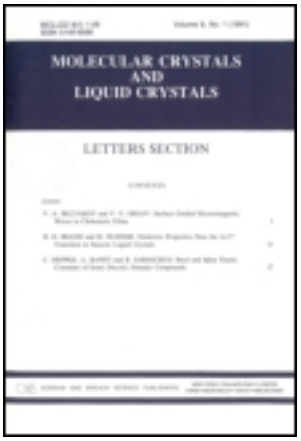

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The Synthesis and Characterizations of Thermally-Stable Yellow Metal Complex Dyes for LCD Color Filters

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Eight kinds of yellow metal (III) complex azo dyes were synthesized using different diazo component, coupling component and metal ion. The effect on the thermal stability of the synthesized dyes by azo ligand with two different functional groups, alcohol and carboxylic acid, was studied.

The characteristics of the synthesized dyes were examined by their absorption maxima, thermal stability by a thermogravimetric analysis (TGA), and the chromatic characteristics of the fabricated films were measured. It was also explained that the effect of functional groups on the thermal stability of the dyes as well as their chromaticity values.

Keywords Absorption maximum; chromaticity diagram; color filter; metal complex dye; thermal stability

Introduction

The metal complexes of azo compounds containing two coordinating groups present in ortho positions in such a way as to form two annelated chelate rings with the metal ions (especially the complexes with copper(III) cobalt(III) and chromium(III)), have been used as pigments, paints and other coloring materials [1]. Yellow-orange dyes are used in color filters most widely, both as absorbing agents in cutting filters and as additives to blue, green, and red dyes for suppressing "parasitic" transmission in the blue range. Such dyes include monoazo dyes derived from five-membered heterocyclic rings: such as pyrazole, thiophene, furan, etc [2–5].

The LCD has become an important display device in mobiles, monitors and high-definition televisions, which requires high resolution and color properties for big screen size [6–9]. The LCD color filter consists of red, green, and blue color pixels that can

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be manufactured by a photolithographic process using photo resists containing polymeric binder, dispersant and corresponding pigments.

In these days, ink-jet printing method using conventional pigment-based inks has been studied to simplify the complicated process and to reduce manufacturing cost of LCD color filters. However, this method has the limitation due to the blocking of ink-jet nozzles as well as low chromatic properties of pigment particles. In order to solve these problems, an ink-jet printing method where dyes are used for higher solubility and superior color saturation property has been proposed as an alternative way.

In particular, metal-azo complexes are one of the important molecules can improve thermal stability of organic dyes, therefore have attracted much attention in both academic and applied research [10–11].

This paper builds on the aforementioned study, reporting work in which eight new dyes have been synthesized (see Fig. 1,2) and characterized using an elemental analysis. The absorption characteristics and chromatic values of the synthesized dyes have been also investigated. Thermal stability of the dyes has been determined by a thermogravimetric analysis (TGA), comparing with that of C. I. Pigment Yellow 150 (see Fig. 3).

Experimental

Dye Synthesis

The diazo component (4-aminoantipyrine, 0.0049 mol) was added to a solution of concentrated hydrochloric acid (35%, 20 ml). The mixture was stirred for 5 hr at room temperature then was cooled to 5°C. Sodium nitrite (97%, 0.0049 mol) was added to the mixture above portionwise at 5–10°C and then stirred for 2 hours at the same temperature with regular checking by Thin Layer Chromatography (TLC) (stationary phase : silica gel, mobile phase : n-hexane/EtOAc = 1/2). The resulting solution was used immediately in the following coupling reaction. The coupling component (3-aminophenol, 0.0049 mol) was dissolved in water (30 ml) and sodium hydroxide solution (25%, 10 ml) and then cooled to 0–5°C by the addition of ice. The diazonium solution previously prepared was added dropwise over 30 min at the same temperature. The mixture was stirred for a further 3 hours at 5–10°C and then aqueous sodium hydroxide solution (25%) was added slowly below 10°C until the pH rose to within the range of 7–8. The precipitated product was filtered off, washed with water until the filtrate was pH 6–7 and dried at 70–75°C. The crude dyes were purified by recrystallization from ethanol. The resulting ligand (0.0031 mol) was dissolved in 20ml of ethanol together with sodium carbonate(0.0047 mol). After heating up to reflux, the chromium(III) acetate hydroxide (0.00156 mol) was added portionwise under vigorous stirring, whereupon a suspension of the chromium(III) complex dye formed. The precipitated solid was collected by filtration, then washed with water and then vacuum dried to obtain the chromium(III)-azo complex. The crude dyes were purified by recrystallization from ethanol. The filtered solid was dried under vacuum to obtain dye **1a** in 48% yield.

