

Naked-eye detection of inorganic fluoride in aqueous media using a new azo-azomethine colorimetric receptor enhanced by electron withdrawing groups†

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A new azo-azomethine receptor, containing active phenolic sites, has been designed and synthesized for quantitative detection and colorimetric sensing of inorganic fluoride ion in aqueous media. The introduction of four electron withdrawing groups into the backbone of the receptor makes the two phenolic groups efficient hydrogen bonding sites. Hence, the receptor is capable of competing with water molecules to detect trace amounts of inorganic fluoride ions in aqueous solutions. Accordingly, the receptor showed a remarkable colour change from light yellow to orange upon the addition of aqueous solution of NaF, enabling naked-eye F⁻ sensing without any spectroscopic instrumentation. The recognition details of F⁻ sensing were also evaluated using UV-Vis spectroscopy and ¹H NMR titration techniques. The ¹H NMR titration revealed that the colorimetric response was considered to be the direct consequence of hydrogen-bond formation between the phenolic groups of the receptor and fluoride ions followed by deprotonation. Importantly, the current sensor can detect inorganic fluoride in water even at 0.058 ppm, which is lower than the World Health Organization (WHO) permissible level. To the best of our knowledge, there have been very few examples of detection limits lower than the WHO permissible level for detecting fluoride ion in drinking water (below 1 ppm). The designed sensor has also shown highly promising results for the qualitative and quantitative detection of fluoride in real samples like sea water, toothpaste and mouthwash.

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Introduction

Anions have been recognized as playing key roles in a wide range of chemical and biological processes.¹ Thus, the design and also construction of molecular sensors for the recognition and sensing of physiologically important anions have been in the forefront of chemistry research.² In particular, the design of sensors for the colorimetric detection of anions is increasingly appreciated since naked eye detection is low cost and does not require any spectroscopic instrumentation.^{3a-c} Among the biologically important anions, fluoride has attracted the interest of chemists owing to its established role in dental care and the treatment of osteoporosis.^{3d-j}

To date a number of colorimetric receptors which are capable of detecting the fluoride ion with high affinity, have been reported.⁴ The common recognition moieties of the reported receptors involve amide, urea and thiourea, amidourea, phenol, pyrrole, imidazolium and indole.⁵ Generally, the formation of hydrogen bonds between active sites, N-H and/or O-H, of these subunits with F⁻ plays a pivotal role in anion sensing. However, most receptors are restricted to the detection of tetrabutylammonium fluoride (TBAF) in organic solvents and there is a paucity of reports regarding the colorimetric detection of fluoride ion in aqueous media.⁶ This obstacle is attributed to the fact that water is a highly competitive solvent and participates in the detection process of F⁻ by mediating interactions between the binding partners. In this regard, F⁻ becomes solvated strongly even with a trace amount of water.⁷ The mentioned blockages limit the discrimination and detection of inorganic fluoride anion in water.

On the other hand, highly selective fluoride ion receptors are strongly favoured for practical applications. However, it is quite difficult to design colorimetric chemosensors for the recognition of F⁻ in water. Indeed, only a few examples of sensors capable of detecting fluoride ion in water have been reported.⁶ Furthermore, most of the determination processes are limited to either recognition of TBAF or use of test papers which need

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† Electronic supplementary information (ESI) available: Characterization data of all compounds, UV-Vis spectrophotometric titrations, stoichiometric determination by Benesi-Hildebrand method, Job's plot, UV-Vis spectral changes upon addition of protic solvent, figures and photographs showing the sensing behavior, procedure details of interference study and details of qualitative and quantitative detection of fluoride by prepared sensor. See DOI: 10.1039/c3ra42709a

several minutes to complete detection and are far away from real-life applications.⁸

Therefore, the development of sensors for the direct detection of inorganic fluoride in aqueous media accompanied by a visually striking colour change, naked eye sensing, is an important target for real-life applications. Kruger *et al.* developed a 1,8-naphthalimide-based colorimetric anion sensor containing the aminothiurea group for the recognition of NaF in aqueous solutions.⁹ Subsequently, Das *et al.* have designed a receptor for the selective and quantitative extraction of fluoride anions from aqueous solution of sodium fluoride.¹⁰ Nevertheless, the evaluation and discrimination of inorganic fluoride in aqueous media still remains as important a challenge to chemical analysis.

