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ARTICLE TYPE

Reversible photo-responsive vesicle based on the complexation between azobenzene contained molecule and α-cyclodextrin

Jianjia Liu,[a] Liang Yan,[b] Jie Wang,*[a] Tao Li,[a] Hanqing Zhao,[a] Li Li,[a] Stephen F. Lincoln,*[b] Robert K. Prud'homme[c] and Xuhong Guo*[a]

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Amphiphilic molecule (Azo-Cl) was successfully synthesized and found to be able to construct reversible spherical vesicles in water. The assembled vesicles were disappeared with the addition of equimolar α-cyclodextrin (α-CD) while reformed with UV irradiation due to the exclusion of cis azobenzene (Azo) group from α-CD's hydrophobic cavity. With alternative Vis irradiation, the vesicles were demolished again as α-CD combined with the Azo group again. These reversible photo-responsive vesicles based on the complexation between Azo-Cl and α-CD should be ideal switchable biomimetic membranes or carriers for photo-controllable release of functional matters like drugs.

Introduction

Amphiphilic molecules have been the hot focus for many years because they could self-assemble into different kinds of well-defined microstructures such as micelles[1, 2], vesicles[3-5], lamellar nanotubes[6, 7] and so on[8]. Normally, they could form these special kinds of structure spontaneously with certain concentration[9, 10]. Among these self-assembly microstructures, vesicles have drawn significant attention to the field of chemistry and biology because they could mimic living cell membranes composed of bilayer structures very well to realize compartmentalization[11, 12].

The assembly structure which was responsive to non-invasion stimulus such as light[13] and heat[14] could help the amphiphilic molecules being used widely in the fields of gene delivery[15, 16], controlled release[17, 18], nanoreactors[19-21] and so on[22-24].

To realize the reversible supramolecular assembly system, azobenzene was commonly used for photo-responsive structures due to their alternate trans-cis isomerization irradiated by UV/Vis light[25-27]. It is well known that α-cyclodextrins (α-CD) which consists of six glucose units forming as a hydrophobic cavity while its outside is hydrophilic[28-30] could bind trans azobenzene very well instead of cis form due to the size effect[31, 32]. Therefore, many kinds of photo-responsive assembly structures have been found in combination of azobenzene derivatives and α-CD[33-36].

Here we synthesized a novel kind of amphiphilic molecule Azo-Cl to construct spherical self-assembly vesicles (**Fig. 1**). Importantly, the photo-responsive vesicles could be obtained and damaged with alternate UV and Vis irradiation in the presence of α-CD.

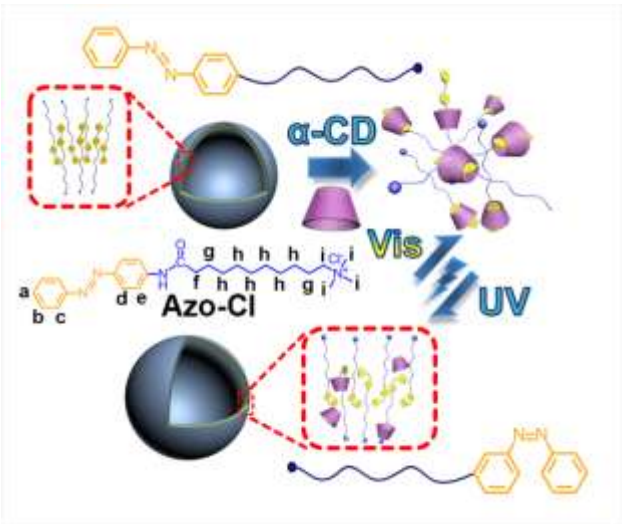

Fig. 1. Chemical structure of amphiphilic molecule Azo-Cl and its photo-responsive self-assembly in the presence of equimolar α-CD in water.

Experimental

Materials

4-Aminoazobenzene (98%), 1-hydroxybenzotriazole (HOBT, 99%), 11-aminoundecanoic acid (97%) and trifluoroacetic acid (TFA, 99%) was obtained from Sigma-aldrich. *N*, *N*'-Dicyclohexylcarbodiimide (DCC, 98%), dichloromethane (DCM, 99.8%), ethanol (EtOH, AR grade), methanol (MeOH, AR grade) and potassium hydroxide (KOH, 85%) were all bought from Merck. Sodium sulfate (Na_2SO_4, 99%), hexane (99%), tetrahydrofuran (THF, 99%) and methyl iodide (99%) were obtained from Chem-supply. Ethylacetate (99.8%), chloroform (99.8%) and hydrochloric acid (HCl, 37%) were obtained from RCI Labscan. Di-tert-butyl-dicarbonate (DTBD, 97%) was manufactured by Acros while diethyl ether (98%) was supplied by Vetec. All the above chemicals were used as received without any further purification. All the deionized water used in the

