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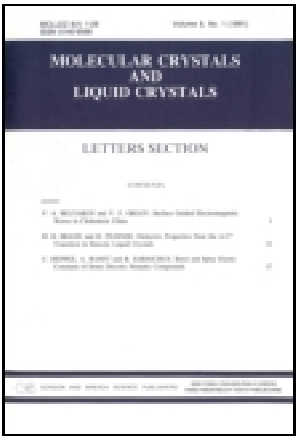

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New Anthraquinone Dyes with Different Side Group Positions for LCD Color Filters

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New Anthraquinone Dyes with Different Side Group Positions for LCD Color Filters

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Quinoline group was substituted in 1,4-position, 1,5-position, and 1,8-position of anthraquinone to synthesize three new chemical compounds for color filters. A systematic study was conducted on changes in physical properties of the synthesized compounds in the substituted positions in terms of optical properties and thermal properties. The extinction coefficient (ε) was extremely high, which was more than 4.22 in log scale for the synthesized compounds, and the value of T_d was higher than 300°C. Both optical properties and thermal stability are qualified as commercial compounds.

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

Introduction

With rapid development of the display industry, dyes and pigments which 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]. With a huge demand, LCDs areimportant devices for mobile displays and high definition televisions which require high resolution and desirable color properties [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 properties in competition with other displays such as organic EL, it is required to research new dyes used as main materials in CF.

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

Many studies have been conducted on AQs in order to apply diverse colors according to the type and position of substituent groups. There are, however, difficulties in developing and applying AQs with color characteristics, optical properties, and thermal stability.

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

Experimental

Measurements

^{1}H-NMR spectrum was measured by using Bruker, Avance 300 Pectrometer. FAB^{2+}-Mass spectrum was measured with JEOL, JMS-AX505WA. An elemental analysis was performed with EA1110 and EA1112 of CE Instrument. Optical absorption (UV) spectrum was measured by HP 8453 UV-VIS-NIR Spectrometer, and a thermo gravimetric analysis (TGA) was conducted on thermal properties by using Seiko Exstar 6000 (TG/DTA6100).

Synthesis

Synthesis of 1,4-bis-(quinolin-8-ylamino)-anthraquinone (1,4(8QL)AQ).

After putting 1 g (3.6 mmol) of 1,4-dichloroanthraquinone, 2.40 g (16.7 mmol) of 8-aminoquinoline, 5.5 g (16.7 mmol) of Cs_2CO_3, and 0.3 g (1.81 mmol) of copper acetate in a 100 ml three-neck-flask, 30 ml of DMF (N,N-Dimethyl formamide) is added and the flask is agitated for 19 hours at 190°C after nitrogen substitution. When the reaction ends, the solvent is removed through distillation and the product is obtained through column chromatography. (16.3% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm) : 13.06(s,2H), 9.06–9.05(d,2H), 8.47–8.44 (m,2H), 8.19–8.16(t,2H), 8.09(s,2H), 7.77–7.75(t,4H), 7.52–7.26(m,6H). (see Fig. 1) Fab$^+$-MS 492m/z. Anal. Calcd. for $C_{32}H_2ON_4O_2$: C, 78.03: H, 4.09: N, 11.38: O, 6.50. Found: C, 78.36: H, 4.10: N, 11.37: O, 6.27.

Synthesis of 1,5-bis-(quinolin-8-ylamino)-anthraquinone (1,5(8QL)AQ).

After putting 1 g (3.6 mmol) of 1,5-dichloroanthraquinone, 2.40 g (16.7 mmol) of 8-aminoquinoline, 5.5 g (16.7 mmol) of Cs_2CO_3, and 0.3 g (1.81 mmol) of copper acetate in a 100 ml three-neck-flask, 30 ml of DMF (N,N-Dimethyl formamide) is added and the flask is agitated for 19 hours at 190°C after nitrogen substitution. When the reaction ends, the solvent is removed through distillation and the product is obtained through column chromatography. (5.6% yield).

