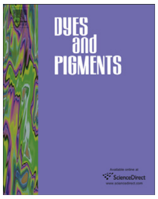
Dyes and Pigments 131 (2016) 293–300

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



The effect of fluorescence of perylene red dyes on the contrast ratio of LCD color filters

Jeong Yun Kim [a], Chun Sakong [a], Sang-a Choi [a], Hyeyoun Jang [a], Se Hun Kim [a], Kil Seong Chang [b], Myoung Sic Han [b], Jeong Su Lee [b], Jae Pil Kim [a, *]

[a] *Lab. of Organic Photo-functional Materials, Department of Materials Science and Engineering, Seoul National University, Seoul, 151-744, Republic of Korea*
[b] *Department of Electronic Material, Alphachem Corporation, 280-3, Donghwa-ri, Bongdam-eup, Hwaseong-si, Gyeonggi-do, Republic of Korea*

ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form
18 March 2016
Accepted 22 March 2016
Available online 23 March 2016

Keywords:
Color filter
Dye-based color filter
Pigment-dye hybrid color filter
Perylene
Fluorescence

ABSTRACT

Dye-based and pigment-dye hybrid color filters are recommended to overcome the drawbacks such as light scattering of traditional pigment-based color filters. However, dyes used as colorants for LCD color filters may exhibit strong fluorescence. Fluorescence lowers the contrast ratio of color filters by increasing brightness in the full-black state and affects optical performance of displays. In this study, the correlation between dye fluorescence and the optical properties of color filters was investigated. Six perylene-based dyes were synthesized, and dye-based and pigment-dye hybrid color filters were prepared with each dye. The fluorescence properties of the synthesized dyes in solution and the prepared color filters were evaluated. The maximum brightness and the contrast ratio of the color filters were measured, from which the minimum brightness of the color filters was calculated. All dye-based and pigment-dye hybrid color filters showed greater minimum brightness than pigment-based one due to emission in the visible region.

1. Introduction

Color filters are essential components of liquid crystal displays (LCDs) [1–8]. The desirable properties of color filters are color purity, contrast ratio, and brightness [9–12]. High-contrast color filters are the most important components in the manufacture of displays with superior optical properties [9,10].

Contrast ratio is the proportion of maximum brightness to minimum brightness [6,9,10]. To obtain a high contrast ratio, light should not be transmitted when the polarizers are closed to produce a dark image (full-black state) [9]. In traditional pigment-based color filters, a small amount of light is transmitted in the full-black state due to light scattering [5,6,10]. The problem, which is caused by the large size of the pigments, can be resolved by replacing pigments with dyes of smaller particle size [2,4,10]. However, many dyes that are used as colorants in LCD color filters exhibit fluorescence, which significantly brightens the full-black state of the device due to their emission. Consequently, dye-based color filters may exhibit a lower contrast ratio than expected.

Perylene-based dyes are suitable colorants for LCD color filters due to their strong color strengths and high thermal stabilities [2–4,10,12]. However, perylene derivatives with bulky substituents commonly exhibit strong fluorescence, because these groups can prevent intermolecular interactions and irradiative energy transfers that are the most important mechanisms of fluorescence quenching [13–15].

This paper will discuss the effect of fluorescence on the contrast ratio of dye-based and pigment-dye hybrid color filters. Perylene-based red dyes were synthesized with bulky substituents at terminal- and bay-positions to improve their solubilities in industrial solvents [2,10]. Color filters were prepared with low color content to minimize the effect of aggregation on optical properties for the obvious investigation about the influence of the fluorescence on the contrast ratio. The fluorescence of the synthesized dyes in solution and the fabricated dye-based and pigment-dye hybrid color filters were measured and compared. The maximum brightness and the contrast ratio of the color filters were measured, and the minimum brightness was calculated from the results. Finally, the correlation between fluorescence and optical properties of the color filters was analyzed.

---

* Corresponding author. Tel.: +82 2 880 7187.
E-mail address: jaepil@snu.ac.kr (J.P. Kim).

http://dx.doi.org/10.1016/j.dyepig.2016.03.041
0143-7208/© 2016 Elsevier Ltd. All rights reserved.

2. Experimental

2.1. Materials and instrumentations

Perylene-3,4,9,10-tetracarboxylic dianhydride, 4-*tert*-octylphenol, iodine, sulfuric acid, bromine and acetic acid purchased from Sigma–Aldrich, 2,6-diisopropylaniline, 2,4,6-trimethylphenol and 2-allylphenol purchased from TCI, K_2CO_3 anhydrous, methylene chloride and other chemical solvents purchased from SAMCHUN pure chemical were used without any additional purification. Transparent glass substrates were purchased from Paul Marienfeld GmbH & CO. KG.

^{1}H NMR and ^{13}C NMR spectra were recorded by a Bruker Avance 500 spectrometer at 500 MHz using chloroform-d and TMS as the solvent and internal standard. Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI-TOF) mass spectra were recorded by a Voyager-DE STR Biospectrometry Workstation with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix. Elemental analysis (EA) was completed on a CE Instrument EA1112. Absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. Fluorescence spectra were measured using a Perkin Elmer LS 55 Fluorescence spectrometer. Contrast ratio and brightness of color filters were measured using a CT-1 of TSUBOSAKA and MC-3700:28C of OTSUKA ELECTRONICS. The thickness of the spin-coated film was measured using a Nano System Nanoview E-1000.

2.2. Synthesis

The dyes **PI2-AP**, **PI2-TMP**, **PI2-S2**, and **PI1-S2** were already reported in our previous study [2,10]. The syntheses of these dyes are detailed in this paper.

2.2.1. 1,(7)-(di)bromoperylene-3,4,9,10-tetracarboxydiimide (1,2); bromination

Perylene-3,4,9,10-tetracarboxylic dianhydride (32.0 g, 81.4 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, bromine (7.5 ml, 146.65 mmol) was added dropwisely for 1 h. The mixture was reacted for 16 h. Then, it was cooled to room temperature and bromine gas was displaced by nitrogen gas. The mixture was slowly poured into 3L of ice-water, producing precipitate collected by suction filtration in crude product form. The crude product was washed with distilled water several times. Then, the crude product was dried at 100 °C under reduced pressure and used in the next step without further purification. The crude containing both **1** and **2** was separated by column chromatography in next step, after importing derivatives in terminal-position to increase solubility.

