

Synthesis of Novel Near-infrared Absorbing Metal Complex Dyes with Indoaniline-type Ligands

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New metal complex dyes with *N,O*-bidentate indoaniline-type ligands, 5-(4'-dialkylaminophenyl-imino)quinolin-8-ones (**3**), have been prepared, which have intense absorption bands in the near-i.r. region and were isolated as stable compounds. A film of complex dye which was prepared from 5-(4'-diethylamino-2'-methylphenylimino)quinolin-8-one and Ni(BF₄)₂aq showed a λ_{max} value of 772 nm and reflected 54.3% of the incident light intensity at 830 nm; these metal complex dyes have potential as a diode-laser optical storage medium.

Recently, near-i.r. absorbing dyes have attracted considerable attention in the field of diode-laser optical storage.¹ The optical recording is effected by a thermal deformation of the recording layer, such as the decomposition, evaporation, or dissolution, which occurs by absorption of the laser beam energy at the irradiated portions of the recording layer. As a diode-laser used in this field emits near-i.r. light at 780–830 nm, the optical recording media need to absorb near-i.r. light efficiently. Only a few near-i.r. absorbing metal complex dyes, such as metallo-phthalocyanines² and metal dithienes,³ are known.

Earlier,⁴ we found that new *N,O*-bidentate indoaniline-type ligands can easily form complexes with several ions, and this complexation with metal ions causes a large bathochromic shift of the absorption bands and an increase in molecular extinction coefficients. These large spectral changes encouraged us to design new near-i.r. absorbing metal complex dyes.

In this paper, we report the synthesis of such metal complex dyes with indoaniline-type ligands. We examined the film properties of one of these dyes for potential use as an optical storage material.

Results and Discussion

Preparation of Indoaniline-type Ligands.—The indoaniline-type ligands were synthesized by condensing quinolin-8-ol (**1**) with 4-dialkylaminoaniline hydrochlorides (**2**) in the presence of an oxidizing agent under alkaline conditions at 5 °C for 10 min (see Table 1). The reaction was promoted by the oxidizing agent and in the presence of sodium hypochlorite gave 5-(4'-diethylamino-2'-methylphenylimino)quinolin-8-one (**3a**) (64%) together with 7-chloro-5-(4'-diethylamino-2'-methylphenylimino)quinolin-8-one (**4a**) (9%) (entry 1). The dye (**4a**) was identified on the basis of the spectral data of an authentic sample obtained by the reaction of 5,7-dichloroquinolin-8-ol (**5**) with 4-diethylamino-2-methylaniline hydrochloride (Scheme 1). Use of ammonium peroxydisulphate as an oxidizing agent gave an increased (95%) yield of (**3a**) (entry 2). The dye (**3b**) was also obtained in good yield under similar conditions (entries 3,4). From these results, the reaction is considered to proceed by oxidation of 4-dialkylaminoaniline, *via* a semiquinone ion, the ease of formation of which may be dependent upon the nature of the oxidizing agent. The dyes (**3a**) and (**3b**) showed λ_{max} values of 625 nm (ϵ_{max} 18 400 dm³ mol⁻¹ cm⁻¹) and 596 nm (ϵ_{max} 15 700 dm³ mol⁻¹ cm⁻¹) in chloroform, respectively. The introduction of a chlorine atom at the 7-position of the quinonoid ring caused a bathochromic shift of the absorption band, that is, (**4a**) and (**4b**) absorbed visible light at 654 nm (ϵ_{max}

23 900 dm³ mol⁻¹ cm⁻¹) and 623 nm (ϵ_{max} 16 800 dm³ mol⁻¹ cm⁻¹) in chloroform, respectively.

