Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Unusual Structural Transformation and Luminescence Response of Magic-Size Silver(I) Chalcogenide Clusters via Ligand-Exchange

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Synthesis:

Triphenyl phosphorus sulfur, 3,3-Dimethyl-1-butyne and silver hexafluoroantimonate were purchased from Saen Chemical Technology Co., Ltd (Shanghai, China). Thionyl chloride and other reagents employed were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals and solvents for synthesis were of analytical grade and used without further purification. The solvents used were of analytical grade. Polymeric [AgC≡C^{t}Bu]n were prepared according to the literature procedure.

Synthesis namely [$Ag_{32}S_3(C{\equiv}C^tBu)_{23}](SbF_6)_3$: $AgSbF_6$ (0.1 mmol, 34.3 mg) and AgC≡C^{t}Bu (0.2 mmol, 37.8 mg) were mixed and dissolved in 10 ml methanol, followed by the addition of $Ph_3P{=}S$ (0.1 mmol, 1 mL) and heated at 60 ℃ for 60 min. A yellow solution collected by filitration. By slowly vaporizing the solvent in the dark, yellow blocky crystalswere obtained within 4-5 days. Interestingly, we can still get a relatively pure sample byprecipitation of the above yellow solution through water precipitation method, with a yield of 77.4% (based on silver).

Crystal Data for **$Ag_{32}S_3$**: $C_{138}H_{207}Ag_{32}F_{18}S_3Sb_3$ (M =6121.29 g/mol): triclinic, space group P-1 (no. 2), a = 19.1661(9) Å, b = 19.2822(10) Å, c = 28.4193(13) Å, α = 93.851(2)°, β = 98.460(2)°, γ = 117.901(2)°, V = 9069.1(8) Å^3, Z = 2, T = 120.0 K, μ(MoKα) = 3.891 mm^{-1}, *Dcalc* = 2.242 g/cm^3, 129189 reflections measured (4.236° ≤ 2Θ ≤ 52.8°), 36993 unique (R_{int} = 0.0305, R_{sigma} = 0.0328) which were used in all calculations. The final R_1 was 0.0787 (I > 2σ (I)) and wR_2 was 0.2407 (all data). CCDC: 2116414.

Synthesis namely [$Ag_{45}S_6(C_8H_4Br)_{32}](C_8H_5Br)_3(SbF_6)_3$: $Ag_{32}S_3$ (0.010 g) was dissolved in a mixture of methanol and dichloromethane (1:1, 4 mL), and 3-bromophenylacetylene (0.2 mmol, 24 μl) was added, after stirring for one hour, filter the yellow flocculent precipitate, the orange crystals precipitate separate out of the mother liquor after two days with a yield of 58.4% (based on silver).

Crystal Data for **$Ag_{45}S_6$**: $C_{265}H_{130}Ag_{45}Br_{33}Cl_2F_6S_6Sb$ (M =11303.88 g/mol): triclinic, space group P-1 (no. 2), a = 18.8242(13) Å, b = 20.2627(13) Å, c = 40.783(3) Å, α = 77.983(2)°, β = 87.539(2)°, γ = 63.769(2)°, V = 13626.7(16) Å^3, Z = 2, T = 160.0 K, μ(MoKα) = 8.202 mm^{-1}, *Dcalc* = 2.755 g/cm^3, 104377 reflections measured (2.3° ≤ 2Θ ≤ 47.06°), 40435 unique (R_{int} = 0.0636, R_{sigma} = 0.0992) which were used in all calculations. The final R_1 was 0.0927 (>2sigma(I)) and wR_2 was 0.2692 (all data). CCDC: 2116415.

