

# Fluorescence and Morphology Modulation in a Photochromic Diarylethene Self-Assembly System

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Supporting Information

**ABSTRACT:** Switchable supramolecular self-assemblies on the basis of interaction between melamine group containing photochromic diarylethene unit (DTE) and naphthalimide derivate (1) were designed and fabricated. 1 can gelate several aprotic solvents with different morphologies. The gel turned into partial gel in ethyl acetate with the addition of DTE as a guest molecule.



Both the absorption and fluorescence spectra of the assembly can be reversibly switched by alternating UV/visible light irradiation. Meanwhile, the morphology of the coassembly of  $1_2 \cdot DTE$  changed to film from original pieces of gel 1 in ethyl acetate. When  $1_2 \cdot DTE$  was irradiated by UV light, the film morphology was converted into aggregated flakes. Moreover, the surface wettability of the complex can also be switched by light irradiation. The photochromic diarylethene unit is able to modulate the fluorescence and morphology of the assembled system only by virtue of light irradiation. Therefore, these results provide further insights into fluorescence and morphology controlling, especially application in upscale smart responsive materials.

# ■ INTRODUCTION

Spontaneous self-assembly of small molecules into complex superstructures by various noncovalent interactions is abundant in nature; meanwhile, it is a powerful approach toward the development of new materials and devices.<sup>1</sup> The structural and functional properties of the final supramolecular assemblies are determined by the assembling information stored in the molecular components, which are dictated by the interplay of both geometrical and conformational constraints, and by the presence of complementary recognition end groups.<sup>2</sup> It is well-known that the driving force in the supramolecular self-assembly process involves hydrogen-bonding,  $\pi$ -stacking, metal-ligand, and van der Waals interactions.<sup>3</sup> However, the regulation and control of the self-assembly process to realize a specific functionality and to obtain well-defined smart materials is still a significant challenge to scientists. Nowadays, more and more interest has been paid to smart materials whose morphology and functionality can be tuned by outside stimuli. Our group previously reported a class of naphthalimide derivative gels which formed various morphologies in response to sonication or chemical input.<sup>4</sup> Reversible light-responsive self-assembly systems are most desirable since only light is used as the input stimulus without other additives needed. Diarylethenes have been proven to be the most promising candidates for applications within those classical photochromic systems owing to the good thermal stability and  $\bar{\rm high}$  fatigue resistance of both isomers.<sup>3</sup> A photochromic diarylethene moiety can act as a photoreversible switch in molecular devices or as a switchable probe for imaging live cells.<sup>6</sup> Irie et al. had reported a surface morphology change in a diarylethene single crystal upon photoirradiation determined by atomic force microscopy,<sup>7</sup> while there is little research concerning the morphology change of a self-assembled system based on photochromic diarylethene

induced by external light stimulus. In fact, smart materials that reversibly change shape and/or size in response to external stimuli have attracted interest due to their potential application as micro actuators, molecular pumps, and so on.<sup>8</sup> This prompted us to obtain photochromic diarylethene self-assembly materials with highly modulating control of both fluorescence and morphology.

In the present study, we designed and synthesized a new diarylethene compound with a melamine group on its side (DTE) and a naphthalimide based gelator (1) which had the ability to form triple hydrogen bonds with melamine. The morphology changes of the self-assembly of 1 in the absence and presence of a complementary DTE were investigated. The complex  $1_2 \cdot DTE$  could be reversibly switched by alternate UV/visible light, giving obvious morphology and fluorescence changes.

# EXPERIMENTAL SECTION

**Materials.** All starting materials were obtained from commercial suppliers and used as received. Moisture-sensitive reactions were performed under an atmosphere of dry argon. 6-Chloro-1,3,5-triazine-2,4-diamine was provided from Sigma-Aldrich; 4-bromo-1,8-naphthalic anhydride (95%), ethane-1,2-diamine (CP), and other chemicals were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). Column chromatography was carried out on silica gel (200–300 mesh).

