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COMMUNICATION

Optical modulation of supramolecular assembly of amphiphilic photochromic diarylethene: from nanofiber to nanosphere†

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A diarylethene derivative with histamines as side chains was synthesized and the morphology of self-assembled supramolecular architecture can be tuned from nanofiber to nanosphere by photo irradiation. The theoretical calculation and model of the self-assembled nanostructure are presented to illuminate the possible self-assembly mechanism.

Organic photochromic molecules have gained much attention for potential applications in optical memory and photo-switches.[1–3] So far, considerable attention has been focused on photochromic diarylethenes due to a high conversion efficiency of reversible photochromic reactivity, excellent thermal stability of both isomers and good fatigue resistance.[4–7] Diarylethenes have shown great promise as new materials for optoelectronic devices and molecular switches.[8–12]

The construction of a supramolecular architecture by a spontaneous self-assembly of molecules is currently a subject of great interest in various areas that range from chemistry, biology to materials science.[10] A supramolecular amphiphile is a useful building block to fabricate soft materials with controlled structure and functions on the basis of noncovalent interactions including amphiphilicity, hydrogen bonding, π–π interaction and so on. Among the self-assembly architecture, a nanostructure with stimuli responsive properties has stimulated special interest as a promising candidate for smart materials.[12] Therefore, it is very important for a reasonable design of externally dressable, responsive molecules that contain self-assembly elements, as these can construct a highly organized nanostructure and give rise to so-called "smart soft materials" for material chemistry.

Photoirradiation is an attractive stimulus since it provides a very broad range of tunable parameters, *e.g.*, wavelength, duration and intensity, which can be modulated in the potential applications.[13–15] The photo triggered self-assembled structure by using various types of photochromic compounds has been previously reported by Zhang group, Zhang group and Hamachi group.[11] The open-ring isomer of the diarylethene possesses a relatively loose twisted conformation, whereas the closed-ring isomer has a stiff planar structure. Although the geometrical structure change of diarylethene is relatively small, the difference in rigidity and conjugation associated with photochromism is anticipated to induce change of non-covalent interaction. Therefore, this change results in the formation, dissociation and reformation of the self-assembled supramolecular architecture.[16]

The semi-fluorinated group is a highly amphiphobic group, which has been widely used for achievement of a hydrophobic surface.[17] It is highly reasonable to anticipate that a diarylethene amphiphile with a semi-fluorinated group and an amphiphilic group will self-assemble into a responsive supramolecular architecture. However, to the best of our knowledge, the investigation of supramolecular behavior of the diarylethene amphiphile with a semi-fluorinated group and an amphiphilic group moiety still remains rare. Herein, in this communication, the synthesis and self-assembly machinery of a diarylethene derivative that bears a substitute of histamine is presented (Scheme 1). We demonstrate that the morphology of a supramolecular architecture could be tuned from nanofiber into nanosphere by photoirradiation.

Photochromic reactivity of diarylethene **1** was examined in methanol. It indicates that the diarylethene is molecularly dispersed in the methanol solution. There exists minor possibility for formation of an aggregate (Fig. S1, ESI†).

Photochromic behavior was also observed in aqueous solution (Fig. S2, ESI†). With increasing pH value, the intense absorption intensity of the open-ring isomer at 220 nm reduced, in the meanwhile, the absorption of the visible region enhanced and the solution became turbid (Fig. S3, ESI†). The phenomenon may indicate a successful self-assembly in the solution. For the aqueous solution of the closed-ring isomer, the absorption of the visible region also enhanced as the pH value was increased and the color of the solution converted from turkey red to dim red correspondingly. Furthermore, the absorption band of the photochromic diarylethene is gradually blue-shifted, indicating corresponding self-assembly in the aqueous solution of the closed-ring isomer.

