

Synthesis, Spectral Property and Dyeing Assessment of Azo Disperse Dyes Containing Carbonyl and Dicyanovinyl Groups

Yun Seok Choi,^{†,‡} Kun Su Lee,[§] Hye Jin Kim,[§] Jong Yun Choi,[§] Soon Bang Kang,[‡] Eui Jae Lee,[§] and Gyochang Keum^{†,‡,*}

[†]Department of Biological Chemistry, University of Science and Technology, Daejeon 305-350, Korea

[‡]Center for Neuro-Medicine, Brain Science Institute, Korea Institute of Science and Technology, Seoul 136-791, Korea

*E-mail: gkeum@kist.re.kr

[§]Central Research Institute, KISCO's Research Institute, Kyung-In Synthetic Corporation, Seoul 157-860, Korea

Received November 19, 2012, Accepted December 19, 2012

A series of azo disperse dyes having dicyanovinyl groups was synthesized by the Knoevenagel condensation with malononitrile from carbonyl substituted phenylazo disperse dyes which were prepared by conventional diazo coupling reaction of aniline derivatives as diazo components. A variety of coupling components such as anilines, an indole and a pyridone were used. The azo disperse dyes were evaluated for their spectral properties and dyeing assessment on the polyester fabrics. The azo disperse dyes containing dicyanovinyl groups showed bathochromic shifts and darker colors due to increased electron withdrawing strength in their azo components and extended conjugation by dicyanovinyl groups than their parent carbonyl substituted azo dyes. The dyes containing 2-acetyl-amino-5-methoxy substituent in the coupling component exhibited higher wavelength of maximum absorbance (λ_{max}) and significant negative solvatochromism than those of other dyes due to intramolecular hydrogen bonding.

Key Words : Azo disperse dyes, Extended conjugation, Spectral properties, Dyeing assessment, Dicyanovinyl

Introduction

Disperse dyes are aromatic compounds and soluble in organic solvents but sparingly soluble in water. They can dye hydrophobic fibers such as nylon, polyester, and acetate at high pressure and temperature, and are structurally based on an azo, anthraquinone or diphenylamine molecule with attached functional groups such as amine, nitro, cyano, etc.

Azo dyes, containing at least one N=N structure in molecule, are the most important group of disperse dyes and globally comprise over 50% of disperse dyes because of its strong tinctorial strength compared to anthraquinone dyes, ease to make, and a low cost of manufacture. Azo dyes have a vivid color in the yellow to blue-green region by varying between azo components with electron withdrawing groups and coupling components with electron donating groups such as aminobenzene. The representative azo disperse dyes are shown in Figure 1.¹⁻⁶