**Synthesis.** The synthetic methodology for compound **1** and DTE is depicted in Scheme 2. Compounds **2**, **3**, and **5** were prepared according to the previously reported method.<sup>9</sup> First; compound **2** was obtained through methyl gallate reaction with bromooctane in the presence of potassium carbonate in acetone. Compound **2** reacted with ethane-1,2-diamine and

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Scheme 2. Synthetic Route for 1 and DTE



purified by column chromatography to give compound **3**. Compound **4** was obtained by the reaction of 4-bromo-1,8-naphthalic anhydride and aqueous ammonia in 2-methoxyethanol. The target compound **1** was synthesized by reaction of compounds **3** and **4**. The target compound DTE was obtained from compound **5** and 5-chloro-3-(2-(5-chloro-2-methylthiophen-3-yl) cyclopent-1-enyl)-2-methylthiophene in a one-pot method.

Preparation of 4-(*N*-(3,4,5-Trisoctyloxy)benzamide)ethylamino-1,8-naphthalimide (1). Compounds 3 (1.0 g, 1.82 mmol), 4 (0.50 g, 1.82 mmol), and CuBr (0.1 g, 0.70 mmol) were dissolved in 50 mL of DMSO. Then, the mixture was heated to 100 °C and stirred for 24 h under N<sub>2</sub> atmosphere. When the reaction was over, the mixture was poured into 300 mL of water. The aqueous phase was extracted with ethyl acetate three times. The combined organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with acetic ester/petrol ether (1:3, v/v) as the eluent, giving a 15% yield of 1. Mp: 191–193 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.49–8.51 (d, *J* = 8.0 Hz, naphthalene-H, 1H), 8.44 (s, -NHCH<sub>2</sub>, 1H), 8.32–8.34 (d, J = 8.0 Hz, naphthalene-H, 2H), 7.60–7.64 (t, J = 8.0 Hz, naphthalene-H, 1H), 7.44 (s, –CONHCO-, 1H), 7.06 (s, ArH, 2H), 6.93–6.95 (t, J = 4.0 Hz, –CH<sub>2</sub>-NHCO-, 1H), 6.48–6.50 (d, J = 8.0 Hz, naphthalene-H, 1H), 3.93–4.02 (m, -OCH<sub>2</sub>CH<sub>2</sub>–, 8H), 3.53 (m, -CH<sub>2</sub>-, 2H), 1.70–1.81 (m, -OCH<sub>2</sub>CH<sub>2</sub>-, 6H), 1.41–1.45 (m, –CH<sub>2</sub>CH<sub>2</sub>-, 6H), 1.25–1.29 (m, -CH<sub>2</sub>-, 24H), 0.85–0.88 (t, J = 6.6 Hz, -CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.5, 164.0, 153.2, 150.7, 141.8, 134.3, 131.2, 128.1, 124.8, 122.5, 120.8, 109.3, 105.9, 103.2, 73.6, 69.5, 46.7, 39.4, 31.8, 29.3, 26.0, 22.6, 14.0. HRMS (ESI<sup>+</sup>) calcd for C<sub>45</sub>H<sub>65</sub>N<sub>3</sub>NaO<sub>6</sub> (M+Na<sup>+</sup>) 766.4771, found 766.4773.

**Preparation of**  $N^2$ **-(4-Bromophenyl)-1,3,5-triazine-2,4,6-triamine (5).** A solution of 4-bromoacetalide (1.2 g, 6.87 mmol) and 2-chloro-4,6-diamino-1,3,5-triazine (1.0 g, 6.87 mmol) in water (25.0 mL) was heated to reflux. To this mixture, 2 × 1.75 mL of 2 M NaOH was added dropwise over 2 h, and the heating was maintained for a total of 4.5 h. After cooling, the precipitate was filtered and washed with water to obtain 1.8 g of

white powder **5** (yield 90%). Mp: 254–256 °C. <sup>1</sup>H NMR (D<sup>6</sup>-DMSO, 400 MHz):  $\delta$  6.32 (s, 4H), 7.33–7.35 (d, *J* = 8.0 Hz, 2H), 7.75–7.77 (d, *J* = 8.0 Hz, 2H), 8.99 (s, 1H). <sup>13</sup>C NMR (D<sup>6</sup>-DMSO, 100 MHz):  $\delta$  167.5, 165.1, 140.7, 131.3, 121.6, 112.8. HRMS (ESI<sup>+</sup>) calcd for C<sub>45</sub>H<sub>65</sub>N<sub>3</sub>NaO<sub>6</sub> [M+H<sup>+</sup>] 281.0150, found 281.0157.

