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Synthesis of a Phenylhydrazone-based Colorimetric Anion Sensor with Complementary IMP/INH Logic Functions

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A dinitrophenyl hydrazone colorimetric anion sensor (receptor **1**) was synthesized and its recognition properties towards various anions were investigated by naked eye observation and spectroscopic methods, namely UV-vis and ^{1}H NMR titrations in DMSO. The addition of AcO^-, F^- and $H_2PO_4^-$ to receptor **1** resulted in marked red shift of the charge-transfer absorbance band ($\Delta\lambda$=91 nm, 407 nm to 498 nm) concomitant with a 'naked-eye' detectable colour change from yellow to pink. However, both the colour and spectral changes were reversible by the addition of cations (M^{II}) of $3d^{5\text{-}10}$ as well as Cd^{II}, Hg^{II}, Mg^{II} and Ca^{II}. Subsequently, complementary IMP/INH logic functions based on colour and spectral switching (ON/OFF) were affirmed. The sensor can, thus be utilized as a colorimetric molecular switch modulated by F^-/M^{II}.

Keywords colorimetric sensor, hydrazone, anion recognition, logic function

Introduction

The sensing and the recognition of anions have been receiving a great deal of attention due to their wide range of applications in bio-chemical systems, environmental processes and molecular switch designs.[1] Colorimetric sensors are of great interest in practical applications due to their simplicity in use and they can provide quantitative signal rapidly, which allows naked-eye detection of anions without resorting to any spectroscopic instrumentation.[2] Generally, a colorimetric sensor molecule consists of two parts: the anion binding part (receptor) and the chromophore.[3] The binding part may be based on various combinations of amides,[4] urea,[5] pyrroles,[6] thiourea,[7] pyrazoles,[8] indoles,[9] hydrazones,[10] imidazoles[11] and carbazoles[12] because their NH groups are known to interact with anions. The chromophore part is responsible for transducing binding induced changes into optical signals such as colour changes. With the reference to the binding parts, only a limited number of reports of hydrazone-based receptors are available. Among others, hydrazone receptors along with indoles and carbazoles and their derivatives are better hydrogen bond donors and both are prone to deprotonation at higher anionic guest concentration.[12f] Hydrazones are characterized by one or more nitro-groups (NO_2), a molecular framework of electron withdrawing group (EWG), which polarizes the NH fragment, thereby increasing hydrogen-bond donor strength. In these cases, highly basic anions like AcO^-, F^- and $H_2PO_4^-$ interact with the sensor through the NH group by means of hydrogen-bonding.[10] The presence of an excess anion may even cause deprotonation, resulting in a classical Bronsted acid-base type reaction.[13]

Alternatively, the functional principles of molecular switches are similar to chemosensors, whereby the introduction of an anion acts as external stimulus in a molecular system,[14] which triggers the change (chemical or physical) of components. These changes can be detected spectrally and/or visually (color changes), which in turn are used to monitor the operation of the system. The essential feature of the molecular switches is their ability to reverse the changes brought by external stimulus such as to restore the initial state of the sensor by means of opposite stimulus. Thus, since the pioneering work on molecular AND logic gates by de Silva and coworkers,[14n] other logic functions such as NAND, OR, XNOR, XOR, NOR, NOT and INHIBIT logic operations have been explored, and remarkable progress has been made in the development of molecular logic gate.[14f-14m] Acknowledgingly, there is a significant number of reports elaborating combinatorial multiple logic functions, based on both Boolean and non-Boolean[14o-14s] logic systems in the literature, however, combinatorial molecular systems with complementary logic functions remain continuously illusive.[15]

In this paper, an anion sensor (receptor **1**) based on a hydrazone moiety was synthesized (Scheme 1). It was

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prepared by the condensation of an aldehyde and a hydrazine. The results showed that receptor **1** was able to selectively recognize AcO^-, F^- and $H_2PO_4^-$ through the formation of a 1∶1 hydrogen-bonding complex, concomitant with a 'naked-eye' detectable colour change during the recognition. However, the changes observed during anion recognition can be significantly reversed by the addition of cations (M^{II}) of $3d^{5\text{-}10}$ as well as Cd^{II}, Hg^{II}, Mg^{II} and Ca^{II} (nitrate, chloride and perchlorate salts) as compared to protic solvents. Subsequently, logic operation properties based on anion-cation as inputs were investigated, and as a result, the outputs of receptor **1** were in accordance with complementary IMP/INH logic functions.[15]

