

## Study on the Controlled Gel Formation and Photochromic Properties of a New Cholesterol-bridge-naphthopyran Dyad

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A cholesterol-bridge-naphthopyran dyad (NP-MCB) was designed and synthesized. NP-MCB can readily self-assemble into gels under ultrasound-radiation in several organic solvents and the formed gels easily transfer to solution by heat. This reversible process can be repeated many times. Scanning Electron Microscopy results showed that the morphologies of all formed xerogels in different solvents have fibrillar microstructure. The gels formation was due to energy and pressure afforded by the ultrasonic process, resulting in formation of molecular hydrogen bonding and molecular aggregation. NP-MCB displayed the normal photochromism both in solution and gel states. The kinetic results confirm that the colored merocyanine in gels show a slower fading speed than that in solution due to the compact aggregation of NP-MCB molecules in gels. The xerogel film formed in polar gelling solvent had large surface wettability than that in nonpolar gelling solvent.

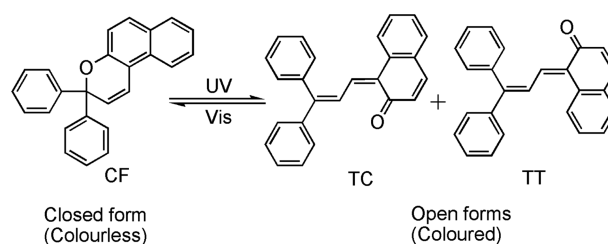
**Key Words :** Gel, Ultrasound, Photochromic, Naphthopyran, Cholesterol

### Introduction

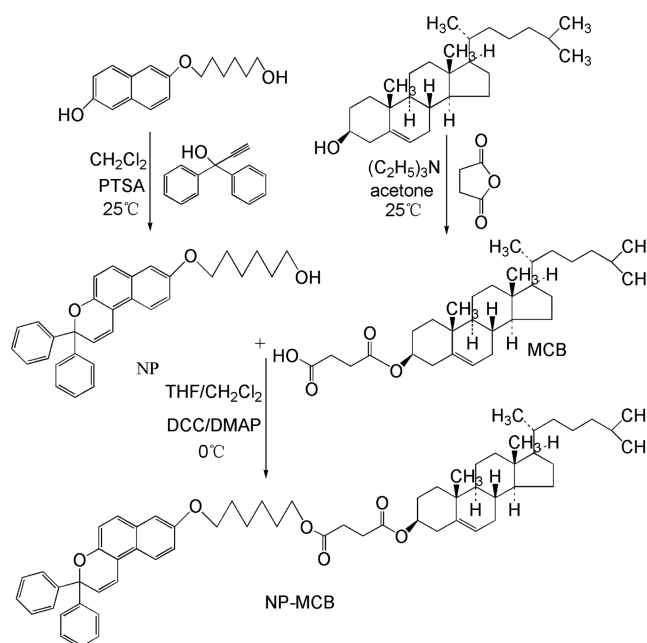
In recent years, low-molecular-mass organogels (LMOGs) attract an increasing interest due to their unique features and the increasingly potential applications of soft matters as smart materials.<sup>1-4</sup> In suitable solvents, LMOGs could autonomously assemble into the three-dimensional networks through the non-covalent interaction, such as hydrogen bond, electrostatic force, hydrophobic force,  $\pi$ - $\pi$  stacking etc. Up to now, a mass of organogels that can respond to the external stimuli,<sup>5</sup> such as light,<sup>6,7</sup> temperature,<sup>8</sup> sound,<sup>9</sup> pH,<sup>10</sup> mechanical stress,<sup>11</sup> anions,<sup>12</sup> metal ions,<sup>13</sup> redox,<sup>14</sup> proton<sup>15</sup> and small molecules,<sup>16</sup> have been reported. However, designing controllable gelation system based on reversible changes of a gelator molecule induced by external stimuli is still a significant challenge to scientists.

