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Design and synthesis of a new organic receptor and evaluation of colorimetric anion sensing ability in organo-aqueous medium

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ABSTRACT

A new organic receptor has been designed and synthesized by the combination of aromatic dialdehyde with nitro-substituted aminophenol resulting in a Schiff base compound. The receptor exhibited a colorimetric response for F^- and AcO^- ion with a distinct color change from pale yellow to red and pink respectively in dry DMSO solvent and yellow to pale greenish yellow in DMSO:H_2O (9:1, v/v). UV–Vis titration studies displayed a significant shift in absorption maxima in comparison with the free receptor. The shift could be attributed to the hydrogen bonding interactions between the active anions and the hydroxyl functionality aided by the electron withdrawing nitro substituent on the receptor. ^1H NMR titration and density functionality studies have been performed to understand the nature of interaction of receptor and anions. The lower detection limit of 1.12 ppm was obtained in organic media for F^- ion confirming the real time application of the receptor.

1. Introduction

The design of organic receptors for the colorimetric detection of anions has seen progressive path in the last two decades and has enriched the field of supramolecular chemistry [1,2]. Considerable research interest in the detection of anions is due to their ubiquitous nature and utility in the field of biology [3], medicine [4], environmental science [5] and catalysis [6]. Anions play a vital role in the biological and environmental system by being a part of the biochemical and physiological reactions [7]. Fluoride ion (F^-) is important in the maintenance of dental and enamel health. Deficiency of fluoride ion leads to dental carries and enamel demineralization while excess of it results in diseases such as fluorosis and osteoporosis. Acetate ion (AcO^-), being one of the components of acetyl coenzyme A, has an important role to play in metabolic process and has gained considerable attention of the chemists too [8–10].The rate of production of AcO^- and its oxidation decides the rate of decomposition of organic matter in marine sediments [11].

Detection of anions by colorimetric technique has grown into an area of great interest for the relative ease in the visual detection of the signaling event [12]. In this view, anion receptor chemistry has gained significant interest in the last two decades and is still considered to be a fertile area of research [13–19]. Researchers have so far developed a wide array of neutral receptors and positively charged receptors for the detection of anions. Among them, neutral receptors bearing hydrogen bond donor functionalities such as imine [20–22], phenol [23–25], amide [26–28], urea [29–33], thiourea [34–38], imidazole [39], pyrrole [40] and 1,3,4-oxadiazole [41–43] have been widely studied. Binding of anions by the receptor has been ascribed to three possible mechanisms, (a) hydrogen bonding interaction [44,45], (b) deprotonation of -NH or –OH functionalities of receptor due to polarization effect in the presence of electron withdrawing substituents [46–48] or (c) chemical reaction [49–51]. Positively charged receptors interact through electrostatic interactions where their hydrogen bond donor tendency is sufficiently enhanced due to the polarization effect (e.g., alkylpyridinium) [52]. Yet, there are reports in the literature where dye based fluorescent sensors have been successfully applied in the detection of aqueous halide ions at physiological level [53].

Choice of solvent has been one of the greatest challenges in the field of anion receptor chemistry. Most of the neutral and positively charged receptors reported so far have proven to sense anions in non-competitive organic media (e.g. DMSO, CH_3CN, CH_2Cl_2, etc.) [54,55]. Very few reports are available in the literature based on the detection process in competitive protic solvents such as H_2O, CH_3CH_2OH [56]. Besides, receptors generally lack in differentiating the anions having similar basicity and surface charge density such as F^-, AcO^- and $H_2PO_4^-$ and thus the selective detection of anions is hindered [57,58]. The introduction of various substituents on the receptor could be a better solution in this regard in tuning the selectivity of the receptor.

Considering the above mentioned issues, herein we report the design and synthesis of a Schiff base organic receptor based on the combination of an aromatic dialdehyde and nitro substituted aminophenol. The receptor has been designed with an attempt to detect anions in competitive media producing visual color response upon anion reception. Further, the electron withdrawing nitro group present in the receptor has been visualized to play vital role as a signaling unit as well

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as aiding the effective binding of anions by increasing the acidity of the hydroxyl proton.

2. Experimental

2.1. Materials and methods

All the chemicals used in the present study were procured from Sigma-Aldrich, Alfa Aesar or Spectrochem and were used as received without further purification. All the solvents were purchased from SD Fine, India, were of HPLC grade and used without further distillation.

Melting point was measured on Stuart SMP3 melting-point apparatus in open capillaries. Infrared spectra were recorded on Jasco FTIR spectrometer. UV/Vis spectroscopy was performed with analytik jena Specord S600 spectrometer in standard 3.5 mL quartz cell with 1 cm path length. The ^{1}H NMR spectra were recorded on Bruker Ascend (400 MHz) instrument using TMS as internal reference and DMSO-d_6 as solvent. Resonance multiplicities are described as s (singlet), d (doublet), t (triplet) and m (multiplet). Mass spectrum was recorded on Bruker Daltonics ESI Q TOF.

