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Modulation of color change and photocyclization of diarylethene with metal complex

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Modulation of color change and photocyclization of diarylethene with metal complex is described. A diarylethene derivative with 4-(ethylideneamino) phenol group 1a is prepared and photochromic behavior is investigated. It is found that 1a exhibits ring-opening and ring-closing photoisomerization with UV/Vis light irradiation in solution. Addition of $Cu(OAc)_2$ to the solution of 1a produces a metal complex 1a–Cu, which generates not only marked color change but also significant promotion in photocyclization. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: color modulation; diarylethene; metal complex; photochromism; photocyclization regulation

INTRODUCTION

Molecules that undergo reversible photoreactions between two isomers with different UV–Vis absorption characteristics are termed photochromic and the process is referred to as photochromism.[1,2] Photochromic diarylethenes are one of the most promising candidates[3–12] for photoelectronic applications because of their thermo-irreversible and fatigue-resistant photoisomerization performances. A lot of applications exist for photochromic diarylethenes that take advantage of their inherent ability to produce switches between two isomers by UV–Vis phototrigger.[13–26] Basic requirements for photoswitch are bistability, suitable wavelength, high efficiency of photoreaction, and fatigue resistance.

Modulation of color change is one of interesting subject for photochromic materials due to the applications such as displays and inks. Both open isomers and closed isomers of diarylethenes have distinct absorption.[27–31] In general, the open isomers have absorption bands at UV region and are colorless, and the closed isomers have absorption bands at visible light region and are colored. Most diarylethenes show very large spectral shifts upon photocyclization of open isomers to closed isomers due to π-electrons delocalization throughout the two condensed thiophene rings and further extension of the substituents. Modulation of the absorption bands (color) of closed isomers are usually due to the modification of the electron properties of substituents[32–35] and the extent of conjugation linked to thiophene rings.[36–38]

Improvement of photochemical reaction efficiency is important and hard subject for photochromic materials. A diarylethene with five-membered heterocyclic rings has two conformations with the two rings in mirror symmetry (parallel conformation) and in C_2 symmetry (anti-parallel conformation). The photocyclization reaction can proceed only from the antiparallel conformation.[39–41] In general, the population ratio of the two conformations is 1:1; therefore, the photocyclization quantum yield cannot exceed 0.5. There are two main approaches to increase the yield of diarylethene photocyclization. One way is to change diarylethene structure by introducing bulky substituents to the thiophene rings or by modifying the bridge unit,[42–44] and another is to incorporate the dithienylethenes into a polymer backbone.[45,46]

In this paper, we report a simple and efficient approach to modulation the color change and to improvement of photocyclization efficiency by diarylethene–metal complex. It is found that by binding with metal ion, the color of closed isomer was changed from blue to purple. Meanwhile, it is also found that the photocyclization of open isomer to closed isomer was promoted with metal complex. The chemical structure of the diarylethene derivative **1a** and its ring-opening and ring-closing photoisomerization is presented in Scheme 1.

EXPERIMENTAL

General Information

^1H NMR spectrum was recorded at 400 MHz with TMS as an internal reference and $CDCl_3$ as solvent. MS spectra were recorded with TOF-MS spectrometer. Absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3010). All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. The reaction was monitored by TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). A 365 nm lamp (36 W) and a Xenon light (500 W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively.

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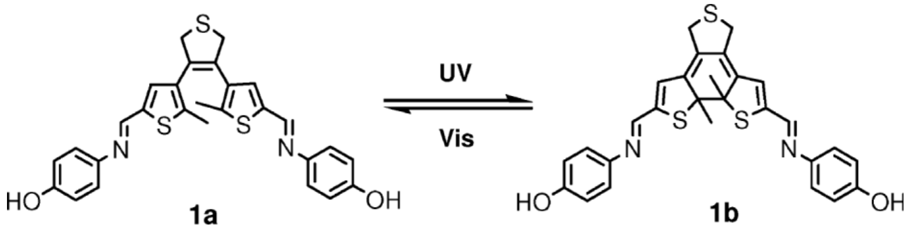
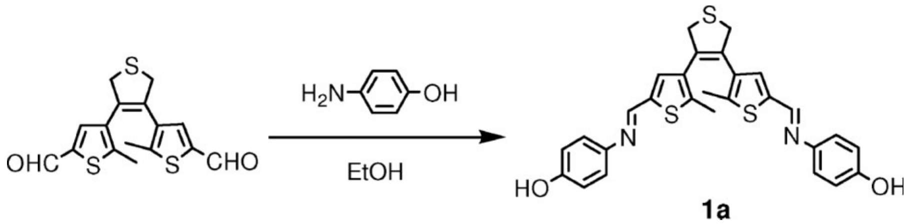


