Colorimetric Chemosensor for Sulfide Anion Detection Based on Symmetrical Nitrovanillin Azine

Diana Lestari, Tutik Dwi Wahyuningsih, and Bambang Purwono*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

*** Corresponding author:**

email: purwono.bambang@ugm.ac.id

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Abstract: *The nitrovanillin azine (**NA**) has been successfully synthesized and examined as a colorimetric chemosensor for sulfide anion detection. The **NA** was synthesized using two steps reaction. Vanillin was reacted with concentrated nitric acid to form 5-nitrovanillin (**NV**) then the **NV** was condensed with hydrazine hydrate to produce the **NA**. The **NA** was obtained and fully elucidated by FTIR, ^{1}H-NMR, ^{13}C-NMR, and GC-MS spectrometer. The **NA** activity for anionic chemosensor was then carried out on several anions such as F^-, Cl^-, Br^-, I^-, S^{2-}, CN^-, HCO_3^-, AcO^-, H_2PO4^-, N_3^-, NO_2^-, SCN^-, ClO_3^-, and NO_3^-. The chemosensor tests showed **NA** was only selective for S^{2-} in DMF:HEPES buffer (9:1, v/v, 10 mM, pH = 7.4) giving color change from light yellow to dark green. The LOD value was 1.43×10^{-5} M and the interaction model of **NA**-S^{2-} indicated deprotonation mode between the -OH group with sulfide anion in a ratio of 1:1. The **NA** chemosensor can be applied for qualitatively analysis of sulfide anion using filter paper strips and quantitatively analysis of sulfide anion in tap water.*

Keywords: *5-nitrovanillin; hydrazine; azine; colorimetric; chemosensor*

■ INTRODUCTION

Hydrogen sulfide (H_2S) is one of the most toxic, corrosive, and flammable gases with the characteristic odor of rotten eggs. In high concentrations, this gas causes serious problems such as hypertension, diabetes, liver cirrhosis, chronic kidney, Down Syndrome, and Alzheimer's disease [1-3]. According to the National Institute of Occupational Safety and Health, the concentration of H_2S harmful to life or health is up to 150 ppm, and the recommended exposure limit is 10 ppm for a maximum duration of 10 min [4]. Hydrogen sulfide is also involved in pathological and physiological functions, including inhibition of insulin signaling, regulation of inflammation, and relaxation of the smooth muscle of blood vessels [5]. Several methods for detecting sulfides are potentiometry [6], chromatography [7], and electrochemistry [8]. However, the use of those instruments requires a complicated sample preparation, expensive, and difficult to operate. Therefore, it is necessary to develop simple, efficient, and faster methods with a high level of sensitivity and selectivity. The colorimetric chemosensor is the most often used to detect anions through color changes [9]. Visually, the detection process is more profitable because it can provide qualitative and quantitative information in a relatively short time [10], and it is possible to be seen directly with the naked eye. This method is not expensive and easy to operate their instruments [11].

Chemosensor compounds have two main parts: signal site in the form of chromophore groups acting as color carrier such as azine (RHC=N-N=CHR) [12], and binding sites such as -OH playing a role in interacting with anions through hydrogen bonding or deprotonation [13]. Research for anion chemosensor in recent years continues to grow. Acetophenone azine derivative has been synthesized as a colorimetric and fluorescence sensor to detect CN^-, F^-, and AcO^- in DMSO [14]. Azines from vanillin and 2-hydroxy-5-phenylazo-benzaldehyde have been used as a colorimetric sensor of S^{2-} anion in DMF: HEPES (v/v = 9:1, 10 mM HEPES, pH = 7.4) [15-16]. Another unsymmetrical azine of dicyanoisophorone-

based derivatives has been designed as a colorimetric and fluorescence of Cu^{2+} toward S^{2-} in DMSO/HEPES buffer (v/v = 2:1, 20 Mm HEPES, pH = 7.4) [17].

In this study, we synthesized the nitrovanillin azine (**NA**) from vanillin as a sulfide anion colorimetric chemosensor. Investigation for **NA** colorimetric chemosensor was carried out by sensing properties measurement to various anion, time interaction, anion interferences, pH effect, reversibility, and LOD. A qualitative test of sulfide anion has also been performed with a filter paper strip, while a quantitative analysis of sulfide anion in tap water shows the application of **NA**.

■ EXPERIMENTAL SECTION

Materials

Materials used for the synthesis were vanillin, nitric acid 37%, dichloromethane (DCM), hydrazine hydrate 80%, methanol, ethanol, chloroform, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), HEPES buffer solution (HBS) in deionized water, acetone, acetonitrile, aquadest, sodium fluoride, sodium chloride, sodium bromide, sodium iodide, sodium sulfide, sodium cyanide, sodium hydrogen carbonate, sodium acetate, sodium dihydrogen phosphate, sodium azide, sodium nitrite, potassium thiocyanate, potassium chlorate, and potassium nitrate. All materials used have a Merck p.a quality, while deionized water is from Onemed.

Instrumentation

The characteristics of the synthesized compounds were carried out using a melting point determination apparatus (Electrothermal-9100), FTIR spectrophotometers (Shimadzu Prestige-21), ^{1}H-NMR (Agilent, 500 MHz and JEOL JNM ECA-500, 500 MHz), ^{13}C-NMR (Agilent, 125 MHz), GC-MS and DI-MS (Shimadzu QP-2010S). The color change was measured using a UV-Vis spectrophotometer (Shimadzu UV-1800).

