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Simple 1,8-diaminonaphthalene-based fluorescence chemosensor for hypochlorites and its practical application

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ABSTRACT

In this work, we have successfully provided a novel strategy for employing commercially available fluorescent reagent as probe for hypochlorite. The strategy is based on a specific reaction promoted by hypochlorite: namely, hypochlorite oxidizes aminos of probe to imines, which has not yet been used in the fluorescent hypochlorite probe design. Interestingly, the probe showed a fluorescent response to hypochlorite with the emission shift from blue to green. Furthermore, the probe displayed high selectivity for hypochlorite over other species. The probe can be used in detecting practical sample and bioimagings. The probe developed herein made it become possible that organic complexes containing amino can be used to design fluorescence probes for hypochlorite.

1. Introduction

Sodium hypochlorite (NaOCl) is used extensively as a bleaching agent and disinfectant at concentrations ranging from 10^{-5} to10^{-2} mol/L [1–3]. However, concentrated hypochlorite solutions are a potential health hazard to human and animals [4,5]. On the other hand, hypochlorite anion is one of the biologically important reactive oxygen species (ROS) [6–9], and it plays a critical role in the immune system. Endogenous ClO^- is essential to life and has important antibacterial properties. However, the abnormal production of hypochlorite can lead to tissue damage and diseases, such as hepatic ischemia-reperfusion injury [10], atherosclerosis [11], lung injury [12], rheumatoid [13,14] cardiovascular diseases [15], neuron degeneration [16], arthritis [17], and cancer [18,19]. Therefore, sensitive and selective probes are required for the detection of hypochlorite (ClO^-). And its determination in environmental and biological samples such as natural water and tap water can be of interest in biochemical research. So far, there are a number of methods available for the hypochlorite determination, such as the normalized and well-known iodometric titration [20], many colorimetric methods based on reaction of hypochlorite with organic reagents [21–27], chemiluminescence methods such as that based on fluorescein test strip [28–30], coulometric [31], polarographic, bromination of fluorescein [32], and radiolysis. In recent years, the optical probe is particularly attracted much attention [33,34,5,35–47]. However, most of these probes generally involved complicated organic synthesis process and high costs. In this work, we employed a commercially available and cheap compound, 1,8-diaminonaphthalene (Scheme 1) to detect HClO/ClO^- by fluorescence spectrometer. The ability of probe to detect ClO^- in living cells (HepG2 cells) via a change (from blue to green) of the fluorescence was proved.

2. Experimental

2.1. Materials

4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Sigma-Aldrich (St. Louis, MO). Analytical grade 1,8-diamino naphthalene was purchased from Aladdin Chemistry Co. Ltd. Sodium hydroxide solution (0.1 mol/L) was added to aqueous HEPES (10 mmol/L) to adjust the pH to 7.0. Metal ions salts were purchased from Shanghai Experiment Reagent Co., Ltd. (Shanhai, China). All other chemicals used were of analytical grade.

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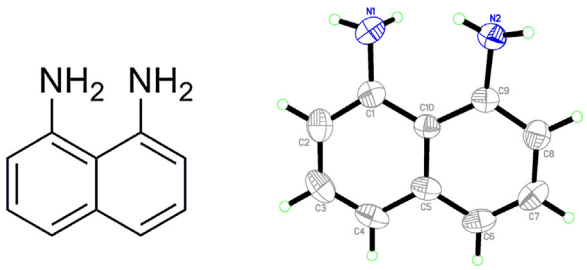

Scheme 1. The structure (top) and thermal ellipsoids of probes are drawn at the 50% probability level.

2.2. Instruments

A pH meter (Mettler Toledo, Switzerland) was used to determine the pH. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. Ultraviolet–visible (UV–vis) spectra were recorded on a Cary 50 Bio UV–vis spectrophotometer. A PO-120 quartz cuvette (10 mm) was purchased from Shanhai Huamei Experiment Instrument Plants, China. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE-300 MHz and 75 MHz NMR spectrometer, respectively (Bruker, Billerica, MA). ESI was measured with an LTQ-MS (Thermo) instrument. The ability of probe reacting to ClO^- in the living cells was also evaluated by laser confocal fluorescence imaging using an Olympus FV1000 laser scanning microscope.

2.3. General fluorescence and general UV–vis spectra measurements

A ClO^- solution was prepared by dissolving sodium hypochlorite in deionized water. Probe stock solution was prepared in ethanol. Aqueous anion salts solutions were also prepared using deionized water. Fluorescence measurements were carried out with a slit width of 5 nm (λ_{ex} = 325 nm). UV–vis and fluorescence spectra were obtained in HEPES aqueous buffer (10 mmol/L, pH 7.0) solutions.

2.4. Detection range

Fluorescence spectra were measured from 350 to 600 nm with excitation at 325 nm, and the sensitivity for ClO^- was 10^{-7} to 10^{-4} mol/L. The main band in the UV–vis spectrum was centered at about 230, 262 nm. The detection threshold for ClO^- was 10^{-5} to 10^{-4} mol/L, and at this level the color change was very obvious.

