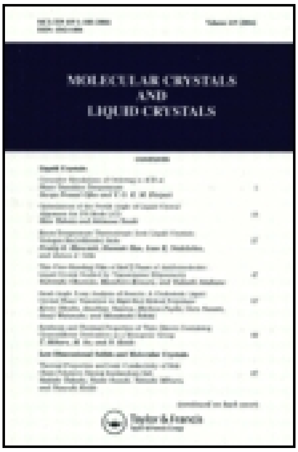

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Synthesis of New Dye Compounds Based on Anthraquinone Moiety for Color Filter Colorants

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Methoxy-pyridine group was substituted in 1,4-position, 1,5-position, and 1,8-position of anthraquinone to synthesize three new chemical compounds for color filter. Systematic study was conducted on changes in physical property of the synthesized compounds in the substituted positions in terms of optical property and thermal property. Extinction coefficient (ε) was extremely high above 4.03 in log scale for the synthesized compounds, and the value of T_d was above 300°C. Both optical property and thermal stability were qualified as the commercial compound.

Keywords Anthraquinone; color filter; dyes; high molar extinction coefficient; pigment

Introduction

With rapid development of display industry, dyes and pigments that had been mainly used in paints, inks, plastics, and fabrics in the past are now used as core compounds of color filter (CF) materials in full color liquid crystal displays (LCDs) [1–3]. LCDs are the devices with the large scale demand deemed important for mobile displays and high definition televisions that require high resolution and desirable color property [4]. In addition, CF is an important component of LCD panel making color image as well as image sensors [5]. High contrast, high color repetition, high color saturation, high color purity, low reflectivity, and low production cost must be included in performance and functions of CF [6]. In order to acquire such performance of CF, improvement in quality, and better spectral property in competition with other displays such as organic EL, new dyes used as main materials in CF must be studied.

Anthraquinone derivatives (AQs) has been used for about one-third of all organic dye products over the world [7]. C. I. Pigment Red 177 is an anthraquinone compound well known and widely used in commerce. In addition, AQs are organic dyes widely used in different fields such as quantum dots in semiconducting industry and medicine field [8–11].

AQs have been continuously studied to apply diverse colors according to the type and position of substituent groups. However, there are difficulties in developing and applying AQs with color characteristics, optical property, and thermal stability.

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In this study, anthraquinone core was used as dye material for new color filter and image sensor to substitute methoxy-pyridine group in 1,4-position, 1,5-position, and 1,8-position of anthraquinone, synthesizing new three anthraquinone derivatives.

Experimental

Measurements

^{1}H-NMR spectrum was measured using Bruker, Avance 300 Pectrometer. Optical absorption (UV) spectrum was measured by HP 8453 UV-VIS-NIR Spectrometer, and thermo gravimetric analysis (TGA) was done on thermal property using Seiko Exstar 6000 (TG/DTA6100).

Synthesis

Synthesis of 1,4-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,4(MeOPY)AQ).

After placing 2 g (7.2 mmol) of 1,4-dichloroanthraquinone, 6-Methoxy-pyridin-3-ylamine (5 eq), Cs_2CO_3 (2.5 eq) and copper Acetate (0.1 eq) in a 250 ml three-neck-flask, add 50 ml of DMF (N,N-Dimethyl formamide) and agitate for 19 hours at 190°C after nitrogen substitution. After reaction was finished, evaporated the solvent by distillation and purified by using column chromatography with THF : n-hexane (1 : 2).

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 11.98 (s,1H), 8.41–8.38 (m,1H), 8.13–8.12 (d,1H), 7.80–7.77 (m,1H), 7.52–7.48 (m,1H), 7.26–7.21 (d,1H), 6.82–6.79 (d,1H), 3.96 (s,3H).

Synthesis of 1,5-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,5(MeOPY) AQ).

