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Highly selective colorimetric receptors for detection of fluoride ion in aqueous solution based on quinone-imidazole ensemble—Influence of hydroxyl group

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ABSTRACT

Two new quinone-imidazole ensembles are prepared, characterized and their fluoride ion sensing properties are investigated in aq. HEPES buffer-DMSO (70–30 v/v) medium (pH = 7.26). Introduction of phenolic hydroxyl group, as an additional H-bond donor moiety, is found to dramatically increase the selectivity of the receptors towards fluoride ion and also accommodates 70% of water in the sensing medium. The hydroxyl group is also found to reduce the acidity of the imidazole N—H proton significantly through its strong electron releasing resonance effect (Swain Lupton Constant R = −0.70). The colour of the solutions of these receptors instantaneously changes from yellow to red upon addition of fluoride ion, while it remains unaffected upon addition of other common anions. This observation is well supported by UV–vis, fluorescence titration and quantum yield determination studies. ^{1}H NMR titration indicates that the mechanism of sensing involves formation of H-bonding between fluoride ion and imidazole N—H and phenolic O—H moieties simultaneously with fairly high binding constants (10^5 M^{-1}). The results of electrochemical and theoretical studies substantiate the proposed mechanism.

1. Introduction

In recent years, recognition of anions by chemosensors has received considerable attention not only because of their important functions, but also for their potential toxicity to the environment and biological systems [1–3]. Among various anions, the detection of fluoride ion is most important because it plays vital role in biological system and is one of the essential trace elements required to form bones and teeth in human [4–7]. However, excessive intake of fluoride ion can cause many problems such as bone disorder, collagen breakdown, thyroid activity and depression etc. which are collectively known as fluorosis disease [8,9]. That is the beneficial or detrimental role of fluoride ion is concentration dependent. According to the World Health Organization (WHO) the maximum permissible limit of fluoride ion in drinking water is 1.5 mg/L [10]. Hence, it is important to develop highly selective, sensitive and rapid sensor for the detection of fluoride ion in aqueous solutions.

Review of literature revealed that molecules that possess functional groups such as urea/thiourea [11,12], amides [13,14], guanidinium [15], ammonium derivatives [16], indoles [17,18] and imidazoles [19,20] are proven to be effective because of their ability to bind fluoride ion using H-bonding interactions. The attachment of these type of functional groups with a suitable signaling unit such as nitro phenyl [21,22], azo dye [23,24] and quinone [25–27] provides complete receptors which can give the information of binding between the receptor and fluoride ion either by the change in colour, fluorescence or both. Recently we are in the process of developing fluoride ion sensors possessing quinone as the signaling unit that can work in aqueous medium [25,28,29], as fluoride ion sensing in aqueous medium is difficult due its very high hydration energy (−505 kJ/mol) [30,31].

Review of literature also revealed that when compared to receptors containing single hydrogen bond donor (HBD) groups, the one with multiple HBD moieties may possess increasing selectivity and also can accommodate substantial amount of water from the solvent [2,32–34]. Based on these observations, in this present work, we have developed two new receptors (**R1** and **R2**) for fluoride sensing by introducing a hydroxyl group as an additional HBD site in a previously reported naphthoquinone-imidazole hybrids **I** and **II** [35]. It was reported, by us, that the receptors **I** and **II** showed a colour change from yellow to red with both fluoride and cyanide ion in pure DMSO.

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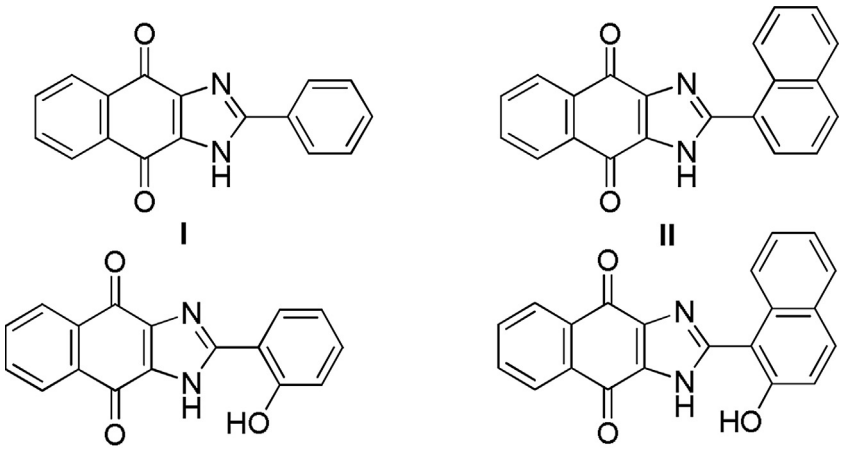

I II

R1 R2

As we presumed, to our delight, the receptors **R1** and **R2** sense fluoride ion selectively in aqueous medium. The main objective, therefore, of the present endeavor is synthesis, characterization and investigation on fluoride ion sensing behaviour of **R1** and **R2** in aqueous solution. The anion sensing properties of these receptors were carried out using visual detection experiment, various spectral techniques (UV–vis, fluorescence and ^{1}H NMR) and electrochemical and theoretical studies.

