Selective colorimetric sensing of fluoride ion and its use for insitu cyclization of the sensor

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ABSTRACT

Sensor **1** (a Schiff base) obtained by the condensation of 4-nitro-*o*-phenyldiamine and 2-hydroxy-1-naphthaldehyde can detect fluoride ion selectively through visual color change. Moreover, insitu cyclisation of sensor **1** to benzimidazole derivative **2** takes place by the help of fluoride ion as evidenced by X-ray crystal structure. The crystal structures of the sensor **1** and benzimidazole derivative **2** show that several types of weak C–H...X (X = O, N), C–H...π and π...π interactions play a crucial role along with intra/inter molecular H-bonding interactions for the stabilization of crystal lattice.

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1. Introduction

In recent years, the design and recognition of receptors capable of selective sensing of anions is an important research area of supramolecular chemistry for their crucial role in biological, industrial and environmental science [1–4]. Specially, development of colorimetric anion sensors is an appreciated field for qualitative and quantitative detection of anions. There are some examples of highly selective, sensitive and easy to use colorimetric anion sensor [5,6].

Among various important anions fluoride ion detection is most important because it plays vital role in biological system [7–12]. A number of compounds/sensors that are able to detect fluoride ion have been reported till now [13–16]. However, the challenge of selective detection and amplifying the fluoride ion sensing event to produce a measurable output still remains demanding. In this regard our interest is to synthesis colorimetric anion sensors that would allow the naked-eye detection of fluoride without using any spectroscopic instrumentation. Here, we report a remarkable chromogenic chemosensor (Schiff base **1**) synthesized by the condensation between 2-hydroxy-1-naphthaldehyde and 5-nitro orthophenyl diamine, which detects fluoride ion selectively. This work not only focus on a new naked-eye selective F⁻ ion sensor but also during this detection process fluoride ion helps in situ cyclization of the sensor to form a pharmaceutically important benzimidazole derivative **2** [17,18]. Furthermore, the formation of chemosensor **1** and benzimidazole derivative **2** have been supported by X-ray crystal structures.

Surprisingly, the crystal structure of the sensor (Schiff base) **1** shows that it exists in the keto form rather than enol form. Moreover, it forms a 3D supramolecular structure through different types of H-bonding interactions and π...π stacking interactions. On the other hand, the crystal lattice of compound **2** and tetrabutyl ammonium ion is stabilized by several C–H...O, C–H...N and C–H...π interactions.

2. Experimental

2.1. Reagents

All reagents and solvents were used as received from commercial sources without further purification. 4-nitro-*o*-phenyl diamine, 2-hydroxy 1-naphthaldehyde and 1-naphthaldehyde were purchased from Sigma Aldrich Chemicals. Spectroscopic grade solvents were purchased from Spectrochem and were used after proper distillation. The anions, tetrabutylammonium fluoride ($Bu_4N^+F^-$) hydrate (98%), tetrabutylammonium acetate ($Bu_4N^+AcO^-$) (97%), tetrabutylammonium dihydrogenphosphate ($Bu_4N^+H_2PO_4^-$) (97%),
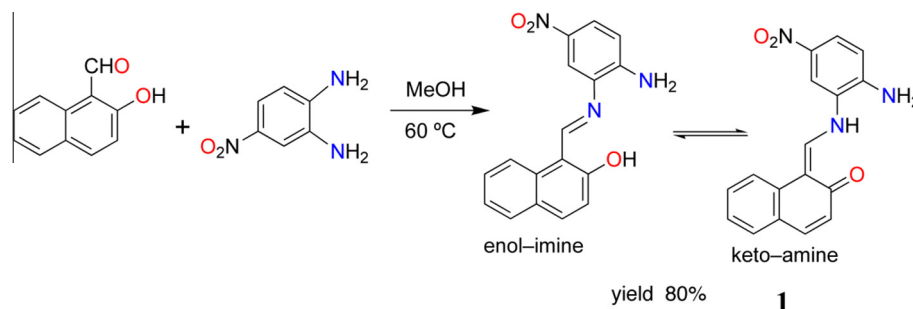
Scheme 1. Synthetic route of sensor **1**.

tetrabutylammonium chloride ($Bu_4N^+Cl^-$) hydrate (98%), tetrabutylammonium bromide ($Bu_4N^+Br^-$) (98%), tetrabutylammonium bromide ($Bu_4N^+I^-$) (98%), tetrabutylammonium nitrite ($Bu_4N^+NO_2^-$) (97%), and tetrabutylammonium cyanide ($Bu_4N^+CN^-$) (95%) were received from Sigma–Aldrich Chemical Company Pvt. Ltd.

2.2. Apparatus

Electronic absorption spectra were recorded on a Hitachi UV–Vis (Model U-3501) spectrophotometer. IR spectra (KBr pellet, 4000–400 cm^{-1}) were recorded on a Parkin Elmer modal 883 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker, Avance 300 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as internal standards.

