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The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters

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ABSTRACT

Although dyes have superior spectral characteristics, they are not widely used as coloring materials for liquid crystal display color filters owing to their low thermal stability. Four perylene and four phthalocyanine dyes of high thermal stability were synthesized and then used to fabricate color filters. The spectral and thermal stabilities of the color filters were investigated by comparing them with pigment-dispersed color filters. The transmittance and color properties of the prepared color filters were higher and the thermal stability was similar to those of the pigment-dispersed color filters. The results showed that the prepared dyes could be successfully applied in ink-jet printed liquid crystal display color filters.

1. Introduction

A color filter (CF) is a key component for rendering color images in liquid crystal display (LCD) panels. The color filter layer is fabricated with colorants of red (R), green (G), and blue (B) from either dyes or pigments. These colorants convert white backlight into R, G, B colors [1,2].

In manufacturing CFs, there are four traditional processes, which include dyeing, pigment dispersion, printing and electrodeposition method [3,4]. Among these technologies, the pigment dispersion method has been widely used in mass production of CF for LCD since it can produce CFs of high durability and good color reproducibility. However, this method has spectral drawbacks such as decreased transmittance of light and contrast ratio caused by aggregation of pigment particles [5].

In order to manufacture LCD panels of higher resolution and larger-size, some innovative methods for CF have been tried such as ink-jet printing, latent pigment technology and acid proliferation type pigment dispersion [6–10]. Among these technologies, researches on ink-jet printing method are active nowadays, thanks to the full development of digital printing technology. However, all these approaches use pigments, therefore, they have the aforementioned limitation of transmittance and contrast ratio.

On the other hand, dye-based CF (D-CF) can have higher transmittance and contrast ratio due to lower light scattering since dyes can be dissolved in a media and exist in molecular phase. Especially, for the ink-jet system which needs highly concentrated ink, the dye-based ink is more suitable than pigment-based ink. Thus, to overcome the limited optical performance of CF with pigments, applying dyes to CF can be an attractive alternative.

It was previously studied that CF fabricated by dyeing method was characterized by high transmittance and good color purity. However, the dyeing method using dyes as coloring materials is not widely used for commercial manufacturing process of CF due to the unsatisfactory thermal, light and chemical resistance of dyes [11]. Thermal stability of dyes is a main drawback while light and chemical stabilities are not so serious problems. In case of photostability, the light emitted from the backlight unit loses considerable energy as it passes through first polarizing film, glass, TFT array and liquid crystal. Also, the light entered from outside is blocked by frontal anti-UV-coating film, second polarizing film, indium tin oxide (ITO) and overcoat layer, thereby preventing photo-fading of the colorants [12,13]. Moreover, the photo-fading can be decreased by mixing auxiliaries such as antioxidants containing benzophenone moiety [14,15]. The chemical stability of colorants can also be compensated by the overcoat layer. However, many dyes are not as resistant to heat as pigments. Discoloration of dye easily occurs

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during the alignment layer forming step performed at 230 °C for an hour. Thus, it is indispensable to improve thermal stability of dyes for commercial production of dye-based CF.

In this study, we have designed and synthesized perylene and phthalocyanine based dyes of high thermal stability and superior spectral property for ink-jet printed CF. The structures of the dyes are designed so that they can induce sufficient intermolecular packing. In addition, the dyes are designed to have high water solubility so that they can be dissolved into the main media of the ink i.e. water. With the synthesized dyes, CF was fabricated via direct ink-jet printing on the black matrix-patterned glass. The heat-resistance, transmittance and color gamut of the prepared CF were investigated and compared with those of pigment-based CF.

2. Experimental

2.1. Materials and instrumentation

3,4,9,10-Perylene-tetracarboxylic dianhydride, 4-chloroaniline, 4-bromoaniline, sulfanilic acid, *m*-cresol, fuming sulfuric acid (oleum) of 20% SO_3 from Sigma–Aldrich, and 6-amino-2-naphthalene-sulfonic acid, isoquinoline, Co-phthalocyanine, Cu-phthalocyanine, Ni-phthalocyanine, Zn-phthalocyanine, 2,4-dinitro-1-naphthol-7-sulfonic acid disodium salt (C.I. Acid Yellow 1), C.I. Acid Violet 43 from TCI were used. ORASOL® Yellow 4GN (C.I. Solvent Yellow 146) was supplied by Ciba Korea Ltd. Pigment-based color resists of NF-R017D (red), NF-G022M (green), NF-B016M (blue) were supplied by Dongwoo Fine-Chem. All other reagents and solvent were of reagent-grade quality and obtained from commercial suppliers. Transparent glass substrate was provided from Paul Marienfeld GmbH & Co. KG. Commercial acrylic binders of LM100, LM300, LM500 and Cr-based black matrix-patterned glass were supplied by LG Micron Co., Ltd.

^{1}H NMR spectra were recorded by Bruker Avance 500 at 500 MHz using DMSO-d_6, as solvent and TMS as the internal standard. Fourier transform-infrared (FT-IR) spectra were recorded as KBr pellets on a Perkin Elmer Spectrum 2000 FT-IR spectrometer. Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI–TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation with α-cyano-4-hydroxy-cynamic acid (CHCA) as matrix. Absorption and transmittance spectra were measured on a HP8452A spectrophotometer. Chromatic characteristics of CFs were analyzed by Otsuka Electronics LCF A2000 spectrometer. Thickness of the CFs was measured using Nano System Nanoview E-1000. Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate 10 K min^{-1} with a TA Instruments Thermogravimetric Analyzer 2050.

