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A simple naphthalene-based colorimetric sensor selective for acetate

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ABSTRACT

A new naphthalene based receptor (**L**) has been designed and synthesized which shows a remarkable color change from colorless to pink on selective binding with acetate. The anion recognition property of the receptor via hydrogen bonding interactions is monitored by UV–vis, fluorescence, and ^{1}H NMR titrations. It is observed that in each case, the receptor shows a specific selectivity toward the acetate ion over other interfering anions. Thus, a significant bathochromic shift in UV–vis spectrum with a sharp pink color in '*naked-eye*' makes the receptor suitable for the detection of the acetate ion.

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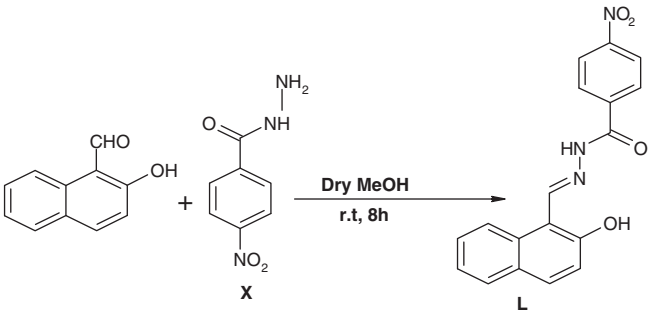
Anions play an important role in the field of supramolecular chemistry. Anions are mainly recognized through hydrogen-bonding interactions,[1] electrostatic interactions,[2] and coordination through metal ions[3]. Among various non-covalent interactions, hydrogen-bonding interactions are particularly useful and effective in this regard. Receptors bearing functional groups such as amides,[4] ureas,[5] thioureas,[6] imidazolium,[7] and positively charged groups[8] have been widely used to recognize anions via hydrogen-bonding interactions.

Recently, neutral organic molecules which are capable of creating highly directional hydrogen bonding interactions have been successfully used in the design of novel anion receptors. The acetate anion plays an important role in biochemistry, environmental, and pharmaceutical science.[9–11] For example, acetate production and oxidation rate have been frequently used because the acetate anion is considered as an indicator of organic decomposition in marine sediments.[12] A great effort has been made to the development of sensing devices for AcO^- involving fluorescence chemosensors, chromogenic chemosensors,[13] and sensors based on electrochemical devices.[14] Even with these remarkable achievements, there are many downsides being recognized. Generally, the recognition of anions are studied in less polar organic solvents[15,16] (e.g. CH_2Cl_2, DMSO, CH_3CN etc.) and sometimes also in the mixture of protic solvents (e.g. H_2O, CH_3CH_2OH). Normally the acetate chemosensors will display response to other anions such as fluoride and dihydrogenphosphate, especially the former,[17] but the sensitivity of our receptor **L** to the fluoride ion as well as dihydrogen phosphate is negligible and does not show any '*naked-eye*' detectable color.

In this Letter, we report a designed Schiff base between the phenyl hydrazine compound (**X**) and 2-hydroxy-1-naphthaldehyde and its anion binding properties were investigated by means of UV–vis, fluorescence, and ^{1}H NMR and as well as by '*naked-eye*'. The amine was synthesized between *p*-nitro benzoate ester and hydrazine hydrate in dry methanol medium under refluxing condition by the reported procedure.[18] The target deep yellow imine receptor **L** was formed in one step by the facile Schiff base condensation reaction of 2-hydroxy-1-napthaldehyde with the yellowish



Scheme 1. Synthesis of the receptor (**L**).

