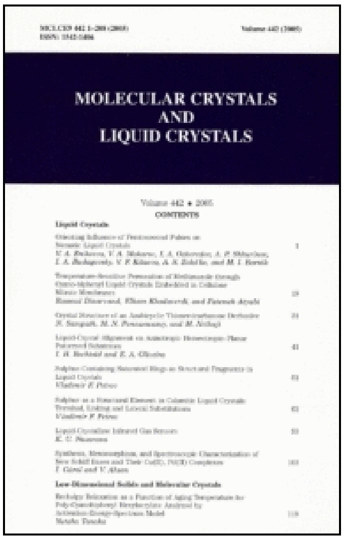

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Synthesis of New Single Black Pigments Based on Azo and Anthraquinone Moieties for LCD Black Matrix

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Based on azo group and anthraquinone moiety, new black matrix pigment materials AAQ and DAAQ were synthesized for the first time through Suzuki C-N coupling. As a result of verifying UV-visible absorption spectra of the synthesized materials, DAAQ was found to absorb the entire visible region in 400 ~ 800 nm in solution state with high extinction coefficient of 8.1×10^3 *L/cm · mol. Realization of black color using a single material is expected to be useful for black matrix application. Also in film state made through spin coating, both AAQ and DAAQ absorbed the entire visible region.*

Keywords Anthraquinone; azo group; black matrix; LCD

Introduction

Liquid crystal display (LCD) has been the spotlight for long time as a flat panel display. For full color realization of LCD, a color filter (CF) is necessary to change white back light into red (R), green (G) and blue (B) lights. In such CF a black matrix (BM) materials are between each R, G, B color pixels for high contrast [1–3]. BM improves the contrast of red, green and blue lights converted from white back light through prevention of external incident light. BM is also used to prevent malfunction of thin film transistor (TFT) by minimizing reflection of light [4,5]. Although Cr/CrO_x with sputtering process has been in use as BM, Cr is a heavy metal element that causes environmental problems itself. And high cost and complicated sputtering process are increasing the necessity of an organic BM [6,7]. Carbon black can also be candidate as a BM, but high dielectric constant limits future use because of TFT malfunction and the new organic BM materials have been recently

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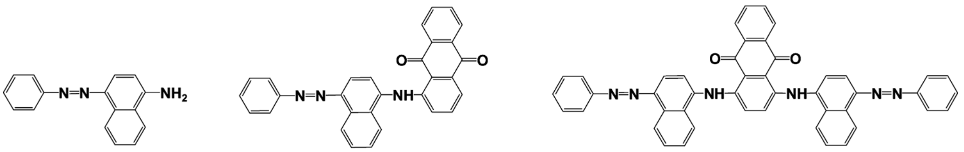


4PhNa AAQ DAAQ

Scheme 1. Chemical structures of 4PhNa, AAQ and DAAQ.

highlighted [8]. Therefore, it is important to develop black pigment which is the core material of organic BM.

In order to make a black pigment used as BM, absorption of external light and reflection of white back light must be blocked. Ideally, light should be absorbed throughout the entire visible region overall even between 400~800 nm as well as high absorption coefficient are also required. In addition, the pigment must have excellent thermal stability because it should not change by heat at the highest temperature of 250°C during the LCD manufacturing process [2,9]. Also, red, blue and green mixture method and single BM material method are available for BM. In case of single organic material method, it is extremely difficult for a material to absorb the entire spectrum, and single material method is hardly in practical use.

Accordingly in this study, a single black pigment was designed as follows using representative functional groups of dyes and pigments with high absorption coefficient, azo and anthraquinone groups [10,11]. First, azo pigment called 4-phenylazo-1-naphthylamine (4PhNa) has high extinction coefficient in the blue region of 440 nm. Anthraquinone has diverse substitution positions and can adjust absorption spectrum according to substitution position [12]. In particular, positions 1 and 4 of anthraquinone can induce absorption of long wavelength region through intramolecular hydrogen bonding with the carbonyl group [13]. A new black pigment was designed and synthesized as shown in Scheme 1 through absorption of 440 nm by azo group and long wavelength absorption other than 440 nm by intramolecular hydrogen bonding of anthraquinone. Optical characteristics of the synthesized material were measured using UV-visible spectrum, and thermal stability was also measured with thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Experimental

