

Supporting Information for:

Functionalized Gold Magic Clusters: Au₂₅(SPhNH₂)₁₇

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Nanoscale

Chemicals

4-aminothiophenol was purchased from TCI. Tetrachloroauric acid hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 52% Au basis), LiBH_4 solution (2 M in THF) and THF (Chromasolv®) were purchased from Aldrich Chemical Company, Inc. All reagent and solvents were of commercial quality and used without further purification. The glassware used in the synthesis were cleaned with *aqua regia* (*aqua regia* is a very corrosive product and should be handled with extreme care) and then rinsed with copious amount of distilled water, then dried overnight prior to use. All reactions were carried out in atmospheric conditions.

Synthesis of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ by simultaneous addition

Typically, tetrachloroauric acid hydrate (200 mg, 1 eq, 528 μmol Au basis) was dissolved in 20 mL of tetrahydrofuran. This mixture and a lithium borohydrate solution (2.112 mmol; 1.06 mL, 4 eq of the 2M commercial solution in 20 mL THF) were added dropwise and simultaneously with two distinct dropping funnels, to a stirred solution of 4-aminothiophenol (139.7 mg; 2 eq., 1.056 mmol in 20 mL THF) into a 100 mL trineck round-bottom flask over a 30 minutes period. After the end of the addition of LiBH_4 and HAuCl_4 the mixture was left under stirring (300 rpm) for five hours.

The mixture turned quickly from yellow to a brown solution and afterwards to a black solution plus the formation of a black precipitate, which indicates the aggregation of the prepared functionalized gold clusters.

Tetrahydrofuran is removed by rotary evaporation and ethanol is added. The black precipitate is collected by centrifugation (15 minutes, 11 000 rpm). The product is then washed with ethanol and collected via centrifugation again (15 minutes, 11 000 rpm). The last step is done three times to completely remove the 4-aminothiophenol excess and salts. The washed black precipitate is dried at air under atmospheric conditions and stored under these conditions.

The so-obtained product (112 mg) is poorly dispersible in almost all solvents except *N,N*-dimethylformamide (DMF). The average yield obtained is 70% based on gold and the characterisations are done without further purifications.

Synthesis of Au₂₅(SCH₂CH₂Ph)₁₈

Synthesis of this nanocluster has been done by following previous reported experiments.^{1,2} The first step was to get the anionic cluster Au₂₅(SCH₂CH₂Ph)₁₈TOA, and the second step was to leave it under ambient atmosphere in CH₂Cl₂ in order to get the neutral nanocluster. ESI-MS has been carried out to check its purity (Figures S1 and S2).

Characterizations

The mass spectra were recorded in a positive ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The gas flow of spray gas is 0.6 bar and the capillary voltage is 4.5 kV. Mild conditions were used for the ions transfer to keep intact the functionalized nanoclusters. The solutions are infused at 180 μL/h in a mixture of solvents (methanol/dichloromethane/water 45/40/15). The mass range of the analysis is 800-5000 m/z and the calibration was done with cesium iodide and tune mix (Agilent).

Thermogravimetric analysis (TGA) was performed with a TGA/SDTA 851° from Mettler Toledo. Around 5 mg of sample was heated at a rate of 10 °C.min⁻¹ from 25 to 1200°C, in a 150 μL alumina crucible, under N₂ atmosphere (50 ml.min⁻¹). Shining droplets of bulk gold were observed at the end of the experiment.

Gold loading is determined by inductively coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa ICP-OES). Sulphur percentage is determined by full combustion at 1320-1360 °C under O₂ stream and analysis of SO₂ and is titrated in a coulometric-acidimetric cell. Carbon and hydrogen percentage is determined by full combustion at 1030-1070 °C under O₂ stream and transformed into CO₂ and H₂O and is titrated on a coulometric detector. Nitrogen percentage is determined by full combustion under He:O₂ stream (3% in O₂) and is titrated on a catharometer. Analysis precision is 0.3% absolute for carbon, sulphur, nitrogen and hydrogen.

X-ray diffraction (XRD) is carried out on a Bruker D8 Advance A25 diffractometer using Cu Kα radiation equipped with a 1-dimensional position-sensitive detector (Bruker LynxEye). Small angle XR scattering was recorded between 0.45° and 7° (2θ) with 0.01° steps and 2 s per step (25 min for the scan). Automatic variable divergence slit was set to 20 mm and the

detector aperture to 59 channels (0.9°). Wide angle XR scattering was recorded between 4° and 90° (2θ) with 0.02° steps and 0.5 s per step (28 min for the scan). Divergence slit was fixed to 0.2° and the detector aperture to 189 channels (2.9°).

