

Supporting Information

Thermally Reversible Self-assembly of Nanoparticles via Polymer Crystallization

*Calum Kinnear, Sandor Balog, Barbara-Rothen Rutishauser, Alke Petri-Fink**

Experimental Section

All chemicals were purchased from Sigma Aldrich and used without purification, unless otherwise specified. End-thiolated PEO was purchased from CreativePEGWorks. Ultrapure water (18.2 MΩ cm) from a Sartorius arium[®] pro system was used throughout. Absolute ethanol was purchased from Honeywell.

GNP synthesis

All glassware was cleaned with freshly prepared aqua regia and extensively rinsed with ultrapure water before use. A citrate synthesis was used to make 16 nm gold NPs, hereafter referred to as Au₁₆.^[1] A solution of HAuCl₄·3H₂O (500 mL, 1 mM) was brought to the boil under magnetic agitation before the rapid addition of a solution of sodium citrate (50 mL, 38.8 mM). Heating was continued for 15 min to ensure complete reduction of all gold. To synthesize larger NPs, hereafter referred to as Au₃₃, a seed-mediated growth from the preformed Au₁₆ NPs was used, as previously published.^[2] Briefly, hydroxylamine hydrochloride (13.45 mL, 2.62 mM) was added to the Au₁₆ dispersion (19.4 mL) followed by the dropwise addition of HAuCl₄·3H₂O (5.33 mL, 25.4 mM) under vigorous stirring. As a weak reducing agent, the hydroxylamine hydrochloride reduces the additional gold salt onto the surface of the preformed seed NPs.

Smaller NPs, hereafter referred to as Au₅ were also synthesized via a published route.^[3]

Briefly, a solution of sodium citrate (4 mL, 38.8 mM) was added to an agitated solution of HAuCl₄·3H₂O (19.38 mL, 2.62 mM). The rapid addition of freshly prepared sodium

borohydride (1 mL, 40 mM) under vigorous stirring reduces the gold ions to form small citrate stabilized NPs.

Functionalization

Au₅ NPs (0.29 mM) were functionalized with two different molecular weights of PEO (5000 and 10,000 g mol⁻¹) by mixing the suspension (17.5 mL) as prepared with 5.73 and 11.45 mg of PEO respectively. This equated to an effective surface concentration of 10 PEO nm⁻². The NPs were concentrated to approximately 0.2 mL via ultrafiltration using a Sartorius Vivaspin with a molecular weight cutoff of 30 kDa, and then added to absolute ethanol (4.8 mL).

Remaining water was removed by activated 3Å molecular sieves, and confirmed through the decrease in the water absorption band in the NIR, by UV-Visible spectroscopy. The final dispersion (5 mL) was sealed under dry argon at a concentration of 1 mM or 200 µg mL⁻¹.

Based on the above purification, we estimate the concentration of residual ungrafted polymer to be less than 2.4 µM (1% of initial polymer concentration).

Au₁₆ NPs (0.93 mM) were functionalized with two different molecular weights of PEO (5000 and 10,000 g mol⁻¹) by mixing the suspension (5.5 mL) as prepared with 1.63 and 3.25 mg of PEO respectively. This equated to an effective surface concentration of 10 PEO nm⁻². Water was replaced by absolute ethanol via two rounds of centrifugation at 20,000 × g for 1 h at 28 °C. The final dispersion (5 mL) was sealed under dry argon at a concentration 1 mM or 200 µg mL⁻¹. Based on the above purification, we estimate the residual ungrafted polymer to less than 0.15 µM (0.2% of initial polymer concentration).

Au₃₃ NPs (0.23 mM) were functionalized with two different molecular weights of PEO (5000 and 10,000 g mol⁻¹) by mixing the suspension (21.7 mL) as prepared with 0.86 and 1.73 mg of PEO respectively. Water was replaced by absolute ethanol via two rounds of centrifugation at 8,000 × g for 0.5 h at 28 °C. The final dispersion (5 mL) was sealed under dry argon at a concentration 1 mM or 200 µg mL⁻¹. Based on the above purification, we estimate the residual ungrafted polymer to be less than 0.01 µM (0.03% of initial polymer concentration).

