A Diarylethene Derived Chemosensor for Colorimetric Sensing of $\text{Cu}^{2+}$

Shouzhi Pu, a Qi Sun, Chunhong Zheng a  
Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, 30013 Nanchang Jiangxi PR China

E-mail: a pushouzhi@tsinghua.org.cn (S. Pu), ezirobot@163.com (C. Zheng)

Abstract. A diarylethene bearing a 8-hydroxyquinoline-linked salicylhydrazide Schift base unit has been synthesized. In CH$_3$CN, the compound displayed a highly selective and sensitive response to $\text{Cu}^{2+}$ via perceptible color and UV–vis absorbance changes among the other tested metal ions. In the presence of $\text{Cu}^{2+}$, the peak at 341 nm disappeared and concomitantly a new charge transfer absorption band emerged at 381 and 450 nm. Moreover, the compound formed host-guest complex in 1:1 stoichiometry.

1. Introduction
Development of chemosensors for the selective recognizing and sensing of bioactive cations is one of the most burgeoning areas in current research because of their different analytical applications in biological, industrial and environmental processes [1,2]. $\text{Cu}^{2+}$ is known as a catalytic cofactor in a variety of metallo-enzymes which includes superoxide dismutase, cytochrome oxidase, and tyrosinase etc. [3]. However, despite its biological significance, imbalance in its required concentration can lead to serious detrimental effects in the human body. The over accumulation of $\text{Cu}^{2+}$ in humans is responsible for a lot of neurological diseases such as Alzheimer's, Wilson's and prion disease [4,5]. Owing to the importance and hazardous roles played by $\text{Cu}^{2+}$ ions, numerous efforts have been undertaken to develop efficient and selective methods to assess $\text{Cu}^{2+}$ ions in cells and organisms [6].

Using optical techniques to detect $\text{Cu}^{2+}$ ions has resulted in fruitful work in the past several decades [7]. However, most of these techniques depend on fluorescent sensors due to their sensitivity [8]. Compared to fluorometric sensors, colorimetric sensors have attracted much attention for allowing so-called “naked-eye” detection in a straightforward and inexpensive manner, offering qualitative and quantitative information without using expensive equipment.

To date, a number of photochromic compounds as versatile sensors for ions have been reported [9]. As one of the most promising photoresponsive materials, diarylethene are especially attractive due to their excellent thermal stability, remarkable fatigue resistance, and rapid response [10]. Most chemosensors based on diarylethene derivatives were obtained by introduce an ion recognizing group into the molecular structures [11-13]. Herein, a colorimetric chemosensor based on a novel diarylethene with 8-hydroxyquinoline-linked salicylhydrazide Schift base has been designed and synthesized, in which act as a recognition unit. It showed selective colorimetric and UV–vis spectral changes in the presence of $\text{Cu}^{2+}$ in CH$_3$CN. The photochromism of 1o is shown in Scheme 1.
2. Experimental

2.1. General
NMR spectra were collected on a Bruker AV400 (400 MHz) spectrometer by using tetramethylsilane (TMS) as an internal standard and with CDCl₃ as the solvent. Elemental analysis was carried out with a PE CHN 2400 analyzer. UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectrophotometer. TLC plates were visualized by 254 nm UV irradiation. Fluorescence spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer. Photo-irradiation experiments were performed using an SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Mass spectra were performed using on Bruker AmaZon SL spectrometer. The solutions of metal ions (0.1 mol L⁻¹) were obtained by the dissolution of their respective metal nitrates in distilled water, except for Mn²⁺, Hg²⁺, K⁺, and Ba²⁺ (their counter ions were chloride ions). Chemical reagents were purchased from either Alfa or TCI and used without further purification. Solvents were from Beijing Chemical Works. Anhydrous solvents were of spectro-grade and purified by distillation prior to use. All solution-phase reactions were performed under an atmosphere of dry argon or nitrogen.

2.2. Synthesis
The synthetic route to the target compound was shown in Scheme 2. 3-5 were synthesized by the similarly reported methods [14,15].

