SUMMARY

PHOTORESPONSIVE MOLECULAR CHEMOSENSORS AND CHEMIONICS BASED ON (HETERO)-AROMATICS

The need to develop chemosensors for different target analytes is well-recognised and is confirmed by the considerable research efforts spent for the preparation of more and more efficient sensory devices\(^1\). The ease to monitor in situ analyte concentrations in real time and, eventually, in real space has enabled wide-spread applications of chemosensors in many fields, such as environmental monitoring, process control, food and beverage analysis, medical diagnosis, and lately, in monitoring toxic gases and explosives for security reasons. It is evident that all these fields are of great importance from a social and economic point-of-view, and this makes the demand for the development of sensory devices even more urgent.

In the present research work, the tailor made design and synthesis of photoresponsive (absorption or emission or both) molecules has been carried out. The photophysical behavior of the synthesized molecules towards varied in-puts viz. anions, cations, pH, acid or base etc. has been investigated. The optical out-puts achieved during these investigations have been elaborated in terms of applications of these molecules in selective qualitative / quantitative analysis of the target analytes and as chemionics. The results of these investigations have been presented in chapters 2-4 which is preceded by brief review of literature on anion sensors in chapter 1

CHAPTER-2

Quaternary Ntirogen Based Chromo-fluorescent Anion Sensors

For the development of anion receptors, the molecular architectures involving at least one of the ligating sites as the positively charged centre have found the special attention. The presence of relatively stronger electrostatic interactions with negative charged species in cooperation with other binding sites has caused remarkably increased binding affinities in comparison to the neutral receptors. The presence of such a charged centre creates further the

advantage in terms of higher solubility of the respective receptor in polar media and water. The varied approaches used for creating such entities involve the alkylation of various nitrogen containing heterocyclic moieties leading to pyridinium, imidazolium, benzimidazolium etc functionalities or the (multiple) alkylation of primary, secondary or tertiary amines to built quaternary ammonium salts. In the present investigations, the chemosensor possessing quaternary amine, imidazolium and pyridinium groups as one of the interacting sites have been synthesized and the findings have been discussed in three sections as given below.

Section 2.2 Quaternary ammonium salt based chromogenic and fluorescent chemosensors for fluoride ion

The chemosensors 5-7 have been synthesized by the reaction of amines 1 and 2 with aryl halides in ethanol at 80 °C (scheme 1).

![Scheme 1](image)

Chemosensors 5-7 possessing quaternary ammonium nitrogen and N-H units undergo visible color change from yellow to pink on addition of fluoride ions. The absorption bands of 5 and 6 centered at 310 nm and 480 nm underwent red shifts to 340 nm (Δλ_max = 30 nm) and 515 nm (Δλ_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 hours, the color of the solution turned fluorescent green (figure 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 with its tail extended to 710 nm closer to near IR region.

Chemosensors 5 and 6 on excitation at 450 nm exhibited emission band at λ_em 580 nm. On addition of F⁻ ions to 5 and 6 the intensity of 580 nm emission band completely turned off along with appearance of two new blue shifted fluorescence emission bands at 505 and 540 nm.

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nm. However, chemosensor 7 on addition of fluoride ions shows only the fluorescence quenching. The addition of the other anions, e.g. Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3\)\(^-\), CH\(_3\)COO\(^-\), HSO\(_4\)\(^-\), H\(_2\)PO\(_4\)\(^-\) and ClO\(_4\)\(^-\) do not cause any significant change in the absorption and emission spectra of 5-7.

![Figure 1: (a) UV-Vis spectra of 5 (50 \(\mu\)M) in CH\(_2\)CN : DMSO (9:1) (a) 5 only, (b) 5 + F\(^-\) (500 \(\mu\)M) (immediately), (c) 5 + F\(^-\) (500 \(\mu\)M) (after 24 h). Inset shows the respective colour changes.](image1)

![Figure 2: Fluorescence emission spectra of (a) 5 (50 \(\mu\)M) (b) 6 (50 \(\mu\)M) in CH\(_2\)CN: DMSO (9:1) upon addition of fluoride ions.](image2)

On incremental addition of F\(^-\) ions to chemosensor 5, 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 can be used for estimation of 1000 – 1500 \(\mu\)M fluoride ions and other anions do not interfere in its estimation.

**Section 2.3 Imidazolium based chromofluorescent probes for the selective estimation of acetate ions in protic medium\(^3\)**

The chemosensors 9 and 10 have been synthesized on heating 1-(chloroacetylamido)-anthracene-9,10-dione with respective 1-benzylimidazole and 1-dodecylimidazole in DMSO (scheme 2).

