# A simple ratiometric and colorimetric chemosensor for the selective detection of fluoride in DMSO buffered solution

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# A simple ratiometric and colorimetric chemosensor for the selective detection of fluoride in DMSO buffered solution

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## Abstract

A derivative of squaramide (cyclobuta[b]quinoxaline-1, 2(3H, 8H)-dione) has been synthesized for the ratiometric and colorimetric sensing of $F^-$ in aqueous solution in competitive fashion. With $F^-$, probe **1** showed a highly selective naked-eye detectable color change along with a characteristic UV-Vis absorbance over other tested ions, which probably originates from the deprotonation occurred between **1** and $F^-$, as proved by the $^1$H NMR titration experiments and DFT calculations.

*Key words: Chemosensor; Fluoride detection; Ratiometric; DFT calculation*

The field of anion receptor chemistry initiated in the late 1960s by Shriver and Biallas[1] and by Park and Simmons[2] has blossomed to develop over the past two decades. To achieve the central theme which is the rapid, sensitive and selective detection of analytes, much effort has been made on the development of new receptors that are able to quantitatively detect anions in competition fashion.[3] Specifically, colorimetric or ratiometric chemosensors have attracted a large number of focuses because they not only can identify the target species but also provide qualitative and quantitative analysis without the help of any spectroscopic instrumentation.[4,5] As reported, plenty of anions which can influence environmental, medical career and physical condition have provoked excessive attentions to researchers,[6] especially in aqueous solutions for monitoring environmental pollution, medicinal diagnostic and health quality standard. Among the various anions, fluoride ions are omnipresent in daily life which is widely used as additives in water and toothpastes to enamel demineralization and prevent dental caries wearing orthodontic appliances.[7] Thus, fluoride detection is of rapidly increasing interest in virtue of its special significance in many fields.[8] So far, there are three main mechanisms between anions and sensors: Lewis acid-base interactions,[9-12] hydrogen-bond interactions,[13,14] and fluoride anion-induced chemical reactions, including a large body of deprotonation reactions.[15-18] Though considerable fluorescent sensors have been designed for detecting fluoride ions depending on the above mechanisms, most of them need a help of chemical tests or the synthesis of probe compound was extremely complicated. In addition, ion-selective electrodes and colorimetry acting as the most widespread methods for recognizing fluoride ions are also special instrumentation dependent and relatively high cost. Therefore, there is a demand for developing a simple, cost-effective and reliable method to detect fluoride ions in aqueous environments.

Herein, a derivative of squaramide (cyclobuta[b]quinoxaline-1, 2(3H, 8H)-dione) probe **1** was designed and simply synthesized for the desirable detection of fluoride ions in aqueous solution, and its advanced performance have been listed in Table 1. Acting as an absorption-based colorimetric chemosensor, probe **1** not only can identify the fluoride ions selectively and sensitively but also detect fluoride ions by naked-eye owing to its distinct visual color change.

**Table 1** A comparison of probe **1** with other reported presentative easy-to-prepare fluoride sensors.

| *Representative Easy-to-prepare Fluoride sensors* | Detection method | Detection medium | Detection limit |
|---|---|---|---|
| Probe **1** | Naked-eye/Test strip | DMSO/$H_2O$ | 4.8 μM |
| Sensor **A** (E.J. Cho)[19] | Naked-eye | DMSO/$CH_3CN$ | Not given |
| Sensor **B** (Y.P. Zhang)[20] | Naked-eye | DMSO/$H_2O$ | Not given |
| Sensor **C** (Y.P. Zhao)[21] | Fluorescence | $CDCl_3$ | Not given |

# Experimental

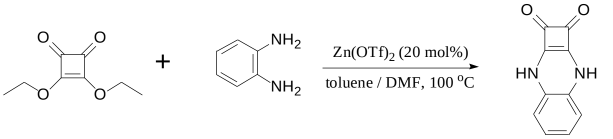
## Synthetic materials and instrumentation

All the chemicals used for the synthesis of probe **1** were of AR grade unless otherwise stated. All the reagents and solvents were purchased from commercial sources and used without further treatment. The aqueous stock solutions of anions of concentration $1.5 \times 10^{-1}$ mol/L were prepared from their *n*-tetrabutylammonium (TBA) salts. The stock solution of probe **1** was prepared by dissolving an accurately weighed probe **1** in DMSO, and then diluted to $5 \times 10^{-5}$ mol/L with buffer solution (pH = 7.24, DMSO / buffer = 90 / 10, v / v, aq. buffer = 0.1 M Tris-$ClO_4$).

