

การสังเคราะห์สารประกอบเชิงซ้อนโลหะพริดีลพอร์ไฟริน

นายธนา อรุณวัฒน์โชค

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF PYRIDYLPORPHYRIN METAL COMPLEXES

Mr. Thana Arunwattanachok

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ธนา อรุณวัฒน์โชค : การสังเคราะห์สารประกอบเชิงซ้อนโลหะพริดีลพอร์ไฟริน (SYNTHESIS OF PYRIDYLPORPHYRIN METAL COMPLEXES) อ.ที่
 ปรึกษา: ผศ.ดร.วรวรรณ พันธุมนาวิน; อ.ที่ปรึกษาร่วม: ผศ.ดร.ยงศักดิ์ ศรีธนาอนันต์; 114
 หน้า

ได้สังเคราะห์เทตระแอริลพอร์ไฟรินที่ประกอบด้วยหมู่พริดีล (Py) และหมู่เฟนิล (P) เป็น
 หมู่แทนที่ที่ตำแหน่งมีโซ และพิสจูนิโครงสร้างโดยวิธีทางสเปกโตรสโกปีต่างๆ การสังเคราะห์
 กระทำโดยใช้ อัตราส่วนของ พิวโรล เบนซิลดีไฮด์ และ 4-พริดีนคาร์บอกซัลดีไฮด์เท่ากับ 4:2:2 ซึ่งได้
 ผลิตภัณฑ์หลักคือ 5-(4-พริดีล)-10,15,20-ไตรฟีนิลพอร์ไฟริน (MPyTPP, **8**) คิดเป็นปริมาณร้อยละ
 36 สารประกอบพอร์ไฟรินที่สังเคราะห์ได้ 2 ชนิดคือ 5,10,15,20-เทตระฟีนิลพอร์ไฟริน (TPP,
1) และ MPyTPP (**8**) มีสมบัติในการเกิดสารประกอบเชิงซ้อนกับเกลืออะซิเตทของ แมงกานีส
 (II) โคบอลต์(II) นิกเกิล(II) คอปเปอร์(II) ซิงค์(II) และเกลือคลอไรด์ของเหล็ก(III) ในตัวทำละลาย
 คลอโรฟอร์มหรือเอิน,เอิน-ไดเมทิลฟอร์มาไมด์ โปรตอนเอ็นเอ็มอาร์ของสารประกอบเชิงซ้อน
 โลหะที่สังเคราะห์ได้ทั้งหมดไม่ปรากฏสัญญาณที่ตำแหน่งระหว่าง -2.70 ถึง -2.90 พีพีเอ็ม ซึ่ง
 สนับสนุนการแทนที่โปรตอน N-H ภายในวงพอร์ไฟรินด้วยอะตอมของโลหะ ส่วนผลของยูวี-วิสิ
 บิลสเปกตรัมนั้นได้แสดงให้เห็นว่า แถบการดูดกลืนคลื่นแสงที่ตำแหน่งควว-แบน 4 แถบของวง
 พอร์ไฟรินเดิมลดลงเหลือ 1 หรือ 2 แถบเมื่อเกิดสารประกอบเชิงซ้อน นอกจากนั้นยังได้สังเคราะห์
 สารประกอบเชิงซ้อนพอร์ไฟริน 2 หน่วยในลักษณะ side-to-face ได้แก่ (ZnTPP)(MPyTPP)
 (**22**) และ (CoTPP)(MPyTPP) (**23**) ได้ในหลอดเอ็นเอ็มอาร์ สัญญาณโปรตอนเอ็นเอ็มอาร์บ่ง
 ชี้ให้เห็นว่า โปรตอนของหมู่พริดีลของ MPyTPP เกิดการเลื่อนไปทางสนามแม่เหล็กมาก
 (upfield) มวลโมเลกุลของสารประกอบเชิงซ้อนโลหะและของพอร์ไฟริน 2 หน่วยสามารถยืนยัน
 ได้โดยใช้เทคนิคมัลติทอพ-แมสสเปกโตรเมทรี และฟิล์มบางของ ZnTPP (**2**) ได้ทดลองนำไปใช้
 เป็นวัสดุอันทรงกิริยาเคมีที่มีการตอบสนองทางแสงในการตรวจจับไอแอลกอฮอล์ต่างๆ

สาขาวิชา.....ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

ปีการศึกษา..... 2549

ลายมือชื่อนิสิต..... *วิชา อรุณวัฒน์โชค*

ลายมือชื่ออาจารย์ที่ปรึกษา..... *อ.ดร. วรวรรณ พันธุมนาวิน*

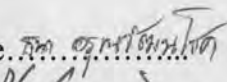
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..... *อ.ดร. ยงศักดิ์ ศรีธนาอนันต์*


4772317623: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE


KEYWORD: PYRIDYLPORPHYRIN / METALLOPORPHYRIN / SIDE-TO-FACE COMPLEXATION / OPTICAL GAS SENSING

THANA ARUNWATTANACHOK: SYNTHESIS OF PYRIDYL PORPHYRIN METAL COMPLEXES. THESIS ADVISOR: ASST. PROF. WORAWAN BHANTHUMNAVIN, Ph.D., THESIS CO-ADVISOR: ASST. PROF. YONGSAK SRITANA-ANANT, Ph.D., 114 pp.

