Supporting Information

Multicomponent Nanoparticles via Self-Assembly with Cross-Linked Block Copolymer Surfactants

Byeong-Su Kim and T. Andrew Taton

A. Representative Procedure for [CdSe/ZnS$_{Blue}$-CdSe/ZnS$_{Red}$]@PS-*b*-PAA$_{XL}$ Micelles

To maximize the co-encapsulation efficiency while maintaining the quantum yield unaffected from cosolvent like DMF, we used only THF for micelle solution before the water addition. However, water addition rate was optimized to form relatively uniform sized micelles.[1]

Initially, predetermined amount of TOPO-stabilized CdSe/ZnS nanoparticles with different diameter, 2.9 and 6.1 nm, respectively, were mixed before addition to the polymer solution. Freshly prepared 100 μL PS$_{250}$-*b*-PAA$_{13}$ stock solution (1.0 mg/mL in THF) was added slowly with vigorous stirring to the nanoparticle solution, such that [CdSe/ZnS$_{Blue}$]$_{initial}$ = 1.0 × 10^{-3} mg/mL, [CdSe/ZnS$_{Red}$]$_{initial}$ = 2.0 × 10^{-3} mg/mL and [PS$_{250}$-*b*-PAA$_{13}$]$_{initial}$ = 0.10 mg/mL in THF (total volume of solution 1.0 mL). Then, 4.0 mL of H_2O was added to the solution at a rate of 400 mL/h with vigorous stirring. After stirring for 30 min, the resulting suspension was subjected to the dialysis against Millipore water (18 MΩ·cm) for over 24 h (Spectra/Por® 4 Regenerated Cellulose Membrane, MWCO = 12-14K) to remove any residual solvent. Assuming no material loss during dialysis, the concentration of each component at this stage was, [PS$_{250}$-*b*-PAA$_{13}$]$_{final}$ = 2.0 × 10^{-2} mg/mL = 0.741 μM, [CdSe/ZnS$_{Blue}$]$_{final}$ = 2.0 × 10^{-4} mg/mL = 11.7 nM, and [CdSe/ZnS$_{Red}$]$_{final}$ = 4.0 × 10^{-4} mg/mL = 2.0 nM, respectively. After micelle formation,

the cross-linking and centrifugal purifications were followed as described previously. After the purification steps, 2.0 μL of the resulting solution was diluted with water and deposited on the TEM grid, dried in air before taking TEM images.

B. Representative Procedure of [Au-Fe_3O_4]@PS-*b*-PAA_{XL} Micelles

B1. Synthesis of oleylamine-stabilized Au nanoparticles

Monodisperse Au nanoparticles were prepared following modified method from the literature protocol.[2] Au precursor, $HAuCl_4 \cdot 3H_2O$ (100 mg, 0.294 mmol) was suspended in 10 mL of toluene. Upon the introduction of oleylamine (1.0 mL, technical grade), insoluble Au precursor dissolved to produce a clear red solution. Temperature was slowly heated to 100 ^oC with stirring under nitrogen, where it became colorless again. After 30 min, the solution was cooled to room temperature in which the solution changed back to a red-violet. The excess surfactant was removed by sequential centrifugal separation. The resulting purified Au nanoparticles were well-dispersed in the organic solvent including hexane, toluene, and THF. The average diameter of Au nanoparticle prepared was determined to be around 13 nm by TEM investigations.

B2. Synthesis of oleylamine-stabilized Fe_3O_4 nanoparticles

Monodisperse 4.5 nm sized Fe_3O_4 nanoparticles were prepared following the method from the literature protocol by Sun et al.[3] Their average diameter and the crystalline structure were determined with TEM.

