NJC

PAPER

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Cite this: *New J. Chem.*, 2014, **38**, 1484

Dual colorimetric receptor with logic gate operations: anion induced solvatochromism†

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Received (in Montpellier, France) 8th October 2013,
Accepted 12th December 2013

DOI: 10.1039/c3nj01229h

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A receptor R1 was designed and synthesised for colorimetric detection of F^- ions as well as Cu^{2+} ions *via* intramolecular charge transfer mechanism. Upon addition of F^- ions in dry DMSO, the color of the receptor R1 changed from pale yellow to blue. The receptor showed a unique property of solvatochromism by displaying different coloration with different solvents only in the presence of F^- ions, which were applied to determine the percentage composition of binary solvent mixtures. The receptor R1 was able to detect Cu^{2+} ions colorimetrically where it exhibited a color change from pale yellow to orange-red. In addition, the receptor was subjected to molecular logic gate applications, wherein it showed 'ON–OFF' switching operations.

Introduction

The design and synthesis of organic chemoreceptors for selective detection of anions and metal ions has gained the attention of scientists due to their prospective applications in the fields of biochemistry and environmental science.[1] In addition, the anions are associated with many other important aspects of supramolecular chemistry such as supramolecular gels, controlling pharmaceutical crystal growth and polymer templating in a simple organogelator.[2] Among all the anions, fluoride plays a vital role in clinical applications although there are disadvantages associated with it.[3] Therefore, the detection of fluoride has significance. Though instrumental methods such as fluoride ion monitor probes are available for the detection of fluoride ions, it consumes much time and requires skilled efforts to operate. On the other hand, colorimetric method of detection is instantaneous, and is equally selective and sensitive. Consequently, for the last couple of decades colorimetric anion receptor chemistry has been studied extensively.[4]

Similarly, researchers have devoted their efforts towards the design and synthesis of various receptors for the detection of hazardous metal ions.[5] Amidst the widespread transition metal ions, copper is distinctive as it is essential to the normal growth of living organisms.[6] However, at high concentration copper is toxic to various organisms including humans.[7] Generally, the detection of copper ion is carried out using complicated instrumental methods such as inductively coupled plasma mass spectroscopy,[8] atomic absorption spectroscopy[9] and X-ray photoelectronic spectrometry.[10] On the other hand, recently the detection of copper ions by colorimetric methods have attained prominence[11] due to various advantages such as selectivity, sensitivity and rapid detection over conventional methods of analysis using instruments. In addition, the quest for effective dual receptors that can detect both anions and cations are emerging and extensive efforts have been put forth to achieve the same.[12] Nevertheless, the colorimetric detection of both F^- and Cu^{2+} using the same chemoreceptor is a challenging task due to their different binding phenomena and needs to be explored. To introduce a dual sensing property to a receptor, the molecule should contain different binding sites that can accommodate F^- ions or/and Cu^{2+} ions.[13]

Being an essential component of molecular computing operations and molecular devices, molecular logic gates for converting chemical input signals into measurable output signals has become an exciting research area in supramolecular chemistry. Subsequently, increasing attention has been paid to logic gate applications based on anion/cation detecting receptors.[14] Various types of logic gate functions can be achieved by applying two-input systems. Even though molecular analogues of many logic gate functions (based on two-input systems) are reported in the literature,[15,16] only a few of them are based on colorimetric receptors.[17] Accordingly, the colorimetric receptor

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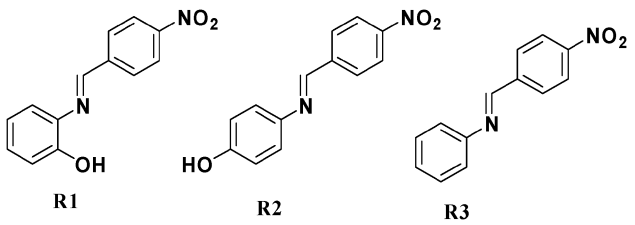
† Electronic supplementary information (ESI) available: ^1H NMR spectra of R1–R3, photographs, UV-vis spectroscopic titration studies of receptors R1, R2 with F^- ions and Cu^{2+} ions. UV-vis changes of R1, R2 and R3 with different anions and different cations. CCDC 912057 and 939305. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj01229h



Scheme 1 Molecular structure of receptors.

based molecular logic gates developed interest among supramolecular chemists.

As a part of our on-going research in designing the colorimetric receptors,[18] herein we report a receptor R1 (Scheme 1), which is capable of detecting anions as well as cations, to be specific F^- ions and Cu^{2+} ions with the naked eye instantaneously.

The receptor R1 encompasses a hydroxyl (–OH) functional group, which detects the F^- ion by a deprotonation mechanism, and phenolic oxygen (–O) along with imine nitrogen (=N) for the detection of Cu^{2+} *via* complex formation.[11e] R1 served as an effective receptor for the detection of the F^- ion as well as Cu^{2+} with the logic gate function. In addition, this receptor showed remarkable solvatochromic property by displaying different colors in different solvents only in the presence of F^- ions. This solvatochromic property of the receptor molecule has indispensable applications in many fields of chemistry including characterization of mixed solvent systems, solid surfaces and polymers, chemical sensors to detect the presence of water in polymers and to study the behaviour of solute–solvent interactions in supercritical fluids.[19] The receptor R2 was synthesised to verify the substitution position of –OH functional group in detection process and receptor R3 was synthesised to examine the role of –OH as a binding site.

