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Synthesis of high-soluble and non-fluorescent perylene derivatives and their effect on the contrast ratio of LCD color filters



PIĞMĔNTS

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ABSTRACT

We designed and synthesized perylene-based dyes for dye-based LCD color filters that highly soluble in organic industrial solvents, exhibit very weak fluorescence, and can be easily synthesized due to their simple molecular structures. The synthesized dyes were designed containing methoxy groups in the terminal-, bay-, or both positions for developing fluorescence quenched dyes. And, dyes with strong fluorescence and similar molecular structures to the fluorescence quenched dyes were also synthesized to clearly compare and analyze the effect of fluorescence on the optical properties. Finally, we fabricated dye-based color filters using the synthesized dyes and analyzed the optical performances of the color filters. The methoxy group in the bay-substituents has an enormous effect on the fluorescence quenched dyes have remarkable effects in minimizing the increment of minimum brightness and prohibiting the contrast ratio decrease.

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1. Introduction

Liquid crystal displays (LCDs) have captured a larger portion of the display market share than other types of displays [1–4]. Research into high-performance LCD devices is very important in order to exploit next-generation display industries such as large format and low power consumption screens [5,6]. LCDs with traditional pigment-based color filters have some advantages in mass production and price competitiveness. However, pigmentbased color filters have draw backs with respect to contrast ratio and brightness owing to their large particle size after heat treatment in the manufacturing process [7–9]. Therefore, research and development toward dye-based and pigment-dye hybrid color filters has been in demand in order to develop displays that exhibit superior optical properties.

Perylene-based dyes have many merits for use as colorants in

dye-based color filters due to their strong color strengths and thermal stabilities [10–13]. However, perylene-based dyes show powerful fluorescence likewise the other dyes that are commonly used for LCD color filters [14,15]. Generally, in almost every report, bulky substituents were introduced to increase the solubilities of the dyes [5,6,16–18]. These bulky substituents usually make the fluorescence of the dyes stronger by broadening the intermolecular distance [19–23]. Therefore, the fluorescence of produced perylene derivatives that have bulky substituents would be naturally increased [24–28]. As mentioned in our previous study [3,9], the fluorescence of the dyes can enhance the brightness of the color filters, meanwhile, that is a key factor of contrast ratio decrease by the unexpected increment of minimum brightness.

In this study, we designed and synthesized perylene-based dyes exhibiting sufficient solubilities in organic industrial solvents as well as significantly inhibited fluorescence. Dye-based color filters using the synthesized dyes were fabricated, and the influence of dye fluorescence on optical performance of the prepared color filters was investigated. Dyes have to be soluble at least



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4-5 wt% in organic industrial solvents to be used for LCD color filters [5,6,8,9]. Therefore, we introduced bulky substituents at the terminal- and bay-positions of the perylene moiety. These substituents could enhance their solubilities by molecular distortion and intermolecular steric hindrance [29,30]. However, the fluorescence of the synthesized dyes could be increased due to the bulky substituents which prevent dye aggregations and intermolecular interactions [21,24–26]. Therefore, we designed the dves to have substituents containing methoxy groups to reduce the fluorescence of the dyes [31]. Moreover, dyes with strong fluorescence and similar molecular structures to the fluorescence quenched dyes were also synthesized to clearly compare and analyze the effect of fluorescence on the optical properties. The dye-based color filters were fabricated in 1-3 wt% color content concentration to accurately investigate the relationship between the fluorescence of the dyes and the optical properties of the prepared color filters.

2. Experimental

2.1. Materials and instrumentation

Perylene-3,4,9,10-tetracarboxylic dianhydride, iodine, sulfuric acid, bromine, and acetic acid were purchased from Sigma-Aldrich; 2,6-diisopropylaniline, 2-methoxy-6-methylaniline, 4methoxyphenol, and 4-ethylphenol were purchased from TCI; potassium carbonate anhydrous, methylene chloride, and other chemical solvents were purchased from Samchun Pure Chemical. All chemicals were used without any additional purification.

Elemental Analysis (EA) was completed on a CE Instruments EA1112 analyzer. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 500 spectrometer running at 500 MHz using chloroform-d as a solvent with TMS as an internal standard. Matrix Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE STR Biospectrometry Workstation using α -cyano-4-hydroxycinnamic acid (CHCA) as a matrix.

Absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. Fluorescence spectra and quantum yield were measured on a Perkin Elmer LS 55 and a PTI Quanta Master 40 fluorescence spectrometer, respectively. A Becker & Hickl SPC-150 equipped with a Time-Correlated Single Photon Counting (TCSPC) board was used to measure the time-resolved fluorescence decay with a time channel of 17.1 ps? Contrast ratio and brightness of color filters were measured by CT-1 of Tsubosaka and MC-3700:28C of Otsuka Electronics.

2.2. Syntheses of the dyes

All synthetic procedures were carried out by following our previous reports [8,9]. We had reported previously that bay-position substitution is possible at much lower temperature and in a shorter reaction time than the widely known method.

2.2.1. 1,7-Dibromoperylene-3,4,9,10-tetracarboxydiimide: bromination

Perylene-3,4,9,10-tetracarboxylic dianhydride (32.00 g, 81.40 mmol), iodine (0.78 g, 3.04 mmol) and sulfuric acid (98%, 450 ml) were mixed and stirred for 2 h at room temperature. The temperature of the mixture was raised to 80 °C and bromine (8.33 ml, 162.80 mmol) was added dropwise over 1 h. The resulting mixture allowed to react for 16 h, upon which time, it was cooled to room temperature and the remaining bromine gas was displaced by nitrogen gas. The mixture was slowly poured into 3 L of ice water and the crude precipitate formed was collected by suction filtration

followed by washing several times with distilled water. The crude product was dried at 80 °C under reduced pressure and used in the next step without further purification. The crude product containing both mono- and di-bromoperylene derivatives was separated by column chromatography in next step, after introducing bulky substituents in the terminal-position to increase their solubilities.

2.2.2. N,N'-bis(R₁)-1,7-dibromoperylene-3,4,9,10-

tetracarboxydiimide: terminal-position substitution

1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide Crude (8.00 g, 14.55 mmol), R₁-NH₂ (45.00 mmol), acetic acid (4.60 ml) and N-methyl-2-pyrrolidone (NMP; 100 ml) were mixed and heated to 120 °C under nitrogen atmosphere for 96 h. Water was added to the mixture and the resulting precipitate was collected by suction filtration. The crude product was washed with water and dried under reduced pressure. The crude product was purified by column chromatography in silica gel using CH₂Cl₂ as an eluent. Three bands were collected. The first band contained a small amount of tribrominated diimide, the second band contained the dibrominated diimide, and the third contained the monobrominated diimide. Detailed structural analysis was conducted after the next step. To obtain the **PI-series**, 2,6-diisopropylaniline was used as R1-NH2 and to obtain PM-series, 2-methoxy-6methylaniline was used.

2.2.3. N,N'-bis(R₁)-1,7-bis(R₂)-perylene-3,4,9,10-

tetracarboxydiimide: bay-position substitution

N,*N'*-*bis*(R₁)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (0.58 mmol) was mixed with anhydrous potassium carbonate (0.35 g, 2.54 mmol), R₂-OH (1.60 mmol) and NMP (60 ml). The mixture was heated at 40 °C under nitrogen and was stirred for 1.5 h. The mixture was cooled to room temperature, and then poured into HCl (400 ml, 5% aqueous). The precipitate was collected by suction filtration, washed with water and dried under vacuum at 80 °C. The crude product was purified by column chromatography in silica gel using CH₂Cl₂ as an eluent to obtain the products as red solids.

2.3. Geometry optimization of the dyes

Density functional theory (DFT) calculations were carried out with the GAUSSIAN09 package. We used the 6-311++G(d,p) Pople basis set for all elements and the conventional B3LYP exchange-correlation function. The intermolecular interactions were analyzed by examining the core twist angles and the size of substituents. Dihedral angles of perylene main body were calculated by measuring the distortion angle of benzene ring in the center of perylene main body. Calculated lengths of bay-substituents were indicated by measuring the lineal distance from oxygen atom of ether linkage to farthest atom in the substituents. And, calculated lengths of terminal-substituents were indicated by measuring the longest lineal distance in the substituents.

