

Preparation of Solvent Soluble Dyes Derived from Diketo-pyrrolo-pyrrole Pigment by Introducing an *N*-Alkyl group

Se-Hwa Choi, Oh-Tak Kwon, Na-rim Kim, Chun Yoon,[†] Jae-Pil Kim,[‡] and Jae-Hong Choi*

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

*E-mail: jaehong@knu.ac.kr

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

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

Received January 15, 2010, Accepted February 9, 2010

Key Words: Diketo-pyrrolo-pyrrole (DPP), Thermal stability, *N*-Alkylation, Color filter, Solvatochromism

Three primary colors, red, green and blue, for LCD color filters are mainly produced by the corresponding pigments, such as C. I. Pigment Red 254, C. I. Pigment Green 36 and C. I. Pigment Blue 15:6, utilizing a photolithographic process.¹⁻⁴ However the use of pigments can cause both reflection and scattering of the light due to the presence of insoluble pigment particles patterned in the each sub-pixels causing the reduced transmittance of the light, thus gives rise to lower contrast ratio.⁴⁻⁵

In terms of manufacturing process for color filter with pigment based photo resists, there have been a number of patents describing the use of ink jet printing in the fabrication of color filter as a means to reduce the cost of color filter manufacture by avoiding the need for lengthy process and repetition in conventional photolithography.^{4,6-7} As the ink jet printing method requires only one-third the number of manufacturing steps comparing with a photolithography, the soluble dyes for primary colors should be used rather than insoluble pigments. To respond this requirement, some patents⁸⁻¹¹ claimed new anionic azo dyes could be applied to ink jet printing for color filter fabrication.

As a red color, a symmetrical molecule (C. I. Pigment Red 254) based on Diketo-pyrrolo-pyrrole (DPP), which was first

synthesized by Ciba-Geigy, has been usually used due to its excellent thermal stability and bright red shade.¹²⁻¹⁴ Single crystal X-ray structural studies¹⁴⁻¹⁶ on DPP clearly reveal the existence of chains of hydrogen bonds between the N-H of one molecule and the oxygen of another molecule which mainly contributes to excellent thermal stability and lack of solubility in most solvents. Therefore, the cancellation of the intermolecular hydrogen bonding *via N*-methylation¹⁶⁻¹⁸ or *N*-arylation^{19,20} of DPP yields not only more soluble derivatives, in the order DPP \ll *N*-monomethyl-DPP \ll *N,N'*-dimethyl-DPP, but also less thermal stable analogues.

In the previous study,²¹ the authors reported that increase of color purity by using additive pigments, C. I. Pigment Red 177, C. I. Pigment Yellow 150 and C. I. Pigment Violet 23, gives rise to undesirable decrease of brightness indicating the need of new soluble dyes which give high level of robustness. This paper builds on the aforementioned study, reporting work in which 10 new dyes with C₂-C₉ *N*-alkyl functions in the DPP ring have been synthesized (see Figure 1) and characterized using elemental analysis. The absorption characteristics of the synthesized dyes in the visible region as well as their fluorescence emission spectra have been investigated. Thermal stability of the dyes has also been determined by a thermogravi-

