

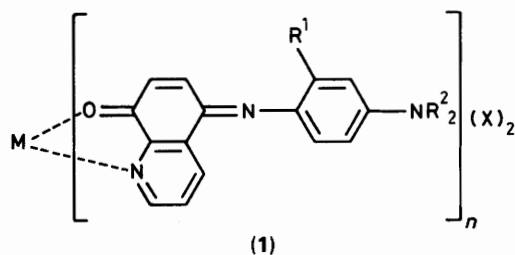
New Near-infrared absorbing Metal Complex Dyes with Heterocyclic Phenyliminoquinone-type Ligands

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N,N-Bidentate pyrido[2,3-*a*]phenothiazine (or phenoxazine)-type ligands have been prepared. Formation of metal complexes causes a large bathochromic shift of the absorption bands and an increase in the molar extinction coefficient. The metal complex dyes have absorption bands in the near-infrared region at 746–842 nm and were isolated as stable compounds. The reaction of 5-(4-dialkylaminophenylimino)-7-chloroquinolin-8(5*H*)-ones with *o*-phenylenediamine in acetic acid gave the corresponding leuco dyes.

In recent years, interest in near-infrared absorbing dyes which show absorption maxima beyond *ca.* 700 nm has been intense because of their many applications in such areas as diode-laser optical storage, laser printing, optical filters, *etc.* Only a few near IR absorbing metal complex dyes, such as metallo-phthalocyanines¹ and metal dithienes,² are known. We have found that the first absorption bands for some quinonoid derivatives have a large bathochromic shift with an increase in the molar extinction coefficient on metal chelate complexation. Using this phenomenon, we have synthesized new types of near-IR absorbing metal complex dyes containing quinonoid ligands.^{3–5} Particularly, some metal complex dyes (1) with



N,O-bidentate indoaniline-type ligands, 5-(4-dialkylamino-phenylimino)quinolin-8(5*H*)-ones,^{3,4} have intense absorption bands ($\epsilon_{\max} > 10^5$) in the near-IR region, and good physical and chemical properties for practical use in diode-laser optical storage.⁶ However, the colour–structure relationships for these chromophoric systems have not been clarified yet and are under investigation. For further progress, it is important to synthesize related metal complex dyes.

We have recently reported the preparation of another type of *N,N*-bidentate heterocyclic phenyliminoquinone-type ligand, the 5-(4-dialkylaminophenylimino)-5*H*-pyrido[2,3-*a*]phenothiazines (2*a*) and (2*b*), which can easily form complexes with nickel (II) ions. The resulting nickel(II) complex dyes were found to absorb near-IR light at 782–838 nm.

We now report metal complex dyes with *N,N*-bidentate heterocyclic ligands (2), and discuss their absorption properties.

Results and Discussion

Preparation of *N,N*-Bidentate Heterocyclic Phenyliminoquinone-type Ligands (2).—The ligands (2) were prepared from the iminoquinolinones (3) as shown in the Scheme. Ring-closure of (3) with 2-aminobenzenethiol (4*a*) (2 equiv.) in the presence of KOH under reflux for 10 min gave the pyrido[2,3-

Table 1. Light absorption properties of dyes (2), (5), and (6).