B3. Preparation of [Au-Fe_3O_4]@PS-*b*-PAA_{XL} micelles

The optimized encapsulation procedure is almost identical to that of [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles. Initially, 13 nm oleylamine-stabilized Au (1.0 mg/mL THF) and 4.5 nm Fe_3O_4 magnetic nanoparticle solutions (1.0 mg/mL in THF) were mixed before addition to the polymer

solution. Freshly prepared 10 μL PS_{250}-*b*-PAA_{13} stock solution (10.0 mg/mL in DMF) was added slowly with vigorous stirring to the nanoparticle solution, such that $[Au]_{initial}$ = 0.10 mg/mL, $[Fe_3O_4]_{initial} = 2.0 \times 10^{-3}$ mg/mL, and $[PS_{250}\text{-}b\text{-}PAA_{13}]_{initial}$ = 0.10 mg/mL in 50:50 mixture of DMF/THF (total volume of solution 1.0 mL). Then, 4.0 mL of H_2O was gradually added at a rate of 140 mL/h to the solution with vigorous stirring. After stirring for 30 min, the resulting suspension was subjected to the dialysis against Millipore water (18 MΩ·cm) for over 24 h (Spectra/Por® 4 Regenerated Cellulose Membrane, MWCO = 12-14K) to remove any residual solvent. After micelle formation, the outer PAA shell was cross-linked (50%) as described previously. Au-Fe_3O_4 micelle solutions were subjected to centrifugation (16000 × *g* RCF_{avg}, 30 min). The upper 90% of the solution was discarded and the same volume of Millipore water was added to the solution. This procedure was repeated three times to remove any aggregates and/or empty micelles in the suspension. Purified [Au-Fe_3O_4]@PS-*b*-PAA_{XL} micelles were readily redispersed in water. After the purification steps, 2.0 μL of the resulting solution was diluted with water and deposited on the TEM grid, dried in air before taking TEM images.

