

Dithiol-Induced Contraction in Ag₁₄ Clusters and Its Manifestation in Electronic Structures

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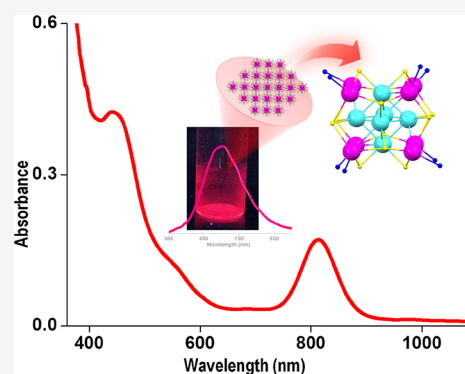


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ABSTRACT: We report a dithiol-protected silver cluster, Ag₁₄(BDT)₆(PPh₃)₈ (BDT = 1,2-benzene dithiol), abbreviated as Ag₁₄DT, which exhibits distinctly different optical properties than the analogous monothiol-protected Ag₁₄(SC₆H₃F₂)₁₂(PPh₃)₈, abbreviated as Ag₁₄MT. Replacement of monothiol by dithiol, keeping the composition constant, has not been possible so far. The inner cores of both Ag₁₄DT and Ag₁₄MT are composed of octahedral Ag₆, but because of the presence of dithiol, the outer cubic Ag₈ shell became distorted in the former. Consequently, Ag₁₄DT showed a unique absorption in the near-infrared (NIR) region, which is mainly due to transitions derived from ligands. It exhibits dual visible/NIR emission, at around 680 and 997 nm. Ag₁₄DT exhibited greater thermal stability because of the rigidity provided by dithiol ligands. The clusters with NIR absorption and emission open up a possibility for their application in solar thermal conversion and medical imaging. NIR luminescence in the range of 1000 nm in ultrasmall clusters is very new.



INTRODUCTION

Surface ligands play a pivotal role in directing the structures of atomically precise nanoclusters (NCs).^{1–6} For years, researchers have been studying the effect of surface ligands on tuning the structure and properties of silver clusters. The availability of single crystal structures provides us with opportunities to study the structure–property relationships in greater detail, and such studies are further enriched by computations.^{7–11} The use of different ligands resulted in the formation of varying silver NCs of different atomicity, namely, Ag₂₅(SPhMe₂)₁₈, Ag₂₉(BDT)₁₂(TPP)₄ (BDT = 1,3-benzene dithiol), Ag₄₄(SR)₃₀ (SR = *p*-fluorothiophenol, *p*-mercaptobenzoic acid), and so forth.^{12–16} Sometimes, the same ligand results in the formation of different NCs depending on the synthetic conditions, such as Ag₂₉(BDT)₁₂(TPP)₄ and Ag₅₁(BDT)₁₉(TPP)₃, which were coprotected by BDT and TPP(PPh₃) ligands.¹⁷ A small change in the structure of the ligand can change the nuclearity of NCs.¹⁸ For example, two isomers of DCBT (dichlorobenzenethiol), namely, 2,4-dichlorobenzenethiol and 2,5-dichlorobenzenethiol, resulted in two different NCs, Ag₄₄(2,4-DCBT)₃₀ and Ag₅₉(2,5-DCBT)₃₂, respectively, under similar conditions.¹⁹ Also, our recent report showed the formation of a single silver cluster, Ag₄₆(SPhMe₂)₂₄(TPP)₈, using 2,5-DMBT (DMBT = dimethylbenzenethiol), while the isomeric thiol, 2,4-DMBT produced a cocrystal, composed of Ag₄₀(DMBT)₂₄(PPh₃)₈ and Ag₄₆(DMBT)₂₄(PPh₃)₈.²⁰ The origin of properties of NCs has been studied for long, among which the evolution of photoluminescence (PL) has

