

Synthesis of Novel Hemicyanine Dyes for Color Compensating Film in Plasma Display Panels

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Received March 3, 2014, Accepted April 28, 2014

Five novel cyanine dyes containing julolidine and indole moieties were synthesized. Several color compensating films for plasma display panels (PDP) were prepared using these dyes. The spectroscopic and physicochemical properties of the synthesized dyes in both solution and film state were evaluated. For each color compensating film, the optimum ratio of dye to binder was determined on the basis of transmittance, half band width, and photo-stability of the color compensating film. The five synthesized dyes showed sharp absorption peaks near 590 nm (orange light) and had molar extinction coefficients above $1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. The melting point of the dyes was above 200 °C and photo-stability of the color compensating films was improved by introducing substituents at the 5th position on the indole derivatives.

Key Words : Cyanine dye, Hemicyanine dye, Synthesis, Color compensating film, Plasma display panel

Introduction

The PDP filter is an optical component composed of color compensating film, NIR (near infrared light) shielding film, EMI (electromagnetic interference) shielding film, AR (Anti reflection) film, and so on. Color compensating films serve to increase the color spectrum of PDP TV by absorbing the orange light ($\lambda_{\max} = 590 \text{ nm}$) discharged from neon gas in PDP. Color compensating films have been manufactured by spin-coating of the dye in the binder on the substrate film. All dyes used in color compensating films should meet spectroscopic and physicochemical requirements as follows: maximum absorption wavelength at $590 \pm 3 \text{ nm}$, molar extinction coefficient (ϵ) above $1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, half band width below 50 nm, high affinity to binder and substrate film, and high photostability. Also, transmittance of color compensating film should be more than 70% in the visible wavelength range (380-780 nm) except at 590 nm.

To date, most of the color compensating films have been made with cyanine, porphyrin, squarylium dyes.¹⁻³ Especially, symmetric cyanine dyes have often been employed. Although they usually achieve the small half band width and high molar extinction coefficient, it is well known that cyanine has some challenges due to poor photo-stability. Increases in the length of the central methine chain induces a significant degradation factor when exposed to light.^{4,5} Although many structures for color compensating films have been introduced, there has been little research regarding the relationship of spectroscopic properties between solution and film state.

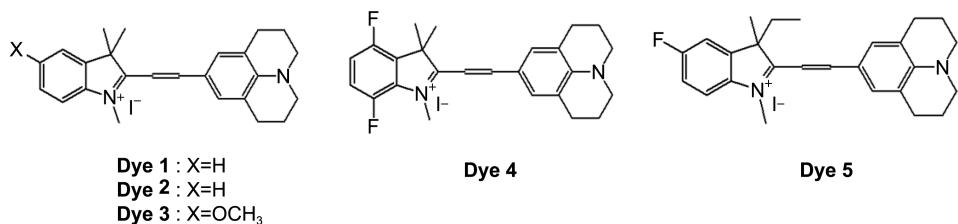
Therefore, this paper focuses on changes in the spectro-

scopic and physicochemical properties of color compensating film with respect to the nature of the substituents and the compatibility of the dye with the binder. Due to the negative photo-stability of the methine chain, we focused on one double bond (common name: astrazine) motif which has been little explored as a conjugation unit. In practice, we designed novel asymmetrical hemicyanine dyes containing julolidine and indolenium iodide^{6,7} bridged by ethylene (Scheme 1). Julolidine was introduced, instead of a simple amine, as a means to give a planar structure which generally ensures a high molar absorption coefficient. The 3,3'-dimethyl substitution at the 3rd position of indolenium iodide ensures greater resistance to light as compared to the sulfur (S) or selenium (Se) substitution at the same position.⁸ Other functional groups were also introduced at the 5th position of indole derivatives to minimize the inevitable color change. Herein, we synthesized five novel dyes for use in PDP color compensating films and fabricated compensation films using the synthesized dyes. Their spectroscopic properties, physicochemical properties, and photo-stability were investigated.

Experimental

General Methods. All reagents were purchased from Sigma-Aldrich or TCI. Moisture-sensitive reactions were performed under nitrogen. All reactions were followed by thin-layer chromatography (TLC) using Analtech silica gel GHLF. ¹H NMR spectra were obtained using Avance 500 spectrometer. Elemental analyses for **Dye1-Dye5** were performed with an elemental analyzer (CE instrument, Italy). Melting point of dyes was recorded on a DSCQ-100. The absorption and transmittance spectra were recorded on HP 8452A UV-visible spectrometer. Aggregation behavior

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**Scheme 1.** Structures of the synthesized dyes.

of dye molecules in the film was observed using SEM (JEOL, JSM-T200). Photo-stability of color compensating films was measured under dry condition at 25 °C using Fade-O-Meter (Arc Lamp, 6.5 mW/cm²).

Fabrication and Characterization of Color Compensating Film. For the preparation of color compensating films based on hemicyanine dye, the synthesized dyes were combined with binder (APEC, ASC-100N) and were spin-coated on PET film (Toyobo, 125 μm) at a speed of 800 rpm. The resulting films were dried initially at room temperature and subsequently at 120 °C for 10 min.