2.2.1. Synthesis of 1-[2-methyl-5-(4-hydroxymethylphenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (3). To a stirred solution of compound 2 (2.47 g, 5.00 mmol) in THF (50 mL), NaBH₄ (0.27 g, 7.00 mmol) was added and continuously stirred. After refluxing for 2 hrs, the mixture was cooled to room temperature and quenched with water (40 mL). The mixture was extracted with ethyl acetate, dried over MgSO₄, filtered, and evaporated. The residue was purified by chromatography on silica gel using the mixture solvent of petroleum ether and ethyl acetate (v/v = 2:1) as the eluent to give 3 (2.16 g, 4.35 mmol) as a light yellow solid in 87% yield. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.77 (s, 3H), 1.98 (s, 3H), 3.60 (s, 3H), 4.71 (s, 2H), 6.93 (s, 1H), 7.23 (s, 1H), 7.38–7.35 (m, 2H), 7.53–7.55 (m, 2H).
2.2.2. Synthesis of 1-[2-methyl-5-(4-bromomethylphenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrrol)perfluorocyclopentene (4). To a stirred anhydrous CH₂Cl₂ (40 mL) of compound 3 (0.99 g, 2.00 mmol) was added MsCl (0.26 ml, 3.20 mmol), TEA (0.50 ml, 3.60 mmol) with vigorous stirring in the cold water bath. Stirring was continued for 5 min at 273 K, 10 mL anhydrous THF containing LiBr (0.69 g, 8.00 mmol) was added and the reaction mixture was stirred for 30 min. at this temperature. The reaction was warmed to room temperature and stirred for 12 hrs. The product was extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate and water, then dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using the mixture solvent of petroleum ether and ethyl acetate (v/v = 6/1) as the eluent to afford 4 as a yellow solid in 70% yield. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.70 (s, 3H), 1.89 (s, 3H), 3.54 (s, 3H), 4.52 (s, 2H), 6.86 (s, 1H), 7.08–7.10 (m, 1H), 7.18 (s, 1H), 7.41–7.48 (m, 6H), 8.01–8.03 (m, 1H), 8.22–8.24 (m, 1H), 10.26 (s, -CHO).

2.2.3. Synthesis of 1-[2-methyl-5-(2-formylquinoline-8-methoxy)dimethyl]-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrrol)perfluorocyclopentene (5). To a stirred solution of 4 (1.12 g, 2.00 mmol) in anhydrous acetonitrile (30 mL), 8-hydroxyquinoline-2-carboxaldehyde (0.28 g, 1.60 mmol), K₂CO₃ (0.66 g, 4.00 mmol), and KI (0.80 g, 2.20 mmol) were added and continuously stirred. After refluxing for 6 h, the mixture was cooled to room temperature and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 6/1) as the eluent to afford 5 as a yellow solid in 70%. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.76 (s, 3H), 1.96 (s, 3H), 3.61 (s, 3H), 7.25 (s, 1H), 7.30 (m, 1H), 7.37 (m, 2H), 7.65 (d, J = 8.0Hz, 1H), 7.83 (s, 1H), 8.17–8.19 (m, 1H), 8.33–8.35 (d, J = 4.0Hz, 1H), 12.31 (s, 1H), 15.81 (s, 1H).

2.3. Procedures for metal-ion sensing
Stock solutions of the metal ions (0.1 mol L⁻¹) were prepared in deionized water. A stock solution of 1o (1.0 × 10⁻³ mol L⁻¹) was prepared in CH₃CN, and was then diluted to 2.0 × 10⁻⁵ mol L⁻¹. Titration experiments were performed by placing 2 mL of 1o in a quartz cuvette of 1 cm optical path length, and then adding the Cu²⁺ stock solution incrementally by means of a micro-pipette. Spectra were recorded 3 sec after the addition. Test samples for selectivity experiments were prepared by adding appropriate amounts of metal ion stock solutions to 2 mL of 1o. In competition experiments, Cu²⁺ was added to solution containing 1o and the other metal ions of interest.

