

Inorg. Chem. Res., Vol. 2, No. 1, 32-39, June 2019

DOI: 10.22036/icr.2019.185320.1048

Naphthalene-based Azo-azomethine Chemosensor: Naked Eye Detection of Fluoride in Semi-aqueous Media

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(Received 11 May 2019, Accepted 2 July 2019)

A new azo-azomethine chemosensor containing active phenolic sites, H₂L, has been designed and synthesized for rapid detection of inorganic fluoride over the other anions such as Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, NO₃⁻, N₃⁻ in DMSO/water (90/10) media. The ¹H NMR titration revealed that the colorimetric response was considered to be the direct consequence of hydrogen-bond formation between phenolic groups of the receptor and fluoride ion followed by deprotonation. The anions recognition ability of H₂L was also evaluated using UV-Vis spectroscopy. Importantly, H₂L can detect inorganic fluoride even at 2.04 × 10⁻⁶ M level, which is lower than the World Health Organization (WHO) permissible level. Interestingly, H₂L was used for qualitative detection of fluoride anion in commercially available mouthwash and toothpaste.

Keywords: Azo-azomethine, Colorimetric detection, Chemosensor, Fluoride ion recognition

INTRODUCTION

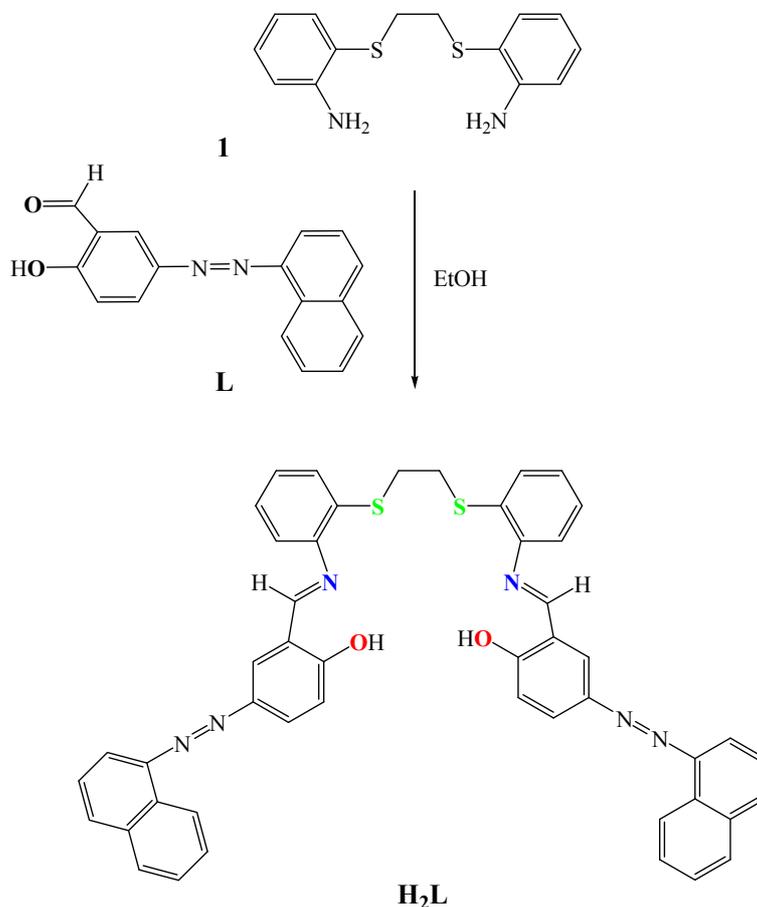
Paramount attention has been laid over last few decades on development of molecular sensors for chemically and biologically relevant anions [1-3]. Among various anions, fluoride has been intensively researched owing to its imperative roles in a broad range of chemical, biological and environmental processes [4,5]. For instance, fluoride ions show beneficial effects in human health. Fluoride plays a crucial role in protecting dental health and treating osteoporosis. On the other hand, excessive fluoride intake may cause collagen breakdown, bone disorders, thyroid activity, depression and immune system disruption [6-8]. Thus, the impetus for development of synthetic chemosensors proficient for sensing fluoride ion is compelling.

