## Preparation of Red Dyes Derived from Diketo-pyrrolo-pyrrole Based Pigment and Their Properties for LCD Color Filters

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Trichromat pigments, such as C. I. Pigment Red 254, C. I. Pigment Green 36 and C. I. Pigment Blue 15:6, have been used for primary colors of LCD color filter utilizing a photolithographic process.<sup>1-4</sup> In order to reduce the manufacturing cost and simplify the complicated process of fabrication for color filters, an ink-jet printing method can be studied,<sup>5-7</sup> where thermally stable trichromat dyes are required to replace conventional pigments.

1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole and some of its derivatives, simply called diketo-pyrrolo-pyrrole(DPP), represent high-performance red pigments due to their excellent thermal stability and brilliant shades and exhibits exceptional resistance to chemical, heat, light, and weather.<sup>8-9</sup> Single crystal X-ray structural studies<sup>10-12</sup> on DPP indicated that the intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one contribute high thermal stability and solvent resistance.

A qualitative inspection of 3,6-diaryl-substitued diketo-pyrrolo-pyrroles reveals several reactive centers.<sup>13</sup> Appropriately substituted phenyl rings should be capable of undergoing electrophilic and nucleophilic aromatic substitutions, and the bicyclic chromophore unit incorporates three different functional groups, namely C=C bonds, C=O groups, and NH groups, each amenable to chemical transformation.

In the previous study,<sup>14</sup> the authors reported that 10 new dyes with  $C_2$ - $C_9$  *N*-alkyl functions in the DPP ring have been prepared by *N*-alkylation. The thermal stability of the dyes can be highly contributed by both the carbon number and their shapes of *N*-alkyl groups in DPP ring, in particular the dyes substituted by a normal  $C_8$  or  $C_9$  alkyl group exhibited extremely high stability. However, absorption maxima of the synthesized dyes shifted to shorter wavelength than those of C. I. Pigment Red 254.

To obtain the appropriate absorption maxima of the red dyes which should be similar to that of C. I. Pigment Red 254, in this study, four red dyes containing an *N*-alkyl or *N*-acyl group in the DPP ring were further synthesized, as shown in Figure 1. The effects of *N*-substituent in the DPP ring on the absorption maxima were also studied. Stronger electron withdrawing group (-CN) was introduced at the *p*-position on the phenyl ring replacing the chloro atom to exhibit a red shift. The structures of



Figure 1. Synthetic scheme of the red dyes.

these dyes were characterized using an elemental analysis and mass spectrophotometer. Absorption maximum ( $\lambda_{max}$ ) and thermal stability of the synthesized dyes were analyzed using by a UV-vis spectrophotometer and thermogravimetric analysis (TGA), respectively. The chromatic characteristics of the fabricated film with the red dyes prepared were analyzed by a spectrometer.

The absorption maxima, chromatic data and transmittance values of C. I. Pigment Red 254 (1a) and synthesized dyes (1b-2c) are summarized in Table 1. Absorption maxima ( $\lambda_{max}$ ) of dyes 1b and 1c were measured to be 504 nm in 1-methyl-2-pyrrolidone which were hypsochromic shifts (12 nm) to that of C. I. Pigment Red 254. A hypsochromic shift observed with dyes 1b and 1c can be best explained by the decrease of planarity and conjugation between DPP ring and adjacent phenyl group caused by the introduction of alkyl group.<sup>15</sup> The dyes 1d and 1e substituted with an electron withdrawing group in the DPP ring also exerted a hypsochromic shift that maximally absorbed at

Dye number	λ <sub>max</sub> (nm)	Chromaticity diagram		Transmittance
		Х	у	(70, at 050 lill)
1a (C.I. Pigment Red 254)	516	0.577	0.336	98.9
1b	504	0.539	0.448	99.9
1c	504	0.565	0.452	100
1d	461	0.403	0.434	100
1e	470	0.398	0.455	99.8
2b	524	0.538	0.351	100
2c	525	0.552	0.356	99.9

**Table 1.** Absorption maxima ( $\lambda_{max}$ ), chromaticity diagram (x,y) and transmittance (%) of the synthesized dyes **1b-2c** 

Determined in N-methyl-2-pyrrolidone (NMP)

