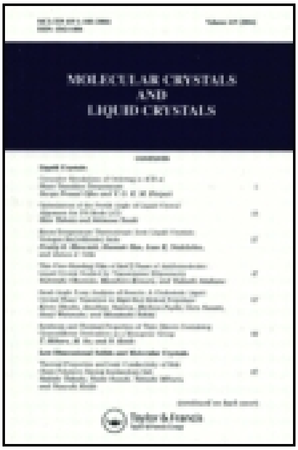

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PHOTOCHROMIC AND FLUORESCENCE STUDIES OF SPIROPYRAN INDOLINE DERIVATIVES IN THE PRESENCE OF ACIDS

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We synthesized 3′,3′-dimethyl-1′-octadecyl-6-nitrospiro-[2H-1-benzopyran-2,2′-indoline] (SP-18) and examined its photochromic behavior and fluorescence in the presence of acid. When strong acids such as HCl and dodecylbenzenesulfonic acid (DBSA) were present, the merocyanine (MC) form generated via heterolytic cleavage of oxygen-carbon bond of the spiropyran (SP) by the irradiation of UV light was protonated to produce the complex MCH^+. The MCH^+ had a yellow color with the absorption maxima at between 410 ~ 430 nm. Since ring-closing reaction of the MC form to produce the SP form was retarded by the protonation of the phenolate in the MC form, MCH^+ had better stability than the MC. Emission peak of the MCH^+ form was observed at 645 nm with HCl and 600 nm with DBSA, respectively. Polymethylmethacrylate (PMMA) films containing the MCH^+ retained about 75% of its original absorbance even after 48 h.

Keywords: acids effect; photochromism; protonated merocyanine; spiropyran

INTRODUCTION

Photochromism of spiropyran [1] and its derivatives has been extensively investigated due to their wide potential applications in optical information storage [2–5], molecular switching devices [6], and others [7,8]. The photochromism of spiropyran is based on the reversible color change between the closed colorless spiro (SP) structure and the open colored merocyanine (MC) form. The mechanism of the photochromism involves

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*Corresponding author. E-mail: cjlee@krict.re.kr heterolytic cleavage of the 1,2 single bond of the pyran ring to give the colored photoisomer MC form, which reverts to the original colorless form upon heating or by irradiation with visible light. When the thermodynamically less stable state is the more deeply colored form, the system is called a "positive" photochromic system, otherwise it is called a "negative (or inverse)" photochromic system. Most spiropyran and related compounds show a positive photochromism. They can be photochemically transformed by UV irradiation into an intensely colored merocyanine and then decolorated to the colorless form by ring closure in the dark or under visible irradiation.

Since the short lifetime of the colored MC species is one of the major obstacles to restrict the applications of the spiropyran, many researchers have focused their efforts on stabilizing the MC state. One of the approaches is to incorporate spiropyrans into rigid matrix such as polymer films, organogels, and clays, in order to improve stabilization of MC state by restricting the mobility of the MC species [9,10]. Another one is to adopt a polar environment such as polyion complex and acidic media [11–13] in order to stabilize the highly polar character of zwitterionic MC form.

In this work we investigated the photochromic behavior of spiropyran indoline derivatives in solution as well as in polymer films in the presence of acid. The produced MC form was protonated by the acid and the protonated MC form (MCH^+) was examined by absorption and emission spectra. Such studies on photochromic behaviors of spiropyrans and their controls are important for applications such as optical recording.

