- Electronic Supplementary Information -

Controllable Oligomerization: Defying Step-Growth Kinetics in the Polymerization of Gold Nanoparticles

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Materials

All chemical reagents were used without further purification. Hydrogen tetrachloroaurate (III) hydrate, 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; amphiphilic diblock copolymer polystyrene-*block*-poly(acrylic acid) (PS_{154}-*b*-PAA_{49}, Mn = 16000 for the PS block and Mn = 3500 for the PAA block, Mw/Mn = 1.15) and thiol-terminated polystyrene (PS-SH, Mn = 2000) were purchased from Polymer Source, Inc. Hydrochloric acid was purchased from P. P. Chemicals Sdn Bhd. Sodium hydroxide was purchased from Sinopharm Chemical Reagent Co. ltd; Deionized water (resistance > 18.2 MΩ/cm) was used in all reactions. All other chemicals were purchased from Sigma Aldrich. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing Zhongjingkeyi Technology Co., Ltd.. $(NH_4)_6Mo_7O_{24}$ was used as negative stain (3.4 mM) in all TEM images reported in this study.

Methods

Characterization. TEM images were collected from a HT7700 Transmission Electron Microscopy operated at 100 kV and a Talos L120C model operated at 120 kV. SEM images were collected from a Quanta 250 FEG Scanning Transmission Electron Microscopy operated at 30 kV. UV-Vis spectra were collected on a Lambd 750 UV-Vis spectrophotometer. Raman spectra were collected from colloidal nanoparticle samples in a cuvette (path length = 1.00 cm) on a PEK-785 spectrometer (PeakerSeeker^{TM}) using Red light-emitting diode (LED) laser (λ = 785 nm) at 290 mW.

Encapsulation of AuNPs with PSPAA shells. The method used here was based on our previous report with minor modifications. 3 mL AuNP solution (d_{Au} = 17 nm) were concentrated to ~ 10 μL by centrifugation at 16000 *g* for 15 min. The deep red solution collected at the bottom of the eppendorf tubes was diluted with H_2O (180 μL). Then the mixture was added into 730 μL DMF solution containing PS_{154}-*b*-PAA_{49} (80 μL, 8 mg/mL in DMF). Finally, thiol-terminated polystyrene (40 μL, 2 mg/mL in DMF) was added to the mixture. The mixture was heated at 110 ^{o}C for 2 h and then allowed to slowly cool down till room temperature.

When using 2-naphthalenethiol (ligand **2**) or 1-dodecanethiol (ligand **3**) as ligands, the deep red suspension (~ 6 μL) collected at the bottom of the eppendorf tube was dispersed into 720 μL

DMF, and the ligand 2-naphthalenethiol in DMF (30 μL, 3 mg/mL) or 1-dodecanethiol in DMF (40 μL, 2 mg/mL) was added. The mixture was then incubated at 60 °C for 2 h. After that, 80 μL PS_{154}-b-PAA_{49} (8 mg/mL in DMF) and 180 μL H_2O were added in sequence. The mixture was further heated to 110 °C for 2 h and then allowed to slowly cool down in the oil bath till room temperature.

Self-assembly of AuNP@PSPAA into dimers. The synthetic method is based on our previous report. The as-prepared AuNP@PSPAA were diluted (600 μL diluted by 8.4 mL water), divided into individual eppendorf tubes, and then centrifuged at 16000 *g* for 30 min to remove the supernatant. The final concentrated solution (~ 25 μL) contained the desired AuNP@PSPAA monomers, DMF and empty PSPAA micelles. After purification via centrifugation, the concentrated AuNP@PSPAA were dispersed into a DMF/H_2O solution (1 mL, $V_{DMF}/V_{H2O} = 6:1$). HCl (5 μL, 1 M) was then added into the solution, and the final concentration is $[HCl]_{final} = 5$ mM. The mixture was incubated at 60 °C for 2 h to facilitate the shape transformation of PSPAA polymer shell.

