

Supporting Information

Time-resolved Monitoring of Dynamic Self-assembly of Au(I)-thiolates Coordination Polymers

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Experimental details and characterizations

Materials. All of the chemicals are commercially available and used without further purification. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, AR grade) was purchased from Shenyang Jinke reagent company, 3-mercaptopropionic acid ($\text{MPA} \geq 99\%$) from Alfa Aesar Company, citric acid ($\geq 99.5\%$) from Tianjin Bodi reagent company, Sodium hydroxide ($\geq 96\%$) and hydrochloric acid (36-38 wt%) from Beijing reagent company. Sodium 3-mercaptopropionate (MPA-Na) was obtained by 1:1 molar ratio neutralization of MPA with NaOH. CA-Na was obtained by 1:3 molar ratio neutralization of citric acid with NaOH. Water was purified by a Milli-Q system.

Preparation and purification methods. All of glass flasks and burettes were cleaned thoroughly with aqua regia before use.

Bulky Au(I)-MPA lamellar structures: HAuCl_4 in aqueous solution (0.2 mL, 0.05 M) was first of all added to 20 mL of water in an Erlenmeyer flask and heated to boil on a hot plate, then MPA-Na aqueous solution (0.8 mL, 0.05 M) was injected, generating white precipitates immediately. The mixture was allowed to boil for another 5 min to complete the reaction. The products were purified by centrifugation to remove the residues before characterization.

Nanosized Au-MPA lamellar structures: The preparation and purification procedure for nanosized structures was the same as those for bulky counterpart, except that CA-Na aqueous solution (1 mL, 0.05 M) was mixed with MPA-Na aqueous solution (0.8 mL, 0.05M), before being injected into the HAuCl_4 solution. The products were in a colloidal solution.

Monitoring the assembly: HAuCl_4 aqueous solution (0.5 mL, 0.05 M) was added to 50 mL water in an Erlenmeyer flask and heated to 80 °C in a water bath. A mixed solution of MPA-Na (2 mL, 0.05 M) and CA-Na (2.5 mL, 0.05 M) was injected into the above solution and maintained at 80 °C for 20 min. Then, the reaction was brought quickly to boil on a hot plate for 7 minutes. A volume of 0.25 mL of sample was taken out timely for measurements of UV-Vis absorption spectra, TEM and AFM images.

Control the reversible assembly: Nanosized Au-MPA lamellar structures were first of all prepared with the same recipe and procedure as before, except that the reaction system was 2.5 times larger. Then, NaOH (0.5 M) and HCl (~0.5 M) were added at boiling temperature to adjust the pH to desired values. 1 mL - 2 mL sample was taken out at different intervals of time for measurements of UV-Vis absorption spectra and TEM images.

Characterizations: UV-Vis absorption spectra were measured using a Shimadzu UV-Vis 2550 spectrophotometer (wavelength resolution: 0.1 nm) with 1 cm light path cuvettes, utilizing Mili-Q water as reference. The scan step is set as 1 nm.

Infrared spectra were recorded on a VERTEX 80/80v spectrometer using the KBr method.

XPS Measurements were carried out at 15 kV and 17 mA, using a Thermo ESCALAB 250 spectrometer with a twin-anode Al K α (1486.6 eV) X-ray source.

Transmission electron microscopy (TEM) images were obtained using a JEOL-2010 electron microscope operating at 200 kV. Samples were deposited onto carbon-coated copper grids for measurements.

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM 6700F electron microscope operating at 200 kV. Samples were deposited onto silicon wafers for measurements.

