

Supporting Information

Interparticle Reactions between Silver Nanoclusters Leading to Product Cocrystals by Selective Cocrystallization

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Experimental Section

Synthesis of $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ nanocluster

Phosphine and hydride co-protected $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ nanocluster (TPP – triphenylphosphine) assigned as Ag_{18} was synthesized by a reported method.¹⁻² 20 mg of AgNO_3 was dissolved in the mixed solvents of 5 mL methanol and 9 mL of chloroform. After that 70 mg of TPP, dissolved in 1 mL of CH_3Cl , was added to the above reaction mixture under stirring condition. After 20 min of stirring, 6 mg of NaBH_4 in 0.5 mL of ice cold water was added. Upon addition of the reducing agent, colourless solution changes to yellow. The reaction mixture was kept for continuous stirring for 3 h under dark condition. After 3 h the yellow colour solution changes to dark green which indicated the formation of the Ag_{18} cluster. The reaction mixture was allowed for solvent evaporation under reduced pressure. The green solid product collected was washed several times with water to remove excess silver precursor and the reducing agent. After washing, the pure material was extracted using methanol. The green colour solution of NC was characterized using UV-vis and ESI MS and was used for further reaction.

Instrumentation

(a) UV/Vis spectroscopy

UV-vis spectra were recorded using a Perkin Elmer Lambda 25 instrument in the range 200 – 1100 nm.

(b) General instrumental parameters used for ESI measurements

Cluster sample was analysed by Waters Synapt G2Si High Definition Mass Spectrometer equipped with electrospray ionization (ESI) and ion mobility (IM) separation. The sample was analysed in positive ESI mode. The optimized conditions for the sample analysed is given below:

Sample concentration: 10 µg/mL

Solvent: CH₃CN

Flow rate: 30 uL/min

Capillary voltage: 2- 3 kV

Cone voltage: 30 V

Source offset: 20 V

Trap collision Energy: 0 V

Transfer collision Energy: 0 V

Source temperature: 100°C

Desolvation temperature: 200°C

Desolvation gas Flow: 400 L/h

Trap gas flow: 10 L/h

(c) X-ray crystallography

Single crystal data were measured using a Bruker Kappa APEX III CMOS diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) 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.

Single crystal X-ray diffraction (SCXRD) analysis

Structure was solved using SHELXT-2017 and least-squares refined using SHELXL-2017. Crystal data and refinement conditions are shown in Table S1. Suitable restraints were applied during the least-squares (LS) refinement. Upon refinement, it was observed that Ag_{16} and Ag_{17} were not disordered. The existence of two types of molecules in the same site results in the additional symmetry related disorders in both the molecules. Three of the CF_3 moieties are doubly disordered and one acetonitrile was also disordered. Their disorders have been resolved. The molecule has a crystallographic $\text{P}2_1/\text{n}$ space group. A more detailed explanation of Ag_{16} and Ag_{17} structure reveals the atom Ag in the shell centre of Ag_{17} which has occupancy of $1/3$ (33.33%). This depicts that in the co-crystal structure $2/3$ (66.66%) NC molecules have 16 Ag atoms and $1/3$ molecules have 17 Ag atoms. The difference Fourier map towards the end showed the presence of acetonitrile molecule in the lattice.

Electron count formula

The total valence electron count (M) for each intermediates, $[\text{Ag}_p(\text{TBT})_q(\text{TFA})_r(\text{CH}_3\text{CN})_s\text{Cl}_t]^+$ is counted by the formula, $M = p - q - r - t - c$, where p, q, r, t and c are the number of silver atoms, thiolate, trifluoroacetates, chloride and net positive charge on the molecule, respectively (Table S3-S5).³

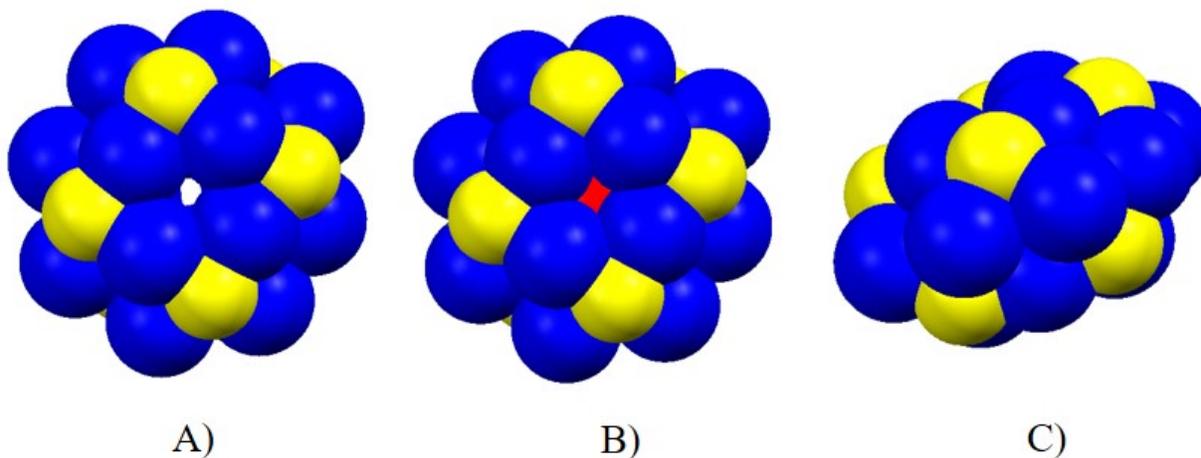


Figure S1. Space-filling model of Ag_{16}S_8 shell in (A) Ag_{16} and (B) Ag_{17} NCs. (C) Lateral view of the Ag_{16}S_8 shell.