2.2.2. N,N′-Bis(2,6-diisopropylphenyl)-1,(7)-(di)bromoperylene-3,4,9,10-tetracarboxydiimide (3,4); terminal-position substitution

The crude 1,(7)-(di)bromoperylene-3,4,9,10-tetracarboxydiimide (8.0 g, 14.5 mmol), 2,6-diisopropylaniline (8.28 g, 46.7 mmol), acetic acid (4.6 ml), and N-Methyl-2-pyrrolidone(NMP) (100 ml) were mixed and heated at 120 °C under the nitrogen atmosphere for 96 h. The precipitate was obtained by adding water to the mixture and be collected by suction filtration. The crude product was washed with water and dried. The crude product was purified by column chromatography in silica gel using CH_2Cl_2 as the eluent. The first reddish band containing tribrominated diimide could be separated. Second reddish band containing dibrominated diimide and third one containing monobrominated diimide could be collected. Detailed structure analysis was done after next step.

2.2.3. N,N′-Bis(2,6-diisopropylphenyl)-1,7-bis(o-allylphenoxy)-perylene-3,4,9,10-tetracarboxydiimide (PI2-AP); bay-position substitution

N,N′-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (0.50 g, 0.575 mmol) was mixed with potassium carbonate anhydrous (0.35 g), 2-allylphenol (0.20 g, 1.50 mmol) and NMP (50 ml). The mixture was heated at 40 °C under nitrogen atmosphere and was stirred at for 1.5 h. The mixture was cooled to room temperature, and then poured into 400 ml of 5% HCl aqueous solution. The precipitate was filtered, washed with water, and dried in vacuum at 80 °C. The crude product was purified by column chromatography in silica gel using CH_2Cl_2 as the eluent to obtain **PI2-AP** as red solid.

Yield 71.5%; ^{1}H NMR ($CDCl_3$, ppm): 9.72 (d, 2H), 8.67 (d, 2H), 7.46 (t, 2H), 7.35 (d, 2H), 7.30 (m, 10H), 6.97 (t, 2H), 6.06 (septet, 2H), 5.14 (d, 2H), 5.07 (d, 2H), 3.59 (d, 4H), 2.71 (septet, 4H), 1.14 (d, 24H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.18, 24.22, 29.40, 34.61, 116.82, 119.54, 122.53, 123.94, 124.24, 125.80, 125.96, 128.70, 129.33, 129.83, 129.93, 130.68, 130.86, 131.75, 131.98, 133.98, 136.42, 145.83, 152.98, 155.74, 163.12, 163.69; MALDI-TOF MS: *m*/*z* 976.3 (100%, $[M+2K]^+$); EA Found(%): C, 81.51; H, 6.14; N, 2.80; O, 9.56. Calc.(%) for $C_{66}H_{58}N_2O_6$: C, 81.29; H, 5.99; N, 2.87; O, 9.84.

2.2.4. N,N′-Bis(2,6-diisopropylphenyl)-1,7-bis(2,4,6-trimethylphenoxy)-perylene-3,4,9,10-tetracarboxydiimide (PI2-TMP)

PI2-TMP was synthesized in the same manner with **PI2-AP** using N,N′-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (0.50 g, 0.575 mmol), potassium carbonate anhydrous (0.35 g) and 2,4,6-trimethylphenol (0.21 g, 1.50 mmol). The reaction temperature was set at 60 °C for 2 h.

Yield 78.0%; ^{1}H NMR ($CDCl_3$, ppm): 9.69 (m, 2H), 8.72 (d, 2H), 7.48 (t, 2H), 7.32 (m, 6H), 7.03 (s, 4H), 2.74 (septet, 4H), 2.34 (s, 6H), 2.18 (m, 12H), 1.19 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.62, 24.15, 24.21, 24.26, 29.38, 29.48, 120.17, 122.13, 122.76, 124.16, 124.21, 124.92, 125.27, 128.17, 129.17, 129.30, 129.50, 129.98, 130.15, 130.24, 130.41, 130.50, 130.54, 130.72, 130.77, 133.62, 133.93, 136.46, 138.65, 145.83, 147.79, 162.97, 163.12; MALDI-TOF MS: *m*/*z* 980.3 (100%, $[M+2K]^+$); EA Found(%): C, 80.96; H, 6.14; N, 2.98; O, 9.91. Calc.(%) for $C_{66}H_{62}N_2O_6$: C, 80.95; H, 6.38; N, 2.86; O, 9.80.

2.2.5. N,N′-Bis(2,6-diisopropylphenyl)-1,7-bis(p-tert-octylphenoxy)-perylene-3,4,9,10-tetracarboxydiimide (PI2-S2)

PI2-S2 was synthesized in the same manner with **PI2-AP** using N,N′-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (0.50 g, 0.575 mmol), potassium carbonate anhydrous (0.35 g) and 4-tert-octylphenol (0.31 g, 1.50 mmol).

Yield 76.9%; ^{1}H NMR ($CDCl_3$, ppm): 9.66 (d, 2H), 8.69 (d, 2H), 8.38 (d, 4H), 7.45 (m, 2H), 7.32 (m, 4H), 7.25 (s, 2H), 7.10 (d, 4H), 2.72 (septet, 4H), 1.39 (s, 4H), 1.16 (d, 24H), 0.75 (s, 18H), 0.73 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.18, 24.22, 29.39, 31.72, 32.00, 32.63, 38.66, 57.38, 118.89, 119.02, 122.49, 123.34, 124.12, 124.20, 124.26, 124.58, 124.75, 126.00, 128.18, 128.45, 129.25, 129.83, 129.92, 130.73, 130.90, 131.98, 133.97, 145.88, 147.47, 147.59, 152.78, 155.71, 162.94, 163.10, 163.71; MALDI-TOF MS: *m*/*z* 1120.5 (100%, $[M+2K]^+$); EA Found(%): C, 81.76; H, 7.41; N, 2.47; O, 8.35. Calc.(%) for $C_{76}H_{82}N_2O_6$: C, 81.54; H, 7.38; N, 2.50; O, 8.58.

2.2.6. N,N′-Bis(2,6-diisopropylphenyl)-1-o-allylphenoxy-perylene-3,4,9,10-tetracarboxydiimide (PI1-AP)

PI1-AP was synthesized in the same manner with **PI2-AP** using N,N′-Bis(2,6-diisopropylphenyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (0.50 g, 0.575 mmol), potassium carbonate anhydrous (0.21 g) and 2-allylphenol (0.15 g, 1.13 mmol).

