A Fluorescently Ratiometric Natural Probe for Selective Detection of Sulfur Dioxide Derivative and Host-Guest Supramolecular Regulation

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Natural sanguinarine (SG) was first used as a fluorescent probe to develop a novel ratiometric sensor for selective HSO_3^- detection. The nucleophilic addition reaction of HSO_3^- occurs at the $\text{C}=\text{N}^+$ group of SG, and subsequent breakage of the conjugated π cycle leads to a decrease in the SG iminium fluorescence that is accompanied by an increase in the alkanolamine fluorescence. Therefore, a ratiometric fluorescence method with a large wavelength shift can be established for HSO_3^- detection. Furthermore, cucurbit[8]uril was used as an efficient host to encapsulate SG for an improved selectivity for HSO_3^- detection over H_2S . Our method benefits include little interference from other common anions and cations for HSO_3^- detection, suggesting a promising application in real sample analysis. Besides sensor development, the interaction of the natural SG with HSO_3^- was first demonstrated in this work to further get an insight into SG's pharmacology.

Keywords Sanguinarine, ratiometric fluorescence, HSO_3^- , detection, cucurbit[8]uril, selectivity

(Received September 23, 2019; Accepted October 21, 2019; Advance Publication Released Online by J-STAGE November 1, 2019)

Introduction

As major environmental pollutants, $\text{SO}_2/\text{H}_2\text{S}$ derivatives (including sulfurous acid (H_2SO_3), sulfite (SO_3^{2-}), bisulfite (HSO_3^-), hydrogen sulfide (H_2S), sulfion (S^{2-}), etc.) can cause heavy damages to the ecological environment and human health, especially with a long-term exposure.^{1–6} To prevent oxidation, some foods and beverages are stored also using sodium sulfite as an efficient preservative. However, asthma and other allergic symptoms can arise with an excess of sulfite involved in foods and beverages.⁷ Furthermore, it is accepted that endogenous SO_2 and its derivatives in mammals can modulate a wide range of physiological processes.⁸ Therefore, there is great demand to develop a straightforward method for reliable detection of SO_2 derivatives.

Variant fluorescent probes have been utilized for the detection of SO_2 derivatives by nucleophilic addition to double bonds ($\text{C}=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$, and $\text{N}=\text{N}$), reduction of azide, nitryl, and selenoxide groups, and the Michael addition reaction.^{3–5,9,10} The probes with fluorescent ratiometric responses have received much attention due to their ability to eliminate fluctuations of the measuring environments by self-calibration. Special efforts must be made to synthesize the ratiometric probes. For example, fluorophores with the levulinate moiety can be selectively deprotected by $\text{SO}_3^{2-}/\text{HSO}_3^-$ to allow the occurrence of excited-state intramolecular proton transfer (ESIPT) or internal charge

transfer (ICT) with a subsequent red-shifted emission.^{11–13} The nucleophilic addition of $\text{SO}_3^{2-}/\text{HSO}_3^-$ to double bonds interrupts the intramolecular charge-transfer (ICT) process or the fluorescence resonance energy transfer (FRET) process, which leads to a ratiometric change of the fluorescence signal.^{14–19} However, developing ratiometric probes for selective $\text{SO}_3^{2-}/\text{HSO}_3^-$ detection without an elaborate synthesis procedure, but with a large emission wavelength shift, is still under the way.

We have continued to search for natural products that have selective molecular-recognition capacities^{20–23} along with promising theranostic potentials. Sanguinarine (SG), a natural benzophenanthridine alkaloid, is well known for its antitumor property and cancer treatment.^{24–28} It has been reported that the $\text{C6}=\text{N5}^+$ double bond in SG can be attacked by a nucleophilic reagent (for example, OH^-) towards converting the positively charged iminium form to the alkanolamine form (Scheme 1).^{20,29,30} These two forms emit at two bands with a wavelength separation of at least 100 nm. Therefore, SG can serve as a natural ratiometric probe for the straightforward SO_2 derivative detection without any elaborate probe synthesis procedure. In this work, we first investigated the possibility of SG interacting with HSO_3^- for HSO_3^- detection by converting the iminium form to the alkanolamine form. Interestingly, the supramolecular encapsulation of SG with cucurbit[8]uril (CB[8])³¹ can improve the selectivity for HSO_3^- detection.

