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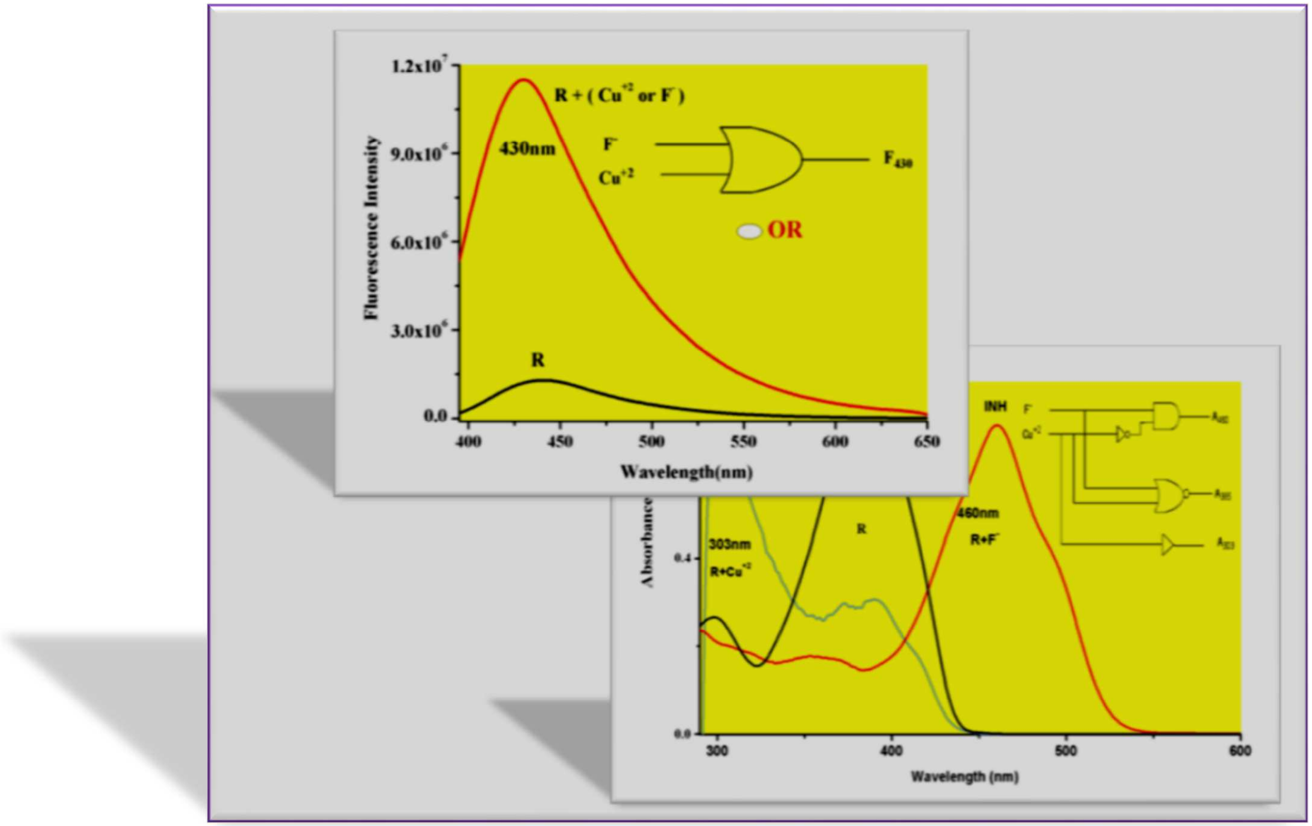
Napthyl-based Schiff base mimics logic functions through selective dual-ion recognition and fluorescence "ON" at a single wavelength.



