Molecular Design, Synthesis and γ ray Detection of Novel Color Formers Having Phenazine Moiety

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Novel color formers 2 containing phenazine moiety for γ ray detection were designed based on the shades of chromophore 1. Color formers 2a-2c were synthesized from aromatic amines 4, 5 and 6 or dye 9· Cl or 10· Cl as starting materials. Acetonitrile solution of 2a, 2b or 2c was changed into corresponding colored form 1a-1c by γ irradiation. Identification of the structures of 1 was carried out with electronic absorption and mass spectrometry. 1a, 1b or 1c showed magenta, red or yellow shade respectively. Substituent R1-R4 introduced into 1 affected a remarkable shift of absorption maximum within visible range.

Keywords: phenazine derivate, γ rays, color former

1. Introduction

We have been studying on γ ray detective materials including color formers having fluorene[1], benzodioxanthen[2] and phenoxazine[3] moieties. Here we report molecular design, and γ ray detection of a novel color former which has phenazine precursor as a chromophore.

2. Results and Discussion

2.1 Molecular design of color former 2

Substituents R1-R4 in compound 1 will affect a remarkable shift of absorption maximum (λmax) within visible range[4,5]. The sum Σσ', of the Hamnett's para-substituent constant σ', of R1-R4 will provide estimation of λmax of 1. Alan G. Miller has demonstrated that increase of Σσ' results in decrease of λmax[4,5] (Table 1).

We designed chromophores 1a-1c using this relationship (Table 2). Electron-donating substituents CH3 or C2H5 will provide magenta 1a, on the other hand, electron-withdrawing substituent C=O or CH3CICl, hereinafter denoted by Troc (2,2,2-trichloroethoxycarbonyl), in 1b or 1c will provide its shade as yellowish red to reddish yellow.

On the basis of these estimations, color former 2a, 2b or 2c was designed. Colorless form 2 was expected to give colored form 1 by the effect of γ ray irradiation.

Table 1 The relationships between Σσ' and λmax in compound 1 (R1=R4=H)

| Σσ'      | λmax (nm) |
|---------------------------------------|
| ≥ about - 0.52                        | ≤ 575     |
| about - 0.52 ≤ 0                      | about 530 ≤ 575 |
| > 0                                   | ≤ 530     |
Table 2  Molecular design of phenazines 1a-1c

<table>
<thead>
<tr>
<th>No.</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>R⁵</th>
<th>Σσ⁺</th>
<th>Shade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>-0.52</td>
<td>magenta</td>
</tr>
<tr>
<td>1b</td>
<td>H</td>
<td>Troc</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>H</td>
<td>0.18</td>
<td>reddish yellow</td>
</tr>
<tr>
<td>1c</td>
<td>H</td>
<td>Troc</td>
<td>Troc</td>
<td>H</td>
<td>H</td>
<td>1.80</td>
<td>yellowish red</td>
</tr>
</tbody>
</table>

1a: R⁰= CH₃ ; 1b: R⁰= H ; 1c: R⁰= H; Troc= C(=O)(OCH₂CCl₃)

2.2 Synthesis of color former 2

Color former 2a was synthesized by the method indicated in Scheme 1[3,6]. Compound 2b or 2c was prepared according to Scheme 2. The yield of 2a, 2b or 2c was 3, 42 or 12% respectively. Purification of 1a was difficult enough to decrease its yield. The reason why only one 2,2,2-trichloroethoxy carbonyl (Troc) group is substituted to each primary amino group at 3 or 7 position is based on the lower basicity of substituted secondary amine than unsubstituted primary amine[7].

2.3. Irradiation of γ rays for 2 in acetonitrile

Acetonitrile solution of 2a (0.25 mM) was irradiated with ⁶⁰Co γ rays at room temperature. The colorless solution turned magenta. Similar experiment for 2b or 2c gave red or yellow shade respectively. Electronic absorption spectra are shown in Figure 1. The coloration was recognized by the naked eye at an absorbed dose of 10 Gy.

