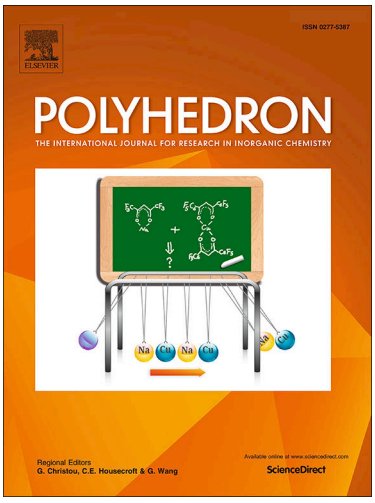

A simple but sensitive and efficient fluorescent probe for "turn-on" sensing of ClO^-

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PII: S0277-5387(20)30220-5
DOI: https://doi.org/10.1016/j.poly.2020.114563
Reference: POLY 114563

To appear in: *Polyhedron*

Received Date: 22 January 2020
Revised Date: 10 April 2020
Accepted Date: 11 April 2020

Please cite this article as: X. Yang, W. Shi, X. Dong, C. Cui, X. Huang, X. Wang, H. Xie, Y. Li, M. Yan, Y. Cui, G. Sun, A simple but sensitive and efficient fluorescent probe for "turn-on" sensing of ClO^-, *Polyhedron* (2020), doi: https://doi.org/10.1016/j.poly.2020.114563

A simple but sensitive and efficient fluorescent probe for "turn-on" sensing of ClO^-

Xiaofeng Yang[a,*], Wendi Shi[a], Xiaoling Dong[a], Chuanyang Cui[a], Xin Huang[a], Xue Wang[a], Hangxin Xie[a], Yexin Li[a], Mei Yan[a], Yu Cui[a], and Guoxin Sun[a]

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Abstract

A simple but sensitive and efficient fluorescent probe **YXF** for "turn-on" detecting ClO^- had been developed. For compound **YXF**, the benzothilazole unit was the efficient fluorophore, and the C=N unit was the recognition site for ClO^-. It could detect ClO^- with a high selectivity and sensitivity over other 29 kinds of common analytes including some reactive oxygen molecules. After addition of 30 equiv. NaClO to the solution of **YXF**, the fluorescent intensity at 452 nm enhanced with an approximately 37-fold within seconds. The fluorescence intensity of the reaction between **YXF** and NaClO showed a good linearity in the NaClO concentration range of 1-180 μM and **YXF** had a low detection limit of 1.8×10^{-8} M. In addition, NaClO-promoted oxidation cleavage of C=N unit of probe **YXF** was verified by HR-MS and NMR spectrometry analysis. Moreover, probe **YXF** could be successfully applied for detection of ClO^- concentration in several tap water and 84 disinfectant samples.

Keywords: ClO^-; "turn-on"; fluorescent probe; benzothilazole

1. Introduction

Hypochlorous acid (HClO) is a weak acid with strong oxidation, and it can be partially ionized as hypochlorite (ClO^-) and H^+ in aqueous solution. Its sodium/calcium salts are widely used as bleach, fungicide and disinfectant [1]. In life, tap water is commonly used chlorine gas (adding about 0. 0029 g chlorine gas into 1 L water can generate hypochlorous acid) to sterilize. Hypochlorous acid is one of the highly reactive oxygen species (ROS), which is produced in the normal oxygen metabolism of organisms and plays an important role in various physiological and pathological processes [2-6]. In the biological environment, the normal concentration of hypochlorous acid is beneficial to human body and is necessary to maintain the normal function of living cells [7]. However, excessive or uncontrolled hypochlorous acid can cause tissue damage and lead to cardiovascular disease, lung damage, atherosclerosis, osteoarthritis and cancer [8-10]. Therefore, microdetection of HClO/ClO^- is very important and significant.

Due to its high sensitivity, low detection limit, simplicity, and especially suitable for real-time and online analysis, fluorescent probes are favored by scientists and have been developed in large quantities from only the literatures review in the past five years [11-24]. It is well known that HClO is a strong oxidizing reagent and it can selectively oxidize some special functional groups, such as oxime, C=C double bond, spiro ring of rodamine (or fluorescein), phenylselenium (or phenyltellurium), phenothiazine, and so on. Inspired by the special oxidation properties of HClO, several fluorescent probes for HClO/ClO^- have reported [25-29]. It is very important and significant to realize the real-time, in-situ, rapid, efficient and specific detection of HClO/ClO^-. Although some reported probes could meet the above requirements, it is necessary to develop new HClO/ClO^- probes to enrich this field.

Benzothiazole molecules are fused by thiazole and benzene ring. As small molecular compounds, benzothilazole-based fluorescent probes have been successfully used in the detection of many substances due to their good optical properties [30-48]. However, to the best of our knowledge, only one HClO/ClO^- fluorescent probe based on benzothiazole fluorophore had been reported [48]. It was known that C=N double bond which was connected to an organic fluorophore could be oxidized by HOCl, resulting in the fluorescence change [48-50]. Base on this design strategy, we designed a simple, facile synthesize benzothilazole-derived fluorescent probe (**YXF**) for turn-on sensing of ClO^-. Experimental results showed that compound **YXF** could

quantitatively response to ClO^- with a good selectivity and sensitivity over other 29 kinds of common analytes. In addition, it showed a rapid response within seconds and a low detection limit (1.8×10^{-8} M). NaClO-promoted oxidation cleavage of C=N unit of probe **YXF** was verified by HR-MS and NMR spectrometry analysis. Moreover, probe **YXF** could be successfully applied for detection of ClO^- concentration in several tap water and 84 disinfectant samples.