Yield 73.4%; ^{1}H NMR ($CDCl_3$, ppm): 9.71 (d, 2H), 8.83 (d, 2H), 8.75 (t, 2H), 8.26 (s, 1H), 7.48 (t, 2H), 7.34 (m, 8H), 6.06 (septet, 2H), 5.12 (d, 1H), 3.56 (d, 2H), 2.77 (septet, 4H), 1.19 (d, 24H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.18, 24.22, 28.71, 29.44, 34.55, 116.87, 119.84, 122.79, 122.85, 123.19, 123.40, 124.15, 124.27, 124.30, 124.38, 124.62, 124.75, 126.08, 126.46, 127.65, 128.77, 129.06, 129.26, 129.38, 129.87, 130.09, 130.51, 130.84, 131.73, 131.86, 132.06, 132.85, 134.50, 135.06, 135.27, 136.34, 145.81, 145.89, 146.41, 152.60, 156.72, 162.90, 163.70, 163.94; MALDI-TOF MS: *m*/*z* 844.2 (100%, $[M+2K]^+$); EA Found(%): C, 81.21; H, 5.95; N, 3.57; O, 9.27. Calc.(%) for $C_{57}H_{50}N_2O_5$: C, 81.21; H, 5.98; N, 3.32; O, 9.49.

2.2.7. N,N′-Bis(2,6-diisopropylphenyl)-1-2,4,6-trimethylphenoxy-perylene-3,4,9,10-tetracarboxydiimide (PI1-TMP)

PI1-TMP was synthesized in the same manner with **PI2-AP** using N,N′-Bis(2,6-diisopropylphenyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (0.50 g, 0.575 mmol), potassium carbonate anhydrous (0.21 g) and 2,4,6-trimethylphenol (0.16 g, 1.13 mmol). The reaction temperature was set at 60 °C for 2 h.

Yield 77.3%; ^{1}H NMR ($CDCl_3$, ppm): 9.89 (d, 2H), 8.83 (t, 2H), 8.05 (s, 1H), 7.50 (m, 2H), 7.34 (d, 4H), 7.04 (s, 4H), 3.03 (s, 1H), 2.78 (septet, 4H), 2.35 (s, 2H), 2.18 (s, 6H), 1.19 (m, 24H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.49, 21.05, 23.09, 23.46, 24.13, 28.38, 28.71, 29.36, 29.44, 120.02, 121.01, 122.40, 122.63, 123.18, 123.25, 123.37, 124.29, 124.39, 124.73, 125.81, 127.66, 127.77, 129.49, 129.95, 130.16, 130.66, 130.75, 130.90, 131.66, 131.86, 132.93, 134.91, 135.07, 135.45, 145.81, 147.81, 157.28, 163.03, 163.76, 164.01; MALDI-TOF MS: *m*/*z* 846.3 (100%, $[M+2K]^+$); EA Found(%): C, 81.22; H, 6.07; N, 3.42; O, 9.29. Calc.(%) for $C_{57}H_{52}N_2O_5$: C, 81.02; H, 6.20; N, 3.32; O, 9.47.

2.2.8. N,N′-Bis(2,6-diisopropylphenyl)-1-p-tert-octylphenoxy-perylene-3,4,9,10-tetracarboxydiimide (PI1-S2)

PI1-S2 was synthesized in the same manner with **PI2-AP** using N,N′-Bis(2,6-diisopropylphenyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (0.50 g, 0.575 mmol), potassium carbonate anhydrous (0.21 g) and 4-tert-octylphenol (0.23 g, 1.12 mmol).

Yield 79.2%; ^{1}H NMR ($CDCl_3$, ppm): 9.68 (d, 2H), 8.82 (d, 2H), 8.76 (d, 4H), 8.39 (s, 1H), 7.49 (m, 4H), 7.34 (m, 4H), 2.78 (septet, 4H), 1.40 (s, 2H), 1.18 (d, 24H), 0.74 (s, 15H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.22, 29.42, 29.45, 31.72, 32.00, 32.64, 57.40, 119.12, 122.75, 122.81, 123.38, 124.08, 124.31, 124.61, 125.37, 126.56, 127.66, 128.54, 129.08, 129.24, 129.85, 130.06, 130.51, 130.86, 131.70, 132.91, 134.51, 135.07, 135.28, 147.82, 152.43, 156.80, 162.89, 163.70, 163.95; MALDI-TOF MS: *m*/*z* 916.3 (100%, $[M+2K]^+$); EA Found(%): C, 81.40; H, 6.85; N, 3.00; O, 8.74. Calc.(%) for $C_{62}H_{62}N_2O_5$: C, 81.37; H, 6.83; N, 3.06; O, 8.74.

2.3. Fabrication of dye-based color filters

The red inks for dye-based color filters composed of the synthesized dye (0.01 g), propylene glycol methyl ether acetate (PGMEA) (0.1 g), and acrylic binder (0.8 g). The prepared dye-based inks were coated on a transparent glass substrate using a MIDAS System SPIN-1200D spin coater. The rotating speed was initially set at 100 rpm for 10s, and then increased to 500 rpm for 20s. The dye-coated color filters were dried at 80 °C for 20min, pre-baked at 150 °C for 10min and post-baked at 200 °C for 1 h. All spin-coated dye-based color filters were 1.6 μm thick.

2.4. Fabrication of pigment-dye hybrid color filters

The red inks for pigment-dye hybrid color filters were composed of the pigment red 177 (13–15%), acrylic polymer dispersant (3–5%), acrylic polymer (3–5%), propylene glycol methyl ether acetate (PGMEA) (75–80%), and synthesized dyes (0.5wt% or 1.0wt % compared with pigment red 177). The concentrations of color content were adjusted to show appropriate color coordination as red color filters. The prepared inks were coated on a transparent glass substrate using a spin coater. The spin-coated color filters were pre-baked at 80 °C for 10min and post-baked at 230 °C for 30min. The contrast ratio of the color filters were measured by CT-1 instrument of TSUBOSAKA and the brightness of them were measured by MC-3700: 28C of OTSUKA ELECTRONICS.

3. Results and discussion

3.1. Design concept and synthesis of the dyes

Perylene-based dyes have many advantages as colorants in optical devices including high color strength and thermal stability [2,4,10,12]. However, their applications are limited by low solubility in industrial solvents due to their planar molecular structures [10,12].