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Scheme 1 Structure conversion of SG from the iminium form to the alkanolamine form upon its interaction with OH^- (at alkalic solution) and HSO_3^- (at acidic solution) following the emission wavelength shifts. The CB[8] binding with the iminium form of SG highly favors the nucleophilic addition of HSO_3^- over H_2S .

Experimental

Reagents and chemicals

Cucurbit[n]urils (CB[n], $n = 5, 6, 7, 8$) were purchased from Strem Chemicals, Inc. (MA, USA). SG and metal ions were purchased from Aladdin Reagent Co. (Shanghai, China). Na_2SO_3 and Na_2S (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used as the sulfur-containing species. At the optimized pH 6.2, they exist mainly at HSO_3^- and H_2S ($\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ for H_2SO_3 are about 1.9 and 7.2, while those for H_2S are about 6.9 and 14.1, respectively). In this work, for convenience, we nominate them as HSO_3^- and H_2S throughout the text, although they should not exist in these states at pH, other than 6.2. Other reagents were of analytical grade (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and used without any purification. Milli-Q water (18.2 M Ω ; Millipore Co, Billerica, USA) was used in all of the experiments.

Fluorescence measurements

Fluorescence spectra were acquired with a F-2700 spectrofluorometer (Hitachi High-Technology Corp, Japan). The fluorescence was measured in a quartz cell with a path length of 1 cm under excitation at 327 nm. SG at the specified concentration was added into the solution buffered with 50 mM PBS (0.1 M K^+) at the specified pH, and the resulting solutions were allowed to incubate for 30 min before the addition of CB[n]. Fluorescence measurements were measured at 20°C after incubating the resultant solution with HSO_3^- or other species for 30 min.

Absorption spectra measurements

Absorption spectra were determined with a UV2550 spectrophotometer (Shimadzu Corp., Japan), equipped with a temperature-controlled circulator (Julabo Labortechnik GmbH, Seelbach, Germany) at 20°C and a quartz cell with a path length of 1 cm.

^1H NMR experiments

^1H NMR experiments were acquired with a Bruker Avenice

600 MHz NMR spectrometer. Samples were prepared by dissolving SG in 0.5 mL D_2O (4 mM). After NMR scanning, 20 mM HSO_3^- was then added to allow incubation for 30 min before the NMR measurements.

Sample detection

Tap water and rainwater samples were determined using the standard addition method. The final SG and CB[8] concentrations were maintained at 1 and 5 μM , respectively. Into the water samples were added PBS buffer (50 mM, 0.1 M K^+ , pH 6.2) containing SG and CB[8] before a fluorescence measurement. Then, an appropriate Na_2SO_3 standard was added to allow incubation for 30 min before recording the fluorescence. The calibration curve was used to obtain the recovery and sample results.

Results and Discussion

In aqueous solution, SG exists in the iminium and alkanolamine forms with their populations dependent on the pH.^{20,29,30} As shown in Fig. 1A, increasing the solution pH (from 4.5 to 9.2) causes an increase in the alkanolamine emission band (F_{a}) as well as a decrease in the iminium emission band (F_{i}) of 1 μM SG because of an OH^- attack with the $\text{C6}=\text{N5}^+$ bond (Scheme 1).^{18,29,30} The F_{a} band at 409 nm and the F_{i} band at 565 nm can be obtained with excitation at 327 nm.²⁰ The fluorescence intensity at 409 nm as a function of the pH predicts a $\text{p}K_{\text{a}}$ of about 7.6 (Fig. 1D), which is in good agreement with previous reports.^{20,29,30} Such a large emission wavelength shift (156 nm) due to breakage of the conjugated π cycle (Scheme 1) is advantageous in developing novel sensors with an ideal contrast in signal response, although up to now, only the nucleophilic addition reaction of OH^- has been investigated. In this work, we tried to use this property to develop a fluorescent sensor for selective detection of HSO_3^- . To regulate the response behavior of SG towards HSO_3^- , we also investigated the supramolecular host-guest interaction of SG by complexation with cucurbit[n]urils (CB[n], $n = 5, 6, 7, 8$) at pH 6.2. SG mainly exists in the iminium form at this condition. We found that CB[8] cavity is

