

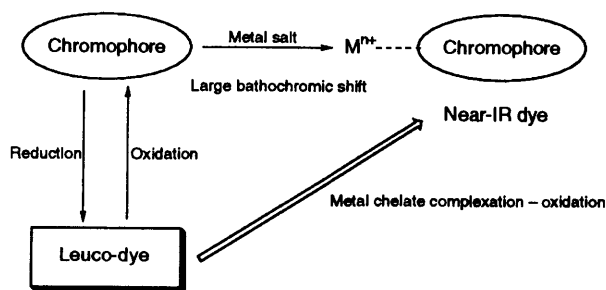
Synthesis and Colour Development Properties of Indoaniline-type Near-IR Colour Formers¹

Yuji Kubo

Department of Applied Chemistry, Faculty of Engineering, Saitama University, Urawa, Saitama 338, Japan

New indoaniline-type near-IR colour formers have been synthesized as stable compounds, which on metal chelate complexation–oxidation, immediately exhibit intense absorption in the near-IR region. This colour development has been investigated using the stopped-flow technique.

Heat- or pressure-sensitive dyes have been widely used in colourless copy papers and special papers for thermal-head printers. These dyes are essentially colourless but have a colour development function, which has been designated as the *colour former*. The colourless triphenylmethane lactones² and leuco-quinones³ are examples. Lactones develop a colour in contact with a Lewis acid such as phenol, and have been widely used as colour formers for heat- or pressure-sensitive applications. However because of their instability, the use of leuco-quinones in colour-former recording media has been less studied. Previously, we found that the *N,O*- or *N,N*-bidentate indoaniline-type ligands **1**⁴ readily form complexes with metal ions, and this complexation causes a large bathochromic shift of the absorption bands with an increase in molecular extinction coefficients, so that these metal complex dyes have intense absorption bands in the near-IR region. The specific absorption properties of the dyes have inspired the molecular design of new types of near-IR colour formers based on the incorporation of such metal chelate complexation into the redox process of the dyes **1** as shown in Scheme 1. Leuco-dyes having such spectral properties are of great value currently as heat- and pressure-sensitive functional dyes in electrooptical applications utilizing diode-laser technology.⁵ To the best of our knowledge, the synthesis of quinone-type near-IR colour formers is limited to our recent reports.^{1,6} In this paper, the synthesis and the colour development properties of the title compounds are described in detail.



Scheme 1

Results and Discussion

Metallochromic Properties of the Indoaniline-type Ligands 1.—The ligands **1**, which show λ_{\max} values in the range 596–648 nm in CHCl_3 solution, react readily with metal ions to form complexes which exhibit large bathochromic shifts and an increase in molecular extinction coefficient. For example, Fig. 1 shows the spectral changes for the complexation of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with **1a** in 99% EtOH. The absorption at 600 nm decreased while a new band appeared in the near-IR region on addition of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. A set of isosbestic points were observed at 470 and ca. 640 nm. At a ratio of $[\text{Cu}^{\text{II}}]/[\mathbf{1a}] = 0.8$,

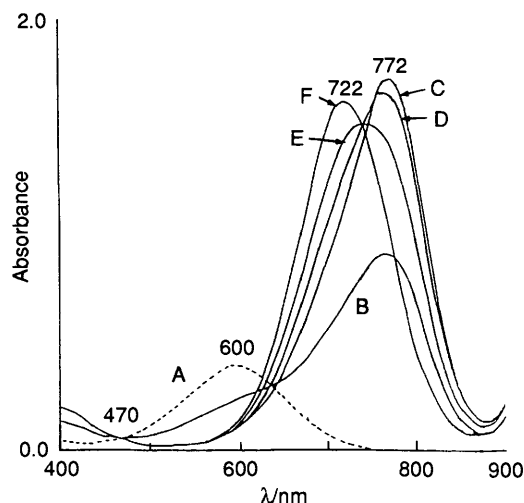


Fig. 1 Influence of added $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ on the absorption spectra of **1a** ($2.5 \times 10^{-5} \text{ mol dm}^{-3}$) in 99% EtOH. Molar ratio $[\text{Cu}^{\text{II}}]/[\mathbf{1a}]$: A, 0.0; B, 0.5; C, 0.8; D, 1.0; E, 1.2; F, 1.8–2.5.

