

Confining an Ag₁₀ Core in an Ag₁₂ Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization

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Supporting Information

ABSTRACT: We introduce a cluster coprotected by thiol and diphosphine ligands, $[Ag_{22}(dppe)_4(2,5-DMBT)_{12}Cl_4]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane; 2,5-DMBT= 2,5-dimethylbenzenethiol), which has an Ag_{10} core encapsulated by an Ag₁₂(dppe)₄(2,5-DMBT)₁₂Cl₄ shell. The Ag₁₀ core comprises two Ag₅ distorted trigonal bipyramidal units and is uncommon in Au and Ag nanoclusters. The electrospray ionization mass spectrum reveals that the cluster is divalent and contains four free electrons. An uncommon crystallization-induced enhancement of emission is observed in the cluster. The emission is



weak in the solution and amorphous states. However, it is enhanced 12 times in the crystalline state compared to the amorphous state. A detailed investigation of the crystal structure suggests that well-arranged C-H··· π and π ··· π interactions between the ligands are the major factors for this enhanced emission. Further, in-depth structural elucidation and density functional theory calculations suggest that the cluster is a superatom with four magic electrons.

KEYWORDS: nanocluster, crystallization induced emission enhancement, 1,2-bis(diphenylphosphino)ethane, 2,5-dimethylbenzenethiol, superatom, magic electron, photoluminescence

tomically precise analogues of noble metals, also called as nanoclusters (NCs), have become an emerging category of nanomaterials, shown to be important in diverse applications such as sensing, catalysis, energy storage, drug delivery, cancer treatment, etc.^{1–8} NCs have been used as nanoscale building blocks for creating solid-state materials.^{9,10} Among these, Au NCs have been long studied due to their higher stability and biocompatibility. The synthesis of stable Ag NCs with well-defined structure and luminescence has drawn intense attention of researchers in the recent past.^{11–15} Precision in their compositions and their structural diversity suggest possible structure-property relationships.^{16,17} The properties of NCs can be tuned by changing the core structure as in the case of $Au_{38}(PET)_{24}$ (PET = 2-phenylethanethiol) NCs.¹⁸ Two isomeric Au₃₈(PET)₂₄ NCs having different core structures exhibit different stability and catalytic activity. The sphere (icosahedral core) and rodlike (biicosahedral core) Au₂₅ NCs also display different catalytic activity for CO₂ electroreduction.¹⁹ The protecting ligands such as thiols, phosphines,²² alkynyls,²³ calixarenes,²⁴ etc. also control the

properties of NCs.²⁵⁻²⁹ Enhancement of photoluminescence (PL) after ligand modification in $[Au_{22}(SG)_{18}]$ (SG = glutathione)³⁰ and $[Au_{23}(SR)_{16}]^{31}$ has been noted. Other than these, NCs are also protected with mixed ligands as in $[Ag_{67}(2,4-DMBT)_{32}(PPh_3)_8]^{3+}$ (2,4-DMBT = 2,4-dimethylbenzenethiol),³² $[Ag_{50}(dppm)_6(SR)_{30}]$ (dppm = 1,1-bis- $(diphenylphosphino)methane),^{33} [Ag_{14}(SC_6H_3F_2)_{12}-(PPh_3)_8],^{34} [Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-} (BDT = 1,3-benzenedi$ thiol),³⁵ etc.³⁶ The mixed-ligand-protected NCs exhibit higher stability with enhanced properties as compared to single ligand protected ones.^{34,35,37} Such an example is [Ag₂₉(BDT)₁₂- $(PPh_3)_4]^{3-}$, which is less reactive to $[Au_{25}(PET)_{18}]^{-}$ compared to $[Ag_{25}(2,4-DMBT)_{18}]^-$ and $[Ag_{44}(SR)_{30}]^{4-.38}$ Further, by varying the secondary ligands, one can modulate the PL of this kind of NCs by keeping the cluster atomicity unaltered.³⁹

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The stability of NCs is expressed in terms of the superatom structure which has been described by the jellium model. According to the spherical jellium model, shell-closing electron counts are 2, 8, 18, 20, 34, 40, 58, 68, 70, *etc.*, which are known as magic numbers. But change in shape and dimensionality result in other magic numbers such as 4 and 6 electrons for prolate and oblate systems, respectively.⁴⁰ Due to mixed ligand protection, NCs can show different shapes and structures. Hence, the underlying diversity of mixed ligand protected Ag NCs need to be explored in terms of their structures and properties and also to discover cluster systems with unknown geometric and electronic structures.