2. Experimental section

2.1. Materials and instruments

2-Aminothiophenol (98%), glycolic acid (97%), Dess-Martin Periodinane (97%), diaminomaleonitrile (99%) and other chemicals for synthesis were purchased from Energy Chemical supplier. Solvents were treated with standard methods prior to use. The water used in the whole experiment was secondary distilled water. The NaOCl solution used in the experiment was 11% by mass. Reaction was monitored by thin-layer chromatography (TLC). ^{1}H NMR and ^{13}C NMR spectra were measured in acetone-d_6 with tetramethylsilane (TMS) as the internal standard on a Bruker Avance III 400 MHz spectrometer. UV-vis absorption spectra were recorded on a Shimadzu 3100 spectrometer. Fluorescence emission spectra were recorded on an Edinburgh Instruments Ltd-FLS920 fluorescence spectrophotometer.

*2.2. Synthesis of compound **YXF***

Compounds **1** and **2** were synthesized according to the reported method [51]. As illustrated in **Scheme 1**, compound **2** (163 mg, 1.0 mmol) and diaminomaleonitrile (108 mg, 1.0 mmol) were completely dissolved in 10 ml of EtOH, respectively. Then, the solution of compound **2** was added dropwise into the diaminomaleonitrile solution. After the reaction mixture was stirred with refluxing for 4 h, a yellow-green solid was precipitated, collected, and washed with EtOH to afford compound **YXF** (164 mg, yield 65%). ^{1}H NMR (400 MHz, acetone-d_6), δ H 8.54 (s, 1H), 8.12 (t, J = 6.4 Hz, 2H), 7.74 (br, 2H), 7.64-7.54 (m, 2H) ppm (**Fig. S1**); ^{13}C NMR (100 MHz, Acetone-d_6), δ C 165.77, 154.19, 149.17, 135.71, 128.91, 127.14, 126.85, 124.23, 122.21, 113.21, 112.17, 103.67 ppm (**Fig. S2**); HR-MS: m/zcalcd for $C12H8N5S^+$ $[M+H]^+$: 254.0495, found: 254.0491 (**Fig. S3**).

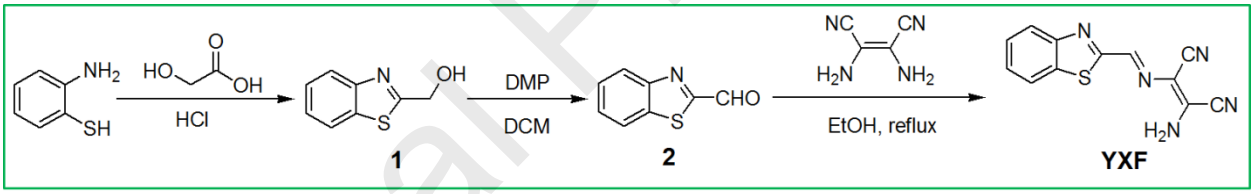
2.3. Spectroscopic experiments

Probe **YXF** 0.1265g was accurately weighed and transferred into a 5 mL volumetric flask. The probe mother liquor with a concentration of 1×10^{-1} M was prepared with DMSO constant volume. Then accurately measure the 50 μL probe mother liquor with a pipette into a 500 mL volumetric flask, and fix the volume with DMSO-PBS buffer (v/v, 1:1, pH 7.4) to prepare a probe solution with a concentration of 1×10^{-5} M. The final composition of the test solution was 10 μM in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution. The test solution was shaken and reacted at room temperature for 10 min, followed, the UV-vis and fluorescence spectra were determined. Fluorescence emission spectra were excited with a wavelength of 360 nm. The slit width of the excitation and emission were 10 nm and 20 nm, respectively.

The response conditions of **YXF** in the absence and presence of NaClO (100 equiv.) in DMSO/0.01 M PBS buffer (pH 7.4) solution with different water content was tested (**Fig. S6**). Results showed that the optimal test condition was in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution, which was used in all following experiments.

3. Results and discussion

*3.1. Synthesis and optical property of compound **YXF***



Scheme 1. Synthesis of compound **YXF**.

As shown in **Scheme 1**, the target compound **YXF** was synthesized by a simple condensation reaction of benzothiazole aldehyde **2** [51] and diaminomaleonitrile, and characterized by ^{1}H NMR and ^{13}C NMR spectra (**Figs. S1-S2**). The $[M+H]^+$ peak at m/z 254.0491 (calcd: 254.0495) in the HR-MS spectrum further verified the formation of the expected adduct (**Fig. S3**). Next, the optical property of compound **YXF** was studied. As shown in **Fig. S4A**, the maximum absorption band of **YXF** was at about 397 nm, and a very weak fluorescence emission peak at about 445 nm was observed under excitation of 360 nm (**Fig. S4B**).

