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Spectral and electrochemical studies on anion recognition by ferrocene based imidazoles possessing different electron acceptor moieties

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ABSTRACT

A series of four ferrocene based imidazoles (**R1**–**R4**), in which the imidazole is attached to different electron acceptor moieties were designed, synthesized and characterized. The anion binding studies were carried out using various techniques including electrochemistry, fluorescence and ^{1}H NMR spectroscopy. Fluorescence studies indicated the formation of strong complexes (Binding constant K_A in the order of 10^6 M^{-1}) between the receptors and cyanide ion selectively. ^{1}H NMR titrations demonstrated that **R1**–**R4** bind cyanide ion through imidazole N–H…CN^- hydrogen bond formation. Electrochemical studies using cyclic voltammetric technique displayed "two-wave behaviour" with a cathodic shift of the ferrocene/ferrocenium redox couple ($\Delta E_{1/2}$) up to 269 mV with cyanide ion with a high selectivity. The practical applicability of the receptor has also been investigated.

1. Introduction

In recent decades increasing attention has been devoted to the development of anion recognition systems, as anions are ubiquitous in biological milieus. Among various anions, cyanide is one of the most studied anions because of its extreme toxicity and usage in various industrial processes such as electroplating, plastic manufacturing, tanning and metallurgy [1,2]. One of the popular strategies adopted for the design of sensors for cyanide is based on the use of H-bonding interaction between the anion and the receptor moiety. But the selectivity of these sensors toward cyanide ion is only modest [3–5]. A survey of literature revealed that a large range of anion sensors that provide either optical or electrochemical responses have been reported [6–8]. Among examples of electrochemical anion sensors, molecules that incorporate ferrocene (Fc) moiety have enjoyed considerable popularity. This is due to good thermal stability and excellent redox properties of ferrocene [9–11]. As a result many ferrocene based anion sensors with electrochemical sensing properties, have been constructed incorporating receptor units such as (thio)urea [12,13], amide [14], dendrimers [15] and imidazole [16].

Very recently we have reported two chromogenic sensors possessing two redox-active centres, ferrocene and quinone (I and II) bridged by imidazole anion recognition group [17]. Both these receptors exhibited dramatic colour change from yellow to intense red upon addition of cyanide and fluoride ions in DMSO.

It is presumed that, though these two compounds exhibited striking colour change and excellent spectral and electrochemical changes, the absence of selectivity towards either one of the anions may be due to the presence of strong electron withdrawing quinone as the signalling unit directly attached to the receptor moiety (N–H). Therefore, we thought of constructing newer receptor molecules by replacing the quinone moieties (in I and II) with relatively weaker electron withdrawing moieties. By doing so we feel that one can tune the H-bond donor property of the N–H moiety and thus may increase the selectivity of the receptor towards any one of anions. Keeping this strategy in mind, we, in the present endeavour, have designed the following four ferrocene based receptors for electrochemical recognition of anions.

Though ferrocene containing imidazopyridine and imidazophenazine have been reported as multichannel probes for selective and sensitive sensing for Pb(II) ions [18], to the best of our knowledge, none of the above four receptors have been tried in anion recognition investigations. The main objective therefore, of the present endeavour is to investigate the anion recognition

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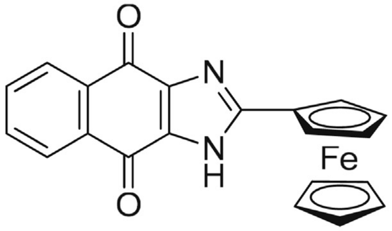
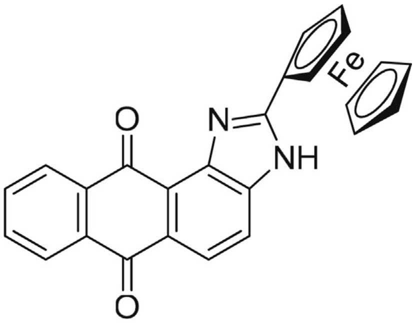


I



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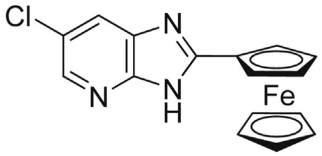