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LETTER

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A Molecular Boolean mimic with OR, NOR, YES and INH functions: Dual-ion Recognition driven Fluorescence “turn on”†

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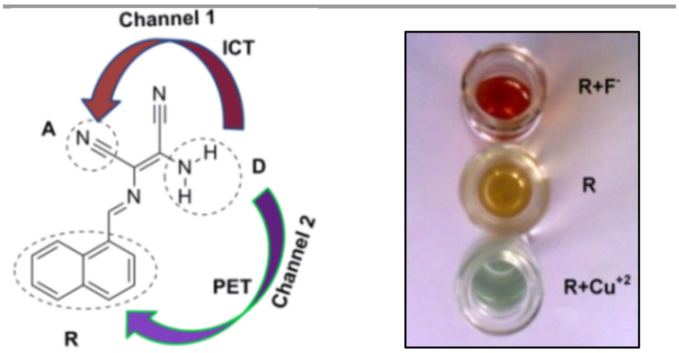
Napthyl-based Schiff base (R) has been explored as a dual-ion receptor for Cu^{+2} and F^{-} with fluorescence “turn on” response at a single wavelength. The changes are attributed to the modulation of ICT and PET processes. The recognition behaviour demonstrates R as a Boolean mimic for computation of OR, NOR, YES and INH functions with a convenient reset mechanism.

Miniaturization of information storage and processing technology has urged integration of logical functions at molecular level in recent decades.[1] Despite a lot of efforts, [2,3] molecular-scale electronics is undergoing a gradual evolution via simple molecular switches, or logic gates.[4] Construction of multiple and complex Boolean operations, such as INH, OR, NOR, etc., from these simple and minute molecular architectures remains an important goal to suffice the above requirement. Although some success has been achieved through functional integration,[5]but these strategies result in molecular complexity, compute logical functions in absorption or emission mode only, require tedious and sophisticated fabrication procedures which are costly and suffer with resetting problems.[6] Apart, there are only a few reports wherein simple molecular systems were designed, which are capable of integrating simple logic gates into combinatorial circuits and performing complex logical functions in dual mode.[7] Such type of operations are important for realization of complex information processing.[8] So there is a need for development and exploration of new and simple molecular scaffolds with ease of fabrication, multiply-configurable, capable of computing complex logical operations and convenient to reset.[9] Receptor molecules obtained through simple synthetic procedures with colorimetric and fluorescence ‘turn on’ behaviour, simultaneously performing dual-ion recognition and hence multiple logical arithmetic are the first choice for any chemist perceiving modulation of molecular devices.

In our endeavour to develop a simple molecular arithmetic machine sufficing above criteria, we looked forward to π-conjugated organic chromophores with extended charge transfer (ICT) and electron transfer (PET) properties.[10, 11] These systems usually exhibit very high sensitivity to the external perturbations in the form of anions and cations.[12] With these considerations in mind, 2-amino-3-((E)-(napthalen-1-ylmethylene) amino) maleonitrile (**R**) was brought under study (Fig. 1a). The later has been intensively studied for non-linear optics (NLO), optical data storage devices and organic light emitting diodes (OLED). However, to the best of our knowledge, there are no reports with the same moiety in the realm of ion recognition and molecular arithmetic.



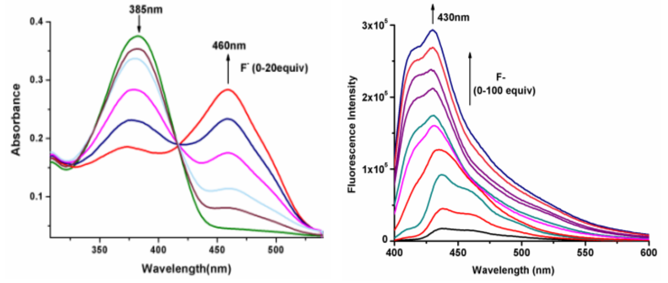
(a) (b)

Fig. 1 (a) Molecular structure of receptor **R** with PET and ICT channels assigned. (b) Visual changes of **R** with Cu^{+2} and F^{-}.

R was obtained by a new and simplest ever synthetic procedure. It involves equimolar addition of methanolic solution of diaminomalenonitrile (DMN) to a stirring solution of 1-napthaldehyde in water, containing a catalytic amount of concentrated HCl. A yellow-colored solid got precipitated immediately.

