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Rapid detection of HSO₄⁻ in water: Novel immobilized azoazomethine colorimetric anion receptors on solid supports

Saba Mahdavi Hezaveh, Hamid Khanmohammadi *, Mojgan Zendehdel

Department of Chemistry, Faculty of science, Arak University, Arak 38156-8-8349, Iran

Abstract

The immobilized azo-azomethine receptors on amorphous SiO₂, S-B, SiO₂ nanoparticles, S-NPs, and NaY zeolite, S-ZY, have been prepared and applied as solid phase sensors for detection of HSO_4^- , over other interfering anions, in 100% aqueous media. Remarkably, S-B and S-ZY show unique and rapid sensitivity towards HSO_4^- , which could it easily visualized through naked eye detection even at 5×10^{-4} molL⁻¹ and 4×10^{-4} molL⁻¹, respectively. The fabricated solid phase sensors were characterized using powder XRD diffraction, TGA-DTA, FE-SEM and also FT-IR techniques. Moreover, the related molecular anion receptor, HL, has been prepared and used for naked eye detection of F⁻ and AcO⁻, in dry DMSO. The anions recognition ability of HL was also evaluated using UV–Vis and ¹H NMR spectroscopic methods.

Keywords: Azo-Azomethine; Bisulfate detection; Colorimetric sensor; Schiff base; NaY zeolite.

^{*} Corresponding author: h-khanmohammadi@araku.ac.ir; Tel: +98-86-34173431; Fax: +98-86- 34173406.

1. Introduction

To date, there are so many reported molecular Schiff-base receptors which are able to detect and colorimetric sensing of biologically important anions, such as F^- , AcO^- , $H_2PO_4^-$, in aqueous/semiaqueous media [1-3]. However, some of Schiff base receptors, based on hydrogenbonding motifs, have displayed poor selectivity against basic anions in aqueous media [4-6]. The major bottlenecks of that receptors are insolubility in water and also water intolerance which restricts their use for real samples analysis in aqueous media [7,8].

Among variety important anions, HSO_4^- is of particularly interest owing to its established role in biological and industrial areas [9, 10]. For instance, HSO_4^- is present in many agricultural fertilizers, industrial raw materials and nuclear fuel waste, which eventually get into the environment [11, 12]. The generated toxic sulfate ions, from dissociation of HSO_4^- in water, cause irritation of skin, eyes and respiratory paralysis [13].

Therefore, design and synthesis of anion receptors that are able to sense HSO_4^- , in aqueous media, has currently been evolving as a forefront research topic [14, 15]. Up to date, many of molecular Schiff-bases receptors, as chemosensor have reported which are quite successful for detection of HSO_4^- anions in aqueous/semiaqueous solutions [16-18]. While that existing sensors have proven to be considerably effective in solution, they can't applied to the continuous online detection owing to the intrinsic limitations of HSO_4^- anions in device fabrication. Actually, hydrolysis of -C=N-bond in the presence of HSO_4^- , and also formation of aldehyde and amine, presented as mechanism of HSO_4^- anion sensing in water using Schiff base receptors [19, 20].

To date, there have been few reports of solid colorimetric chemosensors for detection of $HSO_4^$ anion in water [21]. As a new approach, this motivated us to design new receptors based on lowcost molecular azo-azomethines, for rapid detection of HSO_4^- anion in water. However, one major

question perturbed us: although the most molecular Schiff bases are water-insoluble, how can we apply a Schiff base receptor to detect HSO_4^- anion in water? For this purpose, we design and prepare new covalently immobilized molecular Schiff base receptors on solid supports for detection of HSO_4^- anion in water.

