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Synthesis and characterization of novel triazatetrabenzcorrole dyes for LCD color filter and black matrix



PIGMENTS

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ABSTRACT

We have synthesized three novel triazatetrabenzcorrole dyes via a ring-contraction reaction to be applied as colorants for dye-based liquid crystal display color filter and black matrix. The absorption peaks of the synthesized dyes showed a red-shifted Soret band and a blue-shifted Q-band compared to phthalocyanine dyes, and this can be extremely beneficial when applied for liquid crystal display color filter and black matrix. These dyes exhibited enhanced solubility in the industrial solvents by the introduction of bulky axial substituents. The dyes were successfully spin-coated with binders on the substrate showing a lowered aggregating tendency as illustrated in the field emission scanning electron microscopy images. The spin-coated films prepared with these dyes exhibited superior optical and chromatic properties compared to the phthalocyanine-based or pigment-based ones for green color filter, even without the addition of a yellow compensating dye. In addition, they showed satisfactory dielectric properties for the black matrix of color filter on array mode.

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1. Introduction

Liquid crystal display (LCD) modules, which are widespread media in today's information age, are composed of a backlight unit, a color filter (CF), and a thin-film transistor (TFT) board, with a liquid crystal between CF and TFT board. The CF, which converts the white backlight into various colored lights, consists of RGB (red, green, and blue) pixels, a black matrix (BM) for prevention of light leakage, an overcoat for improving the flatness of the pixel surface, and a column spacer to control the gap between cells [1–4].

Currently, various dye molecules are under extensive investigation for the manufacturing of RGB pixels and BM to improve the performance of LCD. The pigments, being used for the main colorants of RGB pixels, show superior thermal and photo-chemical stabilities, but have low optical and chromatic properties due to their aggregation behavior [5,6]. Dyes can be attractive alternatives to overcome this limitation due to the reduced light scattering resulting from the fact that they can be dissolved in the media and exist in molecular form. Recently, their superior optical properties for higher brightness have outweighed the inferior thermal stabilities because the LCD manufacturing process temperature has been decreasing [7]. The colorants for LCD BMs should not interfere with the electrical signals of TFT to be applied for color filter on array (COA) mode that CF is patterned right onto the TFT array. Therefore, extensive investigation is currently being performed on colorants with low dielectric constants such as dyes, so that LCD BMs can replace the carbon black with high dielectric constant [8,9]. Recently, our group applied the phthalocyanine (PC) derivatives with high color strength and thermal stability to LCD CF and BM by improving their solubility [10,11]. In this study, the novel triazatetrabenzcorrole (TBC) dyes were designed and synthesized through the ring-contraction process of PC dyes. They exhibited more advantageous absorption peaks for LCD CF and BM, and enhanced solubility to the industrial solvents by the introduction of bulky axial substituents. For the above purpose, the thermal stability, optical properties, and solubility of the prepared dyes as the colorant materials for LCD CF and BM were investigated according to their characteristic structures. In addition, the transmittance, color gamut, and dielectric constants of the spin-coated films with these dyes were examined.

2. Experimental

2.1. Materials and instrumentation

1,8-Diazabicyclo-7-undecene (DBU), 3(4)-nitrophthalonitrile, 2,5-bis-(1,1-dimethylbutyl)-methoxyphenol purchased from TCI,



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and 4-methylphenol, PBr₃, CuCl₂ purchased from Sigma–Aldrich were used as received. All the other reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Transparent glass substrates were provided by Paul Marienfeld GmbH & Co. KG. Commercial pigment-based CF and acrylic binder DW1 were supplied by NDM Inc.