Procedure

Synthesis of 5-nitrovanilin (5-NV)

The 5-nitrovanillin (**5-NV**) was synthesized based on previous methods [18]. Vanillin (13.79 g, 70 mmol) was dissolved in 55 mL of dichloromethane (0–5 °C) and 12 mL of HNO_3 was added dropwise at 0–5 °C. The reaction mixture was stirred at room temperature for 20 min and then cold distilled water (25 mL) was added and left for 2 h. Subsequently, the solid was filtered and recrystallized with ethanol. The synthesized product was obtained as a pale-yellow powder in yield of 72.1% (m.p. 176–178 °C). FTIR (KBr) (cm^{-1}): 3209 (-OH group), 3078 (Csp^2-H), 2887 (Csp^3-H), 1681 (C=O), 1543 (-NO_2), 1612 and 1465 (C=C aromatic), 1111 and 1049 (C-O-C). *m/z* [M^+] = 197.

Synthesis of nitrovanillin azine (NA)

The synthesis of **NA** compound is based on a previous method with some modifications [15]. The **5-NV** (0.390 g, 1 mmol) was dissolved in 25 mL of ethanol and mixed with (0.5 mmol) hydrazine hydrate 80% in 5 mL of ethanol. The reaction mixture was stirred at room temperature for overnight and the progress of reaction was monitored by TLC. The solid was filtered and washed with ethanol several times and then crystallized with ethanol:DMSO (2:1). The product was obtained as a yellow solid in yield of 76.14% (m.p. 293–394 °C). FTIR (KBr) (cm^{-1}): 3448 (-OH group), 3078 (Csp^2-H), 2947 (Csp^3-H), 1627 (-C=N-), 1543 (-NO_2), 1472 (C=C aromatic), 1273 (C-O-C). *m/z* [M^+] = 390. ^{1}H-NMR (500 MHz, DMSO-d_6) (δ) (ppm): 3.96 (3H, s, OCH_3), 7.74 (1H, s, ArH), 7.96 (1H, d, ArH), 8.71 (1H, s, -CH=N-), 11.16 (1H, s, ArOH). ^{13}C-NMR (δ) (ppm): 56.69 (OCH_3), 112.73 (C_{aryl}), 118.19 (C_{aryl}), 124.10 (C_{aryl}), 137.18 (C_{aryl}-NO_2), 145.72 (C_{aryl}-OH), 150.03 (-C=N-), 160.10 (C_{aryl}-OCH_3).

Study of NA selectivity as anion chemosensor

A solution of **NA** (2×10^{-5} M) was prepared in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) and solution of anion (0.2 M) such as F^-, Cl^-, Br^-, I^-, S^{2-}, CN^-, HCO_3^-, AcO^-, $H_2PO_4^-$, N_3^-, NO_2^-, SCN^-, ClO_3^-, and NO_3^- in HEPES Buffer Solution (HBS). The 4 mL of **NA** were placed in a cuvette and each (150 µL) anion solution was added. The color change was recorded and determined with a UV-Vis spectrophotometer.

Study of competition of sulfide anions with different anions

A solution of **NA** (2×10^{-5} M) was prepared in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) and

different anion solutions with a concentration of 0.2 M in HBS. The 4 mL of **NA** were put in a cuvette and different anions (0.2 M, 100 µL) of F^-, Cl^-, Br^-, I^-, CN^-, HCO_3^-, AcO^-, H_2PO4^-, N_3^-, NO_2^-, SCN^-, ClO_3^-, and NO_3^- were added, then into each mixture added S^{2-} (100 µL). Color changes were recorded and monitored at a wavelength of 613 nm.

Sensitivity study of NA as a sulfide anion sensor

A solution of **NA** (2×10^{-5} M) was prepared in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) and a solution of S^{2-} (0.2 M) in HBS. The 4 mL of **NA** was put in a cuvette and added S^{2-} (0–100 µL). The color change for each addition of S^{2-} was recorded and monitored at a wavelength of 613 nm. Determination of detection limit using the 3σ/m equation [19].

Study of interaction time of NA-sulfide anions

The 4 mL of **NA** solution (2×10^{-5} M) was prepared in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) and a solution of S^{2-} (0.2 M, 115 µL) was added in HBS. Changes in UV-Vis absorbance were monitored at wavelengths of 613 nm with different time intervals at room temperature.

Reversibility study of NA toward sulfide anions

The 4 mL of **NA** solution (2×10^{-5} M) was prepared in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) and a solution of S^{2-} (0.2 M, 116 µL) was added in HBS followed by the addition of HCl (2 M, 23 µL). Changes in UV-Vis absorbance were monitored at wavelengths of 613 nm before and after adding S^{2-} and HCl several times with different time intervals at room temperature.

pH Dependent study of NA toward sulfide anions

A solution of **NA** (2×10^{-5} M) was prepared in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 3, 5, 7.4, 9 and 11) and a solution of S^{2-} (0.2 M) in HBS. The 4 mL of **NA** with various pH was placed in a cuvette and added S^{2-} (150 µL). Changes in UV-Vis absorbance were monitored at wavelengths of 613 nm before and after the addition of S^{2-}.