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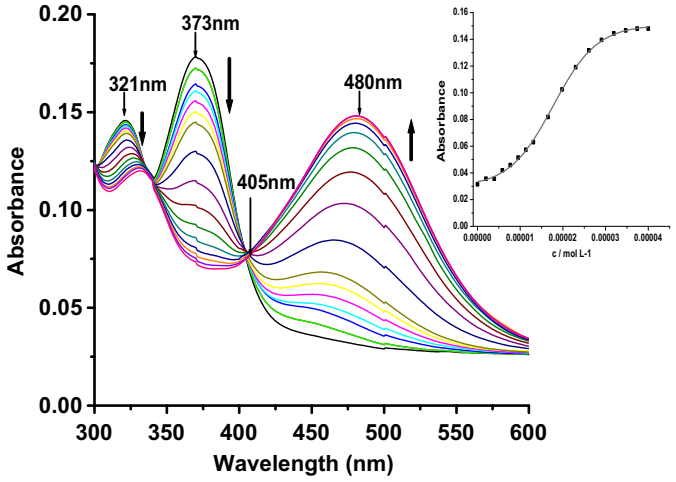


Figure 1. UV–vis absorption spectra of **L** (1×10^{-5} M) in CH_3CN upon titration with tetrabutylammonium acetate (*n*-Bu_4NOAc, 5 equiv). The arrows show changes due to the increasing concentration of AcO^-. Inset, binding isotherms were recorded at 300 and 600 nm with AcO^-. The solid line is global least-squares fit to the experimental data.

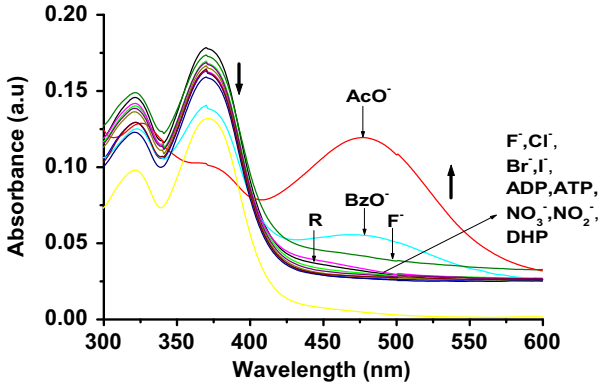


Figure 2. UV–vis absorption spectra of **L** (1×10^{-5} M) in CH_3CN upon titration with 3 equiv of each of the different guests (2×10^{-4} M).

amine (**X**) in methanol medium (Scheme 1) and was produced in an 80% yield after recrystallization from ethanol. Its molecular structure and purity were established from different spectroscopic studies like ^1H NMR, HRMS, and FT–IR and also from crystallography analysis (Supplementary data).

The binding behavior of receptor **(L)** with different anions was studied in acetonitrile solvent. The titration was carried out in CH_3CN at 1×10^{-5} M concentration of receptor **L** upon the addition of incremental amounts from 0–500 μl of tetrabutylammonium acetate (2×10^{-4} M).

The UV–vis spectrum of the receptor **(L)** is characterized by two bands centered at 321 and 373 nm (Fig. 1). As shown in Figure 1, upon gradual increase of the acetate ion concentration, the bands at 321 and 373 nm gradually weaken and a new band appears at 480 nm with an isosbestic point at 405 nm, indicating the formation of a new complex between the receptor (**L**) and the acetate anion (Fig. 1) which is also responsible for the generation of pink color after the addition of tetra butyl ammonium acetate to the solution of the receptor**.** Inset of Figure 1 actually indicates the change of absorbance with the concentration of acetate. From the UV–vis titration data it is revealed that minimum 5.83 μM of AcO^- can be detected by using 10 μM of receptor **L**. The receptor shows linearity up to 2.61×10^{-5} M concentration of acetate (Supplementary data).

After the addition of 5 equiv of tetra-butyl-ammonium acetate, it reaches a saturation level. Titrations were also carried out with various anions like F^-, Cl^-, Br^-, I^-, and $C_6H_5COO^-$ as their tetra butyl ammonium salts and ADP, ATP, KDHP, $NaNO_3$, $NaNO_2$ etc. Interestingly there is no obvious change observed in the UV spectrum except with benzoate ion, which shows slight interference (Supplementary data). There is a small appearance of a new peak at 480 nm which indicates that the receptor **(L)** has a slight response to benzoate ion due to the same carboxylate binding mode as acetate anion. The cavity of **L** binds selectively to AcO^- over $C_6H_5COO^-$ which may be due to the basicity difference (weaker basicity of benzoate over acetate and also steric bulk of the phenyl ring) (Fig. 2).