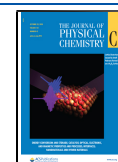
been studied extensively.^{6,21–23} Among the silver NCs reported so far, Ag₁₄(SC₆H₃F₂)₁₂(TPP)₈ is the first crystallized silver NC as per previous references to journals and books.^{8,24,25} Interestingly, it exhibits yellow emission (with a peak maximum at 536 nm).²⁵ The cluster contains an octahedral Ag₆ metal core. Recently, Ag₁₄ was used as a building block to create cluster-based metal–organic frameworks (MOFs).²⁶

Increase in denticity of the ligands increases the structural rigidity of inorganic complexes, which enhances their stability. Replacement of monothiol by dithiols in NCs can enhance the electronic confinement which would be reflected in optical properties. Ligand reconstruction also promoted the formation of NC-based MOFs, which exhibit interesting properties.²⁷ Furthermore, the change in the protecting ligand can vary the properties of NCs keeping their structures unaltered as in the case of Au₂₂(SG)₁₈. Surface engineering of this cluster resulted in 60% enhancement in PL quantum yield.²⁸ Other properties such as chirality, catalytic activity, and reactivity can also be tuned via surface ligand modifications.^{29–34}

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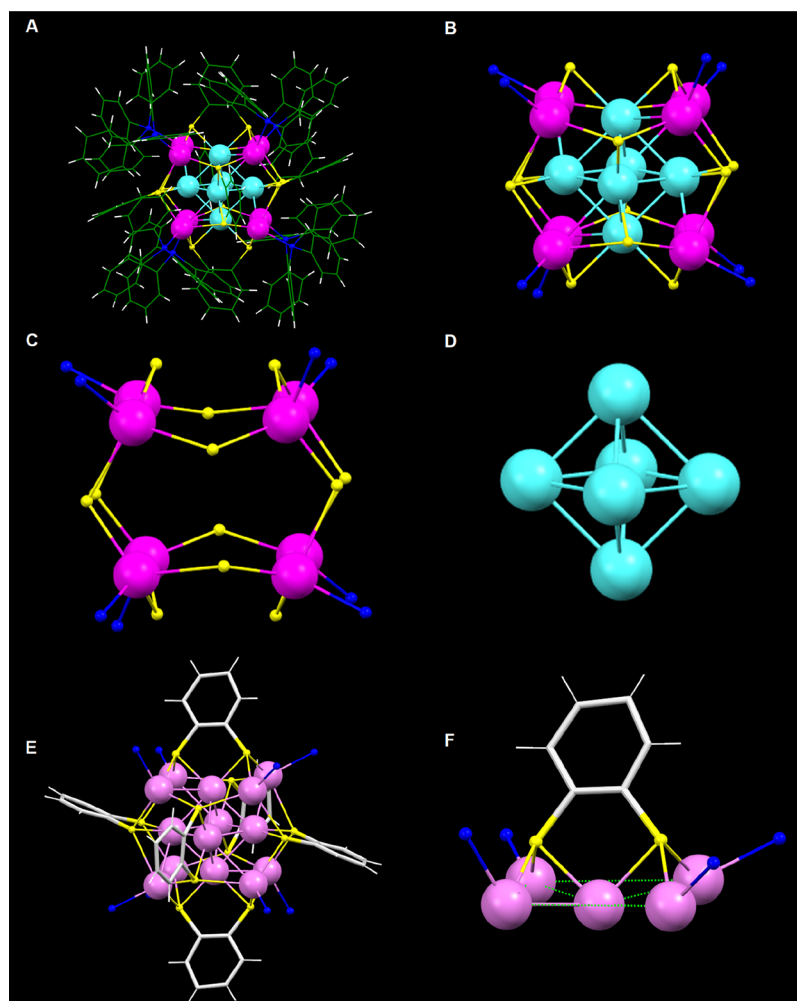


Figure 1. Structural anatomy of Ag_{14}DT clusters. (A) Full structure of Ag_{14}DT . (B) Structure of $\text{Ag}_{14}\text{S}_{12}\text{P}_8$ and (C) cubic shell of $\text{Ag}_8\text{S}_{12}\text{P}_8$. (D) Octahedral Ag_6 inner core. (E) Structure of the unit, $\text{Ag}_{14}(\text{BDT})_6\text{P}_8$. Six faces cover the inner core. One such face is shown in (F). Color code: cyan, magenta, and violet, silver; yellow, sulfur; blue, phosphorous; green, carbon; and grey, hydrogen.

