Synthetic Routes to Multiporphyrin Arrays

Anthony K. Burrell,* David L. Officer,* Paul G. Plieger, and David C. W. Reid

Institute of Fundamental Sciences-Chemistry, Massey University, Private Bag 11-222, Palmerston North, New Zealand

Contents

I. Introduction

Tetrapyrrolic macrocycles[1] play a number of critical biological roles such as molecular binding,[2] reaction catalysis,[3] energy and electron transfers,[4,5] and light harvesting.[6] The importance of these functions has provided the impetus for intensive research toward artificial tetrapyrrolic macrocycle systems that may be able to model or mimic their natural counterparts. However, the synthesis of suitable tetrapyrrolic macrocycles and assemblies of tetrapyrrolic macrocycles has proved to be problematic.

Nature uses a myriad of biosynthetic pathways to make both the tetrapyrrolic macrocycles and the associated proteins and then to assemble them into arrays for energy- and electron-transfer purposes. The tetrapyrrolic macrocycles are bound to the proteins by a variety of interactions such as covalent thioether bonds, metal–ligand axial coordination, hydrophobic or hydrophilic interactions, and hydrogen bonding. It is virtually impossible to synthetically reproduce the intricate and specific protein matrix.

While some research groups have produced porphyrin–peptide conjugate assemblies as models for natural systems,[7–10] many researchers interested in mimicking these systems have constructed artificial, generally covalently linked, tetrapyrrolic macrocyclic arrays. Thus, nature has created a huge impetus for the synthesis of a wide variety of multiporphyrin assemblies.

Largely as a consequence of this, tetrapyrrolic macrocycles have also been found to be of great interest in areas outside modeling and mimicking natural systems. Molecular sensing,[11] molecular recognition,[2] medicine (photodynamic therapy,[12] boron nuclear capture therapy,[13] and DNA cleavage[14,15]), and optical applications (data storage,[16] nonlinear optics,[17] electrochromism,[18] and optical limiting[19]) are just a few of the many areas that have inspired the synthesis of porphyrin assemblies. The development of tetrapyrrolic molecular materials with the potential to undergo controlled energy or electron transfer has led to the production of prototypical molecular-scale devices such as wires,[20,21] logic devices, switches, and gates,[22] essential for the miniaturization of electronic componentry and technology. The increasing importance of these applications provides a continuous stimulus for intensive research toward artificial porphyrin assemblies.

II. Scope and Limitation of This Review

Most reviews on the synthesis of porphyrin assemblies or arrays[23] have placed emphasis on porphyrin size, in particular, diporphyrins, or on specific synthetic methods. The first review on covalently linked diporphyrins was undertaken by Dolphin et al.[24] in 1981 with a focus on heteroatom linkers, a common linkage at the time. Smith et al. summarized synthetic approaches to forming mostly dimer *meso-meso*, *meso-β*, *β–β*, and fused π-system linkages,[25] and more recently, Arnold summarized his significant contribution in the field of dimeric porphyrins containing alkyne, ethene, and ethane bridges.[26] The only current review of noncoordinated multiporphyrin assemblies is that of Shinmori and Osuka, who reviewed synthetic approaches to forming multiporphyrins with particular emphasis on aromatic-, ethynyl-, and *meso-meso*-linked porphyrin arrays.[27] Wasielewski reviewed photoinduced electron-transfer supramolecular systems of which a number are porphyrin dimer, trimer, and tetramer arrays,[5] while Sauvage et al. published a similar review of rotax-
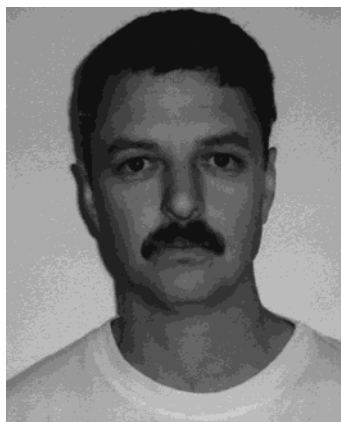
Anthony K. Burrell completed a Ph.D. at the University of Auckland, in 1990, under the direction of Professor Warren Roper. He worked with Professor Jonathan Sessler (UT), from 1990 to 1992, and then at Los Alamos National Laboratory (1992–1994) before obtaining an academic position at Massey University, in 1994, where he is currently Professor of Synthetic Chemistry. He was the recipient of the 1998 New Zealand Association of Scientists Research Medal, The Royal Society of New South Wales Walter Burfitt Prize for 1998 and the JPP Young Investigator Award in Porphyrin and Phthalocyanine Chemistry, 2000.
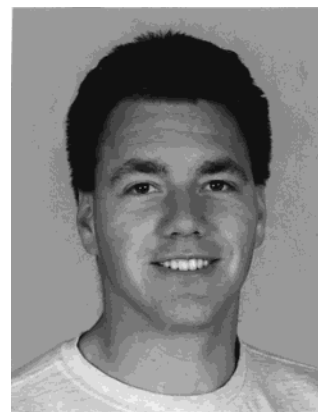
Paul G. Plieger received his B.Sc. with Honors (1994) and Ph.D. (1998) degrees in Synthetic Inorganic Chemistry from the University of Otago in Dunedin, New Zealand, under the supervision of Associate Professor Sally Brooker. He is currently working as a postdoctoral research fellow with Professor Anthony K. Burrell and Associate Professor David L. Officer. His current research interests are focused on the synthesis and coordination chemistry of porphyrin arrays.

