การสังเคราะห์เมทัลโลพอร์ไฟรินที่มีคาลิกซ์[4]เอรีนและคาลิกซ์[4]พิร์โรลเพื่อเป็นไอโอโนฟอร์ในอิเล็กโทรดแบบเลือกจะเพาะต่อแอนไอออน

นางสาวณัฐภรณ์ ลาบึง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SYNTHESIS OF METALLOPORPHYRIN CONTAINING CALIX[4]ARENE AND CALIX[4]PYRROLE AS IONOPHORES IN ANION SELECTIVE ELECTRODES

Miss Nattaporn Labung

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemistry
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Thesis Title	SYNTHESIS OF METALLOPORPHYRIN CONTAINING CALIX[4]ARENE AND CALIX[4]PYRROLE AS IONOPHORES IN ANION SELECTIVE ELECTRODES
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ณัฐภรณ์ ลาบึง : การสังเคราะห์เมทัลโลพอร์ไฟรินที่มีคาลิกซ์[4]เอรีนและคาลิกซ์ [4]พิร์โรลเพื่อเป็นไอโอโนฟอร์ในอิเล็กโทรดแบบเลือกจะเพาะต่อแอนไอออน . (SYNTHESIS OF METALLOPORPHYRIN CONTAINING CALIX[4]ARENE AND CALIX[4]PYRROLE AS IONOPHORES IN ANION SELECTIVE ELECTRODES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร.บัญชา พูลโภคา , อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ศ.ดร. ธวัชชัย ตันฑุลานิ, 121 หน้า.

ในงานวิจัยนี้เป็นการสังเคราะห์สารประกอบเมทัลโลพอร์ไฟรินที่มีหน่วยคาลิกซ์ [4]เอรีน (ML1) และคาลิกซ์[4]พิร์โรล (ML2) เป็นองค์ประกอบในโมเลกุล แต่มีเพียงโมเลกุล ML1 เท่านั้นที่ใช้เป็นไอโอนอฟอร์ในเมมเบรนอิเล็กโทรด โมเลกุล ML1 สังเคราะห์จากการทำปฏิกิริยาเมทัลเลชันของโลหะทรานซิชันกับโมเลกุล L1 ที่สังเคราะห์จากการรวมตัวกันของสารประกอบคาลิกซ์[4]เอรีนที่มีหมู่ไดไพโรลมีเทนสองหมู่ (4) กับเบนซาลดีไฮด์ โดยมีกรดเป็นตัวเร่งปฏิกิริยา และนำโมเลกุล ML1 (ZnL1, CuL1, CoL1, FeL1 และ SnL1) ที่สังเคราะห์ได้ไปใช้เป็นไอโอโนฟอร์ในการศึกษาการตอบสนองทางเคมีไฟฟ้าของแอนไอออนแต่ละตัวและการเลือกจำเพาะต่อแอนไอออนของเมมเบรนที่เตรียมได้จากสารประกอบเมทัลโลพอร์ไฟริน พบว่าเมมเบรนอิเล็กโทรดที่มี ZnL1, CuL1, CoL1 และ FeL1 ทำหน้าที่เป็นไอโอโนฟอร์ในอิเล็กโทรดแบบเลือกจำเพาะต่อแอนไอออน สามารถเลือกจับกับไอโอไดด์ได้ดีที่สุด แต่มีเปอร์คลอเรตและไทโอไซยาเนตที่เป็นไอออนรบกวน และเมมเบรนอิเล็กโทรดที่มี SnL1 หน้าที่เป็นไอโอโนฟอร์ในอิเล็กโทรดแบบเลือกจำเพาะต่อแอนไอออนสามารถเลือกจับกับซาลิซิเลตได้ดีที่สุด โดยมีไอโอไดด์เป็นไอออนรบกวน

สาขาวิชา............เคมี..............................ลายมือชื่อนิสิต..
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This thesis reported the synthesis of metalloporphyrins containing calix[4]arene (**ML1**) and calix[4]pyrrole (**ML2**) However, only **ML1** was used as ionophores in anion selective electrodes. **ML1** was synthesized by metallation of **L1** and metal salts. The **L1** was obtained from the acid catalyzed condensation of benzaldehyde and 1,3-calix[4]arene-bis-dipyrromethane (**4**). Compound **ML1** (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**) was used as ionophore in ion selective electrodes. The potentiometric response of anions for ionophores (**ZnL1**, **CuL1**, **CoL1** and **FeL1**) showed the selectivity toward iodide with perchlorate and thiocyanate as interference ions. Moreover, the potentiometric response of anions for ionophores **SnL1** exhibited selectivity toward for salicylate more than other anions, with iodide as an interference ion.

Department: Chemistry Student's Signature……………………….

Field of Study Chemistry Advisor's Signature……………………

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LIST OF ABBREVIATIONS

Å	Angstrom
^{13}C NMR	Carbon Nuclear Magnetic Resonance
°C	Degree celsius
calcd	Calculated
g	Gram (s)
β	Beta position
δ	Chemical shift
^{1}H NMR	Proton Nuclear Magnetic Resonance
J	Coupling constant
K	Kelvin
s,d, dd, t,m	Splitting patterns of ^{1}H NMR (singlet, doublet, doublet of doublet, triplet and multiplet)
MALDI-TOF-MS	Matrix Assisted Laser Desorption/ Ionization-Time of Flight Mass spectrometry
MeOH	Methanol
EtOH	Ethanol
RT	Room temperature
DMF	Dimethylformamide
ppm	Parts per million
$CDCl_3$	Deuterated chloroform
DMAP	4-Dimethylaminopyridine
TsCl	Toluene-4-sulfonyl chloride
M	Molar
M^{-1}	Per molar
m/z	Mass to charge
Hz	Hertz (s)
FT-IR	Fourier Transform Infrared Spectroscopy

HCl	Hydrochloric acid
µL	Microliter (s)
TFA	Trifloroacetic acid
CH_2Cl_2	Methylene chloride
CH_3COOH	Acetic acid
K_2CO_3	Potassium carbonate
Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium sulfate
$NaHCO_3$	Sodium hydrogencarbonate
NaOH	Sodium hydroxide
NaBr	Sodium bromide
NaCl	Sodium chloride
NaI	Sodium iodide
KF	Potassium fluoride
$NaClO_4$	Sodium perchlorate
KSCN	Potassium thiocyanate
NaSal	Sodium salicylate
NaOAc	Sodium acetate
NaH_2PO_4	Sodium dihydrogenphosphate
$NaNO_3$	Sodium nitrate
$NaNO_2$	Sodium nitrite
Na_2HPO_4	Sodium hydrogenphosphate
mL	Milliliter (s)
mg	Milligram (s)
kg	Kilogram
EA	Elemental Analysis
λ_{abs}	Absorption wavelength
EtOAc	Ethyl acetate
$CHCl_3$	Chloroform

TLC	Thin Layer Chromatography
h	Hour (s)
nm	Nanometer
TDMACl	Tridodecylmethylammonium chloride
KT*p*ClPB	Potassium tetrakis(4-chlorophenyl)borate
MES	4-Morpholinoethanesufonic acid
Gly	Glycine
PVC	Poly(vinyl chloride)
o-NPOE	*o*-Nitrophenyloctylether
TEA	Triethylamine
THF	Tetrahydrofuran
ISE	Ion Selective Electrode (s)
mmol	Millimole (s)
T	Temperature
UV/Vis	Ultraviolet and Visible Spectrophotometry
mV	Millivolt (s)
min	minute
v/v	volume by volume
XRD	x-ray diffraction

CHAPTER I

INTRODUCTION

1.1 Ion Selective Electrodes

The ion selective electrode (ISE) is a potentiometric chemical sensor composing of a membrane whose potential demonstrates the activity of the ion to be defined in a solution (the analyte). Membranes of ISEs consist either of liquid electrolyte solution or glassy or solid that usually have insignificant electron conductivity under the conductions of measurements. ISEs have many undoubted advantages such as low cost, portable and suitable for direct determinations and sensing of ions in solution.(1)

The beginning of ion selective electrodes (ISEs) is connected to the search for biological membrane models. In 1906 Cremer found that a thin glass membrane separating the two electrodes of a galvanic cell made the electromotive force (EMF) of this cell dependent on hydrogen ion concentration. After more than sixty years of study of liquid membrane electrodes was produced which, the first liquid membrane electrodes provided the means for the determination of the activity of Ca^{2+} ions in solution.(2)

The main demand for an organic liquid membrane was that it should be insoluble in water, low volatility, interacted reversibly with the ion of interest and presented some degree of charge conduction which, hypothetically, occurred by the transport of ions by organic molecules.(3)

Probably the most essential advance in liquid membrane electrodes, other than the original discovery, occurred in 1970 when it was exhibited that the organic liquid of the liquid membrane ion selective electrodes (ISEs) could be immobilized into poly(vinyl chloride), PVC, to make a polymer film with sensing properties. These was possible because the reagents and organic liquids used for preparing the liquid membrane were, commonly, excellent plasticizers for PVC. Then plasticizers lower the glass transition temperature of PVC producing fructify homogeneous and flexible films with good mechanical stability. PVC-based membrane electrodes all contain an important reagent which selectively binds the interested ion. This reagent is generally referred as an ionophore or ion carrier. Considerable research has been carried out on these types of membranes and there were many reports of sensors for verious ions and species.(1,2)

The typical PVC membrane ion selective electrode was shown in Figure 1.1. The membrane can be casted onto a glass slide surface, cut as a disc and glued onto the end of a tube. A suitable inner filling solution was then added. These were the configuration which ordinarily used in commercial polymer membrane electrodes although some producers have modified the electrode for easiness of use.

Figure 1.1 Schematic diagram of a membrane electrode measuring circuit and cell assembly.(1)

The potentiometry with ion selective electrodes (ISEs), it was usually the EMF of cell of the following general type that is measured.(2)

reference electrode 1 (Hg/Hg_2Cl_2) || solution 1 | membrane | solution 2 || reference electrode 2 (Ag/AgCl)

The solution 1 (the analyte) contained the ion to be measured. The actual potentiometric system consisted of internal reference electrode 2, inner filling of the ISE, and the membrane. The reference electrodes, electrodes of the second kind (silver/silver chloride electrode, calomel electrode) were normally used.

The EMF responding to only one type of ions can be described by the Nernst equation(1,4):

$$E_{\mathrm{M}} = E^{\circ} + (RT/z_{\mathrm{I}}F)\ \mathrm{In}\ a_{\mathrm{I}}(\mathrm{aq}) \qquad (1)$$

Where E_{M} is the membrane potential, E° incorporates all potential contributions of the measuring cell that are constant for this measurement and is unique for each measured ion. While a_{I} and z_{I} are the activity and the charge of the measured ion, respectively, and the symbols *R*, *T* and *F* are the universal gas constant, the absolute temperature and the Faraday constant, respectively.

The selectivity is one of the most important characteristics of a potentiometric sensor. It often defined whether a credible measurement in the analyte sample is possible. The theoretical selectivity description allows researchers to identify the key parameters for optimizing the performance of potentiometric sensors, for example adjusted weighting parameters (i.e., absolute membrane concentrations) or choosing different plasticizers.

The determination of selectivity coefficients(1,4), can be performed using two different methods defined from Nicolskii coefficients of ion selective electrodes (ISEs) so-called separate solution method (SSM) and fixed interference method (FIM). The separate solution method (SSM) associated the measurement of two separate solutions, each contained a salt of the determined ion only. The Nicolskii coefficient was then calculated from the two observed potential values shown in eq 2

$$K_{IJ}^{\mathrm{pot}} = \frac{a_I}{a_J^{z_I/z_J}} \exp\left\{\frac{E_J - E_I}{RT} z_I F\right\} \qquad (2)$$

Where K_{IJ}^{pot} was the selectivity coefficient, E_I and E_J were the potential response of the primary ion and the interference ion, respectively, a_I and a_J were the activity of the primary ion and the interference ion, respectively, and z_I and z_J were the charge of the primary ion and the interference ion, respectively.

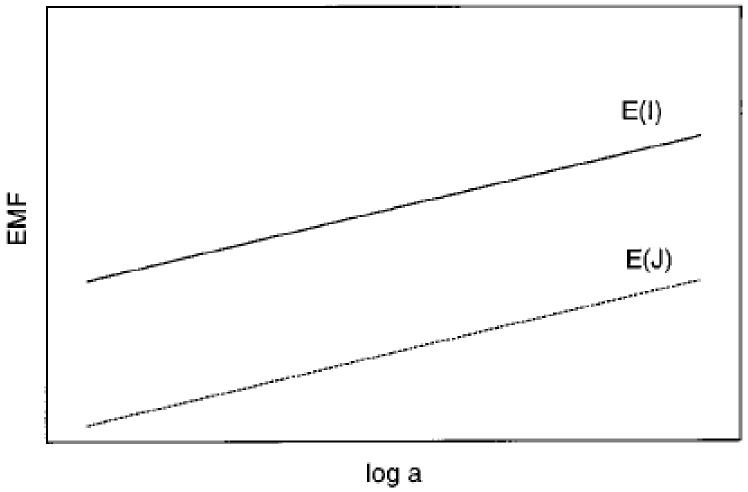


Figure 1.2 Determination of the Nicolskii coefficients according to the separate solution method (SSM).(1)

For the fixed interference method (FIM)(1,4), calibration curves of the primary ion, I, were determined by using adjusted primary ion in the solution contained a constant concentration of interfering ions, J, in the solution until a Nernstian slope to the primary ion is observed. This linear response part was extrapolated to the emf for the background interference only and a primary ion activity, a_I(DL), at the detection limit, which together with the interfering ions activity in the background, a_J(BG) as seen in eq 3.

$$logK_{I,J}^{pot} = \log\left(\frac{a_I(DL)}{a_J(BG)^{Z_I/Z_J}}\right) \qquad (3)$$

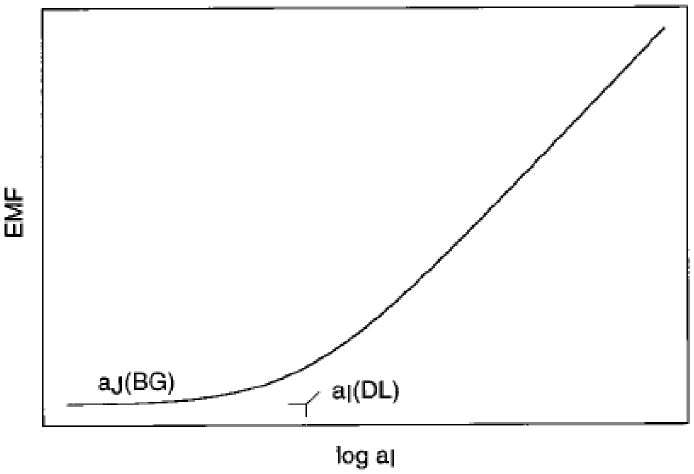


Figure 1.3 Determination of the Nicolskii coefficients according to the fixed interference method (FIM).(1)

1.2 Ionophores of Anion Selective Electrodes

Ionophores or ion-carriers were important reagents in the membrane electrode. It acted as complexing agent, often composed of marcroclyclic structures and transition metal complexes exhibited potentiometric selectivity toward particular ions. The emf response of the membrane based on complexes was believed to occur from binding to the axial position of the metal center. Metal complexes composing of different ligands for examples, cobyrinate(5), phthalocyanine(6), salophen(7), salen(8), and porphyrin(9) have been reported to be good ionophores for anions.

1.2.1 Porphyrin Based Anion Sensors

The porphyrin(10) was a macroclyclic molecule, which showed a very important role in the metabolism of living organisms. It contained four pyrrole rings linked via methane bridges as shown Figure 1.4.

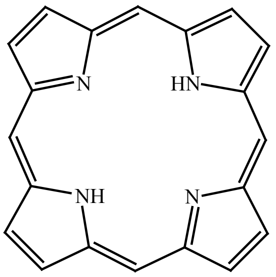
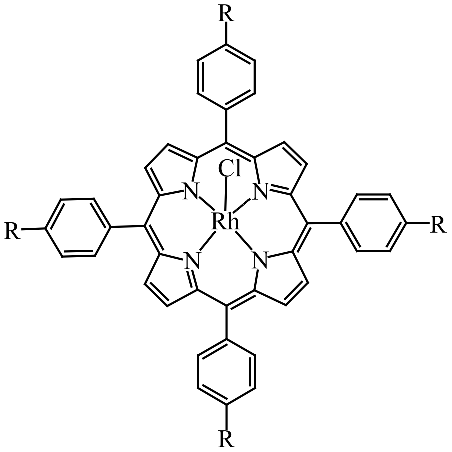


Figure 1.4 The structure of porphyrin[10]

The porphyrin ring displayed aromatic characters and was very stable. Porphyrin and metalloporphyrin derivatives displayed many key roles in essential biological process such as storage, photosynthesis and oxygen transport, for example, cobalt complex in Vitamin B_{12}, magnesium complex in chlorophyll and iron complex in haemoprotien. The porphyrin ring with Lewis acid such as zinc could become produce selective redox active reagents for anions. Metalloporphyrin exhibited potentiometric anions selectivity.

Pietrzak *et al.*(11) synthesized ionophores based on rhodium(III) porphyrins and rhodium(III) salophens as doped polymer membrane electrodes which were selective to nitrite as shown in Figure 1.5 that both anionic additives or cationic additives in the polymer membrane gave highest response to nitrite. The detection limit was in the order of 5×10^{-6} M and selectivity order for the membrane was NO_2^- > SCN^- > Sal^- > ClO_4^- > Br^- > NO_3^- > Cl^- ~ F^-.

a)



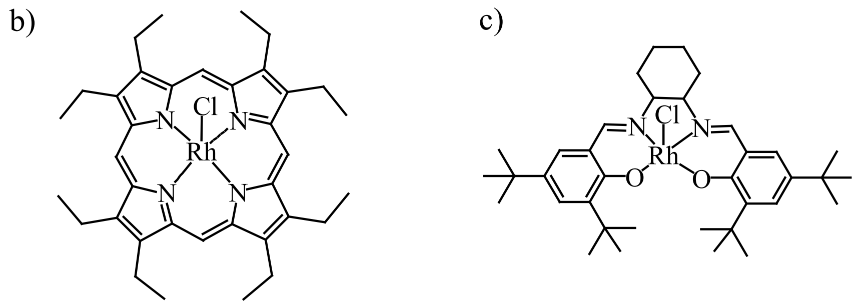
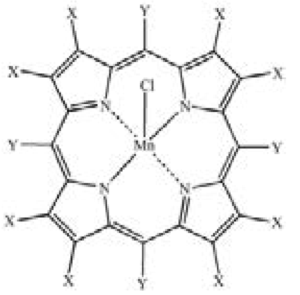


Figure 1.5 Structures of ionophores (a) rhodium(III) 5,10,15,20-tetraphenylporphyrin chloride (Rh-TPP) when R = H, or (Rh-tBTPP) when R = *tert*-butyl; (b) rhodium(III) 2,3,7,8,12,13,17,18-octaethylporphyrin chloride (Rh-OEP); (c) rhodium(III) (*S*,*S*)-(+)-*N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine(Jacobsen's ligand).(11)

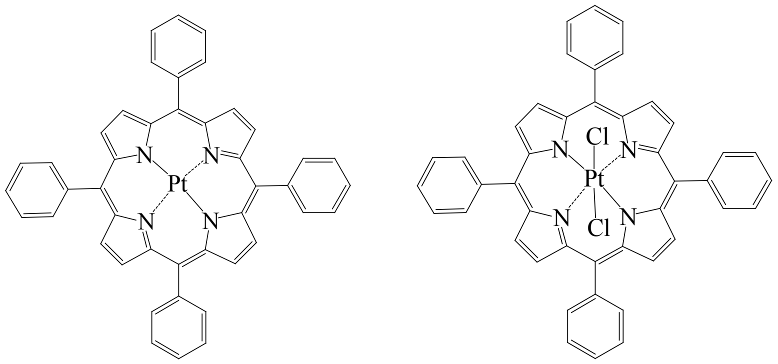
Khorasani *et al.*(12) synthesized new ionophores, 5,10,15,20-tetrakis(4-aminophenyl)porphine manganese(III) chloride (Mn(TNH$_2$PP)Cl) (**1**), 5,10,15,20-tetratolylporphine manganese(III) chloride (Mn(TTP)Cl) (**2**), 5,10,15,20-tetrakis(pentafluorophenyl)porphine manganese(III) chloride (Mn(TF$_5$PP)Cl) (**3**), and two previously reported thiocyanate ionophores, octabromo-5,10,15,20-tetraphenylporphine manganese(III) chloride (Mn(Br$_8$TPP)Cl) (**4**), and 5,10,15,20-tetraphenylporphine manganese(III) chloride (Mn(TPP)Cl) (**5**) in PVC membrane electrodes. They found that electrodes recognized thaiocyanate and exhibited a wide linear range 10^{-7} to 10^{-1} M of SCN^- in phosphate buffer pH 4.5. The detection limit was in the order of 5×10^{-8} M and a wide pH range 3-8. It could be applied to determine SCN^- in urine samples.



1 X =H, Y = *p*-aminophenyl, Mn(TNH$_2$PP)Cl
2 X =H, Y = *p*-tolyl, Mn(TPP)Cl
3 X =H, Y = pentafluorophenyl, Mn(TF$_5$PP)Cl
4 X =Br, Y = phenyl, Mn(Br$_8$TPP)Cl
5 X =H, Y = phenyl, Mn(TPP)Cl

Figure 1.6 Structures of new ionophores manganese(III) porphyrin complexes.(12)

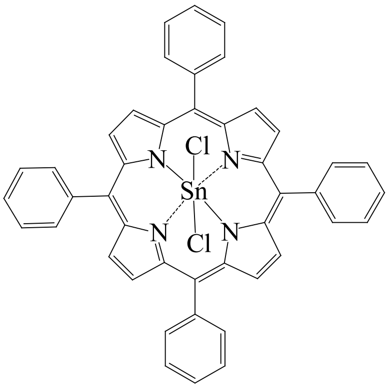
Lvova *et al.*(13) reported that they prepared platinum porphyrin core as ionophores for iodide selective electrodes as shown in Figure 1.7. Pt(II) porphyrins acted as neutral carriers with cationic additives (TDMACl).



6 **7**

Figure 1.7 Structures of platinum porphyrine complexes as ionophores.(13)

Santos *et al.*(14) reported the synthesis of ionophores 5,10,15,20-tetraphenyl(porphyrinato)-tin(IV) (Sn(IV) [TPP]Cl_2) and 2,3,7,8,12,13,17,18-octaethyl(porphyrinato)tin(IV) (Sn(IV)[OEP]Cl_2) (Figure 1.8) *via* metallation of the free porphyrin (H_2[TPP] or H_2[OEP]) using $SnCl_2$. It was found that polymer membrane doped with Sn(IV) [TPP]Cl_2 and Sn(IV)[OEP]Cl_2 selectively recognized phthalate ion more than other anions using cationic additives (TOABr) and anionic additives (NaTPB and KTFPB) as shown in Figure 1.9. Both ionophores 8 and 9 were found to operate *via* a neutral mechanism.



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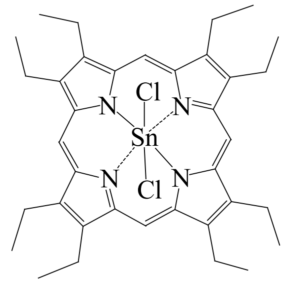


9

Figure 1.8 Structures of Tin(IV) porphyrine complexes as ionophores A) Sn(IV)[TPP]Cl_2 ; B) Sn(IV)[OEP]Cl_2.(14)

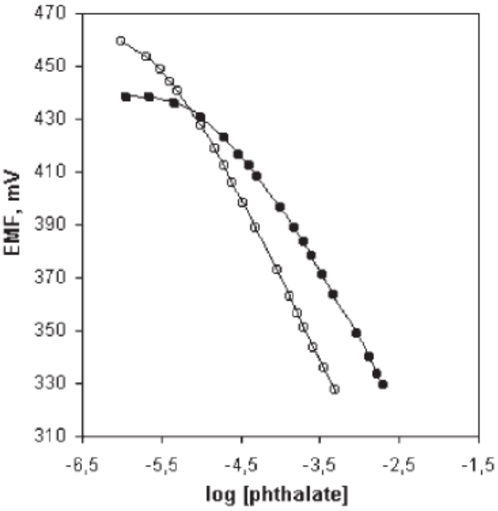


Figure 1.9 The calibration curves for the emf responses toward phthalate of membranes prepared with (O) Sn(IV)[TPP]Cl_2 and ●) Sn(IV)[OEP]Cl_2 no ionic additives.(14)

Sensing mechanisms of metalloporphyrin[15] as ionophores in membrane electrodes containing cationic, anionic or no ion additives are shown in Figure 1.10.

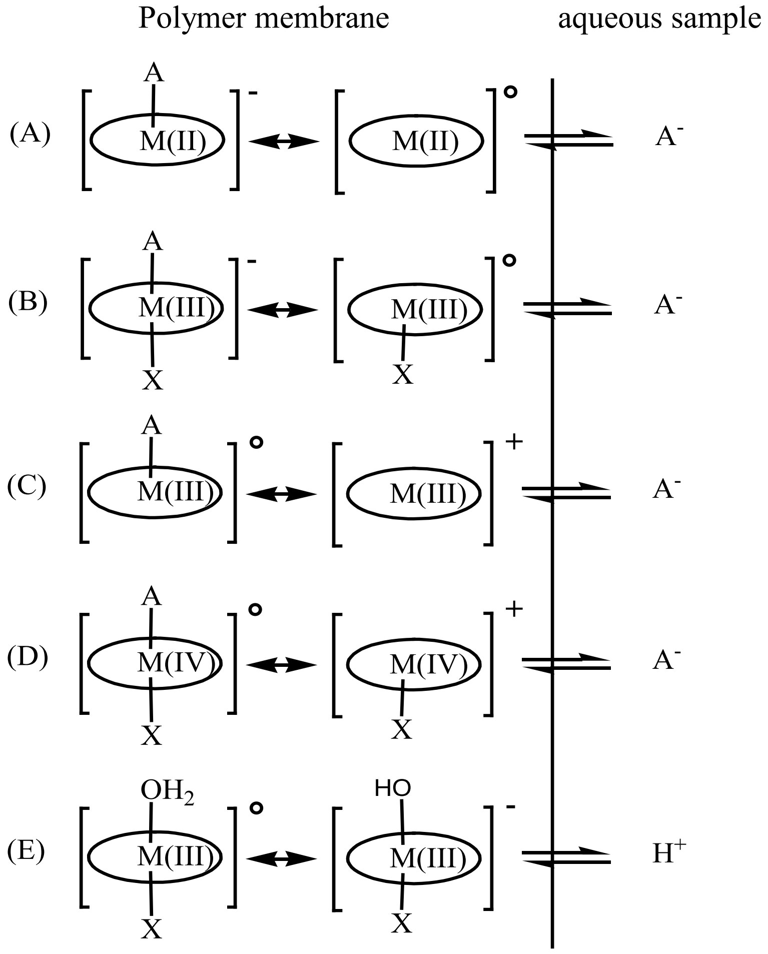


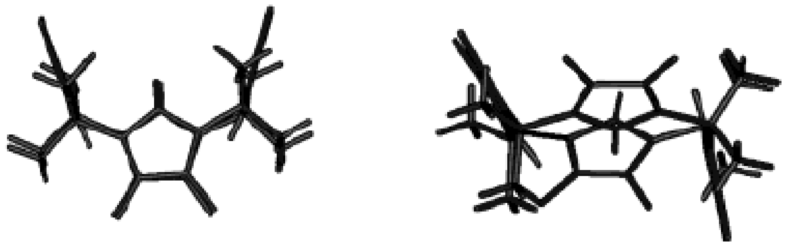
Figure 1.10 Possible mechanisms by which an anion can interacted with metalloporphynrins doped into the polymer membrane of an anion-selective electrodes.(15)

In many cases, possible sensing mechanisms of metalloporphyrins based polymer membranes can occur via coordination to axial ligand with metal center porphyrin ring. When the metal ion is in +2 oxidation state (Figure 1.10 A), such as zinc, cobalt and copper, the total charge is zero. The metalloporphyrin can act as neutral carriers. When the metal ion is in +3 oxidation state as shown Figure 1.10 B and C, for instance Mn(III), In(III), Co(III) or Fe(III) porphyrins can undergo two possible mechanisms. In the case of B, anion as an axial ligand resulted in a negative charged complex, and case C exhibited a charge carrier mechanism. Moreover, when the metal ion is in +4 oxidation state (i.e., Sn(IV) and Pt(IV) porphyrins) they operated via charge mechanism as seen in Figure 1.10 D. In addition, the interaction of water molecules as exial ligands of the metal center porphyrin can be controlled by the pH of the sample solution as shown in Figure 1.10 E.

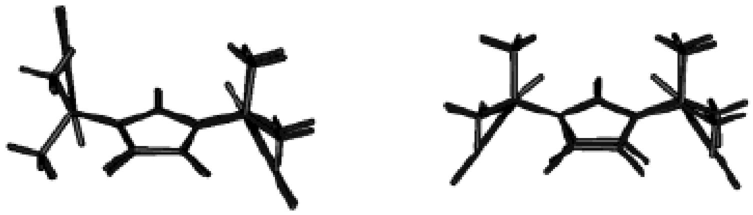
1.2.2 Calix[4]pyrrole Based Anion Sensors

Calixpyrroles was employed as anion receptors because it possesses high affinity and selectivity for specific anions.(16) Calix[4]pyrrole can bind chloride, fluoride, and phosphate anion in organic solutions.(17)

Calix[4]pyrrole is very flexible because the pyrrole unit can rotate around the interpyrrole bonds. Calix[4]pyrrole exists in four conformations cone, partial cone, 1,2-alternate and 1,3-alternate as shown in Figure 1.11(18), but 1,3-alternate conformation was more preferable than others. However, the cone conformation is the most favorite form when calix[4]pyrroles form 1:1 complexes with small anions(19) as seen in Figure 1.12.



1,3-alternated **1,2-alternated**



Partial cone **Cone**

Figure 1.11 Conformations of calix[4]pyrrole.(18)

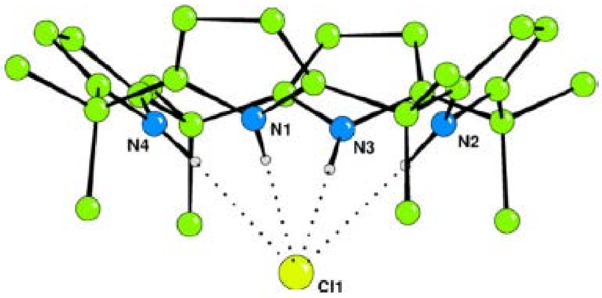
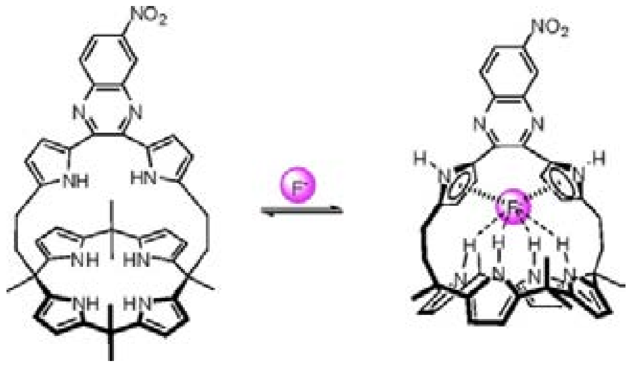


Figure 1.12 Conformation of calix[4]pyrrole binding with chloride.(19)

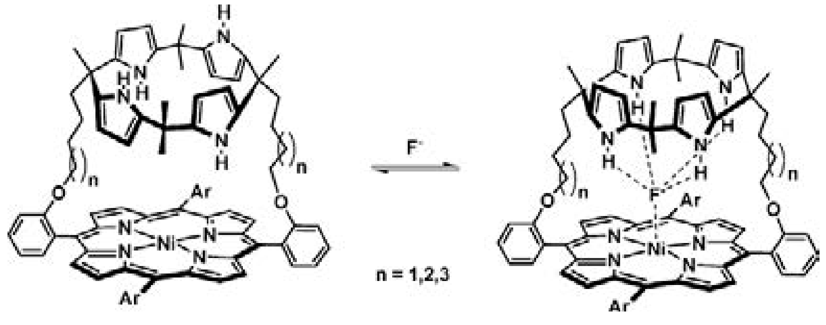
In 2009, Yoo *et al.*(20) synthesized a new calix[4]pyrrole containing dipyrrolylquinoxaline as a chromogenic sensor. When it bound fluoride, acetate, and dihydrogen phosphate anions, the molecule exhibited colorimetric responses. ^{1}H NMR titration of receptor **10** upon adding fluoride, signal of protons N*H* of calix[4]pyrrole moiety showed downfield shifted, stemming from H-bonding interactions as shown in Figure 1.13.



10 **10**+F$^-$

Figure 1.13 Structures of compound **10** binding with F$^-$.(20)

Panda *et al.*(21) reported that synthesis metalloporphyrin stapped calix[4]pyrrole as a receptor for anions. The compound **11** was found to bind fluoride selectivity. (see Figure 1.14).