9-Julolidine Carboxaldehyde (1). Dry *N,N*-dimethylformamide (DMF) (3.4 mL, 43.9 mmol) was charged into a round bottom flask fitted with a magnetic stirrer and pressure-equalizing dropping funnel. The flask was purged with dry nitrogen and cooled in an ice bath. Phosphorus oxychloride (0.79 mL, 8.5 mmol) was then added slowly to the DMF. A solution of 2,3,6,7-tetrahydro-1*H*,5*H*-benzo-quinolizine (julolidine) (1.47 g, 8.5 mmol) in DMF (1.36 mL) was then added with vigorous stirring to the mixture and the resulting mixture was heated at 80–100 °C for 2 h. The solution was allowed to cool to room temperature and was poured into ice water. The solution was neutralized to pH 6–8 by addition of saturated sodium acetate. The desired aldehyde precipitated out of solution as a greenish-yellow solid. The solid was filtered, washed with water and hexane, and dried to obtain pure aldehyde **1** (0.731 g). Yield: 42.7%. ¹H NMR (500 MHz, CDCl₃) δ 1.37 (p, 2x2H), 2.8 (t, 2x2H), 3.3 (2x2H, t), 7.29 (2x1H, s), 9.6 (s, 1H, CHO).

5-Fluoro-2,3,3-trimethyl Indolenine (2b). 4-Fluorophenyl hydrazine hydrochloride (1 g, 6.15 mmol) with 3-methyl-2-butanone (0.988 mL, 9.23 mmol) in ethanol (10 mL) was refluxed at 85 °C for 5 h. The solution was allowed to cool to room temperature and the solvent was removed by rotary evaporation. A solution of glacial acetic acid (5 mL) and HCl (5 mL) was added and refluxed at 110 °C for 3 h. The solution was neutralized to pH 6–8 by addition of 10% sodium hydroxide and cooled to room temperature. The resulting white precipitate was filtered and washed with water and dried. Pure indolenine (**2b**) can be recrystallized in acetonitrile. Yield: 55%. ¹H NMR (500 MHz, DMSO) δ 1.3 (2x3H, s), 2.3 (3H, s), 6.9–7.5 (3x1H, m, Ar'-H)

5-Methoxy-2,3,3-trimethyl Indolenine (2c). The compound **2c** was prepared using the same procedure as **2b** except that 4-methoxy-phenyl hydrazine was used instead of 4-fluorophenyl hydrazine. After neutralization, the material was dissolved in ethyl acetate. The combined organic extract was

dried over anhydrous MgSO₄ and solvent was removed by rotary evaporation and dried. The resulting indolenine was obtained as an oily dark brown product. Yield: 33%. ¹H NMR (500 MHz, DMSO) δ 1.3 (s, 2x3H) 2.2 (s, 3H), 3.9 (s, 3H, OCH₃-H) 6.9–7.5 (m, 3x1H, Ar'-H).

4,7-Difluoro-2,3,3-trimethyl Indolenine (4a). 2,5-Difluoro phenyl hydrazine (1 g, 6.94 mmol) and 3-methyl 2-butanone (0.892 mL, 1.784 mmol) were dissolved in ethanol (0.5 mL) and refluxed at 85 °C for 5 h. The solution was allowed to cool to room temperature and anhydrous ZnCl₂ (2.75 g) was added with vigorous stirring. The mixture was heated to 215 °C for 5 min. After this white vapor was generated and the solution was further refluxed with an additional 2% HCl (20 mL). Solvent was removed by rotary evaporation and the material was purified by column chromatography over silica gel using hexane/ethyl acetate (1:1 v/v) to yield a brown solid (0.9 g). Yield: 66.5%. ¹H NMR (500 MHz, DMSO) δ 1.3 (2x3H, s), 2.3 (3H, s), 7.4 (1H, d, Ar'-H), 7.6 (1H, d, Ar'-H).

2,3-Dimethyl-3-ethyl-5-fluoro Indolenine (5a). The compound **5a** was prepared using the same procedure as **2b** except that 3-methylpentan-2-one was used instead of 3-methyl-2-butanone. The crude product was used in the next step without further purification.

1,2,3,3-Tetramethyl Indolenium Idodide (3a). 2,3,3-Trimethylindolenine (1 g, 12.56 mmol), acetonitrile (50 mL), and methyl idodide (0.94 mL, 15.072 mmol) were refluxed at 80 °C for 7 h. The resulting pink precipitate was filtered and washed with ice-cooled chloroform. Yield: 37%. ¹H NMR (500 MHz, DMSO) δ 1.5 (s, 2x3H), 2.7 (3H, s), 3.9 (s, 3H, s, N-CH₃-H) 7.6–7.9 (3x1H, m, Ar'-H).

5-Fluoro-1,2,3,3-tetramethyl Indolenium Iodide (3b). The compound **3b** was prepared using the same procedure as **3a** except that 5-fluoro-2,3,3-trimethyl indolenine was used instead of 2,3,3-trimethylindolenine. Yield: 40%. ¹H NMR (500 MHz, DMSO) δ 1.5 (s, 2x3H), 2.7 (s, 3H), 3.9 (s, 3H, N-CH₃-H), 7.4–7.9 (m, 3x1H, Ar'-H).

5-Methoxy-1,2,3,3-tetramethyl Indolenium Iodide (3c). The compound **3c** was prepared using the same procedure as **3a** except that 5-methoxy-2,3,3-trimethyl indolenine was used instead of 2,3,3-trimethylindolenine. Yield: 30%. ¹H NMR (500 MHz, DMSO) δ 1.5 (s, 2x3H), 2.7 (s, 3H), 3.9 (s, 3H, N-CH₃-H), 7.1–7.8 (m, 3x1H, Ar'-H).

