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**SYNTHESIS AND PROPERTIES  
OF FULLY CONJUGATED  
PORPHYRIN ARRAYS  
FOR LIGHT HARVESTING**

**A thesis presented in partial fulfillment of the requirements  
for the degree of**

**Doctor of Philosophy  
in  
Chemistry**

**at Massey University, Palmerston North, New Zealand.**

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# Abstract

This thesis presents the synthesis of porphyrin arrays for light-harvesting applications using Wittig chemistry, which allows the construction of covalently bound systems that are conjugated, stable and easy to characterize. This was achieved using a dendrimer strategy utilizing tetraarylporphyrins as building blocks, monofunctionalized with either aldehyde or phosphonium salt groups at the  $\beta$ -pyrrolic position, and benzenes, polyfunctionalized with either aldehyde or phosphonium salt groups; stepwise control of the addition of each porphyrin moiety was thus obtained. In this way, different porphyrins in different metallated states were arranged in a determinate geometrical relationship, which is of great importance in the investigations on electron/energy transfers. Arrays containing up to five metalloporphyrin units (two kinds of porphyrins coordinating two different metals) were synthesized and characterized.

The unexpected chromatography behaviour and  $^1\text{H-NMR}$  spectra of a Zn porphyrin functionalized with a 1,3-bis(methyl(diethylphosphonate)) benzene were the reason for an investigation, which uncovered, mainly with the use of NMR spectrometry, the first case of intramolecular coordination between the Zn centre and a phosphonate group of the same porphyrin. The dynamic nature of this coordination was characterized and chemical-physical parameters for Zn porphyrin/phosphonate binding were determined.

In order to establish the photophysical properties of our conjugated arrays, we synthesized a series of dyads containing Zn and free-base tetraphenylporphyrins (TPPs) connected through variable length phenylenevinylene-type bridges; along with this series, the preparation of the Zn and free-base homometallic homologue dyads and two series of monomers carrying the conjugated linker were realized. Collaboration with IFOS-CNR in Bologna, Italy was established in order to investigate the intramolecular photophysics of those systems, which involve efficient intramolecular energy transfer from the Zn to the free-base porphyrin.

Finally, dyads composed of Fe(III) and Zn porphyrin were prepared as part of a project in collaboration with the University of Pennsylvania for the investigation of new artificial photosynthetic systems. Two series of dimers were prepared in order to obtain incorporation in both the classes of hydrophobic and hydrophilic proteins. TPPs were used for the making of the hydrophobic dyads while hydrophilicity was achieved by employing tetraester porphyrin derivatives, which can be quantitatively hydrolyzed to afford the correspondent water soluble acids. A new monosubstituted porphyrin was also synthesized and incorporated in the arrays to minimize steric hindrance inside the protein binding sites.

# Declaration

This is to certify that the work described in this thesis has not been submitted for a higher degree at any other university or institution.

Fabio Lodato

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I'd like to thank the people who have had an influence on this experience, likely the most life-changing in my first 30 years.

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# Table of Contents

## 1. Introduction

1.1.	Porphyrins	1
1.2.	Porphyrin arrays	3
1.3.	Covalently linked porphyrin arrays	6
1.4.	Porphyrin and porphyrin array applications	7
1.5.	Porphyrins and porphyrin arrays for light harvesting	11
1.6.	Object and structure of the thesis	18

## 2. Array syntheses

2.1.	Introduction to porphyrin array preparations	21
2.2.	Dendrimers	27
2.3.	Porphyrin synthesis and functionalization	30
2.4.	Wittig chemistry	32
2.5.	Dendrimer syntheses	37
2.6.	Mixed array preparations	44
2.7.	Array characterizations	47
2.8.	Experimental procedures	56

## 3. Coordination of pendant phosphonate groups in Zn porphyrins

3.1.	Introduction	74
3.2.	<sup>1</sup> H-NMR investigation of Zn coordination in Zn-22 isomers	75
3.3.	Phosphonate coordination to Zn porphyrins	79
3.4.	Low temperature NMR experiments	84
3.5.	Identification of the coordination around the metal in Zn porphyrins	88
3.6.	Conclusions	92
3.7.	Experimental procedures	93

