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Supporting Information

Patchy Metal Nanoparticles with Polymers: Controllable Growth and Two-Way Self-Assembly

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1. Materials and Instruments

Styrene, α-bromoisobutyl bromide, poly(ethylene oxide) monomethyl ether (PEO_{114}-OH, M_n=5000 g/mol), 4-dimethylaminopyridine (DMAP), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (CuBr), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), poly(acrylic acid) (PAA, M_n =1800 g/mol), poly(vinylpyrrolidone) (PVP, M_n =40000 g/mol), ascorbic acid (AA), sodium citrate, cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium chloride (CTAB), n-butyl amine, sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), N,N-dimethyl formamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane (DCM), ethanol, *n*-hexane and anisole were purchased from Sigma Aldrich. Styrene was passed through a basic aluminum oxide column prior to use for the removal of inhibitors. The reversible addition-fragmentation chain transfer polymerization (RAFT) agent, 3-(benzylthiocarbonothioylthio)propanoic acid (BCTPA), was synthesized according to the previous report.[1] The ultra-pure water was double distilled with a High-Q distillation system (model # 103S). Anhydrous DCM was prepared by refluxing DCM in the presence of CaH_2 for 8 hours.

2. Synthesis of thiol-terminated polystyrene (PS-SH) and poly(ethylene oxide)-*b*-polystyrene (PEO_{114}-*b*-PS_{40})

PS_{200} (M_n= 20.8 kg/mol, PDI=1.08) was synthesized by reversible addition fragmental chain transfer polymerization (RAFT) using BCTPA as the chain transfer agent and followed by the reduction of trithiolate-terminal groups to thiols as reported previously.[2]

PEO_{114}-*b*-PS_{40} was synthesized via atom transfer radical polymerization (ATRP). Firstly, the macromolecular initiator PEO_{114}-Br was synthesized by the esterification between PEO_{114}-OH and α-bromoisobutyl bromide. PEO_{114}-OH (10 g, 2 mmol, 1 eq) and 4-dimethylaminopyridine (24 mg, 0.2 mmol, 0.1 eq) were dissolved into 50 mL anhydrous DCM, the flask was cooled by ice-bath and purged with dry nitrogen gas for 10 min. Then α-bromoisobutyl bromide (1.15 g, 5 mmol, 2.5 eq) was dissolved into 5 mL anhydrous DCM, which was added dropwise into the flask. The reaction was stopped by adding 150 mL chloroform after 24 hours. The combined DCM solution was washed by saturated $NaHCO_3$ aqueous solution for 2 times and dried over Na_2SO_4. Then the solvent was removed by rotatory evaporator, the polymer was purified by precipitation into cooled hexane for 2 times and dried under vacuum. The PEO_{114}-Br macroinitiator was obtained as a white solid.

PEO_{114}-Br (1.5 g, 0.3 mmol, 1 eq), CuBr (65 mg, 0.45 mmol, 1.5 eq), styrene (1.87 g, 18 mmol, 60 eq) and 8 mL anisole and were added into a 25 mL Schlenk flask. Then three times freeze-pump-thaw were conducted by using liquid nitrogen. At the last time, PMDETA (104 mg, 0.6 mmol, 2 eq) was quickly added into the Schlenk flask, which was sealed after filling with nitrogen again. The ATRP of styrene was carried out at 92 ºC for 8 hours. Afterwards, 15 mL of DCM was added to quench the reaction when the flask was cooled down to room temperature. The copper catalyst was removed by passing a short silica gel column. To ensure the lowest residual copper, the column procedure was repeated for 2-3 times until the solution was colorless. The block copolymer was obtained by precipitation with cooled *n*-hexane three times and dried under vacuum. The molecular weight of the block copolymer is 9.2 kg/mol based on NMR spectrum and the dispersity index is 1.1 as measured gel permeation chromatography (GPC).

3. Synthesis of citrate capped AuNPs

Citrate capped AuNPs was synthesized using a previously reported method.[3] Briefly, 100 mg of $HAuCl_4$ was dissolved into 1 L water, which was heated to boiling. Then 30 mL of sodium citrate aqueous solution (1 wt%) was quickly injected into the above solution. After refluxing for 30 min, AuNPs were collected as the stock solution without any further purification. The concentration of AuNPs was measured as 2.39 nM (0.046 mg/mL), and the diameter of AuNPs was measured as 14.6 ± 13 nm.

4. Synthesis of *p*AuNPs

We used a previously published method to synthesize the Janus patchy AuNPs (*p*AuNPs). Briefly, 1 mg/mL PS_{200}-SH and 2 mg/mL PEO_{114}-*b*-PS_{40} DMF solution were prepared at least 1 h before experiment to ensure fully relaxed polymer chains. Then 0.28 mL PS_{200}-SH (0.28 mg, 1.14 μM), 4 mL PEO_{114}-*b*-PS_{40} (8 mg) and 3.72 mL pure DMF were added into a 10 mL glass vial. In the meanwhile, 40 mL citrate capped AuNPs (14.6 ± 13 nm, 2.39 nM) was centrifuged at 9700 rpm

to remove most of the water, the precipitate was collected with a total volume as 80 μL. The concentrated AuNPs was then added dropwise into the glass vial with gentle shaking. The mixing solution was incubated at room temperature overnight. Then 1.54 mL DI water was added to quench the ligand exchange. The glass vial was sealed and heated at 100 ºC for 1 hour, which was cooled down to RT slowly in oil bath. The mixing solution was added into 50 mL DI water, which was centrifuged at 9500 rpm for 3 times to remove free polymer. The *p*AuNPs were stored in water at a concentration of 2.59 nM (0.05 mg/mL).

5. Determination of the concentration of AuNPs

The concentration of citrate capped AuNPs was determined using the molar absorptivity (ε) as reported previously.[4] The ε for 15 nm AuNPs is $2.18 * 10^8\ L\ mol^{-1}cm^{-1}$ at 450 nm with a path length of 1 cm. The original concentration of citrate capped AuNPs is calculated to be $2.39 * 10^{-9}\ mol\ L^{-1}$, that is 2.39 nM. Thus, the mass concentration of citrate capped AuNPs can be calculated as 0.046 mg/mL. The concentration of *p*AuNPs was calculated as 2.59 nM based on the comparison of LSPR intensity, and the mass concentration was 0.05 mg/mL.

6. Seed mediated growth from *p*AuNPs

6.1 CTAB capped *p*AuNPs

The growth of *p*AuNPs was carried out using a seed-mediated growth method in the presence of CTAB as surface ligand and ascorbic acid as reductant. Firstly, the growth solution was prepared with the following procedure. Briefly, certain amount of CTAB and 4 mL H_2O were added into a 10 mL glass vial with a stir bar, which was then placed in a water bath with temperature as 30 ºC. After CTAB was dissolved into water (~ 5 min, clear solution), various amount of $HAuCl_4$ aqueous solution (10 mg/mL) was added, which would afford an orange solution. Then, specific amount of ascorbic acid (10 mg/mL) aqueous solution was added and the solution turned into colorless immediately. The colorless growth solution was stored at 30 ºC and used after preparation. Finally, 0.5 mL Janus AuNPs aqueous solution (2.59 nM, m(Au) = 0.025 mg) was injected in one shot to initiate the secondary growth. The solution was stirred at 400 rpm for 2 hours. The amount of $HAuCl_4$ and ascorbic acid are the key to tune the size of grown *p*AuNPs, the relationship between precursor and the diameter can be seen in Table S1.

Table S1. Synthetic conditions for *p*AuNPs with different sizes.

$HAuCl_4$ (10 mg/mL)	Au (eq)	CTAB (mg)	ascorbic acid (10 mg/mL)	Diameter (nm)
0.12 mL	24	60	80 μL	38.9 ± 2.2
0.06 mL	12	30	40 μL	30.8 ± 1.6
0.045 mL	9	25	30 μL	28.4 ± 2.1
0.03 mL	6	15	20 μL	24.6 ± 1.3
0.015 mL	3	10	10 μL	19.9 ± 1.9

6.2 CTAC capped *p*AuNPs

The CTAC capped Janus AuNPs were prepared in a similar method compared to CTAB. Firstly, 40 mg CTAC (TCI), 0.3 mg $HAuCl_4$ (Au (eq) = 6, m(Au)=0.15 mg) and 0.3 mg ascorbic acid were dissolved into 4 mL water, then 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg) was added in one shot. The solution was stirred at RT for 30 min. The obtained *p*AuNPs still have a spherical Au core, the diameter of which is 24.4 ± 2.5 according to our analysis of TEM images. ‘

6.3 PVP capped *p*AuNPs

The PVP capped Janus AuNPs were prepared with the following method: 4 mL PVP (Sigma Aldrich, M_n = 40000) aqueous solution (2 mg/mL) was prepared, to which 0.3 mg $HAuCl_4$ (Au (eq) = 6, m(Au)=0.15 mg) and 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg) were added. The solution was stirred at RT for 5 min then 0.3 mL ascorbic acid aqueous solution (1 mg/mL) was added in one shot. The solution was further stirred at RT for 30 min. The diameter of *p*AuNPs is 23.4 ± 2.7 according to our analysis of TEM images.

6.4 PAA capped *p*AuNPs

PAA capped Janus AuNPs were prepared with the following method: 4 mL PAA (Sigma Aldrich, M_n = 1800) aqueous solution (2 mg/mL) was prepared, to which 0.3 mg HAuCl4 (Au (eq) = 6, m(Au)=0.15 mg) and 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg) were added. Then 0.3 mL ascorbic acid aqueous solution (1 mg/mL) was added in one shot, the solution was further stirred at RT for 30 min.

6.5 Citrate capped *p*AuNPs

Citrate capped Janus AuNPs were prepared with the following method: 4 mL sodium citrate (0.1 mg/mL) aqueous

solution was prepared, to which 0.3 mg $HAuCl_4$ (Au (eq) = 6, m(Au)=0.15 mg) and 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg) were added. Then 0.3 mL ascorbic acid aqueous solution (1 mg/mL) was added in one shot, the solution was further stirred at RT for 30 min.

6.6 Ag@*p*AuNPs

The preparation of polymer-Au-Ag ABC-type nanostructure was conducted with the following procedure. 4 mL PVP aqueous solution (2 mg/mL) was prepared first, to which 0.23 mg $AgNO_3$ (m ($Ag_{precursor}$) / m (Au_{seed}) = 6) and 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg) were added. Then 0.3 mL ascorbic acid solution (1 mg/mL) was added in one shot, the solution was further stirred at RT for 2 hours.

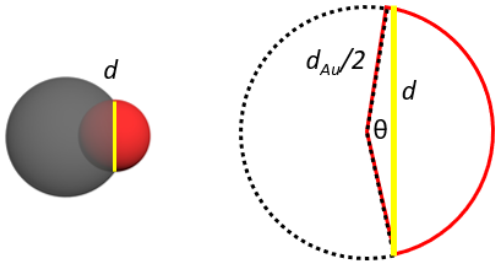
6.7 Pd@*p*AuNPs

The preparation of polymer-Au-Pd ABC-type nanostructure was done with the following procedure. 40 mg CTAB and 4 mL water were added into a 10 mL glass vial, which was put into a water bath (30 ºC). A clear and colorless solution should be afforded 10 min later after all the CTAB was totally dissolved. Then 0.46 mg K_2PdCl_4 (m ($Pd_{precursor}$) / m (Au_{seed}) = 6) was added to the solution, followed by the addition of 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg). Finally, 0.3 mL ascorbic acid (1mg/mL) was added, and the solution was further stirred at RT for 2 hours.

