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RESEARCH ARTICLE

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A turn-on fluorescent probe based on quinoline and coumarin for rapid, selective and sensitive detection of hypochlorite in water samples

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Abstract

A fluorescent probe **L**-Cu^{2+} based on quinoline, coumarin and Cu^{2+} has been synthesized and characterized for hypochlorite determination. After copper ion was added to the solution of ligand **L**, the fluorescence quenching at 490 nm might result from a ligand–metal charge transfer (LMCT) process and its strong coordination ability for Cu^{2+}. In the presence of hypochlorite, the structure of ligand **L** was destroyed to form 7-(diethylamino)-coumarin-3-carboxylic acid, and the fluorescence was restored at 460 nm. In this case, **L**-Cu^{2+} complex could be used as a fluorescent probe to detect hypochlorite, with the advantages of rapid, selective, wide linear range and low detection limit.

KEYWORDS

fluorescent, hypochlorite, water samples

1 | INTRODUCTION

Hypochlorous acid (HClO)/hypochlorite (ClO^-), as a proverbial biological reactive oxygen species (ROS),[1] plays an indispensable part in many biochemical processes.[2,3] It is a biological agent and common disinfectant in daily life that can kill a variety of pathogens.[4,5] However, abnormal hypochlorite concentration in the body could give rise to many illnesses like Alzheimer's disease, angiocardiopathy, nephropathy and even cancer.[6] In October 2017, the international institution for research on cancer has published the list of carcinogens regarding it as a category 3 carcinogen. Therefore, exploiting a rapid and accurate method to detect hypochlorite is an extremely urgent task.[7]

Up to now, with the development of analytical technology, lots of methods for hypochlorite determination have been researched, including iodometry,[8] phosphorescence analysis,[9] electrochemistry,[10] colorimetric method,[11] high performance liquid chromatography (HPLC),[12] and fluorescence analysis.[13] Among them, because of its merits such as fast, well specificity and low detection limit, fluorescence analysis has drawn more attention in the field of research recently.[14–17] Therefore, it already has been reported that hypochlorite can be detected by many fluorescent probes. Nevertheless, most of them have adverse characters of large self-interference, narrow linear range and long reaction time etc. To overcome these shortcomings, we report a sensor for rapid detection of hypochlorite (2 s) with a wide linear range (1.00×10^{-6} mol L^{-1} – 8.00×10^{-3} mol L^{-1}).

2 | EXPERIMENTATION

2.1 | Reagents

4-N,N-Diethylaminosalicylicaldehyde, 2-Quinolinecarboxaldehyde and Diethylmalonate were acquired from Energy Chemical Co., Ltd (Shanghai, China). All the other reagents and chemicals were obtained from reagent sales agency. All reagents, without any prior purification, were analytical reagent grade unless otherwise specified.

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2.2 | Apparatus

Hitachi F-2700 fluorescence spectrophotometer (Hitachi, Japan) was used to perform fluorescence measurements. Sartorius PB-10 digital pH meter was used to make all pH measurements. Varian Mercury YH-300 spectrometer operated at 400 MHz was used to perform Nuclear magnetic resonance (NMR) spectra. Agilent 1,290 Infinity LC System interfaced with the Bruker micrOTOF-Q II mass spectrometer instrument was used to obtain electrospray ionization (ESI) mass spectra.

2.3 | Synthesis

The synthetic pathway for G2 and G3 were based on the previous work.[18,19] Probe **L** was synthesized conveniently from the reaction of G3 and 2-Quinolinecarboxaldehyde, which was shown in scheme 1. It was characterized by ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H, N-C=O), 8.78 (s, 1H, quinoline H-3), 8.58 (s, 1H, coumarin H-3), 8.44 (d, *J* = 8.7 Hz, 1H, quinoline H-5), 8.13 (d, *J* = 8.6 Hz, 1H, quinoline H-8), 8.06 (d, *J* = 8.5 Hz, 1H, C_9H_6NCH=N), 8.03 (d, *J* = 8.1 Hz, 1H, quinoline H-2), 7.81 (t, *J* = 7.7 Hz, 1H, quinoline H-7), 7.76 (d, *J* = 9.0 Hz, 1H, quinoline H-6), 7.66 (t, *J* = 7.4 Hz, 1H, coumarin H-5), 6.86 (d, *J* = 9.1 Hz, 1H, coumarin H-6), 6.68 (s, 1H, coumarin H-8), 3.58–3.47 (m, 4H, NCH_2CH_3), 1.17 (t, *J* = 7.0 Hz, 6H, NCH_2CH_3). ESI-MS: m/z Calculated for $C_{24}H_{22}N_4O_3$ [M] = 414.47, Found [M + H^+] = 415.03. Figure S3 and Figure S4 (a).

