Dosimetric Chromogenic Probe for Selective Detection of Sulfide via Sol–Gel Methodology

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Supporting Information

ABSTRACT: Dinitrobenzenesulfonyl-protected naphthyl azo pyridine conjugate 1 has been designed and synthesized. Compound 1 acts as a nongelator in dimethyl sulfoxide (DMSO)–H₂O (1:1, v/v) while its hydroxy counterpart 2 can form a nice gel in the same solvent. In the presence of sulfide, compound 1 undergoes rapid sulfonate ester hydrolysis and results in the formation of azo-naphthol 2 that responds in instant gelation. Such deprotection was extremely selective to sulfide; other analytes did not show measurable response. The sensing mechanism has been established by various spectroscopic techniques. Compound 1 in solution (DMSO–H₂O) also shows a selective response toward sulfide over a series of other anions with a color change. Preparation of test kit with compound 1 allows detection of sulfide in solution and vapor states. Such kind of dosimetric sensing of chemical analytes by improvising the protection/deprotection of functional groups in gelator structure is rare in the literature, and to the best of our knowledge, this is the first example of a stimuli-responsive low-molecular-weight gelator which dosimetrically senses sulfide over other nucleophilic substrates.

1. INTRODUCTION

Over the last few decades, development of new stimuli-responsive low-molecular-weight gelators (LMWGs) has gained immense interest in the area of supramolecular chemistry. 1-31 Supramolecular gelators with necessary functional groups form self-aggregation involving different weak forces such as hydrogen bonding, π-stacking, hydrophobic, and van der Waals forces. 7-14 Modulation of these weak interactions by means of different physical or chemical inputs (heat, light, redox, pH, ions, etc.) brings phase changes (gel-to-sol transition or vice versa). 3, 7-9, 14-31 Such a phase transition stimulated by different chemical substrates encourages the development of LMWG-derived sensor devices. 7, 14-31

In regard to development of molecular sensors for biologically relevant species, design of reaction-based probes is always beneficial over fluorogenic or chromogenic probes. 32-34 Dosimetric sensing probes are usually highly specific and selective to a single analyte and do not experience any interference from other analytes during the sensing process. However, exploitation of dosimetric approach in developing analyte-responsive LMWGs is rare in the literature. 29-31 Gels of this category draw attention for their operational simplicity and visual detectability involving no instrumental aids (advantages of supramolecular gels) with high degree of sensitivity and specificity (advantages of dosimetric sensing).

During our ongoing research in developing new dosimetric probes by exploiting LMWGs for sensing of biologically relevant chemical analytes, 27-31 we previously reported a pyridyl azo-based naphthyl acetate derivative for sensing and discrimination of hydrazine and perborate in a sol–gel medium. 31 The sensing mechanism relied on the acetyl deprotection of the naphthol –OH group. In continuation, we wish to report here another simple architecture 1 for sulfide sensing utilizing the similar methodology involving a sol–gel technique (Figure 1). Sensing and detection of sulfide draw attention for its toxicity and biological relevance. Hydrogen sulfide is usually known for its bad smell (rotten egg smell). However, it is extensively used in research laboratory for qualitative detection of metal ions and so forth. It plays vital roles in many biological processes (in modulating blood pressure, suppression of oxidative stress, as an antioxidant of reactive oxygen species, etc.). 35, 36 and also linked to a number of diseases (Down’s syndrome, Alzheimer’s disease, liver cirrhosis, etc.). 37-39 Thus, development of sensing probes for sulfide is worth trying. During the past few decades, many chemical methods such as colorimetry, 40, 41 gas chromatography, 42 electrochemical analysis, 43 and use of fluorescent
H2SO4, (f) H2PO4−, (g) HPO42−, (h) SO42−, (i) HS−, (j) BO3−, (k) HSO4−, (l) F−, (m) NO3−, (n) HSO3−, (o) L-cysteine, (p) L-valine, and (r) L-alanine. Cl−, AcO− are used as K-salts, and other anions are used as Na-salts].