¹H NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz using chloroform-d and TMS, as the solvent and internal standard, respectively (Seoul National University National Center for inter-University Research Facilities). Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI-TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation with a-cyano-4-hydroxy-cynamic acid (CHCA) as the matrix. Absorption and transmittance spectra were measured using an HP 8452A spectrophotometer. Fluorescence spectra were measured using a Shimadzu RF-5301PC spectrofluorometer. Elemental analysis was carried out with a Flash EA 1112 CNH analyzer. Cyclic voltammetry was performed using a three-electrode cell and a VersaSTAT 3-100. Chromatic characteristics of the spin-coated films were analyzed on a Scinco color spectrophotometer. Dielectric constants were measured using Edward E306 thermal evaporator and Agilent 4294A precision impedance analyzer. Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10 °C min⁻¹ using a TA Instruments Thermogravimetric Analyzer 2050. The thickness of the spin-coated film was measured using a Nano System Nanoview E-1000. Field emission scanning electron microscopy (FE-SEM) images of spin-coated films were taken by JSM-840A microscope.

2.2. Synthesis

2(3)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)phthalocyanine (**2**) was synthesized according to the previously reported procedures [11], 2(3)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-phthalocyaninatocopper(II) (**2b**) and N,N'-Bis(2,6-diisopropylphenyl)-5-phenylbenzoperylene-2,3,8,9tetracarboxdiimides (**3**) were synthesized according to the procedures reported elsewhere [10].

2.2.1. Hydroxyphosphorus(V)2(3)-Tetrakis(2,5-Bis(1,1dimethylbutyl)-4-methoxyphenoxy)-triazatetrabenzcorrole Hydroxide (**RC1**)

2 (1.24 g, 0.74 mmol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in 20 mL of pyridine. An amount of PBr₃ (9.0 g, 33.0 mmol) was added and the resulting solution heated to 120 °C and stirred for 2 h. After 2 h, approximately 3/4 of the solvent was allowed to evaporate under a flow of argon. The mixture was then poured into a water/ice bath and the resulting suspension filtered to give a green solid. The solid was purified on a silica gel column using 1/6 ethyl acetate/hexane as the eluent. The bright green band was collected and concentrated producing **RC1** as a bright green solid (0.45 g, 35%). MALDI-TOF MS: *m*/*z* 1725.0 (100%, [M + OH]⁺); Found: C, 75.07; H, 8.15; N, 5.75. Calc. for C₁₀₈H₁₃₈N₇O₁₀P: C, 75.19; H, 8.06; N, 5.68.

2.2.2. Dimethoxyphosphorus(V)2(3)-Tetrakis(2,5-Bis(1,1dimethylbutyl)-4-methoxyphenoxy)-triazatetrabenzcorrole (**RC2**)

2 (1.24 g, 0.74 mmol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in 30 mL of pyridine. An amount of PBr₃ (9.0 g, 33.0 mmol) was added and the resulting solution heated to 120 °C and stirred for 2 h. After 2 h, the volume of the reaction mixture was reduced by vacuum distillation to 1–2 mL and then treated with a 50/50 solution of CH₂Cl₂/MeOH for 2 h. The resulting green solid was dissolved in CH₂Cl₂ and

filtered to remove excess pyridinium bromide as a white crystalline solid. The filtrate was reduced in volume under reduced pressure and loaded onto a silica gel column for purification with 1/7 ethyl acetate/hexane as the eluent. The bright green band to elute was collected and dried under vacuum to give **RC2** as a bright green solid (0.75 g, 58%). MALDI-TOF MS: m/z 1752.4 (100%, [M⁺]); Found: C, 75.17; H, 8.20; N, 5.65. Calc. for C₁₁₀H₁₄₂N₇O₁₀P: C, 75.35; H, 8.16; N, 5.59.

2.2.3. Di(4-methylcyclohexoxy)phosphorus(V)2(3)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-triazatetrabenzcorrole (**RC3**)

2 (1.24 g, 0.74 mmol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in 30 mL of pyridine. An amount of PBr₃ (9.0 g, 33.0 mmol) was added and the resulting solution heated to 120 °C and stirred for 2 h. After 2 h, the volume of the reaction mixture was reduced by vacuum distillation to 1-2 mL and then treated with a 50/50 solution of CH₂Cl₂/4methylcyclohexanol for 12 h. The resulting green solid was dissolved in CH₂Cl₂ and filtered to remove excess pyridinium bromide as a white crystalline solid. The filtrate was reduced in volume under reduced pressure and loaded onto a silica gel column for purification with CH₂Cl₂ as the eluent. The second bright green band to elute was collected and loaded onto a silica gel column for purification again with 3/40 ethyl acetate/hexane as the eluent. The first bright green band to elute was collected and dried under vacuum to give **RC3** as a shiny bright green solid (0.78 g, 55%). MALDI-TOF MS: *m*/*z* 1917.8 (100%, [M⁺]); Found: C, 76.11; H, 8.56; N, 5.13. Calc. for C₁₂₂H₁₆₂N₇O₁₀P: C, 76.41; H, 8.52; N, 5.11.