Results and discussion

All the synthesised molecules were characterized by standard techniques. The single crystal of the receptors R1 suitable for X-ray difraction analysis was obtained by slow evaporation of dichloromethane solution at room temperature and the single crystal of receptor R3 was obtained directly from reaction media (ethanol used as solvent). The ORTEP diagrams (50% probability) of the receptor R1 and R3 are given in Fig. S7 (ESI†). The receptors R1 and R3 were crystallised in a monoclinic lattice. Detailed crystallographic data of receptor R1 and R3 are given in Table S1 (ESI†).

Colorimetric study of anions

Initially, the receptors R1 and R2 were evaluated for colorimetric detection of F^- ions over other anions (chloride, bromide, iodide, nitrate, hydrogensulfate, dihydrogenphosphate and acetate) in dry DMSO solvent. Both the receptors have hydroxyl (–OH) functionality as electron donors and nitro ($-NO_2$) functionality as electron acceptors. Due to this donor–acceptor (D–A) interactions these receptors are pale yellow in color. These receptors (5×10^{-5} M) were treated with tetrabutylammonium (TBA) salt of different anions (1 equiv.) in DMSO. A significant color change from pale yellow to blue (receptor R1) and greenish

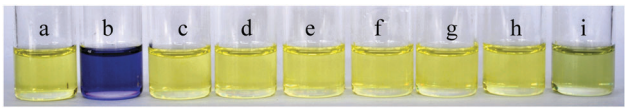


Fig. 1 Change in color of receptor R1 after addition of 1 equiv. of different anions as TBA salt to the receptor solution in DMSO (5×10^{-5} M). (a) Receptor R1, (b) F^-, (c) Cl^-, (d) Br^- (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) AcO^-.

blue (receptor R2) was observed instantaneously with the addition of F^- ions. A slight color variation from pale yellow to greenish yellow in the case of receptor R1 and pale yellow to dark yellow in the case of receptor R2 was observed upon adding the acetate ion. On the other hand, no color change was noticed upon addition of other anions (Fig. 1 and Fig. S9, ESI†). This colorimetric selectivity of receptors R1 and R2 for the detection of F^- ion was further confirmed using UV-vis spectroscopy (Fig. S25 and S26, ESI†).

In order to examine the selectivity towards F^- ion over other anions, 1 equiv. of F^- ion was added to the receptor R1 in the presence of other anions such as Cl^-, Br^-, I^-, NO_3^-, HSO_4^- and $H_2PO_4^-$ ions. The presence of any other anions makes virtually no difference on the colorimetric detection of the F^- ion (Fig. S15, ESI†). Thus, the receptor R1 could selectively detect the fluoride ion even in the presence of other competing anions.

UV-vis studies and binding mechanism

As part of the quantitative analysis, the UV-vis spectrophotometric titration of receptor R1 with TBAF in dry DMSO was carried out. Upon gradually increasing the concentration of F^- ions, the intensity of the peaks at 282 nm, corresponding to imine (–N=C–) linkage, and 385 nm, corresponding to –OH group, decreased gradually. This was followed by the appearance of new bathochromic bands at 339 nm and 555 nm (Fig. 2). The development of the new band at 339 nm was attributed to the formation of an exocyclic imine when the receptor undergoes enol to keto tautomerisation (due to the deprotonation of 2-hydroxy

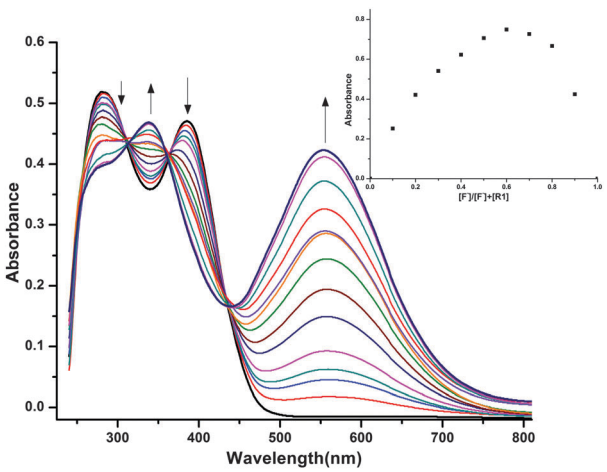


Fig. 2 UV-vis titration spectra of R1 (5×10^{-5} M) with increasing concentration of TBAF (0–25 equiv.) in dry DMSO. Inset: Job's plot for R1 with F^- ion at 555 nm in dry DMSO.

group) and the new band at 555 nm was ascribed to the development of an intramolecular charge transfer (ICT) transition. This constant decrease of two absorption bands and generation of two new absorption bands resulted in the formation of three clear isosbestic points at 309 nm, 361 nm and 433 nm, which evidently suggests the generation of two species in the system during the detection process.

To ensure that the detection process follows deprotonation and not complex formation, receptor R1 was titrated with TBA hydroxide (Fig. S18, ESI†). Upon incremental addition of TBAOH a constant decrease in the peaks at 282 nm and 385 nm was seen along with a gradual increment in the peaks at 351 nm and 572 nm being observed. This confirms that the deprotonation of –OH proton is responsible for the colorimetric change and not complex formation.

In case of receptor R2, the titration resulted in a constant decrease in the intensity of the absorption band at 388 nm due to the deprotonation of the hydroxyl group. Simultaneously, a new bathochromic band at 558 nm appeared, which was attributed to the generation of ICT transition (Fig. S19, ESI†).

