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Cascade detection of fluoride and bisulphate ions by newly developed hydrazine functionalised Schiff bases



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ABSTRACT

Two hydrazine functionalized Schiff bases have been synthesized through the reaction between hydrazine and *o*-vanillin/salicylaldehyde compounds employing a green-chemical approach and characterized spectroscopically including XRD study. Crystal structure analysis reveals that both the chemosensors, *N*,*N*'-bis(*o*-vanilidine)hydrazine (P17) and *N*,*N*'-bis(salicylidene)hydrazine, (HARB) crystallize in monoclinic system with $P_{1/n}$ space group and exist in the locked forms through intramolecular H-bonding (~1.90 Å) between phenolic-OH and N atom of hydrazine. The chemosensors display excellent selectivity towards fluoride followed by bisulphate ions, over other potential competitor anions in acetonitrile. Binding stoichiometry of the individual chemosensor with F⁻ is confirmed to be 1:1 and assessed with absorption study and ¹H NMR analysis. Systematic DFT analysis reveals that the contribution of hydroxyl oxygen atoms to the HOMO increases sharply from the chemosensor to chemosensor-F⁻ adduct (17% to 28%) leading to deprotonation of one hydroxyl group and consequently involvement in conjugation impeding the C=N isomerisation. Thus, the hydroxyl proton captured by F⁻ restricts the C=N isomerisation as well as ICT character of both the chemosensors and confirms the cascade sensing mechanism for fluoride and bisulphate ions.

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1. Introduction

Designing and development of receptors and chemosensors with the ability to recognize the anions with extreme selectivity are of high demand in modern science as anions play fundamental roles in a varied range of biological and chemical processes [1]. Fluoride (F^{-}) is an extremely important anion in the living world. It is an essence to sustain dental health and in curing osteoporosis [2–4]. On the flip side, excess consumption of fluoride causes severe diseases like gastrointestinal dysfunction, dental and bone fluorosis [5]. Focusing on this serious concern, the World Health Organization (WHO), in a guideline has directed to maintain fluoride concentration below 1.5 mg/mL in drinking water [6-8]. On the other hand, bisulphate (HSO₄) is also a useful anion and it is a constituent of many agricultural fertilizers, industrial raw materials, and nuclear fuel waste. Bisulphate has also an adverse effect on the environment as a pollutant and in this context, sensing of this anion over the entire group of oxo-anions is still an emerging area of modern research [9]. Irritation of the skin and eyes and even respiratory paralysis is affected by the toxic sulphate ion (SO_4^{2-}) which is produced from this amphiphilic anion at high pH [10]. To remove such adverse effects, design of an efficient chemosensor for the selective detection of HSO_4^- is a promising challenge to the supramolecular chemists.

Therefore, design and synthesis of environmentally and medicinally important anion, selective probe is still an unsolved challenge. During the last two decades, different scientific groups have synthesized fluoride selective [11-22] as well as bisulphate selective [23-36] probes for the selective and sensitive colorimetric detection of these two ions individually. But, none of the probes was able to detect both the fluoride and bisulphate anions in a cascade manner. Mallick and co-workers [37, 38] exploited the cascade detection of F⁻ and HSO₄⁻ ions employing a single "Off-the-shelf" or commercially available probe molecule. Literature survey indicates that different scientists have been utilized hydrazine functionalized Schiff base to develop chemoreceptor colorimetrically for the detection of F⁻, CH₃COO⁻, and other anions in nonaqueous solution [39-42]. Most of them have synthesized the compounds without reporting their crystal structures. It is well documented that Ziolek et al. studied important spectroscopic and photophysical properties of the conformers of different photochromic Schiff base ligands in a number of differently interacting solvents and micellar systems [43-45]. In this context, herein, we have designed and synthesized two hydrazine functionalized Schiff bases (P17 and

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HARB) using a green-chemical approach. Subsequently, the chemosensors have been efficiently utilized in relay detection of F^- and HSO₄ anions in acetonitrile (MeCN) medium. Further, the binding aspects are established through ¹H NMR analysis and extensive density functional theoretical (DFT) computations. The most attractive part of the present report lies in the fact that structurally simple, easily synthesizable and cost-effective hydrazine functionalized simple Schiff bases can be synthesized just in an undergraduate laboratory to detect both the F⁻ and HSO₄⁻ anions with extreme selectivity and eminent efficiency. Both of the chemosensors in presence of F⁻ display a pronounced yellow colour in MeCN and the naked eye colour change may be observed effortlessly with millimolar solutions.

2. Experimental

2.1. Chemicals, solvents and starting materials

Highly pure o-vanillin (Aldrich, USA), salicylaldehyde (SRL, India) and hydrazine (TCI, Japan) were procured from the respective commercial sources. All the anions in the form of tetrabutylammonium salts (TBAX) were purchased from Sigma-Aldrich and were used without further purification. All the solvents used in the present experiments were spectroscopic grade from Spectrochem, India. All the reagents and solvents were of commercially available A.R grade quality.

