

Synthesis and Photochromism of Novel Spiro(indoline-2,3'-naphtho[2,1-b][1,4]oxazine)

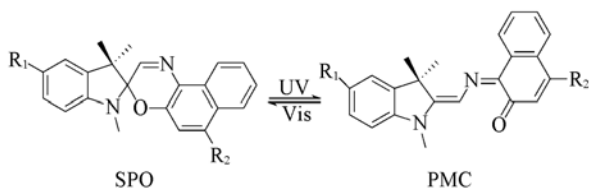
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Abstract A series of novel spirooxazine(SPO) derivatives containing nitrogen heterocycles was synthesized and characterized by ^1H NMR spectra, Fourier transform infrared(FTIR) spectra, mass spectra(MS) and elemental analysis, and their photochromic behaviors were fully investigated in solvents and polymer media. In solvents, they displayed excellent photochromism properties such as high photochromic response and fast thermal bleaching rate. Especially, compounds **1** and **4** exhibited strong fluorescence intensities in dichloromethane solution. It was additionally found that compound **4** showed high fatigue resistance in poly(methyl methacrylate)(PMMA) film, and the thermal decay curves were fitted with biexponential function in PMMA film.

Keywords Spirooxazine; Photochromism; Acidichromism; Fatigue resistance

1 Introduction

Photochromic materials have attracted much interest due to their potential applications in optical memories and switching devices^[1–8]. Up to date, many types of photochromic compounds have been reported. Among thermally reversible photochromic compounds, spirooxazines(SPOs) are well known for their interesting photochromic behavior^[9–11]. Compared to other photochromic compounds such as spiropyrans and azobenzenes, SPOs exhibit more excellent chemical stability, photosensitivity and high photofatigue resistance^[12–15]. As depicted in Scheme 1, the photochromism of SPO is attributed to the photochemical cleavage of the C—O spiro-bond upon ultraviolet(UV) light, which results in the extension of π -conjugation in the colored photomerocyanine(PMC)^[16], which reverts to SPO after thermal treatment or visible(Vis) light irradiation.



Scheme 1 Structural interchange between SPO and PMC isomers

In the present investigation, a new kind of SPO derivatives(**1—6**) were reported. And a remarkable characteristic is that nitrogen heterocyclic groups were appended on the skeleton of the synthesized compounds in order to increase the electronic density of the molecular system and improve the photochromic properties. Interestingly, several merits turned out inherent for compounds **1—6**: (i) in solvents, they could interchange rapidly between SPO form and PMC form when UV

irradiation was switched on and off; (ii) they exhibited excellent acidichromism properties in solvents; (iii) compounds **1** and **4** showed strong fluorescence intensity in dichloromethane solution; (iv) after being embedded into poly(methyl methacrylate)(PMMA) media, they tolerated many switching cycles without decomposing, indicative of an excellent fatigue resistance. These compounds show great prospects in future development of high-performance photochromic materials.

2 Experimental

2.1 Materials and Instruments

All the chemicals were purchased from commercial sources, and the solvents used were dried and purified by distillation before use. The spectrophotometric grade solvents were used in the spectrophotometric measurements.

Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer. Ultraviolet-Visible(UV-Vis) spectra were measured using a Shimadzu UV-2101PC spectrophotometer. The melting points were determined with an X4 Micro-melting point apparatus and were uncorrected. The ^1H NMR spectra were recorded using a Bruker AC-P500(400 MHz) instrument with tetramethylsilane(TMS) as internal standard. Infrared(IR) spectra were recorded on a Bio-Rad FTS 135 spectrophotometer *via* KBr pellets. Mass spectra(MS) were recorded on a Thermo Finnigan LCQ advantage spectrometer. Elemental analysis was performed on a Yanaco MT-3CHN elemental analyzer.

