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Colorimetric chemosensor for multi-signaling detection of metal ions using pyrrole based Schiff bases

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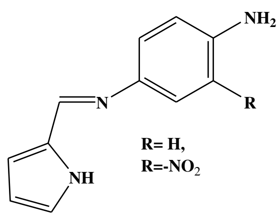
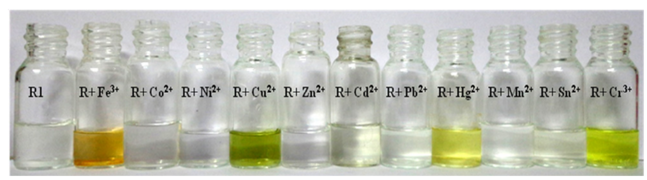
HIGHLIGHTS

- R**1** and R**2** acts as fluorescent and colorimetric sensor for Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+}.
- The binding constant of R**2** was higher than R**1** with 2:1 stoichiometry.
- R**1** and R**2** detect Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} metals at micromolar levels.
- R**1** and R**2** exhibits fluorescence quenching via PET mechanism.

GRAPHICAL ABSTRACT





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ABSTRACT

Pyrrole based Schiff bases act as a highly sensitive probe for metal ions in aqueous medium. Both receptors R**1** and R**2** are sensitive towards Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} among the other metal ions. The sensing ability of the receptors are investigated via colorimetric, optical and emission spectroscopic studies. The binding stoichiometries of R**1** and R**2** with metal ions have been determined as 2:1 by using Job's plot. The colorimetric receptors exhibited high sensitivity with a low detection limit of μM levels. In the presence of metal ions both receptors shows fluorescence quenching. This might be due to the photo induced electron transfer mechanism. The quenching constant was further determined using Stern–Volmer plot.

Introduction

The development of new molecular systems for the colorimetric detection of cations has gained prime importance due to their significance in biological and environmental processes [1–3]. Currently, there is an active effort to develop molecular complexation systems that binds with cation. Generally, pyrrole, –OH, $–NH_2$, urea, thiourea, –CONH centers etc., act as binding sites for cations [4–16]. In particular, the sensing of metal ions has attracted growing attention because of its great potential for biological and industrial applications. During recent years, there is an upsurge in the field of colorimetric sensing of alkali, alkaline–earth and transition metal ions by organic molecules [17,18]. Among the cations, special attention is devoted to develop chemo sensors for transition metal ions and toxic 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 a biological system where mercury, chromium are very toxic metal ions. Iron is one of the important metal ions for most organisms, plays an important role in many biological processes and electron transfer processes in DNA and RNA synthesis [19,20]. Furthermore, iron homeostatic is an important factor involved in neuro-inflammation and progression of Alzheimer's disease and iron deficiency (hypoferremia) can be harmful [21–27]. Copper is a third most essential element, present in plants, animals and human. When the concentration of Cu^{2+} increases its limit it causes Alzheimer's, Parkinson's, and Wilson diseases [28–30]. As mercury has an extremely toxic

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impact on the environment and human health. It is well-known; mercury can lead to dysfunctions of the brain, kidney, stomach, and central nervous systems [31–33]. Trivalent chromium plays an important role in the metabolism of carbohydrates, proteins, lipids and nucleic acids. The excess of chromium causes genotoxic effects and the deficiency of chromium increases the risk for diabetes and cardiovascular diseases [34,35]. Many spectroscopic techniques are used for detecting metal ions. However, these methods are complicated and expensive. The chemosensors are very convenient, sensitive detection, low-cost of equipment and direct visual perception. In addition, some sensors can only be applied in organic solvents, which limit their application in environmental systems. Therefore, it is essential to develop visual eye sensors for sensitive detection of Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} in physiologically suitable solvents. R**1** and R**2** were earlier reported by us as colorimetric and fluorescent chemosensors for fluoride and hydroxide anions [36]. Herein, we report the detection of Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} ions in aqueous analyte solution by R**1** and R**2**. They exhibit a pronounced absorbance behavior toward Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} over other common interfering metal ions. R**1** and R**2** with Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} shows higher binding constant with 2:1 stoichiometry. The receptors R**1** and R**2** detect the metal ions in micromolar levels and they exhibits fluorescence quenching, this might be due to the photoinduced electron transfer mechanism.

Experimental

Materials and methods

Pyrrole-2-carboxaldehyde, 2-Nitro-1,4-phenylene diamine, 1,4-phenylene diamine, iron (III) chloride, cobalt (II) chloride, nickel (II) chloride, copper (II) chloride, zinc (II) chloride, cadmium (II) acetate, tin (II) chloride, lead (II) acetate, mercury (II) nitrate, manganese (II) acetate, chromium (III) chloride, and analytical grade solvents such as acetonitrile (CH_3CN) and ethanol (EtOH) were purchased from Sigma Aldrich and used as such. Shimadzu UV-2600 UV–vis spectrophotometer was used to record UV–visible spectra using quartz cell with 1 cm path length. Fluorescence emission spectra were recorded in a Shimadzu RF-5301 PC spectrofluorophotometer at a scan rate of 500 nm/slit width with Ex: 10 nm Em: 10 nm. Excitation wavelength set was 300 nm. 5×10^{-5} M solution of R**1**, R**2** in CH_3CN and 1.5×10^{-3} M solutions of the cations in H_2O were prepared. 0.2 eq. (10 μL) – 2 eq. (100 μL) of guest solution was added to 3 ml of R**1** and R**2** taken in the UV cuvette.

