New Indoaniline-type Near-infrared Colour Former

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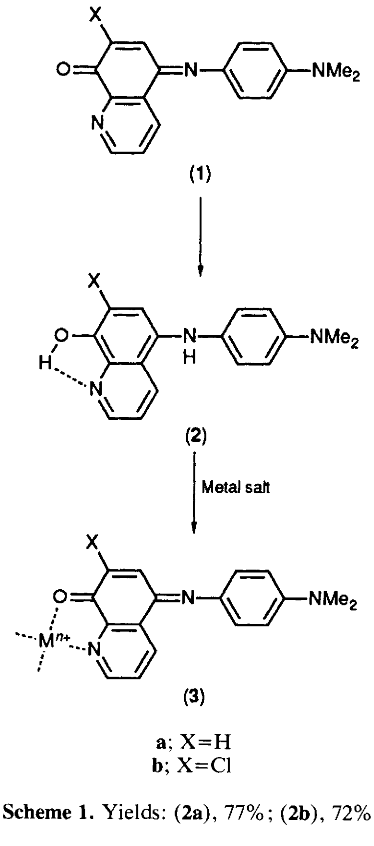
New indoaniline-type near-IR colour formers were prepared as stable compounds, producing intense absorption bands immediately in the near-IR region on metal chelate complexation–oxidation, the spectral characteristics of which were investigated by using the stopped-flow technique.

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 lactones[1] and leuco-quinones[2] 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, the use of leuco-quinones in colour-former recording media has not been studied extensively because of the instability of leuco-quinonoid dyes.

We found previously that the *N,O*-bidentate indoaniline-type ligand, 5-(4-dimethylaminophenylimino)quinolin-8-(5*H*)-one (**1a**),[3] readily forms complexes with metal ions, and this complexation causes a large bathochromic shift of the absorption bands with an increase in molecular extinction coefficients. These metal complex dyes have intense absorption bands in the near-IR region. Hence, the incorporation of the metal chelate complexation into the redox process of the dyes (**1**) is of particular interest for developing new near-IR colour-former systems. Leuco-dyes having such spectral properties are of great value currently as heat- and pressure-sensitive functional dyes in electro-optical applications utilizing diode-laser technology.[4] However, quinone-type near-IR colour formers are as yet unknown.



a; X=H
b; X=Cl

Scheme 1. Yields: (**2a**), 77%; (**2b**), 72%.

In this paper, we report the syntheses of indoaniline-type near-IR colour formers. Colour development in the presence of metal ions was investigated by using the stopped-flow technique.

Reduction of (**1**) with $Na_2S_2O_4$ in alkaline conditions gave the leuco-dyes (**2**)† in 72—77% yield, which have weak absorption maxima at 403 nm in 99% EtOH and are colourless. Interestingly, the leuco-dyes (**2**) could be isolated as stable compounds. Since the leuco-dye of 4-(4-diethylamino-2-methylphenylimino)naphthalen-1(4*H*)-one is unstable and reoxidized immediately, the stability of the leuco-dyes (**2**) may be attributed to an intramolecular hydrogen bond between the 1-nitrogen atom and 8-hydroxy group. With the aim of developing a new colour-former system, we investigated the oxidation behaviour of (**2**) in the presence of metal ions. Figure 1 shows spectral changes upon addition of $Cu(ClO_4)_2 \cdot 6H_2O$ to a solution of (**2a**) in 99% EtOH. Addition of $Cu(ClO_4)_2 \cdot 6H_2O$ 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,[3] suggesting that the oxidation of the leuco-dye (**2a**) accompanying metal chelate complexation produced (**3**). From the functional colour-formers 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 by using the stopped-flow technique. Figure 2 shows the time dependence of the increase in absorbance at 724 nm observed when a 3.0×10^{-5} mol dm^{-3} solution of (**2a**) in 99% EtOH was mixed with a 3.0×10^{-3} mol dm^{-3} solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in 99% EtOH [1 : 1 v/v; final concentration of (**2a**) 1.5×10^{-5} mol dm^{-3}]. After *ca.* 2 s the final stable absorbance at 724 nm was observed. Similar colour development was also observed in the formation of other chelate complexes (**3**) (Table 1). In order to estimate the

