

## Supporting Information

### **The morphology transformation from helical nanofiber to helical nanotube in a diarylethene self-assembly system.**

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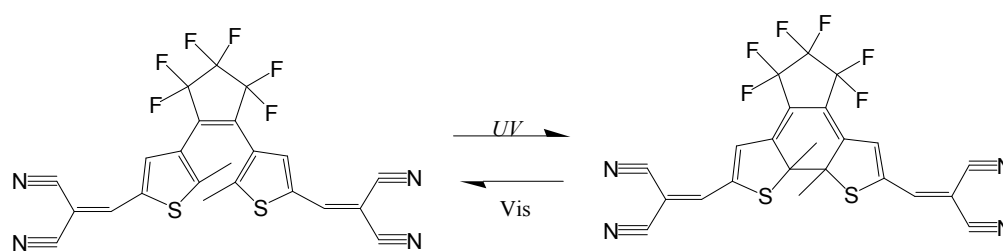
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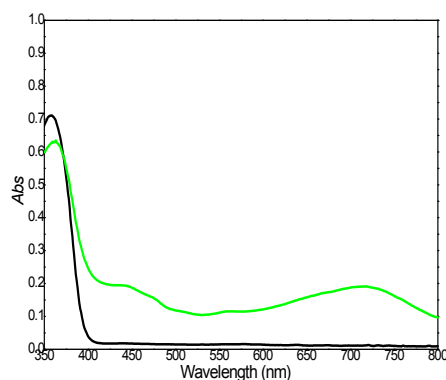
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## Molecule structure and ultraviolet - visible (UV-Vis) Absorption Spectrum

The molecule presented here is based on a diarylethene photochromic unit functionalized with two malononitrile groups. UV-visible spectra were recorded on a Varian Cary 5 UV-Visible spectrophotometer. Photochromic reactivity of the diarylethene was examined in tetrahydrofuran(THF) induced by 365 nm UV light. Fig. S1 shows absorption spectra of the diarylethene in THF before and after UV irradiation. Upon irradiating the colorless solution of open-ring isomer turned cyan due to the appearance of the new visible absorption band centered at 725 nm attributable to the closed-ring isomer. The cyan solution converted to colorless upon irradiation with visible light, indicating that close-ring isomer returned to the initial state. This process could be repeated several times with no sign of photochemical damage. This indicates that the diarylethene is molecularly dispersed in the THF solution.



**Scheme S1.** The structure change of the diarylethene when irradiated with ultraviolet light or visible light.



**Figure S1.** The UV-Vis absorption spectrum of the diarylethene in the THF solution ( $1 \times 10^{-5}$  mol/mL), black line: before UV irradiation, green line: after 365 nm UV irradiation.

## Self-assembly method

Helical nanostructure (Figure. S2)

Helical nanofiber self-assembly by the open-ring isomer:

THF solution (1 mg/mL) was dripped to distilled water slowly at the temperature between 30°C and 50°C, then stood for 6 hours at confined conditions and naturally cooled to room temperature, and then helical nanofiber was obtained.

Helical nanotube self-assembly by the photo stationary state:

THF solution was irradiated with 365 nm UV light for 15 minutes then dripped to distilled water slowly at 30°C and 50°C, the sample was left standing in the dark conditions and naturally cool to room temperature after 6 hours.

#### **Scanning electron microscopy (SEM):**

SEM was performed with a Hitachi mode S-4800 apparatus with an accelerating voltage of 3 kV. The self-assembly structure of the diarylethene formed in the solution at different temperature (30°C, 40°C, 50°C) was dropped to the mica plat, and then natural drying at room temperature, the sample were dealt with the high vacuum gold jetting for one minute before SEM observation.

