Supplementary Information for

**Thiol-Stabilized Atomically Precise, Superatomic Silver Nanoparticles for Catalyzing Cycloisomerization of Alkynyl Amines**

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**Materials and Methods**

**Raw materials**

Silver hexafluoroantimonate (AgSbF$_6$, 98%), cyclohexanethiol (C$_6$H$_{12}$S, 97%) were purchased from Alfa Aesar. (Tianjin, China), sodium borohydride (NaBH$_4$, 98%), triethylamine (C$_6$H$_{15}$N, 99.5%), dichloromethane (CH$_2$Cl$_2$, A.R.), 1,2-dichloroethane (C$_2$H$_4$Cl$_2$, A.R.), toluene (C$_6$H$_8$, A.R.), chlorobenzene (C$_6$H$_5$Cl, A.R.), acetonitrile (C$_2$H$_3$N), ethanol (C$_2$H$_5$OH, A.R.) and TiO$_2$ (P25) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Vulcan XC-72 carbon powder (abbreviated as C) was purchased from Cabot. The water used in all experiments was ultrapure. All reagents were used as received without further purification.

**Synthesis Procedures**

**Synthesis Procedure of [Ag$_{206}$(SR)$_{68}$F$_2$Cl$_2$]$^q$ (1, q = +2, +3, +4 and +5) nanoparticle**

In a typical preparation, 40 mg of AgSbF$_6$ was dissolved in 1 ml of methanol, followed by the addition of 4 ml of dichloromethane. The mixture was cooled to 0 °C in an ice bath and 10 μL of cyclohexanethiol were then added. After 20-min stirring, 1 ml of an aqueous solution of
NaBH₄ (40 mg/mL) and 50 μl of triethylamine were added quickly to the reaction mixture under vigorous stirring. The reaction mixture was aged for 12 h at 0 °C. The aqueous phase was then removed. The organic phase was washed several times with water and evaporated for further analysis. Dark single crystals suitable for X-ray diffraction study were grown by a double-layer of hexane/CH₂Cl₂ solution of crude product at 4 °C for two weeks. The yield of 1 was ~25 % (based on Ag).

**Synthetic procedures for the preparation of N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (2a)**

Compound 2a was prepared according to the known procedures.¹⁻³

1H NMR (400 MHz, CDCl₃) δ 7.71 – 7.67 (m, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.24 – 7.19 (m, 2H), 7.04 – 6.98 (m, 1H), 3.37 (s, 1H), 2.37 (s, 3H).

**1-tosyl-1H-indole (2b)**

1H NMR (400 MHz, CDCl₃) δ 7.99 (dd, J = 8.0 Hz, J = 0.4 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.55 (d, J = 3.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.23 – 7.16 (m, 3H), 6.63 (dd, J = 3.6 Hz, J = 0.8 Hz, 1H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 135.4, 134.8, 130.7, 129.8, 126.8, 126.3, 124.5, 123.2, 121.3, 113.5, 109.0, 21.47.

**Characterizations**

The UV-vis spectra were measured by Shimadzu UV-2550 Spectrophotometer with dichloromethane as solvent. Mass spectra were recorded on an Agilent Technologies ESI-TOF-MS (6224). Thin-layer chromatography (TLC) was carried out with silicycle pre-coated silica gel plates. ¹H NMR and ¹³C NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d₅ with TMS (0.0 ppm) and chloroform (77.0 ppm) signal as an internal reference. Raman spectra were
acquired using a confocal Raman system (Xplora, Horiba) using a 532 nm laser as the excitation light with the power around 0.15 mW. TEM spectra were recorded on a TECNAI F-30 transmission electron microscope operating at 300 kV.

**Electrochemistry**

Electrochemical measurements of nanoparticle were performed with an electrochemical workstation (CHI 760e) using a glass carbon working electrode (diameter 0.1 mm), a Pt counter electrode, and a SCE-reference electrode in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$. Nanoparticle solutions were degassed and blanketed with a high-purity N$_2$ atmosphere during measurement. Ferrocene (Fc$^{0+/+}$) was used as an internal reference for the SCE-reference electrode. The Fc$^{0+/+}$ couple was found to be 0.554 V versus SCE in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$. All potentials in this article are reported with respect to Fc$^{0+/+}$. Voltammograms of the nanoparticle solutions were acquired at 0 °C using an ice bath.

