

Reversible conversion between phosphine protected Au₆ and Au₈ nanoclusters under oxidative/reductive conditions

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Experimental section

Chemicals

All the chemicals were used without further purification. Tetrachloroauric(III) acid (HAuCl₄·4H₂O, 99.99%, Acros), 1,3-Bis(Diphenylphosphino)propane (DPPP, 98%,), sodium borohydride (NaBH₄, 99.99%, Sinopharm), ethanol (99%), hexane (99%), dichloromethane (CH₂Cl₂, 99%), hydrogen peroxide (H₂O₂, 30%, Sinopharm). All ligands were purchased from Adamas. All organic solvents were purchased from Sinopharm.

The synthesis of [Au₂(C₃P₂Ph₄)Cl₂] precursor

2 mmol HAuCl₄·4H₂O was dissolved in 20 mL ethanol. Then 2 mmol DPPP was added into the solution and stirred for several hours. The reaction was stopped when white precipitate appeared. The precursor was washed with ethanol for 3 times and dried in vacuum oven. The white powder is [Au₂(C₃P₂Ph₄)Cl₂] precursor.

Synthetic procedure of [Au₆(dppp)₄]²⁺ nanoclusters

78.4 mg [Au₂(C₃P₂Ph₄)Cl₂] precursor was dissolved in 15 mL ethanol and stirred for 15 min. The precursor is insoluble in ethanol, which formed white precipitate. 6 mg NaBH₄ alcoholic solution was quickly added to reduce the precursor. The color of solution turned brown immediately. After reaction 30 min, the reaction was finished and the product was washed with hexane for 4 times. The [Au₆(dppp)₄]²⁺ was collected by separating the product with ethanol and hexane (Volume ratio is 3:25).

Conversion of [Au₆(dppp)₄]²⁺ to [Au₈(dppp)₄Cl₂]²⁺ nanoclusters

1 mg [Au₆(dppp)₄]²⁺ nanoclusters was dissolved in 2 mL ethanol **at room temperature**. The 0.15 mL H₂O₂ was added to oxidize [Au₆(dppp)₄]²⁺ nanoclusters and stirred for several hours. The blue solution turned into pink after 40 min of reaction. The as-prepared product was dried and washed with ethanol and hexane.

Conversion of [Au₈(dppp)₄Cl₂]²⁺ to [Au₆(dppp)₄]²⁺ nanoclusters

1 mg [Au₈(dppp)₄Cl₂]²⁺ nanoclusters was dissolved in 2 mL ethanol **at room temperature**. To this solution, **different quantities (10 μL, 20 μL, 30 μL, 50 μL) of NaBH₄ alcoholic solution (1 mg NaBH₄ dissolved in 0.5 mL ethanol)** was added to reduce [Au₈(dppp)₄Cl₂]²⁺ nanoclusters and stirred for several minutes. The pink solution turned into blue immediately, indicating the [Au₈(dppp)₄Cl₂]²⁺

was converted to $[\text{Au}_6(\text{dppp})_4]^{2+}$ nanoclusters. The product was dried and washed with ethanol and hexane.

Characterization

UV-Vis spectra of Au nanoclusters (dissolved in ethanol) were performed on a UV-8000s spectrophotometer at room temperature. The mass was measured on a LTQ Orbitrap Elite (ion source is HESI). The product was dissolved in methanol and ethanol.