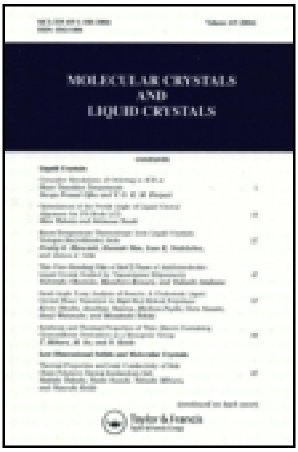

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The Synthesis of Novel Asymmetrical Benzoins and Bis(dithiobenzil) Metal Complex Dyes Containing Ethoxyethoxy Groups and Their Absorption Characteristics

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*Asymmetrical bis(dithiobenzil) metal complex (**BMC**), as a NIR(Near Infra-Red) absorbing dye, was synthesized via preparation of asymmetric benzoin intermediates. Four synthesized dyes were characterized by elemental analyses and GC-Mass, ^{1}H-NMR(nuclear magnetic resonance) analysis. The absorption characteristics of the synthesized dyes in the NIR region were measured using UV-VIS spectrophotometer. Maximum absorbing wavelength was shifted depending on the character and position of substituents in the bis(dithobenzil) metal complex.*

Keywords Bis(dithiobenzil) metal complex; NIR absorbing dye; asymmetrical benzoin; absorption maximum

Introduction

Bis(dithiobenzil) metal complex (Figure 1) is known to be effective in inhibiting the laser-induced fading of colored thin layers on recording disks. It has also been applied to the optical filter on PDP (Plasma Display Panel) panel for NIR absorbing [1,2]. NIR radiations from the PDP affects the electronic equipment located around the PDP, such as a cordless television or a video deck making use of a near infrared light remote controller, and causes malfunctions. Therefore, it is necessary to use NIR dyes which absorb maximally in the range of 850 ∼ 950nm for the optical filter of PDP. However, most symmetric nickel complexes containing the same four substituents in the phenyl ring or unsubstituted phenyl groups show the absorption maximum to be shorter than 850 nm which are not suitable for the optical filter [3].

In this work, some different substituents have been introduced into the phenyl rings to make the nickel complex dyes to be bathochromically shifted in comparison with that of unsubstituted bis(dithiobenzil) metal complex. As shown in Figure 2, ethoxyethoxy groups were introduced to phenyl ring of intermediate **1** by O-alkylation reaction. Then, electron withdrawing group(chloro) or electron donating group(methoxy) was further introduced into the phenyl groups of bis(dithiobenzil) metal complexes.

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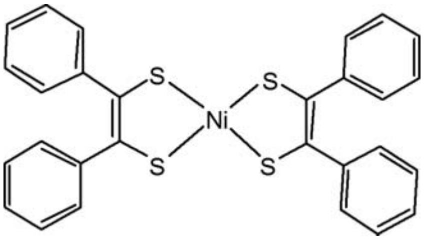

Figure 1. Chemical structure of unsubstitued bis(dithiobenzil) metal complex (**BMC**).

The structures of complex dyes prepared were confirmed using an Elemental Analyzer and GC-Mass, ^{1}H-NMR and their optical properties were measured by means of UV-VIS Spectroscopy.

Experimental

Synthesis

3,4-Bis(2-ethoxyethoxy)benzaldehyde (compound 1). 3,4-dihydroxybenzaldehyde (30.0 g, 0.22 mol), sodium carbonate (46.04 g, 0.43 mol), potassium iodide (7.21 g, 0.04 mol) and 1-chloro-2-ethoxyethane (58.95 g, 0.54 mol) were dissolved in DMF (Dimethylformamide, 150 g) and stirred for four hours at 13°C When the reaction completed and cooled to room temperature, methylene chloride (150 g) and distilled water (150 g) were added. The methylene chloride layer was separated from the aqueous layer, followed by drying with $MgSO_4$, anh., and filtered. Evaporation of the methylene chloride gave a 3,4-bis(2-ethoxyethoxy)benzaldehyde (compound **1**). Yield: 84%. $C_{15}H_{22}O_5$ Found C:62.68 H:7.03 O:27.65, Calculated C:63.81 H:7.85 O:28.33, MS 282.33(M+)

