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# Pterin-based highly selective, ratiometric, and sensitive 'naked-eye' sensor for acetate

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The design and synthesis of a new pterin-based ratiometric and sensitive 'naked-eye' sensor **R** for highly selective recognition of acetate are reported. The acidic lactam NH and the NH of 2-*N*-pivaloyl group of receptor **R** along with 2,4-dinitrophenyl hydrazone group having the other acidic NH moiety lead to the binding of acetate anion in a 1:2 ratio by change of spectroscopic behavior on complexation (UV–vis and $^1$H NMR studies) which is also proven by Job plot. The sharp color change from light yellow to violet promises **R** to be a useful chromogenic ratiometric sensor for acetate amongst other common anions.

Over the past few years, the recognition and sensing properties of anions have attracted considerable attention for their diversity of functions.[1–8] Anions also play a fundamental role in a wide range of chemical, biological, and environmental processes. Among the various biologically important anionic analytes, acetate and dicarboxylate are among the most critical components of numerous metabolic processes. Without them, many enzymes and antibodies are unable to function properly. Therefore, the easily synthesizable anion chemosensor has a greater priority due to the important role of acetate in biology and clinical diagnostics.[9–12] Acetate is one of the carboxylate anions with the unique trigonal structure which can form strong hydrogen-bond interaction with hydrogen bond donors. Therefore, noncovalent hydrogen-bonding interaction is one of the most useful and effective in this regard. Receptors bearing functional groups such as amides,[13] ureas,[14] thioureas,[15] imidazolium,[5] and positively charged groups[16] have been widely used to recognize anions via hydrogen-bonding interactions. A variety of receptor molecules which selectively recognize acetate anion are available in the literature,[17–19] including many capable of luminescent sensing. Generally, the recognition of anions is studied in less polar organic solvents[20,21] (e.g., $CH_2Cl_2$, DMSO, $CH_3CN$ etc.) and sometimes also in the mixture of protic solvents (e.g., $H_2O$, $CH_3CH_2OH$). It is also known that the rate of $AcO^-$ production and oxidation usually acts as an indicator of organic decomposition in marine sediments[22] and transmetalation of tetrapyrroles.[23–25]

On the other hand, ratiometric probes should enable the measurement at two different wavelengths, providing a built-in rectification for environmental effects and raising the dynamic range of measurement. This was considered as a high-quality approach to defeat the major problem of absorption based probes, in which variations in the environmental sample and probe sharing were problematic for quantitative measurements. However, so far, ratiometric probes for acetate are still very scarce.

In this work, pterin has been chosen as an ideal component of a chemosensor due to its biological importance,[26] good platforms for sensing,[27] and also its ability to form charge transfer complexes.[28]

Therefore, we have designed and synthesized a chromophore in our laboratory whose physicochemical properties can be utilized as a ratiometric sensor for acetate both qualitatively and quantitatively.

At first, 2,5,6-triaminopyrimidine hydrochloride is condensed with monoacetal of tricarbonyl compound according to Grabrel–Isay condensation.[29] Then the crude product under pivaloylation gives the soluble product which affords 6-formyl pterin with deprotection of acetal group at 6-position. The receptor **R** was prepared by applying simple Schiff's base condensation reaction between 6-formyl pterin and 2,4-DNP in ethanol which afforded **R** as a yellowish precipitate with a good yield (Scheme 1).

Molecular structure and purity level of the receptor **R** were established from different spectroscopic studies like $^1$H NMR and HRMS analysis (Supplementary data).

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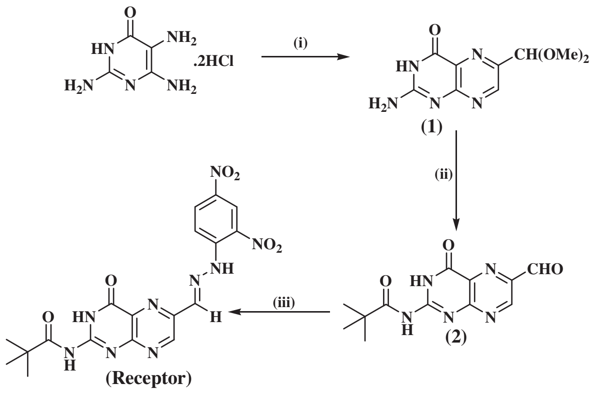


**Scheme 1.** Synthetic outlook of the receptor. Reagents and conditions: (i) $Na_2SO_3$, $H_2O$, $OHC(CO)CH(OMe)_2$, rt,12 h. (ii) (a) Pivalic anhydride, DMAP (cat.), 120 °C, 6 h; (b) TFA, $CH_2Cl_2$, rt, overnight. (iii) 2,4-DNP, EtOH, few drops of acetic acid, 80 °C, 2 h.

