

การสร้างขั้วไฟฟ้าแบบเลือกจำเพาะต่อแอนไอออนจากสารประกอบเชิงซ้อนคอปเปอร์(II)
กับไตรโพลด์แอมีนที่มีฐานเป็นแอนทราซีนและคาลิกซ์[4]เอรีน

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FABRICATION OF ANION-SELECTIVE ELECTRODES FROM ANTHRACENE-BASED
AND CALIX[4]ARENE-BASED COPPER(II) COMPLEXES CONTAINING TRIPODAL
AMINE PENDANTS

Miss Phetlada Kunthadee

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Chemistry

Department of Chemistry

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เพชรลดดา กันทาดี : การสร้างขั้วไฟฟ้าแบบเลือกจำเพาะต่อแอนไอออนจากสารประกอบเชิงซ้อนคอปเปอร์(II) กับไตรโพลด์แอมีนที่มีฐานเป็นแอนทราซีนและคาลิกซ์[4]เอรีน. (FABRICATION OF ANION-SELECTIVE ELECTRODES FROM ANTHRACENE-BASED AND CALIX[4]ARENE-BASED COPPER(II) COMPLEXES CONTAINING TRIPODAL AMINE PENDANTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ศ.ดร. รัชชชัย ต้นทุลา นิ, 71 หน้า.

ได้ออกแบบและสังเคราะห์ไอโอโนฟอรั 3 ชนิดที่มีจำนวนแขนด้านข้าง ตัวเชื่อม และฐานโครงสร้างแตกต่างกัน แล้วเปรียบเทียบผลของโครงสร้างที่มีต่อสมบัติการตรวจวัดแอนไอออน การสังเคราะห์ไอโอโนฟอรั I ได้ร้อยละผลผลิตเท่ากับ 73 โดยเชื่อมต่อสารประกอบเชิงซ้อนโมโนนิวเคลียร์คอปเปอร์ (II) กับไตรโพลด์แอมีนเข้ากับแอนทราซีนโดยตรง ในขณะที่การสังเคราะห์ไอโอโนฟอรั II และ III ทำได้โดยเชื่อมต่อหน่วยของสารเชิงซ้อนคอปเปอร์ (II) จำนวน 2 หน่วยกับพารา-เทอร์เซียร์-บิวทิลคาลิกซ์[4]เอรีนด้วยตัวเชื่อมที่เป็น 2-อัลคอกซีเบนซิลและเอไมด์ ได้ร้อยละผลผลิตเป็น 42 และ 58 ตามลำดับ ทำการสร้างเซ็นเซอร์เมมเบรนพอลิเมอร์ที่มีไอโอโนฟอรัเหล่านี้แล้วทดสอบความไว ความจำเพาะต่อไอออน องค์ประกอบเมมเบรนที่เหมาะสม ตลอดจนลักษณะเฉพาะที่สำคัญอื่นๆ ของขั้วไฟฟ้าโดยแปรผันชนิดและปริมาณของตัวแลกเปลี่ยนไอออน การวิเคราะห์ทางโพเทนชิโอเมตริกชี้ให้เห็นว่าไอโอโนฟอรั I ไม่สามารถทำหน้าที่เป็นตัวพาแอนไอออนที่เหมาะสมในขั้วไฟฟ้าเมมเบรน เนื่องจากโครงสร้างมีแขนด้านข้างเพียง 1 แขนและมีความไม่ชอบน้ำต่ำ ในทางตรงกันข้าม ไอโอโนฟอรั II และ III แสดงความไวและความจำเพาะที่ดีต่อไอโอไดด์ถึงแม้ไม่ใช้ตัวแลกเปลี่ยนไอออน เนื่องจากสารประกอบเชิงซ้อนไดนิวเคลียร์คอปเปอร์ (II) เป็นหน่วยพาไอออนที่มีประสิทธิภาพโดยมีช่องว่างที่พอเหมาะกับไอโอไดด์ ขั้วไฟฟ้าที่ดีที่สุดที่จำเพาะต่อไอโอไดด์ประกอบด้วยไอโอโนฟอรั II (10 มิลลิโมลต่อกิโลกรัม) และไตรโพลด์ซิลเมทิลแอมโมเนียมคลอไรด์ (TDMACI) เป็นตัวแลกเปลี่ยนแอนไอออนปริมาณ 25 เปอร์เซ็นต์โมลสัมพันธ์กับปริมาณของไอโอโนฟอรั ในเมมเบรนที่มีพอลิเมอร์ PVC และ o-NPOE เป็นพลาสติกไฮดรอกซี โดยมีการตอบสนองต่อไอโอไดด์ที่ค่าความชันแบบเนินสต์ -54.9 ± 0.2 มิลลิโวลต์ต่อดีเคด ช่วงการทำงานเชิงเส้นระหว่าง 10^{-5} ถึง 10^{-2} โมลาร์ เวลาการตอบสนองที่รวดเร็วน้อยกว่า 5 วินาที ด้วยขีดจำกัดการตรวจวัดเท่ากับ 3.3×10^{-6} โมลาร์ จากนั้นได้ศึกษาทางยูวี-วิสิเบิลสเปกโทรโฟโตเมตรี พบการเลื่อนไปของสเปกตรัมซึ่งเป็นการยืนยันการเกิดอันตรกิริยาระหว่างไอโอโนฟอรัและไอโอไดด์ นอกจากนี้ ขั้วไฟฟ้างกล่าวสามารถนำมาใช้ในช่องพีเอชที่กว้างระหว่าง 4.7-8.6 ด้วยการผันกลับที่ดีเยี่ยม และยังสามารถนำไปประยุกต์ใช้ในการตรวจหาความเข้มข้นของไอโอไดด์ในน้ำตัวอย่าง ได้แก่ น้ำแร่และน้ำประปา โดยให้ผลเปอร์เซ็นต์การกลับคืนที่น่าพอใจ

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PHETLADA KUNTHADEE: FABRICATION OF ANION-SELECTIVE ELECTRODES FROM ANTHRACENE-BASED AND CALIX[4]ARENE-BASED COPPER(II) COMPLEXES CONTAINING TRIPODAL AMINE PENDANTS. ADVISOR: PROF. THAWATCHAI TUNTULANI, Ph.D., 71 pp.

Three types of ionophores were designed and synthesized with different number of side-arms, linkers and building blocks, and the effects of their structures on anion sensing properties were then comparatively examined. Ionophore **I** was synthesized in 73% yield by attaching tripodal amine mononuclear Cu(II) complex directly to the anthracene, while two units of such complex were connected to the *p*-*tert*-butylcalix[4]arene with 2-alkoxybenzyl and amide linkers to give ionophores **II** and **III** in 42 and 58% yield, respectively. The polymeric membrane sensors containing these ionophores were fabricated and then the sensitivity, selectivity, optimal membrane composition, as well as the important characteristics of electrodes were then explored by varying types and amounts of ion exchangers. The potentiometric investigations indicated that ionophore **I** could not function properly as an anion carrier due to its low lipophilic single-sided arm structure in membrane electrodes. On the other hand, ionophores **II** and **III** exhibited good sensitivity and selectivity toward iodide even in the absence of ion exchangers, resulting from the dinuclear Cu(II) complexes as an effective ion-carrier unit, providing a suitable cavity for iodide. The best iodide-selective electrode was achieved when using ionophore **II** (10 mmol kg⁻¹) in the presence of 25 mol% of tridodecylmethylammonium chloride (TDMACl) anion exchanger related to the ionophore incorporated in the *o*-NPOE plasticized PVC membrane, with the Nernstian slope of -54.9 ± 0.2 mV decade⁻¹ of iodide response, the linear working range from 10⁻⁵ to 10⁻² M, the fast response time less than 5 s, and the limit of detection of 3.3×10^{-6} M. UV-Visible spectrophotometric studies were also carried out and the spectral shift was observed to affirm the interaction between ionophore and iodide. Moreover, this electrode could be used over a wide pH range of 4.7-8.6 with great reversibility, and also applied to determine the concentration of iodide in the real water samples, mineral water and tap water, with satisfactory recoveries.

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

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LIST OF ABBREVIATIONS

°C	Degree Celsius
¹³ C NMR	Carbon nuclear magnetic resonance
d	Doublet (¹ H NMR spectrum)
EMF	Electromotive force
g	Gram
h	Hour
¹ H NMR	Proton nuclear magnetic resonance
HRMS-ESI	High resolution mass spectrometry-electrospray ionization
Hz	Hertz
ISE	Ion selective electrode
<i>J</i>	Coupling constant
KTpCIPB	Potassium tetrakis[<i>p</i> -chlorophenyl] borate
m	Multiplet (¹ H NMR spectrum)
M	Molar
mL	Millilitre
mmol kg ⁻¹	Millimole per kilogram
mV decade ⁻¹	Millivolt per decade
<i>o</i> -NPOE	<i>o</i> -Nitrophenyl octyl ether
ORTEP	Oak ridge thermal ellipsoid plot
PVC	Poly(vinyl chloride)
R ⁻	Cation exchanger
R ⁺	Anion exchanger
s	Singlet (¹ H NMR spectrum)
SSM	Separate solution method
t	Triplet (¹ H NMR spectrum)
TDMACl	Tridodecylmethylammonium chloride
THF	Tetrahydrofuran

v/v	Volume by volume
wt %	Percent by weight
β_{ILn}	Stability constant for ion-ionophore complex
δ	Chemical shift

CHAPTER I

INTRODUCTION

It is well-known that a number of analytical techniques have been proposed and reported so far for the determination of anions at low concentration levels. Unfortunately, there are still some disadvantages among these methods, for example, complicated techniques, expensive instruments, and sample pretreatment requirements. Therefore, ion-selective electrode (ISE) has been considered as an alternative technique for the measurement of anions due to its several advantages such as simplicity, low cost, good sensitivity and selectivity, high speed and non-destructive analysis [1]. The design of anion-selective electrodes gains a lot of interest and challenge recently due to the pH sensitivity, high hydration energy, and variable size and shape of anions [2-4]. There is especially a high demand for new ion carriers (or ionophores) with greater selectivity in the area of anion-ISEs.

Due to the lipophilic property of calixarenes, they have been widely used as chemical building blocks to increase the stability of compounds in organic phase [5-7]. In addition, from our previous observations while searching for a good carrier for Cd^{2+} -selective electrode, we found that the calix[4]arene containing tripodal amines (TPAs) formed a very strong and nonreversible complex with Cu^{2+} and the fabricated membrane electrode gave the time trace line in a negative EMF direction upon the addition of $\text{Cu}(\text{NO}_3)_2$ [8]. As a result, we expect that this tripodal amine $\text{Cu}(\text{II})$ complexes based on calix[4]arene may be employed as anion-selective ionophores.

In this work, we are interested in examining the anion sensing properties of ionophores derivatized from the calix[4]arene and also anthracene scaffolds attached to copper(II) complexes which are the recognition units for anions. We expect that the difference in topologies among these ionophores would play an important role in determining the most selective anion. Our synthesized ionophores will be incorporated into plasticized polymeric membranes and then the optimal membrane

composition, the ion-transfer mechanism across membranes, as well as important characteristics of membrane electrodes are investigated using potentiometric method in order to obtain a new suitable anion-selective electrode which exhibits good performance without the interference by other common anions. Moreover, the possibility of using our optimized electrode for real applications is explored by determining the target anion concentration in real water samples.

1.1 Research Objective

This research aims to fabricate new anion-selective electrodes using anthracene-based and calix[4]arene-based copper(II) complexes as ionophores and then apply the fabricated electrodes for determination of anions in real samples.

1.2 Scope of the Research

Three ionophores derivatized from the anthracene and calix[4]arene scaffolds attached to copper(II) complexes containing tripodal amine pendants are incorporated into polymeric membranes and then their anion sensing properties are comparatively examined. We expect that the difference in topologies such as the number of side arms, types of linkers and building blocks which affect the arrangement of recognition units as well as the stability of ionophores in polymeric membranes would play important roles in determining the most selective anion. The synthesized ionophores are incorporated into plasticized PVC membranes in the absence and the presence of various amounts of ion exchangers for studying the sensitivity and selectivity of the proposed electrodes toward anions. Moreover, two types of ion exchanger, *KTpCIPB* (as cation exchanger) and *TDMACl* (as anion exchanger), are used to observe the ion-transfer mechanism across membranes. Compositions of the membrane are optimized by keeping a constant amount of ionophore and also a constant ratio of PVC and plasticizer at 1:2 by weight. The important characteristics of proposed ISEs such as the potentiometric response, selectivity coefficient, working concentration range, response time, limit of detection, working pH range, and membrane reversibility are subsequently investigated in order to obtain a new suitable anion-selective electrode which exhibits good characteristics without the interference by lipophilic anions. The

optimized ISEs are then applied to determine the target anion concentration in water samples.

1.3 Benefits of the Research

We have expected to obtain great performance anion-ISEs fabricated from polymeric membranes using novel types of ionophores that can be applied for determining of target anions in real samples with satisfying recoveries.

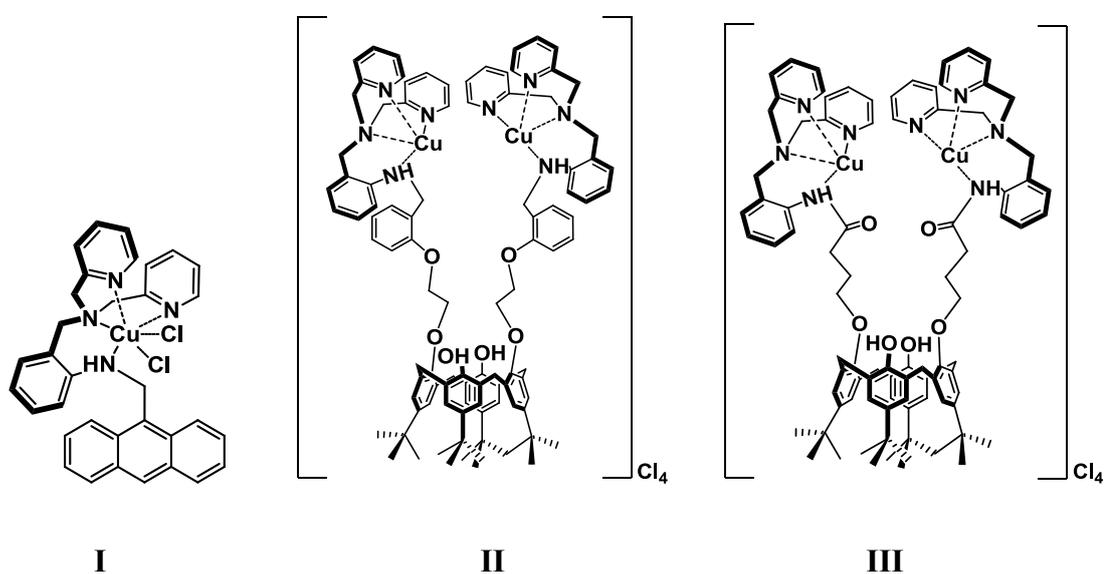


Figure 1.1 Structures of three synthesized ionophores (I-III).

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 A brief concept of supramolecular chemistry

Supramolecular chemistry was originally defined in terms of the non-covalent interactions using the host-guest concept [9-10]. This concept describes complexes composed of two or more molecules or ions that are held together in unique structural arrangement using the idea of molecular recognition and interactions through non-covalent bonding. “Host” is typically a large molecule that contains a cavity or a hole possessing convergent binding sites for a specific guest. “Guest” is a smaller molecule possessing divergent binding sites which can be fit inside a cavity of a host molecule. Guest can vary in size from a single atom/ion to a complex molecule/ion. Molecular recognition between the host and guest may be simply illustrated in Figure 2.1.

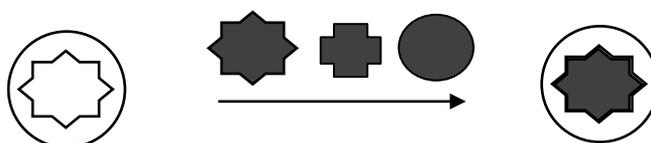


Figure 2.1 Molecular recognition between a host and its complementary guest.

There are four common types of non-covalent interactions: hydrogen bonds, van der Waals forces, electrostatic, and hydrophobic interactions that are utilized to create high selectivity between guest and host compounds [9-11]. In biological systems, the analogous terms of host and guest are commonly referred to enzyme and substrate, respectively. Equilibrium between the unbound state, in which the host and the guest are separate from each other, and the bound state, in which there is a structurally defined host-guest complex is presented as follows:



Where H = host, G = guest, HG = host-guest complex.

The stability of a host-guest complex at equilibrium may be described in terms of the association constant, K_a .

Syntheses of new host molecules having the ability of specific recognition with a guest molecule have been currently developed and utilized in a variety of applications, for example, chemical sensing, medical, biological and environmental analyses [12-16]. Another challenging application is the development of chemical sensors based on supramolecular chemistry for the selective detection of ions.

2.2 Ion-Selective Electrodes (ISEs)

A chemical sensor can be basically defined as a small device that allows the transformation of chemical information into an optical or electrical signal that can be processed by an instrument [17]. Ion-selective electrodes (ISEs) are electrochemical sensors based on ion-selective membranes that allow the potentiometric determination of the activity of an ionic species in the presence of other kinds of ions [18]. It is designed to respond selectively to a particular ion in a solution by measuring an electric potential difference developing across a semi-permeable membrane and a solution of analyte ion in different concentrations relative to a reference electrode. ISE is one of the interesting and effective analytical techniques due to its simplicity, high sensitivity and selectivity. In addition, it is a cheap device and usually does not need a sample preparation. Therefore, ISEs have been applied in a wide range of applications such as chemical sensors, clinical laboratories, physiology, biology, process control, biomedical science, and environmental analysis over the last several decades [1]. Several types of ion-selective membrane are known including glass [19], plasticized polymers [20], or various crystalline materials [21-22]. However, at present, the most versatile ion-selective membrane is a polymeric liquid membrane. The use of plasticized polymeric membrane has been frequently proposed in order to achieve high sensitivity and fast response. The field of ISE therefore bridges fundamental membrane science with fundamental host-guest chemistry.

2.2.1 Components of the polymeric membrane ISEs

The sensitivity and selectivity of electrode mainly depend on the composition and polarity of membrane. The ion-sensitive polymeric membrane is physically a water immiscible liquid of high viscosity consisting of a lipophilic complexing agent (as an ion carrier/ ionophore), a lipophilic ionic salt (as an ion exchanger), an organic polymer such as PVC, and a plasticizer (as a membrane solvent) as listed below [17].

Ionophore

Ionophore, or ion carrier, is a key component of the membrane for assisting the ion-transport across a hydrophobic membrane. It can form relatively strong, selective, and reversible complexes only with the target ion over other interfering ions present in the sample phase. Moreover, the ionophore structure must contain appropriate lipophilic groups in order to keep its leaching rate out of the membrane as low as possible.

Ionic additive

Ionic additive, or ion exchanger, is a lipophilic ionic salt which is added into the polymeric membrane for keeping the charge balance between inside and outside the membrane and help reducing the membrane resistivity. The presence of ion exchanger also prevents the co-extraction of counter ions from the sample phase into the membrane phase together with the primary ions. This means the membrane is permeable only for ions with the same charge sign of the measuring ion as known as “the membrane permselectivity” (or Donnan exclusion). As a result, cation-selective membranes normally contain tetraphenylborate derivatives as lipophilic sites whereas anion-selective membranes require tetraalkylammonium salts.

Polymer

The polymer matrix is ideally inert and has no chemical interaction with the sensed ions. Polymeric membranes for ISEs are commonly prepared with PVC (poly(vinyl chloride)) due to its elasticity and mechanical stability.

Plasticizer

Plasticizer is used as a membrane solvent and must be compatible with other membrane components in order to provide the homogeneity of organic phase. The polarity and dielectric constant of the membrane solvents play a role in reducing the viscosity and enhancing the mobility of the membrane constituents. Moreover, the plasticizer should have high lipophilicity and low vapor pressure [23]. Bis(2-ethylhexyl) sebacate (DOS, apolar) or ortho-nitrophenyl octyl ether (*o*-NPOE, polar) are the common plasticizers employed in ISE membranes [24].

2.2.2 Response mechanisms

The electrochemical measuring cell (Figure 2.2) consists of two galvanic half-cells: the ion selective electrode and the reference electrode [18]. The total potential difference (electromotive force, EMF) measured under zero-current conditions between the two electrodes is the sum of potential differences, arising at each electrochemical interface.

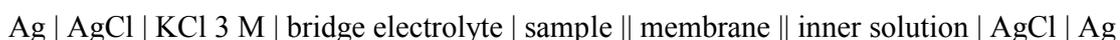
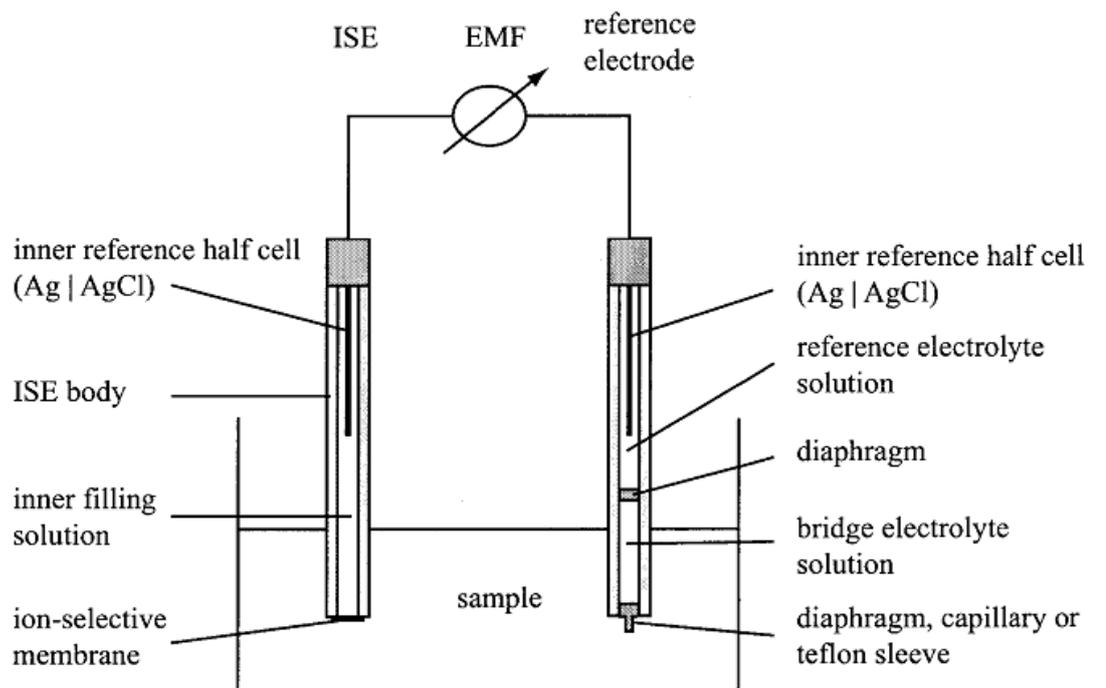


Figure 2.2 Schematic representation of an ISE measuring cell [18].