Figure 2. Photographs showing the phase changes of 1 (c = 0.04 M) upon addition of equivalent amount of different analytes (c = 0.2 M) after 1 h in DMSO−H2O (1:1, v/v) [(a) S2O32−, (b) Cl−, (c) Br−, (d) I−, (e) AcO−, (f) HPO42−, (g) HPO42−, (h) SO42−, (i) HS−, (j) BO3−, (k) HSO4−, (l) F−, (m) NO3−, (n) HSO3−, (o) L-cysteine, (p) L-valine, and (r) L-alanine. Cl− and AcO− are used as K-salts, and other anions are used as Na-salts].

2. RESULTS AND DISCUSSION

2.1. Synthesis. Scheme 1 represents the synthetic route to the synthesis of compound 1. The azo-naphthol 2 was prepared according to the reported procedure via diazotization of 3-aminopyridine and its subsequent coupling with 2-naphthol.31 Sulfonylation of phenolic −OH in 2 in the presence of NaH in dry tetrahydrofuran (THF) gave the desired compound 1 in an appreciable yield. All the compounds were characterized by usual spectroscopic techniques.

2.2. Gelation Study and Chemical Responsiveness of 1. The gelation ability of 1 was investigated in various organic and semiaqueous solvents (Table S1). Compound 1 did not form gel in any of the solvents tested. However, the azo-naphthol 2 produced gels from different solvents that mostly included semiaqueous compositions (Table S1). Then, we checked whether the removal of DNBS group in 1 by a suitable chemical analyte that resulted in intermediate 2 could produce a gel or not. Such type of gelation of progelator 1 could be an elegant approach in developing a naked-eye molecular sensor.27 To demonstrate this, we selected DMSO−H2O (1:1, v/v) as the desired solvent. The effect of different analytes on sol-to-gel transformation of 1 is shown in Figure 2. When aqueous solutions of different probes44−46 have been developed for the detection and quantification of sulfide/H2S. On the contrary, use of a suitable gelator or a progelator for sensing and detection of sulfide involving sol−gel methodology is unexplored.

However, different functional segments of compound 1 are highlighted in Figure 1. The naphthalene moiety is likely involved in gelation through the π−π stacking between the naphthalene rings,29,31 and the pyridyl moiety is introduced in regulating and interlinking the molecules through coordination of water molecules.26,31 The naphthol −OH group is protected by dinitrobenzenesulfonyl (DNBS) moiety. The removal of DNBS by suitable nuclophilic analyte(s) is expected to influence the gelation properties of 1, which will be beneficial for visual sensing of analyte (either gel-to-sol transition or vice versa). The presence of azo-linked chromogenic unit displays optical response upon deprotection reaction.

Interestingly, compound 1 acts as a progelator in dimethyl sulfoxide DMSO−H2O (1:1, v/v), and upon sulfide-stimulated deprotection of naphthol −OH group, it produces a nice gel. The DNBS protection/protection of phenolic −OH moiety in developing chromofluorogenic sensing probes (usually for biothiols and sulfide) is reported in the literature.32−34,47−49 However, pursuance of this dosimetric technique in developing stimuli-responsive supramolecular gelator is unknown in the literature.
Such a large red-shifted absorption band was possibly due to extensive charge delocalization in 2 (obtained from the removal of DNBS group in 1), which resulted in lowering of $\pi-\pi^*$ transition energy.\textsuperscript{31}

The proposed desulfonylation reaction was confirmed by $^1$H NMR, Fourier transform infrared (FTIR), and mass spectrometry analysis. In $^1$H NMR study, after addition of sulfide (taken in D$_2$O) to the d$_6$-DMSO solution of 1, the aromatic proton of type Hb underwent a large upfield chemical shift (from 7.60 to 6.91 ppm) (Figure 4). In addition, the signal for the proton of $-\text{OH}$ (Ha) was found at 15.37 ppm. Such an upfield chemical shift of naphthyl proton (Hb) and appearance of $-\text{OH}$ (Ha) proton signal was a clear indication of the removal of DNBS group. Interestingly, the newly appeared proton signals in the presence of sulfide were matched with the proton signals of compound 2, which undoubtedly confirmed the in situ formation of 2 in the medium.

