



Supporting Information

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Interfacial Assembly of Nanoparticles in Discrete Block-Copolymer Aggregates**

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1. Synthesis of Block-Copolymers

Poly(*tert*-butyl acrylate)₄₁-*block*-polystyrene₁₉₃ (PtBA₄₁-*b*-PS₁₉₃) was synthesized via sequential reversible addition-fragmentation chain transfer (RAFT) polymerization of *tert*-butyl acrylate and styrene.^[1] Briefly, the polymerization reaction was carried out in acetone at 78 °C using 2, 2'-azobisisobutyronitrile (AIBN) as an initiator. The reaction was quenched by dipping the container in iced water and exposing the product to air. The PtBA-*b*-PS was purified by the precipitation with methanol, and the precipitates were collected and dried under vacuum. The molecular weight of the synthesized PtBA-*b*-PS was estimated by gel permeation chromatography (Shimadzu) equipped with Polymer Laboratories columns (guard: 10⁶, 10⁴, and 5 × 10² Å) and a refractive index detector (RID-10A) calibrated with linear polystyrene standards in THF. The molecular weight (M_n) and polydispersity index (PDI) of the polymer were determined to be 25.600 g/mol and 1.13, respectively. Subsequently, the synthesized PtBA-*b*-PS was dissolved in 1,4-dioxane and hydrolyzed by HCl under reflux condition for about three hrs to generate PAA-*b*-PS.^[2] The PS end of the polymer is terminated with a dodecyl trithiocarbonate group introduced from the RAFT catalyst. Finally, the PAA-*b*-PS was purified by repeated precipitations into hexane and characterized by ¹H NMR and FT-IR.

2. Size Distribution of Synthesized Nanoparticle-Block-Copolymer Assemblies (NBA)

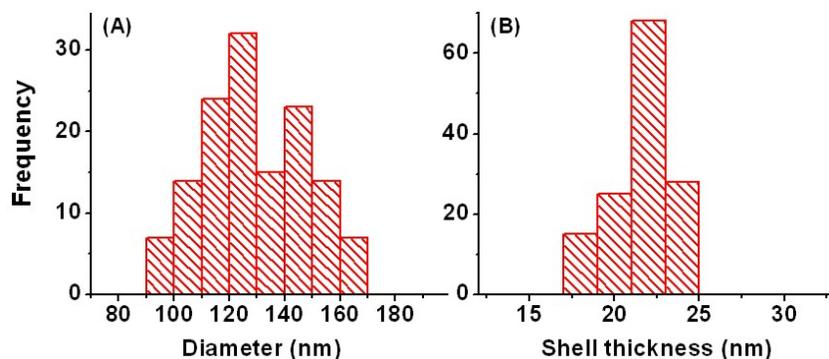


Figure S1. Histograms of (A) the diameter of NBA and (B) the thickness of the polymer shell.

3. Structural Analysis of Nanoparticle-Block-Copolymer Assemblies

The calculated radial intensity (*i.e.*, grey scale of TEM images) profile presented in Figure 2C was generated by combining the radial intensity profile of the two-dimensional projection of semi-transparent dots randomly distributed on the surface of a sphere and the intensity profile of a solid spherical polymer aggregate (Figure S2). The intensity at the background (*i.e.*, carbon layer of TEM grid) was set to one and the relative intensities at the assemblies were calculated and plotted in Figure 2C. In addition to the assembly structure described in Figure 2A, other structures such as the emulsion model where the core of the assembly is filled with a solvent instead of polymers were also considered (Figure S2). For the emulsion model, the intensity at the core region was assumed to be the midpoint between the intensity at the darkest point of the shell and the intensity at the background.^[3] As shown in Figure S2, the radial intensity profile calculated based on the emulsion model did not fit with the experimental data well. In addition, emulsion-like assemblies were occasionally observed in a

few batches of syntheses (Figure S3). Indeed, the emulsion-like assemblies show clearly different contrasts from the typical assemblies with the solid polymer core.

