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Experimental and theoretical study of urea and thiourea based new colorimetric chemosensor for fluoride and acetate ions

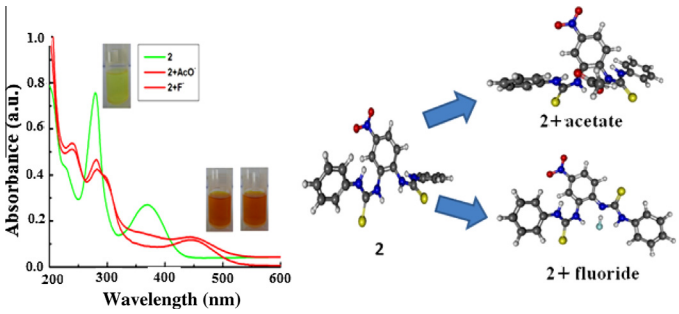
Eramoni Saikia, Manash Protim Borpuzari, Bolin Chetia *, Rahul Kar *

Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India

HIGHLIGHTS

- Two new anion receptors have been reported here.
- Anion recognition was done by naked eye, ^{1}H-NMR and UV visible spectroscopy.
- Theoretical study was performed to know the relative binding mode between receptor and anions.
- Time dependent DFT (TD-DFT) calculations qualitatively match the experimental UV–Vis spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new anion receptors 1,1-(4-nitro-1,2-phenylene) bis(3-phenylurea) (**1**) and 1,1-(4-nitro-1,2-phenylene) bis(3-phenylthiourea) (**2**) have been reported here. The binding and colorimetric sensing properties of receptors **1** and **2** with different anions were investigated by naked-eye, ^{1}H-NMR and UV–Vis spectroscopy. They showed effective and selective binding with two biologically important anions F^- and CH_3COO^-, in presence of other anions, such as Cl^-, Br^-, I^-, NO_2^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, N_3^-, CN^- in acetonitrile. The relative binding mode of fluoride and acetate anions towards receptors **1** and **2** were studied using density functional theory (DFT), in gas phase and in acetonitrile solvent. Computational studies revealed that receptor **1** formed complexes by two intermolecular hydrogen bonds while receptor **2** by three intermolecular hydrogen bonds. In addition, time dependent DFT (TD-DFT) calculations qualitatively match the experimental UV–Vis spectra.

1. Introduction

In many chemical and biochemical phenomena, one of the key process is anion binding. Indeed, more than 70% of co-factors and substrate in biology are anionic in nature, and they play a vital role in enzymes activity, hormones transportation, protein synthesis and DNA regulation along with various chemical and environmental processes [1]. Thus, the design and synthesis of simple receptors that bind anions specifically is the subject of forceful chemical research, in recent years, in the field of supramolecular chemistry [2]. Following the approach of the covalent attachment of signaling subunits viz. p-nitrophenyl [3], o-phenylenediamine [4], anthraquinones [5], acridone [6], calix[4]arenes [7], naphthalimide [8], benzophenone [9], anthracene [10], and ions binding sites, many neutral chemical sensors have been synthesized. In particular, neutral receptors for anions, such as ureas [11], thioureas [12], pyrroles [13], amides [14], benzimidazole [15], most of them contain highly polarized —NH fragments at the binding site, act as a hydrogen bond donor. Contrary to the merely electrostatic interactions, directional H-bonding interactions of such receptors allow to

* Corresponding authors.
E-mail addresses: bolinchetia@dibru.ac.in (B. Chetia), rahul.kar.dib@gmail.com (R. Kar).

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differentiate between anions with different geometries and hydrogen-bonding requirements. Furthermore, selectivity can be enhanced by polarizing the —NH fragment through the insertion of the electron-withdrawing substituent onto the molecular framework, which increases its H-bond donor tendencies. As an extreme polarization, deprotonation may occur from the receptor. This may lead to a substantial delocalization of negative charge, usually a large red shift, and resulting in drastic color change which helps in naked-eye detection of the anion [16]. Therefore, it could open various possibilities of developing anion receptors by fine tuning of polarity of the —NH fragment with the help of naked-eye detection.

With these ideas in mind, we have designed two new simple bis-urea (**1**) and bis-thiourea (**2**) based anion receptors, having a $—NO_2$ group to the ortho-phenylenediamine moiety, to enhance both hydrogen-bond donor tendency and acidity. Thus, anion binding properties of the receptors **1** and **2** were investigated by UV–Visible spectroscopy, ^{1}H-NMR titration and naked-eye detection experiment. In addition, we have performed theoretical studies to understand the receptor–anion interaction at the molecular level which may provide additional information, as reported in some recent publications [17]. We utilized the density functional theory (DFT) to study the binding mode of the receptors towards fluoride and acetate in the presence of acetonitrile solvent. Such studies unrevealed valuable insights into the structures of the receptor–anion complexes and their UV–Vis spectra.