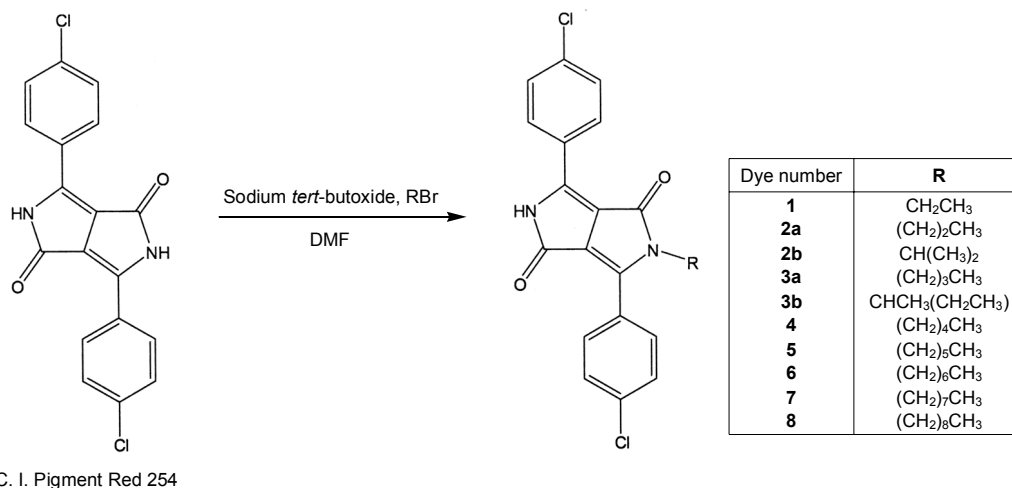


Figure 1. Synthetic scheme and the structures of the dyes 1-8 prepared.

Table 1. Absorption maxima of the synthesized dyes **1-8** in different solvents

Dye number	λ_{\max} (nm)			
	Chloroform	Acetone	Ethanol	DMF
1	497	495	493	501
2a	498	496	492	500
2b	495	492	489	499
3a	498	496	493	502
3b	495	494	491	498
4	498	495	493	501
5	497	493	487	500
6	496	496	492	501
7	496	497	491	501
8	496	495	491	500
Red 254	516 ^a			

^aDetermined in 1-Methyl-2-pyrrolidone

metric analysis (TGA) comparing with that of C. I. Pigment 254.

As shown in Figure 1, 10 dyes have been prepared starting from C. I. Pigment Red 254 by a conventional S_N2 type alkylation reaction using C₂-C₉ alkyl bromides. Optimum conditions for the formation of *N*-anion of DPP were observed with a strong base, sodium *tert*-butoxide and a polar aprotic solvent, DMF where insoluble starting material was readily dissolved in the reaction mixture. Irrespective of amount of alkyl bromide, the mixed products, such as *N*-monoalkyl and *N,N'*-dialkyl derivatives, were formed together need to be further separated by a crystallization in a mixture of *n*-hexane and chloroform. Therefore the final yield of *N*-monoalkyl products ranged in 21 ~ 33%. A general synthetic procedure is described in Experimental Section.

As previously mentioned, the starting material is sparingly soluble in most solvents, but the mono-*N*-alkylated analogues **1-8** were found to have an appropriate solubility in 4 kinds of organic solvents which might be expected to have properties intermediate between C. I. Pigment Red 254 and corresponding *N,N'*-dialkyl derivatives. As shown in Table 1, absorption maxima of the dyes **1-8** were in the range of 495 ~ 498 nm in CHCl₃, whereas 498 ~ 502 nm in DMF, indicating very small effect of the carbon numbers of *N*-alkyl groups on the absorption maximum. Furthermore, the dyes **2a**, **3a** containing a normal group of C₃ or C₄ tended to have a small red shift comparing to corresponding dyes **2b**, **3b** substituted by a branched group, but the small extent of the shifts were observed.

The effect of a solvent upon the color of a dye can be generally explained by a solvatochromism, i. e. bathochromic and hypsochromic shifts of bands with increasing solvent polarity.²² Generally, in many dye molecules, the ground state is less polar than the excited state so that a polar solvent will tend to stabilize the excited state more than the ground state, leading to a bathochromic shift in the absorption maximum. For a series of dyes **1-8**, the absorption maxima tend to shift hypsochromically in both acetone and ethanol those have a similar dielectric constant. These shifts can be attributed to a stabilization effect of the ground state of the dyes by hydrogen bonding between the solvent and N-H group in the DPP molecule. Existence of O-H group in ethanol resulted in more hypsochromic shifts, ranged

Table 2. Substituent effects on the absorption (λ_{\max}) and fluorescence spectra (F_{\max}) of the synthesized dyes **1-8** determined in CHCl₃

Dye number	λ_{\max} (nm) Absorption	F_{\max} (nm) Emission	Stokes shifts (nm)	Transmittance (% at 630 nm)
1	497	524	27	99.99
2a	498	523	25	99.68
2b	495	524	29	99.82
3a	498	528	30	99.49
3b	495	525	30	99.68
4	498	511	13	100.0
5	497	526	29	100.0
6	496	512	16	99.34
7	496	511	15	99.91
8	496	521	25	100.0

in 2 to 6 nm, comparing to those of acetone. However, in polar aprotic solvent, DMF, red shifts were exerted by the stabilization effect of the excited state of the dyes which can be attributed to the higher polarity of the solvent. It was also found that the introduction of an *N*-alkyl group in the DPP ring led to hypsochromic shifts comparison with unsubstituted analogue, as shown in Table 1. For example, dye **7** and dye **8** absorbed maximally at 504 nm in *N*-methyl-2-pyrrolidone, whereas unsubstituted analogue absorbed at 516 nm.