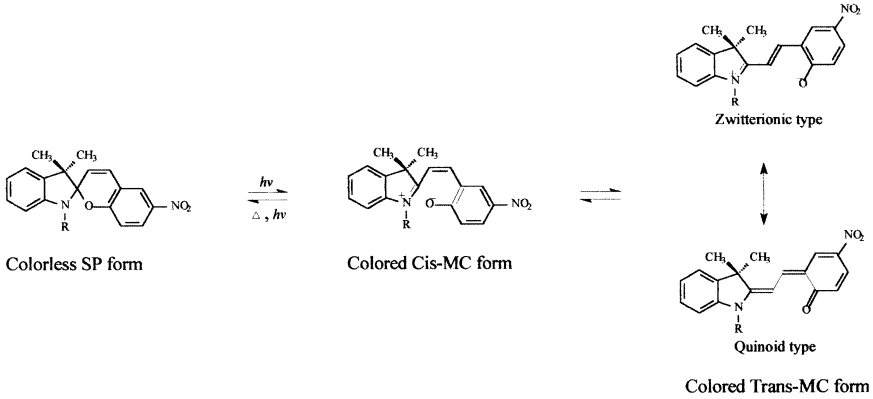
EXPERIMENTAL

Materials

3′,3′-Dimethyl-1′-octadecyl-6-nitrospiro-[2H-1-benzopyran-2,2′-indoline] (SP-18) was synthesized according to the literature procedure [14]. Polymethylmethacrylate (PMMA, Mw: 120,000), hydrochloric acid (HCl), dodecylbenzenesulfonic acid (DBSA), and benzoic acid were purchased from Aldrich and used without further purification. All solvents were purchased SAMCHUN Chemical Co., Ltd. and purified by distillation before use.

Preparation of SP-18

The synthesis of SP-18 was performed following the reaction steps illustrated in Scheme 1.



SCHEME 1

Preparation of 1-Octadecyl-2,3,3-trimethylindoleninium Iodide

A solution of 2,3,3,-trimethylindolenine (0.0314 mol) and octadecyl iodide (0.0471 mol) in chloroform was refluxed at 65 ~ 75°C for 48 hr. The solvent was evaporated and the residue was washed two times with cold diethyl ether. A reddish solid was separated by filtration and dried to give a pale red solid of 1-octadecyl-2, 3, 3-trimethylindoleninium iodide. Yield: 92%; ^{1}H NMR ($CDCl_3$) δ 7.58(s, 4H), 4.69(t, 2H), 3.12(s, 3H), 1.66(s, 6H), 1.25 (m, 30H), 0.87(t, 3H).

Preparation of 3,3-Dimethyl-1-octadecyl-2-methyleneindoline

1-octadecyl-2,3,3-trimethyl indoleninium iodide(0.04 mol) was suspended in water and a concentrated solution of sodium hydroxide was added. After stirring at room temperature for 2 hr, the mixture was extracted with diethyl ether and the organic layer was dried with $MgSO_4$. The organic solution was concentrated using a rotary evaporator to give viscous red liquid of 3,3-dimethyl-1-octadecyl-2-methyleneindoline, which was used directly to the next step without further purification. Yield: 50%; ^{1}H NMR ($CDCl_3$) δ 7.11 ~ 6.50(m, 4H), 3.85(s, 2H), 3.46(t, 2H), 1.62 ~ 1.25 (m, 36H), 0.87(t, 3H).

Preparation of 3′, 3′-dimethyl-1′-octadecyl-6-nitrospiro-(2H-1-benzopyran-2,2′-indoline)

To a warm solution of an 2-hydroxy-5-nitrobenzaldehyde(0.0218 mol) in ethanol was added slowly a solution of a 3,3-dimethyl-1-octadecyl-2-methyleneindoline(0.026 mol) in ethanol. The mixture was refluxed at

70 ~ 75°C for 12 hr. The resultant mixture was cooled in an ice water-bath and the generated solid was collected by filtration. The collected solid was washed several times with cold ethanol and recrystallized two times from ethanol to give 57% of SP-18 as a colorless power. ^{1}H NMR ($CDCl_3$) δ 7.99(m, 2H), 7.18 ~ 6.55(m, 6H), 5.87(d, 1H), 3.14(t, 2H), 1.55(m, 35H), 1.25(s, 3H), 0.87(t, 3H).

Preparation of Samples for Spectrophotometric Measurments

Acids (3.0×10^{-3} M) were added in the solution of SP-18 (3.3×10^{-5} M) in THF. The solution was irradiated with the UV light of 365 nm to convert the closed form to colored open form. Dodecylbenzenesulfonic acid (0.12 g) was added into the chloroform solution of SP-18 (0.04 g) and poly (methylmethacrylate) (PMMA) (0.06 g). The clear solution was spincast on the glass substrate after filtration through 0.45 μm syringe filter. The films were irradiated with 365 nm light before measuring absorption spectrum. The decoloration of the samples stored in the dark state was monitored over several days with UV/Vis absorption spectroscopy.