2.2. Synthesis

2.2.1. Synthesis of dye intermediates (**1a–d**)

N,N′-Bis-(4-chlorophenyl)-3,4,9,10-perylenebis(dicarboximide) (**1a**) was prepared according to the following procedure. A mixture of 3,4,9,10-perylene-tetracarboxylic dianhydride (19.6 g, 0.05 mol), 4-chloroaniline (12.8 g, 0.1 mol), *m*-cresol (300 ml) and isoquinoline (30 ml) was stirred at 50 °C for 2 h. The solution was heated at 130 °C for 5 h, the temperature was raised to 150 °C and kept for 4 h. The reaction was then completed by stirring at 200 °C overnight. The warm solution was poured into 250 ml of acetone, and the precipitate was filtered out and dried at 100 °C under vacuum. The crude product was washed with 5% NaOH until the characteristic green fluorescent color of perylene dianhydride disappear and the unreacted 4-chloroaniline and high boiling point solvents, *m*-cresol and isoquinoline were cleared by ethanol reflux for 2 h. Dyes of **1b–d** were synthesized in the same manner with dye **1a** using 4-bromoanilene, sulfanilic acid and 6-amino-2-naphthalene-sulfonic acid (Scheme 1). The yields, ^{1}H NMR, FT-IR and Mass data of the dyes are given below.

*2.2.1.1. Compound **1a**.* Yield 83.2%; ^{1}H NMR (DMSO-d_6, ppm): 9.12 (d, 4H), 8.65 (d, 4H), 7.62 (d, 4H), 7.50 (d, 4H); FT-IR (KBr, cm^{-1}): 1705 (C=O), 1356 (C–N); MALDI–TOF MS: *m*/*z* 649.94 (100%, $[M+K]^+$).

*2.2.1.2. Compound **1b**.* Yield 81.5%; ^{1}H NMR (DMSO-d_6, ppm): 9.00 (d, 4H), 8.60 (d, 4H), 7.55 (d, 4H), 7.44 (d, 4H); FT-IR (KBr, cm^{-1}): 1703 (C=O), 1357 (C–N); MALDI–TOF MS: *m*/*z* 685.38 (100%, M^+).

*2.2.1.3. Compound **1c**.* Yield 75.7%; ^{1}H NMR (DMSO-d_6, ppm): 8.62 (d, 4H), 8.53 (d, 4H), 8.25 (d, 4H), 8.20 (d, 4H); FT-IR (KBr, cm^{-1}): 1700 (C=O), 1358 (C–N), 1255, 1181 (S=O), 642 (S–O); MALDI–TOF MS: *m*/*z* 746.90 (100%, $[M+2Na]^+$).

*2.2.1.4. Compound **1d**.* Yield 77.8%; ^{1}H NMR (DMSO-d_6, ppm): 8.42 (s, 2H), 8.07 (d, 4H), 7.82 (d, 4H), 7.67 (d, 2H), 7.58 (d, 2H), 7.35 (d, 2H), 7.16 (s, 2H), 7.10 (d, 2H); FT-IR (KBr, cm^{-1}): 1704 (C=O), 1348 (C–N), 1200, 1096 (S=O), 615 (S–O); MALDI–TOF MS: *m*/*z* 824.78 (100%, $[M+Na]^+$).

2.2.2. Synthesis of 1,7-disulfo-3,4,9,10-perylenebis(dicarboximide) derivatives (**2a–d**)

Since the synthetic procedures of perylene dyes **2a–d** are all similar, only **2a** is given as a representative example (Scheme 1). A total of 6 g (0.01 mol) of *N,N′*-bis-(4-chlorophenyl)-3,4,9,10-perylenebis(dicarboximide) (**1a**) with 30 ml of oleum (20% SO_3) were refluxed at 145 °C for 6 h under Ar atmosphere. The hot solution was cooled at room temperature and dropwised into 200 ml of *N,N*-dimethylmethanamide. Then, the mixture solution was poured into 1400 ml of acetone, and the precipitate of **2a** was filtered out and dried at 40 °C under vacuum. In order to remove the remaining sulfuric acid, the product was dissolved in 800 ml of distilled water. After addition of sodium chloride (50 g) to the solution, the precipitate formed was filtered, washed with ethanol and dried in a vacuum oven at 40 °C. The purity of **2a** was confirmed by thin layer chromatography using isopropyl alcohol/acetone/ammonia (1:2:1). The yields, ^{1}H NMR, FT-IR and Mass data of the dyes are given below.

*2.2.2.1. Compound **2a**.* Yield 68.8%; ^{1}H NMR (DMSO-d_6, ppm): 8.80 (d, 4H), 8.50 (d, 4H), 7.91 (s, 2H), 7.58 (d, 2H), 7.43 (d, 2H); FT-IR (KBr, cm^{-1}): 1701 (C=O), 1360 (C–N), 1233, 1069 (S=O), 625 (S–O); MALDI–TOF MS: *m*/*z* 772.05 (100%, $[M+2H]^+$).