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm) : 12.58(s,2H), 9.06–9.04(m,2H), 8.20–8.17 (m,2H), 8.07–8.04(m,2H), 7.96–7.93(m,2H), 7.89–7.86(m,2H), 7.65–7.60(t,2H), 7.53–7.48(m,6H). (see Fig. 2) Fab$^+$-MS 493m/z. Anal. Calcd. for $C_{32}H_2ON_4O_2$: C, 78.03: H, 4.09: N, 11.38: O, 6.50. Found: C, 78.07: H, 4.12: N, 11.16: O, 6.61.

Synthesis of 1,8-bis-(quinolin-8-ylamino)-anthraquinone (1,8(8QL)AQ).

After putting 1 g (3.6 mmol) of 1,8-dichloroanthraquinone, 2.40 g (16.7 mmol) of 8-aminoquinoline, 5.5 g (16.7 mmol) of Cs_2CO_3, and 0.3 g (1.81 mmol) of copper acetate in a 100 ml three-neck-flask, 30 ml of DMF (N,N-Dimethyl formamide) is added and the flask is agitated for 19 hours at 190°C after nitrogen substitution. When the reaction ends, the solvent is removed through distillation and the product is obtained through column chromatography. (16.8% yield).

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm) : 12.52(s,2H), 8.98–8.96(m,2H), 8.17–8.13 (m,2H), 8.06–8.03(m,2H), 7.84–7.79(m,4H), 7.58–7.56(t,2H) 7.53–7.44(m,6H). (see