2.2. Preparation of Schiff bases/chemosensors (P17 and HARB)

The Schiff bases were synthesized under solvent-free conditions using a green-chemical approach following a reported procedure [46–48]. Both P17 and HARB were synthesized by mixing of *o*-vanillin (6.190 g, 40.1 mM or salicylaldehyde (4.820 g, 39.99 mM), respectively, with hydrazine in (0.640 g, 19.98 mM) in a 250 mL bi-necked flat bottom flask under the solvent-free condition at 40 °C with slow stirring for ~4 h. Both the reaction produced bright yellow crystalline products. The yellow crystalline compounds were isolated and dried over CaCl₂. TLC of the reactions was performed using DCM solution of the crystalline yellow products which strongly recommend the formation of a single-phase pure products for both the reactions. The yields were obtained as 6.13 g (89.7%) for P17 and 4.83 g (88.4%) for HARB. The single crystals of the compounds P17 and HARB were obtained from the saturated methanol solution of the compounds following the slow evaporation technique at room temperature.

Anal cal. For $C_{14}H_{16}N_2O_2$ (P17): C, 63.99; H, 5.37; N, 9.33; Found: C, 64.06; H, 5.41; N, 9.39. IR (KBr pellet, cm⁻¹): 3437(v_{OH}), 1612 (v_{C=N}); UV–Vis (1 × 10⁻⁴ M, λ_{max} (abs), nm, MeCN): 227(0.419), 312(0.504), 366(0.171); ¹H NMR (CDCl₃) $\delta = 11.56$ (s, 2H), 8.70 (s, 2H), 6.90–7.01 (m, 6H), 3.93 (s, 3H) ppm; ¹³C NMR (300 MHz, DMSO-*d*₆): 164.97 (HC=N); 149.82 (Ar-OCH₃); 148.48 (Ar-OH); 124.19 (Ar-N=C); 124.19, 119.57, 117.48, 115.24, 114.40, 112.07 (Ar-C); 56.35 (-OCH₃); HRMS (*m*/*z*): 300.09.

Anal cal. For C₁₄H₁₂N₂O₂ (HARB): C, 69.99; H, 5.03; N, 11.66; Found: C, 70.03; H, 5.01; N, 11.69. IR (KBr pellet, cm⁻¹): 3421(v_{OH}), 1630(v_{C=} N); UV–Vis (1 × 10⁻⁴ M, λ_{max} (abs), nm, MeCN): 221(0.584), 293 (0.663), 355(0.590); ¹H NMR (CDCl₃) δ = 11.23 (s, 2H), 8.90 (s, 2H), 6.9–7.5 (m, 8H) ppm; ¹³C NMR (300 MHz, DMSO-*d*₆): 163.66 (HC= N); 158.96 (Ar-OH); 132.80,131.60 (Ar-N=C); 119.23, 117.41, 116.38, (Ar–C); HRMS (*m*/*z*): 240.52.

2.3. Physical measurements

Infra-red spectra of P17 and HARB were recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range of 400–3600 cm⁻¹ with KBr pellet. ¹H and ¹³C NMR spectra of the compounds were obtained on a Bruker Advance 400 MHz spectrometer at 25 °C in CDCl₃. All the ground state absorption and spectrophotometric titrations were recorded on a JASCO V-730 UV–Vis spectrophotometer. Fluorescence

spectra were recorded on Hitachi F-7000 spectrofluorometer. High resolution mass spectra were recorded using a Q-tof-micro quadruple mass spectrometer. The pH values of the solutions were measured by Labman pH meter at room temperature. Elemental analyses were performed on a Perkin Elmer 2400 CHN microanalyser.

2.4. Crystal structure determination and refinement

Single crystal X-ray diffraction data of P17 and HARB were collected using a Rigaku XtaLABmini diffractometer equipped with Mercury 375R (2 × 2 bin mode) CCD detector. The data were collected with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 100.0(2) K using ω scans. The data were reduced using CrysAlisPro 1.171.38.46 [49] and the space group determination is done using Olex2. The structure is resolved by dual space method using SHELXT-2015 [50] and refined by full-matrix least-squares procedures using the SHELXL-2015 [51] software package through OLEX2 suite.

2.5. Anion sensing experiments

Stock solutions of 1.2 mM chemosensors, 10 mM TBAB, and 10 mM TBAF in MeCN were prepared. Other stock solutions of similar anions (tetrabutylammonium salts) were also prepared accordingly in MeCN. About 2400 μ L of solvent (pure MeCN) was taken first in a Teflon stoppered quartz cuvette, then 2 μ L probe was added, stirred on a magnetic stirrer, thermally equilibrated to 300 K. Afterward, appropriate volume fractions of the respective tetrabutylammonium salt stock solutions of bisulphate or/and fluoride or/and others were added as required to the final mixture, stirred well and the absorbance spectra were recorded. These steps were repeated until spectral saturation.

The chemosensory responses of the receptors were examined through spectrophotometric spectral analyses upon the addition of trace amounts of TBAX within MeCN medium. The selectivity for both the receptors towards F^- followed by HSO_4^- anions over other anions of TBA salts was studied in detail [52,53]. All the spectrophotometric analyses were carried out in triplet. The spectrofluorimetric responses of the chemosensors were studied in the absence and presence of the TBAX salts in MeCN medium. P17 was found as a fluorescence inactive molecule both in the presence and absence of TBAX salts. Noteworthy, HARB displayed poor fluorescent behaviour in MeCN. Although, in presence of TBAF, HARB exhibited improved fluorescence intensity.

