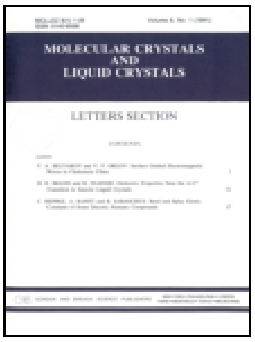

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Preparation and Characterizations of Solvent Soluble Dyes Based on Dimerized Diketo-pyrrolo-pyrrole Pigment

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We have prepared three pigments and six soluble dyes with thermal stability derived from diketo-pyrrolo-pyrrole (DPP) pigment by N*-alkylation and dimerization. Synthesized dyes and pigments were measured by an absorption maximum (λ_{max}) and thermal stability using a UV-VIS spectrophotometer and thermogravimetric analysis (TGA) respectively, comparing with C.I. Pigment Red 254. These dyes exhibited superior solubility to the organic solvents by introducing the linking group (n-octyl). DPP pigments have inferior thermal and solvent stability, which has so far inhibited their commercial adoption in color filter fabrication. The thermal stability of the* N*-alkylated dyes can be highly contributed by both the carbon number and their shapes of* N*-alkyl group in DPP ring.*

Keywords Diketo-pyrrolo-pyrrole (DPP); solubility; absorption maxima; thermal stability; dimerization.

1. Introduction

Liquid crystal display (LCD) modules, which are widespread media in today's information age, are composed of a backlight unit, a color filter (CF), and a thin-film transistor (TFT) board, with a liquid crystal between CF and TFT board. The color filter, which converts the white backlight into various colored lights, consists of RGB (red, green, blue) pixels, a black matrix (BM) for prevention of light leakage, an overcoat for improving the flatness of the pixel surface, and a column spacer to control the gap between cells[1–2].

Currently, various dye molecules are under extensive investigation for the manufacturing of RGB pixels and BM to improve the performance of LCD. The pigments, being used for the main colorants of RGB pixels, show superior thermal and photo chemical stabilities but cause both reflection and scattering of the light due to the presence of

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insoluble pigment particles patterned in the each sub-pixels causing the reduced transmittance of the light, thus gives rise to lower contrast ratio. Dyes can be attractive alternatives to overcome this limitation due to the reduced light scattering resulting from the fact that they can be dissolved in the media and exist in molecular form. Recently, their superior optical properties for higher brightness have outweighed the inferior thermal stabilities because the LCD manufacturing process temperature has been decreasing[3–5].

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. 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.

As a red color, a symmetrical molecule (C. I. Pigment Red 254) based on DPP, which was first synthesized by Ciba-Geigy, has been usually used due to its excellent thermal stability and bright red shade. DPP derivatives are known for being poorly soluble in common organic solvents due to their tendency to form strong $\pi - \pi$ interactions and hydrogen bondings and many efforts have been carried out on their functionalization to improve their solubility[6–7].As a consequence, during the last few years, several studies have been reported in the literature on the use of these soluble DPP derivatives in various application fields.

Herein, we describe efficient synthesis of several DPP dimmers through dimerization reaction of synthesized DPP pigments precursors as well as their spectroscopic characterization. In order to satisfy solubility requirements, alkyl chain was introduced between two *N*-alkylated dyes molecules.

2. Experimental

Synthesis of Pigments

Synthesis of 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (pigment 1). Under nitrogen condition, potassium *tert*-butoxide (2.25 g, 0.02 mol) was dissolved in 150 mL of *tert*-amyl alcohol for 15 min and the mixture was heated to 110°. Iron(III) chloride (s.a) was added and stirred for 30 min then 4-chlorobenzonitrile (1.5 g, 0.01 mol) was added and stirred for 1 hr at the same temperature. Diisopropyl succinate (1.01g, 0.005 mol) was dissolved in 30 mL of *tert*-amyl alcohol and dropwised to the mixture for 3 hr. Then 60 mL of water was poured into mixture and stirred for 20 hr at the same temperature. After reaction, the mixture was cooled to room temperature. The mixture was filtered off and washed by water, methanol. The red pigment was purified by 50 mL methanol and stirred for 30 min at 60°. After stirring, the solution was filtered off and dried under vacuum to obtain Pigment **1** in 43% yield. $C_{18}H_{10}Cl_2N_2O_2$, Found C: 60.21 H: 2.84 N: 7.73, MS (*m/z*) 356(M+).

