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Synthesis and photochromic properties of a multiple responsive diarylethene and its selective binding affinity for copper(II) ion

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ABSTRACT

A multiple responsive photochromic diarylethene, 1-[2,5-dimethyl-3-thienyl]-2-[2-methyl-5-(2-pyridyl)-3-thienyl]perfluorocyclopentene (**1**) with excellent fatigue resistance has been successfully synthesized. Easy and reversible conversion is observed between the two open- and closed-ring isomers of **1** upon irradiation with UV and visible light. Addition of trifluoroacetic acid to these two isomers gives two new protonated products featuring distinctively different color changes. Photochromic diarylethene **1b** is found to have selective interaction with copper(II) ion. With increasing amount of copper(II) ion, the absorption maximum of the photostationary state at 563 nm decreases and disappears eventually, and the color of the solution changes from purple to colorless. Upon UV light irradiation, the solution color remains colorless and can no longer be restored. UV–vis absorption spectroscopy, fluorescence, and NMR spectroscopy were used to investigate the selective interaction between diarylethene **1b** and copper(II) ion with results indicating that diarylethene **1b** exhibits selective binding affinity for copper(II) ion.

1. Introduction

Photochromic materials have recently received increasing attention due primarily to their potential applications in optoelectronic devices, such as optical memories [1–6] and photoinduced switches [7–16]. Diarylethene derivatives are one of the most promising candidates for their notable thermal irreversible photochromic behaviors, remarkable fatigue resistance [1,2] and high photochemical quantum yields [7,17]. The open- and closed-ring isomers of diarylethenes feature different absorption characteristics and many different physical and chemical properties such as photoluminescence [18–21] and refractive index [22,23]. These differences have reportedly been utilized to realize their applications with desired functions.

In recent years, several attempts have been made toward the engineering of multiple responsive switching systems based on modulating the photochromism of diarylethenes for practical applications. Conventional approaches include changing the acid strength [24,25], tuning the intramolecular proton transfer [26], complexing with metal cation ions and anion ions [27–29], and uptaking and releasing of Cu^{2+} and Ag^{+} to and from the monolayer-modified electrode by the cyclic photostimulated [30]. For example, Chen et al. [25] constructed a multiple responsive switching system that gave distinguished color changes upon addition of trifluoroacetic acid and sodium hydroxide. Tian and his coleagues [27], synthesized two new chemosensors based on photochromic dithienylcyclopentene, their photochromic properties can be modulated by Hg^{2+} and F^{-} ions, respectively. Moreover, the two diarylenthenes in photostationary states become promising sensors for Hg^{2+} and F^{-} with high selectivity. Li et al. [31] synthesized an organoboron functionalized diarylethene derivative and demonstrated the modulation of its spectral properties with fluoride and mercuric ions. All the diarylethenes mentioned above are limited to photo or ion induced color changes.

Cu(II) ion, on the other hand, is one of the most important environmental pollutants and an essential trace element in various biological systems. Alteration in the cellar homeostasis of cupric ions is commonly associated with serious diseases, such as Menkes and Wilson disease [32–34], Alzheimer's disease [35], familial amyotropic lateral sclerosis [36,37], and prion diseases [38]. In particular, long-term exposure to high level copper would cause liver or kidney damages [39]. Thus, the recognition and detection for the highly noxious element is of growing interest [40]. The Cu^{2+} selective fluoroionohpores reported so far contain many kinds of moieties as integral parts, such as anthracene [41], macrocyclic dioxotetraamine and 1,8-naphthalimide derivative [42], and urea groups [43]. In this regard, Li and his colleagues [44] developed a rhodamine B derivative as a fluorescence turn-on chemodosimeter

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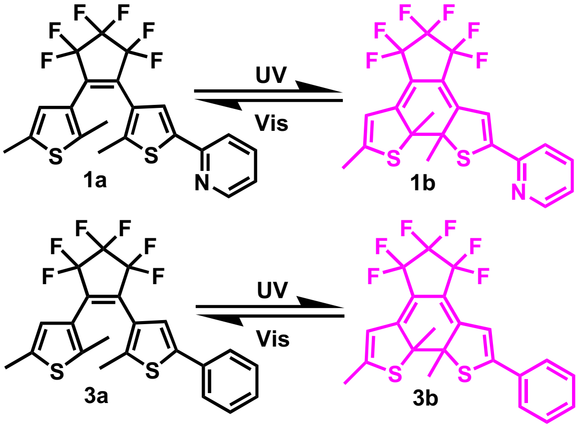

Fig. 1. Photochromism of diarylethenes **1** and **3**.

that responded stoichiometrically, rapidly, and highly sensitively to Cu^{2+} in aqueous media, and it could also be applied in live cell imaging.

Herein, we design and synthesize a simple diarylethene that not only exhibits multiple responsive photochromism with trifluoroacetic acid and triethylamine, but also shows selective binding affinity for copper(II) ion. The diarylethene is found to convert reversibly between the open- (**1a**, colorless) and closed-ring (**1b**, purple) isomers upon irradiation of UV and visible light (Fig. 1), while upon addition of trifluoroacetic acid, the solution color changes from purple (**1b**) to blue (**2b**). The blue solution (**2b**) returns completely back to purple (**1b**) after neutralization with triethylamine. With addition of Cu^{2+}, the purple solution (**1b**) is bleached to colorless, and the fluorescence emission of diarylethene **1b** is greatly quenched. Meanwhile, upon irradiation of ultraviolet light again, the colorless solution can no longer change. The special binding between diarylethene **1b** and copper is believed to be responsible for these findings. The diarylethene promises potential applications in environmental copper(II) ion sensoring and in vivo fluorescence imaging.