2.4. Preparation of dye-based inks and color filters

The red inks for the dye-based color filters were composed of propylene glycol methyl ether acetate (PGMEA; 0.1 g), acrylic binder (0.8 g) and synthesized dye (1, 2 or 3 wt% of the acrylic binder). The prepared dye-based inks were coated on a transparent glass substrate using a MIDAS Systems SPIN-1200D spin coater. The rotation speed was initially set at 100 rpm for 10 s, and then increased to 500 rpm for 20 s. The dye-coated color filters were dried at 80 °C for 20 min, pre-baked at 150 °C for 10 min and postbaked at 200 °C for 1 h.

3. Results and discussion

3.1. Design concept of the synthesized dyes

Synthetic routes and molecular structures of the synthesized dyes are shown in Scheme 1 and Fig. 1. Generally, perylene-based dyes have strong color strengths and thermal stabilities due to their high degree of planarity [10,11,15,32]. However, they usually show inferior solubility in organic industrial solvents such as propylene glycol methyl ether acetate (PGMEA), a commonly used organic solvent in the LCD manufacturing process [5,8,30]. Bulky substituents containing a benzene ring were introduced in the terminal- and baypositions of the perylene main body in order to reduce planarity and intermolecular interactions, as well as to increase the steric hindrance of the synthesized dyes [33–35]. The solubilities of the synthesized dyes in some organic solvents are listed in Table 1. All the dyes show sufficient solubilities as colorants for LCD color filters due to the contribution of the introduced bulky substituents.

All of the dyes were designed to have similar conjugation length. Therefore, it can be regarded that they would exhibit similar spectral properties [9,36–40]. Hence, the effect of the spectral properties of the dyes on the optical performance of fabricated color filters would be minimized. The size and structure of the introduced substituents are also similar, thus, the geometrical structures of the synthesized dyes would be naturally analogous to each other. Geometry-optimized structures of the synthesized dyes are shown in Fig. 2 and dihedral angle of the perylene main body and calculated lengths of the substituents are listed in Table 2 (Details related to the measurements of Table 2 are presented in supplementary data). As shown in Table 2, the differences in the geometrical structures of the synthesized dyes were very small to relate the influences on the intermolecular interactions. Especially, all synthesized dyes show almost identical the dihedral angles that mostly affect the planarities of them [8,41,42]. Therefore, the differences in optical properties of the color filters resulting from dye aggregation and intermolecular interactions would also be minimized.

Introduction of bulky substituents is the most popular method to enhance the fluorescence of dyes by inhibiting both aggregation quenching and energy transfer such as Förster resonance energy transfer (FRET) [21,26,43]. Therefore, in addition to enhancing the solubilities with structure distortion and steric hindrance, the fluorescence of the dyes would be naturally increased when bulky substituents were introduced to the pervlene main body [14]. However, as mentioned in our previous study [9], dves for LCD color filters have to be highly soluble in organic solvents and show minimized fluorescence. Accordingly, we designed dyes containing methoxy groups in the terminal-, bay-, or both positions for developing fluorescence quenched dyes. Generally, methoxy groups are used to cause bathochromic shifts by electron donating effects or to sterically broaden the intermolecular distance [44–47]. And, in some preceding reports [45,46], it has been reported that the introduction of a methoxy group leads to decreased fluorescence in certain dyes. A methoxy group in the para-position of the bay-substituents is highly efficient at decreasing dye fluorescence [48]. Therefore, we designed dyes having a methoxy group at this position. As a result, we successfully designed dyes that highly soluble in organic solvents, exhibit very weak fluorescence, and can be easily synthesized due to their simple molecular structures. Dyes showing strong fluorescence were designed to contain alkyl groups that have a similar geometrical size as methoxy groups in order to minimize the differences in molecular behavior among them.

3.2. Spectral and fluorescence properties of synthesized dyes

The absorption spectra of the synthesized dyes in chloroform are shown in Fig. 3. As mentioned before, the conjugation systems of all synthesized dyes are similar to each other. Therefore, the synthesized dyes exhibit similar spectral properties as shown in Fig. 3 and Table 3 [37,39,49]. Namely, the effect of the spectral properties of synthesized dyes on the optical properties of the fabricated color filters would be minimized. Although, the dyes with methoxy groups in bay-positions show a small bathochromic



Scheme 1. Syntheses of the designed dyes.



