

Supporting Information

Star-like Copolymer Stabilized Noble-Metal Nanoparticle Powders

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Calculation:

Molecular Weight of PEI10k-b-PCL12 = 10,000 + 114.14 × 143 × (10.84 + 1) = 203.3 kDa

143: the number of PCL arms. Please see reference [1] for details.

(10.84 + 1): the degree of polymerization per PCL arm. The number is based on the integration of NMR spectrum as shown in Figure 1.

The average number of gold atoms in a gold nanoparticle can be calculated according to equation

$$N_c = \frac{\pi \rho D^3}{6M}$$
 according to reference [2], where ρ is the density of the fcc gold (19.3 g/cm³), D is the average core diameter of the particles, and M is the atomic weight of gold (197 g/mol), and $N_c = 30.89602D^3$, when D is the average diameter of particle (nm).

As a result, for the AuNPs with average diameter of 16.5 nm, the average number of gold atoms in a gold nanoparticle is

$$N_c = 30.89602 \times D^3 = 30.89602 \times (16.5)^3 = 1.388 \times 10^5$$

For a AuNPs aqueous solution with gold atom concentration of 2.50×10^{-4} mol/L, the gold nanoparticle concentration

$$c(\text{AuNPs}) = 2.50 \times 10^{-4} / (1.388 \times 10^5) = 1.80 \times 10^{-9} \text{ (mol/L)}$$

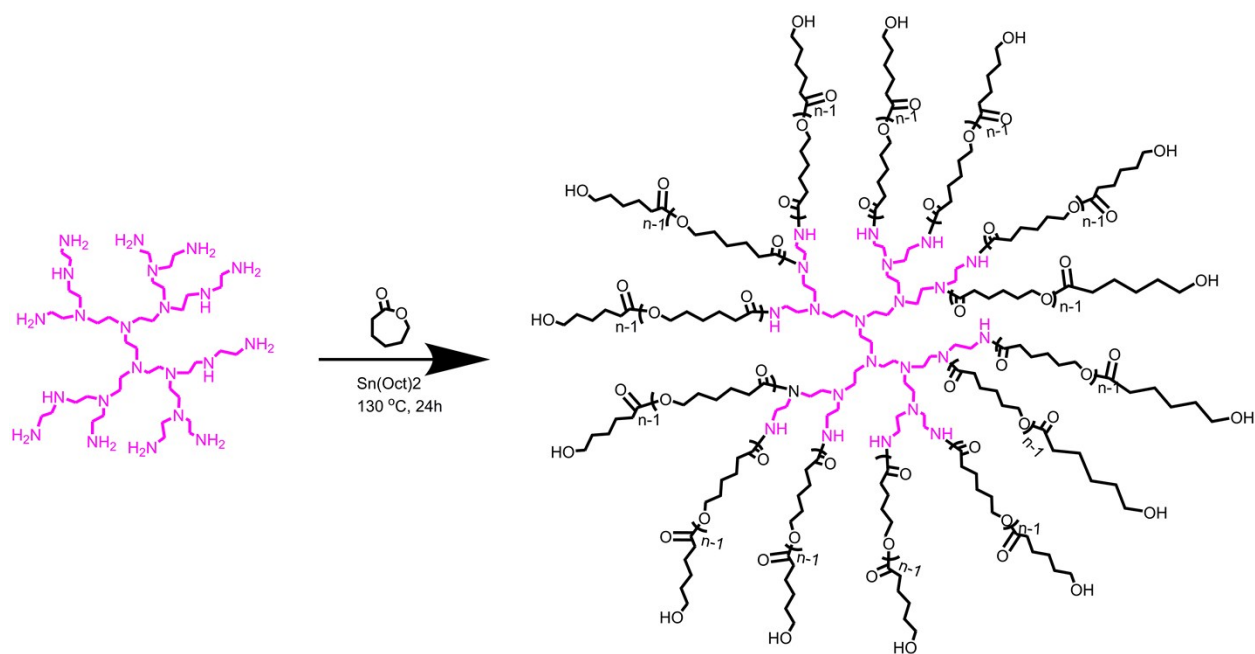
The minimal polymer concentration to transfer all of the AuNPs in aqueous solution is 0.05 mg/mL, the molar concentration of star-like copolymer $c(\text{PEI-b-PCL}) = 0.05 \text{ mg/mL} = 0.05 \text{ g/mL} = 0.05 / (203.3 \times 10^3) \text{ mol/L} = 2.46 \times 10^{-7} \text{ (mol/L)}$

Since equivalent amount of polymer solution and AuNPs solution was employed for phase transfer, the minimal polymer number to stabilize one AuNP is

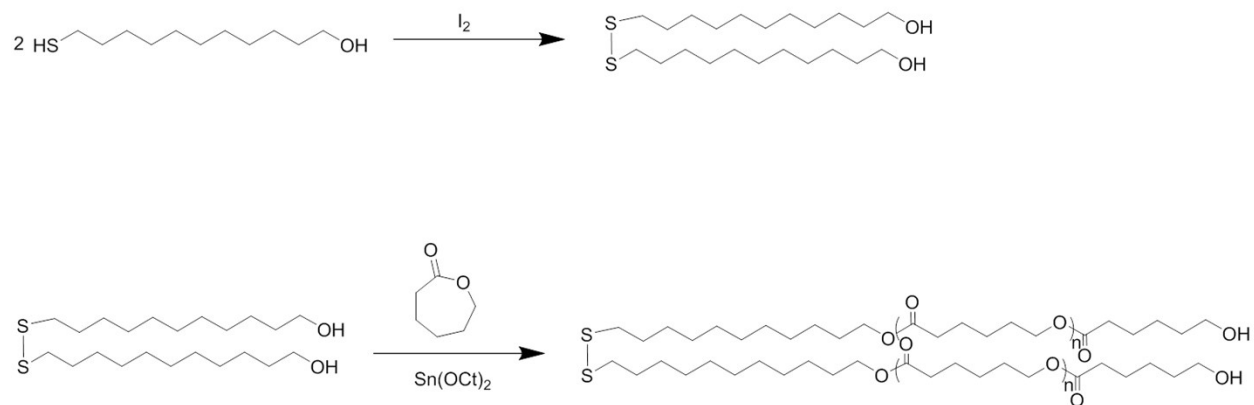
$$(2.46 \times 10^{-7}) / (1.80 \times 10^{-9}) = 137$$

Further discussion on the experiment performed to study the assembly of polymers on AuNPs

Further experiment was conducted to confirm the polymer arrangement of the SPS-AuNPs (right in Scheme 1). In this specific experiment, the AuNPs with smaller size were utilized (12.2 ± 0.9 nm) for a larger difference in size. Negatively charged phosphotungstic acid (PTA) could selectively stain the PEI segment of the amphiphilic star-like copolymer PEI-*b*-PCL. This is due to the presence of electrostatic affinity between the cationic PEI and PTA, while this interaction would be impossible between the hydrophobic PCL and PTA. As expected, the measured average diameter of the PEI10K-*b*-PCL12-stabilized AuNPs increased to 16.8 ± 1.3 nm (see Supporting Information Figure S7) because the surrounding PEIs would also appear as part of the “AuNPs”. When keeping the PEI core with the same molecular weight and changing the DP_n of star-like copolymer from 12 to 6, no significant difference in the measured diameter of “AuNPs” was observed (see Supporting Information Figures S7 and S8). Further evidence was provided by the “light organic shells” around the “AuNPs” in the TEM images of the PEI10K-*b*-PCL12-stabilized AuNPs (inset of Figure S7 (B)). This can be explained that the hydrophobic PCLs surrounding the “AuNPs” would prevent the PTAs from screening those areas.



Scheme S1. Synthesis of star-like block copolymer PEI-*b*-PCL.