Determination of NA-S^{2-} interaction through Job's Plot

A solution of **NA** in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) and solution of S^{2-} in HBS were prepared in a constant concentration of 7×10^{-5} M. Host-Guest solution comparison (1:9–9:1) were prepared by mixing of 0.4–3.6 mL of **NA** solution (Host) with 3.6–0.4 mL of S^{2-} (Guest) with a total solution of 4 mL. Changes in UV-Vis absorbance were monitored at wavelengths of 613 nm and plotted as [G]/[H] vs absorbance.

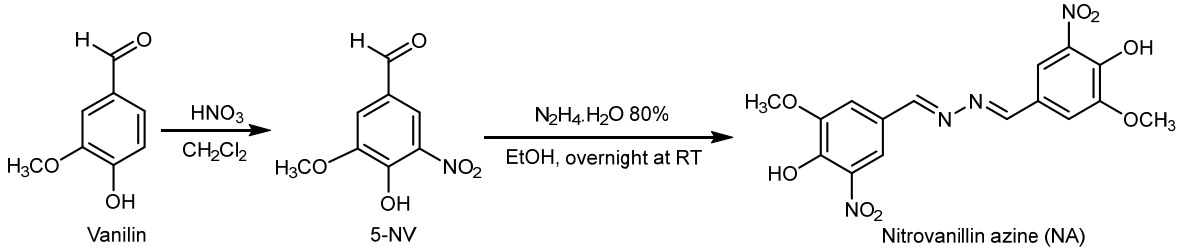
Filter paper strip study of NA toward sulfide anions

Filter paper strip (Whatman no. 42) with a size of 1 × 3 cm were immersed in a solution of **NA** 1×10^{-3} M in DMF:HBS (9:1, v/v, 10 mM HEPES, pH = 7.4) for 2 h. The paper strip was dried in an oven, and then two drops of S^{2-} solution (0.2 M) in HBS were added to the paper strip and allowed to react. Color change was recorded visually and under a 366 nm UV lamp.

■ RESULTS AND DISCUSSION

Chemosensor **NA** was synthesized by condensation reaction between **5-NV** with 80% hydrate hydrazine (Scheme 1) and purified through recrystallization from a solvent mixture of ethanol:DMSO (2:1) to produce a golden yellow solid. All products of synthesis are agreed with spectroscopy data.

Chemosensor **NA** has a binding site in the form of phenol groups that can interact strongly with anions through the hydrogen bond interaction. Here, the -OH group can be deprotonated with strong basic anions such



Scheme 1. Schematic formation of the reaction of **NA** Chemosensor

as CN^-, HCO_3^-, and AcO^- [20]. Sulfide anion also has basic properties that allow the same deprotonation mechanism. Hydrogen sulfide (H_2S) dissolves in water and dissociates to form H^+, HS^- and S^{2-}. Under physiological conditions, it forms about 20% as H_2S and 80% as HS^-/S^{2-}. In this study, sulfide anion (S^{2-}) is a mixture of $H_2S + HS^- + S^{2-}$ in solution [21].

Selectivity and Sensitivity of NA toward S^{2-}

Chemosensor **NA** in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4) has interacted with different anions such as F^-, Cl^-, Br^-, I^-, S^{2-}, CN^-, HCO_3^-, AcO^-, $H_2PO_4^-$, N_3^-, NO_2^-, SCN^-, ClO_3^-, and NO_3^-. The color changes were recorded and confirmed using a UV-Vis spectrophotometer. The addition effect of each anion showed that only the S^{2-} anion gave a color change from light yellow to dark green, whereas other anions did not give a significant color change. The absorbance spectra of **NA** showed two peaks at 388 and 459 nm. After addition of S^{2-} showed a bathochromic shift with the appearance of a new absorbance at 613 nm. This shift indicated the interaction of **NA** with S^{2-}. The phenol group of **NA** experienced deprotonation and then followed by delocalization of π electrons to produce a color change (Fig. 1) and emerging wavelength at λ_{max} 613 nm (Fig. 2).

Detection Limit Calculation

The **NA** sensitivity was confirmed using a UV-Vis titration. Changes in UV-Vis absorbance after the addition of S^{2-} (0–5 mM) in DMF:HBS showed an increase in absorbance with increasing S^{2-} concentration at λ_{max} 613 nm (Fig. 3(a)).