David L. Officer obtained his Ph.D. from Victoria University of Wellington in 1982 under the direction of Professor Brian Halton. He joined the staff at Massey University in 1986 following postdoctoral research at The Australian National University and the University of Cologne as an Alexander von Humboldt Research Fellow. He is currently an associate professor and Director of the Nanomaterials Research Centre. He has active research programs in the synthesis and use of porphyrins for photovoltaic and molecular devices, and the development of new organic-based intelligent materials using functionalized thiophenes and carbon nanotubes.

David C. W. Reid completed his B.Sc. with Honors (1992) and Ph.D. (1998) in Chemistry in the Department of Chemistry at Massey University under the supervision of Professor Tony Burrell and Associate Professor David Officer. He is currently a Research Technologist at the New Zealand Dairy Research Institute in Palmerston North, New Zealand. His current research interests are focused on the behavior of the protein components in processed cheese systems.

anes which include some porphyrin dimer and trimer arrays.[28] Anderson summarized the causes and effect of interporphyrin conjugation on a number of fused and alkyne-linked porphyrin arrays.[29] Reviews on the role of the coordination bond in forming multiporphyrin structures have been covered in some detail by Wojaczynski and Latos-Grazynski,[30] Imamura and Fukushima,[31] and Sanders.[32]

This review aims to give comprehensive coverage to the synthetic methods utilized to form multiporphyrin arrays classified according to the various linkers between porphyrin units in the arrays. Emphasis has been placed on arrays containing *more* than two porphyrins and is organized by type of linker. In large arrays there is commonly more than one type of linkage, and therefore, the array synthesis can fall into more than one linker category. It should

be noted that in such cases the linkage created in the final coupling step has been used to classify the linker type. In a number of cases, this has not been possible as the final synthetic step involves the formation of the porphyrin ring rather than the linker. In such instances, these arrays have been classified according to the most prolific linkage. Every effort has been made to ensure a comprehensive coverage of the literature through the end of 2000.

The review begins with covalent linkers, specifically the carbon—heteroatom linkages. These links are regarded as the historical beginnings of porphyrin arrays and include such examples as the ester-linked di- and triporphyrins of Anton et al,[33] the amide-linked tetraporphyrins of Dubowchik and Hamilton,[34–35] and the ether-linked pentaporphyrin of Milgrom.[36] More recently, this type of linkage has been further exploited, with the ester-linked nonaporphyrin of Sanders[37] and the ether-linked triporphyrin arrays of Osuka[38] being two such examples. The review then examines carbon—carbon linkers. Alkane, alkene, alkyne, and aromatic links are all