![Scheme 2](image3)

\(^3\) Kumar, S.; Luxami, V.; Kumar, A. *Org. Lett.* **2008**, *10*, 5549-5552
The chemosensor 9 (50 μM, CH₃CN:DMSO (20:1)) exhibited two absorption bands at $\lambda_{\text{max}}$ 308 nm ($\varepsilon$ 8200) and 405 nm ($\varepsilon$ 6600). On addition of tetrabutylammonium fluoride (TBA F) (100 μM, 2equiv.) to the solution of 9, the colour of the solution changed from light yellow to orange and the absorbance at 405 nm underwent gradual decrease in its intensity with concomitant increase at 480 nm with isobestic points at 370 nm and 440 nm (figure 2a).

![Figure 2](image)

**Figure 2**: (a) Effect of incremental addition of fluoride ions on UV-Vis spectrum of 9 (50 μM) in CH₃CN: DMSO (20:1) (b) Effect of incremental addition of acetate ions on UV-Vis spectrum of 10 (50 μM) in CHCl₃: MeOH (1:1).

In order to evaluate the role of the dodecyl chain in 10 on its association with anions in the presence of protic solvents, solution of 10 in CHCl₃ – MeOH (1:1) does not show any spectral or colour change on addition of F⁻ ions but on addition of AcO⁻ ions, the absorbance at 405 nm underwent gradual decrease in its intensity with concomitant increase at 475 nm (figure 2b) and other anions do not affect the absorption spectrum of 10.

![Figure 3](image)

**Figure 3**: Fluorescent color changes on addition of anions (left). Effect of incremental addition of fluoride ions on fluorescence spectrum of 9 (10 μM) in CH₃CN. Inset shows plot of fluorescence intensity Vs [F⁻] (points show the experimental results and line is curve fit) (right).
Chemosensor 9 (10 µM, CH$_3$CN: DMSO (20:1)) on excitation at 410 nm exhibited an emission band at $\lambda_{em}$ 480 nm. On addition of fluoride ions (20 µM), the fluorescence intensity at 480 nm (green emission) was turned off and simultaneously a new red shifted fluorescence emission band at 580 nm (red emission) appeared ($\Delta\lambda_{max}$ 100 nm) (figure 3). The colour of the solution under UV-Vis radiations appeared red due to 580 nm emission band. Similarly, in case of chemosensor 10 the addition of acetate shows the new emission band at 580 nm with simultaneous quenching of emission band at 480 nm.

The switching “OFF-ON” behavior at 480 nm and 580 nm on addition of F$^-$ to solution of 9 and acetate ions to solution of 10 provides a dual emission channel for elaborating a ratiometric approach. The ratio of emission intensities ($I_{580}$ / $I_{480}$) of 9 (CH$_3$CN) shows 60-fold emission ratio change and can be used to estimate F$^-$ ions between 2 µM – 40 µM. The chemosensor 10 (CHCl$_3$-MeOH :: 1:1) shows 23-fold emission ratio change and can be used to estimate acetate ions between 2 µM - 25 µM.

**Section 2.4 Pyridinium based internal electric field driven chromofluorescent chemodosimeter for fluoride ion**

The chemosensor 12 has been synthesised by heating 1-(chloroacetylamido)-anthracene-9,10-dione with pyridine in DMSO (scheme 3)

Probe 12 (50 µM, CH$_3$CN: DMSO:: 20:1) exhibits two absorption bands at $\lambda_{max}$ 310 nm ($\varepsilon$ 13720) and at 410 nm ($\varepsilon$ 5760). On addition of tetrabutylammonium fluoride (TBAF) (75 µM, 1.5 equiv.) to the solution of 12, its color changed from pale yellow to dark pink (figure 4b), which on further addition of TBAF (500 µM) turned bright green (figure 4c).

**Scheme 3**

![Scheme 3](image)

**Figure 4:** UV-Vis spectra of 12 (50 µM) in CH$_3$CN : DMSO (20:1) (a) only 12 (b) 12 + F (75 µM) (c) 12 + F (500 µM) (d) 12 + F (500 µM) after 24 hrs.

4 Luxami, V.; Kumar, A.; Hundal, M. S.; Kumar, S.; *Sensor Actuator B*, 2009, 0000
The addition of water to dark pink solution of 12-F mixture reversed the colour change to colourless. The bright green colour obtained at higher concentrations of F\textsuperscript{-} ions was not reversed on addition of water but turned to fluorescent green with $\lambda_{\text{max}}$ 460 nm on standing for 24 hrs (figure 4d). Therefore, chemosensor 12 behaves as a chemosensor for [F\textsuperscript{-}] < 75 µM and as a chemodosimeter for [F\textsuperscript{-}] > 75 µM.