*Synthesis and characterization of sensors R**1** and R**2***

*Sensor R**1**: N-[(1E)-1H-pyrrol-2-ylmethylene] benzene-1,4-diamine*

1,4-Phenylene diamine (0.5 g, 1 mmol) was stirred with pyrrole 2-carboxaldehyde (0.435 g, 1 mmol) in dry dichloromethane (DCM) at 25 °C for 20 h. The reaction mass was concentrated under vacuum. The residue was triturated with n-hexane and filtered. This solid was again triturated with DCM, filtered and dried to yield pure (R**1**). (60% yield). ^{1}H NMR (δ ppm, 400 MHz, DMSO-d_6): 11.4 (1H, s), 8.3 (1H, s), 6.9–7.1 (3H, m), 6.3 (3H, m), 6.1 (1H, m), 5.0 (d, 2H) ^{13}C NMR (δ ppm, 100 MHz, DMSO-d_6): 149.5, 149.1, 130.7, 123.7, 121.5, 116.2, 109.6 IR (KBr, cm^{-1}): 3658, 3232, 3108, 2972, 3043, 2897, 2558, 2742, 2562, 2403, 1689, 1625, 1550, 1490, 1452, 1419, 1334, 1311, 1246, 1203, 1164, 1012 LCMS: *m*/*z* 262.9, 185.8.

*Sensor R**2**: (4-amino-3-nitrophenyl) [(1E)-1H-pyrrol-2-ylmethylene] amine*

2-Nitro-1,4-phenylene diamine (0.6 g, 1 mmol) was refluxed with pyrrole 2-carboxaldehyde (0.435 g, 1 mmol) in ethanol (10 ml) for 16 h. Reaction mixture was concentrated under vacuum and the residue was triturated with n-hexane. The residue was filtered and dried to yield pure (2) (73% yield) ^{1}H NMR (δ ppm, 400 MHz, DMSO-d_6): 11.6 (1H, s), 8.3 (1H, s), 7.7 (1H, d), 7.4 (3H, m) 7.0 (1H, d), 6.9 (1H, d), 6.6 (1H, d), 6.1 (1H, d). ^{13}C NMR (δ ppm, 100 MHz, DMSO-d_6): 148.6, 144.3, 140.0, 130.5, 130.1, 129.9, 123.6, 120.0, 116.0, 115.7, 109.6. IR (KBr, cm^{-1}): 3480, 3429, 3395, 3254, 3119, 2892, 1772, 1634, 1596, 1557, 1503, 1451, 1369, 1339, 1249, 1095 LCMS: *m*/*z* 231.0.

Results and discussion

Cation sensing by colorimetric analysis

Receptors **1** and **2** (Fig. 1) were synthesized by simple condensation of pyrrole-2-carboxaldehyde with 1,4-phenylene diamine and 2-nitro-1,4-phenylene diamine respectively in good yields following the procedure reported by us and well characterized by ^{1}H, ^{13}C NMR, LCMS, FT IR and UV–vis spectroscopic techniques [36]. R**1** and R**2** are very good sensor for biologically important anions like F^- and ^-OH ions. R**1** turned from colorless to yellow and R**2** showed dramatic color change from yellow to permanganate color in presence of F^- and HO^- ions without any interference from other anions. To extend the scope of the R**1** and R**2**, its sensitivity towards metal ions in complete aqueous medium was probed. We investigated the recognition ability of the R**1** and R**2** (5×10^{-5} M in CH_3CN) by naked-eye colorimetric experiments for transition metal ions such as Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Mn^{2+}, Sn^{2+} and Cr^{3+}. When the metal ion solution in H_2O (1.5×10^{-3} M) was added to the R**1**, the color of the solution changed from colorless to pale orange for Fe^{3+}, olive green for Cu^{2+}, yellow for Hg^{2+} and green for Cr^{3+} as seen in Fig. 2a. The promising feature of the present sensor systems is that it gives different color for different metal ions. Thus a single receptor can sense multi metal ions without any overlap. The receptor solution does not show any visible color changes even with a large excess of other metal ions like Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+} and Sn^{2+}. Upon the addition of metal ions into R**2**, the color was changed from colorless to dark yellow for Fe^{3+}, pale olive for Cu^{2+} and pale yellow for Hg^{2+} and Cr^{3+} (Fig. 2b). The color change can be attributed to the complex formation. Thus R**1** and **R2** are able to sense Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} in aqueous medium, physiologically suitable condition which is an added advantage.

Optical spectroscopic studies

The binding interaction studies or R**1** and R**2** in CH_3CN against cations of environmental relevance, such as Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Mn^{2+}, Sn^{2+} and Cr^{3+} shows sensitive response to Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+} in H_2O. The change in the UV–vis absorbance spectrum of R**1** and R**2** due to the addition of 200 μL of metal

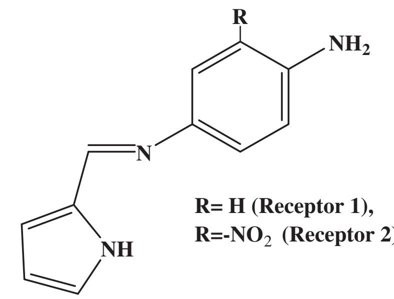

Fig. 1. Structure of R**1** and R**2**.