Scheme 1. Condensation of Pyrrole and Arylaldehydes To Form TAPs

tetraarylporphyrinogen

TAP
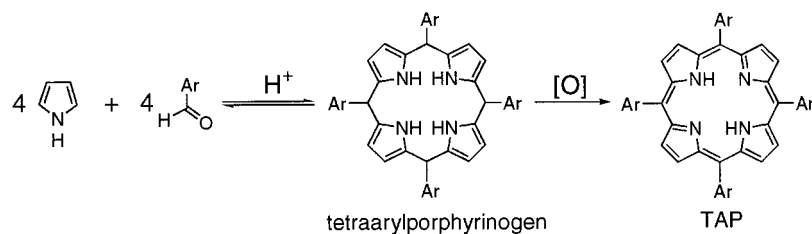
Scheme 2. Mixed Aldehyde Condensation To Give a Mixture of Products

desired porphyrin
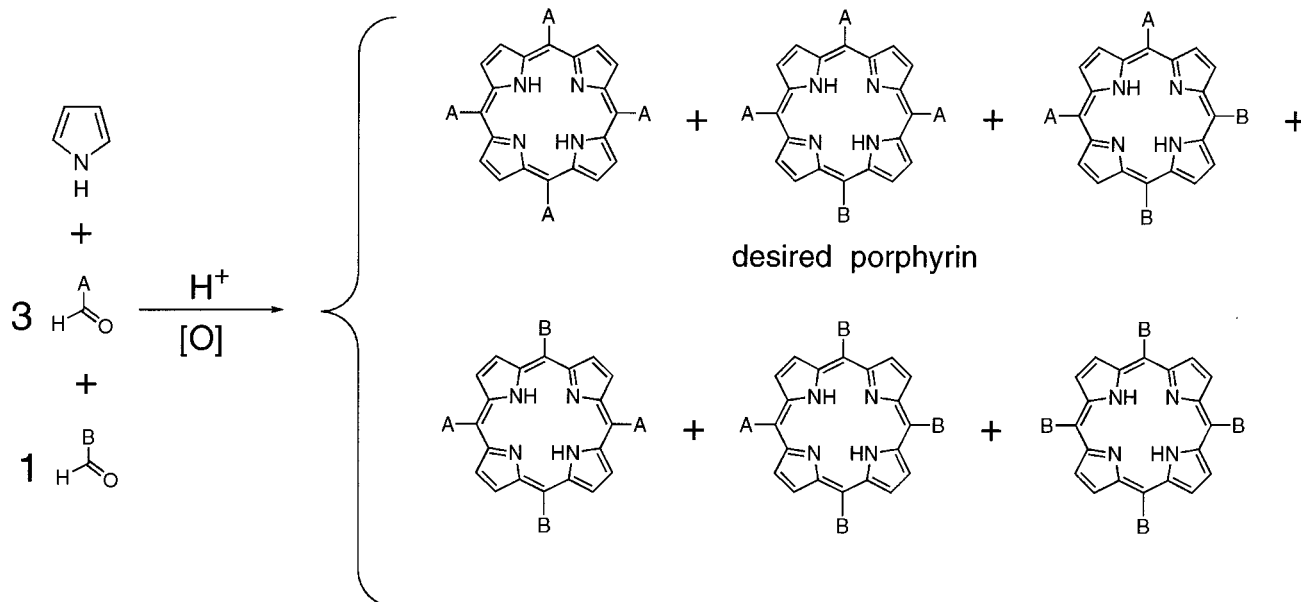
Scheme 3. 2 + 2 Condensation of Dipyrrylmethanes—The MacDonald Method[56]
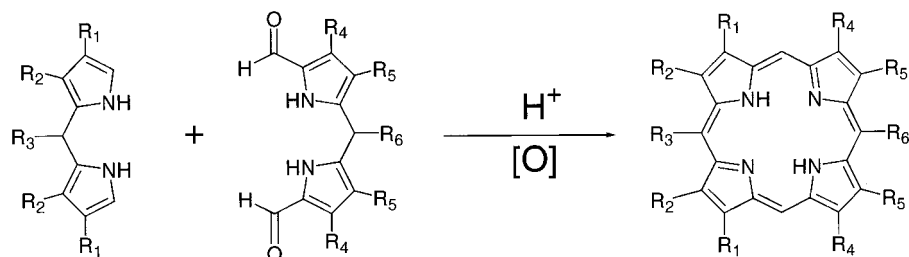
Scheme 4. 2 + 2 Condensation of α-Free Dipyrrylmethanes with Aldehydes
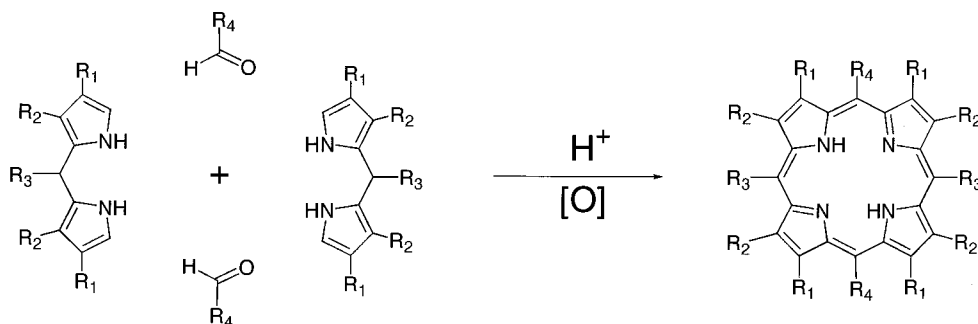
covered and include such examples as the Osuka group's direct single-bond-linked nonamer 'wind-mill'[39] and the alkene-linked nonamer of Officer et al.[40] Given the previous coverage,[30−32] only a select few examples of linkages using metal—metal and metal—ligand coordination have been highlighted, namely, those containing visually stimulating structural arrangements or coordination. To a lesser extent, porphyrin arrays have been synthesized using hydrogen bonding,[41] and the review concludes by detailing a number of such examples.

