



Supporting Information

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Core-Shell Gold Nanoparticles via Self-Assembly and Crosslinking of Micellar, Block-Copolymer Shells**

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A. Chemicals

All chemicals were purchased from Aldrich Chemical. Styrene (99%), *t*-butyl acrylate (98%), and methyl methacrylate (99%) were dried over CaH₂ for 24 hours, and then distilled under vacuum over CaH₂. The vacuum-distilled monomers were then stored at 2 °C under argon (99.99%). Methyl-2-bromopropionate (98%), Cu(I)Br (99.999%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA; 99%), HAuCl₄·*x*H₂O (99.99%) and sodium citrate dihydrate (99%) were used as received.

B. Characterization

¹H NMR spectra (in CDCl₃) were recorded on a Varian Inova 300 MHz spectrometer with the solvent proton signal as a standard. Gel permeation chromatography (GPC) was performed on a Waters 717 high performance liquid chromatography (HPLC) instrument equipped with a Waters 590 HPLC pump, Waters 410 differential refractometer and Spectroflow 757 absorbance detector. Three Polymer Laboratories PL gel columns (Mixed-C, 5 μm) connected in series were used with tetrahydrofuran (THF) as the solvent. Polystyrene was used as the molecular-weight calibration standard. UV-vis spectra were obtained on a Hewlett-Packard series 8453 UV-vis spectrophotometer equipped with an Agilent 89090A Peltier temperature

controller. Transmission electron microscopy (TEM) images were obtained on a JEOL 1210 electron microscope equipped with a Gatan video camera and a Gatan Multiscan CCD camera (1024×1024 pixels). Nanoparticle solutions (5 μ L) were dropped onto Formvar-graphite-coated copper grids (300 mesh, Electron Microscopy Science) and air-dried to prepare them for TEM imaging. All images were obtained at an operating voltage of 120 kV.

C. Synthesis

Polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) and poly(methyl methacrylate)-*block*-poly(acrylic acid) (PMMA-*b*-PAA) were synthesized via atomic transfer radical polymerization (ATRP) as previously reported.^[1] Au nanoparticles (12 nm or 31 nm) were prepared by trisodium citrate reduction^[2] or by growth from nanoparticle seeds.^[3]

Synthesis of poly(*t*-butyl acrylate) (PtBA): An oven-dried 100 mL Schlenk tube fitted with a stirbar was charged with Cu(I)Br (66 mg, 0.46 mmol) under argon flow. The Schlenk tube was connected to a reflux condenser and a double manifold. The tube was evacuated with heating for 5 min, and then carefully flushed with argon (99.99%). These processes were repeated twice more. *t*-Butyl acrylate (10 mL, 68.9 mmol) and PMDETA (95.8 μ L, 0.46 mmol) were transferred into the Schlenk tube, which was immersed in a liquid nitrogen bath, using a gas-tight syringe. This mixture was exposed to three cycles of freeze-pump-thaw to remove dissolved gas. Methyl 2-bromopropionate (512.5 μ L, 4.6 mmol) was added to the mixture, and then additional two cycles of freeze-pump-thaw were performed. The mixture was allowed to stir at room temperature until temperature was equilibrated and the mixture became homogeneous. The Schlenk tube was immersed into a 60 °C pre-set oil bath, and allowed to polymerize with stirring for 1 hour under argon flow. After completion of the reaction, the Schlenk tube was

immersed into liquid nitrogen to quench the polymerization, and then 100 mL of acetone was added to dissolve the polymer product. The cold, bluish-green solution was passed through a column of neutral alumina three times to yield a colorless solution. Evaporation of solvent under vacuum yielded a clear, viscous polymer oil. The isolated polymer was dried in a vacuum oven for three days at room temperature. Yield (PtBA₁₃): 6.2 g (70%). $\overline{M}_n = 1737$, $\overline{M}_w = 2100$, $\overline{M}_w / \overline{M}_n = 1.21$, $\overline{X}_n = 13.6$ (theoretical $\overline{X}_n = 15$). ¹H NMR (CDCl₃): $\delta = 4.0-4.2$ (multi, -CHBr-), 3.65 (s, CH₃O-, initiator endgroup), 2.2-2.4 (broad, polymer backbone), 1.4-1.6 (broad, C(CH₃)₃), 1.15 (small, CH₃OOCCHCH₃-, initiator).

