Supplementary Information for

Co-assembly Behavior of Janus Nanoparticles and Amphiphilic Block Copolymers in Dilute Solution

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1. Interfacial energy

In order to explain the shifted distributions of Janus nanoparticles (JPs) at the core-corona interfaces (see Fig. 3d-g), we calculated the interfacial energy $g(\theta)$ for JPs at various values of ε, where θ and ε are the contact angle and the curvature of interface, respectively (see Eq. 11 and Eq. 12). The results are shown in Fig. S1. Similar to the wrapping fraction $f_{w(core)}$, the contact angle θ can also be used to characterize the spatial localization of nanoparticles at the interfaces (see Fig. S1a-c). Here, we denote the contact angle corresponding to the anchoring position as θ_{an}, and $\theta < \theta_{an}$ and $\theta > \theta_{an}$ indicate that the nanoparticle is shifted toward the solvent and the aggregate core, respectively. Fig. S1d displays the relationship between the interfacial energy and the contact angle at various ε. It is worth noting that, at high values of ε, the contact angle θ_m corresponding to the minimum of interfacial energy is smaller than the θ_{an}. Therefore, the shifted distributions of nanoparticles toward the corona and solvent are favored to minimize the interfacial energy. As shown in Fig. S1e, such observation holds for ε larger than 0.2. For the amphiphilic block copolymers with equal sizes of hydrophilic and hydrophobic blocks, the curvature of core-corona interfaces in spherical and rod-like micelles formed at lower particle loadings is larger than 0.2, which leads to the shifted distributions of Janus nanoparticles which are shown in Fig. 3d-g.
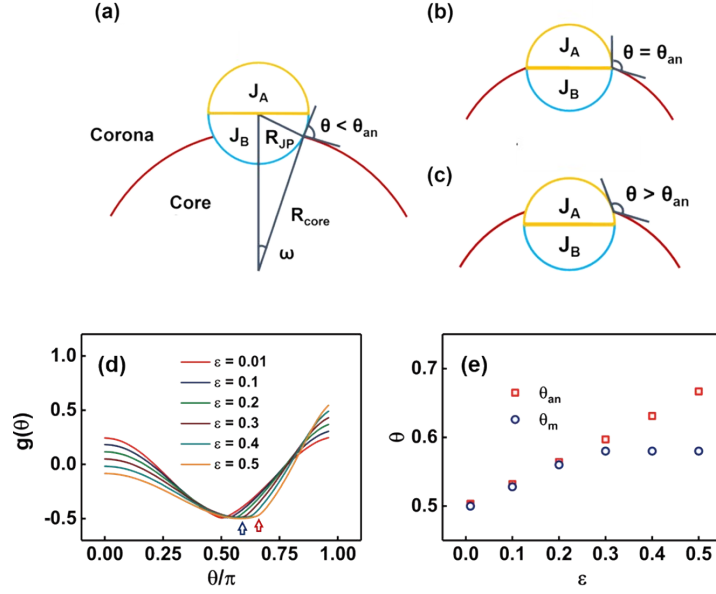
Figure S1. (a-c) Schematic illustration of Janus nanoparticles with a J_A hemisphere (colored in yellow) and a J_B hemisphere (colored in blue) located at the core-corona interface (colored in red) of a spherical micelle. (a) Particle is shifted toward the corona and solvent. (b) Particle is exactly located at the interface (anchoring position). (c) Particle is shifted toward the core. Radii of the particle and the core are denoted by R_{JP} and R_{core}, respectively. Central angle is denoted by ω. Contact angle is denoted by θ. Contact angle corresponding to the anchoring position is denoted by θ_{an}. (d) Dependence of interfacial energy $g(\theta)$ on the contact angle at various curvatures ε of core-corona interfaces. Contact angles corresponding to the anchoring position (θ_{an}) and the minimal interfacial energy (denoted by θ_m) at $\varepsilon = 0.5$ are denoted by red and blue arrows, respectively. (e) Dependence of θ_{an} and θ_m on the value of ε.

