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Semicarbazone and thiosemicarbazone appended 4-diethylamino-2-hydroxybenzyl compounds as highly selective bifunctional chemosensors: An experimental and computational approach

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Highlights

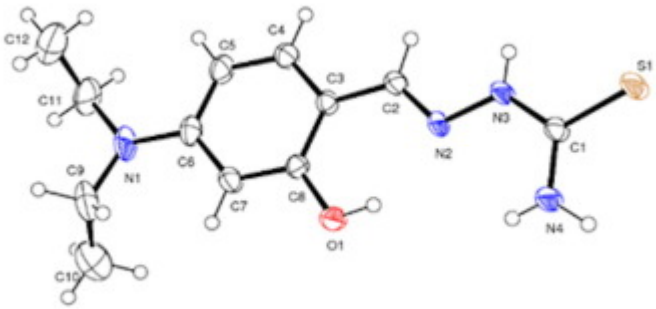
- Three Semicarbazone/thiosemicarbazone-based chemosensors were synthesized.
- Single crystal structure of one of the receptors was solved.
- All the three receptors sensed selected cations and fluoride anion.
- The computational approach supported the experimental sensing studies.

Abstract

Three bifunctional chemosensors, 2-(4-(diethylamino)-2-hydroxybenzylidene)hydrazinecarboxamide (S1), 2-(4-(diethylamino)-2-hydroxybenzylidene)hydrazinecarbothioamide (S2) and 2-(4-(diethylamino)-2-hydroxybenzylidene)-*N*-methylhydrazinecarbothioamide (S3) have been designed and synthesized for recognition of inorganic cations and anions in solution at room temperature. The structure of the receptor S2 was confirmed by single crystal X-ray diffraction technique, which crystallizes in the monoclinic $P2_{1/n}$ space group. The selectivity and sensitivity of cations (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}) and anions (F^-, Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$) were investigated using colorimetric, UV–vis absorption, emission and ^1H NMR studies. The receptors (S1–S3) with ONO/ONS donors allow bare-face recognition of Co^{2+}, Ni^{2+} and Cu^{2+} cations, and F^- anion in a mixture of solvent, CH_3CN:CH_3OH (8:2, v/v). The receptor S3 possesses high sensitivity and selectivity in comparison with the receptors S1 and S2. The binding constant and limit of detection of the receptors with sensed cations and anion showed high sensitivity and selectivity towards Co^{2+} cation with order of magnitude 6, greater than the other sensed cations. In addition, the receptors S3 also shows 6 order of magnitude for Cu^{2+} cation and F^- anion. The optimized geometry determined by DFT studies shows that the receptors in its conjugated state provide binding sites for cations and F^- anion. The HOMO-LUMO energy gap between the receptors and the Co^{2+} cation was found to be the least among the studied receptors-cations binding interaction, possibly due to charge transfer effect.

Graphical abstract

Three bifunctional chemosensors (S1–S3) with two binding sites for selective and sensitive recognition of inorganic cations (Co^{2+}, Ni^{2+} and Cu^{2+}) and anion (F^-) were synthesized and investigated by colorimetric, absorption, emission, ^1H NMR and theoretical studies. The strong binding affinity towards cations and F^- anion evidences the bifunctional behaviour of the synthesized receptors, which may act as the promising candidates for sensor application.



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Introduction

In the field of host–guest chemistry, the bifunctional chemosensors that are capable of recognizing inorganic cations and anions have attracted much attention in recent decades [1], [2], [3]. These binding processes are achieved by flexible linear molecules, which upon recognition of ions align themself in a particular conformation. Hence, while designing the bifunctional receptors, pre-organisation of binding sites with defined shape complimenting the structure for target analytes, and rigid units with clefts and cavities imposes an improvement in recognising the target ions. In general, ion recognition occurs by independent binding or by cooperative binding or through dual binding capability of the receptor. The recognition properties of synthetic receptors mostly involve signalling by optical changes or perturbation in potential signals [4], [5], [6]. Among the different sensing methods, colorimetric sensing is particularly challenging as it involves the recognition of analytes through color change without any instrumentation, and widely employed due to its low cost and easy detection [7], [8]. The development of colorimetric and fluorimetric sensors for the recognition of different ions have emerged with mounting importance in research field because of their potential usages in biological, industrial and environmental applications. The selective sensing of cations and anions is particularly interesting in molecular recognition due to the contamination by heavy transition metals and anions in biological, industrial and environmental samples, which may lead to the serious environmental and health problems [9]. In this regard, the search of better and efficient procedures to detect various ions, which are potentially harmful to both human life and environment, has aroused interest towards sensor studies. For example, the recognition and sensing of fluoride ion has attracted researchers as the excess fluoride may lead to fluorosis, a type of fluoride toxicity that increases bone density [10], [11].