Until now, a number of azo sensors for the detection of fluoride have been reported. However, most of these sensors have been designed for use in noncompetitive organic solvents.^{3a,4i-k} Recently, Mahapatra and co-workers reported new chromogenic azo-azomethine receptors for the recognition of fluoride.^{4f} Although the synthesized receptors have been shown to possess good selectivity and sensitivity for fluoride ion in CH₃CN, the sensory system was not able to compete with water. Thus, F⁻ sensing in aqueous media was restricted to the use of test strips which requires several minutes for the detection process. In pursuit of these, we report here a new member of the azo-azomethine sensors, receptor **1**, (Scheme 1) for the rapid detection and colorimetric sensing of inorganic fluoride ion in aqueous media. To the best of our knowledge, this is the first azo-azomethine receptor used for the qualitative and quantitative detection of fluoride in water and real samples. The prepared molecular sensor, **1**, contains azo phenol moieties serving as sensing units to form hydrogen bonds *via* the disposal of OH groups in the presence of anions. In particular, the presence of four electron withdrawing substituents in the molecular structure of **1** enhances the acidity of its active sites and hence allows the formation of stronger hydrogen bonds

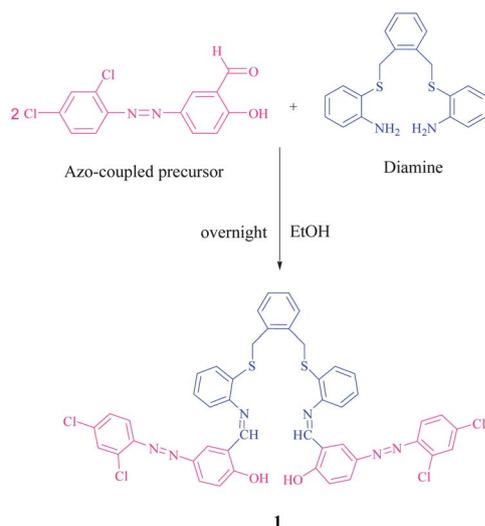
between the OH groups of the sensor and the anionic guest. Therefore, receptor **1** can compete with water for the naked-eye detection of inorganic fluoride in aqueous media.

Results and discussion

The synthesis of receptor **1** was achieved by the straightforward condensation reaction of α,α' -bis(*o*-aminophenylthio)-1,2-xylene with 1-(3-formyl-4-hydroxyphenylazo)-2,4-dichlorobenzene as depicted in Scheme 1. The prepared receptor was characterized using standard spectroscopic techniques (ESI⁺).

As an initial test, we checked the colour changes of receptor **1** in DMSO upon the addition of 10 equiv. of tetrabutylammonium (TBA) salts of F⁻, Cl⁻, Br⁻, I⁻, H₂PO₄⁻, ClO₄⁻, N₃⁻, NO₂⁻, NO₃⁻, AcO⁻ and HSO₄⁻. As shown in Fig. 1(a), a noticeable colour change was observed from light yellow to red in the presence of F⁻, AcO⁻ and H₂PO₄⁻. In contrast, other anions caused no obvious changes in colour. To further study the colorimetric behaviour of receptor **1**, UV-Vis absorption experiments were also performed upon the addition of 10 equiv. of tetrabutylammonium salts of anions to **1** (2×10^{-5} mol L⁻¹ in DMSO), Fig. 1(b). Free receptor **1** exhibited one absorption band at 369 nm and a weak tail at ~490 nm. A distinct change was observed in the spectral pattern in the presence of F⁻, AcO⁻ and H₂PO₄⁻; the extent of the changes was much more for F⁻. Moreover, the addition of anion-based salts to the DMSO solution of **1** gave a bathochromic shift from 369 nm to *ca.* 500 nm with F⁻, AcO⁻ and H₂PO₄⁻. While other anions induced negligible spectral responses.

