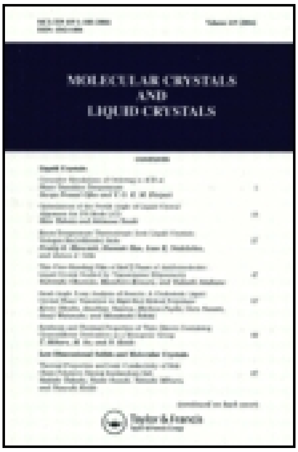

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Preparation of Red Dyes Derived from Quinacridone Pigment by Introducing N-substituent and Their Characteristics as a Colorant for LCD Color Filter

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Preparation of Red Dyes Derived from Quinacridone Pigment by Introducing *N*-substituent and Their Characteristics as a Colorant for LCD Color Filter

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Six red dyes derived from quinacridone pigment (C. I. Pigment Red 122) were prepared by introducing an N-*alkyl group or* N-*acyl group in the quinacridone ring. The characteristics of the synthesized dyes were examined by absorption maxima, solubility and thermogravimetric analysis (TGA). The introduction of* N-*alkyl group gave very little bathochromic shift of 2∼3 nm, whereas the presence of a withdrawing group at the nitrogen exhibited a large hypsochromic shift of 60∼45nm comparing to that of C. I. Pigment Red 122 which is unsubstitued at the nitrogen atom. In terms of weight reduction at 250°C,* N-*alkyl groups withstood to the thermal decomposition in comparison with the behavior of withdrawing groups at the position of nitrogen atom. The solubility of six dyes was dramatically increased by the introduction of* N-*substituent which clearly indicates their character as a dye rather than a pigment.*

Keywords Absorption maximum; *N*-acylation; *N*-alkylation; quinacridone(QA); solubility; thermal stability

Introduction

The LCD (Liquid Crystal Display) has become an important display device in mobiles, monitors and high-definition televisions, which requires high resolution and color properties for big screen size [1–4]. The color filter consists of red, green, and blue color pixels that can be manufactured by a photolithographic process using photo resists containing polymeric binder, dispersant and corresponding pigment [5].

These days, ink-jet printing method using conventional pigment-based inks has been studied to simplify the complicated process and to reduce manufacturing cost of LCD color filters [6–8]. However, this method has the limitation due to the blocking of ink-jet nozzles as well as low chromatic properties of pigment particles. In order to solve these problems,

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an ink-jet printing method where dyes are used for higher solubility and superior color saturation property has been proposed as an alternative [9].

In the previous study [10], the authors reported the preparation of new red dyes containing *N*-substituent in the DPP (diketo pyrrolo pyrrole) ring starting from commercial red pigment (C. I. Pigment Red 254). The thermal stability of the dyes prepared can be greatly increased by both the carbon number and their shapes of *N*-alkyl group in DPP ring, which exhibited extremely high stability up to 250°C. However, absorption maxima of the synthesized dyes shifted to slightly shorter wavelengths than commercially used red pigment. In this study, six new red dyes were prepared in order to obtain appropriate absorption maximum in the range of 520∼530 nm.

Quinacridone and its derivatives have been widely used as organic pigments and they display excellent fastness properties as well as pronounced photovoltaic and photoconductive activities [11, 12]. Their low solubility and high thermal stability of quinacridones are attributed to strong intermolecular H-bonding between the favorably positioned C=O and NH groups, as corroborated by X-ray analysis and by the observation that the solubility of *N*-mono- and *N,N'*-di-alkylated quinacridone strongly increase, the latter being completely soluble [13].

This paper builds on the aforementioned study, reporting work in which six new dyes have been synthesized (see Fig. 1) and characterized using an elemental analysis. The absorption characteristics and solubility of the synthesized dyes have been investigated. Thermal stability of the dyes has also been determined by a thermogravimetric analysis (TGA), comparing with that of C. I. Pigment Red 122.

