Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Self-assembly of an *in silico* designed dipeptide derivative to obtain photo-responsive vesicles

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Table S1. Parameters of Lennard-Jones potential [1,2] for coarse-grained bead types used in this work

Bead type	Q_d (for N-terminal main-chain)	Q_a (for C-terminal main-chain)	N_0 (for azo)	SC_4 (for benzene ring)	P_4 (for water)
Q_d	ε = 5.0 kJ/mol σ = 0.47 nm				
Q_a	ε = 5.6 kJ/mol σ = 0.47 nm	ε = 5.0 kJ/mol σ = 0.47 nm			
N_0	ε = 3.5 kJ/mol σ = 0.47 nm	ε = 3.5 kJ/mol σ = 0.47 nm	ε = 3.5 kJ/mol σ = 0.47 nm		
SC_4	ε = 2.7 kJ/mol σ = 0.47 nm	ε = 2.7 kJ/mol σ = 0.47 nm	ε = 3.5 kJ/mol σ = 0.47 nm	ε = 2.625 kJ/mol σ = 0.43 nm	
P_4	ε = 5.6 kJ/mol σ = 0.47 nm	ε = 5.6 kJ/mol σ = 0.47 nm	ε = 3.5 kJ/mol σ = 0.47 nm	ε = 2.7 kJ/mol σ = 0.47 nm	ε = 5.0 kJ/mol σ = 0.47 nm

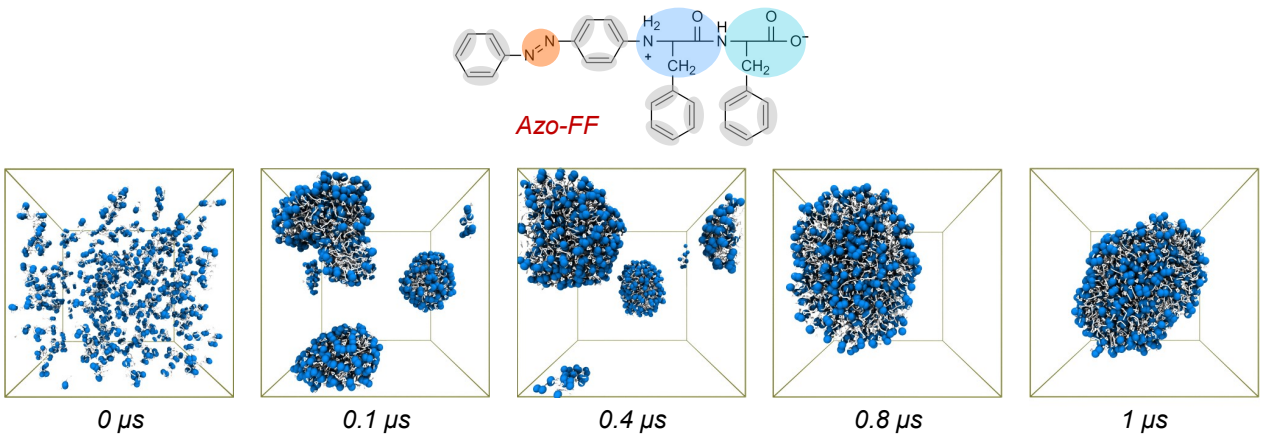

Figure S1. Self-assembly process of Azo-FF molecules. Initially, Azo-FF molecules were randomly distributed in water. As the simulation goes on, Azo-FF molecules quickly aggregate into solid spheres. Also, the core of the spheres is the mixture of hydrophobic groups and hydrophilic groups, indicating that they cannot be separated in space due to the disordered molecule structure. Hydrophilic groups are rendered using blue spheres, and hydrophobic parts are shown in white lines.

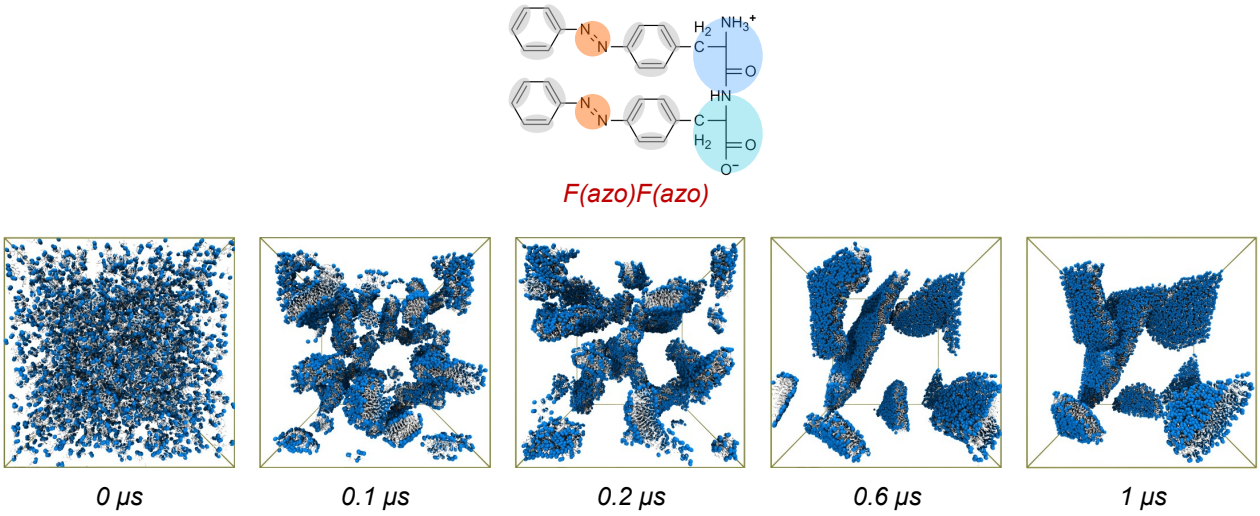

Figure S2. Self-assembly process of F(azo)F(azo) molecules. Randomly distributed F(azo)F(azo) molecules quickly aggregate into small disks and spheres. Then, they further fuse into large lamellae. These lamellae are very flat, indicating extremely high bending rigidity. Hydrophilic groups are rendered using blue spheres, and hydrophobic parts are shown in white lines.

