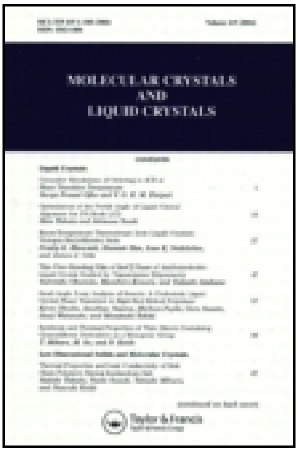

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Se-Hwa Choi [a], Ga-Hye Kil [a], Na-Rim Kim [a], Chun Yoon [b], Jae-Pil Kim [c] & Jae-Hong Choi [a]

[a] Department of Textile System Engineering, Kyungpook National University, Daegu, 702-701, Korea

[b] Department of Chemistry, Sejong University, Seoul, 143-747, Korea

[c] School of Materials Science and Engineering, Seoul National University, Seoul, 151-742, Korea

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Preparation of Thermally Stable Red Dyes Derived from Diketo-Pyrrolo-Pyrrole Pigment for LCD Color Filter

SE-HWA CHOI,[1] GA-HYE KIL,[1] NA-RIM KIM,[1] CHUN YOON,[2]
JAE-PIL KIM,[3] AND JAE-HONG CHOI[1,*]

[1]Department of Textile System Engineering, Kyungpook National University,
Daegu 702-701, Korea
[2]Department of Chemistry, Sejong University, Seoul 143-747, Korea
[3]School of Materials Science and Engineering, Seoul National University,
Seoul 151-742, Korea

6 dyes derived from Diketo-pyrrolo-pyrrole pigment were prepared by introducing an N-*alkyl group, an* N-*acyl group or an* N-*aryl group to the DPP-ring. Absorption maxima, thermal stability by a thermogravimetric analysis (TGA), and the chromatic characteristics of the fabricated films were measured. It was explained that the observed hypsochromic shift and the effects of* N-*substituent on thermal stability of the dyes as well as a chromaticity diagram.*

Keywords Diketo-pyrrolo-pyrrole (DPP); absorption maxima; thermal stability; *N*-acylation; color filter; chromaticity diagram

Introduction

The following pigments, such as C. I. Pigment Red 254, C. I. Pigment Green 36 and C. I. Pigment Blue 15:6, have been used as primary colors (red, green and blue) for LCD color filters, utilizing a photolithographic process [1–4].

C. I. Pigment Red 254, a symmetrical molecule based on DPP, was first developed by Ciba-Geigy, can be widely used for color filters due to its excellent thermal stability and bright shade [5–7]. However, this compound is insoluble in the most of common solvents. The lack of solubility is presumed to result from extensive inter-molecular hydrogen bondings in the solid [8–10], as well as derived in part from π-π stacking, a phenomenon which is obvious from X-ray crystallography [10]. Therefore, the cancellation of the inter-molecular hydrogen bondings via *N*-methylation [11–13] or *N*-arylation [14–16] of DPP yields not only more soluble derivatives (in the order DPP $\gg$ *N*-monomethyl-DPP $\gg$ *N,N'*-dimethyl-DPP), but also less thermal stable analogues.

In general, dyes exhibit superior brightness and contrast ratio compared to those of pigments, however, dyes are poor in thermal resistance and photo-stability. The authors reported [17] that soluble DPP derivatives with thermal stability can be prepared upon *N*-monoalkylation in the DPP ring. The thermal stability of the dyes can greatly attributable

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[*] Corresponding author. E-mail: jaehong@knu.ac.kr

to both the length of carbon chain and their shapes of *N*-alkyl groups in DPP. In particular, dyes substituted by a normal C_8 or C_9 alkyl group exhibited extremely high stability which seems to be competitive to C. I. Pigment Red 254.

In this paper, four electron withdrawing groups were introduced into the DPP-ring so as to compare the absorption maxima, thermal stability and chromaticity values between the dyes based on *N*-alkyl groups (dyes **1** and **2**) and *N*-electron withdrawing groups (dyes **3–6**). Synthesized dyes were measured by an absorption maximum (λ_{max}) and thermal stability using 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 spectrophotometer.