Instrumentation

A spectra View 2000 UV-Visible spectrophotometer and FluoroMax-2 fluoro spectrophotometer were used to record the absorption and emission spectrum, respectively. All samples were exposed to UV light (365 nm) using TLC lamp to convert SP to MC form.

RESULTS AND DISCUSSION

Figure 1(a) shows UV-Vis absorption spectra of SP-18 dissolved in several solvents with a different polarity after irradiation of UV light of 365 nm. The SP-18 with the UV irradiation produced absorption peaks at 580 nm in THF and at 600 nm in toluene, respectively. In more polar solvent such as ethanol, the colored MC form has an absorption maximum at 540 nm. The MC form of spiropyran has been known to have two canonical forms as depicted in Scheme 2: non-polar quinoid type and dipolar zwitterionic type [15], thus partial charges are developed in the molecule. The MC form with partial developed charges in the ground state are more stable in polar solvent than in non-polar solvent. As an electron is transited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), the excited state of MC form becomes less polar than the ground state. Thus, the energy difference between ground state and excited state of MC form in polar solvent is larger than that in

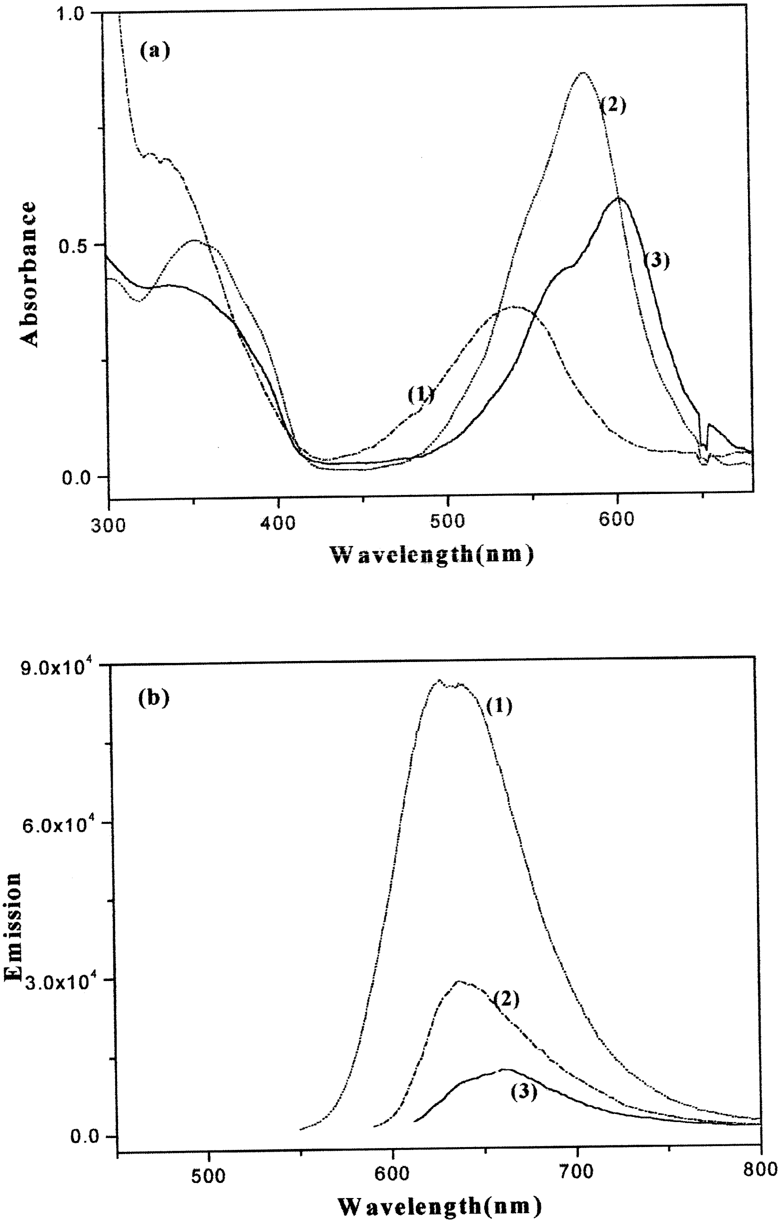
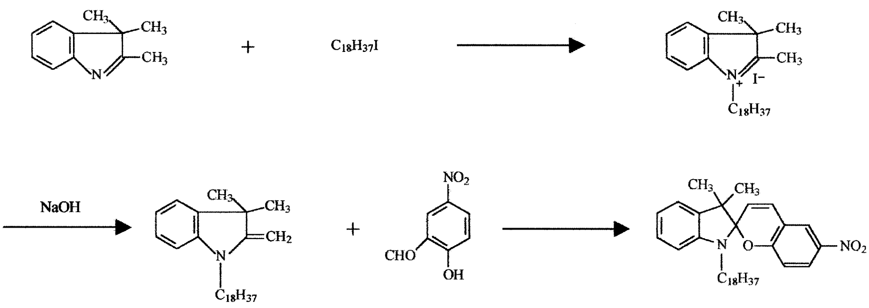