2.6. Colorimetric test

The chemosensors, P17 (0.0340 g, 1 mmol) and HARB (0.030 g, 1 mmol) were dissolved in MeCN (10 mL) separately to get 0.1 mM solution. The colourimetric tests were designed and developed by the addition of a drop of TBAF solution in acetonitrile (1 mM) to the chemosensor solution in MeCN [54]. The colour change (instant yellowish-red colour) was observed and recorded with a digital camera in slow-motion mode. The TBAX salts containing different anions were also dissolved in MeCN (10 mL) to set up the concentration to 0.1 mM. No changes of colouration were observed for other anions.

2.7. Computational details

All mentioned computational calculations were executed using Gaussian 09 W programme suite [55] ignoring symmetrical constraints and GaussView 5.0 [55] was used as user-interface. The ground state and excited state calculations were performed employing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method respectively. Moreover, widely used B3LYP computational model was compiled with 6-311G basis set [56]. Initially, all the probes, anions and probe-anionic complexes were optimized in the gas phase ($\epsilon = 1.0$) and then in MeCN ($\epsilon = 35.688$) employing integral equation formalism polar continuum model (IEFPCM) [57–60] solvent model.



Scheme 1. Preparative route of Schiff bases, P17 and HARB under the solvent-free condition.

The global minimum of each structure was confirmed through stability calculation and IR frequency check-up with no imaginary frequency. For binding energy calculations of the probe-anionoic complexes in vacuum, correction due to basis set superposition error (BSSE) was considered employing a counterpoise method [61–63]. The images of molecular electrostatic potential (MEP) plots and frontier molecular orbitals (FMOs) were extracted from corresponding check point files. Further details of computational methods could be found somewhere else [64,65]. GaussSum [66] program was used to calculate the fractional contributions of various groups to each molecular orbital for the complexes.

3. Results and discussion

3.1. Synthesis of the chemosensors (P17 and HARB)

The Schiff bases P17, and HARB were synthesized under the solventfree condition by the reaction between hydrazine and carbonyl compounds (o-vanillin and salicylaldehyde) separately. The bright yellow crystalline products were recrystallized in methanol using a slow evaporation technique. The synthetic route for the Schiff bases is shown in Scheme 1.

3.2. Spectroscopic characterization of P17 and HARB

Different spectroscopic and analytical techniques were employed to establish the structural compositions of the probes. The formulations of the Schiff bases (P17 and HARB) were determined by infrared, ultraviolet visible, nuclear magnetic resonance, and high-resolution mass spectrometry spectral analysis. The probes were well soluble in acetonitrile. dichloromethane. etc.

The functional sites of P17 and HARB were examined by careful analysis of the stretching vibrations of the corresponding functional groups through infrared spectra. The IR spectra of P17 and HARB (Fig. S1 and S2) exhibited important broad peaks at 3411 and 3421 cm⁻¹ which were assignable to phenolic-OH groups in the probes respectively. The appearance of strong peaks at 1621 and 1630 cm⁻¹ indicated the presence of azomethine groups for P17 and HARB respectively. Other strong peaks at 1462 and 1256 cm⁻¹ for P17, and 1491 and 1280 cm⁻¹ for HARB were attributed to phenoxo (–OPh) groups in the probes. These characteristic peaks resemble well the reported values of the corresponding functional groups [67,68].

The electronic spectra of P17 and HARB were also recorded in MeCN in the 200–900 nm range. The UV–Vis spectrum of P17 displayed the absorption bands at 227, 312, and 366 nm while HARB showed the absorption bands at 221, 293, and 355 nm (Fig. S3). The observable electronic bands within 320 nm may be attributed to intra-ligand π - π */n- π * electronic transitions for both the probes. On the flip side, the optical bands at 366 and 355 nm for P17 and HARB are originated from intra-ligand charge transition. The reported electronic bands for P17 and HARB were in good agreement with the reported values [69].

The NMR spectral analysis of the probes P17 and HARB was carried out in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Figs. S4-S7 displayed the ¹H and ¹³C NMR spectra of P17 and HARB respectively. It was observed that a sharp proton signal (singlet) assignable to phenolic-OH appeared at 11.56 and 11.21 ppm for P17 and HARB respectively (Figs. S4,S6). Another characteristic singlet appeared at 8.70 and 8.90 ppm for P17 and HARB which corresponds to the proton for azomethine group. Other characteristic signals for the aromatic–H of both P17 and HARB correlated with the signals found in 6.90–7.01 and 6.9–7.5 ppm respectively. A singlet at 3.93 ppm was assignable to methoxy proton of P17 (Figs. S4,S6).

The signal and splitting patterns in ¹³C NMR spectra (Figs. S5,S7) ensure that azomethine-C produced the signal at 164.97 and 163.66 ppm for P17 and HARB respectively. Noteworthy, one signal appeared for ipso carbon of P17 and HARB correspond to Ph–OH group at 148.48 and 158.96 ppm. Other characteristics signals assignable to aromatic carbons in ¹³C spectra were observed in the range of 124.19–112.07 and 119.23–116.38 ppm. The signals appeared in proton and carbon NMR spectra index well with the previously reported data [70].

