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Fluorescence sensing of peracetic acid by oxidative cleavage of phenylselenyl ether of 4-hydroxynaphthalimide

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ABSTRACT

A new fluorescent probe for the selective detection of industrially important peracetic acid (PAA) was developed via oxidative cleavage of the phenylselenyl ether derivative of the 4-hydroxynaphthalimide. The probe showed no noticeable changes towards common oxidants and environmentally relevant metal ions and anions. Furthermore, PAA signaling was not influenced by the presence of background ionic species, except for certain redox-active species. Practical application of the probe to the determination of PAA in tap water and atmosphere was successfully executed using a smartphone as a stand-alone signal capturing and processing device.

The selective and sensitive signaling of chemically and industrially important oxidants is one of the most pertinent topics in modern analytical chemistry.[1] Peracids, such as peracetic acid (PAA) and *m*-chloroperbenzoic acid (mCPBA), are important oxidants in many industrial processes and synthetic organic chemistry.[2] For instance, these organic peroxy acids are largely used as reagents in the Baeyer-Villiger oxidation and in the oxidation of alkene carbon-carbon double bonds to generate epoxides.[3] PAA is also employed in a wide variety of industrial and daily applications, including disinfectants for medical facilities, agricultural premises, food establishments, and beverage processing plants, as well as bleaching agents in the textile industry, where PAA functions as a peroxide and oxidizing agent.[4]

However, PAA is a strong oxidizing agent (E^0 = 1.762 V vs. Ag/AgCl)[5] and a primary irritant. Exposure to PAA can cause irritation to the eyes, skin, and respiratory system, and higher or long-term exposure can cause severe lung damage.[6] In 2010, the United States Environmental Protection Agency (US EPA) published Acute Exposure Guidelines (AEGL) for PAA, with 0.17 ppm as an acceptable 8-h occupational exposure limit (OEL).[7] Therefore, the rapid analysis and the selective and sensitive monitoring of PAA are important pursuits for ensuring industrial and laboratory safety. At present, PAA assay is routinely carried out by iodometric redox titration and spectrophotometry using the chromogenic reagent *N*, *N*-diethyl-*p*-phenylenediamine (DPD).[8] Other determination methods using standard instruments include gas chromatography,[9] liquid chromatography,[10] and electrochemical methods.[11] Although optical methods using selective analyte-induced spectral changes are more desirable regarding convenience, selectivity, and sensitivity, signaling systems for PAA relying on fluorescence changes of the probes are relatively unexploited.[12,13]

Recently, several attractive fluorescent probes have been developed for the detection of oxidants such as hypochlorous acid (HOCl) and peroxynitrite by harnessing the unique redox properties of selenium.[14,15] The specific oxidation of boron-dipyrromethene (BODIPY)-based diphenyl selenide[16] and phenylselenyl-appended aminonaphthalimide[17] has been successfully employed for the detection of chemically and biologically important oxidant HOCl. On the other hand, a BODIPY-bearing fluorescent probe modulated by a selenoxide spirocyclization reaction[18] and a near-IR reversible fluorescent probe based on selenide-selenoxide conversion are developed for the imaging and monitoring of peroxynitrite in living cells.[19]

Herein, we report a new PAA-selective fluorescent probe based on the oxidative transformation of phenylselenyl ether-derivatized 4-hydroxynaphthalimide to naphthalimide-diol. The basic platform of naphthalimide-based dyes exhibits exploitable absorption and emission properties and has been extensively used for the construction of chemical probes.[20–24] Designed probe showed pronounced PAA-selective signaling behavior over other oxidants as well as environmentally important metal and anionic species. Particularly, the response of the probe towards another important oxidant, hypochlorite, is readily suppressed using DMSO as a

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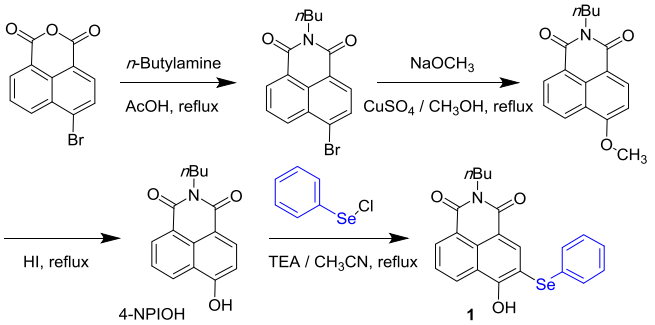
hypochlorite scavenger. As a practical application, determination of PAA in tap water and atmosphere was demonstrated by utilizing a smartphone as a stand-alone signal processing device.

