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Supporting information for

High-yield synthesis and crystal structure of a green Au_{30} cluster co-capped by thiolate and sulfide

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Experimental Details

Reagents: *tert*-butylthiol (*t*BuSH, 98%) was purchased from Alfa Aesar. (Tianjin, China), Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$, 99.9%), Sodium sulfide ($Na_2S \cdot 9H_2O$, 98%), Sodium borohydride ($NaBH_4$, 98%), Triethylamine ($C_6H_{15}N$, 99.5%), toluene (C_7H_8, A.R.) and tetrahydrofuran (C_4H_8O, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The water used in all experiments was ultrapure. All reagents were used as received without further purification.

Synthesis of $Au_{30}S(StBu)_{18}$: For a typical synthesis of $Au_{30}S(StBu)_{18}$, 10 mg $HAuCl_4 \cdot 4H_2O$ and 5.5 μL *tert*-butylthiol (molar ratio $HAuCl_4$:HS*t*Bu = 1:3) were mixed in 3 ml tetrahydrofuran. The mixed solution was kept stirring for 15 minutes at 55 ℃. 1 mL NaBH4 aqueous solution (9 mg/mL) ($HAuCl_4$:$NaBH_4$ = 1:10) and 0.12 mg Na2S ($HAuCl_4$:Na_2S = 50:1) were then added quickly to the above mixture under vigorous stirring. The color of the solution changed from yellow to brown immediately. The reaction was aged for 1 hour at 55 ℃. After the aqueous layer was removed, 2 mL toluene and 1 mL *tert*-butylthiol were added to to the organic phase. The mixed solution was heated to 60 ℃ and the color of the solution became dark green after 6-h aging. Brown sheet-like crystals were crystallized from CH_2Cl_2/hexane at 4 ℃ after 10 days.

Brown sheet-like single crystals of $Au_{30}S(StBu)_{18}$ were recrystallized by diffusing hexane into the cluster solution in CH_2Cl_2 at 4 °C over 15 days. The crystals were readily redissolved in toluene to give a green solution.

Single Crystal Analysis: The diffraction data of $Au_{30}S(StBu)_{18}$ were collected on an Agilent Technologies SuperNova system. X-ray single crystal diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100 K. The data were processed using CrysAlis^{Pro}.[S1] The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97[S2] within Olex2.[S3]

Single Crystal Analysis of $Au_{30}S(StBu)_{18}$: black rodlike crystal, 0.25×0.15×0.03 mm, space group *P*-1 a = 14.7299(4) Å, b = 21.2699(5) Å, c = 25.8105(5) Å, α = 111.285(2) º, β = 92.8643(17) º, γ = 93.898(2) º, V = 93.898(2) Å^3, Z = 2, Cu Kα, T = 100 K, $2\theta_{max}$=147.148 °. 29269 reflections were measured, of which 21922 were unique with R_{int} = 0.0599 Final R_1=9.21%, wR_2= 0.1025 for 719 parameters and 19357 reflections with $I > 2\sigma(I)$.

References:

S1. CrysAlis^{Pro} Version 1.171.35.19. (2011). Agilent Technologies Inc. Santa Clara, CA, USA.

S2. Sheldrick, G. M. (2008). A short history of SHELX. *Acta Cryst*. **A64**, 112-122.

S3. Dolomanov et al. (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*. **42**, 339-341.

