APPLICATION OF ANIONIC PORPHYRIN AS CHROMOGENIC INDICATOR AND METALLOPORPHYRIN CATALYSTS FOR OXIDATION OF BENZYL ALCOHOL

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Specially dedicated to my dearest parents, sister, brother and beloved Wilson Loh

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ABSTRACT

In recent years, extensive research has been carried out on the synthesis of anionic water-soluble porphyrin, *meso*-tetrakis(4-sulphonatophenyl)porphyrin (TSPP) due to the potential applications in photodynamic therapy, sensors, optical devices and catalysis. However, the information on anion recognition properties of free-base TSPP and performance of TSPP metalloporphyrin complexes in heterogeneous catalytic oxidation are relatively scarce. Hence, this research is divided into two main parts. Firstly, free-base TSPP was utilized as chromogenic reagent for recognition of acetate and citrate ions in aqueous solutions and the optical properties were characterized by ultraviolet-visible (UV-Vis) and fluorescence spectroscopies. The interaction of TSPP with the acetate and citrate ions was quantitatively analyzed at pH 4 using different acids (H_2SO_4, HCl, HNO_3, H_3PO_4 and CH_3COOH) for the pH adjustments. The anion sensing mechanism was based on protonation of the imino nitrogens of TSPP porphyrin core in the presence of acids (pH~4), whereby the optical changes observed in the absorption and emission spectra of the pH 4 TSPP solution were the effects of pH changes induced by acetate or citrate anion during deprotonation of TSPP. The Stern-Volmer constant based on the fluorescence quenching spectra revealed that the sensitivity of pH 4 TSPP was almost unaffected by the different acids used for the pH adjustment. For the UV-Vis spectroscopy method, the lowest limit of detection (LOD) of acetate ion (5.61×10^{-6} M) was obtained using nitric acid, while for the fluorescence spectroscopy method, the LOD (4.66×10^{-6} M) of acetate ion was obtained when sulphuric acid was used. Detection of citrate ion was only possible when acetic acid was used for the pH adjustment, with LOD of 9.59×10^{-6} M and 9.79×10^{-6} M for UV-Vis and fluorescence spectroscopies, respectively. Matrix anions (chloride, nitrate, phosphate, carbonate and sulphate ions) effects on the acetate and citrate detection were also studied. The linear range of the fluorescence detection was wider ($2–19 \times 10^{-5}$ M) as compared to the UV-Vis detection ($4–18 \times 10^{-5}$ M). Besides, no significant matrix anion effect could be observed in the fluorescence spectra. The microspecies distributions of TSPP, acetate and citrate ions were simulated using the Marvin Bean ChemSketch® analysis. The results suggested that the pH of the TSPP solution was instantaneously increased upon the addition of acetate or citrate anion. Consequently, the –2 charge TSPP was converted to –4 charge TSPP, accompanied with significant optical changes. In the second part of this work, TSPP was coordinated to Mn(III), Fe(II), Co(II) and Cu(II) ions to yield the *meso*-tetrakis(4-sulphonatophenyl)porphyrinato metal complexes (TSPP-M) for catalytic oxidation of benzyl alcohol to benzaldehyde with *tert*-butyl hydroperoxide as oxidant. The neat TSPP-M showed superior catalytic performance (~60% conversion) as compared to that of free-base TSPP (4.8% conversion). Subsequently, TSPP-M was immobilized on the mesoporous silica support *Santa-Barbara Amorphous-15* (SBA-15) via post-synthesis method to afford the heterogeneous catalysts TSPP-M/SBA-15 (M: Mn, Fe, Co and Cu). The TSPP-M/SBA-15 catalysts exhibited high BET (Brunauer-Emmett-Teller) surface areas > 150 $m^2 g^{-1}$ with average pore diameters > 5 nm. The effects of reactant to oxidant molar ratio, reaction temperature, solvent, and reaction time were further investigated. Under the optimal conditions, the catalytic trend was in the order: Mn(III) > Fe(II) > Co(II) > Cu(II). The TSPP-Mn/SBA-15 catalysts gave > 99% selectivity and turn over frequency of 665 h^{-1} after 3 hours of reaction. In addition, all the TSPP-M/SBA-15 catalysts could be reused up to three recycles without significant loss of catalytic activity. The catalytically active species leached out of TSPP-M/SBA-15 surface was extremely small and generally, can be considered negligible. Findings of present studies are significant because the anionic free-base TSPP was reported for the first time as chromogenic reagent for anion recognition. Furthermore, the TSPP-M/SBA-15 has great potential as an environmental friendly heterogeneous catalyst that offers the prospect of commercialization in the production of chlorine-free benzaldehyde.

