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Synthesis of hetero-bi-functional dye having photochromism and electrochromism. Part 2: Optical properties and behaviors

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Abstract

In the previous study, we synthesized and characterized the novel hetero-bi-functional chromic dye having spiroxazine moiety as a photochromic part and viologen moiety as an electrochromic part within the single dye molecular structure. This novel multi-functional chromic dye showed photochromic and electrochromic properties and DMSO solution. When UV irradiation and electric energy-on/off states were repeated, these photochromism and electrochromism properties were represented with a fairly good reversibility. First-order kinetics indicates that the open-to-close reaction of spiroxazine occurred more rapidly than the redox system reaction of viologen. Structural change of the spiroxazine to the merocyanine form was in difficulties due to the inclusion complex between dye and β-cyclodextrin, which displayed the dramatic decrease of absorption peaks.

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

1. Introduction

In the previous research [1], synthesis and characterization of the novel hetero-bi-functional dye having photochromism and electrochromism properties were examined. Because most chromic dyes are confined to the single chromic property purpose, only less attention has been given to the application of multi-functional chromic properties using single dye structure. In this context, synthesis and characterization of the hetero-bi-functional dye using only single dye structure were carried out in previous part of this work [1].

As explained previously, functional dyes [2–5] showing chromic properties are well known among the important classes of synthetic coloring materials and have attracted much attention due to their potential functions for specialty and high-technology applications. In this context, the research focusing on the hetero-bi-functional chromic properties using only single dye structure was conducted to investigate the absorption spectral changes with DMSO and the first-order kinetics for spontaneous decoloration rate, including the changes in absorbance in response to UV light and electric potential-on/off states.

Formation of inclusion complex and its corresponding optical properties using β-cyclodextrins were also studied. In general, cyclodextrins [6–10] are cyclic oligosaccharides made up of 6–12 α-D-glucopyranose monomers connected at 1 and 4 carbon atoms. Cyclodextrin are of great importance as useful host molecules due to their characteristic structure, namely interior hydrophobic cavity and exterior hydrophilic groups, and thus find wide applications in photophysics, photochemistry as well as photobiology area [6]. In this work, the interaction and absorption behavior between this novel hetero-bi-functional chromic dye and β-cyclodextrin were discussed and its resulting spectral changes were monitored.

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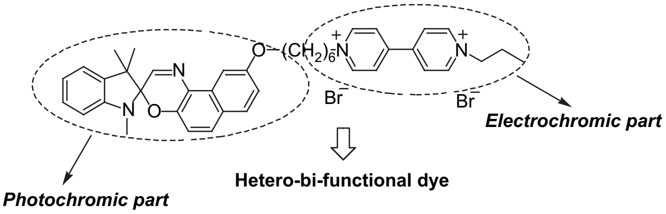

Fig. 1. Synthesized hetero-bi-functional dye structure.

2. Experimental

2.1. Preparation of the hetero-bi-functional dye

The novel hetero-bi-functional dye having photochromism and electrochromism properties within single dye structure was prepared. Its structure is shown in Fig. 1. The methods for synthesis of the hetero-bi-functional dye and its resulting analysis data were described in previous part of this paper [1].

2.2. Photochromic and electrochromic optical changes

Photochromic and electrochromic effects of the prepared hetero-bi-functional dye were investigated. UV irradiation (range 365 nm) and electric energy (2 V) were induced to the dye solution with DMSO. Absorption peak changes and reversible absorption decrease were monitored with time dependence factor.

2.3. Decoloration rate evaluation

First-order kinetic model was fitted and analyzed for the data, when the rate of decoloration of the hetero-bi-functional dye was calculated. Chromism reversibility and optical coloration–decoloration response were also determined.

2.4. Effect of β-cyclodextrin-inclusion complex

Cyclodextrin can react with dye molecules to form an inclusion complex which can influence on absorption intensity and chromism properties. Chromism behavior of the hetero-bi-functional dye in the presence of β-cyclodextrin was investigated and discussed.

