Electronic Supplementary Information for:

Acetylide for Thiolate and Thiolate for Acetylide Exchange on Gold Clusters

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Materials and Methods

Chemicals. Tetrachloroaurate trihydrate (Sigma-Aldrich, ACS reagent, ≥49.0% Au basis), chloro(dimethylsulfide)gold(I) (TCI America, >97% Purity) tetra-*n*-octylammonium bromide (Acros Organics, 98% purity), sodium borohydride (Sigma-Aldrich, ≥98.0% purity), 2-phenylethanethiol (Sigma-Aldrich, ≥99% Purity), phenylacetylene (Alfa Aesar, 98+% Purity), lithium phenylacetylide (Sigma-Aldrich, 1.0M in THF), 3,5-bis(trifluoromethyl)phenylacetylene (Sigma-Aldrich, 97%), tetrahydrofuran (Fisher Scientific, certified, stabilized with 0.025% butylated hydroxytoluene), dichloromethane (Sigma-Aldrich, ACS grade, ≥99.5%, stabilized with 40-150 ppm amylene), toluene (Sigma-Aldrich, ACS reagent, ≥99.5%), methanol (Fisher Scientific, certified ACS, 99.9% assay), acetone (Industrial Chemical Corporation, tech grade), chloroform (EMD Millipore, ≥99.8% assay, stabilized with ethanol), ethanol (Pharmco-Aaper, 200 proof), and *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenyliden]malononitrile (Sigma Aldrich, ≥99.0% [HPLC]) were all used without further purification. Triethylamine (Fisher, ≥99.0%), pyridine (Fisher, ≥99.0%), and diethyl ether (Fisher, ≥99.0%, BHT stabilized) were purified using a SG Water USA glass contour solvent system prior to use. Water was obtained using a Thermo Scientific Barnstead Nanopure set to 18.2 MΩ·cm.

MALDI-MS data collection. 2 mg *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile was dissolved in 0.2 mL dichloromethane. To this solution was added 2.0 µL of nanocluster sample dissolved in dichloromethane. 0.2 µL of the combined solution was spotted on a metal plate for MALDI-MS and allowed dry for one hour. Data was collected using a Bruker Microflex LFR MALDI-TOF. Positive mode spectra were collected as they provided better signal-to-noise ratios relative to negative mode spectra.

Synthesis of $Au_{25}(PET)_{18}TOA$. A previously published method was adapted for the synthesis of $Au_{25}(PET)_{18}TOA$.[1] In brief, 2.0 g $HAuCl_4 \cdot 3H_2O$ and 3.12 g tetra-*n*-octylammonium bromide were added to 140 mL tetrahydrofuran in a 300 mL roundbottom flask. The solution was stirred for 30 minutes until a dark orange color was observed. 3.6 mL of 2-phenylethanethiol was then added to flask, and the resulting solution was stirred overnight. A separate solution containing 1.94 g sodium borohydride and 48 mL H_2O was produced in a 125 mL Erlenmeyer flask. This solution was cooled to 0 °C prior to adding it to the gold-containing solution. The combined solutions were then stirred for 48 hours, followed by separation and evaporation of the organic layer. The resulting brown oil was re-dissolved in several milliliters of dichloromethane and separated into four 50 mL conical vials. The conical vials were filled with methanol and placed in a centrifuge at 4000 RPM for 30 minutes. The supernatant was decanted and the precipitate was washed twice more by addition of methanol and centrifugation. The final product was extracted from the resulting powder using dichloromethane and evaporated to dryness.

Synthesis of gold(I)-phenylacetylide. Synthesis conditions were utilized from a previously published report.[2] In brief, 100 mg chloro(dimethylsulfide)gold(I) was added to 10.0 mL dichloromethane, 47.8 µL phenylacetylene, and 60.3 µL triethylamine in a 20 mL scintillation vial and stirred in the dark for two hours. The solution was then evaporated to approximate dryness and the resulting powder was washed with excess water, ethanol, and diethyl ether.

