

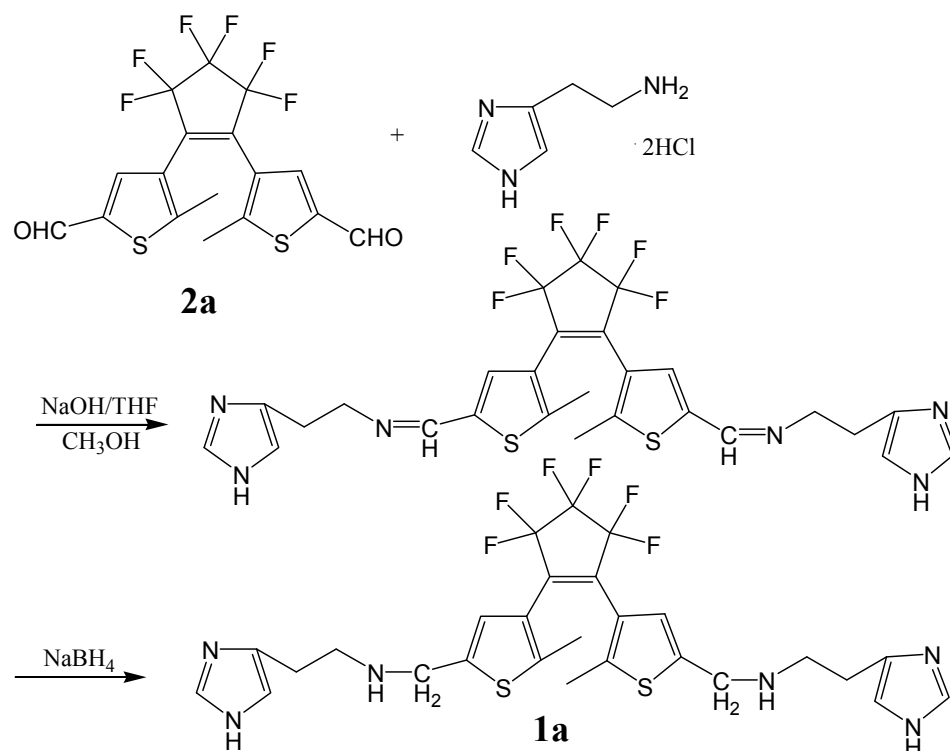
Supplementary Information for

Optical Modulation of Supramolecular Assembly of Amphiphilic Photochromic Diarylethene: from Nanofiber to Nanosphere

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1. Synthesis and assembly of the diarylethene

Diarylethene 1a was prepared from 2a (Scheme S1). First, the histamine dihydrochloride (1.84 g) and sodium hydroxide (0.8 g) were dissolved in freshly distilled diethylene oxide (10 mL) and absolute methanol (30 mL). Then diarylethene 2a (0.6 g) was added to the solution. The resultant mixture was stirred at room temperature for ten hours after sodium borohydride (0.5 g) was added. And the final solution was stirred for twelve hours at 0 °C, then was diluted with methylene dichloride (25 mL) and washed with saturated sodium chloride solution. The methylene chloride was removed and the residue was chromatographed over alkaline alumina with CH₂Cl₂:CH₃OH = 2:1. Yield 0.51 g (58 %) of 1a. MS: m/z (M⁺) 615.16; ¹HNMR (Figure S11): (600 MHz, DMSO): δ 1.84 (s, 6H), δ 2.78 (d, 4H), δ 2.88 (d, 4H), δ 4.12 (s, 4H), δ 6.85 (s, 2H), δ 7.15 (s, 2H), δ 7.60 (s, 2H). Diarylethene 2a was synthesized from 5-methyl-2-thiophenecarboxaldehyde according to previously reported literatures¹.



Scheme S1 Synthetic route of diarylethene with histamine as side chain.

The pH value of the aqueous solution containing the diarylethene was adjusted with HCl and NaOH correspondingly, 2 mg diarylethene was dissolved into 5 ml aqueous solution containing 10^{-3} mol/L hydrochloric acid, then the pH value was adjusted with NaOH solution. The aqueous solution was put for twelve hours at room temperature for good assembly. When the pH value was larger than 6.4, the aqueous solution became turbid (the concentration of the solution is 0.02 mg/mL).

