RAPID COMMUNICATION

A Novel Benzimidazolyl-based Receptor for the recognition of Fluoride and Cyanide Anion

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Abstract. A novel benzimidazole based ligand (**1**) has been synthesized and studied its anion recognition properties. The binding of anion with **1** was studied using UV-Visible spectroscopy, fluorescence spectroscopy and ¹H-NMR techniques at very low concentrations. The results obtained from the spectroscopic studies indicate that ligand **1** is an efficient anion receptor providing changes in chemical shift and optical signals for the detection of two most environmentally important anions, fluoride and cyanide.

Keywords. Anion recognition; fluoride; cyanide; benzimidazole; fluorescence quenching.

1. Introduction

Molecular hosts for the selective recognition of anionic guests are highly sought after in supramolecular chemistry due to their vital role in many biological, chemical and environmental processes such as enzyme-mimic, catalysts, extractants and molecular probes for medicinal diagnostics and monitoring of anionic pollutants.¹ Since, anions are ubiquitous in nature their sensing by newly designed and synthesized artificial receptors have been gaining immense interest.² Among the anions, fluoride and cyanide sensing is a popular topic of interest in supramolecular chemistry owing to their association with diverse array of biological, medical and environmental processes. Fluoride having the smallest ionic radius, highest charge density and a hard Lewis base plays a positive role in dental health and in treatment of osteoporosis but overexposure to it can have detrimental effect such as kidney failure and debilitating skeletal defects.³ On the other side, cyanide detection is important due to its acute toxicity in physiological system as well as a continuing environmental concern caused by its widespread industrial use. One of the well-known adverse effects of cyanide is its inhibition of respiration, which occurs due to inhibition of terminal oxidase (cytochrome oxidase) of the mitochondrial respiratory chain.⁴

To design a specific anionic host, some challenges still have to be faced due to large size of anions compared to cations, effect of chemical environment and pH of the medium on the host-guest interactions. Despite all such challenges, many receptors bearing ureas,⁵ thioureas,⁶ pyrroles,⁷ amides,⁸ benzimidazole,⁹ etc., all of which containing –NH binding site, and other neutral chemical sensors attached with signaling subunits viz. p-nitrophenyl,¹⁰ o-phenylenediamine,¹¹ anthraquinones,¹² acridone,¹³ calix[4]arenes,¹⁴ naphthalimide,¹⁵ benzophenone,¹⁶ anthracene,¹⁷ and hydroxymethylphenol¹⁸ with ion binding sites, have been reported. Although chemosensor with –NH of benzimidazole as binding site are quite limited, they have been gaining importance due to its self signaling property and peculiar acidity of the –NH proton caused by electronic effect of the benzene ring which is responsible for the substrate selective binding.

Here, we wish to introduce a new, simple benzimidazolyl based neutral anion receptor (2,2'-(1,3-phenylene) bis(1*H*-benzo[d]imidazole-5,2-diyl)) bis(phenylmethanone) (**1**) which selectively binds two most important anions, F[–] and CN[–] among the other anions such as Cl[–], Br[–], I[–], NO₂[–], HSO₄[–], HCO₃[–], H₂PO₄[–], N₃[–], AcO[–], ClO₄[–], etc. Receptor **1** has two –NH fragments to act as hydrogen bond donor sites and to form an internal cavity which perfectly selects appropriate guest during the host-guest interaction. It is structurally simple, heat/ air-stable and can be readily prepared in one-step reaction from commercially available starting materials.

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2. Experimental

2.1 Materials and methods

All general analytical grade chemicals and reagents were purchased from Merck-India Chemical Company and Sigma-Aldrich. Spectroscopic grade solvents were used for spectroscopic studies. FT-IR spectra were recorded in KBr pellets on a Shimadzu IR- Prestige-21 FT-IR spectrophotometer operating from 400 to 4000 cm^{-1} . Electronic absorption spectra were obtained with Shimadzu UV-1700 at room temperature. Fluorescence spectra were recorded on a Horibajobin Yovon Fluoromax-4 spectrophotometer. ^1H NMR spectra were obtained with a 400 MHz Bruker Avance II FT spectrometer. Chemical shifts (ppm) were referenced to the residual solvent peaks.

