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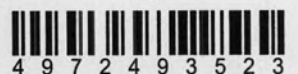
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SYNTHESIS OF ALKYNE-LINKED PORPHYRIN COMPLEXES
FOR ORGANIC NANOSENSOR

Mr. Wuttichai Reainthippayasakul

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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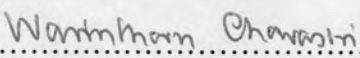
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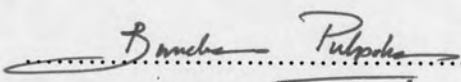
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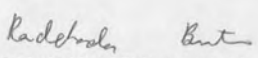
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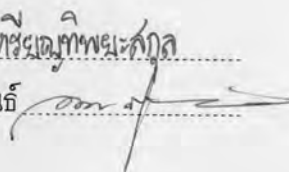
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ชุดของสารประกอบเชิงซ้อนโลหะของพอร์ไฟรินที่เชื่อมต่อกับแอลไคน์ สังเคราะห์ได้จากปฏิกิริยาไซโนกาซิริคัปปลิงในเปอร์เซ็นต์ผลิตภัณฑ์ที่น่าพึงพอใจ (11-88 เปอร์เซ็นต์) โดยหมู่เมธิลิลถูกเลือกใช้เป็นหมู่แทนที่ด้านข้างเพื่อเพิ่มความสามารถในการละลาย ขณะที่หมู่แอลไคน์ถูกต่อที่ตำแหน่งมีไซเพื่อขยายระบบพายคอนจูเกตของพอร์ไฟริน พอร์ไฟรินที่สังเคราะห์ได้ทั้งหมดถูกพิสูจน์เอกลักษณ์ด้วยเทคนิคโปรตอนเอ็นเอ็มอาร์สเปกโทรสโกปี และมวลดิทอพแมสสเปกโทรเมทรี ทั้งยังถูกวิเคราะห์สมบัติกายภาพเชิงแสงด้วยเทคนิคยูวี-วิซิเบิลสเปกโทรสโกปี และฟลูออเรสเซนซ์สเปกโทรสโกปี จากการวิเคราะห์พบว่า ทั้งโลหะไอออนและหมู่แทนที่ที่ตำแหน่งมีไซ โดยเฉพาะอย่างยิ่งหมู่แอลไคน์ ส่งผลต่อสเปกตรัมของการดูดกลืนและการคายแสงของพอร์ไฟริน โดยพอร์ไฟรินที่เชื่อมต่อกับแอลไคน์แสดงระบบพายคอนจูเกตที่มากขึ้นเมื่อเทียบกับพอร์ไฟรินตั้งต้น ดังที่ได้แสดงจากผลการดูดกลืนและการคายแสงในช่วงความยาวคลื่นที่สูงขึ้น สมบัติการเกิดโคออร์ดิเนชันของพอร์ไฟรินที่สังเคราะห์ได้ถูกศึกษาเบื้องต้นโดยใช้เทคนิคโปรตอนเอ็นเอ็มอาร์ ยูวี-วิซิเบิล และฟลูออเรสเซนซ์ไทเทรชันโดยใช้พิริดีนเป็นลิแกนด์ จากผลของโปรตอนเอ็นเอ็มอาร์ไทเทรชันพบว่า สารประกอบเชิงซ้อนโลหะของพอร์ไฟรินเกิดเป็นสารประกอบเชิงซ้อนกับพิริดีนได้แบบ 1:1 นอกจากนี้ การดูดกลืนแสงในช่วงความยาวคลื่นที่สูงขึ้น และการลดลงของความเข้มสัญญาณฟลูออเรสเซนซ์เมื่อเติมพิริดีน ใช้ยืนยันการเกิดสารประกอบเชิงซ้อนระหว่างพอร์ไฟรินและพิริดีนได้

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KEYWORDS : ALKYNE-LINKED PORPHYRIN / COUPLING REACTION /
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WUTTICHAIR EAINTHIPPAYASAKUL : SYNTHESIS OF ALKYNE-
LINKED PORPHYRIN COMPLEXES FOR ORGANIC NANOSENSOR.
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A series of *meso*-alkyne-linked porphyrin metal complexes has been synthesized by Sonogashira coupling reactions in satisfactory yield (11-88%). The mesityl groups were chosen to use as side chains in order to improve the solubility, whereas the alkynyl groups were linked at *meso*-positions to extend the π -conjugated system of porphyrins. All synthesized porphyrins were characterized by ^1H NMR spectroscopy and MALDI-TOF mass spectrometry. Their photophysical properties were also investigated by UV-visible spectroscopy and fluorescence spectroscopy. It has been demonstrated that central metal ions as well as *meso*-substituents, especially alkyne linkers, affected the absorption and emission spectra of porphyrins. The spectroscopic data revealed that alkyne-linked porphyrins exhibited higher π -conjugation compared to porphyrin building blocks resulting in the red shifts in both absorption and emission spectra. Coordination properties of synthesized porphyrins have been preliminarily studied by ^1H NMR, UV-visible, and fluorescence spectroscopic titration with pyridine as axial ligand. The ^1H NMR titration results indicated the 1:1 complexation of porphyrin metal complexes with pyridine. In addition, the significant red shifts in absorption spectra and decreasing of the fluorescence intensity upon an addition of pyridine also supported the formation of porphyrin-pyridine complexes.