The molecular Schiff base, **HL**, was also prepared from the condensation reaction of 2-hydroxy-3-methoxy-5-((4-nitrophenyl)diazenyl)benzaldehyde, **1**, with 3-aminopropyl triethoxysilane (3-APTES) in EtOH (Scheme 1). Although **HL** is an excellent receptor for detection and colorimetric sensing of F⁻ and AcO⁻ in DMSO, no significant color change appeared in the presence of the mentioned anions as well as HSO₄⁻ in water. Then, we prepared new, based on **HL**, using solid supports (amorphous SiO₂, **S-B**, nano SiO₂, **S-NPs**, and also NaY Zeolite, **S-ZY**) for rapid and high selective detection of anions in water (Scheme 2). Surprisingly, **S-B** and **S-ZY** show excellent sensitivity and selectivity against HSO₄⁻ over other anions, such as F⁻. AcO⁻, SO₄²⁻, Cl⁻, CN⁻, NO₃⁻, H₂PO₄⁻, in 100% aqueous media. Indeed, **S-B** and **S-ZY** would be especially suitable for the detection of HSO₄⁻ anion in water and show significant, discernible and rapid color change, even with naked eye at 5×10^{-4} molL⁻¹ and 4×10^{-4} molL⁻¹, respectively. The structures of all prepared sensors were also characterized using powder XRD diffraction, TGA-DTA, FE-SEM and FT-IR technique.

Scheme 1

Scheme 2

2. Experimental

2.1. Materials

All of the reagents and solvents involved in synthesis were of analytically grade and used as received without further purification. 3-Aminopropyl triethoxysilane (3-APTES), 4-Nitroaniline, Tetraethylorthosilicate (TEOS) and 2-Hydroxy-3-Methoxybenzaldehyde (*O*-Vanillin) obtained from Aldrich and Merck. Amorphous SiO₂ (mesh 60) was obtained from Merck and used as received. NaY Zeolite obtained from SPAG (Tehran, I. R. IRAN).

2.2. Instrumentation

¹H NMR spectra recorded on a Bruker Avance 300 MHz spectrometer. FT-IR spectra recorded as pressed KBr discs, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400-4000 cm⁻¹. Melting points determined on Electrothermal 9200 apparatus. C. H. N. analyses were performed on a Vario EL III elemental analyzer. Electronic spectra carried out using Optizen 3220 UV-Vis in the range 200-700 nm. X-ray diffraction patterns of the prepared samples recorded using a Philips PW1730 X-ray diffractometer with Cu K α radiation (0.15418 nm) operated at 30 kV and 15 mA at a scan speed of 1° min⁻¹ and 20 range of 0–80°.

2.3. Synthesis

2.3.1. Azo-coupled O-vanillin precursor, 1

Azo-coupled *O*-vanillin precursor was prepared according to the modified literature procedure 22]. *O*-Vanillin (10 mmol) dissolved in water (20 mL) containing (10 mmol) of sodium hydroxide and (40 mmol) of sodium carbonate during the period of 30 min at 0 °C. The resulted solution added, slowly, to a solution of diazonium chloride (10 mmol) in water at 0–5 °C. The reaction mixture stirred for one h at 0 °C and then allowed to warm slowly to room temperature. The product was collected by filtration and washed with 100 mL of NaCl solution (10%) under vacuum. The obtained solid dried in air. Yield: 2.77 g (92%), m.p. 209-211 °C. ¹H NMR (d₆-DMSO, 300 MHz,

ppm): δ 3.97 (s, 3H), 7.69 (s, 1H), 7.92 (s, 1H), 8.02 (d, 2H, J=8.41 Hz), 8.39 (d, 2H, J=8.4 Hz), 10.37 (s, 1H), 10.52 (br, 1H). IR (KBr, cm⁻¹); 1655 (CHO), 1613 (C=C), 1586 (phenol ring), 1516 (NO₂), 1340 (NO₂) 1458 (N=N), 1269 (C-O), 1130, 960 and 756. EI-Ms: MW (C₁₄H₁₁N₃O₅)= 301.25, experimental m/z (M⁺)=301.07.

2.3.2. 2-methoxy-4-(-(4-nitroohenyl)diazenyl)-6-(-(3-triethoxysilyl)propylimino)methyl)phenol, HL

A solution of 3-APTES (4 mmol) in dry ethanol (10 mL) added to a stirring solution of azo-coupled precursors, **1**, in dry ethanol (20 mL) at 60 °C. The mixture heated over 24 h at 80 °C under N₂ atmosphere and then filtered whilst hot. Dark red solid, m. p. >290 °C. IR (KBr, cm⁻¹); 2932 (C–H), 1647 (C=N), 1609, 1547 (phenol ring), 1516 (NO₂), 1454 (N=N), 1337 (NO₂), 1259 (C–O), 1132, 1101 and 856. ¹H NMR (d₆-DMSO, ppm): δ 0.68 (br, 2H), 1.05 (t, 9H), 1.73 (br, 2H), 3.70 (m, 8H), 4.30 (s, 3H), 7.26 (s, 1H), 7.75 (m, 2H), 8.11 (m, 2H), 8.28(br, 1H), 10.07 (s, 1H). $\lambda_{max}(nm)$ (ϵ (M⁻¹ cm⁻¹)): 280 (18875) and 455 (33700) in THF. EI-Ms: MW (C₂₃H₃₂N₄O₇Si)= 504.61, experimental m/z (M⁺)=504.20.

