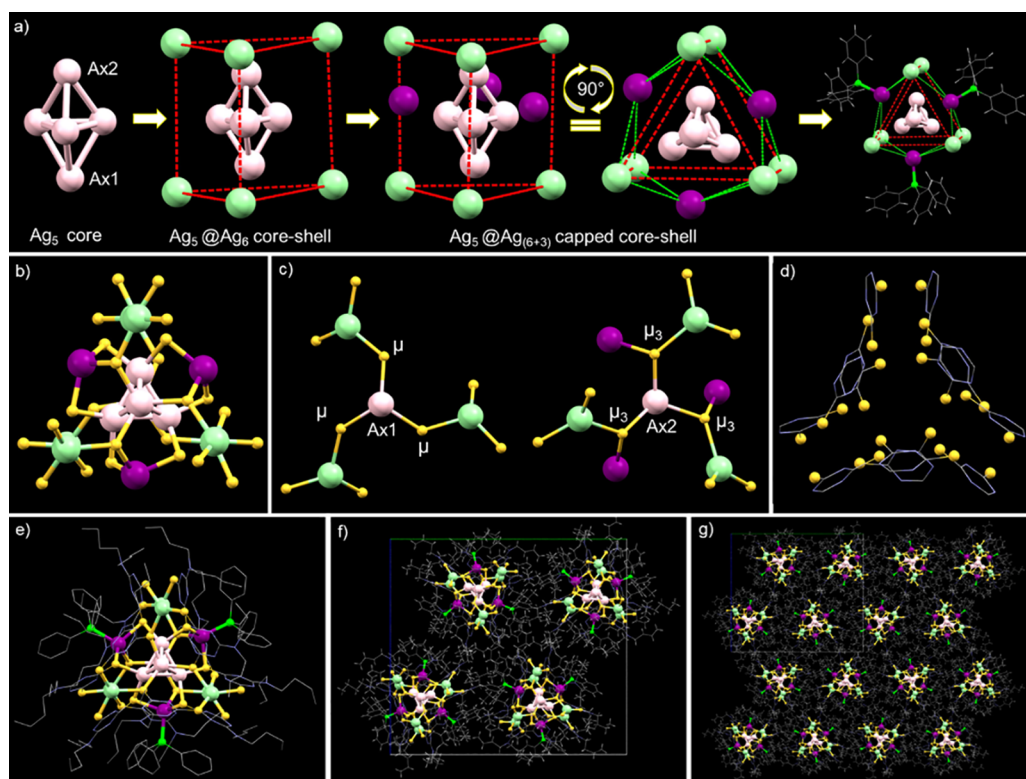


Figure 2. (a) Structural anatomy of the Ag_{14} cluster having a trigonal bipyramidal Ag_5 inner core protected by a trigonal prismatic Ag_6 shell, with the $\text{Ag}_5@ \text{Ag}_6$ core-shell unit being capped by three other Ag atoms. Three TPP ligands are solely connected to these capping silver atoms. (b) Silver sulfide skeleton of the cluster possesses an overall trigonal bipyramidal shape. (c) Connectivity pattern of the two peripheral Ag atoms of the inner TBP core. (d) Location of the twelve TRZ ligands outside the cluster. $-\text{N}(\text{n-butyl})_2$ chains are omitted for clarity. (e) Complete molecular structure of the cluster without H atoms. (f) Packing of the clusters in the unit cell, viewed along the crystallographic *a* axis. (g) View of a $(2 \times 2 \times 2)$ supercell to illustrate the continuation of the packing. Atom color code: pink = silver (TBP core), green = silver (TP shell), purple = silver (capping), green = phosphorus, yellow = sulfur, gray = carbon, blue = nitrogen and white = hydrogen.

stepwise construction of the cluster. Notably, the structure differs from the metal–shell structure in the previous papers reporting a cubic Ag_8 arrangement (see the summary in Table S2). Hence, the new Ag_{14} cluster lacks an fcc core structure but instead has a (near) C_{3v} molecular symmetry. It is worth noting that the three TPP ligands connected to the capping Ag atoms (at Ag–P distances of 2.48 Å) together form an equilateral triangle. An average distance of the centroid of the cluster to the capping Ag atoms is 3.9 Å (Figure S13). The presence of an odd number of TPP ligands is also unprecedented in silver NC chemistry (see the summary in Table S3). A detailed structural analysis reveals that the Ag_5 core is linked to the rest of the Ag atoms via thiolate bridges (shown in Figure 2b). One of the two axial Ag atoms of the inner TBP unit (marked as Ax1 in Figure 2c) is connected with three μ -S atoms, while the other axial Ag atom (marked as Ax2) is connected to a μ_3 -S atom of the thiolate ligands. The resulting bond lengths (2.6 Å on average) reflect an intermediate Ag–S bond strength. The coordination environment of the capping Ag atoms is slightly distorted due to the presence of these two coordination modes of the tri-angulantly oriented triazine rings (shown in Figure 2d). The complete molecular framework of the NC exhibits a triangular shape comprising fourteen silver atoms and twelve surface-anchored TRZ and three TPP ligands (see Figure 2e).

Next, we have investigated the packing of the clusters in the crystal (Figure 2f). According to crystal symmetry, the molecules are packing in layers with the A–B...A–B sequence (shown in Figure 2g). Each cluster is surrounded by six adjacent clusters, with an average (center-to-center) distance of ~ 22 Å (Figure S14). Careful analysis reveals that a large number of dispersive C–H...H–C (distances of 2.1–2.3 Å) and C–H...C (distances of 2.7–3.7 Å) interactions, originating from the n-butyl chains of the TRZ ligands, seem to contribute to the packing of the clusters (see Figure S15). Other minor interactions, such as C–H...S, C–H... π (TRZ) and C–H... π (TPP) (distances of ~ 2.8 Å), originating from the Ag–S skeleton and TRZ and TPP ligands, add to the structure-directing interactions.

Density functional theory (DFT) calculations using the Vienna Ab initio Simulation Package (VASP) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional were performed to compare the intermetallic bonding capabilities of our Ag_{14} cluster with the fcc counterparts.^{61,62} The calculated cohesive energies are -0.78 and -1.09 eV/atom for the new Ag_{14} cluster and the reported fcc- Ag_{14} structure, respectively (Figure 3). This suggests weaker Ag...Ag

interactions in the new arrangement as compared to the fcc cluster structure. This implies that the stability of the new Ag_{14} cluster likely stems from the metal–thiolate coordination rather than from the metal–metal interactions alone. To understand the nature of the bonding within the cluster core, we have carried out a Bader charge analysis of the metal atoms. The atomic charges in the Ag atoms are shown in Figure S16, which confirms the separation of the Ag_{14} substructure into a core and two shells. Atoms of the capping Ag_3 shell feature the least positive charge, which can be attributed to their Ag...P and Ag... S_3 coordination environment. The charge of the five Ag atoms with the Ag_5 TBP core is lower as compared to the Ag_6 TP shell, which can be ascribed to the mixture of Ag...Ag interactions and Ag–S bonding, in an Ag... Ag_4S_2 fashion or an Ag... Ag_3S_3 fashion, whereas the remaining six Ag atoms of the Ag_6 shell are engaged in Ag–S bonding alone, as Ag... S_6 . The presence of different charges in different parts of the Ag_{14} core reveals that these atoms can be expected to behave differently with reactants and contribute to various extent toward the stability of the cluster.

Theoretical Understanding of Electronic Structure of the Ag_{14} Cluster

Time-dependent density functional theory (TD-DFT) calculations were performed (using the Gaussian 09 D.01 program) to investigate the origin of the optical absorption features and the underlying electronic structure of the Ag_{14} cluster. To minimize the computational cost, the calculations utilized a simplified structural model, substituting surface ligands PPh_3 (TPP) and $(n\text{-Bu})_2\text{N-C}_3\text{N}_3\text{-S}_2$ (TRZ) with PMe_3 and $(\text{Me})_2\text{N-C}_3\text{N}_3\text{-S}_2$, respectively. DFT-optimized structural parameters of the cluster are summarized in Table S4. The optical absorption spectrum of the cluster simulated using TD-DFT is shown in Figure 4a. The primary absorption peak appearing at 410 nm is in reasonable agreement with the experimental data. Minor deviation could be attributed to the structural simplification, resolution differences, and implicit solvent consideration in the TD-DFT simulation. The frontier molecular orbital (FMO) analysis showed that this electronic transition is associated with the deeply occupied (HOMO-93) to the LUMO excited state of the cluster (Figure 4b). The outer $\text{Ag}_{(6+3)}$ shell, the Ag–S interface, and the aromatic parts of the ligands are primarily involved in this transition. A similar distribution of electron density is also observed in the electron density maps of the frontier orbitals, centered around the inner $\text{Ag}_{(6+3)}$ region of the cluster (shown in Figure S17a).

