

A simple and efficient colorimetric anion sensor based on a thiourea group in DMSO and DMSO–water and its real-life application

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Abstract

An efficient colorimetric sensor with a thiourea moiety as binding sites and *p*-nitrophenylhydrazine as a signaling unit has been synthesized by only one single-step procedure. Selectivity for anions with the distinct geometry (tetrahedral, trigonal planar and spherical) has been investigated in dry DMSO and even in DMSO/H₂O (95:5, v/v) solutions through the naked-eye experiment, UV–vis titration and ¹H NMR titration techniques. In particular, the fluoride of toothpaste can be detected qualitatively by the sensor 1.

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1. Introduction

In the recent years, considerable interest has been attracted in selective recognition and sensing of anions species via artificial receptors [1,2], because anions play important roles in the environment (pollutant anions from over use of agricultural fertilizers cause eutrophication of lakes and inland waterways) [3], in biological systems (misregulation of anion transport is responsible for a number of medical conditions including cystic fibrosis) [4], and in the clinic (the maintenance of sulfate anion concentration in dialysis patients continues to be problematic) [5]. In particular, more and more importance is attached to colorimetric anion sensors [6,7] since the colorimetric anion sensing system would allow the so-called ‘naked-eye’ detection of anions without resorting to any spectroscopic instrumentation, being simple and convenient for detection. One successful approach for preparing chromogenic sensors involves the formation of molecular architectures, which contain one or more optical-signaling chromophoric groups that are covalently or

noncovalently linked to the receptor moiety, and thus colorimetric sensing of anions with both temporal and spatial resolution would be achieved. Hydrogen-bonding sites typically used in chromogenic or fluorogenic chemosensors are urea [8], thiourea [9], amide [10], phenol [11], or pyrrole subunits [12]. Among them, the thiourea group often chosen as anion binding sites as a functional group is a good hydrogen-bond donor and therefore results in quite stable strongly hydrogen-bonded complexes with different anions such as acetate, phosphate or fluoride. Therefore, large numbers of anion receptors containing the thiourea subunits have been designed, synthesized and tested for anion recognition and sensing during the past decades. For example, Kim et al. [7] have synthesized some receptors by integrating two *p*-nitrophenylthiourea groups into 4, 5-dimethyl-1,2-diaminobenzene, which have been proven to be efficient and colorimetric chemosensors for fluoride and acetate. However, the colorimetric change is observed upon addition of excessive equivalents of anions (65 eq. for fluoride and acetate) only in noncompetitive organic solvents. Up to now, few receptors, which can bind anions in competitive solvents such as H₂O and CH₃CH₂OH, are reported. So the challenges faced for the development of colorimetric sensors capable of anion binding within competitive media still remain.

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Recently, 4-nitro (and 2,4-dinitro) phenylhydrazine [13,14] is proven to be an optical-signaling group for anion recognition site. All these prompted us to develop a novel, sensitive and colorimetric sensor with thiourea unit as anion recognition sites and *p*-nitrophenylhydrazine unit a chromophore for color change. Sensor 1 was obtained (Fig. 1) by reacting *p*-nitrophenylhydrazine with phenylisothiocyanate as a slight red solid in 80% yield. As expected, it was sensitive to anions and showed a unique color change in the presence of F^- , CH_3COO^- and $H_2PO_4^-$. And it was more interesting that the recognition of the biologically important F^- , CH_3COO^- and $H_2PO_4^-$ anions was achieved in DMSO–water solution via hydrogen-bonding at charge-neutral sites. These results imply that the host 1 has a higher capability of competing with H_2O for anion binding, a character significant for anion receptors for practical detection of analyte of interest.

2. Experimental

2.1. Materials

All reagents for synthesis were obtained commercially and 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 Sigma–Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH_2 and then distilled in reduced pressure. And CH_3CN was dried with P_2O_5 (0.5–1:100, v/v) stirring at room temperature overnight and then distilled.

