A highly selective Hg²⁺ fluorescent chemosensor based on photochromic diarylethene with quinoline unit

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Research Article

Keywords: Diarylethene, Hg²⁺ detection, fluorescent chemosensor, logic circuit

Posted Date: February 4th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1282041/v1>

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Abstract

A novel diarylethene-based fluorescent chemosensor containing a quinoline unit (**1o**) had been designed and synthesized. **1o** display good photochromic ability and fluorescent switch property by alternately irradiating UV/vis light. The chemosensor showed high “Turn-off” fluorescent selectivity for Hg^{2+} by competitive tests of the fluorescence reaction in the presence other ions in acetonitrile solution. The stoichiometry between the compound **1o** and Hg^{2+} was 1:1 by Job’s plot curve and HRMS analysis. In addition, the LOD for Hg^{2+} was calculated as 60 nM. The fluorescence emission can be back to the “Turn-on” state by adding EDTA. Based on these facts, a molecular logic gate that including four input signals (UV/vis and Hg^{2+} /EDTA) and one output signal (fluorescent intensity at 491 nm) was designed.

Introduction

Environmental pollution from heavy metal ions is an urgent problem in human society. For example, copper, mercury, cadmium and other toxic heavy metals can be transformed into soluble cations in water and soil, which are directly or indirectly absorbed by the human body through the food chain and other channels, threatening human health^[1–3]. Especially for Hg^{2+} , it is a highly toxic substance due to which can be absorbed by the human body through the skin, digestive system, and respiratory system, and can accumulate in most tissues and organs of the human body^[4–7]. Fluorescent chemosensor is a sensing test method that has developed rapidly in recent years and used in the identification and detection of analytes such as cations, anions, and neutral molecules^[8–9]. Compared to other methods, such as atomic spectroscopy, electrochemical analysis, x-ray fluorescence spectroscopy, cold atomic fluorescence spectroscopy, isotope mass spectrometry, and chromatography^[10–14], fluorescent detection not only has outstanding advantages in sensitivity, selectivity and real-time in-situ detection, but also didn’t need expensive testing instruments and cumbersome analysis steps. Therefore, it is important to study a rapid and efficient fluorescent chemosensor for Hg^{2+} detection^[15–20].

As one of the research hotspots in recent years, diarylethene derivatives have reversible conversion between opened-ring and closed-ring, and display excellent fatigue resistance, remarkable thermal stability, fast response time and brilliant fluorescence conversion performance^[21–28]. At present, diarylethene-based fluorescent chemosensors have been studied extensively by conjuncting different fluorophore, such as rhodamine^[29], coumarin^[30–31], fluorescein^[32–33], etc. Thereinto, quinoline group is a good fluorophore and commonly used as metal complexing agents, which can change its fluorescence signal by adding metal ions to achieve the detection of target metal ions. Therefore, conjuncting quinoline group into diarylethene to construct new chemosensor to detect various ions is a feasible and noteworthy approach.

In this study, a new type of diarylethene-based fluorescence sensor (**1o**) based on diarylethene and quinoline derivative was designed and its structure was determined through ^1H NMR, ^{13}C NMR and ESI-MS. Diarylethene as the parent and quinoline unit was attached to the side of diarylethene in molecular

1o. The chemosensor **1o** are capable of interconversion between opened-ring and closed-ring states under UV/vis light stimulation and the fluorescence intensity can be significantly modulated. In terms of ion selection, **1o** could recognize Hg^{2+} in acetonitrile solution with high “Turn-off” selectivity and a lower detection limit (60 nM). Besides, “Turn-on” fluorescence can be realized again by adding EDTA. Based on the above discussion, a molecular logic circuit was also constructed.

Experimental

General methods

All off chemical reagents used in the experiments were purchased from commercial companies, unless otherwise specified, no purification treatment before use. The ^1H and ^{13}C NMR spectra were tested on the Bruker AV400 (400 MHz) spectrometer, using DMSO as the solvent and the internal standard is tetramethylsilane. The melting point was collected by the WRS-1B melting point device. Acquired of mass spectral data by Bruker-Amazon SL ion trap mass spectrometer. Agilent 8453 UV/vis spectrophotometer was used for the measurement of the absorption spectra, and the equipments of photoirradiation are MUL-165 UV lamp and MVL-210 visible lamp. Hitachi F-4600 spectrophotometer was used to get the fluorescence spectra. Dissolved nitrates of various ions in deionized water to obtained the ionic solutions used, excepted for Ba^{2+} , K^+ , Pt^{2+} and Hg^{2+} (their counter ions were chloride ions).