The IR spectra were recorded on a Fourier Transform Infrared Spectrometer with KBr as discs and the IR bands are expressed in frequency ($cm^{-1}$). The $^1$H-NMR and $^{13}$C NMR were recorded on a Varian mercury-plus 400 NMR spectrometer at room temperature using $d_6$-DMSO as solvent and tetramethylsilane (TMS) as internal standard. The $^{19}$F NMR was recorded on the same instrument using $d_6$-DMSO as solvent and trichlorofluoromethane ($CFCl_3$) as standard. Elemental analyses were determined on a vario EL cube elemental analyzer. Absorption spectra were performed on a TU-1810 ultraviolet spectrophotometer.

## Synthesis of cyclobuta[b]quinoxaline-1, 2(3H, 8H)-dione (Probe 1)

The probe **1** was synthesized as shown in scheme 1. O-phenylenediamine (59 mg, 0.55 mmol), suquaric acid diethyl ester (81 μL, 0.50 mmol), zinc trifluoro-methanesulfonate (40 mg, 0.11 mmol), and mixture (10 mL) of toluene and DMF (toluene: DMF = 19:1) were added in a 100 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and thermometer socket. The reaction temperature was kept at 100 ℃ for 12 h. After cooling to room temperature, a red-brown precipitate was observed and isolated by filtering. The obtained solid was further washed with methanol (3×5 mL) to produce the target compound probe **1** as yellow powder in 74% yield (69 mg). IR ($cm^{-1}$) [KBr]: 3121, 2950, 1656, 1656, 1611, 1548, 1479, 1356; $^1H$ NMR (400 MHz, DMSO-$d_6$, δ ppm): 6.34-6.36 (2H, m, ArH), 6.63 (2H, m, ArH), 10.00 (2H, S, NH); $^{13}C$ NMR (100 MHz, DMSO-$d_6$, δ ppm): 116.4, 124.9, 131.7, 174.4, 178.2. Anal, calcd for $C_{10}H_6O_2N_2$: C, 64.52; H, 3.23; N, 15.05. Found: C, 64.41; H, 3.26: N, 14.87.



**Scheme 1.** The synthetic route for the preparation of probe **1**

## Computational study

The structural optimization and theoretical UV-Vis spectral of probe **1**, **1**-2F⁻ and fully deprotonated form $\mathbf{1}^{2-}$ were performed using the computer program Gaussian 09W by applying the DFT (density functional theory) and TD-DFT methods with a hybrid functional B3LYP using the basis sets 6-31G (d,p).

## Results and discussion

### Sensing of F⁻ by probe 1

The selective detection of fluoride ions can be seen from the observed color change of probe **1** solution from pale-yellow to orange-yellow (Fig. 1). In order to perform these naked-eye experiments, 10 equivalents of various ions (10 μL, 1.5 × $10^{-1}$ mol/L, in buffer) including F⁻ ions were added to the solution of probe **1** (3 mL, 5 × $10^{-5}$ mol/L) in 0.1 M Tris-$ClO_4$ buffer solution (pH = 7.24, DMSO: buffer = 90 / 10, v / v). As show in Fig. 1, no significant color change was observed with other ions except CN⁻ and F⁻ , but the color change caused by CN⁻ can be ignored completely compared with the color change caused by F⁻, which indicate the ability of probe **1** to recognize F⁻ ions selectively from aqueous system.