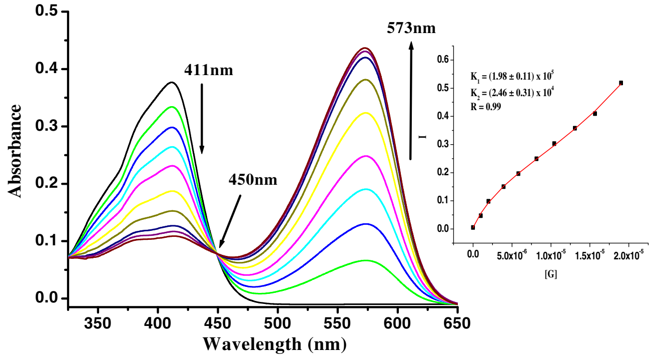


**Figure 1.** UV–vis absorption spectra of **R** ($C = 1 \times 10^{-5}$ M) upon titration with TBAA (tetrabutylammonium acetate) ($C = 2 \times 10^{-4}$ M) in $CH_3CN$ at 25 °C. Inset: nonlinear 1:2 fitting isotherm recorded at 573 nm.

The binding and recognition properties of receptor **R** were studied by UV–vis and NMR titration methods. The UV–vis spectroscopic titration of **R** was carried out in acetonitrile ($C = 1 \times 10^{-5}$ M) with acetate and other anions. There is a characteristic band at 411 nm of the receptor **R** in the UV–vis spectrum (Fig. 1). Surprisingly, it is observed that the intensity of the band at 411 nm decreases upon gradual addition of tetrabutylammonium acetate (TBAA) ($C = 2 \times 10^{-4}$ M) and the intensity of a new band at 573 nm increases, forming a distinguished naked-eye color change from light yellow to violet. The formation of a new complex between **R** and acetate anion is also indicated by the isosbestic point at 450 nm. Additionally, the characteristic structured absorption band at 411 nm is almost completely minimized suggesting that significant electronic perturbation occurred in the ground state of **R**.[30]

The change of color in the presence of acetate ion is attributed by the probable hydrogen bonding formation between **R** and acetate ion (Scheme 2). It is also observed that the enhancement of ratiometric value of absorbance of the **R** ($1 \times 10^{-5}$ M) is near about 19-fold on addition of 5 equiv TBAA after which it gets saturated. From the UV–vis titration data, it is also clear that minimum 2 μM of acetate can be detected by using 10 μM of receptor.

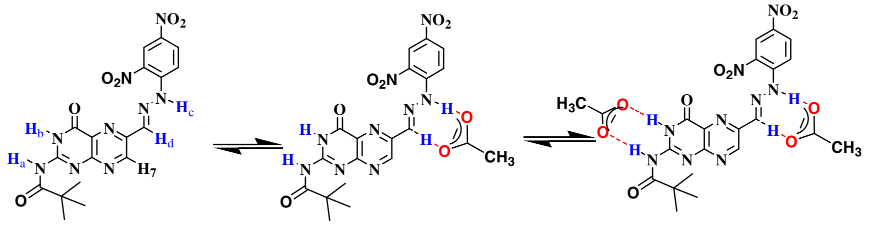
Titrations were also carried out with various anions like $F^-$, $I^-$, and $C_6H_5COO^-$ as their tetrabutylammonium salts and ADP, ATP, KDHP, $NaNO_3$, $NaNO_2$, $K_3PO_4$, $Na_2SO_3$, Na-aspartate, and Na-lactate. Interestingly there is no observable change detected in the UV spectrum except with fluoride and benzoate ion, which show very little interference (Supplementary data). There is a small appearance of a new peak at 573 nm which indicates that the receptor (**R**) has an insignificant response toward fluoride ion. In the presence of benzoate the peak at 411 nm slightly decreases (Fig. 2). Possibly the basicity difference, that is, weaker basicity of benzoate over acetate and the steric effects are the main cause of the selectivity of $AcO^-$ over $C_6H_5COO^-$ toward **R** (Fig. 2).

