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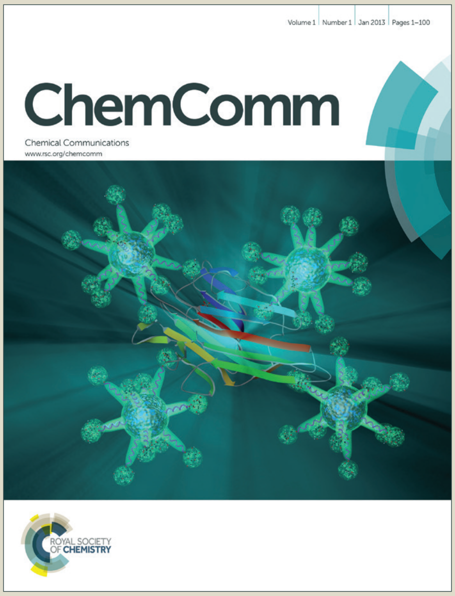

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**ARTICLE TYPE**

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

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**A helical nanostructure can be obtained by self-assembly of a diarylethene derivative that bears two malononitrile substitutes in the tetrahydrofuran/water medium. It is revealed that the helical nanostructure changed from helical nanofiber to helical nanotube when the diarylethene monomer changed from the open-ring isomer to the closed-ring isomer as irradiated with 365 nm ultraviolet light, meanwhile, the helix angle of the nanostructure changed from 50 ° ± 5 °to 75 ° ± 5 °. There is great possibility that the helical nanofibers and the helical nanotubes are assembled from the dimer as the base units based on the theoretical calculation and the experiments results.**

Helical structures are common structural motifs in biomolecules and played a pivotal role in structural stability, signal transduction, genetic reading out and transcription which are involved in the storage of genetic information in biological systems such as protein and DNA[1]. Artificial construction of a helical structure is significant to fabricate functional materials[2] and understand the non-covalent forces that hold the helical structures together[3]. The creation of artificial helical structures in relation to control self-assembly has received great interest in the past decades[4-7]. However, the structure feature of the helix have received relatively little attention and the architecture control of the helical structures remains a great challenge[8].

As an optical switchable molecule, diarylethene has a widespread application in many fields such as molecular electronics[9], molecular magnetism[10], cell biology[11] and surface wettability[12] but there are rare studies about the helical self-assembly of diarylethene molecules as we know[13]. Because the cyclization reaction of the diarylethene can generate a new chiral center, the photochromic ring closure will produce a pair of enantiomers if the molecule has no chiral center[14]. The optical switching between different chiral aggregated states or the optical switching between molecular chirality and supramolecular chirality may offer new prospects for the development of molecular memory materials or smart functional materials. So far as we know it is the first time to construct of a helical nanofiber and a helical nanotube by self-assembly from the same diarylethene molecule.

The molecule presented here is based on a diarylethene photochromic unit functionalized with two malononitrile groups (scheme S1), the synthesis of the compound was initially reported by J.-M. Lehn [15]. The ultraviolet-visible absorption spectra of both isomers were shown in figure S1. In a tetrahydrofuran (THF) solution, irradiation with 365 nm ultraviolet light in a few minutes resulted in photo-cyclization to a photo stationary state (PSS), meanwhile, the colour of the solution changed to cyan from colourless as a stiffer planar closed-ring isomer was generated. Subsequent irradiation with visible light led exclusively to the open-ring isomer and the colour faded to the initial state

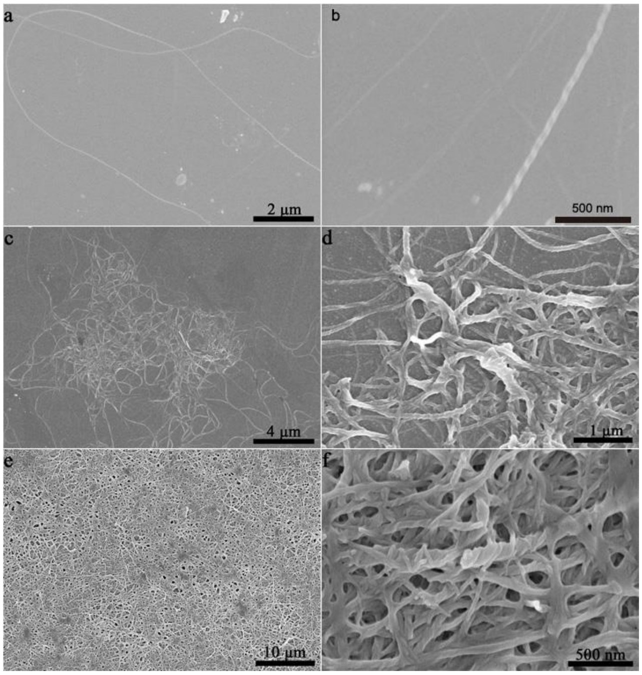


**Figure 1.** Typical SEM image and its enlarged image of the helical nanofiber formed from the open-ring isomer of the diarylethene at different temperature. (a, b) 30℃, (c, d) 40℃, (e, f) 50℃

