

# An efficient novel anion sensor for the recognition of acetate

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**Abstract** A novel colorimetric compound anthracene-9, 10-dicarbaldehyde bis-(phenyl-semithiocarbazon) as sensor **1** is synthesized and characterized. It showed significant color changed from light yellow to purple upon the presence of acetate. This outstanding property was also bolstered by UV–Vis and fluorescent titrations experiments in DMSO or DMSO–H<sub>2</sub>O (95:5, v/v) solution. In addition, <sup>1</sup>H NMR experiments were carried out to explore the nature of interaction between sensor **1** and acetate.

**Keywords** Acetate · Anion recognition · Naked-eye · Colorimetric

## Introduction

Anions are ubiquitous in nature. Recently, recognition and sensing of anions have attracted considerable attention for their diversity of functions [1–8]. Among various important anionic analytes, acetate is one of the most significant species due to its specific biochemical functions in the enzymes and antibodies [9]. In enzymes and antibodies the functions of carboxylates ascribe to their specific

biochemical behavior, and make them the critical components for numerous metabolic processes [10]. In addition, acetate is the anion with strong basicity, and has the trigonal chemical structure, which can form hydrogen-bond interaction with hydrogen-bond donors. Many examples are available about the selective sensor molecules for acetate anion in the literatures [11–13]. At the moment, a lot of researchers have focused on the neutral chromogenic and/or fluorescent anion sensors. Especially, colorimetric-based sensing is very attractive, as it may allow naked-eye detection of the analyte without resorting to any expensive equipment [14].

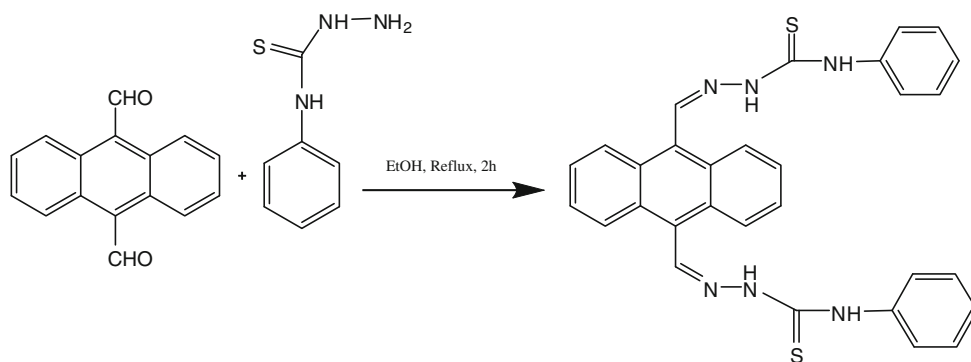
In our previous studies, we prepared a colorimetric anion sensor based on an anthracene derivative, which showed significant color changes upon the presence of fluoride [15]. With this information, we have designed and synthesized another novel sensor **1** by a simple reaction of anthracene-9, 10-dicarbaldehyde and 4-phenylthiosemicarbazide (see Scheme 1). This sensor contains four recognition sites and has good selectivity for recognizing acetate.

Generally speaking, the recognition studies of the past were usually performed in aprotic media (e.g. DMSO, acetonitrile, CHCl<sub>3</sub>, etc.), to avoid the competition from the protic solvent (e.g., water or alcohols) working as another hydrogen-bonding donor [16, 17]. Thus, it is urgent to develop sensors that are able to bind anions within the competitive media, and to be simultaneously accompanied with the ‘naked-eyed’ detectable color changes. Sensor **1** is selective and effective to recognize AcO<sup>−</sup> in dry DMSO. More importantly, it also presents recognition ability in aqueous medium: DMSO–H<sub>2</sub>O (95:5, v/v) solution. The processes of sensing can literally be seen through the ‘naked-eye’ for the sharply color changes from light yellow to purple.

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**Scheme 1** General synthetic routes to the target sensor **1**



## Experimental

### Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH<sub>2</sub> and then distilled in reduced pressure.

### Apparatus

<sup>1</sup>H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS were performed with a MARINER apparatus. C, H, N elemental analyses were made on an elemental vario EL. UV-Vis spectra were recorded on a Shimadzu UV-2450 Spectrophotometer (Shimadzu 2.1 Apparatus Corp., Kyoto, Japan) with a quartz cuvette (path length = 1 cm) at 298.2 ± 0.1 K and the width of the slits used is 10 nm. Fluorescent spectra were recorded on an FP-750 fluorescence spectrometer at 298.2 ± 0.1 K and the width of the slits used is 10 nm.