2.3. Preparation of dye-based inks and spin-coated films

Dye-based ink for a CF and BM was composed of the propylene glycol methyl ether acetate (PGMEA) (2.8 g), acrylic binder (2.0 g), and dye (0.07 g). The prepared dye-based inks were coated on a transparent glass substrate using a MIDAS System SPIN-1200D spin coater. The coating speed was initially 100 rpm for 10 s, which was then increased to 600 rpm and kept constant for 20 s. The wet dye-coated glasses were then dried at 80 °C for 20 min, prebaked at 150 °C for 10 min, and postbaked at 230 °C for 1 h. After each step, the coordinate values of the dye-coated glasses were measured.

2.4. Investigation of solubility

Solubility of the synthesized dyes in propylene glycol methyl ether acetate (PGMEA) was examined to determine the effects of peripheral and axial substituents. The prepared dyes were added to the solvents at various concentrations, and the solutions were sonicated for 5 min using an ultrasonic cleaner ME6500E. The solutions were left to stand for 48 h at room temperature, and checked for precipitation to determine the solubility of the dyes.

2.5. Measurement of spectral and chromatic properties

Absorption spectra of the synthesized dyes and transmittance spectra of pigment-based and dye-based CFs were measured using a UV–vis spectrophotometer. Fluorescence spectra of the synthesized dyes were measured using a Shimadzu RF-5301PC spectrofluorometer. Chromatic values were recorded on a color spectrophotometer (Scinco colormate).

2.6. Measurement of dielectric properties

The prepared dye-based inks were coated on a aluminum substrate using a MIDAS System SPIN-1200D spin coater. The coating speed was initially 100 rpm for 10 s, which was then increased to 800 rpm and kept constant for 20 s. Aluminum electrodes were deposited by Edward E306 thermal evaporator and capacitances were measured by Agilent 4294A precision impedance analyzer.

2.7. Measurement of thermal stability

Thermal stability of the synthesized dyes was evaluated by TGA. The prepared dyes were heated to 110 °C and held at that

temperature for 10 min to remove residual water and solvents. The dyes were then, heated to 220 °C and held at that temperature for 30 min to simulate the processing thermal conditions of CF manufacturing. The dyes were finally heated to 400 °C to determine their degradation temperature. The temperature was raised at the rate of 10 °C min⁻¹ under nitrogen atmosphere.

To check the thermal stability of the dyes in spin-coated films, the fabricated spin-coated glasses were heated in a forced convection oven (OF-02GW Jeiotech Co., Ltd.). The color difference



Scheme 1. Synthesis of triazatetrabenzcorrole dyes.

values (ΔE_{ab}) before and after heating were measured on a color spectrophotometer (Scinco colormate) in CIE L'a'b' mode.

