

Schiff base derived from salicylaldehyde-based azo dye as chromogenic anionic sensor and specific turn-on emission sensor for cyanide ion

Nilanjan Chakraborty¹ | Arijit Chakraborty² | Suman Das¹

¹Biophysical Chemistry Laboratory, Department of Chemistry, Jadavpur University, Kolkata, India

²Department of Chemistry, Acharya Brojendra Nath Seal College, Cooch Behar, India

Correspondence

Suman Das, Biophysical Chemistry Laboratory, Department of Chemistry, Jadavpur University, Kolkata, West Bengal 700032, India. Email: sumandas10@yahoo.com

Funding information

University Grants Commission; Ministry of Human Resource Development, Grant/ Award Number: R-11/101/19; Science and Engineering Research Board, Grant/ Award Number: SR/FT/CS-116/2010

1 | INTRODUCTION

Anion sensing and detection have been a progressing arena in the field of host-guest interaction studies in the last two decades.^[1-16] This approach has overwhelming applications in the medical, biological, environmental, and industrial areas. The importance of colorimetric and fluorescent sensors is increasing day by day owing to nonexpensive instrumentation and naked-eye signaling of the event.

Cyanide, being the most toxic among anions, demands its detection in lower concentrations^[17]; 0.2 to 0.5 mg/kg body weight of cyanide ion is extremely fatal to human beings.^[18] The cellular respiration in mammalian cells is inhibited owing to interaction of cyanide with active site of cytochrome a_3 .^[19] We are exposed to cyanide ion via industrial pollution, as cyanide is involved in various chemical processes like electroplating, tanning, and extraction of metals like gold and silver.^[8,20–23] Fluoride ion is benign in nature owing to its beneficial effect in

Abstract

A novel Schiff base has been derived from condensing 4-aminoantipyrine with diazotized salicylaldehyde. The derived compound acted as a colorimetric sensor for hazardous aqueous anions like CN^- , F^- , and CH_3COO^- among a list of anions. The colorimetric changes were further verified through absorption titrations. The detection limits were of the order of 10^{-10} M, which makes the sensor significant. The interaction of the anions with the sensor was stoichiometrically 1:1 with good binding constants. The sensor turns out to be a specific turn-on emission sensor for CN^- even in competitive environments. The F⁻ ion sensing ability was extended to the determination of F⁻ in a commercial toothpaste with good results.

preventing tooth decay and in osteoporosis treatment.^[24] In surplus amount, fluoride ion exposure can lead to deleterious outcomes like fluorosis, weakening of bones and ligaments, hypocalcaemia, and variation in thyroid hormone status.^[25] Fluoride ion is also released from hydrolysis of chemical warfare agent sarin, and it is also present in many psychiatric drugs, and hypnotic and anesthetic agents.^[26] Acetate ion plays a pivotal role in living systems as acetyl coenzyme.^[27] Acetate ion in form of (11)C-acetate acts as a specific and sensitive radiotracer in positron emission tomography (PET) imaging of hepatocellular carcinoma (HCC) and evaluation of other liver masses^[28] and in protein-ion binding measurements.^[29] Thus, these ions require efficient detectors.

Earlier in our works, we have shown an azo dye derived from fluorophore 4-hydroxy coumarin to be a sensing element for F^- and CH_3COO^- ions^[11] and a Schiff base from 4-aminoantipyrine with pyrene-1-carboxaldehyde as Cu^{2+} sensors.^[30] From our previous knowledge, we have diazotized salicylaldehyde with 4-nitroaniline and derived a ² WILEY Schiff base with 4-aminoantipyrine in our present piece of work. The resulting moiety was investigated for anion sensing where it was responsive towards CN⁻, F⁻, and CH₃COO⁻ ions colorimetrically. The application of F⁻

2 | EXPERIMENTAL SECTION

2.1 | Materials

toothpaste samples.

The solvents are of analytical grade and were obtained from Merck, India; and reagents were purchased from Spectrochem, India, and used without further purification.

ion sensing was extended for the determination of F⁻ in

2.2 | Methods

2.2.1 | Physical measurements

Bruker 300 MHz (Bruker AVANCE 300) spectrometer was used to record ¹H nuclear magnetic resonance (NMR) and ¹³C NMR at an ambient temperature. The melting points were determined on a LabX, India, digital melting point apparatus and are uncorrected. Mettler Toledo Analytical Balance Band (model MS 2045) was used for all weightings.