4,7-Difluoro-1,2,3,3-tetramethyl Indolenium Iodide (4b). The compound **4b** was prepared using the same procedure as **3a** except that 4,7-difluoro-2,3,3-trimethyl indolenine was used instead of 2,3,3-trimethylindolenine. Yield: 40%. ¹H

NMR (500 MHz, DMSO) δ 1.5 (s, 2x3H), 2.7 (s, 3H), 3.9 (s, 3H, N-CH₃-H), 8.2-8.3 (m, 2x1H, Ar'-H).

3-Ethyl-5-fluoro-1,2,3-trimethyl Indolenium Iodide (5b). The compound **5b** was prepared using the same procedure as **3a** except that 2,3-dimethyl-3-ethyl-5-fluoro indolene was used instead of 2,3,3-trimethylindolene. Yield: 42%. ¹H NMR (500 MHz, DMSO) δ 0.4 (t, 3H), 1.5 (s, 2x3H), 2.2 (q, 1H), 2.1 (q, 1H), 2.7 (s, 3H), 4.0 (s, 3H, N-N-CH₃), 7.5-7.9 (m, 3x1H, Ar'-H).

Dye 1. 1,2,3,3-Tetramethyl indolenium iodide (0.24 g, 0.8 mmol) and 9-julolidine carboxaldehyde (0.16 g, 0.8 mmol) were refluxed in acetic anhydride (10 mL) for 5 min. The resulting violet precipitate was filtered and dried. Yield: 30%. ¹H NMR (500 MHz, DMSO) δ 1.7 (s, 2x3H), 1.9 (t, 2x2H), 2.7 (t, 2x2H), 3.4 (t, 2x2H), 3.8 (s, 3H, N-CH₃-H), 7.0-8.15 (m, 8x1H, Ar'-H, -CH=CH-).

Dye 2. The compound **Dye 2** was prepared using the same procedure as **Dye 1** except 5-fluoro-1,2,3,3-tetramethyl indolenium iodide was used instead of 1,2,3,3-tetramethyl indolenium iodide. Yield: 33%. ¹H NMR (500 MHz, DMSO) δ 1.7 (s, 2x3H), 1.9 (t, 2x2H), 2.7 (t, 2x2H), 3.4 (t, 2x2H), 3.8 (s, 3H, N-CH₃-H), 7.0-8.15 (m, 7x1H, Ar'-H, -CH=CH-).

Dye 3. The compound **Dye 3** was prepared using the same procedure as **Dye 1** except 5-methoxy-1,2,3,3-tetramethyl indolenium iodide was used instead of 1,2,3,3-tetramethyl indolenium iodide. Yield: 31%. ¹H NMR (500 MHz, DMSO) δ 1.7 (s, 2x3H), 1.9 (t, 2x2H), 2.7 (t, 2x2H), 3.4 (t, 2x2H), 3.8 (s, 3H, N-CH₃-H), 7.0-8.15 (m, 8x1H, Ar'-H, -CH=CH-).

Dye 4. The compound **Dye 4** was prepared using the same procedure as **Dye 1** except 4,7-difluoro-1,2,3,3-tetramethyl indolenium iodide was used instead of 1,2,3,3-tetramethyl indolenium iodide. Yield: 34%. ¹H NMR (500 MHz, DMSO)

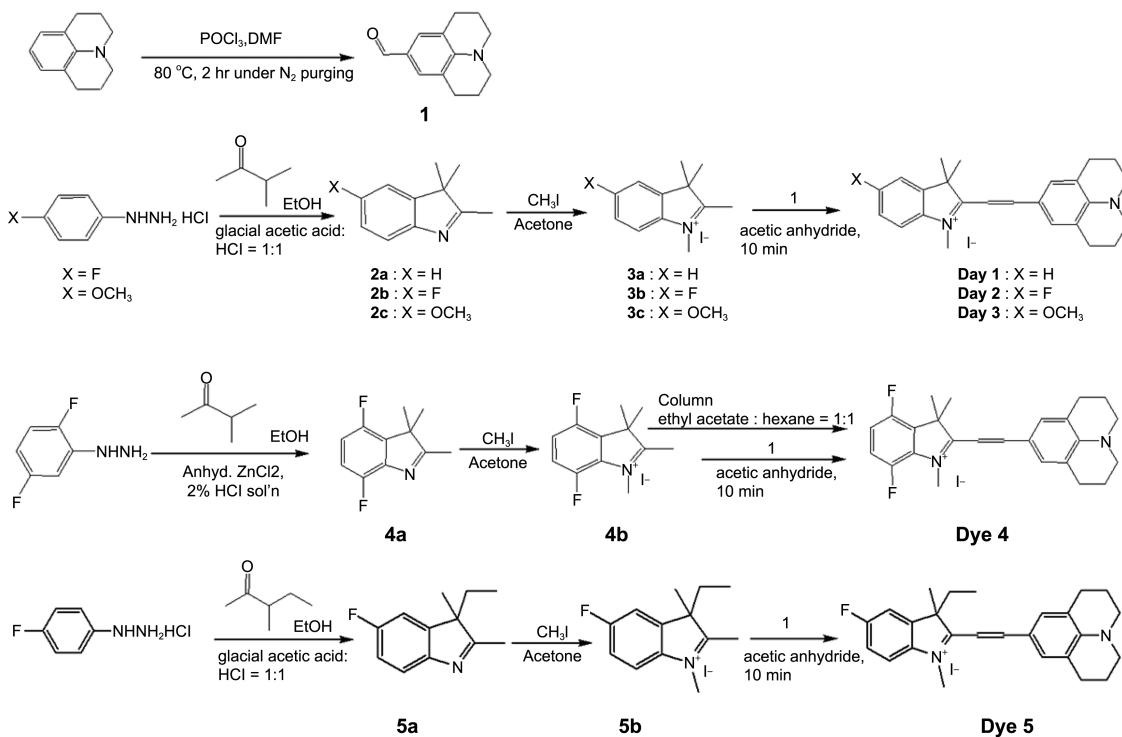
δ 1.7 (s, 2x3H), 1.9 (t, 2x2H), 2.7 (t, 2x2H), 3.4 (t, 2x2H), 3.7 (s, 3H, N-CH₃-H), 6.9-8.1 (m, 6x1H, Ar'-H, -CH=CH-).