Fig. 1 Effect of the solution pH on the emission spectra of 1 μM SG in 50 mM PBS (0.1 M K^+) in the (A) absence and (C) presence of 5 μM CB[8]. (B) Fluorescence spectra of SG (1 μM) in 50 mM PBS (0.1 M K^+ , pH 6.2) upon increasing the CB[8] concentration. Inset: Fluorescence intensity at 544 nm upon increasing the CB[8] concentration and photographs under UV illumination in the (left) absence and (right) presence of 5 μM CB[8]. (D) Dependence of the fluorescence intensity at 409 nm (F_a) on the solution pH in the absence and presence of CB[8].

the best host in lighting up the SG fluorescence (Fig. S1), although CB[7] has also been reported to be able to encapsulate SG.^{31–33}

As shown in Fig. 1B, at pH 6.2, increasing the CB[8] concentration up to 6 μM shifts the emission band of SG (1 μM) from 565 to 544 nm, accompanying a final 12-fold fluorescence increase. This host-guest interaction can be confirmed by the solution color change under UV illumination (inset of Fig. 1B). This indicates that the CB[8] cavity provides a hydrophobic microenvironment to protect SG from attacking by water molecules and other species, since SG at pH 6.2 is positively charged, as confirmed by other SG analogues with a solvent polarity-sensitive fluorescence behavior.³⁴ pH-dependent experiments with CB[8] (Fig. 1C) show that the iminium form still remains, even increasing the solution pH to 9.2, suggesting a strong binding of the SG iminium form with CB[8] and inhibition of the nucleophilic interaction of OH^- to produce the alkanolamine form. For example, at pH 9.2, the fluorescence of the SG alkanolamine form in the presence of CB[8] is 2.4-fold lower than that obtained in the absence of CB[8]. Since CB[n] has a weak binding with the SG alkanolamine form³² and the fluorescence of the alkanolamine form is not strongly affected by CB[8], we can estimate that at pH 9.2, only 42% SG (totally 1 μM) is converted to the alkanolamine form in the presence of 5 μM CB[8]. Because the used PBS buffer can't be extended to a higher pH, we extrapolated the pK_a value of the CB[8]-bound SG to be about 9.4, which is about 1.8 pK_a unit higher than that obtained without CB[8]. However, a pK_a shift of 3.7 has been observed in a previous report for the SG encapsulation by CB[7] in water solution without a substantial amount of cation ions.³² This is caused by the high ion strength of 0.1 M K^+ used in this work thus to weaken the encapsulation binding with CB[n] due

to the competitive electrostatic binding of cation ions with the electronegative portals of CB[n].³⁵ On the other hand, this host-guest encapsulation will decrease the background fluorescence in developing a SG-based ratiometric sensor when operating in a weakly acidic solution at which SO_2 can exist dominantly as HSO_3^- (pK_{a1} and pK_{a2} for H_2SO_3 are about 1.9 and 7.2). For example, at pH 6.2, the presence of CB[8] leads to a 6.8-fold decrease in the fluorescence of the alkanolamine form (Fig. 1D). We thus used pH 6.2 as the optimal buffer condition to prevent the OH^- reaction with SG.