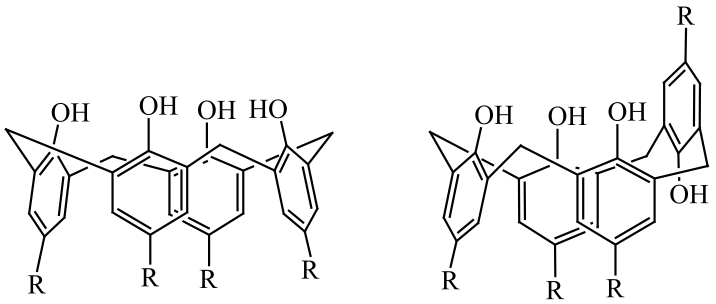
11 **11**+F$^-$

Figure 1.14 Structures of receptor **11** binding with F$^-$.(21)

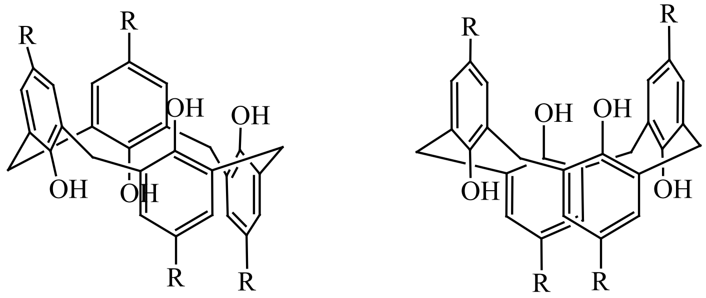
1.2.3 Calix[4]arene Based Anion Sensors

Calixarenes were cavity-possessed macrocylic molecules synthesized from base catalyzed condensation of formaldehyde and *p*-*tert*-butylphenol. In many cases, calix[4]arenes have acquired chemist interests as host molecules in supramolecular chemistry. Therefore, modification at the lower and upper rims of calix[4]arene by attaching groups with different binding abilities enables them to form inclusion complexes with a widely diversity of guest species.(22)

At room temperature in the solution, calix[4]arene existed in four conformations cone, partial cone, 1,2-alternate and 1,3-alternate as shown in Figure 1.15.(23)



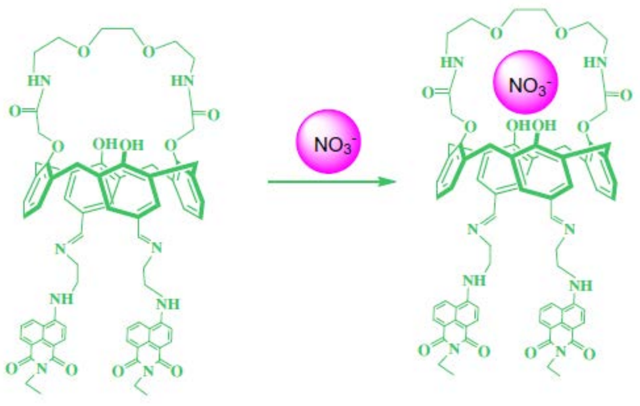
cone **partial cone**



1,2-alternate **1,3-alternate**

Figure 1.15 Conformations of calix[4]arene.(23)

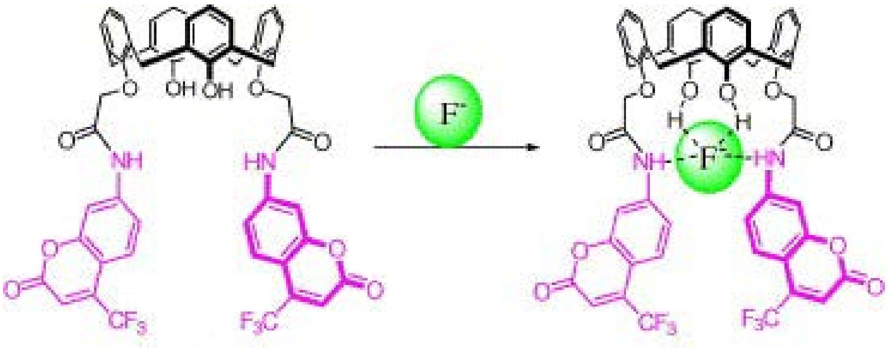
The calix[4]arene derivatives can form complexes with anions *via* H-bond interactions at hydroxyl groups (Figure 1.16). The nitrate ion was encapsulated inside the cavity of 1,8-naphthalimide based calix[4]arene.(24)



12 **12**+NO$_3^-$

Figure 1.16 Structures of compound **12** binding with NO$_3^-$.(24)

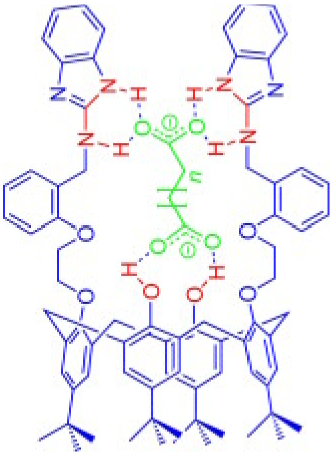
Lee *et al.*(25) synthesized a novel calix[4]arene containing two coumarin signaling units (**13**) for binding of anions. It was found that compound **13** acted as a PCT-based chemosensor upon addition of F^-. The ^1H NMR spectrum showed the amide N-H of **13** disappeared upon adding with F^-. Similarly, the OH protons are upfield shifted with possible H-bonding with F^- as shown in Figure 1.17.



13 **13+F⁻**

Figure 1.17 Structures of compound **13** and compound **13** binding with F^-.(25)

In 2008, Singh *et al.*(26) reported that the receptor **14** posessing cone conformation of calix[4]arene based dipodal has formed complexs with dicarboxylate anions for example glutarate, malonate, pimelate, succinate, adipate, and suberate. The complexation of receptor **14** and pimelate by comparing the ^1H NMR spectrum displayed signals of protons in N-H and OH, the both acted downfield shifts. In this regard, the binding mode for the encapsulation of pimelate in receptor **14** was proposed as shown in Figure 1.18.



14

Figure 1.18 Structures of receptor **14** binding with dicarboxylate.(26)

Moreover, Dudič *et al.*(27) synthesized calixarenes containing two Zn(II) porphyrins units (see Figure 1.19) which can interact with 1,4-diazabicyclo[2.2.2]octane (DABCO) by two different pathways. The complexation studied showed quite diverse behaviour of thiacalixarene diamide **16** when compared with the corresponding calix[4]arene **15**. A plausible explanation of this phenomenon stemmed from differences in the cavity size. The larger cavity of thiacalixarene **16** fitted the steric requirements of DABCO, which resulted in the complexation in intramolecular 1:1 stoichiometry. In contrast, the smaller cavity of compound **15** preferred the 2:1 complex.

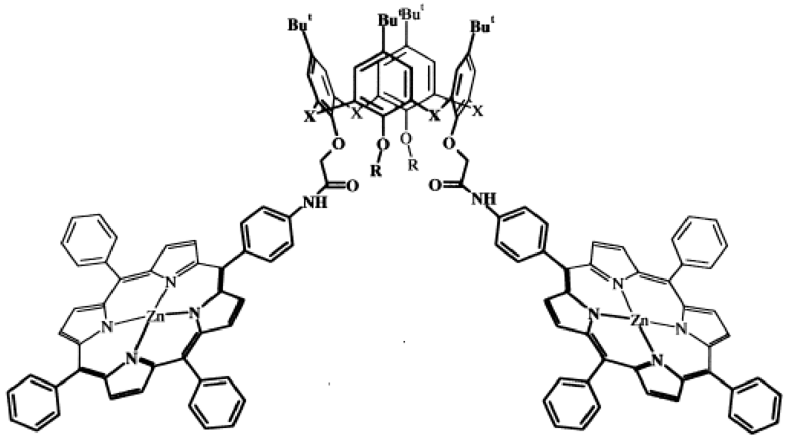
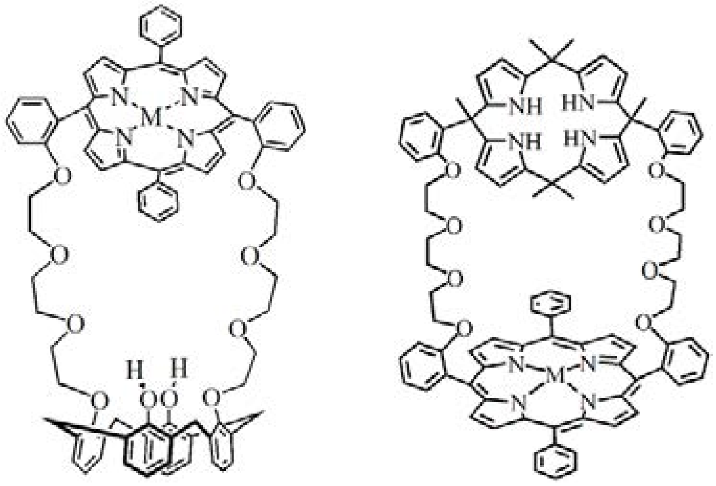


Figure 1.19 Structures of conpound **15** (X = CH_2, R = H) and compound 1**6** (X = S, R = H).(27)

1.3 Objectives and scope of the research

In this research, synthesis of metalloporphyrins containing calix[4]arene and calix[4]pyrrole as ionophores in polymer membrane anion selective electrodes are carried out. The synthesized compounds are then used to fabricate membrane ISEs. Studies of potentiometric response of the ISEs towards anions (ClO_4^-, SCN^-, I^-, OAc^-, F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, $H_2PO_4^-$, HCO_3^- and salicylate) are carried out.



ML1 **ML2**

(M = transition metal)

Figure 1.20 Structures of desired ionophores.

CHAPTER II

EXPERIMENTAL SECTION

2.1 General Procedures

2.1.1 Analytical instrument

UV-vis absorption spectra were measured with a Varian Cary 50 UV-Vis spectrophotometer. MALDI-TOF mass spectra were recorded on Bruker Daltonic by using 2-cyano-4-hydroxy cinnamic acid (CCA) as a matrix. Crystal Data was obtained by Bruker Smart CCD diffractometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus (400 MHz) for ^{1}H and a Bruker Auance 400 (100 MHz) for ^{13}C. In all cases, samples were dissolved in deuterated chloroform except titration of Zn(II) porphyrin-calix[4]arene with tetrabutylammonium fluoride which was dissolved in deuterated acetonitrile. The chemical shifts were recorded in part per million (ppm) using a residual proton or carbon signals in deuterated solvents as internal reference. Infrared spectra were obtained on a Nicolet Impact 400 FT-IR spectrophotometer (Thermo Fisher Scientific company, USA. Elemental analysis was obtained by CHNS/O Analyzer, Perkin Elmer PE2400 Series II.

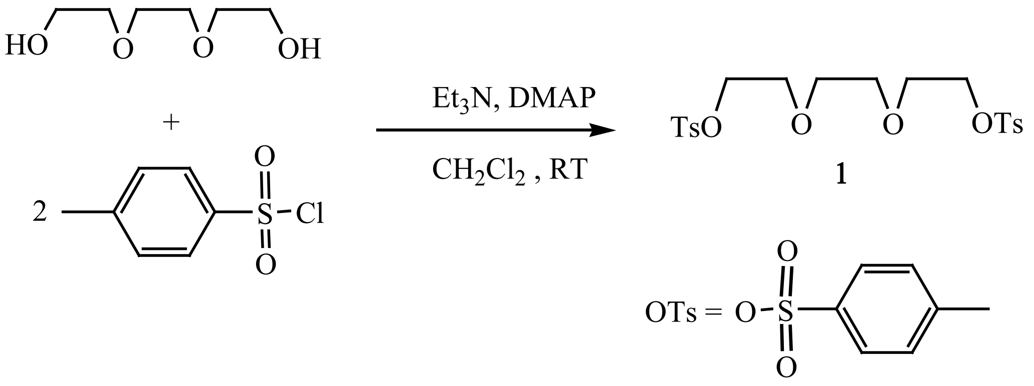
2.1.2 Meterials

All materials were standard analytical grade, purchased from Merck, Fluka, Sigma-Aldrich, Lab scan, BDH or Carlo Erba and used without further purification. Commercial grade solvents such as dichloromethane, methanol, ethyl acetate, hexane and acetone were distilled before use. Dimethylformamide and acetonitrile were dried over calcium hydride and freshly distilled under nitrogen atmosphere prior to use. Thin layer chromatography (TLC) was performed on silica gel plates (Kieselgel 60 F_{254}, 1 mm, Merck). Column chromatography was carried out using silica gel (Kieselgel 60, 0,063-0.200 mm, Merck). Tridodecylmethylammonium chloride (TDMACl), high molecular weight polyvinyl chloride (PVC), *o*-nitrophenyloctyl ether (*o*-NPOE), potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB) and tetrahydrofuran (THF) were obtained from Fluka with Selectophore® grade. Aqueous solutions were prepared with ultrapure water from Milli-Q (Bedford, MA, USA) water purification system (Millipore). Acetate buffer pH 4.0, phosphate buffer pH 7.4, glycine-HCl pH 3.5 and 4-morpholinoethanesulfonic acid (MES) pH 5.5 were used in potentiometric measurements. Calix[4]arene was prepared following literature procedures.(28)

2.2 Synthesis of ionophores

2.2.1 Synthesis of Metalloporphyrin-calix[4]arene (ML1)

2.2.1.1 Synthesis of triethyleneglycol ditosylate (1)$^{(29)}$

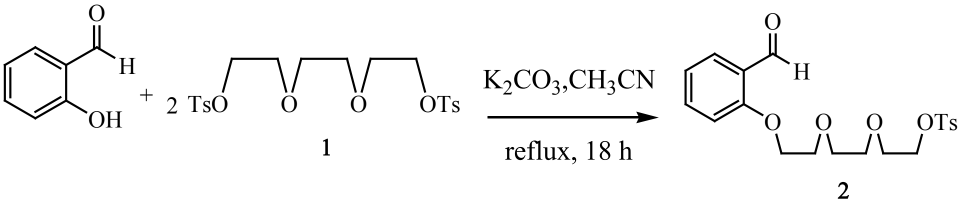


A solution mixture of anhydrous triethyleneglycol (3.0 g, 28 mmol), triethylamine (11.8, 85 mmol) and a catalytic amount of DMAP in 50 mL of freshly distilled dichloromethane was chilled to 0 ºC with an ice bath. The solution of tosylchloride (11.86 g, 62 mmol) in freshly distilled dichloromethane (100 mL) was then added dropwise. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 4 hours. After the reaction was complete, the solution of 3 M hydrochloric acid was added until the pH of the solution reached 1. Then the mixture was extracted with dichloromethane (100 mL) and water (2×100 mL). The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed using a rotary evaporator. The residue was dissolved in a minimum amount of dichloromethane and methanol was added to precipitate triethyleneglycol ditosylate (**1**) as a white solid (9.1 g, 71%yield).

Characteristic data for 1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 7.79 (d, J = 8.0 Hz, 4H, o-ArHSO$_2$), 7.34 (d, J = 8.0 Hz, 4H, m-ArHSO$_2$), 4.13 (t, J = 4.8 Hz, 4H, SO$_2$OCH_2CH$_2$OCH$_2$), 3.65 13 (t, J = 4.8 Hz, 4H, SO$_2$OCH$_2$CH_2OCH$_2$), 3.52 (s, 4H, SO$_2$OCH$_2$CH$_2$OCH_2), 2.44 (s, 6H, ArCH_3)

IR spectrum (***ν***, cm^{-1}): 3063 (CH, st (aromatic)), 2947, 2874 (CH, st), 1595, 1452 (C=C, st), 1356, 1170 (S=O, st).

2.2.1.2 Synthesis of 2-(8-tosyltriethyleneglycol)benzaldehyde (2)



The synthetic procedure was adapted from the previously reported documents.$^{(29)}$ A solution of triethyleneglycol ditosylate (**1**) (9.16 g, 20 mmol) in acetonitrile (100 mL) was added dropwise to a solution mixture of salicylaldehyde (1.05 mL, 10 mmol) and K_2CO_3 (13.82 g, 100 mmol) in freshly distilled acetonitrile (50 mL). The reaction mixture was refluxed with stirring under nitrogen atmosphere for 18 hours. After cooling to room temperature, the solvent was removed under reduced pressure to give a yellow viscous oil. The residue was dissolved in dichloromethane (100 mL) and extracted with water (2×100 mL) The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by a rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc : CH_2Cl_2 = 10:90) to give 2-(8-tosyltriethyleneglycol)benzaldehyde (**2**) as a colourless oil (2.5 g, 61% yield).

Characteristic data for 2: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 10.43 (s, 1H, ArC*H*O), 7.75 (d, *J* = 1.6 Hz, 1H, *o*-Ar*H*CHO), 7.72 (d, *J* = 8.4 Hz, 2H, *o*-Ar*H*SO$_2$), 7.49 (dd, *J* = 1.6, 8.4 Hz, 1H, *p*-Ar*H*CHO), 7.26 (d, *J* = 8.4 Hz, 2H, *m*-Ar*H*SO$_2$), 6.97 (d, *J* = 8.4 Hz, 1H, *m*-Ar*H*CHO), 6.94 (d, *J* = 8.4 Hz, 1H, *m*-Ar*H*CHO), 4.17 (t, *J* = 4.8 Hz, 2H, SO$_2$OC*H*$_2$), 4.09 (t, *J* = 4.8 Hz, 2H, OC*H*$_2$), 3.82 (t, J = 4.0 Hz, 2H, OCH_2), 3.62 (t, J = 4.8 Hz, 4H, OCH_2), 3.54 (t, J = 4.0 Hz, 2H, OCH_2), 2.35 (s, 3H, $ArCH_3$).

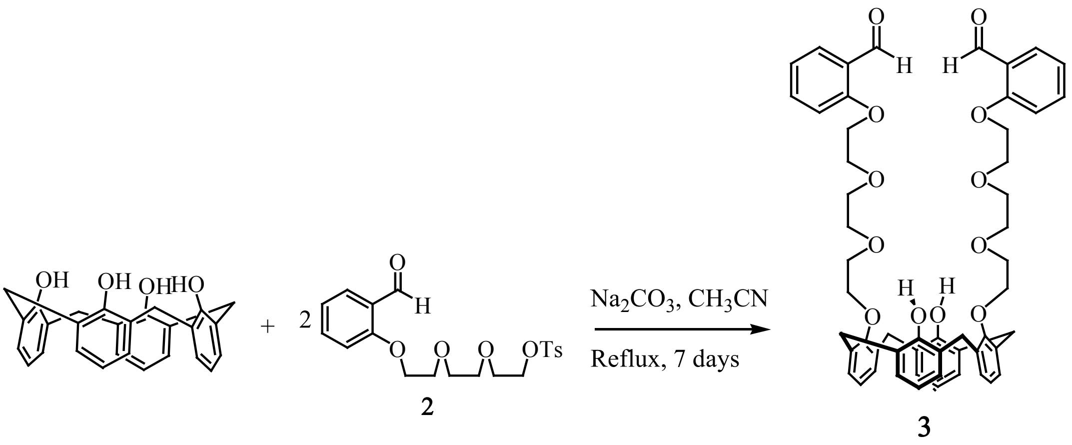
^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 189.7, 161.2, 144.9, 135.9, 132.9, 129.8, 128.1, 127.9, 125.1, 120.9, 113.0, 70.8, 70.7, 69.5, 69.3, 68.7, 68.3, 21.6

IR spectrum (ν, cm^{-1}): 3066 (CH, st (aromatic)), 2867 (CH, st), 1688 (C=O, st), 1595, 1482, 1453 (C=C, st), 1353, 1173 (S=O, st).

Elemental analysis: *Anal calcd* for $C_{20}H_{24}O_7S$: C, 58.81; H, 5.92

Found: C, 58.87; H, 5.93

2.2.1.3 Synthesis of 1,3-calix[4]-dibenzaldehyde (3)



The synthetic procedure was adapted from the previously reported documents.(29) A solution of 2-(8-tosyltriethyleneglycol)benzaldehyde (**2**) (4.08 g, 10 mmol) in acetonitrile (100 mL) was added dropwise to a solution mixture of calix[4]arene (2.12 g, 5 mmol) and Na_2CO_3 (10.6 g, 100 mmol) in freshly distilled acetonitrile (50 mL). The reaction mixture was refluxed with stirred under nitrogen atmosphere for 7 days. After cooling to room temperature, the solvent was removed under reduced pressure to give a brown viscous oil. The residue was dissolved in dichloromethane (100 mL) and extracted with water (2×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solution was removed by a rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc : CH_2Cl_2 = 10:90) to give 1,3-calix[4]-dibenzaldehyde (**3**) as a colourless oil (2.37 g, 53% yield).

Characteristic data for 3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 10.52 (s, 2H, ArC*H*O), 7.82 (d, *J* = 1.6 Hz, 2H, *o*-Ar*H*CHO), 7.81 (s, 2H, ArO*H*), 7.46 (dd, *J* = 1.6, 8.0 Hz, 2H, *p*-Ar*H*CHO), 7.06 (d, *J* = 7.6 Hz, 4H, *m*-Ar*H*OH), 6.98 (t, *J* = 7.6 Hz, 1H, Ar*H*CHO), 6.84 (d, *J* = 7.6 Hz, 4H, *m*-Ar*H*OH), 6.83 (d, *J* = 8.4 Hz, 1H, , *m*-Ar*H*CHO), 6.66 (t, *J* = 7.6 Hz, 2H, *p*-Ar*H*OH), 6.65 (t, *J* = 7.6 Hz, 2H, *p*-Ar*H*OH), 4.23 (d, *J* = 13.0 Hz, 4H, ArC*H*$_2$Ar), 4.17 (t, *J* = 4.4 Hz, 4H, OC*H*$_2$), 4.04 (t, *J* = 4.4 Hz, 4H, OC*H*$_2$), 3.98 (t, *J* = 4.8 Hz, 4H, OC*H*$_2$), 3.90-3.85 (m, 8H, OC*H*$_2$), 3.81-3.79 (m, 4H, OC*H*$_2$), 3.35 (d, *J* = 13.0 Hz, 4H, ArC*H*$_2$Ar)

^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 189.8, 161.3, 153.3, 151.9, 135.9, 133.2, 130.4, 128.8, 128.7, 128.2, 125.3, 125.1, 121.2, 119.0, 113.3, 75.5, 71.2, 71.0, 70.1, 69.6, 68.2, 31.8

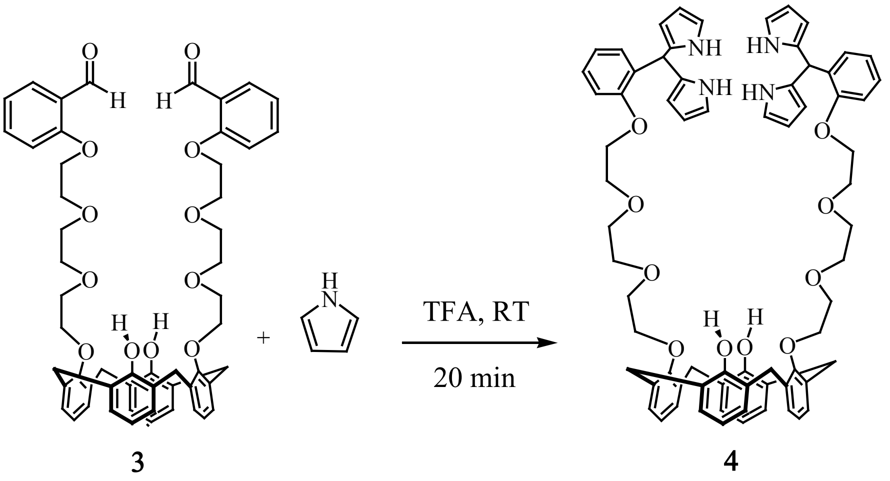
MALDI-TOF MS calcd for $[C_{54}H_{56}N_6O_{12}]^+$ 896.36 m/z, found 919.42 [M+Na$^+$].

IR spectrum (**ν**, cm^{-1}): 3349 (OH, st), 3063 (CH, st (aromatic)), 2920, 2864 (CH, st), 1685 (C=O, st), 1598, 1479, 1449 (C=C, st).

Elemental analysis: *Anal calcd* for $C_{54}H_{56}O_{12}$: C, 72.30; H, 6.29

Found: C, 72.54; H, 6.55

2.2.1.4 Synthesis of 1,3-calix[4]arene-bis-dipyrromethane (4)

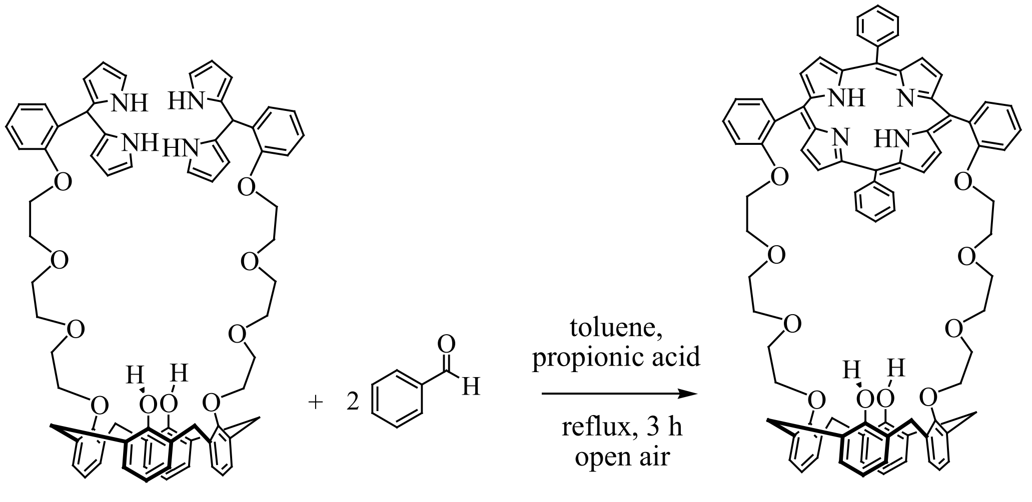


A mixture of 1,3-calix[4]-dibenzaldehyde (**3**) (1.125 g, 1.26 mmol) and freshly distilled pyrrole (7.0 mL, 100 mmol) was degassed by bubbling with nitrogen for 20 minutes, and then trifluoroacetic acid (0.05 mL, 0.62 mmol) was added. The solution was stirred for 20 minutes at room temperature. The reaction mixture was diluted with dichloromethane (50 mL), washed with 0.1 M NaOH (50 mL) and water (2×100 mL), respectively. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, Et_3N : EtOAc : CH_2Cl_2 = 1:2:98) to give 1,3-calix[4]arene-bis-dipyrromethane (**4**) as a brown oil (0.54 g, 38% yield).

Characteristic data for 4: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 8.95 (s, 4H, pyrrole-N*H*), 7.76 (s, 2H, ArO*H*), 7.26 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.20 (d, *J* = 4.4 Hz, 2H, Ar*H*), 7.12 (t, *J* = 7.6 Hz, 4H, Ar*H*), 6.93 (t, *J* = 7.2 Hz, 2H, Ar*H*), 6.85 (d, *J* = 7.6 Hz, 4H, Ar*H*), 6.75 (t, *J* = 8.0 Hz, 4H, Ar*H*), 6.65 (d, *J* = 8.0 Hz, 6H, Ar*H* and pyrrole-*H*), 6.14 (dd, *J* = 2.8, 2.8 Hz, 4H, pyrrole-*H*), 5.98 (s, 4H, pyrrole-*H*), 5.71 (s, 2H, *meso-H*), 4.44 (d, *J* = 12.8 Hz, 4H, ArCH_2Ar), 4.09 (t, *J* = 3.2 Hz, 4H, OCH_2), 3.89 (s, 8H, OCH_2), 3.84 (t, *J* = 3.6 Hz, 4H, OCH_2), 3.73 (t, *J* = 4.4 Hz, 4H, OCH_2), 3.63 (t, *J* = 4.0 Hz, 4H, OCH_2), 3.38 (d, *J* = 12.8 Hz, 4H, ArCH_2Ar)

^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 155.5, 153.0, 151.6, 132.9, 132.4, 131.6, 129.7, 128.7, 128.3, 127.9, 127.7, 125.0, 121.0, 118.8, 116.4, 112.0, 107.5, 106.1, 75.1, 70.7, 70.4, 69.5, 69.4, 66.8, 46.0, 30.9

2.2.1.5 Synthesis of porphyrin-calix[4]arene (L1)



4 **L1**

1,3-Calix[4]arene-bis-dipyrromethane (**4**) (0.54 g, 0.48 mmol) and benzaldehyde (0.07 ml, 0.96 mmol) were dissolved in toluene (40 mL) in a two-necked round-bottomed flask. Propionic acid (40 mL) was added into the solution which turned to a dark color. The reaction was heated at reflux for 3 hours in the open air. After cooling to room temperature, solvents were removed under reduced pressure. The residue was dissolved in dichloromethane (100 mL), washed with saturated $NaHCO_3$ solution and then washed with water (2×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed to give a black viscous residue. The residue was purified by column chromatography (silica gel, EtOAc : CH_2Cl_2 = 5:95) to give **L1** as a purple solid (74 mg, 12% yield).

Characteristic data for L1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 8.83 (d, *J* = 4.4 Hz, 4H, *β*-pyrrole-*H*), 8.77 (d, *J* = 4.4 Hz, 4H, *β*-pyrrole-*H*), 8.13 (d, *J* = 6.8 Hz, 2H, Ar*H*), 8.10 (m, 1H, Ar*H*), 8.08 (m, 1H, Ar*H*), 7.97 (d, *J* = 6.8 Hz, 2H, Ar*H*), 7.77 (m, 1H, Ar*H*), 7.75 (m, 1H, Ar*H*), 7.73 (m, 1H, Ar*H*), 7.72 (s, 2H, ArO*H*), 7.70 (m, 1H, Ar*H*), 7.68 (m, 1H, Ar*H*), 7.66 (m, 1H, Ar*H*), 7.40 (m, 1H, Ar*H*), 7.39 (m, 1H, Ar*H*), 7.36 (m, 2H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.85 (d, *J* = 7.6 Hz, 4H, Ar*H*OH), 6.73 (d, *J* = 7.6 Hz, 4H, Ar*H*OH), 6.64 (dd, *J* = 8.0, 6.8 Hz, 2H, Ar*H*), 6.49 (t, *J* = 7.6 Hz, 2H, Ar*H*), 3.86 (t, *J* = 4.4 Hz, 4H, ArOCH_2), 3.68 (d, *J* = 13.0 Hz, 4H, ArCH_2Ar), 2.97 (d, *J* = 13.0 Hz, 4H, ArCH_2Ar), 2.92 (t, *J* = 4.4 Hz, 4H, ArOCH_2), 2.52 (t, *J* = 4.4 Hz, 4H, OCH_2), 2.17 (t, *J* = 4.4 Hz, 4H, OCH_2), 1.98 (t, *J* = 4.4 Hz, 4H, OCH_2), 1.74 (t, *J* = 4.4 Hz, 4H, OCH_2), -2.75 (s, 2H, N*H*)

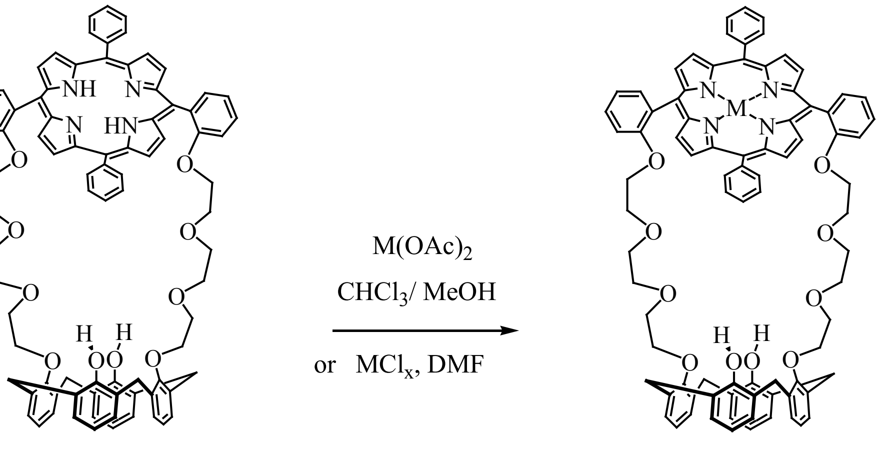
^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 158.9, 153.1, 151.3, 142.1, 135.4, 134.6, 134.3, 133.2, 131.3, 129.9, 128.6, 127.7, 127.6, 125.0, 119.7, 119.6, 118.4, 116.3, 111.9, 69.5, 69.3, 69.2, 69.0, 68.8, 68.4, 30.8

MALDI-TOF MS calcd for $C_{84}H_{74}N_4O_{10}$ m/z 1299.53, found 1299.83.

UV-vis (THF): λ_{max}/nm (logε) : 418 (5.41), 514, 546, 595, 652

IR spectrum (**ν**, cm^{-1}): 3354 (OH, st), 3319 (NH, st),3053, 3025 (CH, st (aromatic)), 2923, 2866 (CH, st), 1467, 1441 (C=C, st), 963 (C-C, st)

2.2.1.6 Synthesis of Metalloporphyrin-calix[4]arene (ML1) (ZnL1, CuL1, CoL1, FeL1 and SnL1)



L1

ML1
(M = Zn, Cu, Co, FeCl and $SnCl_2$)

Generally, a solution mixture of free base porphyrin-calix[4]arene (**L1**) (100 mg, 0.077 mmol) and metal acetate (10 molar equiv.) in $CHCl_3$/MeOH (3:1 v/v) was refluxed with stirring under nitrogen atmosphere for 2 days. After the reaction mixture was cooled to room temperature, dichloromethane (100 mL) was added to the mixture. The mixture was then extracted with 0.1 M HCl (50 mL) and water (2 × 100 mL). The organic layer was dried using anhydrous Na_2SO_4 and evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane, and methanol was added to precipitate. Metalloporphyrin-calix[4]arene (**ML1**) was obtained as a pink solid (81 mg, 78% yield), red solid (89 mg, 85% yield) and orange solid (77 mg, 74% yield) of **ZnL1**, **CuL1** and **CoL1**, respectively.

In the case of **FeL1** and **SnL1**, they were synthesized by refluxing free base porphyrin-calix[4]arene (**L1**) (100 mg, 0.077 mmol) and metal chloride (100 times molar excess of $FeCl_3$ and 50 times molar excess of $SnCl_2$) in DMF (15 mL) under nitrogen atmosphere for 5 days. The reaction solution was cooled to room temperature and suspended in ethyl acetate (100 mL). The solution was washed with 0.1 M HCl (50 mL) and water (2×100 mL).The organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The product was recrytallized from CH_2Cl_2/MeOH to obtain a brown solid (54 mg, 51% yield) and green solid (57 mg, 54% yield) of **FeL1** and **SnL1**, respectively.

Characteristic data for ZnL1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 8.88 (d, *J* = 4.4 Hz, 4H, *β*-pyrrole-*H*), 8.82 (d, *J* = 4.4 Hz, 4H, *β*-pyrrole-*H*), 8.21 (d, *J* = 6.4 Hz, 2H, Ar*H*), 8.07 (d, *J* = 7.2 Hz, 2H, Ar*H*), 8.00 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.76-7.60 (m, 8H, Ar*H*), 7.42 (t, *J* = 7.2 Hz, 2H, Ar*H*), 7.18 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.06 (s, 2H, Ar*H*), 6.82 (d, *J* = 7.6 Hz, 4H, Ar*H*), 6.68 (dd, *J* = 8.0, 6.8 Hz, 2H, Ar*H*), 6.61 (t, *J* = 7.2 Hz, 2H, Ar*H*), 3.70 (s, 4H, ArOCH_2), 3.54 (d, *J* = 12.8 Hz, 4H, ArCH_2Ar), 2.92 (d, *J* = 12.8 Hz, 4H, ArCH_2Ar), 2.83 (s, 4H, ArOCH_2), 2.44 (s, 4H, ArOCH_2), 2.03 (s, 4H, ArOCH_2), 1.92 (t, *J* = 4.0 Hz, 4H, OCH_2), 1.66 (t, *J* = 4.4 Hz, 4H, OCH_2).

^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 159.1, 152.9, 151.1, 150.3, 149.9, 143.1, 134.9, 134.5, 134.3, 132.9, 132.8, 131.7, 131.6, 129.5, 128.7, 128.1, 127.7, 127.2, 126.4, 126.3, 125.1, 120.4, 119.9, 118.4, 116.8, 112.8, 73.7, 69.3, 69.2, 68.9, 68.8, 68.7, 30.8

MALDI-TOF MS calcd for $[C_{84}H_{72}N_4O_{10}Zn]^+$ 1362.89 m/z, found 1363.15.

UV-vis (THF): λ_{max}/nm (logε) : 424 (5.67), 556, 594.

IR spectrum (ν, cm^{-1}): 3341 (OH, st), 3050, 3015 (CH, st (aromatic)), 2918, 2855 (CH, st), 1461, 1438 (C=C, st), 998 (C-C, st).

Elemental analysis: *Anal calcd* for $C_{84}H_{72}N_4O_{10}Zn$: C, 74.03; H, 5.32; N, 4.11

Found: C, 73.78; H, 5.35; N, 4.16

Characteristic data for CuL1:

MALDI-TOF MS calcd for $[C_{84}H_{72}N_4O_{10}Cu]^+$ 1361.04 m/z, found 1361.73.

UV-vis (THF): λ_{max}/nm (logε) : 415 (5.61), 539.

IR spectrum (ν, cm^{-1}): 3348 (OH, st), 3056, 3021 (CH, st (aromatic)), 2918, 2863 (CH, st), 1464, 1438 (C=C, st), 1000 (C-C, st).

