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Synthesis and photochromism of a spirooxazine derivative featuring a carbazole moiety: Fast thermal bleaching and excellent fatigue resistance

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1. Introduction

Considerable effort has been made to develop organic photochromic materials that change their chemical and physical properties upon irradiation with certain wavelengths of light and containing photo-generated species that can be reversed to the initial species either thermally or by irradiation with a different wavelength of light [1]. In particular, thermally reversible photochromic compounds facilitate setting and resetting physicochemical properties of the compounds by simply turning a light source on and off [2].

Among thermally reversible photochromic compounds, spiroindolinonaphthooxazine (SO) derivatives are most promising candidates for applications as multifunctional optoelectronic materials, such as smart windows, ophthalmic lenses, optical data processing and optical switching, as well as displays [3]. This owes to their good coloring power and remarkable fatigue resistance. These compounds are composed of two heterocyclic nearly planar

** Corresponding author. Tel.: +46 8 55378417; fax: +46 8 55378590. E-mail addresses: qzou@shiep.edu.cn (Q. Zou), lixin@theochem.kth.se (X. Li). moieties (indoline and naphthooxazine) linked by a tetrahedral spiro-carbon which prevents the two π -electron systems from conjugation. Such structural characteristics result in colorless or pale yellow solutions of the spiro-compounds since the lowest electronic transition of the molecule occurs in the near ultraviolet (UV) region [4]. As illustrated in Scheme 1, the photo-cleavage of the C–O spiro-bond takes place upon exposure to UV light and subsequent rotation around the C–C bond to give rise to an open merocyanine (MC) structure that absorbs in the visible light region along with the intensively colored solution [5]. The MC isomer is denoted here by its *trans-trans-cis* (TTC) conformation [1a]. The solution returns thermally back to the original state when the UV light irradiation ceases.

For commercial application of multifunctional optoelectronic materials, it is essential to maintain photochromic molecules with highly efficient photoresponse, large steady-state optical density and fast-bleaching speed at ambient temperature, as well as fatigue-resistance [6]. Herein, we report a convenient synthesis of a novel spirooxazine derivative **SOC** (Scheme 2) featuring a carbazole moiety that is usually applied in effective electron-donor and hole-transporting materials [7], for the sake of expanding the photochromic properties and possibly the commercial applications of

trans-trans-cis conformation was found to be several times faster t conformation. This type of fast-bleaching and fatigue-resistent photoching pave an exciting avenue in future development of high-performance pl © 2014

ABSTRACT

A novel photochromic spirooxazine derivative bearing a carbazole moiety (**SOC**) was synthesized and studied in solution under flash photolysis conditions. It is found to exhibit excellent characteristics like high photochromic response, large steady-state optical density, fast thermal bleaching rate and good fatigue-resistance. The effect of different solvents on the photochromic properties of the compound was evaluated, revealing that the photochromic properties can be modulated by different solvents based on the corresponding polarity. The mechanism and kinetics of the thermal fading process of compound **SOC** were additionally investigated by theoretical simulations, where the isomerization pathway from the *trans-trans-cis* conformation was found to be several times faster than that from the *cis-trans-cis* conformation. This type of fast-bleaching and fatigue-resistent photochromic compounds is expected to pave an exciting avenue in future development of high-performance photochromic materials.

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Scheme 1. The structural interchange between the SO and MC isomers.

spirooxazine derivatives. Several merits with good photochromic properties turn out inherent in compound **SOC**: (i) its intensively colored form (MC isomer) possesses relatively large optical density; (ii) it can interchange rapidly between the SO and MC forms when luminous UV irradiation is switched on and off; (iii) it tolerates hundred switching cycles without decomposing, indicative of an excellent fatigue resistance; (iv) its photochromic properties regularly change with respect to the polarity of different solvents, suggesting that the photochromic properties can be modulated by solvent interaction. These merits are highly desired for use in optoelectronic materials, for instance, ophthalmic lenses and smart windows, and provide insight for the future design of functional photochromic materials.