ABSTRAK

Sejak tahun kebelakangan ini, penyelidikan meluas telah dijalankan ke atas sintesis porfirin anionik terlarut dalam air, *meso*-tetrakis(4-sulfanatofenil)porfirin (TSPP) disebabkan oleh potensi aplikasinya dalam terapi fotodinamik, sensor, peranti optik dan pemangkinan. Namun begitu, maklumat mengenai sifat pengecaman anion TSPP bebas logam dan prestasi kompleks metaloporfirin TSPP dalam pengoksidaan pemangkinan heterogen secara relatifnya jarang ditemui. Maka penyelidikan ini terbahagi kepada dua bahagian utama. Pertamanya, TSPP bebas logam telah digunakan sebagai reagen kromogenik bagi pengecaman anion asetat dan sitrat dalam larutan akueus dan ciri optik telah dicirikan menggunakan spektroskopi ultralembayung-nampak (UV-Vis) dan pendafluor. Interaksi antara TSPP dan ion asetat dan sitrat telah dianalisis secara kuantitatif pada pH 4 dengan menggunakan asid yang berlainan (H_2SO_4, HCl, HNO_3, H_3PO_4 dan CH_3COOH) bagi pelarasan pH. Mekanisme pengecaman anion adalah berasaskan protonasi nitrogen imino pada teras porfirin TSPP dengan kehadiran asid (pH~4), di mana perubahan optik yang dicerap dalam spekrum penyerapan dan pemancaran larutan pH 4 TSPP adalah kesan perubahan pH yang diaruh oleh anion asetat atau sitrat semasa penyahprotonasi TSPP. Pemalar Stern-Volmer berdasarkan spekrum pelindapan pendarfluor mendedahkan bahawa kepekaan TSPP pH 4 hampir tidak terjejas dengan penggunaan asid berlainan untuk pelarasan pH. Untuk kaedah spektroskopi UV-Vis, had pengesanan (LOD) paling rendah (5.61×10^{-6} M) untuk ion asetat diperoleh dengan menggunakan asid nitrik, manakala bagi kaedah spektroskopi pendafluor, LOD (4.66×10^{-6} M) untuk ion asetat diperoleh apabila asid sulfurik digunakan. Pengesanan ion sitrat hanya dapat dilakukan apabila asid asetik digunakan untuk pelarasan pH, dengan LOD 9.59×10^{-6} M dan 9.79×10^{-6} M untuk spektroskopi UV-Vis dan pendafluor, masing-masing. Kesan anion matriks (ion klorida, nitrat, fosfat, karbonat dan sulfat) terhadap pengesanan asetat dan sitrat turut dikaji. Julat linear pengesanan pendafluor didapati lebih luas ($2–19 \times 10^{-5}$ M) berbanding dengan pengesanan UV-Vis ($4–18 \times 10^{-5}$ M). Di samping itu, tiada kesan anion matriks yang ketara boleh diperhatikan pada spektrum pendafluor. Taburan mikrospesies TSPP, ion asetat dan sitrat telah disimulasi menggunakan analisis Marvin Bean ChemSketch®. Keputusan kajian mencadangkan bahawa pH larutan TSPP meningkat secara serta-merta semasa penambahan anion asetat atau sitrat. Akibatnya, cas –2 TSPP bertukar kepada cas –4 TSPP, disertai dengan perubahan optik yang jelas. Di bahagian kedua kajian, TSPP telah dikoordinasikan dengan ion Mn(III), Fe(II), Co(II) dan Cu(II) untuk menghasilkan kompleks logam *meso*-tetrakis(4-sulfanatofenil)porfirinato (TSPP-M) bagi pemangkinan pengoksidaan benzil alkohol kepada benzaldehid menggunakan *tert*-butil hidroperoksida (TBHP) sebagai oksidan. Mangkin TSPP-M tulen menunjukkan prestasi pemangkinan yang cemerlang (penukaran ~60%) berbanding dengan TSPP bebas logam (penukaran 4.8%). Seterusnya, TSPP-M dipegunkan ke atas penyokong silika mesoliang *Santa-Barbara Amorphous-15* (SBA-15) melalui kaedah pasca-sintesis bagi menghasilkan mangkin heterogen TSPP-M/SBA-15 (M: Mn, Fe, Co dan Cu). Mangkin TSPP-M/SBA-15 mempamerkan luas permukaan BET (Brunauer-Emmett-Teller) yang tinggi > 150 $m^2 g^{-1}$ dengan purata diameter liang > 5 nm. Kesan reaktan terhadap nisbah molar pengoksida, suhu tindak balas, pelarut dan masa tindak balas telah dikaji. Di bawah keadaan optimum, tren pemangkinan ialah dalam turutan: Mn(III) > Fe(II) > Co(II) > Cu(II). Mangkin TSPP-Mn/SBA-15 memberikan kepilihan >99% dan frekuensi pusingan balik 665 h^{-1} selepas 3 jam bertindak balas. Di samping itu, kesemua mangkin TSPP-M/SBA-15 boleh diguna semula hingga tiga kitaran tanpa kehilangan aktiviti pemangkinan yang signifikan. Spesies aktif mangkin yang larut lesap dari permukaan TSPP-M/SBA-15 juga didapati amat sedikit dan pada umumnya, boleh diabaikan. Hasil kajian ini adalah penting kerana TSPP anionik bebas logam julung kali dilaporkan sebagai reagen kromogenik untuk pengecaman anion. Tambahan pula, TSPP-M/SBA-15 sangat berpotensi sebagai mangkin heterogen mesra alam yang menawarkan prospek komersialisasi dalam penghasilan benzaldehid bebas klorin.