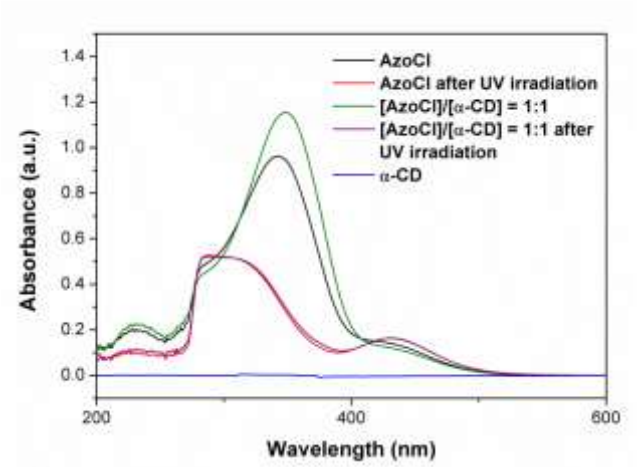

Fig. 2. UV-vis spectrum of 1.2×10^{-4} M Azo-Cl (irradiation with UV light) and UV-vis spectrum of 1.2×10^{-4} M Azo-Cl in the presence of equimolar α-CD (also irradiation with UV light). UV-vis spectrum of 1.2×10^{-4} M α-CD was also included.

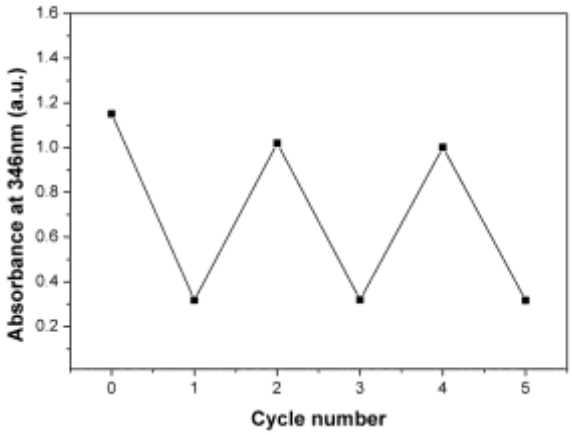

Fig. 3. Absorbance changes at 346 nm of Azo-Cl (1.2×10^{-4} M) in the presence of α-CD (molar ratio 1:1) with alternate UV and Vis irradiation.

experiment was purified by Milli-Q water purification system (10 MΩ/cm). α-CD was obtained from Nihon Shokuhin Kako company and recrystallised three times in H_2O before use.

Synthesis of N-BOC-11-aminoundecanoic acid

The synthesis procedure was based on the literature[37] with some modifications. 2 g 11-aminoundecanoic acid (10 mmol) and 0.7261 g KOH (11 mmol) were dissolved in a mixture solution of 80 mL H_2O and 8 mL THF. 2.4 g DTBD (11 mmol) was added to the above solution. The solution reacted at 50 ^oC for 3 h and then reacted at room temperature overnight. HCl was used to adjust pH as 5. The solution was extracted with ethylacetate. Na_2SO_4 was used to dry the organic layer. The solvent was then evaporated and the product was recrystallised in hexane. ^{1}HNMR (ppm, 500MHz, $CDCl_3$, 298.2K) : 4.55 (br s, 1H), 3.10 (t, J=7.1Hz, 2H), 2.35 (t, J=7.4Hz, 2H), 1.64 (m, 2H), 1.45 (s, 11H), 1.28 (s,12H) (**Fig. S1**).

Synthesis of Azo 11 amide

A mixture of 1 g N-BOC-11-aminoundecanoic acid (3.32 mmol), 0.6548 g 4-aminoazobenzene (3.32 mmol) and 0.4486 g HOBT (3.32 mmol) was dissolved in 100 mL ethylacetate. 1.0276 g DCC (4.98 mmol) was added to the above solution under reflux to react for 24 h. Afterwards the solution was cooled down to 4 ^oC, filtrated and washed with H_2O. The raw product was dried under vacuum after evaporating the organic phase. The product was dissolve in 60 mL TFA/DCM (v/v=15/45) solvent with stirring for 24 h at room temperature. Most of the solvent was removed and the oily liquid obtained was poured in 500 mL diethyl ether to precipitate the product. The product was then dried under N_2. ^{1}HNMR (ppm, 500 MHz, CD_3OD, 298.2 K): 7.52-7.89 (m, 9H), 2.89 (t, 2H), 2.40 (t, 2H), 1.8-1.6 (m, 4H), 1.37 (m, 12H) (**Fig. S2**). ESI-MS, Azo 11 amide: calculated 381.26, found 381.3 (**Fig. S4**).