3. Results and discussion

3.1. Synthesis (see Supporting Information †)

The novel three TBC phosphorus compounds with enhanced solubility and broadened absorption peak were designed and synthesized as shown in Scheme 1. Each precursor of metal-free PC (1)was synthesized through a nucleophilic aromatic substitution reaction between nitro phthalonitriles and phenols with the functional groups having affinity with the industrial solvent, PGMEA, and its structure was confirmed by ¹H NMR [12]. The metal-free PC (2) was synthesized by a cyclotetramerization reaction of the precursors and purified via column chromatography [13]. The PCs synthesized from monosubstituted phthalonitriles can theoretically have constitutional isomers, and their properties were observed without further attempts to separate these isomers in this work [14]. The TBC phosphorus compounds were synthesized via a ringcontraction reaction mediated by PBr₃ in pyridine in which a meso-nitrogen atom is extruded from an appropriate metal-free PC precursor. In order to ensure a good yield of TBC, the pyridine must be carefully distilled over CaH₂, and the phthalocyanine starting material must be dried in a heated (50 °C) vacuum oven for several hours immediately prior to use [15]. After the ring-contraction reaction, the TBC compound RC1 was successfully precipitated by quenching with an ice/water mixture. Purification by silica gel chromatography was carried out by using ethyl acetate/hexane solution as the eluent, rather than ROH/CH₂Cl₂ solution, to avoid any axial ligand exchange with alcohols. The TBC compounds RC2 and **RC3** were synthesized by quenching with an appropriate ROH/ CH₂Cl₂ mixture. The structures of synthesized TBCs were confirmed by MALDI-TOF spectroscopy and elemental analysis.

3.2. Characterization of dyes

3.2.1. Solubility of dyes

For dyes to be successfully applied as colorants for LCD CF or BM, they should exhibit high solubility in industrial solvents. Regardless of the compatibility with binders, dye molecules should dissolve more than 5 wt% in industrial solvents to have the desired optical properties [10.11.16]. Especially, to prevent the reaggregation behavior between the dye molecules after the post baking process, bulky substituents should be introduced and indeed such molecules are therefore normally also better soluble in organic solvents. Such a reaggregation between molecules is believed to be the primary cause of the decline of transmittance of LCD CFs. The solubility data of the synthesized dyes in industrial solvent, PGMEA, are listed in Table 1. In the case of PC dye **2b** (Scheme 2), as found in the previous work, the bulky functional groups substituted at the peripheral positions caused steric hindrance to reduce intermolecular aggregation and the ether linkages in its structures enhanced its miscibility with PGMEA [10]. However, the introduction of bulky axial ligands was considerably more effective in hindering the intermolecular $\pi - \pi$ stacking between phthalocyanine hetero cycles [17-22]. The RC1-3 dyes, with bulky axial ligands at the phosphorus atom, showed considerably higher solubility than PC dye **2b** with only peripheral substituents in PGMEA. In particular, RC3 exhibited the highest solubility contributed by the bulkiest axial substituent, the methylcyclohexoxy group. The increased solubility can be advantageous for the RC1-3 series to show excellent optical properties as the colorant materials for LCD.

3.2.2. Spectral properties of dyes

The UV–vis absorption spectra of PC dye **2b** and TBC dyes **RC1**–**3** are shown in Fig. 1 and the corresponding data are listed in Table 2. As reported elsewhere, the absorption peaks of TBC compounds **RC1–3** had a red-shifted Soret band and blue-shifted Q-



Scheme 2. Synthesis of phthalocyanine dye.

Table 1 Solubility of the synthesized dyes at 20 $^\circ\mathrm{C}$ in PGMEA.

Synthesized dyes	Solubility (g/100 ml)		
2b	6		
RC1	9		
RC2	9		
RC3	10		

band compared to the corresponding PC dye **2b** [23–25]. These traits can be extremely beneficial for dyes **RC1–3** to be applied as colorants of green CF and BM of an LCD.

For dye-based LCD CF, the green dyes should strongly absorb the range above 630 nm [10]. The absorption peaks of the three synthesized TBC dves started from 600 nm and showed extremely strong and sharp maxima in the range of 650–680 nm as shown in Fig. 1. In addition, the growth and bathochromic shift of the Soret bands induced from the conversion from PC compounds to TBC compounds is extremely crucial for these TBC compounds to exhibit vivid green colors. This very strong and sharp absorption at 450 nm cut off the transmittance before 480 nm, replacing the role of the yellow compensating dyes, as shown in Fig. 4 [10,26]. As reported in our previous work, the synthesis of stable yellow dye with strong absorption is very difficult because, in general, the stability and color strength of dye molecules often increase with increasing size of the aromatic system, which inevitably causes a bathochromic shift in their absorption [27]. However, the synthesized TBC dyes RC1-3 can eliminate the addition of yellow compensating dye, which can simplify the manufacturing process, omitting the need to consider the content ratio, compatibility, and thermal deterioration accompanied with the blending of a green main dye and yellow compensating dye.

