Supporting Information:

Chiral Au_{25} Nanopheres and Nanorods: Synthesis and Insight into the Origin of Chirality

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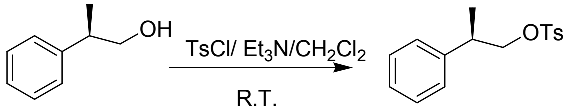
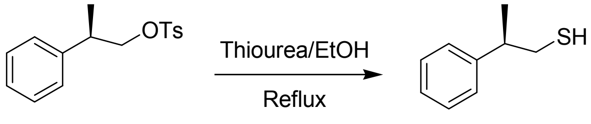
1. Experimental

Chemicals (R)-2-phenylpropane-1-thiol and (S)-2-phenylpropane-1-thiol (denoted pet*) were synthesized according to literature. Tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, >99.99% metals basis, Aldrich), Tetraoctylammonium bromide (TOAB, ≥98%, Fluka), Sodium borohydride (99.99% metals basis, Aldrich). Solvents: Toluene (HPLC grade, ≥99.9%, Aldrich), Ethanol (absolute, 200 proof, Pharmco), Methylene chloride (HPLC grade, ≥99.9%, Aldrich), Acetonitrile (HPLC grade, ≥99.9%, Aldrich). All chemicals were used as received. Nanopure water (resistance 18.2 MΩ·cm) was purified with a Barnstead NANOpure DIwater™ system. All glassware was thoroughly cleaned with aqua regia (HCl: HNO_3=3:1 vol %), rinsed with copious Nanopure water, and then dried in an oven prior to use.

Synthesis of (R)- and (S)-2-phenylpropane-1-thiol. The synthesis comprises two main steps. The first step is shown in the reaction below.

