Sulfonamide-imines as selective fluorescent chemosensors for the fluoride anion†

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Two new sulfonamide-type fluorescent chemosensors in organic media are reported. The two receptors, [*N*,*N*′-bis(2-tosylaminobenzylidene)-1,2-diaminoethane and *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-diamino-2-propanol], display marked changes in the fluorescence emission intensities as a result of deprotonation by basic anions, and show high selectivity for fluoride over other inorganic anions, such as acetate or dihydrogenphosphate. These results suggest that the presence of the imine group as an intramolecular H-bond acceptor enhances the selectivity of these sensors compared to previous examples in the literature. The deprotonation mechanism has been demonstrated by spectrophotometric and spectrofluorimetric titrations as well as by NMR spectroscopy. The X-ray structures of both receptors are also discussed.

Introduction

The importance of inorganic anionic analytes in numerous biological and chemical processes has stimulated the search for improved molecular recognition and sensing of these species.[1] The monitoring of fluoride anions is of particular interest due to their fundamental role in dental care and in osteoporosis treatment, as well as their significant contribution to environmental pollution.[2] Although a number of sensors for fluoride anions have been reported,[3] there is still a need for simple and easily accessible receptors with improved optical response and specificity.

Most of the fluoride chemosensors described in the literature are neutral H-bond donor receptors based on N–H proton transfer from the donor unit to the acceptor component.[4] These systems include ureas,[5] thioureas,[6] amides,[7] sulfonamides[8] and pyrroles,[9] with the fluoride acting as an acceptor. The more acidic the donor, the stronger the receptor-anion interaction and, in a limiting situation, exceptionally acidic donor moieties may suffer deprotonation on interaction with strongly basic anionic species.[10] For fluoride ions the deprotonation process is also favoured due to the formation of the particularly stable HF_2^- dimer.[11] However, highly basic inorganic anions such as $CH_3CO_2^-$ or $H_2PO_4^-$ can also promote the deprotonation of N–H receptors,[10,12] making these two anions the most significant complication for the construction of specific receptors for the fluoride ion.[13]

Herein we describe two new examples of sulfonamide-based fluorescent chemosensors (Scheme 1, $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$) that are capable of detecting fluoride anions in CH_3CN solution. These compounds show high sensitivity and, at the same time, display exceptional selectivity without interference from acetate or phosphate.

Experimental section

General information

Chemicals and solvents of the highest commercial grade available were used without further purification. FAB mass spectra were recorded on a Micromass Autospec spectrometer, employing *m*-nitrobenzyl alcohol as the matrix. Elemental analyses were performed on a Carlo Erba EA 1108 analyzer. NMR spectra were recorded on a Bruker DPX-250 using CD_3CN as solvent. UV/Vis spectra were recorded on HP 8452A or on Jasco V-630 spectrometers. Fluorescence emission spectra were recorded on a Jobin-Ivon Fluoromax-3 spectrometer. Titrations were performed on 1 or 2 mL samples of solutions of the receptors (10 or 40 μM) in CH_3CN, by addition of CH_3CN stock solutions of the appropriate anion in the form of tetrabutylammonium salts.

The structure determination of $\mathbf{H_3L^b}$ was performed at low temperature with a Bruker Appex II CCD diffractometer, using graphite-monochromated Mo-Kα radiation from a fine focus sealed tube source. Intensities were corrected for absorption (SADABS). The structures were successfully solved by direct methods (SIR97),[14] which gave the positions of most of the non-hydrogen atoms. The remaining atoms were identified by successive Fourier difference synthesis. Refinements were carried out on F2 by full-matrix least-squares techniques using SHELXL-97.[15] The positions of all H atoms were calculated geometrically and a riding model was used in their refinement except for those H