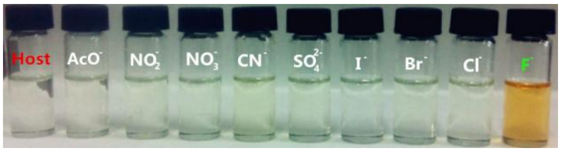


**Fig. 1** Naked-eye detection of F⁻ ion by probe **1** in the presence of other ions under visible.

The sensing properties of probe **1** combine with various anions were investigated by UV-Vis absorption spectroscopy (Fig. 2). The probe **1** showed three peaks at 264 nm, 312 nm and 347 nm in 0.1 M Tris-$ClO_4$ buffer solution (pH = 7.24, DMSO: buffer = 90 / 10, v / v). The peak at 264 nm was observed due to the π→π* electronic transition while the absorption at 312 nm and 347 nm appeared due to the n→π* transition. Upon the addition of equivalent anions into the buffered aqueous solution of probe **1**, the characteristic red shift (from 347 nm to 372 nm) of absorption wavelength could only be observed in the case of F⁻, while addition of other anions did not cause any significant change in the absorption profile except CN⁻ shown a tiny inessential hump proved by following competition experiments. Therefore, it can be concluded that probe **1** can recognize F⁻ selectively over other anions.

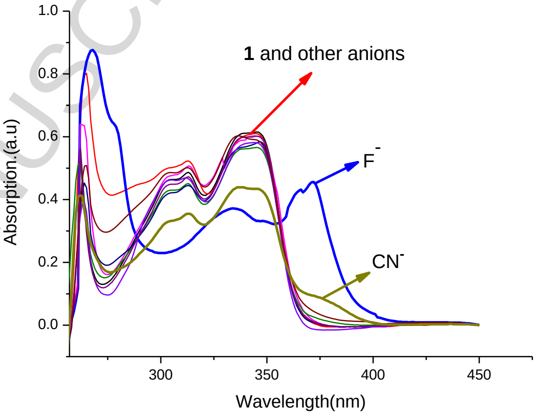


**Fig. 2** UV-Vis spectral changes of probe **1** (5 × $10^{-5}$ mol/L) in 0.1 M Tris-$ClO_4$ buffer solution (pH = 7.24, DMSO: buffer = 90 / 10, v / v) upon addition of 10 equivalents of different anions in TBA salts.

In order to eliminate the interference of other anions, selectivity of probe **1** for F⁻ over other anions were further examined by competitive experiments which were carried out by reacting probe **1** with 10 equivalents F⁻ in the presence of 10 equivalents other anions. By comparing the absorption intensity at 372 nm, no obvious interference was found from the histogram (Fig. 3). These results revealed that **1** showed excellent selectivity towards the fluoride ions even in the present of other competitive anions and thus can be used for the efficient detection of fluoride ions in the samples of different origins.

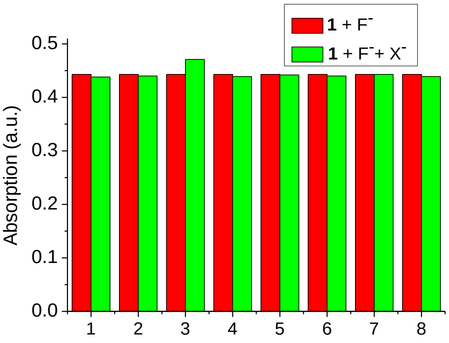


**Fig. 3** UV-Vis of probe **1** (5 × $10^{-5}$ mol/L) at 372 nm upon the addition of 10 equivalents F⁻ and 10 equivalents other anions (X⁻ = $SO_4^{2-}$ (1), $NO_3^-$ (2), CN⁻ (3), $NO_2^-$ (4), Cl⁻ (5), Br⁻(6), I⁻ (7) , AcO⁻ (8).