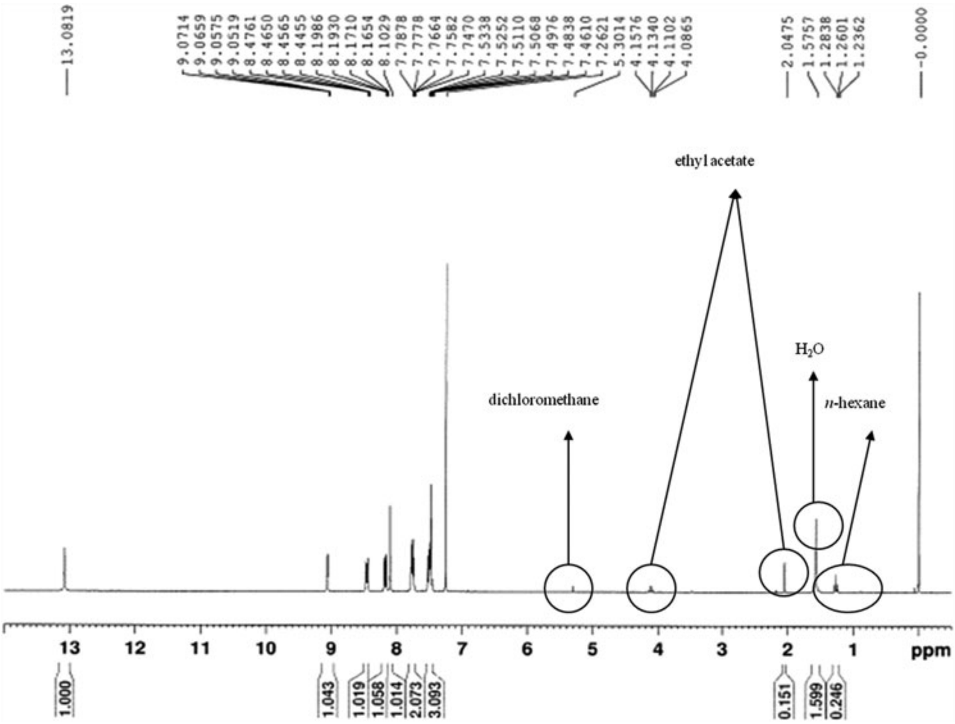


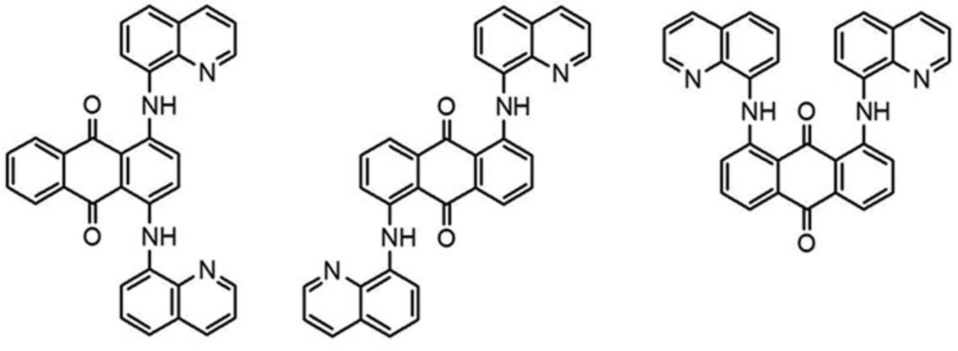
Figure 1. NMR spectrum of 1,4(8QL)AQ.

Fig. 3) Fab$^+$-MS 493m/z. Anal. calcd. for $C_{32}H_2ON_4O_2$: C, 78.03: H, 4.09: N, 11.38: O, 6.50. Found: C, 78.01: H, 4.04: N, 11.37: O, 6.58.

Results and Discussion

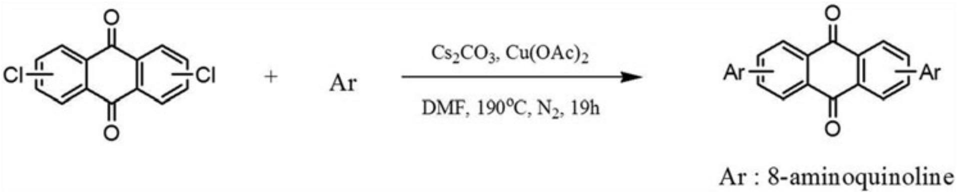
1,4-bis-(quinolin-8-ylamino)-anthraquinone (1,4(8QL)AQ) was synthesized as a green dye with quinoline substituted in 1,4-position of anthraquinone core. 1,5-bis-(quinolin-8-ylamino)-anthraquinone (1,5(8QL)AQ) and 1,8-bis-(quinolin-8-ylamino)-anthraquinone (1,8(8QL)AQ) were made as new violet dyes by changing the position of substituent to 1,5 and 1,8 numbers. Molecular structures are summarized in Scheme 1. Anthraquinone moiety has been used in many studies with various advantages such as an easy synthetic method and limited manufacturing costs. An anthraquinone group was selected as the core in this study as its chemical structure is appropriate to include carbonyl, amine, and hydroxyl which allow hydrogen bonding inside of dye [4]. In addition, an anthraquinone structure can easily have one or more substituents through the typical reaction and even two or three anthraquinone moietiesmay be simply combined [12].

Optical properties of the synthesized compounds were verified through UV-visible absorption (UV-Vis.) spectrum and they are summarized in Fig. 4 and Table 1. The synthesized compound 1,4(8QL)AQ shows UV-Vis. maximum values in THF solution at 441, 618, and 649 nm as well as the green color in a solid state. The molar extinction coefficient values at absorption wavelengths were 56,200, 27,500, and 26,200 L/mol·cm, respectively. Absorption wavelengths of 1,5(8QL)AQ were 376 and 536nm and it exhibited violet color



1,4(8QL)AQ 1,5(8QL)AQ 1,8(8QL)AQ

Scheme 1. Chemical structures of the synthesized dye compounds.



Scheme 2. Synthetic routes of anthraquinone derivatives.