Herein, we report the synthesis, crystal structure, optical and electronic properties of $[Ag_{22}(dppe)_4(2,5-DMBT)_{12}Cl_4]^{2+}$ (I) (dppe = 1,2-bis(diphenylphosphino)ethane), also referred to as Ag₂₂ in the subsequent text. The cluster crystallizes in a tetragonal crystal system with an $I4_1/a$ space group. The cluster has three characteristics: (i) it contains an uncommon Ag10 core which is formed by the combination of two perpendicularly connected Ag₅ distorted trigonal bipyramidal (tbp) units, (ii) the 4e cluster displays $1S^21P^2$ electronic shell closure as it has a prolate shaped structure which has not been observed in previously published Ag NCs,⁴¹ and (iii) it exhibits crystallization-induced emission enhancement (CIEE). Apart from single-crystal X-ray diffraction study, I was thoroughly characterized by high-resolution electrospray ionization mass spectrometry (HRESI MS), scanning electron microscopy/ energy dispersive spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR). In addition, the electronic structure and optical properties are understood in detail by density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

The cluster I was prepared by a one-pot synthetic method which involved the reduction of silver-thiol-phosphine complexes (a detailed synthetic procedure is given in the Experimental Section). Briefly, AgNO₃ was reduced by NaBH₄ in the presence of 2,5-DMBT and dppe in MeOH/DCM (DCM= dichloromethane) under ice-cold conditions. Upon stirring the reaction product with PPh₄Cl and triethylamine for 12 h, absorption spectrum of the crude product was measured and exhibited distinct features at 415 and 497 nm along with a small hump at 635 nm, as presented in Figure S1A. HRESI MS in the positive mode revealed that a mixture of clusters was present in the solution (Figure S1B). Hence, the solution was kept for size focusing for 2-3 days at 4 °C, and the final purified cluster was obtained in MeOH. The optical absorption spectrum of I presented in Figure 1A manifests well-defined sharp peaks at 368 and 512 nm along with two broad shoulder peaks centered at 445 and 670 nm. The cluster shows a sharp peak at m/z 2876 in the HRESI MS, which suggests the formation of a monodispersed cluster (Figure 1B). No other prominent features were observed up to m/z 10000. The cluster was divalent as confirmed by the characteristic difference between two successive peaks of the isotopic distribution, which was 0.5 (Figure S2A). Therefore, the peak at m/z 2876 was assigned as $[Ag_{22}(dppe)_4(2,5-$ DMBT)₁₂Cl₄]²⁺ whose experimental isotopic pattern matched well with the theoretical one (Figure 1B). The assignment was consistent with the single-crystal X-ray diffraction (SCXRD) data.



Figure 1. (A) Optical absorption spectrum of I. Inset: image of single crystals under a microscope. (B) HRESI MS of I which displays a peak at m/z 2876. Inset: Comparison of the theoretical and the experimental isotopic distributions of I.

The collision-induced dissociation (CID) study of $[Ag_{22}(dppe)_4(2,5-DMBT)_{12}Cl_4]^{2+}$ (m/z 2876) is presented in Figure S2B. A systematic loss of four dppe ligands is shown. Initially, two dppe ligands were lost followed by a $[Ag(dppe)]^+$ unit (panel b of Figure S2B). Hence, the cluster became singly charged (the formed species is $[Ag_{21}(dppe)(2,5-$ DMBT)₁₂ Cl_4]⁺ which was abbreviated as II), and a further increase in collision energy (CE) resulted in the removal of the remaining one dppe ligand which gave rise to a peak at m/z4052 (panel c of Figure S2B). At higher collision energies, detachments of Ag–Cl (panel b) and Ag–DMBT (panel c) units from II were observed. The crystals of I were obtained by layering hexane on the surface of the DCM/MeOH solution (1:1 v/v) and was kept for 2 weeks at 4 °C (a photograph of the crystals is shown in Figure 1A). Rectangular-shaped crystals appeared black in color and were of 150-300 μ m in dimension. Cluster I crystallizes in a body-centered tetragonal unit cell under the $I4_1/a$ space group (detailed crystallographic analysis is given in the Supporting Information (SI)) containing four clusters per unit cell (Figure S3A). The atomic structure of I is presented in Figure S3B,C.