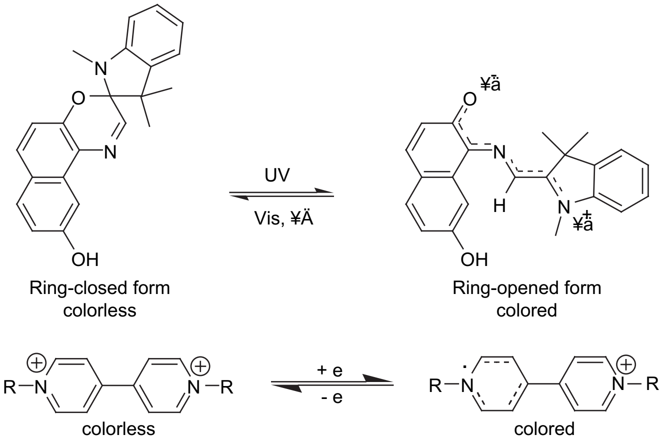

Fig. 2. Examples of photochromic structural change of spiroxazine and electrochromic structural change of viologen.

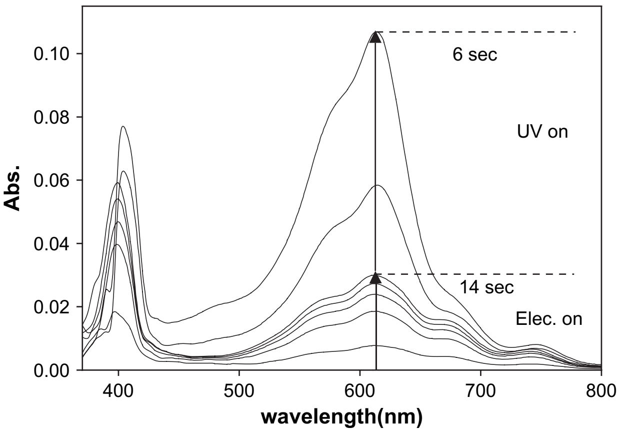

Fig. 3. Visible spectral changes of the dye in DMSO by electric potential (2 V) and UV light.

3. Results and discussion

The spiroxazine part absorbs UV light and shows absorption peak at $\lambda_{max} = 605$ nm as a photochromic change caused by ring open isomerization. The visible range absorption increased gradually by UV irradiation which is ascribed to the generation of the open merocyanine form from the closed spiro form. Electrochromism is the phenomenon of reversible change in color produced electrochemically. Viologen undergoes one-electron reduction to provide a colored radical cation. The redox system of viologen is already proposed in the previous part [1]. Fig. 2 shows the photochromic structural change of spiroxazine and electrochromic structural change of viologen.

Fig. 3 shows the visible spectral changes of the dye caused by the two chromic moieties in DMSO using electric energy and successive UV irradiation. The absorption spectra of the colored viologen part with electric potential appeared first: the applied voltage for the electrical coloration was about

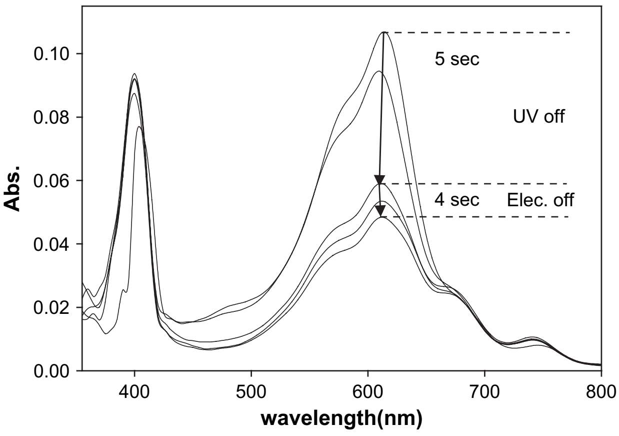

Fig. 4. Spontaneous decoloration of the absorption spectra in DMSO.

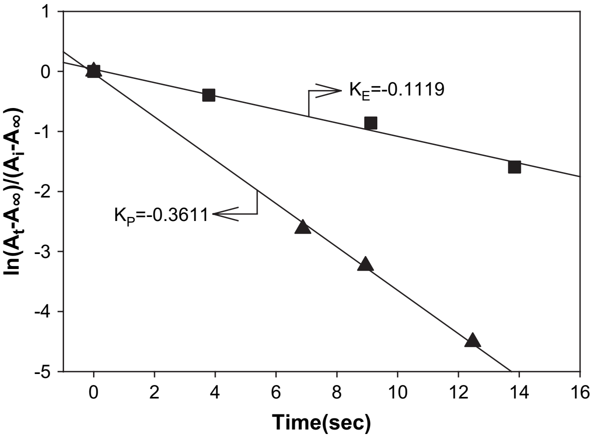

Fig. 5. First-order decoloration kinetic plots of the dye in DMSO.