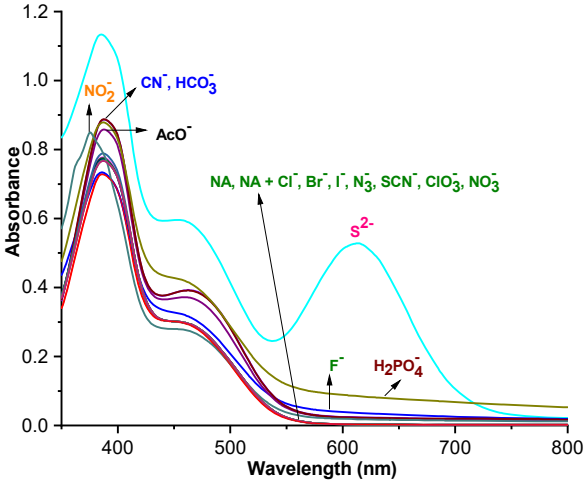


Fig 2. UV-Vis absorbance spectra of **NA** (2×10^{-5} M) with several anions in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4)

Fig 1. Color change of **NA** solution (2×10^{-5} M) with several anions

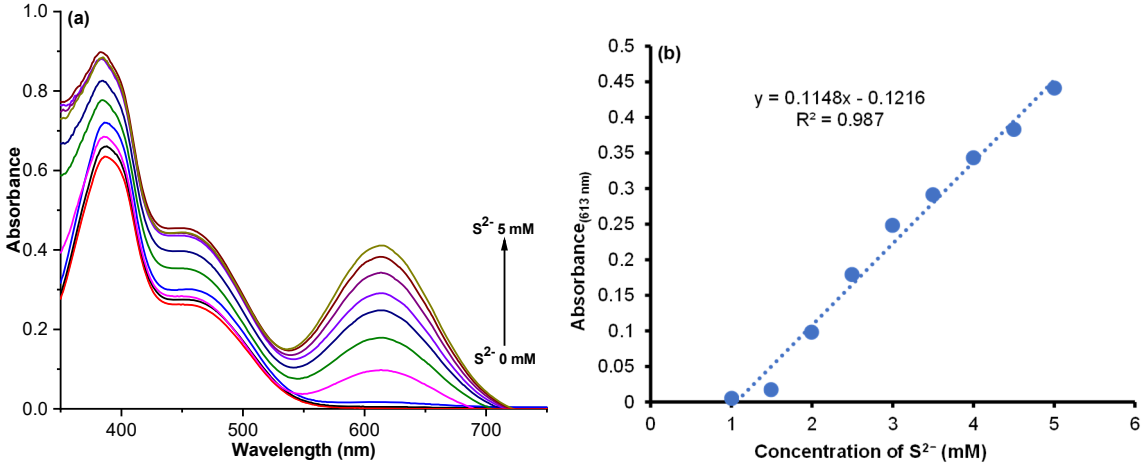


Fig 3. (a) Absorbance spectra of **NA** (2×10^{-5} M) after the addition of concentration variations S^{2-} and (b) Linear regression curve of **NA** with S^{2-}

The calculation of the detection limit used equation 3σ/m, where the σ is the standard deviation obtained from an empty signal without S^{2-} and m is the slope value of the calibration curve [19]. The ratiometric calibration curve has an R^2 of 0.987 (Fig. 3(b)), so the detection limit value (LOD) S^{2-} is 1.43×10^{-5} M (14.3 μM). This **NA** value is smaller than previous LOD values reported by Kaushik et al. [15] and Rokhmah et al. [16].

Competition Study with Other Anions

Examination of possible interference S^{2-} with other anions such as F^-, Cl^-, Br^-, I^-, CN^-, HCO_3^-, AcO^-, $H_2PO_4^-$, N_3^-, NO_2^-, SCN^-, ClO_3^-, and NO_3^- was studied. The results showed that almost all other anions have no interference effect in detecting S^{2-} anions except for CN^- and HCO_3^- (Fig. 4). These anions, CN^- and HCO_3^- are strong bases which interfere sulfide detection process [22]. Sulfide with CN^- and HCO_3^- competes with each other in interacting with the binding site of the chemosensor. Therefore, there is a slight increase in absorbance. This indicates that S^{2-} is not bound to the **NA** binding site due to the presence of CN^- and HCO_3^-, which causes no color change to occur.

Study of Interaction Time Effect of NA-S^{2-}

The study of the interaction time effect of **NA**-S^{2-} was monitored at λ_{max} 613 nm for 30 min (Fig. 5). The measurement results showed that the absorbance change at the peak of 613 nm occurred within one minute after the addition of S^{2-} and reached a maximum absorbance in 15 min and then decreased over time. The absorbance decreases occurred because the S^{2-} was in another form after 15 min. This study confirmed that **NA** toward S^{2-} has a reasonably fast response.

Reversibility Study

The study of **NA** reversibility was examined by adding S^{2-} followed by the addition of a dilute acid solution of HCl (2 M) at λ_{max} 613 nm. Absorbance at λ_{max} 613 nm is a form of **NA** deprotonation by S^{2-}, and then after the addition of dilute acid, the absorbance at λ_{max} 613 nm is lost (**NA** is not deprotonated). Based on the absorbance at λ_{max} 613 nm, **NA** chemosensor can be used as a sulfide sensor with repeatability for up to four cycles (Fig. 6). This shows that **NA** has good reversibility to S^{2-} and H^+ ions.

