Photo-controlled molecular recognition of α-cyclodextrin with azobenzene containing polydiacetylene vesicles†

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Herein, photo-controlled inclusion and exclusion reaction of azobenzene-containing polydiacetylene vesicles with α-cyclodextrin were used to act as driving force to induce chromatic transition of PDA vesicles, which provided a novel model system that combines photochemistry and host–guest chemistry for a photo-stimulus-responsive vesicle.

Biological systems such as cell membranes and chameleons adapt to their surroundings by undergoing reversible structural and functional changes in response to external stimulus. Polydiacetylene (PDA) exhibits intense chromatic switch from blue to red in response to external stimuli including temperature, pH, ions, solvent, stress or ligand interaction.[1] These colorimetric changes can be easily perceived by the UV-absorption spectrum, fluorescence or even the naked eye, which makes PDA an ideal candidate for sensing materials.[2] To date, PDA materials in the forms of liposomes, vesicles and films have been synthesized.[3] However, most of these chromatic responses are irreversible, and limit their application in sensing. To the best of our knowledge, only a few PDA materials with reversible chromatic responses have been reported.[4] Although significant efforts have been given to the issue,[1,4] the exact mechanism of blue-to-red and red-to-blue colorimatic transition have not yet been clearly explained.

Cyclodextrins are intriguing molecules because they form inclusion complexes with a variety of substances.[5] Different binding specificities of α-, β- and γ-cyclodextrins make these substances attractive model systems for studying ligand–receptor interactions. For instance, Kim *et al.* observed that α-cyclodextrin (α-CD) disrupted the ordered structures of PDA vesicles by forming inclusion complexes and induced blue-to-red color transition of PDAs in a selective and predictable way.[6] However, these chromatic transitions of PDA induced by α-CD were irreversible.

As we know, two isomers of azobenzene mesogen, the *trans* and *cis* forms, can be reversibly switched to each other upon photo-irradiation. Driven by hydrophobic and van der Waals interactions, the *trans*-azobenzene can be well-recognized by α-CD.[7] However, when the *trans*-azobenzene is transformed to the *cis*-azobenzene, α-CD cannot include the bulky *cis* form any more due to the mismatch between the host and guest. Therefore, the host–guest assembly and disassembly between the azobenzene and α-CD by an external photo-stimulus can act as a driving force to induce a chromatic transition of the azobenzene containing PDA vesicles. To the best of our knowledge, the light-triggered red-to-blue chromatic response of the PDA materials has not yet been realized. In this communication, we attempted to make use of photo-controlled inclusion and exclusion reaction of the azobenzene-containing PDA vesicles with α-CD to fabricate a novel light-triggered colorimetric transition system (Fig. 1).

To realize the photo-controlled inclusion and exclusion reaction, a diacetylene monomer (10,12-pentacosadiynoic acid, DA) containing a *p*-nitrophenyl azobenzene moiety (NADA) was synthesized in analogy to the previous procedure.[1f] NADA/DA complex vesicles with mol ratios of NADA : DA = 1 : 5 were prepared following similar procedures as in ref. 1*h* (as shown in Fig. 1). As expected, the resulting NADA/DA complex vesicles could be polymerized under 254 nm light irradiation for 10 min at room temperature. The transparent colorless NADA/DA complex vesicles solution was converted into blue PNADA/PDA complex vesicles solution upon UV irradiation. A strong blue-to-red color transition was observed for PNADA/PDA vesicles solution mixing with 2 mM α-CD solution. This colorimetric transition can be ascribed to the inclusion reaction of α-CD with the PNADA/PDA vesicles. UV-Vis absorbance spectra shown in Fig. 2 confirmed that the observed color changes were mainly related to specific association of α-CD with the azobenzene moiety within the PNADA/PDA matrix. Fig. 2(a) shows the blue-to-red colorimetric transition of the PNADA/PDA vesicles induced by α-CD. It was apparent in UV-Vis spectra, that the ratio between the absorbance at ~540 nm (red band) and 630 nm (blue band) increased in the presence of NADA within the complex vesicles. These quantitative colorimetric responses (%CR) data are shown in Fig. 2(b), which depicts the blue-to-red chromatic kinetics of the pure PDA vesicles and PNADA/PDA complex vesicles with α-CD. These blue-to-red color changes were more pronounced (higher %CR and more rapid response) in the presence of NADA within the complex vesicles. We must point out that the stronger colorimetric responses of the PNADA/PDA vesicles with α-CD supported the proposal that these colorimetric changes were indeed mainly related to specific association of α-CD with the azobenzene moiety. Further evidences for above interpretation were provided by the analysis of the colorimetric transitions induced by

