

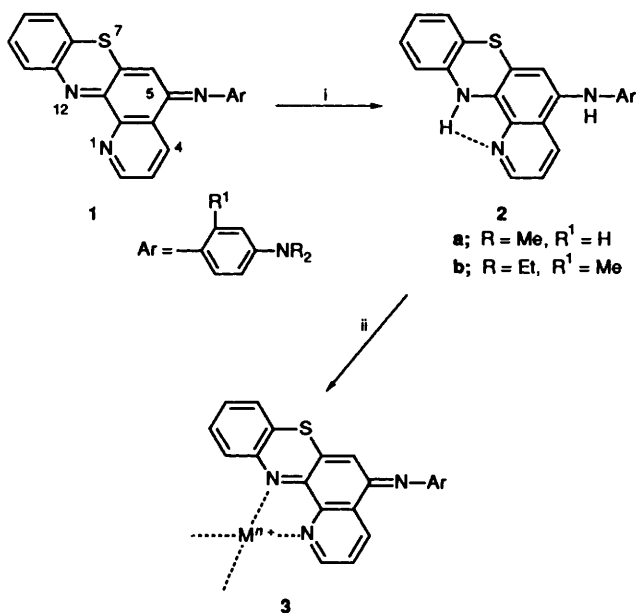
Syntheses of Pyrido[2,3-*a*]phenothiazine-type Near-IR Colour Formers

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New pyrido[2,3-*a*]phenothiazine-type near-IR colour formers† have been synthesized, 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.

Near-IR colour formers are of considerable interest as heat- and pressure-sensitive dyes with electro-optical applications utilizing diode-laser technology.¹ To date, triphenylmethane lactone-type near-IR colour formers† are the best known compounds in this field. The use of leuco-quinones as near-IR colour formers has been little studied because of the instability of leuco-quinonoid dyes. However, recently, we found that 5-(4-dimethylaminophenylimino)quinolin-8(5*H*)-ones give rise to stable leuco-dyes and that these produced intense absorption in the near-IR region, in the presence of metal salts, as a result of metal chelate complexation–oxidation.² In furtherance, of our interest in other types of stabilized leuco-dyes, we have synthesized the title compounds and investigated their colour development in the presence of metal ion by the stopped-flow technique.



Scheme 1 Reagents: i, Na₂S₂O₄; ii, metal salt, EtOH

Reduction of 5-(4-dialkylaminophenylimino)-5*H*-pyrido[2,3-*a*]phenothiazines, **1**³ with Na₂S₂O₄ under alkaline conditions at 70 °C produced the leuco-dyes **2** (65–69% yield) (see Scheme 1) as stable compounds, the absorption spectra of which show weak absorption at 454–459 nm in 99% EtOH. The stability of **2** might be due to an intramolecular hydrogen bond between the 12-NH proton and the 1-nitrogen of the phenothiazine ring.

As shown in Fig. 1(a), addition of 10 equiv. of Cu(ClO₄)₂·6H₂O to a 99% EtOH solution of **2a** immediately produced new absorption at ca. 800 nm, the character of which was consistent with the presence of a Cu^{II}·**2a** complex, **3**, formed

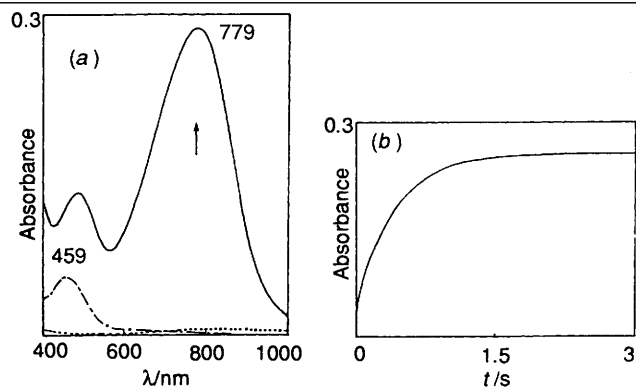


Fig. 1 (a) Spectral changes upon additions of Cu(ClO₄)₂·6H₂O (1.5 × 10⁻⁴ mol dm⁻³) to 99% EtOH solution of **2a** (1.5 × 10⁻⁵ mol dm⁻³): **2a** (---); **3a** (—); Cu(ClO₄)₂·6H₂O (----). (b) Formation of Cu^{II}·**2a** complex dye in 99% EtOH at 25 °C; plot of absorbance at 800 nm vs. time; [Cu(ClO₄)₂·6H₂O]/[**2a**] = 10, [**2a**] = 1.5 × 10⁻⁵ mol dm⁻³.