Synthesis of **1o**

The synthesis route and photochromic properties of **1o** is shown in Scheme 1. According to the previous method, compound **4**^[34] and compound **5**^[35] were synthesized pre-prepared. In a 10 mL single-necked flask, compound **5** (0.27 g, 0.50 mmol) and compound **4** (0.18 g, 0.50 mmol) were dissolved in 5 mL ethanol solution, stirred and refluxed at 78°C for 6 hours to obtain a blue solid compound **1o** (0.30 g, 0.34 mmol) with 69% yield. M.p.: 338-339 K. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 11.74 (s, 1H), 8.62-8.55 (m, 1H), 8.48 (t, $J = 8.0$ Hz, 1H), 8.33 (s, 1H), 8.17 (t, $J = 8.0$ Hz, 2H), 8.04 (s, 1H), 7.80-7.71 (m, 3H), 7.71-7.56 (m, 6H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 5.60 (s, 1H), 5.05 (s, 1H), 1.97 (d, $J = 4.0$ Hz, 6H) (Fig. S3). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ (ppm): 169.9, 169.7, 169.5, 154.4, 154.3, 149.9, 149.6, 143.5, 142.3, 142.2, 141.7, 141.5, 139.7, 138.3, 138.2, 136.3, 134.1, 134.1, 132.9, 130.5, 129.7, 128.8, 128.6, 128.4, 128.2, 127.1, 127.1, 126.7, 126.6, 126.0, 125.9, 125.7, 125.4, 124.0, 123.7, 123.0, 123.0, 121.5, 120.8, 118.8, 118.6, 116.2, 112.9, 68.7, 66.9, 14.5 (Fig. S4). MS (m/z): Calculated for $\text{C}_{46}\text{H}_{30}\text{F}_6\text{N}_4\text{O}_2\text{S}_3$ $[\text{M}]^+$: 880.1435, found: 881.1480 for $[\text{1o} + \text{H}]^+$, 903.1303 for $[\text{1o} + \text{Na}]^+$ (Fig. S5).

Results And Discussion

Photochromic and fluorescent properties of diarylethene **1o**

The photochromic property of **1o** in acetonitrile solution at room temperature were first investigated. As shown in Fig. 1A, two absorption bands was observed with the maximum absorption peak at 335 nm and 296 nm respectively, which was due to n- π^* transition^[36] mixed with π - π^* transition^[37] of the chemosensor **1o**. Meanwhile, the color of the solution was colorless. Irradiated by 297 nm UV light, the absorption peaks at 296 nm and 335 nm decreased slowly and a new visible absorption band with the maximum absorption peak at 598 nm appeared, due to the closed-ring isomer **1c** formed, the larger electron can be delocalization in the molecule. The photocyclization reaction reached a photostationary state (PSS) and the solution's color changed from initial colorless to blue. On the contrary, the absorption spectrum of **1c** completely returned to the initial state **1o** under visible light ($\lambda > 500$ nm) irradiation, and the solution's color changed from blue to colorless at the same time. In the reversible structural transformation process, the isoabsorption point was observed at 357 nm, indicating the photochromism was a reversible two-component photochromic reaction. Taking 1,2-bis(2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene as the reference, the quantum yields of cyclization and ring reversion of diarylethene **1o** were calculated as 0.36 and 0.027, respectively. In addition, after alternately irradiated **1o** with UV and visible light for ten times, **1o** descended only 9% degradation after ten decolorization cycles (Fig. 1B), suggested that **1o** having the good fatigue resistance.

The fluorescent emission spectral change of **1o** in acetonitrile under photoirradiation at room temperature is shown in the Fig. 1C. Under the excitation of 350 nm, a strong fluorescent peak of **1o** centering at 491 nm was observed. When **1o**'s solution was irradiated by 297 nm UV light, the non-fluorescent closed-ring isomer **1c** was generated, resulted in the fluorescent emission of compound **1o** decreased significantly, the color of the solution changed from bright blue to dark blue, the fluorescence was quenched by 84.9% when reached the photostationary state, and the fluorescence quantum yield of **1o** to **1c** decreased from 0.326 to 0.008 in the process. When irradiated renewedly with visible light, **1c** returned to the original **1o**, and the fluorescent color of **1o**'s solution became bright blue again. These results suggested that **1o** bearing notable light-switching characteristics.