Dye 5. The compound **Dye 5** was prepared using the same procedure as **Dye 1** except 3-ethyl-5-fluoro-1,2,3-trimethyl indolenium iodide was used instead of 1,2,3,3-tetramethyl indolenium iodide. Yield: 33%. ¹H NMR (500 MHz, DMSO) δ 0.3 (t, 3H) 1.5 (s, 3H), 1.9 (t, 2x2H), 2.2 (q, 1H), 2.1 (q, 1H), 2.7 (s, 3H), 2.7 (t, 2x2H), 3.4 (t, 2x2H) 3.8 (s, 3H, N-CH₃-H), 7.0-8.1 (m, 7x1H, Ar'-H, -CH=CH-).

Computational Study. DFT (density functional theory) calculations were conducted using Gaussian 03 software. Geometries were optimized using the B3LYP hybrid functional (Beck's three-parameter functional and Lee-Yang-Parr functional) as an exchange-correlation functional 91 and 6-31+G(d,p) was used as the basis set. HOMO and LUMO were determined using optimized geometries. Transition energies were calculated using TDDFT (time-dependent density functional theory). B3LYP, BHandH, and CAM-B3LYP were implemented to study electronic transitions.

Results and Discussion

Synthesis of Dyes. **Dye 1-Dye 5** were prepared by the stepwise synthetic protocol illustrated in Scheme 2. Hemicyanine dyes were synthesized using the Knoevenagel reaction⁹⁻¹² of indolenium iodide with aldehyde **1**. 9-julolidine carboxaldehyde **1** was synthesized using the Vilsmeier reaction^{13,14} including the Vilsmeier-reagents (phosphorus oxychloride, DMF) under nitrogen gas. Compounds **2a-2c**, **5a** were prepared in 2 steps starting from substituted phenyl hydrazine reacted with ketone using a conventional Fisher Indole formation.¹⁵ 4,7-Difluoro-2,3,3-trimethyl indole **4a**



Scheme 2. Schematic diagram for the synthesis of **Dye 1-Dye 5**.

was synthesized by a modified Fisher Indole reaction¹⁶ using 2,5-difluoro phenyl hydrazine and 3-methyl-2-butanone. This was further reacted using anhydrous ZnCl₂ and was followed by purification with silica gel column chromatography. Indolenium iodides **3a-3c**, **4b**, **5b** were prepared by methylation of indole derivatives **2a-2c**, **4a**, **5a** using methylene iodide in acetone. The coupling reaction (Knoevenagel reaction) of indolenium iodide **3a-3c**, **4b**, **5b** with 9-julolidine carboxaldehyde **1** in acetic anhydride for 5-10 min produced **Dye 1-Dye 5**.

Spectroscopic and Thermal Studies of Dyes Synthesized. Absorption spectra of **Dye 1-Dye 5** in chloroform are shown in Figure 1. The absorption spectra of **Dye 1**, **Dye 2**, and **Dye 3** showed an absorption maxima at 592 nm, 592 nm, and 598 nm, respectively. The red-shifted band, at about 6 nm of **Dye 3** having methoxy group at the 5th position of indole moiety as compared to that of **Dye 2** having a fluoro group, is due to the increase of electron donating ability of the functional group. On the other hand, the absorption band of **Dye 4** having the 4,7-difluoro indole group exhibited a red-shift of 10 nm as compared to that of **Dye 1**. **Dye 5** is a modified version of **Dye 2** generated by changing the methyl group to an ethyl group. Introducing an ethyl group at the 3rd position of indole to **Dye 2** caused a slight red-shift to 594 nm.

Optical and thermal properties of **Dye 1-Dye 5** are listed in Table 1. All the dyes showed high molar extinction coefficients above $1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. This high molar absorption coefficient, which is an important factor for cost effectiveness and thickness of the PDP filter, is achieved by the planar structure through the methine unit.

