A fluorescent chemosensor for Sn\textsuperscript{2+} and Cu\textsuperscript{2+} based on a carbazole-containing diarylethene†

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A novel diarylethene containing a carbazole moiety was developed for the highly selective and sensitive detection of Sn\textsuperscript{2+} and Cu\textsuperscript{2+} in methanol. Its fluorescence was enhanced with a 76 nm blue shift and selective fluorescence quenching occurred upon the addition of Sn\textsuperscript{2+} and Cu\textsuperscript{2+}, respectively, over a wide range of tested cations. The compound formed complexes with Sn\textsuperscript{2+} and Cu\textsuperscript{2+} in a 1:1 stoichiometry and has the detection limits of 1.9 μM and 1.2 μM, respectively. Moreover, the compound can be applied to detect Sn\textsuperscript{2+} and Cu\textsuperscript{2+} in natural water samples with high accuracy.

Introduction

Fluorescent sensor design is an active field of supramolecular chemistry due to potential practical advantages in biomedical, analytical, and environmental chemistry, and in the construction of optical and electronic signaling channels towards targeted molecular or ionic species. In the last few decades, significant efforts have been made to develop novel fluorophore chemosensors, capable of distinguishing and sensing biologically and environmentally significant cations and anions. Among these, the detection of heavy and transition metal ions is significant due to these ions playing crucial roles in living systems and also simultaneously having tremendous detrimental effects when exceeding the normal permissible limits.

Sn\textsuperscript{2+}, an essential trace mineral for humans, is involved in growth factors and cancer prevention. Deficiency of tin may result in poor growth and hearing loss, whereas excess tin accumulation can abnormally affect respiratory and digestive systems. Recent reports have revealed that Sn\textsuperscript{2+} can be readily taken up by human white blood cells and cause DNA damage. Thus, it is of great importance to establish a method for the determination of Sn\textsuperscript{2+} in the environmental and biological systems. Similarly, Cu\textsuperscript{2+} is also of significant importance as it acts as a catalytic cofactor for a variety of metalloenzymes and is an essential trace element for many biological processes and systems. The over-accumulation of Cu\textsuperscript{2+} in humans is responsible for many neurodegenerative diseases such as Menkes syndrome, Wilson’s disease, Alzheimer’s disease, and prion disease. Therefore, enormous attempts have been dedicated to the development of Cu\textsuperscript{2+} fluorescent sensors since they facilitate sensitive, easy, and rapid detection.

As one of the most promising photoresponsive materials, diarylethenes have been well-recognized for their remarkable fatigue resistance, excellent thermal stability, and rapid response. Upon alternating the irradiation between UV and visible light, a reversible transformation between the open-ring and closed-ring isomers occurred, accompanied by many obvious changes in the physical properties such as absorption spectra, fluorescence, refractive indices, electronic conduction, oxidation-reduction potentials, and so on. It is very convenient to construct a molecular switch using diarylethenes. Diarylethene derivatives that exhibit good fluorescence performance have become star molecules due to their fluorescence signalizing, high detection sensitivity, and simplicity. However, most diarylethene sensors show weak or no fluorescence. Thus, linking a suitable fluorescent chromophore into the diarylethene structure offers new possibilities for developing fluorescent sensors. To date, many fluorescent sensors for Zn\textsuperscript{2+}, Al\textsuperscript{3+}, Cu\textsuperscript{2+}, Fe\textsuperscript{3+}, Al\textsuperscript{3+}, Mg\textsuperscript{2+}, and Hg\textsuperscript{2+} are based on diarylethene derivatives and have been widely studied. However, there are relatively few reports on the fluorescent sensors for Sn\textsuperscript{2+}.

Carbazole possesses a rigid fused-ring structure and its N atom has a lone pair of electrons forming π–π conjugate with benzene rings. It has been widely investigated as a donor due to its potential value for solar energy storage and efficient luminescence. However, the carbazole moiety has rarely been used in diarylethene derivatives. Herein, a novel carbazole-containing diarylethene 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(3-amine-9-ethyl-carbazolyl)-3-thienyl]perfluorocyclopentene (10) was successfully synthesized. 10 showed dual channel fluorescence signals (‘turn-on’ and ‘turn-off’) for the selective detection of Sn\textsuperscript{2+} and Cu\textsuperscript{2+} in methanol. To the best of our knowledge, this is a new chemosensor for multi-cations (Sn\textsuperscript{2+} and Cu\textsuperscript{2+}) with discrimination in
the fluorescence response. Considering the open- and closed-ring isomeric states, the photochromism and ion sensing of the six states was studied to clarify the mechanism of recognition, as shown in Scheme 1.

