

Supporting Information

Camouflaging Structural Diversity: Co-crystallization of Two Different Nanoparticles having Different Cores but the Same Shell

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Experimental Section

Chemicals

Silver nitrate (AgNO₃) was purchased from Rankem chemicals. Sodium borohydride (NaBH₄, 98%), 2,4 & 2,5-dimethylbenzenethiol (DMBT), tetrabutylammonium hexafluorophosphate and triphenylphosphine (TPP) were purchased from Aldrich. All chemicals were used as received without further purification. All the solvents such as dichloromethane (DCM), methanol (MeOH), n-hexane and chloroform (CHCl₃) were purchased from Rankem chemicals and were of analytical grade. Milli-Q water was used for the synthesis.

Synthesis and purification of $[Ag_{18}H_{16}(TPP)_{10}]^{2+}$

This cluster was synthesized by a reported procedure.¹⁻² 20 mg of AgNO₃ was dissolved in 5 mL methanol (MeOH) and 9 mL of chloroform (CHCl₃) was added. Then 70 mg of triphenylphosphine, dissolved in 1 mL of chloroform, was added to the above reaction mixture under stirring condition. After 20 minutes of stirring, 6 mg of sodium borohydride in 0.5 mL of ice cold water was added. Upon addition of the reducing agent, color of the solution changed instantly to yellow from colorless. The reaction was continued for three hours under dark condition. The final color of the solution was dark green which indicated the formation of the cluster. Mixture of solvents was removed by evaporation under reduced pressure. The green solid material was washed with water to remove excess silver precursor and the reducing agent. After being cleaned with water, the material was extracted with methanol. This green colored material was characterized by UV-vis and ESI MS (Figure S1) and used for further reaction. The yield of the synthesis was 20% in terms of silver.

Synthesis and purification of a mixture of I and II

It was synthesized by a LEIST process. $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ was taken as the precursor in this procedure. 5 mg of the clean precursor cluster was taken in MeOH in a reaction bottle and 0.75 µL of 2,4-dimethylbenzenethiol (DMBT) was added under stirring condition. Just after addition, an instant color change was observed and the reaction was allowed to continue for 12 hours. The final reddish brown color of the reaction mixture indicated the formation of the product cluster. Then the reaction mixture was centrifuged at 5000 rpm for 5 minutes to remove all the insoluble precipitates and the solvent was removed under reduced pressure. Minimum amount (around 1 mL) of MeOH was added to precipitate the material and it was

centrifuged. After centrifugation, the supernatant was discarded and the precipitate was dried under reduced pressure and washed several times with hexane to remove excess triphenylphosphine. This cleaned material was dried under vacuum and dissolved in DCM and methanol which were used for characterization. Yield of the synthesis was 10% in terms of silver.

Synthesis and purification of I

It was synthesized and purified by almost the same procedure as described above. The only difference was in the amount of 2,4 dimethylbenzenethiol used. Here 0.25 μ L of thiol was used instead of 0.75 μ L. Yield of the synthesis was 5% in terms of silver.

Synthesis and purification of [Ag₄₆(2,5-SPhMe₂)₂₄(PPh₃)₈]²⁺

The synthesis and purification procudures were almost same as described for the mixture. Here an isomeric thiol was used, 2,4-dimethylbenzenethiol was changed to 2,5-dimethylbenzenethiol. Yield of the synthesis was 15% in terms of silver.

Crystallization of a mixture of I and II clusters

Cleaned 40 mg of the solid cluster was dissolved in 2 mL of distilled DCM, filtered by syringe filter of pore size 0.22 μ m and layered by distilled hexane at 1:1 (by volume) ratio and kept at 4°C. After approximately one-week, black crystals were observed which were suitable for SCXRD.

Crystallization [Ag₄₆(2,5-SPhMe₂)₂₄(PPh₃)₈]²⁺ cluster

Cleaned 40 mg of the solid cluster was dissolved in 1.5 mL of distilled DCM and 0.5 mL of MeOH, filtered by syringe filter of pore size 0.22 μ m and layered by distilled hexane at 1:1 (by volume) ratio and kept at 4°C. After approximately one-week, black hexagonal crystals were observed which were suitable for SCXRD.

Instrumentation

UV/Vis spectroscopy:

UV/Vis spectra were recorded using a Perkin Elmer Lambda 25 instrument in the range of 200 - 1100 nm.

ESI MS

The ESI MS spectra were measured using a Waters Synapt G2Si HDMS instrument. The Synapt instrument is equipped with an electrospray source, quadrupole ion trap, ion mobility cell and time of flight detector. Samples were measured in positive ion mode.

X-ray crystallography

(i) Mixture of Ag_{40} and Ag_{46}

Single crystal data were measured using a Bruker Kappa APEX III CMOS diffractometer using Cu $K\alpha$ ($\lambda = 1.54178$ Å) radiation. Indexing was performed using APEX III. Data integration and reduction were performed using SAINT V8.37A. Absorption correction was

performed by multi-scan method implemented in SADABS (Bruker, 2016). Space group was determined using XPREP implemented in APEX III.

