

SYNTHESIS AND CHARACTERIZATION OF ZINC PORPHYRIN
COMPLEX HETEROGENIZED IN FUNCTIONALIZED SBA-15 FOR LIQUID
PHASE EPOXIDATION OF LIMONENE

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LIQUID PHASE EPOXIDATION OF LIMONENE

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Thank you ALLAH
Specially dedicated to lovely beloved emak abah,
En. Saadon Saad and Pn. Siti Tumiah Sanusi

Thank you so much for the love, support and prayers

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ABSTRACT

Long-range ordered mesoporous silica SBA-15 of high surface area and uniform pore size was obtained by hydrothermal synthesis using tetraethyl orthosilicate (TEOS) as silica source and Pluronic P123 copolymer as surfactant in acidic media. Functionalization of SBA-15 with 3-aminopropyltriethoxysilane (APTES) via sol-gel reaction gave NH₂-SBA-15 which was qualitatively confirmed with FTIR spectroscopy. Meanwhile, tetra-(*p*-chlorophenyl)porphyrin (TCIPP) was synthesized using modified Alder-Longo method. Insertion of zinc(II) into metal-free TCIPP was achieved using zinc(II) acetate to obtain ZnTCIPP. The successful complexation of zinc(II) in porphyrin molecule was supported by the disappearance of two Q bands and the presence of Soret band in the UV-Vis spectra. ZnTCIPP was also characterized using ¹H NMR spectroscopy, MALDI-TOF MS and elemental CHN analysis. Heterogeneous catalyst NH₂-SBA-15-ZnP was synthesized by incorporating various loadings of the ZnTCIPP into NH₂-SBA-15 and characterized by DR-UV Vis spectroscopy, N₂ adsorption-desorption isotherm, SAXS, FESEM and TEM. The DR-UV Vis spectra of NH₂-SBA-15-ZnP exhibit absorption peaks similar to free ZnTCIPP indicating that porphyrin molecule is confined in the SBA-15. Furthermore, the intensity of Soret and Q bands increases with increasing of ZnTCIPP loading. The hexagonal mesopore structure of SBA-15 was still intact after the modification treatments as shown by the SAXS patterns, FESEM and TEM images. The catalytic activity of homogeneous catalysts ZnTCIPP was compared with the heterogeneous NH₂-SBA-15-ZnP in the epoxidation of limonene in the presence of H₂O₂ oxidant. GC-FID and GC-MS detection analysis showed that the activity of heterogeneous catalysts NH₂-SBA-15-ZnP were active in the formation of limonene oxide as main product. The limonene conversion (34.72%) when catalyzed by free ZnTCIPP is comparable to NH₂-SBA-15-ZnP (26.24%) with ~95% selectivity. The catalytic activity of NH₂-SBA-15-ZnP increases with the increase of ZnTCIPP loading on the SBA-15 support. For the liquid-phase epoxidation of limonene over NH₂-SBA-15-ZnP catalyst in acetonitrile, the optimum conditions for the highest percentage of limonene conversion was at reaction temperature of 80°C during 24 h and using H₂O₂ as oxidant.