Theoretical XRD intensities for Au₂₅ isolated nanoclusters are obtained, within a classical description of the scattering process, using the Debye scattering equation:³

$$I(s) = \sum_m \sum_n f_m f_n \frac{\sin(2\pi s r_{mn})}{2\pi s r_{mn}}$$
$$s = \frac{2 \sin \theta}{\lambda}$$

where n , m are atom indexes, r_{mn} is the magnitude of the distances of each atom from every other atom with f_m and f_n scattering factor, θ is the scattering angle. Atomic positions are taken from the previously reported structure of Au₂₅(SCH₂CH₂Ph)₁₈ crystal.²

X-ray photoelectron spectroscopy (XPS) experiments are carried out on a Kratos Axis Ultra DLD spectrometer using monochromated Al K α X-rays (1486.6 eV, 150 W), a pass energy of 20 eV, a hybrid lens mode and an indium sample holder in ultra-high vacuum ($P < 10^{-9}$ mbar). The analyzed surface area is 700 $\mu\text{m} \times 300 \mu\text{m}$. Charge neutralization is required for all samples. The peaks (Au 4f, S 2p, O 1s, N 1s) are referenced to the C–(C, H) components of the C 1s band at 284.6 eV. Shirley background subtraction and peak decomposition using Gaussian–Lorentzian products are performed with the Vision 2.2.6 Kratos processing program.

The infrared spectra were obtained were carried out on a Bruker Vector 22 FT-IR spectrometer in KBr pellets at room temperature and registered from 4000 cm^{-1} to 400 cm^{-1} .

Transmission electron microscopy (TEM) is carried out on a JEOL 2010 LaB6 microscope operating at 200 kV. To observe individual particles, sample is first dispersed in *N,N*-dimethylformamide (average 0.3 mg per mL), then, one drop of this colloidal solution is dispersed in 3 to 5 mL ethanol and quickly filed on a carbon-coated copper grid. Solvent is then let evaporated at ambient temperature for at least one hour before TEM analysis. To characterize the aggregates of nanoclusters, the same preparation is used but using only EtOH. Sintering of the nanoparticles under the electron beam and formation of bigger gold particles

has been observed. To prevent this growing, the image has to be taken quickly, within a few seconds, on a unexposed area.

N₂ adsorption–desorption isotherms at 77 K were obtained on an ASAP 2010 (Micromeritics) after desorbing the samples at 100 °C for 24 h. Final weight was 22.7 mg. Surface area has been estimated by BET equation.

The UV-vis spectra of solutions were carried out on an Agilent 8453 diode-array spectrophotometer and registered from 300 nm to 900 nm. Spectrophotometer interval is 1.0 nm and integration time is 0.5 s.