The self-assembled behaviour was performed in the THF/water mixture solution. The SEM characterization was performed on a mica chip. Figure 1 revealed that in this mixture solution helical nanofibers were formed by self-assembly. For the open-ring isomer, when the two solutions spread to each other slowly at 30 °C, nanofibers more than 20 um with obvious helix features was obtained. When the temperature was raised to 40 °C, the helical nanofibers generated a slight aggregation. Moreover, it is demonstrated that the flocks were generated from the helical nanofibers aggregation as the temperature was raised to 50 °C. We think this may be because raising the temperature makes the molecules move faster, increasing the rate of the aggregation. In the flocks, the diameter of the nanofiber ranged from tens to hundreds of nanometer and the crude helical nanofibers were winded by the fine nanofibers, which coiled superhelix structures and its secondary self-assembly properties have been reported previously[13, 16].

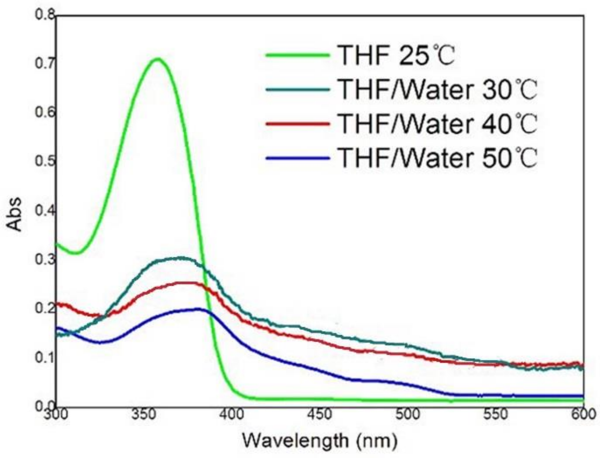


**Figure 2.** Temperature-dependent UV-Vis of the diarylethene in THF/water system.

Temperature-dependent UV-Vis was performed in order to investigate the self-assembling properties of the diarylethene derivative in the THF/water system (Fig. 2). These molecules' aggregate was indicated by the 10 nm red shift and the reduction of the maximum absorption in the UV spectrum. The maximum absorption peak gradually red shifts when increasing the self-assembly temperature, owing to the increasing aggregating of the nanostructure. The PSS solution was obtained after irradiating the THF solution with 365 nm UV light for ten minutes, the PSS of this diarylethene also had a similar self-assembly behaviour in the THF/water system by the same method. The closed ring isomer of the diaryleyhene is thermal instability in solution because of the strong electron-withdrawing group[17], but the forming of the dimers or the multimers is very fast and the colored isomer is very stable in aggregate state. From the atomic force microscope (AFM), it is clearly observed that the nanostructure self-assembled by the PSS is more uniform and the helical pitch is more compact compared with the open-ring isomer (Fig. S2). The diameter of all nanostructures is about 90 nm and the pitch of the helix is about 42 nm. Furthermore, the helical angle of the nanostructures changed from 50 °±5 °to 75 °±5 °after UV irradiation (Fig. 3). Transmission electron microscopy (TEM) observation confirmed that the as assembled nanostructure from the open-ring isomer was a helical fiber structure, To our surprise, after UV irradiation a tubular nanostructure was observed as shown in Figure 3 and Figure S3 in the Supporting Information, to the best of our knowledge, so far a helical nanotube structure was very rare in a self-assembly system[18]. In aggregate state, the isomer is very stable and cannot be switched, so the nanofiber and the nanotube cannot be direct transformed by light.