### General method

All experiments were carried out at 298.2 ± 0.1 K, unless otherwise mentioned.

A 2.0 × 10<sup>-3</sup> M solution of the sensor **1** in DMSO was prepared and stored in the dry atmosphere. A 2.0 × 10<sup>-5</sup> M solution of the sensor **1** in DMSO-H<sub>2</sub>O (95:5, v/v) was also prepared. Solutions of 1.0 × 10<sup>-2</sup> and 1.0 × 10<sup>-1</sup> M tetrabutylammonium salt of the respective anion were prepared in dried and distilled DMSO and were stored under a dry atmosphere.

<sup>1</sup>H NMR titration experiments were carried out in the DMSO-*d*<sub>6</sub> solution (TMS as an internal standard). 2.5 mL of 0.01 M solution of the sensor **1** in the DMSO-*d*<sub>6</sub> was

prepared, into which the increased amount of acetate anion (1.0 M in DMSO-*d*<sub>6</sub>) was added and <sup>1</sup>H NMR of the host-guest system was recorded.

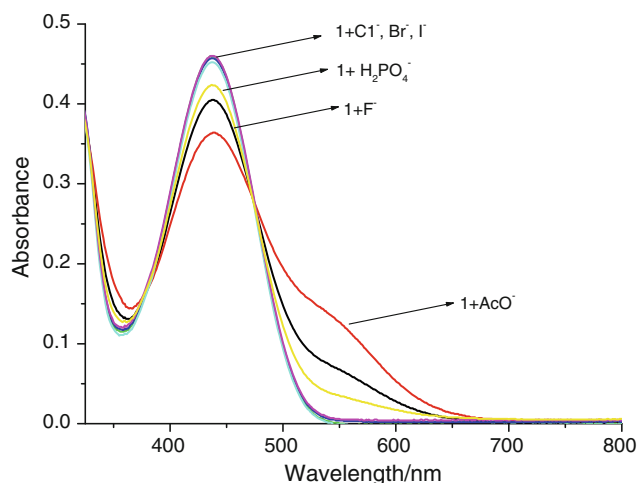
### Synthesis of anthraceno-9, 10-dicarbaldehyde bis-(phenyl-semithiocarbazono)

The sensor **1** was synthesized in three steps (see Scheme 1) starting from anthracene-9, 10-dicarbaldehyde [18, 19] and 4-phenylthiosemicarbazide [20] that were prepared according to the literature. A mixture of 0.234 g (1 mmol) anthracene-9, 10-dicarbaldehyde, 0.334 g phenyl-semithiocarbazono (2 mmol) and three drops of acetic acid were dissolved in 60 mL CH<sub>3</sub>CH<sub>2</sub>OH and then the resulting solution was heated and refluxed for 2 h. The formed precipitate was immediately filtered, and then 0.452 g red solid was obtained after recrystallization from CH<sub>3</sub>CN. This procedure yields 0.452 g (85%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Me<sub>4</sub>Si) δH 7.16 (pseudo-t, *J*<sub>1</sub> = 7.2 Hz, 2 H, Ph-H), δH 7.33 (pseudo-t, *J*<sub>1</sub> = 7.4 Hz, 2 H, Anthracene-H), 7.56 (d, *J*<sub>1</sub> = 7.8 Hz, 4 H, Ph-H), 7.68 (dd, *J*<sub>1</sub> = 2.9 Hz, *J*<sub>2</sub> = 6.8 Hz, 4 H, Anthracene-H), 8.59 (dd, *J*<sub>1</sub> = 3.1 Hz, *J*<sub>2</sub> = 6.8 Hz, 4H, Ph-H), 9.37 (s, 2 H, NC-H), 10.01 (s, 2 H, NNCS-H), 12.12 (s, 2 H, PhNCS-H). ESI-MS (*m/z*): calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>S<sub>2</sub> [M]<sup>+</sup>: 522.11, found: 522.15. Elemental analysis calcd for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>S<sub>2</sub>: C, 67.64; H, 4.54; N, 15.78. Found: C, 67.86; H, 4.51; N, 15.59.

