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Synthesis of New Dilactone-type Fluorescent Dyes and Their Fluorochromic Properties

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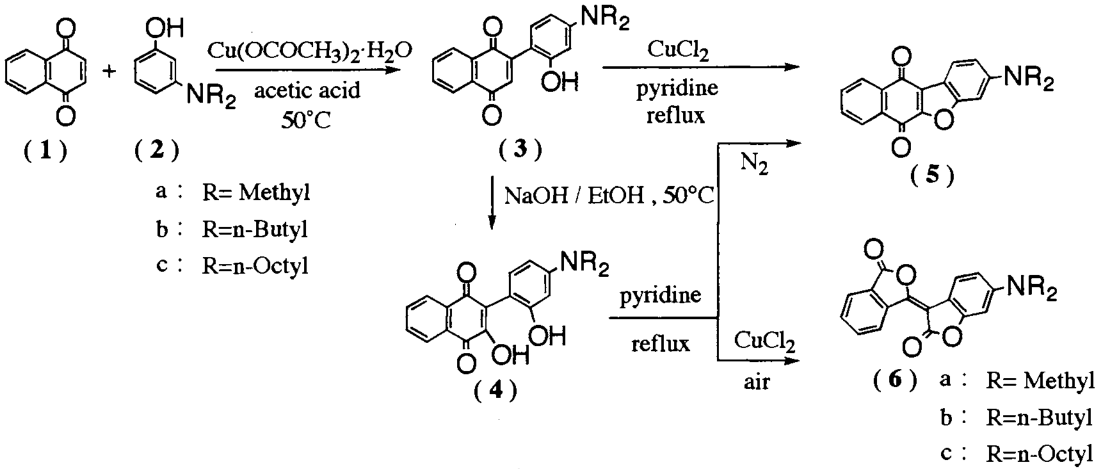
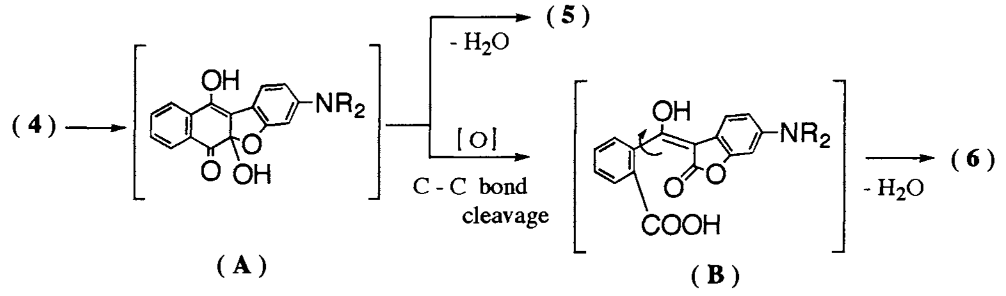
New dilactone-type fluorescent dyes have been synthesized starting from 1,4-naphthoquinone and *m*-(dialkylamino)phenols. Both the fluorescence maxima and intensities of the dyes were drastically changed depending on solvent polarity. The dyes also showed good fluorescent dichroic properties in an ordered nematic liquid crystal.

Fluorescent dyes have attracted much attention because of their practical applications such as dyestuffs and analytical reagents, and emissive materials for new use in dye lasers, solar collectors, and color display systems for electronic devices in recent years.[1, 2] Therefore, research for new fluorescent dyes with appropriate functional properties is very active. We report here the synthesis of new dilactone-type fluorescent dyes with a novel dye skeleton and the study of their absorption and emission properties in organic solvents and an ordered nematic liquid crystalline system.

The synthetic route of the dilactone-type dyes(**6**) is outlined in Scheme 1. The arylation of 1,4-naphthoquinone(**1**) with *m*-(dialkylamino)phenols(**2**) in the presence of $Cu(OCOCH_3)_2 \cdot H_2O$ in acetic acid at 50 °C afforded 2-[4-(dialkylamino)-2-hydroxyphenyl]-1,4-naphthoquinones(**3**) in 74-79% yields. We have previously reported[3] that the compounds(**3**) undergo intramolecular cyclization by refluxing in pyridine in the presence of $CuCl_2$ to give benzofuranoquinone-type dyes, 3-(dialkylamino)benzo[b]naphtho-[2,3-*d*]furan-6,11-diones(**5**), which have appropriate dichroic properties and good solubility in an ordered nematic liquid crystalline system. Here, the compounds(**3**) were reacted with three equivalent of NaOH in aqueous ethanol at 50 °C to give 3-hydroxy-2-[4-(dialkylamino)-2-hydroxyphenyl]-1,4-naphthoquinones(**4**) in 45-73% yields together with **5** in 21-35% yields. It was found that heating the compound(**4**) in refluxing pyridine in the presence of $CuCl_2$ produced smoothly new dilactone-type dyes(**6**) as a main product together with a small amount of **5**. The structure of the new dyes(**6**) were assigned on the basis of IR, ^1H- and ^{13}H-NMR, and mass spectrometry and elemental analysis.[4]



Scheme 1.



Scheme 2.

Table 1. Heating **4b** in refluxing pyridine under various conditions

	Reaction conditions			Yield / %	
Run	Atmosphere	Additive	Time / h	**5b**	**6b**
1	air	none	20	24	23
2	air	$CuCl_2$ a)	4	6.5	42
3	air	$CuCl_2$ b)	1	0.6	62
4	N_2 bubbling	none	20	62	3

a) Molar ratio : $[CuCl_2]$ / [**4b**] = 0.5 , b) Molar ratio : $[CuCl_2]$ / [**4b**] = 1.0.