2.2 Preparation of Receptor (2,2'-(1,3-phenylene)bis(1H-benzod[imidazole-5,2 diyl])bis(phenylmethanone) **1**

Isophthalic acid (0.50 g, 3 mmol) and 3,4-diaminobenzophenone (0.90 g, 6.6 mmol) were charged in 250 mL round bottom flask in orthophosphoric acid (10 mL), and refluxed for 6 h at 220°C (Scheme 1). Then, the resulting hot reaction mixture was poured into ice-cold distilled water (100 mL) with vigorous stirring. A blue precipitate was obtained, which was collected by filtration, then dispersed in 500 mL of hot 10% (w/v) Na_2CO_3 and stirred for 30 min. The insoluble material was collected by filtration, mixed with ice-cold distilled water (800 mL), and adjusted to pH 4 using 10% (v/v) HCl; then recovered by filtration and recrystallized from minimum amount of methanol. The final product obtained was a white powder. Yield: 80%. CHN analysis: experiment: C 78.72, H 4.31, N 10.75, O 6.22 %; calculated: C 78.75, H 4.28, N 10.80, O 6.17%. FT-IR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3246 (benzimidazolyl -NH), 1645 (C=O stretching), 1609 (C=N stretching), 1471 (aromatic C=C stretching), 1316 (C-N stretching), 720 (C-H out of plane bending). ^1H -NMR (400 MHz, $\text{DMSO}-d_6$), δ (ppm): 8.215 (d, 2H_b) 7.979 (s, 2H_d) 7.780 (d, 4H_e) 7.771 (s, 1H_c) 7.706 (d, 2H_e) 7.695 (t, 2H_i) 7.613-7.577 (m, 7H_(a, f, h)). ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$), δ (ppm): 195.2, 154.3, 144.5, 138.2, 137.5, 133.5, 130.6, 129.8, 128.3, 127.9, 127.2, 125.8, 123.7, 120.1, 115.2. Mass calculated for $\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_2$: 518.17; found 518.18.

3. Results and Discussion

Receptor **1**, a benzimidazole based ligand with two -NH binding sites was synthesized using isophthalic acid and

3,4-diaminobenzophenone in orthophosphoric acid and characterized by ^1H -NMR, ^{13}C -NMR and FT-IR spectroscopy. The anion binding property of the receptor **1** was investigated by UV-Visible spectroscopy, ^1H -NMR titration and fluorescence titration experiments.

3.1 UV-Visible titration experiment

UV-Vis absorption spectroscopy is used for examining host/guest interactions by spectral changes of the host. The UV-Vis titration experiment was carried out by concomitant addition of various anions, in the form of tetrabutylammonium salts (TBAX) ($[\text{Bu}_4\text{N}]^+ \text{X}^-$; $\text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CH}_3\text{COO}^-, \text{NO}_2^-, \text{ClO}_4^-, \text{HSO}_4^-, \text{H}_2\text{PO}_4^-, \text{N}_3^-, \text{CN}^-$), to a 1 μM solution of receptor **1** in acetonitrile. The spectra changes were evaluated by titrating 0.2 equivalents of anion aliquots to a solution of receptor and recording the changes in the UV-Vis spectra. The receptor **1** showed two characteristic peaks at 263 nm and 316 nm in the absorption spectrum. Upon addition of fluoride, the band at 263 nm progressively decreased with the formation of a new peak at 289 nm and the band at 316 nm was red shifted to 361 nm with clear isosbestic points at 277 nm and 334 nm (Figure 1a). Similarly, upon addition of cyanide, the bands at 263 nm and 316 nm progressively decreased in intensity with the formation of new peaks at 292 nm and 362 nm and clear isosbestic points at 279 nm and 335 nm were observed (Figure 1b). Both F^- and CN^- ions formed four isosbestic points with the receptor. As reported in literature, formation of isosbestic points shows the formation of a distinct species (complex) between the anion and the receptor. This complex may be formed through strong hydrogen bonding between anion with N-H and aromatic C-H of the receptor. Analogous investigations were carried out with $\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CH}_3\text{COO}^-, \text{NO}_2^-, \text{ClO}_4^-, \text{HSO}_4^-, \text{H}_2\text{PO}_4^-$ and N_3^- ions, as their tetrabutylammonium salts and the titration experiments were monitored by UV-Vis spectra. In all these cases, the absorption bands at 263 nm and 316 nm were not perturbed on addition of the anion, as was observed with fluoride and cyanide anions; neither was there any formation of clear isosbestic point, indicating poor interaction between all these anions with the receptor **1**. The spectral variations were observed for **1** on titrating only with fluoride and cyanide. The limit of detection