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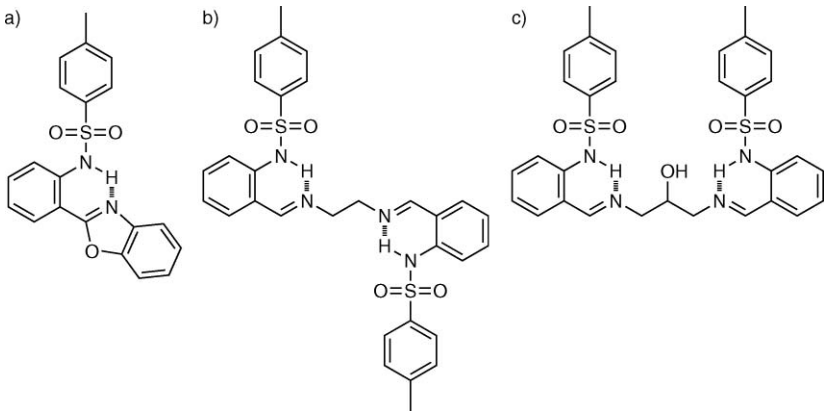
† Electronic supplementary information (ESI) available: Crystallographic data for $\mathbf{H_3L^b}$, selected bond distances and angles for $\mathbf{H_3L^b}$, ^{1}H NMR titrations of $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ with fluoride ions and spectrophotometric and spectrofluorimetric titrations of $\mathbf{H_2L^a}$ with OH^-, acetate and dihydrogenphosphate ions and of $\mathbf{H_3L^b}$ with OH^-, fluoride, acetate and dihydrogenphosphate ions. CCDC reference number 746892. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b916040j



Scheme 1 a) TABO;[13] b) $\mathbf{H_2L^a}$; c) $\mathbf{H_3L^b}$

atoms involved in the intramolecular and intermolecular hydrogen bonds, which were found in a difference electron-density map and then refined with their coordinates riding on the corresponding carrier heteroatom.

Synthesis

2-Tosylaminobenzyl alcohol (I). Triethylamine (1.7 mL, 12.2 mmol) was added to a solution of 2-aminobenzyl alcohol (1.5 g, 12.2 mmol) in CH_2Cl_2 (100 mL). The mixture was heated at 30 °C and tosyl chloride (2.5 g, 13.1 mmol) was added to the mixture after the alcohol had completely dissolved. The reaction mixture was heated under reflux for 8 h. The resulting red solution was filtered through Celite and washed with aqueous HCl (pH = 4; 3 × 100 mL). The combined organic fractions were dried over Na_2SO_4 and partially concentrated under reduced pressure at 25 °C. The product was precipitated with Et_2O. The resulting pale yellow solid was recrystallized from CH_2Cl_2. Yield: 75%. Mass spectrometry (ESI): $m/z = 278.1$ $[I + H]^+$.[16]

2-Tosylaminobenzaldehyde (II). γ-MnO_2 (0.552 g, 6.3 mmol) was added to a solution of 2-tosylaminobenzyl alcohol (0.440 g, 1.6 mmol) in dry CH_2Cl_2 (50 mL) under argon. The suspension was stirred at r.t. for 15 h and then filtered through Celite. The filtrate was partially concentrated on a rotatory evaporator at 25 °C and the product was precipitated with Et_2O. The resulting pale yellow solid was recrystallized from CH_2Cl_2. Yield: 78%. Mass spectrometry (ESI): $m/z = 276.1$ $[II + H]^+$.[16,17a]

***N*,*N*′-Bis(2-tosylaminobenzylidene)-1,2-diaminoethane ($\mathbf{H_2L^a}$).** 1,2-Diaminoethane (0.030 mL, 0.45 mmol) was added to a solution of tosylaminobenzaldehyde (0.25 g, 0.91 mmol) in chloroform (25 mL). The mixture was heated under reflux and the volume of the solution was reduced to about 5 mL over a period of 4 h in a Dean–Stark trap. The resulting bright yellow solution was filtered through a thin Celite bed and concentrated under reduced pressure at 40 °C. The product was precipitated with methanol as a bright yellow solid and this was collected by filtration, washed with Et_2O and dried *in vacuo*. Yield: 95%. Anal. Found: C, 62.65; H, 5.14; N, 9.59; S, 10.38; Calc. for $C_{30}H_{30}N_4O_5S_2$: C, 62.72; H, 5.05; N, 9.75; S, 10.76. Found: Mass spectrometry (FAB): m/z = 575.3 $[\mathbf{H_2L^1} + H]^+$. ^{1}H NMR data (see ESI†). λ_{max} (ε, CH_3CN) = 220 (35984 M^{-1} cm^{-1}), 264 (10350), 316 (2986) nm.[17b,18]