Acetylide exchange reactions on $Au_{25}(PET)_{18}$. Ligand exchange was performed on $Au_{25}(PET)_{18}TOA$ by adding 12.0 mg (1.53 µmol) $Au_{25}(PET)_{18}TOA$ to 3.03 mL dichloromethane in a 20 mL scintillation vial at room temperature. 0.450 mg (1.53 µmol) gold(I)-phenylacetylide was added to the solution containing the Au_{25} cluster and stirred for 30 minutes, after which the solvent was evaporated. The crude product was then extracted using dichloromethane to remove any remaining gold(I)-phenylacetylide and evaporated to dryness.

A similar procedure was used to generate a higher amount of ligand exchange but using 4.50 mg (15.3 µmol) or 450 mg (153 µmol) of gold(I)-phenylacetylide.

Exchange of lithium phenylacetylide with $Au_{25}(PET)_{18}$. Ligand exchange was performed by purging a sealed 20 mL scintillation vial containing 20.0 mg (2.54 µmol) $Au_{25}(PET)_{18}TOA$ and a stir bar with argon for 30 minutes. To this vial was added 25.4 µL (25.4 µmol) lithium phenylacetylide. The solution was stirred for 30 minutes under argon at room temperature, after which a 2.0 µL aliquot of the solution was removed for MALDI-MS analysis.

Synthesis of $[Na][Au_{25}(CCAr)_{18}]$. Synthesis conditions were adapted from a previously published report.[3] In a foil-wrapped 20 mL scintillation vial, 200 mg chloro(dimethylsulfide)gold(I) was added to 10 mL acetone under vigorous stirring. 126 µL 3,5-bis(trifluoromethyl)phenylacetylene and 99 µL triethylamine were then added sequentially, and this mixture was stirred for 2 hours. The resulting precursor Au(I)-CCAr was isolated by drying the solution under rotary evaporation and washing twice with water. 208 mg Au(I)-CCAr was subsequently added to 30 mL of a chloroform:methanol mixture (5:1) in a 100 mL foil-wrapped roundbottom flask under vigorous stirring. A freshly-prepared aqueous solution of sodium borohydride (5.4 mg in 4.7 mL water) was added dropwise followed by 94 µL triethylamine. The mixture was allowed to stir for 20 hours, whereupon a dark solid was obtained following rotary evaporation. This solid was extracted in methanol, which after brief centrifugation gave crude $Au_{25}(CCAR)_{18}$ in the supernatant. For crystallization, this crude was dried and re-suspended in 1:1 dichloromethane:toluene and layered with hexanes in 20 mL scintillation vials. Crystals were observed in a few days at room temperature. All characterizations and post-synthetic modifications described herein for $Au_{25}(CCAr)_{18}$ were performed with

crystal-pure sample. MALDI-MS and UV/Visible absorbance measurements further confirm the purity of the sample (Figures S9, S10).

Thiolate ligand exchange on [Na][$Au_{25}(CCAr)_{18}$]. 13 mg () $Au_{25}(CCAr)_{18}$ was suspended in 1 mL dichloromethane in a 20 mL scintillation vial at room temperature. A solution of 1 µL 2-phenylethanethiol in 100 µL dichloromethane was prepared. 19 µL of this solution, equating to 1 equivalent per cluster, was added to the $Au_{25}(CCAr)_{18}$ solution under vigorous stirring. An aliquot of this mixture was removed for MALDI-MS analysis following a period of 30 minutes.

Synthesis of $Au_{44}(PA)_{28}$. $Au_{44}(PA)_{28}$ was synthesized according to a previously published report.[4] In brief, 44.7 mg gold(I)-phenylacetylide was added to 4.0 mL chloroform and stirred. A solution of 0.95 mg sodium borohydride in 1.0 mL ethanol was prepared and added to the solution containing gold(I)-phenylacetylide. The combined solutions were stirred in the dark for 16 hours. Afterwards, 0.3 mL phenylacetylene and 0.3 mL pyridine were added and stirred for 24 hours in the dark. The solution was subsequently evaporated to near dryness and washed with 15 mL hexanes to afford a dark powder. This powder was purified by size exclusion chromatography to afford the purified product.