**Catalyst Preparation**

**Preparation of (AgSR)$_n$ polymer.** 1 mmol cyclohexanethiol was added into 10 ml silver hexafluoroantimonate CH$_2$Cl$_2$ dispersion (0.1 M) under vigorous stirring. The suspension was aged at r.t. for 3 h. The resulting white precipitate, (AgSR)$_n$ polymer, was collected via centrifugation, washed with CH$_2$Cl$_2$ for five times and then dried in vacuum.

**Preparation of 1 wt% Ag$_{206}$/TiO$_2$ and Ag$_{206}$/C.** 5 ml monodisperse CH$_2$Cl$_2$ solution of Ag$_{206}$ nanoparticle (2 mg/mL) was slowly dropped into 20 ml TiO$_2$ or C CH$_2$Cl$_2$ dispersion (1g TiO$_2$ or C) under vigorous stirring. The suspension was aged at r.t. for 6 h. The solid was collected via centrifugation, washed with CH$_2$Cl$_2$ for five times and then dried in vacuum.

**Preparation of 1 wt% Ag$_{44}$/TiO$_2$ and Ag$_{374}$/TiO$_2$.** Other monodisperse Ag$_{44}$ and Ag$_{374}$ nanoparticles were prepared according to the protocol demonstrated in refs. 22 and 23 (main text). The obtained nanoparticles were loaded on TiO$_2$ as same as the preparation of 1 wt% Ag$_{206}$/TiO$_2$.

**Catalytic Experiments**

Cyclization Reaction of N-(2-ethynylphenyl)-4-methylbenzenesulfonamide (2a) was carried out in a vial. For each reaction, a mixture of reactant, catalyst and solvent was placed into reactor. Then reaction mixture was vigorously stirred at the designed temperature for required time. After cooling the room temperature, the supernatant was collected via centrifugation, and purified by flash chromatography or preparative chromatography on a silica gel. The yields of 1-tosyl-1H-indole (2b) were calculated with reference to the obtained product. The product identification was carried out using $^1$H and $^{13}$C NMR.
**Recycling procedure for 2a**

The reused 5 mol% catalyst (1 wt% Ag$_{206}$/TiO$_2$), 2a (0.1 M), chlorobenzene (2 ml) and a magnetic stir bar were charged. The vial was sealed with a septum and placed into an oil bath, which was preheated to 80 °C. The reaction mixture was held at this temperature for 2 h. The reaction mixture was worked up and purified to afford 2b. The 1 wt% Ag$_{206}$/TiO$_2$ was washed several times with hexane, then dried in 80 °C, and used again in the next round of recycling.

**DFT calculations**

All the atomistic and jellium DFT computations were done by using the real-space code package GPAW.$^{56}$ The experimental crystal structure of Ag$_{206}$(SR)$_{68}$F$_2$Cl$_2$ (SR = cyclohexanethiol) was used as the starting point, and total energies of [Ag$_{206}$(SR)$_{68}$F$_2$Cl$_2$]$^q$ with 4- ≤ $q$ ≤ 5+ were evaluated via single-point calculations, i.e., ignoring the structural relaxation. For a cluster of this size, this is a reasonable approximation. The electron-electron interactions were described by the PBE-functional. The real-space grid spacing was 0.25 Å. Auxiliary DFT calculations were done within the jellium description without explicit atoms, but smearing the positive background charge uniformly in a polyhedral shape taken from the outermost Ag$_{90}$ layer in the core of (1). The real-space grid spacing in these calculations was set to 0.4 Å. The electronic structure of both the atomistic [Ag$_{206}$(SR)$_{68}$F$_2$Cl$_2$]$^q$ and jellium model of the core with $q$ = 4- (corresponding to 138 free electrons) was analyzed via projection of the Kohn-Sham orbitals to spherical harmonics as described previously.$^{57}$

