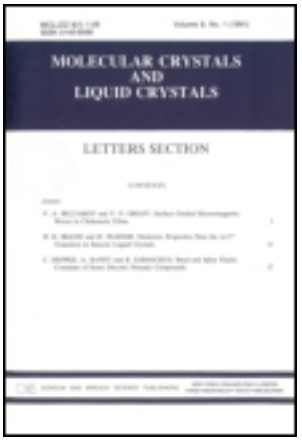


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# A Study on Synthesis of New Blue and Red Color Dyes Based on Anthraquinone Moiety

Junghyo Park [a] , Suyeoun Park [a] & Jongwook Park [a]
[a] Department of Chemistry , The Catholic University of Korea , Bucheon , 420-743 , Korea
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# A Study on Synthesis of New Blue and Red Color Dyes Based on Anthraquinone Moiety

JUNGHYO PARK, SUYEOUN PARK,
AND JONGWOOK PARK*

Department of Chemistry, The Catholic University of Korea, Bucheon 420-743, Korea



*Three new compounds are synthesized as color filter dyes by substituting a pyridine group into 1,4-position, 1,5-position, and 1,8-position of anthraquinone core moiety. Changes in physical properties of the synthesized compounds according to the substitution position are systematically investigated in terms of optical properties and thermal properties. The extinction coefficient value (ε) of the synthesized materials is extremely high and is above 4.22 in a log scale, and $T_d$ is above 300°C with high thermal stability.*

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

## Introduction

With the rapid development of the display industry, dyes and pigments that were mainly used in paints, inks, plastics, and fabrics in the past are currently applied as core materials of color filter (CF) realizing full color in liquid crystal displays (LCDs) [1–3]. Based on a large demand, LCDs are important devices used in mobile displays and high definition televisions which require high resolution and fine color properties [4]. Also, CF is an important element which generates color images in an LCD panel and it is applied to image sensors in addition to LCD [5]. Performance and functions of CF must include high contrast, high color repetition, high color saturation, high color purity, low reflectivity, and low production cost [6]. A study on pigments and dyes used as main materials is essential for CF application.

Anthraquinone derivatives (AQs) have been widely used for a variety of chemical structures and their applications [7]. C. I. Pigment Red 177 is an anthraquinone compound well known for commercial use. In addition, AQs are extremely useful substances not only used as organic dyes but also in many fields such as quantum dots in the semiconducting industry and in the field of medicine [8–11].

AQs have been continuously studied to apply diverse colors according to the type and position of substituent groups. It is, however, difficult to develop and to commercialize AQs equipped with color property, optical property, and thermal stability.

*Address correspondence to J. W. Park, Department of Chemistry/Display Research Center, The Catholic University of Korea, 43-1, Yeokgok, Wonmi, Bucheon, 420-743, Korea (ROK). Tel.: (+82)2-2164-4331; Fax: (+82)2-2164-4764. E-mail: hahapark@catholic.ac.kr

In this study, three new compounds are synthesized by substituting pyridine group in 1,4-position, 1,5-position, and 1,8-position of anthraquinone as the core for new color filter materials.

## Experimental

### *Measurements*

Bruker, Avance 300 Pectrometer was used for $^1$H-NMR spectrum. FAB$^{2+}$-Mass spectrum was measured by using JEOL, JMS-AX505WA. Elemental analysis was measured using EA1110 and EA1112 of CE Instrument. HP 8453 UV-VIS-NIR Spectrometer was used for optical absorption (UV-Vis.) spectrum, and a thermo gravimetric analysis (TGA) was conducted for thermal properties by using Seiko Exstar 6000 (TG/DTA6100). Cyclic voltammograms were measured with Autolab Model NOVA 1.4 in 0.1mol/L tetra(n-butyl)ammonium tetrafluoroborate /Acetonitrile(AN).



### *Synthesis*

Synthesis of 1,4-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,4(3PY)AQ).

Put 1,4-diaminoanthraquinone (2 g, 0.00839 mol), $Cs_2CO_3$ (13.6 g, 0.0419 mol), and copper acetate (0.30 g, 0.00164 mol) in a 250 ml three-neck-flask and melt it in 80 ml of DMF (N,N-Dimethyl formamide). Add 3-bromopyridine (4.09 ml, 0.0419 mol) in nitrogen atmosphere and heat it up to 190°C for 19 hours of agitation. After the reaction is completed, remove the solvent (DMF) through distillation. This product is obtained by re-precipitation after a short column. (16% yield).

