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ORIGINAL ARTICLE

Anion recognition based on phenolic hydroxyl group in competitive media

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Abstract Two novel artificial receptors, one containing phenolic hydroxyl group and diamide (1), the other only containing diamide (2), were designed and synthesized. The binding ability evaluated by UV–vis and fluorescence titration experiments in dry DMSO revealed that compound 1 could selectively recognize AcO^-. In particular, the binding ability can also be detected in the DMSO/H_2O solution by UV–vis. The interference experiment result showed that the binding ability was not influenced by the existence of other anions. In contrast, there were no detectable interaction between receptor 2 and anions. The further insights to the nature of interaction between receptor 1 and AcO^- were investigated by ^1H NMR titration experiments and theoretical investigation, which demonstrated receptor **1** complexed AcO^- through the synergistic hydrogen bonding interaction of OH and NH.

Keywords Anion recognition · Acetate anion · Phenolic hydroxyl group · Diamide

Introduction

Anion recognition by artificial receptors has attracted considerable attention in the field of host–guest chemistry due to the important roles of anions in biomedicinal and chemical processes [1–10]. Artficial anion receptor has shown prospects of unique application in the synthesis of anion sensors [11, 12], membrane transmit carriers [13, 14] and mimic enzyme catalysts, etc. The structural design of receptors is important in anion recognition. With regard to the binding sites, the functional groups such as amide [15], urea [9, 16] and hydroxyl groups [17–20] are numerously used owing to their ability to perform as hydrogen donors. However, the interaction mechanism based on the binding sites of hydroxyl group and amide has been less studied in anion recognition [21–23].

Among various biologically important anions, acetate anion has attracted growing attention for its established role in the enzymes and antibodies. Acetate is also the significant component of numerous metabolic processes. The sensing of acetate anion has aroused great interest and several types of synthetic chemosensors have been developed to date [24, 25]. However, the recognition of acetate anion in aqueous solution is still a challenge work owing to the competitive protic solvent which interacts with the host by H-binding prior to the anion [26–28].

According to this, we synthesized two novel receptors (Scheme 1), one containing phenolic hydroxyl group and diamide (1), the other containing only diamide (2), to examine the difference of anion binding ability based on the hydroxyl group and diamide recognition sites and explore the interaction mechanism. Results indicated receptor 1 showed high selectivity to acetate anion in DMSO and the mixture solution DMSO/H_2O. And the UV–vis spectral interference experiment in DMSO/H_2O (95:5, v/v) showed the binding ability of AcO^- with(and) receptor 1 was not influenced by the existence of other anions. In addition, the ^1H NMR, UV–vis and theoretical investigation proved that the hydroxyl group played an indispensable role in anion recognition.

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Experimental

Chemicals

All reagents obtained commercially for synthesis were used without further purification. In the titration experiments, all the anions added in the form of tetrabutylammonium (TBA) salts were purchased from Sigma–Aldrich Chemical and dried fully. DMSO was dried with CaH_2 and then distilled under reduced pressure.

Apparatus

^{1}H NMR spectra were obtained on a Varian UNITY Plus-400 MHz spectrometer. ESI–MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an Elementar Vario EL. UV–vis spectra were recorded on a Shimadzu UV2450 spectrophotometer with quartz cuvette (path length = 1 cm) and fluorescent spectra were recorded on a Shimadzu RF-5301 PC spectrophotometer at 298.2 ± 0.1 K and the width of the slits used is 5 nm.

Synthesis

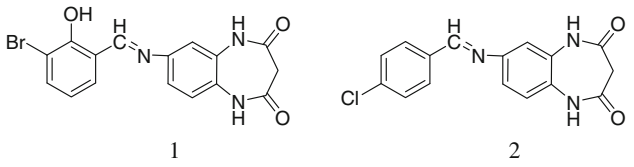
Receptor **1**, **2** were prepared according to the route shown in Scheme 2.

Benzo-1,4-diazacycloheptane[2,3-d]-5,7-dione (3)

1,2-Phenylenediamine (10.8 g, 0.1 mol), diethyl malonate (16 mL, 0.1 mol) and pyridine (200 mL) were put in a 250 mL three-neck flask. The mixture was refluxing under N_2 for 72 h. After cooling, the mixture was filtrated and the white solid was obtained. The solid was washed with ethanol and ether sequentially, and dried in vacuum. Yield: 72%. ^{1}H NMR(DMSO-d_6, 298 K) $\delta = 10.38$ (s, 2H), 7.11–7.18 (m, 4H), 3.17(s, 2H). Elemental analysis: Calc. for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90; Found: C, 61.69; H, 4.59; N, 15.96. FAB-MS (m/z): 177 $(M + H)^+$.