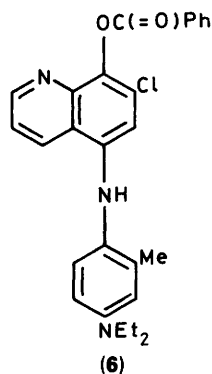
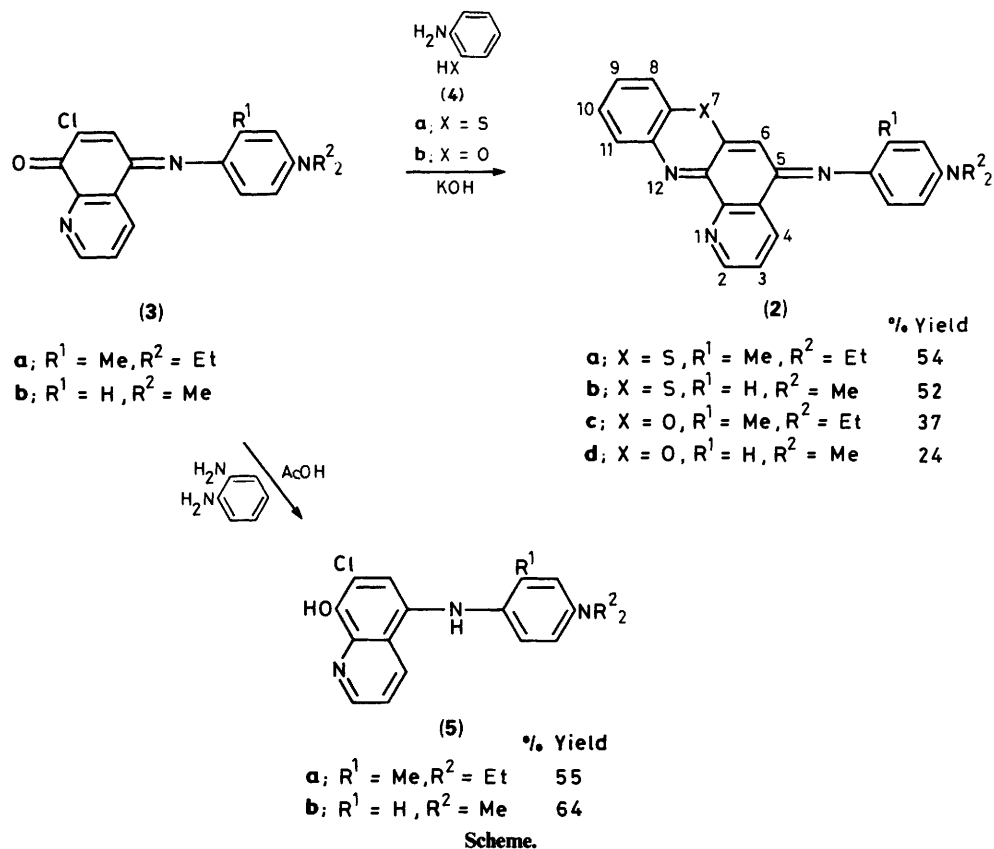
Dye	λ_{\max}/nm	$(\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})^a$
(2 <i>a</i>)	648	(11 200)
(2 <i>b</i>)	613	(10 400)
(2 <i>c</i>)	634	(8 140)
(2 <i>d</i>)	601	(6 670)
(5 <i>a</i>)	398	(3 300) ^b
(5 <i>b</i>)	404	(2 830) ^b
(6)	364	(5 950)

^a Measured in CHCl_3 . ^b Measured in EtOH.

a]phenothiazines (2*a*) and (2*b*) in 54 and 52% yields, respectively. On the other hand, the reaction of (3) with *o*-aminophenol gave the pyrido[2,3-*a*]phenoxazines (2*c*) and (2*d*) in low yield together with many by-products. The low nucleophilicity of 2-aminophenolate may account for this decrease in ring-closure reactivity. Ligands (2) containing the powerful electron-donating aniline ring and the phenothiazine (phenoxazine) group are new chromophoric systems, and showed λ_{\max} at 601–648 nm in chloroform (see Table 1). The absorption maxima of phenothiazines (2*a*) and (2*b*) were at slightly longer wavelengths (by 12–14 nm) than those of the phenoxazines (2*c*) and (2*d*). These results suggested that the electron-accepting power of the quinonoid moiety depended upon the electron-donating ability of the heteroatom in the ring fused to the quinonoid moiety.