461 nm and 470 nm, respectively, which were in the range of  $55 \sim 46$  nm shift in comparison with that of N-unsubstituted analogue (C. I. Pigment Red 254). This great blue shift can be attributable to the inductive effect arisen from electron withdrawing groups (acyl group) led to the destabilized excited state. In this case, both effects of the decrease of planarity and conjugation, which was observed with dyes 1b and 1c, and inductive effect resulting in destabilized excited state occurred simultaneously. However smaller shift was found in  $\lambda_{max}$  of dve 1e due to weak electron withdrawing power of N-substituent (-CH<sub>2</sub>CO<sub>2</sub>Et) compared to that of corresponding dye 1d. Dyes 2b and 2c substituted with an alkyl group in the DPP ring and a CN group at the *p*-position of phenyl ring exhibited absorption maxima at 524 nm and 525 nm, respectively, which shifted to longer wavelength of  $20 \sim 21$  nm in comparison with those of chloro analogues 1b and 1c. Smaller shifts were observed when compared with that of C. I. Pigment Red 254 which were 8 and 9 nm, respectively, indicating a substituent at p-position of phenyl ring works as an acceptor.

The presumable role of electron withdrawing group for hypsochromic shift by an *N*-substituent and bathochromic shift by substituent at *p*-position of phenyl ring can be calculated using a PPP-MO method, as shown in Figure 2. Electron density



Figure 2. Electron density alteration of red dyes 1b, 1c, 2b and 2c on excitation into singlet state.

Notes

Table 2. Comparison of absorption maxima of dyes 1a and 2b between calculated by a PPP-MO method and observed

Dye number.	R	$\lambda_{max}\left(nm\right)^{cal.}$	$\lambda_{max}\left(nm\right)^{obs.}$
1a	Cl	521	516
2b	CN	558	524

alteration on excited state of DPP system indicated that electron density at *p*-position of phenyl ring increases, whereas that of nitrogen atom in the DPP ring decreases. Therefore, it can be explained that the introduction of a CN group, that is more conjugated in  $\pi$ -systems and can accommodate efficiently the electrons than chloro group, at *p*-position of phenyl ring readily stabilizes the excited state leading to a bathochromic shift as observed. Conversely, the *N*-substitution of an electron withdrawing group, such as acyl group, in the DPP ring causes the destabilizing effect on the excited state resulting in a hypsochromic shift.

Both the absorption maxima of dyes **1a** and **2b** by a PPP-MO calculation and observed in NMP were summarized in Table 2. The calculation more exactly matched for dye **1a**, where calculated  $\lambda_{\text{max}}$  was 521 nm and observed absorption was 516 nm. Larger difference was observed with dye containing a CN group at *p*-position of phenyl ring which can be explained that the PPP-MO method was originally constructed for the planar  $\pi$ -conjugated system, therefore it is not appropriate to apply for non-planar molecules (*N*-substituted dyes).<sup>16</sup>

As indicated in Table 1, the chromaticity diagram of all synthesized dyes exhibited lower x values and higher y values than that of C. I. Pigment Red 254 (1a). But the chromaticity diagram of dye 2b and dye 2c showed comparatively closer y values to that of C. I. Pigment Red 254 than other dyes. It was also found that x values of dyes containing an *N*-alkyl group were higher than that of *N*-acyl analogues. A same trend was found in x values of dyes 2b and 2c. Comparing the y values between chloro substituted dyes and CN analogues, quite lower values were observed with dyes 2b and 2c, but very similar x values were obtained. Therefore, it can be concluded that, in this series, dye 2c features in similar color to conventional red pigment 1a.

In terms of transmittance at 630 nm for synthesized dyes, all materials exhibited over 99.8% up to 100% which indicated a more efficient transmittance of red light in comparison with C. I. Pigment Red 254. In case of color filter, transmittance of the light greatly contributes the contrast ratio and brightness of the LCD panel, therefore more efficient performance exerted by the dyes prepared could be a highly valuable property.

