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A novel colorimetric HSO_4^- sensor in aqueous media

Ping Li[a,b,c], You-Ming Zhang[a,b,c], Qi Lin[a,b,c], Jun-Qiang Li[a,b,c], Tai-Bao Wei[a,b,c,*]

[a] Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Lanzhou, Gansu 730070, PR China
[b] Key Laboratory of Polymer Materials of Gansu Province, Lanzhou, Gansu 730070, PR China
[c] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, PR China

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ABSTRACT

A novel and sensitive anion receptor **3**, bearing Schiff base structure, nitrophenyl azobenzol and carboxyl groups, was developed and characterized as a single chemosensor for the recognition of HSO_4^- anion. The different responses of UV–vis spectra and color changes of **3** could be applied to the recognition for HSO_4^- over other anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ and ClO_4^- by the naked eye. Furthermore, the anion binding interaction of receptor-anion was also studied using UV–vis and ^1H NMR titration which revealed that **3** displayed a remarkable binding ability for the HSO_4^- with an association constant $K_a = 6.59 \times 10^4\ M^{-1}$. And the detection limitation of HSO_4^- with the receptor **3** was 2.0×10^{-6} mol L^{-1} in aqueous solution. Most importantly, the qualitative detection of HSO_4^- using receptor **3** was attempted with test kit which was made from receptor **3**.

1. Introduction

The sensing and recognition of anions has emerged recently as a key research field within the generalized area of supramolecular chemistry for the important role placed by anions in a wide range of industrial, agricultural, biological systems and environmental problems [1–3]. Therefore, the recognition and sensing of anionic analytes has attracted considerable attention recently and as a significant goal of research programs [4–10]. In addition, hydrogensulfate anion can be found in many agricultural fertilizer, industrial raw materials and their deleterious effect as pollutants [11]. For example, hydrogensulfate anion is present in nuclear fuel waste along with other oxoanions, which eventually get into the environment. Given that the hydrogensulfate anion has a large standard Gibbs energy of hydration (-1080 kJ mol^{-1}), the recognition and separation of the hydrogensulfate anion from an aqueous media is a challenging task [12]. However, only few examples of hydrogensulfate anion recognition have been reported in recent years. In nature, the hydrogensulfate anion is recognized and transported by the hydrogensulfate-binding protein through hydrogen bonds [13]. Accordingly, the hydrogen bond complexes were widely used in design of anion sensor because a stable object hydrogen bonding complexes could be formed to use the amides [14–16], thioureas [17–19], ureas [20–23] and imidazolium [24] which regarded as the hydrogen donor to form R—H···X^- anion hydrogen bonds and the tautomeric azophenol-containing receptors. However, the detection of anions based on tautomeric azophenol-containing receptors is rarely reported in the literature, although such cation receptors which undergo azophenol to quinone-hydrazone tautomerization upon presence of cations, have been successfully shown [25–27]. Hence, there is a need for us to develop colorimetric anion receptor with anion-induced azophenol to quinone-hydrazone tautomerization as signaling mechanism.

On the other hand, in biological and environmental systems, anion-receptor interactions commonly occur in aqueous media. Therefore, much attention has been paid to develop anion sensors that work in the aqueous phase [28–32]. The challenge is that strong hydration in the aqueous phase stops the sensors from recognizing the anions. So far, only a few receptors have been synthesized that are able to recognize anions in the aqueous phase.

Herein, as one part of our research interesting in anion recognitions [26,31,33–36], we attempted to design an easy to synthesis, highly selective and sensitive sensor for HSO_4^-. Thus, the design of receptor as the chemosensor was mainly based on the fact that: (i) the receptor contains both carboxyl group and Schiff base structure as the binding sites that could recognize HSO_4^- anion selectively; (ii) in order to achieve "naked-eye" recognition, the nitrophenyl azobenzol group as the chromophore was designed. We further anticipated that compound **3** could display azophenol to quinone-hydrazone tautomerization, stimulated by anionic species in solution. Just as expected, the remarkable color change from orange to light yellow was seen during the spectral titration process.

* Corresponding author at: College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, PR China.
Tel.: +86 931 7973191; fax: +86 931 7971216.
E-mail address: weitaibao@126.com (T.-B. Wei).

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2. Experimental

2.1. Apparatus

Melting points were measured on X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. UV–visible spectra were recorded on a Shimadzu UV-2550 spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer with DMSO as solvent and TMS as an internal reference of analytical grade. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer.

2.2. Chemicals

All reagents obtained commercially for synthesis were used without further purification. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Alfa-Aesar Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using.

2.3. General method

2.3.1. General procedure for UV–vis

All the UV–vis experiments were carried out in DMSO or DMSO/H_2O binary solution on a Shimadzu UV-2550 spectrometer at 298.5 K, unless otherwise mentioned. Any changes in the UV–vis spectra of the synthesized compound were recorded on addition of tetrabutylammonium salt while keeping the ligand concentration constant in all experiments. Tetrabutylammonium salt of anions (F^-, CI^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^-), were used for the UV–vis experiments. Affinity constants of receptor **3** for anionic species were determined by non-linear fitting analyses program ORIGIN according to the equation reported by Valeur, 1:1 host–guest complexation [37].

2.3.2. General procedure for ^{1}H NMR

For ^{1}H NMR titrations, two stock solutions were prepared in DMSO-d_6 solution (TMS is used as an internal standard), one of them containing host (0.01 M) only and the second one containing an appropriate concentration (0.5 M) of guest. Aliquots of the two solutions were mixed directly in NMR tubes and ^{1}H NMR of the host–guest system was detected.