A major problem in reviewing the porphyrin literature in this fashion is the lack of much of the information (experimental details, yields, purity) that would allow comparisons of the synthetic routes. Consequently, we have largely avoided comparisons

Scheme 5. General Synthetic Scheme for Porphyrin Array Formation
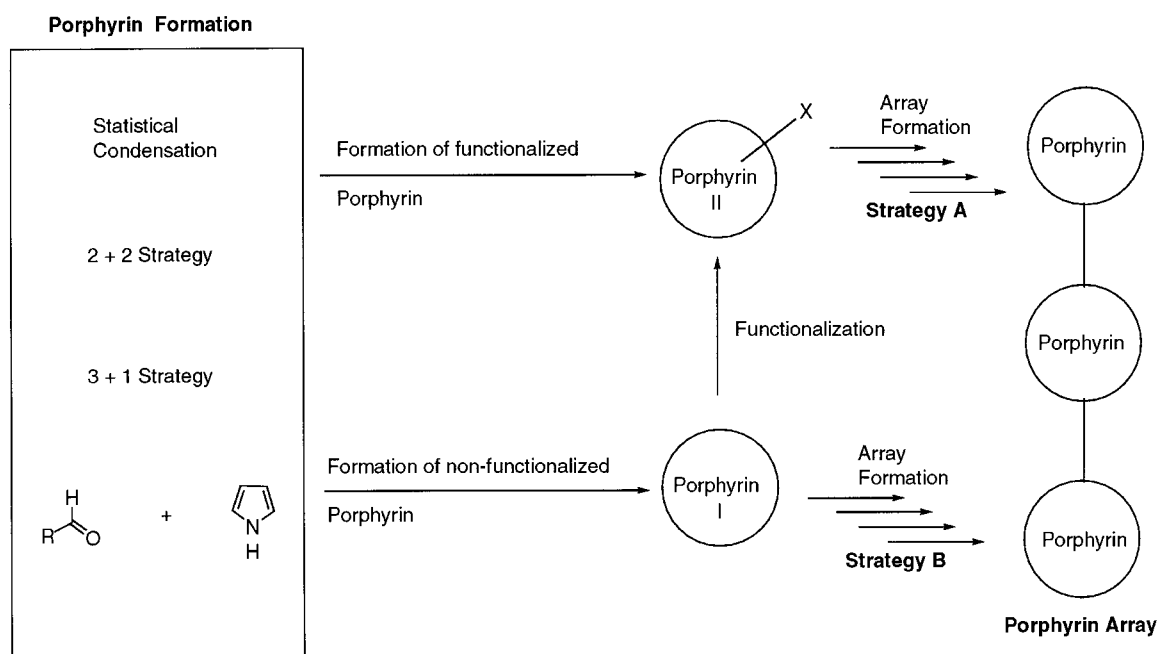
Scheme 6. Synthesis of Triporphyrin Cu-3[a] of Anton et al.[33]

