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Selective fluorescence signaling of hypochlorite in tap water by oxidative hydrolysis of sulfonhydrazone

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ABSTRACT

A new hypochlorite-selective fluorescence signaling probe based on the sulfonhydrazone of 2-acetyl-6-methoxynaphthalene was investigated. The probe was easily prepared by the simple one-step reaction of 2-acetyl-6-methoxynaphthalene with *p*-toluenesulfonylhydrazide. The probe exhibited off/on-type fluorescence signaling behavior toward hypochlorite in aqueous solution via hypochlorite-triggered oxidative hydrolysis of the sulfonhydrazone to yield strongly fluorescent 2-acetyl-6-methoxynaphthalene. Selective hypochlorite signaling over other common oxidants with a large fluorescence enhancement (76-fold) was possible, with a detection limit of 2.0×10^{-8} M. Hypochlorite signaling was not affected by the presence of other common metal ions or representative anions. As a practical application, the methoxyacetylnaphthalene sulfonhydrazone probe was used to determine hypochlorite levels in a tap water sample using a standard smartphone as the detection tool.

1. Introduction

The detection and control of biological and/or organic pollutants in drinking and industrial water, especially water intended for human consumption or food production, are of the utmost importance [1,2]. Hypochlorite (OCl^-), the ionized form of hypochlorous acid (HOCl), is particularly important because it is widely used as cleaning agents, disinfectants, and sanitizers in households and industry [3]. Because of its widespread usage and the potential dangers to human and animal health associated with excess levels of OCl^-, the development of simple and convenient signaling methods for its industrial and environmental detection is imperative.

Recently, a number of sophisticated hypochlorite-selective probes have been developed. These probes are generally based on hypochlorite-induced deoximation [4–6], dediaminomaleonitrile reactions [7], the oxidation of *p*-methoxyphenol to quinone [8], spirolactam ring-opening processes [9–11], or ether cleavage [12]. In addition, several nanomaterial-based fluorescence signaling probes for the determination of hypochlorite have also been developed [13,14]. However, most research efforts have been focused on hypochlorite signaling in biological systems [15]. The signaling of hypochlorite in practical samples, especially domestic tap water, has received less attention (Table S1, Supplementary data) [16–26].

Hydrazones and their metal complexes have attracted much research interest, and have been widely applied in biological, pharmaceutical, analytical, and industrial fields [27–29]. They have also been utilized in the creation of combinatorial libraries [30,31], as auxiliaries in organic synthesis [27], and as hole-transporting materials in optoelectronic devices [27]. The lability of hydrazones toward acid has led to them playing important roles as linkers in drug design [32]. Furthermore, they have recently been frequently employed as the basic platform for the construction of molecular switches, sensors, and other functional materials [33,34]. However, to the best of our knowledge, sulfonhydrazones have hardly been used as reaction-based probes, despite their potentially useful lability toward a range of important chemical species.

In synthetic organic chemistry, hydrazones and semicarbazones are very useful in the protection, purification, and characterization of aldehydes and ketones [35–41]. Consequently, considerable research effort has focused on the development of selective and efficient deprotection methods for hydrazones. In fact, as a design strategy for reaction-based probes, the regeneration of carbonyl compounds from hydrazones of coumarin and 1,8-disubstituted anthraquinone has been successfully used for the signaling of Cu^{2+} ions [42,43]. In addition, we recently reported a hypochlorite-selective signaling probe based on selective oxidative hydrolysis of a sulfonylhydrazide derived from a rhodamine–dansyl conjugate [26].

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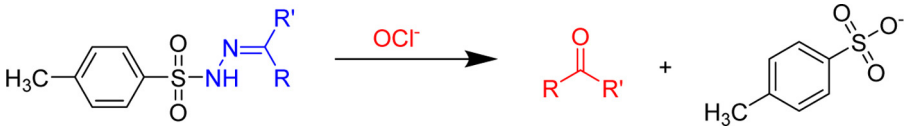
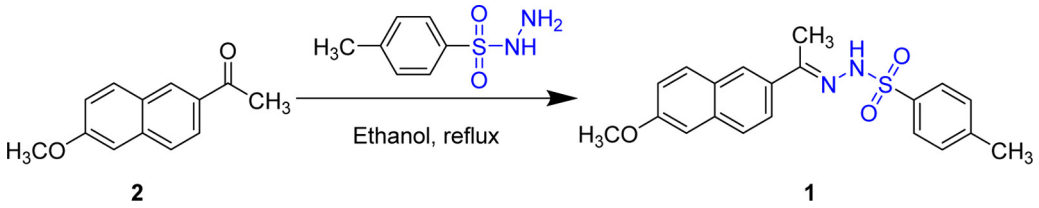


Scheme 1. Hypochlorite-assisted regeneration of ketones from tosylhydrazones.



Scheme 2. Preparation of sulfonhydrazone probe **1**.