Scheme 1. Synthesis of receptor **1**.

Figure 1. UV-Visible spectra of receptor **1** ($1 \mu\text{M}$) in acetonitrile during titration with (a) tetrabutylammonium fluoride. (b) tetrabutylammonium cyanide. Inset: Job plots indicating 1:1 complex formation between receptor **1** with F^- and CN^- .

Table 1. Comparison of detection limit of receptor **1** with other reported sensors.

Type of sensor	Detection limit	references
N-Phenyl-N'-(3-quinoliny)urea receptor	$50 \mu\text{M}$ for F^-	5(b)
Urea receptor with azobenzene group	$2.0 \mu\text{M}$ for F^-	5(c)
Pyrrole based receptor	$50 \mu\text{M}$ for F^-	7(a)
Azobenzene based receptor	$1.1 \mu\text{M}$ for CN^-	8(c)
N-imidazolyl-1,8-naphthalimide based receptor	1.0 mM for F^-	15 (c)
4-Chloro-2,6-bis(Hydroxymethyl) Phenol receptor	1.38 mM for F^-	18
Benzimidazolyl Based receptor	$0.1 \mu\text{M}$ for F^- / CN^-	This work

of fluoride and cyanide is $0.1 \mu\text{M}$. Stoichiometric 1:1 complex formation between receptor **1** and F^- and CN^- was confirmed by Job plots (inset of Figure 1). Table 1 shows a comparison of the detection limit of our receptor **1** with some other receptors/sensors for fluoride and cyanide sensing. Receptor **1** has better limit of detection in comparison to other receptors.

The association constants (K_a)¹⁹ calculated from the UV-Vis spectroscopic data at λ_{max} 316 nm show very strong binding of **1** with fluoride and cyanide ions as compared with other anions. The association constants were found to be $2.3 \times 10^5 \text{ (M}^{-1}\text{)}$ and $2.5 \times 10^5 \text{ (M}^{-1}\text{)}$ for fluoride and cyanide ions, respectively (Figure 2).

3.2 ^1H -NMR Titration Experiment

To understand the binding event further, ^1H -NMR titrations were carried out to study the anion recognition property of receptor **1** with tetrabutylammonium salts of fluoride and cyanide. ^1H -NMR titrations at room temperature were carried out in $\text{DMSO-}d_6$ solvent and the

Figure 2. UV-Visible spectra of receptor **1** ($1 \mu\text{M}$) in acetonitrile during titration with tetrabutylammonium salts of various anions.

changes in the chemical shifts were examined. The ^1H -NMR titration spectra for receptor **1** with cyanide and fluoride anion are shown in Figure 3. Since we have not

observed any $^1\text{H-NMR}$ peak for benzimidazole $-\text{NH}$; so, we studied the host-guest interaction of the receptor **1** with the anions *via* the changes in chemical shift in the aromatic region of receptor **1**. The largest change in chemical shift observed for the aromatic protons which is proximate to the $-\text{NH}$ group which provides evidence for the strong interaction of receptor **1** with fluoride and cyanide anions. The peaks for the protons H^e , H^i , H^f and H^h at 7.706, 7.695, 7.613 and 7.577 ppm, respectively, shifted downfield and all the peaks merged upon addition of fluoride to form a multiplet at 7.753–7.694 ppm, and at 7.750–7.668 ppm upon addition of cyanide which point out that these protons are taking part in complexation between receptor **1** and fluoride and cyanide anion.