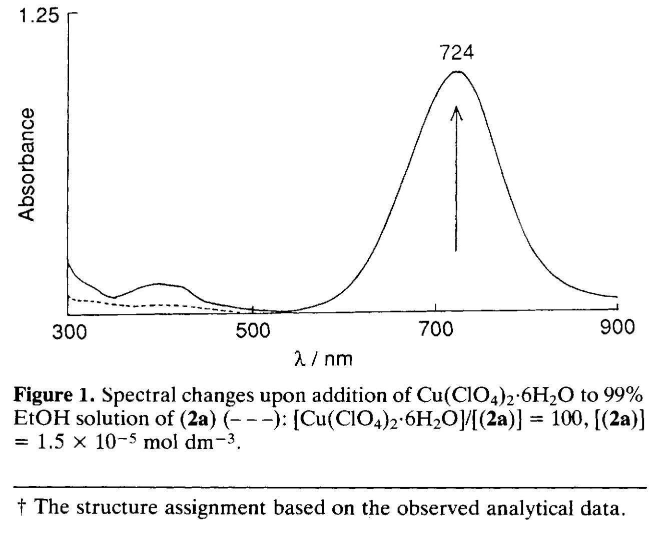


Figure 1. Spectral changes upon addition of $Cu(ClO_4)_2 \cdot 6H_2O$ to 99% EtOH solution of (**2a**) (– – –): $[Cu(ClO_4)_2 \cdot 6H_2O]/[(\mathbf{2a})] = 100$, $[(\mathbf{2a})] = 1.5 \times 10^{-5}$ mol dm^{-3}.

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† The structure assignment based on the observed analytical data.

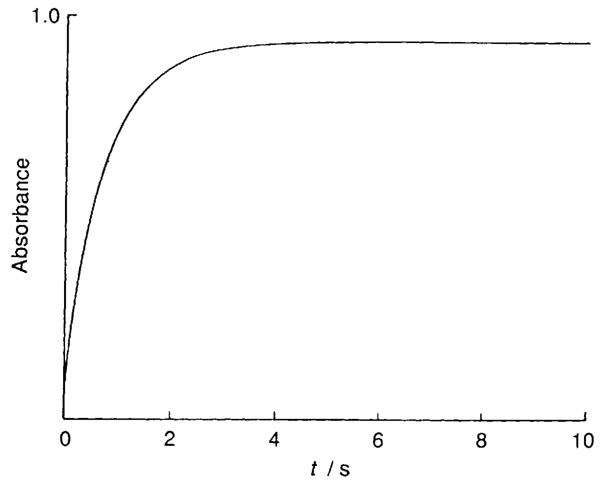

Figure 2. Formation of Cu^{II}—(**1a**) complex in 99% EtOH at 25 °C: plot of the absorbance at 724 nm *vs.* time; [$Cu(ClO_4)_2 \cdot 6H_2O$]/[(**2a**)] = 100, [(**2a**)] = 1.5×10^{-5} mol dm^{-3}.

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

Run	Leuco-dye[a]	Metal salt[b]	Complex dye (**3**), λ_{max}/nm	$T_{1/2}$/s^{1} [c]
1	(**2a**)[d]	$Cu(ClO_4)_2 \cdot 6H_2O$	724	0.50
2	(**2a**)	$FeCl_3 \cdot 6H_2O$	750	0.060
3	(**2a**)	$Fe(ClO_4)_3 \cdot 6H_2O$	734	0.58
4	(**2a**)	$Ni(ClO_4)_2 \cdot 6H_2O$	727	13 000
5	(**2b**)[e]	$FeCl_3 \cdot 6H_2O$	745	0.054

[a] [Leuco-dye] = 1.5×10^{-5} mol dm^{-3}. [b] [Metal salt] = 1.5×10^{-3} mol dm^{-3}. [c] Time for $A/A_\infty = 0.5$; A is the absorbance at λ_{max} of (**3**). [d] λ_{max} (99% EtOH) = 403 nm; ε_{max} = 2800. [e] λ_{max} (99% EtOH) = 403 nm; ε_{max} = 3500.

apparent rate of colour development, we used the half-value period [$T_{1/2}$: time for $A/A_\infty = 0.5$; A is the absorbance at λ_{max} of complexes (**3**)]. As shown in Table 1, $T_{1/2}$ decreases in the order: $Ni(ClO_4)_2 \cdot 6H_2O \gg Fe(ClO_4)_3 \cdot 6H_2O > Cu(ClO_4)_2 \cdot 6H_2O > FeCl_3 \cdot 6H_2O$ (runs 1—4). In the case of $FeCl_3 \cdot 6H_2O$, $T_{1/2}$ values of 0.054—0·060 s were obtained (runs 2 and 5). The activity of $FeCl_3 \cdot 6H_2O$ is considered to be due to its effect as an oxidant. These results imply that the leuco-dyes (**2**) have good chemical properties as near-IR colour formers by the use of appropriate metal salts having oxidation properties.

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