

Synthesis, characterization, and solvent-independent photochromism of spironaphthooxazine dimers

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ABSTRACT

Specifically angled, conjugated spiroindolinonaphthooxazine dimers (SNOD) have been synthesized. The photochromic reactions of two types of SNOD were studied under continuous UV irradiation in solvents of different polarity. Comparison of these results with the single unit provides the examination of the specific effect of substituents on their photochromic properties and relaxation kinetics. The photomerocyanine isomers showed positive solvatochromism, supporting the premise for a less polar quinoidal structure. The thermal closing rate at 25 °C ranged from 0.2 to 1.6 s⁻¹ depending on the compound and solvent. Photochromism of these new compounds showed little dependency on solvent polarity and stable cyclability.

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1. Introduction

Photochromic materials have shown practical applications in the latest technologies such as optical switching, sensor, drug delivery, data storage, and recording [1,2]. The use of spirooxazine based materials has become of increasing interest due to their excellent photostability, compatibility in a variety of matrices, and distinctive changes in structure and absorption spectra upon irradiation. The photoresponsive site of the spirooxazine is the center sp³ spiro carbon. When irradiated with UV light, the carbon oxygen bond cleaves and achieves sp² hybridization, yielding a conjugated zwitterionic or quinoidal system [3,4]. This conjugated isomer, called merocyanine (MC) is metastable and readily isomerizes via ring closing into the spiro (SP) form either thermally in dark conditions or under visible light [5].

As an approach to improve the applicability of spirooxazine based compounds, joining two of the species through a spacer offers unique bi-photochromic molecules with distinctive photokinetic properties [6–8]. A challenge faced with designing bi-photochromic molecules is that these dimer systems often exhibit different or deficient photochemical properties from those of the single components. Photochromic properties and the rate of thermal closing are affected by the nature of the spacer, e.g., inducing a loss of

thermal reversibility, yielding different isomers from the starting material, and/or extensive photodegradation [7,8]. In addition, bi-photochromic systems have shown to be either too rigid or flexible for further application.

Recently, we reported a shape specific photochromic dimer, called SPOD, consisting of two spiro-phenanthro-oxazine moieties connected via triple bond at the indoline portion of the spirooxazine moieties [9]. This SPOD has shown interesting binding ability with palladium catalyst. The open MC form of this molecule showed a bathochromic shift at the maximum wavelength of absorption and higher colourability due to the increased conjugation. It exhibited excellent reversibility; however, the data from thermal bleaching illustrates that the rate of thermal closure increased dramatically with increasing solvent polarity. Thermal closing rates ranged from 0.12 s⁻¹ in nonpolar methylcyclohexane to 4.48 s⁻¹ in polar solvent, dimethylformamide. Reports suggest that the solvent dependency for phenanthrene systems is due to a loss in pseudo pi-conjugation between the indoline and oxazine moieties in its transition state. As the electronic charge on the indoline nitrogen and oxazine oxygen atoms increases, the molecular dipole moment increases causing the accelerated closing with polarity of solvent [10,11].

In this work, we have improved our bi-photochromic systems by replacing the phenanthro-oxazine with naphtho-oxazine to create molecules having environmentally independent optical properties. We report the synthesis and photochromic properties of two types of spiro-naphtho-oxazine dimers: Debald-SNOD(2) and Deba-SNOD(3). The chemical structures and typical

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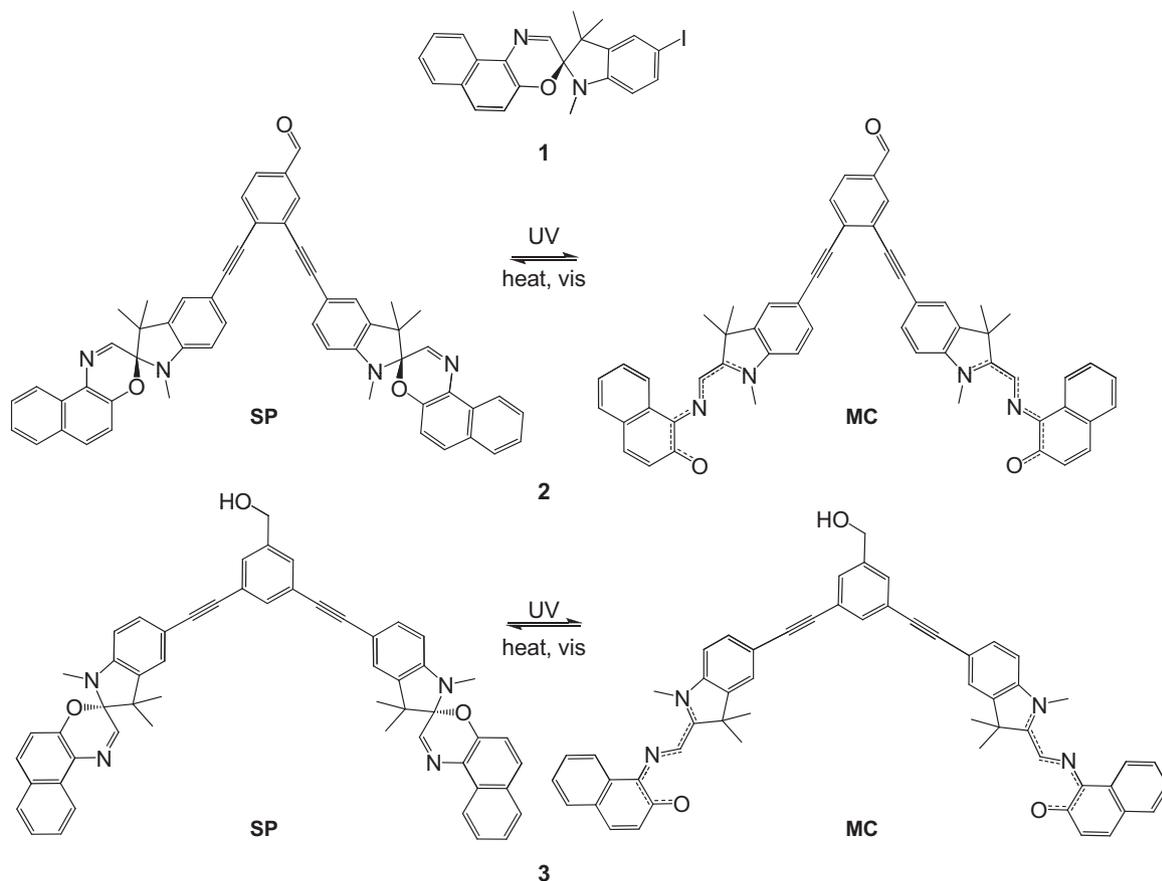