In addition, the sensitive recognition and binding mode of probe **1** with F⁻ was demonstrated by carrying out absorption titration experiment. With the progressive addition of fluoride ions from 0-10 equivalents to the solution of probe **1** ($5 \times 10^{-5}$ mol/L) in 0.1 M Tris-$ClO_4$ buffer (pH = 7.24, DMSO: buffer = 90 / 10, v / v), the absorption intensity at 266 nm and 372 nm was increased gradually along with the simultaneous intensity decrease of two broad shoulder centered at 307 nm and 342 nm. The resulting significant bathochromic shift (around 30 nm) of absorption peak and the two forming absorption isosbestic points at 284 nm and 356 nm were clearly seen. (Fig. 4) According to the following analysis of experimental results, we can conclude that these spectral changes are caused by the deprotonation of amino by $F^-$. The occurrence of deprotonation would suggest that HF and the negatively charged $\mathbf{1}^{2-}$ were formed. This causes an obvious increase in the charge density on the amino nitrogen which is verified by our computational study.

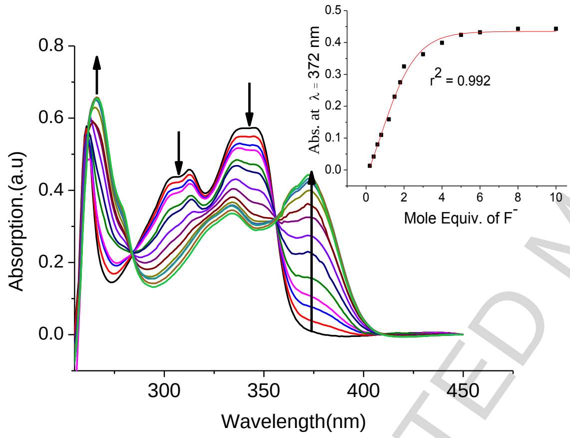


**Fig. 4** UV-Vis titration experiments of **1** ($5 \times 10^{-5}$ mol/L) in 0.1 M Tris-$ClO_4$ buffer solution (pH = 7.24, DMSO / buffer = 90 / 10, v / v) with the addition of 0-10 equivalents of *n*-$Bu_4NF$. Inset: The absorption intensity (I) of **1** at λ = 372 nm as a function of mole equivalents of $F^-$ ions.

To determine the stoichiometry between probe **1** and $F^-$, Job's plot (Fig. 5) was employed and the 1:2 stoichiometry was found, suggesting the deprotonation[22] of amino by basic $F^-$ was possibly occurred. Moreover, the association constant K between **1** and two $F^-$ is determined from eq (1)[23] to be $4.006 \times 10^8$ $M^{-2}$ (Fig. S4).

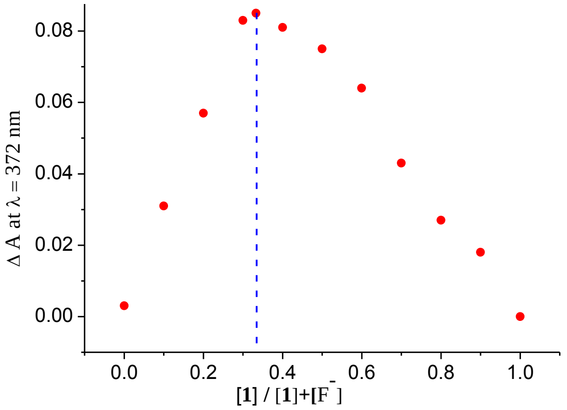


**Fig. 5** Job plot for the interaction between **1** and TBA·F: the change in absorption intensity (ΔA) at λ = 372 nm as a function of mole equivalents of [**1**] / ([**1**] + [$F^-$]).

$$\frac{1}{A-A_0}=\frac{1}{K(A_{max}-A_0)[F^-]_0^2}+\frac{1}{A_{max}-A_0} \qquad (1)$$

$A_0$ and A present the absorbance of **1** before and after addition of $F^-$, respectively, and $A_{max}$ is the absorbance obtained with excess amount of $F^-$. K is the association constant ($M^{-2}$), and $[F^-]_0$ is the concentration of $F^-$ added (M).

