Sensors and Actuators B 215 (2015) 544–552

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Amino-naphthoquinone and its metal chelates for selective sensing of fluoride ions

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ARTICLE INFO

Article history:
Received 2 February 2015
Received in revised form 16 March 2015
Accepted 21 March 2015
Available online 17 April 2015

Keywords:
Sensors
Naphthoquinone
Fluoride
Complex
H-bonding

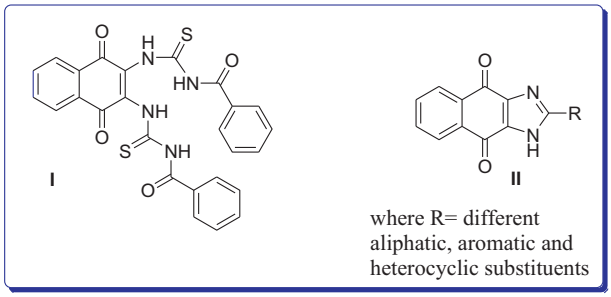
ABSTRACT

The fluoride ion sensing ability of 2-(2-(dimethylamino)ethylamino)-3-chloronaphthalene-1,4-dione (**R1**) and its metal chelates viz. [Cu(**R1**)Cl_2], [Co(**R1**)Cl_2].3H_2O, [Zn(**R1**)Cl_2] and [Ni(**R1**)Cl_2] was studied through visual detection experiment, UV-Vis, fluorescence and ^{1}H NMR titrations. The receptors were highly selective and sensitive for distinguishing fluoride ions from other common anions through a conspicuous change of UV–Vis and fluorescence spectra. The sensing mechanism, as confirmed by ^{1}H NMR titration, involves formation of H-bond between the N-H moiety and F^-ions. The coordination of metal ions was found to increase the H-bond donor ability of the receptor unit (N—H). The binding constant for the [Zn(**R1**)Cl_2] + F^- complex was found to be 6.2×10^4 M^{-1} which is 15 times higher than that of **R1** + F^- complex. The sensing mechanism was further supported by electro chemical studies and DFT calculations using Gaussian 03 program. The detection limits of the probes in the determination of F^- ions were found to 0.05–0.4 μM, which are lower than the World Health Organization (WHO) permissible level (1.5 mg L^{-1}).The test strips prepared using [Zn(**R1**)Cl_2] was found to impart striking colour change instantaneously with F^-ions in water.

1. Introduction

Owing to its important roles in preventing dental caries and in the treatment of osteoporosis [1,2], fluoride ions are widely used as an essential ingredient in toothpaste, pharmaceutical agents and even drinking water. As an essential element of the body, the World Health Organization (WHO) affirmed the optimal level to be 1.5 mg L^{-1} [3]. However, excessive intake of fluoride may cause fluorosis and also lead to nephrotoxic changes and urolithiasis in humans [4–6]. Thus, the diversity of its functions, both beneficial and otherwise, makes the detection of fluoride ions important. Consequently, during recent past, considerable effort has been devoted to the design of sensors for fluoride ions [7–12].

Receptor molecules that sense fluoride ion can be divided into two main classes: (i) Lewis acidic receptors that can bind covalently with fluoride ion and (ii) receptors capable of H-bonding with fluoride ion. In the second class of receptors the most common binding site used for sensing fluoride ion is N—H fragment such as urea/thiourea, imidazole, pyrrole, indole, amine and amide which can interact with fluoride ion through the formation of H-bond. The stability of the receptor-anion complex is strictly related to the acidic nature of the receptor (the N—H proton in particular) and the basic nature of the anion [13–15]. Recently, we have reported thiourea base receptor (I) for selectively sensing of fluoride ions in which the H-bond donor N—H fragment is directly attached to electron deficient quinone moiety (This also serves as the optical signaling unit).



It was observed that such an assembly substantially enhances the H-bond donor ability of the N-H fragment and the binding constant for receptor + F^- ion complex was as high as 10^{15} M^{-1} [16]. We have also reported a series of imidazole based receptors (II) with similar assembly where we are able to tune the acidity of the imidazole N—H fragment by varying the substituent (R) [13]. It is

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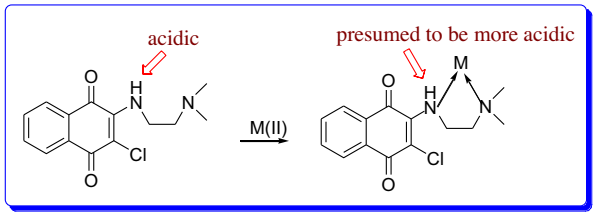
http://dx.doi.org/10.1016/j.snb.2015.03.105
0925-4005/

presumed that when the N-atom of such a N—H fragment is coordinated to a metal ion, the acidity of the N—H fragment (i.e. the H-bond donor property) would enhance further as shown below and also introduction of metal ions into the receptor molecule would take the whole molecule into aqueous solutions.



In line with our perception, recently we have reported a preliminary study on the fluoride ion sensing behavior of a amino quinone based receptor and its metal complexes [15,17]. In continuation of these studies here in the present endeavor we report an easy to make amino-naphthoquinone based receptor and its metal chelates as simple and highly selective fluoride ion receptors. The receptor and its metal [Cu(II), Co(II), Zn(II), Ni(II)] chelates were synthesized and characterized using elemental analysis (CHN), UV–Vis, FT-IR and ^{1}H NMR techniques. The structure of the receptor was confirmed by single crystal XRD study. The fluoride ion sensing properties of these receptors have been investigated using several spectral techniques such as UV–Vis, fluorescence and ^{1}H NMR in addition to electrochemical and theoretical studies.