## **4. Porphyrin photophysics**

4.1.	Introduction	100
4.2.	Intramolecular photophysics	104
4.3.	Time-resolved spectroscopy	109
4.4.	Zn/fb and Zn/Fe(III) porphyrin dyads photophysics	113
4.5.	Monomer models syntheses	114
4.6.	Monomer models spectroscopy and photophysics	119
4.7.	Zn/Zn, fb/fb, and Zn/fb dyad syntheses	127
4.8.	Dyad spectroscopy and photophysics	133
4.9.	Conclusions	137
4.10.	Experimental procedures	138

## **5. Porphyrin arrays for Maquette incorporation**

5.1.	Porphyrins in biological systems	162
5.2.	Porphyrins and maquettes	163
5.3.	Fe(III) porphyrins	167
5.4.	Fe/Zn dyads syntheses	170
5.5.	Water soluble porphyrins	173
5.6.	Water soluble porphyrin dyads	180
5.7.	Water soluble Fe/Zn dyads	186
5.8.	Fe(III) porphyrin array characterizations	189
5.9.	Preliminary investigation into porphyrin/maquette binding	190
5.10.	Conclusions	190
5.11.	Experimental procedures	191

## **6. References**

224

# Abbreviations

z	
anal.	analysis
aq.	aqueous
Ar	aryl
calc.	calculated
CV	cyclic voltammetry or cyclic voltammogram
DMF	dimethylformamide
DSSC	dye-sensitized solar cell
Et	ethyl
EtOH	ethanol
$\epsilon$	extinction coefficient
ep	ethylphosphonate
eq.	equivalents
exc.	excitation
ext	extended
FAB-MS	fast atom bombardment mass spectroscopy
Fig.	Figure
HOMO	highest occupied molecular orbital
HRMS	high-resolution mass spectrometry
h	hour
ipp	isopropylphosphonate
IR	infrared
$J$	coupling constant
LUMO	lowest unoccupied molecular orbital
$\mu\text{L}$	microlitre
MALDI-MS	matrix assisted laser desorption of ions mass spectroscopy
max	maximum
Me	methyl
mep	meta-ethylphosphonate
min	minutes
M	molarity



mmol	millimole
mol	mole
NMR	nuclear magnetic resonance
pep	para-ethylphosphonate
Ph	phenyl
phos	phosphonate
Pr	propyl
ps	phosphonium salt
sat.	saturated
THF	tetrahydrofuran
TLC	thin layer chromatography
TPP	tetraphenylporphyrin
TXP	tetraxylporphyrin
UV	ultraviolet

# Index of Compounds

1	benzaldehyde
2	xylylaldehyde
3	TPP
4	TXP
5	TPP-CHO
6	TXP-CHO
7	TPP-CH <sub>2</sub> -OH
8	TXP-CH <sub>2</sub> -OH
9	TPP-CH <sub>2</sub> -Cl
10	TXP-CH <sub>2</sub> -Cl
11	TPP-ps
12	TXP-ps
13	terephthalaldehyde
14	TPP-Ph-CHO
15	TXP-Ph-CHO
16	1,3,5-tribromomethylbenzene
17	benzene-tricarboxaldehyde
18	(TXP) <sub>2</sub> -Ph-CHO
19	mesitylenetris-(triphenylphosphonium bromide)
20	xylenebis-(triphenylphosphonium chloride)
21	1,3,5-mesitylenetris(diethylphosphonate)
22	TPP-Ph-(ep) <sub>2</sub>
23	(TPP) <sub>2</sub> -Ph-ep
24	(TPP) <sub>3</sub>
25	(TPP) <sub>2</sub> -Ph-CHO
27	(TPP-Ph) <sub>2</sub> -Ph-ep
28	1,3,5-mesitylenetris(diisopropylphosphonate)
29	(TPP-Ph) <sub>2</sub> -Ph-ipp
30	(TXP-Ph) <sub>2</sub> -Ph-ipp
31	((TPP) <sub>2</sub> -Ph) <sub>2</sub> -Ph-ipp

