CHEMISTRY LETTERS, pp. 2027-2030, 1991.

New Metallochromic and Fluorescence Compounds Obtained from the Reaction of 5,8-Quinolinedione with 2-[3-(Dimethylamino)phenyl]propene

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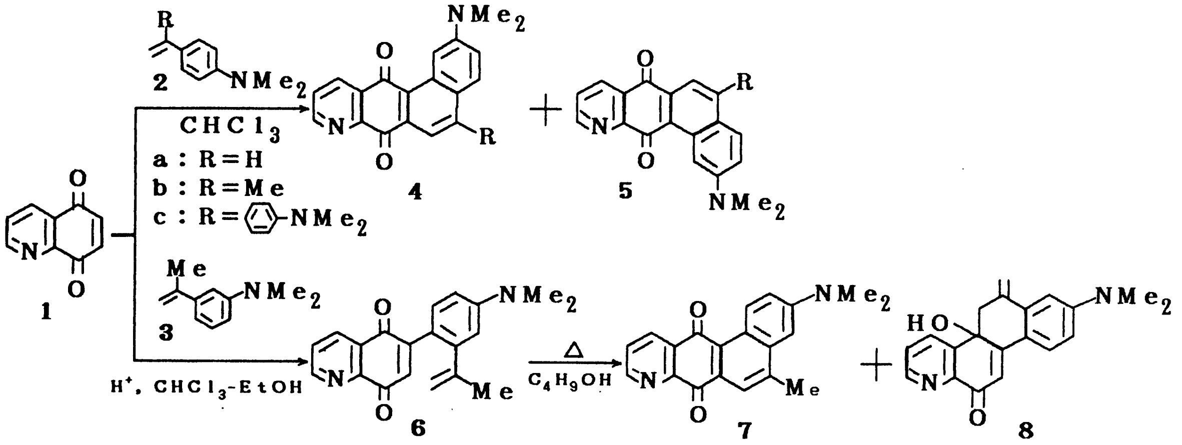
The reaction of 5,8-quinolinedione with 2-[3-(dimethylamino)phenyl]propene was initiated by HCl to give 6-[4-(dimethylamino)-2-(2-propenyl)phenyl]quinoline-5,8-dione, which subsequently underwent intramolecular cyclization to produce new compounds with remarkable metallochromism and intense fluorescence.

The Diels-Alder type reaction of 1,4-naphthoquinone with some substituted styrenes is known to produce benz[a]anthracene-7,12-dione derivatives.1-3) As shown in Scheme 1, we recently synthesized two isomeric heterocyclic quinone dyes (4 and 5) by the Diels-Alder reaction of 5,8-quinolinedione 1 with p-(dimethylamino)styrenes 2a-2c, which showed quite different metallochromic behaviors: only one of the two isomers showed drastic spectral changes induced by metal chelate complexation.4) Snthesis of other related isomers was demanded to investigate the relations between the structure and the metallochromic properties. Hence, we further investigated the reaction of 1 with 2-[3-(dimethylamino)phenyl]propene 3 and obtained new metallochromic and intense fluorecence compounds.

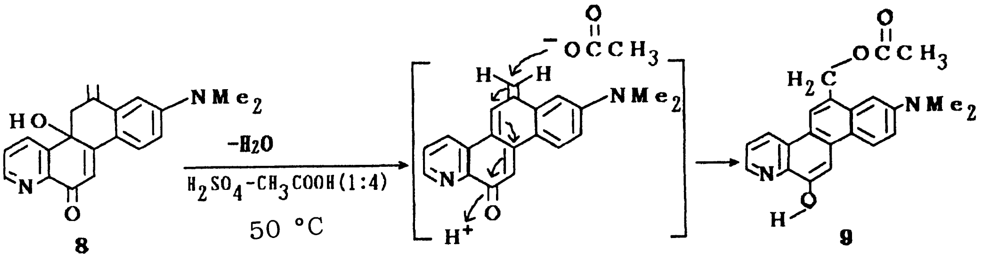


Scheme 1.

In the case of the reaction of 1 with 3, the Diels-Alder reaction did not proceed at all and the starting materials were recovered. However, the reaction was initiated by an addition of HCl to give not the Diels-Alder product but the 6-arylated product, 6-[4-(dimethylamino)-2-(2-propenyl)-phenyl]quinoline-5,8-dione 6,[5] in ca. 50% yield. The corresponding 7-substituted isomer was not observed. We have already found that the regioselective 6-arylation of 1 with N,N-dialkylanilines was efficiently promoted by addition of copper(II) ion in acetic acid,[6] however, the addition of HCl in $CHCl_3$-C_2H_5OH (6:1 v/v) was preferable for the formation of 6. With the aim of getting another isomeric quinone dye 7 , we investigated the intramolecular cyclization of the intermediate 6 and found that 6 underwent cyclization by refluxing in 1-butanol to give a mixture of 3-dimethylamino-5-methylnaphtho[1,2-g]quinoline-7,12-dione 7 (12% yield)[7] and 8 (77% yield).[8] The new compounds(7 and 8) were characterized by mass and ^1H- and ^{13}C-NMR spectra and by elemental analysis. The structure of 8 was also supported by the following result: 1-aza-6-acetoxymethyl-8-dimethylamino-12-hydroxychrysene 9[9] was obtained by the treatment of 8 with H_2SO_4-CH_3COOH (1:4 v/v) at 50 °C for 30 min (Scheme 2).

