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Colorimetric recognition of acetate anions in aqueous solution using charge neutral azo derivatives

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Two novel highly sensitive colorimetric acetate anion receptors: 4-phenylazo-2-hydroxy-benzaldehyde 4-nitrophenylhydrazone (**1**) and 4-phenylazo-2-hydroxy-benzaldehyde 2,4-dinitrophenylhydrazone (**2**) based on azo derivative have been designed and synthesized. UV–vis experiments show that receptor **1** and receptor **2** can selectively recognize acetate in DMSO and even in 9/1 DMSO/H_2O (v/v) mixtures. Meanwhile the color changes induced by anions can provide a way of detection by 'naked-eye'. The further insights to the nature of interactions between receptor **1**, **2** and AcO^- have been investigated by ^1H NMR titration experiments.

1. Introduction

Recently, recognition and sensing of anions have attracted considerable attention for their diversity of functions [1–9]. Among various important anionic analytes, acetate is one of the most significant species due to its specific biochemical functions. For example, acetate plays important roles in organic, environmental, biological processes, etc. In enzymes and antibodies the functions of carboxylate ascribe to their specific biochemical behavior, and make them the critical components for numerous metabolic processes [10–14]. In this regard, highly selective and easy-synthesis receptors of carboxylate anion are badly needed. According to the previous research, the phenylhydrazone-based azo receptors have been observed as an effective receptor for acetate anion in dry DMSO. Thus, unfortunately, most experimental works have to be restricted in the organic solvents which are noncompetitive toward acetate ions [15–17]. Because in protic solvents, the priority of the receptor's interaction will be given to anions with tighter H-binding, the recognition of acetate anions in aqueous solution remains a challenging work.

Significant interest has been inspired by the demanding of developing artificial optical receptors for the selective anion recognition. Meanwhile, a great deal of research on developing colorimetric [18,19] and fluorescent [20,21] receptors has been done.

Recently, colorimetric-based sensing is especially attractive, for it allows naked-eye detection of the analyte without resort to any expensive equipment [22]. In general, these chemoreceptors play the role through a receptor-chromophore general binomial, based on electron-donor–acceptor interaction and possessing a push–pull character [23]. The interaction of a special anion substrate with receptor sites could affect the optical signals emitted by chromophore and lead to the color variation of the system [22]. Among various kinds of interactions, H-bond interaction is more useful and effective than electrostatic interaction. The moieties such as amides [24,25], ureas [26], thioureas [27,28] and other positively charged groups [29,30] have been widely used in recognizing anions via forming H-bond.

However, the research of anion receptors is faced with a host of difficulties. Above all, the design and synthesis of an artificial receptor which possesses high binding affinity for certain anion still present a great challenge in supermolecule chemistry, because the orientation structure of selective anionic chemoreceptors has to match that of anions which exhibits such a wide range of geometries [31–33]. Secondly, as a good receptor, it is not enough to possess only a single interaction site, because the needed selectivity and sensitivity call for relatively strong and directional bonding forces, which is hard to offer simultaneously in aqueous solution. Anyway, hydrogen bonding only could not make compounds efficient receptors for the anions in aqueous solution because of the fierce competition between the protic solvent and the receptor. Besides, the neutral receptors for anions are typically soluble in organic solvent instead of in aqua, which also limits the recognition in aqueous solution.

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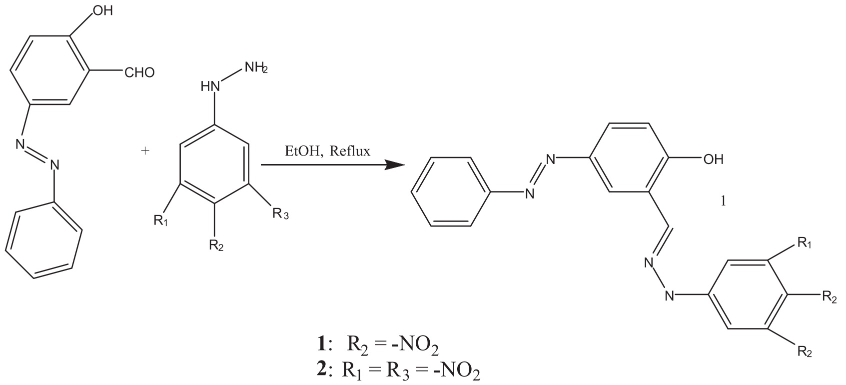


1: R_2 = -NO_2
2: $R_1 = R_3$ = -NO_2

Scheme 1. General synthetic routes to the target receptor **1**.