(ii) [Ag₄₆(2,5-SPhMe₂)₂₄(PPh₃)₈]²⁺

Single crystal X-ray diffraction data was collected in a Bruker APEX-III CMOS diffractometer equipped with Mo K α radiation and photon pixel detector. Unit cell parameters were determined using 36 frames collected from different zones of the reciprocal lattice. The intensity was integrated using SAINT V8.37A software. Multi-scan absorption correction was done using SADABS (Bruker 2016).

ESI MS conditions

The conditions for resolved electrospray ionization mass spectra were as follows:

Sample concentration: 10 µg/mL Solvent: MeOH Flow rate: 30 uL/min Capillary voltage: 3 kV Cone voltage: 0 V Source offset: 0 V Source Temperature: 80-100°C Desolvation Temperature: 150-200°C Desolvation gas flow: 400 L/h Trap gas flow: 10 L/h

Experimental conditions for differential pulse voltammetry

Differential Pulse Voltammetry (DPV) was performed using Biologic SP200 potentiostat in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in dichloromethane at 0-5 °C. Prior to the electrochemical measurements, solutions were degassed for 10 min in five necked reaction vessel which was equipped with three electrodes (both Pt wire used as working and counter electrode and Ag quasi reversible electrode as a reference electrode) and two gas inlet outlet provisions. DPV was performed within a potential window -2V to +2V and the potential was applied to the working electrode (Pt wire) with respect to the reference electrode. In the course of measurements, pulse height and pulse width were maintained as 5 mV and 50 ms, respectively. Solutions of Ag_{40} and Ag_{46} clusters were taken in an electrolyte solution of Bu_4NPF_6 in dry DCM.

Computational details

The Ag (4d¹⁰5s¹), S (3s²3p⁴), P (3s²3p³), C (2s²2p²) and H (1s¹) electrons were treated as valence and the inner electrons were included in a frozen core with scalar-relativistic effects being included for Ag. The exchange-correlation functional employed was the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) and the basis set was double zeta plus polarization (DZP) in all our calculations. We used a 0.2 Å grid spacing for calculating the electron density and a convergence criterion of 0.05 eV/Å, for the residual forces on atoms was used in all geometry optimizations, without any symmetry constraints. The linear combination of GPAW were used to carry out the efficient structure optimization. The optimized structures from the finite-difference real-space grid method of GPAW were used to carry out the efficient structure optimization. The optimized structures from the finite-difference real-space grid method were used for the optical absorption calculation using LR-TDDFT.³ In order to plot the theoretical absorption spectrum for mixture, the amplitude (oscillator strength) of both the clusters was scaled by a factor of 0.5 and then added to each other, to yield the normalized amplitude for the mixture.

The lowest 20 to 50 transitions were considered in order to determine the optical gap of the clusters based on their oscillator strength. The absorption spectra were plotted with a Gaussian broadening of 0.05 eV in the energy range of 0.95-3.3 eV. The distribution of electron density in molecular orbitals corresponding to the optical gap transition was plotted (iso-surface value 0.016-0.018), to analyze the changes in the electronic structure of the clusters. Furthermore, the Bader charge analysis was also carried out to study the charge transfer between the cluster and the ligands. The molecular orbitals were visualised using VESTA software.

For the density of states calculations, the DFT geometry optimization was performed using the crystal structure of the clusters with reduced H ligands, $[Ag_nS_{24}P_8H_{48}]^{2+}$ (n = 46, 40). The hybrid functional, PBE1PBE and LANL2DZ effective core potential (ECP) methodology was used as implemented in Gaussian09 software⁴. Later, the total density of states and projected density of states calculations were analyzed using the Multiwfn3.3.5 package⁵. For all the spectra, the Fermi level (E_F) was centred at the middle of HOMO-LUMO gap.

Analysis of superatomic orbitals

In order to understand further the superatomic orbitals of the atomically-precise monolayer protected Ag₄₆ cluster, the density of states (DOS) spectra were analysed in detail and the configurations of superatomic orbitals $(1S^2, 1P^6, 1D^{10} \text{ and } 2S^2)$ identified are shown in Figure S29. A description of our method of identifying the superatomic orbitals is as follows.

It has been shown for bare gold and silver clusters that the superatomic orbitals have a dominant contribution from 6s atomic orbitals in the case of gold and 5s atomic orbitals in the case of silver, compared to the p- and d-atomic orbital contributions (Wanrun Jiang, Yang Gao, Dexuan Xu, Fang Liu, Zhigang Wang; *J. Electron. Mater.* **2017**, *46*, 3938; Takashi Yumura, Mitsuhiro Kumondai, Yasushige Kuroda, Takashi Wakasugi, Hisayoshi Kobayashia, *RSC Adv.* **2017**, *7*, 4950). Therefore, superatomic orbitals in ligand protected clusters may also be expected occur at the energies where there are peaks in the s-orbital

contribution to the DOS, and where this contribution dominates over the p atomic orbital contribution (for the case of P superatomic orbitals), and over the d atomic orbital contribution (for the case of D superatomic orbitals). The superatomic orbitals of any symmetry mainly contain contributions from the metal s atomic orbitals (AOs) because of the greater delocalization of an overlapping system of s-orbitals, which is a necessary requirement for a state describing a free electron.

