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Synthesis of hetero-bi-functional dye having photochromism and electrochromism. Part 1: Characteristics and its sensing properties

Young-A Son [a], Young-Min Park [a], Myung-Sik Choi [b], Sung-Hoon Kim [b,*]

[a] *BK21 FTIT, Department of Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, South Korea*
[b] *BK21 NBIT, Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, South Korea*

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Abstract

In this study, we prepared a novel hetero-bi-functional chromic dye and evaluated the photochromic and electrochromic properties. With based on spiroxazine as a photochromic part and 4,4′-bipyridinyl derivative, namely, viologen as an electrochromic part within the single dye molecular structure, this novel multi-functional chromic dye showing both photochromism and electrochromism was synthesized and characterized. The absorption spectra of the colored viologen part after electrocoloration are shown: the prominent peak appeared at 610 nm and was colored blue. Further absorption spectral increases were determined using successive UV irradiation.

Keywords: Hetero-bi-functional; Multi-functional chromism; Absorption spectra; Photochromism; Electrochromism; Spiroxazine; Viologen

1. Introduction

Functional dyes [1–4] showing chromic properties are well known and important classes of the synthetic coloring materials and have attracted much attention due to their potential functions for specialty and high-technology applications. In recent years, the most prominent developments in dye chemistry and dye application have been announced in these areas. For example, unprecedented demands for the use of written text copies, photographic images, sensor probes and displays are greatly increasing towards the subject matter of these concerns [2,3]. In general, chromic dye shows a corresponding single chromic property. In this context, the research of synthesis and characterization for multi-chromism effects only using single dye structure has been increasingly required for many color formation systems, including chromic property application in respond to increased consumer and producer demands.

For chromic dyes, spiroxazine dyes [4–8] as photochromic materials have played a great role to the color occurring reaction in so many new high-technology applications. Photochromism effect has attracted much attention recently from the viewpoint of optical applications because of interests in refractive index or absorbance changes through optical extraction. In the case of electrochromic materials, viologens (*N*,*N*′-disubstituted-4,4′-bipyridinium dications) [9,10] have been extensively studied in the past decade due to their potentials as prototypical electron-transfer reagents, herbicides and materials for electrochromic displays [9,10]. The reduction of the dication of viologens to a highly colored cation radical led us to propose its use as an organic electrochromic compound.

In this context, with based on spiroxazine as a photochromic moiety and 4,4′-bipyridinyl derivative, viologen, as an electrochromic moiety within the single dye molecular structure, the novel hetero-bi-functional dye showing both photochromism and electrochromism at the same time was synthesized and

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* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

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characterized. Their optical properties and absorption spectral changes are also discussed.

2. Experimental

Visible spectra were recorded on Shimadzu UV 2100 spectrophotometer. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu OP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as the internal standard.

2.1. Synthesis of compound **2**

After dissolving NaOH (2.50 g, 62.4 mmol) in 100 ml H_2O, 2,7-dihydroxynaphthalene **1** (10.00 g, 62.4 mmol) and $NaNO_2$ (4.46 g, 6.46 mmol) were added to the solution and stirred for 1 h at 60 °C. This solution was cooled to 0 °C. The mixture of conc. 8 ml H_2SO_4 and 15 ml distilled water was added dropwise to the reaction solution with sustaining 0 °C. The reaction was continued for 1 h. After reaction, the bright brown powder **2** was obtained. Yield: 92%; m.p.: 243 °C; MS *m/z* (M^+) 189; Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.40. Found: C, 63.68; H, 3.79; N, 7.65.