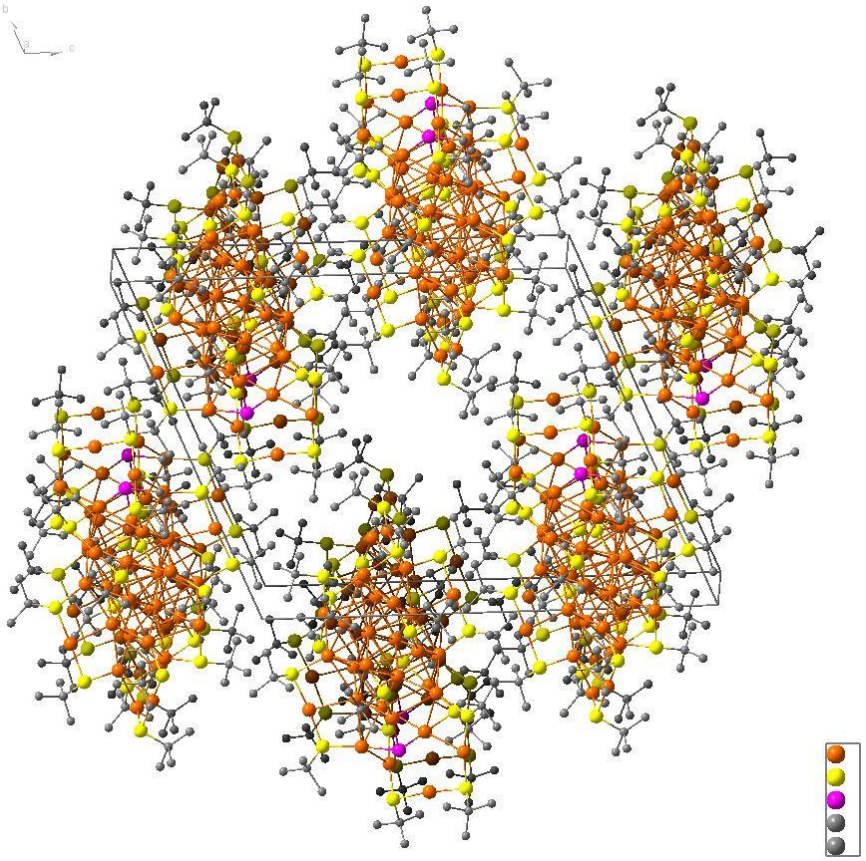

Figure S1 The packing structure of $Au_{30}S(StBu)_{18}$ clusters.

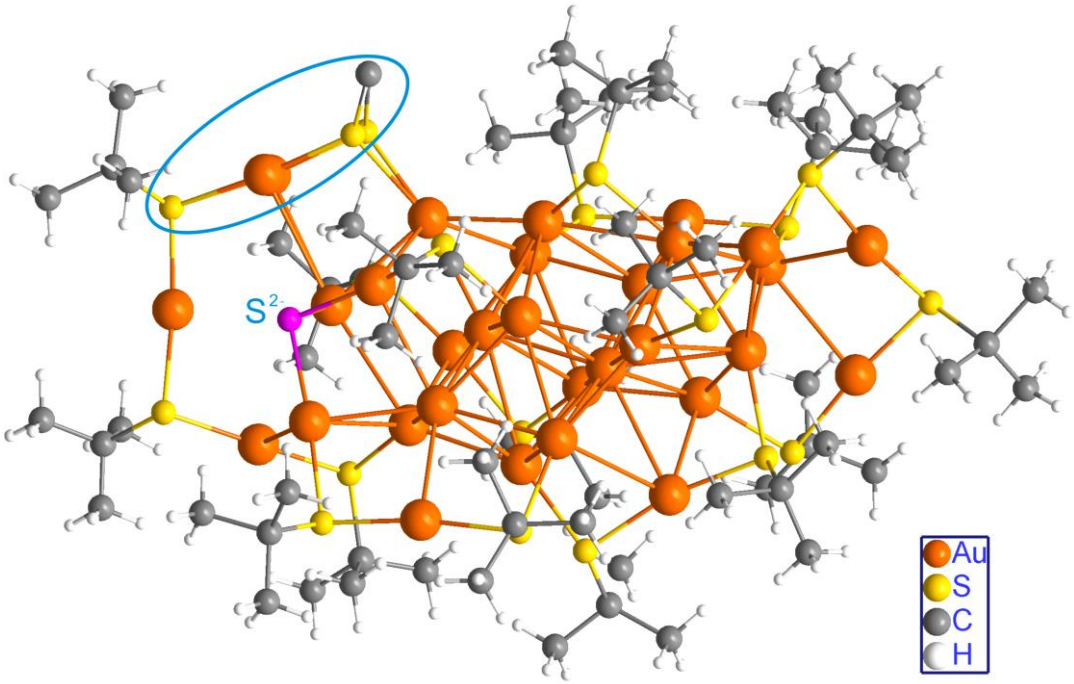

Figure S2 The molecular structure of $Au_{30}S(S\mathit{t}Bu)_{18}$ from X-ray diffraction analysis. The disordered parts are highlighted.

