pH-programmable self-assembly of plasmonic nanoparticles: hydrophobic interaction *verse* static electronic repulsion

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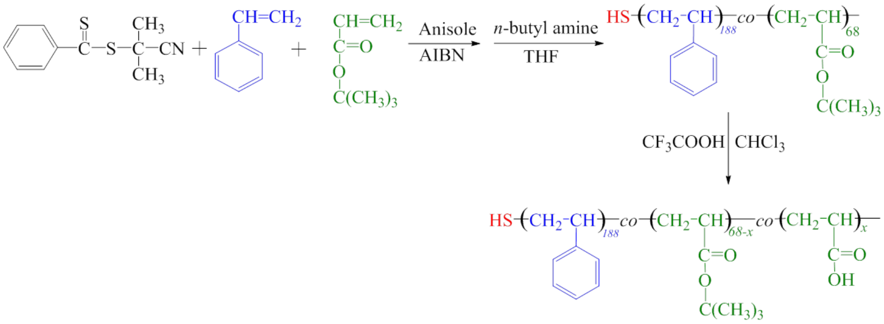
1. Materials

Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, >99.9%), cetyltrimethylammonium bromide (CTAB, 99%), ascorbic acid, sodium borohydride ($NaBH_4$, >99%), trisodium citrate, and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. *tert*-Butyl acrylate (98%) and styrene (99%) were passed through a basic aluminum oxide column prior to use. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The RAFT chain transfer agent (CTA), 2-(2-cyanopropyl) dithiobenzoate (CPDB), was prepared according to the previous reported method.[1] Deionized water (High-Q, Inc. 103S Stills) with resistivity of >10.0 MΩ was used in all experiments. The pH values of the solution were adjusted by adding either a standard 1.0 M of KOH solution or 1.0 M of HCl solution, both calibrated by a pH meter.

2. Polymer synthesis and characterizations



Scheme S1. The synthetic route of thiol-terminated PSt_{188}-*co*-P(tBA_{1-x}-*co*-AA_x)$_{68}$.

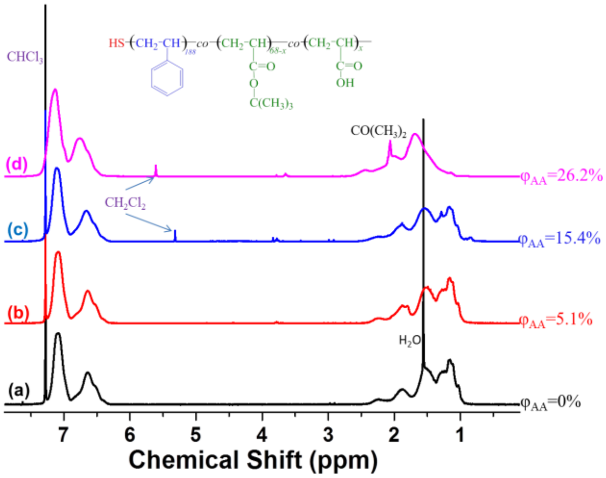


Figure S1. ^1H NMR spectra of P1/P3/P5/P7 in $CDCl_3$ to monitor the different hydrolysis degree of the *tert*-butyl esters using TFA at room temperature. (a) φ_{AA} = 0% (P1), (b) φ_{AA} = 5.1% (P3), (c) φ_{AA} = 15.4% (P5) and (d) φ_{AA} = 26.6% (P7) in D_6-acetone. *Note that*, P7 (d) is insoluble in $CDCl_3$.

3. Synthesis, surface modification and self-assembly of AuNPs

3.1 Synthesis of AuNPs

The glassware for AuNP synthesis were cleaned by aqua regia and rinsed with deionized water prior to all experiments. AuNPs with size of 8.5±0.7 nm were synthesized by seeding growth approach.[2] To prepare the seed solution of AuNPs, 4.9 mg of $HAuCl_4$ (0.014 mmol) and 3.7 mg of sodium citrate (0.013 mmol) were first dissolved in a 100 mL of aqueous solution. 1.5 mL of ice-cold, freshly prepared 0.1 mol/L of $NaBH_4$ (0.15 mmol) solution was quickly injected into the solution under strong stirring. The seed solution was stirred for an additional 2 hr. For 8.5±0.7 nm AuNP, the growth solution was prepared by mixing 144 mL of a 0.2 M CTAB (10.48 g) solution was mixed with 9 mL of a $HAuCl_4$ aqueous solution 10 mM (30.6 mg). To the above solution, 2.4 mL of ascorbic acid solution (0.1 M, 42.2 mg) was added dropwise and the dark yellow solution turned colorless. Finally, 75 mL of a 2-hour-aged seed solution of AuNPs was added to the above growth solution. After growth for 3 hr, AuNPs with size of 8.5±0.7 nm were obtained.

AuNPs with size of 15.1±1.0 nm were synthesized by the previously reported citrate reduction method.[3] Briefly, a 10 mg of $HAuCl_4$ was dissolved in 100 mL of deionized water and heated to boiling under stirring. A 3 mL of sodium citrate (1 wt %) aqueous solution was then quickly added in the above solution. After refluxed for 30 min, AuNPs with size of 15.1 ± 1.0 nm were obtained.

To synthesize AuNPs with a size of 29.6 ± 2.8 nm,[4] initially, AuNPs with size of 15.1±1.0 nm were used as seeds. 30 mg of $HAuCl_4$ was dissolved in 500 mL of deionized water heated to boiling under constant stirring. A 1 mL aqueous solution of sodium citrate (0.349 M, 90 mg) (9 wt%) was then quickly added to the above solution. The solution was refluxed for 30 min, and then the solution temperature was decreased to 85 ^{o}C. Another 1 mL of sodium citrate (0.349 M, 90 mg) (9 wt %) was added, followed by 1 mL of $HAuCl_4$ solution (0.088 M, 30 mg) (3 wt. %). These additions were repeated every 15 minutes until the total mass of $HAuCl_4$ and sodium citrate was 210 mg and 630 mg, respectively.

