

The Synthesis and Absorption Character of New Bis (dithiobenzil) nickel Complex NIR Dyes

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Abstract: A series of new NIR dyes bearing 4-(4-morpholinyl) phenyl and substituted phenyl, were synthesized. The maximum absorption wavelengths of these dyes range from 928 nm to 990 nm.

Keywords: Synthesis, maximum absorption, bis(dithiobenzil) nickel complex, NIR dyes.

Bis(dithiobenzil) nickel complex compounds are an important group of metal complex dyes. Since the first synthesis by Schrauzer¹ and structural determination by X-ray analysis², many kinds of dithiolene metal complexes have been obtained. They absorb in the near infrared region, beyond about 700 nm, and have been widely used for the Q-switch dye laser^{3,4} in infrared absorbing films. Also they are used as antioxidants for polymers^{5,6}. As reported they are superior quenchers to prevent the photofading of dyes and the photodegradation of polymers^{7,8}.

The metal complex dyes have special superior singlet oxygen quenching effect⁹, and they have gained increasing attention of chemists in all fields. Herein, we reported the synthesis of eight new bis(dithiobenzil) nickel complexes and the effect of substituting groups in these complexes on their absorption spectra.

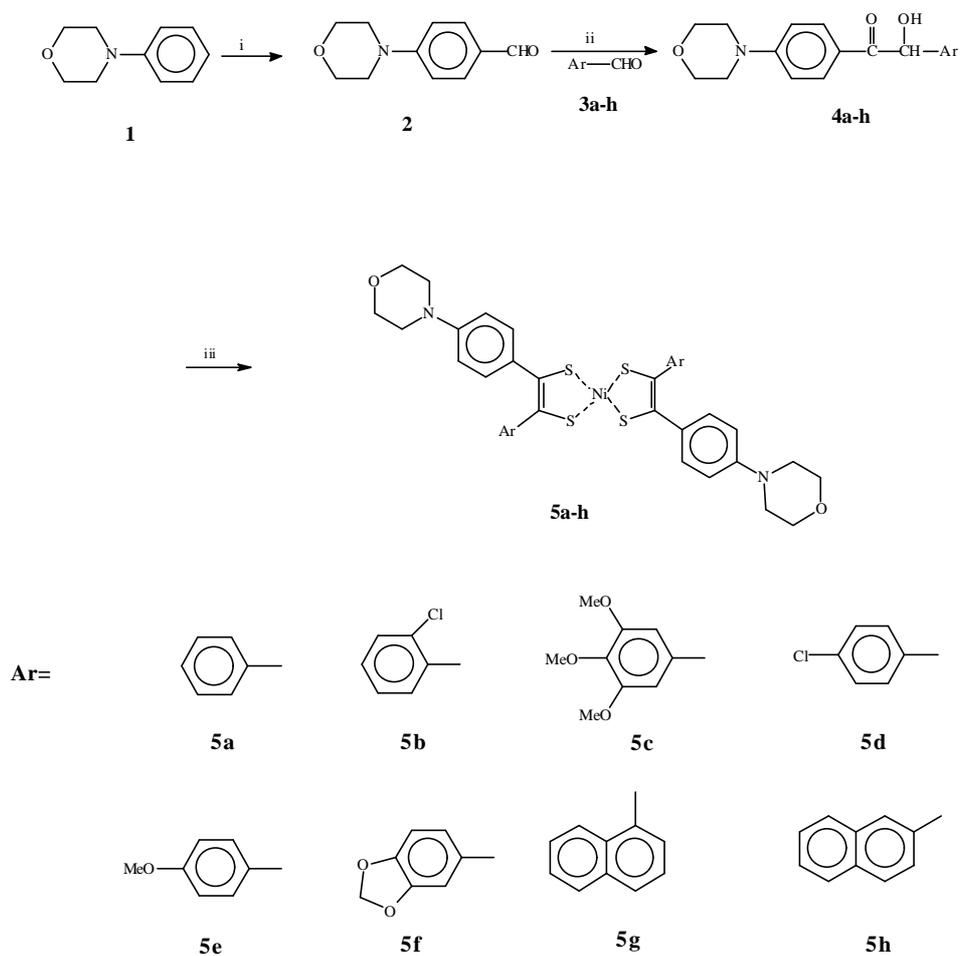
Our synthetic route was shown in **Scheme 1**. We selected 4-phenylmorpholine **1**¹⁰ as the starting material because morpholinyl group is a powerful electron-donating substituent. After a Vilsmeier reaction¹¹, we obtained 4-(4-morpholinyl) benzaldehyde **2** in good yield (81%). Then we prepared eight unsymmetrical benzoin **3a-h** by the benzoin condensation of eight different aromatic aldehydes **3a-h** with compound **2** in the presence of potassium cyanide in 95% ethanol. Treatment of benzoin **3a-h** with P₂S₅ and NiCl₂·6H₂O in 1,4-dioxane¹² afforded the desired complexes **5a-h** in yield over 30%. Furthermore complexes **5g** and **5h** bearing naphthyl groups have larger conjugation plane and their absorption maximum are supposed to have an obvious bathochromic shift. And introducing larger conjugation plane to the complex molecules is a very important part of our molecular design strategy.

The structures of complexes **5a-h** were confirmed by ¹HNMR¹³, MS, IR

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spectrometry and elemental analysis. The infrared spectra of complexes **5a-h** show C=C stretch at 1350 cm^{-1} , bands at 880 cm^{-1} suggest the presence of S-C-C bond. The absorption maximum¹⁴ and $\log \epsilon$ of complexes **5a-h** were shown in **Table 1**. Their spectra data were shown in **Table 2**.