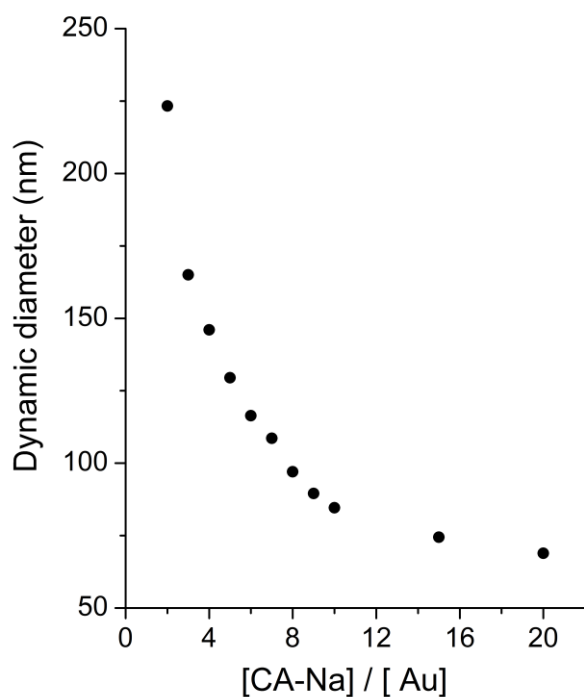
Atomic force microscopy (AFM) imaging in solution was carried out on a NanoWizardII BioAFM (JPK instrument AG, Berlin, Germany). Samples were electrostatically adsorbed on silica wafers modified with an amino-terminated silane coupling agent. The probe is NP-S10 from Bruker, tip radius: 10 nm (nom), 40 nm (max); resonant frequency: 40-75 kHz; spring constant: 0.58 N/m. Because the size of the probe is much larger than the diameter of the strings (TEM), the width of the strings measured by such probes appears much larger than it is, and the height information is used to determine the diameter of the strings in solution.

XRD data was collected with a Rigaku D-Max 2550 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Tube voltage and current were 50 kV and 200 mA, respectively; scan range (2θ) was from 3.0° to 70.0° , scan step was 0.02° .

Dynamic light scattering (DLS) data were measured with a Malvern Zetasizer-nano ZS light scattering particle size distribution analyzer.

Thermogravimetric analyses were carried out on a NETZSCHSTA 449C thermogravimetric analyzer with a heating rate of 2°C min^{-1} from 25°C to 600°C in an air atmosphere.

(a)



(b)

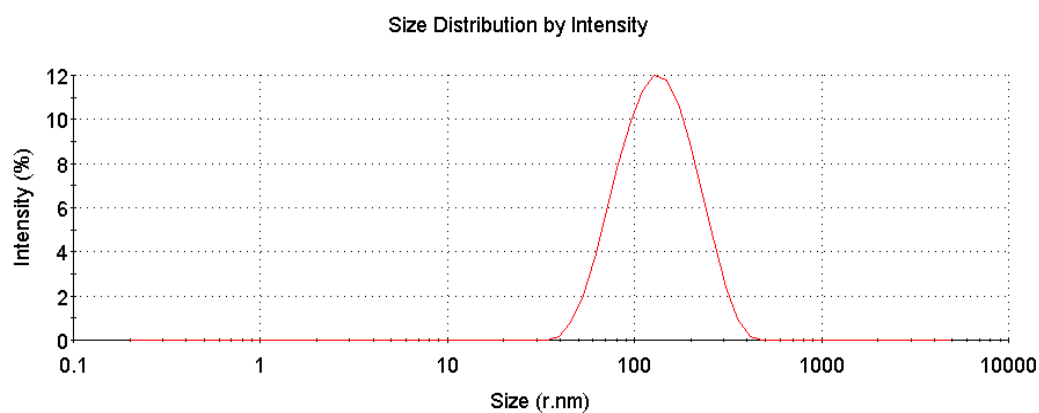


Fig. S1 (a) Variation of the dynamic diameter of the products with the ratio of CA-Na to Au, [Au]= 0.005 M, [MPA-Na]= 0.02 M. (b) DLS result for a typical nanosized sample prepared with CA-Na:MPA-Na: Au=5:4:1, [Au]= 0.005 M which shows the average hydrodynamic diameter at 110 nm, there is about 10 nm deviation from batch to batch synthesis.