3.2 Calculation of the polymer grafting densities on AuNPs

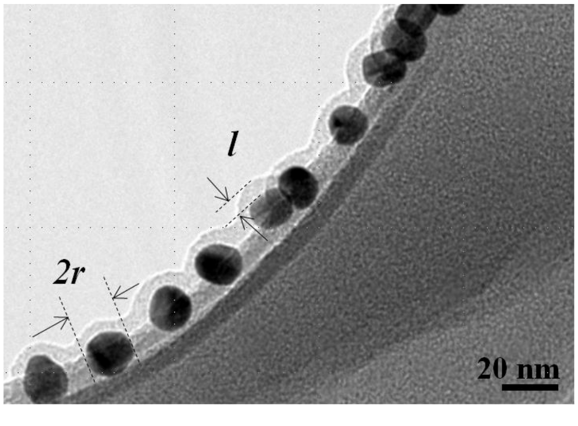


Figure S2. High-magnification TEM image of AuNP-15-P5. TEM grid coated with ultrathin carbon film supported by a lacey carbon film was used to enhance the contrast of polymer shell. As marked in the Figure, 2*r* is the diameter of AuNPs and *l* is the thickness of polymer shell.

From TEM image of P5-grafted AuNPs (Fig S2), we measured the average thickness of the spherical polymer shells (*l*) as well as the diameter of the AuNP cores (2*r*). The grafted polymer had an average volume of 5841 nm^3 from *eq 1*:[5]

$$V_{polymer} = \frac{4\pi}{3}\left[(r+l)^3 - r^3\right] \qquad \textit{eq 1}$$

Using the molecular weight of hydrolyzed P5, 28.4K, the average number of polymer chains on each shell is calculated using *eq 2*:

$$N_{polymer} = \frac{\rho V_{polymer} N_{Av}}{M_n} \qquad \textit{eq 2}$$

where N_{Av} and ρ are the Avogadro's number and the density of the polymer, respectively. The density of the polymer shell is assumed to remain similar to the density of pure PS, 1.05 g/cm^3. An average of 130 polymer chains was estimated to be present on each AuNP after solving equation 2.

The average grafting density (σ) is therefore 0.18 chains/nm^2.

3.3 Self-assembly of ACMs in the DMF/water solution

The self-assembly of ACMs was triggered by the slow addition of water as a selective solvent. Briefly, 0.5 mL of water/DMF solution with an initial water concentration (C_w) of 30 vol% was slowly added to 0.5 mL of ACM solution (0.05 mg/mL in DMF). The final concentration of water was C_w=15 vol% for the self-assembly. The mixed solution was slowly shaken for 2 hr, and then a drop of solution (2-5 μL) was cast on a carbon coated copper grid for TEM observation. The different pHs of self-assembly solution were adjusted by a standard 1.0 M of KOH solution or 1.0 M of HCl solution. *Note that,* the pH values used in this study are the pHs of the initial water.

3.4 Calculation of the interparticle distance in multi-chains

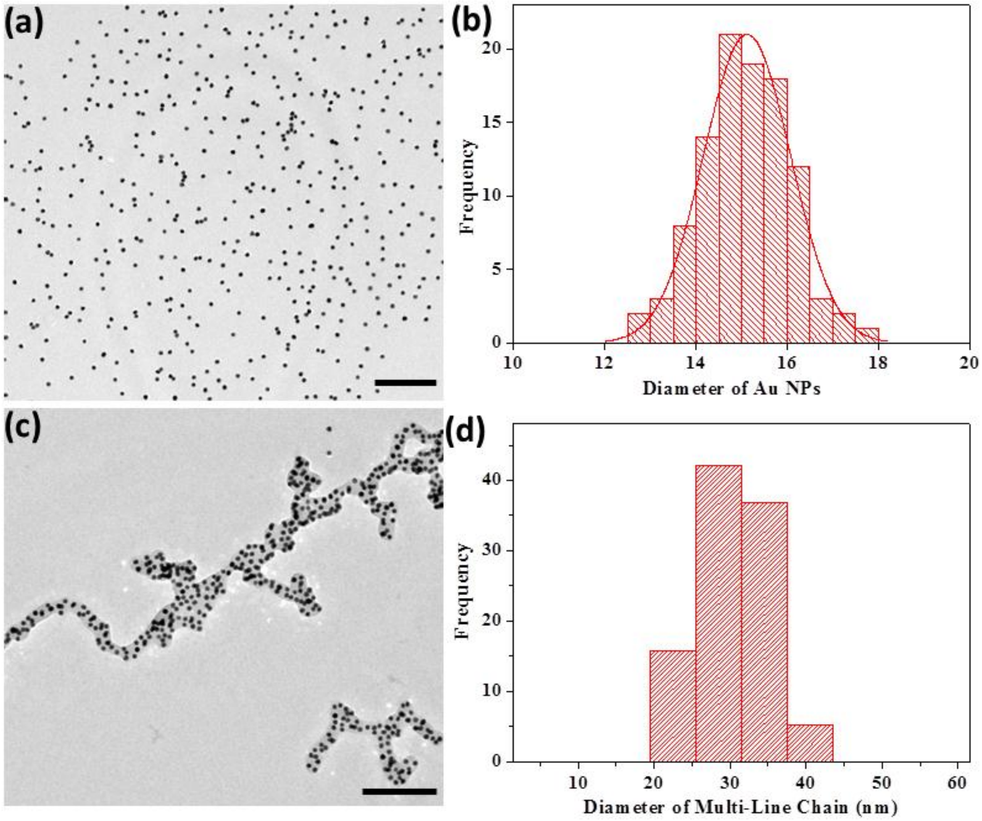


Figure S3 (a) TEM images of trisodium citrate-stabilized AuNPs with a diameter of 15.1 nm. (b) The size distribution of Au NPs core measured from TEM images by averaging over 100 particles. (c) TEM images of multi-line chains of AuNP-15-P5. (d) The diameter size distribution of multi-line chains which was obtained from TEM analysis. The average diameter of multi-line chain is 28.7 nm. Scale bars are 200 nm.