Interestingly, the very large (absorption shift: $\Delta A = 162$ nm) difference between the two wavelengths not only contributes to the accurate measurement of the two absorption peaks, but it also results in a huge ratiometric value. In fact, almost 60-fold enhancement in the ratiometric value ($I_{573}/I_{411}$, from 0.06 to 4.02) is achieved with respect to the acetate-free solution in the presence of 5.0 equiv of acetate (Fig. 3). The change of absorbance with the concentration of acetate also maintained a linear relationship from 2 μM to 10 μM (Fig. 3).

On the addition of acetate ion, the color changes are most likely due to the creation of hydrogen bonds and deprotonation of amide proton of receptor (**R**) which is illustrated in Scheme 2. These hydrogen bonds or deprotonations influence the electronic properties of the chromophore which result in the transformation of color from light yellow to violet, along with a new charge-transfer communication between the acetate bound NH moieties and the electron deficient nitro group.[31] Furthermore, the $\Pi$ delocalization is improved due to the strong hydrogen-bonding interaction between receptor **R** and acetate ion, which was predictable to reduce the energy of the $\pi$–$\pi^*$ transition and therefore accounts for the appearance of a new absorption band at a higher wavelength, that is, at 573 nm resulting in the formation of a violet color. A distinct isosbestic point at 450 nm emerged during the spectral titrations, which confirmed the formation of the stable complex with a definite stoichiometric ratio between the receptor and the anion resulting in a new ICT (internal charge transfer) band that appeared at 573 nm.

The 1:2 stoichiometry for the host–guest complexation was elaborated by the profile of the intensities of the diminishing band centered at 411 nm and rising band at 573 nm which was also confirmed by Job plot analysis (Fig. 4). The association constant was estimated to be $K_1 = 1.98 \pm 0.11 \times 10^5\ M^{-1}$ and $K_2 = 2.46 \pm 0.31 \times 10^4\ M^{-1}$ by nonlinear regressive analysis method[32] using absorption titration data. The calculated detection limit is 0.604 μM based on $K \times Sb1/S$,[33] where Sb1 is the standard deviation of blank measurements and $S$ is the slope of the calibration curve (Fig. S1: Supporting information).

We carried out fluorescence titration experiments of the receptor **R** ($1 \times 10^{-5}$ M) with the $AcO^-$ ($2 \times 10^{-4}$ M) in acetonitrile. The fluorescence response of the receptor **R** with $AcO^-$ was recorded



**Scheme 2.** Probable binding mode of the receptor with acetate.

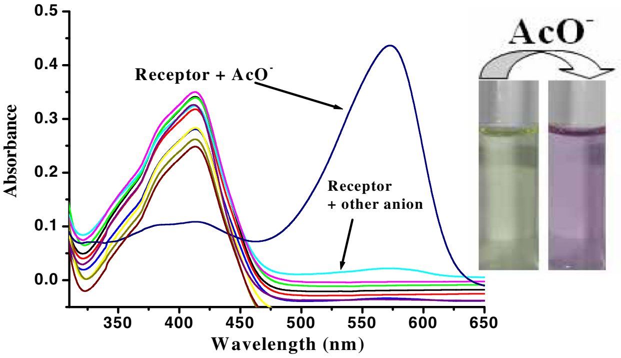


**Figure 2.** UV–vis absorption spectra of **R** upon titration with all the tested anions in $CH_3CN$ with the naked-eye color change of **R** in the presence of acetate.

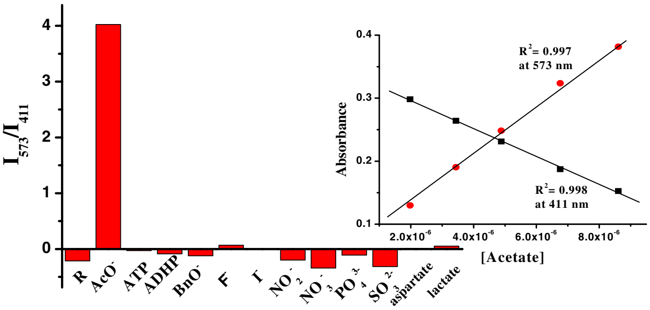


**Figure 3.** The bar plot of ratiometric response of **R** in the presence of all the tested anions (left) and plot of absorbance versus [AcO⁻] at two different wavelengths (right).