Furthermore, to confirm the mechanism of action of probe **1** with $F^-$, $^1H$ NMR titration experiments were carried out, in which spectra were recorded by adding 0-6.0 equivalents fluoride ions into the solution of probe **1** in DMSO-$d_6$. It is observed that the peak corresponding to -NH proton at δ = 10.00 ppm was weakened with the increase of fluoride ions and the peak disappeared when 2.0 or more equivalents fluoride ions were added into the solution of **1** (Fig. 6). The result clearly showed that the –NH proton of probe **1** was captured by $F^-$ which was proved by the observing bifluoride anion ($HF_2^-$) signal at around δ = -141 ppm[24] in $^{19}F$ NMR spectroscopy (Fig. S5) and characteristic absorption peak of $HF_2^-$ around 16.5 ppm[25] in $^1H$ NMR spectroscopy (Fig. S6). These results further confirmed our conclusion that the color change was caused by the deprotonation of amino.

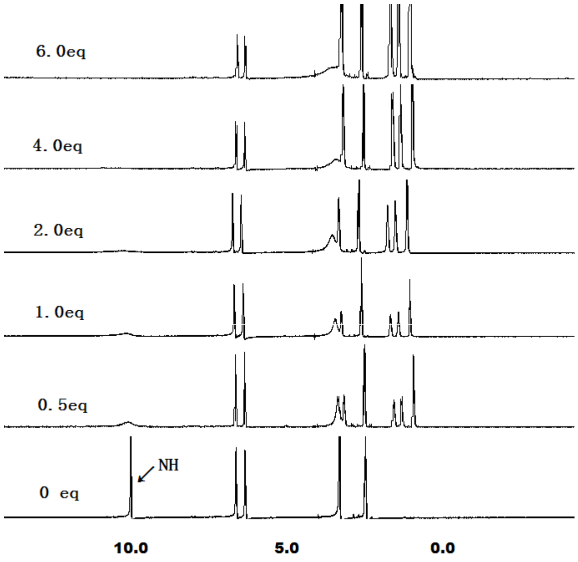


**Fig. 6** $^1H$ NMR spectrums of probe **1** in the presence of 0-6 equivalents of TBA·F.

The limit of detection of the receptor **1** was calculated for $F^-$ ions by using absorption titration[26]. Before calculated the relative standard deviation, the absorption measurements of ten blank samples were taken. The detection limit is then calculated with the following equation: detection limit = $3\delta_{bi}/m$ ($\delta_{bi}$ is the standard deviation of blank measurements, and m is the slope between intensity versus sample concentration). The calculated LOD value of probe **1** for $F^-$ ions is 4.8 μM.

## Application of probe 1

In order to explore the application for the recognition of $F^-$, the test strip with probe **1** was prepared. The test trip was prepared by soaking small strips of cellulose paper in the solution of probe **1** ($1 \times 10^{-2}$ mol/L) in Tris-$ClO_4$ buffer solution and dried in air.

When the strip was dipped in aqueous solution of $F^-$ ($5\times10^{-2}$ mol/L) the colorless (A) strip turned into dark yellow (B) immediately. (Fig. 7)

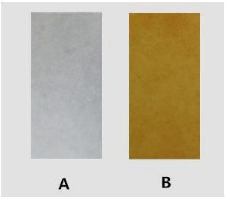


**Fig. 7** Application of probe **1** for detection of $F^-$ by test strip method

## Theoretical results

To understand the intermolecular charge transfer process that occurred between probe **1** and $F^-$, DFT calculations were performed using the B3LYP/6-31G (d,p) basis set. The optimized structure of the receptor probe **1** and the stable structure after adding fluoride ions and fully deprotonated form of the probe **1** were shown in Fig. 8. The calculated interaction energy ($E_{int} = E_{complex} - E_{receptor} - E_{F^-}$) was -125.44 kcal/mol which indicated the formation of stable structure. In the optimized structure, the distance (1.47Å) between N and H beyond the bond length scope (1.01Å) of -NH and the distance (1.00Å) between F and H is nearly equal to the bond length (0.92 Å) of HF.