Scheme S2. Synthesis of disulfide-poly(ϵ -caprolactone)

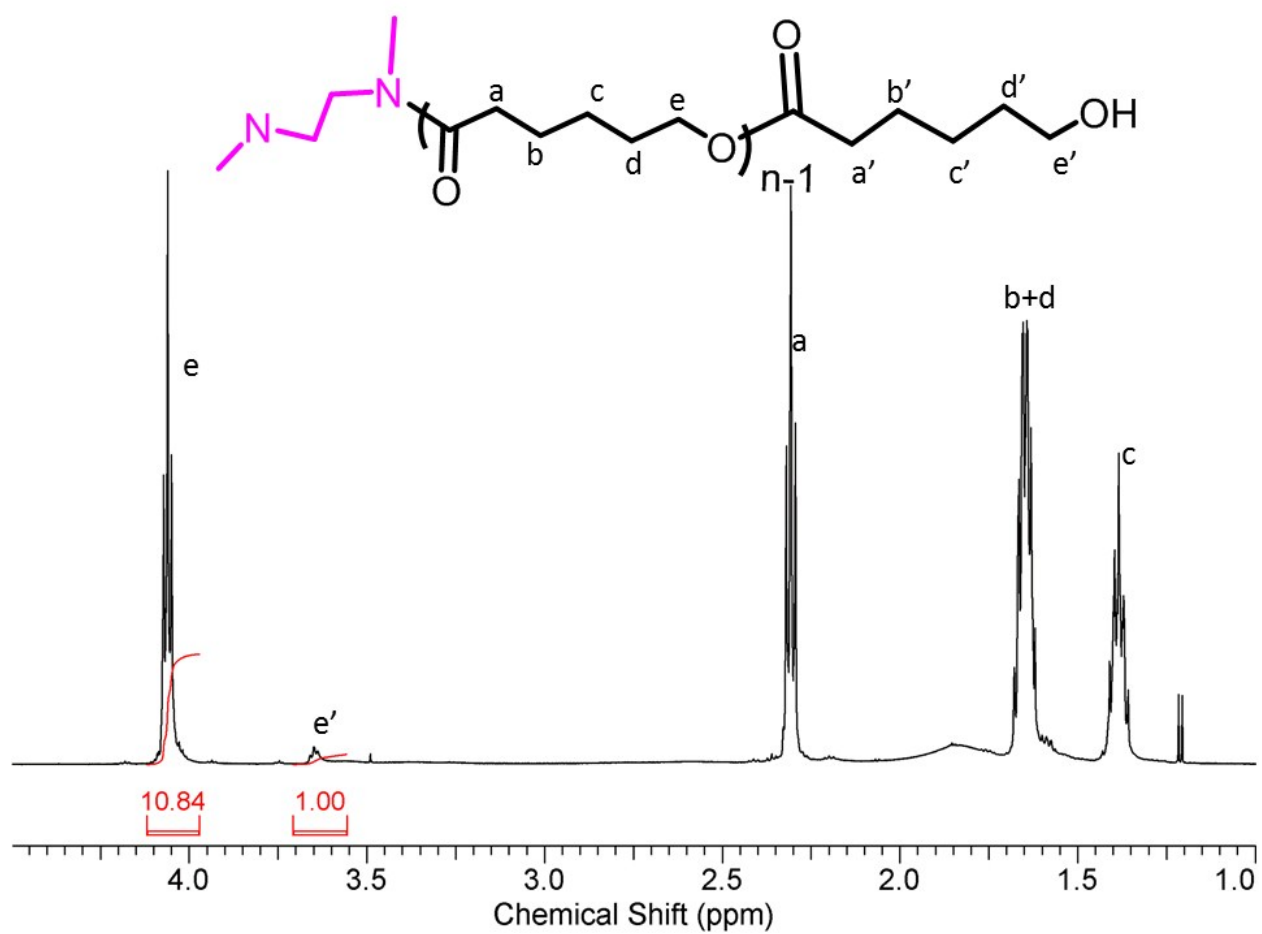


Figure S1. ^1H NMR spectrum (600 MHz, CDCl_3) of star-like copolymer PEI10K-*b*-PCL12.

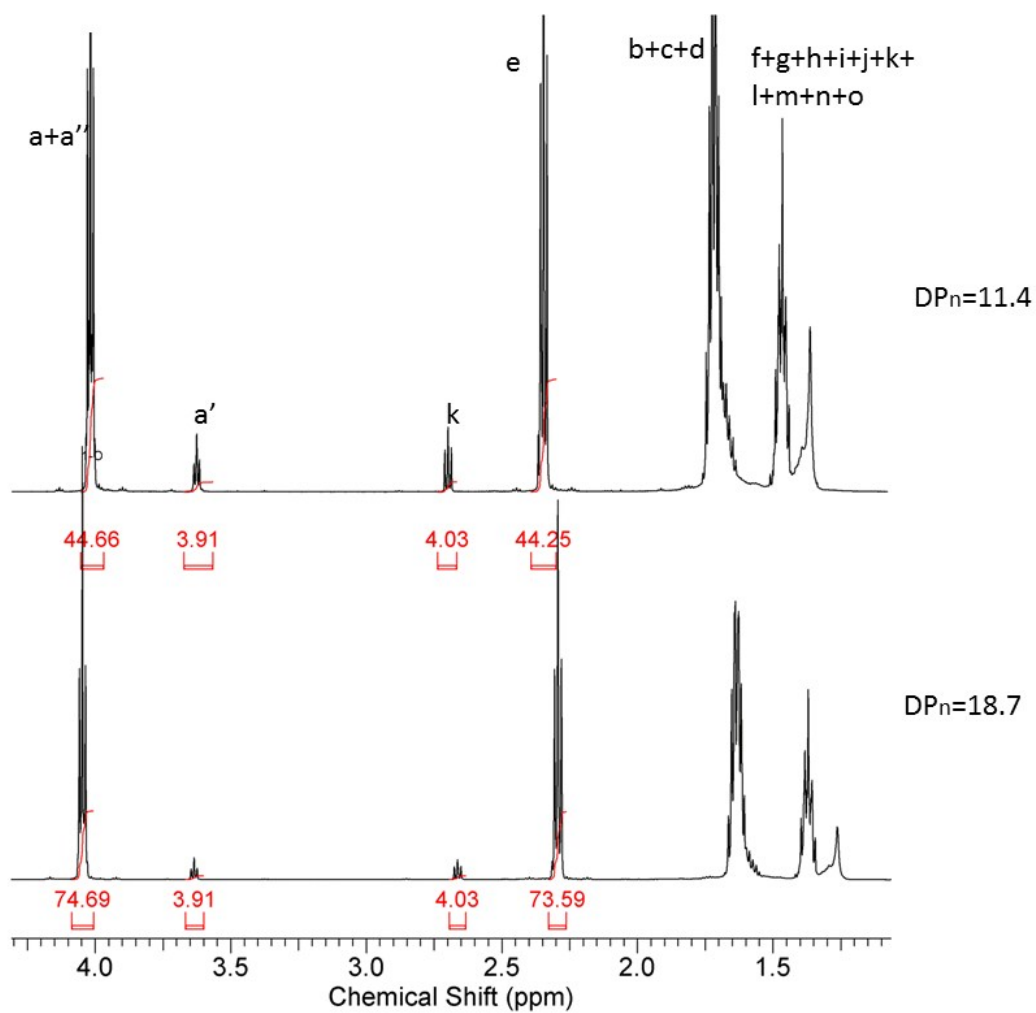
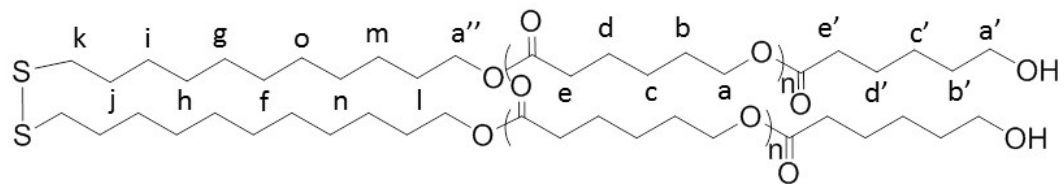