2. Experimental section

2.1. Materials and instrumentations

2,7-Dihydroxynaphthalene and 3,3-dimethyl-2-methylene-1phenylindoline were purchased from Sigma—Aldrich and used without further purification. Other starting materials were commercially available and purified before use. All other reagents were of analytical purity and used without further treatment. Thinlayer chromatography (TLC) analyses were performed on silica-gel plates, and flash chromatography was conducted by using silica-gel column packages purchased from Qing-dao Haiyang Chemical Company, China.

¹H NMR and ¹³C NMR spectra in CDCl₃ were recorded on Brucker AM-400 spectrometers with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded on a Waters LCT Premier XE spectrometer with methanol as solvent. Photochromic reaction was induced in situ by a continuous wavelength irradiation Hg/Xe lamp (Hamamatsu, LC6 Lightingcure, 200W) equipped with narrow band interference filters of appropriate wavelengths (Semrock Hg01 for lirr = 365 nm, Semrock BrightLine FF01-575/25-25 for lirr = 575 nm). UV–vis absorption changes were monitored by a charge-coupled device (CCD) camera mounted on a spectrometer.

2.2. Kinetic measurements in solution

A solution of compound **SOC** in the appropriate solvent, with a concentration of 6.0×10^{-5} M was measured in a well-stirred quartz cell (light-path length: 10 mm). The thermal decay at λ_{max} was studied for all of the samples until 3 s after photoirradiation. The thermal decay curves were fitted with exponential functions of Origin 8.0 software to obtain the pre-exponential constants (A_{th} , A_{1} , and A_{2}) and kinetic constants (k_{1} and k_{2}) of the biexponential kinetic equation to study the photochromic kinetics of compound **SOC**.

2.3. Computational methods

The thermal fading (ring-closure) process of the spirooxazine derivative (compound **SOC**) was investigated by first-principles calculations. The geometries of the spirooxazine isomers and transition states along reaction coordinates were optimized by density functional theory (DFT) calculations, using the M06 functional [8] and the 6-31G** basis set [9] as implemented in the Gaussian 09 program package [10]. Solvent effects of tetrahydro-furan (THF) were taken into account by the polarizable continuum model (PCM) [11] in all calculations. At optimized geometries, frequency analyses were performed and thermodynamic data were computed at 290 K.

2.4. Synthesis

The synthesis route of compound SOC is shown in Scheme 2.



Scheme 2. Synthetic routine of photochromic compound SOC.

2.4.1. Synthesis of 7-bromonaphthalen-2-ol (2)

A synthetic procedure was based on the literature method [12]. To a vigorously stirred mixture of triphenylphosphine (31.5 g, 120 mmol) in acetonitrile (50.0 mL), bromine (19.2 g, 120 mmol) was added dropwise at 0 °C. The reaction mixture was allowed to reach room temperature, and 2,7-dihydroxynaph thalene **1** (16.0 g. 100 mmol) was added in one portion. The mixture was heated to 70 °C for 30 min. after which the solvent was removed by rotary evaporation. The flask was equipped with a gas trap, and the black residue was heated to 250 °C for 1 h. After cooling to room temperature, the mixture was dissolved in 200 mL of dichloromethane and the viscous liquid was obtained after column chromatography (silica gel, petroleum ether/ dichloromethane 1:1). The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 3:2) to give the compound **2** (18.8 g, 84.3 mmol, 84%) as a beige powder. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.09 (s, 1H, -OH), 7.06 (d, 1H, J 2.4 Hz, naphthalene-H), 7.10 (dd, 1H, J 8.8, 2.8 Hz, naphthalene-H), 7.24 (dd, 1H, J 8.8, 2.0 Hz, naphthalene-H), 7.63 (d, 1H, J 8.8 Hz, naphthalene-H), 7.72 (d, 1H, J 8.8 Hz, naphthalene-H), 7.84 (d, 1H, J 1.2 Hz, naphthalene-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 108.7, 118.1, 120.8, 127.0, 127.3, 128.3, 129.4, 129.9, 135.7, 154.0. HR-ESI-MS m/z: [M-H]⁻ calcd. for C₁₀H₆BrO, 220.9602; found, 220.9601.