Results and discussion

N,*N*′-Bis(2-tosylaminobenzylidene)-1,2-diaminoethane ($\mathbf{H_2L^a}$, Scheme 1) was prepared by a modification of a previously reported method.[16] The first step involved the *N*-tosylation of 2-aminobenzyl alcohol with tosyl chloride in CH_2Cl_2 in the presence of NEt_3 to give tosylamidobenzyl alcohol (I).[16] Subsequent oxidation of the OH group in I with γ-MnO_2 afforded 2-tosylaminobenzaldehyde (II).[16,17a] The final step involved the condensation between aldehyde II and 1,2-diaminoethane in chloroform.[17b,18] Likewise, *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-diamino-2-propanol ($\mathbf{H_3L^b}$ Scheme 1) was synthesized following a reported procedure.[16]

The acidity and poor hydrogen-bonding donor ability of the sulfonamide group made it easy to deprotonate with basic acceptors. In the TABO chemosensor recently reported by Peng's group (Scheme 1),[13] the acidity is enhanced by a strong intramolecular H-bond between the N–H fragment of the sulfonamide group and the nitrogen atom of the adjacent benzimidazole moiety. This feature allows fluoride and even acetate (which is a little less basic) to deprotonate the amide group with comparable effectiveness. We envisaged that the replacement of the benzimidazole moiety of the TABO receptor by a weaker H-bond acceptor unit like the imine group (C=N) would diminish the acidity of the N–H donor fragment of the sulfonamide moiety, resulting in increased selectivity between fluoride and acetate ions.

X-ray studies

Yellow crystals of $\mathbf{H_2L^a}$ were formed by slow evaporation at room temperature of a solution of the receptor in chloroform.[17b] $\mathbf{H_2L^a}$ exhibits two strong intramolecular H-bonding N(amide)–H···N(imine) interactions, one on each of the 2-tosylaminobenzylidene moieties (Fig. 1). The distances between these N atoms are 2.705(3) and 2.681(3) Å for N1···N2 and N3···N4, respectively (H1A···N2 = 1.84 Å and H4A···N3 = 1.80 Å). It is also worth mentioning that intermolecular H-bonds or aromatic interactions between neighboring molecules were not observed in the crystal cell.

Single crystals of $\mathbf{H_3L^b}$ suitable for X-ray diffraction studies were formed by slow evaporation of a CH_3CN solution of the receptor at room temperature. The main crystallographic data and bond distances are listed in the ESI.† There are two independent

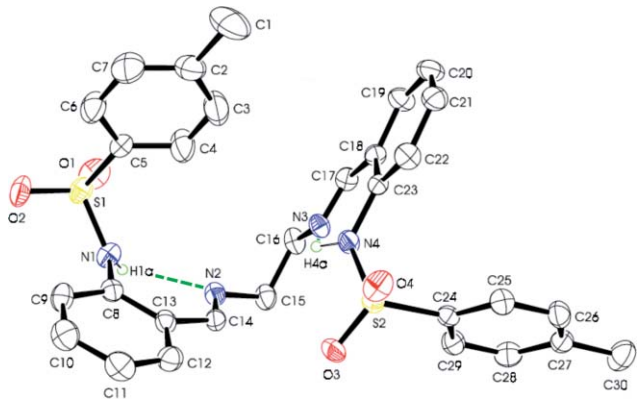


Fig. 1 ORTEP representation of the crystal structure of receptor $\mathbf{H_2L^a}$.[17b] H atoms, except for those involved in intramolecular hydrogen bonds, have been omitted for clarity. Thermal ellipsoids are at 30% of probability.

molecules with opposite chirality in the asymmetric unit of the crystal cell of $\mathbf{H_3L^b}$, giving rise to nearly identical intra- and intermolecular hydrogen-bonding interactions, and therefore we will only discuss one of them.

