Synthesis, Characterization, Evaluation & Complexation of sensors containing imine and hydroxyl groups

A major portion of this chapter has been published as given below:

In the supramolecular chemistry, there is a perpetual effort to construct systems that can bind both the cation and the anion.\(^1\) From the literature, in the biological context, the O-H···anion/cation interactions are almost as crucial as the ubiquitous NH···anion/cation interactions, but still, hydroxyl group containing compounds are less explored comparatively for sensing purposes.\(^2\) However, the incorporation of hydrophilic –OH groups in sensors may improve their effectiveness in aqueous medium. For cation sensing, the presence of hydroxyl groups in the vicinity (preferably ortho position) of carbonyl/imine groups, provides a pre-organized coordination environment for selective metal ion detection in both organic and aqueous medium as discussed in chapter I. For e.g., multiple hydroxyl groups\(^2(d)\) containing (I) provides highly selective detection of Cu\(^{2+}\) ions even at 1ppm in aqueous medium. A naphthalene-based chemosensor\(^2(e)\) with hydroxyl groups elicits detection of Al\(^{3+}\) ions through CHEF phenomena. For anion sensing, hydroxyl group containing sensors generally rely on the resonance-assisted H-bonding (RAHB) phenomenon, existing ubiquitously between the carbonyl/imine group and hydroxyl group at the ortho position\(^2(f)\) to it, as reviewed (section 1.6). This H-bonding causes activation of carbonyl/imine groups and leads to nucleophilic addition reactions at these groups generating chemodosimeters. Kim and Hong \textit{et al.}\(^2(g)\) developed a coumarin-based fluorescent chemodosimeter for selective CN\(^-\) detection, which contains a salicyaldehyde group in the vicinity of carbonyl group and thus provides activation of the carbonyl group by the adjacent phenolic hydrogen through the formation of intramolecular hydrogen bond. Simple deprotonation of the phenolic proton of hydroxyl group containing sensors also provides a detection mechanism for various analytes e.g., F\(^-\), CN\(^-\), CH\(_3\)CO\(_2\)\(^-\) as reaction with these basic anions causes bathochromic shift and hence gives naked-eye sensors. E.g. a series of tripodal sensors\(^2(h)\) is reported, which contains hydroxyl groups in vicinity of the imine groups, along with different electron withdrawing/donating groups and azophenol moiety. These sensors display selective color changes from yellow to deep purple only in the presence of F\(^-\) ions in acetonitrile solution, due to the deprotonation of proton of the hydroxyl group.

Examples of ion sensing using mesitylene based di/tripodal ligands with hydroxyl groups in the vicinity of imine groups; with and without appended azo groups and those containing urea/thiourea moieties have been earlier reported by our lab.\(^3\)
Continuing on that line three new di/tripodal designs (10,11a-b), with variations from the previously reported work are presented here for cation/anion sensing. At the same time, dipodal molecules with hydroxyl groups in conjunction to the imine (-CH=N-), on anthracene anchor (13a-c) and their use for anion sensing purposes, is being reported for the first time here. It was envisaged that the rigid anthracene group may direct the two podes to different sides and thus affect the reactivity/sensitivity/selectivity of the sensors vis-a-vis their benzene/mesitylene based counterparts. Depending upon the type of ion recognition observed, these sensors have been divided into two categories:

(i) Mesitylene based tripodal Schiff base (10) with 5-nitrophenol groups as binding and signalling unit for sensitive and selective Cu$^{2+}$ detection in aqueous medium (Scheme 3.1).

(ii) Dipodal Schiff bases with hydroxyl groups as binding and signalling subunit. These can be subdivided further on the basis of anchor used:

(a) Mesitylene based dipodal chromo-fluorogenic sensors (11a) and (11b) for F$^-$ and CN$^-$ ions in DMSO and semi aqueous medium (Scheme 3.1).

(b) Anthracene based dipodal chromogenic sensors (13a), (13b) and (13c) for F$^-$ and CN$^-$ ions in DMSO (Scheme 3.1).

3.1 Reaction Methodologies used for the synthesis of compounds/sensors
3.2 Experimental

General information

Experimental methods and instruments used are the same as explained in chapter II, section 2.2. Fluorescence microscopy was performed on a ZEISS Axiovert 200 inverted microscope.
X-ray measurement and structure determination

The crystals of compound (11b) were grown by slow evaporation from mixture of CHCl$_3$ and CCl$_4$ and those of (12) from chloroform and (13b) from mixture of acetonitrile and methanol were grown. X-ray data of the compound (11b) was collected on a Bruker’s Apex-II CCD diffractometer using Mo Kα (λ=0.71069 Å) at room temperature. The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. A total of 19836 reflections were measured out of which 5877 were independent and 3146 were observed [I>2σ(I)] for theta 25°. The structures was solved by direct methods in a trigonal R-3 space group, using SIR-92 and refined by full-matrix least squares refinement methods based on F$^2$, using SHELX-97. The refinement showed a disordered CCl$_4$ molecule in the structure with C and one Cl atom lying on the three fold axis with site occupancy of 0.3333. The disorder in other Cl atom was resolved by splitting it in two positions and refining anisotropically with restraints on C-Cl bonding and Cl···Cl non-bonding distances. The hydrogens of the -OH groups were located from the difference Fourier synthesis and were refined isotropically with Uiso values 1.2 times that of their carrier oxygen atoms, with restraints on the O-H distance. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U$_{iso}$ values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbons. All calculations were performed using Wingx package. The crystals of (13b) were highly sensitive and tend to became opaque soon and gave poor diffraction. The data were measured many times on different crystals, in oil. The used data set was the best out of them. Consequently only 19% reflections were observed and R$_{int}$ was high. The molecule could be refined anisotropically but a few atoms showed high thermal parameters. Apart from the molecule there was some much diffused electron density around 0.66 eÅ$^3$ which could not be modelled nicely. Therefore it was removed using the SQUEEZE routine of PLATON. The volume of the void thus created was 63 eÅ$^3$ and the number of electron recovered was 20. This matched well with a molecule of methanol in the asymmetric unit.
UV-vis and Fluorescence studies
Molecular interaction of (10) with 19 different metal nitrates under study were investigated using UV–vis spectroscopy at 5×10⁻⁶ M and Fluorescence spectroscopy at 10⁻⁶ M in HEPES buffer (pH 7.0, containing 20% THF as a co-solvent). The UV-vis studies of 11a/11b/13a/13b/13c 10⁻⁵ M with various tetrabutylammonium anions under study were performed in DMSO. The fluorescence studies of (11a) and (11b) were performed at 5×10⁻⁶ M and at 10⁻⁵ M respectively in DMSO. The binding stoichiometry of various cation and anion complexes [(10)-Cu²⁺, 11a/11b/13a/13b/13c with F⁻ and CN⁻ ions] was determined by the method of continuous variation (Job’s plot).⁵

Calculation of Quantum yield for cation analysis.
The method used for the calculation of fluorescence quantum yield Φₕ for (10) (λₜₐₓ =355 nm) is same as explained in chapter II, section 2.2.

Cell Imaging Studies.
A microbe (Saccharomyces cerevisiae) was cultured in normal broth and secondly in experimental media containing Cu(II). The cells cultured in normal broth as well as cultured in a media containing Cu (II) were treated with (10) dissolved in a DMSO/H₂O (7:3, v/v) solvent mixture. Before performing microscopy observations, the microbe cells were washed with a DMSO/H₂O (7:3, v/v) solvent mixture.

3.3 Synthesis and Characterization of compounds/sensors
Synthesis of receptors
The compound (10) was synthesized by Schiff base condensation reaction of 2,2',2''-(((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(sulfanediyl))trianiline with 2-hydroxy-5-nitrobenzaldehyde in acetonitrile at room temperature in the presence of a catalytic amount of Zn(ClO₄)₂. Similarly, the compounds (11a) and (11b) were synthesized by the Schiff base condensation of 2,2'-(((2,4,6-trimethyl-1,3-phenylene)bis(methylene))bis(sulfanediyl))dianiline with 2,3-dihydroxybenzaldehyde and 2-hydroxybenzaldehyde respectively. The compound (12) was already reported in the literature⁶ prepared by the reduction of a –NO₂ derivative of 12 but in the present work, this compound was prepared in a modified manner. Further, these compound
(12) was used for Schiff base condensation reaction with 2,3-/2,4-/2,5-dihydroxybenzaldehyde in chloroform-methanol mixture to construct compounds (13a), (13b) and (13c).

Characterization of compounds/sensors

All of these compounds have been characterized by \(^1\)H, \(^{13}\)C, IR, mass and X-ray analysis (in some cases). The sensing behaviour of these sensors has been evaluated by using naked-eye, UV-vis, fluorescence and NMR spectral techniques in solution at 25 °C.