The ion recognition event generates a phase boundary potential at membrane-sample interface according to the Nernst's equation [25]:

$$E_M = E^0 + \frac{RT}{zF} \ln a_I(\text{aq}) \quad (2.2)$$

Where E_M is the electrode potential, E^0 is the sum of all constant potential differences in the measuring cell. R , T and F are the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), absolute temperature (K) and Faraday constant (9.648×10^4 coulombs per mole of electron), respectively. z is the charge of the analyte and $a_I(\text{aq})$ is the activity of the analyte in the aqueous sample. It can be seen from the equation that the electrode potential is proportional to the logarithm of the activity of the ion monitored. The inner phase boundary potential is usually independent of the sample. The Nernstian slope of the response function is $2.303 RT/zF = -59.2 \text{ mV}/z$ for $z = -1$ at 298 K.

The uncomplexed form of ionophore can be either charged or electrically neutral. A classification of ion transfer mechanisms based on their charge type is presented in Figure 2.3 (adapted from a published paper of Bakker and coworkers [1]). For example, when the uncomplexed carriers are neutral and the complexes have the same charge as the analyte ions, the membrane requires the additional incorporation of lipophilic ions of opposite charge to ensure permselectivity (see Figure 2.3(a)).

2.2.3 Electrode characteristics

2.2.3.1 Selectivity

Membrane selectivity is one of the most important characteristics of an ISE. It is related to the equilibrium of the exchange reaction of primary ion (I) and interfering ion (J) between organic and aqueous phases, which is usually called the selectivity coefficient ($\log K_{I,J}^{pot}$). According to the IUPAC commission of 1994, potentiometric selectivity coefficient describes the ability of ion-selective electrode to distinguish a particular ion from others [26]. Basically, in the presence of foreign ions, the effective electrode should have preferable selectivity toward primary ion over such interfering

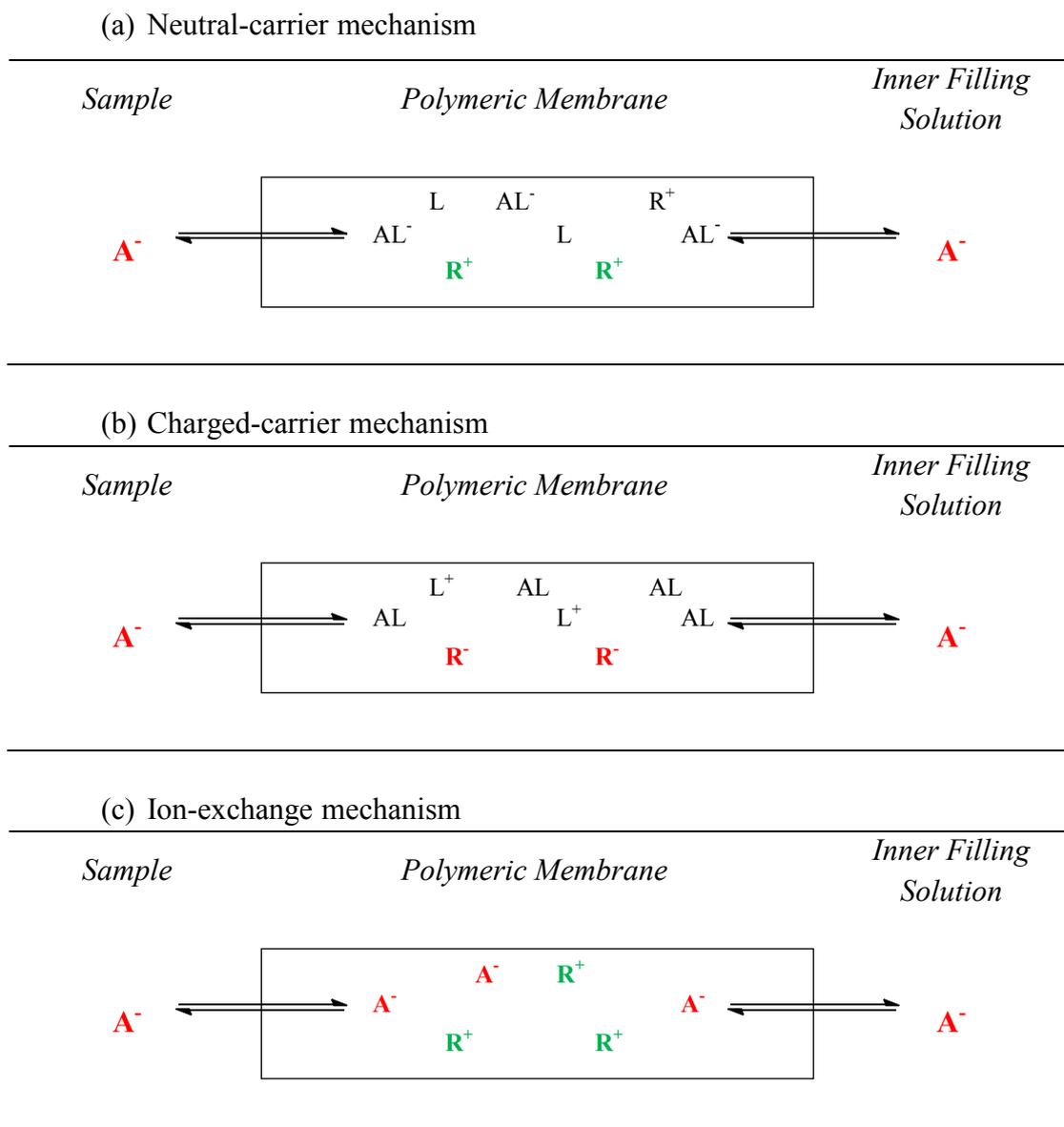


Figure 2.3 Schematic view of the equilibria between sample, ion-selective membrane, and inner filling solution based on (a) neutral-carrier, (b) charged-carrier, and (c) ion-exchange mechanisms, (Note: L = neutral ionophore, L^+ = charged ionophore, R^+ = lipophilic cation (or anion exchanger), R^- = lipophilic anion (or cation exchanger), A^- = analyte anion)

ions without biased signals. The value of $K_{I,j}^{pot}$ is defined by the modified Nikolsky-Eisenman equation (2.3). For an ideally ISE, the value should be zero indicating no interference. However, no electrode is truly specific for one ion. The smaller the value

of $K_{I,j}^{pot}$ the more selective is the electrode toward primary ion (I). The IUPAC commission of 1994 also recommended the use of two different procedures to determine the selectivity coefficients of ISEs, namely the so-called separate solution method (SSM) and the fixed interference method (FIM).

$$E = \text{constant} + \frac{2.303RT}{Z_I F} \log [a_I + K_{I,J}^{pot} a_J^{Z_I/Z_J} + K_{I,K}^{pot} a_K^{Z_I/Z_K} + \dots] \quad (2.3)$$

Separate solution method (SSM)

The SSM involves the measurement of two separate solutions, one containing a salt of primary ion, and another one containing a salt of interfering ion. The selectivity coefficient, $\log K_{I,j}^{pot}$, is then calculated from the two observed EMF values as illustrated in Figure 2.4 and equation (2.4). This method is highly recommended if the electrode exhibits a Nernstian response for the studied ions.

$$\log K_{I,J}^{pot} = \frac{Z_I F \{E(J) - E(I)\}}{2.303 RT} + \log [a_I(I) / a_J(J)^{Z_I/Z_J}] \quad (2.4)$$

where $E(I)$ and $E(J)$ are the recorded potentials in separate solutions for primary ion I and interfering ion J and $a_I(I)$ and $a_J(J)$ are the activities of I and J in separate solutions.

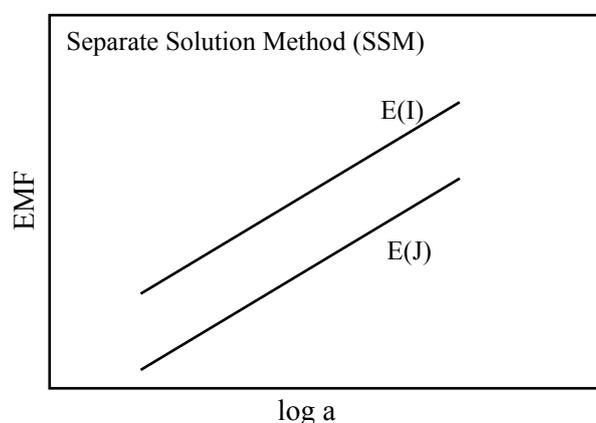


Figure 2.4 Schematic representation of ISE selectivity as determined by the separation solution method [1, 26].

Fixed interference method (FIM)

In the FIM, the potential is measured with the solution of constant interfering ion and varying activity of the primary ion. This method shows the ability of an ISE to distinguish between different ions in the same solution. The selectivity coefficient is calculated using equation (2.5). As shown in Figure 2.5, $a_j(\text{BG})$ is the activity of the constant interfering ion in the background. $a_i(\text{DL})$ is the low detection limit (LDL) of the Nernstian response curve of the electrode as a function of the primary ion activity. The SSM and FIM require Nernstian response of both interfering ion and primary ion. However, the FIM can always be used to determine a minimum primary ion concentration level at which the effect of interference can be neglected. The interfering ions should be present in relatively very low concentration, preventing the biased signals and error readings due to the loss of linearity of primary ion [1, 25-28].

$$\log K_{I,J}^{\text{pot}} = \log [a_i(\text{DL})/a_j(\text{BG})^{Z_I/Z_J}] \quad (2.5)$$

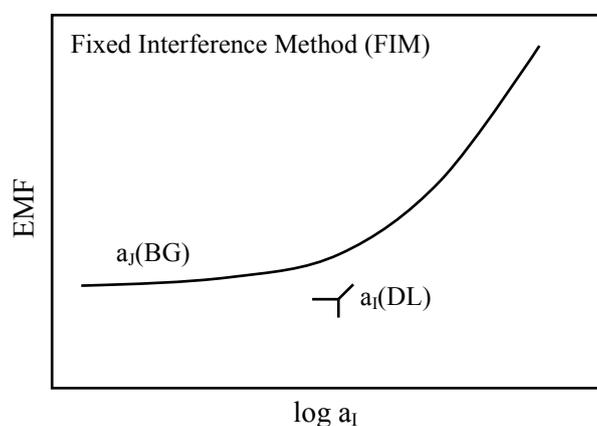


Figure 2.5 Schematic representation of ISE selectivity as determined by the fixed interference method [1, 26].

2.2.3.2 Detection limits

A limit of detection can be simply defined as the concentration for which, under the specified conditions, the cell EMF, E , deviated from the linear EMF response at high and low activities of the measuring ion. According to the IUPAC

recommendation [26], the detection limit is determined by the cross-section of the two extrapolated linear calibration curves as illustrated in Figure 2.6. For ISE, the detection limit can be sometimes dictated by the interference of a competing ion present in the sample or by the leaching of primary ions from the membrane phase into the sample.

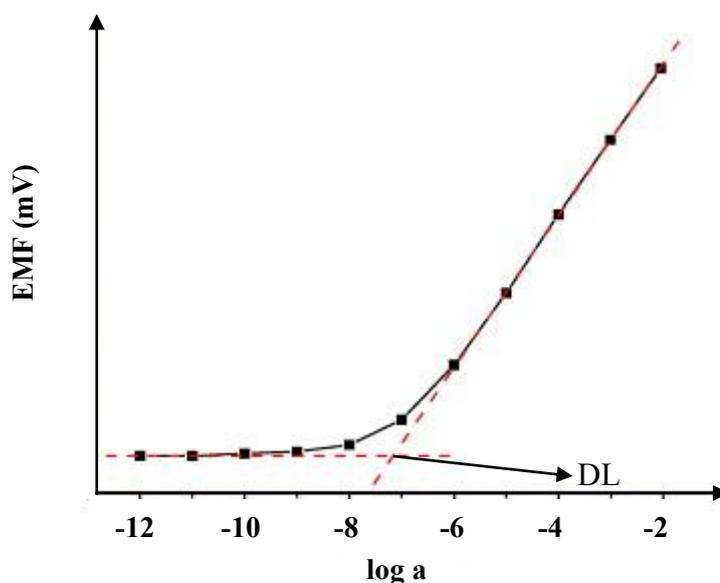


Figure 2.6 The detection limit (DL) of ISE defined according to the IUPAC recommendations [26] by the cross-section of the two extrapolated linear segments of the calibration curve.

2.2.3.3 Response time

The response time is another important characteristic of electrode. A good ISE should have fast response time toward the measured ions. According to IUPAC, as illustrated in Figure 2.7, response time ($\Delta E/\Delta t$) is the time between the instant when an ISE and a reference electrode are contacted with a sample solution (or when the activity of the ion of interest in a solution is changed) and the first instant at which the EMF/time slope ($\Delta E/\Delta t$) becomes equal to its steady-state value within 1 mV [26] or has reached 90% of the constant value at equilibrium [29]. The stirring rate should be controlled during the experiments.

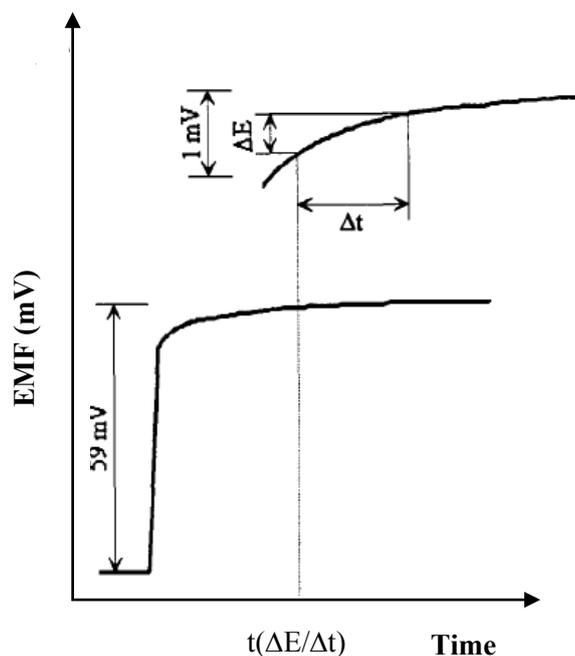


Figure 2.7 The determination of response time $t(\Delta E/\Delta t)$ [26].

2.3 Ionophores for anion-selective electrodes

There have been many reviews about anion receptors based on macrocyclic polyamines [30], amides [31], guanidiniums [32], crown ethers [33], or lanthanoids [34]. In addition, urea and thiourea functions are often employed due to their ability to form strong hydrogen bonds to organic carboxylates [35]. Porphyrins and their derivatives are also frequently used in the design of many supramolecular receptors. Sessler and coworkers have studied many expanded porphyrins including sapphyrins, which are known for their ability to bind anions such as F^- and PO_4^{3-} [36-37]. Moreover, metal-containing ligands have been widely proposed for anion sensing nowadays. The most recent advances in this field are the use of metallo-receptors in dendrimer, functionalized nanoparticle, and surface-bound anion sensors [38].

Ionophores with different functional groups have been designed, synthesized, and used to construct PVC-based membrane electrodes for detecting a variety of anions. Calixarenes and polycyclic aromatic hydrocarbons are one of potentially interesting choices as chemical building blocks which can improve the stability and lipophilicity of ionophores in organic polymer phase.

2.3.1 Anthracene as a building block for ISEs

Anthracene is one type of polycyclic aromatic hydrocarbons, PAHs. It is a solid compound consisting of three fused benzene rings, and used to make dyes because it exhibits a blue fluorescence under UV light. Calix[4]azacrown containing blue-light emitting anthracene fluorophore was studied in terms of luminescent properties and was then published in 2006 [39]. Anthracene and its derivatives are also employed in many chemical syntheses. However, there have been few reports on using anthracene for sensing anions, especially in the electrochemical device like ISE.

N-(4-benzo-15-crown-5)-anthracene-9-imine was incorporated into the fluorescent optode membrane and exhibited the good sensitivity and selectivity to cesium (I) ion [40]. Jeong and his coworkers reported that the anthracene present in a Schiff base compound, 1,2-bis(*E*-2-hydroxy benzylidene amino)anthracene-9,10-dione, could be used as a Cu^{2+} -selective ionophore [41]. Moreover, in our previous report [8], one tripodal amine (TPA) group was connected to an anthracene and examined as cation carrier using PVC membrane ISE (see Figure 2.8 (e)). Unfortunately, the result was unsatisfied because its lipophilicity was not high enough to retain the ionophore in the membrane phase. However, in this work, the Cu(II) complex of this compound (Chapter 1, Figure 1.1) was prepared and expected to be more stable and show a good performance as anion carrier.

2.3.2 Calix[4]arenes as building blocks for ISEs

Calix[n]arenes are a class of cyclic oligomers formed via a phenol-formaldehyde condensation [42]. They exist in a cup-like shape with a defined upper and lower rim and a central annulus (see Figure 2.9). Their rigid conformation possesses cavities and enables calixarenes to act as host molecules. It is therefore possible to prepare various derivatives with differing selectivities for various guest ions by functionally modifying either the upper and/or lower rims.

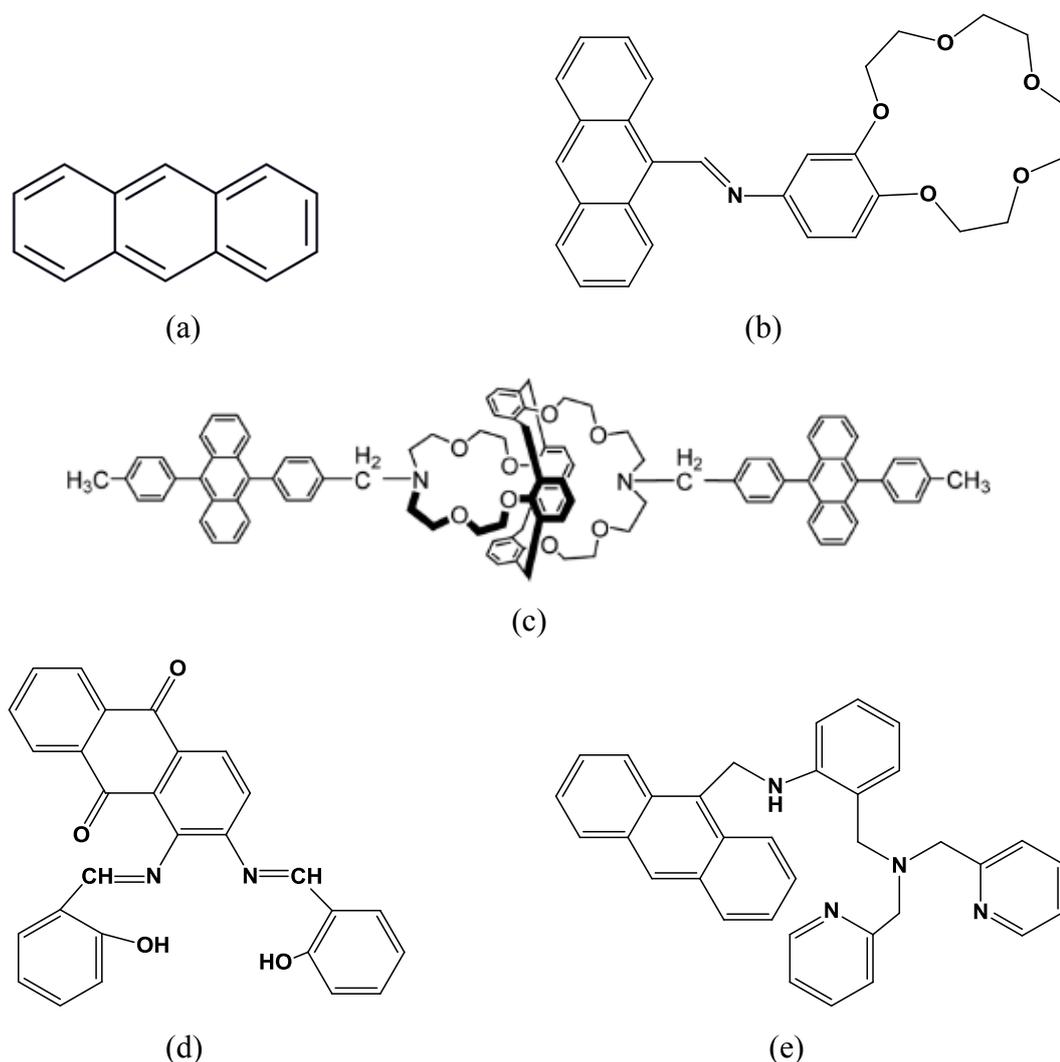


Figure 2.8 The structure of anthracene and its some previously reported derivatives, (a) anthracene, (b) *N*-(4-benzo-15-crown-5)-anthracene-9-imine [40], (c) *N,N*-bis[9-[10-(*p*-tolyl)anthracenyl benzyl]-calix[4]-bisazacrown-5 [39], (d) 1,2-bis(*E*-2-hydroxy benzylidene amino)anthracene-9,10-dione [41], and (e) *N*-(anthracene-9-ylmethyl)-2-(((pyridin-2-ylmethyl)(pyridin-3-ylmethyl)amino)methyl)aniline [8].