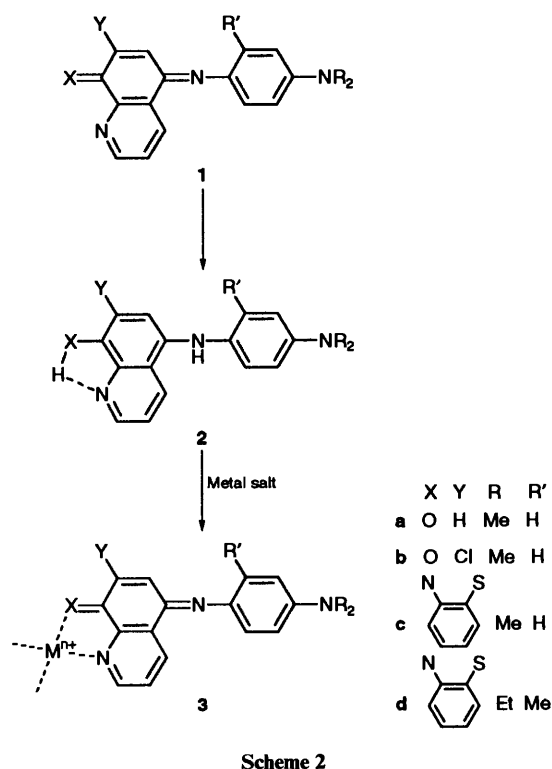
the absorption maximum at 600 nm disappeared completely while a single absorption band at 772 nm was observed (curve C). On further addition of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to this system ($[\text{Cu}^{\text{II}}]/[\mathbf{1a}] > 0.8$), the absorption at 772 nm decreased as another absorption band at around 720 nm increased; a new isosbestic point was also observable, at 740 nm. The final absorption spectrum ($[\text{Cu}^{\text{II}}]/[\mathbf{1a}] = 1.8$, curve F) had an absorption band at 722 nm. Use of the continuous variation method⁷ indicated a 1 : 2 $\text{Cu}^{\text{II}}-\mathbf{1a}$ complex for the absorption at 772 nm, and a 1 : 1 $\text{Cu}^{\text{II}}-\mathbf{1a}$ complex for the absorption at 722 nm, respectively. Similar metallochromic properties were also observed in the complex formation with other ligands (see Table 1). The values of the bathochromic shift ($\Delta\lambda$) were in the range of 80–188 nm. From these results, the synthesis of the leuco-dye **2** is of great interest since the colour development of **2** in the presence of a suitable metal ion would produce a new function as a colour former.

Synthesis and Colour Development Properties of Leuco-dyes 2.—Reduction of **1** with $\text{Na}_2\text{S}_2\text{O}_4$ under alkaline conditions produced the leuco-dyes **2** in 65–77% yields as stable compounds (see Scheme 2), the absorption spectra of which show weak absorption bands at 403–459 nm in 99% EtOH (see Table 2). The structures of **2** were fully assigned on the basis of observed analytical data. The stability of the leuco-dye **2** may be attributed to an intramolecular hydrogen bond between the N-1 and 8-OH group of the quinoline segment for **2a** and **2b**, or between N-1 and the 12-NH proton of the phenothiazine ring for **2c** and **2d**; this is because the leuco-dye of 4-(4-diethylamino-

Table 1 Spectral data for complex formation of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with **1** in 99% EtOH

	Ligand 1		Molar ratio ^a	Complex 3		
	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$		$\lambda_{\text{max}}/\text{nm}$	M:L ^b	$\Delta\lambda_{\text{max}}^c$
a	600	16 600	0.8	772	1:2	172
			2.5	722	1:1	122
b	632.5	20 900	1.0	759	— ^d	126.5
			2.5	712.5	— ^d	80
c	616	10 800	0.6	794	1:2	178
d	654	11 100	0.6	842	1:2	188

^a Molar ratio = [metal ion]/[ligand]. ^b Determined by continuous variation method. ^c $\Delta\lambda_{\text{max}} = \lambda_{\text{max}}(\text{complex}) - \lambda_{\text{max}}(\text{ligand})$. ^d Unable to be determined using continuous variation method.

**Scheme 2****Table 2** Electronic absorption spectra of **2** in 99% EtOH

Compound	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
2a	403	2800
2b	403	3500
2c	459	3700
2d	454	3000

2-methylphenylimino)naphthalen-1(4H)-one is unstable and reoxidizes immediately. With the aim of developing a new colour-former system, the oxidation behaviour of **2** in the presence of metal ions was investigated. Addition of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ resulted immediately in the growth of an intense absorption band in the near-IR region at 724 nm, which was essentially in agreement with the spectral features of a 1:1 Cu^{II} -**1a** complex, suggesting that the oxidation of the leuco-dye **2a** accompanying metal chelate complexation produced **3a** (see Scheme 2). From the functional colour former viewpoint, it is notable that the production of an intense absorption band in the near-IR region, due to the formation of **3**, occurs very rapidly. The spectral characteristics were investigated using the stopped-flow technique. An increase in the absorption at 724 nm was observed when a $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ solution of **2a**

