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Light-Activated Intercluster Conversion of an Atomically Precise Silver Nanocluster

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anes, a 12-vertex, nearly icosahedral boron–carbon framework system, have received immense attention due to their different physicochemical properties. We have synthesized *ortho*-carborane-1,2-dithiol (CBDT) and triphenylphosphine (TPP) coprotected $[Ag_{42}(CBDT)_{15}(TPP)_4]^{2-}$ (shortly Ag_{42}) using a ligand-exchange induced structural transformation reaction starting from $[Ag_{18}H_{16}(TPP)_{10}]^{2+}$ (shortly Ag_{18}). The formation of Ag_{42} was confirmed using UV–vis absorption spectroscopy, mass spectrometry, transmission electron microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and multinuclear magnetic resonance spectroscopy. Multiple UV–vis optical absorption features, which exhibit characteristic



patterns, confirmed its molecular nature. Ag₄₂ is the highest nuclearity silver nanocluster protected with carboranes reported so far. Although these clusters are thermally stable up to 200 °C in their solid state, light-irradiation of its solutions in dichloromethane results in its structural conversion to $[Ag_{14}(CBDT)_6(TPP)_6]$ (shortly Ag_{14}). Single crystal X-ray diffraction of Ag_{14} exhibits Ag_8-Ag_6 core-shell structure of this nanocluster. Other spectroscopic and microscopic studies also confirm the formation of Ag_{14} . Time-dependent mass spectrometry revealed that this light-activated intercluster conversion went through two sets of intermediate clusters. The first set of intermediates, $[Ag_{37}(CBDT)_{12}(TPP)_4]^{3-}$ and $[Ag_{35}(CBDT)_8(TPP)_4]^{2-}$, were formed after 8 h of light irradiation, and the second set comprised of $[Ag_{30}(CBDT)_8(TPP)_4]^{2-}$, $[Ag_{26}(CBDT)_{11}(TPP)_4]^{2-}$, and $[Ag_{26}(CBDT)_7(TPP)_7]^{2-}$ were formed after 16 h of irradiation. After 24 h, the conversion to Ag_{14} was complete. Density functional theory calculations reveal that the kernel-centered excited state molecular orbitals of Ag_{42} are responsible for lightactivated transformation. Interestingly, Ag_{42} showed near-infrared emission at 980 nm (1.26 eV) with a lifetime of >1.5 μs , indicating phosphorescence, while Ag_{14} shows red luminescence at 626 nm (1.98 eV) with a lifetime of 550 ps, indicating fluorescence. Femtosecond and nanosecond transient absorption showed the transitions between their electronic energy levels and associated carrier dynamics. Formation of the stable excited states of Ag_{42} is shown to be responsible for the core transformation.

KEYWORDS: carboranes, silver nanoclusters, intercluster conversion, near-infrared emission, luminescence, ultrafast electron dynamics

INTRODUCTION

Atomically precise nanoclusters (NCs) of noble metals with core dimension <3 nm, composed of a few tens to hundreds of atoms, are an emerging class of nanomaterials with specific properties, which represent a distinct category of materials between atoms and traditional nanoparticles.^{1,2} Different noble metal based NCs, especially of gold, silver, copper, and platinum, protected by various types of surface ligands such as thiols, imine-thiols, phosphines, alkynes, sulfonates, DNAs, proteins, etc., have been synthesized by following different synthetic protocols.^{3–13} Among different noble metal NCs,

gold NCs have been prominent due to their facile synthesis and stability. Although silver NCs are reported less commonly, perhaps due to their higher reactivity, they have received increasing attention recently due to their functional proper-

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Figure 1. Synthesis and characterizations of Ag_{42} NC. (a) Molecular structure of the *ortho*-carborane 1,2-dithiol ligand. Color code for atoms: pink = boron, gray = carbon, yellow = sulfur, blue = hydrogen. (b) Time-dependent UV-vis absorption spectra of Ag_{42} NC in DCM indicating its stability. (inset) Photograph of the respective DCM solution. (c) Full range negative ion-mode ESI-MS spectrum of Ag_{42} NC. Two TPP losses were observed from the parent NC which are shown by the \Rightarrow symbols. (inset) Exact matching of the isotopic distribution of the experimental and theoretical spectra. (d) Systematic losses of four TPP were observed from the peak at m/s 4337.11 with a charge state of 2– up to CE 30. (inset left) Schematic representation of TPP losses. (e) Fourteen sequential mass losses of carborane (C₂B₁₀H₁₀, M 142) units, along with a few silver sulfide loss peaks (marked as \Rightarrow). (inset right) Schematic representation of carborane losses.

ties.¹⁴ Therefore, it is of interest to explore a family of stable silver NCs with tunable properties. Various physicochemical properties such as narrow energy gap and associated multiple electronic transitions, luminescence, chirality, etc., have been used in numerous fields, including optoelectronics, nanosensors, nonlinear optics, circularly polarized luminescence, and nanocluster sensitized solar cells, etc.¹⁵⁻²² Different silver NCs have been characterized through mass spectrometric studies. However, some of them, such as Ag₆, Ag₉, Ag₂₅, Ag₂₉, Ag44, Ag56, Ag67, and Ag141, etc., with specific ligand structure and overall charge, have also been characterized structurally using single crystal X-ray diffraction.^{23–30} Some recent studies have also reported synthesis and structural characterization of bimetallic and polymetallic NCs following coreduction of mixed metal precursors and intercluster reactions.³¹⁻³³ Different transition metal-doped silver NCs, especially Ti and Cd, with varying numbers of dopant atoms showed different electronic features in comparison to the undoped ones.^{34,35}

During crystallization of nanoclusters, more than one silver NC was crystallized within the same unit, forming cocrystals, such as $Ag_{16}-Ag_{17}$, $Ag_{40}-Ag_{46}$, $Ag_{210}-Ag_{211}$, etc.^{36–38} A detailed understanding of their synthesis, and associated structures, and properties has become an important research direction.