Substantial efforts have devoted to fabrication of colorimetric anion sensors, since naked eye detection without requiring spectroscopic instrumentation is low cost

and highly desirable for applications in immediate screen processes [9-11]. Most of these chemosensors employ common recognition moieties for anion sensing include amide, urea and thiourea, amidourea, phenol, pyrrole, imidazolium and indole [12,13]. In most reported chemosensors either hydrogen bonding or complete deprotonation of active N-H or O-H protons of the subunits plays pivotal role in recognition phenomenon. However, most of the reported sensors are chromogenic and their color change upon the addition of fluoride ions is quite similar to those upon the addition of acetate and dihydrogenphosphate [14-16]. In the other hands, the most molecular chemosensor are restricted to detect of fluoride ions in aqueous media [17,18]. This obstacle is attributed to the fact that water is a highly competitive solvent and participates in detection process of F⁻ by mediating interactions between the binding partners. In this regard, F⁻ get solvated strongly even with a trace amount of water [19]. The mentioned blockages limit the discrimination and detection of inorganic fluoride anion in water.

The mentioned obstacle prompted us to develop a new naphthalene-based chromogenic azo-azomethine

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Scheme 1. Synthesis of sensor H₂L

chemosensor for facile detection and discrimination of inorganic fluoride anions. Herein, we report synthesis, characterization and detailed anion binding studies of a new colorimetric azo-azomethine chemosensor, H₂L, for rapid detection and naked eye sensing of fluoride anion in semiaqueous media (Scheme 1). The affinity of H₂L toward fluoride was also evaluated by means of UV-Vis and ¹H NMR spectroscopies. The H₂L was also used for qualitative detection of fluoride anion in commercially available mouthwash and toothpaste.

EXPERIMENTAL

Materials

All of the reagents and solvents involved in synthesis

were of analytically grade and used as received without further purification. All chemicals purchased from Sigma-Aldrich and Merck.

Instrumentation

The structure of all synthesized compounds was confirmed by ¹H NMR spectra, recorded on a Bruker Avance III 300 MHz spectrometers. FT-IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400-4000 cm⁻¹. Melting points were determined on Electrothermal 9200 apparatus. Elemental analyses were performed on a Vario EL III elemental analyzer. Electronic spectral measurements were carried out using Optizen 3220 UV spectrophotometer in the range of 200-900 nm.

Synthesis

1,2-Bis(2-aminophenylthio)ethane, **1**. The 1,2-bis(2-aminophenylthio)ethane, **1**, prepared *via* reaction of 2-aminothiophenol with 1,2-dibromoethane as reported before [20].

1-(3-Formyl-4-hydroxyphenylazo) naphthalene, **L**. The **L** was prepared according to the well-known literature procedure [21].

Synthesis of Chemosensor, H₂L

A solution of **1** (0.28 g, 1 mmol) in absolute EtOH (10 ml) was added to a stirring solution of **L** (0.55 g, 2 mmol) in absolute EtOH (40 ml) during a period of 20 min at 60 °C. The solution was heated in water bath for ~ 4 h at 80 °C with stirring. The mixture was filtered whilst hot and the obtained precipitate was washed with hot ethanol (three times) and then with diethyl ether. The resulted product was dried in air. Brown solid, Yield: 90%, m. p.: 237-240 °C. ¹H NMR (DMSO-*d*₆, 300 MHz, ppm): δ 3.27 (s, 4H), 7.17 (d, 2H, J = 8.70 Hz), 7.29-7.44 (m, 6H), 7.54-7.80 (m, 10H), 8.05-8.18 (m, 6H), 8.43 (s, 2H), 8.88 (d, 2H, J = 8.70 Hz), 9.18 (s, 2H), 13.77 (s, 2H). IR (KBr, cm⁻¹): 1608 (C=N), 1579 (phenol ring), 1467 (N=N), 1282 (C-O), 1105, 802 and 756. Anal. Calcd. % for C₄₈H₃₆N₆O₂S₂: C, 72.70; H, 4.58; N, 10.60. Found: C, 72.46; H, 4.36; N, 10.90. λ_{max} (nm) (ε (M⁻¹ cm⁻¹)): 270 (56200), 385 (89000) in DMSO.