A number of studies on azo dyes have been carried out to

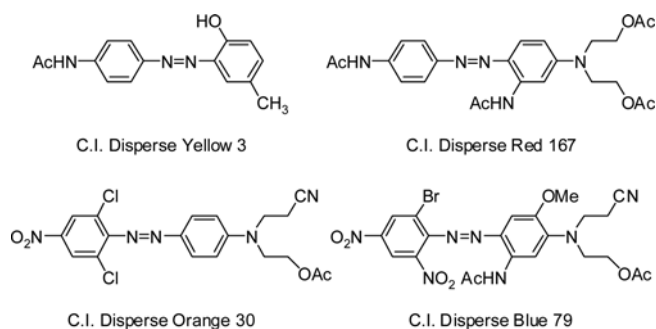


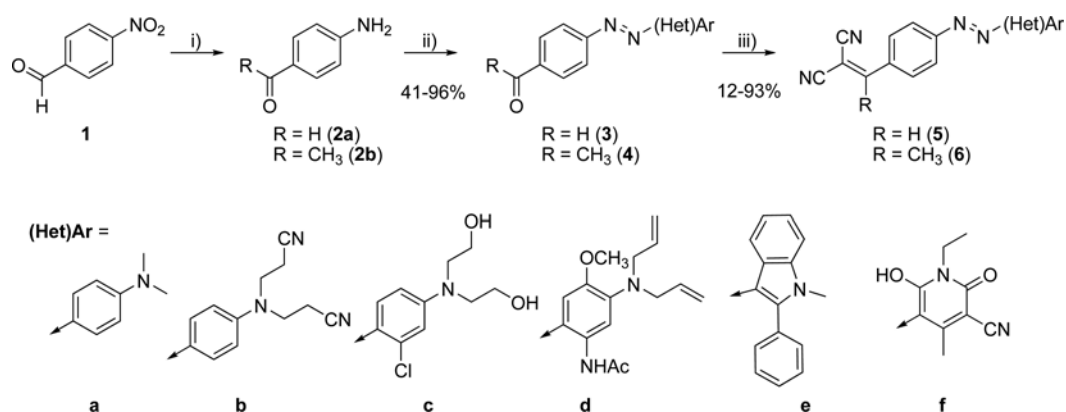
Figure 1. Representative azo disperse dyes.

improve their dyeing properties such as color and fastness to meet the technical and economic requirements,^{1,7,8} also to apply for non-textile uses such as reprography, non-linear optics, solar cells, chemosensors and biology.⁹⁻¹²

In this paper we describe the azo disperse dyes containing carbonyl or dicyanovinyl groups in the *para*-position of diazo components in order to make an impact on bathochromism and solvatochromism of the azo dyes through extending conjugation and increasing electron withdrawing strength. The azo dyes substituted with aldehyde and acetyl group respectively were prepared by diazo coupling with coupling components such as anilines, an indole and a pyridone, and subsequent the Knoevenagel condensation with malononitrile gave the corresponding dicyanovinyl substituted phenylazo dyes. The spectral properties of the dyes and their colorimetric evaluation on polyester fabrics were investigated.

Results and Discussion

The synthesis of azo disperse dyes containing carbonyl and dicyanovinyl groups in the *para*-position of diazo components was shown in Scheme 1. As a precursor of diazo components having aldehyde and acetyl group at the *para*-position, *p*-aminobenzaldehyde **2a** and 4'-nitroacetophenone **2b** were used. Notably, *p*-aminobenzaldehyde **2a** was prepared by reduction of nitro group according to the literature,¹³ and was used for the next step before complete evaporation of solvent because it was easily polymerized by self-condensation upon concentration. The diazo dyes substituted with aldehyde **3b-3f** and acetyl **4a-4f** were synthesized by

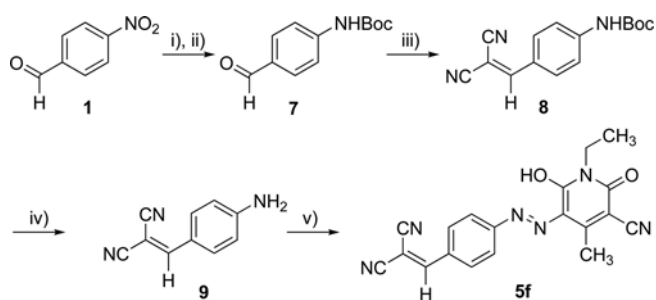


Scheme 1. i) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, EtOH, 70 °C, 1 h; ii) 1 N HCl (aq), NaNO_2 , H_2O , 0 °C, 30 min; then corresponding (Het)Ar, acetone, acetic acid, 0 °C, 4–7 h, 41–94% for aldehyde (2 steps from **5**) and 57–96% for ketone, yields: 48% (**3b**), 41% (**3c**), 43% (**3d**), 56% (**3e**), 94% (**3f**), 78% (**3a**), 62% (**3b**), 72% (**3c**), 58% (**3d**), 57% (**3e**), 96% (**3f**); iii) malononitrile, pyridine, rt for aldehyde or 95 °C for ketone, 3–24 h, 12–93%. Yields: 72% (**5b**), 93% (**5c**), 76% (**5d**), 53% (**5e**), 12% (**6a**), 57% (**6b**), 60% (**6c**), 40% (**6d**), 76% (**6e**), 43% (**6f**).

diazotization using hydrochloric acid and sodium nitrite at 0 °C, followed by a coupling reaction in a one-pot process^{14–17} with various commercially important coupling components such as dialkylanilines (**a–d**), indole (**e**) and pyridone (**f**). As anticipated, the coupling reactions occurred selectively at the *para*-position of anilines **a–d**, and at the 3- and 5-position of the indole **e**¹⁸ and pyridone **f** component respectively.