FIGURE 1 (a) Absorption and (b) fluorescence spectra of SP-18 in (1) ethanol, (2) toluene, and (3) THF.



SCHEME 2

non-polar solvent, which causes the blue shift of absorption (or hypsochromic shift) with the increase of solvent polarity.

The lifetime of the colored MC form was also influenced by the polarity of solvents. The decoloration was much slower in ethanol than in THF as shown in Figure 2. The half-life of the MC form in ethanol ($\tau_{1/2} = 24\,\text{min}$) observed to be ~16 times larger than that in THF ($\tau_{1/2} = 100\,\text{sec}$). Such longer lifetime of the MC form in ethanol is due to the stabilization of the polar zwitterionic form in the solvent with a high polarity. This was manifested in the fluorescence measurement [Fig. 1(b)] as the fluorescence intensity increased in the order of toluene, THF and ethanol. Since the fluorescence were measured almost at the same time interval with the same irradiation time, the difference of the emission intensity in different solutions was directly related to the concentration of the MC form in solution. In ethanol, more MC form remained to give higher fluorescence intensity.

The MC form, ring-open form of SP, has a structure similar to the nitrophenolate and could be protonated in the presence of acid. We added several acids with a different acidity to the THF solution of SP-18. Figure 3(a) shows the absorption spectra of SP-18 solution with acids after UV irradiation. When the added acids were strong acids such as HCl and dodecylbenzenesulfonic acid (DBSA), the protonated MC form (MCH^+) was produced showing absorption peaks at between 410 ~ 430 nm. The MC form was not protonated effectively with weak acid such as benzoic acid and hence showed absorption maximum not much different from that of the MC form without acid. It was very interesting to note that the protonated MC forms were much more stable and showed longer lifetime than the non-protonated MC form. This is due to the retardation of ring-closing reaction of the MCH^+ form to the SP form. More interesting features were found in the fluorescence spectra of the protonated form. The protonated MC form with HCl and DBSA showed strong emissions at 645 and 600 nm,

