



Study on a highly selective colorimetric chemosensor for Cu^{2+} detection and its indirect sensing for hypochlorite



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ABSTRACT

A highly-selective colorimetric chemosensor (**CS1**) for Cu^{2+} detection is prepared and characterized. This Cu^{2+} sensor can act as a potential probe towards ClO^- , by taking advantage of the oxidation property of hypochlorite and different coordinating property of Cu^+ and Cu^{2+} with **CS1**. Upon addition of ClO^- , the absorption maximum band of **CS1** in the presence of Cu^+ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) shows a large red shift from 398 to 552 nm ($\Delta = 154$ nm), and a visually color change from orange to purple is very easy to observe by naked-eyes, while other commonly-coexisting anions can not induce such similar changes. **CS1** mimic an AND logic gate function with Cu^+ and ClO^- as inputs and $A_{552\text{ nm}}/A_{398\text{ nm}}$ as output ($A = \text{absorbance}$), and this function can be easily reset by S^{2-} .

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1. Introduction

The development of selective and sensitive signaling systems for the determination and visualization of metal ions or anions with biological interest is a very attractive research topic in chemosensing and molecular imaging fields [1,2]. Among the various transition metal ions Cu^{2+} , as the third most abundant trace element in human body, plays a critical role as an important trace element for biological processes, and recently many works have been published which emphasize the role of Cu^{2+} in biological processes [3–8]. However, when levels of Cu^{2+} exceed cellular needs, it can be harmful and even highly toxic to biological systems [9,10]. On the other hand, hypochlorite anion (ClO^-) is one important reactive oxygen species (ROS), and could be produced in organisms by the reaction of H_2O_2 with Cl^- ions under the catalysis of a heme enzyme, myeloperoxidase [11]. Endogenous ClO^- is

essential to living lives and has an important antibacterial property. However, excessive or misplaced production of hypochlorite can cause serious damages to biological systems, and even lead to some diseases, including atherosclerosis, arthritis, and cancers [12–14]. Thus, there is a need for a rapid and sensitive method for the determination of Cu^{2+} or ClO^- [15,16].

In the past few decades, we have researched a number of methods for the detection of Cu^{2+} ions at trace quantity levels, such as atomic absorption spectrometry (AAS), ion selective electrodes (ISE), inductively coupled plasma mass spectroscopy (ICPMS) and inductively coupled plasma-atomic emission spectroscopy (ICP–AES) [17]. Although these methods can provide good detection limit in wide concentration ranges, they require costly apparatus and are not suitable for assays because of destruction of the samples. Most of those methods are usually complicated and time-consuming, and can not be used for in-spot, real-time and on-line detection. Consequently, increasing attentions have recently been focused on the development of colorimetric chemosensors for the detection of Cu^{2+} ions due to the simplicity of assay [18], which allows the “naked-eyes” detection of Cu^{2+} . So far, only a few colorimetric and fluorescent chemosensors for Cu^{2+} ions have been reported [19]. Consequently, there is a need to develop colorimetric chemosensors for Cu^{2+} ion detection.

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On the other hand, there are a number of methods available for hypochlorite determination. A few samples are as follows: the normalized and well-known iodometric titration [20], many colorimetric methods based on the reaction of hypochlorite with organic reagents [21–26], chemiluminescence methods that based on fluorescein test strip [27–29], coulometric [30], polarographic, bromination of fluorescein Refs. [31], and radiolysis. For all above methods, colorimetric methods are often preferred since they involve less expensive instrumentation when appropriate chromogenic reagents are available, as suggested by Narayana et al. [25].

Compared with the probes for Cu^{2+} or ClO^- reported [19–31], this is the dual-function and highly selective chemosensor based on a small molecule that can detect both Cu^{2+} and ClO^- . In this paper, we have successfully obtained a new colorimetric chemosensor (**CS1**) for Cu^{2+} with high selectivity. Based on the fact that different coordinating behaviors of Cu^+ and Cu^{2+} with **CS1** and that Cu^+ ions can be oxidized to Cu^{2+} ions by ClO^- , **CS1** can act as a potential probe for hypochlorite. The sensing property of **CS1** for ClO^- is investigated. Moreover, an AND logic gate system has been designed based on oxidation property of hypochlorite, with small molecules as inputs and outputs. Hereby, we have realized molecular logic operations. We conduct an AND logic gate function with Cu^+ and ClO^- as inputs and $A_{552\text{ nm}}/A_{398\text{ nm}}$ as output, and this function can be reset by S^{2-} .