(4′-Nitrobenzo)[1′,2′-d]-1,4-diazacycloheptane[2,3-d]-5,7-dione (4)

Benzo-1, 4-diazacycloheptane[2, 3-d]-5, 7-dione(10 mmol, 1.7 g) was dissolved in concentrated H_2SO_4 (43 mL). Fuming HNO_3 (1.1 mL) was added dropwise with stirring at 273 K. After that, the mixture was stirred for 2 h and then poured into ca. 200 mL ice-water. The solution was filtered and washed with distilled water, then the solid was recrystallized from methanol and dried in vacuum to give a yellow solid. Yield: 85%. ^{1}H NMR (DMSO-d_6, 298 K) $\delta = 10.96$ (s, 1H), 10.74 (s, 1H), 8.04, 7.3(3H), 3.3 (s, 2H), Elemental analysis: Calc. for $C_9H_7N_3O_4$: C, 48.88; H, 3.19; N, 19.00; Found: C, 48.76; H, 3.58; N, 18.61.



1 2

Scheme 1 Chemical structure of receptor 1 and 2

(4′-Aminobenzo)[1′,2′-d]-1,4-diazacycloheptane[2,3-d]-5,7-dione (5)

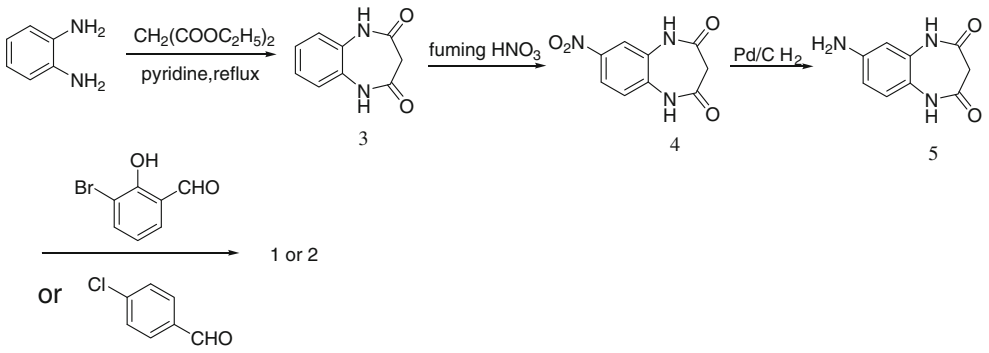
A slurry of compound (4′-nitrobenzo)[1′,2′-d]-1,4-diazacycloheptane [2,3-d]-5,7-dione (221 mg) and Pd/C (10%, 70 mg) in dry ethanol (200 mL) was maintained under hydrogen with stirring for 12 h. The mixture was filtered through a bed of Celite and then washed twice with ethanol (2 × 20 mL). The solvents were removed under reduced pressure and the yellowish solid was dried in vacuum. Yield: 92%. ^{1}HNMR (DMSO-d_6, 298 K) $\delta = 10.15$ (s, 1H), 9.91(s, 1H), 6.76 (d, 1H), 6.38 (m, 1H), 6.27 (d, 2H), 5.16 (s, 2H) 3.08 (s, 2H). Elemental analysis: Calc. for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98; Found: C, 56.41; H, 4.96; N, 21.87.

N-(2′-Hydroxyl-3′-bromophenyl-methylene-yl)-4′-imino-benzo[1′,2′-d]-1,4-diazacycloheptane[2,3-d]-5,7-dione (receptor 1)

(4′-Aminobenzo)[1′,2′-d]-1,4-diazacycloheptane[2,3-d]-5, 7-dione (1 mmol, 191 mg) and 3,5-dibromo-salicylaldehyde (1 mmol, 278 mg) were suspended in dry ethanol (100 mL). The mixture was refluxed for 8 h and the orange-yellow precipitate was separated by filtration. The solid was washed with diethyl ether and dried under vacuum. Yield: 88%. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) $\delta = 12.79$ (s, 1H), 10.46 (s, 2H), 8.96 (s, 1H), 7.88(d, 1H), 7.51 (m, 1H), 7.26 (m, 1H), 7.21 (m, 1H), 7.12(s, 1H), 6.95 (m, 1H), 3.23 (s, 2H). Elemental analysis: Calc. for $C_{16}H_{12}BrN_3O_3$: C, 51.36; H, 3.23; N, 11.23; Found: C, 51.32; H, 3.24; N, 11.28. ESI–MS(m/z):374.92 $[(M + H)^-$, Calcd. 375.00].

