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A colorimetric and absorption ratiometric anion sensor based on indole & hydrazide binding units



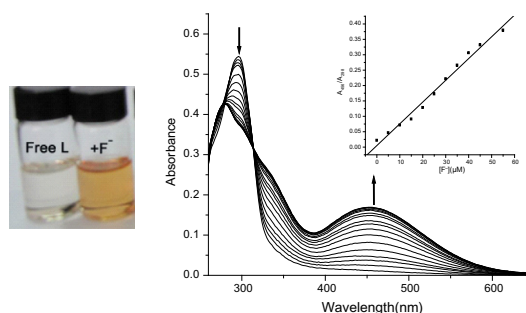
Linbo Zou, Boren Yan, Dingwu Pan, Zan Tan, Xiaoping Bao*

State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Center for Research and Development of Fine Chemicals, Guizhou University, Guiyang 550025, People's Republic of China

HIGHLIGHTS

- An effective anion sensor **L** bearing indole & hydrazide units was synthesized.
- Sensor **L** displayed the colorimetric and absorption ratiometric responses towards F^- , AcO^- and $H_2PO_4^-$ in DMSO.
- Sensor **L** underwent NH deprotonation event upon addition of excessive F^- in DMSO- d_6 .

GRAPHICAL ABSTRACT



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ABSTRACT

A colorimetric and absorption ratiometric anion sensor (**L**) based on indole and hydrazide binding units was designed and synthesized, and its recognition & sensing properties towards different anions were studied by naked-eye observations, UV-vis and 1H NMR titration spectra. Sensor **L** could selectively recognize biologically important F^- , AcO^- and $H_2PO_4^-$ in DMSO over other anions, along with a significant change in its color and absorption spectrum, resulting from the formation of corresponding 1:2 (L/F^-) and 1:1 (L/AcO^- and $L/H_2PO_4^-$) complexes. The 1H NMR titration experiments proved that sensor **L** experienced deprotonation of NH fragment and produced $[HF_2]^-$ species, whereas a stable H-bonding complex was formed in the presence of AcO^- and $H_2PO_4^-$.

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Introduction

More and more attention has been focused on the development of anion receptors or sensors due to key roles of anions in many chemical and biological processes [1–5]. Among common anions, fluoride, acetate and dihydrogenphosphate ions received the most concerns because of their special physiological & biochemical functions in the human body. For example, fluoride was proved to be associated with dental care, osteoporosis and environmental pollution [6]. Acetate ion in the human protein components works as a “molecular switch” in diverse cellular processes,

such as cell division, DNA inheritance and cell aging [7]. Dihydrogenphosphate and its analogues play key roles in signal transduction and energy storage of biological system [8].

Compared with fluorescent and electrochemical sensors, colorimetric sensors had some obvious advantages, such as its convenience, low cost and good visualization [9]. On the other hand, ratiometric sensors could provide more reliable quantitative information since they utilized the ratio of absorption/emission intensity at two different wavelengths as a function of analyte concentration, relative to conventional sensors only depending on a single wavelength for quantitative analysis [10–12]. Most of colorimetric anion sensors were composed of two parts, that is, binding unit and chromophore unit. The extensively-used binding units include amide, urea, thiourea, pyrrole, indole and

* Corresponding author. Tel.: +86 851 8292170; fax: +86 851 3622211.
 E-mail address: baoxp_1980@aliyun.com (X. Bao).

sulfonamide. And recently, a few anion sensors based on hydrazide NH unit were reported, which displayed remarkable differences in their recognition behaviors in spite of small variations in their chemical structures (having nearly the same binding unit and chromophore moiety for these sensors). For example, Shi et al. [13] reported diacylhydrazine-based colorimetric receptors for selective sensing of F^- and AcO^- (from colorless to yellow) over other anions (including $H_2PO_4^-$) in acetonitrile solution, with the formation of a 1:1 stoichiometric complex between the receptors and the anions. Chen and co-workers [14] developed an organogelator containing a hydrazide unit, and its chloroform gel was transferred into a red solution after treatment with F^- , AcO^- and $H_2PO_4^-$, due to the disruption of intermolecular H-bonding interactions among receptor molecules via deprotonation of hydrazide NH. Trivedi et al. [15] synthesized a benzohydrazide-based anion receptor with one *p*-nitrophenyl chromophore, which demonstrated obvious color and spectral changes in DMSO solution only in the presence of F^- and AcO^- (excluding $H_2PO_4^-$). Very recently, Bai and co-workers [16] prepared a *p*-nitrobenzohydrazide derivative and it formed 1:1 H-bonded complexes with AcO^- and $H_2PO_4^-$ in DMSO. For F^- , an initial H-bonding interaction was followed by deprotonation of NH. The addition of F^- , AcO^- and $H_2PO_4^-$ into DMSO solution of the receptor induced a remarkable color change from colorless to red. To our best knowledge, there was no example of integrating hydrazide NH and other NH units into a single anion receptor, which afforded colorimetric & absorption ratiometric responses upon addition of anions.

Herein, we developed an effective anion sensor **L** (Scheme 1) with indole & hydrazide NHs as binding units and *p*-nitrobenzene moiety as a chromophore. Different with the previously reported hydrazide-based anion sensors [13–16], **L** demonstrated a good selectivity towards F^- (1:2 complex), AcO^- and $H_2PO_4^-$ (1:1 complex) over other anions in DMSO, along with a marked color change and absorption ratiometric responses during the recognition process.