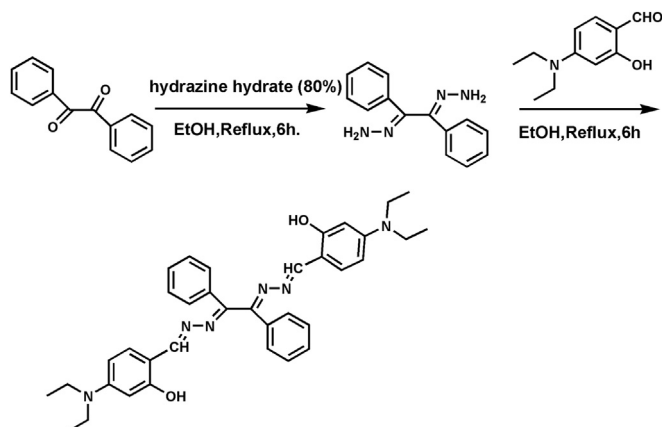
2. Experimental section

2.1. Instruments and reagents

All experiments were carried out at 298 K, unless otherwise mentioned. All the materials for synthesis were purchased from commercial suppliers and used without further purification. Redistilled water was used throughout all experiments. ^1H NMR was recorded using a mercury-300BB spectrometer (Varian, USA) operated at 300 MHz with tetramethylsilane (TMS) as internal standard. Mass spectra were performed on Agilent 1100 MS series and AXIMA CFR MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) MS (COMPACT). Absorption spectra were measured using an ultraviolet–visible spectrophotometer, UV-3000 (Shimadzu Corp, Kyoto, Japan).

2.2. Synthesis of chemosensor **CS1**

The chemosensor **CS1** was synthesized according to Scheme 1. 4-diethylaminosalicylaldehyde (0.386 g, 2 mmol) and benzylhydrazine



Scheme 1. Synthesis and structure of chemosensor **CS1**.

(0.24 g, 1 mmol) were mixed in EtOH solution and refluxed for 6 h. A yellow solid was precipitated and filtered, and then washed with methanol and water several times. It was dried under vacuum. Yield: 73%. Anal. Calc. for $\text{C}_{36}\text{H}_{40}\text{N}_6\text{O}_2$: H 6.85, C 73.44, N 14.27, Found: H 6.90, C 72.37, N 14.18%. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 11.39 (s, 2H, $-\text{OH}$); 8.62 (s, 2H, $-\text{N}=\text{CH}$); 7.81 (d, 4H, Ar-H); 7.46 (d, 6H, Ar-H); 7.08 (d, 2H, Ar-H); 6.07 (d, 2H, Ar-H); 6.16 (d, 2H, Ar-H); 3.32 (m, 8H, $-\text{CH}_2-$); 1.15 (m, 12H, $-\text{CH}_3$).

2.3. General spectroscopic procedures

2.3.1. Preparation of solutions of metal ions and anions

All metal ions stock solutions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ag^+ , Cd^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} and Cu^{2+} were prepared by dissolving their salts nitrate in H_2O with concentration of 10^{-3} M. All anions stock solutions of NO_3^- , HSO_3^- , SO_4^{2-} , ClO_4^- , I^- , Br^- , F^- , HPO_4^{2-} , CO_3^{2-} , AcO^- and sodium ascorbate were obtained by dissolving their sodium salts in H_2O in the order of 10^{-2} M.