Characterization

UV-Vis-NIR spectra were measured on a Jasco V-670 spectrophotometer, with sealed quartz cuvettes and a liquid cooled Peltier element. As an example of a heating-cooling cycle, spectra were collected at 40 °C and 15 °C after allowing the self-assembly for 15 min at the desired temperature. Isothermal measurements were conducted at 20 °C on either dispersed or self-assembled systems. The concentration of the gold NPs with different core sizes was determined using UV-Vis-NIR spectroscopy, and known size dependent extinction coefficients.^[49]

TEM micrographs were obtained on a Philips CM100-Biotwin microscope operating at 80 kV. Samples were prepared by dropcasting 4 μL of either the dispersed or self-assembled particles on a carbon-coated copper grid at either room temperature or 4 °C respectively.

A 3D LS Spectrometer (LS Instruments, Fribourg, Switzerland) equipped with a He–Ne laser ($\lambda = 632.8$ nm) was used for all samples. Measurements were carried out on samples dispersed in ethanol in sealed glass tubes, at a scattering angle of 90° and at various temperatures. The temporal correlation function was fitted with a 2nd order cumulant giving the hydrodynamic radius.

Small- and wide-angle X-ray scattering (SAXS/WAXS) spectra were recorded with an S-MAX3000 and a NanoMax camera, respectively, operating with $\lambda = 0.1524$ nm of photon wavelength (Rigaku Innovative Technologies, Auburn Hills, USA). Raw data were processed according to standard procedures, and the isotropic scattering spectra are presented as a

function of the momentum transfer: $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$. The SAXS spectrum of well-dispersed NPs was recorded by adding 10 vol % of water to the dispersion in ethanol, and sealing the sample in a glass capillary with epoxy resin. The PEO functionalized NP system in absolute ethanol was already self-assembled at RT, therefore the sample was simply sealed in a glass capillary

with epoxy resin before recording the SAXS spectrum. WAXS spectra were similarly collected.

- [1] J. Turkevich, P. C. Stevenson, J. Hillier, *Discuss. Faraday Soc.* **1951**, *11*, 55.
- [2] K. R. Brown, D. G. Walter, M. J. Natan, *Chem. Mater.* **2000**, *12*, 306.
- [3] W. Haiss, N. T. K. Thanh, J. Aveyard, D. G. Fernig, *Anal. Chem.* **2007**, *79*, 4215.

