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A new application of bromopyrogallol red as a selective and sensitive competition assay for recognition and determination of acetate anion in DMSO/water media

Hossein Tavallali[*], Gohar Deilamy Rad, Abolfath Parhami, Elham Abbasiyan

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

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Bromopyrogallol red, BPR, (2-(2,7-dibromo-4,5,6-trihydroxy-3-oxo-3H-xanthen-9-yl) benzenesulphonic acid, Scheme 1) as a new chromogenic anion receptor, can selectively and efficiently be applied for detection of AcO^- over wide range of anions such as BzO^-, F^-, Cl^-, Br^-, OH^-, I^-, NO_3^-, HSO_4^-, CN^- and CO_3^{2-} in mixed DMSO/H_2O media. Increasing the amount of H_2O up to 50% (v/v) caused a dramatic development in selectivity of AcO^-. The developed BPR enabled the determination of acetate in the linear concentration range of 19.0–42.0 μM (1.12–24.8 μg mL^{-1}) with the detection limit of 2.5 μM (0.147 μg mL^{-1}) and the relative standard deviation (RSD, $C = 19.4$ μM, $n = 5$) of less than 1%. This enables the design and development of reusable optical receptors for monitoring trace amounts of acetate ion in vinegar samples and the values agreed with those mentioned by the manufacturers.

1. Introduction

Anions are ubiquitous in both the organic and mineral worlds, and play important roles in biology, medicine, catalysis, and in the environment [1–3]. Among the chemosensors for the detection of anions, the colorimetric chemosensors have attracted considerable attention due to specific color change of solutions upon anion complexation [4]. Acetate (AcO^-) is a critical component of numerous processes. The rate of AcO^- production and oxidation has been frequently used as an indicator of organic decomposition in marine sediments [5] and transmetalation of tetrapyrroles [6]. Therefore, the search for a chromophore, whose changes in color can be used to sense acetate both qualitatively and quantitatively in the presence of several other coexisting anions, is highly desirable [7–11]. Some of these colorimetric receptors for acetate ion in organic media such as DMSO have been reported [9,11,12]. In biological and environmental systems, interactions between anions and sensors occur commonly in aqueous media [13–18]. However it has been shown that strong hydration of sensor molecules in aqueous phase stops the sensor from AcO^- recognition [10]. Therefore the development of anion receptors compatible with aqueous conditions has found considerable attention. Another problem usually encountered as a limitation with AcO^- receptors, is their stronger affinity for F^- [13,14,19]. 2-(2,7-dibromo-4,5,6-trihydroxy-3-oxo-3H-xanthen-9-yl) benzenesulphonic acid (BPR), a metal sensitive dye, is a widely used xanthene ligand and has been applied for the spectrophotometric determination of many cationic substances, such as molybdenum [20], tin [21], ammonium ion [22] and bismuth [23,24]. However, according to our knowledge, BPR has not been applied for detection of anionic species so far. Herein, we report BPR as a novel and selective anionic receptor for selective recognition and determination of AcO^- in high water concentrations (DMSO/H_2O 50:50 v/v). Moreover, a few efforts have been performed to develop anion receptors bearing OH as the binding site such as BPR [25–29].

2. Experimental

2.1. Reagents

Analytical grade reagents and demineralized water were used in solutions preparation. All reagents were obtained commercially and were used without further purification. In the titration experiments, all the anions were added in the form of tetra- butyl ammonium (TBA) salts, unless carbonate was added in the form of sodium salt which were purchased from Sigma–Aldrich Chemical, and stored in vacuum desiccators containing self-indicating silica and were fully dried before use. Nitrate salts of some cations such as Na^+, K^+, Ca^{2+}, Cd^{2+}, Ba^{2+}, Mg^{2+} and Li^+ were purchased from Merck and aqueous solution of 1.0×10^{-2} M of nitrate salts related to the described cations were prepared and used for complexation

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[*] Corresponding author. Tel.: +98 917 315 3520; fax: +98 711 6303230.
E-mail addresses: Tavallali@pnu.ac.ir, Tavallali@yahoo.com (H. Tavallali).