The stoichiometry of the receptor–F^- ion system was determined by a Job's plot obtained from UV-vis spectrophotometric titration data at 555 nm for receptor R1 in DMSO solution (Fig. 2, inset). A maximum absorbance was observed when the mole fraction was 0.66 and this confirms the formation of 1 : 2 (host/guest) stoichiometric ratio between R1 and F^- ions. Hence, it is evident that F^- ion detection using receptor R1 is a two-step process as shown in Scheme 2. In the first instance, a F^- ion binds through hydrogen bonding to the hydroxyl proton of receptor R1, resulting in a 1 : 1 adduct to give a R1$\cdots F^-$ complex.[20] In the next step, the second F^- ion induces deprotonation of the phenolic –OH proton of receptor R1 and as a result, the electron density over the deprotonated receptor R1 was increased. Thus, the charge separation in the receptor was introduced, which resulted in ICT transition between the electron deficient $-NO_2$ group at the *p*-position and the electron rich $-O^-$, which leads to intense colorimetric change.[21]

^{1}H NMR titration was carried out in dry DMSO-d_6 to confirm the binding mechanism.

Upon addition of 0.5 equiv. TBAF, the –OH peak at δ 9.26 (H_a) disappeared completely, thus confirming deprotonation of phenolic –OH.[22] The peak H_b at δ 8.88 corresponding to imine –CH– shifted upfield to δ 8.45 due to the formation of exocyclic double bond and aromatic protons of 4-nitrophenyl group at δ 8.3 and δ 8.33 shifted upfield to δ 8.1 and δ 7.98, respectively (H_c). These upfield observations represent the increase in electron density over the 4-nitrophenyl group of receptor molecule upon F^- ion binding. In contrast, the protons of the 2-aminophenol group shifted downfield from the δ range 6.86–7.29 (H_d) to δ range 7.30–8.87. This shift was due to the decrease in electron density over the 4-aminophenol group of the receptor R1, which resulted in the deshielding of the corresponding protons upon F^- ion binding. Therefore the hydroxyl phenyl group acts as an electron donor and the nitrophenyl group acts as an electron acceptor, thus forming an ICT transition. Furthermore, at 0.5 equiv. and 1.0 equiv., the ^{1}H NMR illustrates both structures R1 and R1′ (Scheme 2), wherein the receptor undergoes keto–enol tautomerism. Finally, the keto tautomer is stabilized at 2 equiv. of F^- ion (Fig. 3).

Solvatochromic study

To our surprise, when 1 equiv. of F^- ion was added to the receptor R1 solution in dry ACN (5×10^{-5} M), a color change from pale yellow to pink was observed. This dissimilarity in color change (in DMSO pale yellow to blue and in ACN pale yellow to pink) was due to the solvatochromic effect of receptor R1. This study was further extended to other aprotic solvents such

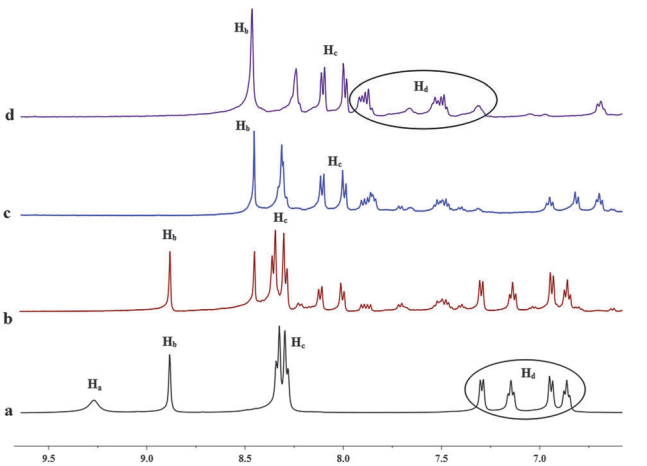
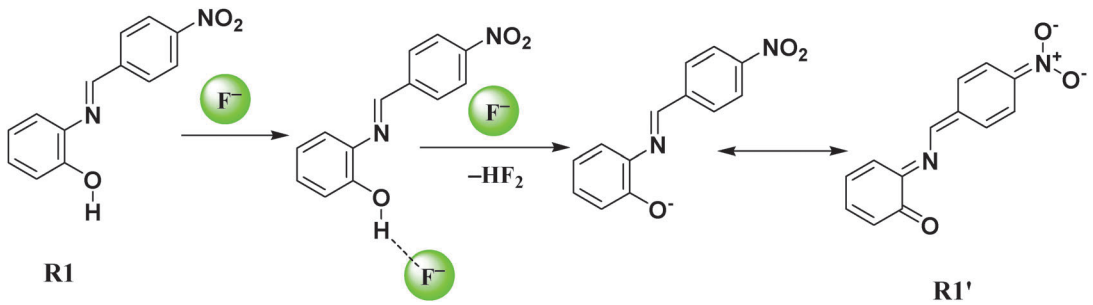


Fig. 3 Partial ^{1}H NMR titration spectra of receptor R1 with F^- ion at different concentrations in DMSO-d_6. (a) 0, (b) 0.5, (c) 1.0 and (d) 2.0 equiv. TBAF.



Scheme 2 Proposed mechanism for the fluoride ion binding to receptor R1.