RESULT AND DISCUSSION

New dipodal azo-azomethine chemosensor, H₂L, has been synthesized *via* condensation reaction of 1,2-bis(2-aminophenylthio)ethane with 1-(3-formyl-4-hydroxyphenylazo) naphthalene in ethanol in good yield (Scheme 1). The resultant product was characterized using common standard spectroscopic techniques (Supplementary materials, S2-S4). The total absence of ν(C=O) absorption band of azo-coupled precursor, **L**, in the IR spectra of azo-azomethine compound, H₂L, together with the appearance of a new absorption band at 1608 cm⁻¹ obviously indicate that Schiff-base was formed [22]. In the ¹H NMR spectrum of H₂L, the CH=N protons exhibit a singlet at 9.18 ppm. Moreover, the signal at 13.77 ppm, assigned to the OH protons, as was confirmed by deuterium exchange when

D₂O was added to DMSO-*d*₆ solution (Supplementary materials, S5). Furthermore, the elemental analyses are also in accordance with the molecular formula. The B3LYP/6-31G* geometry optimized structure of H₂L is displayed in Fig. 1.

As an initial test, the anion sensing properties of H₂L (2 × 10⁻⁵ M) were assessed visually and then by UV-Vis spectrophotometry in DMSO by adding 10 equiv. of the various anions. As shown in Fig. 2, the free H₂L displayed a band at 385 nm. Upon the addition of F⁻, intensity of absorption band at 385 nm decreased and a new band at 505 nm formed and increased obviously. Simultaneously, the yellow color of H₂L in DMSO instantly turned to red (Fig. 2).

To estimate the further details of binding characteristics of H₂L, we carried out UV-Vis spectroscopic titrations upon the addition of standard solutions of F⁻ as its tetrabutylammonium (TBA) salt to dry DMSO solution of the H₂L (2 × 10⁻⁵ M). As shown in Fig. 3, the free H₂L exhibited an intense absorption band centered at 385 nm attributed to the π→π* transition of the chromophores. On incremental increase of F⁻, the absorption band at 385 nm remarkably decreased. This change was accompanied with significant growth of the absorbance at 505 nm. A distinct isosbestic point was observed at 420 nm.

Furthermore, the stoichiometry between H₂L with fluoride anion was determined from UV-Vis spectral changes with the help of Benesi-Hildebrand method [23]. As shown in Fig. 4, the plot of 1/[A-A₀] vs. 1/[F⁻] for the titration of H₂L with tetrabutylammonium fluoride (TBAF) provided a straight line, corroborating that F⁻ interacts with H₂L in a 1:1 stoichiometry with binding constant of 3.92 × 10³ M⁻¹. The stoichiometry of host-guest interaction was also confirmed by use of continuous-variation plots (Job's plots). The variation of measured absorbance at 505 nm reaches to a maximum value when the molar fraction of [H₂L]/[F⁻]+[H₂L] is ≈0.5, indicating 1:1 stoichiometric ratio of the sensor H₂L to the fluoride anion, Fig. 5. Moreover, judging from titration findings, it has been established that the estimated detection limits of sensor H₂L towards F⁻ is 2.54 × 10⁻⁶ M.

Generally, the protic solvents, such as water, compete with anionic guest for binding sites of the host thereby disturbing the interactions between host and guest [2,24,25].