High-Resolution (HR) mass spectral study of the synthesized probes in MeCN was in good agreement with the theoretical molecular mass of the compounds (Figs. S8, S9) and confirmed the solution stability of the probes. P17 and HARB displayed the characteristic base peaks at m/z300.0924 and 240.5225 a.m.u respectively.

3.3. Description of crystal structures of P17 and HARB

Single crystal X-ray diffraction study revealed that both the Schiff bases, P17 and HARB crystallize in monoclinic crystal system with $P2_1/n$ space group. The thermal ellipsoidal plot of P17 and HARB are shown in Figs. 1 and 2. The structural refinement parameter is summarized in Table 1. The bond distances and bond angles of P17 and HARB are presented in Tables 2 and 3 respectively. Both the hydrazine



Fig. 1. Thermal ellipsoidal plot of P17.



Fig. 2. Thermal ellipsoidal plot of HARB.

Structural refinement parameter for P17 and HARB.

Parameters	P17	HARB
Empirical formula	C ₁₆ H ₁₆ N ₂ O ₄	C ₁₄ H ₁₂ N ₂ O ₂
Formula weight	300.31	240.26
Temperature (K)	100.0(2)	100.0(2)
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21/n
a (Å)	6.0167(7)	8.3572(5)
b (Å)	18.2464(17)	6.2970(4)
c (Å)	6.8349(7)	11.6179(6)
α	90	90
β	107.280	106.749(4)
γ	90	90
Volume (Å3)	716.49(14)	585.46(6)
Z	2	2
ρ (gcm-3)	1.392	1.363
μ(mm-1)	0.101	0.093
F (000)	316	252
θ ranges (°)	3.3-32.8	3.0-27.6
Number of unique reflections	2531	1453
Total number of reflections	8269	3712
Final R indices	0.0660, 0.2185	0.050, 0.1167
Largest peak and hole (eA°-3)	0.72, -0.29	0.29, -0.28

functionalized Schiff bases exist in a locked state with strong intramolecular H-bonded interactions and adopt *anti* conformation. In P17, the azomethine bond distance between C8 and N1 atoms was found as 1.289 Å while N1-N1a bond distance value was noted as 1.403 Å. The bond distance values correspond to a pure double and single bond character for the bonds C8-N1 and N1-N1a in P17 (Tables 2). The same structural parameter for C4-N2 and N2-N2a in HARB was found as 1.288 Å and 1.4006 Å respectively (Tables 3). The presence of an additional methoxy group in P17 makes a little deviation in bond distances and bond angles between P17 and HARB. 3.4. Spectrophotometric relay recognition of fluoride and bisulphate ions

The binding propensity of the chemosensors P17, HARB towards the anions of tetrabutylammonium salts (TBAX) were examined in pure MeCN medium at room temperature. The binding properties were explored through detailed spectrophotometric investigation. The electronic spectra of P17 displayed the optical bands at 227, 312, and 366 nm (Fig. S3) while the other analogue HARB exhibited the absorption bands at 221, 293, and 355 nm (Fig. S3). Upon gradual addition of TBAF from 0 to 24.3 µM concentration within P17 solution in MeCN medium, a new absorption band with increasing absorbance was initiated to develop at 472 nm with the appearance of three distinct isobestic points. Fig. 3a presents the absorption spectra of P17, treated with TBAF in MeCN. With the progressive rise in the absorption band at 472 nm, the resultant pale yellow solution of P17 became intensified from yellow to reddish-yellow. In the course of spectrophotometric titration, the electronic band at 314 nm quenched drastically and another band at 355 nm almost vanished after the completion of the titration (Fig. 3a). The observed isobestic points at 282, 345, and 397 nm in the course of titration suggested that the interaction between P17 and TBAF proceeded through a single component reaction.

On the flipside, HARB on interaction with TBAF in pure MeCN under identical reaction conditions developed a new optical band at 462 nm with a concurrent decrease of absorbance values of the existing electronic bands at 294 and 355 nm (Fig. 4a). Three distinct isobestic points were also observed in the course of a spectrophotometric titration between HARB and TBAF within the concentration range of 0–29.0 μ M. The isobestic points at 283, 319, and 387 nm indicated a dynamic equilibrium was also established between the chemosensor, HARB, and its HARB-F⁻ complex. These ratiometric spectral changes might be utilized qualitatively and quantitatively to detect F⁻ in the real samples. In the MeCN medium, the naked eye colour change from yellow to reddishyellow, upon addition of TBAF within HARB was also observed.

Table 2	
Selected bond distances (Å) and angles (°) for P17.	