### Experimental

#### Materials and chemicals

Reactions were monitored by analytical thin-layer chromatography on the plates coated with 0.25 mm silica gel 60 F254 (Qingdao Haiyang Chemical). Flash column chromatography employed silica gel (32–63 μm, Qingdao Haiyang Chemical) and Al2O3 (37–74 μm, J&K). Melting points were measured using a WRS-1B melting point apparatus and are uncorrected. Infrared spectra were obtained using a Bruker Vertex-70 spectrometer. NMR spectra were obtained using a Bruker AV-400 spectrometer with teramethylsilane (TMS) as the internal reference and CDCl3 and DMSO-d6 as solvents. Elemental analysis was carried out using a PE CHN 2400 analyzer.

#### Reagents

Chemical reagents were purchased from either Alfa or TCI and used without further purification. 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.

#### Synthesis

The synthesis of 1o started with the preparation of the intermediates 2 and 3. 3 was lithiated and coupled with 2 followed by hydrolysis to give 4, which was further coupled with 9-ethyl-9H-carbazol-3-amine to afford 1o. The synthetic route is shown in Scheme 2.

#### Synthesis of 4

To a stirred THF solution (50 mL) of 3 (2.04 g, 10 mmol), 2.5 mol L⁻¹ n-BuLi/hexane solution (4.40 mL, 11 mmol) was slowly added at 195 K under a nitrogen atmosphere and the mixture was stirred for 30 min. 2 (2.93 g, 8 mmol) was added and the mixture was further stirred for 2 h at this temperature. The reaction was allowed to warm to room temperature and quenched by the addition of water. The product was extracted with diethyl ether and evaporated in vacuo. It did not require further purification and was used for the next step reaction. The crude product was dissolved in acetone/water (v/v = 1/1) solution (50 mL) with pyridine (0.79 g, 10 mmol) and p-toluenesulfonic acid (2.85 g, 15 mmol). The resulting mixture was refluxed for 6 h and then cooled down to room temperature. The mixture was then sequentially washed with aqueous NaHCO3 and water. After being extracted with ether, the organic layer was dried over MgSO4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyle acetate (v/v = 1/1) as the eluent to give 4 (2.12 g) in 45.0% yield. 1H NMR (CDCl3, 400 MHz): δ (ppm) 1.86 (s, 3H, –CH3), 1.98 (s, 3H, –CH3), 2.16 (s, 1H, thiophene-H), 7.30–7.32 (m, 1H, phenyl-H), 7.44–7.46 (m, 2H, phenyl-H), 7.47 (d, 2H, phenyl-H, J = 8.0 Hz), 7.70 (s, 1H, thiophene-H), 9.78 (s, 1H, –CHO); 13C NMR (DMSO-d6, 100 MHz): δ (ppm) 14.6, 14.7, 123.6, 124.6, 124.8, 125.7, 128.0, 128.4, 129.6, 130.0, 130.6, 133.3, 140.1, 141.5, 183.5.

#### Synthesis of 1o

4 (0.236 g, 0.5 mmol) and 9-ethyl-9H-carbazol-3-amine (0.105 g, 0.5 mmol) were dissolved in methanol (10 mL). The reaction mixture was refluxed for 6 h, and then cooled down to room temperature. The raw product was condensed and purified by recrystallization with methanol to obtain 0.40 g 1o as a yellow solid in 59% yield. M.p. 378–388 K; 1H NMR (DMSO-d6, 400 MHz): δ (ppm) 1.38 (t, 3H, –CH3, J = 8.0 Hz), 2.06 (s, 3H, –CH3), 2.08 (s, 3H, –CH3), 4.47–4.54 (m, 2H, –CH2), 7.26 (s, 1H, thiophene-H), 7.40 (s, 1H, thiophene-H), 7.48–7.52 (m, 3H, –CH3).
Preparation of the metal ions

The solutions of metal ions (0.1 mol L⁻¹) were prepared by the dissolution of their respective metal nitrates in distilled water, except for K⁺, Hg²⁺, Mn²⁺, and Ba²⁺ (where the counter ion was chloride). Distilled-deionized water was used throughout the experiment.