**X-ray single-crystal analysis**

The diffraction data of the single crystals grown from the solutions of 1 were collected on an Agilent Technologies SuperNova system X-ray single-crystal diffractometer with Mo (λ =0.71073 Å) and Cu Kα radiation (λ = 1.54184 Å) at 100 K. The data were processed using CrysAlisPro.$^{58}$ The structure was solved and refined using Full-matrix least-squares based on $F_2$ using ShelXT$^{59}$ and ShelXL$^{60}$ in Olex2$^{61}$ and Shelxle.$^{62}$ Detailed crystal data and structure refinements for both compounds are given in Supplementary Table S1.
**Supplementary Table S1. Crystal data and structure refinement for [Ag\textsubscript{206}(SR)\textsubscript{68}F\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{q}**.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | [Ag\textsubscript{206}(SR)\textsubscript{68}F\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{q} |
| Empirical formula                             | C\textsubscript{408}H\textsubscript{748}Ag\textsubscript{206}Cl\textsubscript{2}F\textsubscript{2}S\textsubscript{68} |
| Formula weight                                 | 30164.90                                   |
| Temperature/K                                 | 100.01(10)                                 |
| Crystal system                                | monoclinic                                 |
| Space group                                   | I2/a                                       |
| a/\textdegree                                   | 46.5160(6)                                 |
| b/\textdegree                                   | 33.3992(5)                                 |
| c/\textdegree                                   | 57.8561(11)                                |
| α/°                                           | 90                                         |
| β/°                                           | 95.577(2)                                  |
| γ/°                                           | 90                                         |
| Volume/\textdegree                            | 89460(2)                                   |
| Z                                             | 4                                          |
| \rho\textsubscript{calc} / cm\textsuperscript{3} | 2.240                                      |
| \mu / mm\textsuperscript{1}                  | 36.923                                     |
| F(000)                                        | 56072.0                                    |
| Crystal size/mm\textsuperscript{3}            | 0.15 \times 0.1 \times 0.08                |
| Radiation                                     | CuKα (λ = 1.54184)                         |
| 2Θ range for data collection/°                | 6.31 to 129.856                            |
| Index ranges                                  | -50 \leq h \leq 54, -37 \leq k \leq 38, -66 \leq l \leq 66 |
| Reflections collected                         | 158097                                     |
| Independent reflections                       | 74145 [R\textsubscript{int} = 0.0710, R\textsubscript{sigma} = 0.0952] |
| Data/restraints/parameters                    | 74145/4824/2969                            |
| Goodness-of-fit on F\textsuperscript{2}       | 1.060                                      |
| Final R indexes [I\geq2σ (I)]                 | R\textsubscript{1} = 0.1083, wR\textsubscript{2} = 0.3030 |
| Final R indexes [all data]                    | R\textsubscript{1} = 0.1667, wR\textsubscript{2} = 0.3990 |
| Largest diff. peak/hole / e Å\textsuperscript{3} | 5.60/-2.78                               |
Supplementary Table S2. A summary of average bond lengths of important bonds in plasmonic Ag\textsubscript{206} nanoparticle.

| Bond Length(Å) | Ag206 Bond Length(Å) |
|----------------|-----------------------|
| Ag-Ag(all)     | 2.996 (990)           |
| Ag-Ag(kernel)  | 2.873 (189)           |
| Ag(1)-Ag(1)   | 2.878 (42)            |
| Ag(1)-Ag(2)   | 2.857 (62)            |
| Ag(2)-Ag(2)   | 2.877 (64)            |
| Ag(2)-Ag(3)   | 2.879 (108)           |
| Ag(3)-Ag(3)   | 2.870 (192)           |
| Ag(3)-Ag(4)   | 2.926 (301)           |
| Ag(4)-Ag(4)   | 3.181 (805)           |
| Ag-S           | 2.531 (196)           |
| Ag-Cl          | 3.091 (273)           |
| Ag-F           | 2.536 (26)            |