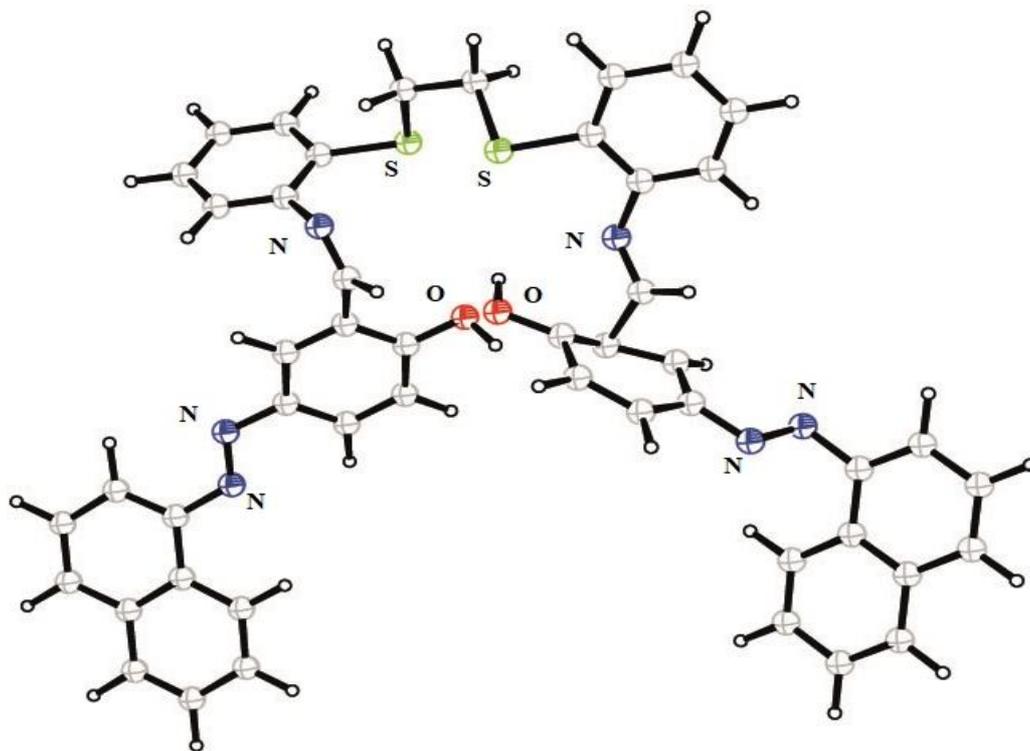


Fig. 1. The B3LYP/6-31G* geometry optimized structure of H₂L.

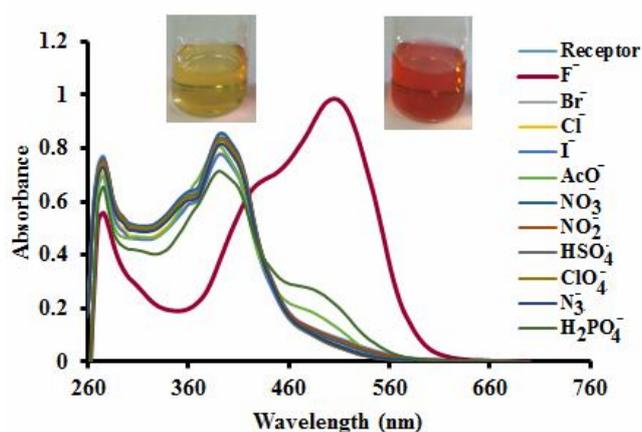


Fig. 2. Color changes of sensor H₂L (2×10^{-5} M in DMSO) after addition of 10 equiv. of different anions.

This is the reason why the direct detection of inorganic anions in water constitutes to be a quite difficult task. To evaluate the applicability of the chemosensor in aqueous environment, we recorded the UV-Vis spectroscopic titration of H₂L (2×10^{-5} M) in 90:10 DMSO-water with

standard solution of TBAF (Fig. 6). Progressive addition of F⁻ was resulted gradual decrease in the intensity of absorption band at 385 nm and simultaneous growth of band at 485 nm. These changes were accompanied by the dramatic color change from yellow to red. Obviously, the

