

ไดโตนิกแอนไอออนเซ็นเซอร์ทางเคมีไฟฟ้าที่มีคาลิกซ์[4]เอรีน

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DITOPIC ANION ELECTROCHEMICAL SENSORS CONTAINING CALIX[4]ARENE

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นิสาชล เนื่องจำนงค์ : ใดโทปิกแอนไอออนเซ็นเซอร์ทางเคมีไฟฟ้าที่มีคาลิกซ์[4]เอรีน.

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อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร.ธวัชชัย ต้นจตุลानी, 95 หน้า.

งานวิจัยนี้ทำการสังเคราะห์ใดโทปิกแอนไอออนเซ็นเซอร์ 1 และ 2 ซึ่งเป็นอนุพันธ์ของคาลิกซ์[4]เอรีน ที่มีหมู่เอไมด์, ซูโครราน์อีเทอร์ และเฟอร์โรซีนเป็นองค์ประกอบ สำหรับหมู่เอไมด์เป็นส่วนที่ใช้เป็นตัวรับสำหรับแอนไอออน ซูโครราน์อีเทอร์เป็นส่วนที่ใช้เป็นตัวรับสำหรับแคตไอออน และหมู่เฟอร์โรซีนเป็นตัวให้สัญญาณทางไฟฟ้า โดยสารประกอบ 1 และ 2 มีหมู่เอไมด์อยู่บนวงเบนซีนในตำแหน่งที่ต่างกัน การสังเคราะห์ 1 และ 2 มีทั้งหมด 4 ขั้นตอน โดยสุดท้ายได้ผลิตภัณฑ์ 1 และ 2 คิดเป็นร้อยละ 12 และ 14 ตามลำดับ

เมื่อทำการศึกษาคูณสมบัติการเกิดสารประกอบเชิงซ้อนของ 1 และ 2 ด้วยเอ็นเอ็มอาร์ 1H เทอเรชัน ในตัวทำละลายผสม 5% ของคิวเทอเรเทตแอสีโตไนไตรด์ ในคิวเทอเรเทตคลอโรฟอร์ม ที่อุณหภูมิห้อง พบว่า สารประกอบ 1 และ 2 สามารถจับกับโลหะแอลคาไลที่ตำแหน่งของซูโครราน์อีเทอร์ และแอนไอออนสามารถเกิดพันธะไฮโดรเจนกับหมู่เอไมด์ได้ นอกจากนี้พบว่าสารประกอบ 1 และ 2 มีความสามารถในการจับกับแอนไอออนได้ดีขึ้นเมื่อมีโลหะแอลคาไลอยู่ โดยอาศัยผลจากแรงระหว่างประจุของโลหะแอลคาไลกับแอนไอออนช่วยเพิ่มประสิทธิภาพในการจับ สารประกอบทั้งสองพบว่ามีเฉพาะเจาะจงกับโบรมไนด์เมื่อมีโซเดียมอยู่ การศึกษาคูณสมบัติทางเคมีไฟฟ้าของสารประกอบ 1 และ 2 ด้วยเทคนิคไซคลิกโวลแทมเมตรีและสแควเวฟโวลแทมเมตรี ซึ่งใช้สารละลาย 0.1 โมลาร์ของเตตระบิวทิลแอมโมเนียมเฮกซะฟลูออโรสเฟต ใน 40% ของแอสีโตไนไตรด์ ในไดคลอโรมีเทน เป็นสารละลายอิเล็กโทรไลต์ โดยใช้ขั้วไฟฟ้าหลักเป็นขั้วไฟฟ้าแพลทินัม ขั้วไฟฟ้าอ้างอิงเป็นขั้วไฟฟ้าซิลเวอร์-ซิลเวอร์ในเทรต และขั้วไฟฟ้าเคาน์เตอร์เป็นแท่งแพลทินัม พบว่าในการจับกับแอนไอออน โดยเฉพาะคลอไรด์และแอสีเตต สารประกอบ 2 มีการเปลี่ยนแปลงทางเคมีไฟฟ้ามากขึ้นเมื่อมีโซเดียมอยู่ ในขณะที่สารประกอบ 1 แทบไม่เห็นการเปลี่ยนแปลงของสารประกอบเมื่อจับกับแอนไอออนทั้งที่มีและไม่มีโซเดียมอยู่ ซึ่งอาจเกิดจากระยะที่ห่างเกินไประหว่างตัวรับสำหรับแคตไอออนและแอนไอออน กับหมู่เฟอร์โรซีน ทำให้การจับการแคตไอออนและแอนไอออนไม่มีผลต่อการเปลี่ยนแปลงทางเคมีไฟฟ้าของหมู่เฟอร์โรซีน

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ลายมือชื่อนิสิต..... *นิสาชล เนื่องจำนงค์*

ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก..... *ธวัชชัย ต้นจตุลानी*

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

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% CD₃CN:CDCl₃ 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⁻ in the presence of Na⁺. However, in the presence of Na⁺, 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% CH₃CN:CH₂Cl₂ with 0.1 M TBAPF₆ as supporting electrolyte and using a Pt working electrode, a Ag/Ag⁺ 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⁺ 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

| | |
|---------------------------|--|
| δ | Chemical Shift |
| ΔG^0 | Standard Gibbs Free Energy |
| μL | Microliter |
| $^1\text{H-NMR}$ | Proton-Nuclear Magnetic Resonance |
| $^{13}\text{C-NMR}$ | Carbon-13-Nuclear Magnetic Resonance |
| \AA | Angstrom |
| AcO^- | Acetate |
| Br^- | Bromide |
| 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 |
| H_2PO_4^- | Dihydrogenphosphate |
| 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 ₃ | Triethylamine |
| NMR | Nuclear Magnetic Resonance |
| ppm | Part per million |
| R | Gas Constant |
| RNA | Ribonucleic Acid |
| s, d, t, m | Splitting patterns of ¹ H-NMR (singlet, doublet, triplet, multiplet) |
| T | Temperature |
| TBA | Tetrabutylammonium |
| THF | Tetrahydrofuran |
| UV-Vis | Ultraviolet-Visible |