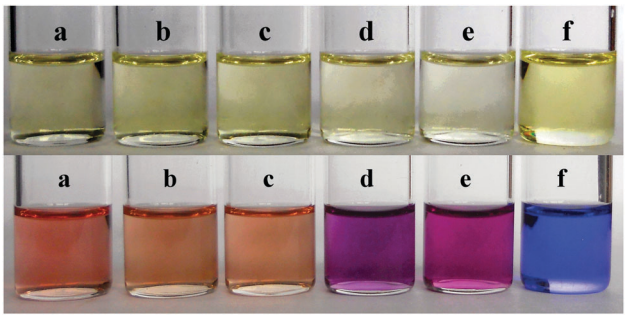


Fig. 4 Solvatochromism in receptor R1 upon addition of 1 equiv. of F^- ions in different solvents. Top row: R1 solution (5×10^{-5} M) in different solvents. Bottom row: R1 + F^-. (a) 1,4-dioxane, (b) THF, (c) DCM, (d) acetone, (e) ACN and (f) DMSO.

as 1,4-dioxane, THF, DCM, acetone and DMSO where the receptor R1 showed different coloration (Fig. 4) only in the presence of F^- ion with respect to the solvent polarity. The color of the receptor R1 was changed from pale yellow to red in 1,4-dioxane, brown in THF and DCM, purple in acetone, pink in ACN and finally blue in DMSO. As the receptor solution does not have any charge separation and charge transfer (CT) transitions, it did not show any solvatochromism in the absence of F^- ions.

However, addition of F^- ions to the receptor solutions induced charge separation. Hence, a charge transfer transition was established, due to which the receptor attains different dipole moments in its ground and lower energy singlet excited states. These newly established dipole moments interacted with the solvent dipole moments to change the energy levels of the receptor and as the solvent polarity increased, these energy levels decreased. As a result the peaks corresponding to CT transitions red shifted (positive solvatochromism)[23] with increasing solvent polarity. This solvatochromism was compared with the dielectric constant of solvents, which are compiled in Table 1. The polarity of any solvent is dependent on its dielectric constant. Greater the dielectric constant, the greater the polarity and as a result, with increasing dielectric constant the red shift increased.

The same trend was observed in case of R2 where the color changed from pale yellow to orange in 1,4-dioxane, dark yellow in THF and DCM, dark brown in acetone, light brown in ACN and blue in DMSO upon addition of 1 equiv. of F^- ions (Fig. S17, ESI†).

The percentage composition of a solvent mixture is generally determined by measuring its physical properties such as viscosity, refractive index or density. On the other hand, photophysical properties such as solvatochromism are not well explored to determine the composition of the solvent mixture. The receptor R1, being solvatochromic in presence of F^- ions, was applied to determine the percentage composition of two different solvents. This experiment was demonstrated by inspecting the color change of receptor R1 upon adding F^- ions in proportionate mixtures of DCM and DMSO. The receptor R1 was dissolved in a mixture of two solvents (by varying compositions between 0% and 100% of DMSO in DCM) to prepare 5×10^{-5} M solution. Upon adding F^- ions (10 equiv.) to each solution, a color change between brown and blue was observed (Fig. 5).

Table 1 Change in absorption maxima (λ_{max}) of receptor R1–F^- complex in different solvents on adding TBAF

Solvent	Dielectric constant	λ_{max} (nm)
1,4-Dioxane	2.21	500
Tetrahydrofuran	7.58	504
Dichloromethane	8.93	505
Acetone	20.70	510
Acetonitrile	37.5	511
Dimethylsulfoxide	46.8	555

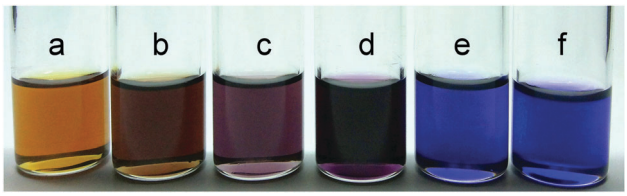


Fig. 5 The color change of receptor R1 with varying composition of DMSO in DCM on adding F^- ions (10 equiv.) (a) 0% *i.e.* 100% DCM, (b) 20%, (c) 40%, (d) 60%, (e) 80% DMSO in DCM and (f) 100% DMSO.

This colorimetric change was confirmed with UV-vis spectroscopy wherein a bathochromic shift of λ_{max} was observed with increasing the percentage of DMSO in DCM (Fig. 6). A shift of approximately 7.5 nm in the λ_{max} was observed for each 20% increase of DMSO in the solvent mixture. A calibration curve was plotted with this bathochromic shift and the percentage composition of DMSO in DCM (Fig. 6, inset).

A linear graph was obtained with the increasing percentage of DMSO in DCM. The percentage composition of unknown solvent mixture (DMSO/DCM) can be easily determined using this calibration curve.

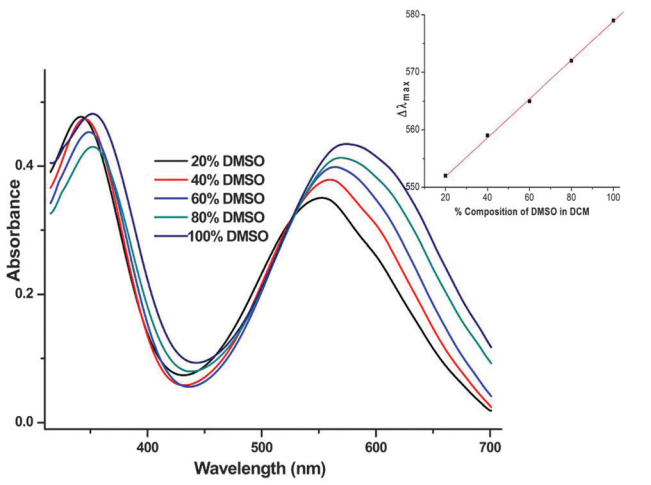


Fig. 6 UV-vis spectral changes of receptor R1 (5×10^{-5} M) on adding 10 equiv. of F^- ions with varying compositions of DMSO in DCM. Inset: calibration curve plotted with % composition of DMSO in DCM *vs.* Shift in λ_{max}.