We then measured the fluorescence response of SG (1 μM) to HSO_3^- and H_2S at pH 6.2 with their concentrations up to 300 μM . As shown in Fig. 2A, the addition of HSO_3^- causes a decrease in the iminium band at 565 nm and an increase in the alkanolamine band, but appearing at 435 nm. This suggests a specific interaction of SG with HSO_3^- to produce a product different from the reaction occurring with OH^- (Scheme 1). Note that this 130 nm emission wavelength shift provides an ideal contrast in developing a ratiometric method for HSO_3^- detection, as confirmed by the clear color change under UV illumination (inset of Fig. 2A). The fluorescence ratio at 435 and 565 nm (F_a/F_i) is linear to the HSO_3^- concentration between 0 and 30 μM (Fig. 2E). The detection limit is estimated to be about 1.2 μM , assuming a signal-to-noise ratio of 3. However, addition of H_2S within the same concentration range similarly leads to the alkanolamine band emitting, but at 430 nm, and brings smaller F_a/F_i values (Fig. 2B). Within the linear response range, the response slope ($\Delta(F_a/F_i)$ vs. ΔC) for HSO_3^- is only 11-fold higher than that for H_2S (Fig. 2E). These facts suggest that HSO_3^- has a stronger nucleophilic addition reaction with SG compared to H_2S (Scheme 1), most likely because of the higher electron density of the sulfur atom in HSO_3^- .

Fig. 2 Fluorescence spectra of SG (1 μM) in 50 mM PBS (0.1 M K⁺, pH 6.2) upon increasing the concentration of (A, C) HSO₃⁻ or (B, D) H₂S in the (A, B) absence and (C, D) presence of 5 μM CB[8], respectively. Photographs under UV illumination in the absence (left) and presence (right) of HSO₃⁻ without and with CB[8] are shown in the inset of (A, 50 μM HSO₃⁻) and (C, 200 μM HSO₃⁻), respectively. Also shown are the F_a/F_i changes upon increasing the HSO₃⁻ or H₂S concentration (E) without and (F) with CB[8], respectively.

Fig. 3 Fluorescence spectra of SG (1 μM) and CB[8] (5 μM) with HSO₃⁻ alone (180 μM) and coexisting with H₂S.

To improve the response specificity of SG to HSO₃⁻, we then checked the fluorescence response of SG (1 μM) to HSO₃⁻ and H₂S in the presence of 5 μM CB[8]. As shown in Fig. 2C, the CB[8] addition causes a more noticeable increase and decrease in the fluorescence of SG at 435 and 544 nm in response to HSO₃⁻ at pH 6.2, although this host-guest encapsulation blunts the response with the linear range for the HSO₃⁻ response increasing up to about 200 μM (Fig. 2F). This suggests that this encapsulation can expand the HSO₃⁻ response range. The change in the solution color under UV illumination upon HSO₃⁻ addition becomes much more distinct (inset of Fig. 2C). The detection limit in this case is estimated to be about 16 μM, assuming a signal-to-noise ratio of 3. However, H₂S is much less efficient in decreasing the iminium band and increasing the alkanolamine band (Fig. 2D). Within the linear response range, the response slope ($\Delta(F_a/F_i)$ vs. ΔC) for HSO₃⁻ in the presence of CB[8] is 45-fold higher than that for H₂S (Fig. 2F). Furthermore, the coexistence of H₂S (up to 8 mM) with 180 μM

Fig. 4 ¹H NMR spectra of SG (4 mM) and its interaction with HSO₃⁻ (20 mM) in D₂O.

HSO₃⁻ only slightly increases the F_a/F_i value (Fig. 3). These facts demonstrate that the CB[8] encapsulation can improve the selectivity of the SG response to HSO₃⁻ against H₂S because of the stronger inhibition of the nucleophilic addition³² by CB[8] with the sulfur atom in H₂S that has a lower electron density than that in HSO₃⁻. Thus, less interference from H₂S is expected for the HSO₃⁻ detection. Note that upon addition of HSO₃⁻ or H₂S in the absence and presence of CB[8], the absorption band of SG almost exists at about 327 nm (Fig. S2), suggesting that the ratiometric sensor for the HSO₃⁻ detection can be operated at a single excitation wavelength.

