A highly selective and sensitive fluorescent chemosensor for Zn$^{2+}$ based on a diarylethene derivative†

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A promising photochromic fluorescent chemosensor 1o linked with Schiff base unit was synthesized. It displayed outstanding photochromism and a superb fluorescence turn-on response toward Zn$^{2+}$. Upon the addition of Zn$^{2+}$ to 1o, the fluorescent color of the solution obviously changed from blue to bright green with a 27-fold fluorescent intensity increase. The combination of 1o–Zn$^{2+}$ with 1:1 stoichiometry was verified by Job's plot and MS analysis. The detection limit for 1o toward Zn$^{2+}$ was measured to be $8.10 \times 10^{-8}$ M. Furthermore, logic gate research was established with Zn$^{2+}$, UV and visible light as input signals and the emission intensity as the output signal.

1. Introduction

It is well known that zinc is the second most plentiful transition metal in cells as well as the requisite ingredient to maintain life. Many research studies reveal that Zn$^{2+}$ plays a crucial role in a number of biological metabolic processes, such as enzyme regulation, neural signal modulation and apoptosis. Free Zn$^{2+}$ exist in some tissues, acting as signal transporters for nerve transmission and necrocytosis. Micro quantities of zinc are essential with about 2–4 g distributed over the human body, but its excess may damage the organism. For instance, overmuch Zn$^{2+}$ in the body will suppress the ingestion of other essential trace metal ions such as Fe$^{3+}$ and Cu$^{2+}$. The inconsistency of Zn$^{2+}$ concentration with the normal levels in the human body will cause diverse diseases, e.g., diabetes, Alzheimer's disease, epilepsy and so forth. Hence, studies focused on Zn$^{2+}$ detection are of great significance. Up to now, conventional ways used for identifying Zn$^{2+}$, such as atomic absorption spectrometry and inductively coupled plasma mass spectrometry, generally require precision instruments, high cost and inconvenient operation. Therefore, it is worthwhile to develop new methods with low cost, easy operability and high selectivity for Zn$^{2+}$ detection.

In recent decades, fluorescent chemosensors have developed rapidly to monitor special species in numerous fields such as environmental analysis and clinical diagnosis due to its high selectivity, efficient sensitivity, real-time detection and easy sample preparation. Up to now, a considerable amount of fluorescent sensors targeting transition and heavy metal ions with transient response and splendid selectivity have been reported. As known to all, quinoline as an important fine chemical raw material, mainly used for the synthesis of pharmaceutical, dyes and a variety of chemical catalysts. On the other hand, an increasing number of photochromic molecular systems have been used as fluorescent probes to detect metal ions in recent years. Among these photochromic materials, diarylethenes have attracted increasing attention due to its excellent anti-fatigue for switching the intensity of fluorescent emission as well as its potential applications in molecular switching devices. Herefore, a variety of Zn$^{2+}$ fluorescence chemosensors decorated with diarylethenes have been reported. However, these sensors either have poor detection limits or disturbances of other metal ions, such as Cd$^{2+}$ exhibiting similar chemical properties.

Herein, we designed a novel fluorescent turn-on chemosensor 1o based on a diarylethene derivative for detecting Zn$^{2+}$ with high selectivity and sensitivity. Besides, the recognition of Zn$^{2+}$ did not have any disturbance from Cd$^{2+}$. The synthetic route and photochromism of target sensor 1o were shown in Scheme 1. Related substances in this paper are characterized by $^1$H NMR, $^{13}$C NMR and mass spectrum as seen in the ESI (Fig. S9–S17†).

2. Experimental

2.1 General methods

All reagents were analytical grade without further purification and all other solvents used in properties testing were spectroscopic grade. The solutions of the metal ions were prepared from the nitrates (0.1 M) of Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Fe$^{3+}$, Pb$^{2+}$, Ca$^{2+}$, Co$^{3+}$, Cr$^{3+}$, Ni$^{2+}$, Mg$^{2+}$, Sr$^{2+}$ and Al$^{3+}$, except for K$^+$, Ba$^{2+}$, Mn$^{2+}$, ...
Hg²⁺ (their counter ions were chloride ions), in distilled water (2 mL). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with tetramethylsilane (TMS) as its internal standard. Melting points were obtained on a WRS-1B melting point apparatus. Mass spectra were measured on an AB SCIEX Triple TOF 4600 instrument. Elemental analysis was performed with a PE CHN 2400 analyzer. The fluorescence quantum yield was recorded with an Absolute PL Quantum Yield Spectrometer. Melting points were obtained on a WRS-AV400 (400 MHz) spectrometer with tetramethylsilane (TMS) as its internal standard. The photochromism of compound 1o was measured on a Hitachi F-4600 fluorescence spectrophotometer. Photo-irradiation was performed with a SHG-200 UV lamp, Cx-21 ultraviolet cabinet and a BMH-250 visible lamp.