As a result, many types of interaction and their combination are being taken into account. One of these we considering are the multiple binding sites involving several different binding groups in certain positions. For example, we link the groups (providing the H-bond and the electrostatic interaction) together, to meet the requirements of anions' special geometry, so as to improve the sensitivity and selectivity of the anion receptors in aqueous solution. Among anion receptors, the azo anion receptors, with multiple binding sites, are especially attractive to us.

In this paper, we designed and synthesized two novel carboxylate anion receptors **1**, **2** that include both the hydrogen-bond-donor group (phenylhydrazone) and colorimetric group (azo). Their recognition behaviors are studied by UV–vis spectrum in dry DMSO and in aqueous solution DMSO/H_2O (9/1), and the sensing processes can be seen by naked-eyes due to the quickly obvious color response shown. Experimentally, we found that these two receptors present higher selectivity to AcO^- than other anions investigated in experiment. The nature of interactions between receptor **1**, **2** and AcO^- were investigated by ^{1}H NMR titration experiments. Besides, changing the number of their "–NO_2" group does not make much impact on their recognition behaviors.

2. Experiments

2.1. Materials

All reagents for synthesis obtained commercially 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.

2.2. Apparatus

^{1}H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer. C, H, N elemental analyses were made on an elementar varuo EL. UV–vis spectra were recorded on a Shimadzu UV-2450 Spectrophotometer with a quartz cuvette (path length = 1 cm) at 298.2 ± 0.1 K and the width of the slits used is 10 nm.

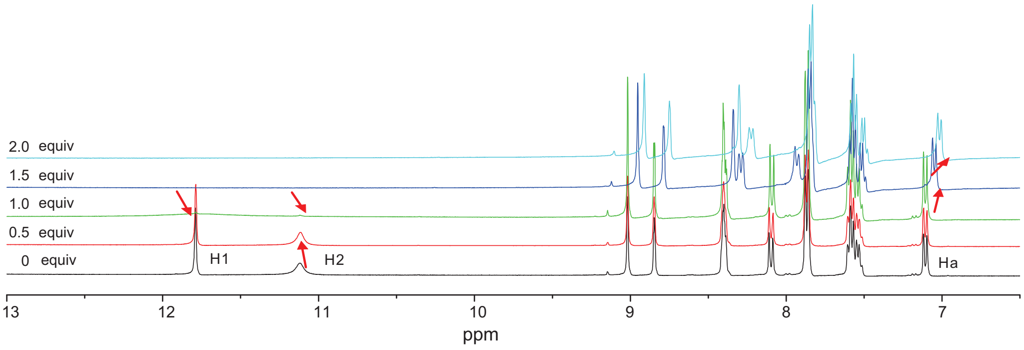
2.3. General method

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 5.0×10^{-4} M solution of the receptor **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^{-3} M tetrabutylammonium salts of the respective anions were prepared in dried and distilled DMSO and were stored under a dry atmosphere.

^{1}H NMR titration experiments were carried out in the DMSO-d_6 solution (TMS as an internal standard). A 0.01 M solution of the receptor **1** in the 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 ^{1}H NMR of the receptor–guest system was tested.

2.3.1. Synthesis of 4-phenylazo-2-hydroxy-benzaldehyde 4-nitrophenylhydrazone

The structures and synthesis of receptor **1** are shown in Scheme 1. 0.226 g 4-phenylazo-2-hydroxy benzaldehyde (1 mmol), 0.153 g *p*-nitrophenylhydrazine (1 mmol) and four drops of acetic acid were dissolved in 60 mL CH_3CH_2OH and then the resulting solution was heated and refluxed 2 h (see Scheme 1). The



Scheme 2. The proposed **1**–guest binding mode in solution.