2.3.3. Preparation of SiO₂ NPs

SiO₂ NPs prepared by using modified Stöber method [23] which involves hydrolysis of TEOS and polyethylene glycol in the presence of ammonia in ethanol as follow: Polyethylengelycol (5 g) added to a solution of ethanol (20 mL) and double distilled water (100 mL) in 250 mL round bottom boiling flask. The flask put into the ultrasonic bath at ambient temperature for 30 min. After this, NH₃ (12.5 mL) and TEOS (10 mL) added to the mentioned flask. The mixture kept at 90 °C in an oil bath under N₂ atmosphere over a period of 24 h. The obtained gel centrifuged and washed with ethanol and double distilled water. The product dried in vacuum oven at 100 °C for 24 h.

2.3.4. General procedure for preparation of amino-modified solid supports

All amino-modified solid supports prepared with similar procedure. The solid support (1 g) added to a solution of 3-APTES (1 mmol) in anhydrous toluene (100 mL). After ultrasonication, for 30 min, the mixture refluxed for 24 h under N_2 atmosphere. The product separated by centrifugation at 2000 rpm for 10 min. The collected solid washed several times with EtOH by repetitive dispersion and precipitation cycles to rinse away raw material.

2.3.5. Preparation of functionalized amorphous SiO₂ sensor, S-B

The functionalized amorphous SiO_2 sensor prepared based on previous publications of similar materials with minor modifications [24]. In brief, 0.1 mmol of **1** in dry EtOH (50 mL) added to amino-modified amorphous SiO_2 support (1 g) in dry EtOH (20 mL) and the mixture incubated under stirring for 24 h at 80 °C under N₂ atmosphere. The obtained mixture washed by repeated centrifugation (2000 rpm) and resuspension three times with chloroform and ethanol to get rid of unbound azo precursor.

2.3.6. Preparation of functionalized SiO2 nanoparticles sensor, S-NPs

The functionalized SiO₂ nanoparticles sensor prepared based on method for preparation of **S-B**. Herein, varying amounts (0.1, 0.3 and 0.5 mmol) of **1** were used for reaction with amino-modified SiO₂NPs support (1 g) in dry EtOH (20 mL), separately. In each case, the mixture incubated under stirring for 24 h at 80 °C under N₂ atmosphere. The obtained mixture washed by repeated centrifugation (2000 rpm) and resuspension three times with chloroform and ethanol to get rid of unbound azo precursor.

2.3.7. Preparation of functionalized NaY Zeolite sensor, S-ZY

The functionalized NaY Zeolite sensor prepared via reaction of **1** (0.5 mmol) with amino-modified NaY Zeolite support [25] (1 g) in dry EtOH (20 mL). The mixture incubated under stirring for 24 h at 80 °C under N₂ atmosphere. The obtained mixture washed by repeated centrifugation (2000 rpm) and resuspension three times with chloroform and ethanol to get rid of unbound azo precursor.