Thiolate ligand exchange on $Au_{44}(PA)_{28}$. Ligand exchange was performed on $Au_{44}(PA)_{28}$ by adding 2.8 mg (0.24 µmol) $Au_{44}(PA)_{28}$ to 0.48 mL dichloromethane in a 20 mL scintillation vial at room temperature. 0.59 µL (0.61 mg, 4.41 µmol) 2-phenylethanethiol was added to the solution containing the Au_{44} cluster and stirred for 5 minutes, after which an aliquot of the solution was removed for MALDI-MS analysis.

Intercluster exchange between $Au_{25}(PET)_{18}$ and $Au_{44}(PA)_{28}$. 1.16 mg (0.148 µmol) $Au_{25}(PET)_{18}$TOA and 1.70 mg (0.148 µmol) $Au_{44}(PA)_{28}$ were combined in 0.29 mL dichloromethane and stirred for five minutes. The solution was then evaporated to dryness and re-dissolved in a minimal amount of DCM for MALDI-MS analysis.

Supporting Figures

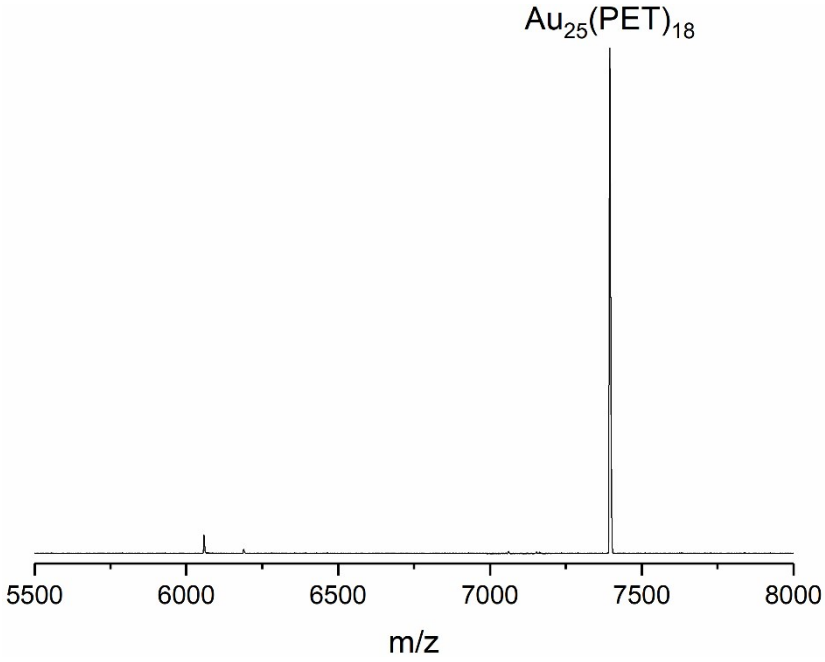

Figure S1: Positive ion MALDI-MS of $Au_{25}(PET)_{18}$. The peak corresponding to this compound is labelled. Other peaks correspond to fragmentation products.