6.8 Pt@*p*AuNPs

The preparation of polymer-Au-Pt ABC type nanostructure was done with the following procedure. 4 mL PVP aqueous solution (3 mg/mL) was prepared first, to which 1.6 mg K_2PtCl_4 (m ($Pt_{precursor}$) / m (Au_{seed}) = 30) and 0.5 mL Janus AuNPs seed (2.59 nM, m(Au) = 0.025 mg) were added. Then 0.1 mL ascorbic acid aqueous solution (10 mg/mL) was added and the solution was further stirred at RT overnight. The reduction of Pt was much slower than Ag and Pd, so the amount of precursor and ascorbic acid were increased dramatically to afford the polymer-Au-Pt heterotrimers.

7. Measurement of the surface coverage of *p*AuNPs with different size



Schematics to illustrate the determination of the interface size (d) and the covered surface area (A_c).

Firstly, the surface coverage (A_c) of *p*AuNPs-14 can be estimated by the following equation:

$$\theta = 2 * \arcsin[\frac{d}{d_{Au}}] \quad (1)$$

$$A_c = 1 - \frac{\theta}{2\pi} \quad (2)$$

The interface distance (d) between the polymer patch and Au core was measured as 13.6±1.2 nm, then θ can be calculated as 2.38 (rad) according to equation (1). Since the polymer patch covered more than a half of the Au core (**Figure S4 a**), the A_c of *p*AuNPs-14 can be obtained as 62% by equation (2), which is about 415 nm^2. Secondly, the A_c of *p*AuNPs with larger size could be determined by equation (3) assuming the covered surface was always constant during the seed-mediated growth:

$$A_c = \frac{415\ nm^2}{4\pi r^2} \quad (3)$$

With increased size of *p*AuNPs, the A_c would decrease accordingly, and the results were summarized in **Table S2**:

Table S2 Summary of the A_c for *p*AuNPs with different Au sizes.

Sample	Surface area (nm^2)	Covered area (nm^2)	A_c (%)
*p*AuNPs-14	669.7	415	62.0
*p*AuNPs-19	1244.1	415	33.3
*p*AuNPs-24	1901.1	415	21.8
*p*AuNPs-28	2551.8	415	16.3
*p*AuNPs-30	2980.2	415	13.9
*p*AuNPs-38	4753.9	415	8.7

8. Self-assembly in the mixture of ethanol and water

1 mL of *p*AuNPs aqueous solution was centrifuged in water twice before assembling to reduce the CTAB concentration. The initial concentration for *p*AuNPs-28 and *p*AuNPs-38 is 0.288 nM, while the *p*-AuNPs-14 concentration is 2.59 nM. At the last time, 0.1 mL water was added to redisperse the *p*AuNPs, the concentration of CTAB should be lower than 0.5 μM. Then 0.9 mL ethanol was quickly added and mixed with 0.1 mL *p*-AuNPs aqueous solution. The mixing solution was transferred to a cuvette for the subsequent in situ UV-vis monitoring.

9. Self-assembly induced by hydrophobicity

Firstly, 4 mL *p*AuNPs-14 (2.59 nM) and *p*AuNPs-28 (0.288 nM) were centrifuged to reduce the surface ligand concentration for the subsequent PEO-SH grafting. Then PEO_{44}-SH was added to the *p*AuNPs aqueous solution, the final concentration of PEO_{44}-SH is 2 mg/mL. The solution was incubated at RT for 24 hours. Then the aqueous PS-*p*AuNP-PEO solution was centrifuged to remove water, and DMF was added to redisperse the PS-*p*AuNP-PEO. To remove the PEO_{114}-*b*-PS_{40}, the nanoparticle DMF solution was centrifuged three times. Finally, the PEO-*p*AuNP-PS DMF solution was dialyzed against water to induce the self-assembling process. UV-vis spectra of NPs were recorded at each stage.

10. Spectra, TEM images and histograms.

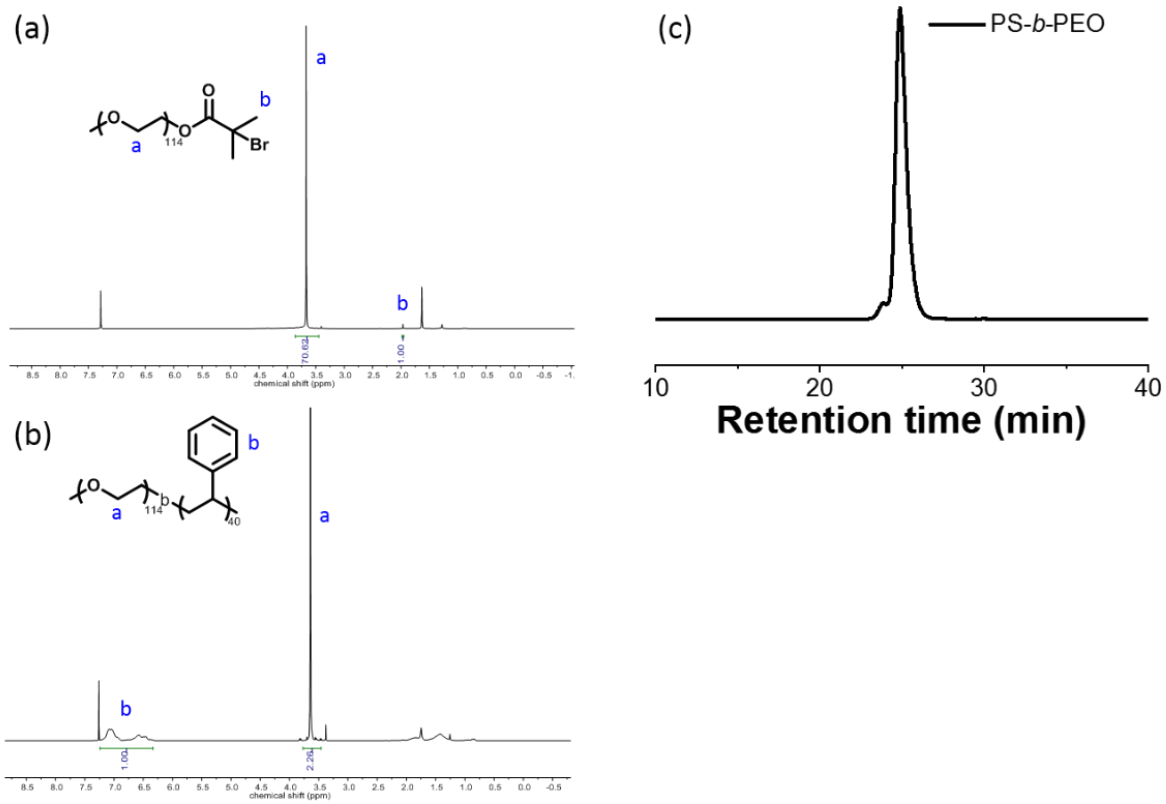


Figure S1. (a-b) NMR spectra ($CDCl_3$) of PEO_{114}-Br (a) and PEO_{114}-*b*-PS_{40} (b); (c) GPC curve of PEO_{114}-*b*-PS_{40}.

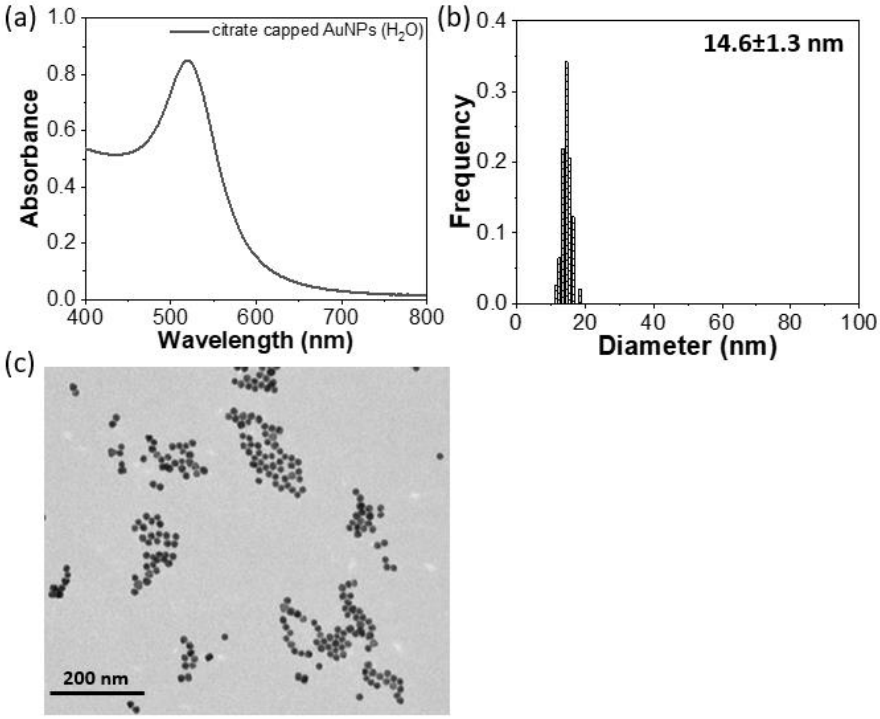


Figure S2. UV-vis absorption spectrum (a), diameter distribution (b) and TEM image (c) and of citrate capped 14.6 nm AuNPs.

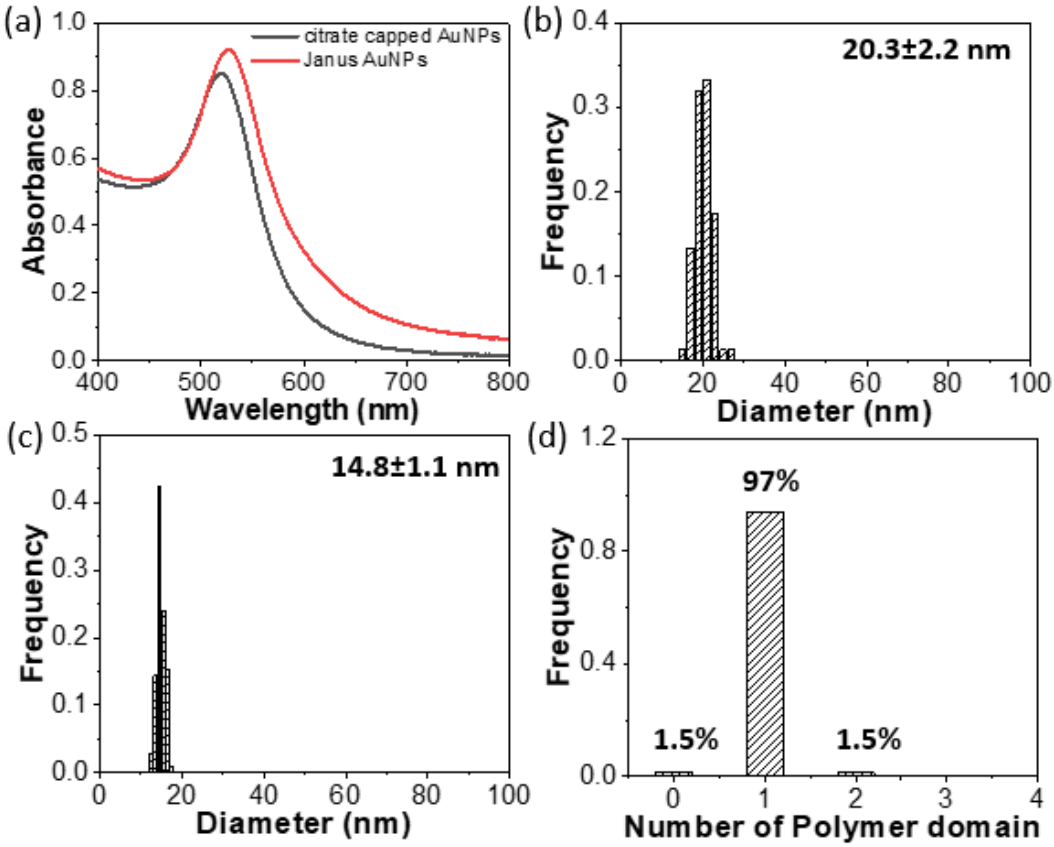


Figure S3. UV-vis absorption spectrum (a), polymer patch diameter distribution (b), Au core diameter distribution (c) and distribution of $N_{polymer}$ (average over 300 *p*AuNPs) (d) of *p*AuNPs-14 nm.