Calix[*n*]arenes are very popular as attractive and excellent ionophores because they provide a platform for the attachment of convergent binding groups to create host molecules, mainly for the attraction of simple cations, anions and small molecules. Due to the lipophilicity of calixarenes, they have been functionalized and widely used as chemical building blocks to increase the stability of compounds in organic phase

and prevent the water dissolution of ionophores from the device in aqueous analysis. Moreover, the presence of the *p-tert*-butyl groups in the upper rim makes the molecule more lipophilic and also forces the calixarene into a permanent cone conformation, giving a specific cavity to recognize specific guest molecules [5, 42-43].

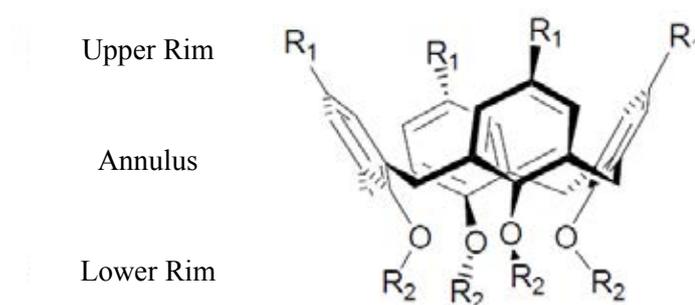


Figure 2.9 Cone conformation of a typical calix[4]arene [42].

There have been several research studies on using ionophores based on calix[n]arene derivatives for sensing anions. Nevertheless, some limitations and disadvantages were observed and it is then still challenging to find more suitable anion sensors which can be employed in real applications. In this work, we expect that the functionalized compounds of *p-tert*-butyl calix[4]arene incorporated in polymeric membranes would give the excellent anion-sensing properties. The response characteristics of some previously reported anion carriers based on calix[4]arene are summarized in Table 2.1 and their structures are presented in Figure 2.10.

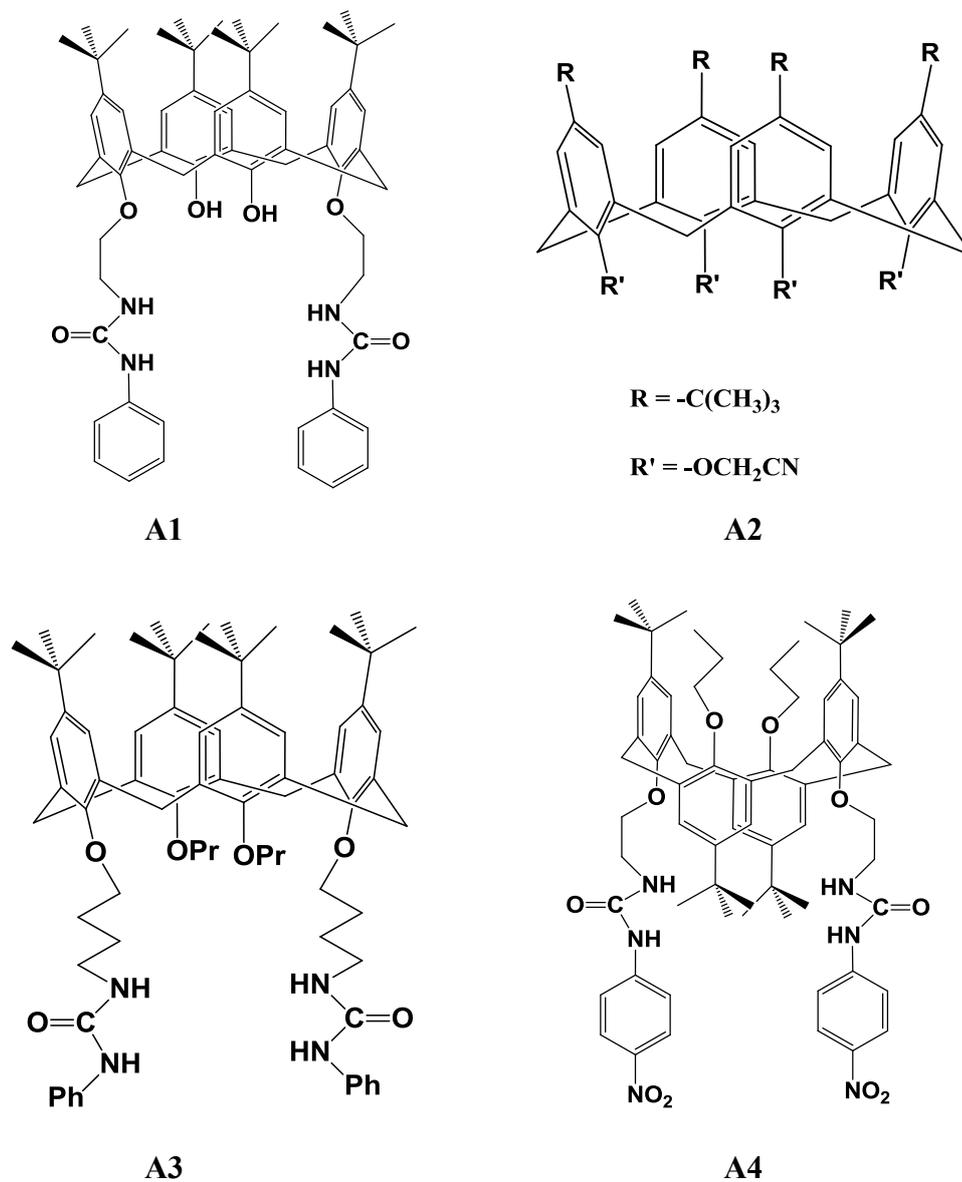


Figure 2.10 Structures of previously reported anion-selective ionophores based on calix[4]arene derivatives [44-47].

Table 2.1 The response characteristics of some previously reported anion-selective ionophores based on calix[4]arene.

Ionophore	Anions	Linear working range (M)	Slope (mVdecade⁻¹)	Detection Limit (M)	Response Time (s)	Working pH range	Lifetime	Ref.
A1	CO ₃ ²⁻	5.0 × 10 ⁻⁴ - 1.0 × 10 ⁻¹	-22.9	1.2 × 10 ⁻⁴	-	-	-	[44]
A2	ClO ₄ ⁻	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻¹	-48.7 ± 0.5	5.0 × 10 ⁻⁶	10-15	2.0 - 2.9	4 months	[45]
A3	HPO ₄ ²⁻	5.0 × 10 ⁻⁵ - 1.0 × 10 ⁻¹	-33.0	5.0 × 10 ⁻⁵	-	7.13	-	[46]
A4	Cl ⁻	5.0 × 10 ⁻⁵ - 1.0 × 10 ⁻¹	-55.69	2.51 × 10 ⁻⁵	-	-	-	[47]

CHAPTER III

EXPERIMENTAL

3.1 General Procedures

3.1.1 Apparatus

Crystallographic data of ionophore **I** were collected on a BRUKER APEX CCD diffractometer (graphite-monochromated Mo-K α radiation with $\lambda = 0.71073$ Å). The structures were solved by direct methods using the program SHLEXS-97 [48] and refined by full-matrix least squares techniques against F^2 using the SHELXL-97 through WinGX [49] crystallographic software package. Non-hydrogen atoms were refined with anisotropic thermal parameters in the latter stage of refinement. Hydrogen atoms are refined anisotropically. Nuclear magnetic resonance (NMR) spectra were recorded on a varian Mercury Plus 400 MHz nuclear magnetic resonance spectrometer. MALDI-TOF mass spectra were recorded on a Micromass Platform II. Absorption spectra were obtained from an Agilent 8453 UV-Visible spectrophotometer. A 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA) was used to record EMF measurements. A reference electrode Ag/AgCl (Metrohm 6.0726.100) was used with 1 M LiOAc as salt bridge electrolyte. pH values were determined with an Orion 2-Star Benchtop pH meter (Thermo Fisher Scientific).

3.1.2 Materials

All materials and reagents were standard analytical grade, and used without further purification. Commercial grade solvents such as methanol, ethanol, and dichloromethane, were purified by distillation. Dichloromethane and toluene were dried over CaH₂ and freshly distilled under nitrogen for set up the reaction. Column chromatography was carried on silica gel (Kieselgel 60, 0.063-0200 mm). Thin layer chromatography (TLC) was performed on silica gel plates (Kieselgel 60, F₂₅₄, 1 mm). Compounds on TLC plates were monitored by the UV-light.

Anthracene-9-carbaldehyde was purchased from Aldrich. Chemicals used for membrane preparation; tetrahydrofuran (THF), chloroform (CHCl_3), high molecular weight poly(vinyl chloride) (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(*p*-chlorophenyl) borate (KTPCIPB), and tridodecylmethylammonium chloride (TDMACl) were purchased in selectophore® grade form Fluka. Potassium and sodium salts of anions were of analytical grade obtained from BDH, Fluka, Carlo Erba, and Merck. The pH 8.2 phosphate buffer and pH 4.4 acetate buffer solutions were used for potentiometric measurements of HCO_3^- and H_2PO_4^- , respectively. All solutions for ISE experiments were prepared with ultrapure water from Milli-Q (Bedford, MA, USA) water purification system (Millipore).

The synthesis and characterization of ionophores **I-III** were illustrated in appendix A.

3.2 Ion Selective Electrode Studies

3.2.1 Preparation of the electrode

Polymeric membranes prepared for ISE measurements consisted of ionophore (10 mmol kg^{-1}), various amounts of ion exchangers, KTPCIPB or TDMACl (0, 10, 25, 50, and 75 mol% relative to ionophore), and PVC: *o*-NPOE plasticizer (1: 2 w/w), in the total amount of 220 mg. All components were dissolved and stirred in 2.5 mL of THF for an hour. Inversely, ionophore **III** needed to be dissolved in a small volume of chloroform before mixing with the solution of other components in THF because of its low solubility. The resulting clear mixture was then cast in a 30 mm-i.d. glass ring fixed on a glass plate. The solvent was allowed to slowly evaporate overnight at room temperature to give a transparent membrane (~0.2-0.3 mm thickness). The membrane was punched into 7.5 mm-i.d. discs and then conditioned overnight in 10^{-2} M of the primary ion solution before the measurements.

3.2.2 The EMF measurements

The conditioned membrane was attached to an electrode body. The electrode was then filled with the mixed internal solution of the primary anion (10^{-2} M) and

NaCl (10^{-3} M). The membrane potentials were measured at ambient temperature with the following galvanic cell:

Ag, AgCl/3 M KCl//1 M LiOAc// sample solution/ membrane/ inner filling solution (IFS)/AgCl, Ag

The reference electrode Ag/AgCl with double junction was used (type 6.0726.100, Metrohm AG, CH-9010 Herisau, Switzerland) with 1 M LiOAc as salt bridge electrolyte. Continuous EMF measurements were carried out with a 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA). EMF values for the ISEs versus reference electrode were measured in stirred solution in the concentration range from 10^{-7} M to 10^{-2} M. The activities of anions in aqueous sample solutions were calculated according to the Debye-Hückel approximation [50]. The detection limit was determined according to IUPAC recommendations.

3.2.3 Selectivity measurements

The potentiometric selectivity coefficients of the electrode for primary anion with respect to other interfering anions were determined by the separate solution method (SSM) as recommended by the IUPAC commission [27-29]. The membranes were conditioned in the solution of interfering anions (sodium or potassium salt) overnight. The potentiometric responses were measured in two separate solutions, one containing interfering anions (j) at the concentration range from 10^{-7} to 10^{-2} M, followed by the other containing primary anions (i) at the same concentration range. The mixed solution of the same interfering anion (10^{-2} M) and NaCl (10^{-3} M) was used as inner filling solution throughout the experiment. The pH 8.2 phosphate buffer and pH 4.4 acetate buffer solutions were employed for determination of the selectivity coefficients of primary anion against HCO_3^- and H_2PO_4^- as interfering anions, respectively.

3.2.4 UV-Visible spectrophotometric measurements

In order to investigate the interaction between the central metal of ionophore and the primary anion, UV-Vis spectrophotometric studies were carried out with the Agilent 8453 UV-Visible spectrophotometer. The ionophore (10 mmol kg^{-1}) was

dissolved in 2.5 mL THF in the presence of the optimal formulation of ion exchanger, PVC, and *o*-NPOE plasticizer in the total amount of 90 mg. The absorbance was then measured over the wavelength range of 400-850 nm. The ionophore-free solution in the same other components was used as a blank solution for absorbance measurements. Subsequently, the aqueous solution of primary anions was added to the ionophore solution to have the concentration of 1.0×10^{-3} M. The mixture was shaken thoroughly at least 5 minutes before measuring the absorbance of the resulting complex solution.

3.2.5 Effects of the solution pH

The effect of pH on membrane potentials was examined by measuring the EMF of the optimized ISE along with the pH of primary ion solutions. The pH of the solution was varied from 3 to 11 by gradually adding 2% HCl, followed by 0.01-0.10 M NaOH. The concentrations of the sample solution were varied from 10^{-4} to 10^{-2} M.

3.2.6 Reversibility

The membrane reversibility was observed by measuring the EMF of the optimized ISE in a 10^{-4} M primary ion solution. The electrode was then rinsed and immersed in a 10^{-3} M primary ion solution, and the potential was measured continually. The measuring cycle was repeated four times. The experiment was then repeated again for the reversibility of another two concentrations of primary ions, 10^{-3} and 10^{-2} M.

3.2.7 Electrode lifetime

After conditioning a membrane overnight in 10^{-2} M primary ion solution, EMF responses of the optimized electrode were recorded over the concentration range of 10^{-7} to 10^{-2} M primary anions. This procedure was repeated several times. The slopes and response potentials during a period of 60 days were recorded. The electrodes were kept in the dark after use.

3.3 Application of the optimized anion-ISE in real samples

The proposed anion-ISE was employed for determining the concentration of primary anions in real water samples; mineral water and tap water. The sample was filtered through the nylon 0.45 μm membrane and examined immediately. The recovery of primary ions in such water samples was explored by spiking primary ion solution into the sample to have the concentrations of 5.0×10^{-5} and 1.0×10^{-4} M. From the resulting EMF data, the concentrations of primary anions in spiked samples were compared with those in non-spiked samples and the percentage recoveries were then obtained.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Design and Syntheses of Ionophores

4.1.1 Design of ionophores

In this work, we have designed and synthesized three Cu(II) complexes possessing one and two Cu(II) centers in the structures for binding anions. Ionophore **I**, a mononuclear Cu(II) complex, was prepared by attaching the tripodal amine Cu(II) complex to the anthracene scaffold. Ionophores **II** and **III** consisted of *p*-*tert*-butylcalix[4]arene as a building block connecting to two units of Cu(II) TPA complexes with 2-alkoxybenzyl- and amide linkers, respectively. The structures of these ionophores were already presented in Chapter 1 (Figure 1.1).

In our previous observations while searching for a good carrier for Cd(II) selective membrane electrode [8], we found that calix[4]arenes containing tripodal amines (TPAs) formed very strong and non-reversible complexes with Cu²⁺ and the fabricated membrane electrode gave a negative potential response upon the addition of Cu(NO₃)₂. Therefore, we have expected that calix[4]arene-based tripodal amine Cu(II) complexes could be employed as anion carriers in polymeric membrane electrodes. The anthracene-based Cu(II) complex was also synthesized and examined using the potentiometric methods in order to compare the ion-carrier properties toward anions. Moreover, the optimal membrane formulation and membrane characteristics were explored in order to obtain a most suitable anion sensor.

4.1.2 Syntheses of ionophores

4.1.2.1 Synthesis of ionophore I

Simplified synthetic routes and percentage yields for ionophores **I-III** are summarized in Figure 4.1-4.3, respectively (the detailed syntheses and

characterization of all ionophores are outlined in Appendix A). The receptor molecule, **L1**, was prepared by the reaction between anthracene-9-carbaldehyde and tripodal amine [8]. Then the complexation between **L1** and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ gave green block-shaped single crystals of ionophore **I** in 73% yield (Figure 4.1(a)).

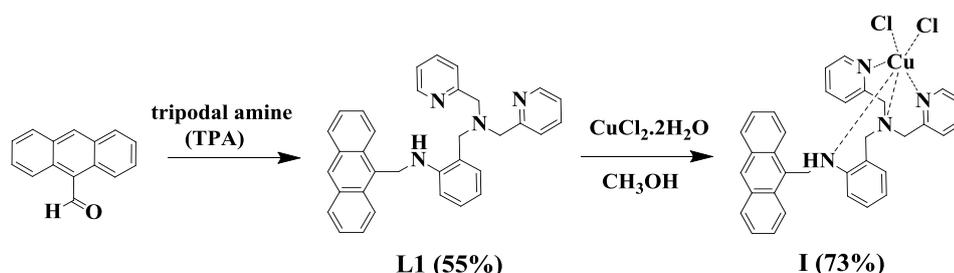


Figure 4.1 Synthetic routes of ionophore **I**.

X-ray crystal structure of this ionophore (see Appendix A, Figure A1) shows that the geometry around the Cu(II) center is best described as tetragonal structure with one chloride, a tertiary nitrogen atom, and two nitrogen atoms of pyridine rings occupying the equatorial coordination sites, and the secondary amine nitrogen atom together with the other chloride in the axial position. Due to the Jahn-Teller effect, the structure of **I** shows an elongated Cu-N(1) and Cu-Cl(2) bond distances of 2.541(2) Å and 2.791(3) Å, respectively along the axial position as compared to those of equatorial ligands: Cu-N(2) , 2.068(2) Å, Cu-N(3) 2.019(2) Å Cu-N(4) 2.012(2) Å and Cu-Cl(1) 2.273(2) Å.

4.1.2.2 Synthesis of ionophore **II**

Bis-calixaldehyde (**a**) [8, 51] was reacted with the tripodal amine (**b**), followed by reduction with NaBH_4 to yield **L2** in 20%. The HRMS-ESI spectrum of **L2** shows a parent peak at m/z 1521.8715 assigning to a molecular ion $[\text{L2}+\text{H}]^+$ and provides evidence that it was a 1:2 condensation product (see characterization data for **L2** in Appendix A). This calix[4]arene derivative is in a cone conformation, as supported by its NMR spectra (Appendix B, Figure B1 and B2). The ^1H NMR spectrum of **L2** shows a pair of doublets at 3.32 ppm and 4.43 ppm corresponding to the equatorial and axial protons of methylene bridging groups, respectively. The addition of CuCl_2

to **L2** in methanol gave a green complex of ionophore **II** in 42% (Figure 4.1(b)). The mass spectrum of **II** shows a parent peak at m/z 1751.6365 corresponding to the molecular ion of dinuclear complex $[\text{Cu}_2\text{L2Cl}_3]^+$.

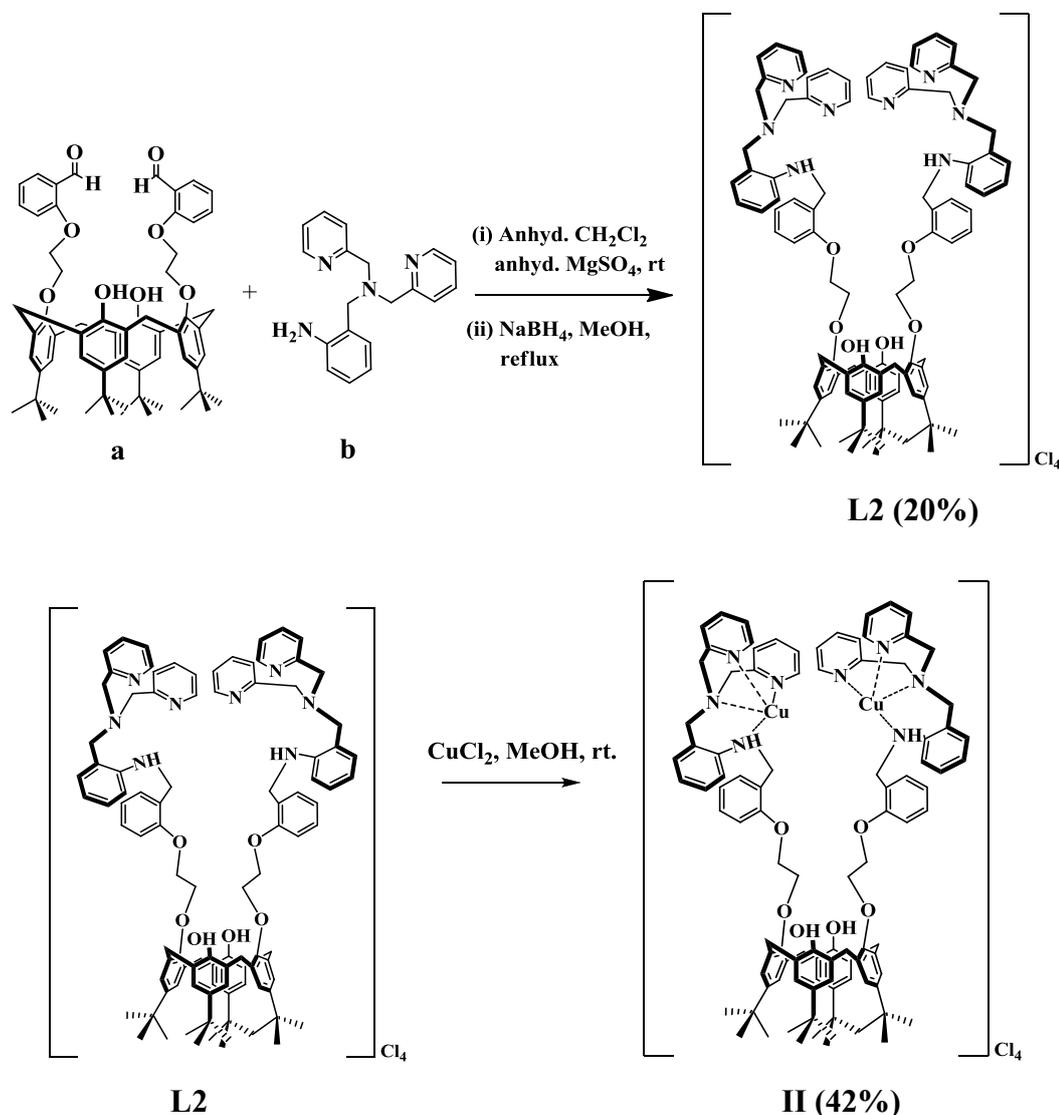


Figure 4.2 Synthetic routes of ionophore **II**.

