Supplementary data for

Cooperative Assembly of Janus Particles and Amphiphilic Oligomers: The Role of Janus Balance

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I. Interaction parameters of bead–bead pairs α_{ij}

In this study, we set the interaction parameter α_{ij}, and the detailed values are shown in Table S1. W stands for water bead, H stands for hydrophilic bead of oligomer, T stands for hydrophobic bead of oligomer, I stands for hydrophilic bead of Janus particle, and O stands for hydrophobic bead of Janus particle.

Table S1 Interaction parameters of bead–bead pairs α_{ij}

α_{ij}	H	T	W	I	O
H	25	80	25	25	80
T	80	25	80	80	25
W	25	80	25	20	80
I	25	80	20	25	80
O	80	25	80	80	25

II. Computational details of the solvent-accessible surface area and the order parameter

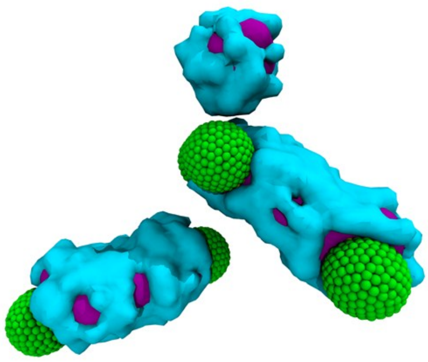

Fig. S1 Representative snapshot of hybrid assemblies in the formation process (20/80 JPs system). Color code: hydrophobic side of JPs in yellow; hydrophilic side of JPs in green; hydrophobic part of amphiphilic oligomer in purple; hydrophilic part of amphiphilic oligomer in cyan.

To get a deep insight into the kinetic pathway of hybrid aggregates formation, the solvent-accessible surface area (SASA) and the order parameter are investigated. Generally, the effect of hydrophobic interaction is to minimize the contact between solvent and hydrophobic part of amphiphiles. The decrease of SASA is favorable to lowering the free energy [1]. In this study, the SASA is obtained by subtracting hydrophobic surface area from total surface area. In the formation process of hybrid disk, the exposed hydrophobic parts are shown in Fig. S1.

The order parameter is relevant parameter to estimate the aggregation structures and the molecular orientation [2], which is expressed as follow:

$$S_m = \frac{1}{2}(3cos^2 q - 1) \tag{1}$$

If order parameter is equal to 1, meaning that the molecules in a state of perfect alignment. If order parameter is equal to 0, meaning that the molecules in a state of complete disorder.

III. The variation of the density of micelle

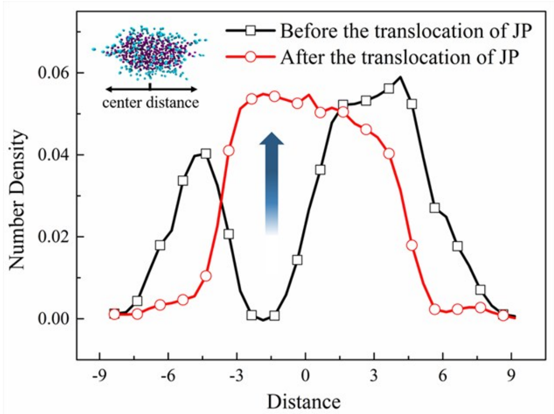

Fig. S2 The variation of the density of micelle.

In order to investigate the translocation of 20/80 JPs, the density of micelle is analyzed, as shown in Fig. S2. It can be seen that there is a non-uniform density distribution before the translocation of 20/80 JPs, and the gradient of density of micelle is significantly reduced after the translocation of 20/80 JPs. We infer the Marangoni effect is the driving force in this process.

IV. The exposed hydrophobic area during curling process

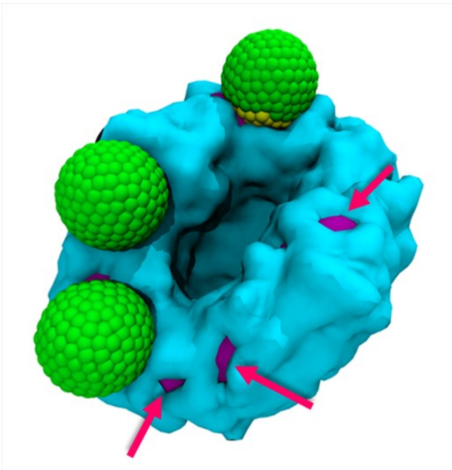

Fig. S3 Representative snapshot of transformation from hybrid disk to hybrid vesicle (20/80 JPs system). The red arrow marks the exposed hydrophobic area during the transformation process.