3. Results and discussion

3.1. Fluorescence and UV–vis spectra

Fig. 1 shows the change in the fluorescence spectra when the $ClO^-$is gradually added to the HEPES aqueous buffer (10 mmol/L, pH 7.0) solution, containing probe 1,8-diaminonaphthalene (2.5 μmol/L) (λ_{ex} = 325 nm). Upon increasing ClO^- concentration, the initial fluorescence intensity of 440 nm gradually decreased with the simultaneous appearance of a new redshifted emission band centered at 518 nm. A visual fluorescence change (from blue to green) for 1,8-diaminonaphthalene, upon the addition of ClO^- to the HEPES aqueous buffer was observed under illumination with a UV 365 nm lamp. Fig. S1 shows the change in the UV–vis spectra when $ClO^-$was added to the HEPES buffer (10 mmol/L, pH 7.0) solution containing the probe (10 μmol/L), As the ClO^- concentration increased, the maximum absorption peak at 230 nm gradually decreased in intensity up to be silent, then a new absorption peak

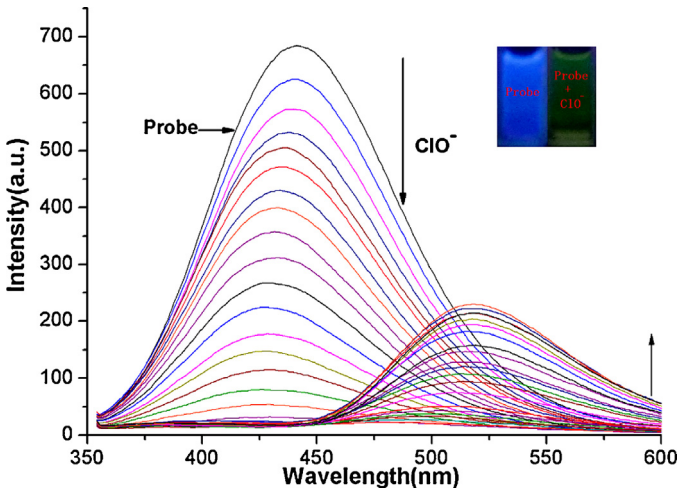

Fig. 1. Fluorescence spectral change for the probe upon the addition of ClO^- in 10 mmol/L HEPES at pH 7.0 as an aqueous buffer with [ClO^-] = 0–125 μmol/L. Inset: visual fluorescence change photographs for probe upon the addition of ClO^- in a HEPES (pH 7.0) buffer solution under UV illumination (365 nm).

come out at 262 nm and also constantly increased with increased concentration of ClO^-.

3.2. Selectivity over other analytes

To evaluate the hypochlorite-selective nature of probe, possible influences caused by other analytes were investigated for probe using the fluorescence spectra of solutions containing probe and analytes (100 equiv.) in HEPES aqueous buffer (10 mmol/L, pH 7.0). The results showed that whereas analytes such as F^-, ClO_3^-, NO_2^-, CN^-, S^{2-}, SCN^-, $P_2O_7^{4-}$, AcO^-, CO_3^{2-}, ClO_4^-, N_3^-, HSO_3^-, H_2O_2, ClO_2^-, MnO_4^-, $ONOO^-$ do not result in any apparent changes in fluorescence intensity, there is notable change when ClO^- is involved (λ_{ex} = 325 nm). Fig. 2 shows that fluorescence spectra when various analytes are added and fluorescence color change. In addition, other oxidizing species have no response to probe see Fig. S2. And among metal ions, surely, only paramagnetic Cu^{2+} can quench the fluorescence of probe (Fig. S2).

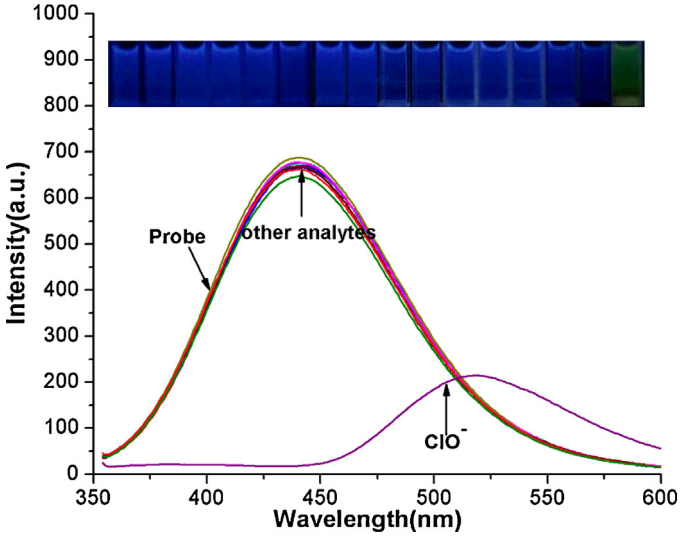

Fig. 2. Fluorescence spectra of probe (2.5 μmol/L) in the absence and presence of various analytes (2500 μmol/L) in 10 mmol/L HEPES solution (pH 7.0) (λ_{ex} = 325 nm, λ_{em} = 440, 518 nm, slit: 2 nm/5 nm). Inset: a visual fluorescence change photograph under illumination with a 365 nm UV lamp.