2.2 Synthesis of Target Compounds

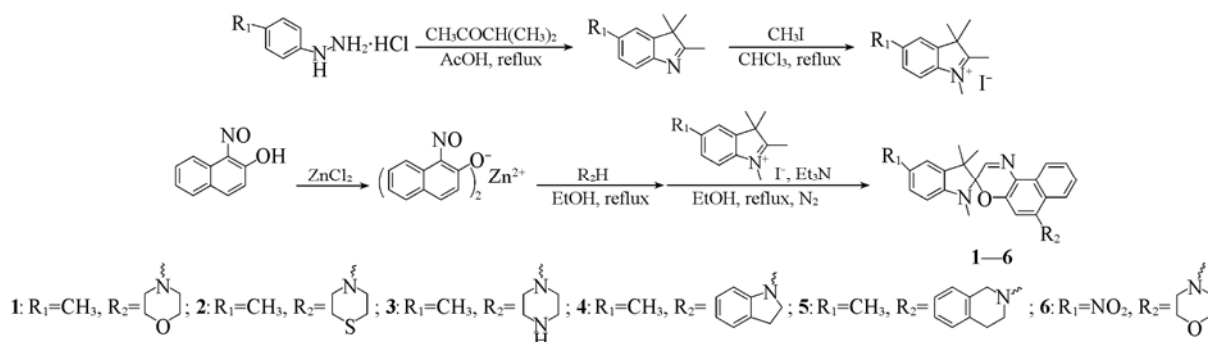
The synthetic routes of target compounds **1—6** are shown in Scheme 2.

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Scheme 2 Synthetic routes of SPO derivatives

2.2.1 General Method for Synthesis of 5-Substituted-2,3,3-trimethyl-3H-indole

The synthetic procedure was based on the literature method^[17].

2.2.2 General Method for Synthesis of 5-Substituted-1,2,3,3-tetramethyl-3H-indolium Iodide

The synthetic procedure was based on the literature method^[18].

2.2.3 Synthesis of 1-Nitroso-2-naphthol Zinc Salt

ZnCl₂ (1.36 g, 0.01 mol) in water (40 mL) was added to 80 mL of mixed solution of tetrahydrofuran and water (1:1, volume ratio) containing 1-nitroso-2-naphthol (3.98 g, 0.024 mol) while stirring. The reaction was completed after 20 min at room temperature, the raw product of 1-nitroso-2-naphthol zinc salt was filtered, then washed with water, and dried under an infrared heat lamp to give the title compound as a brown solid (3.90 g, yield 96%).

2.2.4 Synthesis and Characterization of Novel SPO Derivatives 1—6

1-Nitroso-2-naphthol zinc salt (0.42 g, 1.0 mmol) and morpholine (0.26 g, 3.0 mmol) were added to ethanol (20 mL). The resulting solution was stirred for 1.5 h at reflux. The mixture of 5-methyl-1,2,3,3-tetramethyl-3H-indolium iodide (0.57 g, 1.8 mmol) and triethylamine (TEA, 3.0 mL) that was stirred for 30 min in ethanol (20 mL) was added to the solution under nitrogen atmosphere, and stirred for 8 h at reflux. After removal of the solvent, the residue was purified by column chromatography [silica gel with ethyl acetate-petroleum ether (volume ratio 1:5) as the eluent] to give the desired product 1,3,3,5-tetramethyl-6'-morpholinospiro(indoline-2,3'-naphtho[2,1-b][1,4]oxazine)(1).

Compounds 1,3,3,5-tetramethyl-6'-thiomorpholinospiro(indoline-2,3'-naphtho[2,1-b][1,4]oxazine)(2), 1,3,3,5-tetramethyl-6'-(piperazin-1-yl)spiro(indoline-2,3'-naphtho[2,1-b][1,4]oxazine)(3), 1,3,3,5-tetramethyl-6'-indolinospiro(indoline-2,3'-naphtho[2,1-b][1,4]oxazine)(4), 1,3,3,5-tetramethyl-6'-1,2,3,4-tetrahydroisoquinolinospiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine](5) and 5-nitro-1,3,3-trimethyl-6'-morpholinospiro(indoline-2,3'-naphtho[2,1-b][1,4]oxazine)(6) were synthesized in the same manner.