ABSTRAK

Silika mesolias SBA-15 bertertib julat jauh dengan luas permukaan tinggi dan saiz liang yang seragam telah diperolehi secara sintesis hidroterma menggunakan tetraetilortosilikat (TEOS) sebagai sumber silika dan kopolimer Pluronic P123 sebagai surfaktan dalam medium berasid. Pemfungsian SBA-15 dengan 3-aminopropiltrioksisilana (APTES) melalui tindak balas sol-gel menghasilkan NH₂-SBA-15 yang disahkan secara kualitatif menggunakan spektroskopi FTIR. Manakala, tetra-(*p*-klorofenil)porfirin (TCIPP) telah disintesis menggunakan kaedah Alder-Longo terubahsuai. Penyelitan zink(II) ke dalam TCIPP tanpa logam terhasil menggunakan zink(II) asetat untuk menghasilkan ZnTCIPP. Kejayaan pengkompleksan zink(II) dengan molekul porfirin telah disokong oleh kehilangan dua jalur Q dan kehadiran jalur Soret pada spektrum UV-Vis. ZnTCIPP juga telah dicari menggunakan spektroskopi ¹H NMR, spektroskopi MALDI-TOF MS dan analisis unsur CHN. Mangkin heterogen NH₂-SBA-15-ZnP telah disintesis dengan memasukkan pelbagai muatan ZnTCIPP ke dalam NH₂-SBA-15 berfungsi amino dan dicirikan menggunakan spektroskopi DR-UV Vis, analisis isoterma penyerapan-penyahjerapan N₂, SAXS, FESEM dan TEM. Spektrum DR-UV-Vis bagi NH₂-SBA-15-ZnP mempamerkan puncak penyerapan yang serupa dengan ZnTCIPP bebas yang menunjukkan molekul porfirin terkurung dalam SBA-15. Tambahan lagi, keamatan jalur Soret dan Q turut meningkat dengan peningkatan muatan ZnTCIPP. Struktur heksagon mesolias SBA-15 masih utuh selepas perawatan pengubahsuaian seperti yang ditunjukkan oleh pola SAXS, imej FESEM dan TEM. Aktiviti pemangkinan untuk mangkin homogen ZnTCIPP telah dibandingkan dengan mangkin heterogen NH₂-SBA-15-ZnP dalam pengoksidaan limonena dengan kehadiran oksidan H₂O₂. Analisis pengesanan GC-FID dan GC-MS menunjukkan mangkin heterogen NH₂-SBA-15-ZnP adalah aktif dalam pembentukan oksida limonena sebagai produk utama. Penukaran limonena adalah lebih kurang sama (34.72%) apabila dimangkin oleh TCIPP bebas jika dibandingkan dengan NH₂-SBA-15-ZnP (26.24%) dengan ~95% kepilihan. Aktiviti pemangkinan NH₂-SBA-15-ZnP bertambah dengan pertambahan muatan ZnTCIPP ke atas penyokong SBA-15. Bagi pengoksidaan fasa cecair limonena menggunakan mangkin NH₂-SBA-15-ZnP dalam pelarut asetonitril, keadaan optimum untuk menghasilkan peratus penukaran limonena tertinggi adalah pada suhu tindak balas 80°C dalam tempoh 24 jam dan menggunakan H₂O₂ sebagai oksidan

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LIST OF ABBREVIATIONS

CAN	-	Acetonitrile
APTES	-	(3-aminopropyl)triethoxysilane
BET	-	Brunauer- Emmet Teller measurement
CHN Analysis	-	Carbon, Hydrogen, Nitrogen Analysis
CTAB	-	Cetyltrimethylammonium bromide
DCM	-	Dichloromethane
H	-	Hour
H ₂ O ₂	-	Hydrogen peroxide
IUB	-	International Union of Biochemistry
IUPAC	-	International Union of Pure and Applied Chemistry
MALDI-TOF MS	-	Matrix Assisted Laser Desorption Ionization Time-Of-Flight Mass Spectrometer
MCM	-	Mobil Composition of Matter
NH ₂ -SBA-15	-	Amino functionalized SBA-15
NH ₂ -SBA-15-ZnP	-	ZnTCIPP immobilized into amino functionalized SBA-15
Nm	-	Nanometer
Pluronic P123	-	Poly(ethylene glycol)–block-poly(propylene glycol)–block- poly(ethylene glycol) copolymer
SBA	-	Santa Barbara Amorphous
TBHP	-	<i>tert</i> - butyl hydrogen peroxide
ZnTCIPP	-	[Tetra-(<i>p</i> -chlorophenyl) porphyrinato] Zn(II)
Λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In the past recent years (Adam and Ooi, 2012; Madadi and Rahimi, 2012; Sabour *et al.*, 2013), there are extensive researches on green and environmental friendly catalysts. Apart from being selective and effective, this type of catalyst will fulfil the needs from economic, political and environmental perspectives. Green catalyst would increase the efficiency of the reaction, and beneficiary to the environment through minimization of waste and dangerous byproducts (Anastas *et al.*, 2000). One of the well-recognized environmental catalysts is biomimetic catalyst such as metalloporphyrins. Natural metalloporphyrins complexes were found in chlorophyll, heme and cytochrome P450 which play the major roles in oxygen and electron transport as well as for storage. They have been widely produced synthetically in mimicking the natural occurrence bio-system.