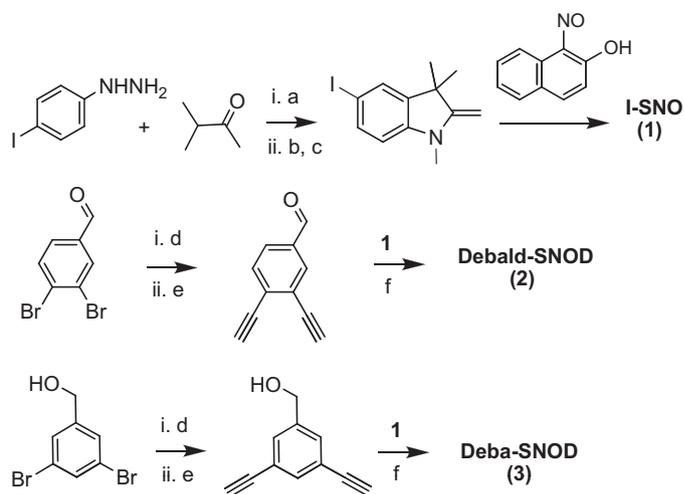
Fig. 1. The structure of I-SNO(1) and typical photoreactions of Debald-SNOD(2) and Deba-SNOD(3).

photoreactions for these compounds are given in Fig. 1. Two SNO units in these dimers were connected to different positions of a phenyl ring spacer, which would create different conjugation systems. Additionally, both dimers possess a functional group on the center phenyl ring to offer further modifications such as grafting on the surface and polymers. The investigation in this report includes studies on the effects of solvent and structure on the absorption properties, fatigue resistance, and closing rate kinetics of the merocyanine of the dimers as compared to the single unit, Iodo-SNO(1).

2. Experimental

2.1. General methods

All reactants (Fisher Scientific, Pittsburg, PA, USA) and deuterated solvents (99.9 atom% D, Sigma–Aldrich, St. Louis, MO, USA) were purchased and used as received. The reaction solvents were purified by Vacuum Atmospheres solvent purifier system. Flash column chromatography was performed on silica gel (200–400 mesh, 60A, Fisher Scientific). A 200 W Mercury Xenon lamp housed in a light box containing a 340 nm colored glass filter (FSR-U340) was directed at a right angle towards a cuvette containing a 10 mL solution of photochromic species maintained at room temperature. Absorption spectra were recorded with an Ocean Optics USB4000 Fiber Optic Spectrometer with UV–vis Dip Probe, capable of recording spectra in the UV to visible region every 0.1–1 s. ^1H and ^{13}C spectra were recorded for CDCl_3 solutions on JOEL 270 MHz and Varian 500 MHz instruments. Mass spectroscopy data were collected with positive mode of the ESI source on an LCQ-Advantage.



Scheme 1. Synthetic route of I-SNO(1), Debald-SNOD(2), and Deba-SNOD(3). Reagents and conditions: (a) H_2SO_4 , EtOH; (b) MeOTf, ACN; (c) NaOH; (d) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, Et_3N ; (e) TBAF, THF; (f) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, NMP; and (g) K_2CO_3 , MeOH.

2.2. Synthesis of photochromic compounds 1, 2, and 3 (Scheme 1)

The synthetic methods shown in Scheme 1 are adapted and modified from a previously published procedure [9]. The bi-photochromic systems were synthesized in five steps with an overall yield of 29% for Debald-SNOD(2) and 38% for Deba-SNOD(3). The synthesis started with the conversion of

4-iodophenylhydrazine to 5-iodo-2,3,3-trimethylindole via Fischer cyclization followed by a methyl triflate in acetonitrile. The product was treated with base and reacted with 1-nitrosophthalen-2-ol in trichloroethane to yield I-SNO(1). The single unit spirooxazine was then reacted with 3,4-diethynylbenzalcohol or 3,4-diethynylbenzaldehyde using Sonogashira coupling to generate the respective spirooxazine dimer.

2.2.1. 5-Iodo-2,3,3-trimethylindolenine

Isopropylmethylketone (1.8 mL, 16.7 mmol) followed by conc. H₂SO₄ (0.6 mL) was added to a solution of 4-iodophenylhydrazine (1.8 g, 7.57 mmol) and ethanol (20 mL) at room temperature. The reaction was allowed to reflux for 12 h. The reaction mixture was allowed to cool to room temperature and 10% sodium bicarbonate was added dropwise until a biphasic mixture was formed. The mixture was extracted with diethyl ether (2 × 20 mL) and washed with deionized water (20 mL). The organic layer was dried over Na₂SO₄ and evaporated to yield a brown viscous liquid. The product was purified using column chromatography with 1:1 diethyl ether and hexane to give a brown viscous liquid (1.72 g, 76.2%). ¹H NMR (270 MHz, CDCl₃, δ): 7.63–7.59 (m, 2H), 7.28 (d, 1H, *J* = 8 Hz), 2.26 (s, 3H), 1.29 (s, 6H).

2.2.2. 1,2,3,3-Tetramethyl-5-iodo-3H-indolium triflate

Methyl triflate (1.4 mL, 13.0 mmol) was added to a solution of 5-iodo-2,3,3-trimethylindolenine (1.7 g, 5.89 mmol) and acetonitrile (ACN) (20 mL) under nitrogen atmosphere and allowed to reflux for 8 h. The solvent was evaporated and the residue was washed with diethyl ether (50 mL) to yield a reddish solid (1.3 g, 73.8%). ¹H NMR (270 MHz, CDCl₃, δ): 8.14 (d, 1H, *J* = 1.5 Hz), 8.01 (dd, 1H, *J* = 8.5 Hz), 7.53 (d, 1H, *J* = 8.5 Hz), 3.91 (s, 3H), 2.69 (s, 3H), 1.56 (s, 6H).

2.2.3. 5-Iodo-1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine] (I-SNO(1))

A solution of 1,2,3,3-tetramethyl-5-iodo-3H-indolium triflate (1.3 g, 4.34 mmol) in aqueous NaOH (1 M, 100 mL) was stirred to 15 min at room temperature. The product was extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and evaporated to yield a bright pink solid. The red solids (1.71 g, 5.68 mmol) and 1-nitrosophthalen-2-ol (1.21 g, 6.99 mmol) were taken into a reaction vessel. Trichloroethane was added to the reaction vessel under nitrogen atmosphere. The reaction mixture was refluxed for 12 h and cooled to room temperature. After the solvent was evaporated, the product was purified using column chromatography with 1:2 dichloromethane and hexane to give a green solid (1.45 g, 56.4%). ¹H NMR (270 MHz, CDCl₃, δ): 8.52 (dd, 1H, *J* = 8.5 Hz), 7.76 (d, 1H, *J* = 8 Hz), 7.73 (s, 1H), 7.65 (d, 1H, *J* = 8.5 Hz), 7.57 (t, 1H, *J* = 7.3 Hz), 7.46 (dd, 1H, *J* = 8 Hz), 7.39 (t, 1H, *J* = 8 Hz), 7.31 (s, 1H), 6.98 (d, 1H, 8.5 Hz), 6.36 (d, 1H, *J* = 8 Hz), 2.73 (s, 3H), 1.36 (d, 6H, *J* = 19 Hz). MS (*m/z*): calcd. [M+H]⁺ 455.1; found 454.2.

