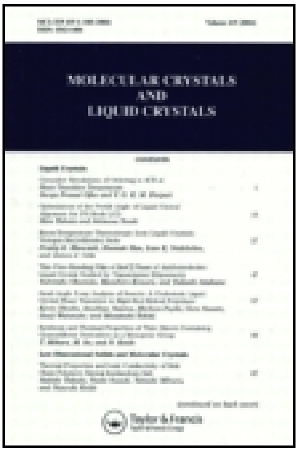

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Synthesis and Physical Property Measurement of New Red Pigment based on Anthraquinone Derivatives for Color Filter Pigments

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In this study, two red compounds for CF pigment bearing piperidine or morpholine group at 1,5-postion of anthraquinone were newly synthesized. It was observed that maximum values of UV-visible absorption of 1,5-DMAQ and 1,5-DPAQ were 488 and 498 nm, respectively, where 1,5-DMAQ has shown higher blue-shifted value than 1,5-DPAQ. These compounds show high molar extinction coefficient values of 10^3 L/mol·cm and can be processed in spin-coating method. The synthesized materials are expected to be candidates for CF pigments in solution process. In temperature study, 1,5-DPAQ and 1,5-DMAQ were decomposed at 184°C and 225°C.

Keywords: Anthraquinone; 1; 5-position; pigment; color filter; molar extinction coefficiency; solution process

1. Introduction

In the past, dyes and pigments have been mainly used as paint, ink, plastics, and fabrics, etc.[1–3] However, in recent years, these materials are increasingly applied as the core material of color filter (CF) generating full color spectrum for liquid crystal display (LCD), as a display industry is growing so rapidly due to fast development of information technology. Furthermore, nowadays the same dye and pigment materials are widely applied in image sensors to be used in charge-coupled device (CCD) camera and web-camera.[4] The dyes and pigments in CF generate a full color spectrum by reflecting or absorbing light of particular wavelength, when white-backlight is injected to CF, red, green and blue pigments.[5–7] Therefore, since the lights of a desired wavelength should be penetrated massively and those of the rest wavelength be filtered to maximum extent, the pigments used in CF should have a high molar extinction coefficient on the wavelength that is required to be absorbed.[4] The pigments also require improvement of thermal stability since CF manufacturing process requires thermal stability of 200°C or above and solution-processible material to simplify process, reduce material loss and improve productivity. The molecular structure of the new colorant materials was designed mainly based on this concept.

In this study, two kinds of pigments for color filter were newly synthesized by placing piperidine or morpholine group at 1,5-position of anthraquinone. Also their physical properties such as optical, thermal and electrochemical characteristics were investigated.

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2. Experimental

2-1. General Method and General Syntheses of New Red Pigments[8]

The following compounds have been synthesized following literature procedures.

In a three-necked flask, under nitrogen atmosphere, 1g (3.6mmol) of 1,5-dichloroanthracene-9,10-dione was allowed to react with 3.56ml (36mmol) of piperidine (3.56ml, 36 mmol) in dimethyl sulfoxide (DMSO) (30 ml) at 70°C for 1 h. The mixture was then allowed to cool down at room temperature. Water (30ml) was then added and red solid precipitated. After filtration, the red solid obtained was recrystallized from dichloromethane (MC) and methanol.

2-2. 1,5-di(piperidin-1-yl)anthracene-9,10-dione (1,5-DPAQ)

The yield 52% ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83-7.80(d, 2H), 7.58-7.52(t, 2H), 7.28(s, 2H), 3.16-3.13(t, 8H), 1.83(s, 8H), 1.67-1.57(t, 4H). Fab$^+$-MS m/e : 374.

2-3. 1,5-dimorpholinoanthracene-9,10-dione (1,5-DMAQ)

The yield was 78.7%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.92-7.90(d, 2H), 7.66-7.61(t, 2H), 7.30-7.28(d, 2H), 4.02-3.99(t, 8H), 3.20-3.17(t, 8H). Fab$^+$-MS m/e : 378.