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λ - Wavelength
°C - Degree Celcius
^{13}C NMR - Carbon-13 nuclear magnetic resonance
^{1}H NMR - Proton nuclear magnetic resonance
^{29}Si NMR - Silica-29 nuclear magnetic resonance
2θ - Bragg angle
Å - Ångström
AcO$^-$ - Acetate ion
a_o - Unit cell parameter
APTES-SBA-15 - (3-aminopropyl)triethoxysilane functionalized SBA-15
BJH - Barrett-Joyner-Halenda
BmimBF$_4^-$ - 1-butyl-3-methylimidazolium tetrafluoroborate
CDCl$_3$ Deuterated chloroform
c-Hex - Cyclohexane
cmc - Critical micellar concentration
CoA - Coenzyme A
CP MAS - Cross polarization magic angle spinning
CTAB - cetyltrimethylammonium bromide
Cu K$_\alpha$ - X-ray diffraction from copper K$_\alpha$ energy levels
DCC - N,N’-dicyclohexylcarbodiimide
DCM - dichloromethane
DDQ - 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMSO - Dimethyl sulfoxide
DR - Diffuse reflectance
ε - Molar absorptivity
FeTPyP - Iron(III)-5,10,15,20-tetrakis(4-pyridyl)-porphyrin
FIA - Flow-injection Analysis

FTIR	-	Fourier transform infrared
GC-FID	-	Gas chromatography-flame ionization detector
h	-	Hour
H_2O_2	-	Hydrogen peroxide
H_2TSPP^{2-}	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrin dication
H_3TSPP^{-}	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrin trication
HOMO	-	Highest occupied molecular orbital
HPLC	-	High performance liquid chromatography
ICP-OES	-	Inductively coupled plasma-optical emission spectroscopy
IUPAC	-	International Union of Pure and Applied Chemistry
J	-	Coupling constant
K-M	-	Kubelka-Munk
K_{sv}	-	Stern-Volmer constant
LMCT	-	Ligand-to-metal charge-transfer
LOD	-	Limit of detection
LUMO	-	Lowest unoccupied molecular orbital
m	-	*Meta-*
M	-	Molarity
MCM	-	Mobil composition of matter
Me	-	Methyl
MLCT	-	Metal-to-ligand charge-transfer
nm	-	nanometer
o	-	*Ortho-*
p	-	*Para-*
PDT	-	Photodynamic therapy
pK_a	-	Acid dissociation constant
ppm	-	Part per million
R.T.	-	Room temperature
SBA	-	Santa-Barbara Amorphous
TBHP	-	*Tert*-butyl hydroperoxide
TCPP	-	*meso*-Tetrakis(4-carboxyphenyl)porphyrin
TEM	-	Transmission electron microscopy

TMPyP	-	*meso*-Tetrakis(N-methylpyridyl)porphyrin
TOF	-	Turnover frequency
TON	-	Turnover number
TPP	-	*meso*-tetrakis(4-phenyl)porphyrin
TPyP	-	*meso*-Tetreakis(pyridyl)porphyrin
TSPP	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrin
$TSPP^-$	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrin monoanion
$TSPP^{2-}$	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrin dianion
TSPP-Co	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrinato cobalt(II)
TSPP-Cu	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrinato copper(II)
TSPP-Fe	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrinato iron(II)
TSPP-M	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrinato metal
TSPP-M/SBA-15	-	*meso*-Tetrakis(4-sulphonatophenyl)-porphyrinato metal immobilized SBA-15
TSPP-Mn	-	*meso*-Tetrakis(4-sulphonatophenyl)porphyrinato manganese(II)
UV-Vis	-	Ultraviolet-visible
XRD	-	X-ray Diffraction
β	-	Beta
δ	-	Chemical shift
μmol	-	Micromole
π	-	pi

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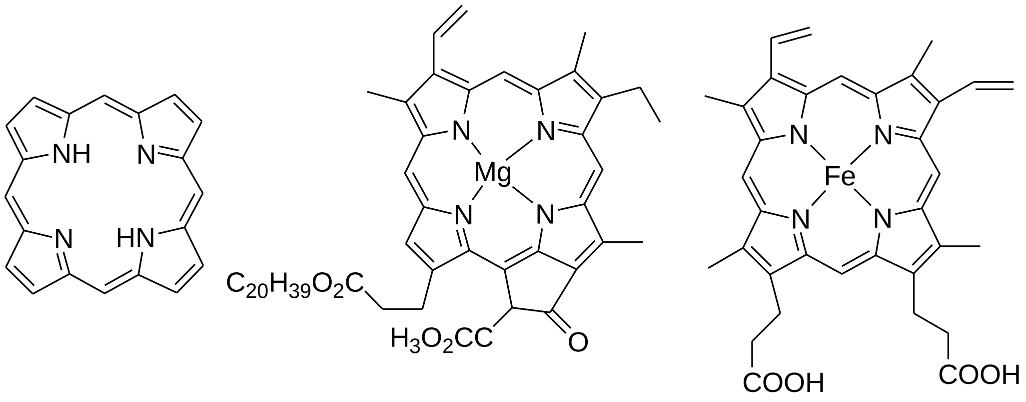
CHAPTER 1

INTRODUCTION

1.1 Background of Research

Porphyrins are natural occurring compounds consisting of tetrapyrrolic macrocycle as shown in **Figure 1.1 (a)**. Porphyrins are essential for living organism as they involve in various biological processes such as oxygen binding, electron transfer, biocatalysis and photochemical routes (Cragg, 2005). Metals in biological system are often bound to porphyrin forming metalloporphyrins. For example, magnesium binds to porphyrin to form chlorophyll (**Figure 1.1 (b)**) that plays the role as a light harvesting agent in the photosynthesis process. While iron binds to porphyrin to form haemoglobin (**Figure 1.1 (c)**) which is responsible for sophisticated oxygen transport in mammals (Donald, 2001).



(a) **(b)** **(c)**

Figure 1.1 Molecular structure of **(a)**: porphyrin, **(b)**: chlorophyll and **(c)**: haemoglobin

The abundance and importance of porphyrin in nature make it interesting scaffold for technological and scientific studies. The π electrons rich macrocycle of porphyrin makes its structure rigid and stable. In addition, the four nitrogen atoms in the macrocycle readily coordinate to wide variety transition metals. Besides, the large macrocycle in porphyrin provides spaces for further functionalization. Its properties can be fine-tuned by introducing substituents or changing the central metal ion.

