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A simple colorimetric sensor for biologically important anions based on intramolecular charge transfer (ICT)

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ABSTRACT

A sensitive colorimetric sensor (**1**) based on 4,5-dinitrobenzene-1,2-diamine was designed and synthesized. Binding of anions such as AcO^-, F^- and $H_2PO_4^-$ results in a notable change in the visible region of spectrum (an approximately 90 nm red shift), which can be detected by the 'naked-eye'. Furthermore, the binding ability was evaluated by UV–vis titration experiments as following: $AcO^- > F^- > H_2PO_4^- \gg Cl^-, Br^-, I^-$. The nature of the color change of **1** induced by AcO^- was due to the intramolecular charge transfer (ICT) which was confirmed by X-ray crystal structure and ^1H NMR titration spectra.

1. Introduction

Anions play an important role in a wide range of biological system. For example, chloride anions are present in large quantities in the oceans; high-energy anionic phosphate derivatives are at the centre of power processes as diverse and important as biosynthesis, molecular transport, and muscle contraction; and carbonates are key constituents of biomineralized materials [1–3]. Despite their popularity in biological system, the design of 'substrate specific' synthetic receptors still reveals a great challenge due to: (i) the large size of anions compared to the cations, (ii) the chemical environment that determines the strength of interaction, and (iii) the pH of the medium. Thus, the development of designing anion receptors is crucial and emergent.

One convenient and efficient strategy to this is the development of neutral optical chemosensors for anions by combining an anion receptor with a chromogenic and/or auxochromic moiety that is capable of signaling the binding event through intramolecular charge transfer (ICT) processes which leads to a change of color visible by eye [4,5]. Generally, such receptors may contain electron-withdrawing groups or be π-conjugated moleculars [6] that enhance the acidity of the anion binding subunits. In some cases, the acidity of them is too strong to binding anions for the hydrogen-bonding donor is deprotonated or proton transferred to a basic anion [7].

However, the boundary between a hydrogen-bonding donor binding to an anion and a process in which the hydrogen-bonding donor is deprotonated and proton transferred to a basic anion is not easy to clearly distinguish [8]. This problem is challenging because these processes are complicated and may be controlled by several factors: (i) the acidity of binding sites in receptor, (ii) the basicity of anion, and (iii) the strength and amount of hydrogen bonding, which may be highly related to the charge numbers and the geometrical shape of the match between the hydrogen-bonding donor and acceptor groups.

In our pursuit for appropriate receptors for the design of colorimetric anion ICT sensors and distinction between hydrogen bonding and proton transfer, we present an anion receptor, 1,2-bis-(*p*-nitrophenylsulfonamido)-4,5-dinitrobenzene (**1**), whose DMSO solution changed to red from yellow after the inducement of AcO^-, F^- or $H_2PO_4^-$ while Cl^-, Br^- or I^- cannot bring the color change of the solution of **1**. This result was confirmed by UV–vis experiments and, also, its ICT characteristic was validated by X-ray crystal structure, IR and ^1H NMR titration spectra.

2. Experimental section

2.1. Reagents

Most of the starting materials were obtained commercially and all reagents and solvents used were of analytical grade. All anions, in the form of tetrabutylammonium salts, were purchased from Sigma–Aldrich Chemical Co., stored in a desiccator under vacuum

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containing self-indicating silica, and used without any further purification. Dimethyl sulfoxide (DMSO) was distilled in vacuo after dried with $CaSO_4$. Tetra-*n*-butylammonium salts (such as $(n\text{-}C_4H_9)_4NF$, $(n\text{-}C_4H_9)_4NCl$, $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_4H_9)_4NI$, $(n\text{-}C_4H_9)_4NAcO$, and $(n\text{-}C_4H_9)_4NH_2PO_4$) were dried for 24 h in vacuum with P_2O_5 at 333 K before use C, H, and N elemental analysis were made on an elementary vario EL.

2.2. General methods

UV–vis absorption spectra were recorded on Shimadzu 2450 with TCC-240A controller. ^{1}H NMR spectra were recorded on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a Mariner apparatus. C, H, and N elemental analyses were made on elemental vario EL. The IR spectra were recorded on MAGNA-560 FT-IR, solid was mixed in KBr pellet and liquid was dropped on the flake of KRS5. The crystal structure was measured on a Rigaku Saturn CCD.