2.3.2. UV absorption changes of **CS1** + Cu^{2+} , **CS1** + Cu^+ , **CS1** + Cu^+ + ClO^- , **CS1** + Cu^+ + other anions and **CS1** + Cu^+ + ClO^- + S^{2-}

A solution of **CS1** (10 μM) was prepared in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v), then 5.0 mL of the solution of **CS1** was placed in a 10-mL tube and the UV absorption spectrum was recorded before and after the addition of sodium ascorbate and Cu^{2+} or Cu^+ to the solution of **CS1**. After the solution of sodium ascorbate and Cu^+ was added to **CS1**, the solution of NaClO or other anions was introduced in portions and the UV absorption changes were recorded at room temperature each time. UV absorption changes of **CS1** (10 μM) + Cu^+ (20 μM) + sodium ascorbate (2 μM) + ClO^- were recorded before and after the addition of S^{2-} to the solution. All the UV–Vis behaviors of **CS1** are studied in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) solution and the **CS1** stock solution concentration is 10 μM .

3. Results and discussion

3.1. Spectral characteristic of **CS1** and its response to metal ions

In the absence of metal ions, the maximum absorption of **CS1** is at about 398 nm, which is attributed to the $n \rightarrow \pi^*$ transitions of the (diethylamino) phenol moiety. As shown in Fig. 1, when 1 equiv

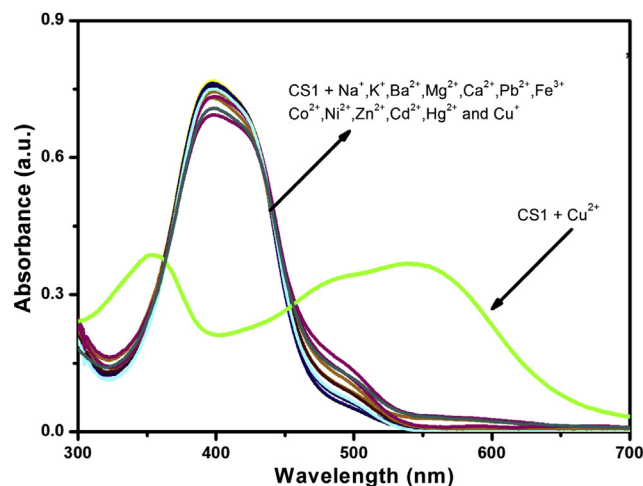
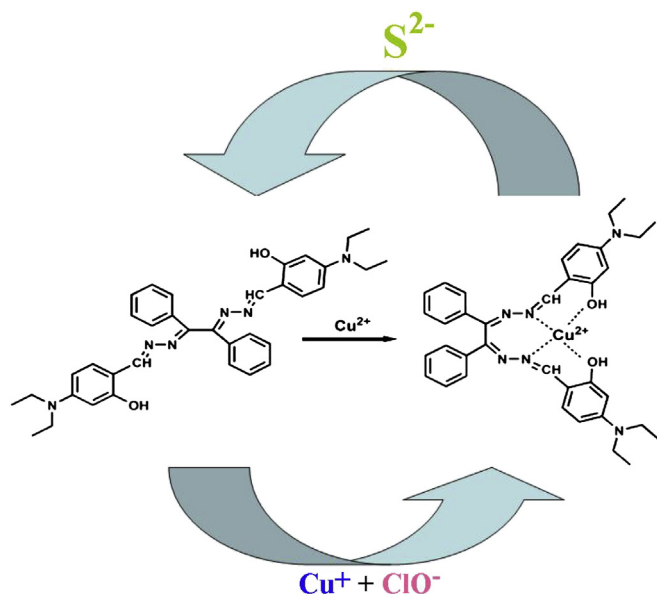


Fig. 1. Absorption spectra changes of chemosensor (10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) upon addition of different metal ions (10 equiv).



Scheme 2. The possible binding model of chemosensor **CS1**.

of Cu^{2+} is added to the solution of **CS1** (10 μM), the peak at 398 nm disappears and a new band peaking at 552 nm appears, and the possible binding model of chemosensor **CS1** is shown in Scheme 2 [32,33]. However, no significant spectral changes can be observed when 10 equiv of other metal ions, such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ag^+ , Cd^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} and Hg^{2+} , are added. This result indicates that the chemosensor **CS1** has a high selectivity for Cu^{2+} ion.