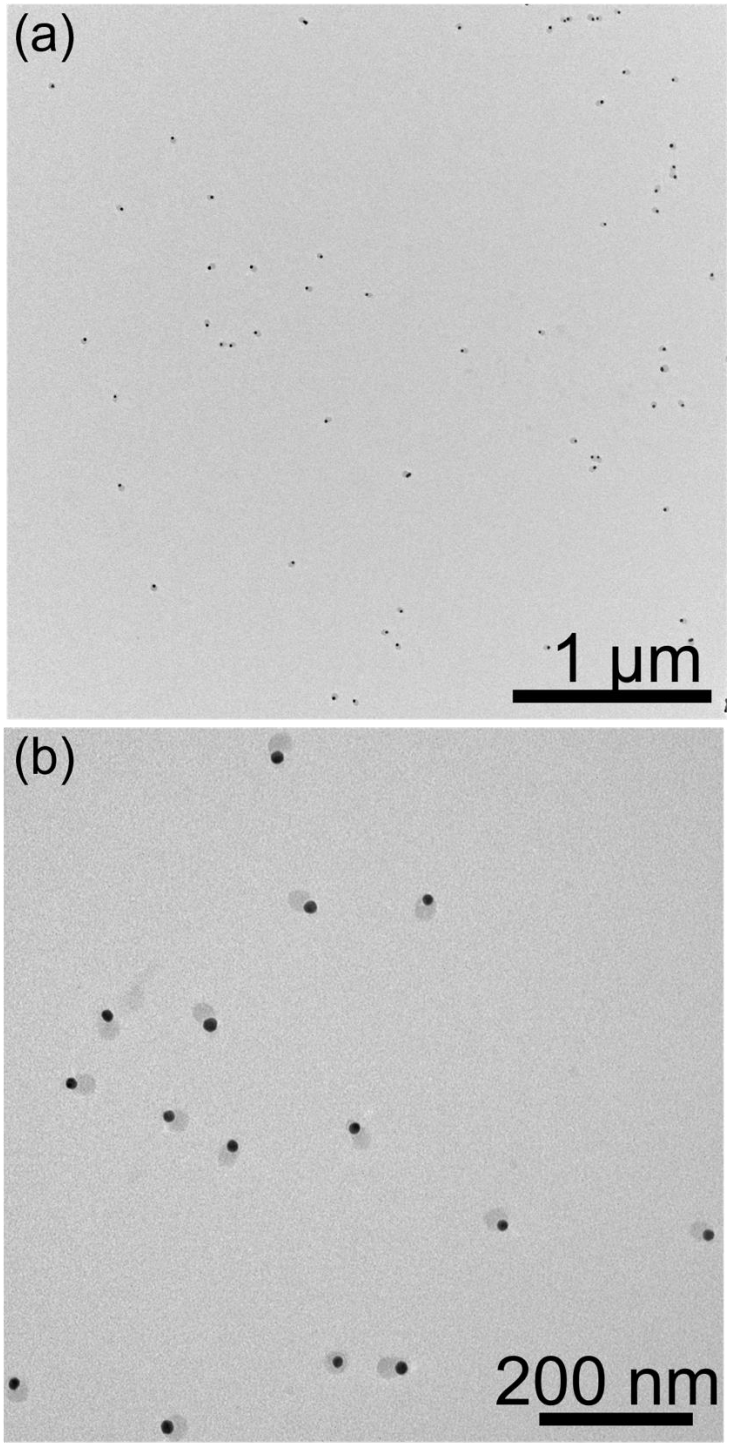


Figure S4. Low resolution (a) and high resolution (b) TEM image of *p*AuNPs-14.

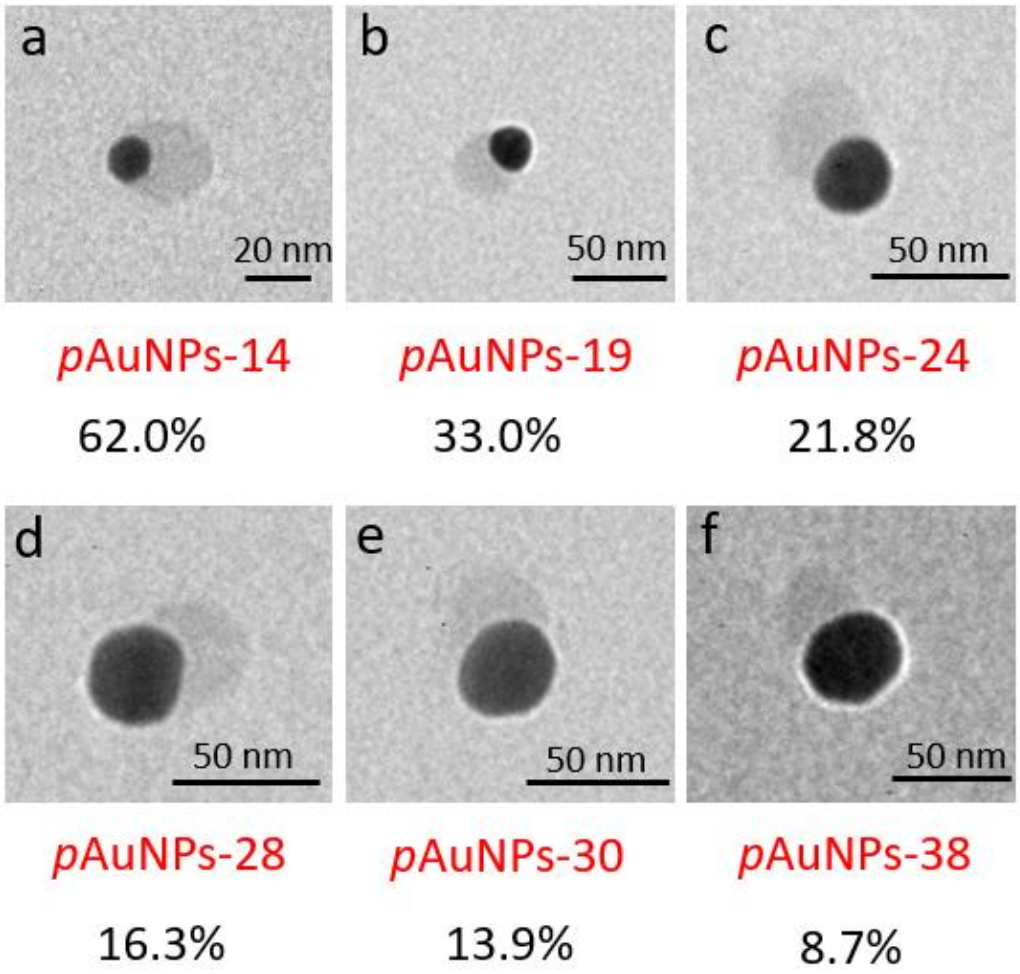


Figure S5. Typical TEM image of *p*AuNPs with different size and their corresponding surface coverage. (Details of calculation can be found at SI-7)

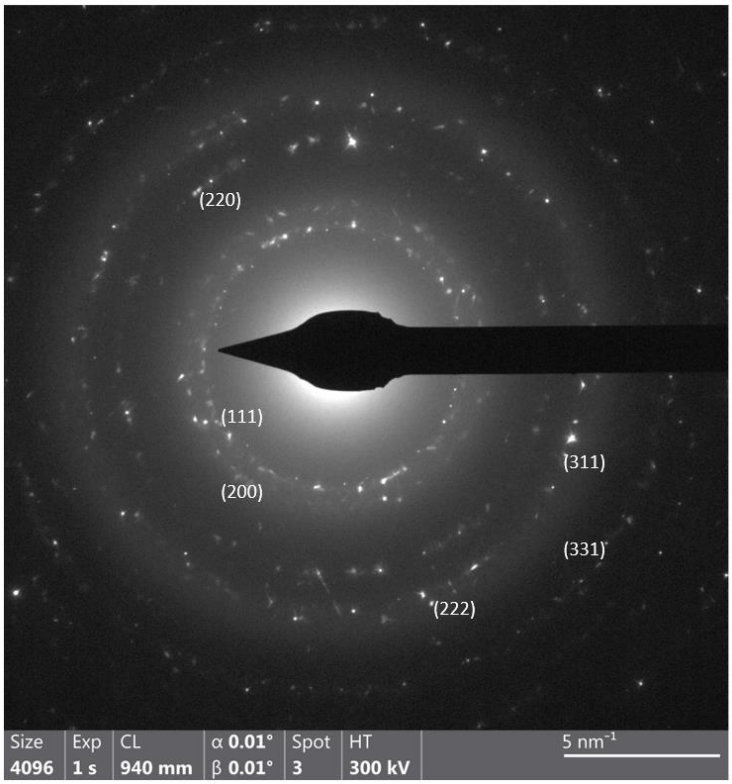


Figure S6. Electron diffraction pattern of *p*AuNPs-38 showing the polycrystalline of the grown *p*AuNPs-38.