Figure S2. ^1H NMR spectra of disulfide-PCL11 and disulfide-PCL19

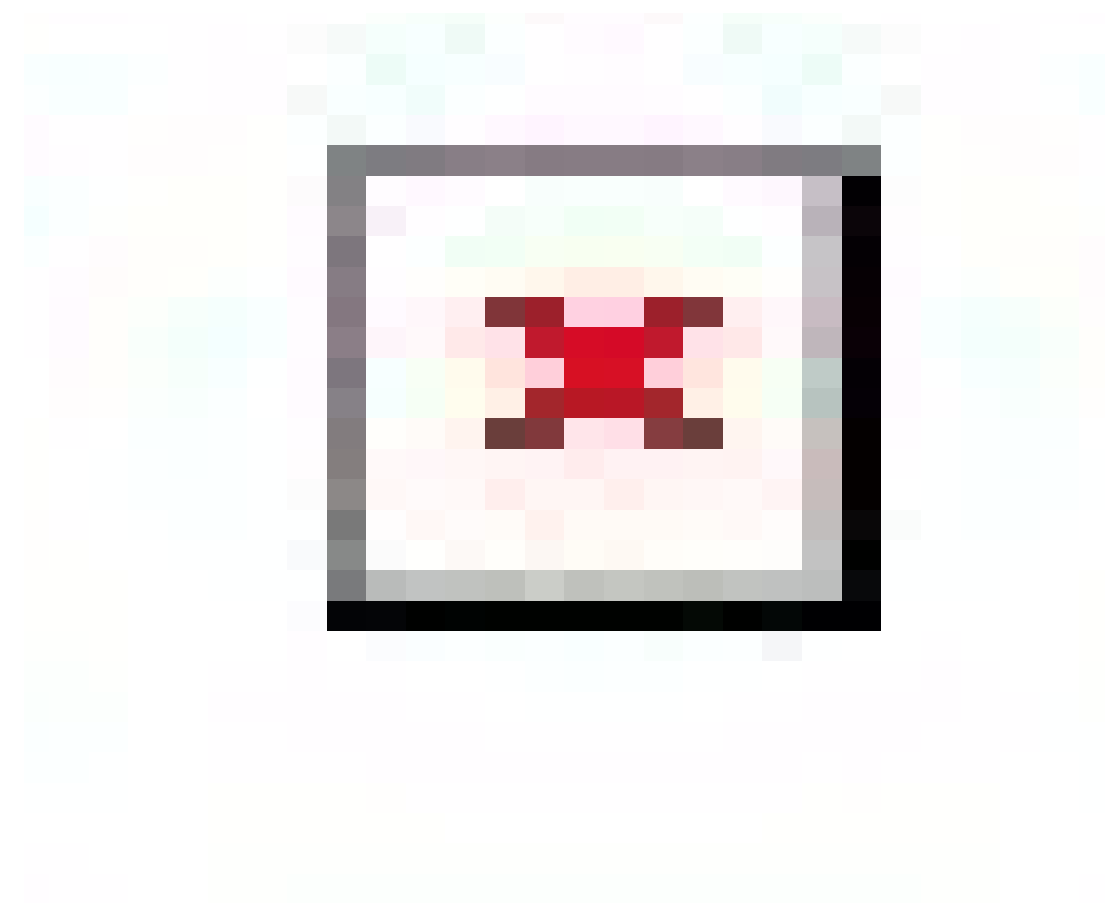


Figure S3. Comparative UV-Vis spectra of citrate-capped AgNPs in aqueous layer and PEI10K-*b*-PCL12 protected AgNPs in chloroform layer.

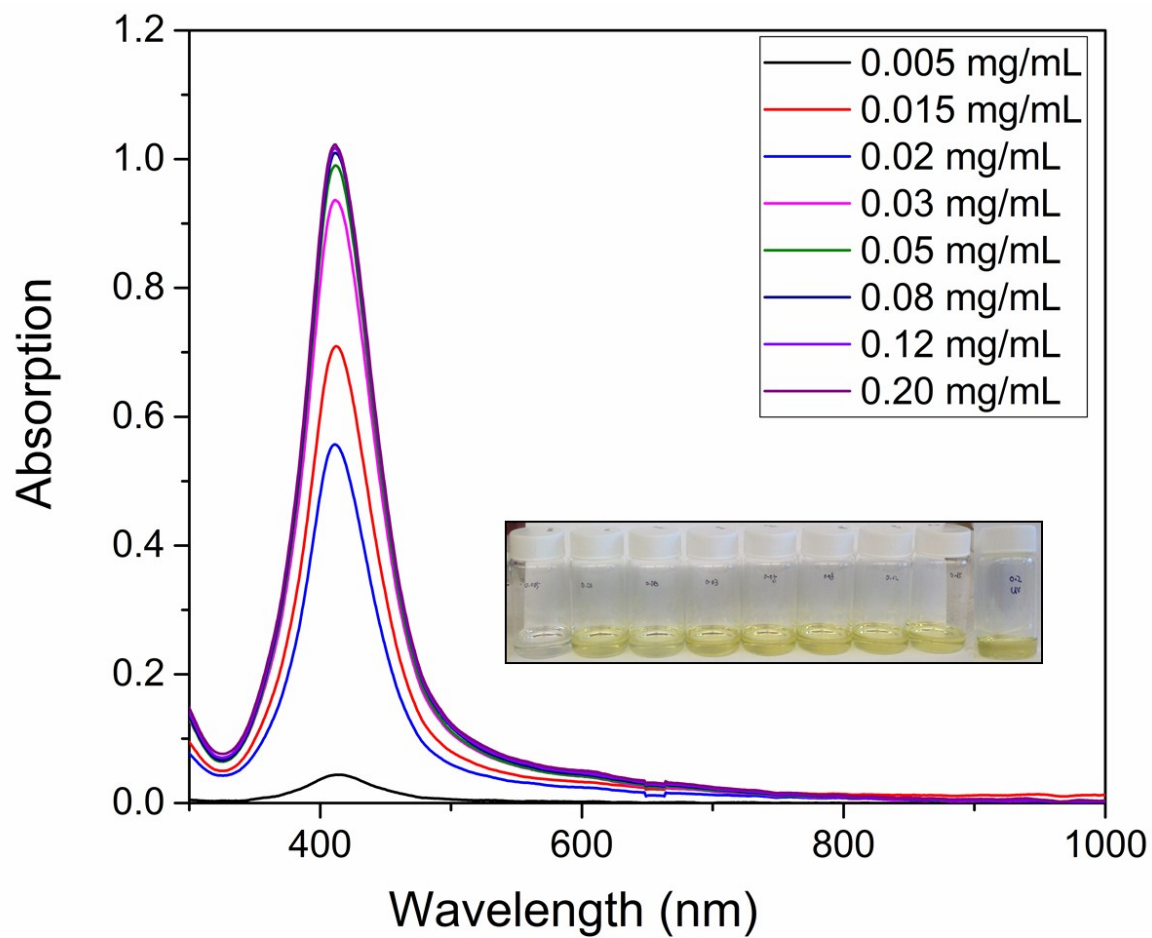


Figure S4. UV-Vis spectra of the chloroform solution of the PEI10K-*b*-PCL12 with different concentration after mixing with the aqueous solution of AgNPs. The inset is the photograph of the organic layer after mixing (increased polymer concentration from left to right as labeled)