3. Results and Discussion

3.1. Characterization of molecular receptor

The molecular azo-azomethine receptor, HL, synthesized via condensation reaction of azocoupled O-vanillin precursor, 1, and 3-aminopropyl triethoxysilane in EtOH (Scheme 1). The HL characterized by Mass, IR and NMR spectroscopic methods. The total absence of v(C=O) absorption band of 1 in the IR spectrum at 1655 cm⁻¹ together with the appearance of a new absorption band at 1647 cm⁻¹ indicate that the new azo-azomethine, HL, formed. Also, the infrared spectrum of **HL** exhibits strong bands at 1337 and 1516 cm⁻¹ assigned to the NO₂ group [26]. In the ¹H NMR spectra of **1**, the CH=O proton exhibit a singlet resonance at 10.37 ppm. The presence of a broad signal at ca. 11.50 ppm assigned to the OH proton, as confirmed by deuterium exchange when D_2O added to d_6 -DMSO solution of **1**. In the ¹H NMR spectrum of **HL**, the CH=N proton exhibit a resonance at 10.07 ppm. Also, the ¹H NMR spectrum show the signals at $\delta_{\rm H}$ 0.68-3.80 ppm assigned to the 3-aminopropyl triethoxysilane moiety in molecule (Supplementary materials). The electronic absorption spectrum of HL, recorded in DMSO at room temperature, display mainly two intense bands. The first UV band located at ca. 280 nm can assigned to the moderate energy $(\pi \rightarrow \pi^*)$ transition of the aromatic rings while the second band at ca. 450 nm is due to low energy $(\pi \rightarrow \pi^*)$ transition involving the π -electrons and also the charge transfer transitions involving whole molecule of the receptor [27].

3.1.2. Anion recognition properties of HL

Initially, the sensing ability of **HL** towards various anions was investigated qualitatively by visual examination of the anion-induced color changes of the receptor in dry DMSO. As exemplified in Fig. 1 (a), upon the addition of 10 equiv. of various anions, as tetrabutylammonium (TBA) salt, to a solution of **HL** in DMSO (5×10^{-5} molL⁻¹), only a vivid colour change observed drastically from light orange to deep blue and red in the presence of F⁻ and AcO⁻, respectively. Conversely, the addition of other surveyed anions failed to cause any conspicuous color change which reflects the capability of molecular **HL** to detect F⁻ and AcO⁻ anions in dry DMSO. However, anion recognition ability of molecular **HL** failed when a few drops of water added to the DMSO solution. To provide fundamental insights into the suitability of **HL**, the anions recognition behaviour of **HL** explored using UV-Vis spectroscopy upon the addition of 10 equiv. of different anions to **HL** solution in DMSO (5×10^{-5} molL⁻¹), Fig. 1 (b). Most significantly, upon the addition of various anions, only F⁻ and AcO⁻ were able to have a profound effect on the electronic spectrum of **HL**.

Figure 1

The effect of interference of other anions was also evaluated. The result shows that the fluoride and acetate ions, individually, could detected by naked eyes without interference from other anions (Supplementary materials).

Moreover, to get quantitative insights into **HL-F** interaction, sensing mechanism and also study of absorption spectra changes, the spectrophotometric titration experiment carried out. For this purpose, absorption spectra changes probed after gradually addition of different concentrations of F^- (0.2–9 equiv.) to a solution of **HL** (5×10⁻⁵ molL⁻¹) in dry DMSO. As shown in Fig. 2 (a), the addition of F^- caused to gradually decreases intensities of the bands at ca. 280 nm and ca. 450 nm and simultaneously formation of new band at ca. 600 nm, attributed to the charge transfer (CT)

from interaction between fluoride anion and **HL**. Correspondingly, one clean isosbestic point observed at 555 nm. Contrary, similar isosbestic point was not observed for AcO⁻ anion (Supplementary materials).

Plotting of $1/(A-A_0)$, which A and A_0 are the absorbance of **HL** in the presence and absence of F^- , respectively, versus $1/[F^-]$ showed a linear relationship, Fig. 2 (b), indicating **HL** bound with F^- in 1:1 binding stoichiometry. The binding constant, K_a , as obtained from Benesi–Hildebrand equation [28] is $1.3 \times 10^4 \,\text{M}^{-1}$ and detection limit of F^- is $1.13 \times 10^{-6} \,\text{molL}^{-1}$.

Figure 2

To further study of the interaction between molecular receptor and fluoride, ¹H NMR titration experiments conducted by addition the different amounts of tetrabutylammoniumfluoride, TBAF, to d_6 -DMSO solution of **HL** (Supplementary materials). It is clear that the OH proton signal of the azo phenol moiety at, 13.87 ppm, thoroughly disappeared when only 0.5 equiv. of F⁻ added into a solution of **HL**. This indicates that strong hydrogen bond formed between fluoride anion and active OH group, as previously reported [29]. Interestingly, a typical HF₂⁻ signal, at ca. 16.0 ppm, observed in ¹H NMR titration experiments at higher concentration of F⁻, indicating that deprotonation of **HL** occurred

Moreover, deprotonation of phenolic OH proton was further supported by titration of **HL** with standard solution of tetrabutylammonium hydroxide (TBAOH) in DMSO. Fig. 3 indicates the OH⁻ induced spectral changes of **HL**. Evidently, the titration profile afforded similar spectral pattern as observed for other basic anions, AcO⁻ corroborating the deprotonation phenomenon [30].