UV irradiation by the use of Ushio 100 W mercury lamp for 6 h to 25 μM acetonitrile solution of 2 was carried out until no absorbance change was observed (Table 3). The resultant electronic spectra are completely coincided with the new peaks in Figure 1. From the mass spectrum data of these chemical species obtained by UV irradiation, we concluded that color former 2a, 2b or 2c changed into colored form 1a, 1b or 1c by UV or γ irradiation.

Table 3  Electronic absorption and mass spectra of 1 resulting after UV irradiation of 2

<table>
<thead>
<tr>
<th>No.</th>
<th>λₘₐₓ (nm)</th>
<th>m/z (M+H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>568</td>
<td>357</td>
</tr>
<tr>
<td>1b</td>
<td>427, 540</td>
<td>517</td>
</tr>
<tr>
<td>1c</td>
<td>460</td>
<td>663</td>
</tr>
</tbody>
</table>
3. Conclusion

From the estimation of the colors of phenazine derivate 1, we designed color former 2. Compounds 2 were synthesized from aromatic amines 4, 5 and 6 or dye 9-Cl or 10-Cl as starting materials. Acetonitrile solutions of 2 were changed into corresponding colored forms 1 by γ irradiation. Compound 1a, 1b or 1c showed magenta, red or yellow shade respectively. Electron-donating substituents introduced into 1 at 3 or 7 amino group causes a bathochromic shift. Discussion is given based on perturbational molecular orbital theory.

4. Experimental

4,4'-bis(dimethylamino)diphenylamine (3)

A cold solution of N,N-dimethyl-p-phenylenediamine (4) (13.6 g, 100 mmol), N,N-dimethyl-aniline (5) (12.1 g, 100 mmol), conc. HCl aq (48 ml) in water (240 ml) was added to a cooled (5 °C) stirring solution of potassium dichromate (6.93 g, 33.0 mmol) in water (200 ml). The temperature of the reaction mixture was kept at 5-10 °C. Zinc chloride (60.0 g, 440 mmol) was then added to the mixture. A green precipitate was collected by filtration and dissolved in warm water. The filtrate of the mixture was added to a solution of sodium dithionite (Na2S2O4, 10.0 g, 57.0 mmol), sodium hydroxide (10.0 g, 180 mmol) in water (40 ml). The green color disappeared and the resultant precipitate was filtered and washed with water. The 4,4'-bis(dimethylamino)diphenylamine (3) was obtained in 21 % yield (5.20 g, 20.4 mmol). Gray powder: 1H NMR (300 MHz, CDCl3) δ (ppm) 6.91 (4H, m, aromH), 6.72 (4H, m, aromH), 5.14 (1H, br, sec-amineH), 2.87 (12H, s, CH3); MS (EI, m/z) 255 (M+); m. p. 112-113 °C.

3,7-bis(dimethylamino)-5-(4-methylphenyl)phenazinium chloride (7 - Cl)

A mixture of 3 (3.87 g, 15.0 mmol), p-toluidine (6) (1.97 g, 16.0 mmol), water (5 ml) and glacial acetic acid (50 ml) was stirred over a water bath at 80 °C. Powdered manganese dioxide (3.00 g, 35.0 mmol) was added in one portion to the reaction.
mixture. After 2 h, an additional MnO₂ (2.00 g, 23.0 mmol) was added. The reaction mixture was stirred for additional 4 h, and filtered hot into water (200 ml) containing potassium chloride (40.0 g, 536 mmol). Precipitated purple red solid was filtered and purified through successive Soxhlet extraction with toluene and methanol. The dye containing 7·Cl (3.94 g) was obtained from the methanol extract.