2.4.2. Synthesis of 7-bromo-2-methoxynaphthalene (3)

A procedure slightly modified from the one described in Ref. [13] was followed. To a mixture of 7-bromonaphthalen-2-ol 2 (3.00 g, 13.0 mmol) and potassium carbonate (5.38 g, 39.0 mmol) in acetone (80.0 mL), iodomethane (9.00 g, 65.0 mmol) was added under stirring. The reaction mixture was refluxed under argon for 10 h. After cooling to room temperature, the mixture was filtered, and the filtrate was concentrated under vacuum. The crude product was purified by column chromatography (silica gel, petroleum ether) to give the compound 3 (2.87 g, 12.1 mmol, 93%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.92 (s, 3H, $-OCH_3$), 7.03 (d, 1H, J 2.4 Hz, naphthalene-H), 7.15 (dd, 1H, J 8.8, 2.8 Hz, naphthalene-H), 7.40 (dd, 1H, J 8.8, 2.0 Hz, naphthalene-H), 7.63 (d, 1H, J 8.8 Hz, naphthalene-H), 7.70 (d, 1H, J 8.8 Hz, naphthalene-H), 7.90 (d, 1H, J 1.6 Hz, naphthalene-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 55.8, 104.6, 119.1, 120.4, 127.5, 129.0, 129.6, 130.2, 132.6, 158.3. HR-ESI-MS m/z: $[M + H]^+$ calcd. for C₁₁H₁₀BrO, 236.9915; found, 236.9912.

2.4.3. Synthesis of 9-(7-methoxynaphthalen-2-yl)-9H-carbazole (4)

A mixture of 7-bromo-2-methoxynaphthalene **3** (1.00 g, 4.20 mmol), carbazole (2.10 g, 13.0 mmol), copper powder (0.270 g, 4.20 mmol), and potassium carbonate (3.00 g, 21.0 mmol) in trichlorobenzene (50.0 mL) was refluxed under argon for 24 h. After cooling to room temperature, the mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/dichloromethane 4:1) to give the compound 4 (0.360 g, 1.10 mmol, 27%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.85 (s, 3H, -OCH₃), 7.15 (d, 2H, J 5.2 Hz, carbazole-H), 7.21 (t, 2H, J 7.2 Hz, carbazole-H), 7.33 (t, 2H, J 5.4 Hz, carbazole-H), 7.38 (d, 2H, J 8.0 Hz, naphthalene-H), 7.42 (dd, 1H, J 8.6, 1.8 Hz, naphthalene-H), 7.83 (d, 1H, J 1.6 Hz, naphthalene-H), 7.87 (d, 1H, J 8.4 Hz, naphthalene-H), 7.98 (d, 1H, J 8.0 Hz, naphthalene-H), 8.08 (d, 2H, J 7.6 Hz, carbazole-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 55.5, 109.5, 110.0, 119.5, 120.4, 120.6, 123.6, 123.8, 123.9, 126.2, 128.0, 128.9, 129.1, 134.9, 140.9, 158.4. HR-ESI-MS m/z: $[M + H]^+$ calcd. for C₂₃H₁₈NO, 324.1388; found, 324.1384.

