

Research paper

An efficient colorimetric and absorption ratiometric anion sensor based on a simple azo-azomethine receptor

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ABSTRACT

An efficient colorimetric and absorption ratiometric azo-azomethine receptor N'-((E)-2-hydroxy-5-((E)-(4-nitrophenyl)diazenyl)benzylidene)picolinohydrazide (**L**) based on phenolic and acyl hydrazine binding units was synthesized and characterized by FT-IR, ¹H NMR, ¹³C NMR and HRMS method. The optical response of **L** towards different anions was studied by colorimetric, UV-vis and ¹H NMR titration method. The results revealed that **L** had a selective colorimetric sensing ability for biologically important F⁻, AcO⁻ and H₂PO₄⁻ by changing color from pale yellow to blue by naked-eye. Interestingly, the sensor **L** demonstrated an absorption ratiometric response towards F⁻ (1:2 complex) and H₂PO₄⁻ (1:1 complex) during the recognition process. The detection limit of the sensor **L** towards F⁻, AcO⁻ and H₂PO₄⁻ was estimated to be 2.94 μM, 4.12 μM and 12 μM respectively. The recognition mechanism was attributed to hydrogen bonding and subsequent deprotonation process according to ¹H NMR titration experiments.

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1. Introduction

Anions play an essential role in the field of biology, industry and environmental science [1,2]. Therefore, More and more attention has been laid over the last few decades on the development of anion sensors [3–5]. Among all the anions, fluoride, acetate and dihydrogenphosphate ions receive the most concerns due to their crucial roles in a broad range of chemical and biological processes [6,7]. For instance, fluoride ion is biologically active and utilised for the treatment of osteoporosis, dental care, anesthetics and psychiatric drugs [8,9] Acetate ions also play an important role in living system as acetyl coenzyme A. In addition, the production of acetic acid from the fermentation process is the main ingredient present in vinegar used in foods [10,11]. Similarly, phosphate and its analogs play a vital role in signal transduction, energy storage and gene construction in biological systems [12,13]. Accordingly, the design and preparation of effective sensors for biologically relevant anions with high selectivity is urgently needed.

Compared with fluorescent and electrochemical sensors, colorimetric sensors have some obvious advantages, such as its convenience, low cost and good visualization. On the other hand, ratiometric sensors could provide more reliable quantitative information since they utilize the ratio of absorption/emission intensity

at two different wavelengths as a function of analyte concentration. However, traditional sensors often depend on a single wavelength for quantitative analysis. In the last few decades, a number of azo-based colorimetric sensors for anions have been reported [14,15]. Velmathi et al. [16] reported a azo-schiff base receptor containing a phenolic OH unit for selective sensing of F⁻/AcO⁻ with the formation of a 1:1 stoichiometric complex. Hamid et al. [17] developed diaminomaleonitrile-based azo receptors and they formed 1:1H-bonded complexes with F⁻ in CH₃CN solution. Rezaeian et al. [18] prepared a new chromogenic azo-azomethine sensor containing active phenolic sites for biologically important anions such as F⁻, AcO⁻ and H₂PO₄⁻ over other anions which formed a 1:2 stoichiometric complex. To the best of our knowledge, there was no example of offering colorimetric and absorption ratiometric responses upon addition of anions by integrating acyl hydrazine N—H and phenolic OH units into a single anion receptor.

Herein, as a part of our ongoing research, we designed and synthesized a new azo-azomethine receptor (as shown in Fig. 1) equipped with nitro-azobenzene group as signal subunit and phenolic OH & hydrazide N—H as binding units. The sensing ability of **L** towards different anions was investigated by means of naked-eye, UV-vis spectroscopy as well as by ¹H NMR titration method. Interestingly, the sensor **L** demonstrated a good selectivity towards F⁻ and AcO⁻ (1:2 complex) and H₂PO₄⁻ (1:1 complex) along with a vivo color change and absorption ratiometric responses during the recognition process.

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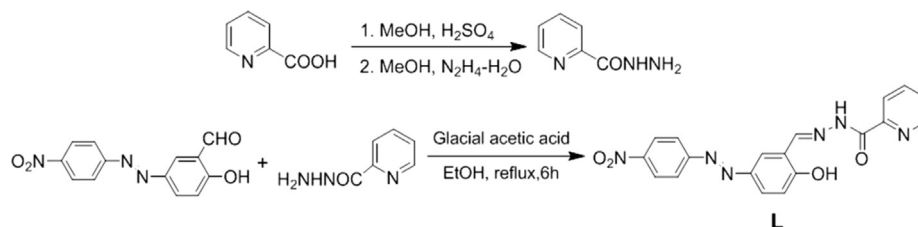


Fig. 1. Synthesis of the sensor **L**.

2. Experimental section

2.1. Materials and methods

Picolinic acid, hydrazine hydrate, p-nitroaniline, salicylic aldehyde, tetra-*n*-butyl-ammonium (TBA) salts (F^- , Cl^- , Br^- , I^- , NO_3^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- , AcO^-) were purchased from Sigma-Aldrich and used without further purification. Other reagents were purchased from commercial source and used as received.

Melting points were determined on a Beijing X-4 microscopic melting point apparatus without correction (Beijing Tech Instrument Co., China). Infrared spectrum were recorded on a Shimadzu IR Prestige-21 spectrometer in KBr disk. UV–vis absorption spectra were recorded on a UV-2550 spectrophotometer in the region 300–600 nm. High-resolution mass spectra (HRMS) were measured by using a Shimadzu LCMS-IT-TOF spectrometer. 1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) and used tetramethylsilane as internal standard substance.