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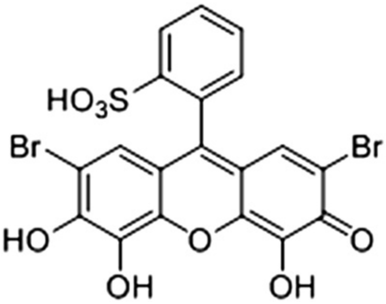


Scheme 1. The molecular structure of BPR.

studies. DMSO (Merck) was dried with CaH_2 and then distilled in reduced pressure. BPR was purchased from Fluka and used in DMSO or DMSO/H_2O solutions. Solutions of BPR with concentration of 5.0×10^{-5} M in DMSO and DMSO with various volumes of water were prepared. These solutions were used for all spectroscopic studies after appropriate dilution. Solution of 1.0×10^{-3} M of TBA salts related to the described anions were prepared in dried and distilled DMSO.

2.2. Apparatus

UV–Vis spectra were recorded on a Perkin Elmer Lambda2 Spectrophotometer containing a thermoelectrically temperature controlled cell holder at 298.2 ± 0.1 K in the wavelength range of 300–700 nm with a quartz cuvette (path length = 1 cm). ^{1}HNMR spectra were measured with Varian unity plus 400 MHz spectrometer using tetramethylsilane (TMS) as the internal standard. A Hamilton microlitre syringe was used for titration experiments.

3. Results and discussion

Despite remarkable achievements in anion detection, there are still many disadvantages in large numbers of examples throughout the literature. For example, the recognition or/and sensing of anions only ever occurred in the noncompetitive organic solvents [2,30,31] (e.g. DMSO, CH_3CN, etc.) but not in the competitive protic solvents such as H_2O, CH_3CH_2OH. Or there were no color changes in the titration experiments at all [31]. Consequently, there is a need to develop receptors capable of anion binding within competitive media, which is simultaneously accompanied with the 'naked-eye' color changes [13]. The sensors based on anion-induced changes in color in aqueous media appear particularly attractive because they offer the potential in many biological and analytical applications.

As the main part of our study, we investigated the effect of water concentration. So, the UV–Vis titration of ionophore was firstly performed in dry DMSO and the results obtained were compared with subsequent titrations in different DMSO/H_2O solutions. UV–Vis titrations of BPR with AcO^-, BzO^- and F^- in dry DMSO as a non-aqueous media were accompanied by similar color changes from red to violet; however other anions (Cl^-, Br^-, I^-, OH^-, NO_3^-, HSO_4^-, CN^- and CO_3^{2-}) did not show any color change (shown in Fig. 1). Addition of water to the medium resulted in a clear increase in selectivity toward the detection of AcO^-. UV–Vis titrations of BPR with AcO^- in DMSO/H_2O (increasing the amount of water up to 50% v/v) as an aqueous media were accompanied by color changes from red to violet; however other anions (F^-, Cl^-, Br^-, I^-, OH^-, NO_3^-, HSO_4^-, BzO^-, CN^- and CO_3^{2-}) did not show any color change (Fig. 2). The higher volume percentages than 50 of water had a disruptive effect on the results. Strong hydration in the absolute aqueous phase stops the receptors from recognizing the anions [10]. In other words binding of anion through hydrogen bonding is really difficult in water as anions become highly solvated in water and there exists a competition of water and anions toward binding with the host molecules.

The effect of solvent system was rather investigated by using ethanol/water mix solvent in which any spectral changes and so any color changes were observed even in the presence of much higher concentrations of AcO^- (about 10-fold excess concentration than previously used in DMSO/water media). As it is evident, the use of aprotic solvents could not be completely avoided due to the competitive solvent effects which interrupt the receptor–anion interactions [32].

3.1. UV–Vis studies in DMSO

BPR (5.0×10^{-5} M) showed an intense absorption band centering at 412 nm and a stronger broad peak at about 523 nm. Upon addition of 0.0–63.6 μM standard solution of TBA salts of anions (F^-, Cl^-, Br^-, I^-, OH^-, NO_3^-, HSO_4^-, AcO^-, BzO^-, CN^-) and sodium salt of CO_3^{2-} only F^-, AcO^- and BzO^- remarkably changed the absorption spectrum of BPR, however CO_3^{2-} also induced a negligible response, which is shown in Fig. 3. During the titration of BPR with a solution of AcO^-, BzO^- and F^-, the intensity of the absorptions at 412 nm decreased and a new absorption band centering at 584 nm appeared which was due to simultaneous color change of the solution of BPR from red to violet (Fig. 1). The presence of acetate, benzoate and fluoride anions resulted in a wavelength shift in maximum absorption from 523 nm (BPR) to 584 nm (BPR-anions) with a gradual decrease in the intensity of the absorbance band at 412 nm and also an increase in the absorbance band at 523 nm which is shown in Fig. 3. These shifts were accompanied simultaneously with significant color change from red to violet (Fig. 1). On the contrary, addition of an excess amount of chloride, bromide, iodide, hydroxide, nitrate or hydrogen sulfate did not produce any notable spectrum changes.

