Rationally designed helical nanofibers *via* multiple non-covalent interactions: fabrication and modulation†

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Building well-defined hierarchical architectures *via* supramolecular chemistry is one of the challenges in nanotechnology and is crucial to our understanding of biological self-assembly and biological phenomenon. In this work, a well-ordered one-dimensional (1 D) helix is fabricated with a novel sugar-based lipid by virtue of multiple non-covalent interactions (*i.e.* hydrophobic interaction, aromatic stacking, and hydrogen bond). The robust helical nanostructure is evidenced by negative-staining TEM, cryo-TEM and circular dichroism (CD). A series of amphiphilic molecules are also synthesized to explore molecular structure-performance relationship and elucidate intermolecular forces that contribute to complex architectures. Moreover, the supramolecular nanohelices in this work are demonstrated to be "smart nanostructures" which can be shaped into spherical micelles, vesicles or unfolded nanofibers by external stimuli, such as pH, light, and surfactant addition.

Introduction

The discovery of DNA double helix by Watson and Crick[1] provides a natural explanation for information transfer during the replication of DNA and transcription of DNA into messenger RNA. This discovery is considered as a milestone in the 20th century's life sciences, which has promoted greatly the biomedical research, the naissance of gene engineering technology and the development of clinical medicine, and turned into a great landmark during the life sciences history. Chemically, DNA is a double-stranded polymer that is twisted into a helix like a spiral staircase. Each strand is comprised of a sugar-phosphate backbone and numerous base chemicals attached in pairs. The four bases that make up the stairs in the spiral staircase are adenine (A), thymine (T), cytosine (C) and guanine (G). The perfect structure of DNA's complementary double helix is of significant importance to the storage and transfer of genetic information.[2]

Inspired by the functionality and complexity of DNA double helix, chemists have endeavoured in the artificial creation of double helical architectures in a controllable manner *via* supramolecular self-assembly. In contrast to a large number of single-stranded helix by synthetic polymers, oligomers or small molecules,[3–9] only a limited number of double helices are reported. Two strategies have been described in the literature. One approach is to join two linear polymer chains into double helix by virtue of inter-chain affinity, which is similar to the way DNA forms. For example, Yashima and coworkers have reported the first heterostranded double helix held together by inter-strand amidinium–carboxylate salt bridges of two complementary homopolymers.[10] This work provides a design rationale for unique double-stranded helical polymers. An alternative approach towards double helix is to take advantage of *bottom-up fabrication*. In this route, polymer-like or one-dimensional aggregates formed by molecular self-assembly (*i.e.* small molecules or polymers) can be jointed in a helical fashion. For example, Frankel and O'Brien prepared amphiphilic diacetylenic aldonamides which can self-organize into helical structures in aqueous solution.[11] Yanagawa *et al.* have found a duplex structure in the self-assembled solution of a phospholipid–nucleoside conjugate containing two long alkyl chains and a nucleotidyl residue.[12] Recently, Jinnai and coworkers and Liu and coworkers have reported the visualization of three-dimensional (3D) double and triple helical morphology of triblock polymers in the mixed solvent.[13] Besides, supramolecular quadruple helices have also been discovered in nonpolymeric systems involving sugar–lipid and peptide amphiphiles.[14]

Despite the study dedicated to artificial double helices, there are still some issues that need to be addressed. On one hand, the structural factors at the molecular level that precisely control the supramolecular self-assembly of a double helix are still vague. People are still incapable of rationalizing the creation of a self-assembled double helix and the supramolecular fabrication of double helices are still rare. Therefore more efforts are needed to reveal molecular structure–performance relationships in double helix systems. On the other hand, one of the advantages in supramolecular chemistry is to build molecular assemblies in a controllable fashion.[15] These supramolecular structures are held together by relatively weak non-covalent interactions and thus might be easily reconfigurable into a variety of morphologies by external stimuli. Such smart stimuli-responsive supramolecular assemblies are attractive for potential applications in

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nanotechnology. Yet few works have focused on the morphological modulation or stimuli-response of a supramolecular double helix.

