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Research Paper

Dual signaling of hypochlorite in tap water by selective oxidation of phenylselenylated dichlorofluorescein

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ABSTRACT

A novel hypochlorite-selective signaling probe based on the oxidative transformation of phenylselenylated 2′,7′-dichlorofluorescein **1** to its selenoxide analogue was investigated. In a pH 7.0 phosphate buffer system (containing 1% DMF as a solubilizer), the designed probe **1** exhibited pronounced colorimetric and fluorogenic hypochlorite signaling behavior over other representative oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide, perborate, and percarbonate as well as a range of environmentally relevant metal ions and anions. The signaling was due to the hypochlorite-assisted oxidation of the probe's selenyl moiety to selenoxide. Hypochlorite signaling was unaffected by the presence of common metal ions and anions as a background. The hypochlorite-selective fluorescence signaling of probe **1** has a detection limit of 3.9×10^{-8} M (0.002 ppm). Finally, the determination of hypochlorite concentration in tap water using a smartphone as a stand-alone portable signaling detection and processing tool was successfully demonstrated.

1. Introduction

The development of selective and sensitive signaling methods for biologically and environmentally important chemical species has attracted ever-increasing research interest [1]. Over the last decades, many sophisticated signaling and visualization probes with colorimetric and/or fluorescent signaling properties have been designed for the selective recognition of metal ions, anions, and various oxidants [2,3]. Undoubtedly, using optical signaling methods is a more attractive option for this purpose than using conventional heavy instrument-based methods such as atomic absorption or atomic emission spectroscopy (AAS/AES), inductively coupled plasma mass spectrometry (ICP-MS), and electrochemical techniques as these techniques typically require expensive instrumentation and/or complicated sample preparation procedures, which complicate on-site and real-time detection. Among the many current optical signaling approaches, fluorescence spectroscopy is the most attractive analytical tool for the detection of metal ions, anions, and oxidants as a result of its capabilities for high sensitivity, selectivity, reproducibility, and real-time monitoring [4]. Particularly, many intriguing reaction-based chemical probes have been developed [5–7] in recent times owing to their unique advantages such as cumulative and specific signaling capabilities [8]. In general, they exploit prominent spectroscopic changes induced by specific reactions that occur between the probes and their target analytes.

Hypochlorous acid (HOCl), a powerful oxidizer and deproteinizer produced by neutrophils, is an important reactive oxygen species (ROS) and has essential roles in biological systems [9]. For example, endogenous hypochlorite, which is produced from the myeloperoxidase (MPO) enzyme-catalyzed reaction between hydrogen peroxide (H_2O_2) and chloride ion (Cl^-), protects the living system from the invasion of pathogens [10,11]. Hypochlorite (OCl^-) is also widely used for industrial applications, functioning as a bleaching agent in paper and textile processing and as a control material to remove slime and algae in piping and tubes [12]. Moreover, hypochlorite is used as a safe sanitizer for the treatment of drinking water and swimming pool [13]. To ensure safe community water supplies, the World Health Organization (WHO) has established 0.2 mg/L (0.2 ppm) as the guideline for the minimum free chlorine level in drinking water in the role of disinfecting agent for bacteria and other microbes [14]. However, excess amounts of hypochlorite can damage protein, DNA, and RNA in cells via oxidative stress [15], and can cause severe diseases of the human body such as cancer and neurodegeneration [16,17].

Owing to these severe side effects of hypochlorite, the development of a selective and sensitive hypochlorite signaling system is crucial. For this purpose, many sophisticated hypochlorite signaling probes that exploit the oxidative properties of hypochlorite

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have been developed [18]. Representative examples are colorimetric and/or fluorescent hypochlorite signaling probes that act via the oxidative hydrolysis of rhodamine hydroxamic acid [19], rhodamine sulfonhydrazide [20], rhodamine hydrazide derivatives [21–23], triphenylamine–diaminomaleonitrile [24], oxime derivatives [25–27], hydrazones [28–30], and boronic acid derivatives [31]. In parallel to these probes, a number of sulfur-containing hypochlorite signaling probes based on the desulfurization of thiolactones [32–34], oxidation of thioethers [35–37], and deprotection of oxathiolane [38] or dithiane [39] have also been developed. However, most of these previously reported probes have focused overwhelmingly on the determination of hypochlorite in biologically relevant systems [40], while those mean that practical applications such as tap water analysis are much less investigated.

Recently, a number of selenium-containing chemical probes with selective signaling properties toward metal ions, anions, thiols, and reactive oxidants have been developed [41]. They are based on the redox properties of selenium and its strong affinity toward Hg^{2+}, Cu^{2+}, and Ag^{+} ions, as well as thiol groups [42]. For instance, Hg^{2+}-selective signaling probes have been designed by exploiting the prominent affinity of mercury to selenium via the opening of the spirolactone ring of rhodamine B, followed by the deselenation and conversion of phosphane selenide to phosphane oxide by the selective deselenation process [43–45]. Moreover, by making use of the strong affinity of selenium for thiol functions, glutathione (GSH) signaling probes were developed through the nucleophilic substitution of the sulfhydryl group to selenylated rhodamine 6G derivative, and the cleavage of the diselenide bond of the fluorescein derivative to give selenylsulfide and selenol [46,47]. Many Se-based chemodosimeters for oxidants based on the facile oxidation of the selenyl moiety have also been developed. The oxidative transformation of selenide to selenoxide was employed for the creation of BODIPY- [48,49] and 1,8-naphthalimide-based [50] hypochlorite probe, and the same method has also been applied to the determination of other important reactive oxygen and nitrogen species such as hydrogen peroxide [51], peroxynitrite [52], superoxide [53], and hypobromous acid [54]. In this study, we have developed a novel hypochlorite-selective chromogenic and fluorescence signaling system based on the hypochlorite-induced oxidative transformation of selenyl moiety of the dichlorofluorescein-based probe to selenoxide. The developed probe showed prominent dual signaling behavior toward hypochlorite over other commonly used oxidants, as well as other environmentally relevant metal ions and anions. Furthermore, the designed probe was successfully applied to the determination of hypochlorite in tap water using a smartphone as a stand-alone portable colorimetric and fluorescence signaling detection tool.