	XRD	DFT		XRD	DFT		XRD	DFT
Bond distances (Å)								
C1-O1	1.3708(19)	1.3860	N1-N1a	1.4036(18)	1.4053	C3-C4	1.410(2)	1.4172
C7-01	1.436(2)	1.4511	C1-C6	1.384(2)	1.3907	C3-C8	1.456(3)	1.4442
C2-02	1.3568(18)	1.3632	C1-C2	1.410(2)	1.4146	C4-C5	1.380(3)	1.3815
C8-N1	1.289(2)	1.3062	C2-C3	1.406(2)	1.4167	C5-C6	1.401(3)	1.4081
Bond angles (°)								
C1-01-C7	115.95(13)	118.74	01-C1-C2	114.88(12)	115.28	C2-C3-C8	121.54(14)	121.15
N1a-N1-C8	112.98(14)	115.17	02-C2-C3	122.85(15)	122.23	C4-C3-C8	118.46(15)	119.37
01-C1-C6	124.87(16)	124.86	C1-C2-C3	119.11(13)	119.48	C2-C3-C4	120.00(16)	119.46
C2-C1-C6	120.25(14)	119.85	02-C2-C1	118.04(13)	118.28	C3-C4-C5	119.90(17)	120.44
C4-C5-C6	120.38(18)	120.02	C1-C6-C5	120.28(17)	120.73	N1-C8-C3	121.88(16)	122.09

Table 3

Selected bond distances (Å) and angles (°) for HARB.

	XRD	DFT		XRD	DFT		XRD	DFT
Bond lengths (Å)								
C5-O1	1.354(2)	1.368	C3-C6	1.398(3)	1.413	C7-C9	1.396(3)	1.405
C4-N2	1.288(2)	1.306	C3-C4	1.446(3)	1.443	C8-C9	1.377(3)	1.390
N2-N2 a	1.4006(18)	1.405	C5-C8	1.390(3)	1.399			
C3-C5	1.415(2)	1.422	C6-C7	1.379(3)	1.386			
Bond angles (°)								
N2a-N2-C4	113.25(14)	115.09	N2-C4-C3	120.88(15)	121.85	C3-C5-C8	120.00(16)	120.04
C4-C3-C5	121.87(16)	121.68	01-C5-C8	118.14(15)	118.16	C3-C6-C7	121.58(16)	121.21
C5-C3-C6	118.20(16)	118.49	01-C5-C3	121.86(16)	121.78	C6-C7-C9	119.28(17)	119.37
C5-C8-C9	120.33(16)	120.80	C7-C9-C8	120.60(17)	120.79			

Most captivatingly, upon addition of other competitive anions to the chemosensors, P17 and HARB in the MeCN medium didn't display any noticeable changes in absorption spectra. Further expansion of our chemosensing approach with the addition of tetrabutylammonium bisulphate (TBAB) to these fluorinated complexes (P17–F and HARB-F⁻) result in promising aspects in dualion recognition. Interestingly, with selective addition of TBAB to the MeCN solution of these TBAF treated chemosensors, the newly developed absorption bands at 472 and 462 nm for P17–F and HARB-F⁻ systems, respectively, started to decrease and ultimately disappeared to lead the original absorption spectra for the pure P17 and HARB (Fig. 3b and 4b). Thus, upon the addition of HSO₄⁻ ion within the fluorinated chemosensors, pure states of P17 and HARB was restored.

The association constant of the chemosensors, P17 and HARB with F⁻ ion was determined to be 2.54×10^4 M⁻¹ and 2.56×10^4 M⁻¹, respectively, using the Benesi-Hildebrand method [71,72] considering a 1:1 stoichiometry (Fig. 3a inset and Fig. 4a inset, respectively). To check the reversibility of the responses, a protic solvent like H₂O was used to make the solution of the chemosensors. Interestingly, when a small amount of water (1%, v %) was added, the colour of the solutions of the fluorinated receptors P17 and HARB changed back to colorless which suggested that the protic solvents destroyed the hydrogen bonding between chemosensors P17 and HARB and F⁻ anion. The above results indicated that the interaction between the chemosensors, P17 and HARB and F⁻ anion could be hydrogen bonding interaction. To understand the recognition properties of the chemosensors, P17 and

HARB, ¹H NMR titration with TBAF was carried out in CDCl₃. It was evident that upon addition of 1 equivalent of F⁻, the proton signal corresponds to the phenolic-OH of P17 and HARB disappeared completely (Fig. 5). This experiment ensured that F⁻ makes an effective interaction with phenolic O-H protons of P17 and HARB. In contrast, other proton signals shifted upfield due to hydrogen bonding interaction increasing the electron density of the o-vanillin/ salicylaldehyde moieties (through-bond effect) [73-75]. The chemical shift of phenolic O-H protons in P17 was at 11.56 ppm which corresponds to the formation of intramolecular hydrogen bond between phenolic O-H protons and imine. The phenolic O-H protons disappeared completely upon the addition of F⁻ anion, and the other H signals moved upfield significantly which may point to the through-bond electronic propagation effect induced by the hydrogen bonding (Fig. 5). From the UV–Vis and ¹H NMR titrations spectra. possible binding models of chemosensors P17 and HARB with F⁻ was proposed, which was shown in Scheme 2. Upon binding of F⁻ anions, the -C=N- isomerization of the chemosensors P17 and HARB were restricted and the ICT (intramolecular charge transfer) interaction between electron-rich imine (C=N-) and electrondeficient fragments was enhanced, which might be responsible for the observed spectral behaviours. The populations of electrons on the whole conjugate of the chemosensors may result in fluorescence enhancement. As for chemosensors HARB, about 10 equiv. of F⁻ needed to destroy the internal hydrogen bond between phenolic OH protons and imine nitrogen which induced the conformational switching of C=N that might result in the sensitive fluorescence response of the receptor, HARB (Fig. S10).