Experimental

Instruments

^{1}H NMR spectra were acquired on a Varian Mercury VX-300 MHz spectrometer. UV-vis spectra were recorded using a Tu-1901 UV-vis spectrophotometer (1 cm quartz cell). C, H, N elemental analyses were acquired on a Perkin-Elmer 240C analytical instrument.

Reagents

Commercially available solvents and reagents were used without further purification, and were all of analytical grades. Deuterated dimethyl sulfoxide (DMSO)-d_6 for ^{1}H NMR was bought from Aldrich. All TBA salts (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$) and other reagents (including the mobile phase) were purchased from Sigma-Aldrich and dried in silica gel desiccators before use. All other reagents, salts were dried before use in a desiccators containing P_2O_5 or distilled in reduced pressure. All UV-vis titrations were performed in 1.0×10^{-5} mol•L^{-1} solution of receptor **1** in DMSO except the Job plot (1.0×10^{-4} mol•L^{-1}) or unless mentioned otherwise. ^{1}H NMR titrations were performed on molar ratio solutions of receptor **1** and tetrabytylammonium (TBA) salts of F^-. Reversibility studies were carried-out using salt cation solutions of $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2$ and $CoCl_2$ (hydrated), which were all dried prior to use.

Synthesis of receptor 1

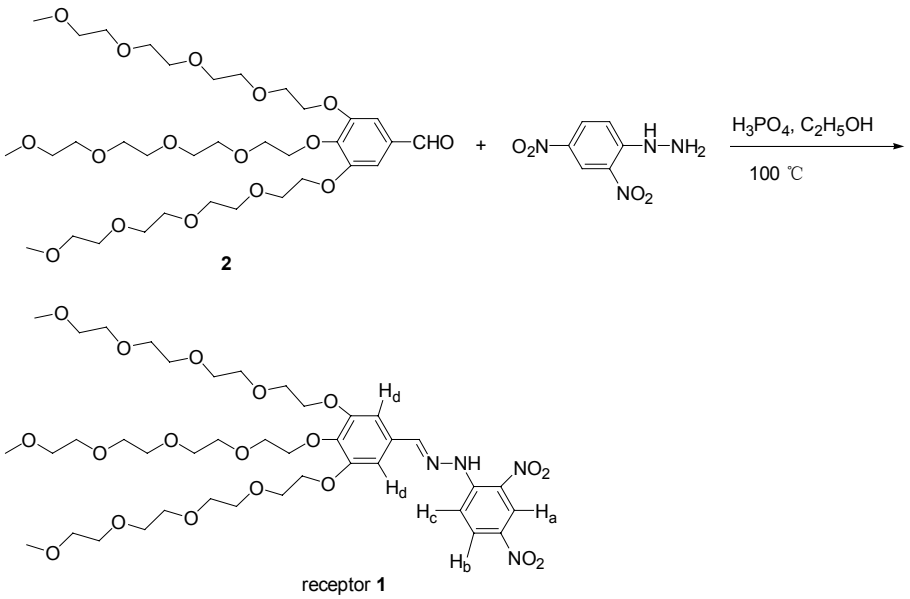
2,4-Dinitrophenylhydrazine (50 mg, 0.25 mmol) in warm phosphoric acid (10 mL) and ethanol (25 mL) was added to 3,4,5-tris(2,5,8,11-tetraoxatridecan-13-yloxy)benzaldehyde[16] (180 mg, 0.25 mmol) and heated to reflux for 6 h. After removing ethanol, water (100 mL) was added, then extracted with methylene dichloride. The combined extract in methylene dichloride was washed with a saturated solution of sodium chloride and dried over sodium sulfate. After removing methylene dichloride, the oily deep red compound was obtained. The oily product was purified in a silica gel column (60 cm) and collected in CCl_4∶$CHCl_3$∶CH_3OH (2∶2∶1) mobile phase as an orange red compound (yield 78%, 176 mg). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 11.70 (s, 1H, NH), 8.87 (s, 1H, N=CH), 8.56 (s, 1H, ArH_{NO2}), 8.35 (d, J=9 Hz, 1H, ArH_{NO2}), 8.14 (d, J=9.6 Hz, 1H, ArH_{NO2}), 7.10 (s, 2H, ArH), 2.50—4.30 (m, 57H, OCH_2-CH_2O). The UV-Vis spectrum of receptor **1** exhibits a band at 407 nm (ε=24 470 dm^3•mol^{-1}•cm^{-1}) due to the π-π* transition. Elemental analysis calcd for $C_{39}H_{56}N_4O_{19}$: C 52.9, H 6.4, N 6.3; found C 53.1, H 6.2, N 6.3.

