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Synthesis and electrochemical sensing behaviour of a new ferrocene functionalized tet 'a' macrocyclic receptor towards transition metal ions

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A new ferrocene functionalized macrocyclic receptor 1,8-bis(ferrocenylmethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (R) has been designed and synthesized to study its potential application as chemosensor. The receptor has been characterized by spectral techniques and X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pcab* with four molecules in a unit cell (half-a-molecule in the asymmetric unit). The electrochemical studies of the receptor in dioxane–water (7 : 3 v/v, 25 °C) indicate that the receptor is pH-dependent with a displacement of $E_{1/2}$ to more anodic potentials with a decrease in the pH from 12 to 5. The electrochemical behaviour of R was also studied in the presence of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in dioxane–water (7 : 3 v/v, 25 °C, $[Bu^n{}_4N][ClO_4]$), showing that upon complexation the ferrocene–ferrocenium half-wave potential shifts anodically in relation to that of the free receptor. The maximum electrochemical shift ($\Delta E_{1/2}$) of 46 mV was found in the presence of Cu^{2+}, followed by Co^{2+} (20 mV), Mn^{2+} (15 mV), Ni^{2+} (13 mV) and Zn^{2+} (9 mV). Moreover, the receptor R is able to electrochemically and selectively sense Cu^{2+} in the presence of the other transition metal cations studied. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: chemosensors; X-ray structure; copper (II) ion sensor; ferrocene; electrochemistry

INTRODUCTION

The design of molecular receptors having the ability to selectively bind and sense cationic, anionic, or even neutral guests via a macroscopic physical response is an area of intense activity.[1–4] The receptor incorporates a redox centre near binding sites, which gives the ability to recognize substrates electrochemically. Owing to the nature of the binding domains, cation/anion recognition studies have been carried out and emphasis has been placed on the potential selective redox recognition. The commonly employed redox-active centres in electrochemical chemosensors are ferrocenes, nitrobenzenes and quinines.[5] Electrochemical sensors containing the ferrocene entity have been reported and those studies indicate that the cation selectivity could be achieved by tailoring the cavity size (Scheme 1).[6–12] Although ferrocene appended to cyclam and other polyaza and polyoxaaza macrocycle have been reported, the ferrocene-functionalized tet'a' macrocycle has not yet been reported.

The main interest in the present work is the incorporation of the redox centre, ferrocene, near the macrocyclic binding sites, namely tet'a' (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) to obtain the receptor (R) for the determination of biologically important guest molecules. The binding properties of the macrocycle may differ with different cations and anions, and these differences can affect the redox properties of the ferrocene moiety, which is in close proximity to the macrocycle via electrostatic interactions. In this paper, the synthesis and characterization of receptor R and its electrochemical behaviour towards first-row transition

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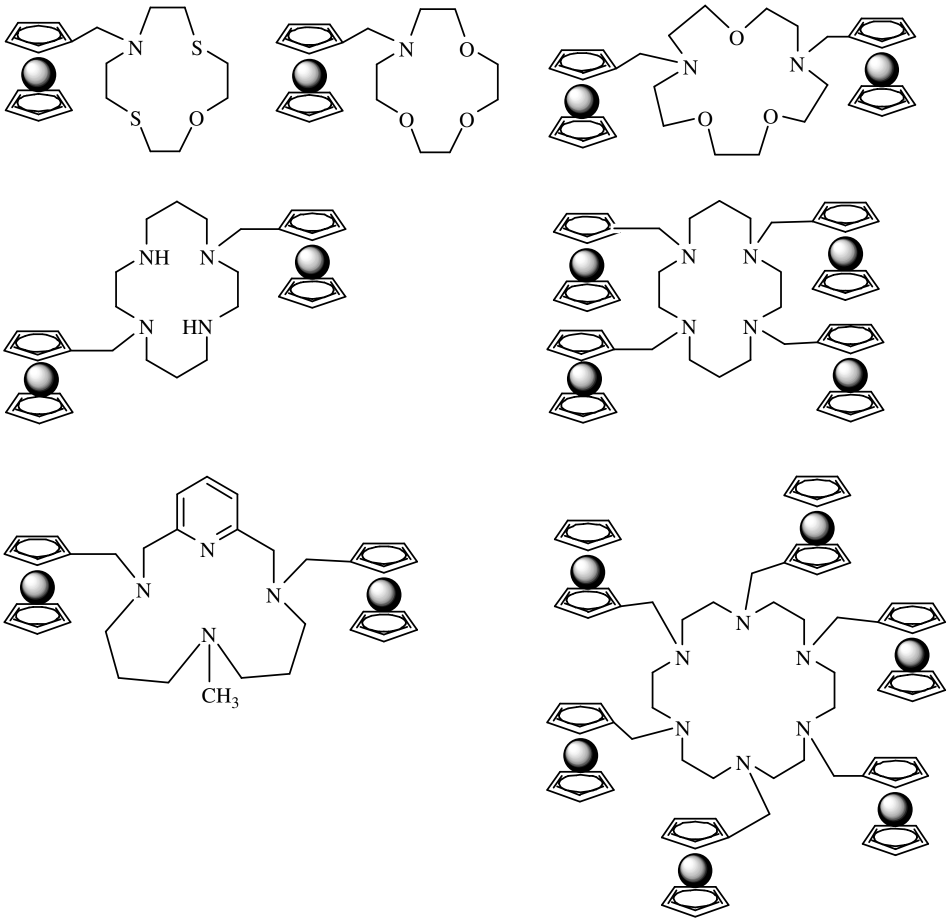