**Compound (10).** 200 mg (0.376 mmol) of tripodal amine was dissolved in 10 ml acetonitrile, to which was added 190 mg (1.12 mmol) of 2-hydroxy-5-nitrobenzaldehyde in 40 ml of acetonitrile along with 2-3 mg of zinc perchlorate. The color of the solution changed immediately to turbid yellow and precipitates separates out within half an hour. These precipitates were filtered, washed with methanol and dried. Yield 70%; mp = 175-177 °C; \(^1\)H NMR (300 MHz, DMSO-d\(_6\), \(\delta\)): 2.21 (s, 9H, -CH\(_3\)), 4.05 (s, 6H, -CH\(_2\)), 7.08 (d, 3H, -Ar, J = 9.3 Hz), 7.38 (t, 6H, -Ar, J = 6 Hz), 7.59 (d, 3H, -Ar, J = 7.2 Hz), 7.57 (d, 2H, -Ar, J = 8.1 Hz), 8.25 (d, 3H, -Ar, J = 9.0 Hz), 8.62 (d, 3H, J = 2.7 Hz) 9.03 (s, 3H, -CH=N), 14.21 (s, 3H, -OH); \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\), \(\delta\)): 15.3 (-CH\(_3\)), 32.7 (-CH\(_2\)), 118.1 (-Ar), 118.3 (-Ar), 118.5 (-Ar), 127.1 (-Ar), 128.4 (-Ar), 128.8 (-Ar), 130.8 (-Ar), 132.7 (-Ar), 136.3 (-Ar), 139.2 (-Ar), 144.9 (-Ar), 161.1 (CH=N), 166.1 (-C-OH); FTIR (KBr, cm\(^{-1}\)): 3049, 2894, 1602, 1475, 1340, 1284, 1094, 749; Elemental analysis calculated for C\(_{51}\)H\(_{42}\)N\(_6\)O\(_9\)S\(_3\) : C, 62.56; H, 4.32; N, 8.58; S, 9.82%. Found: C, 62.34; H, 4.28; N, 8.30; S, 9.65%; HRMS m/z: 979.2226 [M+1]\(^{+}\) ion (calc. 979.2248).

**Compound (11a).** Same procedure as for (11a) except that 0.15 g (1.08 mmol) of 2,3-dihydroxybenzaldehyde was used instead of 2-hydroxybenzaldehyde. Yield 76%; mp = 165-167°C; \(^1\)H NMR (300 MHz, DMSO-d\(_6\), \(\delta\)): 2.23 (s, 6H, -CH\(_3\)), 2.38 (s, 3H, -
Compound (11b). 0.20 g (0.331 mmol) of dipodal amine was dissolved in 10 ml chloroform, to which was added 0.0810 g (0.663 mmol) of 2-hydroxybenzaldehyde in 40 ml of methanol along with 3-4 mg of zinc perchlorate. The reaction mixture was stirred for 2h, after the completion of reaction solvent was evaporated and product was recrystallized from methanol as yellow solid. Yield 60%; mp = 110-112ºC; $^1$H NMR (300 MHz, DMSO-d$_6$, δ): 2.23 (s, 6H, -CH$_3$), 2.30 (s, 3H, -CH$_3$), 4.09 (s, 4H, -CH$_2$), 6.82 (s, 1H, -Ar). 6.88 (d, 2H, -Ar, J = 8.1 Hz), 6.95 (t, 2H, -Ar, J = 7.5 Hz), 7.32 (t, 4H, -Ar, J = 6.3 Hz), 7.40 (t, 4H, -Ar, J = 8.1 Hz), 7.54 (d, 2H, J = 6.3 Hz), 7.60 (d, 2H, J = 6.9 Hz), 8.84 (s, 2H, -CH=N), 12.92 (s, 2H, -OH); $^{13}$C NMR (75 MHz, DMSO-d$_6$, δ): 14.8 (-CH$_3$), 19.2 (-CH$_3$), 31.7 (-CH$_2$), 116.6 (-Ar), 118.0 (-Ar), 126.4 (-Ar), 127.6 (-Ar), 129.9 (-Ar), 130.3 (-Ar), 132.7 (-Ar), 133.1 (-Ar), 133.4 (-Ar), 136.3 (-Ar), 136.7 (-Ar), 145.7 (-Ar), 160.2 (-Ar), 162.7 (CH=N); FTIR (KBr, cm$^{-1}$): 3411, 1608, 1627, 1184, 752; Elemental analysis calculated for C$_{37}$H$_{34}$N$_2$O$_4$S$_2$: C, 70.00; H, 5.40; N, 4.41; S, 10.10%. Found: C, 69.99; H, 5.31; N, 4.30; S, 10.08%; HRMS m/z 657.2140 [M+Na] ion (calc. 657.1852).

Compound (12). Dipodal amine (12) was prepared by taking 1g of K$_2$CO$_3$ in dry acetonitrile along with 149 mg of 2-aminothiophenol (2 mmol). The reaction mixture was refluxed for 30 minutes and then 200 mg of 9,10-dibromoanthracene (1 mmol)
was added slowly. The reaction mixture was refluxed for another 24 hours and the progress of the reaction was monitored by TLC. After the completion of the reaction, K$_2$CO$_3$ was filtered off and filtrate was concentrated. The crude product was recrystallized from CHCl$_3$ to get yellow crystals. Yield 80%; mp = 198 - 200ºC; $^1$H NMR (500 MHz, DMSO-d$_6$, δ): 5.43 (s, 4H, -NH$_2$), 6.23 (m, 4H, -Ar), 6.74 (d, 2H, -Ar, J = 8.0 Hz), 6.83 (t, 2H, -Ar, J = 6.5 Hz), 7.67 (q, 4H, -Ar, J = 6.5 Hz), 8.88 (q, 4H, -Ar, J = 7.0 Hz); $^{13}$C NMR (125 MHz, DMSO-d$_6$, δ): 115.5 (-Ar), 117.6 (-Ar), 120.0 (-Ar), 127.5 (-Ar), 127.7 (-Ar), 128.0 (-Ar), 129.0 (-Ar), 131.0 (-Ar), 134.7 (-Ar), 146.4 (Ar); FTIR (KBr, cm$^{-1}$): 3433, 3352, 1603, 1485, 1297, 1029, 753; Elemental analysis calculated for C$_{26}$H$_{20}$N$_2$S$_2$: C, 73.55; H, 4.75; N, 6.60; S, 15.10%. Found: C, 73.49; H, 4.73; N, 6.62; S, 15.02%; HRMS m/z: 444.0934 [M+Na]$^+$ (calc. 447.0960).

**Compound (13a).** 0.20 g (0.471 mmol) of dipodal amine (12) was dissolved in 10 ml chloroform, to which was added 0.130 g (0.942 mmol) of 2,3-dihydroxybenzaldehyde in 40 ml of methanol along with 3-4 mg of zinc perchlorate. The reaction mixture was stirred for 2h, after the completion of reaction solvent was evaporated and product was recrystallized from methanol as red solid. Yield 85%; mp = 258 - 260ºC; $^1$H NMR (300 MHz, DMSO-d$_6$, δ): 6.12 (d, 2H, -Ar, J = 7.8 Hz), 6.90 (q, 4H, -Ar, J = 8.4 Hz), 7.03 (d, 2H, -Ar, J = 7.5 Hz), 7.22 (m, 4H, -Ar), 7.60 (d, -Ar, J = 7.8 Hz), 7.71 (dd, 4H, -Ar, J$_1$ = 6.9 Hz, J$_2$ = 3.3 Hz), 8.83 (dd, 4H, -Ar, J$_1$ = 6.6 Hz, J$_2$ = 3.0 Hz), 9.16 (s, 2H, -CH=N), 9.29 (s, 2H, -OH), 13.24 (s, 2H, -OH); $^{13}$C NMR (75 MHz, DMSO-d$_6$, δ): 118.2 (-Ar), 119.1 (-Ar), 119.5 (-Ar), 123.1 (-Ar), 126.2 (-Ar), 126.9 (-Ar), 127.8 (-Ar), 128.1 (-Ar), 128.8 (-Ar), 133.4 (-Ar), 134.7 (-Ar), 144.1 (-Ar), 145.7 (-Ar), 149.1 (-Ar), 163.9 (CH=N); FTIR (KBr, cm$^{-1}$): 3480, 1620, 1352, 1462, 1269, 1196, 744; Elemental analysis calculated for C$_{40}$H$_{28}$N$_2$O$_4$S$_2$: C, 72.27; H, 4.25; N, 4.21; S, 9.65%. Found: C, 72.05; H, 4.36; N, 4.19; S, 9.57%; HRMS m/z: 665.1531 [M+1]$^+$ (calc. 664.1490).
**Compound (13b).** Same procedure as for (13a) except that 2,4-dihydroxybenzaldehyde was used instead of 2,3-dihydroxybenzaldehyde. Yield 67%; mp = 190 -192ºC; ¹H NMR (300 MHz, DMSO-d₆, δ): 6.08 (d, 2H, -Ar, J = 8.1 Hz), 6.40 (s, 2H, -Ar), 6.50 (dd, 2H, -Ar, J = 8.25 Hz), 6.86 (t, 2H, -Ar, J = 7.0 Hz), 7.17 (t, 2H, -Ar, J = 7.5 Hz), 7.55 (m, 4H, -Ar), 7.70 (dd, 4H, -Ar, J₁ = 6.9 Hz, J₂ = 3.0 Hz), 8.80 (dd, 4H, -Ar, J₁ = 7.2 Hz, J₂ = 3.3 Hz), 9.03 (s, 2H, -CH=N), 10.40 (s, 2H, -OH), 13.47 (s, 2H, -OH); ¹³C NMR (75 MHz, DMSO-d₆, δ): 102.4 (-Ar), 108.2 (-Ar), 112.1 (-Ar), 118.0 (-Ar), 126.1 (-Ar), 126.9 (-Ar), 127.1 (-Ar), 128.0 (-Ar), 128.9 (-Ar), 133.0 (-Ar), 134.7 (-Ar), 134.9 (-Ar), 144.3 (-Ar), 162.6 (-Ar), 162.8 (-Ar), 163.0 (CH=N); FTIR (KBr, cm⁻¹): 3361, 1513, 1322, 1261, 1200, 1083, 756; Elemental analysis calculated for C₄₀H₂₈N₂O₄S₂: C, 72.27; H, 4.25; N, 4.21; S, 9.65%. Found: C, 72.25; H, 4.21; N, 4.19; S, 9.61%; HRMS m/z: 665.1532 [M+1]⁺ (calc. 664.1490).

