CHAPTER 1

General Overview of Dissertation

1.1 Background of Project

1.1.1 *Introduction*

Metallophthalocyanines have continued to be one of the most studied classes of macrocyclic organometallic functional materials. They exhibit remarkable redox[1-4] and physico-chemical properties that are of interests in fundamental and applied research fields such as electrocatalysis and sensing,[1,5-7] electrochromic and electroluminescent display devices,[8] liquid crystal display devices,[9] photodynamic therapy[10] and other photosensitisation processes,[11,12] and in the development of energy storage and conversion systems such as fuel cells,[13] oxygen reduction reaction,[14] lithium ion battery,[15,16] and supercapacitor development.[17,18,19] The importance of MPc complexes in these technologically important applications has remained the major motivation for the intense search for novel MPc complexes. Thus, in this work, a report is given for the synthesis of nanostructured iron(II) and cobalt(II) phthalocyanine (nanoMPc); iron(II) and cobalt(II) octabutylsulphonyl phthalocyanine (MOBSPc) and novel iron phthalocyanine complex peripherally substituted with platinum, iron(II) tetrakis(diaquaplatinum) octa-carboxyphthalocyanine (PtFeOCPc).

In the area of electrocatalysis and energy storage and conversion systems, the use of transition metal phthalocyanine complexes is crucial. A simple approach is to place a monolayer or a few layers of MPc onto an electrode, for instance a bare edge plane pyrolytic graphite electrode, and measure the response to disturbance by a redox active target, for example molecular oxygen or thiocyanate ion etc.

Considering that many potential applications of the transition MPc complexes, for example in energy systems and heterogeneous catalysis, involve the use of their thin solid films and exchange of electrons between the solid/electrolyte interface, some understanding of the heterogeneous electron transfer kinetics (HET) is important. Thus, the HET of the MPc complexes when supported onto MWCNT-based electrode is also explored. The choice for MWCNT-based electrode is motivated by literature precedents on the ability of carbon nanotubes to enhance the electrochemical performance of the MPc complexes.[17,18,19,20]

1.1.2 *Aim*

This thesis is geared towards the search for potential application of iron(II) and cobalt(II) phthalocyanine complexes immobilised on multi-walled carbon nanotubes modified edge plane pyrolytic graphite electrode in the fields of

- **Electrocatalysis:** Development of electrodes modified with thin films of iron(II) and cobalt(II) phthalocyanine complexes for energy conversion devices such as fuel cell (cathodic oxygen reduction reaction and formic acid oxidation).

- **Electroanalysis:** development of sensors for the detection of biologically and environmentally important molecules such as thiocyanate ion (SCN^-) and nitrite (NO_2).

1.1.3 *Objectives*

- To synthesise nanostructured iron(II) and cobalt(II) phthalocyanine; peripherally substituted iron(II) and cobalt(II) phthalocyanine complexes.
- To interrogate the heterogeneous electron transfer behaviour of the iron(II) and cobalt(II) phthalocyanine complexes in an outer-sphere redox probe ($[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$), using cyclic voltammetry and electrochemical impedance spectroscopy technique.
- To investigate the electrocatalytic oxidation of thiocyanate and nitrite in phosphate buffer solution pH 5 and pH 7.4 respectively, employing cyclic voltammetry and amperometry analysis.
- To study the cathodic reduction of molecular oxygen in 0.1 M NaOH using cyclic voltammetry, linear sweep voltammetry and rotating disk electrode.
- To study the oxidation and stability of formic acid in 0.5 M H_2SO_4 solution, using cyclic voltammetry and amperometry technique.

1.1.4 *Scientific novelty of the work*

- For the first time, iron(II) and cobalt(II) octabutylsulphonyl phthalocyanine (MOBSPc); and iron(II) tetrakis(diaquaplatinum) octacarboxyphthalocyanine (PtFeOCPc) complexes were synthesised and a detailed study of their electrochemical properties provided.

- For the first time, a detailed study of the electrocatalytic reduction of molecular oxygen and formic acid on MWCNT-MPc nanocomposite has been provided.

1.1.5 *Publication of the work*

Some of the materials presented in this thesis have resulted in 6 papers published in international peer-reviewed scientific journals. The results were also presented at 3 international scientific conferences.

1.1.6 *Structure of the thesis*

The thesis consists of 2 sections made up of 6 chapters. Chapter 1 gives a brief summary of the thesis, highlighting the need for carrying out this work and the results obtained. Section A consists of Chapters 2 and 3. Chapter 2 introduces the basics in electrochemistry and a brief review of literature on related works, the experimental procedures and the materials used in this work is presented in chapter 3. Section B is the results and discussion and comprises of chapters 4, 5 and 6. Chapter 4 discusses the results obtained for nanostructured iron(II) and cobalt(II) phthalocyanine, analysis of the result obtained for iron(II) and cobalt(II) octabutyl sulphonyl phthalocyanine is presented in chapter 5, while chapter 6 discusses the result obtained for iron(II) tetrakis(diaquaplatinum)octa-carboxyphthalocyanine.

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