4.1.2.3 Synthesis of ionophore **III**

Ligand **L3** was synthesized starting from the bis-ester derivative of *p*-*tert*-butyl calix[4]arene (**c**). The addition of 15% NaOH gave the diacid derivative (**d**), followed by reacting with SOCl_2 to obtain the bis-acid chloride (**e**). After that, the

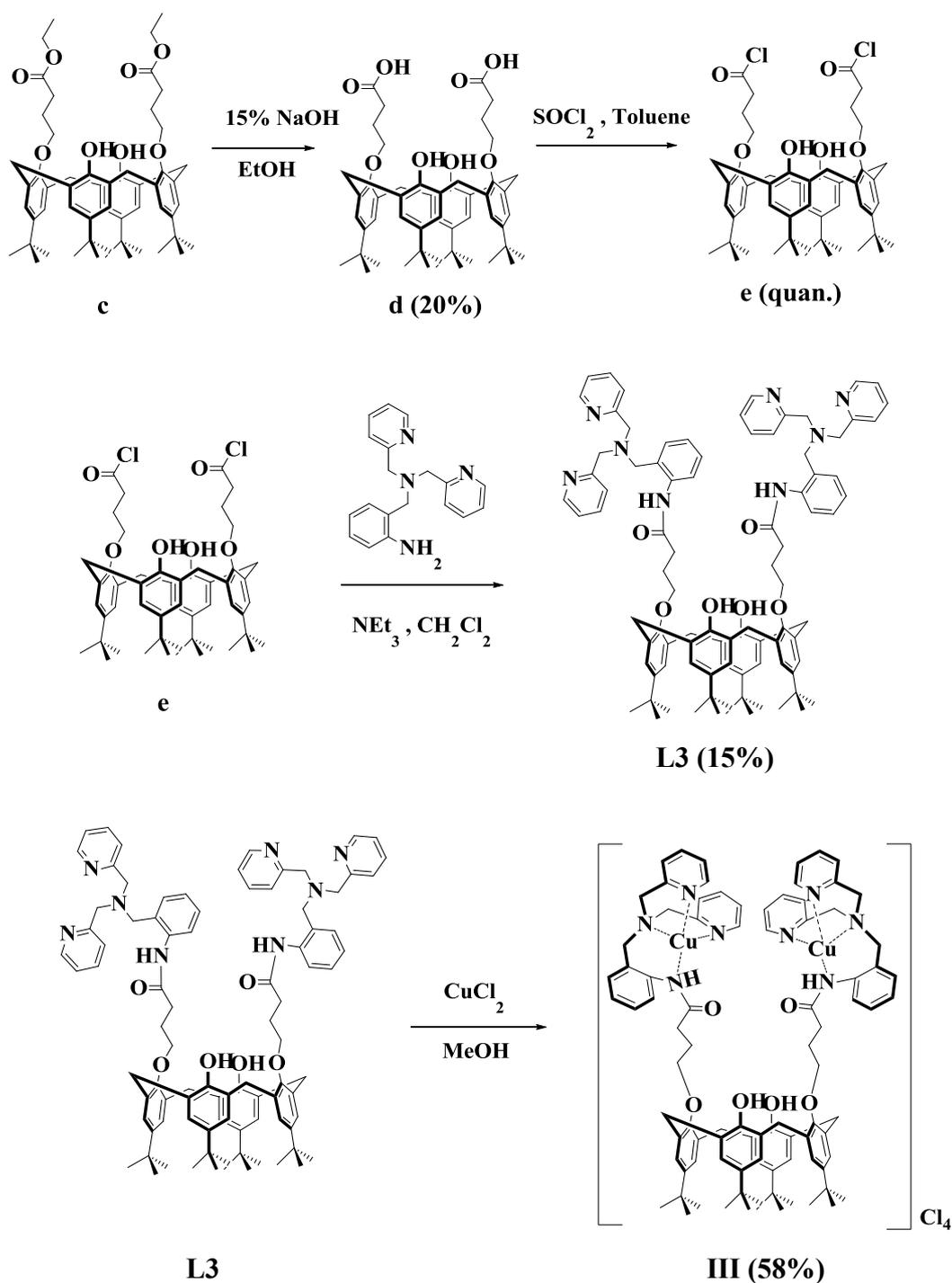


Figure 4.3 Synthetic routes of ionophore **III**.

coupling reaction between bis-acid chloride and tripodal amine yielded **L3** in 15%. The ^1H and ^{13}C -NMR data for **L3** clearly suggests the cone conformation of the calix[4]arene moiety (see Appendix A). The methylenic protons of $\text{Ar-CH}_2\text{-Ar}$ exhibit

two doublet peaks with an AB pattern at 3.31 and 4.33 ppm (1:1 ratio) with geminal coupling constant of 12.8 Hz. The sharp singlet peak at 10.75 ppm belongs to two -NH- amide protons (Appendix B, Figure B7 and B8). HRMS-ESI (positive mode) spectrum features a molecular ion of **L3** at $m/z = 1416.7935$ corresponding to $[\mathbf{L3}+\text{Na}^+]$. The addition of CuCl_2 into the methanolic suspension of **L3** gave the blue solution which was then left at room temperature for 24 hours. The blue solid of ionophore **III** was obtained in 58% yield (Figure 4.1(c)). HRMS-ESI spectrum of **III** shows the parent peak at $m/z = 1623.5339$ designating to the molecular ion of the dinuclear complex $[\text{Cu}_2\mathbf{L3Cl}_3]^+$.

4.2 Fabrication of polymeric membrane ISEs

Ionophore **II** has been previously studied as optical anion sensor and found to be able to detect pyrophosphate using indicator displacement method [51], which the anion recognition occurs in the aqueous system. Thus, we have been interested in examining anion-sensing properties of ionophore **II** and other newly synthesized ionophores, **I** and **III**, as electrochemical sensors using ion-selective membrane electrodes, which the ionophore is incorporated in polymer membrane but the target anion present in aqueous solution.

In experiments, our designed ionophores were incorporated into plasticized PVC membrane in the presence of ion exchangers for studying the effects of ionophore structures on the sensitivity and selectivity of electrodes toward anions. Moreover, two types of ion exchanger, *KTpCIPB* (as cation exchanger) and *TDMACl* (as anion exchanger), were used to observe the ion-transfer mechanism of the prepared membranes. In addition, the sensing characteristic of the fabricated electrode such as the working concentration range, limit of detection, working pH range, reversibility, as well as the application of the optimized electrode in real water samples were investigated.

4.2.1 Potentiometric anion responses

Polymeric membranes were prepared by controlling the ratio of PVC: *o*-NPOE plasticizer at 1:2 by weight, the concentration of ionophore at ca. 10 mmol kg^{-1} , and

varying the amounts of ion exchangers (10, 25, 50, and 75 mol% relative to the ionophore). A comparative study of properties of the synthesized ionophores **I-III** as anion-carriers in PVC was performed by measuring their potentiometric responses toward various anions (F^- , Cl^- , Br^- , I^- , SCN^- , ClO_4^- , NO_3^- , NO_2^- , OAc^- , SO_4^{2-} , HCO_3^- , and $H_2PO_4^-$). Each anion was separately tested without the presence of foreign anions, giving the calibration curves of all studied anions independent of each other. The difference in conditioning anion solutions and internal filling solutions of electrode caused the different background EMFs among these anions, suggesting that the EMF response gave information in terms of anion sensitivity but not yet selectivity.

EMF measurements of the electrodes containing ionophores **I**, **II**, and **III** in different membrane compositions were carried out compared to those of ionophore-free electrode. In preliminary studies, the ionophore-free membrane (based only on 25 mol% TDMACl as anion exchanger) was found to give a strong response toward lipophilic anions such as ClO_4^- , SCN^- , and I^- via ion-exchange mechanism whereas the incorporation of our synthesized ionophores into the membranes gave different results depending on the membrane compositions. Most membranes tended to respond to iodide better than other studied anions, considering from the most negative EMFs discriminating from other anions with a favorable slope in a wide linear concentration range. However, anion-carrier ability of each ionophore and also the optimal membrane composition needed to be attentively considered. For PVC membrane electrodes, it is well known that the type and percentage of each composition are essential parameters that influenced the sensing characteristics of the fabricated electrode. The membrane compositions and their electrode response properties are summarized in Table 4.1.

Figure 4.4 demonstrates the EMF responses of the promising membrane electrodes containing ionophores **I-III** in different types of ion exchangers. Without ion exchanger, the membrane comprising ionophore **I** was not response to most anions, but gave a response slope of $-31.0 \text{ mV decade}^{-1}$ to iodide while membranes using ionophores **II** and **III** gave responses close to theoretical Nernst's equation (-56.5 and $-67.0 \text{ mV decade}^{-1}$, respectively). Therefore, ion exchangers were added in order to reduce the membrane resistivity and improve the response characteristics

toward iodide ions [52]. The addition of cation exchanger, $KTpCIPB$, led to the inferior results, exhibiting the positive slopes of cation response instead of anion response. This is probably because of the induction of Na^+ or K^+ into the membrane faster than the transfer of anions. In the case of iodide, the cation response was mainly observed at the low activities of NaI , followed by the partial iodide response at its higher activities (Figure 4.4(a)). As a result, the cation exchanger was not suitable for fabricating iodide-ISE using ionophore **I**. The addition of anion exchanger, $TDMACl$, could enhance the iodide sensitivity. However, the slopes were improved when using anion exchanger in high quantities, the anion-transfer mechanism was therefore expected to perform mainly by the anion exchanger rather than the ionophore.

In the case of membranes containing ionophores **II** and **III** (Figure 4.4 (b, c)), they gave satisfying slopes (close to the Nernstian slope) of the iodide response. Moreover, it can be seen in Table 4.1 that the electrodes employing ionophores **II** and **III** exhibited the wider linear ranges compared to those of ionophore **I**, indicating the effectiveness of **II** and **III** as iodide carriers in PVC membranes. The membranes prepared from ionophores **II** and **III** also gave the lower detection limits of iodide in the micromolar range.

As mentioned above, potentiometric anion response could give information about sensitivity of individual anion without the presence of other anions. Therefore, the selectivity coefficient ($\log K_{I,j}^{pot}$) needed to be examined in order to study the effect of interfering ions on the selectivity of proposed membranes toward iodide, and also confirm the optimal membrane composition with the anti-Hofmeister behavior.

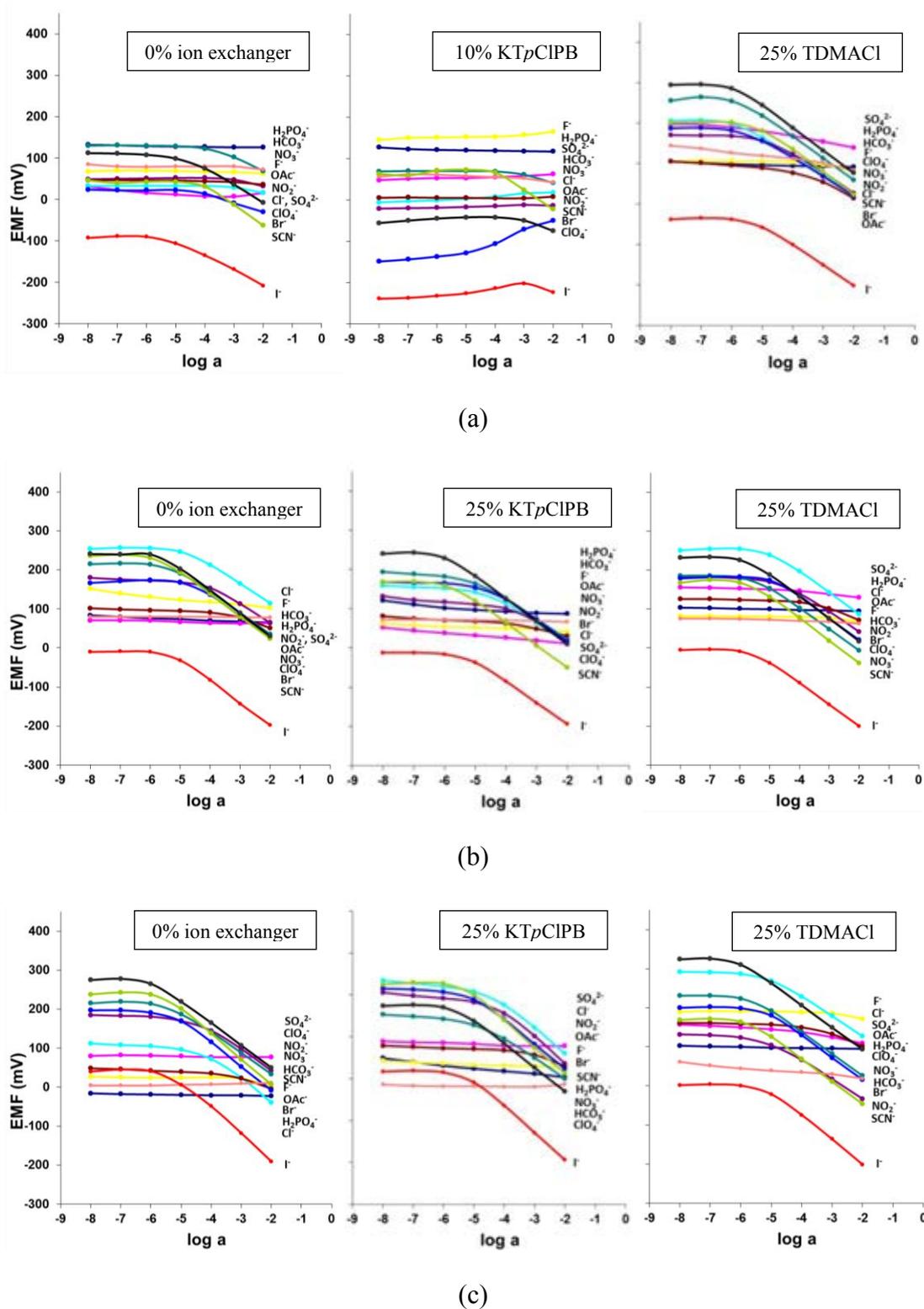


Figure 4.4 Potentiometric EMF responses of the promising membrane electrodes containing ionophores **I** (a), **II** (b), and **III** (c) in different types of ion exchangers (KTpCIPB = cation exchanger, TDMACI = anion exchanger).

Table 4.1 Membrane compositions and electrode response properties toward iodide.

Ionophore	Membrane composition				Slope (mV decade ⁻¹) (±SD, n = 3)	Linear range (M)	Detection limit (M)	
	Ionophore mg (mmol kg ⁻¹)	Ion exchanger		PVC mg (wt%)				Plasticizer <i>o</i> -NPOE mg (wt%)
		KT <i>p</i> CIPB mg (mol%)	TDMACl mg (mol%)					
I	1.39 (10.0)			72.92 (33.1)	146.40 (66.5)	-31.0 (1.3)	10 ⁻⁵ to 10 ⁻³	3.3 × 10 ⁻⁶
	1.39 (10.0)	0.10 (9.2)		73.20 (33.3)	146.89 (66.8)	10.6 (2.1)	10 ⁻⁵ to 10 ⁻³	4.0 × 10 ⁻⁶
	1.38 (10.0)	0.55 (50.4)		72.80 (33.1)	145.63 (66.2)	21.0 (1.5)	10 ⁻⁵ to 10 ⁻³	3.3 × 10 ⁻⁶
	1.39 (10.0)		0.13 (10.3)	72.95 (33.2)	146.22 (66.5)	-44.5 (1.4)	10 ⁻⁴ to 10 ⁻²	5.8 × 10 ⁻⁶
	1.38 (10.0)		0.30 (23.8)	73.11 (33.2)	146.87 (66.8)	-51.4 (0.4)	10 ⁻⁴ to 10 ⁻²	4.6 × 10 ⁻⁶
	1.40 (10.1)		0.63 (50.0)	72.79 (33.1)	146.92 (66.8)	-55.0 (0.4)	10 ⁻⁴ to 10 ⁻²	5.7 × 10 ⁻⁶
II	3.94 (10.0)			72.05 (32.8)	144.95 (65.9)	-56.5 (0.3)	10 ⁻⁵ to 10 ⁻²	4.5 × 10 ⁻⁶
	3.93 (10.0)	0.10 (9.2)		72.25 (32.8)	144.69 (65.8)	-54.4 (0.4)	10 ⁻⁵ to 10 ⁻²	4.0 × 10 ⁻⁶
	3.93 (10.0)	0.28 (25.6)		73.12 (33.2)	145.28 (66.0)	-53.4 (0.2)	10 ⁻⁵ to 10 ⁻²	4.7 × 10 ⁻⁶
	3.94 (10.0)		0.30 (23.8)	71.96 (32.7)	143.95 (65.4)	-54.9 (0.2)	10 ⁻⁵ to 10 ⁻²	3.3 × 10 ⁻⁶
	3.93 (10.0)		0.63 (50.0)	71.94 (32.7)	143.95 (65.4)	-56.0 (0.8)	10 ⁻⁵ to 10 ⁻²	3.0 × 10 ⁻⁶
	3.93 (10.0)		0.99 (78.6)	71.85 (32.6)	144.64 (65.7)	-56.0 (0.4)	10 ⁻⁵ to 10 ⁻²	4.1 × 10 ⁻⁶
III	3.67 (10.0)			72.25 (32.8)	144.97 (65.9)	-67.0 (0.1)	10 ⁻⁵ to 10 ⁻²	3.7 × 10 ⁻⁶
	3.66 (10.0)	0.11 (10.1)		72.35 (32.9)	144.23 (65.6)	-62.7 (1.8)	10 ⁻⁵ to 10 ⁻²	4.5 × 10 ⁻⁶
	3.67 (10.0)	0.27 (24.7)		72.27 (32.8)	145.98 (66.4)	-63.0 (0.0)	10 ⁻⁵ to 10 ⁻²	5.1 × 10 ⁻⁶
	3.67 (10.0)		0.32 (25.4)	72.21 (32.8)	144.59 (65.7)	-61.3 (0.7)	10 ⁻⁵ to 10 ⁻²	4.6 × 10 ⁻⁶
	3.67 (10.0)		0.63 (50.0)	72.04 (32.7)	144.28 (65.6)	-59.5 (1.0)	10 ⁻⁵ to 10 ⁻²	3.5 × 10 ⁻⁶
	3.66 (10.0)		0.94 (74.6)	72.43 (32.9)	144.71 (65.8)	-57.9 (2.3)	10 ⁻⁵ to 10 ⁻²	6.1 × 10 ⁻⁶

4.2.2 Iodide selectivity and structure-selectivity relationship

Potentiometric selectivity is the most crucial characteristic of ISEs and plays an important role in the development of membrane electrodes. Basically, in the presence of foreign ions, the effective ionophore should have preferable selectivity toward primary ion over such interfering ions without biased signals. In this work, the selectivity coefficients of the electrode for iodide with respect to other common anions were determined by the separate solution method (SSM) as recommended by IUPAC [27-29]. Figure 4.5 shows potentiometric selectivity coefficients ($\log K_{I,j}^{pot}$) of polymeric membranes containing ionophores **I-III**, in different types and amounts of ion exchangers. Comparison of the $\log K_{I,j}^{pot}$ values for all membrane compositions are summarized in Appendix C.

Anion selectivity of the membrane based on anion exchanger (without ionophores) was controlled only by the lipophilicity of anions, considering from their hydration energies. The weakly-hydrated anions could easily get into the organic polymer membrane via an ion-exchange mechanism between such anions and anion exchangers in the membrane. The ionophore-free membrane (containing only 25 mol% TDMACl) showed the following order of selectivity: $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{HCO}_3^- > \text{OAc}^- \sim \text{Cl}^- \sim \text{F}^- > \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-}$, and has been compared to the selectivity orders of the membranes employing our proposed ionophores. The results in Figure 4.3 indicates that the electrode based only on ionophore **I** exhibited a very low selective to iodide with a strong interference by most studied anions, seeing from the $\log K_{I,j}^{pot}$ values close to each other. The addition of cation exchanger (KTpCIPB) led to a drastic loss of membrane selectivity toward anion, resulting from a strong induction of cations into the membrane by KTpCIPB which corresponded to the positive slopes of iodide response in Table 1. The addition of anion exchanger, TDMACl, could improve the membrane selectivity. However, the selectivity orders were not significantly different between the ionophore-free membrane and the ionophore **I**-doped membrane, suggesting that TDMACl played a key role in transferring iodide across the membrane because of its high lipophilicity, not the ion carrier function. In agreement with the results in Figure 4.4 and Table 1, ionophore **I**

was not a good carrier for iodide. On the other hand, membranes containing ionophores **II** and **III** showed the similar results in selectivity. Only a slight difference in the order of basic anions such as H_2PO_4^- and HCO_3^- in which the membrane containing ionophore **III** showed higher selectivity order than that of the membrane containing ionophore **II**. The $\log K_{I,j}^{pot}$ values for most studied anions were much lower compared to iodide, indicating strong interactions between such compounds and iodide even in the absence of ion exchangers.