According to the Jellium model-based electron counting rule, this neutral Ag_{14} cluster possesses 2 valence electrons ($\text{NV}_A - M - Z = 14 \times 1 - 12 - 0 = 2$, where N is the number of metal atoms, V_A is the atomic valence, M is the number of electron withdrawing ligands, and Z is the overall charge of the cluster).⁶³ This is expected to give a superatomic electronic configuration of 1S^2 . For analyzing this, we have carried out a molecular orbital analysis of the Ag_{14} part in the optimized geometry of the cluster (Figure S17b). It is seen that the (HOMO-6) features a 1S nature, where the electron density is majorly concentrated on the Ag_5 TBP core, which provides electronic stability to the cluster. We have carried out an electronic structural analysis of the cluster by conducting molecular orbital (MO) and projected density of states (PDOS) analysis. The PDOS of the cluster in terms of the contribution of respective atomic orbitals is represented in Figure 4c.

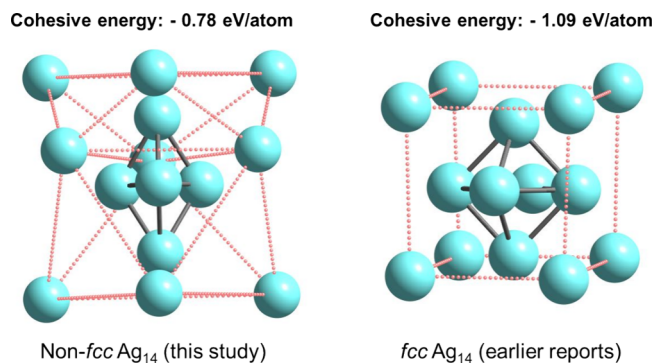


Figure 3. Comparison between the structural stability in terms of cohesive energy of our non-fcc Ag_{14} kernel and the earlier reported fcc Ag_{14} kernel.

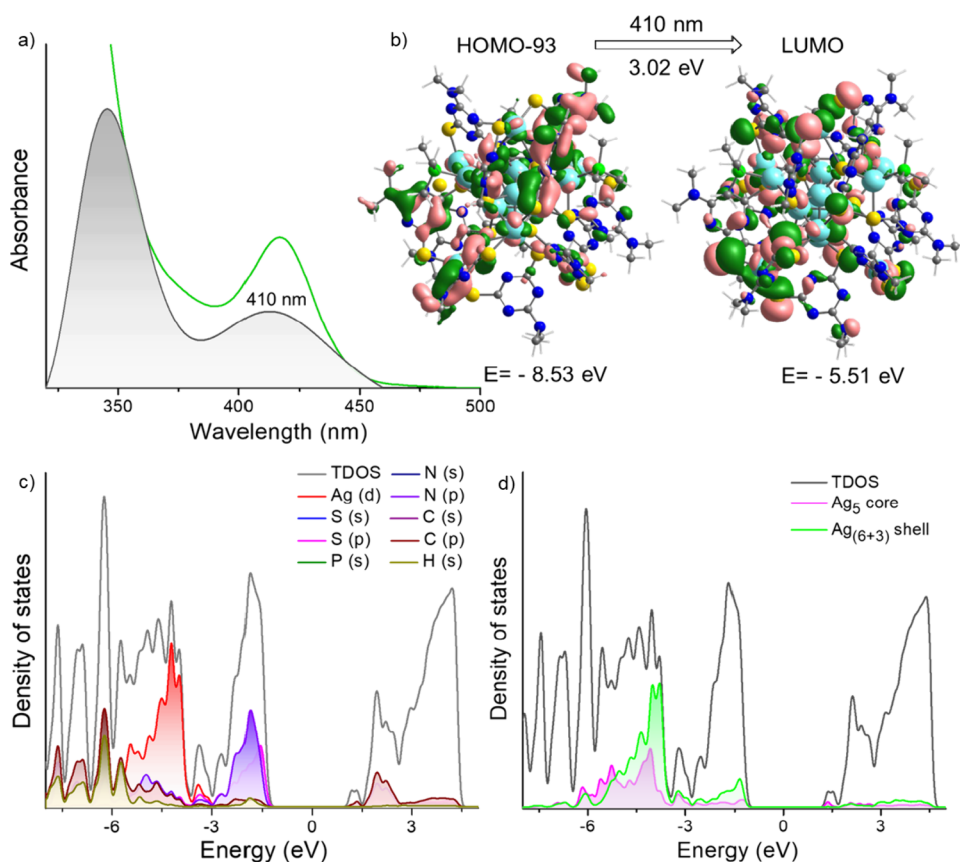


Figure 4. (a) Experimental (green trace) UV–Vis absorption spectrum of the cluster in comparison to the calculated (black trace) spectrum, obtained from TD–DFT calculation of the simplified cluster. (b) Frontier molecular orbitals responsible for the primary optical absorption band, centered at ~ 410 nm. (c) Projected density of states (DOS) analysis showing the contributions of different atomic orbitals present in the cluster. (d) Total density of states in the combination of the Ag_5 core and the $\text{Ag}_{(6+3)}$ shell.

From the PDOS analysis, it can be understood that the valence band was mainly consisting of N(p), S(p), and Ag(d) states and the conduction band has major contribution from C(p) and N(s) states. This suggests that both the silver core and the thiolate ligands contribute to the frontier states. To distinguish the core versus shell contributions and clarify the physical origin of the optical absorption features, we performed a Kohn–Sham (K–S) molecular orbital analysis (Figure S18). Occupied orbitals near the valence band edge are heavily dominated by Ag d-bands hybridized with ligand S (p)-orbitals, with the $\text{Ag}_{(6+3)}$ shell states providing the major contribution—in good agreement with the PDOS analysis. Specifically, the occupied orbital driving the primary 410 nm transition (HOMO-93) consists predominantly of $\text{Ag}_{(6+3)}$ (d) (77%) and Ag_5 (d) (15%) states. In contrast, the unoccupied orbitals shift toward the diffused sp-hybridized orbitals. The LUMO is composed mainly of Ag_5 (sp) core states (65%), with a minor contribution from $\text{Ag}_{(6+3)}$ (d) (20%) states. Consequently, the 410 nm peak is characterized by a dominant interband $d \rightarrow sp$ ligand-to-metal charge transfer (LMCT) excitation, alongside weak intraband $d \rightarrow d$ state mixing owing to the minor d-character present in the low-lying states. Overall, the dominant sp-character of the unoccupied states derived from the central Ag_5 core serves as the primary origin of these interband electronic transitions.

Effect of Oxygenation to the Ag_{14} Cluster

We observed that the non-emitting Ag_{14} cluster turns into an orange-emitting species upon bubbling gaseous oxygen through the solution. This transformation is schematically depicted in Figure 5a (see the Experimental Section for details). The UV–Vis absorption spectrum of Ag_{14} is characterized by a single band centered at 417 nm, which remains unchanged for 30 days in DCM, without oxygen supply (see Figure 5b). Surprisingly, upon bubbling oxygen gas through this solution, the NC exhibits a unique change in absorption and emission characteristics. Photographic images of the Ag_{14} NC in solution and in the solid state during oxygenation are given in Figure 5c, showing the visible orange emission upon oxygenation. Importantly, the effect of oxygenation was not examined in the literature for previously reported fcc Ag_{14} clusters.^{31,53,54,57–60} It has been reported that fluorescent clusters show no impact by oxygen treatment, whereas phosphorescent ones exhibit a reduction in emission intensity when interacting with molecular oxygen.^{64–67} Rather surprisingly, this cluster displays distinctly different physicochemical behavior compared to previously reported systems.