Scheme 1. Structure of diarylethene **1a** and its ring-opening and ring-closing photoisomerization with UV/Vis light irradiation



Scheme 2. Synthesis of diarylethene **1a**

Synthesis of diarylethene *1a*

Diarylethene **1a** was prepared according to synthetic route shown in Scheme 2, and the detailed procedures and spectra data were as follows: a mixture of 3,4-bis (5-formyl-2 -methylthien -3-yl)-2,5-dihydrothiophene[47] (100 mg, 0.3 mmol) and 4-aminophenol (72 mg, 0.66 mmol) in anhydrous ethanol (10 ml) was refluxed. After no starting material was detected by TLC plate, the mixture was cooled, and the yellow product was filtered off, washed with EtOH. Pure diarylethene **1a** was obtained after vacuum drying. Yield: 45% (70 mg). M.p. = 210–211°C. ^1H NMR (400 MHz, DMSO-d_6): 9.48 (s, 2H), 8.58 (s, 2H), 7.43 (s, 2H), 7.14 (d, 4H, $J = 8.7$ Hz), 6.76 (d, 4H, $J = 8.7$ Hz), 4.15 (s, 4H), 1.98 (s, 6H). ^{13}C NMR: 156.2, 149.8, 141.9, 139.9, 139.5, 134.3, 133.0, 132.7, 122.5, 115.7, 42.1, 14.6. TOF-MS EI (*m/z*) calcd. For $C_{28}H_{24}N_2O_2S_3$: 516.1000, found: 516.1000 (100%).

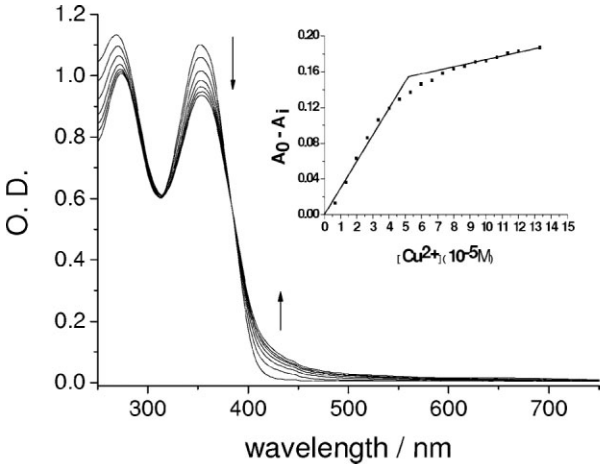


Figure 1. Absorption changes of **1a** (25 μM, CH_3CN) with 365 nm light irradiation (irradiation time: 0, 2, 4, 6 min)

RESULTS AND DISCUSSION

Upon irradiation with UV light, the absorption band ($\lambda_{max} = 353$ nm, $\varepsilon = 4.6 \times 10^4$, in CH_3CN), which attributes to the open-ring isomer **1a**, decreased in intensity, and a new band ($\lambda_{max} = 590$ nm), which corresponds to the closed-ring isomer **1b**, appeared at the same time (Fig. 1). The new band increased in intensity with the irradiation time till the photostationary state (**PSS**) was reached. This process was accompanied by color change of solution from colorless to pale blue. The pale blue solution was bleached back to colorless solution with visible light