In order to further assess the binding characteristics of receptor **1**, we carried out UV-Vis spectrophotometric titrations by adding a standard solution of TBAF to the dry DMSO solution of **1** (2×10^{-5} mol L⁻¹). As shown in Fig. 2, upon the addition of



Scheme 1 Synthesis of receptor **1**.

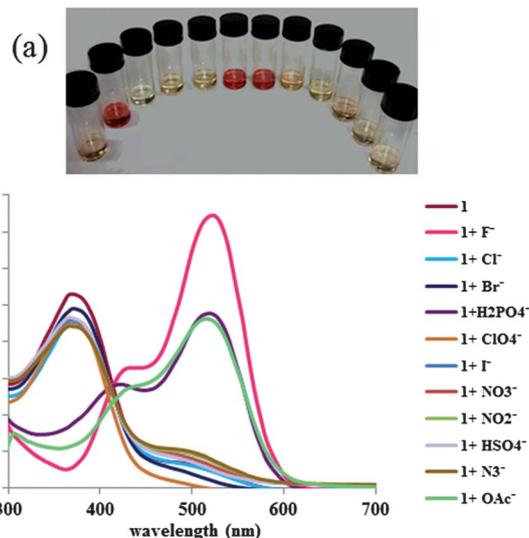


Fig. 1 (a) Colour changes of receptor **1** (2×10^{-5} mol L⁻¹ in DMSO) after addition of 10 equiv. of different anions. From left to right: none, H₂PO₄⁻, ClO₄⁻, Br⁻, Cl⁻, AcO⁻, F⁻, N₃⁻, HSO₄⁻, NO₂⁻, NO₃⁻ and I⁻ (TBA⁺ salts). (b) UV-Vis absorption spectra of receptor **1** (2×10^{-5} mol L⁻¹ in DMSO) in the presence of 10 equiv. of various anions.

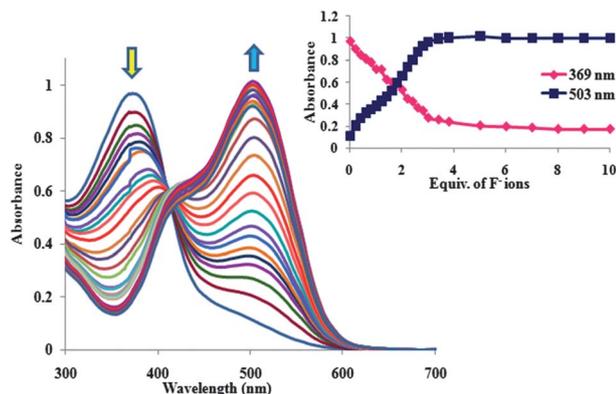


Fig. 2 UV-Vis absorption spectra of receptor **1** ($2 \times 10^{-5} \text{ mol L}^{-1}$) in dry DMSO upon the addition of TBAF (0–10 equiv.). Inset showing the binding isotherm at selected wavelengths in DMSO.

fluoride ion, the band at 369 nm, the $\pi \rightarrow \pi^*$ transition of the chromophores, decreased gradually and simultaneously a new strong absorption band, attributed to the charge transfer (CT), formed at 503 nm indicating interaction between fluoride ion and receptor. An analogous investigation was performed for the addition of the TBA salt of H_2PO_4^- and AcO^- to a solution of **1** in dry DMSO (Fig. S11 and S23, ESI[†]). The Benesi–Hildebrand method¹¹ confirmed 1 : 1 stoichiometry with binding constants of 2.36×10^4 , 1.87×10^4 and $9.54 \times 10^3 \text{ M}^{-1}$ for F^- , AcO^- and H_2PO_4^- , respectively. The 1 : 1 stoichiometry was also determined by Job's plot (Fig. S10, S13 and S24, ESI[†]).

