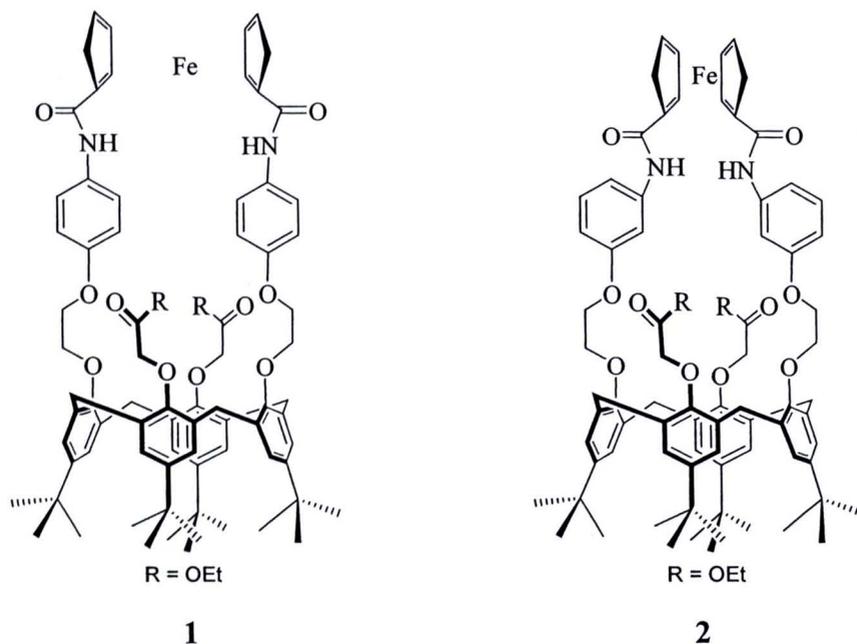


## CHAPTER IV

### CONCLUSION

#### 4.1 Anions Sensing by Heteroditopic Electrochemical Anion Sensors



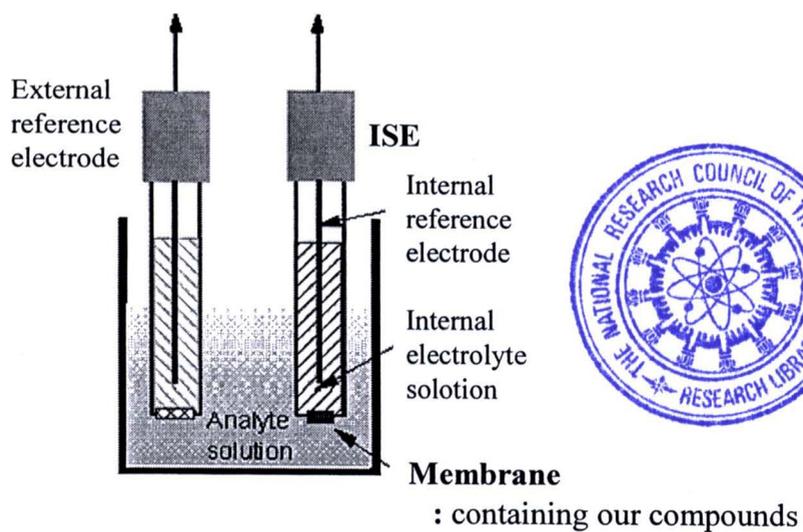
Receptors **1** and **2** can be synthesized in four steps using *p*-*tert*-butylcalix[4]arene as building blocks. To synthesize receptor **1**, *p*-*tert*-butylcalix[4]arene reacted with 2-(4-nitrophenoxy)ethyl 4-methylbenzenesulfonate to yield compound **1a**. The reaction of **1a** with ethylchloroacetate gave compound **1b**. Reduction of **1b** gave compound **1c** which was immediately react with ferrocene diacid chloride to give the final product **1** as orange solid in 12% yield. Receptor **2** can be synthesized in the similar pathway as receptor **1**. The reaction of *p*-*tert*-butylcalix[4]arene with 2-(3-nitrophenoxy)ethyl 4-methylbenzenesulfonate gave compound **2a**. The reaction of **2a** with ethylchloroacetate gave **2b**. Reduction of compound **2b** gave compound **2c** which immediately reacted with ferrocene diacid chloride to give the product **2** as orange solid in 14% yield. <sup>1</sup>H-NMR spectra of receptors **1** and **2** showed a typical AB pattern for the methylene bridge (ArCH<sub>2</sub>Ar) protons. This result confirmed that a calix[4]arene part in receptors **1** and **2** existed in cone conformation.

From  $^1\text{H-NMR}$  studies, receptors **1** and **2** can bind alkali metal cations and anions as the contact ion-pair in which metal cations are encapsulated in pseudo crown ether cavity and anions are hydrogen bonded to amide protons. In the absence of cation, both receptors can bind anions in the same order as following:  $\text{BzO}^-$ ,  $\text{AcO}^- > \text{H}_2\text{PO}_4^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ . However, the binding constants of receptor **2** with anions are lower than that of receptor **1** probably due to intramolecular hydrogen bonding between the amide groups. Interestingly, in the presence of cation, the binding abilities of receptors **1** and **2** towards anions are higher than those of their free forms. Both receptors show high selectivity towards bromide in the presence of sodium.

Electrochemical studies show that no significant increase of  $\Delta E$  for receptor **1** with anions was observed when the cation was added. Moreover, the difference between the  $\Delta E$  of the free receptor **1** and complex  $[\mathbf{1}.\text{Na}^+]$  is small. These observations may be due to the long distance between cation binding sites and ferrocene moiety of receptor **1**. Therefore, the absence and presence of cation have little effect to the electrochemical change of ferrocene moiety in the receptor **1**. For receptor **2**, in the presence of sodium, the magnitudes of changes in the redox potential towards anions, especially with acetate and chloride are higher than those of their free forms. Therefore, sensing properties of receptor **2** will be controlled by both co-bound metal cation and ferrocene moiety in the electrochemically oxidized form. It can be concluded that receptor **2** can act as electrochemical anion sensors for acetate and chloride in the presence of sodium.

## 4.2 Suggestions for Future Works

In the future work, we expect that the synthesized heteroditopic electrochemical anion sensors **1** and **2** can be incorporated into suitable potentiometric devices, for example, using them as ionophores in an ion-selective electrode by addition a compound to the membrane which is mounted on the end of the electrode body (shown in Figure 4.1) for controlled selective detection of anion species.



**Figure 4.1** The ion-selective electrode fabricated from our synthesized compounds.