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CONTENTS

	Pages
ABSTRACT IN THAI	iv
ABSTRACT IN ENGLISH	v
ACKNOWLEDGEMENTS	vi
LIST OF TABLES	xiii
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS	xxiii
CHAPTER I : INTRODUCTION	1
1.1 Porphyrins.....	1
1.2 Structure and Nomenclature of Porphyrins.....	2
1.3 Synthetic Strategies of Porphyrins.....	3
1.3.1 Synthesis of Porphyrins <i>via</i> Monopyrrole Tetramerization.....	4
1.3.2 Synthesis of Porphyrins from Dipyrromethanes.....	6
1.3.3 Synthesis of Porphyrins from Tripyrranes.....	9
1.3.4 Synthesis of Porphyrins from Tetrapyrrolic Intermediates.....	9
1.4 Reactivity Profiles of Porphyrins.....	10
1.4.1 Electrophilic Reactions.....	12
1.4.2 Nucleophilic Reactions.....	12
1.4.3 Reductions, Oxidations, and Other Reactions.....	13
1.4.4 Metallations.....	13
1.4.4.1 Chloroform/Methanol Method.....	14
1.4.4.2 Dimethylformamide Method.....	14
1.4.4.3 Acetic acid/Acetate Method.....	15
1.4.4.4 Pyridine Method.....	15
1.4.4.5 Metal Carbonyl Method.....	15
1.4.4.4 Acetylacetone Method.....	15
1.4.5 Demetallations.....	15
1.5 Photophysical Properties of Porphyrins.....	16

	Pages
1.6 Conjugate-Linked Porphyrins.....	18
1.7 Alkyne-Linked Porphyrins.....	21
1.8 Objectives.....	28
CHAPTER II : EXPERIMENTAL.....	29
2.1 Materials and Chemicals.....	29
2.2 Instruments and Equipments.....	30
2.3 Synthesis of Dipyrromethane Derivatives.....	31
2.3.1 Synthesis of 5-Hexyldipyrromethane (1).....	31
2.3.2 Synthesis of Dipyrromethane (2).....	32
2.3.2.1 Synthesis of Dipyrromethane Using TFA as Catalyst.....	32
2.3.2.2 Synthesis of Dipyrromethane Using MgBr ₂ as Catalyst.....	32
2.4 Synthesis of Ethyne Derivatives.....	33
2.4.1 Synthesis of 1-(4- <i>N,N</i> -Dimethylaminophenyl)-2- trimethylsilylethyne (DMAP-TMSE, 3).....	33
2.4.2 Synthesis of 4- <i>N,N</i> -Dimethylaminophenylethyne (DMAPE, 4).....	34
2.4.3 Synthesis of 1-(4-Nitrophenyl)-2-trimethylsilylethyne (NP-TMSE, 5).....	34
2.4.4 Synthesis of 4-Nitrophenylethyne (NPE, 6).....	35
2.4.5 Synthesis of 1-(4-Cyanophenyl)-2-trimethylsilylethyne (CP-TMSE, 7).....	36
2.4.6 Synthesis of 4-Cyanophenylethyne (CPE, 8).....	36
2.4.7 Synthesis of 1-(4-Formylphenyl)-2-trimethylsilylethyne (FP-TMSE, 9).....	37
2.4.8 Synthesis of 4-Formylphenylethyne (FPE, 10).....	38
2.4.9 Synthesis of 1-(4-Carboxyphenyl)-2-trimethylsilylethyne (CarP-TMSE, 11).....	38