Purification of dimers. The resulting solution contained aggregates of AuNPs, monomers, empty PSPAA micelles, DMF and acid. To isolate the AuNP clusters from the excess reactants, the product solution was diluted (100 μL diluted by 1.4 mL NaOH (pH = 10)), divided into individual eppendorf tubes, and then centrifuged at 14000 *g* for 20 min to remove the supernatant. The red solution at the bottom of eppendorf tube was diluted by NaOH (pH = 10) aqueous solution.

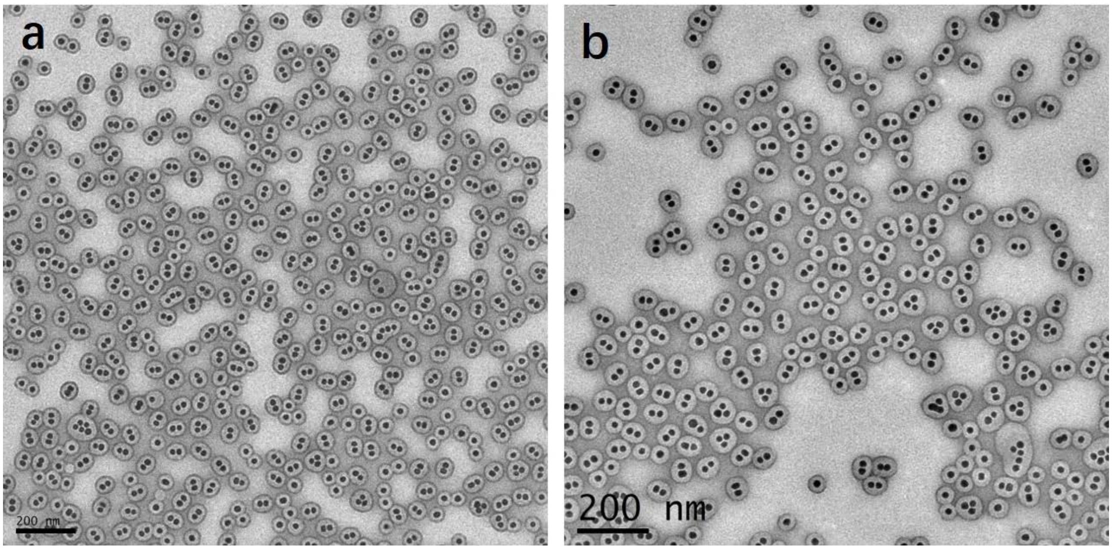

Figure S1 TEM images of the as-synthesized dimers when thiol-terminated polystyrene (ligand **1**) was used as ligand.