2.3. Preparation of sensor 1

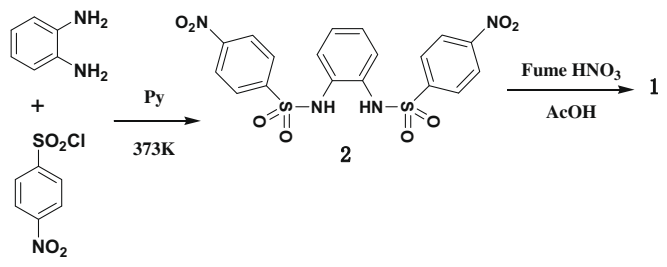
Sensor **1** was synthesized through two steps as shown below in Scheme 1. Firstly, condensation of *o*-diaminobenzene with *p*-nitrobenzenesulfonyl chloride in pyridine gave **2** as a pale yellow solid in 92% yield [9]. Nitration of **2** by fume HNO_3 and AcOH gave pale yellow powder **1** in 80% yield [10].

2.3.1. 1,2-bis-(p-nitro-phenylsulfonamido)-benzene (2)

A solution of *o*-diaminobenzene (2 g, 0.0185 mol) in pyridine (8 mL) was added dropwise to a solution of *p*-nitrobenzenesulfonyl chloride (8.2 g, 0.0370 mol) in pyridine (10 mL) with stirring. After addition, the mixture was heated at 373 K for 5 h. Then cooled, abundance water was added to the mixture. Pale yellow precipitate was filtered and washed with water, then dried in vacuo to afford pure 1,2-bis-(*p*-nitro-phenylsulfonamido)-benzene as pale yellow powder (yield, 95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.70 (s, 2H, –NH), 8.37 (t, 4H, J = 4 Hz and 4 Hz, Ar–H), 7.96 (q, 4H, J = 4 Hz, 4 Hz and 4 Hz, Ar–H), 7.08 (q, 2H, J = 3.6 Hz, 2.8 Hz and 6.4 Hz, Ar–H), 6.94 (q, 2H, J = 3.2 Hz, 2.8 Hz and 3.2 Hz, Ar–H). ESI-mass: m/z 479.34 $(M + H)^+$, (M = 478.05).

2.3.2. 1,2-bis-(p-nitro-phenylsulfonamido)-4,5-dinitrobenzene (1)

1,2-bis-(*p*-nitro-phenylsulfonamido)-benzene (10 g, 0.021 mol) and 15 mL acetic acid (AcOH) were added to a 100 mL three-neck flask. A solution of 2.0 mL fume HNO_3 and 3 mL AcOH was added dropwise to the above mixture at 333 K with stirring. After addition, the mixture solution was going on stirring for another 0.5 h at 333 K. Then after cooled, offwhite solid was filtrated, washed with AcOH and dried in vacuum. m.p. 259–260 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.71 (s, 2H, J = 8 Hz N–H), δ 8.23 (d, 4H, J = 8 Hz, Ar–H), 7.99 (d, 4H, J = 8 Hz, Ar–H), 7.69 (s, 2H, Ar–H). Elemental analysis: Calc. for $C_{18}H_{12}N_6O_{12}S_2$: C, 38.03; H, 2.13; N, 14.78; Found: C, 37.71; H 2.60; N, 14.60. IR (BrK, pellet ν_{max} cm^{-1}): 3292–3242 (m, ν_{as}(–NH)), 3109–3071 (w, ν_{as}(Ar–C–H)), 1540 (s, ν_{as}(–NO_2)), 1337–1355 (s, ν_{as}(–NH)), 1171 (s, ν_s(–NH)). ESI-mass: m/z 569.13 $(M + H)^+$, (M = 568.00).



Scheme 1. The synthetic route of the receptor **1**.

To resolve some powder **1** in DMF solution and after several monthes many single crystals suitable to X-ray analysis were obtained. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.23 (d, 4H, J = 12 Hz, Ar–H), 7.99 (d, 4H, J = 4 Hz, Ar–H), 7.67 (s, 2H, Ar–H), 7.95 (s, H, –(C=O)H), 2.89 (s, 3H, $-CH_3$), 2.73 (s, 3H, $-CH_3$), 2.55 (s, 6H, 2–CH_3). Elemental analysis: Calc. for $C_{23}H_{26}N_8O_{13}S_2$: C, 40.23; H, 3.82; N, 16.32; Found: C, 40.23; H 3.62; N, 16.38. IR (KBr, pellet, ν_{max} cm^{-1}): 3440 (w, br, ν_{as}(–NH···N), 3186–3105 (m, ν_{as}(Ar–C–H)), 1669 (s, ν_s(–C=N)).