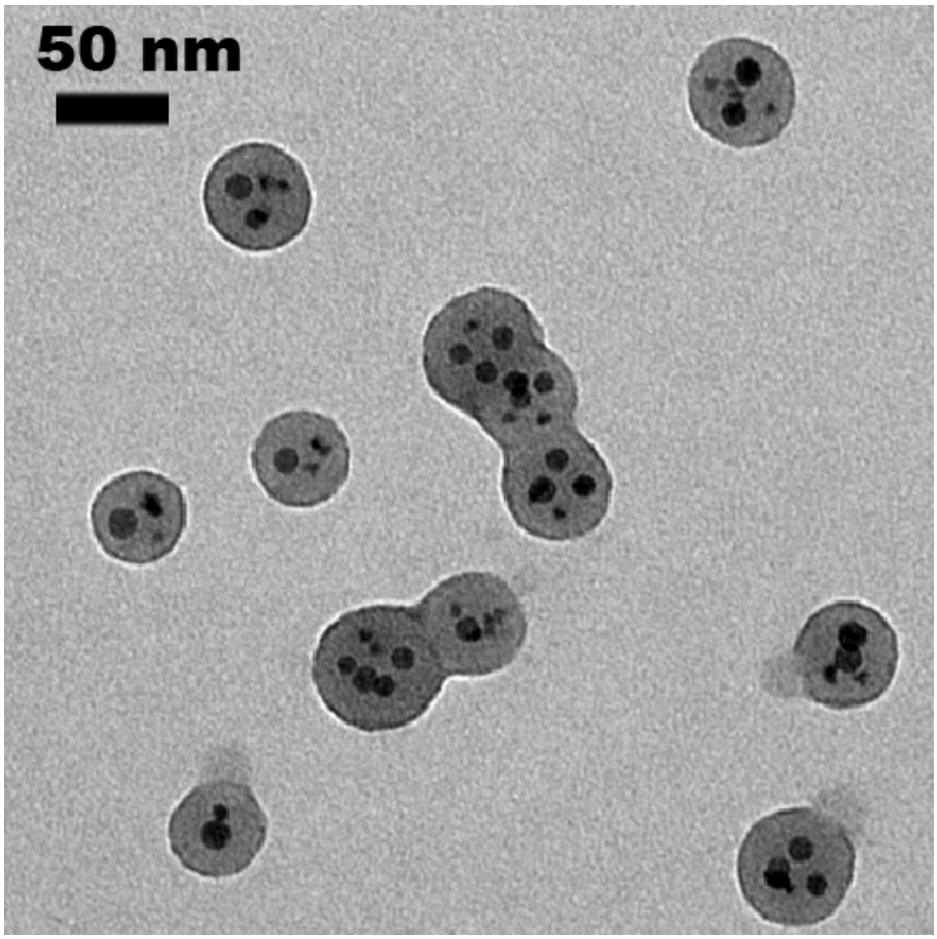

Figure S1. Large area TEM micrograph of [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles obtained at the concentration at $[\gamma\text{-}Fe_2O_3]_{initial}$ = 0.20 mg/mL, $[CdSe/ZnS]_{initial}$ = 2.0 × 10^{-3} mg/mL, respectively (a number ratio of γ-Fe_2O_3 to CdSe/ZnS = 10). Centrifugal purifications were carried out to purify the [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles. Note the multiple micelle aggregation is not by inter-micellar crosslinking, but rather by drying process by which the same aggregation was observed for even non-crosslinked samples. This image corresponds to Figure 1c in the manuscript. Number ratio of each nanoparticle was calculated based on the molecular weight of 10.4 nm of γ-Fe_2O_3 (1.95 × 10^3 μg/nmol) and 6.1 nm CdSe/ZnS (193 μg/nmol).

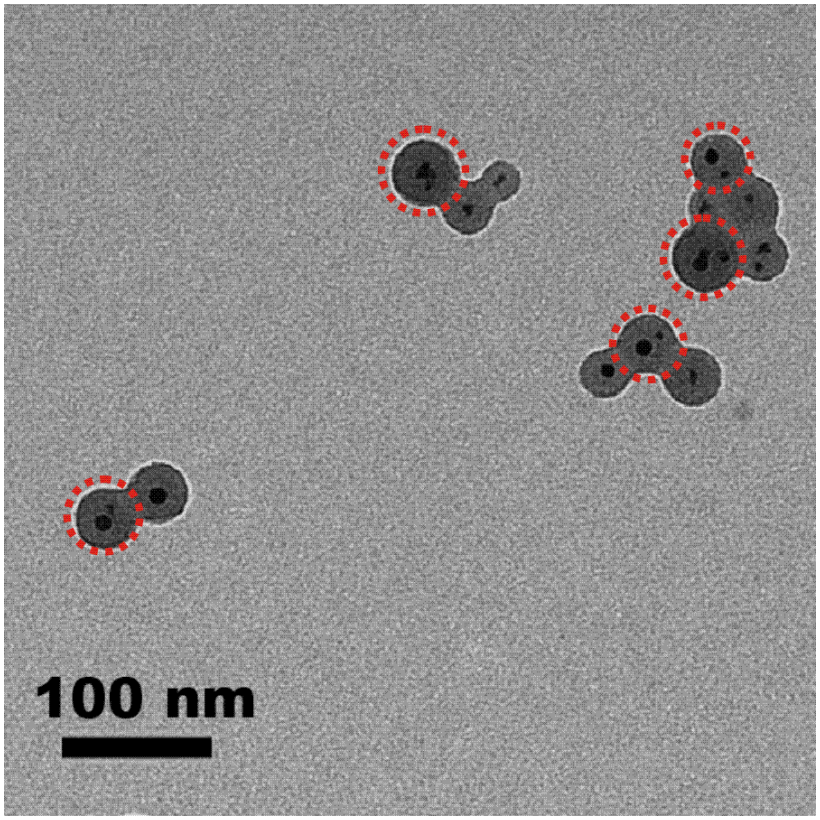

Figure S2. TEM micrograph of [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles obtained at low concentration of nanoparticles at $[\gamma\text{-}Fe_2O_3]_{initial}$ = 0.025 mg/mL, $[CdSe/ZnS]_{initial}$ = 1.0 × 10^{-3} mg/mL, respectively (a number ratio of γ-Fe_2O_3 to CdSe/ZnS = 2.5).; the red-circled micelle represents the colocalization of γ-Fe_2O_3 and CdSe/ZnS in a micelle, while the other single entity encapsulated micelles such that γ-Fe_2O_3 micelle and CdSe/ZnS micelle are still present in the solution even after the centrifugation cycles.