Experimental

General

All chemicals were purchased from commercial suppliers and used without further purification. Dry CH_2Cl_2 and TEA were obtained by refluxing over CaH_2 and distillation before use. All the anions were used as their tetra-*n*-butylammonium salts. Melting points were determined on a XT-4 binocular microscope (Beijing Tech Instrument Co., China). IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer in KBr disk. 1H and ^{13}C NMR spectra were measured on a JEOL-ECX 500 NMR spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded on an Agilent LC/MSD Trap VL. Elemental analysis was performed on an Elementar Vario-III CHN analyzer. UV–vis spectra were recorded on a TU-1900 spectrophotometer (Beijing Pgeneral Instrument Co., China).

Synthesis of sensor **L**

Indole-2-acylhydrazine [17] (100 mg, 0.57 mmol) and *p*-nitrobenzoyl chloride (106 mg, 0.57 mmol) were dissolved in dry CH_2Cl_2 (8 mL) in the presence of dry TEA (0.25 mL), and the

resulting mixture was stirred at room temperature for 18 h. The formed precipitate was filtered off and washed with water, giving **L** as a light-yellow solid in 76% yield (140 mg). Mp > 250 °C. 1H NMR (500 MHz, DMSO- d_6): δ 11.76 (s, 1H, H₁), 10.91 (s, 1H, H₂), 10.65 (s, 1H, H₃), 8.39 (d, J = 9.0 Hz, 2H, H₄), 8.17 (d, J = 9.0 Hz, 2H, H₅), 7.67 (d, J = 8.70 Hz, 1H, H₆), 7.46 (d, J = 8.30 Hz, 1H, H₇), 7.29 (s, 1H, H₈), 7.23 (t, J = 8.20 Hz, 1H, H₉), 7.08 (t, J = 7.50 Hz, 1H, H₁₀); ^{13}C NMR (125 MHz, DMSO- d_6): δ 164.6, 160.9, 149.6, 138.2, 136.8, 129.5, 129.2, 127.1, 124.0, 121.9, 120.1, 112.6, 103.8; IR (KBr, cm^{-1}): 3323 (N–H), 1633 (C=O), 1524 (NO₂), 1346 (NO₂); MS-ESI: 323.1 ([M–H][−]); Anal. Calcd for C₁₆H₁₂N₄O₄: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.13; H, 3.89; N, 17.55.

UV–vis and 1H NMR titration experiments

Stock solution of sensor **L** being studied was prepared in DMSO with the final concentration of 20 μ M. To a 3.0 mL of the above solution was added DMSO solution of each anion (15 mM) using a Hamilton syringe. After each of addition, the UV–vis spectrum was recorded. All the titration experiments were carried out on a Pgeneral TU-1900 spectrometer at 298 K.

To a 0.5 mL of DMSO- d_6 solution of **L** (3.0 mM) was added DMSO- d_6 solution of each anion (60 mM). After each of addition, the 1H NMR spectrum was measured.

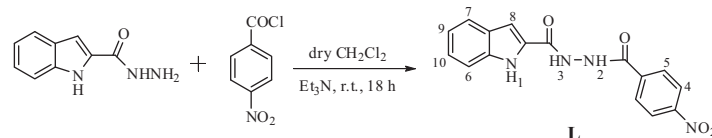
Results and discussion

UV–vis studies

Initially, sensor **L** was examined for its colorimetric sensing capabilities in DMSO upon addition of different anions. As shown in Fig. 1, a significant color change from colorless to yellow was observed in the presence of F^- , AcO^- and $H_2PO_4^-$. In contrast, no perceptible color change happened after addition of other anions, such as Cl^- , Br^- , I^- , ClO_4^- , N_3^- , NO_3^- and HSO_4^- . Subsequently, the selectivity of **L** for various anions was further confirmed by UV–vis spectroscopy. From Fig. 2, addition of F^- , AcO^- or $H_2PO_4^-$ anions to **L** induced the appearance of a new absorption peak around 456 nm (responsible for the vivid color change), concomitant with an evident decrease in the original peak at 296 nm. Upon treatment with other seven anions, very slight or no spectral change was found for **L**.

Encouraged by the above phenomena, the binding interactions of sensor **L** with F^- , AcO^- and $H_2PO_4^-$ were investigated in detail through UV–vis titration spectra. As shown in Fig. 3, upon addition of increasing amounts of F^- to DMSO solution of **L**, the absorbance at 296 nm was gradually decreased and a new absorption peak at 456 nm progressively evolved. A distinct isosbestic point was detected at 312 nm, indicating that only two absorbing species coexisted in the titration mixture [18]. The plot of $1/(A-A_0)$ displayed an excellent linear relationship with $1/[F^-]^2$ according to the Benesi–Hildebrand equation (Fig. 4), proving that **L** bound F^- in a 1:2 stoichiometry with a binding constant of $(1.15 \pm 0.15) \times 10^9 M^{-2}$.

Significantly, there was a good linear relationship between the ratio of the absorbance (A_{456}/A_{296}) in sensor **L** and the concentration of F^- ranging from 0 to 55 μ M, therefore allowing quantitative



Scheme 1. Synthesis of sensor **L**.

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