Herein, we have designed a functional amphiphile bearing a sugar moiety, azobenzene group and butyl chain. In a self-assembled manner, the amphiphile can organize readily into one-dimensional intertwined double helices which were composed of "polymer-like" aggregates or nanofibers in aqueous solution. The self-assembled double helical structures were demonstrated to be stable with respect to dilution, heat, urea or organic solvent. A series of amphiphiles were synthesized to reveal the relationship between molecular structure and self-assembly properties. Meanwhile intermolecular forces that contributed to the formation of one-dimensional double helix were suggested. Morphological modulation of the double helix was realized by external stimuli including pH, light and surfactant addition.

Experimental section

Materials

Sodium dodecylbenzene sulfonate, sodium dodecylbenzene sulfonate and other surfactants were bought from Acros Organics Co. The other reagents are of analytical purity. All the reagents and solvent were used as received.

Amphiphile synthesis

The amphiphiles $C_{10}G$, $C_{12}G$ and $C_{14}G$ were synthesized according to the literature.[16] The synthesis of amphiphile C_4AG is given as below. The other sugar-based amphiphiles are synthesized in a similar way.

(1) 4-Butyl-4′-hydroxyl azobenzene: 14.9 g 4-butylaniline was dissolved in 200 mL water and 25 mL concentrated hydrochloric acid. The solution was cooled to 5 °C in an ice bath and reacted with 15 mL aqueous sodium nitrite (6.67 M) at 5 °C for 1 h. The resulting diazonium solution was then added to a solution containing 9.4 g phenol, 4 g sodium hydroxide, 10 g of sodium carbonate, and 100 mL water at 0 °C for 2 h. The product was collected by filtration, dried in vacuum, and purified by recrystallization in hexane. The yield was 65%. ^{1}H NMR (400 MHz, $CDCl_3$): 0.94 (t, 3H), 1.40 (m, 2H), 1.65 (m, 2H), 2.68 (t, 2H), 6.93 (d, 2H), 7.29 (d, 2H), 7.80 (d, 2H), 7.87 (d, 2H). elemental analysis calcd (%) for $C_{16}H_{18}N_2O$: C 75.56, H 7.13, N 11.01; found: C 75.55, H 7.30, N 11.08.

(2) 4-Butyl-4′-(oxy-2,3-epoxypropyl) azobenzene:[20] 4-butyl-4′-hydroxyl azobenzene (11.31 g, 50.0 mmol) was dissolved in 100 ml of 90% ethanol and sodium hydroxide (2.06 g, 50.0 mmol). Epichlorohydrin (9.34 g, 100 mmol) was slowly added dropwise into the solution at 60 °C. After the mixture refluxed for 2 h, the solvent was removed under reduced pressure. The residue was dissolved in 100 ml of chloroform and sodium chloride was removed by filtration. The filtrate was dried under vacuum and the product was purified by column chromatography using 2% (v/v) ethyl acetate–chloroform as the eluent. The yield was 70%. ^{1}H NMR (400 MHz, $CDCl_3$): 0.95 (t, 3H), 1.38 (m, 2H), 1.63 (m, 2H), 2.68 (t, 2H), 2.80 (dd, H), 2.94 (dd, H), 3.41 (m, H), 4.02 (dd, H), 4.31 (dd, H), 7.02 (d, 2H), 7.30 (d, 2H), 7.83 (d, 2H), 7.91 (d, 2H); elemental analysis calcd (%) for $C_{19}H_{22}N_2O_2$: C 73.52, H 7.14, N 9.03; found: C 73.72, H 7.17, N 9.01.