	Pages
2.4.10 Synthesis of 4-Carboxyphenylethyne (CarPE, 12).....	39
2.5 Synthesis of <i>meso</i> -Dihexylporphyrin Derivatives.....	40
2.5.1 Synthesis of 5,15-Dihexylporphyrin (DHP, 13).....	40
2.5.1.1 Attempts to Synthesize DHP <i>via</i> Monopyrrole Tetramerization.....	40
2.5.1.2 Attempts to Synthesize DHP from 5-Hexyldipyrromethane.....	41
2.5.1.3 Synthesis of DHP from Dipyrromethane.....	42
2.5.2 Synthesis of (5,15-Dihexylporphyrinato)zinc(II) (Zn-DHP, 14).....	43
2.5.3 Synthesis of 5,15-Dibromo-10,20-dihexylporphyrin (Br ₂ DHP, 15).....	44
2.5.4 Synthesis of (5,15-Dibromo-10,20-dihexylporphyrinato)- zinc(II) (Zn-Br ₂ DHP, 16).....	45
2.6 Synthesis of <i>meso</i> -Dimesitylporphyrin Derivatives.....	46
2.6.1 Synthesis of 5,15-Dimesitylporphyrin (DMP, 17).....	46
2.6.2 Synthesis of (5,15-Dimesitylporphyrinato)zinc(II) (Zn-DMP, 18).....	47
2.6.3 Synthesis of (5,15-Dimesitylporphyrinato)manganese(II) (Mn-DMP, 19).....	48
2.6.4 Synthesis of (5,15-Dibromo-10,20-dimesitylporphyrinato)- zinc(II) (Zn-Br ₂ DMP, 20).....	49
2.6.5 Synthesis of (5,15-Dibromo-10,20-dimesitylporphyrinato)- manganese(II) (Mn-Br ₂ DMP, 21).....	50
2.7 Synthesis of Alkyne-Linked Porphyrin Metal Complexes.....	51
2.7.1 Synthesis of [5,15-Bis(trimethylsilylethynyl)-10,20- dimesitylporphyrinato]zinc(II) (Zn-(TMSE) ₂ DMP, 22).....	51
2.7.2 Synthesis of (5,15-Diethynyl-10,20-dimesitylporphyrinato)- zinc(II) (Zn-E ₂ DMP, 23).....	52

	Pages
2.7.3 Synthesis of [5,15-Bis(phenylethynyl)-10,20-dimesityl-porphyrinato]zinc(II) (Zn-(PE) ₂ DMP, 24).....	53
2.7.4 Synthesis of [5,15-Bis(phenylethynyl)-10,20-dimesityl-porphyrinato]manganese(II) (Mn-(PE) ₂ DMP, 25).....	54
2.7.5 Synthesis of [5-Bromo-15-(4'- <i>N,N</i> -dimethylaminophenyl-ethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)(Br)DMP, 26).....	55
2.7.6 Synthesis of [5,15-Bis(4'- <i>N,N</i> -dimethylaminophenyl-ethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE) ₂ DMP, 27).....	56
2.7.7 Synthesis of [5-(4'- <i>N,N</i> -Dimethylaminophenylethynyl)-15-(4''-nitrophenylethynyl)-10,20-dimesitylporphyrinato]-zinc(II) (Zn-(DMAPE)(NPE)DMP, 28).....	57
2.7.8 Synthesis of [5,15-Bis(4'-nitrophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(NPE) ₂ DMP, 29).....	58
2.7.9 Synthesis of [5,15-Bis(4'-cyanophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(CPE) ₂ DMP, 30).....	59
2.7.10 Synthesis of [5,15-Bis(4'-formylphenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(FPE) ₂ DMP, 31).....	60
2.7.11 Synthesis of [5,15-Bis(4'-carboxyphenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(CarPE) ₂ DMP, 32).....	61
2.8 Investigation of Photophysical Properties.....	62
2.8.1 UV-Visible Spectroscopy.....	63
2.8.2 Fluorescence Spectroscopy.....	63
2.9 Investigation of Coordination Properties.....	63
2.9.1 ¹ H NMR Titration.....	63
2.9.2 UV-Visible Titration.....	64
2.9.3 Fluorescence Titration.....	65

	Pages
CHAPTER III : RESULTS AND DISCUSSION.....	66
3.1 Concept of Molecular Design.....	66
3.2 Synthesis of Porphyrin Building Blocks.....	67
3.2.1 Synthesis of <i>meso</i> -Dihexylporphyrin Derivatives.....	68
3.2.1.1 Synthesis of 5,15-Dihexylporphyrin (DHP, 13).....	68
3.2.1.2 Synthesis of (5,15-Dihexylporphyrinato)zinc(II) (Zn-DHP, 14).....	74
3.2.1.3 Synthesis of 5,15-Dibromo-10,20-dihexylporphyrin (Br ₂ DHP, 15).....	75
3.2.1.4 Synthesis of (5,15-Dibromo-10,20-dihexyl- porphyrinato)zinc(II) (Zn-Br ₂ DHP, 16).....	75
3.2.2 Synthesis of <i>meso</i> -Dimesitylporphyrin Derivatives.....	76
3.2.2.1 Synthesis of 5,15-Dimesitylporphyrin (DMP, 17).....	76
3.2.2.2 Synthesis of (5,15-Dimesitylporphyrinato)zinc(II) (Zn-DMP, 18).....	77
3.2.2.3 Synthesis of (5,15-Dimesitylporphyrinato)- manganese(II) (Mn-DMP, 19).....	78
3.2.2.4 Synthesis of (5,15-Dibromo-10,20-dimesityl- porphyrinato)zinc(II) (Zn-Br ₂ DMP, 20).....	78
3.2.2.5 Synthesis of (5,15-Dibromo-10,20-dimesityl- porphyrinato)manganese(II) (Mn-Br ₂ DMP, 21).....	79
3.2.3 Solubility of Porphyrin Building Blocks.....	80
3.3 Synthesis of Alkyne-Linked Porphyrin Metal Complexes.....	81
3.3.1 Attempts to Synthesize Alkyne-Linked Porphyrin from Free Base Porphyrin.....	83
3.3.2 Synthesis of [5,15-Bis(trimethylsilylethynyl)-10,20- dimesitylporphyrinato]zinc(II) (Zn-(TMSE) ₂ DMP, 22).....	84
3.3.3 Synthesis of (5,15-Diethynyl-10,20-dimesitylporphyrinato)- zinc(II) (Zn-E ₂ DMP, 23).....	84
3.3.4 Synthesis of Arylethyne-Linked Porphyrin Metal Complexes	85