The assembling behavior at different pH value was characterized by UV-Vis absorption spectra, dynamic light scattering (DSL), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. Structural and Property characterization

For light-triggered open/closed transition, the sample was irradiated with 254 nm UV mercury lamp (10 W). The sample was placed in a quartz tube, and irradiation was done for a specific duration. For a transition from closed state to open state, irradiation by visible light was performed using an incandescent light bulb (> 440 nm)

UV-Vis absorbance measurements of solution were carried out on the spectrophotometer of Cary50 at 25°C . DLS was performed with a Zetasizer Nano S90 spectrometer. SEM was performed with a Hitachi mode S-4800 apparatus with an accelerating voltage of 3 kV. The aqueous solution of the diarylethene (0.2 mg/mL) with different pH value was dropped to the silicon wafer at different pH value, and then dried in the drier, subsequently for further measurement. The detailed morphology of the sample was obtained by AFM (Agilent AFM 5400).

Photochromic reactivity of diarylethene 1 was examined in methanol. Fig. S1 shows absorption spectra of the diarylethene in methanol with 254 nm light during irradiation. Upon the irradiation the colorless solution of open-ring isomer (1a) turned red due to the appearance of the new visible absorption band centered at 547 nm attributable to the closed-ring isomer (1b). The red solution converted to colorless upon irradiation with visible light, indicating that close-ring isomer returned to the initial state 1a, at the same time, an apparent isosbestic point was observed at 238 nm. This process could be repeated several times with no sign of photochemical damage. This indicates that the diarylethene is molecularly dispersed in the methanol solution. There exists minor possibility for formation of aggregates.

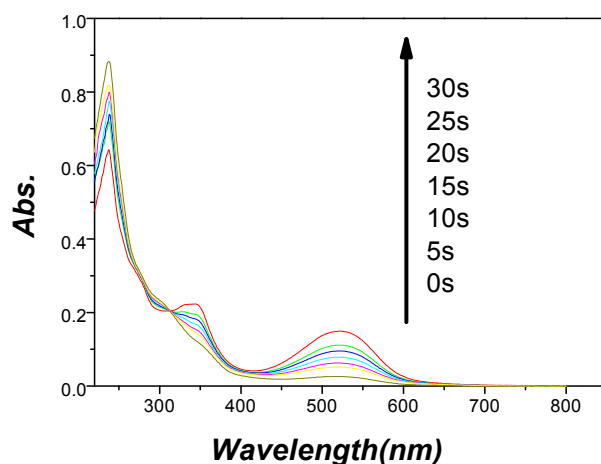


Fig. S1 The absorption spectra of the diarylethene (2.0×10^{-5} M) in methanol solution upon irradiation with 254 nm light.

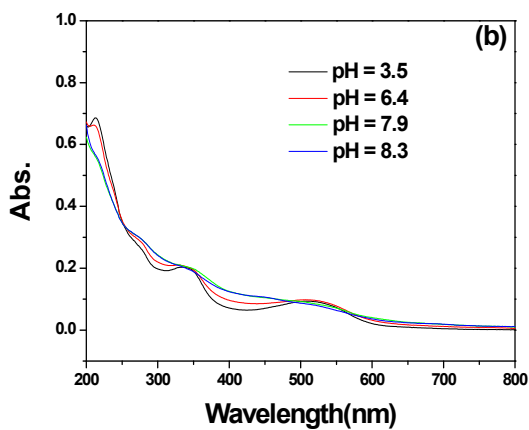
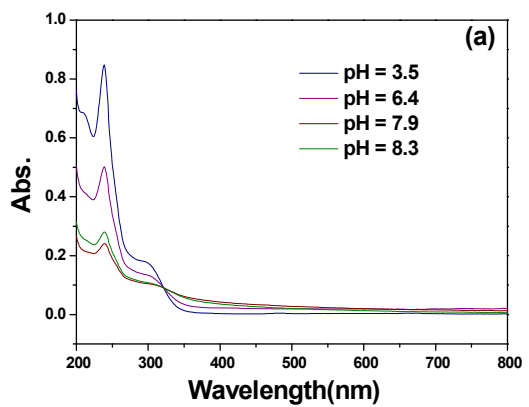


Fig. S2 The absorption spectra of (a) open-ring isomer and (b) closed-ring isomer (2.0×10^{-5} M) at different pH value in water at room temperature.