Other pigments were obtained by same procedure.

Pigment 2 Yield : 15%, $C_{20}H_{16}N_2O_4$, Found C: 67.46 H: 4.22 N: 8.04 O: 18.75, (*m/z*) 348(M+).

Pigment 3 Yield : 38%, $C_{30}H_{20}N_2O_2$, Found C: 81.28 H: 4.54 N: 6.17 O: 7.26, (*m/z*) 440(M+).

Synthesis of Dyes

Synthesis of 3,6-bis(4-chlorophenyl)-2-octylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Dye 1). Under nitrogen condition, 6.27g (14.2 mmol) of 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione was suspended in 90 mL of 1-methyl-2-pyrrolidinone for 2 hr 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 is stirred additionally for two hours. The mixture was poured into 150 mL of water and the red solid was filtered off. Subsequent isolation of the mono-substituted component 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 min 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** was obtained.

Other dyes were obtained by same procedure.

Dye 1 Yield : 45%, $C_{26}H_{26}Cl_2N_2N_2O_2$, Found C: 67.25 H: 5.64 N: 6.47: 6.2 MS (*m/z*) 469(M+).

Dye 2 Yield : 38%, $C_{28}H_{32}N_2O_4$, Found C: 73.21 H: 7.00 N: 6.01 O: 13.77, MS (*m/z*) 460(M+).

Dye 3 Yield : 40%, $C_{38}H_{36}N_2O_2$, Found C: 82.31 H: 6.51 N: 5.03 O: 5.79, MS (*m/z*) 552(M+).

Synthesis of 5,5′-(octane-1,8-diyl)bis(3,6-bis(4-chlorophenyl)-2-octylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) (Dye 4). Under nitrogen condition, obtained 3,6-bis(4-chlorophenyl)-2-octylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(5 g, 0.01 mol) 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 1,8-diiodooctane 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 **4** was obtained. Other dyes were obtained by the same procedure.

Dye 4 Yield : 37%, $C_{60}H_{66}Cl_4N_4O_4$, Found C:69.11 H:5.67 N:5.21 O:5.90, MS(*m/z*) 1048(100)

Dye 5 Yield : 20%, $C_{56}H_{62}N_4O_8$, Found C: 73.11 H: 6.45 N: 6.10 O: 13.78, MS (*m/z*) 919(100).

Dye 6 Yield : 25%, $C_{76}H_{70}N_4O_4$, Found C: 82.13 H: 6.52 N: 5.08 O: 5.91, MS (*m/z*) 1103(100).

Structural Analysis

Structural analyses of synthesized dyes were measured using an EA 1108 (Elemental Analysis) and a Voyager-DE STR Biospectrometry (MALDI-TOF). 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.