2. Experiment

2.1. General methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane as an internal standard. IR spectra were carried out on a Bruker Vertex-70 spectrometer. Mass spectra were measured with an Agilent 1100 ion trap MSD spectrometer. UV–vis absorption spectra were measured using an Agilent 8453 UV–vis spectrometer. Photo-irradiation was carried out with an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Lights of appropriate wavelengths were isolated by different light filters. Fluorescent properties were measured with a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected both at 10 nm. All solvents used were of spectro grade and were purified by distillation prior to use. All other reagents were obtained from J&K Scientific LTD without further purification.

2.2. Synthesis of diarylethene **1a**

Diarylethene **1a** was synthesized according to the synthetic route summarized in Fig. 2, and the detailed procedures and spectral data are as follows: First, (2,5-dimethyl-3-bromo)thiophene (**4**) was synthesized from 2,5-dimethylthiophene referring to the previous literature [45,46]. Lithiation of the mixture of **4** followed by the addition of excess octafluorocyclopentene simultaneously generated compound **5**, which was further treated with the anion generated from 3-bromo-2-methyl-5-(2-pyridyl)thiophene **6** [47] to yield isomeric diarylethene **1a** (42% yield). Its structure was confirmed by NMR, IR, and MS spectrometry. ^1H NMR: (400 MHz, $CDCl_3$, ppm), δ 8.54 (d, $J = 4.6$ Hz, 1H), 7.69–7.72 (m, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.53 (s, 1H), 7.16–7.19 (m, 1H), 6.74 (s, 1H), 2.42 (s, 3H), 1.92 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.37, 14.67, 15.13, 118.49, 122.20, 123.85, 124.45, 124.59, 126.04, 136.74, 137.85, 139.83, 142.59, 144.04, 149.58, 151.66; IR (cm^{-1}): 448, 529, 588, 782, 989, 1083, 1166, 1272, 1401, 1454, 1613, 2053, 2169, 2316, 3182; MS(ESI): m/z 460.0 $(M + H)^+$.

3. Results and discussion

3.1. Photochromism of diarylethene **1**

The ring-opening and ring-closing photoisomerization of diarylethene **1** is illustrated in Fig. 1. The changes in the absorption spectra of diarylethenes **1** induced by photoirradiation at room temperature in hexane is shown in Fig. 3. Upon irradiation with the light of 297 nm, the absorption band ($\lambda_{max} = 307$ nm, $\varepsilon = 2.43 \times 10^4$ L mol^{-1} cm^{-1}), which is attributed to the open-ring isomer **1a**, decreases in intensity, while a new band, which corresponds to the closed-ring isomer **1b**, appears at the same time. The new band increases in intensity with increase in irradiation time until the photostationary state ($\lambda_{max} = 563$ nm, $\varepsilon = 7.98 \times 10^3$ L mol^{-1} cm^{-1}) is reached. Fig. 3 shows typical absorption spectral changes of photochromic diarylethene derivatives in solution. Such process is accompanied by a solution color change from colorless to purple. The purple solution is bleached completely back to colorless upon irradiation with visible light ($\lambda > 500$ nm) and the original absorption spectrum is recovered quantitatively. The quantum yields of the cyclization and cycloreversion are 0.48 and 0.057, respectively [48]. Preliminary fatigue resistance tests show 7% degradation detected by UV–vis absorption (decrease in optical density) after 50 cycles. These findings are indication that, in solution, diarylethene **1** shows remarkable photochromic behaviors with good fatigue resistance.

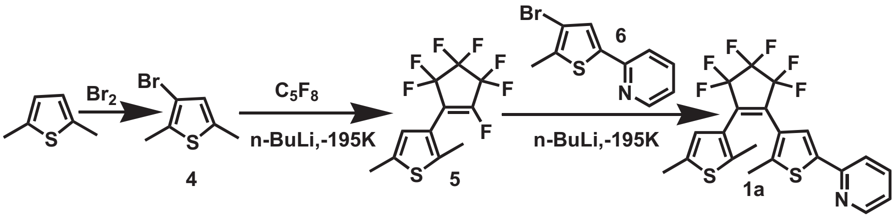

Fig. 2. Synthetic route for diarylethene **1a**.

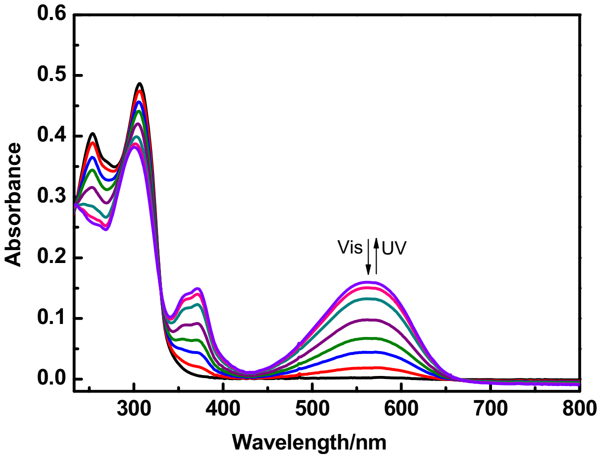

Fig. 3. Absorption spectral changes of diarylethene **1** in acetonitrile.