The ESI mass spectra of the solution recorded after treatment with oxygen showed a molecular ion peak at m/z 2772.23 (charge state 2+), accompanied by an additional peak at m/z 2836.19 (charge state 2+), indicating the presence of a

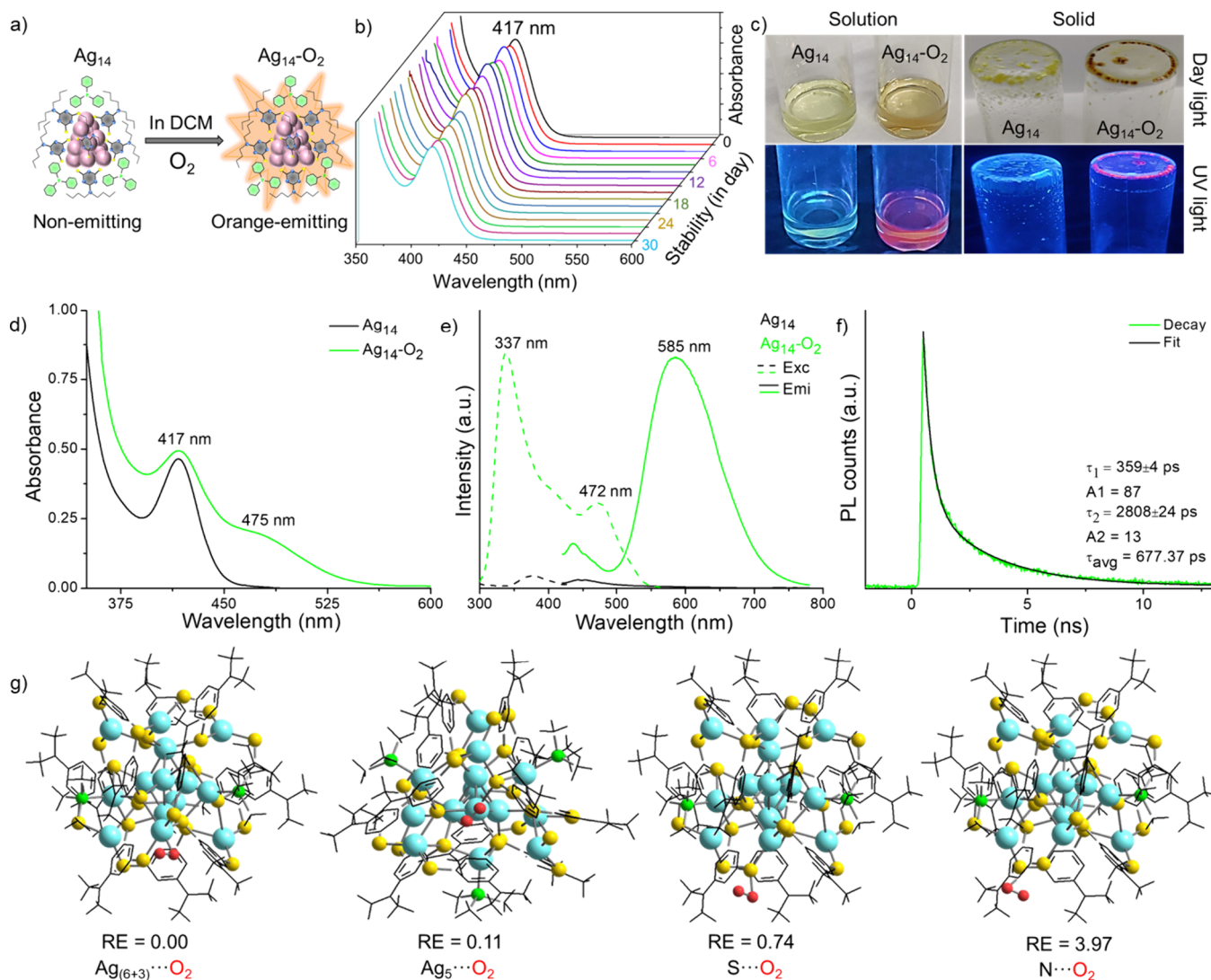


Figure 5. (a) Schematic representation of the oxygenation of Ag_{14} and its effect on luminescence. (b) Time-sequence of UV–Vis absorption spectra of Ag_{14} in DCM solution without oxygen bubbling indicating its stability. (c) Photographs of the cluster before and after oxygen supply in solution (as described in the Experimental Section) and in the solid state under daylight (top) and 365 nm UV light (bottom) exposure. (d) Comparison of UV–Vis absorption spectra of Ag_{14} before and after oxygenation. (e) Photoluminescence excitation and emission spectra of both as-prepared and oxygenated- Ag_{14} in their respective DCM solution. (f) PL decay profile of the oxygenated- Ag_{14} along with fitting of the components. (g) DFT-optimized structures of oxygen attachments (shown in red color) at different binding sites of the Ag_{14} cluster with the relative energies (REs) with respect to the most stable binding site in eV.

cluster adduct comprising four oxygen molecules (shown in Figure S19). Based on the ion intensity of Ag_{14} and oxygenated- Ag_{14} ions, we estimate that approximately $41 \pm 4\%$ of the oxygenated- Ag_{14} species were formed in the solution. Due to the rapid formation and deoxygenation of oxygenated- Ag_{14} clusters in solution, the actual concentration of oxygenated Ag_{14} clusters may exceed the ion concentration measured by mass spectrometry. Furthermore, higher intensity of the Ag_{14} peak may result from the dissociation of oxygenated- Ag_{14} species under the gas-phase conditions present during mass spectrometric analysis. The separation of the oxygenated- Ag_{14} clusters and the growth of single crystals were not successful. The UV–Vis absorption spectrum of the oxygenated species shows an additional band at 475 nm, with an absorption tail up to 540 nm, along with a band at 417 nm for the oxygenated- Ag_{14} cluster (see Figure Sd). In the corresponding PL

spectrum, a strong emission band appears at 585 nm for the oxygenated cluster besides a characteristic photoexcitation band centered around 337 and 472 nm (shown in Figure Se).

We conducted time-dependent PL measurements following a sequential oxygen bubbling interval of 6 h. Comparative PL intensity measurements indicated that emission induced by oxygenation began to manifest after 18 h of bubbling and reached its peak intensity around 48 h (Figure S20). After 48 h of oxygen bubbling, the emission of the oxygenated- Ag_{14} cluster remains persistent for more than two weeks, indicating its stability. Luminescence lifetime measurements of the oxygenated Ag_{14} exhibit a bi-exponential emissive decay with lifetimes of 359 ± 4 , 2808 ± 24 ps and an average lifetime of 677.37 ps (Figure Sf). This extremely short lifetime suggests a fluorescent nature for the oxygenated species, rather than phosphorescence emission. Experimental and computational studies have shown

that oxygen binds to silver clusters through spin pairing and electronic shell closure; however, the effects of this binding on their optical properties have yet to be investigated.^{67,68}

Next, we have investigated the oxygenation affinity of the cluster through DFT calculations. For this, we have calculated the binding of a single O₂ molecule on the simplified model of the Ag₁₄ cluster. Since multiple binding sites are available for O₂ binding, we have considered four possible accessible binding sites: (i) O₂-Ag₅ (core), (ii) O₂-Ag₍₆₊₃₎ (shell), (iii) O₂-S (ligand), and (iv) O₂-N (ligand) on the basis of molecular symmetry. We have compared the relative stability between these binding sites, the results of which are given in Figure Sg.

We find that O₂ binding is most stable in the Ag₍₆₊₃₎ shell. This can be further understood by the PDOS analysis where we find that the Ag₍₆₊₃₎ shell contributes to the valence band of the cluster. As a result, the Ag₍₆₊₃₎(d) states donate electrons to the antibonding molecular orbitals of O₂, leading to its adsorption. To quantify the strength of adsorption, we have calculated the O₂ binding energy according to the following equation:

$$BE = E(\text{Ag}_{14}\text{-O}_2) - [E(\text{Ag}_{14}) + E(\text{O}_2)]$$

where $E(\text{Ag}_{14}\text{-O}_2)$ is the energy of O₂ bound cluster, $E(\text{Ag}_{14})$ is the energy of the bare Ag₁₄ cluster, and $E(\text{O}_2)$ is the energy of the O₂ molecule. The calculated O₂ binding energy of Ag₁₄ is −4.78 eV, suggesting strong binding affinity of oxygens and hence supporting the oxygenation process.

To evaluate the impact of various gaseous species on Ag₁₄ clusters, we performed gas bubbling experiments using argon, nitrogen, and carbon dioxide separately. The comparative UV–Vis absorption spectra (shown in Figure S21) indicated no significant change in the absorption band, which has a maximum wavelength (λ_{max}) of 417 nm, following gas bubbling. Furthermore, we did not observe any visible luminescence after bubbling with these gases. Therefore, we conclude that the Ag₁₄ clusters are not responsive toward these gases.