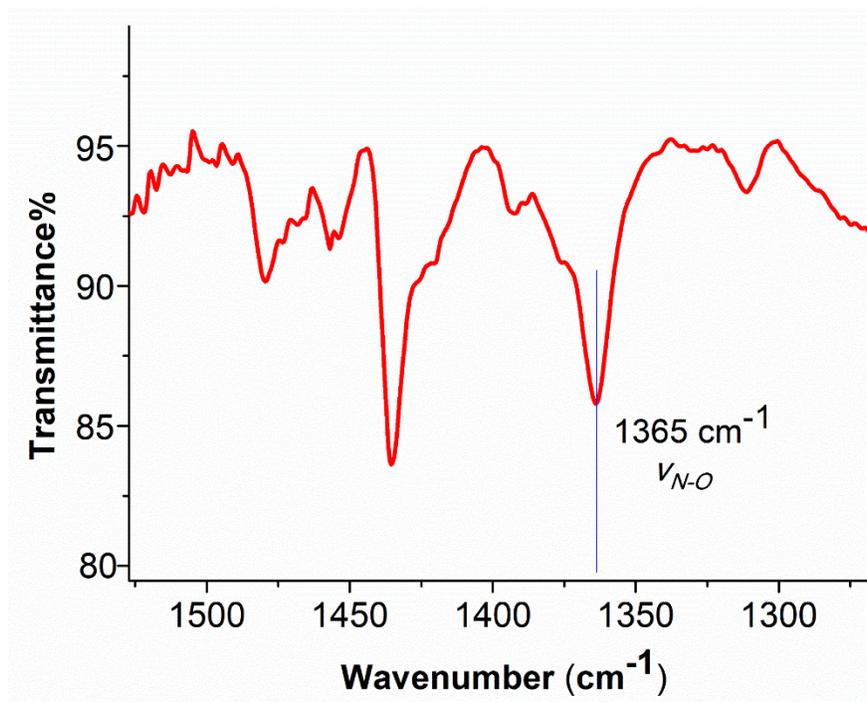
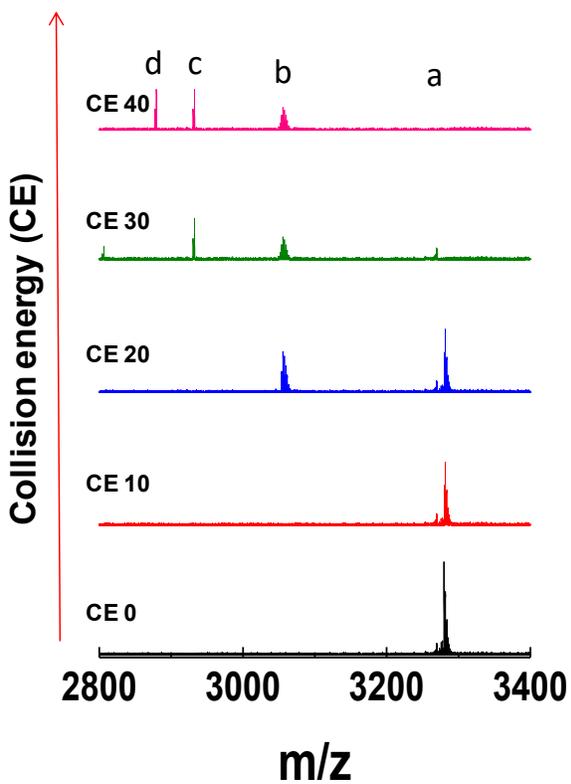


Figure S2. FTIR spectrum of Ag₁₆:Ag₁₇ co-crystal. The absorption band at 1365 cm⁻¹ is assigned to N–O stretching in NO₃⁻.



- (a) $[\text{Ag}_{16}(\text{TBT})_8(\text{CF}_3\text{COO})_6(\text{CH}_3\text{CN})_3(\text{Cl})]^+$
- (b) $[\text{Ag}_{15}(\text{TBT})_8(\text{CF}_3\text{COO})_5(\text{CH}_3\text{CN})_3(\text{Cl})]^+$
- (c) $[\text{Ag}_{15}(\text{TBT})_8(\text{CF}_3\text{COO})_4(\text{CH}_3\text{CN})_3(\text{Cl})]^+$
- (d) $[\text{Ag}_{15}(\text{TBT})_7(\text{CF}_3\text{COO})_6(\text{CH}_3\text{CN})(\text{Cl})]^+$

Figure S3. MSMS spectra of $[\text{Ag}_{16}(\text{TBT})_8(\text{CF}_3\text{COO})_6(\text{CH}_3\text{CN})_3(\text{Cl})]^+$ for different collision energies (I : 0 eV, II : 10 eV, III : 20 eV, IV : 30 eV, IV : 40 eV). With the increase in collision energy the fragmentation occurs in Ag_{16} NC and gives rise to the formation of Ag_{15} species.