[a] (i) C_5H_5N, C_6H_6, reflux, 16 h.
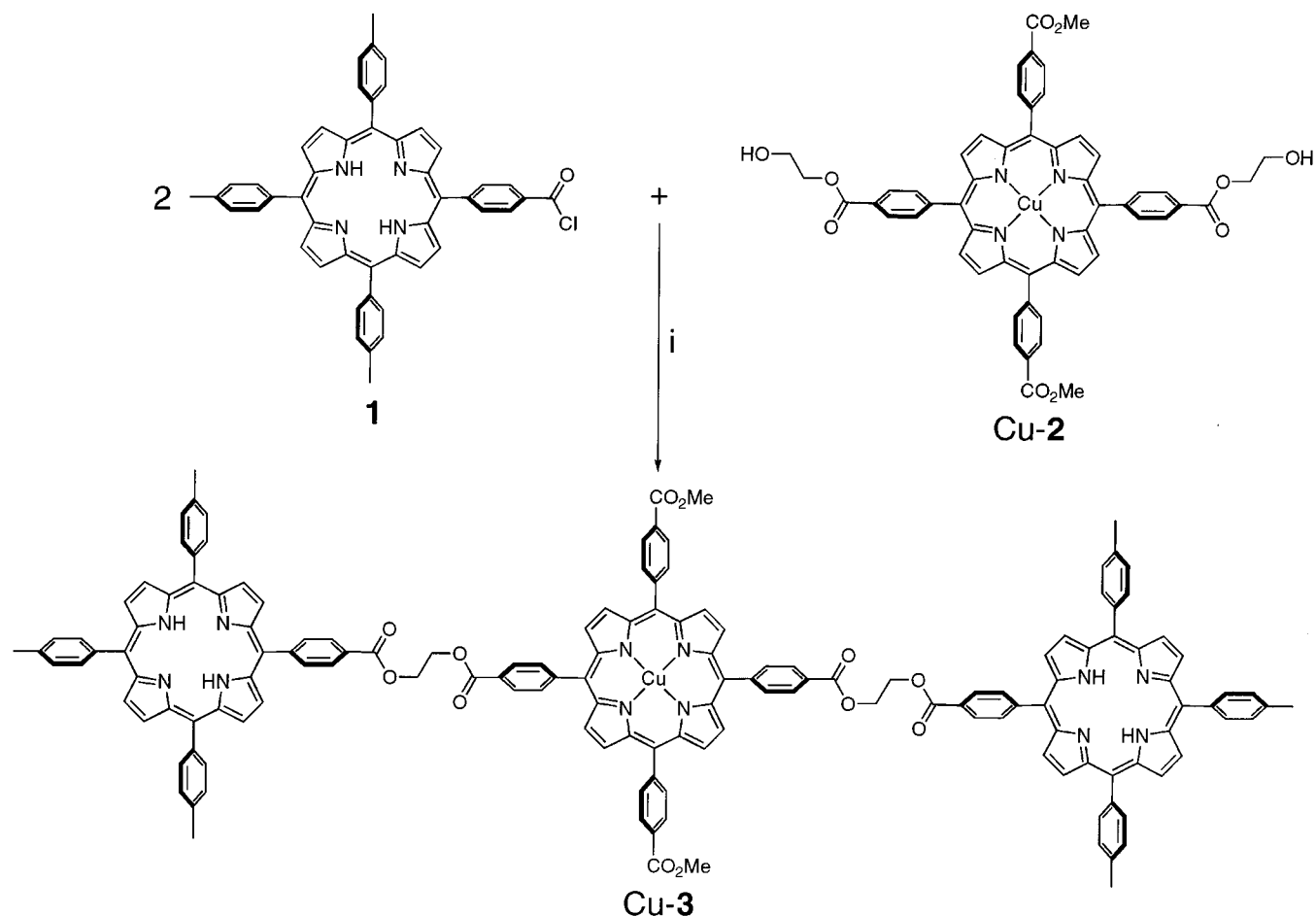
of the effectiveness or efficiency of the various synthetic procedures. Given the obvious strengths of some methodologies, however, it is often clear what chemistry would be most appropriate for the construction of a required array.