The structure (Fig. 2) reveals the formation of the symmetrical Schiff base, with the two tosylamide arms oriented in opposite directions in order to minimize the steric repulsions.

The arrangement of the two 2-tosylaminobenzylidene moieties of $\mathbf{H_3L^b}$ is also highly conditioned by two strong intramolecular N(amide)–H···N(imine) H-bonds. Moreover, there are also hydrogen-bonding interactions between adjacent molecules, which are connected through the oxygen atoms of the tosyl groups and the OH group of the aliphatic spacer (Table 1). The network of

Table 1 Structural parameter of the hydrogen-bonded interactions

Donor–H···Acceptor	Distance (Å) D–H	Distance (Å) H···A	Distance (Å) D···A	Angle (°) (D–H···A)
N(1)–H(1 N)···N(2)	0.84(3)	2.02(3)	2.661(4)	133(3)
N(4)–H(4 N)···N(3)	0.84(4)	1.92(4)	2.642(4)	144(4)
O(5)–H(5O)···O(2)[a]	0.89(3)	1.91(3)	2.686(4)	145(4)
N(5)–H(5 N)···N(6)	0.86(4)	1.90(4)	2.657(4)	146(4)
N(8)–H(8 N)···N(7)	0.85(3)	1.96(3)	2.650(5)	138(3)
O(10)–H(10O)···O(9)[b]	0.93(4)	1.79(2)	2.686(4)	163(5)

Symm Code: [a] (0.5 – x, 0.5 + y, 1.5 – z). [b] (1.5 – x, –0.5 + y, 1.5 – z).

intermolecular hydrogen bonds leads to the formation of zig-zag 1D supramolecular chains (Fig. 3) along the b-direction.

Recently, Gale *et al.* have reported the X-ray structures of some deprotonated sulfonamide receptors.[8b] Unfortunately, all the attempts to obtain single crystals of any of the two anion-sensor complexes described herein were unsuccessful.

Anion binding studies

The interaction of $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ with various anions was systematically studied by UV/Vis and fluorescence emission titrations, which were performed in CH_3CN by addition of a standard solution of the corresponding tetraalkylammonium salt of the anion to a solution of the receptor.

The absorption spectrum of $\mathbf{H_2L^a}$ in CH_3CN has three bands with maxima at 220, 264 and 316 nm. Titration of this ligand with fluoride anions resulted in a bathochromic shift of the spectra with an isosbestic point at 236 nm and the formation of a new absorption band with a maximum at 361 nm (Fig. 4).