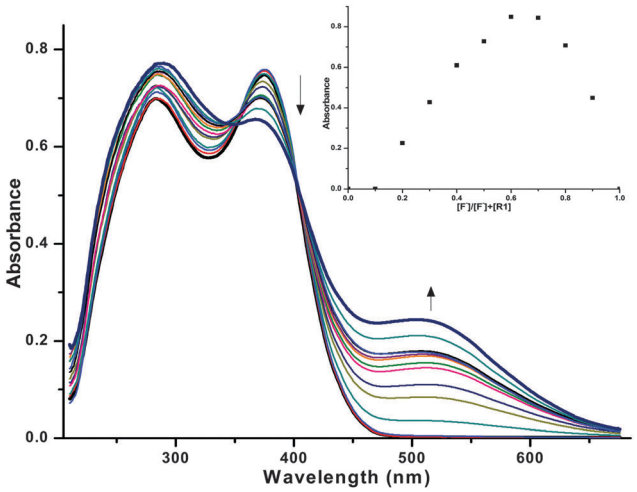


Fig. 7 UV-vis titration spectra of R1 (5×10^{-5} M) with the increasing concentration of TBAF (0–25 equiv.) in ACN. Inset: Job's plot for R1 with F^- ion at 511 nm in dry ACN.

The selectivity of receptor R1 towards F^- ions in ACN follows same trend as in DMSO solution. When the ACN solution of receptor R1 (5×10^{-5} M) was treated with TBA salts of different anions (1 equiv.), only the addition of F^- ions induced an instantaneous color change from pale yellow to pink (Fig. S8, ESI†), whereas the other anions did not show any color change.

The UV-vis titration was carried out for receptor R1 in dry ACN solution. Upon increasing the concentration of F^- ions, the peak at 284 nm increased slightly due to the change in the $\pi \rightarrow \pi^*$ transition. On the other hand, the peak at 375 nm decreased constantly and a new bathochromic band centred at 511 nm was developed, thus forming two clear isosbestic points at 350 nm and 400 nm (Fig. 7). This new peak that developed at 511 nm was ascribed to the formation of ICT transition. The gradual addition of F^- ions to receptor R2 (5×10^{-5} M) in ACN resulted in the bathochromic shift of absorption band from 371 to 393 nm with a broadened band centred at 500 nm, along with the formation of two isosbestic points at 299 nm and 385 nm (Fig. S20, ESI†). In contrast, the molecule R3, which lacks the hydroxyl (–OH) functional group, showed neither any color change (Fig. S11 and S12, ESI†) nor any shift in absorption maxima even after adding 20 equiv. of F^- ions (Fig. S21 and S22, ESI†) in DMSO as well as in ACN. This clearly indicates that the phenolic –OH is the binding site for the F^- ion and hence responsible for colorimetric detection.

The shift in absorption maxima after addition of F^- ions to the receptor solutions in dry ACN and dry DMSO are summarised in Table 2.

The 170 nm shift in DMSO compared with 136 nm in ACN for receptor R1 confirms the stronger binding of the F^- ion in DMSO due to the establishment of a more stable ICT transition. The binding constant was calculated using the Benesi–Hildebrand equation[24] and was found to be $7.15 \pm 0.31 \times 10^6$ M^{-2} for DMSO and $2.13 \pm 0.13 \times 10^6$ M^{-2} for ACN. This indicates the binding of the F^- ion to the receptor is much stronger in the case of DMSO than ACN.

Table 2 Change in absorption ($\Delta\lambda_{max}$) of receptors R1–R3 (5×10^{-5} M) in the presence of TBAF

Receptor	λ_{max} (ACN)[a] (nm)	λ_{max} (DMSO)[b] (nm)	$\Delta\lambda_{max}$ (ACN) (nm)	$\Delta\lambda_{max}$ (DMSO) (nm)
R1	511	555	136	170
R2	500	558	129	170
R3	293	294	0	0

[a] 10 equiv. of TBAF was added to receptor solutions (5×10^{-5} M) in dry ACN. [b] 10 equiv. of TBAF was added to receptor solutions (5×10^{-5} M) in dry DMSO.

Colorimetric study of cations

Further, the receptor R1 was evaluated for its binding ability towards cations in ACN. A colorimetric detection experiment was carried out to check the selectivity of the Cu^{2+} ion over other cations such as Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} (dissolved in water) in the form of their nitrates. The receptor R1 was able to bind selectively to Cu^{2+} ions, which resulted in a remarkable color change from pale yellow to orange-red (Fig. 8), whereas for other cations either yellow color was disappeared or no color change was observed.

The colorimetric selectivity of receptor R1 towards Cu^{2+} ions in the presence of other cations was studied by adding 3 equiv. of Cu^{2+} ions to the receptor R1 (5×10^{-5} M) in the presence of other cations (3 equiv.), such as Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}. The presence of other cations did not have any effect on the colorimetric detection of the Cu^{2+} ions (Fig. S16, ESI†). Accordingly, it is clear that receptor R1 prefers only Cu^{2+} ions for colorimetric detection over other cations.