Cholesterol is a well-known natural product and frequently appears as a versatile building block in gelation and materials chemistry, due to its strong tendency to form aggregates *via* van der Waals interactions,<sup>17</sup> which can not only respond to temperature<sup>18</sup> but also other external stimuli, such as light,<sup>19</sup> redox,<sup>20</sup> acidity,<sup>21</sup> and ultrasound.<sup>22</sup> Some organogels based on cholesterol including photochromic unit such as azobenzene,<sup>23</sup> diarylethene<sup>24</sup> or spirooxazine<sup>25</sup> derivatives have been reported, in which the gelation was controlled by heat, light, acidity *etc.*, as external stimuli. Organogels containing the photochromic unit and cholesterol unit displayed promising application in the fields of optic and electronic smart materials, ophthalmic lenses, optical switches, optical filters, and temporary or permanent memory devices.

As we know, naphthopyrans are an important class of photochromic dyes which show breadth of color generated,



**Scheme 1.** Generic photochromic process for the naphthopyran derivatives.



**Scheme 2.** Synthetic route of compound NP-MCB.

absence of background color, good thermal reversibility, fine control fading kinetics, and good resistance to photochemical fatigue.<sup>26</sup> The photochromic reaction of naphthopyran involves initial heterolytic cleavage of the C-O bond in the pyran moiety upon irradiation with UV-light, resulting in two colored isomeric open forms, a transoid-*cis* (TC) and a transoid-trans (TT) merocyanine isomers<sup>27-29</sup> (Scheme 1). However, among various types of photochromic compounds, there have been relatively seldom reports on naphthopyran used in organogels.

Here, we design and synthesize a new photochromic organogel based on naphthopyran with an alkyl chain unit as a bridge between the naphthopyran and the cholesterol (NP-MCB) through steps shown in Scheme 2. The detailed experiments are presented in the experiment section. The compound could readily self-assemble into gels with nanofiber structure in a few organic solvents. The gels exhibited photochromic properties as well as displayed stimuli-responsive properties, which are presented as below.

## Experimental

**Materials.** All the materials for synthesis and spectra measurement were purchased from commercial suppliers and used without further purification. All the solvents and reagents used in the spectroscopic studies were analytical grade.

**Instrumentation and Methods.** <sup>1</sup>H NMR spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) at room temperature and *d*-chloroform was used as solvent. Mass spectra were recorded on BRUKER AutoflexIII Smart-beam MS spectrometer. Scanning electron microscopy (SEM) pictures of the xerogel were carried out on a Hitachi S-4800 FE-SEM and the samples were sputtered with a layer of gold (*ca.* 10 nm thick) prior to imaging. The xerogel was obtained by freeze-dried with the LGJ-0.5 vacuum freeze dryer. The water contact angle (CA) was measured by the Dataphysics OCA20 Contact Angle System. A CHF-XM35 parallel light system with a 500 W xenon lamp was used as UV source of irradiation. The photochromic properties of the solutions and the gels were examined using a Varian Cary 500 UV-vis spectrophotometer. Absorption spectral changes of solutions and gels were feed into 1 cm quartz vessel. The S-gel was obtained when the prepared sample was treated with ultrasonic radiation (0.31 Wcm<sup>-2</sup>, 40 KHz) for 15 seconds at room temperature

### Synthesis.

**3-Cholesterylloxycarbonylpropanoic acid (MCB):** 3-Cholesterylloxycarbonylpropanoic acid was synthesized by the reported method.<sup>30</sup> A solution of cholesterol (3.89 g, 10 mmol), succinic anhydride (1.27 g, 13 mmol) and triethylamine (1.5 mL, 15 mmol) in dry acetone (60 mL) was heated to reflux under nitrogen atmosphere for 24 h. The acetone was then evaporated and resulting precipitate was recrystallized twice from glacial acetic acid, white solid 3.5 g, 72% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.37 (d, 1H, *J* = 4.0 Hz), 4.63 (m, 1H), 2.68 (t, 2H, *J* = 6.0 Hz), 2.61 (t, 2H, *J* =