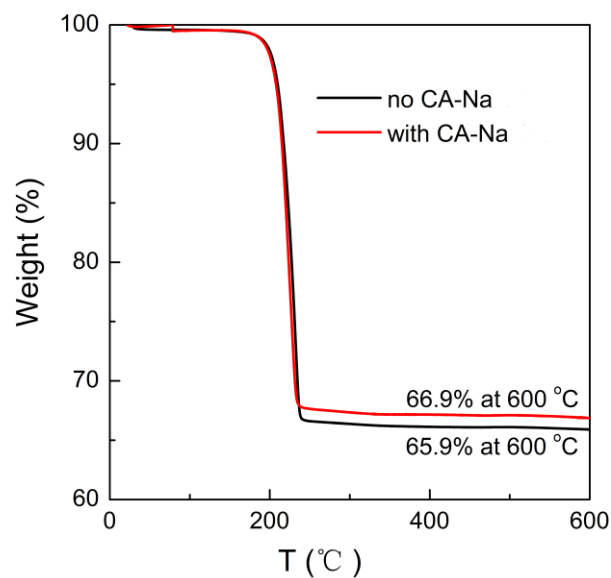


Fig. S2 TGA results for Au(I)-MPA assemblies prepared in presence or absence of CA-Na. The theoretical remaining weight for $(\text{Au(I)-SC}_2\text{H}_4\text{COOH})_n$ is 65.2% assuming only Au is left. The little difference in weight loss results from the very small proportional replacement of H^+ in MPA with Na^+ , which is below the detection limit of XPS.

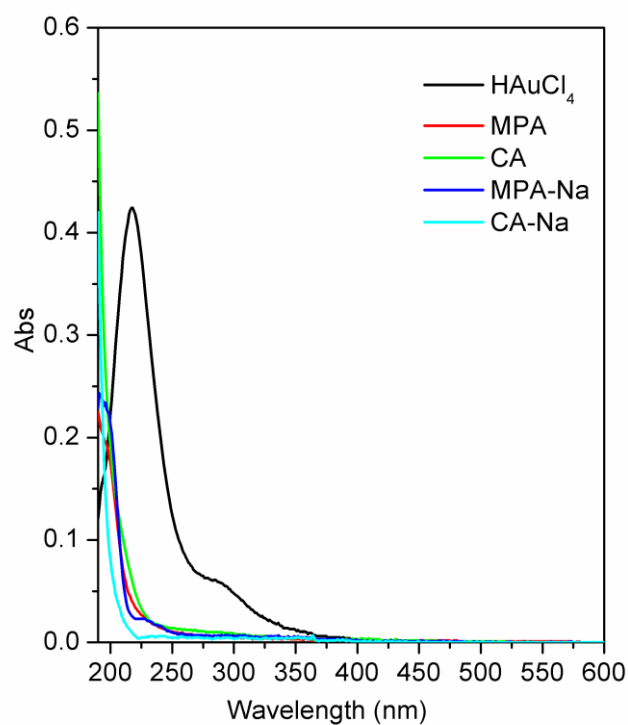


Fig. S3 UV-Vis absorption spectra of reactants of HAuCl₄, MPA, CA, MPA-Na and CA-Na.