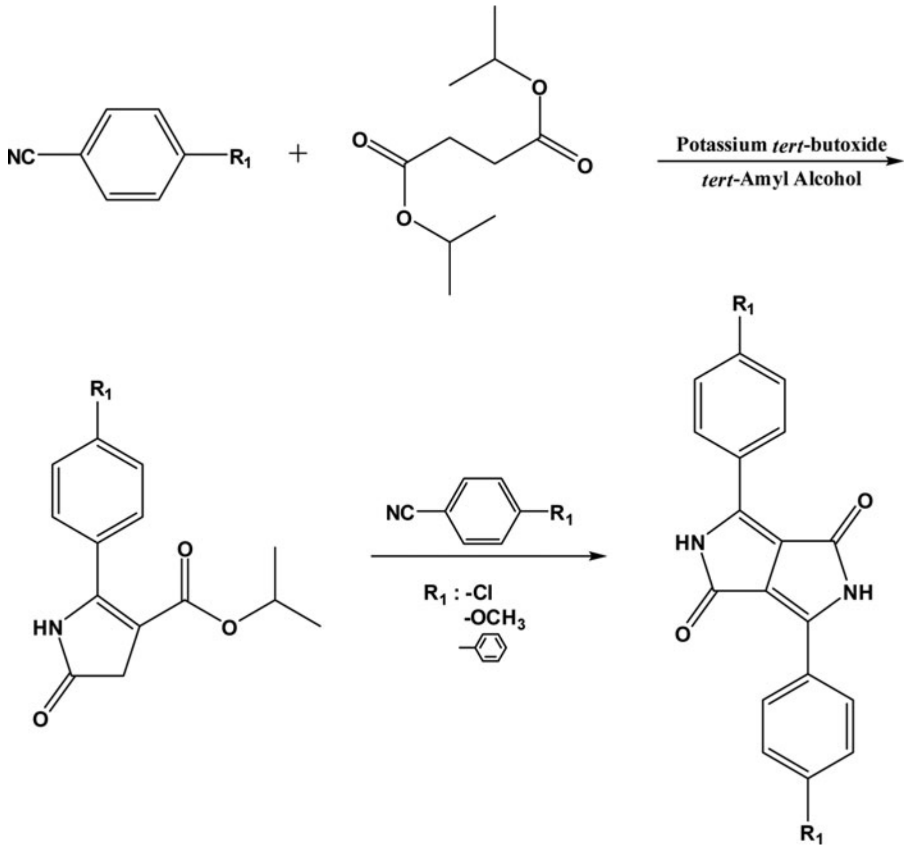


Figure 1. Synthetic scheme and the structures of pigments **1–3**

3. Results and Discussion

Synthesis

To synthesize the dyes, three steps are required. The first step is to prepare pigments. Pigments **1-3** were synthesized through the succinic ester route. In this route, succinic ester is condensed in a Pseudo-Stobbe condensation with an aromatic nitrile in the presence of strong base. It is shown in Figure 1. As in shown Figure 2 and Figure 3, dyes **1-3** were prepared derived from synthesize DPP pigment through typical S_N2 reaction of alkylation. The *N*-alkylated and dimerization DPP derivatives can be easily separated by column chromatography due to their different polarities. Yields of dyes **4-6** were 20% in average.

Spectral Properties of Dyes

The absorption maxima of synthesized pigments and dyes were determined in *N*-methyl-2-pyrrolidone (NMP), as listed in Table 1. The absorption maxima of DPP pigments were observed in the ranged of 516 – 534 nm. It apparently indicated the effects of substituents presented in DPP phenyl ring. Therefore, Pigment 1, substituted by chlorines which acted as an electron-withdrawing group observed at 516 nm. In contrast, Pigment 2