“Turn-off” fluorescent detection of Hg²⁺

The fluorescent response of **1o** to 17 different metal ions of 3.0 eq. (Cu²⁺, Fe³⁺, Al³⁺, Zn²⁺, Ca²⁺, Mg²⁺, Ag⁺, Pb²⁺, Ba²⁺, Mn²⁺, K⁺, Sr²⁺, Co²⁺, Cr³⁺, Ni²⁺, Hg²⁺, Cd²⁺) was measured in acetonitrile solution at room temperature. As shown in Fig. 2A, when excited with 350 nm light, **1o** (2.0×10^{-5} mol L⁻¹) displayed strong fluorescence with maximal emission peak at 491 nm. Only the addition of Hg²⁺ resulted in the complete quenching of its fluorescence. Though 3.0 eq. Fe³⁺ and Cd²⁺ can result in a nearly 72% and 87% decrease in fluorescence intensity and the solution color changes from blue to blue-green (Fig. 2B), the detection effect was much lower than that of Hg²⁺. Considering the interference of other metal ions in the actual detection, the fluorescent competition experiment of Hg²⁺ was carried out. Furthermore, the fluorescence intensity at 491 nm was recorded by adding Hg²⁺ into **1o** solution containing various other metal ions, the result showed the mixed metal ions had little effect on the fluorescence intensity at 491 nm, except Fe³⁺

and Cd^{2+} (Fig. 2C), indicating that the fluorescence detection of **1o** to Hg^{2+} has good anti-interference property.

The relationship of fluorescence intensity between **1o** and Hg^{2+} in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) solution at room temperature was recorded in Fig. 3A and Fig. 3B. With the gradual addition of Hg^{2+} into **1o**'s solution, the fluorescent intensity at 491 nm decreased significantly and the solution color changed from bright blue to dark. When the addition of Hg^{2+} reached 3.0 eq. the fluorescence was almost completely quenched and the fluorescent intensity decreased by more than 99%. Significantly, the fluorescence of the solution completely recovered after 12.0 eq. of EDTA added (Fig. 3C).

The binding stoichiometry of **1o** to Hg^{2+} was calculated from the Job's plot method, as shown in Fig. 4A. When the mole fraction of $[\text{Hg}^{2+}]/([\text{Hg}^{2+}]+[\textbf{1o}])$ was about 0.5, the fluorescence emission intensity reached the minimum value, suggesting the binding stoichiometry was 1 : 1 between **1o** and Hg^{2+} . The association constant (K_a) of **1o** with Hg^{2+} was calculated as $1.6912 \times 10^4 \text{ mol}^{-1} \text{ L}$ according to modified Hildebrand–Benesi equation (Fig. 4B). The limit of detection of compound **1o** for Hg^{2+} was measured as 60 nM (Fig. 4C). Among the probes for Hg^{2+} detection, the detection limit of **1o** was relatively low (Table 1). To sum up, the above data proved that **1o** could acted as a highly selctive fluorescent sensor for Hg^{2+} .

Table 1 Comparison of fluorescent probes for Hg^{2+}

Probe	Stokes shift (nm)	LOD (nM)	References
50	100	38
63	300	39
49	38	40
62	350	41
80	230	42
75	230	43
156	60	This work

Application of **1o** in logic circuits

In general, the fluorescence intensity of **1o** can be regulated by the stimulation of UV/vis light and Hg^{2+} /EDTA in acetonitrile solution. Therefore, an ideal logic gate circuit was created by four input signals (UV-In1, Vis-In2, Hg^{2+} -In3 and EDTA-In4) and a output signal (the change of fluorescence intensity at 491 nm) (Fig. 5). In particular, when the fluorescence intensity at 491 nm is less than 90% of the starting value of **1o**, the output signal can be considered as an "on" state and replaced with "1". Otherwise, it will be treated as "off" and replaced by "0". For example, when the four digital symbols are "1, 0, 1, and 0", the corresponding states of In1, In2, In3, and In4 are "on, off, on, and off". In this case, under the stimulation of Hg^{2+} and UV, the original **1o** was transformed into a closed-loop state **1c'**, and the fluorescence was

quenched. Therefore, the output state was "on" and replaced with "1". Similarly, Table 2 lists each possible logic string of the combinational logic circuit.

