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Synthesis and characterization of some perylene dyes for dye-based LCD color filters

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ABSTRACT

Eight red perylene dyes were synthesized to improve the optical performance of LCD color filters. Among them, dyes with bulky functional substituents at the bay and terminal positions were highly soluble in cyclohexanone, the industrial solvent currently used in the pigment dispersion method. The spectral properties and thermal stability of the dye-based color filters with these dyes were examined by comparing them with pigment-based ones. The prepared color filters exhibited superior spectral properties due to the smaller particle size of the dyes, which led to less light scattering. However, their thermal stability varied with the dye structures, and only the dyes mono-substituted at the bay position had sufficient thermal stability.

1. Introduction

Liquid crystal display (LCD) modules are used widely in a variety of electronic displays, such as computers and TVs. Among the elements of LCD modules, the color filter, which converts the white backlight into red (R), green (G) and blue (B) colored lights, is a vital component [1,2].

Currently, the pigment dispersion method to form RGB patterned pixels using photo lithography has been adopted widely to produce color filters because color filters with superior stability can be achieved [3]. It is also advantageous to scale up the panel size while maintaining its pixel uniformity. Although color filters produced by this method have good thermal and photo-chemical stability, they have low chromatic properties due to the aggregation behavior of pigment particles used as colorants [4]. Dyes can be an attractive alternative to overcome this limitation due to the reduced light scattering because they are dissolved in the media and exist in molecular form. However, in order for the dyes to be applied successfully to a LCD manufacturing process, their low thermal stability needs to be improved [5].

In a previous report [6], water soluble dyes were applied to ink-jetted color filters, but there are few reports on the application of dyes on the currently used photo lithography process.

In this study, a range of highly soluble red perylene dyes were designed and synthesized for dye-based LCD color filters. Perylene-3,4,9,10-tetracarboxylic diimide derivatives show excellent thermal stability originating from their very high resonance stabilization energy [7] and $\pi-\pi$ interactions due to the planar molecular structure [8,9]. In addition, they have very strong and sharp absorption at approximately 530 nm [10]. However, they have low solubility in common industrial solvents, such as cyclohexanone, which limits their applications [11]. In this study, the solubility of the dyes was increased by substituting various bulky functional groups at the bay and terminal positions. The absorbance, solubility and thermal stability of the dyes substituted at one or both of the bay positions were examined and compared. Dye-based color filters were fabricated using both type of dyes, and their chromatic properties and thermal stability were analyzed.

2. Experimental

2.1. Materials and instrumentation

Perylene-3,4,9,10-tetracarboxylic dianhydride, 2,6diisopropylaniline, m-cresol, iodine, sulfuric acid, bromine, acetic acid,

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potassium carbonate anhydrous, phenol, 4-tert-butylphenol, and 4-tert-octylphenol purchased from Sigma–Aldrich, and isoquinoline purchased from TCI 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 color filter and acrylic binder LC20160 were supplied by SAMSUNG Cheil industries Inc.

^{1}H 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. 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 a HP 8452A spectrophotometer. Chromatic characteristics of the color filters were analyzed on a Scinco color spectrophotometer. 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 color filters was measured using a Nano System Nanoview E-1000.

2.2. Synthesis

The dyes **1**, **2a**, **2b**, **4a**, **4b** are already known structures, and we have modified and detailed the synthesis of them in this paper. The dyes **3a**, **3b**, **3c** are new structures.

2.2.1. N,N′-Bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-tetracarboxydiimide (*1*)

A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (3.92 g, 0.01 mol), 2,6diisopropylaniline (5.65 ml, 0.03 mol), m-cresol (60 ml) and isoquinoline (6 ml) was stirred at 50 °C for 2 h. The temperature of the mixture was raised to 200 °C and kept for 12 h. The warm solution was poured into 60 ml of acetone, and the precipitate was filtered out. The collected solution was poured into 1200 ml of n-Hexane and temperature of the mixture solution was dropped to 0 ∼ 5 °C and kept for 24 h. The precipitate was filtered out and dried at 80 °C under vacuum. The crude product was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (40:1) as the eluent to obtain **1** as red solid.

Yield 56.4%; ^{1}H NMR ($CDCl_3$, ppm): 8.80 (d, 4H), 8.75 (d, 4H), 7.50 (t, 2H), 7.36 (d, 4H), 2.75 (septet, 4H), 1.19 (d, 24H); MALDI-TOF MS: m/z 712.10 (100%, $[M + 2K]^+$).

2.2.2. N,N′-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (*2b*)

Perylene-3,4,9,10-tetracarboxylic dianhydride (16.0 g, 40.7 mmol), iodine (0.39 g, 1.52 mmol), and sulfuric acid (98%, 225 ml) were mixed and stirred for 2 h at room temperature. The reaction temperature was set at 80 °C, and bromine (3.58 ml, 70 mmol) was added dropwise over 2 h. The mixture was reacted further at 80 °C for 16 h, cooled to room temperature, and the excess bromine gas was displaced by nitrogen gas. The precipitate obtained after adding ice-water to the mixture was collected by suction filtration. The precipitate was washed with water several times until the aqueous layer became neutral to yield dibromo dianhydride as crude product. The crude product was then dried at 100 °C under reduced pressure and used for the next step without further purification.