Absorption spectra of **R** in dry tetrahydrofuran (THF) shows a characteristic CT band centered at 385nm. UV-Vis titration experiments of R with a pool of competitive anionic species like, F^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, PF_6^-, AcO^- in the form of tetra butyl ammonium salts (TBA) confirmed selective recognition of F^-. Upon addition of TBAF (0.05mM) to R (4µM), a red shift of 75nm was observed with appearance of a new band at 460nm showing a clear isosbestic point at 418nm (Fig. 2a). These changes were visibly marked with intense coloration of R from yellow to red (Fig. 1b). A 1:1 stoichiometry of R and F^- was obtained with the help by Job's plot (SI). The above changes can be attributed to the enhancement in the CT transitions due to hydrogen-bond donor interaction of $–NH_2$ moiety with F^- followed by deprotonation at high concentrations. The deprotonation mechanism was supported by addition of TBAOH to the receptor solution; spectral changes similar to F^- were observed (fig. 5 in SI). The mechanism of interaction can be explained in terms of strong basicity of F^- in non-aqueous environments along with a polarized –N-H moiety as a result of electron withdrawing –CN groups.[13] The equilibrium is further driven by the formation of thermodynamically stable HF_2^- dimer.[14] Unique basicity of F^- in polar aprotic solvents like THF, DMSO, etc. compared to other anions, imparts selectivity for the given interaction.

R on excitation at 385nm in presence of F^- results in fluorescence 'turn on' response at 430nm which intensifies with further additions (Fig. 2b), as a result of strong CT through the Channel 1 resulting in prevention of photo induced electron transfer (PET) from $–NH_2$ to napthyl moiety (Fig. 1a). Apart, very high sensitivity and a near-linear correlation of R with F^- demonstrates its applicability for fluoride analysis within 1-10µM concentrations (figure. 7 in SI).



(a) (b)

Fig. 2 (a) Absorption changes of **R** (4×10^{-6} M) in THF on addition of 0-20 equivalents of TBAF (0.05mM). (b) Emission spectra of **R** (4×10^{-6} M) with 0-100 equivalents of TBAF (0.05mM) on excitation at 385nm. All these experiments were carried at 298K.

The interaction was further probed through ^{1}HNMR titration of **R** in d_6-DMSO with TBAF. Addition of TBAF resulted in broading of $–NH_2$ peak at 8.01ppm along with appearance of new $–NH^-$ signal at 7.36ppm which intensifies with further additions, implicating a clear two-step mechanism of F^- interaction with $–NH_2$ moiety (See Fig. 4 in SI).

R is also associated with a 1, 2-diamine chelating site, well known to bind with heavy transition metal ions like, Cu^{+2}, Fe^{+3},etc.[15] Titration of **R** with different cationic species like, Fe^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}, Mn^{+2}, Fe^{+3}, Pb^{+2}, Cd^{+2}, etc., in dry THF solution, revealed that **R** interacts selectively with Cu^{+2}, even in presence of 100-fold concentrations of others. Addition of Cu^{+2} (0.01mM) resulted in prominent and visible colour change of receptor solution from yellow to blue. In absorption spectra, it was accompanied by decrease in absorption at 385nm with a concomitant appearance of a new broad band at 303nm showing a clear isosbestic point at 364nm. Formation of stable and unsaturated-five membered ring complex **C** blocks the electron- withdrawing ability of –CN groups (Fig. 3), which in turn results in inhibition of CT across the system and hence a shift towards shorter wavelengths shown in figure 4a.

On the basis of Job's studies in absorption experiments at 303nm, a 1:1 complexation was observed between **R** and Cu^{+2} (SI). Similar type of behaviour was observed on addition of Cu^{+2} to the deprotonated state **B** of **R.** Interaction was further evaluated by emission spectra**,** were Cu^{+2} was the only species that resulted in strong emission at 430nm (Fig. 4b). These observations confirm the PET process through channel 2 due to coordination of Cu^{+2} with **R** and formation of Receptor-metal complex **C** and hence a fluorescence " turn on" response.

The instantaneous response of Cu^{+2} binding event with **R** reflects its importance for Cu^{2+} analysis within 10-20µM concentrations (figure. 6 in SI).