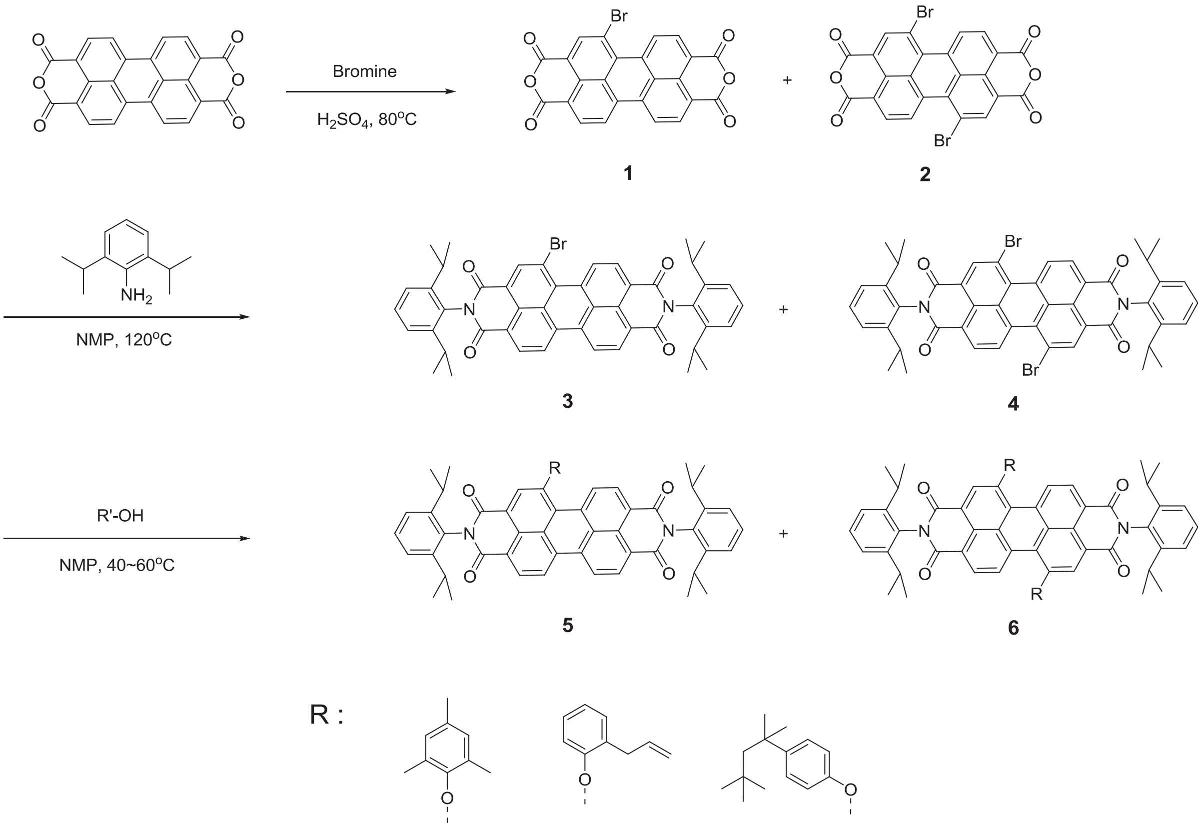
The synthetic routes and molecular structures of the synthesized dyes are shown in Scheme 1 and Fig. 1. All dyes are designed to have increased solubility in organic solvents. Un-substituted perylene dyes are not soluble in industrial solvents such as PGMEA and cyclohexanone [2,10,12]. Introduction of substituents at their terminal- and bay-positions increases the solubility of the dyes in organic solvents. The substituents introduced on perylene-based dyes effectively decrease the intermolecular interactions and planarities of the dyes [2,10]. Solubilities of the synthesized dyes are listed in Table 1. Dyes should have solubilities greater than 5 wt % in industrial solvents to be used as colorants in color filters [2,10,12]. As indicated in Table 1, most of the synthesized dyes showed suitable solubility in industrial organic solvents.

Bromination and substitution reactions at terminal-positions were carried out by well-known procedures [1,2,4,16–18]. Bay-position substitution reactions were performed at a lower temperature and for a shorter time than the standard method by the procedure reported in our previous study [10]. The reaction yields of all bay-position substitution reactions exceeded 70%.

3.2. Spectral properties of the synthesized dyes

All dyes were designed to have a similar length of conjugation. Therefore, they exhibited similar absorption spectra as shown in Fig. 2 [19,20]. Consequently, the spectral properties of the synthesized dyes rarely affected the optical properties of the color filters. However, the varied size and shape of the substituents affected the planarity and crystal packing structure of the dyes. Therefore, the synthesized dyes exhibited different fluorescence properties depending on their molecular structures [21].

As shown in Fig. 3, the synthesized perylene dyes exhibited strong fluorescence over 500–700 nm [16,22–24]. Fluorescence was measured at an excitation wavelength corresponding to the wavelength of maximum absorption, respectively. The emission spectra of synthesized dyes exhibited different maximum wavelengths and intensities depending on their molecular structures. The bay-substituted dyes with three methyl groups at *ortho*- and *para*-positions exhibited the highest fluorescence intensity than other dyes. Furthermore, di-bay-substituted dyes showed stronger fluorescence than mono-bay-substituted dyes. This behavior evidently results from the difference in conjugation length and crystal packing of the dyes [13,15,25,26]. All emission maxima are shifted bathochromically from the wavelength of maximum absorption by 18–30 nm. The intensity at the wavelength of maximum emission and the total emission intensity within the visible region (400–700 nm) are listed in Table 2. The total emission intensity of the most strongly fluorescent dye (**PI2-TMP**) was about twice as large as that of the most weakly



Scheme 1. Synthetic routes of the designed dyes.