2.2 Synthesis of compound 3

The synthetic route was shown in Scheme 1. Compound 2 (ref. 39) (0.54 g, 1 mmol) and a catalytic amount of acetic acid were added dropwise. The mixture was heated at 353 K and stirred for 12 h. A solution of ethanol (10 mL) and then hydrazine hydrate (99%, 2 mL) was added dropwise. The mixture was heated at 353 K and stirred for 12 h until no compound was detected by separating on a silica gel chromatography column with petroleum ether/ethyl acetate (10/1). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 1.39 (t, 3H, -CH₃), 1.97 (s, 3H, -CH₃), 2.31 (s, 3H, -CH₃), 3.45-4.40 (m, 2H, -CH₂), 7.25 (s, 1H, Ar-H), 7.29-7.37 (m, 2H, Ar-H), 7.45 (d, 2H, Ar-H), 7.57 (d, 1H, Ar-H), 7.73 (d, 1H, Ar-H), 7.99 (d, 2H, Ar-H). ¹³C NMR (100 MHz, CDCl₃, TMS), δ (ppm): 14.42, 14.91, 61.14, 120.37, 122.17, 122.21, 124.14, 124.69, 125.10, 125.26, 125.64, 129.75, 130.38, 137.43, 138.41, 140.69, 142.59, 143.09, 166.17. Anal. calc for C₂₈H₂₀F₆O₂S₂ (%): C, 59.36; H, 3.56. Found: C, 59.31; H, 3.59. ESI-MS: m/z = 565.0721 [M – H]⁻ (calcd 565.0731).

2.3 Synthesis of compound 4

Compound 3 (0.57 g, 1 mmol) was suspended in anhydrous ethanol (10 mL) and then hydrazine hydrate (99%, 2 mL) was added dropwise. The mixture was heated at 353 K and stirred for 12 h. After removing the solvent by evaporation under reduced pressure, the crude product 4 was purified by column chromatography using petroleum ether/ethyl acetate (3/1, 1% Et₃N) as the eluent to acquire the compound 4 (0.25 g, yield: 45%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 1.96 (s, 3H, -CH₃), 2.31 (s, 3H, -CH₃), 3.49 (s, 2H, -NH₂), 7.25 (s, 1H, Ar-H), 7.30-7.38 (m, 3H, Ar-H), 7.48 (d, 2H, Ar-H), 7.57 (d, 1H, Ar-H), 7.71-7.76 (m, 3H, Ar-H). ¹³C NMR (100 MHz, CDCl₃, TMS), δ (ppm): 14.76, 14.84, 120.24, 122.05, 122.09, 122.15, 122.37, 124.62, 125.02, 125.42, 125.49, 127.78, 136.46, 138.24, 138.32, 140.49, 142.56, 142.90, 167.86. Anal. calc for C₂₈H₂₂F₆O₂S₂ (%): C, 56.52; H, 3.28; N, 5.07. Found: C, 56.44; H, 3.31; N, 5.09. ESI-MS: m/z = 551.0684 [M – H]⁻ (calcd 551.0686).