## Results and discussion

### UV-Vis anion titration studies

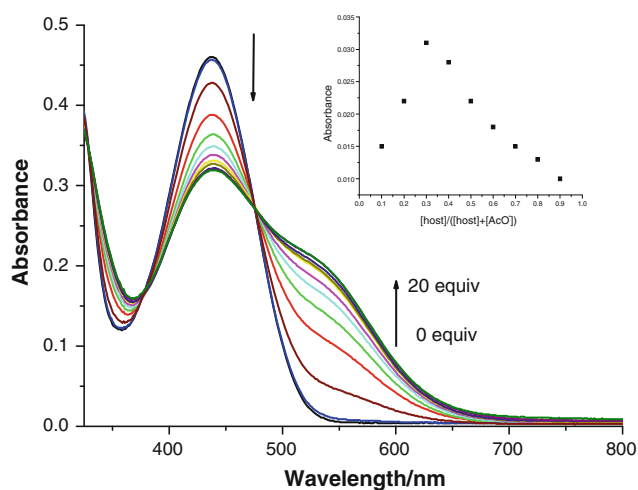
First, to evaluate the binding ability of sensor **1** to anions, the UV-Vis titration experiments of the sensor **1** were carried out in dry DMSO solvent using standard solution of tetrabutylammonium salts of AcO<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> anions at 298.2 ± 0.1 K. In the process, we observed obviously spectra changes after adding AcO<sup>-</sup> and



**Fig. 1** UV-Vis spectrum of **1** ( $2 \times 10^{-5}$  M) in the presence of 10 equiv of AcO<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> in DMSO

the color of the solution of **1** changed from light yellow to purple. A similar spectral change was observed upon the addition of F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, but the change were not significant like that of acetate. However, as the Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> were titrated into **1**, the spectra were hardly changed even the anions were excessive (see Fig. 1).

Then UV-Vis titrations were carried out in DMSO at a certain concentration of **1** ( $2.0 \times 10^{-5}$  M) with the addition of the tetrabutylammonium salt of AcO<sup>-</sup> to study the anion-binding properties (see Fig. 2). In the absence of the anion, an absorption maximum was found at 439 nm. Upon addition of AcO<sup>-</sup>, the peak at 439 nm decreased gradually while the new formed peak at 548 nm increased, at the same time, an isosbestic point at 476 nm was observed.

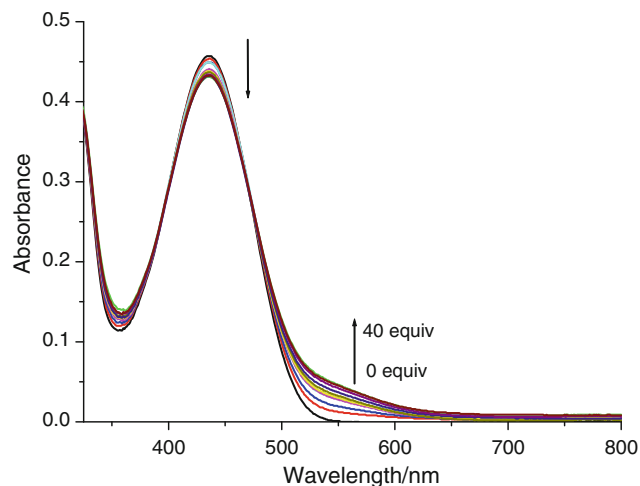


**Fig. 2** Evolution of the UV-Vis spectrum of sensor **1** ( $2.0 \times 10^{-5}$  M) during the titration with AcO<sup>-</sup> in DMSO. *Inset*: Job's plot for sensor **1** with AcO<sup>-</sup> determined by UV-Vis in DMSO, [1] + [anion] =  $2.0 \times 10^{-3}$  M