3.2. *Multiple response of diarylethene **1***

Addition of trifluoroacetic acid (CF_3COOH) in CH_3CN (1.0 M) to the solution of **1a** produces a protonated diarylethene **2a**, whose absorption band bathochromic shifted to 345 nm ($\varepsilon = 1.85 \times 10^4$ L mol^{-1} cm^{-1}, in CH_3CN). Compound **2a** also undergoes photoisomerization under light irradiation (Fig. 4). Upon irradiation of UV light to compound **2a**, the absorption band at 345 nm decreases in intensity, while a new band, corresponding to the closed-ring isomer **2b**, appears at the mean time (Fig. 5). The absorption of the new band increases with increase in irradiation time until the photostationary state ($\lambda_{max} = 600$ nm, $\varepsilon = 1.05 \times 10^4$ L mol^{-1} cm^{-1}) is reached, and this process is coupled with a solution color change from colorless to blue. Presented in Fig. 5 are typical absorption spectral changes of photochromic diarylethene derivatives in solution. The blue solution is bleached completely back to colorless with visible light ($\lambda > 500$ nm) irradiation and the original absorption spectrum is fully recovered. The quantum yields of the cyclization and cycloreversion are measured at 0.095 and 0.015, respectively [48]. The fatigue resistance tests show about 8% degradation detected by absorption after 50 cycles of photoisomerization.

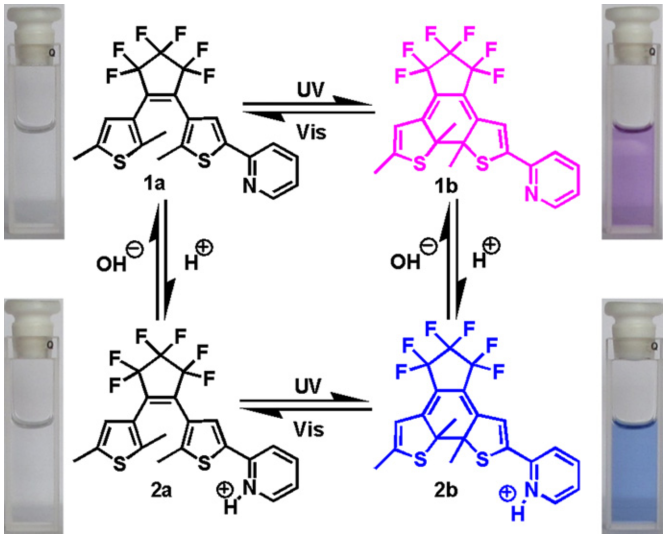

Fig. 4. Structural and color changes between **1a**, **2a**, **1b**, and **2b**.

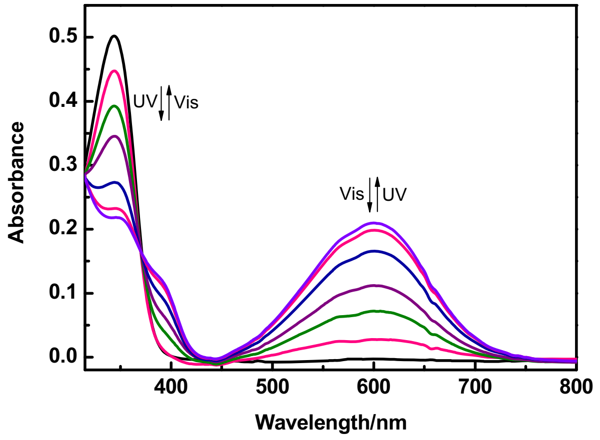

Fig. 5. Absorption spectral changes of diarylethene **2** in acetonitrile.

The switching of **1a** and **1b,** with **2a** and **2b**, respectively, were investigated by protonation of **1a** and **1b** with an acid (CF_3COOH in CH_3CN, 1.0 M) and subsequent back-neutralization of **2a** and **2b** with a base ($(CH_3CH_2)_3N$ in CH_3CN, 1.0 M). The purple solution of **1b** is found to change to a blue solution of **2b** with the addition of trifluoroacetic acid, while the blue solution returns completely back to purple upon neutralization with triethylamine. As presented in Fig. 6, the absorption profile of **2b**, resulted from **1b** after protonation, resembles that of **2b** shown in Fig. 5, which is in turn resulted from **2a** upon UV light irradiation. The blue solution of **2b** either returns completely back to purple (**1b**) after neutralization with the amine or gets bleached to colorless (**2a**) upon visible light irradiation. On the contrary, with the addition of the acid to the solution of **1a**, no color change is observed in the colorless solution of **2a**, although the λ_{max} bathochromic shifts from 307 (**1a**) to 345 nm (**2a**). The transformation of chemical structures and color changes between them are summarized in Fig. 4.

3.3. *Interaction between **1b** and Cu^{2+}*

The interaction between **1b** and copper(II) ion was investigated by UV–Vis absorption spectroscopy in acetonitrile. When $Cu(NO_3)_2$ solution is added to **1b** dropwise, the absorbance centered at 563 nm decreases gradually and levels off after total addition of about 4.0 equivalents (Fig. 7A), with final total 91.5% of decrease in the absorbance band detected by UV–vis absorption. A Sigmoidal

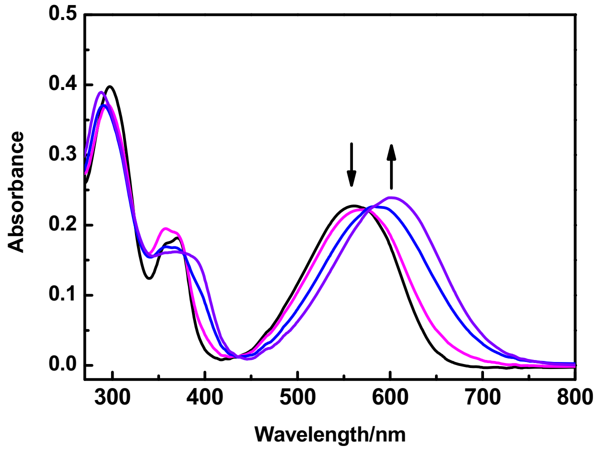

Fig. 6. The absorption changes of **1b** with addition of trifluoroacetic acid.