Scheme 1. Examples of ferrocene containing chemosensors.

metal ions such as Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} has been reported. The crystal structure of the free receptor R is also reported.

EXPERIMENTAL

Materials

Acetonitrile (CH_3CN) was pre-dried over molecular sieves (4–8 mesh) and then distilled under nitrogen from calcium hydride. 1,4-Dioxane and water were of HPLC grade. *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraaza cyclotetradecane and *N*,*N*′-dimethylaminomethyl ferrocene methiodide were prepared by the literature methods.[13,14] Tetra(*n*-butyl) ammonium perchlorate (TBAP), used as the supporting electrolyte in the electrochemical measurements, was purchased from Fluka and recrystallized from hot methanol. (*Caution!* TBAP is potentially explosive; hence, care should be taken in the handling of the compound.) Metal (II) ions such as Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were used as their perchlorate salts. All other chemicals and solvents were of analytical grade and used as received.

Physical measurements

Elemental analysis was carried out on a Carlo Erba model 1106 elemental analyzer. ^1H NMR and ^{13}C NMR spectra were recorded using a model FX-80-Q Fourier transform nuclear magnetic resonance spectrometer. FT-IR spectra were recorded on a Perkin-Elmer RX1 model spectrophotometer on KBr discs in the wavenumber range 4000–250 cm^{-1}. Electronic spectral studies were conducted on a Perkin-Elmer Lambda 35 Model spectrophotometer in the wavelength range 200–800 nm. Electrochemical studies were carried out using CHI600A electrochemical analyser. The measurements were carried out under oxygen-free conditions using a three-electrode cell, in which a glassy carbon electrode was the working electrode, a saturated Ag–AgCl electrode was the reference electrode and a platinum wire was used as the auxiliary electrode. Tetra(*n*-butyl) ammonium perchlorate was used as the supporting electrolyte. The pH of the solutions was adjusted with millimolar solutions of $HClO_4$ and KOH and monitored using a pH meter. The electrochemical response was recorded after progressively adding aliquots of stock solutions in suitable solvent mixture dioxane : water (7 : 3 v/v) containing sub-stoichiometric or stoichiometric equivalents of metal ions.

Synthesis of 1,8-bis(ferrocenylmethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane R

