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Preliminary communication

Ammonium redox-responsive receptors containing two or three ferrocene redox-active centres attached to di- and tri-aza crown ether macrocycles

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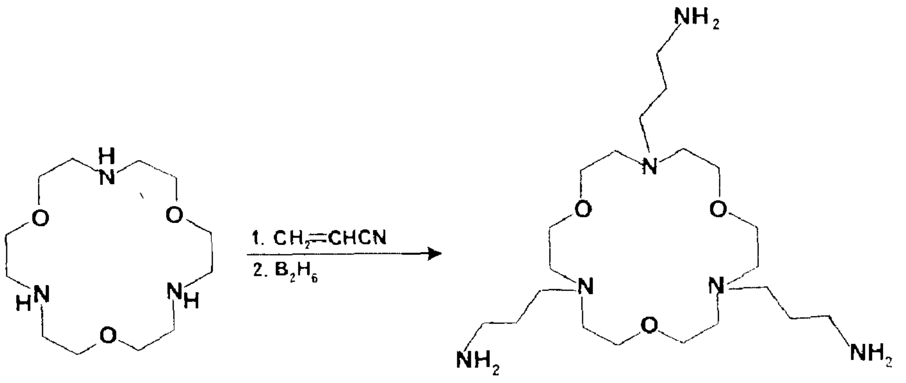
Abstract

The binding of NH_4^+ to novel ferrocenyl aza crown ethers **7** and **6**, respectively, containing two and three ferrocene redox-active centres attached to amine functionalised di- and tri-aza crown ether macrocycles, results in large anodic shifts of the ferrocene/ferricinium redox couple, by up to 220 mV with **6**.

With a view to advancing chemical sensor technology, considerable interest is being shown in the syntheses of redox-active macrocyclic receptor molecules that contain a redox centre in close proximity to a cation binding site [1–8]. These systems can be designed to recognise electrochemically the binding of a metal guest cation either through space interactions or via various bond linkages between the receptor site and redox centre. In contrast to the alkali metal coordination studies of electrochemically reducible [2,4,5] and oxidisable [3,6,7,8] redox-active macrocycles the design and syntheses of prototype amperometric ammonium cation sensor systems have yet to be reported. This communication describes the syntheses of novel ferrocenyl aza crown ethers **7** and **6**, respectively, containing two and three ferrocene redox-active centres attached to new amine functionalised di- and tri-aza crown ether macrocycles, and demonstrates by use of electrochemical techniques for the first time that ammonium guest cation binding at the aza crown ether moieties perturbs the redox potential of the ferrocene/ferricinium couple.

Lehn and co-workers [9,10] first reported the synthesis of 4,10,16-triaza-18-crown-6 (**1**), and subsequently showed that this macrocycle forms very stable ammonium and primary ammonium complexes by the formation of three complementary $\overset{+}{N}H \ldots N$ hydrogen bonds between host and guest. Following this prece-



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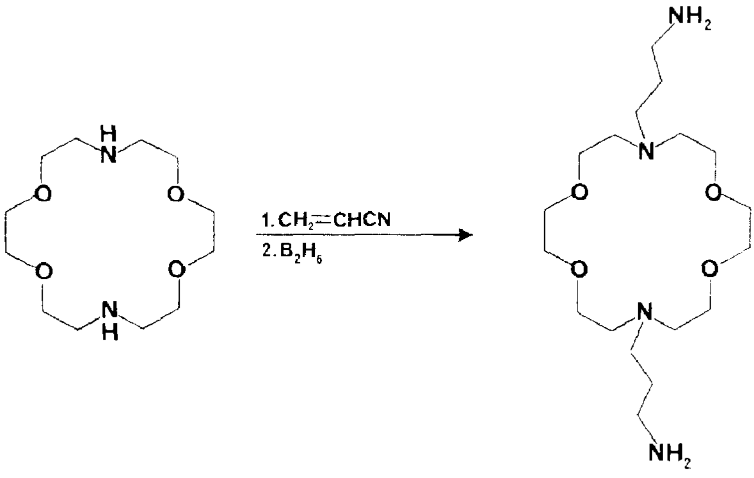

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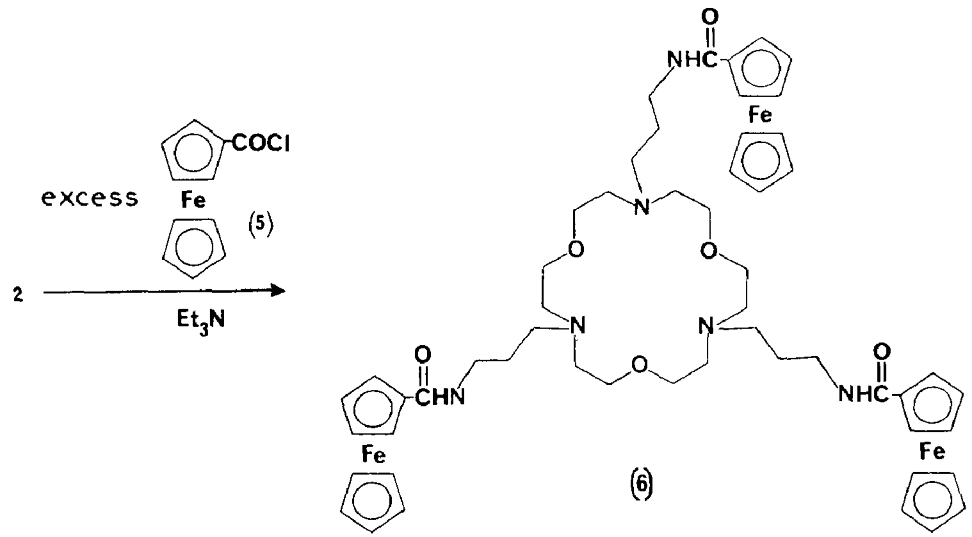
dent we decided to incorporate ferrocenyl redox-active centres into this type of macrocyclic structural framework.