Based on UV-Vis measurements, the detection limits of receptor **1** towards F^- , AcO^- and H_2PO_4^- in DMSO were found to be 2.06×10^{-6} , 3.39×10^{-6} and $2.22 \times 10^{-6} \text{ mol L}^{-1}$, respectively. The surprising results of our present study were that upon the addition of competitive protic solvents such as methanol or water to the solution of **1** + 10 equiv. F^- in DMSO, the colour and also absorption spectrum were not reversed¹² (Fig. S14, ESI[†]). However, progressive addition of a protic solvent to the solution of **1** + 10 equiv. H_2PO_4^- in DMSO caused the colour of the solution to turn from red to yellow. Correspondingly, the absorption band recovered from 497 nm to 369 nm with a clean isosbestic point at 407 nm (Fig. S15, ESI[†]). Similar behaviour was also observed for AcO^- (Fig. S25, ESI[†]). This phenomenon is attributed to the fact that protic solvents would compete with H_2PO_4^- and AcO^- anions for the binding sites of the host and disturb the interaction between the host and guest.^{4f}

From the above findings we concluded that receptor **1** is capable of detecting fluoride ions in aqueous solution. Hence, to investigate the applicability of **1**, further UV-Vis spectrophotometric titrations were performed to detect sodium fluoride in water. Fig. 3 depicts the UV-Vis titration of **1** ($2 \times 10^{-5} \text{ mol L}^{-1}$) in 9 : 1 DMSO–water, with a standard solution of NaF in water. Upon addition of increasing concentrations of NaF, the colour changed dramatically from light yellow to orange (Fig. S18, ESI[†]), this was associated with a gradual decrease in the characteristic absorption band at 369 nm and the simultaneous growth of a new intense band at 467 nm. Clearly, the distinct isosbestic point at 397 nm indicates the interaction between **1**

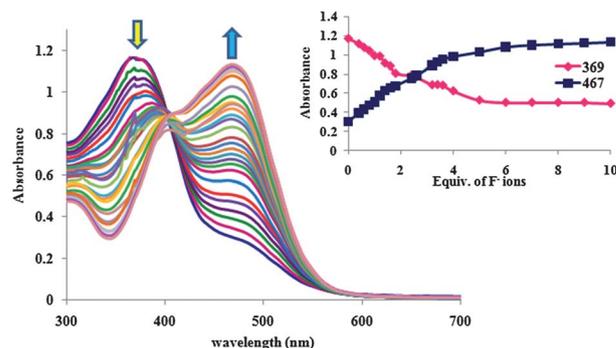


Fig. 3 UV-Vis titration of the receptor ($2 \times 10^{-5} \text{ mol L}^{-1}$) in 9 : 1, DMSO–water with increasing concentrations of NaF (0–10 equiv.) in water. Inset showing the binding isotherm at selected wavelengths in 9 : 1, DMSO–water.

and F^- ion. These findings corroborate that the addition of inorganic fluoride to an aqueous solution of **1** produces absorption spectral changes similar to those seen when TBAF is added to a receptor solution in dry DMSO. Furthermore, titration of 10% aqueous solution of **1** with TBAF afforded similar spectral changes with a binding constant of $2.25 \times 10^4 \text{ M}^{-1}$ close to that found in organic solution (Fig. S16, ESI[†]). In fact, the presence of four electron withdrawing chlorine substituents improved the ability of the phenolic OH protons of **1** to form strong hydrogen bonds⁷ with F^- , present either as inorganic fluoride or TBAF in competitive aqueous media. The Benesi–Hildebrand plot¹¹ of $1/[A - A_0]$ vs. $1/[\text{F}^-]$ for the titration of receptor **1** with NaF provided a straight line (Fig. 4), corroborating the formation of a 1 : 1 H-bonded complex with a binding constant of $1.50 \times 10^4 \text{ M}^{-1}$.

