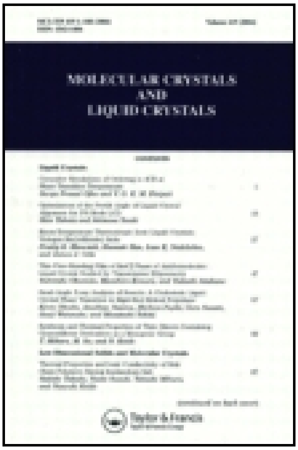

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Synthesis and Photochromic Behavior of Bi-Functional Photochromic Compound

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Bi-functional photochromic compound (SpAz) was synthesized with spirobenzopyran and azobenzene derivatives by DCC coupling reaction. In chloroform solution, a novel photochromic compound showed four kinds of isomer depending on the wavelength of the light irradiated. It was suggested that SpAz has four digital codes for optical memory. When SpAz was dispersed in poly(methyl methacrylate), on the other hand, the photoisomerization of SpAz was limited in polymer matrix due to the poor mobility of Azobenzene moiety with high steric hindrance.

Keywords: azobenzene moiety; bi-functional photochromic compound; multi-photochromism; spirobenzopyran moiety

INTRODUCTION

Photochromic compound is characterized by the ability to undergo a reversible transformation between two different chemical forms having different absorption spectra in response to light of appropriate wavelength [1–4]. One of the most widely studied classes of photochromism is the intense absorption of the colored form in the visible region, which is of great importance for practical applications of photochromic compounds. Recently, much attention has been paid to developing optical devices capable of signal processing such as switching and

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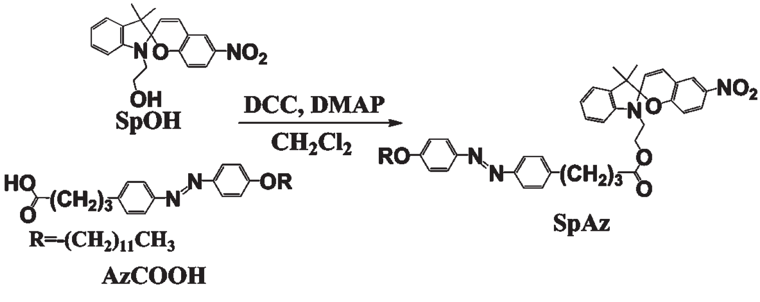
memory. Photochromic compounds have high potential in this field because they can represent “0 (light off)” or “1 (light on)” of two digital codes corresponding to each isomer. If several photochromic moieties can be introduced into certain molecule, the digital code will be increased by 2 × (number of photochromic moieties).

In this study, bi-functional photochromic compound was synthesized with spirobenzopyran and azobenzene derivatives. The photochromic behavior of novel compound was investigated under various light irradiation conditions.

EXPERIMENTAL

2′-Hydroxyethyl-3′, 3′-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2′-indoline] (SpOH) and 4-dodecyloxy-4′-(3-corboxy-trimetylene)azobenzene (AzCOOH) used as a starting material were prepared by the method in the literatures [5–7]. Coupling reaction with SpOH and AzCOOH is carried out according to Scheme 1. A solution of 80.0 mg (0.188 mmol) of AzCOOH, 60.8 mg (0.188 mmol) of SpOH, 2.3 mg (0.0188 mmol) of 4-dimethylaminopyridine (DMAP) and 36.5 mg of *N*,*N*′-dicyclohexylcarbodiimide (DCC) in 20 ml of dry dichloroethane was stirred in the dark at room temperature for 24 h under Ar atmosphere. After removal of the dichloromethane, the residue was separated by chromatography over silica gel with chloroform. Crude product (SpAz) was recrystallized from hexane and a purified SpAz was obtained as an orange powder.

Yield 50 mg (35%), mp 84.5–85.2°C. 1H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (s, 3H, CH_3), 0.88 (t, $J = 6.6$ Hz, 3H, $\mathrm{PhO(CH_2)_8\underline{CH_3}}$), 1.27–1.55 (m, 18H, $\mathrm{PhOCH_2CH_2\underline{(CH_2)}_9}$), 1.15 (s, 3H, CH_3), 1.82 (tt, $J =$ 6.5, 6.5 Hz, 2H, $\mathrm{PhOCH_2\underline{CH_2}}$), 1.94 (tt, $J = 7.5$, 7.5 Hz, 2H, $\mathrm{PhCH_2\underline{CH_2}}$), 2.27 (t, $J = 7.5$ Hz, 2H, $\mathrm{PhCH_2CH_2\underline{CH_2}}$), 2.29 (t, $J = 6.3$ Hz,



SCHEME 1 Synthesis of SpAz.