Asymmetrical benzoins (**3a–e**) were obtained by condensation reaction of compound **1** and corresponding aromatic aldehydes (**2a–e**). Under the presence of potassium cyanide (6.83 g, 0.10 mol) in 65% ethanol (30 g), compound **1** (20.0 g, 0.07 mol) and benzaldehyde (**2a**) (7.5 g, 0.07 mol) were stirred for four hours at room temperature. 2-(3,4-Bis(2-ethoxyethoxy)phenyl)-2-hydroxy-1-phenylethanone (**3a**) was extracted with methylene chloride (30 g) and obtained after drying ($MgSO_4$, anh.) and evaporation under reduced pressure of the methylene chloride solution. Other asymmetrical benzoins (**3b–e**) were obtained using the same procedure.

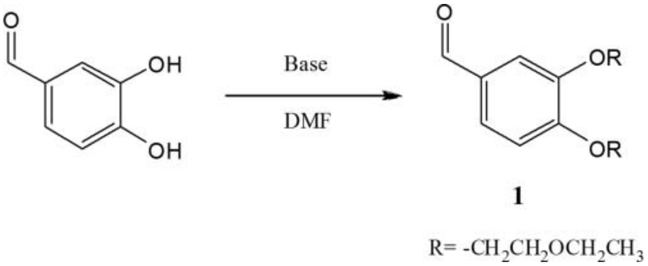

Figure 2. The synthetic method for compound **1**.

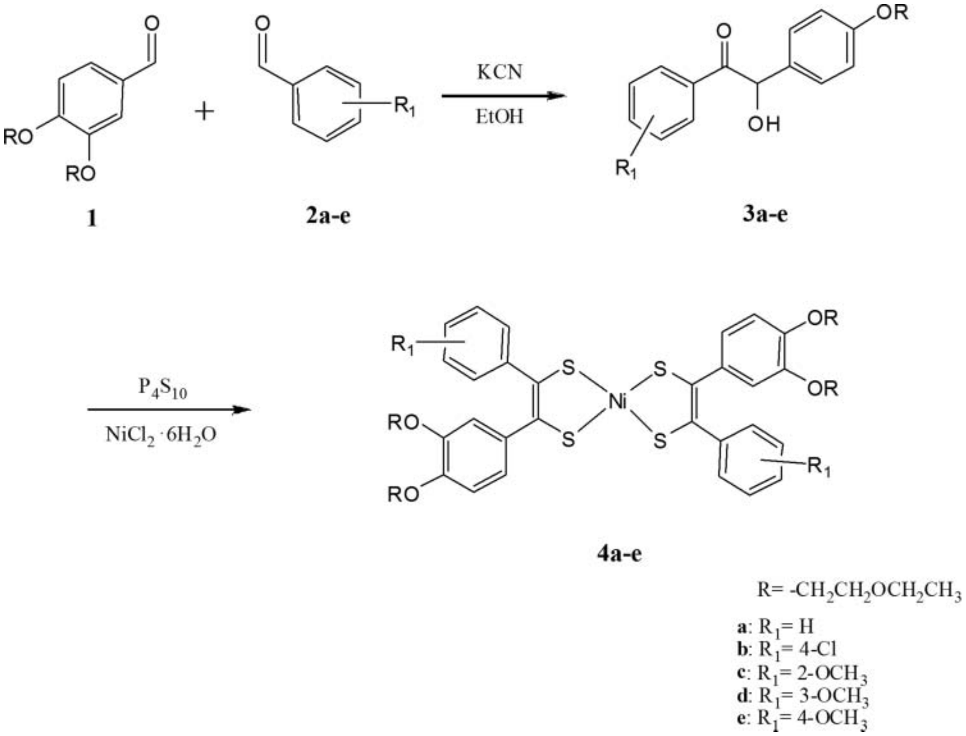

Figure 3. Synthetic scheme and the structures of the dyes **4a–e**.