We find an interesting phenomenon during the investigation of the curling process of hybrid disk, which is the exposed hydrophobic parts appeared mainly in the edge of disk-like micelle, as shown in Fig. S3. Hence, the 20/80 JPs at the edge of micelles can help to reduce the exposed hydrophobic parts of micelles, which is favorable for decreasing free energy.

V. The slippage of 20/80 JPs at micellar edge

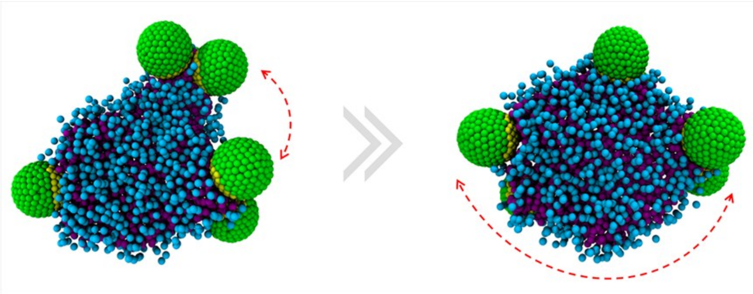

Fig. S4 Representative snapshots of the slippage of 20/80 JPs.

The investigation of the mobility of the JPs can provide clues for further understand the properties of hybrid nanostructures. We find that the 20/80 JPs can move at the micellar edges in equilibrium without breaking the micellar structure. The mobility of the JPs is an important reflection of the fluidic behaviours of micellar surface.

VI. The radial distribution functions of each kind of beads as a function of distance from the vesicle's mass center

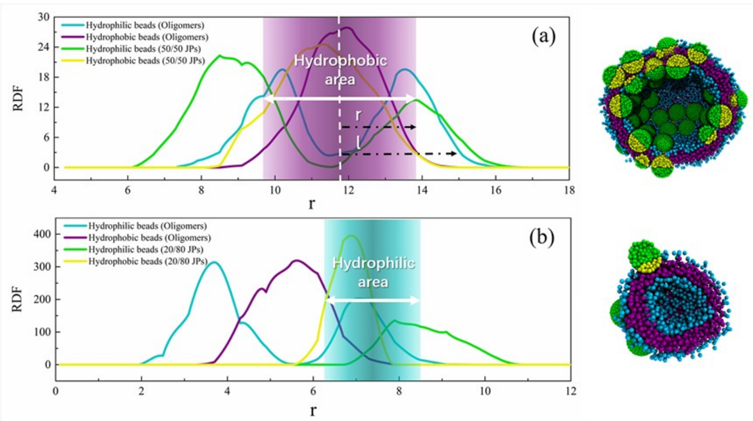

Fig. S5 The radial distribution functions of each kind of beads as a function of distance from the hybrid vesicle's mass center. The hybrid vesicles are obtained by the cooperative assembly of oligomers and (a) 50/50 JPs, (b) 20/80 JPs, respectively.

To analyze hybrid micelles quantitatively, the radial distribution functions (RDFs) of each kind of beads as a function of distance from the vesicle's mass center are plotted in Fig. S4. The value of RDFs provide the basis for determining the thickness of the hydrophobic interior and hydrophilic corona. It can be seen that the thickness of the hydrophobic interior is around 4 r_c and the thickness of the hydrophilic corona is around 2 r_c for both cases.

Reference

1. P. Wang, S. Pei, M. Wang, Y. Yan, X. Sun and J. Zhang, *Physical Chemistry Chemical Physics*, 2017, **19**, 4462-4468.
2. M. Wang, T. Fang, P. Wang, Y. Yan, J. Zhang, B. Liu and X. Sun, *Langmuir*, 2017, **33**, 5291-5297.