Compound *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza cyclotetradecane (1.6 g, 0.005 mol) was dissolved in dry acetonitrile (100 cm^3) with anhydrous potassium carbonate (6.9 g, 0.05 mol). To this was added *N,N′*-dimethylaminomethyl ferrocene methiodide (3.85 g, 0.01 mol) and the solution was refluxed under nitrogen atmosphere for 36 h. During this time trimethylamine evolved, which was detected by pink litmus paper. After cooling, the precipitate was filtered off, the solvent evaporated and the residue dissolved in dichloromethane (100 cm^3). This solution was washed with several portions of water ($3 \times 100\ \text{cm}^3$). The organic phase was dried with $MgSO_4$, filtered and evaporated to dryness. The brown oil obtained was purified by silica column chromatography using dichloromethane, then dichloromethane–methanol with increasing amounts of methanol (5–20%). The dark brown compound eluted in the final fractions, after evaporation of the solvent, was recrystallized from chloroform. Yield: 2.55 g (75%) m.p. 178 °C. FT-IR (cm^{-1}) (KBr): 3250 (N-H Str.), 3090 (C-H str. of ferrocene), 2950, 2800 (alkyl C-H str.), 2250 (CN Str.). ^{1}H NMR ($CDCl_3$): δ 4.1 (18H, s, **H** of ferrocene), 3.50 (4H, s, $C_5H_4C\mathbf{H}_2N$), 2.77 (2H, s, N**H**), 2.70 [2H, t, $J = 3$ Hz, NC**H**(CH_3)], 2.50–2.67 (8H, m, $NC\mathbf{H}_2C\mathbf{H}_2N$) and 1.35 [4H, m, C(CH3)2-C**H**2-CH(CH3)], 0.92–1.08 (18H, m, all CH_3 protons). EI mass spectrum: *m*/*z* 680 (M^+) (calcd for $C_{38}H_{56}Fe_2N_4$: C, 67.1, H, 8.2, N, 8.2; found: C, 66.8, H, 8.1, N, 8.1). UV–vis (CH_3CN) [$\lambda_{\max}$, nm (ε, $\text{M}^{-1}\ \text{cm}^{-1}$)]: 433 (305).

RESULTS AND DISCUSSION

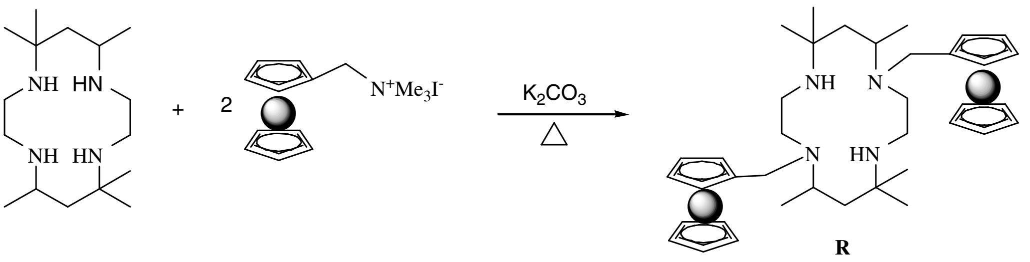
Synthesis and characterization of R

The receptor 1,8-bis(ferrocenylmethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane was synthesized using a simple route in good yields (Scheme 2) when compared with cyclam and other polyaza and polyoxaaza macrocyclic receptors. The R was characterized by IR, NMR and electronic spectral techniques. The elemental analysis generally showed good agreement between the values expected and those obtained. The suitable crystals of R for the single X-ray diffraction analysis were obtained by slow evaporation of the solvent mixture dichloromethane–methanol (v/v, 90 : 10) containing the desired compound. The compound crystallizes in the orthorhombic space group *Pcab* with four molecules in the unit cell (half-a-molecule in the asymmetric unit). The molecular structure was solved by direct methods and refined by full-matrix least-squares procedures. SHELXS97 and SHELXL97[15] programs were used for structure solution and structure refinement, respectively. Full crystal data and structure refinement details, atomic coordinates, equivalent isotropic displacement parameters, full interatomic distances and angles, and anisotropic displacement parameters for the receptor (R) are available from the Cambridge Crystallographic Data Centre CCDC, no. 283261. During the course of the present investigation, the synthesis and X-ray crystal structure of the receptor R were also reported by Tian *et al.*[16]