Various types of metals such Co, Zn, Cu, Mn and Ru can be inserted into the porphyrin cavity by using various metal salts. The metalloporphyrin formed by removal of the inner NH protons that act as multidentate ligand, proficient enough to bind metal ions through multiple sites (Wijesekera and Dolphin, 1994). Zinc metal with d^{10} configuration could form a complex with the porphyrin because Zn^{2+} ion in medium size is suited well to the porphine core (Inamo *et al.*, 1997). In addition, zinc

porphyrin possess an immobilized Lewis acid binding site at Zn^{2+} and four additional urea -NH group (Boa *et al.*, 2007).

There have been many research on application of metalloporphyrin in this field such as enzyme mimicking catalyst, ion receptor (Bao *et al.*, 2007), adsorbent for metal removal (Jeong *et al.*, 2010) and catalysis. In catalysis, these metal complexes provide competent environment for alkene epoxidation and alkane hydroxylation to react. Epoxidation of stilbene and cyclooctane in the presence of iron(III)-(*meso*-tetrakis(fluorophenyl)porphyrin using various oxidants have been reported (Nam *et al.*, 2000). The epoxidation with *m*-chloroperbenzoic acids (MCPBA) gave the highest conversion of the epoxides products but the reaction take place at very low temperature of $-45^{\circ}C$.

So far, metalloporphyrins have been widely studied as homogeneous catalyst. It is reported that the porphyrin ring is liable to oxidative self-destruction, and oxidation of hydrophobic organic substrates by these water-soluble complexes is difficult since the active catalytic species remains dissolved in the aqueous phase (Rosa *et al.*, 2000). Moreover, it is difficult to separate the catalyst and the product of homogeneous catalysis, result in increasing the cost of production.

In contrast, heterogenous catalyst has the advantage of easy separation of the catalyst and products by means of filtration. Therefore, in order to overcome this problem, the metalloporphyrins have to be transformed into heterogeneous catalyst. These metalloporphyrins can be heterogenized by immobilizing them to a solid support, hence directly tuning the liquid phase oxidation from homogeneous to heterogeneous. In heterogeneous catalysis, the metalloporphyrin acts as active site that can be adsorbed physically and bonded chemically to the surface active groups of the solid support.

The immobilization of metalloporphyrin possibly can avoid molecular aggregation or molecular self-destruction reaction which leads to deactivation of

catalytic metalloporphyrin active species. In addition, the improvement to heterogeneous catalysts offers an easy way to recover them from reaction media and reused back (Nakagaki *et al.*, 2000).

Many supports have been used for immobilization of metalloporphyrin. Some of them are clays, silica gel, resin, alumina and modified porous silica (Adam, and Ooi, 2012). In this study, modified mesoporous silica SBA-15 were utilized as the support for porphyrin molecule due to its large pore size (up to 30 nm) and high surface area ($>1000 \text{ m}^2 \text{ g}^{-1}$). This silicate material is thermally and hydrothermally stable, chemically resistant to organic solvent, possesses larger unit cell, well defined morphologies as well as thicker pore size compared to MCM-41 or MCM-48. Mesoporous material SBA-15 also possesses long range ordered structure that make it suitable for application as catalyst support (Zhang *et al.*, 2005).

However, if the metalloporphyrin complex were to attach directly to SBA-15 by weak physical adsorption such as hydrogen bonding, hydrophobic attraction or electrostatic interaction, the adsorbed complex would leach out of the mesoporous channels easily. By covalently bonding the metalloporphyrin on reactive group such as amine, epoxide or thiol group inside the pore, the immobilization stability can be significantly enhanced since it is solid, it can be recycled (Zhao *et al.*, 2012).

Amino-modified mesoporous materials have attracted considerable attention among the variety of organo-functionalized mesoporous materials. The amino-functionality is useful for many practical applications including heterogeneous base catalysis, toxic arsenate ion trapping, biomolecule immobilization, as covalent spacer in the mobilization of catalytically active metal complexes and as a supports for metallic nanoparticles (Sujandi *et al.*, 2006).

In this research, the SBA-15 surface was modified using 3-aminopropyltriethoxysilane (APTES) to produce a terminal amine group ($-\text{NH}_2$). The proposed structure of zinc(II) porphyrin complex immobilized in amino-

functionalized mesoporous silica SBA-15 is shown schematically in Figure 1.1. The amine groups were found to be beneficial for coupling of protein porphyrin to the surface of the silica materials. (Chong and Zhao, 2003) (Serwika *et al.*, 2004). The zinc porphyrin complex contains electron withdrawing group substituents on the *meso*-aryl rings, and its *para*-chloro substituent allows the immobilization via covalent bond with an amine group from functionalized mesoporous silica (Nakagaki *et al.*, 2014).