The subsequent Knoevenagel condensation of carbonyl compounds in the azo dyes containing aldehyde **3b–3e** and acetyl **4a–4f** with malononitrile afforded the corresponding benzylidenemalononitrile derivatives **5b–5e** and **6a–6f** in 12–93% yields. Because of the relatively poor solubility, the final products were isolated by filtration, washed by dichloromethane, and followed by recrystallization.

In case of the pyridone compound **5f**, the reaction gave inseparable mixtures due to its insolubleness in general organic solvents and incomplete conversion. Thus pyridone azo dye **5f** was alternatively synthesized in high yields by the one-pot diazo coupling reaction of pyridone **f** with excess amount (1.25 equiv) of *p*-aminobenzylidene malononitrile **9** which was readily prepared by *in situ* *N*-Boc protection of *p*-aminobenzaldehyde **2a**, the Knoevenagel condensation and sequential *N*-Boc deprotection as shown in Scheme 2.



Scheme 2. i) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, EtOH, 70 °C, 1 h; ii) Boc_2O , TEA, THF, rt, 24 h, 57% (2 steps); iii) malononitrile, pyridine, 95 °C, 12 h, 90%; iv) TFA, DCM, rt, 1 h, 86%; v) 1 N HCl (aq), NaNO_2 , H_2O , 0 °C, 30 min; then pyridone **f**, 0 °C, 6 h, 87%.

Visible absorption spectral data of synthesized dyes containing carbonyl and dicyanovinyl groups recorded in dichloromethane and methanol are given in Table 1. The maximum molar extinction coefficient values (ϵ_{max}) were calculated by the Beer-Lambert law.¹⁹ The wavelength of maximum absorbance (λ_{max}) range of the synthesized dyes were 408–573 nm in dichloromethane and 410–540 nm in methanol within the visible region.

Absorption maxima were exactly dependent on the electron accepting power of *para*-substituents in the azo components, and resultantly increased in the order of ketone (**4**), aldehyde (**3**), ethylidenemalononitrile (**6**), and methylidene-malononitrile (**5**) in the same series of the coupling components.^{2,7} Converting aldehydes (**3**) into its active methylene groups by coupling with malononitrile led to large red shifts of the absorption maxima about 21–66 nm, and the shifts were 2- to 4-fold larger than those of ketones (**4**) except pyridone components (**f**). The substantial bathochromism of dicyanovinyl derivatives probably came from both the extent of conjugation and introduction of two electron-accepting nitrile groups. Methyl substituents on acetyl and 1,1-dicyano-2-propenyl compounds (**6**) reduced the bathochromic shifts probably due to a sterical conformation hindrance and non-planarity between dicyanovinyl and phenyl ring plane with a torsion angle (ω_{torsion}). This observation is consistent with the results of naphthalene analogues as previously reported.²⁰

Azo compounds having *N*-dicyanoethyl aniline group (**b**) as a coupling component absorb maximally at shorter wavelengths by 27–44 nm than the diethanolamine derivatives (**c**), and by 29–50 nm than dimethylamine derivatives (**a**). The tendency is consistent with general phenomena of azo dyes that strength of electron-withdrawing power in the coupling components related to hypsochromic shifts. The indole derivatives (**e**) showed similar absorption maxima with *N*-dicyanoethylamine derivatives (**b**). Especially, dyes **3d–6d** containing 2-acetylamino-5-methoxy substituent in the coupling component showed greater bathochromic shift than those of other dyes. The rationale supporting this phen-

Table 1. Spectroscopic properties (λ_{\max} in nm and ϵ_{\max} in $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and solvatochromic effects