The new primary amine functionalised aza crown ethers **2** and **4** were prepared by reaction of the appropriate aza crown ethers **1** [9,10] and **3** with acrylonitrile followed by diborane reduction. Condensation of **2** and **4** with an excess of ferrocenyl carbonylchloride **5** [11] in the presence of triethylamine followed by column chromatography gave **6** and **7**, respectively, in reasonable yields. The structures of these new air stable compounds were established by elemental analyses, fast atom bombardment mass spectroscopy (FABMS), and ^{1}H NMR spectroscopy.

The electrochemistry of **6**, **7** and model compounds **8** and **9** was investigated in acetonitrile solution by cyclic voltammetry with $[n\text{-}Bu_4N]BF_4$ as the supporting electrolyte. Cyclic voltammograms were also recorded after addition of NH_4^+, K^+ cations to the electrochemical solutions, and the results obtained are presented in Table 1.



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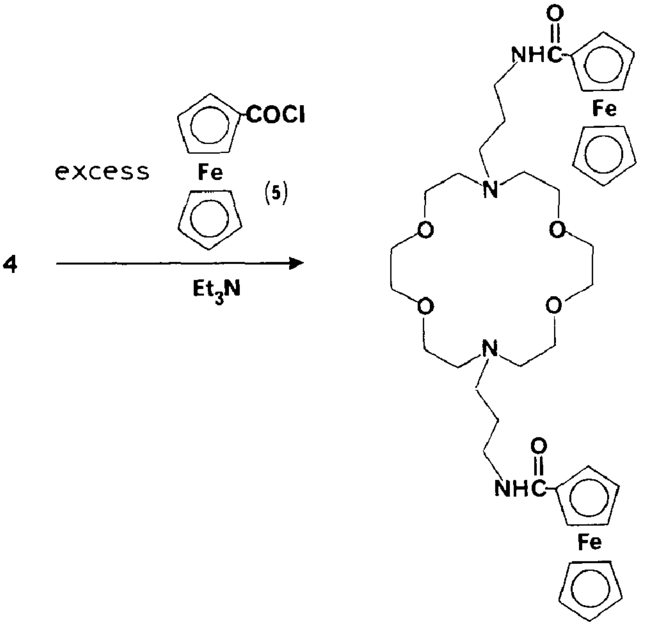

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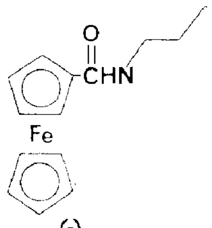
Only in the case of **6** and **7** are significant anodic shifts produced with the two cationic guests, suggesting that a crown ether structural framework containing tertiary amine nitrogen donor atoms is essential for successful guest cation binding. It is noteworthy that the complementary bound NH_4^+ cation exhibits the largest shift, of up to 220 mV with **6**. The interaction between cationic guest and redox-active host probably results from a through-space electrostatic perturbation effect similar to those reported for Gokel's reducible quinone [2] and for nitroaromatic [3,12] lariat crown ethers with alkali metal guest cations. Interestingly

Table 1

Electrochemical data

Compound	**6**	**7**	**8**	**9**
E_f (V) [a]	+0.62 [b]	+0.54 [c]	+0.59	+0.67 [b]
ΔE (NH_4^+) (mV) [d]	220	170	<10	<10
ΔE (K^+) (mV) [d]	50	85	<10	<10

[a] Obtained in MeCN solution containing 0.2 *M* $[n\text{-}Bu_4N]BF_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} *M* in macrocycle and potentials were determined with reference to SCE. [b] Three electron reversible oxidation process. [c] Two electron reversible oxidation process. [d] Shift in oxidation potential produced by presence of guest cation (2 equiv.) added as their thiocyanate salts.



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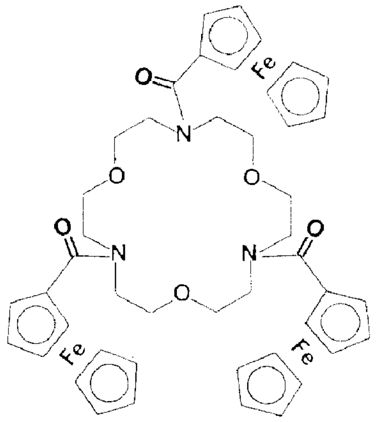

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however, the isolated potassium complex of **7** shows a 10 cm^{-1} shift of the carbonyl amide group to higher frequency in the infrared compared with that for free **7**, suggesting that the K^+ is coordinating to the amide nitrogen of the host in a 'lariat' [13] type fashion. Therefore an amido-cation through-bond electrostatic interaction with the respective ferrocenyl redox centre may also contribute to the overall magnitude of the anodic shift in E_f produced by guest cation binding.

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