2.2.2 | UV-vis and spectrofluorimetric studies

All UV-vis spectra of receptor were recorded in highperformance liquid chromatography (HPLC)-grade acetonitrile on a PerkinElmer UV/VIS spectrometer (model Lambda 25) in matched quartz cells of 1-cm path length.

PerkinElmer fluorescence spectrometer (model LS 55) was used for steady-state fluorescence spectroscopy. Fluorescence-free quartz cell (path length 1 cm) was used. All the measurements were done while keeping excitation wavelength at 363 nm and excitation and emission band passes at 5 and 15 nm, respectively.

2.2.3 | Determination of binding constant

A Benisi-Hildebrand plot^[31] was constructed from the absorption titration data for binding constant determination using the following equation:

$$\frac{\Delta A \max}{\Delta A} = 1 + \frac{1}{K[C]},\tag{1}$$

 $\Delta A = |A_x - A_0|$ and $\Delta A_{\max} = |A_{\infty} - A_0|$. A_0 , A_x , and A_{∞} are the absorbances of sensor **2** in the absence of anions, at an intermediate concentration of anions, and at an anionic

concentration of complete saturation, respectively. *K* represents the binding constant of the complexation between compounds **2** and anions, and [*C*] represents concentration of the anions. The plot was created by plotting $\Delta A_{\text{max}}/\Delta A$ as a function of 1/[C]. The binding constants were determined from the obtained slope of the plot.

2.2.4 | Determination of binding stoichiometry

From the Job's plot^[32] (method of continuous variation), stoichiometry of complexation of anions (CN⁻, F⁻, and CH₃COO⁻) with the analyte was determined. The absorbance differences (ΔA) between the free ligand and after anionic interaction were plotted against the increasing mole fraction of anions. Total concentration of ligand and anion was kept at 50 μ M while varying their mole fraction from 0 to 1. The absorbances at λ_{max} of 364 nm were recorded to obtain Jobs plot. The mole fraction of complexation of the ligand with anions was obtained from the break point in the plot.

2.2.5 | Limit of detection

The limit of detection (LOD) was obtained using calibration curve obtained from the titration profile of absorption studies. The equation mentioned below was utilized to serve the purpose:

$$LOD = \frac{3\sigma}{S},$$
 (2)

where σ is the standard deviation of the blank solution (relative absorbance ratio at shifted maximum to ligand maximum) and *m* is the slope of the plot of relative absorbance versus anionic concentration in the lowest concentration range.

2.2.6 | Anion sensing by NMR spectroscopy

¹H NMR spectra of sensor **2** was procured in DMSO- d_6 both in the presence and absence of various equivalents of F⁻ ion (tetrabutylammonium fluoride) to know the nature of interaction between them using an NMR spectrometer (300 MHz) at room temperature.

2.2.7 | Solvent effects on the spectral properties

To study solvatochromism in the absorption spectra, 25 μ M of compound **2** in various solvents was utilized.

Solvents of varying dielectric constant, viz, ethanol, water, hexane, tetrahydrofuran, toluene, *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), chloroform, and acetonitrile were engaged to figure out the effect of solvent polarities in the absorption spectrum.

2.2.8 | pH dependence of receptor 1 in absorption spectra

pH dependence of sensor **2** was investigated, where 50 μ M of sensor **2** in buffer solutions of various pH values was examined. The changes in wavelength of the absorption were noted. The buffers were as follows: pH 1 to 2, HCl/KCl; pH 3 to 7, citric acid/Na₂HPO₄; pH 8, NaH₂PO₄/NaHPO₄; pH 9, Na₂B₄O₇/H₃BO₃; and pH 10, Na₂CO₃/NaHCO₃.

