Supplementary Information (SI) for ChemComm.
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Supporting Information

Exploring the origin of chirality in Ag_8 clusters based on modular disassembly

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1. Chemicals

All reagents were commercially available and used without further purification. The solvents employed in this study included dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), and acetonitrile (MeCN), all of which were of HPLC grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium borohydride ($NaBH_4$, ≥98%) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Silver p-toluenesulfonate ($C_7H_7AgO_3S$, ≥98%, metal basis), (+)-fenchyl thiols ($C_{10}H_{16}O$, ≥98%), (-)-fenchyl thiols ($C_{10}H_{16}O$, ≥98%),Lawesson's reagent (LR, ≥97%), and 1,1'-bis(diphenylphosphino)ferrocene ($C_{34}H_{28}FeP_2$, ≥97%) were purchased from Shanghai Macklin Biochemical Co.

2. Synthesis of R/S-Ag_8 clusters

Firstly, 60 mg of silver p-toluenesulfonate was added to 7 mL of methanol and ultrasonicated until completely dissolved. Then, 10 mL of dichloromethane was added. Subsequently, 50 μL of (+/-)-fenchyl thiols was added under vigorous stirring. After 15 minutes, the solution became clear. Then, 30 mg of 1,1'-bis(diphenylphosphino)ferrocene was added, and the solution turned golden yellow. After 10 minutes, the solution became turbid. Next, 2 mL of freshly prepared $NaBH_4$ solution (10 mg mL^{-1} in EtOH) was added dropwise. The solution gradually turned black. After the reaction was carried out at room temperature for 17.5 hours, the product was washed several times with methanol and acetonitrile. After diffusing acetonitrile into the dichloromethane solution of the nanoclusters for 1 day, colorless block single crystals could be obtained. The yield of R/S-Ag_8 clusters was 19% based on the initial silver atom.

3. Measurement

The UV-vis absorption spectra of the nanoclusters were recorded using a METASH UV-9000 spectrometer with a 1 cm quartz cell and dichloromethane as the solvent. The spectra were obtained by electrospray ionization mass spectrometry (ESI-MS) using a Waters UPLC h-class/Xevo G2-XSQTOF mass spectrometer. Single crystal X-ray diffraction data were collected on a Stoe Stadivari diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54184). CD spectra were obtained using a JASCO J-1500 CD spectrometer.

4. Computational methods and details

The geometric optimizations and energy calculations for the Ag_4 and Ag_8 clusters were performed using the ORCA 5.0.3 program system,[1-2] at the PBE0-D3(BJ)/def2-SVP and PBE0-

D3(BJ)/def2-TZVP levels of theory,[3-5] respectively. TDDFT calculation is implemented using the ORCA software package at the level of PBE0/def2-SV(P).[5-6] In addition, the solvent effect was considered with 1, 2-dichloroethane in the SMD model.[7] The number of excited states calculated for each cluster is 300. In order to reflect the differences in the electronic structures of Ag_4 and Ag_8, all the above calculations use the overall structure (without any simplification). In addition, the data processing of PDOS and UV-Vis is implemented based on the Multiwfn 3.8 (dev) software package.[8-9]

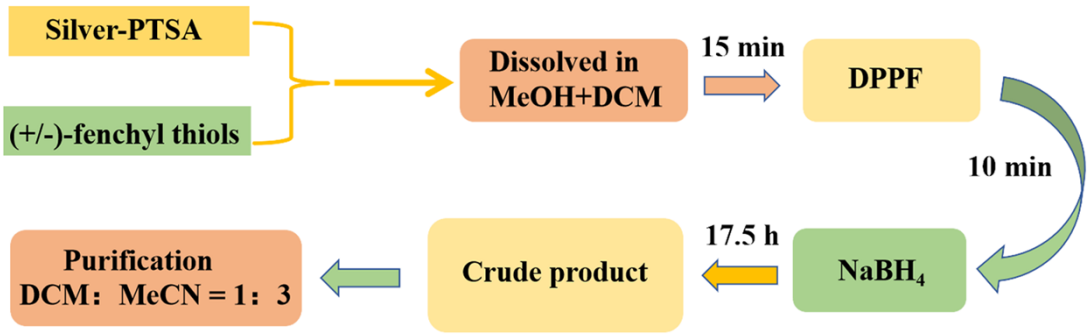

Fig. S1 Synthesis flowchart of R/S-Ag_8 clusters.