7.0 Hz), 2.32 (d, 2H, *J* = 9.0 Hz), 2.02-0.91 (m, 33H), 0.86 (dd, 6H, *J* = 4.0 Hz), 0.68 (s, 3H).

**8-(6-Hydroxy)hexoxy-[3,3-diphenyl]-3H-naphtho[2,1-*b*]pyran (Naphthopyran, NP):** A mixture of 6-(6-hydroxyhexyloxy)naphthalen-2-ol (3.0 g, 11.4 mmol), 1,1-diphenylpropyn-1-ol (2.64 g, 11.4 mmol) and the catalyst of *p*-toluenesulphonic acid (PTSA, 0.06 g) in 50 mL dry CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature under nitrogen atmosphere for 48 h. The mixture was washed with water (6 × 100 mL) and dried over anhydrous sodium sulfate. The crude product was further purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 100:1) to get NP as an orange solid (1.8 g, 35% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, 1H, *J* = 9.0 Hz), 7.52 (d, 1H, *J* = 9.0 Hz), 7.48 (d, 4H, *J* = 3.5 Hz), 7.47-7.30 (m, 4H), 7.29-7.22 (m, 2H), 7.02 (d, 1H, *J* = 2.5 Hz), 7.12 (s, 1H), 7.14 (d, 1H, *J* = 2.5 Hz), 7.16 (d, 1H, *J* = 7.5 Hz), 6.26 (d, 1H, *J* = 10.0 Hz), 4.04-4.02 (m, 2H), 3.68-3.65 (m, 2H), 1.85-1.82 (m, 2H), 1.63-1.59 (m, 2H), 1.50-1.48 (m, 2H), 1.47-1.45 (m, 2H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 155.38, 148.83, 144.84, 130.25, 128.35, 128.02, 127.99, 127.43, 126.96, 124.89, 122.78, 119.63, 119.33, 118.63, 114.25, 107.50, 82.23, 67.79, 62.86, 32.62, 29.16, 25.88, 25.50. HRMS (ESI-TOF), Calcd. for mole ([M+H]<sup>+</sup>): 451.2273, Found: 451.2268.

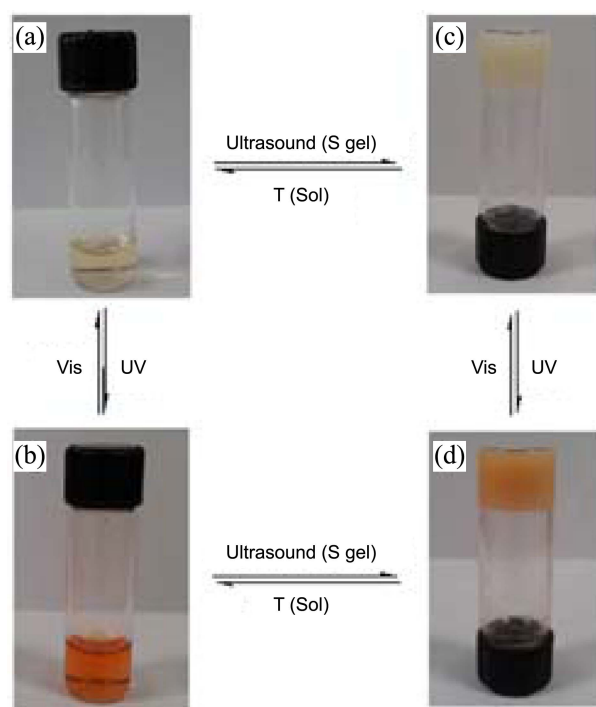
**8-[6-(3-Cholesterylloxycarbonylpropionyloxy)]-[3,3-diphenyl]-3H-naphtho[2,1-*b*]pyran (NP-MCB):** NP (1.36 g, 3.0 mmol), MCB (0.97 g, 2.0 mmol) and 4-dimethylaminopyridine (DMAP, 0.04 g, 0.36 mmol) were dissolved in mixed solvent of purified THF (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (4 mL). After the solution was stirred in ice-water bath for 1 h, *N,N'*-dicyclohexylcarbodiimide (DCC, 0.74 g, 3.6 mmol) was added, and the reaction mixture was allowed to warm up slowly to room temperature and stirred continuously for 24 h. The precipitate was filtered off and solvent was evaporated. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and then washed with 1 N HCl solution, saturated solution of sodium bicarbonate in sequence. After that, the solution was dried over anhydrous sodium sulfate. The crude product was further purified by column chromatography (petroleum ether: ethyl acetate = 15:1), white solid 0.8 g, 44% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (dd, 1H, *J* = 9.5 Hz), 7.53 (dd, 1H, *J* = 9.0 Hz), 7.49 (d, 4H, *J* = 9.0 Hz), 7.32 (m, 5H), 7.26 (m, 2H), 7.17 (m, 1H), 7.14 (m, 1H), 7.02 (d, 1H, *J* = 2.5 Hz), 6.27 (dd, 1H, *J* = 10.0 Hz), 5.36 (d, 1H, 5.5 Hz), 4.63 (m, 1H), 4.12 (t, 2H, 6.5 Hz), 4.03 (t, 2H, 6.5 Hz), 2.60 (m, 4H), 2.32 (d, 2H, *J* = 7.5 Hz), 2.01-0.90 (m, 36H), 0.92 (dd, 4H, *J* = 6.0 Hz), 0.87 (m, 6H), 0.66 (s, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 172.44, 171.70, 155.38, 148.85, 144.85, 139.50, 130.27, 128.37, 128.03, 127.44, 126.97, 124.91, 122.79, 122.68, 119.65, 119.34, 118.64, 114.27, 107.50, 82.24, 74.30, 67.73, 64.68, 56.60, 56.04, 49.89, 42.24, 39.65, 39.47, 38.01, 36.88, 36.52, 36.13, 35.76, 31.83, 31.77, 29.45, 29.20, 29.10, 28.51, 28.21, 28.00, 27.69, 25.76, 25.70, 24.23, 23.79, 22.82, 22.55, 20.96, 19.28, 18.68, 11.81. HRMS (ESI-TOF), Calcd. for mole ([M+H]<sup>+</sup>): 918.5798, Found: 918.5780.