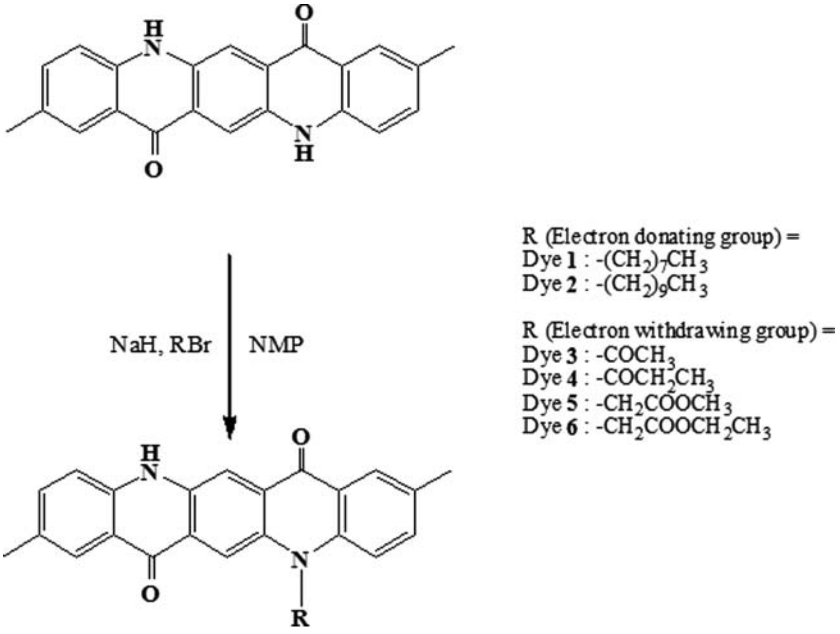

Figure 1. Synthetic scheme and the structures of dyes **1**–**6**.

Experimental

Dye Synthesis

2,9-dimethyl-5-octylquinolino[2,3-b]acridine-7,14(5H,12H)-dione (*dye* ***1***). 2,9-dimethyl-5-octylquinolino[2,3-b]acridine-7,14(5H,12H)-dione (3.4 g, 0.01 mol) and sodium hydride (0.6 g, 0.025 mol) were dissolved in NMP (*N*-Methyl-2-pyrrolidone) 100 ml and stirred for two hours at room temperature, then 1-bromooctane (3.86 g, 0.02 mol) was added. The mixture was heated to 70°C, further stirred for 20 hours at the same temperature with regular checking by thin layer chromatography (TLC) (stationary phase : silica gel, mobile phase : EtOAc/n-hexane = 2/1). When the reaction completed, the mixture was 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. (20 g) and filtered. Evaporation of the ethyl acetate gave a mixture of mono- and di-alkylated products. Subsequent isolation of the mono-alkylated component (dye **1**) was carried out by adding the crude product to a mixture of n-hexane (50 ml) and chloroform (5 ml). After stirring for further 30 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 **1**. The data of structural analysis for synthesized dyes are summarized in Table 1 using a mass spectrometry, elemental analysis and ^1H nuclear magnetic resonance spectroscopy.

Fabrication of color filter. In order to measure optical characteristics, 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 500 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°C) for 5 min to evaporate the solvent.

UV-visible absorption of color filter. UV-visible absorption of synthesized dyes after fabrication using a mixture of resins based on benzyl methacrylate (70%) and methacrylate (30%) was measured.

Structural Analysis

Structural analysis of synthesized dyes were measured using an EA 1108 (Elemental Analysis) and an HP 6890 & Agilent 5973N MSD (GC-Mass). ^1H-NMR spectra were recorded at 25°C on a NMR 400-MHz spectrometer (Bruker, Germany) with $CDCl_3$ as a solvent. UV-visible absorption spectra were obtained from a Shimadzu UV-2100. 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.

Results and Discussion

As shown in Table 2, the absorption maxima (λ_{max}) of the prepared dyes **1**–**6** were in the range of 469∼532 nm in PGMEA(propylene glycol monomethyl ether acetate). Dyes containing an electron withdrawing group at the position of nitrogen atom in the quinacridone ring absorbed maximally at shorter wavelength of 20∼60 nm compared to that of C. I. Pigment Red 122 which was measured to be 529 nm in PGMEA. In the series of dyes **3**–**6**, bigger