$^1$H-NMR (300MHz, $CDCl_3$) $\delta$(ppm): 12.05(s,2H), 8.61(s,2H), 8.43–8.42(d,2H), 8.39–8.37(m,2H), 7.81–7.79(m,2H), 7.61–7.59(d,2H), 7.47(s,2H), 7.35–7.32(m,2H). Fab$^+$-MS 393m/z. Anal. Calcd. for $C_{24}H16N_4O_2$ : C, 73.46; H, 4.11; N, 14.28; O, 8.15 Found: C, 72.65: H, 4.13: N, 14.05: O,8.92.

Synthesis of 1,5-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,5(3PY)AQ)

Place 1.5-dichloroanthraquinone (3 g, 0.01075 mol), $Cs_2CO_3$ (17.51 g, 0.05375 mol), and copper acetate (1.952 g, 0.05375 mol) in a 250 ml three-neck-flask and melt it in 80 ml of DMF (N,N-Dimethyl formamide). Add 3-aminopyridine (2.529 g, 0.02688 mol) in nitrogen atmosphere and heat it up to 190°C for 19 hours of agitation. After the reaction is completed, remove the solvent (DMF) through distillation. This product is obtained by re-precipitation after a short column. (18.15% yield)

$^1$H-NMR (300MHz, $CDCl_3$) $\delta$(ppm): 11.36 (s,2H), 8.66(s,2H), 8.45(s,2H), 7.80–7.78 (d,2H), 7.68–7.66(d,2H), 7.58–7.53(t,2H), 7.45–7.42(d,2H),7.38–7.34(m,2H). Fab$^+$-MS 393m/z. Anal. Calcd. for $C_{24}H16N_4O_2$ : C, 73.46; H, 4.11; N, 14.28; O, 8.15 Found: C, 73.40: H, 4.12: N, 14.27: O,8.20.

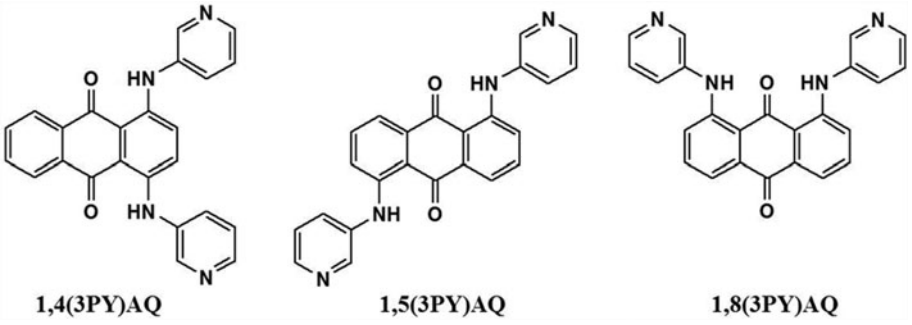
Synthesis of 1,8-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,8(3PY) AQ).

The synthetic procedure is similar to that of 1,5(3PY)AQ. (yield 16.8%).

$^1$H-NMR (300MHz, $CDCl_3$) $\delta$(ppm): 11.25(s,2H), 8.64(s,2H), 8.44(d,2H), 7.79–7.76(m,2H), 7.68–7.65(d,2H), 7.55–7.45(m,4H), 7.37–7.33(m,2H). Fab$^+$-MS 393m/z. Anal. Calcd. for $C_{24}H16N_4O_2$ : C, 73.46; H, 4.11; N, 14.28; O, 8.15 Found: C, 73.47: H, 4.19: N, 14.31: O,8.06.

## Results and Discussion

Newly synthesized blue dye compound is 1,4-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,4(3PY)AQ) which has a pyridine as a substituent in 1,4-position of anthraquinone core. Also, new red dyes of 1,5-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,5(3PY)AQ) and 1,8-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,8(3PY)AQ) are made by changing the position of the substituent group respectively to 1,5 and 1,8. Molecular structures are summarized in Scheme 1. Anthraquinone moiety has been used in many studies for various advantages such as a simple synthetic method and reasonable manufacturing costs. The anthraquinone group was selected as the core in this study because it has an appropriate chemical structure to include carbonyl, amine, and hydroxyl groups which allow hydrogen bonding inside the molecule [4]. In addition, the anthraquinone structure may easily have one substituent or more through the typical reaction and even two or three anthraquinone moieties may be simply combined [12].