2.2. Synthesis of the sensor **L**

Pyridine-2-carbohydrazine was synthesized according to literature method [19]. Azo-coupled salicylaldehyde precursor was prepared according to the well-known literature procedure [20–22].

Pyridine-2-carbohydrazine (1.44 g, 0.0105 mol) and azo-coupled salicylaldehyde precursor (2.71 g, 0.01 mol) were dissolved in 30 mL absolute ethanol followed by the addition of few drops of glacial acetic acid to the reaction mixture. Then the reaction mixture was refluxed for 5 h under stirring. After cooling to room temperature, the mixture was filtered, washed with absolute ethanol, dried in vacuum to obtain red powder. Yield: 82%. m.p. 298–300 °C. FT-IR (KBr, cm^{-1}): 3448 (–OH), 3259 (N–H), 1674 (C=O), 1612 (C=N), 1587 (Ar, C=C), 1511, 1335 (–NO₂), 748 (Ar–H) (Fig. S1). 1H NMR (400 MHz, DMSO) δ 12.66 (s, 1H), 12.09 (s, 1H), 8.95 (s, 1H), 8.75 (d, J = 4.3 Hz, 1H), 8.39 (d, J = 8.6 Hz, 2H), 8.20 (d, J = 1.3 Hz, 1H), 8.16 (d, J = 7.7 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.7 Hz, 1H), 7.78–7.59 (m, 1H), 7.15 (d, J = 8.7 Hz, 1H) (Fig. S2). ^{13}C NMR (101 MHz, DMSO): δ 161.97(s), 161.06(s), 155.79(s), 149.57(s), 149.06(s), 148.43(s), 148.27(s), 145.62(s), 138.51(s), 127.67(s), 127.12(s), 125.45(d), 124.90(s), 123.65(d), 123.36(s), 120.34(s), 118.06(s) (Fig. S3). HRMS: m/z calcd for $C_{19}H_{14}N_6O_4$: $[M+H]^+$ 391.1149; found: 391.1174 (Fig. S4).

2.3. Sensing experiments

2.3.1. UV–vis spectrum of **L** with various anions

Stock solution of the sensor **L** was prepared in CH_3CN solution and the final concentration was 20 μM . To a 3.0 mL of the stock solution was added 60 μL CH_3CN solution of each anion (10 mM). After shaking them for a few seconds, UV–vis spectra of **L** were taken at room temperature.

2.3.2. UV–vis titration of **L** with F^- , AcO^- and $H_2PO_4^-$

To each three 3.0 mL of the stock solution was added 3–30 μL of the tetrabutylammonium of fluoride ion, acetate ion and dihydrogen phosphate ion (10 mM). After mixing them for a few seconds, UV–vis titration spectra were taken at room temperature.

2.3.3. 1H NMR titration of **L** with F^- , AcO^- and $H_2PO_4^-$

Seven NMR tubes of **L** (14.5 mg, 0.05 mmol) with seven different equiv (0, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 equiv) of the tetrabutylammonium salts (F^- , AcO^- and $H_2PO_4^-$) were dissolved in DMSO d_6 (0.6 mL). After shaking them for a minute, there 1H NMR spectra were taken.

3. Results and discussion

3.1. Synthesis and characterization

The sensor **L** has been synthesized via condensation reaction of azo-coupled precursors with pyridine-2-carbohydrazine in absolute ethanol in good yield. The sensor **L** was characterized by FT-IR, HRMS and 1H NMR method. The appearance of a new $\nu(C=N)$ absorption at 1612 cm^{-1} clearly indicated that a new Schiff base compound has been formed. Two absorption bands appeared at 3448 and 3259 cm^{-1} were assigned to the O–H and N–H stretching vibrations respectively (Fig. S1). The IR spectra of **L** exhibits peaks at 1674 cm^{-1} was attributed to C=O stretching vibration. In the 1H NMR, the signal at 12.66 ppm and 12.09 ppm were assigned to the –OH and –NH group separately. The peak at 8.98 ppm confirmed the presence of –CH=N group [23–25] (Fig. S2). The M+1 (protonated molecular ion) peak of the high resolution mass spectrum (HRMS) confirmed the molecular formula of **L** ($C_{19}H_{15}O_4N_6$) without any ambiguity (Fig. S4).

3.2. Colorimetric and UV–vis studies

To investigate the sensing ability of the sensor **L** towards various anions, the colorimetric and UV–vis studies were carried out in CH_3CN solution. Before the addition of different anions (F^- , Cl^- , Br^- , I^- , NO_3^- , AcO^- , HSO_4^- , $H_2PO_4^-$, ClO_4^-), the solution of free **L** was pale yellow and displayed two bands at 316 and 378 nm which were attributed to $\pi \rightarrow \pi^*$ transitions of salicylhydrazone and the chromophore respectively (as shown in Figs. 2 and 3). Upon addition of 10 equiv different anions, only the relatively basic

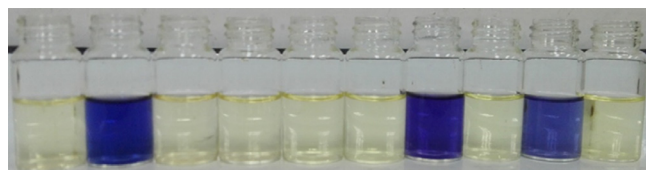


Fig. 2. Color changes of the probe **L** (20 μM) in CH_3CN solution upon addition of 10.0 equiv of different anions (F^- , Cl^- , Br^- , I^- , NO_3^- , AcO^- , HSO_4^- , $H_2PO_4^-$, ClO_4^-).

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