Synthesis of PtBA-*b*-PS: PtBA (0.5 g, 0.30 mmol, $\overline{M}_w = 1737$) and Cu(I)Br (0.043 g, 0.30 mmol) was added to an oven dried Schlenk tube with a stir bar. The Schlenk tube was connected to a reflux condenser and a double manifold. The tube was evacuated with heating for 5 min, and then carefully flushed with argon (99.99%). These processes were repeated twice more. Styrene (9.5 mL, 82 mmol) was transferred into the Schlenk tube, which was immersed in liquid nitrogen bath, using a gas-tight syringe. This mixture was exposed to three cycles of freeze-pump-thaw to remove dissolved gas. PMDETA (63.3 μ L, 0.30 mmol) was added to the mixture, and then additional two cycles of freeze-pump-thaw were performed. The mixture was allowed to stir at room temperature until the temperature equilibrated and the mixture became homogeneous. The Schlenk tube was immersed into a 95 °C pre-set oil bath, and allowed to polymerize for 3.5 hours under argon flow. After completion of the reaction, the Schlenk tube was immersed into liquid nitrogen to quench the polymerization, and then 100 mL of acetone was added to dissolve the polymer product. The cold, bluish-green solution was passed through neutral alumina three times, which gave colorless solution. This clear solution was concentrated *in vacuo* to around 30 mL. White, solid polymer was then isolated by adding methanol to

precipitate. Precipitated polymer was redissolved in a minimal amount of actone and reprecipitated with methanol. The isolated white polymer was dried under vacuum for 2 days at room temperature. Yield (PtBA₁₃-*b*-PS₂₅₀): 5.4 g (60%). $\overline{M}_n = 27685$, $\overline{M}_w = 31837$, $\overline{M}_w / \overline{M}_n = 1.15$, $\overline{X}_n = 250$ (theoretical $\overline{X}_n = 275$). ¹H NMR (CDCl₃): $\delta = 6.30-7.30$ (broad, -CHC₆H₅-), 3.65 (s, CH₃O-, initiator endgroup), 2.2-2.4 (broad, PtBA backbone), 1.70-2.20 (broad, -CHC₆H₅-), 1.4-1.6 (broad, C(CH₃)₃), 1.2-1.7 (broad, -CH₂-C₆H₅-).

Synthesis of PtBA-*b*-PMMA: The same procedure given above for PtBA-*b*-PS was followed for PtBA-*b*-PMMA, substituting methyl methacrylate monomer (8.62 mL, 80 mmol) for styrene. Yield (PtBA₁₃-*b*-PMMA₂₄₀): 5.2 g (61%). $\overline{M}_n = 26069$, $\overline{M}_w = 33629$, $\overline{M}_w / \overline{M}_n = 1.29$, $\overline{X}_n = 240$ (Theoretical $\overline{X}_n = 280$). ¹H NMR (CDCl₃): $\delta = 3.6$ (broad, -OCH₃), 1.8-2.1 (broad, PMMA, PtBA backbone), 1.4-1.6 (broad, C(CH₃)₃), 0.8~1.0 (broad, -CH₃).

Hydrolysis of PtBA-*b*-PS to PS-*b*-PAA: PtBA₁₃-*b*-PS₂₅₀ (4 g, $\overline{M}_n = 27685$) and *p*-toluenesulfonic acid (0.1 g) were dissolved in toluene (100 mL). Then the solution was heated with gentle reflux for 20 hours. The final white solid polymer was isolated by twice of methanol-precipitation. Yield (PS₂₅₀-*b*-PAA₁₃): 3.6 g (92%). ¹H NMR (CDCl₃): $\delta = 6.30-7.30$ (broad, -CHC₆H₅-), 2.2-2.4 (broad, PtBA backbone), 1.70-2.20 (broad, -CHC₆H₅-), 1.2-1.7 (broad, -CH₂-C₆H₅-).

Hydrolysis of PtBA-*b*-PMMA to PMMA-*b*-PAA: The same procedure given above for PS-*b*-PAA was followed for PMMA-*b*-PAA. Yield (PMMA₂₄₀-*b*-PAA₁₃): 3.3 g (85%). ¹H NMR (CDCl₃): $\delta = 3.6$ (broad, -OCH₃), 1.8-2.1 (broad, PMMA, PtBA backbone), 0.8-1.0 (broad, -CH₃).

