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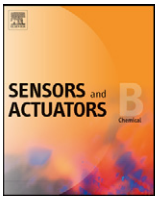

Dual responsive chemosensors for anion and cation: Synthesis and studies of selective chemosensor for F⁻ and Cu(II) ions

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ABSTRACT

New colorimetric chemosensors, 1-[2-{(4-nitrobenzylidene)amino}phenyl]-3-phenylthiourea (**1**), 1-[2-{(2-hydroxy-5-nitrobenzylidene)amino}phenyl]-3-phenyl thiourea (**2**) have been synthesized and characterized by spectroscopic techniques and XRD. The molecular structure of receptor **1** was determined by X-ray crystallography and it has the triclinic space group P_1 with cell parameters $a = 7.2705$ Å (6), $b = 11.0178$ Å (9) $c = 12.0137$ (9) Å and $Z = 2$. Anion binding studies carried out using ^{1}H NMR and UV–visible spectrophotometric titrations revealed that these receptors exhibit selective recognition towards F^- over other halide anions. The selectivity for F^- among the halides is attributed mainly to the hydrogen-bond interaction of the receptor with F^-. Receptors **1** and **2** (5×10^{-5} M) show color change from colorless to brown and yellow respectively in the presence of tetrabutylammonium fluoride (TBAF, 5×10^{-3} M). Moreover, F^--induced color changes remain the same even in the presence of large excess of Cl^-, Br^-, and I^-. Chromogenic receptors **1** and **2** undergo distinct color changes from colorless to violet (**1**) or bluish green (**2**) on gradual addition of Cu(II) and can be used as colorimetric probes for spectrophotometric and visual analysis of Cu(II) in the presence of other transition metal ions such as Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. The binding constant for **2** was found to be higher than that for **1** towards F^- and Cu(II) ion and this may be due to presence of OH group in **2**, which offers extra binding site.

1. Introduction

The development of new molecular systems for the colorimetric detection of anions [1–11], cations [12–21], or neutral molecules [22–27] have gained prime importance due to their significance in biological and environmental processes. Currently, there is an active effort to develop molecular complexation systems that simultaneously bind both the cation and the anion. Generally, pyrrole, -OH, -NH_2, urea, thiourea, -CONH centers act as binding sites for both anions [28–30] and cations [31–34]. In particular, the sensing of fluoride ion has attracted growing attention [35–37], because of its great potential for biological and industrial applications [38,39]. During recent years, there is an upsurge in the field of colorimetric sensing of alkali, alkaline-earth and transition metal ions by organic molecules [40–42]. Among the cations, special attention is devoted to develop chemosensors for transition metal ions: usually they address an environmental concern when present in uncontrolled amount but at the same time some of them like iron, cobalt, copper and zinc are present as essential elements in biological system. On the other hand, over accumulations of copper produce severe or lethal intoxications [43]. Thiourea receptors form effective hydrogen bond interaction with fluoride ions [44] and its derivatives have long history as ligands in coordination to a metal via either sulphur or nitrogen [45–48]. In continuation of our work [49–51], here in we report the synthesis of the receptors **1** and **2** having 4-nitrophenyl substituents and these were appended for two main reasons. (i) Presence of electron withdrawing NO_2 substituents is expected to enhance the acidity and, consequently, the H-bond donor properties of the receptor. (ii) The optical properties of the chromogenic nitrophenyl fragment may be altered following receptor–anion interaction, thus providing colorimetric and spectral sensing of the recognition event. The receptors **1** and **2** allow not only for the selective and sensitive colorimetric detection of F^- in presence of other halide ions and Cu(II) ions in presence of other transition metal ions.

2. Experimental

2.1. Chemicals

All the solvents $CHCl_3$, CH_3CN and DMSO were used as HPLC grade and purchased from Qualigens (Mumbai, India). Tetrabutylammonium salts of halides were purchased from Aldrich chemicals (Mumbai, India).

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2.2. Experimental

The ^1H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer in DMSO-d_6. The IR spectra were recorded on a Perkin-Elmer FT-IR LX-185256 spectrometer. UV–visible experiments were performed on a Perkin-Elmer FT UV–visible λ-35 spectrometer. Elemental analysis of the receptors was obtained in Heraeus CHN rapid analyzer. The EI mass spectra were recorded using JEOL DX 303 mass spectrometer. The crystal data were collected on a BRUKER SMART APEX CCD DIFFRACTOMER equipped with a fine-focus sealed tube employing graphite monochromatised Mo k_α radiation using ω scan mode. The structures were solved using SHELXS-97 and the model was refined using SHELXL-97.

2.3. UV–visible spectroscopic methods

All solutions of receptors **1** and **2** (5×10^{-5} M) were made up with HPLC grade CH_3CN solvent. UV–visible absorption titrations were carried by adding 10 μl aliquots of the titrant as tetrabutylammonium salts (5×10^{-3} M) and cations as its perchlorate salts (5×10^{-3} M). The UV–visible spectra were recorded after each addition.

2.4. Synthesis of receptors [52]

2.4.1. Synthesis of 1-[2-{(4-nitrobenzylidene)amino}phenyl]-3-phenylthiourea

The receptor **1** was synthesized by Schiff base condensation between 1-(2-aminophenyl)-3-phenylthiourea [53] and 4-nitrobenzaldehyde. To the solution of 1-(2-aminophenyl)-3-phenylthiourea (0.3 g, 1.2 mmol) in methanol (25 ml), 4-nitrobenzaldehyde (0.186 g, 1.2 mmol) in methanol (25 ml) was added under stirring. The resulting mixture was refluxed for 3 h and cooled to room temperature. The solid product was collected by filtration and washed with cold methanol. The microcrystalline compound was recrystallized from hot chloroform; yellow colored crystals suitable for XRD were obtained on slow evaporation (Scheme 1).