III. General Synthetic Procedures

The driving force for the design of a porphyrin array is invariably from the requirements for specific array properties or functionality. This will lead the

Scheme 7. Synthesis of Pyropheophorbide Array Zn$_2$-7^a of Boxer and Bucks[68]
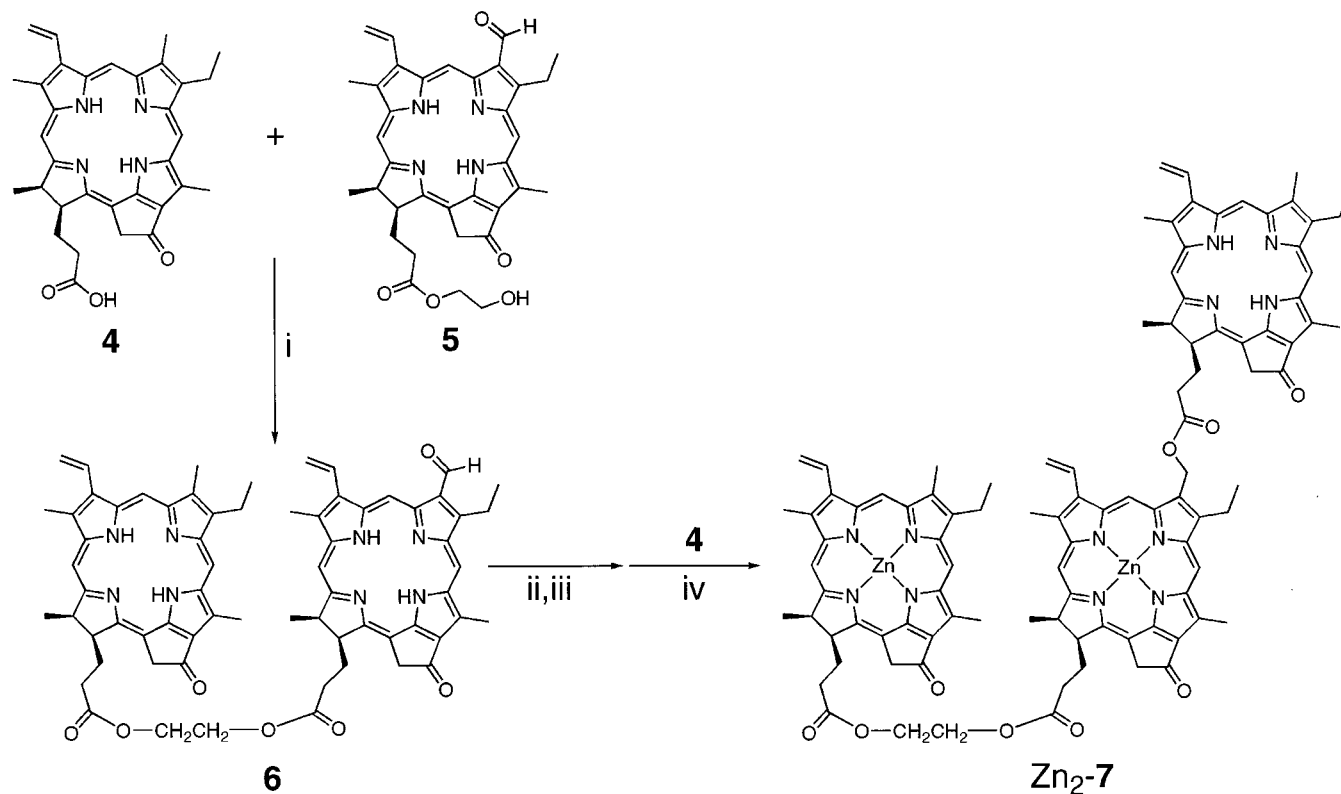
^{a} (i) ClC$_6$H$_5$NMeI, CH$_2$Cl$_2$, reflux. (ii) NaBH$_3$CN. (iii) Zn(OAc)$_2$. (iv) ClC$_6$H$_5$NMeI, CH$_2$Cl$_2$, reflux.