Synthesis of Azo-Cl

0.2643 g Azo 11 amide (0.695 mmol) and 0.50 g KOH (8.91 mmol) was dissolved in 30 mL MeOH. 0.5 mL methyl iodide (8.03 mmol) was added slowly to the above solution and the solution was stirred at room temperature for 3 days. The solution was brought under reflux for a further 24 h and then cooled down to filter. The solid was washed with chloroform, diethyl ether, hexane, EtOH. Then the iodide form was transformed to chloride by Dowex 21K (20-50 mesh Cl) resin column[38]. ^{1}HNMR (ppm, 500 MHz, CD_3OD, 298.2 K) : 7.55-7.91 (m, 9H), 3.13 (m, 11H), 2.44 (s, 2H), 1.75 (m, 4H), 1.41(s, 12H) (**Fig. S3**). ESI-MS, Azo-Cl (minus Cl^-): calculated 423.6, found 423.5, 424.5 (**Fig. S5**).

Characterization

1D ^{1}HNMR spectrum was recorded on Agilent DD2 500 MHz NMR Spectrometer and 2D ^{1}HNMR spectrum was recorded on Varian Inova 600 MHz NMR Spectrometer separately. ESI-MS was obtained from Finnigan MAT LCQ Mass Spectrometer. UV-Vis spectrum was recorded on Cary-5000 UV spectra (Agilent Technologies) with thermo-controlled equipment. Samples were irradiated using 500 W Xe lamp (Ushio Inc.) equipped with cutoff filters to get UV light (Hoya UV 34, 340 ± 10 nm) and visible light (Hoya Y45, 450 ± 10 nm). Surface tension test was performed on Analite Wilhelmy plate surface tension meter. Optical investigations were performed using a polarized light microscope (PLM) DM2500P (LEIKA, Germany) with a CCD camera LEIKA MC120. Transmission electron microscope (TEM) images were taken from FEI Tecnai G2 Spirit TEM operated at 100 Kv accelerating voltage. The samples were prepared as follow: a drop of the solution was added onto the copper grid for two minutes and then the filter paper was used to absorb the excess solution from the grid's edge; this treatment had to be repeated several times and 2% phosphotungstic acid was used to stain the samples.

Results and discussion

Azobenzene (Azo) group could be photoisomerized upon alternate UV and Vis irradiation. As shown in **Fig. 2**, there is an obvious characteristic peak of Azo-Cl at 346 nm which is assigned to π-π^* absorption and it is mainly due to the trans form of Azo-Cl (trans Azo-Cl). However, it decreased with UV irradiation while a new peak at around 440 nm appeared which was ascribed to the n-π^* transition of cis form of Azo-Cl (cis Azo-

Cl)[39]. The change of the spectrum meant there definitely existed

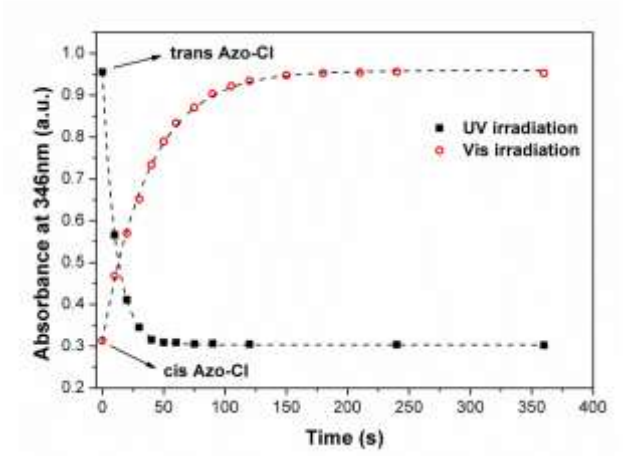

Fig. 4. Absorbance variation at 346 nm of trans Azo-Cl (1.2×10^{-4} M) with the irradiation time of UV and Vis (The dash lines were the fitting curves).

transformation of Azo-Cl with the UV irradiation even as we made some modification of the azobenzene.

