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Supporting Information

Photo-Controlled Reversible Supramolecular Assembly of an Azobenzene-Containing Surfactant with α-Cyclodextrin

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1. Experimental part

Instruments

UV-Vis spectra were obtained using a HITACHI U-3010 spectrophotometer. The irradiation light source for photoisomerization was a high-pressure mercury lamp with an optical fiber (RW-UVA 05-100, purchased from Shenzhen Runwing Mechanical & Electrical Co., Ltd., China), and the intensity was 900 mW/cm^2. The two band-pass filters were of the wavelengths 365 ± 10 and 450 ± 10 nm. The irradiation was carried out in an in-situ mode by irradiating the solutions in the UV-vis spectrophotometer with the optical fiber so as to minimize the errors in the experiments. Surface tension measurements were engaged on a high-sensitive micro-eletromechanical balance system (Dataphysics DCAT21, Germany). The plate used to detect the surface tension is with a length of 19.9 mm and a width of 0.2 mm. The motor speed to drive the plate is 1.00 mm/s. ^{1}H- NMR spectra were recorded in D$_2$O solution on a JEOL JNM-ECA 300 (300 MHz) spectrometer. ESI-MS measurements were performed on a Thermo ELECTRON CORPORATION Finnigan LTQ with deionized water as the solvent. Transmission electron microscopy (TEM) was performed on a MODEL H-800 Electron microscope operating at an acceleration voltage of 100 kV. To prepare TEM samples for the study of the size and the morphology of the aggregation, a drop of the dilute aqueous solution was deposited onto a copper grid, which had been precoated with a thin film of polyvinyl formal and then coated with carbon. Two minutes after the deposition, the excess aqueous solution was blotted away with a strip of filter paper. This process was repeated for several times to ensure that there was enough

sample absorbed on the grid. All the samples were stained with 2% phosphotungstic acid hydrate before observed under TEM. X-ray diffraction (XRD) measurements were performed on a D/max-RB diffractometer with a Cu Kα X-ray irradiation source. X-ray diffractograms were recorded over the range of 2-10º in 2θ degrees and the scanning rate is kept at 1º min^{-1}.

Materials

1, 10-dibromodecane and α-cyclodextrin were purchased from Alfa Aesar and used without further purification. The other reagents used in our work were commercial products from Beijing Chemical Reagent Company. Aniline and pyridine were redistilled under low-pressure before use.
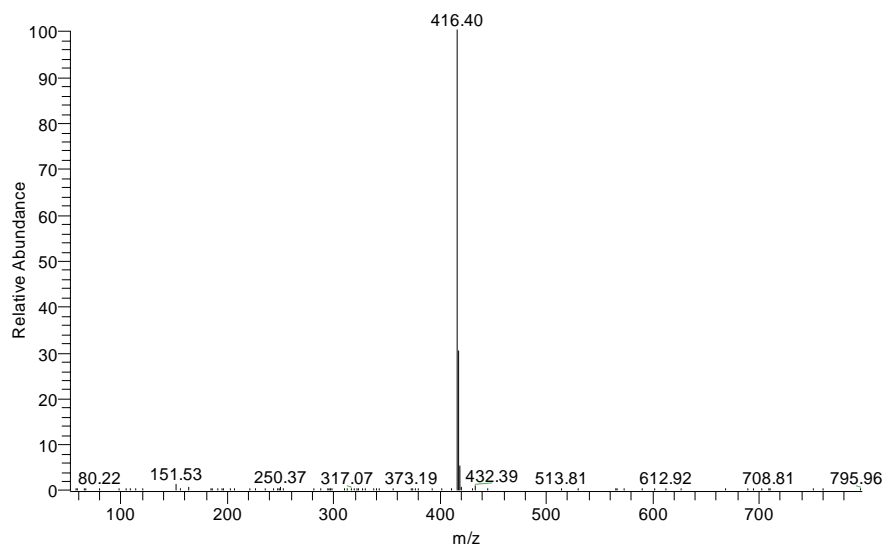
Scheme S1 The synthesis route of AzoC10.