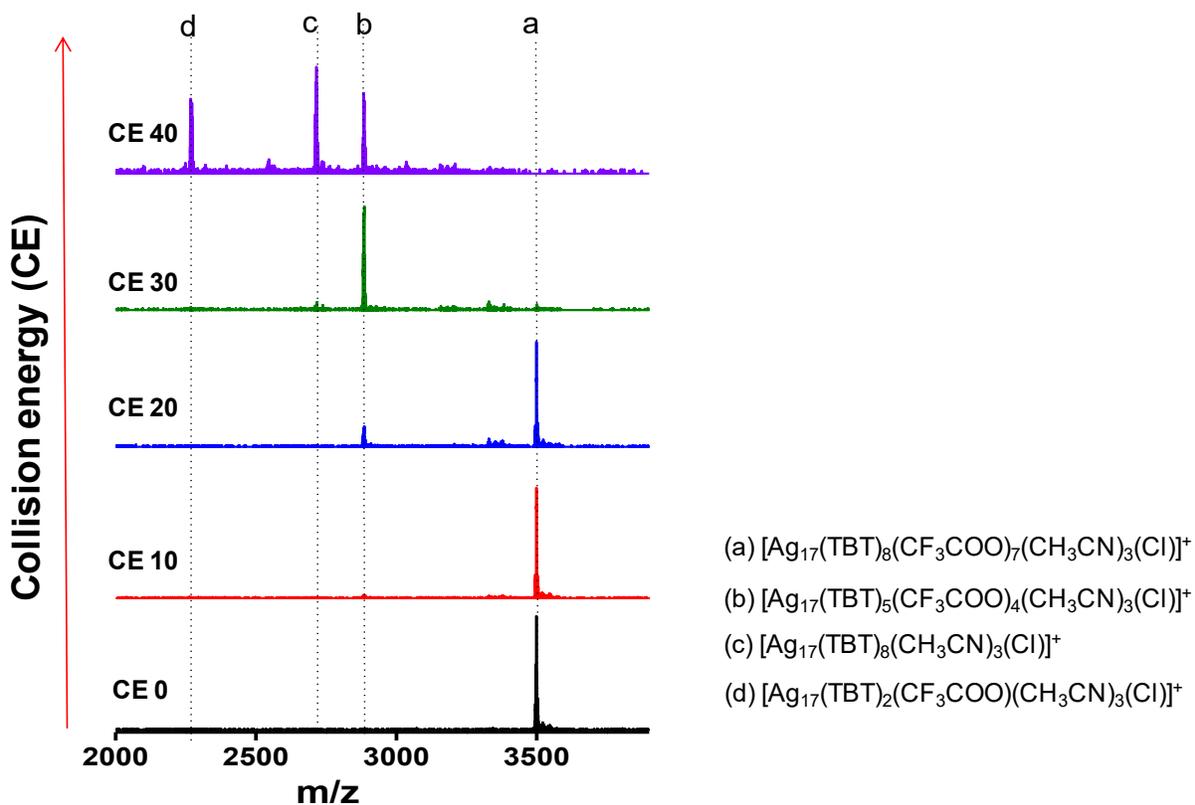


Figure S4. MSMS spectra of $[\text{Ag}_{17}(\text{TBT})_8(\text{CF}_3\text{COO})_7(\text{CH}_3\text{CN})_3(\text{Cl})]^+$ for different collision energies (I : 0 eV, II : 10 eV, III : 20 eV, IV : 30 eV, IV : 40 eV). With increase in the collision energy the ligands are removed and the number of Ag-atoms remains intact indicates Ag_{17} moiety is stable and does not give any Ag_{16} species.

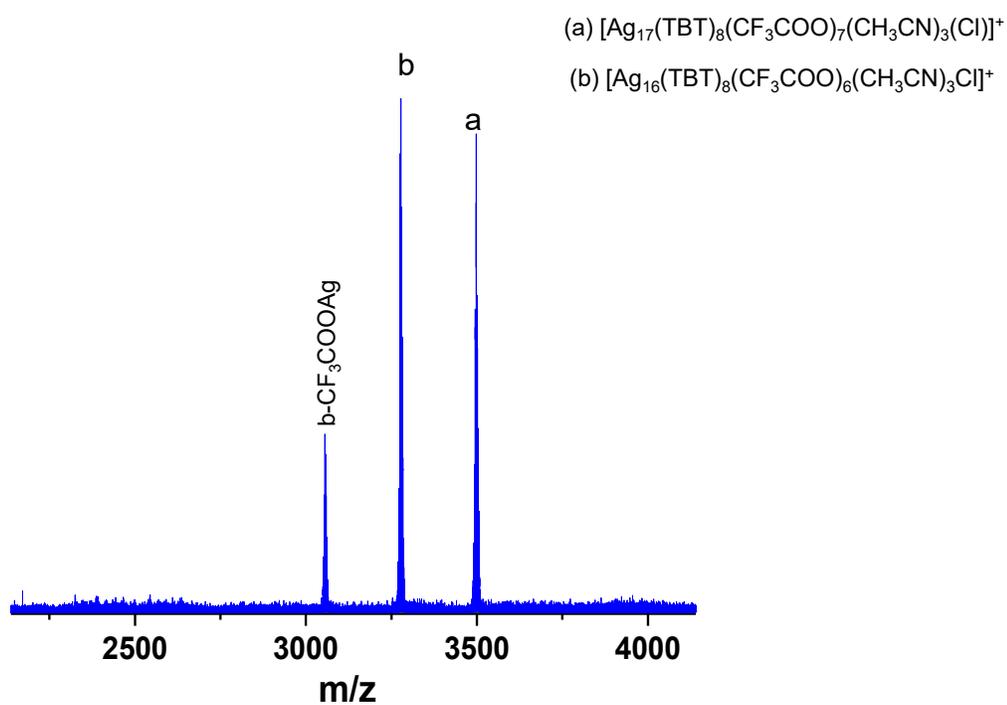


Figure S5. ESI MS of a reaction product in acetonitrile. ESI MS of the reaction mixture shows the population of Ag₁₆ and Ag₁₇ clusters to be almost equal.