2.2.9 | Practical application of fluoride sensing

The practical suitability of sensor 2 was tested to detect concentration of F⁻ in a toothpaste sample. Commercially available toothpaste was weighed and extracted with various amounts of water and centrifuged to obtain a supernatant clear solution. The supernatant solution was further filtered and centrifuged to get clear extracts. The estimation was done in DMSO medium where a known volume of toothpaste extract was added to sensor solution 2 (25 μ M) in DMSO and changes in the absorption spectrum were noted. The estimated fluoride ion concentration was calculated according to the F⁻ amount in the ingredient list of the toothpaste and the dilutions. The found F⁻ ion concentrations in the toothpastes were obtained according to absorbance ratio response and the calibration curve. The calibration curve was plotted from absorption titration profile of sensor $2(25 \,\mu\text{M})$ with aqueous solution of F⁻ in DMSO medium (Figure S10).

2.2.10 | Synthesis of 4-((*E*)-(2-hydroxy-5-((*E*)-(4-nitrophenyl)diazenyl)benzylidene) amino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (2)

4-((*E*)-(2-Hydroxy-5-((*E*)-(4-nitrophenyl)diazenyl)benzylidene)amino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-

one was prepared by condensation of diazotized salicylaldehyde (1) with 4-aminoantipyrine. The salicylaldehyde was diazotized with 4-nitroaniline using reported method.^[29] Diazotized salicylaldehyde (59 mg, 0.22 mmol) in 5 mL of ethanol was refluxed with 4-aminoantipyrine (54 mg, 0.27 mmol) for 8 hours. Catalytic amount of acetic acid was added for better yield. The resulting solid was filtered, washed with chilled

ethanol, and dried over water bath. For purification, the compound was crystallized from acetonitrile. Yield 79.23%; mp 230°C to 235°C. ¹H NMR (300 MHz, DMSO- d_6): δ 13.65 (s, 1H), 9.79 (s, 1H), 8.37 (d, J = 8.58, 2H), 8.18 (s, 1H), 8.01 (d, J = 8.37, 2H), 7.94 (d, J = 7.35, 1H), 7.53 (d, J = 7.05, 2H), 7.39 (s, 3H), 7.11 (d, J = 8.58, 1H), 3.23 (s, 3H), 2.48 (s, 4H), 2.43 (s, 3H), 2.07 (s, 1H) (Fig. S1). ¹³C NMR (75 MHz, DMSO- d_6): δ 163.97, 159.42, 155.80, 150.77, 148.44, 145.59, 134.55, 129.93, 127.93, 126.38, 125.59, 125.53, 123.65, 121.43, 118.29, 114.17, 35.48, 10.34 (Figure S2). High-resolution mass spectrometry (HRMS) (m/z). [M + H] ⁺: calculated 457.16, found 457.11 (Figure S3).

3 | RESULT AND DISCUSSION

3.1 | Synthesis of the colorimetric anion sensor

We have diazotized salicylaldehyde with 4-nitroaniline following a well-established procedure,^[33] where diazonium coupling occurs at the para position. The resulting azo dye of salicylaldehyde was further condensed with 4-aminoantipyrine (Scheme 1). The bright red-colored product obtained was purified by crystallization from acetonitrile, and purity was checked by thin-layer chromatography. The sensor obtained was in good yields.

3.2 | Naked-eye sensing

The chromogenic recognition ability of sensor **2** were checked by addition of aqueous solutions of tetrabutylammonium salts of F^- , Br^- , and I^- and sodium salts of CN^- , CH_3COO^- , $H_2PO_4^-$, HPO_4^{2-} , and NO_3^- into sensor solution in acetonitrile. The colorimetric response was obtained in case of CN^- , F^- and CH_3COO^- where yellow color of the receptor solution was changed to crimson red in case of CN^- and light red in case of F^- and CH_3COO^- (Fig. 1). No such characteristic color



SCHEME 1 Synthesis of sensor 2.

changes were observed in the presence of other mentioned anions. The observations acknowledge ligand **2** as sensor for highly basic anions like CN^- , F^- , and CH_3COO^- and not for the mild ones.