Elemental analysis: *Anal calcd* for $C_{84}H_{72}N_4O_{10}Cu$: C, 74.13; H, 5.33; N, 4.12

Found: C, 74.13; H, 5.42; N, 4.15

Characteristic data for CoL1:

MALDI-TOF MS calcd for $[C_{84}H_{72}N_4O_{10}Co]^+$ 1356.42 m/z, found 1356.69.

UV-vis (THF): λ_{max}/nm (logε) : 416 (5.20), 530.

IR spectrum (ν, cm^{-1}): 3348 (OH, st), 3053, 3021 (CH, st (aromatic)), 2921, 2866 (CH, st), 1461, 1441 (C=C, st), 1000 (C-C, st).

Characteristic data for FeL1:

MALDI-TOF MS calcd for $[C_{84}H_{72}N_4O_{10}FeCl]^+$ m/z 1388.78, 1353.34 [M^+-Cl] found 1353.41[M^+-Cl].

UV-vis (THF): λ_{max}/nm (logε) : 417 (5.04), 501, 569.

IR spectrum (ν, cm^{-1}): 3348 (OH, st), 3054, 3019 (CH, st (aromatic)), 2921, 2865 (CH, st), 1467, 1442 (C=C, st), 1000 (C-C, st).

Elemental analysis: *Anal calcd* for $C_{84}H_{72}N_4O_{10}ClFe$: C, 72.65; H, 5.23; N, 4.03

Found: C, 72.74; H, 4.68; N, 4.07

Characteristic data for SnL1: **^{1}H NMR spectrum** (400 MHz, $CDCl_3$) : δ (ppm) = 9.12 (s, 8H, pyrrole-*H*), 8.32 (m, 4H, Ar*H*), 8.12 (m, 2H, Ar*H*), 7.80 (m, 10H, ArO*H*+ Ar*H*), 7.43 (m, 2H, Ar*H*), 7.34 (m, 2H, Ar*H*), 6.94 (m, 4H, Ar*H*), 6.82 (d, *J*= 7.6 Hz, 4H, Ar*H*), 6.67 (m, 2H, Ar*H*), 6.55 (m, 2H, Ar*H*), 4.10 (d, *J*= 11.2 Hz, 4H, ArCH_2Ar), 4.06 (s, 4H, ArOCH_2), 3.23 (s, 4H, ArOCH_2), 3.17 (d, *J*= 13.2 Hz, 4H, ArCH_2Ar), 2.89 (s, 2H, OCH_2), 2.31 (s, 2H, OCH_2), 1.92 (s, 2H, OCH_2), 1.16 (s, 4H, OCH_2), 0.84 (s, 2H, OCH_2)

^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 152.1, 150.5, 145.6, 145.1, 133.9, 133.8, 132.5, 131.4, 129.8, 127.8, 127.2, 127.0, 126.2, 124.2, 119.5, 117.7, 110.6, 75.7, 73.7, 69.1, 68.4, 68.0, 67.8, 30.1

MALDI-TOF MS calcd for $[C_{84}H_{72}N_4O_{10}SnCl_2]^+$ m/z 1387.29, 1451.74 [M^+-Cl] found 1451.41[M^+-Cl].

UV-vis (THF): λ_{max}/nm (logε) : 429 (5.25), 565, 602.

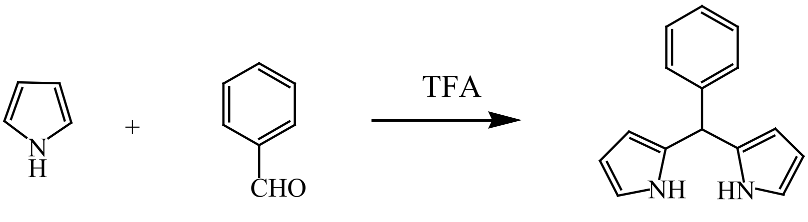
IR spectrum (ν, cm^{-1}): 3341 (OH, st), 3053, 3020 (CH, st (aromatic)), 2920 (CH, st), 1461, 1442 (C=C, st)

Elemental analysis: *Anal calcd* for $C_{84}H_{72}N_4O_{10}Cl_2Sn$: C, 67.84; H, 4.8; N, 3.77

Found: C, 67.57; H, 4.90; N, 3.88

2.2.2 Synthesis of Metalloporphyrin-calix[4]pyrrole (ML2)

2.2.2.1 Synthesis of 5-phenyldipyrromethane (5)⁽³⁰⁾

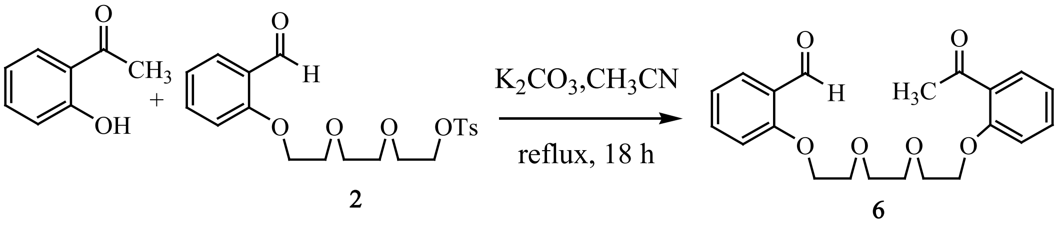


5

A solution mixture of benzaldehyde (0.7 mL, 10 mmol) and freshly distilled pyrrole (13.86 mL, 200 mmol) was degassed by bubbling with nitrogen for 20 minutes. Then, trifluoroacetic acid (0.38 mL, 5.01 mmol) was added. The solution was stirred for 20 minutes at room temperature. The reaction mixture was dissolved in dichloromethane (100 mL), washed with 0.1 M NaOH (50 mL) and water (2×100 mL), respectively. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, Et_3N : EtOAc : hexane = 1:20:80) to give 5-phenyldipyrromethane (5) as a brown oil (0.93 g, 42%yield).

Characteristic data for 5 : ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 7.92 (br s, 2H, pyrrole-N*H*), 7.35-7.22 (m, 5H, Ar*H*), 6.69 (s, 2H, pyrrole-*H*), 6.17 (dd, *J*= 2.8, 2.4 Hz, 2H, pyrrole-*H*), 5.92 (s, 2H, pyrrole-*H*), 5.47 (s, 1H, *meso-H*).

2.2.2.2 Synthesis of 2-(2-(triethylenglycol)bezadehyde)acetophenone (6)



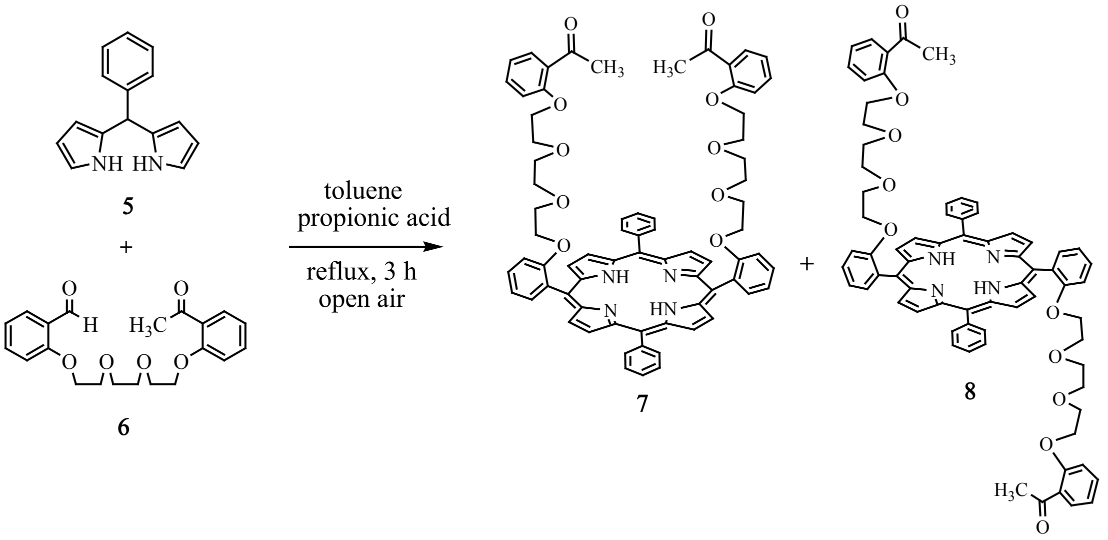
A solution of 2-(8-tosyltriethyleneglycol)benzadehyde (**2**) (4.08 g, 10 mmol) in acetonitrile (100 mL) was added dropwise to a solution mixture of 2-hydroxyacetophenone (1.20 mL, 10 mmol) and K_2CO_3 (13.82 g, 100 mmol) in freshly distilled acetonitrile (50 mL). The reaction mixture was refluxed with stirred under nitrogen atmosphere for 18 hours. After cooling to room temperature, the solvent was removed under reduced pressure to give a brown viscous oil. The residue was dissolved in dichloromethane (100 mL) and extracted with water (2×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed using a rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc : CH_2Cl_2 = 10:90) to give 2-(2-(triethylenglycol)bezaldehyde)acetophenone (**6**) as a yellow oil (2.15 g, 58% yield).

Characteristic data for 6: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) : δ (ppm) = 10.40 (s, 1H, ArC*H*O), 7.68 (d, *J* = 8.0 Hz, 1H, *o*-Ar*H*CHO), 7.62 (d, *J* = 8.0 Hz, 1H, *o*-Ar*H*), 7.39 (t, *J* = 8.4 Hz, 1H, Ar*H*), 7.31 (d, *J* = 7.2 Hz, 1H, Ar*H*), 6.90-6.81 (m, 4H, Ar*H*), 4.12-4.07 (m, 4H,OCH_2), 3.90-3.76 (m, 4H,OCH_2), 3.61 (s, 4H,OCH_2), 2.53 (s, 3H,CH_3COAr)

^{13}C NMR spectrum (100 MHz, $CDCl_3$) : δ (ppm) = 189.7, 178.2, 144.9, 135.9, 132.9, 129.8, 128.1, 127.9, 125.1, 120.9, 113.0, 70.8, 70.7, 69.5, 69.3, 68.7, 68.3, 28.7.

IR spectrum ($\boldsymbol{\nu}$, cm^{-1}): 3070 (CH, st (aromatic)), 2920, 2874 (CH, st), 1685 (C=O, st), 1595, 1479, 1442 (C=C, st).

2.2.2.3 Synthesis of 5,15-di(2-(2-(triethyleneglycol)acetophenone)phenyl)-10,20-diphenylporphyrin (7)

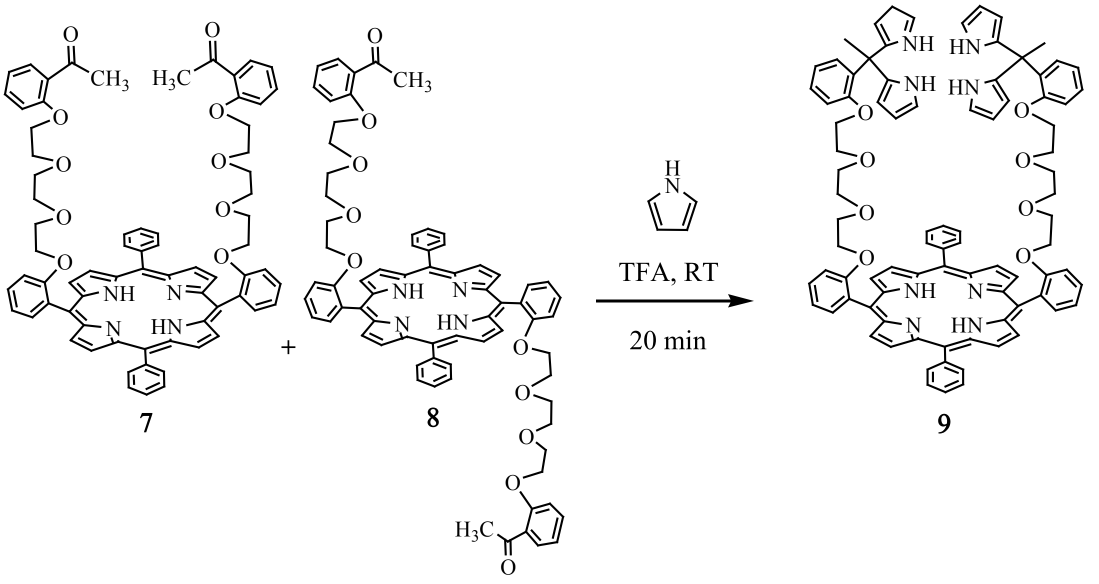


A mixture of 5-phenyldipyrromethane (**5**) (0.93 g, 4.18 mmol) and 2-(2-(triethylenglycol)bezaldehyde)acetophenone (**6**) (1.55 g, 4.18 mmol) was dissolved in toluene (40 mL) in a two-necked round-bottomed flask. Propionic acid (40 mL) was added into the solution which then turned to a dark color. The reaction was heated at reflux for 3 hours in air. After cooling to room temperature, the solvent was removed under reduce pressure. The residue was dissolved in dichloromethane (100 mL), washed with saturated $NaHCO_3$ solution and then washed with water (2×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed to give a black viscous residue. The residue was purified by column chromatography (silica gel, EtOAc : CH_2Cl_2 = 10:90) to give a mixture of compound **7** (TLC, silica gel; $R_f = 0.42$) and compound **8** (TLC, silica gel; $R_f = 0.56$) which cannot be purified by column chromatography.

Characteristic data for 7 and **8:**

MALDI-TOF MS calcd for $[C_{72}H_{66}N_4O_{10}]^+$ 1147.33 m/z, found 1147.68.

2.2.2.4 Synthesis of 5,15-di(2-(2-(triethyleneglycol)-bis-dipyrroethyl)phenyl)-10,20-diphenylporphyrin (9)



A solution mixture of 5,15-di(2-(2-(triethyleneglycol)acetophenone)phenyl)-10,20-diphenylporphyrin **(7** and **8**) (70 mg, 0.061 mmol) in $CHCl_3$ (10 mL) and freshly distilled pyrrole (0.4 mL, 4.88 mmol) was degassed by bubbling with nitrogen for 20 minutes, and then trifluoroacetic acid (0.01 mL, 0.03 mmol) was added. The solution was stirred for 20 minutes at room temperature. The reaction mixture was diluted with dichloromethane (50 mL), washed with saturated $NaHCO_3$ (50 mL) solution and then washed with water (2×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The compound **9** cannot be purified by column chromatography.

2.3 Preparation of PVC membrane electrodes

The PVC membrane was prepared using 10 mmol/kg (1% w/w) ionophore (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**), 1.5, 2.5, 3.5 and 5.0 mmol/kg (15%, 25%, 35% and 50% mol relative to the amount of ionophore) cationic additives (TDMACl) or anionic additives (KT*p*ClPB), 33 wt.% PVC and 66 wt.% plasticizer (*o*-NPOE), in the total mass of 220 mg. Compositions of membranes containing metalloporphyrin-calic[4]arenes (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**) used in this experiment are listed in Table 2.1. The components were dissolved in 2.5 ml (THF) and the mixture was stirred for an hour. The mixture was transferred to a glass ring (30 mm i.d.) fixed on a glass slide. The solvent was evaporated slowly at room temperature for 24 hours to give a membrane. The transparent membrane was punched into small sizes (7.5 mm i.d.) and then conditioned with 0.01 M solution of anions overnight.

Table 2.1. Membrane composition (% w/w) of the constructed electrodes for anions.

Types	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**j**	**K**	**L**	**M**
ZnL1	1	-	-	-	-	1	1	-	-	-	-	-	-
CoL1	-	1	-	-	-	-	-	-	-	-	-	-	-
CuL1	-	-	1	-	-	-	-	1	1	1	-	-	-
FeL1	-	-	-	1	-	-	-	-	-	-	-	-	-
SnL1	-	-	-	-	1	-	-	-	-	-	1	1	1
o-NPOE	66	66	66	66	66	66	66	66	66	66	66	66	66
TDMACl [a]	25	25	25	25	-	15	35	15	35	50	-	-	-
K*p*ClPB [a]	-	-	-	-	25	-	-	-	-	-	-	15	35
PVC	33	33	33	33	33	33	33	33	33	33	33	33	33

[a] % mol relative to the ionophore amount.

2.4 Potential measurement

The electrode body was prepared from the conditioned PVC membranes. In all cases, the mixture of 0.01 M anion and 0.001 M NaCl were used as the inner filling solution except ionophore (**SnL1**) the mixture of 0.01 M anions and 0.01 M NaCl was used as the inner filling solution (IFS). All potential measurements were carried out with the following Voltaic cell:

Ag, AgCl / 3 M KCl // 1 M LiOAc // sample solution / membrane / IFS / AgCl, Ag.

The reference electrode, Ag/AgCl with double junction was used (type 6.0726.100, MetrohmAG,CH-9010 Herisau, Switzerland) with 1M LiOAc as salt bridge electrolyte. Continuous potential measurements were carried out with a 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA).

2.5 Selectivity measurements

The selectivity coefficients were determined by separate solution method (SSM). The interfering ions studied were ClO_4^-, SCN^-, NO_3^-, NO_2^-, Br^-, Cl^-, F^-, OAc^-, SO_4^{2-}, $H_2PO_4^-$ and HCO_3^-. The dynamic response of the electrode was first measured against the same interfering anions (10^{-7} to 10^{-2} M). The electrode was then used to measure the response of iodide solutions for ionophores (**ZnL1**, **CuL1**, **CoL1** and **FeL1**) and used to measure the response of salicylate solutions for ionophores (**SnL1**).

2.6 Effects of pH

The pH electrode, reference electrode and PVC membrane electrode were immersed in the solution of iodide (1.0×10^{-4} M or 1.0×10^{-3} M). The pH range 2.0-10.0 of the solution was adjusted with 0.01 M HCl and 0.01-0.1 M NaOH.

2.7 Reversibility of the PVC membrane potential

The membrane reversibility was examined by measuring the EMF response of I-ISE in a 10^{-4} M I^- solutions. Subsequently, the electrode was rinsed and dipped into a 10^{-3} M I^- solution. The cycle was repeated three times.

2.8 Complexation studies

2.8.1 UV-vis spectrophotometric studies of ZnL1 with anions

A solution mixture of 1.0×10^{-6} M **ZnL1** in CH_3CN and 100 times molar excess of anions in CH_3CN was prepared in a vial and added directly to a cuvette. The UV-vis spectra were recorded after each addition of the solution mixture.

2.8.2 NMR Spectroscopic studies of ZnL1 with Bu_4NF

A solution of 0.005 M **ZnL1** (2×10^{-6} mmol) in a mixture of $CDCl_3$: CD_3CN (1:9 v/v) (0.4 mL) was prepared in a NMR tube. The excess amount of Bu_4NF in CD_3CN (0.4 mL) was prepared in a vial and added directly to the NMR tube by a microsyringe. ^1H NMR spectra were recorded after each addition.

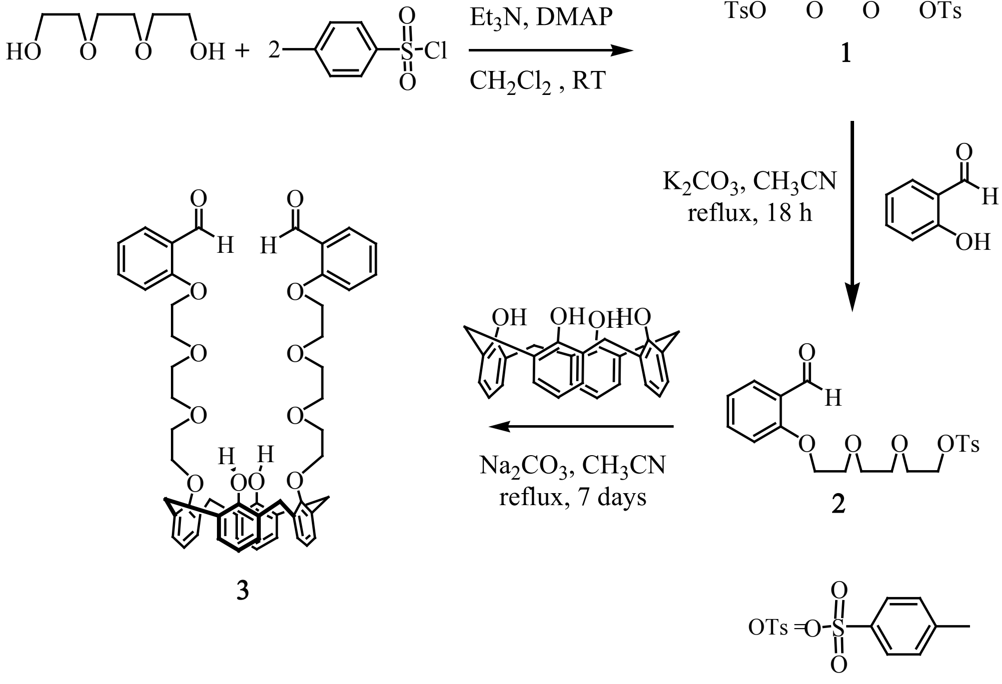
CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis and characterization of ionophores

3.1.1 Synthesis and characterization of metalloporphyrin-calix[4]arene (ML1)

3.1.1.1 Synthesis and characterization of 1,3-calix[4]-dibenzaldehyde (3)



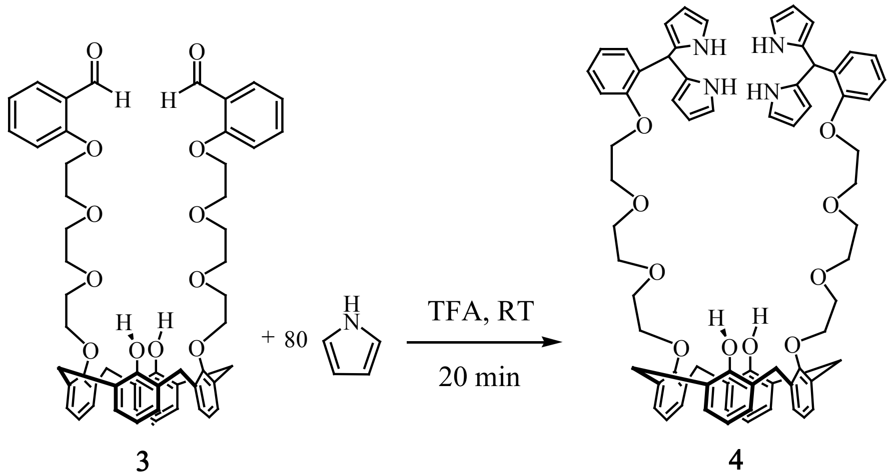
Scheme 3.1 Synthetic patway of 1,3-calix[4]-dibenzaldehyde (**3**)

1,3-Calix[4]-dibenzaldehyde (**3**) was prepared according to the procedure shown in Scheme 3.1.$^{(29)}$ The reaction of anhydrous triethyleneglycol with tosylchloride in the presence of triethylamine as base and a catalytic amount of DMAP in freshly distilled dichloromethane gave a white solid of triethyleneglycol ditosylate (**1**) in 71% yield, after recrytallization from CH_2Cl_2/MeOH. The structures of compound **1** was characterized by ^{1}H NMR spectroscopy and the NMR spectrum showed the characteristic peaks of tosyl groups: a singlet of methyl protons near aromatic ring at 2.44 ppm and two doublets of aromatic protons at 7.79 (*o*-Ar*H*SO_2) and 7.34 (*m*-Ar*H*SO_2) ppm (J = 8.0 Hz). The IR spectrum of compound **1** showed an absorption band at 1356 and 1170 cm^{-1} corresponding to S=O stretching.(31)

The nucleophilic substitution reaction of salicylaldehyde with triethyleneglycol ditosylate (**1**) using excess potassium carbonate as base in freshly distilled acetonitrile provided 2-(8-tosyltriethyleneglycol)benzaldehyde (**2**) as a colourless oil (61% yield). The structures of compound **2** was characterized by ^{1}H NMR spectroscopy and the NMR spectrum showed the characteristic peak of tosyl groups: a singlet of methyl protons near aromatic ring at 2.35 ppm and two doublets of aromatic protons at 7.72 (*o*-Ar*H*SO_2) and 7.26 (*m*-Ar*H*SO_2) ppm (J = 8.4 Hz), the characteristic peaks of benzaldehyde unit: a singlet of ArC*HO* at 10.43 ppm. The ^{13}C NMR spectrum of compound **2** exhibited ^{13}C of aldehyde at 189.7 ppm and ^{13}C of methyl group near aromatic ring at 21.6 ppm. The IR spectrum of compound **2** showed an absorption band at 1688 cm^{-1} for C=O stretching, 1356 and 1170 cm^{-1} corresponding to S=O stretching. The elemental analysis was in accordance with the structure of compound **2**.

Condensation reaction of 2-(8-tosyltriethyleneglycol)benzaldehyde (**2**) (2 equiv.) with calix[4]arene using excess potassium carbonate as base in freshly distilled acetonitrile for 7 days gave a colourless oil of 1,3-calix[4]-dibenzaldehyde (**3**) in 53% yield, after purified by column chromatography. The structure of compound **3** was characterized by ^{1}H NMR spectroscopy that showed the characteristic peaks of benzaldehyde unit: a singlet of ArC*HO* at 10.52 ppm, singlet of hydroxyl protons at 7.81 ppm and methylene protons of calix[4]arene around 4.23 and 3.55 ppm (doublet, J = 13.0 Hz, ArCH_2Ar). These two doublets also indicated that 1,3-calix[4]-dibenzaldehyde (**3**) existed in cone conformation.(28,32) The ^{13}C NMR spectrum of compound **3** exhibited ^{13}C of aldehydic carbon at 189.8 ppm and ^{13}C of methylene of calix[4]arene at 31.8 ppm.⁽³³⁾ The IR spectrum of compound **3** showed an absorption band at 1685 cm^{-1} for C=O stretching. The elemental analysis was in accordance with the structure of compound **3** and MALDI-TOF mass supported the structure of the desired **3** corresponding to intense mass signal at m/z 919.42 [$M+Na^+$].

3.1.1.2 Synthesis and characterization of 1,3-calix[4]arene-bis-dipyrromethane (4)



3

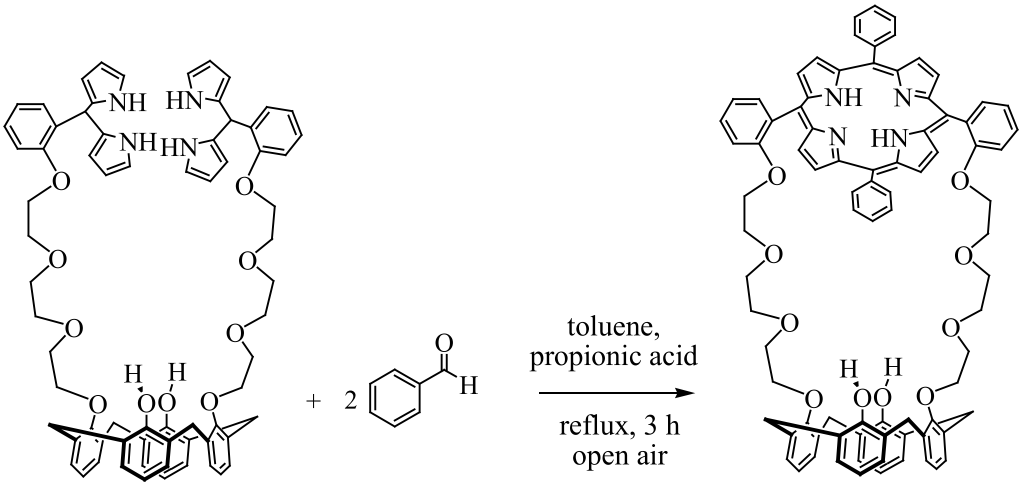
4

Scheme 3.2 The synthesis of 1,3-calix[4]arene-bis-dipyrromethane (**4**)

The synthesis of 1,3-calix[4]arene-bis-dipyrromethane (**4**) was carried out (Scheme 3.2) by treating 1,3-calix[4]-dibenzaldehyde (**3**) with excess pyrrole in the presence of a catalytic amount of CF_3COOH for 20 minutes according to the published procedure.^(34,35) The residue was purified by column chromatography (silica gel, Et_3N : EtOAc : CH_2Cl_2 = 1:2:98) to give 1,3-calix[4]arene-bis-dipyrromethane (**4**) as a brown oil (38 % yield). The structure of compound **3** was characterized by ^1H NMR spectroscopy that showed the characteristic peaks of pyrrole-N*H* as a singlet at 8.95 ppm, a singlet of hydroxyl protons at 7.76 ppm, and four singnals of pyrrolic protons of dipyrromethane at 6.65, 6.14, 5.98 and 5.71 ppm, respectively. Methylene protons of calix[4]arene showed two doublets at 4.44 and 3.38 ppm with *J* = 12.8 Hz

(ArCH_2Ar). These indicated that 1,3-calix[4]arene-bis-dipyrromethane (**4**) was in a cone conformation. The ^{13}C NMR spectrum of compound **4** showed the characteristic peaks of *meso*- position at 46.0 ppm and ^{13}C of methylene of calix[4]arene at 30.9 ppm.

3.1.1.3 Synthesis and characterization of porphyrin-calix[4]arene (L1)

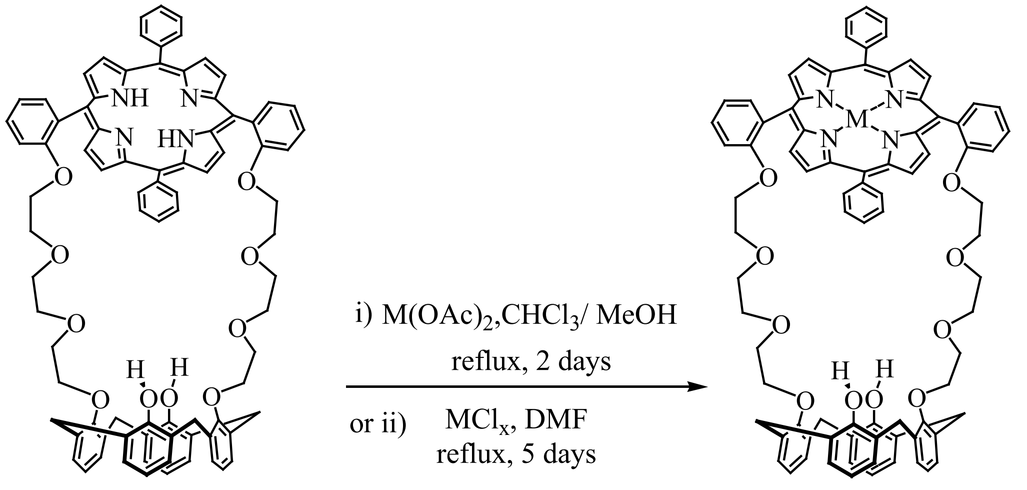


4 **L1**

Scheme 3.3 The synthesis of free base porphyrin-calix[4]arene (**L1**)

Synthesis of porphyrin-calix[4]arene (**L1**) procedure was adapted from the previously reported documents$^{(36)}$ (Scheme 3.3). The obtained by the acid catalyzed condensation of benzaldehyde and 1,3-calix[4]arene-bis-dipyrromethane (**4**) in toluene at reflux in air. The compound **L1** was separated by column chromatography (silica gel, EtOAc : CH_2Cl_2 = 5:95) to give a purple solid **L1** of in 12% yield. The structure of porphyrin-calix[4]arene (**L1**) was supported by ^{1}H NMR, ^{13}C NMR, MS, IR and UV-Vis spectroscopies. The ^{1}H NMR spectrum of porphyrin-calix[4]arene (**L**1) showed the protons signal of β-pyrrolic protons at 8.83 ppm and 8.77 ppm (doublet, J = 4.4 Hz), triethylene protons exhibited groups of signals around 3.86, 2.92, 2.52, 2.17, 1.98 and 1.74 ppm (triplet, J = 4.4 Hz, 24H), methylene protons of calix[4]arene showed signals around 3.68 ppm and 2.97 (doublet, J = 13.0 Hz, ArCH_2Ar). These two doublets also indicated that porphyrin-calix[4]arene (**L**) existed in cone conformation. The protons signals of N*H* in porphyrin appeared around -2.75 ppm (singlet, 2H). The ^{13}C NMR spectrum of compound **L1** showed of triethylene ^{13}C groups of signals around 69.5, 69.3, 69.2, 69.0, 68.8 and 68.4 ppm, ^{13}C of methylene of calix[4]arene at 30.8 ppm. The UV-vis spectrum of **L1** showed a Soret band at 418 nm in THF and four Q bands around 514 nm, 546 nm, 595 nm and 652 nm (Figure 3.1). The IR spectrum of porphyrin-calix[4]arene (**L1**) showed an absorption band at 3354 cm^{-1} corresponding to O-H stretching and at 3319 cm^{-1} for N-H vibrations of the tetrapyrrole system,$^{(37)}$ the strong absorption of the C-C of porphyrin was observed at 963 cm^{-1} and MALDI-TOF mass supported the structure of desired **L1** corresponding to intense mass signal at m/z 1299.53, found 1299.83.

3.1.1.4 Synthesis and characterization of Metalloporphyrin-calix[4]arene (ML1) (ZnL1, CuL1, CoL1, FeL1 and SnL1)



L1

ML1
(M = Zn, Cu, Co, FeCl and SnCl$_2$)

Scheme 3.4 The synthesis of Metalloporphyrin-calix[4]arene (**ML1**) (**ZnL1, CuL1, CoL1, FeL1** and **SnL1**)

Zinc(II) porphyrin-calix[4]arene (**ZnL1**), cuper(II) porphyrin-calix[4]arene (**CuL1**), cobalt(II) porphyrin-calix[4]arene (**CoL1**), ferric(III) porphyrin-calix[4]arene (**FeL1**) and tin(IV) porphyrin-calix[4]arene (**SnL1**) (Scheme 3.4)$^{(38-}$

[42]) were prepared from the metallation of free base porphyrin-calix[4]arene (**L1**) with the corresponding metal salts. All products were recrytallized from CH_2Cl_2/MeOH to obtain as a pink solid (78% yield), red solid (85% yield), orange solid (74% yield), brown solid (51% yield) and green solid (54% yield) of **ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**, respectively. The structures of metalloporphyrin-calix[4]arene (**ML1**) were supported by ^{1}H NMR, ^{13}C NMR, MS, IR and UV-vis spectroscopies. The elemental analysis was in accordance with the structure of compound **ML1.** The UV-vis spectra of metalloporphyrin-calix[4]arene (**ML1**) (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**) displayed only two Q bands substantially different from that of the free base porphyrin-calix[4]arene (**L1**). The Soret band of **ZnL1** and **SnL1** showed a bathochromic shift (424 and 429 nm, respectively). The hypsochromic shift of the Soret bands was found in the case of **CuL1** (415 nm), **CoL1** (416 nm) and **FeL1** (417 nm) (Figure 3.1).