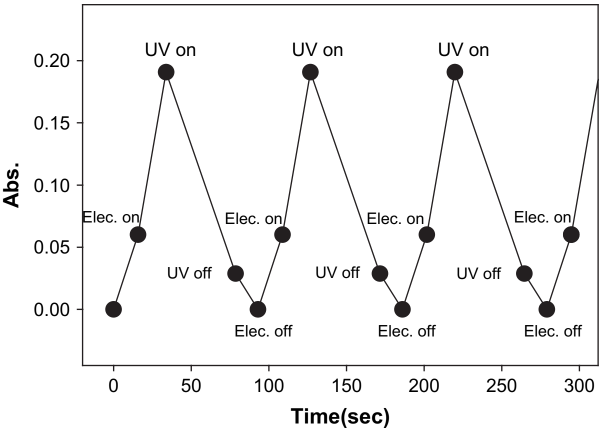

Fig. 6. Absorbance changes at 605 nm of the dye in DMSO using periodic UV and electric potential.

2 V. The major absorption peak was shown at 605 nm and was colored blue. Absorption peak of the electrochromic part increased significantly with increasing applied time. And then, further increase in absorption spectra was observed from successive UV irradiation to the photochromic part. At this point, the open merocyanine structure of spioxazine due to UV energy is responsible for the further increase of the absorption peak at 605 nm. Expected multi-functional chromic effects from the designed dye were clearly observed from Fig. 3. In this context, it is proposed that this novel multi-functional chromic dye was designed and synthesized successfully.

On the other hand, Fig. 4 represents the spontaneous spectral decoloration of the multi-functional chromic dye in DMSO, when UV irradiation and electric energy were phased out. In these spontaneous spectral fading behaviors, each photochromic and electrochromic moiety holds their chromic properties and also shows the multi-functional chromic effects in their stages.

As shown in Fig. 4, when this hetero-bi-functional chromic dye was left in the dark and not engaged in electric energy, the absorbance at 605 nm decreased slowly. Spectra measured after UV irradiation and electric energy supply were proportional to each other in the visible region. This allowed the absorption to be monitored at $\lambda_{\max}$ (605 nm) as a function of time to obtain the color fading rate (k): a first-order fading rate can be obtained by the decoloration properties of the spiroxazine and viologen parts, which is given by Eq. (1) as follows:

$$(A_t - A_\infty)/(A_i - A_\infty) = k \tag{1}$$

where A_i is the absorbance at 605 nm, A_t is the absorbance at 605 nm at any time t after UV irradiation. A_∞ and k refer to the absorbance at 605 nm after 1 h and first-order color changing rate constant, respectively. In this color changing process, the kinetic analysis predicts the logarithm of the difference between A_∞ and A_t at time t to be linear with time, the slope giving the decoloration rate constant, k. First-order plots according to Eq. (1) for the hetero-bi-functional chromic dye are shown in Fig. 5.

The first-order decoloration rate constant of the dye in the viologen part ($k = 0.1119$) was lower than that of spiroxazine part ($k = 0.3611$), which indicates that the open-to-close

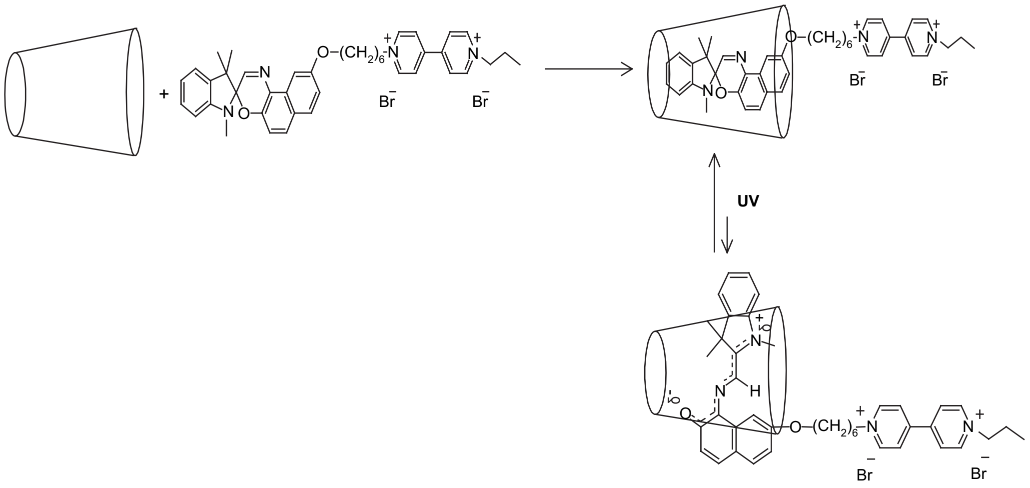

Fig. 7. Example of β-cyclodextrin inclusion and its possible chromism behaviors.