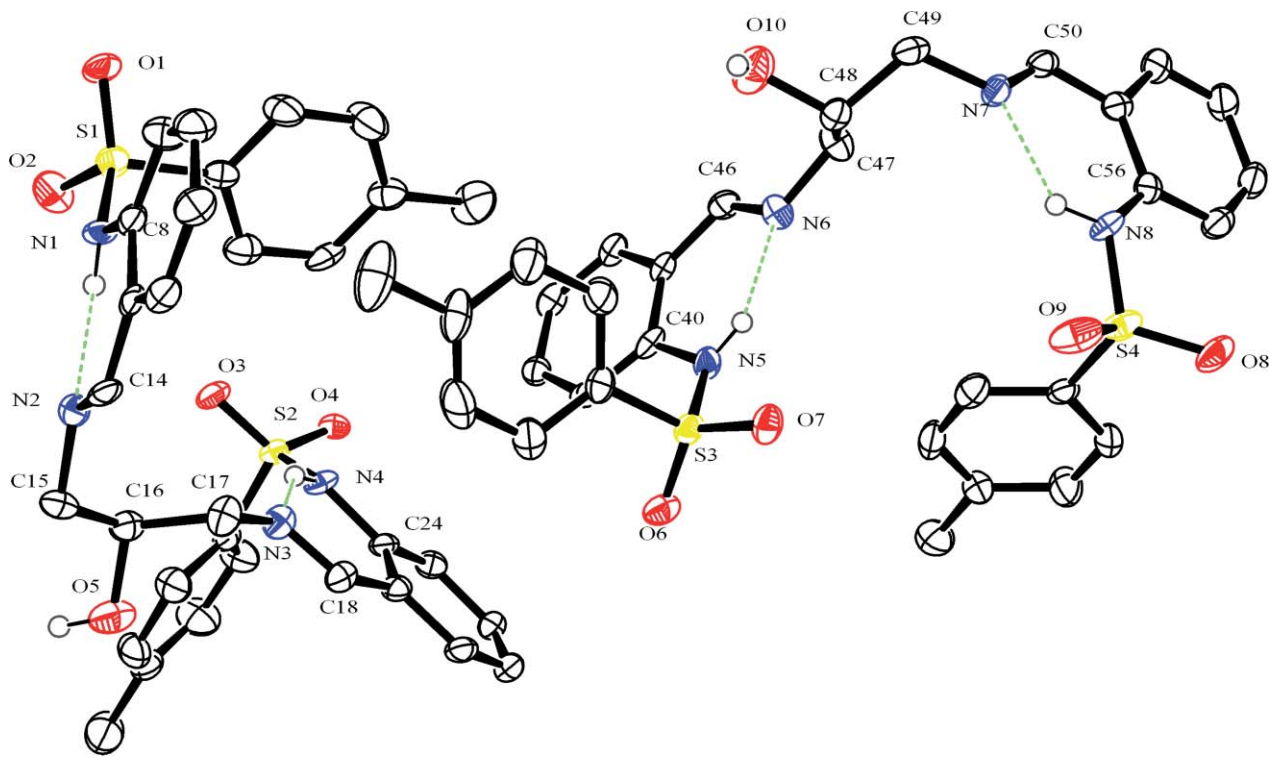


Fig. 2 ORTEP representation of the structures of the two independent molecules of the receptor $\mathbf{H_3L^b}$ founded in the asymmetric unit of the crystal cell. H atoms (except for those involved in inter or intramolecular hydrogen bonds) have been omitted for clarity. Thermal ellipsoids are at 50% of probability.

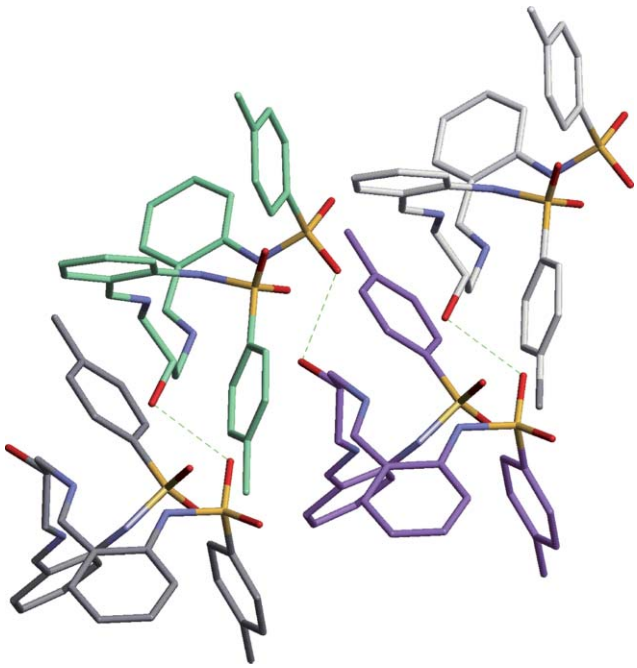


Fig. 3 Stick representation of part of the crystal cell of the receptor $\mathbf{H_3L^b}$, showing the intermolecular H bonds established between the tosyl O atoms and the OH group of the aliphatic spacer in adjacent molecules.