3.3 | Absorption studies on anionic sensing

4____WILEY

To further ratify the naked-eye observations, the whole sensing process was monitored through absorption spectrum. Sensor 2 exhibited an absorption maximum at 364 nm in acetonitrile medium. Upon addition of various anions (50 μ M), a bathochromic shift was observed in the presence of overly basic anions such as CN⁻, F⁻, and CH₃COO⁻ (Fig. 2). No significant changes in the spectrum were noticed in case of other anions that were in the list in our study. Titrations were carried out with 25 μ M of ligand 2 in acetonitrile throughout absorption studies. In case of the most basic CN⁻ ion, the 364-nm peak of the sensor exhibited decrease in intensity with a redshift to 578 nm with increase in intensity (Fig. 3). The changes continued until saturation at 39 µM of analyte concentration. Explicit isosbestic points were absent in the spectrum. While titrating with F⁻ and CH₃COO⁻ ions, the ratiometric changes were perceived with an enhanced redshift to 589 nm (Figs 4 and S4). Distinct isosbestic points were noted at 290, 311, 409, and 438 nm in titration profile with F^- while 313, 407, and 445 nm were isosbestic for titration with CH₃COO⁻. The observed redshift in the presence of CN⁻, F⁻, and CH₃COO⁻ articulates the fact of deprotonation of the phenolic proton at the azo dye part owing to high basicity of anions. Exhibition of sharp isosbestic points stipulates at the equilibrium between phenol and phenolate anion. The deprotonation is also justified as anions that respond are of more basic and least hydrogen bonding character that favors deprotonation over hydrogen-bond formation.

3.4 | ¹H NMR studies

To understand the mechanism of interaction of anions, the study was extended to ¹H NMR experiments.



FIGURE 2 Changes on absorption spectrum of sensor **2** (25 μ M) on addition of various anions (50 μ M) in polar aprotic acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]

The NMR titration was only carried out with tetrabutylammonium fluoride where a complete experiment was performed in DMSO- d_6 (Fig. 5). The antipyrine coupled with azo dye manifests an NMR peak at 13.6 ppm for phenolic OH and at 9.9 ppm for imine bond, and the rest are aromatic protons and protons of the antipyrine part. Upon addition of 1 equivalent of F⁻, the peak at 13.6 ppm disappears and there is a slight upfielded shift of aromatic protons, and on further F⁻ addition, more upfield shift was noted for aromatic protons. The result of NMR titration suggests deprotonation of phenolic hydrogen and formation of phenolate ion, which increases the electron density of the aromatic ring. The 1:1 stoichiometry of interaction can also be predicted from NMR studies.

3.5 | Determination of binding constant, binding stoichiometry, and detection limit

The binding constant was determined from aforementioned Benisi-Hildebrand plot (Figure S5) using data of the absorption titration profile. The binding constants were determined to be 3.66×10^4 M⁻¹, 6.02×10^4 M⁻¹,



FIGURE 1 Colorimetric changes on addition of various anions to 25 μ M of sensor solution in polar aprotic acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 3 Absorption titration of 25 μ M of sensor **2** (curve 1) with aqueous CN⁻ up to 39 μ M (curve 10) in polar aprotic acetonitrile. Inset: Variation in absorbance at 364 and 578 nm with changes in CN⁻ concentration. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 4 Absorption titration of 25 μ M of sensor 2 (curve 1) with aqueous F⁻ up to 45 μ M (curve 10) in polar aprotic acetonitrile. Inset: Ratiometric changes in absorbance at 364 and 589 nm with changes in F⁻ concentration. [Color figure can be viewed at wileyonlinelibrary.com]

and 3.40×10^4 M⁻¹ for CN⁻, F⁻, and CH₃COO⁻, respectively. The forenamed Job's method of continuous variation was employed to obtain the stoichiometry of interaction. The plot (Figure S6) suggests 1:1 stoichiometry for all three ions, viz, CN⁻, F⁻, and CH₃COO⁻. The result acquired complemented the result of the ¹H NMR titration. The important parameter that characterizes a sensor is its detection limit. The detection limit was obtained in the way mentioned in Section 2 from the calibration curve (Figure S7). Sensor **2** has detection limits of 0.604, 0.380, and 0.347 nM for CN⁻, F⁻, and CH₃COO⁻, respectively.



FIGURE 5 ¹H NMR titration of sensor **2** with F^- in highly polar aprotic DMSO- d_6 . [Color figure can be viewed at wileyonlinelibrary. com]

3.6 | Emission studies on sensing

The absence of a good fluorophore in the azo dye of salicylaldehyde makes it very poorly emissive. Herein, the condensed product of the dye with 4-aminoantipyrine induces some rigidity in the structure through the imine bond, which imparts a weak emissive character. Ligand **2** emits at 417.5 nm in acetonitrile medium. The aqueous solutions of anions up to 120 μ M were added to 50 μ M of ligand solution in acetonitrile. Except in CN⁻, no distinct changes were observed for other anions (Fig. 6). Sensor **2** turned out to be turn-on sensor for CN⁻ ion (Fig. 7). The acetonitrile solution of sensor **2** was titrated with increasing CN⁻ ion concentration till saturation at 118 μ M.