*3.2. Sensing behavior of compound **YXF***

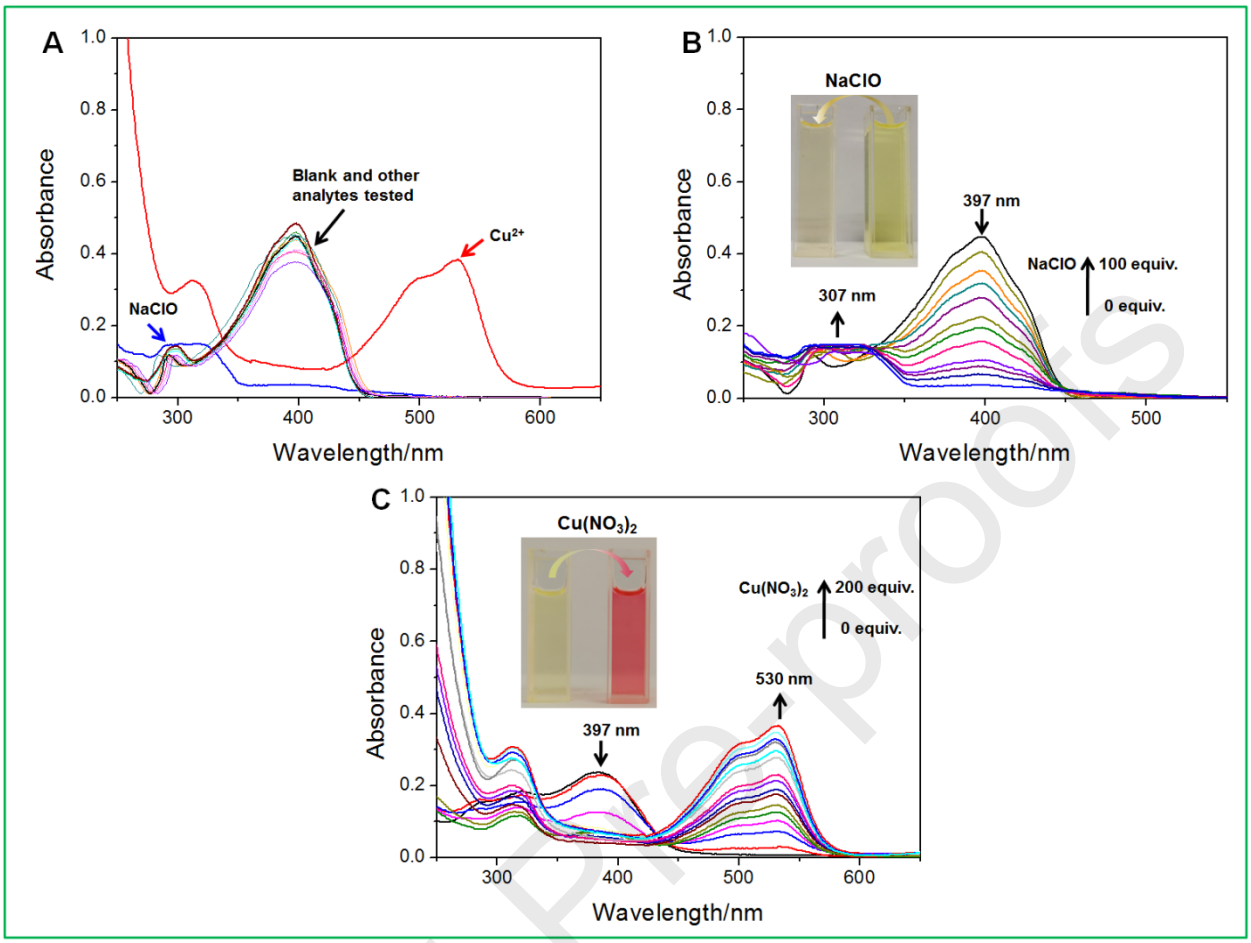


Fig. 1. (**A**) UV-vis absorption spectra of **YXF** (10 μM) to various analytes (100 equiv.) in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution at room temperature. (**B**) Changes in the UV-vis absorption spectra of **YXF** (10 μM) upon addition of 0-100 equiv. of NaClO in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution at room temperature. Inset: photograph showed color change upon addition of NaClO (100 equiv.). (**C**) Changes in the UV-vis absorption spectra of **YXF** (10 μM) upon addition of 0-200 equiv. of $Cu(NO_3)_2$ in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution at room temperature. Inset: photograph showed color change upon addition of $Cu(NO_3)_2$ (200 equiv.).

Firstly, the recognition and sensing properties of compound **YXF** were investigated in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution using UV-vis absorption spectra. As shown in **Fig. 1A**, when different kinds of analytes (100 equiv.), such as $MgSO_4$, $Cu(NO_3)_2$, $FeCl_3$, $CoCl_2$, $CaCl_2$, $ZnCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, NaF, Na_2SO_4, $NaHCO_3$, $NaNO_2$, $NaNO_3$, Na_2SO_3, NaCl, Na_3PO_4, NaI, NaClO, Na_2S, ATP, H_2O_2, $ONOO^-$, $^1O_2$, O_2^-, HO•, GSH, Hcy and Cys, was added, NaClO not only induced an obvious blue shift but also reduced the absorbance