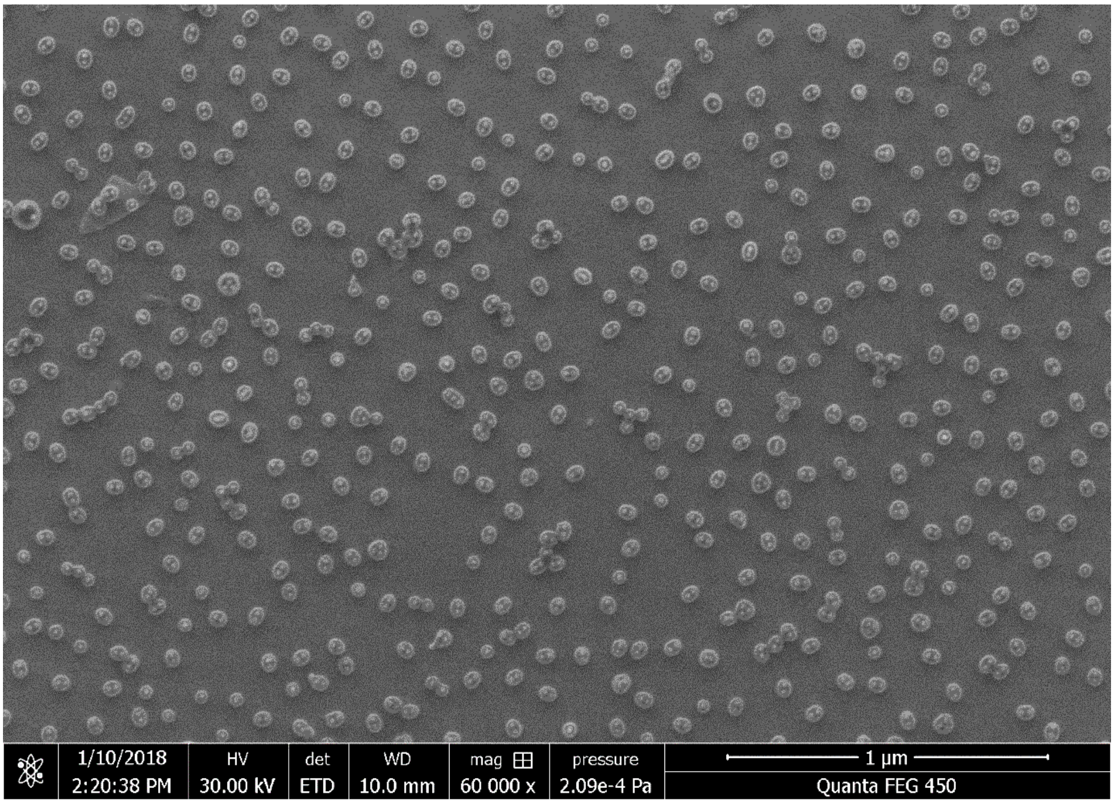

Figure S2 SEM image of the as-synthesized dimers when thiol-terminated polystyrene (ligand **1**) was used as ligand.

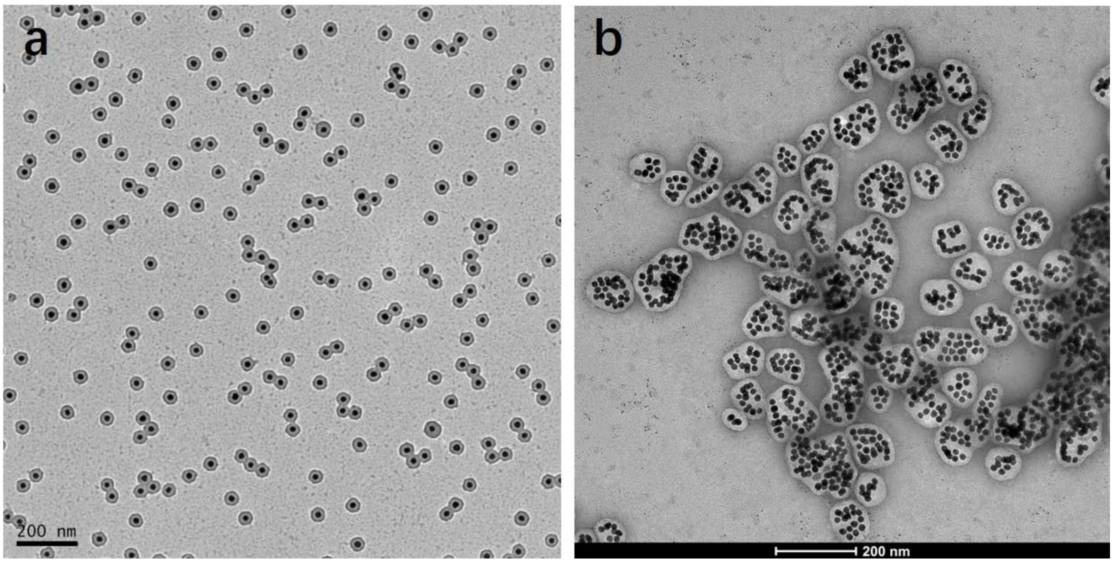

Figure S3 TEM showing the different aggregates of AuNP@PSPAA obtained at different temperatures: a) 25ºC; and b) 95ºC, respectively.