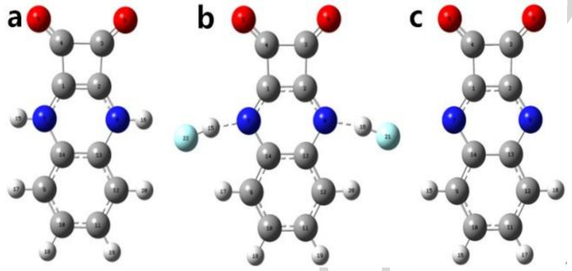


**Fig. 8** Optimized structure of the probe **1** (a), **1**-2F (b) and $\mathbf{1}^{2-}$(c) in the gas phase using DFT calculation at B3LYP/6-31G (d,p) level.

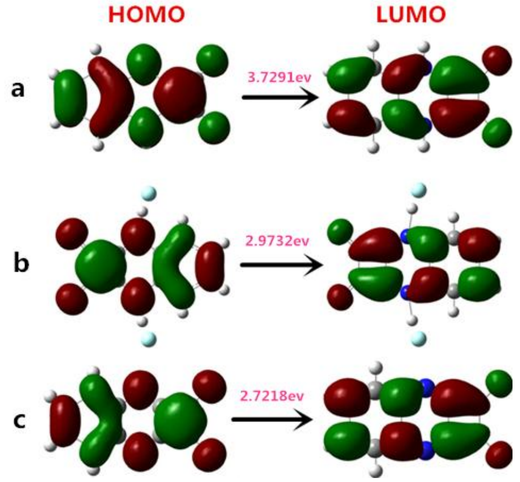


**Fig. 9** DFT computed LUMO and HOMO diagrams of the probe **1** (a), **1**-2F⁻ (b) and $1^{2-}$ (c) in the gas phase.

Apparently, occurrence of deprotonation was attributed to the strong electronegativity of fluoride which induced charge transfer in the probe **1**. These entire phenomena represented a total agreement with the disappearance of -NH in the $^1$H-NMR titration experiments. Furthermore, the HOMO and LUMO diagrams of probe **1**, **1**-2F⁻ and $\mathbf{1}^{2-}$ indicate that the internal charge transfer occurred during the anion recognition process. Also, the HOMO-LUMO band gaps of **1**-2F⁻ and $\mathbf{1}^{2-}$ were approximately equal suggested that occurrence of deprotonation during the recognition. Besides, compared with probe **1**, the HOMO-LUMO band gaps of **1**-2F⁻ and $\mathbf{1}^{2-}$ were decreased, which supports the absorbance at longer wavelength (Fig. 9).

Finally, in order to readily confirm the occurrence of deprotonation during the recognition between probe **1** and $F^-$, TD-DFT calculation was employed to predict the theoretical UV-Vis spectral changes of **1**, **1**-2F⁻ and deprotonated **1,** from which we can also observe three peaks at 171 nm, 245 nm and 312 nm of probe **1** and a obvious shift of absorption from 312 nm to 363 nm after adding $F^-$, which was in agreement with the experimental results. In addition, the appearance of absorption peak at 388 nm for the fully deprotonated form of the probe **1** further indicate that the characteristic red shift of **1**-2F was caused by deprotonation.

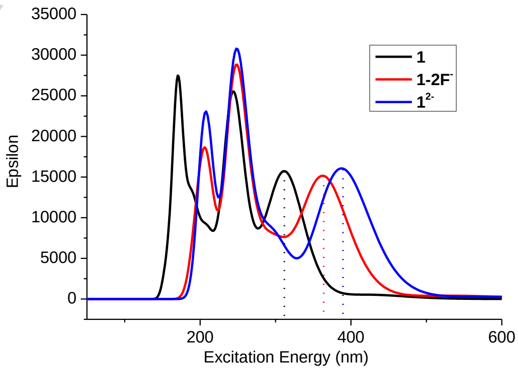


**Fig.10** TD-DFT computed UV spectral diagrams of the **1**, **1**-2F and $\mathbf{1}^{2-}$.

## Conclusion

In summary, we have successfully developed a derivative of squaramide probe **1** as desirable ratiometric and colorimetric chemosensor for the recognition of fluoride ions in aqueous media with high selectivity and sensitivity.