C. Synthesis of Au nanoparticles

Synthesis of Au nanoparticles by sodium citrate reduction: Small Au nanoparticles (<15 nm) were synthesized by sodium citrate reduction of HAuCl₄.^[2] In a representative synthesis, a 250 mL flask was charged with 100 mL of HAuCl₄ (0.01% in H₂O). This solution was heated to reflux with vigorous stirring for 10 min, and then 3 mL of sodium citrate (1% in H₂O) was added quickly to the solution. After refluxing the solution for an additional 30 minutes, a deep-red gold nanoparticle solution was obtained. Finally, the solution was filtered through 0.45 μm nylon membrane filter. The average particle diameter was measured to be 12 ± 1.1 nm by TEM (ellipticity = 0.90); λ_{max} = 519 nm; c ≈ 12 nM, based on an approximate extinction coefficient (ε) of 1.85 × 10⁸ at 530 nm for 12 nm particles.^[4]

Synthesis of Au nanoparticles by growth of seed particles: Larger gold nanoparticles (>15 nm) were synthesized by enlargement of pre-synthesized nanoparticle seeds.^[3] In a representative synthesis, a 250-mL roundbottom flask was charged with 90 mL HAuCl₄ (0.01% in H₂O). The solution was boiled with vigorous stirring in the oil bath for 10 min, and then 2 mL of Au seeds (12 nm diameter, 12 nM in H₂O) and 360 μL of sodium citrate (1% in H₂O) was added to the solution. After boiling the solution for 30 minutes more, deep-reddish gold nanoparticle solution was obtained. The average diameter was measured to be 31 nm by TEM (ellipticity = 0.88), λ_{max} = 529 nm, c = 360 pM, based on an approximate extinction coefficient of 3.27 × 10⁹ at 530 nm for 31 nm particles.^[4]

D. Resuspension of citrate-stabilized Au nanoparticles into DMF

Citrate-stabilized, aqueous Au nanoparticles were transferred into DMF after centrifugation. For example, 1 mL aqueous citrate-stabilized Au nanoparticle solution (31 nm

diameter, ~ 360 pM) was first centrifuged at $3000 \times g$ for 30 min. After carefully pipetting away the upper layer (~ 950 μL), the concentrated, deep red, oily bottom layer was resuspended in 1 mL of DMF. Because excess citrate ion in solution interfered with particle encapsulation, solutions of smaller particles (which usually contain larger citrate concentrations) were centrifuged and resuspended in water prior to dispersion in DMF. DMF suspensions of citrate-stabilized Au nanoparticles were very stable over three months, but were prepared freshly immediately before use.

E. Encapsulation of Au nanoparticles

To encapsulate Au nanoparticles within $\text{PS}_{250}\text{-}b\text{-PAA}_{13}$, 100 μL $\text{PS}_{250}\text{-}b\text{-PAA}_{13}$ solution (10^{-2} g/mL in DMF) was added to 900 μL Au nanoparticle solution (31 nm diameter, ~ 360 pM in DMF) with vigorous stirring. Then, 250 μL of H_2O was gradually added dropwise (8.3 $\mu\text{L}/\text{min}$) via syringe pump with vigorous stirring. As adding H_2O , the solution gradually turned violet in color. Later, 10 μL dodecanethiol solution (1 vol% in DMF) was added to the solution. The resulting solution was stirred for 1 h. Another 3 mL of H_2O was gradually added dropwise (2 mL/h) via syringe pump. DMF was removed by dialysis against water for 24 hours (Spectra/Por #2, MWCO = 12-14K). Polymers with longer PAA blocks ($\text{PS}_{49}\text{-}b\text{-PAA}_{54}$, $\text{PS}_{159}\text{-}b\text{-PAA}_{62}$ or $\text{PS}_{639}\text{-}b\text{-PAA}_{62}$) typically yielded bulk polymer-nanoparticle precipitate rather than stable nanoparticle suspensions at this stage, while polymers with short PAA blocks ($\text{PS}_{250}\text{-}b\text{-PAA}_{13}$, $\text{PS}_{160}\text{-}b\text{-PAA}_{13}$, $\text{PS}_{100}\text{-}b\text{-PAA}_{13}$, $\text{PMMA}_{240}\text{-}b\text{-PAA}_{13}$) yielded stable nanoparticle suspensions that survived addition of water and dialysis. Assuming that no polymer material was lost during dialysis, the copolymer concentration at this stage was calculated to be $\sim 2 \times 10^{-4}$ g/mL. The PAA blocks of the resulting micelles were crosslinked by addition of 2,2'-

(ethylenedioxy)bis(ethylamine) as a difunctional linker and 1-(3-dimethylamino)propyl)-3-ethylcarbodiimide methiodide as an activator. For 50% crosslinking of the PAA blocks in a typical dispersion, the carboxylic acid groups on the PAA blocks were first activated by adding 72 μL 1-(3-dimethylamino)propyl)-3-ethylcarbodiimide methiodide solution (0.1 wt% in H_2O , 24 nmol) all at once. The resulting suspension was left to react with stirring for 30 minutes. The crosslinking of the outer shells of micelles was completed by adding 144 μL 2,2'-(ethylenedioxy)bis(ethylamine) solution (0.1 wt% in H_2O , 96 nmol) in one portion with stirring. After crosslinking, excess reagents were removed by dialysis of the suspension in a polycarbonate membrane (Spectra/Por #2, MWCO = 12-14K) against deionized water for 24 hours.

