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Synthesis and evaluation of simple naked-eye colorimetric chemosensors for anions based on azo dye-thiosemicarbazones

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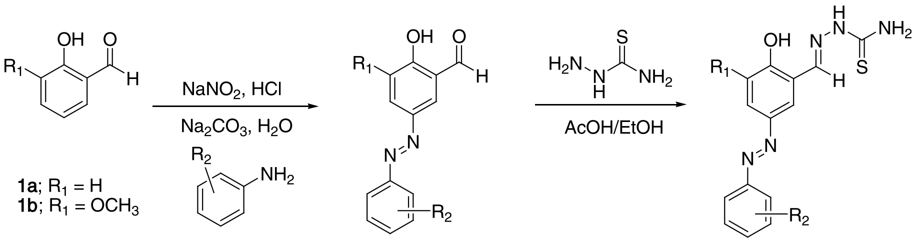
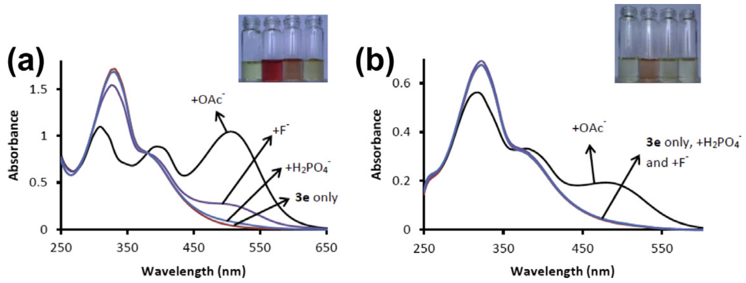
HIGHLIGHTS

- New azo dye-thiosemicarbazone derivatives were synthesized for anion sensor evaluation.
- It is a very good naked eye detection sensor.
- The sensor has detection limit of 0.71 μM for acetate.

GRAPHICAL ABSTRACT





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ABSTRACT

A series of novel, highly selective azo dye-thiosemicarbazones based anion sensors (**3e**–**f**) have been synthesized from the condensation reaction between thiosemicarbazide and six different azo salicylaldehydes. The structure of the sensors was confirmed by spectroscopic methods. The selectivity and sensitivity in the recognition for acetate anion over other anions such as fluoride, chloride, iodide and dihydrogenphosphate anions were determined by naked-eyes and UV–vis spectra. The color of the solution containing sensor had an obvious change from light yellow to orange only after the addition of acetate anion in aqueous solution (water/dimethylsulfoxide, 7:3, v/v) while other anions did not cause obvious color change. The anion recognition property of the receptor via proton-transfer is monitored by UV–vis titration and ^{1}H NMR spectroscopy. Under condition in aqueous solution of sensor **3e** (water/dimethylsulfoxide, 7:3, v/v), linearity range for the quantification of acetate anion was 1–22 μM and limit of detection (LOD) of acetate anion was 0.71 μM.

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Introduction

It is well known that azo colorants are the most versatile class of dyes [1]. While compounds with a thiosemicarbazone structure and their transition metal complexes have a wide range of biological activities, some of them are antiviral [2], antifungal [3], antibacterial [4], antitumor [5], antioxidant [6], analgesic and anti-inflammatory properties [7]. Such thiosemicarbazones have been reported to be useful as chemosensors [8]. The design of host molecules that can recognize and sense anions selectively through visible has received considerable interest in recent years because of the important roles played by the anions in biological, industrial, and environmental processes [9]. In biological and environmental systems, anion–sensor interactions commonly occur in aqueous solution, therefore, much attention has been paid to developing anion sensors that work in the aqueous phase [10]. It is still a challenge to design the anion sensors with high selectivity and sensitivity in a competitive media. As a subset of the anion receptor, the chromogenic anion sensors have shown unique merit, because they can reveal the host-anion binding information through a change of color [11]. Generally colorimetric chemosensor is made up of two main fragments, which involve the binding sites that interact with anions either electrostatically or through hydrogen bonding and the signal parts that connect to the binding sites either directly or intramolecularly linked which show the color changes in the anion recognition procession [12].