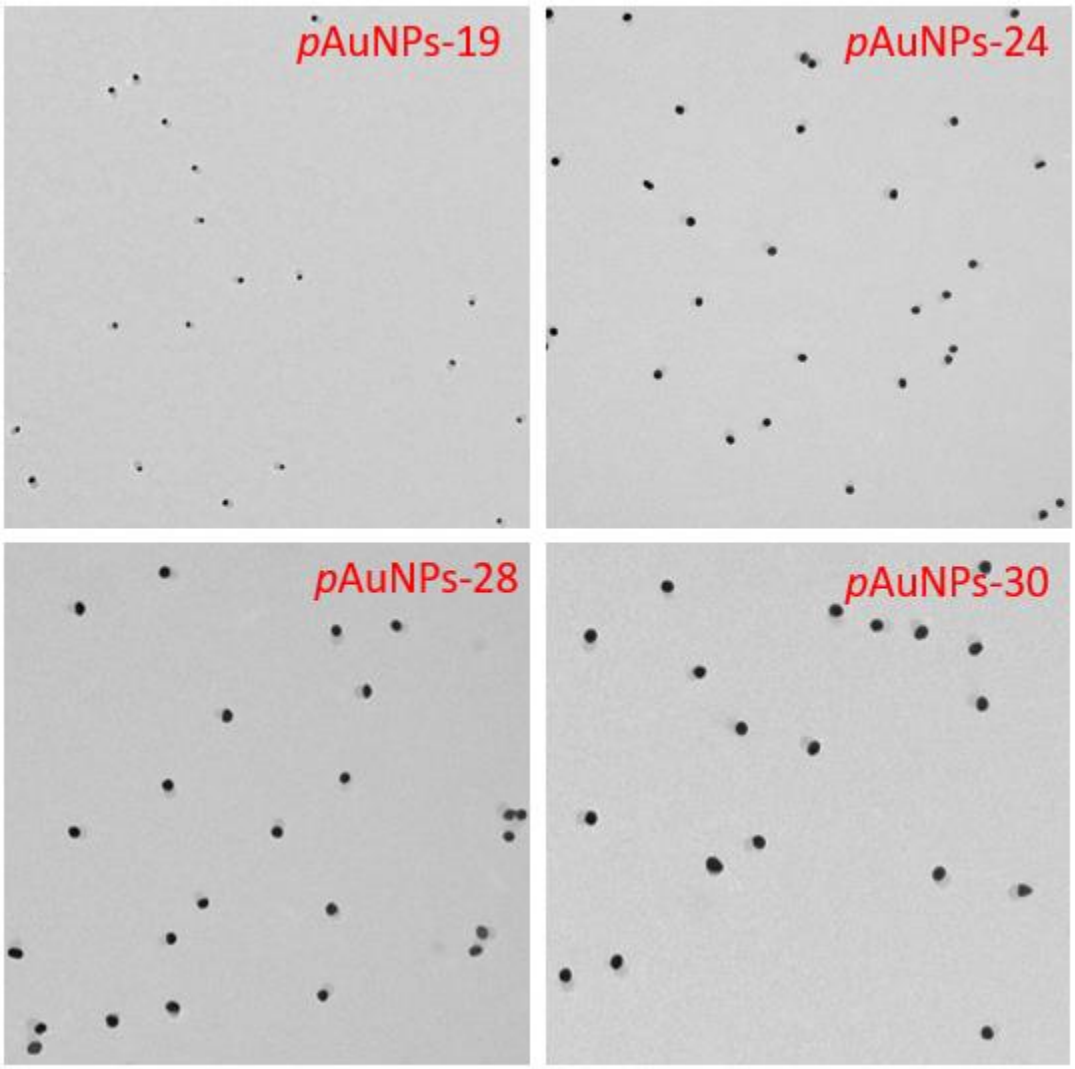


Figure S7. TEM images at a lower magnification of *p*AuNPs with different sizes.

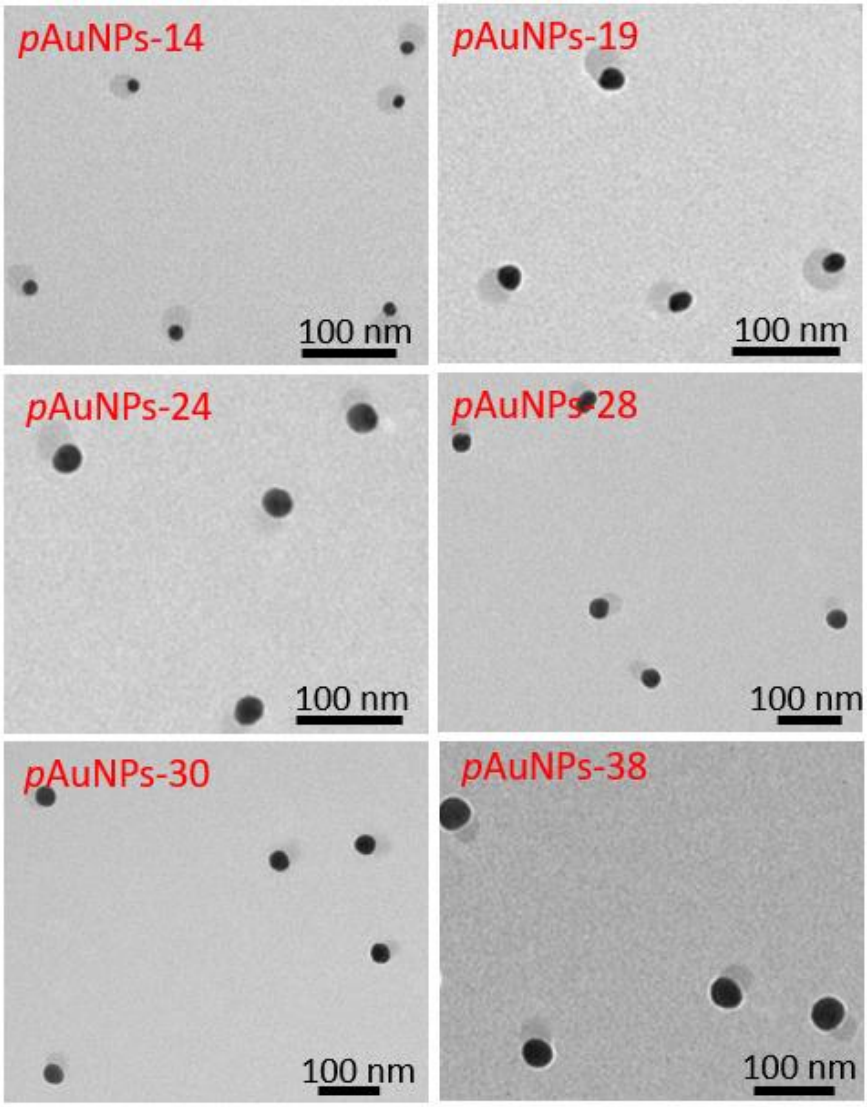


Figure S8. TEM images at a higher magnification of *p*AuNPs with different size.

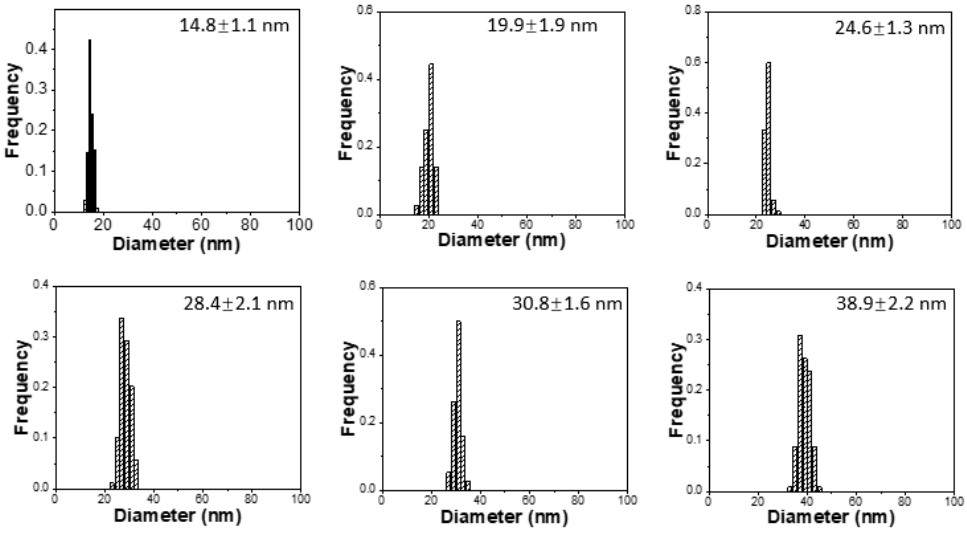


Figure S9. Histograms of the diameter of *p*AuNPs.

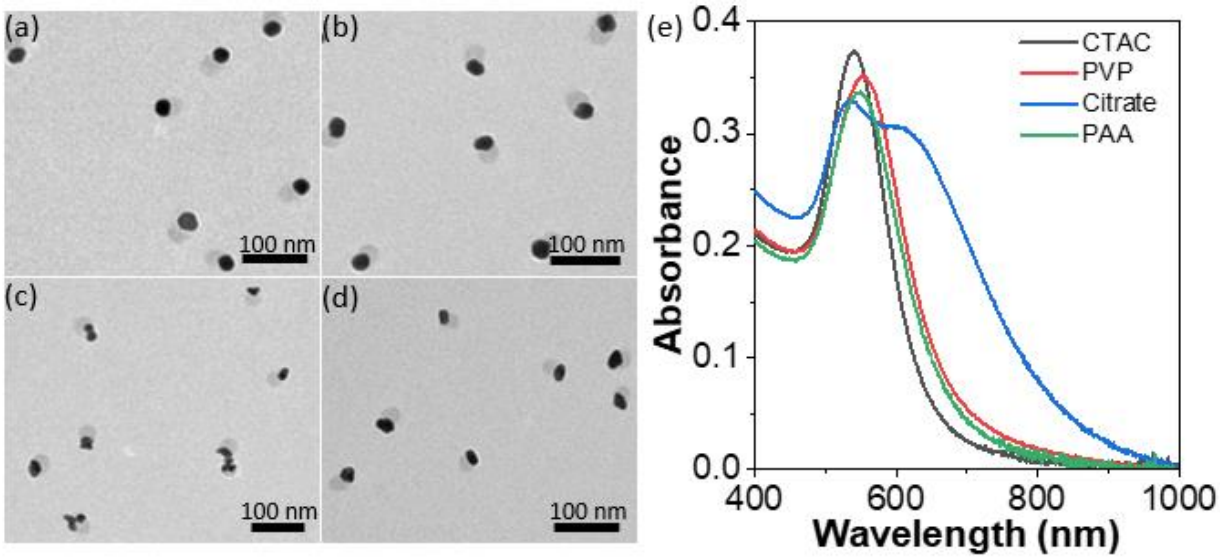


Figure S10. (a-d) TEM images (a, CTAC; b, PVP; c, citrate; d, PAA) and UV-vis absorption spectra (e) of grown *p*AuNPs (Au_{eq}=6) capped with different surface ligands.

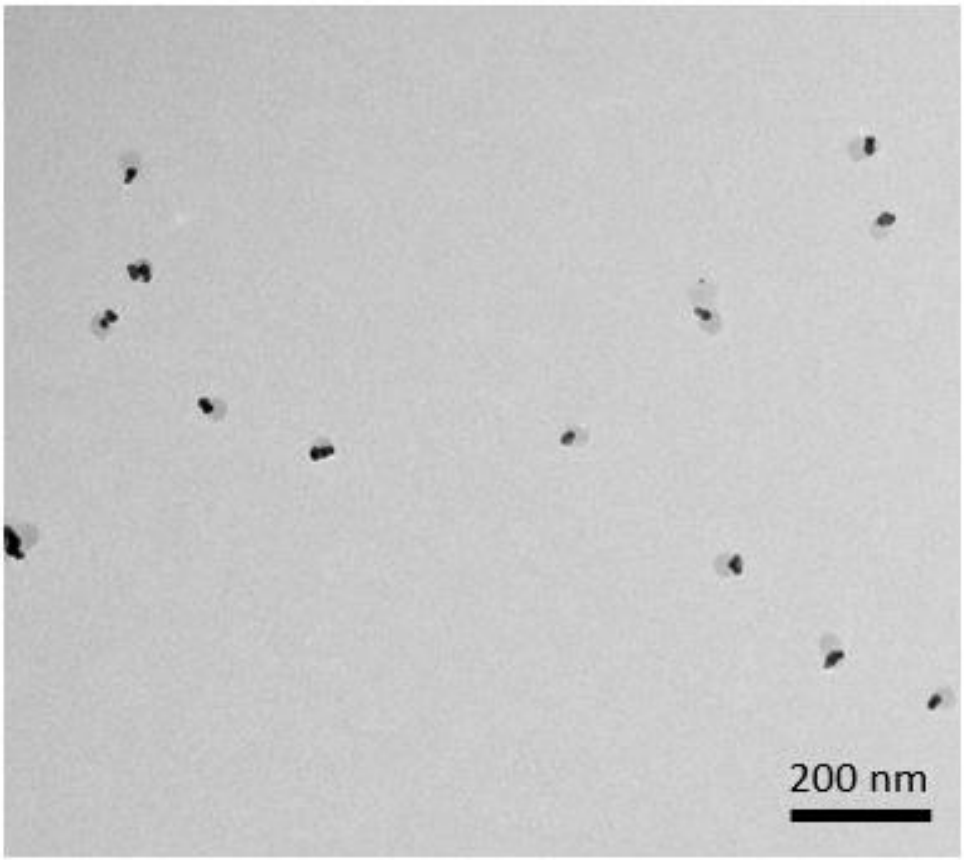


Figure S11. TEM image of grown *p*AuNPs without additional capping ligands.