To design the desired fluorescent probe for PAA, *N*-butyl-4-hydroxynaphthalimide was used as a fluorophore and phenylselenyl ether as a signaling switch. Probe **1** was obtained by the reaction of *N*-butyl-4-hydroxynaphthalimide (4-NPIOH) with phenylselenyl chloride in the presence of triethylamine (TEA) in moderate yield (46%) (Scheme 1). 4-NPIOH was prepared from 4-bromonaphthalic anhydride by a three-step reaction according to the literature procedure.[25] Probe **1** showed a weak emission centered at 537 nm in the phosphate buffered solution containing 2% (v/v) DMSO as a solubilizer. The use of DMSO as a solubilizer for **1**, which has limited solubility in water, was found to be beneficial for suppressing the response of the probe towards OCl^- due to the scavenging effect of DMSO for OCl^- (Fig. S1, Supporting Information). In fact, increasing the DMSO content in the assay solution from 0% to 2% resulted in a dramatic decrease in the OCl^--induced signaling, whereas no measurable decrease was observed for PAA. Based on this, a phosphate buffer solution (pH 7.0) containing 2% DMSO was used to ensure a selective response of probe **1** towards PAA over OCl^-. Meanwhile, a much less informative change in the spectral profile of **1** in response to PAA was observed via UV–vis spectroscopy (Fig. S2, Supporting Information).

Upon treatment of probe **1** with various oxidants under the optimized measurement conditions of phosphate buffer solution containing 2% DMSO, only PAA induced a marked enhancement of the fluorescence of probe **1** at 523 nm (Fig. 1). The color of the solution changed pronouncedly from dark to bright green under illumination with a hand-held UV lamp. Other common oxidants such as H_2O_2, OCl^-, *tert*-butyl hydroperoxide (TBHP), ammonium persulfate (APS, $(NH_4)_2S_2O_8$), perborate (BO_3^-), percarbonate (CO_4^{2-}), *m*-chloroperbenzoic acid (mCPBA), superoxide (O_2^-), peroxynitrite ($ONOO^-$), singlet oxygen ($^1O_2$), and hydroxyl radical ($^{\cdot}OH$) did not induce a measurable response.[26] We also observed that the PAA signaling behavior of probe **1** was not altered in the presence of common oxidants as a background (Fig. S3, Supporting Information). This observation implies that probe **1** may be useful for the discriminative signaling of PAA over H_2O_2 as well as other commonly used practical oxidants. PAA signaling by probe **1** was fast, and nearly instantaneous signaling was observed after sample introduction (Fig. S4, Supporting Information). From the time-trace plot, the rate constant for the signaling process under pseudo-first-order conditions with excess PAA (10 eq.) was calculated as 18.5 min^{-1} (Fig. S5, Supporting Information).

Probe **1** showed satisfactory PAA-selective signaling over common metal ions (Fig. 2), and the response towards most commonly encountered metal ions was negligible. The PAA-selective signaling behavior of **1** under competitive conditions was also assessed. In the presence of background metal ions, PAA-selective signaling by probe **1** underwent a measurable amount of interference in the presence of Fe^{2+}, Co^{2+}, Hg^{2+}, and Ag^+ ions (inset of Fig. 2). The



Scheme 1. Synthesis of naphthalimide-based probe **1**.