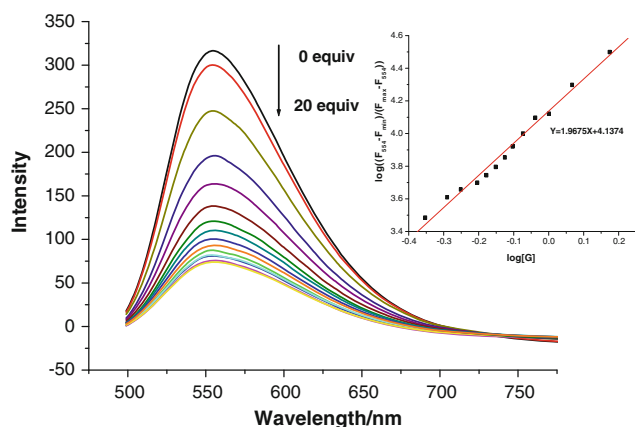
It is well known that protic solvents such as water or methanol will competitively form hydrogen-bonding with the binding site of sensor for anions. In view of the selectivity of sensor **1** in dry DMSO, we have also designed the experiments carried out in DMSO–H<sub>2</sub>O (95:5, v/v) solution to further investigate their performance. Fortunately, a similar phenomenon was actually observed in DMSO–H<sub>2</sub>O (95:5, v/v), so the sensor **1** still has the recognition capability for AcO<sup>-</sup> (see Fig. 3), but similar phenomenon was not observed in DMSO–H<sub>2</sub>O (95:5, v/v) for F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. At the same time, the solution color changed from light yellow to purple, which provide a method to detect AcO<sup>-</sup> by naked-eye conveniently.

#### Fluorescence anion titration studies

The anion binding behavior of the sensor **1** was also investigated by fluorescence titrations in DMSO, which was consistent well with the UV-Vis titrations. Obviously, there was a strong emission band centered at 554 nm, when excited at  $\lambda = 476$  nm. Upon addition of acetate, there was a significant decrease in the emission intensity of **1** (see Fig. 4). Such fluorescence quenching could be ascribed to the increased photoinduced electron transfer (PET) process between the anthracene moiety and the binding site [21]. It was clear that in this system where anthracene moiety and binding site were separated, anion binding to N–H hydrogens caused an in reduction potential of N–H bonds, make the electron transfer more feasible (see Scheme 2). After more acetate anions were added to system, it appeared that the deprotonated species were more electron rich compared with the hydrated acetate anion, and activated the PET



**Fig. 3** Evolution of the UV-Vis spectrum of sensor **1** ( $2.0 \times 10^{-5}$  M) during the titration with AcO<sup>-</sup> in DMSO/H<sub>2</sub>O (95:5, v/v)



**Fig. 4** Fluorescence emission changes of sensor **1** upon the addition of  $\text{AcO}^-$  in DMSO. *Inset*: fluorescence intensity at 554 nm ( $F_{554}$ ) of **1** versus increasing concentration of  $\log[G]$ .  $\lambda_{\text{ex}} = 476$  nm, the concentration of **1** is  $2.0 \times 10^{-5}$  M

process more efficiently, resulting in even greater quenching [22]. This might indicate that the sensor **1** exhibited a good interaction with acetate ions [23].

#### Determination of the binding constant and stoichiometry

Obviously, only one well-defined isosbestic point appeared at 476 nm in Fig. 2, which indicated that the forming stable complex had a certain stoichiometric ratio between sensor **1** and  $\text{AcO}^-$ . Further, from Job's plot [24] of sensor **1** and  $\text{AcO}^-$  in DMSO we found the maximum at a mole fraction of 0.3 (see Fig. 2, inset), which indicated that sensor **1** binded  $\text{AcO}^-$  guest with an 1:2 ratio.

Meanwhile, we also treated the data from fluorescence anion titration in another way as below. The total

fluorescence signal intensity  $F$  can be expressed in the following Eq. 1 [25]:

$$F = \frac{[G]^n F_{\text{max}} + 10^{-B} F_{\text{min}}}{10^{-B} + [G]^n} \quad (1)$$

In the spectrofluorometry of this work,  $F_{\text{min}}$ ,  $F_{\text{max}}$  and  $F$  are the emission intensities of the solution at wavelength 554 nm in the absence of guest, presence of a large excess of guest, and after addition of a given amount of guest to certain concentration, respectively.  $[G]$  is the concentration of guest,  $n$  is the number of  $G$  bound per sensor **1**. The sigmoid curve was obtained and the total binding constant  $B$  was deduced. Practically, this equation can be linearised in the form of Hill plot and the Hill coefficient ( $n$ ) can also be obtained from Eq. 2 [26–29] (see Fig. 4).