2.4.4. Synthesis of 7-(9H-carbazol-9-yl)naphthalen-2-ol (5)

9-(7-methoxynaphthalen-2-yl)-9H-carbazole **4** (0.356 1.10 mmol) was dissolved in anhydrous dichloromethane (20.0 mL) and boron tribromide (4.00 mL of 1 M solution in dichloromethane) was added dropwise under argon for 20 min at 0 °C using a syringe. The solution was stirred for 4 h at 0 °C, before it was poured into icy water (20.0 mL). The mixture was extracted with dichloromethane. The organic layer was dried over MgSO4, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/dichloromethane 1:1) to give the compound 5 (0.174 g, 51%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.31 (s, 1H, -OH), 7.20 (d, 2H, / 7.6 Hz, carbazole-H), 7.30 (t, 2H, / 7.4 Hz, carbazole-H), 7.41 (t, 2H, J 7.6 Hz, carbazole-H), 7.47 (d, 2H, J 8.0 Hz, naphthalene-H), 7.51 (d, 1H, J 8.4 Hz, naphthalene-H), 7.88 (d, 2H, J 6.4 Hz, naphthalene-H), 7.98 (d, 1H, J 8.4 Hz, naphthalene-H), 8.17 (d, 2H, / 8.0 Hz, carbazole-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 109.5, 109.9, 118.3, 120.0, 120.4, 123.0, 123.5, 123.8, 126.0, 127.9, 129.7, 130.0, 135.3, 135.9, 141.0, 154.2. HR-ESIMS m/z: $[M + H]^+$ calcd. for C₂₂H₁₆NO, 310.1232; found, 310.1234.

2.4.5. Synthesis of 7-(9H-carbazol-9-yl)-1-nitrosonaphthalen-2-ol (6)

7-(9H-carbazol-9-yl)naphthalen-2-ol **5** (0.174 g, 0.560 mmol) was dissolved in the solution of acetic acid (10.0 mL) and water (3.00 mL). Then the solution of sodium nitrite (0.039 g, 0.780 mmol) in water (1.00 mL) was added dropwise over 15 min at 0–5 °C using a syringe. The mixture was stirred for 2 h at 0 °C, before the reaction mixture was filtered. The residue was washed with dilute acetic acid in water (5.00 mL), then washed with deionized water (50.0 mL) to give the compound **6** (0.084 g, 44%) as a red solid, which was used directly in the synthesis of compound **SOC**.

2.4.6. Synthesis of 1-phenyl-3,3-dimethyl-9'-(9H-carbazol-9-yl)spiroindolinenaphthoxadine (**SOC**)

7-(9H-carbazol-9-yl)-1-nitrosonaphthalen-2-ol 6 (1.40 g, 4.14 mmol) was gently refluxed in absolute ethanol (50.0 mL) and to the hot solution was added dropwise over 20 min a solution of 3,3-dimethyl-2-methylene-1-phenylindoline (1.00 g, 4.14 mmol) in absolute ethanol (20.0 mL) with triethylamine (2.09 g, 20.7 mmol). The mixture was then refluxed for 24 h. After cooling to room temperature, the mixture was concentrated under vacuum. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 4:1) to give the compound SOC (0.736 g, 32%) as a yellow solid. IR (KBr) v_{max} (cm⁻¹): 749, 984, 1019, 1081, 1092, 1384, 1400, 1447, 1477, 1498, 1594, 1619, 2962, 3145, 3422. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 1.44 (d, 6H, J 6.0 Hz, -CH₃), 6.73 (d, 1H, J 8.0 Hz, benzene-H), 6.95 (t, 1H, J 7.4 Hz, Nbenzene-H), 7.11-7.19 (m, 4H, benzene-H and carbazole-H), 7.28-7.35 (m, 6H, N-benzene-H and carbazole-H), 7.42 (t, 2H, J 7.6 Hz, carbazole-H), 7.50 (d, 2H, / 8.0 Hz, naphthalene-H), 7.55 (dd, 1H, / 8.4, 2.0 Hz, naphthalene-H), 7.62 (s, 1H, -N=CH), 7.76 (d, 1H, J 8.8 Hz, benzene-H), 7.93 (d, 1H, / 8.4 Hz, naphthalene-H), 8.16 (d, 2H, J 7.6 Hz, carbazole-H), 8.65 (d, 1H, J 1.6 Hz, naphthalene-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 19.6, 24.6, 52.1, 97.3, 107.1, 109.0, 116.4, 118.4, 118.9, 119.2, 119.5, 121.0, 122.2, 122.3, 122.4, 124.6, 124.9, 124.5, 126.8, 127.1, 128.3, 128.5, 128.9, 130.7, 134.7, 135.3, 138.2, 140.0, 143.3, 144.9, 150.1. HR-ESI-MS m/z: $[M + H]^+$ calcd. for C₃₉H₃₀N₃O, 556.2389; found, 556.2390.