#### **Transmission electron microscopy (TEM):**

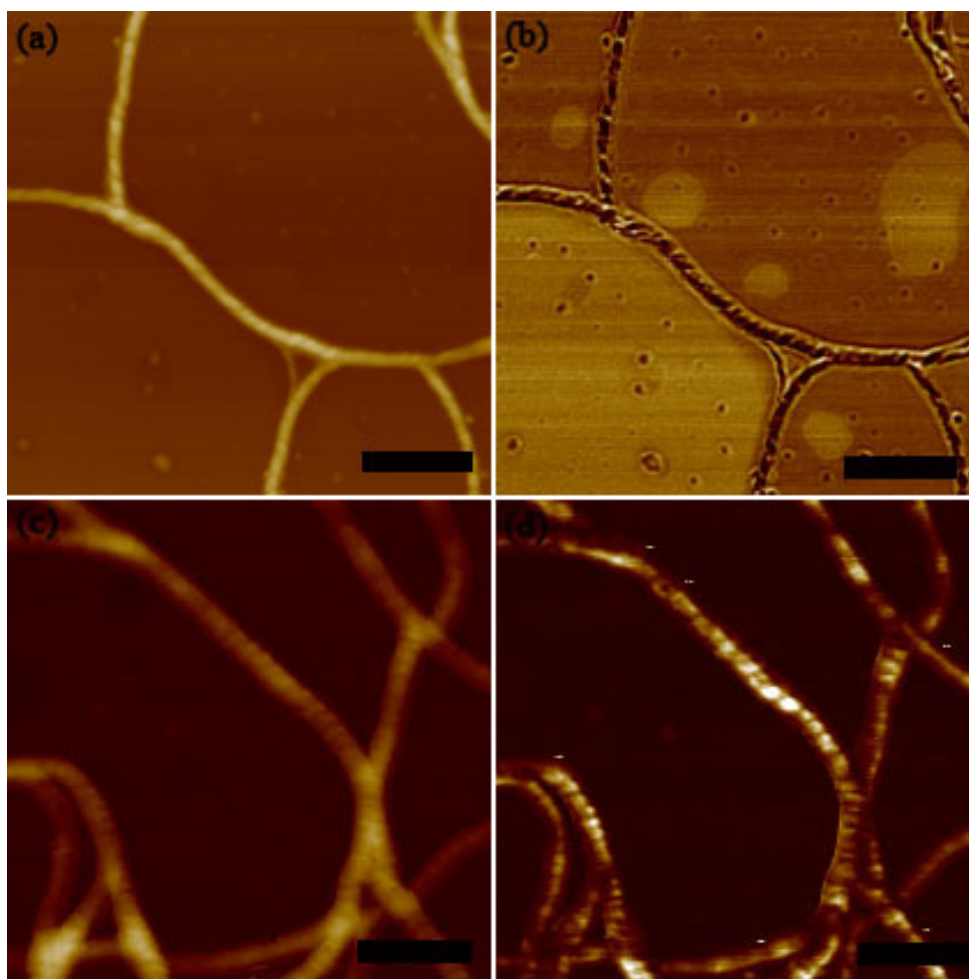
TEM studies were performed by using Hitachi H-7000 TEM operating at 80 kV accelerating voltage. The samples were prepared by drop-casting of the THF/water solution of the diarylethene which was formed before or after UV irradiation at 30°C onto carbon coated copper grids (400 mesh).

#### **Atomic Force Microscopy (AFM):**

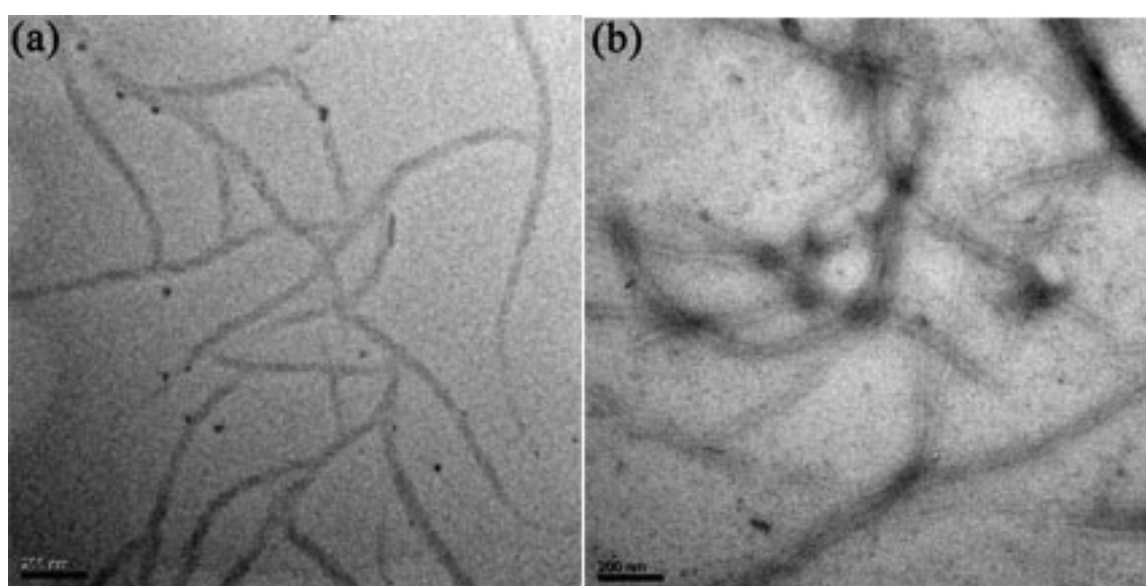
AFM studies were performed with Agilent AFM 5400 by tapping mode, the samples were prepared by drop-casting of the as assembled solution to the mica plat.