2. Experimental section

2.1. General

2′,7′-Dichlorofluorescein and phenylselenyl chloride were purchased from Aldrich Chemical Co. and used without further purification. Meanwhile, sodium hypochlorite was obtained from Aldrich Chemical Co. and used after standardization by iodometry [55]. All solvents were purchased from Aldrich Chemical Co. as 'anhydrous' or 'spectroscopic grade'. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on a Varian VNS NMR spectrometer. UV–vis spectra were recorded with a Scinco S-3100 spectrophotometer equipped with a Peltier temperature controller. Fluorescence spectra were measured with an FS-2 fluorescence spectrophotometer (Scinco). Mass spectra were obtained on a JMS-AX505WA (JEOL) mass spectrometer. Elemental analysis data were obtained using a Thermo Electron Corporation Flash EA 1112 analyzer. Column chromatography was carried out using silica gel (Merck, 240 mesh).

2.2. Preparation of phenylselenyl dichlorofluorescein **1**

Phenylselenyl chloride (0.41 g, 2.2 mmol) was added to a suspension of 2′,7′-dichlorofluorescein (0.40 g, 1.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in DMF (10 mL). The reaction mixture was stirred at 80 °C for 12 h. After the completion of the reaction, the solution was diluted with water and extracted with dichloromethane. The combined organic solution was washed with water, and then evaporated to obtain a brown solid residue. The product was purified by column chromatography (silica gel, CH_2Cl_2:CH_3OH = 9:1, v/v). Yield, 85%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 1H), 7.74 (dd, J = 7.5, 1.1 Hz, 1H), 7.69 (dd, J = 7.5, 1.0 Hz, 1H), 7.36 (s, 2H), 7.33 (dd, J = 8.3, 1.2 Hz, 4H), 7.21 (d, J = 7.6 Hz, 1H), 7.19–7.14 (m, 2H), 7.13–7.08 (m, 4H), 6.85 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 154.9, 151.5, 151.0, 135.7, 130.8, 130.6, 130.6, 129.6, 129.2, 127.6, 126.4, 125.7, 123.9, 116.3, 112.2, 106.2, 82.3; HRMS (FAB); m/z calcd for $C_{32}H_{19}Cl_2O_5Se_2$ $[M+H]^+$: 712.8934, found 712.8937. Anal. Calcd for $C_{32}H_{18}Cl_2O_5Se_2$: C, 54.03; H, 2.55. Found: C, 54.32; H, 2.46.

2.3. Preparation of stock solutions

Owing to the limited solubility of probe **1** in pure water, a stock solution of probe **1** (5.0×10^{-4} M) was prepared in DMF (spectroscopic grade). All stock solutions of tested oxidants (1.0×10^{-2} M), metal ions (1.0×10^{-1} M), and anions (1.0×10^{-1} M) were prepared by dissolving common oxidants (such as hydrogen peroxide, *tert*-butyl hydrogen peroxide, potassium superoxide, sodium perborate, and sodium percarbonate), perchlorate salts of metal ions (such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, and Hg^{2+}), and sodium salts of anions (such as F^-, Cl^-, Br^-, I^-, HPO_4^{2-}, $P_2O_7^{4-}$, SO_3^{2-}, SO_4^{2-}, NO_3^-, OAc^-, HCO_3^-, and ClO_4^-) in distilled water. Hydroxy radical was generated from the reaction of ferrous chloride (1.0×10^{-2} M) with 10 equiv of H_2O_2 [56].

2.4. Measurement of the signaling behavior

All measurements were performed under optimized conditions using a pH 7.0 phosphate buffer solution (10 mM) that contains 1% DMF as a solubilizer. The measuring solutions for hypochlorite signaling were prepared by mixing the stock solutions of probe **1** (30 μL, 5.0×10^{-4} M), analyte (hypochlorite, oxidants, metal ions, or anions) (15 μL, oxidants: 1.0×10^{-2} M, metal ions and anions: 1.0×10^{-1} M), and the pH 7.0 phosphate buffer solution (150 μL, 0.20 M) in a vial. The final concentrations of probe **1**, analyte, and buffer were 5.0×10^{-6} M, 5.0×10^{-4} M, and 1.0×10^{-2} M, respectively. All fluorescence spectra were obtained using an excitation wavelength of 500 nm.

2.5. Evidence for the signaling process

Probe **1** (0.071 g, 0.10 mmol) in 0.10 mL of DMF was added to a solution of sodium hypochlorite (0.017 g, 0.22 mmol) in 5.0 mL of phosphate buffer solution (pH 7.0). After adjusting the solution's pH to 6.0 using a 0.1 N HCl solution, the solution was extracted using dichloromethane. The dichloromethane fraction was passed through a short silica plug (CH_2Cl_2:MeOH = 9:1, v/v) and subsequently, the NMR and mass spectra of the purified product were obtained.