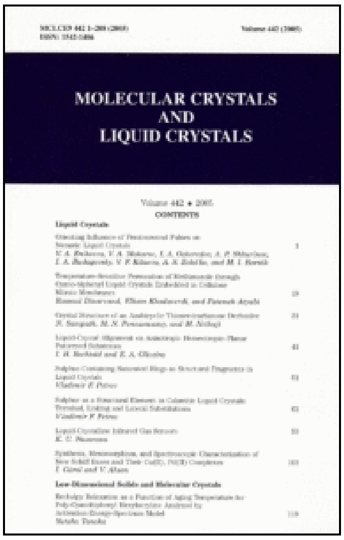

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Synthesis of New Metal Complex Derivatives Based on Azo, Naphthol and Pyrazole Moieties for Color Filter Pigments

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Four Cr and Co based metal complex derivatives for new violet and red color filters were first synthesized by using naphthol and pyrazole groups as well as azo moiety. The UV-visible maximum values of $Co(HPANT)_2$ *and* $Cr(HPANT)_2$*, the naphthol derivatives, were 560 and 561 nm respectively in solution state where both were violet colored solids.* $Co(HPAPMP)_2$ *and* $Cr(HPAPMP)_2$*, the pyrazole derivatives also showed UV-visible maximum values of 465 and 510 nm respectively in solution state, indicating brown and red colored solids. And all these compounds exhibited better clear colors based on higher molar extinction coefficient value compared to the commercial pigments.*

Keywords Azo group; color filter; metal-azo complex; pigment

Introduction

In the past, dyes and pigments were used in general fields like paint, ink, plastic and fabric [1–3]. However, as the display industry has rapidly developed, dyes and pigments have been widely used as core materials of color filter (CF), which is used to make full color in liquid crystal display (LCD). In CF of LCD, the role of dyes and pigments is to express full color by reflecting or absorbing light at specific wavelengths when white-backlight is passing through [4–6]. Therefore, optical characteristics of pigments used in CF must allow light with specific wavelength to pass through and filter remaining wavelengths to the best possible extent. Such pigments are thus required to have specific absorption spectrum and high molar extinction coefficient [7]. Moreover, similar color filter materials are required for image sensors widely being used in charge-coupled device (CCD) cameras and web-cameras [7]. Accordingly, there is a demand for development of new pigment materials to be

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used. This study focuses on the combination of azo group and pyrazole or naphthol group in cobalt and chrome metals for development of new materials.

Azo (–N=N–) has high molar extinction coefficient and can obtain broad range of colors through introduction of diverse aromatic groups using a simple coupling synthesis, resulting in an advantage of realizing diverse colors [8–11]. As an advantage of material system, creation of metal-azo complexes using metallization can adjust absorption wavelength by metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT) [12–15].

In the previous paper, H. Kocaokutgen *et al.* reported the 1-(2-hydroxy-4-methylphenylazo)-2-naphthol [16]. In this study, in order to increase molecular interaction we remove methyl group at para-position of naphthol group as similar chemical structure. The chemical structure removed methyl group is considered as the increased planarity of chemical structure and molecular interaction.

In this report, four pigments for color filter were newly synthesized by synthesizing new azo derivatives which include aromatic groups of naphthol and pyrazole and performing metallization on cobalt ion and chrome ion. UV-visible absorption spectra of synthesized materials were measured with changes in aromatic groups and metal ions to verify changes in absorption property according to pigment structure.

Experimental

Synthesis

1) Synthesis of 1-(2-Hydroxy phenylazo)-2-naphthol (HPANT). 2-Aminophenol (50 mmol, 5.51 g) was mixed with hydrochloric acid (150 mmol, 13 ml) in distilled water (100 ml) and diazotized below 5°C with sodium nitrite (55 mmol, 3.94 g). After stirring for 1 h, 2-naphthol (50 mmol, 7.21 g) was dissolved in 0.1 M sodium hydroxide solution (10 ml) and cooled to 0 to 5°C in an ice bath. Then the above diazo salt solution was stirred into the coupling component solution. The mixture was stirred for 2 h and then filtered. The solid was washed with to of water and recrystallized with ethanol. (7.73 g Yield: 58%).

^{1}H-NMR (300 MHz, Acetone-d$_6$) δ (ppm): 8.52 (d, 1H), 8.00 (d, 1H) 7.97 (d, 1H) 7.76 (d, 1H) 7.64 (d, 1H) 7.59 (t, 1H), 7.43 (t, 1H) 7.16 (t, 1H) 7.01 (q, 2H) 6.85 (d, 1H) FT-IR (KBr cm^{-1}): 3060, 1614, 1567, 1465, 1411, 1299, 1272, 1240, 1213, 1151, 819, 752.