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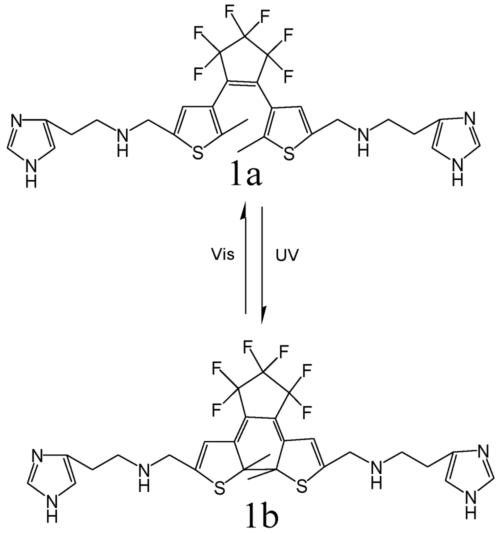
† Electronic supplementary information (ESI) available: Synthesis and characterization of the compound, experimental procedures, UV-vis spectra, the illustration of the color and turbidity change of the aqueous solution when varying the pH value and illumination conditions, DSL of the aqueous solution, AFM image. See DOI: 10.1039/c1cc11385b



Scheme 1 Photochromism of diarylethene with histamines as side chains.

To examine the behavior of the assembly at different pH values in the aqueous solution of the diarylethene, DLS measurements were carried out.[16] For the closed-ring isomer, the peak corresponding to the size of around 650 nm was observed at pH 6.4 (Fig. S4, ESI†). However, when the pH value was 3.5, the light scattering signal was too weak to obtain an apparent size distribution signal. As the pH value increased, the size of the aggregate reduced and the span of the size increased as shown in Fig. S4 (ESI†). This resorts from further reassembly owing to the larger pH value. However, for the open-ring isomer, the change of the size is random and disordered as the pH value increased, which may be originated from a non-spherical morphology.[17] For a fair comparison, the methanol solution of diarylethene **1** was also detected by DLS and no apparent aggregation signal was found, which was consistent with the absorption spectra (Fig. S4, ESI†).

SEM and AFM imaging was used to visualize the self-assembled nanostructure. As shown in Fig. 1, for the open-ring isomer, nanofibers were observed when the pH value was larger than 6.4. The nanofibers stack each other with the length of about 3 μm, which proved the above speculation. It is shown from the AFM image that the width of the nanofiber is about 86 nm (Fig. S5, ESI†). When the solution was irradiated with 254 nm light, the morphology changed from nanofiber to nanosphere (Fig. S6, ESI†). The conversion between nanofiber and nanosphere in the solution is reversed when the irradiation light is tuned after enough time for assembling. The nanostructure is stable upon shaking on the silicon chip. The nanosphere has a solid structure as observed from TEM characterization (Fig. S7, ESI†). The observed diameter of the nanosphere ranged from 600 nm to 700 nm. As can be seen from Fig. 2, the average diameter of the nanosphere could be tuned with the pH value of the solution, transiting from the range between 600 and 700 nm to the range between 200 and 300 nm as the pH value changed from 6.4 to 7.9. These imaging results were substantially compatible with DLS observation. With the pH value increasing, the diameter of the nanosphere becomes smaller. It is obvious that the amphiphile was composed of two main parts: the hydrophobic perfluorocyclopentene group and the hydrophilic histamine group. The intermolecular forces including the hydrophobic effect, π–π stacking and hydrogen-bonding between the molecules and solvent governed the self-assembling behavior. From the above investigation, it can be concluded that the conversion of the self-assembled nanostructure is mainly originated from structural conformational conversion between the open-ring isomer and closed-ring isomer, which influences the change of some weak force, and consequently the change drives the reassembly.

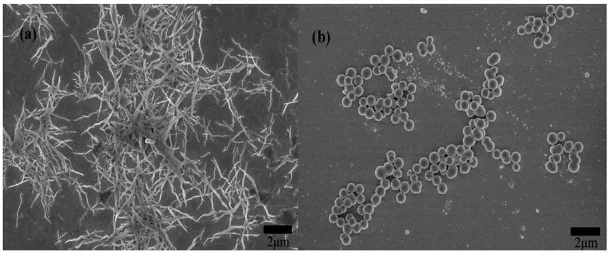


Fig. 1 (a) SEM image of the self-assembled nanofiber of the open-ring isomer in H_2O (0.2 mg mL^{-1}, pH = 6.4); (b) SEM image of the self-assembled nanosphere in H_2O upon irradiation for 30 s.