Fig. 3. (a). Changes in absorption spectra of P17 upon gradual addition of TBAF salt, [P17] = 50 μ M, at 298 K [Inset: B—H plot of P17 with addition of TBAF considering 1:1 binding stoichiometry]; (b). Changes in UV–Vis spectra of the TBAF-treated P17 upon gradual addition of TBAB in MeCN.



Fig. 4. (a). Changes in absorption spectra of HARB upon gradual addition of TBAF salt, [HARB] = 50 μ M, at 298 K [Inset: B—H plot of HARB with addition of TBAF considering 1:1 binding stoichiometry]; (b). Absorption spectra of the mixture of HARB-TBAF upon gradual addition of TBAB in MeCN.

3.5. Selectivity studies

The selectivity of P17 and HARB was verified towards F^- ion over other competitive anions. The ground state absorption was measured separately under identical reaction conditions (Fig. S11a and S11b). Reports on the individual selectivity of the receptors towards different ions were many. However, the selectivity and sensitivity of the receptor molecule are well justified if it can detect a particular anion with different harsh chemical environments. For the real purpose, the receptor molecule must pose the ability to detect a particular ion in presence of other ionic components within the same mixture. Keeping in mind this fact, we studied the selectivity of P17 and HARB towards F^- , in presence of all other competitive anions. Without any uncertainty from the designed spectroscopic selectivity studies (Fig. 6 and S12), it was quite clear that other anions like Cl⁻, Br⁻, I⁻, $PO_4^3^-$, $H_2PO_4^-$, AcO⁻ etc. were ineffective to brought significant spectral changes of both the chemosensors, P17 and HARB. In the contrast, with the immediate addition of F⁻ ion to the respective mixture of anions, new absorption spectra were generated (Fig. S11a and S11b). Therefore, from the selectivity studies of P17 (Fig. 6) and HARB (Fig. S12) towards TBAF, the chemosensors may be assigned as excellent selective and sensitive colorimetric chemosensors for F⁻ ion.

3.6. Computational study on binding aspects of fluoride

3.6.1. Potential energy scan study

The molecular structures of the chemosensors were optimized theoretically in vacuum and MeCN to understand the trans orientation of the



Fig. 5. ¹H NMR titration represents gradual addition of TBAF to P17 in $CDCI_3$ medium [P17] = 49 μ M; [X]_{Final} = 25 μ M].



Fig. 6. Selectivity plot of P17 towards F^- over other competitive anions and their mixture in MeCN medium at 298 K; [P17] = 49 μ M; [X]_{Final} = 25 μ M]

two -OH bonds for P17 and HARB. The optimized structure of P17 (Fig. 7) and HARB (Fig. S13, ESI) are presented in the respective section. The optimized bond lengths and bond angles well reproduced the XRD parameters which provide additional support in favour of trans orientation of two -OH groups (Table 2 and Table 3). Thereafter, the potential energy scan study was performed theoretically to find out the origin behind the existence of specific trans orientation of P17 and HARB. This study was performed by varying the dihedral angle (C11-N13-14 N-15C) from -220° to $+220^{\circ}$ and plotting against the potential energy of the chemosensors in MeCN medium. The plot of variation of potential energy with dihedral angle for P17 (Fig. 8) and HARB (Fig. S14, ESI) molecules displayed a similar type of variation. The plots displayed that potential energy becomes minimum when the dihedral angle along C11-N13-14 N-15C are -180 and +180. Also, there were two saddle points when C11-N13-14 N-15C dihedral angles are -90 and + 90. Also, the stability of both the probes was maximum when the dihedral angle (C11-N13-14 N-15C) was zero. This is because in both the molecules the two hydrogen atoms of -OH group involve in intramolecular hydrogen bonding with two nitrogen atoms. The extent of hydrogen bonding becomes maximum when the two -OH moieties remain in trans position. At trans position due to maximum co-planarity, the extent of conjugation is maximum. This promotes the hydrogen bonding interaction to be maximum.



Fig. 8. Potential energy scan of P17 along potential energy (au) vs dihedral angle (Å), obtained using DFT/B3LYP/6-311G theoretical model and IEFPCM/MeCN solvent system.