Other dyes were obtained by same procedure except reaction time (2hours for dyes **3a–3d**).

Dye **1a** 48% Yield : 48%, $C_{34}H_{34}CrN_{10}O_4$ ^{1}H NMR($CDCl_3$), δ: 2.26(s, 3H), 3.11(s, 3H), 5.04(s, 1H), 5.59(s, 2H), 6.14(s, 1H), 6.19(d, 1H), 6.90(t, 1H), 6.91(d, 1H), 7.12(d,1H), 7.37(t, 1H). Found C:59.26 H:5.02 Cr:7.87 N:21.59 O:9.21 Calculated C: 58.45, H: 4.90, Cr:7.44, N:20.05, O: 9.16, MS 670.69(M+).

Dye **1b** Yield : 51%, $C_{38}H_{42}CrN_{10}O_4$ ^{1}H NMR($CDCl_3$), δ: 2.26(s, 3H), 3.06(s, 3H), 3.11(s, 3H), 5.04(s, 1H), 6.27(s, 1H), 6.32(d, 1H), 6.90(t, 1H), 6.91(d, 1H), 7.12(d,1H),

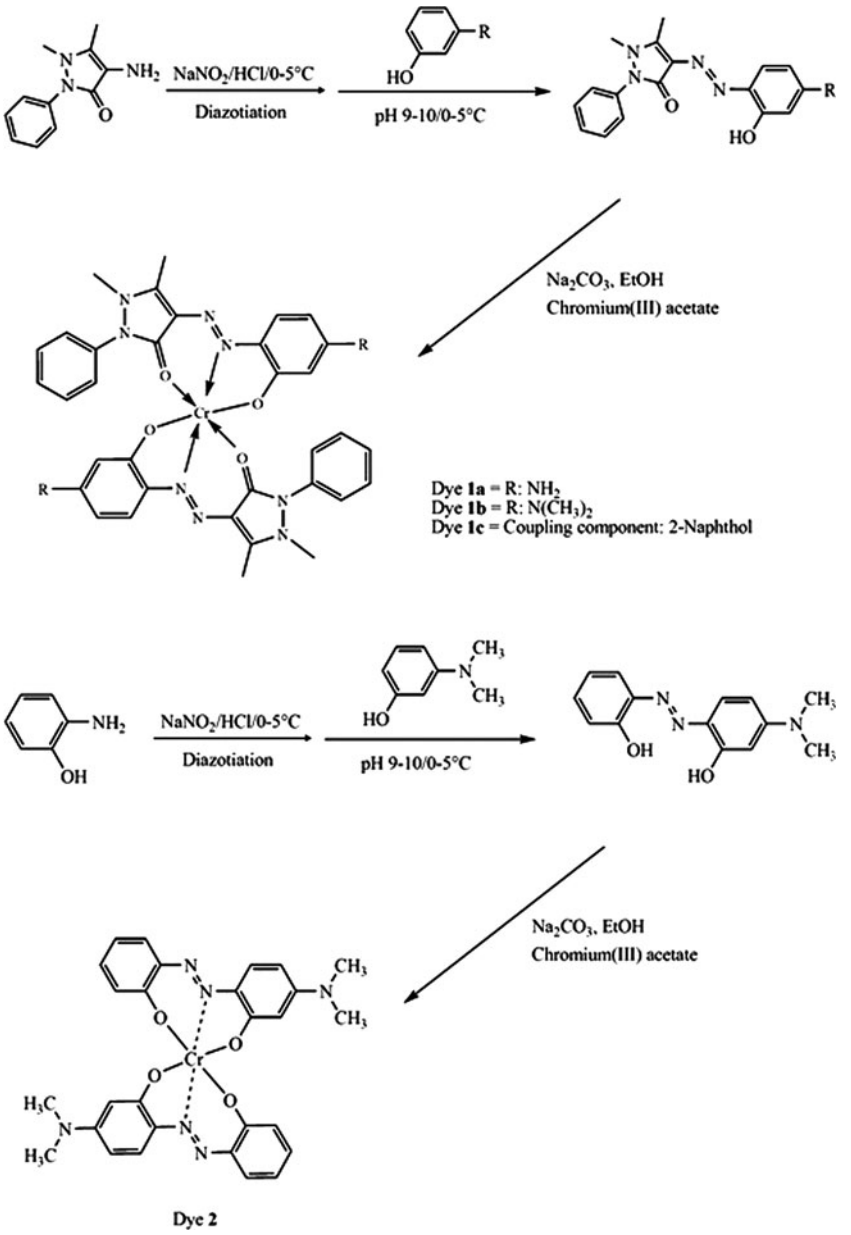

Figure 1. Synthetic scheme of the dye 1a-2.

7.37(t, 1H). Found C:60.87 H:6.11 Cr:6.99 N:19.14 O:9.07 Calculated C, 60.47, H:5.61, Cr:6.89, N:18.56; O, 8.48, MS 755.8 (M+).

Dye **1c** Yield : 43%, $C_{42}H_{36}CrN_{18}O_4$ ^{1}H NMR($CDCl_3$), δ: 2.26(s, 3H), 3.11(s, 3H), 5.04(s, 1H), 6.90(t, 1H), 6.98(d, 1H), 7.12(d,1H), 7.37(t, 1H), 7.37(t, 1H), 7.44(t, 1H), 7.53(t, 1H), 8.04(d,1H), 8.07(d,1H). Found C:65.77 H:4.21 Cr:7.31 N:13.98 O:9.54 Calculated C: 65.62, H: 4.72 Cr:6.76, N: 14.58, O: 8.32, MS 767.7 (M+).

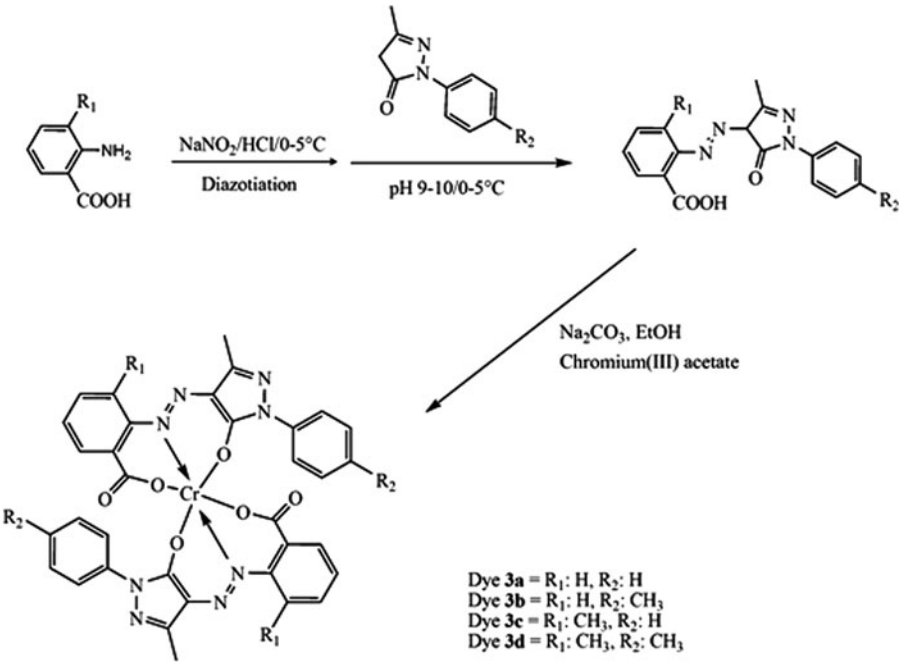

Figure 2. Synthetic scheme of the dye 3a-3d.