For dye-based LCD BM, the dyes should have absorptions that are as strong and broad as possible in the entire visible region [11]. The synthesized TBC dyes exhibited additional strong absorption in the visible range induced from the growth and bathochromic shift of the Soret band, which made their absorption peaks closer to those of the panchromatic dyes. The drawback of PC dyes, as possible candidates for dye-based LCD BM, is their absorption deficiency from 450 nm to 600 nm due to the wide gap between the Soret band and the Q-band [11]. On the other hand, the synthesized TBC dyes **RC1–3** can easily prevent light leakage in the visible range since they have a narrower gap between the Soret band and the Qband. In particular, the bathochromic shift of the Soret band of the

1.4

1.2

1.0

0.8

0.6

0.4

0.2

0.0

300

Absorbance(AU)

RC1 RC2

RC3

400

2b

Table 2

Absorption spectra	a of the synthesiz	zeu uyes ili PGivie	$CA(5 \times 10^{-1})$	IIIOI L).

Synthesized dyes	λ_{\max} (nm)	$\varepsilon_{\rm max}$ (L mol ⁻¹ cm ⁻¹)
RC1	450, 662	183 594, 91 996
RC2	450, 662	158 640, 81 918
RC3	450, 662	244 538, 126 696
2b	340, 680	104 630, 226 736

prepared dyes **RC1–3** was about 110 nm, which was more than that of the general TBC compounds [23–25]. Such a bathochromic shift of the Soret band is likely to be the result of the destabilization of the HOMO-1 (a2u) orbital caused by the removal of a mesonitrogen atom [15]. The Q-bands of the synthesized dyes **RC1–3** were hipsochromic shifted about 18 nm compared to PC dye **2b**, comparable to those of common TBC compounds [23–25]. The molar extinction coefficients of dyes **RC1–3** increased in the order of **RC2** < **RC1** < **RC3**, whereas the absorption maxima (λ_{max}) of the dyes were identical as expressed in Table 2. In particular, the color strength of **RC3** was very strong since its molar extinction coefficient was even higher than that of PC dye **2b**.

3.2.3. Thermal stability of dyes

The dye molecules should have strong intermolecular interactions and form compact aggregates in order to have high thermal stabilities [28-30]. The PC dyes, as the precursor of the TBC dyes as the main colorants for green CFs and BM, are known to be generally very stable. In particular, they have high thermal stability since they consist of extensive aromatic planar and symmetric systems which lead to stacking like rolls of coins [31-33]. The synthesized TBC dyes RC1-3 mostly maintained the superior stability of the PC dyes. However, their stabilities were somewhat deteriorated due to the axial substituents at phosphorus inducing the decreased $\pi - \pi$ stacking interaction. While the peripheral substituents of **RC1–3** are also bulky enough to cause steric hindrance, having the terminal alkoxy group was found to relieve the deterioration of thermal stability [11,34]. The high molecular weight and polar substituents of the synthesized TBC dyes are advantageous for intermolecular interactions, such as Van der Waals Force and dipole-dipole interaction [35]. In order to use dyes as CFs, they should be able to endure a temperature of 220 °C (which is the conventional highest temperature in the LCD manufacturing process) without significant weight loss [36,37]. As shown in Fig. 2, dyes RC2 and



500

600

700

800



Fig. 2. TGA analysis of the synthesized dyes (isothermal 30 min at 220 °C).

40-6

RC3 were stable at the TGA analysis, showing less than 5% weight loss after 30 min at 220 °C. However, the weight loss of **RC1** was relatively larger since the distortion of the **RC1** molecule was induced by the axial substituent introduced asymmetrically as illustrated in Fig. 3. In addition, the hydroxyl axial group of **RC1** is believed to be chemically less stable than the alkoxy axial group of the other dyes. The **RC3** dye showed greater weight loss than **RC2** at the isothermal period, but appeared more stable as the temperature increased.

