Syntheses and Properties of Pyridocarbazole Quinonoid-type Near-infrared Colour Formers

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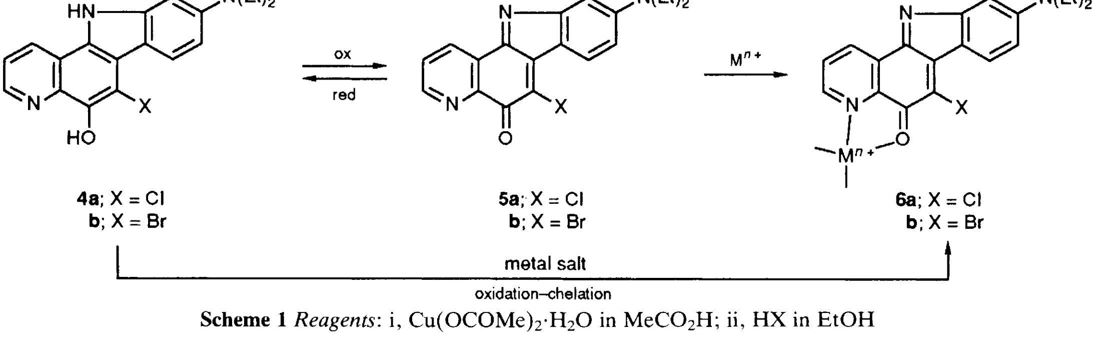
New pyridocarbazole quinonoid-type colour formers that can immediately produce intense absorption bands in the near-IR region on simultaneous metal chelate complexation-oxidation processes are synthesised.

Near-IR colour formers attract considerable attention because of their applications in information recording systems utilizing diode-laser technology. Recently, we have developed new near-IR colour formers that can produce intense absorption bands in the near-IR region immediately on metal chelate complexation–oxidation processes.[1,2] In this paper we further report the syntheses and spectroscopic properties of another new type of stabilized leuco-dyes that become coloured by similar processes.

The reaction of 5,8-quinolinedione **1** with *m*-acetylamino-*N*,*N*-diethylaniline **2** in acetic acid in the presence of copper(II) acetate at 30 °C gave the 6-arylated product **3** in 68%



Scheme 1 *Reagents*: i, $Cu(OCOMe)_2{\cdot}H_2O$ in $MeCO_2H$; ii, HX in EtOH

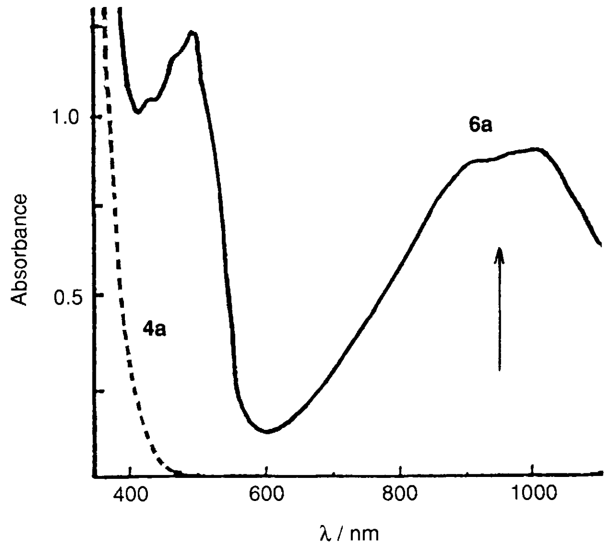


Fig. 1 Spectral changes upon addition of $FeCl_3 \cdot 6H_2O$ to MeCN solution of **4a** (– – –): $[FeCl_3 \cdot 6H_2O]/[\mathbf{4a}] = 10.0$, $[\mathbf{4a}] = 1.0 \times 10^{-4}$ mol dm^{-3}

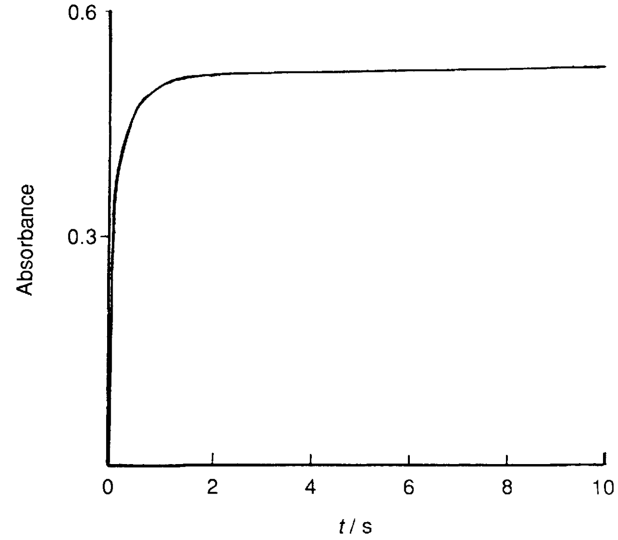


Fig. 3 Formation of Fe^{III}–**5a** complex **6a** in MeCN at 25 °C: plot of the absorbance at 800 nm *vs.* time; $[FeCl_3 \cdot 6H_2O]/[\mathbf{4a}] = 10.0$, $[\mathbf{4a}] = 1.0 \times 10^{-4}$ mol dm^{-3}.