Hence, the energy level positions of the superatomic orbitals emerge exactly in the regimes where the 5s AOs have the greatest contribution corresponding to peaks in the 5s PDOS. Therefore, the partial DOS (PDOS) spectrum of 5s AOs of Ag_{46} cluster was used to identify the configuration of superatomic orbitals and also by comparison of the s-orbital PDOS with the PDOS of the p and d atomic orbitals. We have already shown the PDOS of the Ag s, p and d orbitals in Figure S27. The relative greater contribution of the s atomic orbital compared to p and d can be seen in the regions of energy where the corresponding superatomic orbitals lie.

Based on the above criteria we selected the likely candidates for superatomic orbitals and further checked the symmetry of the overall envelope of the density consistent with the S, P, and D assignment. From the DOS spectrum, it is clear that the frontier orbitals of Ag₄₆ cluster are mainly dominated by the contribution of 5s atomic orbitals (AOs) of silver atoms. From Figure S29, the highest occupied molecular orbital (HOMO) is the 2S superatomic orbital. The calculated isosurfaces of a selection of MOs, with energies located at 5s peaks, that are most likely to correspond to the superatomic orbitals of Ag₄₆ cluster are plotted in Figure S30. For Ag₄₆, the 2S orbital can be clearly identified by its spherical symmetry. The P and D superatomic orbitals, identified by dominant s-orbital contribution over p- and d-orbital contributions, can be visually distinguished from the S superatomic orbitals by the presence of the nodal planes. It is more difficult, however, to distinguish between the features of the P and D orbitals from the density plots alone. A similar analysis was carried out for Ag₄₀ which shows that the HOMO level, shown in Figure S31, coincides with the third D-sublevel. The DOS spectrum of Ag₄₀ cluster clearly shows that there is a splitting in the 1D superatomic orbitals such that three orbitals $(1D^6)$ lie in the occupied region and another two orbitals exist in the unoccupied region. From the calculations, it is clear that Ag₄₀ cluster is also a superatom and all their superatomic orbitals are plotted in Figure S32.

Confirmation of nature of the superatomic orbitals is usually made by the computation of the superatomic DOS which is obtained by projection of the Kohn-Sham states onto clustercentred spherical harmonic functions $(Y_{lm}(\theta,\varphi))$. However, this calculation was beyond our current capabilities. Hence, the superatomic orbital assignments we have presented are approximate, but still reveal the essential superatomic properties of both the clusters.

Analysis of differential pulse voltammetry

We have performed differential pulse voltammetry (DPV) of Ag_{40} and Ag_{46} clusters to estimate the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap. According to earlier studies DPV has been used extensively to determine the HOMO-LUMO gap of atomically precise clusters.⁶⁻¹⁰ DPV results show several peaks in positive and negative potential regions which are assigned as oxidation and reduction peaks, respectively. The first reduction peak (R1) and oxidation peak (O1) of Ag_{40} cluster are -1.19 V and +0.22 V, respectively (Figure S21). Electrochemical gap of Ag_{40} is the difference between the O1 and R1 which is +0.22 - (-1.19) =1.41 V. The actual HOMO-LUMO gap can be obtained by subtracting the charging energy.⁹⁻¹⁰ The charging energy is determined by subtracting the two oxidation potential values (O2-O1=0.71-0.22=0.49 V) (Figure S21A). Hence, the HOMO-LUMO gap for Ag_{40} is 0.92 eV (1.41-0.49). Similarly, the HOMO-LUMO gap of Ag_{46} was determined to be ~1.30 eV (Figure S21B). The predicted (TDDFT) HOMO-LUMO gaps of Ag_{40} and Ag_{46} are 1.0 and 1.43 eV, respectively which are close to the experimental results.