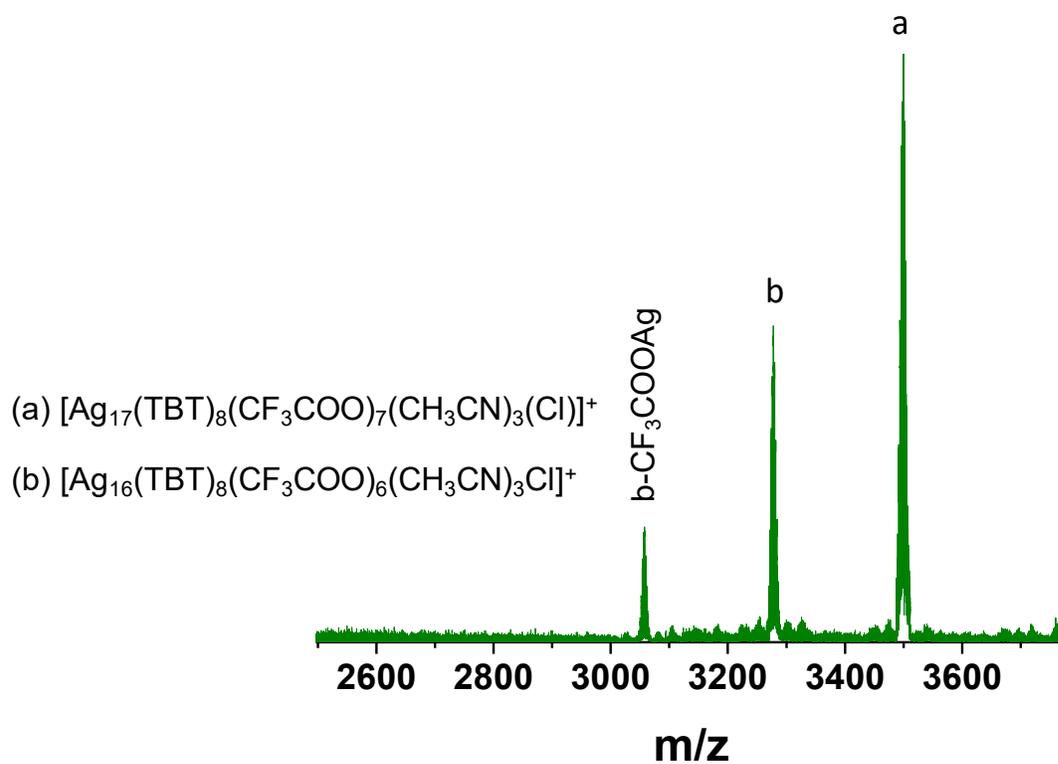


Figure S6. ESI MS of supernatant obtained after crystallization. The intensities of the peaks imply that the population of Ag_{17} is more than Ag_{16} which supports our assumption that selective crystallization occurred.