In order to limit the number of micelles that contained multiple particles, the ratio of empty to filled micelles was kept intentionally high ($N_{\text{empty}}/N_{\text{encapsulated}} \approx 100$, estimated both by TEM counting and by calculation based on the concentration of nanoparticles and polymer and on the aggregation number N_{agg} of micelles). Encapsulated Au nanoparticles were separated from empty micelles by centrifugation. Micelle solution was subjected to centrifugation at $4000 \times g$ for 30 min. The upper 80% of the solution was discarded and the same volume of deionized water was added to the solution. This procedure was repeated three or more times. Purified encapsulated Au nanoparticles were redispersed in pure water. Based on solution absorbance, yields of encapsulated particles (with respect to starting nanoparticle solution) were over 90%.

F. Solubility of fully crosslinked encapsulated 31 nm Au nanoparticles

Relative solubility (A/A_0) is defined as a ratio of the maximum solution absorbance observed for particles in each solvent to the maximum absorbance taken in water (original stock).

The stock solution of 31-nm Au@PS₂₅₀-*b*-PAA₁₃ was prepared with the same procedure given above. The absorbance spectrum of stock solution (A_0) was taken before crosslinking at 547 nm giving the maximum intensity. The fully crosslinked encapsulated Au nanoparticle solution (stock solution) was divided into 1 mL aliquots, and then lyophilized to remove water. Dried each sample was resuspended in 1 mL solvent with the minimum sonication (< 1 min), and then insoluble solid was removed by centrifugation at low speed. The absorbance spectrum of each sample (A) was taken at the wavelength giving the maximum intensity.

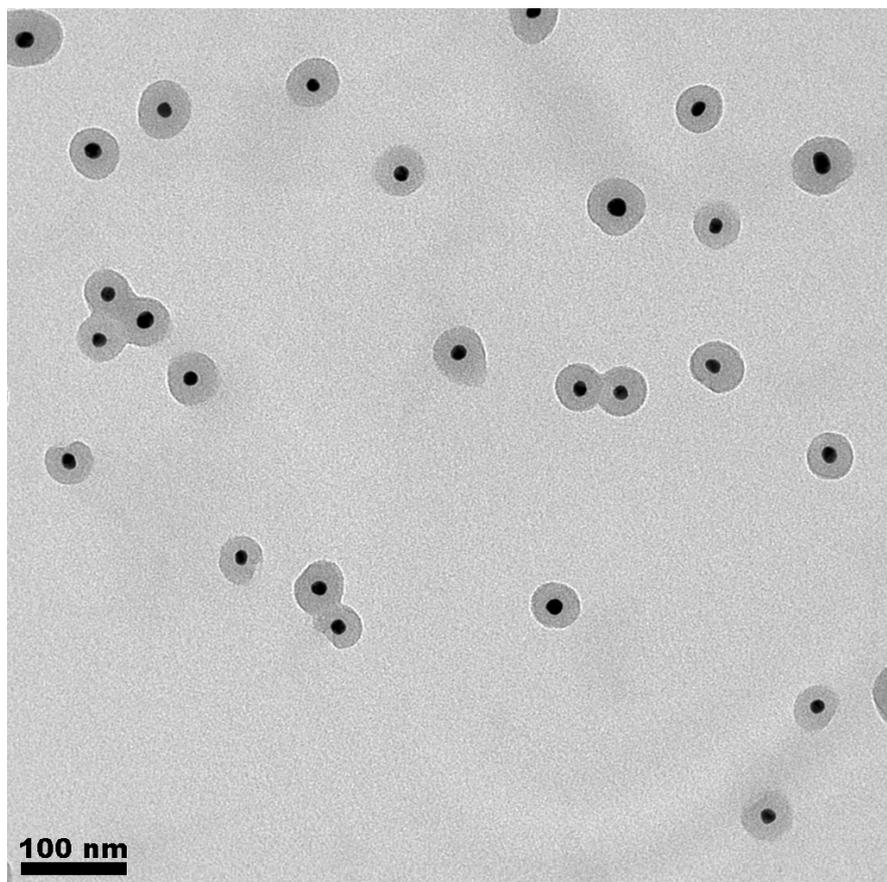


Figure S1. TEM image of encapsulated 12 nm Au nanoparticles within micelles formed from PS₂₅₀-*b*-PAA₁₃, [PS₂₅₀-*b*-PAA₁₃] = 2×10^{-4} g/mL. Histogram in Figure 1f was measured from five such images. The multiple micelle aggregation is not by inter-micellar crosslinking, but by drying process by which the same aggregation was observed for even uncrosslinked samples.

