Reversible colorimetric switching of thiophene hydrazone based on complementary IMP/INH logic functions†

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Received (in Gainesville, FL, USA) 5th February 2010, Accepted 23rd April 2010
DOI: 10.1039/c0nj00097c

We have synthesized a thiophene hydrazone (receptor **1**) that acts as a colorimetric receptor showing a reversible color switching (ON and OFF) function induced by anion and cation recognition. This remarkable color switching is based on two-input complementary IMP/INH logic functions. The (ON and OFF) process of this molecular switch is triggered by an anion (CH_3COO^-, $C_6H_5COO^-$, $HCOO^-$, $H_2PO_4^-$ or F^-), while it is quenched by any one M^{II} ion of 3d (d^5–d^{10}) as well as Cd^{II} and Hg^{II}. A DMSO solution of receptor **1** underwent a bathochromic shift from 407 to 505 nm upon adding any one of the above-mentioned anions, while switch OFF was achieved by the addition of any one of the above-mentioned cations to regenerate a band at 407 nm.

Introduction

The recognition and sensing of anions and cations based on molecular devices have been a subject of extensive and intensive research interest for the last few decades.[1] Such molecular devices are able to perform logic operations based on binary input and output information. Depending on the input/output functionality, different types of molecular logic gates may be constructed using such systems. A major challenge before supramolecular chemists now-a-days is to make these molecular logic gates fast, reversible, stable and more importantly, to explore their mechanistic details.[2] There are 16 different types of logic gate functions for two-input systems,[3] and several examples are available in the literature of these individual molecular logic systems that demonstrate AND,[4] OR,[5] NOT,[6] XOR,[7] NOR,[8] XNOR,[9] NAND,[10] INH,[11] *etc*. logic operations. Two-input IMP functions are rare, and only a few research papers have appeared in literature so far.[12] The IMP logic function output is complementary to an INH gate and is closely related to an "if-then" phrase.

The combination of individual logic systems for their possible use in a unimolecular system has been an emerging area in the field of molecular switches for the last few years. Quite a good number of examples elaborating multiple combinatorial logic functions, leading to integrated circuits *viz*., half-subtractor, half-adder, full-adder, full-subtractor *etc*., have also been reported in the last few years.[13]

Furthermore, molecular systems mimicking various non-Boolean components of electronic devices, performing digital operations such as molecular comparator,[14] digital multiplexer and demultiplexer,[15] encoder–decoder,[16] flip-flop,[17] *etc*., have also been reported. However, reports of combinatorial molecular logic gates having complementary IMP/INH logic functions are rare, and this is only the fourth report of its kind to the best of our knowledge. The first three were by Pischel and Heller,[14] Gupta and van der Boom[19] and Yan *et al*.,[18] respectively.

Receptor molecules obtained through simple synthetic protocols but capable of performing multiple logic operations are the first choice for any supramolecular chemist towards the construction of molecular devices and machines. Hence receptor **1** (thiophene hydrazone), synthesized through a very simple protocol and able to function as a molecular switch by using appropriate combinations of anions and cations in DMSO, is of worth. Thiophene is a heterocyclic ring system that is often used in materials such as conjugated polymers,[20] novel drugs,[21] bio-diagnostic devices[22] and non-linear optical compounds.[23] However, it has been considerably less used as a constituent of molecular chemosensors.

We have studied the logic responses of receptor **1** by using appropriate combinations of anions and cations as inputs. The outputs of this molecular switch (receptor **1**) are in accordance with complementary IMP/INH logic functions (Scheme 1). The present research work is a part of our continuing endeavour over the last few years to synthesize naked eye chemoreceptors through simple reaction protocols.[24]

Experimental

Synthesis of receptor 1

Receptor **1** was synthesized according to a literature procedure[25] by adding a 2 mmol ethanol solution of 2,4-dinitrophenyl hydrazine (DNP) to an equimolar ethanol solution of thiophene-2-carbaldehyde containing one drop of concentrated HCl while stirring. The stirring was continued for ~2 h with mild heating (~60 °C). An orange-colored solid precipitated and was filtered, washed several times with water and a small amount of ethanol, recrystallised from an ethanol–water

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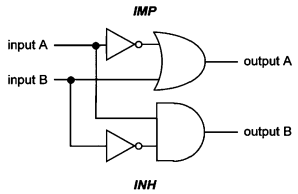
† Electronic supplementary information (ESI) available: General methods, UV-vis titrations of receptor **1** with analytes and their Job's plots, ^{1}H NMR spectra, IR spectra, and CHN data of the receptor. See DOI: 10.1039/c0nj00097c



Scheme 1 A schematic representation of a complementary output IMP/INH circuit.

mixture (50% v/v) and ultimately dried under vacuum over anhydrous $CaCl_2$.