Preparation of N<sup>2</sup>-(4-(4-(2-(5-chloro-2-methylthiophen-3yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)phenyl)-1,3,5triazine-2,4,6-triamine (DTE). To 25 mL anhydrous THF solution of 1,2-bis (5-chloro-2-methylthien-3-yl) cyclopentene (1.0 g, 3.04 mmol), n-BuLi (1.9 mL of 1.6 M solution in hexane, 3.04 mmol) was added dropwise under Ar atmosphere at -5 °C. After the mixture was stirred for 15 min at room temperature, B(OBu)<sub>3</sub> (1.2 mL, 3.4 mmol) was added in one portion. The resulting reddish solution was stirred for 6 h at room temperature and was added to a flask containing 5 (0.89 g, 3.19 mmol), Pd(PPh\_3)\_4 and 10 mL Na\_2CO\_3 solution (20 wt %) at 50 °C. The mixture was refluxed under Ar atmosphere for 18 h. The pure product was obtained by column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/50 (v/v)) as a gray solid (300 mg, 20%). Mp: 127–129 °C. <sup>1</sup>H NMR  $(D^{6}-DMSO, 400 \text{ MHz}): \delta 9.09 \text{ (s, 1H)}, 7.77-7.75 \text{ (d, } J = 8.4 \text{ Hz}, 2\text{H}),$ 7.37 - 7.35 (d, J = 8.4 Hz, 2H), 7.08 (s, 1H), 6.84 (s, 1H),  $\delta$  6.48 (s, 4H), 2.79-2.74 (t, J = 9.8 Hz, 4H), 2.01-1.95 (m, 2H), 1.86 (s, 3H), 1.84 (s, 3H).  $^{13}\mathrm{C}$  NMR (D<sup>6</sup>-DMSO, 100 MHz):  $\delta$  166.5, 164.9, 140.5, 140.1, 136.8, 135.9, 135.7, 133.8, 133.6, 133.0, 128.0, 127.5, 125.5, 124.1, 123.4, 120.6, 38.5, 22.9, 14.6, 14.5. HRMS (ESI<sup>+</sup>) calcd for C<sub>24</sub>H<sub>23</sub>ClN<sub>6</sub>S<sub>2</sub> (M+H<sup>+</sup>) 495.1114, found 495.1181.

**Techniques.** The <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Mercury plus-Varian instrument. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). HRMS was recorded on LTQ-Orbitrap mass spectrometer (ThermoFIsher, San Jose, CA). Melting points were determined on a hot-plate melting point apparatus XT4-100A without correction. Differential scanning calorimetry was carried out by a DSC Q1000 with a heating rate of 10 °C/min. SEM images were obtained using a FE-SEM S-4800 (Hitachi) instrument. Samples were prepared by spinning the samples on glass slices and coating with Au. SAXS diagrams were obtained on a NanoSTAR U SAXS system (Bruker), using a Cu K $\alpha$  radiation source ( $\lambda$  = 0.1542 nm). The SAXS data were corrected for absorption and background scattering. Powder X-ray diffractions were generated by using a Philips PW3830 sealed-tube X-ray generator (Cu target,  $\lambda = 0.1542$  nm) with a power of 40 kV and 50 mA. UV-vis absorption and fluorescent spectra were recorded on a UV-vis 2550 spectroscope (Shimadzu) and an Edinburgh Instruments FLS 900, respectively. Fourier transform infrared (FTIR) spectra were collected by a Nexus 470 spectrometer (Nicolet Company) with a resolution of 2  $\text{cm}^{-1}$ , and 32 scans were accumulated to obtain an acceptable S/N ratio. The samples were prepared with KBr pellets. Original spectra were baseline-corrected by use of Omnic 5.1 software. Confocal laser scanning microscopy was performed with an Olympus ZX81 laser scanning microscopy and a  $60 \times$  oil-immersion objective lens. Water contact angles were performed using the sessile drop method (Dataphysics, OCA 20). The water droplets were introduced using a microsyringe, and images were captured to measure the angle of the liquid-solid interface; each sample was recorded at three different points.