¹H NMR was then used to further confirm the interaction of SG with HSO₃⁻. As shown in Fig. 4, the ¹H NMR chemical shifts of SG alone in D₂O can be assigned to 4.45 (N5-CH₃), 6.13 (C2-O-CH₂-O-C3), 6.35 (C7-O-CH₂-O-C8), 6.96 (H-1), 7.45–7.81 (H-4, H-9, H-10, H-11, H-12), and 9.30 (H-6).³²

Fig. 5 Fluorescence ratio changes of SG (1 μM) in the presence of (A) anions (HSO_3^- at 200 μM and others at 1 mM) and (B) cations (200 μM , EDTA 3 mM) in 50 mM PBS (pH 6.2, 0.1 M K^+) containing 5 μM CB[8]. Also shown are photographs of these solutions under UV illumination in the presence of (C) anions and (D) cations, respectively.

After the addition of 5 equivalent HSO_3^- , these chemical shifts changed to 2.69 (N5- CH_3), 5.53 (H-6), 5.94 – 6.04 (C2-O- CH_2 -O-C3 and C7-O- CH_2 -O-C8), 6.94 (H-1), and 7.10 – 7.68 (H-4, H-9, H-10, H-11, H-12), respectively. These data suggest that the two types of protons in N5- CH_3 and H-6 experience the largest chemical environment alteration by shifting to the high field in the ^1H NMR upon interaction with HSO_3^- , demonstrating that the electron cloud densities around these protons are increased. Therefore, we can conclude that the C6=N5 $^+$ group undergo a nucleophilic addition by HSO_3^- , as depicted in Scheme 1.

The effect of common anions and cations on the HSO_3^- response specificity was then examined. As shown in Fig. 5A, compared with the significant response for 200 μM HSO_3^- , representative anions of F^- , SO_4^{2-} , Cl^- , I^- , Br^- , NO_3^- , Ac^- , and H_2PO_4^- alone in solution at 1 mM still keep the F_a/F_i value at the background level. The coexistence of these anions with HSO_3^- has no obvious effect on the HSO_3^- response. Note that the reductive I^- is inefficient in interacting with SG. The HSO_3^- specificity over other anions can be discriminated by the naked eye under UV illumination (Fig. 5C). Furthermore, typical cations such as Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Al^{3+} , Ca^{2+} , Fe^{3+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , and Hg^{2+} alone and coexisted with HSO_3^- (each cation was at 200 μM and EDTA was added to avoid the direct interaction of cations with HSO_3^-) do not induce significant changes in the F_a/F_i value (Fig. 5B). The solution colors under UV illumination (Fig. 5D) also confirm the specificity for the HSO_3^- response.

Finally, we explored application of our method in detecting HSO_3^- using tap water and rainwater as the typical samples. The standard addition method was used to confirm the feasibility of our method. The recoveries of six samples were close to 100% (Table S1), demonstrating that our method can be used for the real sample analysis. Therefore, our method has potential applications for the selective detection of HSO_3^- in water samples.

Conclusions

In summary, we developed a novel fluorescent method for a selective HSO_3^- assay based on its nucleophilic addition reaction with SG. The reaction occurs at the C=N $^+$ group to bring a decrease in the SG iminium fluorescence and an increase in the alkanolamine fluorescence. Thus, a ratiometric fluorescence method can be established for HSO_3^- detection. Furthermore, the host-guest encapsulation with CB[8] is confirmed to be an efficient way to improve the detection selectivity of HSO_3^- against other species including, for example, H_2S . Other common anions and cations have no interference with the HSO_3^- response, suggesting a promising application of our method in real sample analysis. In this work, we first demonstrated the occurrence of the interaction of the natural benzophenanthridine alkaloid SG with HSO_3^- , and a ratiometric fluorescence method was developed with a large emission wavelength shift. Since SO_2 exists in cells and SG is usually used as an anti-cancer drug, our work also demonstrates the potential SG pharmacology by interaction with SO_2 derivatives.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21675142) and the National and Zhejiang Undergraduate Training Program for Innovation and Entrepreneurship (Grant No. 201810345017).

Supporting Information

Fluorescence spectra of the SG-CB[n] system in the absence and presence of HSO_3^- , and the sample analysis results. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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