Accepted Manuscript

An easy prepared dual-channel chemosensor for selective and instant detection of fluoride based on double Schiff-base

Yan-Li Leng, Jian-Hui Zhang, Qiao Li, You-Ming Zhang, Qi Lin, Hong Yao, Tai-Bao Wei

 PII:
 \$1386-1425(16)30298-0

 DOI:
 doi: 10.1016/j.saa.2016.05.040

 Reference:
 \$\$AA 14461

To appear in:

Received date:23 July 2015Revised date:19 May 2016Accepted date:25 May 2016



Please cite this article as: Yan-Li Leng, Jian-Hui Zhang, Qiao Li, You-Ming Zhang, Qi Lin, Hong Yao, Tai-Bao Wei, An easy prepared dual-channel chemosensor for selective and instant detection of fluoride based on double Schiff-base, (2016), doi: 10.1016/j.saa.2016.05.040

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

An easy prepared dual-channel chemosensor for selective and

instant detection of fluoride based on double Schiff-base

Yan-Li Leng ^{a,b} , Jian-Hui Zhang ^b , Qiao Li ^a, You-Ming Zhang ^a, Qi Lin ^a,

Hong Yao^a, Tai-Bao Wei^{a,*}

E-mail: weitaibao@126.com^{*}

^a Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, College of Chemistry and Chemical Engineering,Northwest Normal University, Lanzhou, Gansu 730070, PR China

^b Department of Metallurgical Engineering, Lanzhou Resources & Environment Voc-Tech College, Lanzhou, Gansu 730021, PR China

Abstract: A colorimetric and fluorescent dual-channel fluoride chemosensor N,N'-bis (4-diethylaminosalicylidene) hydrazine (sensor **S**) bearing two imine groups has been designed and synthesized. This structurally simple probe displays rapid response and high selectivity for fluoride over other common anions (Cl⁻, Br⁻, Γ , AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, CN⁻ and SCN⁻) in a highly polar aqueous DMSO solution. Mechanism studies suggested that the sensor firstly combined with F⁻ through hydrogen bonds and then experienced the deprotonation process at higher concentrations of F⁻ anion to the two Ar-OH groups. The detection limits was 5.78×10^{-7} M of F⁻, which pointing to the high detection sensitivity. Test strips based on sensor **S** were fabricated, which could act as a convenient and efficient F⁻ test kit to detect F⁻ for "in-the-field" measurement.

*Corresponding author

Tel: +8609317973120. E-mail address: weitaibao@126.com

Keywords: Fluoride (F⁻); Chemosensor; Colorimetric; Fluorescent; Imine group; DFT calculations.

1. Introduction

In the past few decades, design and synthesis of organic molecules based on supramolecular concepts for the colorimetric detection in the presence of various anions from industrial effluents, environmental contaminants and the potential for applications in biology and medicine has received current attention [1-5]. Fluoride is considered as a serious health hazard in the environment because it may lead to bone disease in the event of excessive intake of it [6,7]. Therefore, considering the wide application of fluoride, there is a great demand for the development of methods that can rapidly, sensitively and selectively detect the fluoride anion [8-11]. Up to now, many efforts have been made to design simple and low cost chemosensors, several anion receptors such as imidazoles [12,13], pyrroles [14,15], calixpyrroles [16,17], amides [18-20], carbamides [21,22], urea [23,24], and thiourea [25] have been developed.

In many cases, the anion binding unit is primarily composed of H-bonding donors. A variety of neutral receptors have been reported for selective anion recognition based on H-bonding owing to the strength and selectivity of this interaction [26,27]. Meanwhile, H bonding interactions between an anion and the H-bond donors in a sensing system can induce internal charge transfer (ICT), which cause changes in the absorption and emission of the chromogenic probe, thus allowing the naked eye chemosensing [28,29]. Among them, taking the Ar-OH group as the sensing site possesses several merits. For example, it can be used for the hydrogen bond donor site and act as anion binding site. Furthermore, owing to the fact that the acidity of

"Ar-OH" is stronger than that of "H-C=N-", the Ar-OH group can sense F^- not only by forming hydrogen bond (F^- ···HO-Ar) but also by a deprotonation process (deprotonation of Ar-OH). As a result, it can afford two kinds of sense approaches and enhance the sense selectivity for F^- .