Thermal stability of the colorants used for the fabrication of color filters should be required to fulfill the post baking process which is generally carried out at 220 °C, therefore the weight reduction of the colorant should be as small as possible at 200 ~ 250 °C by TGA.<sup>17,18</sup> As shown in Table 3, weight reduction of C. I. Pigment Red 254 was 0.69% at 250 °C, whereas synthesized dye **1b-2c** reduced in the range of 0.01 ~ 17.18% at the same temperature. The least stability was observed with dye **1d** containing an *N*-acyl group which can be attributable to the lower bond dissociation energy of acyl group than that of alkyl groups. Similarly, dye **1e** *N*-substituted by an -CH<sub>2</sub>CO<sub>2</sub>Et group also showed comparatively low stability, however the weight

**Table 3.** Weight reduction of C.I. Pigment Red 254 and dyes prepared at different temperature measured by TGA and color difference ( $\Delta E_{ab}$ )

Deve much on	٨E	Weight (%)		
Dye number	$\Delta E_{ab}$	200 °C	250 °C	
<b>1a</b> (C.I. Pigment Red 254)	-	99.51	99.31	
1b	7.7	99.99	99.99	
1c	6.3	99.85	99.66	
1d	2.8	93.36	82.82	
1e	3.1	96.94	95.22	
2b	2.6	99.12	97.72	
2c	2.9	99.32	99.12	

Table 4. Solubility of synthesized dyes

Dye number –	Solubility (g/100 mL)		
	THF	NMP	
1b	7	9	
1c	8	10	
1d	11	12	
1e	10	11	
2b	11	13	
2c	13	14	

reduced only 4.78% indicating a poor thermal stability of the acy group that directly bonded to nitrogen atom in the DPP system. It was observed that dyes **1b** and **1c** tended to be more resistant to heat in comparison with corresponding dyes **2b** and **2c**, which may be correlated to smaller chloro atom forming shorter bond distance than that of CN group. However all dyes containing an *N*-alkyl group exhibited excellent thermal stability at 250 °C which seems to be competent to C. I. Pigment Red 254.

The color difference ( $\Delta E_{ab}$ ) of synthesized dyes was measured after fabrication using a binder then treated at 250 °C for 60 min. As shown in Table 3, dyes **1b** and **1c** most deviated in  $\Delta E_{ab}$ value after heat treatment compared to that of dyes **1d**, **1e**, **2b**, **2c** which was 7.7 and 6.3, respectively. Considering the maximum allowance of  $\Delta E_{ab}$  value at 250 °C is 3.0, other dyes **1d**, **2b** and **2c** can be used as a thermally stable red component replacing the conventional red pigment, as  $\Delta E_{ab}$  value exhibited less than 3.0. However, for dyes **1b**, **1c** and **1d**, the order of stability in  $\Delta E_{ab}$  value conversed with TGA analysis, which can be assumed most likely by the effect of the monomer included in the binder solution. Therefore, in commercial study, the compatibility of dyes with other additives in photo-resist mixture should be optimized by a trial error.

Solubility in THF was determined as  $10 \sim 13$  g/100 mL for dyes **1d**, **1e**, **2b** and **2c**, but other dyes dissolved in smaller amount of  $7 \sim 8$  g/100 mL. The results in NMP were very similar to THF, thus for the same dyes the solubility showed  $11 \sim 14$  g/ 100 mL. It is generally required that dyes should be dissolved in an appropriate solvent at least 10 g/100 mL for ink-jet printing fabrication. Therefore, dyes **1d**, **1e**, **2b** and **2c** could be proper material to manufacture red ink. Results of solubility test in THF and NMP were shown in Table 4.

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As reported in the previous study,<sup>14</sup> introduction of an *N*-alkyl group into the DPP ring resulted in a hypsochromic shift around 15 nm. In this study, the authors can conclude that substitutions by an N-acyl group also exerted a hypsochromic shift of more than 46 nm depending on the place of acyl group which can be explained by both the inductive effect arisen from electron withdrawing groups and the decrease of planarity and conjugation between DPP ring and adjacent phenyl group. However, the replacement of chloro in the p-position of phenyl ring by a CN group, which is stronger electron withdrawing group, combining with an N-alkylation exhibited very similar absorption maxima to that of corresponding red pigment. In terms of chromaticity diagram, the colors of all dyes prepared were yellower than C. I. Pigment Red 254, two dyes containing a CN group at the *p*-position of phenyl ring showed closer values. As expected, all dyes exerted high transmittance at 630 nm which was more than 99.8%.

Thermal stability of dyes **2b** and **2c** revealed to be equivalent to the red pigment by both methods of TGA and  $\Delta E_{ab}$  value. However, dyes containing an *N*-acyl group tended to be poor in TGA analysis due to the low bond dissociation energy.