From the TEM images, we can measure diameter (*D*) and length (*L*) of multi-line chains, as well as the number of AuNPs per multi-line chains *N*. Assuming that AuNPs were dispersed uniformly in multi-line chains, the volume of AuNPs in multi-line chains was calculated from *eq 3*:

$$V_{AuNPs} = \frac{\pi\left(\frac{D}{2}\right)^2 L}{N} \qquad eq\ 3$$

Using the average radius *r* (7.5 nm) of AuNPs core, the mean interparticle distance (*d*) was estimated from *eq 4*:

$$d = \sqrt[3]{\frac{3V_{AuNPs}}{4\pi}} - r \qquad eq\ 4$$

4. Testing reversibility of the Pickering emulsion

0.22 mL of 0.1mg/mL Au-29-P7 nanoparticles toluene solution was homogenized with 2 mL of water for 3 minutes using ultrasonic bath. Emulsion droplets were imaged with a Nikon Ti-u microscope.

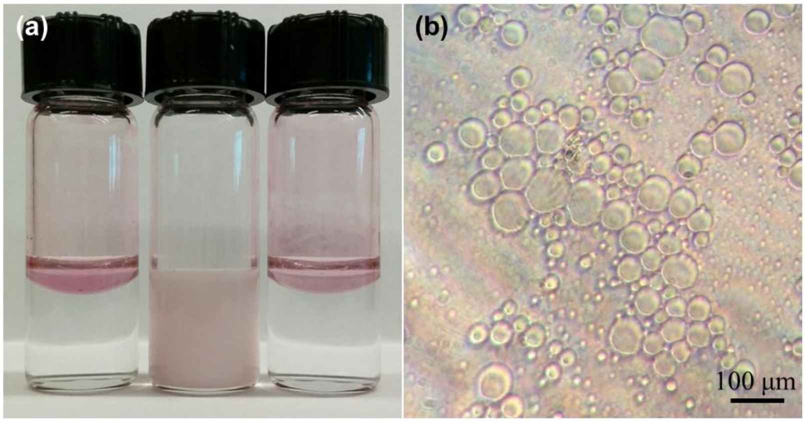


Figure S4 (a) Digital photographs of mixtures with 9:1 (vol) of water and 0.1mg/mL of AuNP-29-P7 in toluene before (left), after homogenization for 4 hr (middle), and two phases appeared again after changing the pH of the aqueous phase to 14. (b) Representative optical microscopic image obtained for toluene-in-water Pickering emulsions stabilized by Au-29-P7 ACMs as the sole emulsifiers.

5. The effect of the content of -COOH groups

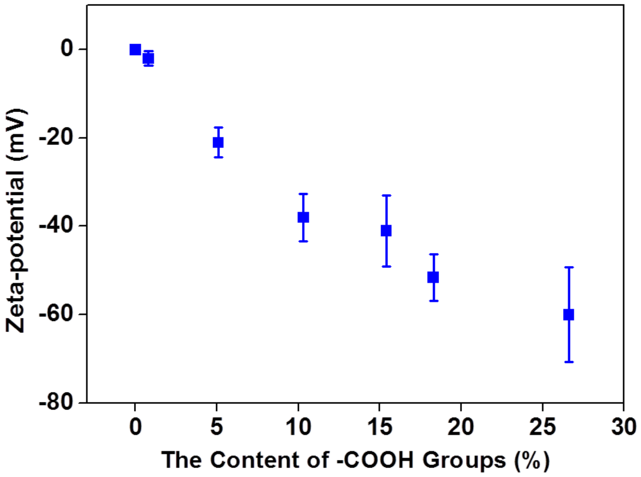


Figure S5. ζ-potentiual of AuNP-15 tethered by polymers with different content of –COOH groups (φ_{AA}) in DMF.

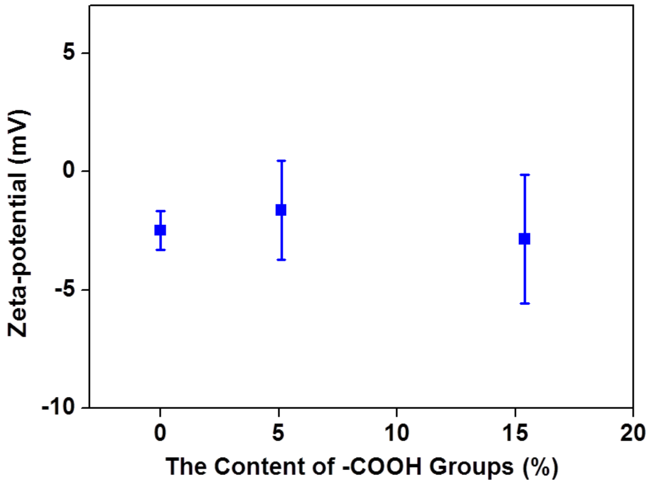


Figure S6. ζ-potential of AuNP-8 tethered by polymers with different content of –COOH groups (φ_{AA}) in DMF.