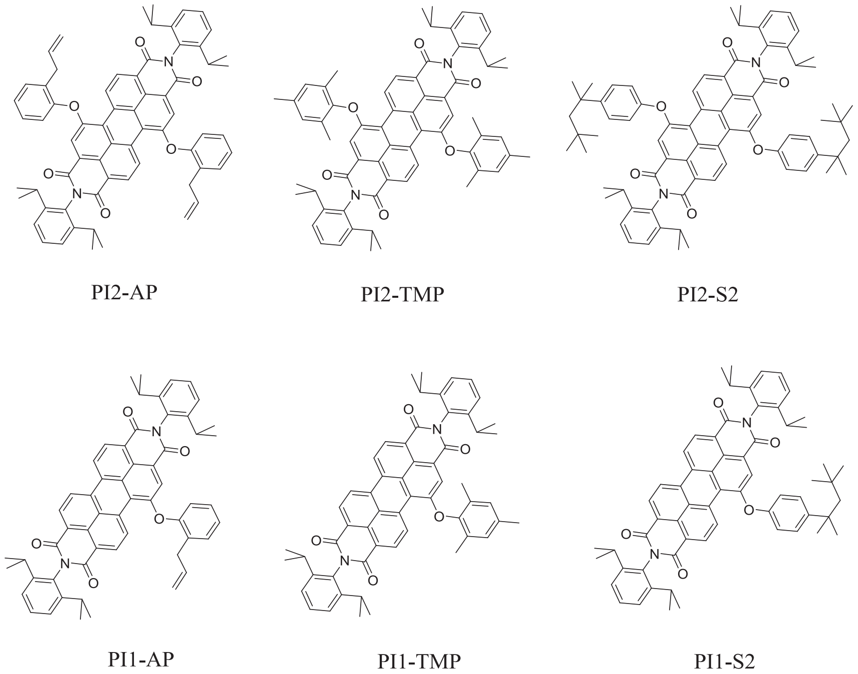


Fig. 1. Structure of the synthesized dyes.

fluorescent dye (**PI1-S2**).

3.3. Optical properties of the fabricated dye-based color filters

Dye-based color filters were prepared with low color content concentrations to minimize the effect of dye aggregation on optical properties of the color filters. As shown in Fig. 4, the fabricated color filters exhibited strong fluorescence in the visible region despite their low color content. The total emission of the color filters in the visible region correlates with the emission of the dyes in

Table 1
Solubility of the synthesized dyes at 20 °C in CH_2Cl_2 and PGMEA (wt%).

Dye	PI2-AP	PI2-TMP	PI2-S2	PI1-AP	PI1-TMP	PI1-S2
CH_2Cl_2	5.1	8.5	6.2	6.0	8.9	6.7
PGMEA	4.4	7.8	5.7	5.0	7.9	6.1

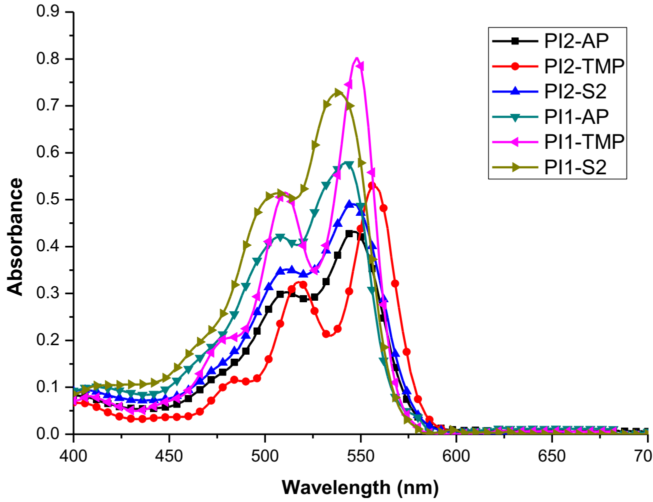


Fig. 2. Absorption spectra of synthesized dyes in chloroform (10^{-5} mol/L).

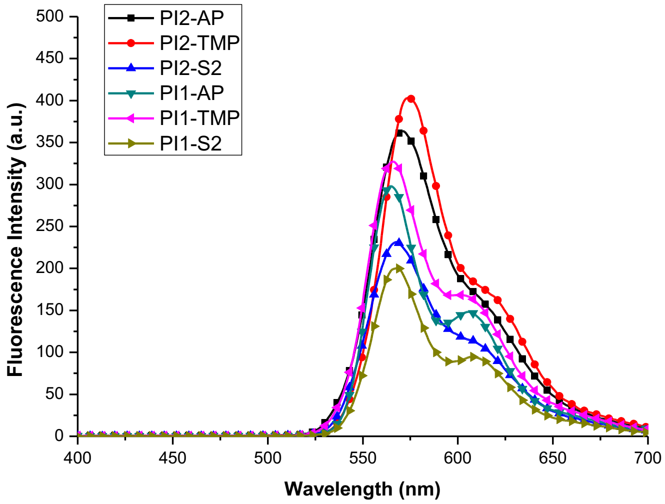


Fig. 3. Fluorescence of synthesized dyes in chloroform (10^{-8} mol/L).

Table 2
Spectral and fluorescence properties of the synthesized dyes.

Dye	PI2-AP	PI2-TMP	PI2-S2	PI1-AP	PI1-TMP	PI1-S2
λ_{em}[a]	571	574.5	567.5	565	566	568
Max. Emission Intensity	363.74	403.16	231.50	298.16	327.48	200.29
Σ(emission)[b]	**45751.41**	**47443.33**	**29065.89**	**32892.27**	**39489.99**	**22455.93**
λ_{abs}[c]	546	556	546	542	548	538
Δss[d]	25	18.5	21.5	23	18	30

[a] λ_{em}: maximum emission wavelength (nm).
[b] Σ(emission): integral of fluorescence intensity in visible-ray region, total emission intensity.
[c] λ_{abs}: maximum absorption wavelength (nm).
[d] Δss: stokes shift.

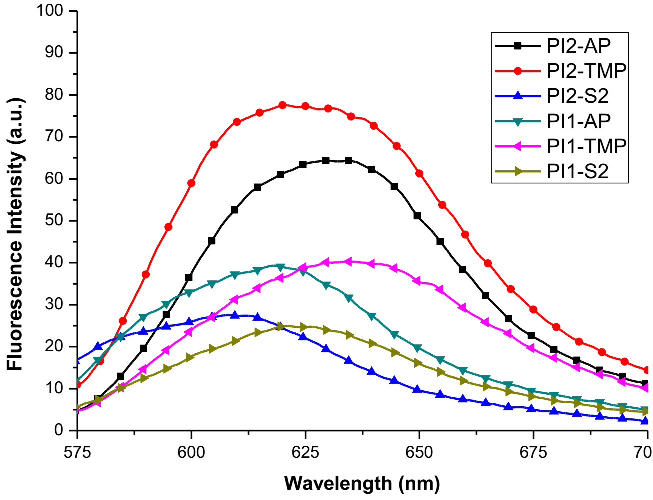


Fig. 4. Fluorescence of fabricated dye-based color filters.

solution as listed in Table 2. Thus, the fluorescence properties of the dyes in solution would be maintained in the film state with similar tendency.