2.2. Apparatus

1H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer using tetramethylsilane (TMS) as an internal standard. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an elemental vario EL. UV–vis spectra were recorded on a Shimadzu UV2450 Spectrophotometer with a quartz cuvette (path length = 1 cm) at 298.2 ± 0.1 K.

2.3. General method

All experiments were carried out at 298.2 ± 0.1 K, unless otherwise mentioned. UV–vis spectra were measured using an ultraviolet–visible spectrophotometer, UV-2450 (Shimadzu

Corp., Kyoto, Japan). A 4.0×10^{-4} M solution of the compound 1 in DMSO was prepared and stored in the dry atmosphere. This solution was used for all spectroscopic studies after appropriate dilution. Solutions of 1.0×10^{-2} M tetrabutyl ammonium salts of the respective anions were prepared in dried and distilled DMSO and were stored under a dry atmosphere. Then, the mixture of 0.5 ml solution of the receptor 1, given amount of anions and 0.25 ml H_2O (H_2O would not be added when titrations were carried out in dry DMSO) was diluted with DMSO to 5 ml, whose absorbance was tested immediately.

1H NMR titration experiments were carried out in the DMSO- d_6 solution (TMS as an internal standard). A 1.0×10^{-2} M solution of the compound 1 in DMSO- d_6 was prepared. Then, the increased amount of acetate anion (1.0 M in DMSO- d_6) was added to the solution above-mentioned and 1H NMR of the host–guest system was tested.

Sample containing toothpaste was prepared as following [15,16]: 1 mg commercially available toothpaste (Crest brand) was added to 1 ml H_2O . After toothpaste was dissolved fully in water, the foam was filtered and 0.25 ml filtrate was added to the solution containing 2×10^{-7} mol sensor 1 and 2×10^{-6} mol tetrabutylammonium fluoride. Then the resulting solution was diluted with DMSO to 5 ml, whose absorbance was tested immediately.

2.4. Synthesis of β -N-(*p*-nitroaniliny)-phenylthiourea

The synthesis route of receptor 1 is shown in Fig. 1. *p*-Nitrophenylhydrazine (0.153 g, 1 mmol) was dissolved in dry 20 ml CH_3CN . To this solution was added phenylisothiocyanate (0.135 g, 1 mmol) dropwise slowly and stirred under inert atmosphere refluxing for 5 h. Then the reaction mixture was cooled to room temperature. Precipitate formed was filtered and washed with CH_3CN and gained 0.22 g. Yield = 80%. 1H NMR (DMSO- d_6) δ H 9.962 (s 1H), 9.922 (s 1H), 9.20 (s 1H), 8.16 (d 2H $J=8$ Hz), 7.46 (d 2H $J=8$ Hz), 7.33 (t 2H $J=13.2$ Hz), 7.17 (t 1H $J=15.2$ Hz), 6.84 (d 2H $J=8$ Hz). Elemental analysis calcd for $C_{13}H_{12}N_4O_2S$ ($M=288.068$): C, 54.15 H, 4.20 N, 19.43; found: C, 54.15; H, 4.17; N, 19.47.

3. Results and discussion

3.1. UV–vis spectral responses of 1

Compound 1 exhibited two main bands at about 372 nm and 532 nm in the UV–vis spectrum in DMSO solution. The weak

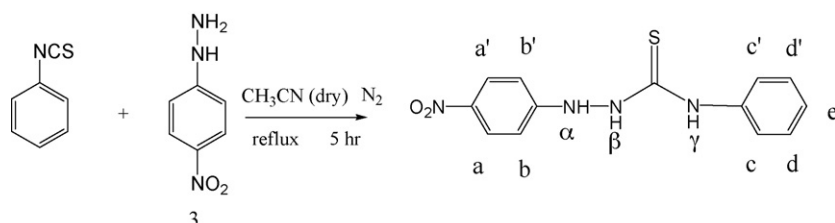


Fig. 1. Synthesis of the sensor 1.

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