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Syntheses of Naphthoquinone Methide-type Near-IR Color Formers

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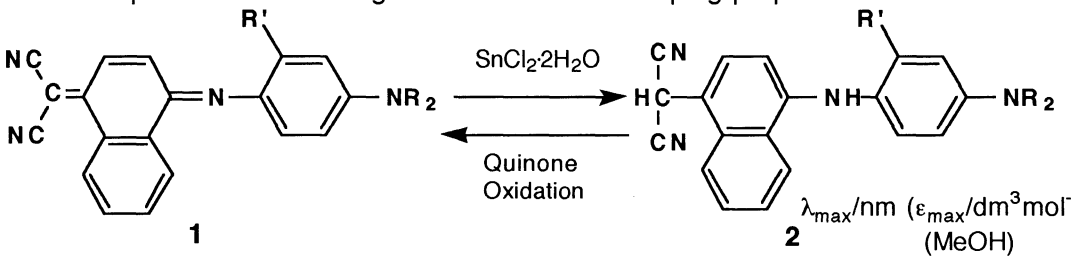
New naphthoquinone methide-type near-IR color formers have been synthesized, which immediately exhibited intense absorption in the near-IR region on oxidation. The color development has been investigated using the stopped-flow technique.

Near-IR color formers are of considerable interest as heat- and pressure-sensitive dyes with electro-optical application utilizing diode-laser technology.[1] To date, triphenylmethane lactone-type near-IR color formers are the best known compounds in this field. The use of leuco-quinones has been little studied because of the instability of the leuco-quinone dyes. However, recently, we found that several types of quinone dyes having metal complexation properties gave rise to stable leuco-dyes and that these produced intense absorption band in the near-IR region in the presence of metal salts.[2] To develop other types of Near-IR color formers, we have attempted to synthesize the title compounds and investigated their color developing properties.



	λ_{max}/nm (ε_{max}/dm^{3}mol^{-1}cm^{-1}) (MeOH)	
a; R = Et, R' = Me	350	(11000)
b; R = Et, R' = H	358	(11000)
c; R = Me, R' = H	359	(11100)

Reduction of 4-(4-dialkylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile (**1**)[3] with $SnCl_2 \cdot 2H_2O$ under acidic conditions produced the leuco-dyes (**2**)[4] in 64 - 74% yield, which have weak absorption maxima at 350 - 359 nm in MeOH. Interestingly, **2** could be isolated as stable yellow compounds. With the aim of developing **2** as a new type of color formers, we investigated the oxidation behavior in the presence of quinone oxidant. As shown in Fig. 1, addition of 10 equiv. of *p*-benzoquinone (BQ) to a MeOH solution of **2a** immediately produced new absorption at ca. 760 nm, the character of which was consistent with the presence of **1a**, formed by oxidation of **2a**. From the functional color-formers viewpoint, it is notable that the production of intense absorption band in the near-IR region occurs very rapidly. The spectral characteristics were investigated using the stopped-flow technique. Figure 2 shows the time dependence of the increase in absorbance at 762 nm observed in the case of a 1×10^{-4} mol dm^{-3} solution of **2a** in MeOH [1:1 v/v; final concentration

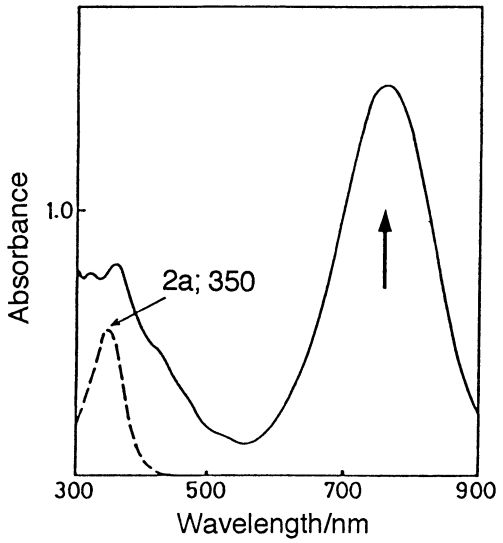


Fig. 1. Spectral changes upon addition of BQ to a MeOH solution of **2a** (----): [BQ]/[**2a**] = 10, [**2a**] = 5 × 10^{-5} mol dm^{-3}.

