

Supporting Information

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

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Instrumentation

UV-Vis absorption spectroscopy

UV-Vis absorption spectra were measured in the wavelength range of 1100-200 nm using Perkin Elmer Lambda 365 UV-Vis spectrometer, equipped with a bandpass filter of 1 nm. The scan rate of the spectral acquisition is 50 nm/min.

Photoluminescence spectroscopy

Photoluminescence spectra were measured using Horiba Jobin Yvon Nanolog spectrofluorometer by applying 3 nm bandpass filter having resolution bandwidth of 5 nm. The Nanolog instrument has a 450 W xenon-arc lamp source, double monochromator with kinetic gratings, associated reflective optics, and CCD detector. Samples were dissolved in DCM (~2.5 ml) was placed in a quartz cuvette having an optical path length of 1 cm to measure the spectrum.

TCSPC measurement

Time resolved PL lifetime measurements were performed using Horiba DeltaFlex time-correlated single photon count (TCSPC) spectrometer equipped with Horiba Delta diode 405 nm laser. Resulted emissive photons were collected using Horiba PPD-850 detector. The biexponential fittings of the decay curve was performed by deconvolution procedure of DAS6 (v. 6.8, Horiba Jobin Yvon) software.

Optical microscopy

Optical microscopic images of single crystals were measured in transmission mode using LEICA light microscope equipped with LAS V4.8 software.

Scanning electron microscopy

The SEM measurements were performed at ultrahigh vacuum using Thermo Scientific Verios G4 UC field emission scanning electron microscope (FESEM) at an operating voltage of 10 kV with a beam resolution of 0.6 nm. The cluster assembled nanostructure samples were applied onto a porous carbon film, followed by a deposition process using gold plasma sputtering lasting for 2 minutes. Q150V Plus gold sputtering instrument from Quorum Technology was used to perform the gold sputtering under a vacuum of 1×10^{-6} mbar.

Scanning transmission electron microscopy and Tomography

The STEM imaging with energy dispersive X-ray spectroscopy (EDS) and elemental mapping were performed using JEOL F200 (S) TEM electron microscope operated at 200 keV. For 3D reconstruction of self-assembled superstructures, tilt series of TEM 2D projections was acquired between $\pm 69^\circ$ with an increment angle of 2° . The images in tilt series were first aligned and processed using IMOD software.¹ The aligned file was further used for 3D reconstruction using a custom-made maximum entropy method (MEM) program.^{2,3} The reconstructed 3D density maps were processed and colored using Chimera software. The images were obtained using Chimera.

X-ray photoelectron spectroscopy

XPS measurements were performed using an ESCA probe TPD equipped with a polychromatic Mg K α X-ray source ($h\nu = 1253.6$ eV). The binding energy of the spectral regions of different elements was calibrated with respect to C 1s (285.0 eV).

NMR spectroscopy

NMR spectra of the Ag₁₄ cluster was measured using a Bruker 500 MHz NMR instrument. Samples were dissolved in CDCl₃ to record the spectrum. Data were analyzed using MestRe-Nova software.

Infrared spectroscopy

FT-IR spectra were measured using a JASCO-4100 FT-IR spectrometer after preparing potassium bromide (KBr) pellets of the respective samples.

Mass spectrometry

High resolution mass spectra was measured using a Waters Synapt G2Si HDMS instrument. The instrument is equipped with an electrospray ionization source, ion trap, ion mobility cell, and time-of-flight mass analyzer. An optimized operating condition such as flow rate 15-20 μ L/min, capillary voltage 2-3 kV, cone voltage 0 V, and source temperature 80-100 $^\circ$ C were used for the measurements. Collision-induced-dissociation (CID) studies were performed upon colliding the selected ions with argon gas inside the trap cell of the instrument. Gradually increasing the collision energy (CE 0 to 55 for Ag₁₄) leads to the fragmentation of the species.

Single crystal X-ray diffraction

Single crystal X-ray diffraction data of $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3]$ cluster was measured using Bruker D8 VENTURE APEX III single crystal X-ray diffractometer equipped with graphite monochromatic Mo (K_α) ($\lambda = 0.71073 \text{ \AA}$) fine focus sealed tube X-ray source and a PHOTON 100 CMOS detector. A crystal was mounted on a Kapton loop with the help of paratone oil and the data collection was performed at 200(2) K. The APEX3-SAINT (Bruker 2018) program was used for integrating the frames and SADABS (Bruker 2018) program was used for multi-scan absorption corrections. The structure was resolved by SHELXT-2018 (Sheldrick) program and refined by full matrix least squares techniques using SHELXL-2018 program. Hydrogens on all carbon atoms were fixed at calculated positions and refined as riding model with $\text{C-H} = 0.93 \text{ \AA}$, and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The electron density of solvent molecules could not be modelled satisfactorily due to difficulty in locating their position. The observed R_{int} was high due to very weak diffraction of crystal at higher Bragg's angles. Therefore a resolution cut at $\sim 1.0 \text{ \AA}$ was made during data reduction process to get a reasonable integration parameters in values/error models. Reflections above $\theta = 25^\circ$ were omitted during refinement to improve R_{int} to a reasonable value. Due to very high thermal and vibrational/rotational disorder of triazine-dithiolate ligand moieties, several restraints (DFIX, SIMU, ISOR, DELU etc.) were applied to their bond distances and thermal parameters (U_{ij}) values during refinement to maintain sensible molecular geometry as well as reasonable anisotropic displacement parameter (ADPs) values.

Femtosecond transient absorption studies

Femtosecond transient absorption (TA) experiment are carried out using the ExciPro spectrometer. In the transient absorption setup Spectra-physics Mai Tai Ti:Sapphire oscillator generate the fundamental 120 fs pulses centered at 800 nm. These pulses send to a Spectra-physics Ti: Sapphire optical amplifier to generate the high energy pulses (4 mJ/pulse) centered at 800 nm with repetition rate of 1 kHz. Then the 800 nm are doubled using the second harmonic β -barium crystal. The generated 400 nm beam is pass through software-controlled chopper and rotating neutral density filter and use to excite the sample. The residual part of 800 nm during the second harmonic generation is send to a time-delayed controller and rotating CaF_2 crystal to produce white light continuum, which is used to probe the pump excited system. To get the better optical sensitivity, in the measurements a reference probe beam along with signal beam is also employed. The intensity of transmitted pulses is measured with the help of MS 2004 (600 lines/mm diffraction

grating blazed at 600 nm) spectrometer, and Si linear photodiode arrays. The group velocity dispersion is calculated by measuring the chirp of ethanol.

Computational details

For molecular level DFT calculations, Gaussian 09 D.01 program was used.⁴ The B3LYP functional with Pople's 6-31G basis set was used for non-metal atoms (C, H, N, P, S) and LANL2DZ-ECP (effective core potential) was employed for Ag.^{5,6} Solvent effects (dichloromethane) were taken into consideration via the polarizable continuum model (PCM).^{7,8} The TD-DFT calculations considered 300 singlet-to-singlet excitation energies.

The Kohn–Sham (K-S) orbital composition analysis and energy level diagrams were constructed using the Multiwfn program^{9,10} by parsing the output (.log) and formatted checkpoint (.fchk) files generated from Gaussian 09 based TDDFT calculations. Electron density contour maps for the frontier molecular orbitals were generated from the .fchk using ChemCraft software at an isosurface value setting of 0.03 a.u.

For periodic boundary condition-based calculations, the Vienna Ab-Initio Simulation Package (VASP) was employed with the Generalized Gradient Approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.^{11,12} Projector augmented wave (PAW) pseudopotentials were used for treating ion-electron interactions.^{13,14} Ionic relaxations were carried out using a conjugate gradient algorithm with convergence criteria of 10^{-4} eV for minimum energy and $0.05 \text{ eV } \text{\AA}^{-1}$ for Hellmann-Feynman forces on atoms. Due to the large size of the unit cell of the NC, the Brillouin zone was sampled at the Gamma point ($1 \times 1 \times 1$). For the PDOS calculation, a higher ($2 \times 2 \times 2$) K-point is used. The atomic charges were calculated using Bader charge analysis.¹⁵ To evaluate intercluster van der Waals interactions in the dimer, calculations were performed using Grimme's DFT-D3 method with Becke–Johnson (BJ) damping.^{16,17}

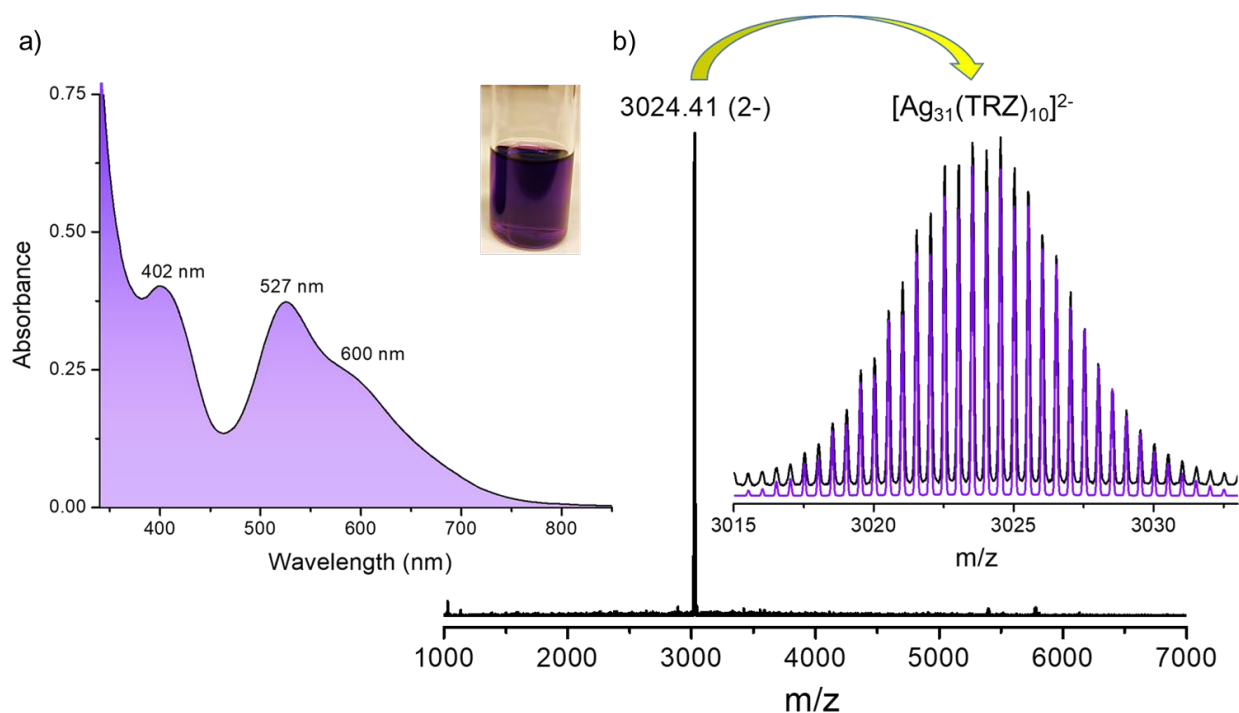


Figure S1. (a) UV-Vis absorption spectrum of $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ nanocluster in DCM solution. Inset shows the photographic image of the cluster in DCM. (b) Negative ion mode ESI-MS spectrum of $[\text{Ag}_{31}(\text{TRZ})_{10}]^{2-}$ nanocluster. Inset shows the exact matching of the isotopic distribution of the experimental with theoretical spectrum.

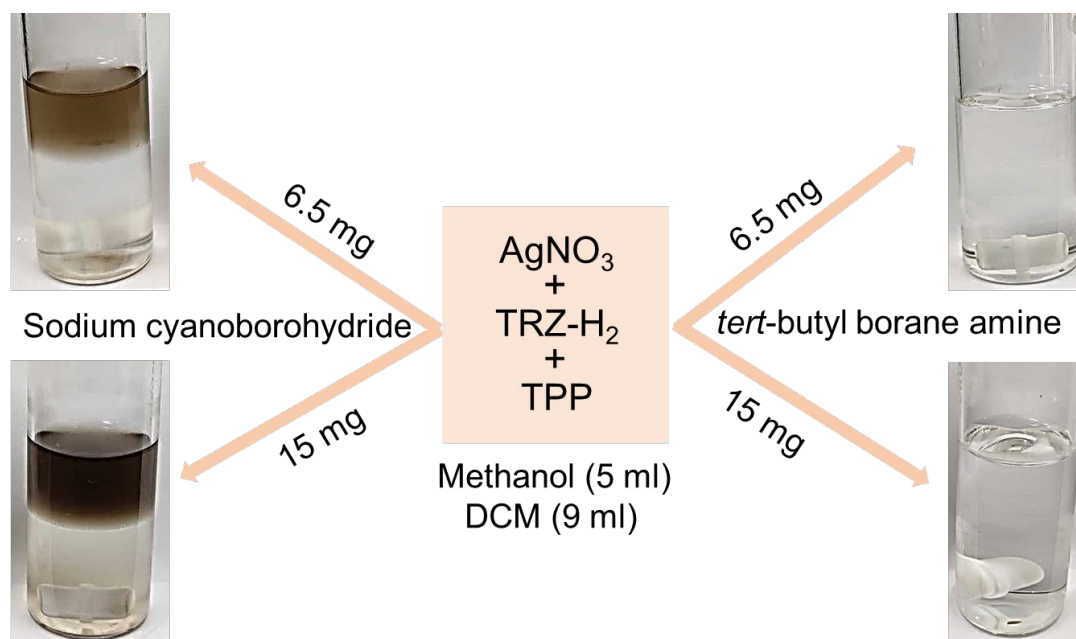


Figure S2. Photographs of the synthetic products formed upon varying the reducing agents in the reaction. No specific clusters were formed in this condition.