Single crystal X-ray diffraction analysis of a mixture of I and II clusters

Structure was solved using SHELXT-2017 and least-squares refined using SHELXL-2017. Crystal data and refinement conditions are shown in Table S4. Suitable restraints were applied during the least-squares (LS) refinement. The molecule has a crystallographic 2/m symmetry which makes the asymmetric unit as ¹/₄ th of the molecule. The structure solution and refinement clearly indicated the existence of disorder for most of the atoms in the asymmetric unit. Successive jobs of least squares refinement followed by Fourier difference map could finally yield the structure and disorder component. As the refinement proceeded, it became evident that Ag₁₁ and Ag₁₂ were not disordered and their actual occupancy refined to 50% of the natural occupancy of the site. The two molecules exist as disorder components in the same site of the X-ray structure, their actual distribution among the unit cells of the crystal cannot be judged from the X-ray as (atomic positions we got from single crystal X-ray structure are only a picture of atom coordinates averaged over all unit cells of the crystal). Apart from disorder caused by the existence of two types of molecules in the same site, there are additional symmetry related disorders in both the molecules. The TPP of P2, P3, P2`, P3` are symmetry disordered. Similarly the thiols S6, S7, S6[°], S7[°] are also disordered. While some hydrogen atoms could be fixed at geometrically idealized positions, majority of the hydrogen atoms were ignored as the disorder did not allow their fixation. The difference Fourier map towards the end showed the presence of water and hexane molecules in the lattice. The oxygen of water could be located and refined. However, hexane molecules were too disordered to be modeled and hence they were ignored. An ortep representation of Ag₄₀ and Ag₄₆ clusters with ellipsoid probability 40% is presented in Figure S27A and B, respectively (carbon and hydrogen atoms are omitted for clarity).

Single crystal X-ray diffraction analysis of $[Ag_{46}(2,5-SPhMe_2)_{24}(PPh_3)_8]^{2+}$ cluster

Structure was solved using SHELXT-2017 and least-squares refined using SHELXL-2017. The cluster was crystallized in trigonal crystal system with space group P-3.¹¹ There is one molecule in a unit cell with 1/6th of the molecule in the asymmetric unit. Along with the compound there are two molecules of triphenyl phosphino oxide in the unit cell. Triphenyl phosphino oxide is the possibly oxidized product of triphenyl phosphine. The cluster is essentially positively charged and nitrate is balancing the charge. However the anions could not be modeled from the difference Fourier Map due to severe disorder.

Table	S1.	Reported	crystal	structures	of	silver	clusters	and	their	inner	core	and	shell
parame	eters												

Cluster	Inner Core	Shell	Ref
$[Ag_{67}(SPhMe_2)_{32}(PPh_3)_8]^{3+}$	Ag ₂₃ (centred	$Ag_{44}S_{32}P_8$	12
	cuboctahedron)		
$[Ag_{14}(SPhF_2)_{12}(PPh_3)_8]$	Ag ₆ (octahedron)	$Ag_8S_{12}P_8$	13
$[Ag_{38}(SPhF_2)_{26}(P^nBu_3)_8]$	Ag_{14} (fcc)	$Ag_{24}S_{26}P_8$	14
$[Ag_{63}(SPhF_2)_{36}(P^nBu_3)_8]^+$		$Ag_{49}S_{36}P_8$	14
$[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$	Ag ₁₃ (centred	$Ag_{16}S_{24}P_4$	15
	icosahedra)		
$[Ag_{78}(SPhCF_3)_{42}(DPPP)_6]$	Ag ₂₂ (three mutually	$Ag_{56}S_{42}P_6$	16
	interpenetrating		
	icosahedra)		
[Ag ₅₀ (DPPM) ₆ (TBBM) ₃₀]	Ag ₁₂ (hollow	$Ag_{38}S_{30}P_6$	17
	icosahedra)		
$[Ag_{25}(SPhMe_2)_{18}]^{-1}$	Ag ₁₃ (centred	$Ag_{12}S_{18}$	18
	icosahedra)		
$[Ag_{44}(FTP)_{30}]^{4-}$	Ag ₁₂ (hollow	$Ag_{32}S_{30}$	19, 20
$[Ag_{44}(p-MBA)_{30}]^{4-}$	icosahedra)		
$[Ag_{62}S_{12}(SBu^{t})_{32}]^{2+}$	Ag_{14} (fcc)	$Ag_{48}S_{44}$	21
$\left[Ag_{141}X_{12}(S-Adm)_{40}\right]^{3+}$	Ag ₁₉ (biicosahedra)	$Ag_{122}S_{40}X_{12}$	22
$[Ag_{23}(SC_2H_4Ph)_{18}(PPh_3)_8]$	Ag ₆ (octahedron)	$Ag_{12}S_{18}P_8$	23
$[Ag_{46}(SPhMe_2)_{24}(PPh_3)_8]^{2+}$	Ag_{14} (fcc)	$Ag_{32}S_{24}P_8$	Present
			work
$[Ag_{40}(SPhMe_2)_{24}(PPh_3)_8]^{2+}$	Ag ₈ (simple cube)	$Ag_{32}S_{24}P_8$	Present
			work

Acronyms of ligands used:

SPhMe₂: 2,4 dimethylbenzenethiol

PPh₃: Triphenylphosphine

SPhF₂: 3,4-difluoro-benzenethiol

PⁿBu₃: Tributylphosphine

BDT: Benzene-1,3-dithiol

SPhCF ₃ :4-(trifluoromethyl)thiophenol
DPPP: 1,3-bis(diphenyphosphino)propane
p-MBA: 4-mercaptobenzoic acid
SBu ^t : <i>tert</i> -butyl mercaptan
TBBM: 4- <i>tert</i> -butylbenzyl mercaptan
DPPM: Bis(diphenylphosphino) methane
X: Cl, Br and I
S-Adm: 1-adamantanethiolate

