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# Improving nanoparticle dispersions of pigment and its application to a color filter: New phthalocyanine derivatives as synergist

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ABSTRACT

Four synergists were synthesized to enhance pigment nanoparticles dispersion and the contrast ratio. The interaction between the synergist and the dispersant was confirmed by infra-red (IR) spectrometry. We demonstrate that the hydrogen bonds forming between the synergist and the dispersant act as a key factor. To analyze the dispersion properties, dynamic light scattering (DLS), and electron microscopic analysis was examined. The spectral and color characteristics was also measured by UV–vis spectrometry and colorimetry, and the contrast ratio of color filters was evaluated. This study confirms that the prepared synergist can increase the contrast ratio of green color filter.

## Introduction

In display devices using a backlight unit such as an LCD, especially, the particle size of the pigments affects not only chromatic properties such as brightness and color but also contrast ratio related to light scattering [1]. The large pigment particles in the color filter scatter the transmitted light. The polarization of the light is changed and becomes uncontrollable, resulting in a transmission of additional light and a decrease in the contrast ratio. Light scattering is related to the particle size, ratio of the refractive indices between the particle and surrounding medium, and particle shape. Among these factors, the particle size exerts a profound influence on the scattering of incident light [2]. Theoretically, larger particles cause more scattering than smaller particles, provided that the refractive index of the particles is the same [3].

For this reason, the solvent-based wet dispersion method with polymer dispersant is used to obtain fine particles, incorporated into an LCD color filter. To obtain a well-dispersed system, preventing the coagulation of the colloidal pigment is very important. This stabilization mainly occurs *via* electrostatic and steric stabilization. However, the former is induced in highly polar systems such as aqueous inks, while the latter is the primary factor in solvent-based systems [4]. Therefore, additives like a polymeric surfactant and synergists are added to obtain stabilized particles in a non-polar solvent, and these additives play a crucial role in producing fine particles. In the wet-dispersion process, the ground pigment powder is stabilized by a dispersing agent. The dispersing agent is adhered to the surface of the pigments after the wetting and grinding stage, and this adsorption of the dispersing agent leads to repulsion between the particles, thereby preventing the flocculation of the particles. The interaction between the dispersant and pigment particles could be induced by different types of force (*e.g.*, ionic, hydrogen-bonding, and electrostatic) [4].

However, in some organic pigments such as phthalocyanine and dioxazine derivatives, the pigment molecules are not responsive to any of the dispersants, owing to their large planar structures. Thus, dispersions of these pigments easily flocculate after grinding. This issue could be resolved by enhancing the interaction between the pigment and dispersant. The synergist can play this role by adsorbing on the pigment surface and then anchoring the dispersant. When the pigments are dispersed by using only the dispersant without a synergist, the dispersion performance including particle size is inferior, and the stability is also considerably reduced. In contrast, when synergists are introduced, the particle size and dispersion stability can then be improved, resulting in better chromatic characteristics [5].

The synergist has a structure capable of interacting with pigments and contains a functional group indicating high affinity with a dispersant, thus increasing the dispersion performance in

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the dispersion matrix [6]. Because chromatic features and transmittance are crucial to image quality, the spectral characteristics of the synergist must be contemplated for the ink of the color filter. Therefore, it is necessary to adopt a synergist, which has similar spectral characteristics to the pigment for the color filter.

Several studies have been carried out to introduce synergists to improve the dispersion of pigments applied to the color filter [5,7–9]. Those studies focused on a blue, a red, and a yellow pigment. To the best of our knowledge, the investigation of a new synergist for green pigments has not been reported. The present study was performed to propose new green synergists that can retain the color properties and increase the dispersion performance of a green pigment used in the color filter. Ultimately, the contrast ratio of the LCD color filter was enhanced by reducing the pigment particle size.

We synthesized synergists for enhancing the dispersion of pigment green 7, which is widely used as a green colorant for the color filter and exhibits inferior dispersion properties. The synergists are designed to ensure the color characteristics of the color filter by showing appropriate spectral characteristics for green. The phthalocyanine was modified to indicate a high intermolecular interaction between the synergist and the pigment. Furthermore, the bathochromic shift of the absorption wavelength was intended by chlorination, and various substituents were added as a dispersant-affinic group to interact with the dispersant: ester, carboxylic acid, primary amine, and tertiary amine. The dispersion characteristics and color properties were investigated by average particle size, polydispersed index (PDI), zeta potential, and UV–vis spectrometer. The interaction between the synergists and a dispersant was demonstrated by using FT-IR spectrometer. The contrast ratio of the green color filter with the pigment dispersion was then examined. Finally, a suitable synergist that can improve the dispersion of pigment green 7 was proposed. The results were used to increase the contrast ratio of a green color filter for LCDs.

## Experimental

### Materials

1,8-Diazabicyclo-7-undecene (DBU), 4,5-dichlorophthalonitrile, ethyl 4-hydroxy-3-methoxybenzoate, *N*, *N*-dimethyl-3-aminophenol, and 3-aminophenol were purchased from TCI, and $ZnCl_2$, potassium carbonate anhydrous, lithium hydroxide monohydrate, and 1-pentanol were purchased from Sigma-Aldrich. The other reagents and solvents were obtained from commercial suppliers. All chemicals were reagent-grade. Transparent glass substrates were provided by NTP, Inc., and acrylic polymer binder [9] was supplied by NDM, Inc.