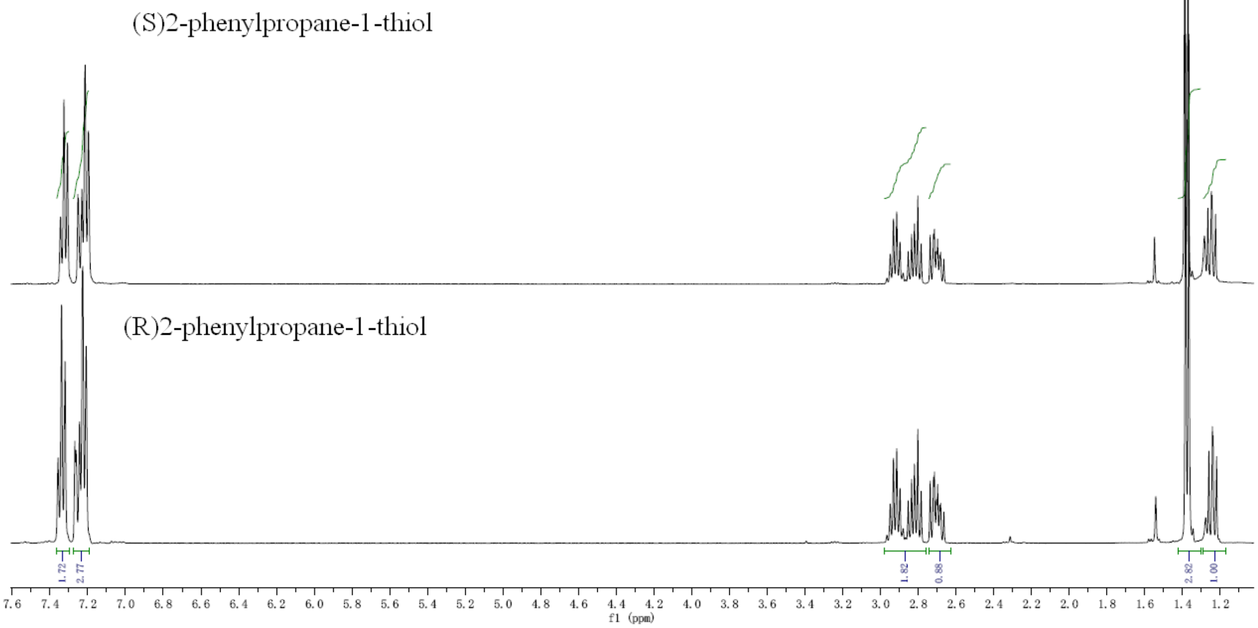


(R)-2-phenylpropane-1-ol (3.5 g) and 4-methylbenzene-1-sulfonyl chloride (5.3 g) were dissolved in CH_2Cl_2 (20 mL), the mixture was stirred at r.t. Triethylamine (6.5 g) was slowly added. Then the stirring was continued for 12 hours. White solid formed was filtered, and the filter was washed with water, and dried over Na_2SO_4. Solvent was removed under reduced pressure to give a pale yellow solid. After recrystalization from EtOAc/petroleum, 6.2 g white solid was obtained (yield: 82%). ^{1}H-NMR ($CDCl_3$, ppm): δ1.31 (d, 3H), 2.45 (s, 3H), 3.12 (m, 1H), 4.07 (m, 2H), 7.13 (d, 2H), 7.13~7.30 (m, 5H), 7.69 (d, 2H).

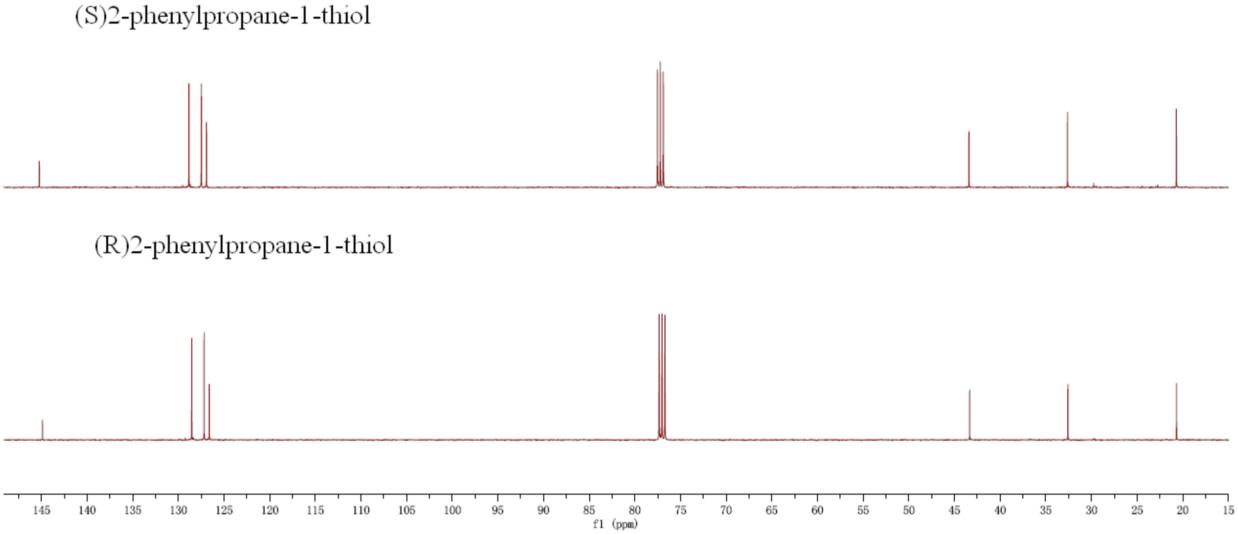


For the second step (see reaction above), (R)-2-phenylpropyl-4-methylbenzensulfonate (2.0 g) and thiourea (0.53 g) was dissolved in 10 mL EtOH, then the mixture was refluxed for 72 hours. Then 7mL, 20% NaOH was added, and the reaction was continued for 1 hour. After the reaction, the mixture was acidified by 10% HCl. The mixture was extracted by petroleum and dried over Na_2SO_4. Solvent was removed under reduced pressure. The product was purified by distillation (75~76 °C/0.1mmHg). NMR spectra are attached below. ^{1}H-NMR ($CDCl_3$, ppm): δ1.22 (t, 1H), 1.56 (d, 3H), 2.68~2.93 (m, 3H), 7.22~7.26 (m, 3H), 7.32~7.37 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm): 20.68, 32.58, 43.34, 126.61, 127.17, 128.53, 144.87. (S)-2-phenylpropane-1-thiol was synthesized by the same method using (S)-2-phenylpropane-1-ol as the starting material. ^{1}H-NMR ($CDCl_3$, ppm): δ1.24 (t, 1H), 1.30 (d, 3H), 2.68~2.93 (m, 3H), 7.23~7.28 (m, 3H), 7.34~7.37 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm): 20.68, 32.58, 43.34, 126.62, 127.18, 128.53, 144.88.