Apparently, the absorbance of α-CD aqueous solution (1.2×10^{-4} M) was almost zero. Importantly, the absorbance of Azo-Cl with equimolar α-CD was higher than Azo-Cl indicating there was association between trans Azo-Cl and α-CD which could strengthen the absorbance[40]. Upon UV irradiation, the absorbance at 346 nm with α-CD dropped and reached almost the same absorbance as the one without α-CD. It meant that all the Azo groups (cis) went out of the cavity of α-CD and no binding between them existed any more. With alternate UV and Vis irradiation, the absorbance at 346 nm would go up and down showing that the photoisomerization between trans and cis could be repeated in the presence of equimolar α-CD according to **Fig. 3**.

It is important to observe the transition kinetics in the absence and presence of α-CD (molar ratio 1:1). Therefore, we used the UV light to irradiate the 1.2×10^{-4} M trans Azo-Cl solution and recorded the spectrum at different time intervals. Similarly, Vis light was exploited to irradiate the cis Azo-Cl and the spectrum was also recorded as before. The absorbance at 346 nm was illustrated in **Fig. 4**.

We assumed this trans-to-cis photoisomerization transition as first order reaction[41]. Therefore,

$$\ln\frac{A_0-A_e}{A_t-A_e}=kt \qquad \textbf{Eq 1}$$

For cis-to-trans photoisomerization, the transition should follow:

$$\ln\frac{A_e-A_0}{A_e-A_t}=kt \qquad \textbf{Eq 2}$$

Both of them could be changed as following equation:

$$A_t=A_e+(A_0-A_e)\times e^{-kt} \qquad \textbf{Eq 3}$$

where A_t was the absorbance at 346 nm at irradiation time t while A_0 and A_e were the ones at time 0 and at equilibrium separately. k was the photoisomerization transition rate (To tell the difference, we defined trans-to-cis transition rate as $k_{t\text{-}c}$ while cis-to-trans transion rate as $k_{c\text{-}t}$).

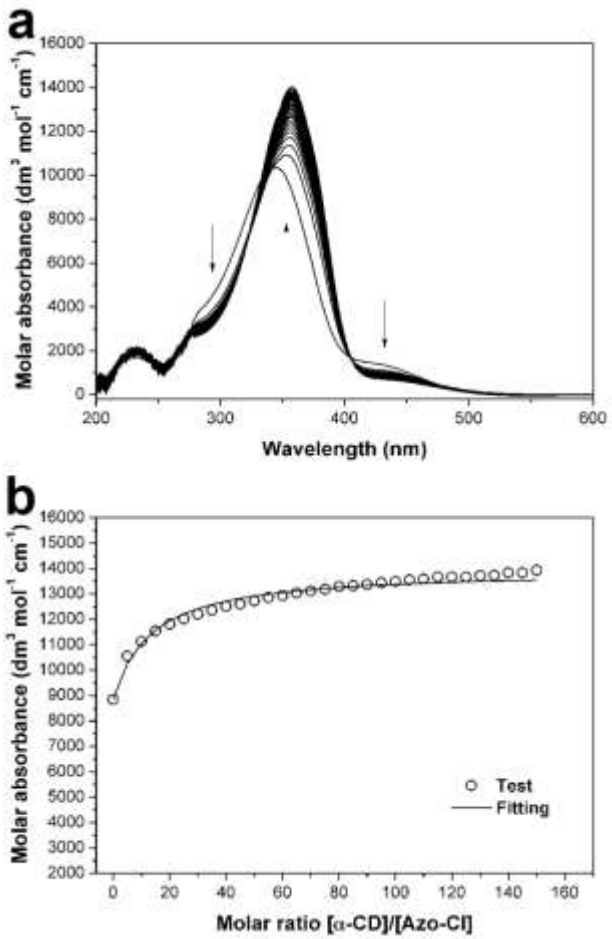

Fig. 5. a. Molar absorbance increase of an Azo-Cl solution (8×10^{-5} M) with 30 sequential additions (50 μL each) of α-CD solution (1.2×10^{-2} M). The arrow indicates the change in absorbance with each addition of α-CD solution; **b**. Molar absorbance variation at 360 nm and the line representing the best fit of an algorithm for a 1:1 host-guest complexation by α-CD over the wavelength range 320-380 nm.

The same calculation was also carried out with the one in the presence of α-CD (molar ratio 1:1) (**Fig. S6**). All the results were listed in **Table 1**.