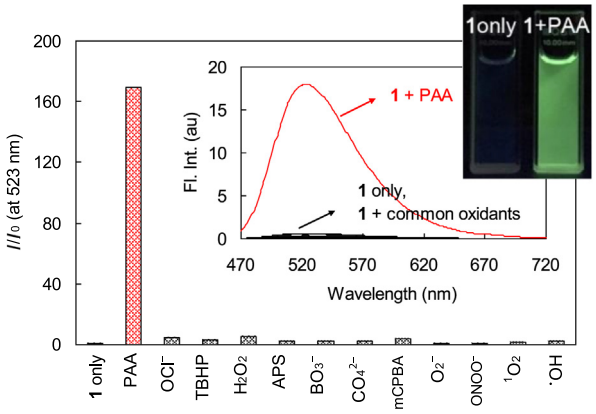


Fig. 1. Selective fluorescence signaling of PAA by **1** over common oxidants. Inset: changes in fluorescence spectrum of **1**. [**1**] = 5.0×10^{-6} M, [oxidant] = 5.0×10^{-5} M in phosphate buffer solution (pH 7.0, 10 mM) containing 2% DMSO. λ_{ex} = 455 nm.

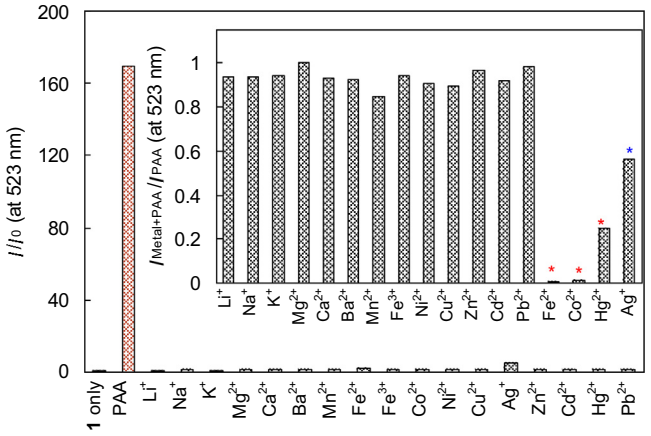


Fig. 2. Selective PAA signaling by **1** in the absence and presence (inset) of coexisting metal ions based on the fluorescence intensity ratio ($I_{Metal+PAA}/I_{PAA}$) at 523 nm. [**1**] = 5.0×10^{-6} M, [PAA] = [M^{n+}] = 5.0×10^{-5} M in phosphate buffer solution (pH 7.0, 10 mM) containing 2% DMSO. λ_{ex} = 455 nm. Interferences in the inset data are due to the redox active (Co^{2+}, Fe^{2+}, and Hg^{2+}) and slightly soluble phosphate complex forming (Ag^+) properties of the metal ions.

reduction of the PAA signaling in the presence of these metal ions is due to the consumption of PAA by the decomposition reaction with these redox-active Fe^{2+}, Co^{2+}, and Hg^{2+},[27–30] as well as the formation of the slightly soluble phosphate complex Ag_3PO_4 ($K_{sp} = 2.8 \times 10^{-18}$) with Ag^+ ions in the phosphate buffer solution.[31] However, this interference is not problematic as PAA assay in various applications generally involves the determination of residual PAA after all the interactions and reactions with background species have occurred. The other metal ions did not significantly affect the fluorescence intensity ratio ($I_{Metal+PAA}/I_{PAA}$) at 523 nm, where the ratio varied between 0.85 for Mn^{2+} and 1.01 for Mg^{2+}. Additionally, from the pH-dependent signaling of PAA by probe **1**, we confirmed that PAA signaling was not significantly influenced by variations in the pH within the range of 4.0–8.0 (Fig. S6, Supporting Information).

Pronounced selectivity of **1** towards PAA over environmentally relevant anions was also observed (Fig. S7, Supporting Information). Furthermore, PAA signaling by **1** under the competitive conditions involving coexisting background anions also showed no discernible interferences, with the exception of that caused by iodide ions (inset of Fig. S7, Supporting Information). The nearly complete suppression of PAA signaling by coexisting iodide ions is due to the reaction of PAA with iodide ions, which resulted in