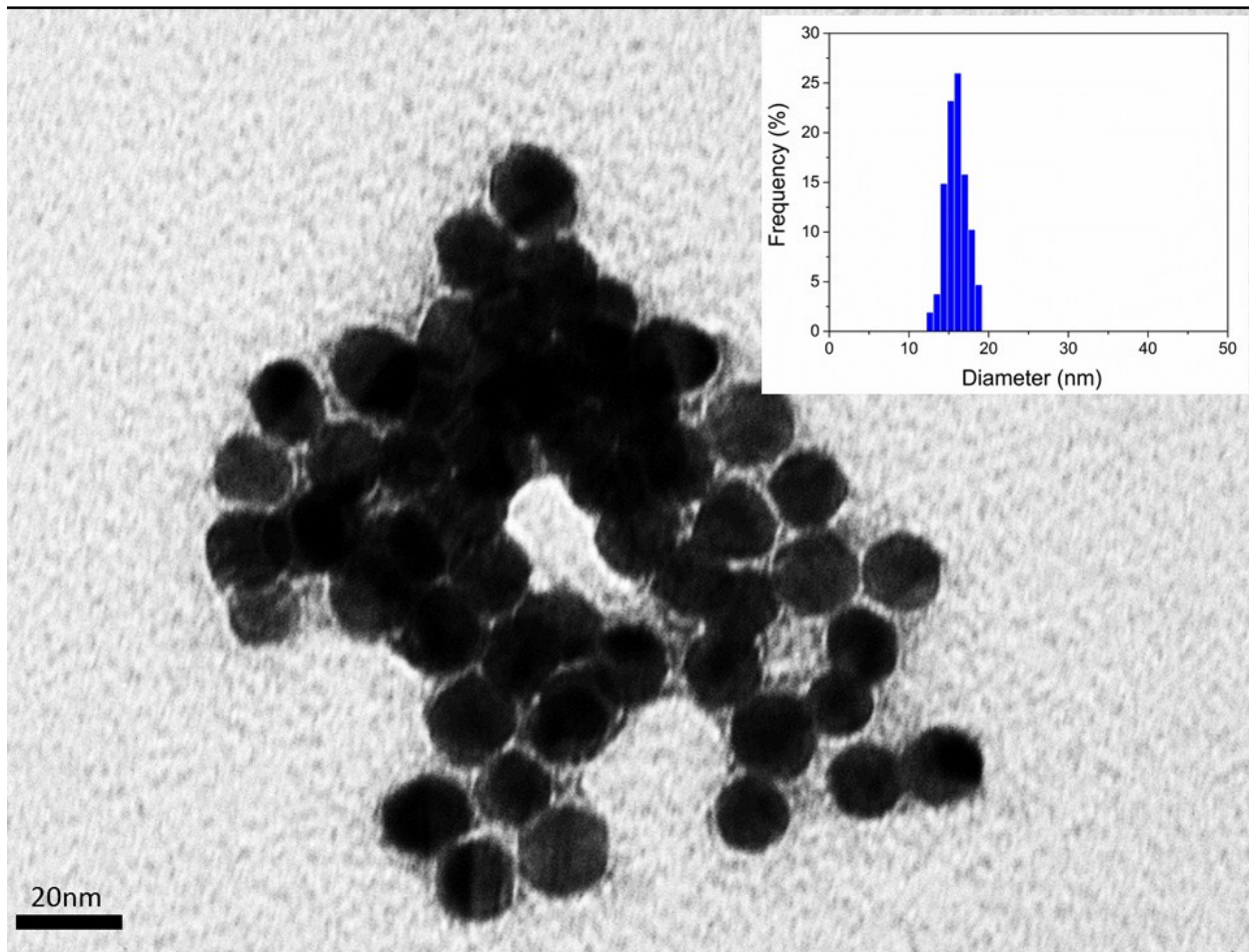


Figure S5. TEM image of the synthesized AuNPs.

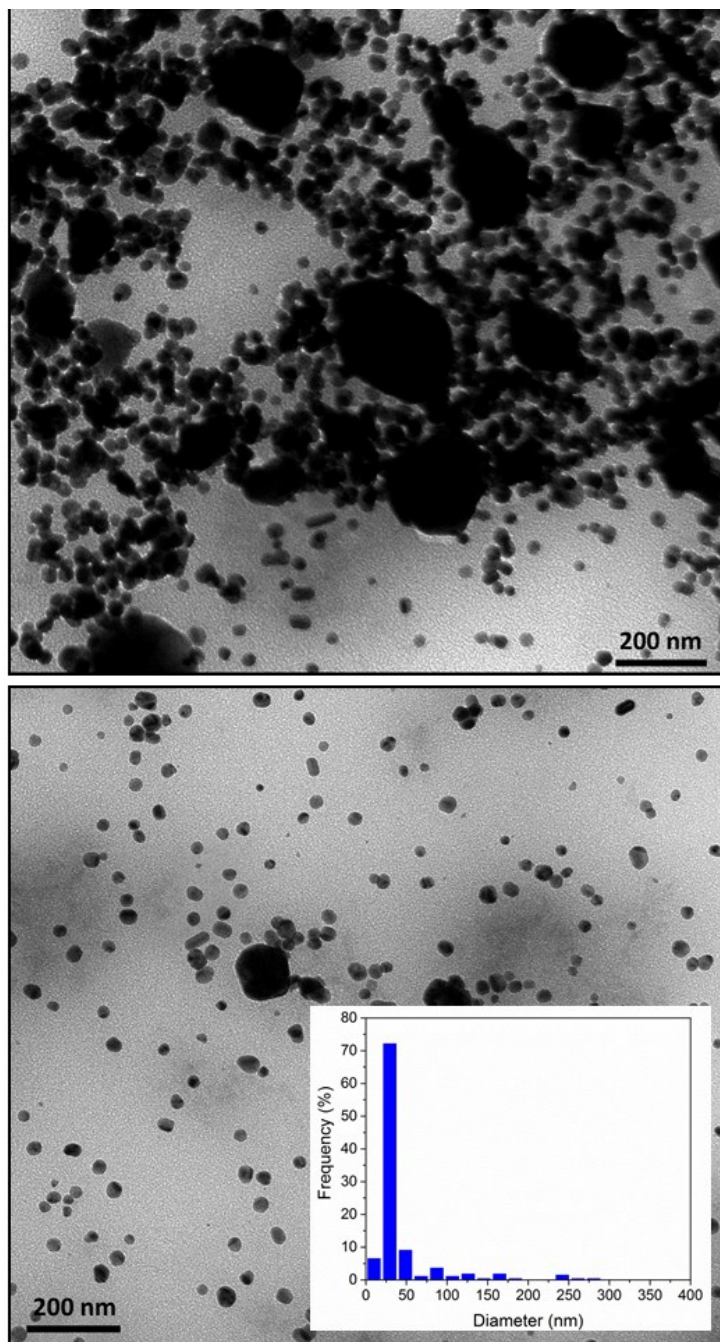


Figure S6. TEM images of synthesized AgNPs in aqueous solution

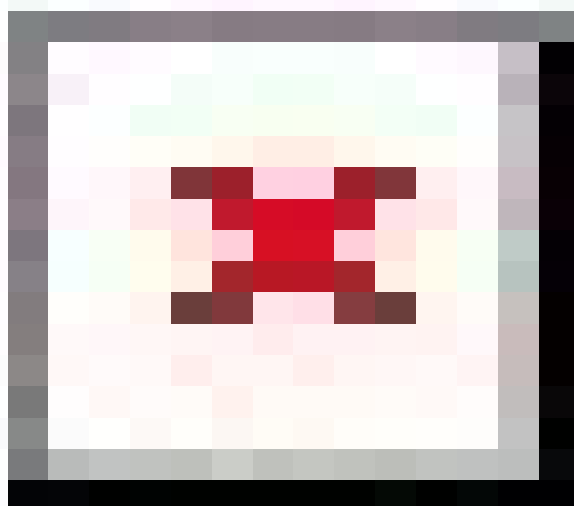


Figure S7. Comparative DLS analysis of citrate-capped AgNPs (CC-AgNPs) in aqueous solution (top) and star-like copolymer stabilized AgNPs (SPS-AgNPs) in chloroform solution (bottom).

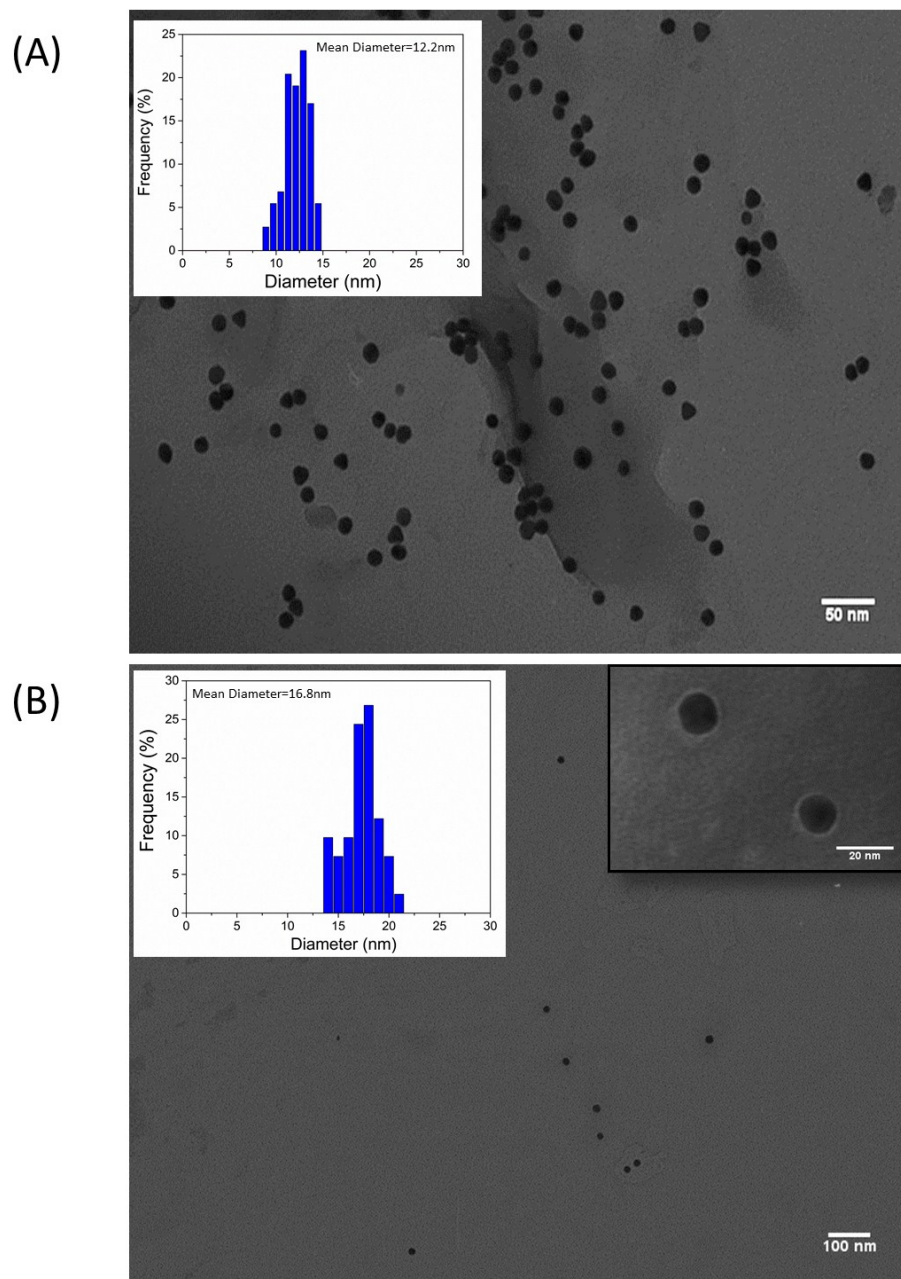


Figure S8. Comparative TEM images of the PEI10K-*b*-PCL12 (PEI Mw=10K, DP_n=12) coated AuNPs with phosphotungstic acid (PTA) as staining agent; insets are the histograms of the diameter of AuNPs and polymer coated AuNPs.