In this paper, we investigate the structure–property relationship between dithiol and monothiol protection in a given cluster core, namely, $\text{Ag}_{14}(\text{BDT})_6(\text{TPP})_8$ and $\text{Ag}_{14}(\text{SC}_6\text{H}_3\text{F}_2)_{12}(\text{TPP})_8$, labeled as Ag_{14}DT and Ag_{14}MT , respectively. We observed that the dithiol (BDT) changes the outer cubic shell structure of the NC and further confines the inner Ag_6 octahedral core. This structural confinement leads to the improvement in optical properties. Introduction of dithiols convert singly emissive Ag_{14}MT to dual emissive Ag_{14}DT . Ligands of this kind can be handy to enhance photophysical properties of many clusters. Incorporation of such ligands enables strong supramolecular interactions, such as $\pi\cdots\pi$ stacking, which were absent in the previously reported Ag_{14} cluster.²⁵ The structure of Ag_{14}DT was determined by single crystal X-ray diffraction (SCXRD), and the composition was confirmed by scanning electron microscopy (SEM)/energy-dispersive analysis (EDS) and elemental analysis measurements. New electronic properties were observed as evidenced from the calculations. A density functional theory (DFT) calculation was performed to obtain deep insights into the electronic structures of Ag_{14}DT . Partial density of states (PDOS) was calculated to analyze the origin of electronic transitions. Further, superatomic orbital calculation revealed that the cluster is a 2e superatom with the electronic

configuration, 1S^2 . Our findings will enhance activities in the area of dithiol-protected NCs leading to their diversity in properties.

EXPERIMENTAL SECTION

Materials. Silver nitrate was bought from Rankem. Sodium borohydride and 1,2-benzene dithiol (BDT) were bought from Sigma-Aldrich. Triphenylphosphine (TPP) was bought from Spectrochem Chemicals. Dichloromethane (DCM), methanol (MeOH), *n*-hexane, and chloroform (CHCl_3) were bought from Rankem and are of analytical grade. Milli-Q water was used for the synthesis.

Instrumentation. Optical absorption measurements were performed in a PerkinElmer Lambda 25 UV–vis spectrophotometer.

A Horiba Jobin Yvon Nanolog spectrometer was used for the PL measurements. The excitation and the emission band pass were set at 3 nm.

SEM and EDS were performed using an FEI QUANTA-200.

SCXRD were measured using a Bruker Kappa APEX III CMOS diffractometer. $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) was used as a source of radiation. Indexing was done by APEX III.

Elemental analysis was done by LECO CS744 and LECO ONH 836 analyzers.

Synthesis and Purification of $[\text{Ag}_{18}\text{H}_{16}(\text{TPP})_{10}]^{2+}$. It was prepared by a known method.^{35,36} 20 mg of silver nitrate was taken in 5 mL of methanol by sonication, and 10 mL of CHCl_3 was added. Then, 70 mg of TPP was mixed to the reaction mixture under stirring condition. After 20 min of stirring, 5.5 mg of cold aqueous solution of sodium borohydride was added. On addition of the reducing agent, the color of the reaction mixture became yellow. The reaction was carried out for 3 h. After 3 h of stirring, it became dark green that confirms the production of the material. Solvents were evaporated under reduced pressure. The solid green material was cleaned several times with water. Then, it was extracted by MeOH to avoid excess phosphine. This green colored material was used for characterization and further reaction.