Table S2. A summary of the average Ag-Ag distances in the two clusters reported in this work

	Bond	length	in	Bond	length	in
Bonds	[Ag ₄₆ (SPl	$hMe_2)_{24}(PPh)$	1 ₃) ₈]	[Ag ₄₀ (S	PhMe ₂) ₂₄ (PPh	1 ₃) ₈]
	(Å)			(Å)		
Ag(P)-Ag(P)	-			2.68		
Ag(F)-Ag(F)	3.80			-		
Ag(O)-Ag(O)	2.88			-		
Ag(F)-Ag(O)	2.70			-		
Ag(S)-Ag(S)	3.0			3.0		
Ag(P)-Ag(S)	-			3.12		
Ag(F)-Ag(S)	2.95			-		
Ag(O)-Ag(S)	3.0			-		
Ag-S	2.64			2.64		
Ag-P	2.45			2.45		

The bonds in the table are defined as follows:

Ag–P bond length between Ag and phosphine

Ag-S bond length between Ag and thiolate

Ag(P) refers to the silver atoms of the Ag₈ perfect cube in Ag₄₀

Ag(F) refers to the silver atoms of the Ag₈ cube in Ag₄₆

Ag(O) refers to the silver atoms of the Ag₆ octahedron in Ag₄₆

Ag(S) refers to the silver atoms of the Ag_{24} outer core present in both the structures

Table S3. A summary of MO transitions to the optical gap of $[Ag_{46}(SCH_3)_{24}(P(CH_3)_3)_8]^{2+}$ and $[Ag_{40}(SCH_3)_{24}(PCH_3)_8]^{2+}$

$\begin{tabular}{ l l l l l l l l l l l l l l l l l l l$	Transition energy (eV)	Oscillator strength
HOMO-4 → LUMO	1.27	0.183
HOMO-1 → LUMO+3	1.33	0.170
HOMO-6 \longrightarrow LUMO+1	1.34	0.135
HOMO-3 → LUMO+2	1.41	0.119
Transition of the optical gap of $[Ag_{40}(SCH_3)_{24}(P(CH_3)_3)_8]^{2+}$	Transition energy (eV)	Oscillator strength
HOMO \longrightarrow LUMO+6	0.96	0.390
HOMO-4 → LUMO+4	0.94	0.414

Table S4. Crystal data and structure refinement for co-crystal

Identification code	SUGI		
Empirical formula	$0.5(C_{336}H_{336}Ag_{46}N_2O_8P_8S_{24})$		
	$+ 0.5(C_{336}H_{336}Ag_{40}N_2O_8I_3)$	P_8S_{24}) + 2H ₂ O+2NO ₃	
Formula weight	10189.69		
Temperature	110(2) K		
Wavelength	1.54178 Å		
Crystal system	Monoclinic		
Space group	C2/m		
Unit cell dimensions	a = 28.053(2) Å	$\alpha = 90^{\circ}$	
	b = 35.669(3) Å	$\beta = 90.6^{\circ}$	
	c = 22.5883(16) Å	$\gamma = 90.0^{\circ}$	
Volume	22602(3) Å ³		
Z	2		
Density (calculated)	1.497 g/cm ³		
Absorption coefficient	16.159 mm ⁻¹		
F(000)	9918		
Crystal size	0.100 x 0.080 x 0.060 mm ³		
Theta range for data collection	3.151 to 52.613°		
Index ranges	-28<=h<=28, -36<=k<=36, -23<=l<=23		
Reflections collected	106189		
Independent reflections	13095 [R(int) = 0.1393]		
Completeness to theta = 52.613°	99.0 %		
Absorption correction	Semi-empirical from equ	ivalents	
Max. and min. Transmission	0.36 and 0.24		
Refinement method	Full-matrix least-squares	on F ²	
Data / restraints / parameters	13095 / 3488 / 2035		
Goodness-of-fit on F ²	1.012		
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.2270		
R indices (all data)	R1 = 0.1475, wR2 = 0.2798		
Extinction coefficient	nction coefficient n/a		
Largest diff. peak and hole $1.170 \text{ and } -1.141 \text{ e} ^{\text{A}-3}$			

	L = L = 2	24(J)01
Identification code	1	
Empirical formula	$C_{372}H_{366}Ag_{46}O_2P_{10}S_{24}$	
Formula weight	10909.79	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P-3	
Unit cell dimensions	a = 24.7173(5) Å	$\alpha = 90^{\circ}$.
	b = 24.7173(5) Å	β= 90°.
	c = 24.6450(6) Å	γ= 120°.
Volume	13039.5(6) Å ³	
Z	1	
Density (calculated)	1.389 g/cm^3	
Absorption coefficient	1.844 mm ⁻¹	
F(000)	5310	
Crystal size	0.100 x 0.100 x 0.050 mm	3
Theta range for data collection	2.855 to 24.988°.	
Index ranges	-29<=h<=29, -29<=k<=29	9, -29<=l<=29
Reflections collected	229996	
Independent reflections	15300 [R(int) = 0.2081]	
Completeness to theta = 24.988°	99.8 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.88 and 0.76	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	15300 / 1035 / 845	
Goodness-of-fit on F ²	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0600, wR2 = 0.153	51
R indices (all data)	R1 = 0.1782, wR2 = 0.238	87
Extinction coefficient	n/a	
Largest diff. peak and hole	1.487 and -0.829 e.Å ⁻³	

