An imine-based colorimetric chemodosimeter for the detection of hypochlorite (ClO^-) in aqueous media: its application in test strips and real water samples

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Abstract. A highly selective colorimetric chemodosimeter **ASAD**, (E)-2-((4-(diethylamino)-2-hydroxybenzylidene)amino)-5-methoxybenzenesulfonic acid, was readily synthesized and characterized. The probe **ASAD** could selectively recognize hypochlorite (ClO^-) through an oxidative cleavage of $\text{C}=\text{N}$ bond with a color change from yellow to colorless and detected it down to a low concentration of $0.95 \mu\text{M}$. Importantly, **ASAD** could be employed as a practical and efficient optical sensor for ClO^- in test strips and water samples. Moreover, the detection process of **ASAD** to hypochlorite was demonstrated by UV-vis spectroscopy, NMR titration and theoretical calculations.

Keywords. Hypochlorite; colorimetric; chemodosimeter; theoretical calculations.

1. Introduction

Reactive oxygen species (ROS) play a significant role in pathological and physiological processes.^{1–5} ClO^- (hypochlorite), one of the significant ROS, is beneficial for our health because it has effective anti-inflammatory and antibacterial properties.^{6–9} Moreover, ClO^- is largely used as a disinfectant or a bleaching chemical.^{10–13} However, excessive levels of ClO^- in an organism are harmful to cellular components, thus resulting in several diseases like inflammation and cardiovascular disease.^{14–18} Therefore, the development of practical and selective sensors capable of monitoring the amount of ClO^- in both living organisms and environment is needed. So, a lot of effort has been devoted to develop ClO^- sensors in the past decade, with various functional moieties like thioether,¹⁹ thioester,^{20–22} thione,^{23,24} *p*-methoxy,^{25,26} hydrazide,^{27,28} oxime,^{29,30} selenide,^{31,32} and $\text{C}=\text{N}$ bond.^{33–35} Chemodosimeter is a molecular probe that recognizes analytes with the irrevocable process.^{36–40} It has the advantage of high selectivity with little interference of other anions, so it has been frequently studied in anion sensing area.^{41–45}

Despite its advantage, it still encounters some problems such as poor detection limit and slow reaction in aqueous media. To surmount the difficulties, we designed sensor **ASAD** having readily cleavable imine moiety ($\text{C}=\text{N}$), which could recognize ClO^- with a low detection limit and fast reaction time.

Herein, we present a novel colorimetric chemodosimeter **ASAD** to monitor the level of hypochlorite (ClO^-). **ASAD** showed high selectivity toward ClO^- among various anions and ROS with the color change (yellow to colorless). The distinct color change can be directly visualized through naked-eye and test strip. In addition, sensor **ASAD** showed a fast reaction and great sensitivity to hypochlorite with a low detection limit ($0.95 \mu\text{M}$). Moreover, the sensing process of **ASAD** toward ClO^- was demonstrated with the diverse spectroscopic investigations and calculations.

2. Experimental

2.1 Chemicals and instruments

Chemicals were commercially provided. A LCQ_{TM} quadrupole ion trap machine and a Varian spectrometer were

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employed to gain ESI-MS, ^1H and ^{13}C NMR spectra. Perkin Elmer spectrometers (2S UV/Vis and LS45) were employed for absorption and fluorescence measurements.

2.2 Synthesis of chemodosimeter ASAD

Methanol (10 mL) was chosen to dissolve 2-amino-5-methoxybenzenesulfonic acid (1×10^{-3} mol, 0.203 g). Then, 4-(diethylamino)salicylaldehyde (**DAS**, 1.2×10^{-3} mol, 0.232 g) was added dropwise to the solution while shaking for 3 h. The yellow powder was filtered and washed with chilly ethyl alcohol and diethyl ether. **ASAD** obtained was 0.273 g (86.8%). ^1H NMR (DMF- d_7 , ppm): δ 13.48 (d, $J = 15.2$ Hz, 1H), 13.15 (s, 1H), 9.13 (d, $J = 14.8$ Hz, 1H), 8.02 (d, $J = 8.8$ Hz, 1H), 7.84 (d, $J = 9.2$ Hz, 1H), 7.66 (d, $J = 2.8$ Hz, 1H), 7.30 (m, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.57 (s, 1H), 4.04 (s, 3H), 3.79 (m, 4H), 1.42 (t, $J = 6.8$ Hz, 6H), ^{13}C NMR (DMSO- d_6 , ppm): δ 163.66, 157.63, 156.09, 154.59, 139.52, 139.33, 127.82, 119.70, 116.18, 112.07, 106.98, 105.14, 95.80, 55.70, 44.85, 12.48. ESI-MS (**ASAD**- $\text{H}^+ + 2\text{MeOH}$): calcd, 441.17 (m/z); found, 441.40.