As shown in Table 1, in the absence of $CuCl_2$, the reaction proceeded slowly to give **5b** in a 24% yield and **6b** in a 23% yield (Run 1). In the presence of $CuCl_2$, the reaction proceeded quickly to give **6b** almost exclusively (Runs 2 and 3). On the other hand, when the reaction was conducted without $CuCl_2$ under bubbling N_2, the formation of **6b** was depressed and **5b** was slowly produced (Run 4). From these results, a possible reaction pathway for the formation of **5** and **6** is illustrated in Scheme 2. An adduct(**A**) formed by intramolecular 1,4-addition may undergo competitive two reactions: one is dehydration to afford **5**, the other is oxidative C-C bond cleavage giving (**B**) followed by intramolecular cyclic condensation to produce the dilactone-type dyes(**6**). The addition of $CuCl_2$ could promote the oxidative C-C bond cleavage tremendously.

The absorption and fluorescence spectra data of the dyes(**6**) are shown in Table 2. The dyes showed intense absorption around 500 nm and emission around 575 nm in benzene. Varying the length of alkyl chain of the dialkylamino group does not affect significantly both the absorption and fluorescence. The effect of solvents on the absorption and fluorescence spectra of **6b** was examined. A bathochromic shift of 27 nm was observed in the absorption maxima on going from cyclohexane to ethanol. A larger bathochromic shift of 79 nm was observed in the fluorescence maxima on going from cyclohexane to ethanol, so that larger Stokes shifts were observed in polar solvents than in nonpolar solvents. These results indicate that the dyes(**6**) become more polar in the excited states than in the ground states. The fluorescence intensities were drastically reduced with increase in solvent polarity. The relative fluorescence intensity of **6b** in cyclohexane is nearly 37-fold greater than that in acetonitrile and 185-fold greater than that in ethanol. These results suggest that the dilactone-type dyes(**6**) have potential as microenvironmental fluorescent proves. Fluorescent dyes having similar fluorochromic properties are known to serve as a fluorescent stain for intracellular lipid droplets.[5]

Table 2. Absorption and fluorescence spectra of **6** in various solvents

Dye	Solvent	Absorption		Fluorescence		
		λmax	εmax	λmax	R.F.I.a)	Δλmaxb)
		nm	dm^{3}mol^{-1}cm^{-1}	nm		nm
6a	benzene	494	(26900)	572	98	78
6b	cyclohexane	485	(31800)	542	278	57
	benzene	505	(29900)	577	100	72
	acetonitrile	510	(29600)	617	7.5	107
	ethanol	512	(29900)	621	1.5	109
6c	benzene	504	(30100)	577	102	73

a) R.F.I. = Relative Fluorescence Intensity : **6b**(benzene) = 100.
b) Δλmax = λmax(Fluorescence) - λmax(Absorption).

Dichroic dyes are now used as guest molecules in a system of guest-host liquid crystal color display divices. The use of dichroic fluorescent dyes as hosts in liquid crystals has been expected for making an optical shutter[6] or an emissive disply.[7-10] As the fluoresent dye(**6**) showed an appropriate dichroic property and good solubility[11] in a nematic liquid (ZLI-1840, Merk), an attempt for controlling fluorescence based on the guest-host interactions in an ordered nematic liquid crystal system was performed. Figure 1 shows the fluorescence spectral changes of the dye for parallel(F//) and perpendicular (F⊥) modes[12] measured by using a GH cell(EHC Co., Ltd.) with a 14 μm thickness of cell gap. The ratios of fluorescence intensities of F// / F⊥ were about 6.0–7.0(conc.; 3x10^{-3}–3x10^{-4} mol dm^{-3}); fairly good values were obtained. The dilactone-type skeleton seems to be useful for designing new fluorescent dichroic dyes. Further synthesis of the related compounds is now under way.

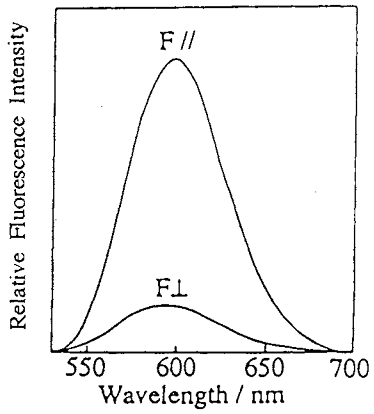


Fig.1. Fluorescence spectra of **6b** in ZLI-1840 for parallel(F//) and perpendicular(F⊥) modes.

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4) **6b**: mp 155-156°C; IR(KBr) 1770 and 1792 cm^{-1} (ester C=O); ^{1}H NMR(CDCl3) δ= 0.98 (6H, t), 1.1-1.9 (8H, m), 3.34 (4H, t), 6.33 (1H, d, J=2.4 Hz), 6.44 (1H, dd, J=2.4, 8.8 Hz), 7.4-8.1 (3H, m), 7.76 (1H, d, J=8.8 Hz), 9.13(1H, d, J=7.7 Hz); ^{13}C NMR δ= 165.7 and 168.0 (ester C=O); MS m/z 391 (M^{+}). Found: C; 73.31, H; 6.51, N; 3.68%. Calcd for $C_{24}H_{25}NO_4$: C; 73.63, H; 6.44, N; 3.58%. The other products(**6a** and **6c**) gave also satisfactory spectral and analytical data; **6a**(53%yield): mp mp 273-274°C; IR(KBr) 1770 and 1792 cm^{-1} (ester C=O), **6c**(59%yield): mp 82-84°C; IR(KBr) 1770 and 1792 cm^{-1} (ester C=O)
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11) The solubility of the dyes(**6**) in ZLI-1840 is remarkably improved by the introduction of longer alkylchains to the dialkylamino group: **6a**(0.4%wt); **6b**(2.6%wt); **6c**(3.0%wt).
12) The method for measurement has been described in the previous paper.[3b]

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