Journal of Photochemistry and Photobiology B: Biology 97 (2009) 18–21

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

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

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ARTICLE INFO

*Article history:*
Received 12 September 2008
Received in revised form 23 April 2009
Accepted 20 July 2009
Available online 24 July 2009

*Keywords:*
Colorimetric
Acetate sensor
ICT
Crystal structure
Naked-eye detection

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 $\pi$-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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doi:10.1016/j.jphotobiol.2009.07.006

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

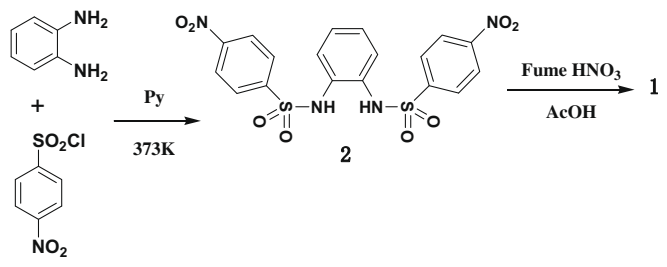
Sensor **1** was synthesized through two steps as shown below in Scheme 1. Firstly, condensation of *o*-diaminobenzene with *p*-nitrobenzenesulfonyl chloride in pyridine gave **2** as a pale yellow solid in 92% yield [9]. Nitration of **2** by fume $HNO_3$ and AcOH gave pale yellow powder **1** in 80% 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-$d_6$): $\delta$ 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-$d_6$): $\delta$ 13.71 (s, 2H, $J$ = 8 Hz N–H), $\delta$ 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 $\nu_{max}$ $cm^{-1}$): 3292–3242 (m, $\nu_{as}$(–NH)), 3109–3071 (w, $\nu_{as}$(Ar–C–H)), 1540 (s, $\nu_{as}$(–$NO_2$)), 1337–1355 (s, $\nu_{as}$(–NH)), 1171 (s, $\nu_s$(–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-$d_6$): $\delta$ 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, $\nu_{max}$ $cm^{-1}$): 3440 (w, br, $\nu_{as}$(–NH···N), 3186–3105 (m, $\nu_{as}$(Ar–C–H)), 1669 (s, $\nu_s$(–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** ($1.0 \times 10^{-5}$ M) recorded upon the addition of $AcO^-$ (see Fig. 1). In the absence of the anion, an absorption peak at the $\lambda_{max}$ of 425 nm, i.e. the $\pi$–$\pi^*$ 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

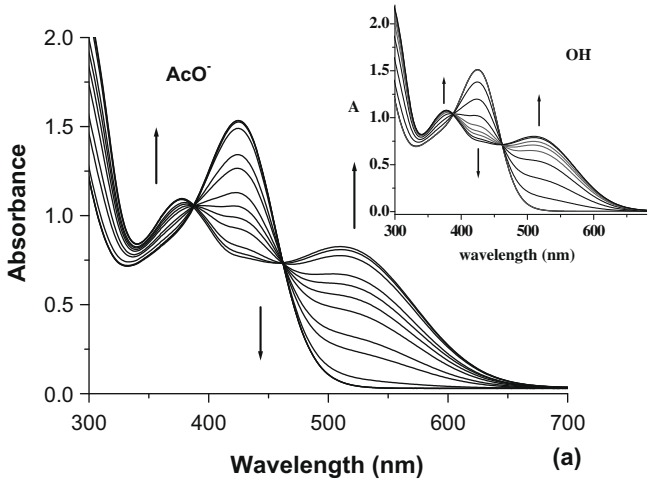



**Fig. 1.** Family of spectra taken in the course of the titration of a $1.0 \times 10^{-5}$ M solution of **1** with a standard solution of $AcO^-$ at 298.2 ± 0.1 K. Inset of Fig. 1: Family of spectra taken in the course of the titration of a $1.0 \times 10^{-5}$ M solution of **1** with a standard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