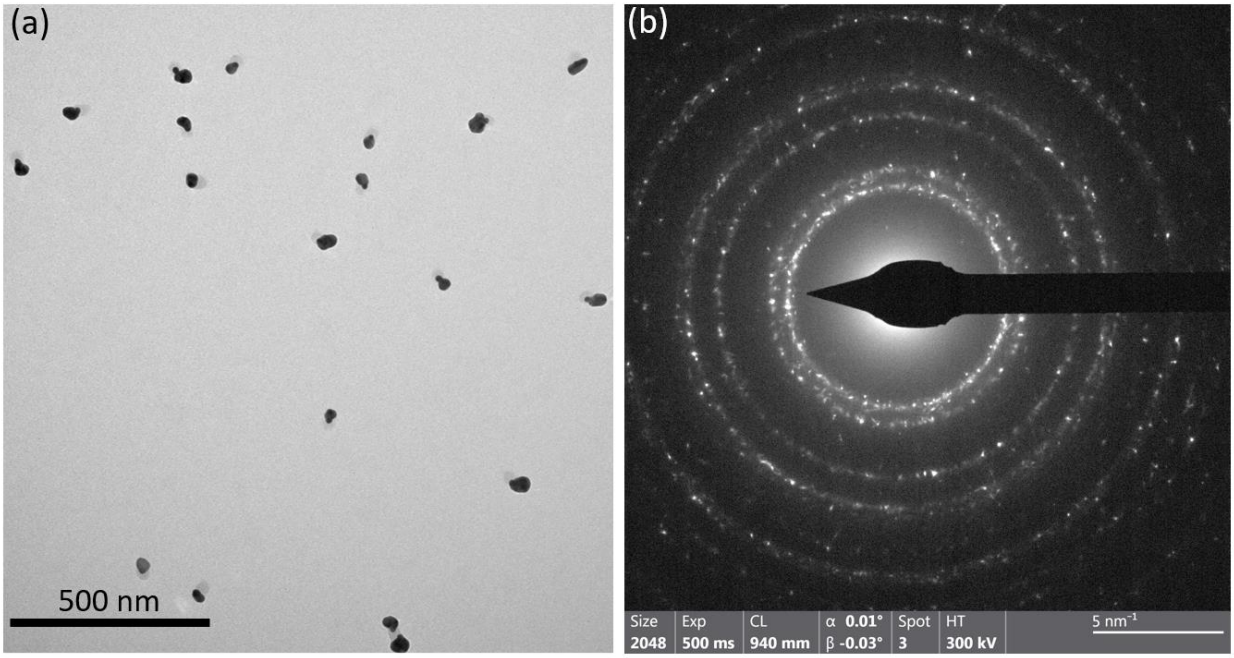


Figure S12. TEM image (a) and electron diffraction pattern (b) of Ag@*p*AuNP-14.

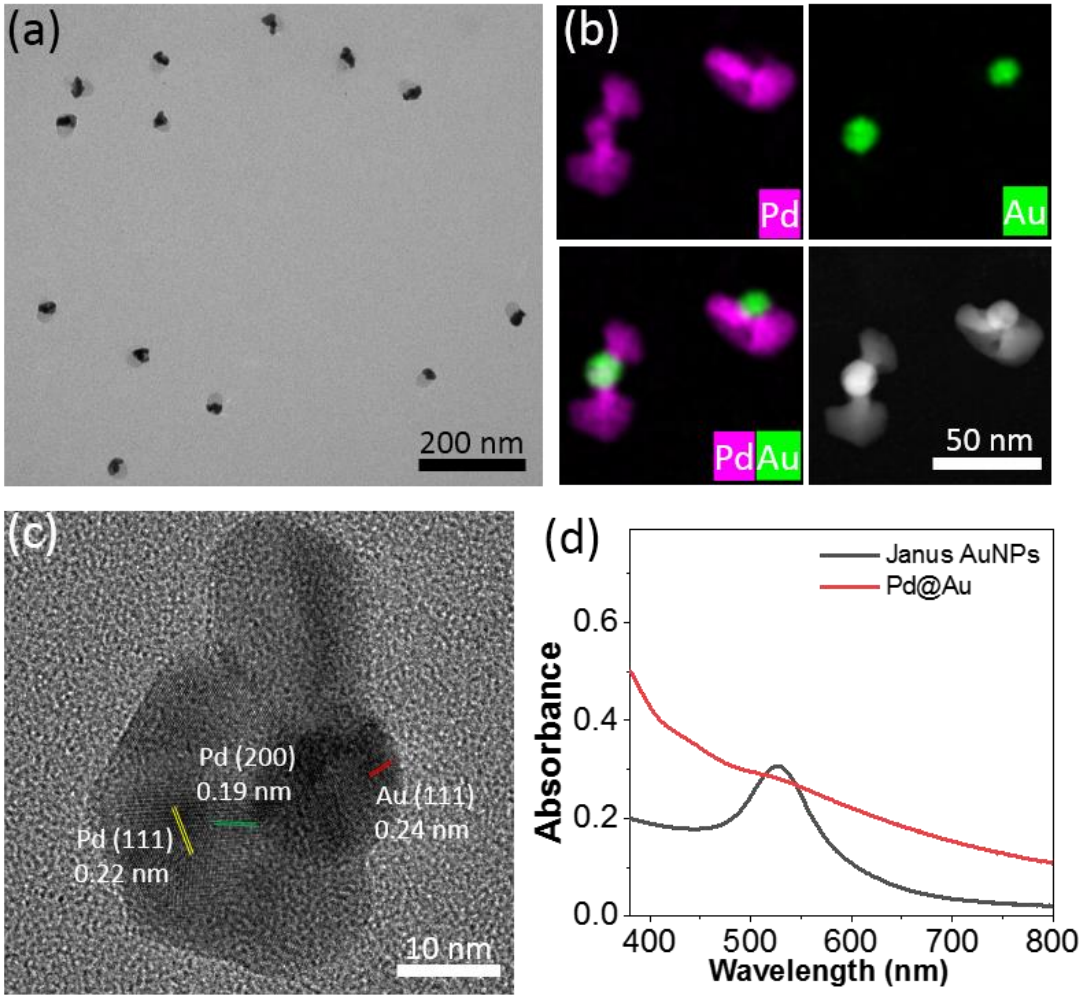


Figure S13. Low resolution TEM image (a), EDX mapping and HADDF (b), high resolution TEM image (c) and UV-vis spectrum (d) of Pd@*p*AuNP-14.

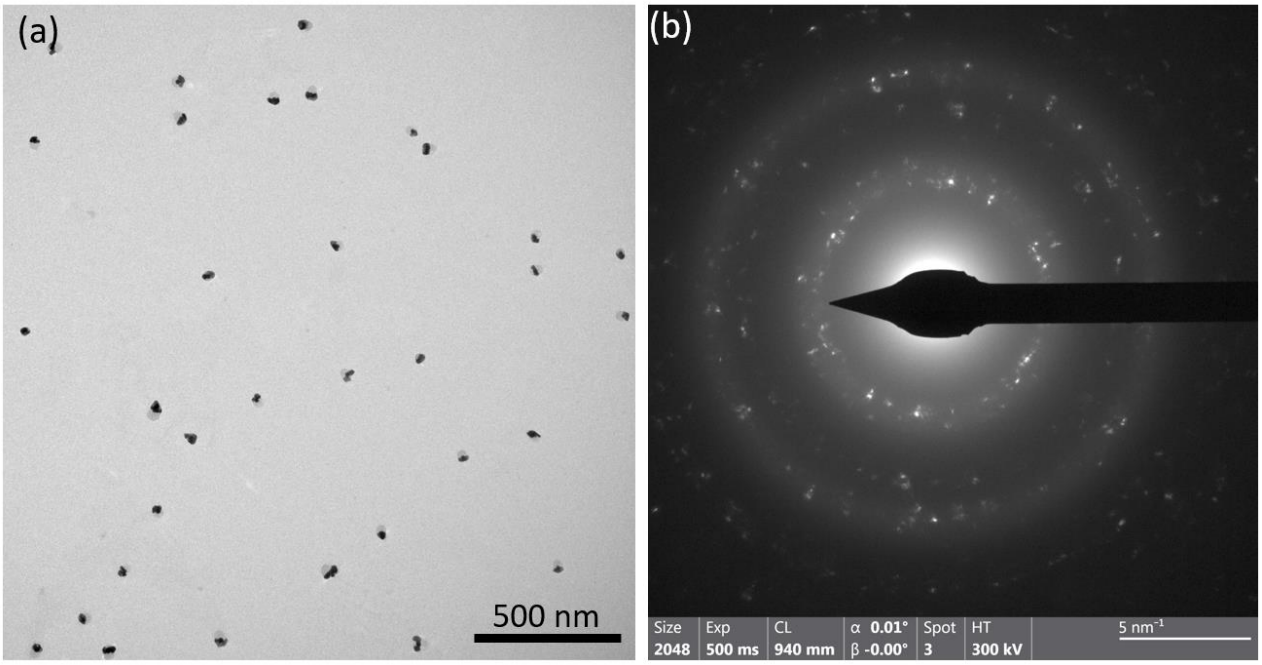


Figure S14. TEM image (a) and electron diffraction pattern (b) of Pd@*p*AuNP-14.

