

Table 1. Solubility of synthesized dyes **1-3** and C.I. Pigment Red 254 at 25 °C in PGMEA

Dye number	Solubility (g/100 mL)
C.I. Pigment Red 254	-
1	0.23
2	0.54
3	14.4

Table 2. Absorption maxima (λ_{\max}) of the synthesized dyes **1-3**, *N*-alkylated Red 254 and C.I. Pigment Red 254

Dye number	λ_{\max} (nm)
C.I. Pigment Red 254	516
<i>N</i> -alkylated Red 254 (Octyl)	504
1	542
2	534
3	527

^aDetermined in NMP (1-Methyl-2-pyrrolidone).

resists, obviating the need for the conventional salt-milling process.

The absorption maxima of C.I. Pigment Red 254 and synthesized dyes **1-3** were determined in NMP, as shown in Table 2. The absorption maximum of *N*-alkylated Red 254 is 504 nm, whereas that of C.I. Pigment Red 254 is 516 nm, as reported in our previous study.¹³ In contrast to the hypsochromic shift of the *N*-alkylated Red 254 analogue compared to C.I. Pigment Red 254, as mentioned above, bathochromic shifts were consistently found with synthesized dyes **1**, **2** and **3**, which absorb at 542, 534, and 527 nm, respectively. These bathochromic shifts are mainly due to the extension of the π -conjugated systems through dimerization of DPP. Further spectral comparisons within the set of dyes **1-3** show that lengthening the linking chains leads to hypsochromic shifts in absorption maximum which can be best explained by the diminished symmetry caused by the extended $-(\text{CH}_2)-$ units.

The chromaticity coordinate values of the spin coated dye-based solutions are summarized in Table 3 and compared to those of C.I. Pigment Red 254. The chromaticity diagram of films from dyes **1-3** exhibited smaller *x* values but larger *y* values than those of C.I. Pigment Red 254 indicating the color shade of synthesized dyes to be yellowish red. In contrast, *x* and *y* values were higher for dyes **1-3** than those of the *N*-monoalkylated Red 254 analogue.

The thermal stability of the colorants used for the fabrication of color filters must be such that they can withstand 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 these kinds of temperature as measured by TGA.^{11,15-17} In the case of C.I. Pigment Red 254, weight reduction was determined to be 0.57 wt % at 230 °C, as shown in Table 4, whereas the weight reduction of the synthesized dyes **1**, **2** and **3** was 1.94%, 1.16%, and 1.52% at 230 °C, respectively. Thus, on the basis of the TGA results, it can be assumed that dyes **1-3** have similar thermal stability

Table 3. Chromaticity co-ordinates (*x*, *y*) of the synthesized dyes **1-3**, *N*-alkylated Red 254 and C.I. Pigment Red 254

Dye number	Chromaticity co-ordinates	
	<i>x</i>	<i>y</i>
C.I. Pigment Red 254	0.588	0.331
<i>N</i> -alkylated Red 254 (Octyl)	0.368	0.361
1	0.387	0.395
2	0.411	0.412
3	0.570	0.425

Table 4. Weight reduction of the dyes **1-3**, *N*-alkylated Red 254 and C.I. Pigment Red 254 at different temperatures measured by TGA

Dye number	Weight (%)	
	230 °C	250 °C
C.I. Pigment Red 254	99.43	99.31
<i>N</i> -alkylated Red 254 (Octyl)	99.99	99.99
1	98.06	96.95
2	98.84	97.68
3	98.48	97.28

Table 5. Comparisons of the color difference (ΔE_{ab}) of films containing synthesized dyes **1-3**, *N*-alkylated Red 254 and C.I. Pigment Red 254 before and after post-baking treatment

Dye number	ΔE_{ab}
C.I. Pigment Red 254	1.65
<i>N</i> -alkylated Red 254 (Octyl)	7.75
1	5.85
2	4.06
3	3.43

to C.I. Pigment Red 254.

In order to develop a more effective method for determining the thermal stability of the dyes in LCD filter applications, the color difference (ΔE_{ab}) value brought about by the fabrication process was examined as shown in Table 5. Industry requires that, for the post baking process at 220 °C followed by a further thermal treatment at 240 °C, ΔE_{ab} should be less than 3. The highest color difference value (7.75) was found, as expected, with *N*-alkylated Red 254, presumably as a consequence of its smaller molecular weight causing more sublimation to occur during the post baking treatment. The dimeric DPP dyes **1-3**, however, exhibited improved thermal stability in the range ΔE_{ab} 3.43-5.85. The size of this difference appears related to molecular weight: an increase in the latter led to a reduction in the former, presumably as the tendency to sublime is diminished. Although ΔE_{ab} values, particularly for dye **3**, are marginally lower than that of C.I. Pigment Red 254, it is likely that further enhancements will be possible through use of longer groups to link the two DPP systems.