The complexation mechanism and the spectral changes associated with the detection process were studied by means of a UV-vis titration experiment of R1 with Cu^{2+}. The UV-vis titration of receptor R1 (5×10^{-5} M) in ACN was carried out by gradually increasing the addition of Cu^{2+} ions in the form of $Cu(NO_3)_2$.

Fig. 9 depicts the UV-vis titration curve of R1 with increasing concentrations of Cu^{2+} ions. Upon increasing the addition of Cu^{2+} ions, the characteristic peak at 375 nm, which corresponds to phenolic –OH, decreased gradually. This observation confirms the participation of phenolic –OH in the complex formation. Along with decrease in the absorption band at 375 nm, a new band centred at 427 nm was observed, which was due to establishment of a charge transfer complex between receptor R1 and the Cu^{2+} ion. The peak at 284 nm, which corresponds to imine (–C═N–), showed a hypsochromic shift to 261 nm. Development of new bathochromic and hypsochromic bands indicates the formation of a new CT stabilized Cu^{2+} complex with the receptor R1.

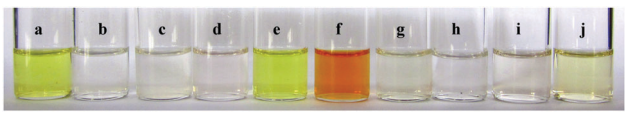


Fig. 8 Change in color after addition of 3 equiv. of different cations to the receptor solution in ACN (5×10^{-5} M). (a) Receptor R1, (b) Mg^{2+}, (c) Ca^{2+}, (d) Co^{2+}, (e) Ni^{2+}, (f) Cu^{2+}, (g) Zn^{2+}, (h) Cd^{2+}, (i) Hg^{2+} and (j) Pb^{2+}.

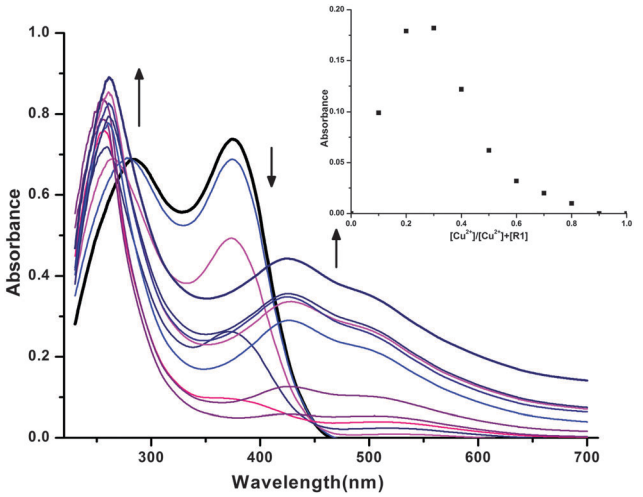
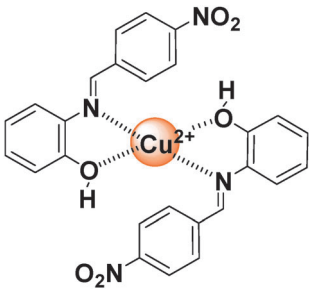


Fig. 9 UV-vis titration spectra of R1 (5×10^{-5} M) with increasing concentration of Cu^{2+} ions (0–25 equiv.) in ACN. Inset: Job's plot for R1 with Cu^{2+} ions at 427 nm.



Scheme 3 Schematic representation of complexation process of Cu^{2+} with receptor R1.

The stoichiometry of the R1–Cu^{2+} system was determined using a Job's plot where the absorbance at 427 nm was plotted against mole fraction of Cu^{2+}, which showed a maximum absorbance when the mole fraction was 0.33 (Fig. 9, inset). This confirms the formation of a 2 : 1 (host/guest) stoichiometric complex and it could be represented as shown in Scheme 3.[25]

In contrast, for other metal ions the extent of CT was diminished, which resulted in the disappearance of the pale yellow color of the receptor.[26] In the case of R2, the –OH group present at the *p*-position of phenyl ring was unable to form any complex with Cu^{2+}. Therefore no color change was observed in the case of R2 upon addition of Cu^{2+} ions. However, the pale yellow color of R2 disappeared (Fig. S13, ESI†) upon addition of Cu^{2+} due to diminished D–A interactions. This result was confirmed by UV-vis spectroscopy where the peak at 371 nm corresponding to the phenolic –OH disappeared (Fig. S23, ESI†) upon addition of Cu^{2+} ions.

Logic gate applications

As stated previously, the receptor R1 changed color from pale yellow to pink upon addition of F^- ions (2 equiv.) in dry ACN and as a result a new band cantered at 511 nm with an absorbance of 0.13 was observed. Surprisingly, adding 1 equiv.