Scheme 1



Reagents and conditions: i) DMF, POCl_3 , steam bath;
 ii) KCN, 95% ethanol, reflux;
 iii) P_2S_5 , 1, 4-dioxane, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, reflux.

Table 1 The UV absorption maximum of complex **5a-h**

5a-h	Ar	λ_{\max} (nm)	log ϵ
5a	Phenyl	982	4.45
5b	2-Chlorophenyl	950	4.40
5c	3, 4, 5-Trimethoxyphenyl	928	4.42
5d	4-Chlorophenyl	966	4.48
5e	4-Methoxyphenyl	983	4.43
5f	3, 4-(Methylenedioxy) phenyl	990	4.42
5g	1-Naphthyl	957	3.73
5h	2-Naphthyl	980	3.75

Table 2 The MS and elemental analysis data of complex **5a-h**

5a-h	MS (FAB)	Elemental Analysis					
		Found: (%)			Calcd: (%)		
		C	H	N	C	H	N
5a	713.3	60.17	4.78	3.86	60.59	4.80	3.93
5b	783.7	54.71	4.08	3.60	55.26	4.12	3.58
5c	893.6	56.02	5.11	3.20	56.44	5.19	3.13
5d	783.7	54.87	4.05	3.47	55.26	4.12	3.58
5e	773.5	59.20	4.87	3.70	58.99	4.95	3.62
5f	801.3	57.61	4.19	3.40	56.93	4.27	3.49
5g	813.1	64.85	4.65	3.40	64.94	4.71	3.44
5h	813.2	64.81	4.59	3.37	64.94	4.71	3.44

The formation of these dithiolene metal complexes involves the interaction between the lowest unoccupied 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 $\pi-\pi^*$ transition and involves molecular orbitals extending over the whole molecule¹⁵.

In general, ligands bearing electron donating groups or a larger conjugation plane can produce a bathochromic shift in absorption spectra^{16,17,18}. As shown in **Table 1**, while the introduction of 3, 4-methylenedioxy in the benzene rings of complex **5f** can produce a bathochromic shift, a hypsochromic shift is caused by 4-chloro atom in complex **5d** compared to complex **5a**. Though complex **5c** has three methoxy groups in benzene rings, the hypsochromic shift in complex **5c** may result from the steric repulsion between the two aryl rings, which makes it difficult to keep the planarity of molecule. The hypsochromic shift in **5b** compared to **5d** (about 16 nm) is caused by the interaction between the benzene ring and the chelate ring. The hypsochromic shift in **5g** compared to **5h** (about 23 nm), results from steric hindrance of naphthlene ring and chelate ring.

In conclusion, eight new near infrared complexes **5a-h** bearing morpholinyl group were synthesized and the effects of substituting groups and molecular structures on their absorption maximum were studied. The absorption maximum of the complexes is in the near-infrared region (over 900 nm).

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13. ¹HNMR (200MHz, CDCl₃) data of complex **5a**: δ 3.29 ppm (t, 8H, J = 4.31 Hz); 3.83 ppm (t, 8H, J = 4.48 Hz); 6.79 ppm (d, 4H, J = 8.80 Hz); 7.33 ppm (s, 10H); 7.86 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5b**: δ 3.28 ppm (t, 8H, J = 4.80 Hz); 3.82 ppm (t, 8H, J = 4.76 Hz); 6.84 ppm (d, 4H, J = 8.80 Hz); 7.22 ppm (m, 8H); 7.85 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5c**: δ 3.29 ppm (t, 8H, J = 4.40 Hz); 3.81 ppm (t, 8H, J = 4.76 Hz); 3.80 ppm (s, 18H); 6.54 ppm (s, 4H); 6.77 ppm (d, 4H, J = 8.80 Hz); 7.85 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5d**: δ 3.28 ppm (t, 8H, J = 4.80 Hz); 3.82 ppm (t, 8H, J = 4.76 Hz); 6.75 ppm (d, 4H, J = 8.80 Hz); 7.28 ppm (s, 8H); 7.82 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5e**: δ 3.28 ppm (t, 8H, J = 4.80 Hz); 3.83 ppm (t, 8H, J = 4.78 Hz); 3.77 ppm (s, 6H); 6.77 ppm (d, 4H, J = 8.80 Hz); 6.80 ppm (d, 4H, J = 8.80 Hz); 7.28 ppm (d, 4H, J = 8.80 Hz); 7.87 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5f**: δ 3.29 ppm (t, 8H, J = 4.31 Hz); 3.83 ppm (t, 8H, J = 4.48 Hz); 5.91 ppm (s, 4H); 6.78 ppm (m, 6H); 6.80 ppm (d, 4H, J = 8.80 Hz); 7.85 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5g**: δ 3.29 ppm (t, 8H, J = 4.31 Hz); 3.83 ppm (t, 8H, J = 4.48 Hz); 6.79 ppm (d, 4H, J = 8.80 Hz); 7.33 ppm (s, 14H); 7.86 ppm (d, 4H, J = 8.80 Hz).
¹HNMR data of complex **5h**: δ 3.29 ppm (t, 8H, J = 4.31 Hz); 3.84 ppm (t, 8H, J = 4.48 Hz); 6.79 ppm (d, 4H, J = 8.80 Hz); 7.35 ppm (s, 14H); 7.86 ppm (d, 4H, J = 8.80 Hz).
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