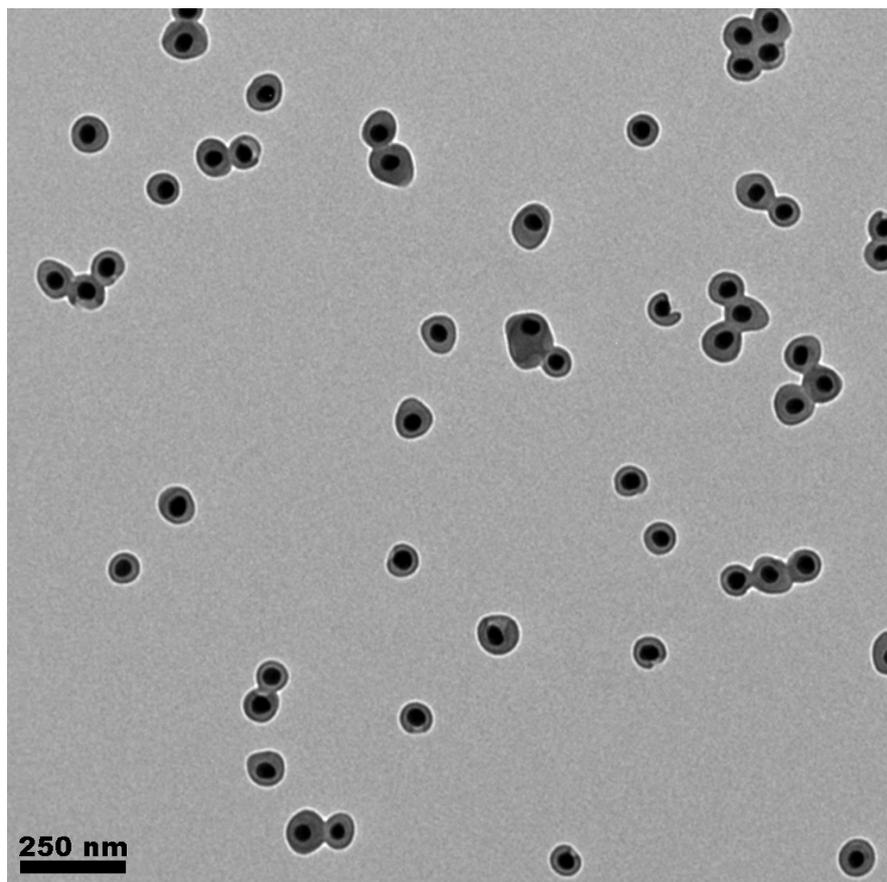


Figure S2. TEM image of encapsulated 31 nm Au nanoparticles within micelles formed from PS₂₅₀-*b*-PAA₁₃, [PS₂₅₀-*b*-PAA₁₃] = 2 × 10⁻⁴ g/mL. Histogram in Figure 1g was measured from five such images.