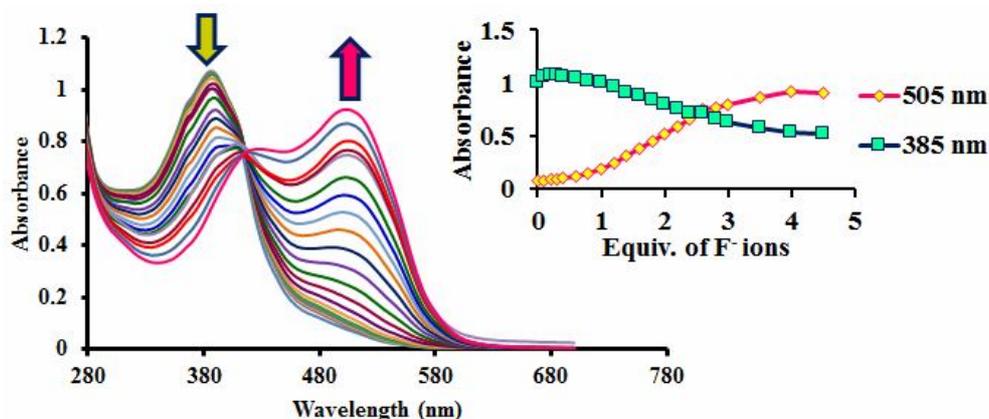


Fig. 3. UV-Vis absorption spectra of H_2L (2×10^{-5} M) in dry DMSO upon the addition of TBAF (0-10 equiv.). Inset shows the binding isotherm at selected wavelengths in DMSO.

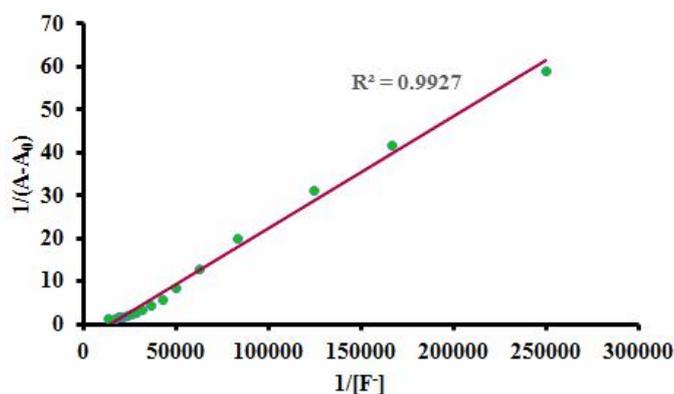


Fig. 4. Benesi-Hildebrand plot of H_2L binding with F^- anion associated with absorbance change at 505 nm in DMSO.

distinct isosbestic point was observed at 410 nm. It is worth noting that on all occasions the number of equivalents of anion required to reach a plateau were exactly the same as those required in DMSO, corroborating that the interaction stoichiometry between H_2L and anion is not affected by the presence of competitive water molecules.

To confirm the 1:1 ratio between H_2L and fluoride anion in aqueous media, Benesi-Hildebrand method was executed (Supplementary materials, S6) [23]. Accordingly, the deprotonation constant for H_2L toward F^- in aqueous media was calculated to be 1.77×10^4 M $^{-1}$. Interestingly, the current system can detect F^- at a low limit of about

2.04×10^{-6} M.

To shed light on the nature of the interaction between H_2L and fluoride anion, 1H NMR spectroscopy was applied. Figure 7 illustrates the 1H NMR spectra of H_2L in the absence and also in the presence of TBAF in DMSO- d_6 . It should be noted that the 1H NMR spectra present the signal at 13.77 ppm, assigned to the OH protons of H_2L , as was authenticated by D $_2$ O exchange experiment. Interestingly, upon the addition of 1 equiv. of F^- , the signal attributed to the OH protons, got thoroughly vanished and simultaneously, the aromatic proton signals underwent upfield shift. The upfield shift is attributed to the

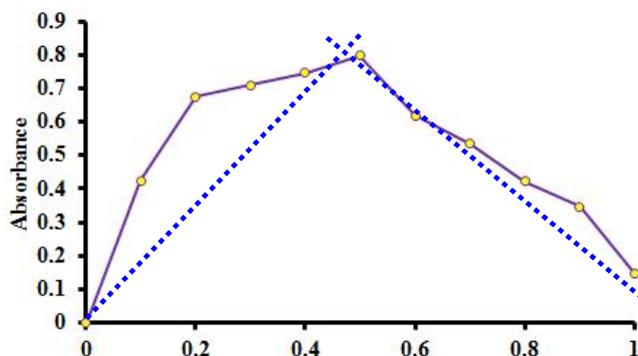


Fig. 5. Job's plot for sensor H₂L with tetrabutylammonium fluoride using UV-Vis.