The crude 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (8.0 g, 14.5 mmol), 2,6diisopropylaniline (8.8 ml, 46.7 mmol), and acetic acid (4.6 ml) were mixed and heated at 120 °C in N-Methyl-2-pyrrolidone(NMP) (100 ml) under the nitrogen atmosphere for 96 h. The precipitate obtained after adding water to the mixture was collected by suction filtration. The crude product was washed with water, dried, and purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. The band containing tribrominated diimide could be separated firstly. Then, the second band containing a mixture of dibrominated isomeric diimides was collected. The mixture was washed with EtOH and toluene and heated at 80 °C for 12 h in toluene (50 ml). The pure diimide, red compound **2b**, was recrystallized from the hot toluene solution [12].

Yield 42.8%; ^{1}H NMR ($CDCl_3$, ppm): 9.56 (d, 2H), 9.01 (d, 2H), 8.80 (d, 2H), 7.52 (t, 2H), 7.36 (d, 4H), 2.74 (septet, 4H), 1.18 (d, 24H); MALDI-TOF MS: m/z 869.83 (100%, $[M + 2K]^+$).

2.2.3. N,N′-Bis(2,6-diisopropylphenyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (*2a*)

2a could be separated by column chromatography from the same crude product of **2b**. After obtaining a mixture of dibrominated isomeric diimides, **2a** was obtained as the third eluted compound. The product **2a** was used for the next step without further purification because there was no isomer.

Yield 36.7%; ^{1}H NMR ($CDCl_3$, ppm): 9.85 (d, 1H), 9.03 (s, 1H), 8.80 (m, 3H), 8.72 (d, 1H), 8.71 (d, 1H), 7.51 (t, 2H), 7.36 (d, 4H), 2.76 (septet, 4H), 1.18 (d, 24H); MALDI-TOF MS: m/z 790.96 (100%, $[M + 2K]^+$).

2.2.4. N,N′-Bis(2,6-diisopropylphenyl)-1-phenoxy-perylene-3,4,9,10-tetracarboxydiimide (*3a*)

2a (1 g, 1.27 mmol) was mixed with potassium carbonate anhydrous (0.7 g), phenol (0.14 g, 1.50 mmol), and NMP (70 ml). The mixture was heated to 120 °C under argon and was stirred at this temperature for 24 h. The reaction mixture was cooled to room temperature and poured into 5% HCl (250 ml). The precipitate was filtered, repeatedly washed with water, and dried in a vacuum at 70 °C. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent to obtain **3a** as red solid.

Yield 85.8%; ^{1}H NMR ($CDCl_3$, ppm): 9.65 (d, 1H), 8.81 (m, 2H), 8.75 (m, 3H), 8.40 (s, 1H), 7.47 (m, 4H), 7.33 (m, 4H), 7.26 (t, 1H), 7.19 (d, 2H), 2.73 (septet, 4H), 1.16 (d, 24H); MALDI-TOF MS: m/z 804.37 (100%, $[M + 2K]^+$).

2.2.5. N,N′-Bis(2,6-diisopropylphenyl)-1-p-tert-butylphenoxy-perylene-3,4,9,10-tetracarboxydiimide (*3b*)

3b was synthesized in the same manner with **3a** using **2a** (1 g, 1.27 mmol), potassium carbonate anhydrous (0.7 g), and 4-tert-butylphenol (0.23 g, 1.50 mmol).

Yield 86.1%; ^{1}H NMR ($CDCl_3$, ppm): 9.68 (d, 1H), 8.82 (m, 2H), 8.75 (m, 3H), 8.42 (s, 1H), 7.48 (m, 4H), 7.33 (m, 4H), 7.13 (d, 2H), 2.74 (septet, 4H), 1.36 (s, 9H), 1.16 (d, 24H); MALDI-TOF MS: m/z 860.28 (100%, $[M + 2K]^+$).

2.2.6. N,N′-Bis(2,6-diisopropylphenyl)-1-p-tert-octylphenoxy-perylene-3,4,9,10-tetracarboxydiimide (*3c*)

3c was synthesized in the same manner with **3a** using **2a** (1 g, 1.27 mmol), potassium carbonate anhydrous (0.7 g), and 4-tert-octylphenol (0.31 g, 1.50 mmol).

Yield 87.8%; ^{1}H NMR ($CDCl_3$, ppm): 9.68 (d, 1H), 8.81 (m, 2H), 8.75 (m, 3H), 8.39 (s, 1H), 7.46 (m, 4H), 7.34 (m, 4H), 7.11 (d, 2H), 2.73 (septet, 4H), 1.75 (s, 2H), 1.40 (s, 6H), 1.16 (d, 24H), 0.75 (s, 9H); MALDI-TOF MS: m/z 916.31 (100%, $[M + 2K]^+$).

