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ARTICLE

Auto-reusable receptors for selective colorimetric recognition of fluoride

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Two new aliphatic oximes featuring additional pyridyl functionality are reported as highly selective colorimetric receptors for fluoride ion recognition. H-bonding mediated binding of fluoride ion to both the receptors are reasonably labile and the fluoride free receptor species are automatically regenerated after a short interval. This allows reuse of both the receptors for colorimetric fluoride recognition upto three cycles without any need for reactivation.

Introduction

Selective recognition of fluoride ion is widely recognized as a topical area of research on account of the vital roles fluoride plays in several important biological and chemical processes.[1] In this context, H-bonding mediated colorimetric recognition of fluoride ion has emerged as one of the most prolific approach for recognition of fluoride ion.[2-12] Fluoride ion can act as an efficient hydrogen bond acceptor and thus induce a partial charge transfer or complete deprotonation in receptor molecule. Consequently, a plethora of fluoride ion receptors based on different hydrogen bond recognition motifs such as thiourea, urea, amide, sulfonamide, imidazoliums/imidazole, indole, pyrrole and Schiff base have been devised.[2-12] However, most of the reported colorimetric fluoride ion receptors show irreversible colour change upon fluoride addition and it limits their application.[13] Nevertheless, a handful of reusable colorimetric fluoride ion sensors have been reported so far.[14] All these receptors are reusable only after addition of an acid which regenerates the initial active host from the host-guest complex.

Tuning the complementarity of interacting sites, size and shape between the receptor and the guest is one of the established routes to enhance selectivity towards fluoride recognition.[15] Proper choice of the acidity of the hydrogen bond donor sites allow designing H-bonding receptors capable of binding fluoride ion even in aqueous environment.[16] Highly acidic H-bonding sites within receptor molecules bind fluoride ion strongly and the resulting species are stable enough that an irreversible colour change of the sample is observed. However, if the H-bonding sites are poorly acidic, the resulting host-guest complex is expected to be labile. Water present in the medium can hydrate fluoride ion from such labile host-guest complex and thus regenerate the free receptor. It is anticipated that the presence of suitable H-bonding acceptor sites within the receptor should facilitate this process. Based on this principle, it should be possible to devise auto-reusable fluoride ion receptors by suitably tuning the acidity of the H-bonding sites within the receptor molecule.

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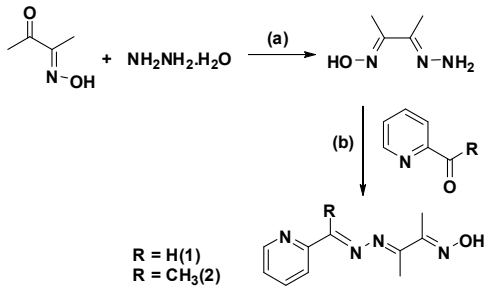
Results and discussion

Synthesis and characterization

The hydroxyl proton in oxime functionality is significantly acidic as compared to water and therefore oxime group can compete with water to bind fluoride ion even in aqueous medium.[17] Indeed a few oxime based fluoride ion receptors are reported recently and they bind fluoride ion selectively even in dimethylsulphoxide (DMSO)-H_2O medium.[18-19] It was anticipated that moderately acidic oxime functionality, when present along with other H-bond acceptor sites may lead to reversible fluoride binding. Both fluoride and the H-boding acceptor site within the receptor will possibly compete to form H-bonding with the oxime H-atom. Therefore, the host-guest complex formed by the fluoride ion with such receptor is expected to be labile. Based on this principle, two new receptors, **1** and **2** were synthesized by a two-step reaction scheme from 2,3-butanedionemonoxime (Scheme 1).



Scheme 1: Synthesis of **1** & **2**: (a) CH_3OH, RT, 2h (b) CH_3CH_2OH, reflux, overnight.