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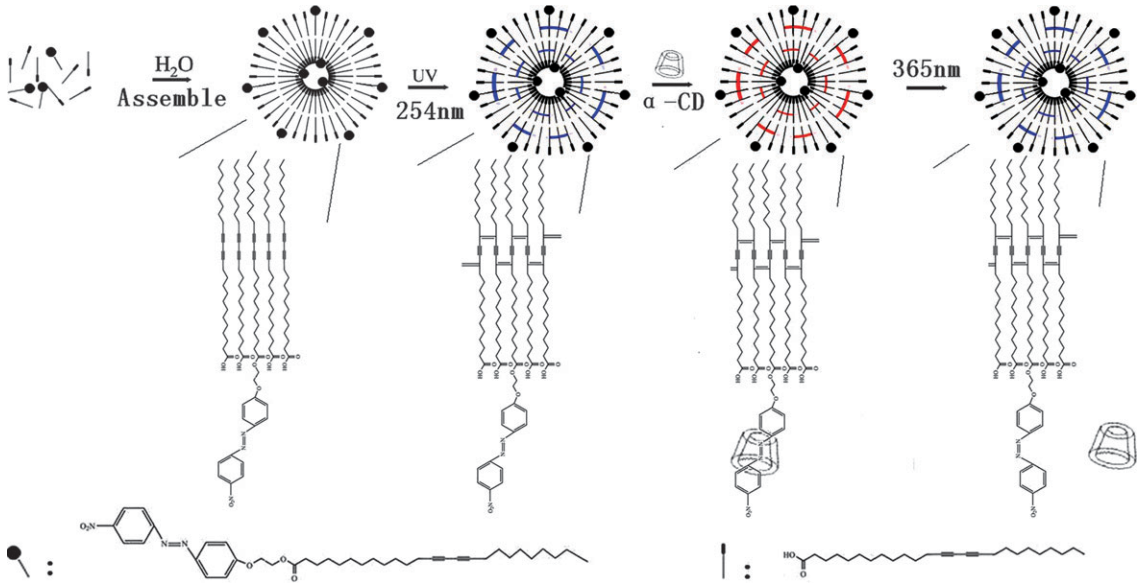

Fig. 1 Illustration of photo-controlled inclusion and exclusion reaction of azobenzene-containing PDA vesicles with α-CD.

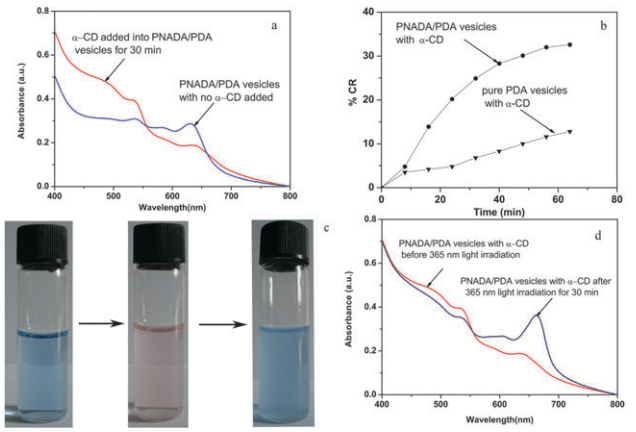

Fig. 2 (a) UV-Vis spectra of PNADA/PDA vesicles solution with no or 2 mM α-CD solution added; (b) quantitative colorimetric response kinetics behavior of pure PDA vesicles and PNADA/PDA complex vesicles with α-CD; (c) Photograph of PNADA/PDA vesicles mixing with α-CD for 20 min and then irradiated with 365 nm light for 30 min; (d) UV-Vis spectra of PNADA/PDA vesicles/α-CD mixing solution before and after 365 nm light irradiation for 30 min.

inclusion and exclusion reaction of α-CD with the azobenzene moiety within the complex vesicles. When mixing with 2 mM α-CD solution for 20 min, the PNADA/PDA complex vesicles solution turned red as mentioned above. Subsequently upon irradiation with 365 nm light for 30 min, the red PNADA/PDA complex vesicles solution turned back to dark blue (as shown in Fig. 2(c)). This colorimetric change could be easily perceived by the UV-absorption spectrum, as the ratio between the absorbance at ~540 and 630 nm decreased (as shown in Fig. 2(d)). This can be ascribed to the disassembly of α-CD and guest molecules, and the changes in conformation order of the side chain within the PDA matrix induced by α-CD could be completely recovered. However, for pure PDA vesicles, no obvious red-to-blue colorimetric transitions could be observed upon 365 nm irradiation. All the above results confirmed that the observed colorimetric transitions were directly related to the specific inclusion and exclusion reaction of α-CD with the *trans*-azobenzene moiety within the PDA matrix, instead of the PDA matrix itself. Previous work has reported that α-CD could form an inclusion complex with *trans*-azobenzene species, while it scarcely interacts with the *cis*-azobenzene moiety because of the mismatch between the host and guest.[7a] α-CD can form an inclusion complex with *trans*-azobenzene isomers due to specific association of α-CD with the *trans* azobenzene moiety and induce a blue-to-red colorimetric transition of the PDA matrix. Upon irradiation with 365 nm light for 30 min, the azobenzene moiety switched from the *trans* to the *cis* state due to the photoisomerization. As discussed above, α-CD might be excluded out of azobenzene group due to the mismatch between the host and guest when the *trans* azobenzene moiety was photo-isomerized to the *cis* state. Therefore, the previous changes in conformation order of the side chain within the polydiacetylene matrix induced by α-CD could be completely recovered and PDA matrix would concomitantly return back to the blue form.