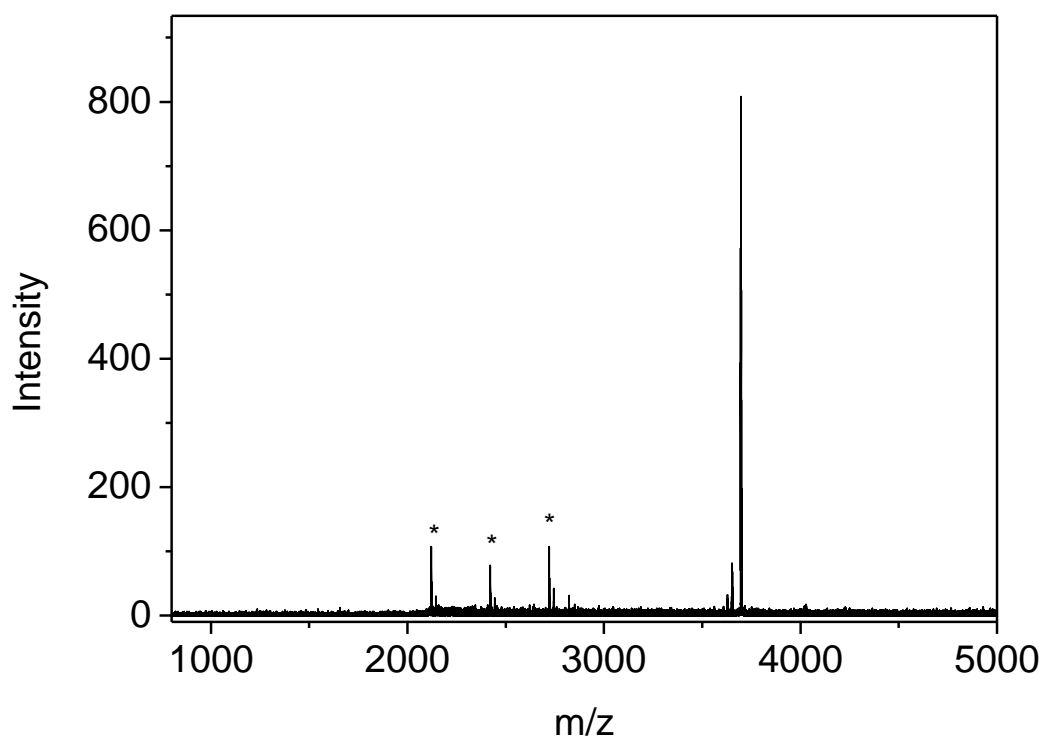


Figure S1. The wide-range ESI mass spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ (main peak at $m/z = 3695.4623$ Th). Peaks marked * correspond to the standard used to calibrate the spectra.

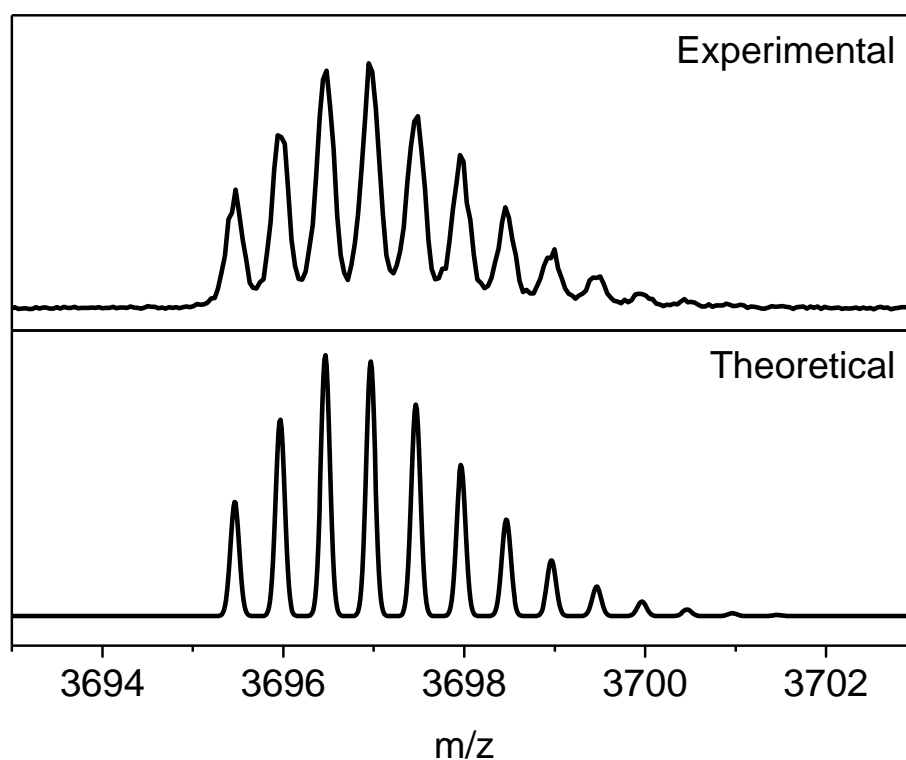


Figure S2. The isotopic pattern of the peak at $m/z = 3695.4623$ Th, corresponding to $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ($m/z_{\text{theoretical}} = 3695.4638$ Th, error = -0.4 ppm), together with the simulated pattern and a resolving power of 15000.