2.2.7. N,N′-Bis(2,6-diisopropylphenyl)-1,7-dilphenoxy-perylene-3,4,9,10-tetracarboxydiimide (*4a*)

4a was synthesized in the same manner with **3a** using **2b** (1 g, 1.15 mmol), potassium carbonate anhydrous (0.7 g), and phenol (0.24 g, 2.50 mmol) (Fig. 1).

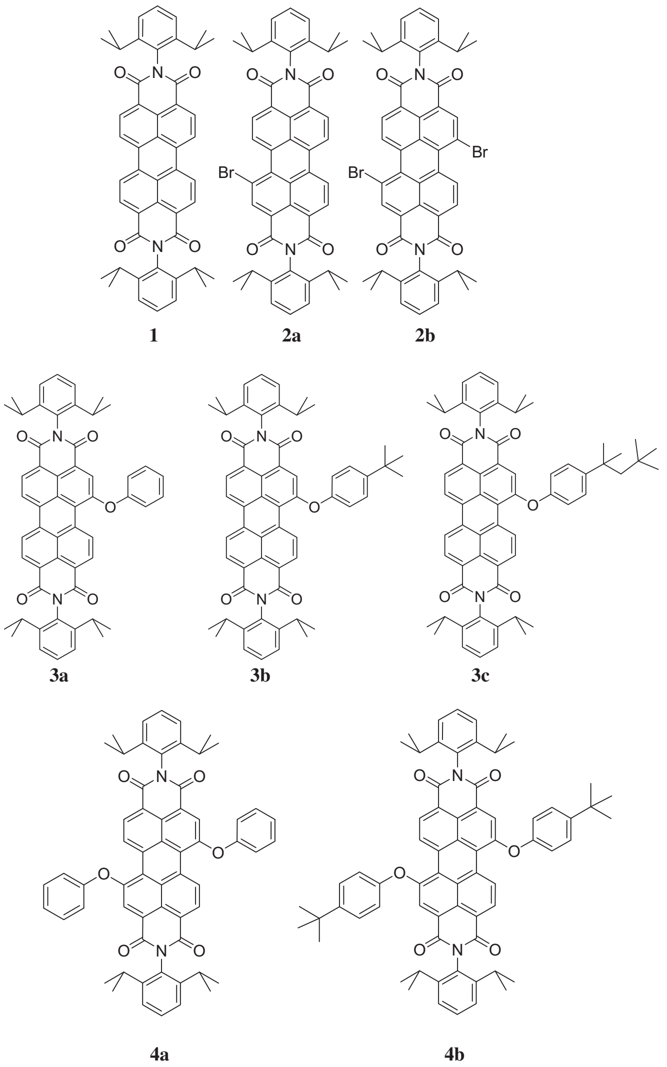


Fig. 1. Synthesized dyes.

Yield 83.1%; ^{1}H NMR ($CDCl_3$, ppm): 9.64 (d, 2H), 8.70 (d, 2H), 8.43 (s, 2H), 7.46 (m, 6H), 7.31 (d, 4H), 7.24 (t, 2H), 7.18 (d, 4H), 2.70 (septet, 4H), 1.14 (d, 24H); MALDI-TOF MS: m/z 896.31 (100%, $[M + 2K]^+$).

2.2.8. *N,N′-Bis(2,6-diisopropylphenyl)-1,7-bis (p-tert-butylphenoxy)-perylene-3,4,9,10-tetracarboxydiimide (**4b**)*

4b was synthesized in the same manner with **4a** using **2b** (1 g, 1.15 mmol), potassium carbonate anhydrous (0.7 g), and 4-tert-butylphenol (0.38 g, 2.50 mmol).

Yield 81.9%; ^{1}H NMR ($CDCl_3$, ppm): 9.66 (d, 2H), 8.71 (d, 2H), 8.45 (s, 2H), 7.46 (m, 6H), 7.31 (d, 4H), 7.12 (d, 4H), 2.71 (septet, 4H), 1.35 (s, 18H), 1.15 (d, 24H); MALDI-TOF MS: m/z 1008.49 (100%, $[M + 2K]^+$).

2.3. *Preparation of dye-based inks and color filters*

The red ink for a color filter was composed of the dye (0.1 g), cyclohexanone (3.2 g), and LC20160 (1.4 g) as a binder based on acrylate.

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 5 s, which was then increased to 300 rpm and kept constant for 20 s. The wet dye-coated color filters were then dried at 80 °C for 20 min, pre-baked at 150 °C for 10 min, and postbaked at 230 °C for 1 h. After each step, the coordinate values of the color filters were measured. All spin-coated dye-based color filters were 1.6 μm thick.