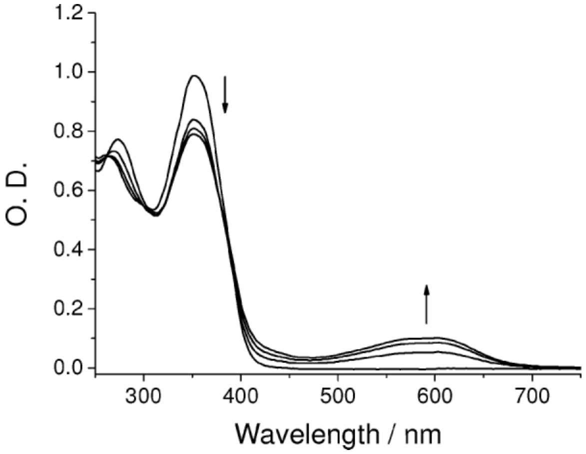


Figure 2. Absorption changes of **1a** (25 μM, CH_3CN) with the addition of $Cu(OAc)_2$ (50 μM). Addition of Cu $(OAc)_2$ to the solution of **1a** produced a complex of **Cu–1a** with a new absorption band at 430 nm as shoulder. The inset is tritration curve of **1a** (25 μM, CH_3CN) with the addition of $Cu(OAc)_2$. A 1:2 complex formation was determined from the absorption spectra changes of **1a**, where the absorption decreased linearly with addition of Cu^{2+} up to 2 equiv

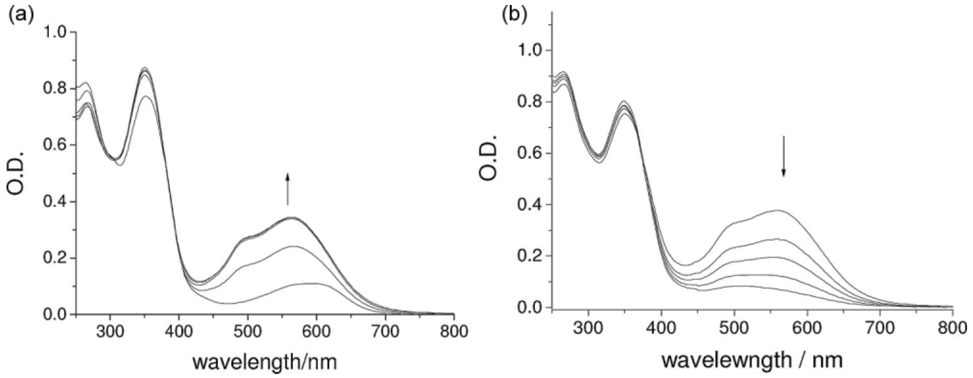


Figure 3. (a) Absorption changes of **1b** with addition of Cu^{2+} (concentration: 0, 13, 25, 38, 50 μM). (b) Photochromic bleaching of **Cu–1b** upon irradiation at ≥450 nm (irradiation time: 0, 11, 22, 36, 54 min)

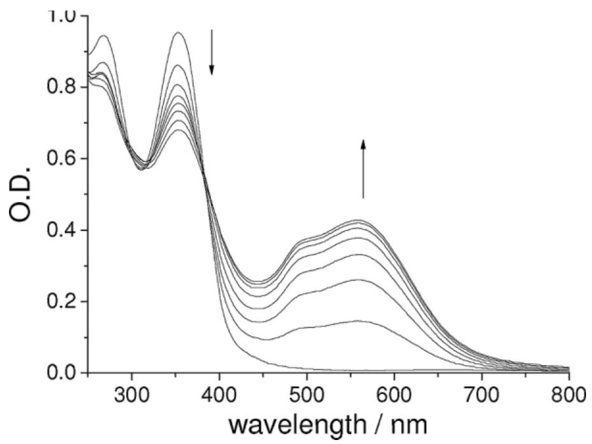


Figure 4. Absorption changes of **Cu–1a** (25 μM, CH$_3$CN) with 365 nm light irradiation (irradiation time: 0, 2, 4, 6, 8, 10, 12, 14 min)

(≥400 nm) irradiation, and the coloration and decoloration can be recycled with UV/Vis light irradiation.