2) Synthesis of 4-(2-Hydroxy phenylazo)-1-phenyl-3-methyl-5-pyrazolone (HPAPMP). 2-Aminophenol (46.3 mmol, 5.0 g) was mixed with hydrochloric acid (138.9 mmol, 8.90 ml) in distilled water (100 ml) and diazotized below 5°C with sodium nitrite (50.963 mmol, 3.623 g). After stirring for 1 h, 3-methyl-1-pyrazolone (46.3 mmol, 7.663 g) was dissolved in 0.1 M sodium hydroxide solution (10 ml) and cooled to 0 to 5°C in an ice bath. Then the above diazo salt solution was stirred into the coupling component solution. The mixture was stirred for 2 h and then filtered. The solid was washed with to of water and recrystallized with ethanol (5.16 g Yield: 38%).

^{1}H-NMR (300 MHz, DMSO-d$_6$) δ (ppm): 13.61 (s, 1H), 10.65 (s, 1H), 7.66 (d, 2H), 7.48 (d, 1H), 7.24 (t, 2H), 7.11 (t, 1H), 7.06 (t, 1H), 6.95 (m, 2H), 2.32 (s, 3H) FT-IR (KBr cm^{-1}): 3353, 1654, 1587, 1546, 1469, 1427, 1349, 1313, 1278, 1145, 1076, 1006, 952, 869, 754.

3) Synthesis of Cobalt-Azo Complex. A solution of cobalt sulfate (1.89 mmol, 0.49 g) and sodium acetate (0.1 g) in 5 ml of DMF was added to a magnetically stirred suspension of the azo compounds (7.56 mmol, 2.0 g) in DMF (10 ml). After the mixture was refluxed for 4 h. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The mixture powder was separated by using column chromatography with ethyl acetate.

Bis(1-(2-hydroxy phenylazo)-2-naphthol) cobalt ($Co(HPANT)_2$). (2.59 g, Yield: 58%) ^{1}H-NMR (300 MHz, Acetone-d_6) δ (ppm): 9.06 (d, 1H), 8.65 (d, 1H) 7.9758 (m, 2H) 7.40 (d, 1H) 7.22 (t, 1H) 6.99 (t, 1H), 6.79 (t, 1H) 6.68 (t, 1H) 6.58 (d, 1H). FT-IR (KBr cm^{-1}): 3401, 1614, 1589, 1544, 1496, 1467, 1384, 1349, 1315, 1276, 1211, 1178, 1145, 1093, 995, 823, 748. FAB-Mass: 583 m/z.

Bis(1-(2-hydroxyphenylazo)-1-phenyl-3-methyl-5-pyrazololne) cobalt ($Co(HPAPMP)_2$). (2.55 g, Yield: 40%) ^{1}H-NMR (300 MHz, Acetone-d_6) δ(ppm): 8.33 (d, 1H), 7.68 (d, 2H), 7.12 (t, 2H), 6.95 (t, 1H), 6.87 (t, 1H), 6.58 (t, 2H), 2.58 (s, 3H). FT-IR (KBr cm^{-1}): 3357, 1587, 1471, 1347, 1311, 1276, 1213, 1145, 1676, 1006, 954, 848, 800, 754. FAB-Mass 645 m/z.

4) Synthesis of Chrom-Azo Complex. A solution of chrome sulfate (1.89 mmol, 2.96 g) and sodium acetate (0.1 g) in 5 ml of DMF was added to a magnetically stirred suspension of the azo compounds (7.56 mmol, 2.0 g) in DMF (10 ml). After the mixture was refluxed for 4 h. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The mixture powder was separated by using column chromatography with ethyl acetate.

Bis(1-(2-hydroxy phenylazo)-2-naphthol) chrome ($Cr(HPANT)_2$). (2.54 g, Yield: 48%). FT-IR (KBr cm^{-1}): 3407, 1662, 1590, 1544, 1498, 1465, 1346, 1309, 1272, 1205, 1178, 1145, 1097, 995, 916, 829, 752. FAB-Mass: 577 m/z.