N-(2′-Hydroxyl-4′-chlorobenzene-methylene-yl)-4′-imino-benzo[1′,2′-d]-1,4-diazacycloheptane[2,3-d]-5,7-dione (receptor 2)

(4′-Aminobenzo)[1′,2′-d]-1,4-diazacycloheptane[2,3-d]-5, 7-dione (1 mmol, 191 mg) and 4-chlorobenzene-salicylaldehyde (1 mmol, 278 mg) were suspended in dry ethanol (100 mL). The mixture was refluxed for 8 h and the orange-yellow precipitate was separated by filtration. The solid was washed with diethyl ether and dried under vacuum. Yield:



Scheme 2 Synthesis route for 1 and 2

88%. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) $\delta = 10.43$ (s, 2H), 8.64 (s, 1H), 7.94(d, 2H), 7.60 (m, 2H), 7.16 (m, 2H), 7.04 (s, 1H), 3.23 (s, 2H). Elemental analysis: Calc. for $C_{16}H_{12}ClN_3O_2$: C, 61.25; H, 3.86; N, 13.39; Found: C, 61.27; H, 3.84; N, 13.40. ESI–MS(m/z):314.12 [$(M + H)^-$, Calcd. 313.06].

Results and discussion

UV–vis titration studies

The anion binding ability of the compounds was firstly investigated through UV–vis titration spectra by adding a standard tetrabutylammonium salt solution of anions to the dry DMSO solution of compounds at 298.2 ± 0.1 K.

In the absence of anions, compound **1** (4.0×10^{-5} M in DMSO) displayed obvious absorption peak at 365 nm. As shown in Fig. 1, the addition of F^-, AcO^- and $H_2PO_4^-$ to DMSO solution of **1** led to obvious changes in the absorption spectrum [29, 30]. The absorption peak at 365 nm decreased obviously and a new absorption peak at about 449 nm developed. The red-shift phenomenon has also been observed with the addition of anions. In contrast, the addition of other anions (Cl^-, Br^-, I^-) did not trigger noticeable spectral change of compound **1** (Fig. 1), indicating very weak or no interaction between these anions and compound 1. Noticeably, colorless DMSO solution of compound **1** turned yellow after interaction with F^-, AcO^- and $H_2PO_4^-$, which contributed to significant development of absorption peak at 449 nm.

Figure 2 showed the significant UV–vis spectral changes of receptor 1 when the acetate concentration changed from 0 to 200×10^{-5} M. The main absorption decreased at 365 nm and increased at 449 nm, and two distinct isosbestic points appeared at 316 nm and 392 nm. The job-plot analysis based on this concentration indicated that the spectral change could be ascribed to the formation of 1:1 host–guest complexation. The association constants and correlation coefficients obtained by noninear least-square calculation method according to UV–vis data were listed in Table 1 [31, 32]. The order of selectivity: $AcO^- > F^- > H_2PO_4^- > Cl^-$, Br^-, I^-. Receptor **1** showed the highest binding ability with acetate anion which could be selectively recognized from other anions based on its association constant. It was likely that **1** could interact with AcO^- through multiple hydrogen bonding [23]. To investigate the effect of hydroxyl groups in receptor 1 on anion recognition, compound 2 was synthesized as a reference compound. Interestingly, there was no change in the absorption spectra of compound 2 (Fig. 3), even though F^- and AcO^- were added, which showed that there was almost no or very weak binding ability between compoud 2 and anions. The above facts fully proved that the receptor 1 interacted with anions through hydrogen bonding. That is to say, the effect of the hydroxyl group on receptor 1 was indispensable for anion recognition.

It is well known that the added protic solvents such as water or methanol will form hydrogen-bonding with the