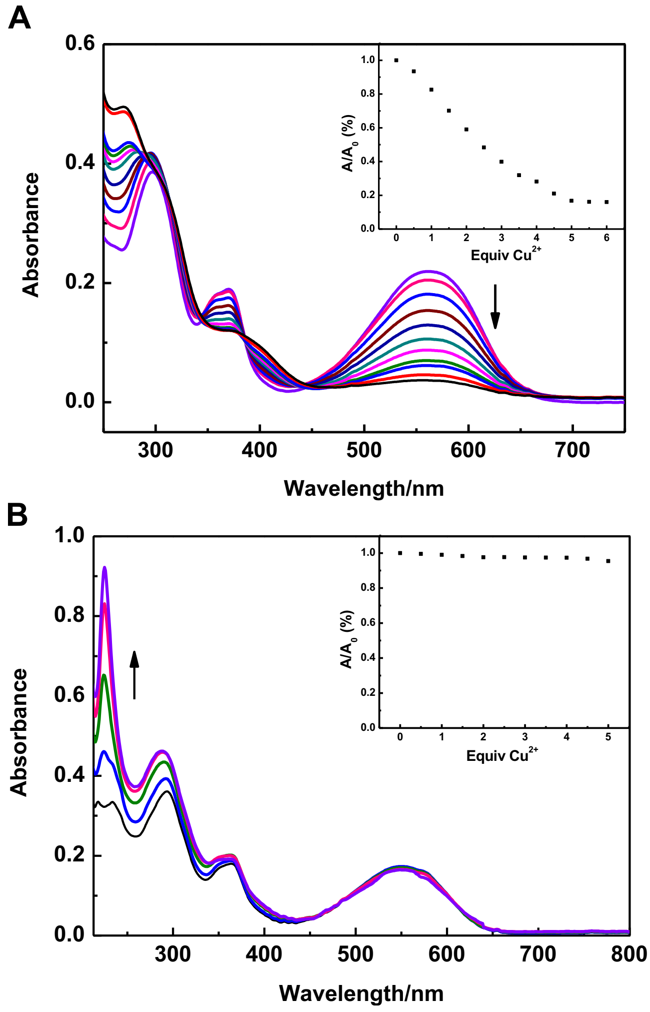

Fig. 7. Absorption spectral changes of diarylethene **1b** (**A**) and **3b** (**B**) (2.0×10^{-5} mol/L) in acetonitrile upon addition of $Cu(NO_3)_2$. The inset shows absorbance at 563 (**A**) and 550 nm (**B**) in the function of equivalents of Cu^{2+}.

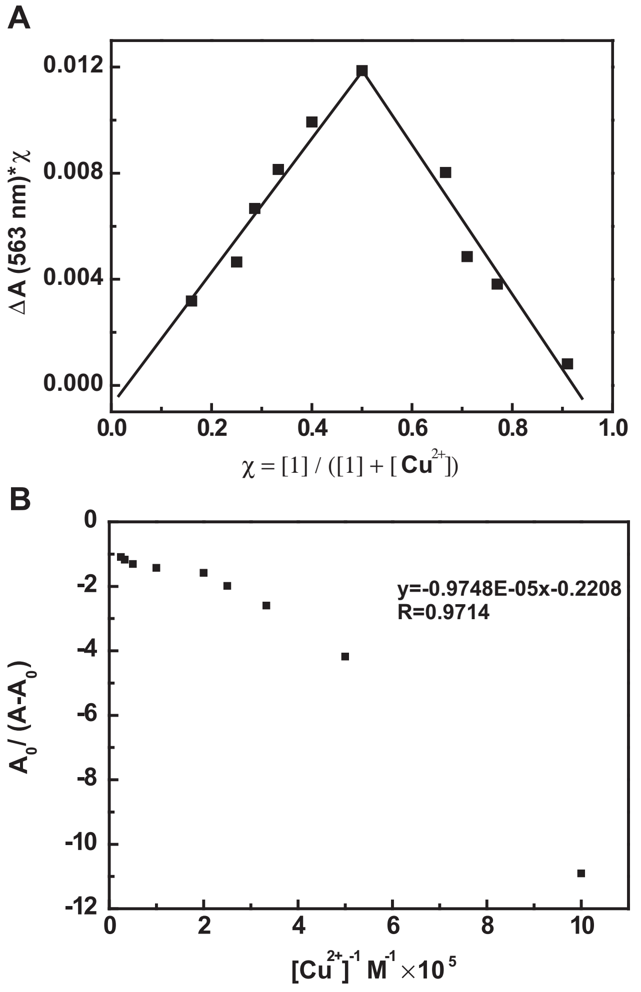

Fig. 8. Job's plot (A) showing 1:1 complex formation for **1b**; Hildebrand–Benesi plot (B) based on the 1:1 for **1b** with Ka = 2.3×10^4 M^{-1}.

curve was also obtained and is shown in the Fig. 7A inset. The absorption band ($\lambda_{max} = 307$ nm), attributed to the open-ring isomer **1a**, increases gradually and then reaches a saturation state with three clear isosbestic points at 344, 385, and 445 nm. Job's plots (Fig. 8A) indicated the 1:1 complex formation in the case and the binding constant for **1b** was found to be 2.3×10^4 M^{-1} (Fig. 8B) using Hildebrand–Benesi equation [49,50]. Meanwhile, a new absorbance centered at 224 nm appears, which originates from the cupric ion. The purple solution is bleached completely to colorless after the addition of Cu^{2+} to the solution. Upon irradiation with the light of 297 nm again, the color of the solution can no longer change. The clear change from purple to colorless can easily be observed by naked eye as revealed in Fig. 9A. The color of the solution are based on the changes in the extent of π-conjugation in diarylethene upon photochromic reaction, on the contrary, the color of the solution change from purple to colorless implies the shorten of π-conjugation. The added Cu^{2+} ions prohibit the π-conjugation extend of compound **1** lead to the color change. These changes were similar to that of a reported publication [51]. These results indicate that copper(II) ion markedly changes the photochromic property of diarylethene **1**.

