

Supplementary Information

Unusual, Photo-Induced Self-Assembly of Azobenzene-Containing Amphiphiles

Table S1. The force field parameters of angle SC4–N0–SC4 for simulating the irradiation of UV and visible light

Irradiation	θ_0 (deg)	K_0 (kcal·mol ⁻¹ ·deg ⁻²)	C (deg ⁻¹)	D (deg ⁻²)
UV	60	98	-0.532	0.080
visible	180	105	0.500	0.073

Table S2. Details (the initial distribution of AzoCO and molecules, the concentration of AzoCO, size, and the simulating force field parameters) of the models used in this work^a

system	model in the main text	the initial distribution of molecules	AzoCO concentration (wt %)	Size (x × y × z, Å)	Force field parameters (Table S1)
1	Figure 3a	random	5	150 × 150 × 150	UV
2	Figure 3b	random	10	150 × 150 × 150	UV
3	Figure 3c	random	15	150 × 150 × 150	UV
4	Figure 3d	random	20	150 × 150 × 150	UV
5	Figure 3e	random	25	150 × 150 × 150	UV
6	Figure 5a	random	10	150 × 150 × 150	UV
7	Figure 5b	random	10	150 × 150 × 150	UV
8	Figure 6a	random	5	150 × 150 × 150	visible
9	Figure 6b	random	10	150 × 150 × 150	visible
10	Figure 6c	random	15	150 × 150 × 150	visible
11	Figure 6d	random	20	150 × 150 × 150	visible
12	Figure 6e	random	25	150 × 150 × 150	visible
13	Figure 8b	pre-assembled	–	150 × 150 × 150	visible
14	Figure 8c	pre-assembled	–	150 × 150 × 150	visible
15	Figure 8d	pre-assembled	–	150 × 150 × 150	visible
16	Figure 9	random	10	150 × 150 × 150	UV, visible

^aFor the initial distribution of molecules, homogeneous mixture of AzoCO and water molecules is called “random”, pre-assembled well-ordered structure is called “pre-assembled”; the force field parameters are shown in Table S1 which was added to the original MARTINI force field.