Redox properties of R

The cyclic voltammograms of R were obtained in dioxane–water (7 : 3 v/v) using 0.1 M TBAP as supporting electrolyte vs Ag–AgCl over a wide pH range from 12 to 4 (Fig. 1). Cyclic voltammograms of the receptor exhibits one well-defined reversible two-electron wave over a large pH range, suggesting that the two ferrocene moieties become oxidized in one step.[17] For example, the receptor shows one oxidation peak at 445 mV and the corresponding reduction peak at 340 mV when the sweep is reversed at pH 7.5. The oxidation–reduction couple appears to be reversible because: (i) there is a separation peak of ca. 105 mV (100 mV found for ferrocene under similar conditions); (ii) there are no shifts of the half-wave potentials with varying scan rates; and (iii) the anodic and cathodic intensities ratios are close to unity. The plots of i_p vs $\upsilon^{1/2}$ (i_p = anodic peak intensity and υ = scan rate) also indicate that the oxidation is controlled by diffusion (data not shown). The controlled potential electrolysis carried out for the receptor at 100 mV more positive to the oxidation potential consumed two electrons per molecule ($n = 1.92$), which is typical of a bis(ferrocenyl) derivative with non-interacting ferrocene units. Therefore, the oxidation process is assigned as follows:

$$2\text{Fe}^{\text{II}} \rightleftharpoons 2\text{Fe}^{\text{III}}$$



Scheme 2. Synthesis of the receptor (R).

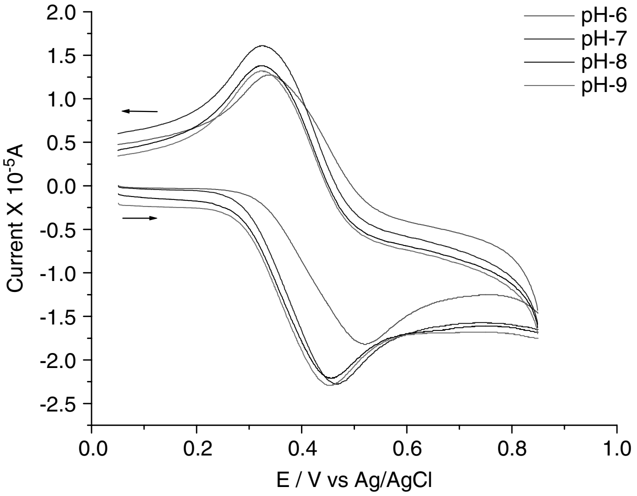


Figure 1. Cyclic voltammograms of the free receptor (R) at pH 6, 7, 8 and 9 {[R] = 10^{-3} M in dioxane : water mixture (7 : 3 v/v); measured by CV at 100 mV s^{-1}; *E* vs Ag/AgCl; GC working and Ag/AgCl reference electrodes; supporting electrolyte, TBAP}.

Influence of pH on electrochemical behaviour of R

The electrochemical studies carried out for the receptor R in dioxane : water mixture (7 : 3 v/v) indicate that the reversible nature and the half-wave potential $E_{1/2}$ of the receptor is pH-dependent. It is observed that the ΔE value for the redox couple of the receptor R at pH 11 is 102 mV and at pH 6 it is 184 mV. These values indicate that the reversibility of the redox couple decreases while decreasing the pH of the medium from 11 to 6. It is also observed that there is a displacement of $E_{1/2}$ to more anodic potentials with a decrease in the pH from 12 to 5 (Figs 1 and 2). The decrease in pH induces the neutral receptor molecule to charged species, resulting in an electrostatic interaction between the charged species and the ferrocenyl moieties, thereby altering its redox potential. The difference between the oxidation potential under basic (pH $\approx$ 12) and acidic (pH $\approx$ 5) conditions was found to be 132 mV. This observation is as expected due to the presence of the charged ammonium groups which make receptor oxidation more difficult; the amine protonation builds up positive charge close to the ferrocene nucleus and this electrochemically repels the ferrocenium cations through space, thermodynamically hindering its oxidation.

It is observed that the change in electrochemical shifts over the pH range 12–5 is not gradual for R. Two deflections in the redox potentials of receptor are observed, the first one between pH 10 and 9 and the second one between pH 7 and 6. These two deflections may be attributed to the difference in protonation behaviour of the strong base-secondary amines and weaker base-tertiary amines present in the receptor respectively.[18] It is also observed that there is no appreciable change in the redox potential of the receptor on further decrease in the pH from 5 to 4. This may be due to the fact that there is no further protonation taking place in the receptor.[19,20] Thus these changes in redox potential of the ferrocene moiety in the receptor with respect to pH of the medium indicate that the receptor R can be used as a good pH responsive electrochemical sensor.