Characterization:

UV–vis spectra were measured on an Analytik Jena S600 UV–visible spectrophotometer. PL spectra were taken on an Edinburgh Instruments FLS980 spectrometer. PL decay dynamics was recorded on a time correlated single-photon counting (TCSPC) spectrofluorometer (FLS980, Edinburgh Instrument) with a 450 nm picosecond pulsed laser at a repetition frequency of 0.1 and 0.5 MHz. Single-crystal X-ray diffraction data was recorded on Bluker D8 VENTURE at 120 kV. High resolution mass spectrometry was recorded on an Agilent 6224 (Agilent Technologies, USA) ESI-TOF-MS spectrometer.

Additional Figures:

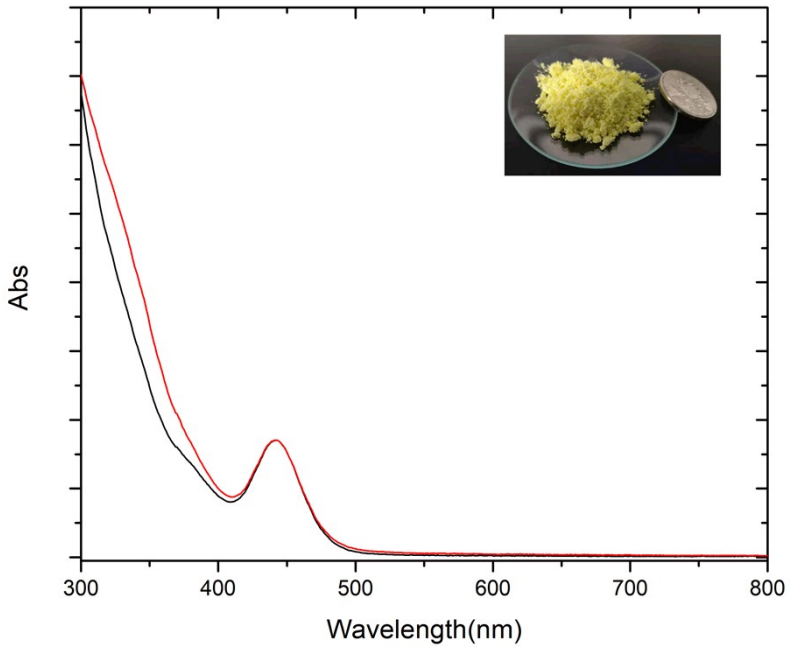

Figure S1. The UV-Vis spectra of solid samples precipitated by water soluble in CH_3OH (red trace), crystal samples (black trace). Inset: 30 g of $[Ag_{32}S_3(C_6H_9)_{23}](SbF_6)_3$ cluster pictured with one coins for scale (each coin is 2.5 cm in diameter and weights 6.1 g). The dishes is 6 cm in diameter.

