Quaternary ammonium salt-based chromogenic and fluorescent chemosensors for fluoride ions

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ABSTRACT

Chemosensors **5–7** possessing a quaternary ammonium cation (for electrostatic interactions) and an N–H group(s) (for H-bonding) as recognition sites and an anthracene-9,10-dione as both a chromogenic and fluorescent moiety exhibit absorption and emission changes with fluoride ions only. No significant response to other anions such as Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, HSO_4^-, $H_2PO_4^-$ and ClO_4^- is observed. The dual emission at λ_{max} 580 nm (free **5/6**) and λ_{max} 510 and 540 nm (**5/6** + F^-) in chemosensors **5** and **6** enables ratiometric analysis of fluoride ions.

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The development of artificial optical receptors for selective anion recognition[1] has attained significant interest, as anions play a fundamental role in a wide range of chemical and biological processes.[2] Binding affinities and thus selectivities between anions and their hosts are generally attributed to hydrogen bonding and/or electrostatic interactions in addition to selectivities arising due to the topologies of the ligating sites,[1e,3] viz. a viz. that of the anion (size and spherical, trigonal or tetrahedral structures). The H-bonding is more influential in providing selective binding through complimentarity and consequently a number of neutral H-bond donor moieties, for example, amide,[4] urea,[1c,5] thiourea[5a,6] and pyrrole[7] or their combinations have been incorporated in the design of anion receptors.

The presence of positively charged ammonium or guanidinium[8] groups or metal ions[9] complements the electrostatic interactions. In such receptors, where the presence of both electrostatic and H-bonding interactions provides a favourable environment, the existence of multiple charged species at neutral pH and the possibility of anion promoted deprotonation complicates the situation. As a result, quaternary ammonium,[10,11] imidazolium,[12] benzimidazolium,[13] pyridinium[14] salts, etc. which are not affected by the pH of the medium have received significant attention. However, a few mixed amine/amide-quaternary amine systems have been explored as the anion receptors. Bowman-James has shown that quaternary ammonium–amide receptors[11] exhibit higher affinities for almost all anions compared to their neutral counterparts.

Recently, we[15] and others[5,16] have shown that the modulation of electron-deficient (amide/urea) or electron-rich (amine/pyridine) functionalities in a host based on anthracene-9,10-dione and 1,8-naphthalimide derivatives led to the development of respective anion and cation chemosensors. In the present study,

we have designed quaternary ammonium cation (for electrostatic interactions) and N–H (for H-bonding) based chromogenic and fluorescent chemosensors **5–7** which are selective for fluoride ions.

A solution of amine **1**[15b] and benzyl chloride **3** in ethanol on stirring at 80 °C for 24 h followed by filtration of separated solid gave the chemosensor **5**,[17] as a red solid in 80% yield (Scheme 1). The downfield shift of NCH_3 and both NCH_2 signals to δ 3.11, δ 3.64 and δ 4.03 in comparison to amine **1** (δ 2.35, δ 2.68, δ 3.43),[15b] and the appearance of a new NCH_2 singlet at δ 4.69 and aromatic protons confirmed the formation of quaternary ammonium salt **5**. Chemosensors **6** (92%) and **7** (85%) were synthesized[17]
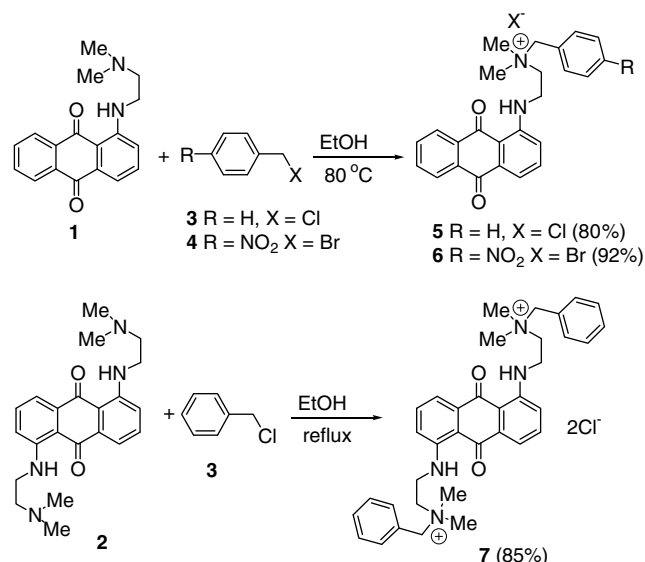
Scheme 1.