2.4. *Investigation of solubility*

The solubility of the synthesized dyes in CH_2Cl_2 and cyclohexanone were examined to determine the effects of substituents at the bay and terminal positions. 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 (Scheme 1).

2.5. *Measurement of spectral and chromatic properties*

Absorption spectra of the synthesized dyes and the transmittance spectra of pigment-based and dye-based color filters were measured using a UV–vis spectrophotometer. The chromatic values were recorded on a color spectrophotometer (Scinco colormate).

2.6. *Measurement of thermal stability*

The thermal stability of the synthesized dyes was evaluated by thermogravimetry (TGA). The prepared dyes were heated to 110 °C and held at that temperature for 10 min to remove the residual water and solvents. The dye was then, heated to 220 °C and held at that temperature for 30 min to simulate the processing thermal conditions of color filter manufacturing. The dyes were finally heated to 400 °C to determine their degradation temperature. The heating was carried out at the rate of 10 °C min^{-1} under nitrogen atmosphere [6,13].

To check the thermal stability of the dyes in color filters, the fabricated color filters were heated to 230 °C for 1 h in a forced convection oven (OF-02GW Jeiotech Co., Ltd.). The color difference values (ΔE_{ab}) before and after heating were measured on a color spectrophotometer (Scinco colormate) in CIE L′a′b′ mode.

2.7. *Geometry optimization of the synthesized dyes*

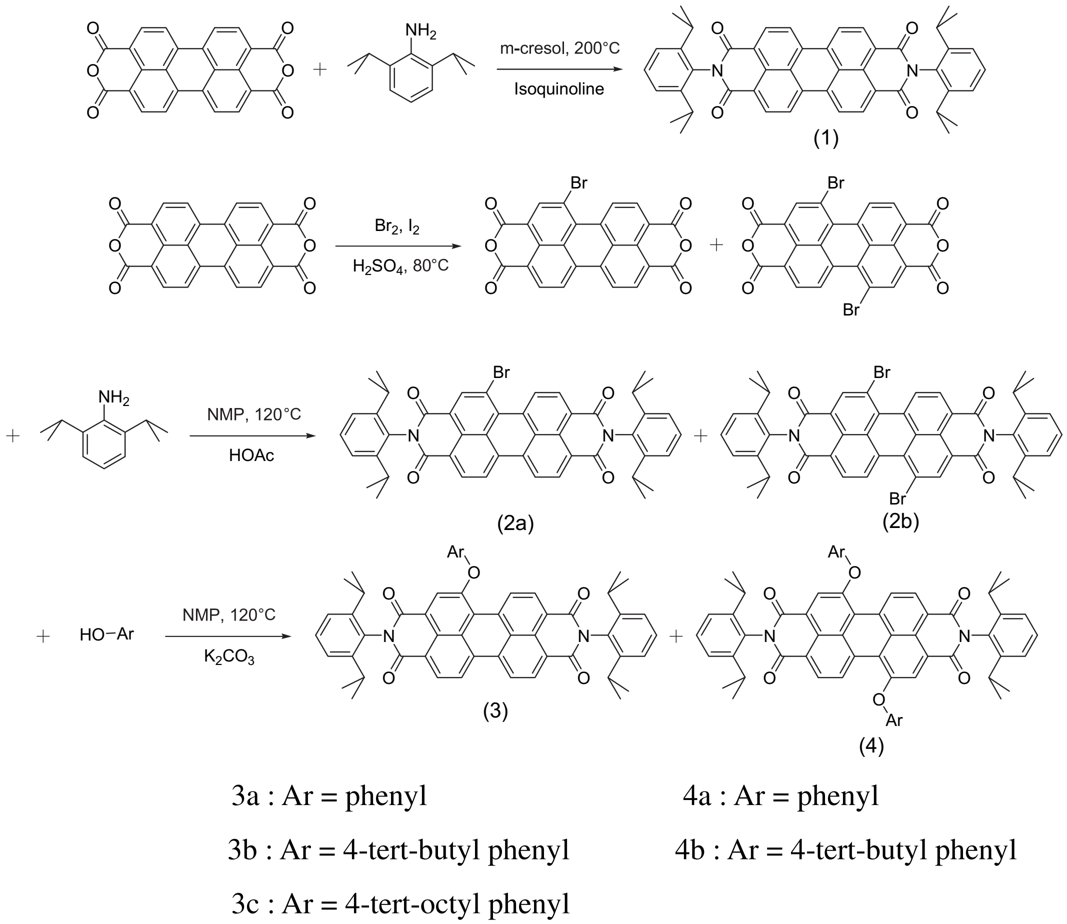
The difference of thermal stability due to the structural differences in the dyes were analyzed by optimizing the dye structures using the Gaussian 03 program, and examining the core twist angles that affect the intermolecular interaction. The optimized geometries of the dye structures were calculated at the B3LYP/6-31G* level.