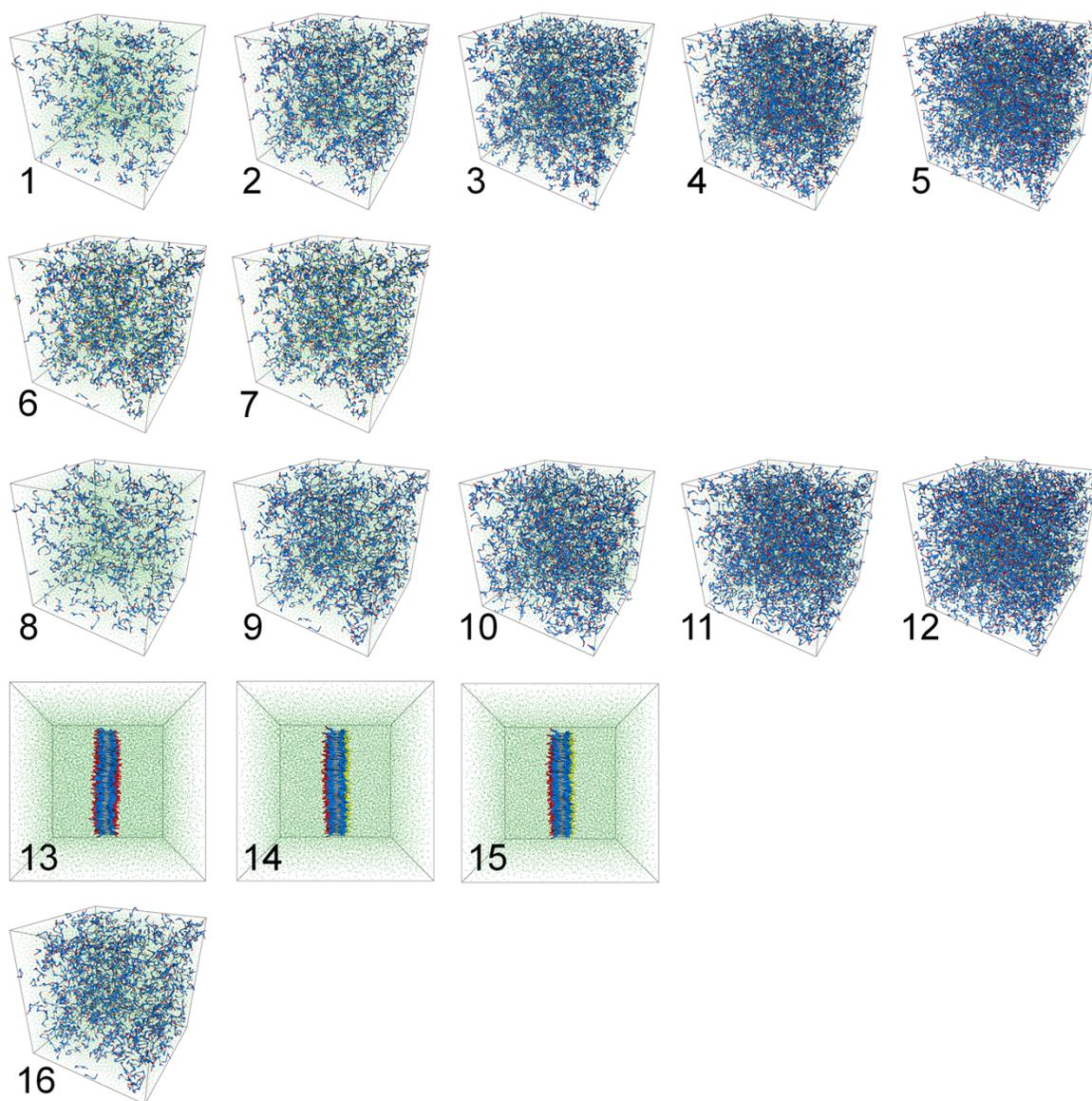


Figure S1. The initial snapshots of system 1-16 listed in Table S2. The color scheme for AzoCO is the same as Figure 1. Water beads are shown in green dots. System 1-12 and 16 are mixtures of AzoCO and water molecules. System 12-15 are pre-assembled AzoCO monolayer flakes. In system 6 and 7, the N0 beads were substituted by SP2 and C2 beads, respectively. In system 14 and 15, the SP2 beads of one side of the monolayer flake were substituted by N0 and C2 beads, respectively. The substituted beads in system 6, 7, 14, and 15 are shown in yellow.