Synthesis of specific nuclearity silver NCs with high purity is always challenging. Many factors such as pH, solvent, temperature, and ligand have profound roles in regulating nuclearity, shape, and surface activity of NCs.^{39,40} Along with conventional coreduction of metal thiolates, other unconventional synthetic strategies such as solid-state gel-based mechanical grinding, microwave irradiation, and ligand exchange induced size focusing as well as fast purification using desalting column techniques were employed to scale up as well as purify NCs.^{41–44} Shape tuning of nanoclusters based on their sensitivity or reactivity to an external solvent environment is possible, resulting in changes in the cluster core and composition.^{45,46} Different photoirradiation methods



Figure 2. Structural studies and thermal stability of Ag_{42} NC. (a) DFT optimized structure of Ag_{42} NC. Atomic color code: blue = inner core Ag atoms, dark pink = outer core Ag atoms, green = phosphorus, pink = boron, yellow = sulfur, gray = carbon, white = hydrogen. (b) Comparison between theoretical and experimental UV-vis absorption spectra. (inset) Electron density map of kernel-centered LUMO + 6. (c) Large area TEM micrograph showing Ag_{42} NCs. (inset) EDS spectrum from such an area. (d) Thermogravimetric and differential thermal analysis data showing thermal stability up to 200 °C. The maximum mass change occurs at 315 °C.

are of interest due to their simplicity and effectiveness in shape engineering.⁴⁷ Various light sources such as UV lamps, sunlight, light emitting diodes (LEDs), fluorescent lamps, and lasers have been used for shape-tuning of nanoparticles and associated properties.^{48,49} We have shown sunlightmediated synthesis of stable silver nanoclusters in a gel matrix.⁵⁰ Although light-induced size growth was observed in gold nanoclusters, there has been no report of light-activated intercluster conversion of silver nanoclusters.⁵¹ In view of the light sensitivity of silver nanostructures, we hypothesized that light may trigger the interconversion of NCs.

Carboranes (dicarba-*closo*-dodecaboranes of general formula $C_2B_{10}H_{12}$) are 12-vertex, nearly icosahedral carbon, and boron cage molecules with electrons delocalized over the molecular framework of CH and BH vertices as well as within the cage.⁵² These types of molecules are promising candidates for synthesizing stable silver NCs with tunable electronic properties. Due to their rigid and robust three-dimensional architectures, chemical, and thermal stability as well as electronic structure, they possess an enormous potential to become key constituents of luminescent polymer materials, catalysts, hypergolic materials, surface-supported self-assembled entities, light-driven molecular nanomachines, etc.^{53–58} Their tunable dipole moment and 3D pseudoaromatic character make carboranes' electronic properties

tunable, unlike other organic counterparts.⁵⁹ There are a few reports of carborane-based metal nanoclusters and their extended framework solids (EFSs) with luminescence properties, but reports on the synthesis of higher nuclearity NCs are rare due to their poor stability and other synthetic limitations.^{60–62}

In this work, we report the synthesis of Ag₄₂ nanoclusters coprotected by ortho-carborane-1,2-dithiol (CBDT), and triphenylphosphine (TPP) ligands through the ligandexchange induced structural transformation (LEIST) protocol. The formation of Ag₄₂ was confirmed using different microscopic and spectroscopic studies. Although Ag₄₂ is thermally stable up to 200 °C, it undergoes light-activated intercluster conversion to $[Ag_{14}(CBDT)_6(TPP)_6]$, through two sets of intermediate NCs. Single crystal X-ray diffraction (SC-XRD) confirmed the atomic structure of the as synthesized Ag_{14} . The Ag_{42} has a NIR emission centered around 980 nm, while as synthesized Ag₁₄ showed red luminescence at 626 nm. Although the luminescence of Ag₁₄ was weak at room temperature, there was >25-fold enhancement in emission with a slight red shift (17 nm) at 77 K. Timedependent density-functional theory (TDDFT) calculations revealed the nature of orbitals responsible for their electronic transitions. To further understand the electronic transition of both the NCs, we have used femtosecond and nanosecond

transient absorption (fs-ns TA) pump-probe measurements, which probed their excited state charge transfer and relaxation dynamics. The Ag₄₂ showed slow decay of excited state charge carriers (3.4 ± 0.6 and $24 \pm 1 \,\mu$ s for 576 nm and 5.7 ± 0.4 and 70 $\pm 10 \,\mu$ s for 685 nm), in comparison to fast (85 ± 9 ps for 565 nm) decay in Ag₁₄.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ag₄₂ NC. We have synthesized ortho-carborane-1,2-dithiol, and triphenylphosphine coprotected Ag₄₂ using a modified LEIST reaction from bipositively charged Ag₁₈ nanocluster protected with 10 TPP and 16 hydride ligands. Details of synthesis and characterization of Ag₁₈, which has been reported previously, are presented in the Supporting Information along with UVvis absorption and mass spectra (Figure S1).⁶³ Mass spectra of CBDT shown in Figure S2 exhibit characteristic isotopic distribution of the molecular ion at $m/z \sim 207.44$ and confirm its purity. A sequence of photographs showing the progression of the LEIST reaction is shown in Figure S3. In brief, following the addition of methanolic solution of CBDT to Ag₁₈, a white precipitate was formed initially. During the progress of the reaction, the precipitate got converted to a brown product in 4 h, indicating the formation of Ag_{42} .