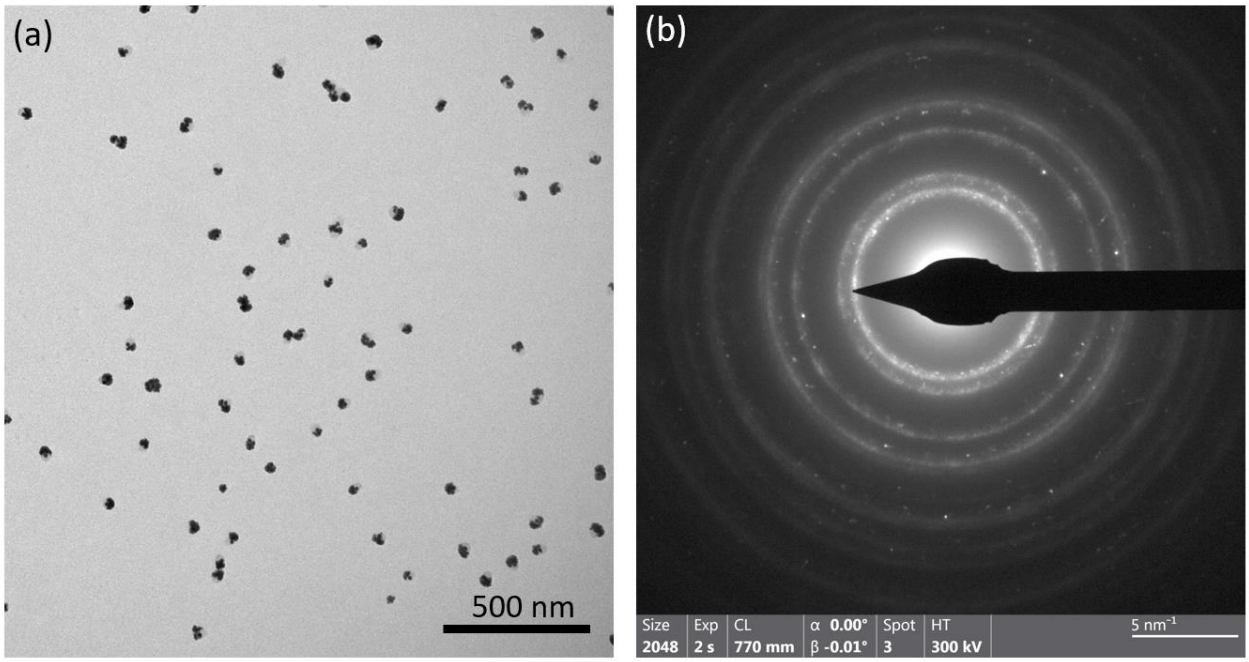


Figure S15. TEM image (a) and electron diffraction pattern (b) of Pt@*p*AuNP-14.

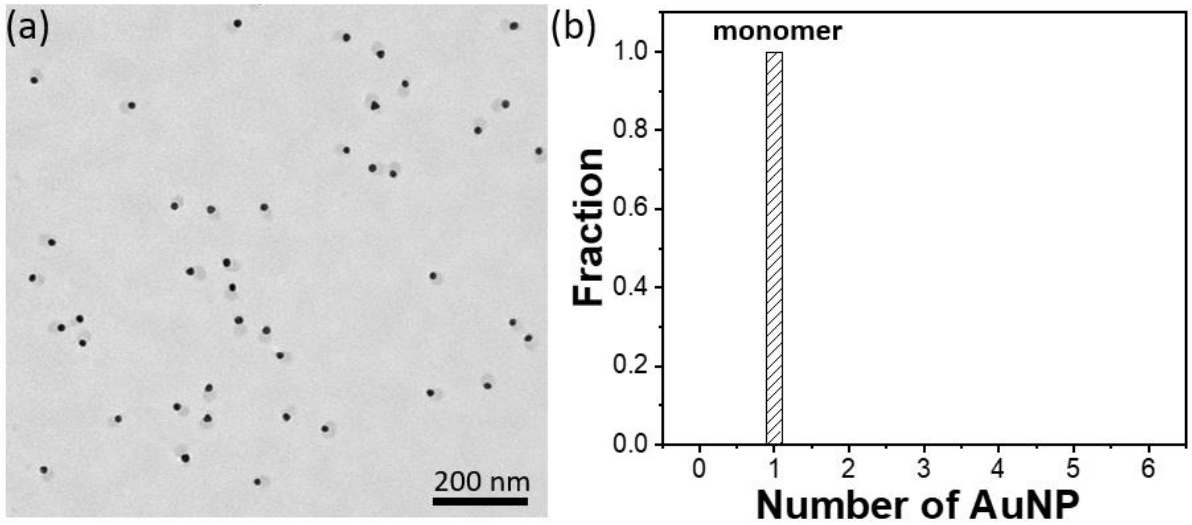


Figure S16. TEM image (a) and product distribution (b) of pAuNPs-14 assembly in ethanol after 24 hours

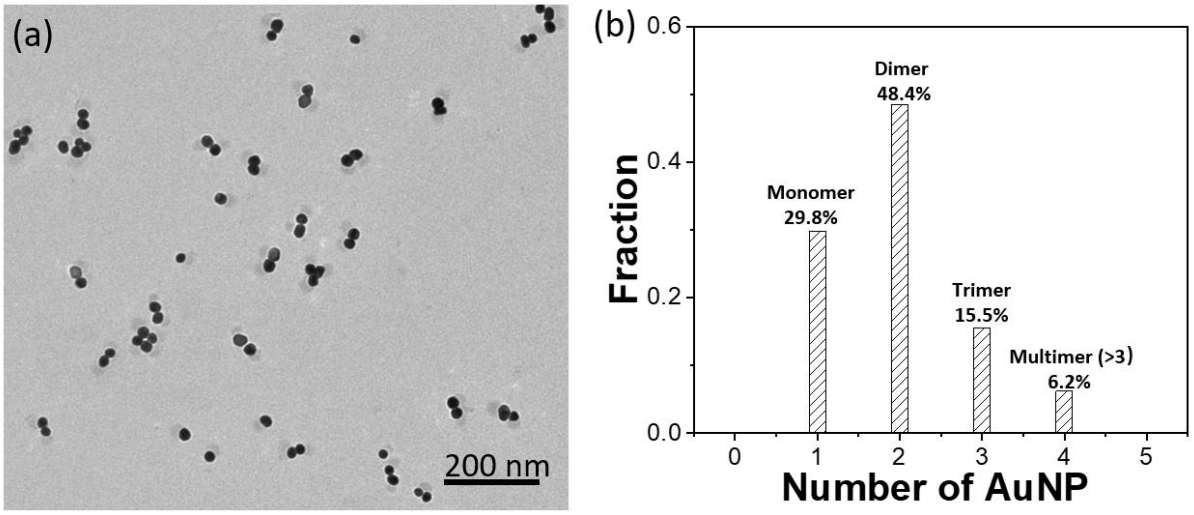


Figure S17. TEM image (a)and product distribution (b) of H-H self-assembly of *p*AuNPs-19.

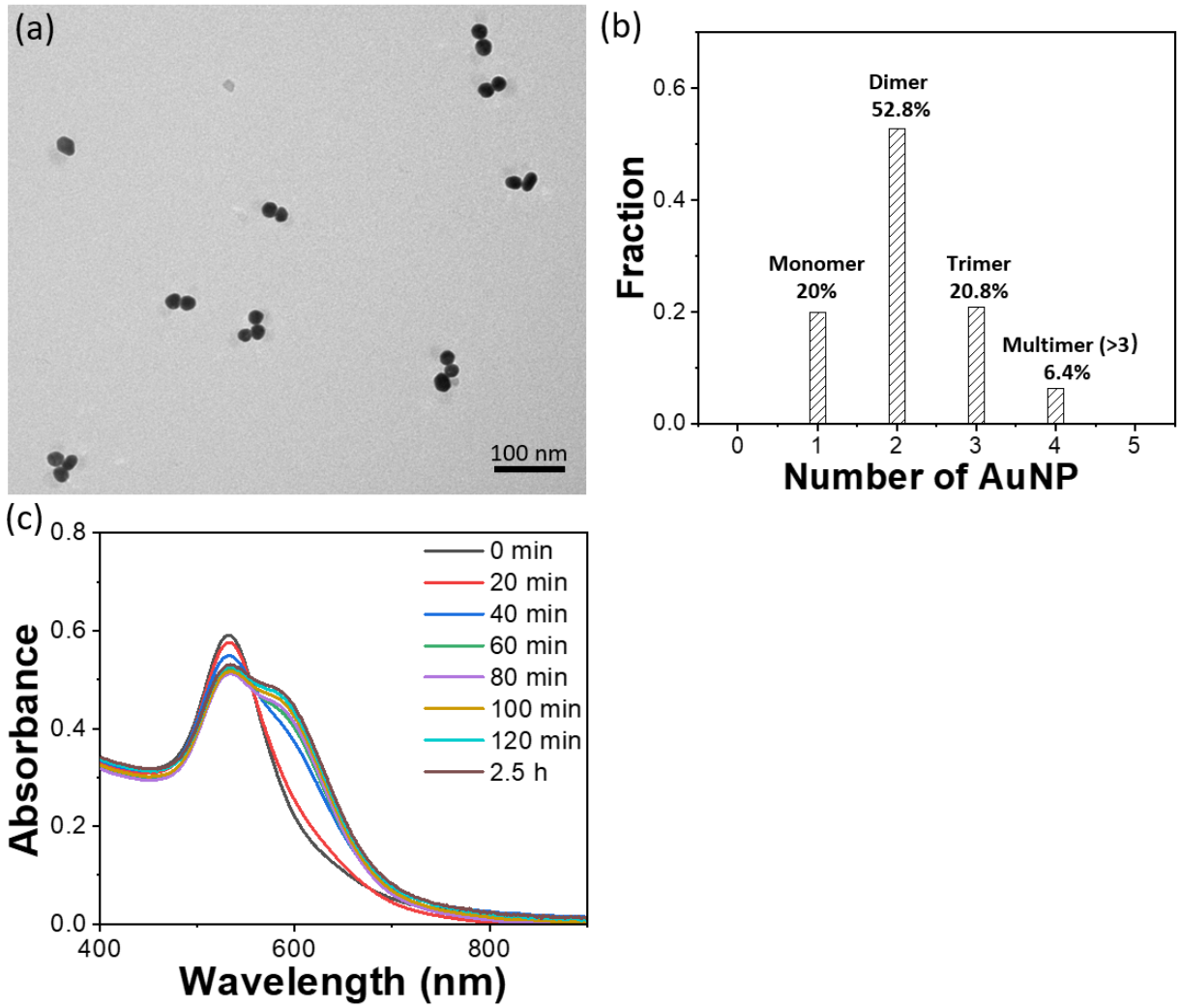


Figure S18. TEM image (a), product distribution (b) and UV-vis evolution (c) of H-H self-assembly of *p*AuNPs-24.