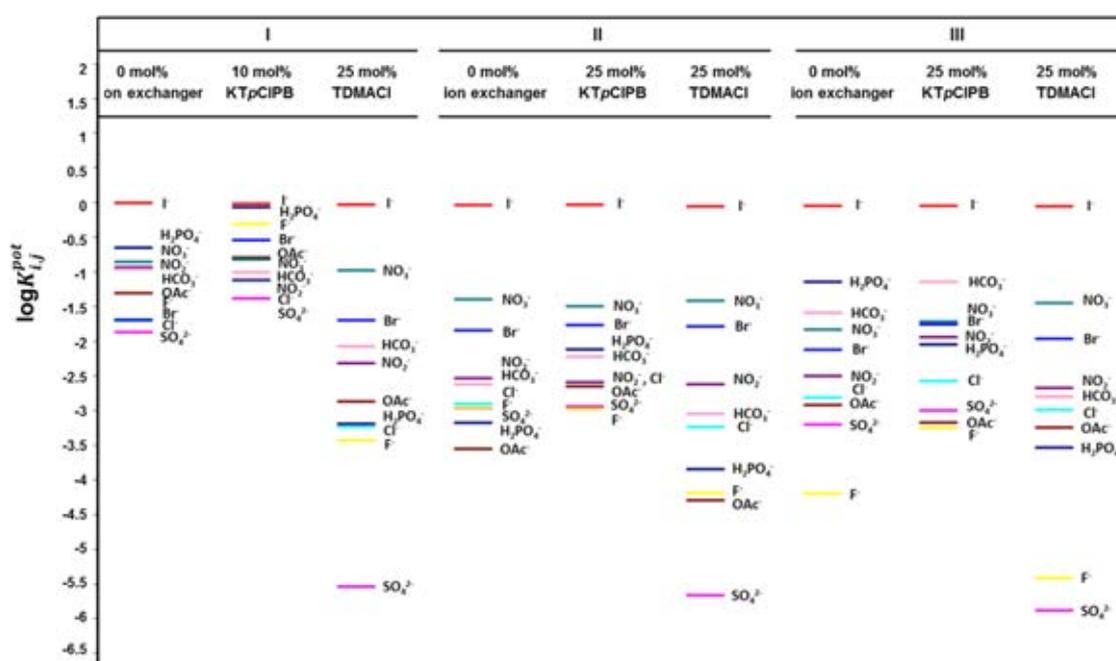


Figure 4.5 Potentiometric selectivity coefficients ($\log K_{I,j}^{pot}$) of membrane electrodes containing ionophores **I-III** in different types and amounts of ion exchangers.

However, strong interferences of ClO_4^- and SCN^- on the iodide selectivity were still commonly observed due to their high lipophilicity and preference to penetrate into the membrane phase. In contrast, the presence of the anion exchanger gave the better selectivity toward I⁻ discriminating from most interfering anions. This signified the importance of two copper centers in both ionophores **II** and **III** and also the anion exchangers added. Moreover, high amounts of the anion exchanger (50 and 75 mol% TDMACI) did not improve the membrane selectivity, but increased the level

of interference by ClO_4^- . Therefore, it was concluded that the membranes employing ionophores **II** and **III** in the presence of 25 mol% TDMACl were suitable for the fabrication of iodide-ISEs.

Structures of ionophores have a strong influence on ion-sensing properties of ISEs. The ion carrier should be generally long-lasting stable in organic polymer membranes and also possess a recognition unit that can reversibly interact with a particular ion discriminating from other ions presented in the sample. In this study, ionophore **I** was demonstrated to function improperly as the iodide carrier in the membrane. The structure of ionophore **I** possessing only one side-arm of the ion receptor unit may not be able to bind iodide effectively, as seen in the requirement of high amounts of the anion exchanger to achieve a Nernstian slope, but the narrow linear concentration range was obtained. Thus, ionophore **I** would not be further studied due to its unfavorable sensitivity and selectivity toward iodide.

Ionophores **II** and **III**, however, showed satisfying results compared to ionophore **I**. The better iodide response was obtained for most membrane compositions even in the absence of the ion exchangers, suggesting that two side-arms of the ion receptor unit probably allowed a stronger coordination of I^- to two copper centers. It was previously reported that the distance between two copper centers would play an important role in anion selectivity [53-55]. Moreover, the side arms attached to the *p-tert*-butylcalix[4]arenes could help controlling the cavity size for the entering of anion guests [56-58]. In the case of ionophore **II**, as mentioned previously, the dinuclear Cu(II) complex was an excellent sensor for pyrophosphate using IDA strategy. The distance between two Cu(II) centers was clearly suitable for the entering of pyrophosphate [51]. However, we found that pyrophosphate did not response to our fabricated membranes at all probably due to its high hydration energy, while iodide could be transferred across the polymer membrane using ionophores **II** and **III** as effective charged carriers. The membrane containing **II** was found to be highly selective towards iodide over other anions.

4.2.3 Response time, working pH range, and reversibility of the membranes prepared from ionophores II and III

The response time of electrode is also an important characteristic of ISEs. The fabricated iodide-ISEs incorporating ionophores **II** and **III** showed a fast response time of less than 5 seconds before reaching a stable EMF value as seen in Figure 4.6. In addition, the potentials were very stable after changing the concentration that indicates a good property of the ISE. However, the EMF signals seemed to gradually decrease over time especially at the high concentrations of iodide for the electrode doped with ionophore **III** (Figure 4.6 (b)).

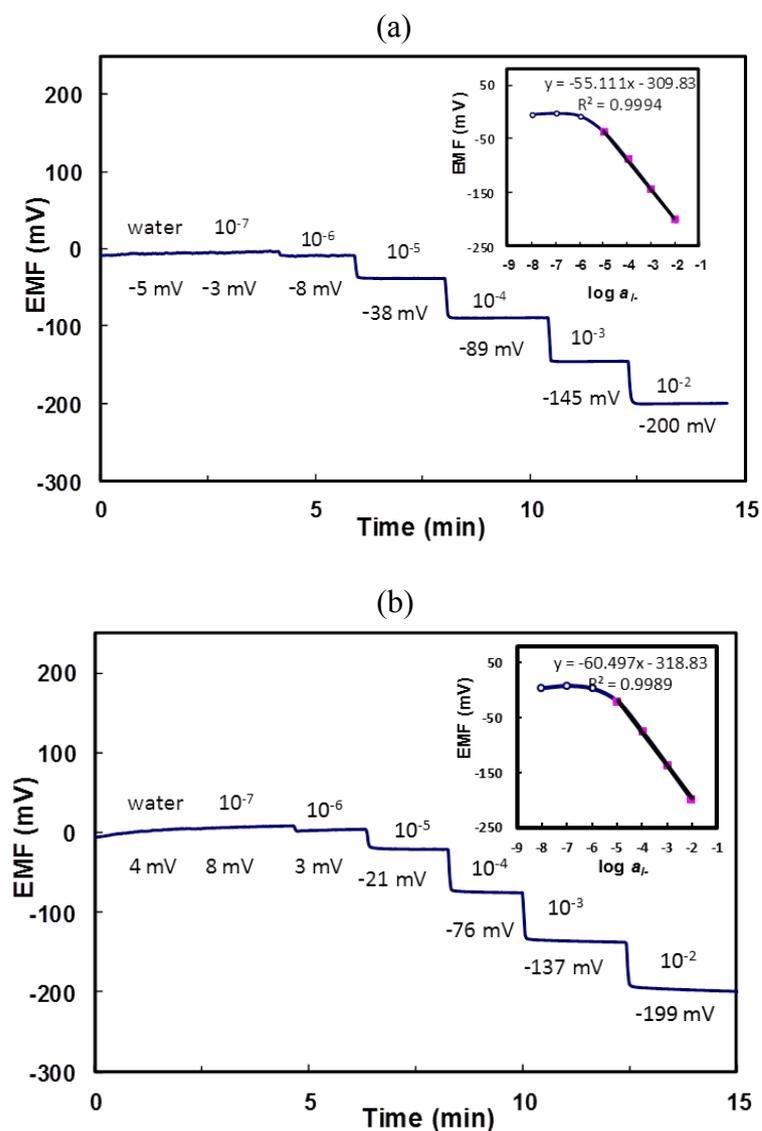


Figure 4.6 Time-dependent response of iodide-ISEs using ionophore **II** (a) and **III** (b)

In order to explore the working pH range of the proposed iodide-selective electrodes, the experiments were carried out over the pH range of 3.0-11.0 using iodide concentrations of 10^{-4} , 10^{-3} , and 10^{-2} M. The pH was adjusted by introducing small drops of 2% HCl followed by 0.01-0.10 M NaOH. Interestingly, although two compounds gave the similar results in sensitivity and selectivity, the EMF signals in variable pH media were significantly different (see Figure 4.7). The electrode response of ionophore **II** toward iodide was independent of pH in the wide range of 4.7-8.6 while the narrow pH range of 4.2-5.8 was observed in the case of ionophore **III** (Figure 4.7 (b)). The latter resulted from a pH-sensitive carbonyl group present in compound spacer that could allow the protonation or reaction with hydroxide depending on the pH of solution, and therefore affected the EMF signals of iodide.

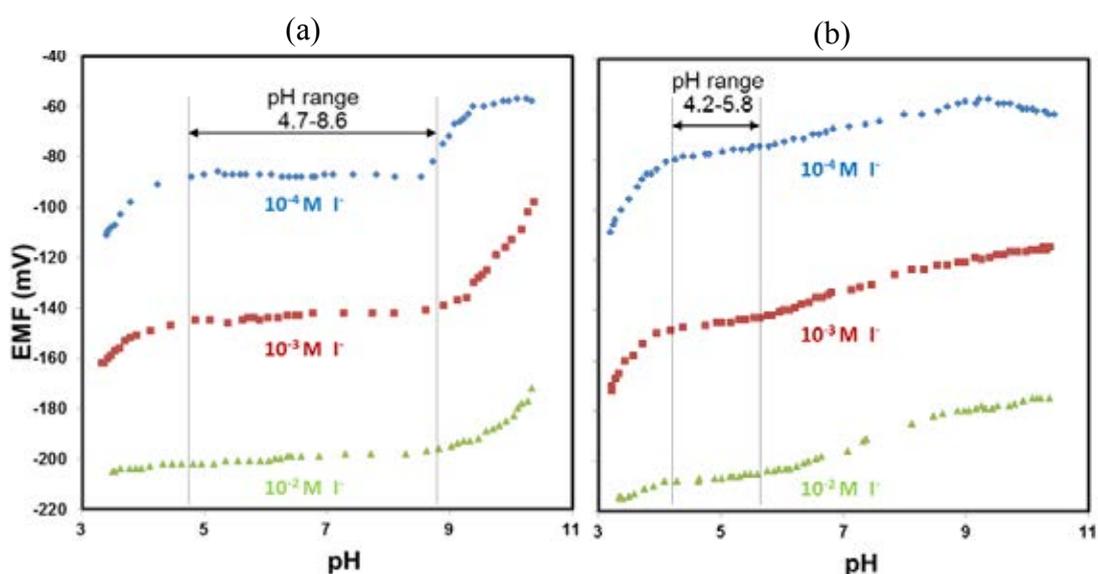


Figure 4.7 The pH effect on EMF signals of the optimized electrodes containing ionophores **II** (a) and **III** (b).

The reversibility of electrode is another important factor that represents the precision of the detection. In the experiments, the optimized iodide electrodes containing compounds **II** and **III** were used to measure the EMF values of two different concentrations of iodide alternatively. As seen in Figure 4.8, the observed reversibility at ambient temperature was excellent, considering from the EMF signals that could be restored at the same concentration in every measuring cycle.

Nevertheless, the signals gradually changed with the time for compound **III**, giving the unstable reversibility of electrode corresponding to the result of pH effect.

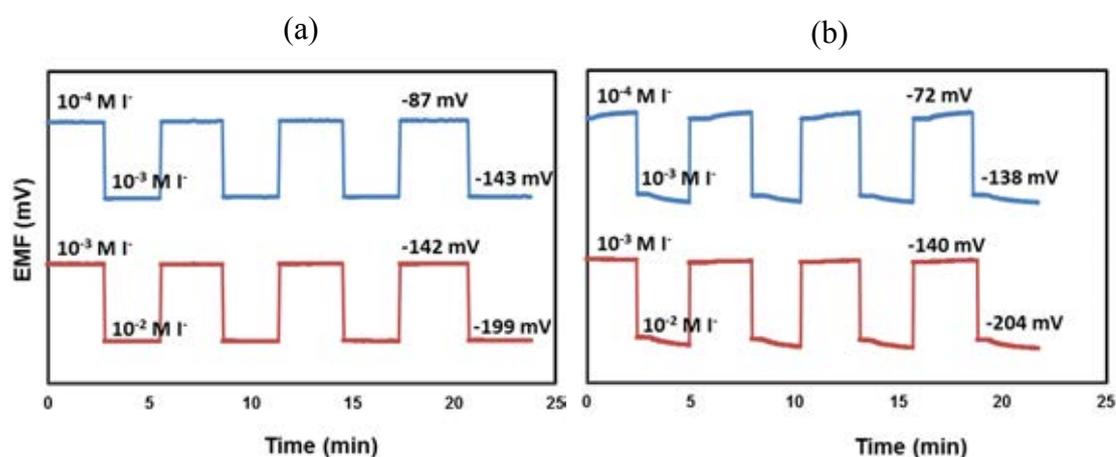


Figure 4.8 Reversibility of iodide-ISEs containing ionophores **II** (a) and **III** (b) at different concentrations.

4.2.4 UV-Vis spectrophotometric studies

It was expected that the successful iodide response resulted from the interaction between the two copper ions of ionophore **II** and iodide. Therefore, we carried out UV-Vis spectrophotometric studies in order to investigate this interaction, and the resulting absorption spectra are presented in Figure 4.9. The solution of **II** in THF in the presence of the ionic exchanger and the polymer matrix exhibited two absorption bands at 451 and 719 nm in the visible region. It was found that, the addition of 10^{-3} M iodide led to the disappearance of the band at 451 nm while the weak d-d transition band at 719 nm was shifted to 650 nm, indicating the coordination of I^- to the Cu(II) centers, which affected the energy gap in d-d splitting of the central Cu(II) ions in ionophore **II**. The color change of the solution from light green to yellow brown after adding iodide solution was also obtained. These results agreed well with those of the previous research [59-60] that the spectral shifts were observed after contacting the ionophore solution with the phase containing iodide ions, suggesting the preferred coordination of iodide to the central metal of **II**. The new

absorption bands and the increase in absorbance also appeared with the increasing concentration of iodide.

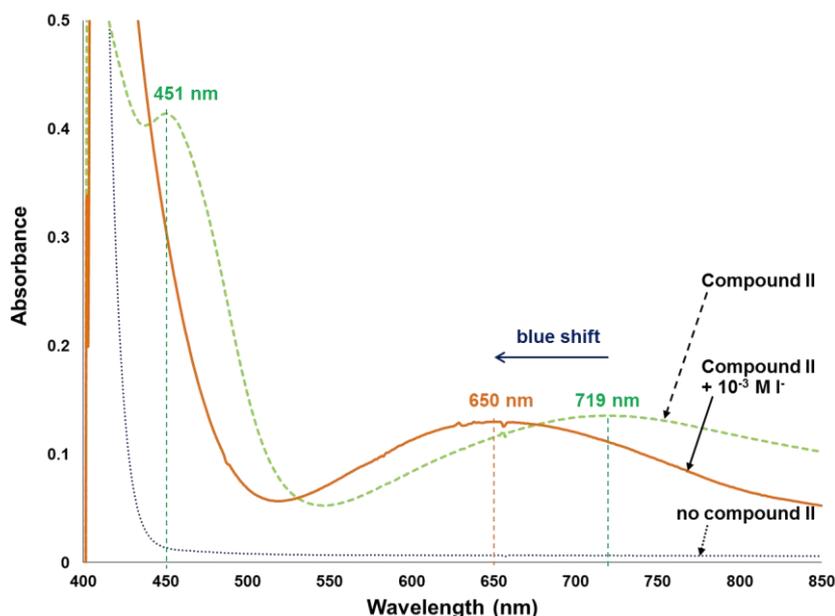


Figure 4.9 UV-Vis absorption spectra of ionophore **II** in THF in the presence of the ionic additive, PVC, *o*-NPOE and the spectral change upon addition of iodide.

4.2.5 Complex formation constant and electrode lifetime

The method for calculating the complex formation constant between primary ions and ionophores in plasticized PVC membrane electrodes is based on the segmented sandwich membrane approach as proposed by Bakker and co-workers [61-63]. The preparation of sandwich membranes and the equation for calculating the ion-ionophore complex formation are demonstrated in Appendix D. In this work, we carried out the experiments to determine the formation constant between I^- and ionophore **II** assuming a 1:1 ion-ionophore stoichiometry. The time response behavior of a two-layer sandwich membrane containing ionophore **II** in the segment facing the 10^{-2} M iodide solution over 3 hours was observed and is shown in Appendix D, Figure D1. The iodide-ionophore **II** complex formation constants ($\log \beta_{Ln}$) of 8.47 ± 0.11 (triplicate experiments) were obtained, indicating a strong and stable complex between our synthesized ionophore **II** and iodide.

Lifetime of the fabricated polymeric membrane electrode is examined since the membrane components may leach or decompose by contact with the measuring or conditioning solutions. The experiments were performed by repeatedly calibrating the same electrode until the slopes of anion response significantly deviate from the first measurement.

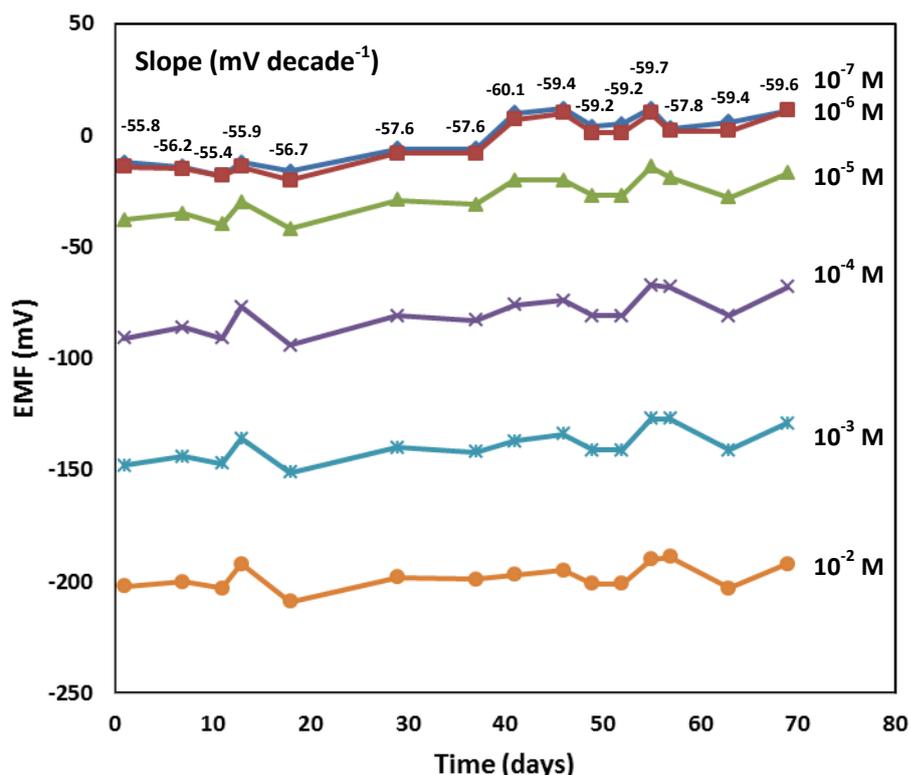


Figure 4.10 Lifetime of the optimized iodide-ISE using ionophore **II**.

As shown in Figure 4.10, the EMF values and also slopes of the optimized iodide-ISE incorporating ionophore **II** were still close to the Nernstian slope and insignificantly changed until 69 days of measurements, suggesting that our optimized electrode could be effectively employed as iodide sensor at least 2 months.

4.3 Application of the optimized iodide-ISE in real water samples

The possibility of using the optimized iodide-ISE containing ionophore **II** in monitoring the concentration of iodide in real water samples was explored. The water samples (mineral water and tap water) were filtered through the nylon 0.45- μm

membrane and freshly examined. The results are summarized in Table 4.2. After spiking standard iodide solution at the concentrations of 5.0×10^{-5} and 1.0×10^{-4} M into the water samples, the percentage recoveries ranging from 81 to 103 % were obtained. These satisfying recoveries showed the accuracy of the electrode and the constituents of the water samples did not significantly interfere in the detection of iodide. In addition, the percentage RSD values for 3 measurements were in acceptable range which confirmed the precision of the detection method.

Table 4.2 Determination of Γ^- in real water samples (n=3) using the electrode fabricated from **II** and 25 mol% of TDMACl.

	Γ^- added ($\times 10^{-5}$ M)	Γ^- found ($\times 10^{-5}$ M \pm SD)	% Recovery \pm SD	% RSD
Mineral water	-	n.d.	-	-
	5.0	5.59 ± 0.13	103 ± 3	2.6
	10	9.72 ± 0.39	93 ± 4	4.2
Tap water	-	n.d.	-	-
	5.0	4.58 ± 0.21	81 ± 4	5.3
	10	9.14 ± 0.38	86 ± 4	4.4

n.d. = not detectable.

CHAPTER V

CONCLUSION

Tripodal amine anthracene- and calix[4]arene-based Cu(II) complexes, compounds **I-III**, were successfully synthesized and used as iodide carriers in polymeric membrane electrodes. Compounds **II** and **III** were very good iodide carriers in PVC membrane electrodes, showing great sensitivity and selectivity toward iodide while compound **I** could not function properly as an iodide carrier. These results suggested that the dinuclear copper(II) centers could bind iodide and were more effective iodide-carrier units than the mononuclear copper(II) complex. Two symmetrical tripodal amine groups on the calix[4]arene framework, along with the assistance of 2-alkoxybenzyl linker, forced two Cu(II) centers to rearrange in a suitable geometry for complexing with iodide. As a result, the best iodide-selective electrode was achieved when using ionophore **II** and 25 mol% TDMACl as anion exchanger in the PVC membrane plasticized with *o*-NPOE 1:2; PVC:*o*-NPOE by weight). This electrode could be used over a wide pH range of 4.7-8.6 with great reversibility, and also applied to determine the concentration of iodide in real water samples with favorable recoveries.