To optimize the quantification of Cu^{2+} in aqueous conditions, the pH of buffer and the CH_3CN fraction in the absorption

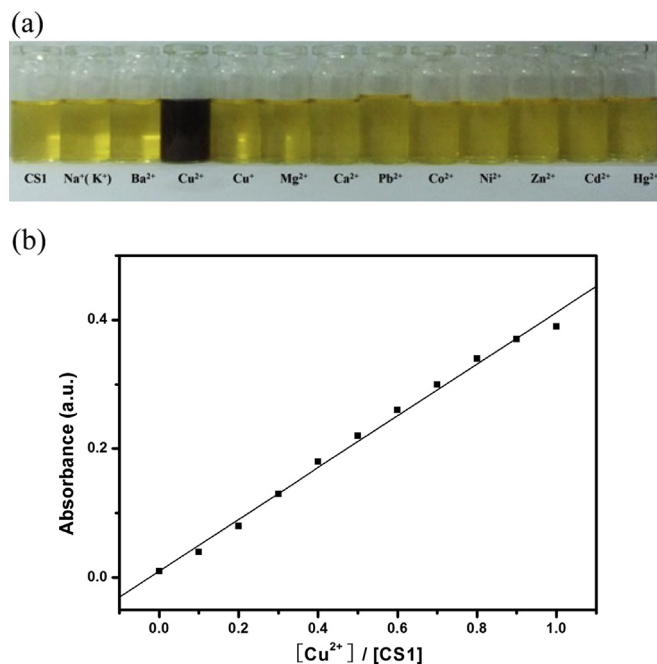


Fig. 2. (a) Color changes upon addition of 10 equiv different metal ions in 50 μM $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) solution of chemosensor **CS1**. (b) Absorbance spectra changes at 552 nm of **CS1** (10 μM) upon addition of Cu^{2+} in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

spectral method are both investigated, and they are used to evaluate the optimized condition of **CS1** for the detection of Cu^{2+} (see Supplementary Data Figs. S1 and S2). Fig. 2a shows the visualization of Cu^{2+} ion recognition and sensing. Each vial contains 20 μM of **CS1** in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v). The addition of one equivalent of Cu^{2+} ion, the color of solution changes from orange to purple, which could be easily used for “naked-eye” detection. Even the addition of 10 equivalents of each interference metal ion doesn’t induce any color change. Fig. 2b shows the absorbance spectra changes at 552 nm of **CS1** (10 μM) upon addition of Cu^{2+} in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v), and the linear response can be expressed by the following formula: $A = 0.01 + 0.40182 \times \{ [\text{Cu}^{2+}] / [\text{CS1}] \}$ ($R^2 = 0.99695$). Here A is the recorded absorbance spectra changes of **CS1** actually measured at a given Cu^{2+} ion concentration.

3.2. Spectroscopic study of **CS1** for ClO^-

Considering the oxidation property of hypochlorite and the spectral change of **CS1** towards Cu^{2+} ion, we are wondering that if **CS1** could be act as a probe for hypochlorite, based on the fact that Cu^+ ions can be oxidized to Cu^{2+} ions by ClO^- . Fig. 3a shows