	Pages
3.4 Investigation of Photophysical Properties.....	88
3.4.1 UV-Visible Spectroscopy.....	88
3.4.1.1 Effect of Metal Ions.....	91
3.4.1.2 Effect of Hexyl and Mesityl Side Chains.....	92
3.4.1.3 Effect of Bromo Substituents.....	94
3.4.1.4 Effect of Alkyne Linkers.....	95
3.4.1.5 Effect of Arylethyne Linkers.....	97
3.4.2 Fluorescence Spectroscopy.....	99
3.4.2.1 Effect of Metal Ions.....	102
3.4.2.2 Effect of Hexyl and Mesityl Side Chains.....	103
3.4.2.3 Effect of Bromo Substituents.....	103
3.4.2.4 Effect of Alkyne Linkers.....	105
3.4.2.5 Effect of Arylethyne Linkers.....	106
3.5 Investigation of Coordination Properties.....	107
3.5.1 ¹ H NMR Titration.....	107
3.5.2 UV-Visible Titration.....	116
3.5.3 Fluorescence Titration.....	120
CHAPTER IV : CONCLUSION.....	123
REFERENCES.....	124
APPENDICES.....	132
VITAE.....	188

LIST OF TABLES

Tables	Pages
2.1 The amounts of porphyrins used in the preparation of the stock solutions.....	62
2.2 The amounts of porphyrins used in the ¹ H NMR titration.....	63
2.3 The amounts of added pyridine and ratio of pyridine:porphyrins in the ¹ H NMR titration.....	64
2.4 The amounts of added pyridine and ratio of pyridine:porphyrins in the UV-visible and florescence titration.....	65
3.1 Effects of acids on the condensation with a 25:1 ratio of pyrrole and paraformaldehyde.....	71
3.2 Effect of pyrrole:paraformaldehyde ratio and reaction time on the yield of dipyrromethane.....	72
3.3 The ¹ H NMR chemical shifts of <i>meso</i> -dihexylporphyrin derivatives.....	76
3.4 The ¹ H NMR chemical shifts of <i>meso</i> -dimesitylporphyrin derivatives.....	79
3.5 The solubility of <i>meso</i> -dihexylporphyrin and <i>meso</i> -dimesitylporphyrin derivatives in common organic solvents.....	80
3.6 Synthesis of aryltrimethylsilylethyne derivatives.....	82
3.7 Synthesis of arylethyne derivatives.....	82
3.8 The structure and yield of symmetric arylethyne-linked porphyrin metal complexes.....	85
3.9 The ¹ H NMR chemical shifts of synthesized arylethyne-linked porphyrin metal complexes.....	87
3.10 The MALDI-TOF mass data of synthesized arylethyne-linked porphyrin metal complexes.....	87
3.11 Absorption maxima of the solutions of all synthesized porphyrins at a 10 ⁻⁵ M concentration in THF.....	89

Tables		Pages
3.12	The excitation and emission wavelength of the solutions of all synthesized porphyrins at a 10^{-5} M concentration in THF.....	100
3.13	Changes in chemical shifts of pyridine and DMP protons in the ^1H NMR titration of DMP with pyridine in CDCl_3	109
3.14	Changes in chemical shifts of pyridine and Zn-DMP protons in the ^1H NMR titration of Zn-DMP with pyridine in CDCl_3	111
3.15	Changes in chemical shifts of pyridine and Zn-(TMSE) $_2$ DMP protons in the ^1H NMR titration of Zn-(TMSE) $_2$ DMP with pyridine in CDCl_3	113