Table 3 Half-value period for the colour development in 99% EtOH at 25 °C

Run	Leuco-dye ^a	Metal salt ^b	Complex dye 3 $\lambda_{\text{max}}/\text{nm}$	$T_{1/2}/\text{s}^c$
1	2a	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	724	0.50
2	2a	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	750	0.060
3	2a	$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	734	0.58
4	2a	$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	727	13 000
5	2b	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	745	0.054
6	2c	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	779	0.14 ^d
7	2d	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}^e$	834	0.26 ^d

^a [Leuco-dye] = $1.5 \times 10^{-5} \text{ mol dm}^{-3}$. ^b [Metal salt] = $1.5 \times 10^{-3} \text{ mol dm}^{-3}$. ^c Time for $A/A_\infty = 0.5$. A is the absorbance at λ_{max} of **3**. ^d A is the absorbance at 800 nm of **3c**. ^e $[\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$.

in 99% EtOH was mixed with a $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 99% EtOH (1:1 v/v; final concentration of **2a** $1.5 \times 10^{-5} \text{ mol dm}^{-3}$). After ca. 2 s, the final stable absorption at 724 nm was observed. Similar colour development was also observed in the formation of other complexes **3** (see Table 3). In order to estimate the apparent rate of colour development, the half-value period ($T_{1/2}$ the time for $A/A_\infty = 0.5$, where A is the absorbance at λ_{max} of complexes **3a** and **3b**, or the absorbance of **3c** and **3d** at 800 nm). As shown in Table 3, $T_{1/2}$ decreases in the order: $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} \gg \text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} > \text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} > \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (runs 1–4). In the case of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $T_{1/2}$ values of 0.054–0.060 s were obtained (runs 2 and 5). The activity of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is considered to be due to its effect as an oxidant. Unfortunately, the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to the 99% EtOH solution of **2c** and **2d** resulted in decomposition reactions in the substrates. The use of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with **2c** and **2d**, however, obtained suitable $T_{1/2}$ values of 0.14–0.26 s (runs 6 and 7). These results imply that the leuco-dyes **2** have good chemical properties as near-IR colour formers by the use of appropriate metal oxidants. The efficient combination of the metallochromic property and the redox process for a quinonoid dye may afford a new molecular design for near-IR colour formers (see Fig. 1).

Experimental

M.p.s were measured on a Mitamura micromelting point apparatus and are uncorrected. Absorption spectra were measured using a JASCO Ubest-30 spectrophotometer. ¹H NMR spectra were taken on a Hitachi R-90H spectrometer. Mass spectra were run on a Hitachi M-80A spectrometer and elemental analyses were obtained using a Perkin-Elmer 240 C, H, N, analyser. The stopped-flow data were obtained on a Photal (Otsuka Electronics) stopped-flow spectrophotometer Model RA-401 by mixing equal volumes of 99% EtOH solutions of leuco-dyes and metal salts.

Materials.—The dyes **1a** and **1b**, 5-(4-dimethylaminophenyl-imino)quinolin-8(5*H*)-ones,^{4a} and **1c** and **1d**, 5-(4-dialkylamino-phenylimino)-5*H*-pyrido[2,3-*a*]phenothiazines,^{4b} were synthesized by the method described previously. Metal salts were reagent grade and used without further purification.

General Procedure for Obtaining Leuco-dyes 2.—To a 95% EtOH solution of **1** (200 cm³, 1.05 mmol) at 70 °C under N₂ was added aqueous Na₂S₂O₄ (20 cm³, 3.14 mmol) and NaOH (5.23 mmol). The mixture was stirred at 70 °C for 1 min and then brought to pH 4 with AcOH (2 cm³). The resulting solution was poured into water (500 cm³) and then neutralized with NaHCO₃. The precipitate was filtered off, dried *in vacuo* and purified by column chromatography on silica gel (Wacogel C-300) using acetone-CHCl₃ as eluent under N₂. The products were recrystallized from tetrahydrofuran-hexane (for **2a**, **b**) or CHCl₃-hexane (for **2c**, **d**).

5-(4-Dimethylaminoanilino)quinolin-8-ol **2a** (yield 77%) had m.p. 174–176 °C; δ_H(CDCl₃ and [2H₆]Me₂SO) 2.85 (6 H, s), 6.35–6.48 (1 H, br d), 6.68 (2 H, d, *J* 9.2), 6.69–6.83 (1 H, m), 6.83 (2 H, d, *J* 9.2), 7.02 (1 H, d, *J* 8.1), 7.12 (1 H, d, *J* 8.1), 7.39 (1 H, dd, *J* 8.6, 4.2), 8.46 (1 H, dd, *J* 8.6, 1.5) and 8.79 (1 H, dd, *J* 4.2, 1.5); *m/z* 279 (M⁺) and 264 (M⁺ – 15) (Found: C, 72.7; H, 6.2; N, 14.8. C₁₇H₁₇N₃O requires C, 73.1; H, 6.1; N, 15.0%).