Dyes	DCM		MeOH		$\Delta\lambda^a$
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	
4a	445	1.04	443	8.28	-2
6a	472	3.61	463	5.78	-9
3b	415	2.57	418	1.85	+3
4b	408	3.92	414	5.03	+6
5b	454	3.25	457	2.16	+3
6b	422	4.48	425	3.94	+3
3c	445	3.29	445	1.97	0
4c	437	2.80	441	4.02	+4
5c	498	2.91	496	3.07	-2
6c	456	3.30	454	4.59	-2
3d	518	1.93	495	2.16	-23
4d	507	10.77	491	1.88	-16
5d	573	7.26	540	5.04	-23
6d	527	7.01	503	3.69	-24
3e	418	3.00	413	2.92	-5
4e	411	4.67	410	0.81	-1
5e	484	4.01	471	8.67	-13
6e	436	4.71	425	0.42	-11
3f	435	7.17	432	7.39	-3
4f	416	4.26	412	7.19	-4
5f	460	5.12	453	5.57	-7
6f	444	2.26	442	9.42	-2

$$^a\Delta\lambda = \lambda_{\max}(\text{MeOH}) - \lambda_{\max}(\text{DCM})$$

omenon is intramolecular hydrogen-bonding between azo nitrogen and hydrogen in the acetylamino group of the coupling component.²¹ Because of lower electron donating effect, pyridone derivatives **3f-6f** showed lower absorption maxima than **3d-6d** irrespective of forming intramolecular hydrogen-bonding of enol tautomer in the coupling components with azo nitrogen attached to phenyl ring of azo component.

For the series of synthesized dyes, ϵ_{\max} as well as λ_{\max} in dichloromethane generally increases as carbonyl groups are converted into dicyanovinyl groups. Acetamide derivatives **3d-6d** showed higher ϵ_{\max} values in dichloromethane, and ϵ_{\max} values of pyridone derivatives **3f-6f** increased in methanol.

Solvatochromic effects in dichloromethane and methanol are also shown in Table 1. Most synthesized dyes exhibited slight negative solvatochromism, except for dyes **3b-6b** and **4c**, because of intermolecular hydrogen bonding between the ground state of dye molecules and the methanol. In particular, dyes **3d-6d** containing the 2-acetylamino-5-methoxy substituent in the coupling components showed significant negative solvatochromism due to higher stabilization of ground states by intramolecular hydrogen bonding of the dyes.

The dyeing assessment of prepared dyes was carried out on polyester fabrics^{4,22} and the results were listed in Table 2. The colors of dyes are well correlated with λ_{\max} values in Table 1. Almost dyes showing λ_{\max} values from 430 nm to

Table 2. Color properties of synthesized dyes on 100% polyester

460 nm represented orange colors, but dyes showing higher or lower λ_{\max} values than that range represented more reddish or yellowish colors, respectively. Depending on the bathochromic shift described above, dicyanovinyl derivatives showed darker colors than its carbonyl compounds.

Conclusion

Novel azo disperse dyes containing dicyanovinyl groups in the azo components were synthesized by the Knoevenagel condensation *via* the corresponding carbonyl derivatives and their spectral properties and dyeing assessment on polyester fabrics were evaluated.

The colors are correlated with their coupling components and spectroscopic properties. All of the dicyanovinyl derivatives exhibited greater bathochromic shift and darker colors than parent carbonyl derivatives due to increase of electron withdrawing power and extended conjugation in azo components.

Among them, the dyes containing 2-acetylamino-5-methoxy substituent in the coupling component exhibited highest red shifts of the absorption maxima and significant negative solvatochromism than those of other dyes due to intramolecular hydrogen bonding.

Experimental Section

Materials. All reagents used were purchased from Sigma-Aldrich Co., Junsei Chemical Co., and TCI. All organic solvents used for reaction were purchased from Sigma-Aldrich Co. and J.T. Baker as HPLC grade. These were used without further purification unless otherwise noted.

Instruments. Melting points were measured on MEL-TEMP[®] Laboratory Devices INC, USA. ¹H-NMR spectra and ¹³C-NMR spectra were recorded on Bruker DPX 300 MHz or Bruker DPX 400 MHz spectrophotometer using CDCl₃, acetone-*d*₆, DMSO-*d*₆ as NMR solvent. TMS was used as an internal standard and chemical shift data are reported in parts per million (ppm) and s, d, t, m, dd, and bs are designated as singlet, doublet, triplet, multiplet, doublet

of doublet, and broad singlet, respectively. Coupling constants (J) were reported in hertz (Hz). The reaction progress was monitored by thin layer chromatography (TLC). UV-Vis spectra were recorded on UV/Vis/NIR spectrophotometer, Perkin-Elmer Lambda 19 Model. All samples were prepared and analyzed at 10 μ M concentration in dichloromethane (DCM) and methanol (MeOH), respectively.