Results and discussion

UV-Vis analysis of receptor 1

The anion binding ability of the receptor **1** was studied in HPLC grade DMSO by adding standard solutions of tetrabutylammonium (TBA) salts of AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^- and I^- at room temperature. Figure 1

Scheme 1 Synthesis of receptor **1**



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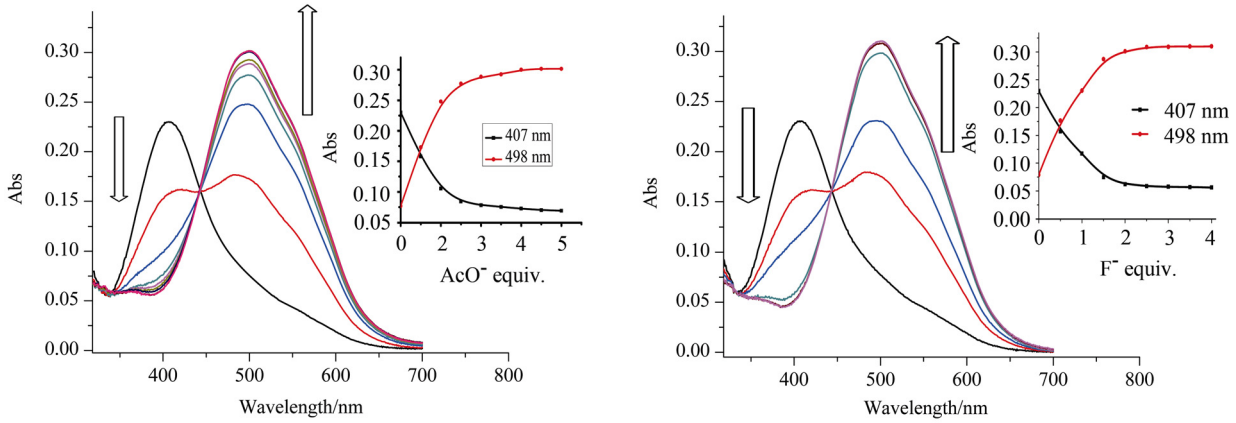

Figure 1 UV-vis spectral changes of receptor **1** (1.0×10^{-5} mol•L^{-1}) in DMSO upon addition of 0—4 equiv. of (a) AcO^- and (b) F^-. Inset: titration profile on the band at 407 nm and 498 nm indicating a 1∶1 adduct (a) AcO^--receptor **1** and (b) F^--receptor **1.**

(a and b) shows the changes in the UV-vis spectra of receptor **1** at a concentration of 1×10^{-5} mol•L^{-1} upon addition of AcO^- and F^- respectively. With the gradual addition of any of these anions, the absorbance peak centered at 407 nm resulting from the π-π* transition of the 2,4-dinitrophenyl hydrazine, disappeared gradually accompanied with the formation of a new band centered at 498 nm, resulting from intermolecular charge transfer (ICT) between the electron rich NH and the electron deficient NO_2.[17] At the same time, the colour of receptor **1** changed from yellow to pink (Figure 2) which could be detected with the naked-eye. The spectral red-shift ($\Delta\lambda$=91 nm) and the colour change (yellow to pink) show that there exists strong hydrogen bonding interactions between receptor **1** and the anions (AcO^- and F^-). The presence of a well-defined isosbestic point at 442 nm indicates the presence of a complex in equilibrium with receptor **1**. The addition of $H_2PO_4^-$ induced similar changes in UV-vis spectra with spectral changes induced by F^- and AcO^-, but with a relatively high volume (ESI, Figure S1). However, no significant spectral responses or colour changes were observed when adding Cl^-, Br^- and I^-, even when large amounts were used (ESI, Figure S2).

