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Controlled synthesis of pure $Au_{25}(2\text{-Nap})_{18}$ and $Au_{36}(2\text{-Nap})_{24}$ nanoclusters from 2-(Diphenylphosphino)pyridine protected Au nanoclusters

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Experimental

Chemical

All the chemicals were used as received without further purification. Tetrachloroauric acid ($HAuCl_4.4H_2O$, 99%) was purchased from Acros (Belgium). 2-Naphthalenethiol (2-Nap, 99%), 2-(diphenylphosphino)pyridine (PPh_2Py, 98%) and triphenylphosphine (PPh_3, 98%) were purchased from Adamas (Switzerland). Sodium borohydride ($NaBH_4$, 99%, Sinopharm), dichloromethane (DCM, 99%), toluene (99%), methanol (99%), 1-hexane (99%) and ethanol (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). The structures of ligands were shown in Figure S4.

Preparation of phosphine protected Au nanoclusters as precursors

[Au(PPh_2py)Cl] and [Au(PPh_3)Cl] complex were obtained at room temperature via reacting $HAuCl_4$ with PPh_2Py or PPh_3 in 20 mL acetone. The [Au(PPh_2Py)Cl] or [Au(PPh_3)Cl] was dissolved in acetone and stirred for 15 min in flask. And then, $NaBH_4$ dissolved in ethanol was added into the reaction solution and stirred for 1 day. After that, the product was washed with hexane four times. At last, the product was extracted with DCM twice, and used as the precursors for further etching treatment.

Synthesis of $Au_{25}(2\text{-Nap})_{18}$ nanoclusters

$Au_{25}(2\text{-Nap})_{18}$ nanoclusters were obtained by heating the Au nanoclusters precursors at high temperature with excess thiols. In details, Au nanoclusters precursors were dissolved in 2 mL DCM and 20 mL toluene. 2-naphthalenethiol (220 mg) was added to solution and vigorously stirred. The solution was heated at 80 ^{o}C for 1 day. When the reaction was finished, the solution was dried and washed with methanol four times. To obtain high-purity product, the crude product was extracted with DCM two times. The purified product was collected by evaporating DCM.

Synthesis of $Au_{36}(2\text{-Nap})_{24}$ nanoclusters

The synthetic procedure of $Au_{36}(2\text{-Nap})_{24}$ is similar to that of $Au_{25}(2\text{-Nap})_{18}$. The Au nanoclusters precursors were dissolved in 2 mL DCM and 20 mL toluene. 200 mg 2-naphthalenethiol was added to reaction solution. The solution was heated at 50 ^{o}C and vigorously stirred. After 1 day, the black solution was formed and dried with vacuum rotary evaporator at 40 ^{o}C. The crude product was washed with methanol and extracted with DCM two times. Finally, the purified product was collected by evaporating DCM at vacuum condition.

Characterization

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was measured on (MALDI-TOF/TOF 5800) using *trans*-2-[3-(4-*tert*-butylphenyl)-2 -methyl-2-propenyldidene] malononitrile (DCTB) as the matrix. 0.5 mg matrix and 0.1 mg Au nanoclusters were dissolved in DCM, respectively, and mixed together. UV-Vis spectra of Au nanoclusters were collected on a Cary 100. 0.2 mg of Au nanoclusters were dissolved in 2 mL DCM**.**

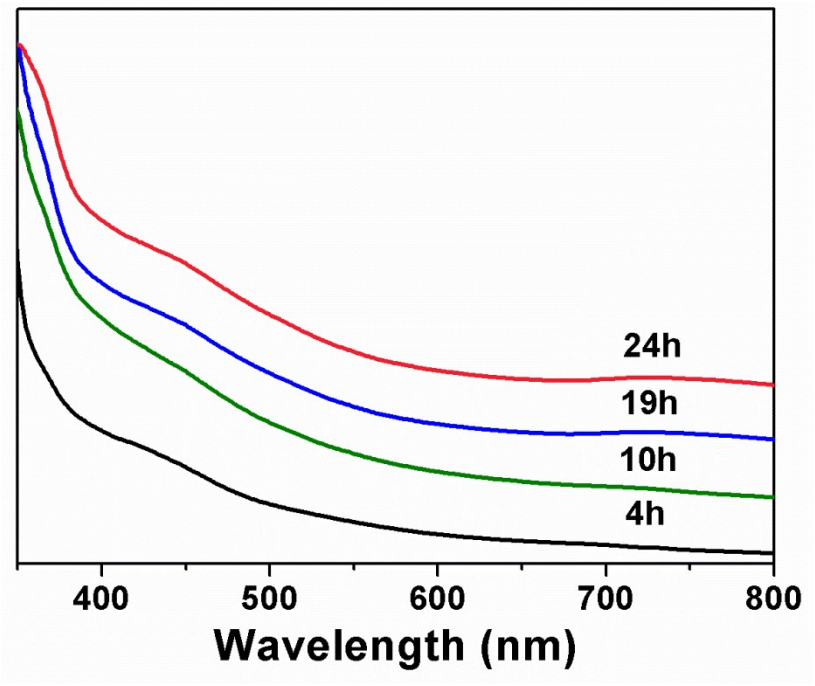


Figure S1 The time-dependent UV-Vis absorption spectra of PPh2Py protected Au nanoclusters during the etching process at 60 ^{o}C.