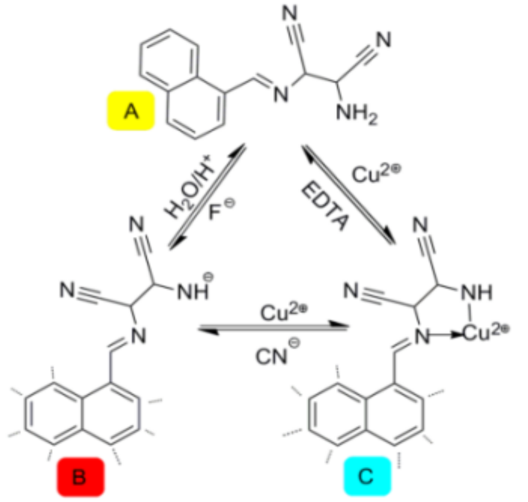
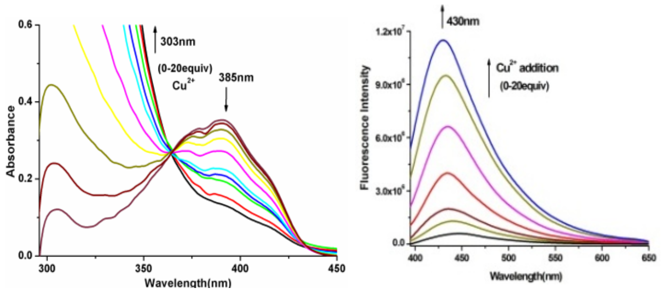


Fig. 3 Interaction of **R** with Cu^{+2} and F^- and reset mechanism.

From the above observations, it is clear that **R** acts a highly selective dual-ion recognition system for F^- and Cu^{+2} with a fluorescence 'turn on' response at 430nm along with multiple colorimetric outputs. On this basis, R was explored for logical arithmetic with Cu^{+2} and F^- as chemical inputs under different combinations. The inputs and outputs were coded with binary digits '0' for 'OFF' and '1' for 'ON'.



(a) (b)

Fig. 4 (a) Absorption changes of **R** (4 × 10^{-6} M) in THF with addition of 0-20 equivalents of Cu^{+2} (0.01 mM). (b) Emission spectra of **R** (4 × 10^{-6} M) with 0-100 equivalents of Cu^{+2} (0.01mM) on excitation at 385nm. All these experiments were carried at 298K.

While monitoring changes in absorption and emission, R performs various logic operations. Presence of either of the inputs (F^- or Cu^{+2}) changes the absorption spectra of R; hence representation of a signal amplification response (YES) at A303 and A460.[16,17] However in two-input operation mode with various combinations of Cu^{+2} and F^-, more complex and multiple logical operations can be obtained through absorption and emission outputs. Absorption signal at 385nm can only be read in the absence of any input, which results in the NOR operation at A385. Presence of F^- results in absorption and emission response at 460nm and 430nm respectively.

However input in the form of Cu^{+2} masks the 460nm absorption signal, but triggers the output signals at 303nm along with 430nm emission. These observations implicate construction of YES and OR logical operations at A303 and F430 in absorption and emission mode respectively. Since presence of Cu^{+2} blocks the output signal generated by F^- in absorption mode. Hence construction of inhibit function (INH) at A460 (Fig. 5a). INH function is neither commutative nor associative, it can be viewed as a two input AND gate, one whose input lines contains an inverter, In the present case input signal Cu^{+2} acts as an inhibitor for absorption signal at A465. Apart from this, strength of INH is also acknowledged in combination with YES and NOR, leading to the construction of an additional combinatorial logical circuit in absorption mode shown in figure 5b.

Finally, each state of **R** can be reset through control inputs in form of H^+/H_2O, EDTA and CN^- to the corresponding initial states as shown in figure 3. Addition of H^+ and trace amount water revert **B** back to **A**. This can be attributed to the protonation of **B** and strong hydration enthalpy of F^-.[18] State **C** can be reverted to **A** with the addition of EDTA and equilibrium is driven by the formation of stable Cu^{+2}.EDTA complex.[19] Similarly, **C** to **B** equilibrium can be reverted back by the addition of CN^- in the form of tetrabutylammonium cyanide (TBACN) solution in dry THF. It is well established that CN^- has a strong binding affinity to Cu (II) ion due to the formation of stable $[Cu(CN)_X]^{n-}$ complex.[20] Hence the given molecular system has a promising reset property which makes it an ideal candidate in the field of ion recognition and molecular electronics.