In order to prepare the related phenazine derivatives, we examined the reaction of (3) with *o*-phenylenediamine. No ring-closure compound was obtained under various conditions. However, the reduction of (3) proceeded in the presence of *o*-phenylenediamine in acetic acid to give 7-chloro-5-(4-dialkylaminoanilino)-8-hydroxyquinolines (5*a*), 55% yield, and (5*b*), 64% yield, which have absorption maxima at 398 nm (ϵ_{\max} 3 300) and 404 nm (ϵ_{\max} 2 830) in ethanol, respectively, and are colourless. The leuco structure was confirmed by preparation of the benzoate derivatives (6). Interestingly, the leuco dyes (5) were stable in the solid state in air, and were gradually oxidized to the coloured form in solution. The spectral characteristics of these leuco dyes are under investigation with a view to the development of a suitable dye for use in heat- and pressure-sensitive applications.

Effect of Metal Ions on the Absorption Spectra of the Ligands (2).—The ligands (2) easily form chelate complexes in which the metal ion binds primarily to the pyridine moiety and N(12), and



the absorption spectra of the complexes show a large bathochromic shift with an increase in molar extinction coefficient compared with the free ligands. For example, Figure 1 shows the spectral change for complex formation of (2a) with Ni(ClO₄)₂·6H₂O in 99% ethanol. Addition of Ni(ClO₄)₂·6H₂O resulted in a decrease in the absorption maximum at 654 nm of (2a) and the growth of a new absorption band in the near-IR region. Isosbestic points were observed at 555 and 700 nm. At a molar ratio of [Ni^{II}]/[(2a)] = 0.6, the absorption maximum at 654 nm disappeared, while a new absorption band at 838 nm was observed [curve (e)]. The continuous variation method indicated the formation of a 1:2 Ni^{II}-(2a) complex. On further addition of Ni(ClO₄)₂·6H₂O {[Ni^{II}]/[(2a)] > 0.6} to this system, the absorption band at 838 nm underwent a slightly hypsochromic shift (21 nm). This shift may be explained on the basis of a change in the co-ordination mode of the complex. Similar spectral changes were observed in complex formation of (2) with metal salts. Table 2 summarizes spectral data for the free ligands (2) and their complex dyes. On addition of aqueous