Effect of Metal Ions on the Absorption Spectra of (3) in 99% EtOH.—These free ligands (**3**) easily form metal chelate complexes in which the metal ion binds primarily to N-1 and O-8, the absorption spectra of which show large bathochromic shifts and increases in molecular extinction coefficient compared with the free ligands. For example, Figure 1 shows the spectral change for the complexation of Cu(ClO₄)₂·6H₂O with (**3a**) in 99% EtOH. The 635 nm absorption band of (**3a**) decreased while a new band appeared in the near-i.r. region on addition of Cu(ClO₄)₂·6H₂O. A set of isosbestic points were observed at 490 nm and 666 nm. At a ratio of [Cu^{II}]/[(**3a**)] = 0.6, the absorption maximum at 635 nm disappeared completely, while a single absorption band in the near-i.r. region at 776 nm was observed (Curve D). On further addition of Cu(ClO₄)₂·6H₂O ([Cu^{II}]/[(**3a**)] > 0.6) to this system, the absorbance at 776 nm decreased while another absorption band appeared at around 720 nm; a new isosbestic point was observable at 750 nm. The final absorption spectrum ([Cu^{II}]/[(**3a**)] = 2.0, Curve H) had an absorption band at 721 nm.

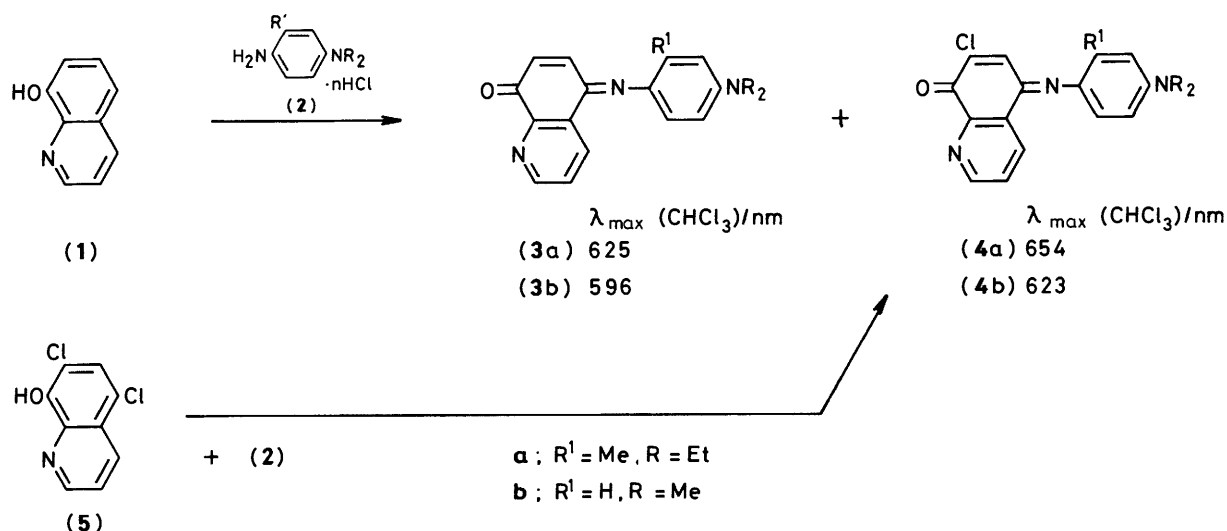
We made further studies of these intricate spectral changes. In Figure 2, continuous variation plots at [(**3a**)] + [Cu(ClO₄)₂·6H₂O] = 2.5 × 10⁻⁴ M are illustrated. The absorption maxima employed (776 nm and 721 nm) were those at which [Cu^{II}]/[(**3a**)] = 0.6 and 2.0 in Figure 1, respectively. As shown in Figure 2, the former maximum occurred when [(**3a**)]/([(**3a**)] + [Cu^{II}]) = 0.67, suggesting the formation of a 1:2 Cu^{II}-(**3a**) complex, while for the latter the formation of a 1:1 Cu^{II}-(**3a**) complex was indicated since the maximum appeared at around 0.5. Similar spectral changes were observed in the formation of complexes with other metal salts. Table 2 summarizes the spectral data for the complex formation of metal salts with (**3**) in

Table 1. Reaction of (1) with anilines^a

Entry	Aniline ^b	Oxidizing agent ^c	Product yield (%) ^d
1	(2a)	NaOCl	(3a)(64), (4a)(9)
2	(2a)	(NH ₄) ₂ S ₂ O ₈	(3a)(95)
3	(2b)	NaOCl	(3b)(63), (4b)(4)
4	(2b)	(NH ₄) ₂ S ₂ O ₈	(3b)(71)

^a Reactions were carried out at 5 °C. ^b Molar ratio of [aniline]/[(**1**)] = 2.