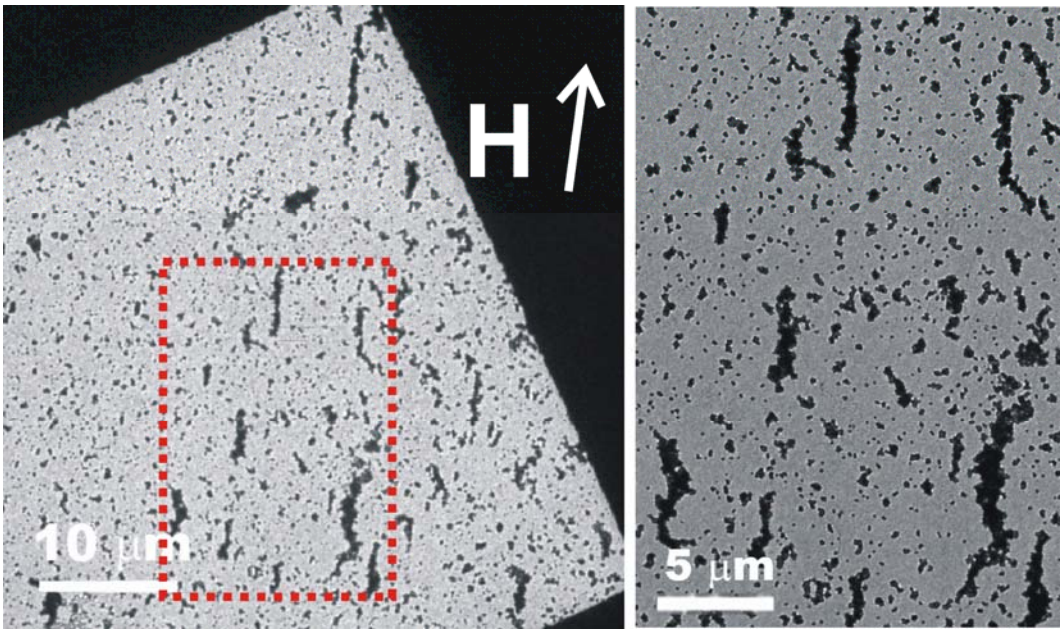

Figure S3. TEM micrograph of aligned [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles with external magnetic field, H, prepared by dropped suspension onto a TEM grid under the influence of a static magnetic field (NdFeB magnet, $H_{estimated}$ = 0.14 T at 1.0 cm). The image on the right shows a magnified view of the selected region. Micelle suspension was prepared at relatively high concentration of nanoparticles such that $[\gamma\text{-}Fe_2O_3]_{initial}$ = 0.30 mg/mL, $[CdSe/ZnS]_{initial} = 2.0 \times 10^{-3}$ mg/mL.