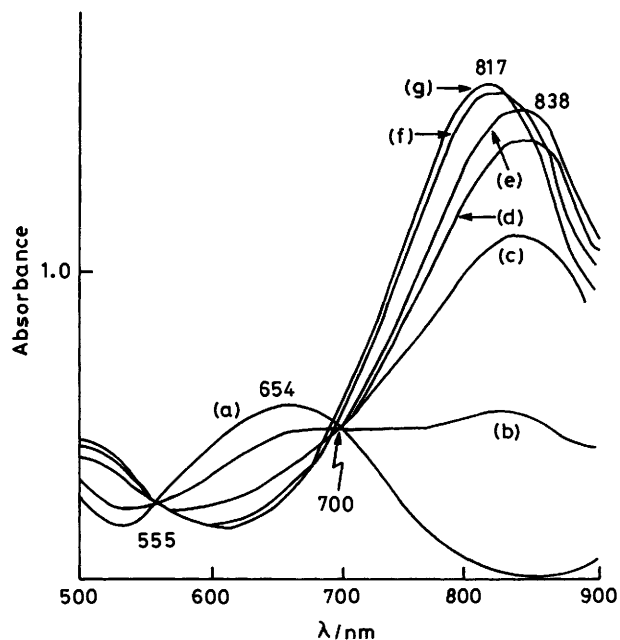


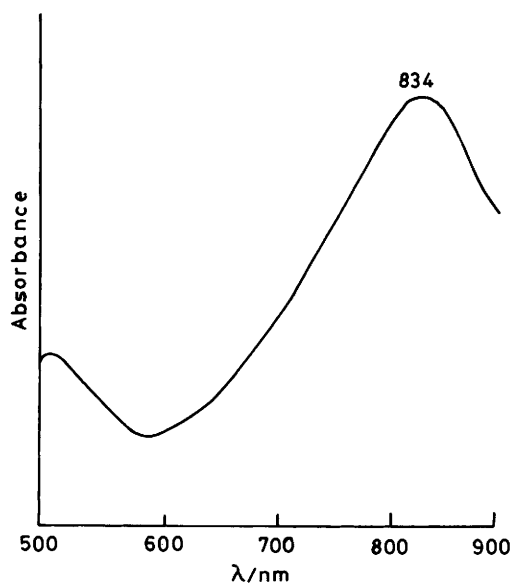
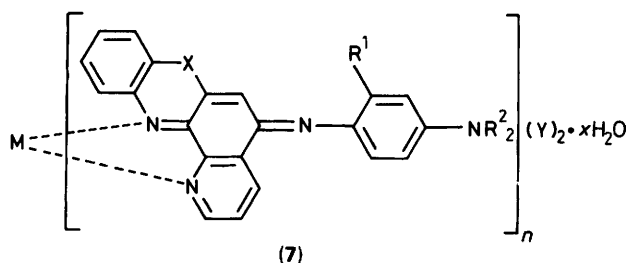
Figure 1. Spectral changes upon addition of Ni(ClO₄)₂·6H₂O to a solution of (2a) in 99% EtOH; [(2a)] = 5.0 × 10⁻⁵ mol dm⁻³. Molar ratio [Ni^{II}]/(2a): (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6; (f) 1.0; (g) 2.0.

Ni(BF₄)₂ to (2a) and (2b) in 99% EtOH solution, 1:1 Ni^{II}-(2a) and (2b) complexes were formed, suggesting that the metal-to-ligand ratio in the complex was affected by the counter-anion of metal ion. These metal complex dyes absorbed near-IR light at 746–842 nm. They showed a bathochromic shift (Δλ_{max}) of 146–188 nm in comparison with the free ligand, with the molar extinction coefficient being 1.8–4.9 times greater. The

Table 2. Spectral data for complex formation between various metal salts and (2) in 99% EtOH.

	Free ligand		λ_{\max}/nm (ϵ_{\max}) ^b	M:L ^c	$\Delta\lambda$ ^d	Re ^e
	λ_{\max}/nm (ϵ_{\max})	Metal salt (mol) ^a				
(2a)	654 (11 100)	Ni(ClO ₄) ₂ ·6H ₂ O (0.6)	838 (54 400)	1:2	184	4.9
(2a)	654 (11 100)	Cu(ClO ₄) ₂ ·6H ₂ O (0.6)	842 (50 400)	1:2	188	4.5
(2a)	654 (11 100)	Ni(BF ₄) ₂ (aq.) (1.0)	828 (23 500)	1:1	174	2.1
(2b)	616 (10 800)	Ni(ClO ₄) ₂ ·6H ₂ O (0.6)	782 (43 600)	1:2	166	4.0
(2b)	616 (10 800)	Cu(ClO ₄) ₂ ·6H ₂ O (0.6)	794 (43 800)	1:2	178	4.1
(2b)	616 (10 800)	Ni(BF ₄) ₂ (aq.) (1.0)	783 (19 400)	1:1	167	1.8
(2c)	646 (10 600) ^f	Ni(ClO ₄) ₂ ·6H ₂ O (0.6)	797 (38 900) ^f	1:2	151	3.7
(2d)	600 (7 860) ^f	Ni(ClO ₄) ₂ ·6H ₂ O (0.5–2.0)	746 ^f	— ^g	146	—

^a Molar ratio, [metal ion]/[free ligand]. ^b Determined by spectral changes upon addition of metal salts. ^c Determined by continuous variation methods. ^d $\Delta\lambda_{\max} = \lambda_{\max}(\text{complex}) - \lambda_{\max}(\text{free ligand})$. ^e $Re = \epsilon_{\max}(\text{complex})/\epsilon_{\max}(\text{free ligand})$. ^f In 17% (v/v) dimethylformamide–chloroform. ^g Unable to be determined owing to broadness of curve.