Supplementary Figures

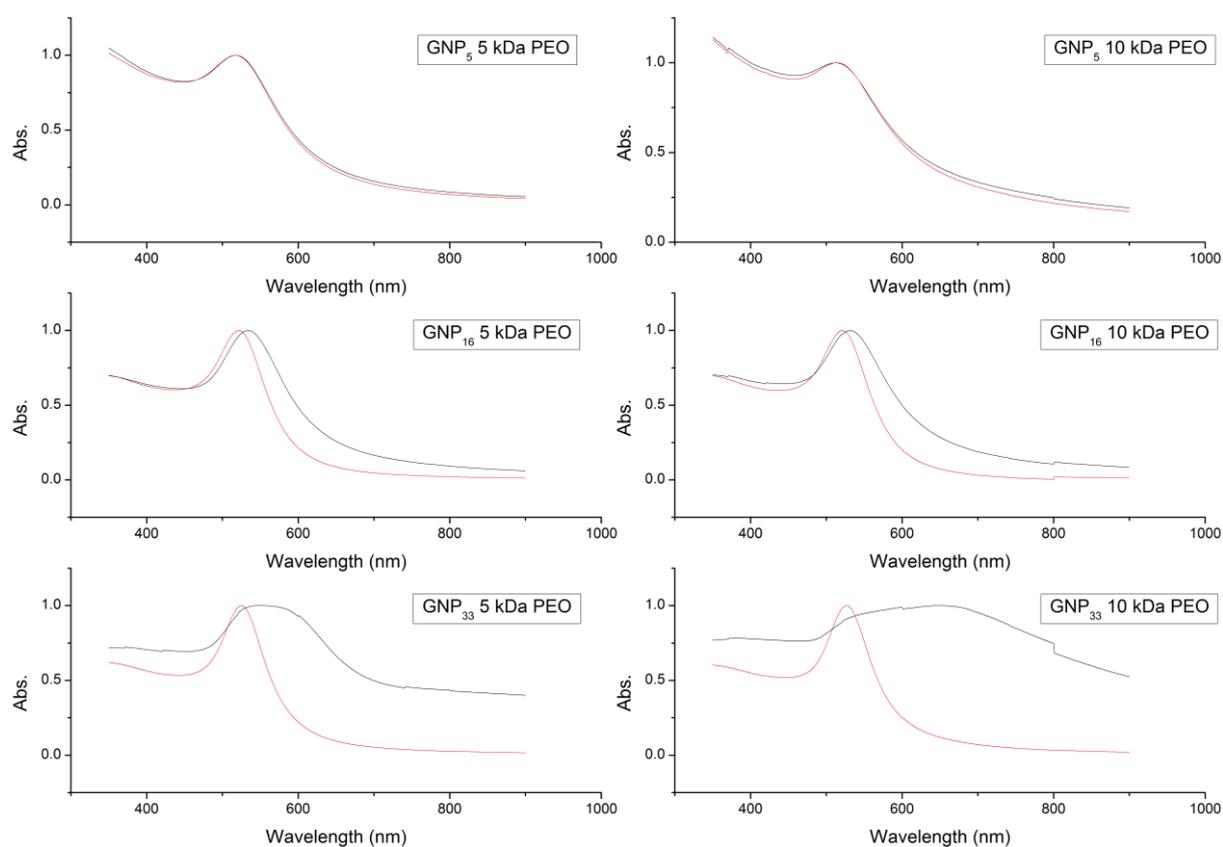


Figure S.1. UV-Vis-NIR spectra of three different gold NP core sizes and two different PEO molecular weights either heated to 45 °C (red) or cooled to 10 °C (black) and held for 15 minutes.

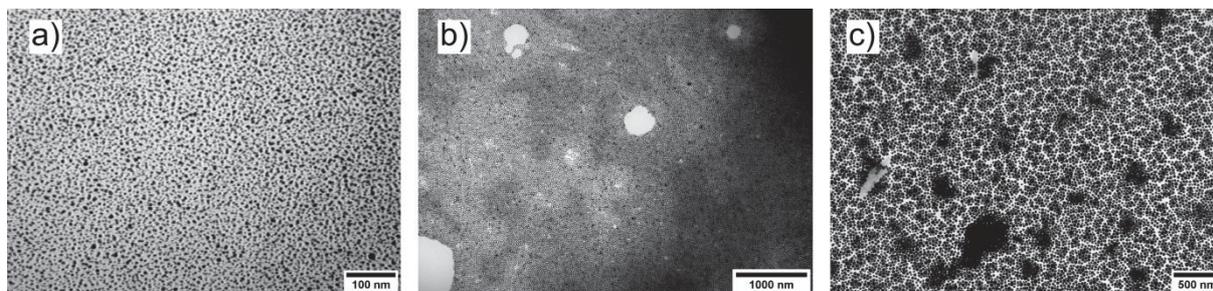


Figure S.2. TEM overviews of self-assembled gold NPs with PEO of a molecular weight 5000 g mol^{-1} : (a) Au_5 , (b) Au_{16} , (c) Au_{33} .