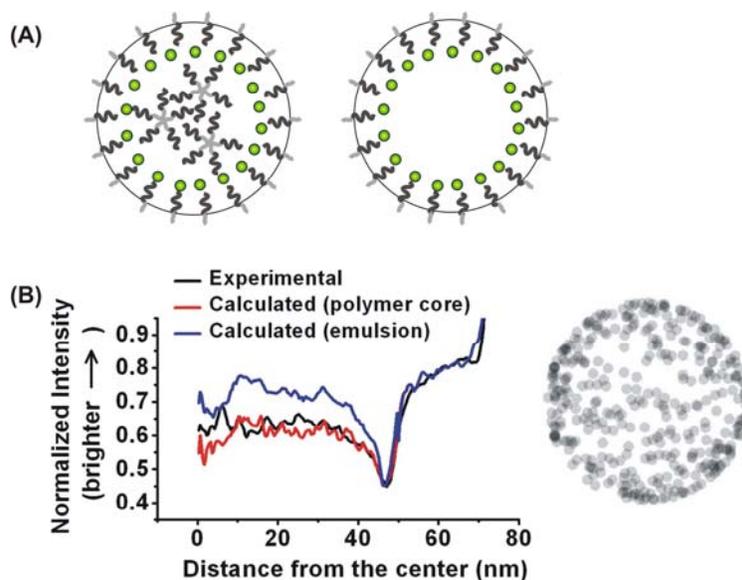


Figure S2. (A) Schematic description of the polymer core model (left) and the emulsion model (right). (B) Radial intensity profiles based on the polymer core model and the emulsion model. The two-dimensional projection of semi-transparent dots distributed on the surface of a sphere used for the calculation is shown on the right.

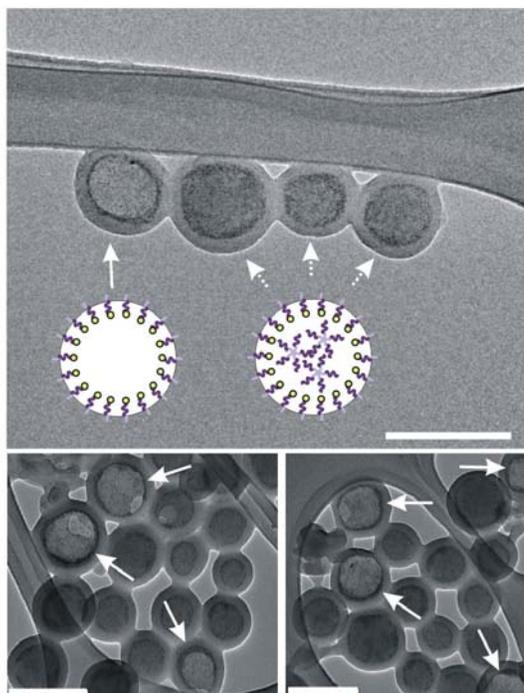


Figure S3. TEM images showing emulsion-type assemblies. Emulsion-type assemblies are indicated with solid-line arrows. It is apparent that the core of emulsion-type assemblies shows a lighter contrast than the core of typical assemblies with the polymer core. Scale bar: 200 nm.

3. Photoluminescent (PL) Properties of NBA

To estimate the quantum yield (QY) of quantum dots (QDs) incorporated in the assemblies, the following two samples were prepared: aq. solution of NBA (Sample I) and QDs in chloroform (Sample II). The two samples contained the same total number of QDs per solvent volume. The number of QDs in Sample I was estimated assuming that there is no loss of QDs during the assembly preparation. The QY of Sample II was estimated to be 34 % using Rhodamine 6G, which has 94 % QY in ethanol, as a standard. We then compared the PL

intensities of Sample I and Sample II. Since the QY of sample II is known, the QY of Sample I can be obtained from the measurement. The PL intensities of prepared NBA solutions varied from batch to batch, but the average QY of QDs in NBA estimated from five different samples was 37 %, which was slightly higher than that of original TOPO-stabilized QDs in chloroform. The QY of QDs is sensitive to the environment and the surface modification. In NBA, the polymer shell effectively protects the nanoparticles from PL quenchers in water, and the surrounding polymer matrix can prevent the surfactants on nanoparticle surfaces from being desorbed.

References

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