2.2. Synthesis of compound **4**

Spiroxazine dye **4** was prepared using 1-nitroso-2, 7-dihydroxynaphthalene **2** (10.00 g, 52.91 mmol) and 1,3,3-trimethyl-2-methyleneindoline **3** (9.17 g, 52.93 mmol) according to the method described in Refs. [11,12]. Yield: 50%; m.p.: 212–214 °C; MS *m/z* (M^+) 344; ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.36 (s, 6H), 2.76 (s, 3H), 6.6 (d, 1H), 6.58 (d, $J = 7.40$ Hz, 1H), 6.84 (d, $J = 8.84$ Hz, 1H), 6.90 (t, $J = 7.46$ Hz, 1H), 7.02 (d, $J = 8.68$ Hz, 1H), 7.22 (t, $J = 7.40$ Hz, 1H), 7.58 (d, $J = 8.60$ Hz, 1H), 7.65 (d, $J = 8.56$ Hz, 1H), 7.71 (s, 1H), 7.88 (s, 1H); Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 75.63; H, 5.67; N, 8.01.

2.3. Synthesis of compound **6**

Prepared spiroxazine compound **4** (5.00 g, 14.52 mmol) was dissolved in 500 ml acetone. K_2CO_3 (1.60 g, 11.58 mmol) was added to acetone solution with stirring and then 1,6-dibromohexane **5** (4.76 g, 14.52 mmol) was added dropwise to the reaction mixture. This system was refluxed for 24 h. After reaction, the solvent was distilled off under reduced pressure. The obtained solid was added to MeOH solution with stirring. The mixture was filtered, washed and dried. The compound **6** was recrystallised in hexane. Yield: 63%; m.p.: 147 °C; MS *m/z* (M^+) 506; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 6H), 1.57 (m, 5H), 1.91 (m, 4H), 3.44 (t, $J = 6.52$ Hz, 2H), 4.18 (t, $J = 6.52$ Hz, 2H), 6.57 (d, $J = 7.52$ Hz, 1H), 6.84 (d, $J = 9.00$ Hz, 1H), 6.89 (t, $J = 8.04$ Hz, 1H), 7.03 (d, $J = 9.10$ Hz, 1H), 7.08 (d, $J = 6.52$ Hz, 1H), 7.20 (t, $J = 7.16$ Hz, 1H), 7.56 (d, $J = 9.04$ Hz, 1H), 7.63 (d, $J = 9.04$ Hz, 1H), 7.71 (s, 1H), 7.84 (s, 1H); Anal. Calcd for $C_{28}H_{31}BrN_2O_2$: C, 66.27; H, 6.16; N, 5.52; O, 6.31. Found: C, 66.95; H, 6.43; N, 6.00.

2.4. Synthesis of compound **9**

4,4′-Bipyridinyl **7** (6.00, 38.4 mmol) was dissolved in 120 ml anhydrous acetonitrile and then 1-bromopropane **8** (4.72 g, 38.4 mmol) was added dropwise to the this solution. This reaction was refluxed under exclusion of moisture for 40 h. After refluxing, the mixture was filtered to remove undesired yellow impurities. The filtrate was then evaporated to obtain the product. The collected compound **9** was recrystallised in anhydrous acetonitrile. The precipitated solid was filtered and dried to give **9**. Yield: 35%; m.p.: 92 °C; MS *m/z* (M^+) 279; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (t, $J = 7.52$ Hz, 3H), 4.53 (m, 2H), 7.08 (t, $J = 7.00$ Hz, 2H), 10.35 (d, $J = 6.52$ Hz, 2H), 10.85 (d, $J = 7.00$ Hz, 2H), 11.22 (d, $J = 5.04$, 2H), 11.41 (d, $J = 7.04$ Hz, 2H); Anal. Calcd for $C_{13}H_{15}BrN_2$: C, 55.93; H, 5.42; N, 10.03. Found: C, 55.26; H, 5.34; N, 10.03.