FTIR analysis showed the disappearance of stretching of S=S bond (1756 cm$^{-1}$) in sulfonate ester and lowering of stretching for signal of azo N=N bond (from 1581 to 1527 cm$^{-1}$) on moving from amorphous state of 1 to the gel state obtained through in situ formation of 2 (Figure 5). These changes in stretching signals were due to removal of electron-withdrawing DNBS moiety. In addition, the gel state showed a broad stretching band at 3418 cm$^{-1}$, indicating the existence of naphthol $-\text{OH}$. The liquid chromatography–mass spectrometry analysis of sulfide-induced gel showed the prominent peak at 250.1 corresponding to the mass of compound 2 [250.0980 (M + H)$^+$] (Figure S1). All this information unequivocally corroborated the successful conversion of compound 1 into 2 through desulfonylation of 1 in the presence of sulfide.

### 2.3. Solution-Phase Interaction

Interactions of 1 with the aforementioned analytes were also investigated in solution and the outcomes were similar to the observations in the gel phase study. UV–vis spectral changes of 1 in DMSO–H$_2$O (1:1, v/v) displayed superior sensitivity of 1 toward sulfide over any other analytes. In the study, addition of sulfide caused ratiometric change in the absorption of 1 (Figure 6a). Upon successive addition of sulfide, the absorption band at 370 nm was gradually red-shifted to 425 nm with the appearance of a new peak at 465 nm.

The absorption peaks at 425 nm corresponded to naphthalene $\pi-\pi^*$ transition. The growth of a new absorption band at 465 nm was attributed to the cleavage of O=S bond, and the intramolecular charge transfer from naphtholic-OH/naphtholic--O$^-$ to pyridyl azo motif introduced the color...
change of the solution from almost colorless to orange-red. The two peaks at 425 and 465 nm progressively reached the maxima in the presence of 4 equiv amounts of sulfi de and merged together to give a broad region near 450 nm.

Importantly, all other analytes were found almost non-interfering. Very little responses were observed for perborate and l-Cys (Figure 6b). These outcomes established high sensitivity of 1 toward sulfi de ions. Such high afﬁnity of 1 for sulfi de was due to a greater nucleophilic character of sulfi de compared to biothiol (l-Cys) that readily cleaved the sulfonate ester in solution. In ﬂuorescence, compound 1 also showed a selective response to sulfi de by introducing substantial quenching of emission. By contrast, other analytes remained silent in the event (Figure S2).

The rapid desulfonylation of 1 using sulfi de was understood from the time-dependent absorption spectral changes of 1. In the presence of 4 equiv amounts of sulfi de, the reaction was completed within ~5 min (Figure 7a). The selectivity of probe 1 toward sulfi de was also investigated by recording absorption spectral changes of 1 with sulfi de in the presence of all other analytes. The spectral comparisons as shown in Figure 7b,c accounted for negligible interference of other analytes during sulfi de sensing.

We also investigated the sensitivity of 1 for sulfi de in solvents like 1:3 and 1:5 DMSO−H2O (v/v) (Figure 8). Addition of 4 equiv amounts of sulfi de also brought similar red-shifted spectral bands as observed for 1:1 solvent composition, suggesting the functioning of the probe in a solvent of higher water content.

The stoichiometry of 1 with sulfi de was determined to be 1:1 (H/G) in all these solvent compositions as indicated by Benesi–Hildebrand plots (Figure S3).50 Corresponding detection limits51 for sulfi de were also calculated (Figure S4). The detection limit values are comparable with the reported sulfi de sensors (Table S2).

Importantly, the UV–vis spectrum of 1 in the presence of sulfi de in DMSO−H2O (1:1, v/v) was almost identical to the absorption spectrum of 2, indicating the successful conversion of 1 into 2 by sulfi de ions. A slight change in the peak positions of absorption bands was possibly due to the presence of DNBS moiety after deprotection (Figure 9a).

**2.4. Test Kit for Sulfi de Detection.** Alongside, for further utility of 1 as a qualitative sulfi de detector, test kit experiment was carried out. The strip was prepared by dipping the fi lter paper into the DMSO−H2O solution of 1 and then dried in air. The paper was next dipped into an aqueous sulfi de solution. The color of the strip was changed into yellowish brown-orange. A similar color change of the strip was noted when the strip was kept in contact with H2S gas. These observations established the beneficial use of compound 1 as a suitable qualitative detector of sulfi de without any instrumental aid (Figure 9b).

