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Multi-signalling cation sensing behaviour of a bis(pyridin-2-yl methyl)aniline based hetarylazo dye

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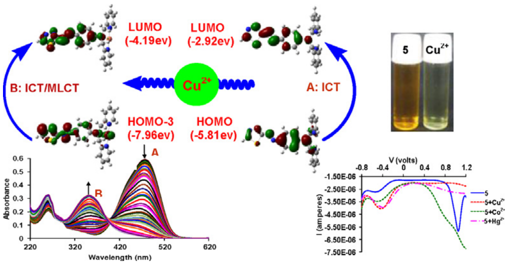
HIGHLIGHTS

- Cation sensing of hetarylazo dye based upon visual, absorption and electrochemical changes is described.
- Sensing mechanism is based upon perturbation in intramolecular charge-transfer upon interaction with cations.
- Sensing protocol is supported by ^{1}H NMR studies as well as theoretical calculations.
- Hetarylazo dye acts as a multichannel sensor.
- Response of the dye towards various cations has also been explored in acidic pH window.

GRAPHICAL ABSTRACT

The chromogenic and electrochemical behaviour of bis(pyridine-2-yl methyl)aniline based hetarylazo dye gets perturbed in the presence of cations, most effective being Cu^{2+}. The conversion of ICT to ICT/MLCT is witnessed by TD-DFT calculations.



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ABSTRACT

We investigated the cation sensing behaviour of a bis(pyridin-2-yl methyl)aniline appended hetarylazo dye via chromogenic and electrochemical transduction channels. The binding pocket constituting both the pyridyl as well as aniline nitrogen atoms acts as recognition site for the cations and consequent perturbation in the intramolecular charge-transfer prevailing in the dye results in the chromogenic response manifested in the form of hypsochromic shift in the intramolecular charge-transfer band and the attendant naked-eye color changes. The dye exhibits significant changes in its electrochemical behaviour in the presence of cations. The experimental results are also rationalized by time-dependent density functional theory (TD-DFT) calculations.

1. Introduction

The intramolecular charge-transfer (ICT) approach has widely been explored for analyte sensing as ICT can easily be perturbed by reducing or enhancing the electron donating character of the donor group [1]. In the previous research from our group, we have successfully explored the perturbation in the ICT of receptors in the presence of guest species and have synthesized chemosensors/chemodosimeters for both cations and anions [2]. One part

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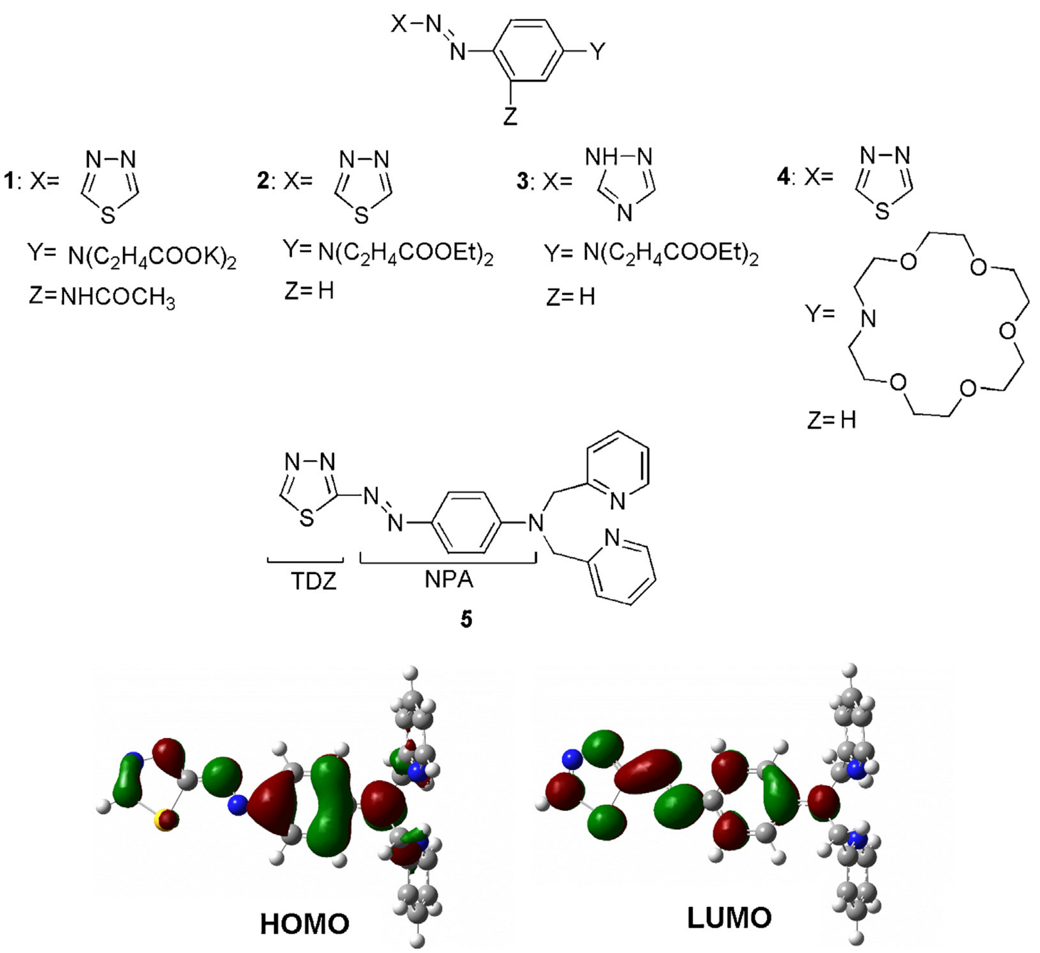