The half band width of **Dye 2** and **Dye 5**, having the fluoro group at the 5th position of indole, was 44 nm which is almost the same as that of **Dye 1**. On the other hand **Dye 3** was broadened to 64 nm relative to **Dye 1**. The half band width of **Dye 4**, having 4,7-difluoro group, was the narrowest with a width of 36 nm. This might be due to the relatively symmetrical structure. In general, it is known that a symmetrical structure or a structure having few functional

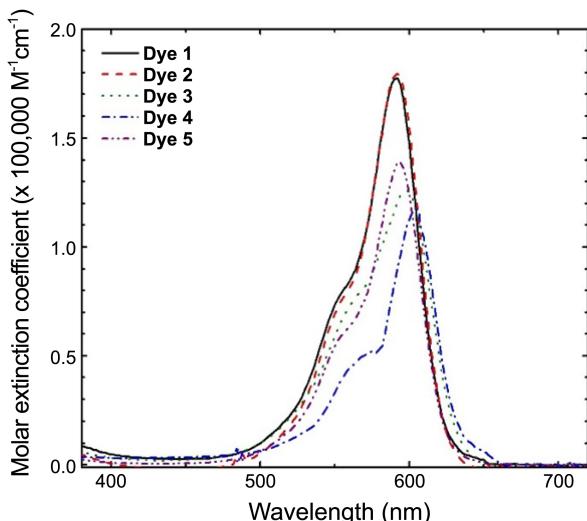


Figure 1. Absorption spectra of **Dye 1-Dye 5** in chloroform.

Table 1. Optical and thermal properties

Dye	λ_{abs}^a (nm)	ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$)	Half Band Width (nm)		T_m (°C)
			in solution ^b	in film state ^c	
Dye 1	592	177,363	44	64	230
Dye 2	592	179,626	44	66	218
Dye 3	598	126,090	64	74	233
Dye 4	604	117,453	36	56	217
Dye 5	594	159,462	46	62	215

^aabsorption spectra measured in chloroform. ^bhalf band width measured in chloroform. ^chalf band width of dyes on film state at optimum composition ratio

groups represents a narrow half band width due to the absorption of light in fewer energy states rather than several energy states.¹⁷ From these results, we can interpret that the fluoro group at the 5th position of indole moiety has little effect on the change in color and half band width. All five dyes, which have absorption maxima of 592-604 nm, and a half band width of near 50 nm, and a molar extinction coefficient of above $1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, can be applied to color compensating films to effectively shield orange light ($\lambda_{\text{max}} = 590 \text{ nm}$). And all dyes displayed melting points of above 200 °C. **Dye 1** and **Dye 3** showed relatively higher melting points of 230 °C and 233 °C, respectively.

Fabrication of Color Compensating Films. Color compensating films using the five dyes were fabricated with PET film (Toyobo, 125 μm). The films were prepared by spin coating of the dye solutions with an acrylate binder (APEC, ASC-100N) at the rate of 800 rpm. The resulting films were dried at room temperature and further baked at 120 °C for 10 min. To gain insight into the optimized composition ratio of the dye to the binder, the composition ratios of the dye to the binder were set in the range of 1:1000-1:2000.

The optimum composition ratio was determined on the basis of transmittance and half band width of the fabricated color compensating film. A high concentration of dye in the binder resulted in difficulty with spin coating and also induced broadening of the half band width accompanied with aggregation. On the other hand, a small amount of dye in the binder makes transmittance high, resulting in ineffectiveness for shielding orange light (590 nm). Therefore, an optimized composition ratio was chosen by finding the composition ratio that has the least half band width and also has the lowest transmittance at around 590 nm.

Figure 2 shows transmittance spectra of color compensating films and SEM showing aggregation behavior based on **Dye 1** and **Dye 3** with different dye/binder ratios. When the ratio of the binder was increased, the half band width was decreased and aggregation of dyes on the film was significantly decreased. However, when the dye content was increased the transmittance of orange light was decreased. Transmittance at visible wavelengths except for orange light represented more than 80%, which means that the film with the synthesized dyes did not interrupt the other portions of visible light, so these dyes are suitable for compensation film if their ratio with binder is optimized.

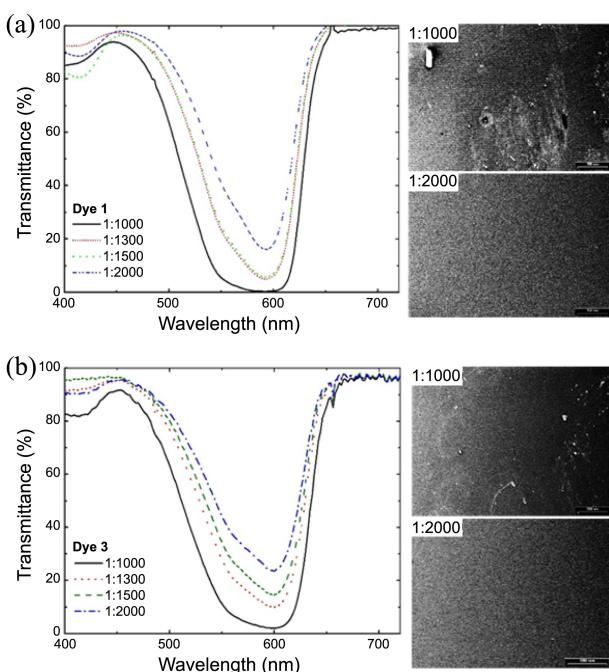


Figure 2. Transmittance spectra of color compensating films based on (a) **Dye 1** and (b) **Dye 3** (Ratio = dye : binder).

Spectroscopic Studies of Color Compensating Films.