Solubility in THF and NMP was determined as more than 10 g/100 mL for dyes 1d, 1e, 2b and 2c, which seems to be capable of adaption of ink-jet printing replacing the complicated lithographic method for color filter fabrication.

Therefore, these dyes prepared could be used as an alternative component for conventional red pigment to increase the contrast ratio and brightness which are crucial requirements in LCD color filter sector.

## **Experimental Section**

2-Acetyl-3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4 (2H,5H)-dione (dye 1d). Under nitrogen condition, 3,6-bis(4chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3.56 g, 0.01 mol) and sodium tert-butoxide (2.88 g, 0.03 mol) were dissolved in DMF (150 mL) and stirred for 1 hr at room temperature, then triethylamine (1 g, 0.01 mol), acetyl chloride (1.2 g, 0.015 mol) and  $I_2(0.2 \text{ g}, 0.001 \text{ mol})$  were added. The mixture was heated to 60 °C, further stirred for 15 hrs at the same temperature with regular checking by TLC (stationary phase : silica gel, mobile phase : *n*-hexane/EtOAc = 2/1). When the reaction completed, cooled to room temperature, then ethyl acetate (150 mL) and water (200 mL) were added. The ethyl acetate layer was separated from the aqueous layer, followed by drying with MgSO<sub>4</sub>, anh. (around 10 g) and filtered. Evaporation of the ethyl acetate gave a mixture of mono- and di-substituted products. Subsequent isolation of mono-substituted component (1d) was carried out by adding the crude product to a mixture of n-hexane (30 mL) and chloroform (3 mL). After stirring for a further 5 minutes at the same condition, the precipitated solid was filtered and subsequently washed with a mixture of *n*-hexane (10 mL) and chloroform (3 mL). The filtered solid was dried under a vacuum to obtain dye 1d in 27% yield. C20H12Cl2N2O3, Found C, 60.78; H, 3.12; N, 6.89; O,12.15. Calculated C, 60.17; H, 3.03; N, 7.02; O, 12.02. MS (m/z) 398 (M+).

Other dyes were obtained by same procedure except reaction temperature (40 °C for dye 1e, 75 °C for dyes 2b and 2c).

Notes

Dye **1b** & Dye **1c** : previously reported in reference 14. Dye **1e** Yield : 36%, Found C, 60.24; H, 3.41; N, 6.45; O, 14.22, Calculated C<sub>22</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub> C, 59.61; H, 3.64; N, 6.32;

O, 14.44, MS 442 (M+) Dye **2b** Yield : 26%, Found C, 74.12; H, 5.64; N, 12.78; O,

7.29, Calculated  $C_{28}H_{26}N_4O_2$  C, 74.65; H, 5.82; N, 12.44; O, 7.11, MS 450 (M+)

Dye **2c** Yield : 24%, Found C, 74.25; H, 6.42; N, 12.01; O, 7.04, Calculated C<sub>29</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub> C, 74.98; H, 6.08; N, 12.06; O, 6.89, MS 464 (M+)

**Fabrication of color filter.** In order to measure optical characteristics and thermal stability, spin-coating was carried out onto glass using a MIDAS System SPIN-1200D spin coater. The glass was spun at a low to moderate speed of 300 rpm for 10 sec to evenly spread the solution. The solution was prepared with synthesized dyes, solvent (1-methyl-2-pyrrolidone) and binder based on acrylate polymer. Once spin-coating was completed, the film was placed quickly onto a hot plate (heated to somewhere around 100  $^{\circ}$ C) for 5 min to evaporate the solvent.

**Thermal stability of color filter.** Thermal stability of synthesized dyes after fabrication was measured by a prebaking at 220 °C for 30 min then by a post-baking at 250 °C for 60 min, thereafter color difference in  $\Delta E_{ab}$  was measured.

Solubility test. The synthesized dyes added into tetrahydrofuran (or NMP, 20 mL) then stirred at room temperature for 30 mins. The supersaturated solution was passed 0.45  $\mu$ m syringe filter. Filtered solid not passed was dried at 65 °C then weighed to calculate the dissolved weight of dye.

**PPP-MO.** The PPP-MO method was used to calculate the excitation energy of  $\pi$  electrons between HOMO and LUMO using PISYSTEM<sup>®</sup> Version 6.2.

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