3a Yield: 62%. $C_{22}H_{28}O_6$ Found C:67.93 H:7.13 O:24.11, Calculated C:68.02 H:7.27 O:24.71, MS 388.45(M+)

3b Yield: 71%. $C_{22}H_{27}ClO_6$ Found C:61.78 H:6.12 O:22.08, Calculated C:62.48 H:6.44 O:22.70, MS 422.90(M+)

3c Yield: 36%. $C_{23}H_{30}O_7$ Found C:67.08 H:7.14 O:25.14, Calculated C:66.01 H:7.23 O:26.76, MS 418.48(M+)

3d Yield: 40%. $C_{23}H_{30}O_7$ Found C:66.12 H:6.99 O:26.38, Calculated C:66.01 H:7.23 O:26.76, MS 418.48(M+)

3e Yield: 61%. $C_{23}H_{30}O_7$ Found C:65.13 H:7.22 O:26.58, Calculated C:66.01 H:7.23 O:26.76, MS 418.48(M+)

2-(3,4-Bis(2-ethoxyethoxy)phenyl)-2-hydroxy-1-phenylethanone (**3a**) (20.0g, 0.05 mol) and P_4S_{10} (7.32g, 0.02mol) were dissolved in dioxane (200g) and stirred for two hours at 60°C. Then, $NiCl_2{\cdot}6H_2O$ (8.31g, 0.04mol) was added uniformly at temperature of 110°C for three hours. Finally, bis(dithiobenzil) metal complex **4a** was obtained. Other bis(dithiobenzil) metal complexes (**4b–e**) were obtained via the same procedure. Prepared dyes were purified with a column chromatography with methylene chloride : methanol (25 : 1) as eluent.

4a Yield: 45%. $C_{44}H_{52}NiO_6S_4$ Found C:58.48 H:5.45 O:14.03, Calculated C:58.99 H:5.85 O:14.29, MS 895.83(M+), ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.10(s, 3H), 3.50(s, 2H), 3.79(s, 2H), 4.31(s, 2H), 6.94(m, 1H), 6.95(m, 1H), 6.99(m, 1H), 7.30(m, 1H), 7.45(m, 1H), 7.50(m, 1H)

4b Yield: 51%. $C_{44}H_{50}Cl_2NiO_8S_4$ Found C:53.98 H:5.12 O:13.98, Calculated C:54.78 H:5.22 O:13.27, MS 964.72(M+), ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.10(s, 3H), 3.50(s, 2H), 3.79(s, 2H), 4.31(s, 2H), 6.94(m, 1H), 6.95(m, 1H), 6.99(m, 1H), 7.49(m, 1H), 7.89(m, 1H)

4c Yield: 42%. $C_{46}H_{56}NiO_{10}S_4$ Found C:56.98 H:6.32 O:17.03, Calculated C:57.80 H:5.90 O:16.74, MS 955.88(M+), ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.10(s, 3H), 3.50(s, 2H), 3.79(s, 2H), 3.83(s, 3H), 4.31(s, 2H), 6.94(m, 1H), 6.95(m, 1H), 6.99(m, 1H), 7.01(m, 1H), 7.19(m, 1H), 7.39(m, 1H)

4d Yield: 44%. $C_{22}H_{27}ClO_6$ Found C:57.75 H:4.95 O:16.57, Calculated C:57.80 H:5.90 O:16.74, MS 955.88(M+), ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.10(s, 3H), 3.50(s, 2H), 3.79(s, 2H), 3.83(s, 3H), 4.31(s, 2H), 6.84(m, 1H), 6.94(m, 1H), 6.95(m, 1H), 7.05(m, 1H), 7.06(m, 1H), 7.64(m, 1H)

4e Yield: 49%. $C_{46}H_{56}NiO_{10}S_4$ Found C:57.16 H:5.95 O:17.02, Calculated C:57.80 H:5.90 O:16.74, MS 955.88(M+), ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.10(s, 3H), 3.50(s, 2H), 3.79(s, 2H), 3.83(s, 3H), 4.31(s, 2H), 6.94(m, 1H), 6.95(m, 1H), 6.99(m, 1H), 7.39(m, 1H)

Structural Analysis

Structural analysis of synthesized dyes were measured using an EA 1108 (E.A.) and an HP 6890 & Agilent 5973N MSD (GC-Mass). ^{1}H-NMR spectra were recorded at 25°C on a NMR 400-MHz spectrometer (Bruker, Germany) with $CDCl_3$ as a solvent.

UV-visible absorption spectra were obtained from a Shimadzu UV-2100.