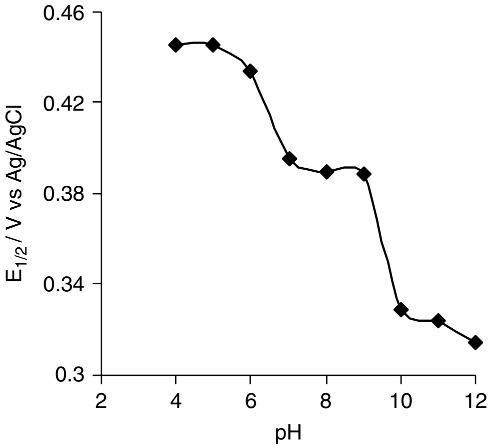


Figure 2. The plot of $E_{1/2}$ vs pH for free receptor (R) over the pH range from 4 to 12 {[R] = 10^{-3} M in dioxane : water mixture (7 : 3 v/v)}.

Electrochemical behaviour of receptor in the presence of transition metal ions

We have electrochemically studied the shift of $E_{1/2}$ vs pH for the L–H^+—M^{2+} systems (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}; M^{2+}: L, molar ratio = 1 : 1) in dioxane : water mixture (7 : 3 v/v). The cyclic voltammograms of the free receptor (R) and in the presence of metal (II) ions (R/M^{2+}) at pH 8 is shown in Fig. 3. In order to rationalize all these data, the difference found between $E_{1/2}$ for the receptor–metal system and that for the free receptor ($\Delta E_{1/2}$), [$\Delta E_{1/2} = E_{1/2}$ (receptor–metal complex)—$E_{1/2}$ (free receptor)] has been monitored at nine different pH values from 4 to 12. The plots of $E_{1/2}$ vs pH and $\Delta E_{1/2}$ vs pH for free receptor and in presence of metal (II) ions are shown in Figs 4 and 5, respectively.

The redox response of this receptor towards these metal cations in the pH range from 12 to 5 at various molar ratios of M^{2+}: R also showed a displacement of half-wave potential, $E_{1/2}$, to more anodic potential (Figs 4 and 5) and it increases with increase in molar ratio (M^{2+} : R) and reaches a maximum at 1 (data not shown). Additions of sub-stoichiometric amounts of metal ions induce a sequential shift of the $E_{1/2}$ values.[10] The complexation of the metal ions with the receptor induces positive charge on the receptor (Scheme 3), making it more difficult to oxidize than free receptor, and shifts the potential of the Fc/Fc^+ redox couple towards the anodic side.[21] This result indicates that the complexed metal (II) cation in the macrocyclic cavity is communicating to the respective covalently appended ferrocene redox centres through space electronic interactions.[22]

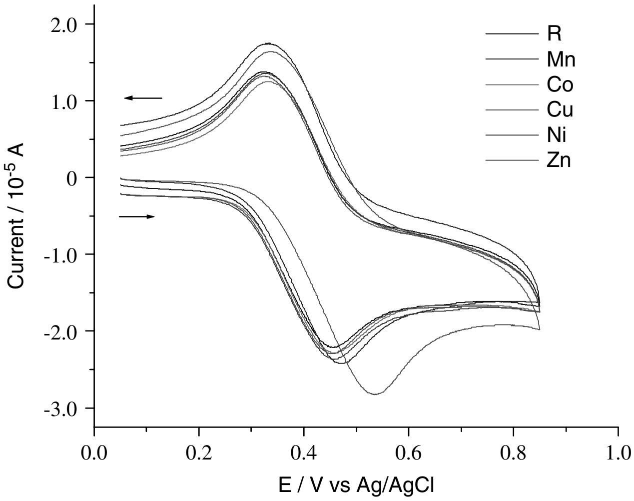


Figure 3. Cyclic voltammograms of the free receptor (R) and in presence of Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} metal ions (M^{2+}: R molar ratio = 1) at pH 8 (measured by CV at 100 mV s^{-1}; E vs Ag–AgCl; GC working and Ag–AgCl reference electrodes; supporting electrolyte, TBAP).