This ability enables porphyrin to be modulated to fit different applications by simple chemical modification of porphyrin multifunctional core, such as protonation by acids. In addition, metal complexes of porphyrins possess photochemically and electrochemically interesting characteristics that can be used to introduce new functionalities of the materials. With these attractive features, porphyrin has been studied intensively in various applications such as sensing, catalysis, photodynamic therapy, energy harvesting and others (Král *et al.*, 2006; Meunier, 1992).

The water solubility of porphyrin is dependent strictly on the functional group substituted at the porphyrin macrocycle. For example, *meso*-tetrakis(4-chlorophenyl)porphyrin with non-polar chlorophenyl- as the substituent group is sparingly soluble in water at room temperature, while *meso*-tetrakis(methylpyridyl)porphyrin with positively charged methylpyridyl- as the substituent is soluble in water. The non-water-soluble porphyrins are not suitable for most of the bio-chemical applications which usually occur in aqueous medium.

Due to the difficulty of preparation, only a limited number of water-soluble porphyrins have been successfully synthesized. In general, water-soluble porphyrin can be divided into three classes, i.e. positively charged porphyrin, negatively porphyrin and neutral porphyrin (Simonnaeux *et al.*, 2011). Examples of water-soluble synthetic porphyrins based on their classes are given in **Table 1.1**.

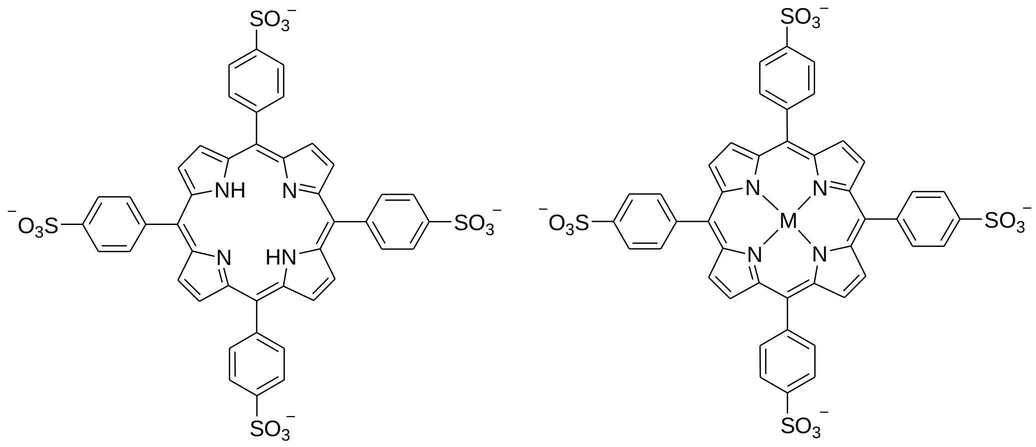
Table 1.1 Examples of water-soluble porphyrins based on their classes

Class of Porphyrin	Examples
positively charged	*meso*-tetrakis(4-pyridyl)porphyrin, *meso*-tetrakis(4-N,N, N-trimethylanilinium)porphyrin
negatively charged	*α, β, γ, δ*-tetraphenylporphine trisulfonate, *meso*-tetrakis-(4-sulphonatophenyl)porphyrin (TSPP)
neutral Porphyrin	glycosylated porphyrins (bearing appended glycol groups)

Compared to other water-soluble porphyrins, the preparation of negatively charged *meso*-tetrakis(4-sulphonatophenyl)porphyrin (hereafter referred as TSPP) was much easier (Fleischer *et al.*, 1971). TSPP is a tetra-anionic porphyrin which consists of four sulphonatophenyl- charge groups (**Figure 1.2(a)**) that enable it to possess excellent water solubility.

When a metal is inserted in the porphyrin core, the resulting complex, *meso*-tetrakis(4-sulphonatophenyl)porphyrinato metal (hereafter referred as TSPP-M), possesses a molecular structure as shown in **Figure 1.2(b)**, which has the potential to undergo redox reactions at the metal centre rather than on the porphyrin ring.

However, not much work has been devoted to the applications of TSPP until a less-tedious protocol was developed by Fleischer *et al.* (1971). Soon after, some TSPP derivatives have been successfully prepared up to gram scale based on the improved version of Fleischer’s method (Srivastava and Tsuisui, 1972; Dong and Scammells, 2007; Simões *et al.*, 2012). This has sparked the interest of researchers to explore more potential applications of TSPP. In general, the TSPP application studies can be grouped into three categories, i.e. sensing, catalysis, and bio-medical applications (Taies and Mohammed, 2013; Cristaldi *et al.*, 2015; Zoltan *et al.*, 2015).



(a) **(b)**

Figure 1.2 Molecular structure of **(a)** *meso*-tetrakis(4-sulphonatophenyl)porphyrin and **(b)** *meso*-tetrakis(4-sulphonatophenyl)porphyrinato metal complex; M: transition metal

In various sensing applications, the TSPPs were used as optical sensing materials for the quantitative analysis by spectrophotometric and high performance liquid chromatography (HPLC) methods (Xu *et al.* 1990). Cation sensing was studied by means of HPLC, UV-Vis and fluorescence spectroscopies while, anion sensing by potentiometric and UV-Vis spectroscopy studies. Besides, neutral molecules and gases were sensed by probes that were modified with TSPP. In the analytical study of cation using TSPP as the host component, the porphyrin structure was reported to undergo a planarity change upon the chelation with the target cation.