Procedures for metal-ion sensing

Stock solutions of the metal ions (0.1 mol L⁻¹) were prepared by means of a micro-pipette. Spectra were obtained 3 s after the addition of the metal ions to the solution. Test samples for the selectivity experiments were prepared by adding appropriate amounts of metal ion stock solutions to 2 mL of 1o in a quartz cuvette of 1 cm optical path length, and then incrementally adding the Sn²⁺ stock solution by means of a micropipette. Spectra were obtained 3 s after the addition. Test samples for the selectivity experiments were prepared by adding appropriate amounts of metal ion stock solutions to 2 mL of 1o. In competition experiments, Sn²⁺ or Cu²⁺ was added to the solution containing 1o and the other metal ions of interest. For fluorescence measurements, excitation was provided at 310 nm, and emission was obtained from 350 to 615 nm.

Determination of cyclization/cycloreversion quantum yields

Quantum yield was measured using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as reference for the cyclization and cycloreversion reactions. The absorbance of the sample and the reference at the irradiation wavelength (297 nm) were observed. For the cyclization quantum yield measurement, absorbance (A) at the absorption maximum of the closed-ring isomer was plotted against time. For the cycloreversion quantum yield measurement, –log A at the absorption of the irradiated wavelength was plotted against time. The measurement was carried out five times, and the value was determined by averaging.

Determination of the stoichiometry of the 1o–Sn²⁺/Cu²⁺ complexes

According to the method for continuous variation, a series of solutions of 1o and Sn²⁺/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 fluorescence spectra were obtained. When plotting the fluorescence intensity against [M²⁺]/([M²⁺] + [1o]), a feature point was obtained at 0.5 on the abscissa, indicating the 1 : 1 stoichiometry of the 1o–Sn²⁺/Cu²⁺ complexes.
287 nm due to the $\pi \rightarrow \pi^*$ transition. Upon irradiation with 297 nm light, the absorption at 287 nm decreased, and a new absorption band centered at 622 nm emerged due to the formation of the closed-ring isomer 1c, accompanied with a color change from colorless to blue. The blue color could be bleached to colorless upon irradiation with visible light ($\lambda > 500$ nm), and the absorption spectrum returned to the initial state of 1o. The cyclization and cycloreversion quantum yields were 0.22 and 0.028, respectively. Moreover, the compound showed good stability at room temperature. No decomposition was detected when the powder was exposed to air for more than six months. After 50 repeat cycles (Fig. S1†), the degradation for 1c was only 7.6%. The fluorescence property of 1o was measured in methanol ($2.0 \times 10^{-5}$ mol L$^{-1}$) at room temperature (Fig. 1B). When excited at 310 nm, the fluorescent emission peak of 1o appeared at 477 nm. Upon irradiation with 297 nm light, the emission intensity decreased due to the formation of weakly fluorescent closed-ring isomers of 1c.† The back-irradiation with appropriate visible light ($\lambda > 500$ nm) regenerated the open-ring isomer of 1o, and the emission intensity returned to the original state. When the photostationary state was achieved, the emission intensity of 1 was quenched to ca. 40%.

The fluorometric responses of 1o towards metal ions was studied in methanol. The fluorescence of 1o was not significantly influenced in the presence of metal ions such as Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, and Ni$^{2+}$. However, the emission intensity of 1o was selectively altered with the addition of Sn$^{2+}$/Cu$^{2+}$. As shown in Fig. 2, a clear fluorescence enhancement of 1o with a 76 nm blue shift was observed with Sn$^{2+}$, whereas a reverse response, i.e. fluorescence quenching, was observed upon the addition of Cu$^{2+}$. The enhancement with Sn$^{2+}$ has been explained based on the inhibition of C=N isomerization due to chelate formation.† Moreover, the blue shift indicated that the possible intra-molecular charge transfer occurred in 1o on interaction with Sn$^{2+}$. In contrast, the fluorescence quenching by Cu$^{2+}$ was most likely due to an energy transfer process occurring from 1o to the open-shell d-orbitals and paramagnetic Cu$^{2+}$, which caused a faster and more efficient nonradiative decay of the excited states of 1o. Moreover, Cr$^{3+}$, Al$^{3+}$, and Fe$^{3+}$ exerted a slight quenching effect with a 76 nm blue shift. However, compared with the strong fluorescence quenching by Cu$^{2+}$, their disturbances were quite minor.