Dye **2** Yield : 42%, $C_{28}H_{26}CrN_6O_4$ ^{1}H NMR($CDCl_3$), δ: 3.06(s, 3H), 6.47(s, 1H), 6.52(d, 1H), 7.15(d, 1H), 7.21(t, 1H), 7.48(t, 1H), 7.83(d, 1H). Found C:60.02 H:4.85 Cr:10.35 N:15.14 O:12.04 Calculated C: 59.78, H: 4.66, Cr:9.24, N: 14.94, O:11.38, MS 563.5 (M+).

Dye **3a** Yield : 39%, $C_{34}H_{26}CrN_8O_6$ ^{1}H NMR($CDCl_3$), δ: 2.34(s, 3H), 7.45(t, 1H), 7.54(d,1H), 7.58(t, 1H), 7.62(d, 1H), 7.79(t, 1H), 8.09(t, 1H), 8.21(d, 1H). Found C:59.23 H:3.96 Cr:7.84 N:16.84 O:14.52 Calculated C:58.79, H: 3.77, Cr:7.49, N: 16.13, O: 13.82, MS 695.6 (M+).

Dye **3b** Yield : 38%, $C_{36}H_{30}CrN_8O_6$ ^{1}H NMR($CDCl_3$), δ: 2.34(s, 3H), 7.50(d, 1H), 7.54(d,1H), 7.79(t, 1H), 8.09(t, 1H), 8.21(d, 1H). Found C:60.13 H:4.81 Cr:7.54 N:15.41 O:13.97 Calculated C: 59.83, H: 4.18, Cr:7.20, N: 15.51, O: 13.28, MS 723.6 (M+).

Dye **3c** Yield : 38%, $C_{38}H_{34}CrN_8O_6$ ^{1}H NMR($CDCl_3$), δ: 2.34(s, 3H), 7.40(t, 1H), 7.45(t,1H), 7.57(d, 1H), 7.58(t, 1H), 7.62(d, 1H), 8.02(d, 1H). Found C:60.34 H:4.51

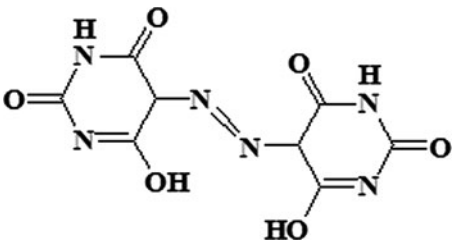

Figure 3. Structure of C. I. Pigment Yellow 150.

Cr:7.48 N:15.74 O:14.02 Calculated C: 59.83, H: 4.18, Cr:7.20,N: 15.51, O: 13.28, MS 723.1 (M+).

Dye **3d** Yield : 41%, $C_{38}H_{34}CrN_8O_6$ ^{1}H NMR($CDCl_3$), δ: 2.34(s, 3H), 7.40(t, 1H), 7.42(d,1H), 7.50(d, 1H), 7.57(d, 1H), 8.02(d, 1H). Found C:60.93 H:5.01 Cr:7.17 N:15.18 O:13.37 Calculated C: 60.80, H: 4.56, Cr:6.93, N: 14.93, O: 12.79, MS 751.7 (M+).

Structural Analysis

Structural analysis of synthesized dyes were measured using an EA 1108 (E.A.) and an HP 6890 & Agilent 5973N MSD (GC-Mass). UV-visible absorption spectra were obtained from a Shimadzu UV-2100. The data of the color properties and transmittance spectra were measured using an MCPD 3700. Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10°C min^{-1} with a Seiko TG/DTA 320 & a SSC 5200H Disk Station.