The self-assembly behavior of Ag₁₄ clusters affected by oxygenation. Aggregates are formed by adding hexane to the DCM solution of the respective clusters (with and without oxygenation). Figure 6a shows schematic illustrations of these self-assembled superstructures in a DCM/hexane solvent mixture with and without oxygen bubbling. High-resolution TEM imaging revealed a spherical assembly of the Ag₁₄ cluster with an average diameter of 600 ± 200 nm (Figure 6b,c), without oxygenation. A large area of TEM and FESEM images showed the formation of numerous spheroids in the aggregation process (shown in Figures S22 and S23).

On the other hand, samples of the oxygenated Ag₁₄ form a ring-like toroidal assembly with a thickness of 20–30 nm (Figures 6d,e, and S24). To gain further insight into the three-dimensional (3D) structural details of self-assembled structures, we performed an electron tomographic (ET) reconstruction of the structures using a series of 2D projections collected from +69° to −69° by tilting the specimen with an increment angle of 2°. The ET reconstruction of the Ag₁₄ aggregate (Figure 6f,g) revealed uniform distribution of

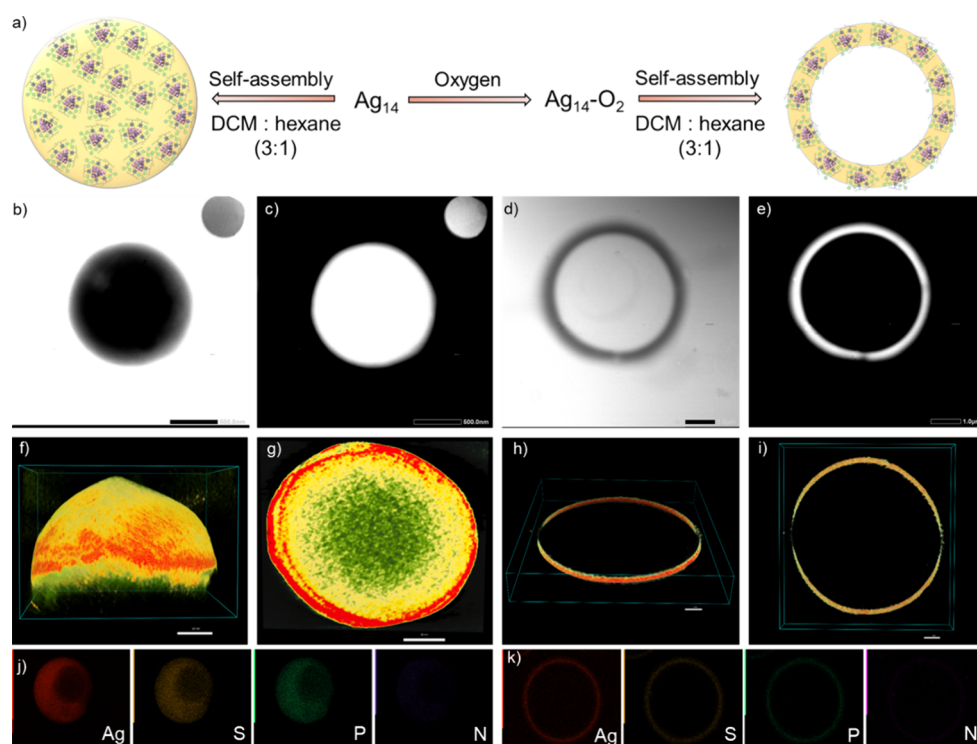


Figure 6. (a) Schematic representation depicting self-assembled superstructures of Ag₁₄ and its oxygenated species. High-resolution (b) TEM and (c) STEM micrographs of a spheroidal assembly of Ag₁₄. High-resolution (d) TEM and (e) STEM micrographs of a toroidal assembly of oxygenated-Ag₁₄. Electron tomographic 3D reconstruction of (f, g) the Ag₁₄ spheroid and (h, i) the oxygenated-Ag₁₄ toroid from different orientations. STEM-EDS elemental mapping of (j) Ag₁₄ spheroid and (k) oxygenated-Ag₁₄ toroid, indicating the presence of Ag, S, P, and N elements.

electron density throughout the structure, implying a densely packed and homogeneous assembly of clusters. However, the structure was deformed presumably owing to drying artifacts during sample preparation and solvent evaporation, as observed previously for self-assembled NCs. The 3D-reconstructed structure of self-assembled oxygenated-Ag₁₄ clusters (in Figure 6h,i) displayed a ring-like structure with a uniform rim diameter and thickness. The EDS spectral profile demonstrates the presence of Ag, S, N, P, and C in both the nanostructures (shown in Figures S25 and S26), and EDS elemental mapping also verified the presence of these elements in the nanostructures (see Figure 6j,k).

Despite these structural insights, the mechanism leading to the observed self-assembled structures is not well understood. However, TRZ ligands with n-butyl chains present on the surface of the cluster show a unique hydrophobic effect of self-aggregation upon oxygenation. The aggregation observed in our clusters seems to be driven by the non-covalent interactions between the ligand motifs of adjacent clusters. In order to study the formation of these superstructures, we have considered a dimer of Ag₁₄ clusters (Figure S27), where two monomer units interact with each other. To quantify the role of van der Waals interactions, we have calculated the thermodynamic feasibility of the formation of dimers from the monomer units by two separate calculations—one without including the van der Waals interactions and another one considering van der Waals interactions via the DFT-D3 method.⁶⁹ For both cases, we have employed full ligand simulation without any simplification as was required to accurately identify the non-covalent interactions. We calculated the dimer formation energy by considering van der Waals interactions and found it to be stable by −0.08 eV. This indicates that the van der Waals interactions mediated by the ligand groups between the molecular cluster units provide essential structural stability of these specific aggregates.

Effect of Excited-State Electron Dynamics upon Oxygenation

Next, we have studied the excited-state behavior of the cluster upon oxygenation through femtosecond TA studies (see the Supporting information for experimental details). In the measurement, samples were excited with 120 fs pump pulses centered at 400 nm. The resulting effects of the system in the non-equilibrium excited state were investigated using a time-delayed probe of a white-light continuum. The obtained result for Ag₁₄ at a pump fluence of 200 μJ/cm² is plotted in Figure 7a–d. We see that the main transient feature of the excited-state system is a broad-band of photoinduced absorption. The non-appearance of ground-state bleaching is well understandable in view of the absence of optical absorption peaks in the investigated regime (Figure 1b). To determine the lifetime of the excited-state absorption (ESA) feature, we look for the temporal profiles of TA (shown in Figures 7c,d and S28a). It reveals a short lifetime of the excited-state carriers with a decay constant of 13–15 ps. To see the effects of oxygenation on excited-state electron dynamics, TA results of oxygenated-Ag₁₄ are plotted in Figures 7e–h and S28b. From the contour and spectral slices, we see that the oxygenated-Ag₁₄ exhibits different TA features than the parent cluster. Along with photoinduced absorption, signature of a negative TA signal is also observed near 475 nm. It is at the position of the absorption peak in the ground-state optical absorption (Figure 5d) and suggests the photobleaching due to a phase-space filling effect.⁷⁰ In addition, the lifetime of the excited-state absorption feature also shows changes in the oxygenated-Ag₁₄, manifested by the prolonged lifetimes, ~862 ps for 550 nm and ~141 ps for 645 nm of the excited-state absorption carriers. Stabilizing the excited-state carriers upon oxygenation might also be responsible for the origin of luminescence in the oxygenated-Ag₁₄ cluster species.