Inputs		Outputs			
F^-	Cu^{2+}	Absorption			Fluorescence
		A_{303}	A_{385}	A_{460}	F_{430}
0	1	1	0	0	1
1	1	1	0	0	1
1	0	0	0	1	1
0	0	0	1	0	0
Functions		YES	NOR	INH	OR

(a)

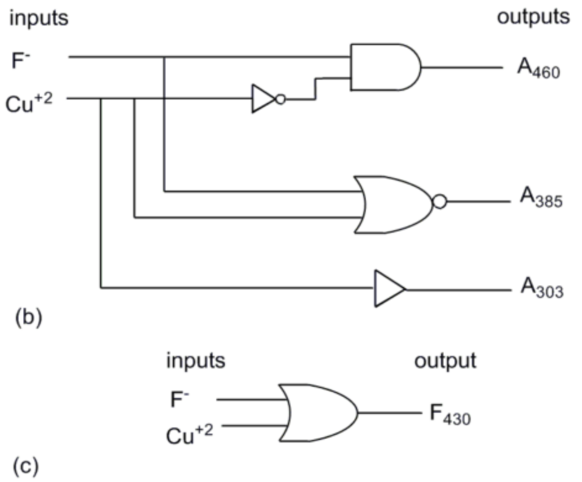


Fig. 5 (a) Truth table for the computation of various logical functions from R with Cu^{+2} and F^- as chemical inputs under different combinations. (b) Representation of combinatorial circuit from YES, INH and NOR gates in absorption mode and (c) OR gate in emission mode.

In summary, we have explored a simple DMN Schiff base (R) as a highly selective receptor for F^- and Cu^{+2} with fluorescence “turn on” at a single wavelength. We demonstrated its application as a Boolean mimic, which can be multiple-configured to construct a number of outputs in dual mode, under various combinations of chemical inputs. As a result, multiple and complex logical operations like OR, NOR, YES and INH have been performed. Apart, a combinatorial logical circuit has also been in absorption mode. Most importantly R can be reset at each and every state with appropriate chemical signals, which is a real drawback with most of the existing molecular mimics. We believe that the given molecular fabrication adds a new direction towards design of potential materials to obtain promising logic information at molecular level.

Experimental Section

Starting materials including 1, 2-Diaminimalenonitrile and 1-napthaldehyde purchased from Sigma Aldrich were used without further purification. However catalytical amount of HCl involved in the reaction was obtained from Merck. Methanol solvent was used as purchased from commercial sources without further purification. Synthesis of compound **R** was carried out in open air conditions at ≈ 298K. THF solvent used for mechanistic study was dried over Sodium metal prior to the use.

Synthetic procedure involves drop wise addition of DMN (50mg, 0.46mmol) (methanolic solution) to same equivalent of 1-napthaldehyde (71mg, 0.46mmol) in distilled water containing 1-2 drops of conc. HCl. An immediately solidified imine **(R)**, was filtered, recrystalization with ethanol/water mixture (v/v 50%) and finally characterized by NMR (^{1}H NMR, ^{13}C NMR) and HR-MS. **R** (Yellow coloured, 95% yield); ^{1}H NMR- (500MHz; d$_6$-DMSO): δ 8.97 (s, 1H), 8.01 (s, 2H), 8.76 (d, J = 10Hz, 1H), 8.42 (d, J = 10Hz, 2H), 8.10 (d, J = 5Hz, 1H), 8.04 (d, J = 5Hz, 2H), 7.70 (t, J = 15Hz, 1H),7.65 (t, J = 10Hz, 1H), 7.62 (t, J = 10Hz, 1H), ^{13}C NMR- (500MHz; d$_6$-DMSO): δ 153.95, 133.87, 132.66, 131.20, 130.60, 129.70, 129.33, 128.39, 127.34, 126.85, 125.99, 123.79, 11.96, 114.31, 104.04. HR-MS (negative mode) found 248.088 for C$_{15}$H$_{10}$N$_4$ and Calcd. 248.106

Structural and mechanistic aspects were confirmed with NMR (^{1}H and ^{13}C NMR), 400 MHz from Bruker. Mass spectral analysis was recorded on a Bruker instrument (HR-MS spectrometer). UV-Vis absorption studies were done with Perkin Elmer spectrophotometer, lambda 25. Emission studies were done with the help of Horiba Jovin Vyon Fluoro log 3-111 spectrophotometer. Graph plotting and curve fitting was done in Origin Pro 8.

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Notes and references

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†Electronic Supplementary Information (ESI) available: [^{1}H NMR, ^{13}C NMR, ^{1}HNMR titration, Jobs plot and absorption studies]. See DOI: 10.1039/c000000x/

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