

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการวิจัยแห่งชาติ



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# โคโตนีออนไฮดรอนเน็ทเซอร์ทางเคมีไฟฟ้าที่มีคาร์บอน[4]เฟอโรน

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DITOPIC ANION ELECTROCHEMICAL SENSORS CONTAINING CALIX[4]ARENE

Miss Nisachol Nerngchamnong

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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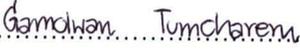
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(DITOPIC ANION ELECTROCHEMICAL SENSORS CONTAINING CALIX[4]ARENE)

อ. ที่ปริกษาวิทยาลัยพนธ์หลัก : รศ. ดร.ชวชัย ตันฑุลานี, 95 หน้า.

งานวิจัยนี้ทำการสังเคราะห์ไดโทปิกแอนไอออนเซ็นเซอร์ 1 และ 2 ซึ่งเป็นอนุพันธ์ของกาลิกซ์[4]เอริน ที่มีหมู่เอไมด์, ซูโดคราวันอีเทอร์ และเฟอร์โรซีนเป็นองค์ประกอบ สำหรับหมู่เอไมด์เป็นส่วนที่ใช้เป็นตัวรับสำหรับแอนไอออน ซูโดคราวันอีเทอร์เป็นส่วนที่ใช้เป็นตัวรับสำหรับแคตไอออน และหมู่เฟอร์โรซีนเป็นตัวให้สัญญาณทางไฟฟ้า โดยสารประกอบ 1 และ 2 มีหมู่เอไมด์อยู่บนวงเบนซีนในตำแหน่งที่ต่างกัน การสังเคราะห์ 1 และ 2 มีทั้งหมด 4 ขั้นตอน โดยสุดท้ายได้ผลิตภัณฑ์ 1 และ 2 กิดเป็นร้อยละ 12 และ 14 ตามลำดับ

เมื่อทำการศึกษาคูสมบัติการเกิดสารประกอบเชิงซ้อนของ 1 และ 2 ด้วยเอ็นเอ็มอาร์ไทเทรชัน ในตัวทำละลายผสม 5% ของคิวเทอเรเทคแอซีไตรไนไตรด์ ในคิวเทอเรเทคคโลโรฟอร์มที่อุณหภูมิห้อง พบว่า สารประกอบ 1 และ 2 สามารถจับกับโลหะแอลคาไลที่ตำแหน่งของซูโดคราวันอีเทอร์ และแอนไอออนสามารถเกิดพันธะไฮโดรเจนกับหมู่เอไมด์ได้ นอกจากนี้พบว่าสารประกอบ 1 และ 2 มีความสามารถในการจับกับแอนไอออนได้ดีขึ้นเมื่อมีโลหะแอลคาไลอยู่ โดยอาศัยผลจากแรงระหว่างประจุของโลหะแอลคาไลกับแอนไอออนช่วยเพิ่มประสิทธิภาพในการจับ สารประกอบทั้งสองพบว่ามีความจำเพาะเจาะจงกับโบรไมด์เมื่อมีโซเดียมอยู่ การศึกษาคูสมบัติทางเคมีไฟฟ้าของสารประกอบ 1 และ 2 ด้วยเทคนิคไซคลิกโวลแทมเมตรีและสแควเวฟโวลแทมเมตรี ซึ่งใช้สารละลาย 0.1 โมลาร์ของเตเตรabutylแอมโมเนียมเฮกซะฟลูออโรฟอสเฟต ใน 40% ของแอซีไตรไนไตรด์ ในไดคลอโรมีเทน เป็นสารละลายอิเล็กโทรไลต์ โดยใช้ขั้วไฟฟ้าหลักเป็นขั้วไฟฟ้าแพลทินัม ขั้วไฟฟ้าอ้างอิงเป็นขั้วไฟฟ้าซิลเวอร์-ซิลเวอร์ในเทรต และขั้วไฟฟ้าเคาน์เตอร์เป็นแท่งแพลทินัม พบว่าในการจับกับแอนไอออน โดยเฉพาะคลอไรด์และแอซีเตต สารประกอบ 2 มีการเปลี่ยนแปลงทางเคมีไฟฟ้ามากขึ้นเมื่อมีโซเดียมอยู่ ในขณะที่สารประกอบ 1 แทบไม่เห็นการเปลี่ยนแปลงของสารประกอบเมื่อจับกับแอนไอออนทั้งที่มีและไม่มีโซเดียมอยู่ ซึ่งอาจเกิดจากระยะที่ห่างเกินไประหว่างตัวรับสำหรับแคตไอออนและแอนไอออน กับหมู่เฟอร์โรซีน ทำให้การจับการแคตไอออนและแอนไอออนไม่มีผลต่อการเปลี่ยนแปลงทางเคมีไฟฟ้าของหมู่เฟอร์โรซีน