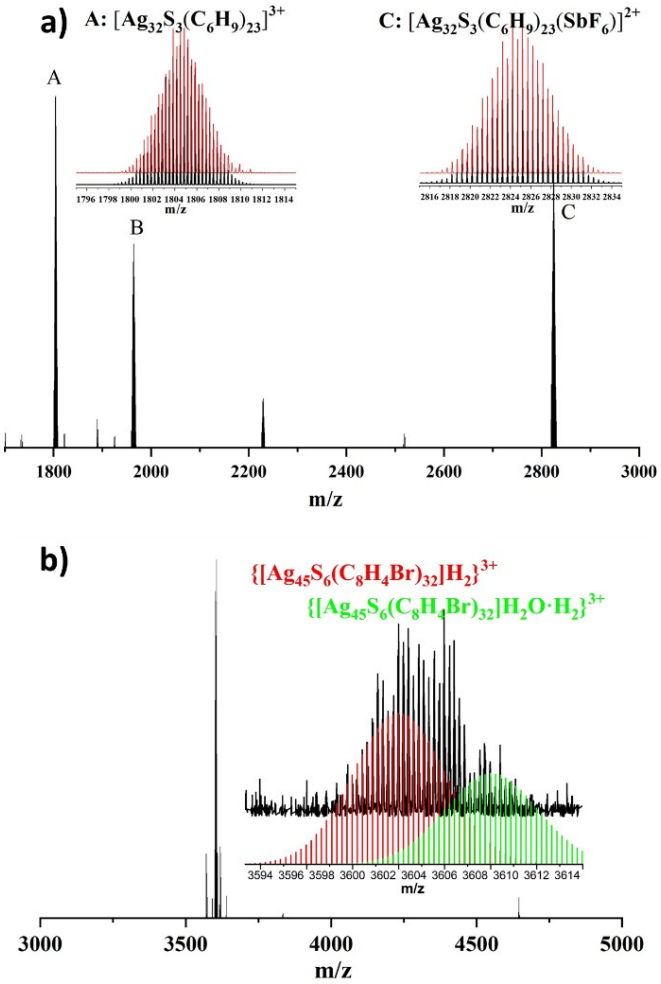

Figure S2. ESI-MS of $Ag_{32}S_3$ (a) and $Ag_{45}S_6$ (b), the measured (black trace) and simulated (red and green trace) isotopic distribution patterns of the corresponding the molecular ion peaks.

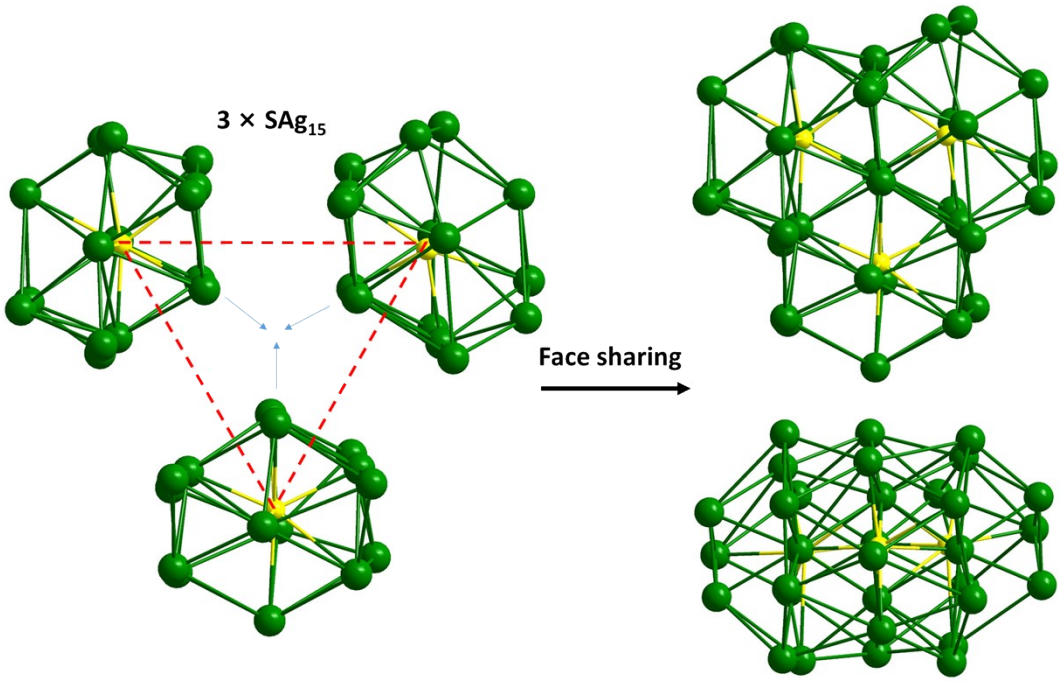

Figure S3. Anatomy of the $Ag_{32}S_3$ cluster, which is constructed by three interpenetrating SAg_{15} unit sharing five Ag atoms.