32	(NiTPP-Ph) <sub>2</sub> -Ph-Ph-ZnTXP
33	(NiTPP-Ph) <sub>2</sub> -Ph-Ph-(ZnTXP) <sub>2</sub>
34	((NiTPP) <sub>2</sub> -Ph) <sub>2</sub> -Ph-Ph-ZnTXP
35	1,3-xylenebis(diethylphosphonate)
36	TPP-Ph-mep
37	toluene(diethylphosphonate)
38	toluene(diisopropylphosphonate)
39	TPP-ext-COOMe
40	TPP-ext-CH <sub>2</sub> -OH
41	TPP-ext-CHO
42	TPP-ext-CH <sub>2</sub> -Cl
43	TPP-ext-CH <sub>2</sub> -ps
44	1,4-xylenebis(diethylphosphonate)
45	TPP-Ph-pep
46	TPP-Ph-TPP
47	TPP-Ph-Ph-CHO
48	TPP-CH=CH <sub>2</sub>
49	TPP-ext-CH=CH <sub>2</sub>
50	TPP-Ph-CH=CH <sub>2</sub>
51	TPP-Ph-Ph-CH=CH <sub>2</sub>
52	<i>trans</i> -4-stilbenecarboxaldehyde
53	<i>trans</i> -4-vinylstilbene
54	(TPP) <sub>2</sub>
55	TPP-ZnTPP
56	TPP-Ph-ZnTPP
57	TPP-ext-Ph-ZnTPP
58	TPP-ext-Ph-TPP
59	TPP-Ph-Ph-ZnTPP
60	TPP-Ph-Ph-TPP
61	FeTPP-Ph-TPP
62	FeTPP-ext-Ph-TPP
63	FeTPP-Ph-ZnTPP
64	FeTPP-ext-Ph-ZnTPP
65	FeTPP-Ph-Ph-ZnTPP

66	tetra(4-sulfonatophenyl)porphyrin, TSPP
67	tetra(4-pyridinyl)porphyrin, T4PyP
68	tetra(3-pyridinyl)porphyrin, T3PyP
69	tetra(4-methylpyridinium iodide)porphyrin, T4MPyP
70	tetra(3-methylpyridinium iodide)porphyrin, T3MPyP
71	TPyP-(Br) <sub>n</sub>
72	3-bromomethyl benzoic acid
73	3-carboxaldehyde benzoic acid
74	3-carboxaldehyde-methylbenzoate
75	3-carboxaldehyde-ethylbenzoate
76	tetra(3'-(methylcarboxylate)phenyl)porphyrin, T3(M)EPP
77	tetra(3'-(ethylcarboxylate)phenyl)porphyrin, T3(E)EPP
78	T3(M)EPP-CHO
79	T3(E)EPP-CHO
80	T3(M)EPP-CH <sub>2</sub> -OH
81	T3(E)EPP-CH <sub>2</sub> -OH
82	T3(M)EPP-CH <sub>2</sub> -Cl
83	T3(E)EPP-CH <sub>2</sub> -Cl
84	T3(M)EPP-CH <sub>2</sub> -ps
85	T3(E)EPP-CH <sub>2</sub> -ps
86	4-bromobenzaldehyde acetal
87	terephthalaldehyde monoacetal
88	2-pyrrole methanol
89	dipyrrylmethane
90	dipyrrylthione
91	monoacetalporphyrin, MAP
92	para-diacetalporphyrin
93	porphine
94	monobenzylporphyrin, MBP
95	MBP-T3EPP
96	MBP-T3CPP
97	MBP-ZnT3EPP
98	FeMBP-ZnT3EPP
99	FeMBP-ZnT3CPP

<b>100</b>	T3(E)EPP-Ph-CHO
<b>101</b>	T3(E)EPP-Ph-ep
<b>102</b>	T3(E)EPP-Ph-Ph-ipp
<b>103</b>	FeMBP-Ph-ZnT3(E)EPP
<b>104</b>	FeMBP-Ph-Ph-ZnT3(E)EPP
<b>105</b>	FeMBP-Ph-ZnT3CPP
<b>106</b>	FeMBP-Ph-Ph-ZnT3CPP
<b>107</b>	FeTPP-Ph-ZnT3(E)EPP
<b>108</b>	FeTPP-Ph-ZnT3CPP