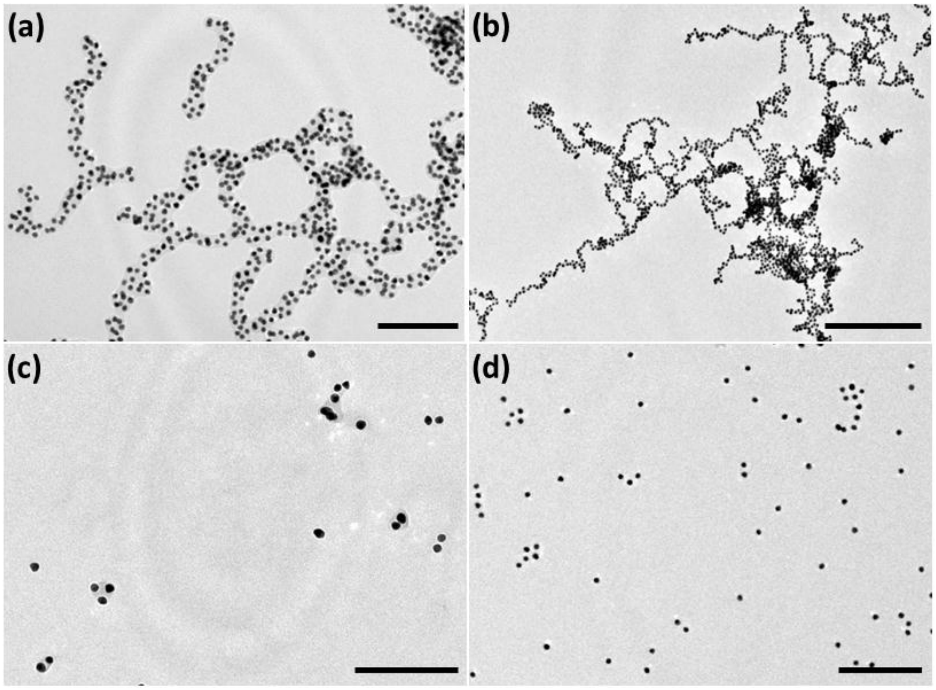


Figure S7. Representative low-magnification TEM images of self-assembly of AuNP-15 by varying φ_{AA} at same pH: (a) φ_{AA} = 0%; (b) φ_{AA} = 5.1%, (c) φ_{AA} = 10.3% and (d) φ_{AA} = 15.4%. All assemblies were obtained at pH=9 with 15 vol% of water. The self-assembly time is 2 hr. Scale bars are 200 nm in (a, c, d) and 500 nm in (b).

6. The effect of pH

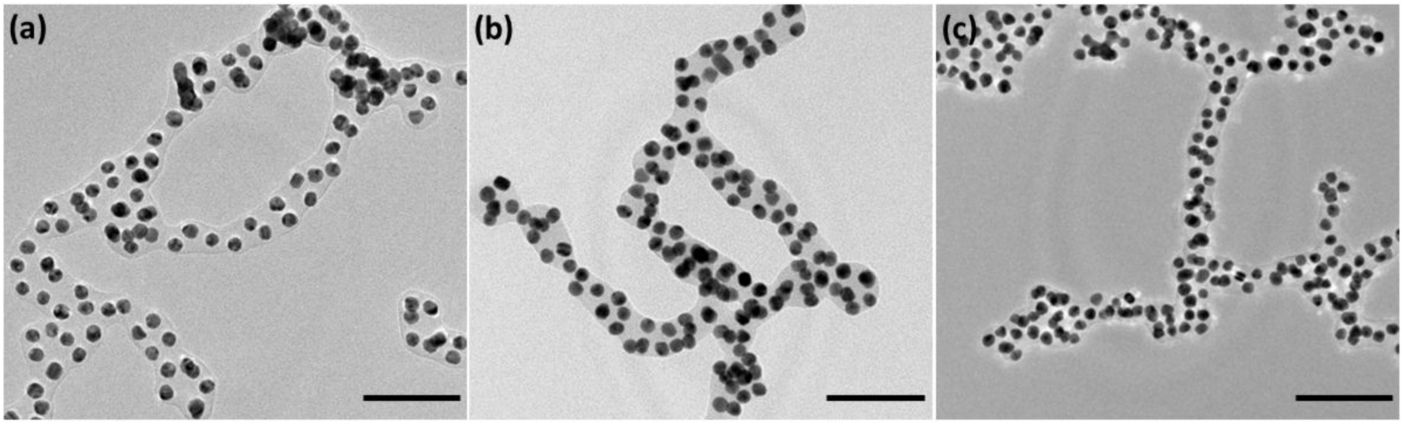


Figure S8. (a-c) TEM images of multi-line chains obtained from AuNP-15-P1 at different pHs in water/DMF (15/85, vol) solution: (a) pH = 5, (b) pH = 7 and (c) pH = 9. Scale bars are 100 nm in (a-c).

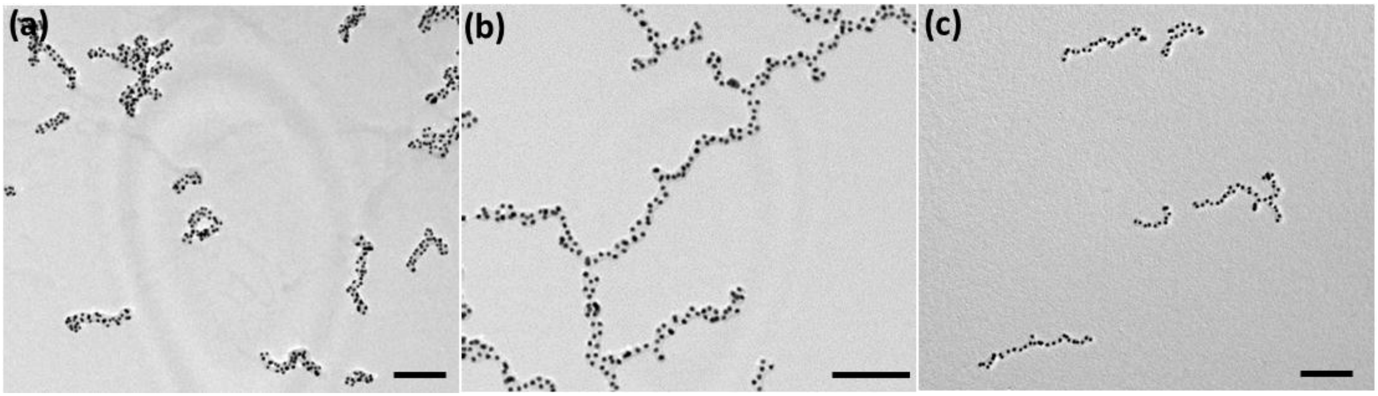


Figure S9. Representative low-magnification TEM images of self-assembly of AuNP-15-P2. (a-c) TEM images of ACM assemblies obtained at different pHs in water/DMF (15/85, vol) solution: (a) multi-line chains at pH=5.0; (b) mixed chains at pH=7.0; and (c) single-line chains at pH=9.0. The self-assembly time of all samples is 2 hr. Scale bars are 200 nm in (a-c).