Synthesis and Purification of $[\text{Ag}_{14}(\text{BDT})_6(\text{PPh}_3)_8]$. The cluster was synthesized by a ligand exchange induced size/structural transformation methodology.^{20,37} Here, $[\text{Ag}_{18}(\text{PPh}_3)_{10}\text{H}_{16}]^{2+}$ was used as a precursor and reacted with 1,2-BDT. 5 mg of $[\text{Ag}_{18}(\text{PPh}_3)_{10}\text{H}_{16}]^{2+}$ was taken in MeOH as a precursor. 1 μL of 1,2-BDT was mixed to the methanolic solution. After adding dithiol, it became brown, and the reaction was continued for 6 h. The reaction mixture was centrifuged, and in the centrifugate, a brown color precipitate was observed. The precipitate was cleaned 2–3 times with MeOH and dissolved in DCM. This solution in DCM was used for further characterizations.

Crystallization Technique. Cleaned 20–30 mg of the material was taken in distilled DCM and filtered by 0.22 μm syringe filter paper. Then, it was layered by distilled hexane (1:1) and kept at 4 $^\circ\text{C}$. After approximately one week, square shape reddish yellow crystals were observed which were suitable for single crystal X-ray crystallography.

Computational Methods. The structural, electronic, and optical properties of the Ag_{14} cluster were investigated computationally by DFT as implemented in the GPAW (grid-based projector-augmented wave method) software package.^{38,39} The chosen GPAW PAW-setups for each element of the cluster's constituent atoms had the valence electronic configurations given in brackets as follows, Ag ($4d^{10}5s^1$), S ($3s^23p^4$), P ($3s^23p^3$), C ($2s^22p^2$), and H ($1s^1$), and scalar-relativistic effects were included for the Ag atoms.

The simulation cell was a cubic box of side 22 $\text{\AA}$, and a grid spacing of 0.2 $\text{\AA}$ was used in real-space finite-difference mode of GPAW. The geometry optimization was carried out with the convergence condition that the forces acting on atoms should be less than 0.05 eV/ $\text{\AA}$ and without imposing any symmetry constraints. All calculations were performed using the Perdew–Burke–Ernzerhof exchange–correlation functional.⁴⁰ The initial geometry of the Ag_{14} cluster for the ground-state optimization was extracted from the atomic coordinates of the unit cell of the crystal structure, and the optimization was performed with complete ligands. The ground-state electronic structure of the optimized cluster structure was characterized by calculating and plotting the molecular orbitals (MOs). The total density of states (TDOSs) and PDOSs were calculated and plotted, and the superatom character of the MOs was analyzed on the basis of the PDOS and also the influence of ligand atomic orbitals (AOs) on the overall electronic structure of the cluster. The absorption spectrum was calculated using linear response time-dependent density functional theory (LR-TDDFT), and the corresponding ground state MOs involved in the optical transitions were identified and plotted.