2. Experimental

2.1. General

All general chemicals and reagents were purchased from Merck-India Chemical Company and some from Sigma–Aldrich. All chemicals used were of analytical grade. Solvents used for spectroscopic studies were of spectroscopic grade. FT-IR spectra were recorded as KBr pellets on a Shimadzu IR- Prestige-21 FT-IR spectrophotometer operating from 400 to 4000 cm^{-1}. Electronic absorption spectra were obtained with Shimadzu UV-1700 UV–Vis spectrophotometer at room temperature.

2.2. General procedure for the synthesis of receptors *1* and *2*

A phenylisocyanate or phenylisothiocyanate (0.35 g, 2.58 mmol) solution was added to a stirred solution of 4-nitro-1, 2-phenylenediamine (0.2 g, 1.3 mmol) in dry THF (15 mL) at room temperature. The reaction mixture was refluxed for 4 h with continuous stirring. After completion of reaction, precipitate was filtered, washed several times with dry THF to give **1** and **2** as light brown and yellow powder respectively.

1,1-(4-Nitro-1,2-phenylene) bis(3-phenylurea) (**1**): Yield: 80%.

IR (KBr): υ_{max}/cm^{-1} 3361 (—NH), 1635 (C=O), 1554, 1438, 1306, 1227, 747.

^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 12.47 (s, 2H, NH), 8.59 (s, 2H, NH), 8.07 (d, 1H), 7.87 (s, 1H), 7.45 (d, 1H), 7.31 (m, 6H), 7.10 (t, 4H). ^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm): 171.4, 142.0, 138.9, 136.7, 131.9, 127.6, 124.1, 123.5, 118.6, 109.0, 104.5 MS for $C_{20}H_{17}N_5O_4$: 391.13.

1,1-(4-Nitro-1,2-phenylene) bis(3-phenylthiourea) (**2**): Yield: 85%.

FT-IR (KBr): υ_{max}/cm^{-1} 3543 (—NH), 1632, 1444, 1379, 1039, 752.

^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 13.12 (s, 2H, NH), 9.79 (s, 2H, NH), 8.27 (d, 1H), 8.12 (s, 1H), 7.90 (d, 1H), 7.51 (m, 6H), 7.20 (t, 4H). ^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm): 172.2, 143.0, 139.9, 137.8, 132.7, 128.8, 124.8, 124.1, 119.4, 109.7, 105.1 MS for $C_{20}H_{17}N_5O_2S_2$: 423.08.

3. Results and discussions

3.1. Synthesis

Receptors **1** and **2** were synthesized by following a general procedure of coupling 4-nitro-1,2-phenylenediamine with phenylisocyanate and phenylisothiocyanate, respectively, in presence of dry THF as a solvent (see Supporting information S1). Finally, the receptors were characterized using ^{1}H NMR, ^{13}C NMR, mass and FT-IR spectral data.

3.2. Naked-eye detection experiment

Host–guest interactions of the receptors **1** and **2** with various anions were studied using naked-eye detection experiment. This was carried out in acetonitrile solvent by addition of corresponding anions to solution of receptors **1** and **2**. The addition of 1 equivalent of tetrabutylammonium fluoride and acetate anions into 2 μM solution of receptor **1** in acetonitrile resulted in a color change i.e., from colorless to light yellow, as shown in the Fig. 1(a). However, the addition of 1 equivalent of fluoride and acetate anions to 2 μM solution of receptor **2** in acetonitrile produced a red color, as shown in Fig. 1(b). On the other hand, addition of Cl^-, Br^-, I^-, NO_2^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, N_3^-, CN^- anions did not give any noticeable color change except a very light color change was observed upon addition of chloride with receptor **1**. So, both receptors **1** and **2** can be used for the visual detection of fluoride and acetate ions at very low concentration.

3.3. UV–Visible titration experiment

The UV–Vis titration experiment was carried out by concomitant addition of various anions, in the form of tetrabutylammonium salts (TBAX) ($[Bu_4N]^+X^-$; X^-=F^-, Cl^-, Br^-, I^-, CH_3COO^-, NO_2^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, N_3^-, CN^-), to a 2 μM acetonitrile solutions of receptors **1** and **2**. The optical changes were evaluated by

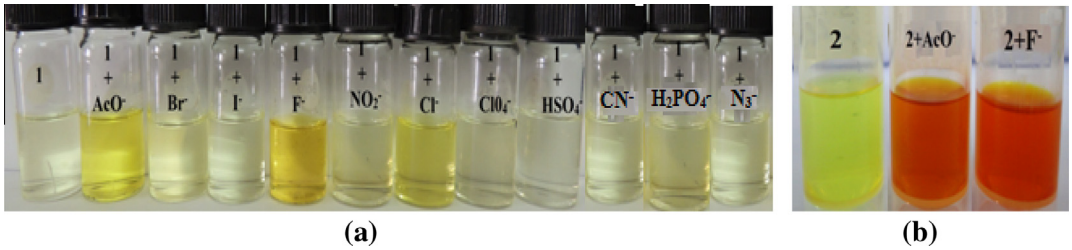

Fig. 1. Color changes observed: (a) receptor **1** on addition of various anions with a visible color change with fluoride and acetate only (b) receptor **2** on addition of fluoride and acetate respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)