(3) Synthesis of C_4AG:[16] In a flask equipped with a reflux condenser, N-methyl glucamine (9.99 g, 49 mmol) was incubated with 4-butyl-4′-(oxy-2,3-epoxypropyl) azobenzene (10.9 g, 49 mmol) in 50 ml methanol and 0.01 ml water at 70 °C. The reaction was finished within 24 h. After cooling, the product was precipitated from methanol solution. The product was further recrystallized from methanol for three times. The yield was higher than 90%. ^{1}H NMR (400 MHz, $CDCl_3$): 0.95 (t, 3H), 1.39 (m, 2H), 1.64 (m, 2H), 2.40 (d, 3H), 2.66 (m, 6H), 3.63 (m, 3H), 3.78 (m, 2H), 3.89 (m, 2H), 4.12 (m, 2H), 7.08 (d, 2H), 7.31 (d, 2H), 7.77 (d, 2H), 7.88 (d, 2H); elemental analysis calcd (%) for $C_{26}H_{39}N_3O_7$: C 61.76, N 8.31, H 7.77; found: C 61.59, N 8.28, H 7.77.

Cryo-TEM image

A small drop of sample was placed on a 400 mesh copper grid, and a thin film was produced by blotting off the redundant liquid with filter paper. This thin film was then quickly dipped into liquid ethane, which was cooled by liquid nitrogen. Observation of the cryo-sample was carried out at −183 °C.

Negative-staining TEM

TEM micrographs were obtained with a JEM-100CXII transmission electron microscope (working voltage of 80–100 kV) by the negative-staining method with uranyl acetate solution (1%) as the staining agent. One drop of the solution was placed onto a carbon Formvar-coated copper grid (230 mesh). Filter paper was employed to suck away the excess liquid. Then one drop of the staining agent was placed onto the copper grid. The excess liquid was also sucked away by filter paper.

UV-vis absorbance

UV-vis absorbance measurements of solution were carried out on the spectrophotometer (Cary 1E, Varian Australia PTY Ltd.) equipped with a thermostated cell holder. The UV-vis measurement was all carried out at 30 °C.

Dynamic light scattering

To prepare dust-free solutions for light scattering measurements, the solutions were filtered through a 0.20 μm membrane filter of hydrophilic PVDF into light scattering cells before the measurements. The light scattering cells had been rinsed with distilled acetone to ensure a dust-free condition before use. DLS was performed with a spectrometer (ALV-5000/E/WIN Multiple Tau Digital Correlator) and a Spectra-Physics 2017 200 mW Ar laser (514.5 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed by using the methods of Contin.

Photoisomeric experiment

For light-triggered *trans*/*cis* transition, solution samples were irradiated with 365 nm UV light from a Spectroline FC-100F fan-cooled, long wave UV lamp. The power of the mercury arc lamp is 100 W. Samples were placed in a quartz tube, and irradiation was done for a specific duration. For *cis*/*trans* transition,

irradiation by visible light was performed using a 200 W incandescent light bulb (> 440 nm).

Results and discussion

Following our interest in the self-assembled nanohelix, we have synthesized a sugar-based amphiphile, denoted as C_4AG. The details of synthetic process were described in the Experimental Section. The novel amphiphile consisted of three parts: azobenzene group, sugar moiety and butyl tail (Chart 1). The hydrophilic sugar headgroup is known to improve the molecular solubility and also generate multiple intermolecular hydrogen bonds. Azobenzene group was chosen because of its planar aromatic structure which may direct one-dimensional molecular packing. Meanwhile, the incorporation of azobenzene is anticipated to impart light-activity to self-assembled systems. Additionally, terminal butyl chain is a good balance for hydrophobic interaction and molecular flexibility. It is worthwhile that sugar–lipids have recently become research focus owing to their biocompatibility, low toxicity, *etc*. In this report, we have utilized a ring-opening reactions of epoxides with N-methylglucamine to give high yield product.[16]

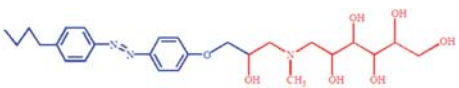

Chart 1 Molecular structure of novel sugar–lipid amphiphile C_4AG (blue part represents hydrophobic group and the red represents hydrophilic group).