RESULTS AND DISCUSSION

The cluster was crystallized in a trigonal unit cell with the space group, $R\bar{3}$. Structural refinement showed that the R_{int} value is higher than that of usual small molecule structures. This is due to weak diffraction of the crystals, and the conclusions drawn are meaningful. The molecule is having an inversion and a 3-fold rotational symmetry. SCXRD showed that the molecular formula of the cluster is $[\text{Ag}_{14}(\text{BDT})_6(\text{PPh}_3)_8]$. The full structure of Ag_{14}DT is presented in Figure 1A. Figure 1B shows the structure after removal of C and H. The structural anatomy suggests its atomic structure to consist of an inner octahedral (Ag_6) core, in which H is surrounded by a distorted cubic (Ag_8) shell. This cubic shell and inner octahedral core are presented in Figure 1C,D, respectively. The Ag–Ag distance in the Ag_6 core is 2.7 $\text{\AA}$ and the same for the Ag_8 cube is 4.5 $\text{\AA}$ as they are linked through S. This indicates that the interactions of silver atoms in the inner core are stronger than in the shell. The six faces of the cubic shell are protected by dithiol moieties (Figure 1E). One such face is shown in Figure 1F. Dithiol ligands pull the corner atoms of the cubic Ag_8 shell closer. Due to this, the edge length and the diagonal distances of the cube get shortened compared to Ag_{14}MT . The centroids of benzene groups of dithiol can be seen as they are placed at the six vertices of an octahedron, as shown in Figure S1A. The edges of the octahedron are shown in green dotted lines. Along with the primary protecting layer, the vertex of the cube is connected by eight PPh_3 ligands. The distortion in the cubic shell is due to the strain on the sulfur atoms. The presence of dithiol ligands shortened the S–Ag–S bond angle. In the case of Ag_{14}DT , the bonding of the Ag_6 core and the sulfur atoms showed an S–Ag–S bond angle of 91.03° , whereas in the case of Ag_{14}MT , it is 119.7° (Figure S1B). This change in bond angle makes a distortion in the cubic shell. The inner-shell silver atoms are coordinated to two thiolates, but in the outer-shell, some of the silver atoms are coordinated with two and the rest are coordinated with three thiolates. These different environments of silver atoms are presented in Figure S2. Hence, the inner-shell silver atoms are strongly interacting with sulfur atoms with an average Ag–S bond length of 2.50 $\text{\AA}$, and it is shorter by 0.17 $\text{\AA}$ than the previous report.²⁵ In contrast, the 2-coordinated Ag–S distances are between 2.55 and 2.66 $\text{\AA}$, and it is longer by 0.10 $\text{\AA}$ than the inner shell. Further, the 3-coordinated Ag atoms with sulfur have an average distance of 2.89 $\text{\AA}$ which shows weaker interactions. As a result of this, the interaction of the PPh_3 ligands is anisotropic on the vertices of the Ag_8 cube. The average Ag–P bond distance is 2.47 $\text{\AA}$. Phosphine ligands bound at 3-coordinated silver atoms is shorter than those bound with 2-coordinated silver atoms. The packing arrangement of Ag_{14}DT shows that there are two molecules in a unit cell. A comparison of unit cell parameters of Ag_{14}DT and Ag_{14}MT is shown in Figure S3. In Ag_{14}DT , the clusters are connected by $\pi\cdots\pi$ interactions of the BDT ligands (Figure S4). As Figure S4 showed, these interactions can also be looked as zigzag structures. The distances between these interactions are ranging from 2.9 to 3.2 $\text{\AA}$. Due to the interlocking of the ligands, the interparticle distance got reduced to 1.7 nm, whereas the overall size of the cluster is 1.9 nm.⁴¹ The octahedron formed by the centroids of the benzene dithiol groups clearly shows the direction of $\pi\cdots\pi$ interactions (red dotted lines in Figure S5A). On the other hand, in Ag_{14}MT , the $\pi\cdots\pi$ interactions are observed in a cluster, and

the clusters have C–H $\cdots\pi$ interactions in the unit cell. Hence, the nature of ligands whether it is dithiol or monothiol is crucial in dictating the nature of supramolecular interactions which determine the packing of the crystal. Along the (001) plane (view from the Z axis), Ag₁₄DT is arranged in a hexagonal lattice where a 3-fold rotational axis passes through the center of the cluster. Along the (100) and (010) planes (viewed from X and Y axes, respectively), NCs are arranged in a rectangular lattice. Moreover, along the Z axis, NCs are assembled along two parallel (00–1) and (001) planes. Every NC on these planes possesses a center of symmetry.