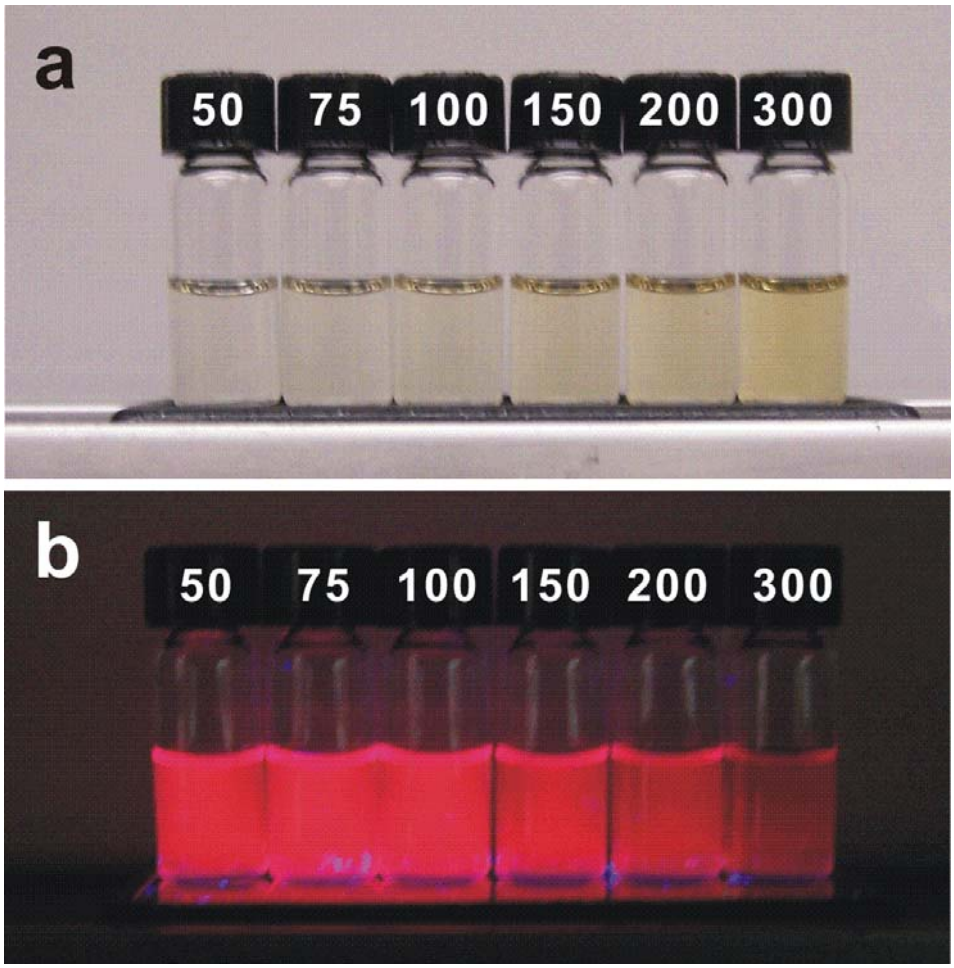

Figure S4. Fluorescence changes of [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles prepared in *pure THF condition* with varying amount of γ-Fe_2O_3 nanoparticles at fixed CdSe/ZnS concentration (2.0 nM) (a, b) Photo of [γ-Fe_2O_3-CdSe/ZnS]@PS-*b*-PAA_{XL} micelles under light, and UV lamp (λ_{ex} = 365 nm), respectively. Numbers on the sample represent the initial concentration of γ-Fe_2O_3 nanoparticles in μg/mL THF.

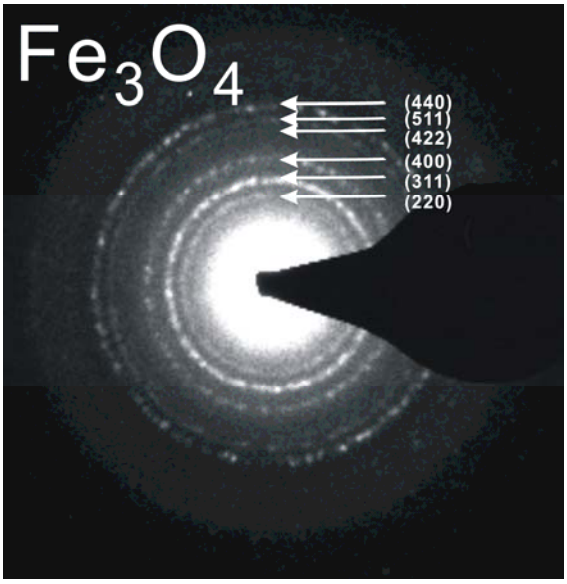

Figure S5. Selected-area electron diffraction (SAED) pattern of oleylamine-stabilized 4.5 nm Fe_3O_4. All the peaks are matching with Fe_3O_4, magnetite (PDF 19-629) was used to assign the diffraction patterns.