Experimental

Dye Synthesis

Under nitrogen condition, 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3.56 g, 0.01 mol) and sodium *tert*-butoxide (2.88g, 0.03 mol) were dissolved in DMF 150 ml and stirred for 1 hr at room temperature, then triethylamine (1g, 0.01mol), propionyl chloride (1.4g, 0.015 mol) and I_2 (0.2g, 0.001 mol) were added. The mixture was heated to 50°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). After completion of the reaction, iodine was destroyed by adding saturated $Na_2S_2O_3$ aq. solution (5 ml). When the reaction completed, cooled to room temperature, then ethyl acetate (150 ml) and distilled water (200 ml) were added. The ethyl acetate layer was separated from the aqueous layer, followed by drying with $MgSO_4$, anh. (around 10 g) and filtered. Evaporation of the ethyl acetate gave a mixture of mono and di-*N*-substituted products. Subsequent isolation of mono-substituted component (Dye **3**) was carried out by adding the crude product into a mixture of n-hexane (30 ml) and chloroform (3 ml). After stirring for a further 5 minutes in 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 **3** in 38% yield. $C_{21}H_{14}Cl_2N_2O_3$ Found C:60.98 H:3.35 N:6.75 O:11.51, Calculated C:61.03 H:3.41 N:6.78 O:11.61, MS 412.04(M+)

Other dyes were obtained by same procedure except reaction temperature (60°C for dyes **4–5**; room temperature for dye **6**).

Dye **1** & Dye **2** : previously reported in the reference 17.
Dye **4** Yield : 36%, Found C:61.77 H:3.75 N:6.61 O:11.21, Calculated $C_{22}H_{16}Cl_2N_2O_3$ C:61.84 H:3.77 N:6.56 O:11.23, MS 426.05(M+)
Dye **5** Yield : 35%, Found C:62.50 H:4.08 N:6.40 O:10.91, Calculated $C_{23}H_{18}Cl_2N_2O_3$ C:62.60 H:4.11 N:6.35 O:10.88, MS 440.07(M+)
Dye **6** Yield : 37%, Found C:54.98 H:2.22 N:10.65 O:18.23, Calculated $C_{24}H_{12}Cl_2N_4O_6$ C:55.09 H:2.31 N:10.71 O:18.35, MS 522.01(M+)

Structural Analysis

Structural analysis of synthesized dyes were measured using an EA 1108 (E.A.) and an HP 6890 & Agilent 5973N MSD (GC-Mass).

UV-visible absorption spectra were obtained from a Shimadzu UV-2100. The data of the color properties and transmittance spectra were measured using an MCPD 3700.

Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10°C min^{-1} with a Seiko TG/DTA 320 & a SSC 5200H Disk Station.

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 seconds to evenly spread the solution (dye-based ink). The solution was prepared with synthesized dyes, a solvent (1-Methyl-2-pyrrolidone) and a binder based on acrylate. Once spin-coating was completed, the film was placed quickly onto a hot plate (heated to around 100°C) for 5 minutes to evaporate the solvent.

Thermal Stability Test as Color Filter

The thermal stability of synthesized dyes after fabrication was measured by pre-baking at 220°C for 30 min and post-baking at 250°C for 60 min, then color differences in $\triangle E_{ab}$ were determined using an MCPD 3700.

Results and Discussion

As shown in Figure 1, four dyes have been prepared starting from C. I. Pigment Red 254 by a typical S_N2 type acylation (Dye **3–5**) and arylation (Dye **6**) reactions using corresponding acyl/aryl chlorides. Reaction conditions for the formation of *N*-anion of DPP were optimized with a strong base, sodium *tert*-butoxide and a polar aprotic solvent, DMF where insoluble starting material (C. I. Pigment Red 254) was readily dissolved in the reaction mixture. The mixture of *N*-monoacyl/aryl and *N,N'*-diacyl/aryl derivatives was formed thus need to