Fabrication of Color Filter

In order to measure optical characteristics and thermal stability, spin-coating was carried out onto glass using a MIDAS System SPIN-1200D spin-coater. The glass was spun at a low to moderate speed of 300 rpm for 10 seconds to evenly spread the solution (dye-based ink). The solution was prepared with synthesized dyes, a solvent (1-Methyl-2-pyrrolidone) and a binder based on acrylate. Once spin-coating was completed, the film was placed quickly onto a hot plate (heated to around 100°C) for 5 minutes to evaporate the solvent.

Thermal Stability Test as Color Filter

The thermal stability of synthesized dyes after fabrication was measured by pre-baking at 100°C for 5 min and post-baking at 250°C for 60 min, then color differences in ΔE_{ab} were determined using an MCPD 3700.

Results and Discussion

As shown in Figs. 1, 2, eight dyes have been prepared by diazotization and coupling reactions and followed by complexation of ligands. All diazo components were sufficiently basic to enable straightforward diazotization using by aqueous sodium nitrite in dilute hydrochloric acid. Coupling reaction was carried out by the addition of the diazonium salt previously prepared to coupler solutions at 0–5°C. Thereafter the resulting ligand was dissolved in ethanol together with sodium carbonate. After heating up to reflux, the chromium(III) acetate hydroxide was added portionwise under vigorous stirring, whereupon a suspension of the chromium(III) complex dye results.

The precipitated solid was collected by filtration, washed with water and then vacuum dried to obtain the chromium(III)-azo complex. After separation, the final yield of products ranged in 38 $\sim$ 51%. The general synthetic procedure is described in Experimental Section.

UV-VIS spectra of azo dyes are generally affected by their chemical structures such as chromophores, substituted groups, number of azo groups, metal ions, pH values, solvents and so on [12–15]. Comparisons of absorption maximum (λ_{max}) of C. I. Pigment Yellow 150, precursor dyes, and synthesized dyes **1a–3d** are listed in Table 1. The spectra of synthesized dyes **1a–3d** were shown in Figs. 4–5. All synthesized dyes showed similar or higher wavelength compared with C. I. Pigment Yellow 150 that was measured to be

Table 1. Absorption maxima (λ_{max}) of the synthesized dyes **1a–3d** and C. I. Pigment Yellow 150

Dye number	Precursor dye λ_{max} (nm)	Metal complex dye λ_{max} (nm)
C. I. Pigment Yellow 150	—	430
1a	435	482
1b	455	517
1c	452	535
2	471	537
3a	391	441
3b	389	442
3c	388	434
3d	385	433

Determined in N-Methyl-2-pyrrolidone (NMP)

430 nm in 1-methyl-2-pyrrolidone. The precursor dyes **1a–1c** and dye **2** that contain a hydroxy group in the *ortho*-positions of azo bond exhibited λ_{max} in the range of 435 ~ 471 nm, whereas corresponding precursor dyes **3a–3d** containing a carboxylic acid group in the *ortho*-position exhibited λ_{max} in the range of 385 ~ 391 nm in 1-methyl-2-pyrrolidone.

Absorption maxima (λ_{max}) of precursor dyes **1a–2** containing a hydroxy group are much higher than those of the corresponding precursor dyes **3a–3d** containing a carboxylic acid group, which can be mainly attributable for the electron donating effect of hydroxy group in *ortho* or *para* position of azo group leading to π electrons are easily moveable so that $\pi \rightarrow \pi^*$ transition exerted easier and absorption maximum shifts to higher wavelength.