Compound 1: a yellow solid. Yield 40%, m. p. 135—137 °C; ¹H NMR (400 MHz, CDCl₃), δ : 1.34(s, 3H, CH₃), 1.35(s, 3H, CH₃), 2.33(s, 3H, CH₃), 2.72(s, 3H, NCH₃),

3.05—3.08[m, 4H, N(CH₂)₂], 3.93—3.96[m, 4H, O(CH₂)₂], 6.48(d, $J=7.7$ Hz, 1H, CH=N), 6.64(s, 1H, ArH), 6.93(s, 1H, ArH), 7.04(d, $J=7.9$ Hz, 1H, ArH), 7.39(t, $J=7.9$ Hz, 1H, ArH), 7.56(t, $J=7.3$ Hz, 1H, ArH), 7.67(s, 1H, ArH), 8.06(d, $J=8.4$ Hz, 1H, ArH), 8.58(d, $J=8.2$ Hz, 1H, ArH); IR (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 2958, 2847, 1586, 1490, 1270, 1105, 1030. MS, m/z : 428.24[M+H⁺]. Elemental anal.(%) calcd. for C₂₇H₂₉N₃O₂: C 75.85, H 6.84, N 9.83; found: C 76.08, H 6.85, N 9.80.

Compound 2: a yellow solid. Yield 33%, m. p. 136—138 °C; ¹H NMR (400 MHz, CDCl₃), δ : 1.34(s, 3H, CH₃), 1.35(s, 3H, CH₃), 2.34(s, 3H, CH₃), 2.72(s, 3H, NCH₃), 2.89—2.92[m, 4H, N(CH₂)₂], 3.30—3.23[m, 4H, S(CH₂)₂], 6.49(d, $J=6.5$ Hz, 1H, CH=N), 6.63(s, 1H, ArH), 6.92(s, 1H, ArH), 7.02(d, $J=6.6$ Hz, 1H, ArH), 7.39(t, $J=7.0$ Hz, 1H, ArH), 7.57(t, $J=7.5$ Hz, 1H, ArH), 7.65(s, 1H, ArH), 8.01(d, $J=8.4$ Hz, 1H, ArH), 8.56(d, $J=8.2$ Hz, 1H, ArH); IR (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 2805, 1730, 1610, 1589, 1489, 1353, 1291, 1116, 1033. MS, m/z : 444.27[M+H⁺]. Elemental anal.(%) calcd. for C₂₇H₂₉N₃OS: C 73.10, H 6.59, N 9.47; found: C 73.29, H 6.60, N 9.45.

Compound 3: a yellow solid. Yield 45%, m. p. 160—162 °C; ¹H NMR (400 MHz, CDCl₃), δ : 1.34(s, 3H, CH₃), 1.35(s, 3H, CH₃), 2.27(s, 3H, CH₃), 2.64(s, 3H, NCH₃), 3.25—3.28[m, 4H, N(CH₂)₂], 3.46—3.49[m, 4H, N(CH₂)₂], 6.47(d, $J=7.8$ Hz, 1H, CH=N), 6.65(s, 1H, ArH), 6.89(s, 1H, ArH), 7.01(t, $J=7.6$ Hz, 1H, ArH), 7.39(t, $J=7.3$ Hz, 1H, ArH), 7.57(d, $J=7.5$ Hz, 1H, ArH), 7.66(s, 1H, ArH), 7.91(d, $J=8.4$ Hz, 1H, ArH), 8.58(d, $J=8.2$ Hz, 1H, ArH); IR (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 3398, 2950, 2817, 1623, 1490, 1362, 1279, 1138, 1022. MS, m/z : 427.24[M+H⁺]. Elemental anal.(%) calcd. for C₂₇H₃₀N₄O: C 76.03, H 7.09, N 13.13; found: C 75.92, H 6.92, N 13.13.