Turn-on CN^- sensing was examined in competitive environments. The competitive anions were firstly added to acetonitrile solution of sensor **2**, an equal amount of



FIGURE 6 Changes on emission spectrum of sensor **2** (50 μ M) on addition of various anions (120 μ M) in polar aprotic acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]

 CN^{-} ion was added, and the emission spectrum was run. The enhancement in emission was well maintained in the presence of other anions (Fig. 8), which signifies the turn-on CN^{-} sensing to be a selective and specific one.

3.7 | Effect of pH and solvent on the sensor

To further extend the utility of the designed sensor, the effect of pH and other solvents must be known. The absorption spectrum of the compound 2 was viewed on various solvents, viz, ethanol, water, hexane tetrahydrofuran, toluene, DMF, DMSO, chloroform, and acetonitrile. In the absorption spectrum of the sensor, there were no



FIGURE 7 Emission titration of 50 μ M of sensor 2 (curve 1) with aqueous CN⁻ up to 118 μ M (curve 13) in polar aprotic acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 8 Turn-on emission of sensor **2** in the presence of aqueous CN⁻ in competitive environment of other anions (solvent: polar aprotic acetonitrile). [Color figure can be viewed at wileyonlinelibrary.com]

significant changes in wavelength with solvent polarity except highly polar electron pair-donating solvents like DMF and DMSO (Figure S8). In DMF and DMSO, the absorption band exhibited a redshifted hump at 600 and 617 nm, respectively. When the absorption spectrum of sensor **2** was taken on various pH values, no noteworthy change in spectrum was noticed (Figure S9). Thus, it can be further exploited in a wide range of pH for future use.

3.8 | Practical application of fluoride sensing

The method to test practical utility of sensor **2** to detect concentration of fluoride in toothpaste has been performed as discussed in Section 2. The working procedures have been already discussed in Section 2. The found fluoride ion concentration in the toothpastes was determined from ratiometric absorbance response and the calibration curve. The calibration curve was obtained from spectrophotometric titration data of sensor **2** with aqueous solution of F^- in DMSO medium (Figure S10). It is noted that the determined fluoride concentrations were in agreement with the estimated data as per the ingredient list (Table 1).

TABLE 1 Results of determination of F⁻ in toothpaste samples.

Estimated [F ⁻], µM	Found [F ⁻], μM	Recovery, %
6.48	7.00	108
9.72	12.73	130
12.94	13.88	107

4 | CONCLUSION

We have designed an azo dye-based Schiff base as a selective chromogenic sensor for aqueous anions such as CN⁻, F⁻, and CH₃COO⁻ via proton abstraction in acetonitrile medium. The stoichiometry of anionic interaction was concluded to be 1:1. Good detection limits of approximately 10^{-10} M were reported for the anions detected. The detection limits are much bellow the maximum allowed limit for CN⁻ and F⁻ in drinking water as recommended by the World Health Organization (WHO). The sensor developed has been inferred to be a specific turnon emission sensor only for CN⁻. The utility of chromophore 2 has been extended to determine F⁻ in an oral care product with good estimation. The compound has also been concluded to be stable in wide range of pH and solvent polarity. Thus, the antipyrine-coupled azo dye of salicylaldehyde is a new attribute to the world of anion sensing, which has a good future prospect.

ACKNOWLEDGMENTS

AC gratefully acknowledges financial supports from Science and Engineering Research Board, DST, Government of India (SERB no. SR/FT/CS-116/2010), and SD gratefully acknowledges the research support under RUSA 2.0 Grant to Jadavpur University, Kolkata, provided by Ministry of Human Resource Development, Government of India (reference no. R-11/101/19 dated 15(19)-02-2019). NC thanks University Grants Commission, Government of India, for Senior Research Fellowship. We also thank the Department of Chemistry, Maulana Azad College (Kolkata, West Bengal, India) and Department of Chemistry, Jadavpur University (Kolkata, India).