Both the compounds were characterized by using standard spectroscopic techniques such as IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis. All efforts to obtain X-ray quality single crystals of compound **1** and **2** failed and this prevented structure elucidation by single crystal X-ray diffraction. IR spectrum of compound **1** and **2** shows sharp and intense peaks appear at ~1615 and ~1596 cm^{-1} due C-N stretching vibration of the two imine C=N groups. A weak signal at ~1570 cm^{-1} can be attributed to C=N stretching vibration of oxime functionality. The N-O stretching vibration of the oxime group is observed as a moderately intense peak centered at ~1358 cm^{-1}. In both the receptors, the recognition unit is connected to a pyridyl ring via a conjugated aliphatic spacer containing imine moiety. ^{1}H NMR spectrum of **1** and **2** in DMSO-d_6 show sharp singlets at 11.95 and 11.71 ppm respectively and these signals can be readily assigned to the oxime N-OH proton. The large down field shift of the oxime proton clearly reveals the highly acidic nature of the oxime proton in **1** and **2**. Signals for all other protons in **1** and **2** appear in expected regions and conform well to the given formulation of the compounds.

Anion binding studies

The interaction of compound **1** and **2** with different anions was investigated by using UV-visible spectroscopy in DMSO medium by addition of standard solution of tetrabutylammonium (TBA) salts of various anions (F^-, Cl^-, Br^-, I^-, CN^-, CH_3COO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-). Optical inspection of solution of compound **1** and **2** in DMSO before and after addition of 50 equivalents TBAF showed dramatic changes in colour from colourless to yellow (Figure 1). The change could be easily detected by naked eye. The intensity of colour gradually increases with increase in anion concentration. It is pertinent to note here that no colour change is observed upon addition of TBA salt of other anions under investigation (e.g. Cl^-, Br^-, I^-, CN^-, AcO^-, HSO_4^-, $H_2PO_4^-$, and ClO_4^-).

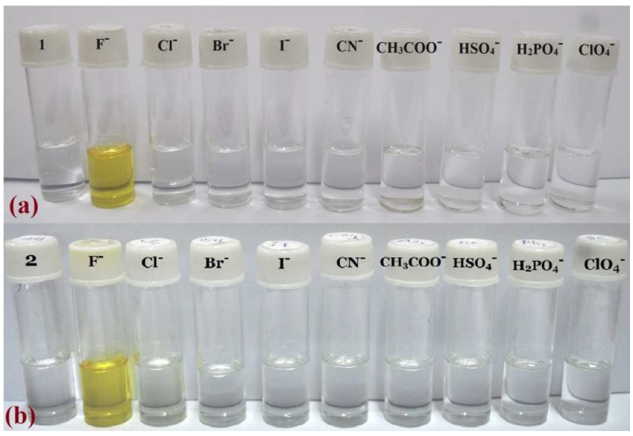


Figure 1: Naked eye view of the colour change after addition of 50 equiv. different anions as their tetrabutyl ammonium salts to 20 μM solution of **1** (a) and **2** (b) in DMSO.

To investigate the modification in electronic structure and selectivity of anion binding, the changes in UV-visible spectrum of the receptors **1** and **2** were recorded in DMSO (20 μM solution), after addition of 50 equivalents of various anions as TBA salts. UV-visible studies clearly reveals that the interaction of compound **1** and **2** with fluoride ion is highly selective as no significant deviation of the UV-visible spectrum is observed upon addition of TBA salt of all other anions (Cl^-, Br^-, I^-, CN^-, AcO^-, HSO_4^-, $H_2PO_4^-$, and ClO_4^-). In case of F^- ion, electronic spectrum of both **1** and **2** show the emergence of a new peak with absorption maxima at ~410 nm (Figure 2). This can be attributed to the change in colour of their solutions upon addition of TBAF, which trigger variation of the electronic environment in **1** and **2**. The bar diagram depicted in Figure 2 unambiguously establish that the intensity of the newly emerged peak is maximum in case of fluoride and negligible for all other anions investigated.

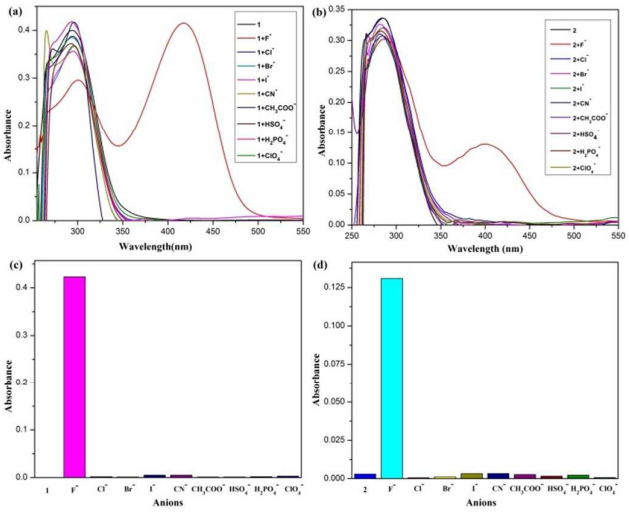


Figure 2: UV-visible absorption spectra of the receptors in dry DMSO (20 μM) after addition of 50 equiv. of different anions in the form of TBA salts: (a) for **1** and (b) for **2**. Intensity of the new peak with λ_{max} ~ 410 nm after addition of 10 equiv. of different anions in the form of TBA salts. (c) for **1** and (d) for **2**.

