

# The Novel Functional Chromophores Based on Squarylium Dyes

Soo-Youl Park,\* Kun Jun, and Sea-Wha Oh

Department of Applied Chemistry, Dye, Dyeing and Finishing Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Daejeon 305-600, Korea. \*E-mail: sypark@kRICT.re.kr

Received November 24, 2004

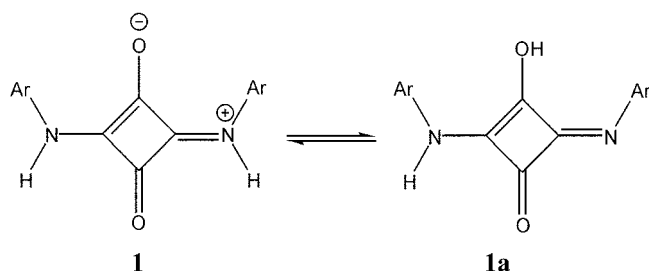
Squarylium or squaraine dyes are derived from 1,2-dihydroxycyclobuten-3,4-dione, otherwise known as *squaric acids*. They are two principal types: the 1,2-bisdonor-substituted derivatives, and the 1,3-bisdonor-substituted derivatives. The former are essentially merocyanines and have no distinctive properties, whereas the latter represent a unique type of chromophore, which is neither a merocyanine nor cyanine and has exceptional light absorption characteristics. They also have many functional applications based on their special properties. Thus it was the objective of this research project to synthesize a range of 1,3-squarylium dyes of widely differing structural types, and to investigate their light absorption and fluorescence properties in general, and the color change properties of appropriate examples in particular. Also in this study, the various pH-induced colour change processes were examined.

**Key Words :** Squarylium, Monoanion, Dianion, Bathochromic shift

## Introduction

The most important squarylium dyes<sup>1</sup> are those with electron donor end groups based on arylamines or heterocyclic derivatives. Both types may be symmetrical or unsymmetrical depending on whether or not the two end groups are the same. X-ray crystallographic analysis of these dyes demonstrates the special delocalized nature of the  $\pi$ -electron system.<sup>2</sup> When the amino group is secondary, there exists the possibility of tautomerism as shown in Scheme 1, so that the dyes may be represented as 1,3-squaraines **1**, or as imino squaramides. In fact, Chemical Abstracts often lists such compounds in the tautomeric form **1a**. However, by analogy with squaric acid amides, such structures are unlikely to be colored. Furthermore, the electronic absorption spectra of these compounds are similar to those of 1,3-bisamino-squaraines based on tertiary amines, which are incapable of such tautomerism, and thus it can be assumed that **1** is the better representation of these compounds.

Particular, some squarylium compounds have a very intense and narrow absorption band. Our results show that squaryliums could be possible to be produced near-infrared absorbing materials with a view to investigate color. All dyes synthesized were shown in Table 1.



Scheme 1. Tautomeric Forms for Dye 1.

## Results and Discussion

The weakly acidic solutions of the dyes ranged in color from pale yellow to red. The molar extinction coefficients

Table 1. Squaryliums Synthesized

No	Ar	m.p. (°C)	Yield (%)
2a		313-316	88
2b		277-280	87
2c		310-314	53
2d		~320 <sup>a</sup>	84
2e		~330 <sup>a</sup>	84
2f		~330 <sup>a</sup>	82

<sup>a</sup>With decomposition.

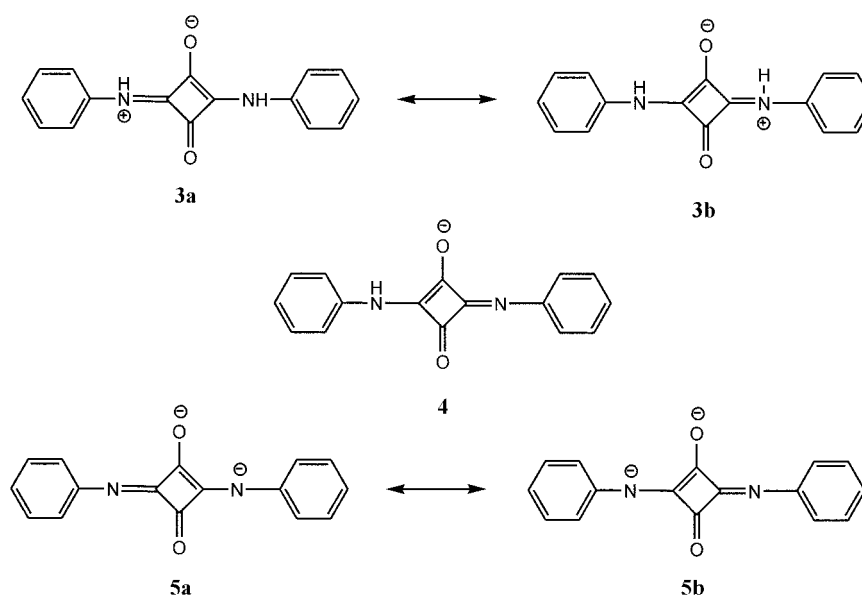
are low in comparison with most squaraine dyes, but were still moderate to very high in comparison with simple azo dyes. Strong electron-withdrawing groups (*e.g.* NO<sub>2</sub>) in direct conjugation with the amino groups had the largest effect on intensity.<sup>4</sup> Absorption bands ranged from narrow to moderately wide (half-bandwidths 54–94 nm). As noted, it became evident that in solution the dyes can exist in the neutral form represented by the resonance structures **3a** and **3b**, or may deprotonate to a greater or lesser degree, giving the monoanionic species **4**, or even the dianions **5a** and **5b** (Scheme 2).