Compound 4: a yellow solid. Yield 42%, m. p. 189—191 °C; ¹H NMR (400 MHz, CDCl₃), δ : 1.36(s, 3H, CH₃), 1.37(s, 3H, CH₃), 2.33(s, 3H, CH₃), 2.74(s, 3H, NCH₃), 3.21—3.25(m, 2H, CH₂), 3.92(m, 2H, NCH₂), 6.29(d, $J=7.7$ Hz, 1H, CH=N), 6.49(d, $J=7.8$ Hz, 1H, ArH), 6.73—6.76(m, 1H, ArH), 6.91(s, 1H, ArH), 6.94(d, $J=3.6$ Hz, 2H, ArH), 7.02(d, $J=7.6$ Hz, 1H, ArH), 7.20(d, $J=6.8$ Hz, 1H, ArH), 7.35(t, $J=7.2$ Hz, 1H, ArH), 7.60(t, $J=7.2$ Hz, 1H, ArH), 7.70(s, 1H, ArH), 7.97(d, $J=8.3$ Hz, 1H, ArH), 8.63(d, $J=8.4$ Hz, 1H, ArH); IR (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 2958, 2871, 1731, 1615, 1594, 1486, 1399, 1385, 1279, 1105, 1026. MS, m/z : 460.31[M+H⁺]. Elemental anal.(%) calcd. for C₃₁H₂₉N₃O: C 81.02, H 6.36, N 9.14; found: C 81.10, H 6.37, N 9.15.

Compound 5: a yellow solid. Yield 39%, m. p.

198—200 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ : 1.34(s, 3H, CH_3), 1.35(s, 3H, CH_3), 2.31(s, 3H, CH_3), 2.73(s, 3H, NCH_3), 3.10—3.14(m, 2H, CH_2), 3.37—3.40(m, 2H, NCH_2), 4.23(s, 2H, NCH_2), 6.49(d, $J=6.6$ Hz, 1H, $\text{CH}=\text{N}$), 6.71(s, 1H, ArH), 6.91(s, 1H, ArH), 7.02(d, $J=7.3$ Hz, 1H, ArH), 7.07(d, $J=5.6$ Hz, 1H, ArH), 7.20(m, 3H, ArH), 7.35(t, $J=6.8$ Hz, 1H, ArH), 7.56(t, $J=6.8$ Hz, 1H, ArH), 7.64(s, 1H, ArH), 8.10(d, $J=7.9$ Hz, 1H, ArH), 8.59(d, $J=7.8$ Hz, 1H, ArH); IR(KBr), $\tilde{\nu}/\text{cm}^{-1}$: 2958, 2822, 1619, 1582, 1494, 1453, 1385, 1287, 1109, 1042. MS, m/z : 474.27[M+H $^+$]. Elemental anal.(%) calcd. for $\text{C}_{32}\text{H}_{31}\text{N}_3\text{O}$: C 81.15, H 6.60, N 8.87; found: C 80.91, H 6.61, N 8.86.

Compound **6**: a yellow solid. Yield 35%, m. p. 237—239 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ : 1.34(s, 3H, CH_3), 1.35(s, 3H, CH_3), 2.81(s, 3H, NCH_3), 3.01—3.04[m, 4H, $\text{N}(\text{CH}_2)_2$], 3.93—3.97[m, 4H, $\text{O}(\text{CH}_2)_2$], 6.48(d, $J=8.5$ Hz, 1H, $\text{CH}=\text{N}$), 6.53(s, 1H, ArH), 7.18(s, 1H, ArH), 7.35(t, $J=7.3$ Hz, 1H, ArH), 7.55(s, 1H, ArH), 7.89(s, 1H, ArH), 8.01(d, $J=8.3$ Hz, 1H, ArH), 8.13(d, $J=8.6$ Hz, 1H, ArH), 8.50(d, $J=8.4$ Hz, 1H, ArH); IR(KBr), $\tilde{\nu}/\text{cm}^{-1}$: 2958, 2817, 1610, 1560, 1506, 1490, 1270, 1158, 1121, 1025. MS, m/z : 459.22[M+H $^+$]. Elemental anal.(%) calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_4$: C 68.11, H 5.72, N 12.22; found: C 68.25, H 5.71, N 12.19.