To determine the binding stoichiometry between 1o and Sn$^{2+}$/Cu$^{2+}$, the continuous variation method was used. Fig. 3 displays the Job’s plot of the fluorescence intensity of 1o and the intensity of the system with the molar fraction of the host $[[1o]/([1o] + [Sn^{2+}/Cu^{2+}])]$ for a series of solutions, in which the total concentration of 1o and Sn$^{2+}$ or Cu$^{2+}$ was constant with the molar fraction of 1o continuously varying. The inflection point was observed when the molar fraction reached 0.5, which indicates a 1 : 1 binding stoichiometry between 1o and Sn$^{2+}$/Cu$^{2+}$. The formation of the 1o–Sn$^{2+}$/Cu$^{2+}$ complex was confirmed by ESI mass spectra (Fig. S2†). The free 1o displayed a characteristic peak at 665.1 m/z. When excess amounts of Sn$^{2+}$ were added to 1o, a new peak at 907.5 m/z emerged that was assigned to 1o–Sn$^{2+}$ (the calculated $[1o + Sn^{2+} + 2NO_3^− - H]$ value was 908.0). When excess amounts of Cu$^{2+}$ were added to 1o, a new peak at 788.1 m/z emerged that was assigned to 1o–Cu$^{2+}$ (the calculated $[1o + Cu^{2+} + NO_3^− - H]$ value was 789.1). The complex formation was further confirmed by IR (Fig. S3†) and $^1$H NMR (Fig. S4†) spectra, respectively. In the IR spectra, the 1669 cm$^{-1}$ ν(C=N) peak of 1o shifted to 1599 cm$^{-1}$ due to the reaction with Sn$^{2+}$ and that of 1o shifted to 1674 cm$^{-1}$ due to the formation of a bond between C=N and Cu$^{2+}$. The new peak at 1380/1388 cm$^{-1}$ indicated that NO$_3^−$ was introduced into 1o–Cu$^{2+}$ and 1o–Sn$^{2+}$, respectively. In the $^1$H NMR spectra of 1o–Sn$^{2+}$, the proton (−CH=N) signal at 9.03 ppm showed up-field shifts upon the addition of Sn$^{2+}$. This indicated that Sn$^{2+}$ binds to the imine moiety. However, the proton signals could not be detected in the presence of the paramagnetic Cu$^{2+}$. The possible complex formation is shown in Scheme 1.

The fluorescence spectral titrations of 1o ($2.0 \times 10^{-5}$ mol L$^{-1}$) were performed with incremental addition of Sn$^{2+}$/Cu$^{2+}$ to obtain a better idea of the binding constants and binding stoichiometry (Fig. 4). When excited at 310 nm, the fluorescence intensity of 1o at 477 nm was enhanced more than 4.5-fold with a 76 nm blue shift for Sn$^{2+}$ and quenched more than 5-fold with

![Fig. 2](image)

**Fig. 2** Changes in the fluorescence of 1o induced by the addition of various metal ions (12 equiv.) in methanol ($2.0 \times 10^{-5}$ mol L$^{-1}$): (A) emission spectral changes and (B) images demonstrating changes in the fluorescence.

![Fig. 3](image)

**Fig. 3** Job’s plot showing the 1 : 1 complex: (A) 1o with Sn$^{2+}$, and (B) 1o with Cu$^{2+}$. 

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Cu\textsuperscript{2+}. The association constant \( K_a \) was graphically evaluated by plotting \( F_0/(F/F_0) \) against \( 1/[M^{2+}] \), as shown in Fig. 5. The fluorescence titration data were linearly fitted according to the Benesi–Hilderbrand equation, \(^{46,47} \) which indicated 1 : 1 binding stoichiometry. The \( K_a \) values were obtained from the slope and intercept of the line and the calculated binding constants were 4.04 \( \times \) \( 10^{-3} \) L mol\(^{-1}\) and 3.40 \( \times \) \( 10^{-4} \) L mol\(^{-1}\) for Sn\textsuperscript{2+} and Cu\textsuperscript{2+}, respectively. The standard deviation for the three repeated measurements of \( K_a \) was 0.88% for Sn\textsuperscript{2+} and 1.48% for Cu\textsuperscript{2+}. Under optical detection, according to the reported method, \(^{48} \) the detection limit of \( 1o \) as a fluorescent sensor for Sn\textsuperscript{2+}/Cu\textsuperscript{2+} was determined from the plot of fluorescence intensity as a function of the concentration of Sn\textsuperscript{2+}/Cu\textsuperscript{2+} (Fig. S5†). \( 1o \) was found to have the detection limits of 1.9 \( \times \) \( 10^{-6} \) and 1.2 \( \times \) \( 10^{-6} \) mol L\(^{-1}\), respectively, which is reasonable for the detection of micromolar concentrations of Sn\textsuperscript{2+}/Cu\textsuperscript{2+}.