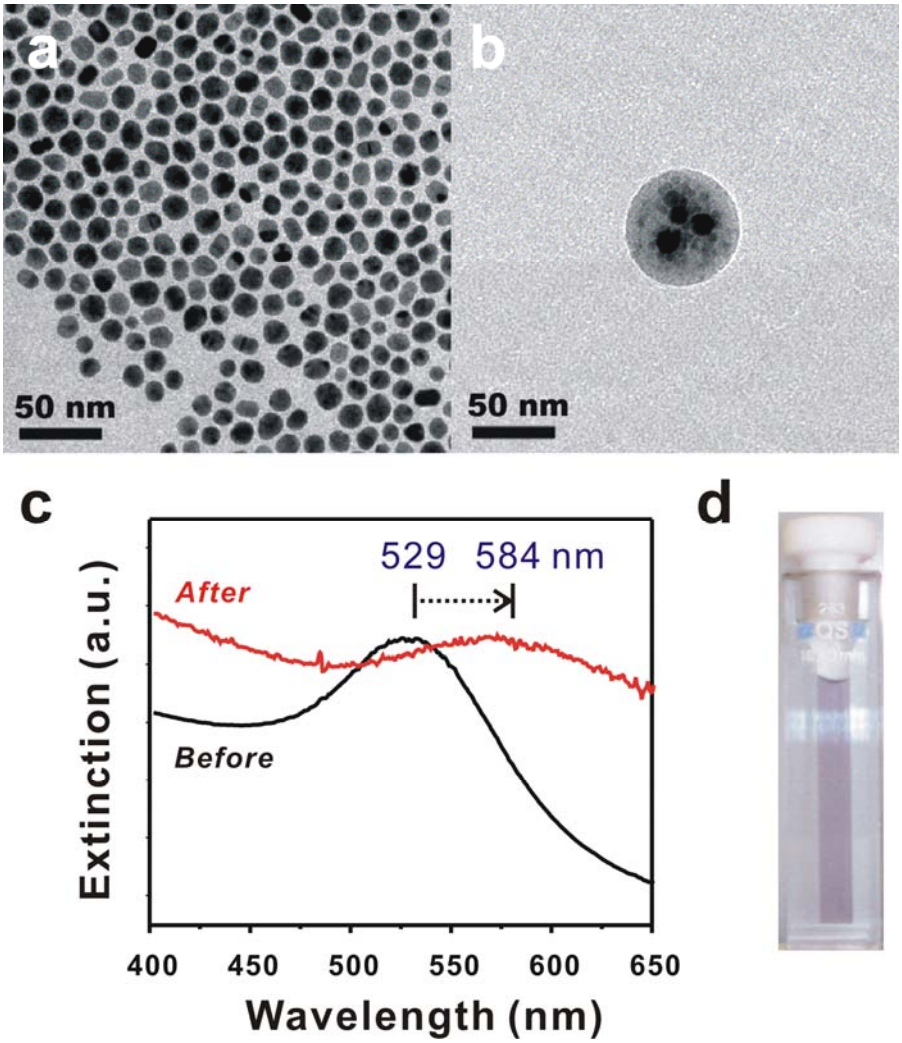

Figure S6. TEM micrographs of (a) oleylamine-stabilized Au nanoparticle (d = 13 nm) (b) [Au-Fe_3O_4]@PS-*b*-PAA_{XL} micelle ($[Au]_{initial} = 1.0 \times 10^{-2}$ mg/mL, $[Fe_3O_4]_{initial} = 2.0 \times 10^{-3}$ mg/mL in THF) (c) UV-vis spectra of Au nanoparticles (black) before encapsulation (red) after encapsulation with Fe_3O_4 in the micelle (d) photograph of [Au-Fe_3O_4]@PS-*b*-PAA_{XL} micelle in water. UV-vis spectroscopy probed the surface-plasmon peak at 529 nm, however, the surface plasmon peak of Au nanoparticle has shifted to 584 nm upon encapsulation, indicating multiple Au nanoparticles encapsulated within a micelle affected the surface plasmon peak of Au nanoparticles red-shifted, and broadened.