The color of DPP system arises not only from the fundamental chromophore but also from π - π stacking, thus DPP derivatives are red in the solid state, whereas are yellow in dilute solution with a fluorescence.^{19,23,24} The observed Stokes shifts for dyes **1-8**, as shown in Table 2, were in the range of 13 ~ 30 nm which seemed to be larger than similar DPP derivatives containing unsubstituted -NH groups, but to be much smaller values than *N,N'*-disubstituted derivatives, for example, Stokes shift of 11 nm was reported for unsubstituted DPP, whereas *N,N*-dimethylated analogue exhibited a greater shift of 43 nm.²⁴⁻²⁶ In this series, the most shifts were found in dyes **2b**, **3a**, **3b**, **5** which indicated their smaller difference of energy between the lowest vibrational level of the excited state S₁ and vibrational levels of the ground state comparing to other dyes.

In terms of transmittance at 630 nm for synthesized dyes, all materials exhibited over 99.34% up to 100% for dyes **4**, **5**, **8** which indicated more efficient transmittance of red light in comparison with C. I. Pigment Red 254 that showed 98.98%. The relevant values have been summarized in Table 2.

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 250 °C, therefore the weight reduction of colorant should be as small as possible at 250 ~ 300 °C by TGA. In case of C. I. Pigment Red 254, the weight reduced 0.69% at 250 °C, as summarized in Table 3, whereas synthesized dyes **1-8** reduced in the range of 0.01 ~ 16.3% at the same temperature. The dyes **7**, **8** *N*-substituted by a longer alkyl group exhibited higher thermal stability that seemed to be as equivalent as that of C. I. Pigment Red 254. Comparatively lower stability was observed with dyes **2b**, **3b** contained a branched substituent. In comparison with corresponding dyes **2a**, **3a** containing an *N*-normal alkyl group at 250 °C, more weight reductions, 5.3% and 9.5%, respectively, occurred. It can be best explained that branched-chain alkyl groups are

Table 3. Weight reduction of dyes **1-8** and C. I. Pigment Red 254 at different temperature measured by TGA

Dye number	Weight (%)			
	200 °C	250 °C	300 °C	350 °C
C. I. Pigment Red 254	99.51	99.31	99.03	97.79
1	96.35	90.82	79.27	61.90
2a	92.61	88.98	82.34	58.16
2b	94.21	83.66	74.87	56.40
3a	98.44	94.05	86.10	64.34
3b	94.68	84.56	73.91	62.73
4	95.68	94.41	92.23	81.40
5	99.33	96.23	81.87	54.48
6	99.99	98.51	87.45	63.90
7	99.99	99.99	96.43	81.96
8	99.85	99.66	98.84	94.56

more nearly spherical than straight-chain alkyl groups, leading to smaller surface areas, and consequently smaller dispersion forces between dye molecules. It was also found that as carbon number of *N*-alkyl group increases, the thermal stability of the dyes at 250 °C increases that is also due to the increased intermolecular dispersion forces. Assuming these results, the carbon number and their shapes of *N*-alkyl groups in DPP system would highly affect the resultant thermal stability.