2.4 | Preparatory work

Stock solution (3 mmol L^{-1}) was gotten by dissolving probe **L** in dimethylsulphoxide (DMSO). The corresponding concentration of the determin and solutions (3 mmol L^{-1}) were achieved by dissolving the species in redistilled water, including K^+, Na^+, Ca^{2+}, F^-, Cl^-, Br^-, HCO_3^-, NO_3^-, SO_4^{2-}, ClO^-, CO_3^{2-}, Fe^{3+}, MnO_4^- and H_2O_2. The real samples were obtained from Changchun Water Supply Company and the lake water of Peony Park Changchun. The add sequence of solutions was 10 μL probe **L** (1 mM), 2090 μL methyl alcohol, 10 μL Cu^{2+}, 890 μL deionized water and 50 μL ClO^-. The gross of solutions marked 3 mL. The emission intensity was recorded at 460 nm with an excitation wavelength at 401 nm. The excitation and emission slits of 5 nm were applied. A sample cell path length was 1 cm.

3 | RESULTS AND DISCUSSION

3.1 | Quenching of fluorescence by Cu^{2+}

With the various concentrations of Cu^{2+} presenting in the solution (CH_3OH/H_2O, 7:3 *v*/v), the fluorescence intensities of **L** were

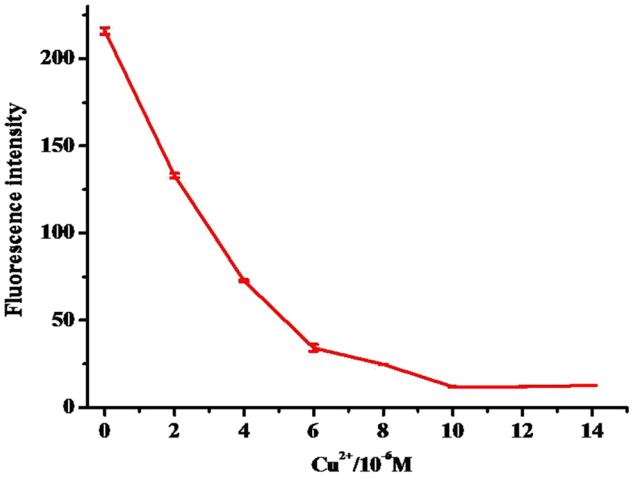
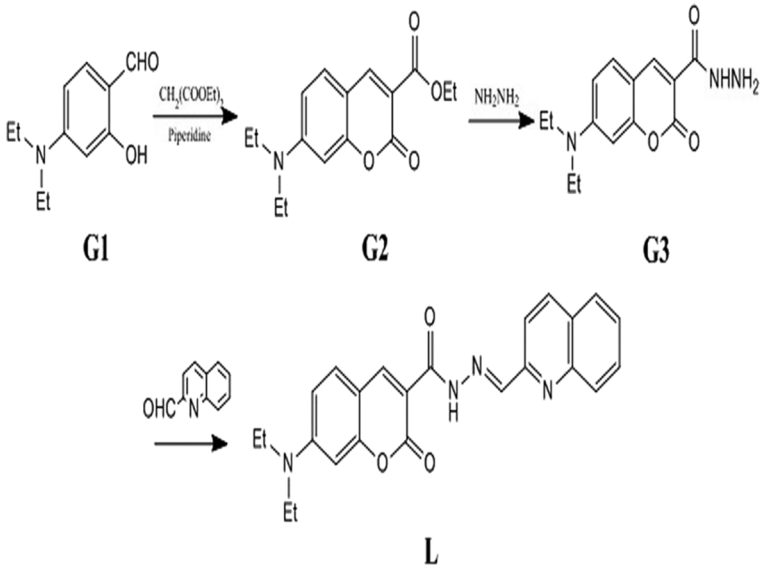