Synthesis

Synthesis of 1-(4-Phenylazo-naphthalen-1-ylamino)-anthraquinone [AAQ]. 4-phenylazo-1-naphthylamine (2.5 g, 10.12 mmol), 1-chloroanthraquinone (2.9 g, 12.14 mmol), $Pd_2(dba)_3$ (0.28 g, 0.30 mmol), [2.2′-bis(diphenylphosphine-1.1′-binaphthyl] (BINAP) (0.75 g, 1.20 mmol), cesium carbonate (9.89 g, 30.35 mmol) and 100 ml toluene were into the 3neck flask. Then the mixture was stirred for 7 h at 100°C under nitrogen. The reaction mixture was quenched with 5 ml water and extracted with chloroform ($CHCl_3$) and dried over magnesium sulfate anhydrous ($MgSO_4$). Evaporation of solvent under vacuum resulted in a brown residue, which was purified by column chromatography using $CHCl_3$ and reprecipitation with methanol. (3.11 g, yield: 67.8%) ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 11.96 (s,1H), 9.07–9.06 (d,1H), 8.40–8.39 (d,1H), 8.33–8.31 (d,1H), 8.28–8.26 (d,1H), 8.07–8.06 (d,2H), 7.93–7.92 (d,1H), 7.84–7.79 (m,3H), 7.73 (t,1H), 7.69–7.66 (m,2H), 7.59–7.56 (t,2H) 7.53–7.51 (m,3H) ; FAB-Mass 453 m/z.

2-2. Synthesis of 1,4-Bis-(4-Phenylazo-naphthalen-1-ylamino)-anthraquinone[DAAQ]. 4-phenylazo-1-naphthylamine (5.6 g, 22.6 mmol), 1,4-dichloroanthraquinone (2.5 g, 9.0 mmol), $Pd_2(dba)_3$ (0.219 g, 0.24 mmol), [2.2′-bis(diphenylphosphine-1.1′-binaphthyl] (BINAP) (0.437 g, 0.70 mmol), cesium carbonate (11.58 g, 35.54 mmol) and 100 ml toluene were into the 3neck flask. Then the mixture was stirred for 24 h at 110°C under nitrogen. The reaction mixture was quenched with 5 ml water and extracted with chloroform ($CHCl_3$) and dried over magnesium sulfate anhydrous ($MgSO_4$). Evaporation of solvent under vacuum resulted in a black residue, which was purified by column chromatography using tetrahydrofuran (THF) and reprecipitation with acetone. (0.90 g, yield: 14.4%) ^1H NMR (500 MHz,$CDCl_3$) δ (ppm): 12.88 (s,2H), 9.07–9.05 (d,2H), 8.48–8.47 (m,2H), 8.36–8.34 (d,2H), 8.05–8.04 (d,4H), 7.92–7.91 (d,2H), 7.84–7.83 (m,2H), 7.75–7.67 (m,4H), 7.60–7.55 (m,8H), 7.51–7.46 (t,2H); FAB-Mass 698 m/z.

