**Controlled synthesis of pure Au$_{25}$(2-Nap)$_{18}$ and Au$_{36}$(2-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$_2$O, 99%) was purchased from Acros (Belgium). 2-Naphthalenethiol (2-Nap, 99%), 2-(diphenylphosphino)pyridine (PPh$_2$Py, 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$_2$Py)Cl] and [Au(PPh$_3$)Cl] complex were obtained at room temperature via reacting HAuCl$_4$ with PPh$_2$Py or PPh$_3$ in 20 mL acetone. The [Au(PPh$_2$Py)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-Nap)$_{18}$ nanoclusters**

Au$_{25}$(2-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 °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-Nap)$_{24}$ nanoclusters**
The synthetic procedure of Au$_{36}$(2-Nap)$_{24}$ is similar to that of Au$_{25}$(2-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 °C and vigorously stirred. After 1 day, the black solution was formed and dried with vacuum rotary evaporator at 40 °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-propenylidene] 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 °C.
Figure S2  The MALDI-mass spectrometry of PPh$_3$ protected polydisperse Au nanoclusters.
Figure S3  The UV-Vis spectrum of PPh$_3$ protected polydispersed Au nanoclusters.
Figure S4  The structure of ligands, 2-(diphenyl-phosphino)pyridine, triphenylphosphine and 2-Naphthalenethiol, respectively.