The most remarkable observation made during anion binding studies was that the solutions of both **1** and **2** containing fluoride ion became colourless after ~45 and ~20 minutes of TBAF addition respectively. UV-visible measurements carried after definite intervals show that the absorbance of the newly generated peak with λ_{max}≈ 410 nm decreases while the same for the peak characteristic of the free receptor with λ_{max} ≈ 300 nm increases with time (Figure 3). Thus, a short duration later the addition of TBAF, the UV-visible spectrum of both the compounds becomes essentially identical to the spectra of free receptors. This reveals the labile nature of the interaction between receptors **1** and **2** with fluoride ion in DMSO medium.

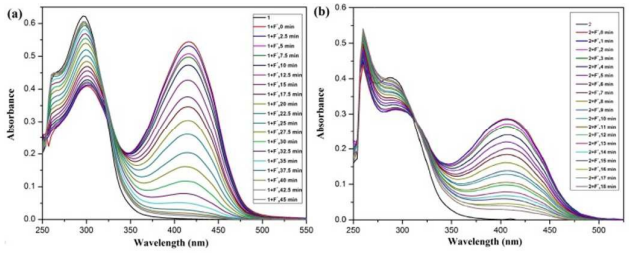


Figure 3: Evolution of UV-visible absorption spectra of the receptors with time in DMSO (30 μM) after addition of 50 equiv. of TBAF salts (a) for **1** and (b) for **2**.

Interestingly, upon addition of TBAF to a decolourized solution of either **1** or **2**, reappearance of yellow colour is observed with naked eyes. Moreover electronic transition with $\lambda_{max} \approx$ 410 nm associated to fluoride binding is also observed. However, the intensity of the colour change and absorbance of the newly generated peak with $\lambda_{max} \approx$ 410 nm associated with TBAF addition decreases during successive cycles and no appreciable change is observed after the third cycle (Figure 4). Thus, both the receptors are reusable in recognizing fluoride ion and can be used up to three cycles for naked eye detection of fluoride (Figure 4). It is pertinent to note here that in case of both **1** and **2**, the active receptor species are automatically regenerated from the host-guest complexes without application of any external stimuli.

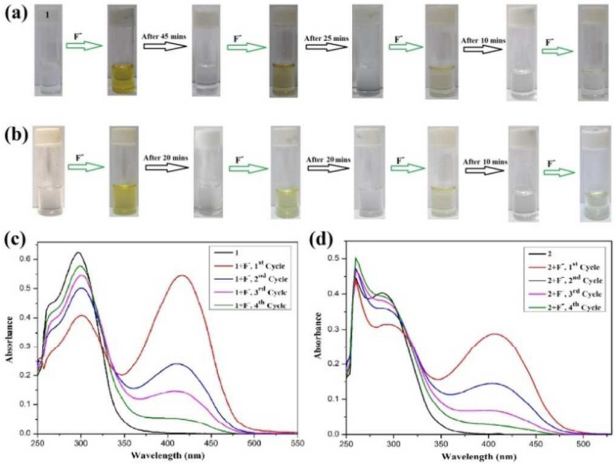


Figure 4: Appearance and disappearance of colour upon addition of 50 equivalents TBAF to solutions of receptors in DMSO (30 μM): (a) for **1** and (b) for **2**. Evolution of UV-visible spectrum of receptors immediately after each cycle of TBAF addition: (c) for **1** and (d) for **2**.

For both the receptors **1** and **2**, plot of $\ln(A_t/A_0)$ against time up to three consecutive cycles are depicted in Figure 5, where A_t is the absorbance after time t and A_0 is the absorbance immediately after addition of TBAF to the respective receptors. In all cases, plot of $\ln(A_t/A_0)$ against time result straight lines with negligible intercept and this establish that the dissociation of the receptor-fluoride complex is a first order process. The rate constants of the dissociation processes were derived for each cycle from slope of the respective plot by using first order rate equation. The values of rate constants increase for successive cycles and indicate enhanced lability of the host-guest complex in the new medium.