The structural change of TSPP was significant and could be observed in both the UV-Vis and fluorescence spectra (Biesaga *et al.*, 2000). Porphyrins usually possess high absorption coefficient at 400–450 nm (visible range) and large stokes shift that minimize the effect of background noise. However, the use of fluorescence spectroscopy for the analysis of target analyte with TSPP is still limited. Hence, the first part of this research highlighted on the application of TSPP in anion recognition studies by UV-Vis and fluorescence spectroscopies. In addition, the distribution of charged species at different pH was simulated using Marvin Bean ChemSketch® to probe the conformational change in TSPP during the anion recognition process.

Since the discovery of cysteine-haem enzyme in cytochrome P450 more than fifty years ago, various types of metalloporphyrins have been developed that aimed to mimic the oxidation properties of cytochrome P450 (Luzgina *et al.*, 1977). Metalloporphyrin coordinated to various transition metals with great variety of new structures have been synthesized (Nakagaki *et al.*, 2013). Some of these metalloporphyrins were TSPP-Ms which were tested as potential catalysts in oxidation, reduction, photodegradation and polymerization reactions (Olaya *et al.*, 2012; Tanimoto *et al.*, 2008; Nabid *et al.*, 2013).

The TSPP-Ms gave good catalytic performances, particularly in oxidation of hydrocarbons (Ren *et al.*, 2009; Ricoux *et al.*, 2009). It was demonstrated that the metal species should be carefully chosen so that the metal-oxo-porphyrin formed could act as active oxidizing species. Noted that most of the TSPP-Ms reported in the literature possessed Mn(III) and Fe(II) as the central metal ion. Oxidative catalyst on TSPP-Ms with Co(II) and Cu(II) core are still scarce. In this study, the physicochemical properties of TSPP coordinated to Mn(III), Fe(II), Co(II) and Cu(II) were synthesized. Their catalytic potential as oxidation catalysts were studied. Their physicochemical properties of these TSPP-Ms were also investigated.

Heterogeneous catalysts are highly desired as they can be easily separated and recovered from the reaction medium. Heterogeneous catalysts based on TSPP-Ms can be obtained by immobilizing the TSPP-Ms onto a solid support. However, the solid support has to be carefully selected so that desirable catalyst properties such as high surface area, good thermal and chemical stabilities can be achieved. Mesoporous silica SBA-15 which consists of high surface area (>500 m^2/g), high hydrothermal stability, easily accessible and uniform mesopores (20 – 100 Å) is an excellent candidate as the solid support for the porphyrin macrocycles. Previous studies have reported that the immobilization of porphyrin catalyst onto SBA-15 enhanced the catalyst stability and selectivity and made the reusability of the catalyst possible (Espinosa *et al.*, 2011; Zhu *et al.*, 2014; Najafian *et al.*, 2015).

Therefore, immobilizing the metalloporphyrin catalyst on a high surface area SBA-15 can lead to the desired catalytic activity. The porphyrin complexes can be introduced onto SBA-15 by two approaches: either by entrapment of the porphyrin in the silica support by *in-situ* synthesis, or immobilization of the porphyrin onto the porous silica surface in a post-synthesis modification step. In the present study, the latter approach was performed to immobilize the TSPP onto SBA-15 via electrostatic interaction between TSPP-M and (3-aminopropyl)triethoxysilane (APTES) functionalized SBA-15 as proposed in **Figure 1.3**.