Scheme 1. Molecular structures of **1**, **2**, **3**, **4** and **5** along with HOMO and LUMO of **5** (isovalue = 0.03).

of our work deals with the hetarylazo derivatives [2b,g,h,l], which are endowed with characteristic intense absorptions in the visible region attributed to strong ICT, responsible for their obvious intense colors, which could easily be modulated on binding with analytes leading to perceptible color changes, desired for a 'naked-eye' chemosensor. Additionally by analyzing the physicochemical parameters, we envisaged that if differential binding sites comprising of combinations of N, S and O are incorporated in a single chromophore, sensing of more than one analytes through 'site-complementarity' might result. Taking advantage of this, we had developed hetarylazo derivatives **1–4** (Scheme 1) as chemosensors for the detection of Zn^{2+}, Hg^{2+} and Fe^{3+}, Cu^{2+}, Hg^{2+} and Pb^{2+} based upon the visual as well as absorption spectral changes [2b,g,h,l].

The detection of various metal ions, especially Cu^{2+}, Hg^{2+} and Co^{2+}, becomes important owing to their importance in our routine life. Copper is the third most abundant transition metal ion in mammals where it plays a crucial role in the growth and development of biological systems as well as in many biochemical processes at the cellular level [3]. However, presence of excess Cu^{2+} can pose serious threats to living organisms especially when it displaces other metal ions acting as cofactor in various enzyme catalyzed reactions [4]. It is also implicated in Alzheimer's disease, Prion diseases, Menkes and Wilson diseases, lipid metabolism and inflammatory disorders [5]. Cobalt is also an essential trace element present in vitamin cobalamin and other metalloproteins where it performs various essential biological roles [6]. But, its increased levels can lead to several health disorders like decreased cardiac output, cardiac and thyroid enlargements, heart diseases, elevated red blood cells, increased blood volume and vasodilation and flushing [7]. It is also responsible for allergic contact dermatitis and even possibly carcinogenic to humans [8]. The detection of mercury has always attracted great interest from chemists because of its highly lethal effects on the environment and living beings [9], which to some extent, result from their affinities toward thiol groups in proteins and enzymes [10] leading to malfunctioning of the living cells. It is considered to be one of the most hazardous species in nature, which may result in prenatal brain damage, cognitive and motion disorders, vision and hearing loss, and even death in extreme cases [11]. The microorganisms can additionally assimilate Hg^{2+} and converted it to methylmercury (CH_3Hg^+), a potent neurotoxin [12]. Thus, the detection of Cu^{2+}, Co^{2+} and Hg^{2+} ions is of great significance.

The receptors containing redox active centers might respond differently upon interaction with the guest species enabling different transduction channels, such as chromogenic or fluorogenic and electrochemical to be operative, thus leading to multichannel receptors [13]. For example, chromogenic response in the form of hypsochromic or bathochromic shifts would be expected if the metal ions interact strongly with the donor or acceptor fragments, respectively, of the receptor. Similarly, electrochemical transduction in the form of e.g. anodic shift in the oxidation wave is expected when the metal ions interact strongly with the donor fragment of the receptor. Likewise, the fluorogenic transduction in the form of emission enhancement or quenching is expected when the metal ions interact (weakly or strongly) with the excited state of fluorophore. In realization of the above, we decided to incorporate a suitable chelating group in the general design of hetarylazo receptors **1–4**, and working on this line, we have