It was first characterized using UV-vis absorption spectroscopy having a characteristic spectrum, as shown in Figure 1b. Three sharp absorption peaks at 688, 572, and 458 nm indicated the closely spaced molecule-like electronic states of the nanocluster. Absorption spectroscopic measurements of the cluster in different solvents (Figure S4) show characteristic spectral bands at 572 and 458 nm. We have observed broadening of the 572 nm peak in DMF and DMSO. The dipolar aprotic nature of these solvents, which leads to favorable interactions with the cluster, is the reason behind this spectral broadening. Long-term stability of the cluster was shown by identical UV-vis absorption features measured over a period of one year. Despite several attempts, we were unable to grow single crystals suitable for diffraction analysis. The grown black solids did not show prominent diffraction peaks in powder X-ray diffraction (Figure S5).

The molecular composition of the Ag₄₂ was confirmed using high-resolution electrospray ionization mass spectrometry (HR-ESI-MS). Detailed instrumentation conditions and sample preparation details are given in the SI. Figure 1c shows the full-range mass spectrum of Ag₄₂ in the negative ionmode, with a characteristic isotopic distribution envelope of a dianionic (2–) cluster centered at m/z 4337.11. A peak separation of m/z 0.5 confirms the charge state as 2–. As no monoanionic species was detected, we assume that the charge state in solution is 2-. A mass of 8674.22 was assigned to the cluster, $[Ag_{42}(CBDT)_{15}(TPP)_4]^{2-}$. Isotopic distribution of the experimental spectrum is in exact agreement with the simulated one. Two other fragments, and their characteristic isotopic envelopes at m/z 4205.67 and 4074.21 indicate sequential losses of 262 amu, corresponding to TPP. In order to gain additional experimental evidence on the composition, we have studied MS/MS fragmentation of the ions derived from the parent cluster by varying the collision energy (CE). Figure 1d and e show the MS/MS fragmentation patterns of Ag₄₂. The parent Ag₄₂ feature at m/z 4337.11 with 2– charge state was selected for the MS/MS fragmentation experiments. Sequential increase of CE from 0 to 30 (in instrumental units) led to four consecutive mass losses, each corresponding to one

TPP (262) unit, which indicates the presence of four weakly bound TPP molecules on the cluster surface. The DFT optimized structure (shown in Figure 2a, to be discussed below) also revealed weak binding of monodentate TPP ligands as a secondary shell through Ag-P bonds on the cluster. Increasing the CE from 30 to 150 did not yield any other fragmentation. At the CE of 150, a set of fragments belonging to carborane (C2B10H10, M 142) units started appearing, which indicate carborane loss from the NC. Further increase of the CE up to 300 showed a total of 15 mass losses of the carborane moiety. This is also supported by the previous results of desorption experiments and time-of-flight secondary ion mass spectrometry data of flat silver surfaces, both pointing at strong Ag-S bonds.^{64,65} Along with the systematic loss of carborane fragments, other peaks in the lower mass range, shown in Figure S6, indicate the detachment of different silversulfide motifs during fragmentation. Spectral analysis reveals the formation of a few smaller carborane-thiolate silver clusters at m/z 1580.82, 1158.96, and 736.28 with the composition of $[Ag_7(C_2B_{10}H_{10}S_2)_4]^-$, $[Ag_5(C_2B_{10}H_{10}S_2)_3]^-$, and $[Ag_3(C_2B_{10}H_{10}S_2)_2]^-$, respectively. A gradual decrease of the intensity of these clusters was observed at higher collision energies. Along with these cluster species, there were several fragmented peaks at m/z 143.27, 175.26, 217.25, 250.20, 314.08, 326.24, 359.40, 391.41, 457.31, and 499.30 assigned to $\begin{bmatrix} C_2 B_{10} H_{11} \end{bmatrix}^{-}, \begin{bmatrix} C_2 B_{10} H_{11} S \end{bmatrix}^{-}, \begin{bmatrix} Ag_2 H_2 \end{bmatrix}^{-}, \begin{bmatrix} Ag C_2 B_{10} H_{10} \end{bmatrix}^{-}, \begin{bmatrix} Ag C_2 B_{10} H_{10} S_2 \end{bmatrix}^{-}, \begin{bmatrix} Ag_3 H_3 \end{bmatrix}^{-}, \begin{bmatrix} Ag_2 (C_2 B_{10} H_{11} \end{bmatrix}^{-}, \\ \begin{bmatrix} Ag_2 (C_2 B_{10} H_{11} S) \end{bmatrix}^{-}, \begin{bmatrix} Ag (C_2 B_{10} H_{11} S) \\ \end{bmatrix}^{-}, and$ $[Ag_3(C_2B_{10}H_{11}S)]^-$, respectively. All of these peaks confirm the presence of different types of silver and CBDT arrangements present in the cluster.

In order to understand the structure, in the absence of single crystal data, theoretical modeling was undertaken. The optimized structure of Ag₄₂ NC is shown in Figure 2a, protected with both CBDT and TPP ligands. We started the optimization from [Ag₄₆(SPhMe₂)₂₄(TPP)₈]²⁺ NC, reported by the group by removing 4 silver atoms, 4 TPPs, and 24 thiolate ligands.³⁷ We have added 15 CBDT ligands to prepare a model of $[Ag_{42}(CBDT)_{15}(TPP)_4]^{2-}$. The optimized structure of Ag₄₂ has a distinct core with 28 silver atoms and a shell of 14 silver atoms (shown in Figure S7). The core is distorted in nature, having Ag–Ag bond distances in the range 2.77-3.10 Å. The distortion of the core is mainly due to the spatial confinement of carboranes. Furthermore, a large number of CBDT ligands create voids between them to adjust their positions, and consequently, the distribution of Ag atoms in the shell is not even. The binding of carborane ligands with the silver core is through AgS2, Ag2S, and Ag3S moieties, having Ag-S bond distances in the range 2.4-2.6 Å. The secondary TPP ligands bind with four Ag atoms with an average bond distance of 2.43 Å. The calculated UV-vis absorption features at 572 nm (shown in Figure 2b) match well with the experimental spectrum, indicative of an optimized structure. Density of states (DOS) calculations reveal that the absorption at 572 nm is due to the electronic transition from HOMOs (HOMO - 10 and HOMO - 9) having the energy of $-0.74\ eV$ to the LUMOs (LUMO + 5, LUMO + 6, and LUMO + 7) with the energy of 1.366, 1.43, and 1.576 eV, respectively (Figure S8a). Electron density plots show that the corresponding transitions are from ligandcentered HOMOs to kernel-centered LUMOs (shown in Figure 2b and S8b). We will come back to this aspect later in the text.



