Novel Color Formers Having a Phenothiazine Moiety

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Leuco methylene blue color formers, 3,7-bis(dimethylamino)-10-(o-nitrobenzyloxycarbonyl)phenothiazine (4) and 3,7-bis(dimethylamino)-10-(tert-butoxycarbonyl)phenothiazine (5) were synthesized in order to obtain novel functional materials. These compounds, (4) and (5), showed good coloring reaction in acetonitrile by UV irradiation. The dimethylsulfoxide (DMSO) solution of 4 showed little change by heating at 70 °C in the presence of p-toluenesulfonic acid. On the other hand, the DMSO solution of 5 showed the blue coloration under the same condition. The acetonitrile solutions of 4 or 5 did not change to blue by γ irradiation.

Keywords: functional dye, leuco methylene blue, photosensitivity, acid sensitivity, deprotection, acid amplifier

1. Introduction

The research in color changing materials by light or thermal conditions have been noteworthy in order to develop novel optical devise.[1] Benzoyl leuco methylene blue (1) is one of the pressure sensitive dyes and gives greenish blue color by the hydrolysis to 2 and following oxidization of 2 to give 3 (Scheme 1).[2]

We designed novel benzoyl leuco methylene blue analogs, 3,7-bis(dimethylamino)-10-(o-nitrobenzyloxycarbonyl)phenothiazine (4) and 3,7-bis(dimethylamino)-10-(tert-butoxycarbonyl)phenothiazine (5). The compounds 4 or 5 have similar structure with typical photo acid generator[3] or acid amplifier[4]. The expected mechanisms of deprotection of 4 and 5 to give colored species (3) are shown in Schemes 2 and 3, respectively. The o-nitrobenzyl ester (4) can be deprotected by ultra-violet (UV) irradiation. The acid-catalyzed deprotection of 5 is expected to be caused by heating in the presence of acid.

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2. Experimental

2.1 Materials

3,7-Bis(dimethylamino)-10-chloroformylphenothiazine (6) was prepared according to the published procedure (Scheme 4).[5] Tetrahydrofuran (THF) and toluene were fractionally distilled over sodium. All other reagents were purchased and used without further purification.

3,7-Bis(dimethylamino)-10-chloroformylphenothiazine (6)

Methylene blue (3•Cl⁻) (392 mg, 1.00 mmol) was dissolved in water (10 ml). Toluene (40 ml), 40% sodium hydroxide solution (10 ml), and sodium dithionite (Na₂S₂O₄, 171 mg, 2.85 mmol) were added to the mixture and stirred at 50 °C until the solution became yellow, which indicates the reduction of cationic dye (3) is complete. Sodium hydrogen carbonate (292 mg, 3.48 mmol) was added to the mixture and toluene (10 ml) solution of bis(trichloromethyl)carbonate ((CCl₃O)₂CO, 272 mg, 0.58 mmol) was added over a period of 90 min at room temperature. The mixture was stirred for another 1 h. The toluene layer was separated from water layer and washed with water and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the solvent was evaporated under reduced pressure. The crude product was digested by addition of methanol. The precipitates were collected by suction filtration and washed with methanol and dried to give 6: yield 154 mg (40 %) white powder; 'H NMR (400 MHz, CDCl₃) δ (ppm) 7.38 (2H, d, aromH), 6.69 (1H, s, aromH), 6.61 (2H, d, aromH), 2.85 (12H, s, CH₃); MS(DI, m/z) 347 (M⁺); IR (HBr, cm⁻¹) 1732.

3,7-Bis(dimethylamino)-10-(o-nitrobenzyloxy carbonyl)phenothiazine (4)

A mixture of 6 (350 mg, 1.00 mmol) and 8 (525 mg, 3.00 mmol) in dry THF (40 ml) was stirred for 3 h at room temperature. The mixture was extracted with toluene several times. The combined toluene layer was washed with water and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel / chloroform-ethyl acetate) and recrystallized from ethanol to give 4: yield 47.3 mg (10 %) pale yellow powder; mp 161 - 162 °C; 'H NMR (400 MHz, CDCl₃) δ (ppm) 8.11 (1H, d, aromH), 7.59 (1H, d, aromH), 7.47 (1H, d, aromH), 7.36 (2H, d, aromH), 6.68 (2H, d, aromH), 6.62 (2H, d, aromH), 5.63 (2H, s, CH₂), 2.94 (12H, s, CH₃); MS (DI, m/z) 463 (M⁺); IR (KBr, cm⁻¹) 1690, 1595, 1505, 1177, 1096; UV-Vis. λmax (nm) 274 (ε = 32000) in acetonitrile (Figure 1 (a)).

Sodium o-nitrobenzylalkoxide (8)

Sodium (690 mg, 30 mmol) and dry toluene (10 ml) was heated and the mixture was stirred until the melted sodium was broken up into fine globules. The mixture was cooled to room temperature. o-Nitrobenzyl alcohol (7) (4.59 g, 30 mmol) was added and the mixture was stirred for 18 h at room temperature. The resulting precipitates were collected by suction filtration and dried to give 8: yield 3.15 g (69 %) yellow powder; 'H NMR (400 MHz, CDCl₃) δ (ppm) 8.11 (1H, d, aromH), 7.74 (1H, d, aromH), 7.67 (1H, dd, aromH), 7.46 (1H, dd, aromH), 5.02 (2H, s, CH₂).