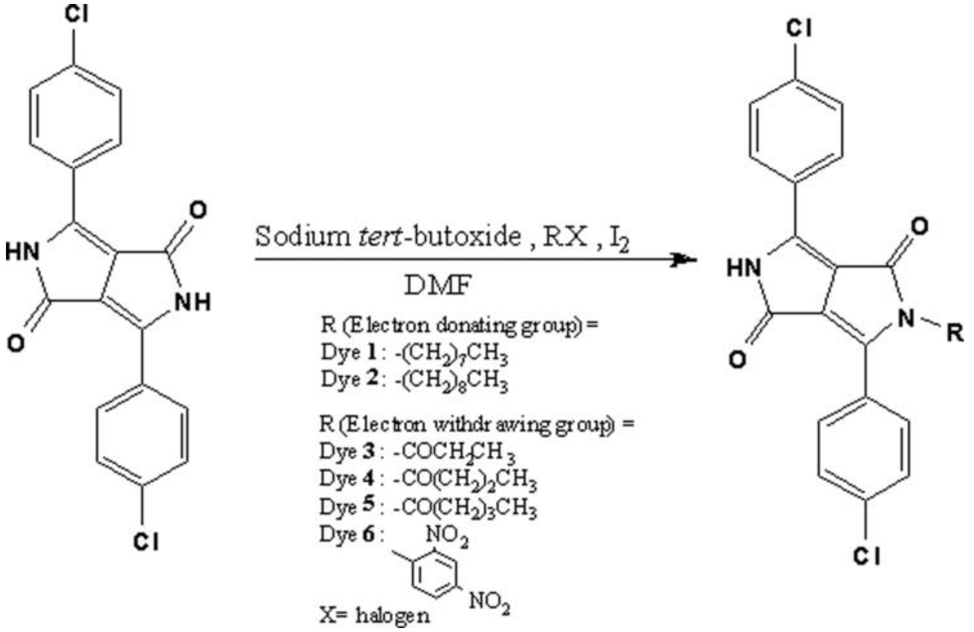

Figure 1.

Table 1. Absorption maxima (λ_{max}) of the synthesized dyes **1–6** and C. I. Pigment Red 254

Dye number	λ_{max} (nm)
Pigment Red 254	516
1	504
2	504
3	461
4	464
5	465
6	476

Determined in 1-Methyl-2-pyrrolidone.

be further separated by a crystallization using with a mixture of n-hexane and chloroform. After separation, the final yield of *N*-monoacyl and aryl products ranged in 35 $\sim$ 38%. A general synthetic procedure is described in Experimental Section.

Comparisons of absorption maxima of C. I. Pigment Red 254 and synthesized dyes **1–6** are listed in Table 1. All dyes **1–6** containing a *N*-substituent absorbed maximally at shorter wavelength compared with that of C. I. Pigment Red 254 that was measured to be 516 nm in 1-methyl-2-pyrrolidone. Both synthesized dye **1** and dye **2** that contain an electron donating group (alkyl group) in the DPP ring exhibited λ_{max} of 504 nm, whereas Dyes **3–6** substituted with an electron withdrawing groups (acyl group for dyes **3–5**, aryl group for dye **6**) in the DPP ring exhibited λ_{max} in the range of 461 $\sim$ 476 nm in 1-methyl-2-pyrrolidone which shifted to much shorter wavelength than those for dyes **1** and **2**. Hypsochromic shift observed with Dyes **1** and **2** 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 [20]. The absorption maxima of dyes **3–5** hypsochromically shifted dramatically in the range of 51 $\sim$ 55 nm in comparison with that of *N*-unsubstituted analogue (C. I. Pigment Red 254). This blue shift could be attributable to the inductive effect arised 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 **1** and **2**, and inductive effect resulted in the destabilized excited state occurred simultaneously. It was also found that the effect of carbon number of acyl group on the absorption maximum to be minimal.

Dye **6** containing an *N*-aryl group exhibited smaller shift compared with dyes **3–5** which may be contributed by the increased conjugation of π-electrons of DPP ring with aryl group leading to smaller energy difference between HOMO and LUMO. Therefore this effect can compensate the negative inductive effect of strong electron withdrawing group exerted by 2,4-dintro group.

As shown in Table 2, chromaticity diagram of all synthesized dyes exhibited smaller x values and higher y values than C. I. Pigment Red 254 indicating the color of synthesized dyes to be overall yellower. It was also found that x values of dyes containing an *N*-alkyl group were higher than those of *N*-acyl and *N*-aryl analogues where dye **6** substituted by stronger electron withdrawing group showed comparatively closer value to dyes **1** and **2**. Similar trend was observed in y values, thus dyes **3–6** exhibited lower y values in comparison with those of dyes **1** and **2**. Among this series, dye **6** seemed to be most similar to that of C. I. Pigment Red 254 in y value.

Table 2. Chromaticity diagram (x,y) and transmittance (%) of the synthesized dyes **1–6** and C. I. Pigment Red 254

	Chromaticity diagram		
Dye number	x	y	Transmittance (%, at 630 nm)
Pigment Red 254	0.577	0.336	98.9
1	0.539	0.448	99.8
2	0.565	0.452	99.8
3	0.408	0.427	100
4	0.393	0.419	99.6
5	0.456	0.432	100
6	0.524	0.401	99.9

Determined in 1-Methyl-2-pyrrolidone.