# Index of Figures

	Page
<b>Figure 1-1</b> Porphine	1
<b>Figure 1-2</b> Aromaticity in free-base, dianionic and metallated porphyrins	2
<b>Figure 1-3</b> UV-visible absorption spectrum of ZnTPP ( <b>Zn-3</b> ) in DCM ( $3.2 \times 10^{-6} \text{M}$ ) with the Q band region expanded	2
<b>Figure 1-4</b> Fused porphyrin tapes by Tsuda and Osuka	3
<b>Figure 1-5</b> Cofacial dimers by Collman <i>et al.</i> and Fletcher and Therien	4
<b>Figure 1-6</b> Coordinated porphyrin arrays by Okumura <i>et al.</i> and Plieger <i>et al.</i>	5
<b>Figure 1-7</b> Coordinated nonaporphyrin array by Mak <i>et al.</i>	5
<b>Figure 1-8</b> Coordinated triporphyrin array by Slagt <i>et al.</i>	6
<b>Figure 1-9</b> Covalently linked array by Sanders <i>et al.</i>	6
<b>Figure 1-10</b> Chiral Ru porphyrin catalyst by Simonnaux and Le Maux	8
<b>Figure 1-11</b> Triple-decker array by Schweikart <i>et al.</i>	9
<b>Figure 1-12</b> Arrays for optoelectronics by Holten <i>et al.</i>	10
<b>Figure 1-13</b> Linear arrays with controlled dihedral angles by Ahn <i>et al.</i>	10
<b>Figure 1-14</b> Three-dimensional grid array by Nakano <i>et al.</i>	11
<b>Figure 1-15</b> Model of the purple bacterial photosynthetic unit by Pullerits and Sundtröm	12
<b>Figure 1-16</b> Schematic representation of a Grätzel cell by Campbell	13
<b>Figure 1-17</b> Schematic representation of an inverted photovoltaic device by Borgström <i>et al.</i>	14
<b>Figure 1-18</b> Polypeptide/porphyrin/fullerene photovoltaic device by Hasobe <i>et al.</i>	14
<b>Figure 1-19</b> Schematic representation of antenna effect in porphyrin arrays	15
<b>Figure 1-20</b> Dendritic multiporphyrin antenna by Choi <i>et al.</i>	16
<b>Figure 1-21</b> Mixed metal pentamer <b>Ni<sub>4</sub>Zn-34</b>	19
<b>Figure 1-22</b> Simulated 3-dimensional structure of <b>Zn-22c</b>	19
<b>Figure 1-23</b> Series of Zn/free base porphyrin dyads	20
<b>Figure 1-24</b> Fe(III)/Zn porphyrin dyads for protein binding	20

<b>Figure 2-1</b>	Meso-meso linked conjugated dimers by Osuka <i>et al.</i>	21
<b>Figure 2-2</b>	Precursor for polyphenylene dendrimers by Diez-Barra <i>et al.</i>	28
<b>Figure 2-3</b>	Polyphenylene dendrimer	29
<b>Figure 2-4</b>	<sup>1</sup> H-NMR spectrum of <b>25</b>	48
<b>Figure 2-5</b>	<sup>1</sup> H-NMR spectrum of the aromatic region of <b>25</b>	49
<b>Figure 2-6</b>	Signal attributions by <sup>1</sup> H- <sup>1</sup> H NMR correlations	50
<b>Figure 2-7</b>	<sup>1</sup> H-NMR resonances of <i>trans</i> , <i>cis</i> and vinyl β-pyrrolic substituents	51
<b>Figure 2-8</b>	<sup>1</sup> H-NMR spectrum of <b>Ni-31</b>	51
<b>Figure 2-9</b>	<sup>1</sup> H-NMR and COSY spectra of <b>Ni-31</b>	52
<b>Figure 2-10</b>	<sup>1</sup> H-NMR and COSY spectra of <b>Ni<sub>4</sub>Zn-34</b>	53
<b>Figure 2-11</b>	MALDI spectrum of <b>Ni<sub>4</sub>Zn-34</b>	54
<b>Figure 2-12</b>	UV-vis absorption spectra of <b>25</b> , <b>Zn-25</b> and <b>Ni-25</b> in DCM	55
<b>Figure 2-13</b>	UV-vis absorption spectra of <b>Ni-25</b> and <b>Ni-31</b> in DCM	56
<b>Figure 3-1</b>	<sup>1</sup> H-NMR (500 MHz) spectra of <b>Zn-22t</b> and <b>Zn-22c</b>	75
<b>Figure 3-2</b>	Ring current effect on proton chemical shifts in annulene and a general porphyrin	77
<b>Figure 3-3</b>	Empirical estimate of ring current shield in porphyrins by Riche <i>et al.</i>	78
<b>Figure 3-4</b>	Computer-generated models of the conformations in <i>trans</i> and <i>cis</i> isomers of <b>M-22</b>	79
<b>Figure 3-5</b>	Phosphonate coordination to a Zn porphyrin	80
<b>Figure 3-6</b>	ZnTPP titration of ligands containing P-O bonds using <sup>31</sup> P-NMR	80
<b>Figure 3-7</b>	<sup>1</sup> H-NMR (500 MHz) spectra of <b>Zn-22t</b> and <b>Zn-22c</b> at concentrations of 10 <sup>-2</sup> M and 10 <sup>-3</sup> M	81
<b>Figure 3-8</b>	Simulated 3-dimensional structure of <b>Zn-22c</b>	82
<b>Figure 3-9</b>	Bond distortion effect on vinyl NMR resonances of <b>Ni-22c</b> and <b>Zn 22c</b>	82
<b>Figure 3-10</b>	<sup>1</sup> H-NMR (400 MHz) resonance of methyl groups in <b>Zn-36c</b>	83
<b>Figure 3-11</b>	<sup>1</sup> H-NMR (700 MHz) and <sup>31</sup> P-NMR (400 MHz) spectra of <b>Zn-22c</b> at various temperatures	84
<b>Figure 3-12</b>	Observed and calculated lineshapes for <sup>1</sup> H-NMR spectra of <b>Zn-22c</b> at various temperatures	86
<b>Figure 3-13</b>	Arrhenius plot for phosphonate exchange in <b>Zn-22c</b>	87