2.4 Synthesis of compound 1o

Compound 4 (0.11 g, 0.2 mmol) was suspended in absolute ethanol (10 mL), followed by the addition of 1-butyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (0.045 g, 0.2 mmol) and a catalytic amount of acetic acid. The mixture was stirred at 353 K for 12 h to complete the reaction. Then the solution was cooled to room temperature and put in a refrigerator overnight. A yellow solid precipitation was observed and then washed with absolute methanol (10 mL x 3) to afford the compound 1o (0.091 g, yield: 60%). Mp: 342–343 K. ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 0.88 (t, 3H, -CH₃), 1.34 (m, 2H, -CH₂), 1.59 (m, 2H, -CH₂), 1.90 (s, 3H, -CH₃), 2.26 (s, 3H, -CH₃), 4.16 (t, 2H, -CH₂), 7.16-7.30 (m, 5H, Ar-H), 7.43-7.53 (m, 4H, Ar-H), 7.64 (d, 1H, Ar-H), 7.69 (d, 1H, Ar-H), 7.78 (d, 2H, Ar-H), 8.47 (s, 1H, -CH═N⁻), 8.61 (s, 1H, Ar-H), 9.89 (s, 1H, -NH–). ¹³C NMR (100 MHz, CDCl₃, TMS), δ (ppm): 14.19, 15.24, 20.84, 30.13, 43.05, 44.16, 114.95, 115.46, 120.62, 121.17, 122.58, 122.76, 123.07, 124.04, 124.57, 125.20, 125.58, 126.02, 130.90, 132.10, 132.80, 133.45, 137.89, 139.01, 140.29, 161.57. Anal. calc for C₁₉H₁₆F₆NO₂S₂ (%): C, 62.90; H, 4.09; N, 5.50. Found: C, 62.83; H, 4.12; N, 5.56. ESI-MS: m/z = 762.1666 [M – H]⁻ (calcd 762.1684).

3 Results and discussion

3.1 Photochromic and fluorescent properties of compound 1o

The photochromism of compound 1o (20 µM in THF) at room temperature was shown in Fig. 1a. In the initial state of 1o, two split absorption peaks were observed at 341 nm and 382 nm, which can be ascribed to π → π* transition, 64 and the solution
was colorless. Upon irradiation with 297 nm light, two sharp bands at 341 nm and 382 nm gradually decreased and a new broad band at 555 nm was observed, indicating the formation of closed ring isomer 1c. When the photostationary state (PSS) was reached, a clear isosbestic spot at 410 nm was observed, and the solution changed from colorless to purple. Relatively, when irradiated with appropriate visible light ($\lambda > 500$ nm), the absorption spectrum intensity at 555 nm recovered to the original state due to the ring cleavage reaction. While in ultraviolet region, a new status different from 1o was reached which may because of C$\equiv$N isomerization (Fig. S1†). A dissimilar open loop isomer ($1o'$) was generated as shown in Scheme 2. Anti-fatigue tests ($\lambda = 555$ nm) were carried out through 15 cycles of coloration–decoloration [Fig. S2†], and the result indicated that 1o had prominent fatigue resistance. Fig. 1b shows the fluorescence spectra changes of 1o (20 $\mu$M in THF) upon irradiation with UV-Vis light. The original state of 1o displayed weak fluorescence at 464 nm when excited at 380 nm with a low quantum yield ($\Phi = 0.008$). Upon irradiation with 297 nm light, the fluorescence emission peak gradually decreased due to the generation of non-fluorescent isomer 1c.† When the PSS was reached, the fluorescent color changed from blue to darkness. Unfortunately, when irradiated with visible light ($\lambda > 500$ nm), the fluorescence intensity hardly changed which may be ascribed to the isomerization of C$\equiv$N bond in excited state.

3.2 Absorption and fluorescence spectra responses of 1o toward Zn$^{2+}$

The detection of Zn$^{2+}$ by sensor 1o was initially assessed by the UV-Vis spectra. The absorption spectra changes of 1o (20 $\mu$M in THF) in the presence of different equivalents of Zn$^{2+}$ (0–1.2 equiv.) were exhibited in Fig. 2a. With addition of increased amount of Zn$^{2+}$, the first band around 341 nm gradually reduced and a new absorption band at 411 nm obviously increased. A plot of absorbance intensity depending on the equivalents of Zn$^{2+}$ showed that the absorption intensity at 411 nm gradually increased until the amount of Zn$^{2+}$ reached 1.2 equivalents (Fig. S3†). Meanwhile, a clear isosbestic point at 369 nm was observed, demonstrating the formation of 1o–Zn$^{2+}$ complex. The solution color changed from colorless to yellow, which was consistent well with the absorption spectra changes. Upon irradiation with 297 nm light, the photochromic properties of 1o–Zn$^{2+}$ were performed in Fig. 2b, a new absorption broad band emerged at 557 nm. At the PSS, the solution color became brown from yellow. Reversely, upon irradiation with visible light ($\lambda > 500$ nm), the absorption spectrum of 1c–Zn$^{2+}$ was restored to its incipient state of 1o–Zn$^{2+}$ and the solution color returned from brown to yellow.