**Compound (13c).** Same procedure as for (13a) except that 2,5-dihydroxybenzaldehyde was used instead of 2,3-dihydroxybenzaldehyde. Yield 60%; mp = 210-212ºC; ¹H NMR (300 MHz, DMSO-d₆, δ): 6.10 (d, 2H, -Ar, J = 8.1 Hz), 6.93 (m, 6H, -Ar), 7.19 (t, 4H, -Ar, J = 6.3), 7.56 (d, 4H, -Ar, J = 7.5), 7.70 (dd, 4H, -Ar, J₁ = 6.9 Hz, J₂ = 3.0 Hz), 8.81 (dd, 4H, -Ar, J₁ = 6.6 Hz, J₂ = 3.3 Hz), 9.07 (s, 2H, -CH=N), 9.20 (s, 2H, -OH), 12.29 (s, 2H, -OH); ¹³C NMR (75 MHz, DMSO-d₆, δ): 117.1 (-Ar), 117.4 (-Ar), 118.2 (-Ar), 119.4 (-Ar), 121.7 (-Ar), 126.1 (-Ar), 127.0 (-Ar), 127.7 (-Ar), 128.1 (-Ar), 128.9 (-Ar), 133.5 (-Ar), 134.7 (-Ar), 144.7 (-Ar), 149.7 (-Ar), 153.2 (-Ar), 163.0 (CH=N); FTIR (KBr, cm⁻¹): 3478, 1622, 1561, 1486, 1361, 1145, 756; Elemental analysis calculated for C₄₀H₂₈N₂O₄S₂: C, 72.27; H, 4.25; N, 4.21; S, 9.65%. Found: C, 72.15; H, 4.06; N, 4.22; S, 9.61%; HRMS m/z: 665.1535 [M+1]⁺ (calc. 664.1490).
X-ray Crystal structure studies

Table 3.1 shows the crystallographic data and refinement parameters for (11b), (12) and (13b). The molecular structure of (11b), which crystallized with a solvent molecule of CCl₄ is shown below in Figure 3.1.

Figure 3.1. ORTEP diagram for (11b) showing the labeling scheme. Hydrogens and solvent CCl₄ have been deleted for clarity.

The structure shows that the dipodal molecule has an approximate ‘U’ shaped conformation with the central anchor phenyl ring forming the base. The torsion angle about C-S bonds are C7-S1 176.35 and C21-S2 159.48° with the dihedral angles between the central ring and the 2-amino-thiophenol ring being 77.2(1) and 51.8(2)°, respectively. The phenyl rings of 2-aminothiophenol and salicylaldehyde moieties on both the arms are rotated by 2.3(2)° and 21.3(2)°, respectively with respect to each other. Two planes passing through the two phenyl rings and the imine group on both the arms showed an interplanar angle of 85.7° (1) between them and are making dihedral angles 75.9° (1) and 60.6(1)° with the central phenyl ring. All these values show that the two arms of the dipodand in the ‘U’ conformation are not parallel but twisted with respect to each other and one of the arms (with C21-S2 bond) is rather gauche than being perpendicular to the central ring (Figure 3.2) unlike the other arm. This distortion is probably there to make room for the CCl₄ solvent molecule which lies close to the latter making C-H···Cl H-bonding interactions and due to the packing requirements (Figure 3.2). There are strong intramolecular H-bonding interactions
between the OH groups and imine nitrogens as well as the S atoms which are supporting this conformation.

**Figure 3.2.** Showing the ‘U’ conformation of the molecule and intramolecular H-bonding interactions in (11b).

The molecules are arranged in the form of H-bonded trimers around the disordered CCl₄ solvent molecule whose one C-Cl bond (C38-Cl1) coincides with the three fold axis along the c axis (Figure 3.3a). Each Cl2 lying in the trigonal plane is H-bonded to C31 and C32 (C31⋯Cl2 a 3.247, C32⋯Cl2 a 3.402, a = x, -1+y,z) whereas each Cl2 is H-bonded to C24 phenylene carbon. Thus the solvent molecule is securely held in the hydrophobic pseudo-cavity of this trimer (Figure 3.3b). Each unit cell contains 6 of
such trimeric units which are further held to each other by C-H···O kind of weak H-bonding interactions as shown in Figure 3.4.

**Figure 3.4.** Showing inter-molecular H-bonding interactions forming the crystal structure of (11b).

The X-ray crystal structure of (12) is shown in Figure 3.5(a). The anthracene lies in a plane with the two fold axis passing through the central ring giving half the molecule in an asymmetric unit. The phenylamine units are almost perpendicular (dihedral angle 73.95(5)°) above and below this plane. This gives a sigmoidal shape to the
molecule as shown in Figure 3.5(b). The crystal packing shows stacking of the molecules down the a axis. There are no H-bonding interactions but S···aromatic ring interactions between S and ring containing (C2-C7) carbon atoms. The centroid to S distance is 3.315 Å with S···S nonbonding distance being 4.698 Å as shown in Figure 3.6.

![Figure 3.6. Showing crystal packing along a axis due to S···π interactions.](image)

Figure 3.6. Showing crystal packing along a axis due to S···π interactions.

The X-ray crystal structure of (13b) is shown in Figure 3.7. The molecule crystallizes in P-1 space group with centre of symmetry passing through the planar anthracene moiety. The two arms attached to it are pointing in opposite directions. In each arm
both the phenyl rings are slightly rotated with respect to each other (dihedral angle 16.8(3)°) whereas both of them are almost perpendicular to the central anthracene ring (dihedral angles 76.0(3) and 79.8(4)° respectively). \textit{Ortho}- hydroxyl group O1 shows strong intramolecular H-bonding with imine N1 (O1···N1 2.571(15)Å, H1A···N1 1.84 Å, \(\angle\)O1-H1···N1 147°) and thioether S1 (O1···S1 3.659(11)Å, H1A···S1 2.89Å, \(\angle\)O1-H1A···S1 141°). The intermolecular H-bonding between the para hydroxyl groups forms a supramolecular arrangement as zig-zag chains (Figure 3.8). Two such parallel chains are attached to each other due to C-H···π interactions between anthracene and the phenyl ring\(^\dagger\) (C8 to C13, \(i = -x,2-y,3-z\)) having H3···centroid\(^i\) and C3···centroid\(^i\) distances of 2.801 Å and 3.627 Å, respectively. This arrangement forms a square grid type of 2D network running diagonally parallel to the \(ab\) plane.

![Zig-zag H-bonded chains of (13b) forming square grid type of 2D network due to C-H···π interactions (a) in ball-n-stick models (b) as space filled model.](image)

**Figure 3.8.** Zig-zag H-bonded chains of (13b) forming square grid type of 2D network due to C-H···π interactions (a) in ball-n-stick models (b) as space filled model.
Table 3.1. Crystal data and structure refinement parameters for (11b), (12) and (13b).

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<td>-9&lt;=h&lt;=9, -12&lt;=k&lt;=15, -33&lt;=l&lt;=28</td>
<td>-7&lt;=h&lt;=7, -11&lt;=k&lt;=10, -23&lt;=l&lt;=23</td>
</tr>
<tr>
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<td>19836</td>
<td>18320</td>
<td>13066</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5877 [R(int) = 0.0261]</td>
<td>4882[R(int) = 0.0291]</td>
<td>4124[R(int) = 0.1888]</td>
</tr>
<tr>
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<td>Semi-empirical from equivalents</td>
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<td></td>
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<tr>
<td>Max. and min. transmission</td>
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<td>0.7471 and 0.6529</td>
<td>0.7455 and 0.4812</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5877 / 5 / 417</td>
<td>4882 / 0 / 136</td>
<td>4124 / 0 / 193</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.996</td>
<td>1.022</td>
<td>0.784</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R1 = 0.0683, wR2 = 0.2042</td>
<td>R1 = 0.0453, wR2 = 0.1280</td>
<td>R1 = 0.1411, wR2 = 0.3288</td>
</tr>
<tr>
<td>[I&gt;2sigma(I)]</td>
<td>R1 = 0.1260, wR2 = 0.2513</td>
<td>R1 = 0.0634, wR2 = 0.1420</td>
<td>R1 = 0.3427, wR2 = 0.3962</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1260, wR2 = 0.2513</td>
<td>R1 = 0.0634, wR2 = 0.1420</td>
<td>R1 = 0.3427, wR2 = 0.3962</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.265 and -0.564 e. Å⁻³</td>
<td>0.467 and -0.507 e. Å⁻³</td>
<td>0.359 and -0.309 e. Å⁻³</td>
</tr>
</tbody>
</table>
Spectral Characterization

All the compounds were characterized by various spectroscopic techniques such as $^1$H NMR, $^{13}$C NMR, IR, elemental analyses and ESI-MS (Figure 3.9 - Figure 3.22). The elemental analysis (CHN data) and mass spectra were in accordance with the molecular formulae.

Figure 3.9. (a) $^1$H NMR of (10) (b) $^{13}$C NMR of (10).

Figure 3.10. (a) IR of (10) (b) ESI-MS of (10).
Figure 3.11. (a) $^1$H NMR of (11a) (b) $^{13}$C NMR of (11a).

Figure 3.12. (a) IR of (11a) (b) ESI-MS of (11a).

Figure 3.13. (a) $^1$H NMR of (11b) (b) $^{13}$C NMR of (11b).
Figure 3.14. (a) IR of (11b) (b) ESI-MS of (11b).

Figure 3.15. (a) $^1$H NMR of (12) (b) $^{13}$C NMR of (12).

Figure 3.16. (a) IR of (12) (b) ESI-MS of (12).
Figure 3.17. (a) $^1$H NMR of (13a) (b) $^{13}$C NMR of (13a).