**Gelation Test.** The gelation properties of NP-MCB were

tested by a previous reported method. The weighed sample was mixed with the corresponding organic solvent (1 mL) in a sealed test tube, and then the mixture was heated until the solid was completely dissolved. After standing the resulting mixture was spontaneously cooled to room temperature. Finally the sealed test tube was inverted to observe if the solution inside could still flow. Gelation was considered to have occurred when a homogeneous substance was obtained, and the solution could not flow, denoted as G (gel). If the solvent and solid-like gel coexist within one system, denoted as PG (partial gel). At the end of the tests, precipitation was obtained which was denoted as P (precipitation). In the same case, only the solution was obtained, denoted as S (solution). On the contrary, the sample could not dissolve even at the boiling point of the solvent, denoted as I (insoluble). If the resulting mixture was able to turn into a gel when cooled to room temperature, this kind of gel is a thermo-reversible gel (T gel). If the hot solution was able to form into a gel immediately with ultrasound treatment, the gel can be thought to be ultrasound-reversible gel (S gel). MGC (minimum gel concentration) was described as a minimum concentration of gelator needed for the formation of stable gel.

## Results and Discussion

**Gel Forming Properties.** NP-MCB was synthesized and expected to be an effective organogelator to form gels by the heating-and-cooling method or heating-and-sonication method. However, as showed in Table 1, NP-MCB could not form organogels in any organic solvents by the heating-and-cooling method. This may be because the unbalanced tendency of the gelator molecules to dissolve or to aggregate in organic solvents. On the contrary, NP-MCB has been found to show the gelation properties in a few organic solvents by the heating-and-sonication method after ultrasound 15 seconds. This change maybe due to energy and pressure which were afforded in the ultrasonic process, resulting in formation of molecular hydrogen bonding and molecular aggregation induced by stacking.<sup>21</sup> The gelation properties were summarized in Table 1 and representative photographs were shown in Figure 1 where the formed gel was opaque



**Figure 1.** Photographs of NP-MCB (15 mg/mL, in 1-butanol) under the cooperative effects of thermal processing, light, ultrasound. (a) sol (closed form) (b) S-gel (closed form) (c) S-gel (open form) (d) sol (open form).

opalescent colloid. Upon irradiation with 365 nm UV light and in the dark, the light pink color of NP-MCB in solution and the opalescent color in gel closed form both could be interconverted with the orange color open form, *i.e.* photochromic processes of NP-MCB. This process could be repeated many times.