Table 1. Photoisomerization transition rate of Azo-Cl (1.2×10^{-4}M) in the presence and absence of equimolar α-CD.

	$k_{t\text{-}c}$ (s^{-1})	$k_{c\text{-}t}$ (s^{-1})
[Azo-Cl]	0.09121	0.02640
R^2	0.99984	0.99916
[Azo-Cl]/ [α-CD]=1:1	0.06258	0.02772
R^2	0.99749	0.99863

As could be seen in **Table 1**, all the fitting degree was above 0.99 which indicated that all the transition followed the first order transition very well. Importantly, $k_{t\text{-}c}$ decreased in the presence of equimolar α-CD. In the presence of α-CD, trans Azo group was mostly included by α-CD and it would be harder for it to get out of the cavity than Azo-Cl itself due to the restriction from α-CD even under UV irradiation[42-44]. However, no big difference was observed when cis Azo group went back to trans form both in the

absence and presence of equimolar α-CD. This indicated the cis Azo group couldn't be complexed by α-CD and it could transform into trans form as free as Azo-Cl itself[40].

To test the complex activity between α-CD and trans Azo-Cl,

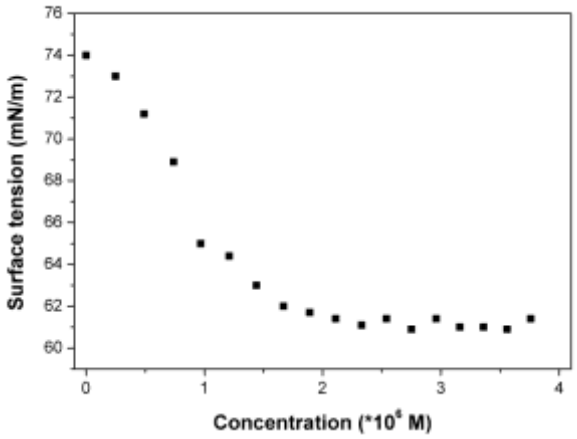

Fig. 6. Surface tension in variation with Azo-Cl concentration. The CAC of Azo-Cl is 2.11×10^{-6} M.

the UV-Vis spectrum was used to record. The model used for determining the apparent complexation constant assumed that there existed equilibrium among α-CD, trans Azo-Cl and their complex formed as host-guest 1:1[45]. Therefore, α-CD complexed trans Azo-Cl according to **Eq 4**.

$$\alpha\text{-}CD + Azo \overset{K}{\rightleftharpoons} \alpha\text{-}CD \bullet Azo \qquad \textbf{Eq 4}$$

The apparent complexation constant, *K*, at equilibrium was given by

$$K = \frac{[\alpha\text{-}CD \bullet Azo]}{[\alpha\text{-}CD][Azo]} \qquad \textbf{Eq 5}$$

Given that $[Azo]_{total}$ and $[\alpha\text{-CD}]_{total}$ were the initial concentrations:

$$[Azo]_{total} = [\alpha CD \bullet Azo] + [Azo] \qquad \textbf{Eq 6}$$

$$[\alpha CD]_{total} = [\alpha CD \bullet Azo] + [\alpha CD] \qquad \textbf{Eq 7}$$

The absorbance at a particular wavelength was given as **Eq 8**

$$A = \varepsilon_{Azo}[Azo] + \varepsilon_{\alpha CD \bullet Azo}[\alpha CD \bullet Azo] \qquad \textbf{Eq 8}$$

where ε represented the molar absorbance. By using HypSpec protocol, the value of *K* was determined by best fitting the variation of the UV-vis spectrum in the range 320-380 nm to an algorithm based on **Eqs 4-8** as the α-CD concentration varied[46-49].

The variation of UV-vis molar absorbance of the Azo-Cl with increasing α-CD concentration (**Fig. 5**) was consistent with the formation of a 1:1 α-CD: Azo-Cl host-guest complex characterized by an apparent complexation constant, K = 912.85 $dm^3\ mol^{-1}$ with λ_{max} = 360 nm. Therefore the binding complex between α-CD and Azo-Cl indeed existed and worked well.