For comparison purposes, 1-[2,5-dimethyl-3-thienyl]-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (**3**) was synthesized according to the previous literature [48]. Compound **3** features similar photochromic properties to diarylenthene **1** as shown in Fig. 1. Similar to diarylethene **1b**, **3b** was also examined in acetonitrile upon addition of Cu^{2+}. As shown in Fig. 7B, the absorbance band at 550 nm has only shown 2.7% degradation detected by UV–vis absorption after addition of 4.0 equivalents of Cu^{2+} to the acetonitrile solution of diarylethene **3b**, and the obtained Sigmoidal curve is revealed in the Fig. 7B inset. No color change is observed by naked eye, and the color change can also be controlled by UV and visible light (Fig. 9B). Such results indicate that the pyridine ring is crucial to the interaction between Cu^{2+} and diarylethene **1b**. Substituting the pyridyl group will eliminate its photochromic properties, and this is also the reason that pyridyl groups are widely used for constructing extended structures through metal coordination [52,53].

3.4. *Selective of **1b** binding affinity for Cu^{2+}*

To explore the selective binding affinity of diarylethene **1b** for Cu^{2+}, comparative experiments were extended to other metal cations in CH_3CN by UV–vis absorption spectroscopy. As depicted in Fig. 10, weak absorption changes of **1b** are observed upon addition of metal cations, such as K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Zn^{2+}, Sn^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+}, Hg^{2+}, Cd^{2+}, compared with the addition of Cu^{2+}. These absorption differences suggest that diarylethene **1b** has strong binding affinity for Cu^{2+} with high selectivity. The good selectivity is likely from the special binding affinity

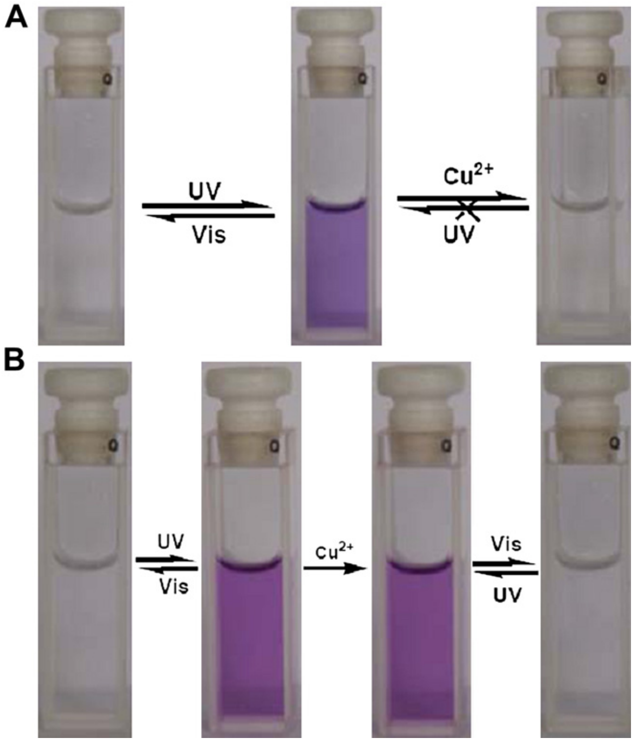

Fig. 9. Color changes of diarylenthene **1** (**A**) and **3** (**B**) upon addition of Cu^{2+} and irradiation with UV/Vis light.

between the copper ion and nitrogen atom of the pyridine ring in diarylethene **1b** [52].

3.5. Fluorescent properties of **1b** with Cu^{2+}

Generally, luminescent emission spectroscopy is more sensitive toward small changes that affect the electronic properties of moleculor receptors [54,55]. Hence, the response of diarylethene **1b** to Cu^{2+} was further investigated with photoluminescence. Diarylethene **1b** in CH_3CN is found to show an intense emission band at 411 nm. As shown in Fig. 11, strong decrease in the emission intensity is observed upon addition of Cu^{2+}. After addition of 4.0 equivalents of Cu^{2+}, the emission of diarylethene **1b** is markedly quenched and only 17% of original remains. Diarylethene **1b** may thus be used as a "turn-off" luminescent molecular probe toward Cu^{2+}. The strong decrease in emission could be explained with energy/electron transfer between an excited complex to an complexed copper cation [56]. The stoichiometry of diarylethene **1b** with Cu^{2+} is consistent with what is obtained by UV–vis absorption. Other ions, such as K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Zn^{2+}, Sn^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+}, Hg^{2+}, and Cd^{2+}, as expected, have no influence on the fluorescence of diarylethene **1b**.

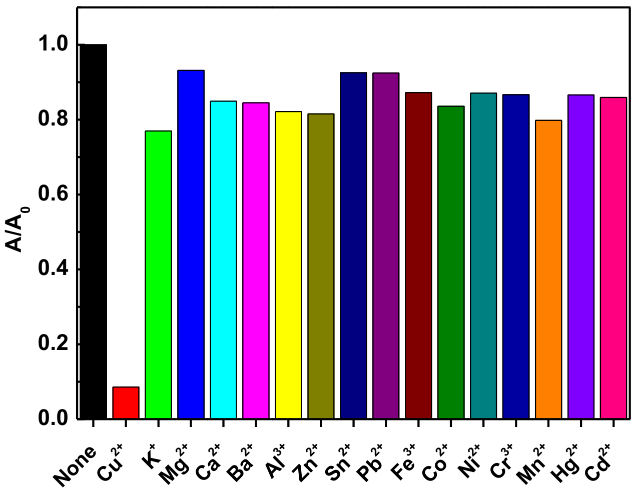

Fig. 10. Comparison of absorbance of diarylethene **1b** in CH_3CN (2.0×10^{-5} mol/L) with addition of 4.0 equivalents of different metal cations.