**Figure 5:** (a) Effect of incremental addition of fluoride ions on fluorescence spectrum of 12 (1 µM, CH\textsubscript{3}CN – DMSO::1000:1). Inset shows plot of fluorescence intensity (FI) Vs [F\textsuperscript{-}] (points show the experimental results and line is curve fit). (b) Effect of incremental addition of fluoride ions on $^1$H NMR spectrum of 12

Probe 12 (1 µM, CH\textsubscript{3}CN – DMSO: 1000:1) on excitation at 400 nm exhibited a weak emission band centered at 510 nm. The intensity of this emission band gradually increased with the gradual increase in concentration of F\textsuperscript{-} ions and a plateau was achieved after the addition of 6 µM fluoride ions (figure 5).

In case of $^1$H NMR spectrum of 12, on addition of fluoride ions, the most of the signals of chemosensor shifted up-field. The most significant up-field shift was observed on H-17, H-18 and H-19 ($\Delta \delta \sim 0.25$) signals (figure 5b). On addition of 6 equiv. of TBAF to 12, the solution became non-fluorescent dark green and a new peak at -84.9 ppm in addition to that at -49.0 ppm appeared in its $^{19}$F spectrum which could be assigned to electric field created by accumulation of fluoride ions around quaternary nitrogen. Its $^1$H NMR spectrum shows the peaks in the region 5-6.5 ppm due to olefinic protons arising due to addition of F\textsuperscript{-} ions on pyridinium ring. Fluorescence changes in probe 12 enables selective estimation of 0.5 µM – 5 µm fluoride ions - the desirable concentration range for the maximum contaminant level of fluoride ions for drinking water (0.2 µM) as suggested by the U.S. environmental protection agency.
CHAPTER-3
Hydroxy-arylbenzimidazole Derivatives as Molecular Sensors

Amongst different emission based signalling mechanisms (ICT, PET, MLCT, ESIPT) available for recognition of target analyte using supramolecular chemistry, the excited state intramolecular proton transfer (ESIPT) attains a special status due to presence of competitive inter and intramolecular H-bonding, dual emission and large stokes shift of the ESIPT band. This phenomenon is quite prominent in case of hydroxyaryl benzimidazoles. In the present chapter it was envisaged that stimuli induced bathochromic or hypsochromic shift of these normal and ESIPT based emission channels can further open new emission channels and thus can provide opportunity for simultaneous estimation of multiple analytes using different emission channels. The findings of these investigations have been discussed in proceeding sections 3.2-3.4.

Section 3.2 Competitive intra- and intermolecular proton transfer in 3-(1H-benzimidazole-2-yl)-naphthenol-2-ol and its derivative: Ratiometric fluorescence sensing of fluoride and zinc ions

Chemosensors 1 and 4 have been synthesized by 1: 1 and 1:2 condensation of 3-hydroxy-2-naphthoic acid and 2,2’-dihydroxy-[1,1’]-binaphthalenyl-3,3’-dicarboxylic acid 3 with 1,2-diaminobenzene, respectively (scheme 1).

![Scheme 1](image)

Chemosensor 1 (0.5 µM, CH₃CN) on excitation at λ_max 330 nm exhibits two emission bands at λ_max 375 nm and 575 nm. The longer wavelength emission at 575 nm is typical of ESIPT emission band and shorter wavelength emission band at 375 nm is due to the normal emission.

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of chemosensor 1. On addition of fluoride ions two new emission bands appeared at 425 nm and 500 nm (figure 1).

**Figure 1**: The effect of incremental addition of F⁻ ions on the fluorescence spectrum of 1 (0.5 µM, CH₃CN)

Figure 2: The effect of incremental addition of F⁻ ions on the fluorescence spectrum of receptor 4 (0.25 µM, CH₃CN).

Chemosensor 4 (0.25 µM, CH₃CN) on excitation at 330 nm mainly exhibits a 586 nm (ESIPT) emission band and only a weak emission around 380 nm. In the solution of 4 (0.25 µM, CH₃CN), on addition of fluoride ions, the fluorescence at 586 nm gradually decreased with increasing concentrations of fluoride (up to 20 equiv.) along with the appearance of a new blue shifted emission band at 515 nm. The intensity of emission band at 515 nm gradually increased with increasing concentration of fluoride (figure 4) and went off scale above 100 equiv. of fluoride anion. The addition of Cl⁻, Br⁻, I⁻, NO₃⁻, CH₃CO₂⁻, HSO₄⁻, H₂PO₄⁻ and ClO₄⁻ anions (1000 equiv.) showed only a small decrease (<15%) in fluorescence spectra of chemosensors 1 and 4.