(*N*-(2,4-Dinitrophenyl)-*N*′-thiophene-2-ylmethylene-hydrazine). Yield 88%; mp 239–241 °C; molecular formula: $C_{11}H_8N_4O_4S$; CHN (%) calc.: C, 45.20; H, 2.76; N, 19.17; CHN (%) found: C, 44.77; H, 2.80; N, 18.49; ν_{max} (KBr)/cm^{-1}: 3421, 3277, 3087, 2922, 1608, 1509, 1421, 1319, 1218, 1133, 1082, 1043, 934 and 829; δ_H (400 MHz, DMSO-d_6,Me_4Si): 11.69 (1 H, s, –NH), 8.93 (1 H, s, –CH=N–), 8.87–8.86 (1 H, d, Ar–H [2,4-DNP]), 8.44–8.41 (1 H, m, Ar–H [2,4-DNP]), 7.93–7.90 (1 H, d, Ar–H [2,4-DNP]), 7.77–7.75 (1 H, d, Ar–H [thiophene]), 7.52–7.51 (1 H, d, Ar–H [thiophene]) and 7.20–7.18 (1 H, m, Ar–H [thiophene]); λ_{max} (DMSO)/nm: 407.

Results and discussion

The structure of receptor **1** in the solid state (Fig. 1) was obtained by X-ray diffraction (XRD) studies of a single crystal grown by slow evaporation of a saturated solution in acetone.[26] Receptor **1** crystallized as monoclinic with the space group $P2_1/c$ and is almost planar. Cell parameters: a = 4.7915(15), b = 9.561(3), c = 25.490(8) Å and Z = 2, along with R and S values of 0.056 and 1.128, respectively.

The molecular structure of receptor **1** is stabilized by N(2)–H···ONO intramolecular hydrogen bonding (2.013 Å). The stability of the crystal structure of receptor **1** is insured by one rarely observed[27] long range intermolecular closed shell O···O interaction involving the $–NO_2$ groups. The interatomic distance for this supramolecular interaction is 2.695 Å, which is considerably smaller than twice the sum of the van der walls radius of an O-atom.

UV-vis studies

A 5 × 10^{-5} M solution of receptor **1** was prepared in HPLC grade DMSO. UV-vis absorption titrations were carried out by adding 0–10 equiv. of the anions as their tetrabutylammonium salts and cations as their chloride salts. The UV-vis spectrum was recorded after each addition.

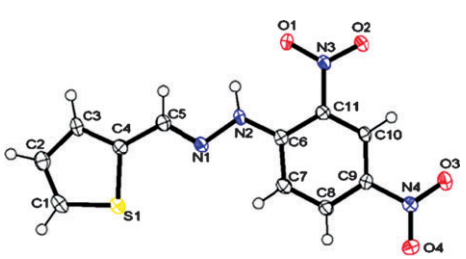


Fig. 1 ORTEP plot of the crystal structure of receptor **1**.

The binding behaviour of receptor **1** with various anions (such as F^-, Cl^-, Br^-, I^-, CH_3COO^-, $C_6H_5COO^-$, $HCOO^-$, $H_2PO_4^-$, BF_4^-, HSO_4^-, ClO_4^- and PF_6^-) was first monitored by visual observation in DMSO. It was found that the receptor **1** exhibited a prominent and instant color change from orange to dark red with CH_3COO^-, $C_6H_5COO^-$, $HCOO^-$ $H_2PO_4^-$ or F^- ions, while the remaining anions did not produce any visual or UV-vis spectral change (see ESI,† Fig. 1). The dark red color of receptor **1** produced upon addition of anions was reversed by addition of any M^{II} of 3d (d^5–d^{10}), as well as Cd^{II} and Hg^{II} (Fig. 3a). The above selection of ions is justified in terms of their biological and environmental relevance.[28] The addition of other metal ions ranging from s to p block examples, such as Na^+, K^+, Ca^{2+}, Mg^{2+} Al^{3+} and Pb^{2+}, did not produce any significant visible color change.