The sensors based on colorimetric determination of anions are still challenges for investigators and they attract much interest. In particular, to develop the naked-eye detection technique for the analytes without using any expensive equipment is of great interest in recent years.

In this paper, we designed and synthesized new and simple anion receptors **3a**–**f** containing both azo dye and thiosemicarbazone unit and studied their anion recognition behaviors. In addition, the sensing processes can be realized by the 'naked-eye' determination as it has a remarkable color response.

Experiment

General

All solvents and reagents were purchased from commercial sources and used as received. IR spectra were recorded on Perkin Elmer SPECTRUM GX, FT-IR spectrophotometer. Spectra were recorded as pressed KBr disc. The ^1H and ^{13}C NMR spectra were measured with a Bruker AVANCE 400 spectrometer operating at 400 and 100 MHz, respectively. The chemical shifts (δ) are reported in ppm, and coupling constants (J) are given in Hz. The spectra were taken in CD_3SOCD_3 and the residual solvent signal of CH_3SOCH_3 at δ 2.50 and 39.5 was used as reference for ^1H and ^{13}C NMR spectra. The HRMS mass spectra were recorded on micrOTOF spectrometer.

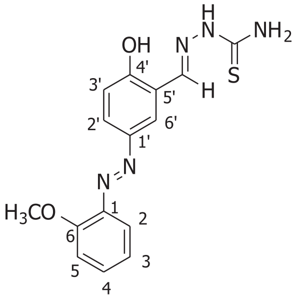
Synthesis

*General procedure for sensors **3a**–**f** synthesis*

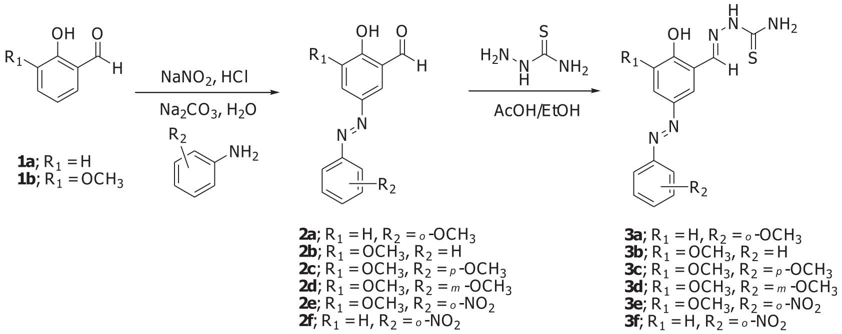
*Synthesis derivatives of azo aromatic aldehyde **2a**–**f**.* The structures of synthesized azo aromatic aldehyde are shown in Scheme 1. A 0 °C solution I of aniline derivatives (10 mmol) in deionized (DI) water (10 mL) and HCl (2 mL) was prepared. A 0 °C solution II of $NaNO_2$ (15 mmol) in DI water (5 mL) was dropwised into the solution I. The mixture was stirred for 10 min. A solution of Na_2CO_3 (30 mmol) in DI water (30 mL) at 0 °C was added aldehyde derivatives **1a** or **1b** (10 mmol). The solution of aldehyde derivatives and Na_2CO_3 was dropwised into the mixture solution of I and II and then the solution was stirred 2 h in cool bath. The reaction was adjusted the pH to 7 by adding the solution of HCl. The precipitated products **2a**–**f** were filtered and heated in the oven.

*Synthesis derivatives of thiosemicarbazone **3a**–**f**.* Thiosemicarbazone (1 mmol) was added into the solution of azo aromatic aldehydes **2a**–**f** (1 mmol) in ethanol (10 mL) and acetic acid (10 drops). The reaction was stirred and refluxed for 6–7 h. After heating, the precipitated products **3a**–**f** were filtered and heated in the oven.

*Sensor **3a***



Yield: 99.91%, m.p. = 197–210 °C. IR (KBr, cm^{-1}); 3432, 3256, 3162, 1602, 1514, 1559, 1107, 762. ^1H NMR (d_6-DMSO,



Scheme 1. Synthetic procedures for sensors **3a**–**3f**.