

## Supporting Information

### The one/two atom size-reduction of $[\text{Au}_{23}\text{SCy}_{16}]^-$ induced by

### $[\text{Au}_6(\text{dppp})_4]^{2+}$ cluster

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# Content

1. Experimental .....	S1
1.1 Synthesis of $[\text{Au}_{23}\text{SCy}_{16}]^{-}[\text{TOA}]^{+}$ .....	S1
1.2 Synthesis of $[\text{Au}_6(\text{dppp})_4]^{2+}\text{Cl}_2$ .....	S1
1.3 Reaction of $[\text{Au}_{23}\text{SCy}_{16}]^{-}[\text{TOA}]^{+}$ with $[\text{Au}_6(\text{dppp})_4]^{2+}\text{Cl}_2$ .....	S1
2. DFT Calculations .....	S1
3. Supporting Figures .....	S2
4. References .....	S4

## 1. Experimental

### 1.1 Synthesis of $[\text{Au}_{23}\text{SCy}_{16}]^{-}[\text{TOA}]^{+}$

Typically, 600  $\mu\text{L}$  of  $\text{HAuCl}_4$  (0.5 M in water) and 190 mg TOAB was mixed in 15 mL of MeOH. After stirring for 15 min, 196  $\mu\text{L}$  cyclohexanethiol (HSCy) was added and further stirred for another 15 min. Then, 114 mg of  $\text{NaBH}_4$  dissolved in 6 mL of cold water was added. The reaction was allowed to further stirring overnight. The raw product was concentrated with rotary evaporation and washed with methanol for one time and n-hexane for three times. The pure  $[\text{Au}_{23}\text{SCy}_{16}]^{-}[\text{TOA}]^{+}$  can be obtained by recrystallization using DCM/n-hexane.

### 1.2 Synthesis of $[\text{Au}_6(\text{dppp})_4]^{2+}\text{Cl}_2$

78.4 mg  $[\text{Au}_2(\text{dppp})\text{Cl}_2]$  was well dispersed in 15 mL ethanol and stirred for 15 min. 6 mg  $\text{NaBH}_4$  was dissolved in an alcoholic solvent and was quickly added to the above solution, with an immediate change of the solution color into brown. The reaction was finished after 30 min (determined by UV-vis spectroscopy). The product, i.e.  $[\text{Au}_6(\text{dppp})_4]^{2+}$ , was washed with hexane 4 times and further purified using a mixed solvent of ethanol and hexane (with volume ratio of 3:25).

### 1.3 Reaction of $[\text{Au}_{23}\text{SCy}_{16}]^{-}[\text{TOA}]^{+}$ with $[\text{Au}_6(\text{dppp})_4]^{2+}\text{Cl}_2$

20 mg  $[\text{Au}_{23}\text{SCy}_{16}]^{-}[\text{TOA}]^{+}$  was dissolved in 15 mL of DCM, and then 8.3 mg of  $[\text{Au}_6(\text{dppp})_4]^{2+}\text{Cl}_2$  was added. Stirring for about 3 hours, the solution color changes from brownish black to crimson black. The reaction mixture was washed with little DCM and excess n-hexane. The crude product was then concentrated and purified by first PTLC with DCM/Hex (1:2) and the second time with DCM/MeOH (10:1).

## 2. DFT Calculations

Density functional theory (DFT) were employed in the Dmol<sup>3</sup> package to calculate dissociation energy of 16 different position bonds of  $[\text{Au}_{23}(\text{SCy})_{16}]^{-}$  cluster.<sup>1, 2</sup> A constrained structural optimization (by fixing Au-S bond distance at 3.5 Å) is used to evaluate the bond dissociation energy.<sup>3</sup> The generalized gradient approximation with the Perdew-Burke-Ernzerhof functional and d-polarization-double basis set (DND).<sup>4, 5</sup> Solution phase single-point energy calculations were conducted at the same level of theory, with dichloromethane as the solvent. The convergence criterion of the geometrical optimization was set as  $2 \times 10^{-5}$  Hartree energy change,  $4 \times 10^{-3}$  Hartree/Å for the gradient, and  $5 \times 10^{-3}$  Å for the displacement, respectively.