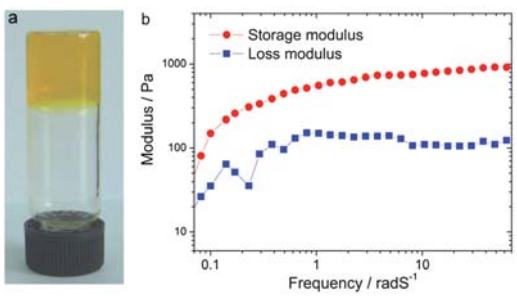

Fig. 1 (a) Macroscopic appearance of self-assembled hydrogel at 20 mM C_4AG. (b) Frequency sweep of elastic hydrogel with 20 mM C_4AG.

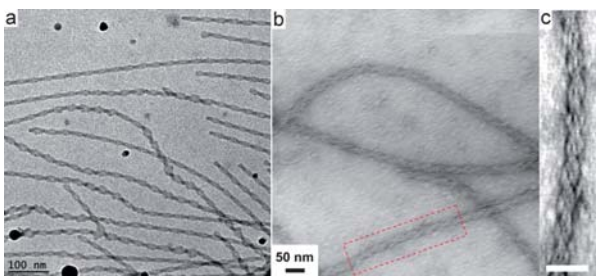

Fig. 2 Double-stranded helix in aqueous solution: (a) cryo-TEM and (b) negative-staining TEM image. (c) Enlarged picture of red line zone in Fig. 2b, which shows left-handed helicity of double helix. The black dot in Fig. 2a is due to the formation of ice crystal during vitrification process. Scale bar in Fig. 2c represents 50 nm.

When elevated to 75 °C, C_4AG can be soluble in aqueous solution. After slowly cooled to room temperature, this solution became bluish and viscous. As the sample concentration was increased to a threshold value, elastic hydrogel can be obtained. This hydrogel can be characterized by up-side-down test (Fig. 1a) and dynamic rheological measurement. From Fig. 1b, it can be seen that the storage modulus (G′) can reach to 10^3 Pa, which was remarkably larger than that of loss modulus (G″). The microstructures formed in C_4AG solution was characterized by cryo-TEM and negative-staining TEM. Large amount of one-dimensional nanofibers were observed in cryo-TEM image, which can be as long as several micrometres (Fig. S1, ESI†). The entanglement of nanofibers was believed to be responsible for solution viscosity enhancement and hydrogel formation. The enlarged cryo-TEM image in Fig. 2a illustrated the existence of double helices with 12–16 nm in width and approximate 25 nm in pitch. Negative-staining TEM also provided evidence of double helix formation (Fig. 2b and 2c).

To investigate helicity of self-assemblies at molecular level, circular dichroism spectroscopy was performed. As Fig. 3a shows, the double helix solution exhibited strong CD signal with a negative Cotton effect (∼ 340 nm) followed by a positive Cotton effect (∼ 290 nm), indicating that dipole moments orientate in an anticlockwise in the aggregates.[17] This microscopic helicity was reflected in the mesoscopic helicity observable under TEM. The intense CD signal revealed strong interaction between azobenzene rings. In a control experiment, no notable CD signal in methanol solution was found, in which the amphiphile will not aggregate (Fig. 3a). It is therefore believed that dichroic signals should not be attributed to molecular chirality but to the supramolecular chirality, which originated from the chiral packing of amphiphiles inside self-assembled aggregates.