2.4. Determination of the stoichiometry of the 1o-Cu²⁺ complex
According to the method for continuous variation. A series of solutions of 1o and Cu²⁺ at ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 were prepared, and the absorption spectra were recorded. When plot the fluorescence intensity against the [Cu²⁺]/([Cu²⁺] + [1o]), a feature point was obtained at 0.5 in abscissa, indicating the 1:1 stoichiometry of the 1o-Cu²⁺ complex.
3. Results and discussion

The absorption spectral and color changes of 1o by photoirradiation in acetonitrile are shown in Fig. 1A. Upon irradiation with 297 nm light, a new absorption band centered at 619 nm emerged due to the formation of the closed-ring isomer 1c, accompanied with a color change from colorless to blue. The blue color faded completely to colorless upon irradiation with visible light ($\lambda > 510$ nm), and the absorption spectrum returned to the initial state of 1o. When the photostationary state was arrived, a clear isosbestic point was observed at 317 nm, indicating that the process was in agreement with a two-component photochromic reaction [16]. The fluorescence property of 1o was measured in acetonitrile ($2.0 \times 10^{-5}$ mol L$^{-1}$) at room temperature (Fig. 1B). When excited with 344 nm light, the fluorescent emission peak of 1o appeared at 472 nm. Upon irradiation with 297 nm light, the emission intensity decreased due to the formation of weakly fluorescent closed-ring isomers of 1c [17]. The back irradiation with appropriate visible light ($\lambda > 500$ nm) regenerated the open-ring isomer of 1o, and recovered the original emission intensity. The emission intensity of 1 was quenched to ca. 33% in the photostationary state.

![Figure 1](image-url)

(A) Absorption spectral change, inset: color changes by stimuli of 297 nm and visible light ($\lambda > 500$ nm); (B) Emission spectral change.

The naked-eye detectable color change of 1o ($2.0 \times 10^{-5}$ mol L$^{-1}$) was observed by adding an equivalent amount of various cations such as (K$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Cr$^{3+}$, Al$^{3+}$, Fe$^{2+}$ and Cu$^{2+}$). 1o showed a perceptible color change from colorless to yellow in the presence of Cu$^{2+}$. In UV–vis absorption study (Fig. 2), 1o alone showed two absorption bands at 252 nm, 293 nm, and 341 nm due to $\pi-\pi^*$ transitions [18]. Upon addition of Cu$^{2+}$, the peak at 341 nm disappeared and concomitantly a new charge transfer absorption band appeared between 358 and 550 nm with absorption maxima at 381 and 450 nm. No noticeable color and spectral changes were observed in the presence of other tested metal ions. The charge transfer promoted color and spectral
changes presumably occurred due to the delocalization of electrons from the quinoline-N, imine-N and salicylhydrazide-OH to Cu$^{2+}$ during complexation.

![Absorption spectra changes of 1o upon addition of Cu$^{2+}$ in acetonitrile (2.0 × 10$^{-5}$ mol L$^{-1}$). Inset: the change of absorbance at 450 nm with the addition of different equiv Cu$^{2+}$.](image)

**Figure 2.** Absorption spectra changes of 1o upon addition of Cu$^{2+}$ in acetonitrile (2.0 × 10$^{-5}$ mol L$^{-1}$). Inset: the change of absorbance at 450 nm with the addition of different equiv Cu$^{2+}$.

For competition studies, 1o was treated with one equivalent of Cu$^{2+}$ ion in the absence and presence of one equivalent of other metal ions (Zn$^{2+}$, Al$^{3+}$, Cr$^{3+}$, Co$^{2+}$, Mn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, K$^+$, Ca$^{2+}$, Fe$^{3+}$, Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$ and Ni$^{2+}$) (Fig. 3). No significant interference was observed in the detection of Cu$^{2+}$ ion in the presence of other metal ions.

![Competitive tests for the absorbance responses of 1o to various metal ions: (A) absorptionspectral change (Bars represent the ratio of absorbance at 450 nm), and (B) color change of 1o upon addition of different cations in acetonitrile (2.0 × 10$^{-5}$ mol L$^{-1}$).](image)

**Figure 3.** Competitive tests for the absorbance responses of 1o to various metal ions: (A) absorptionspectral change (Bars represent the ratio of absorbance at 450 nm), and (B) color change of 1o upon addition of different cations in acetonitrile (2.0 × 10$^{-5}$ mol L$^{-1}$).