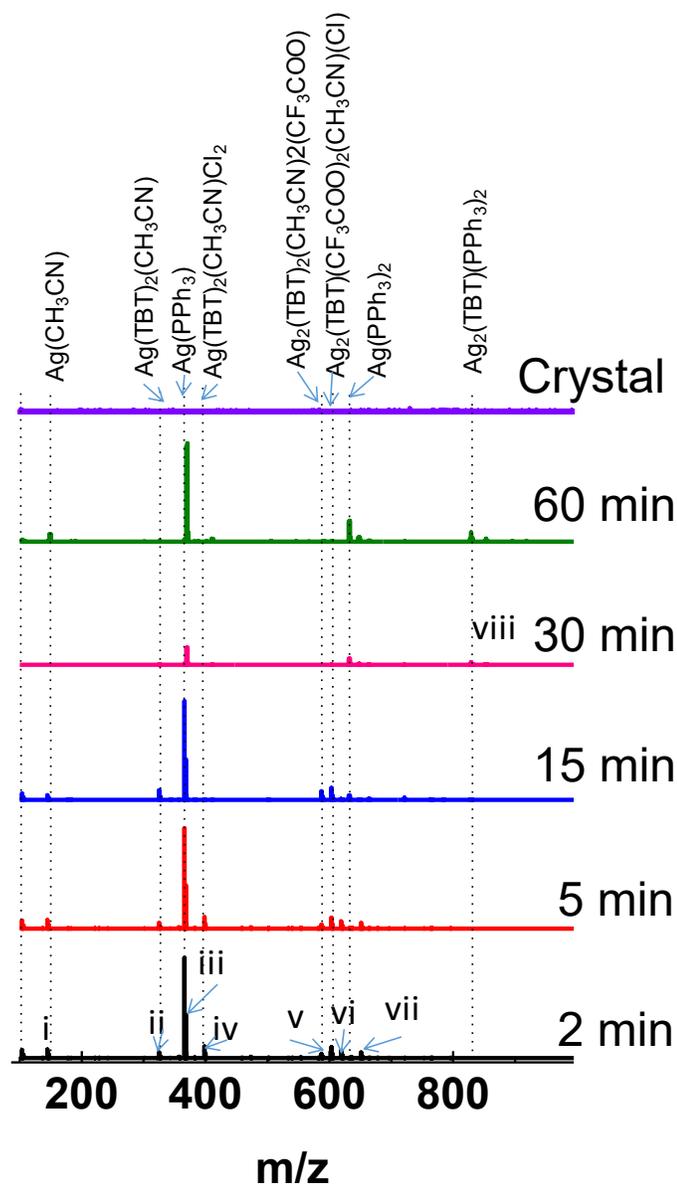
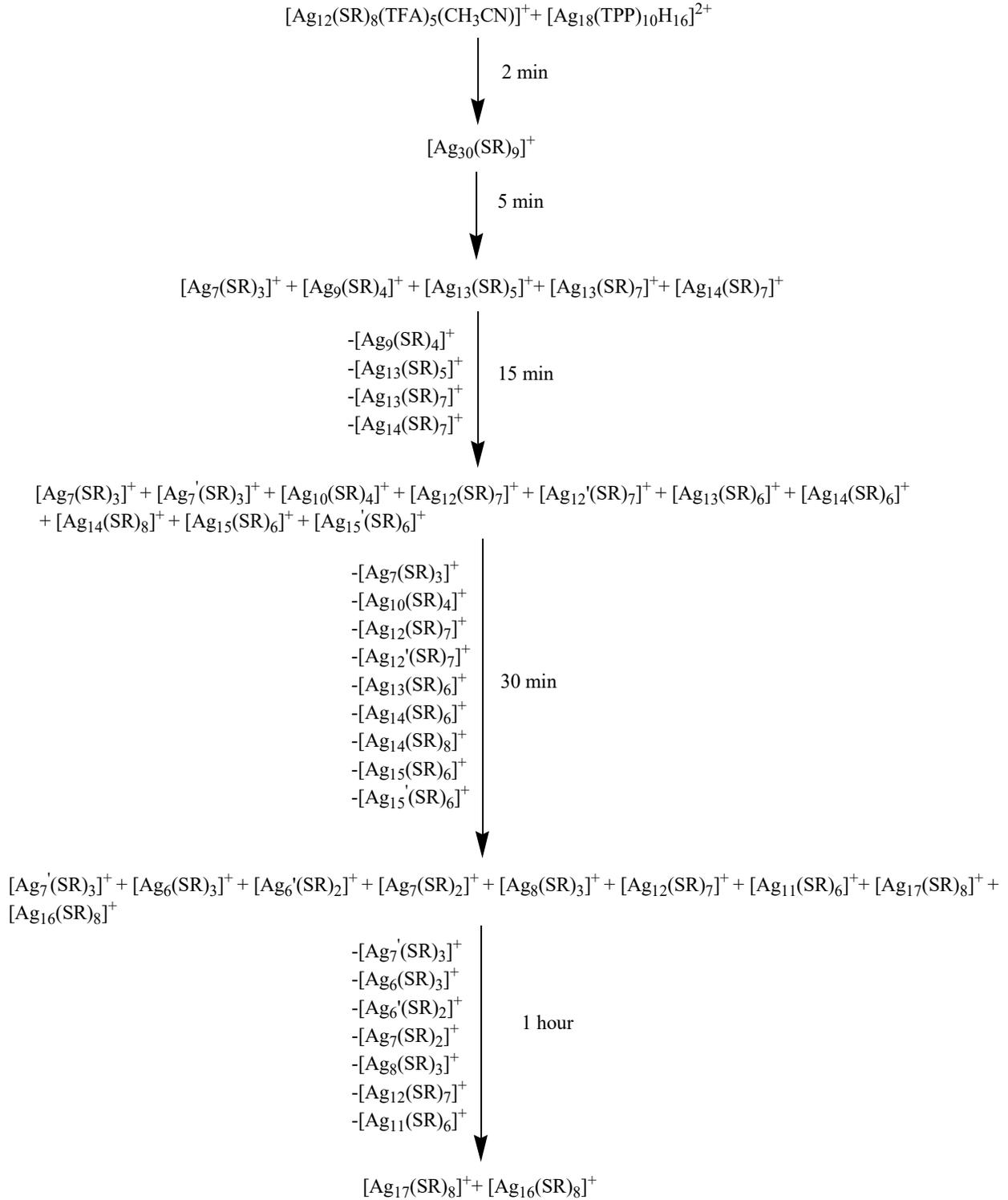


Figure S7. Time-dependent ESI MS spectra from m/z 100-1000. The peaks are assigned and marked by arrow. The species formed in this region are mainly silver-thiolate-phosphine complexes.

Scheme 1: Flow chart of the reaction process



Where SR is tertiary-butylthiolate (TBT). The other ligands (TFA, CH₃CN and Cl) have not been included.