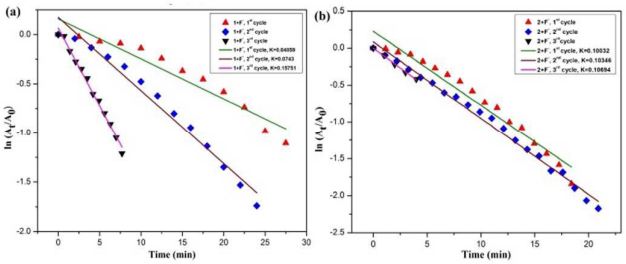


Figure 5: Plot of $ln(A_t/A_0)$ against time of for three consecutive cycles of TBAF addition to receptors: (a) for **1** and (b) for **2**. The solid lines represent best linear fit with good linear correlation ($R^2 > 0.91$).

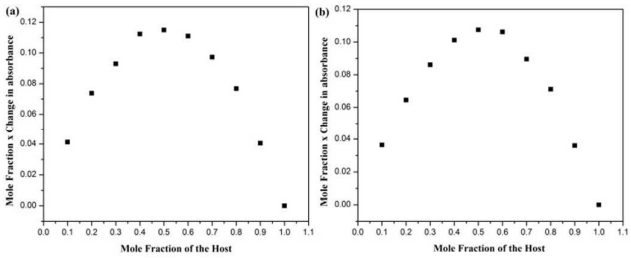


Figure 6: Jobs plot of **1** (a) and **2** (b) against TBAF in DMSO.

In order to elucidate the nature of interaction between the receptors and fluoride ion in DMSO medium, the optimal stoichiometry of interaction was determined by Job plot analysis (Figure 6). Both **1** and **2** showed that host-guest complexes with optimal molar ratio 1:1 are formed in DMSO medium. The mechanism of interaction was further studied with the help of ^{1}H NMR spectroscopy titration in DMSO-d_6. Addition of 0.2 equivalents TBAF displays complete disappearance of the O-H signal in both cases (Figure 7). However, the position of all other protons associated with **1** and **2** are observed at their original positions without any variation of chemical shift. Both of the above two observations point toward highly labile nature of interaction present between the receptors and fluoride ion. Moreover, the exchange rates are faster than NMR timescale and this leads to complete disappearance of oxime proton even when a small amount of TBAF is present. Interestingly, after decolourization of a mixture containing compound **1** and TBAF, the oxime proton reappears at its original position as a broad signal. Thus, NMR studies also support auto-regeneration of the active receptor species after a short time span.

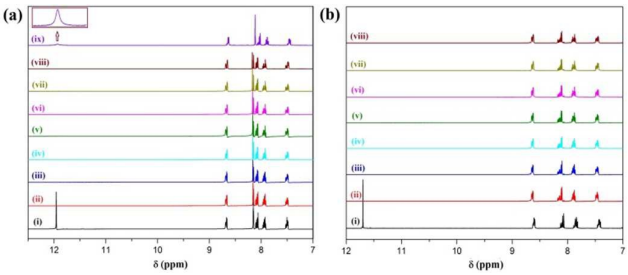


Figure 7: Selected portions of ^{1}H NMR indicating changes in ^{1}H NMR of **1** and **2** upon gradual addition of TBAF in DMSO-d_6: (a) 1 and (b) for 2; (i) host (ii) host + 0.2 equiv. TBAF (iii) host + 0.4 equiv. TBAF (iv) host + 0.6 equiv. TBAF (v) host + 0.8 equiv. TBAF (vi) host + 1.0 equiv. TBAF (vii) host + 1.5 equiv. TBAF (viii) host + 2.0 TBAF (ix) host + 5 equiv. TBAF after decolourization.