2.2.4. 3,4-Bis(trimethylsilylethynyl)benzaldehyde

Trimethylsilylacetylene (4 mL, 28 mmol) was added to a solution of 3,4-dibromobenzaldehyde (0.77 g, 2.9 mmol), Pd(PPh₃)₂Cl₂ (102 mg, 0.15 mmol), and CuI (43.4 mg, 0.23 mmol) in Et₃N (10 mL) at room temperature under nitrogen atmosphere. After stirring for an hour, the temperature was increased to 85 °C and the reaction continued for 12 h. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (20 mL), poured into deionized water (20 mL), to give a biphasic mixture which was extracted with diethyl ether (3 × 20 mL). The organic layer was dried over Na₂SO₄ and evaporated to yield a yellow film (0.564 g, 64.8%). ¹H NMR (270 MHz, CDCl₃): δ 9.97 (s, 1H), 7.59 (d, Ph–H, 1H), 7.71 (dd, Ph–H, 1H), 7.93 (s, Ph–H, 1H), 0.23 (s, Si–(CH₃)₃, 18H).

2.2.5. 3,4-Diethynylbenzaldehyde

3,4-Bis(trimethylsilylethynyl)benzaldehyde (0.45 g, 2.9 mmol) and K₂CO₃ (167 mg, 1.2 mmol) was dissolved in methanol (12 mL) at room temperature. The reaction was stirred for 1 h, diluted with dichloromethane (15 mL), and washed with aqueous sodium bicarbonate (15 mL), and deionized water (2 × 15 mL). The organic layer was collected, dried over Na₂SO₄, and evaporated to yield a yellow solid (0.185 g, 79.6%). ¹H NMR (270 MHz, CDCl₃): δ 9.97 (s, 1H), 7.98 (s, Ph–H, 1H), 7.78 (dd, Ph–H, 1H), 7.63 (d, Ph–H, 1H).

2.2.6. 3,4-Bis((1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine]-5-yl)ethynyl)benzaldehyde (Debal-SNOD(2))

N-Methylpyrrolidine (15 mL) was added to a reaction vessel containing 3,4-diethynylbenzaldehyde (0.18 g, 1.17 mmol), I-SNO(1) (0.797 g, 1.76 mmol), CuI (32.0 mg, 0.117 mmol), and Pd(PPh₃)₂Cl₂ (79.8 mg, 0.117 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 85 °C for 12 h, cooled to room temperature, and diluted with dichloromethane (20 mL). The product was washed with 2% HCl followed by water (2 × 20 mL) and further purified using column chromatography with 2:1 dichloromethane and hexane to give a green solid (0.274 g, 28.3%). ¹H NMR (500 MHz, CDCl₃, δ): 10.0 (s, 1H), 8.55 (d, 2H, *J* = 8 Hz), 8.03 (s, 1H), 7.77 (d, 1H, *J* = 8 Hz), 7.75 (d, 2H, *J* = 8 Hz), 7.73 (s, 2H), 7.71 (s, 1H, *J* = 8 Hz), 7.66 (d, 2H, *J* = 7.75 Hz), 7.65 (d, 1H, 7 Hz), 7.58–7.61 (m, 3H), 7.52–7.56 (m, 3H), 7.41 (m, 2H), 7.32 (s, 2H, *J* = 8 Hz), 7.01 (d, 2H, *J* = 8.5 Hz), 6.92 (dd, 2H, *J* = 9 Hz, 2 Hz), 6.54 (d, 2H, *J* = 7.75 Hz), 2.79 (s, 6H), 1.37 (m, 12H, *J* = 16.5 Hz). MS (*m/z*): calcd. [M+H]⁺ 807.3; found 807.3.

2.2.7. 3,5-Bis(trimethylsilylethynyl)benzalcohol

Trimethylsilylacetylene (4.5 mL, 31.4 mmol) was added to a solution of 3,5-dibromobenzalcohol (1.27 g, 4.78 mmol), Pd(PPh₃)₂Cl₂ (35.2 mg, 0.050 mmol), and CuI (8.81 mg, 0.0458 mmol) in Et₃N (10 mL) at room temperature under nitrogen atmosphere. After stirring for an hour, the reaction temperature was increased to 85 °C and stirred for 12 h. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (20 mL), poured into deionized water (20 mL), to give a biphasic mixture which was extracted with diethyl ether (3 × 20 mL). The organic layer was dried over Na₂SO₄ and evaporated to yield a yellow film (1.83 g). ¹H NMR (300 MHz, CDCl₃): δ 7.51 (t, Ph–H, 1H), 7.41 (m, Ph–H, 2H), 4.63 (s, Ph–CH₂, 2H), 0.23 (s, Si–(CH₃)₃, 18H).

2.2.8. 3,4-Diethynylbenzalcohol

Tetrabutylammonium fluoride (TBAF: 1.0 M solution of THF, 13.7 mL) was added to 3,5-bis(trimethylsilylethynyl)benzalcohol (1.83 g, 6.09 mmol) in anhydrous tetrahydrofuran (THF) (25 mL) at room temperature under nitrogen atmosphere. The reaction was stirred for 8 h, diluted with diethyl ether (25 mL), then washed with 2% HCl (25 mL), brine (25 mL), and deionized water (2 × 25 mL). The organic layer was collected, dried over Na₂SO₄, and evaporated to yield a brown solid. The product was further purified using column chromatography with 3:7 ethyl acetate and hexane to give a golden solid (0.360 g, 33.5%). ¹H NMR (270 MHz, CDCl₃): δ 7.54 (t, Ph–H, 1H), 7.48 (s, Ph–H, 2H), 4.67 (s, Ph–CH₂, 2H), 3.09 (s, –C≡CH, 2H).