Figure 3 actually shows the selectivity for acetate over the other anions which is shown by the green bar. The slight interference of benzoate and fluoride is shown by the violet and olive bars but it cannot be detected by the naked eye which is shown in the inset. From the experimental data, it can be concluded that the receptor **L** possesses high selectivity and sensitivity toward acetate in acetonitrile medium. The other anions except benzoate had no practical significant influence. The color changes are most probably due to the formation of hydrogen bonds or deprotonation of –OH group of receptor **L** on the addition of the acetate ion which is shown in Scheme 2.

These hydrogen bonds or de-protonations affect the electronic properties of the chromophore which result in the change of color from colorless to pink, along with a new charge-transfer interaction between the acetate bound –OH and –NH moieties and the

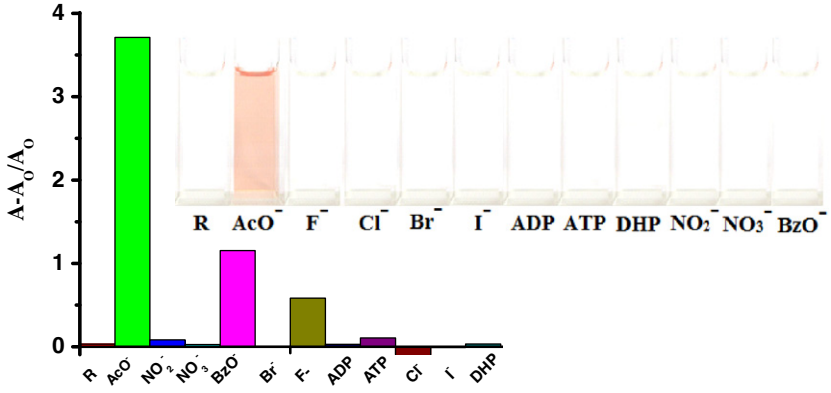
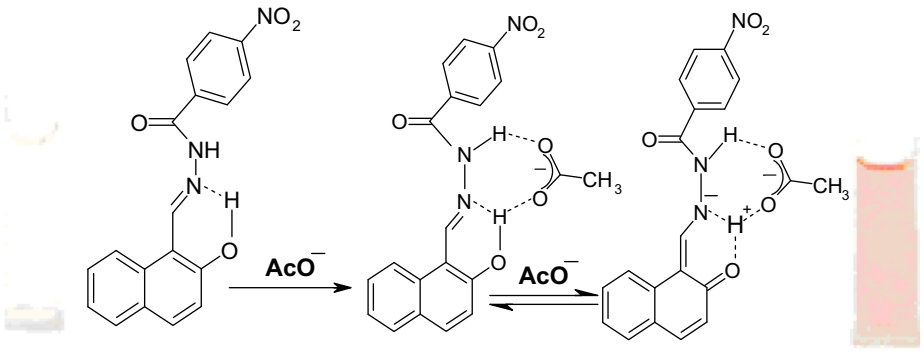


Figure 3. $(A–A_0)/A_0$ ratios of receptor **L** (1×10^{-5} M) after the addition of 3 equiv of each of the various anions (2×10^{-4} M) in acetonitrile. Inset: Color changes of receptor **L** (1×10^{-5} M) upon the addition of 5 equiv of each of the different guest anions (2×10^{-4} M).



Scheme 2. Probable host-guest binding mode in solution phase.