3.2.4. Geometry optimization and electrochemistry of dyes

Geometry optimizations of the synthesized dyes were carried out using Gaussian 09 software. They were calculated with DFT on a B3LYP/6-31 + G (d,p) level. The calculated results were in accord with the solubility and thermal stability data of the prepared dyes. The synthesized TBC dyes **RC1–3** have axial substituents, introduced perpendicular to the main body as illustrated in Fig. 3, believed to be effective to prevent their π – π stacking. This antiaggregation effect was expressed well as their solubilities in Table 1. The influence of the axial substituent gave **RC3** maximum solubility since this methyl cyclohexyl axial group was geometrically even bulkier than other groups. The main body of **RC1** was distorted more than that of **RC2** and **RC3**, as illustrated in Fig. 3, leading to a lower thermal stability.

The oxidation potential data of TBC dyes **RC1–3** are listed in Table 1S (Supporting Information) and are deduced from normalized absorption, fluorescence spectra, and cyclic voltammetry curves shown in Figs. 1S and 2S. The overall electrochemical behavior of the three TBC dyes **RC1–3** appeared similar, as shown in Fig. 2S, suggesting that the influence over their redox potential induced from the axial ligand difference is negligible. The negative values for E_{ox} and $E_{\text{ox}} - E_{0-0}$ of **RC1–3** were greater than those of common PC dyes, impliying that **RC1–3** are easier to oxidize and more difficult to reduce than PC dyes. This is consistent with the notion that the corroles, in general, help stabilize a higher oxidation state [15].



Fig. 4. Transmittance spectra of the pigment-based and dye-based color filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Characterization of spin-coated films

3.3.1. Spectral and chromatic properties of spin-coated films for LCD CFs

The transmittance spectra of spin-coated TBC dyes **RC1–3** are shown in Fig. 4, and the corresponding data are listed in Table 3. These transmittance spectra were compared to the spectrum of the mixture of PC dye **2b** and the yellow compensating dye **3** (see Supporting Information †), and the spectrum of the pigment-based CF. The spin-coated films with TBC dyes **RC1–3** exhibited outstanding transmittance from 490 nm to 580 nm, advantageous to be used as LCD green CFs. In order to achieve a high brightness (Y) for the green color (the most important index for high quality





RC2



RC3

 Table 3

 Transmittance of the pigment-based and dye-based color filters.

Spin-coated dyes	λ_{max} (nm)	Maximum transmittance (%)
RC1	514	93.18
RC2	510	93.25
RC3	520	92.59
2b + 3	538	92.24
Pigment	522	91.30

LCD CF), the square shaped high transmittance spectrum is ideal. The reason why the transmittance spectra of RC1-3 are closer to this ideal transmittance is mainly attributed to their absorption spectra. Firstly, the Soret bands of the absorption peaks of RC1-3, compared to the spectrum of yellow compensating dye 3 [26], were sharper and slightly hipsochromic shifted, leading to the steepshaped transmittance peak and the increase of transmittance in the 490-510 nm region. In addition, the undesirable shoulder before the main transmittance disappeared because of the higher molar extinction coefficients of their Soret bands. Secondly, TBC dyes RC1-3 showed a declined aggregation peak in front of the Qband, resulting from higher solubility, and their Q-bands were slightly less hipsochromic shifted compared to common TBC compounds [17,38]. These factors led to the increased transmittance in the 560–580 nm region. Lastly, RC1–3 with decreased aggregating tendency had smaller particle sizes in the media leading to less light scattering, resulting in an overall rising trend of transmittance [35,39]. In particular, RC2 exhibited 93,25% of the highest maximum transmittance at 510 nm. RC3 cut off the undesirable transmittance most clearly because of the highest molar extinction coefficients.