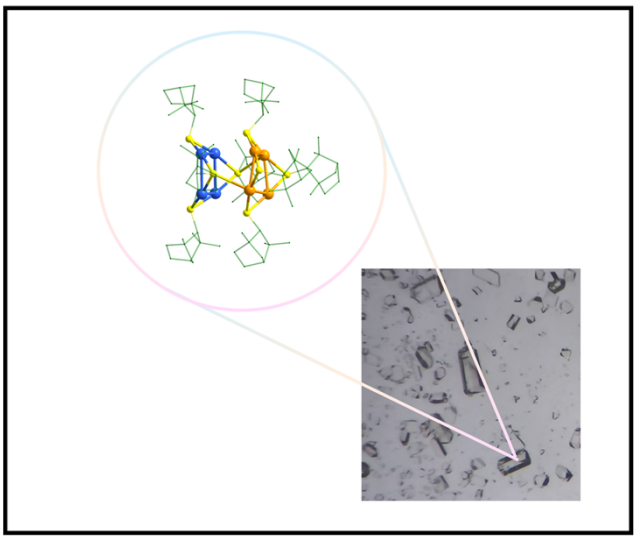

Fig. S2 Crystal photos and structure of R-Ag_8 cluster.

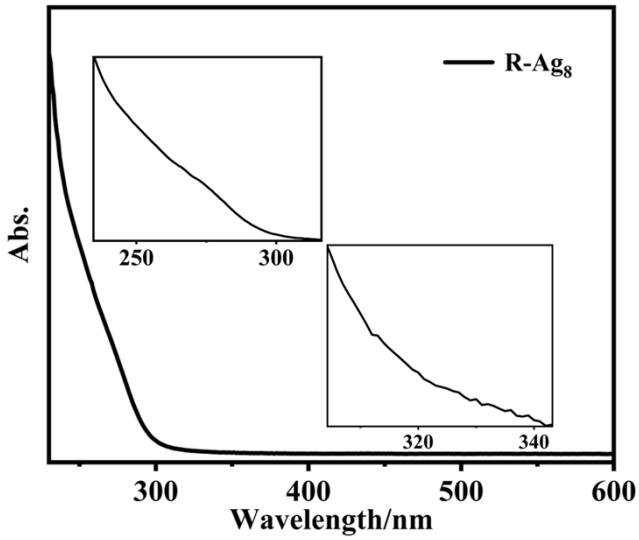

Fig. S3 UV-vis of R-Ag_8 cluster.

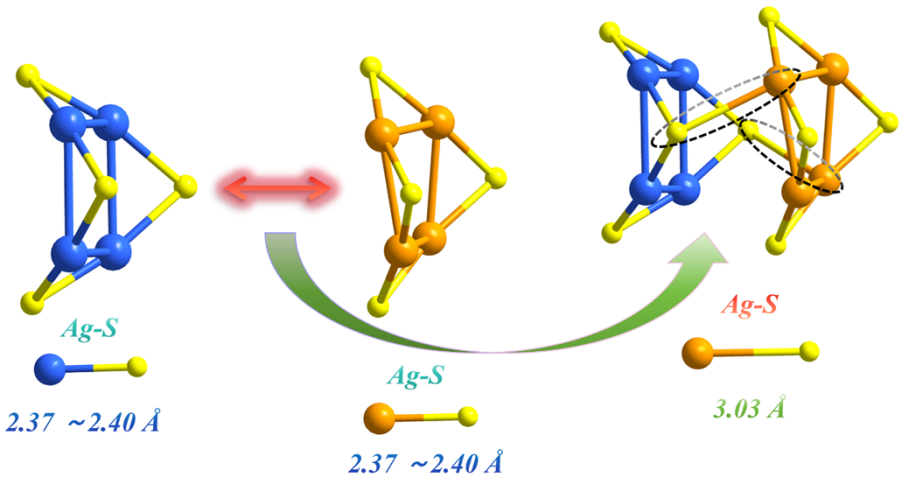

Fig. S4 The bond length of the Ag-S bond in S-Ag_8 cluster.

