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New Near Infrared Absorbing Metal Complex Dyes with N,O-Bidentate Ligands, 6-Substituent-5,8-quinolinediones

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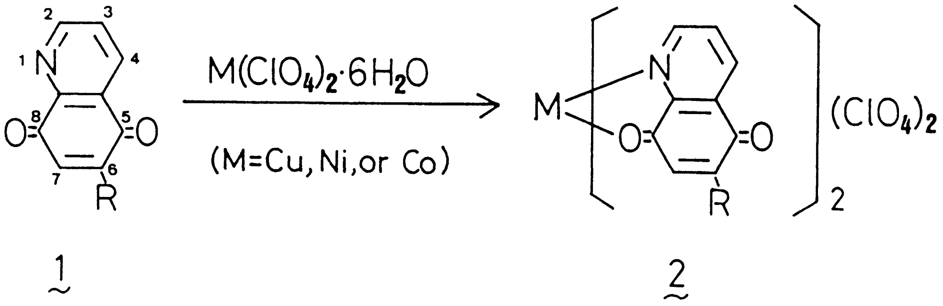
New metal complex dyes were synthesized by the reaction of various 6-substituent-5,8-quinolinediones with transition metal salts. The first absorption bands of these dyes were sensitively shifted to longer wavelength with increase of electron-donating power of the 6-substituents and reached to the near infrared region.

Recently near infrared absorbing dyes have attracted considerable attention, since these organic dyes offer various advantages as optical storage media over inorganic media.[1)] As a diode-laser which is now used in the optical recording systems emits near infrared light (roughly 780-850 nm), the dyes must adequately absorb the near infrared light. An enormous number of organic dyes have been synthesized by dye chemists over a century, however, there are scarcely available dyes which absorb at wavelengths emitted by the diode-laser. Therefore new molecular designs of dyes which can absorb in the near infrared are desired earnestly in this new field. We have previously reported the syntheses and characteristics of two new types of near infrared absorbing dyes, metal complex dyes with indoaniline-type ligands[2)] and naphthoquinone methide near infrared dyes.[3)] In this paper, we now further report on a new type of near infrared absorbing metal complex dyes with N,O-bidentate ligands (2) of which structures are shown in Scheme 1.

The free ligands of the complexes, 6-substituent-5,8-quinolinediones (1a-g), were conveniently synthesized from the regioselective 6-amination[4)] and 6-arylation[5)] of 5,8-quinolinedione promoted by metal ions. We have found that these ligands can easily form metal chelate complexes in which the 1-nitrogen atom and the oxygen atom of the 8-carbonyl group of <u>1</u> coordinate to metal ions (see Scheme 1), and that the absorption spectra of them generally show a large bathochromic shift with increase of absorption intensity for the metal chelate complexation. As a typical example, Fig. 1 shows a spectral change for the complex formation of copper(II) perchlorate hexahydrate with 6-(p-N,N-dimethylaminophenyl)-5,8-quinolinedione (<u>1f</u>) in 99% ethanol. The absorption band around 554 nm (Curve 1) due to the free ligand decreased with increase of a new band around 760 nm. A set of isosbestic points was observed at 452 and 602 nm, which indicated the presence of a simple equilibrium. The continuous variation method indicated the formation of a 1:2 metal-<u>1f</u> complex. In fact, the feature of the final spectrum (Curve 6) was essentially the same as the absorption spectrum of



Scheme 1.

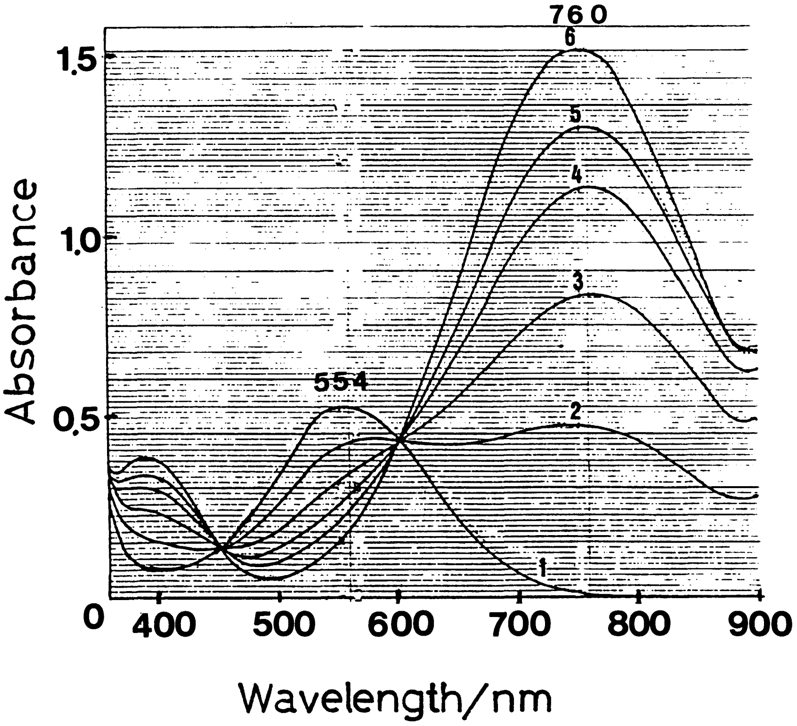


Fig. 1.

Spectral changes upon addition of $Cu(ClO_4)_2 \cdot 6H_2O$ to the 99% (v/v) ethanol-water solution of 6-(p-N,N-dimethylaminophenyl)-5,8-quinolinedione (<u>1f</u>) at 25 °C.