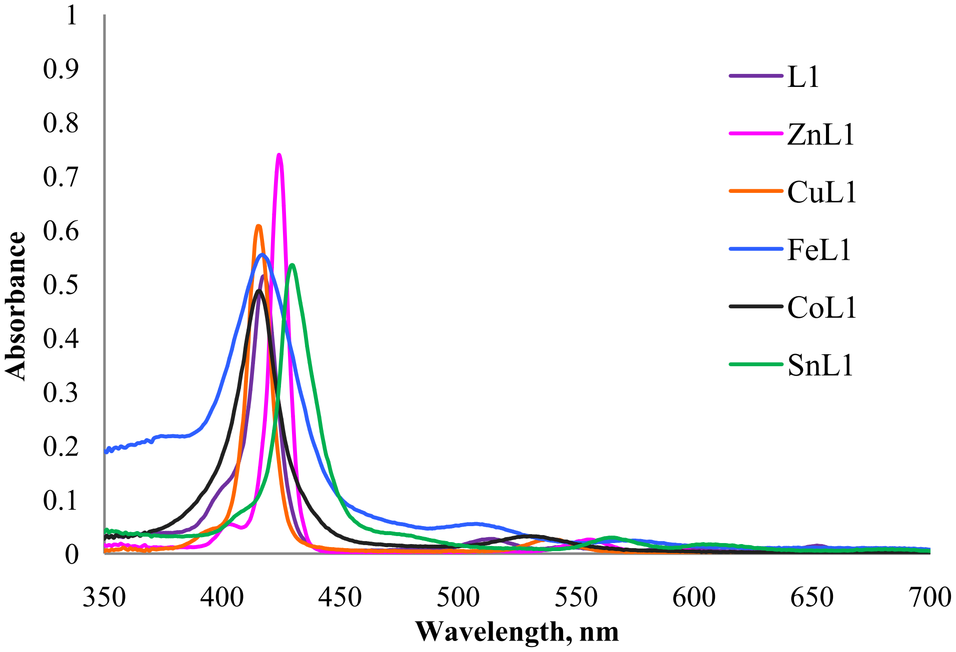


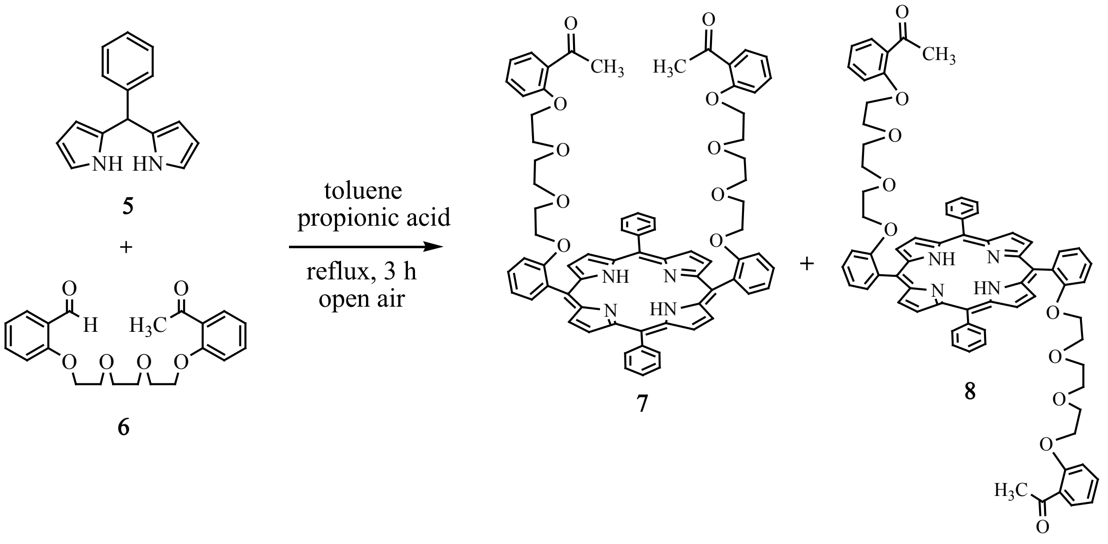
Figure 3.1 UV-vis spectra of **L1**, **ZnL1**, **CuL1**, **FeL1**, **CoL1** and **SnL1** in THF.

The ^{1}H NMR spectrum of Zinc(II) porphyrin-calix[4]arene (**ZnL1**) showed the protons signal of β-pyrrolic protons at 8.88 ppm and 8.82 ppm (doublet, J = 4.4 Hz), triethylene protons exhibit groups of signals around 3.70, 2.92, 2.83, 2.44, 2.03, 1.92 and 1.66 ppm (24H). The protons signals of N*H* in porphyrin disappeared around -2.75 ppm and methylene protons of calix[4]arene showed of signals around 3.54 ppm and 2.92 (doublet, J = 12.8 Hz, $ArCH_2Ar$). These two doublets also indicated that **ZnL1** existed in cone conformation in the same manner as free base porphyrin-calix[4]arene (**L1**). The structures of compound **SnL1** was characterized by ^{1}H NMR spectrum showed the characteristic peaks of the porphyrin unit: a singlet of β-pyrrolic protons at 9.12 ppm and disappeared of N*H* around -2.75 ppm. The ^{13}C NMR spectrum of compound **ZnL1** showed triethylene ^{13}C around 73.7, 69.3, 69.2, 68.9, 68.8 and 68.7 ppm, ^{13}C of methylene of calix[4]arene at 30.8 ppm. Compounds **CuL1**, **CoL1** and **FeL1** could not be characterized by ^{1}H NMR because copper, cobalt and ferric were paramagnetic metal ions. The IR spectra of metalloporphyrin-calix[4]arene (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**) displayed only O-H stretching (at 3351, 3348, 3348, 3348 and 3341 cm^{-1}, respectively), without an absorption band of N-H vibrations.$^{(43)}$

3.1.2 Synthesis and characterization of metalloporphyrin-calix[4]pyrrole (ML2)

The compound **ML2** containing calix[4]pyrrole linked to the porphyrin unit by polyethylene glycol chains was attempted to synthesize by the following procedure.

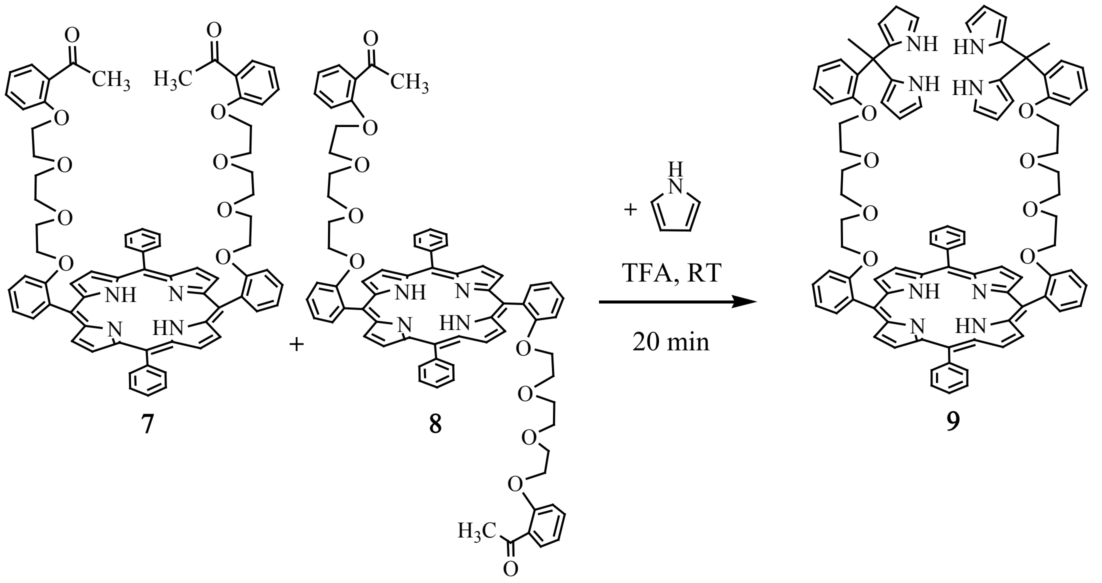
3.1.2.1 Synthesis and characterization of 5,15-di(2-(2-(triethyleneglycol)acetophenone)phenyl)-10,20-diphenylporphyrin (7)



Scheme 3.5 The synthesis of 5,15-di(2-(2-(triethyleneglycol)acetophenone)phenyl)-10,20-diphenylporphyrin (**7**)

The synthetic procedure was adapted from the previously reported documents.(21,44) 5,15-di(2-(2-(triethyleneglycol)acetophenone)phenyl)-10,20-diphenylporphyrin (**7**) (Scheme 3.5) was synthesized by condensation of 5-phenyldipyrromethane (**5**) and 2-(2-(triethylenglycol)bezaldehyde)acetophenone (**6**) to give a mixed atropoisomer of compound **7** (TLC, silica gel; R_f = 0.42) and compound **8** (TLC, silica gel; R_f = 0.56). Both compounds cannot be separated by column chromatography. MALDI-TOF mass spectrum supported the structures of desired atropoisomers **7** and **8** corresponding to intense mass signal at 1147.33 m/z.

3.1.2.2 Synthesis and characterization of 5,15-di(2-(2-(triethyleneglycol)-bis-dipyrroethyl)phenyl)-10,20-diphenylporphyrin (9)



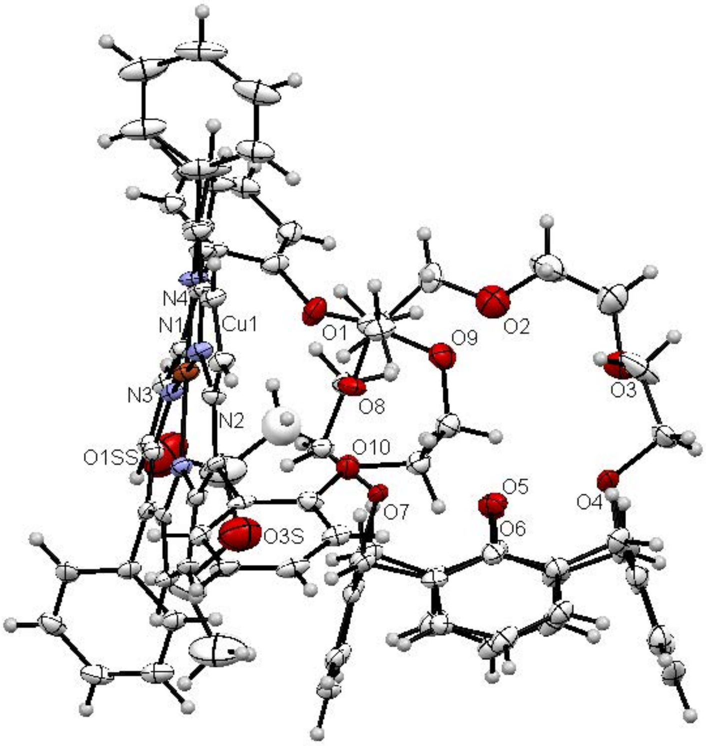
Scheme 3.6 The synthesis of 5,15-di(2-(2-(triethyleneglycol)-bis-dipyrroethyl)phenyl)-10,20-diphenylporphyrin (**9**)

5,15-Di(2-(2-(triethyleneglycol)-bis-dipyrroethyl)phenyl)-10,20-diphenylporphyrin (**9**) was synthesized by the acid catalyzed of 5,15-di(2-(2-(triethyleneglycol)acetophenone)phenyl)-10,20-diphenylporphyrin (**7** and **8**) with 80 time molar excess pyrrole in a presence of catalytic amount of CF_3COOH for 20 minutes according to the published procedure.(35) Unfortunately, the product cannot be purified by column chromatography. Therefore, the desired product, **ML2** cannot be synthesized due to the complication in separation.

3.2 X-ray study of Copper(II) porphyrin-calix[4]arene (CuL1)

Single crystals of **CuL1** were obtained by allowing the solvent (CH_3OH) to slowly evaporate. The X-ray crystal structure of **CuL1** is shown in Figure 3.2. Compound **CuL1** acted the saddle distorted nonplanar porphyrin because the porphyrin ring has many substituents.$^{(45,46)}$ The Cu^{2+} ion is at the center of the porphyrin ring without an axial ligation. The bond lengths from the Cu-N are within 1.976(4)-1.990(4) Å. There is a solvent molecule (ethyl acetate) in the crystal structure of compound **CuL1**. The calix[4]arene unit is in cone conformation in the solid state.$^{(47)}$ The ethylene glycol chain links metalloporphyrin ring and calix[4]arene moiety at 1,3-position and metalloporphyrin bends toward calix[4]arene because of the edge-to-face H-π interactions between the proton (H34) of phenyl at *meso*-position of porphyrin and phenyl ring of calix[4]arene.

a)



b)

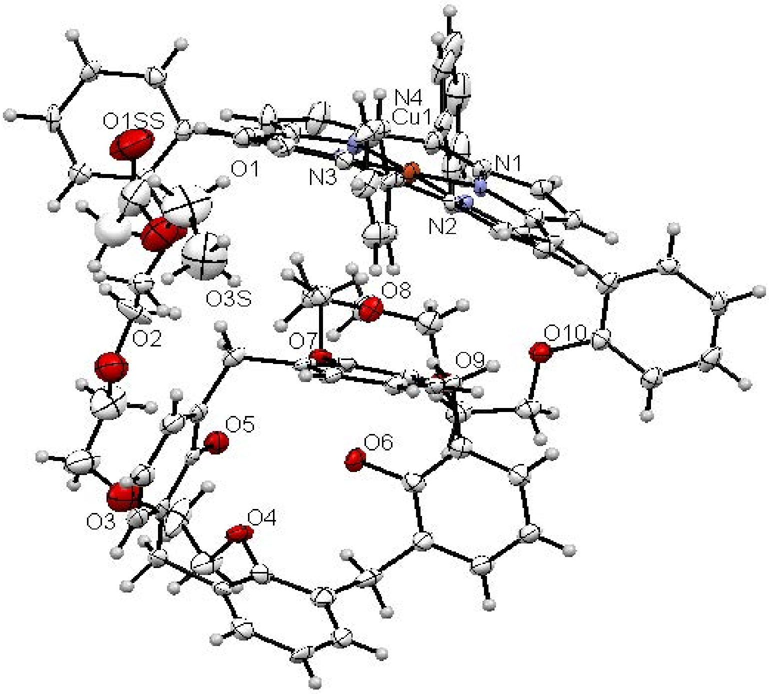


Figure 3.2 Crystal structure of copper(II) porphyrin-calix[4]arene **CuL1** a) side view of **CuL1**, and b) below view of **CuL1**.

3.3 Potentiometric studies of ionophores (ZnL1, CuL1, CoL1, FeL1 and SnL1)

Ionophores **ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1** were then used to fabricate anion selective electrodes

3.3.1 EMF responses of the ISE, prepared for ZnL1, CuL1, CoL1 and FeL1

The emf responses of types A, B, C and D were presented in Chapter 2. (10 mmol/kg (1% w/w) ionophores (**ZnL1**, **CuL1**, **CoL1** and **FeL1**, respectively), 25% mol of TDMACl relative to the ionophore amount, 33 wt.% PVC and 66 wt.% *o*-NPOE). The properties of each membrane electrode were investigated from the calibration curves by plotting between the potential responses for all different of anions species and logarithm of activity. As it was seen from the calibration curves (Figure 3.3-3.6) except for perchlorate, thiocyanate and iodide, the slopes of the obtained curves are much lower than the expected Nernstian slope and plots suffer from limited linear range. However, the iodide ion exhibited the Nernstian response over a concentration range of 1.0×10^{-6} to 1.0×10^{-2} M. The results indicated that these ionophores had good selectivity towards iodide.

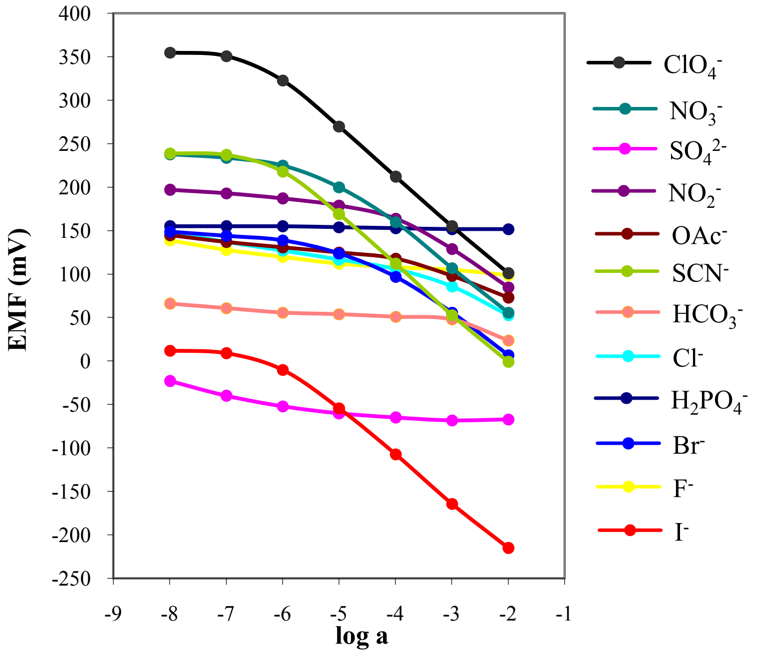


Figure 3.3 Calibration curves of anions responses for type A (**ZnL1**)

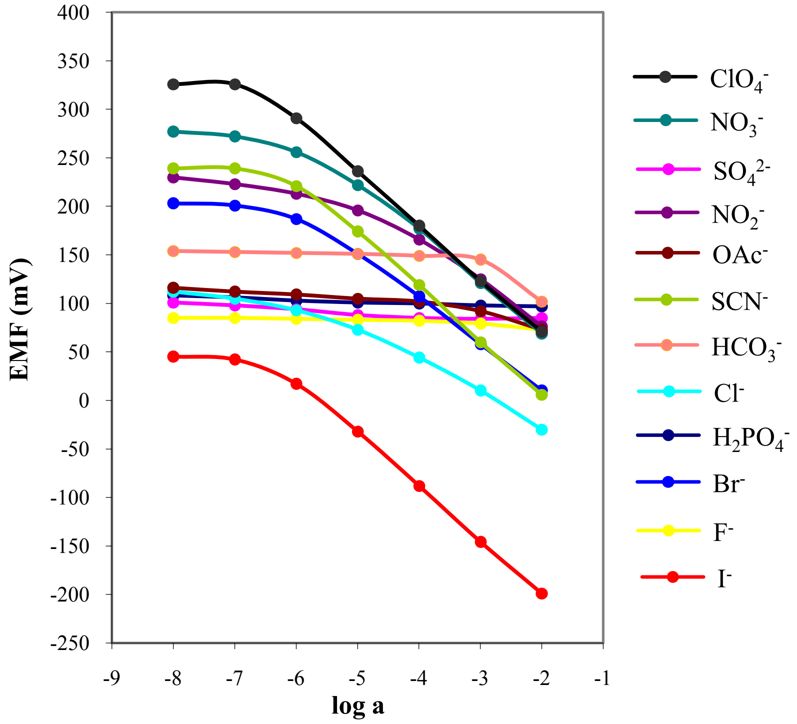


Figure 3.4 Calibration curves of anions responses for type B (**CuL1**)

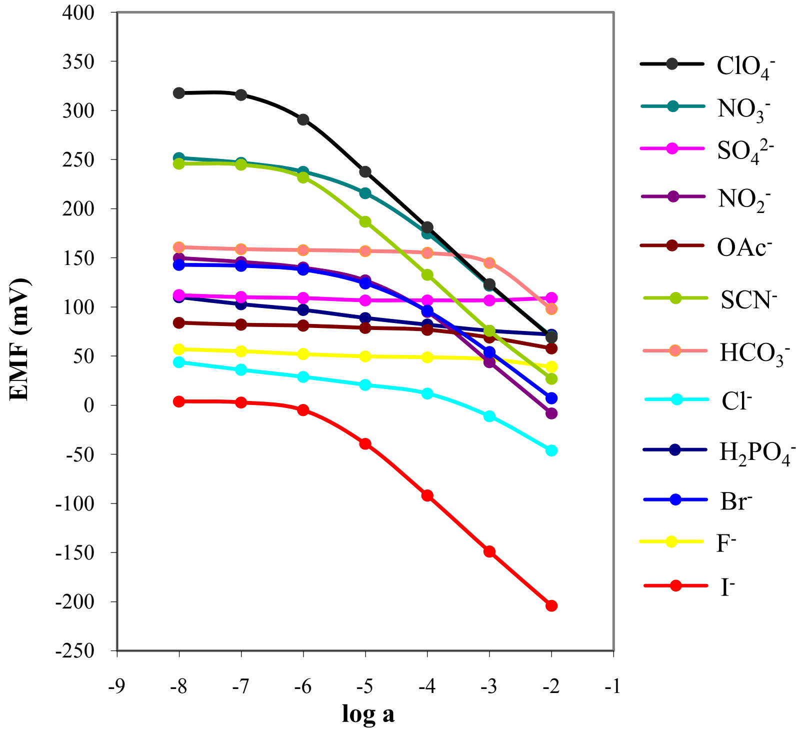


Figure 3.5 Calibration curves of anions responses for type C (**CoL1**)

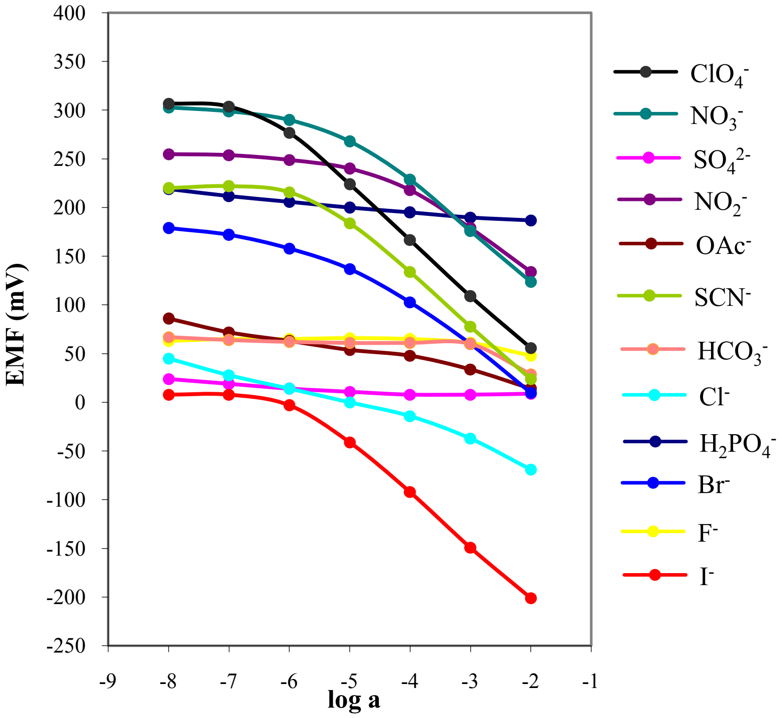


Figure 3.6 Calibration curves of anions responses for type D (**FeL1**)

3.3.2 Effect of solution buffer for iodide responses of the membrane electrode based on ZnL1 using 25% cationic additives

In aqueous solution of milli-Q water, glycine buffer pH 3.5 (0.05 M) and 4-Morpholinoethanesufonic acid (MES) buffer pH 5.5 (0.05 M), the membrane electrode using **ZnL1**, 25% mol of TDMACl relative to the ionophore amount (type A) exhibited a good response and the slope towards I^- in all solution. Moreover, the milli-Q water gave a slope and detection limit of the iodide response better than glycine and MES as shown in Figure 3.7 and Table 3.1.

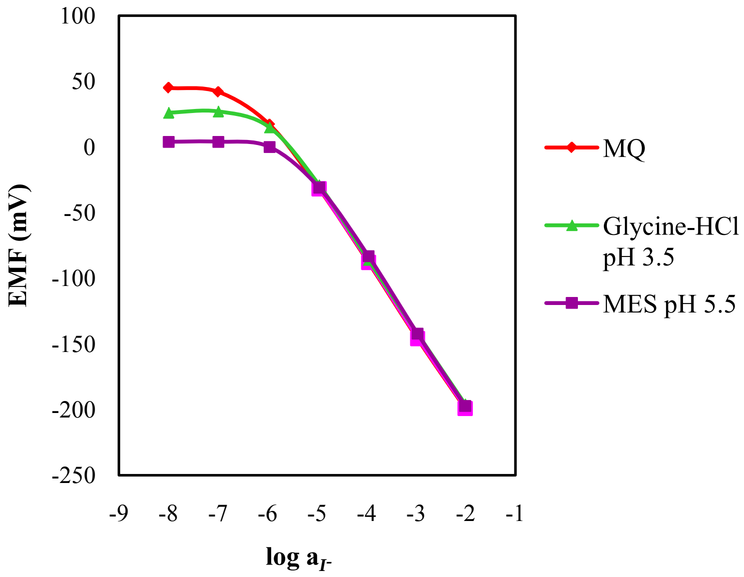


Figure 3.7 Calibration curves of membrane A responses for I$^-$ in milli-Q water, glycine buffer pH 3.5 and MES buffer pH 5.5.

Table 3.1 Characteristics of iodide responses of membrane type A (**ZnL1,** 25% mol of TDMACl) in each aqueous solution.

Type of solution	slope	Linear range	Detection limit
milli-Q	-56.8	1×10^{-6}-1×10^{-2}	5.97×10^{-7}
Glycine pH 3.5	-56.6	1×10^{-6}-1×10^{-2}	1.06×10^{-6}
MES pH 5.5	-56.6	5×10^{-6}-1×10^{-2}	3.35×10^{-6}

3.3.3 Selectivity coefficients of PVC membrane electrodes based on ZnL1, CuL1, CoL1 and FeL1 using 25% mol of cationic additives

One of the most important characteristics of ion selective electrode is its relative response to the primary ion over other ions presented in the solution, which is exhibited in terms of potentiomatric selectivity coefficients. Logarithm of anion selectivity coefficients, $logK_{i,j}^{pot}$ was determined by separate solution method (SSM).

In SSM, i refer to primary ion (iodide) and j refer to interfering ions (other anions) as shown in Figure 3.8

All membrane electrode gave values of log $logK_{i,j}^{pot}$ of ClO_4^- (+1) and SCN^- (+0.5) higher than that of I^- according to the Hofmeister series.(1) However, PVC membranes based on **ZnL1** and **CuL1** (A and B, respectively) gave values of $logK_{i,j}^{pot}$ lower than membranes based on **CoL1** (C) and **FeL1** (D) and the blank membrane (25% TDMACl).

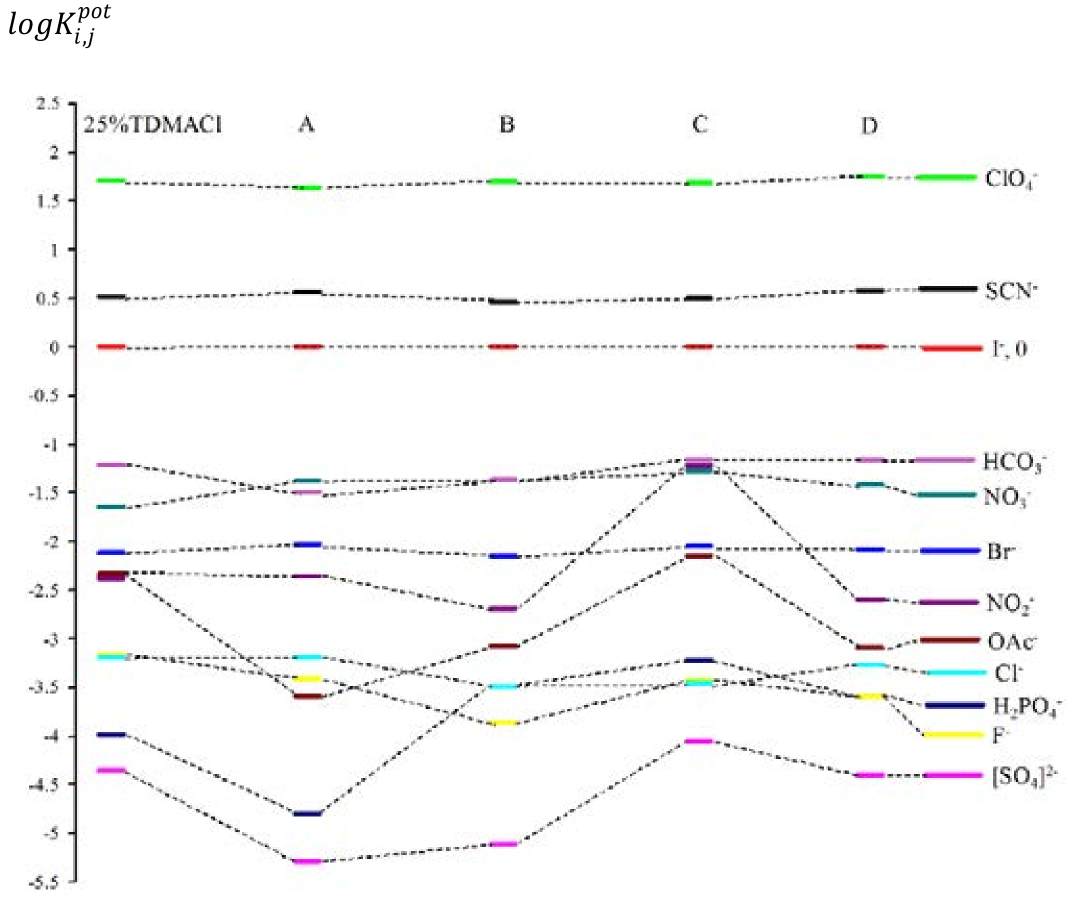


Figure 3.8 Selectivity coefficients of membrane electrodes base on **ZnL1** (type A), **CuL1** (type B), **CoL1** (type C), and **FeL1** (type D). Measurements carried out in milli-Q water. Type refer to membrane composition listed in Table 2.1

3.3.4 Selectivity coefficients of PVC membrane electrode base on ZnL1 and CuL1 using 15%, 25% and 35% mol of cationic additives

For the membrane electrodes based on **ZnL1** with cationic additives (TDMACl) 15%, 25% and 35% mol relative to the ionophore amount (type F, A and G, respectively). The membrane A displayed values of $logK_{i,j}^{pot}$ of SO_4^{2-} and $H_2PO_4^-$ lower than membrane F and membrane G, but other anions (ClO_4^-, SCN^-, NO_3^-, NO_2^-, Br^-, Cl^-, F^-, OAc^- and HCO_3^-) did not differ significantly (see Figure 3.9).

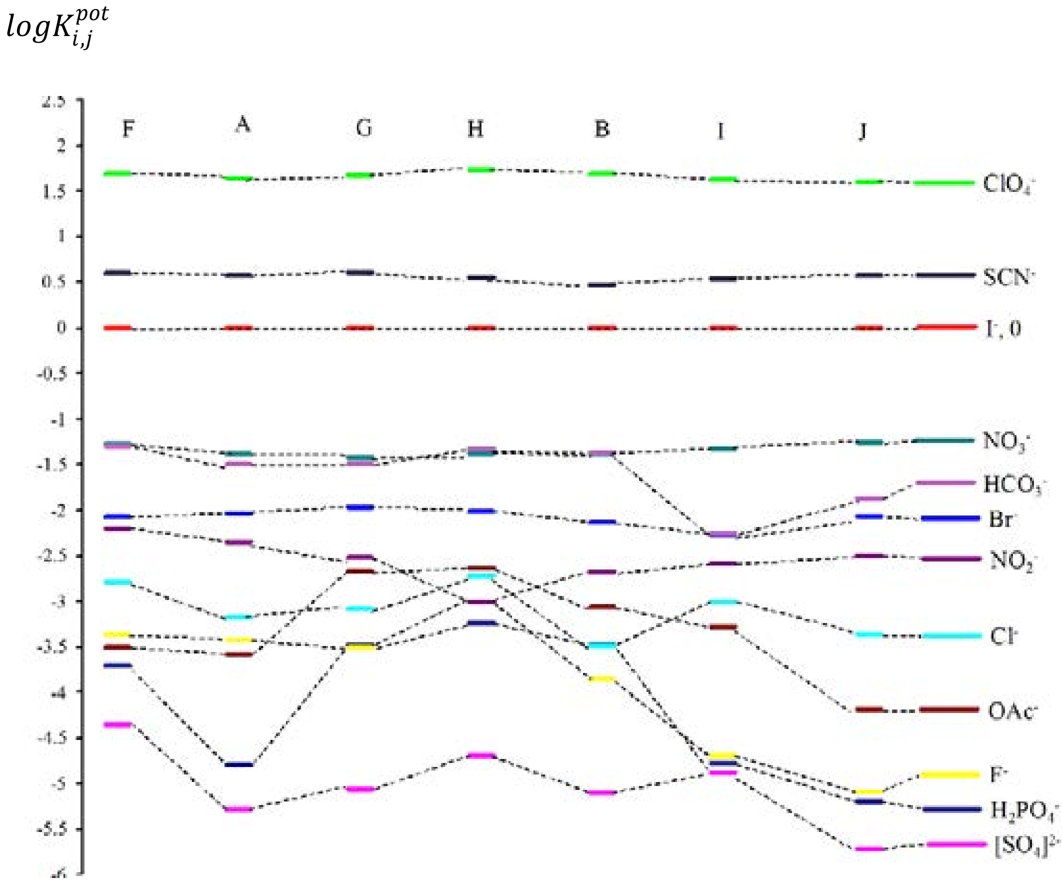


Figure 3.9 Selectivity coefficients of membrane electrodes base on **ZnL1** (type A, F and G), and **CuL1** (type B, H, I and J). Measurements carried out in milli-Q water. Type refer to membrane composition listed in Table 2.1

In the case of membrane electrodes based on **CuL1**, cationic additives (TDMACl) 15%, 25%, 35% and 50% mol relative to the ionophore amount (type H, B, I and J, respectively). The membrane J displayed values of $logK_{i,j}^{pot}$ of SO_4^{2-}, $H_2PO_4^-$, F^- and OAc^- lower than membrane G, membrane B and membrane I. But it is interesting the observe that the membrane I is showing the lowest values of $logK_{i,j}^{pot}$ of HCO_3^-, as presented in Figure 3.9.

3.3.5 Potentiometric studies of ionophore (SnL1)

Due to Lewis acid behavior of the metal center in porphyrin ring, it can bind anions as an axial ligand and exhibits the potentiometric response. Tin(IV) has high oxidation state. Therefore, the synthesized Sn(IV) porphyrin-calix[4]arene (**SnL1**) is studied as an ionophore for anion selective electrodes.

3.3.5.1 EMF responses of SnL1 using 25% mol of anionic additives

Due to Lewis acid behavior of the metal center in porphyrin ring, it can bind anions as an axial ligand and exhibits the potentiometric response. Tin(IV) has high oxidation state. Therefore, the synthesized Sn(IV) porphyrin-calix[4]arene (**SnL1**) is studied as an ionophore for anion selective electrodes.