With this background, as a part of our research interest in molecular recognition [30-34], we reported a simple-to-synthesize, yet sensitive and selective fluoride anion sensor **S**. The strategy employed in the design of this sensor is as follows: firstly, we introduced hydroxyl and imine groups to the sensor molecule as binding sites to detect F^- by hydrogen-bonding interactions. Secondly, in order to achieve high sensitivity for F^- , the fluorescent signal report mode has been adopted, because the fluorescent sensors often provide higher sensitivity than other optic sensors. Therefore, we introduced 4-diethylaminosalicylaldehyde as the fluorescence signal group. Finally, the sensor molecular was designed easily to synthesize with low cost. As a result, sensor **S** could detect F^- with specific selectivity and high sensitivity. Moreover, we also demonstrate that the F^- anion recognition mechanism is both hydrogen bonding and deprotonation with the Ar-OH in sensor **S**, which was investigated by various methods (such as ¹H NMR spectroscopic titration, ESI-MS and Density functional theory (DFT) calculations), both of which give rise to changes in the UV-vis and fluorescent spectra.

2. Experimental section

2.1. Materials and physical methods

All reagents and solvents were commercially available at analytical grade and were used without further purification. ¹H NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz. ¹H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent resonances as internal

standards). UV-visible spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer.

2.2 Synthesis of sensor 1

4-diethylaminosalicylaldehyde (0.424 g, 2.2 mmol), hydrazine monohydrate (0.100 g, 2 mmol), and a catalytic amount of acetic acid (five drops of AcOH) were combined in absolute ethanol (10 mL). The solution was stirred under reflux for 4 h. The reaction mixture was refluxed for 3-4 h and the progress of reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the reaction flask was allowed to cool to room temperature. The solid product that appeared in the flask was filtered and recrystallized with ethanol to get orange crystalline product **S** (0.592 g) in 77% yield (mp: 244-246°C); IR: (KBr, cm⁻¹) v: 2978, 1627, 1590, 1516, 1409, 1355, 1229, 1128, 967, 782; ¹H NMR (DMSO-*d*₆, 400 MHz): δ 1.09-1.13(t, 12H, -CH₃), 3.35-3.39 (t, 8H, N-CH₂), 6.12 (s, 2H, ArH), 6.30-6.32 (d, 2H, ArH), 7.27-7.29 (d, 2H, ArH), 8.61 (s, 2H, N=CH), 11.51 (s, 2H, Ar-OH); Anal. Calcd for C₂₂H₃₀N₄O₂: C 69.08, H 7.91, N 14.65. Found: C 69.20, H 7.89, N 14.62. ESI-MS: m/z calcd for C₂₂H₃₀N₄O₂, [M-H]⁺ = 382.24, found [M-H]⁺ = 383.29.

2.3. General procedure for UV-vis experiments

The solution of sensor S $(2.0 \times 10^{-4} \text{ M})$ in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each anions $(1.0 \times 10^{-2} \text{ M})$ were prepared, respectively, via tetrabutylammonium salts for F⁻, Cl⁻, Br⁻, Γ , AcO⁻, H₂PO₄⁻, HSO₄⁻,

 ClO_4^- and the sodium salts for CN^- , SCN^- . Any changes in the UV-vis spectra of sensor **S** were recorded upon the addition of salts while keeping the concentration of sensor **S** (2.0×10⁻⁵ M) in all experiments.

2.4. General procedure for Fluorescence spectra experiments

The solution of sensor **S** $(2.0 \times 10^{-4} \text{ M})$ in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each anions $(1.0 \times 10^{-2} \text{ M})$ were prepared, respectively, via tetrabutylammonium salts for F⁻, Cl⁻, Br⁻, T⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻ and the sodium salts for CN⁻, SCN⁻. The fluorescence spectra were obtained by excitation at 422 nm. The excitation slit widths were 5 nm and emission slit widths were 5 nm, respectively. Any changes in the fluorescence spectra of sensor **S** were recorded upon the addition of salts while keeping the concentration of sensor **S** $(2.0 \times 10^{-5} \text{ M})$ in all experiments.

2.5. General procedure for ¹H NMR experiments

For ¹H NMR titrations, the appropriate concentrated solution of sensor **S** and the guest were both prepared in DMSO- d_6 . Aliquots of the two solutions were mixed directly in NMR tubes.

3. Results and discussion

In this work, F^- chemosensor **S** was synthesized by the condensation of 4-diethylaminosalicylaldehyde and hydrazine monohydrate (Scheme 1) which has been characterized by ¹H NMR, ESI-MS and elemental analyses. The structure of **S** was further confirmed by X-ray crystallography, as shown in Figure 1 (Summary of Data CCDC 1060898). A summary of the crystallographic data and structural refinements for **S** are listed in Figure 1, Table S1 (see supporting information).