To check the interference of other metal ions in the detection of Sn\textsuperscript{2+} and Cu\textsuperscript{2+}, the interference studies were carried out by monitoring the change in the emission profile of \( 1o \)-Sn\textsuperscript{2+}/Cu\textsuperscript{2+} in the presence of other interfering cations (Zn\textsuperscript{2+}, Al\textsuperscript{3+}, Cr\textsuperscript{3+}, Co\textsuperscript{3+}, Mn\textsuperscript{2+}, Hg\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Fe\textsuperscript{3+}, Mg\textsuperscript{2+}, Ba\textsuperscript{2+}, Sr\textsuperscript{2+}, and Ni\textsuperscript{2+}). As shown in Fig. 6, the fluorescence profile of \( 1o \) with Sn\textsuperscript{2+} was not affected by the coexistence of other interfering metal ions except Cu\textsuperscript{2+}. In the presence of Cu\textsuperscript{2+}, the fluorescence intensity decreased almost 5-fold, which may be ascribed to the high association constant of \( 1o \) for Cu\textsuperscript{2+}. Even in the presence of Sn\textsuperscript{2+}, the fluorescence intensity obviously decreased upon the addition of Cu\textsuperscript{2+}. These studies show that no other metal ions are interfering in the detection of Sn\textsuperscript{2+} except Cu\textsuperscript{2+} and the specific response for Cu\textsuperscript{2+} is not disturbed by other competing metal ions.

To understand the reversibility of \( 1o \) towards Sn\textsuperscript{2+}/Cu\textsuperscript{2+}, a reversibility experiment was carried out using disodium salt of ethylenediaminetetraacetate (Na\textsubscript{2}EDTA), which has a strong binding ability towards metal ions. As shown in Fig. 7, upon the addition of 12 equiv. of EDTA to \( 1o \) containing Sn\textsuperscript{2+}, the emission intensity immediately decreased. Further addition of Sn\textsuperscript{2+} could restore the fluorescent state. The cycle (Sn\textsuperscript{2+}–EDTA) can be repeated several times without any reduction in sensitivity.
be carried out four times. This regeneration indicates that 10 can be reused with proper treatment, whereas the fluorescence could not be regained by further addition of excess EDTA, indicating irreversible sensing for Cu²⁺.

The effect of pH on the fluorescence intensity of 10 was investigated in the absence and presence of Sn²⁺/Cu²⁺. As shown in Fig. S6,† no obvious fluorescence intensity change of 10 was observed between pH 2.4 and 11.5, suggesting that the compound is stable over a wide range. In the pH range of 4.0–11.5, a marked fluorescence enhancement was observed upon the addition of Sn²⁺. In the presence of Cu²⁺, the quenched fluorescence was almost unaffected over a wide range, from pH 2.4 to 12.9. Therefore, 10 can detect Sn²⁺ and Cu²⁺ over a wide pH range with a high selectivity and specificity.

Moreover, 10–Sn²⁺ exhibited a notable fluorescent switch by photoirradiation, as shown in Fig. 8. The emission intensity of the complex 10–Sn²⁺ notably decreased upon irradiation with 257 nm light due to the formation of the closed-ring isomer of 1c–Sn²⁺. When arriving at the photostationary state, the emission intensity was quenched ca. 52%. The back irradiation with appropriate visible light regenerated the open-ring isomer 10–Sn²⁺ and recovered its original emission intensity.

To demonstrate the real application of 10, Sn²⁺/Cu²⁺ in real water samples from the Ganjiang River of Nanchang City were determined according to the reported methods.⁹⁻¹⁰ Different amounts of Sn²⁺/Cu²⁺ were spiked into the real water sample. The sample was filtered through a 0.2 mm membrane. Tables 1 and 2 show the results obtained using the fluorescent sensor 10 with appropriate added amounts of Sn²⁺/Cu²⁺. The recovery for both Sn²⁺ and Cu²⁺ was over 90%. Therefore, 10, which can detect Sn²⁺/Cu²⁺ in real water samples with high accuracy, has practical value.

### Table 1 Detection of Sn²⁺ in natural water samples

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### Table 2 Detection of Cu²⁺ in natural water samples

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Conclusions

A novel diarylethene with a carbazole unit, which shows high sensitivity and selectivity for Sn²⁺ and Cu²⁺ in methanol over a wide range of metal ions tested, was designed and synthesized. The sensing of Sn²⁺ and Cu²⁺ was not affected in the presence of other interfering cations. The 1 : 1 stoichiometry complexes were confirmed from Job’s plot with the detection limits were 1.9 μM for Sn²⁺ and 1.2 μM for Cu²⁺. Moreover, the compound showed high accuracy for Sn²⁺ and Cu²⁺ in natural sample testing. The results indicate that diarylethene derivatives can be used for practical applications in sensory research.

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Notes and references