The coordinate values of the spin-coated dye-based CFs are compared with a pigment-based CF as shown in Table 4 and Fig. 5. The all dye-based CFs are so efficient that they showed similar or larger color gamuts in spite of the much lower colorant contents in the inks due to the much higher tinctorial strength [10,16]. The TBC dyes **RC1–3** showed a superior brightness (Y) value compared to PC dye **2b** and the pigment-based CF owing to the higher transmittance in the green region. Especially, **RC2** exhibited 62.84 of the highest brightness value. **RC3** showed the widest color gamut with the highest y value. Judging from this result, the transmittance and brightness of **RC3** can increase further since the amount of **RC3** in the color ink can be reduced for obtaining the same color strength.

3.3.2. Dielectric properties of spin-coated films for LCD BMs

The synthesized TBC dyes **RC1–3** have excellent optical properties to be applied for LCD BM since the gap between the Soret band and Q-band is narrow. In recent years, the dielectric properties of the colorants have been considered very important for satisfactory application to COA mode, in which CF is patterned right onto the TFT array. Accordingly, colorants with low dielectric constants such as dyes are under extensive investigation for LCD BMs since the conventional carbon black-based BM with high dielectric constant interferes with the electrical signals of TFT [8,9]. The

 Table 4

 The coordinate values corresponding to the CIE 1931 chromaticity diagram and the color difference values of the pigment-based and dye-based color filters.

Spin-coated dyes	Y	x	у	ΔE_{ab}
RC1	60.33	0.279	0.516	4.90
RC2	62.84	0.298	0.509	2.95
RC3	62.29	0.275	0.523	3.03
2b + 3	60.14	0.299	0.519	1.87
Pigment	57.86	0.244	0.504	0.85



Fig. 5. CIE 1931 chromaticity diagram of the pigment-based and dye-based color filters.

demanded dielectric constant with the current commercialized thickness of BM (1–1.5 µm) is smaller than 7, whereas the dielectric constant of the carbon black-based BM is larger than 20 [40]. The dielectric constants of the TBC dyes **RC1–3** spin-coated on the aluminum substrate are listed in Table 5. Their dielectric constants were calculated according to the following equation. The symbol C refers to capacitance (F), ε_0 refers to dielectric constant under vacuum (8.854 \times 10⁻¹⁴ Fcm⁻¹), t refers to thickness (cm), and A refers to the area of the electrode (cm²).

$\varepsilon_{\rm r}({\rm dielectric\ constant}) = C/\varepsilon_0 \times t/A$

The dielectric constants of the spin-coated films with the TBC dyes of **RC1–3** were less than 7 and satisfactory for industrial application, owing to the low dielectric character of the dye molecules. In particular, **RC3** showed the lowest dielectric constant of 3.33 at 10 kHz frequency. The dielectric constants of the spin-coated films decreased as the applied frequency increased due to the lag in the charge transfer of the dye molecule caused by the rapid change in the external electronic field [39].

3.3.3. Thermal stability and FE-SEM images of spin-coated films

The practical thermal stability of spin-coated CFs and BMs needs to be discussed with color difference (ΔE_{ab}) values as expressed in Tables 4 and 6 since it is affected by the compatibility with industrial solvents and binders as well as the inherent thermal stability of dye molecules [10]. The criterion of sufficient thermal stability for commercial applications was that the ΔE_{ab} values of the spincoated films should be less than 3 after heating for one hour at 230 °C [16]. However, the baking temperature decrease in the LCD

Table 5
Dielectric constants of the dye-based black matrices.

Spin-coated dyes	t/A	Frequency (kHz)	Capacitance (pF)	Dielectric constant
RC1	0.46	1	0.94	4.88
		10	0.88	4.57
RC2	0.63	1	0.55	3.91
		10	0.51	3.63
RC3	0.44	1	0.72	3.58
		10	0.67	3.33

Table 6

The coordinate values corresponding to the CIE 1931 chromaticity diagram and the color difference values of the spin-coated films in reformed conditions.