In summary, three dyes containing a linking (specifically, methyl, butyl or octyl), connecting two DPP systems, were prepared starting from C.I. Pigment Red 254 through *N*-

alkylation followed by a typical S_N2 reaction. Dyes **1** and **2** had limited solubility, whereas dye **3**, based on an octyl linking group exhibited dramatically increased solubility in PGMEA which is required if an alternative manufacturing process is to replace the conventional milling method of insoluble pigments. The absorption maxima of synthesized dyes **1-3** were in the range 527-542 nm in NMP and consistently red-shifted compared to that of *N*-alkylated Red 254 mainly due to the extended π orbitals throughout two DPP aromatic systems.

All the synthesized dyes gave smaller x values and higher y values than C.I. Pigment Red 254. Further research is therefore needed to adjust the color of the synthesized dyes, perhaps by utilizing a linking group that is longer than C_{10} alkyl.

Dyes **1-3** showed a similar level of weight reduction (1.2-1.9% at 230 °C), which was slightly higher than that of C.I. Pigment Red 254. Even more importantly, the color difference brought about by high temperature processing was an improvement over that of *N*-alkylated Red 254 and was as low as 3.4 for dye **3**. Our work shows that increasing molecular weight by dimerizing DPP systems leads to greater colorant resilience towards the thermal processing involved in color filter production.

Experimental Section

3,6-Bis(4-chlorophenyl)-2-octylpyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (*N*-alkylated Red 254). 6.27 g (14.2 mmol) of 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-[3,4-*c*]pyrrole was suspended in 90 ml of 1-methyl-2-pyrrolidinone for two hours at room temperature. 3.87 g (34.5 mmol) of potassium *tert*-butoxide was added to this slurry under a nitrogen atmosphere. After stirring for one hour, 5.79 g (30 mmol) of 1-bromooctane was added to the reaction mixture and then the mixture stirred additionally for two hours. The mixture was poured into 150 mL of water and the red solid filtered off. Subsequent isolation of the mono-substituted component (*N*-alkylated Red 254) 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 *N*-alkylated Red 254.

N-Alkylated Red 254: Yield: 45%, Found C: 67.25 H: 5.64 N: 6.47 O: 6.23 Calculated $C_{26}H_{26}Cl_2N_2O_2$ C: 66.53 H: 5.58 N: 6.82 O: 6.82, MS469 (M+).

5,5'-Alkylenebis(3,6-bis(4-chlorophenyl)-2-octylpyrrolo[3,4-*c*]pyrrole-1,4(2H,2H)-dione) (Dye 1). The obtained 5 g (1.1 mmol) was slurried in 70 mL of 1-methyl-2-pyrrolidinone for 15 min at room temperature. 1.673 g (1.5 mmol) of potassium *tert*-butoxide was added to the slurry under a nitrogen atmosphere. After stirring for one hour, 2.04 g (0.6 mmol) of diiodinemethane was added to the reaction mixture and then the mixture stirred additionally for three hours. The mixture was poured into 100 mL of water and the red

solid filtered off and purified by column chromatography (silica gel, dichloromethane as an eluent). After drying, 0.98 g of a red solid of Dye **1** was obtained.

Dye **1**: Yield: 27%, Found C: 67.01 H: 6.02 N: 5.42 O: 6.34 Calculated $C_{53}H_{52}Cl_4N_4O_4$ C: 66.95 H: 5.51 N: 5.89 O: 6.73, MS 950 (M+).

Other dyes were obtained by same procedure except reaction temperature (Dye **2**: 1,4-diiodobutane, Dye **3**: 1,8-diiodoctane).

Dye **2**: Yield: 31%, Found C: 68.32 H: 6.01 N: 5.32 O: 6.10 Calculated $C_{56}H_{58}Cl_4N_4O_4$ C: 67.74 H: 5.89 N: 5.64 O: 6.45, MS 992 (M+).

Dye **3**: Yield: 37%, Found C: 69.11 H: 5.67 N: 5.21 O: 5.90 Calculated $C_{60}H_{66}Cl_4N_4O_4$ C: 68.70 H: 6.34 N: 5.34 O: 6.10, MS 1048 (M+).

Solubility Test. The dye was added PGMEA (20 mL) and then stirred at room temperature for 30 mins. The supersaturated solution was passed through a 0.45 μ m syringe filter. The filtered solid was dried at 65 °C and then weighed to determine the amount of dissolved dye in order to calculate the solubility of the dye.

Fabrication of Color Filter. 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 (PGMEA) and a binder based on acrylate. Once spin-coating was completed, the film was placed quickly onto a hot plate and 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 90 °C for 90 seconds and post-baking at 220 °C for 40 mins, then additionally heating for 1 h at 240 °C, thereafter color differences in E_{ab} were determined using an MCPD 3700.

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