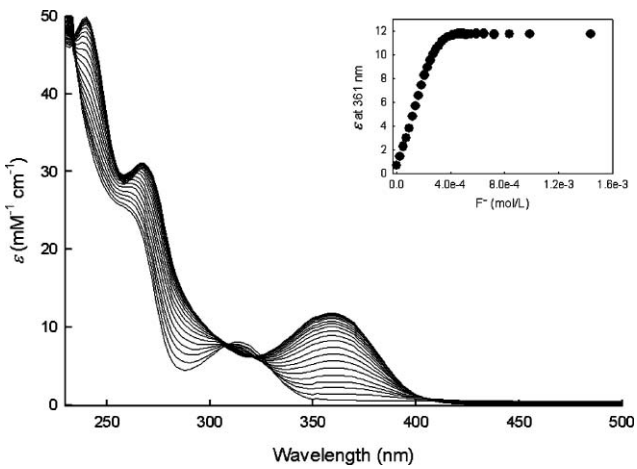


Fig. 4 Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_2L^a}$ with a standard solution of fluoride ions. Inset: absorbance at 361 nm *vs.* concentration of fluoride ions.

The new band at 361 nm matches well with the absorption band formed in the presence of tetrabutylammonium hydroxide and can be assigned to the deprotonated anion $\mathbf{(L^a)^{2-}}$. Analogous titrations were also carried out with $CH_3CO_2^-$, $H_2PO_4^-$, HSO_4^-, Cl^-, Br^-, I^- and NO_3^-. However, the receptor $\mathbf{H_2L^a}$ could only be deprotonated at very high concentrations of $CH_3CO_2^-$ and $H_2PO_4^-$. Changes in the spectra were not observed on the addition of any of the other anions.

Spectrofluorimetric titrations of $\mathbf{H_2L^a}$ with the same series of anions were also carried out in CH_3CN. $\mathbf{H_2L^a}$ shows very weak fluorescence, with an emission band centered at 510 nm (λ_{ex} = 313 nm). As expected, the addition of fluoride anions induced a significant blue shift of this band (454 nm) and the

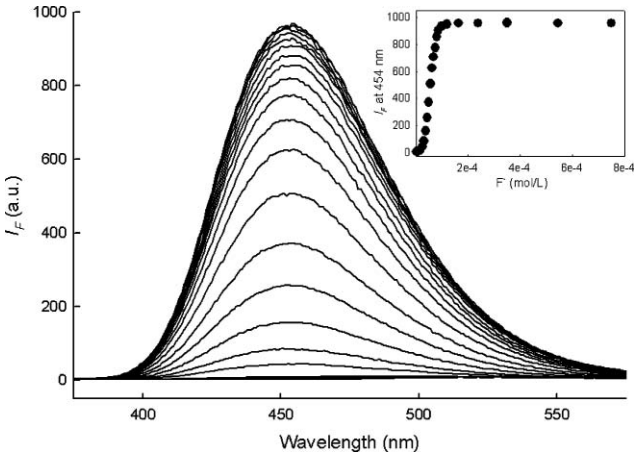


Fig. 5 Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_2L^a}$ with a standard solution of fluoride ions. Inset: fluorescence intensity at 454 nm *vs.* concentration of fluoride ions (λ_{ex} = 313 nm).

fluorescence emission increased markedly (Fig. 5).[13] This new fluorescence emission band matches well with the band formed in the presence of tetrabutylammonium hydroxide, suggesting that it can be ascribed to the deprotonated anion $\mathbf{(L^a)^{2-}}$. The fluorescence titration profile at 454 nm presents a slow increase at low concentrations of fluoride, resulting form the displacement experimented by the emission band. As with the UV titrations, we observed that $CH_3CO_2^-$ and $H_2PO_4^-$ only induced comparable signal changes at much higher concentrations than fluoride, and none of the other anions investigated (HSO_4^-, Cl^-, Br^-, I^- or NO_3^-) induced any noticeable fluorescence emission changes.

The UV/Vis and fluorescence emission titrations were repeated with the receptor $\mathbf{H_3L^b}$, which contains a 2-propanol spacer. This moiety was selected because it was found that the hydroxyl group encourages the formation of an intermolecular H-bond between neighbouring molecules through the oxygen atoms of the tosyl groups.[18,19] Furthermore, we were interested in studying the effect that these intermolecular interactions could have on the acidity of the N–H donor fragments of the receptor. The participation of the OH group of $\mathbf{H_3L^b}$ in intermolecular H-bonding was confirmed by the X-ray data, as indicated above (Fig. 3).