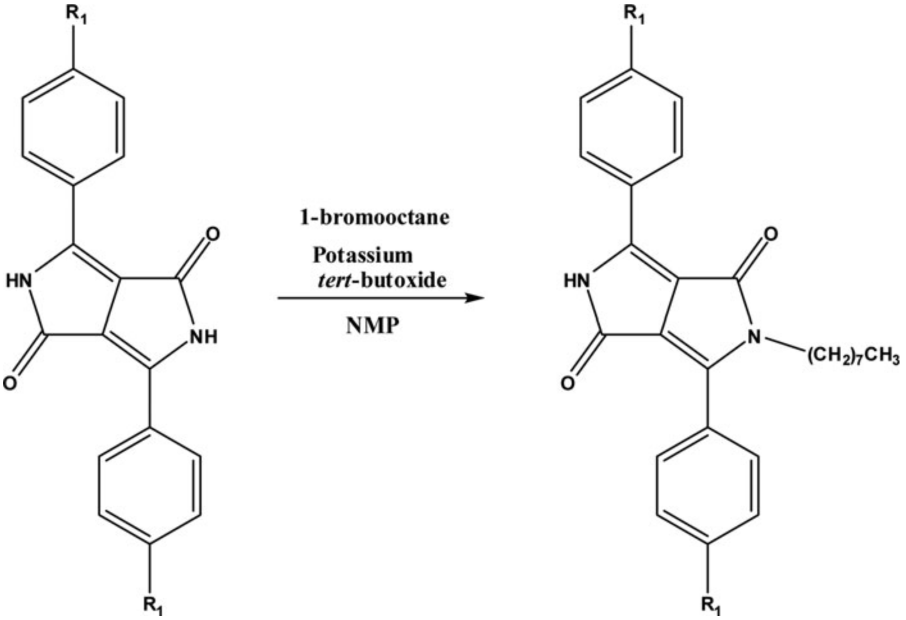


Figure 2. Synthetic scheme and the structures of dyes **1–3**

exhibited a hypsochromic shift of 2 nm that caused by electron-donating substituent(-OMe). Correspondingly, Pigment 3 showed a bathochromic shift in 18 nm comparing to that of Pigment 1 which caused by extension of conjugation between DPP ring. The absorption maximum of *N*-alkylated dyes (4–6) showed a hypochromic shift by 21 – 42 nm. It can be best explained by the decreased planarity and conjugation length between DPP rings caused by the introduction of alkyl group[8]. Contrastively, Dye 4 absorbed at 527 nm which was red shifted by 22 nm compared to Dye 1. It is mainly due to the extension of the π-conjugated systems through dimerization of DPP. Two series of dye substituted methoxy group or benzene ring respectively, were observed in different tendency that was more

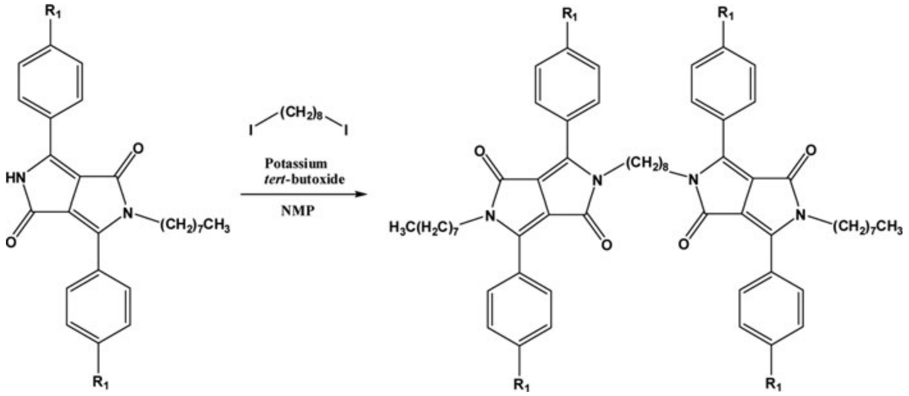


Figure 3. Synthetic scheme and the structures of dyes **4–6**

Table 1. The absorption maxima (λ_{max}) of the synthesized pigments and dyes

Name	λ_{max} (nm) Absorption	ε_{max} (L mol^{-1} cm^{-1})
Pigment1	516	—
2	514	—
3	534	—
Dye1	505	15,100
2	485	16,000
3	492	11,000
4	527	16,200
5	489	18,300
6	494	11,000

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

hypochromic shift than dye substituted chlorine. It is effect of small decrease in planarity and conjugation length between DPP rings[9–12].

Solubility of Dyes

For dyes to be successfully applied as colorants for LCD color filter, they should exhibit good solubility in industrial solvents. Regardless of the compatibility with binders, dye molecules should dissolve more than 5wt% in industrial solvents to have the desired optical properties. Especially, to prevent the aggregation behavior between the dye molecules after post baking process, bulky substituents should be introduced and indeed such molecules are therefore normally also better soluble in organic solvents. The solubility data of the synthesized dyes in organic solvent, PGMEA, are listed in Table 2. The dyes **4-6** with linking group between the two *N*-alkylated dyes showed that solubility in the range of 9–14%. Especially, dye **5** was observed to have the highest solubility at 14.4%. The alkyl chain substituents of dimerized dyes caused by the steric hindrance to reduce intermolecular stacking and ether linkages in its structure enhanced its solubility in industrial solvents. The introduction of alkyl groups considerably effective on hindering the intermolecular $\pi - \pi$ stacking between DPP chromophores. *N*-alkylated dyes **1-3** have smaller solubility compared with dyes **4-6** which caused by introduction of bulky alkyl chain and planner structure (Figure 4). The increased solubility is advantageous for good optical properties