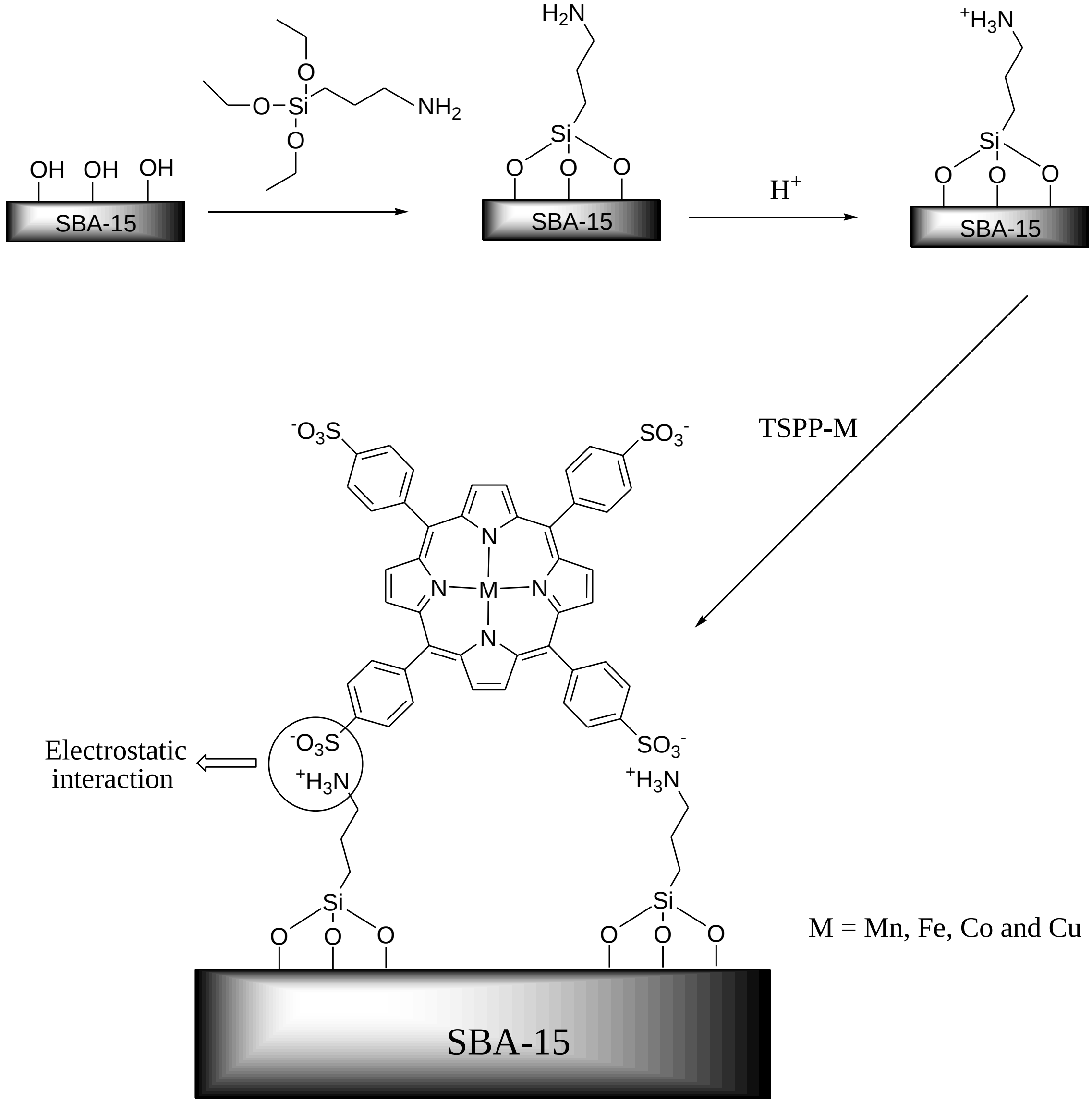


Figure 1.3 TSPP-M (M: Mn, Fe, Co and Cu) immobilized onto APTES functionalized SBA-15 by post-synthesis modification step

1.2 Problem Statement

As anion interactions play a vital role in chemistry and biology, the development of new, sensitive method for the determination of extremely small amounts of anions in solution is deemed important. For example, the concentration of acetate ion is utilized to monitor the fermentation process in sediment and sludge reactor (Orcutt *et al*., 2013; Chua *et al.*2003); while the concentration of citrate ion in urine can be used to diagnose nephrolithiasis and nephrocalcinosis disease (Schell-Feith *et al*., 2006).

Because of the relevance to the needs, a wide variety of methods have been devised to analyse acetate and citrate ions such as capillary ion electrophoresis (Wiliams *et al.*, 1997) isotope labelling method (Morrision *et al.*, 2004), flow injection analysis (Forman *et al.*, 1991) and ion-chromatography methods (Erdema and Bedir, 2014). All of these known methods required tedious sample pre-treatment and complicated instrument set up which limited their widespread applicability. Consequently, UV-Vis absorption and fluorescence spectroscopy techniques are considered as effective tools owing to their sensitivity, simple instrument implementation, as well as safe and short response time (Chahal and Sankar, 2015; Kiefer *et al.*, 2010).

In order to prepare anions sensing material, numerous chromogenic and fluorogenic indicators consist of functional groups such as amide (Goswani *et al.*, 2012), phenolic hydroxyl (Hijji, 2012) and thiourea derivatives (Liu *et al.*, 2012) have been developed for acetate and citrate ions analyses. Most of the indicators were only soluble in aprotic solvents such as acetonitrile, hence limiting their applications for detecting anions in aqueous samples (Huang *et al.*, 2010). This is because non-water-soluble molecular scaffolds tend to agglomerate in aqueous medium. Furthermore, the physicochemical properties of the anion, such as large size and high solvation energy often make the design of anion indicator/receptor more challenging. Because of the larger size of anion as compared to cation, a bigger host is required for the binding of anion.

Currently, quantitative determination of anions can be carried out using commercially available bio-chemical sensors based on enzymes (Keevil *et al.*, 2005). However, many enzymes are very sensitive to sample conditions and unstable at high temperature and extreme pH. As a result, the enzyme-based sensors are not suitable to be applied to samples that are without any pre-treatment. On the other hand, porphyrins have been used in sensor applications due to their high sensitivity. As mentioned in **Section 1.1**, the rich photochemistry of TSPP would enable it to be used as a chromogenic indicator for cation and anion analysis.

Spectral shifts of porphyrins could be used as a “marker” for the presence of different anions. With the high sensitivity of porphyrin to the pH change, the optical behaviour can be altered through modification of the porphyrin structure. In the case of TSPP, owing to its low pK_a (~4.86), the porphyrin can be easily protonated and deprotonated at the pyrrolic nitrogen (-NH), which depends on pH change of the medium (Delmarre et al. 1999). The protonation and deprotonation processes during interactions with the target analytes can affect the conformations of porphyrin macrocycle which may also result in observable changes in the UV-Vis and fluorescence spectra. Therefore, it is possible to use TSPP as anion recognition material for basic anions such as acetate and citrate; without tedious macrocycle modification.

To the best knowledge of the author, using TSPP as fluorogenic indicators for quantitative fluorescence spectroscopic analysis of anion has not been reported yet. Only quantitative absorption spectrophotometric technique has been explored so far. In addition, the application of TSPP, especially free-base TSPP, as chromogenic and fluorogenic indicators for quantitative anion analysis is still scarce. Hence, in the first part of this study, the conformational change of water-soluble TSPP during diprotonation and deprotonation by acids was being utilized for anion analysis in aqueous medium.