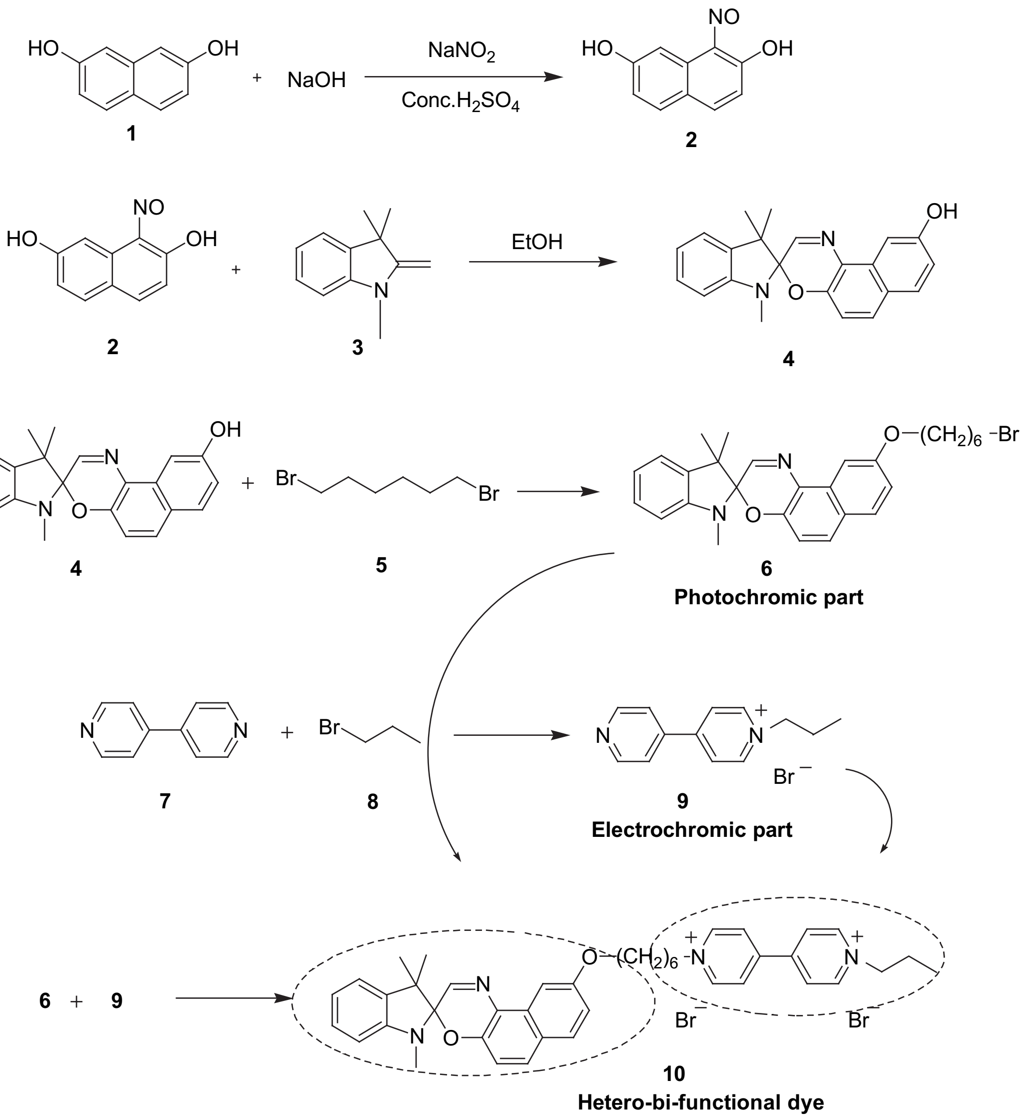
2.5. Synthesis of compound **10**

Spiroxazine compound **6** (3.00 g, 6 mmol) and 4,4′-bipyridinyl derivative **9** (1.70 g, 6 mmol) was refluxed in anhydrous acetonitrile under exclusion of moisture for 30 h. The reaction mixture was filtered and dried to give final product **10**. Yield: 41%; m.p.: 248 °C; MS *m/z* (M^+) 787; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.92 (t, $J = 7.04$ Hz, 3H), 1.24 (s, 3H), 1.27 (s, 3H), 1.43 (m, 2H), 1.54 (m, 2H), 1.82 (m, 2H), 2.03 (m, 4H), 2.68 (s, 3H), 4.14 (t, $J = 6.00$ Hz, 2H), 4.67 (t, $J = 7.00$ Hz, 2H), 4.73 (t, $J = 7.00$ Hz, 2H), 6.66 (d, $J = 8.04$ Hz, 1H), 6.83 (t, $J = 7.56$ Hz, 1H), 6.91 (d, $J = 8.56$ Hz, 1H), 7.02 (d, $J = 9.00$ Hz, 1H), 7.14 (t, $J = 6.56$ Hz, 2H), 7.18 (s, 1H), 7.70 (d, $J = 8.52$ Hz, 1H), 7.75 (d, $J = 8.56$ Hz, 1H), 7.79 (s, 1H), 7.84 (s, 1H), 8.81 (d, $J = 6.52$ Hz, 4H), 9.41 (d, $J = 6.56$ Hz, 2H), 9.44 (d, $J = 6.56$ Hz, 2H); Anal. Calcd for $C_{13}H_{15}BrN_2$: C, 55.93; H, 5.42; N, 10.03. Found: C, 55.26; H, 5.34; N, 10.03.

3. Results and discussion

In recent years, photochromic and electrochromic dyes have attracted much attention as interesting dye classes for functional color materials. This interesting viewpoint with photosensitive and electrosensitive dye material can be expected from the reversible transformations of the molecular structure using photochromic spiroxazine part and electrochromic viologen part. In this work, these two parts are combined together to provide multi-functional chromism effects only using single dye molecular structure (Scheme 1).