**Gelation Test for Organic Fluids.** The gelators and solvents were put in a septum-capped test tube and heated (>75 °C) until the solid was dissolved. The sample vial was then cooled to 25 °C (room temperature). Qualitatively, gelation was considered successful if no sample flow was observed upon inversion of the container at room temperature (the inverse flow method).

## RESULTS AND DISCUSSION

**Morphology of Gel 1 and Complex 1\_2 \cdot \text{DTE.}** Compound 1 is soluble in chloroform, methylene chloride (<50 mg mL<sup>-1</sup>), and

Table	e 1.	Gelation	Abili	ty of	1	and	12	DTE	Ì
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solvent	$1^{b}$	$1_2 \cdot DTE^{b}$	$1_2 \cdot \text{DTE} / \text{UV}^c$
Carbon tetrachloride	G (10)	Р	Р
Methylene chloride	S	S	S
Tetrahydrofuran	S	S	S
Ethyl acetate	G (8.5)	PG	PG
Chloroform	S	S	S
Dioxane	G (50)	Р	Р
Acetonitrile	P(12.5)	Р	G (100)

<sup>*a*</sup> G: gel; PG: partial gel; P: precipitation; S: solution. The critical gelation concentrations of the gelators are given in parentheses (mg mL<sup>-1</sup>). <sup>*b*</sup> Heated to dissolve and cooled to room temperature then aged for 15 min (25 °C). <sup>*c*</sup> Irradiation of 365 nm light for 10 min. The concentrations for other gelation experiment are 50 mg mL<sup>-1</sup>.



**Figure 1.** CLSM and SEM images of gels of 1 (a,d) from ethyl acetate with the concentration of 8.5 mg mL<sup>-1</sup>; (b,e) from 1,4-dioxane with the concentration of 50 mg mL<sup>-1</sup> and (c,f) from carbon tetrachloride with the concentration of 10 mg mL<sup>-1</sup> (scale bar: 30, 10, 20, 5, 2, and 20  $\mu$ m for a, b, c, d, and e and f, respectively).

tetrahydrofuran, but can gelate some aprotic solvents such as ethyl acetate, carbon tetrachloride, and dioxane with the critical gelation concentration of 8.5, 10, and 50 mg/mL, respectively (Table 1). To obtain a photoresponsive self-assembly system, melamine attached diarylethene DTE was added to 1. After addition, the complex became easily soluble in nonproton solvent because of the formation of a complementary hydrogen-bonded complex.<sup>11</sup> The highly twisted structure of the dithienylethene unit in DTE destroyed the molecular packing of 1 and simultaneously improved the solubility of the complex.<sup>1</sup> So, the gels were changed into partial gels in ethyl acetate. Even the concentration of 1 up to 300 mg mL<sup>-1</sup>, stable gel was not formed. In other solvents such as dioxane and carbon tetrachloride, the complex was soluble in higher temperature (>100 °C), but precipitate gradually turned up after cooling to room temperature, which means the network for gelation could not be formed by the complex. The gelation process of 1 and  $1_2 \cdot \text{DTE}$  was investigated by differential scanning calorimetry with temperature range from 20 to 110 °C in ethyl acetate (Supporting Information Figure S2). The result showed two endothermic peaks at 45 and 74 °C in the heating process of gel 1 (50 mg mL<sup>-1</sup>). The former was the gel to sol transformation point; the latter was the volatilization of ethyl acetate, while in the complex, only several