Figure 3. Studies of light-activated intercluster conversion. (a) Schematic representation of light-activated intercluster conversion of Ag_{42} to Ag_{14} through different intermediates. (b) UV-vis absorption spectra of both the NCs along with their mixed intermediate NCs. (inset) Photographic images of the color change during the light-irradiation. (c) Respective mass spectra showing the formation of intermediate nanoclusters during light exposure (each \Leftrightarrow indicates TPP ligand loss from the respective parent NCs).

The Ag_{42} was further characterized by TEM. TEM micrographs are shown in Figures 2c, S9, and they show uniform particles in between 1.2 and 1.5 nm, confirming their cluster size. Although electron beam-induced damage is common in such clusters, individual clusters were readily seen in such images, possibly due to the high thermal stability of the system. The EDS spectrum confirmed the presence of B, C, P, S, and Ag with their atomic concentrations (%) of 41.83, 51.41, 2.22, 1.68, and 2.86, respectively. To further understand ligand binding, we studied multinuclear NMR spectra of the NC in CDCl₃. The ¹¹B NMR spectrum shown in Figure S10 displays four peaks at -10.32, -7.45, -3.35, and 20.23 ppm, which can be assigned to four nonequivalent boron atoms of the carborane ligands. The broadness of the peaks is due to the high electron density of the metallic core close to the carborane molecule. Furthermore, ¹H-decoupled ¹³C NMR spectrum shown in Figure S11 exhibits two peaks at 53.45 and 58.49 ppm assigned to the carbon atoms of carborane ligands, along with several peaks characteristic of the TPP ligands in the range of 128.49-133.92 ppm. The ³¹P NMR spectrum in Figure S12 shows a broad peak at 5.31 ppm, indicating TPP binding to the NC, in contrast to a free TPP exhibiting a sharp ³¹P NMR signal at -5.66 ppm. XPS spectra of Ag₄₂ in Figure S13 show the binding energy values of Ag $3d_{5/2}$ and $3d_{3/2}$ to be 368.5 and 374.6 eV, respectively. These values are close to the typical values of Ag(0). Other characteristic binding energy values of 162.2, 189.5, 284.8, 131.5 eV were correlated with S 2p, B 1s, C 1s, and P 2p spectral regions, respectively. To further understand ligand binding, the FT-IR spectrum of Ag₄₂ was measured and compared with that of the free CBDT ligand, both shown in Figure S14. Two vibrational bands at 2601, and 2578 cm⁻¹ for the free CBDT ligand, which got shifted to a single band at the lower frequency of 2561 cm⁻¹

upon binding in the Ag_{42} , were observed. To comprehend these experimental data, we used DFT calculations to investigate the effect of silver binding to the CBDT ligand in this spectral region. The calculated IR spectra, shown in Figure S15, are dominated by the collective stretching modes of boron-hydrogen bonds. The stretching vibrations of the free SH groups of CBDT fall in this region too but produce only weak infrared lines covered by overlapping BH bands. The differences in the spectra of the free and Ag_{42} -bound CBDT ligand can therefore be attributed mainly to the specific way in which the individual BH bonds, and especially those that are adjacent to the vertices substituted by sulfur atoms, combine into the active vibrational modes. The shift of the band maximum of Ag_{42} to a lower wavenumber compared to free CBDT suggests chemically bound thiolate moieties.

Thermal Stability and Light-Activated Intercluster **Conversion.** To investigate the thermal stability, we have measured thermogravimetric analysis (TGA) of purified Ag₄₂ powder. A detailed experimental procedure of the TGA measurement is presented in the SI. Figure 2d shows the TGA plot of Ag₄₂, which indicates thermal stability up to 200 °C and shows superior thermal stability compared to known silver NCs. To better understand the structural transformation in the solid state, we performed UV-vis absorption spectroscopy and differential scanning calorimetry (DSC) of the cluster during heating. Sample heated in the solid state was dissolved in DCM to measure the absorption spectra. Spectra shown in Figure S16 remained unchanged up to 125 °C, which supports structural stability. At 150 °C, the heated sample appears to have decomposed as the absorption spectrum shows no characteristic features except a background. In the DSC measurement (Figure S17), we observed a continuous exothermic heat flow up to 190 °C, which implies no



Figure 4. Single crystal structure of Ag_{14} NC. Optical micrographs of a single crystal (a) without a polarizer and (b) with a polarizer. (c-h) SEM-EDS elemental mapping of a single crystal proving the presence of all respective elements. (i) Single crystal structure of Ag_{14} nanocluster protected with six CBDT and six TPP ligands. (j-l) $Ag_8@Ag_6$ core-shell geometry from different orientations. (m, n) Supramolecular structure showing the packing of Ag_{14} in different orientations. The $[Ag_2S(TPP)_6]$ fragments are removed for clarity. Atomic color code: blue, dark pink = silver, yellow = sulfur, green = phosphorus, faint pink = boron, gray = carbon, white = hydrogen.

prominent phase transformation of the cluster below 200 $^{\circ}$ C. The continuous exothermic peak is attributed to ligand ordering, which also manifests a weak structural transition at 227 $^{\circ}$ C.