As it might be assumed that BPR pH-sensitivity would affect the color changes, and to settle the resulting misconception, we have studied the effect of OH anion separately. It is noteworthy to mention the initial pH of the BPR solution is 3.34 and since the anions are intrinsically bases, so we preferred to perform the pH-titration through addition of bases including TBAOH. To assess the effect of the acidity of the medium on the color change, we added OH (in the form of TBAOH) into the solution during the determination of AcO^-. It is noteworthy that no color change was

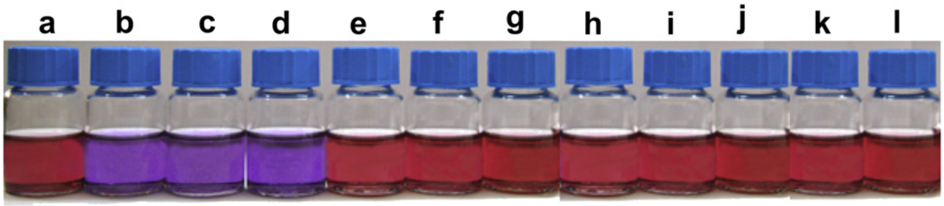


Fig. 1. Photographs of solution of BPR (5.0×10^{-5} M in DMSO) a) No additives b) AcO^-; c) BzO^-; d) F^-; e) Cl^-; f) Br^-; g) I^-; h) NO_3^-; i) HSO_4^-; j) OH^-. k) CN^- and l) CO_3^{2-}. (All anions were added in the form of TBA salts unless CO_3^{2-} in the sodium salt in DMSO and quantity of salts is 63.6 μM).

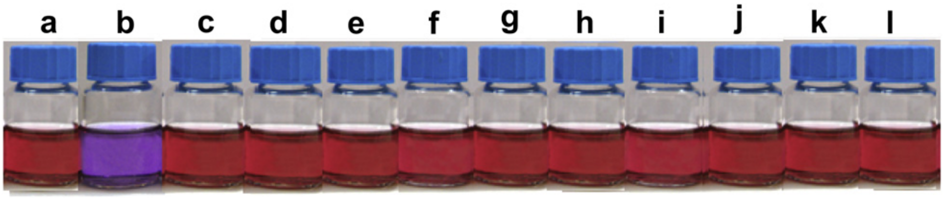


Fig. 2. Photographs of solution of BPR (5.0×10^{-5} M in (v/v)) a) No additives b) AcO^-; c) BzO^-; d) F^-; e) Cl^-; f) Br^-; g) I^-; h) NO_3^-; i) HSO_4^-, j) OH^-, k) CN^- and. l) CO_3^{2-}. (All anions were added in the form of TBA salts unless CO_3^{2-} in the sodium salt in DMSO/H_2O 50:50(v/v and quantity of salts is 63.6 μM).

observed up to 10-fold concentration of acetate anion. However the color of BPR changes in basic pHs which is owing to the conversion into its related conjugate base, interestingly the AcO^- is able to do the same change even in acidic media which confirms the independent nature of the process when AcO^- is applied instead of hydroxide. An experimental fact which should be also taken into consideration is the negligible changes in pH occurred during the addition of AcO^- while the color obviously changes despite the pH is constant. Considering the above reasons it can reasonably be proved that the color change in AcO^- determination is through a hydrogen-bonding process and so completely independent of pH. Upon titrating BPR in DMSO with OH^- (in the form of TBAOH) up to 10-fold concentration of acetate anion no significant change was observed in the UV–Vis spectrum of BPR at 584 nm (Fig. 4). The association constant (described in Section 3.4) for interaction of AcO^- and BPR was calculated to be as 5.31×10^7 M (see Table 1). On the other hand, the addition of AcO^-, BzO^- and F^-, were calculated respectively as 5.12×10^7 M and 4.97×10^7 M, led to the similar changes of the absorption spectrum compared with that of acetate.