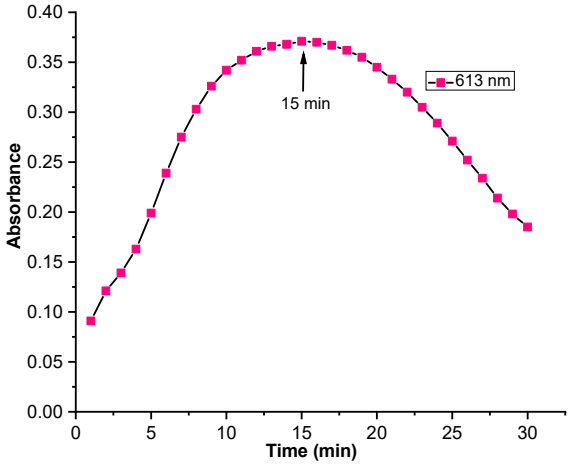


Fig 5. Interaction time and absorbance relationship curve at λ 613 nm of **NA** (2×10^{-5} M) to S^{2-}

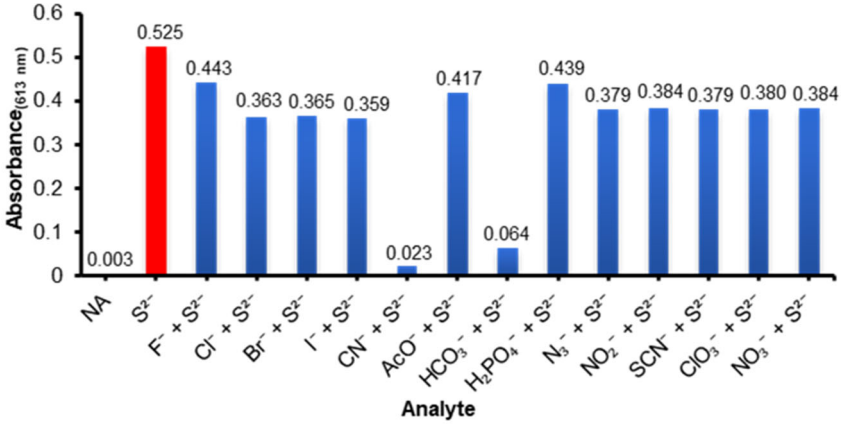


Fig 4. Bar diagram of the competition of several anions with S^{2-}

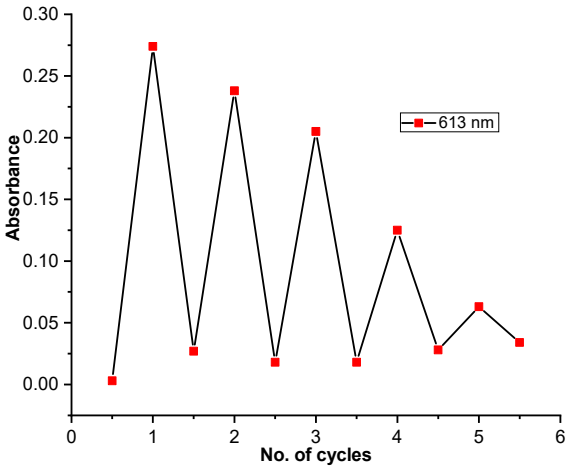


Fig 6. Reversibility absorbance spectra of **NA** with S^{2-} after the addition of HCl (2 M)

pH Effect Study

The pH effect in DMF:HEPES buffer (9:1, v/v, 10 mM HEPES, pH = 3, 5, 7, 4, 9, and 11) was carried out to determine the feasibility of working sensor at different pH. The UV-Vis spectra before the addition of S^{2-} showed two absorptions at 393 and 464 nm for pH of 7.4, 9, and 11. While at pH 3 and 5 produced absorptions at 336 and 337 nm, respectively (Fig. 7(a)). After the addition of S^{2-} at a pH of 7.4 produced the highest maximum absorbance at 613 nm, while at pH 9 and 11, there was no color change and wavelength shifts (Fig. 7(b)).

This shows that **NA** works effectively to detect S^{2-} at a solvent pH 3–8 because the main sulfide species at an acidic pH is H_2S, and pH > 7 is dominant in the form of HS^- from the equilibrium of the S^{2-} species from the salt solution which allows to bind to the **NA** binding site [23]. At pH 9–11, H_2S is in the form of HS^-. The presence of excess HS^-causes higher basicity so that the sulfide interaction with the **NA** binding site does not occur, similar to the interferent of CN^- and HCO_3^-.

Job's Plot Study and NMR Titration

This experiment was conducted to determine the stoichiometric ratio of interactions between **NA** (host) and S^{2-} using the Continuous Variant methods (Job's Plot) [24]. The results from Job's Plot curve showed the ratio of 1:1 (Fig. 8). The **NA**-S^{2-} interaction was also studied by ^{1}H-NMR titration in DMSO-d_6 (Fig. 9). The results showed that the addition of S^{2-} (1 eq.) in D_2O