<b>Figure 3-14</b> Zn-3 <sup>1</sup> H-NMR titrations of phosphonate <b>38</b>	90
<b>Figure 3-15</b> Zn-3 <sup>31</sup> P-NMR titration of phosphonate <b>37</b>	90
<b>Figure 3-16</b> Zn-O distances in complexes with C.N. = 5 and C.N. = 6	91
<b>Figure 3-17</b> Possible difference in the coordination geometry between ZnTPP + phosphonate and <b>Zn-22c</b>	92
<b>Figure 4-1</b> Porphyrin electronic transitions after excitation in the UV-visible region	100
<b>Figure 4-2</b> Exciton coupling in non-conjugated linear porphyrin arrays by Piet <i>et al.</i>	102
<b>Figure 4-3</b> UV-visible-near IR absorption spectra of a series of porphyrin ‘tapes’ by Kim and Osuka	102
<b>Figure 4-4</b> Zn and free-base dyads and monomers for photophysical investigation	103
<b>Figure 4-5</b> Porphyrin-perylene dyad by Tomizaki <i>et al.</i> and porphyrin-fullerene dyad by Schuster <i>et al.</i>	104
<b>Figure 4-6</b> Förster vs. Dexter energy transfer mechanisms	105
<b>Figure 4-7</b> Homometallic dyads by Kadish <i>et al.</i>	106
<b>Figure 4-8</b> Zn/free base dyads by Hsiao <i>et al.</i> and Osuka <i>et al.</i>	106
<b>Figure 4-9</b> Zn/Fe(III) dyads by Helms <i>et al.</i>	107
<b>Figure 4-10</b> Zn/Fe(III) dyad by Fujita <i>et al.</i>	108
<b>Figure 4-11</b> β-Pyrrolic alkynyl linked porphyrin arrays by Therien <i>et al.</i>	108
<b>Figure 4-12</b> Schematic representation of a ns time-resolved absorbance spectrometer	110
<b>Figure 4-13</b> Schematic representation of a ps time-resolved absorbance spectrometer	111
<b>Figure 4-14</b> Schematic representation of a ns time-resolved emission spectrometer	111
<b>Figure 4-15</b> Schematic representation of single photon counting apparatus	112
<b>Figure 4-16</b> Schematic representation of a ps time-resolved emission spectrometer	113
<b>Figure 4-17</b> Photophysics of Zn/free base and Zn/Fe(III) porphyrin dyads	114
<b>Figure 4-18</b> <sup>1</sup> H-NMR spectrum of the vinyl region in <b>Zn-45</b>	119