3.2. UV–Vis studies in DMSO/H_2O

Generally speaking, most spectrum changes and color changes would disappear quickly upon the addition of competitive hydrogen-bonding solvents such as ethanol or water [33]. To our surprise, the distinctive color change, which is shown in Fig. 2, for AcO^- was also observed in DMSO/H_2O solution. However, upon addition of 0.0–63.6 μM standard solution of TBA salts of F^- and BzO^- did not show any color changes under these conditions. To explore the potentiality and analytical applications of BPR for the anions tested, the UV–Vis titrations were carried out in 90:10 (v/v), 75:25 (v/v) and 50:50 (v/v) DMSO/H_2O mixtures. As could be observed, exceptional results were obtained during the titration of BPR with AcO^- which led to substantial selectivity recognition of anions. Upon UV–Vis spectrometric titration in 90:10 DMSO/H_2O, little selectivity was indicated for AcO^- over other anions including F^- and BzO^-. Afterward, we investigated the effect of increasing the percent volume of water. As it was expected, the titration of BPR with AcO^- in higher concentrations of water (25 and 50%v/v of H_2O) showed greater selectivity compared with solutions including other anions. Fig. 5 shows the UV–Vis spectral titration in 50:50 (v/v) DMSO/H_2O, with addition of anions. BPR showed high selectivity for AcO^- over other anions including F^- and BzO^-. The presence of other anions such as F^- and BzO^- did not interfere in the changes of the absorption bands. During the titration of BPR with a solution of AcO^-, the intensity of the absorption at 412 nm decreased and a new absorption band centering at 584 nm appeared which was responsible for color change of the solution of BPR from red to violet. The presence of acetate anion resulted in a wavelength shift in the maximum absorption from 523 nm (BPR) to 584 nm (BPR-anions) with a gradual decrease in the intensity of the absorbance band at 412 nm and a gradual increase in the absorbance band at 523 nm (Fig. 6). These shifts were accompanied simultaneously with significant color change from red to violet (Fig. 2). In addition, a Job plot using mixtures of BPR and AcO^- in DMSO solution also showed the 1:1 stoichiometry (inset Fig. 6) of the adduct and association constant (described in Section 3.4) as 3.4×10^7 M (see Table 1). The results imply that the receptor can selectively sense AcO^- in mixed DMSO/H_2O medium in the presence of F^- and BzO^- which usually are interferences for AcO^- (Table 1). Fig. 7 shows the absorbance measured at 584 nm versus the increasing amount of different anions added. These optical results confirmed that BPR is sensate to acetate ions.

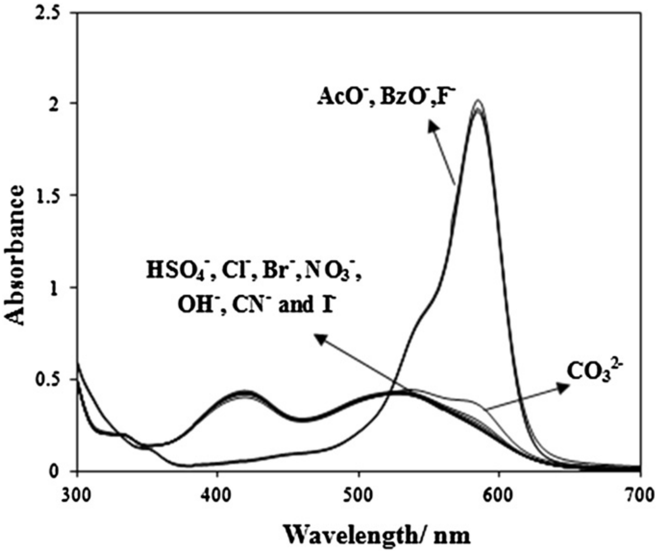


Fig. 3. UV–Vis changes of BPR operated in DMSO (5.0×10^{-5} M) after addition of 63.6 μM of anions.

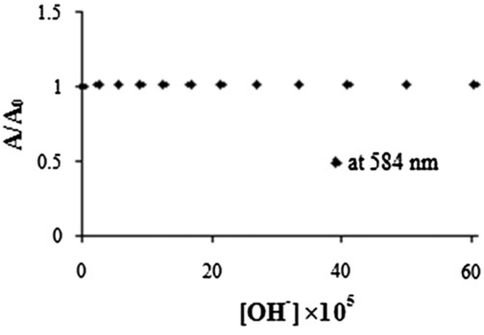


Fig. 4. Changes in the UV–Vis spectrum at 584 nm of BPR in DMSO media upon addition of 0.0–620.0 μM standard solution of TBAOH.