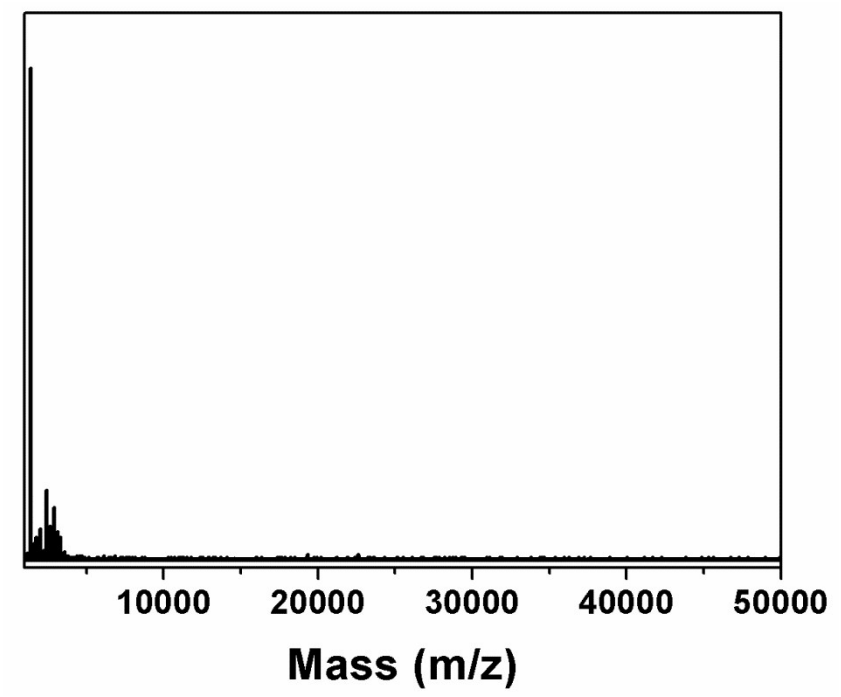


Figure S2 The MALDI-mass spectrometry of PPh_3 protected polydispersed Au nanoclusters.

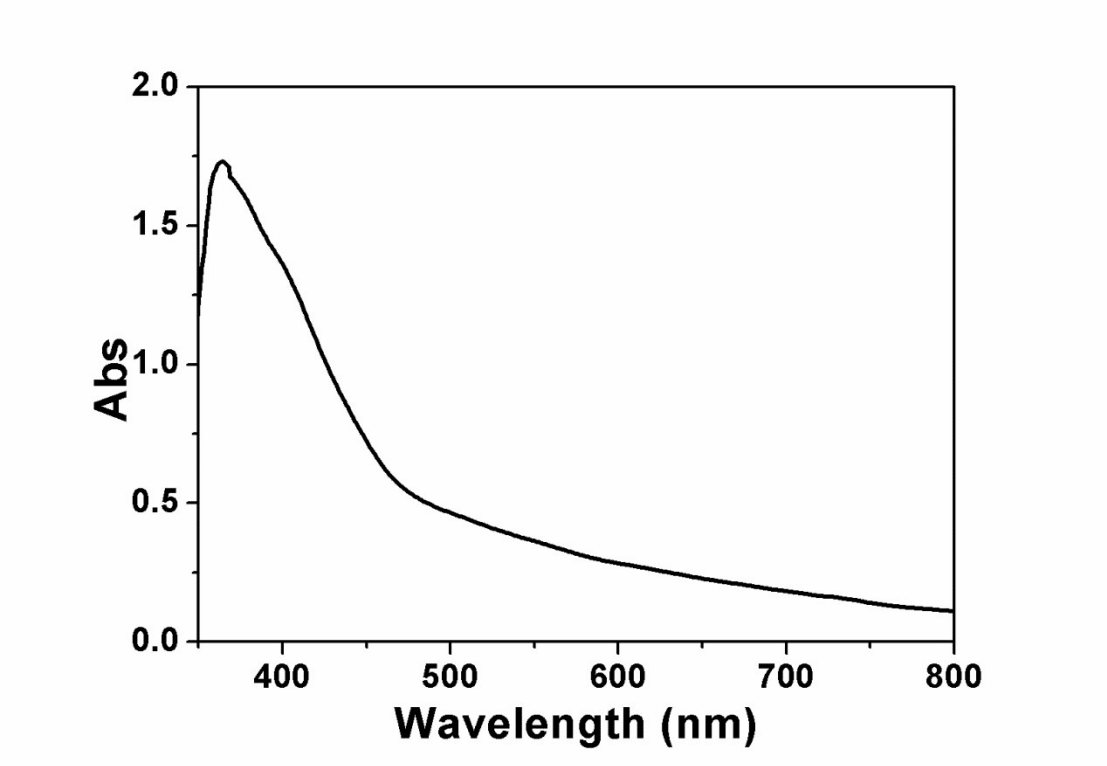
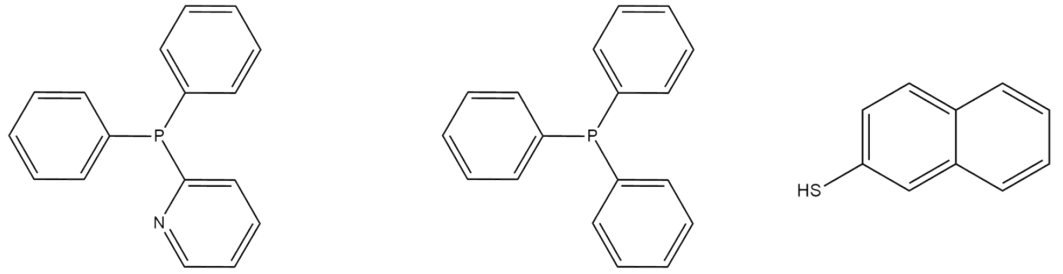


Figure S3 The UV-Vis spectrum of PPh_3 protected polydispersed Au nanoclusters.



2-(diphenyl- phosphino)pyridine Triphenylphosphine 2-Naphthalenethiol

Figure S4 The structure of ligands, 2-(diphenyl-phosphino)pyridine, tripheylphosphine and 2-Naphthalenethiol, respectively.