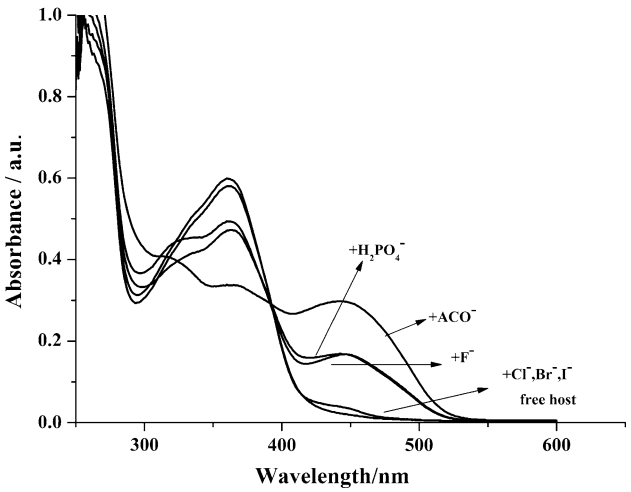


Fig. 1 UV–vis spectra of $1(4 \times 10^{-5}$ M) in DMSO in the presence of 50 equiv. of AcO^-, F^-, $H_2PO_4^-$ and miscellaneous anions including Cl^-, Br^- and I^-

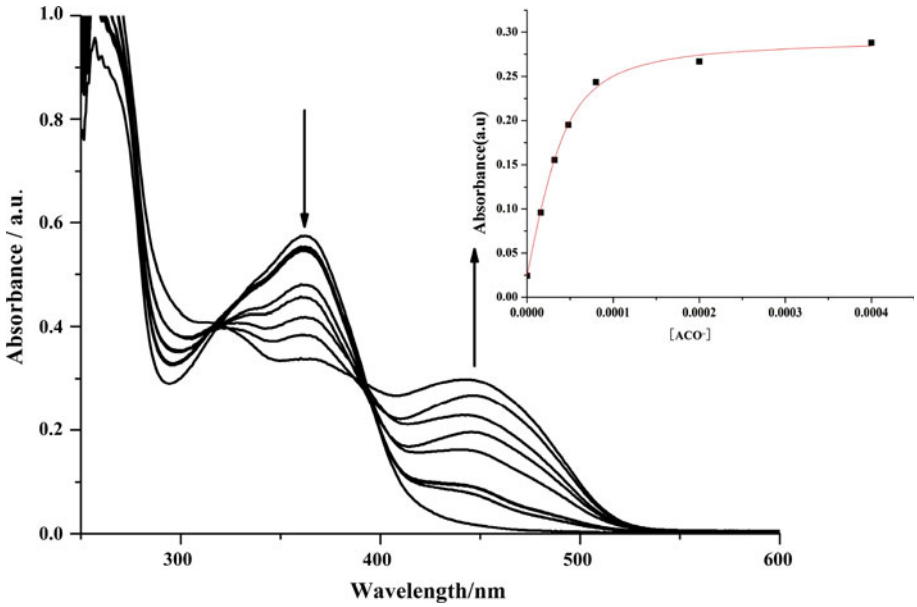


Fig. 2 Evolution of UV–vis spectrum of receptor 1 (4×10^{-5} M) on addition of $[AcO^-] = 0–200 \times 10^{-5}$ M in DMSO. The inset showed the changes of absorbance at 448 nm against the added AcO^-

Table 1 Association constants (Kass, M^{-1}) of the receptor 1 with anions in DMSO and DMSO/H_2O (95/5, v/v) at 298.2 ± 0.1 K

Anions[a]	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
Kass[b]	$8.62 \pm 0.37 \times 10^4$	$1.60 \pm 0.19 \times 10^3$	329 ± 76	ND[c]	ND	ND
Kass[d]	$7.86 \pm 0.85 \times 10^4$	$2.47 \pm 0.48 \times 10^3$	281 ± 41	ND	ND	ND
Kass[e]	$1.81 \pm 0.26 \times 10^4$	$1.56 \pm 0.19 \times 10^3$	ND	ND	ND	ND

[a] The anions were added as their tetrabutylammonium salts

[b] Association constant was determined in DMSO by fluorescence in dry DMSO

[c] Association constant could not be determined due to very weak complexation

[d] Association constant was determined by UV–vis in dry DMSO

[e] Association constant was determined by UV–vis in DMSO/H_2O (95/5, v/v)

binding site of receptor, which influences the interaction of receptor-anion. In view of the high selectivity of receptor 1 in the dry DMSO, we also design experiments in DMSO/H_2O (95:5, v/v) solution to further investigate their performance. In DMSO/H_2O solution, receptor 1 revealed a different spectrum which showed two bands at 320 nm and 366 nm due to 5% protic water. With the addition of AcO^-, the bands centered at 428 nm were gradually enhanced and a well-defined isosbestic at 395 nm appeared. Receptor 1 still had recognition ability for AcO^- in DMSO/H_2O (95:5, v/v) as shown in Fig. 4. The binding ability of receptor 1 with AcO^- was the strongest among the anions studied according to association constant (see Table 1).