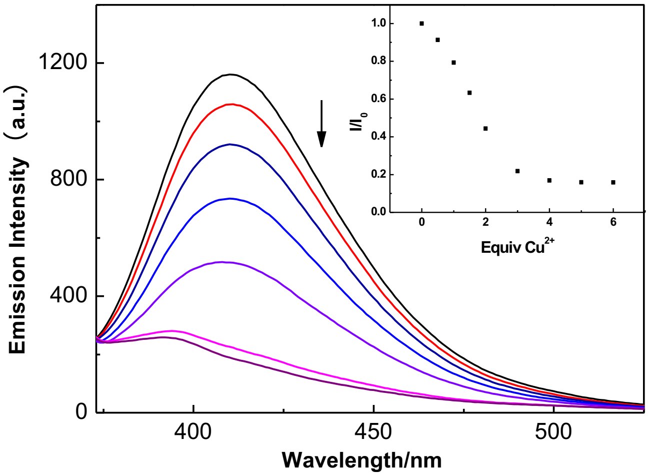

Fig. 11. Changes in the fluorescence emission spectra of diarylethene **1b** in CH_3CN with various amounts of Cu^{2+} ions; $\lambda_{ex} = 350$ nm. The inset shows the fluorescence intensity at 411 nm in the function of equivalents of Cu^{2+}.

In order to confirm the strong binding affinity between Cu^{2+} and diarylethene **1b**, a strong chelant ethylene diamine tetraacetic acid disodium salt (Na_2EDTA) was carried out in the experiments. Upon addition of a Na_2EDTA solution and after irradiation with the light of 297 nm, the colorless solution of diarylethene **1b** and Cu^{2+} cannot change color any more, suggesting that diarylethene **1b** has high affinity for copper(II) ions and the process is irreversible upon addition of Na_2EDTA.

3.6. NMR study the binding affinity of **1b** for Cu^{2+}

NMR spectroscopy was also employed to further investigate the binding affinity of diarylethene **1b** for Cu^{2+}. ^1H NMR experiments were carried out in DMSO-d_6. Fig. 12 compares a portion of ^1H NMR spectra of diarylethene **1b** before and after addition of Cu^{2+}. Significant upfield shifts are observed in the resonance of the pyridine group of **1b** with varied extent occurred in ^1H NMR spectra upon addition of Cu^{2+}. For example, resonances of peaks **a**, **b**, **c**, **d**, **e**,

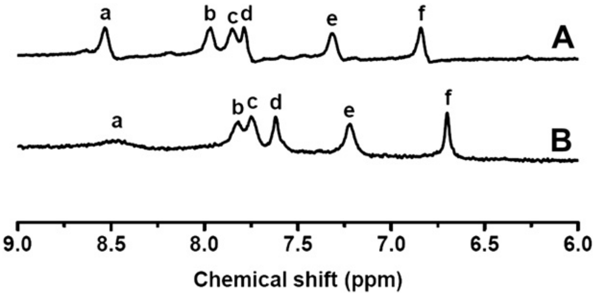

Fig. 12. Partial ^1H NMR spectral changes of diarylethene **1b** in DMSO-d_6 before (**A**) and after (**B**) addition of Cu^{2+}.

and **f**, denoted in Fig. 12, shows upfield shifts about 0.07, 0.14, 0.10, 0.16, 0.10, and 0.13 ppm, respectively. The change of chemical shift indicated that diarylethene **1b** should bind with Cu^{2+}. Moreover, diminishing and broadening effects in peak **a** are observed. Such spectral results indicate that the formed complex between diarylethene **1b** and Cu^{2+} (denoted **Cu-1b**) is fluxional, which may explain its poor recrystallization behaviors [57,58]. The Cu^{2+} binding site is likely the pyridine nitrogen atom, whereas the thiophene ring that links to the pyridine ring may be sterically distorted and keep away from another thiophene ring, causing complex **Cu-1b** to lose its photochromic performances.

4. Conclusion

In summary, a new photochromic diarylethene was successfully synthesized, and its multiple responsive photochromism and selective binding affinity for Cu^{2+} were examined. The results indicate that the diarylethene shows excellent photochromic properties with distinctive color changes, excellent fatigue resistance, and special binding selectivity to Cu^{2+}. It has been demonstrated that with right engineering and construction of a suitable diarylethene, a multiple responsive photoswitch can be achieved. Tuning of photochromic diarylethene spectral properties promises further applications, such as environmental copper(II) ion sensoring with naked eye and in vivo fluorescence imaging.

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References

[1] Irie M. Diaryethene for memories and switches. Chemical Reviews 2000;100: 1685–716.

[2] Tian H, Yang S. Recent progresses on diarylethene based photochromic switches. Chemical Society Reviews 2004;33:85–97.

[3] Wang S, Qi QZ, Li CP, Ding GH, Kim S-H. Photoswitching of bisthienylethene using 2D-p-A type pyran-based fluorescent dye for rewritable optical storage. Dyes and Pigments 2011;89:188–92.

[4] Kawata S, Kawata Y. Three-dimensional data storage using photochromic materials. Chemical Reviews 2000;100:1777–88.