The optical properties of dyes coated on PET film (color compensating film) are shown in Figure 3 and Table 1. The optical values for these dyes on PET film were obtained under optimized composition ratios of the dye to the binder. The absorption spectra of all dyes on PET film were broadened as compared to those of the dye solution in the range of 10–20 nm, whereas the maximum absorption wavelength was conserved. A likely reason for this may be aggregation amongst the dye molecules on the PET film or in the binder.

The difference between the half band width of the dyes in the film state and that in solution was decreased in the order of **Dye 1** ≈ **Dye 4** ≈ **Dye 2** > **Dye 5** > **Dye 3** (Table 1). The degree of broadening of half band width of color compensating film based on **Dye 3** showed a minimum value amongst the five dyes. One possible explanation for this is due to the inhibition of stacking between dye molecules by the good compatibility with the binder or minimal inter-

action between dyes in binder. Considering the molecular structure of **Dye 3**, which has a bulky group at the terminal side of the molecule, this group may serve to prevent aggregation. Moreover, it is also speculated that **Dye 3** is the most compatible with this type of acrylate binder because of the polar methoxy substituent. This results in the smallest broadening of half band width in film state. Similar prevention of broadening has been reported in organic dyes on film state.¹⁸

To further elucidate these differences in broadening of half band width in connection with their substituents effects, we evaluated the aggregation behavior of dyes in the film state through SEM (Scanning Electron Microscope). As shown in Figure 4, **Dye 3** represented a relatively homogeneous dispersion of dye particles in the film, which minimizes the decrease in the spectroscopic properties of color compensating films.

From these results, when fabricating a color compensating film, it is important to prevent or minimize aggregation of dye molecules *via* molecular stacking in the film state. Minimal aggregation could be achieved by using a binder which has the best compatibility with the dye.

Also, because the broadening of the half band width in the film state is inevitable, the structure of cyanine dye to be applied to polymer film as a color compensating film should be designed to have a half band width 10–20 nm less than the target half band width.

Effect of Compatibility of Dyes with Binder on Light.

Figure 5 shows photo stabilities of dyes both in solution and in film state. As shown in Figure 5, the photo-stabilities of the dyes in film states was different from that in solution. In solution, **Dye 5** and **Dye 4** were more stable than the other dyes.

Unlike the results in solution, the photo-stabilities of the dyes in film state were improved by introducing substituents at the 5th position of indole derivatives. **Dye 3** containing a methoxy substituent displayed the best photo-stability in the film. This result indicates that the used binder has an effect on the photo-stabilities of the dye. Generally, the two most important pathways for dye fading are known to be oxidation and reduction. In the case of cyanine dyes, relatively little is known about their fading mechanism, but what is known suggests that fading proceeds by oxidative routes.^{19–21} Singlet oxygen (${}^1\text{O}_2$) plays a significant role in photo-fading and can

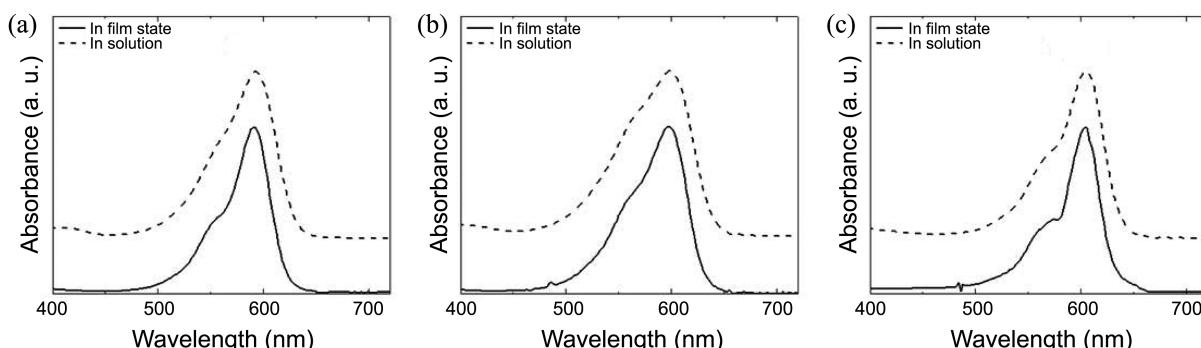


Figure 3. Absorption spectra of **Dye 1** (a), **Dye 3** (b), and **Dye 5** (c) on the film. Composition ratio of the dye to the binder in film state is the optimum composition ratio.

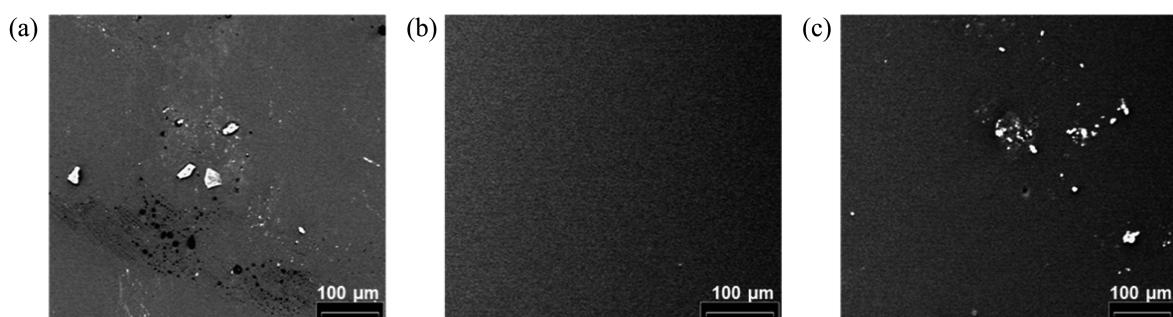


Figure 4. Scanning electron microscopy image of **Dye 2** (a), **Dye 3** (b), and **Dye 5** (c) on the film.