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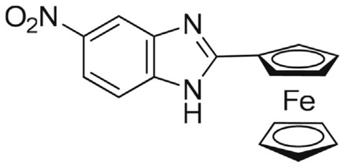

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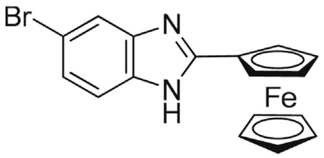
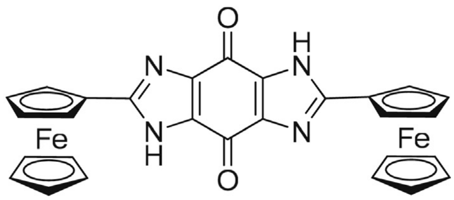


R3



R4

properties of these receptors using spectral (fluorescence and ^{1}H NMR) and electrochemical techniques and theoretical studies.

2. Experimental section

2.1. Chemicals and apparatus

All the reagents for synthesis of the receptors **R1**–**R4** were obtained commercially and were used without further purification. Spectroscopic grade solvents were used as received. UV–Vis spectral studies were carried out in a double beam spectrophotometer. Steady state fluorescence spectra were obtained on a spectrofluorimeter. The excitation and emission slit width (5 nm) and the scan rates (250 nm) were kept constant for all of the experiments. Nuclear magnetic resonance spectra were recorded in DMSO-d$_6$ (^{1}H NMR 300 MHz, ^{13}C NMR 75 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). The ^{13}C NMR spectrum of **R4** was not recorded due to its low solubility. The cyclic voltammetric (CV) 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 DMF containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte at a scan rate of 100 m Vs^{-1}.

2.2. Synthesis and characterization of **R1**

5-Chloropyridine-2,3-diamine was prepared as reported earlier [19]. To a mixture of ferrocene-2-carboxaldehyde (0.5 g, 2.3 mmol) and 5-chloropyridine-2,3-diamine (0.34 g, 2.3 mmol) in ethanol (5 ml) 0.1 ml of concentrated sulphuric acid was added and heated at 80 °C with stirring for 24 h. After cooling to room temperature, water was added to the reaction mixture and the precipitate obtained was filtered through a filter paper and washed with ethylacetate and diethylether to get the pure product as a brownish yellow solid (0.45 g, Yield = 57%). The product was characterized using ^{1}H and ^{13}C NMR and LC-MS spectral techniques.

δ_H (300 MHz; DMSO-d_6; Me$_4$Si): 4.13 (s, 5H), 4.55 (s, 2H), 5.12 (s, 2H), 8.06 (s, 1H), 8.25 (s, 1H), 13.26 (s, 1H) (Fig. S1); δ_C (75 MHz; DMSO-d_6; Me$_4$Si): 68.26, 70.06, 71.06, 73.18, 122.17, 124.89, 132.91, 141.43, 143.24, 158.87. (Fig. S2); Elemental Analysis. Calcd. for $C_{16}H_{12}ClFeN_3$ (%): C, 56.93; H, 3.58; N, 12.45. Found (%): C, 57.04; H, 4.08; N, 12.51. LC-MS (ESI-APCI) *m*/*z*: $[M-H]^+$ Calcd. for $C_{16}H_{12}ClFeN_3H$, 336.0, found, 336.0 (Fig. S3).

2.3. Synthesis and characterization of **R2**

The receptor **R2** was prepared by adopting the same procedure as that of **R1** by using ferrocene carboxaldehyde (0.5 g, 2.3 mmol) and 4-nitrobenzene-1,2-diamine (0.36 g, 2.3 mmol). The pure product obtained is a brownish yellow solid (0.48 g, Yield = 59%). The product was characterized using ^{1}H and ^{13}C NMR and LC-MS spectral techniques.

δ_H (300 MHz; DMSO-d_6; Me$_4$Si): 4.13 (s, 5H), 4.57 (s, 2H), 5.11 (s, 2H), 7.64 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H), 13.08 (s, 1H) (Fig. S4); δ_C (75 MHz; DMSO-d_6; Me$_4$Si): 68.33, 70.08, 71.07, 72.95, 116.24, 117.92, 121.68, 136.00, 138.28, 142.64, 153.11. (Fig. S5); Elemental Analysis. Calcd for $C_{17}H_{13}FeN_3O_2$ (%): C, 58.82;