3. Results and Discussion

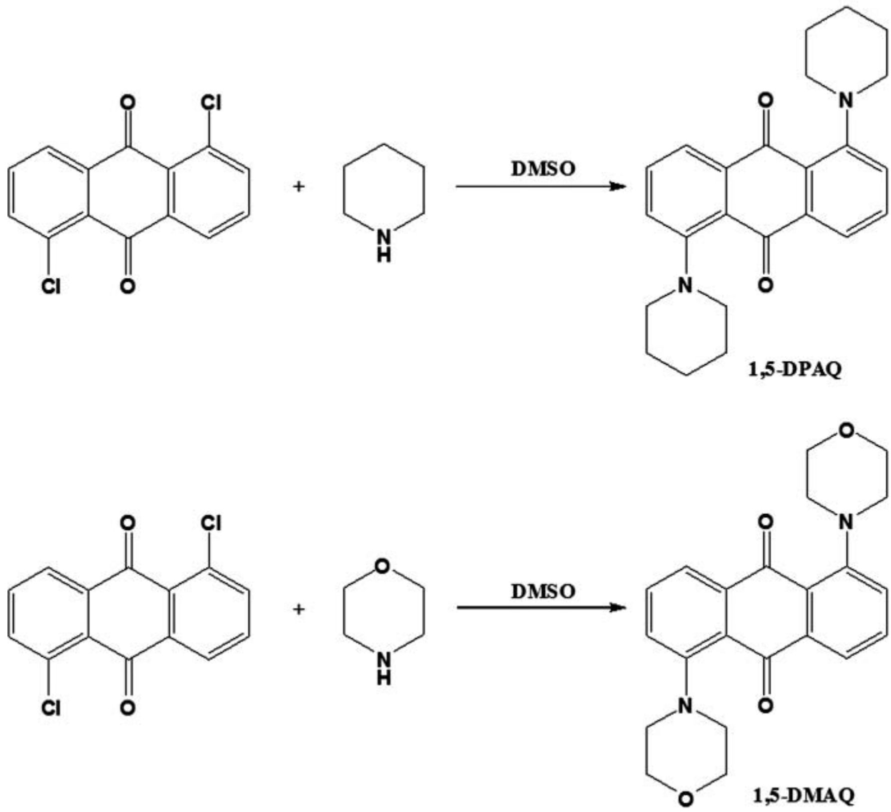
The synthesized materials, substituents of anthraquinone to 1,5-position, are two new red pigments that adopted piperidine and morpholine groups. Their molecular structure and reaction scheme were arranged in Scheme 1.

The optical properties of the synthesized materials were measured with the use of UV-visible (UV-Vis.) absorption spectrum, which were summarized in Figure 1 and Table 1. As shown in Figure 1, UV-Vis. absorption maximum values of 1,5-DMAQ and 1,5-DPAQ were 488 and 498 nm where 1,5-DMAQ showed more blue-shifted value compared to 1,5-DPAQ. These compounds exhibit the molar extinction coefficient values in the range of $3.4 \times 10^3 \sim 4.9 \times 10^3$ L/mol·cm. In the case of other anthraquinone derivative, 1-(dimethylamino)-9,10-anthraquinone has a value of 4900, which means that the values of our synthesized compounds are similar with other conventional 1-substituted anthraquinone derivative.[9] As shown in Table 1, these values are also slightly higher than 1,5-diaminoanthraquinone which does not have a ring.

Table 1. Optical and electrochemical properties of anthraquinone derivatives.

Compound	UV^a_{max} (nm)	ε^b (L/mol·cm)	HOMO (eV)	LUMO (eV)	Band gap (eV)
1,5-DPAQ	498	4.86×10^3	5.38	3.26	2.12
1,5-DMAQ	488	3.36×10^3	5.45	3.23	2.22

a: 2.5×10^{-4} M in THF solution.
b: 1,5-diaminoanthraquinone 2.5×10^{-4} M in THF solution $\varepsilon = 2.32 \times 10^3$ (L/mol·cm).



Scheme 1. Synthetic route of 1,5-DPAQ, 1,5-DMAQ.

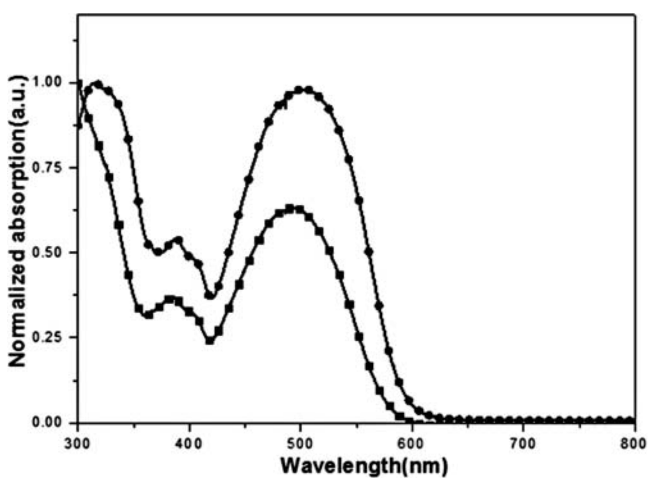


Figure 1. Normalized UV-Visible spectra of 1,5-DPAQ(■), 1,5-DMAQ(•) in THF solution.