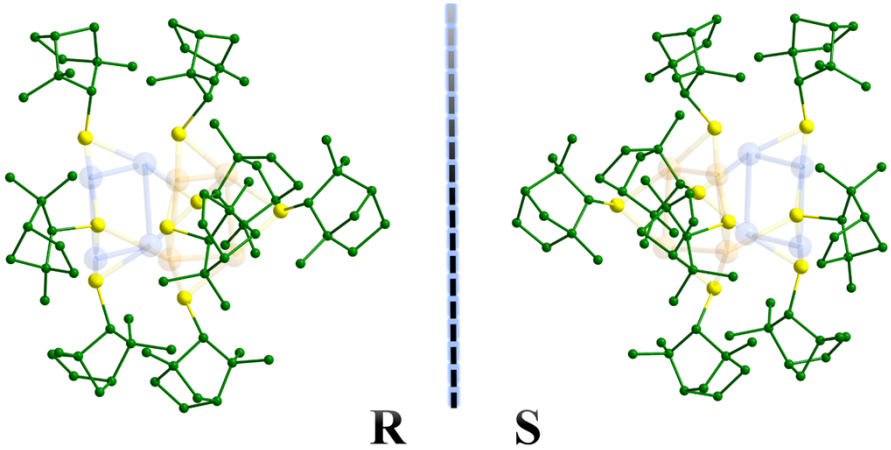

Fig. S5 Structure of chiral ligands in R/S-Ag_8.

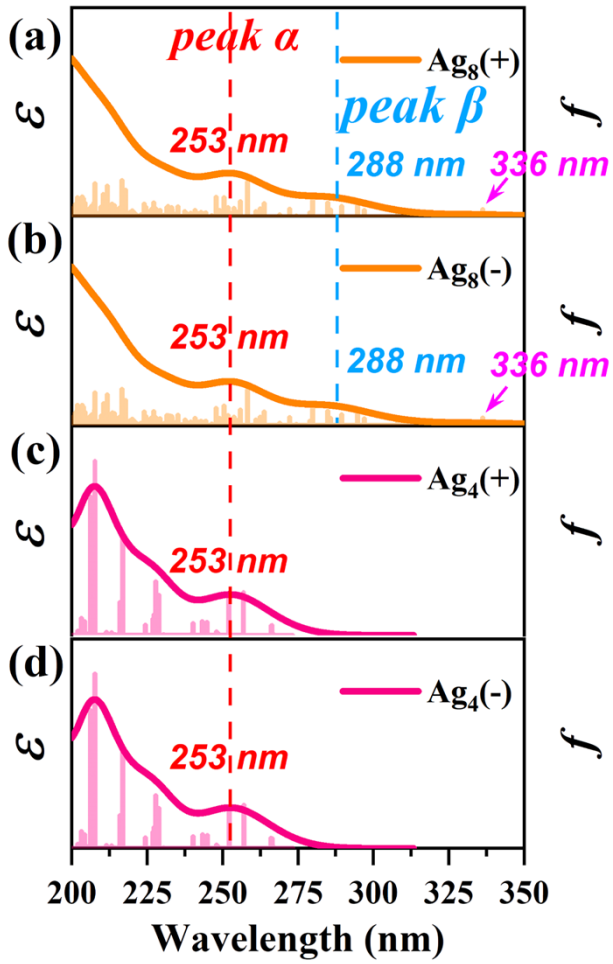

Fig. S6 Calculated UV-Vis spectra of (a,b) Ag_8 and (c,d) Ag_4 clusters.