Table 2. Solubility of synthesized dyes in PGMEA

Name	Solubility(g/100ml)
Dye1	9.4
2	8.4
3	6.5
4	12.8
5	14.4
6	9.5

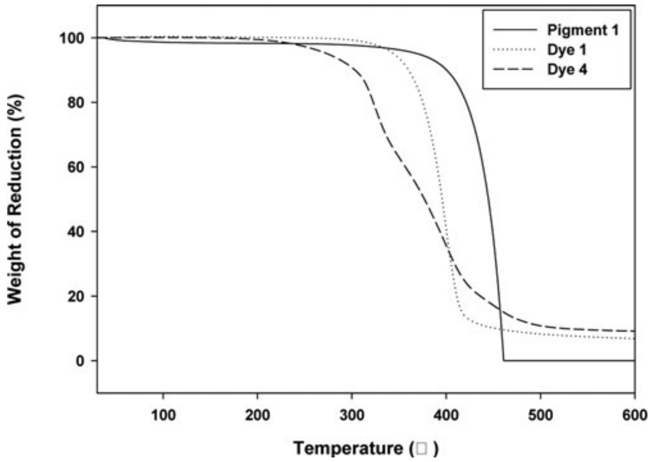
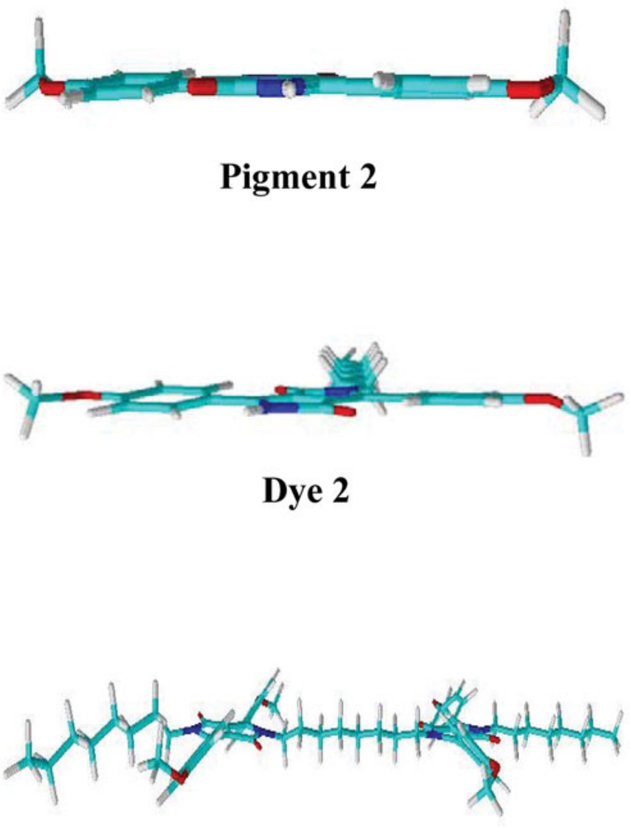


Figure 4. Weight reduction of some pigments and dyes by TGA.



Pigment 2

Dye 2

Dye 5

Figure 5. Geometry-optimized structures of the synthesized pigment 2 and dye 2.

Table 3. Weight reduction of synthesized dyes pigments at different temperature measured by TGA

	Weight (%)	
Name	200°	250°
Pigment 1	99.43	99.08
2	98.3	98.17
3	99.24	99.31
Dye 1	99.62	99.57
2	96.17	94.89
3	97.57	95.99
4	98.48	97.28
5	95.26	93.77
6	96.83	94.48

as the colorant materials for LCD color filters. Therefore, two series of dye were sufficient colorants expected high transmittance and contrast ratio for LCD.