The ease of deprotonation will be determined by the presence of substituents in the aryl rings, electron-withdrawing groups favoring higher pK<sub>a</sub> values. When there are no strong electron-withdrawing groups present, the neutral species corresponding to **3a** and **3b** are present, and the addition of base produces monoanion, which generally absorbs at slightly shorter wavelengths and has a broader absorption band. The latter is a consequence of the lower degree of electronic symmetry of the monoanion. Formation

of the dianion cannot be seen with normal bases, *e.g.* NaOH. This situation in our study is demonstrated for the 4-*n*-hexylphenyl dye **2c** in Figure 1, the spectral shifts being completely reversible.

When derivatives with strong electron-withdrawing groups in the aryl ring are examined, the color properties are somewhat different. Deprotonation to the monoanion is much easier, and in DMF this may occur to some extent without adding any base. Addition of dilute acid will reverse this. Furthermore, formation of the dianion is relatively easy, and thus by careful addition of base it is possible to observe three distinct visible absorption peaks with characteristic isosbestic points. Interestingly in these cases the sequence of bathochromic shift is *dianion* > *monoanion* > *neutral species*. The spectral shifts can be quite dramatic, as exemplified with compound **2f**, shown in Figure 2, the color of which changes from yellow to red to intense blue-green on the addition of increasing amounts of sodium hydroxide solution.

Although these spectral changes are fully reversible by



Scheme 2. pH Equilibria of **3a**.

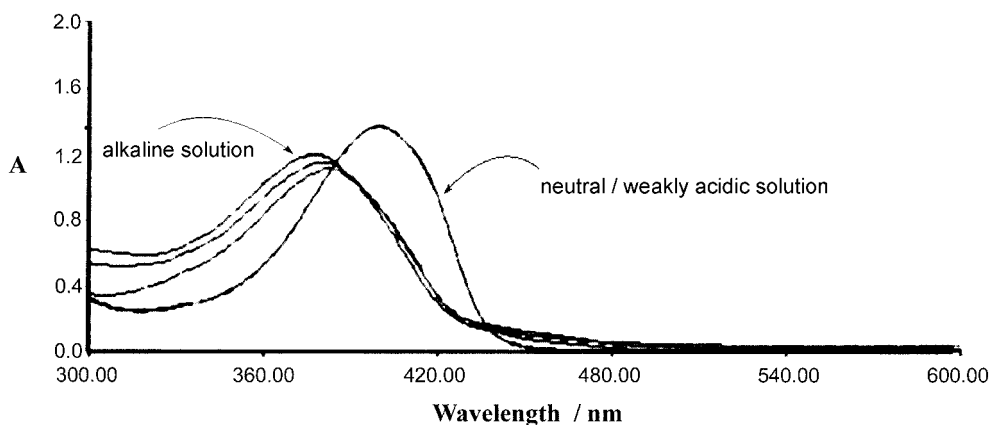
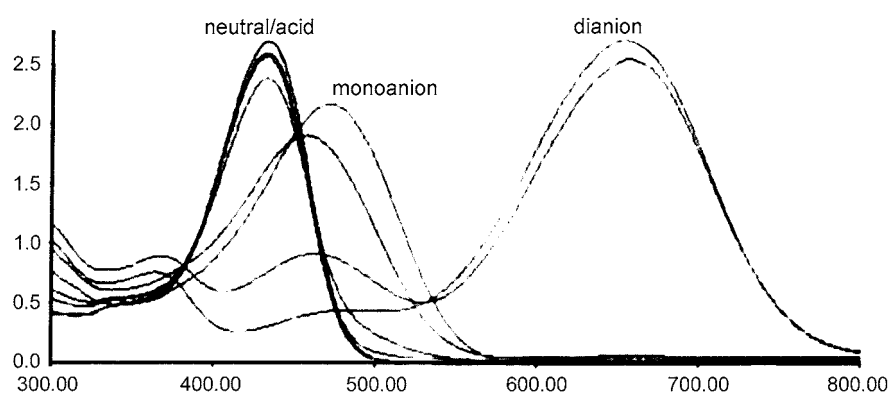