3. Results and discussion

3.1. *Design concept of dyes*

The steric restriction caused by the imidization of bulky aryl groups at the terminal positions of Perylene-3,4,9,10-tetracarboxylic dianhydride decreases the crystal packing density of the dyes, which in turn increases their solubility [14]. In particular, *ortho*-alkyl-substituted aromatics maximize this effect. However, substitution at the terminal position does not affect the UV–Vis absorption spectra significantly because the conjugation nodes along the long axis of the molecule limit the electronic interactions between the main body of the molecule and corresponding substituents [15,16].

Although the solubility of dye **1** in common organic solvents, such as CH_2Cl_2, was increased significantly, it was not soluble enough in industrial solvents, such as cyclohexanone, to be suitable as a color filter (Table 1). Additional bulky substituents were



Scheme 1. Synthesis of the prepared dyes.

introduced at their bay positions to further improve their solubility. The solubility was increased remarkably when the bulky aryl groups were substituted at the bay positions because they deviated from the plane of the molecule and the planarity of the main body was broken [14].

The introduction of substituents at the bay positions was demonstrated to alter the UV–Vis absorption spectra of dyes significantly [17]. Substituents with an ether linkage group were chosen to minimize the bathochromic shift in the absorption spectra and have high affinity with industrial solvents. In particular, phenoxy substituents were considered to be superior to alkoxy ones due to the lower bathochromic shift [18] and greater steric hindrance for high solubility.

3.2. Solubility of dyes

The dyes need to be dissolved in industrial solvents to a concentration of at least 4 ~ 5wt% to be suitable for LCD color filters. Table 1 lists the solubility data of the four representative dyes. Without the appropriate modification of the molecular structure, perylene derivatives have low solubility due to the planar structure, which facilitates the formation of crystals with high lattice energy [14].

The solubility of dye **1** in CH_2Cl_2 was significantly higher than Perylene-3,4,9,10-tetracarboxylic dianhydride due to the terminal bulky aryl groups that rotate 90° out of the plane of the molecule. However, the solubility of dye **1** in cyclohexanone was still very low. The molecular structure of dye **2b** is no longer planar due to the presence of Br atoms at the bay positions, which in turn decrease the crystal packing density [19]. Therefore, the solubility of dye **2b** in CH_2Cl_2 and cyclohexanone was higher than that of dye **1** but was still insufficient for use in LCD color filters.

There were significant improvements in the solubility of dye **3b** and **4b** when the Br atoms were replaced with bulky phenoxy substituents that induce further twisting of the two naphthalene subunits in the perylene core [20]. The core twisting effect of the mono-substituted dye was less than 1,7-di(substituted) dye (Fig. 7). Consequently, dye **3b** would have higher crystallinity than dye **4b**, but the asymmetric molecular structure of dye **3b** could offset this effect. Therefore, the solubility of both dyes was similar in both solvents and sufficient for use in LCD color filters. In particular, their high solubility in cyclohexanone was attributed to the affinity between the ether linkage of the dyes and solvent molecules.

Table 1
Solubility of the dyes at 20 °C.

	1	2b	3b	4b
CH_2Cl_2	+	++	+++	+++
Cyclohexanone	−	+	+++	+++

+++: $5.0 \times 10^4 \sim 1.0 \times 10^5$ mg L^{-1}; ++: $5.0 \times 10^3 \sim 5.0 \times 10^4$ mg L^{-1}; +: $5.0 \times 10^2 \sim 5.0 \times 10^3$ mg L^{-1}; −: $<5.0 \times 10^2$ mg L^{-1}.

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

Fig. 2 and Table 2 show the absorption spectra of dyes **3a** ~ **4b** in CH_2Cl_2. To apply a dye to LCD red color filters, the dye needs to

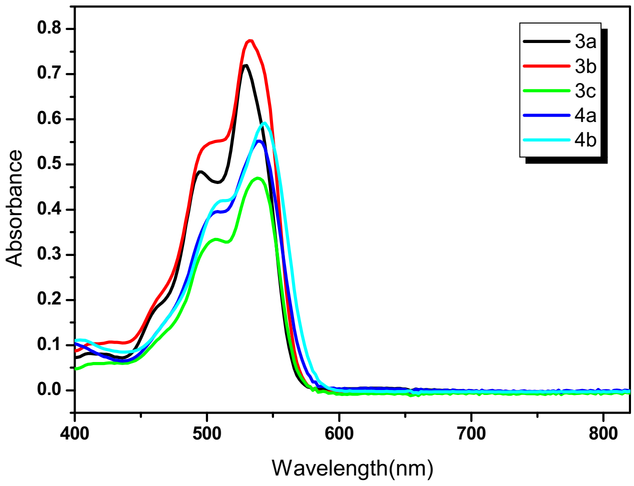


Fig. 2. Absorption spectra in CH_2Cl_2 (10^{-5} mol L^{-1}).