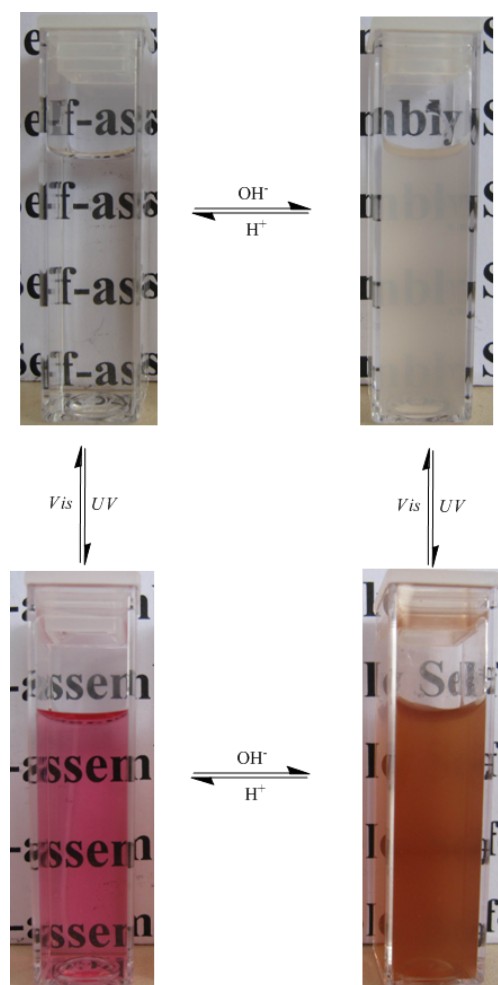


Fig. S3 The illustration of the color and turbid change of the aqueous solution when varying the pH value and illumination condition.

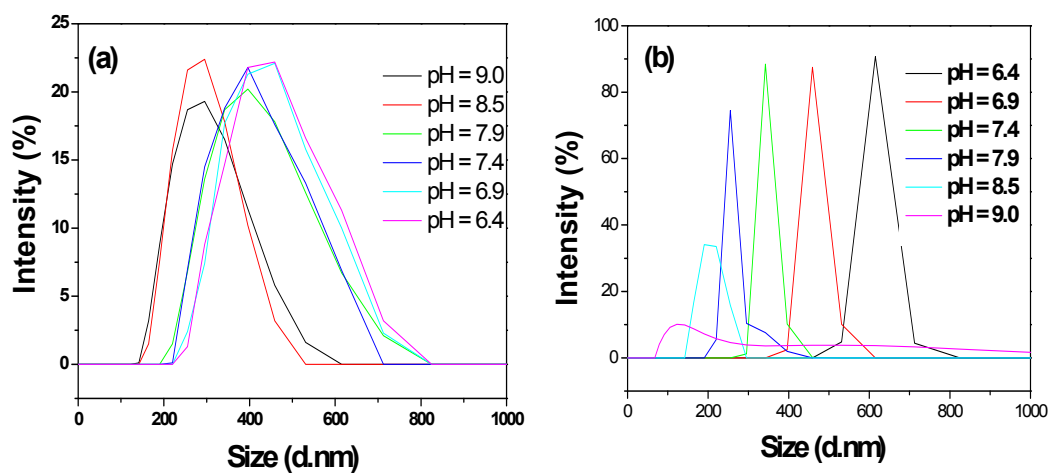


Fig. S4 DSL of the aqueous solution of diarylethene 1 (a) open-ring isomer and (b) closed-ring isomer (0.2 mg/mL) at different pH value.

