Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Ion-precursor and ion-dose dependent anti-galvanic reduction

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Experimental

Chemicals. All chemicals and reagents are commercially available and used as received. Dithizone (DTZ, 98%) was obtained from Aladdin. 2-Phenylethanethiol (PET, 99.0%) and Ethylenediaminetetraacetic acid disodium salt dehydrate ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$, 98%) were purchased from Sigma-Aldrich. Silver nitrate ($AgNO_3$, 99.8%) was purchased from Shanghai chemical reagent co., ltd. Acetonitrile (CH_3CN, 99.0%), toluene (99.5%), dichloromethane (AR), petroleum ether (AR) and were purchased from Sinopharm chemical reagent co., ltd. $Au_{25}(PET)_{18}^{-}TOA^{+}$ were synthesized following the previous methods (see Ref.48 in the main text).

Preparation of the precursor solution

$AgNO_3$ (85mg, 0.5mmol) was directly dissolved in 1 mL H_2O for subsequent AGR reaction. 8 mL water solution containing Ethylenediamine tetraacetic acid disodium salt (0.6mmol, 79.3mg) was added to 7 mL water solution of $AgNO_3$ (85mg, 0.5mmol) under vigorous stirring for 1 hour to prepare Ag-EDTA precursor solution. Ag-PET precursor solution was made by adding 2-Phenylethanethiol (80.5ul，0.6mmol) into 15 mL acetonitrile solution of $AgNO_3$ (85mg, 0.5mmol) under vigorous stirring for 1 hour. Ag –DTZ precursor solution was prepared by adding 7 mL acetonitrile solution of $AgNO_3$ (85mg, 0.5mmol) into 8 mL acetonitrile solution containing Dithizone (0.6mmol, 153.792mg) under vigorous stirring for 1 hour.

AGR reaction

$Au_{25}(PET)_{18}^{-}TOA^{+}$ (7.86 mg, 0.001 mmol) was dissolved in toluene (3ml), then a freshly prepared Ag-L (L=NO_3, EDTA, PET, AR) solution (0.002mmol, 60ul) was added rapidly under vigorous stirring. The reaction was allowed to proceed for 1 hour and the product was precipitated using petroleum ether and washed thoroughly with methanol. After that, the as-obtained products were analyzed by thin-layer chromatography (TLC) or separated by preparative thin-layer chromatography (PTLC) for subsequent characterization. (note: the entire experimental process is conducted under room temperature without avoiding of air and light).

Characterizations. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on an autoflex Speed TOF/TOF mass spectrometer (Bruker) using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. The UV/vis/NIR absorption was measured on a UV-2550 spectrophotometer (Shimadzu, Japan). The TLC plates were eluted with dichloromethane/petroleum ether mixture and the best separation occurred at a DCM/petroleum ether ratio of 40/60 in this system.