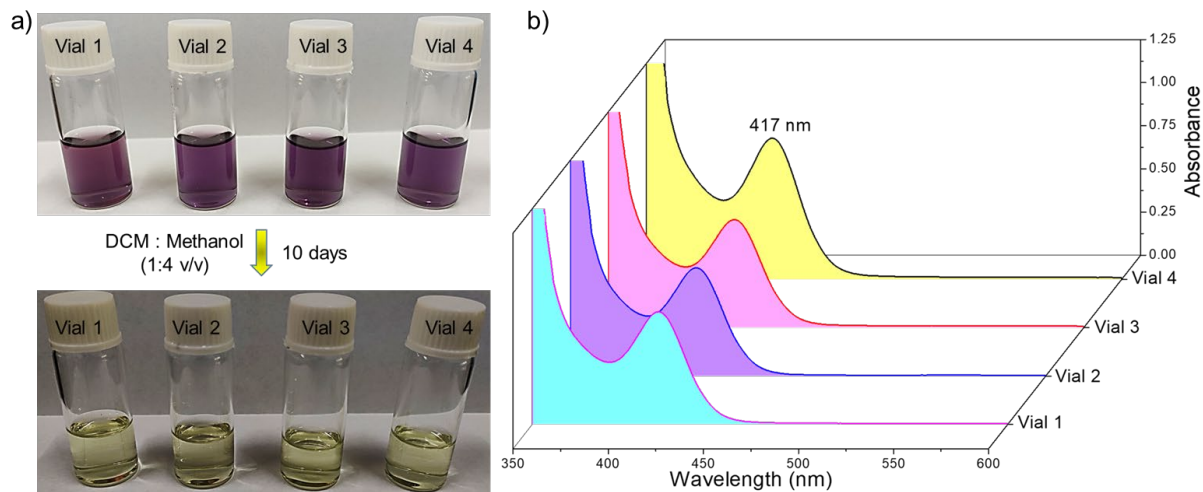


Figure S3. (a) Photographs of the four different vials before and after mixed solvent induced conversion, indicating reproducible nature of the conversion. (b) Identical UV-Vis absorption spectra indicating the reproducible formation of Ag_{14} .

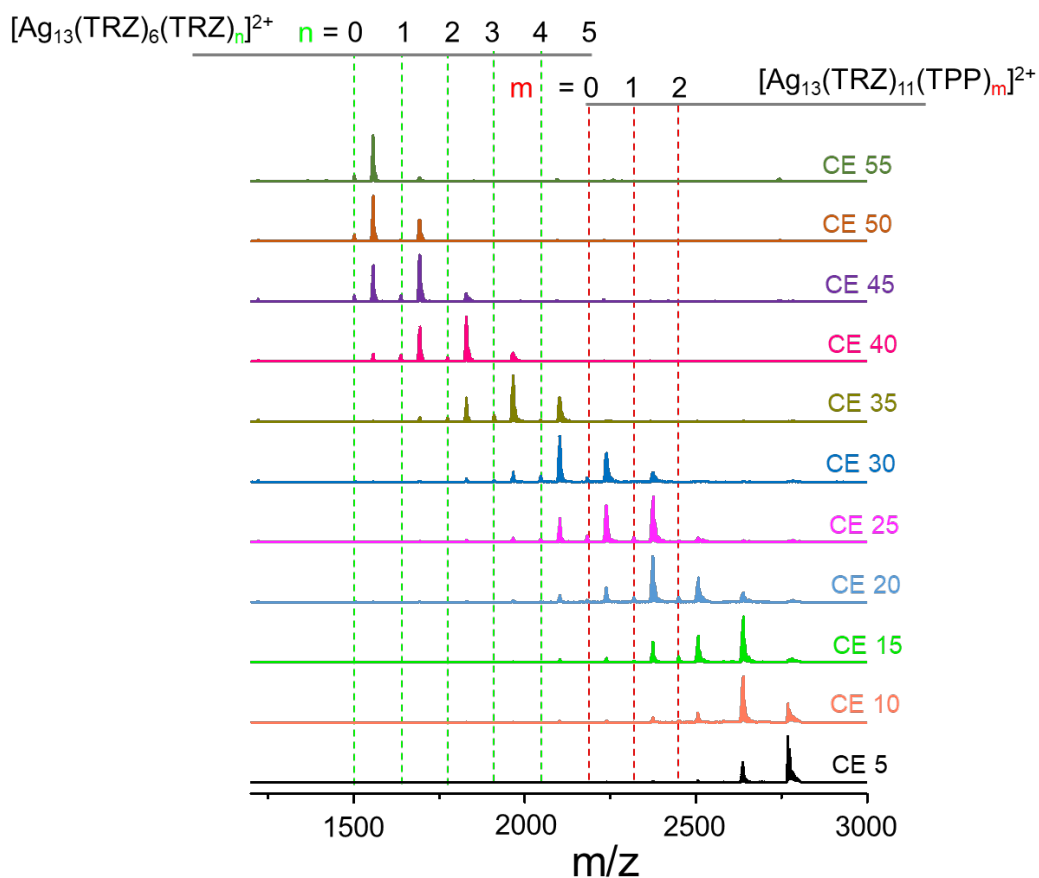


Figure S4. Assignment of the minor fragmentation series in MS-MS spectra of the $[\text{Ag}_{14}(\text{TRZ})_{12}(\text{TPP})_3]$ cluster.

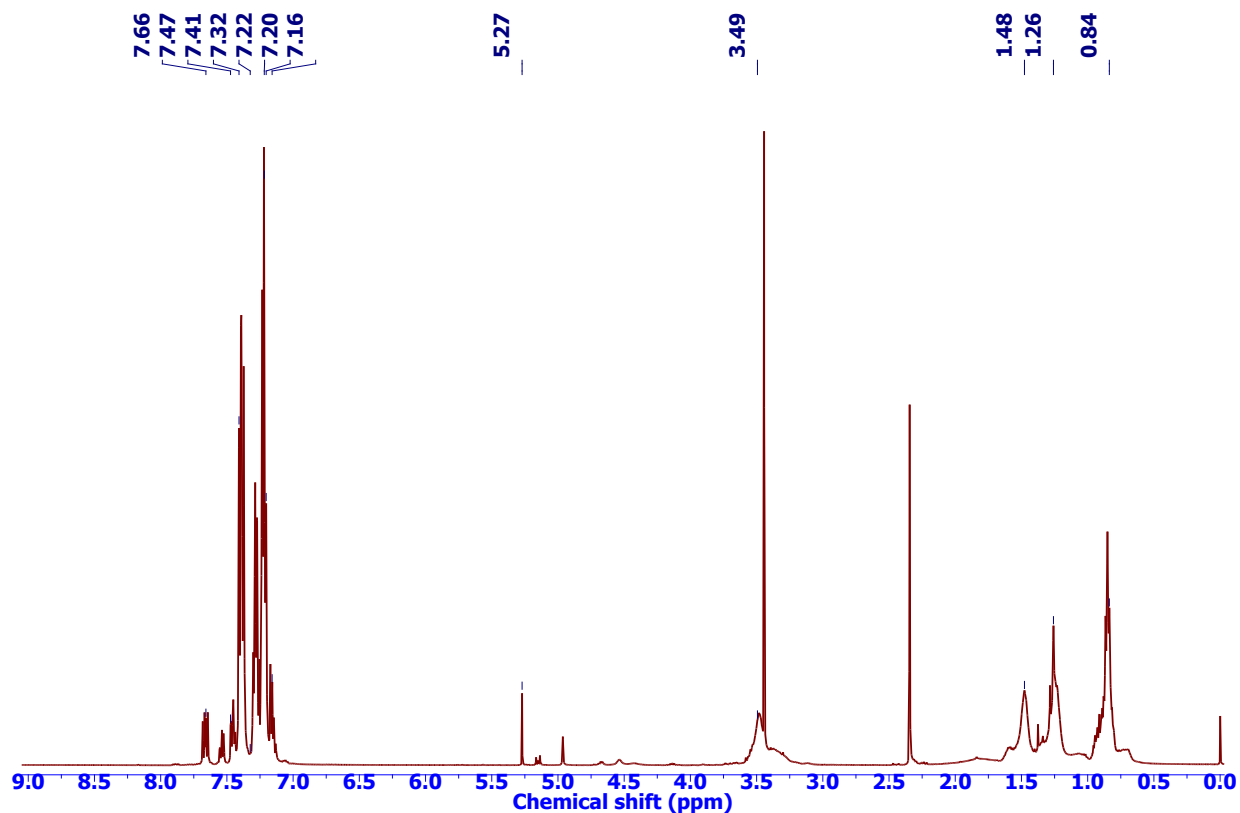


Figure S5. ^1H NMR spectrum of Ag_{14} cluster (measured in CDCl_3). The broad NMR peaks at δ 0.84, 1.26, 1.48 and 3.49 ppm are due to the n-butyl chains of the TRZ ligand. The peak at δ 5.27 ppm is due to the dichloromethane impurity. The chemical shifts in between δ 7.16 to 7.66 ppm are due to TPP ligands.

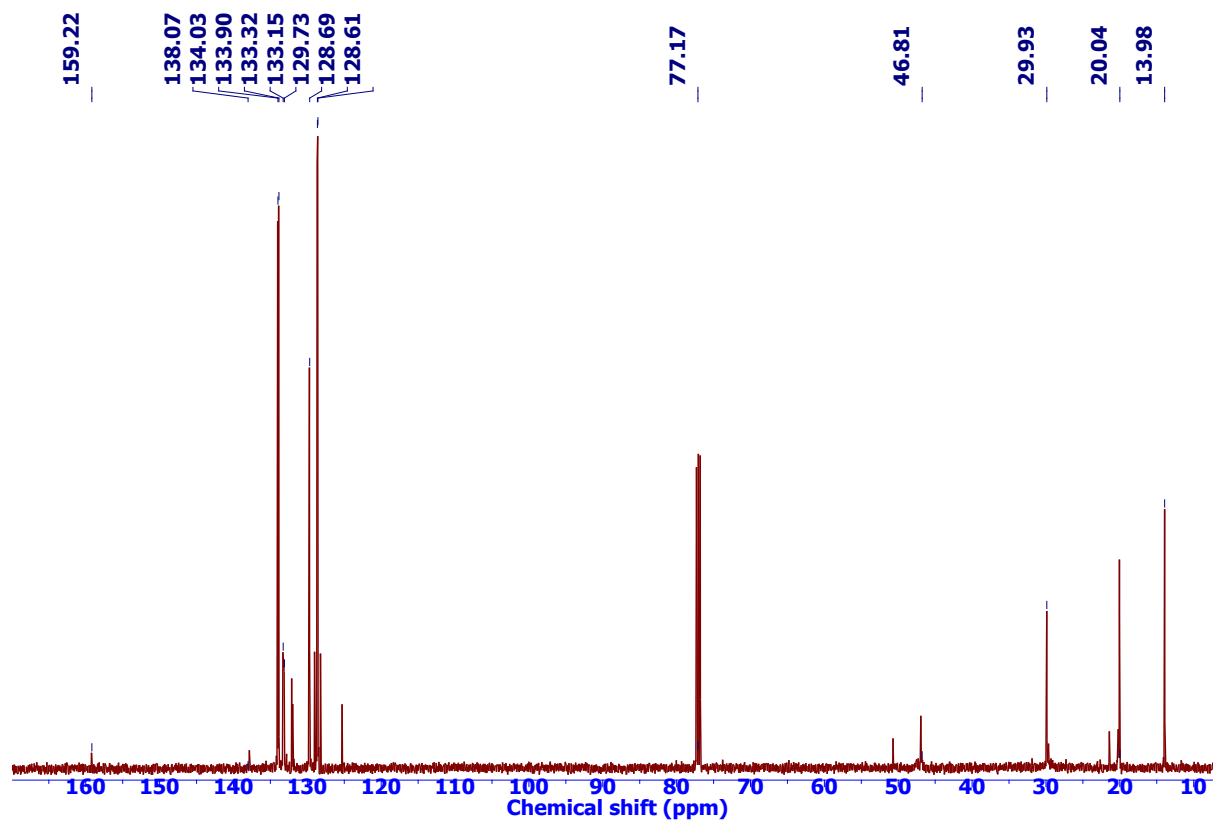


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Ag_{14} cluster (measured in CDCl_3). The triplet peak at δ 77.17 ppm is due to CDCl_3 . The chemical shift at δ 13.98, 20.04, 29.93 and 46.81 ppm are due to n-butyl chains. The multiple peaks in the range of δ 128-134 ppm is for the TPP ligands.