Addition of Cu(OAc)$_2$ (50 μM) to the solution of **1PSS** (**1a/1b**) produced a distinct color of solution: from pale blue to purple. Control experiment showed that no significant color change was observed when a solution of Cu(OAc)$_2$ (50 μM) was added to a solution of **1a**, only a small absorption changes were detected (Fig. 2). The color change resulted from the complexation of **1b** with Cu^{2+}, and further study found that the absorption at 590 nm was gradually blue-shifted to 560 and 495 nm, which corresponds to complex of **Cu–1b**, with increasing concentrations of Cu^{2+} (Fig. 3a). With visible light (≥400 nm) irradiation, the purple solution was bleached to colorless solution (Fig. 3b). The coloration and bleaching could be recycled with UV/Vis light irradiation.

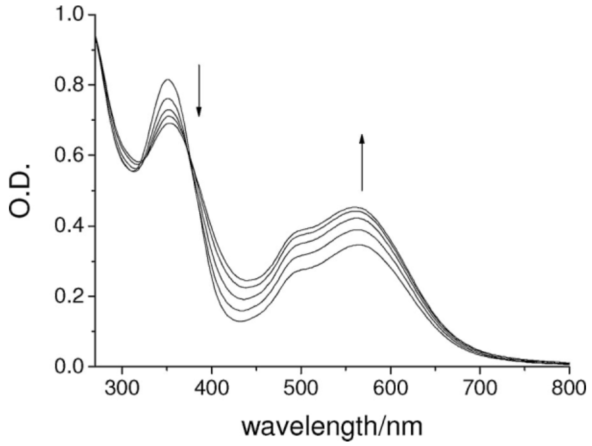
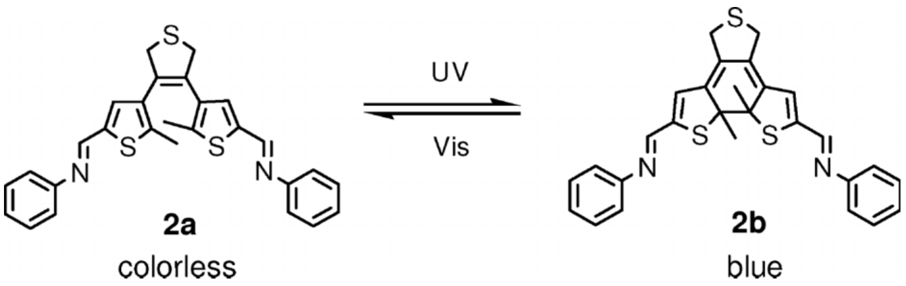


Figure 5. Absorption changes of **Cu–1PPS** (obtained from Figure 3a) with 365 nm light irradiation (irradiation time: 0, 2, 4, 6, 8 min)

Control experiment showed that the complex of **Cu–1a** exhibited photochromic properties: **Cu–1a** converted to **Cu–1b** upon irradiation with 365 nm light till photostationary state was reached, and **Cu–1b** bleached back to **Cu–1a** with visible light ($\lambda \geq 400$ nm) irradiation. As presented in Fig. 4, the absorption at 353 nm, which corresponded to **Cu–1a**, decreased in intensity, and two bands ($\lambda_{max} = 560$, 495 nm), attributed to **Cu–1b**, appeared upon irradiation with 365 nm light. The absorption figure showed the same profile as Fig. 3(a), which confirmed that the complex of **Cu–1a** was converted to **Cu–1b** with 365 nm light irradiation. It is worth noting that the optical density of **Cu–1b** (0.45) at 560 nm in Fig. 4 increased by more than 30% in comparison with that of **Cu–1b** (0.34) in Fig. 3(a), which suggested that the photocyclization of **Cu–1a** to **Cu–1b** was probably promoted by the complexation of **1a** with Cu^{2+}.

To confirm the photocyclization of **Cu–1a** to **Cu–1b** was promoted by the complexation of **1a** with Cu^{2+}, the following experiments were performed. First, upon irradiation with 365 nm light, the solution color of **Cu–1b** resulted from Fig. 3(a), obtained by addition of 50 μM of Cu^{2+} to **1PPS**, darkened. Further investigation found that the optical density of **Cu–1PPS** at 560 and 495 nm increased accompanying the decrease of optical density at 353 nm (Fig. 5), and the largest optical density (0.43) at 560 nm was obtained at photostationary state, which is agreement with the result (0.45) in Fig. 4. Second, the conversion yield of **Cu–1a** to **Cu–1b** (58%) is larger than that of **1a** to **1b** (26%) by calculating the ratio of proton in both open form and closed form in ^{1}H-NMR spectroscopy. All suggested that the complexation of **1a** with Cu^{2+} promoted the photocyclization of **Cu–1a** to **Cu–1b**.