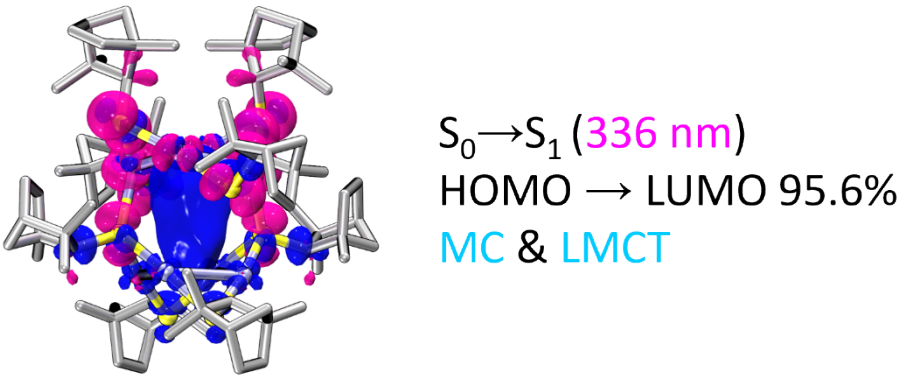

Fig. S7 Hole and electron distributions of the first excited state (S_1) in the R/S-Ag_8 clusters (Blue and pink isosurfaces represent electron and hole, with the value of isosurfaces set at 0.001).

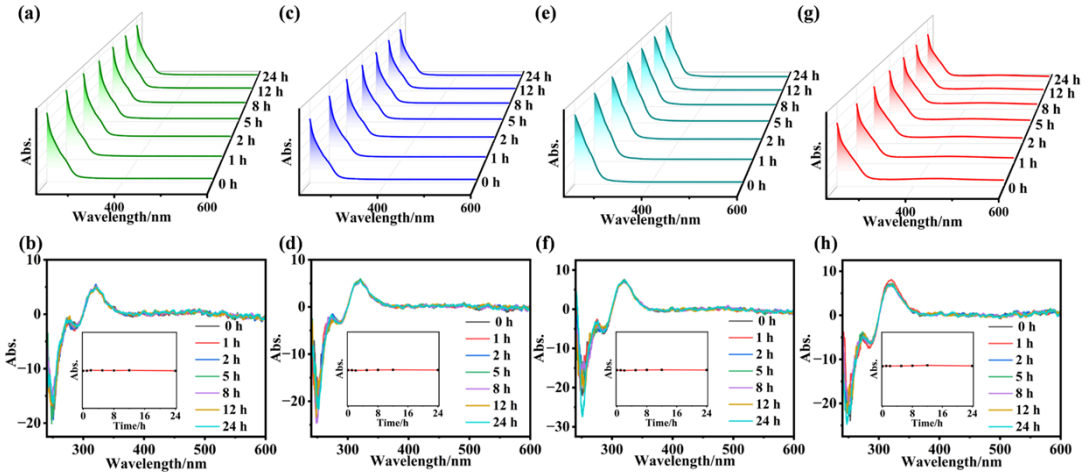

Fig. S8 Time-dependent UV-vis spectra and CD spectra for the stability test of R-Ag_8 in the acidity (a, b), alkalinity (c, d), oxidation (e, f), and thermal (g, h) conditions (Inset: time-dependent absorption coefficient difference curve at 320 nm).

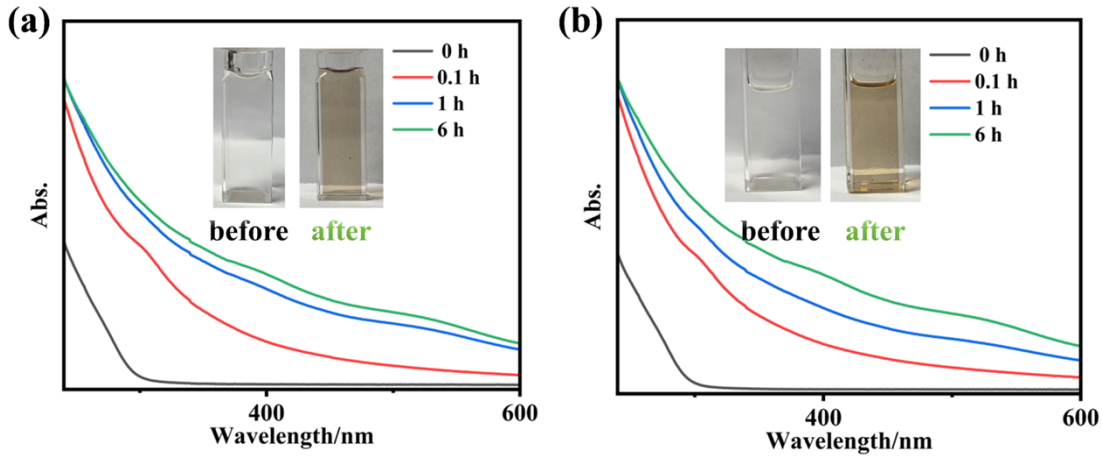

Fig. S9 Time-dependent UV-vis spectra for the stability test of R-Ag_8 (a) and S-Ag_8 (b) under reducing conditions (inset: the color changes of R/S-Ag_8 before and after the addition of a reducing agent).