2. Experimental section

2.1. Chemicals and apparatus

All the reagents for the synthesis of the receptors were obtained commercially and were used without further purification. Spectroscopic grade solvents were used as received. UV–vis spectral studies were carried out on a double beam spectrophotometer. Steady state fluorescence spectra were obtained on a spectrofluorimeter. The excitation and emission slit width (5 nm) and the scan rate (250 mVs^{-1}) were kept constant for all of the experiments. Nuclear magnetic resonance spectra were recorded in DMSO-d_6 (^{1}H NMR 600 MHz, ^{13}C NMR 150 MHz). The ^{1}H NMR spectral data is expressed in the form: Chemical shift in units of ppm (normalized integration, multiplicity, and the value of J in Hz). Electro spray ion mass spectra (m/z) were recorded using LC/MSD TRAP XCT Plus (1200 Agilent).The differential pulse voltammetric (DPV) experiments, of 1 mmol solutions of the compounds, were carried out using GC as working, Pt wire as reference and Ag wire as auxiliary electrodes in DMSO containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 100 mVs^{-1}.

2.2. Synthesis of 2,3-diamino-1,4-naphthoquinone (1)

2,3-Diamino-1,4-naphthoquinone was prepared as reported earlier (Scheme 1) [36]. To a stirred solution of 2,3-dichloro-1,4-naphthoquinone (20 g, 0.09 mol) in aceotonitrile (400 mL), potassium phthalimide (32.6 g, 0.18 mol) was added. The reaction mixture was refluxed for 12 h under nitrogen atm. Afterwards the reaction mixture was cooled to RT and filtered through a filter paper and the residue was washed with water (300 mL). The yellow solid obtained was dried under vacuum. The fine yellow solid was transferred to a 1 L round bottom flask containing 500 mL of distilled water and then 100 mL of hydrazine hydrate (90%) was added to it. The reaction mixture was heated to 60 °C for 12 h. Finally the reaction mixture was cooled to RT, filtered through a filter paper and washed with water to get the pure product as a dark blue coloured powder (12 g, Yield = 72%). ^{1}H NMR (300 MHz, DMSO-d_6) δ_{ppm}: 5.46 (s, 4H), 7.57–7.61 (m, 2H), 7.74–7.77 (m, 2H) (Fig. S1).

2.3. Synthesis and characterization of R1

A mixture of **1** (0.5 g, 2.66 mmol) and salicylaldehyde (0.324 g, 2.66 mmol) in DMSO (5 mL) was heated at 90 °C with stirring for 6 h. After cooling to room temperature, the precipitate obtained was filtered from the reaction mixture using filter paper and was washed with cold ethanol to obtain the pure product (0.48 g, Yield = 62.18%) (Scheme 2). The product was characterized using ^{1}H and ^{13}C NMR and LC–MS techniques. The results are: δ_H (600 MHz; DMSO-d_6; Me_4Si): 6.91–6.94 (m, 1H), 6.95–6.97 (dd, 1H, J = 1.2 Hz, J = 7.8 Hz), 7.31–7.34 (m, 1H), 7.78–7.80 (m, 2H), 8.03–8.04 (m, 2H), 8.11–8.13 (dd, 1H, J = 1.2 Hz, J = 7.8 Hz) 12.312 (s, 2H) (Fig. S2); δ_C (150 MHz; DMSO-d_6; Me_4Si): 117.66, 119.81, 126.74, 127.36, 127.65, 132.63, 133.23, 134.37, 135.51, 158.00, 177.32, 180.63 (Fig. S3); LC–MS (ESI-APCI) m/z: Calcd. for $C_{17}H_{10}N_2O_3$ $[M+H]^+$: 290.07; Found: 291.0 (Fig. S4).

2.4. Synthesis and characterization of R2

A mixture of **1** (0.5 g, 2.66 mmol) and 2-hydroxy-1-naphthaldehyde (0.458 g, 2.66 mmol) in DMSO (5 mL) was heated at 90 °C with stirring for 6 h. After cooling to room temperature, the precipitate obtained was filtered from the reaction mixture using filter paper and was washed with cold ethanol to obtain the pure product (0.5 g, Yield = 55.24%) (Scheme 2). The product was characterized using ^{1}H and ^{13}C NMR and LC–MS techniques. The results are: δ_H (600 MHz; DMSO-d_6; Me_4Si): 7.24–7.25 (d, 1H, J = 9 Hz), 7.26–7.29 (t, 1H, J = 7.2 Hz), 7.36–7.38 (t, 1H, J = 7.2 Hz), 7.70–7.71 (d, 1H, J = 8.4 Hz), 7.78–7.81 (m, 3H), 7.88–7.90 (d, 1H, J = 9 Hz), 8.04–8.06 (m, 2H), 10.445 (s, 1H), 14.063 (s, 1H) (Fig. S5); δ_C (150 MHz; DMSO-d_6; Me_4Si): 109.60, 118.64, 123.66, 124.55, 126.76, 127.64, 128.09, 128.56, 132.25, 133.37, 133.49, 134.30, 150.23, 155.33, 178.39, 181.64 (Fig. S6); LC–MS (ESI-APCI) m/z: Calcd. for $C_{21}H_{12}N_2O_3$ $[M+H]^+$: 340.08; Found: 341.0 (Fig. S7).

3. Results and discussions

The two receptors **R1** and **R2** were synthesized from commercially available 2,3-dichloro naphthoquinone (Scheme 2). The structure of these receptors was characterized by ^{1}H and ^{13}C NMR and LC–MS spectral techniques. The anion binding and recognition ability of the receptors were investigated using UV–vis, fluorescence, ^{1}H NMR, electrochemical studies and DFT computations.