FIGURE 1 The effect of various concentrations of Cu2+ on the fluorescence of L (10 μM), in a mixture solution of water and methanol (CH3OH/H2O, 7:3 *v*/v). The concentrations of Cu2+ are 0, 2, 4, 6, 8, 10, 12, 14 μM, respectively



SCHEME 1 Synthesis of the probe L

recorded and shown in Figure 1 (The RSD data were shown in table S1). According to the following consequences, the fluorescence intensity of **L** declined accompanied by the increasing concentration of Cu^{2+}. The fluorescence intensity remained approximately constant while the concentration of Cu^{2+} increased to 1 equation (10 μM). Thus, 10 μM Cu^{2+} was used as the quenching agent in subsequent experiments.

3.2 | Effect of solvents

Different organic solvents will affect the reactivity of **L**-Cu^{2+} and ClO^- and the solubility of Q1, which will affect the detection effect. In order to survey the fluorescence intensity changes of **L**-Cu^{2+} complex in different organic solvents, four commonly used organic solvents were studied (methyl alcohol, ethyl alcohol, methyl cyanide and DMSO) in the presence or absence of ClO^-. The fluorescence intensity changes were recorded in Figure 2. With or without ClO^-, the difference of fluorescence intensity in methanol–water mixed system was more significant than that in other organic solvent-water systems. This means that the reactivity of **L**-Cu^{2+} with ClO^- and the solubility of Q_1 are both excellent in methanol solvent. Therefore methanol was chosen as the system solvent for subsequent experiments.

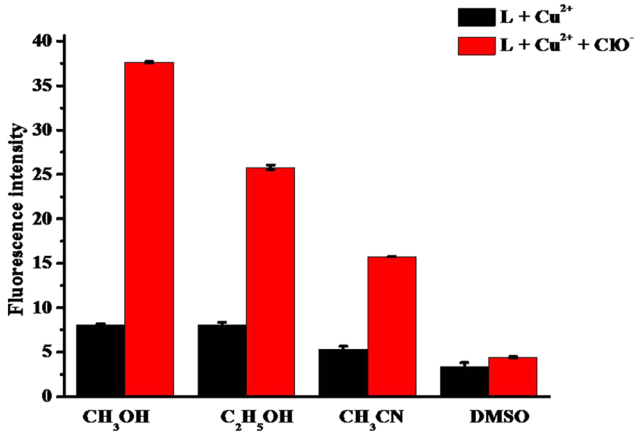


FIGURE 2 The fluorescence intensities of L-Cu2+ (black bars) and L-Cu2++ClO- (50 μM) (red bars) at 460 nm in different solvent/water solutions (7:3, v/v)

3.3 | Effect of water content

The water content of the system will affect the fluorescence intensity. In this experiment, the optimal water content was determined by the double influence factors, one is the reactivity between the L-Cu^{2+} and ClO^- in different water content solvents and the other is the solubility

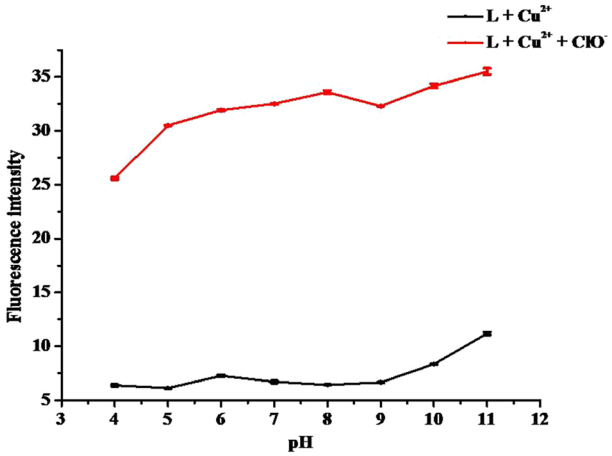


FIGURE 4 The fluorescence of L (10 μM) at 460 nm influenced by various solution pH, in a mixture solution of B.R. buffer solution and methanol (CH3OH/H2O, 7:3 v/v) with (red line) or without (black line) ClO- (50 μM)