3.3. Selectivity studies

The sodium salts of F^-, Cl^-, Br^-, I^-, OH^-, NO_3^-, HSO_4^-, AcO^-, BzO^-, CN^-, CO_3^{2-} and nitrate salts of Na^+, K^+, Ca^{2+}, Cd^{2+}, Ba^{2+}, Mg^{2+} and Li^+ were used to evaluate the selectivity of acetate ion binding properties of BPR in 50:50 (v/v) DMSO/H_2O medium.

Table 1
Association constants (K_{ass}, M^{-1}) of BPR with anions in DMSO and DMSO/H_2O (50:50 v/v) at 298.2 ± 0.1 K.

Anions[a]	AcO^-	BzO^-	F^-	Cl^-, Br^-, I^-, OH^-, NO_3^-, CN^-, CO_3^{2-} & HSO_4^-
K_{ass}[b]	$5.31(\pm0.16) \times 10^7$	$5.12(\pm0.30) \times 10^7$	$4.97(\pm0.17) \times 10^7$	ND[d]
K_{ass}[c]	$3.40(\pm0.18) \times 10^7$	$1.30(\pm0.45) \times 10^3$	$1.20(\pm0.60) \times 10^2$	ND

[a] All the anions were added in the form of tetra-n-butyl ammonium salts.
[b] The association constant was determined in DMSO.
[c] The association constant was determined in 50:50 DMSO/H_2O.
[d] ND indicated that the spectra showed little or no change with the addition of anion so that the association constants cannot be determined using the spectra.

We selected a set of common cations some of them exists as countercations of the salts used like Na^+ and K^+, and the others selected owing to their rampancy in literature like Ca^{2+}, Cd^{2+}, Ba^{2+}, Mg^{2+} and Li^+ Firstly, the effect of each cation on the BPR color change was examined separately, The visible spectrum of the BPR in DMSO/H_2O (50:50 v/v) is characterized by two main bands at about 412 and 523 nm the UV–Vis spectrums in DMSO/H_2O (50:50 v/v) were investigated upon addition of one equivalent of Na^+, K^+, Ca^{2+}, Cd^{2+}, Ba^{2+}, Mg^{2+} and Li^+ nitrate salts. This displayed that the applied cations did not cause any color change and so any relevant change in the absorption spectra of BPR as well. In another parallel experiment the interfering effects of cations on the determination of AcO anion were investigated.

As expected, BPR exhibits excellent selectivity toward acetate over all other anions. The competition experiments were conducted in the presence of acetate mixed with other anions and cations at 40 μM mentioned above (Fig. 8).

Subsequently and to accentuate on the studies performed on pH-effect, as one may relate the color change into pH-fluctuations concomitant with addition of anions, we have also studied the interference effect of OH anion in the presence of AcO^- as well. The results obtained indicated negligible changes solely on the intensity of absorbance bond of AcO^- confirming the independency of color change toward pH fluctuations.

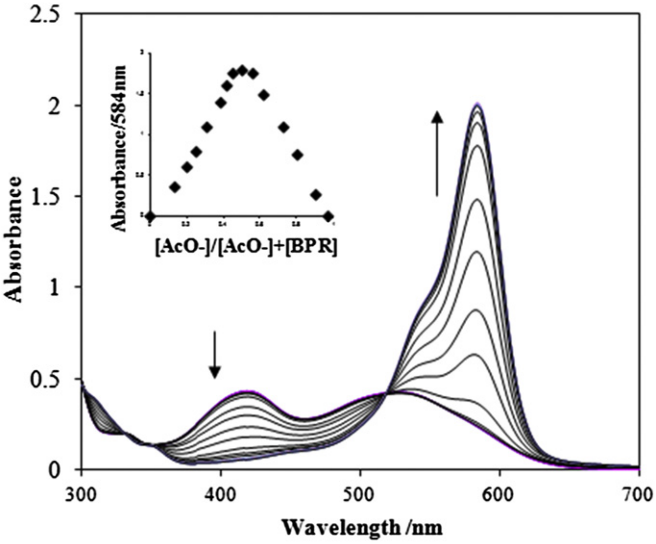


Fig. 6. Titration of 5.0 × 10^{-5} M solution of BPR in DMSO/H_2O (50:50, v/v) upon addition of 0.0–63.6 μM standard solution of TBA acetate. The arrow shows the direction of intensity; inset: the stoichiometry analysis of acetate complex BPR ·AcO^- by job plot analysis; [BPR] + [AcO^-] = 10.0 × 10^{-5} M.