After placing 2 g (7.2 mmol) of 1,5-dichloroanthraquinone, 6-Methoxy-pyridin-3-ylamine (5 eq), Cs_2CO_3 (2.5 eq) and copper Acetate (0.1 eq) in a 250 ml three-neck-flask, add 50 ml of DMF (N,N-Dimethyl formamide) and agitate for 19 hours at 190°C after nitrogen substitution. After reaction was finished, evaporated the solvent by distillation and purified by using column chromatography with ethyl acetate: n-hexane (1 : 4).

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 11.13 (s,1H), 8.17–8.16 (d,1H), 7.73–7.70 (m,1H), 7.58–7.54 (m,1H), 7.52–7.46 (t,1H), 7.17–7.14 (m,1H), 6.85–6.82 (d,1H), 3.98 (s,3H).

Synthesis of 1,8-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,8(MeOPY) AQ).

After placing 2 g (7.2 mmol) of 1,8-dichloroanthraquinone, 6-Methoxy-pyridin-3-ylamine (5 eq), Cs_2CO_3 (2.5 eq) and copper Acetate (0.1 eq) in a 250 ml three-neck-flask, add 50 ml of DMF (N,N-Dimethyl formamide) and agitate for 19 hours at 190°C after nitrogen substitution. After reaction was finished, evaporated the solvent by distillation and purified by using column chromatography with ethyl acetate : n-hexane (1 : 4).

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm) : 11.04 (s,1H), 8.16 (s,1H), 8.15–7.69 (m,1H), 7.69–7.53 (m,1H), 7.47–7.42 (t,1H), 7.20–7.17 (m,1H), 6.84–6.81 (d,1H), 3.98 (s,3H).

Results and Discussion

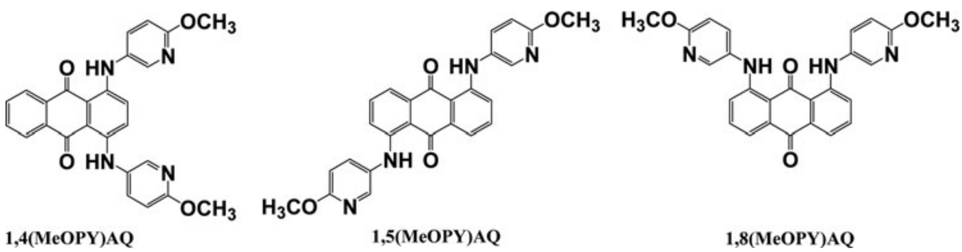
1,4-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,4(MeOPY)AQ) was synthesized as a blue dye with methoxy-pyridine substituted in 1,4-position of anthraquinone core.

Table 1. Optical properties of synthesized materials

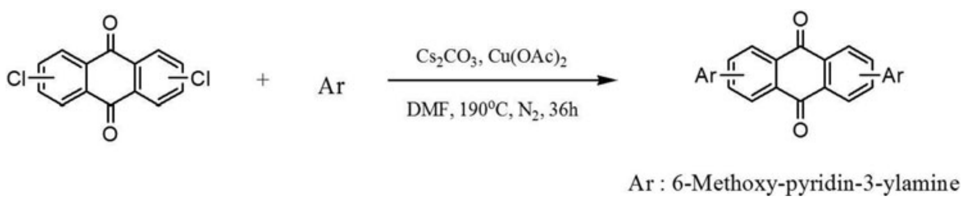
Compounds	Solution[a] UVmax (nm)	Log ε (L/mol·cm)	T_d (°C)
1,4(MeOPY)AQ	594, 628	4.17, 4.18	335
1,5(MeOPY)AQ	521	4.03	320
1,8(MeOPY)AQ	539	4.08	325

a: THF solution (2.5×10^{-5} M).