^c Molar ratio of [oxidizing agent]/[(**1**)] = 2. ^d Isolated yield after column chromatography.



Scheme 1.

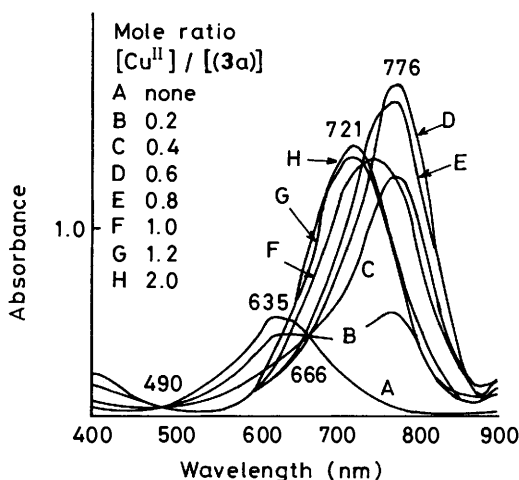


Figure 1. Influence of added $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ on the absorption spectra of (3a) ($2.5 \times 10^{-5}\text{M}$) in 99% EtOH

99% EtOH. The absorption bands which were assigned to 1:2 metal-(3) complexes absorbed near i.r. light at 745–778 nm. The values of the bathochromic shift ($\Delta\lambda_{\max}$) and the ratio of molecular extinction coefficient ($R\epsilon$) were in the range of 140–172 nm and 5.1–8.7 times, in comparison with those of the free ligands (3), respectively. It is worth noting, in view of the many applications in the field of optical data storage technology, optical filters, and so on that some of these complexes (6) have intense absorption bands ($\epsilon_{\max} > 10^5$) in the near-i.r. region. The absorption maxima of 1:1 metal complexes were observed in the range 721–742 nm, shorter than that of the corresponding 1:2 complexes.

Isolation of Metal Complex Dyes.—The metal complexes containing the dye (3) were synthesized as follows: the reaction of (3a) (0.31 mmol) with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.78 mmol) in ethanol–water under a nitrogen atmosphere gave *N,O*-bidentate $[\text{Cu}(\text{3a})_2](\text{ClO}_4)_2 \cdot \text{bis}[5-(4'-\text{diethylamino}-2'-\text{methylphenyl-imino})\text{quinolin-8-one}]$ copper(II) diperchlorate, in 86% yield, and not a 1:1 complex in spite of the use of an excess of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The absorption spectrum of $[\text{Cu}(\text{3a})_2](\text{ClO}_4)_2$ agreed essentially with that for $[\text{Cu}^{\text{II}}]/[(\text{3a})] = 0.6$ in Figure 1, which gives a favourable match with the emission wavelengths of semiconductor lasers. The other 1:2 metal complex dyes were synthesized in a similar manner. However,