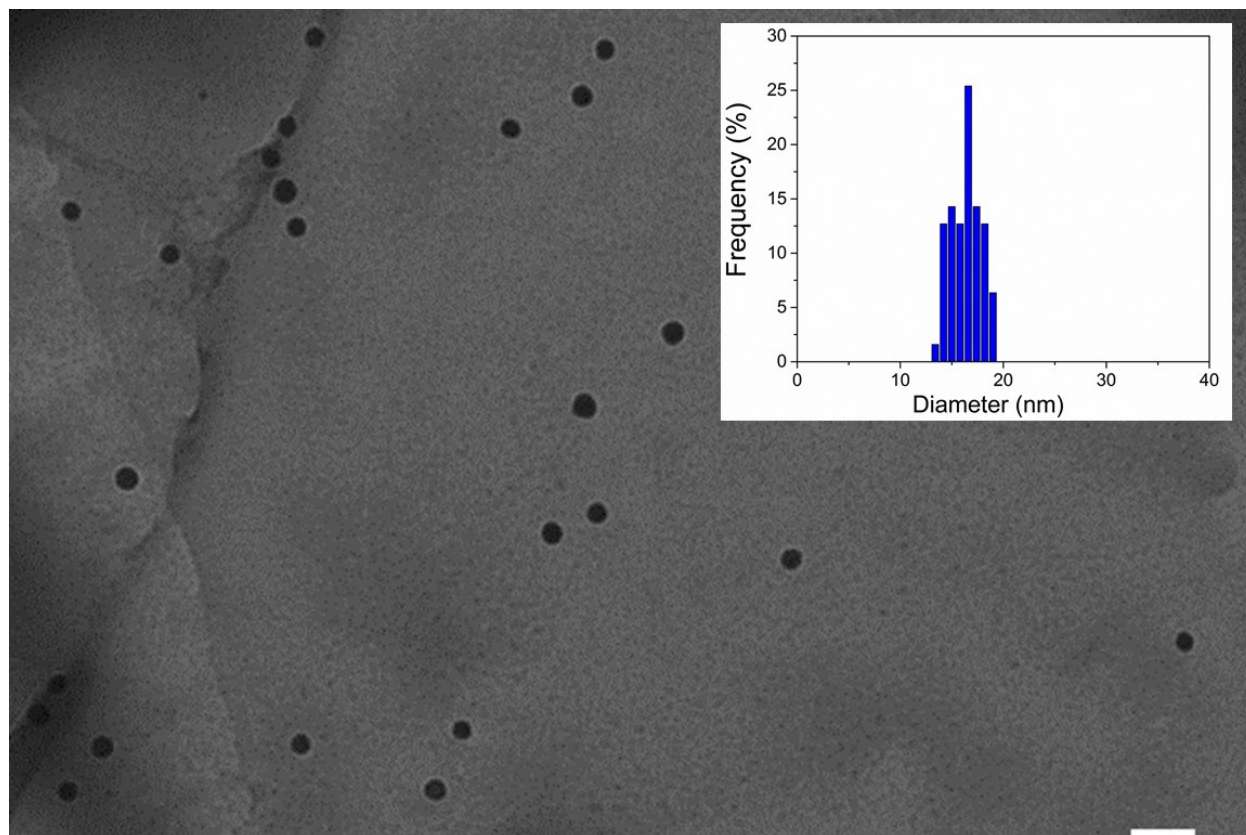


Figure S9. TEM image of AuNPs coated with PEI10K-*b*-PCL6 (PEI Mw=10K, DP_n=6) with phosphotungstic acid (PTA) as staining agent; inset is the histogram.

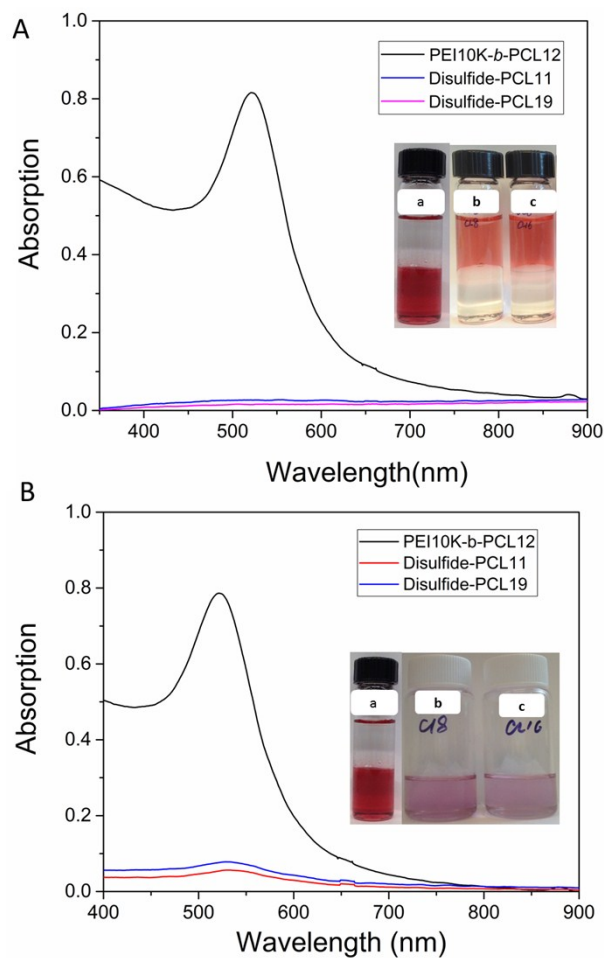


Figure S10. (A) UV-vis spectra of the chloroform solutions of different polymers after mixing with the aqueous solution of the CC-AuNPs (polymer concentration: 0.06 mg/mL); (B) UV-vis spectra of the chloroform solutions of polymer coated AuNPs (polymer concentration: 0.06 mg/mL), ligand exchange method was utilized for polymer disulfide-PCL11 and disulfide-PCL19. Insets are photographs after phase transfer or ligand exchange process.