**Figure 3**: Effect of Zn²⁺ on the fluorescence spectrum of fluorophore 1 (0.5 µM) at pH 7.0 ± 0.1 (10 mM HEPES in CH₃CN:H₂O 4:1, v:v).

**Figure 4**: Effect of Zn²⁺ on fluorescence spectrum of fluorophore 4 (0.1 µM) at pH 7.0 ± 0.1 (10 mM HEPES in CH₃CN:H₂O 4:1, v:v).
Both fluorophore 1 and 4 give ratiometric fluorescent changes on addition of Zn\(^{2+}\) ions. The fluorophore 1 at pH 7.0 ± 0.1 (10 mM HEPES in CH\(_3\)CN:H\(_2\)O 4:1, v:v) shows nearly 50 times increase in ratio of I\(_{590}\)/I\(_{480}\) and can be used to estimate 100 nM to 6 µM of Zn\(^{2+}\). The fluorophore 4 (10 mM HEPES in CH\(_3\)CN:H\(_2\)O 4:1, v:v) shows nearly 120 times increase in ratio of intensity at 585 nm and 480 nm (I\(_{590}\)/I\(_{480}\)) and can be used to estimate 100 nM to 1.3 µM of Zn\(^{2+}\). The emission of 1 and 4 remains unaffected by the addition of other metal ions.

**Section 3.3 3-(3H-Imidazo [4, 5-b]pyridine-2yl)-naphthalen-2-ol and 2-(3H-Imidazo[4,5-b]pyridine-2-yl)-phenol: Ratiometric fluorescence probes for fluoride and copper ions.**

The chemosensor 5 and 6 have been synthesized by the 1:1 condensation of 2,3-diamino pyridine with 3-hydroxy-2-naphthoic acid and 2-hydroxybenzaldehyde respectively (scheme 2).

**Scheme 2**

![Scheme 2](image)

**Figure 5:** Effect of incremental addition of fluoride ions on the fluorescence spectrum of 5 (1 µM, CH\(_3\)CN).

Chemosensor 5 (1 µM, CH\(_3\)CN) on excitation at 300 nm exhibited an emission band at \(\lambda_{em}\) 395 nm. On addition of fluoride ions (2 µM), the fluorescence intensity at 395 nm remained unaffected but lead to the formation of two new emission bands at 540 nm and 340 nm (figure 5). Chemosensor 6 showed the emission band at 480 nm which on addition of fluoride ions is enhanced with addition of 20 nM fluoride ions, which is the lowest concentration of fluoride ions to be estimated by any fluorescent recognition process. The addition of Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3\)\(^-\), CH\(_3\)COO\(^-\), HS\(_2\)O\(_4\)\(^-\), H\(_2\)PO\(_4\)\(^-\) and ClO\(_4\)\(^-\) anions (0.01 M) to solution of 5 / 6 caused insignificant changes to its fluorescence spectrum.

Chemosensor 5 (1 µM, CH\(_3\)CN) on gradual addition of Cu(ClO\(_4\))\(_2\), the emission intensity at 390 nm underwent gradual decrease with concomitant increase at 460 nm (figure 6) and
achieved the plateau with 2 µM of Cu$^{2+}$ ions and provides the opportunity for the ratiometric sensing of copper ions which is the rare phenomenon for the paramagnetic metal ions.

![Figure 6](image1.png)  
**Figure 6:** (a) Effect of incremental addition of Cu$^{2+}$ on fluorescence spectrum of 5 (1µM, CH$_3$CN).

![Figure 7](image2.png)  
**Figure 7:** (a) Effect of incremental addition of Cu$^{2+}$ on absorption spectrum of 6 (10 µM, CH$_3$CN).

However, chemosensor 6 showed only the small fluorescence quenching but in the absorption of chemosensor 6 (10 µM, CH$_3$CN) provides the ratiometric approach for sensing the copper ions (figure 7). The addition of other metal ions does not affect the UV-Vis or fluorescence spectrum of 5 and 6.

**Section 3.4 2-(2-Hydroxyphenyl)-1H-anthra[1,2-d]imidazole-6,11-dione: Differential intramolecular charge transfer (ICT) based ratiometric chromogenic probe for F$, \text{Cu}^{2+}$ and \text{Zn}^{2+}$ ions.**

The receptor 7 has been synthesized by heating the mixture of 1,2-diaminoanthracene-9,10-dione and 2-hydroxybenzaldehyde in PEG (polyethylene glycol) at 120 °C (scheme 3).