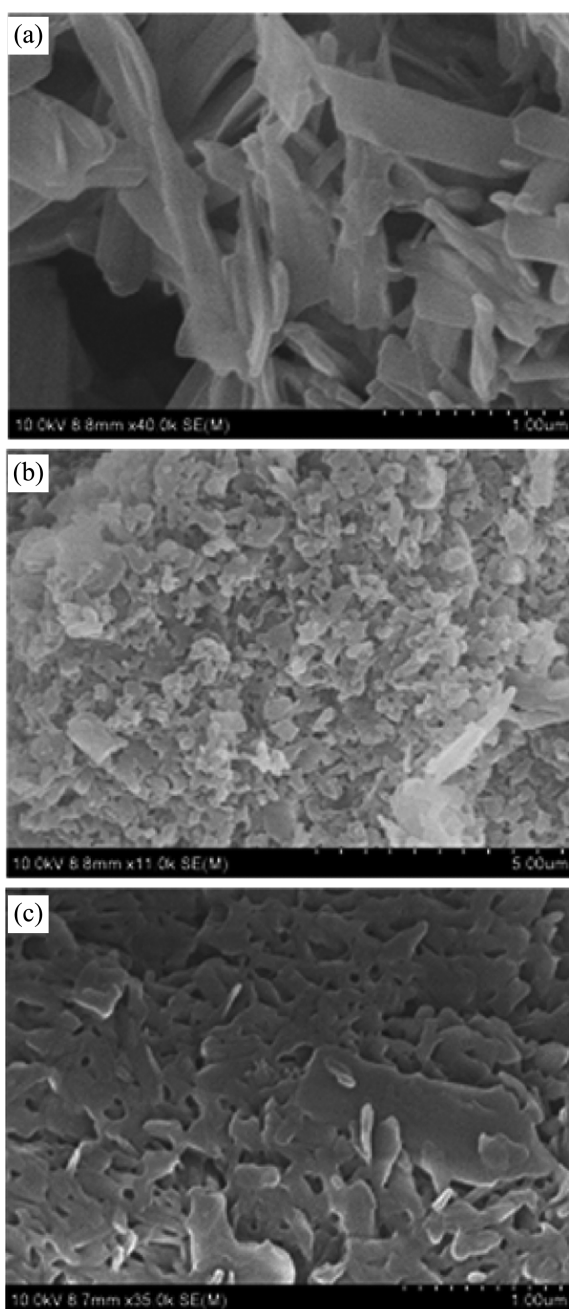
In order to obtain a visual insight into the morphologies of the molecular aggregation mode, the microstructures of NP-MCB in different solvents were examined with SEM (Figure 2). The images demonstrated that the organogelator molecules in the gel phase were self-assembled into 1-D nanofibers with the width ranging from 30 to 200 nm, which further cross-linked into 3-D networks and xerogel morphologies prepared in different solvents were similar, not affected by solvents.

**Photochromic Properties of the NP-MCB.** We took the NP-MCB in 1-butanol as an example to explore the photochromic property by UV-Vis spectroscopy in solution and S gel states. The absorption spectra of NP-MCB in butanol and S gel under irradiation of UV light (365 nm) are shown in Figure 3, respectively. It could be seen that NP-MCB exhibited photochromism upon irradiation of UV light not only in solution but also in gel. The intensity of the ring-opened NP-MCB increased gradually with the time of UV irradiation. The photochromic rate in gel was slower than in solution, which might be caused by the compact aggregation of NP-MCB molecules in S gel. After formation of the S gel, the molecules aggregated more compactly under the enhanced effect of hydrogen bonding.<sup>17,21</sup> Therefore, the free

**Table 1.** Gelation ability of NP-MCB in various solvents

Solvents	Observations	Solvents	Observations
isopropanol	S gel (13)	THF	S
<i>n</i> -hexane	S gel (8)	acetone	S
1-butanol	S gel (15)	CHCl <sub>3</sub>	PG
benzene	S	toluene	S
methanol	I	DMSO	S
<i>p</i> -xylene	S	benzene	S
ethanol	S	CHCl <sub>2</sub>	S
1,4-dioxane	S	xylene	S
ethyl acetate	S	DMF	S