Figure 3.18. (a) IR of (13a) (b) ESI-MS of (13a).

Figure 3.19. (a) $^1$H NMR of (13b) (b) $^{13}$C NMR of (13b).
Figure 3.20. (a) IR of (13b) (b) ESI-MS of (13b).

Figure 3.21. (a) $^1$H NMR of (13c) (b) $^{13}$C NMR of (13c).

Figure 3.22. (a) IR of (13c) (b) ESI-MS of (13c).
3.4 Cation recognition studies of mesitylene anchored Schiff bases containing imine, nitro and hydroxyl groups

The development of highly selective and sensitive fluorescent chemosensors to detect metal ions, such as Cu(II), Pb(II), Hg(II) and Al(III) has gained impetus due to their importance in industrial and biological processes. To date, a number of methods for the detection of Cu(II) in sample have been proposed including atomic absorption spectrometry, quantum dot based assays, inductively coupled mass spectrometry (ICPMS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and electrochemical techniques. However, these methods have limitations that require sophisticated instrumentation and the time consuming techniques. On the contrary, the optical sensors, which involve naked-eye detection and/or fluorescence intensity change, has attracted great research interest as these provide quick, non-destructive and selective results. For practical applications, the need of the hour is to develop Cu(II) sensors that can be prepared easily, have low detection limit and display sensitive and selective recognition in aqueous medium. Many excellent chemosensors and chemodosimeters have been reported for Cu(II) in the past few years. However, some of them have disadvantages such as complicated synthetic procedures, high detection limit, use of organic solvents and interference from other transition metals which often coexist and have similar reactivity towards sensors. In the present report, a tripodal sensor has been constructed which can detect Cu(II) selectively and reversibly in HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, pH 7.0] buffer, with 20% THF as a co-solvent. The copper-induced changes in the fluorescence spectrum of (10) can be used for the quantification of Cu(II) down to a concentration of 3.16 nM. To the best of our knowledge, this is the lowest fluorogenic detection limit achieved at the time of publication for Cu(II) in a mesitylene anchor based tripodal sensor, without any appended fluorophore, in an aqueous medium.

3.4.1 Colorimetric and chromogenic spectral response of (10)

The absorption spectrum of (10) showed two bands centered at \( \lambda_{\text{max}} = 290 \text{ nm} \) (\( \varepsilon_{\text{max}} = 1986 \text{ M}^{-1} \text{ cm}^{-1} \)) and at \( \lambda_{\text{max}} = 354 \text{ nm} \) (\( \varepsilon_{\text{max}} = 2702 \text{ M}^{-1} \text{ cm}^{-1} \)) (Figure 3.23). The latter has been designated as an intraligand or internal charge transfer (ICT) band involving imine and hydroxyl group. With Cu(II), high energy bands showed slight bathochromic shift from \( \lambda_{\text{max}} = 290 \text{ nm} \) to \( \lambda_{\text{max}} = 299 \text{ nm} \) (\( \varepsilon_{\text{max}} = 1052 \text{ M}^{-1} \text{ cm}^{-1} \)) and low
energy band shifted significantly from $\lambda_{\text{max}}$ 354 nm to $\lambda_{\text{max}}$ 404 nm ($\epsilon_{\text{max}} = 1629 \text{ M}^{-1} \text{cm}^{-1}$).

**Figure 3.23.** Changes in the UV-vis spectrum of (10) (5 μM) in HEPES buffer (pH 7.0, containing 20% THF as a co-solvent) on the addition of various metal ions (50 μM). Inset: color changes on addition of Cu(II) to the (10).

**Figure 3.24.** UV-vis spectrum of (10) (5 μM) upon gradual addition of Cu(II) ion. This wavelength change is also accompanied by a color change from very pale yellow to bright yellowish green (Figure 3.23, inset, right) which becomes intense with increase in the concentration of Cu(II) ions. No such color change was observed with any other metal ions under investigation. However the absorption spectrum of (10) showed slight red shifts in the presence (Figure 3.23) of Cd(II), Cr(III), Co(II), Fe(III), Hg(II), Ni(II), Pb(II) and Zn(II). A progressive increase in the intensity of band at 404 nm with bathochromic shift of $\approx 50$ nm was seen (Figure 3.24), on increasing the concentration of Cu(II) ion solution gradually.
3.4.2 Fluorogenic spectral response of (10)

When excited at 355 nm, in THF-H$_2$O (2:8, v/v) with HEPES as the buffer, (10) (1 μM) exhibits a strong fluorescence emission band at 528 nm (Figure 3.25), which gives fluorescent green color under UV lamp (Figure 3.25, inset, right). This band is typical of an excited state intramolecular proton transfer (ESIPT) phenomenon.$^{11,12}$ The general pathway of the photochromism in Schiff bases is as follows: The basal enol form is excited to a $\pi - \pi^*$ (enol*) state from where the hydroxylic proton is quickly transferred to the nitrogen of the imino atom; the resulting geometry corresponds to the fluorescent cis-keto tautomer (also a $\pi - \pi^*$ state or keto*), which may undergo relaxation towards a ground state trans-keto (or keto) isomer form (photochromic tautomer) (Figure 3.26). The steady state emission in such compounds is dominated by the cis-keto tautomer since the decay of the excited enol state is very fast. The emission band of sensor (10) shows a large Stokes shift of 173 nm (from 355 nm to 528 nm) which is due to emission from the cis-keto tautomer formed after photoinduced proton transfer.

Figure 3.25. Fluorescence spectra of (10) (1 μM) and upon addition of 10 equiv (10 μM) of different metal nitrates in HEPES buffer (pH =7.0, containing 20% THF as a co-solvent). Inset: Fluorescent color changes under UV lamp.

Figure 3.26. Mechanism of ESIPT phenomenon involved in fluorescence of (10).
To evaluate the metal binding affinity of (10), the change in fluorescence intensity of (10) upon addition of nineteen metal salts was recorded. The addition of Ag(I), Al(III), Ba(II), Bi(III), Ca(II), Li(I), Na(I), K(I), Mg(II) and Sr(II) ions has no effect on fluorescence emission, whereas Cd(II), Cr(III), Co(II), Fe(III), Hg(II), Ni(II), Pb(II) and Zn(II) showed slight quenching in the fluorescence intensity. In contrast, the addition of Cu(II) significantly quenches the emission band of (10) at 528 nm. This quenching of fluorescence of (10) is also showed by removal of its fluorescent green color as seen under UV lamp (Figure 3.25, inset, right). The co-ordination of paramagnetic Cu(II) to (10) caused energy or charge transfer from (10) to the open-shell d-orbitals of Cu(II) and thus interfere in ESIPT phenomenon, which results in the quenching of the fluorescence of (10). A fluorescence titration (Figure 3.27a) of (10) in the presence of Cu(II) with its varied concentration caused quenching gradually up to the extent of about 94% (Figure 3.27b), which is calculated by using the formula: \[\frac{I_0 - I}{I_0} \times 100\], where \(I_0\) is the original fluorescence intensity and \(I\) is the fluorescence intensity of (10) in the presence of various metal ions. A Stern-Volmer plot (Figure 3.28a) shows a linear dependence of fluorescence intensity ratio (\(I_0/I\)) on the concentration of Cu(II) ions added. The stoichiometry of the (10 - Cu(II)) complex has been found to be 1:3 from Job’s plot (Figure 3.28b) which is further confirmed by the appearance of a peak at m/z 1184.6730, assignable to [(sensor 10–3H)+3Cu+H2O]+, \([C_{51}H_{41}Cu_3N_6O_{10}S_3]^+\) (calc. 1184.7368) in the ESI-Mass spectrum (Figure 3.29). The response parameter \(\alpha\), which is defined as the ratio of free ligand concentration to the initial concentration of the ligand is plotted as a function of the Cu(II) concentration. This plot can be used as a calibration curve for the analytical studies of Cu(II) ions. Li et al. derived a general equation\(^{14}\) to determine stoichiometric ratio of any complex between the ligand and analyte:

\[
[M^{n+}]^m = \frac{1}{nK_a} \cdot \frac{1}{[L]}^{n-1} \cdot \frac{1-\alpha}{\alpha^n}
\]

where \(K_a\) is equilibrium constant for \(M_nL_m\) complex. \([L], [M^{n+}],\) and \([M_nL_m]\) are the concentrations of respective species. Response parameter, \(\alpha\) is the ratio between free ligand concentration, \([L]\), and the initial concentration of ligand, \([L]\)_T. In the present case, the stoichiometric ratio of (10) with Cu\(^{2+}\) is 1:3. So, this equation can be written as
\[ [Cu^{2+}] = \frac{1}{K_a} \cdot \frac{1 - \alpha}{\alpha} \]

The association constant (log \( K_a \)) was calculated to be 7.25. The stability of the complex was also confirmed by the decrease in free energy -19.54 kJ mol\(^{-1}\), calculated from the equation \( \Delta G = -2.303RT \log K_a \).

**Figure 3.27.** (a) Changes in the Fluorescence spectra of (10) in HEPES buffer (5 μM) upon gradual addition of Copper salt (0-10 μM). (b) Fluorescence quenching rate for (10) (1µM) in the presence of various metal nitrates (10 μM).

**Figure 3.28.** (a) Stern-Volmer plot (b) Job’s Plot of (10) with Cu(II) ion.

**Figure 3.29.** ESI-MS spectrum of Copper (II) complex of (3) in titration.
For various practical purposes, the detection limit was determined from the UV-vis and fluorescence titration data based on a reported method.\textsuperscript{15} From absorption studies, the detection limit was found to be $2 \times 10^{-7}$ M (Figure 3.30a) and $3.16 \times 10^{-9}$ M (Figure 3.30b) for fluorescence data, which is quite low for the detection of submicromolar concentration range of Cu(II) ions found in many chemical and biological systems. As to the fluorescence quantum yield,\textsuperscript{16} (10) exhibits nearly 133-fold decrease in quantum yield (from $\Phi_{\text{free}} = 0.668$ to $\Phi_{\text{Cu(II)}} = 0.005$) upon complexation with copper ions.