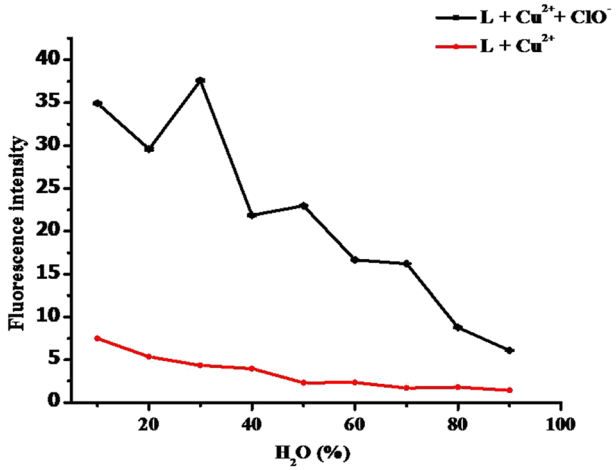


FIGURE 3 The effect of various contents of water on the fluorescence intensity of L-Cu2+ at 460 nm before (red line) and after (black line) the addition of ClO- (50 μM)

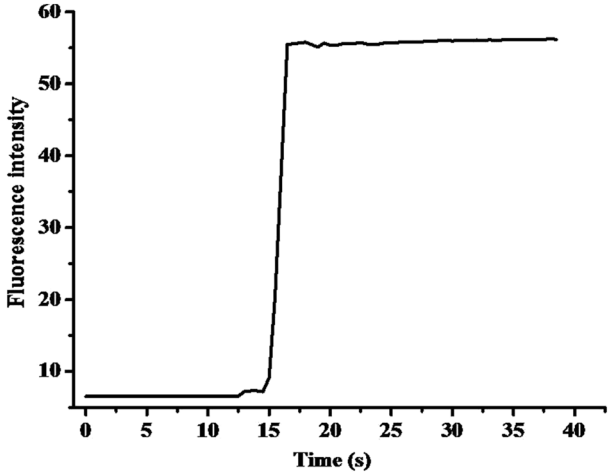


FIGURE 5 The fluorescence of L (10 μM) at 460 nm with reaction time went on, in a mixture solution of water and methanol (CH3OH/H2O, 7:3 v/v) with ClO- (50 μM)

of the Q_1 in solvents. So the fluorescence intensity changes of **L**-Cu^{2+} were investigated in a series of water contents with/without ClO^-. The fluorescence intensity before and after the addition of ClO^- with the water contents ranged from 0 to 100% was presented in Figure 3 (The RSD data were shown in table S2). There was the highest fluorescence enhancement when the water content was 30% (ethanol: water = 7:3). This indicates that the reaction between L-Cu^{2+} and ClO^- is easier when the water content is 30%, and the solubility of the Q1 is not affected in significant. Thus, the 30% water was chosen for subsequent experiments.

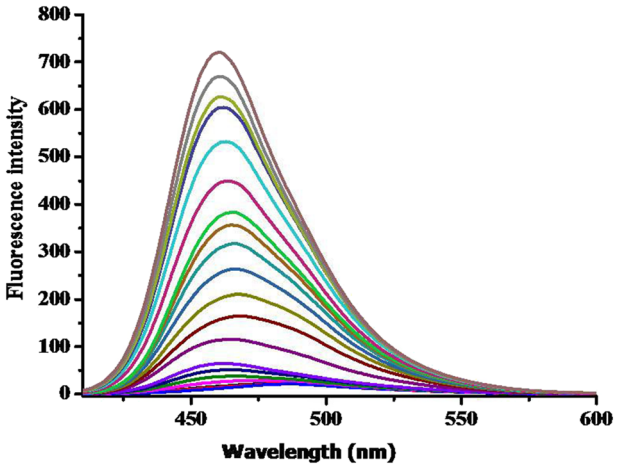


FIGURE 6 Fluorescence spectra of L-Cu2+ titrated with a series of concentrations of ClO- (1.00 × 10−6 − 7.00 × 10−3 Mol L-1) in CH3OH-water solution (7:3, v/v)

3.4 | Effect of pH

It was necessary to explore fluorescence intensity of **L**-Cu^{2+} in different pH solutions. We recorded the fluorescence intensity of **L**-Cu^{2+} in the existence or inexistence of ClO^- within the range of pH 4.0 to11.0 (B.R. buffer of 0.04 mol L^{-1}). As depicted in Figure 4, in the presence of ClO^-, there was no significant change of fluorescence recovery of **L**-Cu^{2+} with different pH (The RSD data were shown in table S3). Therefore, buffer solution is unnecessary in this system. It is more convenient to select pure water for experiments.