General Procedure of Diazo-Coupling Reaction. To 1 N HCl aqueous solution (20 mL) was added 4-aminobenzaldehyde (1.25 g, 10.31 mmol) in 15 mL of acetone dropwise at 0 °C under argon atmosphere. Then sodium nitrite (0.71 g, 10.31 mmol) in 10 mL of water was added dropwise to the solution while maintaining the same temperature. The solution was stirred for 30 min. After that, a corresponding coupling component (10.31 mmol) in 12 mL of acetone and 6 mL of glacial acetic acid was added dropwise to the solution and stirred for additional 4-7 h until the reaction was finished. After completion of reaction, the pH value of diazo liquor was adjusted to pH 5-6 by adding sodium acetate saturated solution and stirred for another 20 min. The solution was extracted with ethyl acetate and water for three times. The combined organic phase was dried over sodium sulfate and concentrated. The resulting mixture was purified by flash column chromatography on silica gel or recrystallization.

Synthesis of 3,3'-((4-Formylphenyl)diazenyl)phenyl)azanediyldipropanenitrile (3b): Compound **3b** was synthesized from compound **2a** according to the similar procedure by the diazo-coupling reaction described above (yield 48%): Dark scarlet solid; mp 159-160 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 10.09 (s, 1H), 8.03-7.97 (m, 6H), 6.79 (d, $J = 6.8$ Hz, 2H), 3.94 (t, $J = 4.9$ Hz, 4H), 2.75 (t, $J = 4.9$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 191.7, 156.3, 147.8, 145.4, 136.9, 130.7, 126.1, 123.0, 117.7, 112.2, 47.9, 16.4.

Synthesis of 3,3'-((4-Acetylphenyl)diazenyl)phenyl)azanediyldipropanenitrile (4b): Compound **4b** was synthesized from commercial compound **2b** according to the similar procedure by the diazo-coupling reaction described above (yield 62%): Orange solid; mp 190-191 °C; ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 8.11 (d, $J = 6.4$ Hz, 2H), 7.87 (dd, $J = 6.6, 10.5$ Hz, 4H), 7.05 (d, $J = 6.9$ Hz, 2H), 3.86 (t, $J = 5.1$ Hz, 4H), 2.84 (t, $J = 5.1$ Hz, 4H), 2.63 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz) δ 197.8, 155.3, 150.1, 144.2, 137.6, 130.0, 125.8, 122.5, 119.7, 112.8, 46.1, 27.4, 15.9.

General Procedure for the Knoevenagel Condensation. A solution of ketone or aldehyde (0.17-0.42 mmol) and an excess of malononitrile (0.85-2.10 mmol) in pyridine was heated at 95 °C (ketone) or room temperature (aldehyde) and stirred for 3-24 h until the reaction was finished. After cooling down to room temperature, pyridine was removed *in vacuo*. The desired product was purified by filtration and washing with dichloromethane, followed by recrystallization.

Synthesis of 2-(4-((4-Bis(2-cyanoethyl)amino)phenyl)diazenyl)benzylidene)malononitrile (5b): Compound **5b** was synthesized from compound **3b** according to the similar procedure by the Knoevenagel condensation described above (yield 72%): Dark purple solid; mp 204-205 °C; ^1H NMR

($\text{DMSO}-d_6$, 300 MHz) δ 8.57 (s, 1H), 8.11 (d, $J = 8.7$ Hz, 2H), 7.96 (d, $J = 8.6$ Hz, 2H), 7.86 (d, $J = 9.1$ Hz, 2H), 3.87 (t, $J = 6.8$ Hz, 4H), 2.85 (t, $J = 6.8$ Hz, 4H); ^{13}C NMR ($\text{DMSO}-d_6$, 75 MHz) δ 160.7, 155.7, 150.5, 144.3, 132.5, 132.4, 126.1, 123.2, 119.6, 114.8, 113.8, 112.9, 81.7, 46.1, 15.9.