As we knew, the amphiphilic molecule could form assembly structure only above CAC (critical aggregate concentration) [24, 50, 51]. Herein surface tension test was used to measure the CAC (**Fig. 6**). Increasing the concentration of Azo-Cl, the surface tension

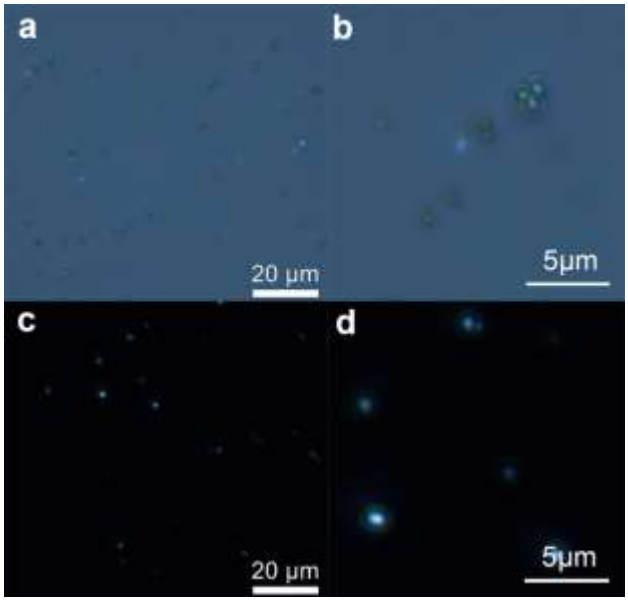

Fig. 7. **a c**. Polarizing light microscope (PLM) images of Azo-Cl (1.2×10^{-4} M); **b**. enlarged image of **a**; **d**. enlarged image of **c**.

kept decreasing as expected. Suddenly it stopped decreasing at around 2.11×10^{-6} M and kept as a constant even higher than this concentration. Therefore, this concentration should be defined as CAC which was much lower than the concentration we used in the other test.

Based on the previous study in this paper, we expected to see some special structure appearing with the concentration higher than CAC. Polarized light microscope (PLM) images were taken in **Fig. 7**. When 1.2×10^{-4} M trans Azo-Cl solution was coated on the glass slide with a glass cover on and observed, yolk-like vesicles showed up with bright greenish cores and dark-colored shells outside the cores and dispersed well. Therefore, we preliminary inferred Azo-Cl could self assembled into vesicle structures.

To further confirm our conclusion, TEM test was conducted and the images were recorded in **Fig. 8**. Obviously, the Azo-Cl itself could assemble into round-shaped structure in **a**. Moreover, we found some vesicle structures not fully stained in **b** and some of them were outlined with colour frame. In enlarge image **c**, the central part was in light colour while the rim of the structure was dark. As we could see from the image, the vesicles' average size was about 210 nm. We came up with a mechanism of vesicle's formation: The hydrophobic part (azo group and carbon chain) would aggregate as a shell and left the hydrophilic part outside and inside of the shell which made the vesicles formed.

With the addition of equimolar α-CD, the big round structure collapsed to small dots and even disappeared (**d**). This was caused by the inclusion activity between trans Azo group and α-CD as previous discussion. The hydrophobic head of Azo-Cl no longer existed which led the vesicles ruined. After then, UV irradiation was upon the sample and the vesicle structure showed up again due to the exclusion of cis Azo group from the cavity of

α-CD (**e**). The amphiphilic molecules could assemble into the vesicle again. Followed by the Vis irradiation, the vesicle structure collapsed again (**f**).

In order to investigate the inclusion assembly between Azo-Cl and α-CD, ^{1}HNMR spectrum was used and collected as **Fig. 9**. Based on related references[41, 52, 53], further information has been obtained from the spectrum. Comparing **a** and **b**, no apparent differences were observed here which meant the original Azo-Cl mostly existed as the trans form.

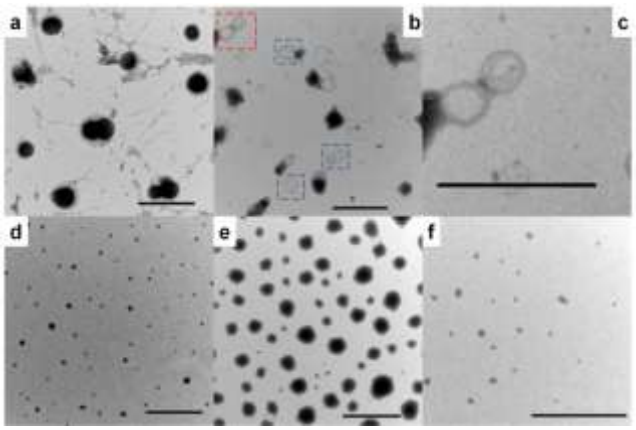

Fig. 8. **a**-**b**. TEM image of Azo-Cl (1.2×10^{-4} M); **c**. Enlarged vesicle image in the red frame from **b**. **d**. TEM image of [Azo-Cl]/[α-CD] = 1:1 (1.2×10^{-4} M); **e**. TEM image of [Azo-Cl]/[α-CD] = 1:1 (1.2×10^{-4} M) under UV irradiation for 30 min; **f**. TEM image of [Azo-Cl]/[α-CD] = 1:1 (1.2×10^{-4} M) under UV irradiation for 30 min and then Vis irradiation for 30 min. (The scale bar indicated 1 μm).