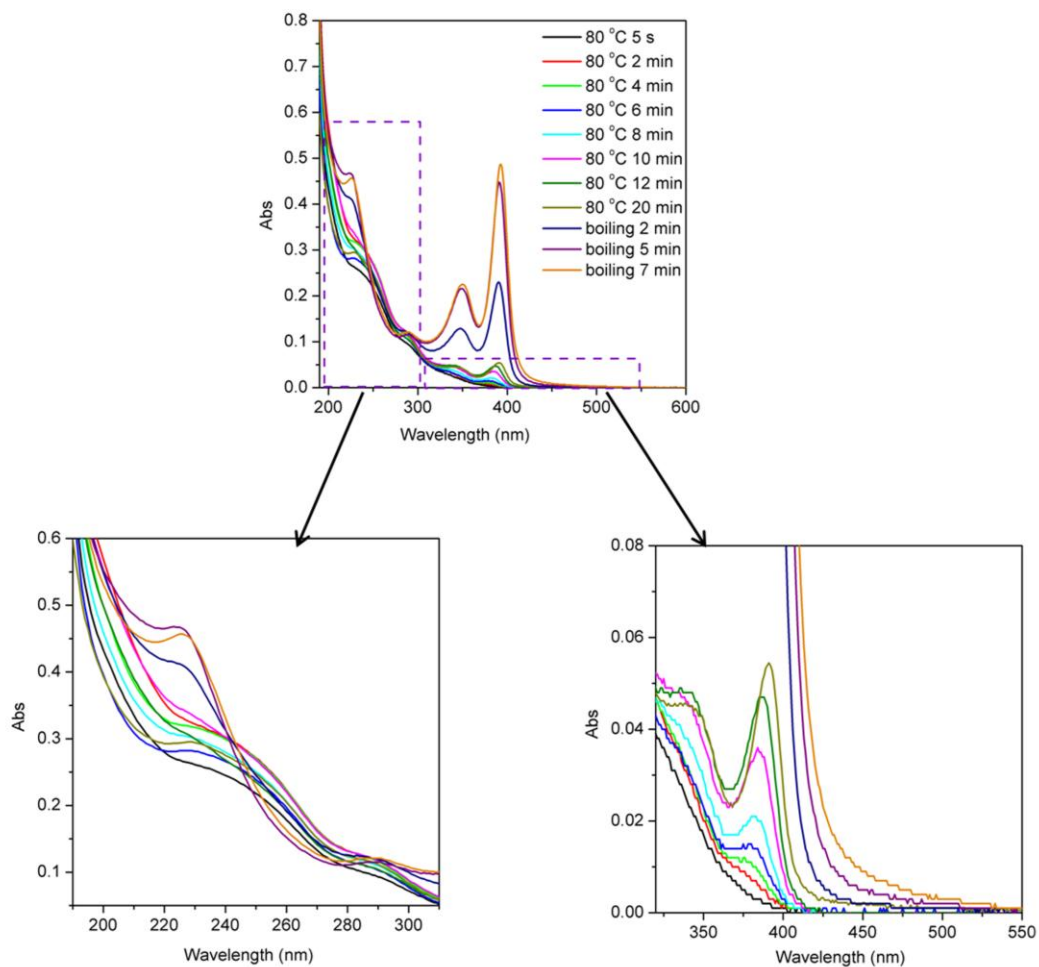


Fig. S4 UV-Vis absorption spectroscopic monitoring of the assembly of Au(I)-MPA CP right after adding the mixture of MPA-Na and CA-Na to Au(III) solution at 80 °C and then brought to boiling temperature quickly.