researcher to choose not only a particular porphyrin unit but also the type of linkage between units that will provide the desired properties and be easily incorporated into the synthetic strategy. Commonly the choice of linker will complement the functionality of the porphyrin unit. Therefore, any array synthetic strategy must take into account both the porphyrin functionalization and linkage implementation.

Procedures for the synthesis and functionalization of monomeric porphyrins have now progressed to the point that virtually any porphyrin can be made.[42] Therefore, linker choice ultimately becomes one of availability of materials, researcher expertise, and ease of implementation. It is not the aim of this section to give a comprehensive insight into the vast multitude of porphyrin fuctionalization reactions; rather, a general summary is presented of both porphyrin and array formation strategies.

A. Porphyrin Formation

There has been a considerable volume of review literature published on the synthetic formation of porphyrins.[42−49] What follows is a summary of the typical synthetic procedures used to form most of the porphyrins used in multiporphyrin assemblies.

A simple path to forming symmetrical synthetic porphyrins such as the TAPs is by the acid-catalyzed condensation reaction of pyrrole with a suitable aldehyde, followed by oxidation of the resulting porphyrinogen (Scheme 1). This procedure, originally developed by Rothemund and Menotti,[50] has been refined to generally give around 20% yields for TAPs.[51] Despite the modest yields, the relative

simplicity of this method has made it well suited to large-scale preparation of TAPs (i.e., >1 g of porphyrin).

Higher yielding and milder reaction conditions have been developed by the Lindsey group.[52,53] Lindsey's group subsequently developed higher reactant concentration conditions (0.1−0.3 mol L^{-1}) that were slightly lower yielding than before but more practical for larger scale preparations.[54] More recently, the group found that the addition of salts, such as sodium chloride, to the condensation reactions could increase (sometimes double) the yields.[55] The specific mechanism for this improvement in yields has not yet been determined.

Other variations on the Rothemund or Lindsey procedure have been published that employ hydroiodic acid, hydrochloric acid, *p*-toluenesulfonic acid (*p*TSA),[56] perchloric acid,[57] trichloroacetic acid (TCA),[58] montmorillonite clays,[59] or high-valent transition metals[60] as catalysts and/or oxidants. A preparation of *meso*-substituted porphyrins was published that employed no solvent or catalyst, reacting the pyrrole and aldehyde together in the gas phase (>200 °C) while admitting oxygen as oxidant.[61] TPP was obtained in a 23% yield in this manner.

While easy to synthesize, these symmetrical porphyrins suffer in that there is no provision to be able to control the functionalization at individual *meso* positions, a severely limiting factor in the quest to form large covalently bonded arrays.