The optical properties of the fabricated dye-based color filters are shown in Table 3. The contrast ratios are very small, because the inks for the color filters have low color content concentrations. The value of RY (Max. Y) is the maximum brightness of the color filter with the polarizer entirely open. Min. Y is the brightness in the full-black state, which is calculated from the maximum brightness and contrast ratio. The minimum brightness shows the same behavior in pre- and post-baked color filters. This phenomenon suggests that the influence of heat treatment on optical properties was minimized by the low color contents [6,10]. Moreover, the sequence of increasing minimum brightness of the fabricated color filters is identical to that of the total emission intensity of the dyes within the visible region. Therefore, it could be argued that the total emission intensity within visible region of the dyes significantly influences the minimum brightness of the fabricated color filters.

3.4. Optical properties of the fabricated pigment-dye hybrid color filters

Pigment-dye hybrid color filters were prepared by adding 0.5 or 1.0 wt% of the synthesized dyes in proportion to Pigment Red 177. The perylene-based dyes are well-known that they would easily exhibit H-aggregation and quench the fluorescence. Therefore, dye concentrations were carefully restricted lower than what is used in industry. FE-SEM images and average particle size were shown in Fig. 5 and Table 4. The fabricated pigment-based and pigment-dye

Table 3
Optical properties of the fabricated dye-based color filter.[a]

Dye		PI2-AP	PI2-TMP	PI2-S2	PI1-AP	PI1-TMP	PI1-S2
Pre-baked	Rx	0.37828	0.35346	0.40584	0.39646	0.39021	0.36881
	Ry	0.23125	0.21607	0.25125	0.26480	0.23116	0.23712
	RY (Max. Y)[b]	37.294	37.022	38.776	40.451	37.263	38.776
	C/R[c]	38	33	57	54.5	47.5	87.5
	Min. Y[d]	**0.9814**	**1.1219**	**0.6803**	**0.7422**	**0.7845**	**0.4432**
Post-baked	Rx	0.37487	0.35348	0.40381	0.39449	0.39130	0.37452
	Ry	0.23423	0.21973	0.25306	0.24776	0.23216	0.23564
	RY (Max. Y)	39.093	36.704	39.606	40.480	37.427	39.151
	C/R	45	35	58	57.5	47	85.5
	Min. Y	**0.8687**	**1.0487**	**0.6829**	**0.7040**	**0.7963**	**0.4579**

[a] The inks for dye-based color filters composed of the synthesized dye (0.01 g), propylene glycol methyl ether acetate (PGMEA) (0.1 g), and acrylic binder (0.8 g).
[b] RY (Max. Y): measured maximum brightness.
[c] C/R: contrast ratio.
[d] Min. Y: calculated brightness of full-black state.

hybrid color filters have similar particle size within the difference of 6–7 nm. Transmittance spectra of the prepared color filters were illustrated in Fig. 6 and Table 5. The transmittance spectra of the hybrid color filters were match up with the spectra of the pigment-based color filter within the whole visible region. By these results, it could be regarded that the added dyes would have very limited effect on the aggregation behavior or optical performance of the color filters.

The fluorescence spectra of the fabricated pigment-dye hybrid color filters are illustrated in Fig. 7. The fluorescence of all hybrid color filters was measured with an excitation wavelength of 530 nm [27]. Therefore, the fabricated hybrid color filters have similar maximum emission peaks. All fabricated pigment-dye hybrid color filters exhibited an absorption maximum at 530 nm, because they consisted primarily of Pigment Red 177. However, the fluorescence properties of the color filters differed as shown in Fig. 7. These properties exhibited tendencies similar to those of dyes in solution and dye-based color filters. Color filters with 1.0 wt% dye showed stronger fluorescence than those with 0.5 wt%. These observations demonstrate that the fluorescence features of the dyes are retained in dye-based color filters and pigment-dye hybrid color filters.

The optical properties of the fabricated pigment-dye hybrid color filters are listed in Table 6. All hybrid color filters showed greater Min. Y values than pigment-based color filter (STD; Pigment Red 177, 100%). This result indicates that the minimum brightness of pigment-dye hybrid color filters was increased by the emission of the added dyes. In addition, the sequence of minimum brightness of the hybrid color filters was the same as that of dye-based ones. As mentioned before, added dyes have limited effect on the aggregation and optical properties of the fabricated color filters. Therefore, the minimum brightness and contrast ratio of pigment-dye hybrid color filters also were affected by the total emission within the visible region. Thus, color filters with strongly emitting dyes would exhibit a high minimum brightness and low contrast ratio.

Table 4
Average particle size in FE-SEM images.

Color filter	Pigment-based	0.5 wt% dye added	1.0 wt% dye added
Average size (nm)	39.667	33.522	34.524

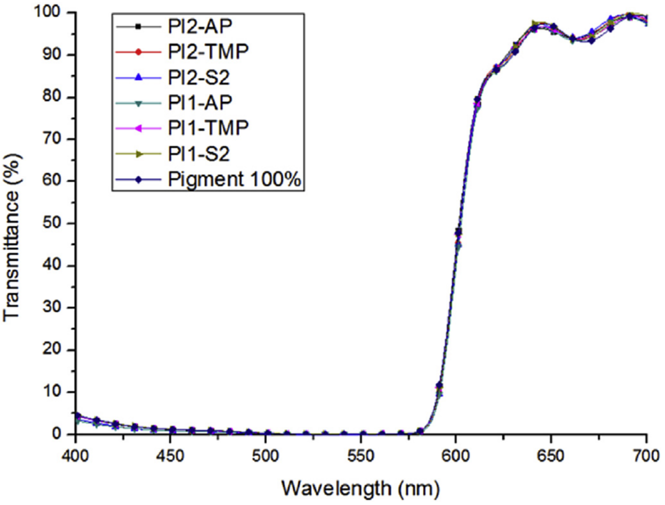


Fig. 6. Transmittance spectra of pigment-based and pigment-dye hybrid color filters.

The fluorescence of a dye could increase maximum brightness.