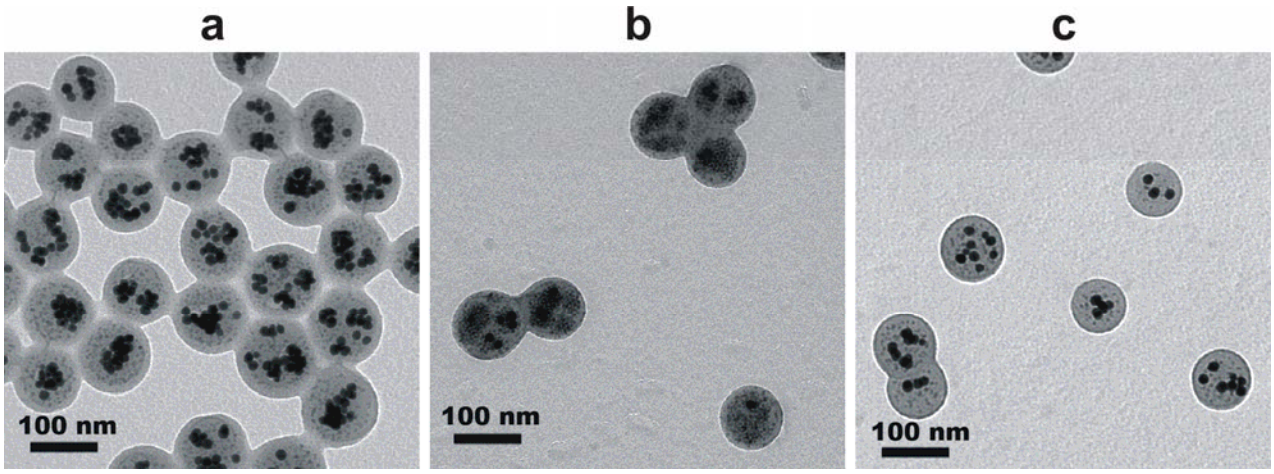

Figure S7. TEM micrographs of [Au-Fe_3O_4]@PS-*b*-PAA_{XL} micelles at different concentration of nanoparticles (a) $[Au]_{initial}$ = 0.175 mg/mL, $[Fe_3O_4]_{initial}$ = 0.025 mg/mL in THF (b) $[Au]_{initial}$ = 0.050 mg/mL, $[Fe_3O_4]_{initial}$ = 0.050 mg/mL in THF (c) $[Au]_{initial}$ = 0.010 mg/mL, $[Fe_3O_4]_{initial}$ = 0.005 mg/mL in THF. By varying the initial concentration of nanoparticles, we can tailor the loading contents of the resulting micelles.

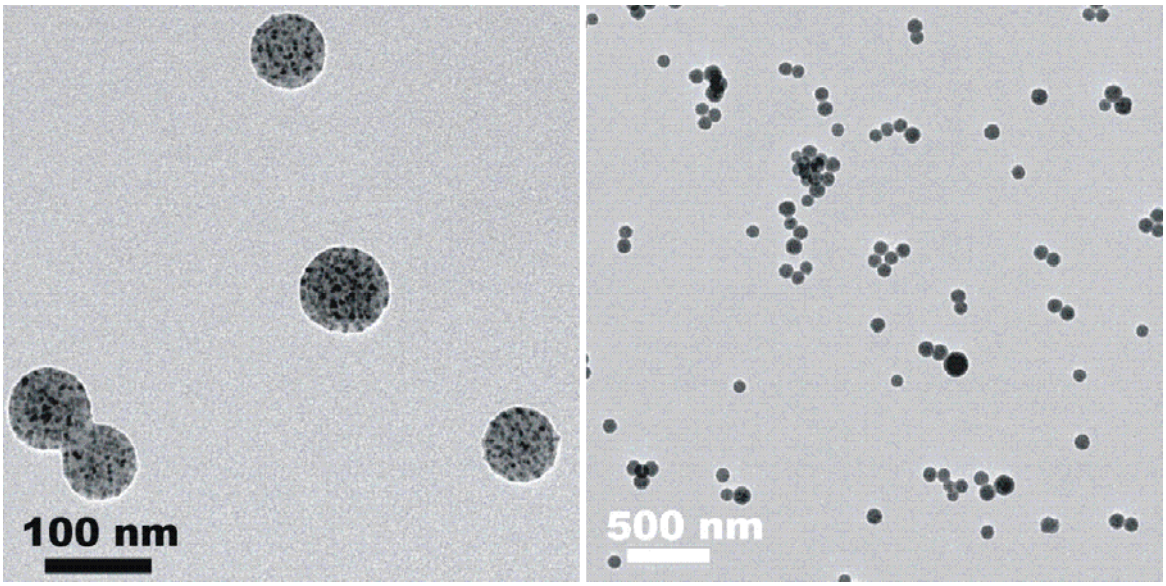

Figure S8. TEM micrographs of [Fe_3O_4-CdSe/ZnS]@PS-*b*-PAA$_{XL}$ micelle at high concentration of nanoparticles; $[Fe_3O_4]_{initial} = 5.0 \times 10^{-2}$ mg/mL, and $[CdSe/ZnS]_{initial} = 5.0 \times 10^{-3}$ mg/mL in THF. This is the same as the inset image in Figure 4c in the manuscript.