Yield: 0.31 g (70.5%) m.p.: 203 °C. Elemental analysis: $C_{20}H_{16}N_4O_2S$ Calcd. (%): C, 63.81; H, 4.28; N, 14.88. Found (%): C, 63.85; H, 4.29; N, 14.86, EI Mass (m/z): 377 $(M+1)^+$; IR (KBr, ν cm^{-1}): 3266 (NH), 1585 (C = N), 1452 (NO_2), 1336 (C = S). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 9.34 (1H, s), δ 9.07 (2H, d, J = 8 Hz), δ 9.03 (2H, d, J = 7.8 Hz), δ 8.55 (1H, s), δ 8.21 (1H, d, J = 7.6 Hz) δ 8.17 (1H, d, J = 7.2 Hz), δ 7.87 (1H, s), 7.5–7.1 (7H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 122.3, 123.7, 124.5, 125.3, 126.6, 127.3, 128, 128.8, 129.9, 132.9, 150, 150.7, 163.7.

2.4.2. Synthesis of 1-[2-{(2-hydroxy-5-nitrobenzylidene)amino} phenyl]-3-phenyl thiourea

The receptor 2 was synthesized by the method as described above from 1-(2-aminophenyl)-3-phenylthiourea (0.3 g, 1.2 mmol) and 5-nitrosalicylaldehyde (0.206 g, 1.2 mmol).

Yield: 0.33 g (71.2%) m.p.: 162 °C. Elemental analysis: $C_{20}H_{16}N_4O_3S$ Calcd. (%): C, 61.21; H, 4.11; N, 14.28. Found (%): C, 61.20; H, 4.13; N, 14.27, EI Mass (m/z): 393 $(M+1)^+$; IR (KBr, ν cm^{-1}): 3436 (OH), 3348 (NH), 1617 (C = N), 1483 (NO_2), 1332 (C = S). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 13.6 (1H, s), δ 8.6 (1H, s), δ 8.39 (1H, s), δ 8.3 (1H, d, J = 8.3 Hz), δ 8.2 (1H, d, J = 7.5 Hz), δ 7.86 (1H, d, J = 7.3 Hz), δ 7.6 (1H, s), δ 7.09-7.40 (9H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 116.7, 119.3, 122.3, 124.5, 125.3, 125.5, 125.8, 126.6, 127.3,128.8, 132.9, 141.1, 150, 163.7, 163.9.

3. Results and discussion

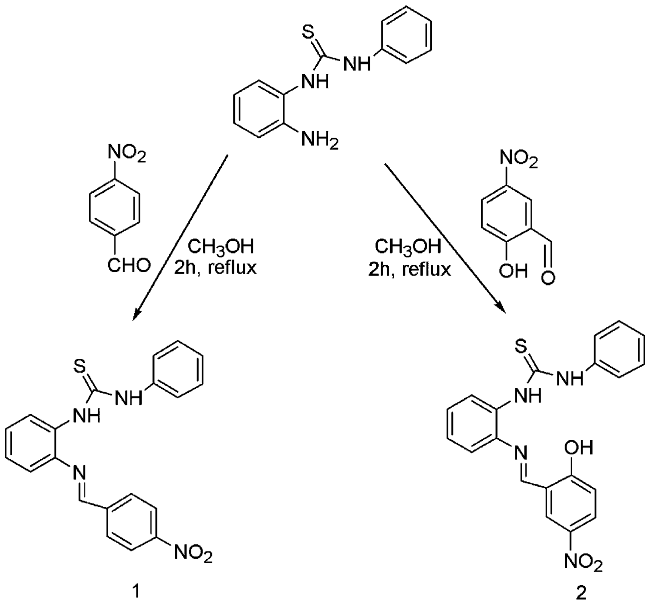
The X-ray quality crystals of receptor **1** were obtained by the slow evaporation of the hot chloroform solution. The molecule crystallizes in triclinic system with the space group P_1. The cell parameters are a = 7.2705 Å (6), b = 11.0178 Å (9), c = 12.0137 (9) Å and Z = 2 [54]. The ORTEP of the receptor **1** is shown in Fig. 1.

3.1. Anion sensing

The recognition properties of the receptors **1** and **2** towards different anions were studied by the several methods such as the naked-eye experiment, the ^1H NMR titration and UV–visible titration.

3.1.1. Colorimetric investigations

Observable color changes also took place in $CHCl_3$ and DMSO solutions. Upon addition of 2 equivalents of fluoride ions, the colorless solutions of **1** became orange brown in $CHCl_3$ and yellow in DMSO. Receptor **2** turned from colorless to brown in $CHCl_3$ and



Scheme 1.

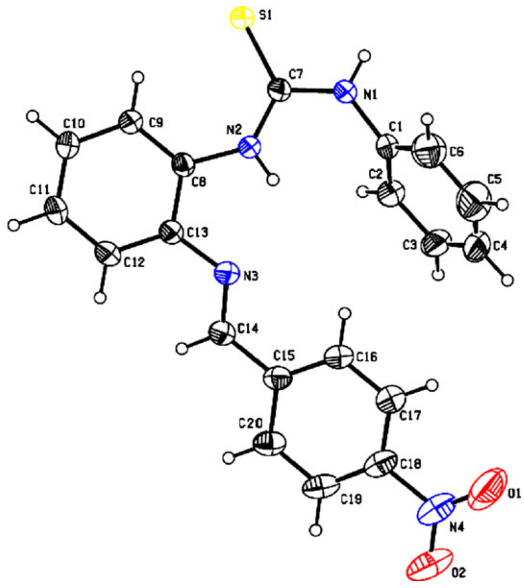


Fig. 1. ORTEP diagram of the receptor **1**.