Here we propose a possible mechanism to elucidate the formation of the helical nanofiber and the helical nanotube based on DFT calculations employing the hybrid B3LYP functional equipped with 6-31G* basis set[19]. The monomeric form of the open-ring isomer has an energy 42 kcal/mol lower than the closed-ring in gas phase, suggesting the former is more stable. Different dimeric conformations were tested (Table S1) and the most stable one has two intermolecular hydrogen bonds between the nitrogen of the C≡N group and the malononitrile C-H hydrogen of the neighboring monomer for both the open-ring and closed-ring isomers (Fig. S5). The difference of the two dimers is the orientation of the free malononitrile groups, which are on the same side of the plane defined by two hydrogen bonds for the closed-ring or different sides for the open-ring. The tetramers were built based on the dimer structures. For the tetramer of the closed-ring isomer, the C-F…H-C hydrogen bonds are formed between the dimers whereas for the open-ring tetramer the C≡N…H-C hydrogen bonds are formed. The formation of the dimer and tetramer lays the foundation for the nanostructure assembly. The optimized structures of 24 monomers at B3LYP/STO-3G are presented in table 1. By extrapolation, the closed-ring assembly with the degree of polymerization (DP) of 72 is also shown in this table. As can be seen, open-ring isomers assemble to form a nanofiber and closed-ring isomers form a nanotube. The small angle X-ray diffraction (SAXD) pattern of the helical nanofiber shows the molecules are arranged with a 1.88 nm interplanar spacing in the monolayer which is in accordance with the 1.8 nm interplanar spacing shown in figure S6. The distances between the layers of the open-ring and the closed-ring assemblies are about 1.0 nm and 0.4 nm respectively, indicate that the open-ring polymer is organized more loosely. The experimental wall thickness of the nanotube is about 10 nm, which is ten times bigger than the monolayer thickness, so we think that the helical nanotube is rolled from several monolayers. The rolling of the nanostructures is similar to the nanotubes which roll from the single bilayer reported by Danino[20].

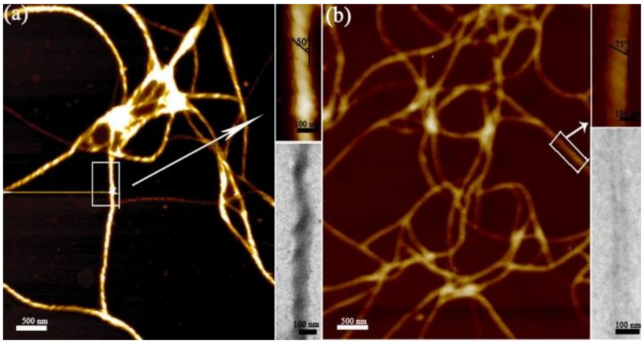
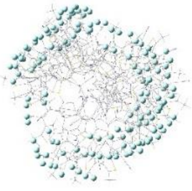
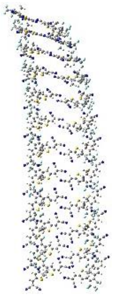
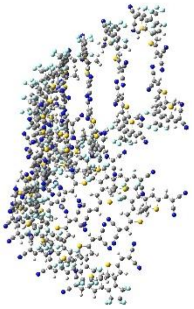
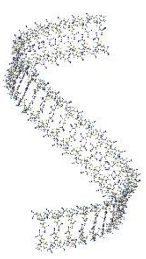
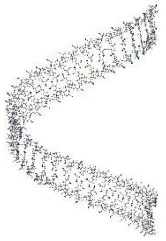
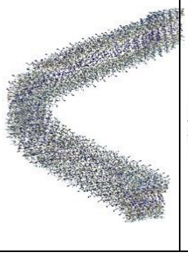
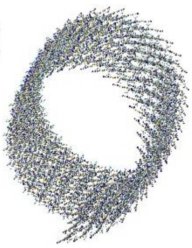


**Figure 3.** The corresponding AFM image, enlarged AFM image (top right corner) and enlarged TEM image (bottom right corner) of the helical fibers and helical tubes formed from the diarylethene before (a) and after (b) UV irradiation.

In summary, we have constructed a helical nanostructure by self-assembly of a diarylethene derivative and successfully tuned the helical properties by light as the molecular shape of the underlying monomer can changed by ultraviolet or visible irradiation. When the diarylethene monomer changed from open-ring isomer to the closed-ring isomer not only the helix angle of the self-assembly structure has a significant change but the morphology of the aggregation states can be transformed from helical nanofiber to helical nanotube. The helical angle of the nanostructures also can be tuned by UV irradiation, which has great potential for smart soft materials and devices. The possible formation mechanism of the nanostructure was presented based on theoretical calculations.

**Table 1**. The ptimized structures at B3LYP/STO-3G of the helical nanotube and helical nanofiber

| | Face view | Side view | Top view |
|---|---|---|---|
| Open-ring DP=24 |  |  |  |
| Closed-ring DP=24 |  |  |  |
| Closed-ring DP=72 |  |  |  |
| Closed-ring DP=72 ,Layer=6 |  |  |  |

[a] closed-ring dimers (DP = 24, 72), open-ring dimers (DP = 24)

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Materials; UV-Vis in THF solution; self-assembly methods; instrument and test method; AFM and TEM images of the helical nanofibers and helical nanotubes; molecular electrostatic potential (ESP) contour maps; relative energy (Erelative) and the binding energy (Ebinding) of the dimers; the images of the dimers employed for the theoretical calculation; See DOI: 10.1039/b000000x/

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