CH_3COO^- and Zn^{II} were taken as representatives of anions and cations, respectively, for studying the logic operations of receptor **1** in view of their high biological relevance among the chosen ions.[28] The same study with Cd^{II} and Hg^{II} instead of Zn^{II} has been appended as supplementary information.†

A DMSO solution of receptor **1** is of an orange color and exhibits a strong absorption band at 407 nm (Fig. 2b) due to the π–π* transition. Upon the addition of CH_3COO^- to the receptor **1** solution, the peak at 407 nm disappears gradually and a new band at 505 nm appears (Fig. 2b). At the same time, the color of the receptor solution also changes from orange to dark red (Fig. 2) with a well-defined isosbestic point at 445 nm, indicating the formation of a stable complex between the receptor **1** and CH_3COO^- during the course of the titration. Similar UV-vis spectral changes were observed upon the respective addition of $C_6H_5COO^-$, $HCOO^-$, $H_2PO_4^-$ or F^- to the receptor **1** solution (see ESI,† Fig. 2).

The Job's plot indicated the formation of a 2 : 1 complex between receptor **1** and all of the above anions (see ESI,† Fig. 3). The corresponding binding constants were determined from their individual spectroscopic UV-vis titration data (Table 1) using the Hyperquad fitting program.[29] The data for CH_3COO^-, $HCOO^-$, $C_6H_5COO^-$ and $H_2PO_4^-$ gave acceptable fits based solely on a 2 : 1 complex (receptor : anion); no contribution from 1 : 1 complexes was required. Other hydrazone-based colorimetric anion sensors involve deprotonation of the hydrazone by basic anions as the basis for color development. A simple 1 : 1 deprotonation does not

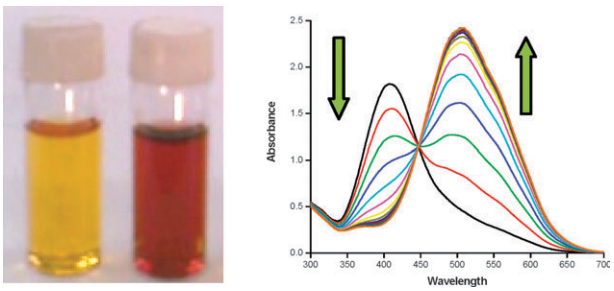


Fig. 2 (a) The visible color changes of receptor **1** from orange to dark red upon the addition of CH_3COO^- ions. (b) The UV-vis spectral pattern of receptor **1** upon the concomitant addition of CH_3COO^-.

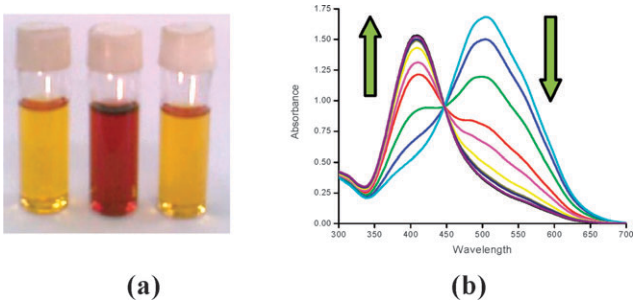


Fig. 3 (a) Color changes of a 5×10^{-5} M DMSO solution of receptor **1**. Left to right: in the absence of ions, in the presence of 1 equiv. of CH_3COO^-, in the presence of 1 equiv. of CH_3COO^- along with 10 equiv. of Zn^{II}. (b) The reversal of the UV-vis spectral pattern of receptor **1** + 0.5 equiv. of CH_3COO^- upon concomitant addition of Zn^{II} ions.

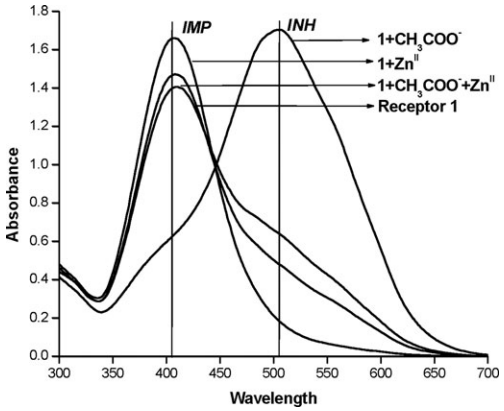


Fig. 4 UV-vis spectra of receptor **1** in DMSO (5×10^{-5} M) with analytes, and molecular logic function IMP (407 nm) and INH (505 nm).

occur in this system, but the color change is consistent with significant proton transfer from receptor **1** to the anion. A bridging complex involving the hydrazone NHs as donors to a common anion is a possible model to explain the observed 2 : 1 stoichiometry. Different molar extinction coefficients are consistent with slightly different extents of proton transfer in the 2 : 1 complexes of the different anions. The formation constants do not directly follow a trend in anion basicity, indicating that the 2 : 1 complex imposes some structural recognition.