Interestingly, a comparison of the binding constant of **1** towards F^- in aqueous media with that found in organic solution revealed that the binding affinity remained strong even in water. It is worth noting that the current system can detect inorganic fluoride even at 0.058 ppm level, which is in accordance with the system reported by Das and co-workers.¹⁰ Remarkably, this limit of detection is much lower than the World Health Organization (WHO) permissible level for the detection of fluoride in drinking water (below 1 ppm).¹³

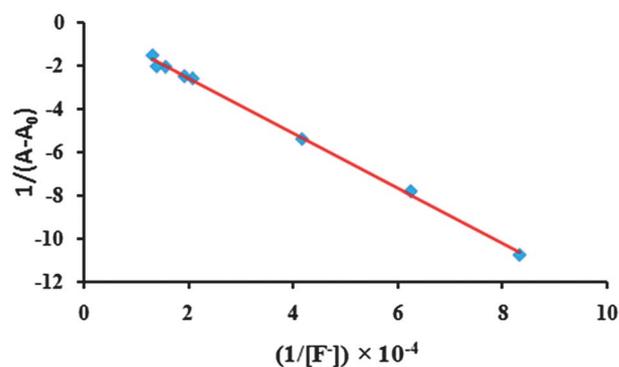


Fig. 4 Benesi–Hildebrand plot of receptor **1** binding with F^- anion associated with absorbance change at 369 nm in 9 : 1, DMSO–water.

It has been reported that excess of fluoride ions not only in potable water but also in toothpaste and osteoporosis drugs is responsible for causing dental problems and skeletal fluorosis.¹⁴ Hence, for practical purposes and also to demonstrate the potential application of the present receptor for the rapid detection of fluoride ion in real samples, we extended our work to the qualitative detection of fluoride in toothpaste. Finally, we were successful in the naked-eye sensing of fluoride ions. The results were also verified using UV-Vis spectroscopy (Fig. S19, ESI†).

Recently, we were inspired by Trivedi and co-workers,¹⁵ who reported the quantitative detection of fluoride ion in real-life applications. Therefore, receptor **1** was tested for the detection of fluoride ion in sea water, collected from the Persian Gulf (latitude 27°49'94", longitude 52°62'19") and in commercial mouthwash. To our surprise, the addition of one drop of sea water to receptor **1**, resulted in a noticeable colour change from light yellow to orange, suggesting that it is possible to use **1** for the naked-eye detection of fluoride ion in sea water. Moreover, F⁻ was detected quantitatively by applying a calibration curve obtained from a plot of absorbance vs. various concentrations of fluoride anions (Fig. 5). The value obtained from the standard plot for sea water, as an unknown sample, was 0.92 ppm, which is in good accordance with the standard value.^{13b} Our control studies showed that there was no interference from phosphate in the colour change resulting from the reaction of **1** with fluoride in sea water (Fig. S21, ESI†). Additionally, the mentioned sensor system allowed the rapid recognition and quantitative detection of fluoride in mouthwash (Fig. S20, ESI†).

To investigate the effect of pH on the host-guest binding affinity, we probed the changes in intensity of the absorption band at 467 nm attributed to the formation of the receptor **1**-F⁻ complex, over a broad pH range 2–12. As indicated in Fig. 6, there is a drastic drop in the intensity of the absorption band in highly acidic conditions, this is probably due to the protonation of fluoride ion, to form weakly ionized hydrofluoric acid, thereby lowering the affinity of fluoride anion to bind to the receptor active sites.¹⁶ As the pH rises, the intensity of the characteristic band increases, this is probably due to an increase in the accessibility of the deprotonated fluoride to form strong hydrogen bonds with the receptor. These pH responses

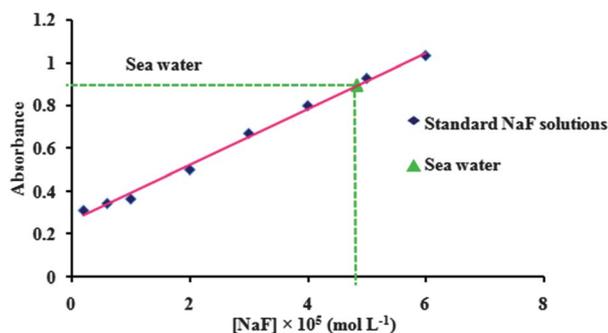


Fig. 5 Calibration curve for the determination of the concentration of fluoride anion in sea water.