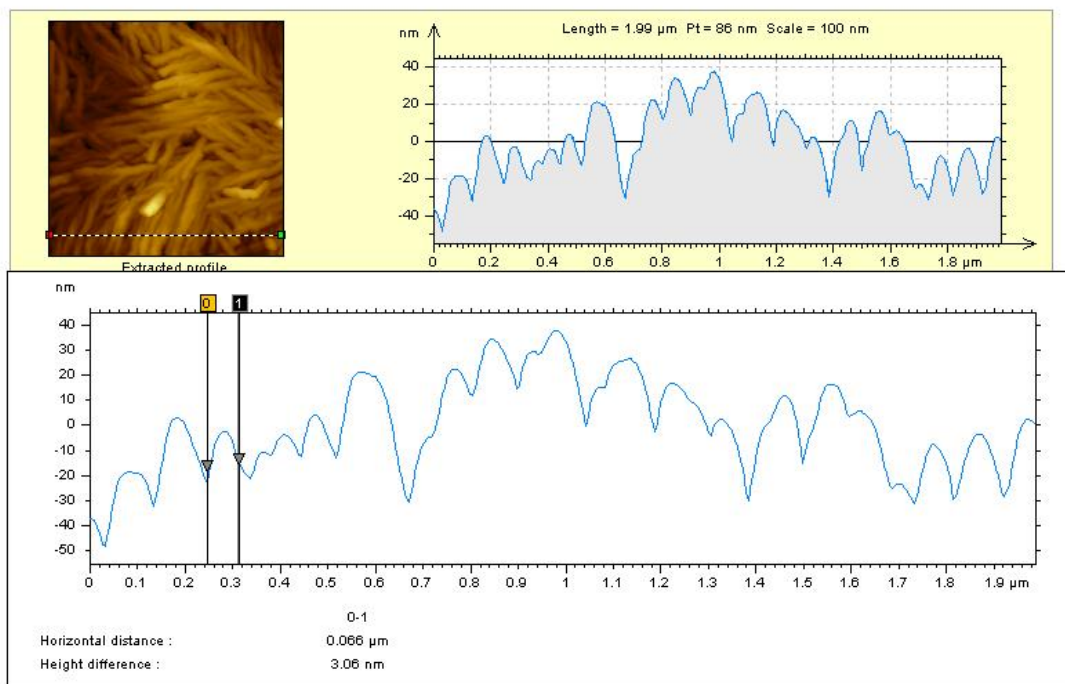


Fig. S5 AFM image of the self-assembly nanofiber of the open-ring isomer in H_2O (0.2 mg/mL pH=6.4).

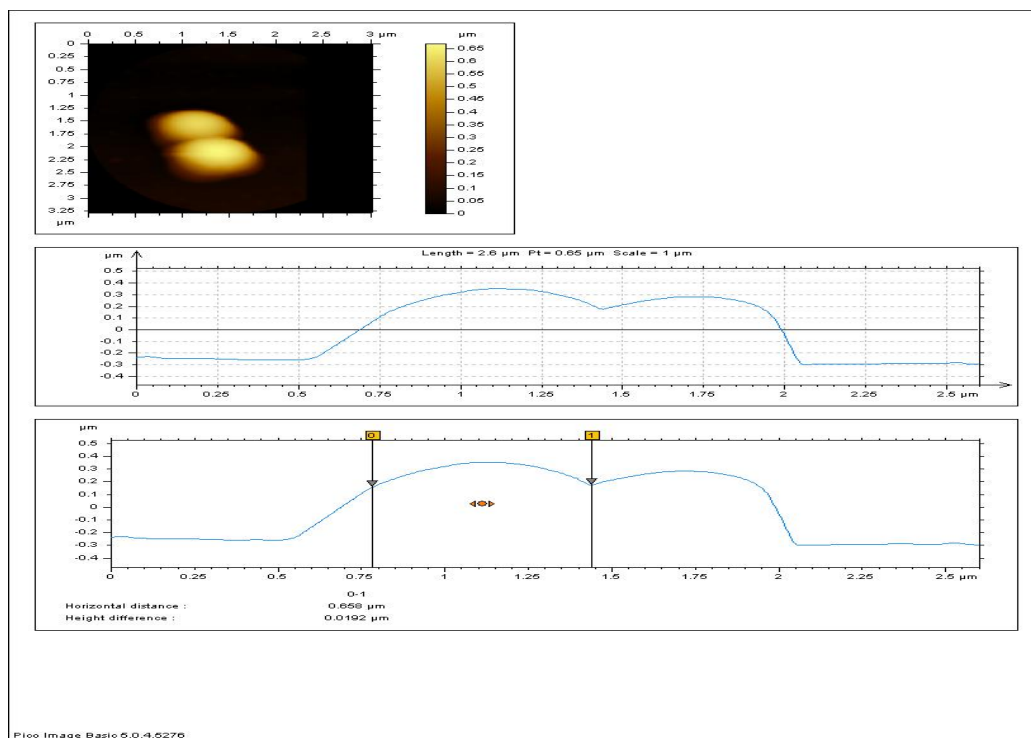


Fig. S6 AFM image of the self-assembly nanosphere in H_2O upon 30 s UV irradiation (0.2 mg/mL pH=6.4).