3.6.2. Binding energy

In order to verify the selectivity of P17 and HARB towards F^- ion over other anions, binding energy analysis was also carried out. Binding energy calculations of different chemosensors-anionic complexes were performed initially in the gas phase (along with BSSE correction) and then in MeCN medium by following Eq. (1).

$$E_{\text{Bind}} = E_{\text{Complex}} - (E_{\text{Probe}} + E_{\text{Anion}}) \tag{1}$$

where E_{Bind} denotes the binding energy of the probe-anion complex, E_{Complex} denotes the optimized energy of the probe and E_{Anion} denotes the optimized energy of the probe and E_{Anion} denotes the optimized energy of the anion. The calculated binding energy values for P17 and HARB with different anions are presented in Tables 4. The BSSE corrected binding energy values of P17–F and HARB-F⁻ complexes in gas phase were remarkably high than other probe-anionic complexes. This fact theoretically established the selectivity of both P17 and HARB towards fluoride ion over other competitive anions. The BSSE corrected binding energy values of P17–F and HARB-F⁻ complexes in gas phase were – 232.7 and – 230.1 kJ mol⁻¹ respectively. Now, for 1:2 binding between the probe and F⁻_i it is quite expected to show almost double binding energy in comparison to the binding energy of



Fig. 7. Optimized geometry of P17 obtained using DFT/B3LYP/6-311G theoretical model and IEFPCM/MeCN solvent system (The dotted lines denote the hydrogen bonds, each atoms are marked with serial number and symbol).

Table 4

Interaction energies (kJ mol⁻¹) of P17-anionic and HARB-anionic complexes in vacuum and acetonitrile medium obtained using the B3LYP/6-311G method (BSSE corrected energies are in the parenthesis).

Complex	Vacuum	MeCN	Complex	Vacuum	MeCN
Binding ener	$rgy (kJ mol^{-1})$				
P17-F	-308.5	-119.6	HARB-F ⁻	-299.3	-113.6
	(-232.7)			(-230.1)	
P17-Cl ⁻	-67.4 (-63.4)	-1.6	HARB-Cl ⁻	-64.7 (-60.8)	-1.4
P17-Br	-66.2(-57.9)	-3.5	HARB-Br	-63.2 (-55.3)	-3.3
P17-AcO	-131.3 (-92.5)	-31.1	HARB-AcO	-114.5 (-85.7)	-32.4
$P17-HSO_4^-$	-36.9 (-50.7)	-24.4	$HARB-HSO_4^-$	-60.5 (-47.2)	-15.4
$P17-H_2PO_4^-$	-85.5 (-64.1)	-20.8	$HARB-H_2PO_4^-$	-81.6 (-60.4)	-20.4
P17-PO ₄ ³⁻	-48.8 (-44.2)	-34.6	HARB-PO ₄ ³⁻	-35.9 (-33.2)	-28.5

1:1 probe-anion complex [76]. However, the BSSE corrected binding energy values of P17–2F and HARB-2F⁻ complexes in gas phase were -272.3 and -268.2 kJ mol⁻¹ respectively. These data clearly indicated the 1:1 binding stoichiometry is more favourable over 1:2. Moreover, the binding energy value of P17–F was found to be larger than HARB-F⁻ complex denoting better binding interaction between P17 and F⁻ over HARB and F⁻.

Table 5

 $O\!-\!H$ and H-X bond length variations of P17 and their anionic complexes in gas phase and MeCN.

Complex	Vacuum		MeCN		
	0-Н	H-X	0-Н	H-X	
Bond length (Å)					
P17	1.002	-	1.006	-	
P17-F	1.561	0.994	1.441	1.020	
P17-Cl ⁻	1.005	4.076	1.007	4.147	
P17-Br ⁻	1.004	4.008	1.006	4.115	
P17-AcO	1.495	1.043	1.085	1.393	
P17-HSO ₄	1.006	2.155	0.999	2.422	
P17-H ₂ PO ₄	1.004	1.787	1.009	3.264	
P17-PO ₄ ³⁻	1.122	1.950	1.190	1.987	

3.6.3. Bond length variation

Bond length variation is an eminent tool to study the hydrogen bonding interaction or proton transfer process and both hydrogen bonding and proton transfer as literally both of them give similar type of bond length variation but differ in the extent of variation. The bond length variations of P17 and HARB are presented in Table 5 and Table S1. The -OH bond length of P17 and HARB will be stretched upon interaction with anions and the highest interacting anion will show the maximum shift. On the other side, the strongest interacting anion will construct the shortest $H-X^-$ distance (X = F, Cl, Br, etc). The -OH bond length of P17 (HARB) in MeCN was 1.006 Å (1.003 Å) that became maximumly elongated upon interaction with F⁻ ion to 1.441 Å (1.426 Å). What's more, the H–F distance squeezed to almost a real H–F bond to 1.020 Å (1.027 Å). Jeffery et al. [77] documented that hydrogen bond distance between 1.2 and 1.5 Å denote strong hydrogen bonding and hydrogen bond length below 1.2 Å indicate the possibility of proton transfer. Hence, the bond length variation data clearly released the possibility of proton transfer from P17/HARB to F⁻ in the ground state.

3.6.4. Frontier molecular orbital analysis

Thereafter, the frontier molecular orbital (FMO) images of P17, HARB, and their fluoride complexes (Fig. 9 and Fig. S15, ESI) were depicted to understand the binding interaction. The energy of HOMO-LUMO energy gap of P17 and HARB were 3.55 and 3.72 eV respectively. The HOMO-LUMO energy gap of P17–F and HARB-F⁻ complexes were 3.17 and 3.20 eV respectively. Such decrease of HOMO-LUMO energy gap obviously denotes strong binding interaction between the probe and F⁻ ion. Also, the decrease of HOMO-LUMO energy gap clearly justified the red shift of absorption maxima observed in the experimental findings.