### 3. Supporting Figures

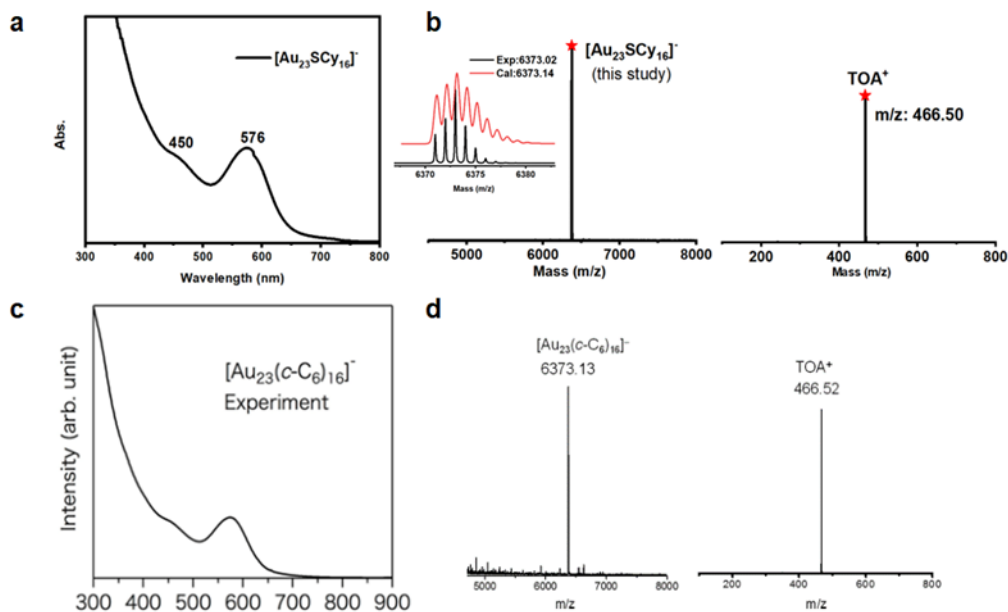


Fig. S1 Comparison of the UV-vis and ESI-MS of the prepared  $\text{Au}_{23}$  precursors in this study (a, b) with the previously reported one (c, d. reproduced from *J. Am. Chem. Soc.* 2013, 135, 18264–1826).