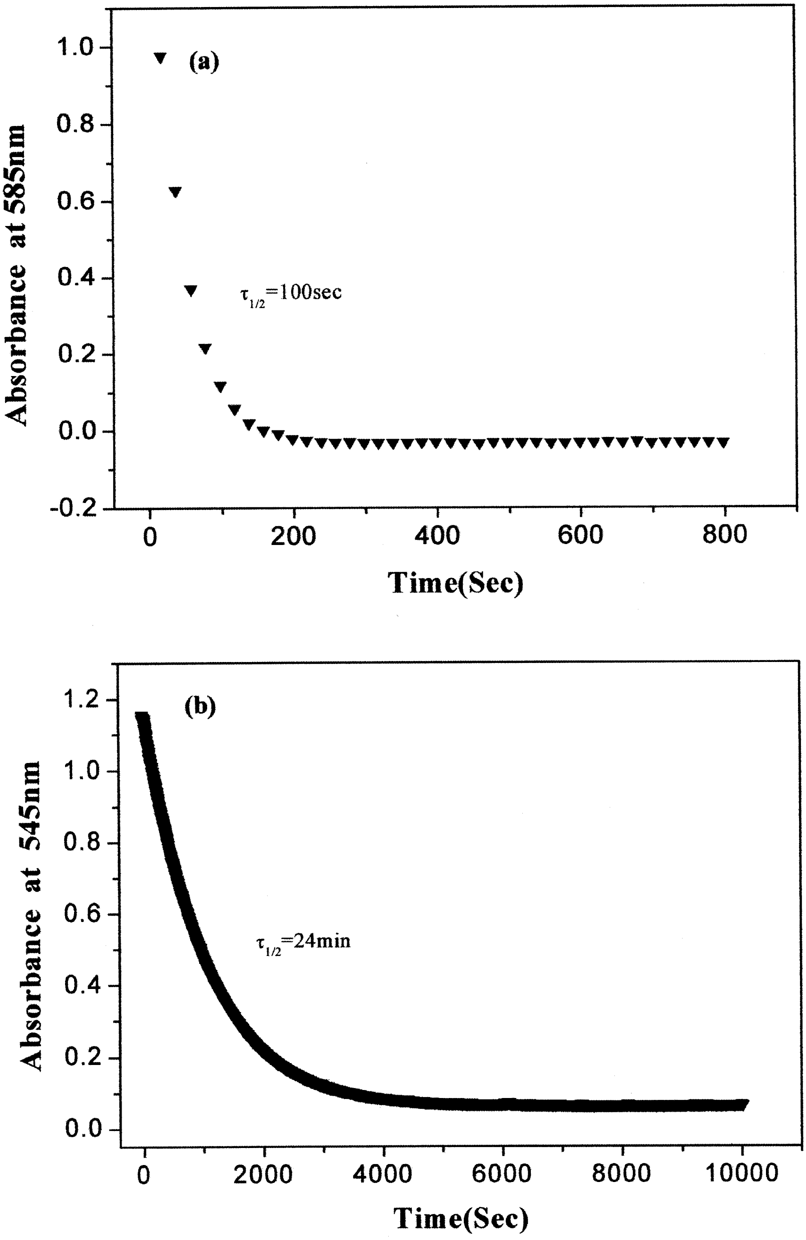


FIGURE 2 Decoloration of SP-18 in solution after UV irradiation (a) THF and (b) ethanol.