3,7-bis(dimethylamino)-5-(4-methylphenyl)-10-(2,2,2-trichloroethoxy carbonyl)-5,10-dihydropyrazine (2a)

The crude dye 7·Cl (756 mg) obtained above was dissolved in 40 ml water. To a mixture of sodium hydroxide (416 mg, 10.4 mmol), sodium dithionite (2.20 g, 6.02 mmol), sodium hydrogen carbonate (NaHCO₃, 889 mg, 10.6 mmol) and water (40 ml), tolune (40 ml) was added. The solution was added to 7·Cl solution. The mixture was vigorously stirred until the purple red color disappeared. Toluene (30 ml) solution of 2,2,2-trichloroethylchloroformate (Troc-Cl) 8 (1.28 mg, 6.05 mmol) was slowly added over 30 min. Stirring was continued for overnight. The toluene layer was separated from water layer and washed with water, then dried over anhydrous sodium sulfate. The solvent of the filtrate was evaporated under reduced pressure. The residue was purified by preparative thin layer chromatography (silica gel, 7 % ethyl acetate/toluene), recrystallized from methanol to give 1a: yield 33.2 mg (3 %): pale yellow powder; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.36 (6H, m, aromH), 6.33 (2H, m, aromH), 5.66 (2H, m, aromH), 4.88 (2H, s, ethoxyH), 2.73 (12H, s, CH₃), 2.47 (3H, s, CH₃); MS (EI, m/z) 532 (M⁺); m. p. 120-123 °C.

3-(2,2,2-trichloroethoxy carbonylamo)-7-diethylamino-5-phenyl-10-(2,2,2-trichloroethoxy carbonyl)-5,10-dihydropyrazine (2b)

3-amino-7-diethylamino-5-phenylpentaazinum chloride (9·Cl) (766 mg, 2.02 m mol) was dissolved in water (40 ml). To a solution of sodium hydrogen carbonate (516 mg, 6.14 mmol) and sodium dithionite (700 mg, 4.02 mmol) in water (20 ml), toluene (30 ml) was added. The solution was added to 9·Cl solution and vigorously stirred until the magenta color became orange, indicating the reduction of cationic dye 9·Cl to its leuco form. Toluene (10 ml) solution of Troc-Cl (8) (1.24 g, 5.84 mmol) was slowly added over 30 minutes. The mixture was stirred for overnight. The toluene layer was separated from water layer, washed with water, and then dried over anhydrous sodium sulfate. The filtrate was evaporated under reduced pressure. The residue was purified by preparative TLC and was recrystallized from methanol to give 1b: yield 586 mg (42 %): colorless crystal; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.63 (2H, m, aromH), 7.52 (2H, m, aromH), 7.37 (3H, m, aromH), 7.07 (1H, m, aromH), 6.65 (1H, s, sec-amineH), 6.30 (2H, m, aromH), 5.51 (1H, m, aromH), 4.88 (2H, s, ethoxyH), 4.72 (2H, s, ethoxyH), 3.71 (4H, q, methyleneH of Et, J=6.8 Hz), 0.96 (6H, t, methylH of Et, J=6.8 Hz); MS(FAB, m/z) 692 (M⁺); m. p. 124-125 °C.

3,7-bis(2,2,2-trichloroethoxy carbonylamino)-2,6-dimethyl-5-phenyl-10-(2,2,2-trichloroethoxy carbonyl)-5,10-dihydropyrazine (2c)

3,7-diamino-2,6-dimethyl-5-phenylpentaazinum chloride (10·Cl) (373 mg, 1.03 mmol) was dissolved in water(20 ml) and treated as above to give 1c: yield 103 mg (12 %): colorless powder; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.54 (7H, m, aromH), 6.75 (2H, s, aromH), 6.46 (2H, s, sec-amineH), 4.88(2H, s, ethoxyH), 4.71 (4H, s, ethoxyH), 2.30 (6H, s, CH₃); MS(FAB, m/z) 842 (M⁺+4); m. p. 210-211 °C.

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References