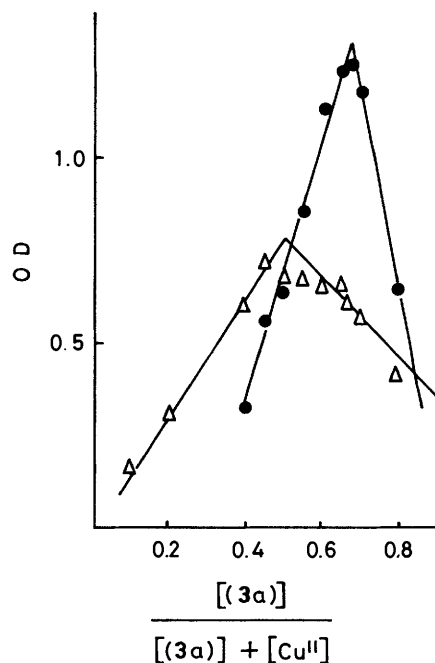
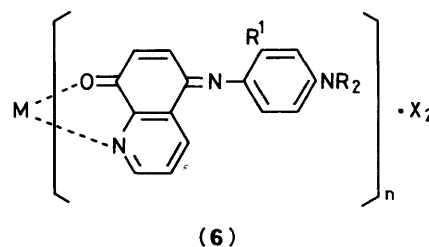


Figure 2. Continuous variation plots for the (3a)- Cu^{II} complex in 99% EtOH: $[(\text{3a})] + [\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}] = 2.5 \times 10^{-4}\text{M}$: ●, o.d. 776 nm, △, o.d. 721 nm



the $\text{Ni}^{\text{II}}-(\text{3})$ crystals which were prepared from (3) and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were found to consist of a mixture of 1:2 and 1:3 $\text{Ni}^{\text{II}}-(\text{3a})$ complexes by elemental analyses as shown in Table 3. All the isolated metal complex dyes (6) have strong absorption bands in the near-i.r. region.

The i.r. spectra (KBr) of these complexes were measured in

Table 2. Spectral data for the complex formation of metal salts with (3) in 99% EtOH

	Free ligand		Metal salt	mol ^a	Complex (6)		M:L ^c	$\Delta\lambda_{\max.}^d$	Re ^e
	$\lambda_{\max.}/\text{nm}$	($\epsilon_{\max.}$)			$\lambda_{\max.}/\text{nm}$	($\epsilon_{\max.}$) ^b			
(3a)	635	(21 300)	Cu(ClO ₄) ₂ ·6H ₂ O	(0.6)	776	(144 000)	1:2	141	6.8
				(2.0)	721	(60 000)	1:1	86	2.8
(3a)	635	(21 300)	Ni(ClO ₄) ₂ ·6H ₂ O	(0.8)	775	(118 000)	1:2	140	5.5
				(3.0)	742	(72 000)	1:1	107	3.4
(3a)	635	(21 300)	Ni(BF ₄) ₂ aq	(0.6)	778	(113 000)	1:2	143	5.3
				(2.5)	742	(69 000)	1:1	107	3.2
(3b)	600	(16 600)	Cu(ClO ₄) ₂ ·6H ₂ O	(0.8)	772	(144 000)	1:2	172	8.7
				(2.5)	722	(69 000)	1:1	122	4.2
(3b)	600	(16 600)	Ni(ClO ₄) ₂ ·6H ₂ O	(0.8)	745	(85 000)	1:2	145	5.1
				(3.0)	728	(60 000)	1:1	128	3.6

^a Molar ratio, [metal ion]/[free ligand]. ^b Determined from spectral changes upon addition of metal salts. ^c Determined by continuous variation method. ^d $\Delta\lambda_{\max.} = \lambda_{\max.}(\text{complex}) - \lambda_{\max.}(\text{free ligand})$. ^e $\text{Re} = \epsilon_{\max.}(\text{complex})/\epsilon_{\max.}(\text{free ligand})$.