Fig. 1. Structure of the synthesized dyes.

| Table 1 |
|---|
| Solubility of the synthesized dyes at room temperature in CH ₂ Cl ₂ , CHCl ₃ and PGMEA |
| (wt%). |

| Dye | PI-4EP | PI-4ME | PM-4EP | PM-4ME |
|---------------------------------|--------|--------|--------|--------|
| CH ₂ Cl ₂ | 5.8 | 5.9 | 5.2 | 5.1 |
| CHCl ₃ | 6.0 | 6.0 | 5.7 | 5.8 |
| PGMEA | 5.0 | 5.1 | 4.7 | 4.8 |

shift of about 4 nm due to the electron donating effect of the methoxy groups [45,46,50]. But, this shift would not seriously influence the optical properties of the manufactured color filters because the color filters were fabricated with low color content concentration.

The fluorescence properties of the synthesized dyes are listed in Fig. 4 and Table 3. All of the measured fluorescence properties except quantum yield were measured at an excitation wavelength corresponding to the wavelength of maximum absorption. The quantum yield was measured with an excitation wavelength of 480 nm [51,52]. Chloroform was used as a solvent for all measurements in Table 3.

In our previous study [9], dyes with various geometrical structures would severely affect their molecular behavior and aggregation resulting in a variation of fluorescence properties. It is wellknown that the two main factors affecting fluorescence quenching of organic dyes are static quenching derived from H-aggregation and energy transfer which occurs via intermolecular interactions [20,22,53–55]. However, as shown in Table 2, the synthesized dyes in this study have similar geometrical molecular structures. Therefore, the intermolecular interactions of the dyes would not be different from each other. In other words, the main factor affecting the fluorescence properties of the synthesized dyes is not H-aggregation or energy transfer. This result also could be verified from the presented data. For example, the solubilities in Table 1 and the fluorescence intensities of the synthesized dyes in Table 3 do not show a correlation. If the fluorescence of the synthesized dyes resulted mainly from intermolecular behavior, the solubility and the fluorescence intensity would show a certain trend. Eventually, it could be concluded that the dyes synthesized in this study exhibit different fluorescence properties which are mainly attributed to the introduced methoxy groups.

The methoxy groups introduced in the terminal-positions have no effect on the fluorescence quenching. On the contrary, methoxy groups in the bay-positions severely diminish the fluorescence. It is widely known that substituents at the bay-positions have a strong conjugation link with the perylene main body [29,33,34]. Contrastively, the terminal-substituents have no or very slight conjugation linkage [5,8]. Therefore, bay-substituents have a strong influence on the π -conjugation system and the electrochemical properties of the dyes. This phenomenon could be verified from the bathochromic shift of the spectral properties of the synthesized dyes with methoxy groups in the bay-positions.

Dyes with bay-substituents containing ethyl groups exhibited more powerful fluorescence in the visible region than dyes with bay-substituents containing methoxy groups. The difference in the total emission intensity is 22–34-fold and the difference in the quantum yield is 12–18-fold between dyes with bay-substituents containing methoxy groups and dyes with ethyl groups. Namely, introduction of methoxy groups in the *para*-position of the bay-substituents is a powerful method to quench dye fluorescence that would rarely affect molecular behavior and aggregation. To sum up, with just a simple modification, we successfully designed and synthesized fluorescence reduced dyes exhibiting sufficient solubilities in organic solvents. These novel perylene-based dyes



Fig. 2. Geometry-optimized structures of the synthesized dyes. (a) PI-4EP, (b) PI-4ME, (c) PM-4EP, and (d) PM-4ME.

Table 2

Dihedral angels of the perylene main body and calculated lengths of the substituents.^a

| Dye | | PI-4EP | PI-4ME | PM-4EP | PM-4ME |
|--|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Dihedral angle of the perylene main body (°) Calculated lengths of substituents (Å) | Bay-substituent Terminal-substituent | 13.13923 7.50721 8.91795 | 13.55246 7.39420 8.85661 | 13.18118 7.50609 7.76817 | 13.51070 7.39358 7.76834 |

^a Dihedral angle and calculated lengths are not symmetric, average values are listed.