(1) [structure] —N≡N **(2)** dibromodecane, K2CO3, refluxing 24 h in actone   **(3)** stirring in pyridine
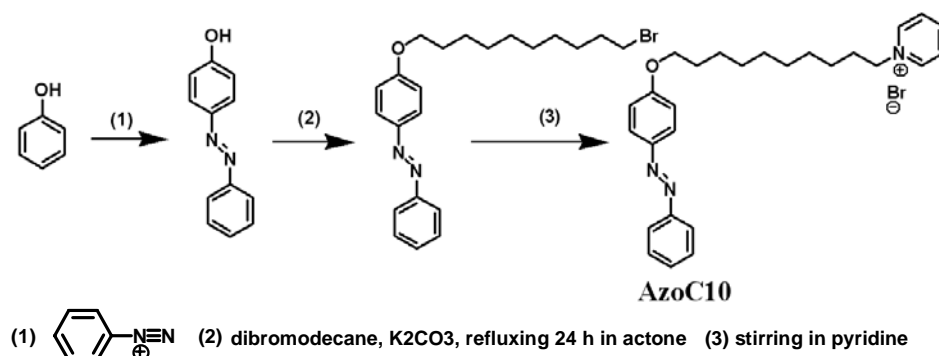
4-Phenylazo-phenol

NaNO$_2$ (4 g, 57.9 mmol) dissolved in 15 mL H$_2$O, was added dropwise into aniline (5 g, 53.8 mmol) mixed with 15 mL HCl (36.5%) at 0°C. The final solution was kept stirring at 0°C for 5 min. Then the clear solution of the diazonium salt was added dropwise into Phenol (4.85 g, 51 mmol) dissolved in 400 mL NH$_3$-NH$_4$Cl buffer solution with pH 9 at 0°C. The reaction was carried out at this temperature for 3 h and then added upon excessive HCl. The precipitation was obtained after filtration and recrystalization twice by 1:1 H$_2$O and ethanol. The final yellow powder 4-Phenylazo-phenol was used for the further reaction.

[4-(10-Bromo-decyloxy)-phenyl]-diazene

4-phenylazo-phenol (0.2 g, 1.01 mmol) was added with magnetic stirring to 1, 10-dibromodecane (3.03 g, 10.1 mmol, 10 equiv.) acetone solution. The mixture was

then added upon K_2CO_3 (0.28 g, 2.02 mmol, 2 equiv.) and trace of 18-C-6. The solution was stirred refluxing for 24 h under Ar protection. Finally the solvent was removed and the combined mixture was purified by silica gel column chromatography eluting with 1:1 dichloromethane: ethyl acetate. The evaporation of the solvent gave a yellow powder.

1-[10-(4-Phenylazo-phenoxy)-decyl]-pyridinium bromide (AzoC10)

Excessive pyridine was added to [4-(10-Bromo-decyloxy)-phenyl]-diazene THF solution. The mixture was kept stirring for 8 h at 60°C under Ar protection. After evaporation of THF and additional pyridine, the yellow solid was dissolved in methanol again. The solution was added stepwise with magnetic stirring to plenty of petroleum ether, and the yellow precipitate was filtered and dried in vacuum oven.

^{1}H-NMR (CDCl$_3$, δ (CHCl$_3$) =7.26): δ 9.47 (d, 2H,); δ 8.47 (t, 1H); δ 8.10 (t, 2H); δ 7.90 (m, 4H); δ 7.50 (m, 3H); δ 7.01 (d, 2H); δ 5.04 (t, 2H); δ 4.04 (t, 2H); δ 2.05-1.31(m, H16). ESI-MS, AzoC10 (minus Br anion): calculated 416.27, found 416.40

Figure S1 ^{1}H-NMR spectrum of AzoC10 in CDCl$_3$.