of compound **YXF**, whereas $Cu(NO_3)_2$ altered the absorption spectrum of compound **YXF** with a large red shift, indicating that compound **YXF** could response to these two ions by different recognition mechanisms. A slight change in absorbance of compound **YXF** was induced by addition of the rest of the other tested analytes. **Fig. 1B** showed that when 0-100 equiv. NaClO was gradually added to **YXF** (10 μM) in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution, the maximum absorption band at about 397 nm gradually decreased and, concomitantly, a new band at about 307 nm gradually increased. This response process was completed within addition of 100 equiv. of NaClO as no further changes were observed with the addition up to 200 equiv. of NaClO. An isosbestic point at 330 nm indicated that only one stable compound was formed from the reaction of **YXF** with NaClO. Meanwhile, the color of the solution changed from dark yellow to pale yellow. **Fig. 1C** showed that upon stepwise addition of Cu^{2+} ions (0-200 equiv.), the maximum absorption band at about 397 nm of compound **YXF** gradually decreased and, concomitantly, a new red-shifted band at about 530 nm gradually increased. Meanwhile, the color of the solution changed from dark yellow to red. These results demonstrated that compound **YXF** was characteristic of a high selectivity toward NaClO and Cu^{2+} ions over other competitive analytes and could serve as a "naked-eye" probe.

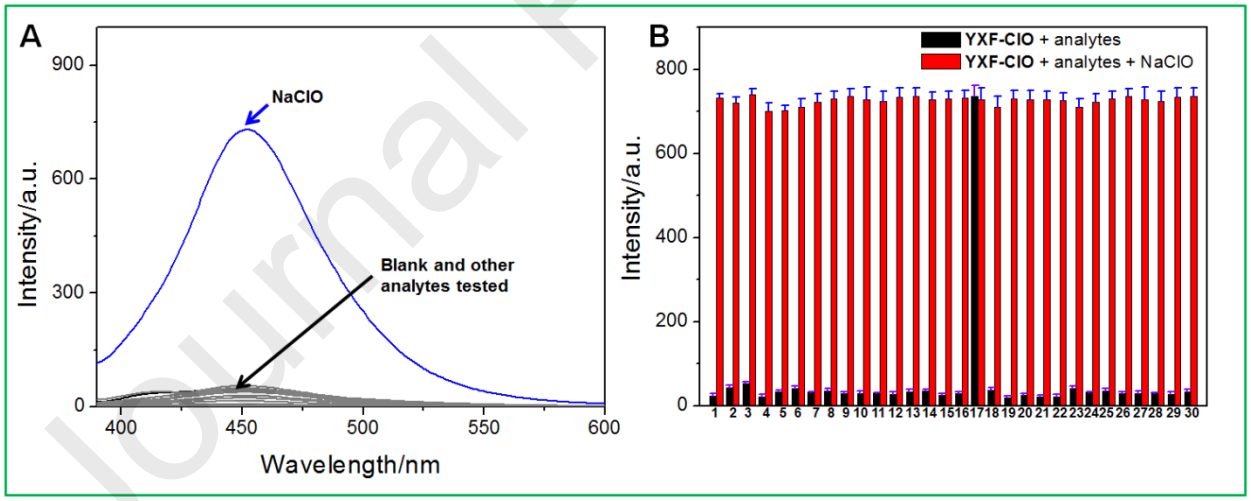


Fig. 2. (**A**) Fluorescence spectra of **YXF** (10 μM) to various analytes (30 equiv.) in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution at room temperature, λ_{em}: 360 nm. (**B**) The fluorescence intensity of **YXF** (10 μM) at 452 nm in response to NaClO (30 equiv.) in the presence of various interfering analytes (50 equiv.) in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution at room temperature, λ_{em}: 360 nm. Interfering analytes, from 1-30: blank,

$MgSO_4$, $Cu(NO_3)_2$, $FeCl_3$, $CoCl_2$, $CaCl_2$, $ZnCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, NaF, Na_2SO_4, $NaHCO_3$, $NaNO_2$, $NaNO_3$, Na_2SO_3, NaCl, Na_3PO_4, NaI, NaClO, Na_2S, ATP, H_2O_2, $ONOO^-$, $^1O_2$, O_2^-, HO•, GSH, Hcy and Cys.

Next, the fluorescence spectra of compound **YXF** (10 μM) in response to different kinds of analytes (30 equiv.) were also observed in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution. When excited at 360 nm, the fluorescence intensity of compound **YXF** was almost unchanged by addition of other analytes including Cu^{2+} ions, while it was significantly enhanced only after adding NaClO with the fluorescence quantum yield increasing from 0.01 to 0.38 (**Fig. 2A**). This indicated that compound **YXF** had a well-defined fluorescence selectivity for NaClO over Cu^{2+} and other analytes. As shown in **Fig. 2B**, the fluorescence response of **YXF** to NaClO was almost no effect on all these typical analytes. Thus, NaClO could be effectively detected by **YXF** in the presence of other analytes including Cu^{2+} ions.