3. Results and discussion

3.1. Synthesis and characterization

The target compound **SOC** was synthesized in six steps (substitution, etherification, Ullmann condensation, Zeisel ether cleavage, nitrosylation, condensation), starting from commercial and known precursors, as illustrated in Scheme 2. In order to prepare the designed compound **SOC**, we devised a new protocol to exploit the key intermediate **6** (1-nitrosonaphthalen-2-ol with a carbazole appendage at C-7 position), and elaborately synthesized it in five steps first. The chemical structures of compound **SOC** and other key intermediate products were well confirmed by ¹H NMR, ¹³C NMR, and HRMS (see the Experimental section and Supporting Information for details).

3.2. Photochromic properties

The evaluation of photochromic behavior for compound SOC involves some relevant parameters, related to the absorption spectra of the closed and open forms, kinetic thermal bleaching rate and fatigue resistance, as well as solvent effects. It is well-known that the photochromic reaction is caused by the reversible spiroheterolytic cleavage of the Csp3-O bond under UV irradiation, yielding the open MC form which can return to the closed SO form upon irradiation at visible light or in the dark [1a]. Under continuous irradiation with the light of 365 nm, the tetrahydrofuran (THF) solution of compound SOC very quickly reached the photostationary equilibrium. The color of the solution changed from lightvellow to blue, indicative of the formation of the open MC form. The optical density of compound SOC at the photostationary state was as high as 0.94, while its intensively colored form was thermally unstable at ambient temperature. The measurement of the transient absorption spectra was initiated immediately after ceasing the irradiation when a photostationary state was reached under illumination with 365 nm light at 290 K. As depicted in Fig. 1, the absorption band centered at 602 nm decreased rapidly after ceasing the irradiation, and a complete fading was achieved within 10 s, accompanied by the blue solution turning back to light-yellow, resulting from the closed SO form. Notably, upon irradiation with 365 nm light, the absorption spectra in the intensively colored form almost covered the whole visible spectrum with a broad absorption band between 300 and 400 nm. This generic nature enabled compound **SOC** to serve as a type of promising materials for extensive applications in the field of eye-protective glasses and smart windows, because both the visible and UV light could be effectively absorbed [14].



Fig. 1. Transient UV–vis absorption changes of compound **SOC** in THF solution $(6.0 \times 10^{-5} \text{ M})$ at 290 K after irradiation with 365 nm light in a well-stirred quartz cell (light-path length: 10 mm). Each of the spectra was recorded at 650 ms intervals within a 10 s period.