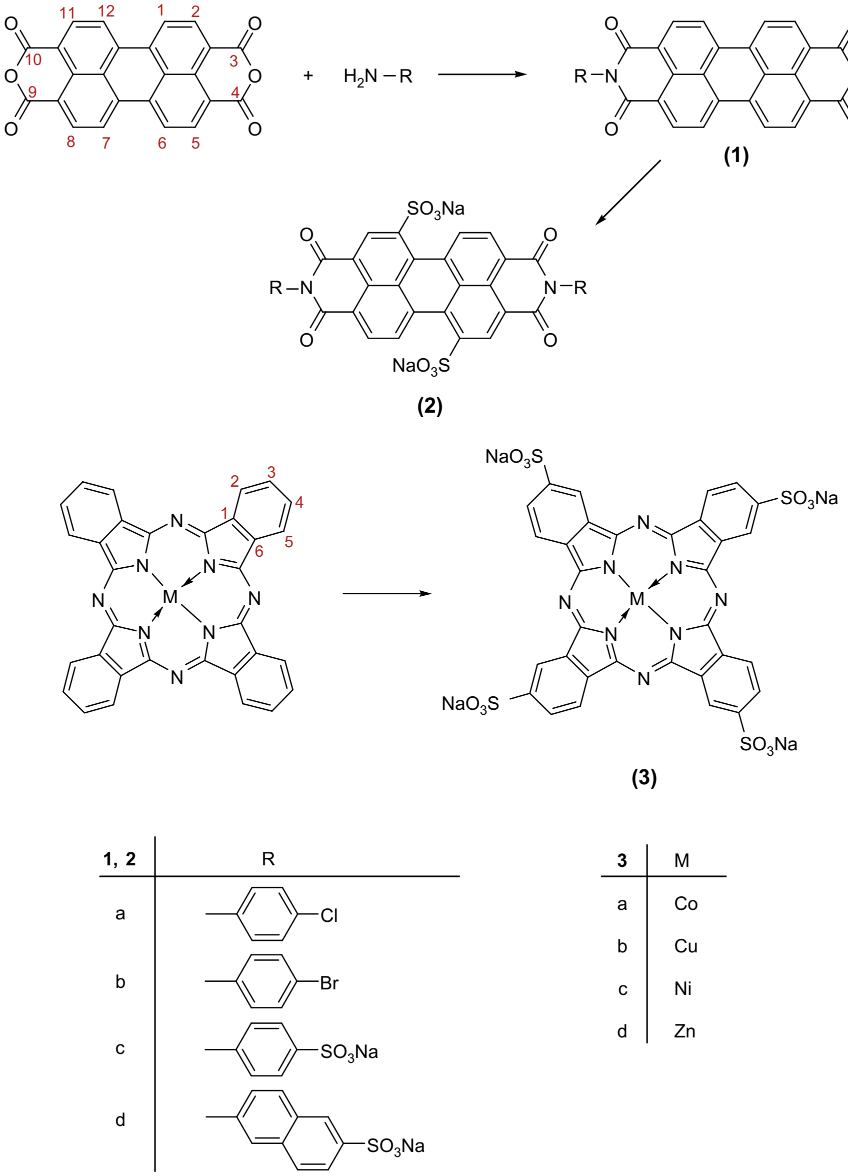
*2.2.2.2. Compound **2b**.* Yield 72.3%; ^{1}H NMR (DMSO-d_6, ppm): 8.73 (d, 4H), 8.45 (d, 4H), 7.94 (s, 2H), 7.76 (d, 2H), 7.33 (d, 2H); FT-IR (KBr, cm^{-1}): 1700 (C=O), 1358 (C–N), 1233, 1058 (S=O), 623 (S–O); MALDI–TOF MS: *m*/*z* 904.89 (100%, $[M+2Na]^+$).

*2.2.2.3. Compound **2c**.* Yield 65.3%; ^{1}H NMR (DMSO-d_6, ppm): 8.90 (d, 4H), 8.67 (d, 4H), 7.79 (s, 2H), 7.74 (d, 2H), 7.53 (d, 2H); FT-IR (KBr, cm^{-1}): 1708 (C=O), 1328 (C–N), 1195, 1041 (S=O), 617 (S–O); MALDI–TOF MS: *m*/*z* 861.93 (100%, $[M+4H]^+$).

*2.2.2.4. Compound **2d**.* Yield 71.2%; ^{1}H NMR (DMSO-d_6, ppm): 9.29 (s, 2H), 9.15 (s, 2H), 9.05 (d, 2H), 8.87 (d, 2H), 8.64 (d, 2H), 8.40 (d, 2H), 8.33 (d, 2H), 8.07 (s, 2H), 7.80 (d, 2H); FT-IR (KBr, cm^{-1}): 1709 (C=O), 1362 (C–N), 1193, 1041 (S=O), 615 (S–O); MALDI–TOF MS: *m*/*z* 961.98 (100%, $[M+4H]^+$).

2.2.3. Synthesis of sulfonated metal-phthalocyanine (**3a–d**)

Water soluble dyes with metal-phthalocyanine moiety (**3a–d**) were synthesized by heating metal phthalocyanines in oleum (Scheme 1). A total of 5 g of metal-phthalocyanine with 20 ml of



Scheme 1. Synthesis of thermally stable dyes.

oleum (20% SO_3) were refluxed at 145 °C for 3 h. In the case of zinc-phthalocyanine, however, the mixture was stirred at 90 °C for 6 h. The solution was added into 500 ml of distilled water. After addition of sodium chloride (80 g) to the solution, the precipitate formed was filtered, washed with ethanol and dried in a vacuum oven at 40 °C. The crude product was refluxed in ethanol for 2 h, hot filtered, washed with hot ethanol and subsequently dried in vacuum oven. The yields, FT-IR and Mass data of the dyes are given below.

*2.2.3.1. Compound **3a**.* Yield 81.3%; FT-IR (KBr, cm^{-1}): 1640 (C=N), 1422, 1145 (S=O), 622 (S–O); MALDI–TOF MS: *m*/*z* 892.58 (100%, $[M+4H]^+$).