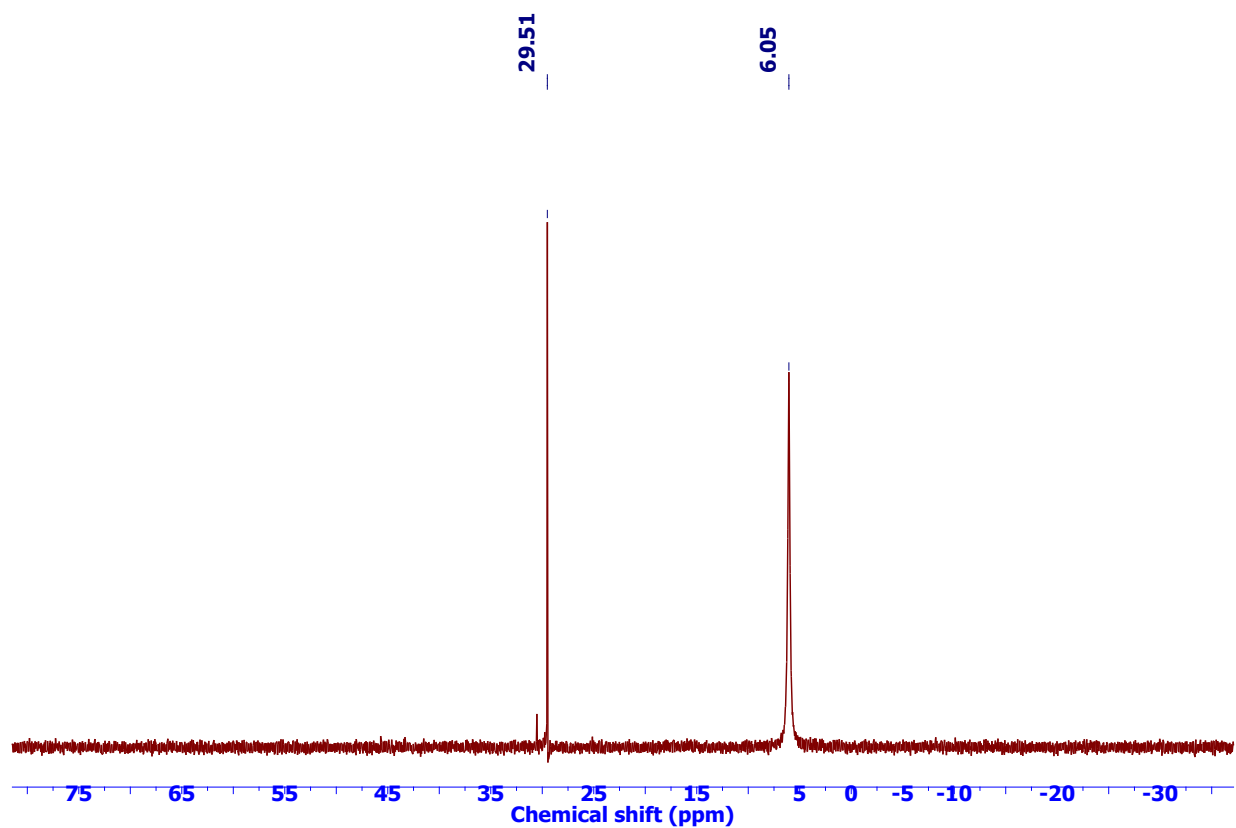


Figure S7. ^{31}P NMR spectrum of Ag_{14} cluster (measured in CDCl_3). The broad peak at δ 6.05 ppm is due to the bonded TPP and the sharp peak at δ 29.51 ppm is due to triphenylphosphine oxide as an impurity.

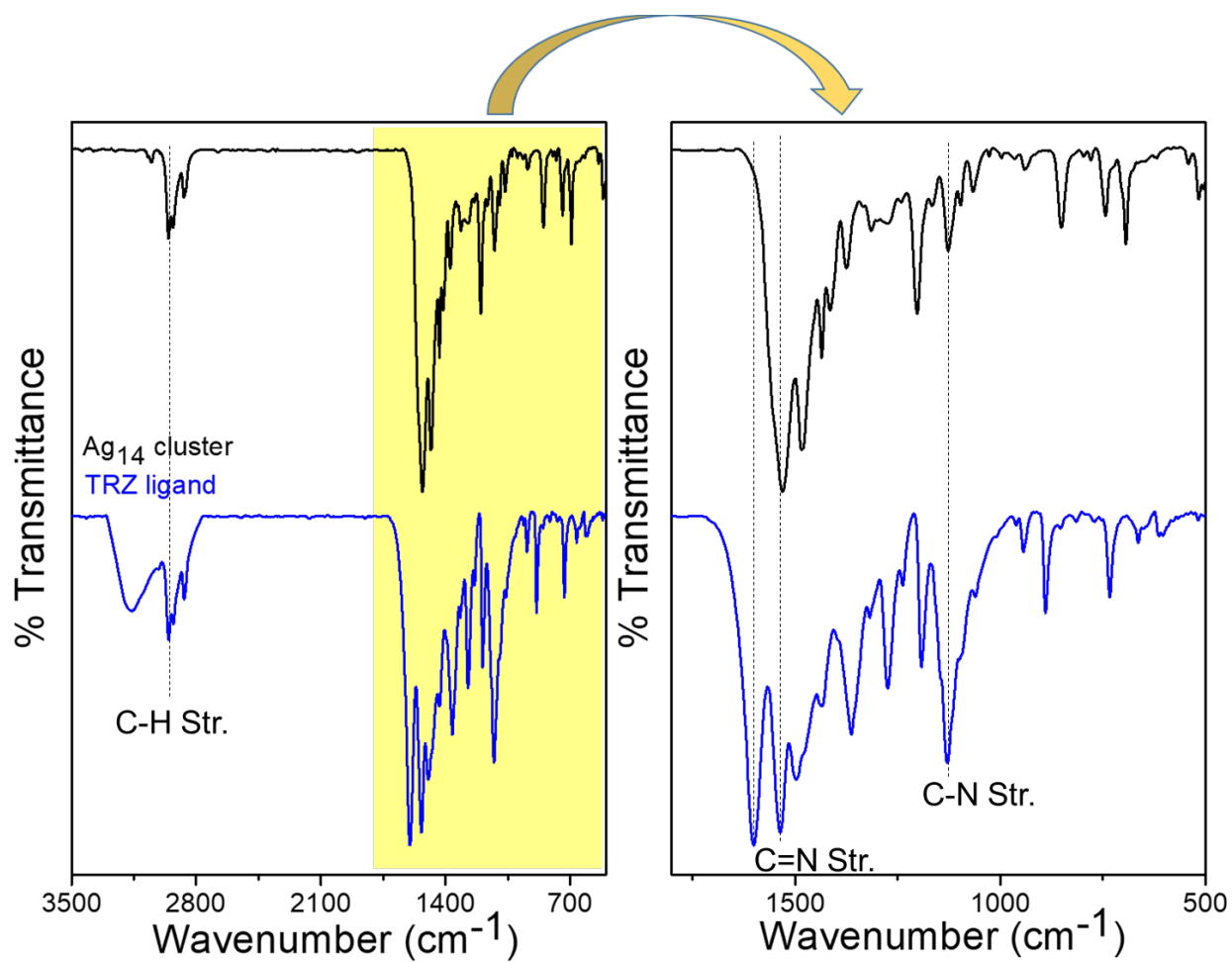


Figure S8. The FT-IR spectra of Ag_{14} cluster in comparison with TRZ- H_2 ligand. An expanded view of the highlighted region with respective assignments of the vibrational bands.

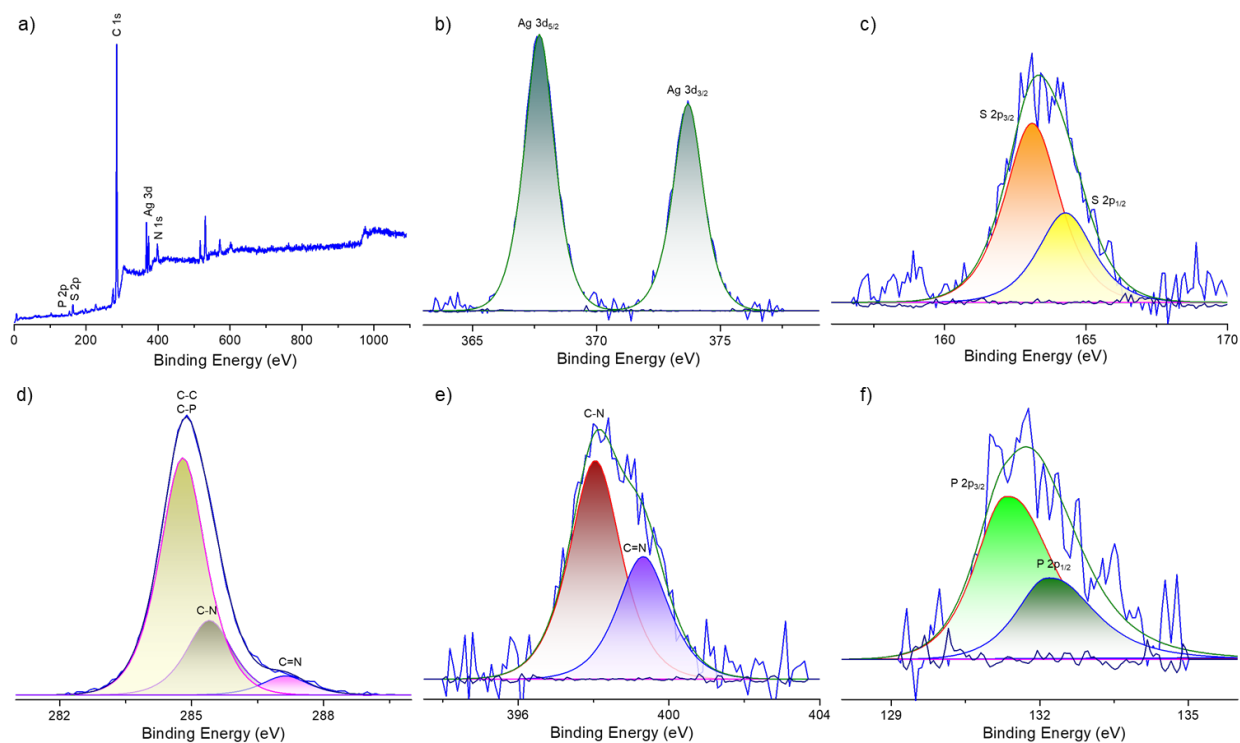


Figure S9. (a) The XPS survey spectrum of Ag_{14} cluster. Spectral fitting of the selected area of (b) Ag 3d, (c) S 2p, (d) C 1s, (e) N 1s and (f) P 2p regions.

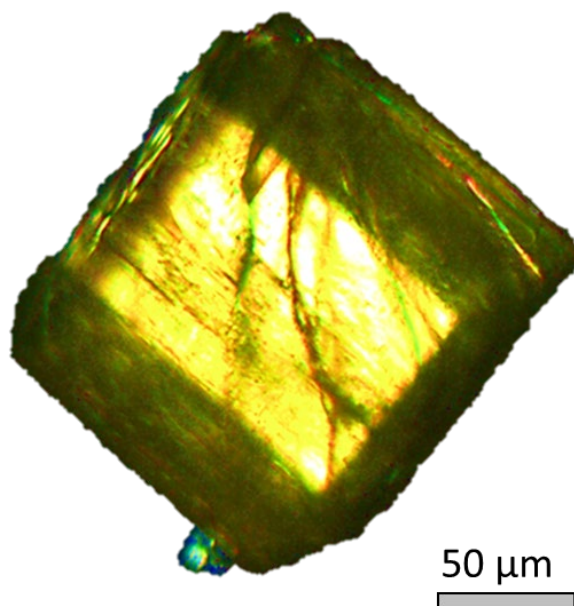


Figure S10. An optical microscopic image of a yellow colored cuboidal Ag_{14} crystal.

Table S1. Crystal data and structural refinement for [Ag₁₄(TRZ)₁₂(TPP)₃] nanocluster.