![Scheme 3](image3.png)  
**Scheme 3**

![Figure 8](image4.png)  
**Figure 8:** Visible color changes on addition of different anions and metal ions and their combinations

![Figure 9](image5.png)  
**Figure 9:** (a) Effect of incremental addition of fluoride ions to 7 (20 µM, CH$_3$CN) on its absorbance spectrum.
Chemosensor 7 (20 µM, CH₂CN) exhibits the absorption band at λ\text{max} 400 nm (ε 15000). On gradual addition of TBA F to the solution of 7 (20 µM, CH₂CN), the absorbance at 400 nm underwent gradual decrease in its intensity with concomitant increase in absorbance at 465 nm (ε = 10850, Δλ = 65 nm) associated with isobestic points at 365 nm and 435 nm. This is also associated with visible change in color from pale yellow to orange (figure 8). The red shift of 65 nm points to the significant stabilization of excited state by ICT due to interaction of 7 with fluoride ion.

Chemosensor 8 (20 µM, CH₂CN) exhibits absorption band at 420 nm and on addition of anions it did not show any visible colour change or change in its absorption spectrum even on addition of TBA OH (10 equiv.). This observation clearly points that the deprotonation from OH is responsible for color change.

Figure 10: Effect of incremental addition of Zn²⁺ ions to 7 (20 µM, CH₂CN) on its absorbance spectrum.

Figure 11: Effect of incremental addition of Cu²⁺ ions to 7 (20 µM, CH₂CN) on its absorbance spectrum.

On addition of solution of Cu²⁺, chemosensor 7 shows the ~140 nm red shift from λ\text{max} 400 nm to 540 nm which induces the colour change from yellow to magenta. However on addition of Zn²⁺, a red shift of ~ 95 nm from 400 nm to 495 nm caused the color change from yellow to pink (figure 8). The addition of other metal ions even at 0.01 M concentration caused negligible responses to the color of the chemosensor 7.

The titration of chemosensor 7 with Cu²⁺ and Zn²⁺ shows that it forms 1:1 stoichiometric complex with Cu(ClO₄)₂ to give new λ\text{max} at 540 nm and with Zn(ClO₄)₂ forms 1:2 (7-Zn²⁺) complex associated with λ\text{max} at 495 nm. The addition of fluoride ions to the 7-Zn(ClO₄)₂ complex restored the original spectrum of chemosensor 7 but in case of 7-Cu(ClO₄)₂ complex on addition of fluoride ions showed the further red shift of absorption band to 600 nm.
CHAPTER 4

Miniaturization of chromo-fluorescent chemionics based on ortho-hydroxyaryl-benzimidazole

The fundamental features in chemionic information system are molecular recognition and changes in the molecular structure. In an attempt to develop bottom-up electronics, there has been an increasing interest in using molecules to construct miniaturized electric circuits that would be 1 million times smaller than the corresponding micrometer-scale digital logic circuits fabricated on conventional solid state semiconductor chips. It will allow to construct ultra-high density molecular circuitry that has great impact in computer science. To achieve this target different molecular devices to perform the AND, OR, XOR, XNOR, INHIBIT, and NAND fundamental Boolean functions have been developed. The combinatorial logic functions have been used to miniaturize the molecular half-adder, half-subtractor, full-adder and full-subtractor etc. The present chapter discusses the elaboration of different logic gates and combinatorial circuits using hydroxyaryl benzimidazoles.

Section 4.4 3,3’-bis-(1H-benzimidazolyl-2-yl)-[1,1’]binaphthenyl-2,2’-dil : Elaboration of molecular half-subtractor and reconfiguration to other fundamental Boolean operators

Fluorophore 1 (0.5 µM, CH₃CN) on excitation at 330 nm gave emission maxima at 585 nm with a stokes shift of 255 nm attributed to ESIPT from phenolic OH to benzimidazole nitrogen. On addition of perchloric acid (HClO₄, as acid) (5 µM), the emission at 585 nm was completely quenched and a new emission band at 435 nm with hypsochromic shift of 150 nm appeared (figure 1b). On addition of tetrabutylammonium hydroxide (TBA OH, as base OH⁻) (5 µM) to the same solution, the emission at 585 nm was reappeared.

![Chemical Structures and Fluorescence Spectrum](image)

**Figure 1**: The effect of acid and base on the fluorescence spectrum of fluorophore 1 in CH₃CN (a) 1 (0.5 µM) (b) 1 + HClO₄⁻ (5 µM) (c) 1 + TBA OH (5 µM) and (d) 1+ HClO₄ (5 µM) + TBA OH (5 µM).