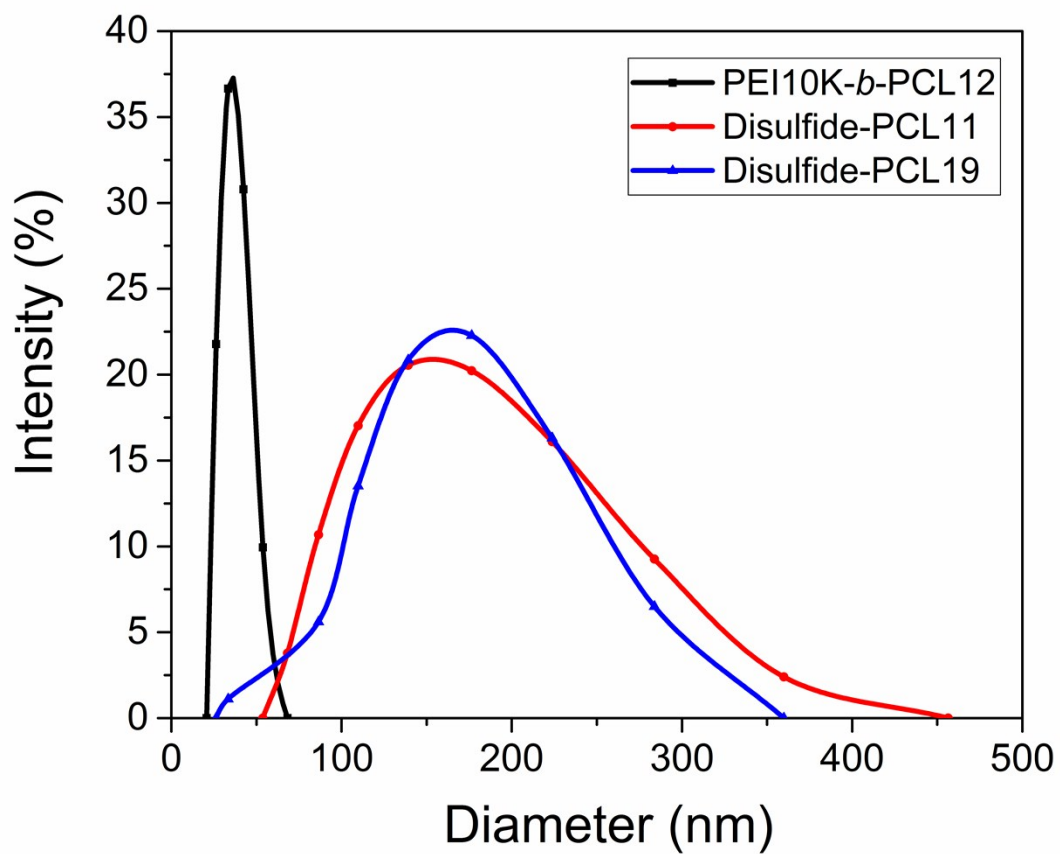


Figure S11. Comparative DLS analysis of AuNPs stabilized by the different polymers as labeled.

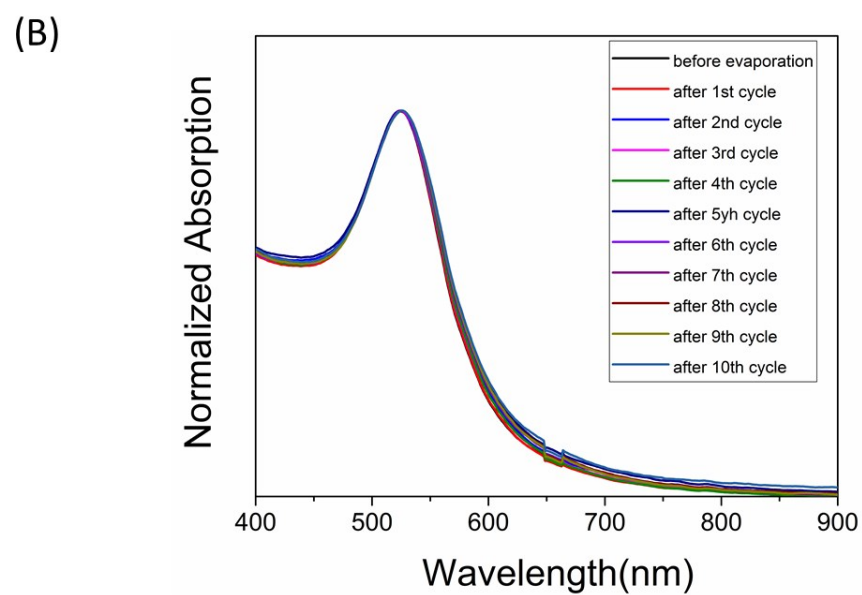
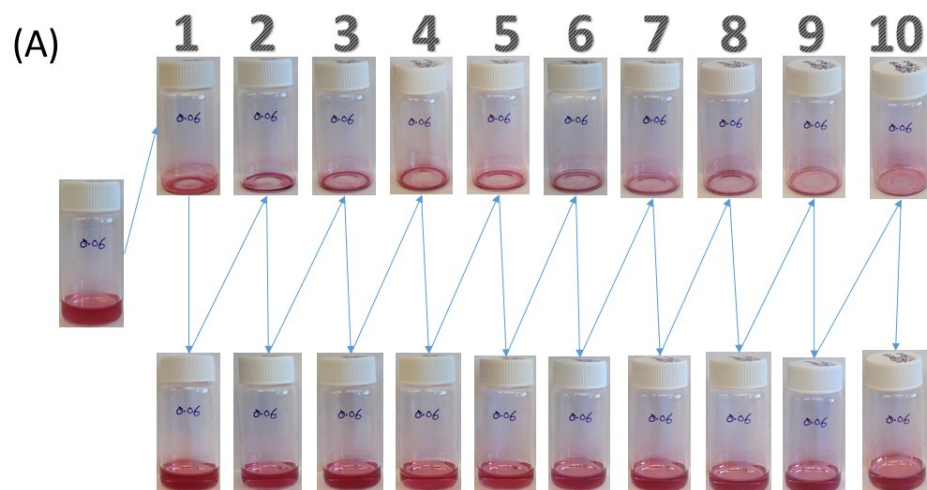


Figure S12. (A) Photographs of the polymer-stabilized AuNPs in chloroform after every evaporation and re-dispersion in chloroform; (B) Localized surface plasmon resonance (LSPR) spectra of the polymer-stabilized AuNPs in chloroform after each cycle's re-dispersion.

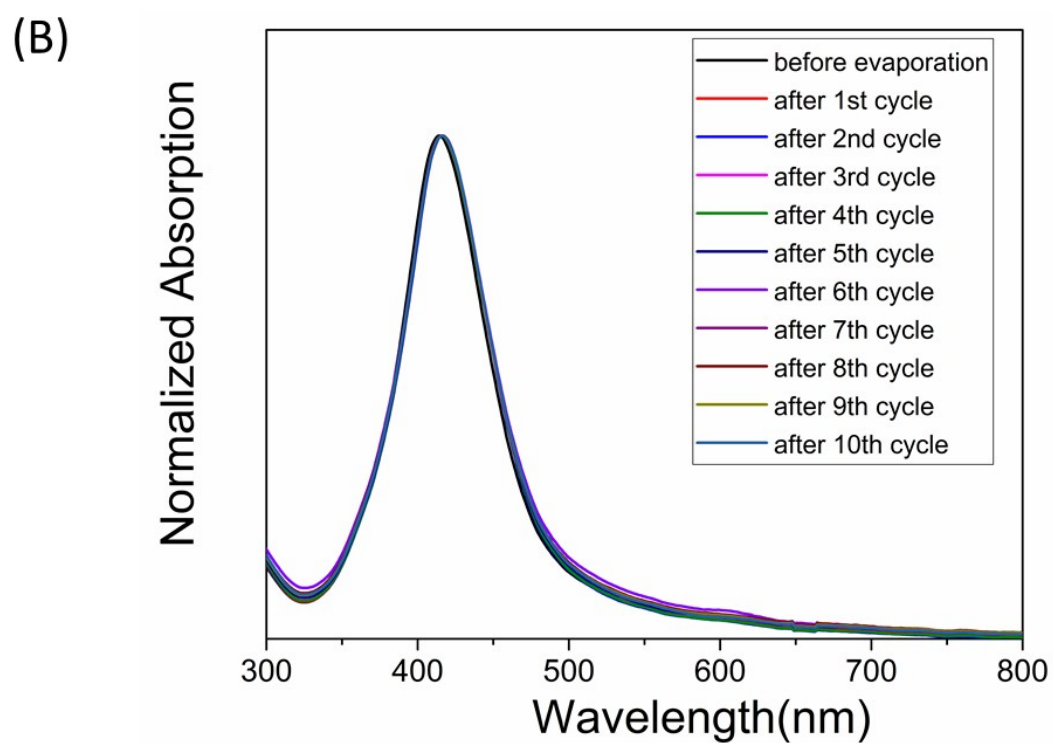
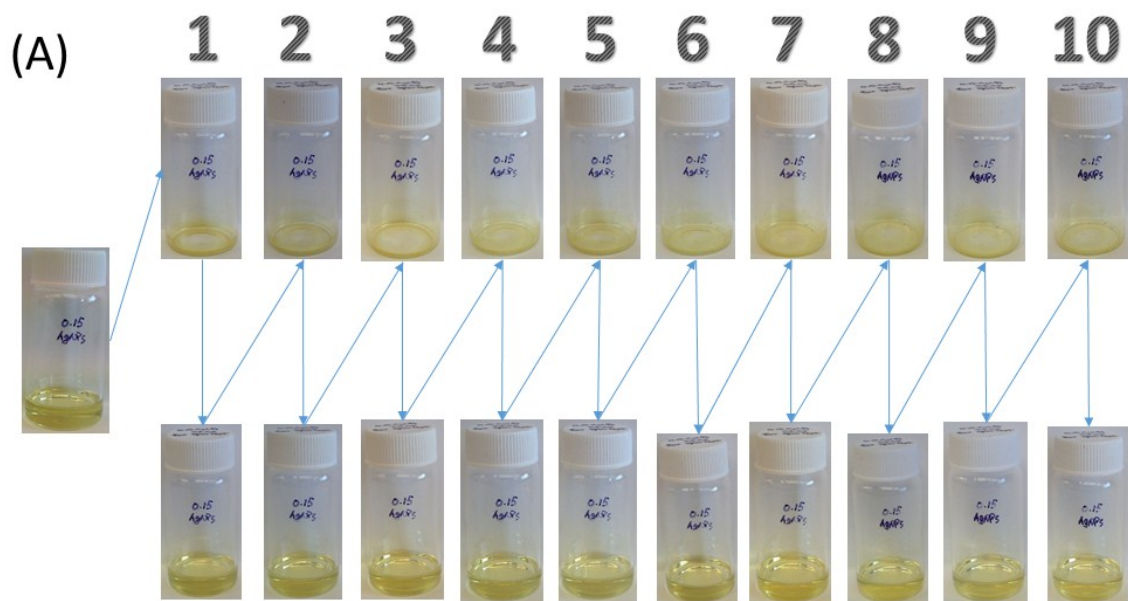