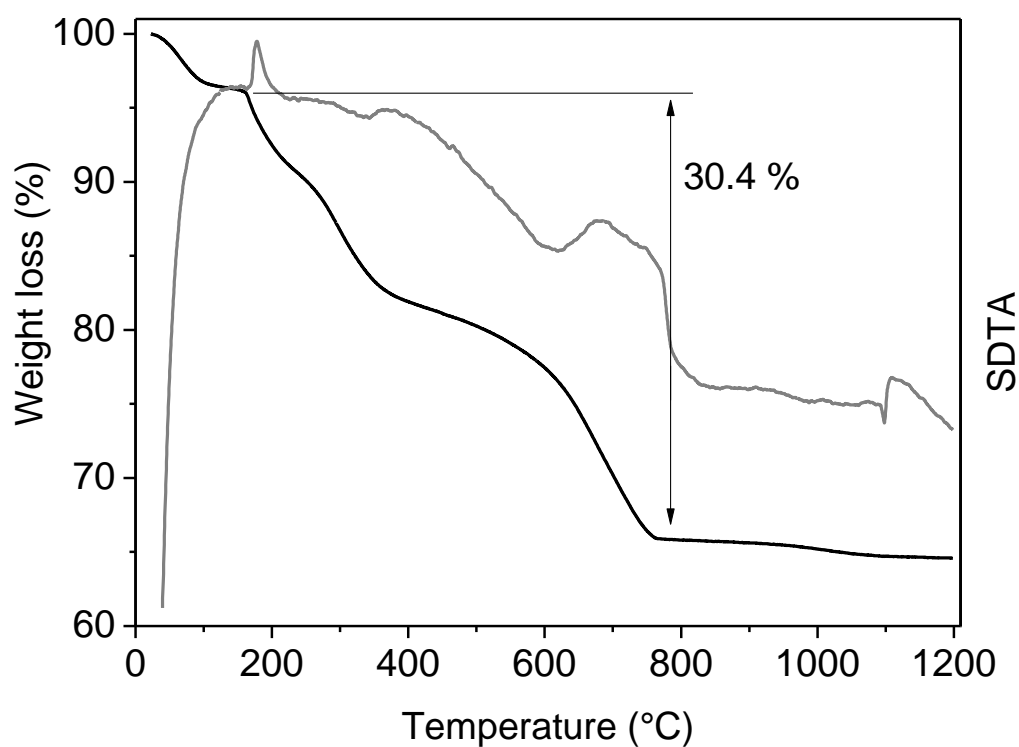


Figure S3. Thermogravimetric (black) and simultaneous differential thermal (grey) analyses of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ carried out under N_2 at $10\text{ }^\circ\text{C}/\text{min}$. Shinning droplets of bulk gold have been observed at the end of the experiment.

Table S1. Elemental analysis of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$:

$\text{Au}_{25}(\text{SPhNH}_2)_{17}\cdot 0.25\text{EtOH}\cdot 0.75\text{H}_2\text{O}$	L / Au	Au (%)	C (%)	H (%)	N (%)	S (%)
Measured	0.66	61.86	16.45	1.51	2.95	6.61
Calculated	0.68	61.94	17.30	2.41	3.00	6.86

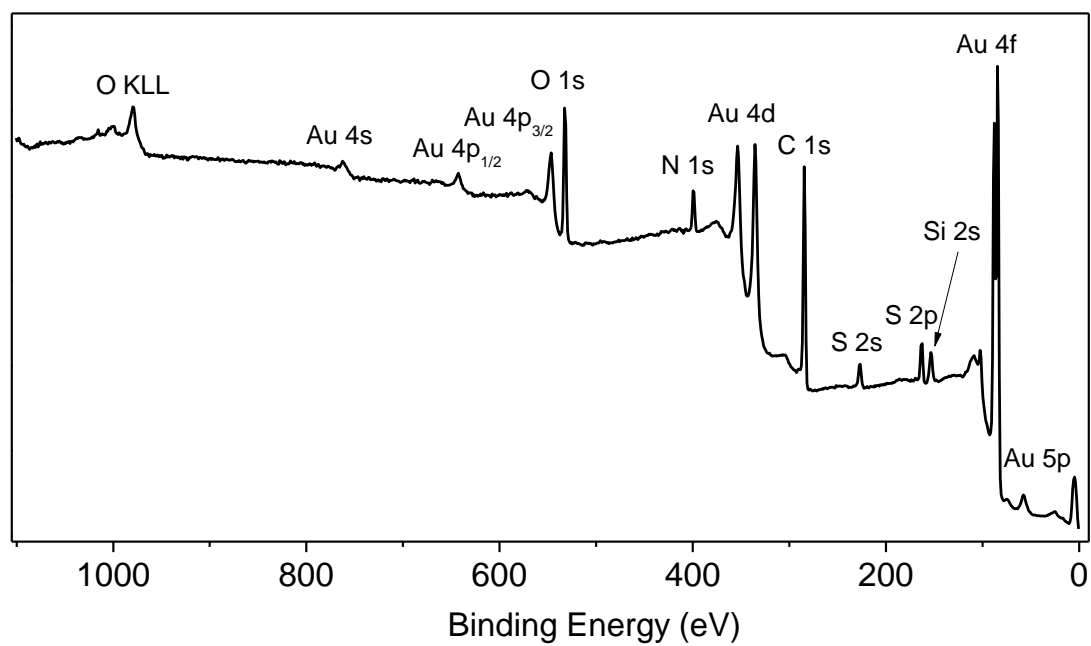


Figure S4. Survey scan of XPS analysis of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ clusters.