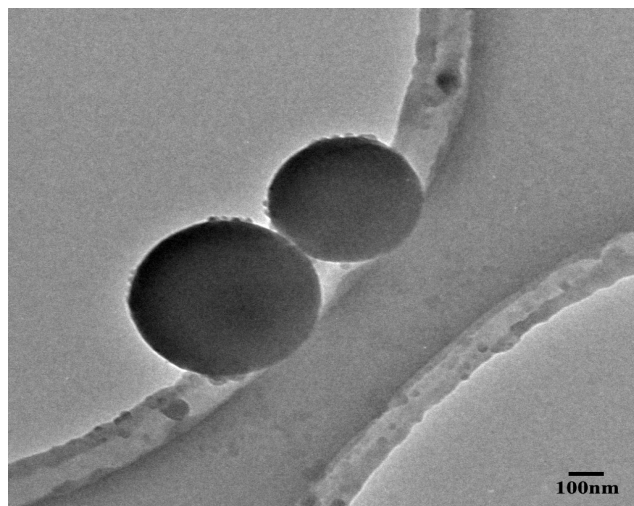


Fig. S7 TEM image of the self-assembly nanosphere of the closed-ring isomer in H₂O (0.2 mg/mL, pH=7.9).

3. SEM image of diarylethene with malononitrile group as the side chain

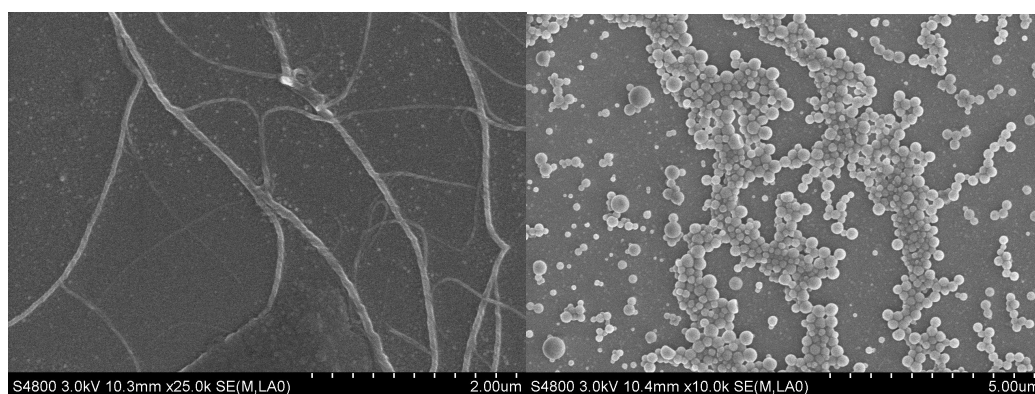
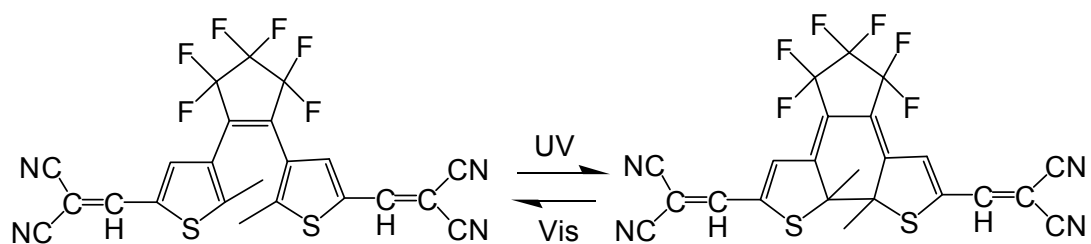


Fig. S8 (a) SEM image of the self-assembled helical nanofiber of the open-ring isomer in H₂O and THF (0.2 mg/mL, pH=6.4); (b) SEM image of the self-assembled nanosphere upon UV irradiation.

Reference

- [1] S. L. Gilat, S. H. Kawai, J.- M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 1439.