2.3 Preparation of Photochromic PMMA Film

PMMA(10 g) was added to toluene(60 mL) and the mixture was heated and stirred until it became a transparent liquid. Then a specified amount(mass fraction, %) of SPO was added to the PMMA solution with vigorous agitation. The mixture was poured into a glass slide and kept in a dark room. After the complete evaporation of the solvent, the PMMA film with SPO was obtained.

3 Results and Discussion

3.1 Photochromic Properties in Solvents

The photochromic properties of compounds **1—6**(0.1 mmol/L) were investigated by transient UV-Vis absorption spectroscopy in a series of solvents with varying polarity index, namely cyclohexane, dichloromethane and ethanol. The results indicated that all the compounds could undergo photochemical reaction within 3 s upon UV irradiation in various solvents. Obviously, compounds **1—6** possessed high photoresponse. As illustrated in Fig.1, UV light irradiating compound **6** at 365 nm in cyclohexane solution led to increase in absorption intensity of the band in the visible region, and the optical density of compound **6** at the photostationary state was as high as 0.54. While the colored form was thermally unstable, and a complete fading was achieved within 5 s, revealing that compound **6** possessed fast thermal bleaching rate.

Table 1 shows the maximum wavelength of the absorption band(λ_{max}) of compounds **1—6** at the photostationary state. As illustrated in Table 1, the λ_{max} of compounds **1—6** show a bathochromic shift with the increase in the polarity of solvents, indicating a positive solvent effect. Moreover, the substituents of indoline moiety alter the photochromic properties of the SPO

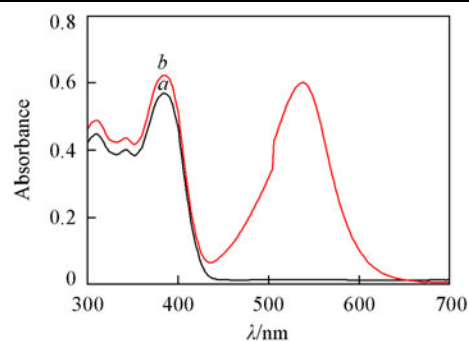


Fig.1 UV-Vis spectra of compound **6** in cyclohexane solution before(a) and after(b) UV irradiation

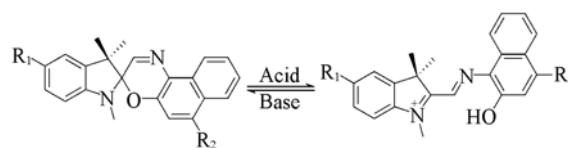
Table 1 Maximum wavelength of compounds **1—6** after UV irradiation in different solvents

Compound	$\lambda_{\text{max}}/\text{nm}$		
	Cyclohexane	Dichloromethane	Ethanol
1	574	593	603
2	570	590	600
3	563	576	605
4	580	610	617
5	568	591	606
6	529	565	584

derivatives. For example, compound **1** exhibit its λ_{max} at 574 nm in cyclohexane solution, whereas the λ_{max} of compound **6** is located at 529 nm. The bathochromic shift of compound **1** is due to a relative increase of electron density in the indoline moiety caused by the electron-donating methyl substituents.

3.2 Acidichromism Properties

Halochromism mainly denotes the color change of a dye on addition of acids or bases. We also investigated the acidichromism property of the representative compound **2** in solvents. The acidichromism processes of SPO derivatives **1—6** are presented in Scheme 3.



Scheme 3 Principle of ring-opening and ring-closing interconversion of SPO derivatives with acid and base trigger

When acid(CF_3COOH) was added into the ethanol solution of compound **2**(0.1 mmol/L), the colorless solution directly turned blue as a result of the formation of a protonated photochromerocyanine(PMCH) and its absorption spectrum changed significantly. PMCH could be kept at room temperature for at least three weeks, revealing that the acid was very effective to stabilize the opened PMC. Interestingly, after base(TEA) was added, it rapidly turned back to colorlessness. It is worth noting that the absorption spectra before addition of acid and after addition of base are almost overlapped(Fig.2), indicating the excellent acidichromism reversibility between SPO and PMCH.