3.4. Association constants

The association constants were determined by nonlinear fitting analysis of the titration curves according to the Eq. (1), for 1:1host–guest complexation [34].

$$A = A_0 + \frac{(A_{\lim} - A_0)\left\{C_H + C_G + 1/K_{ass} - \left[\left(C_H + C_G + 1/K_{ass}\right)^2 - 4C_HC_G\right]^{1/2}\right\}}{2C_H} \tag{1}$$

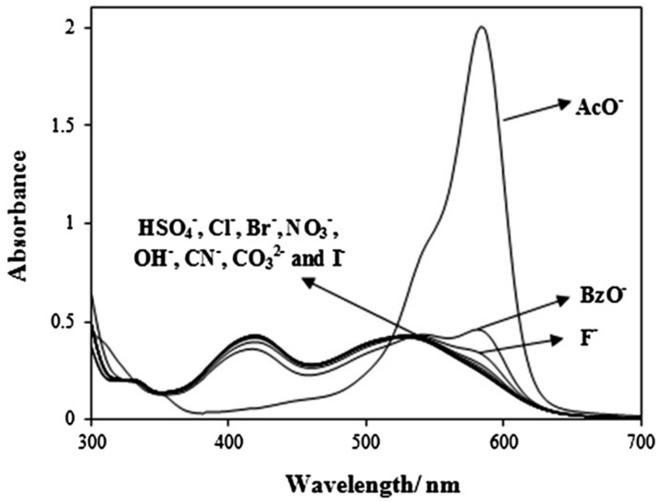


Fig. 5. UV–Vis changes of BPR operated in DMSO/H_2O 50:50(v/v) (5.0 × 10^{-5} M) after addition of 63.6 μM of anions.

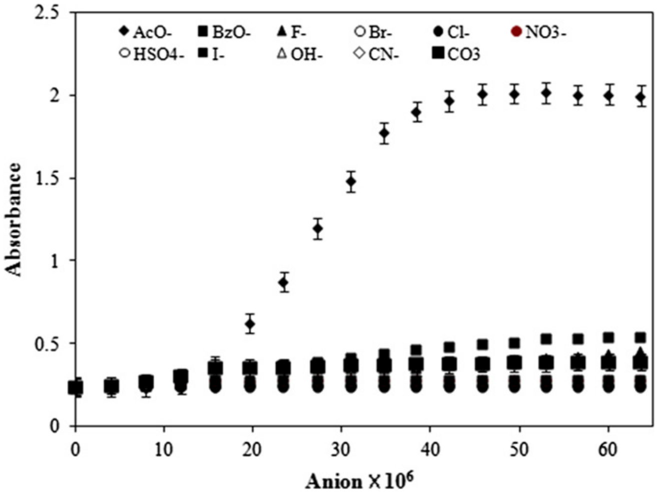


Fig. 7. UV–Vis titration curve of BPR (5.0 × 10^{-5} M in DMSO/H_2O (50:50, v/v)) with increasing quantity of different anions (0.0–63.6 μM); A = molar absorbance at 584 nm.

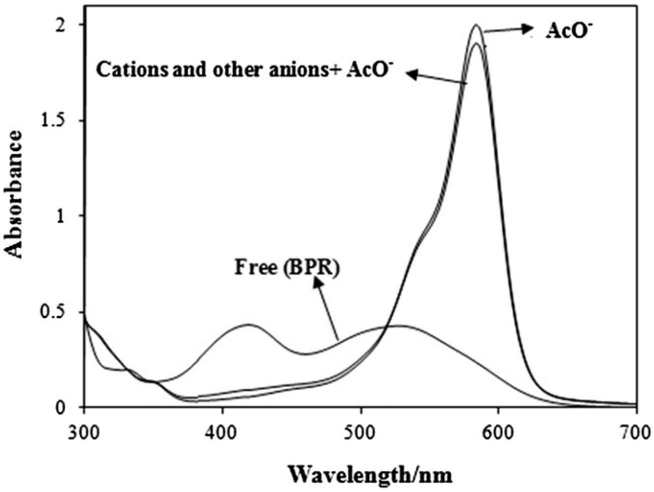


Fig. 8. Absorbance responses of BPR (5.0×10^{-5} M in DMSO/H_2O (50:50, v/v)) to AcO^- (40 μM) in the presence of selected anions (40 μM).