**3. CONCLUSIONS**

In conclusion, DNBS-protected naphthyl azo pyridine 1 that acts as sensing probe for sulfi de in a sol−gel medium has been designed and synthesized. Compound 1 behaves as a nongelator in DMSO−H2O (1:1, v/v) and on desulfonylation forms a gel in the same solvent. In the presence of sulfi de, compound 1 undergoes rapid removal of DNBS moiety and

![Figure 7](image1.png)

Figure 7. (a) Time-dependent absorption spectra (at 450 nm) of 1 (c = 2.50 × 10−5 M) upon addition of 4 equiv amounts of sulfi de (c = 1.0 × 10−3 M) in DMSO−H2O (1:1, v/v); (b) selectivity of 1 (c = 2.50 × 10−5 M) upon addition of 4 equiv amounts of sulfi de (c = 1 × 10−3 M) to the solution of 1 containing other analytes (F−, Cl−, Br−, I−, AcO−, H2PO4−, HPO42−, S2O32−, H5−, BO3−, SO42−, NO3−, HSO3−, l-cysteine, l-glycine, l-valine and l-alanine) in 4 equiv amounts each in DMSO−H2O (1:1, v/v), and (c) the associated bar plot at 450 nm: (i) 1 with all other analytes except sulfi de and (ii) 1 with all analytes including sulfi de and (iii) 1 with sulfi de only.

![Figure 8](image2.png)

Figure 8. Change in the absorbance of 1 (c = 2.50 × 10−5 M) upon gradual addition of equivalent amount of sulfi de in (a) 1:3 DMSO−H2O (v/v) and (b) 1:5 DMSO−H2O (v/v).

![Figure 9](image3.png)

Figure 9. (a) Comparison of normalized UV–vis spectra of 2 and 1 with sulfi de in DMSO−H2O (1:1, v/v) and (b) photograph of the test kits of 1 (c = 2.5 × 10−5 M) for solution- and gas-phase detection of sulfi de.
forms azo-naphthol 2, which produces an instant gel in DMSO–H2O (1:1, v/v). Such gel formation through dosimetric cleavage of sulfonate ester is extremely selective to sulfide, while all other analytes taken in the study remained almost noninterfering and thus finds potential use in selective visual sensing of sulfide. The deprotection reaction has been established by various spectroscopic techniques. Selectivity of compound 1 for sulfide is also found in the solution phase where ratiometric change in absorbance with sulfide introduces colorimetric response from almost a colorless solution to orange-red. Preparation of test kits with compound 1 allows the detection of sulfide in solution and vapor states and suggests its practical utility in qualitative detection of sulfide. Such kind of dosimetric sensing of chemical analytes through protection/deprotection of a functional group in a gelator backbone is less explored in the literature, and to the best of our knowledge, this is the first example of a stimuli-responsive LMWG which dosimetrically senses sulfide over a variety of other nucleophilic substrates (Table S2).

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All the chemicals were purchased from Spectrochem and Sigma-Aldrich. All solvents used in the reaction were purified, dried, and distilled. NMR solvents were obtained from Aldrich. 1H and 13C NMR spectra were recorded in a Bruker 400 MHz instrument. FTIR spectra were recorded in a Bruker 400 MHz instrument. FTIR spectra were recorded using a PerkinElmer LS55 spectrophotometer. Fluorescence and UV–vis spectra were recorded using a PerkinElmer LSS5 spectrofluorimeter and a Shimadzu UV-2450 spectrophotometer, respectively. SEM image was obtained using an EVO LS-10 Zeiss instrument.