2. Materials and methods

2.1. Chemicals

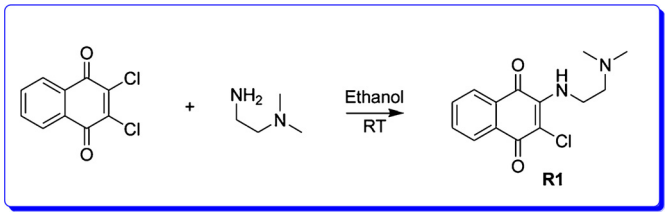
All the chemicals used in the present study were of high purity analytical grade (Aldrich, India) and were used as received. Commercially available spectroscopic grade solvents (Merck, India) were used as received. The solutions of anions were prepared from their analytical grade tetrabutylammonium salts.

2.2. Instrumentation

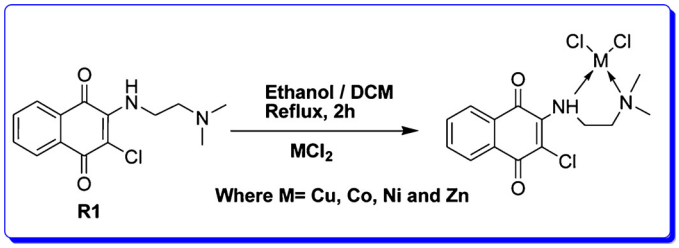
The electronic absorption spectra were recorded on a JASCO (V630, Japan) double beam spectrophotometer using 1 cm matched quartz cells. Steady state fluorescence spectra were obtained on a Caryeclipse fluorescence spectrophotometer (Agilent technologies). Nuclear magnetic resonance spectra were recorded in DMSO-d_6 (Bruker, ^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz). The ^{1}H NMR spectra data is expressed in the form: chemical shift in units of ppm (normalized integration, multiplicity, and the value of J in Hz). FT-IR spectra were recorded in a JASCO (FT-IR 460 Plus, Japan) spectrometer. Elemental analysis for CHN was performed at CSIR-Central Drug Research Institute, Lucknow (EuroVector EA 3000). EPR spectra were recorded at Madurai Kamaraj University, Madurai on JEOL FA3000, X-Band Microwave spectrometer using Mn marker as the standard. The geometrical optimization of the complexes was performed using Density Functional Theory with the B3LYP hybrid functional, by using a basis set of 6-31G. Computations have been performed using the Gaussian 03 Revision D.01 program package.

2.3. Synthesis of the receptor (R1)

To a stirred solution of 2,3-dichloro-1,4-naphthoquinone (1 g, 0.0044 mol) in 10 mL of ethanol, N,N′-dimethylethylenediamine (0.39 g, 0.0044 mol) was slowly added and the reaction mixture was stirred at RT for 1 h. The progress of the reaction was monitored by thin layer chromatography (TLC). Once the reaction has been completed, 20 mL of water was poured into the reaction mixture and extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. The reaction mixture was washed with n-hexane to get the pure product as a red solid 0.95 g (77%). The overall reaction is shown in Scheme 1.



Scheme 1. Synthesis of the receptor (**R1**).



Scheme 2. Synthesis of M(II)-Complexes.

The receptor was characterized using various analytical and spectral techniques and the results are: ^{1}H NMR (DMSO-d_6, 300 MHz) (ppm) δ 7.99-7.94 (t, J = 7.2 & 7.5 Hz, 2H), 7.85-7.72 (m, 2H), 7.22 (s, 1H), 3.83-3.77 (q, 2H), 2.15 (s, 1H); (Fig.S1),^{13}C NMR (DMSO-d_6, 75 MHz) δ 180.00, 135.17, 133.07, 132.40, 130.65, 126.78, 126.20, 58.88, 45.09, 42.06; (Fig.S2), LCMS (ESI-APCI) m/z: $[M+H]^+$calcd for $C_{14}H_{15}ClN_2O_2$, 278.73, found, 279.10 (Fig.S3). ^{1}H NMR (DMSO-d_6/D_2O, 300 MHz) (ppm) δ 7.91-7.87 (t, J = 5.7 & J = 6 Hz, 2H), 7.78-7.74 (t, J = 5.4 & 5.4 Hz, 1H), 7.70-7.66 (t, J = 5.4 & 5.1 Hz, 1H), 3.75-3.72 (t, J = 4.2 & 3.9 Hz, 2H), 2.46-2.43 (t, J = 4.5 & 4.5 Hz, 2H) (Fig. S4).

2.4. General procedure for the synthesis of metal chelates

The receptor **R1** (1.8 mmol) was dissolved in 10 mL of dichloromethane and then 1.8 mmol of chloride salt of metals dissolved in 10 mL of ethanol was added drop-wise and the reaction mixture was stirred and heated at 60 °C for 2 h. The solvent was allowed to evaporate slowly to produce the solid product. The resultant product was collected by filtration and washed with dichloromethane and ethyl acetate (Scheme 2).

3. Results and discussion

3.1. Characterization of receptor R1

Facile condensation of N,N-dimethylethylenediamine with 2,3-dichloro-1,4-naphthoquinone in ethanol yielded the receptor **R1**. The receptor **R1** was characterized using elemental analysis (CHN), FT-IR, UV-Vis, ^{1}H and ^{13}C NMR and LC-MS techniques (see Section 2). The molecular structure of **R1** is determined by X-ray crystallography. The crystal structure of **R1** with atom numbering scheme is shown in Fig. 1 and the crystal data are collected in Table S1. **R1** has the Orthorhombic space group pbca with cell parameters a = 8.6370(3) Å, b = 13.9230(5) Å, c = 24.0680(9) Å and z = 8. The crystal packing of **R1** is depicted in Figure.S6 and the bond lengths and bond angles are collected in Table S2. The two carbonyl bond