[5] Xie N, Chen Y, Yao B, Lie M. Photochromic diarylethene for reversible holographic recording. Materials Science and Engineering: B 2007;138:210–3.

[6] Luo S, Chen K, Cao L, Liu G, He Q, Jin G, et al. Photochromic diarylethene for rewritable holographic data storage. Optical Express 2005;13:3123–8.

[7] Tian H, Wang S. Photochromic bisthienylethene as multi-function switches. Chemical Communications 2007;8:781–92.

[8] Tian H, Feng YL. Next step of photochromic switches. Journal of Materials Chemistry 2008;18:1617–22.

[9] Kim M-S, Maruyama H, Kawai T, Irie M. Refractive index changes of amorphous diarylethenes containing 2,4-diphenylphenyl substituents. Chemistry of Materials 2003;15:4539–43.

[10] Feringa BL, van Delden RA, Koumura N, Geertsema EM. Chiroptical molecular switches. Chemical Reviews 2000;100:1789–816.

[11] Sud D, Norsten TB, Branda NR. Photoswitching of stereoselectivity in catalysis using a copper dithienylethenes complexes. Angewandte Chemie International Edition 2005;44:2019–21.

[12] Mitchell RH, Bandyopadhyay S. Catalytic asymmetric synthesis of hydroxy enol ethers: approach to a two-carbon homologation of aldehydes. Organic Letters 2004;6:1729–32.

[13] Fukaminato T, Sasaki T, Kawai T, Tamai N, Irie M. Digital photoswitching of fluorescence based on the photochromism of diarylethene derivatives at a single-molecule level. Journal of the American Chemical Society 2004;126: 14843–9.

[14] Wigglesworth TJ, Sud D, Norsten TB, Lekhi VS, Branda NR. Chiral discrimination in photochromic helicenes. Journal of the American Chemical Society 2005;127:7272–3.

[15] Whalley AC, Steigerwald ML, Guo X, Nuckolls C. Reversible switching in molecular electronic devices. Journal of the American Chemical Society 2007; 129:12590–1.

[16] Tsujioka T, Sesumi Y, Takagi R, Masui K, Yokojima S, Uchida K, et al. Selective metal deposition on photoswitchable molecular surfaces. Journal of the American Chemical Society 2008;130:10740–7.

[17] Zhu WH, Meng XL, Yang YH, Zhang Q, Xie YS, Tian H. Bisthienylethenes containing a benzothiadiazole unit as a bridge: photochromic performance dependence on substitution position. Chemistry-A European Journal 2010;16: 899–906.

[18] Tian H, Chen B, Tu H, Müllen K. Novel bisthienylethene-based photochromic tetraazaporphyrin with photoregulating luminescence. Advanced Materials 2002;14:918–23.

[19] Norsten TB, Branda NR. Photoregulation of fluorescence in a porphyrinic dithienylethene photochrome. Journal of the American Chemical Society 2001;123:1784–5.

[20] Giordano L, Jovin TM, Irie M, Jares-Erijman EA. Diheteroarylethenes as thermally stable photoswitchable acceptors in photochrome fluorescence resonance energy transfer (pcFRET). Journal of the American Chemical Society 2002;124:7481–9.

[21] Yam VWW, Ko CC, Zhu NY. Photochromic and luminescence switching properties of a versatile diarylethene-containing 1,10-phenanthroline ligand and tts rhenium(I) complex. Journal of the American Chemical Society 2004; 126:12734–5.

[22] Kim EY, Choi YK, Lee MH. Photoinduced refractive index change of a photochromic diarylethene polymer. Macromolecules 1999;32:4855–60.

[23] Bertarelli C, Bianco A, D'Amore F, Gallazzi MC, Zerbi G. Effect of Substitution on the change of refractive index in dithienylethenes: an ellipsometric study. Advanced Functional Materials 2004;14:357–63.

[24] Kawai SH, Gilat SL, Lehn JM. Photochemical pK_a-modulation and gated photochromic properties of a novel diarylethene switch. European Journal of Organic Chemistry; 1999:2359–66.

[25] Liu HH, Chen Y. Construction and properties of multi-addressable switching system based on a photochromic diarylethene. Journal of Materials Chemistry 2009;19:706–9.

[26] Ohsumi M, Fukaminato T, Irie M. Chemical control of the photochromic reactivity of diarylethene derivatives. Chemical Communications; 2005:3921–3.

[27] Zou Q, Jin JY, Xu B, Ding L, Tian H. New photochromic chemosensors for Hg^{2+} and F^-. Tetrahedron 2011;67:915–21.

[28] Tian H, Qin B, Yao RX, Zhao XL, Yang SJ. A single photochromic molecular switch with four optical outputs probing four inputs. Advanced Materials 2003;15:2104–7.

[29] Kopelman RA, Snyder SM, Frank NL. Tunable photochromism of spirooxazines via metal coordination. Journal of the American Chemical Society 2003;125: 13684–5.

[30] Zhang JJ, Riskin M, Tel-Vered R, Tian H, Willner I. Optically activated uptake and release of Cu^{2+} or Ag^+ ions by or from a photoisomerizable monolayer-modified electrode. Langmuir 2011;27:1380–6.

[31] Zhou ZG, Yang H, Shi M, Xiao SZ, Li FY, Yi T, et al. Photochromic organoboron-based dithienycyclopentene modulated by fluoride and mercuric(II) ions. ChemPhysChem 2007;8:1289–92.

[32] Waggoner DJ, Bartnikas TB, Gitlin JD. The role of copper in neurodegenerative disease. Neurobiology of Disease 1999;6:221–30.

[33] Vulpe C, Levinson B, Whitney S, Packman S, Gitschier J. Isolation of a candidate gene for Menkes disease and evidence that it encodes a copper-transporting ATPase. Nature Genetics 1993;3:7–13.