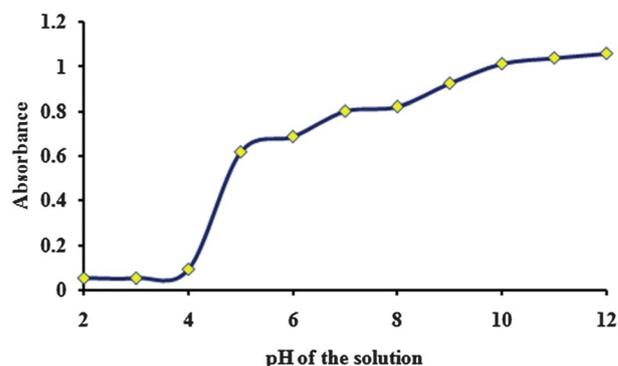


Fig. 6 Absorbance changes of receptor **1** corresponding to various pHs of aqueous solution containing $4 \times 10^{-5} \text{ mol L}^{-1} \text{ NaF}$.

of **1** are not surprising since similar findings have been reported for other colorimetric fluoride sensors.^{8b,9,10}

To further study the nature of the interaction between receptor **1** and fluoride, ¹H NMR titration experiments were conducted. Fig. 7 shows the ¹H NMR spectra of **1** with different amounts of TBAF in DMSO-*d*₆. It is clear that the OH protons of the azo phenol moieties at 13.87 ppm thoroughly disappeared when only 0.5 equiv. of F⁻ was added into a solution of **1**. This

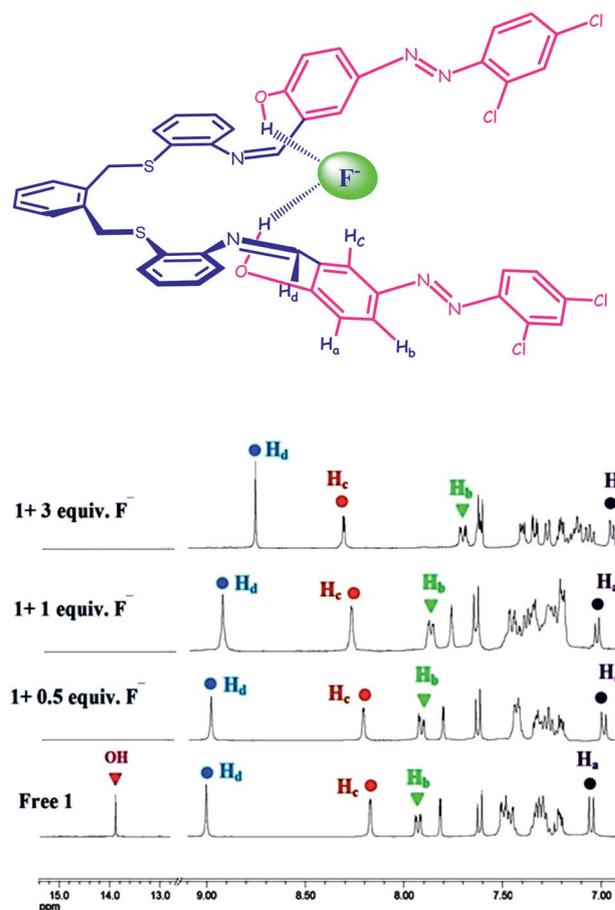


Fig. 7 ¹H NMR spectra of receptor **1** in DMSO-*d*₆ ($2 \times 10^{-2} \text{ mol L}^{-1}$) in the absence and in the presence of different amounts of TBAF.