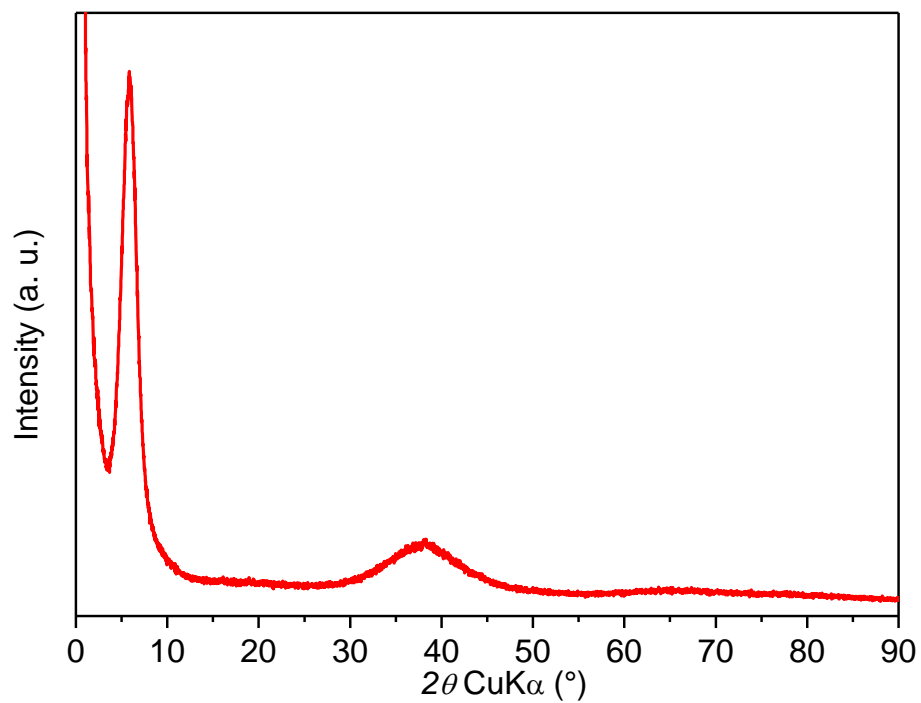


Figure S5. Experimental PXRD patterns of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$.

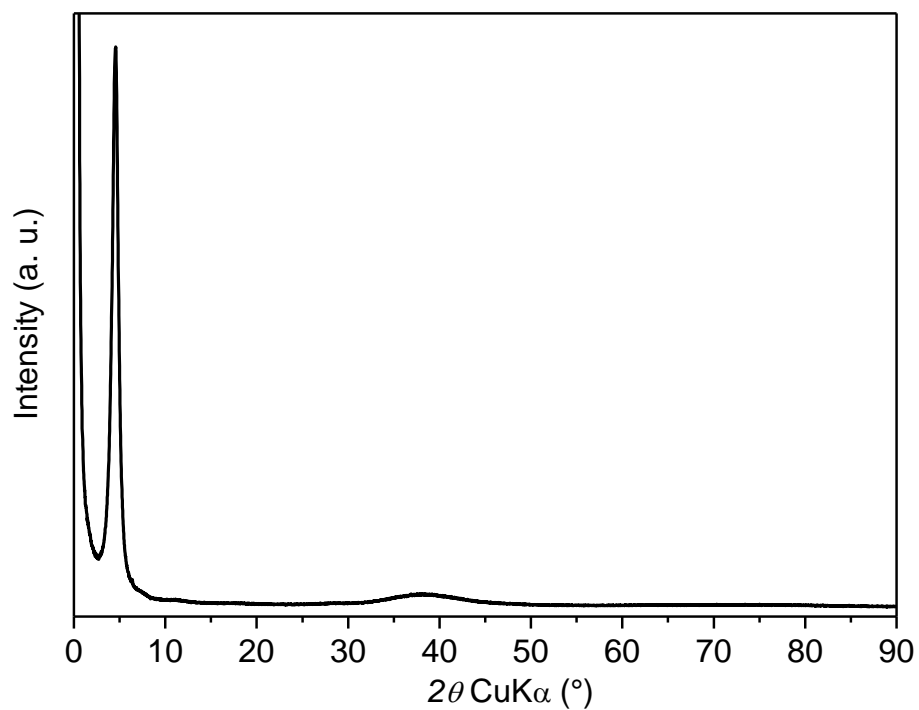


Figure S6. Experimental PXRD patterns of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$.