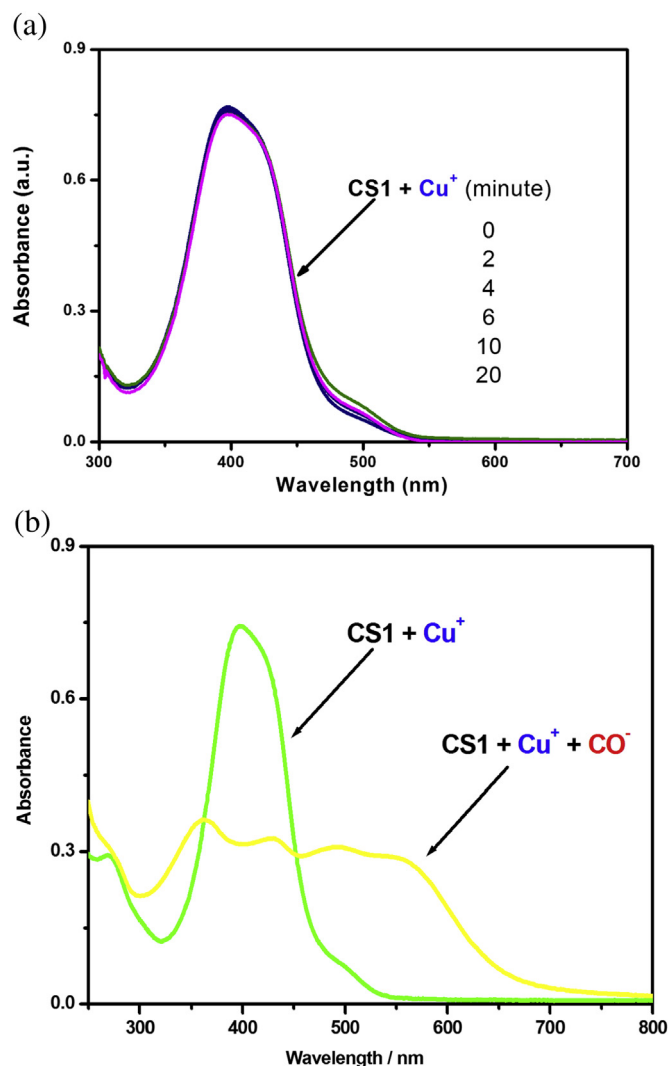


Fig. 3. Absorption spectra of **CS1** (10 μM), CuI (20 μM) and sodium ascorbate (1 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) in the absence (a) or presence (b) of NaClO (3 equiv.).

the absorption spectra of **CS1** (10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) in the presence of Cu^+ (3 equiv.) and sodium ascorbate (stabilizer, which could eliminate the influence of oxygen in the air). It could be observed that there is no obvious spectral change upon Cu^+ addition, suggesting that **CS1** does not react with Cu^+ . The reason is that Cu^{2+} has a bigger polarization capability than Cu^+ and can afford stronger coordination interaction, and the energy of **CS1**- Cu^{2+} is lower than **CS1**- Cu^+ . However, as shown in Fig. 3b, upon addition of 3 equiv of NaClO , the spectrum changes dramatically: the absorbance at 398 nm decreases and a new absorption peaking at 552 nm appears. Correspondingly, a color change from yellow to purple is observed, indicating that **CS1**, in the presence of Cu^+ , can be used a naked-eyes indicator for hypochlorite.

Fig. 4a shows the absorption spectra of **CS1** under Cu^+ ions and sodium ascorbate. As the concentration of ClO^- ions increasing, the absorbance at 398 nm decreases gradually, with the increase of absorbance at 552 nm (Fig. 4b). One isosbestic point at about 455 nm is observed.

As shown in Fig. 5a, only the addition of ClO^- induces a significant spectral change. Other ions such as NO_3^- , HSO_3^- , SO_4^{2-} , ClO_4^- , I^- , Br^- , F^- , HPO_4^{2-} , CO_3^{2-} and AcO^- elicits nearly no changes in the

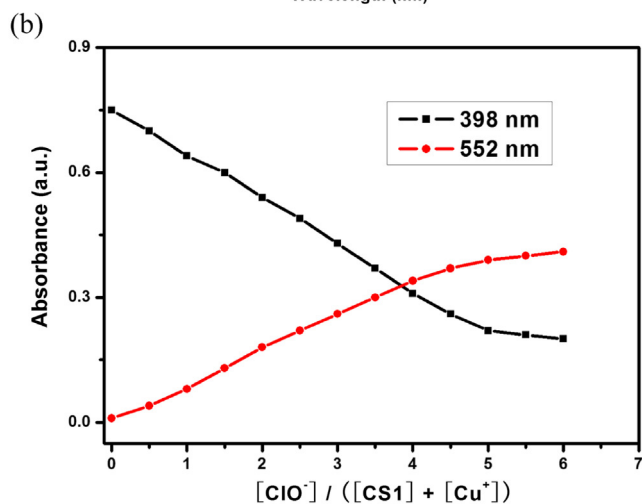
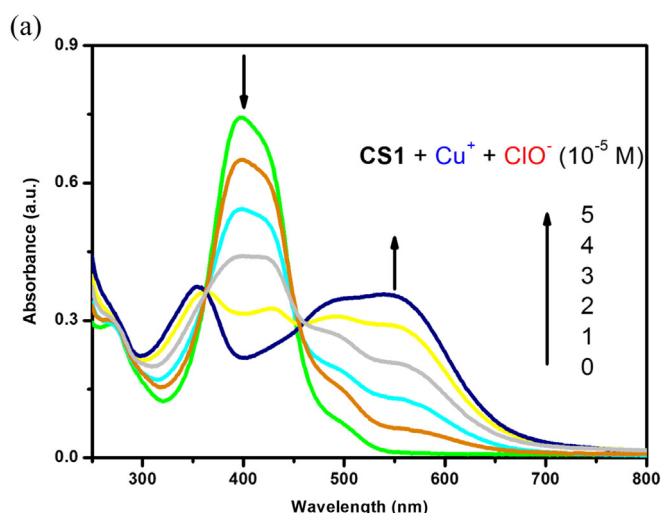