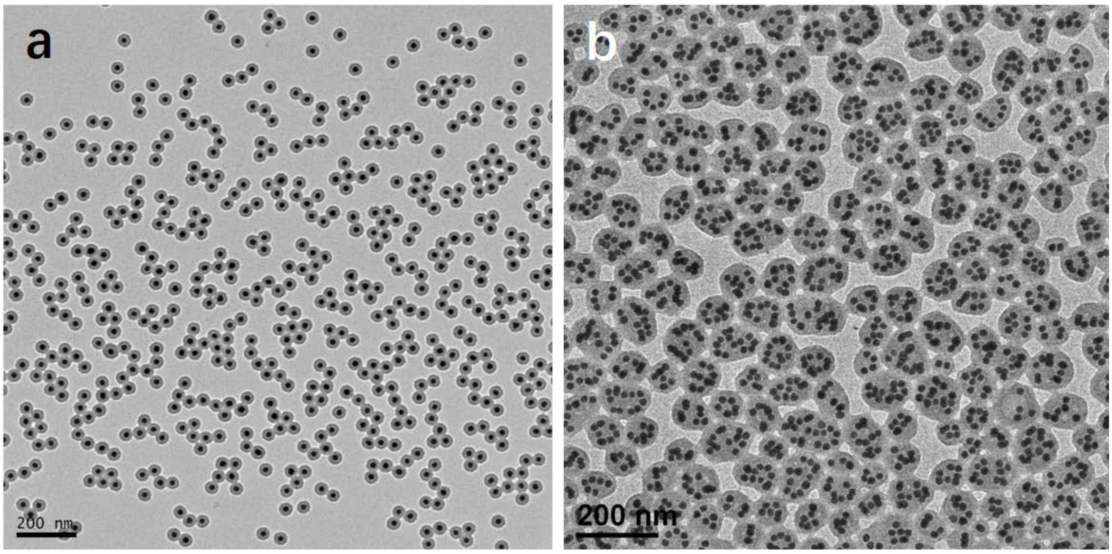

Figure S4 TEM showing the different aggregates of AuNP@PSPAA obtained at different concentration acid: a) [HCl] = 0 mM; and b) [HCl] = 10 mM.