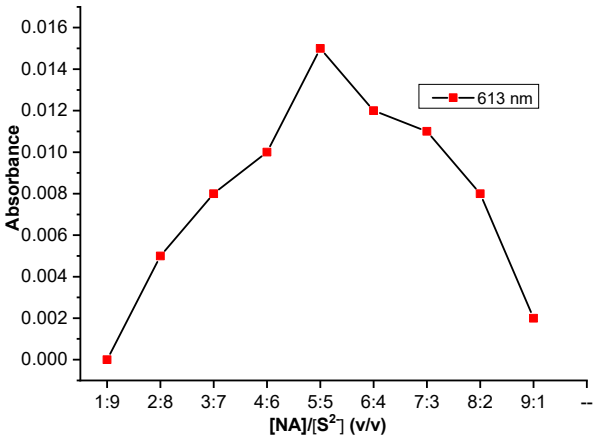


Fig 8. Job's Plot curve of **NA** titration toward the addition of S^{2-}

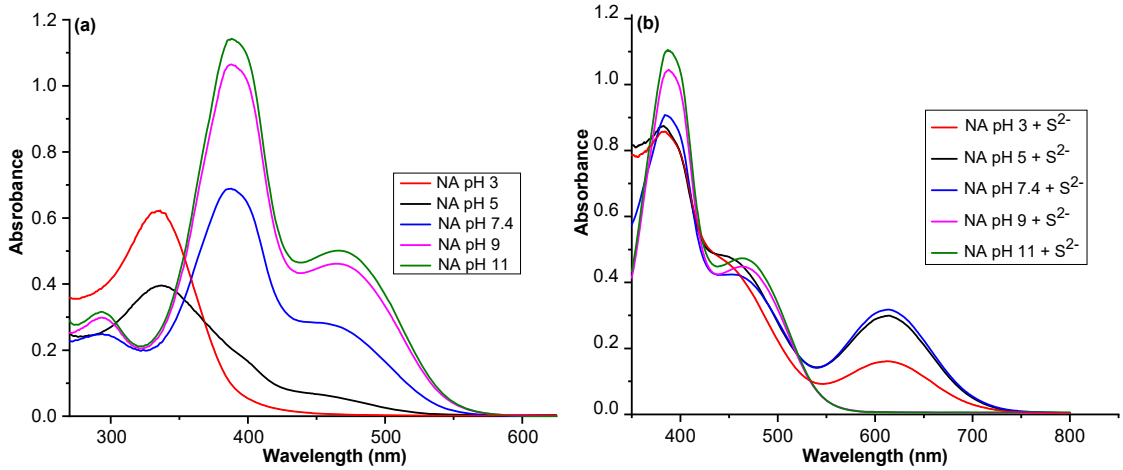


Fig 7. (a) Absorbance spectra of **NA** (2×10^{-5} M) at different pH and (b) Absorbance spectra of **NA** (2×10^{-5} M) after the addition of S^{2-} to different pH

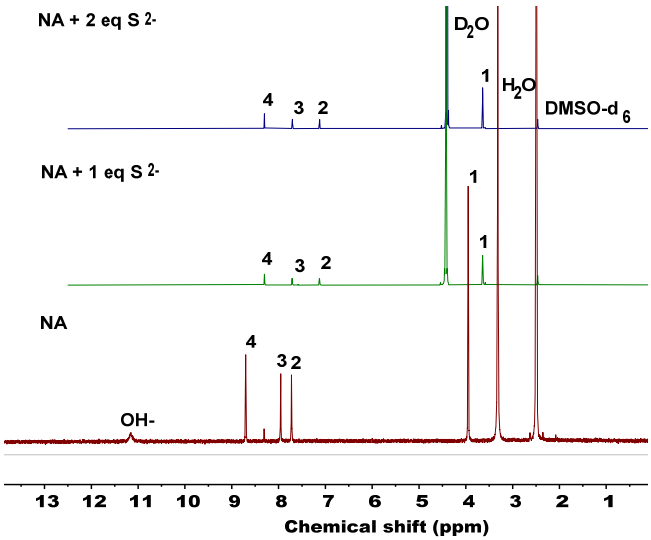
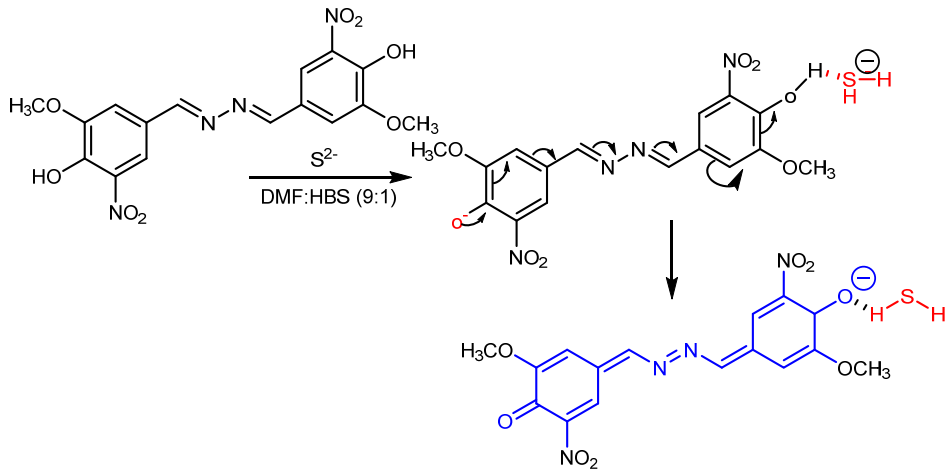


Fig 9. ^{1}H-NMR spectra titration of **NA** with S^{2-}

causes the -OH signal at δ 11.16 ppm to disappear completely, followed by the proton of imine and aromatic ring shifting simultaneously to the up-field area. The addition of S^{2-} (2 eq.) has shifted more up-field than the addition of 1 eq. This shift is caused by -OH deprotonation produced by a resonance phenomenon. The electron density of the aromatic ring increases due to the disconnection of charges in the conjugation system. From the stoichiometric ratio stating one molecule of the binding site (-OH) interacting with one molecule of S^{2-} can be made an interaction model of **NA**-S^{2-} (Scheme 2).