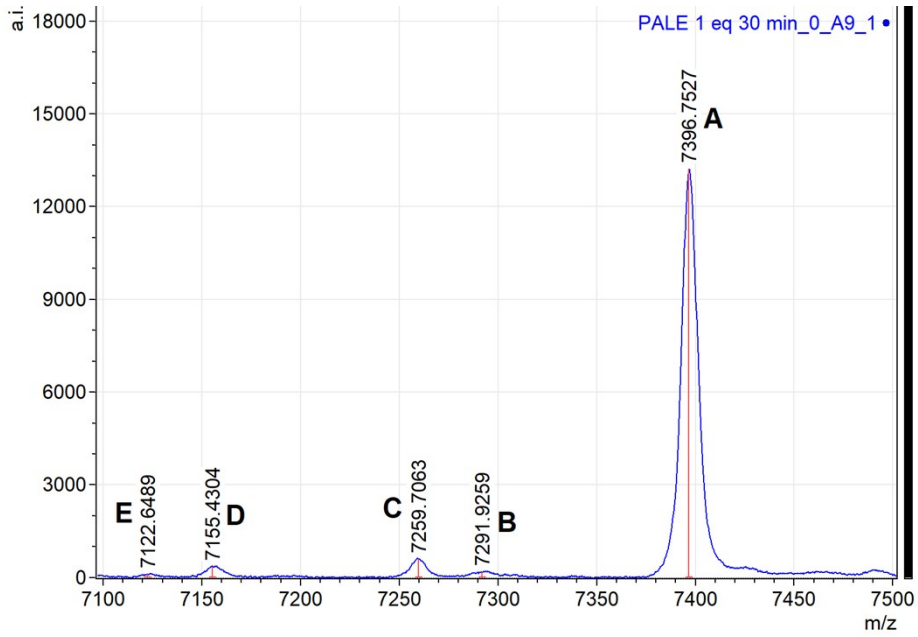

Figure S2: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 1 eq. phenylacetylene in DCM for 30 minutes. The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$ B) $Au_{25}(PET)_{17}S_1$ C) $Au_{25}(PET)_{17}$ D) $Au_{25}(PET)_{16}S_1$ E) $Au_{25}(PET)_{16}$

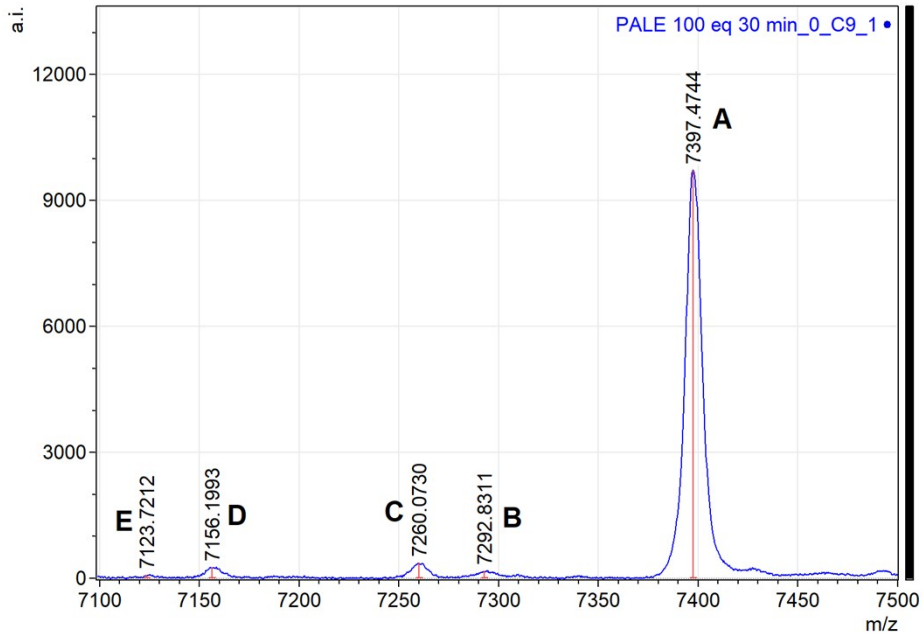

Figure S3: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 100 eq. phenylacetylene in DCM for 30 minutes. The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$ B) $Au_{25}(PET)_{17}S_1$ C) $Au_{25}(PET)_{17}$ D) $Au_{25}(PET)_{16}S_1$ E) $Au_{25}(PET)_{16}$.