Table S5 Crystal data and structure refinement for $[Ag_{46}(2,5 \text{ SPhMe}_2)_{24}(PPh_3)_8]$



Figure S1. Characterization of $[Ag_{18}(PPh_3)_{10}H_{16}]^{2+}$ by UV-vis and ESI MS. (A) Full range ESI MS of a methanol solution of $[Ag_{18}(PPh_3)_{10}H_{16}]^{2+}$ in positive ion mode. The major peak is for $[Ag_{18}(PPh_3)_{10}H_{16}]^{2+}$. (B) Comparison of experimental (red trace) and simulated (black) isotopic distributions of the cluster. Peaks labelled with asterisk (*) correspond to PPh₃ loss. (C) UV-vis absorption spectrum of the cluster. These data presented here is matching with previous report.¹⁻²



Figure S2. Construction of the FCC (Ag_{14}) or octacapped octahedron ($Ag_6@Ag_8$). (A) Ag_8 core which caps the Ag_6 octahedron. (B) Ag_6 octahedron which can be viewed also as square bipyramid. (C) Ag_{14} core which corresponds to FCC or octacapped octahedron. All atoms shown are silver.



Figure S3. Complete crystal facets present in the FCC (Ag_{14}). Facets are shown in ball-and-stick model. (A) Square shaped facet {100}. (B) Rectangular shaped facet {110}. (C) Equilateral triangle shaped facet {111}. The atoms other than facets are shown in wireframe model. All atoms shown are silver. All atoms shown are silver.



Figure S4. Construction of $Ag_{32}S_{24}P_8$ shell, tetrahedrally oriented silver-thiolate-phosphine complexes (AgS₃P) are sitting on the faces of eight hexagons of Ag₂₄ outer core. (A) Eight units of tetrahedrally oriented AgS₃P. (B) Ag₂₄ outer core in ball-and-stick model. (C) Ag₂₄ outer core encapsulated by eight units of AgS₃P. (D) Ag₂₄ outer core in spacefilling model. (E) One AgS₃P unit in ball-and-stick model. (F) Ag₃₂S₂₄P₈ shell. Color legends: yellow, sulphur; blue, red, silver; magenta, phosphorous.



Figure S5. Encapsulation of Ag_6 inner core by Ag_{24} outer core. (A) Ag_{24} outer core consists of six square faces. The faces are shown in six different colours. (B) Ag_6 octahedron. (C) Ag_6 inner core encapsulated by Ag_{24} outer core, which resulted in the formation of six square pyramids. (D) One such square pyramid is shown by an arrow in wireframe model. This kind of architecture is not observed in case of **II** cluster. All atoms shown are silver.



Figure S6. (A) and (B) Organization of $[II](NO_3)_2$ and $[I](NO_3)_2$, respectively in a centred rectangular 2D lattice along z axis. (C) and (D) Packing diagram of the same which exhibits rectangular 2D lattice along x axis. Hydrogen atoms are omitted for clarity. Yellow rectangles correspond to unit cells. Color legends: gray, carbon; magenta, silver; yellow, sulphur; orange, phosphorous; red, oxygen; cyan, nitrogen.



Figure S7. The packing diagram of **[II]**(**NO**₃)₂ and **[I]**(**NO**₃)₂ clusters. It clearly reveals the location of counter ions (**NO**₃⁻) in the packing of both the clusters. Each unit cell is having two clusters (Z = 2 in Table S4) and four counter ions (as each counter ion contributes half per cluster). Hence each cluster contains two counter ions (**NO**₃⁻). (A) and (B) Packing of **[II]**(**NO**₃)₂ and **[I]**(**NO**₃)₂ clusters, respectively. Counter ions are shown in spacefilling model. Hydrogen atoms are omitted for clarity. Crystallographic axes a, b and c are shown by red, green and blue colours, respectively. Color legends: light green, carbon; magenta, silver; yellow, sulphur; orange, phosphorous; cyan, nitrogen; red, oxygen.



Figure S8. The construction of Ag_{32} and Ag_{38} kernels present in **II** and **I** clusters, respectively. (A) Ag_{24} outer core. (B) and (D) Ag_{32} and Ag_{38} kernels, respectively. (C) and (E) One hexagon from (B) and (D), respectively. (a) Ag_8 inner core of **II**. (b) Ag_{14} ($Ag_8@Ag_6$) inner core of **I**. The cubes of simple cubic and face-centred cubic structures are shown in white colour. Ag_6 octahedral inner core is shown in magenta colour. Dotted green lines represent the cube in FCC. All atoms shown are silver.