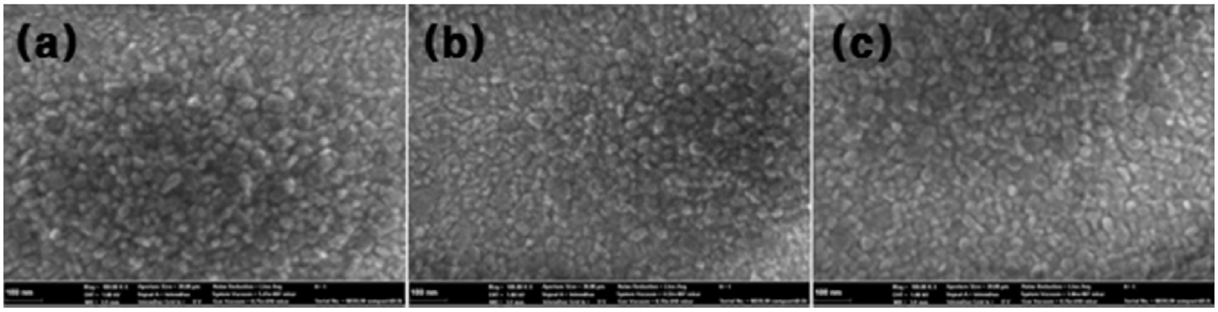


Fig. 5. FE-SEM images of pigment-based and pigment-dye hybrid color filters fabricated with **PI2-TMP** ((a) pigment-based, (b) 0.5 wt% dye added, (c) 1.0 wt% dye added color filter).

Table 5
Transmittance of fabricated pigment-based and pigment-dye hybrid color filters at 645 and 650 nm.

Dye	At 645 nm (%)	At 650 nm (%)
PI2-AP	96.41	95.72
PI2-TMP	97.62	97.02
PI2-S2	97.33	96.48
PI1-AP	96.70	95.99
PI1-TMP	96.81	96.34
PI1-S2	97.90	97.03
Pigment-based	97.46	97.56

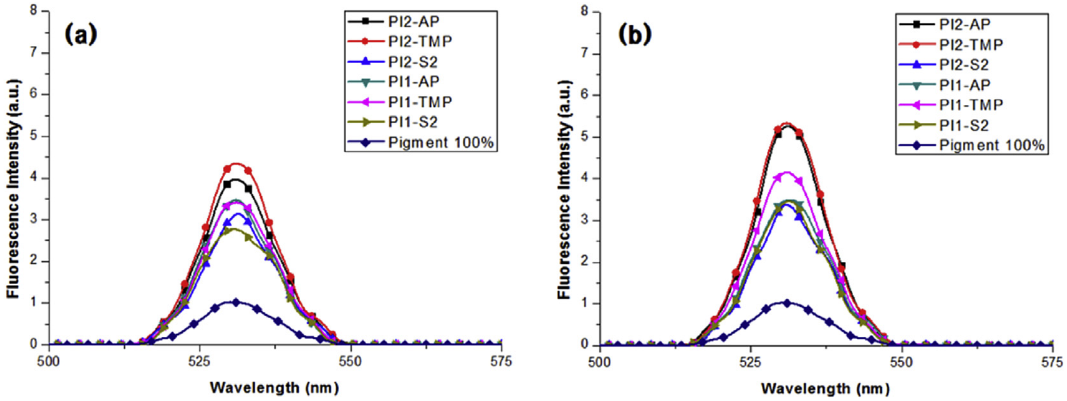


Fig. 7. Fluorescence of fabricated pigment-based and pigment-dye hybrid color filters (dye contents (a) 0.5 wt%, (b) 1.0 wt%).

Table 6
Optical properties of the fabricated pigment-dye hybrid color filters.

Dye		PI2-AP	PI2-TMP	PI2-S2	PI1-AP	PI1-TMP	PI1-S2
0.5 wt%	Rx	0.656	0.656	0.656	0.656	0.656	0.656
	Ry	0.30311	0.30314	0.30362	0.30310	0.30312	0.30283
	RY (Max. Y)[a]	13.187	13.132	13.234	13.110	13.133	13.316
	C/R[b]	11294	11130	11824	11568	11428	11849
	Min. Y[c]	**0.0011676**	**0.0011799**	**0.0011192**	**0.0011333**	**0.0011492**	**0.0011238**
1.0 wt%	Rx	0.656	0.656	0.656	0.656	0.656	0.656
	Ry	0.30392	0.30375	0.30381	0.30394	0.30940	0.30384
	RY (Max. Y)	13.337	13.416	13.351	13.403	13.420	13.445
	C/R	10238	9234	11325	11124	11070	11727
	Min. Y	**0.0013027**	**0.0014529**	**0.0011789**	**0.0012049**	**0.0012123**	**0.0011465**
STD (pigment 100%)[d]		**Rx: 0.656, Ry: 0.30391, RY: 13.492, C/R: 12304, Min. Y: 0.0010966**					

[a] RY (Max. Y): measured maximum brightness.
[b] C/R: contrast ratio.
[c] Min. Y: calculated brightness of full-black state.
[d] STD: pigment-based color filter (Pigment Red 177, 100%).

However, as listed in Table 6, maximum brightness of the fabricated pigment-dye hybrid color filters were maintained in every case. There is no increase of maximum brightness from the added dyes. On the contrary to this result, the minimum brightness of the fabricated hybrid color filters were increased in all cases. Even though the increases in figures were small, they raised the minimum brightness considerably in proportion, which lowered contrast ratio values accordingly.

4. Conclusion

To investigate the effect of fluorescence on the contrast ratio of color filters, six perylene-based dyes were synthesized, and dye-based and pigment-dye hybrid color filters were prepared from them. The fluorescence properties of the synthesized dyes in solution and the fabricated color filters were measured and compared to one another. The total visible-range emission intensity of the synthesized dyes in solution and the prepared color filters showed the same trend regardless of their states. The minimum brightness of the color filters calculated from the maximum brightness and contrast ratio showed a similar trend to the total emission intensity. Therefore, it is concluded that the total emission in the visible region is a key factor in determining the minimum brightness and contrast ratio of color filters. Consequently, color filters fabricated with strongly fluorescent dyes will exhibit high minimum brightness and low contrast ratio.

Acknowledgments

This work was supported by the Advanced Technology Center Program (No.10039098, Development of pigment-dye hybrid type of color mill base with ultra-brightness for LED TV) funded by the Small and Medium Business Administration.