Nevertheless, we observed light-activated intercluster conversion from Ag₄₂ to Ag₁₄ in a DCM solution, accompanied by a visible color change from dark brownish to orange. Experimental details of light-triggered intercluster conversion are discussed in the SI. Figure 3a shows a schematic representation of the conversion. UV-vis absorption spectra and mass spectra measured after specific periods of light exposure (Xe arc lamp, 190 W) unveils that this intercluster conversion proceeds through several intermediate NCs. After 8 h of light exposure, the brownish Ag₄₂ solution became dark reddish, and this change was accompanied by the decrease of the absorption peaks in the range from 500 to 700 nm, along with the appearance of other peaks at 418 and 463 nm, both arising from these intermediates. HR-ESI-MS spectrum (Figure 3c) shows two features at m/z 3239.64, with the charge state of 2-, and at m/z 2504.68, for 3-. These two spectral features correspond to [Ag₃₅(CBDT)₈(TPP)₄]²⁻ and $[Ag_{37}(CBDT)_{12}(TPP)_4]^{3-}$, respectively. Figure S18 shows the exact matching of the experimental and calculated isotopic envelopes for both of these intermediate NCs. Light irradiation after 16 h leads to further changes in the UV-vis absorption

spectra manifested by the appearance of a peak at 525 nm and another sharp peak at 462 nm. HR-ESI-MS measurements of the solution confirm the existence of a mixture of three primary NCs; $[Ag_{30}(CBDT)_8(TPP)_4]^{2-}$, $[Ag_{26}(CBDT)_{11}(TPP)_4]^{2-}$, and $[Ag_{26}(CBDT)_7(TPP)_7]^{2-}$ along with their fragmented peaks due to the loss of phosphine. Simulated isotopic distribution (shown in Figure S19) of these NCs matched well with experimental spectra. After 24 h of light irradiation, the solution became yellowish-orange with two distinct optical absorption peaks at 415 and 486 nm, and the mass spectrum confirmed the formation of Ag₁₄ as an end product (Figure S20). Further exposure of light up to 48 h did not result in any significant change in the absorption features. To understand the effect of the lamp power on the conversion process, we have monitored the absorption features while varying the lamp power. Figures S21-S25 show the time-dependent UV-vis absorption spectra of the conversion at different lamp powers, namely 100, 125, 150, 175, and 200 W. We have observed complete conversion of Ag₄₂ to Ag₁₄ following a similar set of intermediate nanoclusters after 24 h of light exposure, at 175-200 W. Decreasing the lamp power below 150 W slowed down the conversion. For the lamp power of 100 W, the conversion was completed after 48 h. Lamp power below 100 W drastically reduced the rate of transformation.



Figure 5. Theoretical electronic energy levels of Ag_{14} NC. (a) Experimental and theoretical UV-vis absorption spectra of Ag_{14} . (b) Frontier molecular orbitals responsible for the electronic transitions at 486 nm. (c) Total density of states in terms of molecular orbital contribution. (d) Total density of states in terms of atomic orbital contribution.

However, the absorption spectrum of Ag_{42} remained unchanged up to 100 °C. This confirms the thermal stability of the NC not only in its solid-state but also in solution. Figure S26 shows photographs of a DMF solution of Ag_{42} without any significant visible color change after heating to 100 °C. The superior thermal stability of Ag_{42} together with changes activated by light show possibilities leading potentially toward superstable silver NCs.

To better understand the structural stability, we have calculated the valence electrons of both the nanoclusters. According to the superatomic electron counting formula, $N\nu_A$ - M - Z, the $[Ag_{42} (CBDT)_{15} (TPP)_4]^{2-}$ nanocluster has 14 free electrons (42 - 30 + 2) with the superatomic electronic configuration, $1S^2 1P^6 1D^6$ (where N = number of metal atoms, ν_A = atomic valence of the metal atoms, M = number of electron withdrawing ligands, and Z = overall charge of the cluster).66-68 The unpaired electrons present in 1D nonspherical superatomic orbitals may generate paramagnetism in Ag₄₂ clusters. In contrast, the $[Ag_{14}(CBDT)_6(TPP)_6]$ nanocluster has two free electrons (14 - 12 - 0), with an electronic configuration of 1S². The superatomic closed shell electronic configuration may be a reason behind the formation of Ag₁₄ as an end product upon light irradiation. Although due to the lack of closed shell electronic structure, the Ag_{42} nanocluster has less electronic stability, and it is stable over a longer time as well as upon heating, which is most probably due to the heat absorbing capacity of surrounding bulky carborane ligands.

Structure of the Product Ag₁₄. We were able to grow single crystals of Ag₁₄, which gave a detailed understanding of the structural details of the system. Around 50 mg of the product obtained from different sets of light-irradiation were used for the crystallization by slow diffusion of dry hexane into dichloromethane (dichloromethane:hexane = 2.5:1.5, v/v). Yellow cuboid crystals (an optical microscopy image of a single crystal is shown in Figures 4a and b) were obtained. The SEM image of a crystal shown in Figure 4c indicates its cuboid nature. Figures 4d—h shows the EDS elemental mapping of a single crystal, which proves the presence of the respective elements, i.e. B, C, P, S, and Ag in the single crystal.