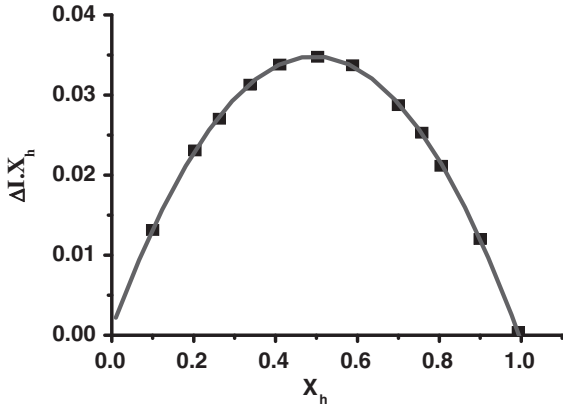


Figure 4. Jobs plot diagram of receptor **L** for anion tetra butyl ammonium acetate (where Xh is the mole fraction of host and ΔI indicates the change of the absorbance).

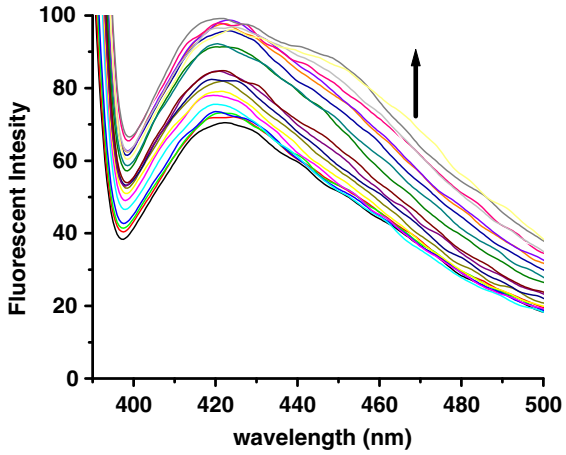


Figure 6. Changes in fluorescence emission for receptor **L** (1×10^{-5} M) upon the addition of 5 equiv. Tetrabutyl ammonium acetate (2×10^{-4} M) in CH_3CN (λex = 373 nm).

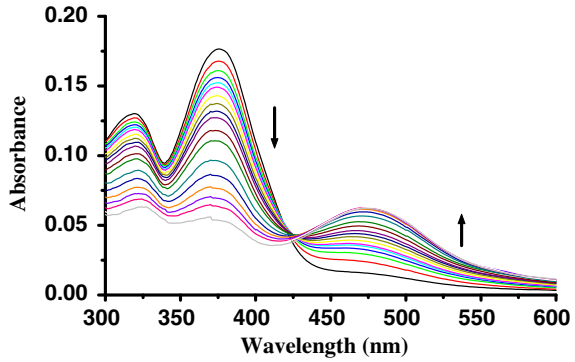


Figure 5. UV–vis absorption spectra of **L** (1×10^{-5} M) in CH_3CN-H_2O (9:1, v/v) upon titration with tetrabutylammonium acetate (n-Bu_4NOAc, 10 equiv).

electron deficient nitro group.[19,20] Furthermore, the strong hydrogen-bonding interaction between receptor **L** and AcO^- could enhance π delocalization, which was expected to reduce the energy of the π–π* transition and therefore accounts for the appearance of a new absorption band near 480 nm resulting in the formation of a pink color.[21] A well-defined isosbestic point at 405 nm emerged during the spectral titrations, which indicated the formation of the stable complex with a certain stoichiometric ratio between the receptor and the anion resulting in a new ICT (internal charge transfer) band that appeared at 480 nm. The 1:1 stoichiometry for the host–guest complexation was elaborated by the profile of the intensities of the decreasing band centered at 373 nm and increasing band at 480 nm which was also confirmed by Job plot analysis (Fig. 4).

The sensing property of the receptor was also investigated in acetonitrile/water (9/1, v/v). As expected, in the presence of water, the sensing behavior of the receptor is slightly diminished (Fig. 5). This may be due to the interaction of the guest with water.

In the case of pure acetonitrile media the absorbance of the receptor **L** (**1** $\times$ **10**$^{-5}$ M) increases fivefold on the addition of 5 equiv of tetrabutylammonium acetate (2×10^{-4} M) while in acetonitrile–water mixture the fourfold increase occurs by the addition of 10 equiv of acetate in same experimental conditions that is there is a loss of some sensitivity in acetonitrile-water media. This is why we choose only acetonitrile for the titration purpose for proper sensing of the receptor.