The structural anatomy of I shows that it possesses an Ag_{10} core (Figure 2A,B) which has not been observed in previous reports of Au and Ag NCs (a list of known Ag structures is given in Table S2). The Ag_{10} core is made up of two Ag_5 units having distorted trigonal bipyramidal (tbp) geometry (Figure 2C) which are connected to each other in a perpendicular fashion through the four axial Ag atoms forming a tetrahedron. The Ag_5 units can also be viewed as a combination of two face-shared tetrahedra (Figure S4). Hence, the alternate structure of the Ag_{10} can be described as a combination of five edge and face-shared tetrahedra (Figure S4). The Ag_5 units possess a chiral C_2 point group while the Ag_{10} core unveils an achiral S_4 point group.

The Ag_{10} core is encapsulated by an $Ag_{12}(dppe)_4(DMBT)_{12}Cl_4$ shell (Figure 2E-G) which is formed by four Ag_2SP_2Cl and four AgS_2 staple motifs (Figure 2G). The shell can also be viewed as a combination of four $Ag_2S_3P_2Cl$ and four Ag atoms (Figure 2H). Out of the four $Ag_2S_3P_2Cl$ staples, two connect the first three layers of the core and the remaining two connect the last three layers in a similar



Figure 2. (A, B) Ball and stick and polyhedral representations of the Ag_{10} core, (C) Ag_5 units having tbp geometry, (D, E) total structure of I with and without C and H atoms of ligands, (F) structure of $Ag_{12}P_8S_{12}Cl_4$ shell, (G) four Ag_2SP_2Cl and AgS_2 motifs, and (H) four $Ag_2S_3P_2Cl$ and Ag atoms. Labels: red, blue, and pink = Ag; yellow = S; orange = P; green = Cl; gray = C; H atoms are omitted for clarity.

fashion, but rotated ~90° along the C_2 axis (Figure S5). The remaining four silver atoms are connected with the third and fourth layers of the Ag₁₀ core and also act as bridging atoms between the tetrameric staples of the first three and the last three layers. Staples are connected to the core in such a way that S_4 symmetry is maintained (Figure S6). The counterions that could be nitrates were not identified due to the disorder present in the crystal. However, the IR spectrum of I display peaks corresponding to N–O and N=O stretching frequencies (Figure S7A). In addition, the HRESI MS of I shows a peak corresponding to NO₃⁻ (Figure S7B). Therefore, the results of HRESI MS and IR confirm the presence of NO₃⁻ as the counterion.

The Ag-Ag bond lengths present in the Ag₁₀ core range between 2.704 and 3.031 Å, which is similar to other thiol/ phosphine-coprotected clusters.^{33,34,42} The Ag–Ag distance in Ag_2SP_2Cl staple motifs is 3.144 Å, which is shorter than that of the other dppe-protected clusters.⁴² The remaining four AgS₂ staples where Ag atoms are directly bonded to the Ag₁₀ core also display a shorter Ag-Ag distance (3.063 Å). The average Ag–S distance is 2.508 Å, which is shorter than that of monothiol-protected clusters^{20,21,27,42} and almost similar to that of the dithiol-protected clusters.³⁵ The Ag–P bond length is 2.417 Å with a distorted P-C-C-P linkage.⁴² The two P-C bonds are 1.861 and 1.777 Å because of the stronger C-H… π interactions between the benzene rings of dppe and 2,5-DMBT on one side (3.266, 2.852, 2.851 Å) than on another side (3.292, 3.072, 3.246 Å) (Figure S8). Other than dppe and 2,5-DMBT, the cluster is stabilized by Cl ligands which connect the Ag atoms of core and staples. In this cluster, Cl is strongly bonded to the metal core (2.491 Å) which is stronger

than bulk AgCl (2.77 Å), though the distance between Ag atoms of staples and Cl is slightly longer than that of the core (2.855 and 3.066 Å). Because of these strong interactions, I exhibits high stability at room temperature (Figure S9). The Cl atoms can be substituted by Br atoms using PPh₄Br which formed $[Ag_{22}(dppe)_4(DMBT)_{12}Cl_{4-n}Br_n]$ with n = 0-4 (Figure S10). This showed the anion-exchange capability of I. Further, the cluster was analyzed by SEM/EDS elemental mapping, which confirms the presence of Ag, S, Cl, and P (Figure S11). In addition, elemental characterization of I was performed using XPS (Figure S12). Peaks corresponding to Ag $3d_{5/2}$, S $2p_{3/2}$, P $2p_{3/2}$, and Cl $2p_{3/2}$ appear at ~367.9, ~162.2, ~131.3, and ~198.0 eV, respectively. Both Ag(0) and Ag(1) should be present in the spectrum, but it is hard to separate them.