Thermal Stability of Dyes

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°, therefore the weight reduction of the colorant should be small as possible at 230 – 250° by TGA[12–14]. The thermal stability of synthesized pigments and dyes are shown in Table 3, and corresponding data shown in Figure 4. Weight reductions of *N*-alkylated dyes **1-3** were in the range of 0.43 - 5.11%, whereas the dyes **4-6** showed slightly higher reductions of 2.72 – 6.23% at 250°. Dye 1 and 3 substituted by a phenyl ring at ρ-position of DPP ring were to be most stable analogues in these series which mainly due to substituted phenyl ring at ρ-position that increased intermolecular $\pi - \pi$ stacking.

Geometry Optimization of Dyes

The synthesized pigment **2** is almost planar structure as shown Figure 5 observed structure from the side. Dye 2 substituted long alkyl chain, is smaller twisted structure than Pigment 2 that is planner structure. However, Dye 5, linked between DPP rings by octyl group, is not planer structure, and twisted structure especially positioned at DPP ring. It indicates that dye structure has steric hindrance and decrease intermolecular $\pi - \pi$ stacking between DPP chromophores. Therefore, it is effect on solubility and thermal stability of dyes.

4. Conclusions

In summary, we have successfully synthesized dyes **4-6** by three-step reaction. *N*-alkylated dyes **1-3** showed hypsochromic shift due to the decrease in planarity and conjugation between DPP ring and adjacent phenyl group caused by the introduction of alkyl group. However the dimerized dyes **4-6** exhibited a bathochomic shift which can be attributable to the extension of the π-conjugated systems through dimerization of DPP. These dyes exhibited enhanced solubility of 6 $\sim$ 14% in PGMEA by introducing alkyl substituents.

The synthesized dyes are less stable than DPP pigments because alkyl substituents readily provide decreased intermolecular $\pi - \pi$ stacking. However, most of dyes showed less than 5% weight reduction by TGA. In conclusion, these dyes can be suitable for use in LCD color filter as a red component.

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References

[1] Sabnis, R. W. (1999). *Displays*, *20*, 29.
[2] Tsuda, K. (1993). *Displays*, *14*, 24.
[3] Carr, K., Freeman, H. S., & Peters, A. T. (2000). *Eds*. Elsevier: London, U.K., 28.
[4] Glaser, F., Herbst, W., & Hunger, K. (1993). *Eds.* VCH: Weinheim, Germany, 50.
[5] Na, D. Y., Jung, I. B., Nam, S. Y., Yoo, C. W., and Choi, Y. J. (2007). *J. Korean Inst. Electron. Mater. Eng.*, *20*, 5.
[6] Choi, S. H., Kwon, O. T., Kim, N. R., Yoon, C., Kim, J. P., & Choi, J. H. (2010). *Bull. Korean. Chem. Soc.*, *31*, 1073.
[7] Kim, Y. D., Kim, J. P., Kwon, O. S., & Cho, I. H. (2009). *Dyes and Pigments*, *81*, 45.
[8] Choi, S. H., Kil, G. H., Kim, N. R., Yoon, C., Kim, J. P., & Choi, J. H. (2010). *Bull. Korean. Chem. Soc.*, *31*, 3427.
[9] Martin, V., Martin, W., Jan, V., Petr T, Stanislav L. (2008). *J. Fluoresc.*, *18*, 81.
[10] Zollinger, H. (2003). Wiley-VCH:Weinheim, Germany, *336*.
[11] Potrawa, T. (1987). *H. Chem. Ber.*, *120*, 5.
[12] Langls, H., Grundei, T., Potrawa, T., & Polborn, K. (1996). *Liebigs Ann. Chem.*, *679*.
[13] Das, S., Basu, R., Minch, M., & Nandy, P. (1995). *Dyes and Pigments*, *29*, 191.
[14] Chunlong, Z., Nianchun, M., & Liyun, L. (1993). *Dyes and Pigments*, *23*, 13.