To make clear whether the binding ability of receptor 1 with AcO^- changed under the condition that all anions studied existed simultaneously, we conducted the UV–vis spectral interference experiment [33] in DMSO/H_2O (95:5, v/v) (Fig. 5). Results indicated that the intensity of spectral response of receptor 1 upon the addition of the mixed anions was almost the same as the addition of only acetate anion, which showed the binding ability of AcO^- with receptor 1 was not influenced by the existence of other anions even though 5% water was added.

Fluorescent titrations

The binding behavior of receptor 1 and anions was investigated by fluorescent titrations in dry DMSO solution. Obviously, compound 1 exhibited weak fluorescent emission peaks at 456 nm (see Fig. 6), upon excitation wavelength at 407 nm. Significant spectral changes were observed upon the addition of F^-, AcO^- and $H_2PO_4^-$ to DMSO solution of compound 1. Interestingly, the addition of AcO^- to DMSO solution of receptor 1 made the emission peak shift to the long-wave direction, concomitant with an obvious increase in its emission intensity (Fig. 6). Similar fluorescence enhancement phenomena were also

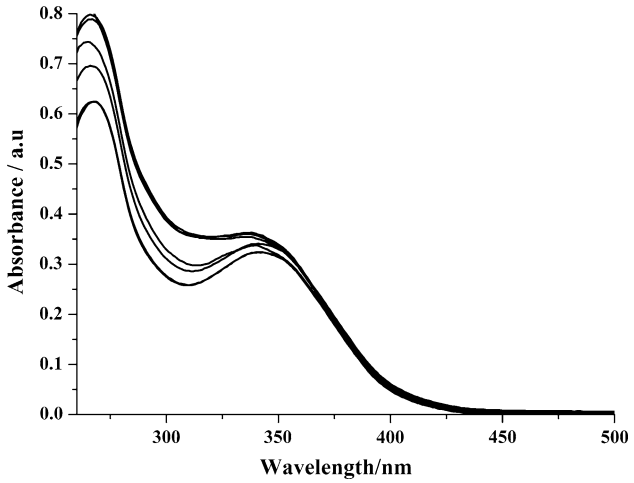


Fig. 3 UV–vis spectra of 2 (2×10^{-5} M) in DMSO in the presence of 50 equiv. of AcO^-, F^-, $H_2PO_4^-$ and miscellaneous anions including Cl^-, Br^- and I^-

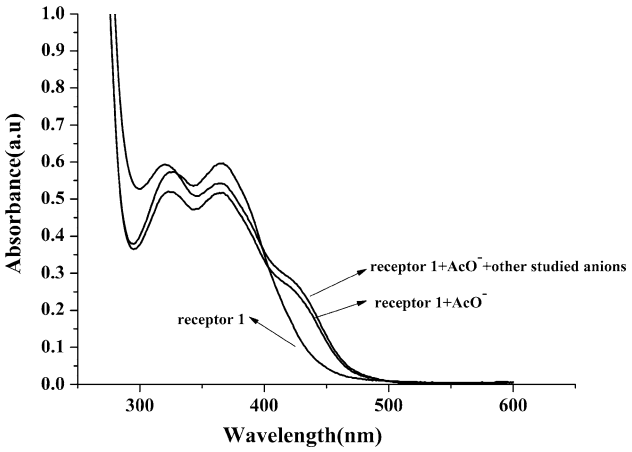


Fig. 5 UV–vis spectrum of receptor 1 (4×10^{-5}) on addition of anion in DMSO:H_2O (95:5 v/v) solution (the concentration of anion is 50 equiv.)

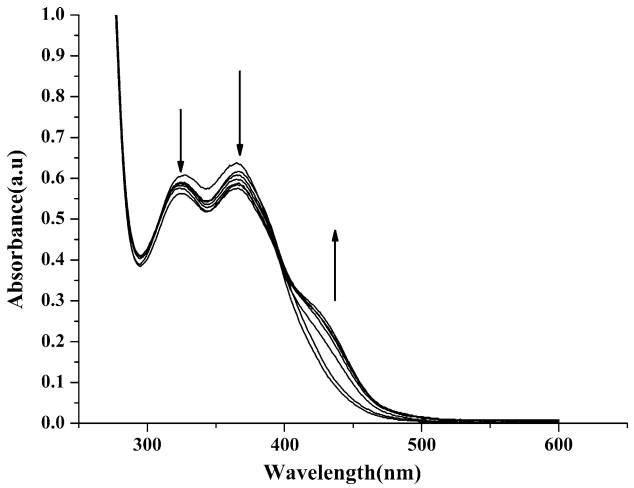


Fig. 4 UV–vis spectrum of receptor 1 (4×10^{-5}) on addition of $[AcO^-] = 0$–200×10^{-5} M in DMSO: H_2O (95:5 v/v) solution. Arrows indicate the direction of increasing anion concentration