Thiosemicarbazones (TSCs) form a class of hard-soft oxygen, nitrogen and sulphur containing compounds, which received considerable attention because of their diverse importance in chemical sciences [12]. These heterocyclic compounds act as complexing agents for metal ions and anions due to the presence of versatile binding sites that act as neutral or monobasic ligands, and may form four or five membered chelate rings through *N*-hydrazinic and S-thiolate atoms [13], [14]. TSCs show promising biological activities because of which many research groups are actively engaged in determining its improved broad spectrum biological activities [15]. Even though they show wide usage in the field of medicinal chemistry, their applications as sensors are still needs to be enlightened. The semicarbazones and thiosemicarbazones as organic receptors with binding sites – NH/ONO/ONS for the coordination of cations and anions are reported [16]. They are widely used as ionophore and also employed as sensor for ion selective electrode system. The introduction of fluorescence group sensitively affects the receptor unit and interacts with cations [17], [18]. However, derivatives of semicarbazones/thiosemicarbazones as dual receptors are scarce in literature. The dual sensing takes part in biological processes involving molecular recognition of cationic and anionic species.

In the present study, we have been interested in exploring the bifunctional behaviour of three receptors (S1–S3) for recognition of inorganic cations and anions in an organic environment. The receptors were synthesized in a good yield by a simple condensation reaction between 4-diethylamino-2-hydroxybenzaldehyde and semicarbazide/thiosemicarbazide/4-methyl-3-thiosemicarbazide. The structures of receptors were authenticated by elemental analysis, UV–vis, NMR and mass spectral techniques, while X-ray diffraction analysis confirms the structure of receptor S2. The selectivity and sensitivity of these receptors towards selected cations (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}) and anions (F^-, Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$) were studied by naked eye vision, UV–vis absorption, fluorescence and ^1H NMR techniques.

Section snippets

Materials

4-Diethylamino-2-hydroxybenzaldehyde, semicarbazide, thiosemicarbazide, 4-methyl-3-thiosemicarbazide and perchloric acid were purchased from Sigma-Aldrich and used as received. Acetonitrile, ethanol, methanol and DMSO were HPLC grade and purchased from AVRA Chemicals (India). Tetrabutylammonium salts of anions such as F^-, Cl^-, Br^-, I^- and HSO_4^- were purchased from AVRA chemicals (India), and used as obtained. The perchlorate salts of cations such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}…

Synthesis of bifunctional chemosensors (S1-S3)

Three bifunctional chemosensors, 2-(4-(diethylamino)-2-hydroxybenzylidene)hydrazinecarboxamide (S1), 2-(4-(diethylamino)-2-hydroxybenzylidene)hydrazinecarbothioamide (S2) and 2-(4-(diethylamino)-2-hydroxybenzylidene)-*N*-methylhydrazinecarbothioamide (S3) were synthesized by the condensation of 4-diethylamino-2-hydroxy-benzaldehyde with semicarbazide, thiosemicarbazide and 4-methyl-3-thiosemicarbazide in ethanol (Scheme 1). The chemosensor molecules were characterized by elemental analysis, FT…

Conclusion

In summary, we have developed three bifunctional receptors (S1–S3) with two binding sites for selective and sensitive recognition of inorganic cations (Co^{2+}, Ni^{2+} and Cu^{2+}) and anion (F^-). These receptors were found to show significant responses upon addition of cations and fluoride anion as investigated by colorimetric, absorption, emission and ^1H NMR studies. The sensing of F^- anion is attributed to deprotonation of NH proton in semicarbazone/thiosemicarbazone moiety, in which F^- anion…

CRediT authorship contribution statement

Sethu Amuthakala: Conceptualization, Investigation, Validation, Writing – original draft. **Sundaram Bharathi:** Data curation, Software, Visualization. **Aziz Kalilur Rahiman:** Conceptualization, Methodology, Supervision, Writing – review & editing.…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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