Table 1 does not include data for fluoride as this system is significantly more complex. The Job's plot clearly indicates a 2 : 1 complex (see ESI,† Fig. 3c) but the evolution of the UV-vis spectrum is not consistent with a direct 2 : 1 complex formation. A 1 : 1 complex can be accommodated by the data, but the statistical significance of the fits remain poor (see ESI,† Fig. 4). Other hydrazone-based colorimetric sensors for fluoride in dipolar aprotic solvents show the formation of the bifluoride ion.[30] It is likely that in the present system, a mixture of 1 : 1, 2 : 1 and 1 : 2 complexation processes occur, with the 2 : 1 complexes dominating in the concentration range of the UV-vis titrations.

The addition of 10 equiv. of Zn^{II} to the above solution (receptor **1** + CH_3COO^-) resulted in the disappearance of the dark red color and the restoration of the original orange color of receptor **1** (Fig. 4a). This naked eye observation was reflected in the form of a vanishing 505 nm (receptor + 1 equiv. of CH_3COO^-) absorption band and the reappearance of the 407 nm (receptor **1**) absorption band (Fig. 4b) upon the concomitant addition of Zn^{II}. Similar UV-vis spectral patterns and color changes were observed upon the respective addition of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II} and Hg^{II} (see ESI,† Fig. 5).

Table 1 Binding constants (log $\beta_{2:1} \pm 0.2$) of receptor **1** with various anions in DMSO solution and the extinction coefficient ($\varepsilon \pm 1000$) of the 2 : 1 complex at 510 nm

Anion	log $\beta_{2:1}$	ε/L mol^{-1} cm^{-1}
CH_3COO^-	10.8	88 000
$C_6H_5COO^-$	9.6	133 000
$HCOO^-$	9.3	66 700
$H_2PO_4^-$	9.0	91 200

As can be seen in Fig. 3a, the color changes (optical outputs) are controlled by the inputs of anion and cation; the CH_3COO^- 'switches ON' the optical output while Zn^{II} 'switches OFF' the optical output. The UV-vis titration data for Zn^{II} addition to the 2 : 1 CH_3COO^- complex could be analyzed by Hyperquad using the known 2 : 1 receptor–CH_3COO^- cumulative formation constant as a fixed parameter. Acceptable fits required two complexation processes: the formation of a 2 : 1 complex of receptor **1** with Zn^{II} and a 1 : 1 ion pairing association of Zn^{II} and CH_3COO^-. The logarithm of the cumulative formation constants were 9.5 ± 0.2 and 4.4 ± 0.2, respectively. Although the maximum absorbance of the 2 : 1 complex of **1** with Zn^{II} is closely similar to the free ligand, the extinction coefficient of the complex is more than twice that of the ligand on a molar basis (32 000 L mol^{-1} cm^{-1} for **1** compared with 71 000 L mol^{-1} cm^{-1} for the complex).

For comparison, the order of guest addition was then reversed by the addition of 10 equiv. of Zn^{II} to a solution of receptor **1** in DMSO (5×10^{-5} M), which brought no color change, except for a small increase in the absorption intensity (hyperchromic shift) at 407 nm (see ESI,† Fig. 6). This was followed by the addition of 2 equiv. of CH_3COO^- to the same solution, leading to the appearance of the dark red color. Therefore, Zn^{II} did not inhibit the chromogenic response of the system to CH_3COO^- ions.

Hence, the process of switch ON and switch OFF is reversible, and is not inhibited either by anion or cation addition, but instead depends on the concentration of ions (see ESI,† Fig. 7). A convenient way of representing these changes through a molecular logic gate is a truth table (Table 2).

The changes in absorbance at 505 nm in response to the inputs are in accordance with an INHIBIT (INH) logic gate,

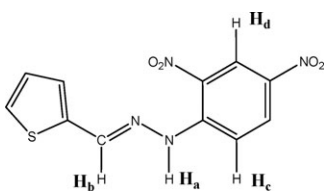


Fig. 5 The proton labelling of receptor **1**.

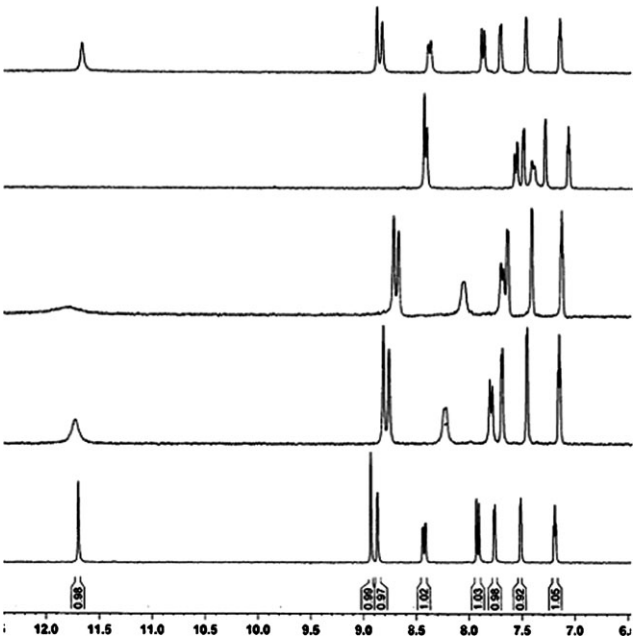
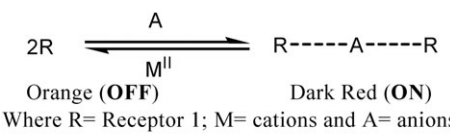