$\mathbf{H_3L^b}$ has a similar UV spectrum to $\mathbf{H_2L^a}$ in MeCN. As with $\mathbf{H_2L^a}$, the addition of fluoride anions induce a bathochromic shift resulting from the formation of the anionic species $\mathbf{(HL^b)^{2-}}$, as demonstrated by the coincidence of the emission spectrum in the presence of tetrabutylammonium hydroxide. Once again, only $CH_3CO_2^-$ and $H_2PO_4^-$ were able to deprotonate the receptor $\mathbf{H_3L^b}$ but these gave only a residual response. The fluorescence response of $\mathbf{H_3L^b}$ also parallels the observations discussed previously for $\mathbf{H_2L^a}$. $\mathbf{H_3L^b}$ displayed very weak fluorescence emission at 509 nm (λ_{ex} = 313 nm) in CH_3CN. The addition of fluoride resulted in the appearance of a strong fluorescence emission band at 461 nm that progressively increased with the addition of the salt and the formation of the deprotonated anion species $\mathbf{(HL^b)^{2-}}$. Once again, $CH_3CO_2^-$ and $H_2PO_4^-$ induce similar spectral changes, but with much less sensitivity. The difference in the behaviour of $\mathbf{H_3L^b}$ in the presence of different anions is clearly distinguishable by the fluorescence intensity, not only quantitatively in the fluorimeter but also under a hand-held UV lamp (λ_{ex} = 365 nm), as shown in Fig. 6.

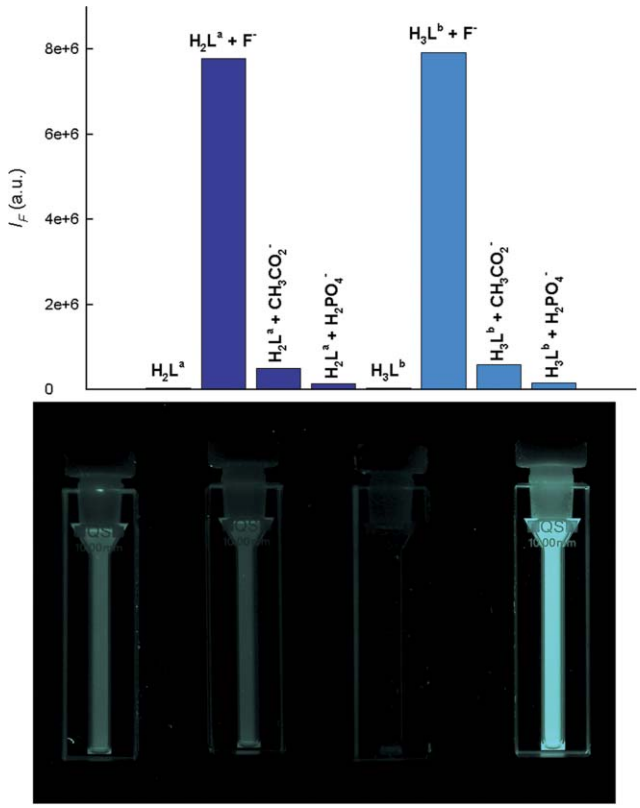


Fig. 6 Relative fluorescence intensities of 10 μM solutions of receptors $\mathbf{H_2L^a}$ ($\lambda_{em} = 454$ nm) and $\mathbf{H_3L^b}$ ($\lambda_{em} = 461$ nm) in the presence of 20 equiv. of F^-, $CH_3CO_2^-$ and $H_2PO_4^-$ in CH_3CN ($\lambda_{ex} = 313$ nm). Bottom, fluorescence visual features of the interaction of inorganic anions with receptor $\mathbf{H_3L^b}$ in CH_3CN solution (10 μM) under a UV lamp ($\lambda_{ex} = 365$ nm); from left to right: +20 equiv. of $CH_2CO_2^-$; +20 equiv. of $H_2PO_4^-$; free receptor; +20 equiv. of F^-.