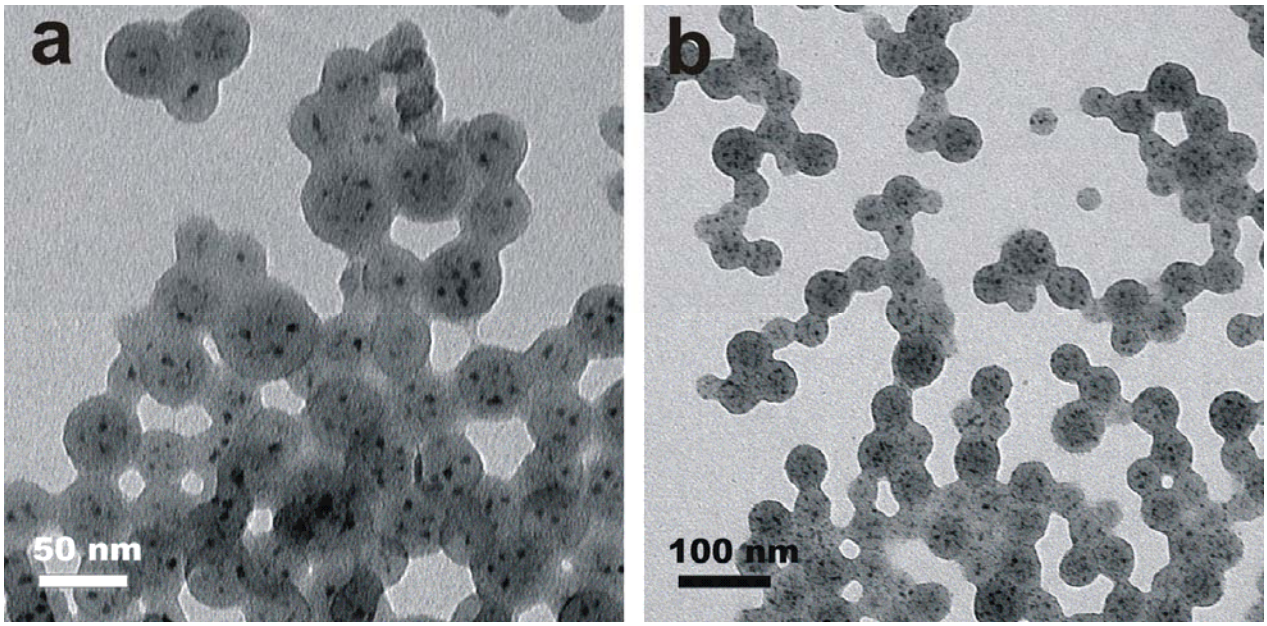

Figure S9. TEM micrographs of [CdSe/ZnS_{Blue}-CdSe/ZnS_{Red}]@PS-*b*-PAA_{XL} micelle at different relative concentration of nanoparticles (a) $[CdSe/ZnS_{Blue}]_{initial}$ = 1.0 × 10^{-3} mg/mL, and $[CdSe/ZnS_{Red}]_{initial}$ = 2.0 × 10^{-3} mg/mL (a number ratio of CdSe/ZnS_{Blue} to CdSe/ZnS_{Red} = 5.6), (b) $[CdSe/ZnS_{Blue}]_{initial}$ = 8.0 × 10^{-3} mg/mL, and $[CdSe/ZnS_{Red}]_{initial}$ = 2.0 × 10^{-3} mg/mL (a number ratio of CdSe/ZnS_{Blue} to CdSe/ZnS_{Red} = 45.1). Number ratio of each nanoparticle was calculated based on the measured molecular weight of CdSe/ZnS_{Blue} (17.1 μg/nmol) and CdSe/ZnS_{Red} (193 μg/nmol). Particles were initially dispersed in 1.0 mL of THF before water addition.

References

(1) Shibasaki, Y.; Kim, B.-S.; Young, A. J.; McCloon, A.; Ekker, S. C.; Taton, T. A. *J. Am. Chem. Soc.* **2006**, submitted.

(2) Yu, H.; Chen, M.; Rice, P. M.; Wang, S. X.; White, R. L.; Sun, S. H. *Nano Lett.* **2005**, *5*, 379-382.

(3) Sun, S. H.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. X. *J. Am. Chem. Soc.* **2004**, *126*, 273-279.