Identification code	Ag ₁₄ nanocluster	
CCDC no	2376263	
Empirical formula	C ₁₈₆ H ₂₆₁ Ag ₁₄ N ₄₈ P ₃ S ₂₄	
Formula weight	5541.94	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 17.6786(6) Å	$\alpha = 90^\circ$
	<i>b</i> = 37.7752(12) Å	$\beta = 95.918(2)^\circ$
	<i>c</i> = 35.2338(9) Å	$\gamma = 90^\circ$
Volume	23404.2(12) Å ³	
<i>Z</i>	4	
Density (calculated)	1.573 gm/cm ³	
Absorption coefficient	1.434 mm ⁻¹	
<i>F</i> (000)	11200	
Crystal size	(0.20 × 0.15 × 0.10) mm ³	
Theta range for data collection	2.504 to 24.999°	
Index ranges	-20 ≤ <i>h</i> ≤ 20, -44 ≤ <i>k</i> ≤ 44, -39 ≤ <i>l</i> ≤ 40	
Reflections collected	245965	
Independent reflections	40379 [<i>R</i> (int) = 0.1460]	
Completeness to theta = 24.999°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7451 and 0.4984	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	40379 / 1362 / 2476	
Goodness-of-fit on <i>F</i> ²	1.090	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0879, <i>wR</i> 2 = 0.1720	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1521, <i>wR</i> 2 = 0.2051	
Extinction coefficient	<i>n/a</i>	
Largest diff. peak and hole	1.124 and -1.023 e.Å ⁻³	

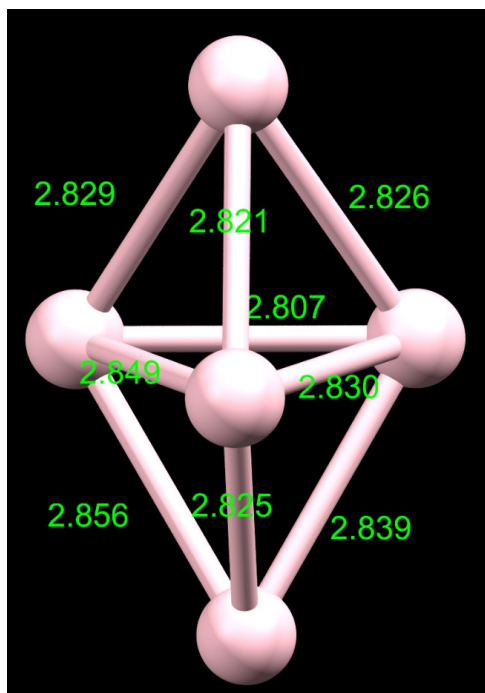


Figure S11. Intermetallic Ag–Ag distances of the trigonal bipyramidal Ag_5 inner kernel of Ag_{14} cluster.

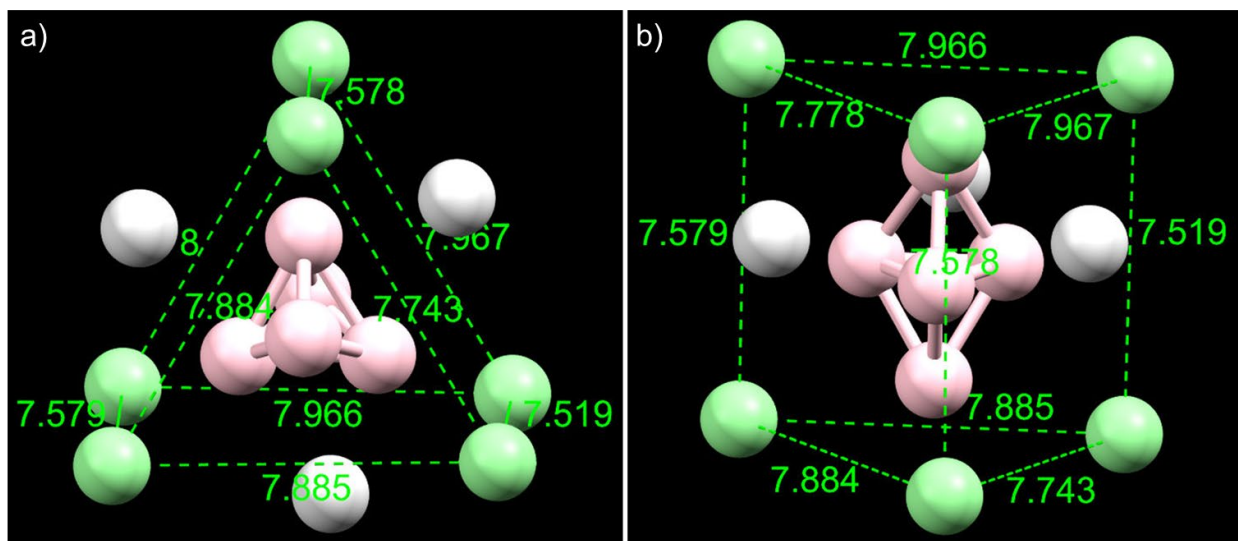


Figure S12. (a, b) Interatomic $\text{Ag}\cdots\text{Ag}$ distances of the trigonal prismatic Ag_6 shell, viewed from two different orientations.

Table S2. A summary of the core-shell structural arrangements for different Ag₁₄ nanoclusters.

Sl. No	Composition	Ligand	Core structure	Shell structure	Ref.
1.	[Ag ₁₄ (DFBT) ₁₂ (TPP) ₈]	3,4-difluoro-benzene thiol [DFBT-H]	Ag ₆ (octahedral)	Ag ₈ (cube)	18
2.	[Ag ₁₄ (BTFTB) ₁₂ (TPP) ₄ (DMF) ₄]	3, 5-bis(trifluoromethyl)-benzene thiol [BTFTB-H]	Ag ₆ (octahedral)	Ag ₈ (cube)	19
3.	[Ag ₁₄ (BDT) ₆ (TPP) ₈]	1,2-benzene dithiol [BDT-H ₂]	Ag ₆ (octahedral)	Ag ₈ (cube)	20
4.	[Ag ₁₄ (PNTP) ₁₀ (DPPH) ₄ Cl ₂]	<i>para</i> -nitro thiophenol [PNTP-H]	Ag ₆ (octahedral)	Ag ₈ (cube)	21
5.	[Ag ₁₄ (CBDT) ₆ (CH ₃ CN) ₈] [Ag ₁₄ (CBDT) ₆ (pyridine) ₈] [Ag ₁₄ (CBDT) ₆ (<i>p</i> -methylpyridine) ₈]	<i>ortho</i> -carborane 1,2-dithiol [CBDT-H ₂]	Ag ₆ (octahedral)	Ag ₈ (cube)	22
6.	[Ag ₁₄ (CBDT) ₆ (TPP) ₆]	<i>ortho</i> -carborane 1,2-dithiol [CBDT-H ₂]	Ag ₈ (bicapped trigonal antiprism)	Ag ₆ (surface atoms)	23
7.	[Ag ₁₄ (TRZ) ₁₂ (TPP) ₃]	6-(dibutylamino)-1, 3, 5-triazine-2, 4-dithiol [TRZ-H ₂]	Ag ₅ (trigonal bipyramidal)	Ag ₆ @Ag ₃ (tricapped trigonal prismatic)	This work

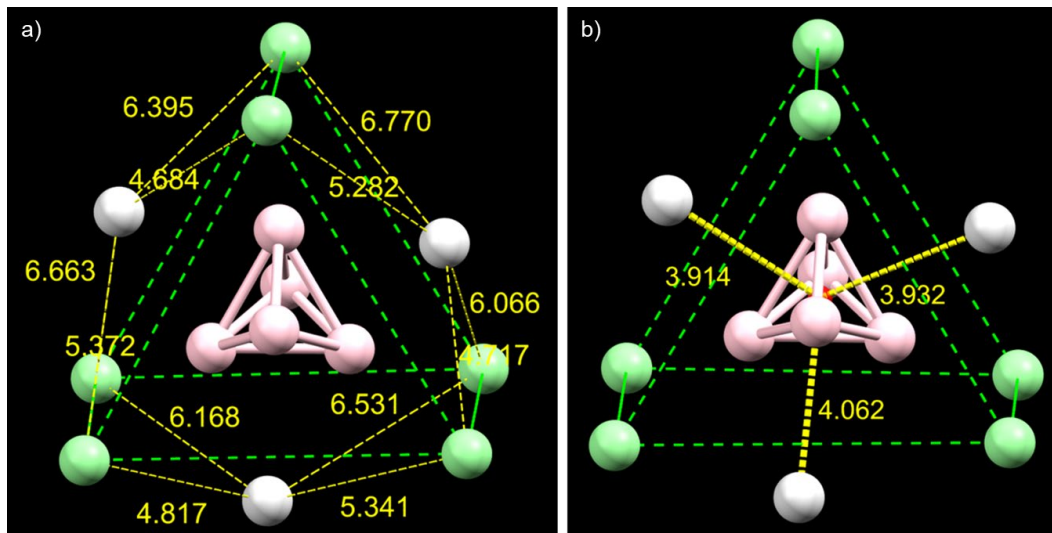


Figure S13. (a) Interatomic distances of the capping Ag atoms with the other Ag atoms present in the Ag₆ shell. (b) Distances between the centroid of the cluster to the capping Ag atoms.

Table S3. A summary of different silver nanoclusters co-protected by thiolates and TPP ligands.

Sl. No	Core	Composition	Ligand	No. of TPP	Ref.
1.	Ag ₁₄	[Ag ₁₄ (DFBT) ₁₂ (TPP) ₈]	3,4-difluoro-benzene thiol [DFBT-H]	8	18
2.	Ag ₁₄	[Ag ₁₄ (BTMBT) ₁₂ (TPP) ₄ (DMF) ₄]	3, 5-bis(trifluoromethyl)-benzene thiol [BTMBT-H]	4	19
3.	Ag ₂₃	[Ag ₂₃ (PET) ₁₈ (TPP) ₈]	phenyl ethane thiol [PET-H]	8	24
4.	Ag ₂₉	[Ag ₂₉ (BDT) ₁₂ (TPP) ₄]	1,3-benzene dithiol [BDT-H ₂]	4	25
5.	Ag ₃₃	[Ag ₃₃ (PET) ₂₄ (TPP) ₄]	phenyl ethane thiol [PET-H]	4	26
6.	Ag ₃₉	[Ag ₃₉ (PFBT) ₂₄ (TPP) ₈]	pentafluoro benzene thiol [PFBT-H]	8	27
7.	Ag ₄₀	[Ag ₄₀ (DMBT) ₂₄ (TPP) ₈] [Ag ₄₆ (DMBT) ₂₄ (TPP) ₈]	2,4-dimethyl benzene thiol [DMBT-H]	8	28, 29
8.	Ag ₄₂	[Ag ₄₂ (CBDT) ₁₅ (TPP) ₄]	<i>ortho</i> -carborane 1,2-dithiol [CBDT-H ₂]	4	23
9.	Ag ₄₄	[Ag ₄₄ (EBT) ₂₆ (TPP) ₄]	2-ethyl benzene thiol [EBT-H]	4	30
10.	Ag ₆₇	[Ag ₆₇ (DMBT) ₃₂ (TPP) ₈]	2,4-dimethyl benzene thiol [DMBT-H]	8	31
11.	Ag ₁₄	[Ag ₁₄ (TRZ) ₁₂ (TPP) ₃]	6-(dibutylamino)-1, 3, 5 -triazine-2, 4-dithiol [TRZ-H ₂]	3	This work

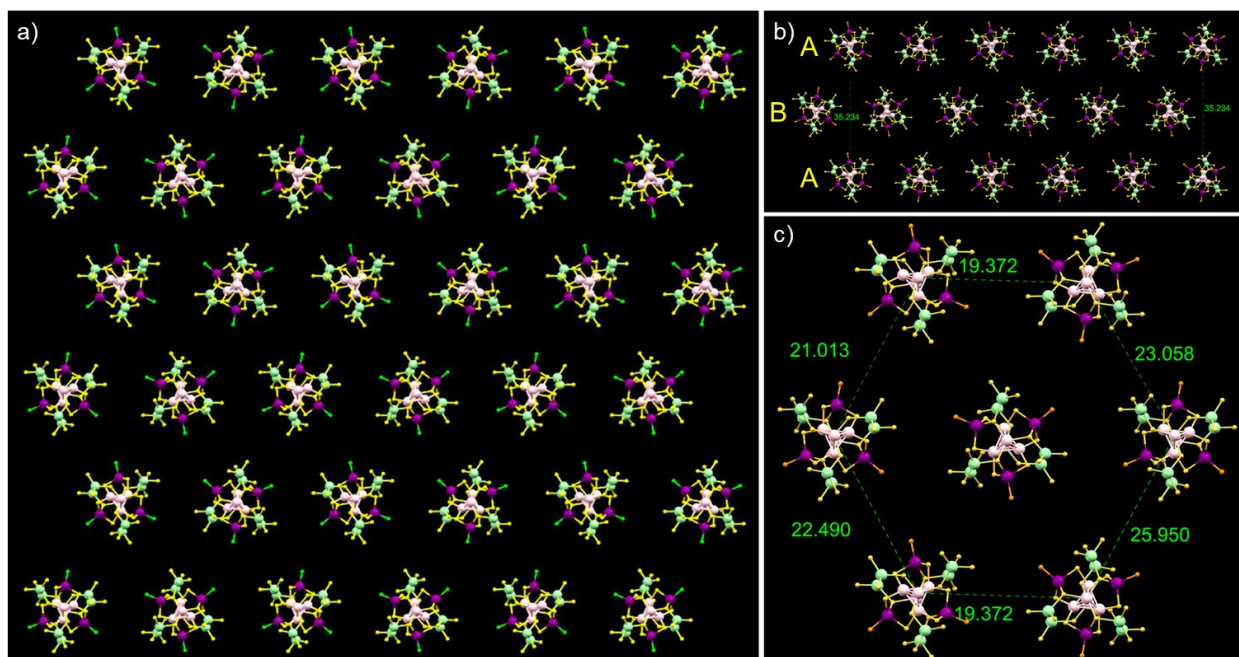


Figure S14. (a) Supramolecular packing of the silver-sulphide skeleton of Ag_{14} cluster along 'a' axis. (b) Expanded view of the packing showed AB...AB layers of clusters. (c) An expanded view of the hexagonal intercluster packing.