Application of NA Chemosensor in Tap Water Samples Analysis

Determination of % recovery was carried out for quantitative analysis of sulfide in tap water samples. Tap water was added S^{2-} (1, 3, and 5 mM), and then **NA** was used as the reagent for quantitative analysis using UV-Vis. Using calibration curves (y = 0.1148x – 0.1216), the % recovery values are 108.5, 98.6 and 91.5%, respectively (Table 1). These results indicate that **NA** can be used to detect S^{2-} with a concentration range of 1–5 mM. From the obtained analysis data of a range % recovery (80–108%) and % RSD (6%) [25], it can be said that **NA** can be used for quantitative analysis by UV-Vis spectrophotometer. The results of % recovery and % RSD values are shown in (Table 1).



Scheme 2. The interaction model of **NA**-S^{2-}

Table 1. Determination of sulfides in tap water samples

Sample	Na_2S added (mM)	Na_2S found (mM)	RSD (%)	Recovery (%)
Tap water	1	1.085 ± 0.02	1.8	108.5
	3	2.958 ± 0.21	3.0	98.6
	5	4.587 ± 0.09	4.6	91.5

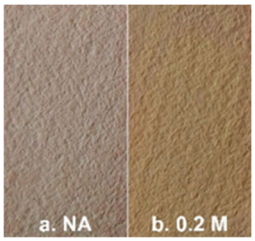


Fig 10. Change in the color of paper strip soaked in **NA** (1×10^{-3} M) after the addition of S^{2-} (0.2 M)

Qualitative Analysis Using Filter Paper Strips

To examine the rapid response of **NA** to S^{2-}, a qualitative analysis was performed using filter paper. Whatman filter paper No. 42 immersed in NA solution (1×10^{-3} M), was added two drops of S^{2-} and dried (Fig. 10). The color of paper strip changes from light pink to yellow. Furthermore, the paper strip was monitored under a 366 nm UV lamp and indicated no luminescence both before and after the addition of S^{2-}. The results indicated that **NA** could be used to detect sulfides in colorimetric analysis.

■ CONCLUSION

We have successfully synthesized a nitrovanillin azine (**NA**) through the condensation reactions of 5-nitrovanillin (**5-NV**) with hydrazine hydrate. Properties of **NA** chemosensor gave high selectivity toward S^{2-} in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4) with color change from light yellow to dark green. The colorimetric LOD of **NA** was 14.3 μM, and the interaction model between host-guests (NA-S^{2-}) is in a 1:1 ratio. A filter paper strip for qualitative and quantitative analysis of S^{2-} in tap water samples indicated that **NA** has potential as a sulfide anion colorimetric chemosensor.

■ ACKNOWLEDGMENTS

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■ REFERENCES

[1] Hammers, M.D., Taormina, M.J., Cerda, M.M., Montoya, L.A., Seidenkranz, D.T., Parthasarathy, R., and Pluth, M.D., 2015, A bright fluorescent probe for H_2S enables analyte-responsive, 3d imaging in live zebrafish using light sheet fluorescence microscopy, *J. Am. Chem. Soc.*, 137 (32), 10216–10223.

[2] Han, Y., Qin, J., Chang, X., Yang, J., and Du, J., 2006, Hydrogen sulfide and carbon monoxide are in synergy with each other in the pathogenesis of recurrent febrile seizures, *Cell. Mol. Neurobiol.*, 26 (1), 101–107.

[3] Lou, Z., Li, P., and Han, K., 2015, "Selenium as a Versatile Center in Fluorescence Probe for the Redox Cycle Between HClO Oxidative Stress and H_2S Repair" in *Advanced Protocols in Oxidative Stress III*, Eds. Armstrong, D., Springer New York, 97–110.

[4] Chan, Y.H., Lock, S.S.M., Wong, M.K., Yiin, C.L., Loy, A.C.M., Cheah, K.W., Chai, S.Y.W., Li, C., How, B.S., Chin, B.L.F., Chan, Z.P., and Lam, S.S., 2022, A state-of-the-art review on capture and separation of hazardous hydrogen sulfide (H_2S): Recent advances, challenges and outlook, *Environ. Pollut.*, 314, 120219.

[5] Dufton, N., Natividad, J., Verdu, E.F., and Wallace, J.L., 2012, Hydrogen sulfide and resolution of acute inflammation: A comparative study utilizing a novel fluorescent probe, *Sci. Rep.*, 2 (1), 499.

[6] Pol, R., Céspedes, F., Gabriel, D., and Baeza, M., 2019, Fully integrated screen-printed sulfide-selective sensor on a 3D-printed potentiometric microfluidic platform, *Sens. Actuators, B*, 290, 364–370.

[7] Shu, J., Qiu, Z., and Tang, D., 2018, Self-referenced smartphone imaging for visual screening of H_2S using Cu_xO-polypyrrole conductive aerogel doped with graphene oxide framework, *Anal. Chem.*, 90 (16), 9691–9694.