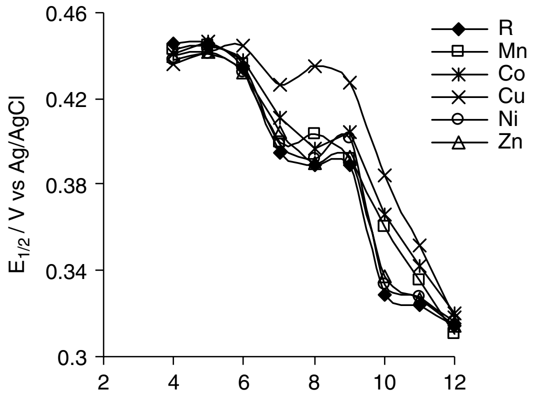


Figure 4. The plot of $E_{1/2}$ vs pH for free receptor (R) and in presence of Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} metal ions {[M^{2+}] and [R] is 10^{-3} M in dioxane : water mixture (7 : 3 v/v), M^{2+}: R molar ratio = 1}.

From the above data, some regions of selectivity of the receptor towards the metal ions can also be detected. For instance, the receptor shows higher selectivity for Cu^{2+} over the pH range from 6 to 11 with the largest electrochemical shift for Cu^{2+} ion at pH ca. 8 (Fig. 5). Further, the receptor shows a lesser shift of $\Delta E_{1/2}$ ($\Delta E_{1/2} < 20$ mV) for all the metal ions except for Cu^{2+} ion ($\Delta E_{1/2} = 46$ mV). This may be due to the fact that the copper (II) ion has higher stability constant value than the other metal ions with a tet'a' macrocycle,[23] which makes more binding towards Cu^{2+} ion and, hence, higher anodic shift of the redox potential of the receptor with this metal ion.

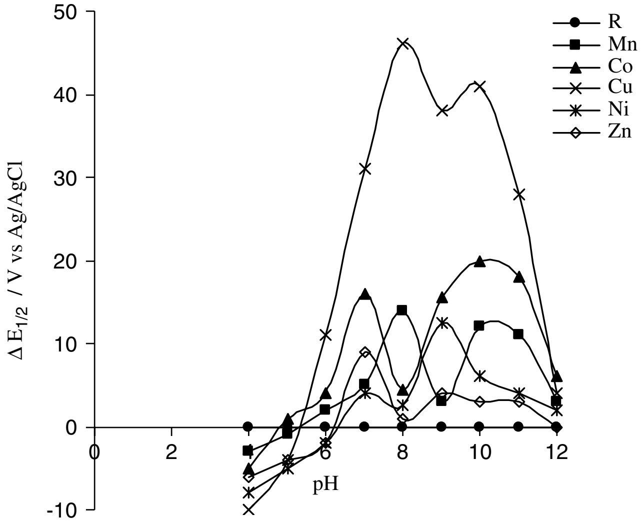
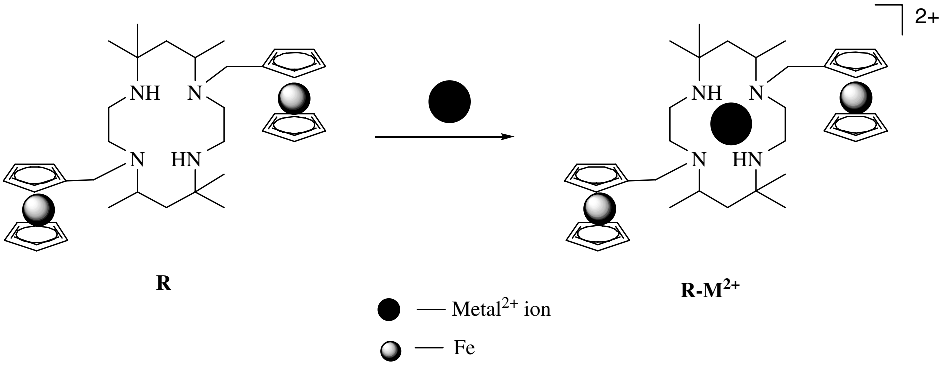


Figure 5. The plot of $\Delta E_{1/2}$ vs pH for free receptor (R) and in presence of Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} metal ions {[M^{2+}] and [R] is 10^{-3} M in dioxane : water mixture (7 : 3 v/v), M^{2+}: R molar ratio = 1}.