(Insert Scheme 1)

(Insert Figure 1)

The absorption spectrum of sensor S in DMSO solution exhibits the absorption band at 422 nm. When 50 equiv. of F was added to the DMSO solution of sensor S, the band at 422 nm is red-shifted to 456 nm (Figure 2). This absorption was responsible for the color change (from yellow to dark-yellow) and perceptible to the naked eyes (Figure 2, insert). To validate the selectivity of sensor S, the same tests were applied using Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, CN⁻ and SCN⁻ anions, and none of these anions induced any significant changes in the UV-vis spectrum. The selective fluorescence response of S to F^- anion was also investigated (Figure 3). The emission of S appeared at the maximum emission wavelength was 488 nm in DMSO solution when excited at $\lambda_{ex} = 422$ nm. When 50 equiv. of F was added to the solution of sensor S, the strong fluorescence emission band at 488 nm is quenched and the fluorescence color changed from blue-green to pale-yellow (Figure 3, inset), which could be easily distinguished by the naked eye under the aid of a normal UV lamp (λ_{ex} =365 nm). To validate the selectivity of sensor S, the same tests were also applied using Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, CN⁻ and SCN⁻ anions, and none of these anions induced any significant changes in the fluorescent spectrum of the sensor.

(Insert Figure 2)

(Insert Figure 3)

The binding affinities of **S** and F^- have been examined through the titration experiments. As shown in Figure 4, with the increasing concentrations of F^- , the strong absorption band of **S** centered at 422 nm gradually decreased along with the appearance of a new absorption band centered at 456 nm. The formation of new band may be due to the hydrogen bond formation of the F^- with Ar-OH protons or

deprotonation of Ar-OH protons [32]. Similarly, in the florescence titration spectrum (Figure 5), while the concentration of F⁻ was increased, the emission maximum at 488 nm gradually decreased. The sensor gives an immediate response to the fluoride anion (see supporting information, Figure S5) and the detection limit of the **S** for the determination of F⁻ was estimated to be 5.78×10^{-7} M, which pointing to the high detection sensitivity (see supporting information, Figure S6). The Job plot between **S** and F⁻ was implemented, demonstrating a 1:4 stoichiometry for the **S** and F⁻, as shown in Figure 6 [35].

(Insert Figure 4)

(Insert Figure 5)

(Insert Figure 6)

To explore the sensing mechanism of sensor **S** to F^- , the ¹H NMR titration were investigated, which illustrated the characteristic structural changes occurring upon interaction with F^- . As shown in Figure 7, before the addition of fluoride anion, the ¹H NMR chemical shifts of the Ar-OH and -HC=N- protons on **S** were at δ 11.51, 8.61 ppm, respectively. Upon the addition of 0.5 and 1.0 equiv. of fluoride anion, the resonance for Ar-OH were gradually decreased and then completely disappeared. Further addition of F^- to 2.0 equiv. resulted in the formation a new peak at 16 ppm which pertained to $[HF_2]^-$ [36]. These observations obviously indicate the deportonation process of the fluoride anion with the two Ar-OH groups in sensor **S**. A plausible mechanism for the formation of **S**-F⁻ has been proposed in Scheme 2.

(Insert Figure 7)

(Insert Scheme 2)

Further to confirm the proposed mechanism of sensor **S** with F^- , we performed DFT calculations done at the B3LYP/6-311+g (2d, p) level of theory [37]. The

optimized stationary structures (minima, saddle points) on the potential surfaces of the reactions are depicted schematically in Figure 8. Calculations results show: 1) the sensor **S** firstly combined with F^- through hydrogen bond and then experienced the deprotonation process at higher concentrations of F^- anion to the two Ar-OH groups; 2) the reaction process of IM1 to IM2 is endothermic by 19.5 kJ·mol⁻¹ on the ground potential energy surface, while the whole reaction is exothermic by 277.7 kJ·mol⁻¹, which showed that the reaction of probe **S** with F^- is easy to carry out. These calculations results are consistent with the experimental results.

(Insert Figure 8)

To investigate the practical application of sensor **S**, test trips were prepared by immersing filter papers into DMSO solution of **S** (0.1 M) and then drying in air. The test strips containing **S** were utilized to sense F^- . As shown in Figure 9, when F^- anion was added on the test kits, the obvious color change was observed both in visible light and under the 365 nm UV-lamp.