Fig. 2. The biexponential (second order) decay model and experimental thermal fading kinetics in THF solution $(6.0 \times 10^{-5} \text{ M})$ at 290 K (black line: data measured; red line: the second order decay model fitted). Inset: the second order decay model parameters. The monitored wavelength was at 602 nm.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The photochromic property of compound SOC was also investigated by transient UV-vis absorption spectroscopy in a series of solvents with varying polarity index, namely toluene, acetonitrile, and methanol. The UV-vis absorption spectral changes of compound **SOC** in other representative solutions were similar to in THF solution, along with the rapid fading rates. The maximum wavelength of the absorption band (λ_{max}) at the photostationary state and corresponding absorbance (Aabs) are listed in Table S1. Interestingly, slight bathochromic shifts of the absorption band derived from the MC form were observed with increasing solvent polarity from 601 nm in the weakly polar toluene to 607 nm in the moderately polar acetonitrile and to 618 nm in the highly polar methanol. The bathochromic shift shown in Table S1 at higher solvent polarity is indicative of a better stabilization of the excited state of the photomerocyanines relative to the ground state, i.e. of an increasing dipole moment upon electronic excitation [4]. Therefore, the ground-state weakly polar molecule should approach the configuration of the quinoid form and the excited state should have a prevalent zwitterionic character, which is in accordance with the $\pi - \pi^*$ character of the singlet excited state of the open form [15]. The quantum yields (ϕ) of the SP \rightarrow MC isomers of compound **SOC** in various solvents were evaluated by the standard procedures [16]. It turned out that the quantum yields gradually increased when the polarity of the solvents decreased in the sequence of methanol ($\Phi = 0.251$), acetonitrile ($\Phi = 0.438$), THF ($\Phi = 0.677$), toluene ($\Phi = 0.701$). In addition, Table S1 showed that

Table 1

Spectrokinetic data^a of thermal fading for compound SOC (6.0 \times 10 $^{-5}$ M) in different solvents at 290 K.

Solvent	$\tau_{1/2}$ (ms)	$\tau_{3/4} (\mathrm{ms})$	$k_1 (s^{-1})$	$k_{2}(s^{-1})$	A_1	<i>A</i> ₂	A _{th}
Toluene	885	1820	0.372	0.361	0.366	0.392	0.0121
THF	675	1742	2.05	0.60	0.369	0.567	0.0046
Acetonitrile	363	786	4.76	0.55	0.244	0.555	0.006
Methanol	185	331	4.85	4.63	0.182	0.212	0.0197

^a Samples initially irradiated at UV light of 365 nm until in the photostationary state (3 s). Thermal decoloration was then monitored at the λ_{max} of the intensively colored form (MC form) at 290 K in the dark.



Fig. 3. Energy barrier for isomerization between TTC and CTC.

the absorbance of compound **SOC** in acetonitrile solution at the photostationary state was as large as 1.25, which was about 2.6 times larger than that of methanol solution (0.49) under the same conditions, indicating that the solvent played a key role in obtaining large photosteady-state optical density of compound **SOC**.

3.3. Thermal fading kinetics

Kinetic studies are important as they concern the behavior of photochromic molecules of applicative interest. The thermal fading kinetics that is determined from the absorption-time data sets was analyzed using the following biexponential equation [17]:

$$A(\tau) = A_1 e^{-k_1 \tau} + A_2 e^{-k_2 \tau} + A_{th}$$
(1)

where $A(\tau)$ is the absorbance at λ_{max} of compound **SOC**; A_1 and A_2 are the contributions to the initial absorbance A_0 ; k_1 and k_2 are exponential decay rate constants of fast and slow components, respectively; and A_{th} is the residual coloration (offset) at the termination of testing time.

This is the most common model used for the analysis of the photochromic system and makes is beneficial to compare with other literature reported values [18]. It was found that the thermal fading kinetics of compound **SOC** is well described by the biexponential function with correlation coefficients >0.99 in all analyses. Additionally, the convenient measurement of thermal fading rate can be described by the $\tau_{1/2}$ and $\tau_{3/4}$ values, which are the time that takes for the absorbance to reduce by 1/2 and 3/4 of the initial absorbance in the MC form, respectively [6].