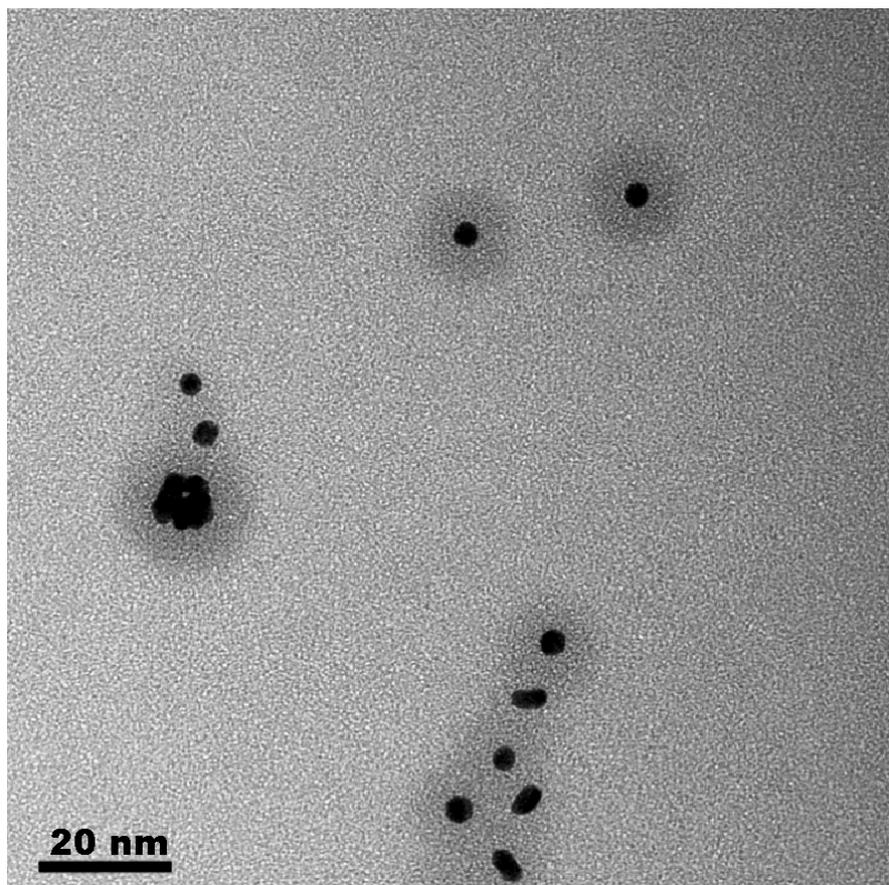


Figure S3. TEM image of encapsulated 4 nm Au nanoparticles within micelles formed from PS₂₅₀-*b*-PAA₁₃, [PS₂₅₀-*b*-PAA₁₃] = 2×10^{-4} g/mL. While some micelles contain single nanoparticles, others contain two or more particles.

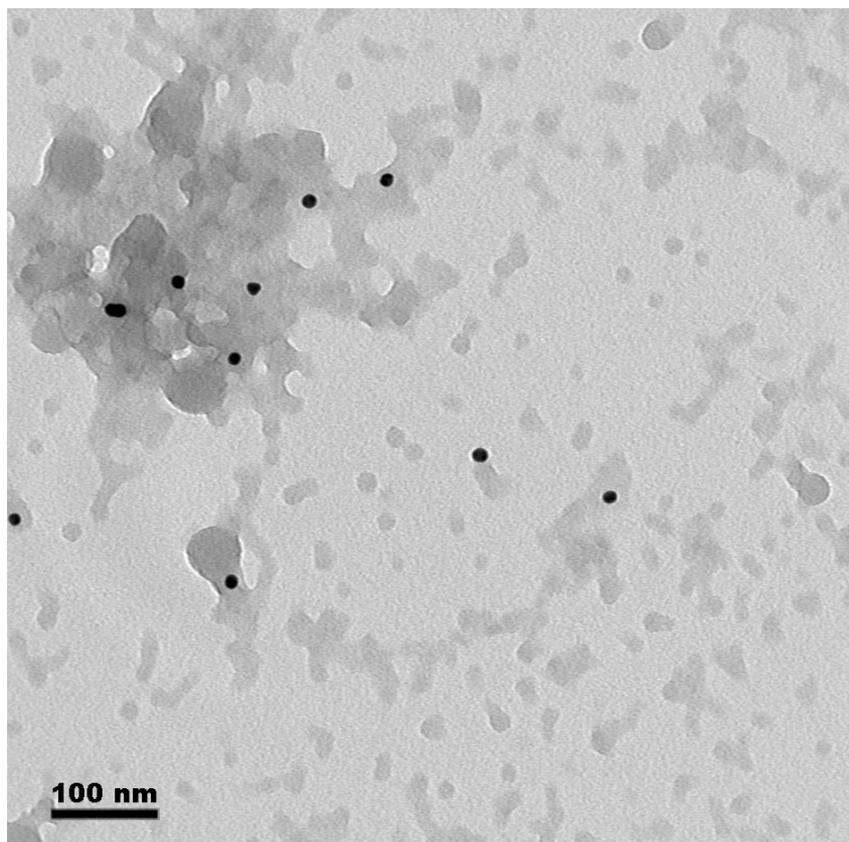


Figure S4. TEM image of material obtained during attempt to encapsulate 12 nm Au nanoparticles within micelles formed from PS₆₃₉-*b*-PAA₆₂, [PS₆₃₉-*b*-PAA₆₂] = 2×10^{-4} g/mL. This image is representative of attempts to encapsulate using polymers with longer PAA blocks. We currently understand that this failure is due to the more dominant formation of empty micelles rather than forming polymer layer on the surface for the polymer with longer PAA blocks.^[5]