The binding site of **1a** with Cu^{2+} was estimated by both NMR spectroscopy and analogue. ^{1}H NMR spectroscopy showed that the signals arising from the aromatic protons (thiophen ring) shift downfield by 0.05 ppm, and from imine protons (N═CH) shift upfield by 0.02 ppm, respectively. The signal of OH ($\delta = 9.5$ ppm) in phenol group, however, disappeared. These suggested that the



Scheme 3. The structural of analogue **2a** and its ring-opening and ring-closing photoisomerization with UV/Vis light irradiation

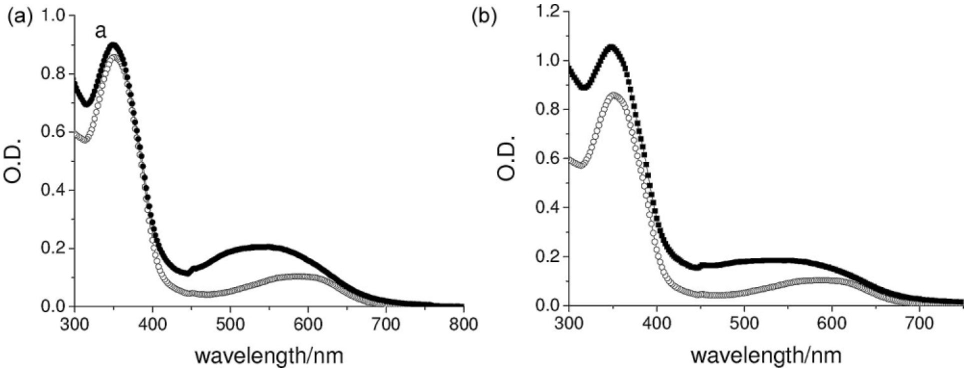


Figure 6. Absorption change of **1b** with addition of Co^{2+} (a) and Mn^{2+} (b) (white: **1b**, black: **1b-metal**)

binding site may be at O atom. To further confirm the binding site, an analogue **2a** (Scheme 3) was prepared and investigated. It was found that **2a** showed ring-opening and ring-closing photoisomerization with UV/Vis light irradiation, and accompanying the photocyclization, the colorless solution of **2a** was changed to blue solution of **2b**. Addition of Cu^{2+} to the solution of **2PPS**, no color change was observed. Further study found that no change in both absorption spectra of **2a** and **2b** was detected upon addition of Cu^{2+}. Results suggested that no complex was formed between **2a** or **2b** with Cu^{2+}, and the binding site occurred at O atom instead of at S and N atoms. The complex **Cu–1a** is probably formed[48] by binding two Cu^{2+} with two phenol units, which prefers to the photocyclization of diarylethene due to the increase of the anti-parallel conformation.[49,50]

The color change and the promotion of photocyclization of **1a/1b** with other with metal ions (Zn^{2+}, Mg^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}) were also explored. Primarily experiments showed that addition of metal ions above to the solution of **1a** and **1b** produced metal-complexes, which resulted in the color change. But only with Co-complex and Mn-complex, the optical density of closed isomer was increased by 16% (Co^{2+}) and 10% (Mn^{2+}) (Fig. 6). The results suggested that the photocyclization of **1a** could also be promoted by binding with other metal ions.

CONCLUSIONS

In summary, an artificial photochromic diarylethene with functional group has been designed and prepared as template. It has demonstrated that not only distinct color change is obtained in photocyclization when diarylethene binds with metal ion but also the photocyclization reaction is significantly promoted with diarylethene-metal complex. This may provide a simple and convenient way to modulate the color and the photocyclization of diarylethene system.

Acknowledgements

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