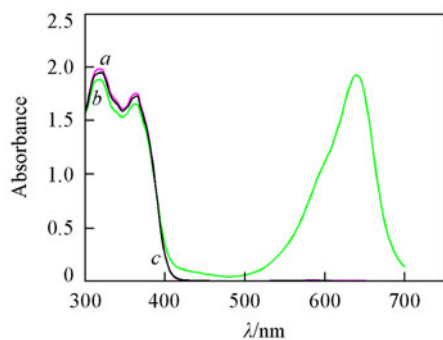


Fig.2 UV-Vis spectra of compound **2** in ethanol solution before addition of CF_3COOH (a), after addition of CF_3COOH (b) and after addition of TEA(c)

Further investigations suggested that the absorption band at λ_{max} increased with increasing the amount of CF_3COOH (Fig.3). Interestingly, the color switching could be cycled with acid and base trigger in cyclohexane(Fig.4), which provides a promising way of manipulating ring-opening and ring-closing interconversion for SPO derivatives.

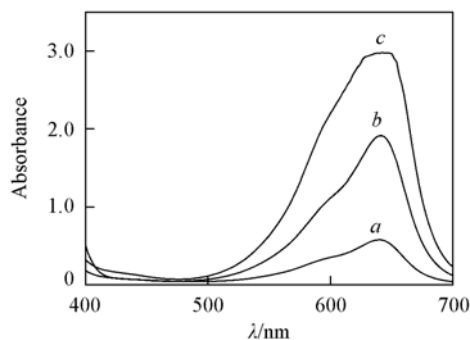


Fig.3 Absorption changes of compound **2** with different addition amounts of CF_3COOH in ethanol

Addition amount of $\text{CF}_3\text{COOH}/\mu\text{mol}$: a. 1; b. 2; c. 3.

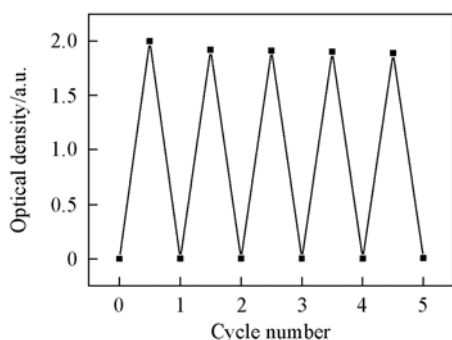


Fig.4 Cycle number of coloration and decoloration of compound **2** with CF_3COOH and TEA trigger in cyclohexane solution

3.3 Fluorescence Properties

Compounds **1** and **4** in dichloromethane solution at room temperature produced strong fluorescence at excitation wavelengths of 399 and 392 nm, respectively, and the fluorescence intensity after UV irradiation was stronger than that before UV

irradiation(Fig.5), this may be explained by the fact that the opened PMC form after UV irradiation produce intense π -conjugation. Especially, compared with compound **1**, compound **4** displayed stronger fluorescence intensities with a maximum fluorescence band around 492 nm both before and after UV irradiation in dichloromethane solution, because compound **4** has bigger conjugate system than compound **1**, which strengthens the fluorescence intensity. The fluorescence properties make them candidates to be applied in anti-counterfeiting technology.