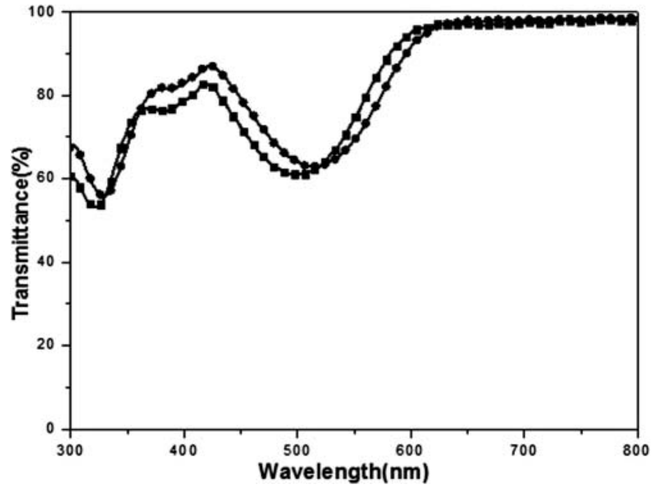


Figure 2. Transparent spectra of 1,5-DMAQ(■), 1,5-DPAQ(●): spin-coating (3 wt% $CHCl_3$ solution) films on glass substrate.

For the reference, Figure 2 shows the transparent spectrum of the synthesized compounds in film state. The synthesized materials are expected to be candidate for CF pigments in solution process. HOMO, LUMO levels and band gap were obtained through measurements of the cyclic voltammetry (CV) and UV-visible spectra of the synthesized material (see Table 1). In the case of HOMO levels, 5.38 and 5.45 eV, were similar regardless of the substituents of the synthesized material.

Thermal stability of the synthesized materials was measured with the thermo gravimetric analysis (TGA) which were summarized in Figure 3. As shown in Figure 3, thermal

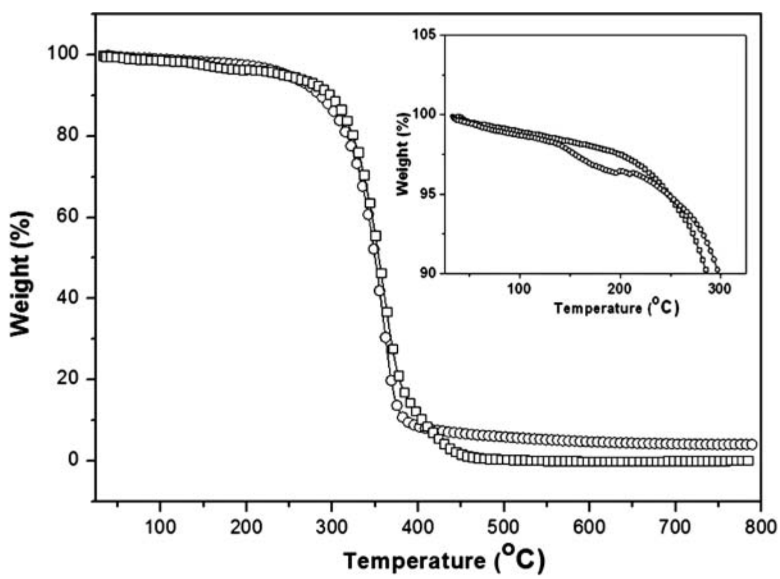


Figure 3. Thermogravimetric analysis (TGA) of 1,5-DPAQ(□), 1,5-DMAQ(○).

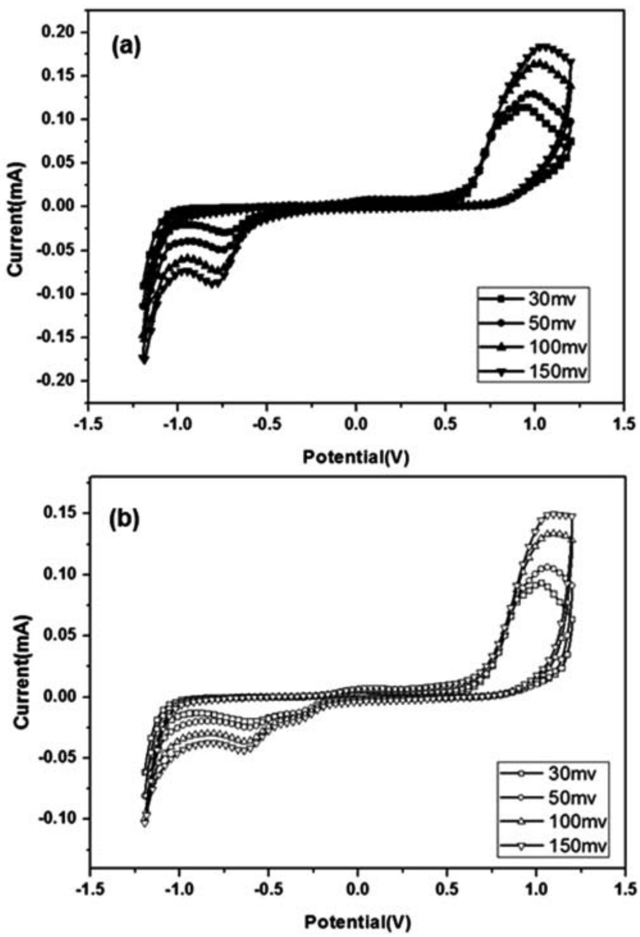


Figure 4. Cyclic voltammograms of (a) 1,5-DPAQ, (b) 1,5-DMAQ [0.1M $(n\text{-}Bu)_4NBF_4$] with various scan rates 30 mV/s –150 mV/s.