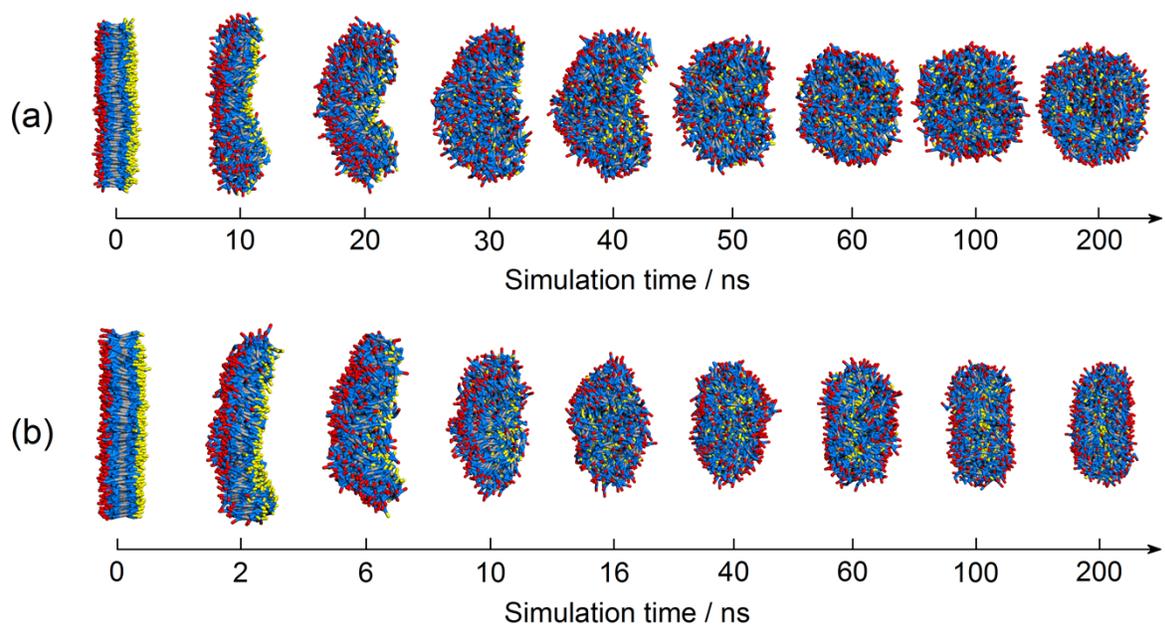


Figure S2. The evolvement of (a) the pre-assembled SP2-Azo-N0, and (b) the pre-assembled SP2-Azo-C2. Obviously, the morphology of the assemblies hardly changes after 60 ns. Thus, the simulation time of 200 ns is enough to reach the equilibrium state. The SP2 beads of one side of the *trans*-AzoCO monolayer are substituted by N0 beads in (a) and C2 beads in (b), which are shown in yellow.

Analyses on the self-assembly under alternating irradiation of visible and UV light (Figure 9)

As shown in Figure 9, simulated with the Vis angle potential, AzoCO molecules assemble into monolayer structure. When the Vis potential is replaced by UV potential, the monolayer structure transforms into spherical structure (we call it “UV-sphere”). Then, the system is simulated with visible potential again. Unexpectedly, the UV-sphere could not re-assemble into monolayer structure, but keeps spherical morphology (we call it “Vis-sphere”). Why couldn’t the morphology transform reversibly? How to trigger the reversible morphology transformation? Analyses are needed to answer these questions.

We have known that the V-shaped *cis*-AzoCO molecules assemble into spherical structure (Figure 3). Thus, does the molecular morphology of AzoCO changes from UV-sphere to Vis-sphere? We calculated the probability distribution of angle SC4-N0-SC4. We find the angle SC4-N0-SC4 of AzoCO molecules in the UV-sphere is $\sim 60^\circ$ (Figure S3a); and the Vis-sphere, $\sim 180^\circ$ (Figure S3d). Therefore, although the spherical morphology was maintained, the photoisomerization of the basic self-assembling components happened. The UV-sphere consists of *cis*-AzoCO molecules; the Vis-sphere consists of *trans*-AzoCO molecules. We have known that *cis*-AzoCO molecules assemble into “chaotic micelle”. Thus, the UV-sphere here is spherical “chaotic micelle” (Figure S3c), which is verified with the RDFs of N0 and SP2 beads (Figure S3b). To uncover the structural details of Vis-sphere, we also calculated the RDFs of N0 and SP2 beads (Figure S3e). For N0 beads, there is also one peak (the same as “chaotic micelle”); but before the peak, a valley exists at ~ 30 Å. Interestingly, there’re two SP2 peaks (A and B), which is different from the “chaotic micelle”. Within 20 Å, the *trans*-AzoCO looks disordered. Scrutinizing the molecular arrangement of the Vis-sphere, with the RDFs shown in Figure S3e, we found the Vis-sphere also possesses a bi-level structure (Figure S3f). There is also a well-ordered shell, but which is assembled by *trans*-AzoCO molecules. The interior surface and the exterior surface of the shell is made up of the two SP2 ends of *trans*-AzoCO, thus generating the

two RDF peaks of SP2 in Figure S3e. N0 beads in the shell are sandwiched by SP2 beads, generating the single N0 peak between the SP2 peak A and B.

Then, why does the “chaotic micelle”/UV-sphere transform into such a structure but not monolayer? Comparing the formation of the monolayer structure and the Vis-sphere, they are all formed under the irradiation of visible light; the difference is on the initial distribution of AzoCO molecules. The monolayer structure is assembled initially from homogeneous mixture of water and AzoCO molecules. But the Vis-sphere is assembled initially from the “chaotic micelle”/UV-sphere. The existence of “chaotic micelle” shows that the disordered core is very stable under the shelter of the ordered shell. The AzoCO molecules interact with each other and maintain extremely stable state despite the disordered arrangement. When the *cis*-AzoCO molecules in the core of “chaotic micelle” transform into *trans* conformation, the molecular interactions and the disordered arrangement are unaltered. Therefore, the disordered core of *trans*-AzoCO molecules is also stable. One side of the exterior *trans*-AzoCO molecules has to be exposed to the water environment, thus leading to the formation of the ordered shell (blue area in Figure S3f). Therefore, once the cluster of AzoCO formed, it is hard to break it. Highly dispersed solution of AzoCO molecules is needed to get the monolayer structure. Therefore, to realize the reversible transition between “monolayer phase” and “chaotic micelle” (of course, it’s easy to reversibly transform between UV-sphere and Vis-sphere), additional excitations (such as heating, and agitation) to break the AzoCO cluster into dispersed fragments are needed.