To confirm the elements present in the cluster, SEM/EDS was performed. It showed the presence of Ag, S, P, and C which is consistent with the single crystal X-ray structure. In order to check the homogeneity of the elements in the crystal, EDS mapping was performed, as shown in Figure S6. CHS elemental analysis was also performed to confirm the composition (Table S3), and it showed good agreement with calculation. Electrospray ionization was carried out in both the ion modes to get the molecular ion peak, but unfortunately, no peak was observed. This indicates the neutral charge of the cluster which was further supported by SCXRD as no counter ion was observed. The cluster solution in DCM showed molecule-like transitions in the UV–vis spectrum. The most intense peak was observed at 425 nm with a broad hump around 600 nm. Along with these features, it had a strong absorption in the near-infrared (NIR) region, centered on 860 nm (Figure 2). The Ag₁₄DT cluster showed dual visible/NIR

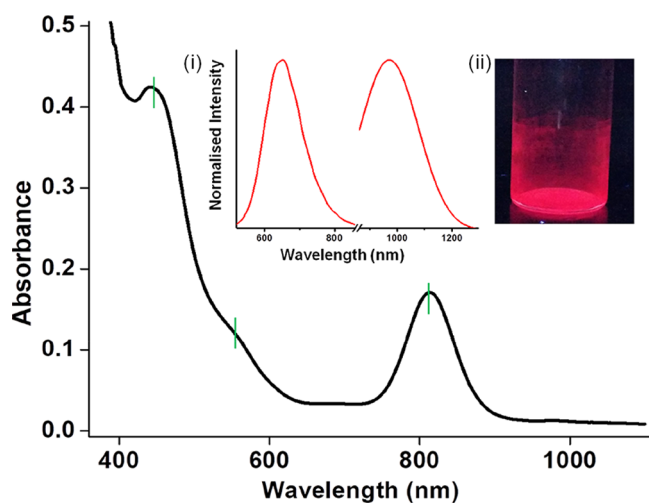


Figure 2. Optical absorption spectrum of Ag₁₄DT dissolved in DCM. Inset (i) shows the PL spectrum of Ag₁₄DT. It exhibits dual visible/NIR emission. The visible and NIR spectra were taken with two detectors, with the same sample. Inset (ii) the photograph of the crystals of Ag₁₄DT under UV light.

PL. These emissions were around 680 and 997 nm, upon excitation at 365 and 860 nm, respectively (inset (i) of Figure 2). Ag₁₄MT was reported with yellow PL at 530 nm. It is worthy to note that the PL of Ag₁₄MT was stable for a few hours, but Ag₁₄DT was stable for a few days at room temperature. The difference in the optical properties of monothiol- and dithiol-protected Ag₁₄ clusters is likely to be due to the change in the ligand shell. The modification of the primary ligand shell alters the electronic structure of the cluster which resulted in new optical properties. Ag₁₄DT and Ag₁₄MT had comparable thermal stability at 40 °C, and their absorption

spectra were recorded as a function of time. After 1 h of heating, the UV–vis features of Ag₁₄MT started to change, and they disappeared almost completely after 2 h, whereas for Ag₁₄DT, there was a slight decrease in the absorbance but no change in the peak shape (Figure S7). This observation implied that Ag₁₄DT is thermally more robust than Ag₁₄MT. This is due to the presence of dithiol which provides more rigidity to the ligand shell.

The electronic and optical properties of Ag₁₄DT were computed by taking the atomic coordinates from the crystal structure as the starting point. The optimized structure of Ag₁₄DT cluster in the reduced form is presented in Figure S8. Bader charge analysis (Table S1) showed that silver atoms in the inner shell accumulate lower positive charges (0.170e) than in the outer shell (0.294e). This analysis proved that the inner shell silver atoms are more confined than the outer shell. The optical absorption spectrum of [Ag₁₄(BDT)₆(P(CH₃)₃)₈] cluster was calculated using LR-TDDFT. A reduced ligand structure was used in the calculations. Theoretical and experimental UV–vis spectra are compared in Figure 3A. The theoretical spectrum shows two distinct peaks at 720 and 471 nm along with a shoulder at 545 nm. There are some shifts between the calculated and measured optical spectra. These shifts between theoretical and experimental spectra might be due to lack of exact coordinates for calculating the spectra of the cluster.⁴² The appearance or disappearance of some peaks might be due to the presence of distortions and intracuster interactions (between the organometallic complexes (AgS₃PPh₃) on the surface of the cluster) in the structure which may not have been properly accounted for in the computations.¹² Another reason for this discrepancy could be due to polymorphism and structural isomers in the solutions.