3. Results and discussion

3.1. UV-vis spectroscopic measurement

Firstly, to evaluate the binding ability of **1**, the UV–vis titration experiments of the receptor **1** were carried out in dry DMSO solution using standard tetrabutylammonium salts of AcO^-, F^-, $H_2PO_4^-$, OH^-, Cl^-, Br^- and I^- at 298.2 ± 0.1 K. UV–vis spectrum of the solution of **1** (1.0×10^{-5} M) recorded upon the addition of AcO^- (see Fig. 1). In the absence of the anion, an absorption peak at the λ_{max} of 425 nm, i.e. the π–π^* transition [11] of the chromophore (4,5-dinitrobenzene-1,2-diamine), disappeared gradually accompanying with the formation of a new band at 515 nm characteristic of deprotonation of the receptor, which was ascribed to the ICT between the deprotonated –NH unite and the electron-deficient –NO_2 moiety. Relatively, the solution of **1** changed to red from yellow. Indeed, titration with OH^- gives the same band (Fig. 1, inset). The similar spectral changes were observed upon the addition of F^- and $H_2PO_4^-$. However, when 1.5 equiv. AcO^-, F^- or $H_2PO_4^-$ were added into the solution of **1** (**1.0** $\times$ **10**$^{-5}$ M), the color changes were different (see Fig. 2). Especially, as the Cl^-, Br^- and I^- were titrated into **1**, the spectra hardly change even the anions were excessive.

Continuous variation method was used to determine the stoichiometric ratios of the receptors to AcO^- anion guest. In Fig. 3, Job Plot [12] of **1** and AcO^- in DMSO shows the maximum at a molar fraction of 0.5. Moreover, similar results can also be obtained for other anions (F^- and $H_2PO_4^-$).

For a ration of 1:1 stoichiometry, the relation in Eq. (1) could be derived easily, where X is the absorption intensity, and C_H or C_G is

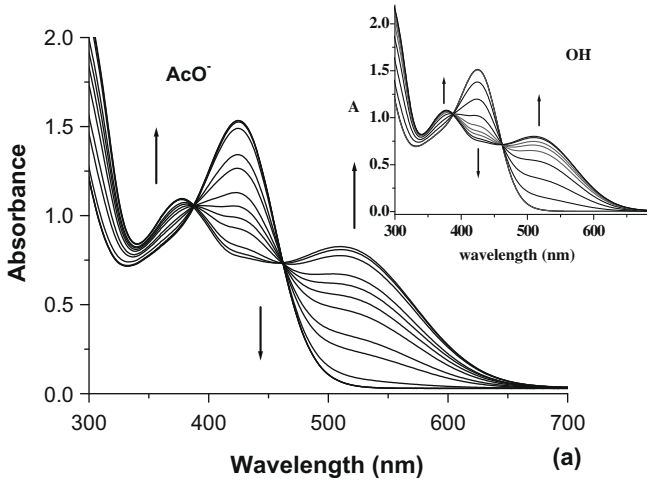


Fig. 1. Family of spectra taken in the course of the titration of a 1.0×10^{-5} M solution of **1** with a standard solution of AcO^- at 298.2 ± 0.1 K. Inset of Fig. 1: Family of spectra taken in the course of the titration of a 1.0×10^{-5} M solution of **1** with a standard solution of OH^- at 298.2 ± 0.1 K.

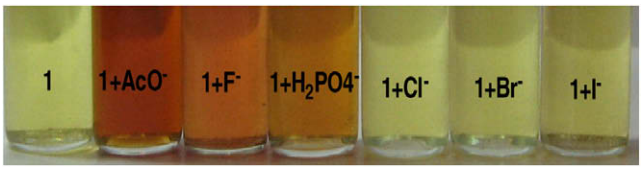


Fig. 2. The color changes of sensor **1** in DMSO solutions.

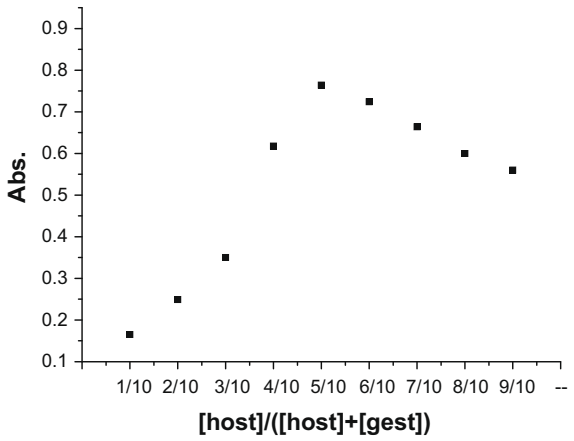


Fig. 3. Job plots for receptor **1** with AcO^- determined by UV–vis in DMSO at 298.2 ± 0.1 K, [host] + [guest] = 2.0×10^{-5} M.

the concentration of the host or the anion guest correspondingly [13].

$$X = X_0 + (X_{lim} - X_0)\{C_H + C_G + 1/K_{ass} - \left[(C_H + C_G + 1/K_{ass})^2 - 4C_HC_G\right]^{1/2}\} \Big/ 2C_H \quad (1)$$

The affinity constants of receptor **1** for anionic species are calculated and listed in the Table 1 below.