Suggestion for future works:

In this research, the optimized iodide-selective electrode gave the limit of detection in micro-molar range that still could not be compared to the commercial electrode. Therefore, the inner filling solution should be optimized by lowering the concentrations of iodide in order to obtain the detection limit down to sub-micromolar range which would be successfully and effectively employed in the future for real applications. The problem of strong interference by lipophilic ClO_4^- and SCN^- should be resolved. The design of other types of ionophores that are more selective to iodide may be considered together with the optimization of proposed electrodes.

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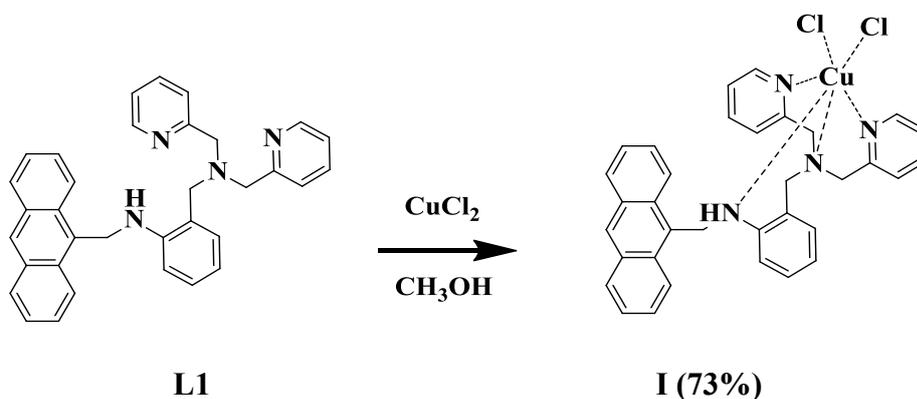
APPENDICES

Appendix A

Syntheses of ionophores I-III

1. Synthesis of Ionophore I

The solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in CH_3OH was added to the suspension of methanolic solution of **L1** [8] giving a deep green solution. The solution was allowed to stand at room temperature for 1 week to obtain green block-shaped X-ray diffraction quality single crystals of ionophore **I** (85 mg, 73%).



Characterization data for ionophore **I**:

ESI-MS (positive mode): $[\text{CuL}_1\text{Cl}]^+$ Calcd for $\text{C}_{34}\text{H}_{30}\text{CuClN}_4$, 592.1455; Found, 592.1460.

X-ray crystallographic data: Cu-N(1) 2.541(2) Å, Cu-Cl (2) 2.791 (3) Å, Cu-N(2) 2.068 (2) Å, Cu-N(3) 2.019 (2) Å Cu-N(4) 2.012(2) Å and Cu-Cl(1) 2.273(2) Å.

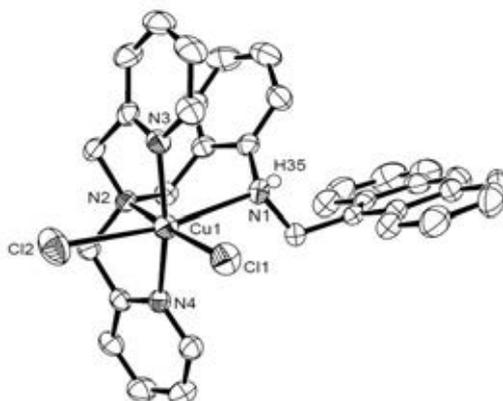


Figure A1. X-ray crystal structure of ionophore **I**.

Table A1. Crystallographic data and final refinement parameters for ionophore **I**.

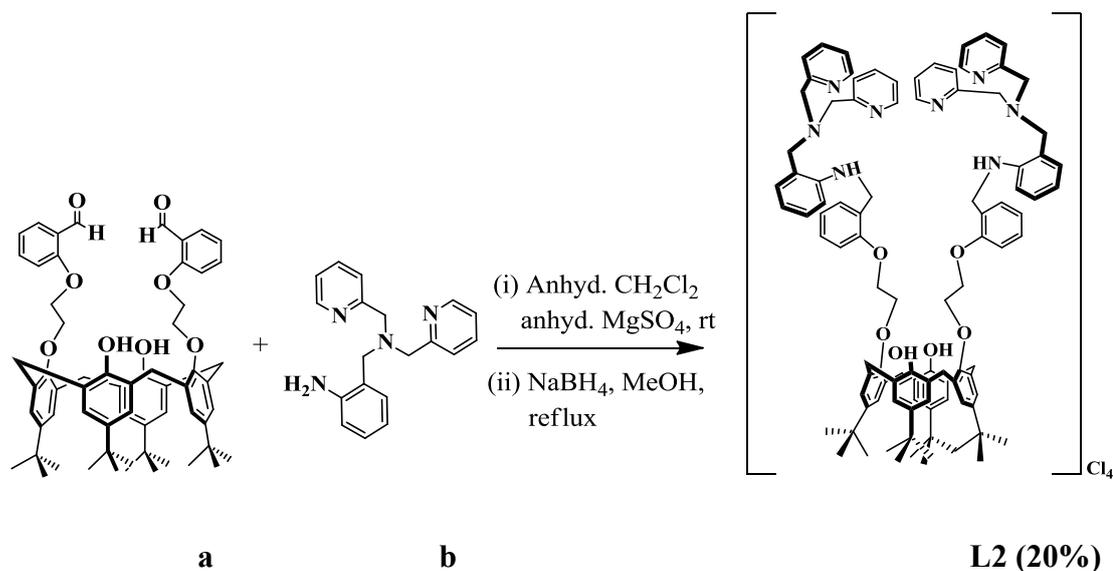
	Compound I
Chemical formula	C ₃₅ H ₃₄ Cl ₂ CuN ₄ O
Formula weight	661.10
Crystal size	0.26 × 0.3 × 0.32
Colour	Green
Temperature (K)	293(2)
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	15.9666(4)
<i>b</i> (Å)	13.5534(4)
<i>c</i> (Å)	28.1590(8)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	6093.7(3)
<i>Z</i>	8
ρ_{calc} (g cm ⁻³)	1.441
μ (mm ⁻¹)	0.928
<i>F</i> (000)	2744

θ range for data collection	1.45 to 28.02°
Index ranges	-21 ≤ h ≤ 21
	-17 ≤ k ≤ 17
	-37 ≤ l ≤ 37
Reflections collected / observed	69843 / 7366
	[$R(\text{int}) = 0.0975$]
Data / restraints / parameters	7366 / 0 / 408
Goodness-of-fit on F^2	1.166
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0721$, $wR_2 = 0.1226$
R indices (all data)	$R_1 = 0.1025$, $wR_2 = 0.1325$
Largest diff. peak and hole ($e^- \text{ \AA}^{-3}$)	0.450 and -0.462

2. Synthesis of Ionophore II

2.1. Synthesis of L2

The solution of compound **a** in dried CH_2Cl_2 was added to a suspension of anhydrous MgSO_4 in CH_2Cl_2 with the tripodal amine, **b**. The reaction mixture was stirred for 12 h under nitrogen atmosphere and the imine product was obtained as a dark solid in a quantitative yield. The imine was dissolved in MeOH, and the solution was cooled to -5 °C. Subsequently, NaBH_4 was added to the brown solution, and the mixture was refluxed for 12 hours under N_2 atmosphere. The crude product was then purified by column chromatography (SiO_2) using 20% MeOH in EtOAc to obtain yellow oil. After recrystallizing in diethyl ether, **L2** was obtained as a white solid (0.85 g, 20%).



Characterization data for **L2**:

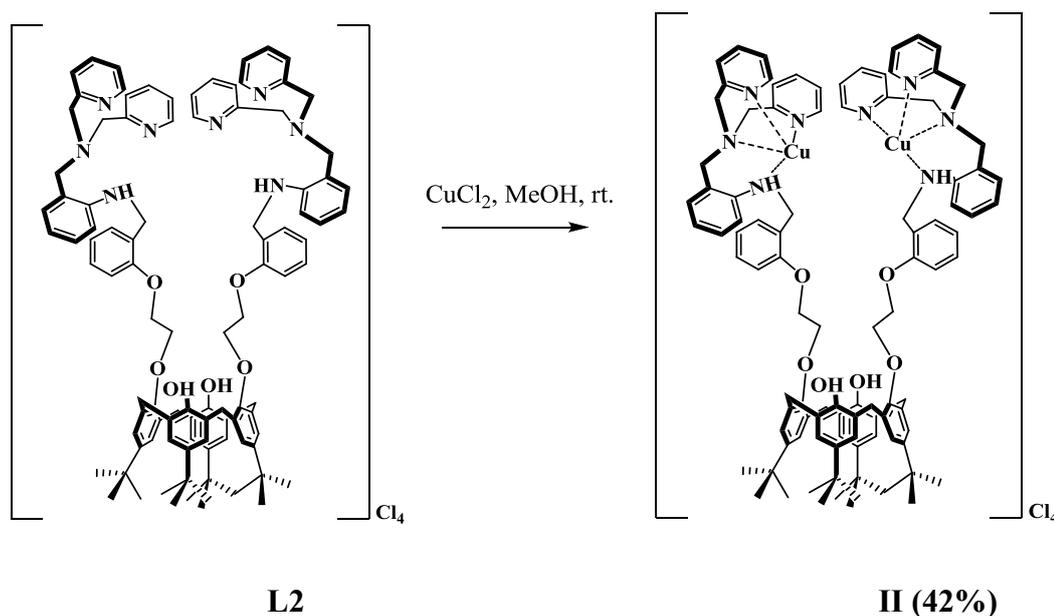
^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.42 (d, 4H, $J = 4$ Hz, ArH), 7.91 (s, 2H, ArOH), 7.65 (d, 2H, $J = 2.4$ Hz, ArH), 7.46 (m, 4H, ArH), 7.35 (d, $J = 7.6$ Hz, 2H, ArH), 7.30 (s, 4H, ArH), 7.19 (m, 2H, ArH), 7.06 (m, 8H, ArH), 7.05 (m, 2H, ArH), 6.95 (d, 4H, $J = 8.4$ Hz, ArH), 6.89 (s, 4H, ArH), 6.86 (d, 2H, $J = 7.2$ Hz, ArH), 6.72 (s, 2H, -NH-), 6.54 (m, 2H, ArH), 6.44 (d, 2H, $J = 8$ Hz, ArH), 4.53 (d, 4H, $J = 4.8$ Hz, $-\text{CH}_2\text{-NH}-$), 4.44 (d, 4H, $J = 12.8$ Hz, Ar- $\text{CH}_2\text{-Ar}$), 4.35 (s, 8H, $-\text{CH}_2\text{-O}-$), 3.80 (s, 8H, $-\text{CH}_2-$), 3.68 (s, 4H, $-\text{CH}_2-$), 3.33 (d, 4H, $J = 13.2$ Hz, Ar- $\text{CH}_2\text{-Ar}$), 1.26 (s, 18H, *p*-*tert*-butyl), 1.03 (s, 18H, *p*-*tert*-butyl).

^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 159.23, 156.24, 150.35, 149.73, 149.07, 148.21, 147.34, 141.69, 136.29, 133.12, 130.97, 128.77, 128.56, 128.52, 127.93, 127.63, 125.72, 125.20, 123.20, 121.91, 121.55, 120.71, 115.35, 110.78, 110.32, 74.16, 66.65, 60.16, 58.47, 41.76, 34.04, 33.84, 31.83, 31.66, 31.10.

HRMS-ESI (positive mode, m/z): [**L2** + H] $^+$ Calcd for $\text{C}_{100}\text{H}_{112}\text{N}_8\text{O}_6$, 1521.8705; Found, 1521.8715.

2.2 Synthesis of ionophore II

The methanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added to the methanolic suspension of **L2** then the color of solution changed to deep green immediately. After standing the green solution at room temperature for 1 week, the obtained deep green solid filtered and washed with MeOH to yield ionophore **II** in 42% (111 mg).



Characterization data for ionophore **II**:

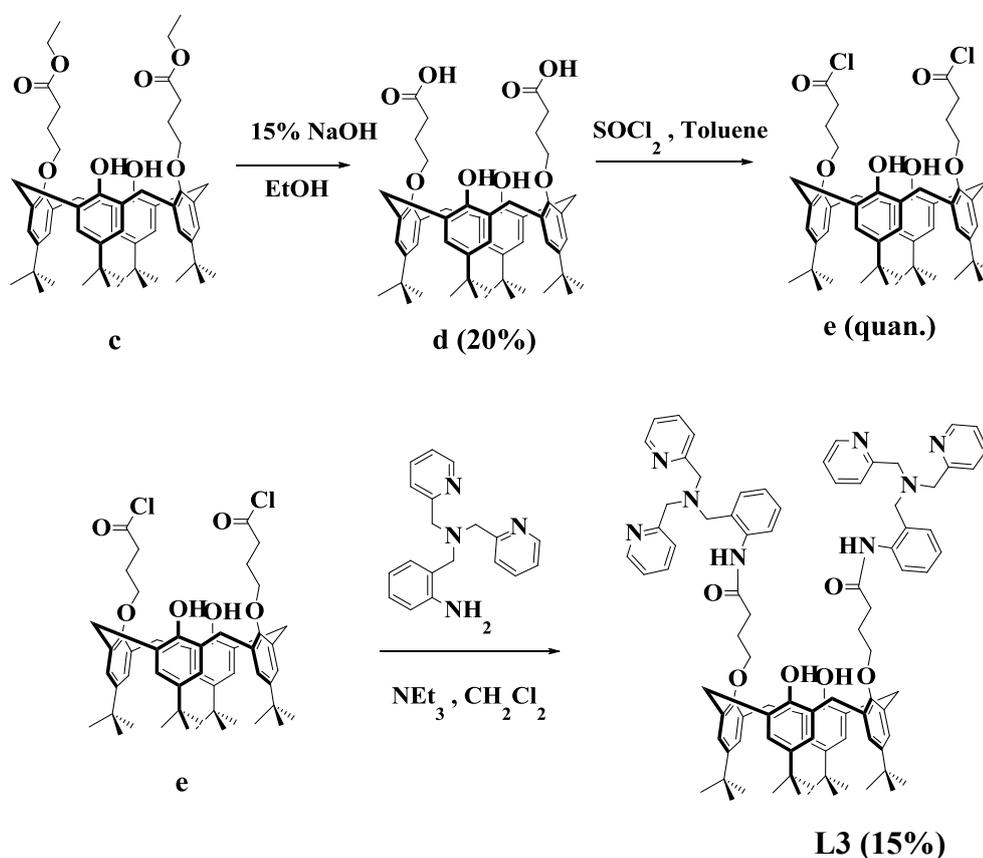
HRMS-ESI (positive mode, m/z): $[\text{Cu}_2\text{L2Cl}_3]^+$ Calcd for $\text{C}_{100}\text{H}_{112}\text{Cl}_3\text{Cu}_2\text{N}_8\text{O}_6$, 1751.6362; Found, 1751.6365.

3. Synthesis of Ionophore III

3.1. Synthesis of L3

The receptor molecule, **L3**, was synthesized in three steps starting from the bis-ester derivative of *p-tert*-butyl calix[4]arene (**c**) Upon addition of 15% NaOH into the solution of compound **c**, the diacid derivative (**d**) was obtained in 20% yield. The calix[4]arene acid chloride derivative (**e**) was synthesized by reacting the diacid derivative (**d**) with SOCl_2 in toluene.

A solution of tripodal amine, **b**, and Et₃N was stirred in dry CH₂Cl₂ under nitrogen. Diacid chloride (**e**) in dry CH₂Cl₂ was added dropwise to the reaction mixture. A white precipitate was formed and stirring was continued for 72 hours at room temperature. The white solid was filtered, and the filtrate was concentrated to dryness. The crude solid was dissolved in CH₂Cl₂, washed with water, and then with brine. The organic layer was dried with anhydrous MgSO₄. Filtrate was concentrated to dryness. The crude product was subjected to chromatography on a silica gel column using 2% MeOH in CH₂Cl₂ as eluent to give a white solid of **L3** (1.85 g, 15%).



Characterization data for **L3**:

¹H-NMR (400 MHz, CDCl₃, ppm): δ 10.75 (s, 2H, -OH), 8.54 (d, 4H, *J* = 0.8 Hz, ArH), 8.33 (d, 2H, *J* = 8 Hz, ArH), 7.52 (m, 4H, ArH), 7.42 (s, 2H, -NH), 7.22 (d, 6H, *J* = 7.6 Hz, ArH), 7.13 (d, 2H, *J* = 7.2 Hz, ArH), 7.06 (m, 8H, ArH), 6.99 (m, 2H, ArH), 6.79 (s, 4H, ArH), 4.33 (d, 4H, *J* = 12.8 Hz, Ar-CH₂-Ar), 4.10 (t, 4H, *J* = 6.4 Hz, -CH₂-), 3.76 (s, 12H, -CH₂-), 3.31 (d, 4H, *J* = 12.8 Hz, -CH₂-), 2.92 (t, 4H, *J* = 7.2

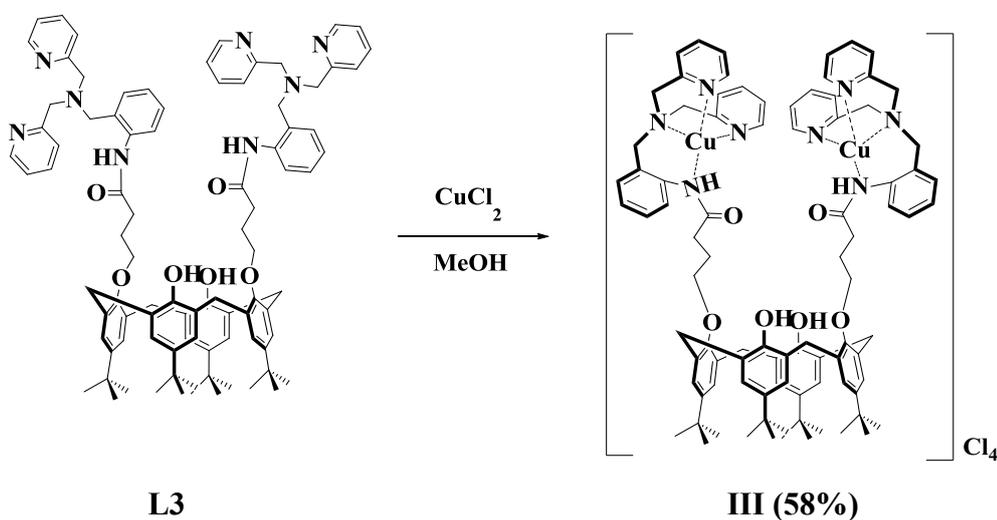
Hz, $-CH_2-$), 2.44 (t, 4H, $J = 6.8$ Hz, $-CH_2-$), 1.31 (s, 18H, *p*-*tert*-butyl), 0.97 (s, 18H, *p*-*tert*-butyl).

^{13}C -NMR (100 MHz, $CDCl_3$, ppm): δ 171.32, 158.20, 150.66, 150.00, 149.22, 146.76, 141.47, 138.63, 136.51, 132.50, 130.48, 128.33, 127.94, 126.11, 125.50, 125.13, 123.48, 123.11, 122.28, 121.33, 76.20, 59.78, 58.15, 33.92, 33.84, 33.80, 31.81, 31.75, 31.04, 25.99.

HRMS-ESI (positive mode, m/z): [$L3 + Na$] $^+$ Calcd for $C_{90}H_{104}N_8NaO_6$, 1415.7977; Found, 1416.7935.

3.2 Synthesis of ionophore III

The methanolic solution of $CuCl_2 \cdot 2H_2O$ was added to the methanolic suspension of **L3**, the color of solution changed to blue immediately. After the blue solution was left to stand at room temperature for 24 hours, the blue solid precipitate was filtered and washed with MeOH to yield compound **III** (94 mg, 58%).



Characterization data for ionophore **III**:

HRMS-ESI (positive mode, m/z): [Cu_2L3Cl_3] $^+$ Calcd for $C_{90}H_{104}Cl_3Cu_2N_8O_6$, 1623.5736; Found, 1623.5339.

