



Spectroscopic, electrochemical and theoretical studies on anion recognition by receptors with redox active ferrocene and quinone centers bridged by imidazole



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ABSTRACT

Two chromogenic sensors possessing two redox-active centers (quinone and ferrocene) bridged by imidazole anion recognition group have been synthesized and screened for their anion sensing properties. Both the receptors exhibited dramatic color change upon the addition of fluoride and cyanide ions so that we could finish anion recognition by visual detection without resorting to any spectroscopic instruments. The evaluation of the receptor interaction with anions was performed by UV–Vis titration experiments in DMSO. UV–Vis titrations revealed that receptor **1**, wherein the imidazole moiety is directly attached to naphthoquinone unit, exhibited a relatively larger bathochromic shift of the intramolecular charge transfer (ICT) band than **2** in which the imidazole receptor unit is away from the quinone moiety. Receptor **1** displays a higher ($\Delta\delta = 0.269, 0.352$ ppm) downfield shift of the imidazole N–H proton than **2** ($\Delta\delta = 0.070, 0.122$ ppm) indicating that the anion binding pattern of these chemosensors was H-bond interaction. Also, the UV–Vis and ^1H NMR results indicated that the receptor– CN^- binding is relatively stronger than receptor– F^- interaction. The redox activities of the quinone and ferrocenyl centers in **1** and **2** have been characterized by cyclic and differential pulse voltammetries. Electrochemical titrations revealed that the receptor **1** sensed CN^- ions with an anodic shift of -198 mV in the oxidation potential of ferrocene moiety when compared to -188 mV with the receptor **2**. Addition of incremental amounts of F^- and CN^- ions, to these two receptors, shifts the $E_{1/2}$ of the quinone redox couple to less negative potentials. DFT (B3LYP/3-21G) calculations performed for both free receptor and receptor–anion complexes are in good agreement with the observed spectroscopic and electrochemical data.

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1. Introduction

Since the ubiquity of anions and their importance as agricultural, fertilizer and industrial raw materials necessitates the development of highly sensitive anion sensors [1]. The reason for this intensive interest is the importance of the detection of anions in disciplines such as biology and environmental sciences [2]. Among the interest in biologically functional anions, fluoride is one of particular importance owing to its established role in dental care [3] and treatment of Osteoporosis [4]. However, excessive use may create fluorosis resulting in the discoloration of teeth [5,6]. Although cyanide has been used as poison for centuries, it was not until 1782 that this anion was first isolated by the Swedish chemist Scheel [7]. The extreme toxicity of cyanide in physiological systems,

as well as the continuing environmental concern caused by its widespread industrial use, has led to considerable reach in to the development of methods for cyanide detection. A large range of anion sensors that provide either optical or electrochemical responses have been reported.

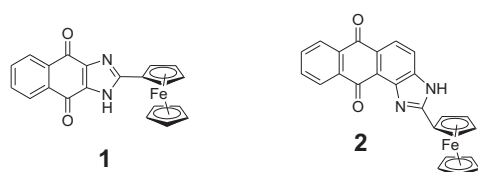
In general chemical sensor composed of two basic parts: recognition unit and signal transduction unit. A survey of literature revealed that, various authors have developed chemosensors containing urea/thiourea [8], calixarene [4]-pyrrole [9], indole [10], imidazole [11], calixarene [12], and hydrazine [13] as receptor units. Moieties such as quinone [14], nitrophenyl [15] and azo dye [16,17] were used as signaling units.

Among examples of electrochemical anion sensors, receptor molecules that incorporate ferrocene (Fc) moiety have enjoyed considerable popularity. This is due to the readily accessible Fc/Fc^+ redox couple and the extensive electrochemistry of Fc that exist in the literature. Literature survey revealed that the redox-responsive ferrocene unit has been incorporated into amide [18], urea [19],

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thiourea [20], dendrimers [21] and imidazole [22] moieties to construct the anion receptors with electrochemical sensing properties. The driving force responsible for the anion binding ability of these receptors in their neutral ferrocene form is usually the H-bonding interaction between the guest anion and H-bond donor groups appended to the receptor. Other redox active moieties such as cobaltacene [23,24] and quinone [25] have also been reported.

Despite the development of these classical optical or electrochemical receptors for anion sensing, there is paucity of use of multi-channel signaling anion chemosensor molecules. Also, the development of simple and easy-to-make chemosensors for anions is strongly desired. From this perspective, we decided to investigate two electro-optical sensors (**1** and **2**) by combining the redox activities of ferrocene and quinone moieties with the strong H-bond donor ability of the imidazole N–H group. The two redox active centers were so chosen that the redox couple of these two moieties would appear at two different well separated potential windows.