2.3 Chromogenic sensing of ClO^-

2.3a UV-vis titration: DMF (N,N-dimethylformamide, 1.0 mL) was chosen to dissolve **ASAD** (5×10^{-6} mol, 1.9 mg). 12.0 μL (5×10^{-3} M) of **ASAD** was diluted in 2.988 mL of PBS buffer (10 mM, pH 7.4) to give 0.02 mM. NaClO (5×10^{-4} mol, 256 μL) was dissolved in distilled water (5.0 mL). 0.3–11.4 μL (0.1 M) of the ClO^- were added to separate **ASAD** solutions (0.02 mM, 3 mL). UV-vis spectra of the solutions were recorded with UV-vis spectrometer.

2.3b Competition experiment: 10.8 μL (0.1 M) of a ClO^- stock solution was diluted in 2.966 mL of PBS to give 18 equiv. 10.8 μL (100 mM) of diverse oxidants and anions (NO_2^- , OH^- , Cl^- , CN^- , OAc^- , F^- , AcOOH , H_2PO_4^- , Br^- , BzO^- , $t\text{-BuOOH}$, N_3^- and H_2O_2) was transferred to ClO^- solution. 12.0 μL (5×10^{-3} M) of the **ASAD** was added into the solution above prepared to make 20 μM . UV-vis spectra of the solutions were recorded with UV-vis spectrometer.

2.3c pH effect: Buffers of pH = 6–8 were provided by mixing HCl and NaOH in the PBS buffer. Sensor DMF (2 mL) was chosen to dissolve **ASAD** (1×10^{-2} mol, 3.8 mg). 12.0 μL (5×10^{-3} M) of **ASAD** was diluted in 2.988 mL of PBS buffer to give 20 μM . Then 10.8 μL (0.1 M) of a ClO^- stock was added to each **ASAD** (0.02 mM). UV-vis spectra of the solutions were recorded with UV-vis spectrometer.

2.3d ^1H NMR titration: To three NMR cuvettes of **ASAD** (0.0025 mmol, 0.95 mg) dissolved in DMF- d_7 (500 μL) were added three different equivalents (0, 1 and 5) of NaClO dissolved in D_2O . Their ^1H NMR spectra were recorded with a Varian spectrometer.

2.3e Analysis of ClO^- : UV-vis analyses of ClO^- in water samples were performed by adding 24 μL (0.005 M) of **ASAD** and 0.60 mL (0.1 M) of a stock PBS buffer to a 5.376 mL sample. Their UV-vis spectra were recorded with UV-vis spectrometer.

2.3f Test strips: **ASAD** test strips were made by soaking filter papers into **ASAD** (5×10^{-3} M), and dried in vacuum. **ASAD** test strips were treated with 3 mM of various oxidant and anions (ClO^- , NO_2^- , OH^- , Cl^- , CN^- , OAc^- , F^- , AcOOH , H_2PO_4^- , Br^- , BzO^- , $t\text{-BuOOH}$, N_3^- and H_2O_2). After dried at room temperature, the photograph of each test strip was taken.

2.3g Theoretical calculations for ASAD and DAS: Energy-optimized structures of **ASAD** and **DAS** were calculated with DFT using Gaussian 09W program. The hybrid functional was 3-parameter, Becke, Lee-Yang-Parr (B3LYP). The basis set was 6-31G(d,p).^{46–49} Since imaginary frequency was not shown in optimized forms of **ASAD** and **DAS**, their geometries displayed local minima. Solvent effect of water was dealt with CPCM.^{50,51} With the optimized structures of **ASAD** and **DAS**, the UV-vis transition investigations were performed using TD-DFT method with thirty lowest singlet states.

3. Results and discussion

ASAD was readily produced by the condensation of 2-amino-5-methoxybenzenesulfonic acid with 4-(diethylamino)salicylaldehyde in methanol (yield 86.8%), as depicted in Scheme 1. It was identified by ^1H NMR, ESI-MS and ^{13}C NMR (Figure S1, Supplementary Information).