For the ionophore **SnL1** (type E), the composition of the membrane differerent from that of **ZnL1**, **CuL1**, **CoL1** and **FeL1**, ionophore (**SnL1**) (10 mmol/kg (1% w/w), 25% mol of anionic additives (KT*p*ClPB) relative to the ionophore amount, 33 wt.% PVC and 66 wt.% *o*-NPOE). The effects of anions on the behavior of membrane electrode was investigated using the calibration curves by plotting between the potential responses for all different of anion species and logarithms of activity. As it was seen from the calibration curves (Figure 3.10) except for salicylate, the slopes of the obtained curves are much lower than the expected Nernstian slope. In contrast, perchlorate and thaiocyanate ion exhibited the slope (-45.2 and -39.4 mV/decade, respectively) of membrane E lower than membranes component of **ZnL1**, **CuL1**,

CoL1 and **FeL1**. However, the salicylate ion exhibited in the Nernstian response over a concentration range of 5.0×10^{-5} to 1.0×10^{-2} M. In this regard, the ionophore is selective towards salicylate compared to other anions. However, the **SnL1** membrane electrode still suffers from a limited linear range for detecting salicylate ion.(9, 48, 49)

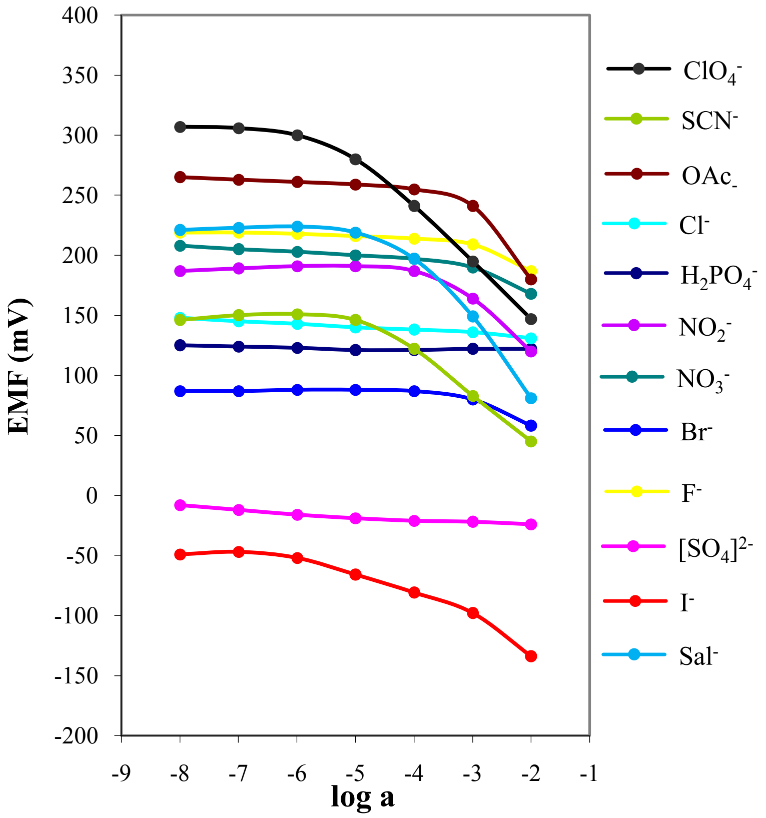


Figure 3.10 Calibration curves of anions responses for type E (**SnL1**). Measurements carried out in glycine buffer pH 3.5 (0.05 M).

3.3.5.2 Effect of the inner filling solution on salicylate responses of membrane E

The effect of the inner filling solution concentration on the emf response of membrane electrode was investigated at different concentrations of I^- and Cl^- as shown in Table 3.2. The results showed various that concentrations of the inner filling solution resulted in different slopes for salicylate. However, at I^- 1.0×10^{-2} M and Cl^-

1.0×10^{-2} M of the inner filling solution, the electrode exhibited the Nernstian slope (-60 mV/decade), while at the concentrations I^- 1.0×10^{-3} M and Cl^- 1.0×10^{-2} M, the electrode displayed super Nernstian response (-64 mV/decade) as shown in Figure 3.11 and Table 3.2.

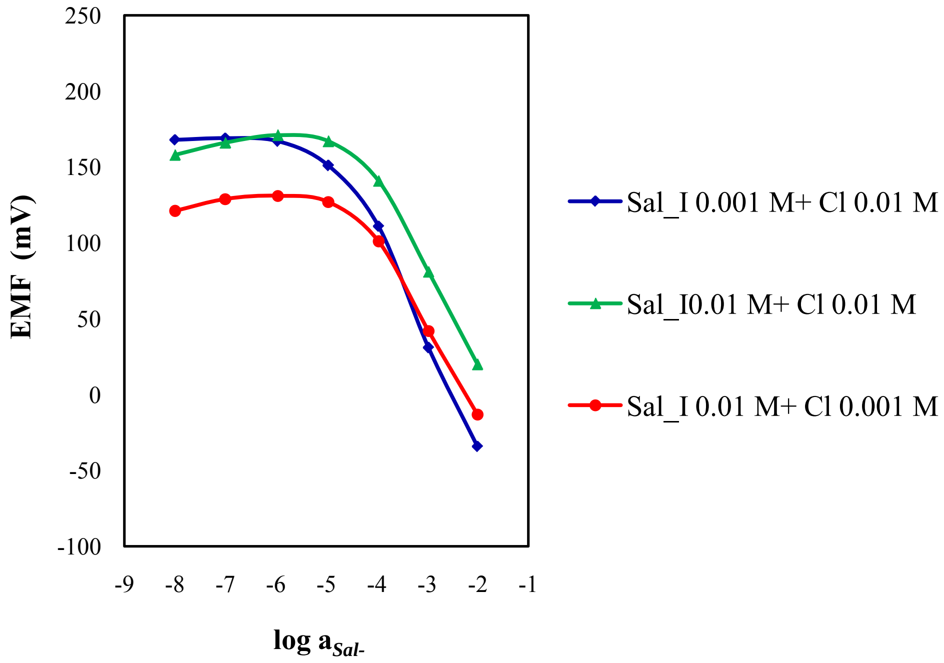


Figure 3.11 Calibration curves of salicylate responses for type E (**SnL1**), different concentrations of I^- and Cl^- of the inner filling solution. Measurements carried out in glycine buffer pH 3.5 (0.05 M).

Table 3.2 Characteristics of salicylate responses of membrane type E (**SnL1,** 25% mol of KT*p*ClPB) in each inner filling solution.

Type of inner filling solution	slope	Linear range
Sal 0.001 M + Cl 0.01 M	-64	5×10^{-5}-1×10^{-2}
Sal 0.01 M + Cl 0.01 M	-60	5×10^{-5}-1×10^{-2}
Sal 0.01 M + Cl 0.001 M	-58	5×10^{-5}-1×10^{-2}

3.3.5.3 Selectivity coefficients of PVC membrane electrode based on SnL1

In the case of membrane electrode fabricated from **SnL1**.Effects of anionic additives (KT*p*ClPB) 0%, 15 %, 25% and 35% mol relative to the ionophore amount (type K, E, L and M, respectively) were studied. The membrane E displayed values of $logK^{pot}_{Sal,j}$ of all interfering ions lower than salicylate ion. However, I^- was found to be the most interfering ion. Furthermore, the membrane electrode using **SnL1** exhibited anon-Hofmeister pattern towards salicylate with an anionic additive, suggesting charge carrier mechanism(17) of the electrode membrane as presented in Figure 3.12.

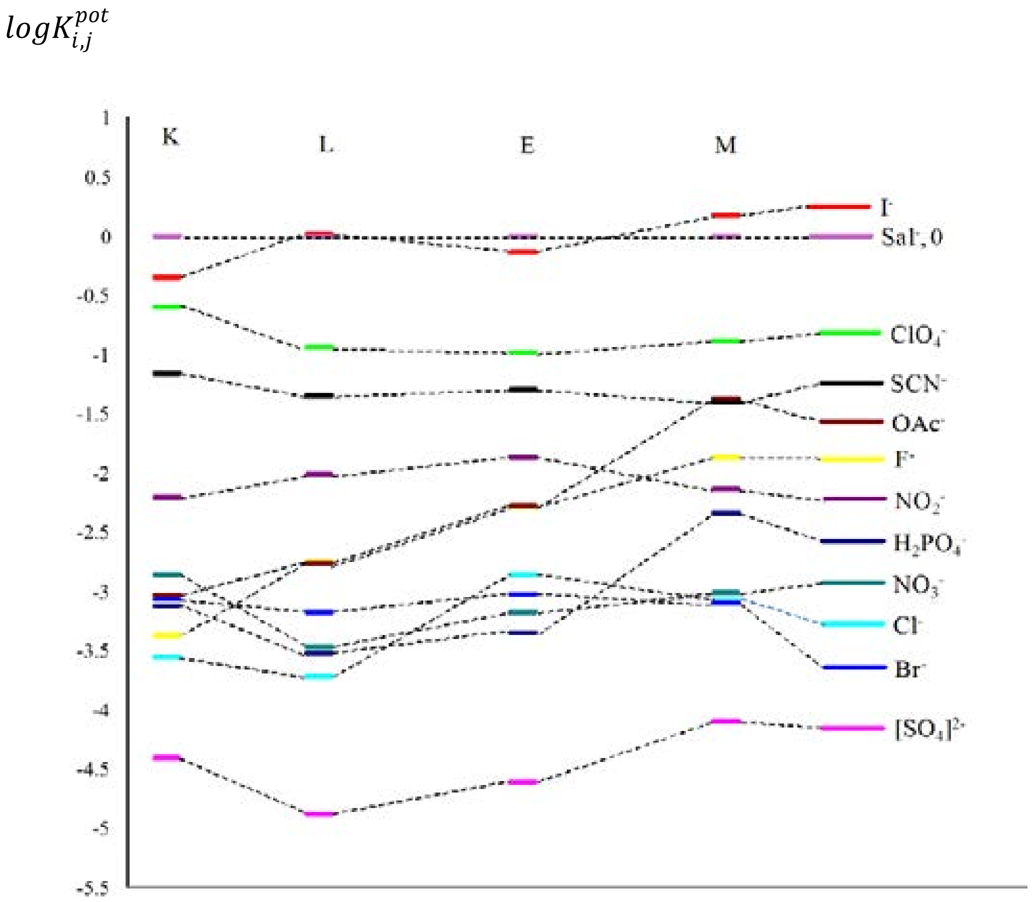


Figure 3.12 Selectivity coefficients of membrane electrodes based on **SnL1,** anionic additives (KT*p*ClPB) 0%, 15%, 25% and 35% mol relative to the ionophore amount (type K, E, L and M, respectively). Measurements carried out in glycine buffer pH 3.5 (0.05 M).

For the membrane electrode using **SnL1** without ionic additives (type K), selectivity coefficients of membrane showed the values of $logK_{i,j}^{pot}$ of NO_3^- lower than NO_2^-. It was found that the membrane K gave a non- Hofmeister series. The membrane electrode has a greater amount of anionic additives (KT*p*ClPB), selectivity coefficients of F^- and OAc^- ion in membrane electrodes using anionic additives corresponding to the values more than the membrane electrode based on **SnL1** only. In contrast, selectivity coefficients decrease for $logK_{i,j}^{pot}$ of ClO_4^- and SCN^-.

3.3.6 Reversibility of the potentiometric iodide response for membrane electrode based on ZnL1 using 25% cationic additives

The reversibility of the membrane electrode was an important property of the ion selective electrodes.

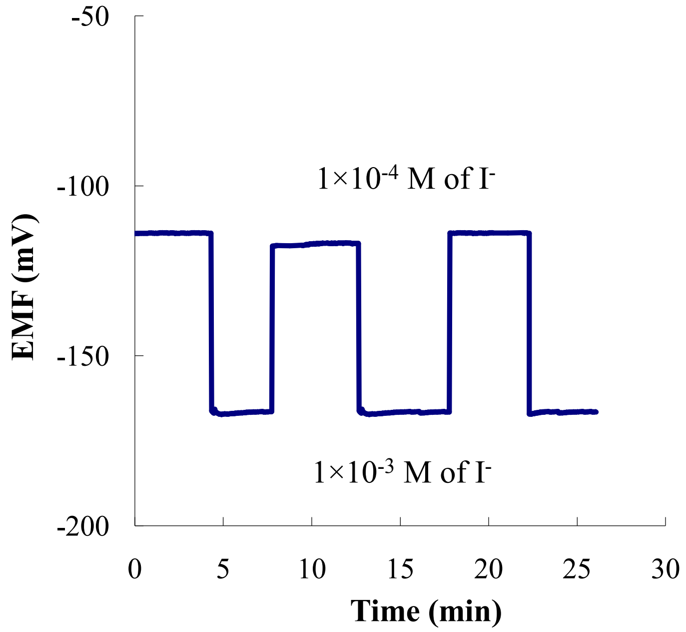


Figure 3.13 The reversibility of emf iodide response for membrane electrode based on **ZnL1** using 25% TDMACl at different concentrations between 1×10^{-4} M and 1×10^{-3} M.

Figure 3.13 showed the emf response toward I$^-$ for the membrane electrode based on **ZnL1** using 25% cationic additives (TDMACl). When changing I$^-$ concentration back and forth between 1×10^{-4} M and 1×10^{-3} M, emf signals can be restored at the same concentration of I$^-$ in every cycle. Accordingly, the membrane electrode be used to measure I$^-$ concentration with a very good reversibility.

3.3.7 Effect of pH on the potentiometric iodide response for membrane electrode based on ZnL1 using 25% cationic additives

The influence of pH of the test solution on the iodide response was tested at 1×10^{-4} M and 1×10^{-3} M concentration of iodide over a pH range of 2.0-10.0 (adjusted with HCl or NaOH) as shown in Figure 3.14. The results showed that the emf response remains constant over the pH range 3.5-6.0. In high pH, OH$^-$ can coordinate as an axial ligand to the metal center porphyrin.(50)

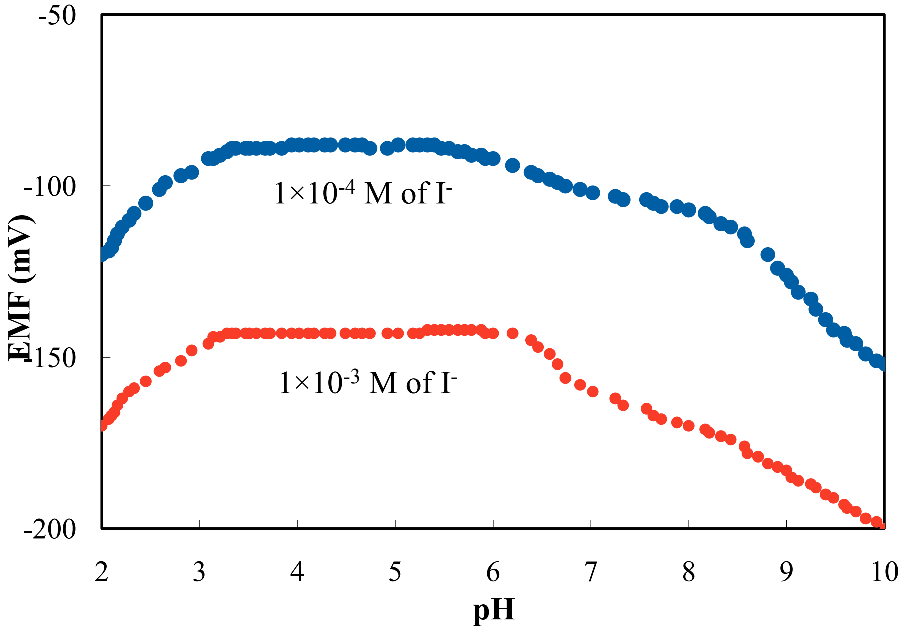


Figure 3.14 Effect of pH of the potentiometric iodide response for membrane electrode based on **ZnL1** using 25% cationic additives. At 1×10^{-4} M and 1×10^{-3} M concentration of I$^-$.

3.4 Complexation studies of Zinc(II) porphyrin-calix[4]arene (ZnL1) with anions in solution

Compound **ZnL1** contains the Zinc center porphyrin strap calix[4]arene which can bind anions and act as a chromophore. Thus, the complexation studies of Zinc(II) porphyrin-calix[4]arene with ClO_4^-, NO_3^-, Cl^-, Br^-, I^-, F^-, CH_3COO^-, $PhCOO^-$, $H_2PO_4^-$, were carried out in acetonitrile. The anion recognition *via* ion-ion interactions to axial ligand of Zinc porphyrin can also be easily monitored by anions complexation induced change in UV-vis absorption spectra by additions of excess (100 equiv.) tetrabutylammonium salts. The obtained spectra were shown in Figure 3.15.

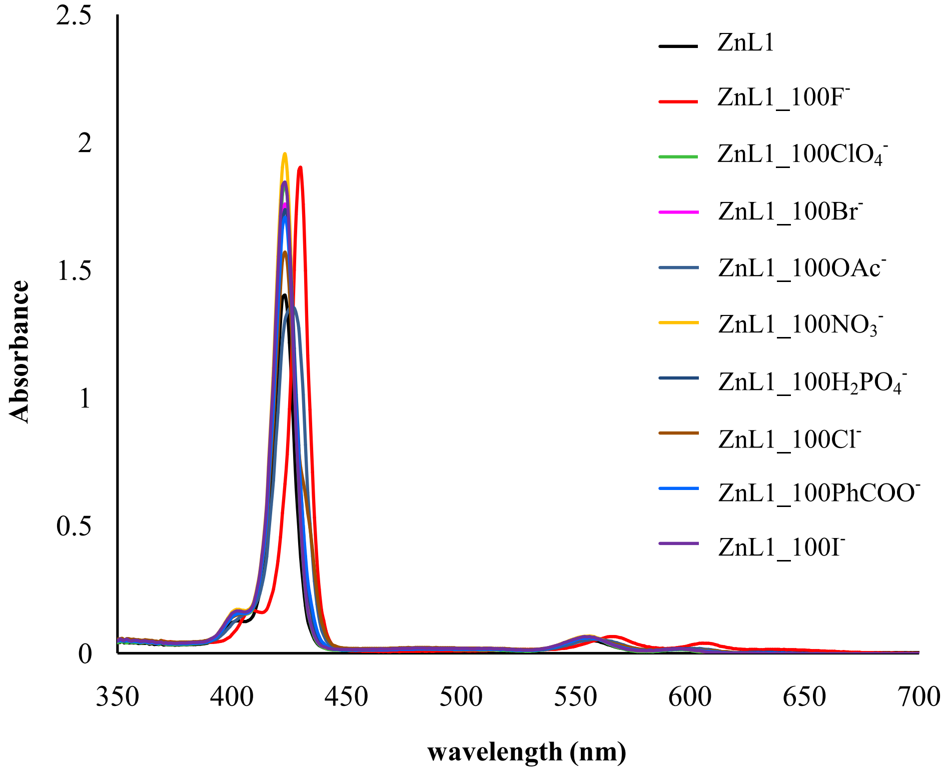


Figure 3.15 UV-vis spectra of Zinc(II) porphyrin-calix[4]arene (**ZnL1**) (5.0 µM) with various tetrabutylammonium salts (100 equiv.).

The UV-vis spectrum of **ZnL1**, in the absence of anions, exhibited the Soret band at 423 nm in acetonitrile. A bathochromic shift of the spectrum was observed at 430 nm upon adding the Bu_4NF, but other anions do not give a new band due to **ZnL1** : anions complexes.

3.4.1 Complexe studies of Zinc(II) porphyrin-calix[4]arene (ZnL1) with Bu_4NF

Complexation studies of Zinc(II) porphyrin-calix[4]arene (**ZnL1**) with Bu_4NF in acetonitrile by UV-vis spectrophotometry were also carried out. UV-vis absorption spectra of **ZnL1** were measured at a 1.0 μM. The job's method(51) was used to determine the binding stoichiometry of the complexes using the absorption spectra data at 423 nm for complex of **ZnL1** with Bu_4NF. The job's plot was plotted between the mole fraction of **ZnL1** in the mixture (X_{ZnL1}) and $\Delta A \times (1-X_{ZnL1})$ calculated from the maximum absorption changes ΔA multiplied by their inverse mole fraction ($1-X_{ZnL1}$). The plots afforded the maximum point at 0.5 for **ZnL1** with Bu_4NF suggesting a 1:1 stoichiometry as shown in Figure 3.16.

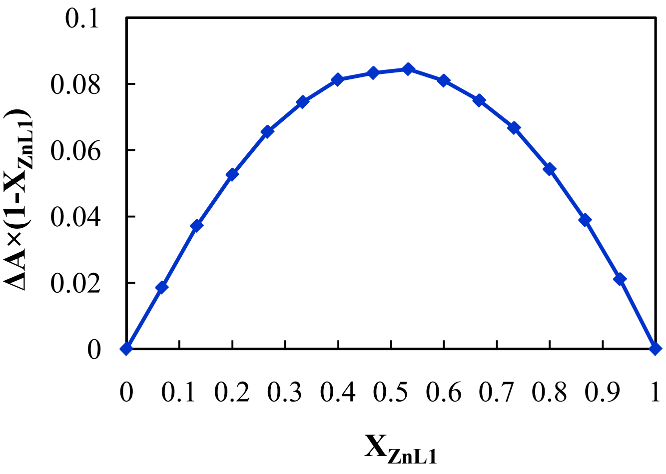


Figure 3.16 The job's plot of the complexation of **ZnL1** with Bu_4NF in CH_3CN.

3.5 ^{1}H NMR studies of Zinc(II) porphyrin-calix[4]arene (ZnL1) with Bu_4NF

^{1}H NMR titrations of 5 µM **ZnL1** (2×10^{-6} mmol) in a mixture of $CDCl_3$: CD_3CN (1:9 v/v) with Bu_4NF as a fluoride anion were carried out. The ^{1}H NMR apectra were illustrated in Figure 3.17 and 3.18. The signals of β-pyrrolic protons at 8.49 and 8.41 ppm to upfield shifts and remained a broad singlet upon adding fluoride (0.7 equiv.). (52,53) Moreover, the signal of ethylene protons at 3.36 ppm were slightly downfield shifted and methylene protons of calix[4]arene showed a doublet at 3.11 ppm which was broadened and downfield shifted. These results suggested that F^- was coordinate as an axial ligand of the Zn-porphyrin complex and located near calix[4]arene cavity.

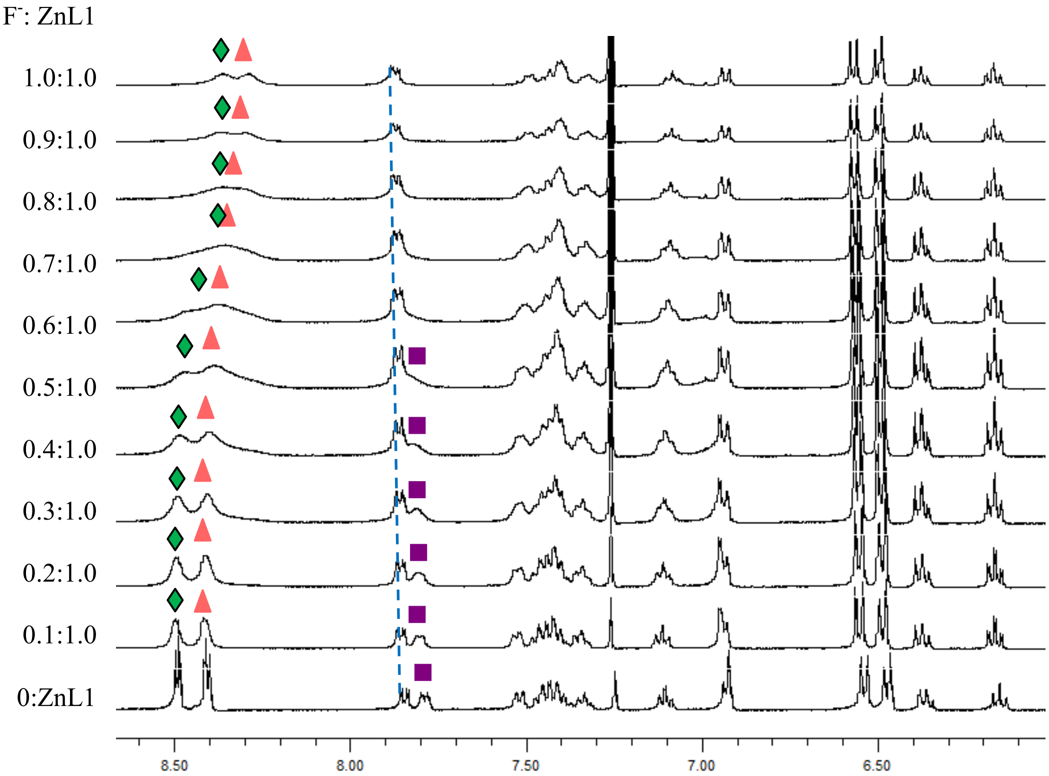


Figure 3.17 ^{1}H NMR titration spectra of **ZnL1** with Bu_4NF in a mixture $CDCl_3$:CD_3CN = 1:9 (v/v) at 9.00-6.00 ppm.

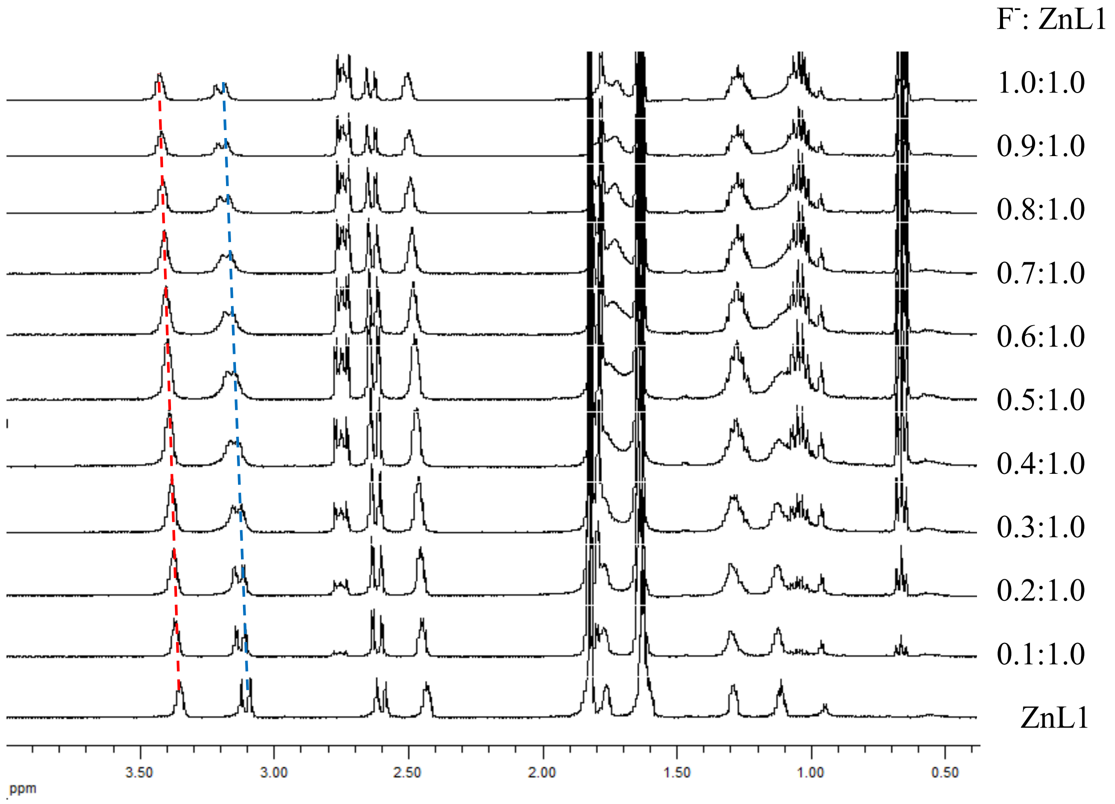


Figure 3.18 ^{1}H NMR titration spectra of **ZnL1** with Bu_4NF in a mixture $CDCl_3$:CD_3CN = 1:9 (v/v) at 4.00-0.05 ppm.

CHAPTER IV

CONCLUSION

Ionophores based on metalloporphyrin-calix[4]arene **ML1** (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**) have been synthesized. The synthetic pathway was beginning with a condensation of 2-(8-tosyltriethyleneglycol)benzaldehyde (**2**) with calix[4]arene by using Na_2CO_3 as a base in refluxing CH_3CN. The 1,3-calix[4]-dibenzaldehyde (**3**) was afforded with 53% yield. The acid catalyzed condensation of 1,3-calix[4]-dibenzaldehyde (**3**) with excess pyrrole afforded 1,3-calix[4]arene-bis-dipyrromethane (**4**) in 38% yield. The porphyrin-calix[4]arene (**L1**) (12% yield) was obtained by the acid catalyzed condensation and oxidation of benzaldehyde and 1,3-calix[4]arene-bis-dipyrromethane (**4**) in toluene at reflux in air. The metallation of free base porphyrin-calix[4]arene (**L1**) with the corresponding metal salts were afforded with metalloporphyrin-calix[4]arene (**ZnL1**, **CuL1**, **CoL1**, **FeL1** and **SnL1**) in 78%, 85%, 74%, 51% and 54% yield, respectively. The X-ray crystal structure of porphyrin-calix[4]arene (**CuL1**) showed the calix[4]arene unit is in cone conformation and copper ion is in the center of porphyrin ring without an axial ligation.

The potentiometric response of polymer membrane electrodes doped with metalloporphyrin-calix[4]arene (**ZnL1**, **CuL1**, **CoL1** and **FeL1**) as ionophores for anions were constructed. In this case, the mentioned ionophores were found to detect iodide selectivity in comparison to other anions. For the potentiometric response of polymer membrane electrodes doped with **SnL1** as ionophores for anions, the slopes of the obtained curves are much lower than the expected Nernstian slope. However, the salicylate ion exhibited the Nernstian response over a concentration range of 5.0×10^{-5} to 1.0×10^{-2} M.

The complexation studies of metalloporphyrin-calix[4]arene (**ZnL1)** with Bu_4NF presented that the complex of **ZnL1** : Bu_4NF were 1:1 stoichiometry. The ^1H NMR titration of **ZnL1** with upon each addition of Bu_4NF as a fluoride. The results suggested the coordination of F^- to the Zn(II) center and it showed locate near the calix[4]arene cavity.