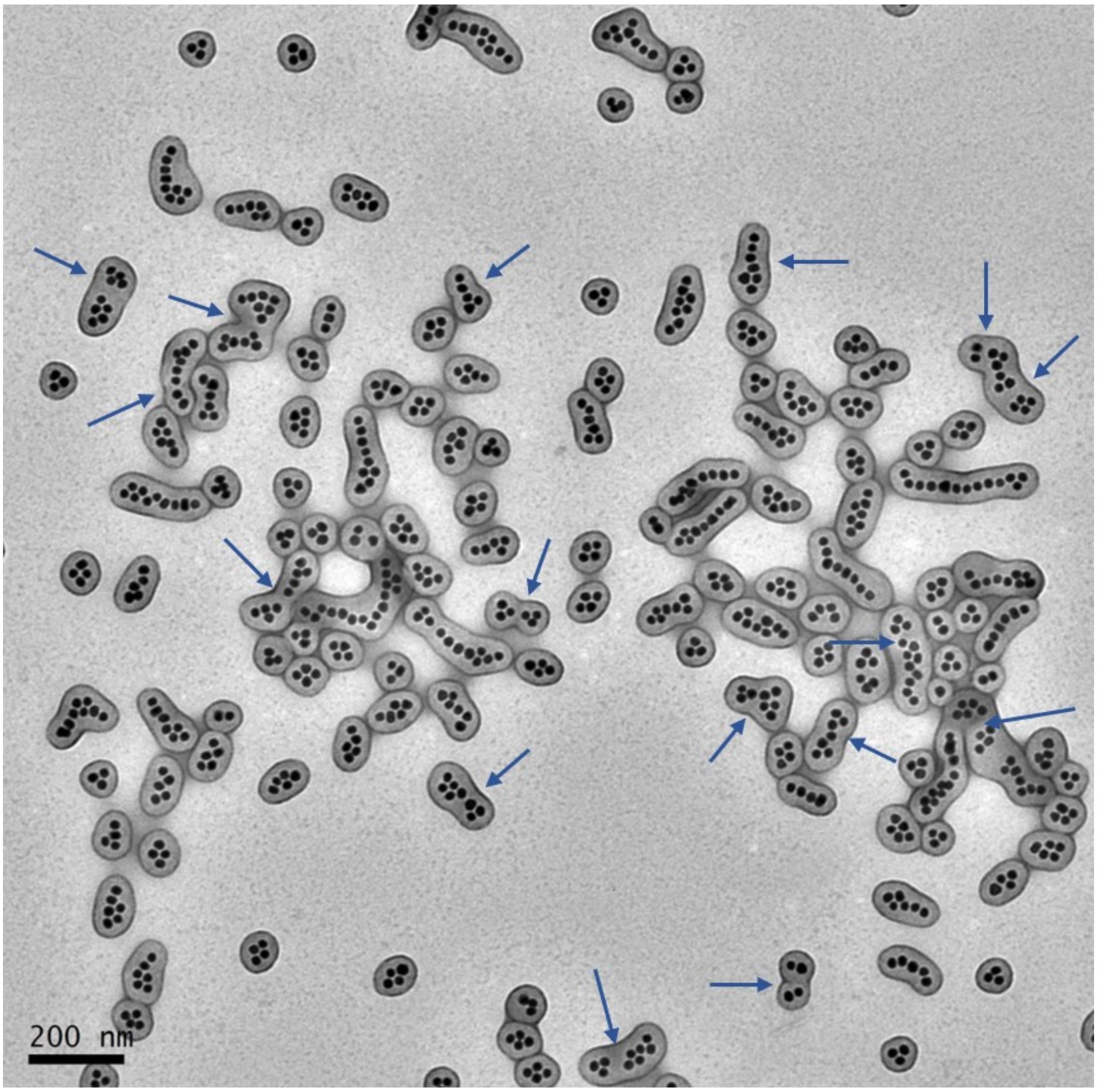

Figure S5 TEM showing the different aggregates of AuNP@PSPAA obtained at V_{DMF}/V_{H2O} = 3:1.