Fig. 4. (a) Absorption spectra of **CS1** (10 μM), CuI (20 μM) and sodium ascorbate (1 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) in the presence of different amounts of NaClO after 30 min. (b) The absorbance was measured at 398 nm and 552 nm, respectively with titration of NaClO .

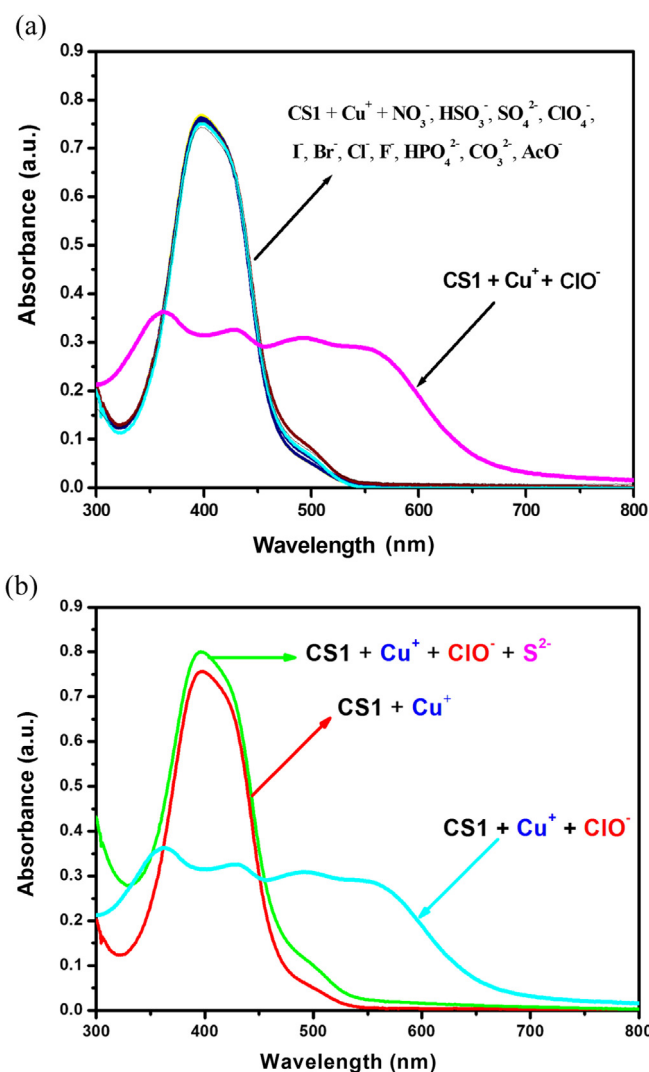


Fig. 5. (a) Absorption spectra of **CS1** (10 μM), CuI (20 μM) and sodium ascorbate (1 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) in the presence of different kind of anions (100 μM). (b) The concentration of S^{2-} was 50 μM .