indicates the formation of strong hydrogen bonds between fluoride anions and active OH groups, as previously reported.¹⁷ With increasing further equiv. of F^- , the signals of H_a and H_b showed progressive upfield shifts, whereas the signal of H_c exhibited a progressive reverse shift toward downfield. Simultaneously, an upfield shift of the imine proton (H_d) from 9.00 to 8.76 ppm was also observed. The evidence above can be attributed to the two possible effects which are responsible for observed chemical shifts upon OH-fluoride interaction:^{46,18} (1) through-bond effects, which increase the electron density on the phenyl ring and promote an upfield shift of the C-H protons and (2) through-space effects, which induce polarization of the C-H bonds, where the partial positive charge creates a downfield shift.

Interestingly, a typical HF_2^- signal was observed in 1H NMR titration experiments at higher concentration of F^- , indicating that deprotonation of receptor **1** occurred (Fig. S26, ESI†).⁴⁷ Consequently, the 1H NMR titration experiments corroborated that F^- recognition occurs through initial hydrogen bond formation between anion and sensor, followed by deprotonation. Furthermore, the formation of an initial $1-F^-$ H-bonding host-guest complex is supported by the pK_a value, determined from spectrophotometric pH titration (Fig. S22, ESI†).

Conclusion

To sum up, we have designed and synthesized a new azo-azomethine based anion-receptor for the facile detection of fluoride present in aqueous media without any spectroscopic instrumentation. Selective binding of the receptor with fluoride ion through hydrogen-bonding interactions gave rise to a dramatic colour change from light yellow to orange with a concomitant bathochromic shift. Our achieved detection limit of F^- ion was 0.058 ppm, which is lower than the WHO recommended level (below 1 ppm) for safe drinking. Notably, we demonstrated that the synthesized sensor can also be considered as a tool for the detection and quantification of fluoride ion in real samples.

Experimental

General

All chemicals were purchased from Sigma-Aldrich and used without further purification. Electronic spectral measurements were carried out using an Optizen 3220 UV spectrophotometer in the range of 200–900 nm. FT-IR spectra were recorded with pressed KBr discs, using an Unicam Galaxy Series FT-IR 5000 spectrophotometer in the region of 400–4000 cm^{-1} . Melting points were determined with an Electrothermal 9200 apparatus. NMR spectra were recorded with Bruker AV 300 MHz and Bruker Avance III 400 MHz spectrometers. C, H, N, analyses were performed using a Vario EL III elemental analyzer. Mass spectra were recorded with a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV.

Synthesis of α,α' -bis(*o*-aminophenylthio)-1,2-xylene

A mixture of 2-aminothiophenol (12.52 g, 0.10 mol) and sodium hydroxide (4.00 g, 0.10 mol) in deionized water (60 mL) was

heated to reflux for 30 min. The mixture was allowed to cool to 60 °C and α,α' -dibromo-*o*-xylene (13.20 g, 0.05 mol) was added dropwise over a period of 30 min. The mixture was then heated to reflux for 2 h. After cooling to room temperature, the reaction mixture was extracted with chloroform. The organic layer was dried over anhydrous $MgSO_4$ and then evaporated to dryness. The obtained product was further washed thoroughly with diethyl ether and dried under vacuum at room temperature. Yield: 70%, m. p. 103–106 °C (lit. 106 °C).¹⁹ 1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 4.02 (s, 4H), 5.31 (br, 4H), 6.46 (t, 2H, $J = 7.60$ Hz), 6.73 (d, 2H, $J = 8.00$ Hz), 7.05 (m, 8H). IR (KBr, cm^{-1}): 3352 and 3449 (NH), 1607 and 1477 (C=Car). MS (EI, 70 eV): m/z (%) = 352 (M^+ , 63), 228 (100), 194 (94), 124 (69), 80 (63).