The new peak at 720 nm is due to the interaction of BDT ligands with the cluster which was not present in Ag₁₄MT. The MOs responsible for ground state electronic structures are plotted which showed the respective MOs for each optical transition. The TDOS and PDOS were also calculated to study the influence of ligand AOs on the overall electronic structure of the cluster. The calculated highest-occupied molecular orbital (HOMO)–lowest-unoccupied molecular orbital (LUMO) gap was 1.72 eV. The peak at 720 nm arises from the transitions of HOMO – 1 and HOMO – 2 to LUMO. PDOS spectra showed that HOMO – 1 is mainly contributed by the 3p AOs of S, 4d AOs of Ag, and 2p AOs of (C), which contribute to some extent. Similarly, the LUMO is also made up of 3p (S), 4d (Ag), and 2p (C) (Figure 3B,C). Hence, the frontier orbitals are mainly influenced by the thiolate ligands, and therefore, the optical absorption is red-shifted than in Ag₁₄MT. The transition for the peak at 545 nm is taking place from HOMO – 8 to LUMO, and this transition is well buried into the valence band. HOMO – 8 is highly dominated by 3p (S) and 2p (C). Finally, the transition at 471 nm takes place from HOMO – 5 to LUMO + 2. HOMO – 5 is mainly contributed by 3p (S), 5s (Ag), 4d (Ag), and 2p (C), while the LUMO + 2 is dominated by 5s (Ag).

In order to understand the contribution of the inner core and outer shell atoms to the optical properties, we have calculated PDOSs of the inner core and outer shell of the Ag₁₄ cluster. This helped us to identify the MOs responsible for optical properties. It is evident from Figure S9 that the MOs responsible for transitions are populated mainly from the outer shell. Thus, the outer shell which is composed of the Ag₈S₁₂ framework is responsible for the optical transition. Introduc-

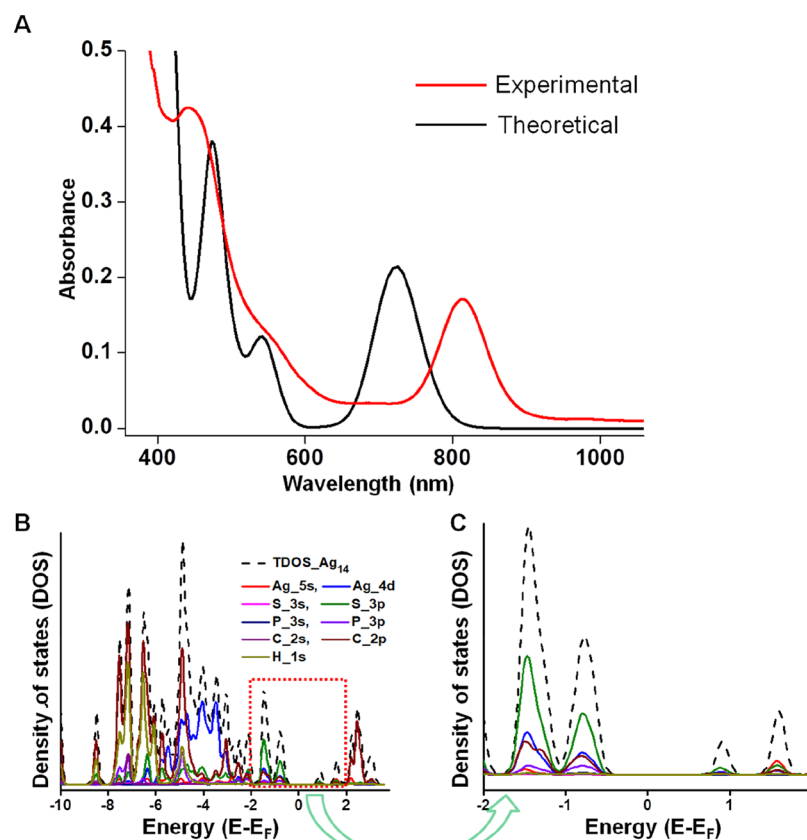


Figure 3. (A) Comparison of the experimental UV-vis spectrum (red trace) with the predicted one (black trace). Inset shows theoretical and experimental PL spectra. (B) TDOSs and PDOSs. HOMO–LUMO gap was kept at zero energy. (C) Expanded view of the selected region of (B).