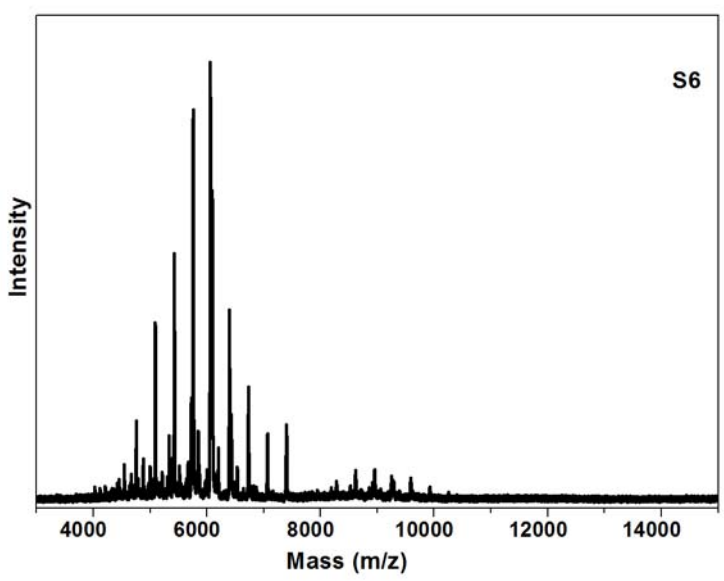

Fig. S1 MALDI-TOF-MS spectrum of S6

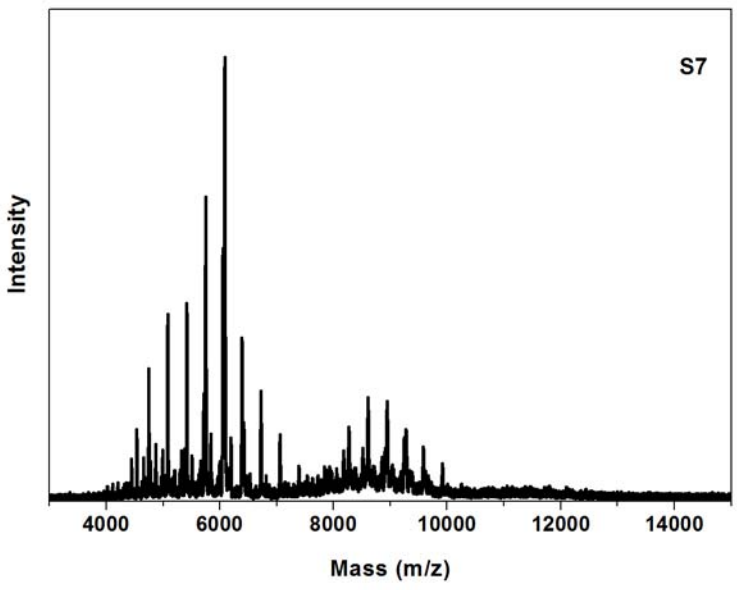

Fig. S2 MALDI-TOF-MS spectrum of S7

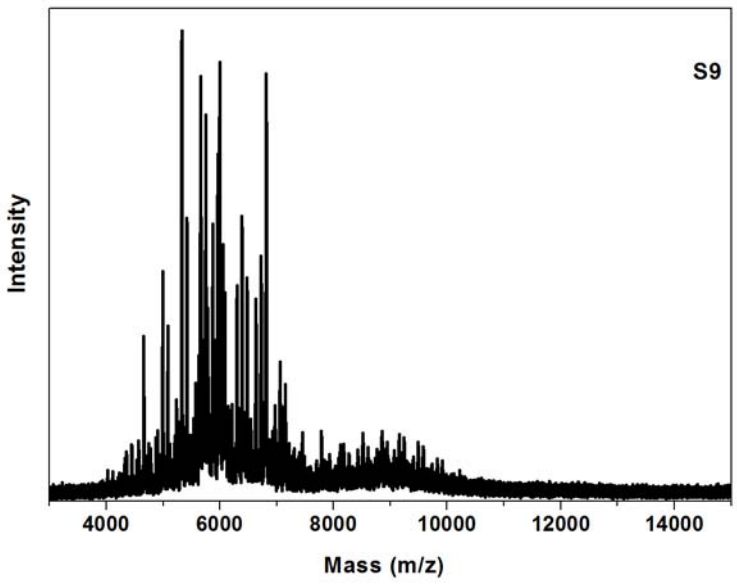

Fig. S3 MALDI-TOF-MS spectrum of S9

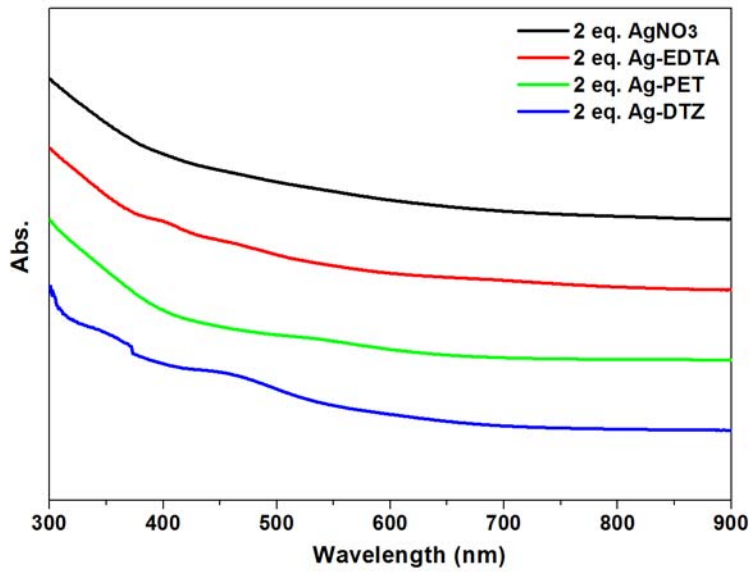

Fig. S4 UV/Vis/NIR spectra of the starting spots in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with various ion precursors