The stability of self-assembled double helix was also studied with respect to dilution, heating, and additives (*i.e.* urea and organic solvent). First, it is found that double helical nanofibers can be observed even when the sample was diluted to low concentrations (Fig. 4). The CD result (not shown here) shows that a Cotton effect can be intense at low concentration of 10^{-4} mol L^{-1}, indicating a notable stability of molecular architectures. Second, it is demonstrated that helical nanostructures can exist at the temperature of 50 °C (Fig. S2, ESI†). At higher temperatures, the helical nanostructures can be well-dispersed which gives a less bluish and viscous solution. At lower temperature, helical nanofibers tend to aggregate leading to strongly turbid solution

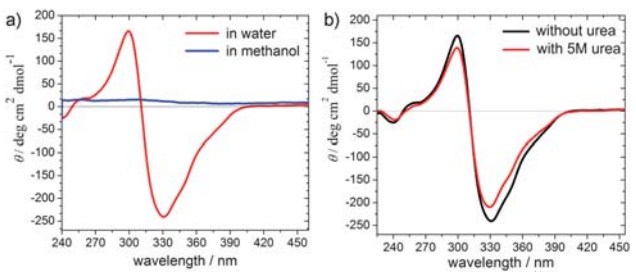

Fig. 3 (a) CD spectra of C_4AG solution in water (light grey) and in methanol (dark grey). (b) CD spectra of C_4AG solution in water: in the presence of urea (light grey) and absence of urea (black).

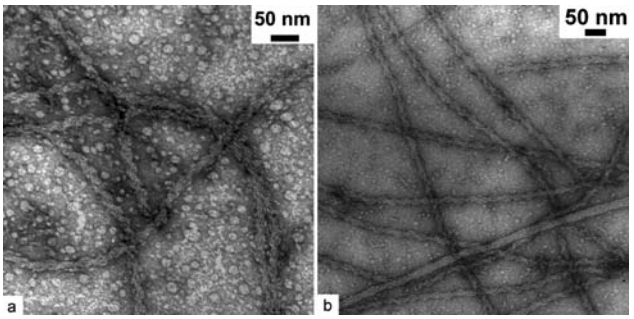

Fig. 4 Negative-staining TEM image of self-assembled double-stranded helix in C_4AG aqueous solution: (a) 0.1 mM and (b) 10 mM.

with low viscosity. Third, the effect of urea addition was also examined. It is well known that urea can break hydrogen-bonds in water which results in proteins being denatured or DNA double chain melt.[18] The self-assembled doubled helix in C_4AG solution seems to be inert to urea addition; even when the concentration of urea reaches 5 M, double helical fibers can be still observed. The circular dichroism spectrum gives evidence for the existence of helical nanostructures in the presence of urea (Fig. 3b). This implies that hydrogen bonds are not the exclusive force driving double helix formation. Finally, it is found that the double helix can survive in the presence of a small amount of organic solvent such as methanol, ethanol, DMSO and DMF.

Exploring the driving force for double helix: structure–performance relationship

In this section, the relationship between molecular structure and mesoscopic assemblies was discussed and the intermolecular forces that governed the self-assembled double helix were suggested. The C_4AG amphiphile was composed of three main parts: hydrophilic sugar, planar azobenzene moiety and hydrocarbon tail. By varying molecular structures, we systematically investigated the structure–performance relationship in a series of compounds. First, the effect of the azobenzene group was considered, which was believed to bring additional π–π stacking to molecular self-assembly. In order to investigate the role of the azobenzene group, we have synthesized three analogous amphiphiles without azobenzene groups (Chart 2a). Helical nanofibers can not be observed in these systems when the azobenzene group is replaced by a saturated aliphatic chain. It is therefore suggested that π–π stacking of azobenzene groups was indispensable for the formation of one-dimensional helix. Second, when the sugar head was replaced by other hydrophilic group (*i. e.* quarter-amino, carboxyl, or glycol), the amphiphilies would self-organize into global micelles or vesicles but not one-dimensional architectures (Chart 2b). This is because sugar group can generate multiple site hydrogen-bonds, which can promote close packing of amphiphiles and simultaneously guild the orientation of molecules within aggregates. The existence of hydrogen-bonding interactions is demonstrated by FT-IR (Fig. S3, ESI†). Finally, we have demonstrated that butyl chain in C_4AG amphiphile was essential for the 1 D nanostructure. Herein we synthesized series of sugar-based amphiphiles with azobenzene moieties (denoted as C_0AG, C_2AG, C_4AG, and C_6AG), in which the hydrocarbon chain was varied (Chart 3). It is found that the amphiphiles with longer hydrocarbon chains (*i.e.* C_4AG and C_6AG) can self-assemble into double helical nanofibers (Fig. 5). However, the amphiphiles with shorter hydrocarbon chains (*i.e.* C_0AG and C_2AG) could not aggregate into well-ordered structures but only thick precipitates. It is proposed that rigid molecules such as C_0AG and C_2AG tend to closely pack into precipitates owing to π–π stacking. The existence of butyl or hexyl groups can interfere with close packing between aromatic groups to avoid precipitate formation.