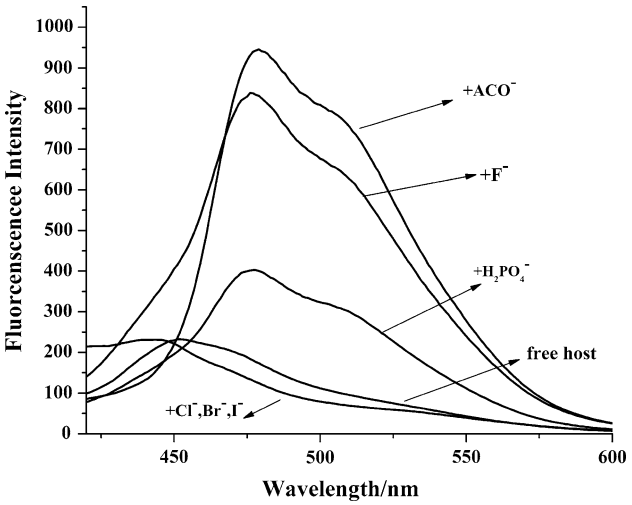
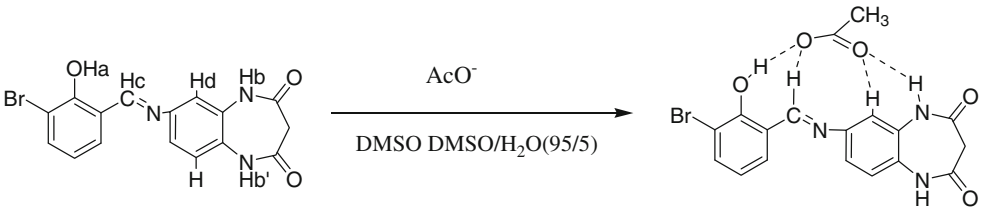


Fig. 6 Fluorensecence spectra of 1 (2×10^{-5} M) in DMSO in the presence of 50 equiv. of AcO^-, F^-, $H_2PO_4^-$ and miscellaneous anions including Cl^-, Br^- and I^-

Scheme 3 The proposed host–guest binding mode in solution



found after the addition of other anion (F^- and $H_2PO_4^-$), but the increasing intensity was not obvious [23]. Otherwise, the addition of excess equiv. Cl^-, Br^-, I^- ions had a slight effect on fluorescence intensity. As demonstrated in Scheme 3, the conformational restriction of receptor 1 was induced upon interaction with acetate ion through hydrogen-bonding. Therefore, there existed astonishingly strong enhancement of the fluorescence intensity observed in Fig. 7, which could be derived from the increase of the rigidity in receptor molecules [23].

The association constants were also calculated according to fluorescence results. As expected, the analytical

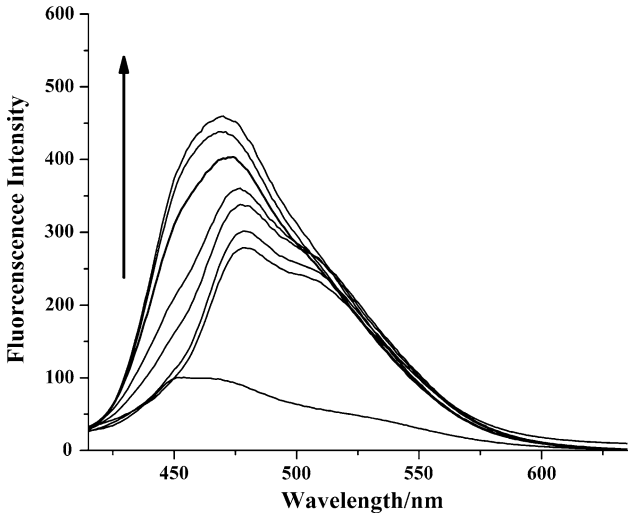


Fig. 7 Fluorescent changes of the sensor 1 in DMSO (2×10^{-5} M) upon addition of AcO^-, *Arrow* indicates the direction of increasing anion concentration