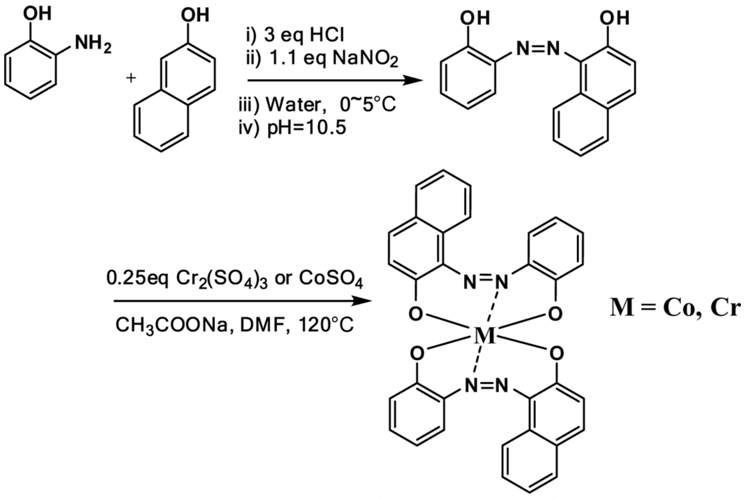
Bis(1-(2-hydroxyphenylazo)-1-phenyl-3-methyl-5-pyrazololne) chrome ($Cr(HPAPMP)_2$). (2.52 g, Yield: 42%) FT-IR (KBr cm^{-1}): 3390, 1656, 1550, 1467, 1340, 1272, 1207, 1170, 1147, 1056, 1004, 842, 752 FAB-Mass: 637 m/z.

Measurements

^{1}H-NMR spectra were recorded on Bruker, Advance-300 and Fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer.

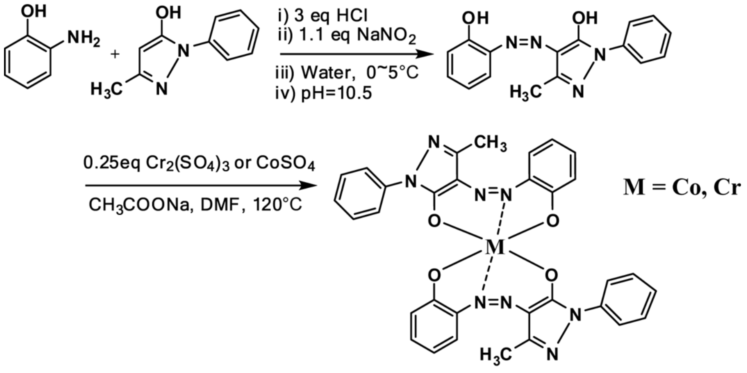
Results and Discussion

Schemes 1–3 are structural formula and synthetic scheme of naphthol and pyrazole derivatives, $Co(HPANT)_2$, $Cr(HPANT)_2$, $Co(HPAPMP)_2$, and $Cr(HPAPMP)_2$ as well as commercial pigments. After synthesizing ligand through azo coupling reaction, Co or Cr complex including azo group can be synthesized by adding cobalt (Co) sulfate or chrome (Cr) sulfate under basic condition. In addition, pyrazole derivatives, $Co(HPAPMP)_2$ and $Cr(HPAPMP)_2$ were synthesized by azo coupling reaction and similar metal-ligand reaction [17].



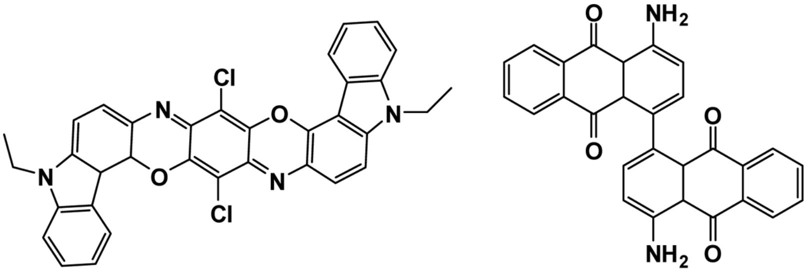
Co(HPANT)$_2$ or Cr(HPANT)$_2$

Scheme 1. Synthetic route of naphthol derivatives.



Co(HPAPMP)$_2$ or Cr(HPAPMP)$_2$

Scheme 2. Synthetic route of pyrazole derivatives.



Pigment Violet 23 **Pigment Red 177**

Scheme 3. Structure of commercial pigments.