2H, NCH_2), 2.86 (t, $J = 7.5$ Hz, 2H, $Ph\underline{CH_2}$), 3.47 (t, $J = 6.3$, 2H, $\underline{CH_2}O$), 4.04 (t, $J = 6.5$ Hz, 2, $PhO\underline{CH_2}$), 4.23 (t, $J = 6.7$ Hz, 2H, $COO\underline{CH_2}$), 5.86 (d, $J = 10.8$ Hz, 1H, −CH=), 6.66–7.21 (m, 6H, 5H Ar and 1−CH=), 6.99 (d, $J =$ 8.9 Hz, 2H, 3′, 5′ −H Ar), 7.24 (d, $J = 8.3$ Hz, 2H, 2,6−H Ar), 7.77 (d, $J = 8.3$ Hz, 2H, 3,5-H Ar), 7.89 (d, $J = 8.9$ Hz, H, 2′,6′ −H Ar), 7.98–8.03 (m, 2H, 5-H Ar and 7-H Ar) ppm. IR (KBr) 2924, 2853, 2366, 2342, 1736, 1703, 1651, 1604, 1581, 1545, 1510, 1479, 1461, 1336, 1273, 1250, 1145, 1089, 1022, 954, 838, 809, 750 cm^{-1}. MS(FAB) 787 (M^+).

The photochromic behavior of SpAz was investigated in chloroform solution with the concentration of 2.0×10^{-4} M and in poly(methylmethacrylate) (PMMA) film prepared on a quartz substrate by the spin-coating. The concentration of SpAz in PMMA film was 4 wt%.

RESULTS AND DISCUSSION

Figure 1 shows the UV-Vis absorption spectra of SpOH and AzCOOH in chloroform solution and the spectral change by UV light irradiation with 365 nm. Main absorption peaks of SpOH appear around at 255 nm and 320 nm. These absorption bands were assigned to π–π^* transitions of benzopyran and of indoline rings in SpOH molecule, respectively. Upon UV light irradiation, the solution changed from

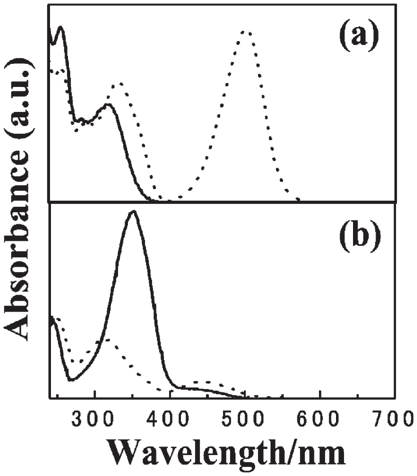


FIGURE 1 UV-Vis absorption spectra of (a) SpOH and (b) AzCOOH in chloroform solution before (solid line) and after (dotted line) UV light (365 nm) irradiation.

colorless to deeply red and a broad absorption peak appeared around at 500 nm. This band is assigned to merocyanine form of SpOH based on the heterolytic cleavage of C–O bond. In the case of AzCOOH, the absorption peak assigned to π–π^* transition of trans-isomer of azobenzene appeared around at 350 nm. After UV light irradiation, a weak absorption peak appeared around at 440 nm due to the overlap of the n–π^* electronic transition of the metastable cis-isomer of azobenzene [8,9].

UV-Vis absorption spectrum of SpAz in chloroform solution shows in Figure 2 with those of SpOH and AzCOOH. There are two main peaks at 245 nm and 350 nm and a shoulder at 270 nm. It is noticable that the spectrum of SpAz is almost equal to the sum of SpOH and AzCOOH spectra. It seems that SpAz has two photochromic moieties in the molecule. The photochromic behavior of SpAz was heavily dependent on the wavelength of the light irradiated. When the SpAz in chloroform solution is irradiated by the visible light with the wavelength range from 390 nm to 400 nm at rt, the absorption intensity at 350 nm decreased and that at around 450 nm increased, as shown in Figure 3(a). This result indicates that only azobenzene moiety in SpAz is photoisomerized from trans-form to cis-one. After standing for 5 min under rt and/or visible light irradiation with 443 nm, the former increased and the latter decreased. The photoisomerization of azobenzene moiety in SpAz was reversible. Upon light irradiation with the wavelength range from 290 nm to 390 nm, the broad absorption peak appears around at 590 nm in addition to similar spectral change observed under above visible light irradiation, as shown in Figure 3(b). This indicates that the