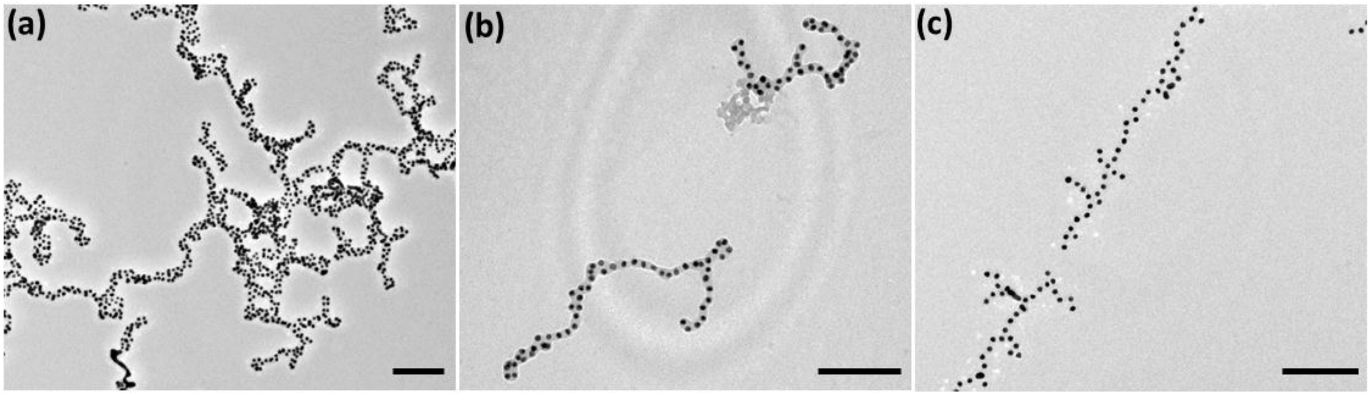


Figure S10. Representative low-magnification TEM images of self-assembly of AuNP-15-P3. (a-c) TEM images of ACM assemblies obtained at different pHs in water/DMF (15/85, vol) solution: (a) multi-line chains at pH=5.0; (b) single-line chains at pH=7.0; and (c) single-line chains at pH=9.0. The self-assembly time of all samples is 2 hr. Scale bars are 200 nm in (a-c).

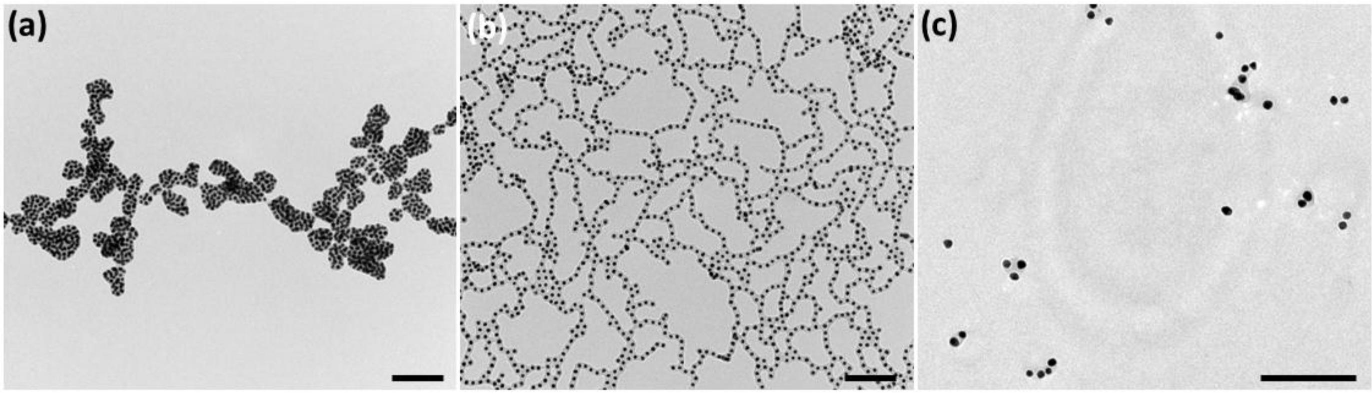


Figure S11. Representative low-magnification TEM images of self-assembly of AuNP-15-P4. (a-d) TEM images of ACM assemblies obtained at different pHs in water/DMF (15/85, vol) solution: (a) multi-line chains at pH=3.0; (b) single-line chains at pH=7.0; and (c) unimolecular micelles mixed with cluster at pH=9.0. The self-assembly time of all samples is 2 hr. Scale bars are 200 nm in (a-c).

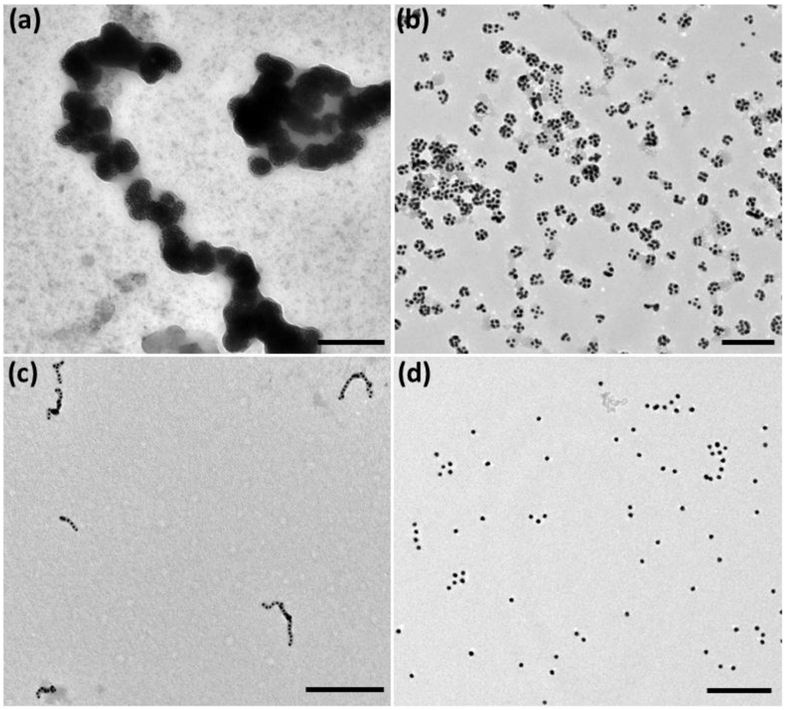


Figure S12. Representative low-magnification TEM images of self-assembly of AuNP-15-P5. (a-d) TEM images of ACM assemblies obtained at different pHs in water/DMF (15/85, vol) solution: (a) multi-line chains at pH=3.0; (b) clusters at pH=5.0; (c) single-line chains at pH=7.0; and (d) unimolecular micelles at pH=9.0. The self-assembly time of all samples is 2 hr. Scale bars are 500 nm in (a, c) and 200 nm in (b, d).