3.5 | Optimum reaction time

Rapid response is an important advantage of analytical method, so we investigated the detection time of **L**-Cu^{2+} for ClO^-. As can be seen from Figure 5, ClO^- was added to **L**-Cu^{2+} at 15 s and the reaction ended about after 2 s. It means that we can test the sample immediately, which is very fast and saves time.

3.6 | Analysis of ClO^- by L-Cu^{2+}

The relationship between fluorescence intensities and ClO^- concentrations was studied under optimal conditions in this part. As depicted in Figure 6, with the increase of ClO^- concentration, the fluorescence intensity gradually recovered companied by a blue shift to 460 nm. There is a linear fitting curve of fluorescence intensities and the concentrations of ClO^- (1.00×10^{-6} mol L^{-1} – 7.47×10^{-3} mol L^{-1}) which is shown in Figure 7. Since the error bars are too small to show, we provided RSD data in table S4. The linear fitting curve is as

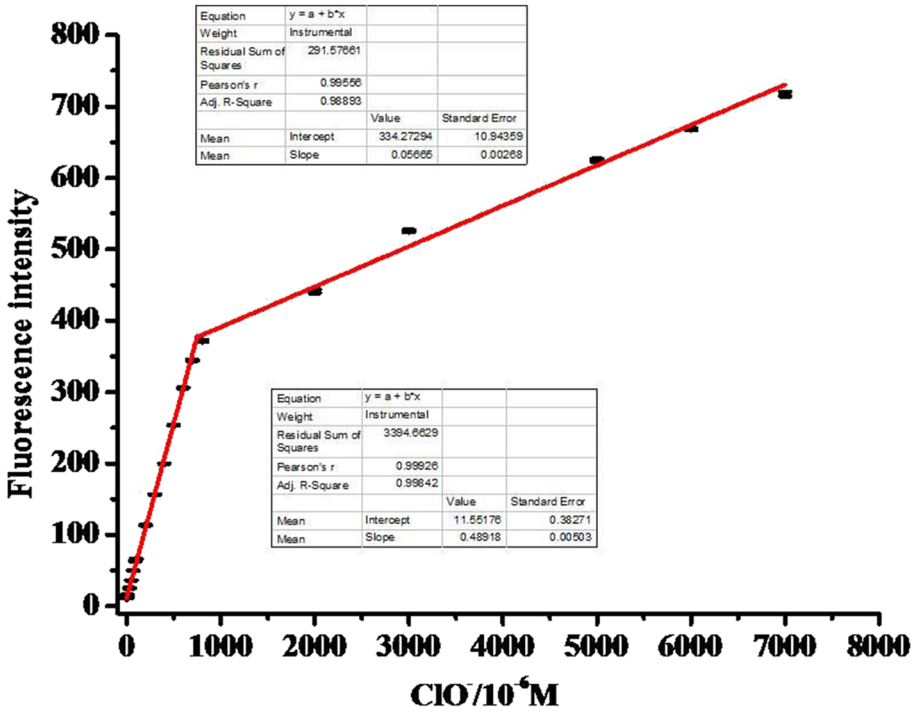


FIGURE 7 The linear fitting curve of fluorescence intensities of L-Cu2+ and a series of concentrations of ClO-

follows: F = 11.55 + 0.49 [ClO⁻] (1.00×10^{-6} mol L^{-1} – 7.47×10^{-4} mol L^{-1}) contained the coefficient of association (R) of 0.9992 (R^2 = 0.9984) and F = 334.27 + 0.057 [ClO⁻] (7.47×10^{-4} mol L^{-1} – 8.00×10^{-3} mol L^{-1}) with the coefficient of association (R) of 0.9956 (R^2 = 0.9889). According to the equation LOD = (3σ/s), LOD for ClO⁻ is calculated to be 5.7×10^{-7} mol L^{-1}. There are two different linear relationships here, probably because that in the lower concentration range of ClO⁻, the concentration of probe is much higher for ClO⁻ to achieve equilibrium easily, while in the higher concentration range of ClO⁻, the concentration of probe is insufficient to some extent, so we need much more ClO⁻ to achieve equilibrium. In other words, the probe has better sensitivity for ClO⁻ in lower concentrations than higher ones.