The target compound 7 showed remarkable metallochromic behaviors: drastic spectral changes were observed upon addition of various metal ions such as Cu(II), Ni(II), Sn(IV), etc. As a typical example, Fig. 1 shows the spectral changes observed upon addition of $SnCl_4$ to the THF solution of 7. The pattern of the spectral changes was similar to that of the isomer 5, but quite different from that of the isomer 4.[4] The detailed relations between the structure and metallochromism of these isomeric dyes (4, 5, and 7) will be reported elsewhere.

On the other hand, the unexpected compound 8, which is a new type of dye, showed not only remarkable metallochromism but also intense fluorescence. Figure 2 shows the absorption spectrum of 8 and those obtained after addition of some metal salts to the 99% ethanol solution: drastic spectral changes were induced by metal chelate complexation between the ring nitrogen atom and neighboring carbonyl group of 8 with various metal ions.[10]



Scheme 2.

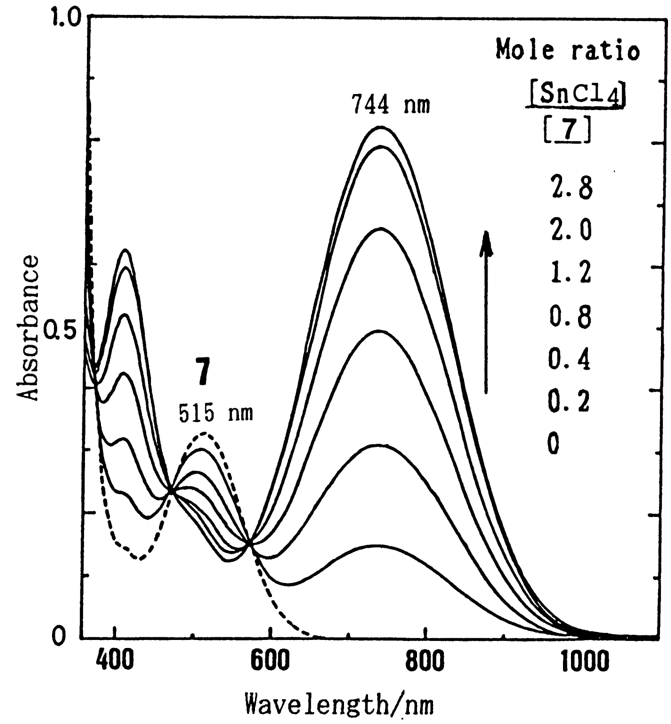


Fig.1. Spectral changes upon addition of $SnCl_4$ to the THF solution of 7: [7]=6.25x10^{-5} M.

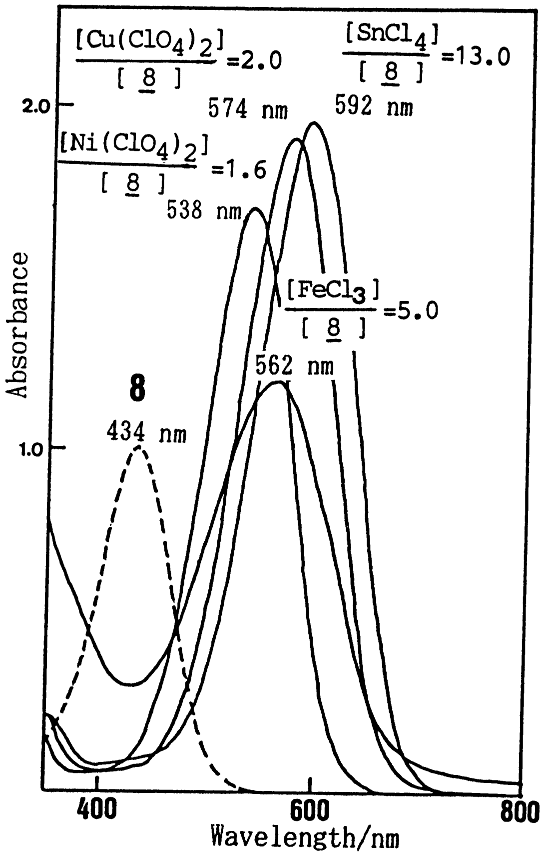


Fig.2. Spectral changes after addition of various metal salts to the 99% ethanol solution of 8: [8]=6.25x10^{-5} M.

