SUPPORTING INFORMATION

Tunable and Reversible Aggregation of poly(ethylene oxide-*st*-propylene oxide) grafted Gold Nanoparticles.

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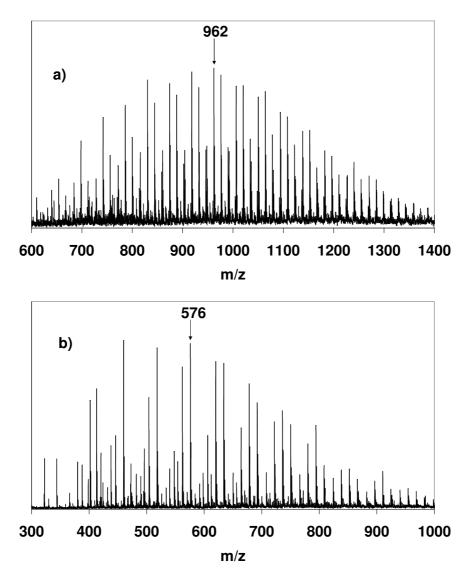
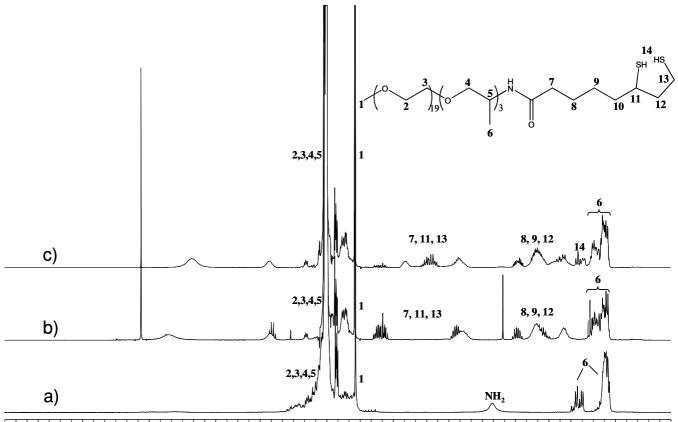
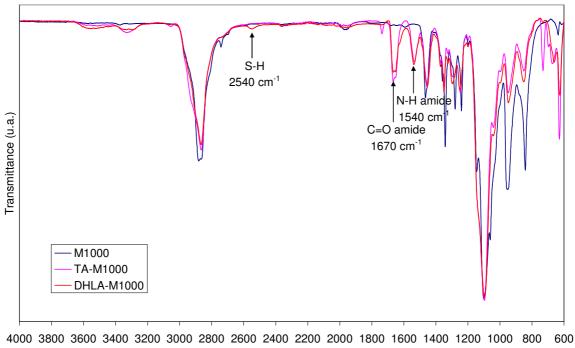


Figure S1. MALDI-TOF mass spectra of Jeffamine (a) M1000 and (b) M600.



6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Figure S2. ¹H NMR spectra of (a) Jeffamine M1000, (b) TA-M1000 and (c) DHLA-M1000 in CDCl₃ (The remaining peaks correspond to residues of solvents).



wavenumber (cm⁻¹)

Figure S3. IR spectra of Jeffamine M1000, TA-M1000 and DHLA-M1000.

Synthesis of AuNP6, CTAB AuNP7 and citrate AuNP13 and AuNP17 :

Acid AuNP6. AuNPs capped by decanoic acid were synthesis following procedure described in Ref. 1. AuCl₃ (7.5 mg, 0.025 mmol, 1eq) was dissolved in DDAB solution (1 mL, 100 mM in toluene) by sonication. Then decanoic acid (43 mg, 0.250 mmol, 10eq), dissolved into toluene (2.5 mL) by sonication, was mixed to the gold salt solution. Finally, TBAB (25 mg, 0.097 mmol, 4eq), dissolved in DDAB solution (1 mL), was injected in to the gold salt solution during vigorous stirring. Dark red color appears immediately.