Figure S13. (A) Photographs of the polymer-stabilized AgNPs in chloroform after every evaporation and re-dispersion in chloroform; (B) Localized surface plasmon resonance (LSPR) spectra of the polymer-stabilized AgNPs in chloroform after each cycle's re-dispersion.

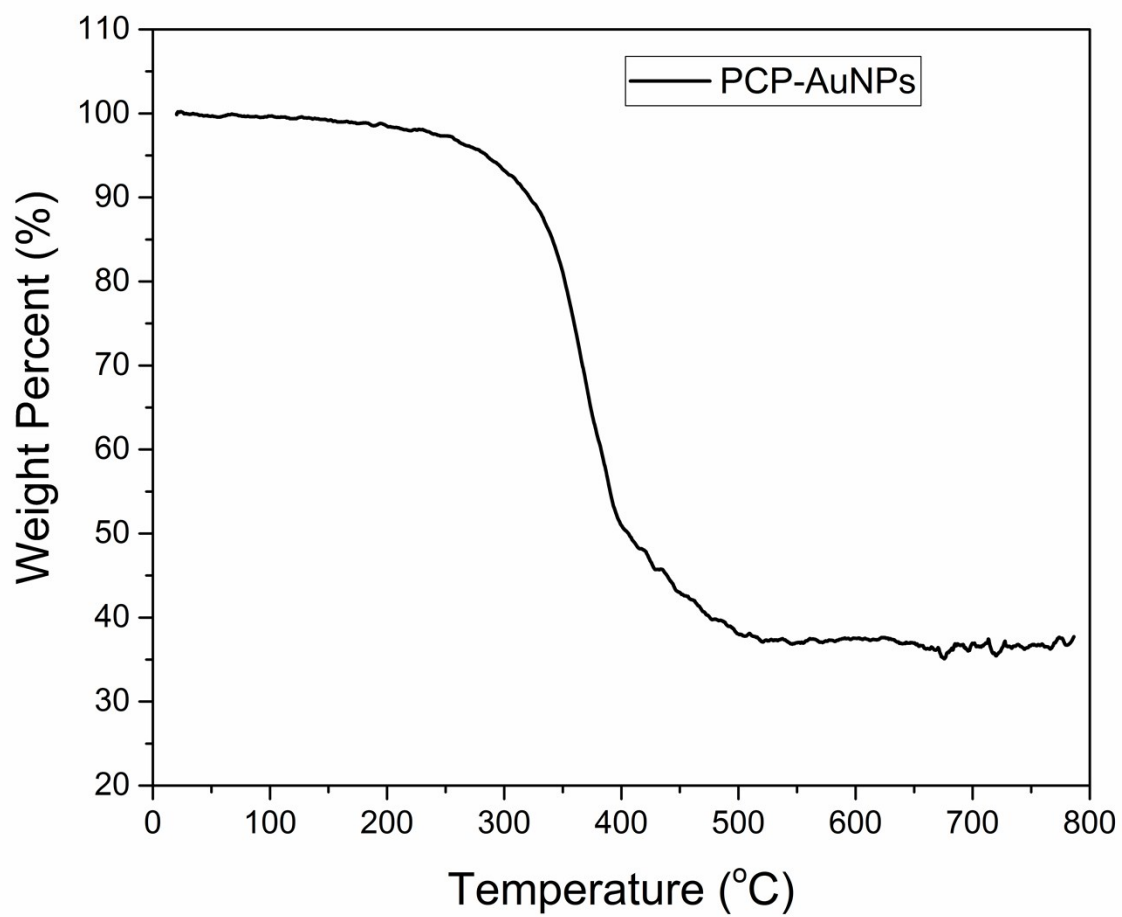


Figure S14. TGA analysis of polymer-coated AuNPs in powder form (PCP-AuNPs)

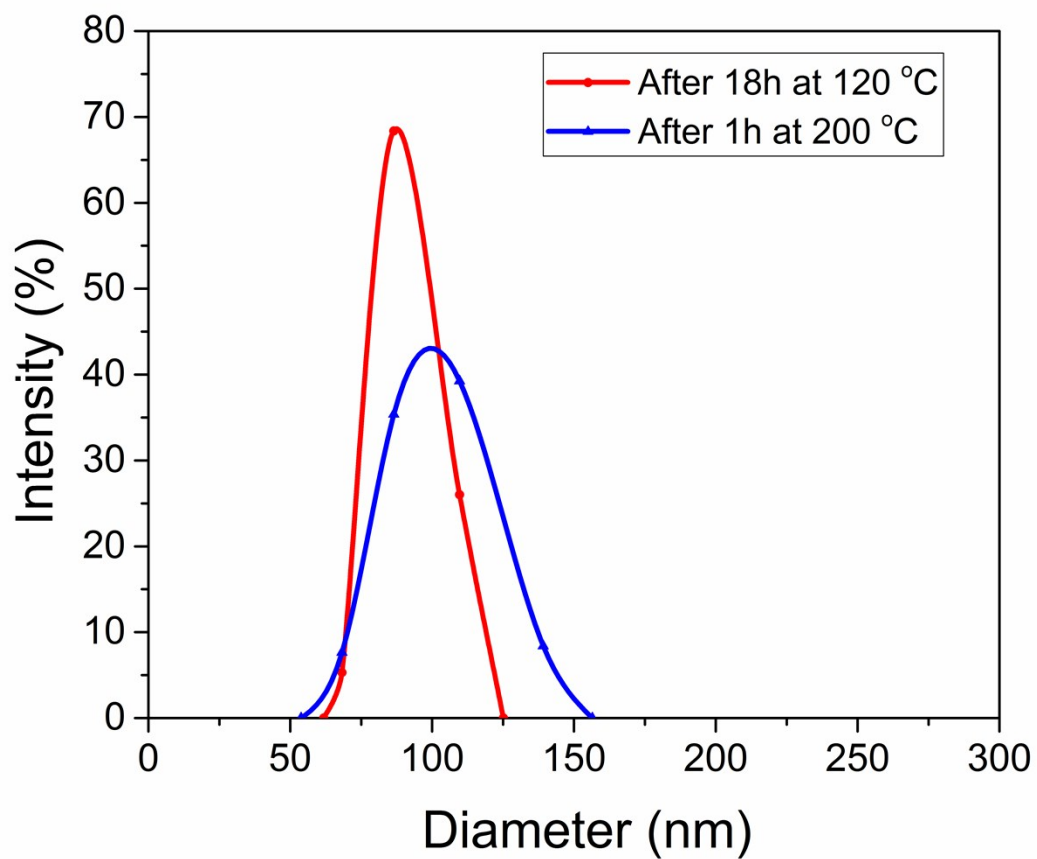


Figure S15. DLS analysis of SPS-AuNPs after 18h at 120 °C and 1h at 200 °C.