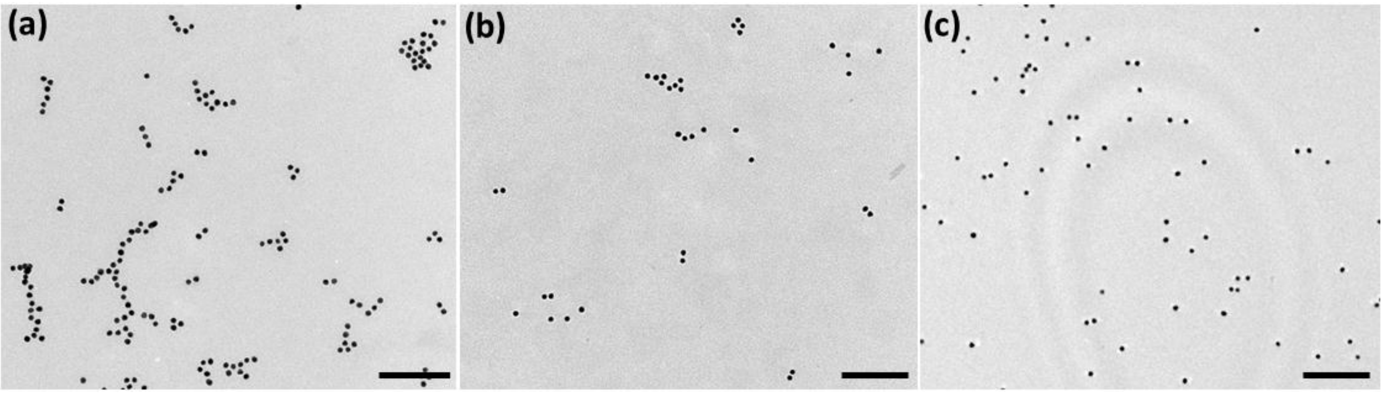


Figure S13. Representative low-magnification TEM images of self-assembly of AuNP-15-P7. (a-c) TEM images of ACM assemblies obtained at different pHs in water/DMF (15/85, vol) solution: (a) single-line chains mixed with unimolecular micelles at pH=5.0; (b) unimolecular micelles at pH=7.0; and (c) unimolecular micelles at pH=9.0. The self-assembly time of all samples is 2 hr. Scale bars are 200 nm in (a-c).

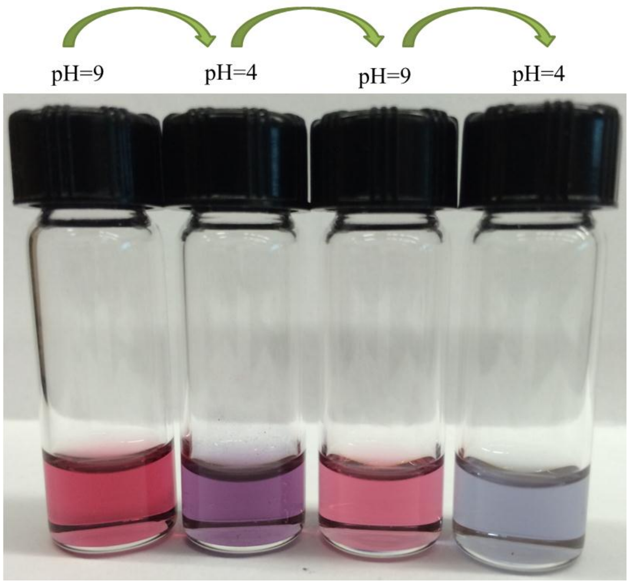


Figure S14. pH-induced reversible self-assembly of AuNP-29-P3 obtained at different pHs in water/DMF (3/97, vol) solution. To disassemble, the addition of DMF was used to reduce C_{water} to ~1.5 vol% and the pH was increased to 9. The disassembly was performed by sonicating at 40 ^{o}C for 15 min. 1mL of the assembly solution was refilled in the above vials for the images.

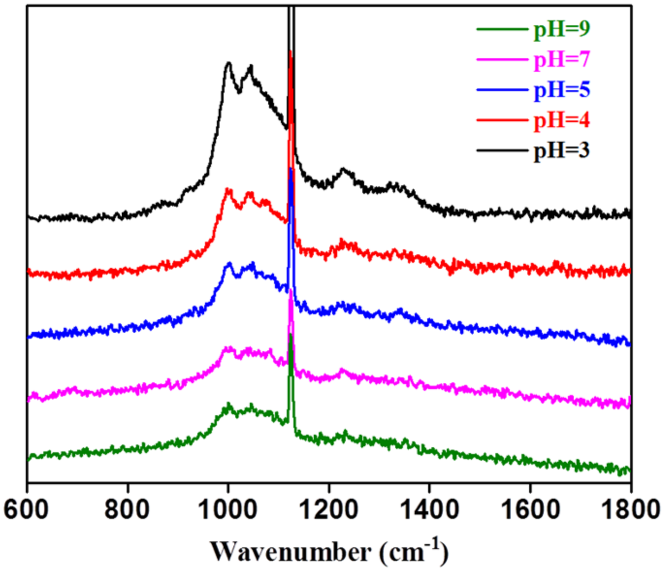


Figure S15. The SERS spectra of 4-mercaptopyridine with different 29 nm ACMs assembled structure after added different pH water/DMF solution.