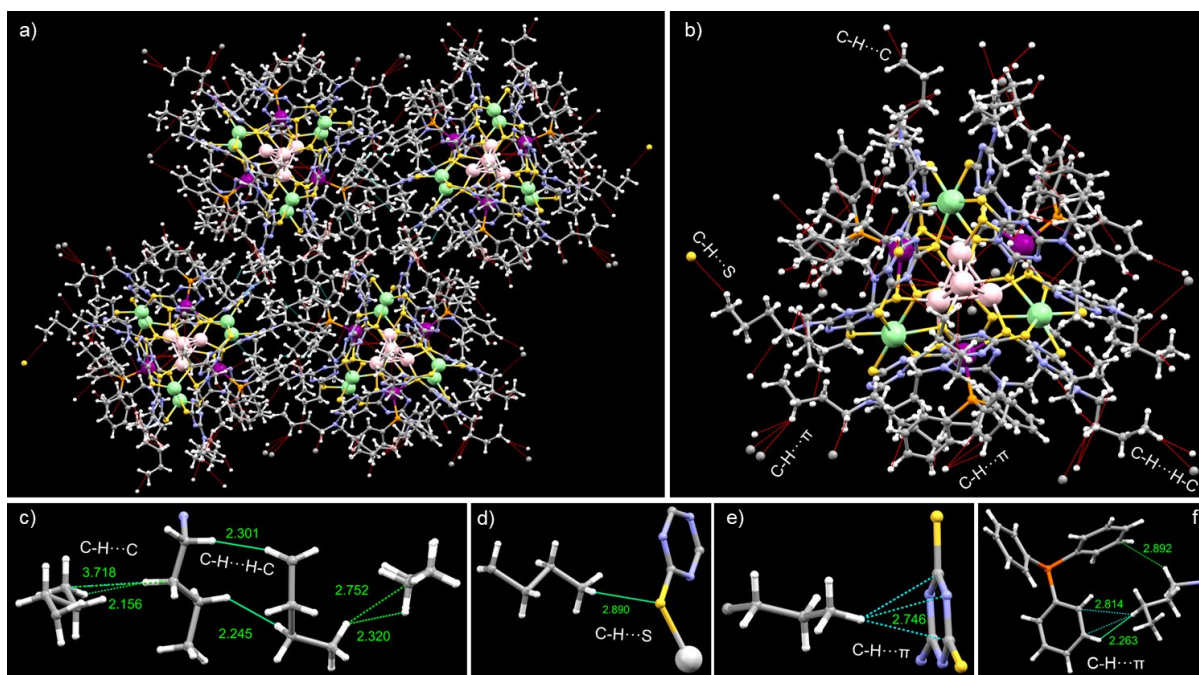


Figure S15. (a) Short contact interactions observed in a unit cell of the Ag_{14} cluster. (b) The same interactions of a single cluster. (c-f) Ligand-centered non van der Waals interactions with marked distances.

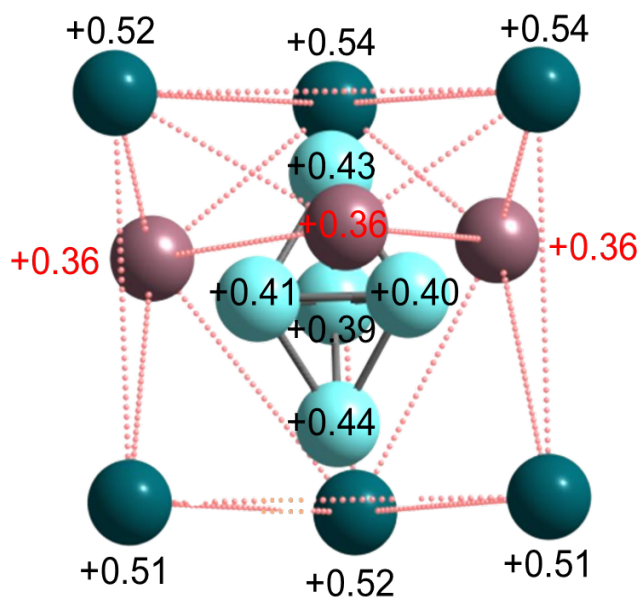


Figure S16. Bader charge analysis shows the distribution of the atomic charges in the non-fcc Ag_{14} skeleton.

Table S4. Structural parameters of DFT optimized Ag_{14} cluster with simplified ligands shell.

Bond Type	Bond Length (Å)
Ag–Ag (Ag_5 TBP core)	2.83
Ag_5 (core)–S(shell)	2.59
Ag_6 (TP shell)–S (shell)	2.45
Ag_3 (shell)–S (shell)	2.65
Ag_3 (shell)–P (shell)	2.48

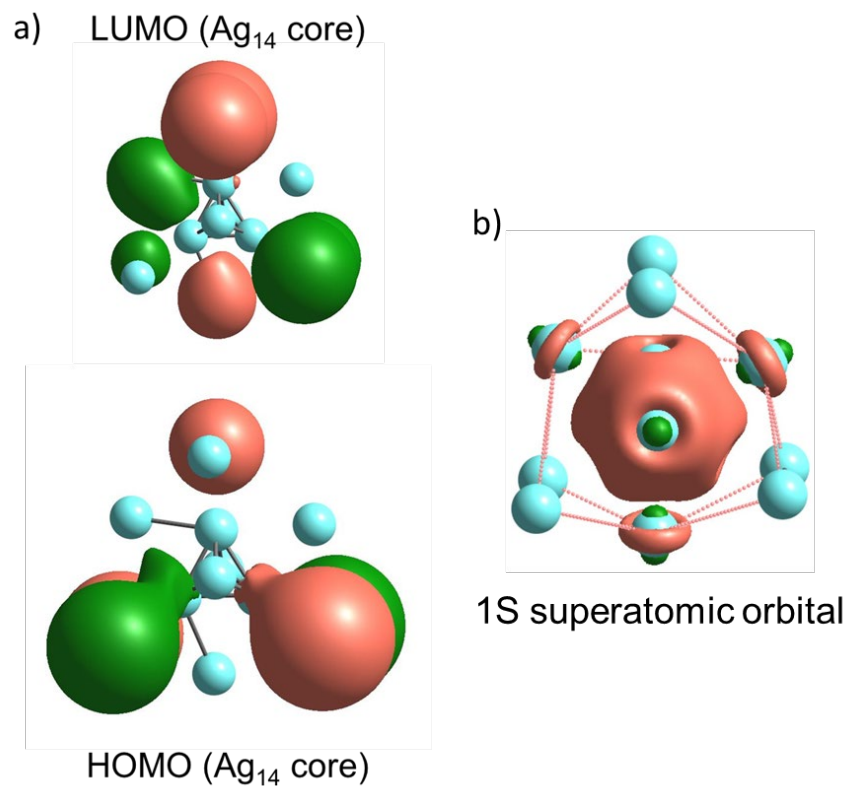


Figure S17. (a) Electron density maps of the HOMO and LUMO orbitals diffuse across the $\text{Ag}_{(6+3)}$ shell. (b) Electron density maps of the 1S superatomic orbital concentrated on TBP Ag_5 inner core. Analysis was performed only on the Ag_{14} metal skeleton.

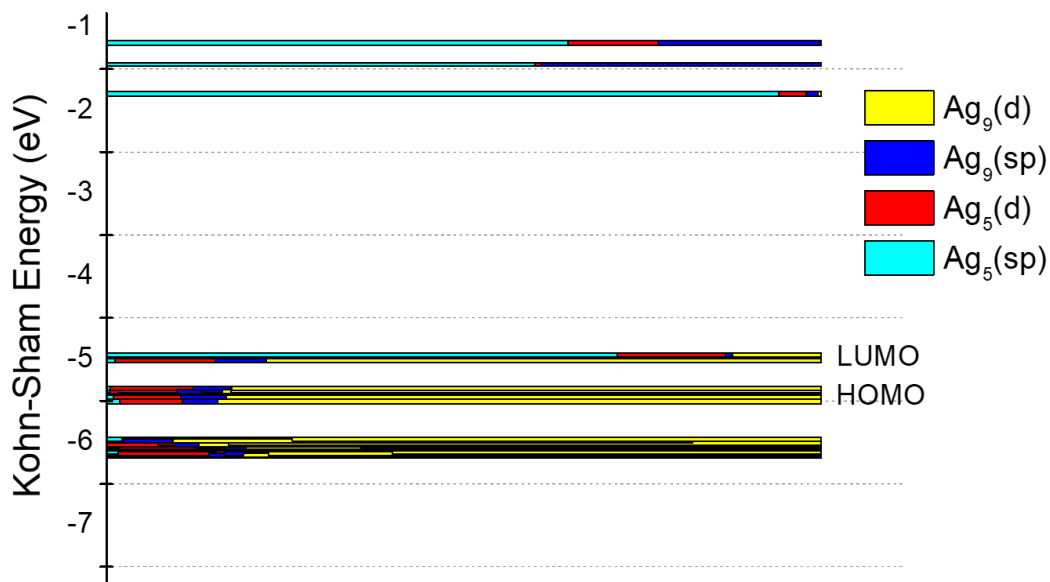


Figure S18. Kohn-sham orbital analysis of the Ag_{14} cluster in terms of the contribution of Ag_5 core and $\text{Ag}_{(6+3)}$ shell.

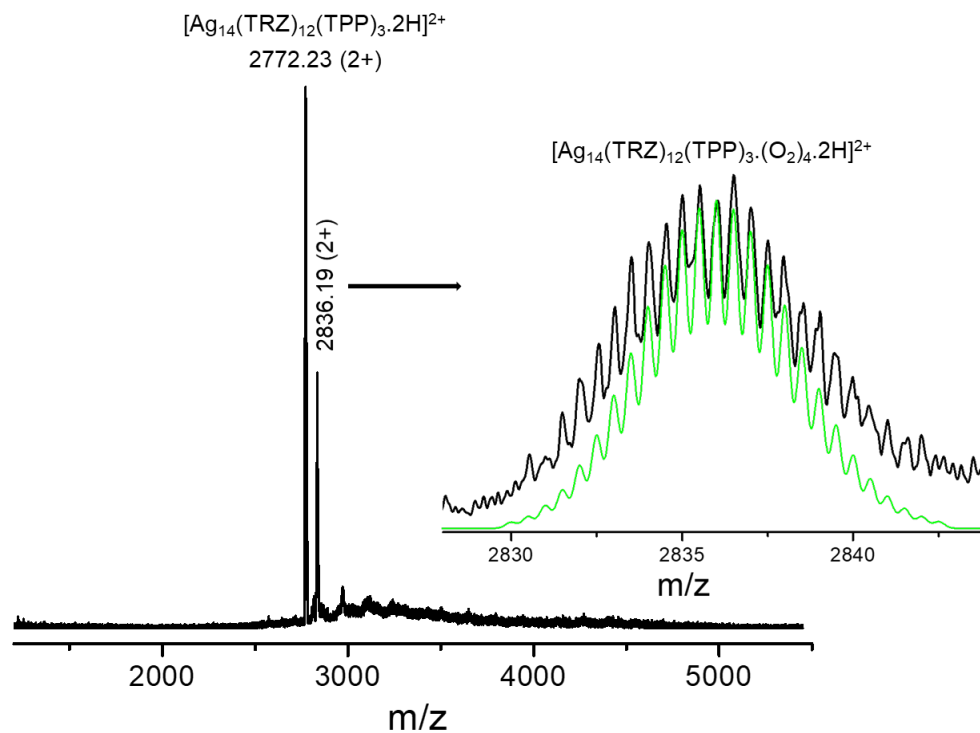


Figure S19. Positive ion mode ESI-MS spectrum of the Ag_{14} cluster after oxygen bubbling. The mass spectrum was recorded after being exposed to oxygen for a duration of 2 days. Along with the molecular ion peak at 2772.23, another major peak at 2836.19 indication the attachment of four oxygen molecules with the cluster. Inset shows the isotopic simulation of the peak. A few weakly resolved peaks at higher m/z values may result from additional oxygen incorporation into the cluster.