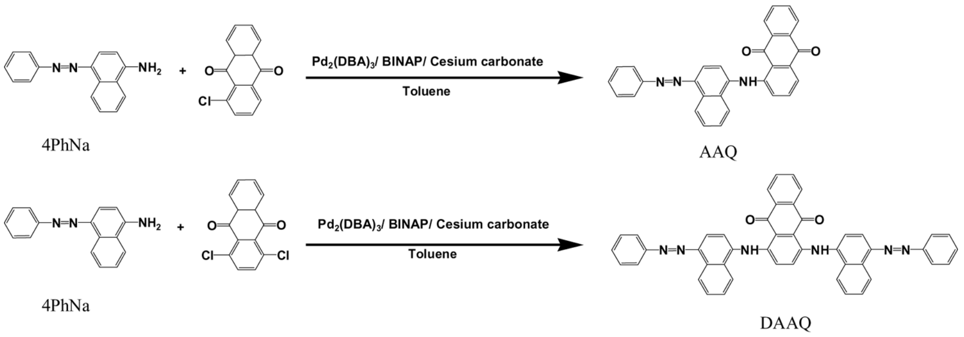
Measurements

^1H-NMR spectra were recorded on Bruker, Advance 500 and fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra of synthesized materials were obtained by HP 8453 UV-VIS-NIR spectrometer. The melting temperatures (T_m), glass-transition temperatures (T_g) and degradation temperatures (T_d) were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) operated at heating rates 10°C/min. Thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). The Thermal stability of samples under a nitrogen atmosphere was determined by measuring their mass losses while heating at a rate 20°C/min. T_d was determined from the 5% degradation points of weight loss of the compounds.

Results and Discussion

As shown in Scheme 2, 4PhNa and mono-substituted or di-substituted anthraquinone with chlorine substituted at position 1 or 1 and 4 were used to synthesize AAQ and DAAQ in facile one step reaction through Suzuki C-N coupling. The structure of synthesized materials was mainly verified by using ^1H NMR and mass spectrum. NH-proton shows intramolecular hydrogen bonding with the carbonyl group of anthraquinone. Therefore, NH_2 peak prior to synthesis was 4.59 ppm and NH-proton peak moved respectively to 11.96 and 12.88 ppm after synthesis in ^1H NMR spectroscopy of the synthesized AAQ and DAAQ [14].

UV-visible spectra of synthesized materials in solution state are summarized in Figure 1 and Table 1. As shown in Figure 1, absorption spectrum of 4PhNa in the visible region (400∼800 nm) has a peak at 440 nm and the synthesized AAQ and DAAQ also respectively showed peak spectrum at 428 and 481 nm. Also in case of 4PhNa, the range of absorption spectrum in the visible region is 400∼550 nm and 1-chloroanthraquinone and 1,4-dichloroanthraquinone absorb UV wavelength light under 400 nm. However, AAQ was found to absorb broader range of spectrum



Scheme 2. Synthetic routes of AAQ and DAAQ.

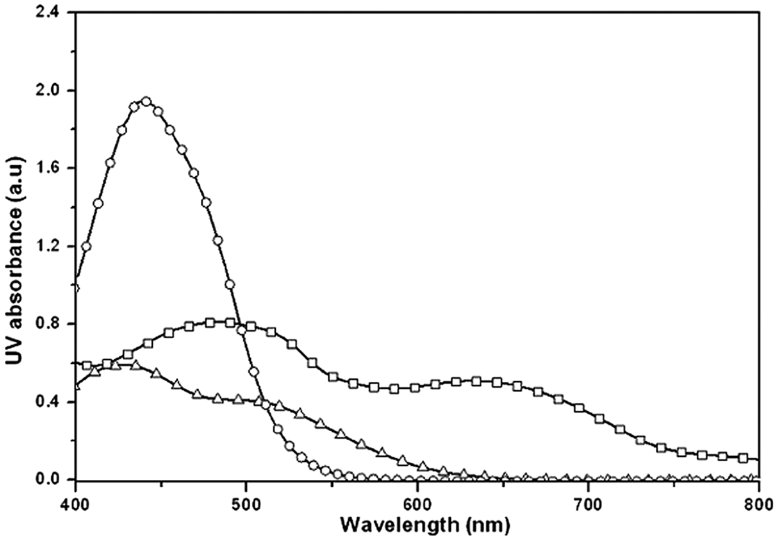


Figure 1. UV-Visible spectra of 4PhNa (-○-), AAQ (-△-) and DAAQ (-□-) (1×10^{-4} M in THF solution).