Figure 2 Colour change displayed upon addition of anions (A^- =AcO^-, F^- and $H_2PO_4^-$) to receptor **1** at 10 μmol•L^{-1} and 100 μmol•L^{-1}.

In addition, the ^{1}H NMR titrations suggested that the interaction of F^- with receptor **1** is a two-step process: (i) the formation of F-HN hydrogen-bond complex at low F^- concentration and (ii) the deprotonation process occurring with excess F^-. The addition of 0.5 to 1 equiv. of F^- where the pink colour appears and persists is a result of hydrogen bonding interaction between F^- and the NH, whereas excess F^- induces the deprotonation of receptor **1**.[17,18] Meanwhile, the limit of detection (LOD) of receptor **1** is at 1×10^6 mol•L^{-1} at 25 ℃.

Interestingly, the spectral shift and the pink colour produced by the addition of anions were significantly reversed by the additions of various cations (M^{II}) of $3d^{5\text{-}10}$ configuration, as well as Cd^{II}, Hg^{II}, Mg^{II} and Ca^{II} (anhydrous salts) as compared to protic solvent such as water, where excessive quantities may be required. Furthermore, the addition of ns^1 cations (anhydrous salts) such as Li^+, Na^+, Ka^+ did not generate any significant change at all, even when different forms (F^-, Cl^-, I^-, ClO_4^-, Br^-) were used, except LiCl which could reverse the changes, the action attributable to the electrostatic interaction between Li^+ and highly electronegative F^- in the solution. Apart from LiCl, no other forms of lithium halide (F^-, I^-, Br^-) or any other compound (ClO_4^-) used could revert the change. Moreover, acidic species such as chloroacetic acid could significantly reverse the spectral and visual changes when added, presumably due to acid-base interaction.[13]

Continuous variation method was used to determine the stoichiometric ratios of the host (receptor **1)** and the specific guest anion.[10g] The experimental procedures consisted of preparing series of solutions of host and guest anions such that the sum of the total concentrations is constant (1×10^{-5} mol•L^{-1}), with the molar fraction continuously varying. The wavelength was chosen where the absorbance was largest upon host-guest complexation (498 nm). The difference between the observed absorbance and the free receptor **1** (498 nm) in each series was plotted against the molar fraction [x=[H]/([H]+[G])].[10b] The Job's plot indicated the formation of a 1∶1 complex between receptor **1** and the three anions (ESI, Figure S3). The statistical data in the non-linear curve fitting for AcO^- and F^- illustrated (Figure 1a and 1b insets), correlate to a 1∶1 host-guest ratio respectively.

The corresponding binding constants for a 1∶1 host-guest complex were determined from their individual spectroscopic UV-vis absorption titration data (Table 1) at 25 ℃ by using a nonlinear least square fit[10c] of the absorbance versus the concentration of the cation added according to the equation:

$$A = A_0 + \frac{(A_{lim} - A_0)\{C_H + C_G + 1/K_a - [(C_H + C_G + 1/K_a)^2 - 4C_H C_G]^{1/2}\}}{2C_H}$$

where A is the intensity of absorbance; A_0 is the intensity of absorbance of the host only; A_{lim} is the maximum intensity of absorbance of host when guest is added; K_a is the affinity constant of host-guest; C_H and C_G are the concentration of the host and guest respectively. The association constants of receptor **1** towards the anions are listed in Table 1. Accordingly, the spectral changes under the same titration conditions, the K_a of receptor **1** for AcO^- should be slightly larger than F^-, a trend well known for hydrazone receptors.[10] The binding affinity trend displayed by receptor **1** in DMSO was: $AcO^- \geqslant F^- > H_2PO_4^- >>>> Cl^- \approx Br^- \approx I^-$.