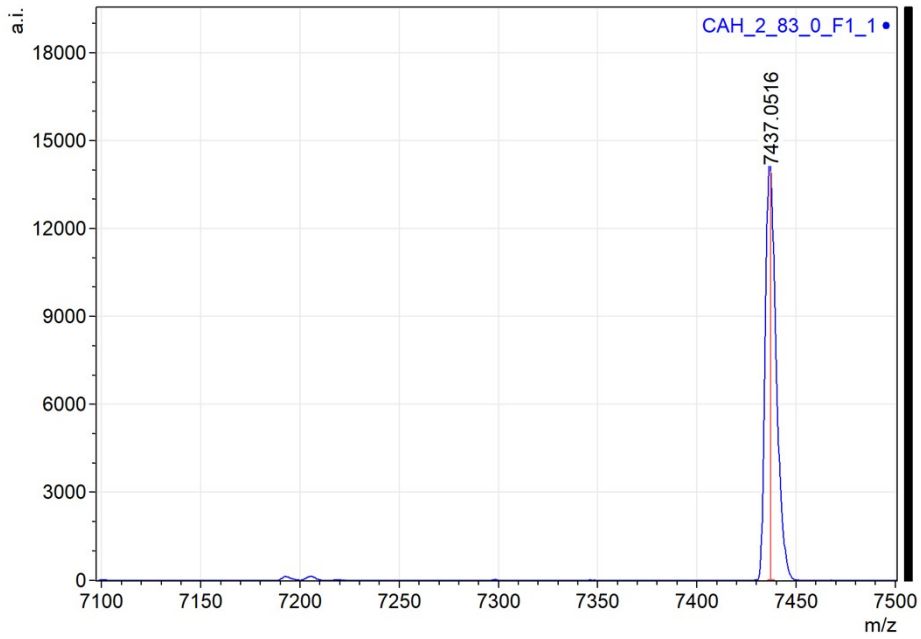

Figure S4: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 10 eq. phenylacetylene and 1 eq. triethylamine in DCM for 30 minutes. A sodium adduct of $Au_{25}(PET)_{18}$ is labelled. The calculated mass spectrometry result for $Au_{25}(PET)_{18}{\cdot}2Na^{+}$ is 7437.91 m/z.

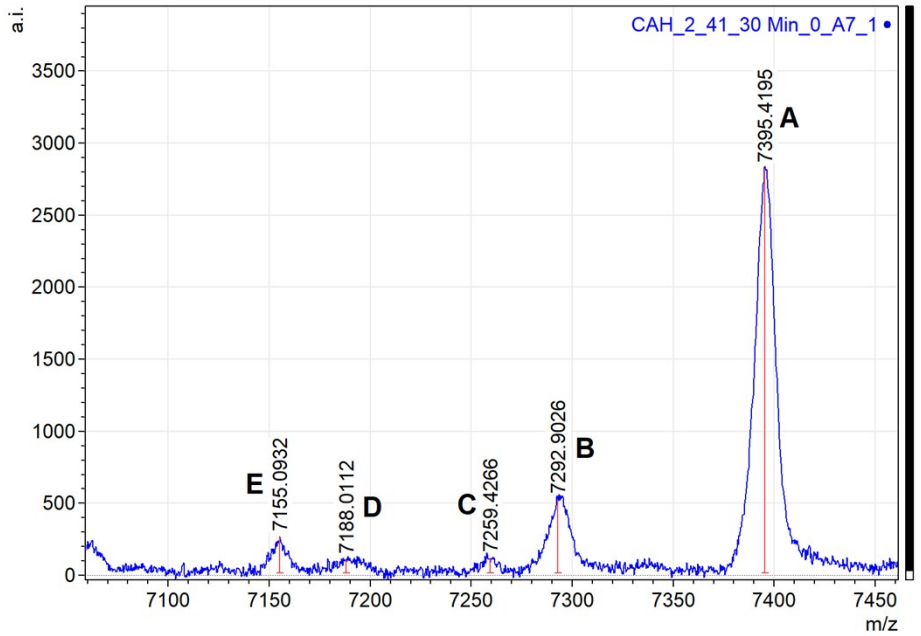

Figure S5: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 100 eq. phenylacetylene in toluene for 30 minutes at 60 °C. The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$ B) $Au_{25}(PET)_{17}S_1$ C) $Au_{25}(PET)_{17}$ D) $Au_{25}(PET)_{16}S_1$ E) $Au_{25}(PET)_{16}$.