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APPENDICES

APPENDIX A

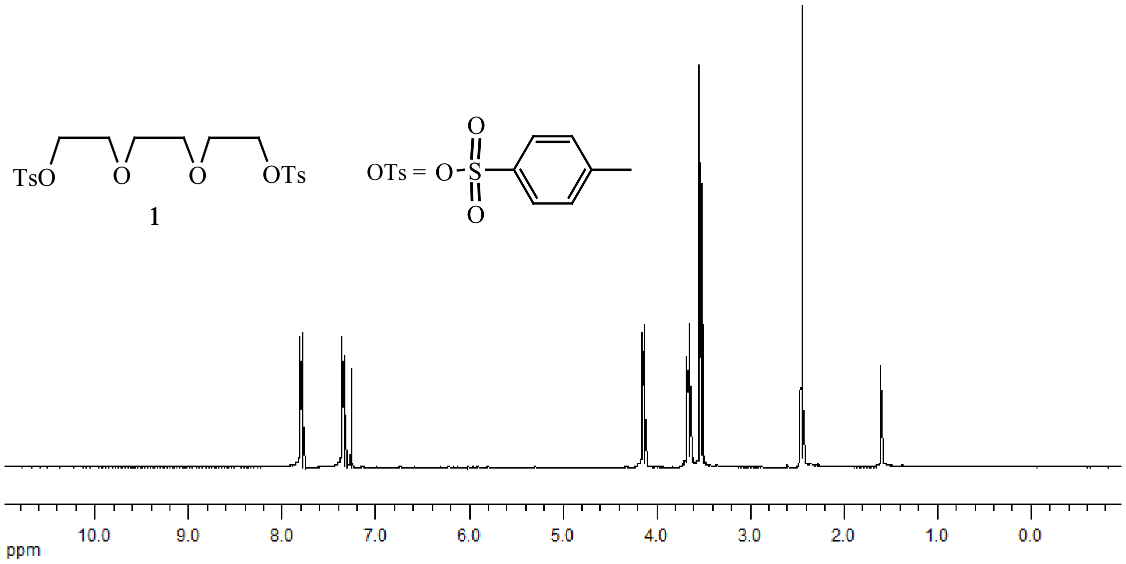

Figure A-1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**

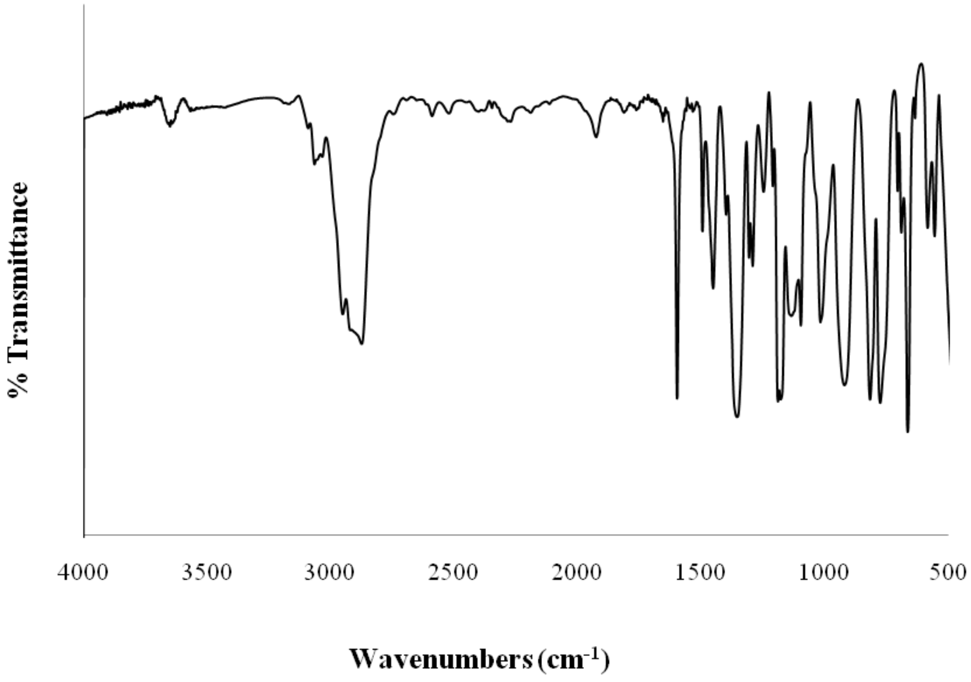

Figure A-2 IR spectrum of **1**

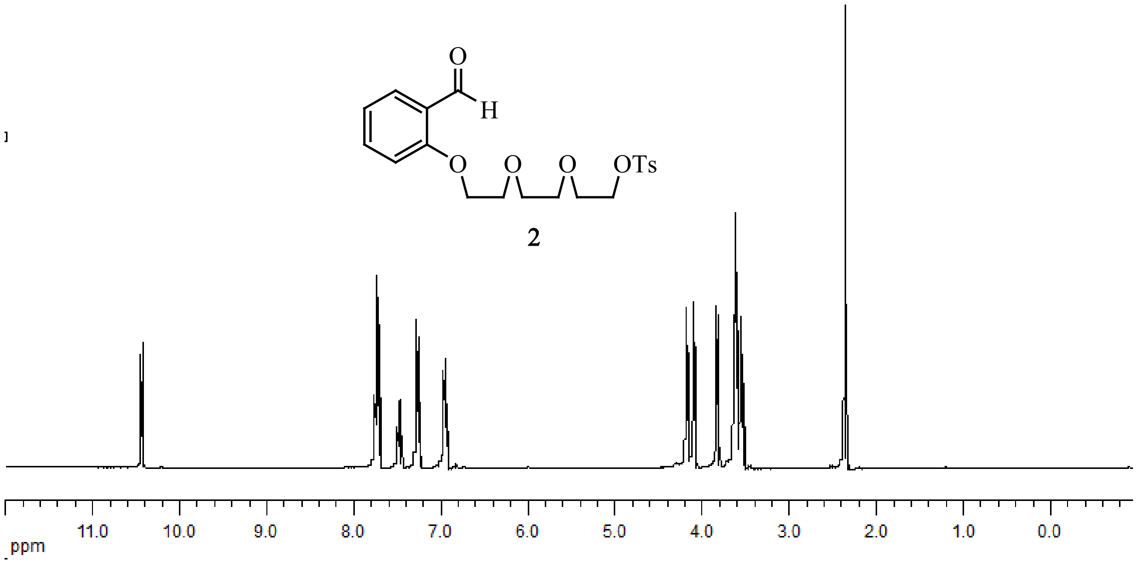

Figure A-3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**

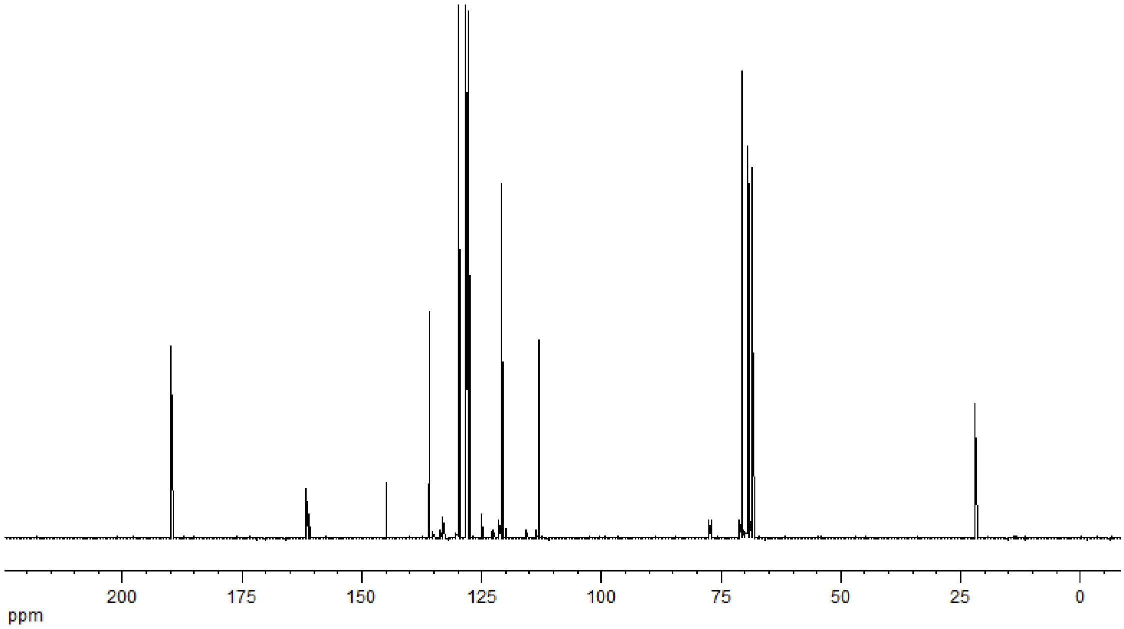

Figure A-4 ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2**

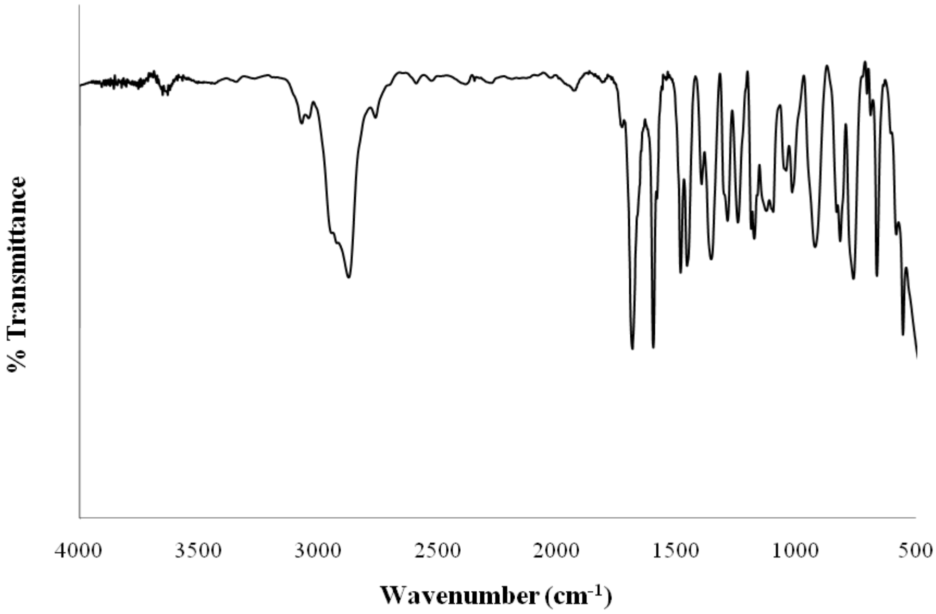

Figure A-5 IR spectrum of **2**

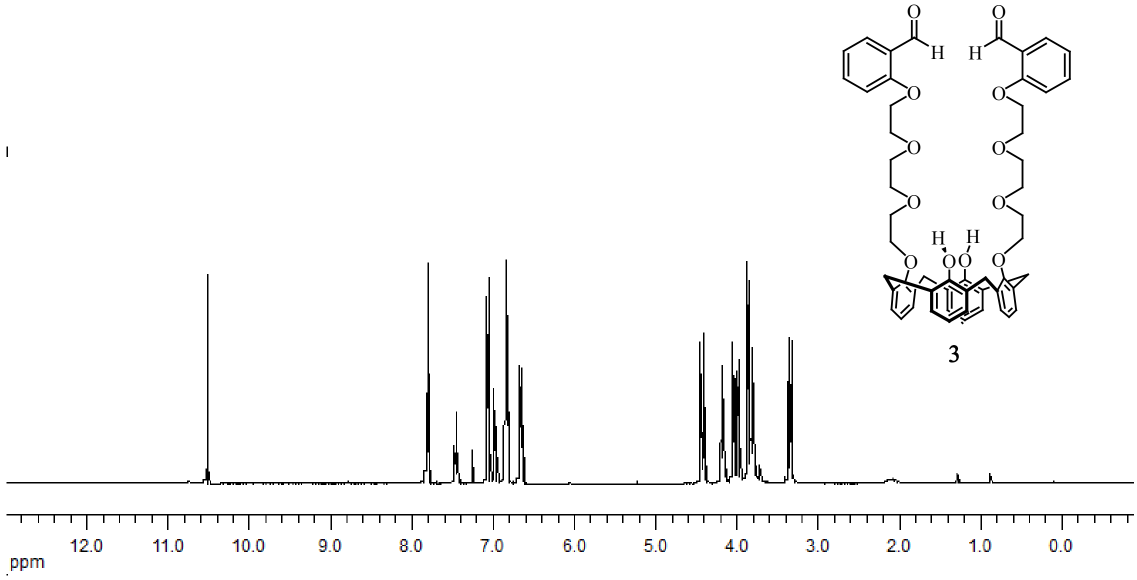

Figure A-6 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **3**

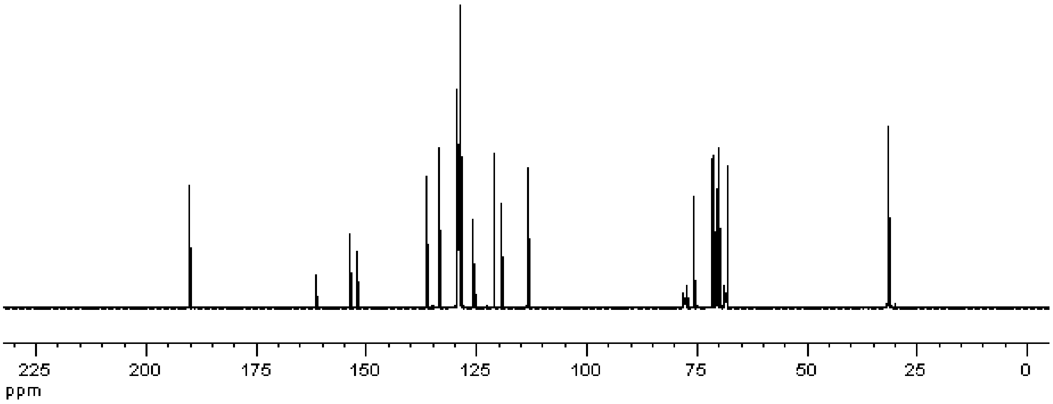

Figure A-7 ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3**

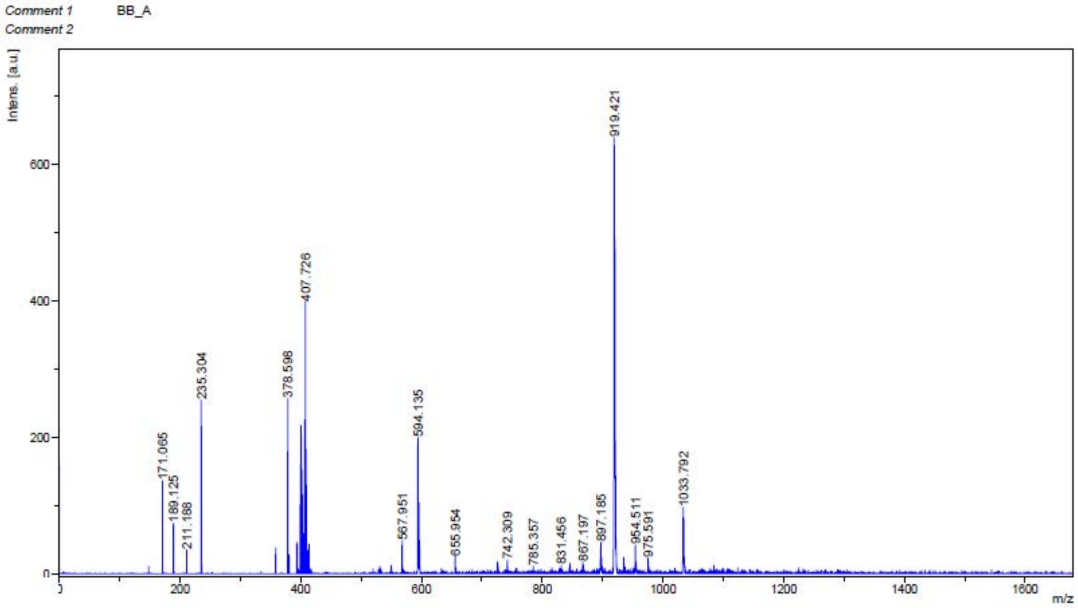

Figure A-8 MALDI-TOF mass spectrum (CCA) of **3**

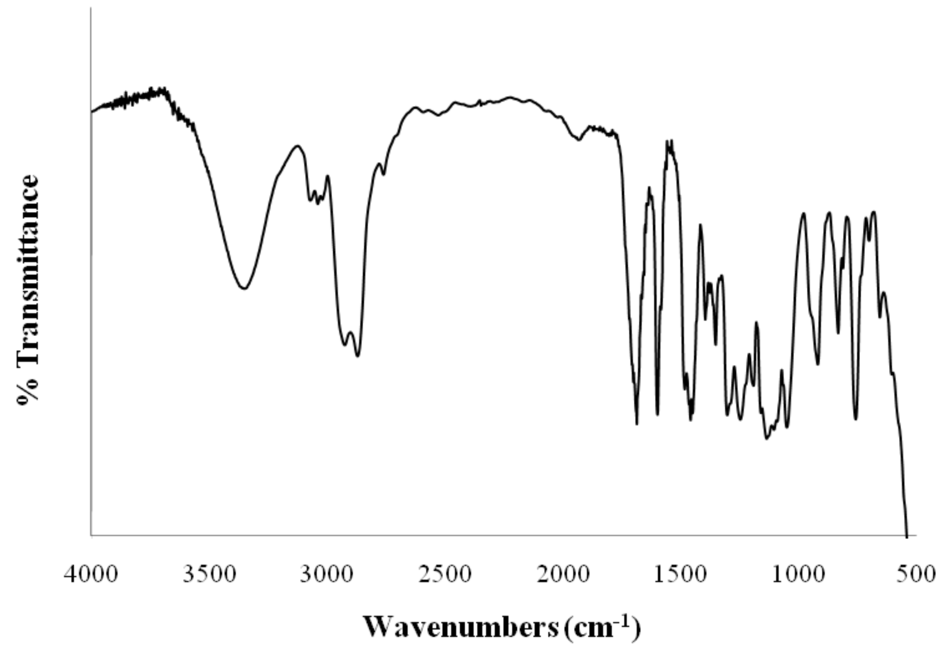

Figure A-9 IR spectrum of **3**

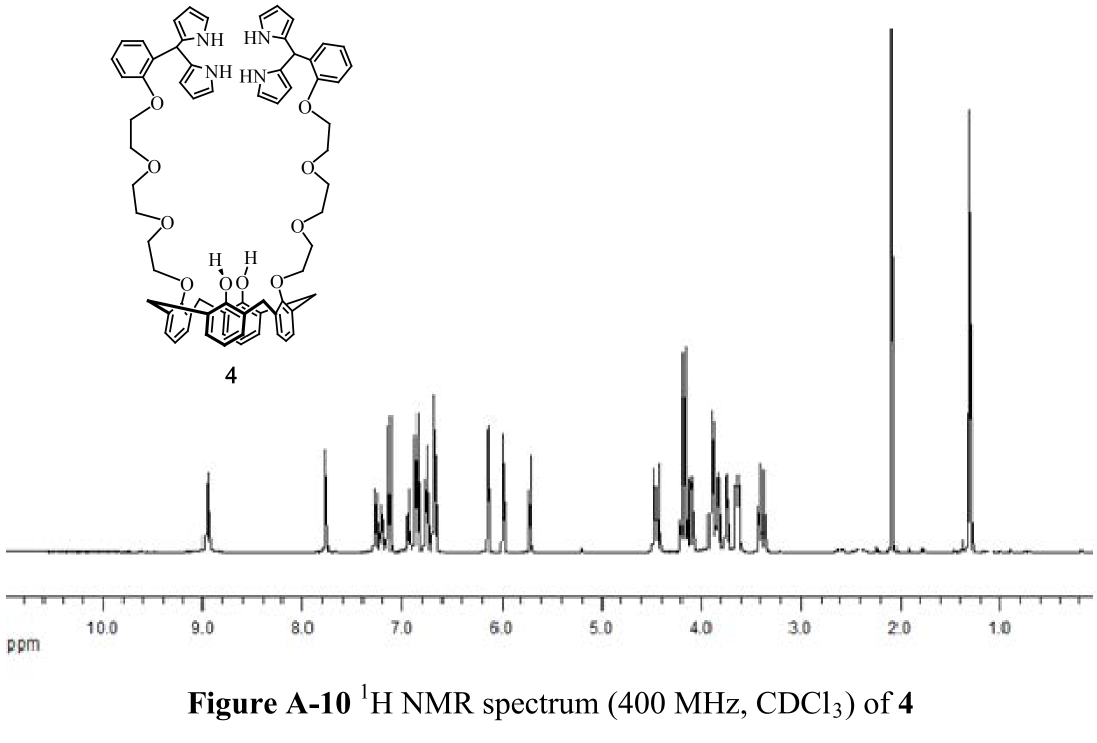

Figure A-10 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**

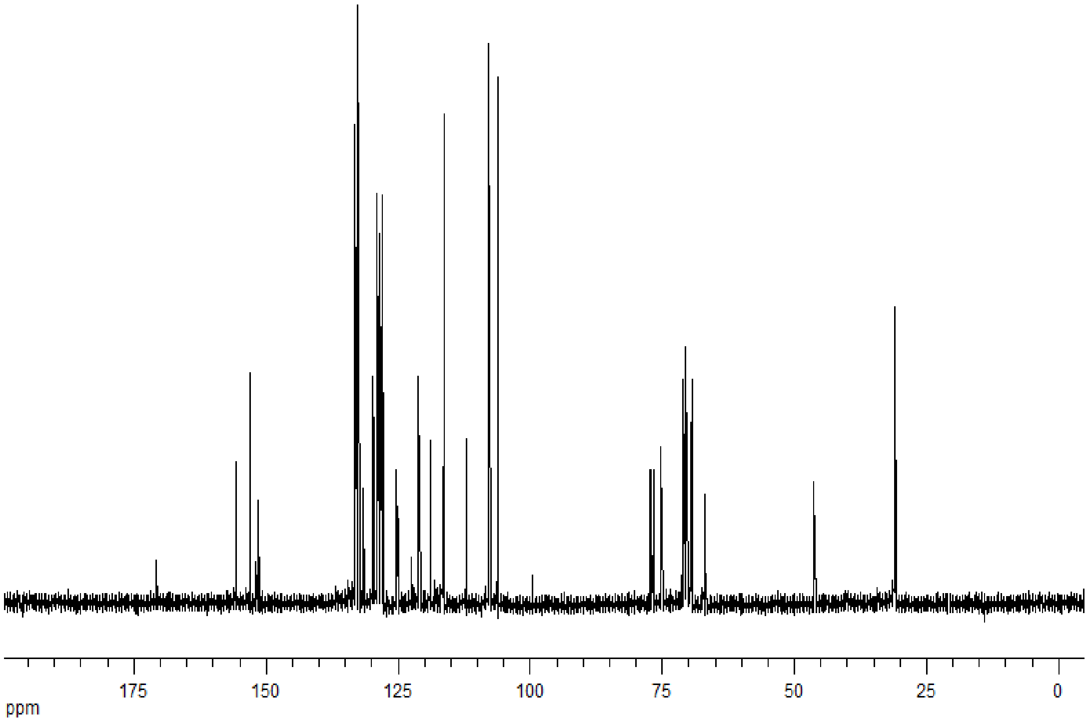

Figure A-11 ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **4**

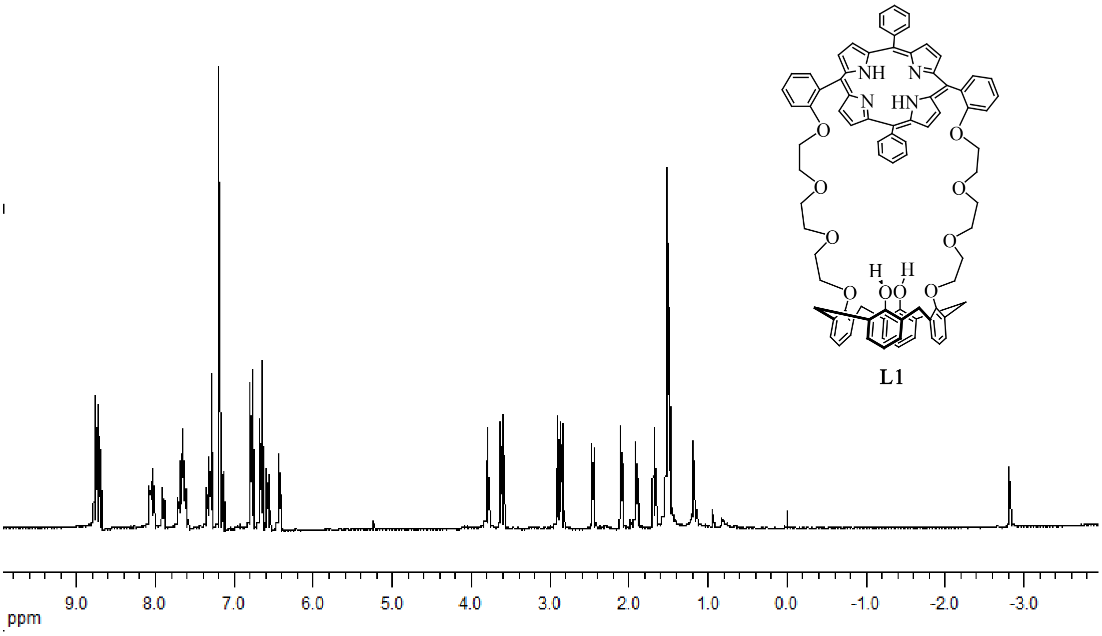

Figure A-12 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **L1**

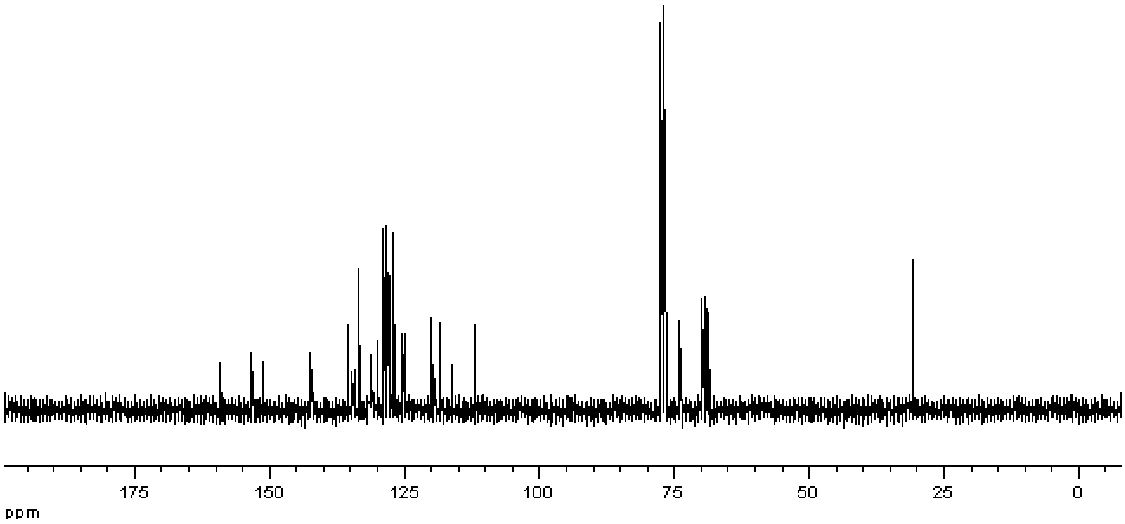

Figure A-13 ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **L1**

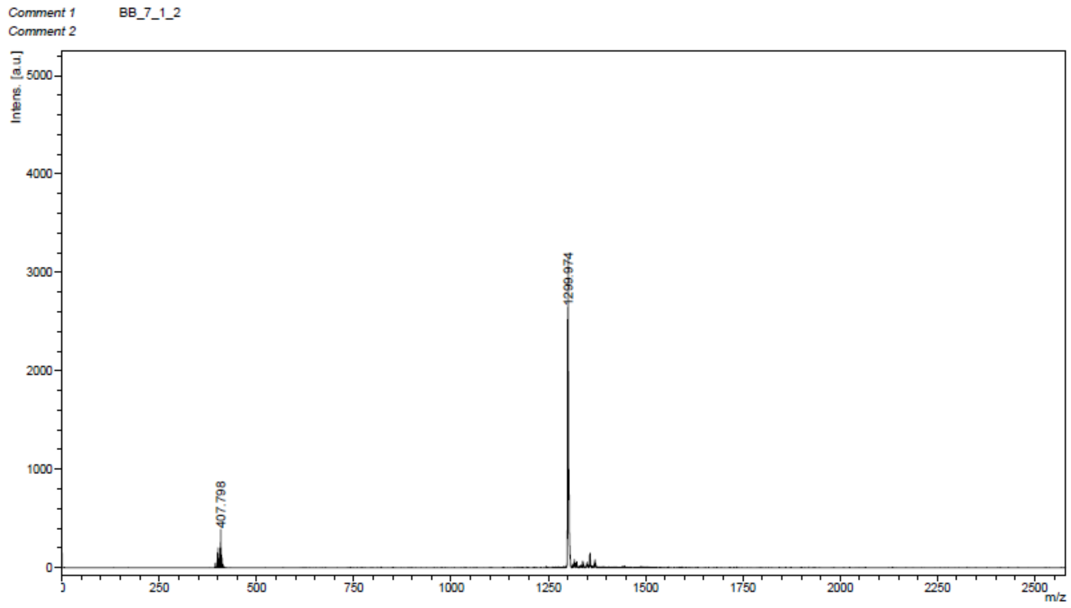

Figure A-14 MALDI-TOF mass spectrum (CCA) of **L1**

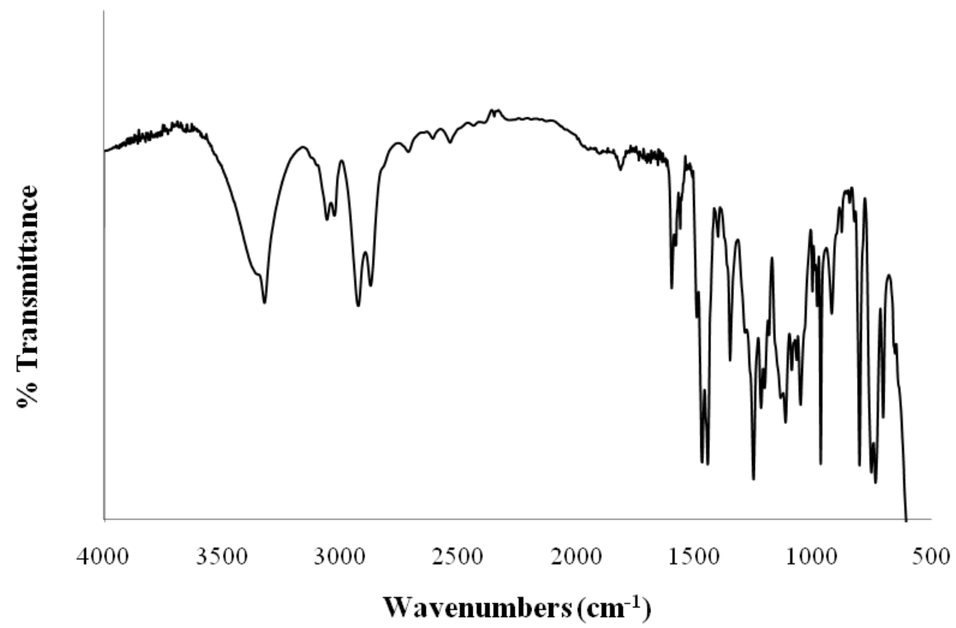

Figure A-15 IR spectrum of **L1**

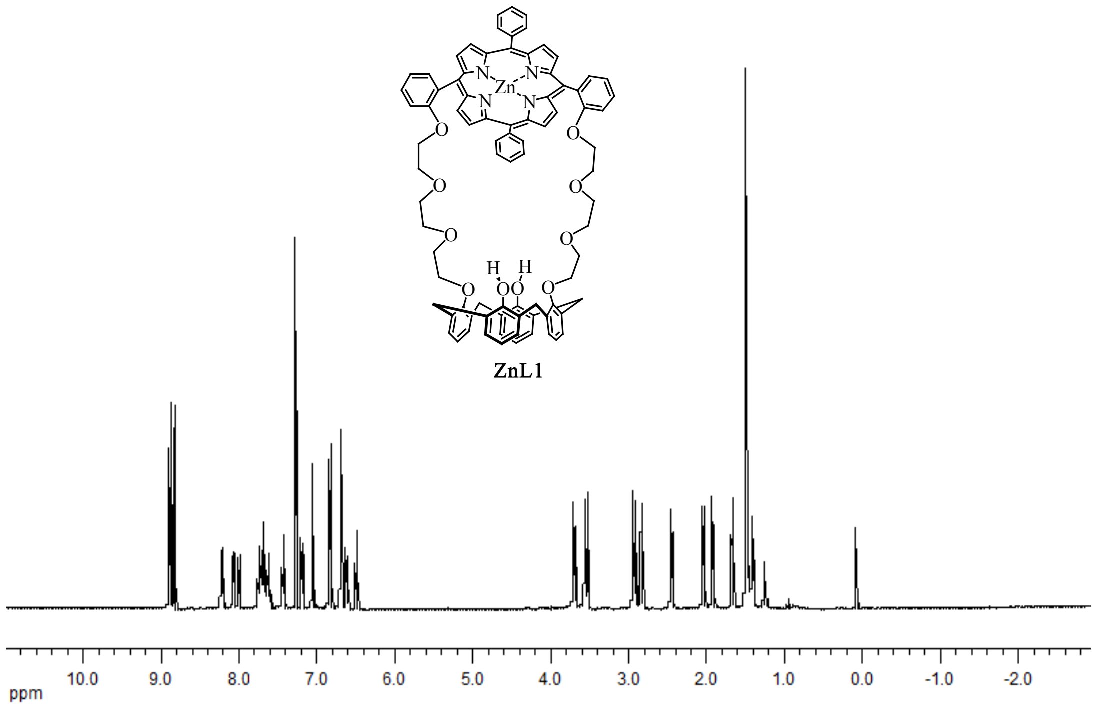

Figure A-16 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **ZnL1**

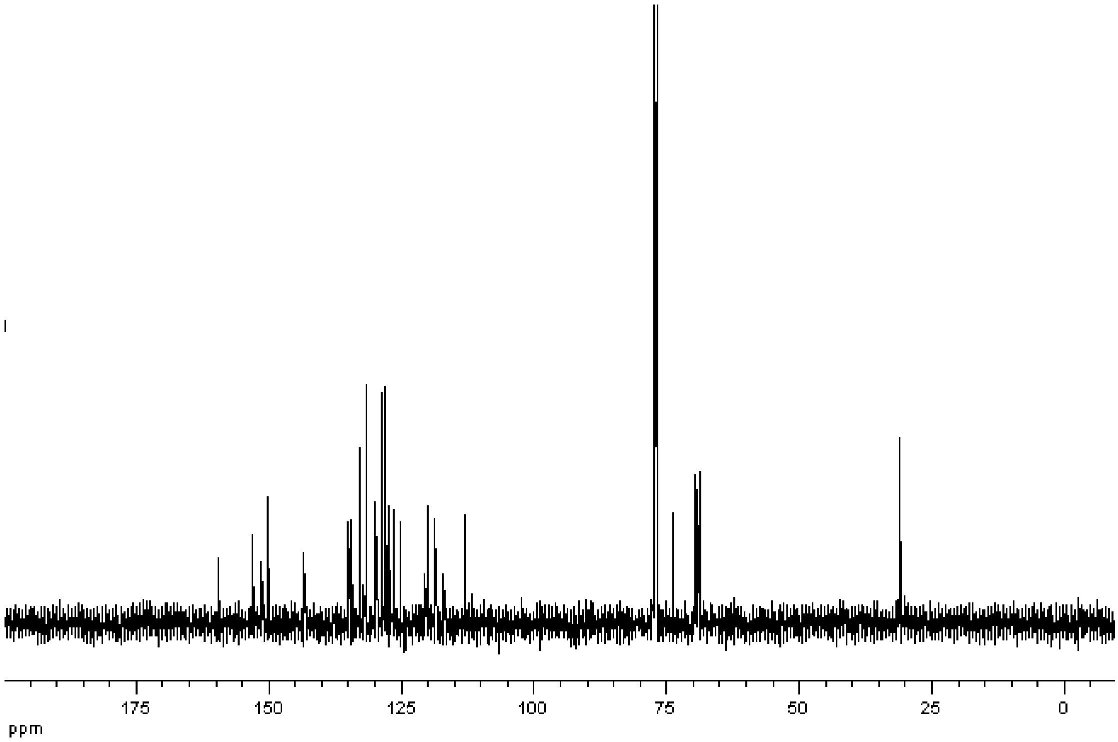

Figure A-17 ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **ZnL1**

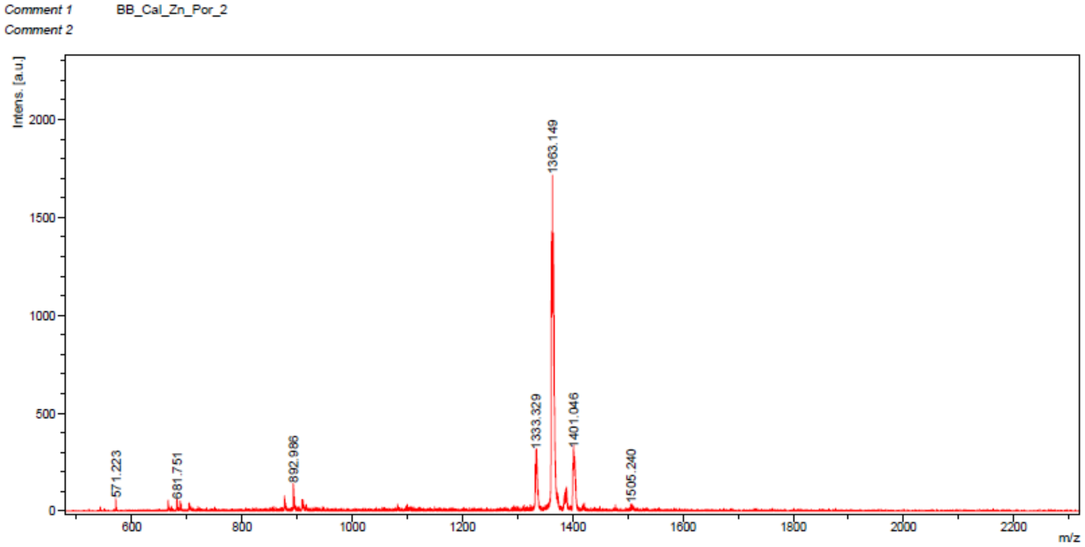

Figure A-18 MALDI-TOF mass spectrum (CCA) of **ZnL1**

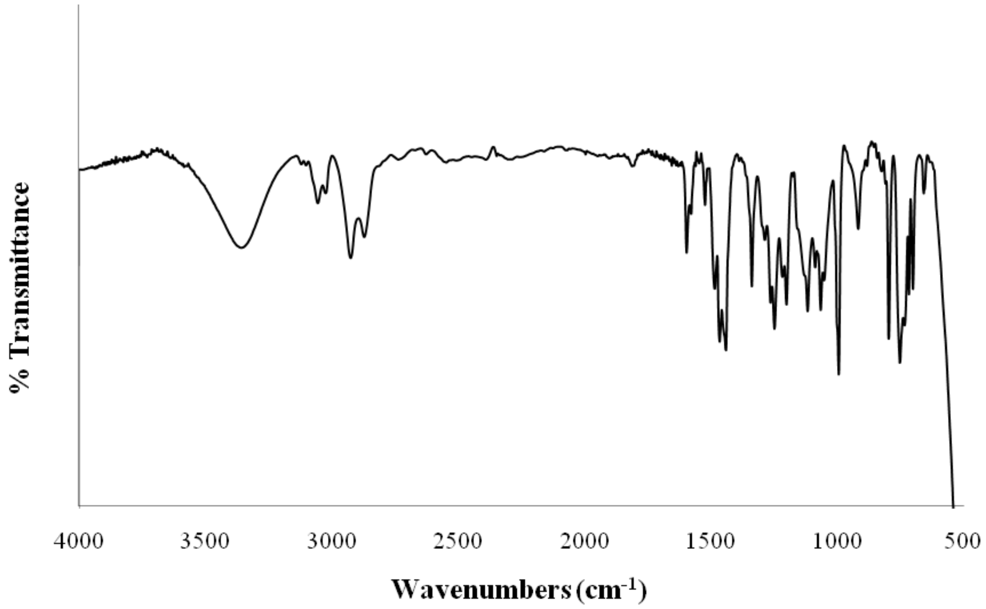

Figure A-19 IR spectrum of **ZnL1**

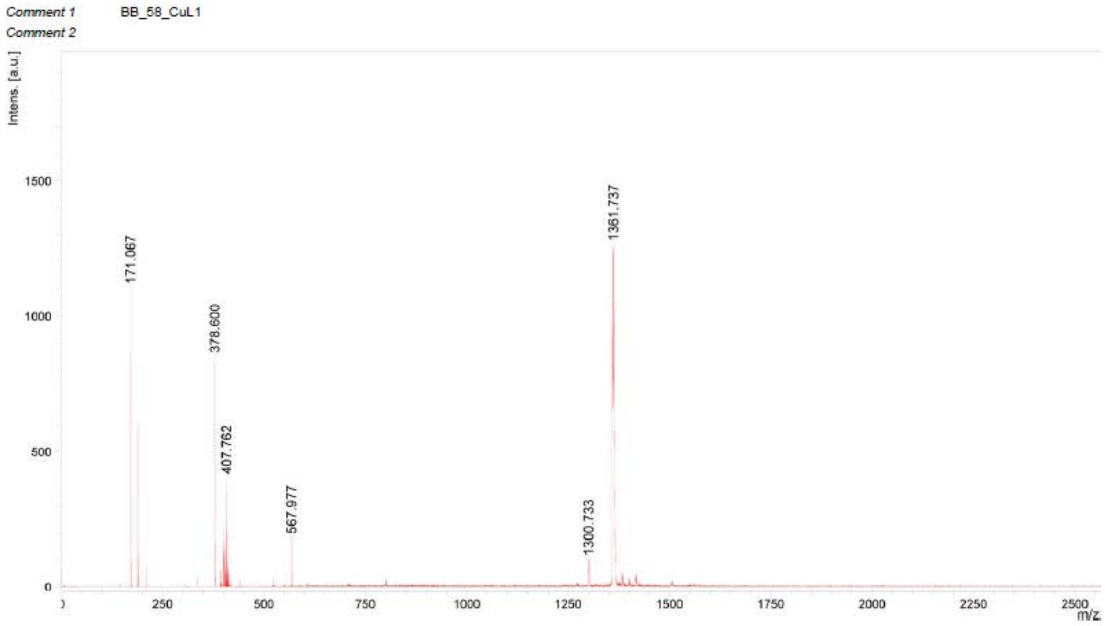

Figure A-20 MALDI-TOF mass spectrum (CCA) of **CuL1**

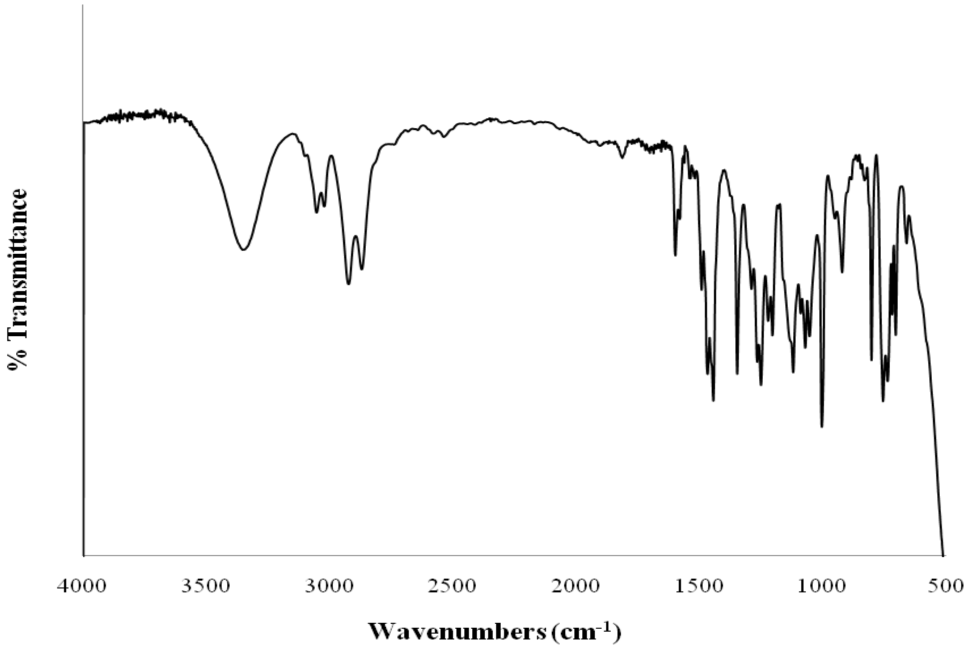

Figure A-21 IR spectrum of **CuL1**

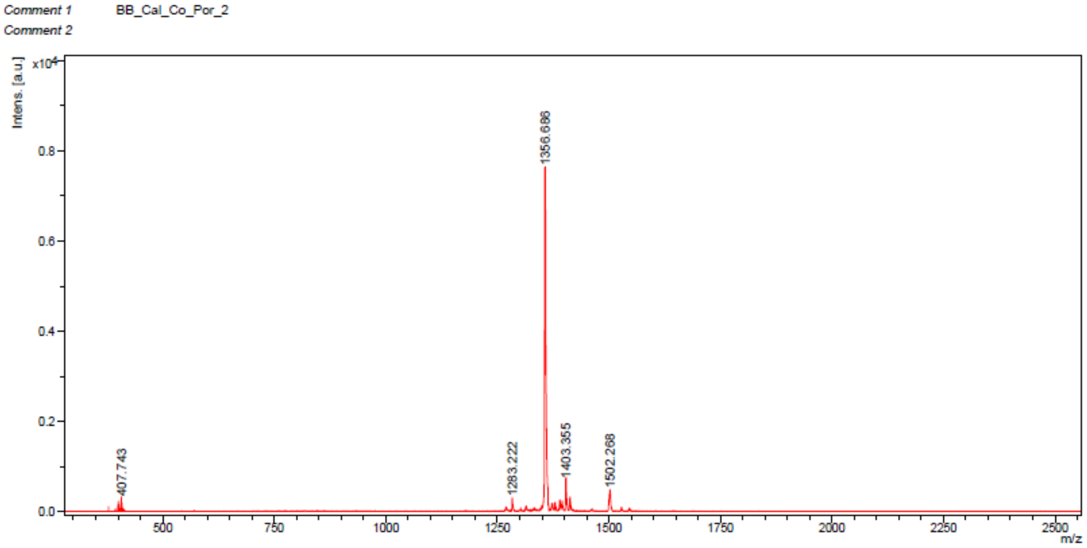

Figure A-22 MALDI-TOF mass spectrum (CCA) of **CoL1**

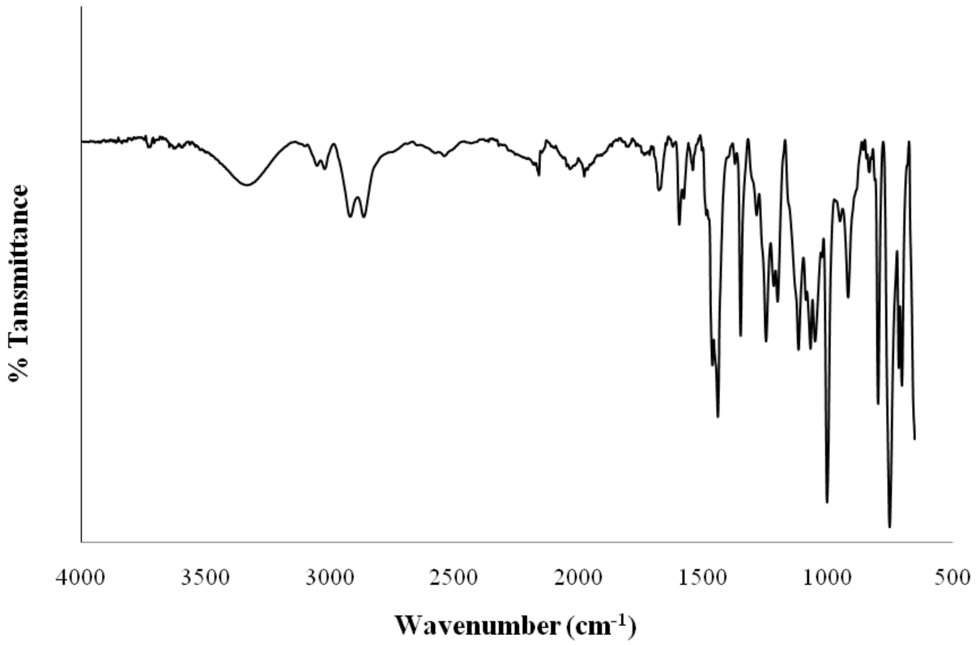

Figure A-23 IR spectrum of **CoL1**

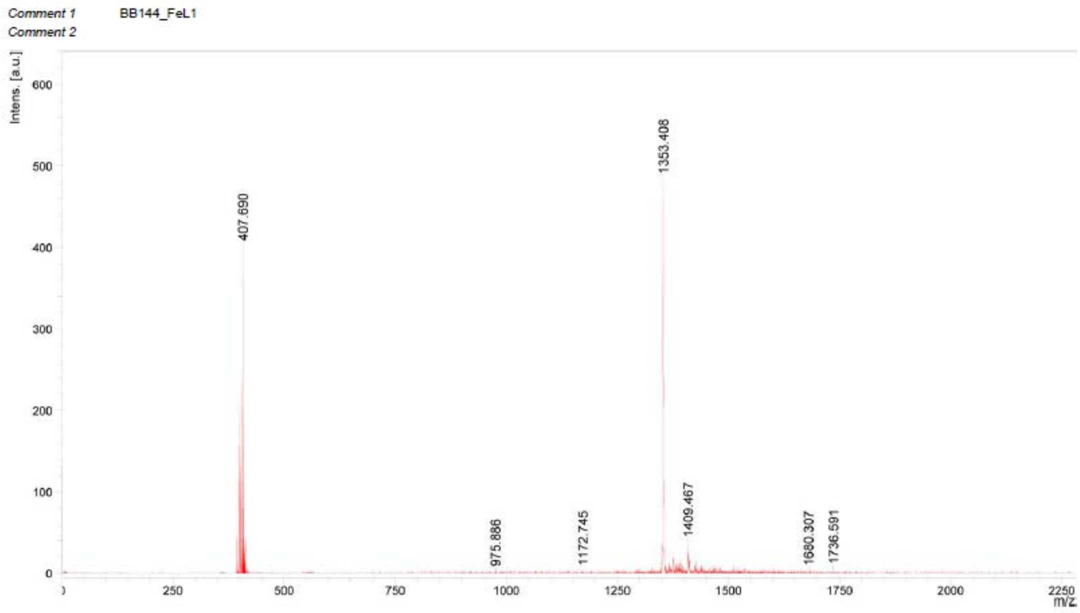

Figure A-24 MALDI-TOF mass spectrum (CCA) of **FeL1**

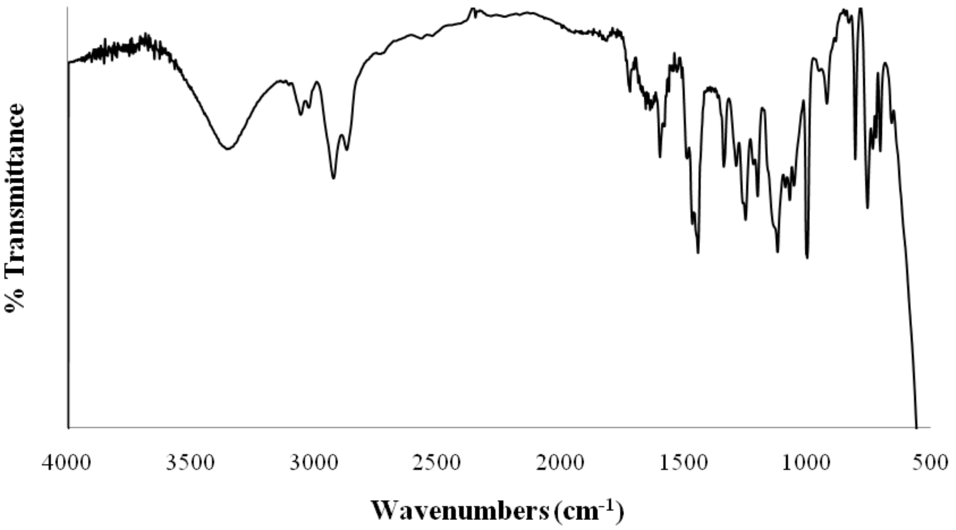

Figure A-25 IR spectrum of **FeL1**

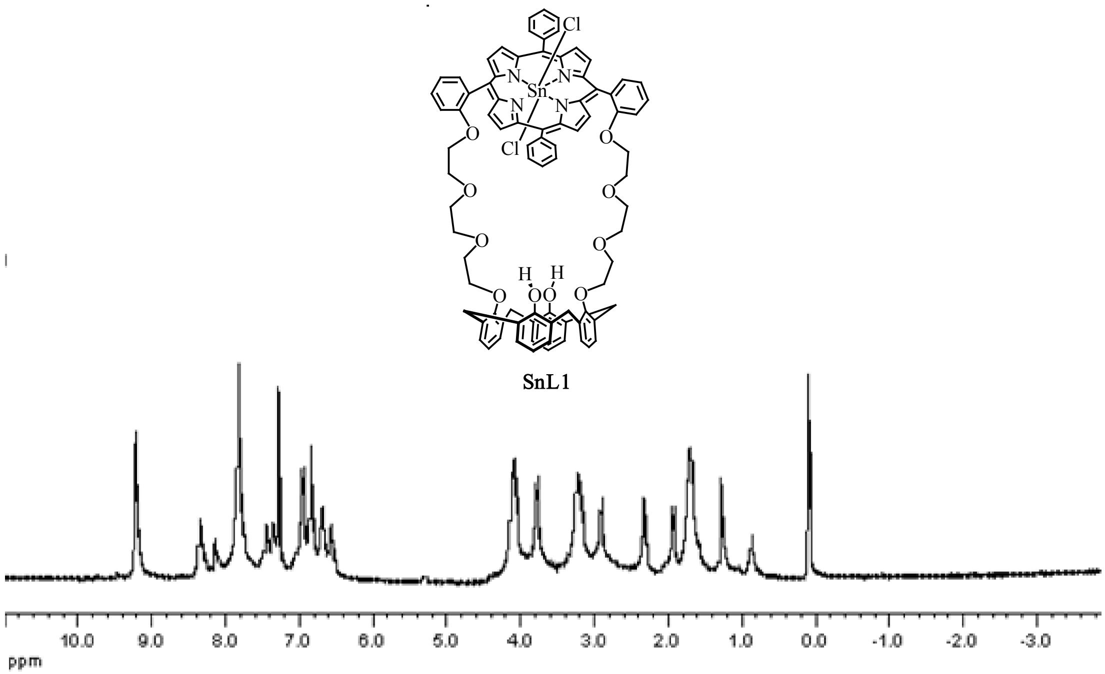

Figure A-26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **SnL1**

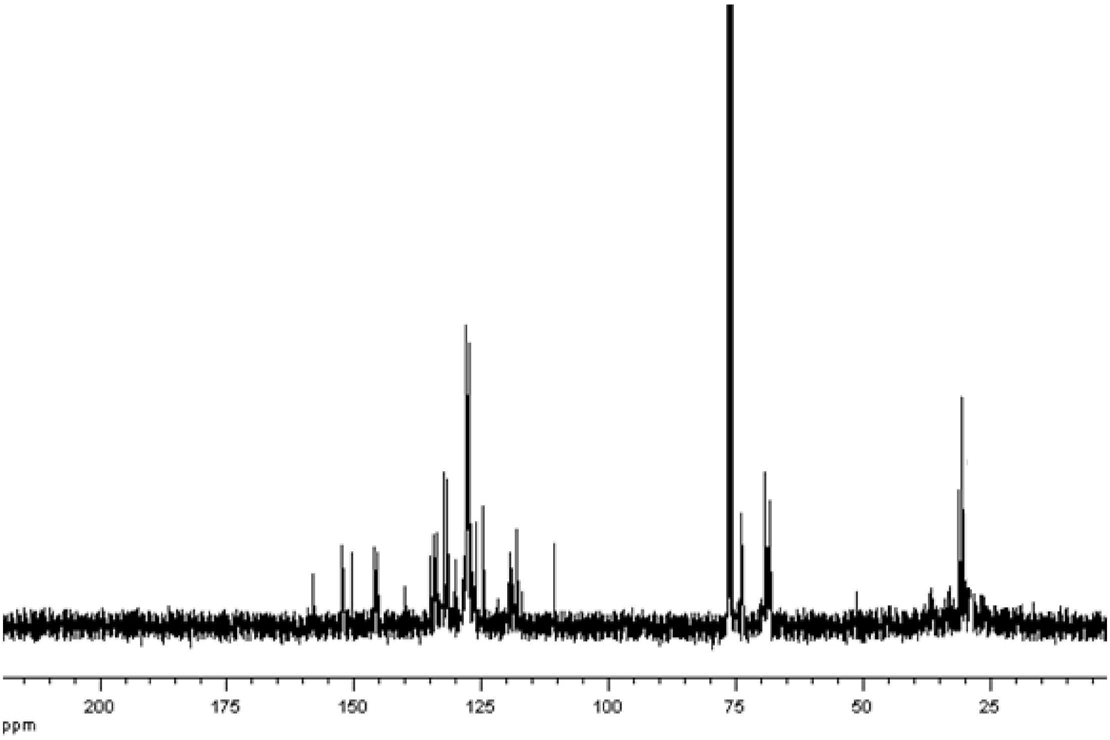

Figure A-27 ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **SnL1**

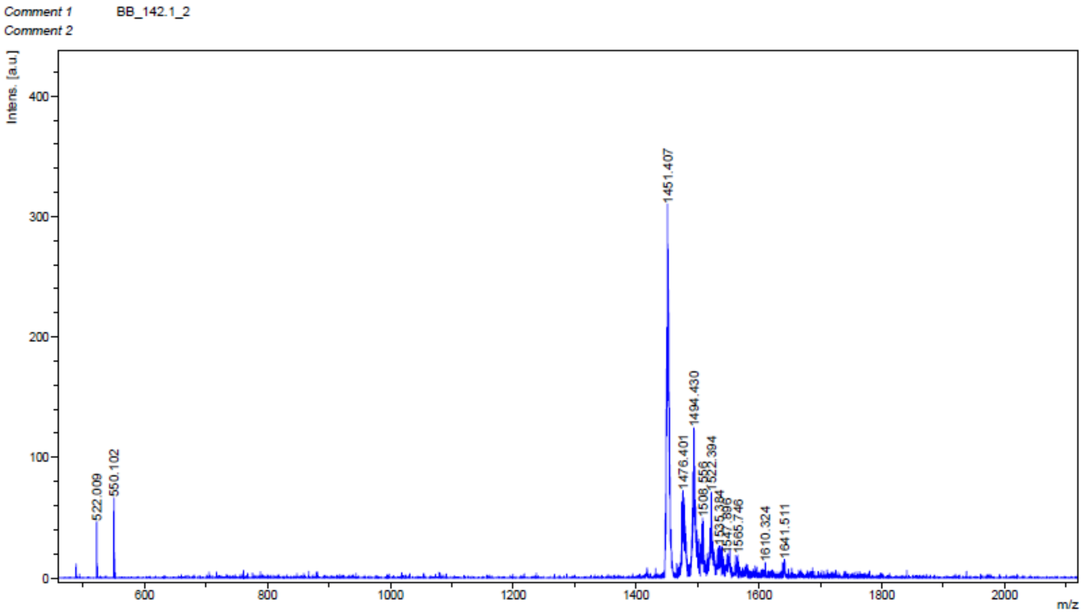

Figure A-28 MALDI-TOF mass spectrum (CCA) of **SnL1**

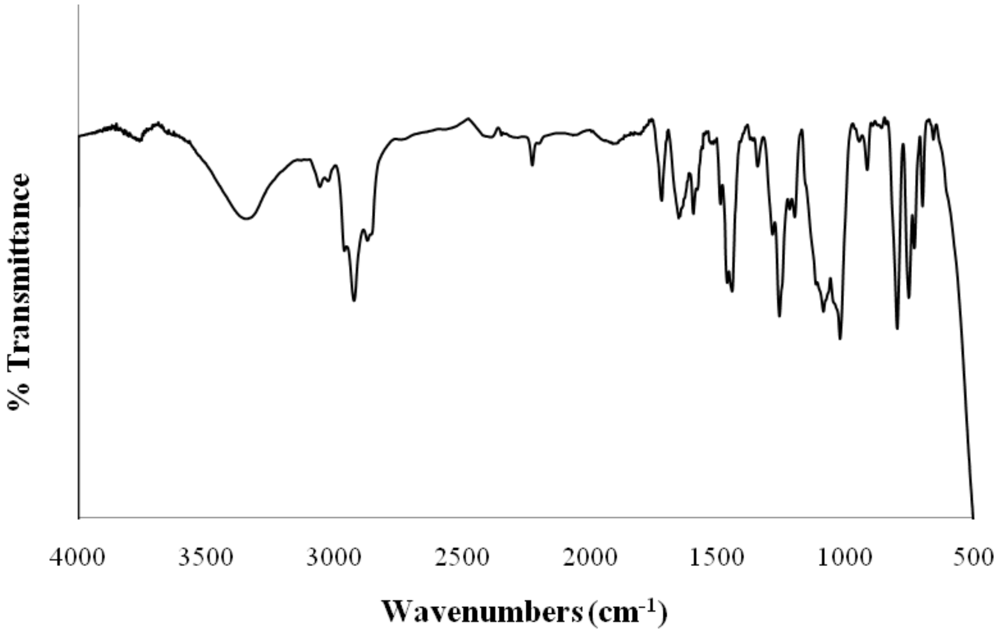

Figure A-29 IR spectrum of **SnL1**

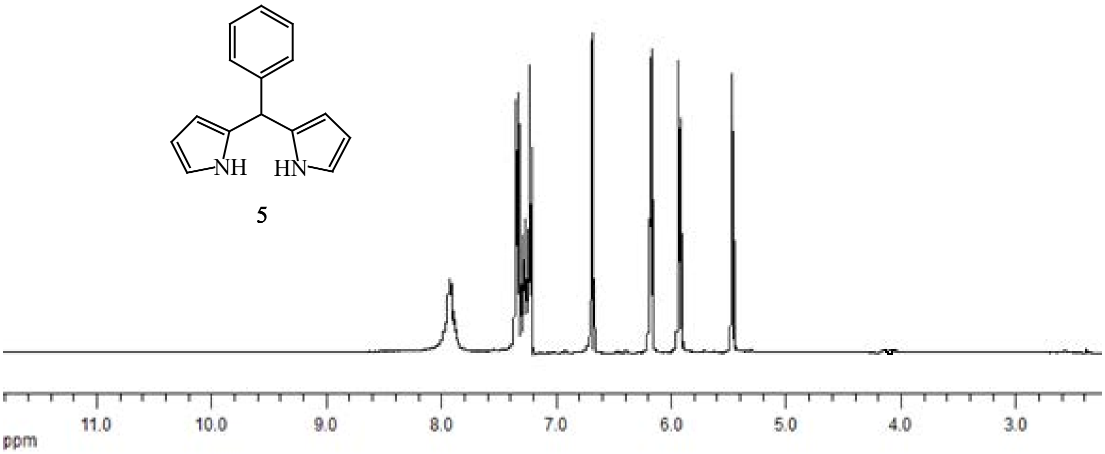

Figure A-30 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**

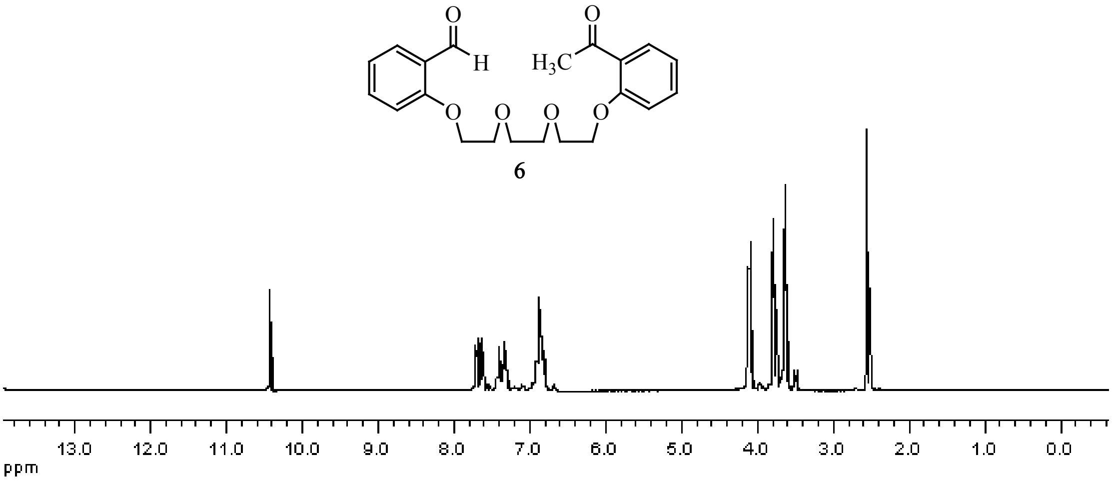

Figure A-31 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**

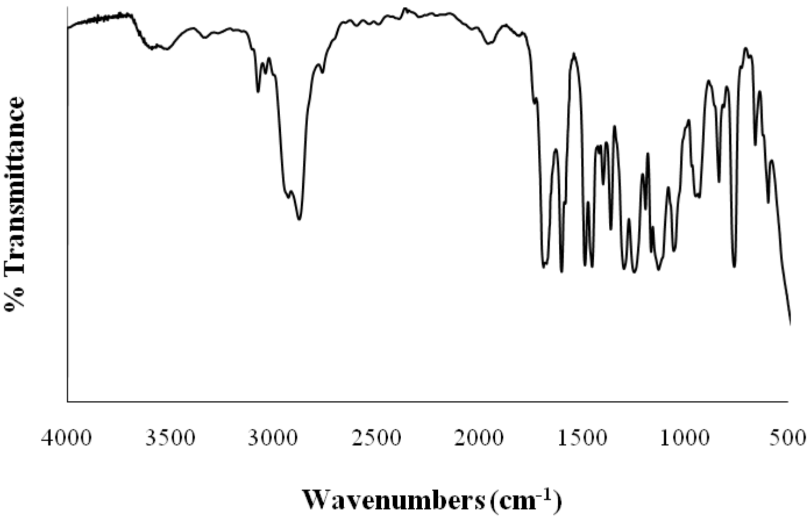

Figure A-32 IR spectrum of **6**

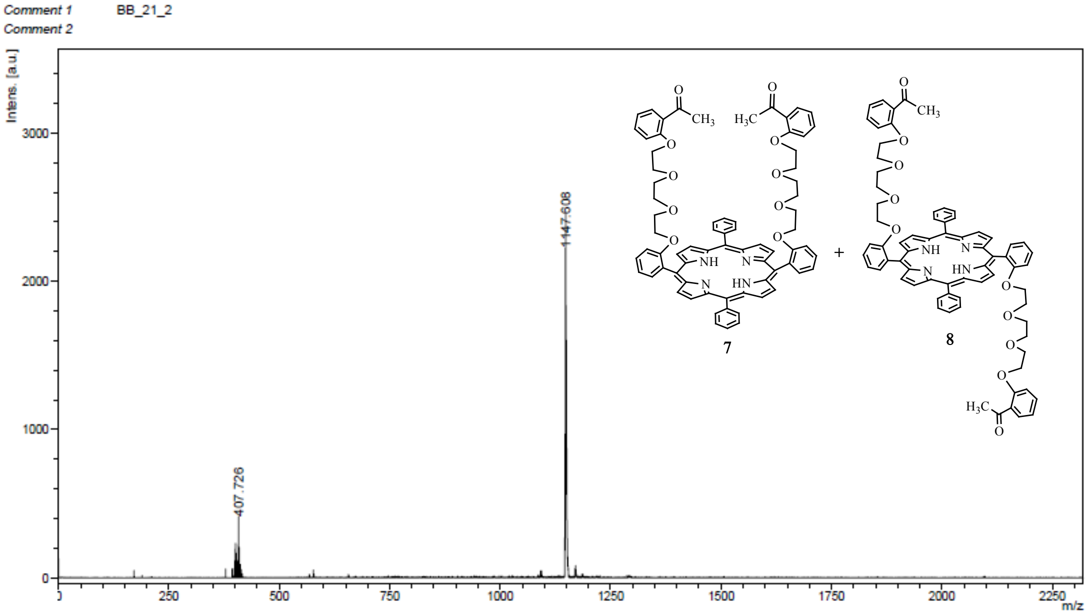

Figure A-33 MALDI-TOF mass spectrum (CCA) of **7** and **8**

APPENDIX B

Table 1. Crystal data and structure refinement for cuper(II) porphyrin-calix[4]arene (CuL1)

Identification code	s543414_01_01
Empirical formula	$C_{88}H_{78}CuN_4O_{12}$
Formula weight	1447.08
Temperature	296(2) K
Wavelength	0.71073 A
Unit cell dimensions	a = 22.437(5) A alpha = 90 deg. b = 13.900(2) A beta = 112.306(4) deg. c = 25.367(6) A gamma = 90 deg.
Volume	7319(3) $Å^3$
Z, Calculated density	4, 1.313 Mg/m^3
Absorption coefficient	0.367 mm^{-1}