The optical functions with photochromism and electrochromism are very interesting subjects from the aspect of the optical applications due to absorbance spectral response



Scheme 1.

under light and electric energy. The photochromic reaction in question is caused by the reversible heterolytic cleavage of the C(spiro)−O bond under UV radiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark. Photochromic reactive system of spiroxazine is shown Fig. 1. Electrochromism is the phenomenon of reversible change in color produced electrochemically. Among organic electrochromic compounds, viologen as a chromophore is particularly attractive due to the possibility of selecting various colors by introducing different substituents into the molecule. This viologen undergoes one-electron reduction to provide a colored radical cation. The redox system of viologen is shown in Fig. 2.

In this work, using spiroxazine compound **6** and 4,4′-bipyridinyl derivative **9**, hetero-bi-functional dye **10** showing both

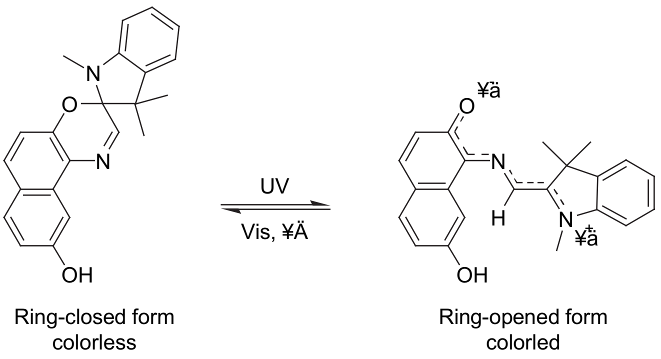


Fig. 1. Photochromic structural change of spiroxazine.

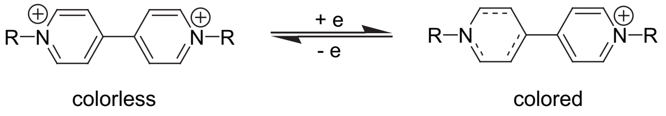


Fig. 2. Electrochromic structural change of viologen.

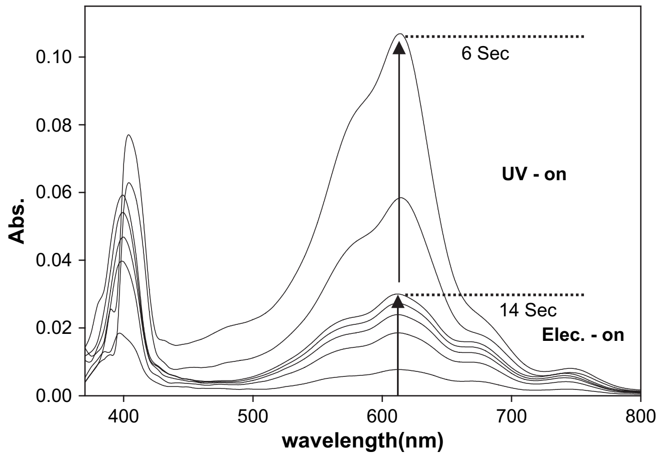


Fig. 3. Visible spectral changes of the dye **10** in DMSO by electric potential (2 V) and UV light.