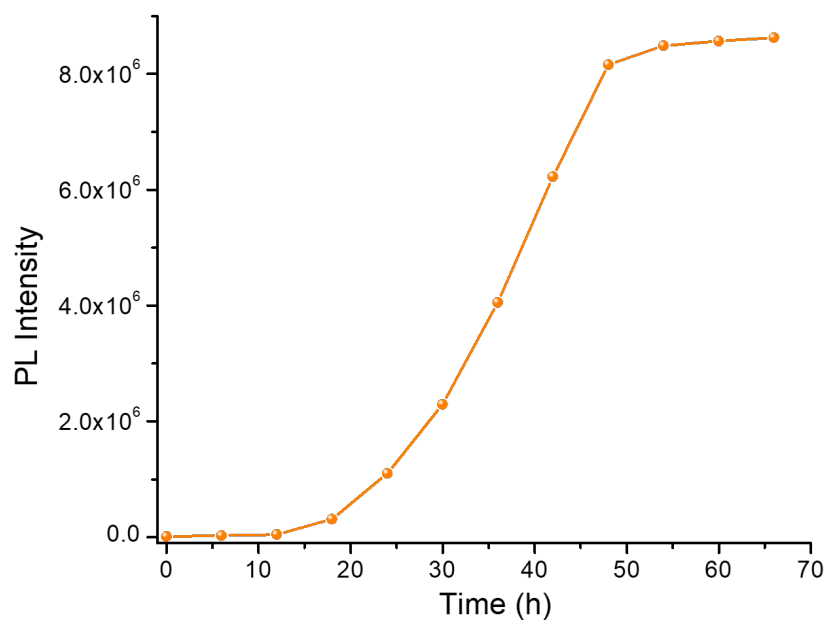


Figure S20. Time-dependent variation of PL intensity in the Ag_{14} cluster following the oxygen bubbling.

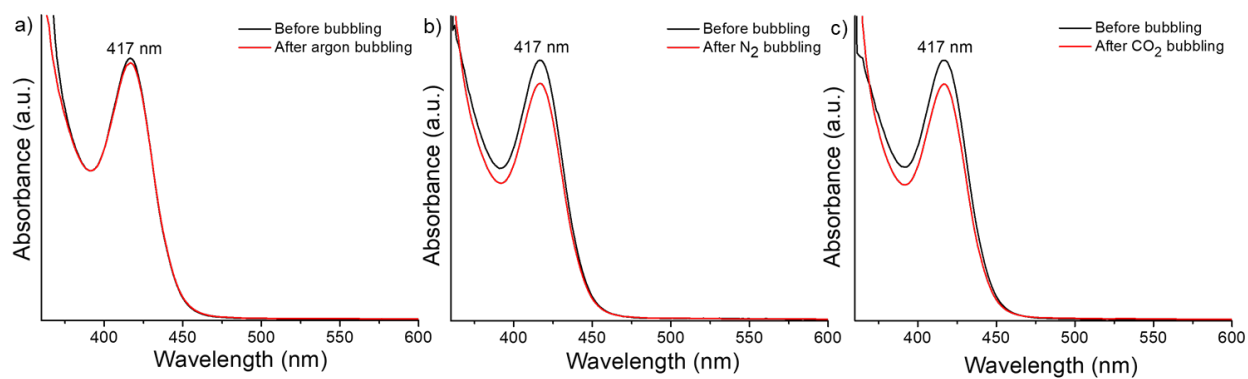


Figure S21. The comparative UV-Vis absorption spectra of the Ag_{14} cluster solution were analyzed before and after bubbling with (a) argon, (b) nitrogen and (c) carbon dioxide. Each gas was bubbled through the solution for a duration of 48 hours. No significant changes were observed in the absorption band (λ_{max} 417 nm) of the Ag_{14} cluster after bubbling with any of the gases.

Self-assembly of Ag₁₄ and oxygenated-Ag₁₄ clusters

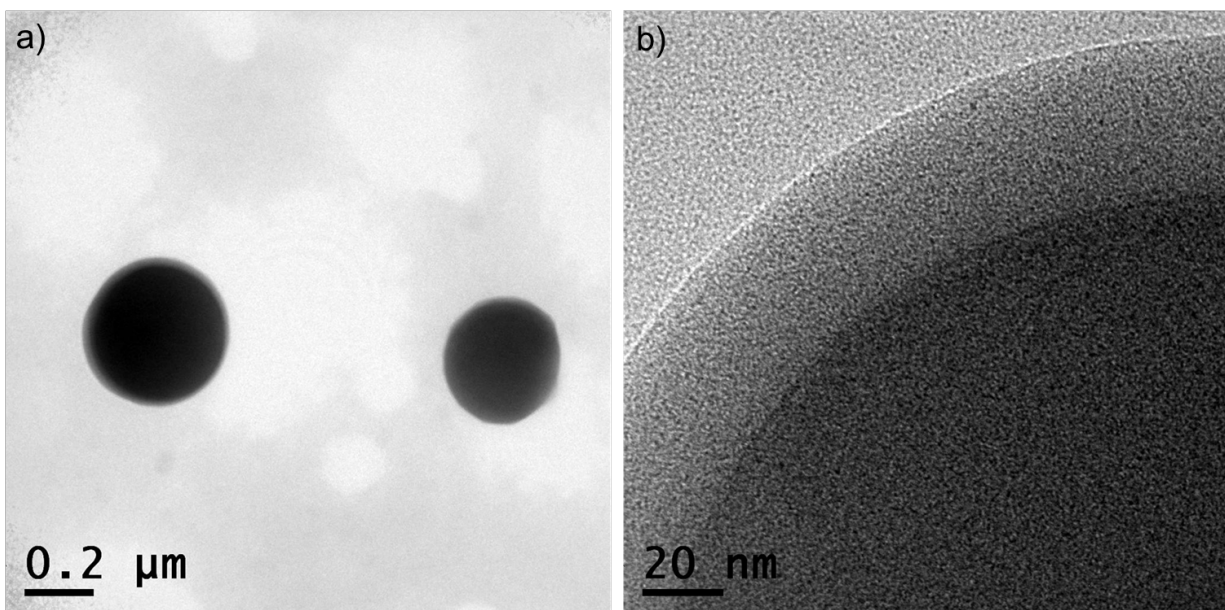


Figure S22. (a) A large area TEM micrograph of Ag₁₄ spheroids. (b) An expanded view of the surface of the spheroid.

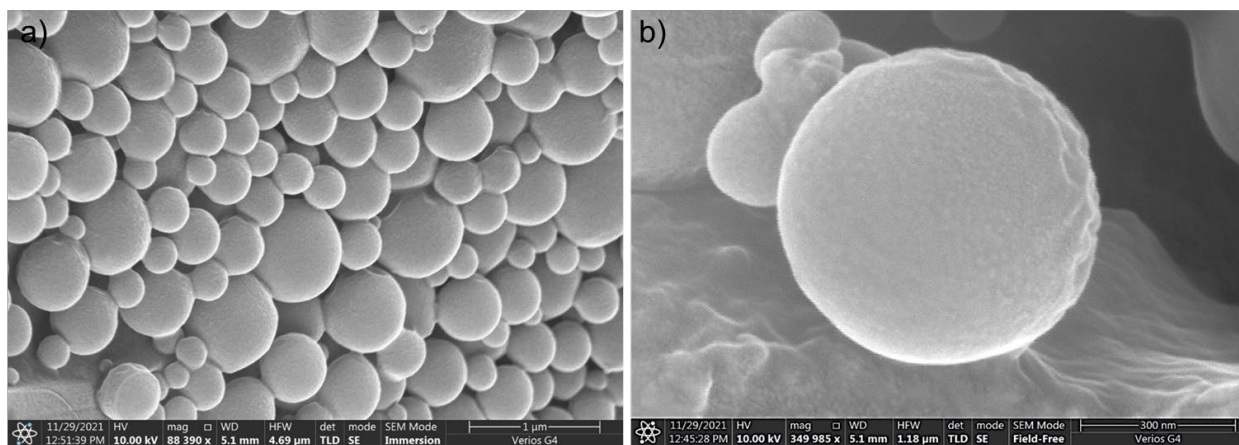


Figure S23. (a) A large area FESEM micrograph shows different Ag₁₄ spheroids assembled on to a carbon film. (b) An expanded view of a single spheroid.

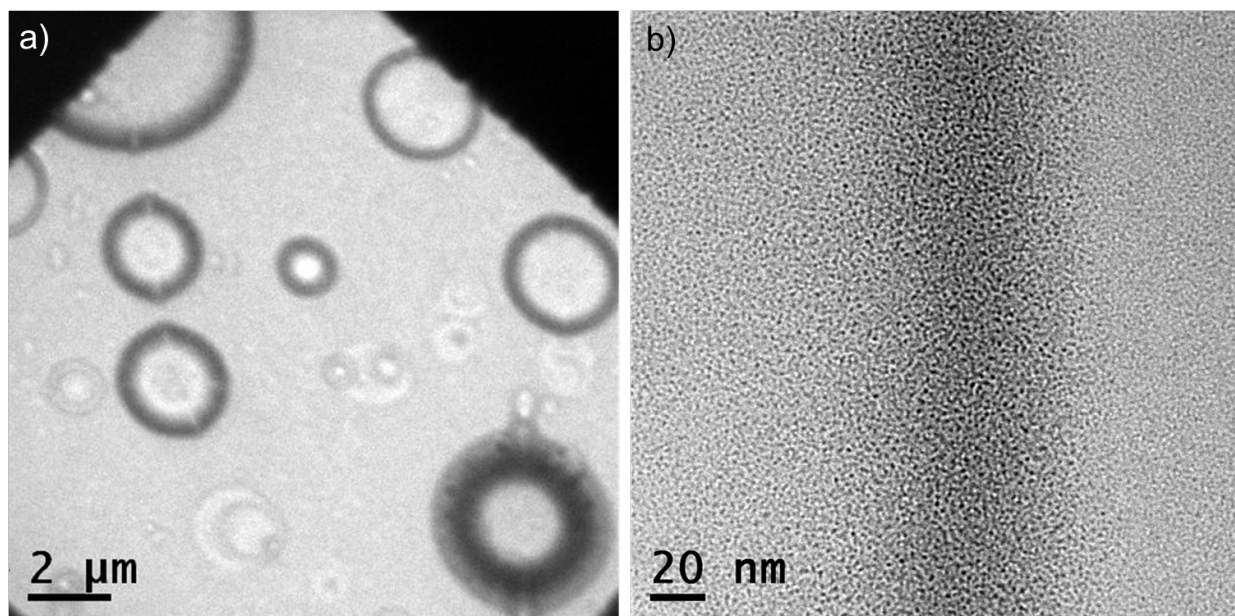


Figure S24. (a) A large area TEM micrograph showing oxygenated-Ag₁₄ toroids. (b) An expanded view of a single toroid showed assembly of clusters.

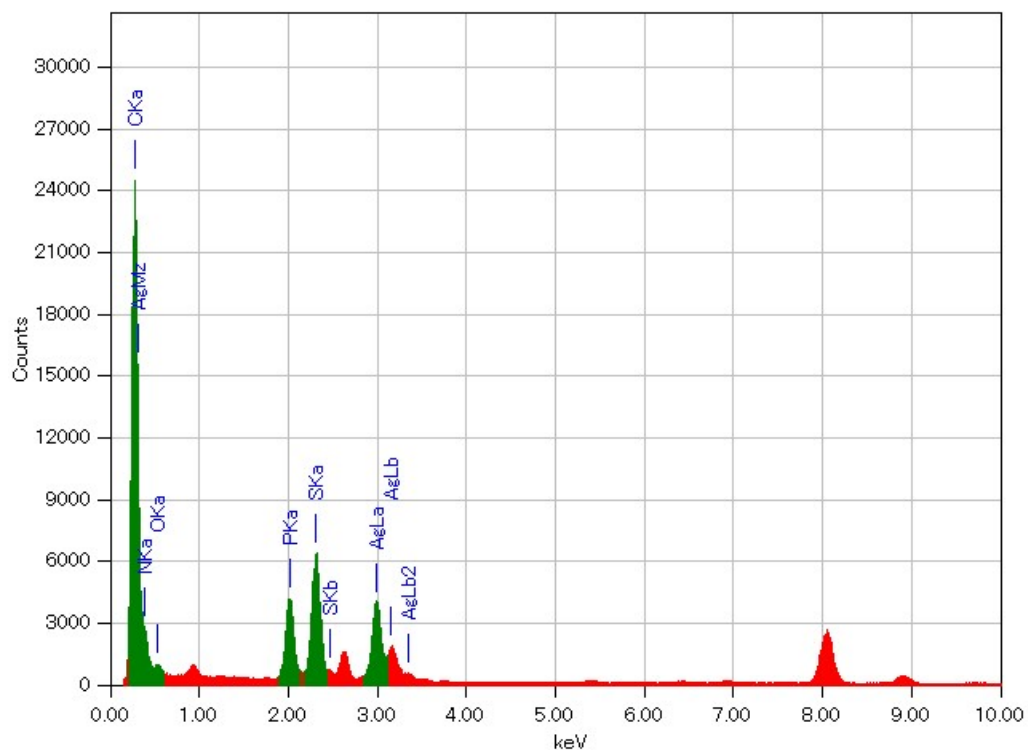


Figure S25. The EDS spectrum of Ag₁₄ spheroid shows the presence of existing elements.