**Figure 2.** Absorption spectrum of the isolated [Ni(2a)₂](ClO₄)₂ in 99% EtOH.

$\Delta\lambda_{\max}$ value depended upon the absorption properties of the free ligands (2) and nature of metal salts; in particular, it increased with the increase in the electron-donating strength of the aniline ring of the free ligands (2). The first absorption band of (2) is due to a $\pi-\pi^*$ transition. Therefore, the absorption properties of these metal complex dyes are considered to be dependent upon intramolecular charge transfer, corresponding to a migration of electron density from the aniline ring to the di-imine segment including the metal ion.

Isolation of Metal Complex Dyes.—The metal complex dyes were prepared as follows: the reaction of (2a) with Ni-

(ClO₄)₂·6H₂O (2.5 equiv.) in ethanol–water under nitrogen gave the *N,N*-bidentate Ni^{II} complex dye bis{5-(4-diethylamino-2-methylphenylimino)-5*H*-pyrido[2,3-*a*]phenothiazine}nickel(II) diperchlorate (7a) in 97% yield. As shown in Figure 2, the absorption spectrum of the isolated metal complex dye (7a) absorbed near-IR light at 834 nm, and was essentially in agreement with the spectral feature at [Ni^{II}]/[(2a)] = 0.6 in Figure 1. Similarly, other metal complex dyes (7b–h) were isolated. On the other hand, the reaction of the ligand with Ni(BF₄)₂ in ethanol–water solution produced a tar and isolation of the complex was unsuccessful. However, when the reaction was conducted in aqueous tetrahydrofuran [Ni (2a) and (2b)] (BF₄)₂·2H₂O were successfully isolated. These results and elemental analyses are in Table 3. Interestingly, the complexes (7c) and (7f) which were prepared from (2a) and (2b) with Cu(ClO₄)₂·6H₂O were found to consist of 1:3 Cu^{II}–(2a) and (2b) complexes in the solid state from their elemental analyses despite the indication that the corresponding 1:2 metal complexes were formed in solution. A similar result was also observed for (7g). In solution the complexes $M(L)^{2+} \rightleftharpoons M(L)_2^{2+} \rightleftharpoons M(L)_3^{2+}$ would be in equilibrium and the complex of lowest solubility would be precipitated. Consequently, in these cases $M(L)_3^{2+}$ was obtained exclusively. All the isolated metal complex dyes (7) have absorption bands in the near-IR region, and have potential as diode-laser optical storage media *etc.* In addition, the free ligands, which show a large bathochromic shift on complex formation, can be used as a metal ion indicator.

Experimental

M.p.s are uncorrected. Absorption spectra were measured using a Hitachi 220A 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.

Materials.—The dyes (3), 5-(4-dialkylaminophenylimino)-7-chloroquinolin-8(5*H*)-ones, were synthesized by the method described previously.⁴ 2-Aminobenzenethiol (4a), *o*-aminophenol (4b), *o*-phenylenediamine, and benzoyl chloride were reagent grade and were used without further purification. Ni(ClO₄)₂·6H₂O⁸ and Cu(ClO₄)₂·6H₂O⁹ were prepared by the literature methods. 40% aqueous Ni(BF₄)₂ was kindly supplied by Mitsubishi Kasei Corporation.

Preparation of Pyrido[2,3-*a*]phenothiazine-type Ligands (2a) and (2b).—To a solution of the iminoquinolinone (3a) or (3b)

Table 3. Elemental analyses for metal complexes (7).