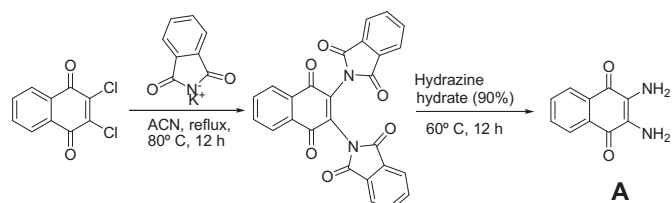
Though the cyanide ion sensing property of the receptor **2** in acetonitrile/water mixture has already been reported [26], we have taken this receptor for comparison in the present study. Such a comparative study is essential because recently we have demonstrated the effect of intensity of intramolecular charge transfer transition on the sensing event with these two quinone based thiourea moieties [27]. Further in the present article a detailed investigation on the electrochemical behavior and theoretical studies of the receptor **2** have been reported which was absent in the earlier report. Also, we have carried out the anion sensing behavior of the receptor **2** in DMSO and observed significantly different results when compared to that of previously reported one [26].

The main objective, therefore, of the present endeavor is to synthesize two imidazole based receptors **1** and **2** (Schemes 1 and 2) and to make use of these molecules as sensors for anions. The sensing behavior of these two receptors has been investigated via multi-channel ways i.e. using visual detection, electronic and ^1H NMR spectral and electrochemical techniques.

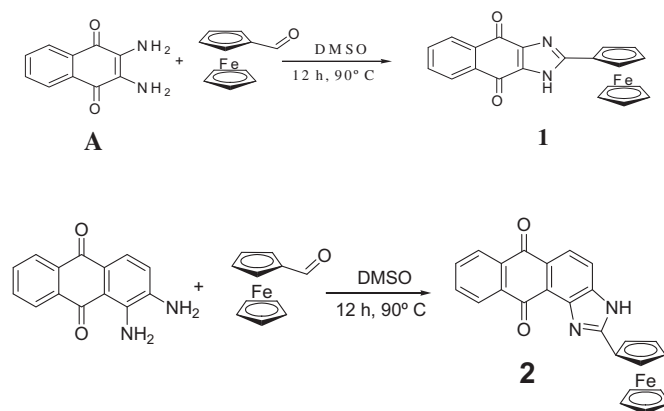
2. Experimental section

2.1. Chemical and apparatus

All reagents for 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 in DMSO on a (JASCO V-630-double beam



Scheme 1. Synthesis of 2,3-diaminonaphthoquinone (**A**).



Scheme 2. Synthesis of receptors **1** and **2**.

spectrophotometer). Nuclear magnetic resonance spectra were recorded in DMSO- d_6 in Madurai Kamaraj University, Madurai (Bruker, ^1H NMR, 300 MHz). The ^1H NMR spectra data is expressed in the form: Chemical shift in units of ppm (normalized integration, multiplicity and the value of J in Hz). Cyclic and Differential Pulse voltammeteries were performed with a conventional three electrode system consisting of a glassy-carbon-disk working electrode which was polished using 0.05 μm (alumina/water slurry) and rinsed thoroughly with double distilled water and DMSO. Solutions for CV and DPV were typically 1.0 mM in the redox-active species and were deoxygenated by purging with nitrogen.

2.2. Synthesis process

2.2.1. Synthesis of 2,3-diaminonaphthoquinone (**A**)

To a stirred solution of 2,3-dichloro-1,4-naphthoquinone (20 g, 0.0881 mol) in ACN (400 mL) potassium phthalimide (19.66 g, 0.1061 mol) was added. The reaction mixture was refluxed for 12 h under nitrogen atm. Afterward the reaction mixture was cooled to RT, filtered through the filter paper and the settled residue was washed with water (300 mL). The getting yellow solid obtained was dried under vacuum. The fine yellow solid was transferred in to a 1 L single neck RB with 500 mL of distilled water, and then 100 mL of hydrazine hydrate (90%) was added to the reaction mixture and heated to 60 °C for 12 h. Finally the reaction mixture was cooled to RT, filtered through the filter paper and washed with water to get the pure product as a dark blue colored powder (**A**) (Scheme 1) (12 g, Yield = 72%).

2.2.2. Synthesis of 2-ferrocene-1H-naphtho[2,3-d]imidazole-4,9-dione (**1**)

A mixture of 2,3-diamino-1,4-naphthoquinone (**A**) (1 g, 0.0053 mol) and ferrocene carboxaldehyde (1.137 g, 0.0053 mol) in 5 mL of DMSO was stirred and heated at 90 °C under nitrogen atmosphere for 12 h. After completion of reaction, the reaction mixture was cooled to RT and the precipitate formed was filtered through the filter paper and washed with cold ethanol to give dark brown solid (1.3 g, Yield = 64.0%).

^1H NMR (300 MHz, DMSO- d_6) δ (ppm) 13.83 (s, 1H), 8.10 (m, 2H), 7.85 (m, 2H), 5.16 (s, 2H), 4.52 (s, 2H), 4.15 (s, 5H). LC-MS m/z ($M + \text{H}$) $^+$ calcd. 382.0, found 383.0. Elemental analysis: Anal. Calcd. for $\text{C}_{21}\text{H}_{14}\text{FeN}_2\text{O}_2$: C, 65.99; H, 3.69; N, 7.33. Found: C, 65.46; H, 3.72; N, 7.37.

2.2.3. Synthesis of 2-ferrocene-3H-anthra[2,1-d]imidazole-6,11-dione (**2**)

Though the receptor **2** has already been reported [26], we have adopted a different methodology to prepare it. A mixture of

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