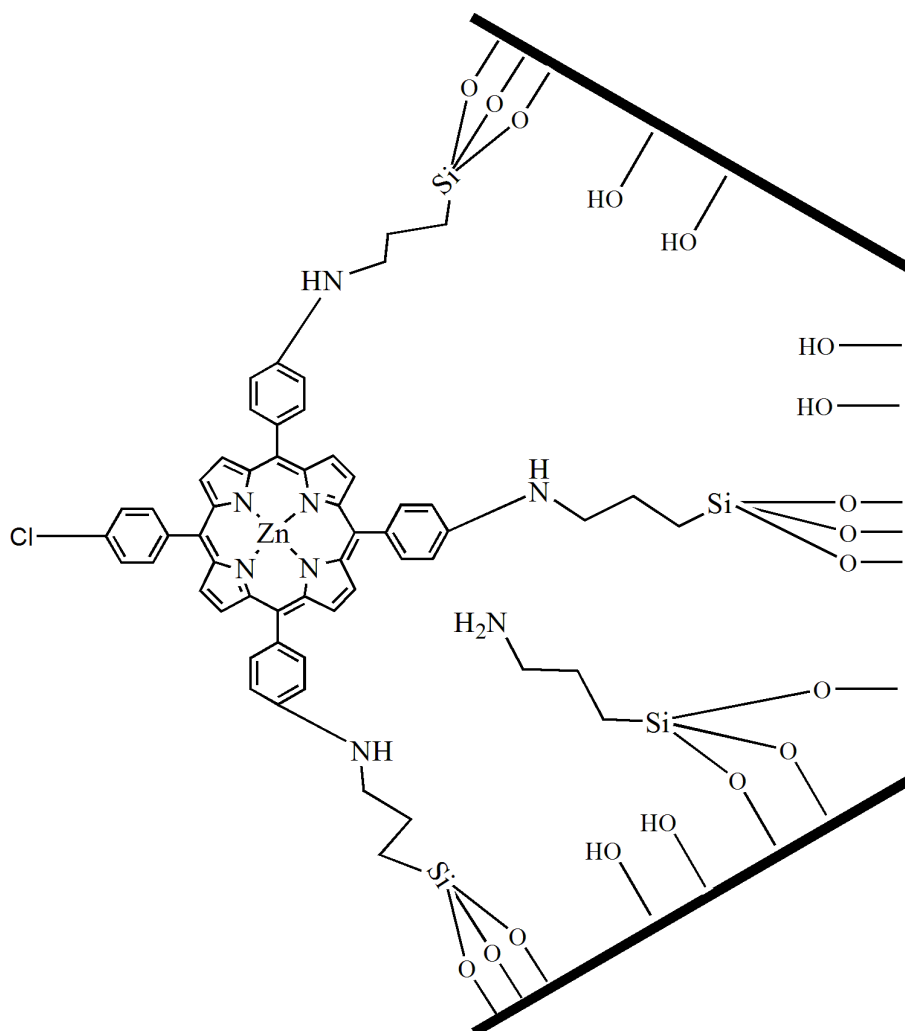


Figure 1.1 Proposed structure of zinc(II) porphyrin complex immobilized in amino-functionalized mesoporous silica SBA-15

The epoxidation of alkene is an oxidation process whereby an oxygen atom is added into the compounds. The olefin epoxidation reaction has fascinated researchers because of the usefulness of epoxide as intermediate agents in organic synthesis,

since the epoxide can be further transformed by ring opening, to form highly functionalized products (Oliveira *et al.*, 2009). Limonene epoxidation product, 1,2-limonene oxide covered many purposes in synthetic chemistry. In addition, the oxygenated compounds derived from terpene and natural terpenoid are crucial in manufacture of fragrance, flavours and food additives (Casuscelli *et al.*, 2004).