[34] Bull PC, Thomas GR, Rommens JM, Forbes JR, Cox DW. The wilson disease gene is a putative copper transporting P-type ATPase similar to the Menkes gene. Nature Genetics 1993;5:327–37.

[35] Barnham KJ, Masters CL, Bush AI. Neurodegenerative diseases and oxidative stress. Nature Reviews Drug Discovery 2004;3:205–14.

[36] Valentine JS, Hart PJ. Misfolded CuZnSOD and amyotrophic lateral sclerosis. Proceedings of the National Academy of Sciences of the United States of America 2003;100:3617–22.

[37] Bruijn LI, Miller TM, Cleveland DW. Unraveling the mechanisms involved in motor neuron degeneration in ALS. Annual Review of Neuroscience 2004;27: 723–49.

[38] Brown DR, Kozlowski H. Biological inorganic and bioinorganic chemistry of neurodegeneration based on Prion and Alzheimer diseases. Dalton Transactions; 2004:1907–17.

[39] Georgopoulos PG, Roy A, Yonone-Lioy MJ, Opiekun RE, Lioy PJ. Environmental copper: its dynamics and human exposure issues. Journal of Toxicology and Environmental Health: Part B 2004;4:341–94.

[40] Schroder JL, Basta NT, Payton M, Wilson JA, Carlson RI, Janz DM, et al. Ecotoxicological risks associated with land treatment of petrochemical waste: I. Residual soil contamination and bioaccumulation by cotton rats (*Sigmodon Hispidus*). Journal of Toxicology and Environmental Health: Part A 2003;66: 305–25.

[41] Kumar S, Singh P, Kaur S. A Cu^{2+} protein cavity mimicking fluorescent chemosensor for selective Cu^{2+} recognition: tuning of fluorescence quenching to enhancement through spatial placement of anthracene unit. Tetrahedron 2007;63:11724–32.

[42] Mu HL, Gong R, Ma Q, Sun YM, Fu EQ. A novel colorimetric and fluorescent chemosensors: synthesis and selective detection for Cu^{2+} and Hg^{2+}. Tetrahedron Letters 2007;48:5525–9.

[43] Yang H, Liu ZQ, Zhou ZG, Shi EX, Li FY, Du YK, et al. Highly selective ratiometric fluorescent sensor for Cu(II) with two urea groups. Tetrahedron Letters 2006;47:2911–4.

[44] Yu MX, Shi M, Chen ZG, Li FY, Li XX, Gao YH, et al. Highly sensitive and fast responsive fluorescenece turn-on chemodosometer for Cu^{2+} and its application in live cell imaging. Chemistry – A European Journal 2008;14:6892–900.

[45] Pu SZ, Liu WJ, Miao WJ. Photochromism of new unsymmetrical isomeric diarylethenes bearing a methoxyl group. Journal of Physical Organic Chemistry 2009;22:954–63.

[46] Liu WJ, Pu SZ, Liu G. Synthesis and optoelectronic properties of unsymmetrical isomeric diarylethene derivatives having a fluorine atom. Journal of Molecular Structure 2009;936:29–36.

[47] Gilat SL, Kawai SH, Lehn J-M. Light-triggered molecular devices: photochemical switching of optical and electrochemical properties in molecular wire type diarylethene species. Chemistry – A European Journal 1995;1:275–84.

[48] Pu SZ, Yan LS, Wen ZD, Liu G, Shen L. Synthesis and chlorine atom position effect on the properties of unsymmetrical photochromic diarylethenes. Journal of Photochemistry and Photobiology A: Chemistry 2008;196:84–93.

[49] Job P. Formation and stability of inorganic complexes in solution. Annales de Chimie 1928;9:113–203.

[50] Benesi HA, Hilderbrand Jh. A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. Journal of the American Chemical Society 1949;71:2703–7.

[51] Zhang JJ, Tan WJ, Meng XL, Tian H. Soft mimic gear-shift with a multi-stimulus modified diarylethene. Journal of Materials Chemistry 2009;19: 5726–9.

[52] Matsuda K, Takayama K, Irie M. Photochromism of metal complexes composed of diarylethene ligands and Zn(II), Mn(II), and Cu(II) hexafluoroacetylacetonates. Inorganic Chemistry 2004;43:482–9.

[53] Matsuda K, Shinkai Y, Irie M. Photochromism of metal complexes composed of diarylethene ligands and $ZnCl_2$. Inorganic Chemistry 2004;43: 3774–6.

[54] Yang YK, Yook KJ, Tae J. A rhodamine-based fluorescent and colorimetric chemodosimeter for the rapid detection of Hg^{2+} ions in aqueous media. Journal of the American Chemical Society 2005;127:16760–1.

[55] Guo X, Qian X, Xia L. A highly selective and sensitive fluorescent chemosensor for Hg^{2+} in neutral buffer aqueous solution. Journal of the American Chemical Society 2004;126:2272–3.

[56] Miller MT, Gantzel PK, Karpishin TB. A photoluminescent copper(I) complex with an exceptionally high CuII/CuI redox potential: $[Cu(bfp)_2]^+$ (bfp = 2,9-bis(trifluoromethyl)-1,10-phenanthroline). Angewandte Chemie International Edition 1998;37:1556–8.

[57] Ngwendson JN, Banerjee A. A Zn(II) selective fluorescence sensor that is not affected by Cd(II). Tetrahedron Letters 2007;48:7316–9.

[58] Ngwendson JN, Amiot CL, Srivastava DK, Banerjee A. Design of a Zn(II) ion specific fluorescence sensor. Tetrahedron Letters 2006;47:2327–30.