Figure S9. (A) Truncated octahedron Ag_{32} shell in wireframe model. (B) Inner core Ag_6 octahedron in spacefilling model. (C) Encapsulation of Ag_6 octahedron, by truncated octahedron Ag_{32} shell to construct Ag_{38} .



Figure S10. Peaks at m/z 5176.25, 4853.5 and 3235.75 are expanded (From main manuscript Figure 4) in A, B and C, respectively. In A and B the characteristic peak separation is m/z 0.5 which confirm +2 charge state. Similarly in C peak separation of m/z 0.33 reveals +3 charge state.



Figure S11. Collision energy dependent mass spectra of \mathbf{I}^{2+} . **II** was not detected in any charge state during the collision induced dissociation experiment of \mathbf{I}^{2+} . (A) Full range spectra show the absence of **II** in +3 and +1 charge state. (B) Expanded region from Figure A show the absence of **II** in +2 charge state. Dotted vertical lines of black, red and blue correspond to the m/z positions of **II** in +3, +1 and +2 charge state, respectively. The collision energy (C.E.) values given are in instrumental units.



Figure S12. Collision-induced dissociation (CID) experiments were performed on both the clusters. (A) and (B) Collision energy dependent mass spectra of \mathbf{I}^{2+} and \mathbf{II}^{2+} , respectively. Systematic losses of secondary ligands (triphenylphosphine) were observed due to weaker binding with the cluster core. CID experiments revealed the maximum loss of eight phosphine ligands which confirm the number of secondary ligands present in the cluster formulae. This observation is consistent with SCXRD results. The symbol asterisk (*) indicates the loss of thiol ligands (SPhMe₂). The collision energy (C.E.) values given are in instrumental units.



Figure S13. (A) and (B) Time dependent ESI MS and UV-vis spectra, respectively of a mixture of **II** and **I** clusters, heated in methanol at 50 °C. UV–vis spectra showed no considerable change with time up to 8 h, only change in the absorbance was observed. After 8 h of stirring at 50 °C, the optical absorption spectrum started to change and the highly structured features disappeared after 12 h. This indicates that the cluster was getting decomposed and this is reflected in the ESI MS also. Time dependent ESI MS revealed the presence of the species, **II** and **I** and no interconversion was seen as their relative intensities were same. This observation established that there is no oxidation product of **I** to form **II**. Studies were also conducted on pure clusters also. No interconversion of one cluster to the other was seen. The peaks marked with asterisk indicate the loss of PPh₃ ligands.



Figure S14. Comparison of UV-vis spectra of a mixture of **II** and **I** clusters along with previously reported clusters.¹⁸⁻¹⁹ Some of the features are comparable with the two reported clusters but the overall spectrum is different. FTP refers to 4-fluorothiophenol.



Figure S15. Comparison of UV-vis spectra of a mixture of **II** and **I** clusters (red trace) with previously reported $[Ag_{67}(SPhMe_2)_{32}(PPh_3)_8]^{3+}$ (black trace).¹² Both the clusters are synthesised by using same ligands but UV-vis spectra are very different. This indicates that synthetic methodology plays major role in determining the size and shape of the nanoclusters.



Figure S16. (A) Positive ion mode ESI MS. Peaks labelled * indicate phosphine loses. (B) Expansion of the selected area is shown by an arrow. The peak corresponding to Ag_{46} was observable only upon magnification.



Figure S17. (A) Full range ESI MS of a methanol solution of crystals in positive ion mode. The peak is due to $[Ag_{46}(2,5-SPhMe_2)_{24}(PPh_3)_8]^{2+}$.(B) The isotopic distribution of experimental spectrum (black) is compared with simulated spectrum (blue). (C) UV-vis absorption spectrum of a solution of crystals in dichloromethane.



Figure S18. Comparison of the crystal structures of Ag_{46} cluster present in the co-crystal and the single component crystal. (A) and (B) Full structure of $[Ag_{46}(2,5-SPhMe_2)_{24}(PPh_3)_8]$ and $[Ag_{46}(2,4-SPhMe_2)_{24}(PPh_3)_8]$, respectively. Counter ions are not shown here. Hydrogen atoms of triphenylphosphine for $[Ag_{46}(2,4-SPhMe_2)_{24}(PPh_3)_8]$ are not fixed. (C) and (D) Structure of $Ag_{46}S_{24}P_8$ present in multicomponent crystal (co-crystal) and single component crystal, respectively. Carbon and hydrogen atoms are not shown for clarity.



Figure S19. Time dependent UV-vis spectra of Ag_{40} and Ag_{46} clusters, heated at 50°C in MeOH. (A) and (B) correspond to UV-vis spectra of Ag_{40} and Ag_{46} , respectively. UV-vis spectra showed the disappearance of highly structured features of Ag_{40} after 1.5 h. In the case of Ag_{46} , the spectral features and absorbance were the same up to 3 h, only change in absorbance was seen afterwards. This observation reveals that Ag_{40} is not thermally very stable as compared to Ag_{46} .