In the second part of this research, the TSPP-M immobilized SBA-15 samples were explored in heterogeneous catalysis of benzyl alcohol in order to understand the structure-catalytic property relationship in this catalyst system. In homogeneous catalysis, oxidation of alcohols to corresponding aldehyde and ketone requires a stoichiometric amount of oxidant such as chromium(VI), permanganate, DMSO and DDQ (Cardona and Permeggiani, 2015). Consequently, all of these oxidants suffer drawbacks of generating high amounts of organic and inorganic toxic side products after the reaction. Furthermore, these methods are usually carried out in halogenated organic solvent that will produce undesirable halogenated waste and caused safety hazardous concern. Hence, the catalytic reaction with little amount of oxidant has attracted attention in the past decade.

In the conventional method, benzaldehyde was produced by hydrolysis of benzyl chloride or oxidation of toluene and styrene with stoichiometric amounts of chromium and manganese salt. These methods generate copious wastes and the chloride inevitably will present in the benzaldehyde as an impurity (Yu *et al.*, 2010; Patel and Pathan, 2012). Moreover, these methods suffer from the drawbacks of lack of selectivity, generation of undesired side product, unenviable toxic waste and usage of toxic reagent. Consequently, an alternative environmentally benign heterogeneous catalyst for the oxidation of benzyl alcohol is required.

In this work, the TSPP was core modified using a series of transition metals such as Mn(III), Fe(II), Co(II) and Cu(II) as oxidation catalyst for conversion of benzyl alcohol as model reaction. Hence, it would be expected that stability of valence electron and oxidative properties of TSPP ligand will affect the catalytic activity trend. Previous studies have shown that various TSPP-Ms were utilized as epoxidation and oxidation catalysts (Ren *et al.*, 2009; Rémy *et al.*, 2009; Nabidi *et al.*, 2013).

However, till date, TSPP-M catalyst has never been reported for its application in the liquid phase oxidation of benzyl alcohol to benzaldehyde. Thus, present study reported for the first time that TSPP-Ms with different metal cores were used as catalysts for the oxidation of benzyl alcohol. In addition, the usage of “clean” oxidant such as *tert*-butyl hyroperoxide (TBHP) for the liquid phase oxidation of benzyl alcohol possesses great potential from the point of view of green chemistry.

Neat metalloporphyrin catalyst typically shows high efficiency and selectivity under mild reaction conditions. This is because the reactant molecules interact with the catalyst molecules in the same reaction phase, generally liquids, which make chemical reactions more efficient and easy to form the desired products. However, the use of metalloporphyrin as a homogeneous catalyst has suffered a few drawbacks such as insoluble in the reaction medium, liable to oxidative self-destruction, mass transfer limitation and aggregation through π-π stacking interaction that lead to deactivation of the catalyst (Rosa *et al.*, 2000).

Furthermore, the difficult recovery of homogenous catalyst leads to the substantial loss of the catalyst and adds significantly to production costs of commercial processes. In order to overcome these drawbacks, immobilization of homogenous catalyst onto mesoporous solid support was demonstrated in this study in order to produce environmentally benign heterogeneous catalyst which could be a very promising, alternative approach.

1.3 Research Objectives

The main goal of this research is to investigate the application of TSPP as anion indicator and oxidation catalyst.

The main objectives of this research are shown as follows:

1. To synthesize and characterize *meso*-tetrakis(4-sulphonatophenyl)porphyrin (TSPP).
2. To investigate the colorimetric and fluorogenic properties of TSPP as anion recognition material.
3. To evaluate and optimize the catalytic condition of *meso*-tetrakis(4-sulphonatophenyl)porphyrinato metal (TSPP-M) immobilized SBA-15 in the synthesis of benzaldehyde by oxidation of benzyl alcohol.

1.4 Scope of Study

In this research, the anionic porphyrin entity, TSPP was used throughout the study. In Chapter 4, the physicochemical properties of TSPP were studied by Fourier Transform Infrared (FTIR) spectroscopy, ^{1}H, ^{13}C NMR spectroscopies and matrix-assisted laser desorption – time of flight (MALDI-TOF) mass spectrometry. The correlations between optical changes of TSPP aqueous solution and anion concentration have been investigated by the addition of different acids and base for pH adjustment in the range of 2 to 7. Furthermore, matrix effect studies were carried out in the presence of additional anions, i.e. chloride, nitrate, phosphate, carbonate and sulphate, respectively. Additionally, the charge species distribution of TSPP during the anion interaction was predicted using the Marvin Bean ChemSketch®.

In Chapter 5, the TSPP was coordinated to different transition metals (Mn(III), Fe(II), Co(II) and Cu(II)) and immobilized onto SBA-15 (TSPP-M/SBA-15) through electrostatic interaction. The physicochemical properties of the resulting organic-inorganic hybrid materials were characterized with Fourier Transform Infrared (FTIR) spectroscopy, diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy, ^{29}Si, ^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopy, X-ray diffraction analysis (XRD), nitrogen absorption measurement, inductively coupled plasma optical emission (ICP-OES) spectrometry, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).

The catalytic properties and reusability of TSPP-M immobilized SBA-15 samples were tested in the oxidation of benzyl alcohol. Various catalytic conditions such as the substrate to oxidant ratio, temperature, solvent, reaction time and catalyst loadings have been optimized. The research outline is illustrated in **Figure 1.4**.