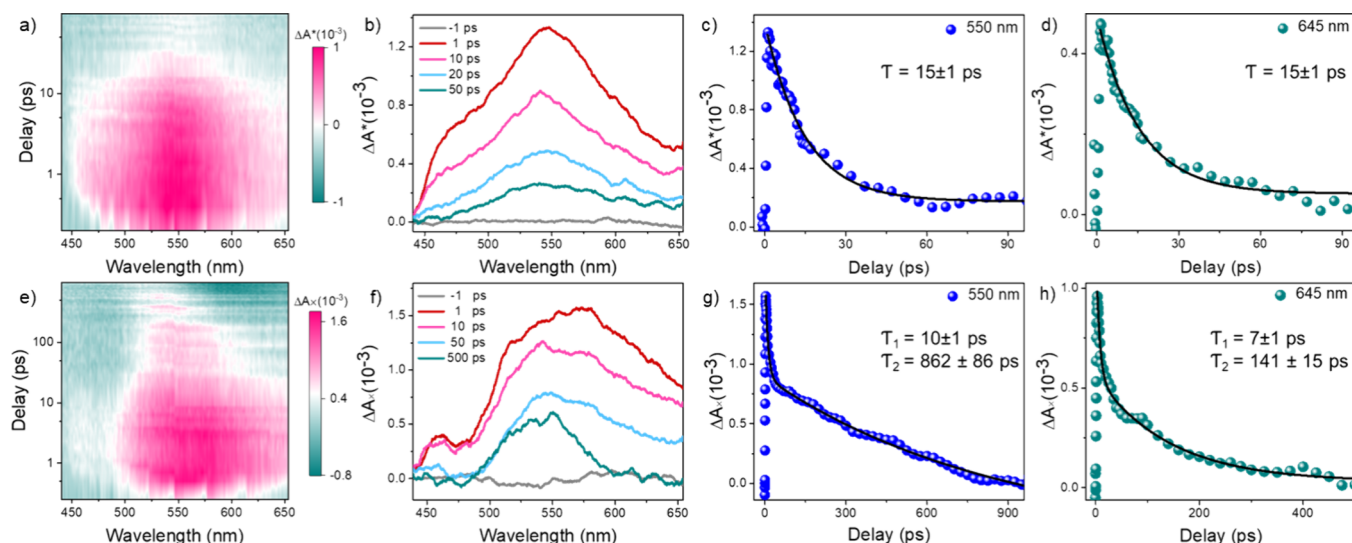


Figure 7. (a) Contour plot of the femtosecond-TA spectrum showing photoinduced absorption as a main feature for Ag₁₄. (b) Spectral profile of the TA for the same NC at selected time delays. TA kinetics decay of the Ag₁₄ sample upon probing at selected wavelengths of (c) 550 and (d) 645 nm. (e) Femtosecond-TA contour plot of the oxygenated-Ag₁₄ species. (f) Selected time evolution of the spectral profile. Kinetics decay of ESA feature of oxygenated-Ag₁₄ at selected wavelengths of (g) 550 and (h) 645 nm.

CONCLUSIONS

In conclusion, we demonstrated the formation of a TRZ- and TPP-co-protected $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3]$ cluster, synthesized by a mixed solvent-induced conversion process, starting from the $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ cluster. This Ag_{14} cluster shows a unique core-shell structure with a trigonal bipyramidal Ag_5 core surrounded by a tricapped trigonal prismatic $\text{Ag}_{(6+3)}$ shell. This non-fcc core-shell structure arrangement is distinctly different from the various reported fcc- Ag_{14} clusters. The presence of an odd number of TPP ligands directly bonded to three capping silver atoms was observed for this silver cluster. Theoretical investigations have demonstrated that although the non-fcc Ag_{14} skeleton exhibits lower structural stability compared to its fcc analogues, the overall stability of the Ag_{14} cluster is significantly influenced by the arrangement of silver-sulfide motifs and bulky TRZ ligands. High-resolution mass spectrometry, along with other spectroscopic and microscopic studies, confirm the molecular composition and ligand environment of the cluster. The Ag_{14} cluster manifests an interesting oxygenation effect in that the non-luminescent as-prepared cluster is converted to an orange-emitting one upon treatment with oxygen. Femtosecond TA studies demonstrated the stabilization of an extremely fast decay of excited-state absorption carriers upon oxygenation resulting in visible luminescence. Self-assembly of the cluster is also tuned by oxygenation. This work highlights a new direction for exploring metal clusters with a distinctive metal framework and a surface-sensitive ligand shell. Additionally, the findings indicate that there are several structurally diverse clusters of the same nuclearity, which enhance the diversity within this family of precision nanomaterials.

EXPERIMENTAL SECTION

Chemicals Used

Silver nitrate and *tert*-butyl borane-amine complex were purchased from Rankem Chemicals. Sodium borohydride (98%), sodium cyanoborohydride, and triphenylphosphine were bought from Aldrich Chemicals. 6-(Dibutylamino)-1,3,5-triazine-2,4-dithiol was purchased from TCI America. HPLC-grade dichloromethane, methanol, and *n*-hexane solvents were purchased from Rankem Chemicals and Finar, India. Milli-Q water was used for the synthesis and purification purpose. Deuterated solvent, CDCl_3 (99.8 atom % D), was purchased from Sigma-Aldrich. Commercially available gases, including 99% pure oxygen, nitrogen, argon, and carbon dioxide (Indogases), were used for the bubbling experiments. All the chemicals were commercially available and used as such without further purification.

Synthesis of $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ NC

The $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ cluster was synthesized at room temperature using triphenylphosphine-assisted co-reduction of silver-thiolate precursors by following our earlier report.⁵² In brief, 40 mg of AgNO_3 (0.235 mM) was dissolved in 9 ml of methanol. After 10 min of reaction, 10 ml of DCM was added. 50 mg (0.183 mM) of TRZ- H_2 was dissolved in 2 ml of DCM and added to the solution under stirring. After additional 15 min of the reaction, 100 mg of TPP (0.381 mM), dissolved in 2 ml of DCM, was added to the reaction mixture, which leads to the formation of a colorless solution. After 10 min, 24–25 mg of NaBH_4 , dissolved in 1 ml of Milli-Q water, was added. Just after the addition of NaBH_4 , a dark reddish solution was formed, which eventually got converted to a blue-violet solution after overnight reaction. After 16 h of reaction, mixed solvents were removed at reduced pressure. The crude oily product was washed multiple times using methanol and hexane. The cluster powder was formed by drop-

casting a DCM solution of the cluster onto a glass slide after which the sample was dried under ambient conditions at 50 °C and stored in a vacuum closed container. The yield of the product was 75% in terms of silver nitrate. UV-Vis absorption spectra and mass spectrometric studies were performed to characterize the cluster (see Figure S1).

Synthesis of $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3]$ NC

Ag_{14} was synthesized using a mixed-solvent-induced conversion method using a previously synthesized Ag_{31} cluster. During the conversion process, 5 mg of Ag_{31} powder and 1 mg of TPP were dissolved in 0.75 ml of DCM, followed by the addition of 3 ml of methanol. The vial was placed under dark conditions at 4 °C. After 10–12 days, the violet-colored Ag_{31} solution gradually turned greenish yellow, indicating the formation of the Ag_{14} cluster as the sole cluster product, along with some silver-thiolate complexes. The solution was dried under reduced pressure, followed by washing using an ice-cold mixture of methanol and ethanol (1:1, v/v), which resulted in the purified cluster. The Ag_{14} cluster dissolved in DCM was used for further studies. The yield of the product was 30–35% in terms of Ag_{31} cluster. Greenish-yellow cuboid crystals were formed after 30 days at 4 °C through vapor diffusion of methanol into the DCM solution of the cluster with a concentration of >35 mg/ml.

Oxygenation to Ag_{14} NC

Oxygenation of Ag_{14} was performed upon bubbling with pure oxygen gas. 5 mg of purified Ag_{14} cluster was dissolved in 3 ml of DCM for oxygenation studies. After 48 h of oxygen bubbling using balloons filled with oxygen gas, we observed a visible color change from greenish-yellow to dark yellow. The as-prepared Ag_{14} did not emit any visible light under a 365 nm UV lamp, whereas the oxygenated- Ag_{14} cluster emitted visible orange luminescence both in solution and also in solid state. Bubbling with oxygen for over 48 h did not enhance the oxygenation process, as we did not observe any significant changes in luminescence afterward. Oxygenated- Ag_{14} clusters were stable under ambient conditions over two weeks as monitored through time-dependent emission studies. As we were unable to completely regenerate the Ag_{14} cluster from the oxygenated sample, we concluded that the oxygenation to Ag_{14} was an irreversible process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.6c11805>.

Instrumentation, computational details, X-ray crystallographic details, and additional experimental results that support the findings of this study (DOCX)

Accession Codes

Deposition Numbers 2376263 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Author Contributions

A.J. carried out the synthesis, crystallization, and the majority of the experimental studies. A.S.N. conducted theoretical calculations under the supervision of B.P. A.K.P. performed ultrafast TA studies on the cluster under K.N.V.D.A.'s guidance. J.R. was responsible for mass spectrometric characterization, while N. conducted the TEM and tomographic reconstruction. V.Y. participated in the experimental investigations. A.J. drafted the initial version of the manuscript, with all authors contributing to its finalization. T.P. and S.D. conceived the idea, supervised the project, and finalized the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Prof. Ashutosh Sharma.