Table 1. Analytical data for the synthesized dyes **1**–**6**

Dye number	Yield (%)	MS MS (*m/z*)	Elemental Analysis	^{1}H-NMR (δ, ppm, in CDCl$_3$)
1	21	452	Calculated for $C_{30}H_{32}N_2O_2$ C:79.61 H:7.13 N: 6.19 O:7.07 Found C:79.45 H:7.76 N:6.59 O:7.12	0.86(s, 3H), 1.27(s, 2H), 1.30(s, 2H), 1.51(s, 2H), 2.34(s, 3H) 3.92(s, 2H), 4.0(s, 1H), 6.57(m, 1H), 6.60(m, 1H), 6.66(m, 1H) 6.72(m, 1H), 7.18(m, 1H), 7.21(m, 1H), 7.25(m, 1H), 7.27(m, 1H)
2	23	480	Calculated for $C_{32}H_{36}N_2O_2$ C:79.96 H:7.55 N:5.83 O:6.66 Found C:80.12 H:7.58 N:5.96 O:6.61	0.87(s, 3H), 1.25(s, 2H), 1.27(s, 2H), 1.29(s, 2H), 1.47(s, 2H), 2.34(s, 3H) 3.93(s, 2H), 4.0(s, 1H), 6.56(m, 1H), 6.61(m, 1H), 6.66(m, 1H) 6.72(m, 1H), 7.17(m, 1H), 7.19(m, 1H), 7.23(m, 1H), 7.27(m, 1H)
3	38	382	Calculated for $C_{24}H_{18}N_2O_3$ C:75.38 H:4.74 N:7.33 O:12.55 Found C:75.26 H:4.86 N:7.45 O:13.74,	2.01(s, 3H), 2.34(s, 3H), 4.0(s, 1H), 6.60(m, 1H), 6.93(m, 1H), 7.15(m, 1H), 7.22(m, 1H), 7.43(m, 1H), 7.46(m, 1H), 7.80(m, 1H), 7.88(m, 1H)
4	36	396	Calculated for $C_{25}H_{20}N_2O_3$ C:75.74 H:5.08 N:7.07 O:12.11 Found C:76.98 H:5.13 N:6.98 O:12.52,	1.02(s, 3H), 2.31(s, 2H), 2.36(s, 3H), 4.0(s, 1H), 6.60(m, 1H), 6.93(m, 1H), 7.19(m, 1H), 7.26(m, 1H), 7.42(m, 1H), 7.49(m, 1H), 7.80(m, 1H), 7.85(m, 1H)
5	28	412	Calculated for $C_{25}H_{20}N_2O_4$ C:72.80 H:4.89 N:6.79 O:15.52 Found C:73.11 H:4.78 N:6.68 O:15.39	2.33(s, 3H), 3.70(s, 3H), 4.0(s, 1H), 4.02(s, 2H), 6.59(m, 1H), 6.63(m, 1H), 6.68(m, 1H) 6.70(m, 1H), 7.17(m, 1H), 7.21(m, 1H), 7.24(m, 1H), 7.28(m, 1H)
6	25	426	Calculated for $C_{26}H_{22}N_2O_4$ C:73.23 H:5.20 N:6.57 O:15.01 Found C:74.86 H:5.31 N:6.42 O:15.20	1.31(s, 3H), 2.34(s, 3H), 4.0(s, 1H), 4.02(s, 2H), 4.16(s, 2H), 6.60(m, 1H), 6.61(m, 1H), 6.68(m, 1H) 6.74(m, 1H), 7.17(m, 1H), 7.22(m, 1H), 7.24(m, 1H), 7.27(m, 1H)

hypsochromic shifts were observed with dyes **3** and **4** substituted by an *N*-carbonyl group compared to those of dyes **5** and **6** substituted by a *N*-$CH_2CO_2CH_3$ or *N*-$CH_2CO_2CH_2CH_3$ group. In particular, absorption maxima of dyes **3** and **4**, those *N*-substituted with an alkyl carbonyl group in the quinacridone ring, hypsochromically shifted in the range of 60∼57 nm in comparison with that of *N*-unsubstituted analogue (C. I. Pigment Red 122). This blue shift can be attributable to the inductive effect arisen from the presence of electron withdrawing group (acyl group) at the nitrogen atom that led to the destabilized excited state. In this case, both effects causing the decrease of planarity and conjugation system [14], which was observed with dyes **3** and **4**, and an inductive effect resulting in a destabilized excited state occurred simultaneously. However, smaller hypsochromic shifts were found in λ_{max} of dye **5** and **6** which due to their weaker electron withdrawing power of *N*-substituent compared to that of corresponding dyes **3** and **4** (acyl group).

In contrast, both dyes **1** and dye **2** containing an electron donating group (alkyl group) in the quinacridone ring exhibited λ_{max} at 531 nm and 532 nm, respectively, which are very

Table 2. Absorption maxima of the synthesized dyes **1–6**

Dye number	λ_{max} (nm)^1	λ_{max} (nm)^2
C. I. Pigment Red 122	529	530
1	531	533
2	532	535
3	469	472
4	472	476
5	509	512
6	509	511

λ_{max} (nm)^1: determined in propylene glycol monomethyl ether acetate (PGMEA)

λ_{max} (nm)^2: determined in solid state using by mixed resins of benzyl methacrylate(70%)/methacrylate(30%)

similar to that of the *N*-unsubstituted analogue (C. I. Pigment Red 122). The minimal effect on absorption maximum exerted by an *N*-alkyl group can indicate that the contribution of alkyl group to the stabilization of the excited state of *N*-substitued dye was very small which can be attributable to their weak electron donating power.