The recognition of fluoride ions was confirmed by obvious color change from pale-yellow to orange-yellow due to the appearance of a new charge transfer band. The remarkable colorimetric sensing of probe **1** confirmed a 1:2 action model. Furthermore, probe **1** can be used to detect $F^-$ in the aqueous media by naked-eye and induce a remarkable spectroscopic response by giving a new intense peak in the absorption spectrum at 372 nm. Considering the good selectivity and sensitivity of chemosensor probe **1** for the detection of $F^-$ from aqueous system, its applications in chemical and daily life will become more convenient.

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## Notes and references

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## Graphical Abstract

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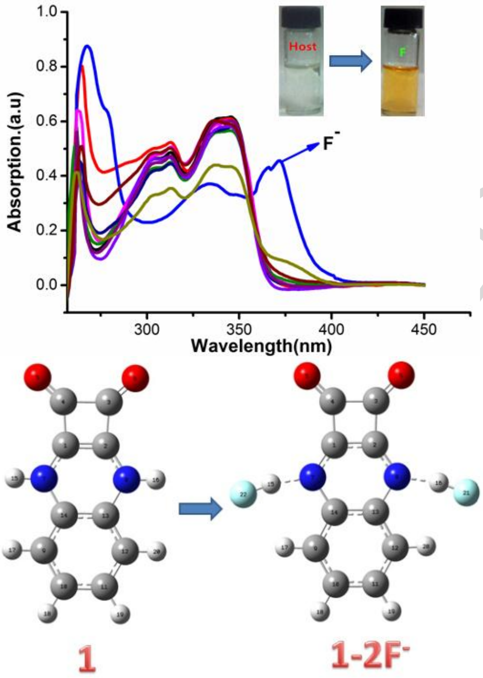

# Highlights:

- An easy-to-prepare fluoride sensor was synthesized.
- Anion recognition phenomenon can be observed by naked-eye.
- Recognition mechanism was proved by the $^1$H NMR titration experiments and DFT calculations.