**Scheme 1.** Chemical structures of the synthesized dye compounds.

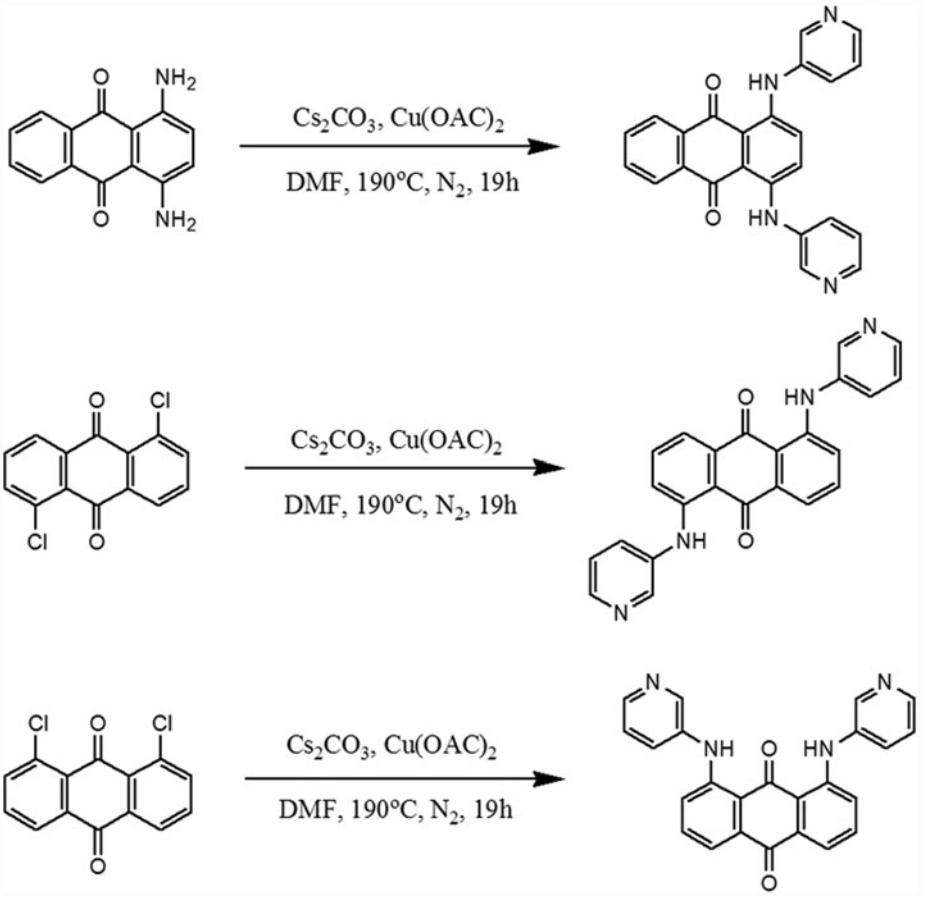
Optical properties of the synthesized compound were verified through UV-visible absorption (UV-Vis.) spectrum as summarized in Fig. 1 and Table 1.

The synthesized 1,4(3PY)AQ shows UV-visible maximum values of 390, 585, and 624nm in THF solution and blue color in a film state due to no absorption in the range between 440 nm and 500 nm. Molar extinction coefficient values of 390, 585, and 624 nm in 1,4(3PY)AQ are 10,400, 16,700, and 16,200 L/mol·cm, respectively. 1,5(3PY)AQ exhibits UV-Vis. maximum value at 515 nm and red color in a solid state. The molar extinction coefficient value of 1,5(3PY)AQ is 22,800 L/mol·cm. 1,8(3PY)AQ also shows UV-Vis. maximum value at 528 nm and red color in a film state. The molar extinction coefficient value of 1,8(3PY)AQ is 18,400 L/mol·cm. 1,5(3PY)AQ and 1,8(3PY)AQ have red color

**Table 1.** Optical properties of synthesized materials

| Compounds | UV-Vis.$_{max}$ (nm)[a] | Log $\varepsilon$ (L/mol·cm) | HO MO (eV) | LU MO (eV) | Band Gap (eV) | Solid color |
|---|---|---|---|---|---|---|
| 1,4(3PY)AQ | 585 | 4.22 | −5.21 | −3.34 | 1.87 | Blue |
| 1,5(3PY)AQ | 515 | 4.36 | −5.52 | −3.36 | 2.16 | Red |
| 1,8(3PY)AQ | 528 | 4.26 | −5.53 | −3.42 | 2.11 | Red |

a : THF solution ($2.5 \times 10^{-5}$ M).