From equation (1) and Fig. 2, $\tau_{1/2}$ and $\tau_{3/4}$ obtained for compound **SOC** in THF solution were 675 ms and 1742 ms with the fading rate constants ($k_1 = 2.05 \text{ s}^{-1}$, $k_2 = 0.60 \text{ s}^{-1}$), respectively. In

order to fully understand the impact of the solvent polarity on the fading thermal kinetics, the fading kinetics of compound **SOC** was analyzed for other solvents using the same method - the spectrokinetic data were summarized in Table 1. By comparison of the data listed in Table 1, it was found that the fading speeds of the MC form in different solvents were dramatically accelerated as the solvent polarity increased in the sequence of toluene ($\tau_{1/2}$ = 885 ms, $\tau_{3/4}$ = 1820 ms), THF ($\tau_{1/2}$ = 675 ms, $\tau_{3/4}$ = 1742 ms), acetonitrile ($\tau_{1/2}$ = 363 ms, $\tau_{3/4}$ = 786 ms), methanol ($\tau_{1/2}$ = 185 ms, $\tau_{3/4}$ = 331 ms). The effects of solvent on the kinetic and thermodynamic parameters of spirooxazine ring opening and closing are generally interpreted in terms of solvation effects. The positive solvatochromism reveals that the thermal bleaching course can be tuned by choosing an appropriate solvent.

As mentioned above, the fast fading kinetics made it possible to change the color of the solution restricted to the position where it was irradiated with UV light, since the diffusion rate of the intensively colored species was slightly slower than the thermal bleaching rate at ambient temperature. Due to the short half-lifetime ($\tau_{1/2} = 185$ ms) of compound **SOC** in methanol solution at 290 K, the blue block of the solution only appeared where 365 nm light beam irradiated, other part of the solution remained light-yellow (see Figure S1). Such fast fading kinetics is indispensable for applications in light modulators and optical data processing.

3.4. Density functional theory calculations

According results presented in the literature [19], the open-ring isomer of spirooxazine derivatives has a number of conformations, among which the two most stable ones are termed as **TTC** and **CTC**. Here "T" and "C" denote the *trans/cis* conformation of the three dihedral angles (1-2-3-4, 2-3-4-5 and 3-4-5-6, see Fig. 3). We



Fig. 4. Energy barrier for ring-closure isomerization between TTC and SOt.



Fig. 5. Energy barrier for ring-closure isomerization between CTC and SOc.

examined the energy barrier for isomerization between **TTC** and **CTC** by scanning the potential energy surface along the rotation of dihedral angle 1-2-3-4 (see Fig. 3 and Table S2), and found that the barrier is actually larger than 84 kJ/mol (or 20 kcal/mol), which is not accessible under ambient temperature. This means that the two open-ring isomers, **TTC** and **CTC**, are not interconvertible. This is also connected to the observation that the thermal fading kinetics of open-ring isomer usually exhibits biexponential decay [17,18].

We further investigated the ring-closure isomerization pathways from **TTC** and **CTC**, respectively. As shown in Fig. 4, the rotation of the dihedral angle 2-3-4-5 gives rise to the closed-ring isomer **SOt**, which is more stable than its open-ring counterpart **TTC**. This process takes place via a transition state with an energy barrier of 72.6 kJ/mol (Table S3). Differently, the ring-closure process of **CTC** goes through two transition states and one intermediate **CCC** (Fig. 5). The rotation of the dihedral angle 2-3-4-5 in **CTC** has to



Fig. 6. Time-dependent photocoloration of compound **SOC** (6.0×10^{-5} M) in different solutions: (a) THF; (b) toluene; (c) acetonitrile; (d) methanol at 290 K by UV irradiation at 365 nm, and the subsequent thermal fading when the irradiation was ceased. The monitored wavelength was at the λ_{max} of the intensively colored form (MC form), respectively.

overcome an energy barrier of 76.8 kJ/mol to reach **CCC** where all the three dihedral angles are all in their *cis* conformations (Table S4). Intermediate **CCC** then overcomes a small energy barrier of 10.9 kJ/mol to reach the ring-closure isomer **SOc** through shortening of the C–O distance (Fig. 5 and Table S4).