*3.3. Fluorimetric recognition of **YXF** for NaClO*

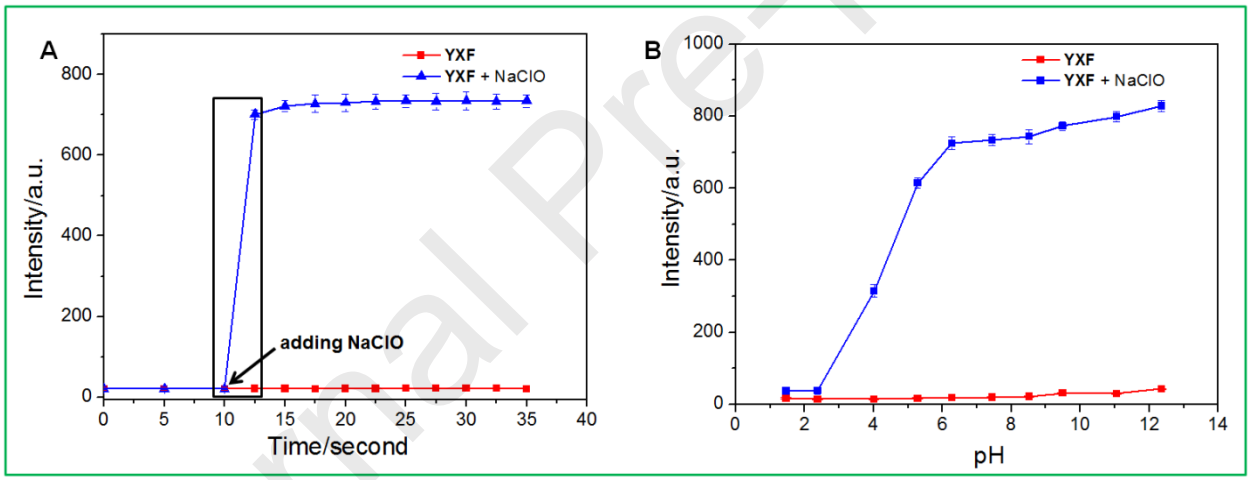


Fig. 3. (**A**) The time course of fluorescence intensity of free probe **YXF** (10 μM) in the absence and presence of 30 equiv. NaClO at 452 nm in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution, λ_{em}: 360 nm. (**B**) Fluorescence response at 452 nm of free probe **YXF** (10 μM) in the absence and presence of 30 equiv. NaClO in DMSO-H_2O (v/v, 1:1) as a function of different pH values, λ_{em}: 360 nm.

Reaction time is an important factor to evaluate the feasibility of probe detection. First, we examined the response time of compound **YXF** in the presence of NaClO. As shown in **Fig. 3A**, the fluorescence intensity of compound **YXF** did not change with time. Once 30 equiv. NaClO was added, the fluorescence intensity of **YXF** at 452 nm significantly increased immediately, indicating the fluorescence response was very fast. The

response signal would reach the maximum value within seconds, which was very important for real-time detection. This was consistent with the fact that the imine group could be cut off by HClO/ClO^- under a relatively mild condition [48-50].

Next, we detected the pH-dependent fluorescence changes of free probe **YXF** and after addition of NaClO (**Fig. 3B**). The fluorescent intensity of probe **YXF** was very low at a pH range from 1.4 to 9.6, whereas after the addition of 30 equiv. NaClO, the fluorescent intensity at 452 nm enhanced significantly when the pH was greater than 4.0, and the fluorescence signal was stronger under alkaline conditions, implying that NaClO played a key role in the response system. These results indicated that **YXF** could be applied to selectively detect NaClO in the physical environment.

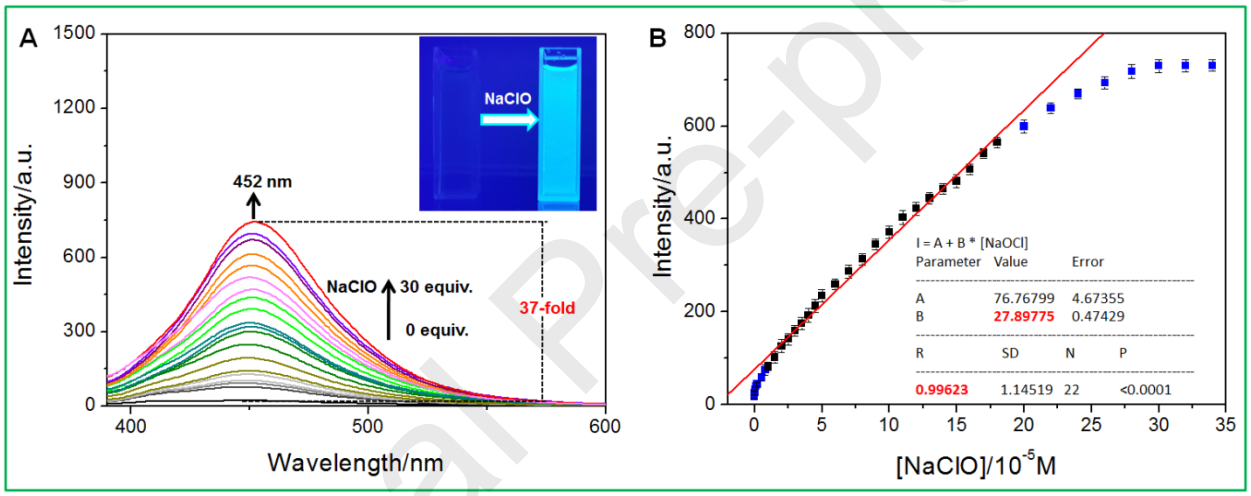
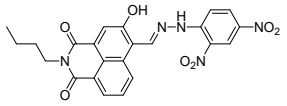
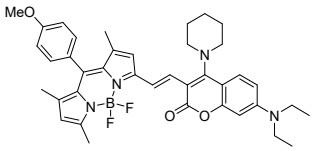
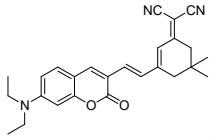
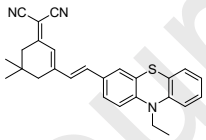
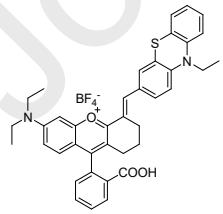