In this report, the authors can conclude that 10 new dyes with C₂-C₉ *N*-alkyl functions in the DPP ring have been prepared by *N*-alkylation with corresponding alkyl bromides where desired mono-alkylated products were readily separated from the mixture with di-alkylated analogues by crystallization. The synthesized dyes were soluble in organic solvents exhibiting absorption maxima of 495 ~ 498 nm in CHCl₃, thus the effect of *N*-alkyl groups onto absorption maximum seemed to be minimal. The observed Stokes shifts for synthesized dyes were in the range of 13 ~ 30 nm which was intermediate between corresponding *N,N'*-unsubstituted DPP derivatives and *N,N'*-disubstituted analogues. The thermal stability of the dyes can be highly contributed by both the carbon number and their shapes of *N*-alkyl groups in DPP, in particular dyes substituted by a normal C₈ or C₉ alkyl group exhibited extremely high stability. Therefore these dyes could be used as an alternative soluble red color for the fabrication of color filter.

Experimental Section

2-Butyl-3,6-bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3a). Under nitrogen condition, 3,6-bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3.56g, 0.01 mol) and sodium *tert*-butoxide (2.53 g, 0.025 mol) were dissolved in DMF 150 mL and stirred for 1 hr at room temperature, then 1-bromobutane (3.45 g, 0.025 mol) was added. The mixture was heated to 60 °C, further stirred for 20 hr 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 distilled water (200 mL) were added. Ethyl acetate layer was separated from the aqueous layer, followed

by drying with MgSO₄, anhyd. (around 10 g) and filtered. Evaporation of the ethyl acetate gave a mixture of mono and di-alkylated products. Subsequent isolation of mono-alkylated component (**3a**) was carried out by adding the crude product to a mixture of *n*-hexane (30 mL) and chloroform (3 mL). After stirring for 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 vacuum to obtain dye **3a** in 27% yield. C₂₂H₁₈Cl₂N₂O₂, Found C, 63.78; H, 4.42; N, 6.59, Calculated C, 63.93; H, 4.39; N, 6.78, MS (*m/z*) 412(M⁺).

Other dyes were obtained by same procedure except reaction temperature (room temperature for dye **1**, 60 °C for dyes **2-5**; 80 °C for dyes **6-8**).

Dye 1: Yield: 24%, C₂₀H₁₄Cl₂N₂O₂, Found C, 62.05; H, 3.64; N, 7.16, Calculated C, 62.35; H, 3.66; N, 7.27, MS (*m/z*) 384(M⁺).

Dye 2a: Yield: 30%, C₂₁H₁₆Cl₂N₂O₂, Found C, 62.95; H, 4.06; N, 7.01, Calculated C, 63.17; H, 4.04; N, 7.02, MS (*m/z*) 398(M⁺).

Dye 2b: Yield: 21%, C₂₁H₁₆Cl₂N₂O₂, Found C, 63.05; H, 4.01; N, 6.95, Calculated C, 63.17; H, 4.04; N, 7.02, MS (*m/z*) 398(M⁺).

Dye 3b: Yield: 25%, C₂₂H₁₈Cl₂N₂O₂, Found C, 63.64; H, 4.47; N, 6.64, Calculated C, 63.93; H, 4.39; N, 6.78, MS (*m/z*) 412(M⁺).

Dye 4: Yield: 27%, C₂₃H₂₀Cl₂N₂O₂, Found C, 64.61; H, 4.83; N, 6.51, Calculated C, 64.05; H, 4.72; N, 6.56, MS (*m/z*) 426(M⁺).

Dye 5: Yield: 31%, C₂₄H₂₂Cl₂N₂O₂, Found C, 65.90; H, 5.10; N, 6.43, Calculated C, 65.31; H, 5.02; N, 6.35, MS (*m/z*) 440(M⁺).

Dye 6: Yield: 32%, C₂₅H₂₄Cl₂N₂O₂, Found C, 66.49; H, 5.26; N, 6.23, Calculated C, 65.94; H, 5.31; N, 6.15, MS (*m/z*) 454(M⁺).

Dye 7: Yield: 33%, C₂₆H₂₆Cl₂N₂O₂, Found C, 66.79; H, 5.63; N, 6.01, Calculated C, 66.53; H, 5.58; N, 5.97, MS (*m/z*) 468(M⁺).

Dye 8: Yield: 29%, C₂₇H₂₈Cl₂N₂O₂, Found C, 66.92; H, 5.89; N, 5.70, Calculated C, 67.08; H, 5.84; N, 5.79, MS (*m/z*) 482(M⁺).

Acknowledgments. This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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