2.2. Synthesis of 2-((E)-((E)-3-((E)-(2-hydroxy-4-nitrophenylimino)methyl)benzylidene)amino)-5-nitrophenol

Isophthalaldehyde (154.12 mg, 1.14 mmol) and 2-amino, 5-nitrophenol (400 mg, 2.29 mmol) were mixed in 5 ml ethanol. A drop of acetic acid was added and the reaction mixture was refluxed at 50 °C for 5 h. The formation of the product was confirmed through TLC by the generation of single spot indicative of the disappearance of starting materials. Yield: 80%, m. p. 210 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 10.31 (s, OH), 8.8 (s, CH = N), 7.7–7.5 (d, Ar-H), 7.49 (s, Ar-H), 7.32 (s, Ar-H,), 6.60–6.62 (d, Ar-H), 6.2 (s, Ar-H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 108.61, 111.12, 115.03, 118.22, 120.58, 129.70, 134.71, 136.59, 145.48, 150.56, 162.32. FT-IR (cm^{-1}): (C-O) 1155, (C-O) 1228, (NO_2) 1342, (C═C) 1513, (C═N) 1625, (C-H) 2902, (C-H) 2984, (OH) 3426. Mass (ESI): *m/z* Calculated: 406.09 Obtained: 428.9 ($M + Na^+$) (Scheme 1).

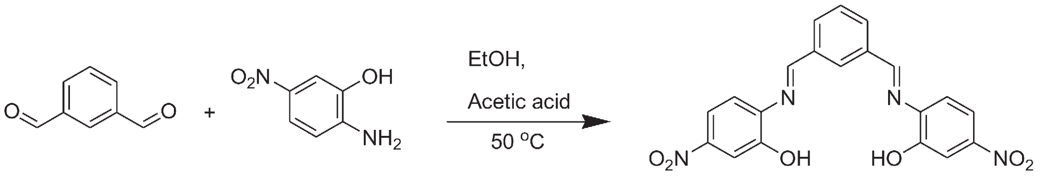
2.3. Computational methods

We have performed the Density Functional Theory (DFT) simulation on the receptor molecule using GAUSSIAN 09 package. A closed shell Becke–Lee–Yang–Parr hybrid exchange-correlation three-parameter functional (B3LYP) [59–61] along with 6-311++G(d) basis set were used in the simulation to derive a complete geometry optimization for isolated receptor as well as the receptor binding with AcO^- and F^- ions. Molecular geometry was fully optimized by using Berny's optimization algorithm, which uses redundant internal coordinates. To confirm the convergence to the minima on the potential energy surface, the harmonic vibrational wavenumbers were calculated using analytic second derivatives and properly scale down to control the systematic errors caused by incompleteness of the basis set. In a second step the time dependent DFT (TD-DFT) method were used considering the same B3LYP exchange-correlation functional with 6-311++G (d, p) basis set to obtain the UV–Visible absorption spectra of free and ion bonded receptor.

3. Results and discussion

3.1. Colorimetric studies

The receptor R, comprising of chromogenic signaling unit and hydrogen bond donor functionality viz., -NO_2 and –OH respectively are likely to exhibit appreciable color change in the detection of anions. Preliminarily, qualitative analysis has been performed to figure out the interaction of various anions with the receptor. Receptor solution of 1×10^{-4} M has been prepared in dry DMSO. Standard solution of anions (TBA salts of F^-, Cl^-, Br^-, I^-, HSO_4^-,$H_2PO_4^-$ and AcO^-) as 1×10^{-2} M has been prepared in dry DMSO. With the addition of 2 equiv. of test anions to the receptor solution, visible color change was observed for F^- and AcO^- ions from pale yellow to pale red and pale pink respectively. There was no appreciable color response upon addition of other anions. In this regard, the receptor could serve the purpose of detecting F^- and AcO^- ions among all as depicted in Fig. 1. UV–Vis absorption spectra was recorded to confirm the color change, with the addition of test anions to receptor solution. Initial absorption peak of the receptor at 325 nm corresponds to the transitions between the π orbitals localized on the azomethine group (C═N) and second absorption peak at 383 nm could be assigned to the intramolecular charge transfer occurring within the Schiff's base moiety. The azomethine and the nitro functionality lead to pale yellow coloration of the receptor. The shift in the λ_{max} was observed for F^- and AcO^- differing by a unit of 135 nm and 145 nm respectively in comparison with the free receptor and a subsequent decrease in the absorption band centered at 383 nm. The shift in the λ_{max} was not observed with the addition of other anions involved in the present study as shown in Fig. 2. The selective response of the receptor has been represented in the form of bar graph where the change in



Scheme 1. Synthesis of receptor R.

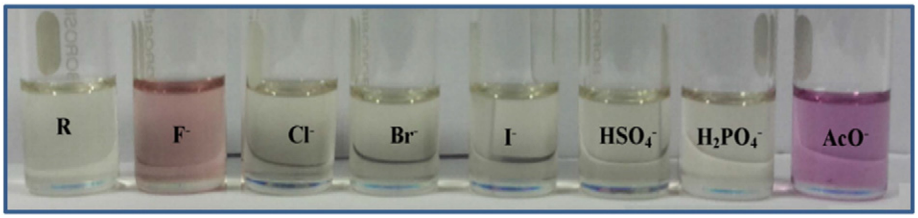


Fig. 1. Color changes of receptor R upon addition of 2 equiv. of various anions in dry DMSO.