Figure 1. The Effect of Added Base (NaOH) on the Absorption Spectrum of **2c** in DMF.



**Figure 2.** Absorption Spectra of **2f** in DMF, with Increasing Addition of NaOH.

adding dilute acid, it should be noted that the anionic species are not stable and over a period of several minutes at room temperature and that acidification does not restore the full original absorbance of the neutral species. Very similar results were observed with the dye **2e**.

The spectral shifts occurring in methanol and in DMF solutions of dyes under acidic, neutral and basic conditions are summarized in Table 2.

It was found that in aqueous DMF the  $pK_b$  for the first dissociation of derivatives **2e** and **2f** was *ca.* 11.5, and for the second dissociation *ca.* 12.5. Although the 3-hydroxyphenyl dye **2a** behaved similarly to dye **2c**, it showed no tendency to form a long wavelength dianion. The 4-hydroxyphenyl analogue **2e** behaved exceptionally, and did produce a

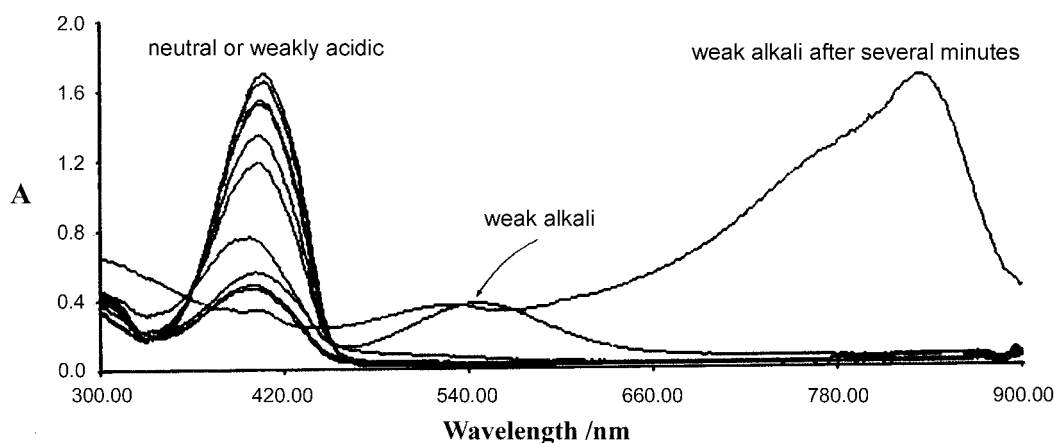
species in alkali absorbing at very long wavelengths, as shown in Figure 3.

It was evident however that the appearance of the long wavelength band was not instantaneous on addition of sodium hydroxide, but developed over a few minutes. Further works showed that the process was one of oxidation. The most likely explanation for this is summarized in Scheme 3. Thus the addition of alkali initially produces the usual monoanion, but there will also occur some further deprotonation of one of the hydroxy groups to give the dianionic species **6**. This will be very prone to air oxidation, giving the hydroxyquinonoid species, which will also ionize in the presence of base to give the dianion **7**.

