

Supporting Information

A Triflate and Alkynyl Protected Ag₄₃ Nanocluster with Passivated Surface

Ting Li,^a § Xiaoqin Cui,^b § Linfeng Liang,^b Cui Luo,^b Huan Li,^{b*} Xian-Ming Zhang,^{ab*}

^aSchool of Chemistry & Material Science, Shanxi Normal University, Linfen, 041000, China

^bInstitute of Crystalline Materials, Shanxi University, Taiyuan, 030006, China

§ These authors contributed equally to this work.

Corresponding authors: 59584340@sxu.edu.cn (H. Li) xmzhang@sxu.edu.cn (X.-M. Zhang)

Experimental section

1 Materials

Tert-butylacetylene ($t\text{BuC}\equiv\text{C}$, 98%) and 1,4-bis-(diphenylphosphino)butane(dppb, 97%) were purchased from Shanghai Macklin Biochemical Co., Ltd (China), silver trifluoromethanesulfonate (AgOTf, 99.8%) and sodium borohydride (NaBH_4 , 98%) were from Energy Chemical (Shanghai, China). All chemicals and solvents were used as received.

2 Instruments

FT-IR spectra were collected on Nicolet iS5 with samples prepared as KBr pellets.

UV-Vis absorption was tested on a domestic spectrophotometer with samples being dispersed in CH_2Cl_2 .

Emission spectra were measured on an Edinburgh FLS-920 equipment in solution at room temperature.

X-ray Crystallography. Data collection for $\text{Ag}_{43}(t\text{BuC}\equiv\text{C})_{24}(\text{CF}_3\text{SO}_3)_8$ was carried on an Agilent Technologies SuperNova Single Crystal Diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 150 K. Absorption corrections were applied by using the program CrysAlis (multi-scan).¹ The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 within OLEX2.²

3 Synthesis of $\text{Ag}_{43}(t\text{BuC}\equiv\text{C})_{24}(\text{CF}_3\text{SO}_3)_8$ (Ag_{43})

Silver trifluoromethanesulfonate (51 mg, 0.2 mmol) was dissolved in ethanol (2 mL), then a CH_2Cl_2 solution (2 mL) containing dppb (1,3-bis(diphenylphosphino)butane, 26 mg, 0.1 mmol) and *tert*-butylacetylene (14 μL , 0.1 mmol) was added under vigorous stirring. A freshly prepared solution of NaBH_4 (0.1 mmol in 1 mL of ethanol) was added dropwise after 35 μL triethylamine was introduced. Upon reduction, the solution changed from colorless to light yellow. The reaction was then aged for 12 hours at ambient conditions, during which the color turned dark green. The mixture was evaporated to dryness to give a dark solid, which was dissolved in CH_2Cl_2 (2 mL) again. The solution was centrifuged for 5 min at 12000 r/min. The supernatant solution was subject to the diffusion with *n*-hexane and diethyl ether (volume ratio, 1:1) to afford black green block crystals after one week.

Characterization

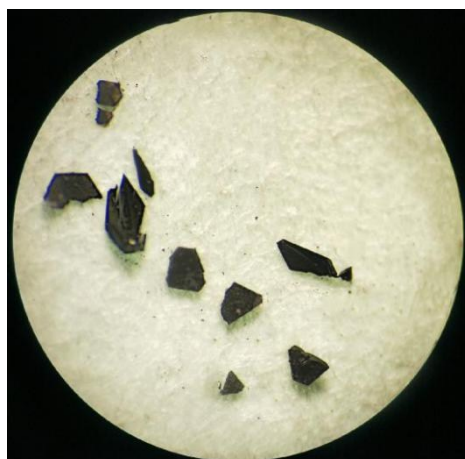


Figure S1. An image of Ag₄₃ crystals (black block) under an optical microscope.