The SC-XRD measurements show that Ag_{14} crystallizes in a triclinic crystal system with a cell volume of 7160 Å³ under the space group of $\overline{P}1$ (detailed crystallographic information is presented in Table S1). The total structure of Ag_{14} (shown in Figure 4i) has diagonally opposite three pairs of carborane and three pairs of triphenylphosphine ligands. The further structural anatomy of the Ag_{14} core is shown in Figures 4j–1 and S27, and it reveals the $Ag_8@Ag_6$ core–shell geometry. The Ag_8 core of the nanocluster is made by two tetrahedrons in a bicapped trigonal antiprismatic fashion along with an Ag_6S_{12} shell, which is further surrounded by six CBDT and TPP ligands. The CBDT and TPP act as the primary and secondary ligands, respectively. The six Ag atoms on the shell are bonded with the TPP ligands through Ag–P bonds. The average Ag– Ag bond distance of 2.6–2.7 Å of the Ag_8 core shown in Figure



Figure 6. Emission properties of Ag_{42} and Ag_{14} NCs. (a) Excitation and emission spectra of the Ag_{42} indicate their NIR emission (inset) Image of the NC under 365 nm UV light, at room temperature. (b) >25-fold enhancement in the emission of the Ag_{14} upon cooling in LN_2 , PL excitation, and emission spectra of Ag_{14} at room temperature. (left inset) Expanded spectra. (right inset) Red emission of the cluster under UV light. The sample was cooled under LN_2 .

S28 is much shorter compared to the bond distance of 3.7-3.9Å between the Ag₈ core and the six surrounding Ag atoms, clearly indicating a core-shell geometry. Careful analysis reveals that Ag₁₄ has C₃ axial symmetry along with two capping Ag atoms of the Ag₈ core. Figures S29 and S30 show the C₃ axial symmetry of the structure from different orientations. The unit cell molecular packing of the crystal shown in Figure S31 reveals that four [Ag₂S(TPP)₆] fragments are packed diagonally opposite to the cluster. Most probably, the $[Ag_2S(TPP)_6]$ fragments are generated from Ag_{42} during light irradiation, and they crystallize along with the Ag₁₄ due to favorable interactions. The average distance of each [Ag₂S- $(TPP)_6$] fragment from the Ag₁₄ centroid is in between 14.4 and 16.4 Å (Figure S31b). There is no covalent bonding between Ag_{14} and the $[Ag_2S(TPP)_6]$ fragments (Figure S32). Molecular packing of Ag_{14} along with $[Ag_2S(TPP)_6]$ fragments is shown in Figures 4m, n and \$33 indicating lamellar packing of the cluster within the lattice. The binding force of Ag₁₄ with $[Ag_2S(TPP)_6]$ fragments (shown in Figure S34) is due to the several intermolecular interactions such as CH- π , BH- π , B-CH, CH-BH, Ag- π , B- π , etc. To provide another independent view on Ag₁₄, we used TEM imaging (Figure S35), which displays uniform particle distribution. Extended beam irradiation produced Ag₂S with a lattice spacing of 2.8 Å, corresponding to the d_{110} . The EDS elemental analysis showed the presence of all the expected elements, i.e. B, C, P, S, and Ag with an atomic % of 38.86, 56.67, 1.54, 1.20, and 1.73, respectively. Figure S36 shows the ¹¹B NMR spectrum of the same with four peaks at -0.69, -7.32, -10.78, and -13.43 ppm in the shielded regions with nearly identical intensity, which was correlated with the symmetrical carborane binding of the Ag₁₄ nanocluster. The proton decoupled ¹³C NMR spectrum, shown in Figure S37, exhibits two peaks at 53.44 and 50.85 ppm assigned to carbon atoms of the carborane ligands, along with different characteristic peaks in the region of 128 to 134 ppm, corresponding to bonded TPP ligands. A broad ³¹P NMR peak (shown in Figure S38) at 4.04 ppm indicates TPP binding with the nanocluster. To further confirm the chemical binding of different atoms in Ag₁₄, we performed XPS studies. The survey spectrum along with individual elements (Figure S39) confirm that the oxidation state of silver is close to Ag(0).

The presence of B 1s and P 2p signatures at 189.8, and 131.5 eV, respectively, confirm the ligand binding in the solid state. FT-IR results (Figure S40) show changes in the BH stretching due to carborane binding with the metallic core.

Electronic Structure of Ag₁₄ through TDDFT. TDDFT calculations were performed to understand the electronic energy levels and associated electronic transitions of Ag₁₄. Detailed structure optimization and details of calculations are presented in the SI. The DFT optimized structure and its anatomy are shown in Figures S41 and S42. The optical absorption spectrum was calculated using linear-response TDDFT and delta SCF methods, using the ground and excited state optimized structures of the NC. The calculated optical absorption spectrum in comparison with the experimental UV-vis spectrum is shown in Figure 5a. For both the spectra, not only the overall trend but also the distinct peak at 486 nm were matched well. The relevant molecular orbitals corresponding to this transition are plotted in Figure 5b. The transition is arising from two occupied molecular orbitals, i.e., HOMO - 4 and HOMO - 3, having energies of -4.413 and -4.405 eV to empty orbitals LUMO + 9 and LUMO + 11 with energies of -1.87 and -1.856 eV, respectively. This excitation is from core to surface states.

Additional density of state (DOS) calculation (shown in Figure 5c) reveals that both the HOMOs (HOMO - 4 and HOMO - 3) having the energy of -1.50 eV contributed equally to the transition to the LUMOs (LUMO + 9 and LUMO + 11) with the energy of 1.04 eV for this transition. The distribution of electron density of these molecular orbitals clearly shows that the metal core localized HOMOs transfer their charge to the delocalized LUMOs centered around the ligands. Therefore, the charge transfer is assigned as a metal core to ligand shell charge transfer (MLCT). However, the lowest transition (HOMO-LUMO gap) for this cluster is at 561 nm. The corresponding transition is taking place between HOMO and LUMO with a gap of 2.207 eV. To comprehend the hybridization of these molecular orbitals, the total and partial density of states were analyzed in the entire energy regime from -9.5 to 2 eV, as shown in Figure 5d. The middle of the gap was set at 0 eV for clarity. From Figure 5d, the doubly degenerate HOMO bands are mainly made up of 3p



Figure 7. Femtosecond and ns-TA pump-probe spectra of Ag_{42} NC. (a) Contour plot, where the region enclosed by dashed lines indicates the photoinduced absorption arising from the Stark effect. (b) Spectral evolution of TA at an early time scale. (c) Formation and decay of bleach and PIA with time constants of 1.6 \pm 0.1 and 1.4 \pm 0.1 ps, showing close association of PIA with hot carriers. (d, e) Spectral and temporal evolution of TA for long time scales at different wavelengths. (f) Nanosecond time evolution recorded with ns laser flash photolysis.