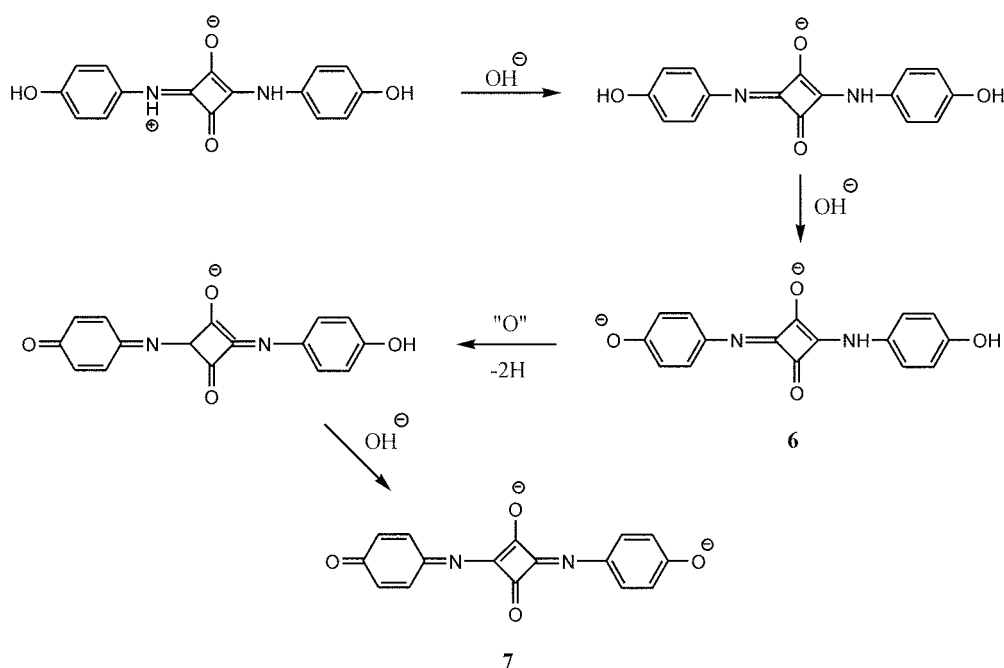
This extensively conjugated chromophoric system would

**Table 2.** Spectra of **2** in Methanol and in DMF at Different pH Values

DYE	$\lambda_{\max}$ (nm) in MeOH			$\lambda_{\max}$ (nm) in DMF			$\epsilon_{\max}$ ( $1 \text{ mol}^{-1}\text{cm}^{-1}$ ) in DMF	
	Acid	Neutral	Base	Acid	Neutral	Base	Acid	Base
<b>2a</b>	391	391	368	403	403	637	49,330	18,210
<b>2b</b>	393	393	741	408	408	839	36,190	60,700
<b>2c</b>	378	378	360	403	403	386	36,850	29,070
<b>2d</b>	360	429	542	370	488	621	16,250	46,540
<b>2e</b>	438	438	593	458	458	626	60,190	48,990
<b>2f</b>	426	426	585	438	438	650	47,040	55,950



**Figure 3.** Spectral Changes on Addition of NaOH to Solution of Dye **2e** in DMF.



Scheme 3. Possible Mechanism for the Oxidation of **2e**.

be expected to absorb at exceptionally long wavelengths and is most probably the species observed spectroscopically.

### Experimental Section

**General Methods.** All the chemicals and solvents used for the reactions were purchased from Aldrich (U.S.A. Chemical Co.), Acros (U.K. Chemical Co), and Junsei (Japan Chemical Co). All reactions were monitored by thin layer chromatography (TLC). Ultraviolet and visible spectra were determined on a Perkin-Elmer Lambda 15 Spectrophotometer. Melting points were measured on an electrothermal melting point apparatus. Elemental microanalysis and mass spectrometric analyses were performed by the EPSRC National Mass Spectrometry Service, using either fast atom bombardment sampling in a *m*-nitrobenzyl alcohol matrix, electron impact ionization, chemical ionization or electro spray.

General procedure for the synthesis of 1,3-bis(*N*-arylamino)squaraines was followed as: Squaric acid (0.290 g, 2.5 mmol)<sup>5,6</sup> was heated under reflux in a mixture of 1-butanol (40 mL) and toluene (20 mL), and water was distilled off azeotropically using a Dean-Stark trap. After 1h, the appropriate primary aromatic amine (5 mmol) was added and the reaction mixture refluxed for additional 4 h. The suspension was then cooled to room temperature and the solvent removed on a rotary evaporator. The residue was crystallized from 1-butanol and the solid dried in an oven at 50 °C.

**1,3-Bis(3-hydroxyphenylamino)squaraine 2a:** This was prepared from 3-aminophenol (0.545 g, 5 mmol), and **2a** was obtained as a yellow solid (0.65 g, 88%), mp. 313-316 °C. Mass Spectrum (FAB): Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, [M] =

264. Found [M] = 264. Anal. Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 64.86; H, 4.08; N, 9.46. Found: C, 65.05; H, 4.1; N, 9.35.

**1,3-Bis(4-hydroxyphenyl)squaraine 2b:** Using 4-aminophenol (0.550 g, 5 mmol), the general procedure gave **2b** as a yellow solid (0.64 g, 87%), mp. 277-280 °C. Mass Spectrum (FAB): Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, [M] = 264. Found [M] = 264. Anal. Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 64.86; H, 4.08; N, 9.46. Found: C, 64.82; H, 4.1; N, 9.0.