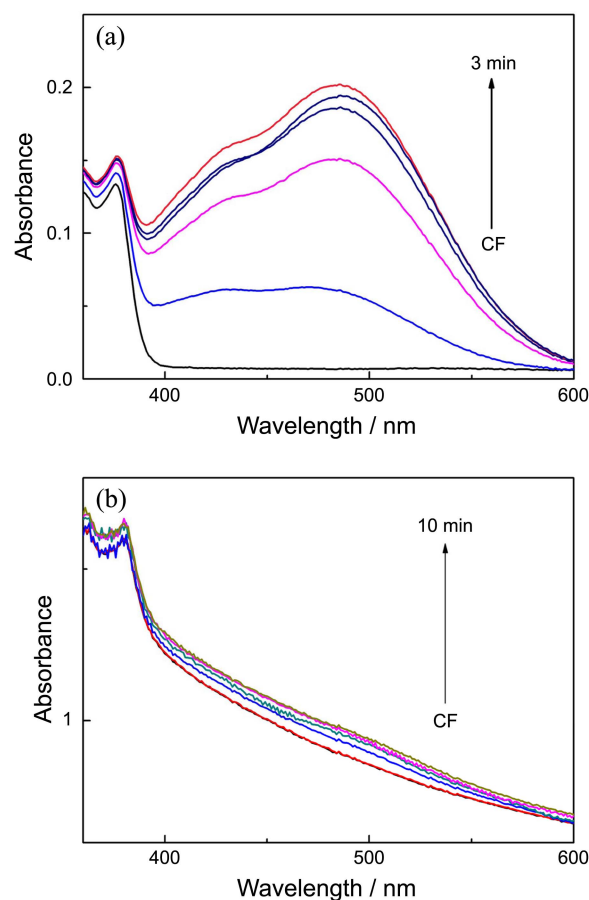
I: insoluble. S: solution. S gel: ultrasound-reversible gel. PG: partial gel. Numbers in parentheses represent the MGC (minimal gelation concentration, mg/mL)



**Figure 2.** SEM images of the xerogels from the S gel (15 mg/mL) in 1-butanol (a), isopropanol (b), *n*-hexane (c).

volume around the NP-MCB molecules and the mobility of the bond rotating were reduced, and then the photochromic performance of NP-MCB was slowed down.<sup>31</sup> The maximum absorption peaks of NP-MCB in solution and S gel were at 486 nm and 499 nm, respectively. The red-shift of absorbance band of open-form NP-MCB also should be attributed to the closely molecular aggregation in gel state.

As shown in the Scheme 1, when naphthopyran is irradiated with UV light and reach to a photostable state, there are two open forms, TC and TT. The open-forms spontaneously fade back to the closed form *via* two steps, TT→TC→CF. The process of TC→CF ( $k_1$ ) is usually rapid, and TT→CF

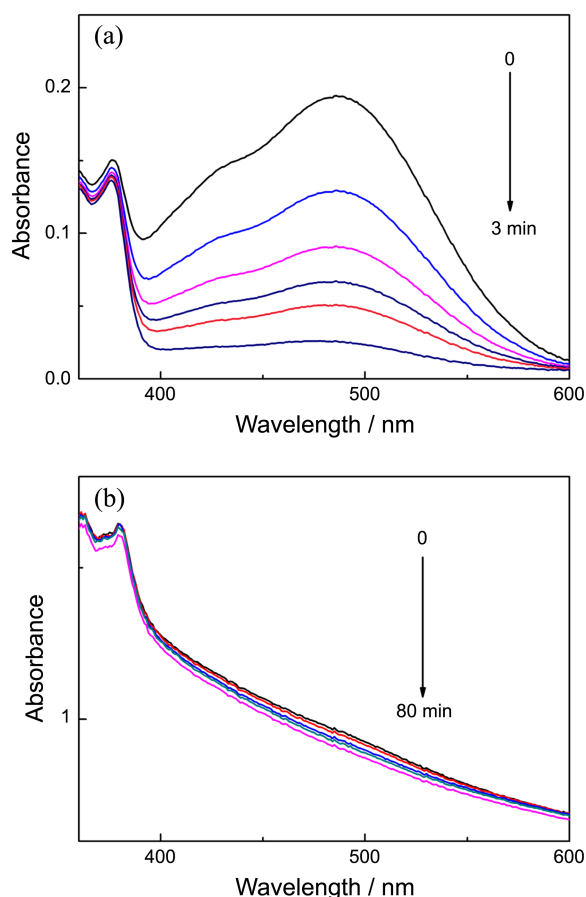


**Figure 3.** The absorbance change of the NP-MCB in butanol solution (a,  $1 \times 10^{-5}$  M) and S-gel (b, 15 mg/mL) with the irradiation time of UV light.