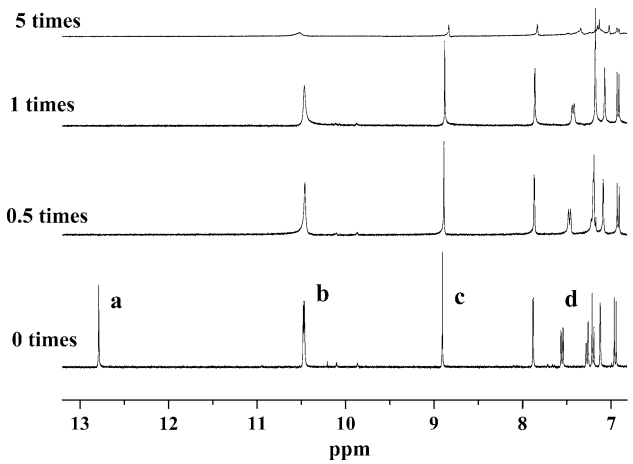


Fig. 8 ^{1}H NMR titration of a 2.0×10^{-3} M solution of 1 in DMSO-d_6 with AcO^-

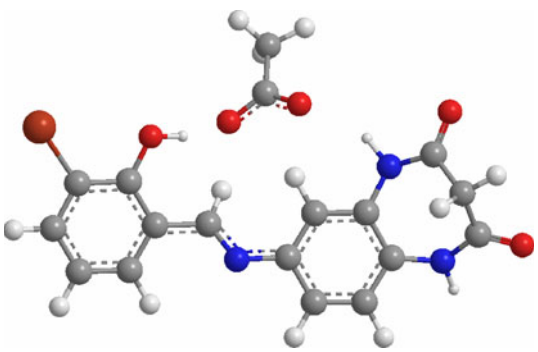


Fig. 9 B3LYP/3-21G-predicted optimized geometry of complex of 1 with acetate

results of the fluorescence titration were very consistent with those results of the UV–vis titration, which can be seen from Table 1 [34].

^{1}H NMR titrations

To shed a light on the nature of the interaction between the anions tested and receptor 1, ^{1}H NMR titrations were carried out in DMSO-d_6. Figure 8 showed ^{1}H spectral changes of receptor 1 (2×10^{-3} M) in DMSO-d_6 in the absence and presence of different equivalent of acetate ions. Obviously, after addition of 0.5 equiv. of AcO^-, the proton signal of the –OH group (Ha) at 12.79 ppm disappeared, which showed the proton of the hydroxyl group formed the hydrogen bonding with acetate ion. The double peak signal at 10.46 ppm (Hb) of amides broadened by addition of the AcO^- from 0 to 1 equiv.. With the further addition of AcO^- (5 equiv.), the resonance signal of the –NH also broadened obviously and exhibited a little downfield shift due to the hydrogen bond formation between the acetate and the diamide in receptor 1. No obvious change was observed in the proton signal of the –CH group at 8.96 ppm (Hc) when the addition of the AcO^- changed from 0 to 1 equiv.. When the concentration of AcO^- was up to 5 equiv., the chemical shift of the –CH shifted to the upfield. With the addition of acetate ions, the phenyl protons especially for the protons Hd (at 7.51 ppm) shifted to upfield significantly, which indicated the increase of the electron density on the phenyl ring owing to the through-bond effects. The phenyl ring proton away from OH at 7.26, 7.12 and 6.95 ppm all moved upfield due to the shielding effect which resulted from the electron density increase of the phenyl rings through the bond spreading. These changes clearly indicated that the host–guest interaction indeed involved the formation of hydrogen-bond by hydroxyl group and diamide (Scheme 3).

Theoretical investigation on the structure

To understand the geometry of the receptor-acetate complex, the structures of receptor were optimized. The calculations were carried out at the B3LYP level of theory with 3-21G as the basis set through Gaussian 03 package [35]. For geometry optimizations, the first guess was fully optimized by AM1 semi-empirical Hamiltonian. Then the models were re-optimized at B3LYP/3-21G level of theory. The B3LYP/3-21G-optimized structures for the complexes of receptor 1 with acetate [36] are represented in Fig. 9. As for acetate, two oxygens participated in the formation of hydrogen bond, one oxygen atom formed hydrogen bond with the protons of OH (dO···H(a) = 1.946 Å) and imine (dO···H(c) = 2.025 Å), another oxygen atom formed hydrogen bond with one (dO···H(b) = 2.072 Å) of two