A) 1H-NMR spectra



B) 13C NMR spectra:



Synthesis of chiral thiol protected $Au_{25}(SR)_{18}$ nanospheres. $HAuCl_4 \cdot 3H_2O$ (0.1612 g, 0.41 mmol) was dissolved in 5 mL Nanopure water, and tetraoctylammoniun bromide (TOAB, 0.2596 g, 0.47 mmol) was dissolved in 10 mL toluene. The two solutions were combined in a 25 mL tri-neck round bottom flask. The solution was vigorously stirred (~1100 rpm) with a magnetic stir bar to facilitate phase transfer of Au (III) salt into the toluene phase. After ~15 min, phase transfer was completed, leaving a clear aqueous phase at the bottom of the flask; the aqueous was then removed using a 10 mL syringe. The toluene solution of Au (III) was purged with N_2 and cooled down to 0 °C in an ice bath over a period of 30 min under magnetic stirring. After stirring was reduced to a very low speed (~50 rpm), (R)-2-phenylpropane-1-thiol (0.17 mL, ~3 equivalents of the moles of gold) was added. The solution was kept stirring after thiol addition, during which the solution color slowly changed from deep red to faint yellow, then gradually phased out and eventually became clear over a ~1 h period. After the solution turned clear, the stirring speed was increased to ~1100 rpm. 10 mL of aqueous solution of $NaBH_4$ (0.1561 g, 4 mmol, 10 equivalents per mole of gold, freshly made in 10 mL ice-cold Nanopure water) was rapidly added to the solution all at once. After $NaBH_4$ addition, the reaction was allowed to further proceed for ~40 hr under N_2 atmosphere.

Post-synthetic treatment: The reaction mixture was washed three times with 60 mL nanopure water. The organic phase was removed by rotary evaporation at room temperature. Methanol (~50 mL) was added to the solution to precipitate the Au nanoparticles. The turbid solution was allowed to stand on bench overnight. The precipitate was collected. Very pure Au_{25} nanoclusters protected by (R)-2-phenylpropane-1-thiol were obtained by extraction of the nearly dried solids with CH_3CN. After evaporation of solvent under reduced pressure, methanol was added to the reaction product to precipitate gold nanoclusters.

The Au_{25} nanoparticles protected by (S)-2-phenylpropane-1-thiol or racemic 2-phenylpropane-1-thiol were synthesized using the same method.

Synthesis of chiral Au_{25} rods. Briefly, polydisperse Au nanoparticles (1-3 nm) were first prepared from the modified Brust−Schiffrin method. To do that, $HAuCl_4 \cdot 3H_2O$ (0.118 g, 0.3 mmol) was dissolved in 5 ml Nanopure H_2O, and tetraoctylammonium bromide (TOAB, 0.190 g, 0.348 mmol) was dissolved in 10 ml toluene. The two solutions were combined in a tri-neck flask, and the mixture was vigorously stirred for ~15 min to effect phase transfer of gold salt into the toluene phase via the formation of charge neutral compounds, $TOA^+[AuCl_{4-x}Br_x]^-$; the clear aqueous phase was then removed. Triphenylphosphine (PPh_3, 0.235 g, 0.9 mmol) was added to the toluene solution under vigorous stirring. The solution immediately became whitish cloudy. Then, an aqueous $NaBH_4$ solution (0.034 g, 0.9 mmol, dissolved in 5 ml ethanol) was rapidly added all at once to the toluene solution. The solution immediately turned dark. The reaction was allowed to proceed for two hours at room temperature. Following rotary evaporation of toluene, a black product was obtained. The black product was washed several times with hexane to remove excess PPh_3 and TOAB. Then, the black product was dissolved in chloroform, and unreacted gold(I) salt was removed by precipitating the nanoparticles by adding pentane to the chloroform solution. The as-obtained product (~100 mg) comprises polydisperse Au nanoparticles.