Figure 3

3.2. Solid state sensors

3.2.1. Anion recognition properties of the solid sensors

The sensing ability of the prepared sensors, **S-B**, **S-NPs** and **S-ZY**, towards various anions, 5×10^{-3} molL⁻¹, such as **F**⁻, AcO⁻, NO₃⁻, CN⁻, H₂PO₄⁻, HSO₄⁻, Cl⁻ and SO₄²⁻, as their sodium salts, has investigated qualitatively by visual examination of the anion-induced color changes of the individual sensors in water. Surprisingly, **S-B** and **S-ZY** were very sensitive toward HSO₄⁻ and exhibited a fast response time, below than 10 s, to detection of bisulfate over other anions in water, Fig. 4 (a) and Fig. 4 (b). Thus, when **S-B** and **S-ZY** added to water solution containing bisulfate, the color of solution was proportional to the amount of bisulfate ions. Fig. 5 (a) and Fig.5 (b) show color scale obtained upon the addition of **S-B** and **S-ZY** solid to bisulfate solutions of different concentration. Actually, in the presence of **S-B** and **S-ZY** the lowest concentration of HSO₄⁻, in water, which can be recognize by naked eye found to be 5×10^{-4} molL⁻¹ and 4×10^{-4} molL⁻¹, respectively. Furthermore to check the practical utility of **S-B** and **S-ZY** the possible interferences by other anions carried out. The result indicated that the mentioned sensors could use for the detection of HSO₄⁻ ion in real samples without any other anion interferences (Supplementary materials).

Figure 4

Figure 5

However, when **S-NPs** used as sensor a significant color change, from dark red to orange-yellow in water solution was observed in the presence of HSO_4^- after 12 h, over other anions (Supplementary materials). In the other hand, the behavior of **S-B** and **S-ZY** in similar acidic condition (in the presence of HCl) examined. As expected, upon the addition of H⁺ ions in aqueous solution, containing **S-B** and **S-ZY**, an obvious color change, quite similar to HSO_4^- , observed, Fig. 6.

Figure 6

3.2.2. FT-IR Spectroscopy

The symmetric stretching and bending frequency bands of Al-O-Si framework of zeolite are appear at ca.791 and 463 cm⁻¹, respectively [31]. The asymmetric stretching of Al–O–Si chain of zeolite is appear at ca.1010 cm⁻¹. The IR spectra of S-ZY before and after functionalized and also after treatment with HSO₄⁻ are given in Fig. 7. The FT-IR spectra of S-ZY indicated an intense band about ca.1015 cm⁻¹ attributable to the asymmetric stretching of Al–O–Si chain of zeolite. The broad band about ca. 3550 cm⁻¹ in is due to stretching vibrations involving OH groups. A comparison of the infrared spectra of the free zeolite Fig.7 (a) and the Schiff base immobilized receptors before, Fig.7 (c), and after, Fig.7 (d), reaction with HSO_4^- ion show remarkable differences in the region 1600–3000 cm⁻¹. The reduce intensity of v(C=N) stretching band, at ca. 1650 cm⁻¹, in the IR spectra of the Schiff base immobilized receptors together with appearance of new band at ca. 1722 cm⁻¹, after reaction with HSO₄⁻, clearly indicated that the immobilized Schiffbase receptor was hydrolysed after reaction with HSO₄⁻, Fig.8. The infrared spectra of free S-B and S-NPs shows strong bands at ca. 1160, ca. 1090 and ca. 800 cm⁻¹ which are characteristic silica network according to the similar literature (Supplementary materials) [32].



