


คาลิกซ์[4]เอรีนที่มีเฟอโรซีนหรือนิกเกิลไดโอรฮาไดเอซาเป็นองค์ประกอบสำหรับเป็นตัวตรวจวัดแอนไอออน



นางสาว บุษยรัตน์ ธรรมพัฒน์กิจ

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CALIX[4]ARENE CONTAINING FERROCENE OR NICKEL DITHIA DIAZA AS ANION SENSOR



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ได้ทำการสังเคราะห์ลิแกนด์ **6** ที่สามารถจับโลหะทรานซิชัน คือ 25,27-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctaneethyl-*p-tert*-butylcalix[4]arene ซึ่งสามารถสังเคราะห์ได้ 2 วิธี วิธีแรกทำการสังเคราะห์โดยปฏิกิริยาระหว่าง dibromoethyl-calix[4]arene (**2a**) กับ Ni(bme-daco) โดยนิกเกิลทำหน้าที่เป็นโลหะเติมเฟลด์ในอะซิโตนไนไตรล์ซึ่งจะได้ผลิตภัณฑ์ของ Ni(bme-daco)calix[4]arene (**4a.Br₂**) โดยในขั้นการสังเคราะห์สารประกอบ **2a** จะได้สารประกอบที่ไม่ต้องการ dimericcalix[4]arene (**3**) ในปริมาณมาก ส่วนวิธีที่ 2 สังเคราะห์โดยปฏิกิริยาระหว่าง dichloroethyl-calix[4]arene (**2b**) กับ Ni(bme-daco) ซึ่งใช้โซเดียมไอโอดด์เป็นตัวเร่งปฏิกิริยาในอะซิโตนไนไตรล์จะได้ผลิตภัณฑ์ของ Ni(bme-daco)calix[4]arene (**4b.I₂**) และ BisNi(bme-daco)calix[4]arene เป็น by-product จากนั้นเอานิกเกิลออกจากสาร **4** โดยการรีฟลักซ์กับโปแตสเซียมไซยาไนด์ ในอะซิโตนไนไตรล์จะได้ลิแกนด์ **6**

ได้สังเคราะห์สารประกอบคาลิกซ์[4]เอรีนที่มีเอมีดเฟอโรซีนสำหรับจับแอนไอออนที่ตำแหน่ง upper rim และเอทิลเอสเทอร์สำหรับจับแคทไอออนที่ตำแหน่ง lower rim ของ 5,7-diamideferrocenyl-25,26,27,28-tetraalkylcalix[4]arene (**5a**, **5b** และ **5c**) โดยการทำปฏิกิริยาระหว่าง tetraalkyldiaminocalix[4]arene (**4a**, **4b** และ **4c**) และ 1,1-Bis(chlorocarbonyl)ferrocene การพิสูจน์โครงสร้างของสารที่สังเคราะห์ได้โดยวิธีเอ็นเอ็มอาร์สเปกโตรสโกปีพบว่าสารประกอบ **5a** และ **5b** มีคอนฟอร์เมชันที่อยู่ในสมดุลระหว่างโคนคอนฟอร์เมชันและพาเซิลโคนคอนฟอร์เมชัน ส่วนสารประกอบ **5c** อยู่ในรูปโคนคอนฟอร์เมชันและผลทางเอกซเรย์พบว่า **5a** จะอยู่ในรูปพาเซิลโคนคอนฟอร์เมชัน ส่วนสารประกอบ **5b** จะอยู่ในรูปโคนคอนฟอร์เมชัน นอกจากนี้ได้ทำการศึกษาความสามารถในการเกิดสารประกอบเชิงซ้อนกับแอนไอออนโดยวิธีโปรตอนเอ็นเอ็มอาร์ไคเตรชัน วิธีไซคลิกโวลแทมเมตรี และวิธีสแควร์เวฟโวลแทมเมตรีในอะซิโตนไนไตรล์พบว่าลิแกนด์ **5a**, **5b** และ **5c** ชอบที่จะจับกับคาร์บอกซิเลตแอนไอออนมากกว่า $H_2PO_4^-$ และ Cl^- และยังพบว่าความสามารถของลิแกนด์ในการจับกับแอนไอออนเป็นไปตามลำดับคือ **5c** > **5a** > **5b** นอกจากนี้พบว่าเอทิลเอสเทอร์ที่ตำแหน่ง lower rim ของลิแกนด์ **5c** สามารถจับกับ โซเดียม โปแตสเซียม รูบิเดียม และซีเซียมไอออน โดยศึกษาจากเทคนิคอิเล็กโตรสเปกโตรสโกปีไอออนในเซชันแมสสเปกโตรเมตรี