Table 3. Elemental analyses of complexes (6)

Complex		C(%)		H(%)		N(%)	
		Calc.	Found	Calc.	Found	Calc.	Found
[Cu(3a) ₂](ClO ₄) ₂		53.31	53.43	4.70	4.69	9.32	9.40
[Ni(3a) _n](ClO ₄) ₂	(n = 2)	53.60	56.70	4.72	5.06	9.38	9.74
	(n = 3)	59.27		5.22		10.37	
[Ni(3a) ₂](BF ₄) ₂		55.15	55.94	4.86	5.01	9.65	9.69
[Cu(3b) ₂](ClO ₄) ₂		49.98	49.65	3.70	3.62	10.29	10.25
[Ni(3b) _n](ClO ₄) ₂	(n = 2)	50.28	53.81	3.73	3.70	10.35	10.90
	(n = 3)	56.22		4.16		11.57	

Table 4. I.r. spectral data of C(8)=O for the complex of metal salts with (3)

Free ligand	$\nu(\text{C}=\text{O})/\text{cm}^{-1}$	Complex	$\nu(\text{C}=\text{O})/\text{cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$ ^a
(3a)	1 655	[Cu(3a) ₂](ClO ₄) ₂	1 595	60
		[Ni(3a) ₂₋₃](ClO ₄) ₂	1 597	58
		[Ni(3a) ₂](BF ₄) ₂	1 597	58
(3b)	1 653	[Cu(3b) ₂](ClO ₄) ₂	1 597	56
		[Ni(3b) ₂₋₃](ClO ₄) ₂	1 599	54

^a $\Delta\nu = \nu(\text{C}=\text{O}) (\text{free ligand}) - \nu(\text{C}=\text{O}) (\text{complex})$

order to obtain further insight into the co-ordination structure. The absorption band of the C(8)=O group of [Cu(3a)₂](ClO₄)₂ was at 1 595 cm⁻¹, which was 60 cm⁻¹ lower than that of the free ligand (3a). Table 4 summarizes the i.r. spectral bands of the C(8)=O group for the complex formation of metal salts with (3), the shifts of which were in the range of 54–60 cm⁻¹, and comparable with that of Cu^{II} complexed with salicylaldehyde (62 cm⁻¹).⁵ These results suggest that the double bond character of the C(8)=O group was decreased by co-ordination of the oxygen atom C(8)=O to a metal ion, in the solid state.

Preparation of a Film of the Metal Complex Dye (6).—As these metal complex dyes (6) were considered to have potential use in diode-laser optical storage, we investigated their film properties. The spin-coating process is used for the application of the film and in order to obtain a smooth homogeneous layer, the metal complex dyes should have a good solubility in the solvent used. A tetrachloroethane solution of the complex was poured on to a poly(methyl methacrylate) (PMMA) substrate, in the case of [Ni(3a)₂](BF₄)₂ the film obtained was found to be optically clear (because of the good solubility of this complex in tetrachloroethane). Figure 3 shows the absorption and reflection spectra of a film of [Ni(3a)₂](BF₄)₂ in the visible and near-i.r. region. The film showed intense absorption in the range 600–900 nm and a $\lambda_{\max.}$ value of 772 nm. The reflection

spectrum exhibited a broad peak at around 930 nm. The film reflected 54.3% of incident light intensity at 830 nm. The results show the potential of these metal complex dyes as diode-laser optical storage media.

Experimental

M.p.s are uncorrected. Absorption spectra were measured using a Hitachi 220A spectrophotometer. ¹H N.m.r. spectra were taken on a Hitachi R-90H spectrometer. I.r. spectra were measured with a JASCO FT/IR-5000 i.r. spectrophotometer in KBr pellet form. Mass spectra were run on a Shimadzu LKB-9000 spectrometer operating at 80eV, and elemental analyses were obtained using a Perkin-Elmer 240C C, H, N, analyser.

Quinolin-8-ol (1), 5,7-dichloroquinolin-8-ol (5), and 4-dialkylaminoaniline hydrochlorides were reagent grade and used without further purification. Ni(ClO₄)₂·6H₂O⁶ and Cu(ClO₄)₂·6H₂O⁷ were prepared according to the literature. 40% Aqueous Ni(BF₄)₂ was kindly supplied by the Mitsubishi Kasei Corporation.