Figure S2 ESI-MS spectrum of AzoC10.

2. Association constant between AzoC10 and α-CD

The association constant between AzoC10 and α-CD in aqueous solution was determined by following the UV absorption at 346 nm, as shown in Figure S3. The concentration of AzoC10 was kept at 1×10^{-5} M. Upon addition of excess α-CD, the absorption of AzoC10 increased remarkably. With an assumption of a 1:1 stoichiometry, the inclusion complexation of α-CD (G) with AzoC10 (H) is expressed by the following equation:
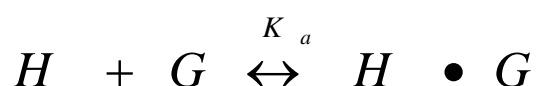
$$H + G \overset{K_a}{\leftrightarrow} H \bullet G$$

We employed the usual double reciprocal plot according to the modified Hidebrand-Benesi equation:

$$\frac{1}{\Delta A} = \frac{1}{K_a \Delta\varepsilon [H][G]} + \frac{1}{\Delta\varepsilon [H]}$$

Where H, G, K_a represents host (AzoC10), guest (α-CD), association constant respectively. ΔA denotes the absorbance difference before and after guest molecules were added. $\Delta\varepsilon$, which denotes the difference of the molar extinction coefficient between the host and host-guest complex at the same wavelength, is 3.7×10^3 M^{-1}cm^{-1} in our work. The association constant K_a was calculated by the equation:

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$$K_a = \frac{1}{k\Delta\varepsilon[H]} = 2.8 \times 10^4 M^{-1},$$

Where k is the slope value of line plot in Figure S3.
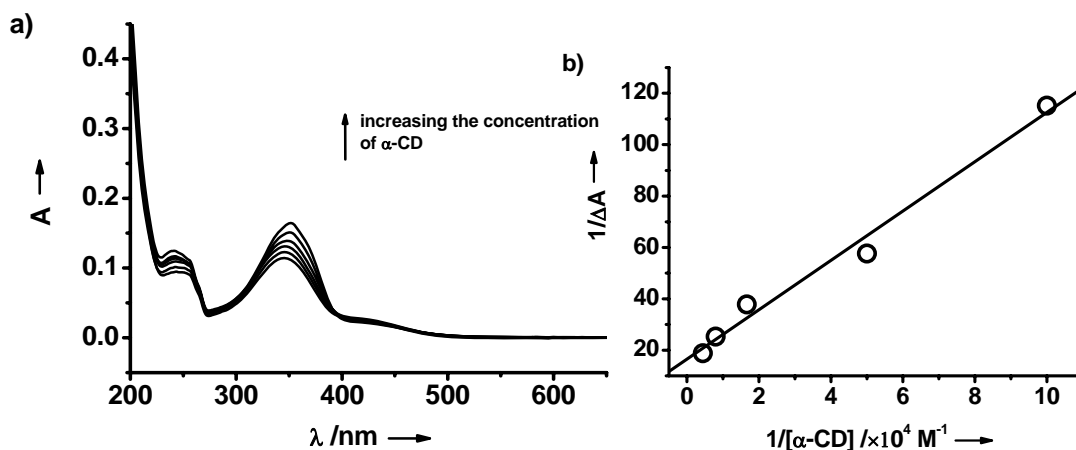
Figure S3 The UV absorption of AzoC10 upon stepwise addition excess α-CD. The concentration of AzoC10 keeps 1×10^{-5} M.