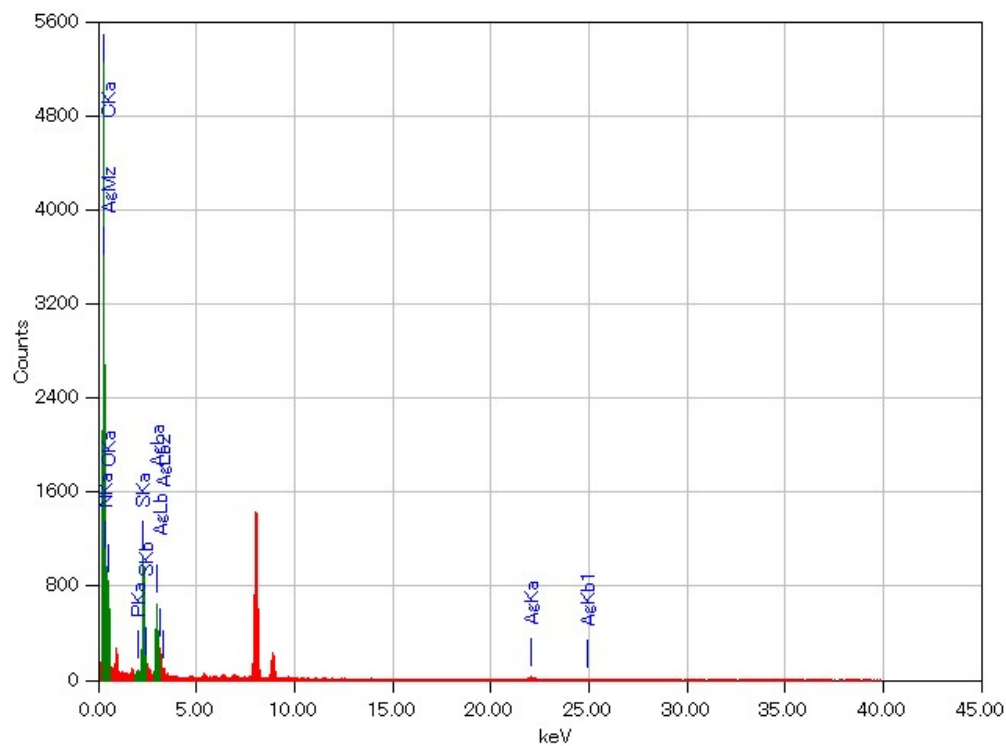


Figure S26. The EDS spectrum of oxygenated- Ag_{14} toroid shows the presence of existing elements.

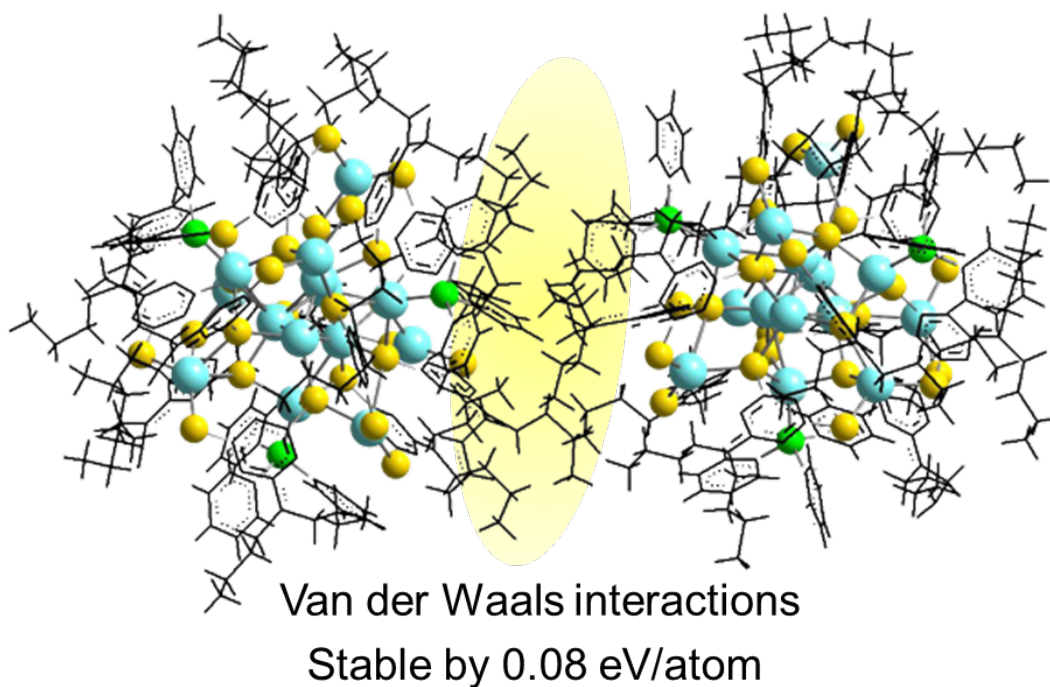


Figure S27. Structural modelling of the supramolecular interactions dominated by the n-butyl chains of TRZ ligand of the cluster.

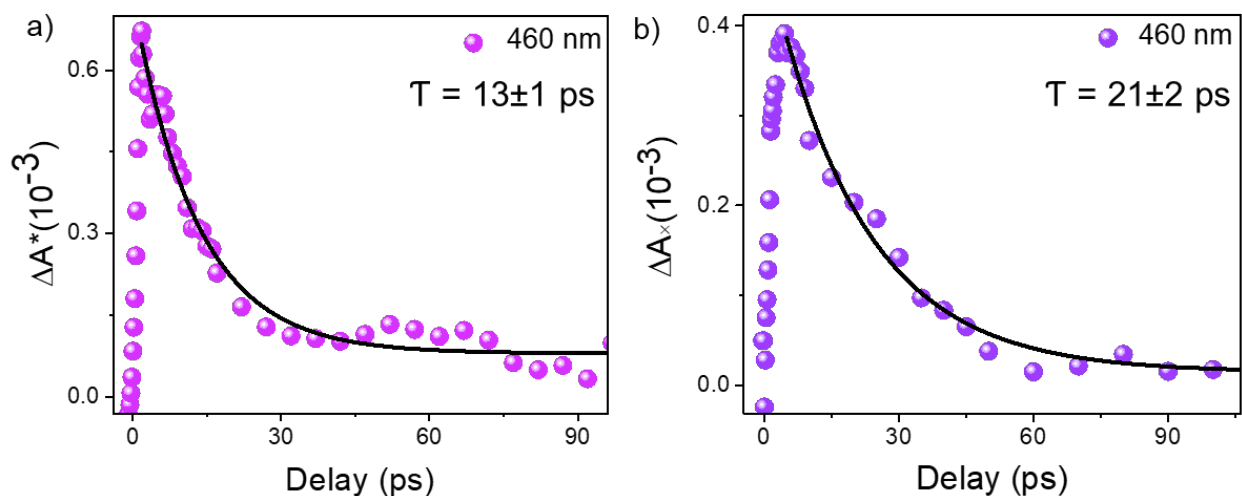


Figure S28. TA kinetics decay trace of (a) Ag₁₄, (b) oxygenated-Ag₁₄ clusters at a probe wavelength of 460 nm.

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Ag₁₄(TRZ)₁₂(TPP)₃] nanocluster. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ag(1)	6082(1)	6267(1)	7116(1)	33(1)
Ag(2)	7387(1)	6278(1)	7666(1)	33(1)
Ag(3)	6099(1)	6706(1)	7760(1)	34(1)
Ag(4)	6025(1)	5963(1)	7853(1)	34(1)
Ag(5)	4758(1)	6334(1)	7499(1)	34(1)
Ag(6)	5392(1)	5451(1)	7023(1)	43(1)
Ag(7)	8282(1)	7358(1)	8243(1)	48(1)
Ag(8)	5661(1)	7169(1)	6962(1)	48(1)
Ag(9)	5368(1)	6353(1)	8640(1)	46(1)
Ag(10)	8136(1)	5287(1)	8501(1)	49(1)
Ag(11)	8253(1)	6073(1)	6478(1)	52(1)
Ag(12)	3958(1)	6207(1)	6159(1)	58(1)
Ag(13)	3984(1)	7462(1)	7910(1)	55(1)
Ag(14)	3865(1)	5377(1)	8232(1)	57(1)
C(1)	5635(7)	4994(3)	7951(3)	34(2)

C(2)	5531(8)	4427(3)	8142(4)	49(3)
C(3)	6690(8)	4693(3)	8292(4)	44(3)
C(4)	8982(7)	6026(3)	8900(4)	41(3)
C(5)	8368(6)	6524(3)	8592(3)	36(2)
C(6)	9189(9)	6586(4)	9122(4)	64(4)
C(7)	8585(6)	6738(3)	7094(3)	35(2)
C(8)	9770(7)	6914(4)	6962(4)	45(3)
C(9)	9299(7)	7168(3)	7476(4)	43(3)
C(10)	5742(6)	7291(3)	8564(3)	33(2)
C(11)	5681(8)	7756(3)	8963(4)	46(3)
C(12)	6854(7)	7614(3)	8784(3)	36(2)
C(13)	3748(7)	7128(3)	6999(3)	37(2)
C(14)	2896(7)	7484(4)	6686(4)	50(3)
C(15)	3056(7)	6958(3)	6410(3)	43(3)
C(16)	6384(6)	5693(3)	6307(3)	34(2)
C(17)	6570(8)	5553(4)	5693(4)	57(4)
C(18)	5404(7)	5769(3)	5795(3)	42(3)
C(19)	7023(7)	6501(4)	5835(4)	48(3)
C(20)	5899(7)	6623(3)	6138(3)	33(2)
C(21)	5935(9)	6696(5)	5506(4)	64(4)
C(22)	8425(6)	5475(3)	7635(3)	34(2)
C(23)	9039(7)	5436(4)	7063(4)	45(3)
C(24)	9517(7)	5163(3)	7607(4)	45(3)
C(25)	2316(7)	5507(4)	6760(4)	47(3)
C(26)	3481(6)	5724(3)	6958(4)	36(2)
C(27)	2791(6)	5377(3)	7372(3)	35(2)
C(28)	6297(7)	5591(3)	8801(3)	36(2)
C(29)	5304(7)	5183(3)	8910(3)	42(3)
C(30)	6487(9)	5134(4)	9214(4)	54(3)
C(31)	3472(7)	6288(3)	8245(3)	38(2)
C(32)	2292(7)	6317(4)	8445(4)	46(3)
C(33)	2809(7)	6836(3)	8251(4)	43(3)
C(34)	6534(7)	7634(3)	7695(3)	31(2)
C(35)	6770(8)	8175(3)	7955(4)	43(3)
C(36)	5524(7)	7995(3)	7892(3)	40(3)
C(37)	6472(9)	7588(4)	6210(5)	63(3)

C(38)	7092(9)	7399(4)	6358(5)	73(4)
C(39)	7699(12)	7343(6)	6150(7)	114(7)
C(40)	7670(16)	7486(8)	5782(9)	156(12)
C(41)	7056(17)	7679(8)	5634(8)	160(12)
C(42)	6460(13)	7725(6)	5835(6)	111(7)
C(43)	4889(8)	7769(4)	6171(4)	52(3)
C(44)	4445(8)	7488(4)	6018(4)	58(3)
C(45)	3826(9)	7548(5)	5749(4)	71(4)
C(46)	3666(11)	7884(5)	5622(5)	81(5)
C(47)	4069(11)	8170(5)	5789(5)	91(6)
C(48)	4677(11)	8117(4)	6051(5)	78(5)
C(49)	5935(9)	8103(4)	6718(4)	59(3)
C(50)	6531(11)	8310(5)	6626(7)	103(6)
C(51)	6652(13)	8657(6)	6783(9)	136(9)
C(52)	6198(15)	8758(6)	7059(7)	118(8)
C(53)	5602(14)	8565(4)	7153(5)	92(6)
C(54)	5469(11)	8240(4)	6983(5)	77(4)
C(55)	6289(9)	4662(3)	6977(4)	58(3)
C(56)	6971(9)	4812(4)	6873(5)	73(4)
C(57)	7681(10)	4735(4)	7065(7)	93(6)
C(58)	7688(12)	4512(5)	7380(6)	95(6)
C(59)	7055(11)	4349(5)	7479(5)	78(4)
C(60)	6328(10)	4429(4)	7275(4)	68(4)
C(61)	4638(8)	4560(4)	6857(4)	52(3)
C(62)	4042(8)	4704(4)	7028(5)	61(4)
C(63)	3408(9)	4502(4)	7078(5)	66(4)
C(64)	3373(10)	4151(5)	6976(5)	79(5)
C(65)	3986(13)	4004(5)	6821(7)	126(9)
C(66)	4594(13)	4209(5)	6750(7)	117(9)
C(67)	5483(8)	4756(3)	6243(4)	51(3)
C(68)	5953(10)	4484(4)	6111(4)	73(4)
C(69)	5932(13)	4421(6)	5711(5)	102(6)
C(70)	5468(13)	4623(6)	5457(5)	96(6)
C(71)	5018(12)	4880(5)	5580(5)	83(5)
C(72)	5012(9)	4949(4)	5967(4)	61(4)
C(73)	5899(10)	6801(4)	9489(4)	60(3)