Theoretical calculations

The binding of fluoride ion with both **1** and **2** were further investigated by quantum chemical calculations using the density functional method (DFT). DFT studies have been earlier employed to successfully predict the ground state structures of different receptor-halide complexes.[20] The geometry optimized structures of **1**, **1.F**$^-$, **2** and **2.F**$^-$ are depicted in Figure 8 along with the pictorial HOMO-LUMO diagrams. The lowest energy conformations predicted for both the free receptors lack any noteworthy intramolecular H-bonding interactions. The calculated O-H bond distances of the oxime moiety in the

free receptors **1** and **2** measure 0.973 and 0.964 Å respectively. Within the host-guest complexes, **1.F**$^-$ and **2.F**$^-$ the O-H···F distances measure 2.467 Å and 2.461 Å while the O-H···F bond angles are 176.33° and 176.42° respectively. These calculated structural parameters are in good agreement with experimental parameters observed in oxime-fluoride species reported earlier.[18] Thus, the host-guest complexes, **1.F**$^-$ and **2.F**$^-$ are formed by moderately strong O-H···F hydrogen bonding interactions between the oxime functionality of receptor and fluoride ion. Moreover, the computed interaction energy between the receptors and fluoride ion are found to be -224 kJ/mol and -202 kJ/mol for **1** and **2** respectively. The absorption spectra of the receptors and their fluoride complexes were calculated using time dependent DFT (TD-DFT) method at B3LYP/6-311+G* level using DMSO as the solvent. For both the receptors **1** and **2**, the computed transition energies of the most intense peaks (309 nm and 285 nm) agree well with the observed value (300 nm and 290 nm respectively). TD-DFT studies predict that upon complexation with fluoride new intense electronic transitions are generated at 406 and 380 nm for **1** and **2** respectively. Both the computed values are in good agreement with the observed spectral changes (416 and 407 nm for **1** and **2** respectively).

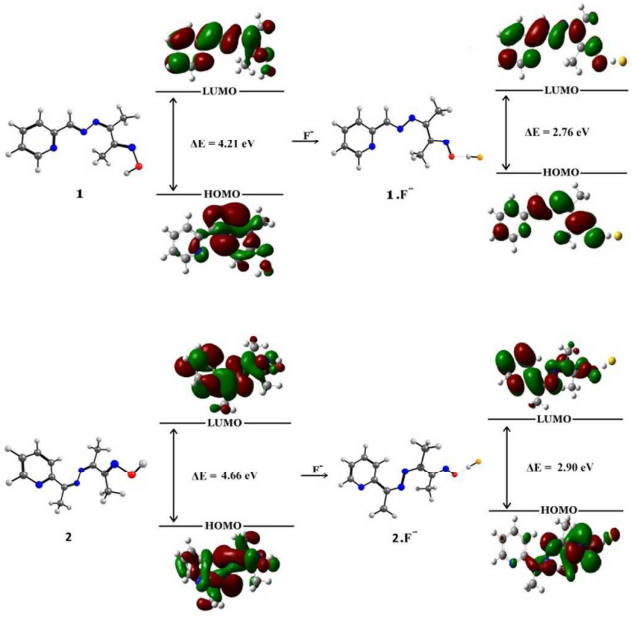
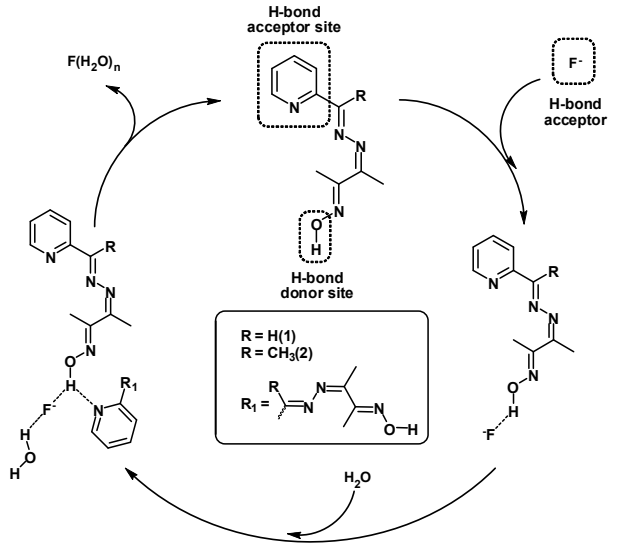


Figure 8: Optimized geometry of **1**, **1.F**$^-$, **2** and **2.F**$^-$ along with pictorial HUMO-LUMO diagrams.