7. The effect of the size of AuNPs and the dielectric constant of solvents

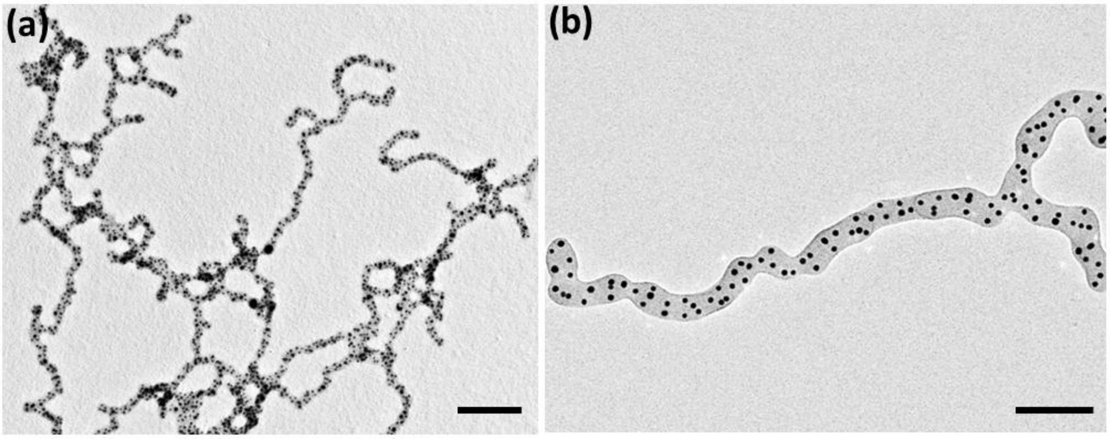


Figure S16. TEM images of multi-line chains of AuNP-8-P3. Scale bars are 200 nm in (a) and 100 nm in (b).

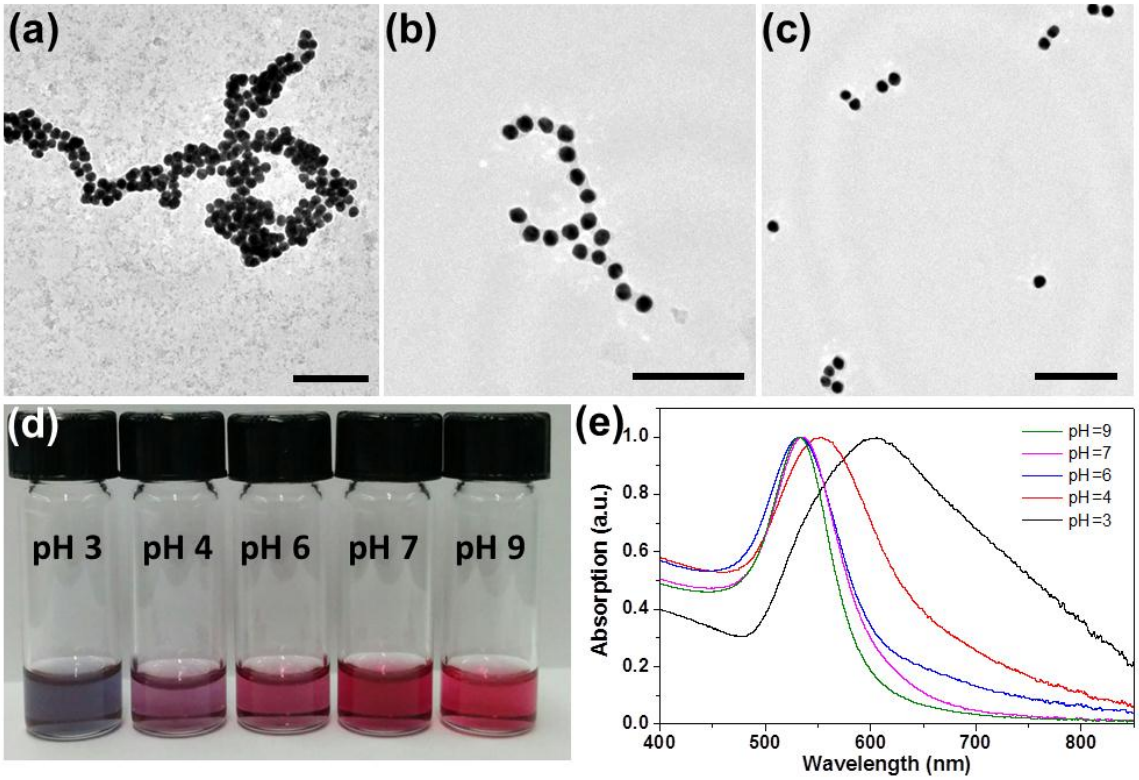


Figure S17. pH-induced programmable self-assembly of AuNP-29-P3. TEM images of ACMs assembled structure after added different pH water/DMF solution: (a) multi-line chains at pH = 4.0; (b) single-line chains at pH = 7.0; (c) unimolecular micelles at pH = 9.0. Scale bars are 200 nm. (d) Digital picture of ACMs assembled structure in response to pH changes. (e) The extinction spectra of P3 tethered ACMs when pH was changed from 9 to 3 at room temperature.