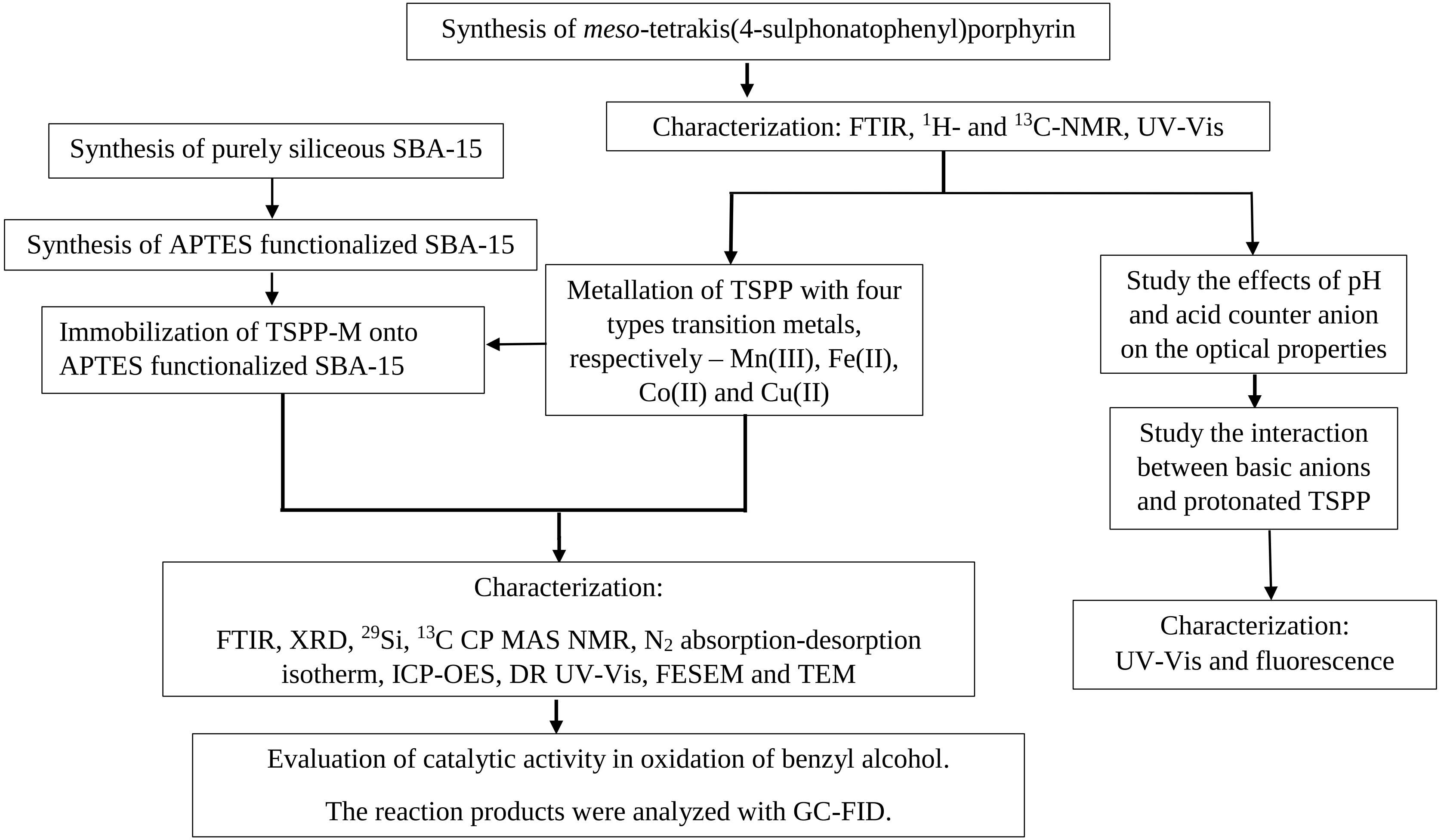


Figure 1.4 Outline of research

1.5 Significance of Study

In this research, the porphyrin *meso*-tetrakis(4-sulphonatophenyl)porphyrin (TSPP) which fulfils the prerequisite of high water-solubility, low toxicity and commercially available up to gram scale is an exciting candidate for a wide variety of research studies involving aqueous samples (Böhm and Gröger, 2015). The TSPP can be prepared in aqueous medium, making it more environmentally friendly as the usage of non-sustainable and flammable organic solvents can be minimised.

Furthermore, a new chromogenic and fluorogenic indicator based on TSPP has been developed for the quantitative analysis of acetate and citrate ions. The rich photochemistry of TSPP allows for the analysis of anions to be carried out by means of UV-Vis and fluorescence spectroscopies which do not require complicated instrument set up. Moreover, new techniques, fluorescence spectroscopy and prediction with Marvin Bean ChemSketch® (Chem Axon) were developed for the anion detection and prediction of TSPP charge species, respectively.

Additionally, the strong coordination properties of TSPP towards various kinds of transition metals allow for the development of selective biomimetic catalysts based on porphyrins. Green synthesis of benzaldehyde using alcohol as precursor and TBHP as oxidant for the transformation of benzyl alcohol to benzaldehyde can possibly reduce the generation of toxic side products and undesired inorganic contaminants. Recyclable and selective oxidation catalysts based on TSPP derivatives offer the prospect of commercialization and the oxidation reaction can be practically implemented to produce chlorine-free benzaldehyde that meets the stringent requirements of cosmeceutical and pharmaceutical industries.

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