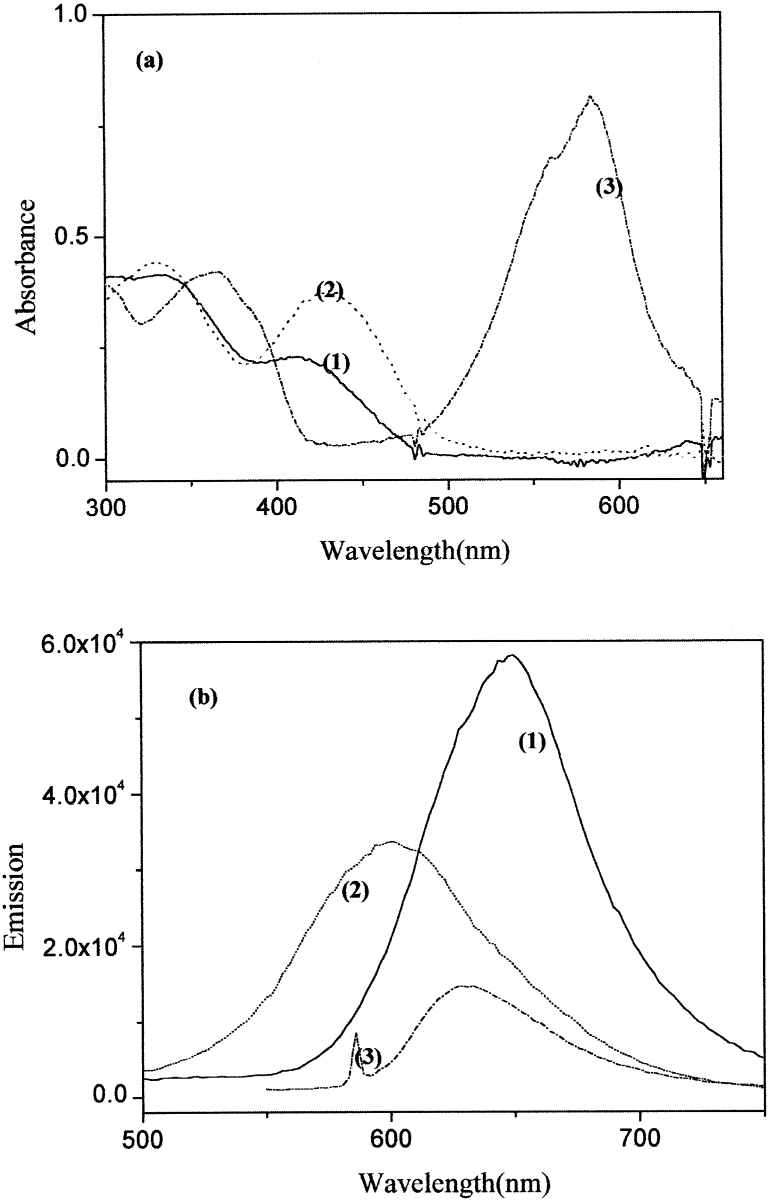
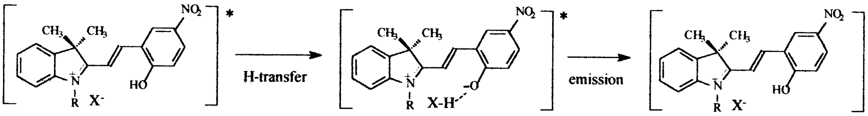


FIGURE 3 (a) Absorption and (b) fluorescence spectra SP-18 in THF in the presence of (1) HCl, (2) DBSA, and (3) benzoic acid. The concentration of SP-18 was 3.3×10^{-5} M.



SCHEME 3

respectively [Fig. 3(b)]. These emissions were almost in the same range of wavelength as the non-protonated MC form. It was assumed that intermolecular excited state proton transfer reaction might be operative in this system as illustrated in Scheme 3. The strength of acidity of the added acids will determine the strength of hydrogen bonding between the phenolate and acid, which can allow the fine control of the emission peak. Figure 4 shows decoloration spectra of the MCH$^+$ between SP-18 and DBSA in THF solution. Decoloration of MCH$^+$ form was much slower than in MC form.

We incorporated the SP-18 with acid into the polymer films, in order to examine the possibility of utilizing this material for optical recording application. Dodecylbenzenesulfonic acid (DBSA) was added to the chloroform solution of SP-18 and PMMA, and the solution was spincast

