Supplementary Material:

Asymmetric Vesicle Constructed by AB/CB Diblock Copolymer Mixture and Its Behavior: A Monte Carlo Study

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S1: The simulation result shows that after running for about more than 5000 time steps (in each time step, 7000 MCS are performed), the structure of artificial asymmetric vesicle still remain unchanged.

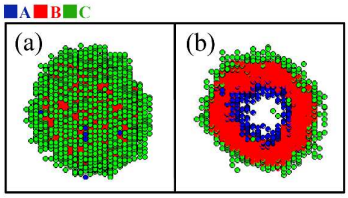

Figure S1. Vesicle structure (a) and its cross-section (b) of artificially made well-layered asymmetric vesicles after running for more than 5000 time steps.

S2: The simulation results show that the asymmetric vesicle membrane structure is independent of the initial state (Figure S2) and the dynamic process (Figure S3-4), which proves that the asymmetric vesicle structure is stable.

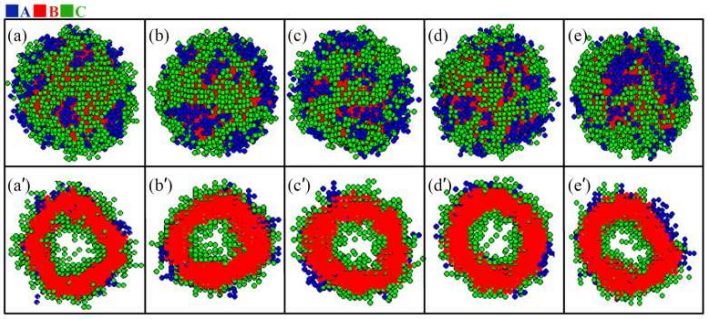

Figure S2. Membrane structures of the asymmetric vesicles formed by A_3B_4/C_3B_4 diblock copolymer mixture with different initial states (f_{A3B4} = 25%). (a')-(e') are the cross-sections corresponding to (a)-(e) respectively.

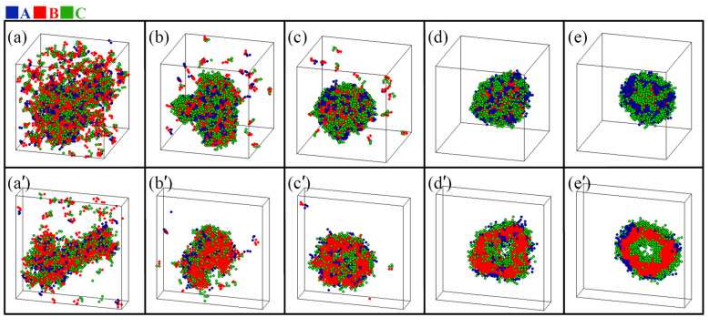

Figure S3. Snapshots showing the pathway of asymmetric vesicle formation of A_3B_4/C_3B_4 diblock copolymer mixture with f_{A3B4} = 25% at a slower annealing speed

(the annealing speed is 0.0002 per time step, 9000 Monte Carlo Steps (MCS) were performed at each time step). Simulation time: (a) 7.2×10^5, (b) 9.0×10^5, (c) 9.9×10^5, (d) 1.4×10^6, (e) 3.6×10^6 MCS. For the purpose of clarity, the cross sections of the micelles are given in (a')-(e').

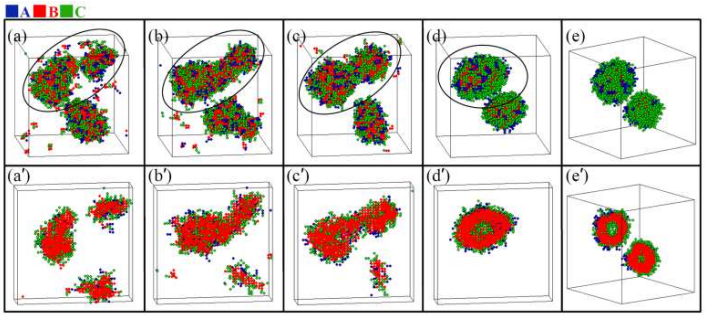

Figure S4. Snapshots showing the pathway of asymmetric vesicle formation of A_3B_4/C_3B_4 diblock copolymer mixture with $f_{A3B4} = 25\%$ at a faster annealing speed (the annealing speed is 0.0008 per time step, 7000 Monte Carlo Steps (MCS) were performed at each time step). Simulation time: (a) 1.6×10^5, (b) 1.9×10^5, (c) 2.0×10^5, (d) 5.6×10^5, (e) 2.1×10^6 MCS. (a')-(d') are the cross sections of the circled micelles in (a)-(d); (e') shown the cross sections for the two vesicles shown in (e).

S3: The simulation results indicate that due to the competition between the effects of the mixed ratio of the two diblock copolymers and the solution pH, some metastable states can be observed when $f_{A3B4} = 40\%$ and 42%.

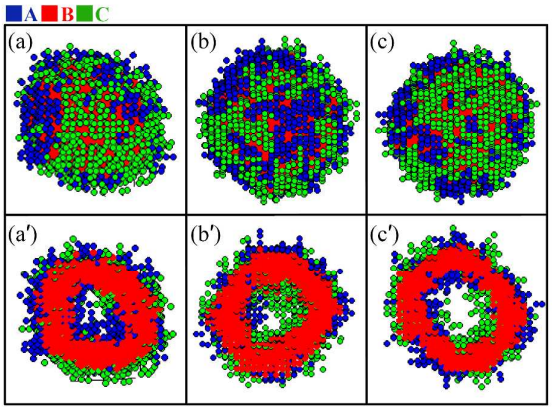

Figure S5. Possible vesicle structures formed by the mixture of A_3B_4/C_3B_4 (blocks C are charged, $\varepsilon_{CC} = 0.5$) with f_{A3B4}=40% (a,b and a',b') and 42% (c,c') when the initial states are changed.