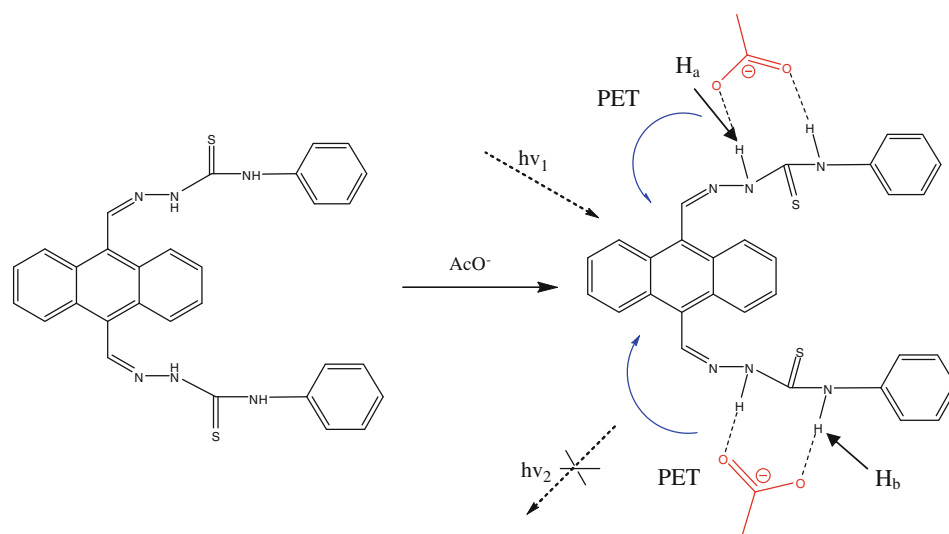
$$\log \frac{F - F_{\text{min}}}{F_{\text{max}} - F} = n \log[G] + B \quad (2)$$

As shown in Fig. 4, the binding constant of sensor **1** to  $\text{AcO}^-$  ( $\log\beta$  or  $B$ ) is 4.1374, and the Hill coefficient ( $n$ ) is 1.9675 indicating sensor **1** binds the acetate anion guest with a ratio of 1:2 which is consistent with Job plots. Therefore, the results drawn from the data of fluorescent titrations are qualitatively matched with that from the UV–Vis spectral titrations. The affinity constants of sensor **1** for anionic species have been calculated and listed in Table 1.

According to the results from UV–Vis titrations and fluorescent titrations, the proposed mode for the host–guest bonding in solution was depicted (see Scheme 2). In the structure, two acetate anions are located at the each side of sensor **1** via hydrogen bonding.

As clearly shown in Table 1, the order of binding affinity of **1** with anions (in DMSO or DMSO-water) is  $\text{AcO}^- \gg \text{F}^- > \text{H}_2\text{PO}_4^- \sim \text{Cl}^- \sim \text{Br}^- \sim \text{I}^-$ . Because

**Scheme 2** The proposed binding mode of **1** with  $\text{AcO}^-$  activating PET process



**Table 1** Affinity constants of sensor **1** with anions in DMSO and DMSO/H<sub>2</sub>O (95:5, v/v)

Anions	AcO <sup>-</sup>	F <sup>-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
lgK <sub>ass</sub> <sup>a</sup>	4.02 ± 0.15	3.31 ± 0.03	3.01 ± 0.11	ND	ND	ND
lgK <sub>ass</sub> <sup>b</sup>	4.13 ± 0.10	3.50 ± 0.10	3.09 ± 0.02	ND	ND	ND
lgK <sub>ass</sub> <sup>c</sup>	3.10 ± 0.13	ND	ND	ND	ND	ND

<sup>a</sup> The affinity constants determined by UV–Vis in dry DMSO

<sup>b</sup> The affinity constants determined by fluorescence in dry DMSO

<sup>c</sup> The affinity constants determined by UV–Vis in DMSO–H<sub>2</sub>O (95:5, v/v) solution

ND cannot determined

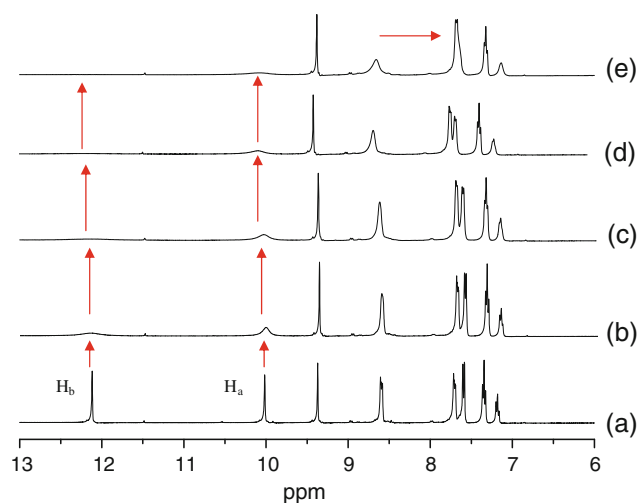
acetate is the anion with strongest basicity among the six tested anions, and has the trigonal chemical structure, which can form hydrogen-bond interaction with hydrogen-bond donors. The angle of O–C–O in AcO<sup>-</sup> is about 120° while the angle of O–P–O in H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is about 108°, so AcO<sup>-</sup> might be more fit to the distance between two –NH on each side of sensor **1**, and forming N–H<sup>+</sup> anion hydrogen bonds. The affinity constants of Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> are very small due partly to their weak basicity.