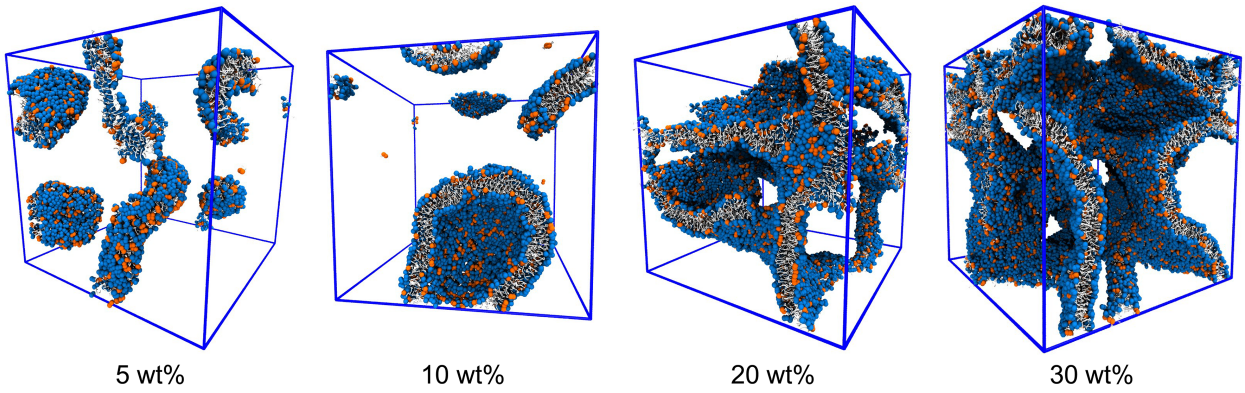

Figure S3. Effect of concentration of peptides on the self-assembly morphology. Taking the F(azo)A:FF=4:1 system for example, peptides form into vesicles at the concentration of 10 wt %. As the concentration decreases, number of peptide molecules is limited to form large assemblies. What we observe at the concentration of 5 wt % are small spheres, disks, and rods. When the concentration is larger (we tested 20 wt % and 30 wt %), peptides assemble into the bicontinuous phase. Taken together, as the concentration increases, the self-assembly morphology transforms from dispersed small flakes into vesicles and bicontinuous phases. The concentration of 10 wt % is an appropriate content to obtain vesicles.

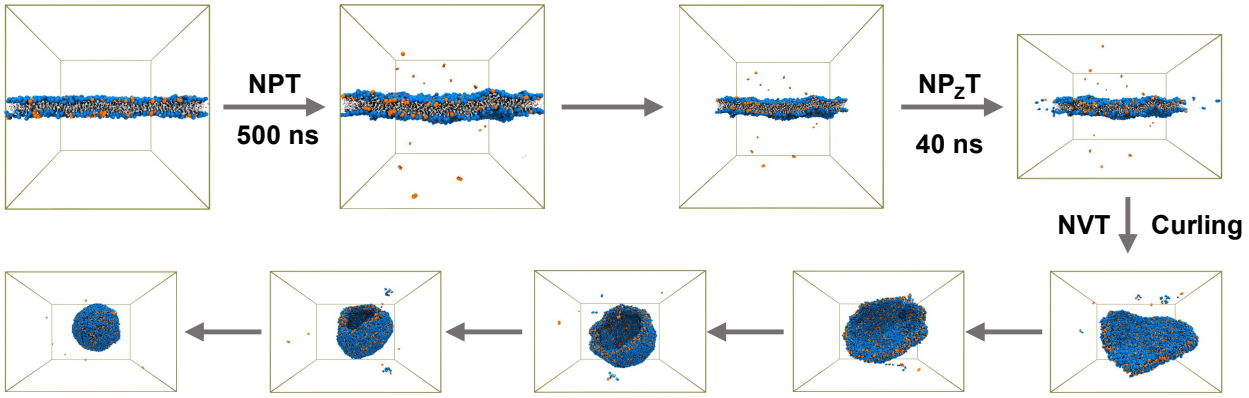

Figure S4. The procedure to construct vesicle models with uniform sizes and balanced numbers of molecules in the inner and outer leaflets. First, a bilayer structure of F(azo)A and FF was constructed and simulated for 500 ns to reach equilibrium. Then, the equilibrated bilayer was placed in a larger water box. The x and y dimension of the water box was fixed, and the box along the z direction was relaxed with 40 ns NP_zT simulation. Finally, a NVT simulation was performed, and the bilayer spontaneously curls into a spherical vesicle. This procedure was used in our previous work to generate a phospholipid liposome model.[3]

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