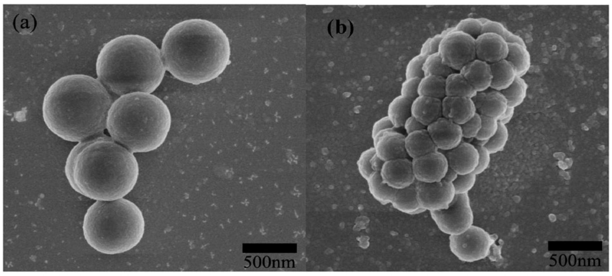
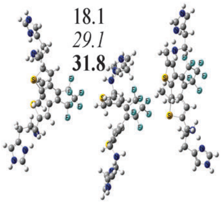
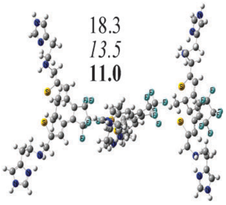
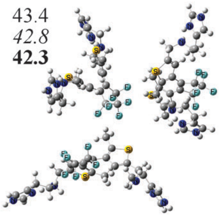
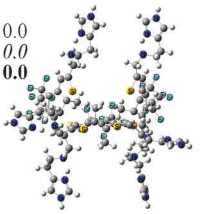


Fig. 2 SEM image of the self-assembly nanoparticles of the closed-ring isomer in H_2O (a) 0.2 mg mL^{-1}, pH = 6.4, (b) 0.2 mg mL^{-1}, pH = 7.9.

To prove the speculation, the histamine group was substituted by the malononitrile group. A similar one dimensional structure with a helical structure assembled at the open-ring isomer and nanosphere morphology at the closed-ring isomer was obtained respectively (Fig. S8, ESI†). It is noted that the morphology is not dependent on the pH value. This observation proved that histamine is essential for the morphology dependent on the pH value.

To understand the tropism of supramolecular architecture, the calculations were carried out employing a B3LYP functional equipped with a 3-21G basis set implemented using a suite of Gaussian 03 program package. The open-ring and the closed-ring isomers are taken as the prototype to illustrate the assemble phenomenon. Solvent effects are estimated on the basis of the gas-phase geometries employing the diethylether and water solutions. The dielectric constant is 4.24 and 78.35, respectively. Taking the energy of the self-assembly nanosphere of the closed-ring isomer in acidic conditions as the respective zero point, the relative energies in gas-phase, diethylether and water solvents are represented in Table 1 with normal, italic, and bold characters. Although the relative energy in different phases is distinct, the open-ring isomer is

Table 1 The energy of the self-assembled nanofiber and nanosphere

Relative energy/ kcal mol^{-1}	**1a**·2H$^+$(open ring)	**1b**·2H$^+$ (closed ring)
Nanofiber	 18.1 *29.1* **31.8**	 18.3 *13.5* **11.0**
Nanosphere	 43.4 *42.8* **42.3**	 0.0 *0.0* **0.0**

composed predominantly of the nanofiber conformation, while the closed-ring isomer prefers the nanosphere structure.

It was reported that histamine possesses two pK_a values (pK_{a1} = 5.8, pK_{a2} = 9.4).[18] Therefore, when the pH value is larger than pK_a, the protonated histamines located on two sides lost the protons. Concomitantly, the dipole moment of the diarylethene decreases significantly, as is reflected in Table 1. Therefore, the intermolecular combination strength weakens under high pH conditions when the assembly occurs. In other words, the degree of polymerization or aggregation under the acidic conditions is larger than that in the basic environment. Thus, it is reasonable that the radii of the self-assembly nanosphere of the closed-ring isomer is larger under low pH conditions.

In summary, we have synthesized an amphiphilic diarylethene derivative with histamines as side chains and investigated its photochromic properties and light triggered self-assembling behavior. The molecule can self-assemble into a nanostructure at an enhanced pH value. For the open-ring isomer, a nanofiber was obtained at a pH value larger than 6.4. After UV irradiation, the morphology was changed from nanofiber into nanosphere. A possible formation mechanism was presented based on theoretical calculations. This responsive architecture is of high potential for smart soft material and devices.

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