(Insert Figure 9)

4. Conclusion

In summary, we have proposed a facile, low-cost, and efficient double Schiff-base example of a highly selective chemosensor for F^- through hydrogen bonding and deprotonation between S and the anion. The sensor gives an immediate response to the fluoride anion both by visible color changes as well as fluorescence turn-off response. Fluoride anion are detectable by hydrogen bonding and deprotonation to the Ar-OH groups and the mechanism of the reaction was investigated by various means (such as ¹H NMR spectroscopic titration, ESI-MS and DFT calculation). Moreover, test strips based on sensor **S** was fabricated, which could serve as practical colorimetric to detect F^- for "in-the-field" measurement and did not require any additional equipment but

just by virtue of "dip-sticks" approach. We believe the test strips could act as a convenient and efficient F^- test kit. More applications of this efficient strategy might be found in extended occasions of this concept, such as with combinations of anion-neutral molecules.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 21064006, 21262032, and 21161018), the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (No. IRT1177), the Natural Science Foundation of Gansu Province (No. 1010RJZA018), the Youth Foundation of Gansu Province (No. 2011GS04735), and NWNU-LKQN-11-32.

References

- [1] H. Yu, J.Y. Lee, S. Angupillai, S. Wang, S.H. Feng, S. Matsumoto, Y.A. Son, A new dual fluorogenic and chromogenic "turn-on" chemosensor for Cu²⁺/F⁻ ions, Spectrochim. Acta A 151 (2015) 48-55.
- [2] H.E. Nicholas, D.B. Paul, Advances in anion supramolecular chemistry: From recognition to chemical applications, Angew. Chem. Int. Ed. 53 (2014) 11716-54.
- [3] K.L. Zhu, S.J. Li, F. Wang, F.H. Huang, Anion-controlled ion-pair recognition of paraquat by a bis(*m*-phenylene)-32-crown-10 derivative heteroditopic host, J. Org. Chem. 74 (2009) 1322-1328.
- [4] K.L. Zhu, L. Wu, X.Z. Yan, B. Zheng, M.M. Zhang, F.H. Huang, Anion-assisted complexation of paraquat by cryptands based on bis(*m*-phenylene)-[32]crown-10, Chem. Eur. J. 16 (2010) 6088-6098.
- [5] M.M.J. Smulders, S. Zarra, J.R. Nitschke, Quantitative understanding of guest binding enables the design of complex host-guest behavior, J. Am. Chem. Soc.

135 (2013) 7039-7046.

- [6] C.B. Yeamans, G.W.C. Silva, G.S. Cerefice, K.R. Czerwinski, T. Hartmann, A.K. Burrell, A.P.J. Sattelberger, Uranium azide photolysis results in C-H bond activation and provides evidence for a terminal uranium nitride, Nucl. Mater. 374 (2008) 75-78.
- [7] G. Villalba1, R.U. Ayres, H.J. Schroder, Exergy sustainability indicators as a tool in industrial ecology, Ind. Ecol. 11 (2007) 85-98.
- [8] C.R. Wade, A.E.J. Broomsgrove, S. Aldridge, F.P. Gabba, Fluoride ion complexation and sensing using organoboron compounds, Chem. Rev. 110 (2010) 3958-3984.
- [9] K. Liu, X.J. Zhao, Q.X. Liu, J.Z. Huo, X. Wang, Y.P. Wu, Investigation on the photophysical properties of ESPT inspired salicylaldehyde-based sensor for fluoride sensing, Spectrochim. Acta A 140 (2015) 198-201.
- [10] M. Cametti, K. Rissanen, Highlights on contemporary recognition and sensing of fluoride anion in solution and in the solid state, Chem. Soc. Rev. 42 (2013) 2016-38.
- [11] L. Wan, Q.H. Shu, J.P. Zhu, S.H. Jin, N. Li, X. Chen, S.S. Chen, A new multifunctional Schiff-based chemosensor for mask-free fluorimetric and colorimetric sensing of F⁻ and CN⁻, Talanta 152 (2016) 39-44.
- [12] F.M. Pfeffer, K.F. Lim, K.J. Sedgwick, Indole as a scaffold for anion recognition, Org. Biomol. Chem. 5 (2007) 1795-1799.
- [13] M. Mazik, H. Cavga, Molecular recognition of N-acetylneuraminic acid with acyclic benzimidazolium- and aminopyridine/guanidinium-based receptors, J. Org. Chem. 72 (2007) 831-838.
- [14] P. Dydio, D. Lichosyt, J. Jurczak, Amide- and urea-functionalized pyrroles and benzopyrroles as synthetic, neutral anion receptors, Chem. Soc. Rev. 40 (2011)

2971-2985.