2.4. Synthesis and characterization of receptor **3**

The synthesis route of receptor molecule **3** is demonstrated in Scheme 1. Intermediate 5-(p-nitro-phenylazo)-salicylaldehyde (**1**) and 5-amino-1,3,4-thiadiazol-2-carboxylic acid (**2**) were prepared according to the literature reported [38,39]. Intermediate 5-(p-nitro-phenylazo)-salicylaldehyde (0.542 g, 0.002 mol) and 5-amino-1,3,4-thiadiazole-2-methane acid (0.290 g, 0.002 mol) were mixed in absolute ethanol solutions (20 mL) with acetic acid as a catalyst. Then, the resulting solution was stirred under refluxed conditions for 5–6 h at 79 °C, then cooled to room temperature and the solvent was removed by evaporation. Finally, the brown crude solid was purified by recrystallistaion from hot solution of DMF/H_2O and the desired pure receptor **3** was obtained in 87% yield. Mp: Intermediate 1: 186–188 °C (lit. 187–189 °C); Intermediate 2: 184–186 °C (lit. 185–187 °C); receptor **3**: 212–213 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.79 (s, 1H, COOH), 10.38 (s, 1H, OH), 8.44 (d, J = 8.8, 2H, ArH), 8.26 (s, 1H, ArH), 8.18 (m, 3H, ArH), 8.16 (m, J = 2.8, 1H, ArH) 7.25(d, 1H, CH); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 206.42, 190.20, 186.64, 183.25, 167.41, 165.94, 164.40, 155.13, 148.10, 144.76, 130.00, 125.00, 124.74, 123.22, 122.80, 118.62. ESI-MS, m/z: 398.1. Anal. Calcd. for $C_{16}H_{10}N_6O_5S$: C, 48.24; H, 2.51; N, 21.11; S, 8.04; Found: C, 48.22; H, 2.48; N, 21.14; S, 8.06.

3. Results and discussion

3.1. UV–vis spectral recognitions and colorimetric signaling

The anion binding affinity of receptor **3** was primly investigated by UV–vis spectra in the absence and presence of adding various anions such as F^-, CI^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^- using tetrabutylammonium (TBA) as a counter cation. The experiment was performed by preparing 2.0×10^{-5} mol L^{-1} solution of receptor **3** in the mixture of dimethylsulphoxide (DMSO) and thirdly distilled water with the volume ratio H_2O/DMSO (3.8:6.2, v/v). There were two characteristic absorption peaks for UV–vis spectra of receptor **3** at 488 nm and 376 nm in the absence of anions. The receptor **3** responded with dramatic color changes when particular TBA anionic salts were added to solution above respectively. Upon the addition of HSO_4^- anion, there was a prominent change that an absorption peak at 488 nm disappeared while a new and strong absorption peak at 300–450 nm appeared (Fig. 1(a)) in the corresponding UV–vis absorption spectra due to complexation between receptor **3**–HSO_4^- molecules. In addition, there appeared a dramatic color change from orange to faint yellow (Fig. 1(c)) for the solution of receptor **3** along with the addition of HSO_4^- (TBA). On the contrary, addition of other anionic species to the solution of receptor **3** (TBA) no significant modulation of color was observed in the UV–vis absorption spectra. The result shows the specificity of the chemosensor **3** for binging HSO_4^- anion was realized successfully (For interpretation of the references to color in the text, the reader is referred to the web version of the article.).

3.2. UV–vis spectral titrations

In order to estimate the specific properties for selective recognition of HSO_4^- and colorimetric changes associated with the receptor **3**, the receptor **3** toward HSO_4^- anion was studied by UV–vis absorption spectra titration experiments. The experiments were conducted using a 2.0×10^{-4} M solution of receptor **3** in aqueous solutions (H_2O/DMSO, 3.8:6.2, v/v) (Fig. 2(a)). Upon the addition of HSO_4^- (0.1 M) anion to the aqueous solution, a significant decreasing of the UV–vis absorbance at 480 nm and a new band centered at 370 nm were observed. There was an isosbestic point at 398 nm, which indicates that receptor **3** reacts with HSO_4^- anion to form a stable complex. By nonlinear least-squares fitting of the spectroscopic titration curves at λ_{max} = 480 nm for the receptor **3**, the association constant K_a of the receptor **3** toward HSO_4^- was calculated as 6.59×10^4 M^{-1} (R = 0.998). Furthermore, the lowest detection limitation of receptor **3** toward HSO_4^- was obtained according to UV–vis titration profile and was at least down to 2.0×10^{-6} mol L^{-1} in aqueous solution [33]. To know the stoichiometry between the receptor and HSO_4^- in the aqueous solution, the Job' plot (Fig. 2(b)) from which 1:1 stoichiometry was found has been drawn. Taken together, these results illustrated that receptor **3** is binding with HSO_4^- as specific chemosensor. Thus, the receptor **3** could potentially be used as an anion probe for monitoring HSO_4^- in physiological and environmental systems.

3.3. ^{1}H NMR titrations

To further elucidate the binding mode of the receptor **3** with HSO_4^-, ^{1}H NMR-titration spectra were undertaken, which illustrated the characteristic structural changes that occurred upon interaction with HSO_4^- (5.0×10^{-1} mol L^{-1}) as their TBA salts in