ABBREVIATIONS

TPP	triphenylphosphine
TRZ	6-(dibutylamino)-1,3,5-triazine-2,4-dithiolate
TTP	tricapped trigonal prismatic
fcc	face-centered cubic
NC	nanocluster
CE	collision energy
PL	photoluminescence
DCM	dichloromethane
NMR	nuclear magnetic resonance
XPS	X-ray photoelectron spectroscopy
TBP	trigonal bipyramidal
DFT	density functional theory
VASP	Vienna Ab initio Simulation Package
PBE	Perdew–Burke–Ernzerhof
TD-DFT	time-dependent density functional theory
FMO	frontier molecular orbital
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
PDOS	projected density of states
TEM	transmission electron microscopy
TA	transient absorption
ESA	excited-state absorption

REFERENCES

- (1) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116*, 10346–10413.
- (2) Chakraborty, I.; Pradeep, T. Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles. *Chem. Rev.* **2017**, *117* (12), 8208–8271.
- (3) Fuhr, O.; Dehnen, S.; Fenske, D. Chalcogenide Clusters of Copper and Silver from Silylated Chalcogenide Sources. *Chem. Soc. Rev.* **2013**, *42* (4), 1871–1906.
- (4) Song, Y.; Lambright, K.; Zhou, M.; Kirschbaum, K.; Xiang, J.; Xia, A.; Zhu, M.; Jin, R. Large-Scale Synthesis, Crystal Structure, and Optical Properties of the Ag₁₄₆Br₂(SR)₈₀ Nanocluster. *ACS Nano* **2018**, *12* (9), 9318–9325.
- (5) Häkkinen, H. Atomic and Electronic Structure of Gold Clusters: Understanding Flakes, Cages and Superatoms from Simple Concepts. *Chem. Soc. Rev.* **2008**, *37* (9), 1847–1859.

- (6) Yadav, V.; Jana, A.; Acharya, S.; Malola, S.; Nagar, H.; Sharma, A.; Kini, A. R.; Antharjanam, S.; Machacek, J.; Nair, K.; Devi, V.; Base, T.; Häkkinen, H.; Pradeep, T. Site-Specific Substitution in Atomically Precise Carboranethiol-Protected Nanoclusters and Concomitant Changes in Electronic Properties. *Nat. Commun.* **2025**, *16*, 1197.
- (7) Jana, A.; Yadav, V.; Kuceřáková, M.; Malola, S.; Kini, A. R.; Acharya, S.; Poonia, A. K.; Macháček, J.; Adarsh, K. N. V. D.; Häkkinen, H.; Base, T.; Pradeep, T. $[\text{Ag}_{62}\text{S}_{12}(\text{CBT})_{32}]^{4+}$: A 2.2 nm Two-Electron Superatomic Carborane-Thiolated Silver Nanocluster Exhibiting Multilayer Charge Separation. *ACS Nano* **2025**, *19*, 35015–35026.
- (8) Kang, X.; Wei, X.; Xiang, P.; Tian, X.; Zuo, Z.; Song, F.; Wang, S.; Zhu, M. Rendering Hydrophobic Nanoclusters Water-Soluble and Biocompatible. *Chem. Sci.* **2020**, *11* (18), 4808–4816.
- (9) Kang, X.; Zhu, M. Tailoring the Photoluminescence of Atomically Precise Nanoclusters. *Chem. Soc. Rev.* **2019**, *48* (8), 2422–2457.
- (10) Lin, H.; Song, X.; Chai, O. J. H.; Yao, Q.; Yang, H.; Xie, J. Photoluminescent Characterization of Metal Nanoclusters: Basic Parameters, Methods, and Applications. *Adv. Mater.* **2024**, *36*, 2401002.
- (11) Diez, I.; Pusa, M.; Kulmala, S.; Jiang, H.; Walther, A.; Goldmann, A. S.; Müller, A. H. E.; Ikkala, O.; Ras, R. H. A. Color Tunability and Electrochemiluminescence of Silver Nanoclusters. *Angew. Chem., Int. Ed.* **2009**, *48* (12), 2122–2125.
- (12) Gao, X.; Tian, Z.; Ren, X.; Ai, Y.; Zhang, B.; Zou, G. Silver Nanocluster-Tagged Electrochemiluminescence Immunoassay with a Sole and Narrow Triggering Potential Window. *Anal. Chem.* **2024**, *96* (4), 1700–1706.
- (13) Feng, A.; Hou, S.; Yan, J.; Wu, Q.; Tang, Y.; Yang, Y.; Shi, J.; Xiao, Z. Y.; Lambert, C. J.; Zheng, N.; Hong, W. Conductance Growth of Single-Cluster Junctions with Increasing Sizes. *J. Am. Chem. Soc.* **2022**, *144* (34), 15680–15688.
- (14) Yuan, P.; Zhang, R.; Selenius, E.; Ruan, P.; Yao, Y.; Zhou, Y.; Malola, S.; Häkkinen, H.; Teo, B. K.; Cao, Y.; Zheng, N. Solvent-Mediated Assembly of Atom-Precise Gold–Silver Nanoclusters to Semiconducting One-Dimensional Materials. *Nat. Commun.* **2020**, *11* (1), 2229.
- (15) Abbas, M. A.; Kamat, P. V.; Bang, J. H. Thiolated Gold Nanoclusters for Light Energy Conversion. *ACS Energy Lett.* **2018**, *3* (4), 840–854.
- (16) Rival, J. V.; Chand, S.; Jana, A.; Nonappa, Biju, V.; Pradeep, T.; Rajamalli, P.; Shibu, E. S. Bimetallic Nanocluster-Based Light-Emitting Diodes With High External Quantum Efficiency and Saturated Red Emission. *Adv. Mater.* **2025**, *37*, 2507893.
- (17) Russier-Antoine, I.; Bertorelle, F.; Calin, N.; Sanader, Ž.; Krstić, M.; Comby-Zerbino, C.; Dugourd, P.; Brevet, P. F.; Bonacic-Koutecky, V.; Antoine, R. Ligand-Core NLO-Phores: A Combined Experimental and Theoretical Approach to the Two-Photon Absorption and Two-Photon Excited Emission Properties of Small-Ligated Silver Nanoclusters. *Nanoscale* **2017**, *9* (3), 1221–1228.
- (18) Sakai, J.; Biswas, S.; Irie, T.; Mabuchi, H.; Sekine, T.; Niihori, Y.; Das, S.; Negishi, Y. Synthesis and Luminescence Properties of Two Silver Cluster-Assembled Materials for Selective Fe^{3+} Sensing. *Nanoscale* **2023**, *15* (29), 12227–12234.
- (19) Cao, M.; Pang, R.; Wang, Q. Y.; Han, Z.; Wang, Z. Y.; Dong, X. Y.; Li, S. F.; Zang, S. Q.; Mak, T. C. W. Porphyrinic Silver Cluster Assembled Material for Simultaneous Capture and Photocatalysis of Mustard-Gas Simulant. *J. Am. Chem. Soc.* **2019**, *141* (37), 14505–14509.
- (20) Luo, Z.; Zheng, K.; Xie, J. Engineering Ultrasmall Water-Soluble Gold and Silver Nanoclusters for Biomedical Applications. *Chem. Commun.* **2014**, *50* (40), 5143–5155.
- (21) Hua, Y.; Huang, J. H.; Shao, Z. H.; Luo, X. M.; Wang, Z. Y.; Liu, J. Q.; Zhao, X.; Chen, X.; Zang, S. Q. Composition-Dependent Enzyme Mimicking Activity and Radiosensitizing Effect of Bimetallic Clusters to Modulate Tumor Hypoxia for Enhanced Cancer Therapy. *Adv. Mater.* **2022**, *34*, 2203734.
- (22) Ma, M. X.; Ma, X. L.; Liang, G. M.; Shen, X. T.; Ni, Q. L.; Gui, L. C.; Wang, X. J.; Huang, S. Y.; Li, S. M. A Nanocluster $[\text{Ag}_{307}\text{Cl}_{62}(\text{SPhBu})_{110}]$: Chloride Intercalation, Specific Electronic State, and Superstability. *J. Am. Chem. Soc.* **2021**, *143* (34), 13731–13737.
- (23) Yuan, Z. R.; Wang, Z.; Han, B. L.; Zhang, C. K.; Zhang, S. S.; Zhu, Z. Y.; Yu, J. H.; Li, T. D.; Li, Y. Z.; Tung, C. H.; Sun, D. Ag_{22} Nanoclusters with Thermally Activated Delayed Fluorescence Protected by Ag/Cyanurate/Phosphine Metallamacrocyclic Monolayers through In-Situ Ligand Transesterification. *Angew. Chem., Int. Ed.* **2022**, *61* (45), e202211628.
- (24) Kulkarni, V. K.; Khirak, B. N.; Takano, S.; Malola, S.; Albright, E. L.; Levchenko, T. I.; Aloisio, M. D.; Dinh, C. T.; Tsukuda, T.; Häkkinen, H.; Crudden, C. M. N-Heterocyclic Carbene-Stabilized Hydrido Au_{24} Nanoclusters: Synthesis, Structure, and Electrocatalytic Reduction of CO_2 . *J. Am. Chem. Soc.* **2022**, *144* (20), 9000–9006.
- (25) Hu, F.; Li, J. J.; Guan, Z. J.; Yuan, S. F.; Wang, Q. M. Formation of an Alkynyl-Protected Ag_{112} Silver Nanocluster as Promoted by Chloride Released In Situ from CH_2Cl_2 . *Angew. Chem., Int. Ed.* **2020**, *59* (13), 5312–5315.
- (26) Liu, K.-G.; Gao, X.-M.; Liu, T.; Hu, M.-L.; Jiang, D. All-Carboxylate-Protected Superatomic Silver Nanocluster with an Unprecedented Rhombohedral Ag_8 Core. *J. Am. Chem. Soc.* **2020**, *142* (40), 16905–16909.
- (27) Yuan, S. F.; Guan, Z. J.; Liu, W. D.; Wang, Q. M. Solvent-Triggered Reversible Interconversion of All-Nitrogen-Donor-Protected Silver Nanoclusters and Their Responsive Optical Properties. *Nat. Commun.* **2019**, *10* (1), 4032–4037.
- (28) Cerretani, C.; Kanazawa, H.; Vosch, T.; Kondo, J. Crystal Structure of a NIR-Emitting DNA-Stabilized Ag_{16} Nanocluster. *Angew. Chem., Int. Ed.* **2019**, *131* (48), 17313–17317.
- (29) Yonesato, K.; Yanai, D.; Yamazoe, S.; Yokogawa, D.; Kikuchi, T.; Yamaguchi, K.; Suzuki, K. Surface-Exposed Silver Nanoclusters inside Molecular Metal Oxide Cavities. *Nat. Chem.* **2023**, *15* (7), 940–947.
- (30) Feng, Y.; Fu, F.; Zeng, L.; Zhao, M.; Xin, X.; Liang, J.; Zhou, M.; Fang, X.; Lv, H.; Yang, G.-Y. Atomically Precise Silver Clusters Stabilized by Lacunary Polyoxometalates with Photocatalytic CO_2 Reduction Activity. *Angew. Chem., Int. Ed.* **2024**, *63*, e202317341.
- (31) Yang, H.; Lei, J.; Wu, B.; Wang, Y.; Zhou, M.; Xia, A.; Zheng, L.; Zheng, N. Crystal Structure of a Luminescent Thiolated Ag Nanocluster with an Octahedral Ag^{6+} Core. *Chem. Commun.* **2013**, *49* (3), 300–302.
- (32) Desiredy, A.; Conn, B. E.; Guo, J.; Yoon, B.; Barnett, R. N.; Monahan, B. M.; Kirschbaum, K.; Griffith, W. P.; Whetten, R. L.; Landman, U.; Bigioni, T. P. Ultrastable Silver Nanoparticles. *Nature* **2013**, *501* (7467), 399–402.
- (33) Luo, X. M.; Li, Y. K.; Dong, X. Y.; Zang, S. Q. Platonic and Archimedean Solids in Discrete Metal-Containing Clusters. *Chem. Soc. Rev.* **2023**, *52* (1), 383–444.
- (34) Kang, X.; Zhu, M. Metal Nanoclusters Stabilized by Selenol Ligands. *Small* **2019**, *15* (43), 1902703.
- (35) Khatun, E.; Bodiuzzaman, M.; Sugi, K. S.; Chakraborty, P.; Paramasivam, G.; Dar, W. A.; Ahuja, T.; Antharjanam, S.; Pradeep, T. Confining an Ag_{10} Core in an Ag_{12} Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization. *ACS Nano* **2019**, *13* (5), 5753–5759.
- (36) Yang, H.; Yan, J.; Wang, Y.; Su, H.; Gell, L.; Zhao, X.; Xu, C.; Teo, B. K.; Häkkinen, H.; Zheng, N. Embryonic Growth of Face-Center-Cubic Silver Nanoclusters Shaped in Nearly Perfect Half-Cubes and Cubes. *J. Am. Chem. Soc.* **2017**, *139* (1), 31–34.
- (37) Yuan, S. F.; Xu, C. Q.; Liu, W. D.; Zhang, J. X.; Li, J.; Wang, Q. M. Rod-Shaped Silver Supercluster Unveiling Strong Electron Coupling between Substituent Icosahedral Units. *J. Am. Chem. Soc.* **2021**, *143* (31), 12261–12267.
- (38) Zhang, M. M.; Dong, X. Y.; Wang, Z. Y.; Luo, X. M.; Huang, J. H.; Zang, S. Q.; Mak, T. C. W. Alkynyl-Stabilized Superatomic Silver Clusters Showing Circularly Polarized Luminescence. *J. Am. Chem. Soc.* **2021**, *143* (16), 6048–6053.
- (39) Nag, A.; Chakraborty, P.; Bodiuzzaman, M.; Ahuja, T.; Antharjanam, S.; Pradeep, T. Polymorphism of $\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4^{3-}$ Cluster: Interactions of Secondary Ligands