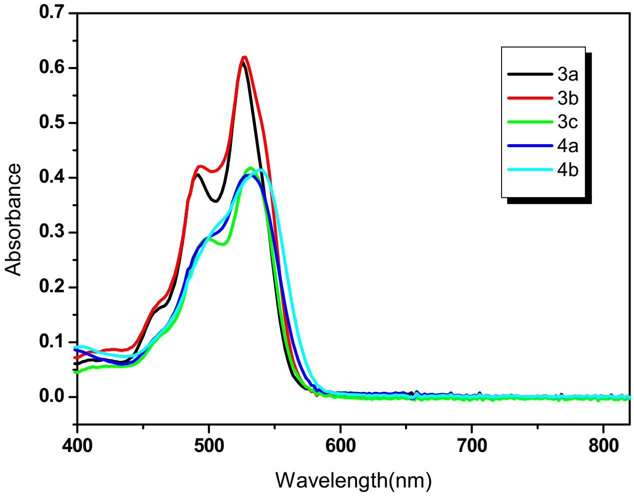


Fig. 3. Absorption spectra in Cyclohexanone (10^{-5} mol L^{-1}).

have a strong and sharp absorption maximum in the 525 ~ 550 nm range. The absorption maxima of the above dyes with various phenoxy substituents at the bay positions were slightly bathochromic compared to Perylene-3,4,9,10-tetracarboxylic dianhydride (λ_{max} = 526 nm) due to the electron donating effect of the substituents [21]. The bathochromic shifts in the mono-substituted dyes (**3a** ~ **c**) were less than those of 1,7-di(substituted) dyes (**4a** ~ **b**) because such an effect of substituents diminishes. As can be seen in comparison with **3a** ~ **c** and **4a** ~ **b**, the bulkier alkyl group at the *para* position produces a larger red-shift in λ_{max} due to the increase in donating power.

The above dyes show spectral-broadening compared to Perylene-3,4,9,10-tetracarboxylic dianhydride but still have satisfactory spectral sharpness for use in LCD color filters. This spectral-broadening was attributed to the increase in conjugation between the substituents and perylene core, as well as to twisting of the perylene core by the substituents [12].

The molar extinction coefficients of the synthesized dyes were quite high and varied with the dye structure. Therefore, the dye-based color filters could have higher tinctorial strength compared to the pigment-based one with considerably lower dye content. The molar extinction coefficients of the mono-substituted dyes were higher than the 1,7-di(substituted) dyes because their structural planarity was less distorted. However, the molar extinction coefficient of dye **3c** was lower than that of dyes **4a** and **4b**, probably due to the steric effect of the tert-octyl group.

Fig. 3 and Table 2 show the absorption spectra of dyes **3a** ~ **4b** in cyclohexanone, the industrial solvent of LCD color filters. There were some differences between the absorption spectra in cyclohexanone and CH_2Cl_2. When the dyes were dissolved in cyclohexanone, the absorption maxima were hypsochromic by approximately 4 ~ 6 nm and the molar extinction coefficients decreased by approximately 10000 ~ 20000 compared to those in CH_2Cl_2. This would be attributed to the difference in affinity between the dyes and solvents.

Table 2
Absorption spectra of the prepared dyes in CH_2Cl_2 and Cyclohexanone.

Solvent	Dye	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})
CH_2Cl_2	**3a**	530	71919
	3b	532	77434
	3c	538	47014
	4a	540	55197
	4b	544	59145
Cyclohexanone	**3a**	526	60980
	3b	528	61991
	3c	532	41830
	4a	532	40529
	4b	538	41431

Fig. 4 shows the transmittance spectra of the pigment-based color filter and the fabricated dye-based color filters with dyes **3a** ~ **4b**. All the dye-based color filters had similar or superior transmittance spectra compared to the pigment-based one because dyes dissolved in the media have a smaller particle size, which leads to less light scattering [6,22]. In particular, the synthesized perylene dyes can maintain a well-dissolved state due to their high molar extinction coefficients so that only small amounts of dyes are needed for LCD color filters. The color filter with dye **4b** showed the highest transmittance over 625 nm because of its two bulky tert-butylphenoxy substituents, which lead to less aggregation of dye molecules. Table 3 shows the transmittance of the pigment-based and dye-based color filters at 650 nm; the dye-based color filters had higher transmittance. However, all the dye-based color filters had undesirable transmittance at 400–500 nm, as shown in Fig. 4, and yellow color compensating dyes are needed to cut off these undesirable transmittance.