2.2.9. 3,5-Bis((1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine]-5-yl)ethynyl)phenylmethanol (Deba-SNOD(3))

N-Methylpyrrolidine (15 mL) was added to a reaction vessel containing I-SNO(1) (0.63 g, 1.39 mmol), 3,4-diethynylbenzalcohol (0.145 g, 0.929 mmol), CuI (17.2 mg, 0.092 mmol), and Pd(PPh₃)₂Cl₂ (64.1 mg, 0.092 mmol) under nitrogen atmosphere. The reaction

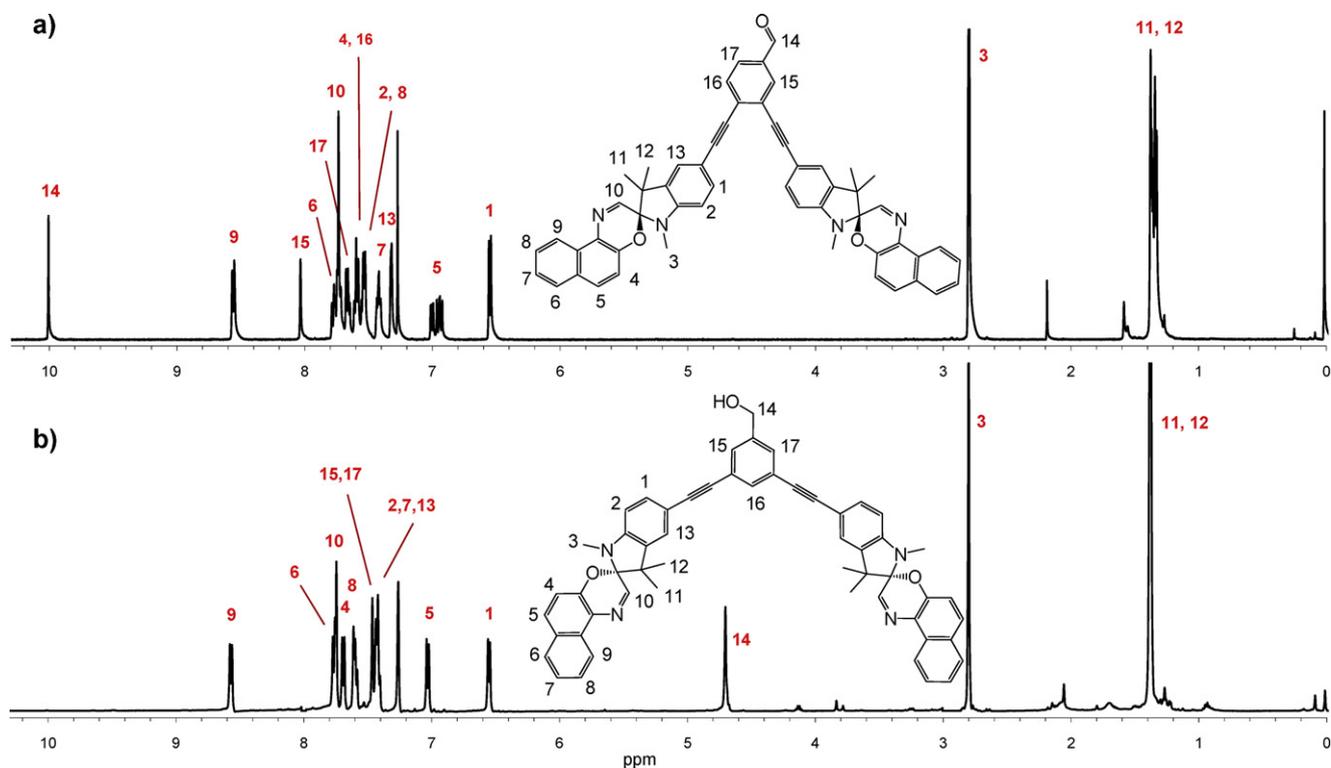


Fig. 2. ^1H NMR spectra of (a) Debald-SNOD(**2**) and (b) Deba-SNOD(**3**) (500 MHz, room temp., CDCl_3).

mixture was stirred at 85°C for 12 h, cooled to room temperature, and diluted with dichloromethane (20 mL). The product was washed with 2% HCl followed by water (2×20 mL) and further purified using column chromatography with 3:7 ethyl acetate and hexane to give a green solid (0.423 g, 37.6%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.56 (d, 2H, $J=8$ Hz), 7.76 (d, 2H, $J=8$ Hz), 7.74 (s, 2H), 7.68 (d, 2H, $J=8$ Hz), 7.60 (m, 3H), 7.47 (s, 2H), 7.40–7.44 (m, 4H), 7.02 (d, 2H, $J=8$ Hz), 6.55 (d, 2H, $J=8$ Hz), 4.70 (s, 2H), 2.80 (s, 6H), 1.38 (d, 6H, $J=10.5$ Hz). MS (m/z): calcd. $[\text{M}+\text{H}]^+$ 809.3; found 809.3.

2.3. Procedures for the determination of photochromic properties

A 10 mL solution was prepared in a vial containing a micro stir bar, maintained at 25°C . Light from a 200 W Mercury Xenon lamp, filtered by 340 nm colored glass filter (FSR-U340), was directed perpendicular to the side of the vial. The absorbance was recorded using the Ocean Optics software. The solution was irradiated and stirred while monitoring the change in absorbance in the visible region.

Solvatochromism was studied using the spiro compounds (10^{-4} M) in solvents of various polarity. The wavelength at the maximum MC absorbance was recorded in each solution. The kinetics of thermal bleaching was studied following the disappearance of the colored form at the wavelength of maximum absorbance. After absorbance maximum was reached for the solutions (10^{-4} M), irradiation was discontinued, and thermal decay was recorded and plotted as absorbance versus time. The measurements were performed at room temperature. First-order rate constants were obtained from the linear dependences of $\ln A/A_0$ versus time. Cyclability was evaluated by plotting absorbance of merocyanine at the wavelength maxima versus time upon repeated irradiation in an on and off manner.

3. Results and discussion

3.1. Synthesis

The approach to improve the photochromic abilities of spirocompounds involved connecting the two spirooxazines directly through a benzyl spacer. The major difference in the two dimers is seen in the positioning of the spirooxazine units. The two photochromic moieties are linked ortho to each other in Debald-SNOD(**2**) while they are meta to each other in Deba-SNOD(**3**). The ortho positioning may offer a longer conjugated system in Debald-SNOD(**2**) which would facilitate in simultaneous activation of both moieties upon irradiation [7]. Both dimers have been designed to have specific angles, so that the photochromic units of the MC form create a cavity for further applications such as sensing or binding.

The new dimers were obtained with high purity and successfully characterized using ^1H , ^{13}C , and 2D-NMR analyses. The ^1H NMR spectra of the compounds **2** and **3** are shown in Fig. 2. Both integration of characteristic spirooxazine signals at 1.37, 2.81, and 7.71 ppm and chemical shifts of protons near triple bond connections assisted in identification of the dimeric structure for each compound. Downfield shifts to 6.5 and 7.3–7.4 ppm in these dimers from the peaks in single I-SNO(**1**) confirm connection to diethynylbenzyl spacer. NMR data offer distinctive difference in structure between asymmetric and symmetric dimers particularly splitting doublets at 7 ppm in Debald-SNOD indicating complex coupling that is not seen in Deba-SNOD.