Synthesis of 2-(1-(4-((4-Bis(2-cyanoethyl)amino)phenyl)diazenyl)phenyl)ethylidene)malononitrile (6b): Compound **6b** was synthesized from compound **4b** according to the similar procedure by the Knoevenagel condensation described above (yield 57%): Blood-red solid; mp 151-152 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.97 (d, $J = 9.1$ Hz, 4H), 7.71 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 9.1$ Hz, 2H), 3.94 (t, $J = 6.5$ Hz, 4H), 2.75 (t, $J = 6.5$ Hz, 4H), 2.7 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 174.3, 154.9, 147.8, 145.3, 136.8, 128.6, 126.1, 123.0, 117.6, 112.8, 112.2, 84.8, 47.9, 24.2, 16.4.

Synthesis of *tert*-Butyl (4-formylphenyl)carbamate (7): A mixture of 4-aminobenzaldehyde (**2a**), prepared from 4-nitrobenzaldehyde (500 mg, 3.31 mmol) described above, Boc_2O (722 mg, 3.31 mmol), triethylamine (402 mg, 3.97 mmol) in THF was stirred at room temperature. After completion of reaction, water was added to the mixture and the solution was extracted with ethyl acetate for three times. The combined organic phase was dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography on silica gel ($\text{EtOAc}/n\text{-Hex}$, 1:5) to yield title product **7** (417 mg, 57% for two steps). ^1H NMR (CDCl_3 , 300 MHz) δ 9.83 (s, 1H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.56 (d, $J = 8.6$ Hz, 2H), 1.43 (s, 9H).

Synthesis of *tert*-Butyl (4-(2,2-dicyanovinyl)phenyl)carbamate (8): Compound **8** was prepared from compound **7** according to the similar procedure by the Knoevenagel condensation described above (yield 90%). ^1H NMR (CDCl_3 , 300 MHz) δ 7.88 (d, $J = 8.7$ Hz, 2H), 7.71 (s, 1H), 7.63 (d, $J = 6.7$ Hz, 2H), 6.95 (s, 1H), 1.54 (s, 9H).

Synthesis of 2-(4-Aminobenzylidene)malononitrile (9): To a solution of *tert*-butyl (4-(2,2-dicyanovinyl)phenyl)carbamate (**8**) (350 mg, 1.30 mmol) in dichloromethane, trifluoroacetic acid (3.71 g, 32.50 mmol) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. After completion of reaction, pH was made slightly basic by addition of 1 N sodium hydroxide aqueous solution. Water was added to the mixture, and the resulting solution was extracted with dichloromethane for three times, and then dried by using sodium sulfate and concentrated. The residue was purified by flash column chromatography on silica gel ($\text{EtOAc}/n\text{-Hex}$, 1:2) to yield title product **9** (189 mg, 86%). ^1H NMR (CDCl_3 , 300 MHz) δ 7.78 (d, $J = 8.7$ Hz, 2H), 7.51 (s, 1H), 6.69 (d, $J = 8.8$ Hz, 2H), 4.52 (bs, 2H).

Synthesis of 2-(4-((5-Cyano-1-ethyl-2-hydroxy-4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl)benzylidene)malononitrile (5f): Compound **5f** was synthesized from 2-(4-aminobenzylidene)malononitrile **9** (180 mg, 1.06 mmol) and compound **f** (152 mg, 0.85 mmol) as a coupling component according to the similar procedure by diazo-coupling reaction described above. After completion of reaction, the resulting mixture was purified by filtration and washing with acetone

to yield title product **5f** (266 mg, 87%), as light orange solid: mp 294-296 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) δ 14.41 (bs, 1H), 8.47 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 3.88 (d, *J* = 6.8 Hz, 2H), 2.54 (s, 3H), 1.23 (s, 3H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 160.5, 160.3, 160.1, 146.2, 133.1, 129.2, 125.7, 118.2, 115.2, 114.1, 80.0, 69.0, 35.1, 16.9, 13.1.