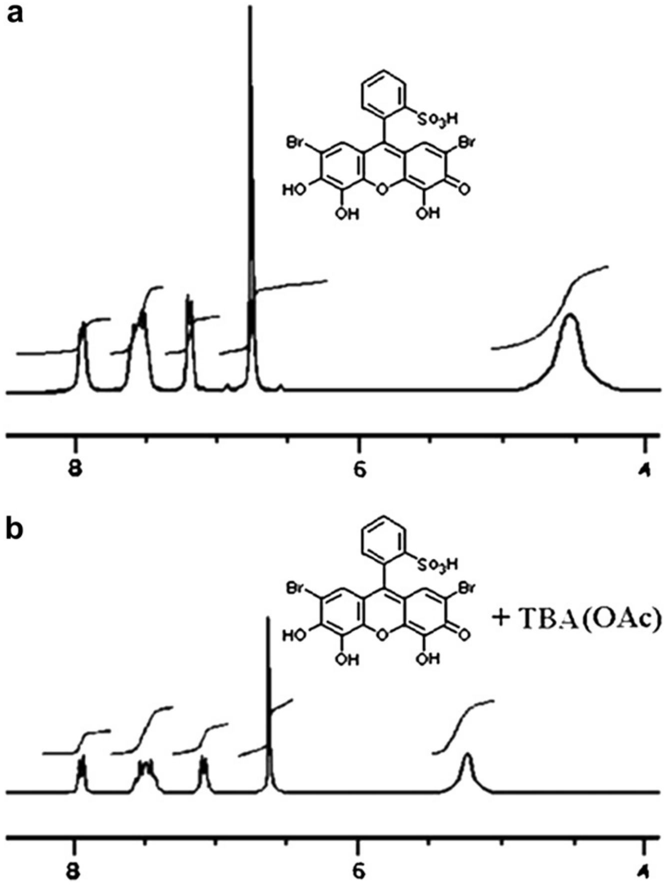


Fig. 9. ^{1}HNMR spectrums: a) BPR in DMSO-d_6 (1.0×10^{-2} M). b) BPR in DMSO-d_6 (1.0×10^{-2} M) in presence of 4.5 eq. AcO^-.

Where C_G and C_H are the concentration of guest and host, respectively and A is the intensity of absorbance at certain concentration of host and guest. A_0 is the intensity of absorbance of host only and A_{lim} is the maximum intensity of absorbance of host when guest is added. K_{ass} is the affinity constant of host–guest complexation. As it is clearly observed in Table 1, the selectivity trends of binding affinities of anions for BPR in DMSO/H_2O solution were determined to be $AcO^- >> BzO^- > F^- > (Cl^-, Br^-, I^-, OH^-, NO_3^-, HSO_4^-, CN^-$ and $CO_3^{2-})$. The selectivity for special analyte of the host molecule could be rationalized on the basis of not only the guest basicity but also shape complementarity between the host and the anionic guests. So, the selectivity for AcO^- could be rationalized on the basis of the guest basicity and structure of the complex. The acetate anion, which is trigonal planar, might be the fittest for binding sites of the BPR among the anions tested to form multitopic hydrogen-bonding interactions with BPR (Scheme 2).

3.5. Possible binding mode and ^{1}H NMR studies

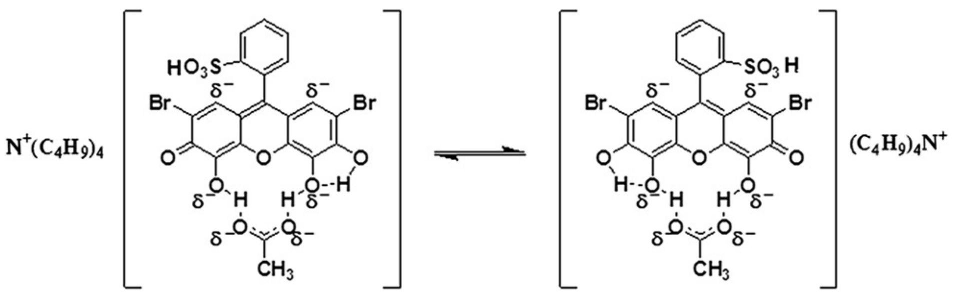
To identify the possible anion binding mode, ^{1}HNMR studies, shown in Fig. 9, were carried out in DMSO-d_6. The ^{1}H NMR spectra of BPR were as follows:

$\delta = 4.55$ (s, br, 3H, OH), 6.76 ppm (s, 2H), 7.18–7.22 (d, 1H), 7.51–7.58 (m, 2H), 7.94–7.96 (d, 1H).