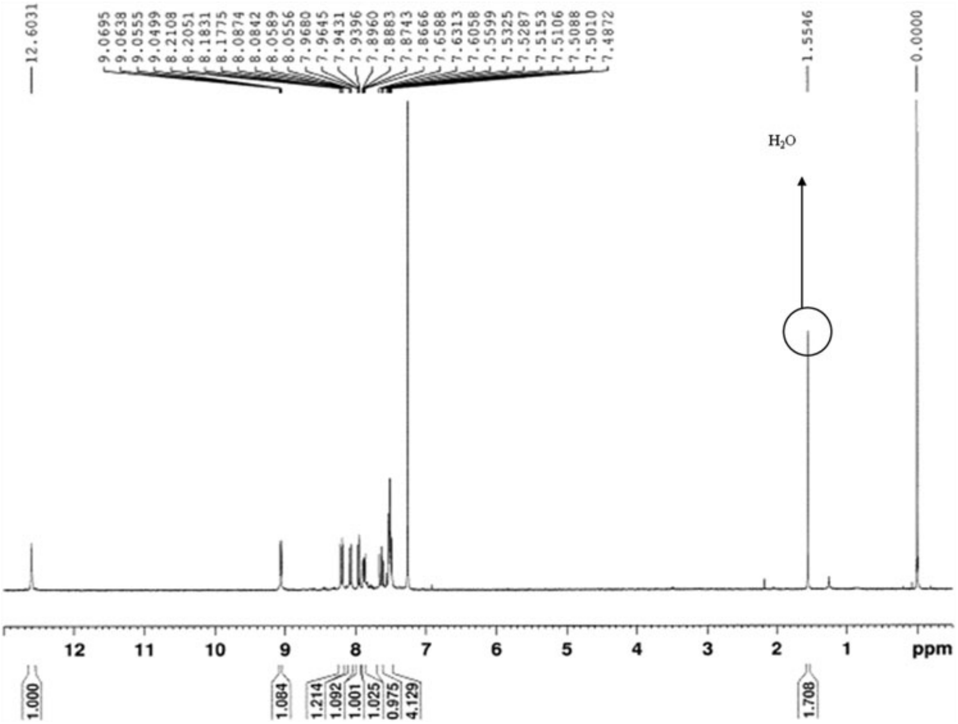


Figure 2. NMR spectrum of 1,5(8QL)AQ.

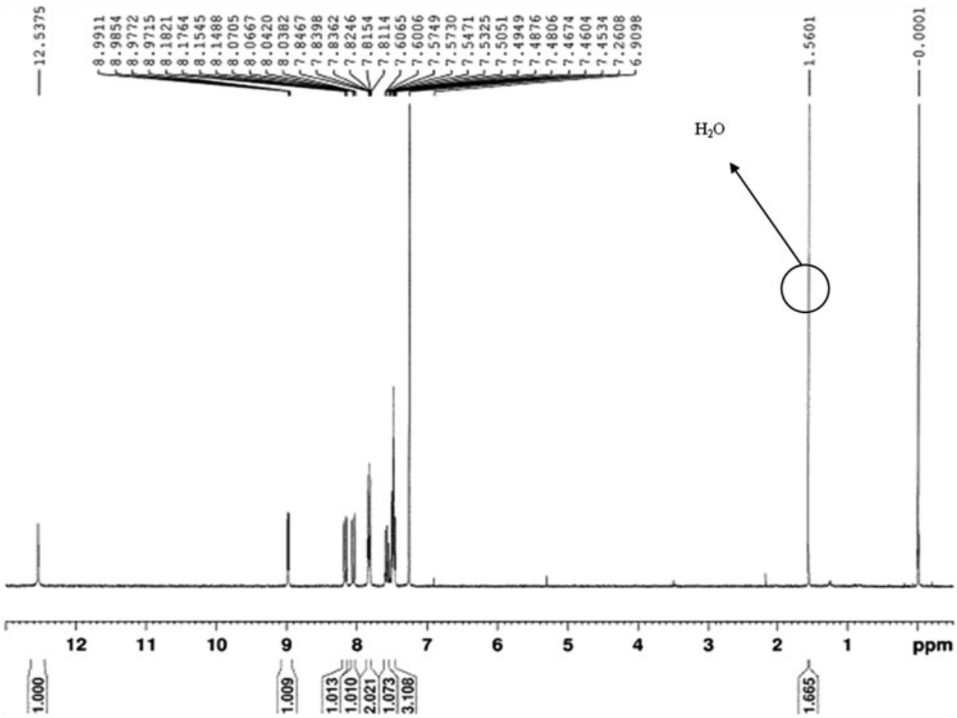


Figure 3. NMR spectrum of 1,8(8QL)AQ.

in a solid state. Molar extinction coefficient values of this compound at absorption wavelengths were 31,300 and 16,800 L/mol·cm. Absorption wavelengths of 1,8(8QL)AQ were 369 and 557nm and it showed violet color in a solid state. Molar extinction coefficient values at wavelengths were respectively 43,200 and 23,500 L/mol·cm. All molar extinction coefficient values of the synthesized compounds are higher than commercial requirement of 10,000 L/mol·cm.