General Procedure for the Preparation of the Substituted Quinolin-8-ones (3) and (4).—An aqueous solution of an oxidizing agent (6.8 mmol) was added dropwise to an aqueous alkaline solution of (1) (3.4 mmol) and (2) (6.8 mmol) at 5 °C

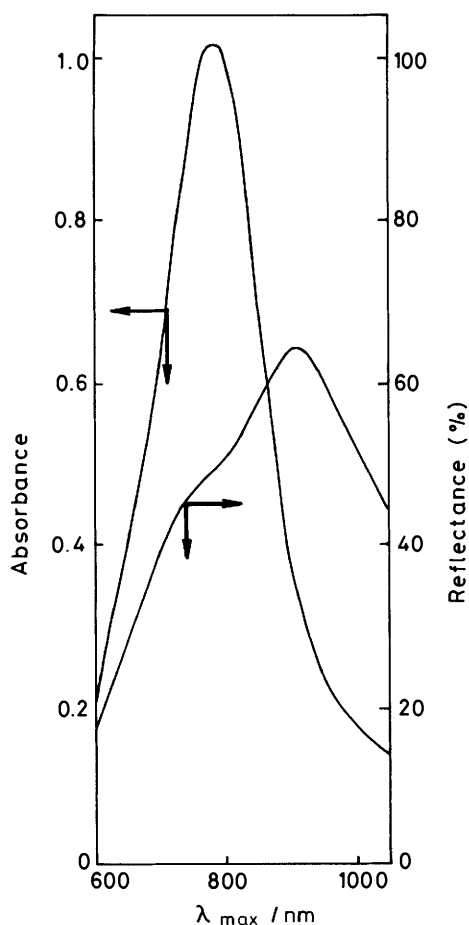


Figure 3. The absorption and reflection spectra of a film of $[\text{Ni}(\mathbf{3a})_2][\text{BF}_4]_2$

and the resulting mixture was stirred for 10 min at 5 °C. The products were then filtered off, dried, chromatographed on silica gel (Wacogel C-300) using ethyl acetate–benzene (1:1) as eluant, and recrystallized from ethanol. The yields are summarized in Table 1.

5-(4'-Diethylamino-2'-methylphenylimino)quinolin-8-one (3a). M.p. 125–128 °C; $\lambda_{\text{max}}(\text{CHCl}_3)$ 625 nm (ϵ_{max} , 18 400 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.20 (6 H, s), 2.36 (3 H, s), 3.40 (4 H, q), 6.56–6.64 (3 H, m), 6.79 (1 H, d, J 10.5 Hz), 7.51 (1 H, d, J 10.5 Hz), 7.64 (1 H, dd, J 8.3, 4.5 Hz), 8.82 (1 H, dd, J 7.5, 1.5 Hz), and 8.86 (1 H, dd, J 5.3, 1.5 Hz) (Found: C, 75.2; H, 6.6; N, 13.1. $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}$ requires C, 75.2; H, 6.6; N, 13.2%).

5-(4'-Dimethylaminophenylimino)quinolin-8-one (3b). M.p. 176–178 °C; $\lambda_{\text{max}}(\text{CHCl}_3)$ 596 nm (ϵ_{max} , 15 700 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.04 (6 H, s), 6.77 (2 H, d, J 9.0 Hz), 6.84 (1 H, d, J 10.6 Hz), 7.04 (2 H, d, J 9.0 Hz), 7.55 (1 H, d, J 10.6 Hz), 7.59 (1 H, dd, J 8.0, 4.4 Hz), 8.85 (1 H, dd, J 8.6, 1.8 Hz) and 8.89 (1 H, dd, J 4.6, 1.8 Hz) (Found: C, 73.9; H, 5.4; N, 15.2. $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}$ requires C, 73.6; H, 5.4; N, 15.2%).

7-Chloro-5-(4'-dialkylaminophenylimino)quinolin-8-one (4).—An aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (4.68 mmol) was added dropwise to an aqueous alkaline solution of (5) (2.34 mmol) and (2) (4.68 mmol) at 60 °C. After being stirred for 10 min at 60 °C, the reaction mixture was filtered, dried, and chromatographed on silica gel (Wakogel C-300) using chloroform–acetone (10:1) as eluant. The dyes (4a) and (4b) were obtained in 87 and 55% yield, respectively.