Appendix B

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

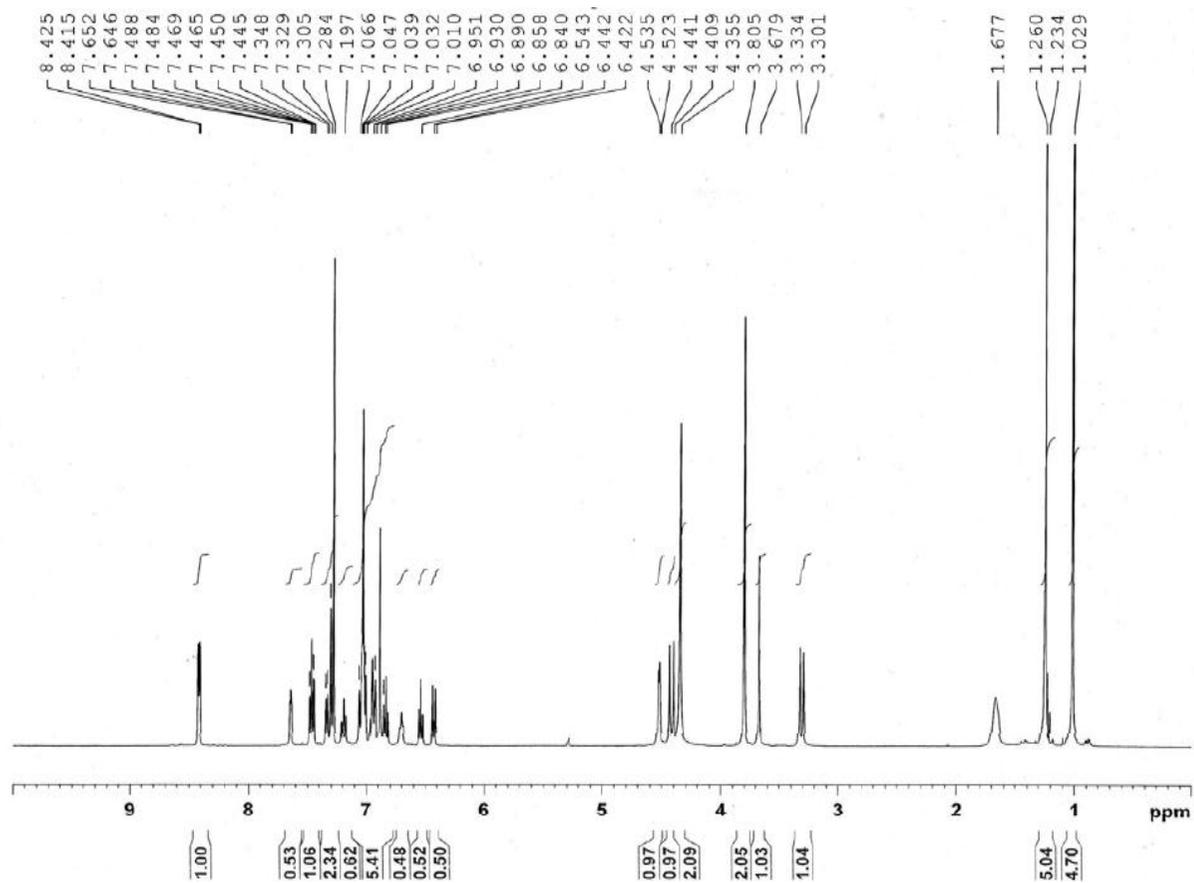


Figure B1. $^1\text{H-NMR}$ spectrum of L2 in CDCl_3 [51].

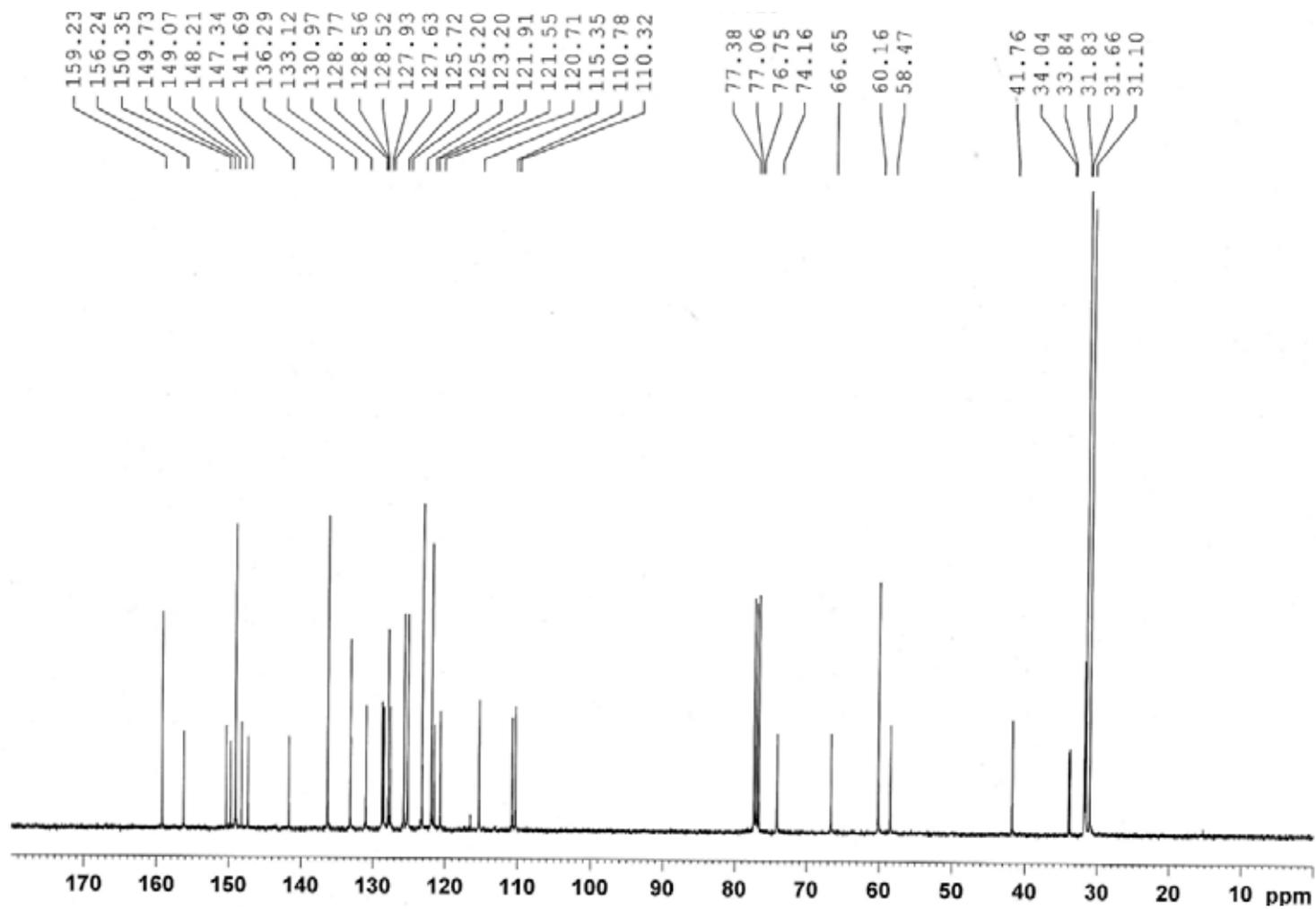


Figure B2. ^{13}C -NMR spectrum of L2 in CDCl_3 [51].

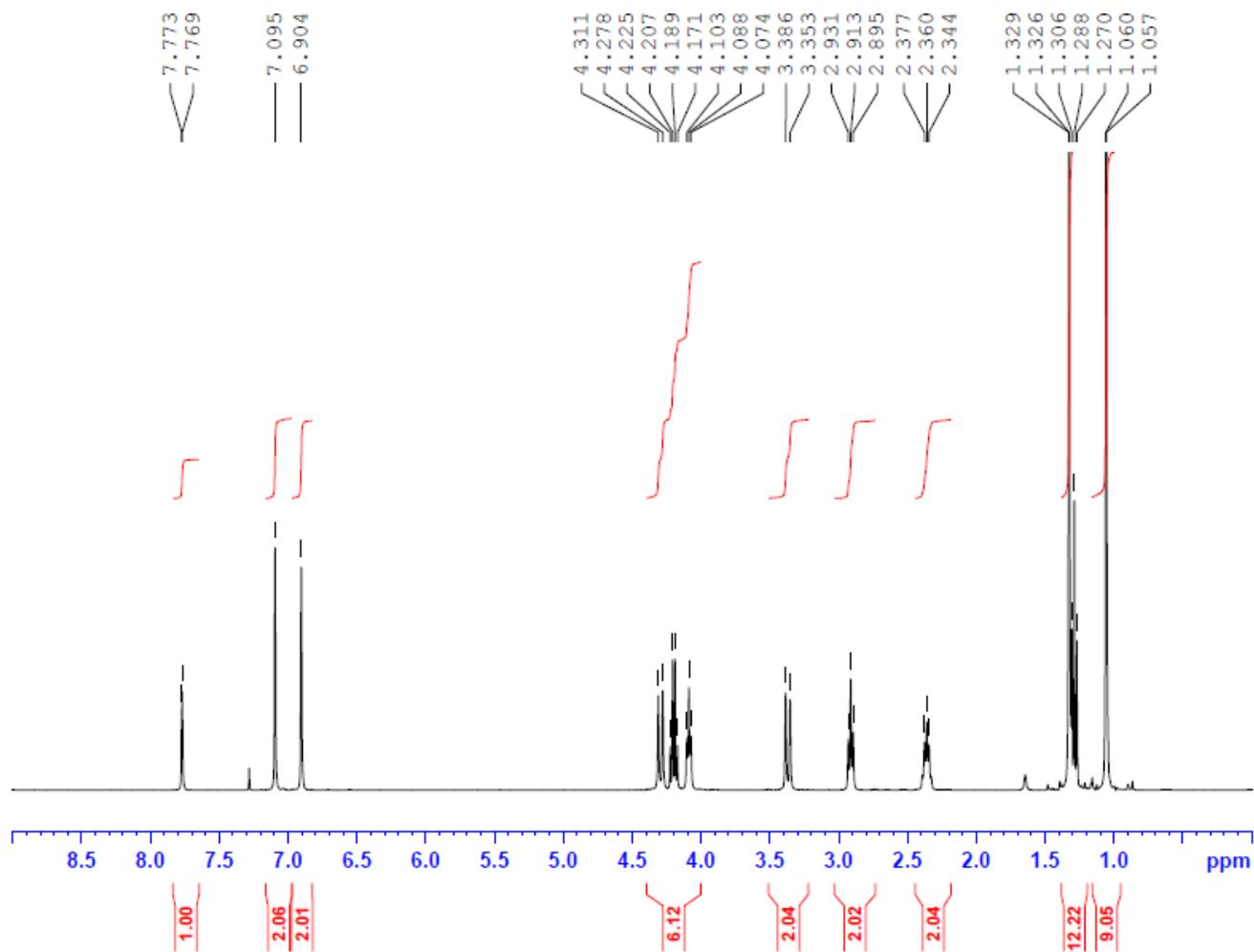


Figure B3. $^1\text{H-NMR}$ spectrum of compound **c** in CDCl_3 .

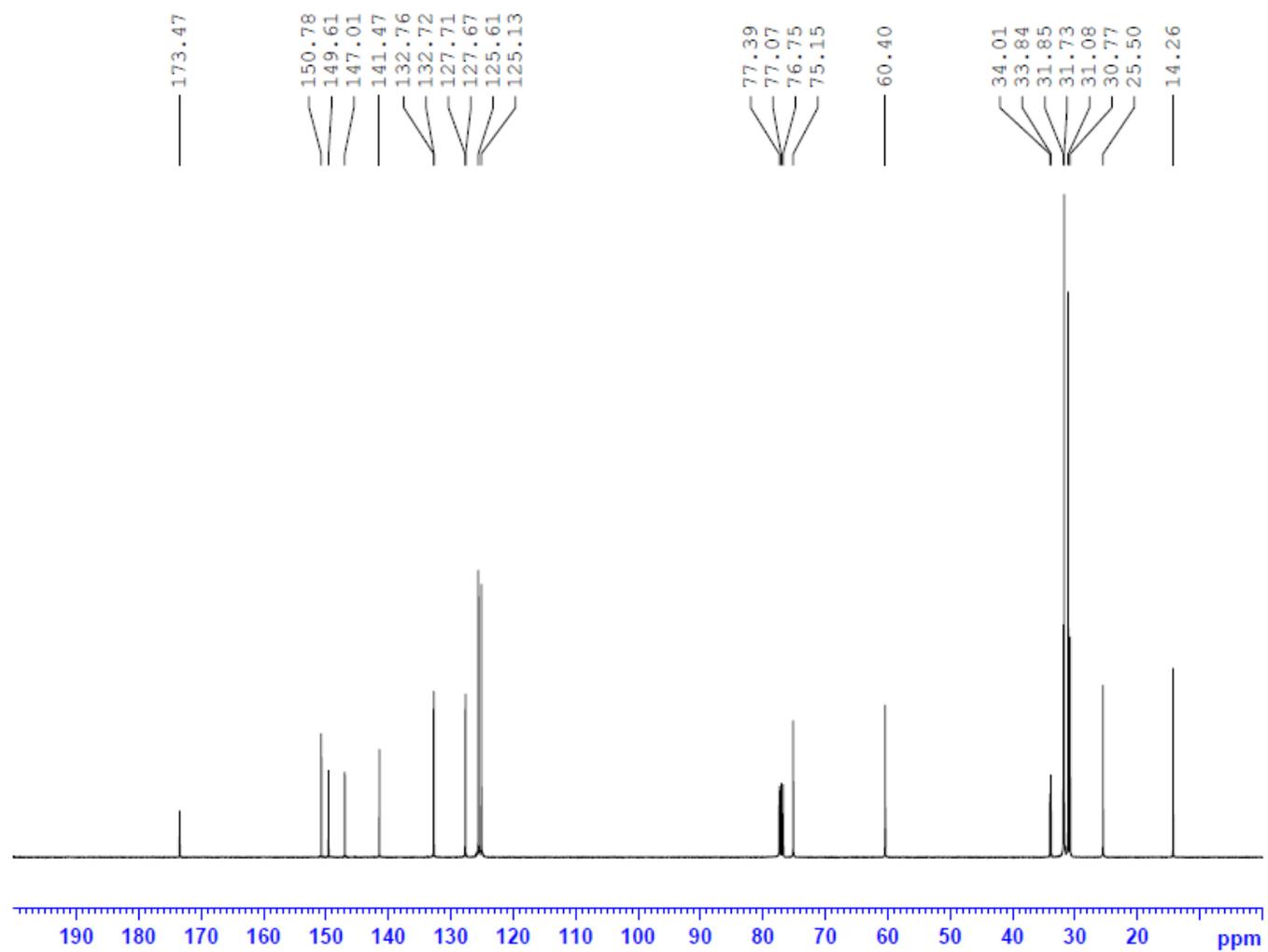


Figure B4. ^{13}C -NMR spectrum of compound **c** in CDCl_3 .

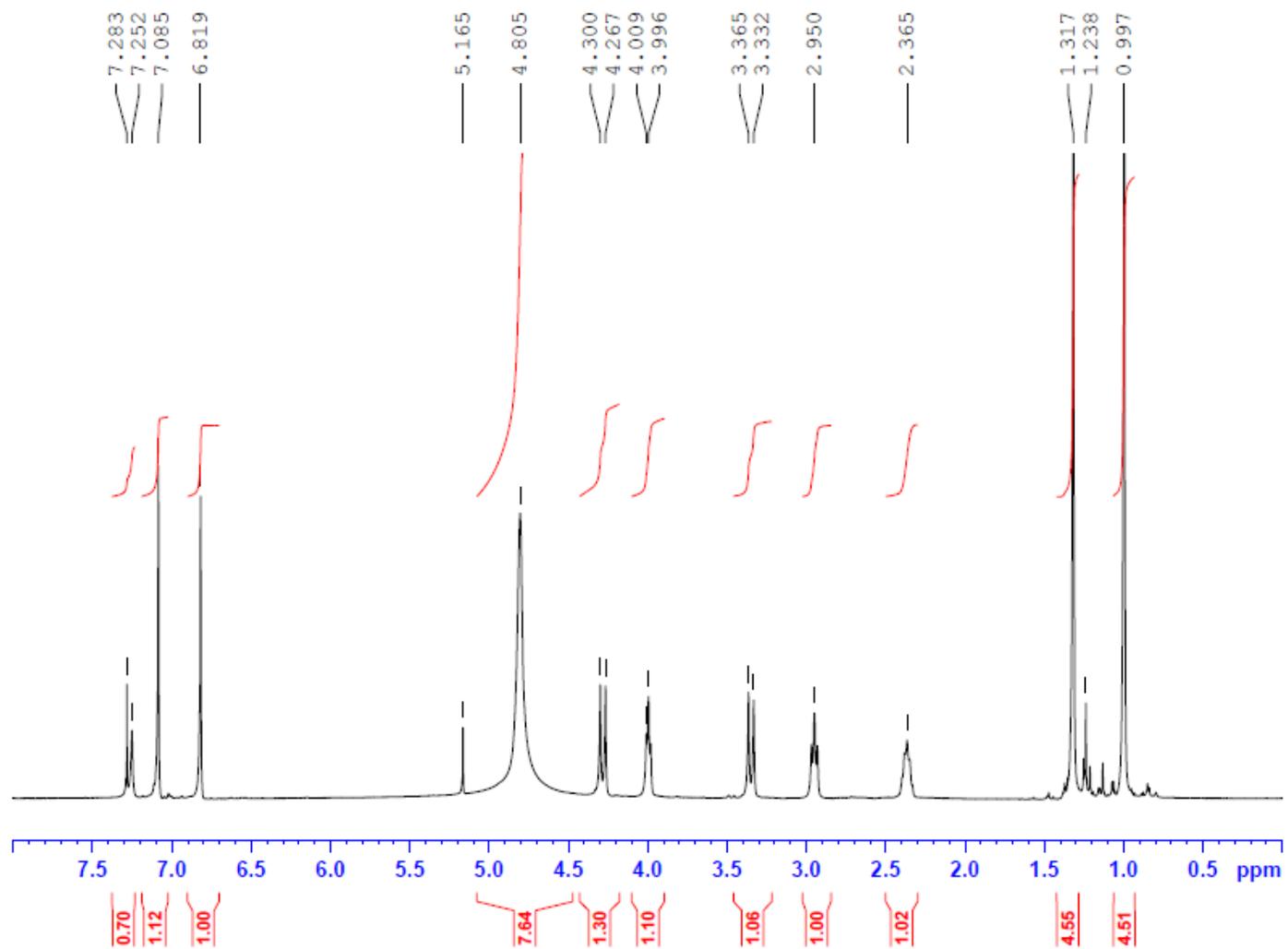


Figure B5. $^1\text{H-NMR}$ spectrum of compound **d** in CDCl_3 .

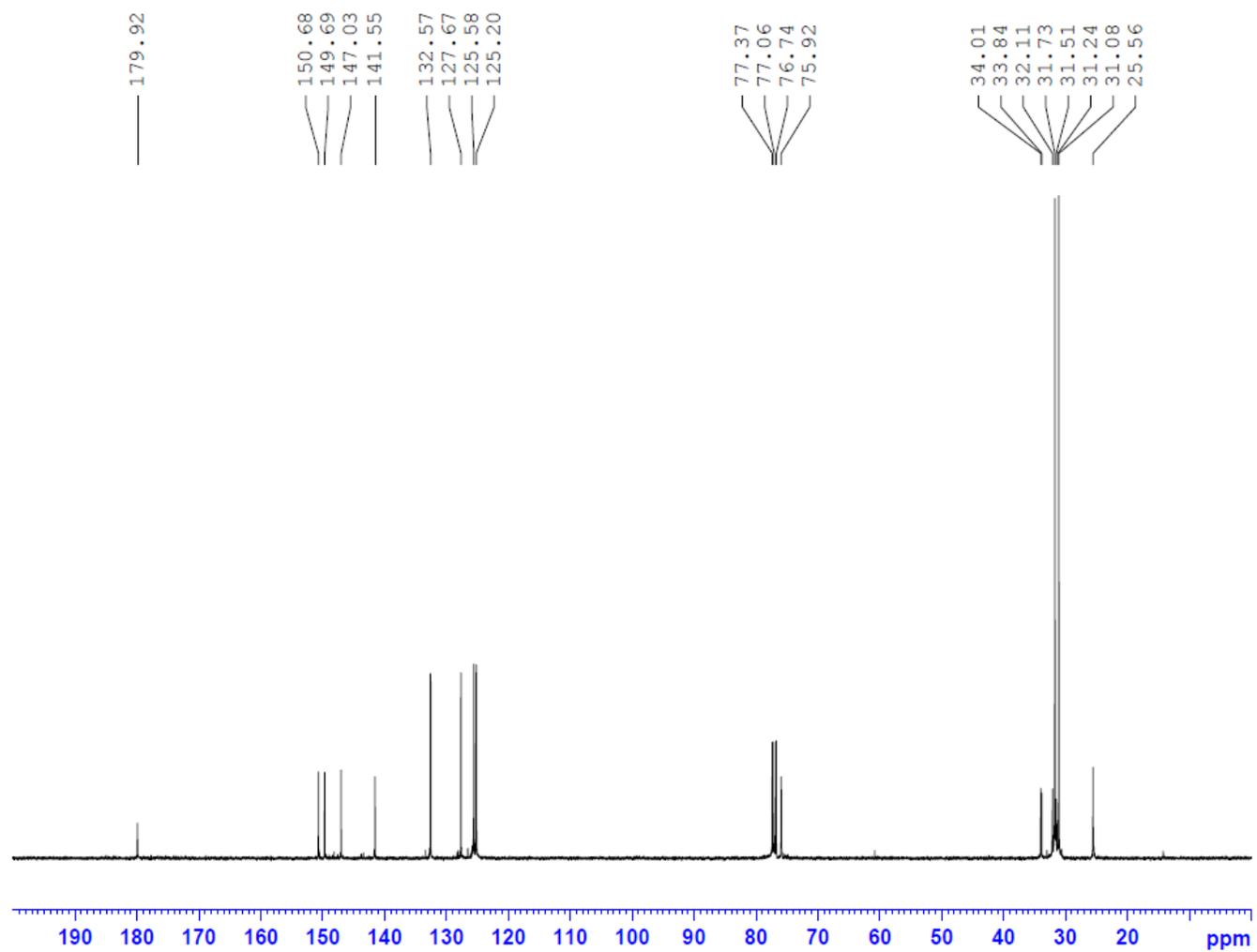


Figure B6. ^{13}C -NMR spectrum of compound **d** in CDCl_3 .