Figure 8

3.2.3. BET analysis

Table 1 shows the BET surface area and pore volumes of, amorphous SiO₂, S-B, NaY and S-ZY. The S-B and S-ZY displayed abrupt decrease of surface area as compared to amorphous SiO₂, and NaY, respectively. This, may be, attributed to most non-porous coverage of solid supports surface

by the azomethine receptor and can lead to restricted access to the pores for adsorption of N₂ gas, Fig. 9 and supplementary materials [33].

Table 1

Figure 9

3.2.4. Thermal analysis

Thermal stability and decomposition behavior of the solid sensors have been studied by TGA from room temperature up to 700 °C. The TGA curve of **S-B** is given in the Fig. 10 (a). The first mass loss until 180 °C, about 2.1%, is attributed to desorption of water molecules. The second step of weight loss, about 200-600 °C, is due to removal of organic fragment from solid surfaces (5.5%). The TGA plots for **S-NPs** and **S-ZY** is shown in Fig. 10 (b) and Fig. 10 (c), respectively. As seen from Fig. 10 (b) and Fig. 10 (c), the weight loss of 5.09 % and 9.31 % between the temperature intervals of 25-200 °C is attributed to desorption of physical and chemical water molecules present in the **S-NPs** and **S-ZY**, respectively. Above this temperature organic fragment comes out with multiple steps in the temperature range 325–500 °C. The second step with 5.27 % and 8.05% weight loss is assigned to decomposition of Schiff base for **S-NPs** and **S-ZY**, respectively. In the last step of **S-ZY** TGA curve, Fig. 10 (c), the structure of zeolite is changed.

Figure 10

3.2.5. Powder XRD analysis

The powder XRD patterns of the solid supports before and after immobilization of Schiff base ligand are given in Fig. 11(a-c). The XRD patterns of zeolite Y is characterized by many sharp peaks due to the framework ordering of zeolite [34], Fig. 11 (a). The diffraction patterns

functionalized support after binding of Schiff base molecule is similar to that of the native support. This provided that only little or negligible loss in crystallinity and morphology of **S-ZY** during the functionalize procedures has taken place and the percentage of amorphization of zeolite Y is small [35]. Interestingly, the change at the intensities of XRD peaks is negligible indicating that the most added Schiff base ligand inserted into and some of them, in agreement with BET data, were in outside of the channels of zeolite [36]. Fig. 11 (b) shows the powder XRD patterns of native amorphous SiO₂ and **S-B**. The presence of several weak peaks, located in the range of 10–55°, indicated that the phase transformation from amorphous to crystalline phase, in **S-B**, was take placed during immobilization process. Fig. 11 (c) represents the powder XRD patterns of nano particles SiO₂ and **S-NPs**. The morphology of **S-NPs** studied using the field emission scanning electron microscopy (FE-SEM) technique. It was observed that the prepared **S-NPs** nanospheres are aligned, dense and non-crystalline phase, with a diameter of ca.100 nm, as shown in Fig. 12. Therefore, the response time of **S-NPs** towards HSO₄⁻ is slower, 12 h, than that of larger size and hollow, **S-B** and **S-ZY**, sensors.

Figure 11

Figure 12

4. Conclusion

New series of molecular and also fabricated sensors on solid-supports have prepared as efficient chromogenic sensing materials for naked eye detection of anions in aqueous and semiaqueous media. The molecular azo-azomethine sensor, **HL**, exhibited discernable color changes upon the

addition of more basic anions, such as F^- and AcO⁻, in DMSO. The recognition details of the anion sensing of **HL** were also assessed using ¹H NMR and UV-Vis spectroscopic methods. Furthermore, the covalently immobilized **HL** on solid supports, amorphous SiO₂, **S-B**, SiO₂ nanoparticles, **S-NPs**, and NaY zeolite, **S-ZY**, were prepared. Remarkably, **S-B** and **S-ZY** sensors show unique and rapid sensitivity towards HSO₄⁻, over other interfering anions such as F⁻, AcO⁻, NO₃⁻, CN⁻, H₂PO₄⁻, Cl⁻ and SO₄²⁻ in water. The fabricated solid sensors characterized using powder XRD diffraction, BET, TGA-DTA, FE-SEM and FT-IR techniques. Hydrolysis of the immobilized Schiff-base receptor, on the surface of the solid support, is responsible for making **S-B** and **S-ZY** as sensors for detection of HSO₄⁻ in water.