In summary, a one-dimensional double helix was fabricated cooperatively by multiple weak interactions including the hydrophobic effect, π–π stacking between azobenzene groups

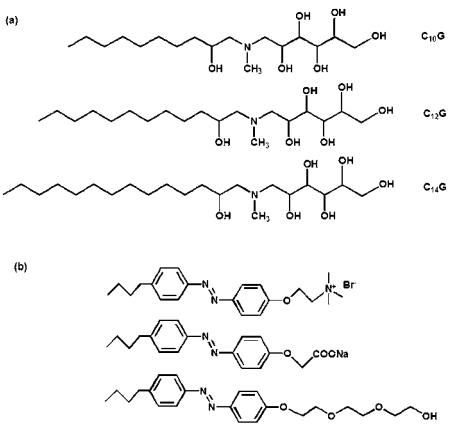

Chart 2 (a) Series of sugar-based amphiphiles without azobenzene group; (b) alkyl azobenzene derivatives without sugar groups.

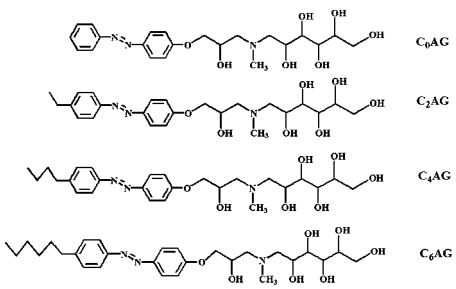

Chart 3 Sugar-based amphiphiles containing an azobenzene moiety with different lengths of hydrocarbon chain, denoted as C_0AG, C_2AG, C_4AG and C_6AG.

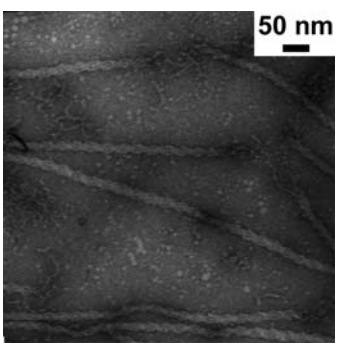

Fig. 5 Negative-staining TEM image of C_6AG in an aqueous solution (1 mM).

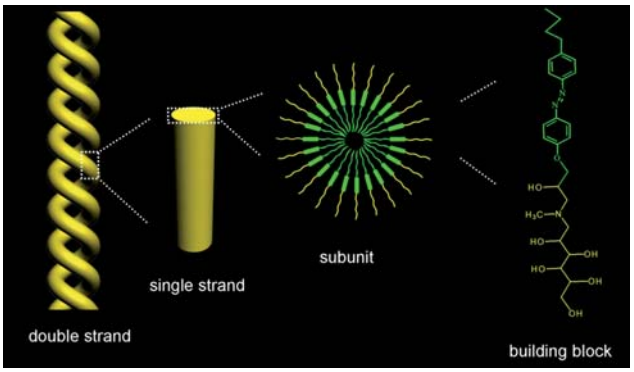

Fig. 6 Representative scheme of double-stranded helix in aqueous solution.