Mechanism of fluoride binding

Experimental and theoretical results presented here establish the thermodynamically strong but kinetically labile nature of interaction between the receptors **1** & **2** with fluoride ion. The moderately strong acidic nature of the oxime proton can be accounted for the strong nature of interaction between the receptors and fluoride. However, to form H-bonded host-guest complex, fluoride ion has to compete with H-bond acceptor pyridine moiety present within the receptor. The labile nature of host-guest interaction is further enhanced by hydration of fluoride ion by water present within the medium due to the hydrophilic nature of the solvent used. It is pertinent to note here that the experimental binding energy for a 1:1 water-fluoride ion complex is -97 kJ/mol.[21-22] The water tolerance levels of both the receptors were determined by monitoring the variation in the absorbance of the λ_{max} ≈ 400 nm peak (Section S4) on addition of calculated amount of H_2O. Colorimetric studies reveal that the water tolerance limit for **1** and **2** are 900 and 450 equivalents water respectively against every equivalent of fluoride present. If water is present above this limit, the binding between the receptors and fluoride is not strong enough to observe any appreciable change in the UV-visible spectrum.

The pKa of oxime protons in DMSO are estimated from the chemical shift (δ_{OH}) of the associated proton by using an established relationship, pKa = 29.10-1.63δ_{OH}.[23] The estimated pKa values of the oxime protons in **1** and **2** are 9.62 and 10.01 respectively. The higher acidity of the oxime proton in **1**, as evident from the smaller pKa value leads to much stronger binding with fluoride ion in this case. Therefore, the water tolerance limit as well as the time required for decolorization of **1** is relatively higher as compared to those observed for **2**. Due to the interplay of two concomitant competitions favouring dissociation, the receptor-fluoride complexes formed by **1** and **2** are significantly labile. This eventually leads to automatic regeneration of the active free receptor species within a short time span (Scheme 2). Thus, the labile receptor-fluoride interactions allow repetitive fluoride detection by using **1** & **2** and in both the cases the associated colorimetric change is observed up to three consecutive cycles. However, the polarity of the medium varies after each successive addition of TBAF and this can be possibly attributed to the lack of any colour change upon TBAF addition after the third cycle.



Scheme 2: Proposed scheme for auto-regeneration of active receptor species from receptor-fluoride complexes.

Conclusions

The present approach to auto-reusable receptors for selective recognition of fluoride relies on incorporation of both H-bond donor and acceptor sites within the receptor. Although the two auto-reusable receptors **1** and **2** can selectively recognize fluoride ion in polar medium *viz.* DMSO, recognition in aqueous medium is not yet possible. However, proper tuning of the acidity/basicity of the H-bonding sites within the receptor may eventually lead to reusable receptors for selective recognition of fluoride even in aqueous medium. Efforts to devise oxime based chromogenic fluoride sensors with enhanced reusability and efficiency are currently underway in our laboratory.

Experimental section

Materials and methods

Melting points were recorded on a JSCW melting point apparatus. Elemental analysis was done by using Perkin Elmer PR 2400 series analyser. Infrared spectra were recorded with a Nicolet Impact I-410 FT-IR spectrometer as KBr diluted discs. The ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a 'JEOL' NMR spectrophotometer in DMSO-d_6 at room temperature. In NMR spectra, chemical shifts are reported in parts per million downfield of Me_4Si (TMS) as internal standard. UV-visible data were recorded with a Shimadzu UV2450 spectrophotometer and a Thermo Scientific Multiskan GO spectrophotometer. ^{1}H NMR spectroscopy based titration studies were carried out on a 600 MHz Bruker Avance III NMR spectrometer in DMSO-d_6. All TBA salts for NMR and UV-visible studies were purchased from Sigma-Aldrich® and used as such. All anions were used in the form of their TBA salts (fluoride as its trihydrate). The receptor solutions were titrated by adding known quantities of concentrated solution of the anions in question. The anion solutions used to effect the titrations contained the receptor at the same concentration as the receptor solutions into which they were being titrated so as to nullify the dilution effect. Rate constants of the decolourization processes were determined by using first order kinetic equation written as

$dC_t/dt = -kC_t$ or $In(C_t/C_0) = -kt$ or $In\ (A_t/A_0) = -kt$

where C_t is the concentration of the receptor fluoride complex at time 't' and k is the rate constant which can be derived from the decrease in absorbance at λ_{max} ~ 410 with time.