Results and Discussion

The absorption maxima (λ_{max}) in the near infrared region of bis(dithiobenzil) metal complexes prepared are shown in Table 1. The absorption characteristic of these bis(dithiolene) metal complexes involves the interaction between the lowest unoccupied π molecular orbitals of the ligand and the occupied orbitals of the central metal. The light absorption in the near-infrared region is assigned to the first allowed π-π^* transition and involves molecular orbitals extending over the whole molecule [4]. The intensity of the absorption band in the near-infrared region of bis(dithiobenzil) metal complex, shown in Figure 1, was sensitive to substituents in the *para*, *ortho*, *meta*-position of phenyl group and is assigned to a π-π^* transition of ligands [5].

Table 1. Absorption maxima of the synthesized dyes **4a–e** and **BMC**

Dye number	λ_{max} (nm)
Unsubstituted **BMC**	855
4a	925
4b	906
4c	888
4d	906
4e	938

*Determined in CH_2Cl_2.

In the symmetrically substituted bis(dithiolene) metal complexes, the close linear relationship exists between the λ_{max} values and the Hammett modified substituent constants, $\sigma_p{}^+$, as shown in decreases of the absorption maxima in the order $OCH_3 < CH_3 < Cl$ [6].

In asymmetrically substituted bis(dithiolene) metal complexes **4a–e**, a non-linear relationship exists between the λ_{max} values and the Hammett substituent constants, σ_p. However, when $(\sigma_p(x) + \sigma_p(H))/2$ is used as a substituent constant for the asymmetric complexes then a linear relationship exists between the $\Delta\lambda_{max}$ values and the σ_p values for asymmetrically substituted bis(dithiolene) metal complexes.

As shown in Table 1, by comparison with unsubstituted **BMC**, the absorption maximum of dye **4a** shifted bathochromically (70 nm) which mainly due to the inductive effect exerted by electron donating substituents (ethoxyethoxy groups) in the *para*- and *meta*-position of the phenyl groups. In the case of dye **4b**, a hypsochromic shift (19 nm) was observed in comparison with that of dye **4a** which can be best explained by the presence of electron withdrawing group (4-chloro atom) at the *para*-position of phenyl ring leading to higher energy level of excited state of dye **4b**.

By the introduction of electron donating group (methoxy group) at *ortho*- or *meta*-position in the phenyl ring, the absorption maxima of dyes **4c** and **4d** were also blue shifted, 37 nm and 19 nm, respectively, which can be attributable to the steric hindrance effect leading to the decrease of conjugation efficiency between the phenyl ring and the chelate ring [7]. In contrast, the absorption maximum of **4e** containing a *para*-methoxy group was observed at 938nm which can be free from any steric hindrance. Therefore, it can be concluded that the position of substituent in the phenyl ring affects the absorption maximum due to its steric hindrance.

However, the bathochromic shift of 13 nm was found in dye **4e** which contains methoxy groups in the *para*-position of the phenyl ring, comparing to that of dye **4a**, indicating more efficient resonance effect arisen between the *para*-methoxy group and other π–electron systems in the dye molecule without a steric hindrance.

Assuming these results, it can be concluded that the presence of an electron donating group in the *para*-position of the phenyl ring can exert a bathochromic shift rather than *ortho*- or *meta*-position. In this case the absorption maximum can be obtained at 938 nm which seems to be very suitable for a NIR absorbing dye for optical filter of PDP.

Conclusions

In this work, five novel asymmetrical bis(dithiobenzil) metal complex dyes were prepared via asymmetric benzoin intermediates. The final yield of bis(dithiolene) metal complex dyes ranged in $42 \sim 51\%$.

The absorption maximum of dye **4a** shifted bathochromically (70 nm) which mainly due to the inductive effect exerted by electron donating substituents (ethoxyethoxy groups) in the *para*- and *meta*-position of the phenyl groups, whereas dye **4b** showed a hypsochromic shift (19 nm) in comparison with that of dye **4a** which can be explained by the presence of electron withdrawing group (4-chloro). However, steric hindrance on *ortho*-position of the phenyl ring for dye **4c** decreased the conjugation between the phenyl ring and the chelate ring leading to further hypsochromic shift. This steric hindrance can be exempt by the introduction of mehoxy group into the *para*-position of the phenyl ring for dye **4e** that absorbed maximally at 938 nm.

Acknowledgment

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