General Procedure of Dyeing. Dyeing of polyester fabric with disperse dyes was carried out using high temperature and high pressure method in IR dyeing machine at a material to liquor ratio of 1:20.^{4,22} Fabric was dyed using 2 wt % of dye in the solution. Additionally dispersing agent Irgasol DAM (1.0 g/L) was added and the pH of the dye bath was adjusted to 4.5 using glacial acetic acid. Dyeing was commenced at room temperature. The dye bath temperature was raised at a rate of 2 °C/min to 130 °C and maintained at this temperature for another 60 min. After cooling down to room temperature rapidly, the dye fabrics were rinsed and reduction cleared in an aqueous solution of 1 g/L sodium hydroxide pellet and 3 g/L sodium hydrosulfite using 50:1 liquor ratio at 80 °C for 15 min. After that, the treated fabrics were rinsed using cold water and then dried in the open air.

Supporting Information. Experimental procedures, melting points, ¹H and ¹³C NMR for the compounds not described in the manuscript, and all UV-Vis spectral data have given as supplementary material.

Acknowledgments. This work was supported by the Technology Innovation Development Program (S1072140) of Korea Small & Medium Business Administration (SMBA), and Grants from Korea Institute of Science and Technology.

References

- Zollinger, H. *Color Chemistry. Syntheses, Properties, and Applications of Organic Dyes and Pigments*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.
- Griffiths, J. *Colour and Constitution of Organic Molecules*; Academic Press: London, UK, 1976.
- Aspland, J. R. *Textile Dyeing and Coloration*; American Association of Textile Chemists and Colorists: North California, U. S. A., 1997.
- Hauser, P. J. *Textile Dyeing*; In Tech, Rijeca, Croatia, 2011.
- Golob, V.; Tušek, L. *Dyes Pigm.* **1999**, *40*, 211.
- Ghaharpour, M.; Rashidi, A.; Tayebi, H. *World Appl. Sci. J.* **2011**, *14*, 1291.
- Koh, J. S.; Greaves, A. J.; Kim, J. P. *Dyes Pigm.* **2003**, *56*, 69.
- Towns, A. D. *Dyes Pigm.* **1999**, *42*, 3.
- Deligeorgiev, T.; Lesev, N.; Kaloyanova, S. *Dyes Pigm.* **2011**, *91*, 74.
- Yan, Y.; Hu, Y.; Zhao, G. *Dyes Pigm.* **2008**, *79*, 210.
- Ledoux, I.; Zyss, J.; Barni, E.; Barolo, C.; Diulgheroff, N.; Quagliotto, P.; Viscardi, G. *Synth. Met.* **2000**, *115*, 213.
- Cheng, X.; Zhou, Y.; Qin, J.; Li, Z. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2133.
- Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839.
- He, L.; El-Shafei, A.; Freeman, H. S.; Boyle, P. *Dyes Pigm.* **2009**, *82*, 299.
- Pirez-Moreno, J.; Zhao, Y.; Clays, K.; Kuzyk, M. G.; Shen, Y.; Qiu, L.; Hao, J.; Guo, K. *J. Am. Chem. Soc.* **2009**, *131*, 5084.
- Singh, A. K.; Das, J.; Majumdar, N. *J. Am. Chem. Soc.* **1996**, *118*, 6185.
- Zhang, D. *Spectrochim. Acta Part A* **2010**, *77*, 397.
- Albar, H. A.; Shawali, A. S.; Abdalialh, M. A. *Can. J. Chem.* **1993**, *71*, 2144.
- Skoog, D. A.; West, D. M.; Holler, F. J.; Crouch, S. R. *Analytical Chemistry: An Introduction (Saunders Golden Sunburst Series)*, 7th ed.; Thomson Learning: London, UK, 1999.
- Petriè, A.; Johnson, S. A.; Pham, H. V.; Li, Y.; Èeh, S.; Golobiè, A.; Agdeppa, E. D.; Timbol, G.; Liu, J.; Keum, G.; Satyamurthy, N.; Kepe, V.; Houk, K. N.; Barrio, J. R. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 16492.
- Cheon, K. S.; Park, Y. S.; Kazmaier, P. M.; Buncel, E. *Dyes Pigm.* **2002**, *53*, 3.
- Metwally, M. A.; Bondock, S.; El-Desouky, S. I.; Abdou, M. M. *J. Korean Chem. Soc.* **2012**, *56*, 348.