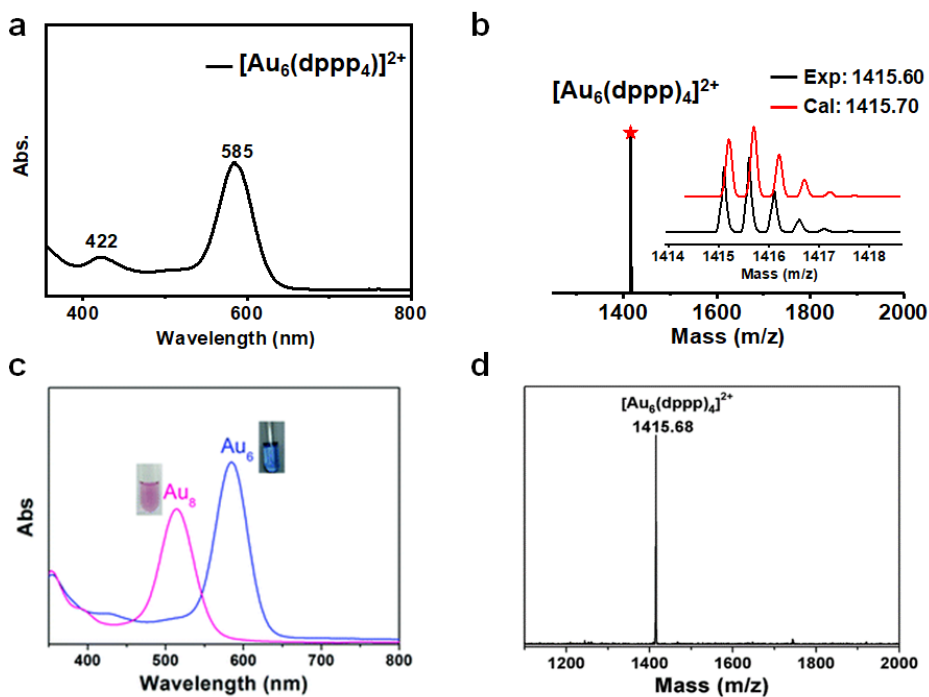
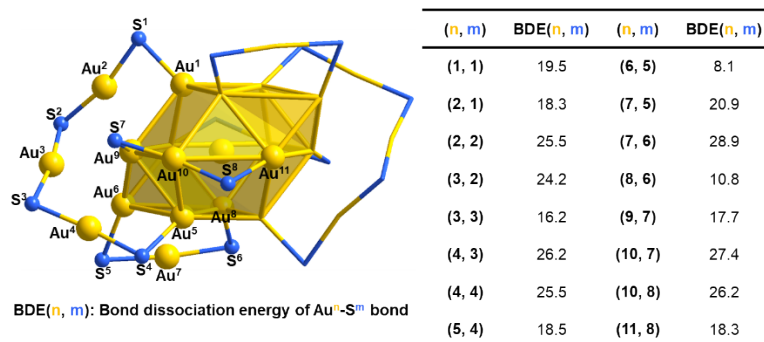
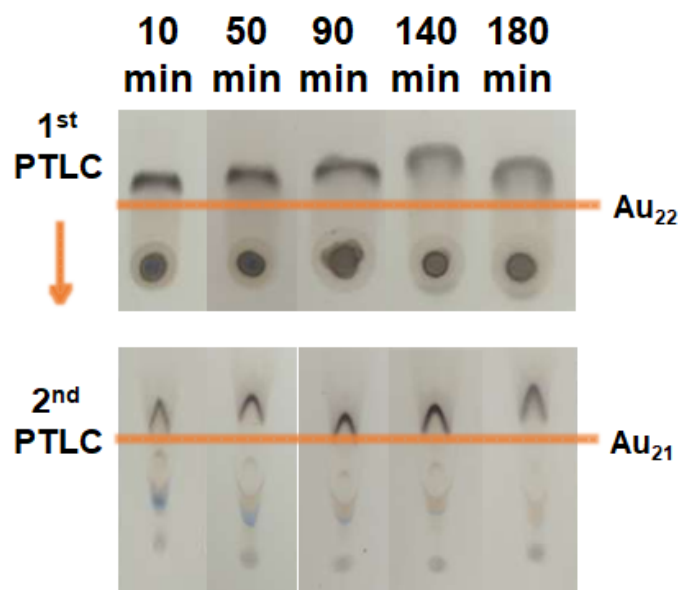


Fig.S2 Comparison of the UV-vis and ESI-MS of the prepared  $\text{Au}_6$  precursors in this study (a,b) with the previously reported one(c,d. reproduced from *Nanoscale*,2017,9,2424–2427). Of note, the

pink and blue line correspond to the UV-Vis of  $[\text{Au}_8(\text{dppp})_4\text{Cl}_2]^{2+}$  and  $[\text{Au}_6(\text{dppp})_4]^{2+}$  (the same as the precursor in our study), respectively.



**Fig. S3** The Au-S bond dissociation energy of  $[\text{Au}_{23}(\text{SCy})_{16}]^-$  clusters calculated with DFT. calculations.



**Fig. S4** The first and second PTLC monitoring at different time during the 1:1 reaction of  $[\text{Au}_{23}(\text{SCy})_{16}]^-$  and  $[\text{Au}_6(\text{dppp})_4]^{2+}$ .

#### 4. References

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