The single crystal of compound **1** and **2** were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.71073 Å) radiation. The crystal was placed at 60 mm from the CCD and 360 frames were measured with a counting time of 5 s. The structure was solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program [19]. All calculations were carried out using SHELXS 97, PLATON 99, ORTEP-32 and WINGX system Ver-1.64 [19].

2.3. Synthesis of sensor **1**

The sensor **1** (1-[(2-amino-5-nitrophenyl)-vinyl]-naphthalen-2-ol) was synthesized by condensation between 4-nitro-o-phenyl diamine (0.34 g, 1 mmol) and 2-hydroxy naphthaldehyde (0.45 g, 1.2 mmol) in methanol (50 ml) at room temperature (Scheme 1). The solution was stirred under reflux conditions for 6 h, and the precipitate was filtered, washed with methanol three times, then recrystallized from chloroform and hexane (v/v, 1/3) to get reddish crystal of **1** (0.58 g) in 80% yield.

^{1}H NMR (300 MHz, d_6-DMSO, 20 °C) δ (ppm): 14.53 (s, 1H), 9.69 (s, 1H), 8.57 (d, J = 9 Hz, 1H), 8.13 (s, 1H), 7.99 (d, J = 9 Hz, 1H), 7.93 (d, J = 9 Hz, 1H), 7.85 (d, J = 9 Hz, 1H), 7.55 (t, J = 9 Hz, J = 9 Hz, 1H), 7.38 (t, J = 9 Hz, J = 9 Hz, 1H), 7.17 (d, J = 9 Hz, 1H), 6.81 (d, J = 9 Hz, 1H), 6.60 (s, 1H); ^{13}C NMR (75.5 MHz, d_6-DMSO, 20 °C) δ (ppm): 110.47, 113.91, 116.38, 119.96, 121.62, 124.19, 124.57, 124.72, 127.83, 128.52, 129.38, 133.07, 133.23, 136.08, 137.08,

149.89, 161.16, 163.66. IR (KBr): 3474, 3345, 1634, 1602, 1561, 1487, 1314, 1266 cm^{-1}.

2.4. Synthesis of compound **2**

The compound **2** (tetrabutyl ammonium salt of 1-(6-nitro-1H-benzoimidazol-2-yl)-naphthalen-2-ol) was obtained by the reaction between **1** (0.10 g, 0.03 mmol) and tetrabutyl ammonium fluoride (0.20 g, 0.06 mmol) in acetonitrile at room temperature. The solution was stirred for 12 h. The resultant solution was then crystallized by ether diffusion. While diethyl ether was diffused into the acetonitrile solution for four days to produce red colored crystals of **2** (0.06 g, 0.01 mmol) (Scheme 2) [20]. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C) δ (ppm): 10.09 (d, J = 8.5 Hz, 1H), 8.48 (s, 1H), 8.02 (d, J = 9 Hz, 1H), 7.61–7.1 (m, 7H), 2.48 (m, 8H), 1.34–0.76 (m, 28H), ^{13}C NMR (75.5 MHz, d_6-DMSO, 20 °C) δ (ppm): 13.89, 19.62, 23.50, 58.03, 110.46, 113.91, 116.32, 120.00, 121.60, 124.19, 124.56, 127.81, 128.55, 128.96, 129.39, 133.05, 133.23, 136.11, 137.08, 149.87, 161.12, 163.75. IR (KBr): 3535, 3165, 2944, 1637, 1443, 1375 cm^{-1}.

3. Results and discussion

The sensor **1** was obtained by the condensation between 4-nitro-o-phenyl diamine and 2-hydroxy 1-naphthaldehyde in methanol (Scheme 1). It was characterized by ^{1}H and ^{13}C NMR, IR spectra and single crystal X-ray analysis (Supporting information, Figs. S1–S4).

The IR spectra of **1** exhibits a peak at 1634 cm^{-1} which might be the carbonyl v(C=O) stretching band. This indicates that sensor **1** (a Schiff base) exists as keto–amine form in the solid state instead of the usual enol form [21]. However, ^{13}C spectra in d_6-DMSO does not exhibit C=O peak. This can be explained in terms of keto–amine tautomerization (—C=N— or =C—NH—) of the Schiff base [21]. Generally, these type of compounds prefer to exist as enol form in polar solvents [22].

To obtain the exact information about the structural features of Schiff base **1**, it was crystallized from chloroform–hexane mixture. The crystal structure shows that compound **1** crystallizes in the space group $P21/n$ (Table 1). Fig. 1 shows the molecular structure of **1**. Generally, most of the Schiff bases were isolated in the enol form in solid state [23]. Interestingly, here the Schiff base **1** exists as keto form rather than enol form as evidenced by the X-ray crystal analysis (Fig. S12). The crystal structure of **1** shows that the C—O bond distance (C101—O1) is 1.297(7)Å which is much shorter compared to the C—OH bond distance in the enol form (C—OH distance 1.3500 Å) [24]. It also supports the keto form of the Schiff base **1** in the solid state. This keto–amine form of **1** contains an intramolecular H-bond (distance 2.512 Å, Fig. 1, Table 2) between O1 (acceptor) and N2H106 (donor) [25].