We carried out fluorescence titration experiments of the receptor (**L**) [10 μM] with the AcO^- (200 μM) in acetonitrile. The fluorescence response of the receptor **L** with AcO^- was recorded with an excitation at 373 nm. As shown in Figure 6, there is no significant change observed in the emission spectrum of the receptor after the addition of excess amount of acetate salt. However, the minor increase of fluorescence intensity suggests that the ICT process operates due to the occurrence of a tautomeric equilibrium during the anion recognition process (Scheme 2).

From NMR study, we have investigated the molecular interaction between the receptor **L** and an acetate ion. The NMR of the receptor **L** shows the existence of two probable forms of the receptor **L** (Form A and Form B) in solution in DMSO-d_6 and probably

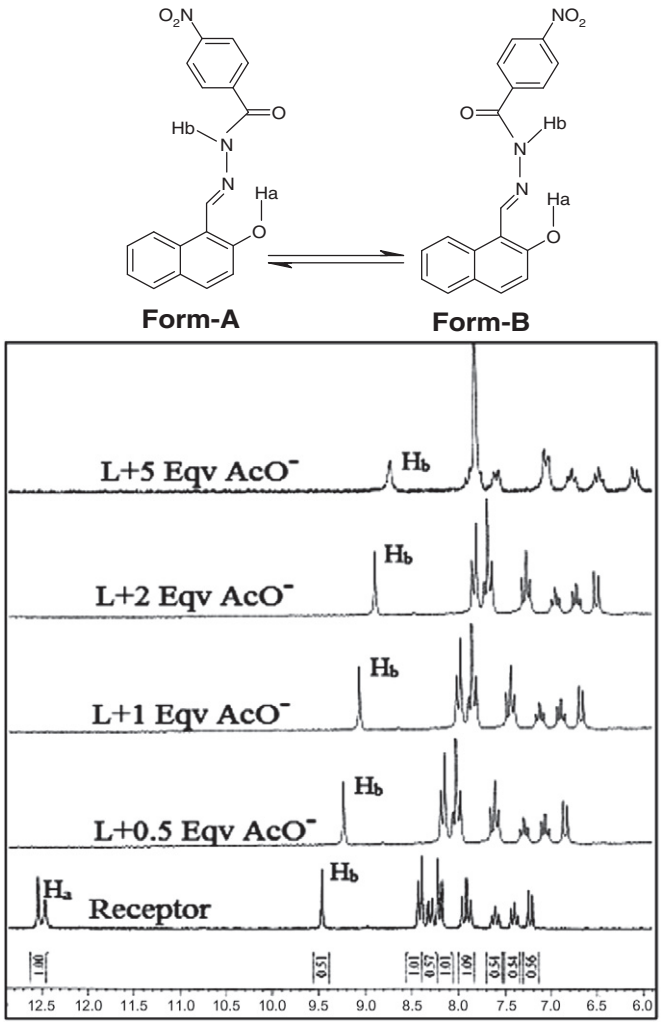


Figure 7. Partial ^{1}H NMR spectrum (200 MHz) of **L** (1.19×10^{-2} M) in DMSO-d_6 at 25 °C and corresponding changes after the addition of different equivalents of tetra butyl ammonium acetate (2.21×10^{-2} M).