Tetraarylporphyrins carrying 4-pyridyl (Py) and phenyl (P) groups at *meso*-positions have been synthesized and characterized by various spectroscopic methods. The synthesis was performed by reacting pyrrole, benzaldehyde, and 4-pyridine carboxaldehyde at a 4:2:2 ratio giving 5-(4-pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) as a major product in 36% yield. Among the porphyrins prepared, 5,10,15,20-tetraphenylporphyrin (TPP, **1**) and MPyTPP (**8**) have been shown to form complexes with acetate salts of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and chloride salt of Fe(III) in either chloroform or *N,N*-dimethylformamide. ¹H NMR measurements of all these metalloporphyrins revealed that the signal of internal N-H protons within the inner core of porphyrin rings between -2.70 to -2.90 ppm was absent, supportive of replacements of these protons by metal atoms. UV-Visible spectra showed that the four Q-bands of the free porphyrin base were reduced to only one or two peaks upon complexations. Dimeric porphyrin formed by a side to face complexation, (ZnTPP)(MPyTPP) (**22**) and (CoTPP)(MPyTPP) (**23**) were synthesized insitu in NMR tubes. ¹H NMR spectra indicated that pyridyl protons of MPyTPP showed large upfield shifts. The corresponding molecular weights of the porphyrin complexes and the dimer complexes were confirmed by MALDI-TOF-MS technique. Finally, ZnTPP (**2**) thin film has been used as optical-responsive chemically interacting materials for the detection of various vaporized alcohols.

Field of study Petrochemistry and Polymer Science Student's signature 

Academic year 2006 Advisor's signature 

Co-advisor's signature 

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LIST OF ABBREVIATIONS

E_a	: activation energy
α	: alpha
β	: beta
cm	: centimeter
δ	: chemical shift
CHCl ₃	: chloroform
COSY	: correlation spectroscopy
°C	: degree Celsius
δ	: delta
CDCl ₃	: deuterated chloroform
DDQ	: 2,3-dichloro-5,6-dicyanobenzoquinone
CH ₂ Cl ₂	: dichloromethane
DMF	: <i>N,N</i> -dimethylformamide
DMSO	: dimethylsulfoxide
d	: doublet (NMR)
g	: gram
γ	: gamma
MALDI-TOF-MS	: Matrix Assisted Laser Desorption/Ionization Time Of Flight mass spectrometry
<i>m</i> -	: meta
μ L	: microliter
mmol	: micromole
mg	: milligram
mL	: milliliter
min	: minute
[<i>M</i>] ⁺	: molecular ion
m	: multiplet (NMR)
nm	: nanometer
NMR	: nuclear magnetic resonance spectroscopy
<i>o</i> -	: ortho
<i>p</i> -	: para

ppm	: part per million
%	: percent
π	: pi
MPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrin
CoMPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrinatocobalt(II)
CuMPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrinatocopper(II)
MnMPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrinatomanganese(II)
FeMPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrinatoiron(II)
NiMPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrinatonicel(II)
ZnMPyTPP	: 5-(pyridyl)-10,15,20-triphenylporphyrinatozinc(II)
<i>cis</i> -DPyDPP	: 5,10-(dipyridyl)-15,20-diphenylporphyrin
<i>trans</i> -DPyDPP	: 5,15-(dipyridyl)-10,20-diphenylporphyrin
TPyMPP	: 5,10,15-(tripyrldyl)-20-phenylporphyrin
<i>k</i>	: rate constant
SAM	: self-assembled monolayer
s	: singlet (NMR)
TPP	: 5,10,15,20-tetraphenylporphyrin
CoTPP	: 5,10,15,20-tetraphenylporphyrinatocobalt(II)
CuTPP	: 5,10,15,20-tetraphenylporphyrinatocopper(II)
FeTPP	: 5,10,15,20-tetraphenylporphyrinatoiron(II)
MnTPP	: 5,10,15,20-tetraphenylporphyrinatomanganese(II)
NiTPP	: 5,10,15,20-tetraphenylporphyrinatonicel(II)
ZnTPP	: 5,10,15,20-tetraphenylporphyrinatozinc(II)
TPyP	: 5,10,15,20-tetrapyrldylporphyrin
ZnTPyP	: 5,10,15,20-tetrapyrldylporphyrinatozinc(II)
TLC	: thin layer chromatography
UV	: ultra-violet
Vis	: visible
λ	: wavelength