Fig. 6 Partial ^{1}H NMR spectra of receptor **1** (5×10^{-3} M) in DMSO-d_6. From bottom to top: receptor **1**, **1** + 0.1 equiv. CH_3COO^-, **1** + 0.25 equiv. CH_3COO^-, **1** + 0.5 equiv. CH_3COO^-, **1** + 1.0 equiv. CH_3COO^- + 10 equiv. Zn^{II}.

whereas the spectral changes at 407 nm are described with an IMPLICATION (IMP) logic gate (Fig. 4). Hence, the high colorimetric output at 407 nm is produced under all circumstances, except in the presence of only anions, whereas the high colorimetric output at 505 nm is produced in the presence of only anions and remains low in all the other combinations of anions and cations.

^{1}H NMR studies

^{1}H NMR spectral studies in DMSO-d_6 were carried out to understand the possible binding mode and reversibility of receptor **1** towards the sensing process. Partial labelling of the protons of receptor **1** is shown in Fig. 5.



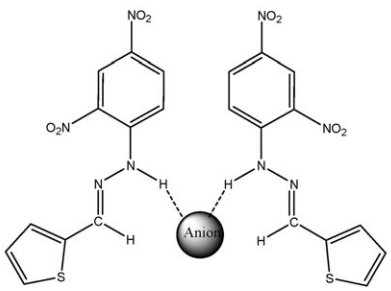


Fig. 7 The proposed binding mode of receptor **1** with anions in solution.

Table 2 Truth table for the complementary IMP/INH logic functions. Inputs: 1 equiv. anion and 10 equiv. cation. Outputs: absorbance intensity at 407 and 505 nm, respectively

Input		Output	
Anion	Cation	IMP 407 nm	INH 505 nm
0	0	**1 (high, 1.47)**	0 (low, 0.46)
0	1	**1 (high, 1.66)**	0 (low, 0.16)
1	0	0 (low, 0.64)	**1 (high, 1.70)**
1	1	**1 (high, 1.40)**	0 (low, 0.61)

A representative ^{1}H NMR titration between receptor **1** and tetrabutylammonium acetate is shown in Fig. 6. Upon adding 0.1 equiv. of acetate, the peak at 11.70 ppm (–NH) (H_a) shifted downfield with broadening, and the Ar–H signals shifted upfield with slight broadening, indicating the formation of hydrogen bonding between CH_3COO^- and the receptor. With the further addition of CH_3COO^-, the phenyl protons, especially H_c and H_d, and the aldimine proton H_b (Fig. 5), shifted upfield significantly, indicating the increase of the electron density on the phenyl ring owing to through-bond effects.[31] At the same time, the –NH signal carried on broadening upon the concomitant addition of CH_3COO^-, and ultimately vanished upon the addition of 0.5 equiv. of CH_3COO^- (significant deprotonation of –NH from the receptor **1**), confirming the 2 : 1 stoichiometry between the receptor and CH_3COO^- throughout the UV-vis titrations.

Furthermore, upon adding 10 equiv. of Zn^{II} as its chloride salt to the DMSO-d_6 solution of receptor **1** with CH_3COO^- (1 equiv.), the almost original spectrum of receptor **1** (having changes only in the second decimal place in the chemical shift values of the protons) was obtained (Fig. 6). Thus, the UV-vis and ^{1}H NMR spectral studies lead us to conclude that an equilibrium involving the reversible formation of a 2 : 1 receptor–anion complex (Fig. 7) is responsible for the function of receptor **1** as a molecular switch.

Conclusion

We have designed a simple, easily accessible colorimetric molecular switch in the form of receptor **1** that undergoes reversible ON–OFF signaling through the detection of anions and cations based on a complementary two-input IMP/INH logic gate. We believe that the present system will provide a useful addition to the range of optical devices that can operate at the molecular level.

Acknowledgements

Authors are thankful to CSIR, New Delhi for financial assistance.

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