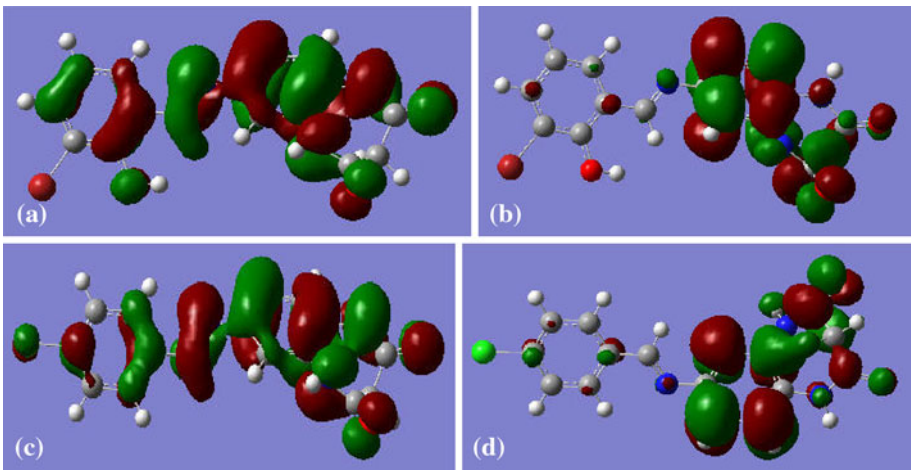


Fig. 10 The selected frontier orbitals. **a** HOMO of 1, **b** LUMO of 1, **c** HOMO of 2, **d** LUMO of 2

–NH protons and the proton of benzene ring (dO···H(d) = 2.041 Å). Finally, the receptor 1 is bound to the acetate anion by four hydrogen bond contacts yielding a highly stable 1:1 complex (Scheme 3).

Theoretical investigation on molecular orbital level using density functional theory at B3LYP/3-21G level with Gaussion03 program can also explain the hydrogen bond interaction (Fig. 10). The calculation results on the energy gap of E_{LUMO}, E_{HOMO} of **1** and **2** were listed in Table 2. From Table 2, the energy gap $\Delta E(E_{LUMO}- E_{HOMO})$ of compound **2** is larger than that of 1, which implies compound **1** has higher reaction activity than compound **2**. Therefore it is easier for compound 1 to interact with anions than compound 2 and has stronger binding ability.

In addition, selected frontier orbitals for compounds are shown in Fig. 10. We introduced molecular frontier orbital in order to explain UV–vis absorption spectra in host–guest interacted process by electron transition of frontier orbital. The HOMO density in compound **1** is localized on the whole molecular while the LUMO density is only localized on diamide moiety, which illustrates the electron transition of the LUMO arouses the red shift phenomenon in UV–vis spectra and the fluorescence enhancement of 1-anion.

In receptor 1, the charge of the oxgyen atom (O) of –OH group is −0.582572, and the charges of the nitrogen atoms of –NH are −0.829401 and −0.830528, respectively. The charges of the nitrogen atoms in receptor 2 are −0.828908 and −0.830347, respectively. The smaller the charge of the oxgyen atom of phenolic hydroxyl group is, the stronger the binding ability is. Thus it is easier for AcO^- to interact with hydrogen of OH than that of NH.

In previous text, the anion binding ability of compound 2 only containing –NH was very weak and could not be used for anion recognition. However, compound 1 containing –OH and –NH showed strong anion binding ability which may be relevant to multiple hydrogen bond [23]. These results proved that the hydroxyl group played an important role in anion recognition.

Table 2 The calculation results on the energy gap of E_{LUMO}, E_{HOMO} of **1** and **2**

Compound	**1**	2
E_{LUMO} (a.u.[a])	−0.03186	−0.03082
E_{HOMO} (a.u.)	−0.22168	−0.22218
ΔE (kJ mol^{-1})	498.37	502.42

[a] 1 a.u. = 2625.5 kJ mol^{-1}

Conclusion

In summary, a new receptor bearing phenolic hydroxyl group and diamide (1) showed anion-binding ability through UV–vis, fluorescent and ^1H NMR titrations in DMSO and DMSO/H_2O (95:5 v/v). The results demonstrated that 1 could bind strongly with anions and selectively distinguish AcO^- from other anions according to the association constants. The experimental results and theoretical investigation proved that receptor 1 interacted AcO^- through multiple hydrogen bonding interaction with the –OH and the –NH. In addition, the binding ability of AcO^- with receptor 1 was not influenced by the existence of other anions even in DMSO/H_2O (95:5 v/v). The experiments and theoretical investigation may contribute to the development of more colorimetric and fluorescent chemosensors.

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