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by similar reactions of amine **1** with halide **4** and amine **2**[18] with halide **3**. In chemosensor **7**,[17] the appearance of only four signals in the aliphatic region confirmed that a bis-quaternary salt has been formed.

The effect of a proximal positive charge on the spectroscopic behaviour of **5–7** was studied using absorption and steady-state fluorescence spectroscopy. In CH$_3$CN–DMSO (9:1), chemosensors **5–7** showed absorption spectra shifted to shorter wavelengths ($\Delta\lambda_{ab}$ 10–20 nm) with respect to their parent amines **1** and **2** (Table 1). In fluorescence spectroscopy, the amine **1** shows a Stokes shift of 30 nm but the diamine **2** and quaternary ammonium salts **5–7** exhibit larger (80–105 nm) Stokes shifts. The emission maxima in the case of **7** (585 nm) appeared at a shorter wavelength ($\Delta\lambda_{em}$ 10 nm) with respect to that of amine **2** (595 nm). However, in the case of amine **1**, λ_{em} was observed at 525 nm which after conversion to ammonium salts **5** and **6** appeared at 580–585 nm. The quantum yields (Φ) of the quaternary ammonium salts **5–7** were between 0.019 and 0.024 which are nearly 4–5 times larger for **5** and **6**, and 19 times larger in the case of **7** than those observed in their parent amines **1** and **2** (Table 1).

This increased Φ in chemosensors **5–7** is consistent with the earlier reported[19] interaction of the anthracene-9,10-dione chromophore with a positively charged species. In anthracene-9,10-dione the low-lying n–π^* transition is generally non-fluorescent which on co-ordination of the chromophore associated non-bonded electrons (C=O of anthracene-9,10-dione) with any of the electropositive centres is destabilized. As a result the π–π^* state becomes the lowest energy transition and emission is switched 'ON'. Chemosensors **5–7** constitute the first examples, where intra-molecular interactions of an anthracene-9,10-dione derivative with a quaternary ammonium cation switches 'ON' the emission.[20] Such inversion of electronic transition states by intermolecular interactions has been used earlier for cations sensing only[19] (Scheme 2).

The chemosensor **5** (50 µM, CH$_3$CN–DMSO (9:1)) exhibits two absorption bands at λ_{max} 310 nm (ε 6000) and 480 (ε 6600) nm. Addition of tetrabutylammonium fluoride (TBAF) (1000 µM) to a solution of **5** resulted in a change in colour of the solution from yellow to pink. The absorption bands of **5** centred at 310 nm and 480 nm underwent red shifts to 340 nm ($\Delta\lambda_{max}$ = 30 nm) and 515 nm ($\Delta\lambda_{max}$ = 35 nm) which reflects the stabilization of the charge transfer excited state following the interaction of **5** with fluoride ions. On keeping the solution for 24 h, the colour of the solution turned fluorescent green (Fig. 1) and the UV–vis spectrum of this solution attained a structured absorption band with maxima at 364, 473, 505, 534, 573 and 646 nm. Addition of the other anions, for example, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, CH$_3$COO$^-$, HSO$_4^-$, H$_2$PO$_4^-$ and ClO$_4^-$ caused no significant change in the absorption spectrum of **5**. Significantly, amine **1** did not show any change in its absorption spectrum even on addition of 0.01 M fluoride and other anions (Figs. S1 and S2). Therefore, the presence of a quaternary ammonium salt as an appendage in chemosensor **5** is conspicuously responsible for its selective interaction towards fluoride anion.