Spin-coated dyes	Y	x	у	ΔE_{ab}
RC1 ^a	60.13	0.282	0.521	3.16
RC2 ^a	62.79	0.294	0.510	1.75
RC3 ^a	62.21	0.277	0.534	1.98
RC1 ^b	60.05	0.278	0.526	3.83
RC2 ^b	62.27	0.293	0.521	2.66
RC3 ^b	61.56	0.275	0.554	2.60

 $^a\,$ Prebaked for 10 min at 90 $^\circ C$ and postbaked for 30 min at 200 $^\circ C.$

 $^{\rm b}\,$ Spin-coated with reduced rpm (100 rpm for 5 s, 300 rpm for 20 s).

manufacturing process is easing this criterion for sufficient thermal stability. Under this criterion, the spin-coated TBC dyes RC1-3 exhibited somewhat less thermal stability compared to the PC dye or pigment-based CF as shown in Table 4. This is because of the relatively reduced aggregating tendency of axially substituted dyes RC1-3, which coincides with the result of solubility discussion. Such a reduced aggregating tendency of **RC1–3** made their particle size smaller than that of PC dye 2b on the spin-coated films as illustrated in FE-SEM images in Fig. 6. This smaller dye aggregate size leads to superior solubility and optical property which are in a trade-off relationship with thermal stability to some degree. As reported in a previous paper, the substituents hindering intermolecular $\pi - \pi$ stacked interaction induced smaller dye aggregate sizes in the FE-SEM images, which in turn reduced the drop of transmittance when the dve contents were increased [41]. However, the thermal stability of dyes improves as the dye aggregate size increases in general [28–30]. As illustrated in Fig. 6, the dve aggregate size decreased as the axial substituents became bulkier in the order of **RC1** > **RC2** > **RC3**. However, the ΔE_{ab} value of **RC1**

appeared to be the largest, probably due to the distortion of the main body and the weak stability of the hydroxyl group. Therefore, the replacement of such hydroxyl group into the alkoxy group is believed to make the TBC dye more stable.

Under the most recent LCD manufacturing process baking condition, the films spin-coated with TBC dves RC1-3 exhibited improved thermal stability as shown in condition **a** of Table 6. Especially, **RC2** and **RC3** exhibited sufficient thermal stability for commercial application. In this condition, the coordinate value y was somewhat increased and the brightness (Y) was somewhat decreased due to the reduced dye degradation. The thermal stability of spin-coated film can also be improved by slowing down the spin-coating speed. The films spin-coated with RC1-3 exhibited improved thermal stability under the condition **b** which had the reduced rpm (100 rpm for 5 s, 300 rpm for 20 s) of spin-coating as shown in Table 6. The improvement of thermal stability, namely the decrease of the ΔE_{ab} value, in this condition was contributed to by the growth of the film thickness resulting from the reduced spincoating speed. Such a growth of film thickness raised the coordinate value y, but resulted in reduced brightness (Y).

4. Conclusions

The three novel TBC phosphorus dyes were successfully synthesized and applied for dye-based LCD CF and BM. They were synthesized via a ring-contraction reaction in which a mesonitrogen atom is extruded from an appropriate metal-free PC precursor. On account of this meso-nitrogen extrusion, the absorption peaks of the synthesized dyes had a red-shifted Soret band and a blue-shifted Q-band compared to the PC dyes, which can be extremely beneficial for application as colorants of green CF and BM



Fig. 6. The FE-SEM images of the spin-coated films.

of LCD. In addition, these dyes exhibited superior solubility to the industrial solvents by introducing the bulky axial substituents at the phosphorus atom.

The synthesized dyes were dissolved in industrial solventbinder composites and spin-coated on the glass or aluminum substrate. In terms of dye-based LCD green CF, the strong and bathochromic shifted Soret bands of the prepared dyes effectively replaced the role of the yellow compensating dye. The spin-coated films exhibited a square shaped ideal transmittance spectrum, leading to excellent brightness contributed by the smaller particle size as illustrated in the FE-SEM images. In terms of dye-based LCD BM, the prepared dyes were advantageous for panchromatic absorption since the gap between their Soret band and Q-band was narrow. In addition, the spin-coated films exhibited low dielectric constants satisfactory for application to the COA mode. They showed slightly inferior thermal stability compared to the PC dye, but could be improved under reformed conditions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.05.026.

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