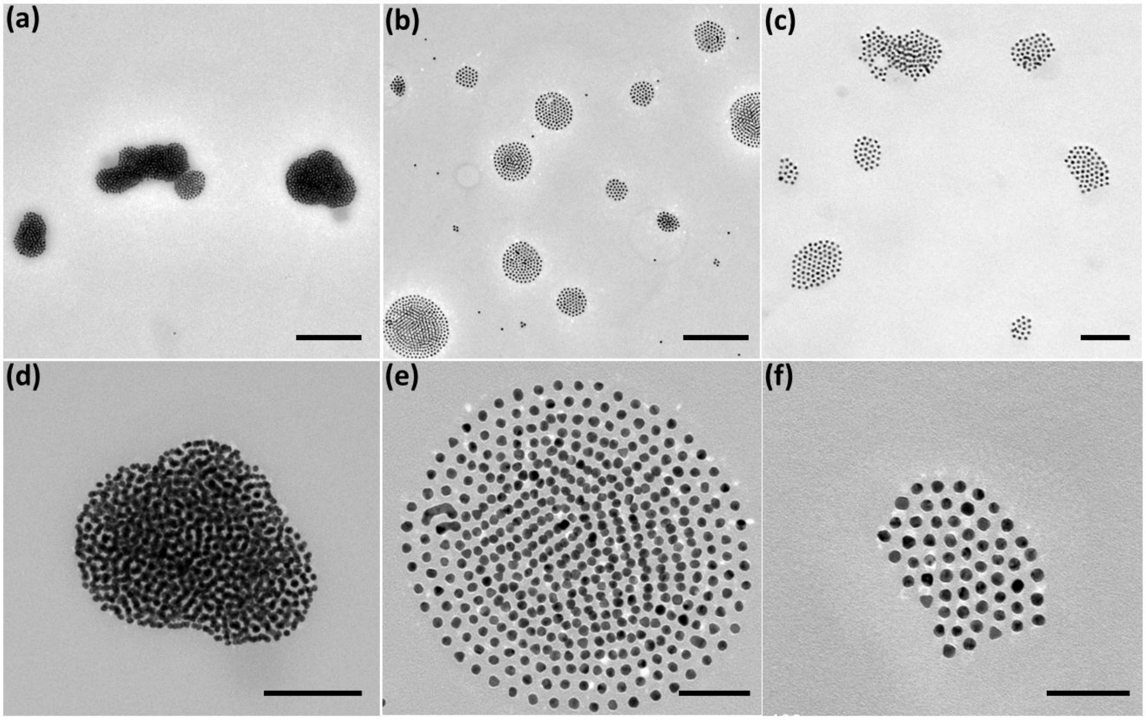


Figure S18. pH-programmable self-assembly of AuNP-15-P4 water/THF. (a-c) TEM images of ACM assemblies obtained at different pHs in water/THF (15/85, vol) solution: (a, d) at pH=4.0; (b, e) at pH=7.0; and (c, f) at pH=9.0.The self-assembly time of all samples is 2 hr. Scale bars are 500 nm in (a, b), 200 nm in (c, d) and 50 nm in (e, f). After adding water to the THF solution of AuNP-15-P4, the circular islands with sizes in the range of 100 to 600 nm were formed. By adjusting the pH of water to 4, the ACMs of AuNP-15-P4 formed closely packed clusters. On the contrary, by changing pH to 9 using NaOH solution, AuNPs could form small single sheet structure with sizes between 50 and 100 nm. That is due to the low dielectric constant of THF compared to DMF, suppressing the electrostatic interactions between NPs. The self-assembly morphology of ACMs changed from chains to spherical clusters. In pH=7 or 9 solution, the ACMs assemble into spherical clusters which is a type of non-closely packed colloidal structure in solution, after collapsing onto the carbon film to form flat disk-like assemblies during solvent evaporation.[6, 7]

8. Self-assembly kinetics by dynamic light scattering

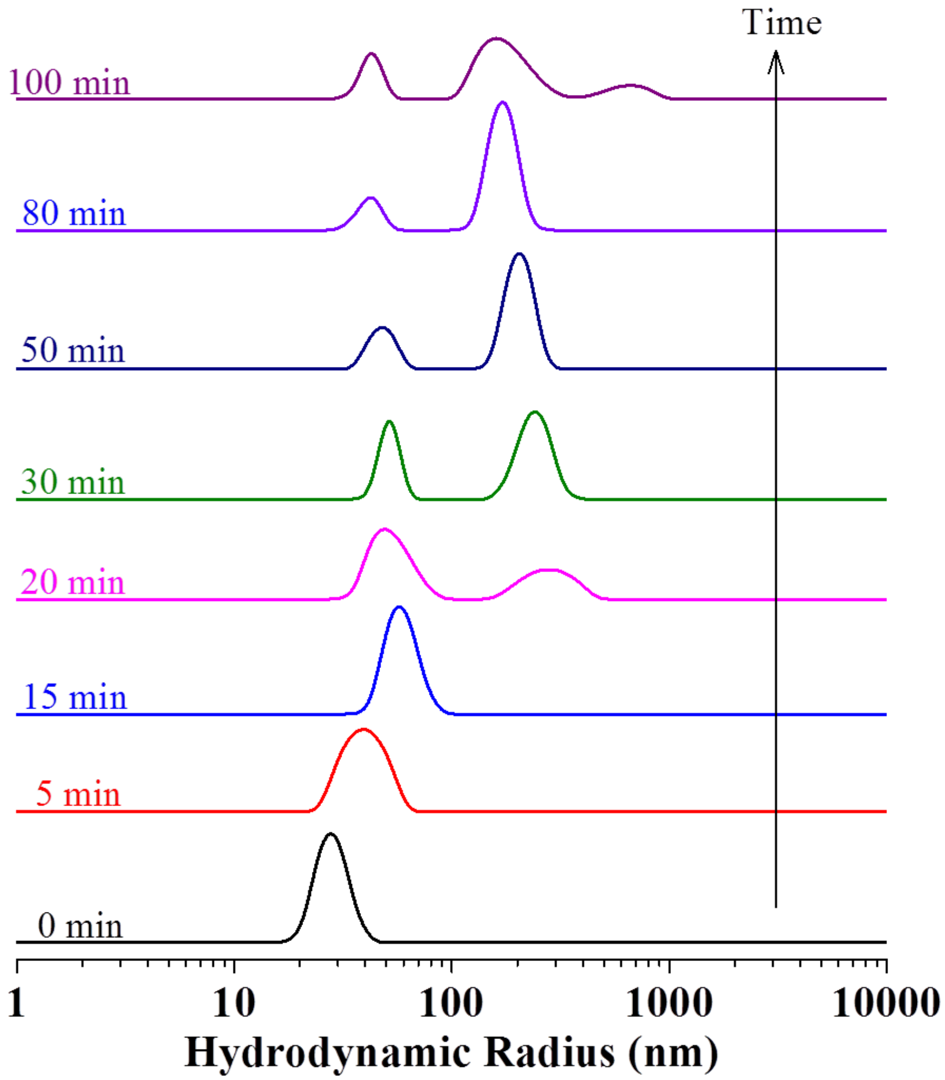


Figure S19. The *in situ* study of self-assembly kinetics of AuNP-29-P3 by following the change of hydrodynamic radius at pH=7 with a C_w of 15 vol%.

References

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