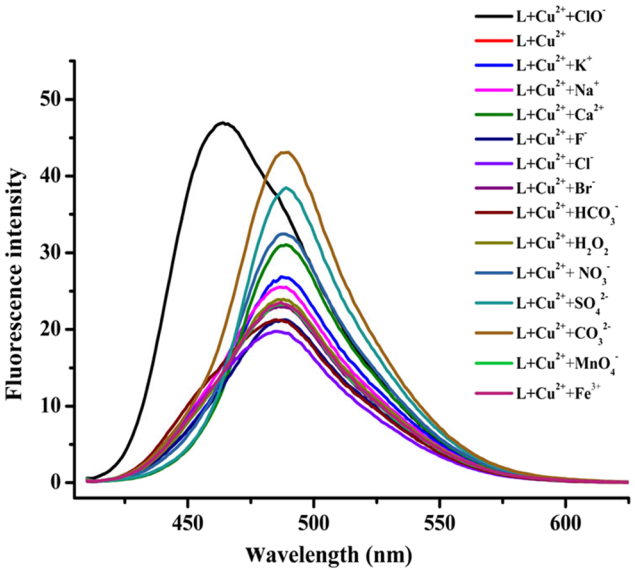


FIGURE 8 The fluorescence recovery of L-Cu2+ after adding 50 μM ClO- or 100 μM other species (K+, Na+, ca+, F-, cl-, Br-, HCO3-, CO32-, NO3-, SO42-, Fe3+, MnO4- and H2O2) in CH3OH-water solution (7:3,v/v)

3.7 | Selectivity and competition

This probe has a specific response to ClO⁻. We used 50 μM ClO⁻ or 100 μM other species (K^+, Na^+, Ca^+, F^-, Cl^-, Br^-, HCO_3^-, CO_3^{2-}, NO_3^-, SO_4^{2-}, Fe^{3+}, MnO_4^- and H_2O_2) for fluorescence recovery of **L**-Cu^{2+}, as shown in Figure 8, only ClO⁻ restored fluorescence at 460 nm and other ions restored fluorescence at 490 nm because of coordination between ions. Meanwhile, the competition experiment shows that the sensor has satisfactory anti-interference performance, which is shown in Figure 9.

3.8 | Compare with other hypochlorite fluorescence probes

We compared this work with several hypochlorite fluorescence probes which published in recent years and the consequences were listed in Table 1. There is indistinctive difference between this work and other hypochlorite probes in detection limit, but it has obvious advantages in linear range and detection time for this work. Therefore, this work has certain potential application value.

3.9 | Actual sample detection and mechanism

In the interest of studying the feasibility of this procedure when applied to practical samples, the probe is used in running water and lake water. In running water the concentration of hypochlorite ions measured is 3.8×10^{-6} mol L^{-1} with RSD of 1.49%. It's reliable according to National standard for water quality of the People's

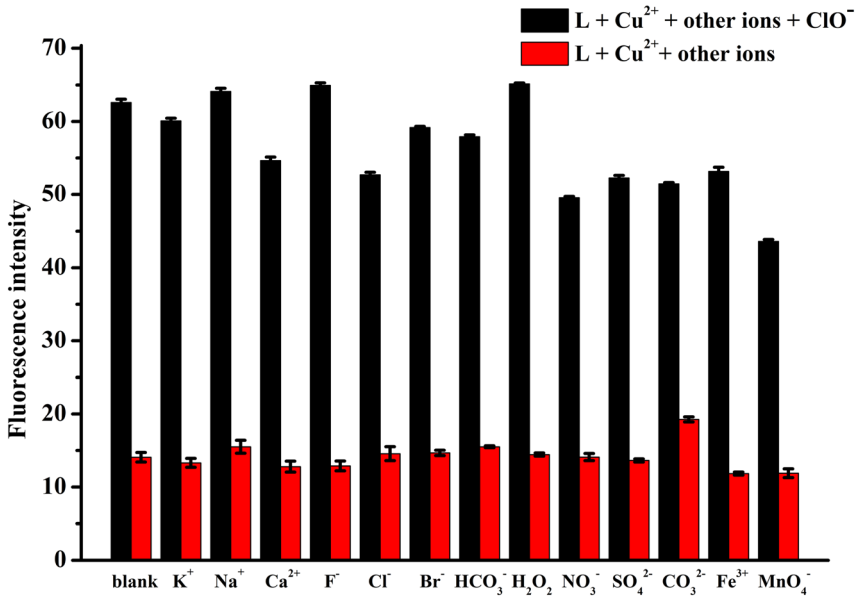


FIGURE 9 In the presence of other species (100 μM), the fluorescence intensity (λem = 460 nm) of L-Cu2+ with ClO- (100 μM, black line) or without ClO- (red line) in CH3OH-water solution (7:3, v/v)