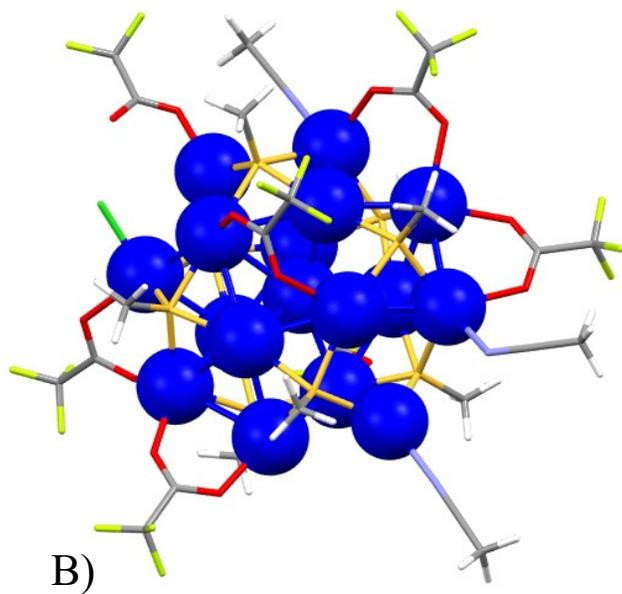
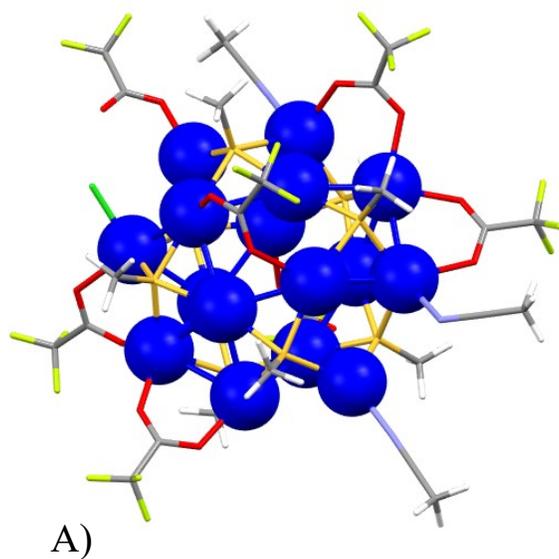


Figure S8. Optimized geometry of (A) Ag₁₆ and (B) Ag₁₇.

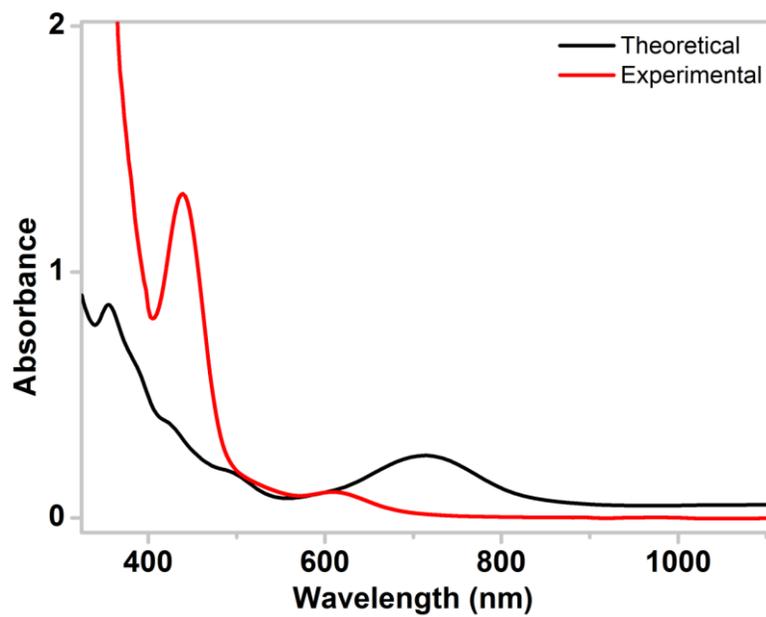


Figure S9. Experimental (red) and theoretical (black) optical absorption spectra of a crystal.