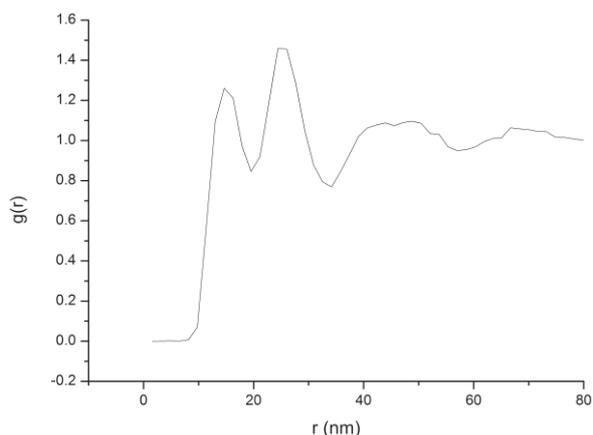


Figure S.3. Radial distribution function of Au_{16} NPs (PEO layer of 5000 g mol^{-1}) from TEM of the self-assembled particles.

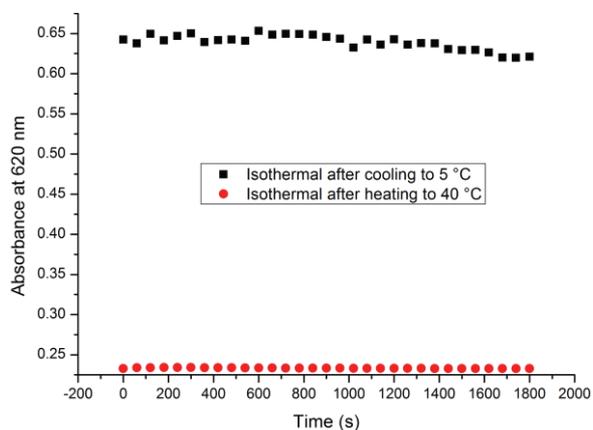


Figure S.5. Isothermal experiment at $20 \text{ }^\circ\text{C}$ for Au_{16} NPs functionalized with PEO of molecular weight $10,000 \text{ g mol}^{-1}$ and dispersed in 1 % water in ethanol. The sample was either heated to $40 \text{ }^\circ\text{C}$ or cooled to $5 \text{ }^\circ\text{C}$ and held at this temperature for 15 min before recording the absorbance at 620 nm and $20 \text{ }^\circ\text{C}$ over a period of 1800 s. The decrease in absorbance for the pre-cooled sample is due to sedimentation; inversion of the cuvette reverts the absorbance back to the value at $t = 0 \text{ s}$.

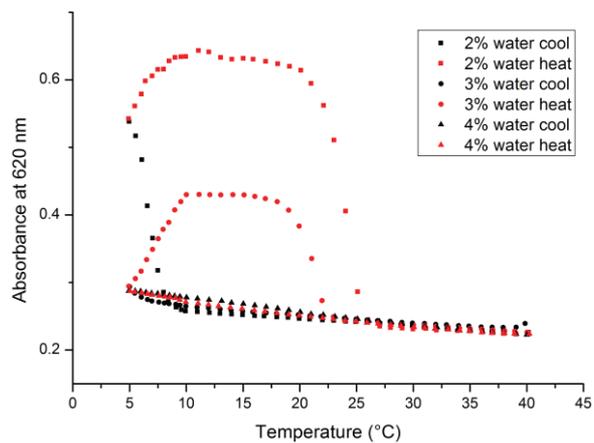


Figure S.6. Change in absorbance at 620 nm for Au₁₆ NPs, functionalized with PEO of molecular weight 10,000 g mol⁻¹, upon a heating and cooling cycle. The amount of water was varied from 2 % to 4 %, with the crystallization transition practically disappearing at 4 % water. Therefore, the melting and crystallizing transitions can be easily tuned by the content of water added.