CTAB AuNP7. AuNPs of 7 nm were prepared following a seeding growth approach². Seed solution: A 20 mL solution containing 0.25 mM HAuCl₄ and 0.25 mM citrate was prepared. 0.6 mL of 0.1 NaBH₄ solution was added while stirring. Growth solution: 1.5 g of CTAB was added to 50 mL of a HAuCl₄ solution (0.25 mM). 18 mL of the growth solution and 0.1 mL of 0.1 M ascorbic acid solution were mixed, and 2 mL of the seed solution was added while vigorously stirring. After 10 min, the solution was deep red.

Citrate AuNP13, AuNP17. Citrate stabilized AuNPs were synthesized using the standard citrate reduction method³. Briefly, 1 mL of a HAuCl₄ solution (25 mM) was added to 100 mL of water. The solution was boiled and then 5 mL for AuNP17 (2.5 mL for AuNP13) of trisodium citrate solution at 1% in weight was added under vigorous stirring. After 20 min of boiling, the solution was allowed to cool to room temperature. Water volume was then completed to 100 mL.

- (2) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Langmuir* **2001**, *17*, 6782-6786.
- (3) Turkevich, J.; Stevenson, P. C.; Hillier, J. Discuss. Faraday Soc. 1951, 55-75.

⁽¹⁾ Jana, N. R.; Peng, X. G. J. Am. Chem. Soc. 2003, 125, 14280-14281.

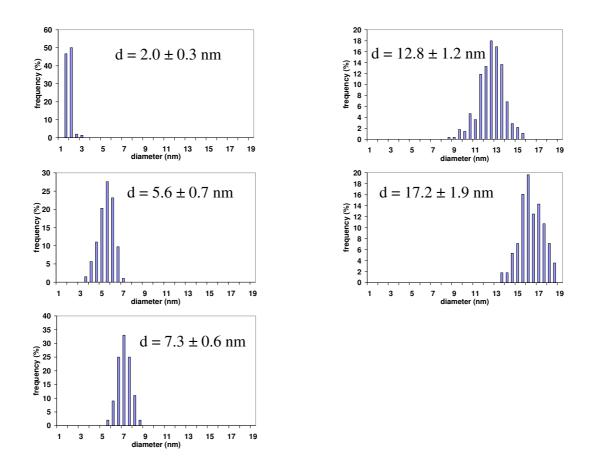


Fig S4. Size distribution of TEM images of polymer-protected AuNPs: AuNP2@DHLA-M600, AuNP6@DHLA-M600, AuNP7@DHLA-M600, AuNP13@DHLA-M600, AuNP17@DHLA-M600. Size distributions were calculated from 100 particles.

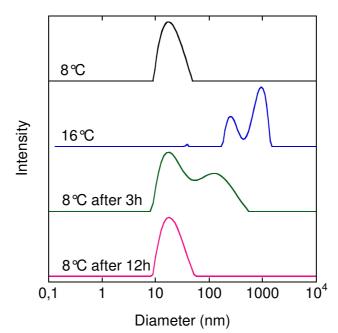


Figure S5. Size distribution (intensity) determined by DLS of AuNP6@DHLA-M600 in 10 mM KCl solution for one heating-cooling cycle.

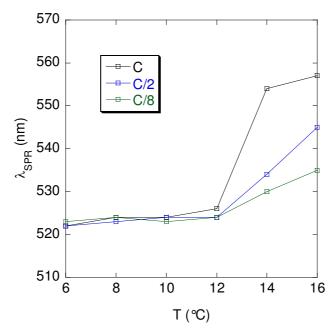


Figure S6. Evolution of maximum wavelength (determined by UV-vis spectroscopy) vs. temperature for AuNP6@DHLA-M600 in 10 mM KCl solutions (ramp 0.4° C/min) in different AuNPs concentrations (C = 1.7 x 10⁻⁶ mol/L of AuNPs).

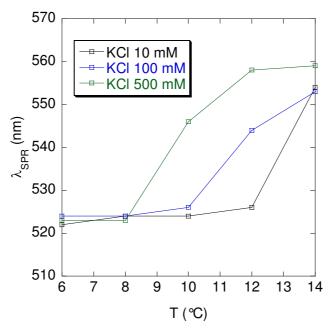


Figure S7. Evolution of maximum wavelength (determined by UV-vis spectroscopy) vs. temperature for AuNP6@DHLA-M600 in different KCl concentrations (ramp 0.4°C/min).