It indicates four different types of aromatic protons in 6.76–7.96 ppm with the relative peak areas of 2:1:2:1 respectively. As indicated in Fig. 8 upon addition of TBA (OAc) as an acetate ion source, a dramatic shift to lower fields (from 4.55 to 5.23) was observed for hydroxyl group. It is suggested to be as a result of inclusion of phenolic OH groups in a strong hydrogen bond interaction with acetate ion (Scheme 2). δ^- in Scheme 2 is used to indicate the minus partial charges as a consequence of the distribution of acetate ion charge in to BPR aromatic ring. The other hydroxyl group has also an interaction since the single peak in $\delta = 6.76$ (related to aromatic ring protons in para-position of described hydroxyl groups) is upfielded to 6.63 as a consequence of increasing electron density on oxygen which has caused a charge incretion on para position via resonance effect.

3.6. Analytical characteristics for acetate anion

BPR can be used as a novel receptor system for detection of acetate anion by absorbance intensity in aqueous solutions. A calibration curve was obtained from plot of absorbance intensity with the single stage addition of known various standard concentrations



Scheme 2. The proposed host–guest binding mode in solution.

Table 2
Concentration of acetate in different sample of known acetate anions.

Sample	Concentration of acetate (μg mL^{-1})		Recovery%
	Acetate content	Found with BPR[a]	
1	1.150	1.096 ± 0.03	95.30
2	1.930	1.816 ± 0.07	94.10
3	2.210	2.082 ± 0.05	94.20

[a] Average of three measurements(±S.D.).

Table 3
Determination of total acetate ion flowing samples.

Sample	Total acetate ion determined (g/100 mL)	
	Determined by proposed sensor[a]	Labeled
Vinegar 1 (brand1)	4.43 ± 0.04	4.0–5.0
Vinegar 2 (brand1)	4.69 ± 0.02	4.0–5.0
Vinegar 3 (brand1)	4.25 ± 0.03	4.0–5.0
Vinegar 4 (brand2)	4.83 ± 0.02	5.0
Vinegar 5 (brand2)	4.79 ± 0.03	5.0

[a] Average of three measurements (±S.D.).

of acetate anions. Calibration graph was obtained with standard solution of TBA acetate prepared in the same solvent (DMSO/H_2O 50:50, v/v). The curve equation was $A = 0.0752C_{AcO^-} - 1.1704$ that C_{AcO^-} unit was μM ($r = 0.9929$). The linear range of quantitative detection for acetate ion was determined to be 19.0–42.0 μM with a detection limit of 2.5 μM (3σ).

4. Analytical application

4.1. Analysis of acetate in sodium acetate

A stock solution of 5.0 mM acetate anion was prepared daily by dissolving 10.5 mg sodium acetate salt (Merck) in 25 ml DMSO/H_2O (50:50, v/v). Working solutions were prepared by appropriate dilution of this stock solution with deionized water and DMSO (50:50, v/v) and absorbance was measured at 584 nm against a blank reagent (DMSO/H_2O 50:50, v/v). The concentration of acetate was established by referring to a calibration graph. The utilization of BPR for the analysis of acetate anion in these samples was tested and the results obtained are shown in Table 2.

4.2. Analysis of acetate in vinegar samples

The proposed receptor was used for the determination of acetate in two commercially available brands of vinegar containing 4.0–5.0 g/100 mL acetic acid. The sample solution was prepared by dilution of 50 μL of vinegar to 50 mL with deionized water and DMSO (50:50, v/v). The analysis was carried out by UV–Vis spectroscopy using a calibration curve (described in Section 3.6). It is seen from Table 3 that there was a satisfactory agreement between the determined values and the labeled acetate content.

Table 4
Comparison of the analytical characteristics of the methods for acetate anion determination.

Method	Detection limit($\times 10^6$)	Authentic sample/matrix	Reference
Potentiometry	1.2	Vinegar	[35]
Amperometry	130	Wine and vinegar	[36]
Colorimetric sensor	Not detect	–	[8–11]
Fluorescent sensor	Not detect	–	[37]
The proposed method	2.5	Vinegar	–

5. Conclusions

To sum up, we have presented a simple and colorimetric receptor, which allows so-called “naked-eye” detection in a straightforward and inexpensive manner in aqueous solutions, offering qualitative and quantitative information without using expensive equipment. In addition, the sensor successfully detected acetate in real sample and is expected to have many opportunities in detection of anions in real-life owing it to the simplicity and sensitivity of the analysis and availability of pure BPR. In the other hand, a comparison of the analytical characteristics between BPR and some of those of literature methods for acetate determination is summarized in Table 4. It can be seen that the proposed method is more superior in terms of sensitivity and simplicity.

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