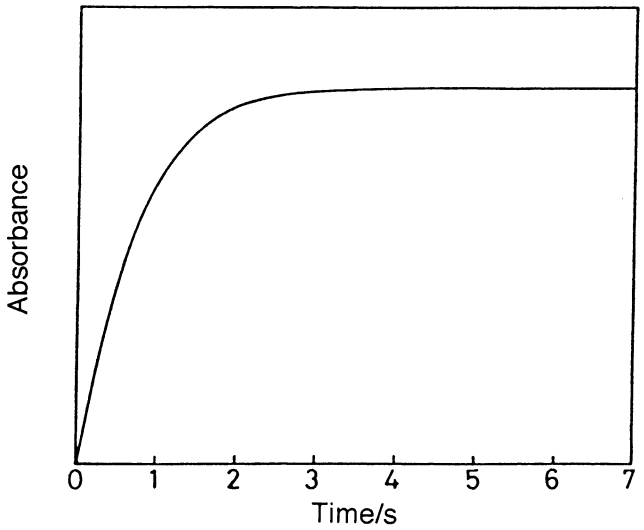


Fig. 2. Formation of **1a** in MeOH at 25 °C: The plot of the absorbance at 762 nm vs. time: [BQ]/[**2a**] = 10, [**2a**] = 5 × 10^{-5} mol dm^{-3}.

Table 1. Half-value period for color development in MeOH at 25 °C[a)]

Leuco-dye[b)]	Near-IR dye (λ_{max}/nm)	$T_{1/2}$/s[c)]
2a	**1a**; 762	0.55
2b	**1b**; 735	0.63
2c	**1c**; 718	0.43

a) In the presence of 10 equiv. of BQ (5 × 10^{-4} mol dm^{-3}). b) [Leuco-dye] = 5 × 10^{-5} mol dm^{-3}. c) Time for A/A∞ ; A is absorbance at λ_{max} of **1**.

of **2a** is 5 × 10^{-5} mol dm^{-3}]. After ca. 2 sec., the absorbance at 762 nm was observed to be saturated. Similar color development was also observed in the case of **2b** and **2c**. In order to estimate the apparent rate of color development, we used the half-value period [$T_{1/2}$: time for A/A∞ = 0.5; A is the absorbance of λ_{max} of **1**]. In the presence of 10 equiv. of BQ, $T_{1/2}$ values of 0.43 - 0.63 sec. were obtained (see Table 1). These values are almost consistent with that of 5-(4-dimethylaminoanilino)quinolin-8-ol in the presence of 100 equiv. of $Cu(ClO_4)_2 \cdot 6H_2O$.[2a)] From these results, the leuco-dyes (**2**) could have potential for use as a suitable near-IR color former.

References

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2) a) Y. Kubo, H. Yasuoka, and K. Yoshida, *J. Chem. Soc., Chem. Commun.,* **1990**, 1253; b) Y. Kubo, H. Yasuoka, Shin-ichi Hamaguchi, and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1,* **1992**, 411; c) K. Yoshida, N. Oga, M. Kadota, Y. Ogasawara, and Y, Kubo, *J. Chem. Soc., Chem. Commun.,* in press.
3) Y. Kubo, F. Mori, K. Komatsu, and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1,* **1988**, 2439.
4) **2a**: Mp 172 - 174 °C; ^{1}H NMR ($CDCl_3$) 1.20 (6H, t), 2.18 (3H, s), 3.38 (4H, q), 5.39 (1H, s), 6.045 (1H, brd.), 6.43 (1H, d, J = 8.13 Hz), 6.52 - 6.63 (2H, m), 7.00 - 7.10 (1H, m), 7.44 (1H, d, J = 8.35 Hz), 7.51 - 7.78 (2H, m), 7.83 - 7.935 (1H, m), 8.035 - 8.14 (1H, m); MS (m/z) 368 (M^+); Anal Found: C, 77.70; H, 6.64; N, 14.80%. Calcd for $C_{24}H_{24}N_4$: C, 78.23; H, 6.56; N, 15.20%.

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