**Scheme 2.** Synthetic route of anthraquinone derivatives.

and this may be explained by the fact that there is no absorption in the range between 600 nm and more.

Also, 1,4(3PY)AQ has longer wavelengths of absorption maximum values in comparison to 1,5(3PY)AQ and 1,8(3PY)AQ. This suggests that a relatively delocalized $\pi$-conjugation length is taken by 1,4(3PY)AQ. The HOMO value of the synthesized materials is found by CV measurement, and the LUMO value is estimated after finding a band gap by using UV-Vis. edge calculation. As a result, while LUMO values of the compounds are similar, the HOMO value of the structure in which side group is substituted in 1,4-position is different from that of the structures in which a side group is substituted in 1,5-position and 1,8-position. This is probably because conjugation in 1,5 or 1,8-position structure is separated from a carbonyl group of anthraquionone and conjugation in 1,4-position structure is connected through a benzene ring of anthraquinone. That is, the structure with substitution in 1,4-position can be assumed to show color differences due to movement towards longer wavelengths in UV-Vis. spectrum with longer conjugation lengths.

In addition, 1,4(3PY)AQ includes another absorption band at 400 nm and does not show absorption in the range between 440 and 550 nm. This is probably because of different hydrogen bonds formed in the three compounds. However, this phenomenon cannot clearly

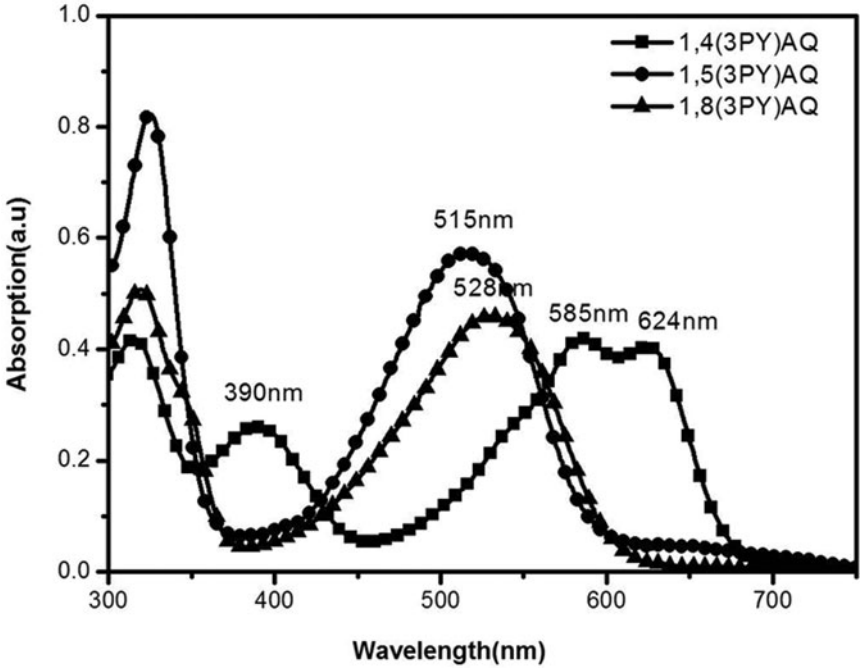



**Figure 1.** UV-Visible absorption spectra of 1,4(3PY)AQ(■), 1,5(3PY)AQ(●) and 1,8(3PY)AQ(▲) in THF solution of $2.5\times10^{-5}$M.