Figure 3.30. (a) Absorbance (b) Fluorescence intensity of (10) for different concentrations of Cu (II), normalized between the maximum emission (0.0 µM Cu (II)) and the minimum emission intensity.

Apart from the sensitivity of the sensor, selectivity is another important property of a fluorescent probe. The selectivity of (10) towards Cu(II) was ascertained by performing competitive experiments with 10 µM (10 equiv) of Cu(II) in the presence of 50 µM (50 equiv) of other interfering metal salts (Figure 3.31a). There is almost negligible interference from other metal ions under investigation. Thus, (10) can be used as a selective fluorescent sensor in the presence of most of the competitive metal ions. This high selectivity of sensor is attributed to a high thermodynamic stability of the copper(II)-sensor complex, due to the presence of chelation sphere of N, O and S atoms and due to its strong tendency to promote deprotonation of OH groups during complex formation, which is confirmed by $^1$H NMR spectroscopy (Figure 3.31b). Reversibility is a pre-requisite in developing a novel chemosensor for practical applications. The reversibility of the reaction of (10) and Cu(II) was performed by the titration of the mixture of (10) and Cu(II) (1:10) with EDTA (Figure 3.32a and b). The increase in the fluorescence intensity at 528 nm indicates the regeneration of free (10). The fluorescence was again quenched on addition of more Cu(II) to the same mixture.
Figure 3.31. (a) Competitive selectivity of (10) (1µM) for Cu (II) ion (10 µM) in the presence of other metal ions (50 µM). (b) (I) full 1H NMR of (10) (5 mM) (II) showing deprotonation of –OH protons, broadening and very small shift in other signals of (10), when treated with Cu(II) (5mM) in DMSO-d6.

Figure 3.32. Showing the reversibility of the response of (10) towards Cu(II).

3.4.3 Mechanism of complexation of (10) with Cu(II)

The complex formation of (10) and Cu(II) by the proposed mechanism (Figure 3.33) is confirmed by ESI-MS, UV and IR spectroscopy. The ESI-MS spectrum of the Cu-complex in the titration in DMSO shows a peak at m/z 1184.6730, which is assigned to \( [C_{51}H_{41}Cu_3N_6O_{10}S_3]^+ \) (calc. 1184.7368) (Figure 3.29). The UV spectrum of this complex in DMSO (Figure 3.34a) shows two bands at 354 nm (\( \epsilon_{\text{max}} = 2999 \text{ M}^{-1} \text{ cm}^{-1} \)) and at 438 nm (\( \epsilon_{\text{max}} = 2738 \text{ M}^{-1} \text{ cm}^{-1} \)), which may be assigned to ligand to metal charge transfer transitions. Another band lies at 684 nm (\( \epsilon_{\text{max}} = 241 \text{ M}^{-1} \text{ cm}^{-1} \)). A broad, low intensity band falling below 700 nm has been assigned to a d-d transition for Cu(II) in a square-pyramidal environment, which may be achieved in the present case due to additional coordination with nitrate and/or water molecules. The IR spectrum of the complex (Figure 3.34b) shows a shift of \( \nu_{C=N} \) band to a lower frequency by 15 cm\(^{-1}\), which clearly indicates the involvement of imine group in co-...
ordination to metal ion. A strong peak at 1385 cm\(^{-1}\) indicates the presence of nitrate ion in the complex.

**Figure 3.33:** Proposed mechanism for the Cu - complex formation of (10).

**Figure 3.34.** (a) UV-vis spectrum of Cu (II) complex (Solid separated) of (10) in DMSO. (b) IR Spectrum overlay of (10) and its Cu-complex.

### 3.4.4 Biological applications of (10)

In order to work as a sensor in biological medium, a compound should have a wide working range of pH. The fluorescence of (10) at 528 nm remains unaffected between pH 2.05 – 8.95 and decreases rapidly from 2.05 to 1.39 and 8.95 to 10.35. Hence, (10) can be used within the pH range 2.05 - 8.95 at room temperature, which is good enough to work in the biological medium. To investigate the applications of (10) as a chemosensor for Cu(II) recognition in biological medium, a microbe (*Saccharomyces cerevisiae*) was cultured in normal broth and secondly in experimental media containing Cu(II). The cells cultured in normal broth as well as cultured in a media containing Cu (II) were treated with (10) dissolved in a DMSO/H\(_2\)O (7:3, v/v) solvent mixture. Before performing microscopy observations, the microbe cells were washed with a DMSO/H\(_2\)O (7:3, v/v) solvent mixture. The microscopy images taken of (A) blank microbe cells, (B) microbe cells cultured in medium enriched with Cu(II)
(0.1M), (C) microbe cells cultured in normal broth and treated with (10) (10 µM), and (D) microbe cells cultured in medium enriched with Cu(II) (0.1M) and treated with (10) (10 µM) are shown in Figure 3.35.

![Microscopic Images](image)

**Figure 3.35.** Microscopic images of: (A) microbe cells cultured in normal medium (B) microbe cells cultured in medium enriched with Cu(II) (C) microbe cells cultured in normal medium and treated with (10) (D) microbe cells cultured in medium enriched with Cu(II) and treated with (10).

The microscopic investigations revealed that probe (10) is capable of binding Cu(II) in a cellular medium. The microscopic image (Figure 3.35) clearly shows that the sensor passed through the membrane of the microbe and bind in the cytoplasm enriched with Cu (II). The cell wall of any cell was not ruptured with the treatment of sensor as evident from the SEM image of the cells cultured with Cu(II) and then treated with (10) (Figure 3.36).

![SEM Image](image)

**Figure 3.36.** SEM images showing the surface morphology of microbe cells cultured with Cu(II) and then treated with (10), before performing microscopy, the cells were washed with a DMSO/H₂O (7:3, v/v) solvent mixture.
3.5 Anion recognition studies of mesitylene/anthracene anchored Schiff bases containing hydroxyl groups

Some neutral dipodal chemosensors containing mesitylene/anthracene as an anchor and hydroxyl (-OH) groups as binding units have been synthesized, characterized and evaluated as selective and sensitive sensors for anions.

3.5.1 Mesitylene based chemosensors and chemodosimeters

The development of anion sensing receptors\textsuperscript{18,19} has gained impetus due to better understanding of the role of anions in biological, environmental and chemical processes. Among various anions, fluoride and cyanide have been extensively studied owing to their importance in our life. There is always a need for developing sensors to monitor these anions, more so for having a multianalyte sensing chemosensor catering to more than one ion with their distinctive and selective responses. As most of the chemosensors for CN\textsuperscript{-} ion suffer from unsolicited interferences of other ions, specially the F\textsuperscript{-} ion therefore the selectivity is a paramount issue.\textsuperscript{20} The chemodosimetry approach for optical sensing involves the occurrence of a specific chemical reaction and a covalent bond formation prior to transducing an optical output signal.\textsuperscript{21} While there are fewer systems studied from this approach for the F\textsuperscript{-} ions it has been quite successfully used in the case of CN\textsuperscript{-} ions owing to its strong nucleophilicity.\textsuperscript{22} Despite all these reports the nucleophilic addition of CN\textsuperscript{-} on Schiff base’s imine bond has scarcely been studied. The closest examples to this system are the two chemodosimeters using salicyaldehyde hydrazone functionality\textsuperscript{23} where addition of cyanide to the imine bond of hydrazones has been suggested. In the present work, the synthesis and characterization of two mesitylene anchor based dipodal Schiff base systems incorporating catechol (11a) and phenol (11b) units as the end groups have been reported and exploited the anion recognizing ability of the -OH group in conjunction with the imine group. Receptor (11a) has been found to act as a naked-eye chromogenic and ratiometric fluorogenic sensor for F\textsuperscript{-} whereas it behaves as a dual channel chromogenic sensor and chemodosimeter depending on the concentration of CN\textsuperscript{-} ion, in DMSO. In water, it behaves as a highly selective sensor for CN\textsuperscript{-} ion only. Thus (11a) can be used to visually discriminate between the two ions. The phenol containing compound (11b) acts as an exclusive, naked-eye, concentration dependent chromo-fluorogenic sensor or a chemodosimeter for cyanide.
ion. Such a chemodosimeter response, to the best of our knowledge has been studied for the first time in a Schiff base and is attributed to the in-situ acid catalysis of the Strecker reaction (at the time of publication), giving addition of CN\(^-\) anion to the imine bond producing the corresponding nitrile [(chemodosimeter-I, CH-I), Scheme 3.2].

**Figure 3.37.** Changes in the UV-vis spectrum of (11a) in DMSO (10 \(\mu\)M) on the addition of various anions (100 \(\mu\)M).