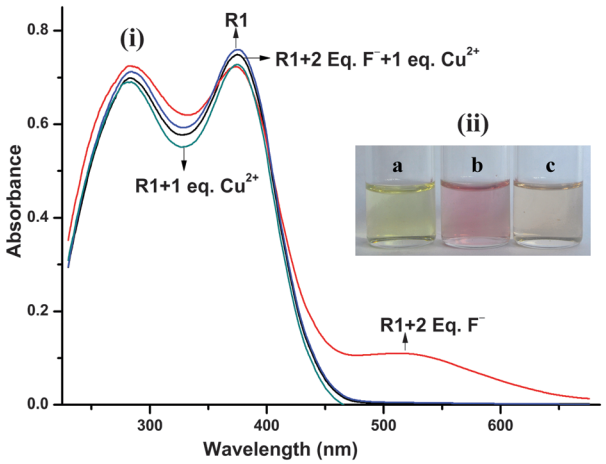


Fig. 10 (i) Reversal of the UV-vis spectral pattern of receptor R1 + 2 equiv. of F^- upon addition of Cu^{2+} ions. (ii) Color changes of a 5×10^{-5} M ACN solution of receptor R1. (a) Receptor R1, (b) R1 + 2 equiv. of F^- and (c) R1 + 2 equiv. of F^- + 1 equiv. Cu^{2+}.

of Cu^{2+} ions to this R1–F^- ion complex resulted in the disappearance of the pink color and the original pale yellow color of receptor R1 was restored (Fig. 10ii). This revertion of the color was confirmed by UV-vis spectroscopy where the band at 511 nm (due to ICT) disappeared and the band at 375 nm corresponding to receptor R1 was restored (Fig. 10i). This property of receptor R1 was further applied for the molecular logic gate and 'ON–OFF' switching operation.

The system is said to be 'switched ON' when receptor R1 shows an optical output from pale yellow to pink in the presence of F^- ions and system is said to be 'switched OFF' when Cu^{2+} ions were added to the same solution and the pale yellow color of the receptor R1 reappears. These observations can be correlated to demonstrate a logic gate operation, where the output signals (change in color) could be controlled by input signals (addition of F^- ions and Cu^{2+} ions). The receptor R1 showed no absorbance at 511 nm, which is accounted for by the Boolean value of "0" and with the addition of F^- ions it showed an absorbance of 0.13, which is accounted for by the Boolean value of "1". The process of 'switch ON' and 'switch OFF' represented in the molecular logic gate is shown through the truth table as shown in Table 3.

Output signals in the form of spectral change at 511 nm were observed upon supplying input signals in the form of F^- ions and Cu^{2+} ions represents an INHIBIT (INH) logic gate.[27] The outputs of the receptor R1 are in agreement with complementary INH logic function (Fig. 11).

Table 3 Truth table for INHIBIT (INH) logic function. Inputs: addition of 2 equiv. F^- ions and 1 equiv. Cu^{2+} ions to a 5×10^{-5} M ACN solution of R1. Outputs: absorbance at 511 nm (high absorbance: 1; low absorbance: 0)

Input A (F^- ion addition)	Input B (Cu^{2+} ion addition)	Output (absorbance at 511 nm)
0	0	0
1	0	1
0	1	0
1	1	0

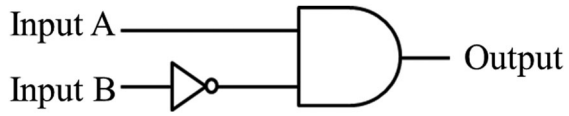
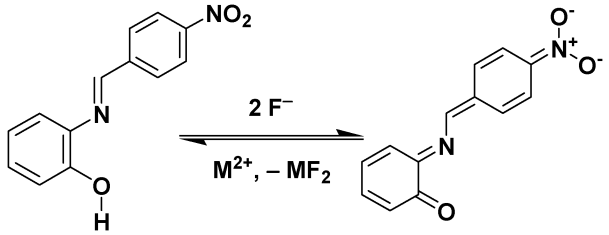


Fig. 11 A schematic representation of a complementary output INH circuit.



Scheme 4 Reversable process of receptor R1 upon addition of Cu^{2+} to the R1 + F^- in ACN solution.

Similar color change was observed upon the addition of other metal ions such as Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} (Mg^{2+}, $Ca^{2+}$and Pb^{2+} salts were not soluble in organic solvents like ACN) instead of Cu^{2+}. This confirms formation of stable MF_2 salts (metal–fluoride salt). Thus, receptor R1 becomes free after the addition of 1 equiv. of M^{2+} ions to the R1 + 2 equiv. F^- solution as demonstrated in Scheme 4.[17e]

However, the addition of 10 equiv. of F^- ion to the R1–Cu^{2+} complex did not show any color change. This confirms the stable complex formation between receptor R1 and Cu^{2+} ion.

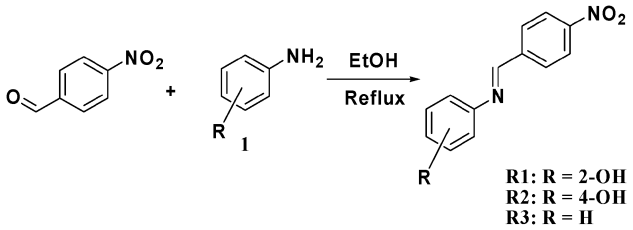
Conclusion

To conclude, receptor R1 was designed and synthesised for the colorimetric dual ion sensing application. The receptor R1 was able to distinguish F^- ions colorimetrically over other anions. This receptor showed this unique solvatochromic property only in the presence of F^- ions as it establishes charge separation in the receptor. The receptor displayed different colorations in different solvents upon adding F^- ions. This colorimetric discrimination in different solvents was successfully applied to determine the percentage composition of binary solvent mixtures. The receptor R1 colorimetrically discriminated Cu^{2+} ions over other cations by showing a color change from pale yellow to orange-red. It acts as a molecular switch which is said to be 'switched ON' in presence of F^- ions and 'switched OFF' when Cu^{2+} ions were added. This switch 'ON–OFF' process was demonstrated by logic gate functions. The receptor R1 gave output signals corresponding to the INH circuit with input signals which can be implemented to molecular computing operations and molecular devices.