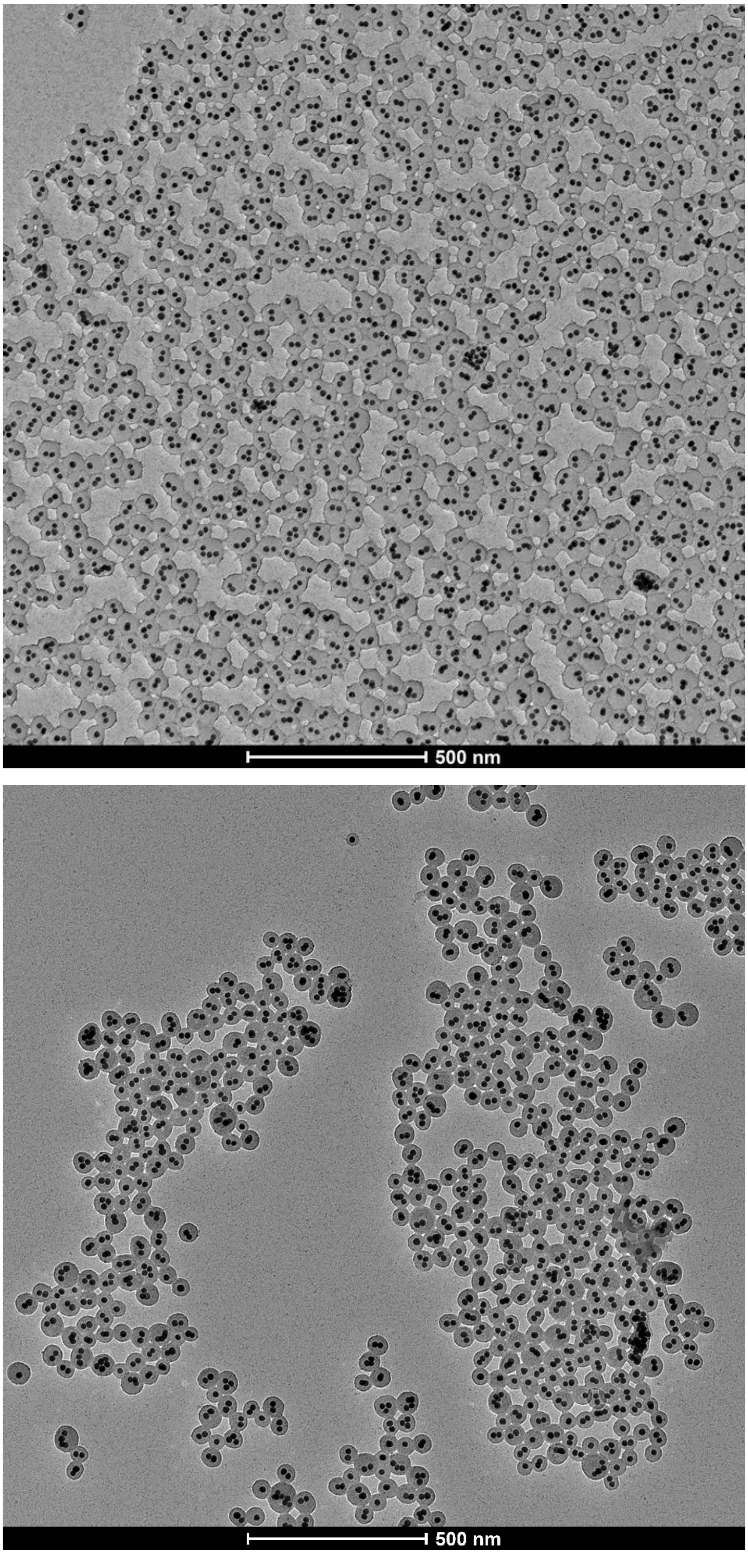

Figure S6 TEM showing dimers were obtained when using 2-naphthalenethiol (ligand **2**) as ligand.

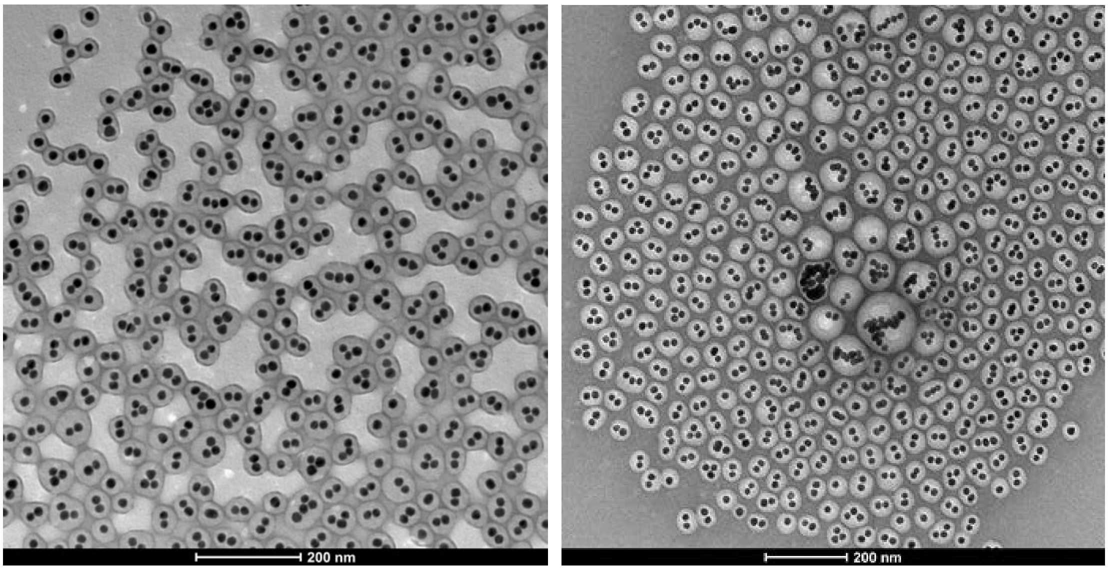

Figure S7 TEM images showing dimers were obtained when using 1-dodecanethiol (ligand **3**) as ligand.