TABLE 1 Comparison of this work with other hypochlorite fluorescence probes

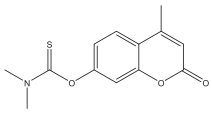
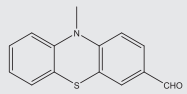
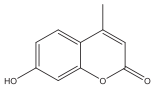
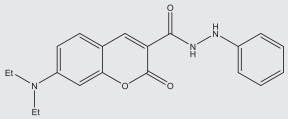
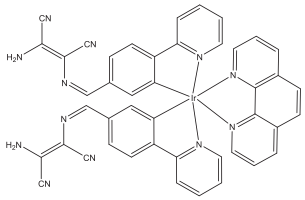
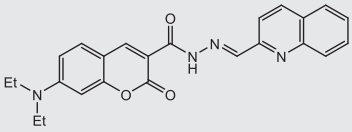
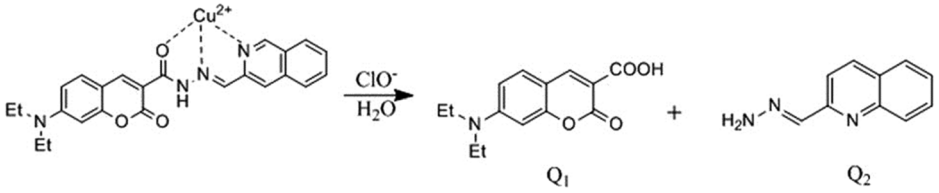
Probe	Response time	Detection limit	Linear range	Reference
	60 s	0.035 μM	5.0–50.0 μM	[20]
	10 s	0.45 μM	0–100 μM	[21]
	60 s	0.067 μM	0–150 μM	[22]
	300 s	0.37 μM	0–60 μM	[1]
	20 s	0.11 μM	60–180 μM	[6]
	2 s	0.57 μM	1–747 μM	This work

TABLE 2 Results of lake water sample determination

Sample	ClO^- added/Mol L^{-1}	ClO^- found/Mol L^{-1}	Recovery/%	RSD/%
Lake water	5.00×10^{-5}	5.67×10^{-5}	113	0.91
	6.00×10^{-5}	6.56×10^{-5}	109	0.37
	7.00×10^{-5}	7.22×10^{-5}	103	0.20

Republic of China. Since hypochlorite ions could not be detected in the lake water, we carried out labeling recovery experiment on the lake water samples and the consequences were listed in Table 2. It is observed that the detection consequences acquired by the sensor are in well agreement with the amount of hypochlorite ions added, and the recovery rates are between 103% and 113%, with RSD of 0.20% - 0.91%. Thus, the sensor is applicable for detecting hypochlorite in actual samples.

SCHEME 2 Detection mechanism



The credible mechanism obtained by ESI-MS of the interaction between probe L-Cu^{2+} and hypochlorite is shown in Scheme 2.[1,23] As shown in figure S4, the peak of Q_1 + Na^+ in mass spectra were at 284.0888 and the peak of Q_2 + H^+ in mass spectra were at 172.0880. After the addition of hypochlorite, the C-N bond was cut and the coumarin was released, which restored the fluorescence intensity.

4 | CONCLUSIONS

All in all, a highly sensitive probe was synthesized to detect hypochlorite specifically and quickly. When the probe reacted with hypochlorite, it showed a large stokes shift, produced a strong fluorescence recovery at 460 nm and the response time is as short as two seconds. There was a linear fitting curve of the intensities of fluorescence recovery and the concentrations of hypochlorite ranging from 1.00×10^{-6} to 7.47×10^{-4} mol L^{-1} with a LOD of 5.7×10^{-7} mol L^{-1}. Moreover, we successfully applied this method to environmental water samples and achieved satisfactory results. Therefore, the probe is a splendid hypochlorite sensor, which is characterized by rapid, selective and sensitive features and can meet practical needs.