( $k_2$ ) is slow. The change of absorption intensity of the open form NP-MCB with time after removing the UV irradiation was shown in Figure 4. The fading time was much longer in gel than in solution, which indicates that the microenvironment around NP-MCB molecules affects the fading rate of open-form NP-MCB.

The biexponential decay equation,  $A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$  is often used to evaluate the kinetic constants  $k_1$  and  $k_2$ . Where  $A(t)$  is the optical density at  $\lambda_{max}$  of the open forms,  $A_1$  and  $A_2$  are the contributions to the initial optical density  $A_0$ , and  $A_{th}$  is the residual coloration at the termination of the testing time.<sup>32,33</sup> The black lines in Figure 5 were the experimental fading curves of NP-MCB in solution and gel, meanwhile, the red lines were the fitted curves obtained by the above equation with Origin software. Other evaluation mode for fading rate is comparing of  $T_{1/2}$  and  $T_{2/3}$ , which were the time taken for the sample to fade to half and two-thirds of the initial absorbance. This evaluation is insightful for comparing overall kinetics. The kinetic constants of NP-MCB were given in Table 2. The fitted data of  $k_1$  and  $k_2$  in solution were much faster than in gel, which were consistent with the experimental result.

The inserts in Figure 5 presented the reversibility of coloration and decoloration at the maximum absorption

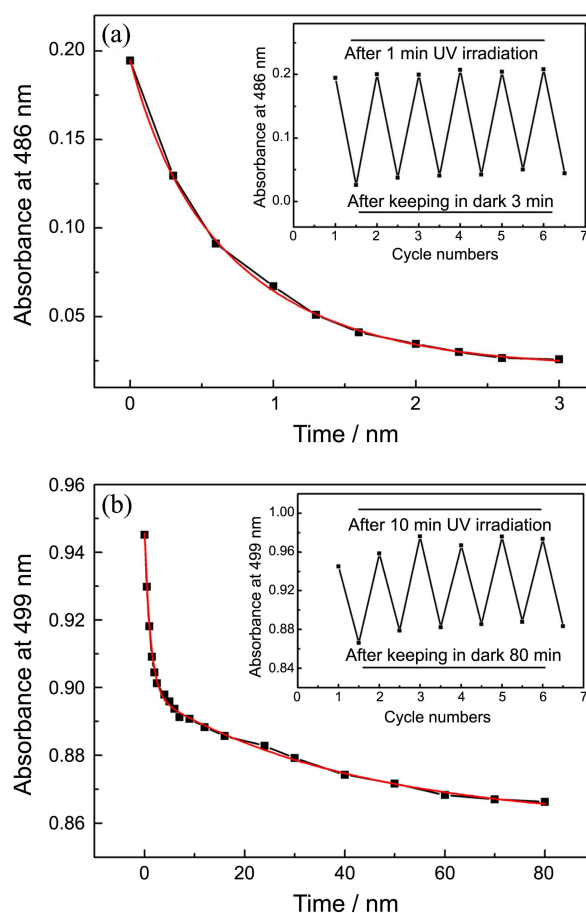


**Figure 4.** The UV-vis absorption spectra of the NP-MCB in butanol solution (a,  $1 \times 10^{-5}$  M) and S-gel (b, 15 mg/mL) after removing the UV irradiation versus time.

wavelengths, 486 nm and 499 nm, respectively. After 6 cycles of coloration/decoloration, the absorbance intensities were almost similar to the initial values, which implied that NP-MCB had good thermal reversibility.