In comparison to 1,5(8QL)AQ and 1,8(8QL)AQ, 1,4(8QL)AQ has a much longer wavelength of about 100 nm in absorption maximum value. This means that 1,4(8QL)AQ has delocalized and expanded π-conjugation length relatively more. It might be due to the two substituent groups attached at one side phenyl ring. The HOMO level of the synthesized compounds was examined through CV measurement, and the LUMO value was calculated after obtaining the band gap by using UV-Vis. spectrum. As a result, LUMO values of the compounds were similar, but the HOMO value of the structure with side group substituted in 1,4-position was different from the value of structures with side group substituted in 1,5-position and 1,8-position. This may explain why there is conjugation separation by carbonyl group in the structure substituted by 1,5 or 1,8-position and more conjugation through benzene ring of anthraquinone in the structure substituted by 1,4-position.

That is, longer conjugation length in the structure substituted in 1,4-position is expected to move towards longer wavelength in UV-Vis. spectrum, resulting in color differences.

When the extinction coefficient (ε) value of the synthesized compounds in THF solution was measured, all dyes had extremely high values between 4.22 and 4.75 in log scale (see Table 1). This is similar to the mean value (log ε: 4.24) shown by the representative red dye, which is widely known as commercial material, diketopyrrolopyrrole (DPP) derivatives

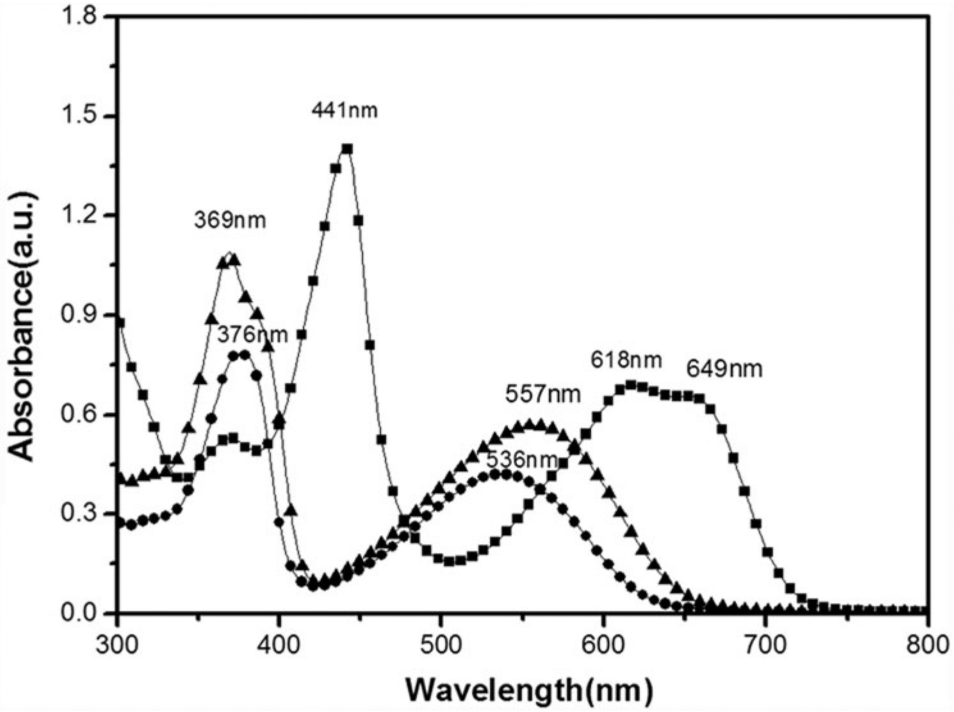


Figure 4. UV-Visible absorption spectra of 1,4(8QL)AQ(■), 1,5(8QL)AQ(•) and 1,8(8QL)AQ(▲) in THF solution of 2.5×10–5M.