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NISACHOL NERNGCHAMNONG : DITOPIC ANION ELECTROCHEMICAL SENSORS CONTAINING CALIX[4]ARENE. ADVISOR : ASSOC. PROF. THAWATCHAI TUNTULANI, Ph. D., 95 pp.

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Two heteroditopic electrochemical anion sensors **1** and **2** have been synthesized. *p*-*tert*-Butylcalix[4]arene was used as a building block. Pseudo-crown ether and amidoferrocene group were attached to the *p*-*tert*-butylcalix[4]arene framework for binding cations and anions, respectively. Compounds **1** and **2** are different in the position of the amidoferrocene units attached to the benzene ring. Syntheses of compounds **1** and **2** were carried out in four steps giving products **1** and **2** as orange solid in 12% and 14% yields, respectively.

The complexation properties of **1** and **2** were studied by NMR titration experiments recorded in 5% CD<sub>3</sub>CN:CDCl<sub>3</sub> at room temperature. We found that both compounds simultaneously complexed alkali metal salts in ion-pair fashions in which metal cations were encapsulated in pseudo-crown ether cavity and anions were hydrogen bonded to amide protons. In the presence of metal cations, the anion binding affinities of the receptors **1** and **2** were enhanced due to the strong electrostatic interactions of co-bound cation and anion. Interestingly, both compounds possessed highest selectivity for Br<sup>-</sup> in the presence of Na<sup>+</sup>. However, in the presence of Na<sup>+</sup>, the binding constants of receptor **2** with anions were much higher than that of receptor **1**. The electrochemical properties of **1** and **2** were studied by cyclic and square wave voltammetry using 40% CH<sub>3</sub>CN:CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and using a Pt working electrode, a Ag/Ag<sup>+</sup> reference electrode and a Pt coil counter electrode. Studies showed that in the presence of metal cations, the interactions of heteroditopic receptor **2** towards anions, especially chloride and acetate are higher than its free form whereas no significant electrochemical change was observed when Na<sup>+</sup> was added to receptor **1**. This may result from the long distance between binding sites and ferrocene moiety of receptor **1**.

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## LIST OF ABBREVIATIONS

$\delta$	Chemical Shift
$\Delta G^0$	Standard Gibbs Free Energy
$\mu\text{L}$	Microliter
$^1\text{H-NMR}$	Proton-Nuclear Magnetic Resonance
$^{13}\text{C-NMR}$	Carbon-13-Nuclear Magnetic Resonance
$\text{\AA}$	Angstrom
$\text{AcO}^-$	Acetate
$\text{Br}^-$	Bromide
$\text{BzO}^-$	Benzoate
$^\circ\text{C}$	Degree Celsius
COSY	Correlation Spectroscopy
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DNA	Deoxyribonucleic Acid
equiv.	Equivalent
F	Faraday constants
g	Gram
HMBC	Heteronuclear Multiple Bond Correlation
HMQC	Heteronuclear Multiple-Quantum Coherence
$\text{H}_2\text{PO}_4^-$	Dihydrogenphosphate
$\text{HSO}_4^-$	Hydrogensulphate
Hz	Hertz
J	Coupling Constant
K	Kelvin
K	Association Constant
kJ	Kilojoule
M	Molar
m/z	Mass per Charge Ratio
mL	Milliliter
mmol	Millimol
mV	Millivolt

NEt <sub>3</sub>	Triethylamine
NMR	Nuclear Magnetic Resonance
ppm	Part per million
R	Gas Constant
RNA	Ribonucleic Acid
s, d, t, m	Splitting patterns of <sup>1</sup> H-NMR (singlet, doublet, triplet, multiplet)
T	Temperature
TBA	Tetrabutylammonium
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-Visible