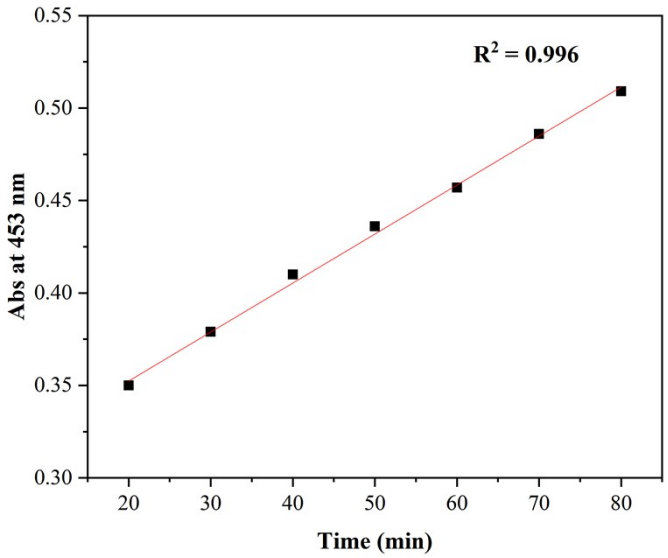

Figure S4. Time plots of the absorption increase at 453 nm of $Ag_{32}S_3$ converting to $Ag_{45}S_6$, fitting the increasing intensity of the 453 nm peak gives a perfect match with a zero-order reaction.

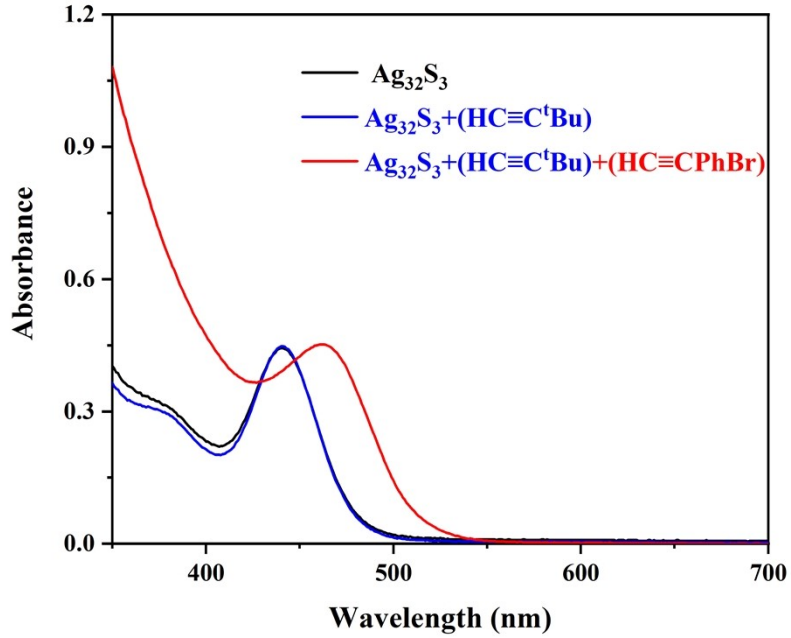

Figure S5. UV-Vis spectra of $Ag_{32}S_3$ by adding in HC≡CBu^t and HC≡CPhBr.

After dissolving $Ag_{32}S_3$ in the mixture of dichloromethane and methanol solvents (black trace), HC≡CBu^t was added to $Ag_{32}S_3$ with 2 h of stirring, the absorption (blue trace) is almost unchanged. while HC≡CPhBr was added with 1 h of stirring, the absorption band of $Ag_{45}S_6$ is obvious (red trace).