and Their Effect on Solid State Luminescence. *Nanoscale* **2018**, *10* (21), 9851–9855.

(40) Kang, X.; Zhu, M. CocrySTALLIZATION of Atomically Precise Nanoclusters. *ACS Mater. Lett.* **2020**, *2* (10), 1303–1314.

(41) Huang, R. W.; Wei, Y. S.; Dong, X. Y.; Wu, X. H.; Du, C. X.; Zang, S. Q.; Mak, T. C. W. Hypersensitive Dual-Function Luminescence Switching of a Silver-Chalcogenolate Cluster-Based Metal-Organic Framework. *Nat. Chem.* **2017**, *9* (7), 689–697.

(42) Das, A. K.; Biswas, S.; Manna, S. S.; Pathak, B.; Mandal, S. An Atomically Precise Silver Nanocluster for Artificial Light-Harvesting System through Supramolecular Functionalization. *Chem. Sci.* **2022**, *13* (28), 8355–8364.

(43) Wang, J. Y.; Li, Y. K.; Jing, X.; Luo, P.; Dong, X. Y.; Zang, S. Q. Co-Assembly of Ag₂₉ Nanoclusters with Ru(Bpy)₃²⁺ for Two-Photon Up-Conversion and Singlet Oxygen Generation. *ACS Mater. Lett.* **2022**, *4* (5), 960–966.

(44) Zou, X.; He, S.; Kang, X.; Chen, S.; Yu, H.; Jin, S.; Astruc, D.; Zhu, M. New Atomically Precise M1Ag21(M = Au/Ag) Nanoclusters as Excellent Oxygen Reduction Reaction Catalysts. *Chem. Sci.* **2021**, *12* (10), 3660–3667.

(45) Li, L. J.; Luo, Y. T.; Tian, Y. Q.; Wang, P.; Yi, X. Y.; Yan, J.; Pei, Y.; Liu, C. Unveiling the Remarkable Stability and Catalytic Activity of a 6-Electron Superatomic Ag₃₀ Nanocluster for CO₂ Electoreduction. *Inorg. Chem.* **2023**, *62* (35), 14377–14384.

(46) Som, A.; Griffo, A.; Chakraborty, I.; Hähl, H.; Mondal, B.; Chakraborty, A.; Jacobs, K.; Laaksonen, P.; Ikkala, O.; Pradeep, T.; Nonappa Strong and Elastic Membranes via Hydrogen Bonding Directed Self-Assembly of Atomically Precise Nanoclusters. *Small* **2022**, *18*, 2201707.