3. The measurement of Critical Aggregate Concentration

We have employed a method of the concentration dependence on surface tension to measure the critical aggregate concentration (CAC) of *trans*- and *cis*-AzoC10. According to the Langmuir model for surface adsorption, below the CAC, some of the surfactants adsorb at the water-air interface, and the others disperse into the bulk solution without aggregation; above the CAC, for the interface is fully covered by the surfactants, the surfactants cannot adsorb at the interface anymore, and instead, they will aggregate spontaneously in solution by self-organization. [1] Figure S4 exhibits the change of surface tension with the variation of concentration of *trans*-AzoC10 and *cis*-AzoC10 at room temperature. For each form of the surfactant, there is a gradual decrease in the surface tension with the increase of concentration. A nearly plateau is obtained when the concentration is above a critical value. The concentration of surfactant at which the surface tension keeps nearly at a constant value is noted as CAC. The CAC of *trans*-AzoC10 is 3.5×10^{-5} M and *cis*-AzoC10 3.9×10^{-5} M. The

difference of the CAC for *trans*- and *cis*-AzoC10 is not evident as expected, which could be rationalized by considering that the azobenzene group is in the end of hydrophobic tail of the surfactant.
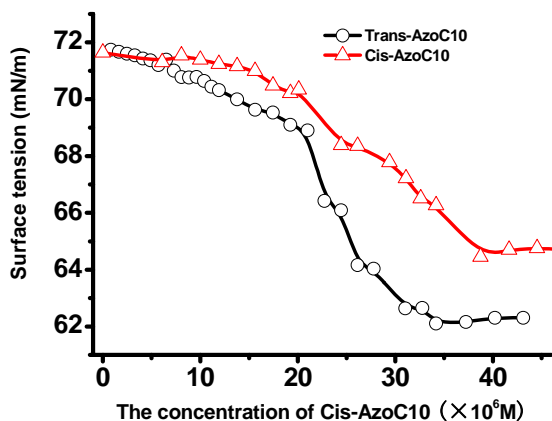
Figure S4 Dependence of the surface tension on AzoC10 concentration. The CAC of *Trans*-AzoC10 is 3.5×10^{-5} M, The CAC of *cis*-AzoC10 is 3.9×10^{-5} M.

4. The photoisomeric behavior of AzoC10

The first-order plots for *trans-cis* photoisomerization of AzoC10 are shown in Figure 5a by the following equation:

$$\ln\frac{(A_0 - A_{eq})}{(A_t - A_{eq})} = k_t t$$

Where A_0, A_t, and A_{eq} are the initial absorbance, the absorbance at time t, and the absorbance at the photostationary state of azobenzene group of AzoC10 at 346 nm, respectively. k_t is the rate constant of the *trans-cis* isomerization. As shown in Figure S5a, although the reason for the isomerization of AzoC10 deviating from the first-order plots at a high concentration is not clear, the different initial *trans-cis* photoisomerization rate of AzoC10 at various conditions agree well with TEM observations.

For the *cis-trans* conversion of azobenzene, the kinetic equation needs to be changed to

$$\ln\frac{(A_{eq} - A_0)}{(A_{eq} - A_t)} = k_c t$$

in which k_c is the rate constant of the *cis-to-trans* photoisomerization. The relation between ln $[(A_{eq} - A_0)/(A_{eq} - A_t)]$ and t fits a direct proportion function, as shown in Figure 5Sb. We have found interestingly that α-CD has little effect on the *cis-trans* isomerization of AzoC10 when above its CAC.
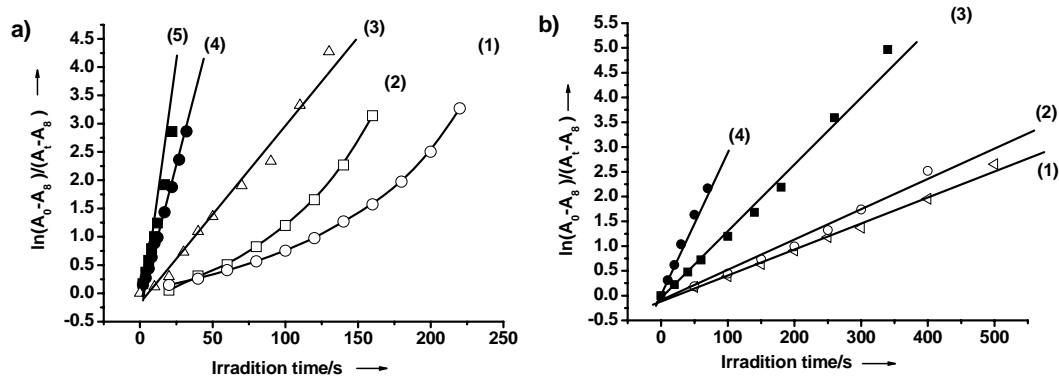