AOs of S atoms and 5p and 4d AOs of Ag atoms, while the LUMO bands are dominated by 3p AOs of P atoms and 5p AOs of Ag atoms.

Luminescence Properties of Ag₄₂ and Ag₁₄ NCs. We have measured the photoluminescence spectra of Ag₄₂ and Ag₁₄ separately. Figure 6a and b shows the excitation and emission spectra of both the NCs. The former one exhibits a NIR emission maximum centered around 980 nm, corresponding to a broad excitation maximum centered around 525 nm. The lifetime of the NIR emission is >1.5 μ s indicating that the emission is phosphorescence, originating from a triplet state (Figure S43). UV-vis absorption peak at 572 nm is close to the excitation maximum at 525 nm. Interestingly, Ag₁₄ shows red luminescence at room temperature (25 °C) with an emission maximum at 626 nm, corresponding to the excitation maxima at 373 and 447 nm. The excitation maximum of the cluster present near to the broad absorption maximum is responsible for this emission at 626 nm. The emission feature of Ag14 enhances significantly upon cooling the sample in liquid nitrogen. The inseparable $[Ag_2S(TPP)_6]$ fragments present with the Ag₁₄ cluster in solution may have a slight contribution in this aggregation process.

Luminescence spectral measurements show a 25.4-fold enhanced emission with 17 nm red-shift of the spectral profile. Luminescence enhancement with slight red-shift is due to the restriction of the nonradiative decay of the NCs, due to aggregation-induced emission, in liquid nitrogen matrix. Literature reports a similar type of emission enhancement in NCs due to enhanced rigidity of the NC in the presence of secondary ligands and lowering of the temperature.^{69,70} Figure S44 presents images of Ag₁₄ crystals under 365 nm UV excitation with clearly observable red emission.

Electron Dynamics of Ag₄₂ and Ag₁₄ through fs- and ns-TA. For better understanding the effect of light-activation

to the electronic energy levels, and associated electronic transitions, we have measured femtosecond-nanosecond transient absorption (fs-ns-TA) of both the NCs. Details of the instrumental setup and measurements are given in the SI. The TA spectra of Ag_{42} are compiled in Figure 7. Upon photoexcitation using a 400 nm laser pump with a fluence of 250 μ J/cm², Ag₄₂ showed ground-state photobleaching (GSPB), centered at 576 and 468 nm. The observed GSPB are at the positions of two states observed in the ground state optical absorption spectrum at 572 and 458 nm. It indicates the Pauli blocking of these two states by pump excited carriers, which reduces the absorption of probe pulse, generating GSPB signals. Along with it, other important features observed are a fast decaying photoinduced absorption (PIA) at 620 nm, redshifted with respect to the GSPB at 576 nm and two nondecaying PIA signals at 685 and 520 nm.

In order to gain additional insight behind the origin of fast decaying PIA, we have plotted the spectral kinetics of TA and temporal profiles at 580 and 620 nm for the early time scales, in Figure 7b and c. From Figure 7b, we observe the simultaneous growth of the GSPB signal and the decrease of the PIA signal. The GSPB growth time generally relates to the time taken by the pump excited hot carriers to reach that state. The close association of GSPB growth with the PIA decay suggest that Coulomb interaction between the hot carriers causes the red shift of the 576 nm resonance. It causes the absorption of probe pulse into these levels, observed as redshifted PIA. It disappears once all the pump-excited carriers reach that state. A similar effect, generally observed in semiconductors, is attributed as a Stark effect.⁷¹ The observation of the Stark effect in our NCs suggests the close similarity of the electronic structure of NCs with semiconductors. The DFT optimized structure of Ag₄₂ (shown in Figure 2a) reveals that it has a layer-like silver core $(Ag_{12} and$ www.acsnano.org

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Figure 8. Femtosecond-TA pump-probe spectra of Ag_{14} NC. (a) Contour plot indicating a broad ESA. (b) Time evolution spectral profile of ESA features. (c) Fast decay time data of ESA corresponding to the 565 nm peak.

Ag₃₀) and surface CBDT and TPP ligand shells, making an anisotropic nature, which generates an inherent electric field gradient. Perturbation of the external electromagnetic field is due to this inherent electric field gradient. The literature shows that an anisotropic gold NC exhibits a similar type of Stark effect.⁷² In order to analyze the lifetime of carriers, we have plotted the time evolution of GSPB and PIA features in Figure 7d and e. It shows almost similar kinetics for GSPB and PIA, not decaying in our fs-TA window, and this has an almost constant magnitude up to 1400 ps. It demonstrates the long lifetime of NC states. To determine their lifetime, we have further studied ns-TA decay kinetics using ns laser flash photolysis. The time evolution of ns-TA is shown in Figure 7f, with a very long lifetime, having average decay constants of 3.4 \pm 0.6 and 24 \pm 1 μ s for 576 nm and 5.7 \pm 0.4 and 70 \pm 10 μ s for 685 nm. The localized long-lived excited states of the silver core of the cluster, an element having inherent light sensitivity, are likely to be contributing to its light-induced core transformation (shown in Figures 2b and S6b).