be produced by irradiation of the dyes. According to previous reports,²² although the intersystem crossing yields for cyanine dyes are quite low, the cyanine dyes react rapidly with singlet oxygen. A myriad of factors such as lifetime at excited state, substituents, aggregation, air, water, solvent, and substrate have an effect on photofading by oxidative routes. In this experiment, it is assumed that the main factors that have an effect on photobleaching of dyes on film might be substituents, degree of aggregation, and lifetime at excited state since conditions such as air, water, solvent, and substrate were controlled. In solution state, a plausible explanation for increased photo-stability through the introduction of two fluoro groups at indole derivatives is that fluorination lowers the oxidation potential (electron density) of the double bond by electron withdrawing. This means a fluorinated dye should be less susceptible to reactions with a singlet oxygen. A similar result was reported by Kanofsky and Sima.²³ On the other hand, **Dye 3** having a methoxy substituent as an electron donating group showed the lowest photo-stability in solution. Unlike the result in solution, it is interesting that **Dye 3** conferred the best photo-stability in film state. It might be explained by other factors. Perhaps, **Dye 3** has the best compatibility with the acrylate binder due to interaction between polar groups, resulting in minimized aggregation. This is supported by the SEM (Fig. 4) which

showed a homogeneous dispersion of particles. Also the smallest broadening (Table 1) of the half band width in film state points to this good compatibility of **Dye 3** with an acrylate binder. From these results, choosing a proper binder which is well compatible with the dye is important for ensuring good photo-stability. In practice, all cyanine dyes for color compensating film are used with additives including antioxidants and UV absorbers to ensure good photo-stability. However, cyanines without additives might play an important role in cost effectiveness and thickness of the PDP filter. In our results, although the photo-stability of films based on cyanine dyes decreased with time, there may be a further study which considers the modification of dyes and variations on the binder for enhancement of photo-stability without additives. It is also suggested that there should be a minimal use of additives having a negatively charged structure. This is because synthesized dyes have positively charged structures. From these results, choosing a proper binder which is well compatible with dye is important for ensuring good photo-stability.

Molecular Modeling. In order to investigate electronic transition energies, the TDDFT (time dependent density functional theory) method was implemented. The exchange correlation functional for optimized geometry was based on B3LYP for all cases. As a step to investigate dependence of

Table 2. Maximum absorption wavelength, oscillating strength (*f*), HOMO, LUMO, and band gap of the dyes obtained by DFT calculations

functional	Dye 1		Dye 2		Dye 3		Dye 4		Dye 5	
	λ_{\max} /nm	<i>f</i>	λ_{\max} /nm	<i>f</i>	λ_{\max} /nm	<i>f</i>	λ_{\max} /nm	<i>f</i>	λ_{\max} /nm	<i>f</i>
Experimental value	592	177,363 ^a	592	179,626	598	126,090	604	117,453	594	159,462
B3LYP	492 (100) ^b	1.6029	493 (99)	1.6077	507 (91)	1.6020	493 (111)	1.6215	493 (101)	1.5907
BHandH	462 (130)	1.6760	465 (127)	1.6390	467 (127)	1.7313	471 (133)	1.5043	466 (128)	1.6163
CAM-B3LYP	474 (118)	1.6371	478 (114)	1.6159	480 (114)	1.6863	484 (120)	1.5396	479 (115)	1.5960
HOMO*	-6.36		-6.40		-6.29		-6.47		-6.39	
LUMO*	-1.75		-1.81		-1.71		-1.94		-1.81	
Band gap*	4.61		4.58		4.59		4.54		4.58	

*The values were calculated with CAM-B3LYP. ^aMolar extinction coefficient ($M^{-1}cm^{-1}$). ^bDifference between the calculated value and the experimental value.

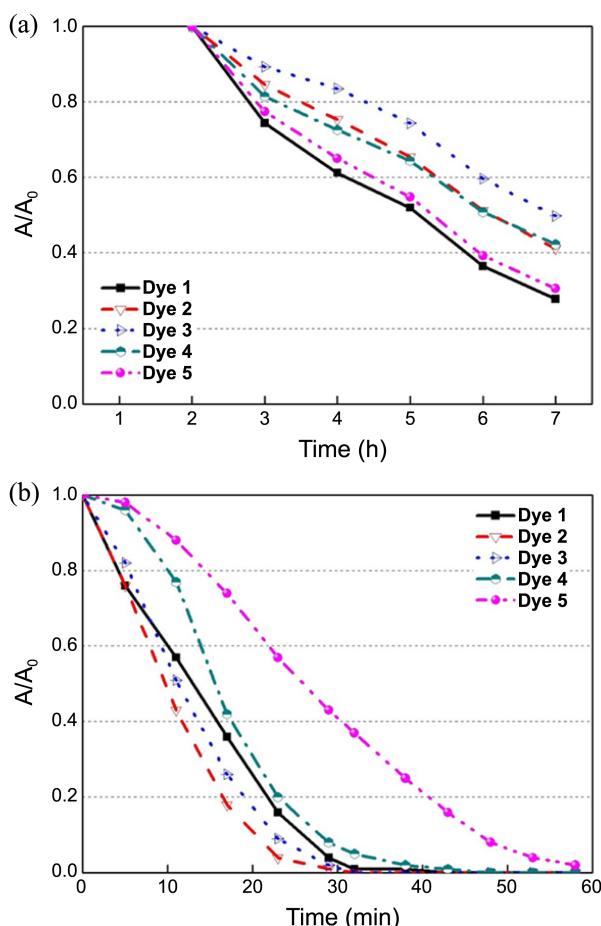


Figure 5. Photo-stability of Dye 1-Dye 5 (a) in film state and (b) in solution (A: Absorbance after irradiation, A_0 : Absorbance before irradiation).