<b>Figure 4-19</b> Comparison between UV-visible absorption spectra of <b>51</b> and the sum of TPP and the conjugated substituent <b>53</b>	120
<b>Figure 4-20</b> UV-visible absorption spectra of free-base porphyrins <b>48-50</b>	121
<b>Figure 4-21</b> UV-visible absorption spectra of Zn porphyrins <b>Zn-48-Zn-51</b>	121
<b>Figure 4-22</b> Emission spectra (at 295 K) of the series <b>48-50</b> in toluene	123
<b>Figure 4-23</b> Emission spectra (at 295 K) of the series <b>Zn-48-Zn-51</b> in toluene	123
<b>Figure 4-24</b> Emission spectra at 77 K of the series <b>Zn-48-Zn-51</b>	124
<b>Figure 4-25</b> Series of homometallic and heterometallic (M = Zn or 2H) porphyrin dyads	127
<b>Figure 4-26</b> <sup>1</sup> H-NMR resonances of the butadiene linker in <b>Zn-54</b>	133
<b>Figure 4-27</b> UV-visible absorption spectra of the series of free-base homometallic dyads <b>54, 46, 58</b> and <b>60</b> in toluene	134
<b>Figure 4-28</b> UV-visible absorption spectra of the series of heterometallic dyads <b>Zn/fb-55, Zn/fb-56, Zn/fb-57</b> and <b>Zn/fb-59</b> in toluene	134
<b>Figure 4-29</b> Emission spectra of the of heterometallic dyad <b>Zn/fb-59</b> and monomer model <b>Zn-51</b> in toluene	136
<b>Figure 4-30</b> Picosecond time-resolved emission spectra of <b>Zn/fb-59</b> in toluene	137
<b>Figure 5-1</b> Maquettes: porphyrin binding maquette and chemical-physical ductility. By Dutton	163
<b>Figure 5-2</b> Maquette models for proton and electron pumps by Discher <i>et al.</i>	164
<b>Figure 5-3</b> Model of a porphyrin array-maquette photoactive system	165
<b>Figure 5-4</b> Fe/Zn porphyrin dyads for amphiphilic maquette binding	165
<b>Figure 5-5</b> Fe/Zn porphyrin dyads for hydrophilic maquette binding	166
<b>Figure 5-6</b> <sup>1</sup> H-NMR spectrum of MAP <b>91</b>	183
<b>Figure 5-7</b> <sup>1</sup> H-NMR spectrum of <b>Zn/fb-97</b>	185

# Index of Synthetic Schemes

	Page
<b>Scheme 1-1</b> Schematic representation of Miyatami and Amao photosynthetic system	17
<b>Scheme 1-2</b> Schematic representation of Amao and Okura photosynthetic system	17
<b>Scheme 2-1</b> Array syntheses by Burrell and Officer and Nagata <i>et al.</i>	22
<b>Scheme 2-2</b> Array syntheses by Anton <i>et al.</i>	22
<b>Scheme 2-3</b> Array syntheses by Campbell	23
<b>Scheme 2-4</b> Array syntheses by Prathaphan <i>et al.</i>	23
<b>Scheme 2-5</b> Ag(I) promoted array syntheses by Park <i>et al.</i>	24
<b>Scheme 2-6</b> Phenylene bridged dimer by Burrell and Officer	24
<b>Scheme 2-7</b> Symmetrically functionalized porphyrin formation by Lindsey <i>et al.</i>	25
<b>Scheme 2-8</b> Functionalized porphyrin formations by Wiehe <i>et al.</i> and Kadish <i>et al.</i>	25
<b>Scheme 2-9</b> Example of porphyrin preparation by mixed aldehyde condensation	26
<b>Scheme 2-10</b> Porphyrin Vilsmeier formylations by Inhoffen <i>et al.</i> and Momenteau <i>et al.</i>	26
<b>Scheme 2-11</b> Dendrimer preparations by Freeman and Frichet, and Zeng and Zimmerman	27
<b>Scheme 2-12</b> Dendrimer formation through Wittig chemistry	29
<b>Scheme 2-13</b> Tetraarylporphyrins (TPP <b>3</b> and TXP <b>4</b> ) synthesis by Adler <i>et al.</i>	30
<b>Scheme 2-14</b> Phosphonium salt TPP-ps <b>11</b> and TXP-ps <b>12</b> syntheses by Burrell and Officer	31
<b>Scheme 2-15</b> Mechanism of the Wittig reaction	32
<b>Scheme 2-16</b> Preparation of porphyrin aldehydes <b>14</b> and <b>15</b> by Burrell and Officer	32
<b>Scheme 2-17</b> Syntheses of trialdehyde <b>17</b> and porphyrin dimer <b>18</b> by Burrell and Officer	33