More than 90% azo group was in trans form from the interegation. However, we still could find there were some quite low peaks at upfield (δ<7.45) which were attributed to the cis form of Azo group. So the trans and cis form were always in dynamic equilibrium which complied with our previous photoisomerization transition rate test.

With UV irradiation, the downfield peaks (δ>7.45) almost disappeared while the upfield peaks intensity increased due to the formation of cis Azo-Cl (**c**). When equimolar α-CD was added to the Azo-Cl, the chemical shifts of peaks at downfield moved which showed the complexion between trans azo group and α-CD (**d**). With UV irradiation, the downfield peaks (δ=8.0-7.6) disappeared and the upfield peaks showed up again (**e**) (δ=7.45-7.0) which were the characteristic peaks of cis Azo group in reference of (**c**). Therefore α-CD couldn't include Azo group any more due to its isomerization. Upon further Vis irradiation again, the spectrum (**f**) recovered almost the same as (**d**) which meant binding complexation was reformed between Azo group and α-CD.

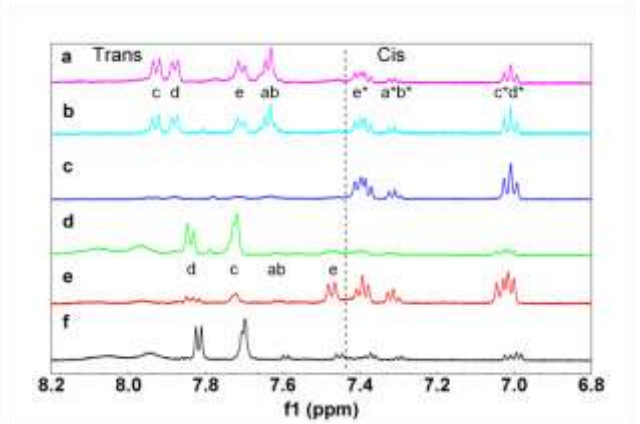

Fig. 9. ^{1}HNMR spectrum (500 MHz, D_2O, 298.2 K) of: **a**. Azo-Cl (1.6 mM); **b**. trans Azo-Cl (1.6 mM, Vis irradiation of **a**); **c**. cis Azo-Cl (1.6 mM, UV irradiation of **a**); **d**. [Azo-Cl]/[α-CD] = 1:1 (1.6 mM); **e**. [cis Azo-Cl]/[α-CD] = 1:1 (1.6 mM, UV irradiation of **d**); **f**. [trans Azo-Cl]/[α-CD] = 1:1 (1.6 mM, Vis irradiation of **e**). (The asterisk means the cis form of Azo-Cl's protons)

2D NOESY ^{1}HNMR spectrum was conducted to study the further details of the complexation (**Fig. 10**). When equimolar α- CD was added to the trans Azo-Cl, the cross peak between Azo group and α-CD (δ=3.1-3.9) was observed (**Fig. 10a**). Apparently, the proton signal of α-CD and the one from trans Azo group (δ>7.45) made the overlapped cross signal which meant the trans Azo group had been included by the cavity of α-CD. Based on the inclusion, the hydrophobic Azo group became hydrophilic instead afterwards led to the collapse of the vesicles. At the same time, the cross peak between α-CD and proton **h** of Azo-Cl (**Fig. 1** and **S3**) was also observed. As a brief summary, α-CD mostly could bind Azo part and would also bind with the carbon chains of Azo-Cl.

With UV irradiation, the cross peak between trans Azo group and α-CD disappeared (**Fig. 10b**) showing that the cis Azo group couldn't be included by the α-CD due to the size effect. Then the Azo part became hydrophobic again and could help to rebuild the vesicle structure. Despite the existing cross peak between α-CD and proton **h** of Azo-Cl, a quite weak cross peak between α-CD and proton **f** of Azo-Cl was also observed surprisingly. It indicated that some α-CDs on the Azo part would slide to the carbon chain with the UV irradiation. At the same time, we couldn't rule out the possibility that some α-CDs would run into water instead.