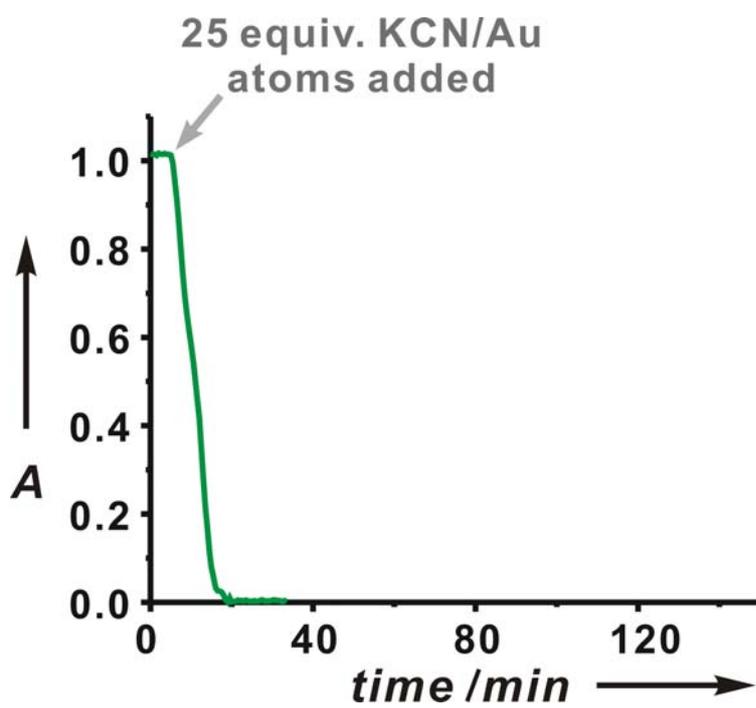


Figure S5. Cyanide-induced decomposition of dodecanethiol-functionalized, 12-nm Au nanoparticles in DMF.

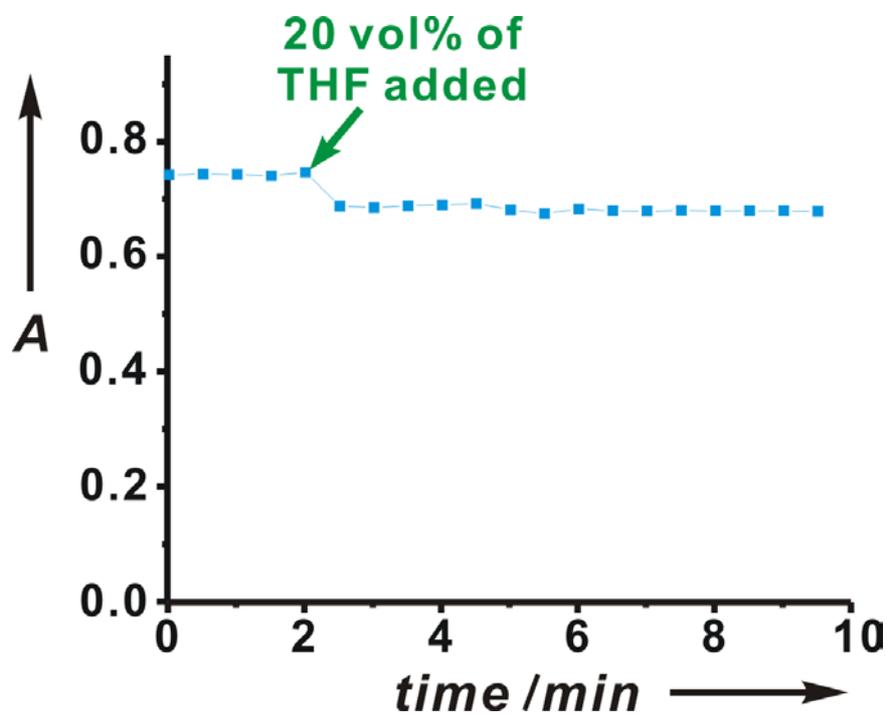


Figure S6. UV-VIS absorbance change of encapsulated 12 nm Au nanoparticles within PS₂₅₀-*b*-PAA₁₃ micelles (50% crosslinked) by adding THF (20 vol% at 2 min). Absorbance was measured at $\lambda_{\text{max}} = 529$ nm. This change in absorbance was used to correct the contribution of solvent to the changes shown in Figure 3.