### 3.5.1.1 Colorimetric and chromogenic response of (11a) and (11b)

The anion binding ability of receptor (11a) (10\(\mu\)M) was determined by the changes in its absorption spectra measured upon addition of various tetrabutyl ammonium anions, TBAX (where X = F, Cl, Br, I, NO\(_3\), CN, ClO\(_4\), ACO, HS\(_2\)O\(_4\) and H\(_2\)PO\(_4\)) in DMSO (100\(\mu\)M) (Figure 3.37). Upon addition of F\(^-\) and CN\(^-\), significant changes in the spectra were observed. With F\(^-\), the intraligand charge transfer (ICT) band\(^{24d,25}\) at \(\lambda_{\text{max}}\) 355 nm disappears and a new peak appears at \(\lambda_{\text{max}}\) 431 nm (\(\epsilon_{\text{max}}\) 7.3 \(\times\) 10\(^4\) M\(^{-1}\) cm\(^{-1}\)) with a concomitant color change from pale yellow to bright yellow. But in case of CN\(^-\), a new absorption peak appears at \(\lambda_{\text{max}}\) 445 nm with a lesser absorption (\(\epsilon_{\text{max}}\) 5.0 \(\times\) 10\(^4\) M\(^{-1}\) cm\(^{-1}\)) which then shifts to 469 nm (\(\epsilon\) = 5.5 \(\times\) 10\(^4\) M\(^{-1}\) cm\(^{-1}\)) which tails well up to 600 nm. The bathochromic shift increases with time (Figure 3.38a) and/ or with further addition of TBACN. The saturation causes the appearance of a new broad band at 500nm (\(\epsilon\) = 6.3 \(\times\) 10\(^4\) M\(^{-1}\) cm\(^{-1}\)). These spectral changes are accompanied with the visual color changes from pale yellow to bright yellow to reddish orange (Figure 3.38b). There are no visual or spectroscopic changes with Cl\(^-\), Br\(^-\), I, NO\(_3\), ClO\(_4\), ACO\(^-\), HS\(_2\)O\(_4\) and H\(_2\)PO\(_4\) ions.
Figure 3.38. Showing changes in (a) absorption (b) colors of (11a) on addition of tetrabutylammonium anions with time.

As (11a) responded to both F\(^-\) and CN\(^-\) ion therefore to have a better insight in the recognition phenomenon UV-vis titrations were performed. On gradual addition of aliquots of TBAF to 10 μM solution of (4) in DMSO (Figure 3.39a), a significant change observed even on addition of 1μM of anion, so the detection limit\(^{26}\) of fluoride has to be less than 1.5 μM. The reaction of (4) with TBAF gives a binding constant, K = 4.68 × 10\(^3\) M\(^{-1}\) and shows a 1:1 stoichiometry (Figure 3.40a and b).

Figure 3.39. Changes in UV-vis spectra of (11a) (10 μM) upon gradual addition of (a) TBAF (0-100μM) (b) TBAF (0-100μM). Inset shows chromogenic determination of (a) fluoride (b) detection after stepwise addition of respective anion in DMSO.

This reaction is completely reversible on addition of water in it as F\(^-\) ion is highly solvated in water and loses its basicity due to hydration. On the other hand, gradual addition of CN\(^-\) anion to (4) leads to a band at 445 nm at lower concentration (<37 μM), but at a higher concentration (from 37 to 700 μM) the latter shifts to a longer wavelength at λ\(_{\text{max}}\) 496 nm (Figure 3.39b). The stoichiometry of the reaction is 1:2 as found by the Job’s plot and a binding constant K =7.27 x10\(^3\) M\(^{-1}\) (Figure 3.41a and b).
The changes are fully reversible at lower concentrations of the anion but irreversible at the higher concentrations i.e. red color once attained does not disappear not even on addition of water. The detection limit of cyanide in solution of (11a) in DMSO was found to be less than 3 μM. Addition of TBAOH to (11a) causes changes similar to TBAF and no band at longer wavelength were found which means that the sensing involves deprotonation of the catechol moieties in the presence of more basic F⁻ ion in DMSO. In the case of CN⁻ ion which is a weaker base but a stronger nucleophile, it is proposed that deprotonation leads to nucleophilic attack at the –C=N bond. Thus (4) acts as a visual chromogenic chemosensor for F⁻ ion and a unique double channel operating sensor which behaves as a chemosensor for CN⁻ at a concentration ~40 μM (4 equivalents) and a ‘naked eye’, concentration or time dependent, chemodosimeter above it. Moreover the visual color changes within 2-3 minutes give selective response to F⁻ and CN⁻ anions and thus may be used for both anions.

Figure 3.40. Stoichiometry and Benesi-Hildebrand plot for (11a) with TBAF.

Figure 3.41. Stoichiometry and Benesi-Hildebrand plot for (11a) with TBACN.
3.5.1.2 $^1$H and $^{13}$C NMR Titration Experiments of (11a)

The proposed chemodosimeter is based upon the $^1$H and $^{13}$C NMR changes found on addition of 10 equivalents of TBAF and TBACN to a solution of (11a) in DMSO-d$_6$. Figure 3.42a shows the changes found in the aromatic region in the $^1$H NMR for (11a) on their addition. In both the cases the –OH signals have disappeared and the spectra show the expected up field shift in almost all the signals. Most significant, however is the disappearance of the imine signal at $\delta$ 8.875 and appearance of a doublet at $\delta$ 5.526 in the case of CN$^-$ but not in the case of F$^-$ ion (Figure 3.42b). These changes have been attributed to the occurrence of a Strecker’s reaction by nucleophilic addition of CN$^-$ ion on the imine bond resulting in the formation of a nitrile (CH-I, Scheme 3.2).

As it is well known that the poor reactivity of the imine bond requires activation for the satisfactory efficiency in the Strecker reaction and hence is generally activated by a Bronsted or Lewis acid by forming iminium ions in case of those imine groups which are not substituted by an activating group. In the present case, the potential H-bonding pocket defined by four catecholic –OH protons which have the potential to bind anions in a chelate mode, tends to bring the cyanide to their vicinity. Deprotonation of the –OH groups results in generation of H$^+$ ions which activates the imine group and a nucleophilic addition reaction of CN$^-$ occurs forming a nitrile.

![Figure 3.42](image_url)

*Figure 3.42.* (a) full (b) partial $^1$H NMR of (11a) in DMSO-d$_6$ (5 mM) showing changes on addition of F$^-$ and CN$^-$ anions. (A) Sensor alone (B) with TBAF (50 mM) (C) with TBACN (50 mM). [Labels used in the diagram are shown in Scheme 2.3].
Scheme 3.2. Proposed reaction mechanism for chemodosimeter (CH-I) formation.

The dependence of change on concentration of the anion suggests that deprotonation is just one step in a multi-step process. The doublet at $\delta 5.526$ is assigned to the amine proton and the corresponding signal due to imine proton disappears. The signal due to the proton attached to the chiral C is overlapped by the signals due to tetrabutyl ammonium cation. As the product (CH-I) obtained is a mixture of diastereomers with diastereomeric excess of one enantiomeric pair, therefore each signal in the NMR is accompanied by another signal of much lesser intensity. These observations are well supported by the changes in the $^{13}$C NMR of the addition product (Figure 3.43a) where the signal at $\delta 162.9$ ppm due to imine carbon is absent but a signal appears at $\delta 155$ ppm corresponding to the carbon of the added CN group (absent in DEPT-135) on the positive side (Figure 3.43b).

Figure 3.43. Showing the (a) $^{13}$C NMR (b) partial DEPT-135 of (11a) in DMSO-d$_6$ with TBACN in it, T represents signals due to TBA.
The signal due to the chiral $\alpha$-C (Scheme 1) is again overlapped by the signals of DMSO in $^{13}$C NMR spectrum but is clearly visible at $\delta$ 39.7 ppm in the DEPT on the positive side (Figure 3.43b). The electrospray ionization mass spectrum (Figure 3.44a) of this solution in DMSO shows a base peak at 786.85 which corresponds to $[(\text{CH-I})+\text{DMSO}+\text{Na}+1]^+$ (calculated 786.15) ion which clearly proves the formation of (CH-I) during the sensing experiment.

**Figure 3.44.** (a) Mass Spectrum of CN$^-$ adduct (CH-I) obtained on addition of TBACN in (11a) in DMSO (b) Showing the triplet characteristic for the presence of [HF$_2$]$^-$ anion on addition of 10 equiv. of TBAF in 5mM of sensor (11a).

Based on the above evidence it may be concluded that (11a) behaves as a chemodosimeter for CN$^-$ induced deprotonation. At low concentrations of the anion the nitrogen of the imine group is not protonated and the imine group is not activated for the nucleophilic attack by the CN$^-$ ion therefore (11a) behaves as a chromogenic sensor only. On the other hand due to the high basicity of the [HF$_2$]$^-$ ion which is produced in the presence of F$^-$ ion and is recognizable by the tell-tale triplet at 16.1 (Figure 3.44b) it acts as a chromogenic sensor for it.

### 3.5.1.3 Fluorogenic spectral response of (11a)

The fluorescence spectral changes of (11a) with various anions (Figure 3.45a and b) make it a highly selective fluorogenic sensor for F$^-$ ion with very small interference only from CN$^-$ ion which vanishes at higher concentration of analyte. The ligand does not have any fluorescence when excited at 350 nm but on the addition of TBAF an emission band appears at 560 nm with high intensity. This gives a fluorescent green color under UV lamp (Figure 3.45c) and the emission has been attributed to well-
known ESIPT phenomenon in such Schiff bases where the steady state emission is dominated by cis-keto tautomer formed after photoinduced proton transfer.\textsuperscript{29}

**Figure 3.45.** Showing (a) changes in the Fluorescence intensity (b) fluorescence ratio $[I/I_o]$ of sensor (11a) (5μM) at $\lambda_{max}$ 560 nm upon addition of various anions (50 μM) with excitation at 350 nm in DMSO. (c) Fluorescence color changes for (11a) with different anions, Sensor : analyte ratio 1:10, sensor conc. 5μM.