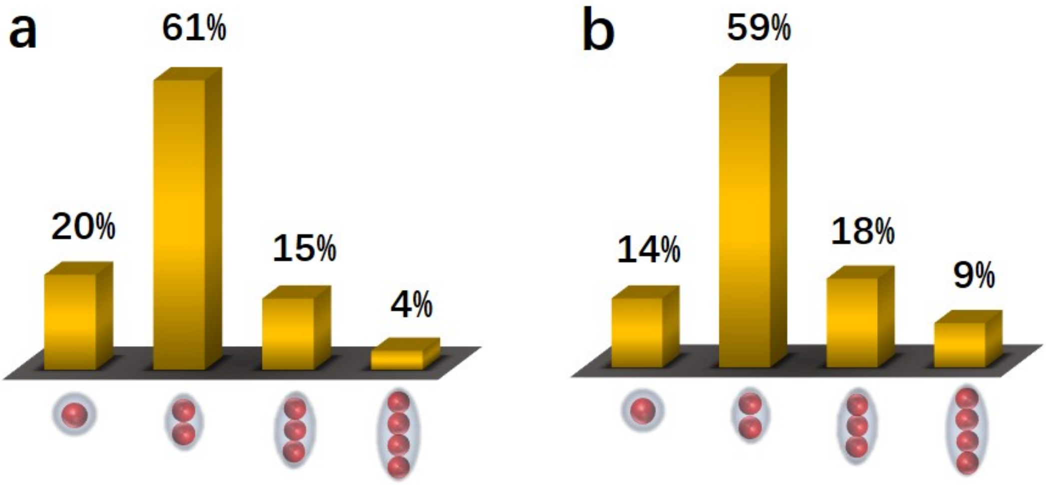

Figure S8 The histograms of the sample a) Figure 4a and S6; b) Figure 4b and S7.

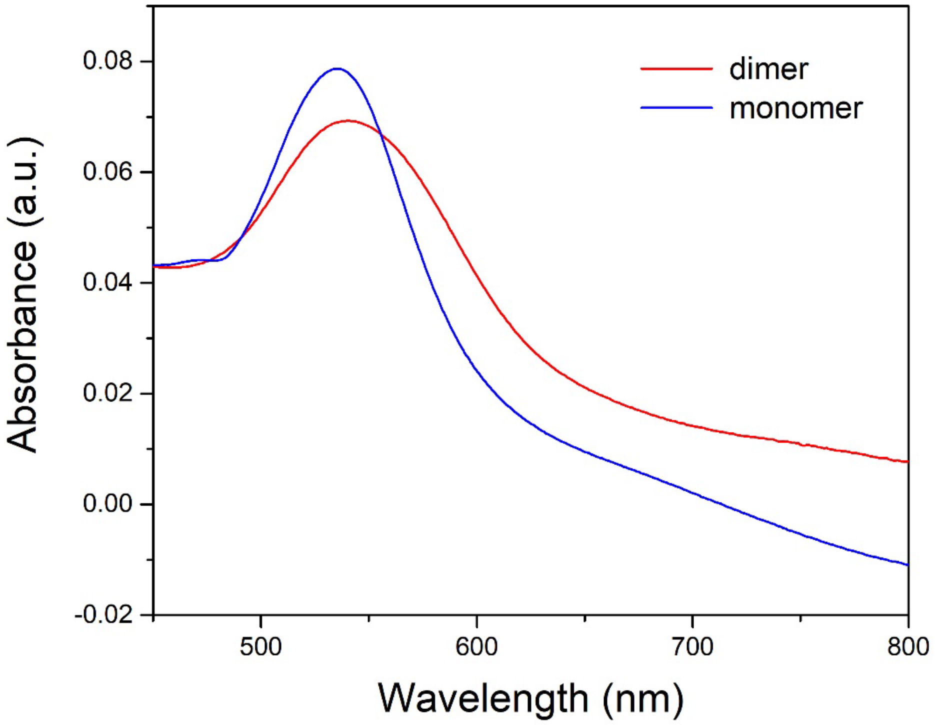

Figure S9 UV-vis spectra of the purified monomer and dimer, when using 1-dodecanethiol (ligand **3**) as ligand.