Table 1 Association constant (K_a, L•mol^{-1}) of receptor **1** with F^-, AcO^- and $H_2PO_4^-$

Anion[a]	K_a
F^-	9.63×10^4
AcO^-	1.05×10^5
$H_2PO_4^-$	0.17×10^2

[a] The anions were added in their tetrabutylammonium salts.

Despite the remarkable response towards the above-mentioned anions, receptor **1** displayed mixed results in acetonitrile solution (CH_3CN). In CH_3CN, similar changes were observed for F^- (like in DMSO), despite a 14 nm hypsochromic shift, however, no significant change was observed for AcO^- and $H_2PO_4^-$ (ESI, Figure S4). Conclusively, the solvent polarity played a major role in host-guest interactions too.

Reversibility studies

Ideally, the recovery of the deprotonated receptor **1** should be possible based on the deprotonation mechanisms. Hydrogen bonding donor solvents such as water and methanol would compete with anion guest anions for receptor sites, the N—H.[5b,19] However, in this case reversibility studies indicated that water could hardly fully restore the deprotonated receptor **1** (ESI, Figure S5) even when large amount was used, however, there was a remarkable response when several cations (Zn^{II}, Cu^{II}, Pb^{II}, Ni^{II}, Co^{II}) were used (ESI, Figure S6). More cations were studied, but only few are presented in the work due to similarity in behaviours (reversibility) to those shown here.

In order to study and further elucidate the reversibility properties of a deprotonated receptor **1**, UV-vis and ^{1}H NMR analysis in DMSO and DMSO-d_6 solutions respectively were carried-out. Zn^{II} among other cations was selected, not only for its environmental friendliness and excellent bio-system roles, but its d^{10} configuration in NMR analysis. The addition of 1 equiv. Zn^{II} as a nitrate solution to the host-guest solution (receptor **1**+F^-) saw the disappearance of the pink colour (Figure 3a) and the restoration of the original yellow colour. The naked eye observed was reflected spectrally by the disappearance of the peak at 498 nm and the reappearance of the absorption band at 407 nm (Figure 3b). The amount of Zn^{II} needed to completely restore receptor **1** suggested that there existed a 2∶1 (F∶Zn) ratio interaction between F^- and Zn^{II}, giving rise to 1∶2∶1 (receptor **1**∶F∶M^{II}). This had eventually demonstrated that Zn^{II} was directly interacting with F^- rather than with the sensor. Similar behaviours were observed when other cations were used (ESI, Figure S6**)**. Virtually, reversibility studies of receptor **1** had just prompted the possibility and curiosity of exploring the molecular logic functions[15] based on colorimetric switch modulated by F^-/M^{II}.

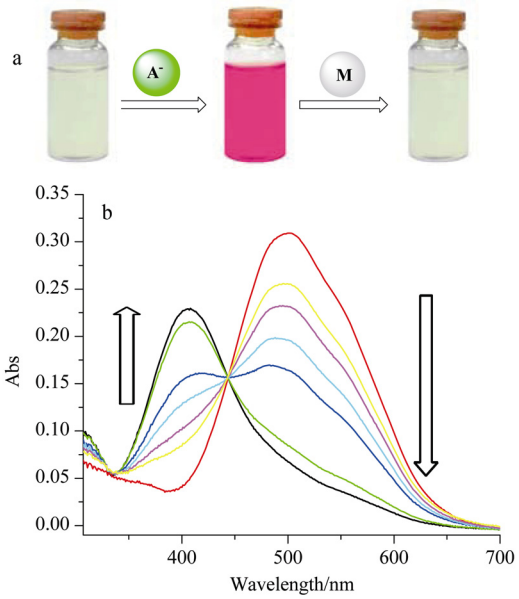

Figure 3 (a) Color changes of receptor **1** (1.0×10^{-5} mol•L^{-1}) in DMSO. Left to right: in the absence of ions, in the presence of 4 equiv. of F^- and in the presence of 4 equiv. of F^- along with 2 equiv. of M (M=M^{II} ($3d^{5\text{-}10}$), Cd^{II}, Hg^{II}, Mg^{II} and Ca^{II}). (b) The reversal of the UV-vis spectral pattern of receptor **1**+4 equiv. of F^- upon concomitant addition of 2 equiv. Zn^{II} ions.