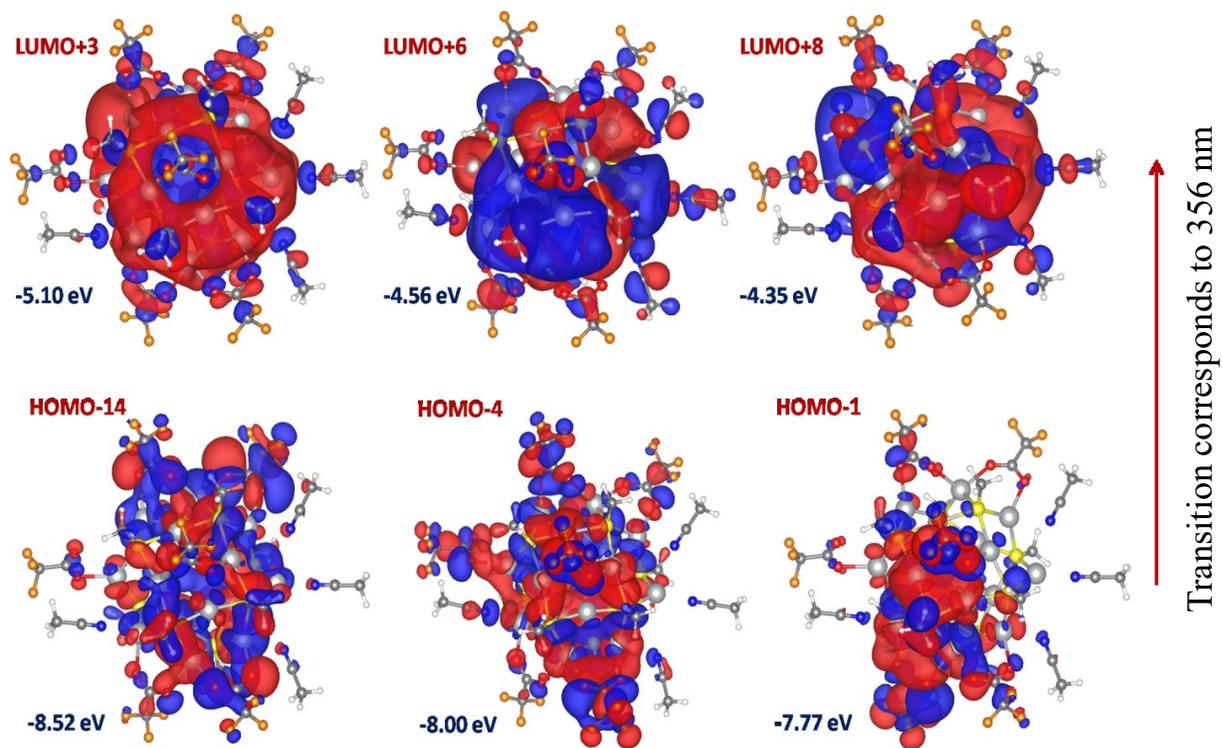


Figure S10. Molecular orbitals responsible for the optical transition of the peak at 356 nm.

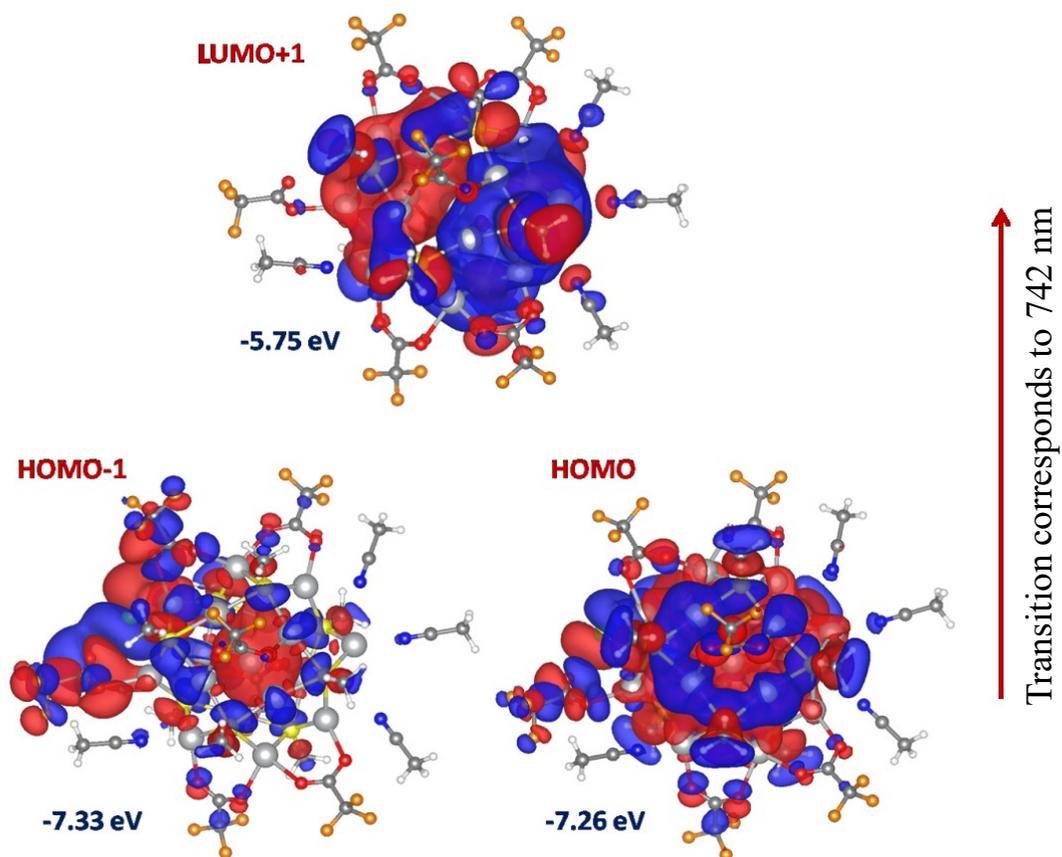


Figure S11. Molecular orbitals responsible for the optical transition of the peak at 742 nm.

Table S1. Crystal data and structure refinement for co-crystal

Identification code	new1	
Empirical formula	C ₅₄ H ₈₁ Ag _{16.33} F ₂₁ N ₄ O ₁₄ S ₈ Cl	
Formula weight	3462.94	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 19.802(9) Å	α = 90°
	b = 22.502(10) Å	β = 98.198(14)°
	c = 22.792(11) Å	γ = 90°
Volume	10052(8) Å ³	
Z	4	
Density (calculated)	2.288 Mg/m ³	
Absorption coefficient	3.381 mm ⁻¹	
F(000)	6587	
Crystal size	0.200 x 0.150 x 0.100 mm ³	
Theta range for data collection	2.856 to 25.000°	
Index ranges	-22 ≤ h ≤ 23, -26 ≤ k ≤ 26, -27 ≤ l ≤ 27	
Reflections collected	137308	
Independent reflections	17664 [R(int) = 0.1507]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.5466	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	17664 / 904 / 1192	
Goodness-of-fit on F ²	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0812, wR2 = 0.2079	
R indices (all data)	R1 = 0.1811, wR2 = 0.3073	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.946 and -1.274 e.Å ⁻³	