	Complex dye						C (%)		H (%)		N (%)		
	M	X	R ¹	R ²	Y	n	x	Calc.	Found	Calc.	Found	Calc.	Found
(7a)	Ni	S	Me	Et	ClO ₄	2	0	56.4	57.4	4.4	4.5	10.1	10.25
(7b)	Ni	S	Me	Et	BF ₄	1	2	45.1	45.4	4.1	4.2	8.1	7.9
(7c)	Cu	S	Me	Et	ClO ₄	3	0	61.0	59.8	4.7	4.3	10.9	10.9
(7d)	Ni	S	H	Me	ClO ₄	2	0	54.0	55.8	3.55	3.7	11.0	11.2
(7e)	Ni	S	H	Me	BF ₄	1	2	42.45	42.6	3.4	3.4	8.6	8.5
(7f)	Cu	S	H	Me	ClO ₄	3	0	58.8	58.2	3.9	3.7	11.9	11.9
(7g)	Ni	O	Me	Et	ClO ₄	3	0	63.2	61.55	4.9	4.8	11.3	11.1
(7h)	Ni	O	H	Me	ClO ₄	— ^a	—	—	—	—	—	—	—

^a Unable to obtain the pure complex.

(2.83 mmol) in refluxing ethanol (200 ml) was added (**4a**) (5.66 mmol) and KOH (5.66 mmol) in ethanol (40 ml). The mixture was stirred under reflux for 10 min then poured into ice-water. The mixture was filtered, and the precipitate was washed with water, dried, and chromatographed on silica gel (Wakogel C-300) using ethyl acetate-benzene (1:1) as eluant. The products were recrystallized from benzene-n-hexane [(**2a**), 54% yield] or ethanol [(**2b**), 52% yield].

5-(4-Diethylamino-2-methylphenylimino)-5H-pyrido[2,3-a]-phenothiazine (**2a**) had m.p. 177–178 °C; λ_{\max} (CHCl₃) 648 nm (ϵ_{\max} 11 200 dm³ mol⁻¹ cm⁻¹); δ_{H} (CDCl₃) 1.20 (6 H, t), 2.28 (3 H, s), 3.38 (4 H, q), 6.56–6.80 (3 H, m), 6.96 (1 H, s), 7.11–7.32 (3 H, m), 7.55 (1 H, dd, *J* 4.5, 8.0 Hz), 7.90–8.00 (1 H, m), 8.94 (1 H, dd, *J* 1.8, 7.8 Hz), and 9.02 (1 H, dd, *J* 2.0, 4.4 Hz) (Found: C, 73.9; H, 5.8; N, 12.9%; *M*⁺ 424. C₂₆H₂₄N₄S requires C, 73.6; H, 5.7; N, 13.2%; *M*, 424).

5-(4-Dimethylaminophenylimino)-5H-pyrido[2,3-a]phenothiazine (**2b**) had m.p. 244–247 °C; λ_{\max} (CHCl₃) 613 nm (ϵ_{\max} 10 400 dm³ mol⁻¹ cm⁻¹); δ_{H} (CDCl₃) 3.00 (6 H, s), 6.78 (2 H, d, *J* 9.0 Hz), 6.975 (1 H, s), 6.98 (2 H, d, *J* 9.0 Hz), 7.10–7.33 (3 H, m), 7.55 (1 H, dd, *J* 4.6, 8.1 Hz), 7.91–8.01 (1 H, m), 8.89 (1 H, dd, *J* 1.8, 8.1 Hz), and 9.03 (1 H, dd, *J* 1.8, 4.5 Hz) (Found: C, 71.9; H, 4.6; N, 14.2%; *M*⁺ 382. C₂₃H₁₈N₄S requires C, 72.2; H, 4.7; N, 14.65%; *M*, 382).