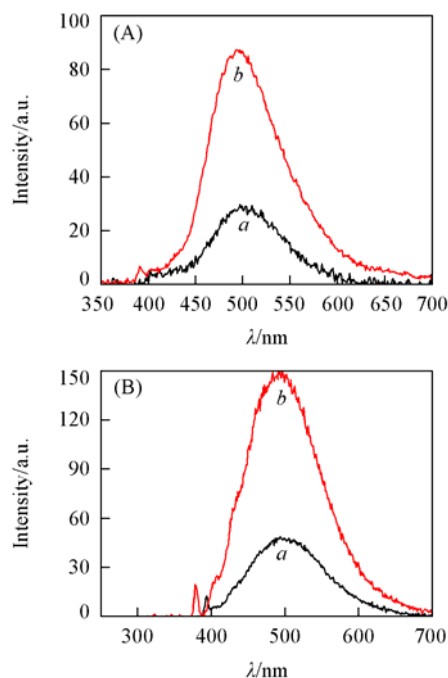


Fig.5 Fluorescence spectra of compounds **1**(A) and **4**(B) before(a) and after(b) UV irradiation in dichloromethane solution at room temperature

3.4 Photochromic Properties in PMMA Film

The effect of PMMA film on photochromism and thermal decay processes of compounds **1**—**6** was investigated. It was found that the λ_{max} of compounds **1**—**6** in PMMA film lies between 550 nm and 620 nm, which was similar to that in solutions. In order to investigate the thermal decoloration process of the synthesized compounds in PMMA film, the A - t decay curve of the representative compound **1** was measured, and the dynamic fitting was carried out(Fig.6). It was turned out that the decoloration process of compound **1** in PMMA films obeyed the equation:

$$A(t)=A_1\exp(-t/t_1)+A_2\exp(-t/t_2)+A_3$$

where A_1 , A_2 and A_3 are coefficients, t_1 is fast process lifetime, t_2 is slow process lifetime. R^2 and Chi^2/DoF (variance) were used to measure the degree of fitting. R^2 (0.99923) was nearly close to 1 and Chi^2/DoF (1×10^{-5}) was close to zero, meaning that the fitting curve was successfully simulated with the equation. Thus the decoloration process follows a biexponentially attenuation law, which had a fast and a slow process^[19].

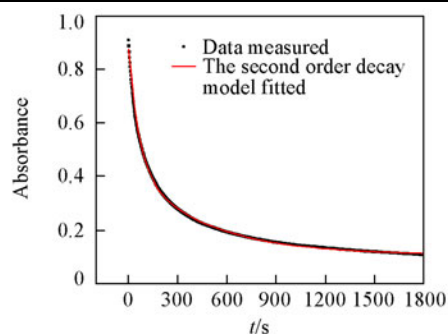


Fig.6 Experimental and fitted $A-t$ decay curves of compound 1 in PMMA film

3.5 Evaluation of the Fatigue Resistance

Fatigue resistance is an important factor for applicable photochromic materials. An investigation of fatigue resistance for the representative compound **4** in PMMA film was performed by turning UV light of 365 nm on and off. As presented in Fig.7, after 10-cycle irradiation, the absorbance ratio (A/A_0) was kept at 98.3% in the presence of molecular oxygen. It showed that compound **4** possessed excellent fatigue resistance.

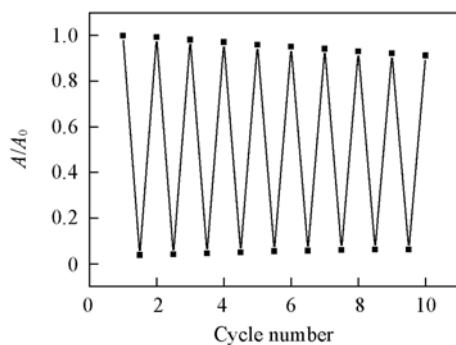


Fig.7 Photoinduced absorption changes for compound 4 in PMMA film

Photoirradiation started at each point of top for visible light and then finished at the point of bottom for UV light.

4 Conclusions

New SPO derivatives were designed and synthesized, and their photochromic properties were investigated. The synthesized compounds exhibited good photochromic properties.

Moreover, they were found to display regular change on the photochromic properties depending on solvent polarity, indicating solvent-tunable photochromic behavior. In PMMA film, these new compounds showed high fatigue resistance. These evidences show that this type of SPO derivatives may be promising for potential applications in molecular switch, information storage, etc.

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