- [15] P.A. Gale, P. Anzenbacher, J.L. Sessler, Calixpyrroles, Coord. Chem. Rev. 222 (2001) 57-102.
- [16] R. Nishiyabu, M.A. Palacios, W. Dehaen, J.P. Anzenbacher, Synthesis, structure, anion binding, and sensing by calix[4]pyrrole isomers, J. Am. Chem. Soc. 128 (2006) 11496-11504.
- [17] J.L. Sessler, J.M. Davis, Sapphyrins: Versatile anion binding agents, Acc. Chem. Res. 34 (2001) 989-997.
- [18] S.O. Kang, M.A. Hossain, K. Bowman-James, Influence of dimensionality and charge on anion binding in amide-based macrocyclic receptors, Coord. Chem. Rev. 250 (2006) 3038-3052.
- [19] H. Niu, Q.H. Shu, S.H. Jin, B.J. Li, J.P. Zhu, L.J. Li, S.S. Chen, A simple ratiometric and colorimetric chemosensor for the selective detection of fluoride in DMSO buffered solution, Spectrochim. Acta A 153 (2016) 194-198.
- [20] C.R. Bondy, S.J. Loeb, Amide based receptors for anions, Coord. Chem. Rev. 240 (2003) 77-99.
- [21] A.P. Davis, Anion binding and transport by steroid-based receptors, Coord. Chem. Rev. 250 (2006) 2939-2951.
- [22] A.P. Davis, J.B. Joos, Structural diversity in coordination chemistry of tridentate and tetradentate polyphosphines of Group 6 to 10 transition metal complexes, Coord. Chem. Rev. 240 (2003) 143-206.
- [23] V. Amendola, L. Fabbrizzi, L. Mosca, F.P. Schmidtchen, Urea-, squaramide-, and sulfonamide-based anion receptors: A thermodynamic study, Chem. Eur. J. 17 (2011) 5972-5981.
- [24] C.M.G. Dos Santos, E.M. Boyle, S. De Solis, P.E. Kruger, T. Gunnlaugsson,

Selective and tuneable recognition of anions using C_{3v} -symmetrical tripodal urea-amide receptor platforms, Chem. Commun. 47 (2011) 12176-12178.

- [25] A.F. Li, J.H. Wang, F. Wang, Y.B. Jiang, Anion complexation and sensing using modified urea and thiourea-based receptors, Chem. Soc. Rev. 39 (2010) 3729-3745.
- [26] H.Y. Kim, H.G. Im, S.K. Chang, Colorimetric and fluorogenic signaling of fluoride ions by thiophosphinated dichlorofluorescein, Dyes Pigments 112 (2015) 170-175.
- [27] Y.P. Li, M. Zheng, J.F. Wang, Y.Y. Gao, B.L. Zhang, W.J. Yang, Two-photon absorption and fluorescence fluoride-sensing properties of *N*-octyl-3,6-bis[4-(4-(diphenylamino)phenyl)phenyl]-1,4-diketo-pyrrolo[3,4-c] pyrrole, Dyes Pigments 104 (2014) 97-101.
- [28] E.A. Katayev, Y.A. Ustynyuk, J.L. Sessler, Receptors for tetrahedral oxyanions, Coord. Chem. Rev. 250 (2006) 3004-3037.
- [29] F.P. Schmidtchen, Reflections on the construction of anion receptors: Is there a sign to resign from design?, Coord. Chem. Rev. 250 (2006) 2918-2928.
- [30] G.Y. Gao, W.J. Qu, B.B. Shi, P. Zhang, Q. Lin, H. Yao, W.L. Yang, Y.M. Zhang, T.B. Wei, A highly selective fluorescent chemosensor for iron ion based on 1H-imidazo [4,5-b] phenazine derivative, Spectrochim. Acta A 121 (2014) 514-519.
- [31] Q. Lin, X. Zhu, Y.P. Fu, Y.M. Zhang, R. Fang, L.Z. Yang, T.B. Wei, Rationally designed anion-responsive-organogels:sensing F-via reversible color changes in gel–gelstates with specific selectivity, Soft Matter. 10 (2014) 5715-5723.
- [32] Q. Lin, B. Sun, Q.P. Yang, Y.P. Fu, X. Zhu, Y.M. Zhang, T.B. Wei, A novel strategy for the design of smart supramolecular gels: Controlling

stimuli-response properties through competitive coordination of two different metal ions, Chem. Commun. 50 (2014) 10669-10671.