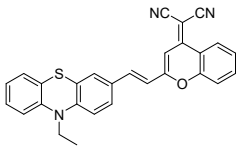
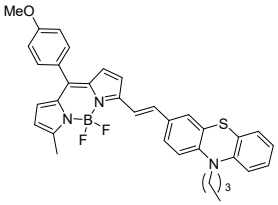
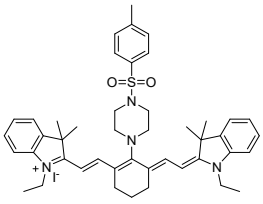
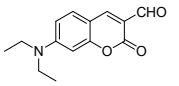
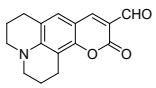
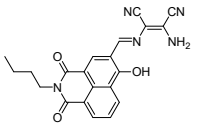
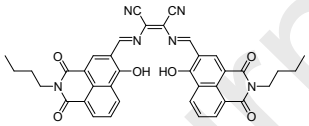
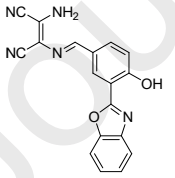
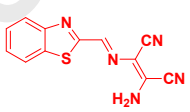
Fig. 4. (**A**) Fluorescence spectra of **YXF** (10 μM) upon addition of 0-30 equiv. of NaClO in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution. Inset: photograph showed color change in fluorescence upon addition of NaClO (30 equiv.). (**B**) Fluorescence intensity *vs.* increasing concentration of NaClO, λ_{em}: 360 nm.

Followed, fluorescence titration of **YXF** with increasing NaClO was performed at pH 7.4. As depicted in **Fig. 4A**, in the absence of NaClO, compound **YXF** exhibited a very weak fluorescence emission in DMSO-PBS buffer (v/v, 1:1, pH 7.4) solution. Once upon addition of NaClO at ambient temperature, a band centered at 452 nm was formed and its fluorescence intensity remarkably increased. When 30 equiv. NaClO was added, the fluorescence intensity of the solution reached saturation representing an approximate 37-fold fluorescent intensity signal response, and a bright cyan fluorescence could be observed. After the linear fitting between the

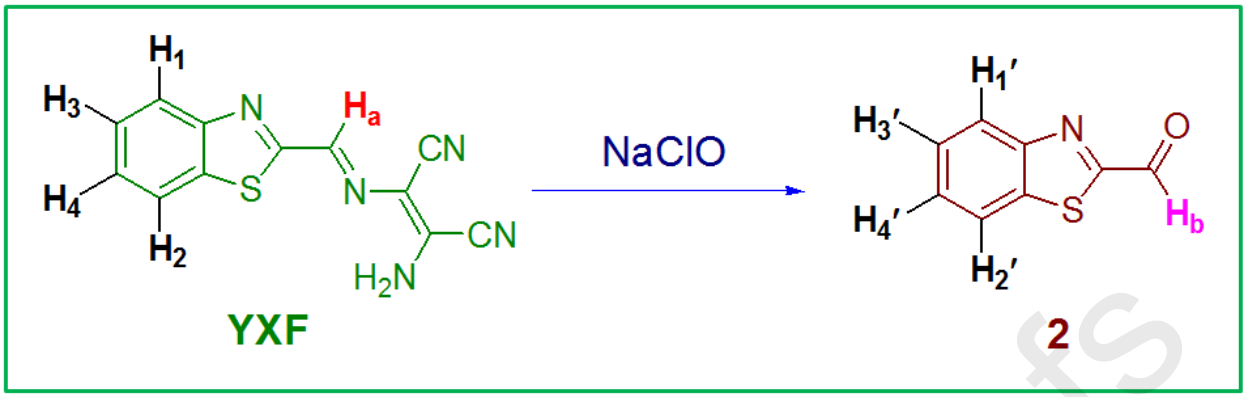
fluorescence intensity of probe **YXF** at 452 nm and the concentration of NaClO, a good linear correlation over a concentration range of 1-180 μM was obtained (**Fig. 4B**). The linear fitting equation was: I = 76.76799 + 27.89775 [NaClO], R = 0.99623, indicating the suitability of probe **YXF** for quantitative detection of NaClO. The low limit of detection (LOD) under this condition was evaluated to be 1.8 × 10^{-8} M (LOD = 3σ/k, σ represented the standard deviation of the fluorescence intensity of probe **YXF** at 452 nm, k represented the slope of linear fitting equation). With regard to a simple structure, a facile synthesis, as well as a high sensitivity and a low LOD response toward ClO^-, **YXF** achieved a potential membership of ClO^- fluorescent probe club, which was comparable with some recently reported fluorescence probes for HClO/ClO^- (**Table 1**).

Table 1. Comparison of some reported fluorescent probes for HClO/ClO^- since the year 2018.