*2.2.3.2. Compound **3b**.* Yield 88.0%; FT-IR (KBr, cm^{-1}): 1638 (C=N), 1396, 1141 (S=O), 622 (S–O); MALDI–TOF MS: *m*/*z* 896.70 (100%, $[M+4H]^+$).

*2.2.3.3. Compound **3c**.* Yield 83.5%; FT-IR (KBr, cm^{-1}): 1633 (C=N), 1331, 1193 (S=O), 637 (S–O); MALDI–TOF MS: *m*/*z* 891.84 (100%, $[M+4H]^+$).

*2.2.3.4. Compound **3d**.* Yield 87.7%; FT-IR (KBr, cm^{-1}): 1638 (C=N), 1326, 1192 (S=O), 658 (S–O); MALDI–TOF MS: *m*/*z* 898.86 (100%, $[M+4H]^+$).

2.3. Preparation of dye-based inks

Aqueous red ink was composed of dye **2a** (1.0 g), C.I. Solvent Yellow 146 (0.5 g), distilled water (7.5 ml), *N*,*N*-dimethylmethanamide (2 ml) and LM100 (0.5 ml) as a binder based on acrylate. Aqueous green ink was prepared with dye **3d** (1.0 g), C.I. Acid Yellow 1 (0.5 g), distilled water (9.5 ml) and LM300 (0.5 ml). Aqueous blue ink was made up of dye **3b** (1.0 g), C.I. Acid Violet 43 (0.5 g), distilled water (9.5 ml) and LM500 (0.5 ml).

2.4. Fabrication of pigment-based and dye-based color filters

2.4.1. Fabrication of pigment-based CFs using spin-coating method

Commercial pigment-based inks were coated on transparent glass substrate using MIDAS System SPIN-1200D spin coater. The coating speed was kept for 5 s at 100 rpm. Then, the speed was raised up to 800 rpm and kept constant for 20 s. Wet pigment-coated CFs were baked at 180 °C for 1 h. Thickness of them was around 1.7 μm.

2.4.2. *Fabrication of dye-based CFs using spin-coating method*

Prepared dye-based inks were coated on transparent glass substrate using MIDAS System SPIN-1200D spin coater. The coating speed was kept for 5 s at 100 rpm. Then, the speed was raised up to 700 rpm and kept constant for 20 s. On the other hand, dye-based red CF was coated at 100 rpm for 5 s and the coating speed was raised to 1500 rpm and kept constant for the same time. Wet dye-coated CFs were baked at 180 °C for 30 min, the temperature was raised to 220 °C and kept for 1 h. All dye-based CFs through spin-coating had 1.7 μm of thickness.

2.4.3. *Fabrication of dye-based CFs using ink-jet printing method*

The Cr-based black matrix was fabricated as previously described [8,9]. To facilitate adherence of the colorant inks in the black matrix-patterned glass of sub-pixels, the patterned glass was previously treated with plasma of CF_4 and O_2 using Korea Vacuum Tech. MEICP before printing [9]. The inks were printed using UJ 100 ink-jet printer made by UNIJET Co., Ltd. The size of the nozzle was around 30 μm. After printing, these inks were heated at 180 °C for 30 min, the temperature was raised to 220 °C and kept constant for 1 h. The dimension of one sub-pixel cell is around 27 μm by 88.0 μm by 1.2 μm which can contain 32.1–42.8 pl of ink, and the thickness of each colorant film in the cell will be 0.8 μm.

2.5. *Investigation of spectral and chromatic properties*

Transmittance spectra of pigment-based CFs and dye-based CFs were examined by UV–vis spectrophotometer. Chromatic properties of them were investigated by color spectrophotometer (LCF A2000). In case of ink-jet printed CFs, monitoring with a CCD camera of LCF A2000, the transmittance and chromaticity of separated sub-pixels on the substrates could be measured.

2.6. *Investigation of thermal stability*

2.6.1. *Thermal stability of synthesized dyes*

Thermogravimetric analysis was used to examine decomposition temperature and relative weight losses of synthesized dyes. The prepared dyes were heated to 110 °C for 10 min to remove any residual water and solvent. Then, it was heated to 220 °C and held there for 30 min to simulate the processing thermal conditions of CF manufacturing. The dyes were finally heated to 450 °C to determine their degradation temperature. All heating was carried out at the rate of 10 °C min^{-1} under nitrogen atmosphere [16].

2.6.2. *Thermal stability of color filters*

Prepared pigment-based and dye-based CFs were heated at 250 °C and kept for 1 h using Jeiotech Co., Ltd. Forced Convection Oven OF-02GW. The chromaticity difference (ΔE_{ab}) values before and after heating was examined by color spectrophotometer (LCF A2000).

3. Results and discussion

3.1. *Synthesis of dyes*

Prepared dyes have the same structures of corresponding thermally stable perylene and phthalocyanine pigments [17,18], but they have sulfonic acid groups. Sulfonation of 3,4,9,10-perylenebis(dicarboximide) derivatives (**2a**–**d**) in oleum gave disulfonate derivatives of 3,4,9,10-perylenebis(dicarboximide). Sulfonation in air gave a mixture of isomeric 1,7-disulfo-3,4,9,10-perylenebis(dicarboximide) and 1,6-disulfo-3,4,9,10-perylenebis(dicarboximide). The proton peaks of 6-position and 7-position of perylene appeared at the same field (7.90–7.95 ppm for **2a**–**d**) and these were confirmed by ^{1}H NMR. On the other hand, the sulfonation with oleum in an inert atmosphere led to the homogeneous 1,7-disulfo-3,4,9,10-perylenebis(dicarboximide).