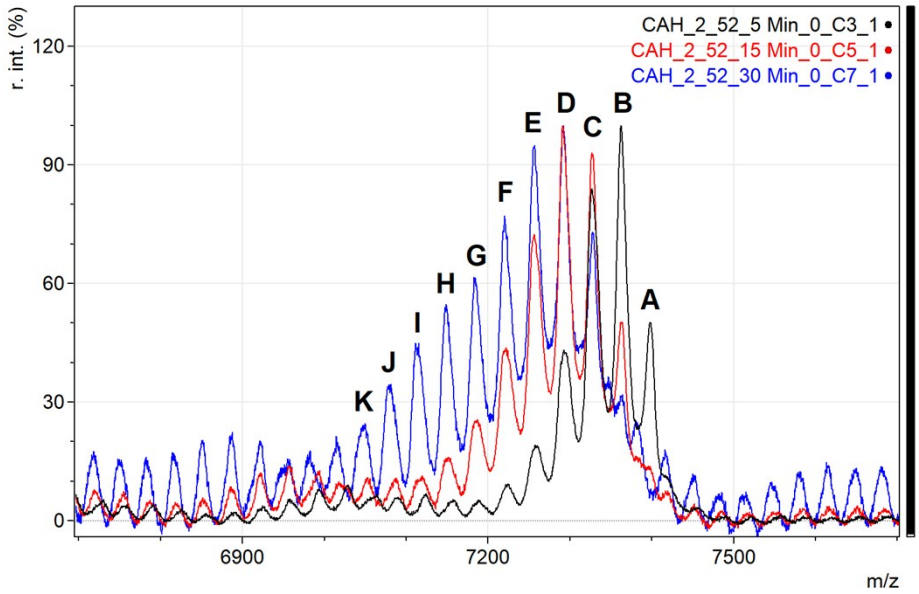

Figure S6: Normalized positive ion MALDI-MS spectra after mixing $Au_{25}(PET)_{18}$ with 10 eq. gold(I)-phenylacetylide in THF for 5 minutes (black), 15 minutes (red), and 30 minutes (blue). The peaks are labelled as the following species: A) $Au_{25}(PET)_{18}$ B) $Au_{25}(PET)_{17}(PA)_1$ C) $Au_{25}(PET)_{16}(PA)_2$ D) $Au_{25}(PET)_{15}(PA)_3$ E) $Au_{25}(PET)_{14}(PA)_4$ F) $Au_{25}(PET)_{13}(PA)_5$ G) $Au_{25}(PET)_{12}(PA)_6$ H) $Au_{25}(PET)_{11}(PA)_7$ I) $Au_{25}(PET)_{10}(PA)_8$ J) $Au_{25}(PET)_9(PA)_9$ K) $Au_{25}(PET)_8(PA)_{10}$