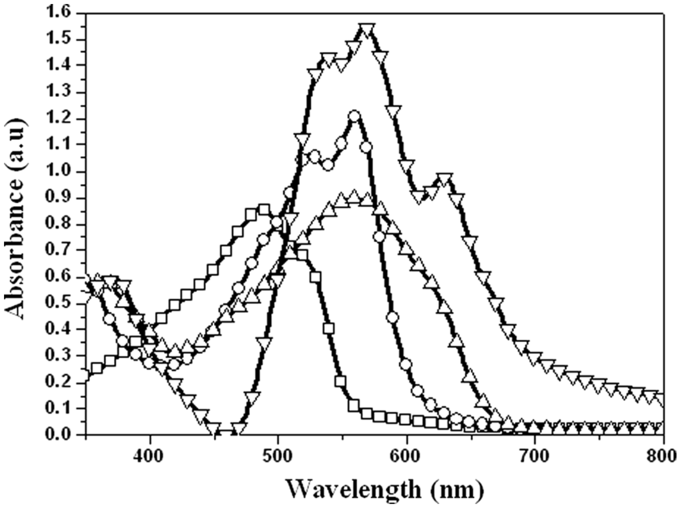


Figure 1. UV-Visible absorption spectra of HPANT (-□-), Co(HPANT)$_2$ (-○-), Cr(HPANT)$_2$ (-△-), and Pigment Violet 23 (-▽-) (three samples: acetone solution of 4×10^{-5} M; Pigment Violet 23: THF solution of 2.5×10^{-4} M).

UV-visible absorption spectra and molar extinction coefficient value of four newly synthesized metal-azo complexes and two ligands in acetone solution were measured under 4×10^{-5} M concentration. The results are shown in Figures 1, 2 and Table 1. As shown in Figure 1, UV-visible maximum of naphthol derivatives Co(HPANT)$_2$ and Cr(HPANT)$_2$ was respectively 560 and 561 nm, which was 74 and 75 nm red shifted compared to 486 nm of ligand HPANT. Therefore, while HPANT was a red colored solid, Co(HPANT)$_2$ and Cr(HPANT)$_2$ were violet

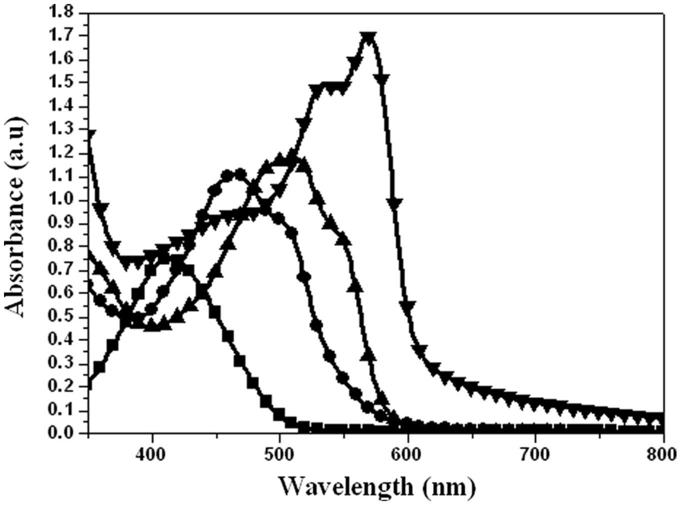


Figure 2. UV-Visible absorption spectra of HPAPMP (-■-), Co(HPAPMP)$_2$ (-●-), Cr(HPAPMP)$_2$ (-▲-), and Pigment Red 177 (-▼-). (three samples: acetone solution of 4×10^{-5} M; Pigment Red 177: THF solution of 2.5×10^{-4} M).

Table 1. Optical properties of synthesized compounds

	Compound	UV_{max} (nm)	Edge (nm)	ε (L/mol · cm)	Log ε	Solid color
Naphthol derivatives	HPANT[a]	486	557	21600	4.33	red
	$Co(HPANT)_2$[a]	560	612	30200	4.48	violet
	$Cr(HPANT)_2$[a]	561	671	22300	4.34	violet
Commercial violet pigment	Pigment violet 23[b]	568	690	6196	3.79	violet
Pyrazole derivatives	HPAPMP[a]	413	517	18700	4.27	orange
	$Co(HPAPMP)_2$[a]	465	566	27500	4.43	brown
	$Cr(HPAPMP)_2$[a]	510	599	29500	4.46	red
Commercial red pigment	Pigment Red 177[b]	570	605	6792	3.83	red

[a] In acetone solution ($4 * 10^{-5}$ M).
[b] In THF solution ($2.5 * 10^{-4}$ M).

colored solids [1]. Solid color of these two metal-azo complexes is similar to absorption maximum wavelength of 568 nm shown by a commercial violet pigment called Pigment Violet 23. Red shift in absorption wavelength according to metal substitution of ligand is probably caused by combination of HPANT with metal ion [15,18]. In addition, metal complex $Cr(HPANT)_2$ was more red shifted than $Co(HPANT)_2$ with the edge of UV-visible spectrum at 671 and 612 nm respectively. This shows a trend of more red shift in chrome ion because chrome ion has larger positive electron ability than cobalt ion and electron push effect in azo group is relatively stronger [18].