Cluster I emitted in the red region with an emission maximum at ~ 670 nm as shown in Figure 3A. The crystal displayed intense red photoluminescence (PL); however, when it was dissolved in MeOH, the intensity was reduced (QY of I in MeOH is $5.3\times10^{-4}).$ In addition, the amorphous powder made by evaporation of MeOH solution of I showed very weak emission. We have compared the luminescence intensities of the amorphous and crystalline forms of I. The densities of these forms are approximately the same. The experiments were done similarly with the same illumination volume and keeping all experimental parameters the same (details are given in the Experimental Section). The crystalline state exhibits 12 times more luminescence intensity than the amorphous powder. Detailed structural investigations showed the presence of strong intramolecular noncovalent C-H··· π and π ··· π interactions between the benzene rings of 2,5-DMBT and dppe in



Figure 3. (A) Emission spectra of I in the crystalline (red), amorphous (pink), and solution (green) states. Inset: photograph under UV light shows red emission. (B, C) Intramolecular noncovalent interactions between protective ligands (metal atoms are omitted). (D) Noncovalent intermolecular interactions between protective ligands of two adjacent clusters.



Figure 4. Experimental (red) and the theoretical (black) absorption spectra of I and the model cluster $[Ag_{22}(SMe)_{12}(Me_4P_2C_2H_4)_4Cl_4]^{2+}$, respectively. K–S MOs are shown in the inset.

the crystal of I (Figure 3B,C). In addition, the clusters are strongly bonded to the neighboring one through strong C– $H \cdots \pi$ interactions between the ligands (Figure 3D). The packing diagrams shown in Figure S13 display that the clusters are packed in a rectangle and square 2D lattices along X/Y and Z axes, respectively. This extended intermolecular interaction gives rise to higher PL intensity in the crystalline state. The lower emission intensity in the amorphous state is because of the random arrangement of clusters which do not allow formation of regular intermolecular as well as intramolecular interactions. Crystallization-induced emission enhancement is one type of aggregation induced emission (AIE) where the aggregation occurs in the crystalline state and molecules are arranged systematically.⁴³

The electronic structure and optical spectrum of I were studied by density functional theory (DFT) and timedependent DFT (TDDFT) calculations using the Gaussian G09 software. For calculations, the reduced model cluster, $[Ag_{22}(SMe)_{12}(Me_2PCH_2CH_2PMe_2)_4Cl_4]^{2+}$ was used where benzene groups of each 2,5-DMBT and dppe were simplified using $-CH_3$ (or -Me) groups (Figure S14). Further details of the computations are included in the Experimental Section. The theoretical and experimental absorption spectra presented in Figure 4 demonstrate that the theoretical spectrum is blueshifted and is consistent with the experimental one (peaks at ~460 and ~395 nm are ~50 nm blue-shifted while the peak at ~650 nm is ~25 nm blue-shifted), which is due to the reduced structure.^{32,35} To analyze the contributions of atomic orbitals (AOs) in the molecular orbitals (MOs), the Kohn–Sham (K– S) MOs (inset of Figure 4) and the density of states (DOS) were calculated (Figure 5). The electronic transitions related



Figure 5. (B) The DOS analysis of MOs of the model cluster, $[Ag_{22}(SMe)_{12}(Me_4P_2C_2H_4)_4Cl_4]^{2+}$.

to the peak at ~650 nm originate from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Hence, the theoretical energy gap is 1.9 eV, which is in accordance with Au₂₂ and is higher than that of recently published Ag₂₃ (1.4 eV).^{44,45} The features at ~460 and 395 nm arose due to the transitions between HOMO to LUMO+2 and HOMO-5 to LUMO+1, respectively (K-S MOs are given in the inset of Figure 4). The partial DOS spectra shown in Figure 5 show that HOMO, LUMO, LUMO+1, and LUMO+2 are mainly composed of 5s and 5p AOs of Ag, while HOMO-5 exhibits predominant contributions from Ag 4d and S 3p. Thus, the peaks at 650 and 460 nm are attributed to sp to sp interband transition while that of 395 nm is attributed to π to sp transition.