In order to prove the above idea, 2D-NOESY experiments were performed for PNADA/PDA vesicles/α-CD complex before and after 365 nm light irradiation. The NOESY spectrum for PNADA/PDA vesicles/α-CD complex before 365 nm light irradiation demonstrated correlation peaks between protons in the α-CD cavity and protons in the *trans*-azobenzene moiety (as shown in Fig. 3(a)), indicating that α-CD formed an inclusion complex with the *trans*-azobenzene moiety within the complex vesicles. After 365 nm irradiation for 30 min, no correlation peaks between protons in the α-CD cavity and protons of the azobenzene moiety were observed (as shown in Fig. 3(b)), indicating host–guest disassembly between the azobenzene moiety and α-CD.[7b] If the NOESY signals had been collected for long time, the thermal isomerization reaction of the azobenzene moiety should lead to partly inevitable recovery of *cis* to *trans*

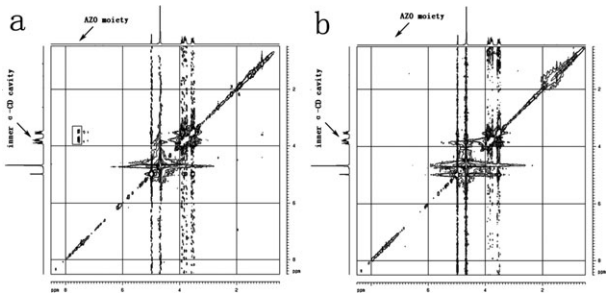

Fig. 3 2D-NOESY spectra of PNADA/PDA vesicles/α-CD complex (a) before and (b) after 365 nm light irradiation for 30 min.

transition of the azobenzene moiety. Here, the interaction between α-CD and PDA matrix was weak and hardly affected these colorimetric transitions. The NOESY results well confirmed the mechanism that the colorimetric transitions in response to the external photo-stimuli were directly related to the specific inclusion and exclusion reaction of α-CD with the azobenzene moiety within the PDA matrix instead of the PDA matrix itself.

Furthermore, the PNADA/PDA vesicles solution in the presence of α-CD were irradiated with UV (365 nm) and visible light (435 nm) for 10 min alternately. The photo-induced partially reversible chromatic response of the PNADA/PDA vesicles in the presence of α-CD were observed.

Upon 365 nm light irradiation, the absorbance at ~540 nm (red band) decreased, while the absorbance at ~630 nm (blue band) increased dramatically. However, when we switched the light irradiation to 435 nm, the absorbance at ~540 nm slightly increased, while the absorbance at ~630 nm slightly decreased; see Fig. 4. On alternating irradiation of the solution with UV and visible light, this partially reversible chromatic response was observed. Unfortunately, upon irradiation at 435 nm for a sufficient time, the absorbance at 540 and 630 nm could not return back to the initial value. The above results indicated that the inclusion complex of α-CD with the PNADA/PDA vesicles was less stable and exclusion reaction of α-CD with the azobenzene moiety within PDA matrix occurred in response to UV irradiation.

In conclusion, the photo-controlled inclusion and exclusion reaction of azobenzene-containing PDA vesicles with α-CD has been used to act as a driving force to induce the chromatic transition of PDA vesicles. Our work provides a novel system that combines photo-chemistry and host–guest chemistry for a photo-stimulus-responsive vesicle system. We hope this model system would be also valuable in understanding the chromatic transition mechanism of the PDA materials.

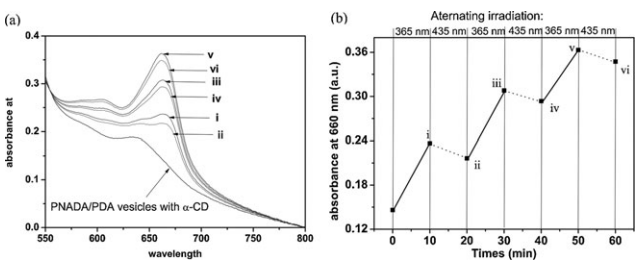

Fig. 4 (a) UV-Vis spectra and (b) absorption maximum at *ca.* 660 nm for PNADA/PDA vesicles with α-CD upon alternating irradiation with 365 and 435 nm light: (i) the mixing solution under 365 nm light irradiation for 10 min; (ii) subsequent irradiation of (i) with 435 nm light for 10 min; (iii) subsequent irradiation of (ii) with 365 nm light for 10 min; (iv) subsequent irradiation of (iii) with 435 nm light for 10 min; (v) subsequent irradiation of (iv) with 365 nm light for 10 min; (vi) subsequent irradiation of (v) with 435 nm light for 10 min.

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