Also as shown by Figure 2, pyrazole derivatives, $Co(HPAPMP)_2$ and $Cr(HPAPMP)_2$ had UV-visible spectrum at maximum value of 465 and 510 nm, which were 52 and 97 nm red shifted compared to 413 nm of ligand HPAPMP. This is a similar trend shown by azo-complexes with naphthol derivatives and more red shift was also shown by $Cr(HPAPMP)_2$ than $Co(HPAPMP)_2$. While ligand HPAPMP was an orange colored solid, $Co(HPAPMP)_2$ and $Cr(HPAPMP)_2$ were brown and red colored solids [1]. In particular, $Cr(HPAPMP)_2$ showed similar absorption wavelength as a commercial red pigment called Pigment Red 177 and is expected to show commercial application.

UV-visible maximum absorption wavelength and molar extinction coefficient value of synthesized materials are summarized in Table 1. Naphthol derivatives, $Co(HPANT)_2$ and $Cr(HPANT)_2$ were more strongly red shifted compared to pyrazole derivatives, $Co(HPAPMP)_2$ and $Cr(HPAPMP)_2$. This could be interpreted as a longer conjugation length of naphthol group. Longer conjugation length effect was shown identically in metal complexes with Co and Cr. These results suggest that pigments with diverse colors can be made by absorbing specific wavelengths and controlling UV-visible absorption spectrum according to the changes in aromatic groups and metal ions.

Molar extinction coefficient value of naphthol derivatives HPANT, $Co(HPANT)_2$ and $Cr(HPANT)_2$ was respectively 21600, 30200 and 22300 L/mol · cm. Converted to log, high molar extinction coefficient of about 4 is obtained.

This is higher than the molar extinction coefficient of 6200 L/mol · cm shown by commercial Pigment Violet 23. Accordingly, since high molar extinction coefficient is expected to show more vivid colors, synthesized materials can possibly be used as pigments for LCD color filter as well as image sensors [7]. In addition, pyrazole derivatives HPAPMP, Co(HPAPMP)$_2$ and Cr(HPAPMP)$_2$ showed molar extinction coefficient of 18700, 27500 and 29500 L/mol · cm, which is higher than about 6800 L/mol · cm of commercial Pigment Red 177. New chemical structural changes in ligand and substitution of metal ion can adjust the maximum value and range of UV-visible absorption spectrum and absorb only the specific wavelengths, thereby realizing pigments with diverse colors. Higher molar extinction coefficients than commercial violet and red pigments will show more clear colors. Synthesized materials can thus be used as pigments for LCD color filter. Mill-base experiment and study on dispersion stability are currently being conducted.

Conclusions

This study synthesized 4 types of new metal-azo complexes by synthesizing 2 types of new azo ligands that include pyrazole and naphthol, an aromatic group based on azo group and metalizing cobalt ion and chrome ion. As a result of measuring UV-visible absorption spectra of synthesized materials, metal-azo complexes were found to be red shifted farther compared to maximum absorption wavelength of ligands.

The UV-visible maximum values of Co(HPANT)$_2$ and Cr(HPANT)$_2$, the naphthol derivatives, were 560 and 561 nm respectively in solution state where both were violet colored solids, and these absorption wavelengths are similar to that of Pigment Violet 23, a commercial violet pigment, 568 nm. Co(HPAPMP)$_2$ and Cr(HPAPMP)$_2$, the pyrazole derivatives also showed UV-visible maximum values of 465 and 510 nm respectively in solution state, indicating brown and red colored solids, and in particular, Cr(HPAPMP)$_2$ showed absorption wavelength similar to that of Pigment Red 177, a commercial red pigment. In addition, the basic colors of Cr and Co were similar, but Cr complex showed more red shift compared to Co complex. These results suggest that mutual minute color tuning can be done based on similar metal-azo complexes structural formula. The molar extinction coefficient values of Co(HPANT)$_2$ and Cr(HPANT)$_2$, naphthol derivatives, were respectively 30200 and 22300 L/mol · cm, both of which were higher than that of Pigment Violet 23, 6200 L/mol · cm, and the values of Co(HPAPMP)$_2$ and Cr(HPAPMP)$_2$, pyrazole derivatives, were 27500 and 29500 L/mol · cm. Particularly, Cr(HPAPMP)$_2$ showed much higher molar extinction coefficient value compared to that of commercial Pigment Red 177, 6800 L/mol · cm. Such high molar extinction coefficient values are expected to show clearer and more vivid colors, suggesting the possibility of use as pigments for LCD color filtering pigment and image sensors.

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