3.2. Photoisomerization in solution

Low temperature NMR spectroscopy was used to observe the merocyanine isomerization of a single SNO unit and the dimers [11–13]. Fig. 3 shows ^1H NMR spectra of I-SNO(**1**) and Deba-SNOD(**3**), before and after 1 min UV irradiation (340 nm) in $\text{THF}-d_6$

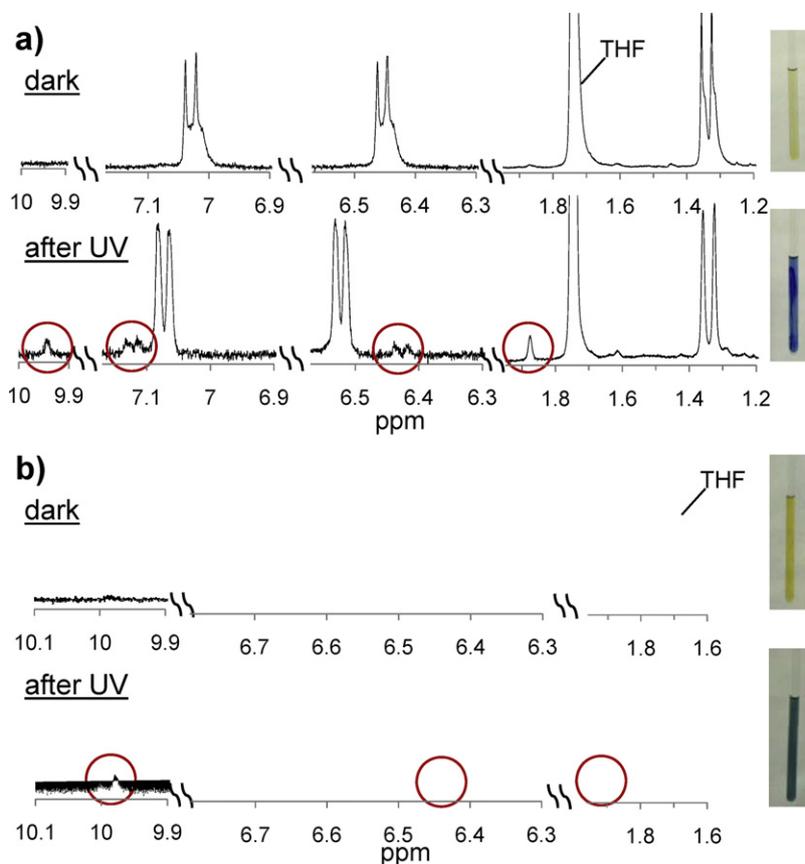


Fig. 3. Low temperature ^1H NMR spectra of (a) I-SNO(**1**) and (b) Deba-SNOD(**3**) in $\text{THF-}d_8$ at -30°C ; before (upper) and after (lower) UV irradiation of each compound. The photographs show the NMR samples.

at -30°C . Upon photo-exposure, similar changes occurred in both structures of **1** and **3**. The opening of spirooxazine is characterized by a peak appearance at 1.88 ppm for two methyl groups as a singlet and for aromatic H at 9.95 ppm for I-SNO (Fig. 3a, after UV). In the closed form, these protons correspond to two methyl singlets at 1.35 and 1.32 ppm, and a singlet at 7.7 ppm, respectively. In addition, the merocyanine peaks of doublets at 6.43 ppm and 7.12 ppm were observed after irradiation shown in lower spectra of Fig. 3a. The doublet signals correspond to aromatic peaks of the closed form meta to the indoline nitrogen and oxazine oxygen, respectively. These doublets shifting upfield from original SP signals to 6.43 ppm and downfield to 7.12 ppm suggest a change in electron distribution indicative of the open form. Besides appearance of these resonance peaks of the MC form, some SP signals were also shifted after UV irradiation. Similar peaks of the MC isomers were observed for the dimers, **2** (data not shown) and **3** (Fig. 3b) after UV treatment. Peaks of low intensity indicate a small conversion to the expected photomerocyanines at this temperature (-30°C) and conditions as consistent with lower quantum yields reported on general SNO series [3,11,14,15].

To examine photochromism and reversibility of compounds **1**, **2**, and **3**, the absorbance spectra were collected. A typical spectrum of each compound in solution resulted in a strong band in the UV region representing the closed form. The absorbance spectra for the two dimers (**2**, **3**) in THF are shown in Fig. 4. Photo irradiation with a UV light (340 nm) resulted in the formation of colored MC isomer with λ_{max} in the range of 550–630 nm. When the light is removed, the absorbance spectrum prior to excitation is restored concluding that isomerization is reversible.

The absorbance in the spectrum of the spiro form consists of localized $\pi-\pi^*$ transitions in UV region of the indoline and oxazine

moieties of the molecule. The absorbance spectra of Debald-SNOD(**2**) exhibit large broad peaks from 300 to 420 nm while the single unit (SNO) and Deba SNOD(**3**) compounds have narrow absorption bands at 300–360 nm. The difference is based on the structure in that the spirooxazine units are linked at ortho position to each other in **2** while they are meta to each other in **3**. The

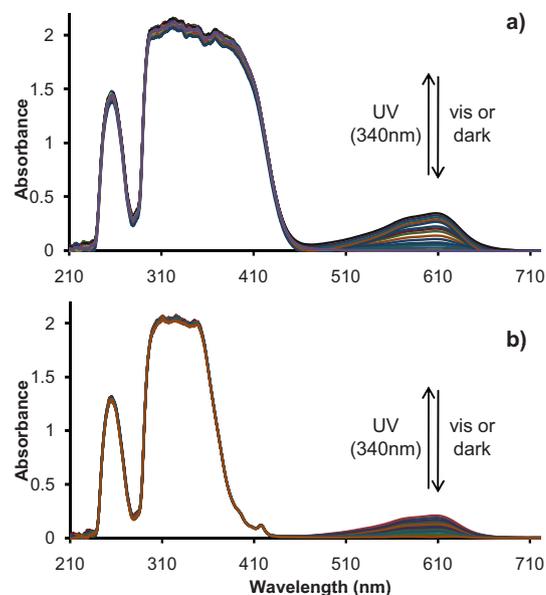


Fig. 4. Absorbance spectra of (a) Debald-SNOD(**2**) and (b) Deba-SNOD(**3**) in THF, 1×10^{-4} M upon irradiation of UV light (340 nm) at room temperature.

ortho position offers longer conjugated system between two indoline units of SNO moieties, which absorbs longer wavelength at the peak about 390 nm.