We utilized a literature method for the oxidative regeneration of ketones from tosylhydrazones to design a novel and selective reaction-based probe for hypochlorite (Scheme 1) [44,45]. The designed compound exhibited pronounced hypochlorite-selective signaling behavior with prominent off/on-type fluorescence signaling. We also investigated the application of the probe to rapid and convenient hypochlorite signaling in tap water samples using a smartphone as an easily accessible detection device. Because of their portable and fast analytical capabilities, many consumer electronic devices, such as flatbed scanners [46], tablet computers [47], web cameras [48], and smartphones [49], have recently attracted much research interest for their use in the detection and analysis of visible and/or fluorescent signaling. In particular, smartphones, which is one of the most easily available and portable tools, have been increasingly used as signaling processors for the analysis of important chemical species, such as O_2 [50], Hg^{2+} [51], nitrite [52], trinitrotoluene [53], and methamphetamine [54]. The ability of smartphones to record, process, and send images in the field is highly desirable to avoid the need for heavy instrumentation [49].

2. Experimental section

2.1. General

2-Acetyl-6-methoxynaphthalene was purchased from Tokyo Chemical Industry Co. *p*-Toluenesulfonylhydrazide was obtained from Sigma-Aldrich Co. Sodium hypochlorite solution was purchased from Sigma-Aldrich Co. and used after standardization by iodometry [55]. All other chemicals and solvents were obtained from commercial sources and used as received. ^{1}H NMR (300 and 600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a Varian Gemini 2000 or a Varian VNS NMR spectrometer using residual solvent signals as a reference. UV–vis spectra were measured with a Scinco S-3100 spectrophotometer equipped with a Peltier temperature controller. Fluorescence spectra were recorded on a PTI QuantaMaster steady-state spectrofluorometer. Mass spectra were measured with a Micromass Autospec mass spectrometer. Column chromatography was performed with silica gel (Merck, 240-mesh). Digital images were captured with a smartphone (Galaxy A7, Samsung Electronics Co.).

2.2. Preparation of sulfonhydrazone probe *1*

2-Acetyl-6-methoxynaphthalene **2** (0.20 g, 1.0 mmol) was dissolved in ethanol (10 mL), and *p*-toluenesulfonylhydrazide (0.38 g, 2.0 mmol) was added. The reaction mixture was heated under reflux for 12 h. The resultant precipitate was collected by filtration and washed with pure ethanol. After purification by column chromatography (silica gel, CH_2Cl_2/CH_3OH = 29:1, *v/v*), the desired product, **1** was obtained as a white solid (0.36 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.91 (m, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.59 (s, 1H), 7.32 (d, J = 8.7 Hz, 1H), 7.14 (dd, J = 8.9, 2.6 Hz, 1H), 7.11 (d, J = 2.5 Hz, 1H), 3.93 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 152.3, 144.1, 135.4, 135.2, 132.4, 130.0, 129.6, 128.25, 128.2, 128.1, 126.9, 126.1, 124.0, 119.1, 110.0, 105.8, 55.3, 21.6, 13.0. HRMS: (FAB$^+$); *m/z* calcd. for $C_{20}H_{21}N_2O_3S^+$ [M+H]$^+$: 369.1267. Found 369.1272. Anal. Calcd. for $C_{20}H_{20}N_2O_3S$: C, 65.20; H, 5.47; N, 7.60; S, 8.70. Found: C: 65.52, H: 5.37, N: 7.46, S: 8.51.

2.3. ^{1}H NMR studies

Sodium hypochlorite solution (1.0 mmol) diluted in distilled water (9.0 mL) was added to a solution of compound **1** (3.7 mg, 0.1 mmol) in acetonitrile (1.0 mL). The mixture was stirred at room temperature for 10 min, and the resulting solution was extracted with dichloromethane. After evaporation of the volatiles, the product residue was purified by short column chromatography (silica gel, CH_2Cl_2/CH_3OH = 29:1, *v/v*), and subsequently characterized by ^{1}H NMR and mass spectrometry.

2.4. Determination of hypochlorite in tap water using a smartphone

Signaling images of the solutions at various hypochlorite concentrations were captured with the smartphone and used to construct a calibration curve. To prevent interference from environmental light, the cells containing the sample solutions were kept in the dark using a handmade dark box. This cubic box, with a rectangular hole in the side, in which the smartphone was fitted and faced the measuring cells, was used to capture the images. In addition, images of the solutions under UV light, from a lamp (UV hand lamp, Wenk Labtec) fitted into the lid of the prepared box, were taken using the smartphone with the following settings: Focus, auto; ISO, 400; white balance, auto; brightness, 0; image size, 6 megapixels (3264 × 1836); color effect, none. In addition, to remove the reflection of highly fluorescent OCl^- signaling solutions, individual cells were compartmented from other cells by placing a handmade U-shaped paper box. Calculated amounts of stock solutions of hypochlorite (or tap water), phosphate buffer solution, and **1** were sequentially added to a vial, and the resulting solutions were diluted to 3.0 mL with distilled water. The final concentrations of **1**, phosphate buffer (pH 7.0), and hypochlorite in the standard solutions were 5.0×10^{-6} M, 1.0×10^{-2} M, and 0–3.0×10^{-6} M, respectively, in aqueous solution containing 1% acetonitrile. The blue channel level in the resulting images was