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'Naked-eye' detection of fluoride and acetate anions by using simple and efficient urea and thiourea based colorimetric sensors

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HIGHLIGHTS

- Novel urea and thiourea-based on colorimetric sensors were synthesized.
- These sensors were characterized with ^{1}H, ^{13}C, APT, COSY NMR, FTIR, elemental, UV–vis data.
- It was found that the receptors are highly selective toward fluoride and acetate anions.

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ABSTRACT

Simple and efficient sensors 1 and 2 possessing azo and nitrophenyl as signaling units and urea and thiourea moieties as binding sites were designed and synthesized. These sensors were characterized by combination of ^{1}H, ^{13}C, APT, COSY NMR, FTIR, elemental analysis, and UV–vis spectral data. The interaction and colorimetric sensing properties of receptor 1 and 2 with different anions were investigated by the naked eye, as well as UV–visible and ^{1}H NMR experiments. It was found that the receptor 1 and 2 are highly selective toward fluoride and acetate anions in $CHCl_3$.

1. Introduction

The selective recognition and sensing of anions via artificial organic chemosensor molecule/probe, containing a suitable receptor site, have attracted considerable attention for chemists in past decades [1]. Anions play significant roles in chemical, environmental and biochemical processes [2–8], hence their recognition is important. The development of simple receptors capable of recognizing biologically relevant anions such as fluoride, chloride, phosphate, and carboxylate has attracted considerable interest [9]. The design of these receptors has focused on the ability to recognize and sense selectively biologically important anions through naked eye, electrochemical and optical responses [10]. The incorporation of fluorescent chromophores into receptors has gained considerable attention owing to their high sensitivities and easy detection [11]. The investigation of anion-selective receptors based on colored chromophores is also studied [12]. In particular, the development of colorimetric anion sensing is important and useful since it allows so-called 'naked-eye' detection of anions without the use of any spectroscopic instrumentation. Such receptors would be more valuable if they could be obtained by a simple synthetic method [13].

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 used in chromogenic or fluorogenic chemosensors are urea [14,15], thiourea [16], amide [17], phenol [18], or pyrrole subunits [19]. The large numbers of anion receptors containing these subunits have been designed, synthesized and tested for anion recognition and sensing during the past decades. For example, Liu and coworkers reported synthesis of a simple and efficient chemosensor containing naphthalene signal moiety and thiourea recognition and that this sensor has proven to be highly selective for fluoride and show a remarkable color change and fluorescence quenching [20]. A novel colorimetric and fluorescent sensor possessing fluorenone and naphthalene moieties as signaling groups for fluoride and pyrophosphate anions was prepared by Thangadurai and coworkers [21].

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Herein, we have designed a new class of urea and thiourea-based receptors 1 and 2 containing azophenol–imine platform and investigated their anion sensing properties towards F^-, Br^-, Cl^-, I^-, AcO^-, ClO_4^-, NO_3^-, HSO_4^-, and $H_2PO_4^-$ anions. The spectroscopic data showed that receptor 1 and 2 are selective colorimetric sensor for fluoride and acetate anions in $CHCl_3$.

2. Experimental

2.1. General

NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer in d_6-DMSO and $CDCl_3$. FT-IR spectra were obtained on a Perkin Elmer Spectrum 100 FTIR spectrometer. UV/Vis spectra were measured with a Perkin Elmer Lambda 25 spectrometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 Mesh). All reactions, unless otherwise noted, were conducted under nitrogen atmosphere. All starting materials and reagents were of standard analytical grade from Fluka, Merck, and Aldrich and used without further purification.

2.2. Synthesis

2.2.1. Synthesis of 5-(4-nitro-phenylazo)-salicylaldehyde (S1)

Synthesis of S1 was carried out according to known procedure [22] For this, to a solution of 4-nitroaniline (3.5 g, 0.025 mol) in water (2 mL) was slowly added 3 ml of 37% aq HCl solution at 0–5 °C. 10 ml of 20% aq $NaNO_2$ solution was added to this mixture and the resulting solution was stirred for 1 h, affording a yellow solution. Salicylaldehyde (2.5 ml, 0.025 mmol) was dissolved in a solution comprising 9 g Na_2CO_3 and 75 ml H_2O and the resulting solution of salicylaldehyde was added dropwise to the bright yellow colored solution over 1 h. After stirring for 4 h, the reaction mixture was neutralized with HCl, the brown crude solid was filtered and recrystallized from ethanol to afford a pure yellow product. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 1H, J = 8.8 Hz, ArH), 8.02 (d, 2H, J = 8.9 Hz, ArH), 8.11 and 8.14 (dd, 1H, J = 2.3 Hz, J = 8.8 Hz, ArH), 8.34 (d, 1H, J = 2.3 Hz, ArH), 8.37 (d, 2H, J = 8.9 Hz, ArH), 10.30 (s, 1H, CHO).

2.2.2. Synthesis of the receptors 1 and 2

To a solution of S1 (0.2 g, 0.74 mmol) in EtOH (20 mL) was added a solution of 4-phenylsemicarbazide or 4-phenylthiosemicarbazide (0.74 mmol) and a catalytic amount of *p*-toluenesulphonic acid in dry EtOH (10 mL). The mixture was refluxed for 24 h under nitrogen. The product, which was precipitated during stirring, was filtered off, washed with ethanol and dried in vacuo.