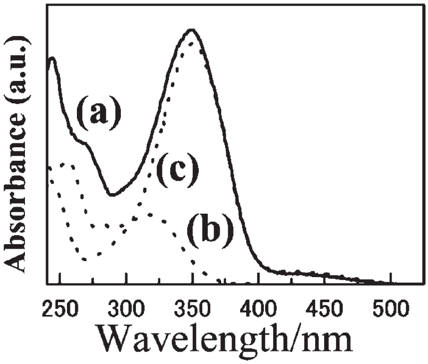


FIGURE 2 UV-Vis absorption spectra of (a) SpAz, (b) SpOH, and (c) AzCOOH in chloroform solution.

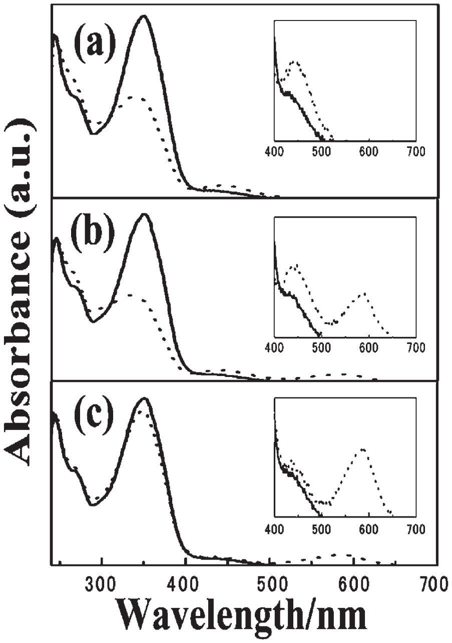


FIGURE 3 UV-Vis absorption spectra of SpAz in chloroform solution before (solid line) and after (dotted line) light irradiation with (a) $390 < \lambda < 400\,\text{nm}$, (b) $290 < \lambda < 390\,\text{nm}$ and (c) $270 < \lambda \leq 290\,\text{nm}$. In the inset, spectra are enlarged.

trans–cis photoisomerization in azobenzene moiety and the Sp (closed-ring form)-PMC (opened-ring form) photoisomerization in spirobenzopyran moiety occurred simultaneously. It is noteworthy that the absorption peak originated from PMC-form in spirobenzopyran moiety is red-sifted to about 90 nm as compared with that of SpOH. The indoline cation in PMC-form of SpAz maybe acts as an electron acceptive part against to the azobenzene moiety. Therefore, PMC-form of SpAz was stabilized. As a result it seems that its absorption peak was red-sifted. When the SpAz in chloroform solution was irradiated by the UV light with the wavelength range from 270 nm to 290 nm, on the other hand, the absorption band around 590 nm increased independently, as shown in Figure 3(c). Therefore only spirobenzopyran moiety was photoisomerized from Sp-form to PMC-form under this condition. The spectral change shown in Figures 3(b) and (c) was also reversible. When the SpAz in chloroform solution was irradiated by the UV light with the wavelength shorter than 270 nm, the absorption

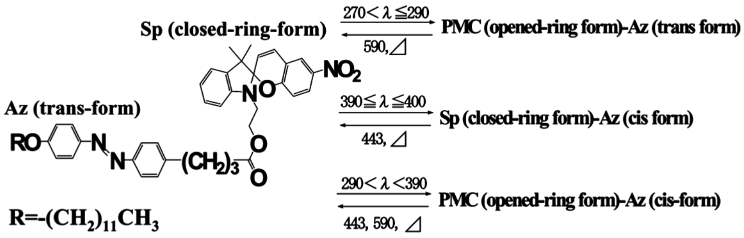


FIGURE 4 Photochromic behavior of SpAz in chloroform solution.

intensity around at 450 nm increased but that at 350 nm scarcely changed. In addition, any spectral change was not observed with heat treatment and/or visible light irradiation. Therefore it is concluded that SpAz was decomposed by UV light irradiation. The absorption peak around at 450 nm is seems to originate from bi-product but further information concerning to its chemical structure can not be obtained. The photochromic behavior of SpAz in chloroform solution is summarized in Figure 4. The Sp (closed-ring form)-Az (trans form) isomer is the most stable in four isomers under ambient condition.