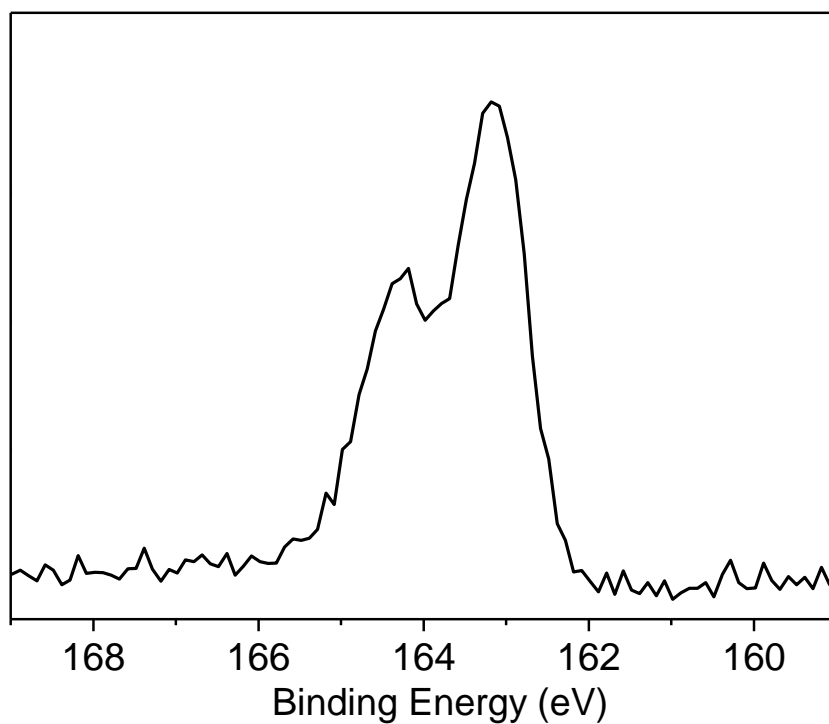


Figure S7. XPS analysis of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ nanoclusters from S_{2p} .

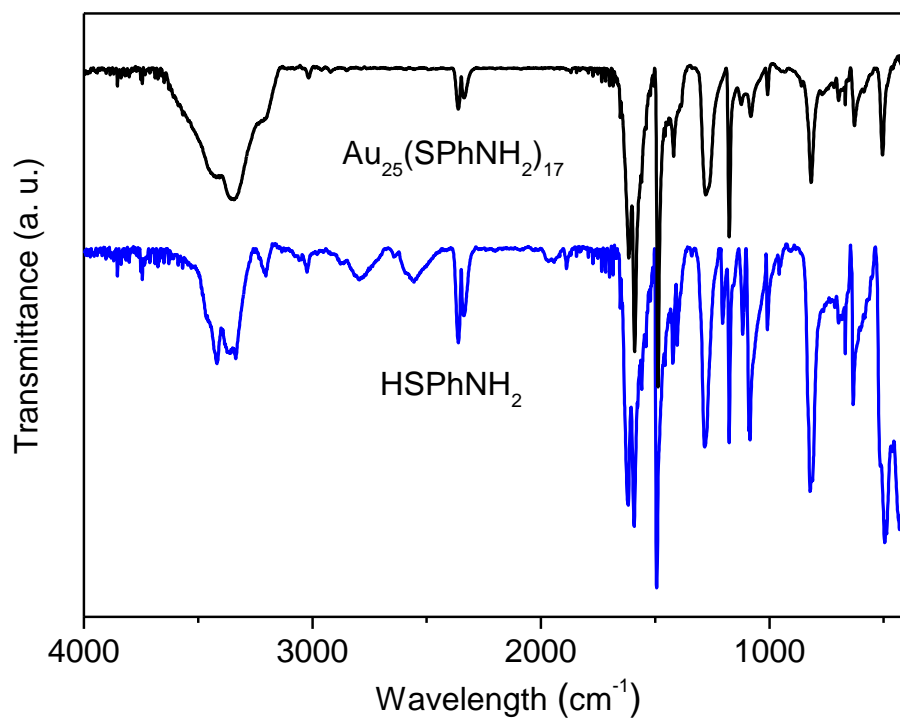


Figure S8. FT-IR spectra of the nanocluster $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ and the free ligand HSPhNH_2 .