The sulfonic acids of metal phthalocyanines were readily accessible by direct sulfonation with oleum. However, by varying the oleum concentration, reaction temperature, and time, up to four sulfonate groups could be introduced in the 4-position of the benzene ring [19,20]. The resulting products were mixtures of different regio-isomers which have slightly different polarities and solubilities. Therefore, in order to obtain the homogeneous tetra-sulfonated metal phthalocyanines, the oleum concentration and reaction condition were controlled closely. In case of Co, Cu and Ni-phthalocyanine (**3a**–**c**), we used 20% of oleum and the sulfonation reaction was carried out at 145 °C for 3 h. Similarly, the tetra sufonated Zn-phthalocyaine (**3d**) was synthesized with 20% oleum at 90 °C for 6 h. The purity of metal-phthalocyanine dyes (**3a**–**d**) were identified in Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI–TOF) mass spectrum.

3.2. *Preparation of ink-jet printed color filter*

Fig. 1 briefly describes the direct ink-jet printing process on black matrix-patterned glass using the synthesized dyes. Compared to the presently commercialized complicated pigment dispersion process, the color stripe can be formed by ink-jet printing of color inks in one simple step. In addition, as this process does not involve photo-lithography, it saves on materials and minimizes the use of toxic solvent such as *N*-methylpyrrolidone.

Fig. 2(a) shows the image of red ink prepared with **2a** dye jetting from the ink-jet printer nozzle and the black matrix-patterned glass. Fig. 2(b) shows the evenly patterned RGB pixel

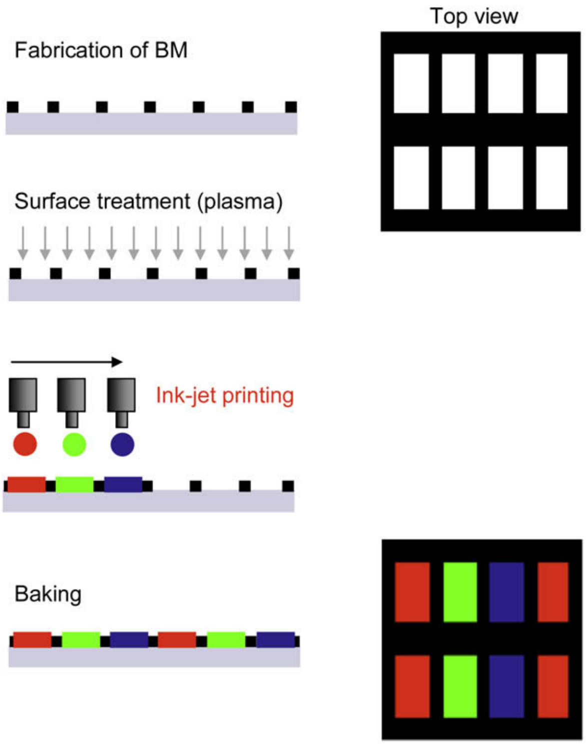


Fig. 1. Schematic representation of ink-jet printing technology for fabrication of color filter.