1,5-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,5(MeOPY)AQ) and 1,8-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,8(MeOPY)AQ) were made as new red dyes by changing the position of substituent to 1,5 and 1,8 numbers. Molecular structures are summarized in Scheme 1. Anthraquinone moiety has been using in many studies with various advantages such as the ease of synthetic method and limitation in manufacturing cost. Anthraquinone group was selected as the core in this study due to its chemical structure appropriate for including carbonyl, amine, and hydroxyl that allow hydrogen bonding inside of dye [4]. In addition, anthraquinone structure can easily have one or more substituents by through the typical reaction and even two or three anthraquinone moiety itself can be simply combined [12].



Scheme 1. Chemical structures of the synthesized dye compounds.



Scheme 2. Synthetic route of anthraquinone derivatives.

Optical property of the synthesized compounds was verified by through UV-visible absorption (UV-Vis.) spectrum and is summarized in Fig. 1 and Table 1. The synthesized compound 1,4(MeOPY)AQ showed UV-Vis. maximum values in THF solution at 594 and 628 nm as well as blue color in solid state. Molar extinction coefficient value at each absorption wavelength was 14,830 and 15,250 L/mol·cm, respectively. Absorption maximum wavelength of 1,5(MeOPY)AQ was 521 nm and it exhibited red color in solid state. Molar extinction coefficient value of 1,5(MeOPY)AQ was 10,730 L/mol·cm. Absorption

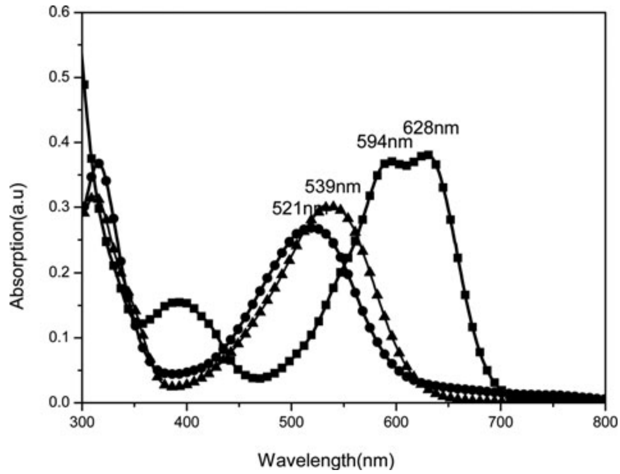


Figure 1. UV-Visible absorption spectra of 1,4(MeOPY)AQ (■), 1,5(MeOPY)AQ (•), 1,8(MeOPY) AQ (▲) in THF solution of 2.5×10^{-5}M.

wavelengths of 1,8(MeOPY)AQ were 539 nm and it showed red color in solid state. Molar extinction coefficient value of 1,8(MeOPY)AQ was 12,030 L/mol·cm. All molar extinction coefficient values of the synthesized compounds are above than commercial requirement of 10,000 L/mol·cm.

In comparison to 1,5(MeOPY)AQ and 1,8(MeOPY)AQ, 1,4(MeOPY)AQ has a much longer wavelength of about 100 nm in absorption maximum value. This means that 1,4(MeOPY)AQ has relatively more delocalized and expanded π-conjugation length. It might be due to the two substituent groups attached at one side phenyl ring. That is, longer conjugation length in the structure substituted in 1,4-position can be predicted to move towards longer wavelength in UV-Vis. spectrum, resulting in color difference.

In addition, 1,4(MeOPY)AQ includes another absorption band at 400 nm and does not show absorption in 450∼550 nm range. This is probably because of different hydrogen bonds formed in the three compounds. However, this phenomenon cannot clearly be explained by the chemical structure. Further studies on the correlation between position of substituent group and absorption wavelength are necessary.

When extinction coefficient (ε) value of the synthesized compounds in THF solution was measured, all dyes had extremely high values between 4.03 and 4.18 in log scale (see Table 1). Such high molar extinction coefficient value provides high possibility of the usage as LCD color filter dyes.