On gradual addition of fluoride anions to a solution of **5** (50 µM, CH$_3$CN–DMSO (9:1)), the absorbance at 340 nm and 515 nm
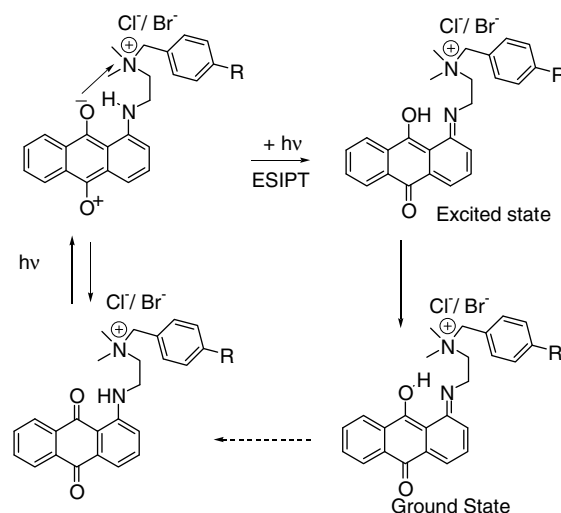
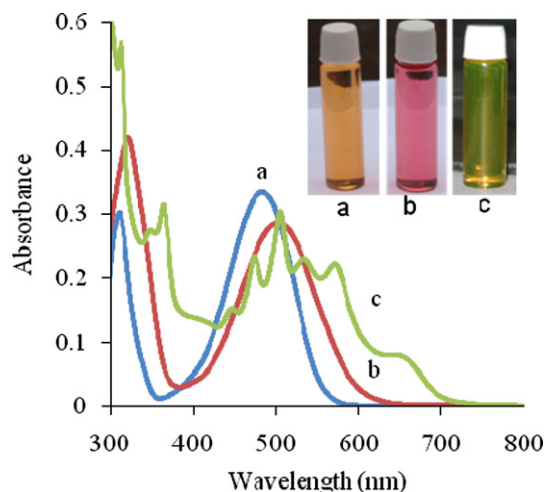**Scheme 2.** Probable mechanism for the enhanced emission in **5**.

Figure 1. UV–vis spectra of **5** (50 µM) in CH$_3$CN–DMSO (9:1) (a) **5** only, (b) **5** + F$^-$ (500 µM) (immediately), (c) **5** + F$^-$ (500 µM) (after 24 h) (inset shows the respective colour changes).

increased gradually. A plot of the absorbance at 340 nm and 480 nm verses concentration of fluoride ions shows a straight line which attains a plateau after addition of 1000 µM fluoride ions (Figs. S3 and S4). The spectral fitting of the absorbance data shows the formation of higher stoichiometric complexes [LF$_4$ (log β_{LF4} = 12.11 ± 0.27) and LF$_6$ (log β_{LF6} = 17.76 ± 0.5)]. Chemosensor **6** possessing a *p*-nitro group showed similar changes on addition of fluoride anions to those observed with **5**.

Chemosensors **5** and **6** (50 µM, CH$_3$CN–DMSO (9:1)) on excitation at 450 nm exhibited emission band at λ_{em} 580 nm. Addition of Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, CH$_3$COO$^-$, HSO$_4^-$, H$_2$PO$_4^-$ and ClO$_4^-$ anions (0.01 M) to solutions of **5** and **6** led to insignificant changes in their fluorescence spectra. However, on addition of fluoride (1000 µM), the fluorescence intensity at 580 nm was completely turned off and a new blue-shifted fluorescence spectrum with two new emission bands at 505 and 540 nm appeared (Fig. 2).

On gradual addition of fluoride to the solution of **5**, the emission intensity at 580 nm decreased slowly up to 600 µM of fluoride ions. On further addition of fluoride, a new structured emission spectrum with two emission maxima at 510 and 540 nm appeared, which went off scale at greater than 1000 µM of fluoride ions.

Table 1
UV–vis and fluorescence data for **1**, **2** and **5–7**

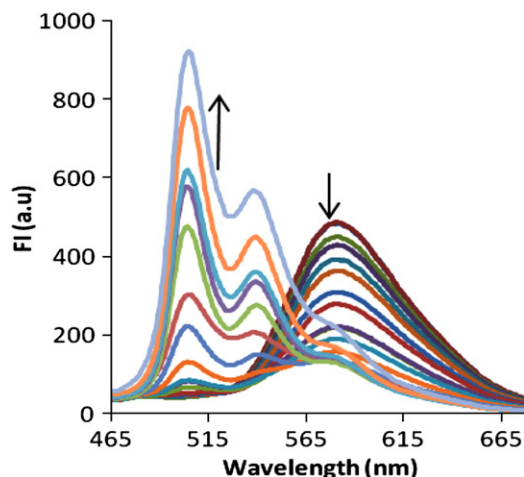|	UV–vis (CH$_3$CN–DMSO; 9:1)		Fluorescence (CH$_3$CN–DMSO; 9:1)	
	λ_{max} (nm)	ε	λ_{max} (nm)	Φ
1	495	8600	525	0.005
5	480	6600	585	0.020
6	485	5400	580	0.024
2	515	14,100	595	0.001
7	495	10,200	585	0.019

Figure 2. Fluorescence emission spectra of **5** (50 μM) in CH$_3$CN–DMSO (9:1) upon addition of fluoride.