Synthesis of 1-(3-formyl-4-hydroxyphenylazo)-2,4-dichlorobenzene

A mixture of 2,4-dichloroaniline (1.62 g, 10 mmol) in hydrochloric acid (9 mL) and water (4 mL) was heated to 70 °C to form a solution. The clear solution was poured into an ice-water mixture and was diazotized at 0–5 °C with sodium nitrite (0.7 g, 10 mmol in water, 10 mL). The cold diazo solution was added to the solution of salicylaldehyde (1.22 g, 10 mmol) in water (20 mL) containing sodium hydroxide (0.40 g, 10 mmol) and sodium carbonate (4.24 g, 40 mmol) over a period of 30 min at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then allowed to warm slowly to room temperature. The product was collected by vacuum filtration and washed with NaCl solution (100 mL, 10%). The obtained solid was dried under vacuum at 80 °C overnight. Yield: 86%, m. p. 120–123 °C. 1H NMR (DMSO- d_6 , 300 MHz, ppm): δ 7.29 (d, 1H, $J = 8.84$ Hz), 8.09 (dd, 1H, $J = 8.84$ Hz, $J = 2.16$ Hz), 7.55 (d, 1H, $J = 8.76$ Hz), 7.68 (d, 1H, $J = 8.76$ Hz), 7.89 (s, 1H), 8.19 (d, 1H, $J = 2.16$ Hz), 10.37 (s, 1H), 11.88 (br, 1H). IR (KBr, cm^{-1}): 1668 (CHO), 1620 (C=C), 1578 (phenol ring), 1485 (N=N), 1287 (C-O), 1246, 1148, 866 and 768. Anal. calcd. for $C_{13}H_8Cl_2N_2O_2$: C, 52.91; N, 9.49; H, 2.73%. Found: C, 52.62; N, 9.38; H, 2.65%. λ_{max} (nm) (ϵ ($M^{-1} cm^{-1}$)): 260 (29950), 356 (49260) and 465 (11853) in DMSO.

Synthesis of 1,2-bis(4-((2,4-dichlorophenyl)diazonyl)-2-((methylthio)phenylimino)methyl)phenol)methylenbenzene (1)

A solution of α,α' -bis(*o*-aminophenylthio)-1,2-xylene (0.35 g, 1 mmol) in absolute EtOH (10 mL) was added to a stirring solution of azo-coupled precursor (0.59 g, 2 mmol) in absolute EtOH (50 mL) during a period of 20 min at 60 °C. The solution was heated in a water bath overnight 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 resulting product was dried in air. Yield: 96%, m. p. 172–175 °C. 1H NMR (DMSO- d_6 , 300 MHz, ppm): δ 4.30 (s, 4H), 7.04 (d, 2H, $J = 8.80$ Hz), 7.20 (m, 2H), 7.30 (m, 6H), 7.46 (m, 6H), 7.60 (d, 2H, $J = 8.71$ Hz), 7.80 (s, 2H), 7.91 (d, 2H, $J = 8.80$ Hz), 8.15 (s, 2H), 8.99 (s, 2H), 13.86 (br, 2H). IR (KBr, cm^{-1}): 1614 (C=N), 1578 (phenol ring), 1470 (N=N), 1288 (C-O), 1097, 831 and 756. Anal. calcd. for $C_{46}H_{32}Cl_4N_6O_2S_2$: C, 60.93; N, 9.27; H, 3.56; S, 7.07%. Found: C, 61.73; N, 9.26; H, 3.16; S,

7.00%. λ_{\max} (nm) (ϵ ($M^{-1} \text{ cm}^{-1}$)): 264 (41200) and 369 (50850) in DMSO:MS (EI, 70 eV): $[M]^+$ = 908 molecular ion peak was not observed. m/z (%) = 399 (25), 226 (94), 198 (44), 161 (61), 145 (100), 124 (89), 80 (69).

Acknowledgements

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