[13]. Such a high molar extinction coefficient value provides a 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 more than 300°C with T_d value of 365°C in 1,4(8QL)AQ, 363°C in 1,5(8QL)AQ, and 397°C in 1,8(8QL)AQ (see Fig. 5). Thermal stability is important when the synthesized compounds are used as dyes in color filters. Color filters 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 have been verified through thermal stability higher than the highest temperature of 250°C in the LCD manufacturing process [5].

Table 1. Optical properties of synthesized materials

Compounds	UV-Vis.$_{max}$ (nm)^a	Log ε (L/mol·cm)	HO MO (eV)	LU MO (eV)	Band Gap (eV)	Solid color
1,4(8QL)AQ	441, 618, 649	4.75, 4.44, 4.42	−5.09	−3.31	1.78	Green
1,5(8QL)AQ	376, 536	4.50, 4.22	−5.40	−3.36	2.04	Violet
1,8(8QL)AQ	369, 557	4.64, 4.37	−5.37	−3.35	1.99	Violet

a: THF solution (2.5×10^{-5} M).

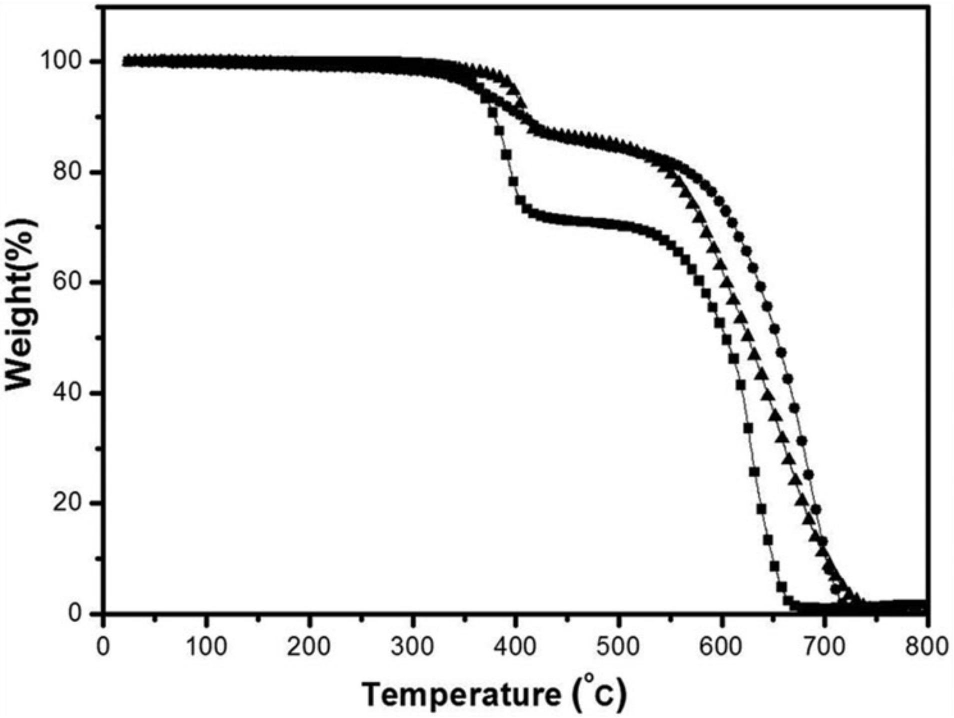


Figure 5. TGA data of 1,4(8QL)AQ (■), 1,5(8QL)AQ (●) and 1,8(8QL)AQ (▲).

Conclusion

With anthraquinone as the core, 1,4-bis-(quinolin-8-ylamino)-anthraquinone (1,4(8QL)AQ) as a green dye with quinoline substituted in 1,4-position was synthesized, and 1,5-bis-(quinolin-8-ylamino)-anthraquinone (1,5(8QL)AQ) and 1,8-bis-(quinolin-8-ylamino)-anthraquinone (1,8(8QL)AQ) were synthesized as new violet dyes in which the position of substituent changed to 1,5 and 1,8 for diverse colors. The three compounds showed excellent results on optical properties and thermal stability. The extinction coefficient (ε) of all dyes was high at 4.22 or above in log scale, and all dyes showed high thermal stability with T_d value more than 300°C.

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