**Figure 2.** FE-SEM images of complex 1+DTE from ethyl acetate with different ratios of 1/DTE before (above) and after (below) UV irradiation: (a,e)  $1 \cdot 0.25$  DTE; (b,f)  $1 \cdot 0.50$  DTE; (c,g)  $1 \cdot 1.0$  DTE (scale bar: 5, 20, 10, 20, 50, and 2  $\mu$ m for a, b, c, e, f, and g, respectively); (d) and (h) are in situ bright field images of confocal laser scanning microscopy of a wet complex in ethyl acetate before and after UV irradiation.

sharp peaks in the range 70-82 °C were observed. These peaks possibly belonged to the solvent volatilizing process.

The morphology of the gels was investigated using scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM). In this case, we found that the morphologies of the xerogels slightly depended on the solvents. SEM and CLSM images of the xerogel obtained from ethyl acetate revealed a flaky texture with a width or length of around several to dozens of micrometers (Figure 1a,e). The gel from 1,4-dioxane had a beltlike morphology with a width of around 300 nm (Figure 1b,f) and the gel in carbon tetrachloride clearly indicated irregular sticks of larger dimension (Figure 1c,g). The solvent dependent morphology of gel 1 may be due to the dipolar structure of 1 and the competition interactions between gelator–gelator and solvent–gelator.<sup>4d,10</sup> For example, in a solvent of lower polarity such as ethyl acetate and carbon tetrachloride, the weaker interaction between gelator and solvent resulted in big aggregation of the gelator molecules. To elucidate the role of the DTE on the aggregation change in self-assembly, the morphology of the complexes with different molar ratio of 1/DTE in ethyl acetate was observed through SEM images. In this experiment, 0.25, 0.5, and 1.0 equiv of DTE were added to 5.0 mg of 1 in 0.1 mL of ethyl acetate, respectively, and then the system was heated, dissolved, and cooled to partial gel. The morphology of the complex was changed from aggregated flakes of gel 1 to a film-like structure with some holes and bubbles on the film, regardless of different molar ratios of DTE/1 (1:4, 1:2, 1:1) in ethyl acetate (Figure 2a-c). In 1,4-dioxane, the belt-like morphology changed to tenuous fiber structure, and in acetonitrile, the worm-like morphology changed to that of small particles, with the addition of DTE by means of CLSM (Figure S1, Supporting Information).

**Chemical Model of the Self-Assembly of 1 and DTE.** In order to clarify the chemical model of the self-assembly of 1 and DTE and the hydrogen bonding in the course of complex formation, <sup>1</sup>H NMR experiment of DTE by titration with 1 was performed (Figure 3a). The signals of the amide proton N-Ha of DTE in THF- $d_8$  shifted downfield from  $\delta = 5.96$  to 6.07, 6.14, 6.20, 6.24, 6.27, and 6.27 ppm with the addition of 1 ratio of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 equiv, respectively. The signals of the other amide proton N-Hb of DTE also downfield shifted from  $\delta = 8.36$  to 8.74 ppm with the increase of 1 ratio from 0 to

2.5 equiv and remained constant after further increase. At the same time, the signal of N-Hc in 1 at 10.27 ppm was downfield shifted to 10.70, 10.76, 10.82, 10.89, 10.98, and 11.12 ppm with the decrease of the 1 ratio of 3.0, 2.5, 2.0, 1.5, 1.0, and 0.5 equiv, respectively. Figure 3b shows the changes in chemical shift of N-Ha, N-Hb, and N-Hc with increasing 1/DTE ratio. We can see the gradual change of the chemical shift even when the ratio of 1 to DTE is larger than 2 since the formation of hydrogen bonding is a dynamic system. However, the other two NH protons (Hd, 7.61 ppm, and He, 8.13 ppm) in 1 show no obvious shifts during the whole experiment process. The <sup>1</sup>H NMR titration data were analyzed in light of the Benesi-Hildebrand equilibrium: 1 + DET  $\leftrightarrow$  1 · DTE ( $K_1$ ) and 1 · DTE + 1  $\leftrightarrow$  1<sub>2</sub> · DTE ( $K_2$ ).<sup>13</sup> The binding constants of the two equilibria were calculated as  $K_1 = 303 \text{ M}^{-1}$  and  $K_2 = 281940 \text{ M}^{-1}$ , which meant that the latter equilibrium was more stable than the former equilibrium. The above results supported the formation of a 12DTE complex via multiple hydrogen bonds involving N-Ha, N-Hb, and N-Hc as presented in Scheme 1.