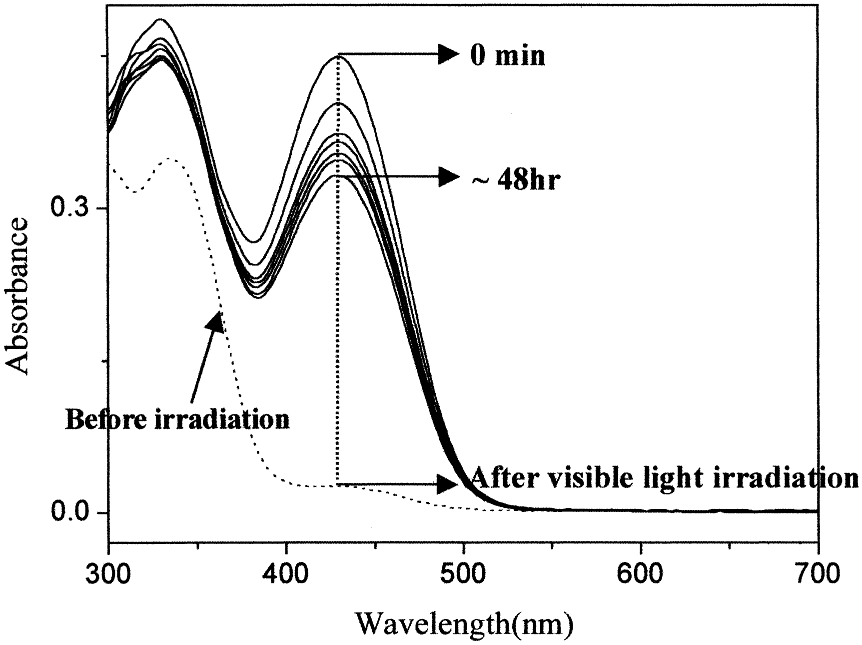


FIGURE 4 Decoloration spectra of complex MCH$^+$ in THF solution.

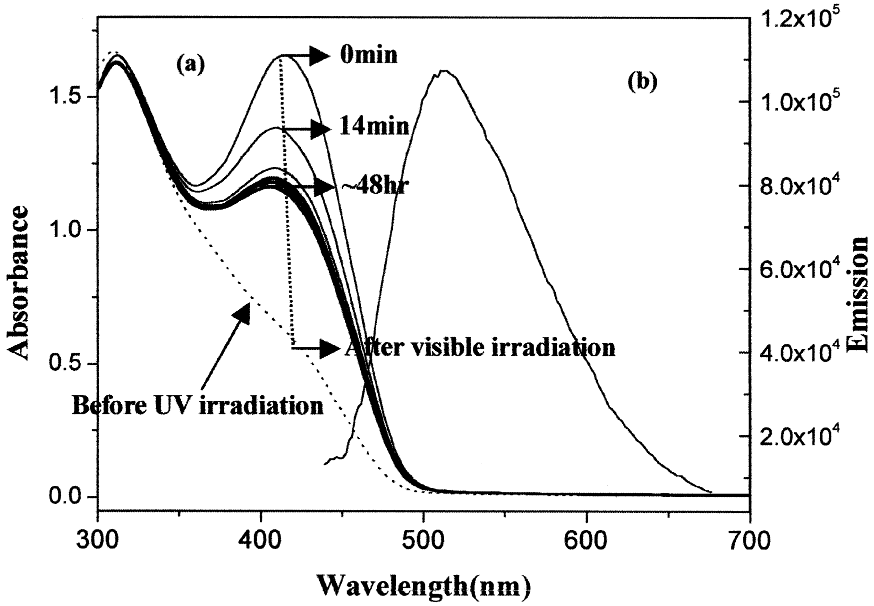


FIGURE 5 Decoloration of complex MCH$^+$/PMMA film; (a) Absorption and (b) fluorescence spectra.

on the glass substrate. The irradiation of UV light of 365 nm of the film produced a transparent and yellow film. The film had a similar absorption characteristics with the protonated MC form with DBSA in solution as shown in Figure 5(a), indicating that the MC form in polymer films was also protonated with the acid. The decoloration characteristics of the film as shown in Figure 5(a) indicated that the films reserved about 75% value of the original absorbance after 2 days of storage in the dark state. The films incorporated with the MCH$^+$ also showed photochromic behavior as shown in Figure 5(a). When irradiated with visible light, the yellow color of the film was faded, and then the yellow color of films was recovered with the irradiation of UV light (365 nm). In addition, the films containing the MCH$^+$ had a strong fluorescence centered at 535 nm as shown in Figure 5(b).

In summary, the stability of MCH$^+$ form, which is the protonated form of MC with strong acids, was highly increased. The MCH$^+$ form showed a absorption maximum at between 400–430 nm with irradiation of UV light of 365 nm and then the color was faded when illuminated with visible light. The decoloration of the protonated form MCH$^+$ in solution was highly retarded as compared with the MC form, due to blocking of the ring-closing reaction by protonating the phenolate ion. The PMMA films incorporated with the protonated MC form also showed high stability of the colored form and possessed strong fluorescence.

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