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Syntheses and Characteristics of Near-Infrared Absorbing Metal Complex Dyes with Indoaniline-type Ligands

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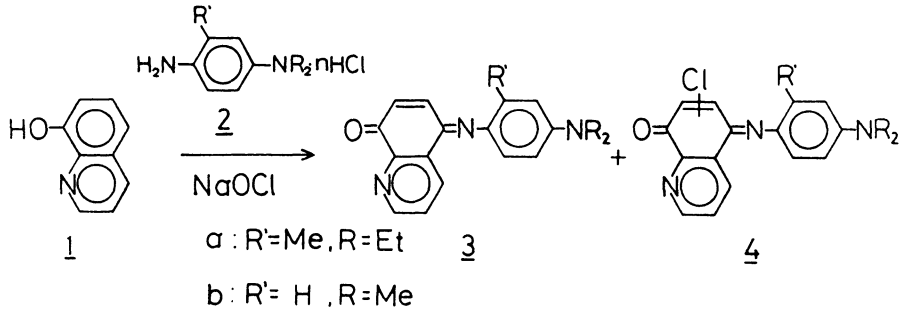
New metal complex dyes with N,O-bidentate indoaniline type ligands have been prepared, which absorb near-infrared light at 745 - 776 nm in EtOH. Some of these complex dye media have excellent characteristics for the practical use as diode-laser optical storage.

Recently, near-infrared absorbing dyes are of remarkable interest since these dyes have prospect of developing many application in the new field of diode-laser optical storage.[1] As the gallium-aluminium-arsenic (GaAlAs) diode-laser emits infrared light at 800 - 830 nm, the dyes have to absorb light in the range of 700 - 830 nm. Some of the metal complex dyes which absorb infrared light, such as metalo-phthalocyanines[2] and metal dithienes,[3] have been known as dyes for optical storage media. However, infrared absorbing metal complex dyes with quinonoid structure have not been known yet.

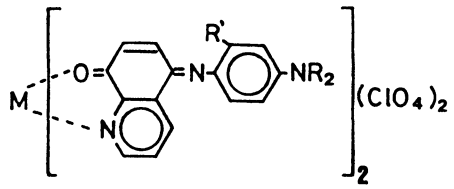
In this paper, we wish to report the syntheses and some characteristics of new metal complex dyes obtained from N,O-bidentate indoaniline-type ligands. The indoaniline-type ligands (3) were synthesized by condensing 8-hydroxyquinoline (1) with the dialkylaminoaniline hydrochlorides (2) (Scheme 1). A 5% sodium hypochlorite solution (6.2 cm^3) was added dropwise to an aqueous NaOH solution of 1 (2.07 mmol) and 2a (4.13 mmol) at 5 °C. The mixture was stirred for 10 min to give 5-(2'-methyl-4'-diethylaminophenylimino)quinoline-8-one (3a)[4] in 64% yield together with 4a[5] in 9% yield. The compounds (3a and 4a) were blue in color and showed λ max values of 625 nm and 654 nm in chloroform, respectively. Similarly, 3b (λ max



Scheme 1.

596 nm in chloroform) and 4b (λ max 623 nm in chloroform) were obtained in 63% and 4% yields, respectively.

We have found that the compounds (3) can easily form complexes with several metal ions. The absorption spectra of the free ligands (3) showed large red shifts with increase of molecular extinction coefficient by complex formation with metal ions. For example, in a spectral change upon addition of copper(II) perchlorate hexahydrate to the ethanol solution of 3a, the absorption band at 635 nm of 3a decreased with increase of a new band in infrared region. A set of isosbestic points was observed at 490 nm and 666 nm. The final spectrum has an absorption maximum at 776 nm (ε max 144000 $mol^{-1}dm^3cm^{-1}$ at $[Cu^{2+}]/[3a]=0.6$). The continuous variation method indicated the formation of 1:2 copper(II)-3a complex. The similar spectral changes were observed in the formation of complexes with other metal(II) ions. Table 1 summarizes the spectral data for the complex formation of metal(II) perchlorates with 3 in 99% EtOH. As shown in Table 1, the values of red shifts, Δλ max=λ max(complex) -λ max(free ligands), were in the range of 140 to 172 nm and the values of molecular extinction coefficients of the complex dyes were about 5 - 9 times in comparison with those of free ligands.



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a : M=Cu, R'=Me, R=Et
b : M=Ni , R'=Me, R=Et
c : M=Cu, R'= H , R=Me
d : M=Ni , R'= H , R=Me

Synthesis of metal complex of 3a was carried out as follows: The reaction of 3a (0.31 mmol) with copper(II) perchlorate hexahydrate (0.78 mmol) in ethanol-water solution under nitrogen atomosphere gave N,O-bidentate copper complex (5a), bis[5-(2'-

Table 1. Spectral Data for the Complex Formation of Metal(II) Perchlorates with 99% EtOH

Metal perchlorate	λ max/nm(ε max/mol^{-1}dm^{3}cm^{-1})		Δλ max[a]	Rε[b]
	Free ligand	Complex[c]		
$Cu(ClO_4)_2 \cdot 6H_2O$	3a, 635(21300)	5a, 776(144000)	141	6.8
$Ni(ClO_4)_2 \cdot 6H_2O$	3a, 635(21300)	5b, 775(118000)	140	5.5
$Cu(ClO_4)_2 \cdot 6H_2O$	3b, 600(16600)	5c, 772(144000)	172	8.7
$Ni(ClO_4)_2 \cdot 6H_2O$	3b, 600(16600)	5d, 745(85000)	145	5.1

a) Δλ max = λ max(complex) - λ max(free ligand).

b) Rε = ε max(complex)/ε max(free ligand).

c) Determined by spectral changes upon addition of metal(II) perchlorates.