C(74)	5740(12)	7081(4)	9739(5)	83(5)
C(75)	6345(14)	7313(5)	9860(6)	100(6)
C(76)	7067(14)	7258(6)	9737(6)	108(7)
C(77)	7170(12)	7001(6)	9504(6)	100(6)
C(78)	6637(10)	6755(5)	9380(5)	82(5)
C(79)	5323(8)	6105(4)	9661(4)	53(3)
C(80)	5766(10)	6137(5)	10005(5)	77(5)
C(81)	5796(12)	5858(6)	10275(6)	101(6)
C(82)	5424(14)	5548(5)	10176(6)	110(7)
C(83)	5018(13)	5513(5)	9828(6)	94(6)
C(84)	4957(10)	5788(4)	9569(5)	70(4)
C(85)	4255(10)	6661(4)	9407(5)	69(3)
C(86)	3902(10)	6896(4)	9147(5)	73(4)
C(87)	3201(11)	7035(5)	9203(5)	89(4)
C(88)	2825(13)	6954(7)	9506(7)	120(5)
C(89)	3162(13)	6728(7)	9774(7)	128(6)
C(90)	3883(12)	6571(6)	9727(6)	108(5)
C(91)	5425(11)	3797(4)	8308(6)	91(5)
C(92)	5791(14)	3563(5)	8009(8)	133(8)
C(93)	5940(20)	3205(7)	8253(10)	250(20)
C(94)	6320(30)	2985(10)	7990(11)	360(40)
C(95)	4264(10)	4135(5)	7993(6)	102(5)
C(96)	3767(11)	4174(6)	8335(7)	131(6)
C(97)	2938(12)	4172(7)	8224(8)	154(8)
C(98)	2515(18)	4225(9)	8571(9)	203(12)
C(99)	9399(13)	7183(5)	9385(7)	130(7)
C(100)	9937(13)	7361(6)	9145(8)	149(7)
C(101)	10585(17)	7291(7)	8926(9)	176(9)
C(102)	11057(15)	7534(7)	8716(8)	172(10)
C(103)	9864(14)	6632(6)	9801(6)	148(9)
C(104)	10640(15)	6563(8)	9718(7)	179(9)
C(105)	10924(19)	6396(7)	10121(8)	198(10)
C(106)	10770(17)	6004(7)	10087(10)	197(12)
C(107)	11064(8)	7071(4)	6845(5)	67(4)
C(108)	11548(9)	6882(4)	7156(5)	72(4)
C(109)	11742(11)	6502(5)	7088(5)	92(6)

C(110)	12235(12)	6334(6)	7400(6)	114(8)
C(111)	10265(9)	6647(6)	6408(5)	103(6)
C(112)	9842(13)	6813(7)	6058(6)	147(7)
C(113)	10176(18)	7144(9)	5908(8)	205(9)
C(114)	9710(20)	7227(13)	5524(9)	283(16)
C(115)	4451(10)	7880(5)	9204(6)	110(6)
C(116)	3836(14)	7947(6)	8908(7)	142(7)
C(117)	3810(13)	8322(6)	8830(6)	138(7)
C(118)	3001(14)	8322(8)	8597(8)	176(10)
C(119)	5537(13)	8280(6)	9356(6)	127(6)
C(120)	5643(19)	8224(7)	9768(7)	185(8)
C(121)	5730(20)	8609(8)	9933(10)	212(9)
C(122)	5280(30)	8935(10)	9771(13)	310(16)
C(123)	2760(14)	8080(5)	6958(6)	123(7)
C(124)	2359(15)	8016(7)	7312(7)	156(8)
C(125)	1566(16)	8037(9)	7364(8)	177(9)
C(126)	1286(18)	8041(8)	7750(8)	179(11)
C(127)	2172(11)	7966(6)	6286(6)	120(6)
C(128)	1323(11)	7977(7)	6261(6)	145(7)
C(129)	1087(14)	8143(8)	5861(6)	162(8)
C(130)	218(15)	8160(10)	5838(9)	215(12)
C(131)	6778(12)	5385(6)	5048(5)	115(7)
C(132)	6873(14)	5729(7)	4840(5)	139(7)
C(133)	6630(17)	5751(8)	4412(5)	173(9)
C(134)	6950(20)	5446(10)	4215(9)	255(15)
C(135)	7793(10)	5251(7)	5595(5)	132(8)
C(136)	8461(10)	5418(7)	5434(7)	154(8)
C(137)	9159(11)	5186(8)	5546(8)	182(9)
C(138)	9808(15)	5357(11)	5391(10)	257(15)
C(139)	4829(11)	6935(6)	5106(5)	97(6)
C(140)	4259(11)	6677(6)	4924(6)	107(7)
C(141)	3470(11)	6831(6)	4830(6)	109(7)
C(142)	2925(15)	6582(8)	4640(9)	186(15)
C(143)	5994(14)	6763(8)	4814(6)	191(11)
C(144)	6548(15)	7070(9)	4800(8)	227(11)
C(145)	7220(17)	7001(10)	4584(9)	239(12)

C(146)	7810(16)	6748(10)	4769(9)	234(14)
C(147)	10152(10)	4939(5)	8230(5)	86(4)
C(148)	9773(12)	4610(5)	8340(5)	101(5)
C(149)	9916(15)	4586(6)	8781(5)	130(6)
C(150)	9640(20)	4232(7)	8898(9)	213(12)
C(151)	10713(12)	4836(6)	7598(7)	143(8)
C(152)	10551(15)	4466(6)	7441(8)	178(8)
C(153)	10930(20)	4182(8)	7234(8)	212(10)
C(154)	11360(20)	3940(10)	7506(10)	259(16)
C(155)	1774(9)	5704(4)	6132(4)	67(4)
C(156)	2190(10)	5540(4)	5839(4)	74(5)
C(157)	2200(13)	5768(6)	5488(5)	104(7)
C(158)	2504(15)	5595(7)	5164(5)	135(9)
C(159)	1022(10)	5323(6)	6544(6)	122(7)
C(160)	836(14)	5021(7)	6293(8)	158(8)
C(161)	1421(16)	4741(7)	6345(9)	175(9)
C(162)	1080(20)	4411(9)	6121(11)	261(15)
C(163)	6707(14)	4640(5)	9660(6)	130(7)
C(164)	6844(19)	4306(6)	9413(8)	172(8)
C(165)	6670(20)	3936(6)	9482(10)	201(10)
C(166)	7070(20)	3726(9)	9202(9)	240(14)
C(167)	7746(11)	5111(5)	9580(5)	106(6)
C(168)	7732(14)	5416(7)	9866(6)	148(7)
C(169)	8475(15)	5573(8)	9992(8)	182(9)
C(170)	8260(20)	5892(9)	10235(10)	238(14)
C(171)	1009(8)	6340(4)	8636(5)	68(4)
C(172)	512(8)	6416(5)	8272(5)	78(5)
C(173)	301(11)	6105(5)	8028(6)	95(6)
C(174)	-193(10)	6191(5)	7678(6)	105(7)
C(175)	1738(10)	5769(4)	8661(5)	79(4)
C(176)	2084(15)	5709(7)	9076(6)	142(6)
C(177)	1750(17)	5378(7)	9248(8)	172(8)
C(178)	2280(20)	5136(8)	9065(10)	213(12)
C(179)	8084(8)	8402(4)	8027(4)	61(4)
C(180)	8595(9)	8468(4)	8395(5)	68(4)
C(181)	9406(10)	8361(5)	8382(6)	92(6)

C(182)	9889(12)	8420(5)	8753(6)	119(9)
C(183)	7011(10)	8773(4)	8203(4)	71(4)
C(184)	6840(13)	8759(4)	8611(5)	95(5)
C(185)	6699(14)	9121(5)	8780(7)	128(7)
C(186)	6002(17)	9282(9)	8586(10)	213(13)
N(1)	6248(7)	4404(3)	8308(3)	51(3)
N(2)	5189(6)	4717(3)	7970(3)	41(2)
N(3)	6384(5)	4994(2)	8100(3)	34(2)
N(4)	5094(8)	4129(3)	8146(4)	81(4)
N(5)	9554(12)	6803(4)	9383(5)	128(7)
N(6)	8728(7)	6746(3)	8839(3)	50(3)
N(7)	9327(8)	6239(3)	9158(3)	65(4)
N(8)	8481(6)	6171(3)	8607(3)	38(2)
N(9)	8653(5)	6963(3)	7396(3)	38(2)
N(10)	9148(5)	6714(3)	6866(3)	41(2)
N(11)	9872(6)	7139(3)	7264(3)	43(2)
N(12)	10341(7)	6880(3)	6741(3)	60(3)
N(13)	6509(5)	7337(2)	8571(3)	33(2)
N(14)	5306(6)	7488(3)	8756(3)	42(2)
N(15)	6423(6)	7828(3)	8977(3)	42(2)
N(16)	5227(8)	7960(3)	9161(4)	76(4)
N(17)	3579(5)	6880(2)	6721(3)	36(2)
N(18)	3419(6)	7434(3)	6992(3)	47(3)
N(19)	2710(6)	7266(3)	6392(3)	47(3)
N(20)	2574(8)	7808(3)	6664(4)	78(4)
N(21)	5656(6)	5787(3)	6178(3)	37(2)
N(22)	5869(7)	5657(3)	5547(3)	53(3)
N(23)	6852(6)	5569(3)	6079(3)	42(2)
N(24)	7042(8)	5416(4)	5456(4)	84(4)
N(25)	5522(6)	6720(3)	5807(3)	47(3)
N(26)	6647(7)	6586(4)	5502(3)	68(4)
N(27)	6637(5)	6528(3)	6163(3)	37(2)
N(28)	5594(8)	6802(5)	5161(4)	103(6)
N(29)	8453(5)	5559(3)	7259(3)	37(2)
N(30)	8962(6)	5278(3)	7818(3)	40(2)
N(31)	9572(6)	5235(3)	7235(3)	51(3)

N(32)	10083(7)	4977(4)	7796(4)	69(3)
N(33)	2233(6)	5338(3)	7097(3)	48(3)
N(34)	3426(5)	5575(3)	7303(3)	38(2)
N(35)	2935(5)	5704(3)	6680(3)	42(2)
N(36)	1735(6)	5506(4)	6489(3)	64(3)
N(37)	5558(6)	5482(3)	8732(3)	42(2)
N(38)	5774(7)	5005(3)	9153(3)	57(3)
N(39)	6775(6)	5418(3)	9039(3)	47(3)
N(40)	6972(8)	4963(4)	9470(4)	76(4)
N(41)	2919(6)	6119(3)	8384(3)	42(2)
N(42)	2222(6)	6671(3)	8387(3)	46(3)
N(43)	3433(5)	6642(2)	8173(3)	39(2)
N(44)	1706(6)	6144(3)	8569(3)	55(3)
N(45)	5771(5)	7682(2)	7728(3)	35(2)
N(46)	6032(6)	8238(3)	8010(3)	45(2)
N(47)	7047(6)	7872(3)	7806(3)	40(2)
N(48)	7269(7)	8432(3)	8059(3)	54(3)
S(1)	7671(2)	5633(1)	7868(1)	35(1)
S(2)	7804(2)	7678(1)	8788(1)	45(1)
S(3)	6806(2)	7240(1)	7485(1)	35(1)
S(4)	7599(2)	4686(1)	8486(1)	54(1)
S(5)	5255(2)	5386(1)	7754(1)	32(1)
S(6)	6650(2)	5724(1)	6795(1)	33(1)
S(7)	5317(2)	6953(1)	8276(1)	35(1)
S(8)	4489(2)	5876(1)	5640(1)	54(1)
S(9)	5401(2)	6610(1)	6542(1)	35(1)
S(10)	7793(2)	6472(1)	7022(1)	38(1)
S(11)	2752(2)	5187(1)	7805(1)	52(1)
S(12)	9130(2)	5581(1)	8923(1)	52(1)
S(13)	4578(2)	8049(1)	7925(1)	53(1)
S(14)	6576(2)	5972(1)	8572(1)	35(1)
S(15)	4363(2)	5070(1)	8823(1)	57(1)
S(16)	9041(2)	5546(1)	6593(1)	67(1)
S(17)	7753(2)	6700(1)	8222(1)	35(1)
S(18)	2915(2)	6650(1)	6060(1)	57(1)
S(19)	9355(2)	7447(1)	7857(1)	60(1)

S(20)	2781(2)	7277(1)	8150(1)	61(1)
S(21)	7938(2)	6368(1)	5862(1)	61(1)
S(22)	4285(2)	6063(1)	8130(1)	36(1)
S(23)	4433(2)	7016(1)	7373(1)	35(1)
S(24)	4308(2)	5958(1)	6886(1)	32(1)
P(1)	5700(2)	7676(1)	6511(1)	48(1)
P(2)	5421(2)	4846(1)	6746(1)	42(1)
P(3)	5186(2)	6472(1)	9316(1)	49(1)

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