FT-IR spectra were also measured for the precursors and the complex  $1_2 \cdot DTE$  to verify the intermolecular hydrogen bonding between 1 and DTE during the self-assembly (see Figure S3, Supporting Information). The peak at 3404 cm<sup>-1</sup> can be assigned to the stretching frequency of free N–H groups existing in DTE. In the complex  $1_2 \cdot DTE$ , this frequency completely disappeared from the original position. The peaks at 3369 and 3332 cm<sup>-1</sup> in the compound 1 were moved to 3323 and 3202 cm<sup>-1</sup>, respectively. This red-shifted changes of N–H stretching frequency in the complex provided evidence for the formation of H-bonding between molecule 1 and DTE.

The absorption and fluorescence of the precursors and the complex were carried out to further understand the self-assembly process. The absorption of 1 in dilute solution of ethyl acetate  $(1.0 \times 10^{-5} \text{ M})$  was at 425 nm and shifted to 453 nm in the gel state (Figure 4a). Meanwhile, the maximum emission of 1 at 500 nm in diluted solution of ethyl acetate  $(1.0 \times 10^{-5} \text{ M})$  was red-shifted to 542 nm in the gel state (Figure 4b). The bath-ochromic shift in both absorption and emission of 1 with the increase of concentration demonstrated the formation of a J-aggregate between naphthaleneimide units in a head to tail mode in the gel state (Supporting Information Figure S4).<sup>16</sup>



**Figure 3.** (a) <sup>1</sup>H NMR spectra of DTE with the increasing addition of 1 (THF- $d_8$ ,  $C_{\text{DTE}} = 1.07 \times 10^{-2}$  M); (b) chemical shift change of N-Ha, N-Hb, and N-Hc (Scheme 1) with the different molar ratio of  $C_1/C_{\text{DTE}}$ .



**Figure 4.** (a) Absorption and (b) fluorescent emission spectra of 1 in solution  $(1 \times 10^{-5} \text{ M})$ , gel  $(2.24 \times 10^{-2} \text{ M}, \text{film})$ , and complex  $1_2 \cdot \text{DTE} (C_1 = 2.24 \times 10^{-2} \text{ M}, C_{\text{DTE}} = 1.12 \times 10^{-2} \text{ M})$  at room temperature ( $\lambda_{\text{ex}} = 425 \text{ nm}$ ); (c) absorption spectral change of  $1 (c = 1 \times 10^{-5} \text{ M})$  under the addition of DTE from 0 to 1.2 equiv in ethyl acetate (cell length, 1.0 cm); (d) absorption change of a dilute solution of DTE in ethyl acetate  $(1 \times 10^{-5} \text{ M})$  upon irradiation of 365 nm light at room temperature (cell length, 0.5 cm); (e) absorption and (f) fluorescence spectral changes of the complex  $1_2 \cdot \text{DTE}$  in ethyl acetate  $(c_1 = 2.24 \times 10^{-4} \text{ M}, c_{\text{DTE}} = 1.12 \times 10^{-4} \text{ M})$  upon irradiation of 365 nm light at room temperature (cell length, 0.5 cm); (e) absorption and (f) fluorescence spectral changes of the complex  $1_2 \cdot \text{DTE}$  in ethyl acetate  $(c_1 = 2.24 \times 10^{-4} \text{ M}, c_{\text{DTE}} = 1.12 \times 10^{-4} \text{ M})$  upon irradiation of 365 nm light at room temperature (cell length, 0.5 cm); (e) absorption and (f) fluorescence spectral changes of the complex  $1_2 \cdot \text{DTE}$  in ethyl acetate  $(c_1 = 2.24 \times 10^{-4} \text{ M}, c_{\text{DTE}} = 1.12 \times 10^{-4} \text{ M})$  upon irradiation of 365 nm light at room temperature (cell length, 0.1 cm;  $\lambda_{\text{ex}}$ : 425 nm).