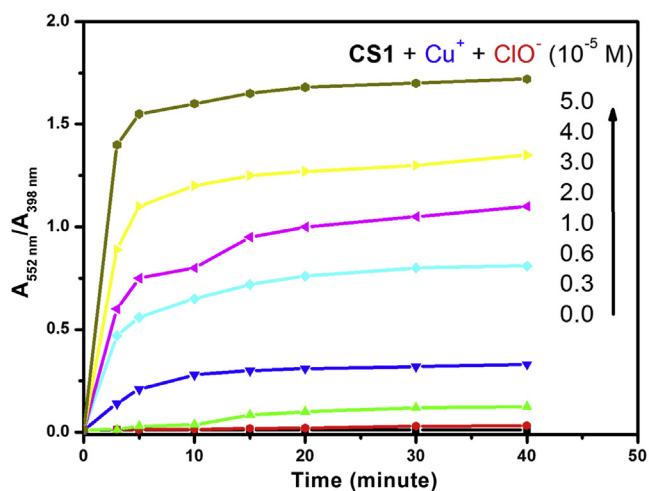


Fig. 6. Reaction-time profile of **CS1** (10 μM), CuI (20 μM) and sodium ascorbate (1 μM) in the presence of different concentrations of hypochlorite anion. Kinetic studies were performed at room temperature.

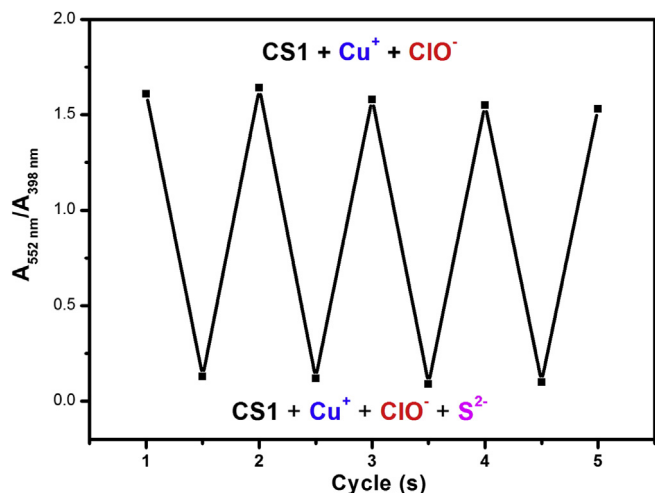


Fig. 7. $A_{552\text{ nm}}/A_{398\text{ nm}}$ responses of **CS1** (10 μM) by alternated adding Cu^+ + ClO^- and S^{2-} (sodium salt) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v). The cyclic index is the number of alternating Cu^+ + $\text{ClO}^-/\text{S}^{2-}$ cycles.

absorbance spectra. Thus, the selectivity for ClO^- over other anions is remarkably high.

Since the color change relies on the chemical reaction from Cu^+ to Cu^{2+} triggered by ClO^- , we thus investigate the influence of reaction time on the sensing behavior, and the obtained result is demonstrated in Fig. 6. It can be seen that the oxidation and recognition can be finished in 30 min when ClO^- concentration is higher than 10 μM , and this short reaction time guarantees a fast detection.

The S^{2-} -adding experiment is conducted to examine the reversibility of **CS1** (Fig. 5b). It is shown clearly that the absorption spectrum can nearly restore to the initial intensity upon the addition of S^{2-} as shown in Fig. 7, which confirms the good reversibility of **CS1**.

3.3. Logic gate

In a silicon-circuitry based computer, electrical signals are used as inputs and outputs. Following the laws of Boolean algebra, this supposition opens the door to use molecular entities on the purpose of mimicking the function of logic gates, which constitute the basis of digital information processing. Molecular logic gates have attracted significant interest recently [34], since they have enabled the development of molecular-scale computers and “autonomously regulated” chemical systems.

The first example of a molecular logic gate is described by de Silva in 1993, mimics an AND function [35]. Here, the UV–Vis absorbance behavior of chemosensor **CS1** in presence of Cu^+ and ClO^- can satisfactorily mimic an AND logic gate function with Cu^+ and ClO^- as inputs and $A_{552\text{ nm}}/A_{398\text{ nm}}$ as output. Free **CS1** shows a low $A_{552\text{ nm}}/A_{398\text{ nm}}$, corresponding to a “0” state. Upon the individual presence of Cu^+ or ClO^- , the $A_{552\text{ nm}}/A_{398\text{ nm}}$ is still low (“0” state). However, the simultaneous presence of Cu^+ and ClO^- can give a high $A_{552\text{ nm}}/A_{398\text{ nm}}$, corresponding to a “1” state. The value change of $A_{552\text{ nm}}/A_{398\text{ nm}}$ in the presence of Cu^+ and ClO^- and the corresponding truth table with logic circuit for AND function are given in Fig. 8. The action can be reset by the addition of S^{2-} , which regenerates the initial state as shown in Fig. 7.