#### **Small angle X-ray diffraction (SAXD):**

SAXD studies were recorded using a Bruker-AXS micro-diffractometer (D8 ADVANCE) with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) from 2° to 7° at a scanning speed of 0.2° min<sup>-1</sup>, the samples were prepared by drop-casting of the as assembled solution of the diarylethene onto the mica plat.



**Figure S2.** Typical AFM image of helical structures formed from the diarylethene. (a) before the UV irradiation, (b) after the UV irradiation, (c,d) the corresponding phase image. Scale bar: 500 nm.

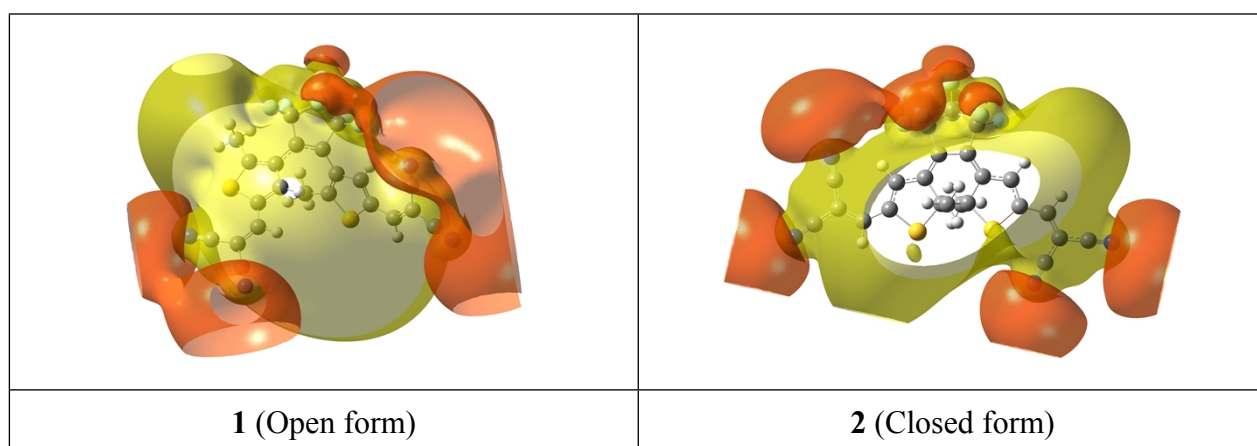


**Figure S3.** Typical TEM image of helical nanofiber and nanotube formed from the diarylethene before and after the UV irradiation.

## Theoretical calculation

The optimizations were performed employing the hybrid B3LYP functional equipped with 6-31G\* basis set. The commonly used polarizable continuum model (PCM) is employed with the tetrahydrofuran (THF) solvent throughout the calculations implemented using a suit of Gaussian 09 program package.

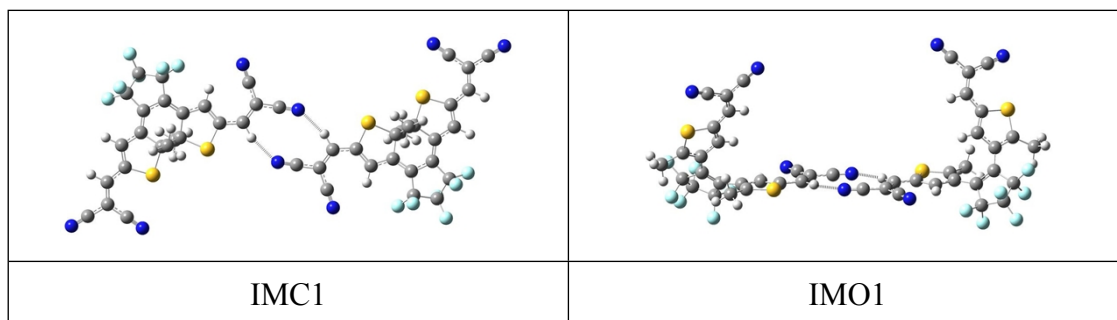
The molecular electrostatic potential (ESP) contour maps of the open and closed form represented in the bellow figures illustrate that it is electronegative around the  $C\equiv N$  groups and the fluorine atoms, while the electropositive potential is generated around the C-H groups. Thus, the  $C\equiv N\dots H-C$  and  $F\dots H-C$  interactions are expected to be function during the self-assembly process. Fortunately, it is the case for the optimized dimer and the tetramer of both the closed form and the open form. The difference between the tetramers of the closed form and the open form lies in their hydrogen bond type, in other words, the  $C-F\dots H-C$  intramolecular hydrogen bond is predominant in the closed tetramer, while the main intramolecular interaction in the open tetramer is the  $C\equiv N\dots H-C$  coupling.