by oxidation of **2a** on metal chelation. It is of great value that the intense absorption band is formed very rapidly, a property which was investigated using the stopped-flow technique. Fig. 1(b) shows the time dependence of the increase in absorbance at 800 nm observed when a 3.0 × 10⁻⁵ mol dm⁻³ solution of **2a** in 99% EtOH was mixed with a 3.0 × 10⁻⁴ mol dm⁻³ solution of Cu(ClO₄)₂·6H₂O in 99% EtOH (1:1 v/v; final concentration of **2a** is 1.5 × 10⁻⁵ mol dm⁻³). After ca. 1.5 s, the final stable absorbance at 800 nm was observed. Similar colour development was also observed in the formation of **3b**. In order to estimate the apparent rate of colour development, we used the half-value period ($T_{1/2}$: time for $A/A_{\infty} = 0.5$; A is absorbance of **3** at 800 nm). In the presence of 10 equiv. of Cu(ClO₄)₂·6H₂O, $T_{1/2}$ values of 0.255–0.26 s were obtained (see Table 1, run 1 and 2). The $T_{1/2}$ value decreases with an increase in the amount of Cu(ClO₄)₂·6H₂O. The use of 100 equiv. of Cu(ClO₄)₂·6H₂O gave a $T_{1/2}$ value of 0.14 s, whose value is equal to 28% of that of the corresponding indoaniline-type near-IR colour former² (runs 3 and 4), suggesting that the colour development of **2** in the presence of Cu^{II} ion might be excellent. From these results, the target molecule **2** could have potential for use as a suitable near-IR colour former. Now, this characteristic in the presence of other metal salts is under investigation.

Experimental

M.p.s were measured on a Mitamuraiken 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 240C C, H, N, analyser. The stopped-flow data were obtained on a Photal (Otsuka Electronics) stopped-flow spectrophotometer

† Colourless compounds which can be rendered coloured by simple acid–base and/or oxidation processes.

Table 1 Half value period for colour development in 99% EtOH at 25 °C^a

Run	Leuco-dye ^b	Complex dye 3 λ_{\max}/nm	$T_{1/2}/\text{s}^c$
1	2a ^d	779	0.255
2	2b ^e	834	0.26
3 ^f	2a	779	0.14
4 ^f	4	724	0.50 ^g

^a In the presence of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($1.5 \times 10^{-4} \text{ mol dm}^{-3}$). ^b [Leuco-dye] = $1.5 \times 10^{-5} \text{ mol dm}^{-3}$. ^c Time for $A/A_x = 0.5$; A is absorbance of **3** at 800 nm. ^d $\lambda_{\max}(99\% \text{ EtOH})/\text{nm}$ 459; $\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 3700. ^e $\lambda_{\max}(99\% \text{ EtOH})/\text{nm}$ 454; $\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 3000. ^f [$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$] = $1.5 \times 10^{-3} \text{ mol dm}^{-3}$. ^g A is absorbance of 5-(*p*-dimethylaminoanilino)quinolin-8-ol **4** at 724 nm.

Model RA-401 by mixing equal volumes of 99% EtOH solutions of leuco-dyes and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Materials.—The dyes **1**, 5-(4-dialkylaminophenylimino)-5*H*-pyrido[2,3-*a*]phenothiazines, were synthesized by the method described previously.³ $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was reagent grade and used without further purification.

General Procedure for Obtaining Leuco-dyes 2.—To a 95% EtOH solution (200 cm³) of **1** (1.05 mmol) at 70 °C under N₂ was added an aqueous solution (20 cm³) of Na₂S₂O₄ (3.14 mmol) and NaOH (5.23 mmol). The mixture was stirred at 70 °C for 1 min and then brought to pH 4 using AcOH (2 cm³). The resulting solution was poured into water (500 cm³) and then neutralized with NaHCO₃. The precipitate was collected, dried *in vacuo* and purified by column chromatography on silica

gel (Wacogel C-300) using acetone-CHCl₃ (1 : 25) as eluent under N₂. The products were recrystallized from CHCl₃-hexane (**2a**, 65% yield; **2b**, 69% yield).

5-(4-Dimethylaminoanilino)pyrido[2,3-*a*]phenothiazine **2a** had m.p. 209–212 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 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-methylanilino)pyrido[2,3-*a*]phenothiazine **2b** had m.p. 196–198.5 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.16 (6 H, t), 2.20 (3 H, s), 3.32 (4 H, q), 5.03–5.33 (1 H, br d), 6.365 (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

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