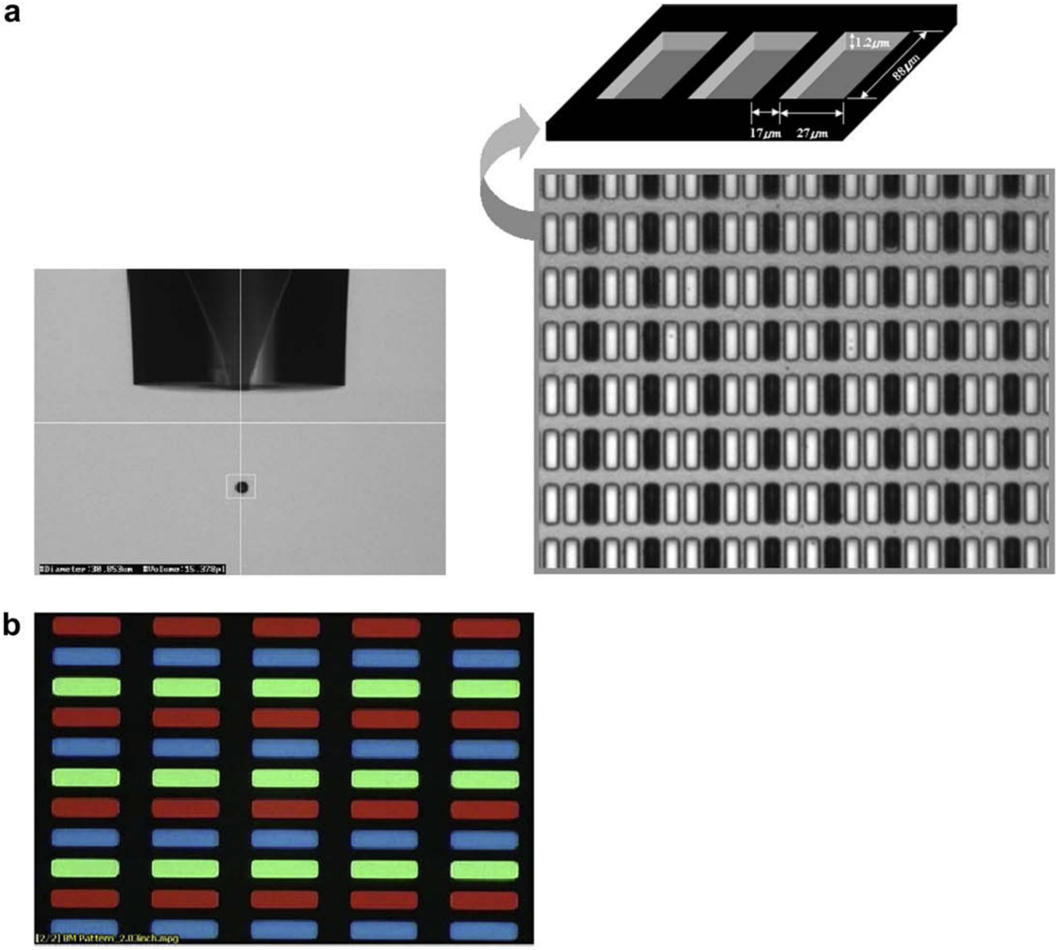


Fig. 2. Optical microscopy (OM) image of ink-jetted sub-pixels. (a) Red ink of **2a** and **Y1** being jetted in black matrix-patterned glass and gray-scale OM image of printed red stripe. (b) RGB patterned color filter using ink-jet printing method.

(27.0 μm × 88.0 μm × 1.2 μm) on a glass where RGB ink with the prepared dyes were successively jetted on.

However, the coating thickness of ink-jetted colorant layer was restricted to less than 1.2 μm which was the height of black matrix. For this reason, the prepared ink-jetted CF had a thickness of 0.8 μm as shown in Table 1.

3.3. *Spectral properties of dyes and dye-based color filters*

Table 2 shows UV–vis absorption spectra of prepared dyes in water. Dyes **2a**–**d** exhibited two characteristic absorption bands between 500 and 550 nm. The absorption maxima (λ_{max}) of dyes **2a**–**d** were not quite dependent upon the substituent, R. As for color strength, **2a** showed the highest molar extinction coefficient (ε_{max}) value among the dyes.

The absorption spectra of metal phthalocyanine dyes **3a**–**d** in water showed an intense absorption band in the range of 650–670 nm depending on the nature of the central metal atom. In these dyes, **3b** had superior absorption properties at 668 nm such as high ε_{max} value and sharp absorption band. On the other hand, **3d** showed two absorption maxima of 634 and 658 nm and it also had some absorption over 700–750 nm to make it more suitable for green colorant.

Based on spectral properties including λ_{max} and ε_{max} values of the prepared dyes, dyes **2a** (Red), **3d** (Green) and **3b** (Blue) have been chosen as colorants for LCD CF. However, these selected dyes themselves did not have accurate RGB transmittance spectra. Fig. 3 shows the transmittance spectra of RGB CFs. For red CF, **2a** showed undesirable transmittance at 400–450 nm even though it had considerable transmittance at over 600 nm. Thus, by adding small amount of C.I. Solvent Yellow 146 (Y1) which could cut down transmittance at 400–450 nm, excellent red spectrum could be

Table 1
Thermal stability of dye-based and pigment-based color filters

	Red (ΔE_{ab})	Green (ΔE_{ab})	Blue (ΔE_{ab})	Thickness (T) (μm)
D-CF[a]	0.15	0.2	0.14	1.5
D-CF	0.21	0.36	0.19	1.5
Ink-jetted D-CF[b]	0.27	0.4	0.21	0.8
P-CF	0.2	0.7	1.9	1.5

[a] Dye-based color filter without color compensating dyes.

[b] Dye-based color filter with prepared and color compensating dyes.

Table 2
UV–vis absorption spectra of the prepared dyes in water

Dye	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})	Hue
2a	500, 542	33 700, 17 500	Red
2b	504, 538	24 100, 20 600	Red
2c	502, 530	27 500, 23 700	Red
2d	500, 536	24 600, 31 100	Red
3a	658	39 000	Blue
3b	668	98 700	Greenish blue
3c	658	83 000	Blue
3d	634, 658	67 400, 68 700	Bluish green