The open form of spirooxazine is characterized by an absorption band in the visible region. The MC absorbance of the dimers **2** and **3** in THF (609 and 606 nm, respectively) showed a shift to longer wavelength than that of the single unit **1** (589 nm) due to increased conjugation. The intensities of the MC forms in those compounds were observed to be lower than previously reported studies of spiro-naphtho-oxazines (SNO) [14,16,17]. The molar extinction coefficient of the MC form in SNOD is still unknown; however, a possible factor for the low intensity is possibly due to a temperature increase of the solution during irradiation. Generally, the ring opening reaction of spirooxazines is temperature sensitive [18]. In addition, substituents exerting an inductive effect on the indoline moiety of spirooxazine affect to destabilize the open form.

The structural differences of the two dimers play a significant role in the opening and closing of each moiety upon irradiation. We speculated that by increased conjugation through two spirooxazine units, the simultaneous activation of both units would occur upon irradiation [7]. To investigate this hypothesis, we extended the UV exposure time and examined the opening and closing upon irradiation in nonpolar and polar solvents. Fig. 5 shows plots of the absorption maxima of the merocyanine of Debald-SNOD(**2**) and Deba-SNOD(**3**) in nonpolar methylcyclohexane (5a) and polar dimethylformamide (5b) versus time. Upon initial excitation, a rapid increase in absorbance followed by decrease is observed in both solvents, which is reported as 'characteristic' for the spiro-naphtho-oxazines, yet the reason is unknown [19]. After this initial projection, the merocyanine absorbance of both dimers in methylcyclohexane (5a) increased stepwise upon

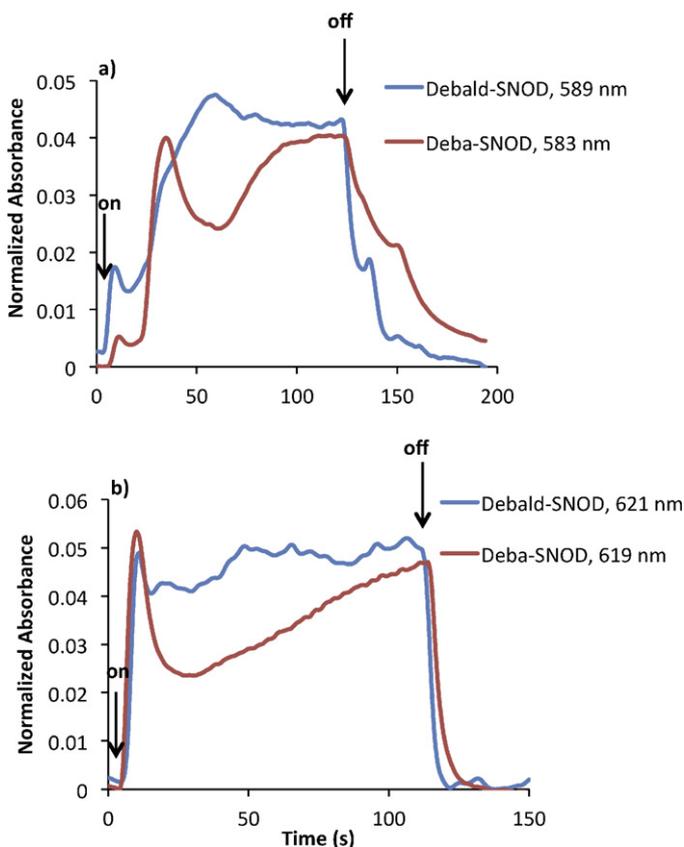


Fig. 5. Plots of the absorption maxima of the merocyanine of Debald-SNOD(**2**) and Deba-SNOD(**3**) in methylcyclohexane (a) and dimethylformamide (b), 1×10^{-4} M versus time subjected to UV irradiation at room temperature.

Table 1

The wavelength of the MC form absorption of I-SNO(**1**), Debald-SNOD(**2**), and Deba-SNOD(**3**).^a

Solvent	Brooker's red parameters (χ_R)	λ_{MC} (nm) ^b		
		1	2	3
Methylcyclohexane	50.1	553	589	583
Diethyl ether	48.3	565	597	593
Toluene	47.2	587	607	603
Tetrahydrofuran	46.6	589	609	606
Acetone	45.7	590	614	612
Dimethylformamide	43.7	610	621	619

^a At 25 °C, concentration of the solution: 1×10^{-4} M.

^b Obtained under UV irradiation at 340 nm.

sustained exposure to UV light. The plot of Debald-SNOD(**2**) shows a shoulder before maximum absorbance is attained, and then maintains a steady absorbance. While, opening to the MC form of Deba-SNOD(**3**) shows a slow two-step process to reach stable absorbance. It is again, unknown why the MC absorbance decreases after the major increase. The difference between Debald-SNOD and Deba-SNOD can be explained by the conjugation of two units of the Debald-SNOD, whose second spirooxazine unit opens faster than non-conjugated Deba-SNOD. In contrast to the behavior in methylcyclohexane, in polar dimethylformamide, Debald-SNOD(**2**) maintains a maximum absorbance of the merocyanine form upon initial opening, while Deba-SNOD(**3**) displays a gradual increase to reach absorbance maximum. After 150 s, the light source was turned off so that isomerization to the closed form could be observed. Upon discontinuation of irradiation, a dual step closing process is observed distinctively in methylcyclohexane (Fig. 5a) in which the dimers generally demonstrate a slower isomerization to the SP form. The decline in intensity is evidently faster for the conjugated dimer, Debald-SNOD than that of Deba-SNOD. This is probably due to the sequential closing of two moieties. In dimethylformamide, the cyclization appears faster due to the non-polar nature of the merocyanine form and its stability in this media [16]. Thus, multistep closing was not observed.

The solvatochromism of the photomerocyanine-based $\pi-\pi^*$ absorption band of **1**, **2**, and **3** were examined in a series of solvents. The wavelength maxima were correlated with the Brooker's red parameters (χ_R) [18,20], which takes into account solvation effects such as dispersion forces and hydrogen bonding, rather than simple solvent polarity parameters. Spectral data indicate positive solvatochromism as wavelength maxima of the MC isomers shift to longer wavelengths with increasing relative solvent polarity as summarized in Table 1. This bathochromic shift indicates that the lowest excited state of the MC is better stabilized by polar solvents resulting in a decrease in transition energy. The normalized absorption spectra of Deba-SNOD(**3**) under UV irradiation are shown in Fig. 6a, along with the plot of wavenumbers of absorption maxima as a function of Brooker's red parameters in Fig. 6b. In addition to bathochromic shift in λ_{max} , a decrease in shoulder intensity with increasing solvent polarity was observed. These data suggest that the quinoidal form of the MC isomer is favored over the zwitterions. Examination of the absorbance of the photomerocyanine forms of single SNO and dimers confirmed positive solvatochromism, but both dimers (**2**, **3**) showed smaller shift compared to the shift seen in I-SNO.