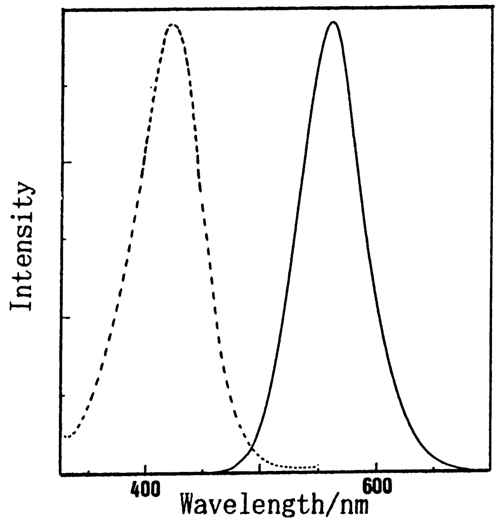


Fig. 3. Excitation (----) and Emission (——) spectra of 8 in CH_3CN: [8]=1.0x10^{-6} M.

Table 1. Absorption and Emission Spectra of 8 in various Solvents

Dye	Solvent	Absorption λmax/nm (ε)	Emission λmax/nm	Δλmax^{a)}/nm
8	C_6H_6	407(17900)	500	93
	$CHCl_3$	431(21000)	540	109
	CH_3CN	423(21000)	561	138
	C_2H_5OH	438(19700)	574	136

a) Δλmax = λmax(Emission) - λmax(Absorption)

In Table 1, the solvent effect on the absorption and the emission spectra of 8 is listed. Though both the absorption and the emission maxima shifted to longer wavelength with an increase in solvent polarity, the bathochromic shift of emission maxima was much larger than that of absorption maxima, which led to the well separated absorption and emission spectra of 8 in a polar solvent as shown in Fig. 2. Such remarkable metallochromism and intense fluorescence together with large solvatochromism of 8, makes this class of compounds very promising in connection with analytical and technical applications.

References

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3) M. Gates, J. Org. Chem., 47, 578 (1982).
4) K. Yoshida, T. Koujiri, E. Sakamoto, and Y. Kubo, Bull. Chem. Soc. Jpn., 63, 1748 (1990).
5) 5: mp 151-151.5 °C; λmax (THF) 509 nm (εmax 4600); ^{1}H NMR ($CDCl_3$) δ= 2.09 (3H, brs), 3.04 (6H, s), 4.75 (1H, brs), 4.95 (1H, m), 6,55-6.75 (2H, d and dd), 7.1-7.3 (2H, s and d), 7.65 (1H, dd), 8.42 (1H, dd) 9.03 (1H, dd); MS m/z 318 (M^+).
6) K. Yoshida, M. Ishiguro, H. Honda, M. Yamamoto, and Y. Kubo, Bull. Chem. Soc. Jpn., 61, 4335 (1988).
7) 7: mp 253-254 °C; λmax (THF) 515 nm (εmax 5400); ^{1}H NMR ($CDCl_3$) δ= 2.68 (3H, s), 3.12 (6H, s), 6.81 (1H, d), 7.25 (1H, dd), 7.64 (1H, dd), 8.15 (1H, s), 8.55 (1H, dd), 9.01 (1H, dd), 9.47 (1H, d); MS m/z 316 (M^+).
8) 8: mp 247 °C(dec); ^{1}H NMR (CD_3SOCD_3) δ=2.70 (1H, brd), 3.03 (6H, s), 3.35 (1H, brd), 5.26 (1H, brs), 5.86 (1H, brs), 5.92 (1H, brs), 6.67 (1H, s), 6.81 (1H, dd), 7.06 (1H, d), 7.5-7.8 (2H, d and dd), 8.33 (1H, dd), 8.75 (1H, dd). MS m/z 318 (M^+).
9) 9: mp 208-209 °C; ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s), 3.13 (6H, s), 5.65 (2H, s), 7.11 (1H, d), 7.26 (1H, dd), 7.60 (1H, dd), 8.19 (1H, s), 8.42 (1H, s), 8.52 (1H, d), 8.82 (1H, dd), 8.92 (1H, dd); MS m/z 360 (M^+).
10) We have previously observed similar spectral changes in the chelate complexation of some quinoid dyes with metal salts in organic solvents: K. Yoshida, M. Ishiguro, and Y. Kubo, Chem. Lett., 1987, 2057; Y. Kubo, K. Sasaki, H. Kataoka, and K. Yoshida, J. Chem. Soc., Perkin Trans. 1, 1989, 1469; K. Yoshida, N. Oga, T. Koujiri, M. Ishiguro, and Y. Kubo, ibid., 1990, 1891.

(Received August 12, 1991)