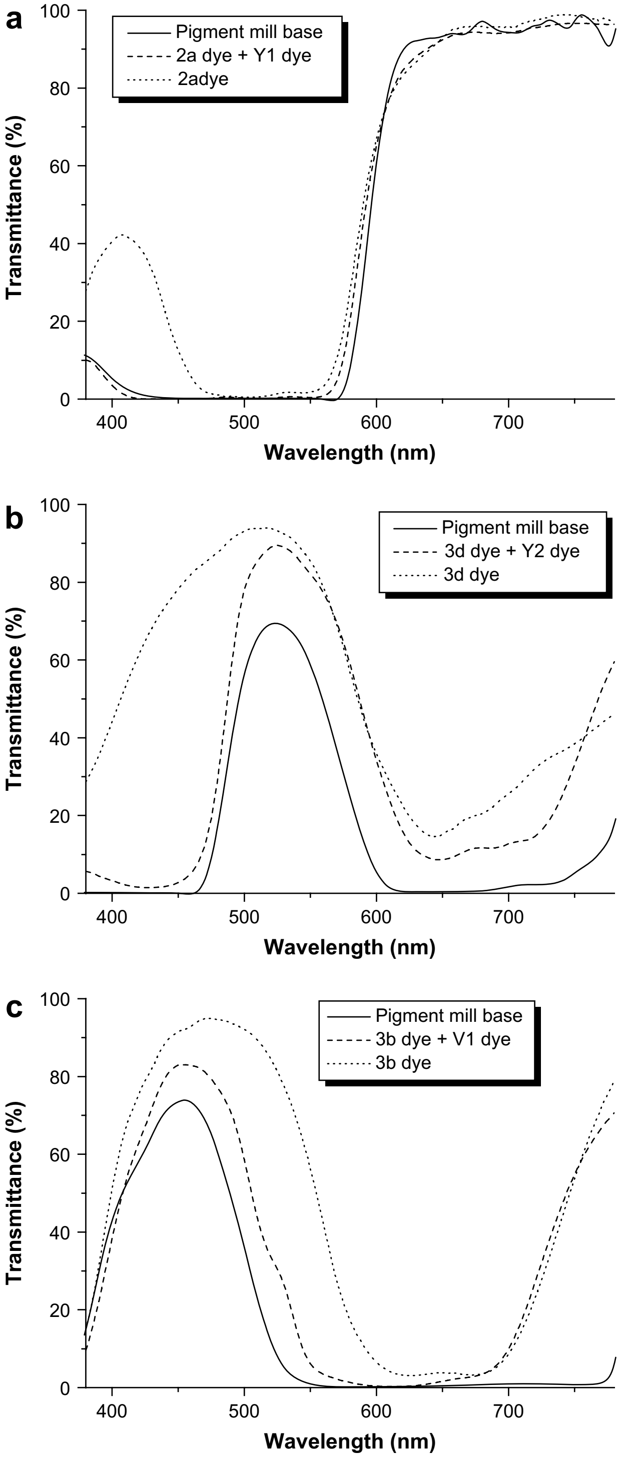


Fig. 3. Transmittance spectra of spin-coated RGB color filters with pigments (solid line), prepare dyes (dotted line), and prepared dyes and color compensating dyes (dashed line). (a) Red color filter, (b) Green color filter and (c) Blue color filter.

obtained. Similarly, we compensated green transmittance spectrum using C.I. Acid Yellow 1 (Y2) which decreased unnecessary transmittance at 400–450 nm. Also, we corrected blue transmittance spectrum by adding C.I. Acid Violet 43 (V1) which effectively cut down transmittance at 500–600 nm. However, transmittance at around 450 nm decreased a little bit due to the absorption of V1 at that region. Although the transmittance of the prepared CF has been somewhat lowered by color compensation, the transmittance of D-CF was higher than that of P-CF. The transmittance of red, green and blue D-CF was 92.4, 82.1 and 82.9% at 650, 550 and 450 nm, respectively.

Fig. 4 and Table 3 compare chromaticity diagrams and coordinate values of NTSC, P-CF and D-CF. D-CF had a slightly wider color gamut than P-CF, which would improve color impression of display. D-CF also had higher brightness (*Y*) values than P-CF. It is known that the scattering power of the pigment particles depends upon particle size and the maximum opacity of the P-CF occurs when the diameter of particles is about half the wavelength of light, that is, about 200 nm. Thus, the smaller particle size of dyes (10 nm) than that of pigments (100 nm) lowers the scattering of incident light as shown in Fig. 5 [21]. These enhanced transmittance and brightness can increase the contrast ratio, and consequently, a high-definition LCD will be obtained [22].

However, the chromatic property of ink-jet printed D-CF was lower than that of spin-coated D-CF. This would be due to the lower color saturation resulting from the thinner thickness (0.8 μm) of ink-jetted CF than that of spin-coated D-CF (1.5 μm). If the dye-based inks can be printed on higher black matrix (>1.5 μm) patterned glass, the chromaticity for ink-jetted D-CF would be enhanced.

3.4. Thermal stability of dyes and dye-based color filters

In general, a material with strong intermolecular interaction has high thermal stability. For the high thermal stability, the dye molecules should have strong intermolecular interaction and form compact aggregates [23–25]. The synthesized perylene (**2a**–**d**) and phthalocyanine (**3a**–**d**) dyes have planar and symmetric molecular structure, which results in effective molecular packing through π–π interaction. In addition, their high molecular weight and polar substituent will make intermolecular interaction such as Van der Waals Force and dipole–dipole interaction strengthened. As a result, all of the prepared dyes showed satisfactory thermal stability for manufacturing of LCD color filter.

Thermal stability of the dyes is investigated through measuring of their change in weight at 220 °C – the highest temperature in LCD manufacturing process [26,27]. Fig. 6 shows the thermogravimetric analysis graph of synthesized dyes. The majority of dyes showed below 5% weight loss for 30 min maintenance at the

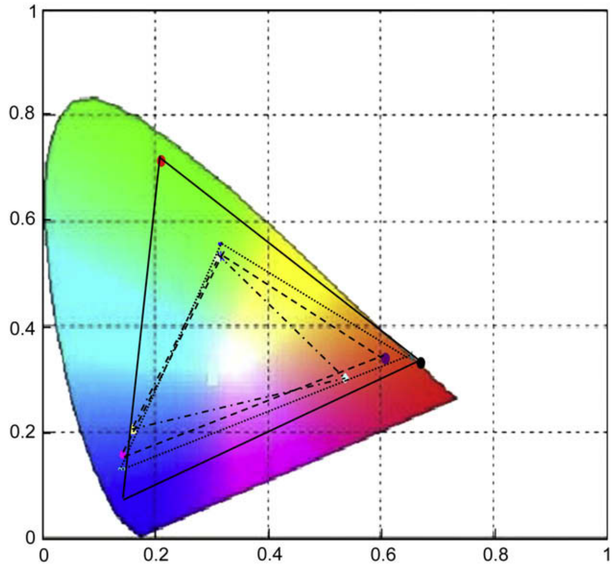


Fig. 4. CIE 1931 chromaticity diagram of NTSC (solid line), pigment-based color filter (dashed line), dye-based color filter using spin-coating (dotted line) and dye-based color filter using ink-jet printing (dash-dotted line).