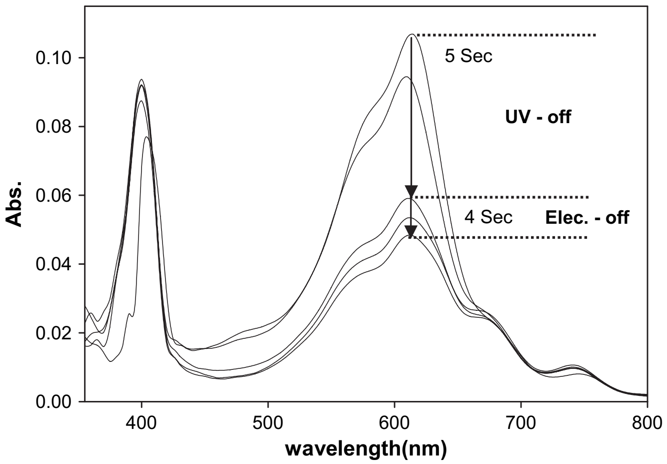


Fig. 4. Spontaneous spectral changes in DMSO.

photochromism and electrochromism at the same time was synthesized and characterized in terms of their designed optical properties. Fig. 3 shows that visible spectral changes of the dye **10** due to the two chromic materials that were determined in DMSO using electric energy and successive UV irradiation. The absorption spectra of the colored viologen part after electrocoloration are shown first: the applied voltage for the coloration was about 2.0 V. The prominent peak appeared at 610 nm and was colored blue. The absorbance of electrochromic part increased significantly with increasing applied time. Further absorption spectra increase was determined using successive UV irradiation. At this point the open merocyanine structure of spiroxazine part due to induced UV energy is attributed to the further increase of the absorption peak at 610 nm. Expected multi-functional chromic effects are clearly observed in Fig. 3. Thus, it is proposed that this novel multi-functional chromic dye was designed and synthesized successfully.

Conversely, Fig. 4 represents the spontaneous spectral changes of the multi-functional chromic dye in DMSO when UV radiation and electric energy were phased out. In these spectral fading behaviors, two chromic compounds hold their chromic properties and also show the multi-functional chromic effects in their stages.

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References

[1] Muthyala R. Chemistry and applications of leuco dyes. New York: Plenum press; 1997.
[2] Waring DR, Hallas G. The chemistry and application of dyes. New York: Plenum press; 1990.
[3] Gregory P. High-technology applications of organic colorants. New York: Plenum press; 1991.
[4] Crano JC, Guglielmetti. Organic photochromic and thermochromic compounds. New York: Plenum press; 1999.
[5] Keum SR, Choi YK, Lee MJ, Kim SH. Dyes Pigments 2001;50:171.
[6] Kim SH, Suh HJ, Cui JZ, Gal YS, Jin SH, Koh K. Dyes Pigments 2002;53:251.
[7] Lim WT, Cui JZ, Suh HJ, Lee HS, Heo NH, Kim SH. Dyes Pigments 2003;56:7.
[8] Kim SH, Ahn CH, Keum SR, Koh K. Dyes Pigments 2005;65:179.
[9] Kim SH, Bae JS, Hwang SH. Dyes Pigments 1996;31:89.
[10] Kim SH, Bae JS, Hwang SH, Gwon TS, Doh MK. Dyes Pigments 1997;33:167.
[11] Kakishita T, Matsumoto K, Kiyotsukuri T, Matsumura K, Hosoda M. J Heterocyclic Chem 1992;29:1709.
[12] Dürr H, Ma Y, Corterllaro G. Synthesis; 1995:294. March.