Figure S5 a) *Trans-cis* isomerization of AzoC10 with the concentration of (1) $7×10^{-5}$ M; (2) $7×10^{-5}$ M and mixed with 1:1 α-CD; (3) $3.5×10^{-5}$ M; (4) $1×10^{-5}$ M mixed with 1:1 α-CD; (5) $1×10^{-5}$ M. ***b)*** *Cis-trans* isomerization of *cis*-rich AzoC10 with the concentration of (1) $7×10^{-5}$ M; (2) $7×10^{-5}$ M and mixed with 1:1 α-CD; (3) $3.5×10^{-5}$ M; (4) $1×10^{-5}$ M.

5. ESI-MS evidence for the association of α-CD with AzoC10

In Figure S6, before UV irradiation, there exists a peak, of which *m/z* is equal to 1387.79, corresponding to the 1:1 inclusion complex of AzoC10 (minus bromine anion) and α-CD. After irradiation at 365 nm, there still exists a peak with *m/z* at 1387.82, suggesting that *cis*-AzoC10 can also form 1:1 inclusion complex with α-CD.
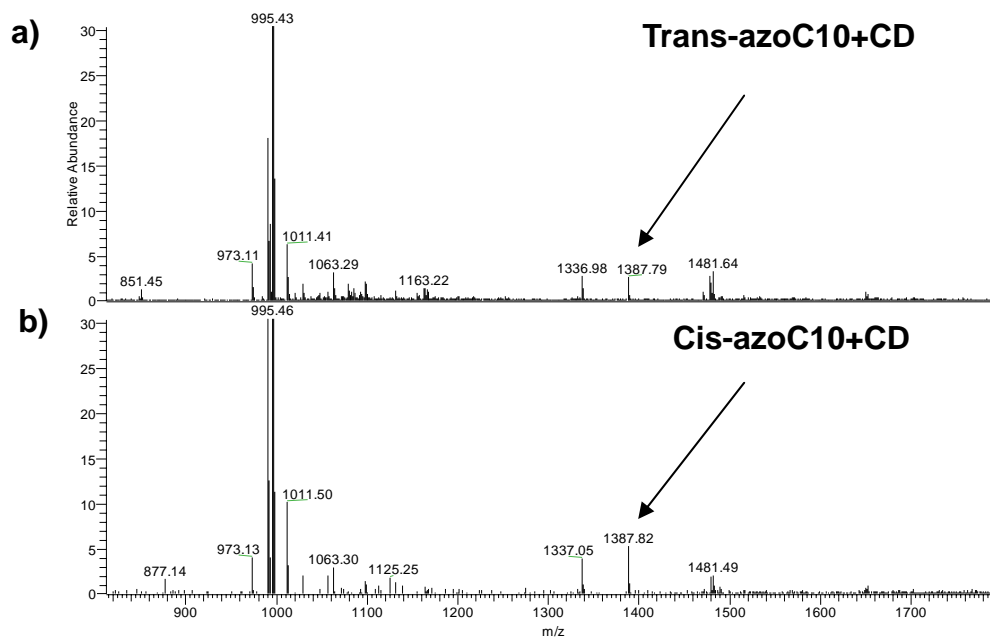
Figure S6 ESI-MS spectrum of the mixture of AzoC10 and 1:1 α-CD *a)* before UV irradiation; *b)* after irradiation at 365 nm for 600 s.

