Supporting Information for

Comparison of chiral counterion, solvent, and ligand in inducing chiroptical response from Au$_{25}^-$ nanoclusters

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Experimental Details

1. Synthesis of (R)- and (S)-2-phenylpropane-1-thiol.

The synthetic routine is illustrated below:

a: (D/L)-phenylalanine (40g, 0.297mol) was dissolved in THF in N$_2$ atmosphere. The solution was cooled to 0°C, and then lithium aluminium hydride powder (14g, 0.371mol) was added in portion. This solution was stirred for 2h at 0°C, before the reaction was quenched by water adding dropwise. After drying under vacuum, the residue was extracted with dichloromethane and washed by water. The dichloromethane layer was evaporated to obtain (R/S)-2-amino-3-phenylpropan-1-ol as yellow oil. At last the product as purified by recrystallization. $^1$H NMR (CDCl$_3$/TMS): δ 1.42 (s, H), 2.4~2.8 (2H, mm), 3.3~3.7 (2H, mm), 3.11 (1H, m), 7.1~7.3 (5H, m). $^{13}$C NMR(400MHz, CDCl$_3$, ppm): δ 138.68, 129.20, 128.58, 126.41, 66.14, 54.20, 40.74.
b. (R/S)-2-amino-3-phenylpropan-1-ol (15.2g, 0.1mol) was dissolved in 1, 4-dioxane and water (v/v=1:1), then (Boc)_2O (24.0g,0.110mol) and NaOH (5.0g,0.125mol) were added slowly at the same time under 0°C. 2 h later, the mixture was kept stirring at room temperature over night. The product was extracted with dichloromethane and washed by water. The dichloromethane solution was dried by evaporation, and the crude material was purified by
recrystallization in dichloromethane and petroleum ether. $^1$H NMR (400MHz, CDCl$_3$, ppm): δ 1.41(9H, s), 1.96(2H, d), 3.5-3.6(2H, dd), 3.87(1H, d), 7.2-7.3(5H, d).

c. A mixture of (S/R)-tert-butyl-1-hydroxy-3-phenylpropan-2-ylcarbamate (5.0 g, 20 mmol), triethylamine (6mL, 40 mmol) and tetrahydrofuran (100 mL) was stirred together at 0°C, then methylsulfonfyl chloride (2.0 mL, 25mmol) was added dropwise. After stirring for 2 h, the solution was extracted by DCM (50ml×3) and washed by water. The organic phase was combined and dried by Na$_2$SO$_4$ then evaporated to give crude product. Then the crude
material was purified by recrystallization in dichloromethane and petroleum ether. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 1.42\) (9H, s), 2.8-2.9(2H, m), 2.91(3H, s), 4.2-4.3(2H, m), 7.2-7.4(5H, m).

d. A solution of (S)-2-(tert-butoxycarbonylamino)-3-phenylpropyl methanesulfonate (4.4 g, 13.4 mmol) and potassium thioacetate (1.8 g, 15.8 mmol) dissolved in 30 mL DMF was stirred at room temperature over 3 d. Then 50 mL cool water was added and the mixture was extracted by DCM. The organic phase was combined and dried by Na2SO\(_4\) then evaporated to give crude product. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta 1.40\) (9H, s), 2.35 (3H, s), 2.8-3.1 (4H, m), 3.98 (H, m), 7.16-7.3 (5H, m).
e. Ammonia (2.0 g) was dissolved in anhydrous ethanol under 0°C. And then (S)-S-2-(tert-butoxycarbonylamino)-3-phenylpropyl ethanethioate (2.0 g, 6.5 mmol) was added into the solution. Then the mixture was stirred at room temperature before TLC shows no raw material exists. Target product was attained by evaporating the solution to dryness. $^1$H NMR (400MHz, CDCl$_3$, ppm): $\delta$ 1.34(H, t), 1.42(9H, s), 2.58-2.68(2H, m), 2.8-2.9(2H, m), 4.0(H, m), 7.1-7.3(5H, m).
f. A mixture of (S)-tert-butyl 1-mercapto-3-phenylpropan-2-ylcarbamate (1.5 g, 5.6 mmol) dissolved in dichloromethane and concentrated hydrochloric acid (3 mL) was stirred at room temperature for 5h. The mixture was evaporated to give crude residue. The impurity was dissolved in dichloromethane and the solid was the target product. $^1$H NMR (400MHz, D$_2$O, ppm): δ 2.6-3.0(4H, m), 3.66(H, m), 7.2-7.4(5H, m).
2. Spectroscopic characterization of products

Fig. S1 \( ^1H \) NMR spectrum of DMEB and \([\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^{-}\) DME\(^+\) in CDCl\(_3\).

Fig. S2 Thermogravimetric analysis of \([\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^{-}\) DME\(^+\) cluster

Fig. S3 \( ^1H \) NMR spectra of \(\text{Au}_{25}(\text{appt})_{18}\)
**Fig. S4** Thermogravimetric analysis of $\text{Au}_{25}^{(\text{appt})_{18}}$ nanoclusters.

**Fig. S5** The Negative-ion MALDI-TOF spectra of (R)-$\text{Au}_{25}$ and (S)-$\text{Au}_{25}$ clusters.