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25,27-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctaneethyl-*p-tert*-butylcalix[4]arene (**6**) can be synthesized by 2 methods. In the first method, coupling reaction of dibromoethylcalix[4]arene (**2a**) and Ni(bme-daco) bearing Ni acting as a metal template in CH₃CN afforded Ni(bme-daco)calix[4]arene (**4a.Br₂**). Interestingly, synthesis of dibromoethylcalix[4]arene (**2a**) produced the large amount of the by-product of dimericcalix[4]arene (**3**). In the second method, the reaction of dichloroethyl-calix[4]arene (**2b**) and Ni (bme-daco) in the presence of NaI as a catalyst in CH₃CN provided the Ni(bme-daco)calix[4]arene (**4b.I₂**) and the by-product, BisNi(bme-daco)calix[4]arene (**5**). Ni(II) was removed by refluxing compound **4** with KCN in CH₃CN to provide compound **6**.

5,7-Diamideferrocenyl-25,26,27,28-tetraalkylcalix[4]arenes (**5a**, **5b** and **5c**) were prepared by coupling reactions of tetraalkyldiaminocalix[4]arenes (**4a**, **4b** and **4c**) and 1,1-Bis(chlorocabonyl)ferrocene in dichloromethane with triethylamine as base. Elucidation of the structures by NMR spectroscopy found that **5a** and **5b** were in the equilibrium of cone and partial cone conformations while **5c** was in cone conformation. Binding abilities were investigated by ¹H-NMR titrations, cyclic voltammetry and squarewave voltammetry in CH₃CN. Ligands **5a**, **5b** and **5c** were found to bind carboxylate anions significantly better than H₂PO₄⁻ and Cl⁻. The binding ability order of ligands towards anions is **5c** > **5a** > **5b**. Additionally, **5c** can bind alkali metals at tetraethyl ester units as studied by electrospray ionization mass spectrometry.

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List of Abbreviations and Signs

Å	Angstrom
K_{ass}	Association constant
$^{13}\text{C-NMR}$	Carbon Nuclear Magnetic Resonance
°C	Degree Celcius
δ	Chemical shift
CIS	Complexation Induced Shift
J	Coupling constant
DEPT	Distortionless Enhancement of NMR signals by Polarization Transfer
g	Gram
Hz	Hertz
MALDI-TOF	Marrix Assistance Laser Desorption/Ionization-Time of Flight
mL	Milliliter
mmol	Millimol
2D	Two-dimentional
NOESY	Nuclear Overhauser Enhancement Spectroscopy
HMQC	Heteronuclear Multiple Quantum Coherence
HSAB	Hard-Soft Acid-Base
HMBC	Heteronuclear Multiple Quantum Bond Correlation
COSY	Correlated Spectroscopy
EXSY	Exchange Spectroscopy
ROESY	Rotation Overhauser Effect Spectroscopy
ppm	Part per million
M^{-1}	Per molar
$^1\text{H-NMR}$	Proton Nuclear Magnetic Resonance
RT	Room Temperature
2D-NMR	Two-Dimentional Nuclear Megnetic Resonance
CV	Cyclic Voltammetry
SW	Square Wave Voltammetry
BEF	Binding Enhancement Factor

List of Abbreviations and Signs (continue)

A	Ampere
V	Volt
E	Potential
ΔG	Gibb's energy
F	Faraday constant
TBAPF	Tetrabutylammonium hexafluorophosphate
AN	Acetonitrile
TBA	Tetrabutylammonium
ESI-TOF MS	Electrospray Ionization Time of Flight Mass Spectrometry
PC	Partial Cone conformation
C	Cone conformation
1,3-alt	1,3-alternate conformation
Fc	Ferrocene



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