**The Surface Wettabilities of Xerogels.** Functional surfaces with controllable wettability have attracted more interest for their great potential in biological and industrial applications.<sup>34</sup> The wettabilities of *n*-hexane, isopropanol and 1-butanol xerogels were characterized by the measurement of the water contact angle (CA) on their surface. The organogels were spin-coated onto glass slices, dried in air for 6 h at room temperature, then in vacuum for 12 h at 35 °C to ensure that no free solvent remains in these xerogels. Figure 6 has shown the shapes of water droplets sitting on different xerogel films. The CAs on surfaces coated xerogels, in 1-butanol, isopropanol and *n*-hexane increase from ( $131.5 \pm 0.7$ ) to ( $136.1 \pm 0.8$ ) and ( $145.3 \pm 0.9$ ), respectively. The polarity of *n*-hexane is the smallest used solvents among *n*-hexane, isopropanol and 1-butanol solvents, so its xerogel has the largest CA, which is consistent with the report.<sup>35</sup> Therefore, the surface wettabilities of xerogels could be modified by using different solvents.

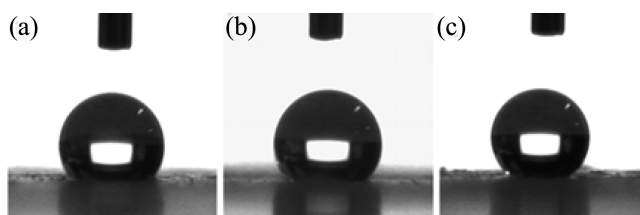
In addition, the effect of UV irradiation on CAs of xerogel films were also investigated. After the measurement of CA,



**Figure 5.** The fading curves of NP-MCB in solution (a,  $1 \times 10^{-5}$  M) and S gel (b, 15 mg/mL) monitored at 486 nm and 499 nm, respectively. The inserts are the photochromic cycles during alternating irradiation of ultraviolet and thermal bleaching in the dark.

**Table 2.** Kinetic data of NB-MCB in solution and gel

	$\lambda_{\max}$ (nm)	$T_{1/2}$ (min)	$T_{2/3}$ (min)	$k_1$ ( $\text{min}^{-1}$ )
solution	486	0.5	0.8	4.39
gel	499	2.1	6.9	0.086
	$k_2$ ( $\text{min}^{-1}$ )	$A_1$	$A_2$	$A_{th}$
solution	1.19	0.14	0.031	0.02
gel	0.024	0.047	0.038	0.86



**Figure 6.** Photographs of the water droplet on glass slices spin-coated with xerogel of NP-MCB from 1-butanol ( $131.5 \pm 0.7$ )° (a), isopropanol ( $136.1 \pm 0.8$ )° and *n*-hexane ( $145.3 \pm 0.9$ )° (c).



the water droplet was erased slightly with soft paper, then the xerogel film was irradiated by UV light (360 nm) for 10 min. The opalescent color of xerogel films became to the orange color, which indicated that the naphthopyrans in NP-MCB isomerized to the open-forms (Scheme 1). Then, the CA was then measured immediately. No obvious changes of CAs obtained from different solvents before and after UV irradiation in all xerogel films. There are two kinds of merocyanine isomers forms of naphthopyran, *i.e.* ketene and zwitterions.<sup>36</sup> If the open-form of naphthopyran is zwitterionic structure, the xerogel film should have better wettability and has smaller CA than that before UV irradiation. However, in our experiments, all CAs had no obvious changes, so it is reasonable to think the open-form of NP-MCB in xerogels is ketene structure.

### Conclusion

In summary, a new photochromic NP-MCB has been synthesized. NP-MCB could form S gel after ultrasound 15 seconds in several organic solvents and the xerogel morphologies prepared in different solvents were similar and presented the 3-D networks. The interconversion between solution and gel of NP-MCB was easily realized by heating and sonication. NP-MCB displayed excellent photochromic performances and good thermal reversibility both in solution and gel. The fading rate of NP-MCB could be tuned by changing its states, solution and gel. Furthermore, the test of the water contact angle of xerogels proved that the surface wettabilities could be modified by using different solvents and the open-forms of NP-MCB in xerogels were ketene structure. Thus, the present study may introduce a new way for preparation of reversible function materials through the supramolecular self-assembly under the effect of ultrasonic stimulation and heating, which makes it promising application in the fields of molecular photonic devices and other smart materials.

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