(47) Rival, J. V.; Mymoona, P.; Lakshmi, K. M.; Nonappa; Pradeep, T.; Shibu, E. S. Self-Assembly of Precision Noble Metal Nanoclusters: Hierarchical Structural Complexity, Colloidal Superstructures, and Applications. *Small* **2021**, *17*, 2005718.

(48) Nonappa; Lahtinen, T.; Johannes.S.Haataja; Tero, T.-R.; Häkkinen, H.; Ikkala, O. Template-Free Supracolloidal Self-Assembly of Atomically Precise Gold Nanoclusters: From 2D Colloidal Crystals to Spherical Capsids. *Angew. Chem., Int. Ed.* **2016**, *55*, 16035–16038.

(49) Wu, Z.; Liu, J.; Li, Y.; Cheng, Z.; Li, T.; Zhang, H.; Lu, Z.; Yang, B. Self-Assembly of Nanoclusters into Mono-, Few-, and Multilayered Sheets via Dipole-Induced Asymmetric van Der Waals Attraction. *ACS Nano* **2015**, *9* (6), 6315–6323.

(50) Bi, Y.; Wang, Z.; Liu, T.; Sun, D.; Godbert, N.; Li, H.; Hao, J.; Xin, X. Supramolecular Chirality from Hierarchical Self-Assembly of Atomically Precise Silver Nanoclusters Induced by Secondary Metal Coordination. *ACS Nano* **2021**, *15* (10), 15910–15919.

(51) Chandra, S.; Sciortino, A.; Das, S.; Ahmed, F.; Jana, A.; Roy, J.; Li, D.; Liljeström, V.; Jiang, H.; Johansson, L. S.; Chen, X.; Nonappa; Cannas, M.; Pradeep, T.; Peng, B.; Ras, R. H. A.; Sun, Z.; Ikkala, O.; Messina, F. Gold Au(I)₆ Clusters with Ligand-Derived Atomic Steric Locking: Multifunctional Optoelectrical Properties and Quantum Coherence. *Adv. Opt. Mater.* **2023**, *11*, 2202649.

(52) Jana, A.; Dar, W. A.; Jana, S. K.; Poonia, A. K.; Yadav, V.; Roy, J.; Chandra, S.; Adarsh, K. N. V. D.; Ras, R. H. A.; Pradeep, T. Photoconversion of Ag₃₁ to Ag₄₂ Initiated by Solvated Electrons. *Chem. Mater.* **2023**, *35*, 7020–7031.

(53) Boduazzaman, M.; Khatun, E.; Sugi, K. S.; Paramasivam, G.; Dar, W. A.; Antharjanam, S.; Pradeep, T. Dithiol-Induced Contraction in Ag₁₄ Clusters and Its Manifestation in Electronic Structures. *J. Phys. Chem. C* **2020**, *124* (42), 23426–23432.

(54) Jana, A.; Jash, M.; Poonia, A. K.; Paramasivam, G.; Islam, M. R.; Chakraborty, P.; Antharjanam, S.; Machacek, J.; Ghosh, S.; Adarsh, K. N. V. D.; Base, T.; Pradeep, T. Light-Activated Intercluster Conversion of an Atomically Precise Silver Nanocluster. *ACS Nano* **2021**, *15*, 15781–15793.

(55) Jana, A.; Unnikrishnan, P. M.; Poonia, A. K.; Roy, J.; Jash, M.; Paramasivam, G.; Machacek, J.; Adarsh, K. N. V. D.; Base, T.; Pradeep, T. Carboranethiol-Protected Propeller-Shaped

Photoresponsive Silver Nanomolecule. *Inorg. Chem.* **2022**, *61*, 8593–8603.

(56) Bootharaju, M. S.; Dey, R.; Gevers, L. E.; Hedhili, M. N.; Basset, J. M.; Bakr, O. M. A New Class of Atomically Precise, Hydride-Rich Silver Nanoclusters Co-Protected by Phosphines. *J. Am. Chem. Soc.* **2016**, *138* (42), 13770–13773.

(57) Deng, G.; Teo, B. K.; Zheng, N. Assembly of Chiral Cluster-Based Metal-Organic Frameworks and the Chirality Memory Effect during Their Disassembly. *J. Am. Chem. Soc.* **2021**, *143* (27), 10214–10220.

(58) Liang, X. Q.; Li, Y. Z.; Wang, Z.; Zhang, S. S.; Liu, Y. C.; Cao, Z. Z.; Feng, L.; Gao, Z. Y.; Xue, Q. W.; Tung, C. H.; Sun, D. Revealing the Chirality Origin and Homochirality Crystallization of Ag₁₄ Nanocluster at the Molecular Level. *Nat. Commun.* **2021**, *12* (1), 4966.

(59) Wang, Z. Y.; Wang, M. Q.; Li, Y. L.; Luo, P.; Jia, T. T.; Huang, R. W.; Zang, S. Q.; Mak, T. C. W. Atomically Precise Site-Specific Tailoring and Directional Assembly of Superatomic Silver Nanoclusters. *J. Am. Chem. Soc.* **2018**, *140* (3), 1069–1076.

(60) Yadav, V.; Jana, A.; Khatun, M.; Nagar, H.; Lebedkin, S.; Mondal, A.; Acharya, S.; Malola, S.; Antharjanam, S.; Egor, M.; Ghosh, P.; Base, T.; Kappes, M.; Häkkinen, H.; Pradeep, T. Isomeric Ag₁₄ Nanoclusters With Distinct Photophysical and Nanomechanical Properties. *Adv. Sci.* **2026**, e76657.

(61) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561.

(62) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.

(63) Walter, M.; Akola, J.; Lopez-acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ha, H.; Ackerson, C. J.; Whetten, R. L.; Nbeck, H. G.; Häkkinen, H. A Unified View of Ligand-Protected Gold Clusters as Superatom Complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (27), 9157–9162.

(64) Dong, X. Y.; Si, Y.; Yang, J. S.; Zhang, C.; Han, Z.; Luo, P.; Wang, Z. Y.; Zang, S. Q.; Mak, T. C. W. Ligand Engineering to Achieve Enhanced Ratiometric Oxygen Sensing in a Silver Cluster-Based Metal-Organic Framework. *Nat. Commun.* **2020**, *11* (1), 3678.

(65) Zhu, C.; Xin, J.; Li, J.; Li, H.; Kang, X.; Pei, Y.; Zhu, M. Fluorescence or Phosphorescence? The Metallic Composition of the Nanocluster Kernel Does Matter. *Angew. Chem., Int. Ed.* **2022**, *134* (31), e202205947.

(66) Jana, A.; Jash, M.; Dar, W. A.; Roy, J.; Chakraborty, P.; Paramasivam, G.; Lebedkin, S.; Kirakci, K.; Manna, S.; Antharjanam, S.; Machacek, J.; Kucerakova, M.; Ghosh, S.; Lang, K.; Kappes, M. M.; Base, T.; Pradeep, T. Carborane-Thiol Protected Copper Nanoclusters: Stimuli-Responsive Materials with Tunable Phosphorescence. *Chem. Sci.* **2023**, *14*, 1613–1626.

(67) Mitsui, M.; Arima, D.; Uchida, A.; Yoshida, K.; Arai, Y.; Kawasaki, K.; Niihori, Y. Charge-Transfer-Mediated Mechanism Dominates Oxygen Quenching of Ligand-Protected Noble-Metal Cluster Photoluminescence. *J. Phys. Chem. Lett.* **2022**, *13* (40), 9272–9278.

(68) Luo, Z.; Gamboa, G. U.; Smith, J. C.; Reber, A. C.; Reveles, J. U.; Khanna, S. N.; Castleman, A. W. Spin Accommodation and Reactivity of Silver Clusters with Oxygen: The Enhanced Stability of Ag₁₃. *J. Am. Chem. Soc.* **2012**, *134* (46), 18973–18978.

(69) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(70) Yang, Y.; Ostrowski, D. P.; France, R. M.; Zhu, K.; Van De Lagemaat, J.; Luther, J. M.; Beard, M. C. Observation of a Hot-Phonon Bottleneck in Lead-Iodide Perovskites. *Nat. Photonics* **2016**, *10*, 53–59.