In terms of transmittance at 630 nm for synthesized dyes, all materials exhibited over 99.6% up to 100% which indicated more efficient transmittance of red light in comparison with C. I. Pigment Red 254 that showed 98.9%. 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 highly valuable property. The relevant values have been summarized in Table 2.

Thermal stability of the colorants used for the fabrication of color filters is one of the crucial requirements to fulfill the post baking process which is generally carried out at 220°C, therefore the weight reduction of colorant should be as small as possible at 200 ∼ 250°C by TGA [18–19]. As shown in Table 3, weight reduction of C. I. Pigment Red 254 was 0.69% at 250°C, whereas synthesized dye **1–6** reduced in the range of 0.01 ∼ 21.53% at the same temperature. As previously reported [17], the dyes **1** and **2** containing a long chain of straight-alkyl group exhibited higher thermal stability (in the range of 0.01 ∼ 0.34%) that seemed to be as equivalent as that of C. I. Pigment Red 254. Comparatively lower stability was observed with dyes **3–5** substituted by an *N*-acyl group, where the stability decreased in order of dye **3** ≫ dye **4** ≫ dye **5**. However, 2,4-dinitrophenyl group

Table 3. Weight reduction of dyes **1–6** and C. I. Pigment Red 254 at different temperature measured by TGA

	Weight (%)	
Dye number	200°C	250°C
Pigment Red 254	99.51	99.31
1	99.99	99.99
2	99.85	99.66
3	97.68	89.45
4	92.62	84.50
5	89.76	78.47
6	98.55	97.83

Table 4. Color difference $\triangle E_{ab}$ of synthesized dyes

Dye number	$\triangle E_{ab}$
1	7.7
2	6.3
3	3.5
4	3.9
5	3.7
6	3.8

present in DPP ring contributed to the increased thermal stability to compare with *N*-acyl groups. Thus the weight reduction of dye **6** was 2.17% which seemed to be very similar to that of C. I. Pigment Red 254. It can be explained that acyl groups have comparatively lower bond dissociation energy than that of alkyl or aryl groups. It was found that as carbon number of *N*-acyl group increases, the thermal stability of the dyes at 250°C decreases that may be due to the decreased intermolecular dispersion forces.

As an alternative method to determine the thermal stability of dyes, the color difference measured in $\triangle E_{ab}$ value after fabrication process was examined, as shown in Table 4. In terms of $\triangle E_{ab}$ value of synthesized dyes, higher color difference (7.7 ∼ 6.3) was found with dyes **1** and **2** those showed lower weight reduction by TGA, whereas smaller $\triangle E_{ab}$ values (3.5 ∼ 3.9) observed for dyes **3–6** containing an electron withdrawing group in DPP. This opposite tendency may be derived from the effects by the monomer and/or binder used in the fabrication process.

Conclusions

In this paper, 6 dyes with *N*-alkyl group, *N*-acyl group or *N*-aryl group in the DPP ring were prepared derived from C. I. Pigment Red 254. The final yield of *N*-monoacyl and aryl products ranged in 35 ∼ 38% after separation from the mixture of mono- and di-substituted derivatives. dyes **1** and **2** that contain an electron donating group (alkyl group) exhibited λ_{max} of 504 nm, whereas Dyes **3–6** substituted with an electron withdrawing groups exhibited λ_{max} in the range of 461 ∼ 476 nm. It can be explained by that both effects of the decrease of planarity and conjugation, and an inductive effect resulted in the destabilized excited state. Dye containing an *N*-aryl group exhibited smaller shift compared with dyes **3–5** which may be contributed by the increased conjugation of π-electrons of DPP ring with aryl group. Chromaticity diagram of all synthesized dyes exhibited smaller x values and higher y values than C. I. Pigment Red 254 indicating the color of synthesized dyes to be overall yellower. In terms of transmittance at 630 nm for synthesized dyes, all materials exhibited over 99.6% up to 100% which indicated more efficient transmittance of red light.

TGA analysis showed that all synthesized dye reduced in the range of 0.01 ∼ 21.53% at 250°C where *N*-alkyl groups exerted higher thermal stability whereas *N*-acyl groups exhibited comparatively lower property which can be mainly attributed to the bond dissociation energy of *N*-substituent. However smaller $\triangle E_{ab}$ values (3.5 ∼ 3.9) observed for dyes **3–6** containing an electron withdrawing group after fabrication of color filter.

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