Logic operation studies with F^- and M as inputs

Logic operation capabilities of receptor **1** were studied based on its reversibility studies (Figure 3b). The addition of appropriate combinations of F^- and Zn^{II} as inputs, produced the outputs (Figure 4a) which are in accordance with complimentary IMP/INH logic functions.[15a,15c,15f] The process is initiated (ON) by the addition of input 1 (AcO^-, F^-, $H_2PO_4^-$) and reversed

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(OFF) by the input 2 (Zn^{II}, Cu^{II}, Pb^{II}, Ni^{II}, Co^{II}, Cr^{II}, Mn^{II}, Fe^{II}, Mg^{II}, Ca^{II}). The spectral changes at 498 nm upon the addition of inputs are complementary to an INHIBIT (INH) logic gate, while at 407 nm are in accordance with an IMPLICATION (IMP) logic gate. Furthermore, no visual observation was detected after 2 equiv. of Zn^{II} was added to receptor **1**, except a slight hyperchromic shift at 407 nm (ESI, Figure S7). The addition of 5 equiv. of F^- to the solution of receptor **1**+2 equiv. Zn^{II} resulted in the appearance of the pink colour as well as the spectral shift from 407 to 498 nm. This did not only suggest a direct 2∶1 (F∶Zn) anion-cation interaction, but showed that the colorimetric activities of receptor **1** are not in any way inhibited by the presence of Zn^{II}. The ON and OFF reversible process sorely depends on the concentrations of the anions. The stability of receptor **1** was further demonstrated when about 4 cycles (ESI, Figure S8) were tested on F^-/Zn^{II} input-output system, which displayed consistent results with regard to anionic-cationic molar interactions. Moreover, apart from the 4 cycle completed only, the system could still carry on with more cycles, as there was still no sign of interference with colour or spectral change patterns, except the increase in input volumes. The IMP (implication) gate which is output-complementary to an INH (inhibition) was affirmed. In Table 2 the corresponding chemical inputs, spectral output signals and their binary encoding are compiled and displayed. IMP logic is closely related to "if…(condition), then…(consequence)" phrases. These logic gates can be combined in a complementary output circuit whose electronic equivalents are indicated in Figure 4b.[15a,15f]

Table 2 Truth table for the logic behavior IMP/INH of receptor **1** (10 μmol•L^{-1} in DMSO)[a]

Input		Output	
		(IMP)	(INH)
Input 1 (F^-)	Input 2 (Zn^{II})	407 nm (Abs.)	498 nm (Abs.)
0	0	1 (0.26)	0 (0.04)
1	0	0 (0.08)	1 (0.29)
0	1	1 (0.28)	0 (0.02)
1	1	1 (0.25)	0 (0.07)

[a] Inputs: 4 equiv. F^- and 2 equiv. Zn^{II}. Outputs: absorbance intensity at 407 and 498 nm, respectively.

^{1}H NMR titrations in DMSO-d_6

In order to investigate and ascertain the binding activities of the receptor, ^{1}H NMR titrations were carried out in the DMSO-d_6 molar solution of receptor **1**. It is noticed that the ^{1}H NMR spectra suggested that the interaction of F^- with receptor **1** is a two-step process: (i) formation of F⋯HN hydrogen-bond complex at low F^- and (ii) the deprotonation when F^- is in excess. According to Figure 5, receptor **1** exhibits one resonance at δ 11.70 attributed to the binding proton (—NH).[4c,5,6c,10c] The NH proton signal broadened downfield and disappeared upon the gradual addition of F^-, before a bifluoride ion $(HF_2)^-$ signal appeared at δ 15—17. Obviously, at low F^- (0.5—1 equiv.) a 1∶1 binding ratio was formed with receptor **1**, suggesting hydrogen-bond formation as shown in equation (1), however, as F^- increased (1.5—2 equiv.) the HF is released from the H-bond complex giving rise to $(HF_2)^-$ complex[17,18] and the deprotonated receptor, shifting the interaction ratio to a 2∶1 (F∶receptor **1**) as indicated in equation (2).[20]