LIST OF FIGURES

Figures	Pages
1.1 Structures of naturally occurring porphyrin derivatives.....	1
1.2 Structure and nomenclature of porphyrin in Fischer's system relative to IUPAC system.....	3
1.3 Synthesis of tetraphenylporphyrin (TPP) from monopyrrole using Adler-Longo's procedure.....	4
1.4 Synthesis of tetraphenylporphyrin (TPP) from monopyrrole using Lindsey's procedure.....	5
1.5 Synthesis of octaethylporphyrin (OEP) from monopyrrole.....	6
1.6 Synthesis of porphyrins from two unsymmetrically substituted dipyrromethanes using the MacDonald [2+2] approach.....	7
1.7 Synthesis of porphyrin from symmetrically substituted dipyrromethane using the MacDonald [2+2] approach.....	8
1.8 Synthesis of porphyrin from symmetrically substituted 1,9-di-unfunctionalized dipyrromethanes and aldehydes.....	8
1.9 Synthesis of porphyrin from tripyrrane and monopyrrole using the [3+1] approach.....	9
1.10 Synthesis of porphyrin from tetrapyrrolic intermediate.....	10
1.11 The inner and outer aromatic subfragments of the porphyrin skeleton.....	11
1.12 The conjugation pathway in the [18]-annulene structure of porphyrins.....	11
1.13 Bromination of porphyrins by using NBS.....	12
1.14 The basic structures of phlorins, porphodimethanes, and chlorins...	13
1.15 The Gouterman's four orbital model and the electronic absorption spectrum of a simple porphyrin.....	17
1.16 The energy level diagram to explain the fluorescence emission.....	18
1.17 Structures of <i>meso</i> -phenylene-linked porphyrin and directly <i>meso-meso</i> bonded porphyrin oligomers.....	19

Figures	Pages
1.18 Structures of <i>meso</i> -substituted porphyrins with conjugated	20
1.19 Model of the definition of torsional angles θ_{AB} and θ_{BC}	20
1.20 The mechanism of Sonogashira coupling reaction.....	22
1.21 Structures of porphyrins containing 4-dimethylaminophenyl as the electron donor group and 4-nitrophenyl, 4-cyanophenyl, and 5-nitrothiazoyl as the electron acceptor group.....	23
1.22 Synthesis of <i>meso</i> -ferrocenylethynyl porphyrins.....	24
1.23 The molecular structure of <i>meso</i> -ferrocenylethynyl porphyrin from the X-ray diffraction analysis.....	24
1.24 The absorption spectra of donor-acceptor porphyrin and its corresponding compounds.....	25
1.25 Structures of asymmetrically 5,15-substituted-(10,20-diaryl- porphyrinato)zinc(II) chromophores.....	26
1.26 Structures of porphyrin-fullerene with ethynylenephenylene subunits.....	27
1.27 Structures of <i>meso-meso</i> , <i>meso-β</i> , and <i>β-β</i> ethyne-linked porphyrin dimers.....	27
1.28 The general structure of target porphyrins.....	28
3.1 The general structure of target porphyrins.....	66
3.2 The general synthetic strategy for the preparation of <i>meso</i> - dibrominated porphyrins as porphyrin building blocks.....	67
3.3 The synthetic pathways of 5,15-dihexylporphyrin.....	68
3.4 Structures and exact masses of predicted porphyrin components in the hexylporphyrin mixture.....	69
3.5 The MALDI-TOF mass spectroscopic data of each fraction from column chromatography of the hexylporphyrin mixture.....	69
3.6 The ^1H NMR spectra of crude mixture, pyrrole, dipyrromethane, and tripyrrane.....	73
3.7 The ^1H NMR spectrum of 5,15-dihexylporphyrin (DHP, 13).....	73
3.8 The ^1H NMR spectrum of 5,15-dimesitylporphyrin (DMP, 17).....	77

Figures	Pages
3.9 The π - π stacking interactions of Zn-Br ₂ DHP and Zn-Br ₂ DMP.....	81
3.10 The MALDI-TOF mass spectrum of product from the reaction between Br ₂ DHP and trimethylsilylacetylene.....	83
3.11 The visual color of the solutions of porphyrins at a 10 ⁻⁴ M concentration in THF.....	90
3.12 UV-visible absorption spectra of DMP, Zn-DMP, and Mn-DMP....	91
3.13 UV-visible absorption spectra of DHP, Zn-DHP, Zn-Br ₂ DHP, DMP, Zn-DMP, and Zn-Br ₂ DMP.....	93
3.14 The distribution of dihedral angles in <i>meso</i> -aryl Zn(II), Cu(II), Ni(II), and free base porphyrins from the CCD.....	94
3.15 UV-visible absorption spectra of DHP, Zn-DHP, Br ₂ DHP, and Zn-Br ₂ DHP.....	95
3.16 UV-visible absorption spectra of Zn-DMP, Zn-(TMSE) ₂ DMP, Zn-E ₂ DMP, and Zn-(PE) ₂ DMP.....	96
3.17 UV-visible absorption spectra of Zn-(PE) ₂ DMP, Zn-(DMAPE) ₂ DMP, Zn-(NPE) ₂ DMP, Zn-(CPE) ₂ DMP, Zn-(FPE) ₂ DMP, and Zn-(CarPE) ₂ DMP.....	97
3.18 UV-visible absorption spectra of Zn-(PE) ₂ DMP, Zn-(DMAPE)(Br)DMP and Zn-(DMAPE)(NPE)DMP.....	98
3.19 Florescence images of the solutions of porphyrins at a 10 ⁻⁴ M concentration in THF under the excitation wavelength at 366 nm...	101
3.20 Fluorescence emission spectra of DMP, Zn-DMP, and Mn-DMP...	102
3.21 Fluorescence emission spectra of DHP, Zn-DHP, DMP, and Zn-DMP.....	103
3.22 Fluorescence emission spectra of Br ₂ DHP, Zn-DMP, Zn-Br ₂ DMP and Zn-(DMAPE)(Br)DMP.....	104
3.23 The photoinduced electron transfer (PET) process.....	105
3.24 Fluorescence emission spectra of Zn-DMP, Zn-(TMSE) ₂ DMP, and Zn-E ₂ DMP.....	105