Probe	Reponse time	LOD (M)	references
	2 seconds	5 × 10^{-8}	Org. Biomol. Chem. 16 (2018) 2074
	10 seconds	1.2 × 10^{-7}	Sensors & Actuators: B. Chemical 273 (2018) 1532
	100 seconds	1.7 × 10^{-7}	Sensors & Actuators: B. Chemical 287 (2019) 453
	10 seconds	3.9 × 10^{-8}	New J. Chem. 42 (2018) 5135
	400 seconds	9.2 × 10^{-8}	Org. Biomol. Chem. 17 (2019) 108

	not mentioned	7.2×10^{-7}	Sensors & Actuators: B. Chemical 255 (2018) 963
	2 minutes	4.1×10^{-9}	Sensors & Actuators: B. Chemical 263 (2018) 137
	20 seconds	1.165×10^{-6}	Anal. Methods 11 (2019) 1751
	16 seconds	7.782×10^{-8}	Sensors & Actuators: B. Chemical 255 (2018) 2378
	12 seconds	6.114×10^{-8}	
	4 minutes	1.2×10^{-7}	Sensors & Actuators: B. Chemical 269 (2018) 180
	7 minutes	2.6×10^{-8}	
	30 seconds	8×10^{-8}	Dyes and Pigments 158 (2018) 526
	**5 seconds**	**1.8×10^{-8}**	**This work**

3.4. Proposed response mechanism



Scheme 2. Proposed response mechanism for **YXF** with NaClO.

The sensing mechanism for **YXF** with NaClO was proposed in **Scheme 2**. As the previous reported literature about oxidation of C=N double bond derivative from diaminomaleonitrile with HClO/ClO^-, the hydrazone group could be transformed by NaClO to give the aldehyde oxide derivative [48-50]. In order to verify the possibility of the above recognition mechanism, the mixture of NaClO and probe **YXF** was tested by HR-MS spectrometry. After reaction with 30 equiv. NaClO for 10 minutes, the mass spectral peak of the reaction product at *m/z* 164.0161 corresponding to the oxidation product [**2**+H]$^+$ was observed, and there was no peak of **YXF** (*m/z* 254.0459) (**Fig. S5**). This result indicated that probe **YXF** was converted into **2** completely. The sensing mechanism was further confirmed by ^{1}H NMR spectrum titration analysis on the mixture of probe **YXF** with NaClO in acetone-d_6. As illustrated in **Fig. 5**, upon the addition of NaClO, the proton signal at 8.64 ppm (H_a) of probe **YXF** which was assigned to the –C**H**=N– group disappeared and, concomitantly, a new proton signal at 10.20 appeared which was consistent with the proton signal of H_b of compound **2**. In addition, the other proton signals generated from the mixture of probe **YXF** with NaClO also corresponded to those of compound **2**. These data strongly supported our proposed mechanism for the manner in which NaClO reacted with probe **YXF** to generate compound **2**.