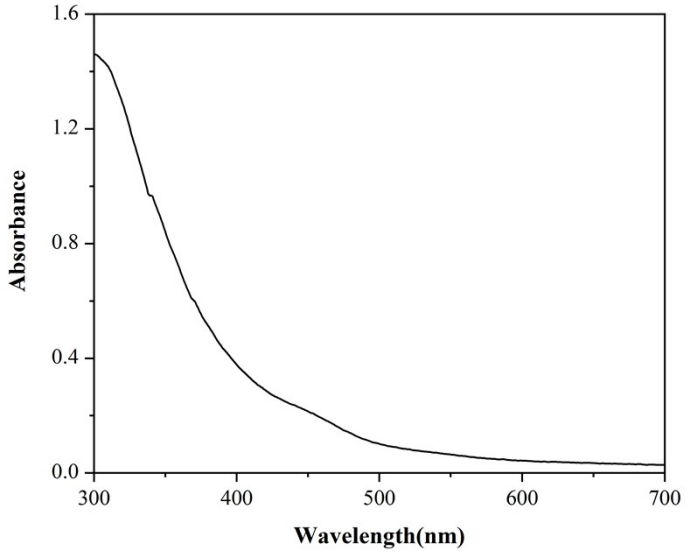

Figure S6. UV-Vis spectra obtained by mixing the polymeric $[AgC{\equiv}CPhBr]_n$ with precursor triphenylphosphine sulfide and $AgSbF_6$ (Under the same experimental condition as $Ag_{32}S_3$ to $Ag_{45}S_6$, heating at 60°C for 1h).

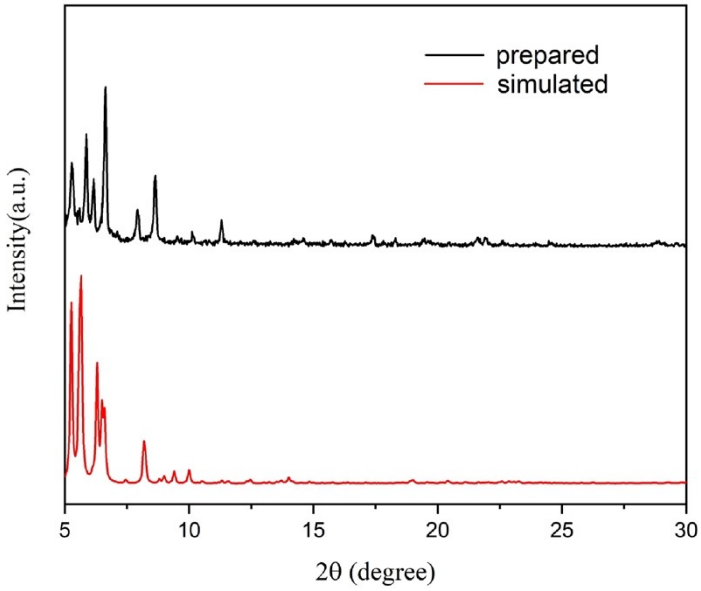

Figure S7. The prepared and simulated PXRD spectra of $Ag_{32}S_3$ crystals.

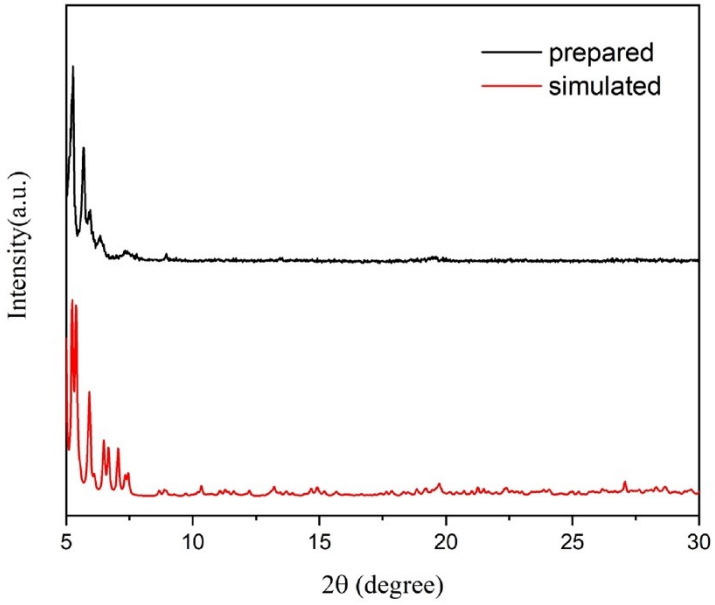

Figure S8. The prepared and simulated PXRD spectra of $Ag_{45}S_6$ crystals.