For the measurement of the absorption maxima for synthesized dyes **1–6** at solid state, each dyes has been fabricated on the glass substrate using a spin coater. The absorption maximum of C. I. Pigment Red 122 exhibited at 530 nm, whereas those of the dyes **1–6** were in the range of 472~535 nm at solid state. The dyes **1–2**, substituted with an electron donating group (alkyl group) in the quinacridone ring exhibited λ_{max} of 533 and 535 nm, respectively, which were very similar to that of C. I. Pigment Red 122. The dyes **5** and **6**, substituted with an electron withdrawing group (ester group) in the quinacridone ring, also exerted a hypsochromic shift that maximally absorbed at 512 nm and 511 nm, respectively. As same as measured in PGMEA solvent, the absorption maxima of dyes **3** and **4**, containing a stronger electron withdrawing group, were observed to be 472 nm and 476 nm, respectively, which were greater hypsochromic shifts compared to that of C. I. Pigment Red 122.

Table 3. Weight reduction of dyes **1–6** and C. I. Pigment Red 122 at different temperature measured by TGA

	Weight (%)	
Dye number	200°C	250°C
C. I. Pigment Red 122	99.50	99.49
1	97.05	95.99
2	98.07	97.33
3	94.06	87.80
4	93.51	90.69
5	86.08	88.45
6	93.40	91.16

Table 4. Solubility of synthesized dyes **1–6**

	Solubility (g/100 mL)	
Dye number	NMP	PGMEA
1	7	6
2	9	8.5
3	4	8
4	5	10
5	5	6
6	7	7

Determined in NMP and PGMEA

In this series of the synthesized dyes, therefore, dyes **1** and **2** could be used as a red component for mill-base in LCD color filter fabrications due to their similar optical properties to that of C. I. Pigment Red 122.

Thermal stability of the colorants used for the fabrication of color filters should be required to fulfill the post baking condition, which is generally carried out at 230°C. Therefore, the weight reduction of colorant should be as small as possible at 200∼250°C by TGA [15]. In case of C. I. Pigment Red 122, the weight reduced 0.51% at 250°C, as summarized in Table 3, whereas synthesized dyes **1–6** reduced in the range of 2.67∼17.55% at the same temperature. Both dye **1** and **2** that *N*-substituted by an alkyl group exhibited higher thermal stability than that of the dyes containing *N*-carbonyl group. The least stability was observed with dye **3**, containing an *N*-acyl group, which can be attributable to the lower bond dissociation energy of acyl group than that of alkyl groups. Similarly, dyes **5–6** *N*-substituted by ester group also showed comparatively low thermal stability. However, dyes containing an *N*-alkyl group exhibited good thermal stability at 250°C which seems to be similar with C. I. Pigment Red 122.

The solubility of the dyes **1–6** in NMP and PGMEA are listed in Table 4. Solubility in PGMEA was determined as 8∼10 g/100 ml for dyes **2–4**, but other dyes were soluble in smaller amounts of 6∼7 g/100 ml. There was a tendency of the introduction of an acetyl group improves the solubility. The most soluble values measured in NMP were observed for dyes **1** and **2** where their solubility was 7 and 9 g/100 ml, respectively. However, lower solubility was observed with dyes **3–5**. By considering the general requirement that dyes should be soluble in an appropriate solvent around 10 g/100 ml for the ink-jet printing fabrication. Therefore, in terms of solubility, the dyes **2–4** could be promising materials to replace the conventional insoluble pigment, such as C. I. Pigment Red 122.

Conclusions

In this study, six red dyes containing an *N*-alkyl group, *N*-acyl group or *N*-ester group in the quinacridone ring were prepared starting from C. I. Pigment Red 122. The synthesized dyes exhibited absorption maxima of 469∼532 nm in PGMEA, whereas 472∼535 nm in solid state. Dyes **1** and **2** that contain an electron donating group (alkyl group) exhibited λ_{max} of 531 nm and 532 nm, respectively, which are very similar to that of the starting analogue, whereas dyes **3–6** substituted with an electron withdrawing group exhibited λ_{max} in the range of 469∼509 nm in PGMEA. This hypsochromic shift can be explained by that both effects of the decrease of planarity and conjugation, and an inductive effect resulted in the destabilized excited state.

In case of C. I. Pigment Red 122, the weight reduced 0.5% at 250°C, whereas synthesized dyes **1–6** reduced in the range of 2.6∼17.5% at the same temperature. Both dye **1** and **2** that *N*-substituted by an alkyl group exhibited higher thermal stability than that of the dyes containing *N*-carbonyl group.

Solubility of synthesized dyes in PGMEA and NMP was determined as 8∼10 g/100 ml for dyes **2–4**, but other dyes were soluble in smaller amounts of 6∼7 g/100 ml. Therefore, these dyes **2–4** could be used as red component to replace the conventional red pigment for the ink-jet fabrication method.

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