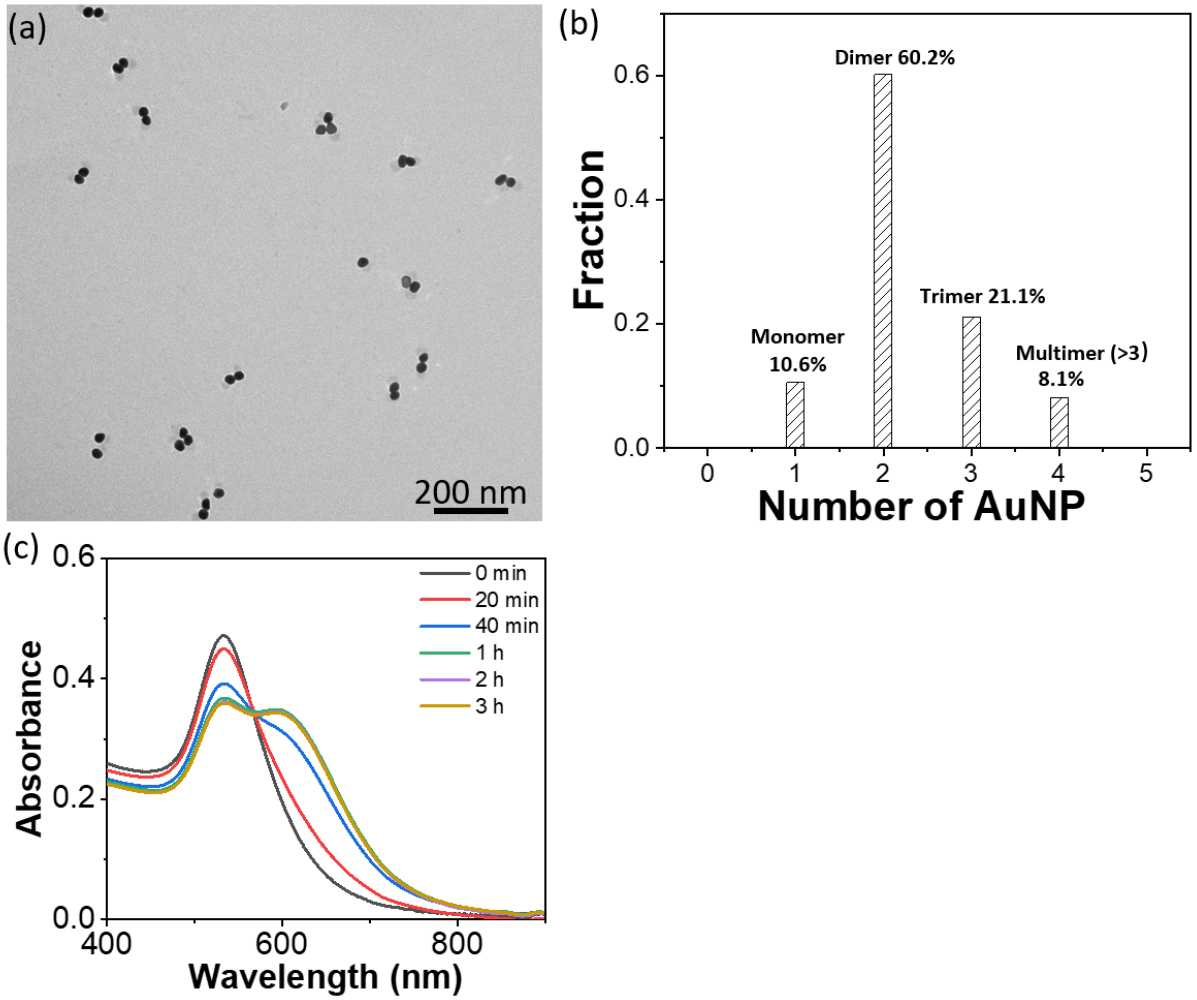


Figure S19. TEM image (a), product distribution (b) and UV-vis evolution (c) of H-H self-assembly of *p*AuNPs-28.

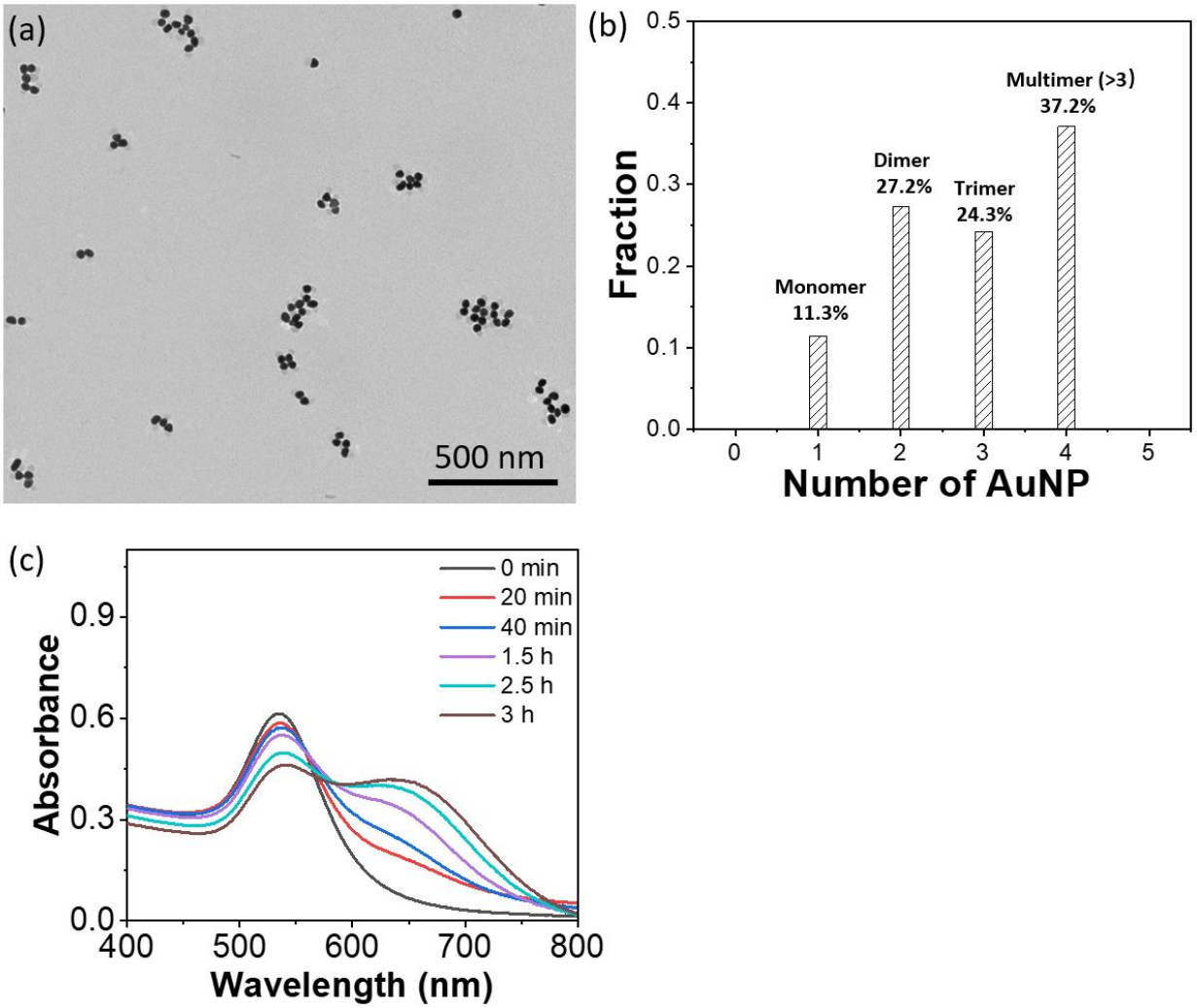


Figure S20. TEM image (a), product distribution (b) and UV-vis evolution (c) of *p*AuNPs-30 H-H self-assembly.

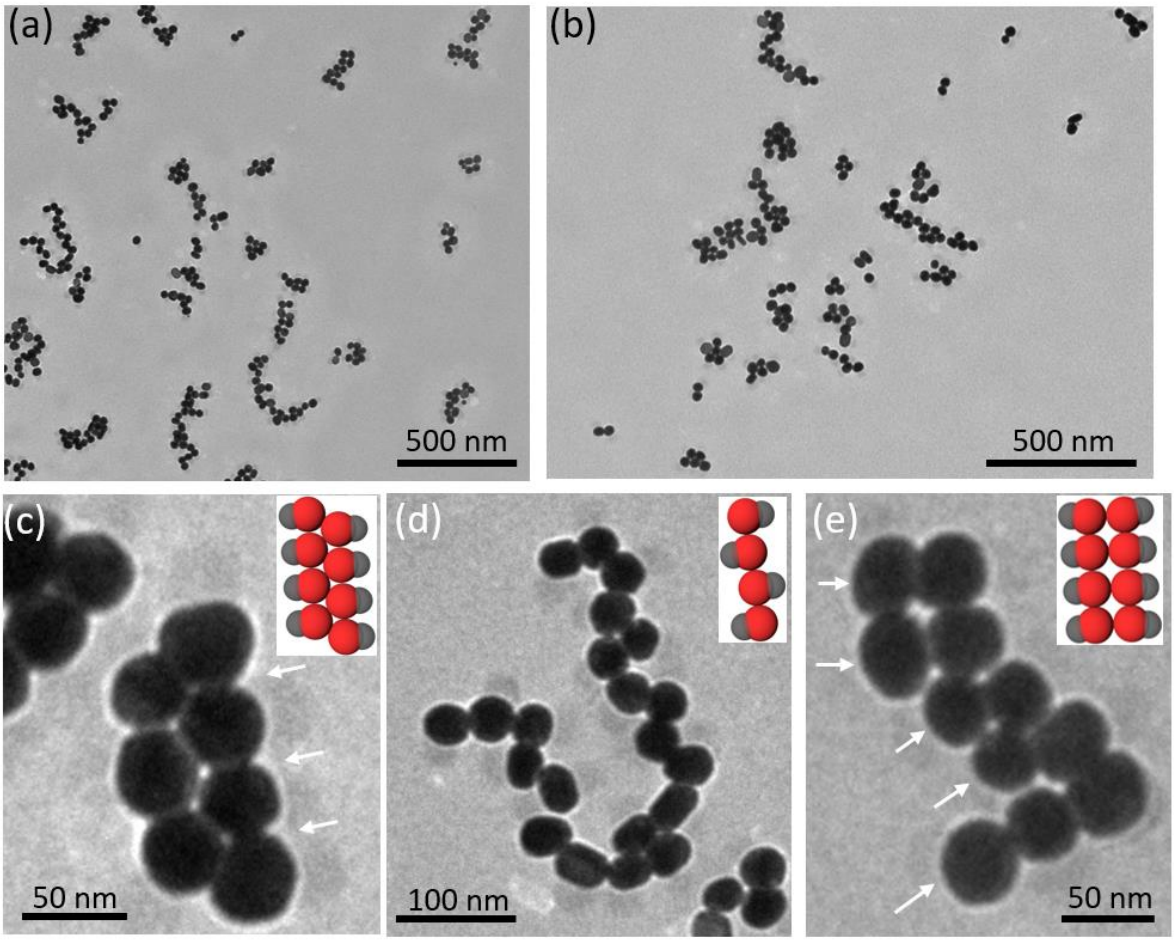


Figure S21. Low resolution TEM image (a and b) of pAuNPs-38 H-H assembly. TEM image and schematic illustration of zig-zag chain (c), linear chain (d), and bundled double chain (e).