1 D. F. Shriver and M. J. Biallas, *J. Am.Chem. Soc.*, 1967, **89**, 1078.
2 C. H. Park and H. E. Simmons, *J. Am.Chem. Soc.*, 1968, **90**, 2431.
3 (a) M. N. Piña, C. Rotger, B. Soberats, P. Ballester, P. M. Deyà and A. Costa, *Chem. Commun.*, 2007, **9**, 963; (b) V. Amendola, G. Bergamaschi, M. Boiocchi, L. Fabbrizzi, and Mi. Milani, *Chem. Eur. J.*, 2010, **16**, 4368; (c) Q. Shu, Jan W. Bats and M. Schmittel, *Inorg.Chem.*, 2011, **50**, 10531; (d) M. Schmittel and Q. Shu, *Chem. Commun.*, 2012, **48**, 2707; (e) M. Schmittel, Q. Shu and M. E. Cinar, *Dalton Trans*., 2012, **41**, 6064; (f) K. Chen and M. Schmittel, *Chem. Commun.*, 2014, **50**, 5756; (g) K. Chen, Q. Shu and M. Schmittel, *Chem. Soc.Rev.*, 2015,**44**, 136.
4 (a) P. A. Gale, *Chem. Commun.*, 2011, **47**, 82; (b) Y.S. Mi, D.M. Liang, Y.T. Chen, X.B. Luo and J.N. Xiang, *RSC Adv.*, 2014, **4**, 42337; (c) H. Khanmohammadi and K. Rezaeian, *RSC Adv*., 2014, **4**, 1032; (d) S.J. Yang, Y. Liu and G.Q. Feng, *RSC Adv.*, 2013, **3**, 20171.
5 M. E. Moragues, R. Martínez-Máňez and F. Sancenón, *Chem. Soc. Rev.*, 2011, **40**, 2593.
6 Y. Zhao, L. Yao and M. Zhang, *Talanta*, 2012, **97**, 343.
7 H. S. J. Horowitz, *Public Health Dent*., 2003, **63**, 3.
8 (a) D. Sharma, R. K. Bera and S. K. Sahoo, *Spectrochim. Acta A* 2013, **105**,477; (b) D. Sharma, S. K. Sahoo, S. Chaudhary, R. K. Berac and J. F. Callan, *Analyst*, 2013, **138**, 3646; (c) D. Sharma, S. K. Sahoo, R. K. Bera and R. Kamal, *J. Fluorescence*, 2013, **3**,387; (d) D. Sharma, A. Moirangthem, S. K. Sahoo, A. Basu, S. M. Roy, R. K. Pati, S. K. Ashok Kumar, J. P. Nandred and U. D. Patil, *RSC Adv*., 2014, **4**, 41446; (e) U. N. Yadava, P. Pant, D. Sharma, S. K. Sahoo and G. S. Shankarling, *Sensors and Actuators B*, 2014, **197**, 73; (f) Y. Zhou, J. F. Zhang and J.Yoon, *Chem. Rev.*, 2014, **114**, 5511.
9 L. Trembleau, T. A. D. Smith and M. H. Abdelrahman, *Chem.Commun*., 2013, **49**, 5850.
10 I.-S. Ke, M. Myahkostupov, F. N.Castellano and F. P. Gabbaï, *J. Am. Chem. Soc*., 2012, **134**, 15309.
11 C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P.Gabbaï, *Chem. Rev.*, 2010, **110**, 3958.
12 Y. Kim and F. P.Gabbaï, *J. Am. Chem. Soc.*, 2009, **131**, 3363.
13 P. Ashokkumar, H. Weishoff, W. Kraus and K. Rurack, *Angew.Chem., Int. Ed.*, 2014, **53**, 2225.
14 F. Y. Wu, M. H. Hu, Y. M. Wu, X. F. Tan, Y. Q. Zhao and Z. J. Ji, *Spectrochim. Acta A* 2006, **65**, 633
15 C. Saravanan, S. Easwaramoorthi, C.Y. Hsiow, K. Wang, M. Hayashi and L. Wang, *Org. Lett*., 2013, **16**, 354.
16 X. Jiang, M. C. Vieweger, J. C. Bollinger, B. Dragnea and D. Lee, *Org. Lett.*, 2007, **9**, 3579.
17 P. Sokkalingam and C. H. Lee, *J. Org. Chem.*, 2011, **76**, 3820.
18 A. K. Atta, I. H. Ahn, A. Y. Hong, J. Heo, C. K. Kim and D. G. Cho, *Tetrahedron Lett*., 2012, **53**, 575.
19 E.J. Cho , Y. Lee , H.J. Bae and Y. J. Lee, *Spectrochim. Acta A* 2015, **151**, 655.
20 Y.P. Zhang and S.M. Jiang, *Org. Biomol. Chem.*, 2012, **10**, 6973.
21 Y.P. Zhao , C. C. Zhao , L.Z. Wu , L.P. Zhang , C.H. Tung and Y.J. Pan, *J. Org. Chem.*, 2006, **71** , 2143.
22 (a) T. Gunnlaugsson, P. E. Kruger, P. Jensen, F. M. Pfeffer and G. M. Hussey, Tetrahedron Lett.,2003, 44, 8909; (b) Q. G. Wang, Y. S. Xie, Y. B. Ding, X. Li and W. H. Zhu, Chem. Commun., 2010, 46, 3669.
23 Y. Shiraishi, S. Sumiya, Y. Kohno, and T. Hirai, J. Org. Chem. 2008, 73, 8571.
24 M. Goursaud, P. D. Bernardin, A. D. Cort, K. Bartik and G. Bruylants, Eur. J. Org. Chem., 2012, 19, 3570.
25 S. Saravan Kumar, S. Bothra, S. K. Sahoo and S. K. Ashok Kumar, J. Fluorine Chem., 2014, 164, 51.
26 C. R. Lohani, J. M. Kim, S.Y. Chung, J. Yoon and K. H. Lee, Analyst, 2010, **135**, 2079.