ORCID

Suman Das D https://orcid.org/0000-0002-4148-1002

REFERENCES AND NOTES

- [1] Beer PD, Gale PA. Angew Chem Int Ed. 2001;40:486.
- [2] Sun SS, Lees AJ. Coord Chem Rev. 2002;230:171.
- [3] Martínez-Máňnez R, Sancenon F. Chem Rev. 2003;103:4419.
- [4] Jiang P, Guo Z. Coord Chem Rev. 2004;248:205-229.
- [5] Gale PA, Garcia-Garrido SE, Garric J. Chem Soc Rev. 2008;37:151.
- [6] Caltagirone C, Gale PA. Chem Soc Rev. 2009;38:520.
- [7] Kim SK, Lee DH, Hong J-I, Yoon J. Acc Chem Res. 2009;42:23.
- [8] Xu Z, Chen X, Kim HN, Yoon J. Chem Soc Rev. 2010;39:127.
- [9] Chandel M, Roy SM, Sharma D, et al. JOL. 2014;154:515.
- [10] Hovath M, Cigan M, Filo J, et al. RSC Adv. 2016;6:109742.

[11] Chakraborty N, Bhuiya S, Chakraborty A, Das S. Indian J Chem. 2018;57A:59.

- [12] Chakraborty N, Bhuiya S, Chakraborty A, Mandal D, Das S. J Photochem Photobiol A. 2018;359:53.
- [13] Reddy PM, Hsieh S-R, Changa C-J, Kang J-Y. J Hazard Mater. 2017;334:93.
- [14] Reddy PM, Hsieh S-R, Lee M-C, et al. Dyes Pig. 2019;164:327.
- [15] Reddy PM, Hsieh S-R, Wu W-C, Chang C-J, Chen Y-S, Lee M-C. React Funct Polym. 2018;123:26.
- [16] Reddy PM, Hsieh S-R, Chen J-K, Chang C-J, Kang J-Y, Chen C-H. Spectrochim Acta Part A. 2017;186:8.
- [17] Matsubara K, Akane A, Maseda C, Shiono H. Forensic Sci Int. 1990;46:203.
- [18] Huang X, Gu X, Zhang G, Zhang D. Chem Commun. 2012;48:12195.
- [19] Solomonson LP, Vennesland B, Conn EE, Knowles CJ, Westley J, Wissing F. Cyanide as a metabolic inhibitor. In: *Cyanide in Biology*. London: Academic Press Ltd.; **1981**.
- [20] Qian G, Li X, Wang ZY. J Mater Chem. 2009;19:522.
- [21] Peng L, Wang M, Zhang G, Zhang D, Zhu D. Org Lett. 2009;11:1943.
- [22] Kim DS, Chung YM, Jun M, Ahn KH. J OrgChem. 2009;74:4849.
- [23] Vallejos S, Estevez P, Garcia FC, Serna F, Jose L, Garcia JM. Chem Commun. 2010;46:7951.
- [24] Horowitz HS. J Public Health Dent. 2003;63:3.
- [25] Dey S, Giri B. Med Clin Rev. 2016;2:1.
- [26] Hudnall TW, Chiu C-W, Gabbai FP. Acc Chem Res. 2009;42:388.
- [27] Qiao YH, Lin H, Shao J, Lin HK. Spectrochim Acta Part A. 2009;72:378.
- [28] Ho CL, Yu SC, Yeung DW. J Nucl Med. 2003;44:213.
- [29] Saifer A, Westley F, Steigman J. Biochemistry. 1964;3:1624.
- [30] Chakraborty N, Chakraborty A, Das S. JOL. 2018;199:302.
- [31] Benesi HA, Hildebrand JH. J Am Chem Soc. 1949;71:2703.
- [32] Job P. Ann Chim Appl. 1928;9:113.
- [33] Ahmadi RA, Amani S. Molecules. 2012;17:6434.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Chakraborty N, Chakraborty A, Das S. Schiff base derived from salicylaldehyde-based azo dye as chromogenic anionic sensor and specific turn-on emission sensor for cyanide ion. *J Heterocyclic Chem*. 2019;1–7. https://doi.org/10.1111/jhet.3693

Wii fv<u>⊥</u>