With the addition of DTE, a new absorption band at 320 nm belonging to open form of DTE was gradually increased (Figure 4c). The absorption of 1 at 425 nm was not altered obviously in dilute solution of the complex, whereas it shifted to 442 nm in a partial gel of  $1_2$ DTE ( $1.12 \times 10^{-2}$  M) (Figure 4a). The maximum emission shifted to 536 nm with the addition of DTE, showing a weakened  $\pi - \pi$  interaction of 1 in the complex than the gel (Figure 4b). This was probably one factor contributing to the gel change to partial gel after DTE addition.

The above spectral study proved that compound 1 can form organic gels because of (a) strong hydrogen-bonding interactions between the amide units; (b)  $\pi - \pi$  interactions between the naphthalene imides. The highly twisted structure of the dithienylethene unit destroys the molecular packing in the 1<sub>2</sub>DTE complex, thus resulting in collapse of the gel. This result was further supported by powder X-ray diffraction (Figure 5). The scattering patterns of 1 xerogel in ethyl acetate showed a sharp peak at 2.49 nm, which was about the same length as 1





(ca. 2.55 nm). At the same time, the various spacings of 2.49, 1.24, and 0.82 nm formed a suite of fractions (d/1:d/2:d/3), a feature that strongly suggested a lamellar structure.<sup>17</sup> The complex 1<sub>2</sub>DTE from ethyl acetate displayed a completely different X-ray diffraction profile, with one broad peak corresponding to *d* spacing of 0.43 nm. The small-angle X-ray scattering (SAXS) patterns of the complex 1<sub>2</sub>DTE before and after UV irradiation showed one peak with the value of *d* spacings of 3.74 and 3.71 nm, respectively (Figure 5b). No peak was found in SAXS pattern of gel 1. The value of *d* spacing in the complex 1<sub>2</sub>DTE pattern was about the same length as 1 + DTE. This result supported the view that the complex 1<sub>2</sub>DTE was formed through three H-bondings between two molar equivalents 1 and DTE.

Fluorescence and Morphology Switch of the Complex. DTE undergoes reversible photochemical ring-closing and ring-opening reactions upon the alternating irradiation of UV/visible light. The structural flexibility of the ring-open state was turned into planar and rigid backbone of the ringclosed state by UV radiation. Reversible photochromic reaction of DTE was carried out in both dilute solution and the complex. The photo isomerization of the dithienylethene unit concerns an intramolecular electron transfer process, resulting in a ring-closed reaction (Scheme 1).<sup>5</sup> A new absorption band at 490 nm appeared in ethyl acetate solution of DTE (1.0 imes $10^{-5}$  M) under 365 nm light irradiation due to the large  $\pi$ electron delocalization in its closed isomer (Figure 4d).<sup>18</sup> The complex  $1_2 \cdot \text{DTE}$  showed almost the same absorption change as that in DTE dilute solution by irradiation of 365 nm light (Figure 4e). According to the absorption of DTE in its closed state and the emission spectra of 1 in ethyl acetate, efficient intermolecular energy transfer was allowed to occur, leading to strong fluorescence quenching.<sup>19</sup> With irradiation of 365 nm light for 90 min, the complex  $1_2 \cdot \text{DTE}$  ( $C_1 = 2.24 \times$  $10^{-2}$  M,  $C_{\text{DTE}} = 1.12 \times 10^{-2}$  M) in ethyl acetate underwent photocyclization and exhibited a distinct fluorescence quenching of more than 80% until reaching the photo stationary state (Figure 4f). This process was also demonstrated by a confocal laser scanning microscopy image. The coassembly solution was dropped onto the surface of a glass slide. The fluorescence of the selected part was guenched by irradiation of 405 nm laser light for 10 s (see Supporting Information Figure S6). The fluorescence reversible cycle experiment was