TDDFT calculations on exchange correlation functional, B3LYP, BHandH, and CAM-B3LYP were employed. Solvent effect was included using the PCM (polarizable continuum model). As shown in Table 2, the results of TDDFT calculations implemented were found to be dependent on the hybrid function employed. A comparison of the calculated values with respect to experimental values, BHandH and CAM-B3LYP showed good estimation of relative trends in optical transition properties. Notably, **Dye 4** showed the lowest band gap and oscillating strength, which is consistent with experimental results. The addition of the two fluorine groups on **Dye 4** might be responsible for the most bathochromic shift by a strong LUMO shift, resulting in band decrease amongst the tested dyes.

Conclusion

All color compensating films, which have absorption maxima of 592-604 nm, small half band width, high molar extinction coefficient, and transmittance of 80% in the visible wavelength range except at the absorption peak of

590 nm were fabricated using five novel hemicyanine dyes. These could be applied to use as color compensating films to effectively shield orange light ($\lambda_{\text{max}} = 590 \text{ nm}$). The best compatibility of the dye with the binder ensures good spectroscopic and physicochemical properties. This results in the smallest broadening of the half band width and enhanced photo-stability. Aggregation of the dyes in film state could be minimized by introduction of bulky substituents or a compatible binder

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (No. NRF-2012R1A5A2051388).

References

1. Harada, T.; Yamada, T.; Suzuki, R.; Yabuki, Y.; Nishigaki, J. **2000**, Patent PCT/JP1999/005785.
2. Harada, T.; Yamada, T. **2001**, Patent US6309564 B1.
3. Ando, T.; Ikuhara, I.; Yamada, T. **2005**, Patent US6849327 B1.
4. Metsov, S.; Simov, D.; Stoyanov, S.; Nikolov, P. *Dyes and Pigments* **1990**, *13*, 11.
5. Lee, K.; Park, S. W.; Ko, M. J.; Kim, K.; Park, N.-G. *Nature Materials* **2009**, *8*, 665.
6. Chen, P.; Sun, S.; Hu, Y.; Qian, Z.; Zheng, D. *Dyes and Pigments* **1999**, *41*, 227.
7. Medina, F.; Poyato, J.; Rodriguez, J. *Journal of Photochemistry and Photobiology A: Chemistry* **1992**, *67*, 301.
8. Jha, B.; Banerji, J. *Dyes and Pigments* **1983**, *4*, 77.
9. Brooker, L.; Sklar, A.; Cressman, H.; Keyes, G.; Smith, L.; Sprague, R., et al. *Journal of the American Chemical Society* **1945**, *67*, 1875.
10. Brooker, L.; Dent, S., Jr.; Heseltine, D.; Lare, E. V. *Journal of the American Chemical Society* **1953**, *75*, 4335.
11. Kramer, D. N.; Bisauta, L. P.; Bato, R. *The Journal of Organic Chemistry* **1974**, *39*, 3132.
12. Jedrzejewska, B.; Kabatc, J.; Pietrzak, M.; Pączkowski, J. *Dyes and Pigments* **2003**, *58*, 47.
13. Cai, G.; Bozhkova, N.; Odingo, J.; Berova, N.; Nakanishi, K. *Journal of the American Chemical Society* **1993**, *115*, 7192.
14. Zammit, M. D.; Davis, T. P.; Willett, G. D. *Macromolecules* **1997**, *30*, 5655.
15. Jackman, L.; Scarmoutzos, L.; Smith, B.; Williard, P. G. *Journal of the American Chemical Society* **1988**, *110*, 6058.
16. Petrova, T.; Mamaev, V.; Akobson, G. *Russian Chemical Bulletin* **1969**, *18*, 609.
17. Hunger, K. *Industrial Dyes: Chemistry, Properties, Applications*; Wiley-VCH: Weinheim, Germany, 2007.
18. Horuchi, H.; Ishibashi, S.; Tobita, S.; Uchida, M.; Sato, M.; Toriba, K., et al. *The Journal of Physical Chemistry B* **2003**, *107*, 7739.
19. Gordon, P. F.; Gregory, P. *Organic Chemistry in Colour*; Springer-Verlag: Berlin, Germany, 1983.
20. Yang, S.; Tian, H.; Xiao, H.; Shang, X.; Gong, X.; Yao, S., et al. *Dyes and Pigments* **2001**, *49*, 93.
21. Kuramoto, N.; Kitao, T. *Dyes and Pigments* **1982**, *3*, 49.
22. Renikuntla, B. R.; Rose, H. C.; Eldo, J.; Waggoner, A. S.; Armitage, B. A. *Organic Letters* **2004**, *6*, 909.
23. Kanofsky, J. R.; Sima, P. D. *Photochemistry and Photobiology* **2000**, *71*, 361.