Figures	Pages	
3.25	Fluorescence emission spectra of Zn-(PE) ₂ DMP, Zn-(DMAPE) ₂ DMP, Zn-(DMAPE)(NPE)DMP, Zn-(NPE) ₂ DMP, Zn-(CPE) ₂ DMP, Zn-(FPE) ₂ DMP, and Zn-(CarPE) ₂ DMP.....	106
3.26	The ¹ H NMR titration spectra of DMP with pyridine in CDCl ₃	108
3.27	The ¹ H NMR titration curve of DMP with pyridine in CDCl ₃	109
3.28	The ¹ H NMR titration spectra of Zn-DMP with pyridine in CDCl ₃ .	110
3.29	The ¹ H NMR titration curve of Zn-DMP with pyridine in CDCl ₃	111
3.30	The ¹ H NMR titration spectra of Zn-(TMSE) ₂ DMP with pyridine in CDCl ₃	112
3.31	The ¹ H NMR titration curve of Zn-(TMSE) ₂ DMP with pyridine in CDCl ₃	113
3.32	The Job's plot of the complexation of Zn-DMP with pyridine.....	115
3.33	The Job's plot of the complexation of Zn-(TMSE) ₂ DMP with pyridine.....	115
3.34	The proposed structure of 1:1 porphyrin-pyridine complex.....	116
3.35	The UV-visible titration spectra of Zn-DMP (10 ⁻⁵ M in THF) with pyridine at 25 °C.....	117
3.36	The UV-visible titration spectra of Zn-Br ₂ DMP (10 ⁻⁵ M in THF) with pyridine at 25 °C.....	117
3.37	The UV-visible titration spectra of Zn-(TMSE) ₂ DMP (10 ⁻⁵ M in THF) with pyridine at 25 °C.....	118
3.38	The UV-visible titration spectra of Zn-E ₂ DMP (10 ⁻⁵ M in THF) with pyridine at 25 °C.....	118
3.39	The UV-visible titration spectra of Zn-(PE) ₂ DMP (10 ⁻⁵ M in THF) with pyridine at 25 °C.....	119
3.40	The UV-visible titration spectra of Mn-DMP (10 ⁻⁵ M in THF) with pyridine at 25 °C.....	119
3.41	The fluorescence titration spectra of Zn-DMP (10 ⁻⁵ M in THF) with pyridine at ambient temperature.....	119

Figures	Pages
3.42 The fluorescence titration spectra of Zn-(TMSE) ₂ DMP (10 ⁻⁵ M in THF) with pyridine at ambient temperature.....	121
3.43 The fluorescence titration spectra of Zn-(PE) ₂ DMP (10 ⁻⁵ M in THF) with pyridine at ambient temperature.....	122
A-1 The ¹ H NMR spectrum of 5-hexyldipyrromethane (1).....	133
A-2 The ¹ H NMR spectrum of dipyrromethane (2).....	133
A-3 The ¹³ C NMR spectrum of dipyrromethane (2).....	134
A-4 The ESI mass spectrum of dipyrromethane (2).....	134
A-5 The ¹ H NMR spectrum of DMAP-TMSE (3).....	135
A-6 The ¹³ C NMR spectrum of DMAP-TMSE (3).....	135
A-7 The ESI mass spectrum of DMAP-TMSE (3).....	136
A-8 The ¹ H NMR spectrum of DMAPE (4).....	136
A-9 The ¹³ C NMR spectrum of DMAPE (4).....	137
A-10 The ESI mass spectrum of DMAPE (4).....	137
A-11 The ¹ H NMR spectrum of NP-TMSE (5).....	138
A-12 The ¹³ C NMR spectrum of NP-TMSE (5).....	138
A-13 The ¹ H NMR spectrum of NPE (6).....	139
A-14 The ¹³ C NMR spectrum of NPE (6).....	139
A-15 The ¹ H NMR spectrum of CP-TMSE (7).....	140
A-16 The ¹³ C NMR spectrum of CP-TMSE (7).....	140
A-17 The ¹ H NMR spectrum of CPE (8).....	141
A-18 The ¹³ C NMR spectrum of CPE (8).....	141
A-19 The ¹ H NMR spectrum of FP-TMSE (9).....	142
A-20 The ¹³ C NMR spectrum of FP-TMSE (9).....	142
A-21 The ESI mass spectrum of FP-TMSE (9).....	143
A-22 The ¹ H NMR spectrum of FPE (10).....	143
A-23 The ¹³ C NMR spectrum of FPE (10).....	144
A-24 The ESI mass spectrum of FPE (10).....	144
A-25 The ¹ H NMR spectrum of CarP-TMSE (11).....	145
A-26 The ¹³ C NMR spectrum of CarP-TMSE (11).....	145