After metal complexation reaction, Some dyes **1a–1c** and dye **2** that contain a hydroxy group in the *ortho*-positions of azo bond exhibited λ_{max} in the range of 482~537 nm,

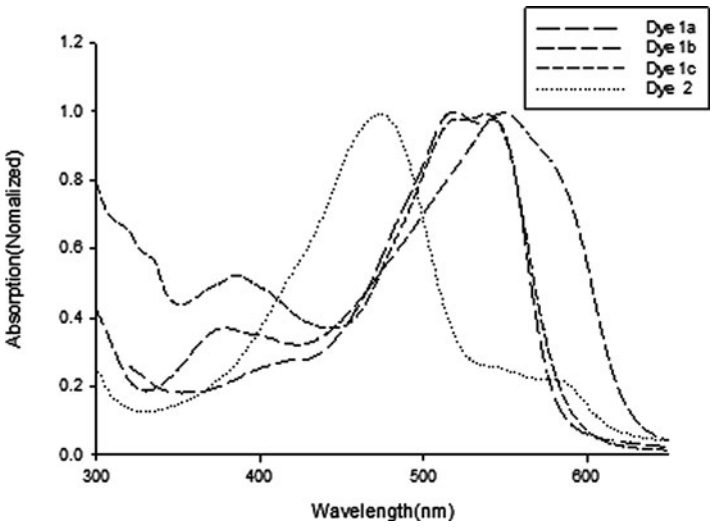

Figure 4. UV-VIS Spectra of the synthesized dyes 1a-2 in NMP.

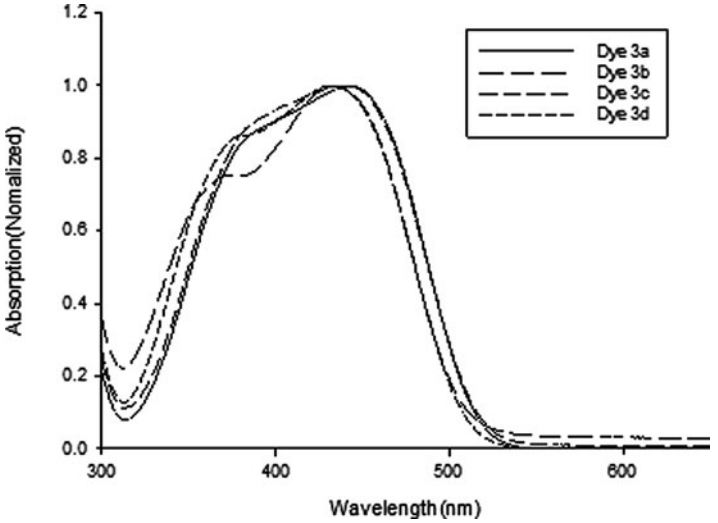

Figure 5. UV-VIS Spectra of the synthesized dyes 3a-3d in NMP.

whereas the corresponding dyes **3a–3d** containing a carboxyl group in the *ortho*-position exhibited λ_{max} in the range of 433 $\sim$ 442 nm in 1-methyl-2-pyrrolidone.

These results can be explained by the formation of ligands by metal ion which connected with the oxygen atom of hydroxy group led to the oxygen atom to be easier to give nonbonded electrons to π -electron system, which attributes to the red shift of absorption maximum of the azo ligand. This can be increased with the increasing of the positive electricity ability of metal ion. It can also probably arose from the energy change of the intense $\pi \rightarrow \pi^*$ transition of the conjugated chromophore due to the chelation between metal ions and azo ligand [16–17].

Table 2. Chromaticity diagram (x,y) of the synthesized dyes **1a–3d** and C. I. Pigment Yellow 150

	Chromaticity diagram	
Dye number	x	y
C. I. Pigment Yellow 150	0.421	0.494
1a	0.401	0.289
1b	0.435	0.273
1c	0.448	0.345
2	0.412	0.263
3a	0.406	0.489
3b	0.347	0.372
3c	0.407	0.426
3d	0.412	0.452

Determined in N-Methyl-2-pyrrolidone (NMP).