Fig. 3. Absorption spectra of the synthesized dyes in chloroform (10^{-5} mol/L).

have more desirable properties than those previously used as colorants in LCD color filters.

Table 3

Spectral and fluorescence properties of the synthesized dyes.

| Dye | PI-4EP | PI-4ME | PM-4EP | PM-4ME |
|---|-----------|--------|-----------|----------|
| $\begin{array}{c} \lambda_{abs}^{a} \\ \epsilon_{abs}^{b} \\ \lambda_{em}^{c} \\ Max. \ Emission \ Intensity \\ \Sigma(emission)^{d} \end{array}$ | 546 | 550 | 548 | 552 |
| | 62,049 | 56,653 | 56,508 | 59,998 |
| | 581 | 586 | 580 | 582 |
| | 241.82 | 7.07 | 226.75 | 10.20 |
| | 29,305.99 | 856,53 | 27,623.99 | 1,257.39 |
| Δss^e | 35 | 36 | 32 | 30 |
| Q_y^f | 0.966 | 0.054 | 0.948 | 0.079 |

^a λ_{abs} : maximum absorption wavelength (nm).

 b ϵ_{abs} : molar extinction coefficient (L/mol cm).

 λ_{em} : maximum emission wavelength (nm).

 d $\Sigma(\text{emission}):$ integral of 'Fluorescence Intensity' in visible-ray region, total emission intensity.

^e Δ ss: stokes shift.

 $^{\rm f}$ Q_v: quantum yield (10⁻⁵ mol/L in chloroform, excited at 480 nm).

3.3. Time-resolved fluorescence properties of synthesized dyes

The results of the time-resolved fluorescence decay of the synthesized dyes measured by a time-correlated single photon



Fig. 4. Fluorescence of the synthesized dyes in chloroform (10^{-8} mol/L) .

counting (TCSPC) system are illustrated in Fig. 5 and Table 4 [56,57]. The represented fluorescence decay data were measured with an excitation wavelength of 520 nm and fitted using a bi-exponential function [58,59].

The dyes with methoxy groups in the bay-positions exhibited shorter fluorescence lifetimes than those with ethyl groups. In other words, the methoxy group in the bay-position affects both fluorescence intensity and lifetime. Therefore, the total emission quantity from the dyes with methoxy groups in the baysubstituents would be much smaller than that of the dyes with ethyl groups. This is the same result as the tendencies of the total emission intensity in the visible region and the quantum yield data that were presented ahead.

Energy injected from the excitation light is released in radiative or non-radiative form [60–62]. The radiative decay rate constant and the non-radiative decay rate constant can be simply calculated from the fitted lifetime (τ) and the quantum yield (Q_y) with the following equations [59,63–66]. The results are listed in Table 5.

$$K_r = \frac{1}{\tau_r} = \frac{Q_y}{\tau} \tag{1}$$

$$K_{nr} = \frac{1}{\tau_{nr}} = \frac{1}{\tau} - \frac{1}{\tau_r} = \frac{1}{\tau} \left(1 - Q_y \right) \tag{2}$$

All synthesized dyes show similar radiative decay constants (K_r),



Fig. 5. Time-correlated single-photon-counting (TCSPC) results of the synthesized dyes and instrumental response function of the TCSPC setup $(10^{-5} \text{ mol/L in chloroform})$.

Table 4

Fluorescence decay time (τ) of the synthesized dyes (ns).

| Dye | PI-4EP | PI-4ME | PM-4EP | PM-4ME |
|------------|--------|--------|--------|--------|
| Decay time | 3.95 | 0.23 | 4.25 | 0.35 |

Table 5

Calculated radiative decay rate constant (K_r) and non-radiative decay rate constant (K_{nr}) (ns^{-1}).

| Dye | PI-4EP | PI-4ME | PM-4EP | PM-4ME |
|-----------------|----------|----------|----------|----------|
| K _r | 0.244557 | 0.234783 | 0.223059 | 0.225714 |
| K _{nr} | 0.008608 | 4.113043 | 0.012235 | 2.631429 |

however, their non-radiative decay constant (K_{nr}) are tremendously different depending on the substituents at the bay-position. The dyes with methoxy groups in the bay-positions show extremely higher value of non-radiative decay constant than that of the dyes with ethyl groups. It could be regarded that the dyes with bay-substituents containing methoxy groups exhibit intensely stronger non-radiative energy release than the radiative form [60,61,67], contrary to the dyes containing ethyl groups in the baypositions. Due to this reason, dyes with methoxy groups in baypositions seem to exhibit quenched fluorescence. The trend is reversed in the case of the dyes with ethyl groups in bay-positions, although all of the synthesized dyes have similar geometrical molecular structures and conjugation systems.