Preparation of Pyrido[2,3-a]phenoxazine-type Ligands (2c) and (2d).—To a solution of the iminoquinolinone (**3a**) or (**3b**) (2.26 mmol) in ethanol (200 ml) at room temperature for (**3a**) and 70 °C for (**3b**) was added a solution of (**4b**) (22.6 mmol) and KOH (22.6 mmol) in ethanol (100 ml). The mixture was stirred for 3 h, then neutralized with acetic acid, evaporated to ca. one-third volume, and poured into ice-water (300 ml). The separated product (fraction A) was filtered off and dried *in vacuo*. The filtrate was extracted with chloroform and the extract (fraction B) concentrated *in vacuo*. Fractions A and B were combined and chromatographed on silica gel (Wakogel C-300) using acetone-chloroform (1:50) as eluant. The products (**2c**) and (**2d**) were recrystallized from benzene-n-hexane and were obtained in 37 and 24% yield, respectively.

5-(4-Diethylamino-2-methylphenylimino)-5H-pyrido[2,3-a]-phenoxazine (**2c**) had m.p. 221–222 °C; λ_{\max} (CHCl₃) 634 nm (ϵ_{\max} 8 140 dm³ mol⁻¹ cm⁻¹); δ_{H} (CDCl₃) 1.12 (6 H, t), 2.18 (3 H, s), 3.30 (4 H, q), 6.58 (1 H, s), 6.48–6.83 (3 H, m), 6.88–7.33 (3 H, m), 7.50 (1 H, dd, *J* 4.6, 8.1 Hz), 7.78 (1 H, dd, *J* 2.1, 7.1 Hz), and 8.87–9.12 (2 H, m); *m/z* 408 (*M*⁺) and 393 (*M*⁺ – 15) (Found: C, 76.2; H, 5.9; N, 13.6. C₂₆H₂₄N₄O requires C, 76.45; H, 5.9; N, 13.7%).

5-(4-Dimethylaminophenylimino)-5H-pyrido[2,3-a]phenoxazine (**2d**) had m.p. 264–265 °C; λ_{\max} (CHCl₃) 601 nm (ϵ_{\max} 6 670 dm³ mol⁻¹ cm⁻¹); δ_{H} (CF₃CO₂D) 3.61 (6 H, s), 7.37 (2 H, d, *J* 9.0 Hz), 7.65–8.58 (6 H, m), 8.61–8.93 (1 H, m), 9.53–9.77 (1 H,

m), and 9.90–10.19 (1 H, m); *m/z* 366 (*M*⁺) and 351 (*M*⁺ – 15) (Found: C, 75.9; H, 5.0; N, 14.7. C₂₃H₁₈N₄O requires: C, 75.4; H, 4.95; N, 15.3%).

Reaction of the Iminoquinolinones (3a) and (3b) with *o*-Phenylenediamine.—To a solution of (**3a**) or (**3b**) (0.57 mmol) in acetic acid (20 ml) at room temperature was added a solution of *o*-phenylenediamine (1.13 mmol) in acetic acid (10 ml). The mixture was stirred for 3 h at room temperature, then poured into water, and the solution neutralized. The products were filtered off, dried *in vacuo*, and chromatographed on silica gel (Wakogel C-300) using methylene chloride as eluant under nitrogen; (**5a**) and (**5b**) were obtained in 55 and 64% yield, respectively.

7-Chloro-5-(4-diethylamino-2-methylanilino)-8-hydroxyquinoline (**5a**) had m.p. 170.5–172 °C; λ_{\max} (EtOH) 398 nm (ϵ_{\max} 3 300 dm³ mol⁻¹ cm⁻¹); *m/z* 355 (*M*⁺) and 340 (*M*⁺ – 15) (Found: C, 67.3; H, 6.3; N, 11.6%. C₂₀H₂₂ClN₃O requires C, 67.5; H, 6.2; N, 11.8%).