F(000)	3036
Theta range for data collection	1.74 to 25.08 deg.
Limiting indices	-26<=h<=26, -16<=k<=9, -30<=l<=30
Reflections collected / unique	41802 / 12899 [R(int) = 0.1826]
Completeness to theta = 25.08	99.2 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12899 / 0 / 944
Goodness-of-fit on F^2	0.801
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1315
R indices (all data)	R1 = 0.1806, wR2 = 0.1640
Extinction coefficient	0.00099(15)

Largest diff. peak and hole	0.655 and -0.593 e.A^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cuper(II) porphyrin-calix[4]arene (CuL1) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	5611(1)	-970(1)	7579(1)	23(1)
O(1)	6825(2)	2080(3)	7427(2)	33(1)
O(2)	6171(2)	4452(3)	7153(2)	54(1)
O(3)	5381(2)	5902(3)	7428(2)	57(1)
O(4)	4801(2)	5176(3)	8194(2)	32(1)
O(5)	5949(2)	4218(3)	8719(2)	28(1)
O(6)	4568(2)	3097(3)	8353(2)	29(1)
O(7)	5666(2)	2136(2)	8559(2)	22(1)
O(8)	4891(2)	1136(3)	7476(2)	27(1)
O(9)	3411(2)	1441(3)	6802(2)	34(1)
O(10)	3536(2)	-23(3)	7738(2)	28(1)
N(1)	4720(2)	-1449(3)	7153(2)	20(1)
N(2)	5510(2)	-1169(3)	8313(2)	19(1)
N(3)	6503(2)	-505(3)	7997(2)	18(1)
N(4)	5717(2)	-741(3)	6851(2)	21(1)
C(1)	4433(3)	-1625(4)	6583(2)	22(1)
C(2)	3782(3)	-1957(4)	6454(2)	25(1)
C(3)	3671(3)	-1928(4)	6936(2)	24(1)
C(4)	4258(3)	-1606(4)	7380(2)	23(1)
C(5)	4345(3)	-1526(4)	7956(2)	21(1)
C(6)	4949(3)	-1369(4)	8395(2)	21(1)
C(7)	5975(3)	-1111(3)	8852(2)	18(1)
C(8)	5699(3)	-1288(3)	9270(2)	21(1)

C(9)	5064(3)	-1441(4)	8988(2)	22(1)
C(10)	6625(3)	-851(4)	8986(2)	20(1)
C(11)	7068(3)	-819(4)	9590(2)	21(1)
C(12)	6980(3)	-177(4)	9971(2)	25(1)
C(13)	7432(3)	-105(4)	10526(2)	34(2)
C(14)	7978(3)	-656(4)	10700(2)	33(2)
C(15)	8070(3)	-1289(4)	10323(3)	32(2)
C(16)	7624(3)	-1378(4)	9777(2)	28(2)
C(17)	6850(3)	-559(4)	8575(2)	21(1)
C(18)	6887(3)	-57(4)	7763(2)	20(1)
C(19)	7500(3)	177(4)	8210(2)	25(2)
C(20)	7474(3)	-135(4)	8702(2)	23(1)
C(21)	6738(3)	150(4)	7199(2)	21(1)
C(22)	6199(3)	-204(4)	6770(2)	25(2)
C(23)	5291(3)	-982(4)	6311(2)	29(2)
C(24)	5517(3)	-596(5)	5898(3)	39(2)
C(25)	6050(3)	-97(4)	6174(2)	35(2)
C(26)	4708(3)	-1456(4)	6188(2)	25(2)
C(27)	4340(3)	-1704(5)	5575(3)	33(2)
C(28)	3775(3)	-1229(4)	5265(3)	38(2)
C(29)	3437(3)	-1453(5)	4693(3)	52(2)
C(30)	3676(4)	-2157(6)	4437(3)	55(2)
C(31)	4239(4)	-2647(6)	4744(3)	55(2)
C(32)	4566(3)	-2414(5)	5318(3)	45(2)
C(33)	7191(3)	777(4)	7044(2)	22(1)
C(34)	7588(3)	411(4)	6786(2)	26(2)
C(35)	8016(3)	994(4)	6659(2)	26(1)
C(36)	8044(3)	1943(4)	6782(2)	27(2)
C(37)	7650(3)	2345(4)	7038(2)	28(2)
C(38)	7226(3)	1768(4)	7163(2)	26(2)
C(39)	6772(3)	3081(4)	7516(3)	35(2)
C(40)	6273(3)	3541(4)	6990(3)	49(2)

C(41)	5656(3)	4958(5)	6724(3)	57(2)
C(42)	5600(3)	5941(5)	6957(3)	56(2)
C(43)	4726(3)	5665(5)	7264(3)	53(2)
C(44)	4543(3)	5901(5)	7757(2)	41(2)
C(45)	4703(3)	5418(4)	8698(3)	30(2)
C(46)	5167(3)	5959(4)	9100(3)	29(2)
C(47)	5804(3)	6206(4)	9044(3)	30(2)
C(48)	6340(3)	5531(4)	9392(3)	29(2)
C(49)	6371(3)	4585(4)	9224(3)	23(1)
C(50)	6854(3)	3953(4)	9558(2)	24(1)
C(51)	6856(3)	2914(4)	9377(2)	26(2)
C(52)	6388(3)	2305(4)	9532(2)	20(1)
C(53)	6511(3)	2126(4)	10107(2)	23(1)
C(54)	6082(3)	1600(4)	10264(2)	23(1)
C(55)	5519(3)	1264(4)	9854(2)	23(1)
C(56)	5370(3)	1444(4)	9283(2)	20(1)
C(57)	4722(3)	1148(4)	8848(2)	23(1)
C(58)	4201(3)	1866(4)	8827(2)	22(1)
C(59)	3742(3)	1606(4)	9060(2)	25(1)
C(60)	3253(3)	2234(4)	9035(2)	31(2)
C(61)	3227(3)	3129(4)	8805(2)	30(2)
C(62)	3671(3)	3424(4)	8579(2)	26(2)
C(63)	3656(3)	4434(4)	8348(3)	34(2)
C(64)	4142(3)	5095(4)	8762(3)	30(2)
C(65)	4064(3)	5379(4)	9260(3)	32(2)
C(66)	4504(3)	5942(4)	9655(3)	35(2)
C(67)	5068(3)	6223(4)	9585(3)	32(2)
C(68)	4157(3)	2783(4)	8604(2)	24(1)
C(69)	5825(3)	1933(4)	9136(2)	20(1)
C(70)	5875(3)	1395(4)	8261(2)	25(2)
C(71)	5518(3)	1544(4)	7634(2)	26(2)
C(72)	4542(3)	1221(4)	6878(2)	34(2)