Based on the energy barriers and Eyring equation, we computed the rate constants for the two ring-closure isomerization pathways, namely **TTC** \rightarrow **SOt** and **CTC** \rightarrow **SOc**. as shown in Table S5. The **TTC** \rightarrow **SOt** ring-closure pathway is found to have a lower energy barrier and is hence several times faster than $CTC \rightarrow SOc$. The computed rate constants are 0.50 and 0.09 s⁻¹ for **TTC** \rightarrow **SOt** and $CTC \rightarrow SOc$, respectively, which are in qualitative agreement (albeit smaller) compared with the experimental observation of 2.05 and 0.60 s⁻¹. According to the Eyring equation, the experimental energy barriers for the two ring-closure isomerization pathways can be estimated as 69.2 and 72.2 kJ/mol, respectively. We can see that the computed energy barriers (72.6 and 76.8 kJ/mol) overestimate the barriers by ~ 4 kJ/mol (or ~ 1 kcal/mol), which is reasonable for a parameterized density functional (M06) and a double-zeta basis set (6-31G^{**}). We further refined the energy barrier for the **TTC** \rightarrow **SOt** ring-closure pathway by recomputing the self-consistent field energy using the triple-zeta basis set 6-311++G** and obtained an energy barrier of 71.6 kJ/mol, which shows better agreement with experimental result.

3.5. Photocoloration/thermal bleaching cycles

The photocoloration investigation showed that compound **SOC** in various solutions could undergo photochemical reaction within 3 s upon UV light irradiation. As depicted in Fig. 6, it took only about 0.92 s in methanol, 1.30 s in acetonitrile, 2.07 s in THF and 2.52 s in toluene, respectively, for compound SOC to reach the photostationary state under the same measurement conditions, which was consistent with its thermal fading rate. Obviously, compound SOC possesses high photoresponse, which is an important precondition in practical applications for ophthalmic plastic lenses and smart windows, as well as optical switching devices. Additionally, fatigue resistance is another important factor to consider for applicable photochromic materials. A preliminary investigation of fatigue resistance for compound SOC in different solvents was performed by simply turning UV light of 365 nm on and off. As presented in Fig. 6, after 10 cycles of coloration/bleaching, no distinct degradation was detected by UV-vis absorption for compound SOC in THF and methanol solution. Compound SOC also showed good fatigue resistance in toluene solution, and less than 15% degradation was detected after 10 cycles. The fatigue resistance of compound SOC in THF and methanol solution was further tested by subjecting it to 100 coloration-decoloration cycles, respectively. As can be seen from Figure S2, there is no sign of degradation after one hundred switching cycles, even in the presence of molecular oxygen, demonstrating very good fatigue resistance of compound SOC in THF and methanol solution, respectively.

4. Conclusions

A spirooxazine derivative **SOC** featuring with a carbazole unit, for the first of their kind, was synthesized and characterized. Its photochromic behaviors were investigated in solvents of different polarity. The compound underwent reversible ring-opening/ closure isomerization between the closed SO form and the open MC form upon irradiation with 365 nm light and in the dark. Benefiting from a special design of molecular structure, the compound displayed fast coloration rate under UV light illumination, large steady-state optical density, and rapid bleaching under dark condition, as well as excellent fatigue resistance at ambient temperature. Moreover, compound **SOC** was found to exhibit regular change on the photochromic properties depending on solvent polarity, indicating solvent-tunable photochromic behavior. Density functional theory calculations provided insight into the mechanism and kinetics of the thermal fading process of the spirooxazine derivative **SOC**. In particular, the **TTC** \rightarrow **SOt** pathway was found to be several times faster than **CTC** \rightarrow **SOc** with the latter pathway containing an intermediate state where the spirooxazine is in its *cis-cis*-cis conformation. This work is expected to provide a promising, robust platform to develop the photochromic materials with promising photoresponsive characteristics, such as rapid switching speed and remarkable stability.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.04.004.

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