stability of the synthesized material, T_d values of 1,5-DPAQ and 1,5-DMAQ were respectively 184 and 255°C. This result indicated that 1,5-DMAQ with oxygen showed relatively higher thermal stability, compared to 1,5-DPAQ with carbon, which means that improved thermal resistance of 1,5-DMAQ is due to the increase of intermolecular interaction by the adoption of oxygen instead of carbon. It was found that 1,5-DMAQ showed improved thermal resistance and satisfied the thermal stability condition 200°C or above which is required in CF manufacturing process.

To evaluate the electrochemical kinetic properties of 1,5-DPAQ and 1,5-DMAQ, the synthesized compounds, CV was measured to various scan rates at 30∼150 mV/s. The peak potentials were shifted gradually to slightly higher potential as scan rate increased as shown in Figure 4. The synthesized 1,5-DPAQ and 1,5-DMAQ showed similar oxidation voltage of about 0.6 V. In addition, 1,5-DPAQ and 1,5-DMAQ showed irreversible reduction. Reduction curve also increased gradually with increase in scan rate. The electrochemical process of the synthesized compounds showed reproducible results in −1.2∼1.2 V potential range under $Ag/AgNO_3$ conditions. One different result between two compounds in CV was that two reduction peaks were found in 1,5-DMAQ, which might be due to oxygen. It

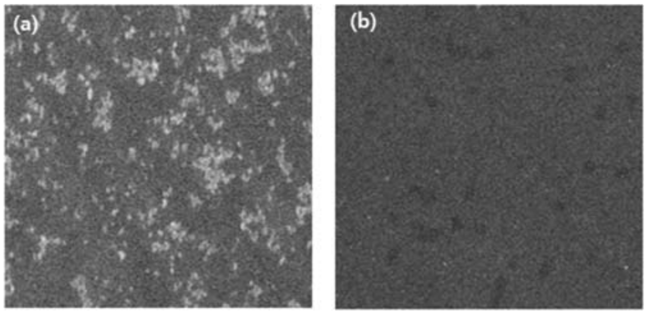


Figure 5. SEM images ($\times 8000$) of 1,5-DMAQ(1×10^{-3}M THF solution), Red 254 spin-coating (0.1 wt%, THF solution) films on glass substrate a) Red 254, b) 1,5-DMAQ.

was empirically known that redox peak was increased by scan rate in power law function. The related exponential values were calculated through re-plotting of CV data. If electrochemical oxidation-reduction reaction is reflected in electron transfer process or reactant diffusion process, exponential value, x is 1 or 0.5, respectively.[10,11] The oxidation current density and scan rate of synthesized compounds showed linearly proportional relationship. Based on the re-plot data in 30mV/s$\sim$ 150mV/S range, the x values of 1,5-DPAQ and 1,5-DMAQ were 0.298 and 0.297. These values mean that they are similarly close to diffusion process.

By capturing SEM images (see Figure 5) after spin-coating, 1,5-DMAQ was found to be superior to commercial red pigment, red 254 in surface. It means that 1,5-DMAQ was a candidate for red solution-processible pigment having the proper thermal property.

4. Conclusions

Two red-colored compounds for CF pigment bearing piperidine or morpholine group at 1,5-postion of anthraquinone were successfully synthesized, and its physical properties were also investigated by the respective substituent of the synthesized materials. Maximum UV-visible absorption values of 1,5-DMAQ and 1,5-DPAQ were 488and 498 nm and particularly 1,5-DMAQ showed values blue-shifted more than 1,5-DPAQ. These compounds showed high molar extinction coefficient values of 10^3 L/mol·cm. The synthesized materials are expected to be candidate for CF pigments. Electrochemical properties of these anthraquinone derivatives were additionally investigated by CV and HOMO levels of the two compounds were 5.38 and 5.45 eV, respectively. In thermal property of the synthesized compounds, T_ds of 1,5-DPAQ and 1,5-DMAQ were 184°C and 225°C. In SEM images, the surface of 1,5-DMAQ material was superior to that of the commercial red pigment, red 254. 1,5-DMAQ could be a good candidate for red solution-processible pigment having the proper thermal property.

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