Epoxidation have been studied extensively but the organic peracids like *m*-chloroperbenzoic acid are still widely used as epoxidation agents. By using peracids as oxidants, the reaction produces acid waste directly as sub-product beside the desired oxidation products. The peracid is also a matter of concern in safety issues (Yi *et al.*, 2009; Wade, 2006; Grigoropoulou *et al.*, 2003).

Therefore, the present work explores the potential of synthetic zinc(II) porphyrin complex immobilized into the amino functionalized SBA-15 as heterogeneous catalyst for liquid phase epoxidation of limonene. The catalytic activity and recyclability of the catalysts were investigated. Reaction parameter such as temperature, oxidant and reaction time were then optimized.

1.2 Problem Statement

Metalloporphyrins attract a great interest to the researchers in catalytic study since the establishment of the well-known iron porphyrin-based cytochrome P450 with high capability in catalyzing many oxidation transformations. However, synthetic metalloporphyrin are extensively used as homogenous catalyst. As compared to heterogeneous catalyst, homogeneous catalyst usually is more active, but it is often difficult to separate the catalyst from reaction mixture resulting in higher cost in commercial processes. Thus, it is highly desirable to improve the metalloporphyrin catalytic properties, which possess equally the high selectivity of homogeneous catalyst and convenience of heterogeneous catalyst. In order to

accomplish this goal, one of the ways is to immobilize the homogeneous catalyst in high surface area solid support. SBA-15 is chosen despite of MCM-41 because SBA-15 has larger mesopore, from 3nm up to 15nm as reported by Zhao *et al.* (1998) compared to MCM-41 only 2nm to 3nm pore size (Schmidt *et al.*, 1995). The large pore obtained from the copolymer surfactant used as the template. The larger pore size of SBA-15 assist porphyrin complex to easily immobilized into the pore of SBA-15. Therefore, in this research, [tetra(*p*-chlorophenyl)porphyrinato]Zn(II) (ZnTCIPP) immobilized in amino-functionalized SBA-15 was synthesized as the recyclable heterogeneous epoxidation catalyst.

In this study, the epoxidation of limonene was used as model reaction to evaluate the catalytic activity of zinc porphyrin supported functionalized SBA-15 materials. This reaction is of interest because the product, 1,2-limonene oxide are essential in various fields such as the flavours and fragrance industries. In addition, most of the known oxidation reactions are not industrial tolerance due to its low selectivity and waste generation. A new trend involving the oxidation process is the use of environmentally friendly oxidant and catalyst. The recycled catalyst and clean H₂O₂ as oxidant will lead to safer and unpolluted oxidation procedures. Therefore, in this study the reactivity of synthesized ZnTCIPP complex incorporated into amino functionalized SBA-15 was investigated in epoxidation of limonene.

1.3 Objectives of Study

The objectives of this study are:

- i. To synthesize [tetra-(*p*-chlorophenyl)porphyrinato] Zn(II) (ZnTCIPP) complex.
- ii. To synthesize (3-aminopropyl)triethoxysilane (APTES) functionalized SBA-15.

- iii. To immobilize ZnTCIPP complex into APTES functionalized SBA-15.
- iv. To evaluate and optimize the catalytic activity of ZnTCIPP complex immobilized into APTES functionalized SBA-15 in liquid phase epoxidation of limonene using H₂O₂ as oxidant in acetonitrile.

1.4 Scope of Study

The zinc(II) porphyrin complex of ZnTCIPP was first synthesized using Alder-Longo modified method and characterized using Fourier Transform Infrared (FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis), ¹H Nuclear Magnetic Resonance spectroscopy (NMR), CHN elemental analysis and Matrix-Assisted Laser Desorption Ionization Time-Of-Flight Mass Spectrometer (MALDI-TOF MS).

Subsequently, SBA-15 was synthesized and functionalized with APTES before ZnTCIPP was immobilized into functionalized SBA-15. The immobilized material then was characterized using Small-Angle X-ray Scattering (SAXS), Diffuse Reflectance UV- Vis Spectroscopy (DR UV-Vis), Field Emission Scanning Electron Spectroscopy (FESEM), Transmission Electron Microscopy (TEM) and N₂ Adsorption- Desorption Isotherm Analysis.