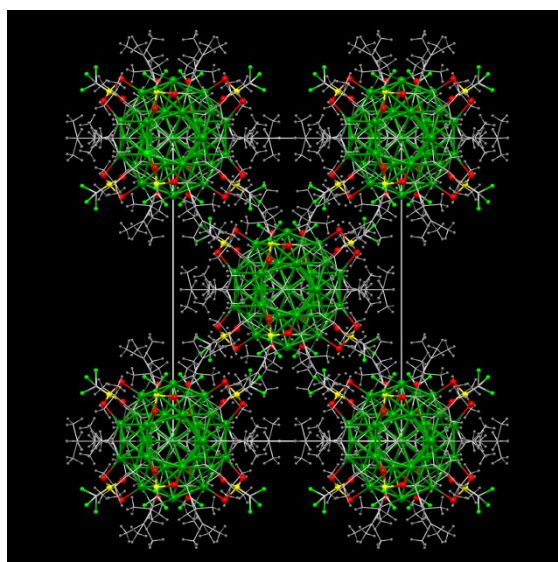


Figure S2. Packing of Ag₄₃ in a unit cell. Color legend: Ag, dark green; S, yellow; O, red; F, light green; C, gray.

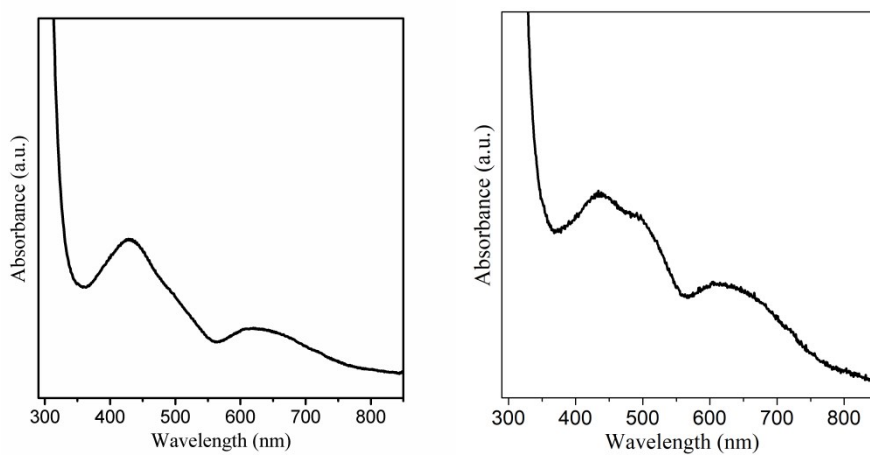


Figure S3. The UV-Vis absorption of Ag₄₃ before (left) and after (right) catalyzing the reaction of silane with H₂O.

Table 1. Crystal data and structure refinement for Ag₄₃.

Identification code	Ag ₄₃ (^t BuC≡C) ₂₄ (CF ₃ SO ₃) ₈
Empirical formula	C ₁₅₄ H ₂₁₀ Ag ₄₃ F ₂₄ O ₂₄ S ₈
Formula weight	7796.10
Temperature/K	150
Crystal system	monoclinic
Space group	I2/m
a/Å	19.8306(5)
b/Å	27.6106(10)
c/Å	20.8093(9)
α /°	90
β /°	91.117(3)
γ /°	90
Volume/Å ³	11391.7(7)
Z	2
ρ calcd/cm ³	2.273
μ /mm ⁻¹	30.120
F(000)	7382.0
Crystal size/mm ³	0.25 × 0.25 × 0.25
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.5 to 159.84
Index ranges	-13 ≤ h ≤ 25, -17 ≤ k ≤ 34, -26 ≤ l ≤ 23
Reflections collected	32054
Independent reflections	12003 [Rint = 0.0503, Rsigma = 0.0504]
Data/restraints/parameters	12003/1015/650
Goodness-of-fit on F ²	1.514
Final R indexes [I > 2σ (I)]	R1 = 0.1238, wR2 = 0.3962
Final R indexes [all data]	R1 = 0.1498, wR2 = 0.4187
Largest diff. peak/hole / e Å ⁻³	2.08/-1.87

References

- 1 CrysAlisPro Version 1.171.35.19. 2011. Agilent Technologies Inc. Santa Clara, CA, USA.
- 2 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J Appl. Crystallogr. 2009, 42, 339.