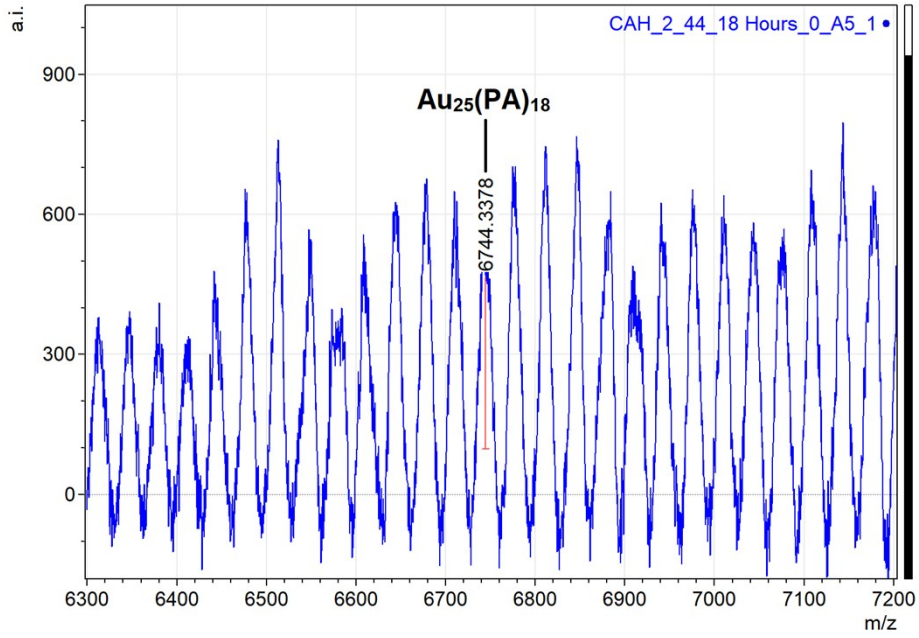

Figure S7: Positive ion MALDI-MS spectrum after mixing $Au_{25}(PET)_{18}$ with 100 eq. gold(I)-phenylacetylide in DCM for 18 hours. The peak corresponding to the mass of $Au_{25}(PA)_{18}$ is labelled.

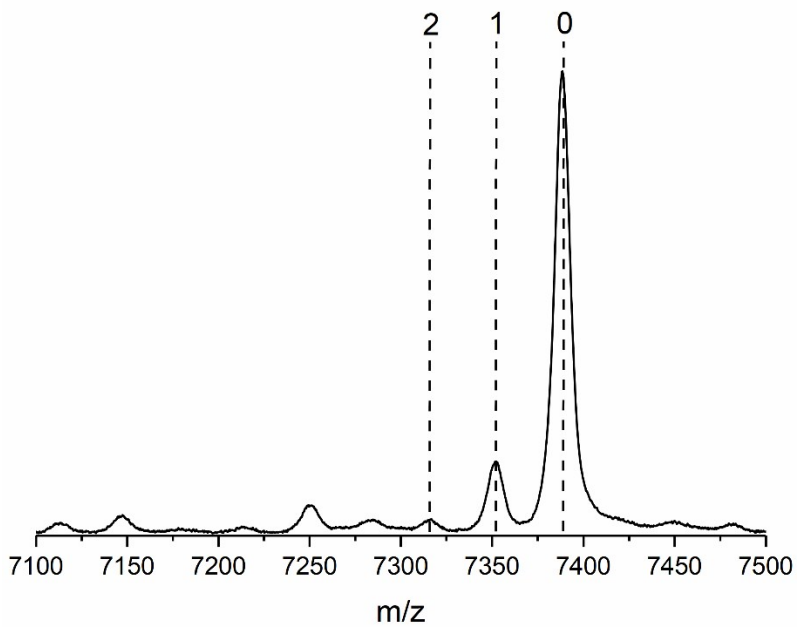

Figure S8: Positive ion MALDI-MS spectrum of $Au_{25}(PET)_{18-x}(PA)_x$ obtained after mixing $Au_{25}(PET)_{18}$ with 10 eq. of lithium phenylacetylide in DCM under argon for 5 minutes. Other peaks correspond to fragmentation products.