and hydrogen-bonding of sugar moieties. In particular, hydrocarbon chains seem to be essential for supramolecular self-assemblies. Combined with the TEM image, CD spectrum and the above discussions, we have described a representative scheme of double helix formation (Fig. 6). Driven by the hydrophobic effect, π–π interaction and hydrogen bonding, C_4AG molecules can self-assemble into 1 D nanofibers which are analogues to "rodlike micelles". Meanwhile the chiral sugar will not pack parallel but rather pack at a non-zero twist angle with respect to their neighbors, leading the whole nanostructure to twist into a helix. On the other hand, hydrogen bonds arising from sugar groups between two adjacent strands were thought to provide the buckling force to join the two cylinders together.

Morphological modulation of double helix by external stimuli

As demonstrated above, the supramolecular double helix was held together by relatively weak non-covalent interactions, which implied that helical nanostructures might be easily reconfigurable into a variety of morphologies. In this section, we have modulated the self-assembled organizations by external stimuli including pH, light irradiation and surfactant addition.

First, the incorporation of an azobenzene moiety can endow light-activity to the double helix. Azobenzene can undergo photo-induced isomerism accompanied by large structural change as reflected in the dipole moment and change in geometry. The isomerization involves a decrease in the distance between *para* carbon atoms in azobenzene from about 9.0 Å in *trans*-form to 5.5 Å in *cis*-form. Likewise, *trans*-azobenzene has no dipole moment while the dipole moment of the nonplanar *cis*-compound is 3.0 D.[19] As shown in Fig. 7, the C_4AG molecule can realize reversible *trans*/*cis* transitions triggered by UV or visible light, leading to remarkable reduction of the CD signal intensity of the C_4AG solution (Fig. 8a). The DLS data clearly indicated the existence of small particles with 3 nm radius, which is comparable to the molecular length of C_4AG (Fig. 8b). Hence it is proposed that global micelle was formed in C_4AG solution after UV irradiation. The effect of conformational change in azobenzene group may involve two aspects. On one hand, the light-triggered *cis*-azobenzene can be more hydrophilic than the *trans*-form owing to the enhancement of dipole moment. On the other hand, the existence of *cis*-azobenzene may restrict close packing of amphiphiles in the aggregates which is responsible for CD signal decrease. These two factors ultimately gave birth to the transition from helical nanofibers to global micelles.

Second, the amino atom in C_4AG can be protonated with addition of acid which imparted pH-sensitivity to C_4AG self-assemblies (Fig. 9). The pK_a of C_4AG in aqueous solution is 8.9. It can be noted that the addition of acid can lead to the trans-formation from helical nanofibers to small micelles, accompanied by the disappearance of Cotton effect (Fig. S4 and S5, ESI†). It is rationalized that the protonation of amino group can greatly enhance molecular hydrophilicity and also brings electrostatic repulsion between amphiphiles, which are not conducive to higher-ordered self-assemblies.

Third, as we have declared that, double-stranded helix was held together by attractive interaction of hydrogen bond. It is hence reasonable that when the repulsive effect was introduced into the double strands, people can unfold the double helix in controllable fashion just as the DNA chains melt. Herein, we have actually succeeded by incorporating ionic surfactant into a double helix. As Fig. 10a shows, fragmentized unfolded

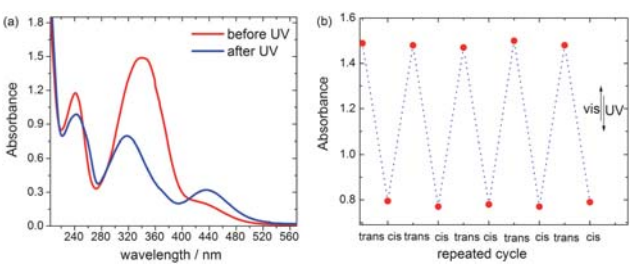

Fig. 7 (a) UV-vis of C_4AG solution before and after UV irradiation; (b) repeated UV-vis absorbance of C_4AG solution, which illustrated the reversibility of photo-triggered *trans*/*cis* transition.