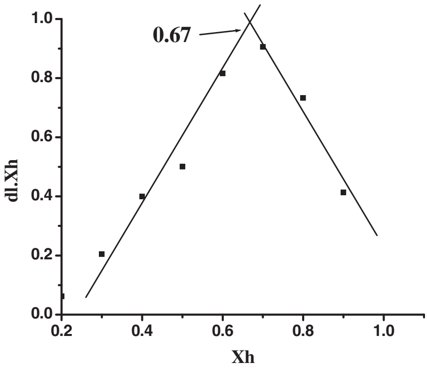


**Figure 4.** Job plot diagram of receptor **R** for anion tetrabutylammonium acetate (where Xh is the mole fraction of host and dI indicates the change of the absorbance).

with an excitation at 411 nm (Fig. S3: Supporting information) and there is no observable change in the emission spectrum of the receptor after the addition of excess amount of acetate salt. However, the slight increase of fluorescence intensity suggests that the ICT process operates due to the occurrence of a tautomeric equilibrium during the anion recognition method (Scheme 2).

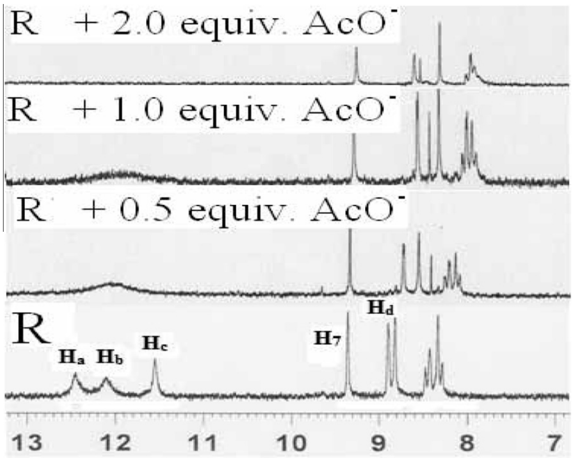


**Figure 5.** Partial $^1H$ NMR spectrum of **R** in DMSO-$d_6$ with addition of different equiv of TBAA.

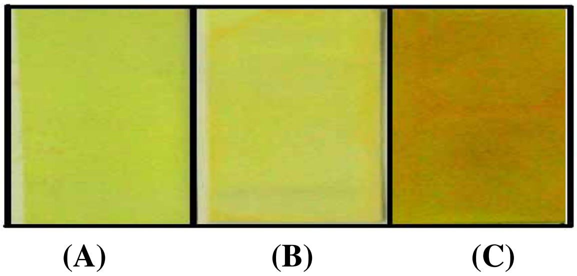


**Figure 6.** Photographs of test strips of **R** toward various concentrations of acetate ($C \times 10^{-3}$ mol/L) $C$ = (A) 0, (B) 2, (C) 10.

Now we describe the $^1H$ NMR titration of receptor **R** with TBAA in DMSO-$d_6$ (Fig. 5) to recognize the nature of interaction between the specific hydrogens of **R** and the acetate ion. It is found that the amides and N—H-(—C=NH—) protons (Ha, Hb, and Hc) of **R** are gradually dispersed with the gradual addition of acetate anion indicating the cyclic intermolecular H-bonding interaction as shown in Scheme 2. Additionally, the –CH– of hydrazone moiety and $H_7$ of **R** are distinguishably shifted upfield in complex 1:1 (0.417 ppm and 0.137 ppm) and complex 1:2 (0.551 ppm and 0.296 ppm), respectively. Besides, the protons of the 2,4-dinitro-substituted aromatic ring of **R** also undergo upfield shift on complexation with acetate in 1:1 and 1:2 complexes.

Many sensors for AcO⁻ detection could only be performed in solution, which would limit their applications. To examine the realistic function of chemosensor **R**, test strips were prepared by immersing TLC plates into a solution of **R** ($2 \times 10^{-3}$ M) and then drying in air. As shown in Figure 6, when acetate solution was added on the test kits in different concentrations, the obvious color changes from greenish yellow to brown were observed. Thus, the test strips could straightforwardly sense acetate. Development of such dipsticks is helpful as immediate qualitative information is obtained without resorting to the instrumental analysis.

Thus we have been able to develop a unique pterin-based hydrazone receptor specific for chromogenic recognition of acetate over many other anions. The electron withdrawing pterin moiety having in one side, the lactam NH and the pivaloylamide N–H, binds one acetate moiety and the other side having 2,4-DNP hydrazone moiety binds the other acetate ion making the sensor **R** a bidentate one for acetate (1:2). Test strips (TLC sticks) of **R** also demonstrated its effective solid surface application as a sensor for acetate.

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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.2014.03.068.

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