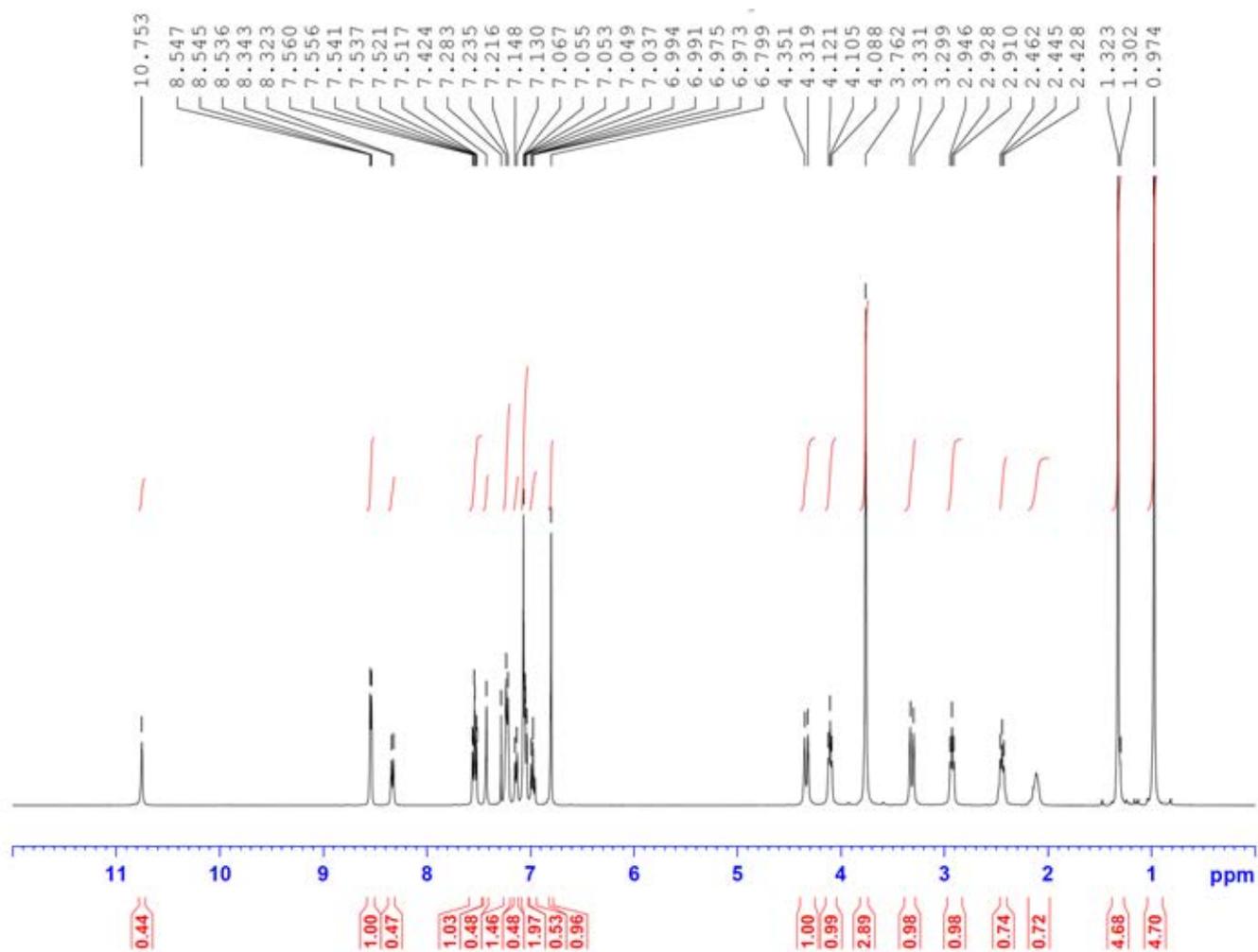


Figure B7. $^1\text{H-NMR}$ spectrum of L3 in CDCl_3 .

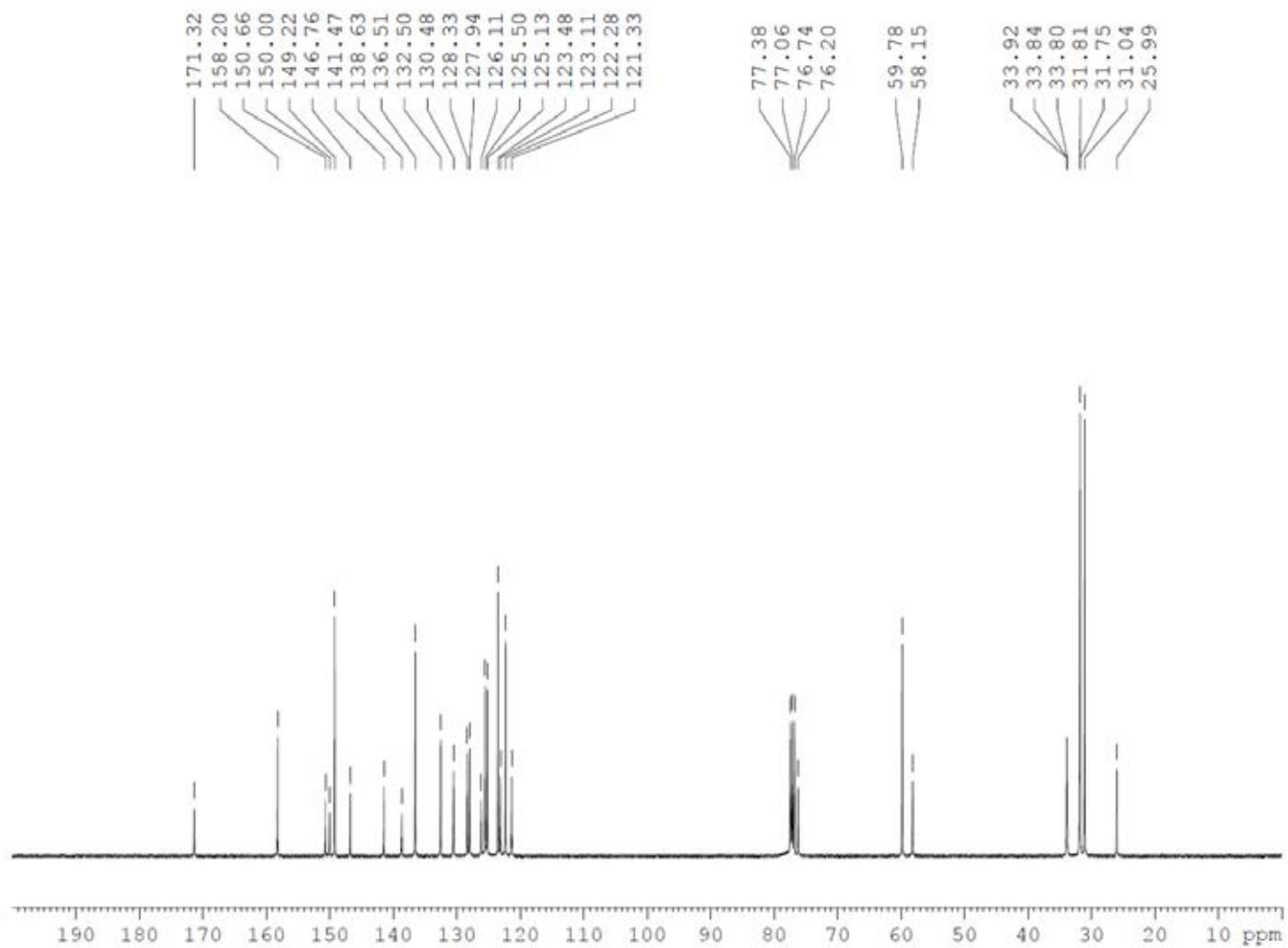


Figure B8. ^{13}C -NMR spectrum of L3 in CDCl_3 .

Appendix C

Comparison of potentiometric selectivity coefficients ($\log K_{I,j}^{pot}$) for all fabricated membrane electrodes

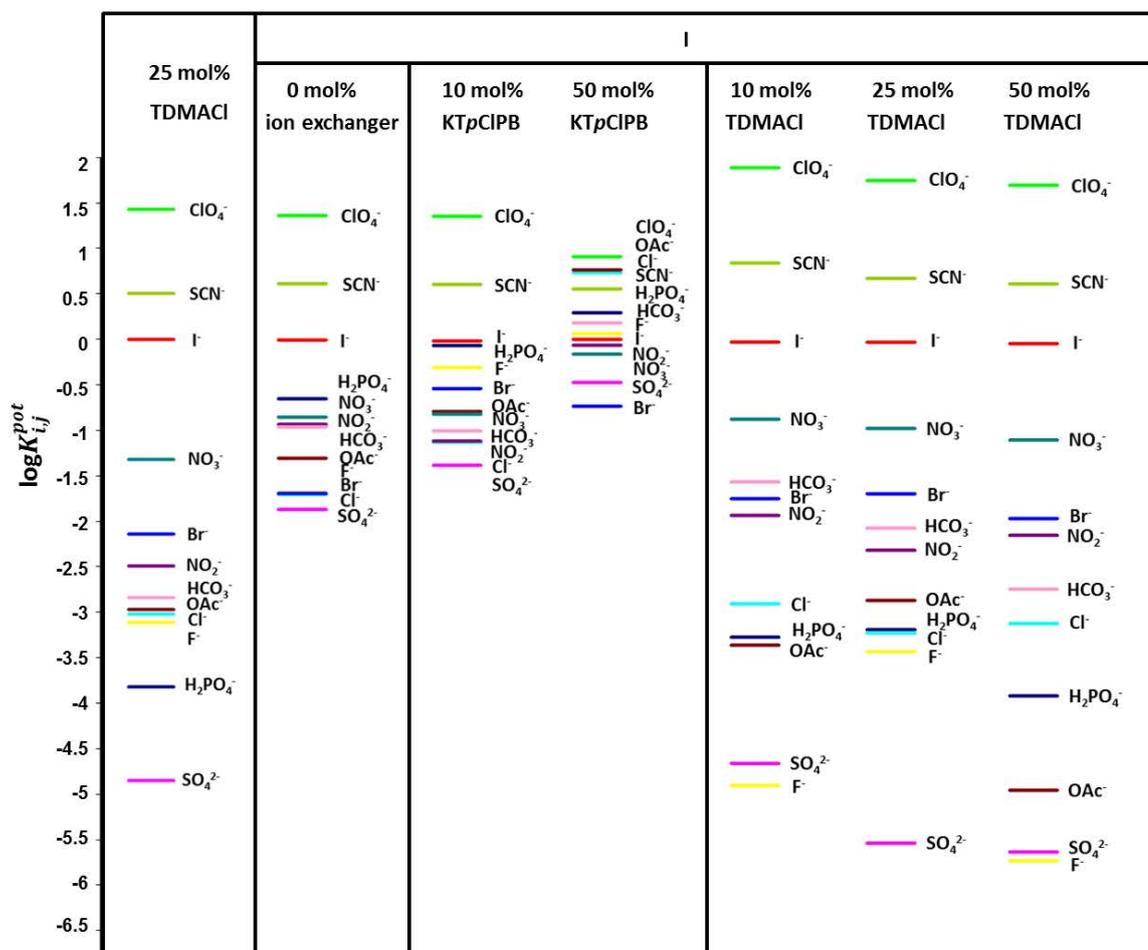


Figure C1. Selectivity coefficients ($\log K_{I,j}^{pot}$) of the membrane electrodes using ionophore I.

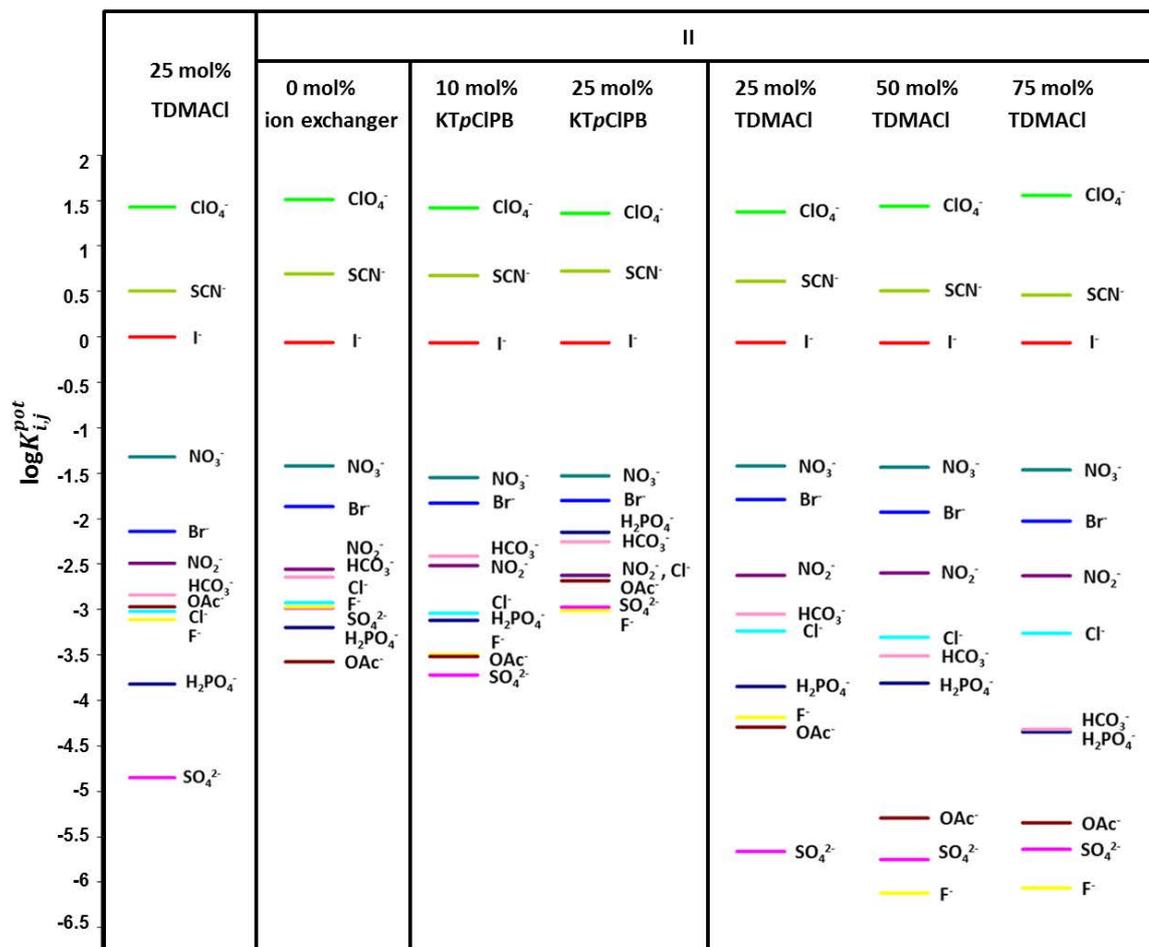


Figure C2. Selectivity coefficients ($\log K_{I,j}^{pot}$) of the membrane electrodes using ionophore II.

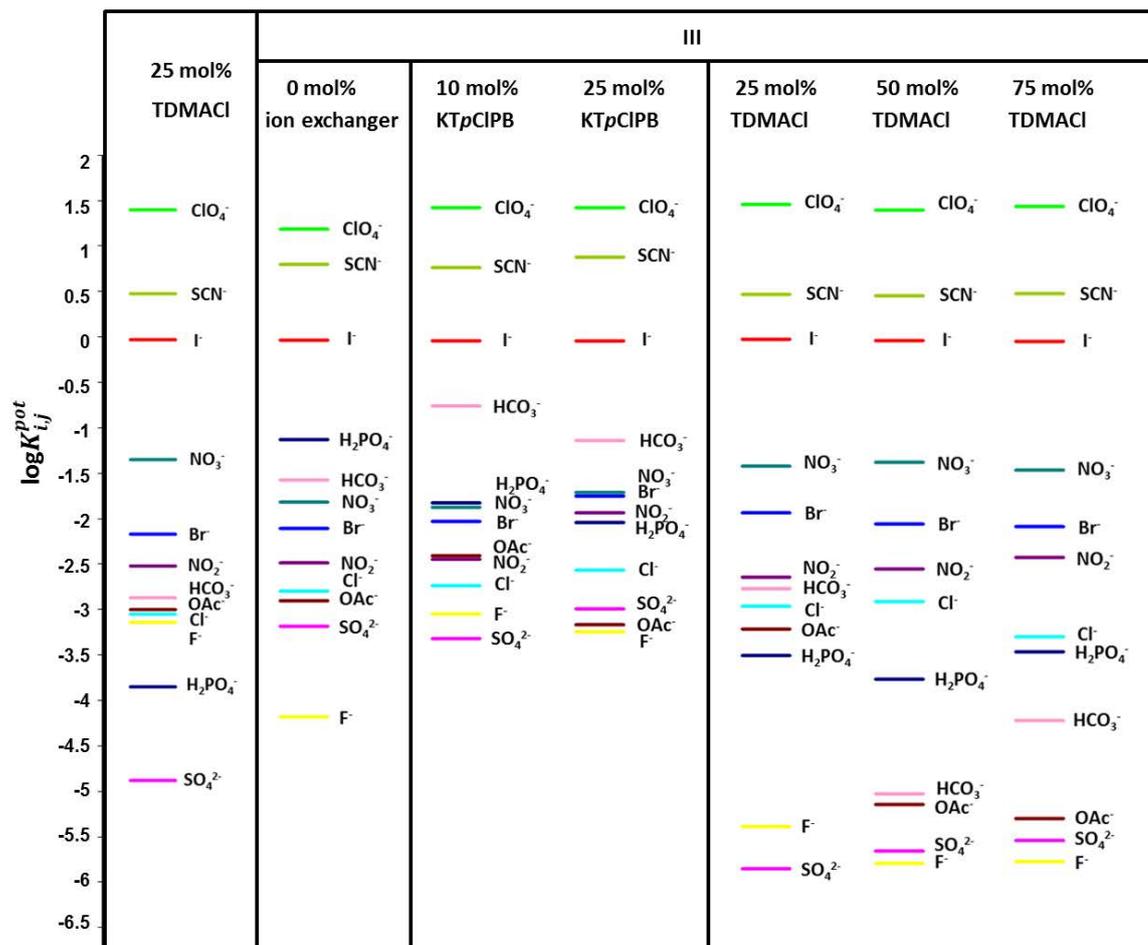


Figure C3. Selectivity coefficients ($\log K_{I,j}^{pot}$) of the membrane electrodes using ionophore III.

Appendix D

Preparation of sandwich membranes

The ion-ionophore complex formation constants in the polymeric membrane were determined by measuring the membrane potentials across two-layer sandwich membranes [61-63], where only one side contains the ionophore.

The prepared polymeric membranes, with and without ionophore, were conditioned in 10^{-2} M primary ions for overnight. Then, the membranes were softly dried on tissue paper without rinsing with water. The sandwich membrane was prepared by attaching two individual membranes together and visibly checked for air bubbles before mounting at the end of electrode. The membrane containing ionophore was exposed to the 10^{-2} M sample solution that is the same solution as the conditioning solutions. The electrode was then filled with the mixed internal solution of the primary anion (10^{-2} M) and NaCl (10^{-3} M). All EMF measurements were performed at ambient temperature in unstirred salt solution with respect to a Ag/AgCl reference electrode with 1 M LiOAc as a salt bridge electrolyte. The prepared sandwich membrane needed to be attached to the electrode body immediately before starting the membrane potential measurement. The EMF values were continuously recorded for several hours until the ion-ionophore formation was completed.

Membrane potential values, E_M , were determined by subtracting the cell potential for ionophore-free membrane from that of the sandwich membrane. The ion-ionophore formation constants were calculated using the following equation;

$$\log \beta_{IL_n} = \left(\frac{E_M z_1 F}{2.303 RT} \right) - n \log \left(L_T - \frac{n R_T}{z_1} \right) \quad (D.1)$$

L_T is the total concentration of ionophore. R_T is the concentration of lipophilic ion exchanger. R , T , F , n and z_1 are gas constant, absolute temperature, Faraday constant, the stoichiometry of complex and the charge of the tested ion, respectively.

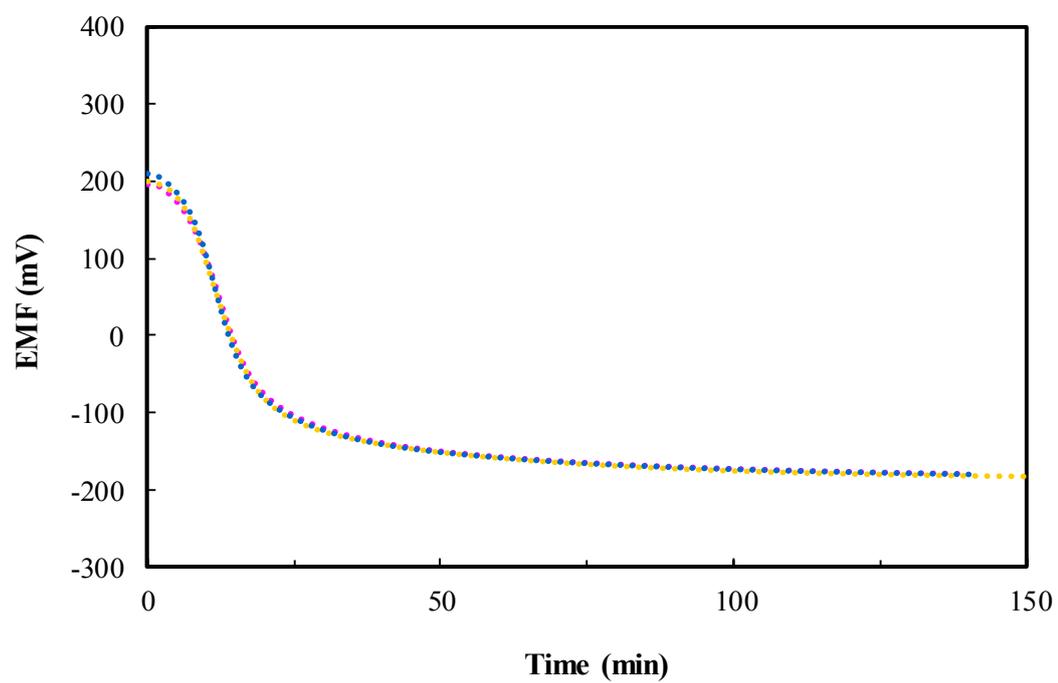


Figure D1. Time response behavior of the sandwich membrane using ionophore **II** to iodide (0.01 M NaI, $n = 3$).

VITA

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