As a result of measuring TGA for thermal stability of the synthesized compounds, all synthesized compounds were found to have high thermal stability above 300°C with T_d value of 335°C in 1,4(MeOPY)AQ, 320°C in 1,5(MeOPY)AQ, and 325°C in 1,8(MeOPY)AQ (see Fig. 2). Thermal stability is important in order to use the synthesized compounds as dyes in color filter. Color filter must withstand heat generated by LCD backlight as well as LCD processing temperature. That is, there is an intimate relationship between thermal stability of dyes used in color filters and sustainable operation of display. Accordingly, possibility of using the synthesized compounds as LCD dyes was verified through thermal stability higher than the highest temperature of 250°C reached in LCD manufacturing process [5].

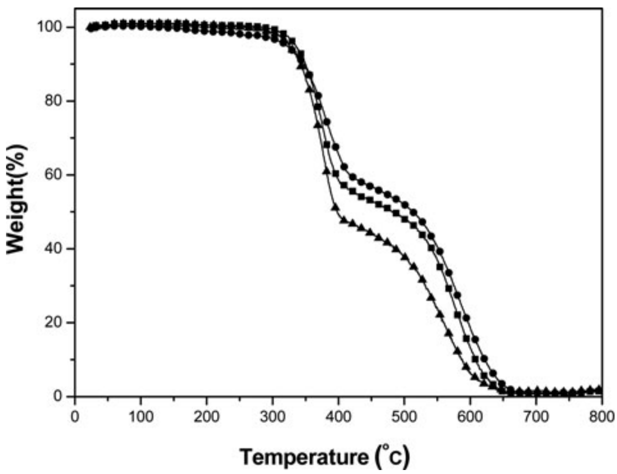


Figure 2. TGA data of 1,4(MeOPY)AQ (■), 1,5(MeOPY)AQ (•), 1,8(MeOPY)AQ (▲).

Conclusion

With anthraquinone as the core, 1,4-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,4(MeOPY)AQ) as a blue dye with methoxy-pyridine substituted in 1,4-position was synthesized, and 1,5-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,5(MeOPY)AQ) and 1,8-Bis-(6-methoxy-pyridin-3-ylamino)-anthraquinone (1,8(MeOPY)AQ) were synthesized as new red dyes in which the position of substituent was changed to 1,5 and 1,8 for diverse colors. The three compounds showed excellent results on optical property and thermal stability. Extinction coefficient (ε) of all dyes was high at 4.03 or above in log scale, and all dyes showed high thermal stability with T_d value above 300°C.

Acknowledgments

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References

[1] Zollinger, H. (1991). *Color Chemistry*, VCH Publishers, Inc., New York.
[2] Gaber, M., Ayad, M. M., & El-Sayed, Y. S. Y. (2005). *Spectrochimica Acta Part A*, *62*, 694.
[3] Wang, S., Shen, S., Xu, H., Gu, D., Yin, J., & Tang, X. (1999). *Dyes and Pigments*, *42*, 173.
[4] Yoon, C., Choi, J. H., & Kim, J. P. (2010). *Mol. Cryst. Liq. Cryst.*, *533*, 102.
[5] Sabnis, R. W. (1999). *Displays*, *20*, 119.
[6] Koo, H., Chen, M., & Pan, P. (2006). *Thin Solid Films*, *515*, 896.
[7] Jacquemin, D., Brémond, E., Ciofini, I., & Adamo, C. (2012). *J. Phys. Chem. Lett.*, *3*, 468.
[8] Tierney, M. T., & Grinstaff, M. W. (2000). *J. Org. Chem.*, *65*, 5355.
[9] Zhu, H., Song, N., & Lian, T. (2011). *J. Am. Chem. Soc.*, *133*, 8762.
[10] Park, J. H., Park, Y. I., & Park, J. W. (2011). *Mol. Cryst. Liq. Cryst.*, *551*, 116.
[11] Iwanaga, H. (2009). *Materials*, *2*, 1636.
[12] Wang, W., Bien, H. S., Stawitz, J., & Wunderich, K. (1985). *Ullmann's Encyclopedia of Industrial Chemistry, 5th edition*, A2, 355.