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6 Luxami, V.; Kumar, S. New J. Chem. 2008, 32, 2074-2079
The addition of TBA OH (5 µM) to solution of 1 gave new hypsochromically shifted emission band at 515 nm ($\Delta \lambda = 70$ nm) (figure 1c) with concomitant quenching at 585 nm. This process was reversed on addition of HClO$_4$ (5 µM) (figure 1d).

<table>
<thead>
<tr>
<th>Input</th>
<th>Output (emission)</th>
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<tbody>
<tr>
<td>OH$^-$</td>
<td>INH (B) 435 nm</td>
</tr>
<tr>
<td>0 0</td>
<td>0 (low, 73)</td>
</tr>
<tr>
<td>0 1</td>
<td>1 (high, 812)</td>
</tr>
<tr>
<td>1 0</td>
<td>0 (low, 126)</td>
</tr>
<tr>
<td>1 1</td>
<td>0 (low, 80)</td>
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</table>

**Figure 2:** Schematic presentation of two in-puts based half-subtractor logic circuit. Truth table for fluorophore 1 for operation of the molecular half-subtractor with INH (B) and XOR (D) combination.

Binary half-subtractor operation of 1 can also be explained by monitoring the emission intensities at two different wavelength 515 nm (INHIBIT) and 475 nm (XOR) (figure 1). In these binary subtraction function, XOR gate output (monitoring wavelength: $\lambda_{\text{em}} = 475$ nm) is the difference digit (D) and the INHIBIT gate (monitoring wavelength: $\lambda_{\text{em}} = 515$ nm / 435 nm) is the borrow digit (B). The integration of XNOR logic at 585 nm with INHIBIT gate at 515 nm leads to half-subtractor (figure 2). Similarly, XNOR (585 nm) can be combined with INHIBIT at 435 nm to make the combinatorial half-subtractor.

**Figure 3:** The effect of acid and base on the fluorescence spectrum of 2 in CH$_3$CN (a) 2 (1 µM) (b) 2 + HClO$_4$ (5 µM) (c) 2 + TBA OH (5 µM) and (d) 2 + HClO$_4$ (5 µM) + TBA OH (5 µM).

Fluorophore 2 (1 µM, CH$_3$CN) on excitation at 330 nm gives two emission maxima at 385 nm and 585 nm respectively due to normal emission and excited state intramolecular proton transfer (ESIPT) emission. The addition of tetrabutylammonium hydroxide (TBA OH
as base) (5 µM) to solution of 2 gave two new emission bands at 440 nm and 510 nm (figure 3c). Both these emission bands were reversed on addition of HClO₄ (5 µM). On addition of perchloric acid (HClO₄) (5 µM) to the solution of 2 (1 µM, CH₃CN) a new emission band at 455 nm with hypochromic shift (Δλ = 130 nm) appeared (figure 3b). Therefore the emission output of 2 at 510 nm is turned “ON” (output = 1) only in the presence of OH⁻ as input. For all other circumstances (figure 3), the output signal at 510 nm is 0 and thus leads to INHIBIT gate at 510 nm. XOR gate in case of 2 is elaborated with output signal at 475 nm. The output at 475 nm is high, i.e., 1, with either of the inputs H⁺ (acid) or OH⁻ (base). These observations of XOR (475 nm) and INHIBIT (510 nm) functions have been compiled and lead to molecular half-subtractor with negative logic function. Fluorophore 5 (0.5 µM, CH₃CN) on excitation at λmax 330 nm gave emission maxima at 455 nm which on addition of HClO₄ underwent quenching with concomitant appearance of new emission band at 405 nm while addition of TBA OH (base) showed only small enhancement in emission at 455 nm. Therefore, 5 cannot be used for elaboration of combinatorial logic gates.

**Figure 4**: (a) Fluorescence emission spectra of fluorophore 1 under input conditions (a) I (0.5 µM, CH₃CN only; b) I + Cu²⁺ (2 µM); c) I + F⁻ (25 µM); d) I + Cu²⁺ (10 µM) + F⁻ (25 µM). (b) Presence of different logic functions on addition of different concentrations of Cu²⁺ ions to the solution of 4 in CH₃CN and F⁻ (25 µM).