The fluorescence response experiments were ulteriorly carried out to investigate the interaction between 1o (20 $\mu$M in THF) and Zn$^{2+}$ by adding various equivalents of Zn$^{2+}$ (0–1 equiv.) to 1o (Fig. 3a). The fluorescence titration experiments showed that the maximum emission intensity was achieved when 1 equivalent of Zn$^{2+}$ was added to the solution, excited by 380 nm light (Fig. S4†). As can be seen from above that the emission intensity of 1c can not recover to that of 1o due to the free rotation around C$\equiv$N bond. The isomerization of C$\equiv$N bond was always considered to be the predominant decay process in excited state.† With the addition of Zn$^{2+}$, the emission intensity dramatically increased associated with a red shift from 464 nm to 513 nm. When the amount of Zn$^{2+}$ reached
1 equivalent, the fluorescence intensity achieved its maximum with a high quantum yield ($\Phi = 0.220$) which is 27-fold larger than that of 1o. At the same time, the fluorescent color apparently changed from blue to bright green, which was coincident with the changes in the fluorescence spectra. The formation of complex 1o–Zn$^{2+}$ should be responsible for these phenomena. By combining with Zn$^{2+}$, the C=$\equiv$N isomerization was suppressed, and the increased rigidity of the molecule led to chelation enhanced fluorescence (CHEF), thereby realizing the fluorescence enhancement of complex 1o–Zn$^{2+}$.

Noteworthily, because of the inhibition of C=$\equiv$N isomerization, the chelate 1o–Zn$^{2+}$ showed prominent fluorescence switch performance by UV-Vis light irradiation (Fig. 3b) as compared with the probe 1o (Fig. 1b). Upon irradiation with 297 nm light, the emission peak gradually decreased due to the formation of closed-ring isomer 1c–Zn$^{2+}$. The fluorescent color changed from bright green to dark green in the wake of the fluorescence intensity reached the minimum. Relatively, the fluorescence spectrum of 1c–Zn$^{2+}$ recovered to its initial state of 1o–Zn$^{2+}$ upon irradiation with visible light ($\lambda > 500$ nm). The fluorescence spectral responses among closed-ring isomer 1c and Zn$^{2+}$ were further studied as shown in Fig. 3c. With the addition of Zn$^{2+}$ (0–1 equiv.), the emission intensity was obviously enhanced accompanied by a red shift from 464 nm to 513 nm. The C=$\equiv$N
isomerization was prohibited through the interaction between 1c
and Zn$^{2+}$, indicating that Zn$^{2+}$ induced fluorescence turn-on
behavior. When the amount of Zn$^{2+}$ reached 1 equivalent, the
fluorescence intensity reached its maximum ($\Phi = 0.030$), and
meanwhile, the fluorescent color changed from darkness to dark
green.

To get a further insight into the binding mode of complex 1o–
Zn$^{2+}$, the Job’s plot analysis experiment was implemented by the
fluorescence titration in THF solution, which distinctly shows
a 1 : 1 stoichiometry between Zn$^{2+}$ and 1o (Fig. S5†). The asso-
ciation constant ($K_a$) for the complex 1o–Zn$^{2+}$ was determined by
the corresponding fluorescence titration data in 1 : 1 binding
equation as $2.27 \times 10^4$ M$^{-1}$ (Fig. S6†). Besides, the detection limit
(LOD) of 1o to Zn$^{2+}$ was evaluated to be $8.10 \times 10^{-8}$ M based on
LOD = 3$\sigma$/s, where “$\sigma$” is the standard deviation of blank sample,
and “s” is the slope between the fluorescence intensity versus Zn$^{2+}$
concentration (Fig. S7†). Mass spectrum and $^1$H NMR spectra
were utilized to further verify the binding fashion of receptor 1o
toward Zn$^{2+}$. The peak located at $m/z = 950.4967$ was coincided
well with the ensemble [1o + Zn$^{2+}$ + 2NO$_3^-$ + H$^+$], proving the
existence of complex 1o–Zn$^{2+}$ with a 1 : 1 stoichiometry (Fig. S8†).
Fig. 4 shows the $^1$H NMR spectra changes upon the addition of