In the second step, the conversion of polydisperse gold nanoparticles to atomically monodisperse Au_{25} rod clusters was carried out by adding (S)-2-phenylpropane-1-thiol or (R)-2-phenylpropane-1-thiol to the starting nanoparticles dissolved in CH_2Cl_2. In a typical experiment, polydisperse Au nanoparticles obtained in the first step were dissolved in 20 ml CH_2Cl_2; thiol was then added to the solution with a molar ratio of thiol/Au = 6:1. The solution was vigorously stirred at room temperature for ~2 days. Over the reaction period, one observes the solution color from initial dark red to final dark green. The final product was collected after rotary evaporation of solvent (CH_2Cl_2), followed by washing with hexanes and subsequent washing with hexane/cholorform 1:1. The monodisperse Au_{25} nanorods were extracted from the precipitates with ethanol.

Characterization All UV-Vis absorption spectra of Au MPCs in either toluene or methylene chloride were recorded using a Hewlett-Packard (HP) 8453 diode array spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyzer (TG/DAT 6300, Seiko instruments, Inc.) with 2-3 mg of MPCs in a SiO_2 pan at a heating rate of 10°C /min. MALDI mass spectra were recorded in negative/positive ion mode on an Applied Biosystems Voyager DE-STR MALDI-TOF. Other parameters are: acceleration voltage: 25 kV, delay time: 350 ns, and a nitrogen laser (337 nm) was used in the linear mode. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) were used as MALDI matrix. ^{1}H-NMR spectra were collected with Bruker Avance 300 MHz, and chloroform-*d* was used as solvent. CD spectra were measured with CD Jasco J-715 Spectropolarimeter.

2. Supporting Figures:

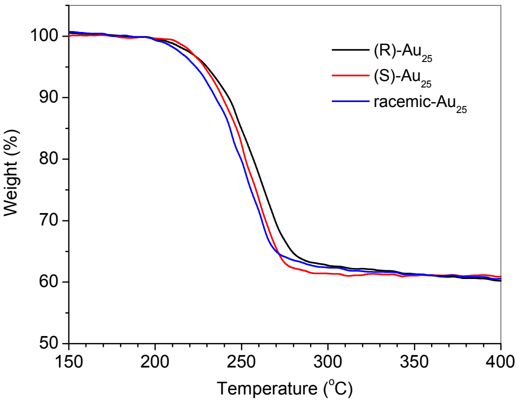


Figure S1. The TGA profiles of the *R*-, *S*- and racemic pet*-protected Au_{25} nanoparticles.