Table S1 Repeatability survey of AuNP aggregates shown in Figure 2b and c.

Sample	$AuNP_1$%	$AuNP_2$%	$AuNP_3$%	$AuNP_{4+}$%
1	34.0	62.0	2.6	1.4
2	27.5	66.7	4.6	1.2
3	28.8	68.1	2.7	0.4

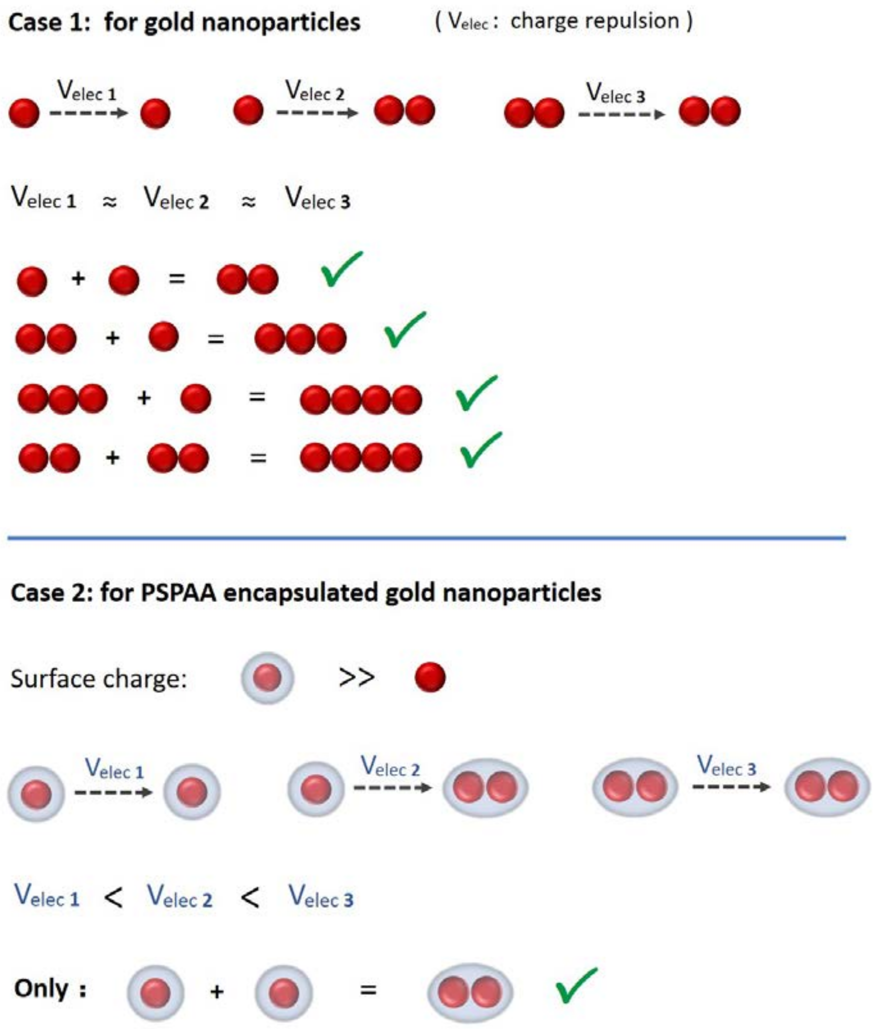

Figure S10 Schematic illustrating the mechanistic causality of oligomerization.