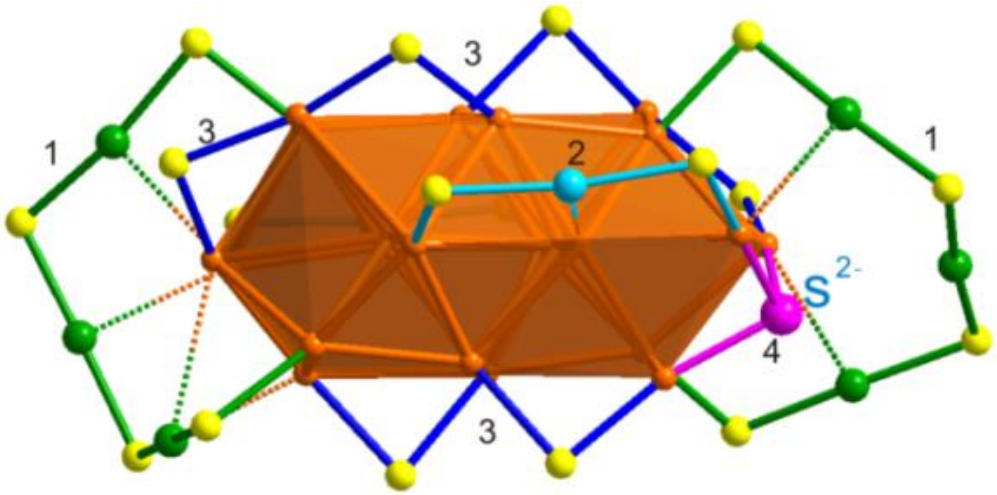

Figure S3 The surface structure profile of $Au_{30}S(StBu)_{18}$. The $Au_3(SR)_4$, $Au(SR)_2$ units, bridging SR, and μ_3-S^{2-} are highlighted with bonds in green, cyan, blue and pink, respectively.

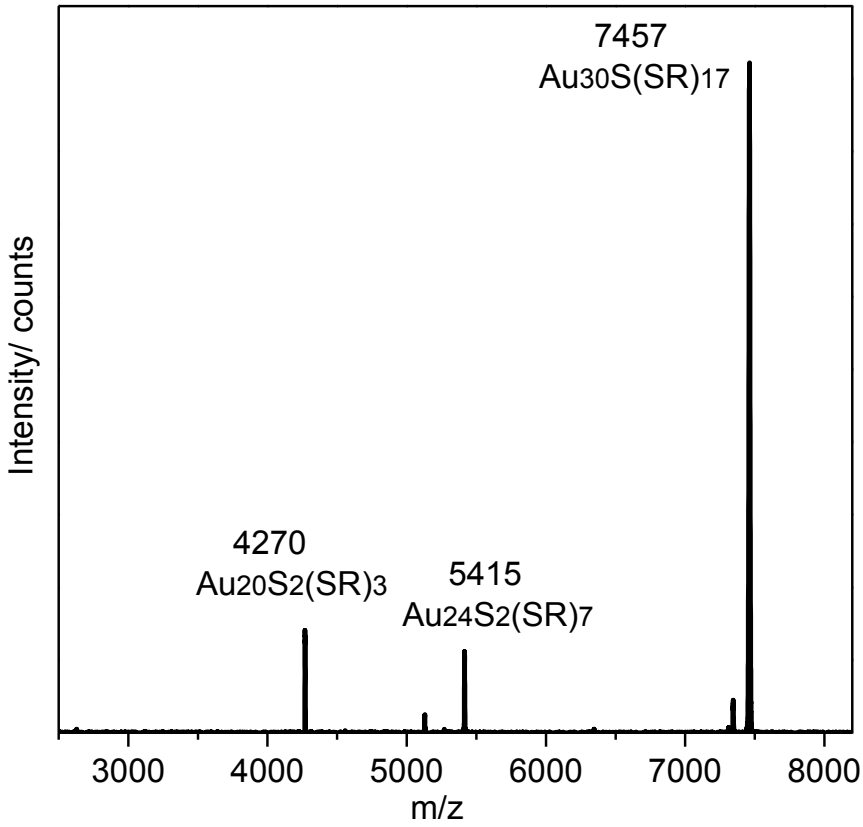

Figure S4 The MALDI–TOF spectrum of the crude product without any purification.