3.1 Colorimetric and spectral studies of ASAD with ClO^-

To investigate the sensing properties of **ASAD** toward various anions including some oxidants (ClO^- , NO_2^- , OH^- , Cl^- , CN^- , OAc^- , F^- , AcOOH , H_2PO_4^- , Br^- , BzO^- , $t\text{-BuOOH}$, N_3^- and H_2O_2), we conducted selectivity test in PBS buffer (Figure 1). Some oxidants such as AcOOH , $t\text{-BuOOH}$ and H_2O_2 were also tested because ClO^- can act as an anion as well as an oxidant. Addition of 18 equiv. of ClO^- induced a great spectral change with the disappearance of the absorbance at 413 nm, accompanied by a noticeable color change from yellow to colorless. On the other hand, none of the other oxidants and anions led to any significant change. These observations signified that **ASAD** had outstanding selectivity to ClO^- over various anions and oxidants.

UV-vis titrations of **ASAD** toward ClO^- were conducted to understand the photophysical properties.

Scheme 1. Synthesis of **ASAD**. **Figure 1.** (a) Absorbance and (b) color changes of **ASAD** (0.02 mM) with the addition of diverse oxidants and anions (18 equiv.).

The reaction of **ASAD** with varied concentrations of hypochlorite was shown in Figure 2, which exhibited the two-step change in the spectra (Figure 2(a)). In the first step, the absorbance band around 413 nm decreased consistently, and then the absorbance of 500 nm continuously increased with a redshift of 87 nm, resulting in a color change from yellow to orange (Figure 2(b)). In the second step, the absorbance of the visible region gradually decreased up to 18 equiv. of ClO^- with a color change from orange to colorless. Based on these results, we assumed that **ASAD** would react with ClO^- through two-step mechanisms. In the first process, there was the oxidative addition of ClO^- to the $\text{C}=\text{N}$ bond and in the second process, the imine bond was cleaved to produce **DAS** (Scheme 2).

To obtain a quantitative appraisal of **ASAD** toward ClO^- , a calibration experiment was carried out in the scope of 0–40 μM and a suitable linear relationship was observed ($R^2 = 0.9994$, $n = 3$, Figure 3). The detection limit of 0.95 μM was obtained on the basis of $3\sigma/\text{slope}$,⁵² which is the second lowest among those for formerly addressed colorimetric sensors for ClO^- in a near-perfect aqueous media, to date (Table S1, Supplementary Information). To assess the feasibility of **ASAD** with ClO^- in water samples, drinking and tap samples were selected and analyzed three times (Table 1). Suitable numbers for relative standard deviations (R.S.D.)

Figure 2. (a) Absorbance changes of **ASAD** (0.02 mM) with ClO^- (0–19 equiv.). (b) Absorbance changes of **ASAD** (0.02 mM), extracted from the range of 0–4 equiv. of ClO^- in (a). (c) Absorbance changes of **ASAD** (0.02 mM), extracted from the range of 5–19 equiv. of ClO^- in (a).

Scheme 2. Probable sensing mechanism of ClO^- by **ASAD**.

Figure 3. Detection limit based on the intensity (413 nm) of **ASAD** as a function of the concentration of ClO^- . $[\text{ASAD}] = 20\mu\text{M}$ and $[\text{ClO}^-] = 0\text{--}40\mu\text{M}$.

and recoveries were obtained. These outcomes indicated that **ASAD** had a good potential for determination of hypochlorite levels in the environment.

In order to explore the sensing process of **ASAD** toward ClO^- , ^1H NMR titrations were performed (Figure 4). Upon the addition of ClO^- (1.0 equiv.) to **ASAD**, the H_3 signal of the diethyl group and H_7 signal of the imine moiety diminished, and the new $\text{H}_{3'}$ signal (1.2 ppm) began to appear. With further addition of ClO^- (5.0 equiv.) to **ASAD**, the H_7 peak (9.1 ppm) gradually

decreased and the new $\text{H}_{7'}$ peak (10.5 ppm) began to appear. The result indicated that the imine bond ($\text{C}=\text{N}$) was cleaved by strong oxidizing agent ClO^- to produce **DAS**, which was proved by ESI-MS (Figure 5). Positive-ion MS of **ASAD** with ClO^- showed that the peak ($m/z = 257.10$) is assignable to **DAS** + Na^+ + MeCN [$m/z = 257.13$, calcd]. Based on the UV-visible and ^1H NMR titrations, and ESI-MS, the conceivable detecting process of ClO^- was proposed (Scheme 2).