$[\underline{1f}]_t = 6.25\times10^{-5}$ mol dm^{-3} ($[\ ]_t$ denotes the total concentration). $[Cu(II)]_t = 0.00$(Curve 1), 2.5×10^{-5} (Curve 2), 3.75×10^{-5}(Curve 3), 5.0×10^{-5}(Curve 4), 6.25×10^{-5}(Curve 5), 1.25×10^{-4}–1.56×10^{-4}mol dm^{-3}(Curve 6)

Table 1. Spectral data for the complex formation of $M(ClO_4)_2 \cdot 6H_2O$ with 6-substituent-5,8-quinolinediones (1) in 99% ethanol at 25 °C

Free ligand (1) 6-substituent -R	(No)	λ max(ε max) nm	Metal ion[a)] M^{2+}	Complex (2) λ max(ε max)[b)] nm	$\Delta\lambda$ max[c)]	Rε max[d)]
$-NH-C_6H_4-Cl$	(1a)	464(4810)	Cu^{2+} e)	500(16200)	36	3.37
$-NH-C_6H_4-OMe$	(1b)	486(4690)	Cu^{2+} e)	528(18100)	42	3.86
$-NH-C_6H_4-NMe_2$	(1c)	548(4470)	Cu^{2+} e)	704(19900)	156	4.45
$-NH-C_6H_4-NMe_2$	(1c)	548(4470)	Ni^{2+} e)	664(16100)	116	3.60
$-NH-C_6H_4-NMe_2$	(1c)	548(4470)	Co^{2+} e)	650(15600)	102	3.49
$-C_6H_4-NHMe$	(1d)	558(7720)	Cu^{2+} f)	743(45390)	185	5.88
$-C_6H_4-NHBu$	(1e)	567(8320)	Cu^{2+} f)	756(48800)	189	5.87
$-C_6H_4-NMe_2$	(1f)	554(8760)	Cu^{2+} f)	760(49200)	206	5.62
$-C_6H_4-NMe_2$	(1f)	554(8760)	Ni^{2+} f)	728(42400)	174	4.84
$-C_6H_4-NMe_2$	(1f)	554(8760)	Co^{2+} f)	713(37500)	159	4.28
$-C_6H_4-NEt_2$	(1g)	579(10710)	Cu^{2+} f)	769(58600)	190	5.47

a) Metal salts [$Cu(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, and $Co(ClO_4)_2 \cdot 6H_2O$] were added. b) Determined by spectral changes upon addition of metal salt. c) $\Delta\lambda$ max = λ max(complex) - λ max(free ligand). d) Rε max = ε max(complex)/ ε max(free ligand). e) The final spectrum of the complex was obtained at [Metal ion]/[1] = 0.5 — 0.7 . f) The final spectrum of the complex was obtained at [Metal ion]/[1] = 2.0 — 3.0 .

the isolated 1:2 copper(II) complex of 1f.[6)] The similar spectral changes were also observed when other 6-substituted derivatives of 5,8-quinolinedione and metal ions were used. Table 1 summarizes the spectral data of various 6-substituent-5,8-quinolinediones and their metal complexes in 99% ethanol. The first absorption bands of the free ligands (λ max(free ligand)) are shifted to longer wavelengths with increasing electron-donating strength of the 6-substituents, which have already observed in the similarly substituted naphthoquinones[7)] and anthraquinones.[8)] Therefore these bands can be ascribed to π - π^* transition of intramolecular charge transfer character from the 6-substituent to the quinone carbonyl groups. The details of color-structure relationships of the metal complex dyes have not been clarified yet and are under investigation, however, it was observed that the values of the bathochromic shifts ($\Delta\lambda$ max) induced by the complex formation become larger with increasing the electron-donating power of the 6-substituent and were in the vast range of 36–206 nm. This result implies that the first absorption bands of the complexes are more sensitively shifted to longer wavelength than those of the free ligands depending on the electronic mobility of a long conjugated system including the 6-substituent. Both the bathochromic shift($\Delta\lambda$ max) and the ratio of molecular extinction coefficients ($R\varepsilon$ max $= \varepsilon$ max(complex)/ε max(free ligand)) were also dependent on the nature of transition metal ions and increased in the following order: Co(II) $<$ Ni(II) $<$ Cu(II). Consequently, the Cu(II) complexes with the ligands having strong electron-donating 6-substituents have stronger absorption bands in near infrared region. These dyes have prospect of many applications not only for optical recording media but also for protectors in optical filter. Some of the free ligands which show large bathochromic shift for the metal complexation can be applied as a metal ion indicator.

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6) The 1:2 copper(II) complex of 1f was synthesized as follows. The free ligand (1f)(0.5 g, 1.8 mmol) was dissolved in 90 ml of 95% ethanol. Metal salt, Cu(ClO_4)$_2$·6H_2O (0.67 g, 1.8 mmol) dissolved in 30 ml of 95% ethanol, was added to the above solution of 1f. After stirred for 1 h at room temperature, the solvent was removed gradually under reduced pressure to ca. 1/2 volumes, and then cooled overnight in a refrigerator. The dark greenish precipitate was filtered, and dried in vacuo over P_2O_5. Found: C, 49.86; H, 3.44; N, 6.76%. Calcd for $Cu(C_{17}H_{14}N_2O_2)_2(ClO_4)_2$ = Cu(1f)$_2$(ClO_4)$_2$: C, 49.86; H, 3.45; N, 6.84%. Other metal complex dyes prepared by the analogous methods also gave satisfactory analytical data.
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