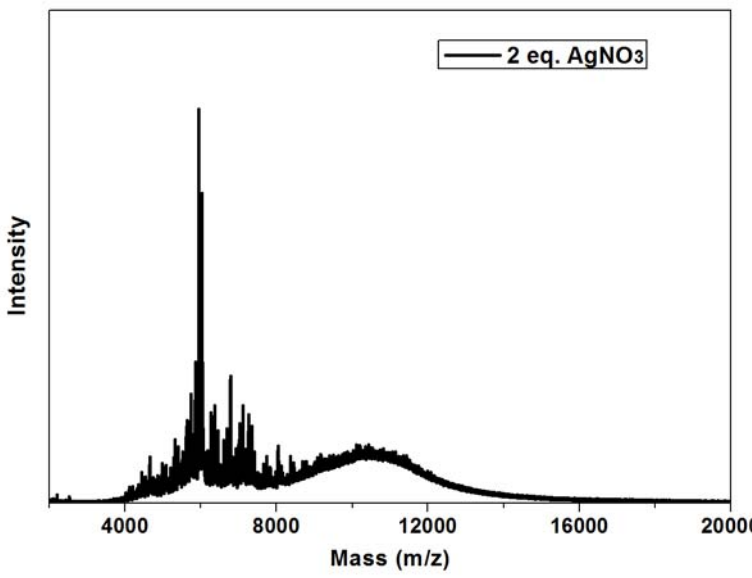

Fig. S5 MALDI-TOF-MS spectrum of the starting spot in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with AgNO3. The mass spectrum was acquired in positive ionization mode.

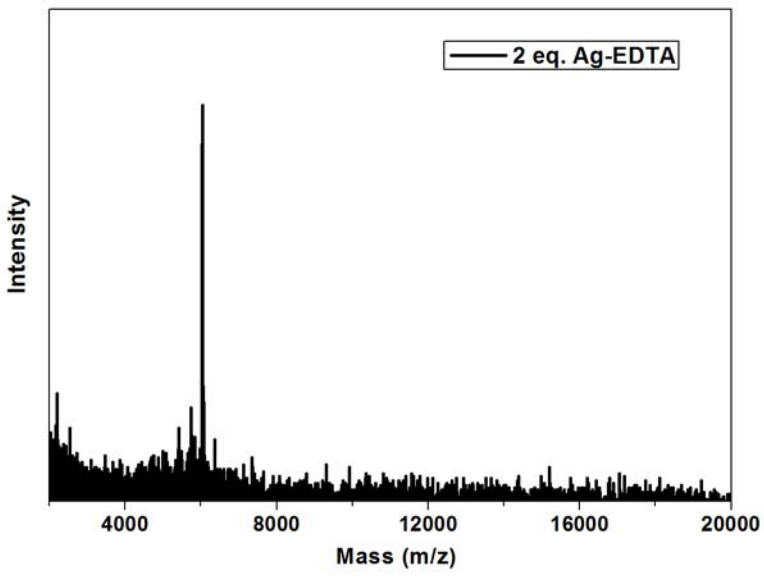

Fig. S6 MALDI-TOF-MS spectrum of the starting spot in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with Ag-EDTA. The mass spectrum was acquired in positive ionization mode.

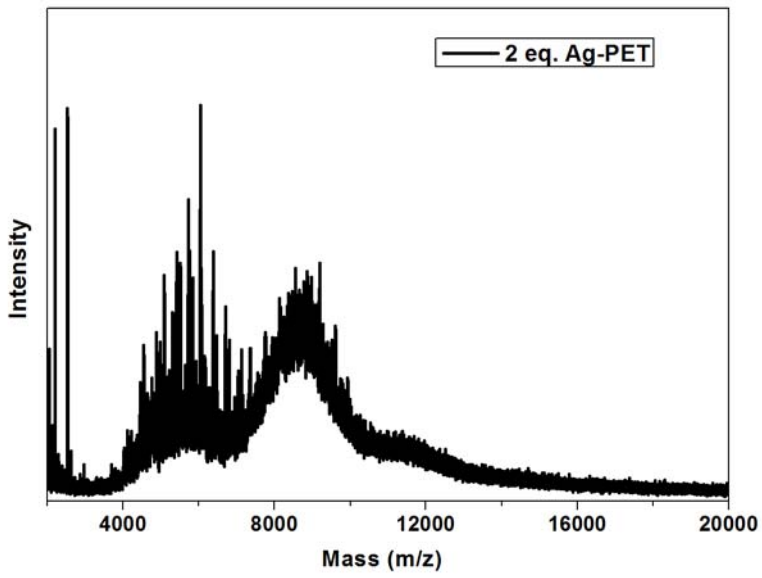

Fig. S7 MALDI-TOF-MS spectrum of the starting spot in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with Ag-PET. The mass spectrum was acquired in positive ionization mode.