The catalytic activity and reusability of the heterogenized zinc(II) porphyrin complex were compared with the homogeneous ZnTCIPP in the epoxidation of limonene. Reaction parameters such as temperature, type of oxidant and reaction time were optimized. The products of limonene epoxidation were analyzed using Gas Chromatography- Flame Ionization Detector (GC-FID) and Gas Chromatography- Mass Spectrometry (GC-MS)

1.5 Outline of Study

Figure 1.2 shows the outline of research activities for the synthesis and characterization of recyclable zinc porphyrin complex heterogenized in functionalized SBA-15 for liquid phase epoxidation of limonene.

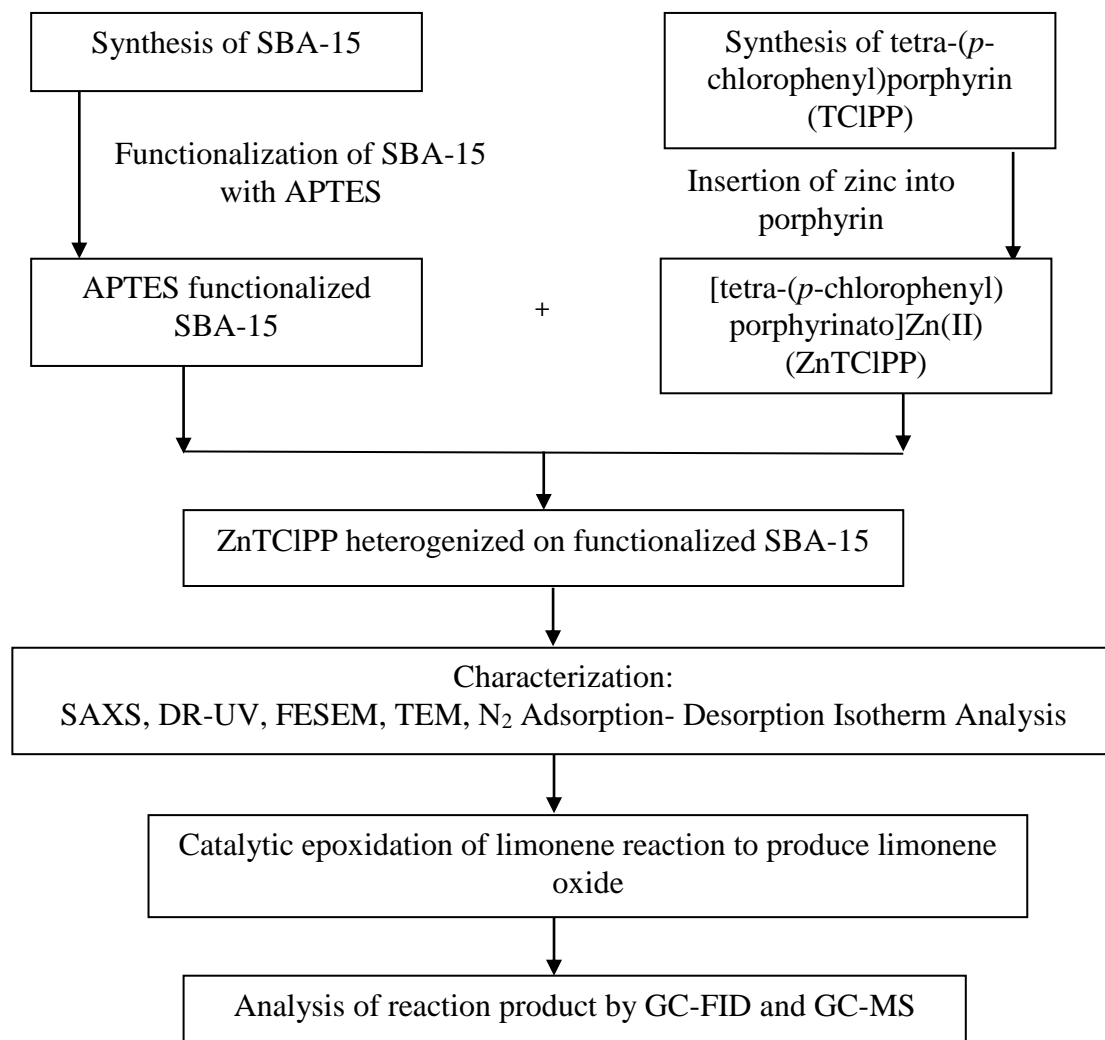


Figure 1.2 The outline of the study

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