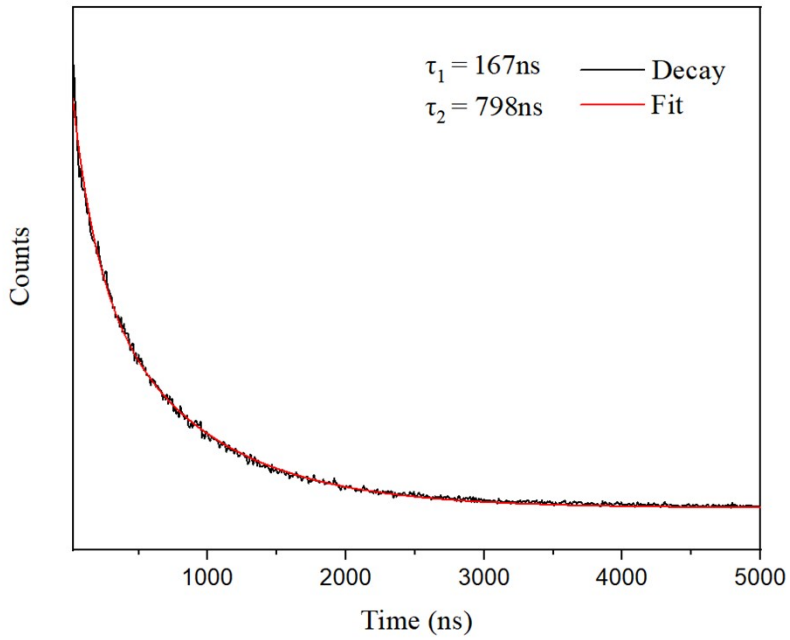

Figure S9. Luminescence decay profiles of $Ag_{45}S_6$ in trichloromethane at room temperature: The final lifetime obtained by ExpDec 2 fitting is 167 ns and 798 ns.

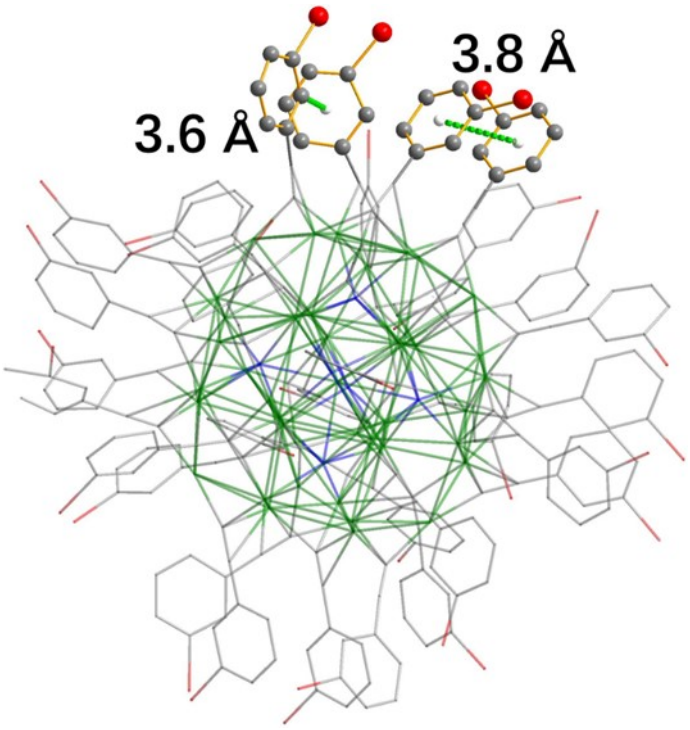

Figure S10. The π – π interaction of aromatic rings in $[Ag_{45}S_6(C{\equiv}CPhBr)_{32}]^+$.