<b>Scheme 2-18</b>	Synthesis of mesitylenetris-(triphenylphosphonium bromide) <b>19</b> by Storck and Manecke	33
<b>Scheme 2-19</b>	Wittig chemistry attempts involving mesitylenetris-(triphenylphosphonium bromide) <b>19</b>	34
<b>Scheme 2-20</b>	Wittig chemistry attempts involving of xylenebis-(triphenylphosphonium chloride) <b>20</b>	34
<b>Scheme 2-21</b>	Phosponates syntheses by Michaelis and Haehne	35
<b>Scheme 2-22</b>	1,3,5-mesitylenetris-(diethylphosphonate) <b>21</b> preparation	35
<b>Scheme 2-23</b>	Triphosponate <b>21</b> Wittig reaction with <b>Zn-5</b>	36
<b>Scheme 2-24</b>	Synthesis TPP dimer aldehyde <b>25</b>	37
<b>Scheme 2-25</b>	Porphyrins Zn-metallation reversible reaction	38
<b>Scheme 2-26</b>	Porphyrin dimer syntheses involving trisphosponate <b>21</b>	39
<b>Scheme 2-27</b>	Comparison between <b>Zn-22c</b> and <b>Zn-22t</b> reactivity	39
<b>Scheme 2-28</b>	Porphyrin dimer syntheses involving triphosponates <b>21</b> and <b>28</b>	41
<b>Scheme 2-29</b>	Porphyrin dimer syntheses involving triisopropylphosphonate <b>28</b>	42
<b>Scheme 2-30</b>	Porphyrin tetramer <b>M-31</b> syntheses	43
<b>Scheme 2-31</b>	Attempts to make 2 <sup>nd</sup> generation aldehyde dendrimers	44
<b>Scheme 2-32</b>	Mixed trimer <b>Ni<sub>2</sub>Zn-32</b> preparation	45
<b>Scheme 2-33</b>	Mixed tetramer <b>Ni<sub>2</sub>Zn<sub>2</sub>-33</b> preparation	46
<b>Scheme 2-34</b>	Mixed pentamer <b>Ni<sub>4</sub>Zn-34</b> preparation	46
<b>Scheme 3-1</b>	Aldehyde <b>Zn-5</b> reaction with triphosponate <b>21</b>	74
<b>Scheme 3-2</b>	Preparations of <b>Ni-22</b> and free base <b>22</b>	76
<b>Scheme 3-3</b>	Porphyrin phosphonate <b>Zn-36</b> synthesis	83
<b>Scheme 3-4</b>	Synthesis of monophosponates <b>37</b> and <b>38</b>	88
<b>Scheme 4-1</b>	Retrosynthetic scheme for the synthesis of porphyrins <b>M-48-M-51</b>	115
<b>Scheme 4-2</b>	Syntheses of “extended” aldehyde <b>41</b> and phosphonium salt <b>43</b>	116
<b>Scheme 4-3</b>	Wittig reaction of aldehyde <b>Zn-5</b> with diphosponate <b>44</b>	117
<b>Scheme 4-4</b>	Wittig reaction of phosphonate <b>Zn-45</b> with dialdehyde <b>13</b>	117
<b>Scheme 4-5</b>	Synthesis of vinylstilbene <b>53</b> via Wittig chemistry	118

<b>Scheme 4-6</b> Syntheses of A series dyads <b>54</b> , <b>Zn-54</b> and <b>Zn/fb-55</b>	128
<b>Scheme 4-7</b> Synthesis of heterometallic dyad <b>Zn/fb-56</b>	129
<b>Scheme 4-8</b> Synthesis of heterometallic dyad <b>Zn/fb-57</b>	129
<b>Scheme 4-9</b> Synthesis of homometallic dyads <b>58</b> and <b>Zn-58</b>	130
<b>Scheme 4-10</b> Synthesis of heterometallic dyad <b>Zn/fb-59</b>	131
<b>Scheme 4-11</b> Synthesis of homometallic dyads <b>60</b> and <b>Zn-60</b>	131
<b>Scheme 5-1</b> Iron insertion in free-base porphyrins	167
<b>Scheme 5-2</b> Iron porphyrin dimerization equilibrium	168
<b>Scheme 5-3</b> Iron porphyrin equilibria in presence of basic water	168
<b>Scheme 5-4</b> Hydrophobic Fe/free base porphyrin dimer syntheses	170
<b>Scheme 5-5</b> Hydrophobic Fe/Zn porphyrin dimer syntheses	171
<b>Scheme 5-6</b> Transmetallation between Zn and Fe porphyrins	172
<b>Scheme 5-7</b> Synthesis of a long chain hydrophobic dimer <b>Fe/Zn-65</b>	172
<b>Scheme 5-8</b> Synthesis of TSPP <b>66</b>	173
<b>Scheme 5-9</b> Syntheses T4PyP <b>67</b> and T3PyP <b>68</b>	174
<b>Scheme 5-10</b> Syntheses of water soluble T4MPyP <b>69</b> and T3MPyP <b>70</b>	174
<b>Scheme 5-11</b> Attempts to insert sulphonic groups in TPP derivatives	175
<b>Scheme 5-12</b> Attempts of Vilsmeier formylation on TPyP <b>Cu-67</b> and <b>Cu-68</b>	175
<b>Scheme 5-13</b> Reversible activation of pyridines by N-oxide formation	176
<b>Scheme 5-14</b> Bromination of tetrapyridylporphyrins	176
<b>Scheme 5-15</b> Attempt of CO insertion in <b>71</b>	177
<b>Scheme 5-16</b> Attempts to introduce formyl groups in <b>71</b> and <b>Zn-71</b>	177
<b>Scheme 5-17</b> Synthesis of T3(R)EPP <b>76</b> and <b>77</b>	178
<b>Scheme 5-18</b> Syntheses of T3EPP aldehyde and phosphonium salt	179
<b>Scheme 5-19</b> Syntheses of functionalized hydrophilic porphyrins	179
<b>Scheme 5-20</b> Retrosynthetic scheme for monosubstituted porphyrin preparation according to the procedure described by Wiehe <i>et al.</i>	180
<b>Scheme 5-21</b> Preparation of the monoprotected terephthalaldehyde <b>87</b>	181
<b>Scheme 5-22</b> Syntheses of dipyrromethane <b>89</b> by Lin <i>et al.</i> (via alcohol) and Brückner <i>et al.</i> (via thione)	181
<b>Scheme 5-23</b> Synthesis of MAP <b>91</b>	182
<b>Scheme 5-24</b> Synthesis and Fe metallation of MBP <b>94</b>	183
<b>Scheme 5-25</b> Synthesis of water-soluble fb/fb porphyrin dimer <b>96</b>	184