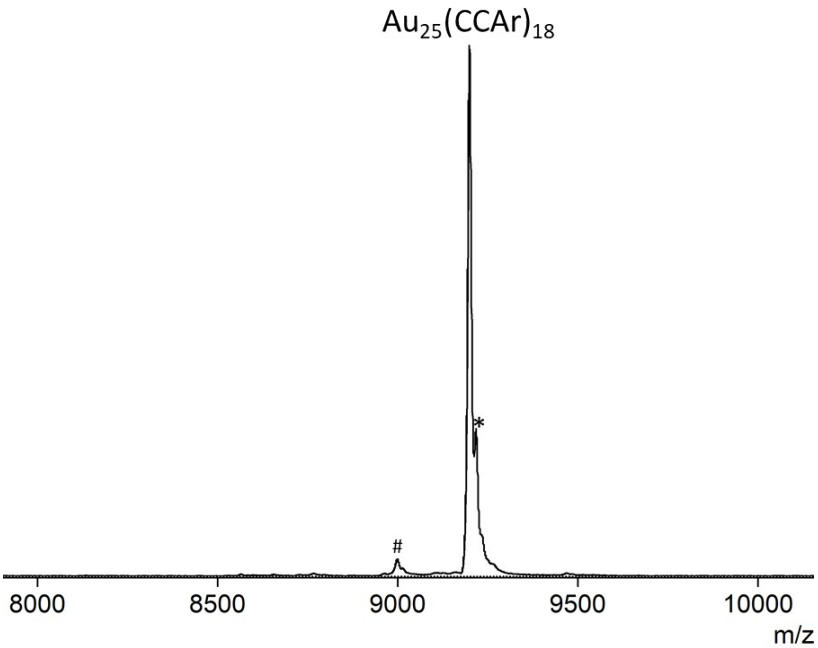

Figure S9: Negative ion MALDI-MS spectrum of crystal-pure $Au_{25}(CCAr)_{18}$. The peak corresponding to the compound is labelled. The peak labelled # is a fragment peak corresponding to the loss of gold from the parent cluster. The peak labelled * is an adduct peak corresponding to the parent peak plus a fluorine.

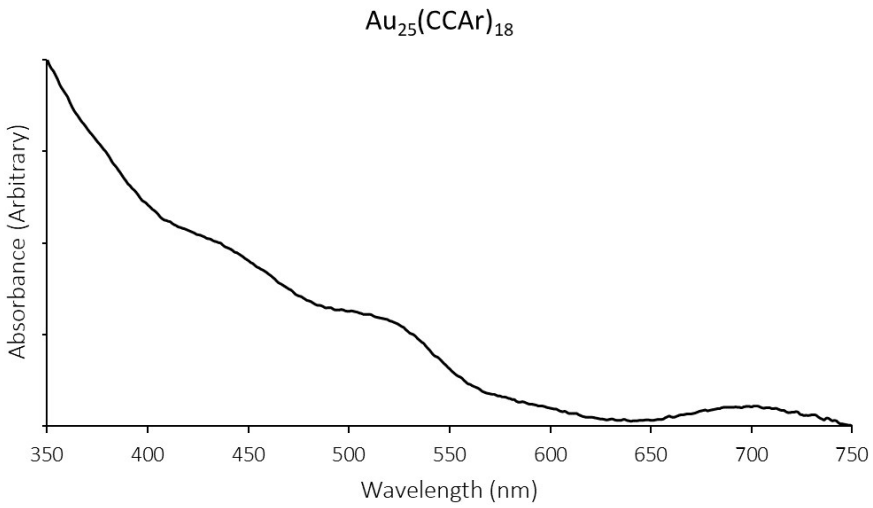

Figure S10: UV/Visible absorbance spectrum of crystal-pure $Au_{25}(CCAr)_{18}$. The position and relative intensity of absorption peaks matches well with that reported by Li et al. (reference 3).

References

1) Parker, J. F.; Weaver, J. E. F.; McCallum, F.; Fields-Zinna, C.A.; Murray, R. W. *Langmuir* **2010**, *26*, 13650.
2) Wan, X.-K.; Tang, Q.; Yuan, S.-F.; Jiang, D.; Wang, Q.-M. *J. Am. Chem. Soc.* **2015**, *137*, 652.
3) Li, J.-J.; Guan, Z.-J.; Lei, Z.; Hu, F.; Wang, Q.-M. *Angew. Chem. Int. Ed.* **2019**, *58*, 1083-1087.
4) Wan, X.-K.; Guan, Z.-J.; Wang, Q.-M. *Angew. Chem. Int. Ed.* **2017**, *56*, 11494.