The binding ability of 1o towards Cu$^{2+}$ was estimated by performing UV–vis absorption titration experiment. Upon successive addition of an incremental amount of Cu$^{2+}$ to the solution, the absorption band was gradually red shifted with the appearance of an isosbestic point at 358 nm indicative of the formation of a single species in solution. Using Job’s plot (Fig. 4), keeping the sum of the initial concentration of Cu$^{2+}$ and 1o at 2.0 × 10$^{-5}$ mol L$^{-1}$ and the changes of Cu$^{2+}$ molar ratio from 0 to 1, the stoichiometry of the 1o and Cu$^{2+}$ was obtained. When excess amounts of Cu$^{2+}$ were added to 1o, a new peak at 786.1967 m/z that was assigned to 1o–Cu$^{2+}$ with a 1:1 binding mode. According to the literature [19], the possible binding mode was shown in Fig. 5.
Figure 4. Job’s plot showing the 1 : 1 complex between Cu$^{2+}$ and 1o. The total concentration of Cu$^{2+}$ and 1o was 2.0 × 10$^{-5}$ mol L$^{-1}$.

Figure 5. The possible binding mode between Cu$^{2+}$ and 1o.

In summary, a new easy-to-prepare and chemosensor derived from a diarylethene for the selective detection of Cu$^{2+}$ was designed and synthesized. The color of the sensor turned from colorless to yellow with the appearance of a new charge transfer band at 381 and 450 nm selectively in the presence of Cu$^{2+}$ which allowed to detect this metal ion. The result is helpful for the design of novel sensor based on photofunctional materials.

References
[1] M. Chhatwal, A. Kumar, V. Singh, R.D. Gupta, S.K. Awasthi, Coord. Chem. Rev. 292, 30 (2015)
[2] G.R.C. Hamilton, S.K. Sahoo, S. Kamila, N. Singh, N. Kaur, B.W. Hyland, J. F. Callan, Chem. Soc. Rev. 44, 4167 (2015)
[3] R. Uauy, M. Olivares, M. Gonzalez, Biomed. Pharmacother. 57, 134 (2003)
[4] U.N. Yadav, P. Pant, S.K. Sahoo, G.S. Shankarling, RSC Adv. 4, 42647 (2014)
[5] U. Fegade, A. Saini, S.K. Sahoo, N. Singh, R. Bendre, A. Kuwar, RSC Adv. 4, 39639 (2014)
[6] K.P. Carter, A.M. Young, A.E. Palmer, Chem. Rev. 114, 4564 (2014)
[7] X.Q. Chen, T. Pradhan, F. Wang, J.S. Kim, J.Y. Yoon, Chem. Rev. 112, 1910 (2012)
[8] Y.E. Spichiger-Keller, Wiley-VCH, New York, 1998
[9] M. Natali, S. Giordani, Chem. Soc. Rev. 41, 4010 (2012)
[10] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 114, 12174 (2014)
[11] S.Z. Pu, H.C. Ding, C.H. Zheng, H.Y. Xu, J. Phys. Chem. C 118, 7010 (2014)
[12] H. Tian, B. Qin, R. Yao, X. Zhao, Adv. Mater. 15, 2104 (2003)
[13] S.J. Xia, G. Liu, S.Z. Pu, J. Mater. Chem. C 3, 4023(2015)
[14] Liu, G.; Pu, S.Z.; Wang, X.M.; Liu, W.J.; Yang, T.S. Dyes Pigm. 90, 71 (2011)
[15] S.Z. Pu., L.L. Ma, G. Liu, H.C. Ding, B. Chen, Dyes Pigm. 113, 70 (2015)
[16] T. Nakashima, K. Miyamura, T. Sakai, T. Kawai, Chem. Eur. J. 15, 1977 (2009)
[17] T. Kawai, M.S. Kim, T. Sasaki, Opt. Mater. 21, 275 (2003)
[18] Z.X. Li, L.Y. Liao, W. Sun, C.H. Xu, C. Zhang, C.J. Fang, C.H. Yan, J. Phys. Chem. C 112, 5190 (2008)
[19] Y.C. Liu, Z.Y. Yang, J. Organomet. Chem. 694, 3094 (2009)

Acknowledgment
The authors are grateful for the financial support from the National Natural Science Foundation of China, 51373072), the Young Scientist Training Program of the Jiangxi Province (20153BCB23008), and the JXSTNU Sci-Tech innovation team (2015CXTDTD002).