In contrast to Ag₄₂ NC, Ag₁₄ did not show any type of photoinduced bleaching effects, the only feature observed was a broad PIA. Most probably, isotropic structure of Ag₁₄ having C₃ axial symmetry (shown in Figures S29 and S30) did not have any inherent electric field gradient. Figure 8A shows the contour plot of Ag₁₄ after 400 nm excitation at a fluence of 250 μ J/cm². The TA spectral profile in Figure 8b did not show any GSB peaks; only it has a broad PIA in the range of 500 to 650 nm. The time evolution of PIA maximum centered around 565 nm is shown in Figure 8c, with the decay time of 85 ± 9 ps indicating fast relaxation, which is also in contrast to Ag₄₂, where we observed long lifetime of carriers.

CONCLUSION

In summary, we have presented the synthesis of *ortho*carborane-1,2-dithiol and triphenylphosphine coprotected Ag₄₂ NC using a LEIST reaction starting with Ag₁₈. This is a carborane-protected silver nanocluster with the highest number of Ag atoms reported so far. Numerous techniques have been used to probe the structure as well as electronic and photophysical properties of the Ag₄₂. Despite several efforts, molecular complexity limited us to get diffractable single crystals. Thermogravimetric measurements showed exceptional thermal stability in them, up to 200 °C. Although the cluster is thermally stable, irradiation with white light leads to a structural conversion to Ag₁₄. UV—vis absorption spectra indicate this structural conversion through some intermediate NCs. The mass spectrometric measurements suggested the interconversion through two sets of intermediate NCs. The first set of NCs were composed of $[Ag_{35}(CBDT)_8(TPP)_4]^{2-1}$ and $[Ag_{37}(CBDT)_{12}(TPP)_4]^{3-}$, and the next had $[Ag_{30}(CBDT)_8(TPP)_4]^{2-}$, $[Ag_{26}(CBDT)_{11}(TPP)_4]^{2-}$, and $[Ag_{26}(CBDT)_7(TPP)_7]^{2-}$. Single crystal XRD confirms Ag_{14} had a Ag₈ bicapped trigonal antiprism core surrounded by six Ag surface atoms through Ag-S and Ag-P bonding. Six CBDT and TPP ligands coprotected the metallic core. TDDFT calculation of Ag₁₄ reveals an electronic transition from the HOMO localized to $\mathrm{Ag}_{\mathrm{14}}$ core to the LUMO centered on CBDT and TPP ligands. Interestingly, Ag₄₂ showed a NIR phosphorescence in comparison to the red emitting Ag₁₄. Femtosecond TA measurements showed a very fast (lifetime of <1 ps) red-shifting of the ESA of Ag₄₂ due to its anisotropic nature. Time-resolved (fs and ns)-TA confirms the slow decay (3.4 \pm 0.6 and 24 \pm 1 μ s for 576 nm and 5.7 \pm 0.4 and 70 \pm 10 μ s for 685 nm) features of Ag₄₂, in comparison to the fast decaying $(85 \pm 9 \text{ ps for 565 nm})$ ESA for Ag₁₄. This long time scale decay suggests slow vibrational relaxation, a potential reason for the observed light-induced core reduction. This work leads to the path toward a detailed understanding of light-triggered intercluster conversion of atomically precise metal nanoclusters and associated electron dynamics. We believe light-irradiated interconversion is a synthetic method to prepare other silver nanoclusters.

EXPERIMENTAL SECTION

Synthesis of Ag₄₂ **NCs.** Ag₄₂ was synthesized from hydride, and TPP coprotected Ag₁₈ using the LEIST reaction. A detailed protocol for the synthesis of Ag₁₈ is presented in the SI. In brief, a methanolic solution of Ag₁₈ was reacted with CBDT, producing Ag₄₂ as a brown precipitate, which was insoluble in common alcohols such as ethanol but soluble in chlorinated solvents. The crude NCs were purified using repeated washing by water, methanol, and ethanol solvents. The purified NCs in the solutions of dichloromethane (DCM), 1,2-dichlorobenzene (DCB), acetone, acetyl acetone (acac), methyl isobutyl ketone (MIBK), acetonitrile (ACN), tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were used for further studies.

Synthesis of Ag₁₄ NCs through Light-Irradiation. Ag₁₄ was synthesized using light-irradiation of Ag₄₂. A DCM solution (5 mL) of purified Ag₄₂ (10 mg) was degassed using argon bubbling prior to exposure to light. A 190 W solar simulator from Newport, India, was used as the source of light. After 24 h of light irradiation, Ag₄₂ got transformed fully to Ag₁₄. There was no transformation Ag₁₄ upon further irradiation. The reaction was accompanied by a change of color from dark brown (Ag₄₂ NCs), to dark red (intermediate NCs), and to a final orange–yellow, typical of Ag₁₄. Diffraction quality single crystals of Ag₁₄ were obtained by slow diffusion of dry hexane into the

concentrated cluster solution in DCM. The grown yellow cuboid crystals were used for single crystal X-ray diffraction.

Additional experimental details and instrumentations are presented in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c02602.

Experimental section, instrumentation, X-ray crystallographic details, computational details, and additional experimental data (PDF)

Single crystal X-ray data for Ag₁₄ nanocluster (CIF)

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Author Contributions

A.J. performed the synthesis, characterization, and most of the experimental studies. M.J. assisted A.J., especially in the crystallization of the samples. P.C. performed mass spectrometric studies. Md.R.I. conducted electron microscopic measurements. All the fs-ns time-resolved studies were conducted by A.K.P. in the laboratory of K.N.V.D.A. S.G. was involved in the discussion of experimental data. G.P. and J.M. performed computational studies. T.B. synthesized the carborane thiols used in this work and conducted all the work relating to those systems. The first draft of the manuscript was written by A.J., and all the authors contributed to improving it. T.P. suggested the problem, supervised the project, and finalized the manuscript. This work is a part of longer-term collaboration aimed at unlocking the potential of materials produced by combining metal nanoclusters and carborane ligands initiated by T.P. and T.B.

Notes

The authors declare no competing financial interest.

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