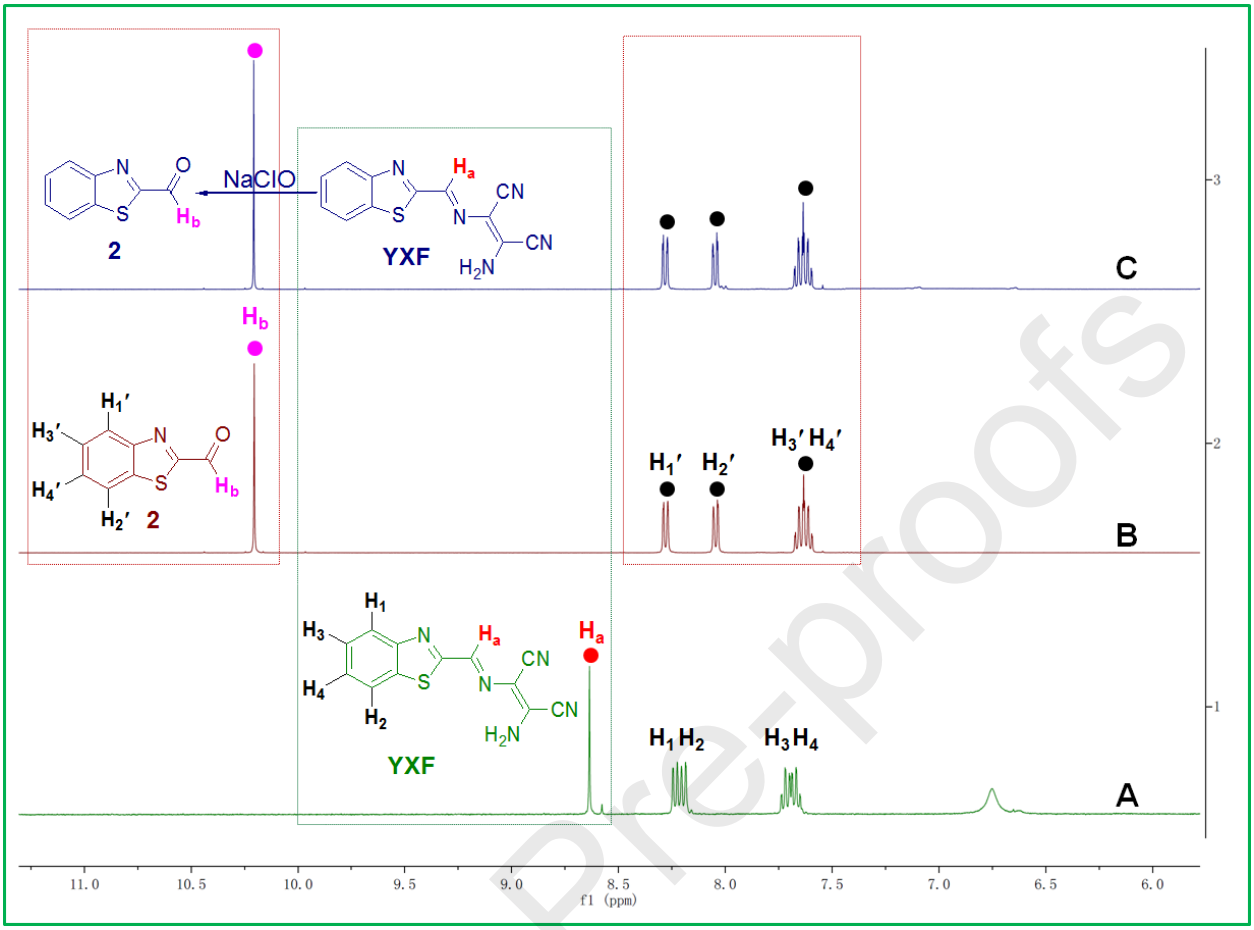


Fig. 5. Partial ^{1}H NMR of **YXF** (**A**), compound **2** (**B**), and **YXF** + NaClO (**C**) in acetone-d_6.

3.7. Detection of ClO^- in tap water

In order to exploit its real application, the performance of probe **YXF** of detecting ClO^- in tap water samples was studied (**Table 2**). The tap water samples were used directly for determination without special treatment. The recovery of ClO^- was determined by the standard addition method through the fluorescence spectra titration. The statistical data in the **Table 2** demonstrated that the average recovery rates of ClO^- in the real water sample were about 98.5~102.1%, indicating that the prepared probe **YXF-ClO** could be successfully used for the analysis and determination of ClO^- in the real sample.

Table 2. Experimental results of real tap water samples recovery.

Sample	Labeled (μM)	Added (μM)	Found	Recovery (%)	RSD * (%)
1	5.00	1.00	6.02	102.1	1.6

2	5.00	3.00	7.91	98.3	2.1
3	5.00	5.00	9.86	98.5	2.6

* Relative Standard Deviation, n=5.

3.8. Detection of ClO^- level in 84 disinfectant samples

The feasibility of probe **YXF** for detecting ClO^- in practical samples was explored. From the fluorescence spectra titration curves (**Fig. S7**) and the calibration curve (**Fig. 4B**), the ClO^- level in the purchased 84 disinfectant sample was calculated to be 1.02 M, which was within the range from 0.95 to 1.30 M of product concentration (the effective chlorine level was 34.0-46.0 g/L). Furthermore, the calculated recovery values of ClO^- were between 94.4% and 102.9%, indicating the accuracy and scientific nature of this method. Therefore, probe **YXF** could be used to detect ClO^- level in 84 disinfectant samples. The corresponding calculated values were listed in **Table 3**.

Table 3. Determination of ClO^- level in 84 disinfectant samples.

Sample	ClO^- level found (M)	ClO^- added (*m*M)	ClO^- found (*m*M)	Recovery (%)	RSD * (%)
84 disinfectan	1.02	1.02	0.98	96.1	0.6
		2.04	2.10	102.9	1.1
		3.06	2.89	94.4	0.8

* Relative Standard Deviation, n=5.

4. Conclusions

In summary, a simple structure and facile synthesis new fluorescence probe, **YXF** for "turn-on" response to ClO^- was developed. It could detect ClO^- with a high selectivity and sensitivity over other 29 kinds of common analytes including some reactive oxygen molecules. After addition of 30 equiv. NaClO to the solution of **YXF**, the fluorescence intensity at 452 nm enhanced with an approximately 37-fold within seconds and, concomitantly, the fluorescence color from dark to bright cyan could be observed. A linear calibration curve was obtained between the fluorescence intensity at 452 nm and the NaClO concentration range of 1-180 μM

indicating this probe was suitable for quantitative determination of ClO^-. Furthermore, it was found that **YXF** had a detection limit of 1.8×10^{-8} M. In addition, NaClO-promoted oxidation cleavage of C=N unit of probe **YXF** was verified by HR-MS and NMR spectrometry analysis. Moreover, probe **YXF** could be successfully applied for detection of ClO^- concentration in several tap water and 84 disinfectant samples.

Conflict of interest statement

The authors have declared that no conflict of interest exists.

Acknowledgments

Financial support by the National Natural Science Foundation of China (Grants 21708013, 21675064, 51473067), the China Postdoctoral Science Foundation (Grants 2017M620288), Natural Science Foundation of Shandong Province of China (ZR2018MB016), Young Taishan Scholars Program of Shandong Province (TSQN20161036), and Major basic research projects of natural science foundation of Shandong province (ZR2018ZC0230).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://

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A simple but sensitive and efficient "turn-on" benzothilazole-based fluorescent probe **YXF** for ClO^- detection was developed. Compared with previous fluorescent probes, the main advantages of this probe were a rapid response time (within 5 seconds), a low detection limit (1.8×10^{-8} M), a high selectivity and an excellent sensitivity.

Highlights

• A simple "turn-on" benzothilazole-based fluorescent probe for ClO^-.

• A rapid-response time within 5 seconds for detection ClO^-.

- A low detection limit of 1.8×10^{-8} M for ClO^-.
- High selectivity and sensitivity for ClO^-.