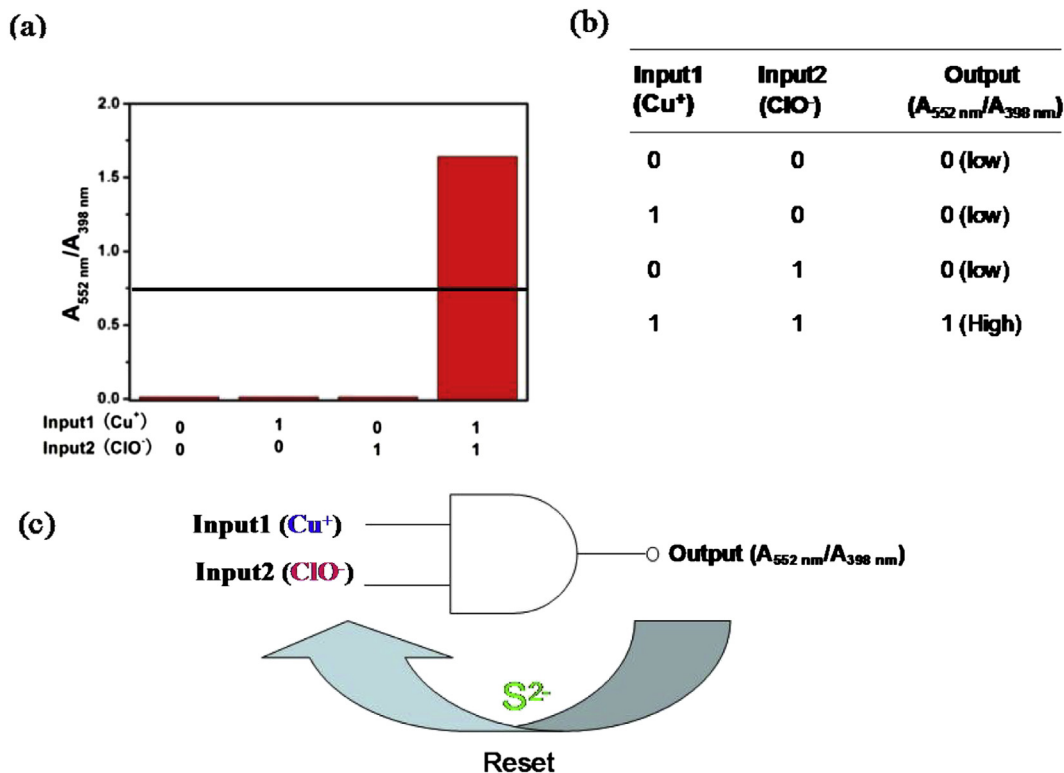


Fig. 8. $A_{552\text{ nm}}/A_{398\text{ nm}}$ responses of **CS1** (10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v) in the presence of Cu^+ , ClO^- and Cu^+ + ClO^- . **CS1** mimic an AND logic gate function with Cu^+ and ClO^- as inputs and $A_{552\text{ nm}}/A_{398\text{ nm}}$ as output, and this function can be easily reset by adding S^{2-} .

4. Conclusions

In conclusion, we have developed a highly selective colorimetric chemosensor (**CS1**) for Cu^{2+} . Based on the absorption spectrum difference of **CS1** towards Cu^+ and Cu^{2+} , **CS1** also can be act as a potential probe for hypochlorite. Furthermore, **CS1** can mimic an AND logic gate function with Cu^+ and ClO^- as inputs and $A_{552\text{ nm}}$ / $A_{398\text{ nm}}$ as output, and this operation can be easily reset by S^{2-} . This may be a novel idea to develop new chemosensors for oxidants.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2013.03.022>.

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