Computational methods

All quantum chemical calculations were performed by using Gaussian 03 software package.[24] The ground state geometry of **1**, **2**, **1.F**$^-$ and **2.F**$^-$ were optimized using the hybrid DFT functional B3LYP and 6-311+G* basis set.[25-26] The energies of the free receptors, corresponding 1:1 host-guest complexes and free fluoride ion were determined from the B3LYP/6-311+G* optimized geometries without any zero-point energy correction. The interaction energy (ΔE_{int}) of the host guest complexes were computed by using the following equation as the difference between the energy of the complex ($E_{[H\text{-}F^-]}$) and the total energy of the free receptor (E_H) and fluoride ion (E_F)[27]

$$\Delta E_{int} = (E_{[H\text{-}F^-]}) - (E_H + E_F^-)$$

Excited state calculation were performed within the time-dependent (TD-DFT) framework[28] at the B3LYP/6-311+G* level using DMSO as the solvent by the self-consistent reaction field (SCRF) method[29] and using the conductor polarized continuum model (cpcm).[30]

Synthesis of 1: 2-pyridinecarboxaldehyde (0.107g, 1 mmol, 100 µL) was taken in a 100 mL round bottom flask and added 40 mL of C_2H_5OH. Then 3-hydrazono-butan-2-one oxime (0.121 g, 1 mmol) was added to the above solution and refluxed overnight with constant stirring. The resultant solution was concentrated to 10 mL by using rotary evaporator. To this concentrated solution distilled water was added and a white crystalline solid precipitated out. The product was filtered, washed with water, dried in air and collected.

Yield: 88%; m.p.: 164-170 °C. FT-IR (KBr, cm^{-1}): ü = 3394(br), 3256(w), 3161(br), 3027(m), 2930(m), 2858(br), 3278(w), 2281(w), 1685(s), 1616(s), 1570(w), 1475(m), 1437(w), 1358(s), 1298(m), 1202(m), 1145(w), 1113(w), 1039(w), 992(s), 932(m), 880(w), 829(w), 778(s), 701(s), 624(w), 536(br), 455(w), 413(m); ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 11.95 (s, 1H), 8.67-8.62 (m, 1H), 8.12 (s, 1H), 8.07-8.01 (m, 1H), 7.93-7.86 (m, 1H), 7.49-7.43 (m, 1H), 2.19 (s, 1H), 2.11 (s, 3H), 2.00 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 162.23, 156.15, 155.14, 153.13, 150.31, 137.57, 125.73, 121.75, 13.33, 8.91. Elemental analysis % calculated for $C_{10}H_{12}N_4O$: C = 58.70, H = 5.91, N = 27.54; Found: C = 60.07, H = 5.67, N = 27.86; UV-visible: (λ_{max}, nm): 300.

Synthesis of 2: 2-acetyl pyridine (280µL, 2.5 mmol) was taken in a 250 mL round bottom flask and added 50 mL of C_2H_5OH. On the above solution, 3-hydrazono-butan-2-one oxime (0.287 g, 2.5 mmol) was added and refluxed overnight with continuous stirring. The resultant solution was concentrated by using rotary evaporator and added distilled water to the concentrated solution. Precipitate comes out and then filtered it, dried in air.

Yield: 85%; m.p.: 134.7 °C. FT-IR (KBr, cm^{-1}): ü = 3850(w), 3805(w), 3752(m), 3689(w), 3629(m), 3181(br), 3061(br), 2919(w), 2871(w), 1993(w), 1570(s), 1473(s), 1432(m), 1357(s), 1308(m), 1245(s), 1110(s), 1007(w), 779(s), 736(m), 682(br), 627(m), 564(s) ; ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) : 11.71 (s, 1H), 8.60-8.59 (d, ^{3}J = 8 Hz, 1H), 8.08-8.06 (m, 1H), 7.86-7.83 (m, 1H), 7.43-7.41 (m, 1H), 2.18 (s, 3H), 2.04 (s, 3H), 1.94 (s, 3H) ; ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 157.52, 156.97, 155.28, 152.51, 149.04, 138.88, 125.92, 121.11, 12.32, 11.77, 8.93 ; Elemental analysis % calculated for $C_{11}H_{14}N_4O$: C = 60.51, H = 6.46, N = 25.58; Found: C = 60.89, H = 6.15, N = 26.08; UV-vis: (λ_{max}, nm): 290.

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Graphical Abstract
For

Auto-reusable receptors for selective colorimetric recognition of fluoride

Two auto-reusable colorimetric receptors for selective recognition of fluoride in polar medium are reported.