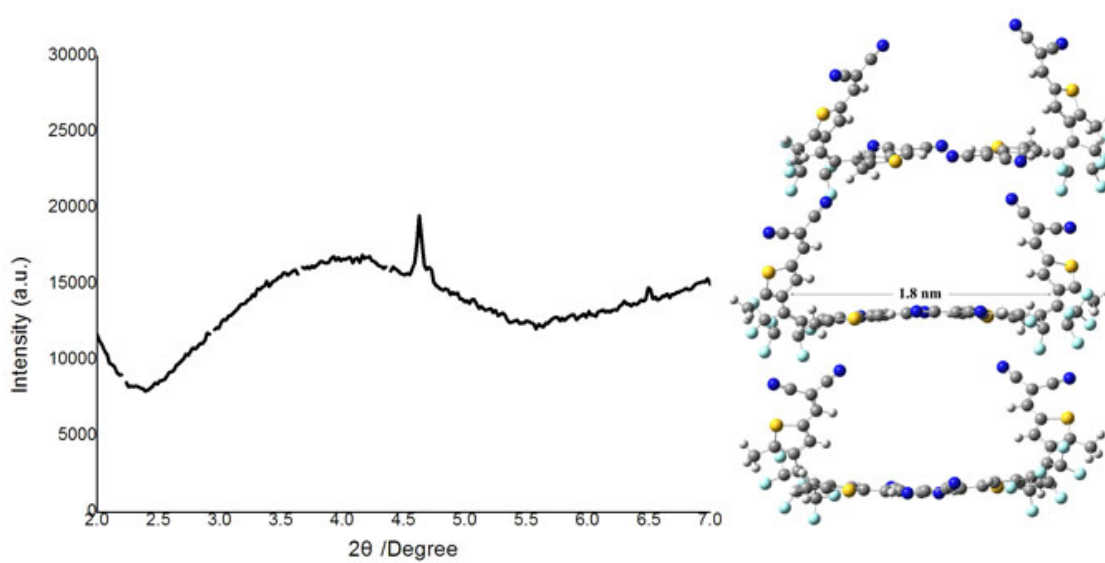
**Figure S4.** The molecular electrostatic potential (ESP) contour maps of the open and closed form

**Table S1.** The relative energy ( $E_{\text{relative}}$ ) and the binding energy ( $E_{\text{binding}}$ ) of the dimers.

| Dimer   |               |                       |                      |         |                |                       |                      |
|---------|---------------|-----------------------|----------------------|---------|----------------|-----------------------|----------------------|
| Complex | HF            | $E_{\text{relative}}$ | $E_{\text{binding}}$ | Complex | HF             | $E_{\text{relative}}$ | $E_{\text{binding}}$ |
| IMC1    | -4993.4349628 | 41.6                  | -4.1                 | IMC2    | -4993.43071603 | 44.3                  | -1.4                 |
| IMC3    | -4993.4320817 | 43.4                  | -2.3                 | IMC4    | -4993.43469274 | 41.8                  | -3.9                 |
| IMC5    | -4993.4333597 | 42.6                  | -3.1                 | IMC6    | -4993.43106056 | 44.1                  | -1.6                 |
| IMC7    | -4993.4306878 | 44.3                  | -1.4                 | IMC8    | -4993.43165667 | 43.7                  | -2.0                 |
| IMC9    | -4993.4304539 | 44.4                  | -1.2                 | IMC10   | -4993.43102775 | 44.1                  | -1.6                 |
| IMO1    | -4993.5012593 | 0.0                   | -4.2                 | IMO2    | -4993.49872463 | 1.6                   | -2.6                 |
| IMO3    | -4993.5007597 | 0.3                   | -3.9                 | IMO4    | -4993.49869646 | 1.6                   | -2.6                 |
| IMO5    | -4993.4963271 | 3.1                   | -1.1                 | IMO6    | -4993.4988234  | 1.5                   | -2.7                 |



**Figure S5.** The mode employed by dimer IMC1 for the closed isomer and the modes of dimer IMO1 for the open form. The hydrogen bonds are represented with the dashed line.



**Figure S6.** The SAXD of the nanofibers self-assembly from the open-ring isomer of the diarylethene and the theoretical simulation interplanar spacing of the partially orderly arranged molecule.