This study may be useful for further investigations on improving the reversibility of stimuli-responsive self-assembling systems. The structural difference of UV-sphere and Vis-sphere is also possibly useful. Here, only some analyses on this result are given. Further studies on this topic is needed.

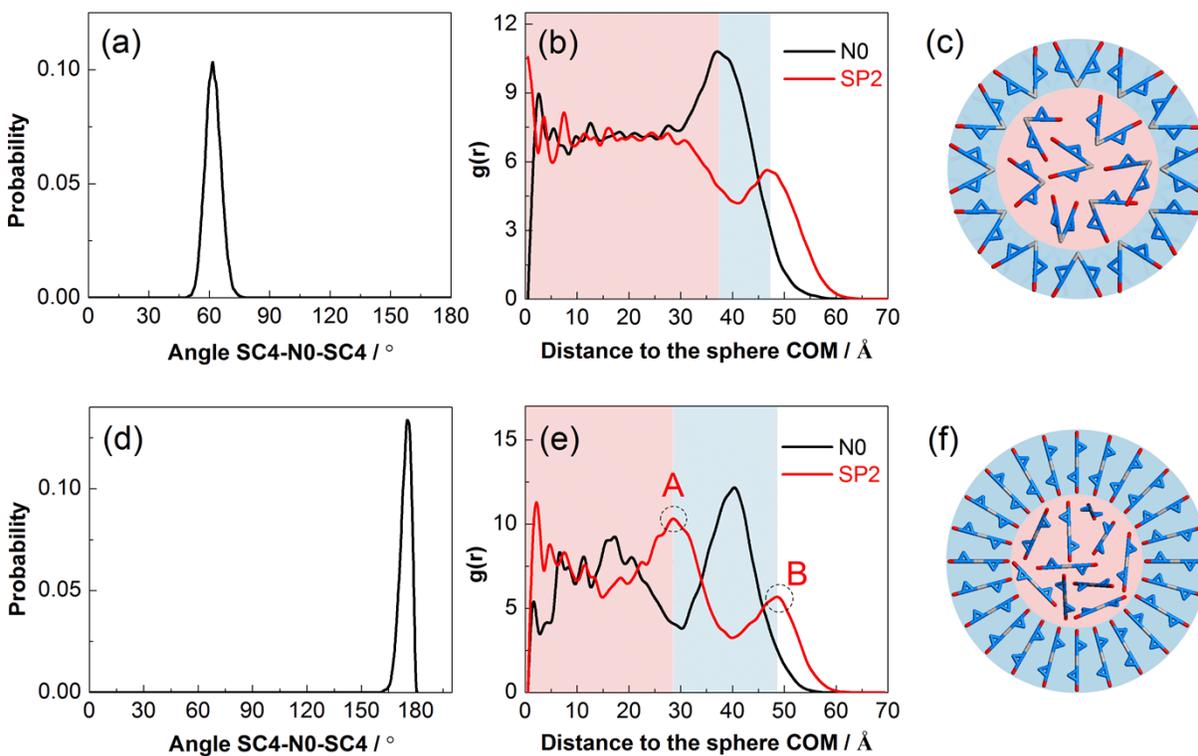


Figure S3. The probability distribution of the angle SC4-N0-SC4 in the (a) UV-sphere and (d) Vis-sphere. The radial distribution functions $g(r)$ of N0 and SP2 beads as a function of distance from the center of mass (COM) of the (b) UV-sphere and (e) Vis-sphere. The schematic representation of the structure of the (c) UV-sphere and (f) Vis-sphere.