At low F^- concentration (hydrogen bonding):

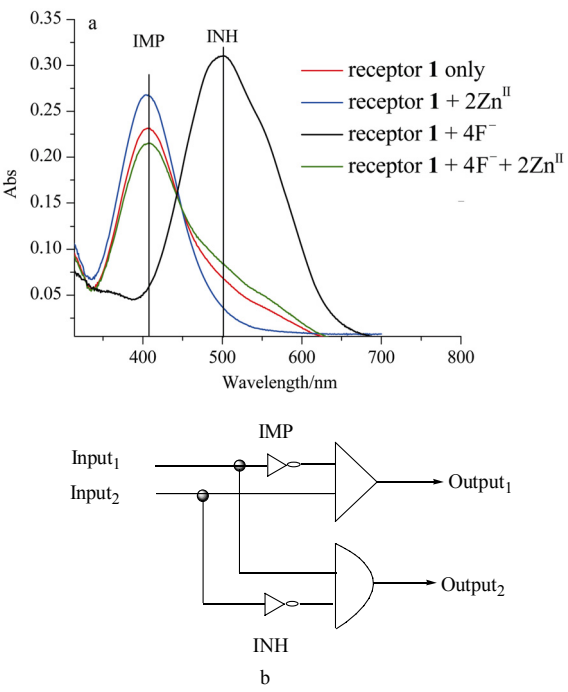

Figure 4 (a) UV-Vis spectra of receptor **1** (1×10^{-5} mol•L^{-1}) in DMSO with F^- and molecular logic function "IMP" (407 nm) and "INH" (498 nm), (I) receptor **1**+4 equiv. F^-, (II) receptor **1** +Zn^{II}, (III) receptor **1**+4 equiv. F^-+2 equiv. Zn^{II}, (IV) receptor **1**. (b) A combinatorial IMP/INH logic circuit.

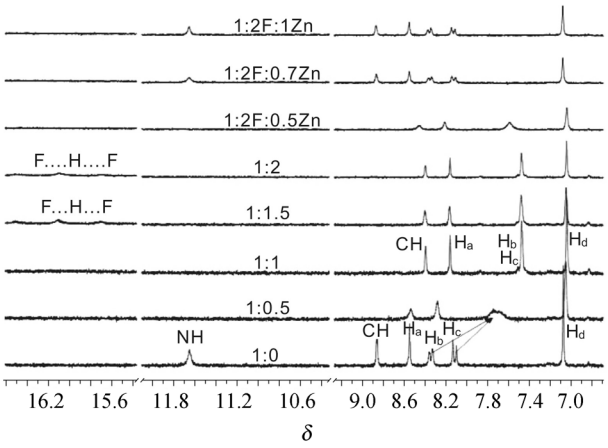

Figure 5 ^{1}H NMR spectra taken during the titration of receptor **1** in DMSO-d_6 solution (1.0×10^{-5} mol•L^{-1}) with a standard solution of TBAF ranging from 1∶0—2 molar equivalents and the addition of Zn^{II} to receptor **1**⋯F reversing the system.

LH (receptor **1**)+F^-↔$[LH\cdots F]^-$ (1)

Excess F^- concentration (deprotonation):

$LH+2F^-\leftrightarrow L+[FHF]^-$ (2)

Moreover, the phenyl ring protons H_a, H_b, and H_c (Scheme 1) all experienced significant upfield shifts, which could be attributed to the increase in electron density on the phenyl ring owing to the through-bond effect.[13a] More details on ^{1}H NMR titration spectra are referred to ESI, Figure S9, 10.

Conclusions

In summary, the phenylyhydrazone based anion receptor **1** was successfully synthesized and analyzed in DMSO. There are two vital points which can be deduced from this sensor: (i) receptor **1** is selective for AcO^- and F^-, displaying visual changes detectable by naked eyes or without any instrument; (ii) receptor **1** displayed a remarkable reversible system based on two input complementary IMP/INH logic functions modulated by F^-/Zn^{II}, which is very rare in literature. The colorimetric switching by appropriate amounts of anion and cation is likened to a molecular logic gate based on two-input functions for ON and OFF system control.

Acknowledgement

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