C(73)	3864(3)	793(4)	6720(2)	32(2)
C(74)	3476(3)	1565(4)	7380(2)	31(2)
C(75)	3140(3)	813(4)	7587(2)	27(2)
C(76)	3343(3)	-802(4)	7965(2)	25(1)
C(77)	3755(3)	-1587(4)	8092(2)	21(1)
C(78)	3585(3)	-2403(4)	8311(2)	22(1)
C(79)	3025(3)	-2454(4)	8413(2)	27(2)
C(80)	2629(3)	-1663(4)	8293(2)	31(2)
C(81)	2777(3)	-832(4)	8075(2)	26(1)
C(82)	7313(3)	4290(4)	10071(3)	35(2)
C(83)	7289(3)	5228(4)	10239(3)	36(2)
C(84)	6811(3)	5837(4)	9905(3)	35(2)
O(3S)	8448(2)	2079(4)	9694(2)	68(2)
C(1S)	8791(4)	1429(6)	10194(3)	87(3)
O(1SS)	8933(3)	1282(4)	9198(2)	85(2)
C(1SS)	8558(4)	1917(6)	9216(3)	65(2)
C(3SS)	8643(4)	1838(6)	10683(3)	93(3)
C(4SS)	8181(4)	2572(5)	8744(3)	69(2)

Table 3. Bond lengths [A] and angles [deg] for cuper(II) porphyrin-calix[4]arene (CuL1)

Cu(1)-N(4)	1.976(4)
Cu(1)-N(2)	1.978(4)
Cu(1)-N(3)	1.985(4)
Cu(1)-N(1)	1.990(4)
O(1)-C(38)	1.380(6)
O(1)-C(39)	1.422(6)
O(2)-C(40)	1.379(7)
O(2)-C(41)	1.434(7)
O(3)-C(43)	1.406(7)
O(3)-C(42)	1.457(7)
O(4)-C(45)	1.416(6)
O(4)-C(44)	1.446(6)
O(5)-C(49)	1.370(6)
O(6)-C(68)	1.375(6)
O(7)-C(69)	1.398(6)
O(7)-C(70)	1.456(6)
O(8)-C(72)	1.423(6)
O(8)-C(71)	1.427(6)
O(9)-C(74)	1.427(6)
O(9)-C(73)	1.431(6)
O(10)-C(76)	1.371(6)
O(10)-C(75)	1.423(6)
N(1)-C(1)	1.365(6)
N(1)-C(4)	1.380(6)
N(2)-C(7)	1.371(6)
N(2)-C(6)	1.379(6)
N(3)-C(18)	1.367(6)
N(3)-C(17)	1.378(6)

N(4)-C(23)	1.381(7)
N(4)-C(22)	1.394(6)
C(1)-C(26)	1.380(7)
C(1)-C(2)	1.446(7)
C(2)-C(3)	1.338(7)
C(2)-H(2)	0.9300
C(3)-C(4)	1.443(7)
C(3)-H(3)	0.9300
C(4)-C(5)	1.404(7)
C(5)-C(6)	1.407(7)
C(5)-C(77)	1.491(7)
C(6)-C(9)	1.430(7)
C(7)-C(10)	1.414(7)
C(7)-C(8)	1.437(7)
C(8)-C(9)	1.346(7)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-C(17)	1.380(7)
C(10)-C(11)	1.477(7)
C(11)-C(12)	1.384(7)
C(11)-C(16)	1.392(7)
C(12)-C(13)	1.391(7)
C(12)-H(12)	0.9300
C(13)-C(14)	1.369(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.371(8)
C(14)-H(14)	0.9300
C(15)-C(16)	1.373(7)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(20)	1.438(7)
C(18)-C(21)	1.372(7)

C(18)-C(19)	1.449(7)
C(19)-C(20)	1.343(7)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(22)	1.373(7)
C(21)-C(33)	1.499(7)
C(22)-C(25)	1.427(7)
C(23)-C(26)	1.389(7)
C(23)-C(24)	1.431(7)
C(24)-C(25)	1.328(7)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
C(26)-C(27)	1.498(8)
C(27)-C(28)	1.381(8)
C(27)-C(32)	1.381(8)
C(28)-C(29)	1.393(8)
C(28)-H(28)	0.9300
C(29)-C(30)	1.391(9)
C(29)-H(29)	0.9300
C(30)-C(31)	1.386(9)
C(30)-H(30)	0.9300
C(31)-C(32)	1.397(8)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
C(33)-C(34)	1.387(7)
C(33)-C(38)	1.406(7)
C(34)-C(35)	1.385(7)
C(34)-H(34)	0.9300
C(35)-C(36)	1.351(7)
C(35)-H(35)	0.9300
C(36)-C(37)	1.397(7)
C(36)-H(36)	0.9300

C(37)-C(38)	1.370(7)
C(37)-H(37)	0.9300
C(39)-C(40)	1.520(8)
C(39)-H(39A)	0.9700
C(39)-H(39B)	0.9700
C(40)-H(40A)	0.9700
C(40)-H(40B)	0.9700
C(41)-C(42)	1.512(9)
C(41)-H(41A)	0.9700
C(41)-H(41B)	0.9700
C(42)-H(42A)	0.9700
C(42)-H(42B)	0.9700
C(43)-C(44)	1.496(8)
C(43)-H(43A)	0.9700
C(43)-H(43B)	0.9700
C(44)-H(44A)	0.9700
C(44)-H(44B)	0.9700
C(45)-C(46)	1.373(8)
C(45)-C(64)	1.402(8)
C(46)-C(67)	1.380(7)
C(46)-C(47)	1.526(7)
C(47)-C(48)	1.517(8)
C(47)-H(47A)	0.9700
C(47)-H(47B)	0.9700
C(48)-C(49)	1.391(7)
C(48)-C(84)	1.395(8)
C(49)-C(50)	1.402(7)
C(50)-C(82)	1.398(8)
C(50)-C(51)	1.516(7)
C(51)-C(52)	1.513(7)
C(51)-H(51A)	0.9700
C(51)-H(51B)	0.9700

C(52)-C(69)	1.381(7)
C(52)-C(53)	1.400(7)
C(53)-C(54)	1.382(7)
C(53)-H(53)	0.9300
C(54)-C(55)	1.377(7)
C(54)-H(54)	0.9300
C(55)-C(56)	1.380(7)
C(55)-H(55)	0.9300
C(56)-C(69)	1.391(7)
C(56)-C(57)	1.511(7)
C(57)-C(58)	1.523(7)
C(57)-H(57A)	0.9700
C(57)-H(57B)	0.9700
C(58)-C(68)	1.383(7)
C(58)-C(59)	1.413(7)
C(59)-C(60)	1.385(7)
C(59)-H(59)	0.9300
C(60)-C(61)	1.365(7)
C(60)-H(60)	0.9300
C(61)-C(62)	1.386(7)
C(61)-H(61)	0.9300
C(62)-C(68)	1.391(7)
C(62)-C(63)	1.516(7)
C(63)-C(64)	1.505(8)
C(63)-H(63A)	0.9700
C(63)-H(63B)	0.9700
C(64)-C(65)	1.396(8)
C(65)-C(66)	1.357(8)
C(65)-H(65)	0.9300
C(66)-C(67)	1.398(7)
C(66)-H(66)	0.9300
C(67)-H(67)	0.9300

C(70)-C(71)	1.499(7)
C(70)-H(70A)	0.9700
C(70)-H(70B)	0.9700
C(71)-H(71A)	0.9700
C(71)-H(71B)	0.9700
C(72)-C(73)	1.539(7)
C(72)-H(72A)	0.9700
C(72)-H(72B)	0.9700
C(73)-H(73A)	0.9700
C(73)-H(73B)	0.9700
C(74)-C(75)	1.497(7)
C(74)-H(74A)	0.9700
C(74)-H(74B)	0.9700
C(75)-H(75A)	0.9700
C(75)-H(75B)	0.9700
C(76)-C(77)	1.387(7)
C(76)-C(81)	1.400(7)
C(77)-C(78)	1.378(7)
C(78)-C(79)	1.380(7)
C(78)-H(78)	0.9300
C(79)-C(80)	1.374(7)
C(79)-H(79)	0.9300
C(80)-C(81)	1.375(7)
C(80)-H(80)	0.9300
C(81)-H(81)	0.9300
C(82)-C(83)	1.379(8)
C(82)-H(82)	0.9300
C(83)-C(84)	1.378(8)
C(83)-H(83)	0.9300
C(84)-H(84)	0.9300
O(3S)-C(1SS)	1.346(8)
O(3S)-C(1S)	1.509(8)

C(1S)-C(3SS)	1.511(10)
C(1S)-H(1S1)	0.9700
C(1S)-H(1S2)	0.9700
O(1SS)-C(1SS)	1.232(9)
C(1SS)-C(4SS)	1.487(10)
C(3SS)-H(3S1)	0.9600
C(3SS)-H(3S2)	0.9600
C(3SS)-H(3S3)	0.9600
C(4SS)-H(4S1)	0.9600
C(4SS)-H(4S2)	0.9600
C(4SS)-H(4S3)	0.9600

N(4)-Cu(1)-N(2)	178.69(18)
N(4)-Cu(1)-N(3)	89.48(18)
N(2)-Cu(1)-N(3)	89.76(18)
N(4)-Cu(1)-N(1)	89.93(18)
N(2)-Cu(1)-N(1)	90.85(18)
N(3)-Cu(1)-N(1)	179.13(18)
C(38)-O(1)-C(39)	119.6(4)
C(40)-O(2)-C(41)	113.6(5)
C(43)-O(3)-C(42)	113.9(5)
C(45)-O(4)-C(44)	111.9(4)
C(69)-O(7)-C(70)	113.3(4)
C(72)-O(8)-C(71)	110.5(4)
C(74)-O(9)-C(73)	115.2(4)
C(76)-O(10)-C(75)	119.6(4)
C(1)-N(1)-C(4)	106.7(4)
C(1)-N(1)-Cu(1)	127.5(4)
C(4)-N(1)-Cu(1)	125.7(4)
C(7)-N(2)-C(6)	104.8(4)
C(7)-N(2)-Cu(1)	127.9(3)
C(6)-N(2)-Cu(1)	127.3(4)

C(18)-N(3)-C(17)	107.0(4)
C(18)-N(3)-Cu(1)	126.3(4)
C(17)-N(3)-Cu(1)	126.7(4)
C(23)-N(4)-C(22)	105.5(4)
C(23)-N(4)-Cu(1)	127.2(4)
C(22)-N(4)-Cu(1)	126.9(4)
N(1)-C(1)-C(26)	125.3(5)
N(1)-C(1)-C(2)	109.1(5)
C(26)-C(1)-C(2)	125.5(5)
C(3)-C(2)-C(1)	107.9(5)
C(3)-C(2)-H(2)	126.1
C(1)-C(2)-H(2)	126.1
C(2)-C(3)-C(4)	106.9(5)
C(2)-C(3)-H(3)	126.6
C(4)-C(3)-H(3)	126.6
N(1)-C(4)-C(5)	126.3(5)
N(1)-C(4)-C(3)	109.4(5)
C(5)-C(4)-C(3)	124.2(5)
C(6)-C(5)-C(4)	123.2(5)
C(6)-C(5)-C(77)	120.0(5)
C(4)-C(5)-C(77)	116.8(5)
N(2)-C(6)-C(5)	125.0(5)
N(2)-C(6)-C(9)	111.2(5)
C(5)-C(6)-C(9)	123.8(5)
N(2)-C(7)-C(10)	125.4(5)
N(2)-C(7)-C(8)	110.3(5)
C(10)-C(7)-C(8)	124.1(5)
C(9)-C(8)-C(7)	107.5(5)
C(9)-C(8)-H(8)	126.3
C(7)-C(8)-H(8)	126.3
C(8)-C(9)-C(6)	106.3(5)
C(8)-C(9)-H(9)	126.9

C(6)-C(9)-H(9)	126.9
C(17)-C(10)-C(7)	122.2(5)
C(17)-C(10)-C(11)	118.7(5)
C(7)-C(10)-C(11)	118.9(5)
C(12)-C(11)-C(16)	118.0(5)
C(12)-C(11)-C(10)	121.7(5)
C(16)-C(11)-C(10)	119.9(5)
C(11)-C(12)-C(13)	120.7(5)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(14)-C(13)-C(12)	120.3(6)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	119.3(6)
C(15)-C(14)-H(14)	120.4
C(13)-C(14)-H(14)	120.4
C(16)-C(15)-C(14)	121.0(6)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	120.6(5)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7
N(3)-C(17)-C(10)	126.9(5)
N(3)-C(17)-C(20)	108.9(5)
C(10)-C(17)-C(20)	123.7(5)
N(3)-C(18)-C(21)	127.1(5)
N(3)-C(18)-C(19)	109.2(5)
C(21)-C(18)-C(19)	123.6(5)
C(20)-C(19)-C(18)	107.0(5)
C(20)-C(19)-H(19)	126.5
C(18)-C(19)-H(19)	126.5
C(19)-C(20)-C(17)	107.8(5)

C(19)-C(20)-H(20)	126.1
C(17)-C(20)-H(20)	126.1
C(18)-C(21)-C(22)	123.0(5)
C(18)-C(21)-C(33)	118.3(5)
C(22)-C(21)-C(33)	118.7(5)
C(21)-C(22)-N(4)	125.0(5)
C(21)-C(22)-C(25)	125.8(5)
N(4)-C(22)-C(25)	109.2(5)
N(4)-C(23)-C(26)	125.2(5)
N(4)-C(23)-C(24)	109.3(5)
C(26)-C(23)-C(24)	125.3(5)
C(25)-C(24)-C(23)	108.1(6)
C(25)-C(24)-H(24)	126.0
C(23)-C(24)-H(24)	126.0
C(24)-C(25)-C(22)	107.8(5)
C(24)-C(25)-H(25)	126.1
C(22)-C(25)-H(25)	126.1
C(1)-C(26)-C(23)	124.0(5)
C(1)-C(26)-C(27)	119.4(5)
C(23)-C(26)-C(27)	116.3(5)
C(28)-C(27)-C(32)	119.7(6)
C(28)-C(27)-C(26)	120.4(6)
C(32)-C(27)-C(26)	119.9(6)
C(27)-C(28)-C(29)	120.4(7)
C(27)-C(28)-H(28)	119.8
C(29)-C(28)-H(28)	119.8
C(30)-C(29)-C(28)	119.3(7)
C(30)-C(29)-H(29)	120.3
C(28)-C(29)-H(29)	120.3
C(31)-C(30)-C(29)	120.9(7)
C(31)-C(30)-H(30)	119.5
C(29)-C(30)-H(30)	119.5

C(30)-C(31)-C(32)	118.5(7)
C(30)-C(31)-H(31)	120.7
C(32)-C(31)-H(31)	120.7
C(27)-C(32)-C(31)	121.1(7)
C(27)-C(32)-H(32)	119.4
C(31)-C(32)-H(32)	119.4
C(34)-C(33)-C(38)	117.8(5)
C(34)-C(33)-C(21)	122.1(5)
C(38)-C(33)-C(21)	120.1(5)
C(35)-C(34)-C(33)	121.5(5)
C(35)-C(34)-H(34)	119.2
C(33)-C(34)-H(34)	119.2
C(36)-C(35)-C(34)	119.4(5)
C(36)-C(35)-H(35)	120.3
C(34)-C(35)-H(35)	120.3
C(35)-C(36)-C(37)	121.1(5)
C(35)-C(36)-H(36)	119.4
C(37)-C(36)-H(36)	119.4
C(38)-C(37)-C(36)	119.4(5)
C(38)-C(37)-H(37)	120.3
C(36)-C(37)-H(37)	120.3
C(37)-C(38)-O(1)	124.5(5)
C(37)-C(38)-C(33)	120.8(5)
O(1)-C(38)-C(33)	114.7(5)
O(1)-C(39)-C(40)	110.5(5)
O(1)-C(39)-H(39A)	109.6
C(40)-C(39)-H(39A)	109.6
O(1)-C(39)-H(39B)	109.5
C(40)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	108.1
O(2)-C(40)-C(39)	105.9(5)
O(2)-C(40)-H(40A)	110.6

C(39)-C(40)-H(40A)	110.6
O(2)-C(40)-H(40B)	110.6
C(39)-C(40)-H(40B)	110.6
H(40A)-C(40)-H(40B)	108.7
O(2)-C(41)-C(42)	108.0(6)
O(2)-C(41)-H(41A)	110.1
C(42)-C(41)-H(41A)	110.1
O(2)-C(41)-H(41B)	110.1
C(42)-C(41)-H(41B)	110.1
H(41A)-C(41)-H(41B)	108.4
O(3)-C(42)-C(41)	113.0(6)
O(3)-C(42)-H(42A)	109.0
C(41)-C(42)-H(42A)	109.0
O(3)-C(42)-H(42B)	109.0
C(41)-C(42)-H(42B)	109.0
H(42A)-C(42)-H(42B)	107.8
O(3)-C(43)-C(44)	106.7(6)
O(3)-C(43)-H(43A)	110.4
C(44)-C(43)-H(43A)	110.4
O(3)-C(43)-H(43B)	110.4
C(44)-C(43)-H(43B)	110.4
H(43A)-C(43)-H(43B)	108.6
O(4)-C(44)-C(43)	109.4(5)
O(4)-C(44)-H(44A)	109.8
C(43)-C(44)-H(44A)	109.8
O(4)-C(44)-H(44B)	109.8
C(43)-C(44)-H(44B)	109.8
H(44A)-C(44)-H(44B)	108.3
C(46)-C(45)-C(64)	123.4(6)
C(46)-C(45)-O(4)	117.9(5)
C(64)-C(45)-O(4)	118.8(6)
C(45)-C(46)-C(67)	118.4(6)

C(45)-C(46)-C(47)	121.8(5)
C(67)-C(46)-C(47)	119.7(6)
C(48)-C(47)-C(46)	111.7(4)
C(48)-C(47)-H(47A)	109.3
C(46)-C(47)-H(47A)	109.3
C(48)-C(47)-H(47B)	109.3
C(46)-C(47)-H(47B)	109.3
H(47A)-C(47)-H(47B)	107.9
C(49)-C(48)-C(84)	117.7(6)
C(49)-C(48)-C(47)	121.9(6)
C(84)-C(48)-C(47)	120.4(5)
O(5)-C(49)-C(48)	122.7(5)
O(5)-C(49)-C(50)	115.7(5)
C(48)-C(49)-C(50)	121.6(6)
C(82)-C(50)-C(49)	118.7(5)
C(82)-C(50)-C(51)	121.0(5)
C(49)-C(50)-C(51)	120.3(5)
C(52)-C(51)-C(50)	111.9(4)
C(52)-C(51)-H(51A)	109.2
C(50)-C(51)-H(51A)	109.2
C(52)-C(51)-H(51B)	109.2
C(50)-C(51)-H(51B)	109.2
H(51A)-C(51)-H(51B)	107.9
C(69)-C(52)-C(53)	117.2(5)
C(69)-C(52)-C(51)	123.5(5)
C(53)-C(52)-C(51)	119.2(5)
C(54)-C(53)-C(52)	120.6(5)
C(54)-C(53)-H(53)	119.7
C(52)-C(53)-H(53)	119.7
C(55)-C(54)-C(53)	120.1(5)
C(55)-C(54)-H(54)	119.9
C(53)-C(54)-H(54)	119.9

C(54)-C(55)-C(56)	121.2(5)
C(54)-C(55)-H(55)	119.4
C(56)-C(55)-H(55)	119.4
C(55)-C(56)-C(69)	117.4(5)
C(55)-C(56)-C(57)	120.0(5)
C(69)-C(56)-C(57)	122.5(5)
C(56)-C(57)-C(58)	111.1(4)
C(56)-C(57)-H(57A)	109.4
C(58)-C(57)-H(57A)	109.4
C(56)-C(57)-H(57B)	109.4
C(58)-C(57)-H(57B)	109.4
H(57A)-C(57)-H(57B)	108.0
C(68)-C(58)-C(59)	117.2(5)
C(68)-C(58)-C(57)	123.5(5)
C(59)-C(58)-C(57)	119.3(5)
C(60)-C(59)-C(58)	120.6(5)
C(60)-C(59)-H(59)	119.7
C(58)-C(59)-H(59)	119.7
C(61)-C(60)-C(59)	119.8(6)
C(61)-C(60)-H(60)	120.1
C(59)-C(60)-H(60)	120.1
C(60)-C(61)-C(62)	121.7(6)
C(60)-C(61)-H(61)	119.1
C(62)-C(61)-H(61)	119.1
C(61)-C(62)-C(68)	117.7(5)
C(61)-C(62)-C(63)	121.3(5)
C(68)-C(62)-C(63)	120.9(5)
C(64)-C(63)-C(62)	113.1(5)
C(64)-C(63)-H(63A)	109.0
C(62)-C(63)-H(63A)	109.0
C(64)-C(63)-H(63B)	109.0
C(62)-C(63)-H(63B)	109.0

H(63A)-C(63)-H(63B)	107.8
C(65)-C(64)-C(45)	116.1(6)
C(65)-C(64)-C(63)	119.8(6)
C(45)-C(64)-C(63)	124.0(6)
C(66)-C(65)-C(64)	121.7(6)
C(66)-C(65)-H(65)	119.2
C(64)-C(65)-H(65)	119.2
C(65)-C(66)-C(67)	120.5(6)
C(65)-C(66)-H(66)	119.7
C(67)-C(66)-H(66)	119.7
C(46)-C(67)-C(66)	119.8(6)
C(46)-C(67)-H(67)	120.1
C(66)-C(67)-H(67)	120.1
O(6)-C(68)-C(58)	121.8(5)
O(6)-C(68)-C(62)	115.3(5)
C(58)-C(68)-C(62)	122.8(5)
C(52)-C(69)-C(56)	123.2(5)
C(52)-C(69)-O(7)	119.1(5)
C(56)-C(69)-O(7)	117.3(5)
O(7)-C(70)-C(71)	107.9(4)
O(7)-C(70)-H(70A)	110.1
C(71)-C(70)-H(70A)	110.1
O(7)-C(70)-H(70B)	110.1
C(71)-C(70)-H(70B)	110.1
H(70A)-C(70)-H(70B)	108.4
O(8)-C(71)-C(70)	108.4(4)
O(8)-C(71)-H(71A)	110.0
C(70)-C(71)-H(71A)	110.0
O(8)-C(71)-H(71B)	110.0
C(70)-C(71)-H(71B)	110.0
H(71A)-C(71)-H(71B)	108.4
O(8)-C(72)-C(73)	109.6(4)

O(8)-C(72)-H(72A)	109.7
C(73)-C(72)-H(72A)	109.7
O(8)-C(72)-H(72B)	109.7
C(73)-C(72)-H(72B)	109.7
H(72A)-C(72)-H(72B)	108.2
O(9)-C(73)-C(72)	113.8(5)
O(9)-C(73)-H(73A)	108.8
C(72)-C(73)-H(73A)	108.8
O(9)-C(73)-H(73B)	108.8
C(72)-C(73)-H(73B)	108.8
H(73A)-C(73)-H(73B)	107.7
O(9)-C(74)-C(75)	114.1(5)
O(9)-C(74)-H(74A)	108.7
C(75)-C(74)-H(74A)	108.7
O(9)-C(74)-H(74B)	108.7
C(75)-C(74)-H(74B)	108.7
H(74A)-C(74)-H(74B)	107.6
O(10)-C(75)-C(74)	108.6(4)
O(10)-C(75)-H(75A)	110.0
C(74)-C(75)-H(75A)	110.0
O(10)-C(75)-H(75B)	110.0
C(74)-C(75)-H(75B)	110.0
H(75A)-C(75)-H(75B)	108.4
O(10)-C(76)-C(77)	115.5(5)
O(10)-C(76)-C(81)	124.1(5)
C(77)-C(76)-C(81)	120.4(5)
C(78)-C(77)-C(76)	118.6(5)
C(78)-C(77)-C(5)	123.0(5)
C(76)-C(77)-C(5)	118.3(5)
C(77)-C(78)-C(79)	122.0(5)
C(77)-C(78)-H(78)	119.0
C(79)-C(78)-H(78)	119.0

C(80)-C(79)-C(78)	118.4(5)
C(80)-C(79)-H(79)	120.8
C(78)-C(79)-H(79)	120.8
C(79)-C(80)-C(81)	121.8(6)
C(79)-C(80)-H(80)	119.1
C(81)-C(80)-H(80)	119.1
C(80)-C(81)-C(76)	118.8(5)
C(80)-C(81)-H(81)	120.6
C(76)-C(81)-H(81)	120.6
C(83)-C(82)-C(50)	120.2(6)
C(83)-C(82)-H(82)	119.9
C(50)-C(82)-H(82)	119.9
C(82)-C(83)-C(84)	120.2(6)
C(82)-C(83)-H(83)	119.9
C(84)-C(83)-H(83)	119.9
C(83)-C(84)-C(48)	121.6(6)
C(83)-C(84)-H(84)	119.2
C(48)-C(84)-H(84)	119.2
C(1SS)-O(3S)-C(1S)	116.7(6)
O(3S)-C(1S)-C(3SS)	105.3(7)
O(3S)-C(1S)-H(1S1)	110.7
C(3SS)-C(1S)-H(1S1)	110.7
O(3S)-C(1S)-H(1S2)	110.7
C(3SS)-C(1S)-H(1S2)	110.7
H(1S1)-C(1S)-H(1S2)	108.8
O(1SS)-C(1SS)-O(3S)	121.0(8)
O(1SS)-C(1SS)-C(4SS)	126.6(8)
O(3S)-C(1SS)-C(4SS)	112.4(8)
C(1S)-C(3SS)-H(3S1)	109.5
C(1S)-C(3SS)-H(3S2)	109.5
H(3S1)-C(3SS)-H(3S2)	109.5
C(1S)-C(3SS)-H(3S3)	109.5

H(3S1)-C(3SS)-H(3S3)	109.5
H(3S2)-C(3SS)-H(3S3)	109.5
C(1SS)-C(4SS)-H(4S1)	109.5
C(1SS)-C(4SS)-H(4S2)	109.5
H(4S1)-C(4SS)-H(4S2)	109.5
C(1SS)-C(4SS)-H(4S3)	109.5
H(4S1)-C(4SS)-H(4S3)	109.5
H(4S2)-C(4SS)-H(4S3)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cuper(II) porphyrin-calix[4]arene (CuL1) The anisotropic displacement factor exponent takes the form: $-2 \pi^2$ [h^2 a^2 ×U11 + ... + 2 h k a× b×U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	27(1)	26(1)	20(1)	-1(1)	15(1)	-4(1)
O(1)	39(3)	23(2)	47(3)	-4(2)	29(2)	0(2)
O(2)	60(4)	51(3)	54(3)	5(3)	26(3)	5(3)
O(3)	75(4)	65(3)	45(3)	11(3)	36(3)	10(3)
O(4)	45(3)	30(2)	35(3)	10(2)	30(2)	16(2)
O(5)	32(3)	31(2)	25(2)	-4(2)	14(2)	-4(2)
O(6)	34(3)	31(2)	31(3)	12(2)	22(2)	3(2)
O(7)	31(2)	19(2)	19(2)	-1(2)	15(2)	4(2)
O(8)	26(2)	37(3)	16(2)	4(2)	7(2)	0(2)
O(9)	28(3)	43(3)	28(3)	6(2)	8(2)	10(2)
O(10)	32(3)	25(2)	32(3)	5(2)	18(2)	5(2)
N(1)	27(3)	17(3)	22(3)	-5(2)	16(2)	-11(2)
N(2)	21(3)	21(3)	20(3)	-1(2)	12(2)	0(2)
N(3)	25(3)	14(3)	19(3)	-4(2)	14(2)	-7(2)
N(4)	25(3)	28(3)	13(3)	-7(2)	11(2)	-10(2)
C(1)	32(4)	24(3)	17(3)	-3(3)	17(3)	-5(3)
C(2)	31(4)	26(3)	20(4)	-5(3)	14(3)	-3(3)
C(3)	25(4)	27(4)	25(4)	-1(3)	15(3)	-3(3)
C(4)	29(4)	24(3)	20(4)	2(3)	14(3)	0(3)
C(5)	32(4)	19(3)	20(4)	-4(3)	19(3)	-1(3)
C(6)	30(4)	17(3)	23(4)	-1(3)	18(3)	0(3)
C(7)	29(4)	11(3)	22(3)	6(3)	19(3)	2(3)

C(8)	27(4)	24(3)	15(3)	-4(3)	12(3)	1(3)
C(9)	34(4)	21(3)	19(4)	3(3)	19(3)	4(3)
C(10)	28(4)	15(3)	23(3)	-1(3)	17(3)	3(3)
C(11)	22(3)	25(3)	22(3)	1(3)	16(3)	1(3)
C(12)	28(4)	27(4)	25(4)	1(3)	17(3)	1(3)
C(13)	42(5)	43(4)	22(4)	-2(3)	17(3)	-4(4)
C(14)	30(4)	50(4)	17(4)	5(3)	7(3)	-1(3)
C(15)	26(4)	45(4)	27(4)	15(3)	15(3)	10(3)
C(16)	38(4)	30(4)	27(4)	11(3)	23(3)	10(3)
C(17)	26(4)	19(3)	20(4)	0(3)	12(3)	0(3)
C(18)	27(4)	14(3)	23(4)	-2(3)	16(3)	-2(3)
C(19)	28(4)	27(4)	25(4)	-5(3)	15(3)	-5(3)
C(20)	23(4)	28(4)	19(4)	2(3)	9(3)	4(3)
C(21)	28(4)	21(3)	20(4)	-3(3)	14(3)	-3(3)
C(22)	33(4)	26(4)	21(4)	1(3)	16(3)	-4(3)
C(23)	35(4)	38(4)	21(4)	1(3)	18(3)	-7(3)
C(24)	38(4)	65(5)	18(4)	-2(3)	14(3)	-16(4)
C(25)	44(5)	45(4)	21(4)	-3(3)	16(3)	-23(3)
C(26)	31(4)	29(4)	23(4)	-3(3)	19(3)	-8(3)
C(27)	30(4)	49(4)	26(4)	-3(3)	18(3)	-15(3)
C(28)	43(5)	45(4)	28(4)	1(3)	16(4)	-21(4)
C(29)	50(5)	74(6)	33(5)	10(4)	16(4)	-28(4)
C(30)	60(6)	87(6)	22(4)	-9(4)	21(4)	-38(5)
C(31)	48(5)	88(6)	42(5)	-23(4)	31(4)	-30(5)
C(32)	35(4)	77(5)	30(4)	-15(4)	20(4)	-26(4)
C(33)	24(4)	25(4)	18(3)	0(3)	12(3)	-4(3)
C(34)	32(4)	24(3)	24(4)	-2(3)	14(3)	-5(3)
C(35)	33(4)	30(4)	22(3)	0(3)	21(3)	-3(3)
C(36)	30(4)	31(4)	25(4)	3(3)	15(3)	-14(3)
C(37)	29(4)	25(4)	33(4)	-1(3)	16(3)	-1(3)
C(38)	25(4)	34(4)	26(4)	-1(3)	16(3)	0(3)
C(39)	43(4)	28(4)	44(4)	2(3)	27(4)	5(3)

C(40)	87(6)	18(4)	42(5)	-4(3)	25(4)	6(4)
C(41)	62(6)	73(6)	38(5)	19(4)	19(4)	13(4)
C(42)	65(6)	57(5)	60(5)	10(4)	39(5)	21(4)
C(43)	31(4)	86(6)	45(5)	41(4)	17(4)	10(4)
C(44)	50(5)	46(4)	35(4)	23(4)	27(4)	24(4)
C(45)	48(5)	20(4)	34(4)	10(3)	30(4)	7(3)
C(46)	46(4)	10(3)	46(4)	3(3)	35(4)	5(3)
C(47)	43(4)	20(4)	42(4)	2(3)	34(4)	0(3)
C(48)	35(4)	26(4)	42(4)	-1(3)	34(4)	-8(3)
C(49)	25(4)	21(4)	36(4)	3(3)	25(3)	0(3)
C(50)	29(4)	25(4)	26(4)	-4(3)	21(3)	-5(3)
C(51)	26(4)	33(4)	24(4)	-1(3)	15(3)	1(3)
C(52)	22(4)	21(3)	21(4)	-1(3)	14(3)	7(3)
C(53)	17(3)	27(4)	28(4)	-5(3)	11(3)	4(3)
C(54)	29(4)	25(3)	20(4)	1(3)	15(3)	2(3)
C(55)	30(4)	17(3)	29(4)	-1(3)	20(3)	1(3)
C(56)	26(4)	15(3)	23(4)	-1(3)	14(3)	3(3)
C(57)	26(4)	24(3)	23(3)	-1(3)	16(3)	4(3)
C(58)	25(4)	27(4)	15(3)	-4(3)	8(3)	-3(3)
C(59)	30(4)	27(3)	20(3)	1(3)	12(3)	0(3)
C(60)	24(4)	36(4)	38(4)	-8(3)	17(3)	0(3)
C(61)	30(4)	32(4)	33(4)	0(3)	18(3)	6(3)
C(62)	26(4)	27(4)	29(4)	3(3)	15(3)	3(3)
C(63)	28(4)	44(4)	36(4)	6(3)	20(3)	16(3)
C(64)	31(4)	27(4)	36(4)	8(3)	16(3)	10(3)
C(65)	30(4)	27(4)	46(5)	7(3)	23(4)	5(3)
C(66)	47(4)	31(4)	48(4)	14(4)	43(4)	15(4)
C(67)	39(4)	23(4)	38(4)	4(3)	20(3)	2(3)
C(68)	29(4)	23(4)	21(4)	-2(3)	9(3)	-1(3)
C(69)	29(4)	18(3)	20(4)	-3(3)	16(3)	2(3)
C(70)	32(4)	27(3)	22(4)	-1(3)	16(3)	-2(3)
C(71)	27(4)	33(4)	25(4)	0(3)	15(3)	-1(3)

C(72)	34(4)	44(4)	27(4)	-1(3)	16(3)	-2(3)
C(73)	33(4)	38(4)	24(4)	-7(3)	11(3)	-4(3)
C(74)	28(4)	35(4)	30(4)	3(3)	14(3)	7(3)
C(75)	28(4)	30(4)	25(4)	-1(3)	12(3)	2(3)
C(76)	29(4)	28(4)	21(3)	3(3)	14(3)	-1(3)
C(77)	20(4)	35(4)	10(3)	-7(3)	7(3)	-4(3)
C(78)	28(4)	22(3)	20(3)	-3(3)	12(3)	1(3)
C(79)	38(4)	29(4)	23(4)	-5(3)	22(3)	-11(3)
C(80)	27(4)	47(4)	24(4)	-9(3)	17(3)	-7(3)
C(81)	26(4)	33(4)	21(3)	-6(3)	12(3)	-5(3)
C(82)	29(4)	42(4)	40(4)	-4(3)	20(3)	2(3)
C(83)	36(4)	38(4)	42(4)	-10(4)	24(4)	-6(4)
C(84)	42(4)	28(4)	51(5)	-11(4)	35(4)	-8(4)
O(3S)	66(4)	88(4)	59(4)	-2(3)	32(3)	2(3)
C(1S)	94(7)	113(7)	43(6)	26(5)	13(5)	27(6)
O(1SS)	64(4)	101(5)	99(5)	-19(4)	42(4)	10(3)
C(1SS)	55(6)	89(7)	58(6)	-7(5)	29(5)	-13(5)
C(3SS)	106(8)	120(8)	47(6)	-23(5)	21(6)	-28(6)

VITAE

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