Figures	Pages
A-27 The ESI mass spectrum of CarP-TMSE (11).....	146
A-28 The ¹ H NMR spectrum of CarPE (12).....	146
A-29 The ¹³ C NMR spectrum of CarPE (12).....	147
A-30 The ESI mass spectrum of CarPE (12).....	147
A-31 The ¹ H NMR spectrum of DHP (13).....	148
A-32 The MALDI-TOF mass spectrum of DHP (13).....	148
A-33 The UV-visible spectrum of DHP (13).....	149
A-34 The fluorescence spectrum of DHP (13).....	149
A-35 The ¹ H NMR spectrum of Zn-DHP (14).....	150
A-36 The MALDI-TOF mass spectrum of Zn-DHP (14).....	150
A-37 The UV-visible spectrum of Zn-DHP (14).....	151
A-38 The fluorescence spectrum of Zn-DHP (14).....	151
A-39 The ¹ H NMR spectrum of Br ₂ DHP (15).....	152
A-40 The MALDI-TOF mass spectrum of Br ₂ DHP (15).....	152
A-41 The UV-visible spectrum of Br ₂ DHP (15).....	153
A-42 The fluorescence spectrum of Br ₂ DHP (15).....	153
A-43 The ¹ H NMR spectrum of Zn-Br ₂ DHP (16).....	154
A-44 The MALDI-TOF mass spectrum of Zn-Br ₂ DHP (16).....	154
A-45 The UV-visible spectrum of Zn-Br ₂ DHP (16).....	155
A-46 The fluorescence spectrum of Zn-Br ₂ DHP (16).....	155
A-47 The ¹ H NMR spectrum of DMP (17).....	156
A-48 The MALDI-TOF mass spectrum of DMP (17).....	156
A-49 The UV-visible spectrum of DMP (17).....	157
A-50 The fluorescence spectrum of DMP (17).....	157
A-51 The ¹ H NMR spectrum of Zn-DMP (18).....	158
A-52 The MALDI-TOF mass spectrum of Zn-DMP (18).....	158
A-53 The UV-visible spectrum of Zn-DMP (18).....	159
A-54 The fluorescence spectrum of Zn-DMP (18).....	159
A-55 The ¹ H NMR spectrum of Mn-DMP (19).....	160
A-56 The MALDI-TOF mass spectrum of Mn-DMP (19).....	160

Figures	Pages
A-57 The UV-visible spectrum of Mn-DMP (19).....	161
A-58 The fluorescence spectrum of Mn-DMP (19).....	161
A-59 The ¹ H NMR spectrum of Zn-Br ₂ DMP (20).....	162
A-60 The MALDI-TOF mass spectrum of Zn-Br ₂ DMP (20).....	162
A-61 The UV-visible spectrum of Zn-Br ₂ DMP (20).....	163
A-62 The fluorescence spectrum of Zn-Br ₂ DMP (20).....	163
A-63 The ¹ H NMR spectrum of Mn-Br ₂ DMP (21).....	164
A-64 The MALDI-TOF mass spectrum of Mn-Br ₂ DMP (21).....	164
A-65 The UV-visible spectrum of Mn-Br ₂ DMP (21).....	165
A-66 The fluorescence spectrum of Mn-Br ₂ DMP (21).....	165
A-67 The ¹ H NMR spectrum of Zn-(TMSE) ₂ DMP (22).....	166
A-68 The MALDI-TOF mass spectrum of Zn-(TMSE) ₂ DMP (22).....	166
A-69 The UV-visible spectrum of Zn-(TMSE) ₂ DMP (22).....	167
A-70 The fluorescence spectrum of Zn-(TMSE) ₂ DMP (22).....	167
A-71 The ¹ H NMR spectrum of Zn-E ₂ DMP (23).....	168
A-72 The MALDI-TOF mass spectrum of Zn-E ₂ DMP (23).....	168
A-73 The UV-visible spectrum of Zn-E ₂ DMP (23).....	169
A-74 The fluorescence spectrum of Zn-E ₂ DMP (23).....	169
A-75 The ¹ H NMR spectrum of Zn-(PE) ₂ DMP (24).....	170
A-76 The MALDI-TOF mass spectrum of Zn-(PE) ₂ DMP (24).....	170
A-77 The UV-visible spectrum of Zn-(PE) ₂ DMP (24).....	171
A-78 The fluorescence spectrum of Zn-(PE) ₂ DMP (24).....	171
A-79 The ¹ H NMR spectrum of Mn-(PE) ₂ DMP (25).....	172
A-80 The MALDI-TOF mass spectrum of Mn-(PE) ₂ DMP (25).....	172
A-81 The UV-visible spectrum of Mn-(PE) ₂ DMP (25).....	173
A-82 The fluorescence spectrum of Mn-(PE) ₂ DMP (25).....	173
A-83 The ¹ H NMR spectrum of Zn-(DMAPE)(Br)DMP (26).....	174
A-84 The MALDI-TOF mass spectrum of Zn-(DMAPE)(Br)DMP (26)..	174
A-85 The UV-visible spectrum of Zn-(DMAPE)(Br)DMP (26).....	175
A-86 The fluorescence spectrum of Zn-(DMAPE)(Br)DMP (26).....	175