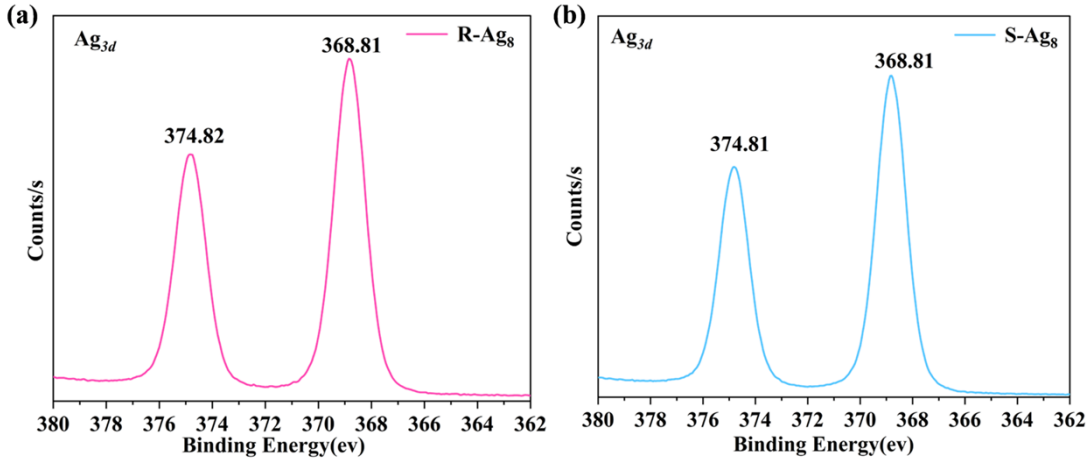

Fig. S10 XPS spectra of Ag 3d for R/S-Ag_8 clusters.

Table S1 Crystal data and structure refinement for R-Ag_8 and S-Ag_8

CCDC Number	2511976	2511975
Identification code	R-Ag_8	S-Ag_8
Empirical formula	$C_{80}H_{136}Ag_8S_8$	$C_{80}H_{136}Ag_8S_8$
Formula weight	2217.32	2217.32
Temperature/K	120.15	120.15
Crystal system	monoclinic	monoclinic
Space group	l2	l2
a/Å	16.90380(10)	16.9196(2)
b/Å	12.78060(10)	12.7575(2)
c/Å	20.16090(10)	20.1848(3)
α/°	90	90
β/°	91.3310(10)	91.2890(10)
γ/°	90	90
Volume/Å^3	4354.40(5)	4355.82(11)
Z	2	2
ρcalcg/cm^3	1.691	1.691
μ/mm^{-1}	16.197	16.192
F(000)	2240.0	2240.0
Crystal size/mm^3	0.65× 0.3× 0.06	0.04× 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.904 to 153.84	6.742 to 153.4
Index ranges	$-21 \le h \le 21$, $-13 \le k \le 15$, $-25 \le l \le 24$	$-19 \le h \le 21$, $-15 \le k \le 13$, $-24 \le l \le 25$
Reflections collected	42035	42202
Independent reflections	8460 [R_{int}= 0.0408, R_{sigma} = 0.0285]	8370 [R_{int} = 0.1316, R_{sigma} = 0.0663]
Data/restraints/parameters	8460/121/445	8370/61/444
Goodness-of-fit on F^2	1.086	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0880	R_1 = 0.0634, wR_2 = 0.1684
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0887	R_1 = 0.0670, wR_2 = 0.1714
Largest diff.peak/hole / e Å^{-3}	1.08/-1.08	1.97/-1.70
Flack parameter	-0.018(6)	0.044(18)

Reference

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