The jellium electron count of I gives 4e, which do not correspond to a shell-closing structure according to the spherical jellium model as electrons cannot be stabilized in spherical geometry. However, the 4e systems having a 1S²1P² configuration can be stabilized in a prolate geometry, which was explained by Mingos on the basis of the structural jellium model.⁴⁶ According to the hypothesis, the stabilization energy to place 2e in po is double that required for placing them in $p_{\pm 1}$, and hence, they have a preference for prolate geometry.⁴⁰ The silver framework in I possesses a prolate geometry similar to the previously reported 4e gold NCs (Figure S15).⁴⁶ The DFT calculation showed that I is a superatom with 4e and the electronic distributions in superatomic orbitals are presented in Figure S16 along with the isosurfaces of superatomic orbitals (analysis of superatomic orbitals are described in the Experimental Section). The higher stability of I may be due

to the presence of four magic electrons. The magic stability of I can also be described in terms of the superatom network (SAN) model which has been used to explain the stability of 4e gold NCs such as $[Au_{18}(SR)_{14}]$, $[Au_{20}(SR)_{16}]$, $[Au_{24}(SR)_{20}]$, *etc.*⁴⁷ Cluster I is composed of the Ag_{10}^{6+} core, which is a combination of two 2e tbp Ag_5^{3+} units. Thus, the core can be viewed as a network of Ag_5^{3+} superatoms according to the SAN model.

CONCLUSION

In conclusion, we have presented a silver cluster, Ag₂₂, with an Ag₁₀ core which was formed by two orthogonal Ag₅ distorted trigonal bipyramid units connected to each other to form an Ag₄ tetrahedron. The Ag₅ units were also expressed as two face-shared Ag₄ tetrahedra. Thus, the Ag₁₀ core was described as an arrangement of five Ag₄ tetrahedra, and it was encapsulated by an outer shell, Ag₁₂(dppe)₄(2,5-DMBT)₁₂Cl₄. Though the cluster was feebly luminescent in solution, the crystal is highly luminescent due to extended C–H··· π and π ··· π interactions. This enhancement has rarely been observed in a pure Ag NC. Theoretical calculations showed that the cluster contains superatomic orbitals with four magic electrons which contribute to the magic stability of Ag₂₂. This work highlights the unknown aspects of mixed ligand protected silver NCs and suggests additional possibilities with them.

EXPERIMENTAL SECTION

Chemicals and Materials. Silver nitrate (AgNO₃), triethylamine, and dppe were purchased from Rankem Chemicals. Tetraphenylphosphonium chloride (PPh₄Cl), 2,5-DMBT, sodium borohydride (NaBH₄, 98%), and triphenylphosphine (PPh₃) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. All the solvents such as DCM, MeOH, *n*-hexane, *N*,*N*-dimethylformamide (DMF), acetonitrile (ACN), and CHCl₃ were purchased from Rankem Chemicals and were of analytical grade.

Synthesis of $[Ag_{22}(dppe)_4(2,5-DMBT)_{12}Cl_4]^{2+}$ (I). In a typical one-pot synthesis, ~20 mg of AgNO₃ was dissolved in MeOH/DCM (5/9 v/v) followed by the addition of 10 µL of 2,5-DMBT. Then 10 mg of dppe was added to the reaction mixture and kept stirring. After 15–20 min, 20 mg of NaBH₄ (in 1 mL of ice-cold water) was added dropwise to the mixture, which changed the color from yellow to dark brown. After that, 10 mg of PPh₄Cl and 30 µL of triethylamine were added. The reaction was kept under stirring for 12 h under ice-cold conditions. After completion of the reaction, it was kept for 2–3 days at 4 °C. The mixture was then thoroughly washed with MeOH/H₂O followed by complete solvent evaporation. Then the cluster was extracted using MeOH and dried on a rotavapor. The obtained purified NC showed high solubility in various organic solvents such as MeOH, DCM, DMF, ACN, CHCl₃, etc. All measurements were performed in MeOH.