4.2. Synthesis. 4.2.1. Compound 2. Compound 2 was synthesized according to the reported procedure.26,31

4.2.2. Compound 1. To the solution of compound 2 (1.0 g, 4.01 mmol) in dry THF (20 mL), NaH (0.3 g, 12 mmol) was added and the solution was allowed to stir for 15 min at room temperature under a nitrogen atmosphere. After that, 2,4-dinitrobenzenesulfonyl chloride (1.18 g, 4.40 mmol) was added and the solution was allowed to stir for 15 min at room temperature to form a gel. For semiaqueous solvents, the reaction mixture was stirred under reflux for 8 h. After completion of reaction as monitored by thin-layer chromatography, THF was removed under vacuum and the residual mass was extracted with CHCl3/CH2OH (2%, v/v) mixture. The organic layer was washed with NaHCO3 solution (3 × 15 mL) and dried over anhydrous Na2SO4. Evaporation of the solvent gave the crude product which, upon purification by column chromatography over a silica gel using 15% ethyl acetate in petroleum ether, afforded the desired compound 1 (0.61 g, yield 72%, mp 142 °C). 1H NMR (CDCl3, 400 MHz): δ 8.89 (d, 1H, J = 2 Hz), 8.70 (t, 1H, J = 4 Hz), 8.44–8.42 (m, 1H), 8.35 (d, 1H, J = 2 Hz), 8.25–8.22 (dd, 1H, J1 = 8 Hz, J2 = 2 Hz), 8.03 (t, 2H, J = 8 Hz), 7.80–7.79 (m, 2H), 7.66–7.61 (m, 2H), 7.50 (d, 1H, J = 8 Hz), 7.42–7.40 (m, 1H); 13C NMR (CDCl3, 100 MHz): 152.7, 150.1, 148.6, 147.9, 145.9, 140.7, 139.9, 134.8, 133.2, 130.0, 132.6, 129.4, 128.3, 127.6, 127.5, 126.18, 126.10, 124.4, 123.9, 121.8, 120.0. FTIR (KBr) ν cm−1: 3053, 1756, 1521, 1584, 1563, 1416, 1295, 1253, 1220; m/z: (ESI+) calcd, 480.0 (M)+; found, 480.0 (M)+.

4.3. General Procedure for Gelation Test. The required amount of compound 1 was first taken in pure organic solvents (1 mL), slightly warmed to dissolve and then cooled to room temperature to form a gel. For semiaqueous solvents, the compound was first dissolved in the organic solvent and then water was added to it. Analyte-responsive behavior of compound 1 was investigated following the same method. In that case, all the guest analytes were taken in water. All the gels were tested via the usual inversion of vial method after ~15 min of sample preparation. Samples of gel for SEM image was dried under vacuum and then coated with a thin layer of gold metal. The gel-to-sol transition temperature (Tg) was determined by the dropping ball method.

4.4. General Procedures of UV–Vis and Fluorescence Titrations. A stock solution of compound 1 was prepared in DMSO–H2O (1:1, v/v) in the concentration range of 10−3 M. The stock solutions of all the analytes were prepared in pure water in the concentration range of 10−3 M. The solution of the compound (2 mL) was taken in a cuvette and different analytes were sequentially added in different amounts. The analyte-induced changes in the absorbance and emission of the compound were recorded.

4.4.1. Stoichiometry of the Interaction.50 The Benesi–Hildebrand plot was adopted to determine the stoichiometry of interaction using the expression: 

\[ \frac{A_0}{\epsilon_0 - A} = \frac{\epsilon_m - \epsilon_c}{(K_{eq}C_\text{g} + 1)} \]

where \( \epsilon_m \) and \( \epsilon_c \) represent the molar extinction coefficients for the probe and the complex, respectively, at a selected wavelength, \( A_0 \) denotes the absorbance of free probe at that specific wavelength, and \( C_\text{g} \) is the concentration of the guest analyte. The measured absorbance \( A_0/(A - A_0) \) as a function of inverse of the analyte concentration fits a linear relationship, indicating a 1:1 stoichiometry of the probe–analyte complex.

4.5. Calculation of Detection Limit.23 The detection limit was calculated from UV–vis titration data. Absorbance of compound 1 was measured five times, and the standard deviation of blank measurement was determined. To have the slope, absorbance values were plotted against concentrations of sulfide. The detection limit was calculated using the equation: detection limit = 3σ/k, where σ is the standard deviation of blank measurement and k is the slope.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02795.

Material having table of gelation tests, FTIR and fluorescence spectra including binding curves and detection limit, comparison table, and characterization spectra (PDF)

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Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS
R.R. thanks DST, India, for providing DST inspire fellowship. A.P. thanks CSIR, New Delhi, India, for a fellowship. M.M. thanks SERB, DST, India, for National Postdoctoral fellowship. K.G. thanks SERB, DST, New Delhi, for financial support (file no. EMR/2016/08006/OC).

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