Experimental section

General information

All chemicals were purchased from Sigma-Aldrich, Alfa Aesar or Spectrochem and used without further purification. All solvents were procured from SD Fine, India, and were of HPLC grade and used without further distillation.



Scheme 5 Syntheses of receptors R1, R2 and R3.

The ^{1}H NMR spectra were recorded on a Bruker Avance II (500 MHz) instrument using TMS as internal reference and DMSO-d_6 as solvent. Resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Melting points were measured on a Stuart-SMP3 melting-point apparatus in open capillaries. Infrared spectra were recorded on a Thermo Nicolet Avatar-330 FT-IR spectrometer; signal designations: s (strong), m (medium), w (weak), br m (broad medium) and br w (broad weak). UV-vis spectroscopy was carried out with an Ocean Optics SD2000-Fibre Optics Spectrometer in standard 3.5 mL quartz cells (2 optical windows) with 10 mm path length. Elemental analyses were done using a Flash EA1112 CHNS analyzer (Thermo Electron Corporation).

General synthetic procedure for the target compounds R1, R2 and R3 (Scheme 5)

A mixture of 4-nitrobenzaldehyde (1.32 mmol) and **1** (2.69 mmol) was reacted in ethanol under reflux for 5 h. The reaction was catalyzed by a drop of acetic acid. The solid product was obtained after cooling and was filtered and washed with ethanol to obtain the target compounds (R1, R2 and R3). All the synthesized compounds were solid and characterized using ^{1}H NMR, IR, elemental analysis and mass spectrometry.

(*E*)-2-(4-Nitrobenzylideneamino)phenol, R1. Yield: 79%. Elemental analysis: calculated for $C_{13}H_{10}N_2O_3$ (%): C 64.46, H 4.16, N 11.56; experimental (%): C 64.26, H 4.30, N 11.60. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.27 (s, 1H, –OH), δ 8.88 (s, 1H, =CH), δ 8.34 (d, 2H, Ar-H, J = 8 Hz), δ 8.30 (d, 2H, Ar-H, J = 8 Hz), δ 7.30 (d, 1H, Ar-H, J = 7.5 Hz), δ 7.16 (t, 1H, Ar-H, J = 7.25 Hz), δ 6.95 (d, 1H, Ar-H, J = 8 Hz), δ 6.86 (t, 1H, Ar-H, J = 7 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.45, δ 152.23, δ 149.11, δ 142.48, δ 137.40, δ 130.24, δ 129.01, δ 124.30, δ 119.98, δ 119.82, δ 116.85. m.p. 165–166 °C. FT-IR in cm^{-1}: 3367.3 (m), 1586.2 (m), 1508.8 (m), 1331.7 (s), 1230.2 (m), 1096.4 (w), 1027.5 (w), 779.9 (m). MS (ESI): m/z: calculated: 243.2375 $[M + H]^+$; experimental: 243.2590 $[M + H]^+$.

(*E*)-4-(4-Nitrobenzylideneamino)phenol, R2. Yield: 80%. Elemental analysis: calculated for $C_{13}H_{10}N_2O_3$ (%): C 64.46, H 4.16, N 11.56, experimental (%): C 64.32, H 4.28, N 11.48. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.72 (s, 1H, –OH), δ 8.77 (s, 1H, =CH), δ 8.32 (d, 2H, Ar-H, J = 8 Hz), δ 8.12 (d, 2H, Ar-H, J = 8.5 Hz), δ 7.32 (d, 2H, Ar-H, J = 8.5 Hz), δ 6.85 (d, 2H, Ar-H, J = 8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.79, δ 155.11,

δ 148.80, δ 142.59, δ 142.06, δ 129.53, δ 124.42, δ 123.61, δ 116.31. m.p. 173–175 °C. FT-IR in cm^{-1}: 3434.3 (s), 1582.7 (m), 1500.6 (s), 1328.4 (s), 1252.5 (m), 1197.9 (m), 1195.7 (w).

(*E*)-*N*-(4-Nitrobenzylidene)benzenamine, R3. Yield: 63%. Elemental analysis: calculated for $C_{13}H_{10}N_2O_2$ (%): C 69.02, H 4.46, N 12.38; experimental (%): C 68.98, H 4.50, N 12.39. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.79 (s, 1H, =CH), δ 8.35 (d, 2H, Ar-H, J = 8.5 Hz), δ 8.19 (d, 2H, Ar-H, J = 8.5 Hz), δ 7.47 (t, 2H, Ar-H, J = 7.5 Hz), δ 7.29–δ 7.35 (m, 3H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.27, δ 151.02, δ 149.27, δ 141.95, δ 130.08, δ 129.76, δ 127.38, δ 124.44, δ 121.71. m.p. 94–95 °C. FT-IR in cm^{-1}: 3063.5 (w), 1588.1 (m), 1510.3 (s), 1330.6 (s).

Acknowledgements

MP, SN and DRT acknowledge the Director and the HOD (Department of Chemistry), NITK, for providing research infrastructure. DRT acknowledges the Department of Science and Technology (DST, Government of India, New Delhi) for financial support. MP is thankful to NITK for the research fellowship. MP and SN thank the Optoelectronics Laboratory, Department of Physics, NITK for spectral analysis and Prof. P. Srinivas, HOD, PPSFT Department, CFTRI, Mysore for his kind help in NMR analysis.

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