Spectral fitting of these data (Fig. S5) showed the formation of higher stoichiometric complexes LF$_3$ and LF$_6$ (log β_{LF3} = 9.43 ± 0.07 and log β_{LF6} = 22.5 ± 0.3) and is in agreement with UV studies.

Therefore, in the case of chemosensor **5**, upon incremental addition of F$^-$ ions, the emission intensity at 580 nm is gradually 'switched off' and at 505 nm is 'switched on'. This situation of dual emission provides the opportunity for elaborating **5** as a ratiometric chemosensor and allows the estimation of analyte independent
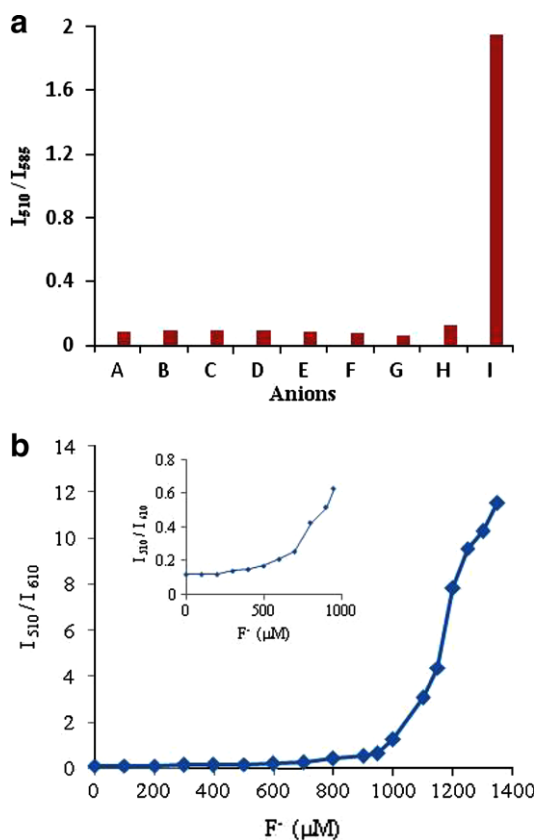

Figure 3. (a) Fluorescence ratiometric response (I$_{510}$/I$_{585}$) of **5** (50 μM) upon addition of tetrabutylammonium salts of anions in CH$_3$CN–DMSO (9:1) [A = NO$_3^-$; B = I$^-$; C = HSO$_4^-$; D = H$_2$PO$_4^-$; E = ClO$_4^-$; F = Cl$^-$; F = Br$^-$; G = AcO$^-$; I = F$^-$]. (b) Ratiometric response of **5** towards F$^-$ anions; inset shows the effect of F$^-$ between 500 and 1000 μM.
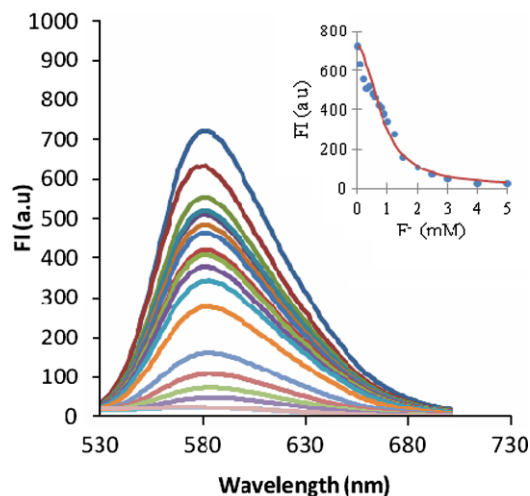

Figure 4. Fluorescence emission spectra of **7** (50 μM) in CH$_3$CN–DMSO (9:1) upon addition of fluoride. Inset shows a plot of fluorescence vs [F$^-$] (points show the experimental results and the line is curve fit).

of the concentration of the receptor. Therefore, chemosensor **5** can be used for estimation of 500–1200 μM fluoride ions and other anions do not interfere in its estimation (Fig. 3).

The appearance of structured band in UV–vis spectrum and enhanced emission at 510 nm, on addition of CsF (solid) to solution of **5** in DMSO and enhanced emission of solution of **5** in pure CH$_3$CN on addition of TBAF, ruled out participation of tetrabutylammonium cation and DMSO in achieving such photophysical changes. Klymchenko et al.[20] have suggested that in a flavone-based sensor, the participation of long range coulomb interactions between quaternary ammonium moiety and added anions is responsible for such behaviour and has proposed its application in developing new chemosensors.