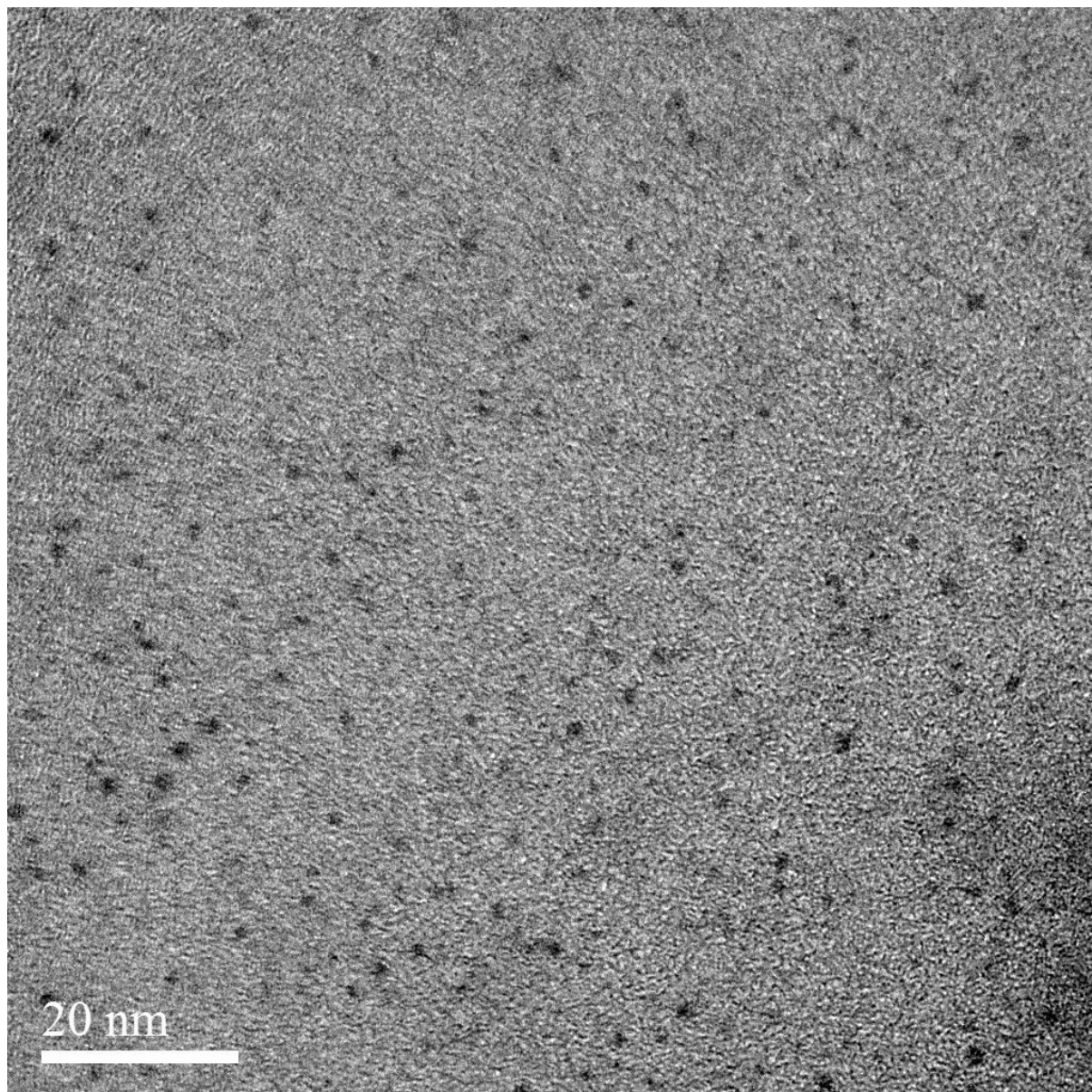


Figure S9. TEM image of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ prepared in DMF. Scale bar represents 20 nm.