Table 3
The coordinate values corresponding to CIE 1931 chromaticity diagram of NTSC, pigment-based and dye-based color filter

	Color	x	y	Y	Gamut (%)
NTSC	Red	0.670	0.330	29.0	100
	Green	0.210	0.710	60.4	
	Blue	0.140	0.080	10.4	
P-CF[a]	Red	0.608	0.339	19.3	45.5
	Green	0.315	0.533	56.3	
	Blue	0.142	0.158	11.7	
D-CF	Red	0.653	0.344	19.63	57.3
	Green	0.312	0.556	63.12	
	Blue	0.141	0.131	16.15	
D-CF[b]	Red	0.535	0.302	25.38	33.6
	Green	0.309	0.528	51.85	
	Blue	0.159	0.207	30.19	

[a] D-CF using spin-coating method ($T = 1.5$ μm).

[b] D-CF using ink-jet printing method ($T = 0.8$ μm).

temperature of 220 °C and they were stable up to 250 °C. Dyes **2a**, **2b** and **3b** exhibited below 1% weight loss.

For commercial applications, CFs should have the chromaticity difference (ΔE_{ab}) values less than three after heating for an hour at 250 °C from the viewpoint of thermal stability [24,25]. As shown in Table 1, the ΔE_{ab} values of D-CF both with and without color compensating dyes were similar to that of P-CF or even lower in some cases. ΔE_{ab} values of D-CF using color compensating dyes were higher than D-CF without them, which implied that the thermal stability of compensating dyes might be lower than that of the synthesized dyes. The ΔE_{ab} values of ink-jetted CFs using dyes were slightly higher than those of spin-coated CFs due to their thinner coating thicknesses. Nevertheless, the ΔE_{ab} values of ink-jetted CFs were generally lower than that of P-CF. Therefore, it can be concluded that the thermal stability of D-CFs with thermally stable dyes were not largely affected by the manufacturing method, and the prepared dyes could be successfully applied to ink-jet printing technology.

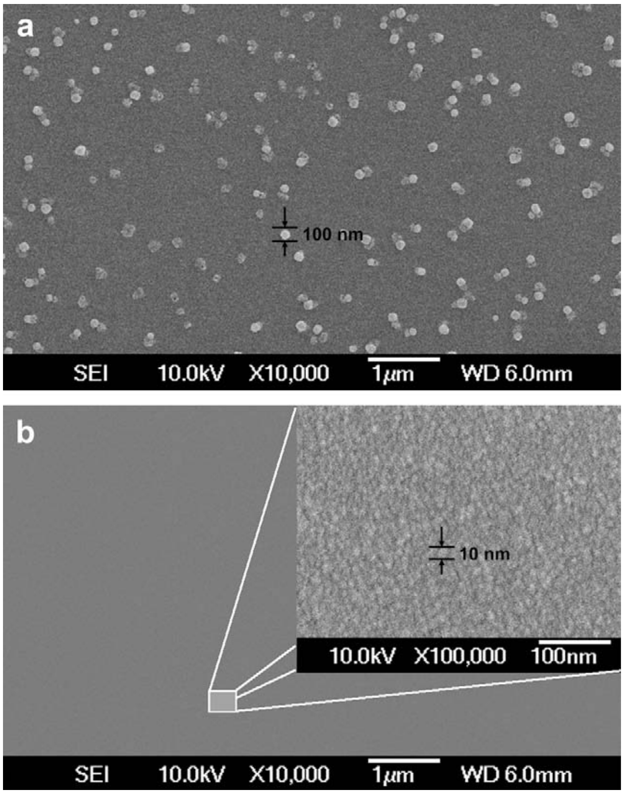


Fig. 5. FE–SEM images of color filters. (a) Pigment-based color filter with pigment-crystalline particles. (b) Dye-based color filter with dye aggregates.

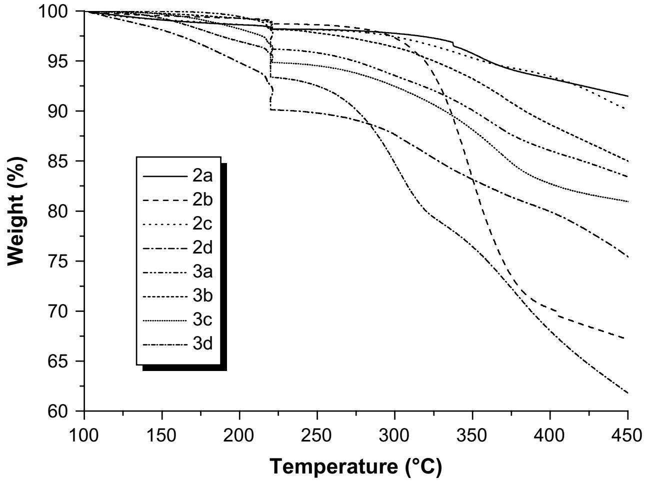


Fig. 6. Thermogravimetric analysis (TGA) of prepared dyes.

4. Conclusions

Eight thermally stable RGB dyes were synthesized and LCD CFs were fabricated using some of these dyes. Adequate RGB transmittance spectra for CF could be obtained by the addition of yellow and violet colors compensating dyes. Since the particle size of dyes is smaller than that of pigments, the prepared D-CF had higher optical performance than the P-CF while it showed a similar thermal resistance to the P-CF. In addition, the synthesized dyes were successfully applied to the ink-jet printing system which would be the new manufacturing technology for LCD CF. Fabricated ink-jet printed CF did not differ significantly from P-CF in terms of its thermal stability.

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