3.3. Thermal fading kinetics of the MC form

Fig. 7 shows a thermal fading of Deba-SNOD(**3**) in ether; the MC absorbance at the wavelength maxima collected immediately after the UV irradiation was terminated. The inserted plot of $\ln(A/A_0)$ versus time exhibited the first order kinetics of the closing rate and gave a rate constant with the relaxation time obtained using

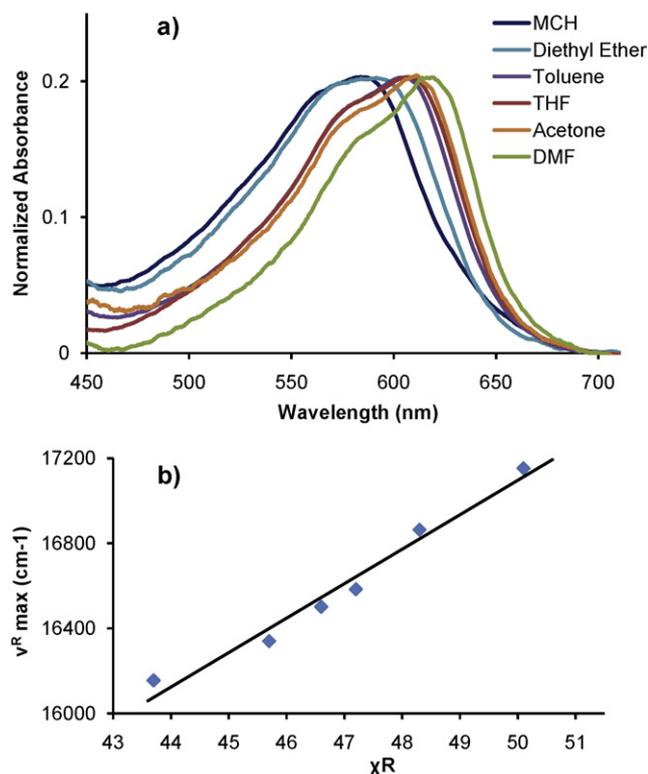


Fig. 6. (a) Absorbance spectra of the MC form of Deba-SNOD(3) in various solvents, and (b) a plot of wavenumbers (cm^{-1}) of the MC maxima as a function of Brooker's red parameters of all solvents.

$t = 1/k$. Data from elongated irradiation revealed a sequential closing of the two spirooxazine moieties (Fig. 5); however, overall thermal closing in all solvents was evaluated to obey first order kinetics. Table 2 summarizes calculated rate constants of the three compounds in various solvents. The relaxation half-life of the merocyanines ($\tau_{\text{MC-SO}}$) given in Table 2 was obtained from the first order rate constant using the expression $t_{1/2} = \ln 2/k$. The results of rate constants indicate relatively slow thermal decay of the MC isomer in methylcyclohexane for all compounds. The single unit, I-SNO(1) showed increased closing rates with an increase in polarity of solvents with the exception of toluene. Thermal closure for the single unit is generally faster than that of the dimers (2, 3) with the exception of diethyl ether, which is consistent with previous studies on other spiro-dimers and partially due to the delay in opening and closing of one moiety of the biphotocromic system [9]. Despite their differences in conjugation between

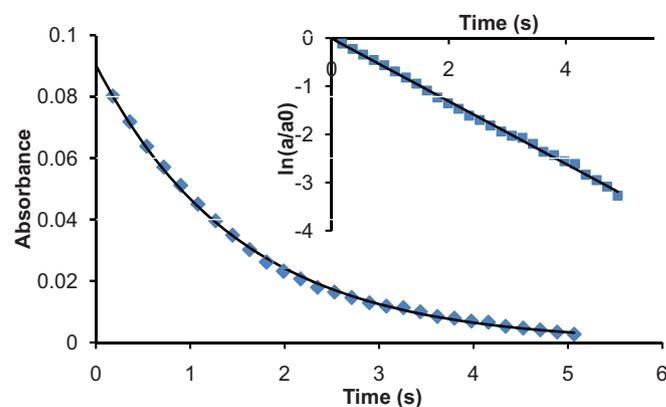


Fig. 7. The thermal decay of the MC absorbance at 593 nm of Deba-SNOD(3) in diethyl ether at 25 °C ($[3] = 1.0 \times 10^{-4}$ M). Embedded graph depicts the first-order kinetic plot of the thermal decay.

moieties, compounds 2 and 3 show relatively similar closing rates with the exception of toluene. The cyclization rate of the MC form in the dimers show smaller dependence upon solvent polarity compared to that of I-SNO.

In general, thermal closing rate varies depending both on structural characteristics and solvent polarity [4,16,18]. It has been reported that substituents influence the photochromism through both electronic and steric effects. The general stability of the MC dimers (2, 3) in solution compared to the single form (1) may be due to the inductive effect of the halogen into the MC indoline moiety destabilizing the merocyanine form of 1.

In our previous report on spiro-phenanthro-oxazine dimer (SPOD), the closing rate constants were extremely different from non-polar to polar solvents [9]. For comparison, the rate constants of SPOD and two SNODs, 2 and 3 were plotted against log scale of solvent dielectric constants in Fig. 8. The closing rate of SPOD (green marks) in methylcyclohexane ($\epsilon = 2.1$) was 0.12 s^{-1} , and in dimethylformamide ($\epsilon = 38$) was 4.48 s^{-1} , and thus, had a significant solvent dependency. It is suggested that for spiro-phenanthro-oxazine systems, the transition state of the ring closing reaction is more polar than either the SP or MC forms [10,11]. The polarity of the transition state is due to a loss of pseudo π conjugation upon rotation of indoline and oxazine moieties, which increases the electronic charge on both the indoline nitrogen and oxazine oxygen. The MC isomer being planar results in delocalization of the charge throughout the molecule and thus loses the bipolar nature. As the polarity of the solvent increases, the quinoidal MC form is destabilized to decrease energy gap with the transition state, and the closing rate is drastically increased for SPOD.

Table 2
Thermal fading rates^a of compounds 1, 2, and 3 (1.0×10^{-4} M) in different solvents of varying polarity.