Figure S20. Comparison of optical absorption spectra of solutions of Ag_{46} , Ag_{40} . UV-VIS-NIR spectra of Ag_{40} and Ag_{46} clusters in DCM. Red and black spectra correspond to Ag_{46} and Ag_{40} , respectively. Inset shows the absorption of Ag_{40} in the NIR region.



Figure S21. (A) and (B) correspond to differential pulse voltammetry (DPV) of Ag_{40} and Ag_{46} clusters in forward and reverse scan mode. It was carried out to determine the HOMO-LUMO gaps of both the clusters. R1 and R2 indicate the 1st and 2nd reduction potential values, respectively. O1 and O2 stand for the 1st and 2nd oxidation potential values.



Figure S22. Reduced model structure of Ag_{40} and Ag_{46} . A and B correspond to $[Ag_{40}(SCH_3)_{24}(P(CH_3)_3)_8]$ and $[Ag_{46}(SCH_3)_{24}(P(CH_3)_3)_8]$, respectively. Color legends: white, hydrogen; cyan, carbon; yellow, sulphur; orange, phosphorous; magenta, silver.



Figure S23. Construction of theoretical optical absorption spectrum from a 1:1 mixture of Ag_{40} and Ag_{46} clusters. Red and black traces indicate the calculated absorption spectrum of $[Ag_{40}(SCH_3)_{24}(P(CH_3)_3)_8]$ and $[Ag_{46}(SCH_3)_{24}(P(CH_3)_3)_8]$, respectively. Green trace indicates the mixture of both the clusters in equal proportion.



Figure S24. Molecular orbital transitions to the optical gap of $[Ag_{46}(SCH_3)_{24}(P(CH_3)_3)_8]$. The calculated HOMO -4, HOMO-1, HOMO-6, LUMO, LUMO+3, LUMO+1 of $[Ag_{46}(SCH_3)_{24}(P(CH_3)_3)_8]$ cluster.



Figure S25. Molecular orbital transitions to the optical gap of $[Ag_{40}(SCH_3)_{24}(P(CH_3)_3)_8]$. The calculated HOMO, HOMO-4, LUMO+4 and LUMO+5 of $[Ag_{40}(SCH_3)_{24}(P(CH_3)_3)_8]$ cluster.



Figure S26. Comparison of the predicted optical absorption spectra of $[Ag_{40}(SCH_3)_{24}(P(CH_3)_3)_8]$ cluster in its 2+ and 3+ charge states.



Figure S27. Comparison of the plot of density of states versus energy of both the clusters, Ag_{40} and Ag_{46} . TDOS correspond to total density of states. (**A**) and (**C**) correspond to density of states of Ag_{40} and Ag_{46} , respectively. (B) and (D) correspond to the expansion of (A) and (C), respectively in the specific energy region. The energies of the corresponding molecular orbitals, responsible for major transitions in both the clusters are marked by black dotted lines. Fermi level (E_F) was centred at the middle of HOMO-LUMO gap. The optical transitions in both clusters basically have the final state consisting of mainly 5p Ag orbitals. Intraband 5s to 5p, and interband 4d to 5p transitions are expected to occur mainly in these clusters with some contribution from Ag 5p or S 3p to Ag 5s.



Figure S28. (A) and (B) correspond to the density of states of Ag_{46} and Ag_{40} , respectively for ligands alone. The atomic orbital contributions of ligands other than 3p of sulphur are not significantly influencing near HOMO-LUMO for both the clusters. The total PDOS contribution arising from the core and shell was calculated by summing over different orbitals of atoms in the core and shell regions for Ag_{40} (S2 D) and Ag_{46} (S2 C).



Figure S29. Plot of density of states versus energy in case of Ag_{46} and the filling of 20 electrons in the superatomic orbitals. The highest molecular orbital is set to be at zero. Dotted lines correspond to the total density of states and solid red lines indicate the desnity of states of Ag_5s .



Figure S30. Isosurfaces of superatomic orbitals in Ag_{46} . The energy values (eV) are shown in the brackets. The highest occupied molecular orbital is set to be at zero.



Figure S31. Plot of density of states versus energy in case of Ag_{40} and the filling of 14 electrons in the superatomic orbitals. The highest molecular orbital is set to be at zero. Dotted lines correspond to the total density of states and solid red lines indicate the desnity of states of Ag_5s .



Figure S32. Isosurfaces of superatomic orbitals in Ag_{40} . The energy values (eV) are shown in the brackets. The highest occupied molecular orbital is set to be at zero. 1D superatomic orbitals are observed to split such that three orbitals (1D⁶) lie in the occupied region and another two orbitals are in the unoccupied orbitals.



Figure S33. Ortep representation of both the clusters with ellipsoid probability 40%. A and B correspond to $Ag_{40}S_{24}P_8$ and $Ag_{46}S_{24}P_8$, respectively. Color legends: silver, blue; green, phosphorus; brown, sulphur. Carbon and hydrogen atoms are omitted for clarity.

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