[8] Satheshkumar, A., El-Mossalamy, E.H., Manivannan, R., Parthiban, C., Al-Harbi, L.M., Kosa, S., and Elango, K.P., 2014, Anion induced azo-hydrazone tautomerism for the selective colorimetric sensing of fluoride ion, *Spectrochim. Acta, Part A*, 128, 798–805.

[9] Wang, Q., Wang, Y., Guan, M., Zhu, S., Yan, X., Lei, Y., Shen, X., Luo, L., and He, H., 2020, A multicolor colorimetric assay for sensitive detection of sulfide ions based on anti-etching of triangular gold nanoplates, *Microchem. J.*, 159, 105429.

[10] Mergu, N., Singh, A.K., and Gupta, V.K., 2015, Highly sensitive and selective colorimetric and off-on fluorescent reversible chemosensors for Al^{3+} based on the rhodamine fluorophore, *Sensors*, 15 (4), 9097–9111.

[11] Rajamanikandan, R., and Ilanchelian, M., 2022, Simple smartphone merged rapid colorimetric platform for the environmental monitoring of toxic sulfide ions by cysteine functionalized silver nanoparticles, *Microchem. J.*, 174, 107071.

[12] Tiwari, K., Kumar, S., Kumar, V., Kaur, J., Arora, S., and Mahajan, R.K., 2018, An azine based sensor for selective detection of Cu^{2+} ions and its copper complex for sensing of phosphate ions in physiological conditions and in living cells, *Spectrochim. Acta, Part A*, 191, 16–26.

[13] Pei, P.X., Hu, J.H., Chen, Y., Sun, Y., and Qi, J., 2017, A novel dual-channel chemosensor for CN^- using asymmetric double-azine derivatives in aqueous media and its application in bitter almond, *Spectrochim. Acta, Part A*, 181, 131–136.

[14] Irmi, M.N., Purwono, B., and Anwar, C., 2021, Synthesis of symmetrical acetophenone azine derivatives as colorimetric and fluorescent cyanide chemosensors, *Indones. J. Chem.*, 21 (6), 1337–1347.

[15] Kaushik, R., Ghosh, A., Singh, A., and Jose, D.A., 2018, Colorimetric sensor for the detection of H_2S and its application in molecular half-subtractor, *Anal. Chim. Acta*, 1040, 178–186.

[16] Rokhmah, N.V., Mardjan, M.I.D., and Purwono, B., 2022, Synthesis vanillin-azine as colorimetric chemosensor of sulfide anion, *Indones. J. Chem.*, 22 (6), 1490–1500.

[17] Li, J.Z., Leng, T.H., Wang, Z.Q., Zhou, L., Gong, X.Q., Shen, Y.J., and Wang, C.Y., 2019, A large Stokes shift, sequential, colorimetric fluorescent probe for sensing Cu^{2+}/S^{2-} and its applications, *J. Photochem. Photobiol., A*, 373, 146–153.

[18] Rahmawati, R., Purwono, B., and Matsjeh, S., 2018, A naked-eye colorimetric receptor for anions based on nitro group featuring with benzimidazole unit, *Asian J. Chem.*, 30 (9), 1933–1936.

[19] Li, Q., Cai, Y., Yao, H., Lin, Q., Zhu, Y.R., Li, H., Zhang, Y.M., and Wei, T.B., 2015, A colorimetric and fluorescent cyanide chemosensor based on dicyanovinyl derivatives: Utilization of the mechanism of intramolecular charge transfer blocking, *Spectrochim. Acta, Part A*, 136, 1047–1051.

[20] Ghosh, T., and Mishra, S., 2020, A natural cyanobacterial protein C-phycoerythrin as an HS^- selective optical probe in aqueous systems, *Spectrochim. Acta, Part A*, 239, 118469.

[21] Tan, B., Jin, S., Sun, J., Gu, Z., Sun, X., Zhu, Y., Huo, K., Cao, Z., Yang, P., Xin, X., Liu, X., Pan, L., Qiu, F., Jiang, J., Jia, Y., Ye, F., Xie, Y., and Zhu, Y.Z., 2017, New method for quantification of gasotransmitter hydrogen sulfide in biological matrices by LC-MS/MS, *Sci. Rep.*, 7, 46278.

[22] Kamli, S., Orojloo, M., and Amani, S., 2021, Design and synthesis of a novel chemosensor for simultaneous detection of CN^-, HCO_3^- and AcO^- anions and Fe^{2+} cation in an organic-aqueous environment: An experimental and Density Functional Theory studies, *J. Mol. Struct.*, 1234, 130708.

[23] Migdisov, A.A., Williams-Jones, A.E., Lakshtanov, L.Z., and Alekhin, Y.V., 2002, Estimates of the second dissociation constant of H_2S from the surface sulfidation of crystalline sulfur, *Geochim. Cosmochim. Acta*, 66 (10), 1713–1725.

[24] Kang, J.H., Chae, J.B., and Kim, C., 2018, A multi-functional chemosensor for highly selective ratiometric fluorescent detection of silver(I) ion and dual turn-on fluorescent and colorimetric detection of sulfide, *R. Soc. Open Sci.*, 5 (6), 180293.

[25] Official Methods of Analysis of AOAC International, 2019, *AOAC Guidelines for Single-Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals*, AOAC International, Gaithersburg, MD, USA, 1–15.