Solvent	Dielectric constant, ϵ	Rate constant, kt/s^{-1}		
		I-SNO(1)	Debald-SNOD(2)	Deba-SNOD(3)
Methylcyclohexane	2.1	0.82 (0.9)	0.41 (1.7)	0.27 (2.6)
Toluene	2.4	1.92 (0.4)	1.02 (0.7)	0.22 (3.2)
Diethyl ether	4.3	0.67 (1.0)	0.77 (0.9)	0.56 (1.2)
Tetrahydrofuran	7.5	2.90 (0.2)	0.57 (1.2)	0.48 (1.4)
Acetone	21	1.51 (0.5)	1.18 (0.6)	1.44 (0.5)
Dimethylformamide	38	1.84 (0.4)	1.59 (0.4)	1.03 (0.7)

^a At 25 °C.

^b The relaxation half-life of the merocyanines.

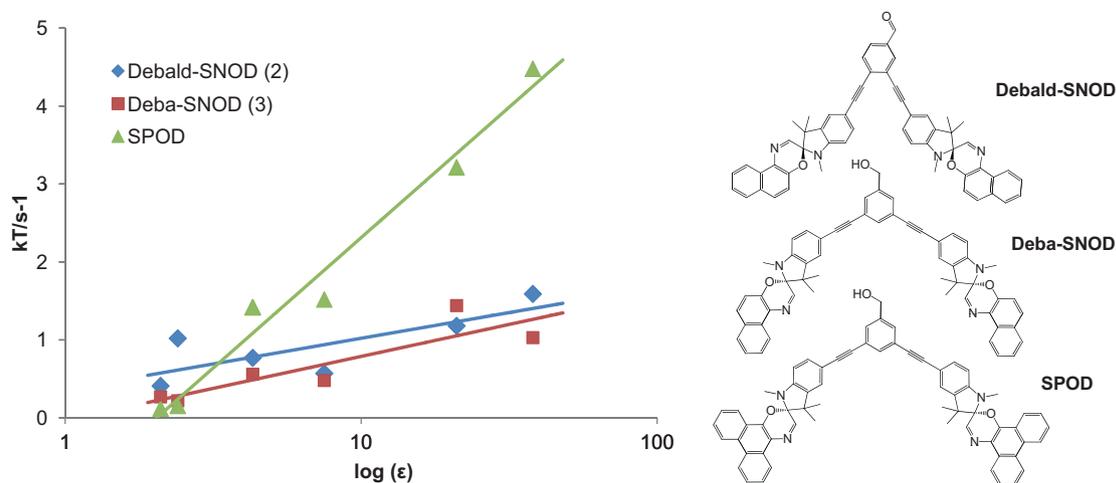


Fig. 8. Solvent dependency of thermal closing rate of Debald-SNOD (diamond), Deba-SNOD (square), and SPOD (triangle) [9] upon solvent dielectric constant.

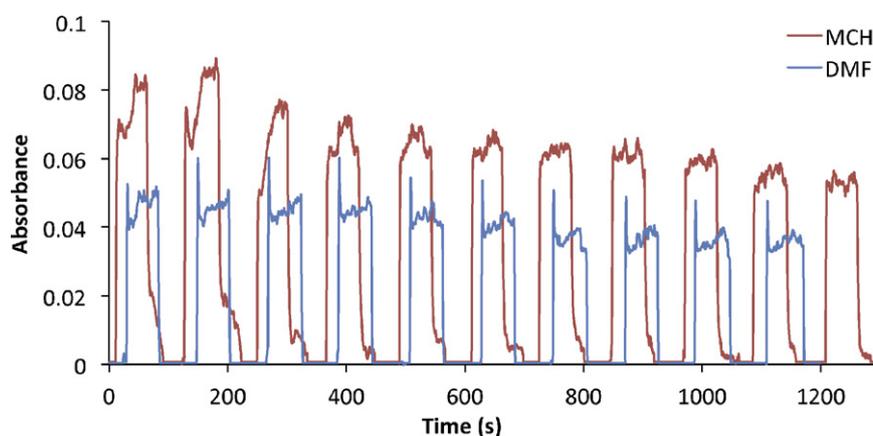


Fig. 9. Cycles of UV irradiation of Debald-SNOD ($[2] = 1 \times 10^{-4}$ M) at 25 °C followed by thermal closing; absorption maxima for the MC isomers at 581 nm in methylcyclohexane (higher absorbance) and 621 nm in DMF (lower absorbance) were plotted.

For the spiro-naphtho-oxazine dimers in this study, the removal of the ring on the oxazine portion of phenanthrene (SPOD) to naphthalene (SNOD) changes the polarity of the molecule itself. Though the linker can exert a substituent effect which increases the electronic charge on the indoline nitrogen, the electron density at the oxazine oxygen is reduced. The loss of electron density upon the rotation for closing makes the transition state of the cyclization reaction less polar, which decreases the polarity gap with either the SP or MC forms. This similarity in compound polarity through photocyclization reaction is a plausible explanation to make the closing rate of SNOD significantly less sensitive to the solvent polarity as Fig. 8 shows.

3.4. Fatigue resistance

To investigate the resistance of SNOD series to photodegradation, solutions of each compound in varying solvents were alternately UV-irradiated and left in the dark. Plots of the absorption maxima of the merocyanine of Debald-SNOD(2) in methylcyclohexane and dimethylformide versus time subjected to an off and on manner of irradiation are shown in Fig. 9. Debald-SNOD in methylcyclohexane exhibited small decrease of MC absorbance over the long, repeated irradiation. In this highly non-polar solvent, precipitation was observed after extended UV exposure, which could be explained as a result of aggregation of the planar MC isomers by π - π stacking. This is typical phenomenon for

relatively polar MC forms such as isomer of spiropyran [15,21]. Except in this particular case, the results of cyclability tests in various solvents indicated no appreciable fatigue or irreversibility under the experimental conditions over 20 min. Deba-SNOD(3) also showed excellent cyclability.

4. Conclusions

The photochromic reactions of two spironaphthooxazine dimers were studied under continuous UV irradiation in solvents of different polarity. The investigation examined the effects of solvent and structure on the absorption properties and closing rate kinetics of the merocyanine. The structural difference of these dimers influenced the activation and deactivation processes of two moieties. The dimer with complete conjugation through the two spirooxazine units showed faster opening and closing of the second unit compared to the dimer whose conjugation was interrupted between two units as we hypothesized. A bathochromic shift and plotting of the absorbance of the photomerocyanine forms of both dimers against empirical Brooker's parameters confirmed a quinoidal merocyanine structure. The rate of cyclization of MC form of the dimers showed very little dependence upon solvent polarity unlike that of the previously examined spirophenanthrooxazine dimer. In summary, spironaphthooxazine dimers prepared in this study exhibited an excellent response to photo induction, reversible isomerization, and high fatigue

resistance which are deemed valuable traits for practical application. Further modification of SNOD molecules such as conjugation on substrate surfaces or to polymers, and investigation of binding interaction of SNOD with guest compounds are underway.

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