No observable change occurred in the peak positions for the protons H^b and H^d , and the peaks for the protons H^a , H^c , H^g shifted a little bit upfield upon addition of each fluoride and cyanide anion signifying that they are not directly involved in complexation. From the $^1\text{H-NMR}$ titration study, it was established that aromatic region of benzophenone moiety is actively taking part in the complexation of receptor **1** with anion and bind through the cavity of the receptor. So, from the above discussion, it is clear that the protons H^e , H^i , H^f , H^h of receptor **1** form strong hydrogen bond with F^-/CN^- (Figure 3).

3.3 Fluorescence Titration Study

The fluorescence titration experiment was also carried out to study the host-guest chemistry of receptor **1** with various anions. During the titration, all anions were added as their tetrabutylammonium salts (TBAX) ($[\text{Bu}_4\text{N}]^+ \text{X}^-$; $\text{X}^- = \text{F}^-$, Cl^- , Br^- , I^- , CH_3COO^- , NO_2^- , ClO_4^- , HSO_4^- , H_2PO_4^- , N_3^- , CN^-) to the acetonitrile solution of receptor **1**. The fluorescence emission spectrum of receptor **1** (conc = $2 \mu\text{M}$) showed a broad band at 345 nm when excited at 263 nm. Significant quenching of the fluorescence was observed on addition of fluoride and cyanide anions only and no quenching was observed upon addition of other anions. The changes observed in the fluorescence spectrum of a solution of receptor **1** in acetonitrile on addition of fluoride and cyanide up to 2.0 equivalents are depicted in Figure 4. A large quenching in intensity of the 345 nm band was observed on addition of 1.0 equivalent of fluoride anion indicating that on the formation of the hydrogen bonded complex, the excited state was modified considerably leading to the quenching of fluorescence. Again, a large quenching in intensity of the 345 nm band was observed on the addition of 1.0 equivalent of cyanide anion, which also indicates the formation of the hydrogen bonded complex between cyanide and receptor **1**. The spectral variations observed for receptor **1**

Figure 3. (A) Hydrogen bonded complex between fluoride/cyanide and receptor **1**; (B) changes in the $^1\text{H-NMR}$ spectrum in $\text{DMSO-}d_6$ of receptor **1**, $1:\text{CN}^-$ (1 equiv.) and $1:\text{F}^-$ (1 equiv.).

Figure 4. Changes in the fluorescence spectrum ($\lambda_{\text{ex}} = 263 \text{ nm}$) for receptor **1** ($2 \mu\text{M}$) in CH_3CN with the addition of, (a) $[(\text{Bu})_4\text{N}]\text{F}$ solution ($0.2 \mu\text{M} - 2 \mu\text{M}$), and (b) $[(\text{Bu})_4\text{N}]\text{CN}$ solution ($0.2 \mu\text{M} - 2 \mu\text{M}$).

Figure 5. Changes in the fluorescence spectrum ($\lambda_{\text{ex}} = 263 \text{ nm}$) for receptor **1** ($2 \mu\text{M}$) in CH_3CN with the addition of tetrabutylammonium salts of various anions ($2 \mu\text{M}$)

on titrating with different anions in 1:1 ratio (Figure 5), demonstrating the selective nature of receptor **1** as a chemical sensor for recognizing fluoride and cyanide anion.

4. Conclusions

In conclusion, a benzimidazole based receptor **1** has been designed and synthesized. Receptor **1** shows strong binding to F^- and CN^- ions via changes in UV-Vis spectrum, ^1H -NMR peaks and fluorescence emission intensity. We can expect that our study may provide guidelines towards the development of new benzimidazole based receptors with $-\text{NH}$ binding sites.

Supplementary Information (SI)

FT-IR, ^1H NMR, ^{13}C NMR and mass spectra of receptor **1** are available at www.ias.ac.in/chemsci.

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