The photoisomerization of SpAz was investigated in the solid state using PMMA as a matrix. SpAz was distributed uniformly in the

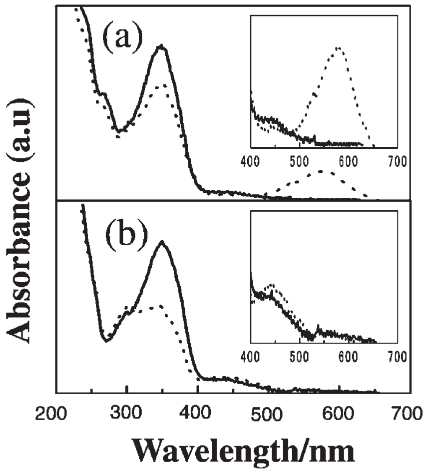


FIGURE 5 UV-Vis absorption spectra of (a) SpAz and (b) AzCOOH in PMMA film before (solid line) and after (dotted line) light ($300 < \lambda < 390$ nm) irradiation. In the inset, spectra are enlarged.

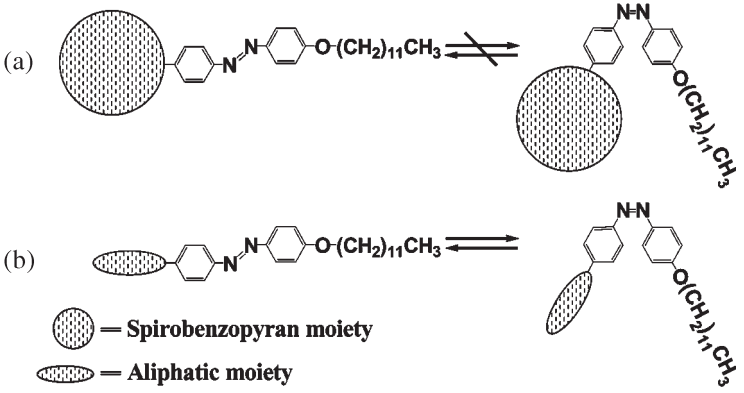


FIGURE 6 Trans–cis photoisomerization of (a) SpAz and (b) AzCOOH in PMMA film.

PMMA film. According to Figure 4, the most serious structural change by light irradiation is the isomerization from Sp (closed-ring form)-Az (trans form) isomer to Sp (opened-ring form)-Az (cis form) one. When the PMMA film containg SpAz was irradiated by the light with wavelength from 290 nm to 390 nm, the absorption intensity around at 590 nm increased but that at 450 nm did not change, as shown in Figure 5(a). Consequently, the photoisomerization occurred at only spirobenzopyran moiety in the film. On the other hand, AzCOOH in the PMMA film isomerized from trans form to cis one under same irradiation condition, as shown in Figure 5(b). It is well-known that trans-cis isomerization in azo group occurred by the following 3 steps; break of π-bond between two nitrogen atoms, rotation around σ-bond of N−N, recombination of π-bond. The easiness of rotation is dependent remarkably on the volume of substituent. It is obvious that the volume of substituent in SpAz is larger than that in AzCOOH. The free volume of SpAz in the PMMA film is also small comparing to that in the solution. Therefore, the trans-cis isomerization of SpAz in PMMA film can not occur by the steric hindrance with bulky substituent, as shown in Figure 6.

CONCLUSIONS

In this study, bi-functional photochromic compound (SpAz) was synthesized with spirobenzopyran and azobenzene derivatives and its photochromic behavior was investigated. In chloroform solution, SpAz showed four kinds of isomers depending on the wavelength of the light irradiated. SpAz has the possibility of four digital codes and the potential of fabrication of multi-addressable system and molecular switching for optical memory. However, such photoisomerization was not observed in the PMMA film. In particular application, photochromic response in the film is very important. We have done further investigation of photochromic behavior of SpAz using another matrix such as silica glass and soft polymers.

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