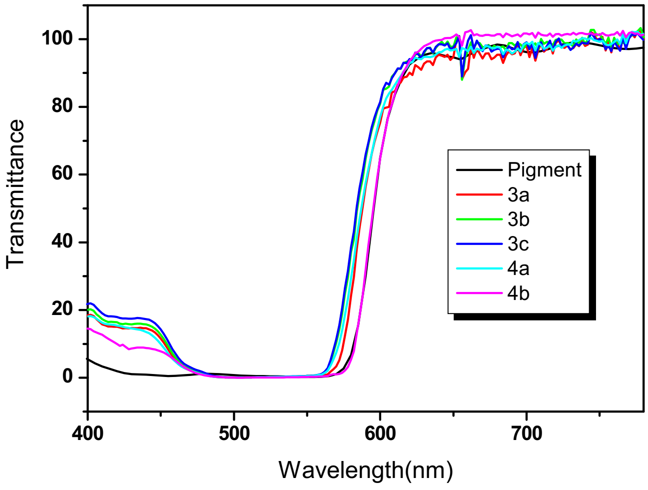


Fig. 4. Transmittance spectra of the spin-coated color filters.

Table 3
Transmittance of the spin-coated color filters at 650 nm.

Color filter	Transmittance (%) at 650 nm
Pigment	94.5997
3a	94.8496
3b	97.7593
3c	97.5466
4a	96.7853
4b	100

Table 4 lists the coordinate values of the pigment-based color filter and fabricated dye-based color filters with dyes **3a** ~ **4b**. Although dye-based color filters had a lower colorant content, they could have a similar color gamut with a pigment-based one due to the high molar extinction coefficients. In particular, the color filters with dyes **3a** and **3b**, which have higher molar extinction coefficients, had larger x values. However, the x, y values of the color filters with dyes **4a** and **4b** decreased after postbaking due to their low thermal stability, as shown in Fig. 5 and Table 4. Compared to the pigment-based color filter, the dye-based ones had smaller y values, which are advantageous for a wide color gamut. In particular, the color filters with more bathochromic dyes had smaller y values. The dye-based color filters also had higher brightness (Y) values than the pigment-based one due to their higher transmittance [6].

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

Dye molecules should have a strong intermolecular interaction and form compact aggregates to have the high thermal stability [23–25]. The synthesized perylene dyes contain many aromatic rings and have a relatively flat molecular structure that contributes to the strong π–π stacked interactions [8,9]. In addition, their high molecular weight and polar substituents at the bay positions are advantageous for intermolecular interactions, such as Van der Waals Force and dipole–dipole interaction [6].

For dyes to be used as color filters, they should endure temperature of 220 °C, which is the highest temperature in the LCD manufacturing process, without significant weight loss [26,27]. Mono-substituted dyes **3a** and **3b** showed less than 1% weight loss after 30 min at 220 °C and were stable up to 250 °C, whereas the 1,7-di(substituted) dyes **4a** and **4b** showed approximately 5% weight loss, as shown in Fig. 6. This was attributed to the lower core twisting and less anti-aggregation effect of the substituents of the mono-substituted dyes, which leads to close packing of the dye molecules for high thermal stability. In a previous report, field emission scanning electron microscopy (FE-SEM) studies of various dyes showed that the dye with less steric hindrance had the bigger aggregate size that led to superior thermal stability [28]. Therefore, the thermal stability of 1,7-di(substituted) dyes is insufficient for use in LCD color filters, even though they exhibited excellent spectral properties. The mono-substituted dye **3c** showed less weight loss than dyes **4a** and **4b** but more weight loss than dyes **3a** and **3b** due to the low thermal stability caused by the tert-octyl alkyl chain.

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.

Color filter		x	y	Y	ΔE_{ab}
Pigment	Prebake	0.644	0.345	22.10	0.248
	Postbake	0.641	0.343	22.16	
3a	Prebake	0.639	0.337	23.01	0.613
	Postbake	0.635	0.335	23.28	
3b	Prebake	0.642	0.335	24.69	0.752
	Postbake	0.640	0.334	25.01	
3c	Prebake	0.623	0.311	25.25	1.823
	Postbake	0.615	0.309	26.20	
4a	Prebake	0.634	0.304	24.72	9.873
	Postbake	0.528	0.262	30.06	
4b	Prebake	0.626	0.303	24.49	9.668
	Postbake	0.527	0.269	29.67	

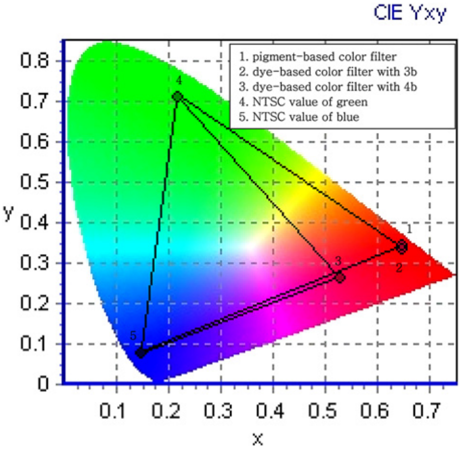


Fig. 5. CIE 1931 chromaticity diagram of the pigment-based and dye-based color filters.