Moreover from Table 6 and Fig. 9, it was observed that the contribution of hydroxyl oxygen atoms to HOMO sharply increased from probe to probe- F^- complex (17% to 27% for P17 and 17% to 28% for HARB) denoting deprotonation of one hydroxyl group and involvement in conjugation impeding the C=N isomerisation. Thus, from frontier molecular orbital analysis, it could be stated that the strongly basic F^- ion captured acidic hydroxyl proton and restricted the C=N isomerisation as well as ICT character. Consequently, upon binding with F^- ion, the probes displayed a sharp red shift of absorption maxima. Thereafter, the addition of HSO₄⁻ facilitates the reprotonation of the probe with



Fig. 9. The HOMO-LUMO images of P17 and P17-F⁻ complex with corresponding energy values calculated using MeCN/IEFPCM solvent model.

Table 6

Energy and % of composition of different group of atoms in FMO's for P17, P17-F, HAR	В
and HARB-F ⁻ complexes in MeCN.	

Compound	Compound FMO's Energy % Composition							
		(eV)	N	Hydroxyl O	Hydroxyl H	С	Other Atoms	F
P17	LUMO	-0.15	0	3	0	95	1	-
	LUMO	-0.30	0	3	0	94	3	-
	+2 LUMO	-1.22	32	3	0	65	0	-
	+ I LUMO	-2.57	14	4	0	82	0	-
	HOMO	-6.12	3	17	0	78	2	-
	HOMO-1	-6.37	7	16	0	76	1	_
	HOMO-2	-6.61	11	2	0	85	2	-
	HOMO-3	-7.34	51	13	3	25	11	_
P17-F ⁻	LUMO	+0.45	1	7	0	86	6	0
	LUMO	+0.03	0	3	0	93	4	0
	+2 LUMO +1	-0.61	29	3	0	67	1	0
	LUMO	-196	15	5	0	79	1	0
	LOMO	5 12	0	5 27	0	61	1	0
	LIOMO 1	-J.15 5.01	0 E	16	0	64	-+ 1 E	0
		-5.91	22	25	1	20	1J 11	1
	HOMO-2	-0.00	15	55	0	20	11	0
	HUMO	-0.15	10	0	0	05	14	0
ПАКЬ	+3	-0.52	1	4	0	95	0	-
	LUMO +2	-0.32	0	4	0	96	0	-
	LUMO +1	-1.21	31	2	0	67	0	-
	LUMO	-2.55	14	4	0	82	0	_
	HOMO	-6.27	15	17	0	68	0	_
	HOMO-1	-6.65	1	23	0	76	0	_
	HOMO_2	-7.00	9	7	0	84	0	_
	HOMO_3	-7 33	65	14	3	9	9	_
HARB $-F^-$	LUMO	+0.45	1	8	0	91	0	0
		-0.13	1	4	0	95	0	0
	T2 LUMO	-0.62	27	2	0	71	0	0
	+1 11M0	1.06	15	4	0	01	0	0
	LONIO	-1.90	10	4 20	0	61	0	0
		-5.15	10	∠ð 20	0	02 12	U G	0
		-0.07	38 12	59 15	2	15	0	2
	HUIVIU-2	-6.13	13	15	0	12	U	0
	HOMO-3	-6.57	5	13	U	82	U	U

recovering the absorption band of the pure probe. Based on the experimental observations and computational results, we could propose the following mechanism (Scheme 2). Here, actually, the switching of the probes from neutral to deprotonated forms was monitored by fluoride and bisulphate ions and resulting corresponding sensing phenomenon.

4. Conclusions

In summary, we report a green-chemical method for the synthesis of hydrazine functionalised Schiff base chemosensors (P17, HARB). Both the structurally simple, easily synthesizable and cost-effective chemosensors consecutively detected F⁻ followed by HSO₄⁻ ions with excellent selectivity over various individuals and a mixture of anions in MeCN medium. The chemosensors display a visible absorption profile with pronounced changes of colour from colorless to reddish-yellow at room temperature. Spectrofluorimetry study suggests that HARB exhibits turn-on fluorescence properties in presence of TBAF perhaps P17 remains fluorescent silent in the presence and absence of TBAB. Most amusingly, the TBAF treated chemosensors displayed a reversible response in presence of TBAB. Extensive DFT calculations and ¹H NMR spectral analysis established the mechanistic aspects of sensing and suggest that the changes in absorption spectra were driven by the hydrogen bonding between the OH and fluoride anions. The hydroxyl proton captured by F⁻ restricts the C=N isomerisation as well as ICT character for both P17 and HARB, and confirm the cascade sensing mechanism for fluoride and bisulphate ions. This strategy for the design of the molecules employing a green-chemical synthetic approach may provide a simple way to develop more efficient dual-channel anion chemosensors.

Declaration of Competing Interest

- All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
- This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.
- The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript
- The following authors have affiliations with organizations with direct or indirect financial interest in the subject matter discussed in the manuscript:



Scheme 2. Proposed binding mechanism of P17 with fluoride and subsequently bisulphate ions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq.2021.115293. Supplementary crystallographic data are available free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) upon request, quoting deposition number CCDC 1957032 for HARB and 2040547 for P17.

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