On using three different concentrations of Cu²⁺ in the presence of 25 µM of fluoride ions and 0.5 µM of fluorophore 1, three different emission channels of logic gates are activated. At 2 µM [Cu²⁺] only NOR gate exists at 585 nm; at 5 µM [Cu²⁺] both NOR (585 nm) and INHIBIT (515 nm) Boolean operations become active and at 10 µM [Cu²⁺] along with NOR (585 nm) and INH (515 nm) operations, an additional emission channel at 400 nm representing AND logic operation is emerged (figure 4).
Section 4.5 3-(3H-Imidazo [4, 5-b] pyridine-2yl)-naphthalen-2-ol and 2-(3H-Imidazo [4, 5-b] pyridine-2-yl)-phenol: Superimposed molecular keypad lock and half-subtractor / adder implications

On excitation at 300 nm, fluorophore 6 (1 µM, CH₃CN) exhibited an emission band at λₑₐₚ 395 nm. On addition of fluoride ions (2 µM), the fluorescence intensity due to 6 at 400 nm remained unaffected but gave two new emission bands; the one with a red shifted emission maxima at 540 nm (Δλₑₚₐₓ 145 nm) and at 330 nm (Δλₑₚₐₓ 65 nm) (figure 5b).

On addition of Cu²⁺ (2 µM) to the mixture of 6 and F⁻ ions, the emission bands at 540 nm and 320 nm were reversed and an emission spectrum similar to that of fluorophore 6 was achieved (figure 5d). On addition of Cu²⁺ (2 equiv) to 6 (1 µM, λₑₓ 300, CH₃CN) the fluorescence intensity at 400 nm was turned off with simultaneous appearance of a new red shifted emission band at 460 nm (green emission) (Δλₑₚₐₓ 60 nm). On addition of F⁻ (2 µM) to the mixture of 6 and Cu²⁺ ions, the emission band at 460 nm due to 6-Cu²⁺ complex remained unaffected (figure 1e). Therefore, the spectral changes achieved on addition of F⁻ ions to the solution of 6 could be reversed on addition of Cu²⁺ ions (sequence-1), but the spectral changes achieved on addition of Cu²⁺ to the solution of 6 remained unaffected by the addition of F⁻ ions (sequence-2). The emission at 400 nm on adding F⁻ (IN₁) and Cu²⁺ ions (IN₂) (the sequence 1) elaborates IMP (IMPLICATION) logic operation.

Figure 5: The effect of F⁻ ions and Cu²⁺ on the fluorescence spectrum of 6 (1 µM, CH₃CN) (a) 6 only; (b) 6 + F⁻ (2 µM); (c) 6 + Cu²⁺ (2 µM); (d) 6 + F⁻ (2 µM) (IN₁) + Cu²⁺ (2 µM) (IN₂); (e) 6 + Cu²⁺ (2 µM) (IN₁) + F⁻ (2 µM) (IN₂).

Figure 6: Visual Sequence dependence password entry to access the fluorescence at 400 nm.

On adding Cu\(^{2+}\) (IN\(_1\)) and F\(^–\) ions (IN\(_2\)) (sequence 2) to the solution of 6, the two inputs act in an non-anhiliating mode leads to molecular scale elaboration of INV (INVERTER) logic function. The sequential logic operation with memory function can be constructed as password entry. The combination of inputs gives the password “NET”. On inverting the addition sequence to Cu\(^{2+}\) and F, an obvious fluorescence quenching (OFF, designated as the character “D”) is observed. This input sequence gives the word “END” which itself shows the end of emission at 400 nm and implies only “NET” password which opens the emission at 400 nm (figure 6).

This addition of F\(^–\) and Cu\(^{2+}\) ions as stimuli to the solution of 6 also elaborates superimposed half-subtractor combinatorial logic circuit with difference digit at 460 nm and borrow digit at either 320 nm or at 540 nm using emission mode (figure 7).

![Figure 7: Molecular scale implementation and truth table for the operation of half-subtractor using fluorophore 6](image)

<table>
<thead>
<tr>
<th>Input</th>
<th>Output (emission)</th>
</tr>
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<tbody>
<tr>
<td>F(^–)</td>
<td>Cu(^{2+})</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
</tr>
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<td>1</td>
<td>0</td>
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<td>1</td>
<td>1</td>
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</table>

![Figure 8: The effect of Cu\(^{2+}\) and base on the absorption spectrum of fluorophore 7 in CH\(_3\)CN (a) 7 (10 \(\mu\)M) (b) 7 + Cu\(^{2+}\) (20 \(\mu\)M) (c) 7 + TBA F (100 \(\mu\)M) and (d) 7+ Cu\(^{2+}\) (20 \(\mu\)M) + TBA F (100 \(\mu\)M).](image)

Fluorophore 7, on using absorbance as output channels and Cu\(^{2+}\) and TBA OH as two inputs provides the opportunity for the simultaneous elaboration of INHIBIT (390 nm), AND (350 nm) and XOR (265 nm) logic operations. INHIBIT and XOR logic function on combination provide the opportunity for the elaboration of molecular half-subtractor and AND and XOR logic functions in combination elaboration of molecular half-adder. Thus, the simultaneous
presence of addition and subtraction functions provides the opportunity for the elaboration of molecular calculator through absorbance (figure 8).