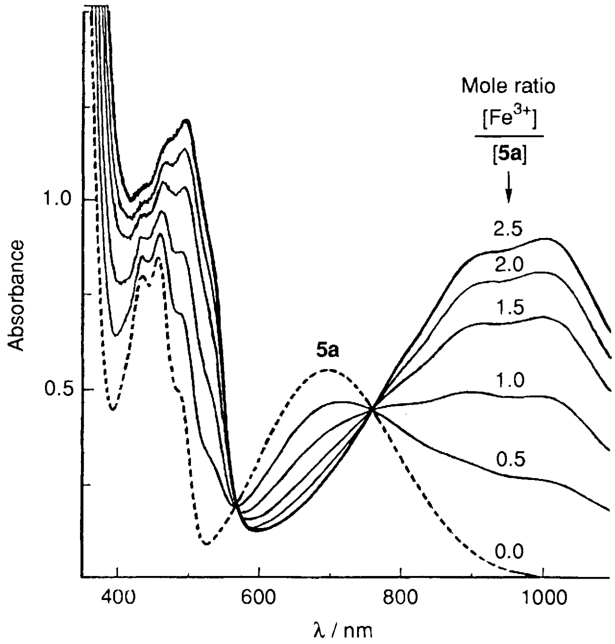


Fig. 2 Spectral changes upon addition of $FeCl_3 \cdot 6H_2O$ to MeCN solution of **5a** (– – –): $[\mathbf{5a}] = 1.0 \times 10^{-4}$ mol dm^{-3}

yield. Hydrolysis of **3** with HX (HCl or HBr) in 99% ethanol under argon resulted in intramolecular cyclization to give the leuco-dyes, 5-chloro (or bromo)-2-diethylamino-6-hydroxy-11*H*-pyrido[3,2-*a*] carbazole **4**[†] (**4a**: λ_{max} 353 nm, **4b**: λ_{max} 341 nm in MeCN), in 90–94% yield. Compounds **4** were stable enough to be purified by column chromatography under an air atmosphere and showed no absorption bands in the visible region (see Fig. 1). Treatment of **4** with oxidants such as PbO_2, $NaIO_4$, or chloranil in organic solvents gave quantitatively the pyridocarbazole quinonoid dyes, 2-diethylamino-5-chloro (or bromo)-pyrido[3,2-*a*]carbazole-6-one **5**,[†] which are green and have two absorption bands in the visible region [**5a**: 435 nm (ε_{max} 8080) and 693 nm (ε_{max} 5530), **5b**: 458 nm (ε_{max} 7560) and 696 nm (ε_{max} 4850) in MeCN]. The cyclic voltammograms for the reduction of **5** in dimethylformamide exhibited two reversible one-electron steps and were reproducible for multiplex scannings. Furthermore, the dyes **5** showed remarkable metallochromic behaviours: notable spectral changes were observed upon addition of various metal ions such as Cu^{II}, Ni^{II}, Co^{II}, Fe^{III} and Sn^{IV} *etc.* As a typical example, Fig. 2 shows the spectral changes observed upon addition of $FeCl_3 \cdot 6H_2O$ to a MeCN solution of **5a**, the formation of a Fe^{III}–**5a** chelate complex in which the 7-nitrogen atom and neighbouring 6-carbonyl group coordinate to the Fe^{III} ion was suggested.[3]

As $FeCl_3 \cdot 6H_2O$ is both an oxidizing and chelating agent, addition of $FeCl_3 \cdot 6H_2O$ to a MeCN solution of the leuco-dyes **4** was expected to produce new absorption bands in the near-IR region. In fact, as shown in Fig. 1, the absorption spectrum (λ_{max} *ca.* 1000 nm), which is almost consistent with that of the [Fe^{III}–**5a**] complex **6a**, was immediately produced when a ten mol ratio of $FeCl_3 \cdot 6H_2O$ was added to the MeCN solution of **4a**, which suggests that both oxidation and chelation processes proceeded almost simultaneously. It is of great value that the intense absorption bands are formed immediately in the near-IR region. Therefore, the apparent rate of colour development was examined by using the stopped-flow technique.[1,2] Fig. 3 shows the time dependence of the increase in absorbance at 800 nm observed when a 2.0×10^{-4} mol dm^{-3} solution of **4a** in MeCN was mixed with a 2.0×10^{-3} mol dm^{-3} solution of $FeCl_3 \cdot 6H_2O$ in MeCN (1:1 v/v; final concentration of **4a** is 1.0×10^{-4} mol dm^{-3}). After *ca.* 1.5 s, the final stable absorbance was observed. These results imply that the leuco-dyes **4** have potential for use as visible or near-IR colour formers by choosing appropriate oxidizing agents.

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References

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2 Y. Kubo, H. Yasuoka, S. Hamaguchi and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1992, 411.
3 We have previously observed similar spectral changes in the metal chelate complexation of some quinonoid dyes with various metal salts in organic solvents: K. Yoshida, O. Miyatake, J. Okamoto, H. Tokuda and Y. Kubo, *Chem. Lett.*, 1991, 2027 and previous papers.

[†] The new compounds **4** and **5** were characterized by mass and ^1H and ^{13}C NMR spectra and by elemental analyses.