Table 1. Optical properties of 4PhNa, AAQ and DAAQ in THF solution (1×10^{-4} M concentration)

	UV_{max} (nm)	UV Absorption-range (nm)	ε (L/cm · mol)	Log ε
4PhNa	440	400∼580	1.9×10^4	4.29
AAQ	428	503∼624	5.9×10^3	3.77
DAAQ	481	400∼800	8.1×10^3	3.91

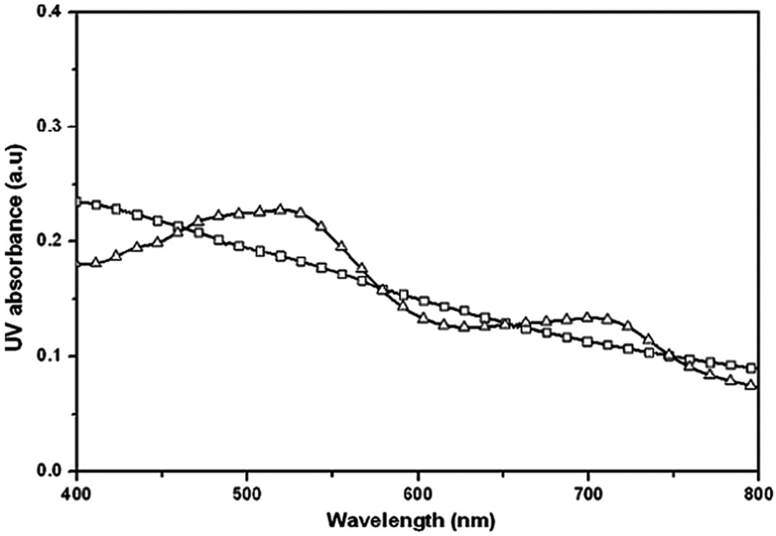


Figure 2. UV-Visible spectra of AAQ (-△-) and DAAQ (-□-) (film on the glass).

including 503 ~ 624 nm and DAAQ showed possibility as a BM material with absorption of the entire visible region between 400~800 nm. This result can be interpreted by that as the number of intramolecular hydrogen bonding between anthraquinone carbonyl group and NH-proton increases, absorption spectrum become wider from 440 nm to longer wavelength [11].

Extinction coefficient value of AAQ and DAAQ was respectively 5.9×10^3 and 8.1×10^3 L/cm · mol. Converted into log, these values were relatively high at 3.77 and 3.91. The two synthesized materials were made into film state by using spin coating on a glass substrate. As a result of measuring UV-visible spectrum in film state, as shown by Figure 2, AAQ absorbs the entire visible region, which is broader range of absorption compared to that in solution state. This result could be due to the absorption of longer wavelength region by molecular packing and stacking in film state. DAAQ was also verified to evenly absorb the whole visible region. Therefore, both AAQ and DAAQ presented possibility as organic black matrix pigments.

Thermal stability of the synthesized materials was measured by TGA and DSC, and the results are summarized in Table 2. T_d of AAQ and DAAQ was 353 and 366°C, respectively. AAQ showed T_m at 267°C. Since this result has higher thermal stability than the highest temperature (250°C) reached during LCD manufacturing process, these materials can be candidate for LCD organic BM material [2,8]. An experiment is currently being conducted on the synthesis which increases the number

Table 2. Thermal property of AAQ and DAAQ

	T_g (°C)	T_m (°C)	T_d (°C)
AAQ	–	267	353
DAAQ	–	–	366

of intramolecular hydrogen bonding in a molecule and on dispersion stability of the synthesized materials for various application.

Conclusions

Black matrix pigments AAQ and DAAQ composed of new single material were synthesized for the first time through Suzuki C-N coupling based on representative dye and pigment functional groups, azo group and anthraquinone moiety. As a result of verifying UV-visible spectrum in solution state, absorption range was shown as 4PhNa (400~580 nm), AAQ (503~624 nm) and DAAQ (400~800 nm). This result could be due to the increased number of intramolecular hydrogen bonding between 1,4 substituted NH-proton and carbonyl group in anthraquinone. Particularly in case of DAAQ, the entire visible region is absorbed with high extinction coefficient of 8.1×10^3 L/cm · mol. As a result of measuring UV-visible spectrum in film state prepared by spin coating, both AAQ and DAAQ absorbed the entire visible region.

For thermal stability of synthesized materials, T_d of AAQ and DAAQ was respectively 353 and 366°C. T_m of AAQ was measured at 267°C. Since synthesized materials have high thermal stability compared to the peak temperature of 250°C during LCD manufacturing process, they can be used as LCD organic BM pigments.

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