Receptor 1; Orange solid, Yield: 85%; Mp = 252-254 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.00 (t, 1H, J = 7.4 Hz, ArH), 7.08 (d, 1H, J = 8.8 Hz, ArH), 7.28 (t, 2H, J = 7.4 Hz, ArH), 7.62 (d, 2H, J = 7.6 Hz, ArH), 7.83 and 7.85 (dd, 1H, J = 2.5 Hz, J = 8.8 Hz, ArH), 8.02 (d, 2H, J = 8.9 Hz, ArH), 8.32 (s, 1H, ArH), 8.40 (d, 2H, J = 8.9 Hz, ArH), 8.66 (d, 1H, J = 2.5 Hz, CHN), 9.01 (s, 1H, NH), 10.74 (s, 1H, NH), 11.25 (br s, 1H, OH). ^{13}C NMR (100 MHz, d_6-DMSO): δ 160.68, 155.85, 153.42, 148.34, 145.90, 139.52, 137.36, 128.87, 125.65, 125.55, 123.71, 123.56, 122.97, 121.90, 120.55, 117.46; Anal. Calcd. for $C_{20}H_{16}N_6O_4$ (404.38): C, 59.40; H, 3.99; N, 20.78. Found: C, 59.67; H, 4.05; N, 20.82.

Receptor 2; Orange solid, Yield: 86%; Mp = 235–237 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.07 (d, 1H, J = 8.8 Hz, ArH), 7.19 (t, 1H, J = 7.4 Hz, ArH), 7.36 (t, 2H, J = 7.4 Hz, ArH), 7.52 (d, 2H, J = 7.6 Hz, ArH), 7.82 and 7.84 (dd, 1H, J = 2.5 Hz, J = 8.8 Hz, ArH), 7.98 (d, 2H, J = 9.1 Hz, ArH), 8.37 (d, 2H, J = 9.1 Hz, ArH), 8.54 (s, 1H, ArH), 8.81 (d, 1H, J = 2.2 Hz, CHN), 10.22 (s, 1H, NH), 11.19 (br s, 1H, OH), 11.86 (s, 1H, NH). ^{13}C NMR (100 MHz, d_6-DMSO): δ 176.53, 161.17, 155.82, 148.29, 145.96, 139.60, 138.90, 128.49, 126.81, 126.77, 125.88, 125.49, 123.52, 123.33, 121.71, 117.52; Anal. Calcd. for $C_{20}H_{16}N_6O_3S$ (420.44): C, 57.13; H, 3.84; N, 19.99. Found: C, 57.25; H, 3.91; N, 20.02.

2.3. UV–vis experiments

The solutions of the receptor 1 and 2 (4.0×10^{-5} M) and the guest anions (2.0×10^{-3} M) were prepared in $CHCl_3$. The volume of the receptor 1 and 2 solutions used in the UV–vis measurements was 3 mL. Absorption spectra were recorded by adding different amounts of anion solution to the receptor 1 and 2 solutions. The colorimetric studies of 1 and 2 towards various anions can be easily observed by the naked eye in $CHCl_3$ at concentration of 4.0×10^{-5} M.

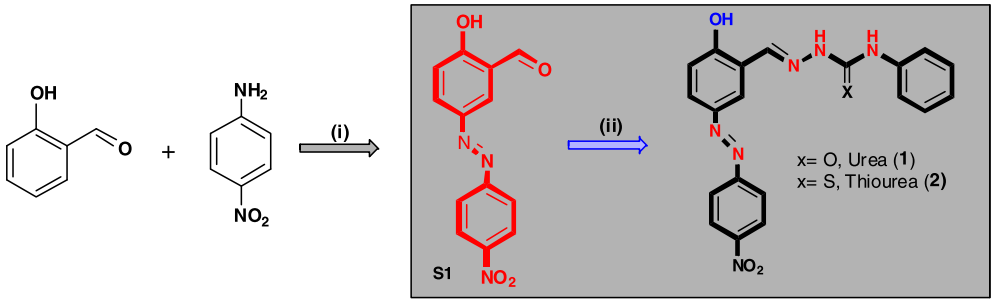
2.4. ^{1}H NMR experiments

^{1}H NMR titrations were performed on a Varian 400 MHz spectrometer at 298 K. The solution of the receptors 1 and 2 (0.0255 M in d_6-DMSO) was titrated by adding known quantities of concentrated solution of tetrabutylammonium fluoride and acetate (0.02 M). The chemical shift changes of the receptors 1 and 2 were monitored. All titrations were repeated at least twice to get the consistent values.

3. Result and discussion

3.1. Synthesis of novel receptors

As can be seen in Scheme 1, the receptors 1 and 2 were obtained in 85% and 86% yields, respectively by reacting 5-(4-nitro-phenylazo)-salicylaldehyde S1 with 4-phenylsemicarbazide or 4-phenylthiosemicarbazide in dry EtOH. Their molecular structures and purities were established from spectroscopic studies including ^{1}H



Scheme 1. Synthesis of the receptors 1 and 2; Reagents and conditions: (i) Na_2CO_3, $NaNO_2$/HCl, H_2O, 0–5 °C; 90%; (ii) 4-phenylsemicarbazide or 4-phenylthiosemicarbazide, EtOH.