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A CERTINAL

Figure Captions

Scheme 1: Synthesis of molecular receptor HL

Scheme 2: The prepared solid sensors

Figure 1: (a) Color change of **HL** (5×10^{-5} molL¹⁻ in DMSO) upon the addition 10 equiv. of various anions, as TBA salt, from left to right: Free **HL**, H₂PO₄⁻, Cl⁻, NO₂⁻, F⁻, HSO₄⁻, AcO⁻, N₃⁻, NO₃⁻ (b) UV–Vis absorption spectra of **HL** (5×10^{-5} molL⁻¹ in DMSO) in the presence of 10 equiv. of the mentioned anions

Figure 2: (a) UV-Vis absorption spectra of **HL** $(5 \times 10^{-5} \text{ molL}^{-1})$ in dry DMSO upon the addition of TBAF (0.2-9 equiv.) (b) Benesi–Hildebrand plot of **HL** binding with F^{-} anion associated with absorbance change at 600 nm in DMSO

Figure 3: UV-Vis absorption spectra of **HL** $(5 \times 10^{-5} \text{ molL}^{-1})$ in dry DMSO upon the addition of TBAOH

Figure 4: (a) Color changes of **S-B** and (b) **S-ZY** in present of various anions, $(5 \times 10^{-3} \text{ molL}^{-1})$ in water. From left to right: (a) none, F⁻, AcO⁻, SO₄²⁻, CN⁻, Cl⁻, NO₃⁻, H₂PO₄⁻, HSO₄⁻ and (b) none, F⁻, AcO⁻, NO₃⁻, HSO₄⁻, CN⁻, SO₄²⁻, Cl⁻, H₂PO₄⁻.

Figure 5: Colorimetric response of H₂O-suspended of (a) **S-ZY** and (b) **S-B** in the presence of HSO₄⁻ (from left to right 5×10^{-3} , 1×10^{-3} , 5×10^{-4} and 1×10^{-4} molL⁻¹)

Figure 6: Colorimetric response of H_2O -suspended of (a) **S-B** and (b) **S-ZY** in the presence of H^+ ions.

Figure 7: The IR spectra of (a) free zeolite NaY, (b) amino modified zeolite H₂N-Y and (c) free **S-ZY** and (d) **S-ZY** when treatment with HSO₄⁻

Figure 8: Possible complexation mode of solid sensors, S-B and S-ZY, with HSO4⁻

Figure 9: The N₂ adsorption/desorption isotherms of S-ZY

Figure 10: TGA-DTA analyses curves of (a) S-B, (b) S-NPs and (c) S-ZY

Figure 11: powder XRD spectra of (a) NaY zeolite, (b) S-ZY, (c) Amorphous SiO2, (d) S-B, (e)

SiO₂ Nanoparticles, (f) **S-NPs**

Figure 12: FE-SEM image of S-NPs

CERTIFICATION MANUSCRAW

Table 1. Textural properties of amorphous SiO₂, NaY, S-B and S-ZY

	Surface area (m^2/g)	Pore Volume (cm ³ /g)
Amorphous SiO ₂	303.04	0.686
S-B	248.92	0.503
NaY	560	0.390
S-ZY	9.088	0.078
R		



Scheme 1























Figure 10



Figure 11



Figure 12

Graphical Abstract

Rapid detection of HSO₄⁻ in water: Novel immobilized azoazomethine colorimetric anion receptors on solid supports

Saba Mahdavi Hezaveh, Hamid Khanmohammadi *, Mojgan Zendehdel

Department of Chemistry, Faculty of science, Arak University, Arak 38156-8-8349, Iran



New immobilized azo-azomethine receptors on solid supports have been prepared and applied as anion sensors for detection of HSO_4^- , over other interfering anions, in 100% aqueous media.

^{*} Corresponding author: h-khanmohammadi@araku.ac.ir; Tel: +98-86-34173431; Fax: +98-86- 34173406.

Highlights

- New covalently immobilized azo-azomethine receptors on solid supports prepared
- The immobilized receptors on amorphous SiO₂ and zeolite-Y show unique and rapid sensitivity towards HSO₄⁻ in 100% aqueous media
- The related molecular receptor prepared and used for naked eye detection of F⁻ and AcO⁻, in dry DMSO.

J. T.