Crystallization of $[Ag_{22}(dppe)_4(2,5-DMBT)_{12}Cl_4]^{2+}$ (I). About 45 mg of the purified cluster was dissolved in 1.5 mL of DCM and 0.5 mL of MeOH. Then the cluster solution was filtered by a syringe filter of 0.22 μ m pore size, and it was layered by 2 mL of hexane. The sample was kept at 4 °C, and the black crystals were formed after 2 weeks. Distilled solvents were used for crystallization.

Characterization. UV–vis spectra were measured using a PerkinElmer Lambda 25 spectrometer. HRESI MS were recorded using a Waters Synapt G2-Si high-resolution mass spectrometer in the positive-ion mode. Emission spectra of the cluster were collected in a Witec GmbH, Alpha-SNOM alpha300S confocal Raman instrument equipped with 532 nm laser as the excitation source. A laser power of 500 μ W with integration time of 0.1 s and two accumulations were used throughout the experiments. IR spectra were recorded using a JASCO-FT/IR-4100 spectrometer. XPS measurements were carried out with an Omicron ESCA Probe spectrometer with polychromatic

Al K α X-rays (hv = 1486.7 eV). During the measurement, pass energy for the survey scans was kept at 50 eV, which was changed to 20 eV for specific regions. Binding energies (BE) of the core levels were calibrated with C 1s BE set at 285 eV. SEM measurements were performed using FEI Quanta 200 operating at 30 kV equipped with EDS. X-ray data collection was performed with Bruker AXS Kappa Apex III CMOS diffractometer equipped with graphite monochromated Mo (K α) ($\lambda = 0.71073$ Å) radiation at 273 K (further details are presented in the SI).

Quantum Yield Measurements. The PL quantum yield (QY) of I in solution (MeOH) was calculated by the integrated luminescence intensity method where emission intensity of I was compared to that of rhodamine 6G (QY is 1 in MeOH). The PL QY of a sample can be calculated from the following equation

$$\varphi_{\rm s} = \frac{F_{\rm s}}{A_{\rm s}} \times \frac{A_{\rm r}}{F_{\rm r}} \times \frac{n_{\rm s}^2}{n_{\rm r}^2} \times \varphi_{\rm r}$$

where "s" and "r" refer to the clusters and the reference; φ_s and φ_r are the QY of the sample and that of the reference; F_s and F_r are the integrated intensity of the samples and the reference; A_s and A_r are the absorbance of the sample and the reference at the excitation wavelength; and n_s and n_r are the refractive indices of the sample and reference solution, respectively.

Computational Details. The structural, electronic ,and optical properties of I were computationally studied using DFT and TDDFT. All of the calculations were performed using the Gaussian09 software package.⁴⁸ Initially, all of the phenyl rings of I in its crystal form were replaced by the reduced model ligands (CH₃), and then the structure was optimized by allowing only relaxation of the C and H atoms in the DFT formalism with a PBE1PBE exchange-correlation functional,⁴⁹ which is extensively used for electronic structure calculations, along with the Los Alamos double- ζ effective core potential (LANL2DZ) basis set.⁵⁰ Further, the vibrational frequency calculations were performed at the same level of theory to check that the structures have any saddle points. The absorption spectrum of the $[Ag_{22}(SMe)_{12}(P_2(CH_2)_2(Me)_4)_4Cl_4]^{2+}$ cluster was calculated by the TD-DFT at the same level of theory. The electronic properties such as superatom orbital analysis, the total DOS, and partial DOS (PDOS) were also calculated and analyzed by using the Multiwfn3.3.5 package.⁵¹ The natural population analysis was utilized to identify the character of superatomic orbital using the NBO 3.1 software. For all of the spectra, the Fermi level (EF) was centered at the middle of the HOMO-LUMO gap. Superatomic orbitals were analyzed following a recent publication of Jiang et al.⁵³ According to this report, all superatomic orbitals should have higher s orbital contribution over the p and d orbital contributions. This is an important requirement as it describes the state of free electrons. The nature of the superatomic orbitals is usually confirmed by the computation of the superatomic DOS, which is obtained by projection of the Kohn-Sham states onto cluster-centered spherical harmonic functions $(Ylm(\theta, \varphi))$, which was beyond our present capabilities. Still, the superatomic orbital assignments made by NBO 3.1 software show the essential superatomic properties of the cluster.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b01189.

Crystallographic analysis and structure of $[Ag_{22}(dppe)_4(2,5-DMBT)_{12}Cl_4]^{2+}$ (CIF)

IR, SEM, and XPS data and theoretical analysis (PDF)

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