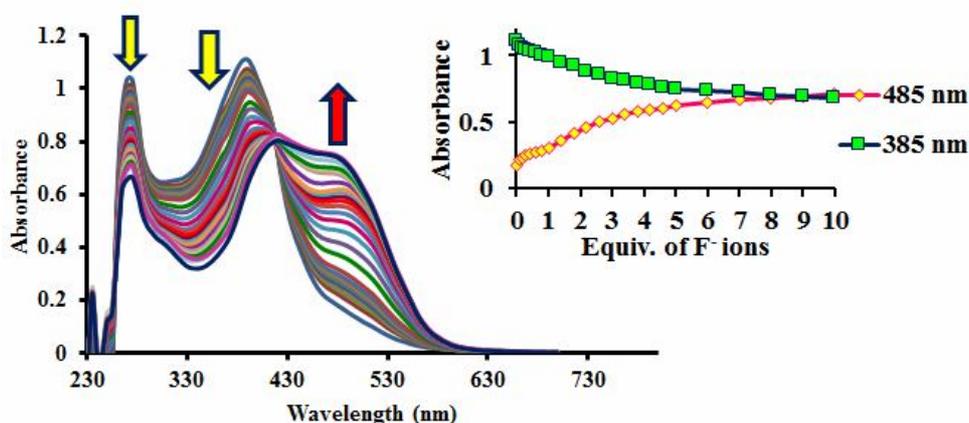


Fig. 6. UV-Vis titration of the sensor H₂L (2×10^{-5} M) in 9:1, DMSO-water with increasing concentration of TBAF (0-10 equiv.). Inset shows the binding isotherm at selected wavelengths in 9:1, DMSO-water.

considerable augmentation of electron density onto the π -conjugated framework, causing shielding effect. The evidence observed above revealed that the colorimetric response was considered to be the direct consequence of hydrogen-bond formation between phenolic groups of the receptor and fluoride ion followed by deprotonation.

Moreover, the deprotonation process was verified by UV-Vis titration experiment of H₂L with a standard solution of tetrabutylammonium hydroxide (TBAOH) [26]. The titration profiles afforded similar spectral pattern as observed for fluoride anion, suggesting deprotonation of phenolic OH protons. The OH⁻ induced spectral changes of H₂L are shown in Fig. 8.

Recently, we were inspired by Hundal and co-workers [5], who reported qualitative detection of anions in aqueous

media. Thus, we wondered if H₂L could be applicable for naked eye sensing of inorganic fluoride in real samples and water. To achieve this ultimate goal, we extended our work for qualitative detection of F⁻ anions in commercially available mouthwash and toothpaste. To our delight, addition of one drop of mouthwash to H₂L, caused a conspicuous color change from light yellow to red, indicating H₂L is capable of detecting inorganic fluoride in aqueous media by the naked eyes. The result was also substantiated using UV-Vis spectroscopy. For this purpose, we employed the 2×10^{-5} M of H₂L in 90:10 DMSO-water solutions. Very remarkably, as is shown in Fig. 9, addition of 5 μ l of commercial mouthwash caused the appearance of new band at 505 nm. Therefore, H₂L can be considered as a highly promising candidate for rapid detection and