because of this, two peaks appear for naphtholic proton (δ 12.520 ppm and δ 12.570 ppm, respectively) (intramolecularly six membered hydrogen bonded with imine nitrogen in both forms) possibly due to different environments in the two conformational forms. Form A and Form B are probably inter-convertible by rotation around the N–N sigma bond and Form A is more stable in the solid phase because it was exclusively crystallized, as proven by single crystal X-ray structure. However, in the solution phase probably Form B binds better to acetate as suggested by NMR titration spectral analysis. The peak at slightly downfield (δ 12.57 ppm) probably belongs to –OH of Form A and the other at δ 12.52 due to –OH of Form B existing in solution. However the other possible tautomer having vinylic –NH is probably not present as the vinylic –NH should not appear at such down field (i.e. around δ 12 ppm). So possibly there is an energy barrier between the two hydrogen bonded conformers A and B showing two peaks. The –OH proton of **L** itself appeared at δ 12.5 (H_a) ppm, downfield from its normal value (δ 10 ppm), due to its intramolecular H-bonding between imine nitrogen and naphthol –OH group which is shown in scheme 2. However, in case of the titration experiments for the receptor **L** and tetrabutylammonium acetate in DMSO-d_6 solvent, the proton signal of the naphthol hydroxyl disappeared after the addition of 0.5 equiv of acetate and there was no appearance of proton signal by naphthol hydroxyl group even after the addition of 1, 2, and 5 equiv of acetate. This indicates that there is a new complex formation between naphthol hydroxyl group and acetate ion.

At the same time, due to complexation process, the –NH (H_b) proton of hydrazide undergoes an upfield shift from δ 9.477 ppm to δ 9.019 ppm because the anionic species induces an upfield chemical shift through diamagnetic shielding. Again noticeable upfield chemical shifts are also shown in the case of protons of benzene as well as in naphthalene rings of receptor **L** which are induced due to complexation after the addition of 5 equivalents of acetate which is shown in NMR titration curves (Fig. 7).

The structure of **L** is further confirmed and characterized by single crystal X-ray diffraction and is shown in Figure 8. However we are so far unable to grow a single crystal for the bound form to confirm the complex structure and we propose the complex structure as shown in Scheme 2. The crystal structure is stabilized by an intramolecular O—H···N hydrogen bond between the naphthalene OH and the imine nitrogen, which forms an $S(6)$ ring motif.[22] In the crystal, molecules are linked into planes parallel to the (001) via intermolecular (N,C)–H···O and (C,C)–H···O bifurcated acceptor bonds, generating $R_2^1(6)$ ring motifs.[22]

In conclusion, herein we report a new receptor which selectively recognizes acetate anion over other interfering anions in acetonitrile solution. Its bold color change only after addition of acetate anion makes it an excellent sensor for detecting acetate anion in 'naked-eye'. The selectivity of the receptor may be due to unique *peri* position (of naphthalene) of the hydrazone and also due to enhanced acidity of the amide NH_b of hydrazone. The selectivity here is greatly influenced based on charge-charge interactions, and the involvement of both N–H···O and O–H···O hydrogen bonds.

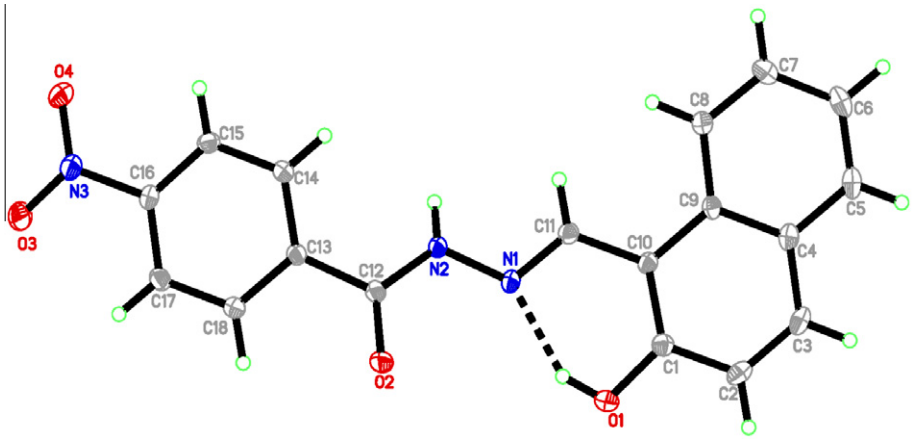


Figure 8. Ortep diagram of receptor **L** (Form A).

The unique binding motif can find a greater utility in the development of new anion receptors/sensors with enhanced binding affinity and substrate specificity, which is actively being investigated.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.06.104.

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