Table 3. Weight reduction of dyes **1a–3d** and C. I. Pigment Yellow 150 at different temperature measured by TGA

	Weight (%)	
Dye number	200°C	250°C
C. I. Pigment Yellow 150	97.97	97.01
1a	94.25	92.81
1b	97.83	97.45
1c	97.09	94.85
2	95.11	93.62
3a	99.50	99.24
3b	98.87	98.57
3c	98.62	98.32
3d	98.97	98.61

In terms of chromaticity diagram of the synthesized dyes, all dyes exhibited lower y values than that of C. I. Pigment Yellow 150, as shown in Table 2, where the chromaticity diagram of dyes **3a** and **3d** showed comparatively closer y values to that of C. I. Pigment Yellow 150 compared to other dyes. The same trend was also found in x values of dyes **3a** and **3d**. By comparing the y values between dyes containing a hydroxy group and corresponding dyes containing a carboxylic acid group, higher values were observed with dye **3a** and dye **3d**. Therefore, it can be concluded that, in this series, dye **3a** features in similar color properties compared to that of the conventional C. I. Pigment Yellow 150.

Thermal stability of the colorants used for the fabrication of color filter is one of the crucial requirements to fulfill the post baking process which is generally carried out at 220°C, therefore the weight reduction of colorant should be as small as possible at 200 ∼ 250°C by TGA [18–19].

As shown in Table 3, weight reduction of C. I. Pigment Yellow 150 was 2.99% at 250°C, whereas synthesized dyes **1a–3d** reduced in the range of 0.76∼6.38% at the same temperature.

Table 4. Color difference in ΔE_{ab} of synthesized dyes after post-baking at 250°C for 60 min

Dye number	ΔE_{ab}
C. I. Pigment Yellow 150	<3
1a	28.1
1b	26.7
1c	9.4
2	21.4
3a	2.5
3b	2.1
3c	4.2
3d	3.8

Dye **3a–3d** containing a carboxyl group exhibited the range of 0.76∼1.68% of weight reduction which seemed to be slightly higher than that of C. I. Pigment Yellow 150.

As an alternative method to determine the thermal stability of dyes, the color difference measured in ΔE_{ab} value after fabrication process was carried out, as shown in Table 4. In terms of ΔE_{ab} value of synthesized dyes, higher color difference (9.4∼28.1) was found with dyes **1a- 2** containing a hydroxy group in metal complex dye those also showed higher weight reduction by TGA, whereas much smaller ΔE_{ab} values (2.1∼3.8) observed for the dyes **3a-3d** containing a carboxyl group in metal complex dye those also showed lower weight reduction by TGA, as mentioned above.

The resultant higher stability of the metal complex dyes based on carboxylic acid groups over those of corresponding hydroxy groups is probably due to the existence of resonance forms in which the negative charge is delocalized over two equivalent oxygen atoms. Since a carboxylate ion is more stable than a hydroxide ion, it is lower in energy and more highly favored in the formation of metal complex.

However, in commercial study, the compatibility of dyes with other additives used for the formulation of photo-resist systems should be optimized by a trial error considering with photo-initiator, monomer, cell stabilizer, binders.

Conclusions

Eight metal complex dyes were prepared via diazotization and coupling reactions followed by a metal complexation reaction. Absorption maxima (λ_{max}) of dyes containing a hydroxy group in the *ortho*-positions of azo bond consistently exhibited a bathochromic shift compared to the corresponding dyes containing a carboxyl group in the *ortho*-position.

The thermal stability of synthesized dyes were examined by both TGA analysis and ΔE_{ab} values after fabrication process. Except three dyes, by TGA, smaller weight reduction was observed with other five dyes compared to that of C. I. Pigment Yellow 150. The synthesized dyes prepared from precursor dyes containing a carboxylic acid group exhibited higher thermal stability in ΔE_{ab} values in comparison with that of the corresponding dyes containing hydroxy groups.

Therefore, it can be clearly concluded that some dyes **3a–3d** could be used as an alternative component to replace the conventional yellow pigment to increase the contrast ratio and the transmittance for the fabrication of LCD color filter.

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