3.4. Optical properties of fabricated dye-based color filters

Color filters are located between two polarizing films in the LCD devices. Light radiated from a back light unit is polarized by the first polarizer when entering into the color filters. Most light that passes through the color filters maintains its polarized state, however, non-polarized light can be generated by scattering or emission. This non-polarized light can passes through the second polarizer even in full-black state, and increases the minimum brightness. As scattering from the traditional pigment-based color filters gives rise to the unexpected increment of minimum brightness, fluorescence emitted from the dye-based color filters also causes the same effect in spite of the smaller particle size compared to pigment-based ones. We reported this phenomenon in our previous study through experimental investigations [9].

Dye-based color filters were fabricated using the synthesized dyes that were added in the proportion of 1, 2 or 3 wt% to the acrylate binder. The measured fluorescence spectrometer results are shown in Fig. 6a. The measurements were obtained with an excitation wavelength corresponding to the wavelength of maximum absorption. Both the incident light that passed through the color filters and the emission from the color filters can be observed in all of the fluorescence spectra. The fluorescence spectrum of the color filter fabricated with PI-4EP with 3 wt% dye content is separately illustrated in Fig. 6b. In the results of the color filters fabricated with PM-4EP, the intensity of the incident light exceeded the detectable range of our instrument. Therefore, the intensity of the incident light is saturated in the maximum detectable value of the instrument in every dye content concentration. The absolute values of the spectra are not precise because the measurements of the fluorescence spectrometer of the fabricated dye-based color filters were operated without consideration of the emission toward every spherical direction. However, it can be argued that the observed trend of incident light and emission varying according to dye content concentration is definitely a meaningful result.



Fig. 6. (a) Fluorescence spectrometer results of the fabricated dye-based color filters (each dye contents were 1, 2 and 3 wt% increasing toward right-side). (b) Detailed fluorescence spectrometer results of the color filter fabricated with **PI-4EP** in 3 wt% dye content. (c) Plot of maximum emission intensity of the fabricated color filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As shown in the spectra, the intensity of the incident light is decreasing with increasing dye concentration. Contrastively, the intensity of the emission from the color filters is increasing according to the dye concentration. The maximum emission intensities from the prepared color filters are plotted in Fig. 6c. As shown in the figures, the emission intensity increase of the color filters depends on the added dye concentration with a certain linear trend. These phenomena result from the fact that the color filters were fabricated with a low color content concentration [9]. In accordance with the dye concentration increase, the increase of the aggregation fluorescence quenching would be smaller than the increase of the emission from the added dyes in the concentration range of our investigation [68,69].

The color filters fabricated with dyes containing ethyl groups in

bay-positions exhibited strong fluorescence within the visible region in the film state. As mentioned in our previous study [9], the fluorescence properties of the prepared color filters show a similar tendency to the properties of the dyes in the solution state. Therefore, the fluorescence of the added dyes would significantly affect the optical properties of the color filters.

The optical properties of the fabricated color filters are listed in Table 6. All represented data were measured 3 times and the average value is provided. The brightness of the color filters decreased with the increase in dye content concentration. This results from the fact that the transmittance of the color filters would decrease with the amount of additionally added dyes. Namely, the effect of the fluorescence from the added dyes on the brightness increase is much weaker than the effect of the

| Table 6 |
|--|
| Optical properties of the fabricated dye-based color filters |