Table S2. Silver complexes, silver thiolates and phosphines observed m/z below 1000

S. No.	[Intermediate] ⁺	code	m/z
1	[Ag(CH ₃ CN)] ⁺	I	150.01
2	[Ag(TBT) ₂ (CH ₃ CN)] ⁺	ii	326.11
3	[Ag(PPh ₃)] ⁺	iii	368.14
4	[Ag(TBT) ₂ (CH ₃ CN)(Cl) ₂] ⁺	iv	398.11
5	[Ag ₂ (TBT) ₂ (CH ₃ CN) ₂ (CF ₃ COO)] ⁺	v	587.21
6	[Ag ₂ (TBT)(CF ₃ COO) ₂ (CH ₃ CN)(Cl)] ⁺	vi	606.20
7	[Ag(PPh ₃) ₂] ⁺	vii	631.18
8	[Ag ₂ (TBT)(PPh ₃) ₂] ⁺	viii	828.89

Table S3. Reaction intermediates formed during the reaction

[Intermediate] ⁺	code	m/z	Electron count (M)
[Ag ₃₀ (TBT) ₉ (CF ₃ COO) ₆ (CH ₃ CN) ₅] ⁺	1	4928.08	14
[Ag ₇ (TBT) ₃ (CF ₃ COO) ₃ (CH ₃ CN) ₃ (Cl)] ⁺	2	1294.97	1
[Ag ₉ (TBT) ₄ (CF ₃ COO) ₂ (CH ₃ CN) ₂] ⁺	3	1635.29	2
[Ag ₁₃ (TBT) ₇ (CF ₃ COO) ₄] ⁺	4	2479.99	1
[Ag ₁₃ (TBT) ₅ (CF ₃ COO) ₆] ⁺	5	2526.24	1
[Ag ₁₄ (TBT) ₇ (CF ₃ COO) ₅] ⁺	6	2703.01	1
[Ag ₇ (TBT) ₃ (CF ₃ COO) ₃] ⁺	7	1361.51	0
[Ag ₁₀ (TBT) ₄ (CF ₃ COO) ₃] ⁺	8	1774.09	2
[Ag ₁₂ (TBT) ₇ (CF ₃ COO) ₃ (CH ₃ CN) ₂ Cl] ⁺	9	2377.02	0
[Ag ₁₂ (TBT) ₇ (CF ₃ COO) ₃ (CH ₃ CN) ₃ Cl] ⁺	10	2418.34	0
[Ag ₁₄ (TBT) ₆ (CF ₃ COO) ₄ (CH ₃ CN)Cl] ⁺	11	2573.86	2
[Ag ₁₃ (TBT) ₆ (CF ₃ COO) ₆] ⁺	12	2615.38	0
[Ag ₁₄ (TBT) ₈ (CF ₃ COO) ₄ (CH ₃ CN)(Cl)] ⁺	13	2751.97	0
[Ag ₁₅ (TBT) ₆ (CF ₃ COO) ₅ (CH ₃ CN)(Cl)] ⁺	14	2795.23	2
[Ag ₁₅ (TBT) ₆ (CF ₃ COO) ₅ (CH ₃ CN) ₂ Cl] ⁺	15	2836.20	2
[Ag ₆ (TBT) ₃ (CF ₃ COO)] ⁺	16	1028.86	1

$[\text{Ag}_6(\text{TBT})_2(\text{CF}_3\text{COO})_2(\text{CH}_3\text{CN})]^+$	17	1092.62	1
$[\text{Ag}_7(\text{TBT})_2(\text{CF}_3\text{COO})_4]^+$	18	1385.95	0
$[\text{Ag}_8(\text{TBT})_3(\text{CF}_3\text{COO})_3]^+$	19	1469.89	1
$[\text{Ag}_{11}(\text{TBT})_6(\text{CF}_3\text{COO})_3(\text{CH}_3\text{CN})]^+$	20	2102.34	1
$[\text{Ag}_{12}(\text{TBT})_7(\text{CF}_3\text{COO})_3(\text{CH}_3\text{CN})]^+$	21	2298.93	1

References

- (1) Ghosh, A.; Bodiuzzaman, M.; Nag, A.; Jash, M.; Baksi, A.; Pradeep, T. Sequential Dihydrogen Desorption from Hydride-Protected Atomically Precise Silver Clusters and the Formation of Naked Clusters in the Gas Phase. *ACS Nano* **2017**, *11*, 11145-11151.
- (2) Bootharaju, M. S.; Dey, R.; Gevers, L. E.; Hedhili, M. N.; Basset, J. M.; Bakr, O. M. A New Class of Atomically Precise, Hydride-Rich Silver Nanoclusters Co-Protected by Phosphines. *J. Am. Chem. Soc.* **2016**, *138*, 13770-13773.
- (3) Stellacci, F.; Tang, Y.; Pan, J.; Dass, A.; McLean, J. A.; Cliffel, D. E.; Kothalawala, N.; Harkness, K. M.; Demeler, B.; Bakr, O. M. $[\text{Ag}_{44}(\text{SR})_{304}]^-$: A Silver–Thiolate Superatom Complex. *Nanoscale* **2012**, *4*, 4269-4274.