7-Chloro-5-(4-dimethylaminoanilino)quinolin-8-ol **2b** (yield 72%) had m.p. 182–184 °C; δ_H(CDCl₃ and [2H₆]Me₂SO) 2.90 (6 H, s), 6.73 (2 H, d, *J* 8.8), 6.87–7.08 (2 H, m), 6.97 (2 H, d, *J* 9.0), 6.99 (1 H, s), 7.41 (1 H, dd, *J* 8.6, 4.2), 8.55 (1 H, dd, *J* 8.6, 1.3) and 8.81 (1 H, dd, *J* 4.2, 1.3); *m/z* 313 (M⁺) and 298 (M⁺ – 15) (Found: C, 64.5; H, 5.1; N, 13.0. C₁₇H₁₆ClN₃O requires C, 65.1; H, 5.1; N, 13.4%).

5-(4-Dimethylaminoanilino)pyrido[2,3-*a*]phenothiazine **2c** (yield 65%) had m.p. 209–212 °C; δ_H(CDCl₃) 2.90 (6 H, s), 5.11–5.50 (1 H, br d), 6.60–7.10 (9 H, m), 7.13–7.40 (1 H, m), 7.70–7.97 (1 H, br d), 8.21 (1 H, dd, *J* 8.6, 1.5) and 8.72 (1 H, dd, *J* 4.2, 1.5); *m/z* 386 (M⁺ + 2) and 384 (M⁺) (Found: C, 71.8; H, 5.2; N, 14.5. C₂₃H₂₀N₄S requires C, 71.85; H, 5.2; N, 14.6%).

5-(4-Diethylamino-2-methylamino)pyrido[2,3-*a*]phenothiazine **2d** (yield 69%) had m.p. 196–198.5 °C; δ_D(CDCl₃) 1.16 (6 H, t), 2.20 (3 H, s), 3.32 (4 H, q), 5.03–5.33 (1 H, br d), 6.37 (1 H, s), 6.40–7.00 (7 H, m), 7.27 (1 H, dd, *J* 8.35, 4.2), 7.62–7.85 (1 H, br d), 8.21 (1 H, dd, *J* 8.5, 1.4) and 8.73 (1 H, dd, *J* 4.2, 1.5); *m/z* 428 (M⁺ + 2), 426 (M⁺) and 411 (M⁺ – 15) (Found: C, 73.15; H, 6.2; N, 12.9. C₂₆H₂₆N₄S requires C, 73.2; H, 6.1; N, 13.1%).

Acknowledgements

Y. K. acknowledges helpful discussions with Associated Prof. K. Yoshida of Kochi University, and Messrs. H. Yasuoka and S. Hamaguchi for their assistance with this work. Y. K. also thanks the Research Centre Mitsubishi Kasei Corporation, for mass and elemental analyses.

References

- 1 Preliminary accounts: (a) Y. Kubo, H. Yasuoka and K. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1990, 1253; (b) Y. Kubo, H. Yasuoka, S. Hamaguchi and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1992, 411.
- 2 T. Iketani, *Tokushu-Kinou-Shikiso*, ed. T. Ikemori and M. Sumitani, CMC, Tokyo, 1986, pp. 138–162.
- 3 M. Matsuoka, Y. Kubo and T. Kitao, *J. Soc. Dyers Colour*, 1987, **103**, 167.
- 4 (a) Y. Kubo, K. Sasaki, H. Kataoka and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1469; (b) Y. Kubo, H. Kataoka, M. Ikezawa and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1990, 585.
- 5 Y. Sato, *J. Jpn. Soc. Colour Mater.*, 1988, **61**, 292.
- 6 K. Yoshida, N. Oga, M. Kadota, Y. Ogasawara and Y. Kubo, *J. Chem. Soc., Chem. Commun.*, 1992, 1114. Some naphthoquinone methide-type near-IR colour formers have also been synthesized; Y. Kubo, K. Kotani and K. Yoshida, *Chem. Lett.*, 1992, 1663.
- 7 K. Ueno, *Numon Chelate Kagaku*, Nankodo, Tokyo, 1969, pp. 56.

Paper 4/00531G

Received 28th January 1994

Accepted 8th March 1994