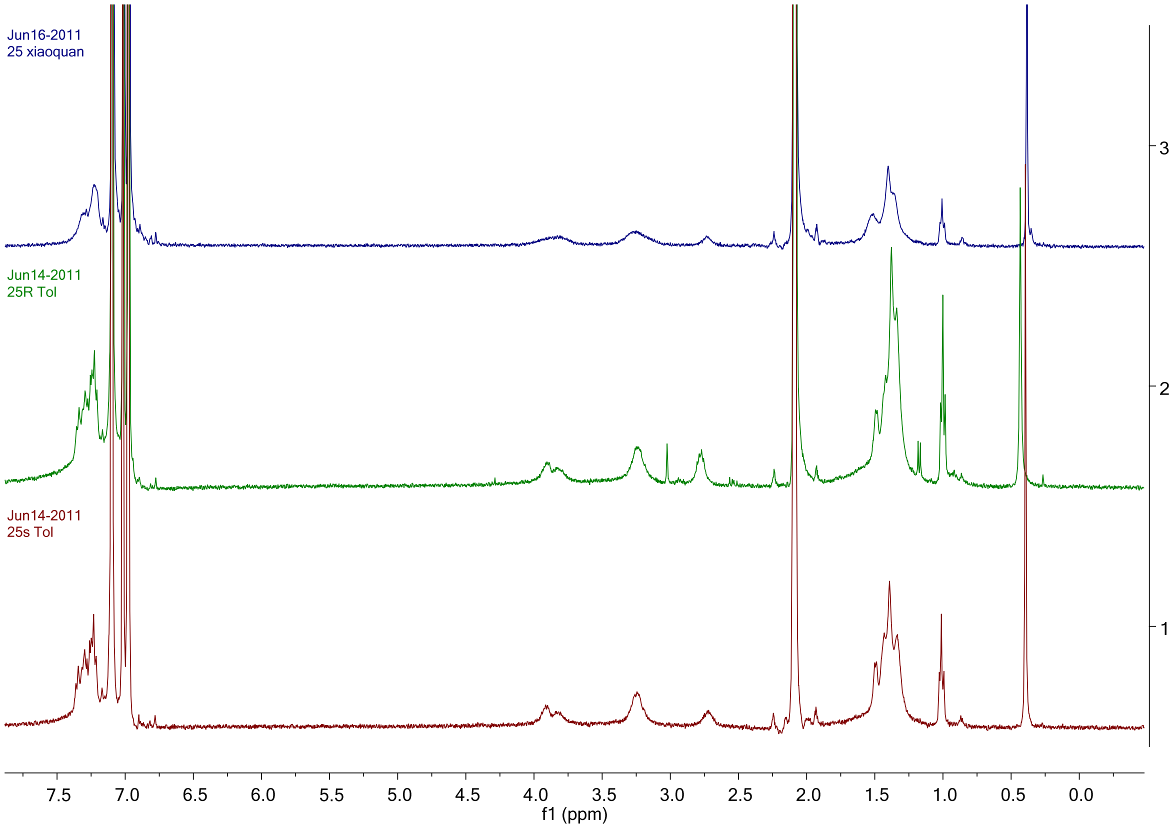


Figure S2. ^{1}H-NMR spectra of the *R*- and *S*-Au_{25} nanoparticles. The multiplet at~ 7 ppm is from the phenyl rings (90H). The triplet at ~ 0.9 ppm is from four CH_3 groups of TOA^+ (12H). The broad signal at 2-4 ppm is assigned to CH_2 and CH of 2-phenylpropane-1-thiol. The multiplet at 1-2 ppm is from mixed CH_2 of TOA (i.e., $(CH_2)_6\times4$) and CH_3 of 2-phenylpropane-1-thiol (i.e., $CH_3\times18$). The signal at 3.6 ppm is assigned to be NCH_2 of TOA ($CH_2\times4$). Note that the CH_2 and CH proton signals of 2-phenylpropane-1-thiol are broadened compared with free ligands, which is due to their spatial proximity to the gold core.

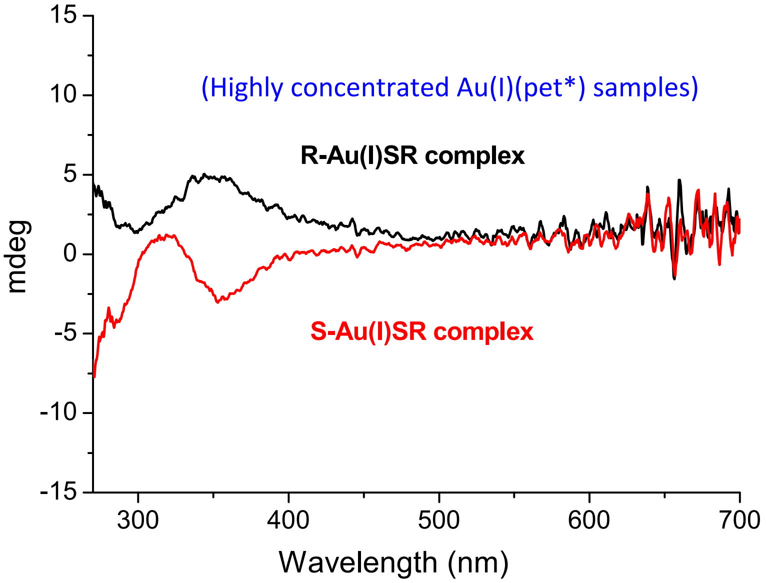


Figure S3. CD spectra of [Au(I)(pet*)]x complexes. Note that the concentrations of complexes are significantly higher than those of $Au_{25}(pet^*)_{18}$.