### 3.5.1.4 Colorimetric, UV-vis and Fluorogenic spectral response of (11b)

Among ten anions tested in DMSO, (11b) responded only to the CN$^-$ ion as is evident from the absorption (Figure 3.46) and emission bands (Figure 3.48a) resulting in a color change from almost colorless to yellow which moves towards reddish with time (Figure 3.47b). From the absorption spectra at 10 equiv of the added anion the band at $\lambda_{max}$ 350 nm is completely vanished and a new, very broad band starts appearing at 465 nm (Inset, Figure 3.47a). The detection limit of cyanide in solution of (11b) was found to be less than 3μM.

**Figure 3.46.** (a) Changes in the UV-vis spectrum of (11b) in DMSO (10 μM) on the addition of various anions (100 μM), Inset. Visual color changes. (b) Showing changes in UV-vis of (11b) (10 μM) in DMSO with gradual addition of TBACN, Inset- expanded increase in absorbance near 465 nm and chromogenic determination of cyanide detection.
Figure 3.47. Showing changes in (a) absorption (b) colors of (11b) on addition of tetrabutylammonium anions with time.

Figure 3.48. Showing Job’s plot and Benesi-Hildebrand Plot for addition of TBACN to (11b).

A comparison with the –OH ion shows that the channel working for sensing is similar to (11b) i.e. H-bonding at low concentration and due to deprotonation and chemodosimetry, at higher concentration (with a 1:2 stoichiometry and binding constant of $3.53 \times 10^2$ M$^{-1}$ (Figure 3.48a and b). The lesser sensitivity of (11b) towards chemodosimetry is expected due to phenol being less acidic than catechol and has one proton only, deprotonation and subsequent activation of the imine nitrogen is achieved at a higher concentration of CN$^-$ ion or after a longer reaction time than (11a). Due to this slow chemodosimeter response (11b) can be used as a very selective and sensitive chromo/fluorogenic sensor for CN$^-$ ion exclusively, transducing different naked eye chromo/fluorogenic responses at low and high concentrations of the anion.
Figure 3.49. Showing (a) changes in Fluorescence intensity of 443 nm band of (11b) on addition of TBACN, conc. 5μM, anions (1-10 equivalents) (b) the relative changes in intensity with various anions (c) Fluorescence color changes in (11b) with various anions.

The fluorescence spectra of (11b) exhibited emission bands at \( \lambda_{\text{ems}} \) 437 nm and \( \lambda_{\text{ems}} \) 545 nm. The intensity of the former band enhances up to ten folds on addition of TBACN (Figure 3.49a) but not with other anions (Figure 3.49b). This gives blue color fluorescence (Figure 3.49c) at very high anion concentration or after 24 hours. This effect may be due to PET phenomenon which is reduced when \(-\text{OH}\) is involved in H-bonding with the anion resulting in enhancement of signal.

Figure 3.50. ESIMS of CN adduct obtained on addition of TBACN in (11b) in DMSO.

3.5.1.5 \(^1\)H NMR Titration Experiments of (11b)

The \(^1\)H NMR and mass spectra (Figure 3.50) of the sensor with 20 and 30 equivalents of CN\(^-\) ion again shows (Figure 3.51) the absence of OH and imine signals, up field shift of aromatic protons, appearance of the \(-\text{NH}\) signal at \( \delta \) 5.69 ppm.
3.5.1.6 Colorimetric response of sensors in semi-aqueous medium

Since the chemodosimetric detection of CN⁻ ion is irreversible in water therefore the efficacy of (11a) and (11b) was checked in water by using aqueous solutions of (100 μM) TBACN, NaCN and NaSCN in a DMSO solution of (11a) and (11b) (10 μM, DMSO : water 2 : 1) which resulted in the similar response as in DMSO in the form of appearance of red color (Figure 3.52) in the solution.

In order to confirm this proposed mechanism (scheme 1), the nitrile product from (11a) and NaCN was synthesized, separated, purified and analyzed by ¹H NMR, IR and mass spectrometry (Figure 3.53). Apparently any hydrolysis of the nitrile formed into amino acid has not occurred because of the absence of any acid in the reaction medium at this stage.
Figure 3.53. (a) $^1$H NMR (b) IR (c) Mass spectra of (CH-I).
3.5.2 Anthracene based chemosensors

3.5.2.1 $^1$H NMR comparison of sensors (13a), (13b) and (13c)

$^1$H NMR spectra of these sensors (13a), (13b) and (13c) demonstrating ortho-para effect as the chemical shifts of two –OH groups in the three isomers (Table 3.2) follow a trend since using the same concentration (5mM), the α and β protons appear at a relatively higher frequency (in the meta isomer (13b) (Figure 3.54) which may be attributed to the –ortho, -para directing effect of the –OH groups, which causes shielding effect on the C atoms bearing them. The aromatic protons ‘q’ of meta isomer are also at a much higher frequency than those of ortho (13a) and para (13c) isomer, as they are shielded due to the presence of partial negative charge on them, owing to the +R effect of –OH groups.

**Table 3.2. Chemical Shifts in α, β protons of (13a), (13b) and 13c).**

<table>
<thead>
<tr>
<th>Sensor 13a(δ (ppm))</th>
<th>Sensor 13b(δ (ppm))</th>
<th>Sensor 13c(δ (ppm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-OH</td>
<td>β-OH</td>
<td>α-OH</td>
</tr>
</tbody>
</table>

**Figure 3.54.** $^1$H NMR of (A) (13a) (B) (13b) (C) (13c) at 5mM concentration of each sensor.

3.5.2.2 Colorimetric and UV-vis response of sensors

The anion binding ability of (13a) was determined by the measurement of changes in absorption spectra of (13a) when titrated with various tetrabutylammonium anions
such as F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, CN⁻, ClO₄⁻, CH₃CO₂⁻, C₆H₅CO₂⁻, H₂PO₄⁻ and HSO₄⁻ in DMSO (10µM) (Figure 3.55). Free sensor (13a) characterized by the presence of three absorption bands centered at $\lambda_{\text{max}}$ 357 nm ($\epsilon_{\text{max}}$ 24,300 M⁻¹ cm⁻¹), at $\lambda_{\text{max}}$ 396 nm ($\epsilon_{\text{max}}$ 23,400 M⁻¹ cm⁻¹) and at $\lambda_{\text{max}}$ 412 nm ($\epsilon_{\text{max}}$ 18,400 M⁻¹ cm⁻¹). These bands may be assigned as an intraligand or internal charge transfer (ICT) bands involving imine and hydroxyl group.³⁴d,2⁵ Upon addition of F⁻ and CN⁻, significant changes in the spectra were observed. With F⁻, the intensity of peak at 357 and 396 nm reduced and the peak at 412 nm showed bathochromic shift by ~23 nm. But in case of CN⁻, peak at 412 nm red shifted by ~10 nm only. These spectral changes are accompanied with the visual color changes from pale yellow to reddish orange. There are no visual or spectroscopic changes with other tetrabutylammonium anions such as CH₃CO₂⁻, C₆H₅CO₂⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, HSO₄⁻ and H₂PO₄⁻ ions. As (13a) showed bathochromic shift with both F⁻ and CN⁻ ion, therefore, to have a better understanding of the sensing mechanism, UV-vis titrations were performed. On progressive addition of aliquots of TBAF and TBACN to a 10 µM solution of (13a) in DMSO, the bands at 357 nm and at 396 decreases gradually and a red shifted band appears at $\lambda_{\text{max}}$ 435 nm ($\epsilon_{\text{max}}$ 37,900 M⁻¹ cm⁻¹) for F⁻ (Figure 3.56a) and at $\lambda_{\text{max}}$ 422 nm ($\epsilon_{\text{max}}$ 24,900 M⁻¹ cm⁻¹) (Figure 3.56b) for CN⁻ ion. This simultaneous change in wavelengths provides ratiometric response of (13a) for both F⁻ and CN⁻ ions (Inset, Figure 3.56(a) and (b)) with detection limits of 0.56 µM for F⁻ and 0.79 µM for CN⁻ ions. The 1 : 2 stoichiometry of the interaction of (13a) with TBAF and TBACN was determined by Job’s plot (Figure 3.57) and binding constants 1.08 x10⁴ M⁻¹ for F⁻ and 5.27 x10³ M⁻¹ for CN⁻ (Figure 3.58).

**Figure 3.55.** (a) Changes in UV-vis spectra (b) (A/A₀) of (13a) (10 µM) upon addition of 10 equivalent of various tetrabutylammonium anions in DMSO.
Figure 3.56. Showing changes in UV-vis of (13a) (10 μM) in DMSO with gradual addition of (a) TBAF (b) TBACN Inset. Titration profiles.

Figure 3.57. Job’s Plot showing 1:2 stoichiometries for (a) TBAF (b) TBACN.

Figure 3.58. Benesi-Hildebrand plot for (13a) with (a) TBAF (b) TBACN.

The above proposed deprotonation mechanism for sensing phenomenon was further confirmed by the $^1$H NMR titrations of (13a) with TBAF (Figure 3.59) and TBACN (Figure 3.60) in DMSO-d$_6$. With F$^-$ ion, the peaks for the α-OH and β-OH observed at 9.29 and at 13.24 ppm disappear completely even before the addition of one equivalent of TBAF, which indicate that the response of (13a) with fluoride ions is
through frozen proton transfer (acid-base process) and not through incipient proton transfer (H-bonding).