The selectivity of **ASAD** for ClO^- with the various oxidants and anions was examined through competitive studies (Figure S2, Supplementary Information). Most of the oxidants and anions did not interfere with the sensing of hypochlorite by **ASAD**. However, AcOOH inhibited about 50% of the absorbance, and H_2PO_4^- , H_2O_2 , CN^- and NO_2^- showed inhibition of more than 80%.

Moreover, the pH effect on sensing capability for ClO^- was studied in a pH scope of 6–8 (Figure S3, Supplementary Information). **ASAD** with ClO^- showed a prominent color change between pH 6 and 8. These consequences indicated that ClO^- can be obviously detected by the UV-visible measurements or naked eye using **ASAD** over physiological pH range. For practicable application, test strips were prepared by coating filter paper with **ASAD** (Figure 6). When the strips were exposed to diverse oxidants and anions, an evident color change appeared only with ClO^- in PBS buffer. To our surprise, this observation is the first case that a sensor

Table 1. Determination of ClO^- ^a.

Sample	ClO^- added (μM)	ClO^- found (μM)	Recovery (%)	R.S.D. (n=3) (%)
Tap water	0.0	0.0	-	-
	20.00	19.82	99.09	1.35
Drinking water	0.0	0.0	-	-
	20.00	20.02	100.08	0.50

^aConditions: $[\text{ASAD}] = 20\mu\text{mol/L}$ in PBS buffer.

Figure 4. ^1H NMR titrations of ASAD with ClO^- (0, 1.0 and 5.0 equiv).

Figure 5. Positive ESI-MS of ASAD (1×10^{-4} M) with ClO^- (1 equiv).

Figure 6. Photographs of ASAD-test strips immersed in various oxidants and anions.

Figure 7. Optimized forms of (a) ASAD and (b) DAS.

could detect ClO^- *via* the test strip in a near-perfect aqueous media, to date (Table S1, Supplementary Information). These results meant that the strip might have practical application for rapid and easy detection of ClO^- .

3.2 Theoretical calculations

To demonstrate the detection mechanism of **ASAD** to hypochlorite, calculations were achieved. The optimized forms of **ASAD** and **DAS** were calculated using B3LYP as a hybrid functional and 6-31G(d,p) as a basis set (Figure 7). The oscillator strengths and major transition energies of the two compounds are shown in Figures S4 and S5, Supplementary Information. The MO of **ASAD** turned out to be the HOMO $\rightarrow$ LUMO transition at the first lowest excited state (417.41 nm, Figures S4 and S6, Supplementary Information). This transition showed ICT (intramolecular charge transfer). The MO of **DAS** also showed the HOMO $\rightarrow$ LUMO transition at the second lowest excited state (299.75 nm, Figures S5

and S6, Supplementary Information). The electron density of both HOMO and LUMO was evenly scattered over the **DAS** showing ICT. Moreover, the increased energy gap of **DAS** was consistent with the blue shift of the UV-visible spectrum (Figure S5, Supplementary Information). Since the blue-shifted spectrum was not observed in the visible region, this calculation was consistent with the color change from yellow to colorless. The results of the theoretical calculations further confirmed the conceivable detection process in Scheme 2.

4. Conclusions

A new selective colorimetric probe **ASAD** was readily synthesized based on the combination of 2-amino-5-methoxybenzenesulfonic acid and 4-(diethylamino) salicylaldehyde. Sensor **ASAD** exhibited the outstanding detection to hypochlorite with the low detection limit ($0.95 \mu\text{M}$), which is the second lowest among those for formerly addressed colorimetric sensors for ClO^- in a near-perfect aqueous media. Oxidative cleavage of the

C=N bond in **ASAD** by hypochlorite resulted in colorimetric sensing from yellow to colorless. Its excellent sensing ability could be applied in real samples and test strips. Importantly, **ASAD** could, for the first time, detect ClO^- via the test strip in a near-perfect aqueous media, to date. Therefore, **ASAD** has a great potential application for recognizing ClO^- .

Supplementary Information (SI)

Supplementary data (Table S1 and Figures S1–S6) associated with this article is available at www.ias.ac.in/chemsci.

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