<b>Scheme 5-26</b>	Synthesis of water-soluble porphyrin dimer <b>Zn/fb-97</b>	184
<b>Scheme 5-27</b>	Synthesis of water-soluble Zn/Fe(III) porphyrin dimer <b>Zn/Fe-99</b>	186
<b>Scheme 5-28</b>	Synthesis of porphyrin aldehyde <b>Zn-100</b>	186
<b>Scheme 5-29</b>	Syntheses of Zn porphyrin phosphonates <b>Zn-101</b> and <b>Zn-102</b>	187
<b>Scheme 5-30</b>	Synthesis of long chain Zn/Fe(III) porphyrin dimers	187
<b>Scheme 5-31</b>	Synthesis of long chain hydrophilic Zn/Fe(III) porphyrin dimers	188
<b>Scheme 5-32</b>	Synthesis of TPP containing water-soluble dyad <b>Fe/Zn-108</b>	188

## Index of Tables

	Page	
<b>Table 2-1</b>	Syntheses of porphyrin phosphonates <b>M-23</b> and <b>M-27</b>	40
<b>Table 2-2</b>	Syntheses of phosphonates <b>M-27</b> and <b>M-29</b>	41
<b>Table 2-3</b>	Syntheses of phosphonates <b>Zn-29</b> and <b>Zn-30</b>	42
<b>Table 2-4</b>	Syntheses of phosphonates <b>Zn-31</b> and <b>Ni-31</b>	43
<b>Table 3-1</b>	<sup>1</sup> H-NMR (400 MHz) chemical shifts of variously metallated <i>cis</i> and <i>trans</i> <b>M-22</b>	77
<b>Table 3-2</b>	Temperature dependence of exchange rate $\tau^{-1}$ between coordinated and uncoordinated phosphonate ligands in <b>Zn-22c</b>	87
<b>Table 4-1</b>	Syntheses of the series of terminal methylene porphyrins <b>48-51</b>	118
<b>Table 4-2</b>	Absorption data for TPP, ZnTPP and porphyrin series <b>48-51</b> and <b>Zn-48-Zn-51</b> in toluene and at room temperature	122
<b>Table 4-3</b>	Luminescence properties of series <b>48-51</b> and <b>Zn-48-Zn-51</b> in toluene	125
<b>Table 4-4</b>	Absorption data for the series of heterometallic dyads <b>Zn/fb-55</b> , <b>Zn/fb-56</b> , <b>Zn/fb-57</b> and <b>Zn/fb-59</b> in toluene and at room temperature	135
<b>Table 4-5</b>	Absorption data for the series of Zn and free-base homometallic dyads <b>M-54</b> , <b>M-46</b> , <b>M-58</b> and <b>M-60</b> in toluene and at room temperature	135