It has been already reported that a selective electrochemical response along with large $\Delta E_{1/2}$ values can be related with the presence of predominant receptor–metal complexes in a wide pH range and the existence of pH ranges of selective complexation.[20,22] The present study indicated that the R was able to electrochemically recognize Cu^{2+} ion over other common metal ions such as Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} over the pH range 6–11. Further, the shift of the anodic peak potential (E_{pa}) is noticeably different from shift of the cathodic peak potential (E_{pc}) when comparing the Cu(II) complex with the receptor R. This is due to the fact that, in the presence of Cu^{2+} ion, the receptor becomes a dipositive charged species $[Cu–R]^{2+}$; consequently an increase in the ferrocene oxidation potentials (E_{pa}) is observed when compared with the free receptor. Qualitatively, we can understand this behaviour by taking into account that highly charged species are more difficult to oxidize due to electrostatic repulsion between the positively charged electrodes and the positively charged species when compared with neutral species. However, the cathodic peak potential (E_{pc}) is not much altered with respect to the free receptor, which may be due to the fact that, after the oxidation process, both the free receptor and metal-complexed systems exist as positively charged species.

Of particular importance for evaluating receptor as a chemical sensor are the results of competition experiments in solutions followed by electrochemical techniques; this means the behaviour of the receptor in the presence of several substrates. When an equimolar mixture of metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} is added to a solution of R, the extent of the anodic shift of ferrocene–ferrocenium couple is approximately equal to that induced by Cu^{2+} alone. Further, competition experiments when carried out in the presence



Scheme 3. Complexation of receptor (R) with various metal (II) ions.

of excess competing cations ($[Cu^{2+}]:[M^{2+}] = 1:2$, where, $M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+} and Zn^{2+}) with respect to the Cu^{2+} ion does not alter the redox potentials of the receptor. Thus, the receptor R can be used as a good chemosensor for the selective recognition of Cu^{2+} ion in the presence of other first row transition metal ions. Although similar behaviour was observed for few other ferrocene incorporated macrocyclic receptors,[22,24] the shift in $E_{1/2}$ values for the tet'a' macrocycle receptor is less than that for the unsubstituted macrocycle receptor, which may be due to the hexamethyl substitution in the periphery of the tet'a' receptors, which affects its flexibility. Thus, the flexibility of the macrocyclic framework plays an important role in the complexing ability of tet'a' ligand and consequently in its behaviour as a redox sensor.

The electrochemical recognition ability of the receptor against transition metal ions was also studied in aprotic solvents such as acetonitrile. The maximum $\Delta E_{1/2}$ value in the presence of Cu^{2+} ion is 110 mV in acetonitrile and 46 mV in dioxane : water mixture. It is also observed that the shifts in electrochemical values were higher in acetonitrile, when compared with that found in dioxane : water for other metal ions studied. This observation is in line with the fact that the dielectric constant of acetonitrile ($\varepsilon = 37.5$) is lower than that of dioxane : water 70 : 30 v/v mixtures ($\varepsilon = 53.3$). [The dielectric constant of the dioxane : water 70 : 30 v/v mixture has been calculated as $\varepsilon = \sum_i X_i\varepsilon_i$, where X_i and ε_i are the molar fractions and permittivities of water and dioxane.] The interaction between the positively charged ammonium groups and the ferrocenyl moieties has been reported to be mainly electrostatic and therefore larger electrochemical shifts are expected in solvents with lower dielectric constants.[25]

CONCLUSION

The receptor R reported in the present work has the ability to recognize first row transition metal (II) ions electrochemically due to the existence of receptor–metal complexes over a wide pH range. The electrochemical studies further indicate that the receptor shows higher selectivity towards Cu^{2+} ion than the other transition metal ions studied. The shift in redox potentials ($E_{1/2}$ for the ferrocene–ferrocenium couple) found for the tet'a' receptor R is less than the cyclam receptor in the presence of metal ions. From the studies, we infer that flexibility and the binding nature of the receptor play an important role in its complexing ability and consequently in its behaviour as a redox sensor.

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