NMR studies

The ^{1}H NMR spectra in CD_3CN of $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ show obvious changes on addition of fluoride ions. In both spectra the NH signal (13.11 ppm for $\mathbf{H_2L^a}$ and 13.25 for $\mathbf{H_3L^b}$) rapidly disappears; the imine proton signal shifts downfield and the aromatic proton signals shift slightly when F^- ions are added. These observations further confirm that the fluoride anion causes deprotonation of the amide groups of both receptors.

Equilibrium constants

From the data collected, it is clear that the changes in the NMR, UV/Vis and emission spectra of $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ in MeCN in the presence of F^- are a consequence of the deprotonation of the sensors and the formation of the anionic species $(\mathbf{L^a})^{2-}$ and $(\mathbf{HL^b})^{2-}$. The deprotonation process of the N–H fragments of $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ promoted by fluoride anions follow the acid–base reaction equilibrium below:[13]

$$\mathbf{H_nL} + 2F^- \rightleftharpoons \mathbf{H_{(n-2)}L^{2-}} + 2HF\ (K_D) \quad (1)$$

Moreover, considering the particularly high stability of the HF_2^- dimer,[11] it can be suggested that the following dimer formation process occurs in the subsequent step:[20]

Table 2 Log K_D for $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ interaction with anions

	log K_D[a]		log K_D[b]	
Anion	$\mathbf{H_2L^a}$	$\mathbf{H_3L^b}$	$\mathbf{H_2L^a}$	$\mathbf{H_3L^b}$
F^-	8.652 ± 0.03	8.911 ± 0.05	8.406 ± 0.09	8.669 ± 0.06
$CH_3CO_2^-$	5.915 ± 0.07	6.203 ± 0.09	5.841 ± 0.12	6.048 ± 0.08
$H_2PO_4^-$	4.284 ± 0.12	4.497 ± 0.08	4.017 ± 0.09	4.486 ± 0.10

[a] From UV/Vis titration spectra. [b] From fluorescence titration spectra.

$$HF + F^- \rightleftharpoons HF_2^- \quad (2)$$

The overall equilibrium, with a stoichiometry of 1 : 4 for $\mathbf{H_n}$L-fluoride interactions, can be obtained combining eqn (1) and (2):[13]

$$\mathbf{H_nL} + 4F^- \rightleftharpoons \mathbf{H_{(n-2)}L^{2-}} + 2HF_2^- \quad (3)$$

This two-step equilibrum can also be applied to the N–H deprotonation processes promoted by the anions $CH_3CO_2^-$ and $H_2PO_4^-$, which can also form relatively stable dimers.[10,12,13]

The UV/Vis and fluorescence emission titration data were fitted to the above model using the SPECFIT/32™ programme.[21] The corresponding K_D values are compiled in Table 2. These K_D values demonstrate that receptors $\mathbf{H_2L^a}$ and $\mathbf{H_3L^b}$ can selectively detect fluoride ions by a fluorogenic "OFF/ON" response with high sensitivity and selectivity. Previously reported sulfonamide chemosensors do not display this level of selectivity.

Conclusions

In summary, we have developed a new family of fluorescent sulfonamide chemosensors for fluoride ions in organic media. These systems are based on the deprotonation of the amide donor fragments in the presence of highly basic inorganic anions. The presence of the imine group as an intramolecular H-bond acceptor enhances the selectivity of these sensors compared to previous examples in the literature. The equilibrium constants for fluoride anions are two orders of magnitude larger than those calculated for acetate, and four orders of magnitude larger than those for dihydrogenphosphate. The deprotonation mechanism has been demonstrated by spectrophotometric and spectrofluorimetric titrations as well as by NMR spectroscopy. The X-ray structures of both receptors are also discussed.

Finally, we observed that the presence of an OH group in the aliphatic spacer of the receptor causes a slight increase in the equilibrium constants. We believe that this effect could be due to hydrogen bonding interactions between the tosyl O atoms and the OH group and the influence of these interactions on the donor properties of the N–H fragments of the receptor. We are currently studying this interaction as a means to modulate the affinity (and selectivity) of this class of chemosensors.

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