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REFERENCES

[1] L. Long, Y. Wu, W. Lin, A. Gong, F. Hu, C. Zhang, *Chem. Commun.* **2015**, *51*, 10435.
[2] C. H. Chang, E. L. Pearce, *Nat. Immunol.* **2016**, *17*, 364.
[3] Y. Zhao, X. B. Zhang, Z. X. Han, L. Qiao, C. Y. Li, L. X. Jian, *Anal. Chem.* **2009**, *81*, 7022.
[4] Z. M. Prokopowicz, F. Arce, R. Biedron, C. L. L. Chiang, M. Ciszek, D. R. Katz, M. Nowakowska, S. Zapotoczny, J. Marcinkiewicz, B. M. Chain, *J. Immunol.* **2010**, *184*, 824.
[5] A. Manna, S. Goswami, *New J. Chem.* **2015**, *39*, 4424.
[6] L. Hou, M. Shangguan, Z. Lu, S. Yi, X. Jiang, H. Jiang, *Anal. Biochem.* **2019**, *566*, 27.
[7] R. Wang, R. Wang, J. Dongyan, W. Lu, C. Jiang, X. Shan, Q. Chen, G. Sun, *Analyst* **2018**, *143*, 5834.
[8] L. C. Adam, I. Fabian, K. Suzuki, G. Gordon, *Inorg. Chem.* **1992**, *31*, 3534.
[9] G. Li, Q. Lin, L. Sun, C. Feng, P. Zhang, B. Yu, Y. Chen, Y. Wen, H. Wang, L. Ji, H. Chao, *Biomaterials* **2015**, *53*, 285.
[10] M. Jović, F. Cortés-Salazar, A. Lesch, V. Amstutz, H. Bi, H. H. Girault, *J. Electroanal. Chem.* **2015**, *756*, 171.
[11] J. Zhang, X. Wang, X. Yang, *Analyst* **2012**, *137*, 2806.
[12] J. M. Boyd, S. E. Hrudey, X.-F. Li, S. D. Richardson, *TrAC Trends Anal. Chem.* **2011**, *30*, 1410.
[13] Y. Koide, Y. Urano, K. Hanaoka, T. Terai, T. Nagano, *J. Am. Chem. Soc.* **2011**, *133*, 5680.
[14] L.-L. Wang, J. Qiao, H.-H. Liu, J. Hao, L. Qi, X.-P. Zhou, D. Li, Z.-X. Nie, L.-Q. Mao, *Anal. Chem.* **2014**, *86*, 9758.
[15] G. Chai, Q. Liu, Q. Fei, J. Zhang, X. Sun, H. Shan, G. Feng, Y. Huan, *J. Biol. Chem. Luminesc.* **2018**, *33*, 153.
[16] J. Zhang, Y. Liu, Q. Fei, H. Shan, F. Chen, Q. Liu, G. Chai, G. Feng, Y. Huan, *Sens. Actuators B* **2017**, *239*, 203.
[17] M. Guan, H. Mi, H. Xu, Q. Fei, H. Shan, Y. Huan, S. Lv, G. Feng, *J. Fluoresc.* **2017**, *27*, 611.
[18] Y. Ma, W. Luo, P. J. Quinn, Z. Liu, R. C. Hider, *J. Med. Chem.* **2004**, *47*, 6349.
[19] H. Takechi, Y. Oda, N. Nishizono, K. Oda, M. Machida, *Chem. Pharm. Bull.* **2000**, *48*, 1702.
[20] Y. Z. XiaoWang, C. Xu, H. Song, L. Li, J. Zhang, M. Guo, *Spectrochim. Acta, Part A* **2018**, *203*, 415.
[21] Y. Z. HaohanSong, C. Xu, X. Wang, J. Zhang, Y. Wang, X. Liu, M. Guo, X. Peng, *Dyes Pigm.* **2019**, *162*, 160.
[22] L. Pang, Y. Zhou, W. Gao, H. Song, X. Wang, Y. Wang, *RSC Adv.* **2016**, *6*, 105795.
[23] D. X. Li, Y. Feng, J. Z. Lin, M. Chen, S. X. Wang, X. Wang, H. T. Sheng, Z. L. Shao, M. Z. Zhu, X. M. Meng, *Sens. Actuators B* **2016**, *222*, 483.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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