### <sup>1</sup>H NMR titrations

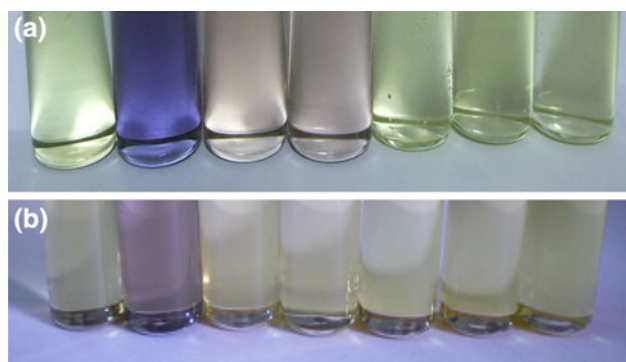
To shed a little light on the nature of the intermolecular interactions between AcO<sup>-</sup> and sensor **1**, <sup>1</sup>H NMR spectral changes upon addition of AcO<sup>-</sup> in DMSO-*d*<sub>6</sub> solution of **1** (1.0 × 10<sup>-2</sup> M) were investigated. Obviously, the proton signals at 10.01 and 12.12 ppm which have been assigned to H<sub>a</sub> and H<sub>b</sub> (marked in Scheme 2) can be observed in the absence of the AcO<sup>-</sup> (see Fig. 5). Upon addition of 0.2 equiv of AcO<sup>-</sup>, the signals of H<sub>a</sub> and H<sub>b</sub> are broadened, and anthryl rings exhibited an upfield shift slightly, which indicates the formation of a host–guest complex [15]. As increasing the addition of AcO<sup>-</sup>, the signals of H<sub>b</sub> eventually disappear, which displays the complete deprotonation of the sensor **1**.

### Analytical application

The potential application of sensor **1** in analytical chemistry field was evaluated in DMSO and DMSO/H<sub>2</sub>O (95:5, v/v). The results show that sensor **1** could be applied in detection of biologically important anions such as acetate ion in DMSO (Fig. 6). Upon addition of five equiv anions, the color of solution of sensor **1** changed from light yellow to purple by the introduction of AcO<sup>-</sup>. It is interesting that the selective recognition ability of sensor **1** for AcO<sup>-</sup> in DMSO/H<sub>2</sub>O (95:5, v/v) mixed solvent is better than dry DMSO, for the naked-eye discrimination between the acetate and other anions. Such methodology would be



**Fig. 5** <sup>1</sup>H NMR titration of a 1.0 × 10<sup>-2</sup> M solution of **1** in DMSO-*d*<sub>6</sub> with [Bu<sub>4</sub>N] AcO<sup>-</sup>. **a** 0 equiv.; **b** 0.2 equiv.; **c** 0.4 equiv.; **d** 0.6 equiv.; **e** 1.2 equiv



**Fig. 6** Color changes of the sensor **1** (2.0 × 10<sup>-5</sup> M) in DMSO (**a**) and DMSO/H<sub>2</sub>O (95:5, v/v) (**b**) in absence and presence of five equiv of anions (from the left to the right: **1** only, **1** + AcO<sup>-</sup>, **1** + F<sup>-</sup>, **1** + H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, **1** + Cl<sup>-</sup>, **1** + Br<sup>-</sup> and **1** + I<sup>-</sup>)

expected to help to extend the development fluorescent sensors for biologically anions in aqueous medium.

### Conclusions

In conclusion, we have successfully presented a new kind of colorimetric sensor which can recognize acetate selectively in DMSO or DMSO–H<sub>2</sub>O (95:5, v/v) solution. UV–Vis and <sup>1</sup>H NMR titration experiments were performed to support this conclusion. It is expected to be applied for detection of acetate in real life for its good recognition ability toward acetate.

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