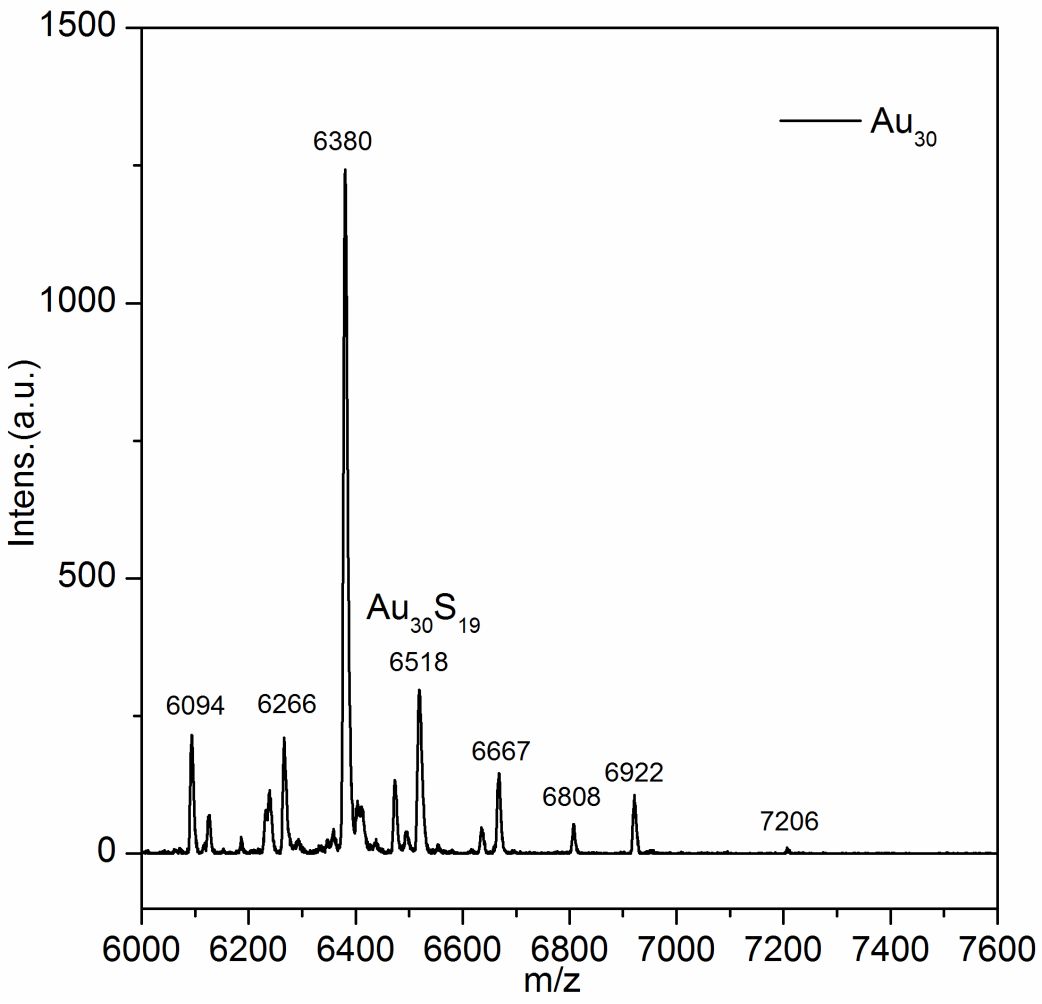

Figure S5 The MALDI mass spectrum of the pure of $Au_{30}S(StBu)_{18}$ obtained with high laser intensity.