- [33] Q. Lin, B. Sun, Q.P. Yang, Y.P. Fu, X. Zhu, T.B. Wei, Y.M. Zhang, Double metal ions competitively control the guest-sensing process: A facile approach to stimuli-responsive supramolecular gels, Chem. Eur. J. 20 (2014) 11457-11462.
- [34] C.O. Ng, S.W. Lai, H. Feng, S.M. Yiu, C.C. Ko, Luminescent rhenium(I) complexes with acetylamino- and trifluoroacetylamino-containing phenanthroline ligands: Anion-sensing study, Dalton Trans. 40 (2011) 10020-10028.
- [35] J.J.B. Nevado, J.A.M. Pulgarin, M.A.G. Laguna, Spectrofluorimetric study of the β-cyclodextrin:vitamin K₃ complex and determination of vitamin K₃, Talanta 53 (2001) 951-959.
- [36] K. Liu, J. Huo, B. Zhu, R. Huo, Fluoride-Triggered ESPT in the Binding with Sal(oph)en, J. Fluoresc. 22 (2012) 1231-1236.
- [37] M.J. Frisch, G.W. Trucks, H.B. Schegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, J.T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakia, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Oritiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Li-ashenko, P. Piskorz, I.R. Komaromi, L. Martin, D.J. Fox, T.M. Keith, A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Chal-lacombe, P.M. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.



Scheme 2 A possible mechanism of the sensor S to F^- .



Figure 1 The single crystal X-ray structure of S.



Figure 2 Absorbance emission data for probe **S** in the DMSO solution. Inset: color changes observed for **S** upon the addition of F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- , CN^- , SCN^- (50 equiv., respectively) in DMSO.



Figure 3 Fluorescence emission data for probe **S** in the DMSO solution (excitation wavelength=422 nm). Inset: Visual fluorescence emissions of **S** upon the addition of F^- , CI^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- , CIO_4^- , CN^- , SCN^- (50 equiv., respectively) in DMSO on excitation at 365 nm using UV lamp at rt.



Figure 4 Absorbance spectra of probe S in the presence of different concentration of F^- in DMSO. Inset: A plot of absorbance depending on the concentration of F^- in the range from 0 to 120.56 equiv. The detection wavelength was 480 nm.



Figure 5 Fluorescence spectra of probe **S** in the presence of different concentration of F^- in DMSO. Inset: A plot of fluorescence intensity depending on the concentration of F^- in the range from 0 to 111.64 equiv. The detection wavelength was 488 nm.



Figure 6 Job's plot of **S** with F^- in DMSO, indicating the 1:4 stoichiometry for **S** and F^- clearly.



Figure 7 Partial ¹H NMR spectra of **S** (0.05M, DMSO- d_6) and in the presence of varying amounts of F⁻.



Figure 8 The optimized stationary structures on the potential surfaces of the reactions. (R1 is sensor **S**, IM1 is intermediate 1, IM2 is intermediate 2, IM3 is intermediate 3, P is \mathbf{S} - \mathbf{F}^- , pale-blue ball is fluoride, grey ball is carbon, blue ball is nitrogen, red ball is oxygen, white ball is hydrogen).



Figure 9 Photographs of S on test papers (a) left: only S, right: after immersion into DMSO solutions with F^- ; (b) left: only S, right after immersion into DMSO solutions with F^- under irradiation at 365 nm.

A CLARANT



Graphical Abstract

A colorimetric and fluorescent dual-channel fluoride chemosensor *N*,*N*'-bis (4-diethylaminosalicylidene) hydrazine (sensor **S**) bearing two imine groups has been designed and synthesized. This structurally simple probe displays rapid response and high selectivity for fluoride over other common anions (Cl⁻, Br⁻, Γ , AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, CN⁻ and SCN⁻) in a highly polar aqueous DMSO solution. Mechanism studies suggested that the sensor firstly combined with F⁻ through hydrogen bonds and then experienced the deprotonation process at higher concentrations of F⁻ anion to the two Ar-OH groups. The detection limits was 5.78×10^{-7} M of F⁻, which pointing to the high detection sensitivity. Test strips based on sensor **S** were fabricated, which could act as a convenient and efficient F⁻ test kit to detect F⁻ for "in-the-field" measurement.

Highlights

- 1. Synthesize an effective F^- chemosensor.
- 2. Study the mechanism by different way.
- 3. Test trips can be used to detect F^- easily.

A CER MAN