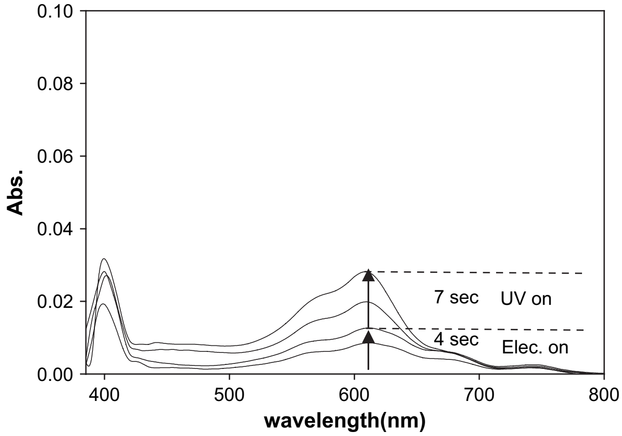

Fig. 8. Effect of β-cyclodextrin on absorption spectral changes of the dye in DMSO: dye concentration 6.35×10^{-4} mol/l, β-CD concentration 1×10^{-3} mol/l.

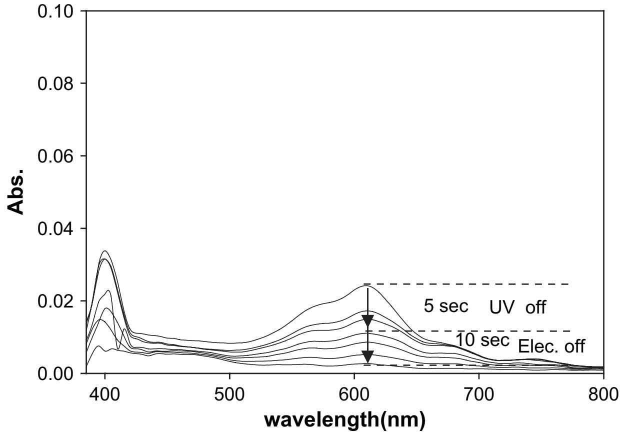

Fig. 9. Effect of β-cyclodextrin on spontaneous decoloration of the absorption spectra in DMSO.

reaction of spiroxazine occurs more rapidly than the redox system reaction of viologen.

Fig. 6 shows the absorbance changes in response to UV/Elec.-on and UV/Elec.-off states. Rapid on-line monitoring of these changes is possible if one records the absorbed intensity as a function of time. These photochromism and electrochromism behaviors represented a fairly good reversibility, as can be seen from Fig. 6, where reversible consecutive coloration–decoloration cycles are confirmed.

Formation and absorption change of the inclusion complex using the dye and β-cyclodextrin were investigated. Cyclodextrins have the property of forming inclusion complex with various guest molecules with suitable polarity and dimension due to their special molecular structure: hydrophobic internal cavity and hydrophilic external surface. Fig. 7 shows the inclusion complex process using the dye and β-cyclodextrin and its possible inclusion way to show photochromic structural transformation. Fig. 7 has shown that hetero-bi-functional chromic dye and β-cyclodextrin can form an inclusion complex, which makes the transformation of spiroxazine moiety from ring closed form to ring open merocyanine form in DMSO be restricted.

For this study, the formation of inclusion complex using the dye and β-cyclodextrin was carried out and confirmed by photochromic spectral changes: β-cyclodextrin was put into the hetero-bi-functional dye solution with sufficient stirring. The spectral changes were then recorded after the solution was kept under UV irradiation and electric energy engagement. The results from Figs. 8 and 9 showed that the absorption spectral intensity dramatically decreased compared to the results from Figs. 3 and 4.

These findings revealed that the inclusion complex between dye and β-cyclodextrin was formed when β-cyclodextrin was added into the dye solution and that the open merocyanine structure formation was restricted by β-cyclodextrin inclusion complex. Intensities in the coloration–decoloration stages due to the inclusion complex were lower than those of the chromic dye itself, which caused for the decrease in absorbance. On the other hand, since spiroxazine part entered into the inner cavity of β-cyclodextrin, the photochemical chromic behavior within the inclusion complex was more difficult than that of spiroxazine moiety itself, which would cause the decrease in absorption peak and also higher activation energy would be required.

Acknowledgement

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