References

[1] Kim YD, Kim JP, Kwon OS, Cho IH. The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters. Dyes Pigm 2009;81(1):45–52.
[2] Choi J, Sakong C, Choi J-H, Yoon C, Kim JP. Synthesis and characterization of some perylene dyes for dye-based LCD color filters. Dyes Pigm 2011;90(1):82–8.
[3] Kim YD, Cho JH, Park CR, Choi JH, Yoon C, Kim JP. Synthesis, application and investigation of structure–thermal stability relationships of thermally stable water-soluble azo naphthalene dyes for LCD red color filters. Dyes Pigm 2011;89(1):1–8.
[4] Sakong C, Kim YD, Choi J-H, Yoon C, Kim JP. The synthesis of thermally-stable

red dyes for LCD color filters and analysis of their aggregation and spectral properties. Dyes Pigm 2011;88(2):166–73.

[5] Choi J, Lee W, Sakong C, Yuk SB, Park JS, Kim JP. Facile synthesis and characterization of novel coronene chromophores and their application to LCD color filters. Dyes Pigm 2012;94(1):34–9.

[6] Choi J, Lee W, Namgoong JW, Kim TM, Kim JP. Synthesis and characterization of novel triazatetrabenzcorrole dyes for LCD color filter and black matrix. Dyes Pigm 2013;99(2):357–65.

[7] Choi J, Kim SH, Lee W, Chang JB, Namgoong JW, Kim YH, et al. The influence of aggregation behavior of novel quinophthalone dyes on optical and thermal properties of LCD color filters. Dyes Pigm 2014;101:186–95.

[8] Lakshmi Praveen P, Ojha DP. Effect of molecular interactions and end chain length on ultraviolet absorption behavior and photo stability of alkoxycinnamic acids: theoretical models of liquid crystal. J Mol Liq 2014;197:106–13.

[9] Yoon C. Choi J-h. Synthesis of tricyanopyrrolidone derivatives as synergists for improving contrast ratio of liquid crystal displays. Dyes Pigm 2014;101:344–50.

[10] Kim JY, Choi J, Namgoong JW, Kim SH, Sakong C, Yuk SB, et al. Synthesis and characterization of novel perylene dyes with new substituents at terminal-position as colorants for LCD color filter. J Incl Phenom Macrocycl Chem. 2015;82(1–2):203–12.

[11] Kim SH, Namgoong JW, Yuk SB, Kim JY, Lee W, Yoon C, et al. Synthesis and characteristics of metal-phthalocyanines tetra-substituted at non-peripheral (α) or peripheral (β) positions, and their applications in LCD color filters. J Incl Phenom Macrocycl Chem. 2015;82(1–2):195–202.

[12] Yuk SB, Lee W, Namgoong JW, Choi J, Chang JB, Kim SH, et al. Synthesis and characterization of bay-substituted perylene dyes for LCD black matrix of low dielectric constant. J Incl Phenom Macrocycl Chem. 2015;82(1–2):187–94.

[13] Langhals H, Ismael R, Yürük O. Persistent fluorescence of perylene dyes by steric inhibition of aggregation. Tetrahedron 2000;56(30):5435–41.

[14] Pu S, Fan C, Miao W, Liu G. The effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a methoxy group. Dyes Pigm 2010;84(1):25–35.

[15] Chakraborty S, Debnath P, Dey D, Bhattacharjee D, Hussain SA. Formation of fluorescent H-aggregates of a cyanine dye in ultrathin film and its effect on energy transfer. J Photochem Photobiol A Chem 2014;293:57–64.

[16] Tsai HY, Chen KY. Synthesis and optical properties of novel asymmetric perylene bisimides. J Lumin 2014;149:103–11.

[17] Wei ZJ, Xu YW, Zhang L, Luo MM. Synthesis and thermal polymerization of perylene bisimide containing benzocyclobutene groups. Chin Chem Lett. 2014;25(10):1367–70.

[18] Qiao Y, Chen J, Yi X, Duan W, Gao B, Wu Y. Highly fluorescent perylene dyes with large stokes shifts: synthesis, photophysical properties, and live cell imaging. Tetrahedron Lett. 2015;56(21):2749–53.

[19] Hutchings MG. Unexpected bathochromic shifts in the visible absorption spectra of arylazo dyes containing the orfho-N-pyridinium-nitro substituent combination. Dyes Pigm 1991;17:227–40.

[20] Durbeej B, Eriksson LA. On the bathochromic shift of the absorption by astaxanthin in crustacyanin: a quantum chemical study. Chem Phys Lett. 2003;375(1–2):30–8.

[21] Lynch DE, Byriel KA. The role of C–H···O hydrogen-bonding interactions in the solid-state packing of squaraine dyes. Cryst Eng 1999;2(4):225–39.

[22] Reghu RR, Bisoyi HK, Grazulevicius JV, Anjukandi P, Gaidelis V, Jankauskas V. Air stable electron-transporting and ambipolar bay substituted perylene bisimides. J Mater Chem. 2011;21(21):7811.

[23] Lee IL, Li SR, Chen KF, Ku PJ, Singh AS, Kuo HT, et al. Synthesis, photophysical properties, and field-effect characteristics of (Ethynylphenyl)benzimidazole-decorated anthracene and perylene bisimide derivatives. Eur J Org Chem. 2012;2012(15):2906–15.

[24] Mazurak Z, Wanic A, Karolczak J, Czaja M. The fluorescence decay times and quantum efficiencies of 1,4,5,8-naphthalisoimides. J Lumin 2015;158:103–9.

[25] Langhals H, Krotz O, Polborn K, Mayer P. A novel fluorescent dye with strong, anisotropic solid-state fluorescence, small stokes shift, and high photostability. Angew Chem Int Ed Engl. 2005;44(16):2427–8.

[26] Biedermann F, Elmalem E, Ghosh I, Nau WM, Scherman OA. Strongly fluorescent, switchable perylene bis(diimide) host-guest complexes with cucurbit[8]uril in water. Angew Chem Int Ed Engl. 2012;51(31):7739–43.

[27] Masuko M, Ohuchi S, Sode K, Ohtani H, Shimadzu A. Fluorescence resonance energy transfer from pyrene to perylene labels for nucleic acid hybridization assays under homogeneous solution conditions. Nucleic Acids Res. 2000;28(8). e34-e.