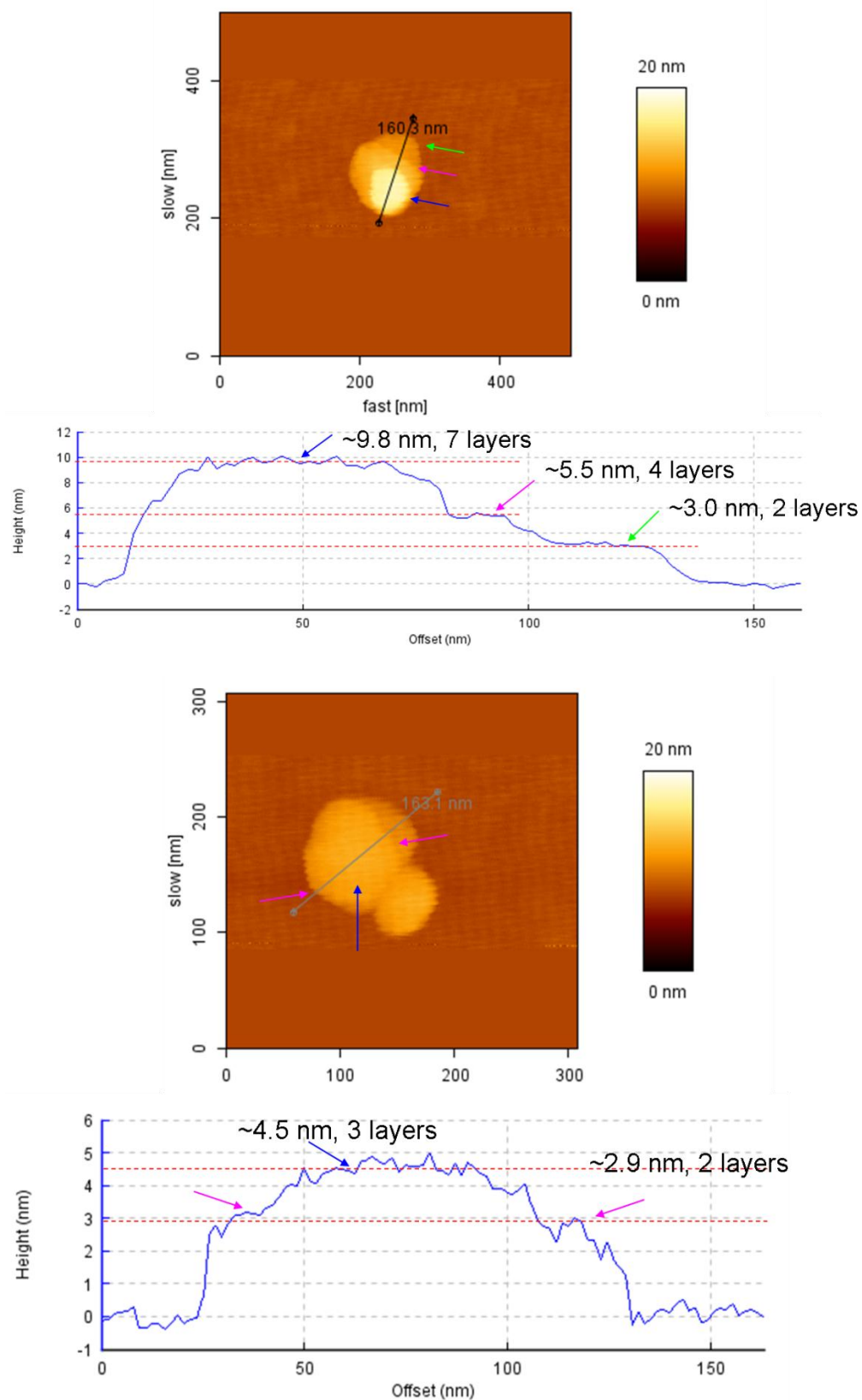


Fig. S5 AFM images and height diagrams of the nanosized Au(I)-MPA lamellar structures. The height of a single layer is about 1.4-1.5 nm.

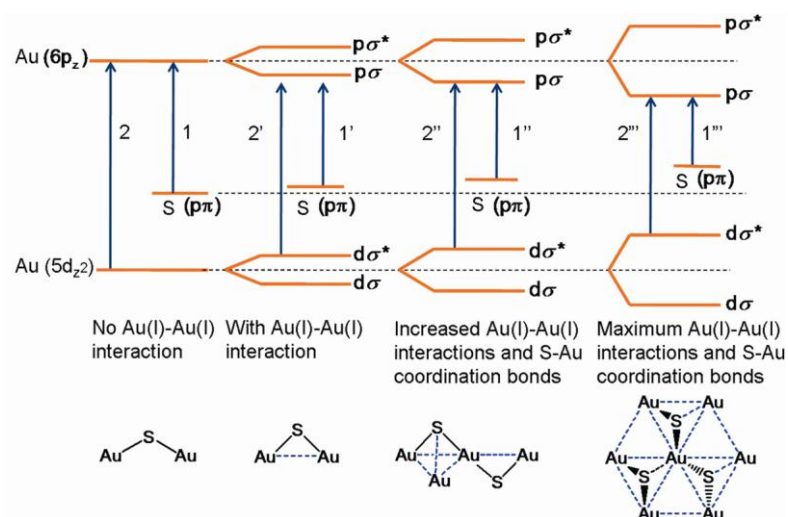


Fig. S6 Diagram of electronic orbits for Au(I)-thiolates affected by some typical forms of Au(I)-Au(I) interaction and S-Au coordination, and the resulted LMCT (1) and MCCT (2) transitions, substituent groups on S are omitted in the illustration, dash lines indicates the Au(I)-Au(I) interactions and additional S-Au coordination bonds.^{1,2}

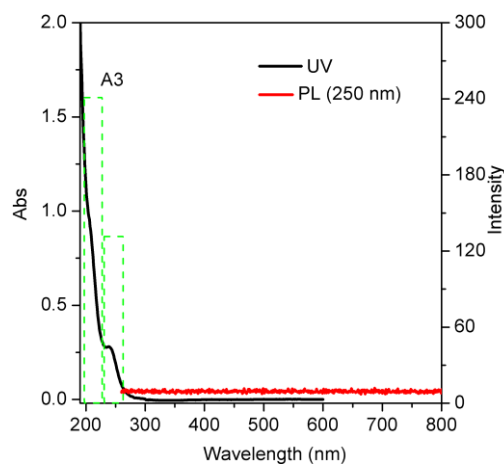


Fig. S7 UV-Vis absorption spectrum and photoemission spectrum of Au(I)-MPA CPs at pH value of 12.05 with absorption in A3 region. The sample does not have photoemission, indicating there are no Au(I)-Au(I) interactions in this sample.

References:

- 1 R. P. Briñas, M. Hu, L. Qian, E. S. Lyman, J. F. Hainfeld, *J. Am. Chem. Soc.* 2008, **130**, 975-982.
- 2 J. M. Forward, D. Bohmann, J. P. Fackler Jr, R. J. Staples, *Inorg. Chem.* 1995, **34**, 6330-6336.