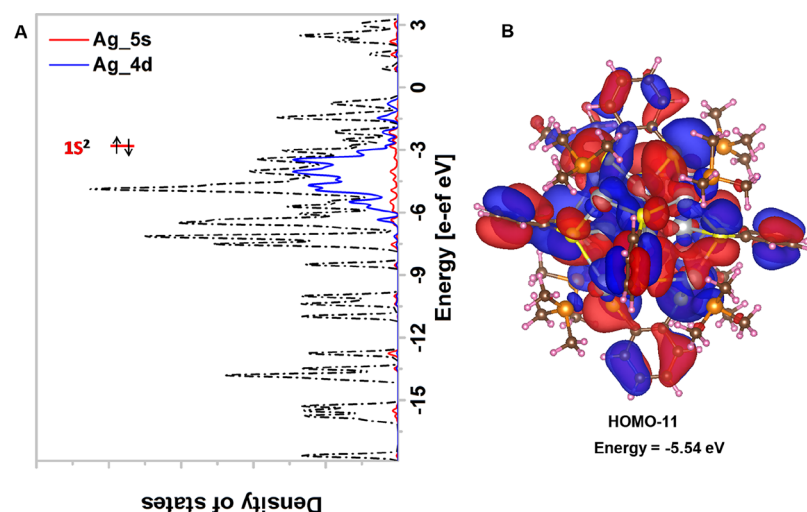


Figure 4. (A) Plot of density of states vs energy of Ag₁₄DT. Dotted lines correspond to the total density of states. Blue and red solid lines indicate the density of states of Ag_{5s} and Ag_{4d}, respectively. (B) Isosurface of the superatomic orbital (1S) and its energy.

tion of benzenedithiol enhances intraligand interactions. Seemingly, there are possibilities of ligand–metal and metal–ligand charge transfer during excitation which affects the emission property.

According to the electron counting rule, the number of free electrons in the cluster is given by $14 - 12 = 2$, which is a superatom configuration. The superatom character of Ag₁₄ cluster is shown in Figure 4. The configuration is 1S², and the superatomic orbital is made up of HOMO – 11 which has S character with the delocalized electron density. It is noted that

the 1P superatomic orbital is empty. Therefore, the optical transition takes place between 1S and 1P superatomic orbitals.

CONCLUSIONS

In summary, we present a structural analogue of Ag₁₄MT, namely, Ag₁₄DT, composed of a core of the same nuclearity, protected with monothiol and dithiol, respectively. Structural details of Ag₁₄DT were obtained by SCXRD which revealed the effect of ligands in the optical properties of NCs having

similar structures and compositions. Unlike the case of Ag_{14}MT which was reported previously, Ag_{14}DT possesses NIR absorption and emission which could be useful in various applications. DFT and PDOS calculations helped us to understand the electronic structures of Ag_{14}DT in greater detail. The large changes in optical properties are brought about by the subtle changes in ligands. Such changes can be very much useful for a whole range of cluster systems which are known now. This study shows the possibility of synthesizing clusters protected by new dithiols with exciting properties. We believe that dithiol-protected clusters can create a new avenue in cluster-assembled solids, and new explorations leading to new properties are likely from future research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c07140>.

Additional measurements of optical spectroscopy, SEM, elemental analysis, Bader charge analysis, and crystal structure refinement (PDF)

Crystallographic data for $\text{Ag}_{14}\text{-3}$ (CIF)

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Notes

The authors declare no competing financial interest.

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