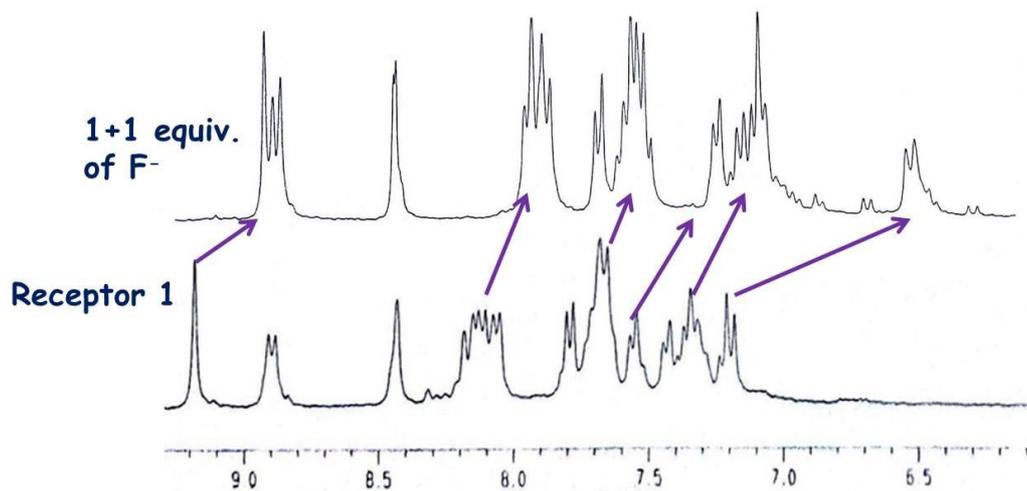


Fig. 7. ¹H NMR spectra of H₂L in DMSO-*d*₆ (2×10^{-2} M) in the absence and presence of 1 equiv. of F⁻.

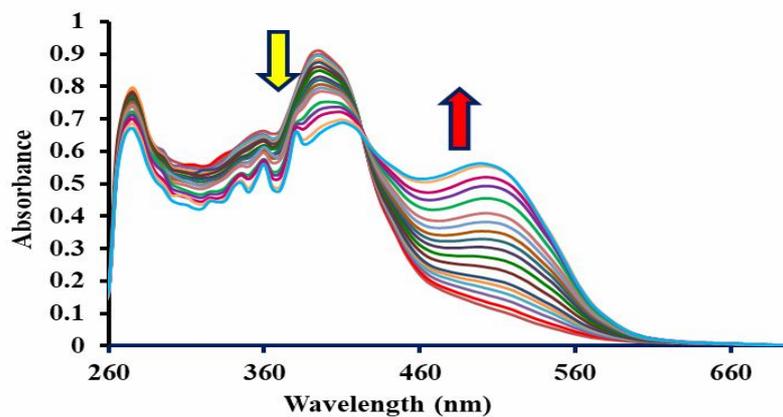


Fig. 8. UV-Vis absorption spectra of sensor H₂L (2×10^{-5} M in DMSO) upon the addition of TBAOH (0-10 equiv.).

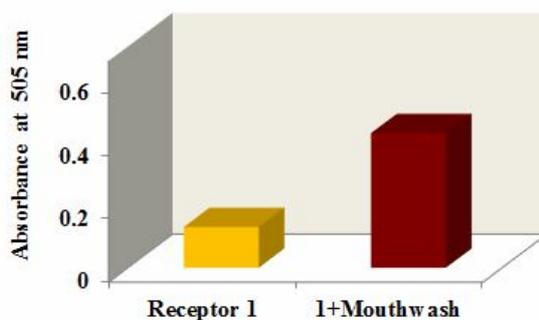


Fig. 9. The proof of concept for detection of fluoride in mouthwash.

colorimetric sensing of anions in real samples.

CONCLUSIONS

To sum up, we present the synthesis, characterization and anion binding behavior of a new dipodal azo-azomethine naphthalene-based chemosensor. The mentioned sensory system allows facile recognition of F⁻ in both DMSO and DMSO-water (90/10) media without any spectroscopic instrumentation. Interaction of the prepared chemosensor with fluoride ion gave rise to the dramatic color change from light yellow to red with concomitant bathochromic shift. The recognition details of anion sensing were also studied using ¹H NMR technique. The ¹H NMR experiments confirmed that the color response was considered to be the direct consequence of deprotonation of OH protons. Notably, the sensory system could as well be served as proficient tool for qualitative detection of anions in real samples.

ACKNOWLEDGEMENTS

We are grateful to the Arak University for financial support of this work (Grant Number No. 93-13597)

SUPPORTING MATERIALS

Supporting information associated with this article can be found free of charge *via* the “Supplementary Content” section of this article’s web page.

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