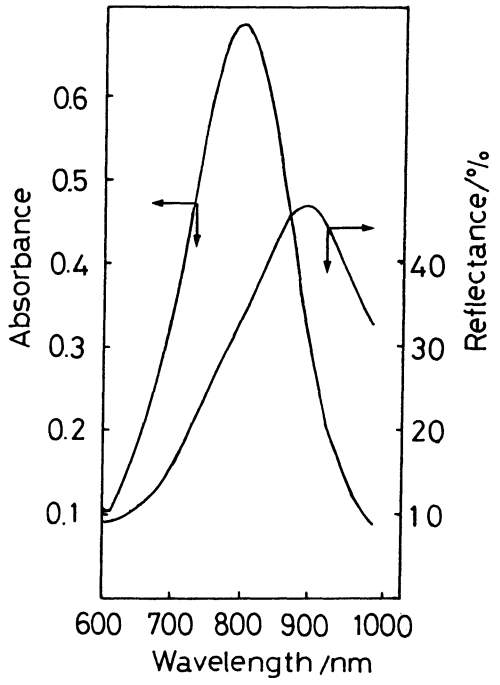

Fig. 1. The absorption and reflection spectra of 50 nm-thick film of 5b.

methyl-4'-diethylaminophenylimino)quinoline-8-one] copper(II) diperchlorate,[6] in 86% yield. The absorption spectrum of the isolated 1:2 copper complex agreed essentially with the spectral feature at [Cu^{2+}]/[3a]=0.6, which has favorable absorption for semiconductor laser. The other corresponding 1:2 complexes of Cu(II) and Ni(II) with N,O-bidentate indoaniline-type ligands were synthesized in a similar manner. All the metal complex dyes (5) have strong absorption bands in infrared region.

Some properties of these new complex dyes for the practical use as optical storage materials were examined. The spin-coating process is a suitable for applying the complex dye films. The tetrachloroethane solution of 5a and 5b was poured on to a polymethyl methacrylate

(PMMA) substrate. The film of 5b was more optically clear than that of 5a because of better solubility of 5b in tetrachloroethane. Figure 1 shows the absorption and reflection spectra of 50 nm-thick film of 5b in a visible and near-infrared wavelength region. The film of 5b showed a intense absorption band in the range of 600 - 900 nm and the λ max value of 808 nm. The reflection spectrum exhibited a broad peak at around 900 nm. The film reflected 38% of incident light intensity at 830 nm. Optical writing on this medium with semiconductor laser(wavelength 830 nm, power 4mW) proved that this complex dye film exhibited clear pit forming characteristic. The details of these characteristics for optical storage media will be reported elsewhere. These complex dyes have good physical and chemical properties for the practical use as diode-laser optical storage.

References

1) M. Umehara, M. Abe, and H. Oba, Yuki Gosei Kagaku Kyokai Shi, 43, 334 (1985).

2) U. S. P. 4298975 (1981); L. Edwards and Gouterman, J. Mol. Spectry., 33, 292 (1970).

3) G. N. Schrauzer, Acc. Chem. Res., 2, 72 (1969).

4) 3a: mp 125 - 128 °C; ^{1}H NMR ($CDCl_3$): 1.20 (6H, t), 2.36 (3H, s), 3.40 (4H, q), 6.56 - 6.64 (3H, m), 6.79 (1H, d, J=10.5 Hz), 7.51 (1H, d, J=10.5 Hz), 7.64 (1H, dd, J=8.3, 4.5 Hz), 8.82 (1H, dd, J=7.5, 1.5 Hz), and 8.86 (1H, dd, J=5.3, 1.5 Hz); Analysis Found: C, 76.03; H, 6.69; N, 13.06%. Calcd for $C_{20}H_{21}N_3O$: C, 75.23; H, 6.58; N, 13.17%.

5) 4a: mp 144 - 145 °C; ^{1}H NMR ($CDCl_3$): 1.22 (6H, t), 2.36 (3H, s), 3.42 (4H, q), 6.58 - 6.70 (3H, m), 7.56 (1H, dd, J=8.3, 4.5 Hz), 7.72 (1H, s), 8.82 (1H, dd, J=8.3, 1.5 Hz), and 8.90 (1H, dd, J=4.5, 1.5 Hz); Analysis Found: C, 67.88; H, 5.75; N, 11.72%. Calcd for $C_{20}H_{20}N_3OCl$: c, 67.89; H, 5.66; N, 11.88%.

6) 5a: mp > 300 °C; Analysis Found: C, 53.43; H, 4.69; N, 9.40%. Calcd for $C_{40}H_{42}O_{10}N_6Cl_2Cu$: C, 53.31; H, 4.70; N, 9.32%.

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