**1,3-Bis(4-*n*-hexylphenyl)squaraine 2c:** Using the general procedure, 4-*n*-hexylaniline (0.90 g, 5 mmol) gave **2c** as a white solid (0.55 g, 53%), mp. 310-314 °C. Mass Spectrum (FAB): Calcd. for C<sub>28</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>, [M] = 432. Found [M] = 432. Anal. Calcd. for C<sub>28</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.74; H, 8.39; N, 6.48. Found: C, 77.28; H, 8.91; N, 6.61.

**1,3-Bis(6-nitrobenzthiazolylamino)squaraine 2d:** 2-Amino-6-nitrobenzothiazole (0.97 g, 5 mmol) gave **2d** as a red solid (1.0 g, 84%), mp. 320 °C with decomp. Mass Spectrum (FAB): Calcd. for C<sub>18</sub>H<sub>8</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>, [M] = 468. Found [M] = 468. Anal. Calcd. for C<sub>18</sub>H<sub>8</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: C, 46.15; H, 1.72; N, 17.94. Found: C, 45.9; H, 1.9; N, 17.75.

**1,3-Bis(3-carboxy-4-nitrophenylamino)squaraine 2e:** 3-Amino-6-nitrobenzoic acid (0.91 g, 5 mmol) gave **2e** as a red solid (0.94 g, 84%), mp. 330 °C with decomp. Mass Spectrum (FAB): Calcd. for C<sub>18</sub>H<sub>10</sub>N<sub>4</sub>O<sub>10</sub>, [M] = 442. Found [M] = 442. Anal. Calcd. for C<sub>18</sub>H<sub>10</sub>N<sub>4</sub>O<sub>10</sub>: C, 48.88; H, 2.28; N, 12.67. Found: C, 49.15; H, 2.50; N, 12.65.

**1,3-Bis(2-chloro-5-methoxy-4-nitrophenylamino)squaraine 2f:** 2-Chloro-5-methoxy-4-nitroaniline (1.02 g, 5 mmol) gave **2f** as a red solid. (1.0 g, 82%), mp. 330 °C with decomp. Mass Spectrum (FAB): Calcd. for C<sub>18</sub>H<sub>12</sub>N<sub>4</sub>O<sub>8</sub>Cl<sub>2</sub>, [M] = 483. Found [M] = 483. Anal. Calcd. for C<sub>18</sub>H<sub>12</sub>N<sub>4</sub>O<sub>8</sub>Cl<sub>2</sub>: C, 44.74; H, 2.50; N 11.59. Found: C, 45.0; H, 2.65; N, 11.35.

### Conclusion

The 1,3-bis(N-arylamino)squaraines were found to have interesting pH indicator properties due to the acidity of the NH protons. If the aryl ring contained no strong electron-withdrawing groups, deprotonation resulted in a small hypsochromic shift of the absorption band. On the other hand, when strong electron-acceptors were present, dissociation occurred more readily, and the absorption band of the monoanion showed a significant bathochromic shift relative to the neutral species. On the addition of more base, a second dissociation was also observable with such compounds, and the resultant dianion showed a further shift to longer wavelengths. For example, derivatives with a 4-nitro substituent in the aryl ring showed a color change from yellow to red to cyan. Dyes of this type can be readily modified with additional substituents to give the requisite solubility and pK properties for pH indicator applications. It was also found that when a 4-hydroxy group was present in the aryl ring, the monoanion was spontaneously oxidized in

air to give a quinonoid species that absorbs at exceptionally long wavelengths (*ca.* 800 nm). The squarylium dyes have found many uses as functional dyes. Functional applications include their use as near-infrared absorbers (*e.g.* for optical data recording materials), laser dyes, light filters, photoconductive materials, long wavelength fluorescent labels and as dichroic dyes for liquid crystal displays.

### References

1. Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 869.
  2. Dirk, C. W.; Herndon, W. C.; Cervantes-Lee, F.; Martinez, H. S.; Kalamegham, P.; Tag, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L. T. *J. Am. Chem. Soc.* **1995**, *117*, 2214.
  3. Reans, F. *J. Chem. Soc.* **1996**, *92(19)*, 3611.
  4. Matsuoka, M.; Yasui, S.; Kitao, T. *Dyes and Pigments* **1988**, *10*, 13.
  5. Junek, H.; Hermetter, A.; Colbrie, H. F.; Aigner, H. *Tetrahedron Letters* **1973**, 2993.
  6. Vogel, A. I. *Textbook of Practical Organic Chemistry*, 4<sup>th</sup> Ed; Longman: London and New York., 1978; p 677.
-