The UV–vis spectrum of **7** on addition of fluoride and other anions showed insignificant changes in its absorbance and λ_{max}. The solution of chemosensor **7** (50 μM, CH$_3$CN–DMSO (9:1)) on excitation at λ_{max} 450 nm exhibited emission at λ_{max} 585 nm. Addition of Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, CH$_3$COO$^-$, HSO$_4^-$, H$_2$PO$_4^-$ and ClO$_4^-$ anions (1000 equiv) resulted in insignificant changes in the emission of **7** but on addition of fluoride ions, the emission was quenched (Fig. 4). Spectral fitting of these data showed the formation of LF$_2$ only (log β_{LF2} = 6.23 ± 0.07).

Thus, chemosensors **5–7** bearing quaternary ammonium and amine NH moieties exhibit unique changes in their absorption and fluorescence properties, on addition of fluoride ions and emulate new dual channel chemosensors for F$^-$ ions. The effect of additional functionalities on sensing behaviour is under investigation.

Acknowledgements

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.04.147.

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17. Compound **5**: red solid; Yield 80%, mp 50 °C; FAB Mass 385 (M$^+$); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.11 (s, 6H, CH$_3$), 3.64 (br s, 2H, CH$_2$), 4.03 (br s, 2H, CH$_2$), 4.69 (s, 2H, CH$_2$), 7.43 (d, J = 8.4 Hz, 1H, ArH), 7.44–7.59 (m, 6H, ArH), 7.74 (t, J = 7.5 Hz, 1H, ArH), 7.84–7.95 (m, 2H, ArH), 8.15 (d, J = 7.5 Hz, 1H, ArH), 8.21 (d, J = 7.5 Hz, 1H, ArH), 9.75 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 36.0, 49.3, 61.7, 68.2, 112.9, 115.7, 118.5, 136.3, 127.8, 128.9, 130.3, 132.3, 133.0, 133.6, 134.1, 134.5, 135.8, 150.4, 182.7, 184.3. Elemental analysis for C$_{25}$H$_{25}$ClN$_2$O$_2$ requires: C, 71.33; H, 5.99; N, 6.66. Found: C, 71.45; H, 5.85; N, 6.50.Compound **6**: red solid; Yield 92%, mp 230 °C; FAB Mass 430 (M$^+$); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.19 (s, 6H, CH$_3$), 3.76 (t, J = 6.3 Hz, 2H, CH$_2$), 4.06 (q, J = 6.3 Hz, 2H, CH$_2$), 4.89 (s, 2H, CH$_2$), 7.39 (d, J = 8.4 Hz, 1H, ArH), 7.58 (d, J = 7.5 Hz, 1H, ArH), 7.69 (t, J = 8.4 Hz, 1H, ArH), 7.80–7.87 (m, 2H, ArH), 7.93 (d, J = 8.4, 2H, ArH), 8.16 (d, J = 7.5 Hz, 1H, ArH), 8.22 (d, J = 7.5 Hz, 1H, ArH), 8.34 (d, J = 8.4 Hz, 2H, ArH), 9.80 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 50.1, 56.8, 63.2, 66.6, 113.9, 116.4, 118.7, 124.2, 124.3, 126.9, 133.1, 134.1, 134.8, 134.9, 135.0, 135.1, 136.3, 149.5, 150.9, 183.4, 185.2. Elemental analysis for C$_{25}$H$_{24}$BrN$_3$O$_4$ requires: C, 58.83; H, 4.74; N, 8.23. Found: C, 58.80; H, 4.78; N, 8.18.Compound **7**: red solid; Yield 85%, mp 280 °C; FAB Mass 563 (M$^+$+1); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.11 (s, 12H, 4 × CH$_3$), 3.64 (t, J = 6.3 Hz, 4H, 2 × CH$_2$), 4.03 (q, J = 6.3 Hz, 4H, 2 × CH$_2$), 4.71 (s, 4H, 2 × CH$_2$), 7.35 (d, J = 8.4 Hz, 2H, ArH), 7.51–7.63 (m, 12H, ArH), 7.72 (t, J = 8.4 Hz, 2H, ArH), 9.71 (br s, 2H, 2 × NH); ^{13}C NMR (DMSO-d_6, 75 MHz): 36.4, 50.0, 62.2, 68.1, 113.2, 116.0, 117.9, 118.1, 129.7, 131.2, 133.6, 136.0, 136.7, 150.6, 185.0. Elemental analysis for C$_{36}$H$_{42}$Cl$_2$N$_4$O$_2$ requires: C, 68.24; H, 6.68; N, 8.84. Found C, 68.25; H, 6.60; N, 8.90.

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