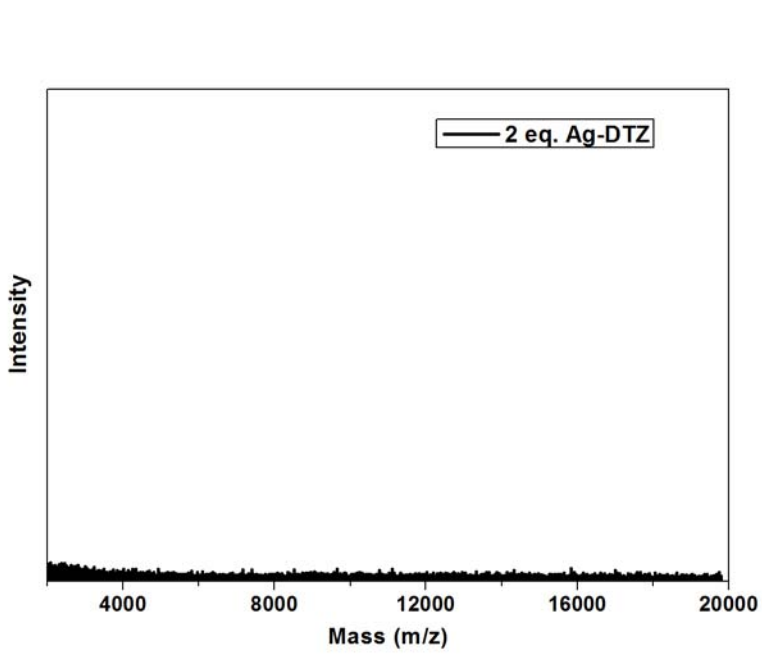

Fig. S8 MALDI-TOF-MS spectrum of the starting spot in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with Ag-DTZ. The mass spectrum was acquired in positive ionization mode.

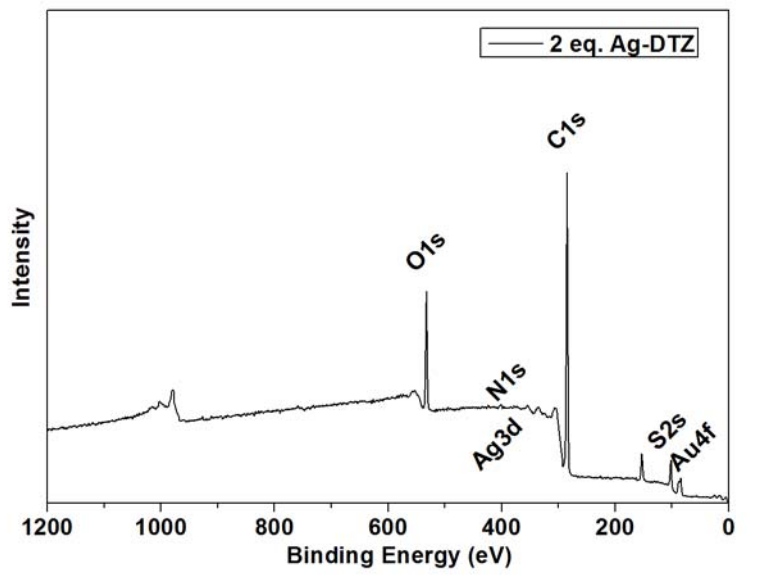

Figure S9. XPS survey spectrum of the starting spot in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with Ag-DTZ.

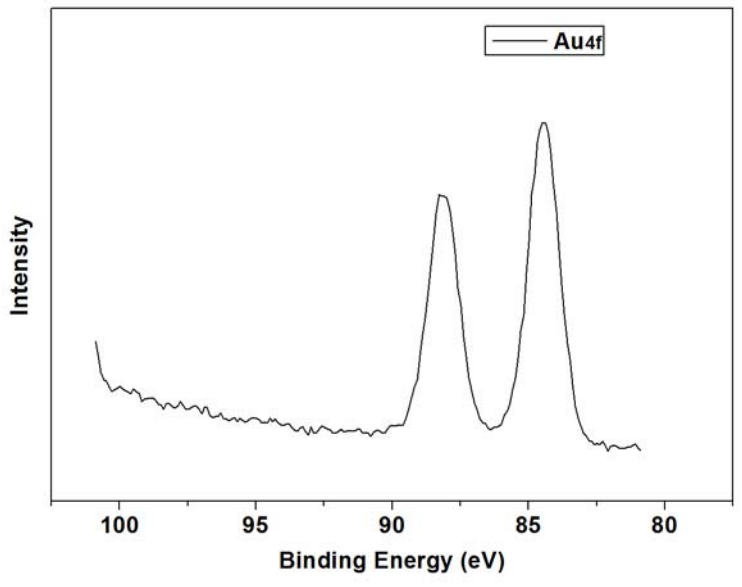

Figure S10. Au4f XPS spectra of the starting spot in PTLC plate when anion $Au_{25}(PET)_{18}$ reacts with Ag-DTZ.