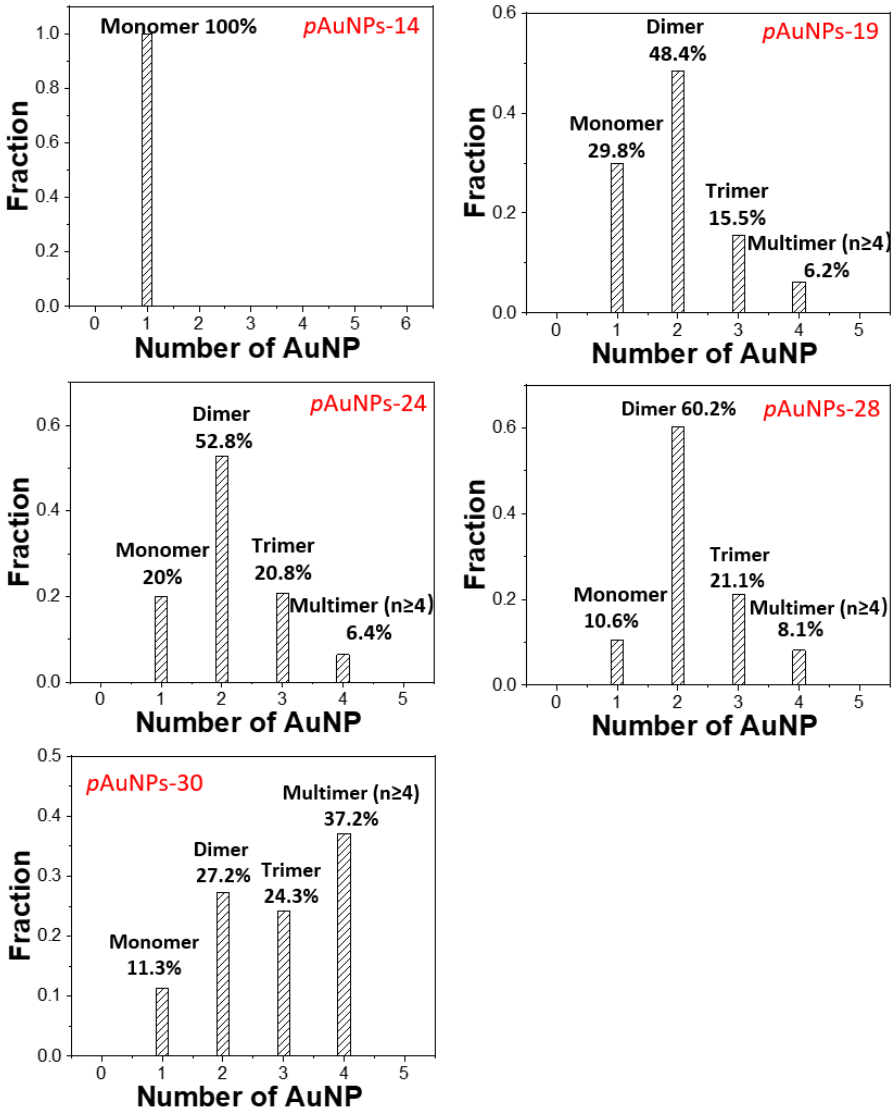


Figure S22. Summary of the production distribution of *p*AuNPs H-H assemblies.

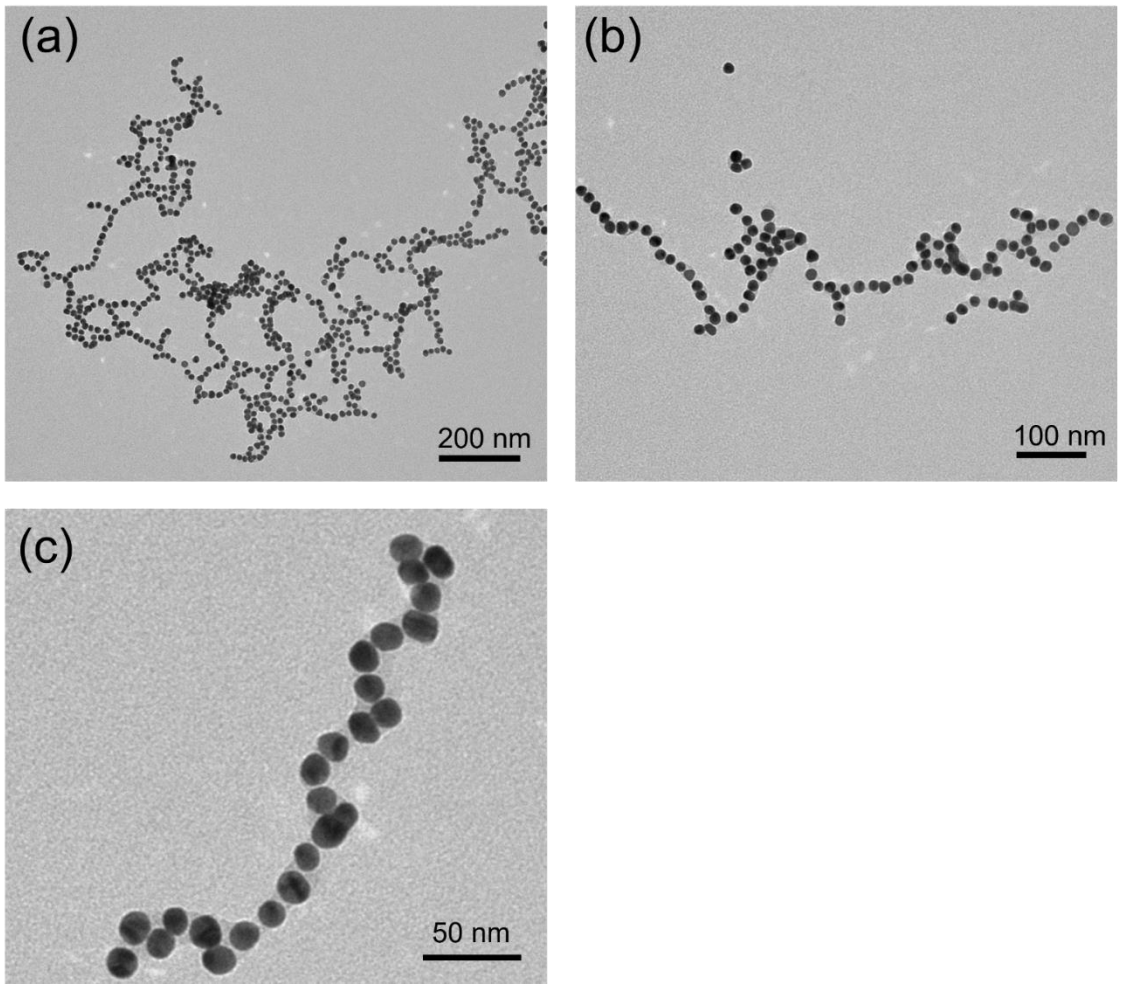


Figure S23. (a-c) TEM images at different magnification of pAuNPs-28 T-T assemblies.

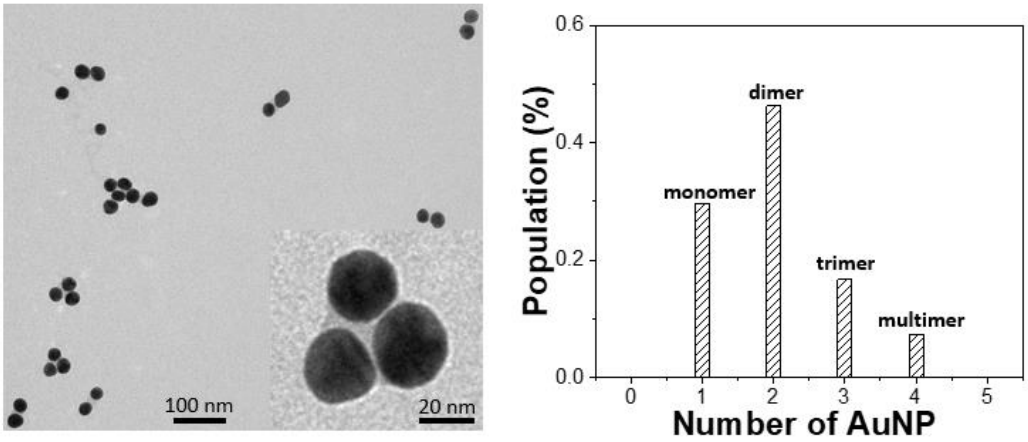


Figure S24. TEM image (left, inset is a zoom-in image where the gap between AuNPs was filled with polymer) and product distribution (right) of *p*AuNP-28 T-T assemblies.

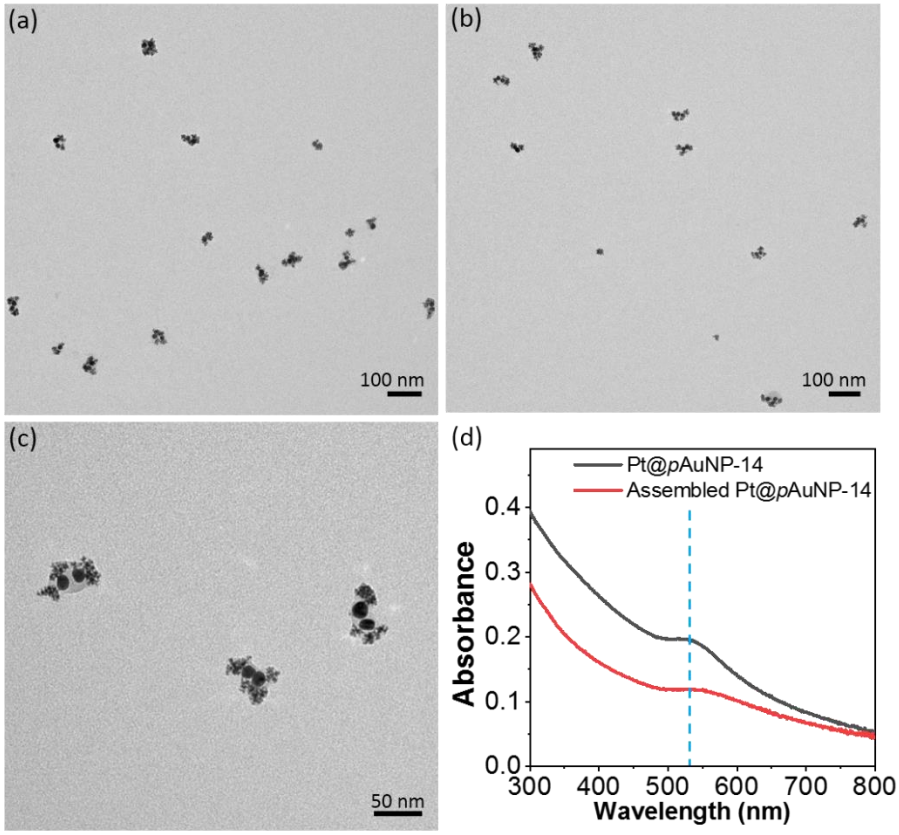


Figure S25. TEM images (a-c) and UV-vis spectrum (d) of the assembly of Pt@*p*AuNP-14. The assembly was carried out by dialysis against water after removal of polymer patches. The UV-vis shows the broadening LSRP peak shift from 530 nm to 544 nm after assembly.

References

1. Hasell, T.; Thurecht, K. J.; Jones, R. D.; Brown, P. D.; Howdle, S. M., Novel one pot synthesis of silver nanoparticle–polymer composites by supercritical CO 2 polymerisation in the presence of a RAFT agent. *Chem. Commun.* **2007,** (38), 3933-3935.
2. Li, W.; Kanyo, I.; Kuo, C.-H.; Thanneeru, S.; He, J., pH-programmable self-assembly of plasmonic nanoparticles: hydrophobic interaction versus electrostatic repulsion. *Nanoscale* **2015,** *7* (3), 956-964.
3. He, J.; Liu, Y.; Babu, T.; Wei, Z.; Nie, Z., Self-Assembly of Inorganic Nanoparticle Vesicles and Tubules Driven by Tethered Linear Block Copolymers. *J. Am. Chem. Soc.* **2012,** *134* (28), 11342-11345.
4. Haiss, W.; Thanh, N. T.; Aveyard, J.; Fernig, D. G., Determination of size and concentration of gold nanoparticles from UV− Vis spectra. *Anal. Chem.* **2007,** *79* (11), 4215-4221.