7-Chloro-5-(4'-diethylamino-2'-methylphenylimino)quinolin-8-one (4a). M.p. 144–145 °C; $\lambda_{\text{max}}(\text{CHCl}_3)$ 654 nm (ϵ_{max} , 23 900 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.22 (6 H, t), 2.36 (3 H, s), 3.42 (4 H, q), 6.58–6.70 (3 H, m), 7.56 (1 H, dd, J 8.3, 4.5 Hz), 7.72 (1 H, s), 8.82 (1 H, dd, J 8.3, 1.5 Hz), and 8.90 (1 H, dd, J 4.5, 1.5 Hz) (Found: C, 67.9; H, 5.7; N, 11.9%).

7-Chloro-5-(4'-dimethylaminophenylimino)quinolin-8-one (4b). M.p. 170–173 °C; $\lambda_{\text{max}}(\text{CHCl}_3)$ 623 nm (ϵ_{max} , 16 800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.07 (6 H, s), 6.78 (2 H, d, J 9.2 Hz), 7.06 (2 H, d, J 9.0 Hz), 7.61 (1 H, dd, J 8.2, 4.4 Hz), 7.76 (1 H, s), 8.84 (1 H, dd, J 8.2, 1.7 Hz), and 8.96 (1 H, dd, J 4.5, 1.6 Hz) (Found: C, 65.6; H, 4.4; N, 13.4. $\text{C}_{17}\text{H}_{14}\text{ClN}_3\text{O}$ requires C, 65.5; H, 4.5; N, 13.5%).

General Procedure for the Preparation of Metal Complex Dyes (6).—To the free ligands (3) (0.31 mmol) dissolved in 99% EtOH under a nitrogen atmosphere were added the metal perchlorate hexahydrates (0.78 mmol) dissolved in water (50 ml). The resulting mixtures were stirred for 30 min at room temperature after which the precipitates were filtered off, washed with water, then with 99% EtOH or ethyl acetate, and dried.

The reaction of (3a) with 40% aqueous $\text{Ni}(\text{BF}_4)_2$ was carried out using the same procedure, the resulting solution being reduced in volume and then poured into water. The precipitate was filtered off and dried.

Metal complex dyes (6). The elemental analyses and i.r. spectral data are given in Tables 3 and 4, respectively. $[\text{Cu}(\mathbf{3a})_2](\text{ClO}_4)_2$; Yield 86%; m.p. > 300 °C. $[\text{Ni}(\mathbf{3a})_{2-3}](\text{ClO}_4)_2$; m.p. 245–246 °C. $[\text{Ni}(\mathbf{3a})_2](\text{BF}_4)_2$; Yield 75%; m.p. > 300 °C. $[\text{Cu}(\mathbf{3b})_2](\text{ClO}_4)_2$; Yield 91%; m.p. > 300 °C. $[\text{Ni}(\mathbf{3b})_{2-3}](\text{ClO}_4)_2$; m.p. > 300 °C.

Preparation of the Film of $[\text{Ni}(\mathbf{3a})_2](\text{BF}_4)_2$.—The complex dye, $[\text{Ni}(\mathbf{3a})_2](\text{BF}_4)_2$ (9 mg) was dissolved in tetrachloroethane (600 mg) and the solution filtered through a 0.22 μm filter. The filtrate was dropped onto a poly(methyl methacrylate) (PMMA) substrate, and coated by the spinner method at a rotational speed of 1 000 r.p.m. The coating layer was dried at 80 °C for 5 min to give a dye film of $[\text{Ni}(\mathbf{3a})_2](\text{BF}_4)_2$. The absorption and reflection spectra of this dye film were recorded on a 323 Hitachi Recording Spectrophotometer.

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