**Figure 3.59.** (a) partial $^1$H NMR of (13a) (5 mM) in DMSO-d$_6$ showing changes on addition of TBAF.

**Figure 3.60.** (a) partial $^1$H NMR of (13a) (5 mM) in DMSO-d$_6$ showing changes on addition of TBACN.

Such deprotonation phenomenon based fluoride ion sensors which also accompanied by colour change are well known for basic anions such as F$^-$ and H$_3$PO$_4$ and
moderately acidic functional groups such as -NH.\textsuperscript{30} The deprotonation process was further confirmed by the appearance of triplet at 16.1 ppm due to formation of HF\textsubscript{2}\textsuperscript{-} after addition of 2 equivalents of TBAF to (13a) in DMSO-d\textsubscript{6}. This anion-induced deprotonation of –OH protons increases the charge density in the system and results in upward shift of aromatic protons and protons of imine group. The polarity of the solvent (DMSO) and intrinsic acidity of sensor (13a) itself provide ideal conditions for double deprotonation of α and β – OH protons. Thus, both \textsuperscript{1}H NMR and UV-vis titrations revealed that the interaction of (13a) with F\textsuperscript{-} ion causes deprotonation of α and β – OH protons. The \textsuperscript{1}H NMR titration of (13a) with TBACN also provided similar results of deprotonation of α and β – OH protons and upward shift of aromatic protons which confirm deprotonation. To further prove this deprotonation phenomenon, the interaction of (13a) with TBAOH was checked in same solvent medium. With addition of 10 equivalents of hydroxide ion, the sensor (13a) showed similar bathochromic shift as in case of TBAF/TBACN (Figure 3.61), which means that the sensing involves deprotonation of the hydroxyl groups of (13a) in the presence of F\textsuperscript{-}/CN\textsuperscript{-} ions in DMSO.

![Figure 3.61. Showing changes in UV-vis spectrum of (13a) with TBA salts of CN\textsuperscript{-}, F\textsuperscript{-} and OH\textsuperscript{-} in DMSO.](image)

The sensing properties of (13b) and (13c) with anions were also explored with UV-vis absorption spectrometry. In the absence of anions, the UV-vis spectrum of (13b) (20 μM) was characterized by the presence of three absorption maxima at λ\textsubscript{max} 364 nm (ε\textsubscript{max} 39,000 M\textsuperscript{-1} cm\textsuperscript{-1}), at λ\textsubscript{max} 385 nm (ε\textsubscript{max} 41,000 M\textsuperscript{-1} cm\textsuperscript{-1}) and at λ\textsubscript{max} 406 nm (ε\textsubscript{max} 35,300 M\textsuperscript{-1} cm\textsuperscript{-1}). When titrated with tetrabutylammonium anions under study in DMSO, it responded only to the F\textsuperscript{-} ion with very small interference only from CN\textsuperscript{-} (Figure 3.62(a) and (b)). From the absorption spectra at 10 equivalents of the F\textsuperscript{-} ion,
the peak at \( \lambda_{\text{max}} 364 \text{ nm} \) was completely vanished and a new peak appears at \( \lambda_{\text{max}} 426 \text{ nm} \) (\( \epsilon_{\text{max}} 61,700 \text{ M}^{-1} \text{ cm}^{-1} \)) (with a 1 : 2 stoichiometry and binding constant of 2.27 \times 10^3 \text{ M}^{-1} ) (Figure 3.63(a) and (b)). This ratiometric response due to simultaneous increase and decrease in intensity of absorption bands was also accompanied with a color change from almost colorless to yellow.

**Figure 3.62.** (a) Changes in UV-vis spectra (b) \((A/A_o)\) of \((13b)\) (10 \(\mu\)M) upon addition of 10 equiv. of various tetrabutylammonium anions in DMSO.

**Figure 3.63.** (a) Showing changes in UV-vis of \((13b)\) (10 \(\mu\)M) in DMSO with gradual addition of TBAF (b) Benesi-Hildebrand plot for \((13b)\) with TBAF.

**Figure 3.64.** (a) Changes in UV-vis spectra (b) \((A/A_o)\) of \((13c)\) (10 \(\mu\)M) upon addition of 10 equiv. of various tetrabutylammonium anions in DMSO.
In case of (13c), free sensor exhibits absorption maximum centered at $\lambda_{\text{max}}$ 398 nm ($\epsilon_{\text{max}}$ 26,700 M$^{-1}$ cm$^{-1}$) along with a shoulder at $\lambda_{\text{max}}$ 417 nm ($\epsilon_{\text{max}}$ 23,700 M$^{-1}$ cm$^{-1}$). Among eleven anions tested in DMSO, (13c) responded only to the F$^-$ ion as revealed from the absorption bands (Figure 3.64(a) and (b)) resulting in color change from almost colorless to reddish yellow. With F$^-$ ion, absorption spectrum showed slight increase in the intensity of band at 398 nm and appearance of a new broad band at $\lambda_{\text{max}}$ 574 nm. The stability constant, $K = 4 \times 10^3$ M$^{-1}$ for the interaction of (13c) with F$^-$ ions (with 1 : 2 stoichiometry) was calculated by using Benesi-Hildebrand plot (Figure 3.65(a) and (b)). The detection limits of (13b) and (13c) for F$^-$ ion were found to be 0.66 $\mu$M and 1.6 $\mu$M respectively.

Figure 3.65. (a) Showing changes in UV-vis of (13c) (10 µM) in DMSO with gradual addition of TBAF (b) Benesi-Hildebrand plot for (13c) with TBAF.

Competitive selectivity of (13b) and (13c) for F$^-$ was determined by UV-vis titrations with F$^-$ in the presence of other TBA anions under study, which revealed that F$^-$ can be detected in the presence of other competitive anions (Figure 3.66(a) and (b)).

Figure 3.66. Competitive Selectivity of (a) (13b) (b) (13c) (10µM) towards F$^-$ ions (10 equivalent) in the presence of 100 equivalent of other anions under study.
3.5.2.3 $^1$H NMR titration experiments of (13a), (13b) and (13c)

The sensing mechanism of interaction of (13b) and (13c) with TBAF was further investigated with $^1$H NMR titrations.

![Figure 3.67](image1.png)

**Figure 3.67.** (a) partial $^1$H NMR of (13b) (5 mM) in DMSO-d$_6$ showing changes on addition of TBAF.

![Figure 3.68](image2.png)

**Figure 3.68.** (a) partial $^1$H NMR of (13c) (5 mM) in DMSO-d$_6$ showing changes on addition of TBAF.

Both sensors show deprotonation of $\alpha$ and $\beta$ – OH protons accompanied with the upward shift of aromatic and imine protons (Figure 3.67 and Figure 3.68). The deprotonation phenomenon was also confirmed by the existence of a triplet at 16.171 ppm for (13b) and at 16.155 ppm for (13c).
The above $^1$H NMR and UV-vis studies revealed that sensor (13a) showed spectral and visible response for both F$^-$ and CN$^-$ ions, (13b) showed significant response for F$^-$ ion with very little interference from CN$^-$ ion whereas (13c) responded to F$^-$ ions. This selectivity trend of sensors may be attributed to the chelating capability of catechol moiety which can chelate both the anions equally well. This fact is supported by the supramolecular arrangement of the sensors owing to the intermolecular H-bonding. As evident from the crystal structure of 13b it consists of zig-zag linear chains due to intermolecular H-bonding between meta –OH groups (Figure 3.8). Though X-ray structures of 13a and 13c are not available but from crystal engineering point of view a similar linear chain type of crystal structure is anticipated for 13c also due to H-bonding between consecutive para –OH groups. Just like 13b, 13c would also have a $R_2^2(4)$ H-bonding synthon$^{31}$ as shown in Figure 3.69 (b) and (c) respectively for this supramolecular arrangement. However, 13a, because of catechol groups would give two such $R_2^2(4)$ synthons for forming linear H-bonded tapes in this case (Figure 3.69(a)). The latter is thus pre-organised to form the well-documented,$^{32}$ chelating environment (Figure 3.70) for the guest anions which is equally suitable for F$^-$ and CN$^-$ ions.

**Figure 3.69.** Showing H-bonding interactions in (a) (13a) (b) (13b) and (c) (13c).

**Figure 3.69.** Interaction of TBAF/TBACN with Sensor (13a).
Conclusions

- A tripodal Schiff base sensor (10) containing mesitylene as anchor and hydroxyl groups and nitro groups as end units in conjugation, elicits high selectivity and sensitivity towards Cu(II) in HEPES buffer.
- The high selectivity of sensor towards Cu(II) is attributed to a high thermodynamic stability of the copper(II)-sensor complex, due to the presence of proper chelation sphere of N, O and S atoms.
- The copper-induced changes can be used for the quantification of Cu(II) down to a concentration of 3.16 nM on fluorimeter and 0.2 µM on spectrophotometer.
- The microscopic studies of (10) reveal that it has no cytotoxic effect and thus can be used as an efficient sensor in biological systems also.

Two mesitylene based Schiff base, dipodal receptors containing hydroxyl groups have developed as F⁻ and CN⁻ ion sensors. Catechol based sensor (11a) works for both F⁻ and CN⁻ ions, albeit through different channels in DMSO. Its colorimetric response may be used to discriminate between the two anions within two minutes whereas its fluorogenic response may do so instantaneously and with high sensitivity. In DMSO: water (11a) behaves as a colorimetric sensor exclusively for CN⁻ ion.

- The phenol based sensor (11b) is a highly selective one for CN⁻ ion and may be used as a semi quantitative chromo/fluorogenic sensor sensing CN⁻ with colorimetric and fluorogenic responses for different CN⁻ ion concentrations.
- The chemodosimeter response of these sensors towards CN⁻ ion is due to the Strecker’s nucleophilic addition to imine bond of the Schiff bases.

Three anthracene based Schiff base receptors appended with hydroxyl groups have been constructed and evaluated as F⁻ and CN⁻ ion sensors.

- (13a) shows spectral and visible response for both F⁻ and CN⁻ ions, (13b) shows significant response for F⁻ ion with very little interference from CN⁻ ion whereas (13c) is highly selective to F⁻ ions only. The change in selectivity from (13a) to (13c) may be attributed to the chelating ability of the catechol group.
References