Table 2 Truth table consisting of four inputs data and corresponding output digits..

Inputs				Output
In1 (UV)	In2 (Vis)	In3 (Hg ²⁺)	In4 (EDTA)	($\lambda_{em} = 491 \text{ nm}$)
0	0	0	0	0
1	0	0	0	0
0	1	0	0	0
0	0	1	0	1
0	0	0	1	0
1	1	0	0	0
1	0	1	0	1
1	0	0	1	0
0	1	1	0	1
0	1	0	1	0
0	0	1	1	0
1	1	1	0	1
1	1	0	1	0
1	0	1	1	0
0	1	1	1	0
1	1	1	1	0

Conclusions

In summary, a novel diarylethene-based Hg²⁺ chemosensor containing a quinoline unit (**1o**) had been synthesized. **1o** displayed high selectivity for Hg²⁺ in acetonitrile solution by fluorescence experiments and good anti-interference capability. The quenching detection of **1o** induced by Hg²⁺ can be recover by adding EDTA. The detection limit of **1o** towards Hg²⁺ was 60 nM. Therefore, the diarylethylene derivative **1o** can be used an effective sensor for the detection of Hg²⁺. Besides, the fluorescence intensity of **1o** can

be modulated by irradiating UV/vis light, based on the fact, a logic gate circuit based on four inputs and one output was designed.

Declarations

Acknowledgements: The authors are grateful for financial support from the National Natural Science Foundation of China (41867052, 21861017, 41867053).

Author Declarations:

Funding: This work was supported by the National Natural Science Foundation of China (41867052, 21861017, 41867053)

Conflicts of interest: No conflict of interest to declare.

Ethics approval: Not applicable.

Consent to participate: All authors given consent for participation.

Consent for publication: All authors agreed to publish.

Availability of data and material: All data generated or analysed during this study are included in this published article (and its supplementary information files).

Code availability: Not applicable

Authors' contributions: All authors contributed to the design and synthesis of this study. All authors performed the experimental material preparation, data testing and analysis of the results. The first draft of the manuscript was written by Liangtao Mao and all authors read and approved the final manuscript.

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Scheme 1

Scheme 1 is available in Supplemental Files section.

Figures

Figure 1

(A) Changes of absorption spectra and color of **1o** in acetonitrile solution ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) under UV/vis light irradiation. (B) Ten decolorization cycles of **1o** in acetonitrile solution at room temperature. (C) Changes of fluorescence spectrum and color of **1o** in acetonitrile solution ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) under UV/vis light irradiation.

Figure 2

(A) The emission spectral changes by adding different metal ions (3.0 eq.) to **1o** (2.0×10^{-5} mol L⁻¹). (B) Fluorescence photos change by adding different ions into **1o**. (C) Competitive test for fluorescence response of **1o** at 491 nm. The red column represents the fluorescence intensity of **1o** solution with various metal ions, and the black column represents the fluorescence intensity of **1o** solution with Hg²⁺ (3.0 eq.) and various other metal ions (3.0 eq.).

Figure 3

(A) Changes in the fluorescence of **1o** in acetonitrile solution induced by Hg^{2+} /EDTA (different amounts of Hg^{2+} titrated with **1o**) at room temperature. (B) Fluorescence intensity at 491 nm of **1o** in acetonitrile under different equiv of Hg^{2+} induction. (C) Fluorescence intensity at 491 nm of **1o**+ Hg^{2+} under different equiv of EDTA induction.

Figure 4

(A) The Job's plot showed the complex ratio of **1o** and Hg^{2+} was 1:1. (B) Hildebrand-Benesi plots were plotted on the basis of 1:1 complexation between **1o** and Hg^{2+} , and the binding constant between **1o** and Hg^{2+} was measured as $1.6912 \times 10^4 \text{ mol}^{-1} \text{L}$. (C) The limit of detection for Hg^{2+} was 60 nM.

Figure 5

Combinational logic circuit equivalent to the truth table given in Table 1. In 1 (UV), In 2 (Vis), In 3 (Hg^{2+}), In 4 (EDTA) and Output (at 491 nm, when the fluorescence quenching exceeds 90%, it is defined as 1. Otherwise, it is defined as 0).

Supplementary Files

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