### Characterization and instruments

$^1$H NMR spectra were recorded on a Bruker Avance 500 spectrometer (National Center for Inter-University Research Facilities at Seoul National University) at 500 MHz using dimethyl sulfoxide-d6, chloroform-d with tetramethylsilane (TMS) Elemental analysis was performed with a Thermo Scientific Flash EA 1112 elemental analyzer. Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation (National Center for Inter-University Research Facilities at Seoul National University). UV–vis absorption spectra were measured using a PerkinElmer Lambda 25 spectrophotometer, and Fourier transform infrared spectroscopy (FT-IR) was conducted using a Thermo Scientific Nicolet 6700. The particle size analysis was performed using a Photal Otsuka Electronics ELSZ-1000, samples were prepared by diluting the dispersion with PGMEA (0.1 wt.%). The thickness of the spin-coated color filter was measured using a KLA-TENCOR Nanospec AFT/200 alpha step. Transmission electron microscopy (TEM) was performed on an FEI Tecnai F20 with an acceleration voltage of 200 kV; samples were prepared according to the literature procedures [7]. Field-emission scanning electronic microscopy (FE-SEM) images were acquired on a Zeiss MERLIN Compact; Pt was coated on the samples using JEOL MSC-101 for 40 secs at a current strength of 40 mA to avoid charging of the surface. Atomic Force Microscopy (AFM) was undertaken using a Park Systems NX-10. The color properties and transmittance spectra of the color filters were measured on a Scinco color spectrophotometer. The contrast ratio were analyzed using Tsubosaka Electric CT-1 BSLE.

### Synthesis

#### Synthesis of compound 1 (ethyl 4-(2-chloro-4,5-dicyanophenoxy)-3-methoxybenzoate)

4,5-Dichlorophthalonitrile (1 g, 5.10 mmol) and ethyl 4-hydroxy-3-methoxybenzoate (1.10 g, 5.61 mmol) were dissolved in dry DMF (50 mL) and anhydrous $K_2CO_3$ (3.52 g, 25.5 mmol) was added portion wise for 3 h. The mixture was stirred at 80 °C for 12 h under nitrogen atmosphere. The solution was then poured into ice water (100 mL) with vigorous stirring to precipitate the product. The resulting suspension filtered to give a white-yellowish powder. Pure product was collected by column chromatography on silica gel using MC/hexane (3:1) mixture as an eluent. Yield 66%; $^1$H NMR ($CDCl_3$, 500 MHz, 25 °C, TMS): δ 7.87 (s, 1H, Ar-H), 7.77 (d, J = 10 Hz, 2H, Ar-H), 7.20 (d, J = 8.5 Hz, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 4.43 (q, J = 7 Hz, 2H, ester-CH2), 3.85 (s, 3H, OCH3), 1.43 (t, J = 7.5 Hz, 3H, CH3); $^{13}$C NMR ($CDCl_3$, 500 MHz, 25 °C, TMS): δ 165.36, 157.24, 150.71, 144.76, 135.41, 130.27, 128.83, 123.38, 122.13, 119.54, 115.35, 114.38, 114.28, 109.83, 61.54, 56.24, 14.32.

#### Synthesis of compound 2 (4-chloro-5-(3-(dimethylamino)phenoxy) benzene-1,2-dicarbonitrile)

The product was synthesized following the same procedure for ethyl 4-(2-chloro-4,5-dicyanophenoxy)-3-methoxybenzoate using 4,5-dichlorophthalonitrile (1 g, 5.10 mmol), 3-(dimethylamino) phenol (0.77 g, 5.61 mmol), DMF (50 mL), and anhydrous $K_2CO_3$ (3.52 g, 25.5 mmol). The crude product was purified by column chromatography on silica gel using EA/hexane (1:4) mixture as the eluent. Yield 73%; $^1$H NMR (d6-DMSO, 500 MHz, 25 °C): δ 8.51 (s, 1H, Ar-H), 7.50 (s, 1H, Ar-H), 7.26 (t, J = 8.5 Hz, 1H, Ar-H), 6.64 (dd, J = 8.5, 2.5 Hz, 1H, Ar-H), 6.48 (t, J = 2.5 Hz, 1H, Ar-H), 6.36 (dd, J = 8.0, 2.5 Hz,1H, Ar-H), 2.91 (s, 6H, amine-CH3); $^{13}$C NMR (d6-DMSO, 500 MHz, 25 °C): δ 157.07, 154.69, 152.25, 136.00, 130.66, 128.53, 121.93, 115.14, 114.98, 109.70, 109.16, 106.28, 103.27, 39.92.

#### Synthesis of compound 3 (4-(3-aminophenoxy)-5-chlorobenzene-1,2-dicarbonitrile)

The product was synthesized following the same procedure for ethyl 4-(2-chloro-4,5-dicyanophenoxy)-3-methoxybenzoate using 4,5-dichlorophthalonitrile (1 g, 5.10 mmol), 3-aminophenol (0.61 g, 5.61 mmol), DMF (50 mL), and anhydrous $K_2CO_3$ (3.52 g,25.5 mmol). The white yellowish solid was obtained that was purified by column chromatography on silica gel using MC/hexane (10:1) mixture as the eluent. Yield 78%; $^1$H NMR (d6-DMSO, 500 MHz, 25 °C): δ 8.51 (s, 1H, Ar-H), 7.56 (s, 1H, Ar-H), 7.09 (t, J = 8 Hz, 1H, Ar-H), 6.49 (d, J = 8 Hz, 1H, Ar-H), 6.28 (t, J = 2.5 Hz, 1H, Ar-H), 6.23 (dd, J = 8, 2.5 Hz, 1H, Ar-H), 5.41 (s, 2H, amine-H); $^{13}$C NMR (d6-DMSO, 500 MHz, 25 °C): δ 156.82, 154.85, 151.06, 136.08, 130.70, 128.91, 122.49, 115.14, 114.96, 111.38, 109.39, 105.92, 104.12.

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