| Dye Dye content | | Brightness | ss | | Contrast ratio - blank 30,000 | | |
|-----------------|---|------------|--------|---------|-------------------------------|-----------------|--------|
| | | Rx | Ry | Value | Max. brightness | Min. brightness | Value |
| PI-4EP | 1 | 0.3237 | 0.2977 | 62.1513 | 1765.1667 | 20.8607 | 84.62 |
| | 2 | 0.3244 | 0.2953 | 59.9033 | 1729.9333 | 22.2023 | 77.92 |
| | 3 | 0.3251 | 0.2886 | 52.3643 | 1617.0000 | 27.6647 | 58.45 |
| PI-4ME | 1 | 0.3228 | 0.3023 | 70.8803 | 1839.9000 | 3.5033 | 525.19 |
| | 2 | 0.3334 | 0.2804 | 56.4173 | 1509.5667 | 4.2287 | 356.98 |
| | 3 | 0.3310 | 0.2765 | 51.4653 | 1428.0000 | 6.6037 | 216.24 |
| PM-4EP | 1 | 0.3157 | 0.3213 | 82.4580 | 2184.0667 | 7.3437 | 297.41 |
| | 2 | 0.3168 | 0.3187 | 80.0553 | 2136.9667 | 10.1030 | 211.52 |
| | 3 | 0.3185 | 0.3157 | 73.0377 | 2032.0000 | 17.5680 | 115.66 |
| PM-4ME | 1 | 0.3310 | 0.2918 | 63.1287 | 1642.8000 | 3.5767 | 459.31 |
| | 2 | 0.3382 | 0.2805 | 55.9787 | 1456.0000 | 3.3073 | 440.23 |
| | 3 | 0.3483 | 0.2674 | 46.2667 | 1228.4333 | 6.4457 | 190.58 |

transmittance reducing that derives the brightness decrease. Therefore, it would be hard to expect a remarkable brightness increase from the fluorescence of the dyes added in dye-based color filters.

Contrast ratio is the proportion of maximum brightness to minimum brightness [5,8,70–72]. The maximum and minimum brightness values are represented after normalization to a blank brightness of 30,000. The minimum brightness of the color filters was increased according to the fluorescence of the added dyes. Both the maximum and minimum brightness of the color filters with highly fluorescent dyes generally show higher values than those with less fluorescent dyes. However, the influence of the fluorescence seems more effective on the minimum brightness. Therefore, the color filters with highly fluorescent dyes exhibited a lower contrast ratio than those with fluorescence quenched dyes.

It can be concluded that the fluorescence properties of the fabricated color filters show the same tendency to those of the dyes in the solution state. Additionally, the fluorescence of the added dyes has a limitative effect on the maximum brightness increase of the fabricated color filters. However, the fluorescence mainly influences the minimum brightness increase and causes the contrast ratio decrease. In conclusion, color filters prepared with synthesized dyes containing methoxy groups in the bay-substituents have remarkable effects in minimizing the increment of minimum brightness and prohibiting the contrast ratio decrease.

4. Conclusions

The most popular method to enhance the solubilities of dyes is the introduction of bulky substituents. However, bulky substituents usually enhance the fluorescence of dyes by preventing both static fluorescence quenching with H-aggregation and energy transfer via intermolecular interaction. Therefore, it is difficult to devise dyes exhibiting both sufficient solubilities in organic industrial solvents and significantly quenched fluorescence.

Dyes have to be sufficiently soluble in organic solvents and show minimized fluorescence to be used as a colorant in LCD color filters. In this study, we successfully designed and synthesized dyes meeting this purpose by introducing substituents containing methoxy groups. Moreover, we also synthesized highly fluorescent dyes which have similar molecular structures to the fluorescence quenched dyes. Finally, we fabricated dye-based color filters using the synthesized dyes and analyzed the optical performances of the color filters.

In conclusion, the methoxy group in the *para*-position of the bay-substituents has an enormous effect on the fluorescence quenching without the conspicuous influences on molecular behavior or dye aggregation. On the contrary, there is no

fluorescence quenching effect by the methoxy group in the terminal-substituents. This difference seems to be caused by the π -conjugation system of the substituents. The color filters fabricated with the synthesized dyes containing methoxy groups in the baypositions exhibited lower minimum brightness than those with ethyl groups. Therefore, they show superior performance in preventing contrast ratio decrease caused by fluorescence of added dyes.

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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.2016.08.061.

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