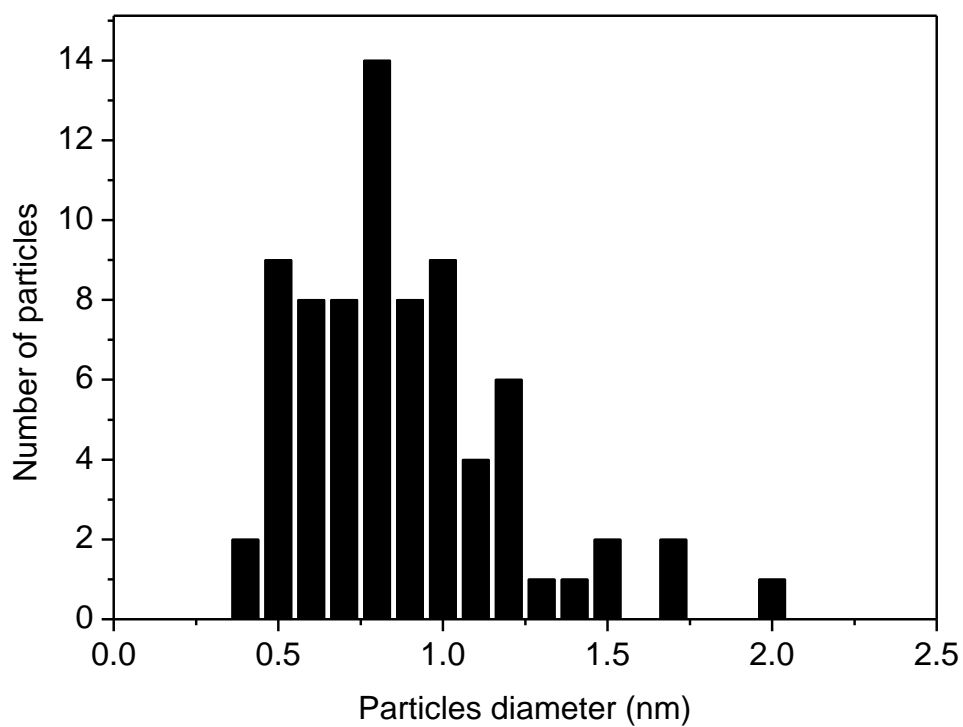


Figure S10. Size distribution from TEM pictures of Au₂₅(SPhNH₂)₁₇ dispersed in DMF. Based on a total of 75 particles the average size is 0.8 ± 0.3 nm.

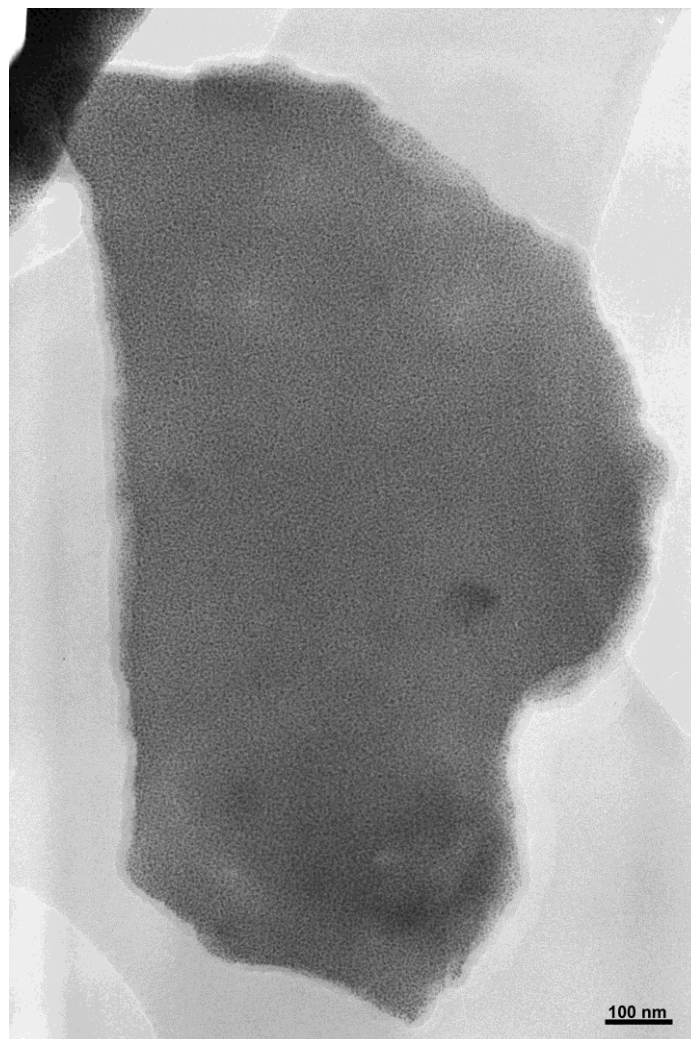


Figure S11. TEM image of $\text{Au}_{25}(\text{SPhNH}_2)_{17}$ prepared in EtOH. Scale bar represents 100 nm.

- (1) Zhu, M.; Lanni, E.; Garg, N.; Bier, M. E.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 1138.
- (2) Zhu, M. Z.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. C. *J. Phys. Chem. C* **2008**, *112*, 14221.
- (3) Dinnebier, R. E.; Billinge, S. J. L. *Powder Diffraction, Theory and Practice*; RSC Publishing: Cambridge, **2008**.