The emission channel of fluorophore 7 using acid and base as inputs are activated to elaborate molecular half-subtractor. Significantly, this molecular half-subtractor is elaborated at 1 nM concentration of the fluorophore 7 and uses only 10 nM concentration of TBA OH or HClO4. This constitutes the molecule which has been elaborated at lowest concentration of any fluorophore.

<table>
<thead>
<tr>
<th>Input</th>
<th>Output (emission)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^+) H(^+)</td>
<td>INH (B) 410 nm</td>
</tr>
<tr>
<td>0 0</td>
<td>0 (low, 67)</td>
</tr>
<tr>
<td>0 1</td>
<td>1 (high, 840)</td>
</tr>
<tr>
<td>1 0</td>
<td>0 (low, 95)</td>
</tr>
<tr>
<td>1 1</td>
<td>0 (low, 93)</td>
</tr>
</tbody>
</table>

**Figure 9**: The effect of acid and base on the fluorescence spectrum of fluorophore 7 in CH\(_3\)CN (a) 7 (1 nM) (b) 7 + HClO\(_4\) (10 nM) (c) 7 + TBA OH (10 nM) and (d) 7 + HClO\(_4\) (10 nM) + TBA OH (10 nM).

Fluorophore 7 exhibits XOR logic function at 450 nm and two INHIBIT logic functions at 410 nm and 520 nm. These functions have been compiled in truth table and lead to molecular half-subtractor (figure 9).

**Section 4.6 2-(2-Hydroxyphenyl)-1H-anthra[1,2-d]imidazole-6,11-dione:**

Reconfigurable, resettable and superimposed moleculator

The absorption output of probe 8 at 465 nm is turned “ON” (output = 1) only in the presence of TBA F as input. For all other circumstances, the output signal is turned “OFF” (output = 0) (figure 10). These outputs correlate well with INHIBIT logic gates at 465 nm. The output at 495 nm is high, ie., 1, with either of the inputs Cu\(^{2+}\) or TBA F. Further, two simultaneous inputs in the form of Cu\(^{2+}\) and F\(^-\) ions work in non-annihilating mode and further shift the absorption band to 600 nm. This observation correlates well with XOR logic gate (500 nm) as it generates an “ON” output when either input is “ON”; but not when both inputs are either “ON” or both are “OFF”. These observations of XOR (500 nm) and INHIBIT (465 nm) functions have been compiled in truth table and lead to molecular half-subtractor.
Figure 10: UV-Vis spectra of probe 8 (20 µM, CH₃CN) (a) only 8; (b) 8 + TBA F (80 µM); (c) 8 + Cu²⁺ (20 µM); (d) 8 + Cu²⁺ (20 µM) + TBA F (80 µM).

<table>
<thead>
<tr>
<th>Input</th>
<th>Output (absorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻Cu²⁺</td>
<td>INH (B) 465 nm</td>
</tr>
<tr>
<td>0 0</td>
<td>0 (low, 0.170)</td>
</tr>
<tr>
<td>0 1</td>
<td>0 (low, 0.231)</td>
</tr>
<tr>
<td>1 0</td>
<td>1 (high, 0.442)</td>
</tr>
<tr>
<td>1 1</td>
<td>0 (low, 0.19)</td>
</tr>
</tbody>
</table>

Figure 11: Molecular scale implementation and truth table for the operation of half-adder and half-subtractor using probe 8.

When the absorption output at 610 nm is monitored, it is in the “ON” state only if both the inputs are present. In all other circumstances it remains in “OFF” state. Thus 610 nm wavelength correlates well with the AND logic function. These observations of XOR (495 nm) and AND (610 nm) functions have been compiled in truth table and lead to molecular half-adder (figure 11).

Figure 12: UV-Vis spectra of probe 8 (20 µM, CH₃CN) (a) only 8; (b) 8 + TBA F (80 µM); (c) 8 + Zn²⁺ (20 µM); (d) 8 + Zn²⁺ (20 µM) + TBA F (80 µM).

When the chemical input is switched from Cu²⁺ to Zn²⁺, the algebraic logic is reconfigured from half-adder and half-subtractor to half-subtractor and comparator because on simultaneous inputs in the form of Zn²⁺ and F⁻ annihilate each other’s action regenerating the absorption spectrum of 8 at 400 nm (figure 12).