7-Chloro-5-(4-dimethylaminoanilino)-8-hydroxyquinoline (**5b**) had m.p. 183–185 °C; λ_{\max} (EtOH) 404 nm (ϵ_{\max} 2 830 dm³ mol⁻¹ cm⁻¹); *m/z* 313 (*M*⁺) and 298 (*M*⁺ – 15) (Found: C, 65.2; H, 5.1; N, 13.4. C₁₇H₁₆ClN₃O requires C, 65.1; H, 5.1; N, 13.4%).

Preparation of 7-Chloro-5-(4-diethylamino-2-methylanilino)-8-quinolyl Benzoate (6).—To a solution of (**5a**) (0.5 mmol) in tetrahydrofuran (1 ml) at room temperature was added benzoyl chloride (0.64 mmol). The mixture was stirred for 4.5 h at 40 °C, then evaporated, washed with aqueous NaHCO₃, dried, and chromatographed on silica gel (Wakogel C-300) using methylene chloride as eluant to give (**6**) in 44% yield. The benzoate (**6**) had m.p. 216–218 °C; λ_{\max} (CHCl₃) 364 nm (ϵ_{\max} 5 950 dm³ mol⁻¹ cm⁻¹); δ_{H} (CDCl₃) 1.20 (6 H, t), 2.19 (3 H, s), 3.37 (4 H, q), 5.69–5.90br (1 H), 6.50–6.61 (3 H, m), 6.98–7.65 (4 H, m), 7.57 (1 H, s), 8.20–8.38 (3 H, m), and 8.83 (1 H, dd, *J* 4.2, 1.5 Hz); *m/z* 459 (*M*⁺) and 444 (*M*⁺ – 15) (Found: C, 70.25; H, 6.0; N, 8.6. C₂₇H₂₆ClN₃O₂ requires C, 70.5; H, 5.7; N, 9.1%).

General Procedure for the Preparation of Metal Complex Dyes, [M(2)_n](ClO₄)₂.—To the free ligand (**2**) (0.47 mmol) in 99% ethanol (100 ml) under nitrogen was added Ni(ClO₄)₂·6H₂O (1.18 mmol) in water (20 ml). The mixture was stirred for 30 min at room temperature, concentrated *in vacuo*, and poured into water. The precipitate was filtered off and dried *in vacuo*. The complex prepared from (**2d**) with Ni(ClO₄)₂·6H₂O decomposed in water. The reactions of (**2a**) and (**2b**) with Cu(ClO₄)₂·6H₂O were carried out by the same procedure. The resulting precipitate was filtered off, washed with water, and dried *in vacuo*.

Elemental analyses are given in Table 3; $[\text{Ni}(\mathbf{2a})_2](\text{ClO}_4)_2$; yield 97%; m.p. 210 °C (decomp.); $[\text{Ni}(\mathbf{2b})_2](\text{ClO}_4)_2$; yield 95%; m.p. > 300 °C; $[\text{Ni}(\mathbf{2c})_3](\text{ClO}_4)_2$; yield 24% m.p. > 300 °C; $[\text{Cu}(\mathbf{2a})_3](\text{ClO}_4)_2$; yield 62%; m.p. 206 °C (decomp.); $[\text{Cu}(\mathbf{2b})_3](\text{ClO}_4)_2$; yield 97%; m.p. > 300 °C.

Preparation of $[\text{Ni}(\text{L})](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$, L = (2a) or (2b).—To the free ligand (2a) or (2b) (0.24 mmol) in tetrahydrofuran (20 ml) under nitrogen was added 40% aqueous $\text{Ni}(\text{BF}_4)_2$ (0.59 mmol) diluted with tetrahydrofuran (20 ml). The mixture was stirred for 30 min at room temperature, then concentrated *in vacuo* and washed with chloroform. The precipitate was filtered off and dried *in vacuo*. Elemental analyses are given in Table 3; $[\text{Ni}(\mathbf{2a})](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$; yield 42%; m.p. 236–238 °C; $[\text{Ni}(\mathbf{2b})](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$; yield 25%; m.p. > 300 °C.

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