From the Table 1, the affinity ability was evaluated as following: $AcO^- > F^- > H_2PO_4^- \gg Cl^-, Br^-, I^-$. The reason was probably that the selective recognition for acetate anion is related to the configuration of the acetate matching with the receptor and the alkalescence of the anion, as well as the basicity of receptor. Because acetate anion was a plane and triangular and the angle of O–C–O was about 120°, the distance of two oxygen atoms might be fit to the two hydrogen atoms on recognition sites of the receptor in the triangular configuration. Furthermore, the alkalescence of acetate anion was also stronger than the other anions (Cl^-; Br^-; I^-). So, the association constant K_{ass} for acetate was maximal. The angle of O–P–O is about 108° for $H_2PO_4^-$ (tetrahedral configuration) and the distance of two oxygen atoms of AcO^- was longer than that of $H_2PO_4^-$; so two oxygen atoms of $H_2PO_4^-$ could not match well with two hydrogen atoms in the receptor. As for F^-, it was global and had the smallest atom radius in halide atom, but the better alkalescence made itself have the higher association constant K_{ass} than $H_2PO_4^-$.

3.2. ^{1}H NMR titration spectra

Proton NMR titration experiments were conducted to further investigate the interaction of **1** with AcO^- in DMSO-d_6. It is noticed that the signals of NH protons disappear on addition of 1.5 equiv. AcO^- and the signals of all the protons in three benzene rings have gone to upfield and without any change in shape (Fig. 4). The two protons in matrix benzene ring have gone to upfield 0.18 ppm (from 7.68 ppm to 7.50 ppm). And the other eight protons at of the two substituted benzene rings shift very lightly to upfield 0.02 ppm (from 8.24 ppm to 8.22 ppm and 8.00 ppm to 7.98 ppm, respectively). These results indicate that the charge flowing to the benzene is obstructed by the group of sulfonamide, but unhindered to the directly linked benzene ring, which caused the solution of **1** changed to red from yellow. The same consequence of titration with F^- and $H_2PO_4^-$ are obtained which means that the interaction mode of the three anions is same. However, the titration of Cl^-, Br^- or I^- brought no changes of the ^{1}H NMR spectra. Furthermore, the mode of interaction between **1** and AcO^- were given in Scheme 2 below.

Table 1
The affinity constants of receptor **1** with anions at 298.2 ± 0.1 K in DMSO.

Anion	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
lgK_{ass} (M^{-1})	5.38 ± 0.27	4.88 ± 0.19	4.86 ± 0.12	[a]ND	[a]ND	[a]ND

[a] ND = cannot be determined.

3.3. Crystal structure of sensor *1*

The straightest and the most believable evidence is the crystal structure. For this reason, we obtained the single crystal of sensor **1**[14].

Interestingly, the crystal structure (Fig. 5) involves three moleculars, deprotoned sensor **1**, a DMF and a protoned *N,N*-dimethylamine. It is well known that DMF is prone to decompose and product *N,N*-dimethylamine and carbon monoxide in acid or basic circumstance [15]. So the protoned *N,N*-dimethylamine should be the decomposition product of DMF in the solution and then accepts the proton from N(3) sulfonamide (in Fig. 4). It can be seen from Fig. 5, the distance of C(13)–N(3)$^-$ (1.369(4) Å) which falls in the distance range 1.34–1.38 Å for C=N [16]. Compared with C(13)=N(3), N(4)–C(14) with the distance of 1.425(2) Å is the undeprotoned sulfonamide H(4)–N(4). Then intramolecular hydrogen bond N(3)···H(4)–N(4) forms with the distance of 2.595(3) Å (CCDC 607917).