carried out to check the resistance to fatigue as shown in Supporting Information Figure S5. In the first cycle of an alternating UV/visible light irradiation, the recovery of the fluorescence intensity is 80%. However, in the following cycles, the decrease of fluorescence is very rare; 75% of the fluorescence intensity still remains after 7 cycles of UV/visible light irradiation.

The morphology of the film of the complex was also switched by UV light irradiation. When the samples of the partial gel from ethyl acetate were irradiated with UV light of 365 nm for 10 min and dropped on the surface of the mica, then dried for 4 h in vacuum in the dark, the film-like morphology of complex  $1_2$  · DTE was changed to flakes (Figure 2e-g). An in situ bright field image of confocal laser scanning microscopy of complex in ethyl acetate was also carried out to elucidate the morphology modulation under the UV light irradiation. The smooth film structure of the complex before irradiation of UV light (Figure 2d) was changed to an irregular nubby structure after irradiation of UV light for 2 h (Figure 2h). However, because of the comparatively larger solubility of the complex than 1, the sol to gel transformation was only observed in acetonitrile with the critical concentration larger than 100 mg/mL after UV light irradiation. Nevertheless, the gelator of 1 plays a key role for preparing a two component switchable film for further application.

Functional surfaces with controllable wettability have come to the forefront of research for their great potential application in daily life, industry, and agriculture.<sup>20,21</sup> Taking into account the specific morphology change of the complex  $1_2$ DTE before and after irradiation of UV light, the surface of the films may possess quite different surface wettability. In fact, the film of complex 12DTE from ethyl acetate before UV light irradiation had a relatively hydrophilic surface with contact angle of 105.5°, advancing contact angle of 107.0°, and receding contact angle of 97.7° (Figure 6a). The contact angle hysteresis, H (the difference between the advancing contact angle and the receding contact angle), was 9.3°. The film obtained by a sample irradiation of 365 nm light for 10 min gave a contact angle of 140.0° with advancing angle of 141.0° and receding angle of 134.3° (Figure 6b). The contact angle hysteresis H was 6.7° after UV radiation.<sup>22</sup> The maximum contact angle change is about 35° and can be reversed by irradiation of visible light of 500 nm (Supporting Information Figure S7). In this way, a tunable surface was



Figure 6. Water contact angle change of the film coating with complex  $1_2$ DTE from ethyl acetate upon alternating UV and visible light irradiation.

prepared whose wettability switched solely by alternate irradiation of UV/visible light with the change of the surface morphology.

#### CONCLUSIONS

We have successfully synthesized a new naphthalimide based gelator (1) whose self-assembly structure varied with different kinds of solvents. The coassembly process of 1 with diarylethene attached melamine (DTE) was studied. DTE plays the role of dual switches for the morphology and fluorescence in the coassembly. After DTE was added to the self-assembly of 1, the morphology of the complex was changed from flaky texture to films, which was turned into aggregated flakes with the irradiation of 365 nm light. The fluorescence of the coassembly of 1 and DTE was quenched and recovered reversibly by alternating irradiation of UV/visible light. The mechanism study of the changing process clarified that the triple parallel H-bonds were essential to the construction of a dual switch to the coassembly of molecule 1 and DTE. Moreover, the wettability of the surface prepared by the complex can be switched by alternate irradiation of UV/visible light with the change of the surface morphology. Thus, the present study may introduce a new way for preparation of reversible function materials responsive to light stimulation through the supramolecular self-assembly, which will be useful in various applications, such as drug delivery systems and smart materials.

# ASSOCIATED CONTENT

**Supporting Information.** Supplementary CLSM images and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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