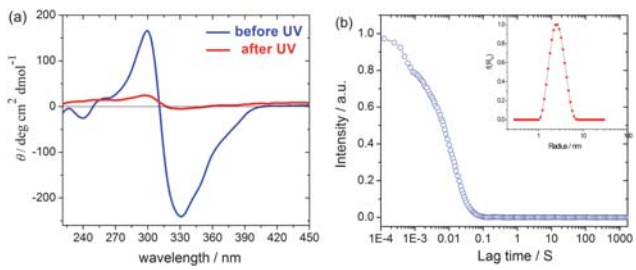

Fig. 8 (a) CD spectrum of C_4AG molecule in aqueous solution before and after UV irradiation; (b) dynamic light scattering of C_4AG solution after UV irradiation, which indicates the existence of small micelles.

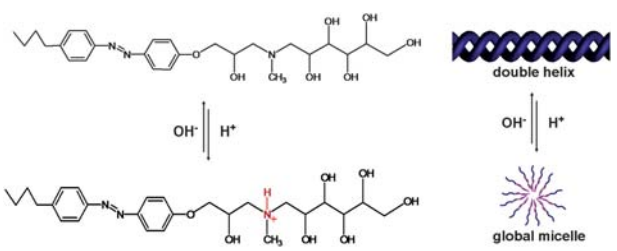

Fig. 9 Structural change of C_4AG molecular with addition of acid or base.

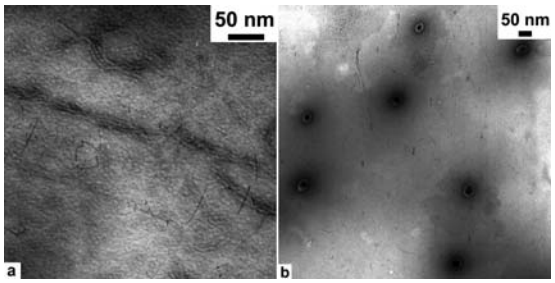

Fig. 10 Negative-staining TEM image of C_4AG solution in the presence of ionic surfactant: (a) fragmentized unfolded single-stranded nanofibers caused by addition of sodium dodecyl sulfonate; (b) global vesicles induced by SDBS.

nanofibers can be clearly observed with the addition of sodium dodecyl sulfonate. This can be rationalized that ionic surfactant can penetrate into helical aggregate owing to hydrophobic effect and impart electrostatic repulsion to the adjacent helix which can result into the unfolding of the double helix. Similar results were also found by using other ionic surfactants. Further addition of ionic surfactants can result into the dissociation of nanofibers. In addition, the double nanohelix can be shaped into global vesicles with the addition of sodium dodecylbenzene sulfonate (SDBS) (Fig. 10b). The vesicles exhibit uniform diameter of 40–50 nm. It is proposed that aromatic group in sodium dodecylbenzene sulfonate may contribute to vesicle formation.

Conclusions

In conclusion, a hierarchical self-assembled double helix was fabricated by a novel amphiphile of glucose-based lipid. The driving forces for the self-assembled architectures are proposed to be multiple weak interactions including hydrophobic interaction, aromatic stacking and hydrogen bond. In addition, morphological modulation of supramolecular double helix can be rationally realized by external stimuli, such as pH, light, and surfactant addition. Triggered by external inputs, double-strand helix can be shaped into spherical micelle or vesicle. Meanwhile we have for the first time realized unfolding double-stranded helix into single-stranded nanofibers by introducing repulsive effect into the aggregates. We hope our work can help to understand helical structures in life (*i.e.* DNA, protein β-sheet, *etc.*) and also the self-assembled complex architectures in nature. In addition, the supramolecular self-assembled double helix is anticipated to be exploited to mimic DNA biomineralization to direct inorganic double-stranded helices synthesis.

Acknowledgements

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