Table S1. Solubility of encapsulated 31 nm Au nanoparticles

Solvent	Relative solubility (A/A_0) ^[a]	
	PS ₂₅₀ - <i>b</i> -PAA ₁₃	PMMA ₂₄₀ - <i>b</i> -PAA ₁₃
toluene	0.92	0.83
<i>o</i> -dichlorobenzene	0.74	0.88
methyl ethyl ketone (MEK)	0.68	-
acetone	0.03	0.85
ethyl acetate	0.71	0.70
chloroform	0.70	0.53
methylene chloride	0.90	0.81
tetrahydrofuran	0.92	0.98
dioxane	0.52	-
cyclohexane	0.36	0.01
dimethylformamide	0.69	0.65
isopropanol (<i>i</i> PrOH)/MEK (1:1)	0.02	0.64

[a] Relative solubility (A/A_0) is defined as a ratio of the solution absorbance measured at λ_{\max} for particles in each solvent (A) to the absorbance measured at λ_{\max} in water (A_0). Each sample was prepared by lyophilizing 1 mL aqueous, encapsulated 31 nm Au nanoparticle solution,^[15] and resuspending the dried material into 1 mL solvent. Absorbance values were measured after removing insoluble solid by centrifugation at low speed. $A/A_0 = 0.61-1.0$ (soluble), $A/A_0 = 0.1-0.6$ (slightly soluble), $A/A_0 = 0.0-0.1$ (insoluble).

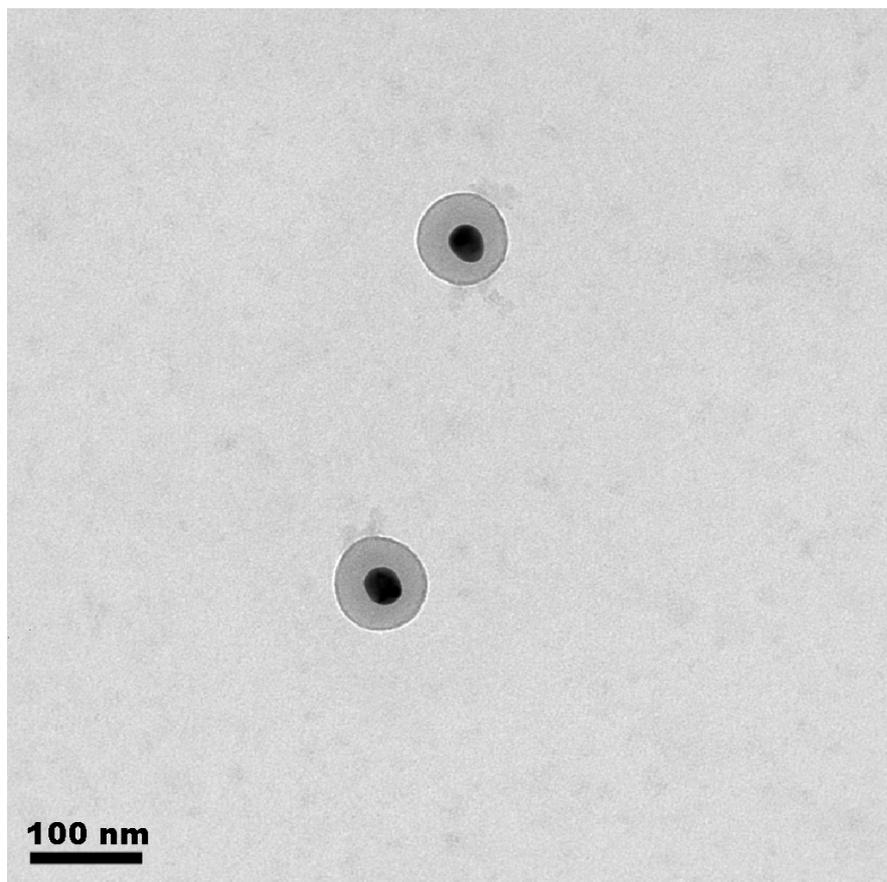


Figure S7. TEM image of encapsulated 31 nm Au nanoparticles, prepared by adding 20 vol% THF to aqueous encapsulated Au nanoparticle solution, waiting 2 hours, and then removing THF by dialysis against H₂O. Particles looked indistinguishable from starting material (shown in Figures 1d, S3), indicating that solvation of topologically linked shell is reversible and does not dissolve away surfactant.

References

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