Compared with the sulfonamide N(4), the geometry of sulfonamide of N(3) group revealed significant changes. Following deprotonation, the N(3)–S(1) (1.5731(18) Å) bond length decreases (N(4)–S(2) 1.6156(18) Å), whereas the distances of S(1)=O(5) and S(1)=O(6) are increased (S(1)–O(5), 1.4382(16) Å, S(1)–O(6), 1.4435(15) Å; S(2)–O(7), 1.42892(17) Å, S(2)–O(8), 1.4308(17) Å), which suggests that the lone pair on the deprotonated nitrogen atom is partly delocalized over the SO_2 fragment. It is described in part by the resonance representation in Scheme 3 (formula c). On the other hand, the electron must also delocalize over the matrix benzene ring, as suggested by the distinct reduction of the

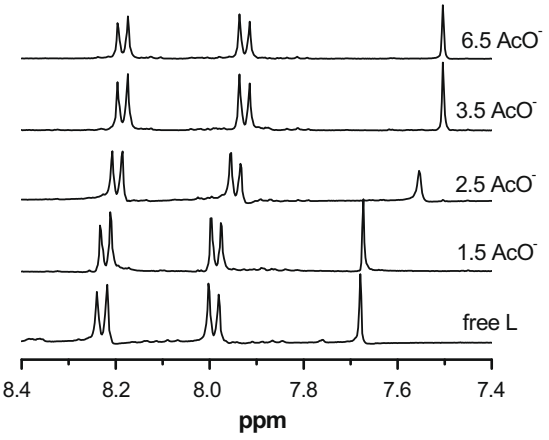
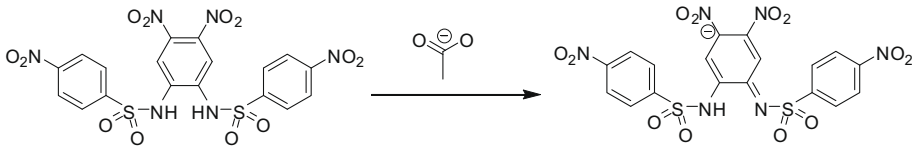


Fig. 4. Partial ^{1}H NMR titration spectra of **1** (5×10^{-3} M) added with AcO^- in DMSO-d_6 at room temperature.



Scheme 2. The mode of interaction between **1** and AcO^-.

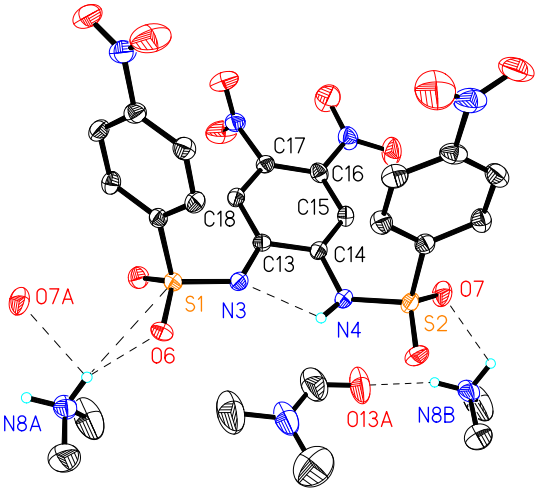
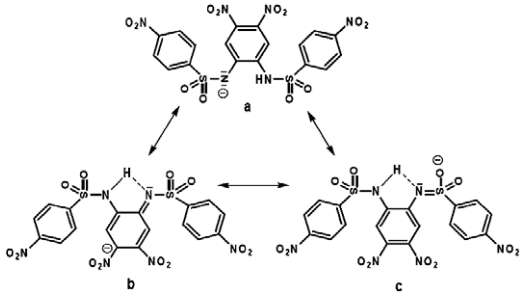


Fig. 5. Molecular structure of **1** (30% probability thermal ellipsoids).



Scheme 3. Resonance representation of the deprotonated form of L. Formula b accounts for the shortening of N–C bond, and c for the lengthening of S=O bonds and shortening of N–S bond.

N(3)–C(13) distance and accounted for by the resonance formula b in Scheme 3 which is one of the several possibilities [17–19]. With the assistance of two electro-drawing groups of $-NO_2$ in the matrix benzene ring, the resonance formula b may be dominant.

Thus, the crystal structure obtained is formula b. This result reveals that the abundant charge of deprotonated –NH unite can transfer to the electron-deficient $-NO_2$ moiety, which corroborated the mode of interaction between **1** and AcO^-.

4. Conclusions

In summary, we have presented an ICT anion sensor for AcO^-. The DMSO solution (1×10^{-5} M) of sensor has an obvious color change from yellow to red upon the addition of AcO^-, $H_2PO_4^-$ or F^-, which reveals that it is a very sensitive sensor for naked-eye. The nature of the sensor sensing anions was corroborated that it is based on ICT by UV–vis, ^1H NMR titration and the single crystal structure analysis.

Acknowledgements

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