Figures	Pages
A-87 The ^1H NMR spectrum of Zn-(DMAPE) $_2$ DMP (27).....	176
A-88 The MALDI-TOF mass spectrum of Zn-(DMAPE) $_2$ DMP (27).....	176
A-89 The UV-visible spectrum of Zn-(DMAPE) $_2$ DMP (27).....	177
A-90 The fluorescence spectrum of Zn-(DMAPE) $_2$ DMP (27).....	177
A-91 The ^1H NMR spectrum of Zn-(DMAPE)(NPE)DMP (28).....	178
A-92 The MALDI-TOF mass spectrum of Zn-(DMAPE)(NPE)DMP (28).....	178
A-93 The UV-visible spectrum of Zn-(DMAPE)(NPE)DMP (28).....	179
A-94 The fluorescence spectrum of Zn-(DMAPE)(NPE)DMP (28).....	179
A-95 The ^1H NMR spectrum of Zn-(NPE) $_2$ DMP (29).....	180
A-96 The MALDI-TOF mass spectrum of Zn-(NPE) $_2$ DMP (29).....	180
A-97 The UV-visible spectrum of Zn-(NPE) $_2$ DMP (29).....	181
A-98 The fluorescence spectrum of Zn-(NPE) $_2$ DMP (29).....	181
A-99 The ^1H NMR spectrum of Zn-(CPE) $_2$ DMP (30).....	182
A-100 The MALDI-TOF mass spectrum of Zn-(CPE) $_2$ DMP (30).....	182
A-101 The UV-visible spectrum of Zn-(CPE) $_2$ DMP (30).....	183
A-102 The fluorescence spectrum of Zn-(CPE) $_2$ DMP (30).....	183
A-103 The ^1H NMR spectrum of Zn-(FPE) $_2$ DMP (31).....	184
A-104 The MALDI-TOF mass spectrum of Zn-(FPE) $_2$ DMP (31).....	184
A-105 The UV-visible spectrum of Zn-(FPE) $_2$ DMP (31).....	185
A-106 The fluorescence spectrum of Zn-(FPE) $_2$ DMP (31).....	185
A-107 The ^1H NMR spectrum of Zn-(CarPE) $_2$ DMP (32).....	186
A-108 The MALDI-TOF mass spectrum of Zn-(CarPE) $_2$ DMP (32).....	186
A-109 The UV-visible spectrum of Zn-(CarPE) $_2$ DMP (32).....	187
A-110 The fluorescence spectrum of Zn-(CarPE) $_2$ DMP (32).....	187

LIST OF ABBREVIATIONS

Å	angstrom
α	alpha
Abs	absorbance
Ar	aryl or aromatic group
β	beta
br	broad (NMR)
Bu	butyl
°C	degree celsius
cm	centimeter
d	doublet (NMR)
dd	doublet of doublet (NMR)
δ	delta
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethylsulfoxide
eq.	equivalence
ESI-MS	Electrospray Ionization mass spectrometry
Et	ethyl
g	gram
γ	gamma
h	hour
HOMO	highest occupied molecular orbital
Hz	hertz
<i>i</i> -	iso
<i>J</i>	coupling constant
<i>k</i>	rate constant
K_a	association constant
LUMO	lowest unoccupied molecular orbital
m	multiplet (NMR)
<i>m</i> -	meta
M	molar

$[M]^+$	molecular ion
MALDI-TOF-MS	Matrix Assisted Laser Desorption Ionization Time-of-Flight mass spectrometry
Me	methyl
mg	milligram
MHz	megahertz
min	minute
mL	milliliter
mmol	millimole
mol	mole
m/z	mass per charge ratio
NBS	<i>N</i> -bromosuccinimide
nm	nanometer
NMR	Nuclear Magnetic Resonance
<i>o</i> -	ortho
OAc	acetate
<i>p</i> -	para
Ph	phenyl
ppm	part per million
Pr	propyl
py	pyridine
rt	room temperature
s	second
s	singlet (NMR)
t	triplet (NMR)
<i>t</i> -	tertiary
TBAF	tetrabutylammonium fluoride
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilane or trimethylsilyl
μ L	microliter
μ mol	micromole
UV	ultraviolet

λ	wavelength
δ	chemical shift
π	pi
%	percent