![Fig. 4](image1)

**Fig. 4** $^1$H NMR (DMSO-$d_6$, 400 MHz) spectra changes of receptor 1o in the presence of 1 equivalent of Zn$^{2+}$.

![Fig. 5](image2)

**Fig. 5** Upon addition various metal ions to 1o (20 $\mu$M in THF): (a) fluorescence emission spectra, (b) fluorescent photos.
Zn\(^{2+}\) to the DMSO-\(d_6\) solution of 10. As can be seen that the signal of the –NH proton at 12.087 ppm became broad and moved slightly toward the low field region in the presence of 1 equivalent of Zn\(^{2+}\). Besides, the signal intensity at 8.490 ppm belonging to –N═CH proton was slightly weaker. In view of above mentioned changes, we proposed the complexation between receptor 10 and Zn\(^{2+}\) was achieved through two oxygen atoms of the carbonyl groups (C═O) as well as one nitrogen of the imine nitrogen group (–CH═N) as demonstrated in Fig. 4.

The fluorescence selectivity of 10 (20 \(\mu\)M in THF) toward different metal ions was investigated as shown in Fig. 5. Receptor 10 showed very weak fluorescence intensity upon excitation at 380 nm. After adding a variety of metal ions (Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Fe\(^{3+}\), Pb\(^{2+}\), Ca\(^{2+}\), Co\(^{2+}\), Cr\(^{3+}\), Ni\(^{2+}\), Mg\(^{2+}\), Sr\(^{2+}\), Al\(^{3+}\), K\(^{+}\), Ba\(^{2+}\), Mn\(^{2+}\) and Hg\(^{2+}\), 1 equiv. each), only Zn\(^{2+}\) caused a prominent fluorescence enhancement centered at 513 nm, indicating an efficient fluorescence turn-on behavior. Besides, it is imperative to note that the recognition of 10 toward Zn\(^{2+}\) was not subject to any interference from Cd\(^{2+}\). Fig. 5b shows the fluorescent photos of 10 upon addition of various metal ions in THF solution. The fluorescent color of 10–Zn\(^{2+}\) was obviously bright green, indicating that sensor 10 could be used for detecting Zn\(^{2+}\) with high selectivity.

### 4. Logic gate research

As mentioned above, sensor 10 (20 \(\mu\)M in THF) exhibited significant fluorescence turn-on response upon the addition of Zn\(^{2+}\), and then can be further adjusted by UV-Vis light irradiation. The selective fluorescence “on–off” conversion of receptor 10 stimulated by Zn\(^{2+}\) and UV-Vis light inspired us to investigate its feasible application in the field of logic gate (Fig. 6). In this research, the fluorescence intensity of 10 was regarded as the initial value, and only if the emission intensity was 10-fold larger than the initial value, the output signal was considered “on” (readout “1”). Thus, the signal turn-on behavior occurred only when Zn\(^{2+}\) was chelated with the open ring isomer 10. In all other input combinations, the output signal remained in “off” state (readout “0”).

## 5. Conclusion

In summary, a new photochromic fluorescent probe 10 was synthesized for the first time. As a diarylethene derivative, probe 10 not only revealed splendid photochromic properties, but also exhibited superb fluorescence selectivity and high sensitivity toward Zn\(^{2+}\). Upon excitation at 380 nm, only Zn\(^{2+}\) induced significant fluorescence enhancement with 27-fold fluorescent intensity increase, and simultaneously, the fluorescent color of 10 obviously changed from blue to bright green. Noteworthily, the selective fluorescence turn-on behavior caused by Zn\(^{2+}\) had no interference from Cd\(^{2+}\). The detection limit was as low as 8.10 \(\times\) 10\(^{-8}\) M. This fluorescence enhancement was ascribed to the inhibition of C═N isomerization and CHEF between receptor 10 and Zn\(^{2+}\). In addition, the logic gate study was established based on the fluorescence intensity of 10 could be modulated by Zn\(^{2+}\), UV and visible light.

### Conflicts of interest

There are no conflicts to declare.

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![Fig. 6](image_url)
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