3,7-Bis(dimethylamino)-10-(o-nitrobenzyloxy carbonyl)phenothiazine (4)

A mixture of 6 (350 mg, 1.00 mmol) and 8 (525 mg, 3.00 mmol) in dry THF (40 ml) was stirred for 3 h at room temperature. The mixture was extracted with toluene several times. The combined toluene layer was washed with water and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel / chloroform-ethyl acetate) and recrystallized from ethanol to give 4: yield 47.3 mg (10 %) pale yellow powder; mp 161 - 162 °C; 'H NMR (400 MHz, CDCl₃) δ (ppm) 8.11 (1H, d, aromH), 7.59 (1H, d, aromH), 7.47 (1H, d, aromH), 7.45 (1H, dd, aromH), 7.36 (2H, d, aromH), 6.68 (2H, d, aromH), 6.62 (2H, d, aromH), 5.63 (2H, s, CH₂), 2.94 (12H, s, CH₃); MS (DI, m/z) 463 (M⁺); IR (KBr, cm⁻¹) 1690, 1595, 1505, 1177, 1096; UV-Vis. λmax (nm) 274 (ε = 32000) in acetonitrile (Figure 1 (a)).
potassium tert-butoxide (336 mg, 3.00 mmol) in dry THF (30 ml) was stirred for 3 h at room temperature. The mixture was extracted with chloroform several times. The combined chloroform layer was washed with water and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel / chloroform-ethyl acetate) and was recrystallized from methanol to give 5: yield 61.4 mg (16 %) colorless needles; mp 192 - 193 °C; 'H NMR (400 MHz, CDCl₃) δ (ppm) 7.33 (2H, d, aromH), 6.64 (2H, s, aromH), 6.61 (2H, d, aromH), 2.91 (12H, s, CH₃), 1.47 (9H, s, tert-butyl); MS (DI, m/z) 385 (M⁺); IR (KBr, cm⁻¹) 2973, 1712, 1597, 1496, 1233, 1049; UV-Vis. λₓₓₓ (nm) 272 (ε = 29400) in acetonitrile (Figure 1(b)).

2.2. Method
UV-Vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Acetonitrile solutions of 1 or 2 (1.0 x 10⁻⁴M) were irradiated with ⁶⁰Co γ rays at room temperature. The 100 W high-pressure Hg lamp was used for UV irradiation.

3. Results and Discussion
3.1. UV irradiation
The absorbance changes at 655 nm for acetonitrile solution of 4 or 5 ([4 or 5]₀ = 1.0 x 10⁻⁴M) in quartz cell by the irradiation of UV light are shown in Figure 2. Both compounds showed the absorbance change caused by the deprotection by UV irradiation to give 3 (λₓₓₓₓ = 655 nm). The spectra of acetonitrile solution of 4, 5, or 3•Cl⁻ are shown in Figure 1. As shown in Figure 2, the absorbance at 655 nm reached to the maximum about 70 or 40 min after the beginning of irradiation for 4 or 5, respectively. The yields of deprotected product 3 calculated from the molecular extinction coefficient (ε) of 3•Cl⁻ were about 40 % (from 4) or 30 % (from 5), respectively. The absorbance at 655 nm of the solution of 5 increased faster than that of 4, showed slight decrease of the absorbance about 40 min after the beginning of irradiation. The decomposition of 3 may occur while the irradiation of UV light.

Fig. 1 UV-Vis spectra of 4 (a), 5 (b), and 3•Cl⁻ (c) in acetonitrile, [4 or 5] = 1.0 x 10⁻⁴M; [3•Cl⁻] = 1.0 x 10⁻⁵M.
3.2 Acid-catalyzed thermolysis

Acid-catalyzed deprotection of 4 or 5 was monitored by the spectral change in the presence of p-toluenesulfonic acid. Neither acetonitrile solutions of 4 or 5 in the presence of 1000 equivalents of p-toluenesulfonic acid showed any spectral change at room temperature.

When DMSO solution of 4 or 5 was heated at 70 °C with 1000 equivalents of p-toluenesulfonic acid, the changes of the absorbance at 655 nm were observed (Figure 3). Compound 4 showed only a slight increase of the absorbance at 655 nm. On the other hand, compound 5 showed a larger increase of the absorbance of 3, indicating the amplified decomposition of tert-butoxycarbonyl moiety by heating with acid.

3.3. Irradiation of γ rays

The o-nitrobenzylester photo acid generators such as 2-nitrobenzyl tosylate (9) and 2-nitrobenzyl methanesulfonate (10) decomposed to give corresponding acid by γ irradiation[6].

Thus, γ irradiation was attempted to the acetonitrile solution of 4 or 5. Figures 4 and 5 show the UV-Vis spectral changes of the acetonitrile solution of 4 or 5 (1.0 x 10^{-4}M) after γ irradiation, respectively. The solution of 4 did not change the absorption intensity at 655 nm, which would be assigned to the absorption of the generated dye (3). The new absorption around 470 nm was observed.
nm appeared after irradiation. The solution turned pale yellow instead of blue. As for the solution of compound 5, the absorption at 655 nm was increased a little and the new broad absorption around 350 - 700 nm appeared after γ irradiation. The compound 4 and 5 would be decomposed by γ irradiation. Poly(butene-1-sulphone) (11) is 50 times as sensitive to electron beam or deep UV radiation as poly(methyl methacrylate) (PMMA, 12).[7]

4. Summary
Leuco methylene blue analogs, 4 and 5 were synthesized in order to obtain novel functional materials. Compound 4 or 5 showed good coloring reaction by UV irradiation. DMSO solution of 5 showed to turn blue by heating at 70 °C in the presence of p-toluenesulfonic acid. The acetonitrile solutions of 4 or 5 did not give the blue color of 3 indicating the decomposition of π-conjugate system of 3 by γ irradiation.

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References