The ΔE_{ab} values of the color filters should be less than 3 after heating for one hour at 230 °C for commercial applications. The color filters with the mono-substituted dyes had satisfactory ΔE_{ab} values that varied according to their structures, as shown in Table 4. In contrast, the color filters with the 1,7-di(substituted) dyes had ΔE_{ab} values bigger than 3, which means that their thermal stability is insufficient.

As shown in Table 4, the x, y coordinate values of the color filters with the 1,7-di(substituted) dyes decreased and their brightness (Y) values increased after postbaking. This suggests that their original red color faded due to degradation of their molecular structure. However, the thermal stability of dye-based color filters can be improved if the commercial binder used for the pigments can be adjusted.

The difference in thermal stability between the two types of dyes was analyzed partially by geometry calculations. Fig. 7 shows the optimized geometries of dyes **3b** and **4b**, which showed molecular core twisting due to the bulky phenoxy substituents at the bay positions [29]. The approximate dihedral angle between the two

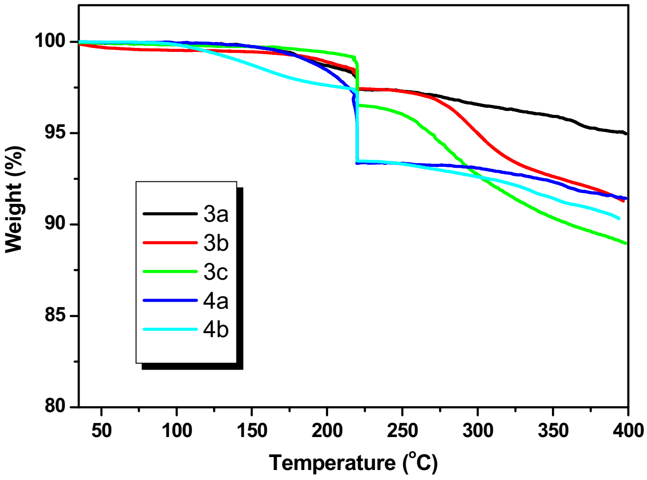


Fig. 6. Thermogravimetric analysis (TGA) of the prepared dyes.

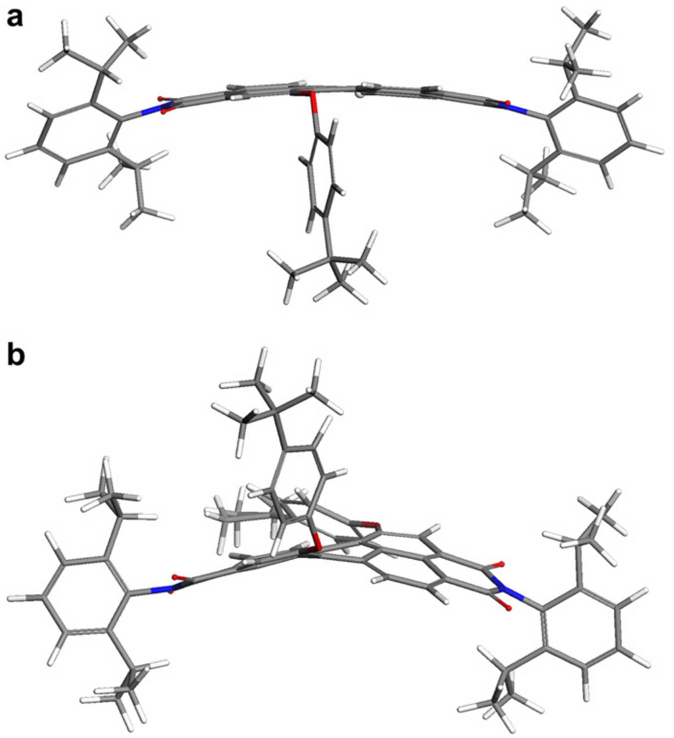


Fig. 7. Geometry-optimized structures of dyes **3b** and **4b**.

naphthalene subunits attached to the central benzene ring was 8.6° and 26.2° for dyes **3b** and **4b**, respectively. Therefore, the core twisting that decreases π–π stacked interaction was more severe in the 1,7-di(substituted) dye, which in turn led to lower thermal stability.

4. Conclusions

Eight red perylene dyes were synthesized, and among them five solubility enhanced dyes were used in color filters. The difference in solubility of the prepared dyes was attributed to the bulky functional substituents at the bay and terminal positions and the core twisting of the molecular structures.

All five dyes showed sharp absorption near 530 nm, and the dye-based color filters could have a similar color gamut to the pigment-based one despite the much lower colorant content used due to their high molar extinction coefficients. In addition, the dye-based color filters with those dyes could have higher transmittance than the pigment-based one because they dissolved in the media, would exist in the molecular phase and could have a smaller particle size that leads to less light scattering.

The mono-substituted dyes had satisfactory thermal stability due to the properly controlled aggregation, whereas the 1,7-di(substituted) dyes did not meet the commercial criterion because their two bulky substituents at the bay positions made them thermally less stable.

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