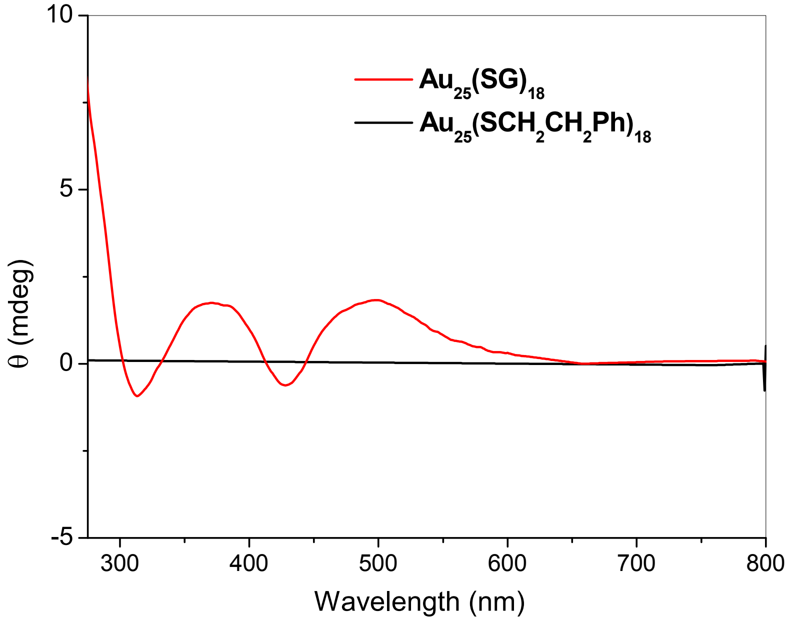


Figure S4. CD spectra of chiral $Au_{25}(SG)_{18}$ and achiral $Au_{25}(pet)_{18}$. Note that –SG represents *L*-glutathionate ligand.

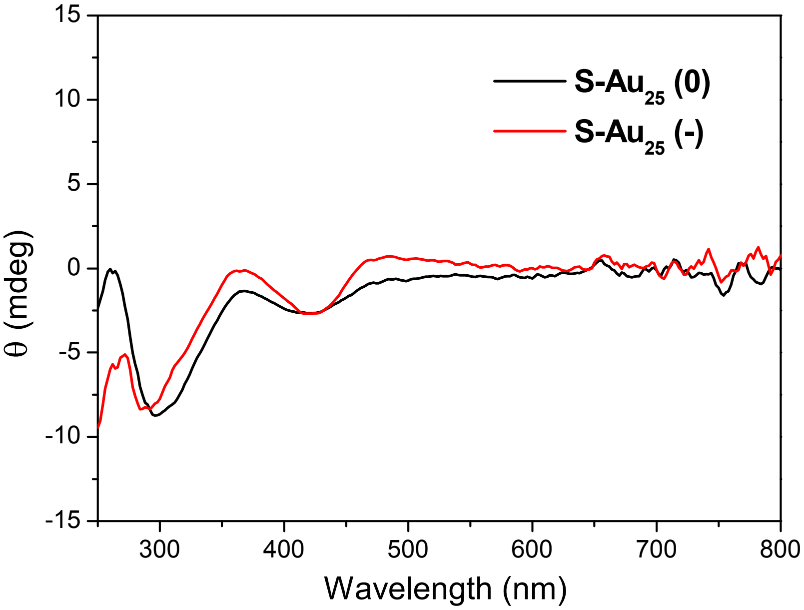


Figure S5. The wide-range (250-800 nm) CD spectra of chiral *S*-Au_{25}(pet*)$_{18}$ and the effect of the charge state on the CD spectrum.