Ag-Ag (all) bond length in the Ag\textsubscript{206} nanoparticle (longer-than-normal bonds (> 4.0 Å) elimination).
Ag-Ag (kernel) bond length in the Ag\textsubscript{116} kernel.
Ag(1)-Ag(1) bond length in the 1\textsuperscript{st} shell.
Ag(1)-Ag(2) bond length between the 1\textsuperscript{st} and 2\textsuperscript{nd} shell.
Ag(2)-Ag(2) bond length in the 2\textsuperscript{nd} shell.
Ag(2)-Ag(3) bond length between the 2\textsuperscript{nd} and 3\textsuperscript{rd} shell.
Ag(3)-Ag(3) bond length in the 3\textsuperscript{rd} shell.
Ag(3)-Ag(4) bond length between the 3\textsuperscript{rd} and 4\textsuperscript{th} shell.
Ag(4)-Ag(4) bond length in the 4\textsuperscript{th} shell (longer-than-normal bonds (> 4.0 Å) elimination).
Ag–S bond length between Ag and thiolate (longer-than-normal bonds (> 2.7 Å) elimination).
Ag–Cl bond length between Ag and chloride.
Ag–F bond length between Ag and fluoride (longer-than-normal bonds (> 2.7 Å) elimination).
All other data are from structures determined by single-crystal analysis.
Supplementary Figure 1. TEM images of as-prepared product of Ag$_{206}$ (1). The inset plot shows the size distribution of the nanoparticles observed by TEM.
Supplementary Figure 2. Structure dissection of the fivefold multiple-twinned kernel $\text{Ag}_{116}$ (a) of 1, consisting of five wedge-shaped units (b).
Supplementary Figure 3. The five-fold twinned boundary (111) faces in the Ag\textsubscript{116} core are not strictly planar. (a) The diagram showing the twisted twinning boundaries. (b) The boundary planes as viewed along the fivefold axis. It should be noted that even the atoms of the (J73)/2 cap (refs. S13) deviate little from these twinned boundary planes.
Supplementary Figure 4. The Ag-S, Ag-Cl and Ag-F bond lengths over 2.7 Å of Ag_{206} nanoparticle 1 at the two poles (a, b) and the equator (c). The longer-than-normal bonds were marked as dotted lines. Color codes: green, Ag; yellow sphere, S; red, Cl; and Pink, F.
Supplementary Figure 5. (a) Thermogravimetric analysis of Ag$_{206}$ nanoparticle. (b) Stability of Ag$_{206}$ solid under air condition monitoring by UV-Vis spectra.
Supplementary Figure 6. Predicted charging behavior of 1. The total energy as a function of charge for [Ag$_{206}$(SR)$_{70-x}$F$_x$Cl$_2$]$^{q-4 \leq q \leq 5+}$ from DFT computations (red circles), compared with a quadratic fit $E(q) = aq^2 + bq + c$ where $a = 0.576 \pm/\ 0.001$ eV/|e|, $b = 3.123 \pm/\ 0.002$ eV/|e|, and $c = 4.202 \pm/\ 0.007$ eV. The quadratic behavior is a manifestation of the metallic character of the nanoparticle. The first derivative of this fit gives a constant charging energy of about 1.15 eV/|e|. 
Supplementary Figure 7. Characterization of the metal core of nanoparticle (1) by polyhedral jellium calculations for a closed-shell 138 electron system. (a, b) projection of the density of electron states into spherical harmonics. (a) shows a zoom-in of the states close to the HOMO-LUMO gap at 138 electrons. Other major gaps at 92, 196, and 198 electrons are noted as well. (c) calculated optical absorption spectrum shows one strong plasmonic peak at 312 nm. The shift to the experimental plasmon peak of 1 measured at 464 nm (Figure 4a) is due to several factors, such as the simplicity of the jellium description taking into account only Ag(5s) electrons and neglecting screening of Ag(4d) electrons, and the missing effect of the ligand shell. (d) shows two views of the polyhedron used to construct the constant positive background. Pink spheres denote the positions of the outermost core shell Ag$_{90}$ in (1).
Supplementary 8. ESI-MS of 1 after ligand-exchange with tert-butylacetylene (TBA) to give \([\text{Ag}_{206}(\text{SR})_{65+y}\text{Cl}_{2-y}\text{TBA}_5]^{4+}\) and \([\text{Ag}_{206}(\text{SR})_{65+y}\text{Cl}_{2-y}\text{TBA}_5]^{4+}\), where \(x,y=0-2\) and \(\text{SR}=\text{cyclohexanethiolate}\).
Supplementary Figure 9. Raman spectra of 1 and 1 after ligand-exchange with tert-butylacetylene (TBA).
Supplementary Figure 10. TEM images of Ag$_{206}$ (1)/TiO$_2$ before (a) and (b) after reaction. Insets show the size distributions of the Ag nanoparticles before (a, inset) and after (b, inset) reaction.
Supplementary Figure 11. UV-Vis-spectra of Ag$_{206}$/TiO$_2$ before (black) and after reaction (red).
Supplementary Figure 12. Proposed catalytic cycle for indole syntheses from 2-ethynylaniline derivatives.
Supplementary Figure 13. ESI-MS of Ag\textsubscript{206} nanoparticle 1 and 1 plus 2a in CH\textsubscript{2}Cl\textsubscript{2} solutions. (a) Comparison of ESI-MS spectra before and after adding 2a in CH\textsubscript{2}Cl\textsubscript{2} solution of 1. (b) Enlarged +4 region is compared with a series of simulated [Ag\textsubscript{206}(SR)\textsubscript{67-x}Cl\textsubscript{2}F\textsubscript{3}(2a)_x]\textsuperscript{4+} (x=0-5) and [Ag\textsubscript{206}(SR)\textsubscript{68-x}F\textsubscript{4}(2a)_x]\textsuperscript{4+} (x=0-5).
Supplementary Figure 14. $^1$H NMR spectrum of 2a.
Supplementary Figure 15. $^1$H NMR spectrum of 1-tosyl-1H-indole (2b).
Supplementary Figure 16. $^{13}$C NMR spectrum of 1-tosyl-1H-indole (2b).
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