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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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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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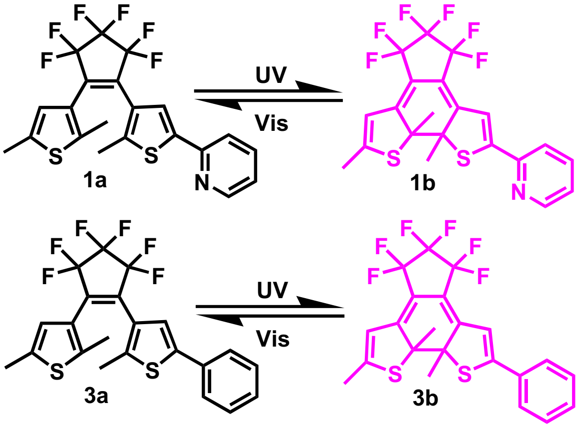

Fig. 1. Photochromism of diarylethenes **1** and **3**.

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.

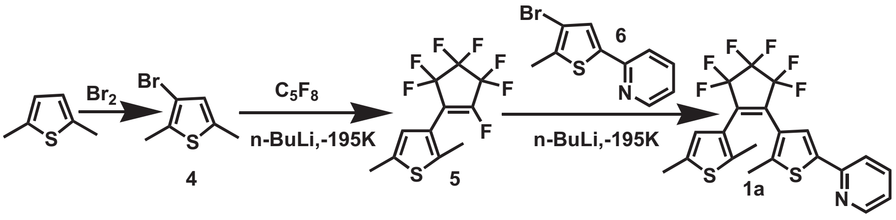

Fig. 2. Synthetic route for diarylethene **1a**.