6. Interdigitated structure of AzoC10 aggregates as indicated by normalized UV spectra and XRD

There is no clear J-aggregate or H-aggregate present when the AzoC10 molecules aggregate together, for the normalized UV absorbance of AzoC10 below CAC and above CAC are nearly same, as shown in Figure S7. Therefore, the most likely structure for the vesicle-like aggregate of AzoC10 could be regarded as an interdigitated bilayer, which can be well supported by the XRD results shown in Figure S8. The low-angle XRD pattern of AzoC10 cast film with the concentration of 7×10^{-5} M shows that there is a Bragg peak 2θ about 3°, corresponding to d-spacing of 29.7 Å. Considering that AzoC10 is about 26 Å in lines, we may draw a conclusion that AzoC10 molecules are well interdigitated in the vesicle-like aggregates.
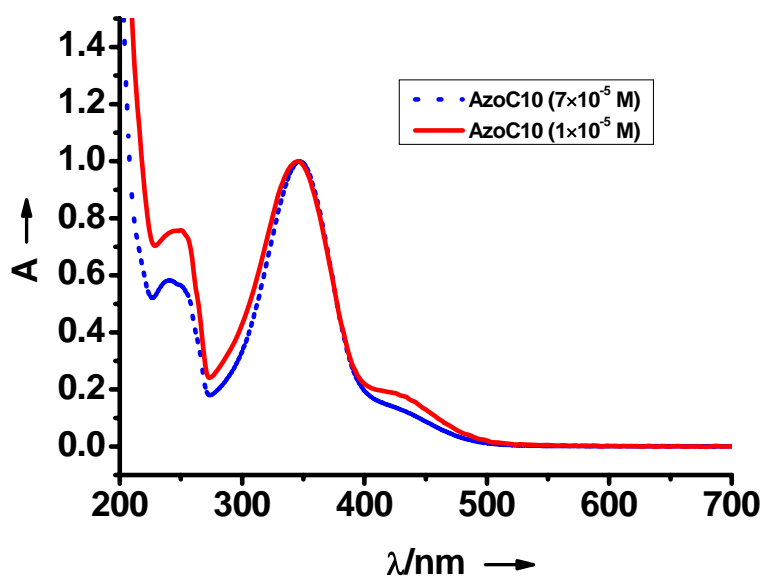
Figure S7 The normalized UV absorbance of AzoC10.

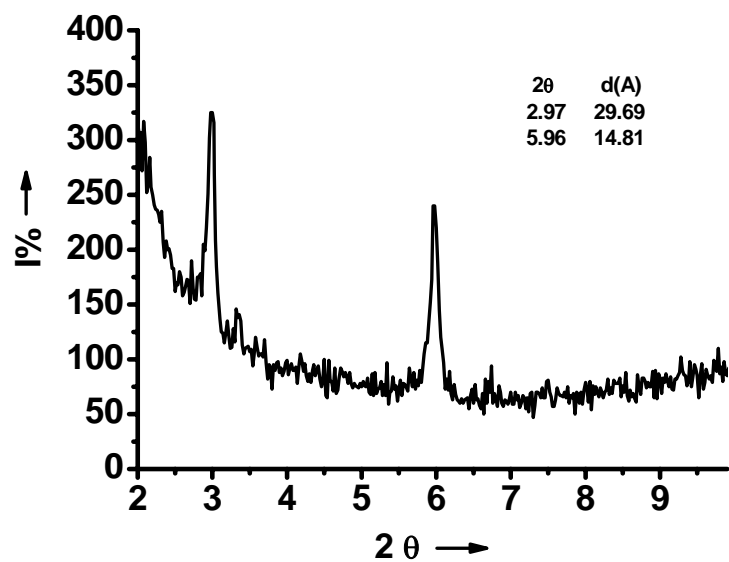| 2θ	d(A)
2.97	29.69
5.96	14.81

Figure S8 Low-angle X-diffraction pattern of AzoC10 cast film on quartz.

Reference:

[1] A. -A. M. A. Omar, *J. Chem. Eng. Data* **1998**, *43*, 117.