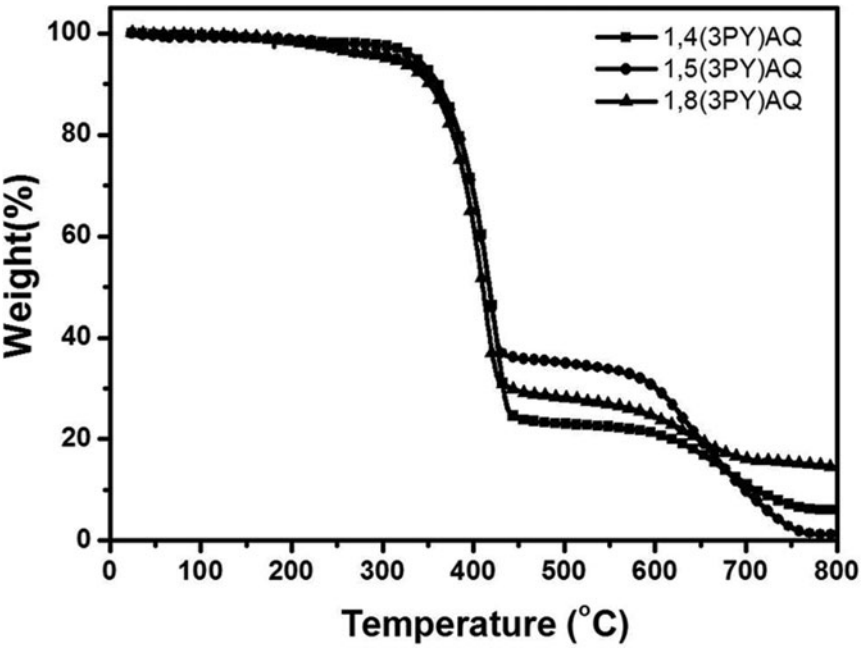



**Figure 2.** TGA data of 1,4(3PY)AQ (■), 1,5(3PY)AQ (●) and 1,8(3PY)AQ (▲).

be explained by a chemical structure. It is required to conduct further studies on the correlation between position of substituent groups and absorption wavelengths.

As a result of measuring extinction coefficient values ($\varepsilon$) of the synthesized substances in THF solution, all dyes have extremely high values between 4.22 and 4.36 in a log scale (see Table 1). Such values are similar to the mean value (log $\varepsilon$: 4.24) of diketopyrrolopyrrole (DPP) derivatives, which are the most widely known red pigments in commercial use [13]. Such high molar extinction coefficients suggest high probability of application as dyes in LCD color filters. As a result of measuring TGA for thermal stability of the synthesized materials, all three compounds show high thermal stability above 300°C with $T_d$ value of 337°C in 1,4(3PY)AQ, 317°C in 1,5(3PY)AQ, and 308°C in 1,8(3PY)AQ (see Fig. 2). Thermal stability is important for use of the synthesized materials as color filter dyes. When fabricating and using LCD, color filters must withstand heat generated by LCD backlight as well as LCD processing temperature. That is, thermal stability of dyes used in color filters is closely related to sustainable operation of display. Accordingly, possibility for application of the synthesized materials as dyes in LCD is verified with thermal stability higher than the highest temperature of 250°C used in LCD manufacturing process [5].

## Conclusion

In order to realize various dye colors by using the anthraquinone moiety as the core, 1,4-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,4(3PY)AQ) is synthesized as blue color by substituting pyridine in 1,4-position, and 1,5-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,5(3PY)AQ) and 1,8-Bis-(pyridin-3-ylamino)-4a,9a-dihydro-anthraquinone (1,8(3PY)AQ) are synthesized as red dyes by changing the position of the substituent group to 1,5 and 1,8. These three compounds show excellent optical properties and thermal stability. The extinction coefficient value ($\varepsilon$) of all three dyes is higher than 4.22 in a log scale, and all three materials show high thermal stability with $T_d$ value above 300°C.

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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, Chun, Choi, Jae-Hong, & Kim, Jae Pil (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, Mark T., & Grinstaff, Mark W. (2000). *J. Org. Chem.*, *65*, 5355.
[9] Zhu, Haiming, Song, Nianhui, & Lian, Tianquan (2011). *J. Am. Chem. Soc. 133*, 8762.
[10] Park, Junghyo, Park, Youngil & Park, Jongwook (2011). *Mol. Cryst. Liq. Cryst.*, *551*, 116.
[11] Iwanaga, Hiroki (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.
[13] Riggs, L., Morton, C. J. H., Slawin, A. M. Z., Smith, D. M., Westwood, N. J., Austena, W. S. D., & Stuart, K. E. (2005). *Tetrahedron*, *61*, 11230.