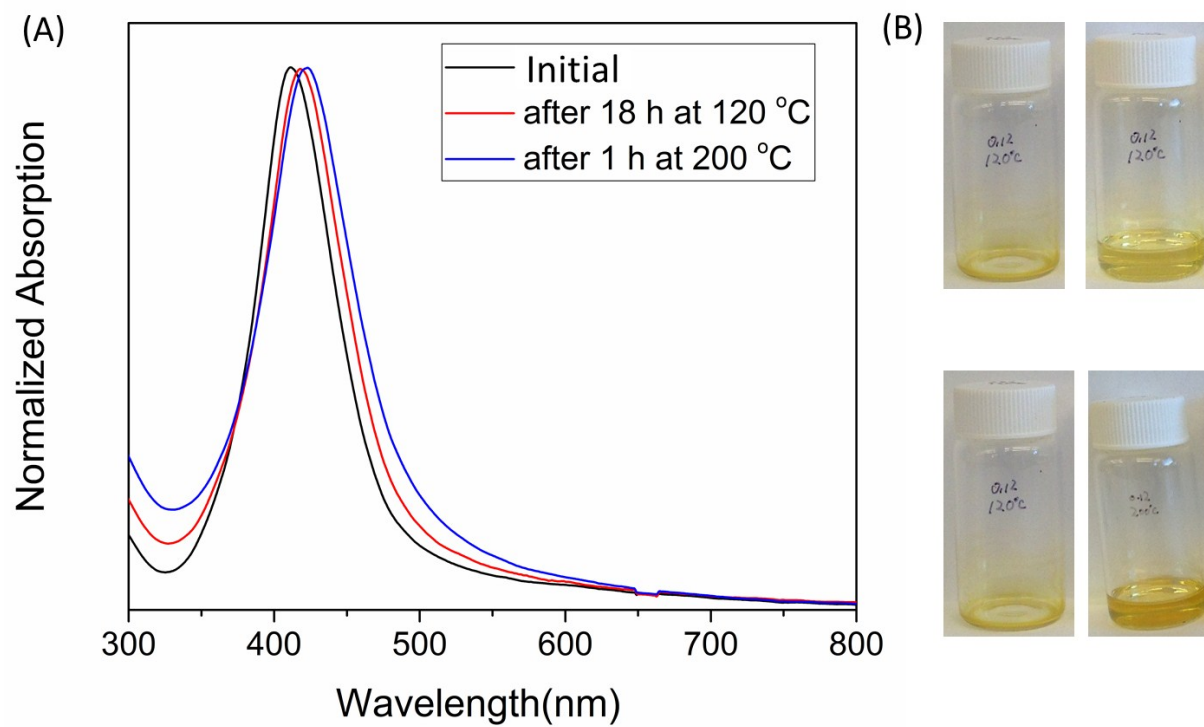


Figure S16. (A) Comparative LSPR spectra of the original polymer-stabilized AgNPs in chloroform, PCP-AgNPs after 18h at 120 °C, and PCP-AgNPs after 1 h at 200 °C; (B) Photographs of the PCP-AgNPs after 18 h at 120 °C and re-dispersion in chloroform solution (top), PCP-AgNPs after 1 h at 200 °C and re-dispersion in chloroform solution(bottom).

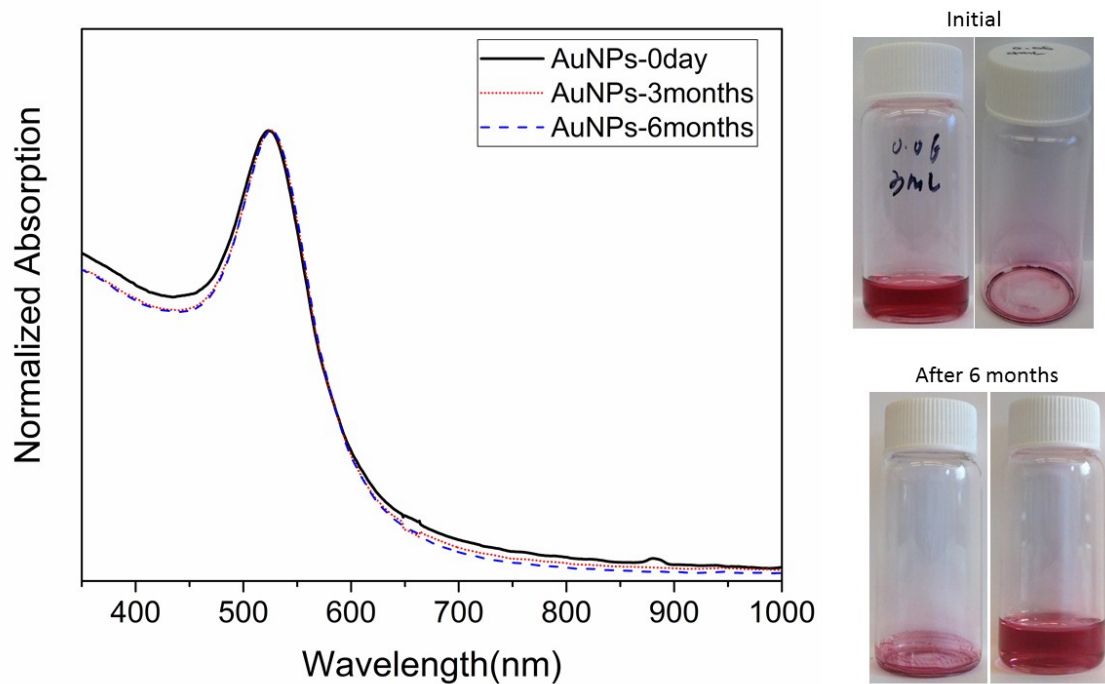


Figure S17. (A) Comparative LSPR spectra of the initial polymer-stabilized AuNPs in chloroform and PCP-AuNPs (redispersion in chloroform) after 3 and 6 months; (B) Photographs of the initial polymer-stabilized AuNPs in chloroform and PCP-AuNPs, and PCP-AuNPs after 3 months and redispersion in chloroform.

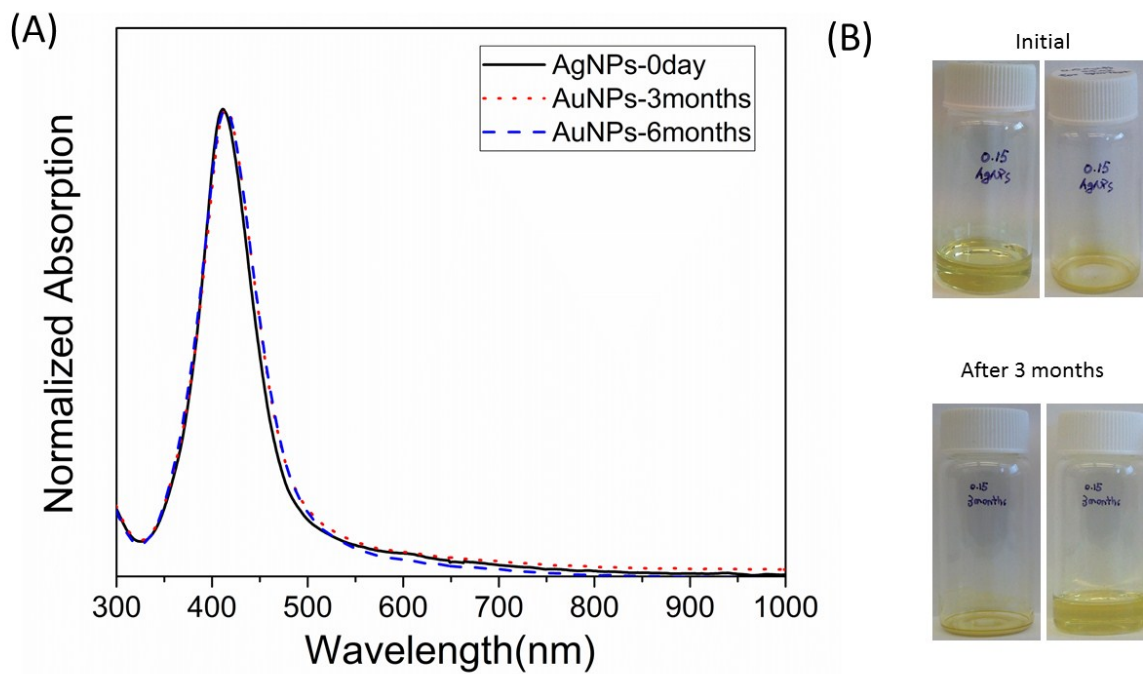


Figure S18. (A) Comparative LSPR spectra of the initial polymer-stabilized AgNPs in chloroform, and PCP-AgNPs (redispersion in chloroform) after 3 and 6 months; (B) Photographs of the initial polymer-stabilized AgNPs in chloroform and PCP-AgNPs, and PCP-AgNPs after 3 months and redispersion in chloroform.

References:

[1] P.-F. Cao, M.J. Felipe and R.C. Advincula, *Macromol. Chem. Phys.*, 2013, 214, 386-395.

[2] Y. Lu, L. Wang, D. Chen, and G. Wang, *Langmuir*, 2012, 28, 9282-9281.