Afterwards, the sample was irradiated with Vis light again, the cross peaks between α-CD and trans Azo group (also proton **h**) showed up again (**Fig. 10c**). However, the cross peak between α-CD and proton **f** didn't exist anymore. Therefore α-CD would slide back to the Azo group. Upon Vis irradiation, the α-CDs (both in water and on proton **f**) came back onto the Azo group. Since some of the α-CDs bound firmly with the middle part of carbon chain which was too far from the Azo group, it was too hard for them to move onto the Azo group even with enough Vis irradiation. The formation mechanism of vesicles was shown in **Fig. 1**.

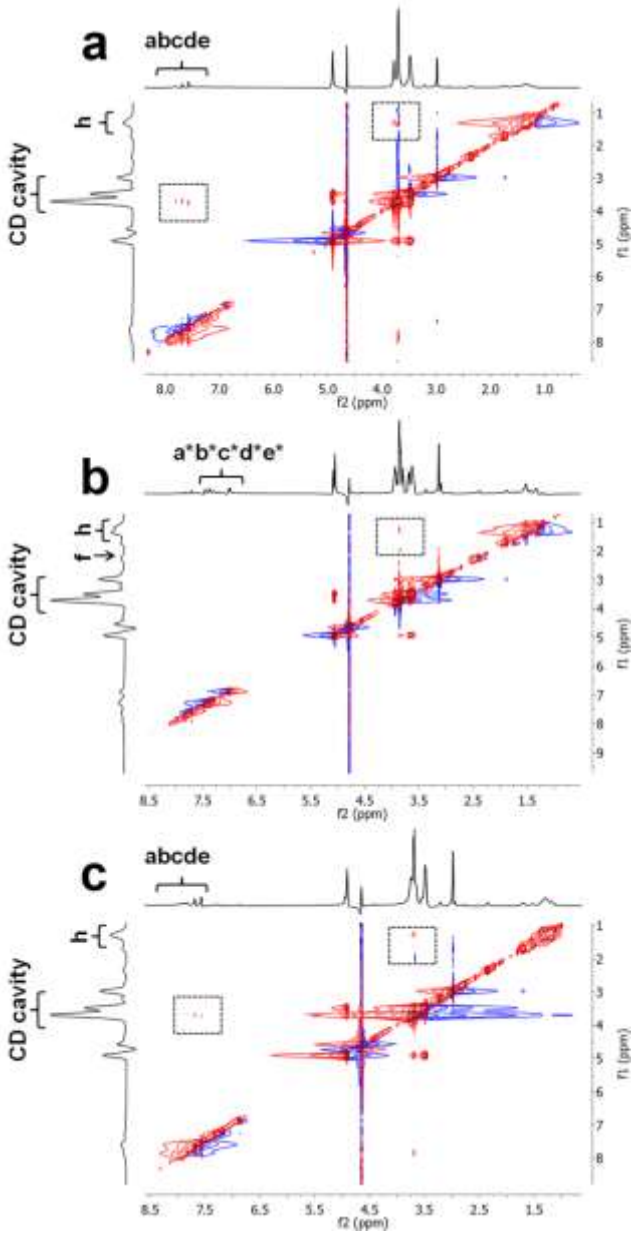

Fig. 10. 2D NOESY NMR spectrum (600MHz, D_2O, 298.2K): **a**. [Azo-Cl]/[α-CD] = 1:1 (1.6mM); **b**. UV irradiation of **a**; **c**. Vis irradiation of **b**. (The asterisk means the cis form of Azo-Cl's protons)

Conclusions

Recoverable spherical vesicles were constructed by the self-assembly of amphiphilic molecule (Azo-Cl) in water. With the addition of equimolar α-CD, assembled vesicles disappeared due to the complexation between trans Azo group and α-CD. Afterwards, they showed up upon UV irradiation due to the exclusion of cis Azo group out of α-CD. With alternative Vis irradiation, vesicles collapsed repeatedly. These reversible assembled vesicles could be used in a board fields such as controlled drug release and biomaterials.

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Notes and references

[a] *State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: jiewang2010@ecust.edu.cn; guoxuhong@ecust.edu.cn*
[b] *School of Chemistry and Physics, University of Adelaide, Adelaide, SA 5005, Australia. E-mail: stephen.lincoln@adelaide.edu.au*
[c] *Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA*

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