2. Penetration of solvent/copolymer beads

In order to check whether the copolymer and solvent beads could penetrate into the model nanoparticles, we calculated the probability $g(r)$ of finding a solvent/copolymer bead at a distance of r away from a nanoparticle center for a system at equilibrium with $f_A = 0.5$ and $c_{JP} = 0.2$, where f_A is the fraction of hydrophilic blocks in the block copolymers, and c_{JP} is the volume fraction of Janus nanoparticles. The result is shown in Fig. S2. The snapshot of aggregates is shown in the inset. It can be seen that there are no solvent and copolymer beads at $r < R_{JP} = 0.5r_c$ (in fact, the range can be extended to about r_c), where R_{JP} is the radius of nanoparticles. This suggests that the possible penetration of solvent/copolymer beads has been well prevented.
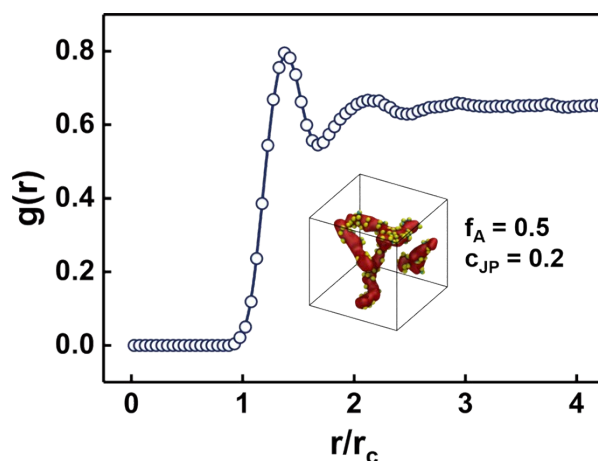

Figure S2. Probability $g(r)$ of finding a solvent/copolymer bead at a distance of r away from a nanoparticle center for a system at equilibrium with $f_A = 0.5$ and $c_{JP} = 0.2$. The snapshot of aggregates is shown in the inset. Aggregate cores are colored in red. J_A and J_B hemispheres are colored in yellow and cyan, respectively. Aggregate coronas and solvents are omitted for clarity.

3. Radius of gyration

The radius of gyration, R_g, of a hydrophilic block or a hydrophobic block is computed as

$$R_g^2 = \frac{1}{2N^2}\sum_{i,j}(\mathbf{r}_i - \mathbf{r}_j)^2$$

where N is the number of beads in each block, $\mathbf{r}_i$ and $\mathbf{r}_j$ are the positions of the ith and the jth beads, respectively. Fig. S3 shows the distributions of R_g for the hydrophilic blocks (Fig. S3a) and the hydrophobic blocks (Fig. S3b) for a system at equilibrium with $f_A = 0.5$ and $c_{JP} = 0.3$. The number-average R_g of the hydrophilic/hydrophobic block is denoted in each panel. By this means, the R_g of copolymer chains can also be obtained. It is found that the R_g of symmetric block copolymers is around $2.05r_c$ and the R_g of hydrophilic (hydrophobic) blocks is around $1.11r_c$ ($1.09r_c$).
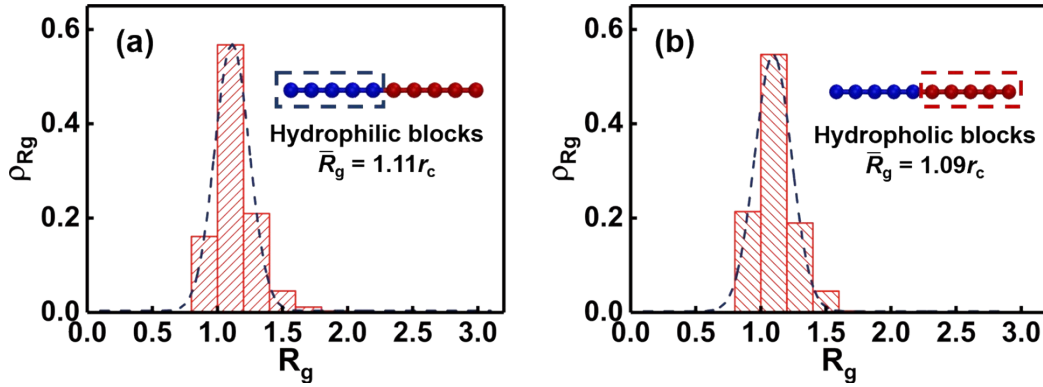
Figure S3. Distributions of the radius of gyration, R_g, of (a) hydrophilic blocks and (b) hydrophobic blocks for a system at equilibrium with $f_A = 0.5$ and $c_{JP} = 0.3$. Insets show the coarse-graining models of the amphiphilic block copolymer. The number-average radius of gyration, $\overline{R}_g$, of two types of blocks are denoted.