It is possible to synthesize unsymmetrically substituted porphyrins via mixed aldehyde condensations. If a mixture of two different aldehyde starting

Scheme 8. Synthesis of Nonaporphyrin 10[a] of Sanders et al.[37]


a (i) DEAD, PPh₃.
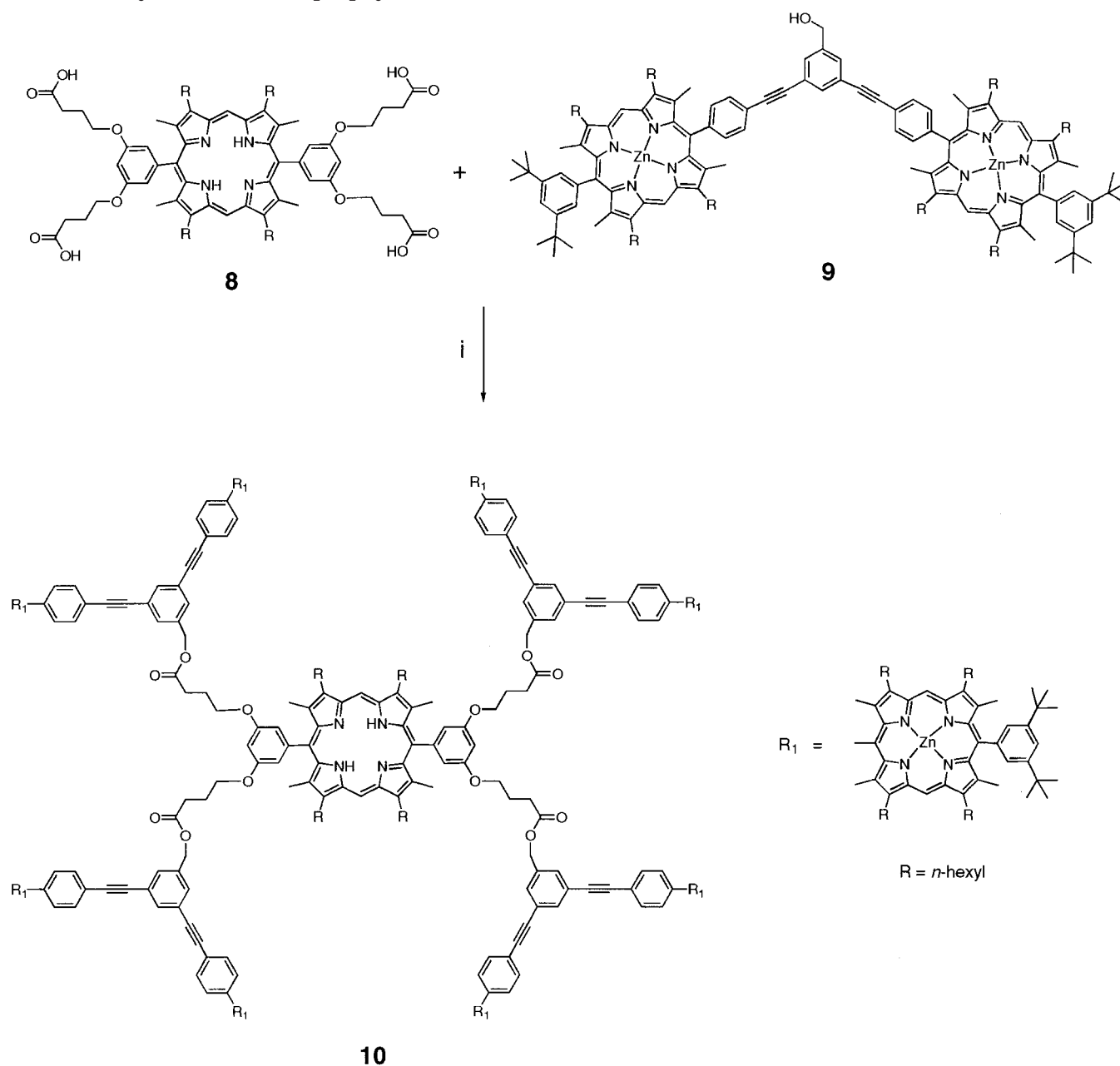
materials is employed in the Adler or Lindsey porphyrin syntheses, then a statistical mixture of products is obtained (Scheme 2). The desired porphyrin is then removed by extensive chromatography. The disadvantages here are that yields are lower by virtue of the statistical outcome of the reaction and the separation procedures can be troublesome, particularly if the reactions are carried out on a significant scale.[62−64]

Alternative approaches for synthesizing substituted porphyrins have been devised in which dipyrrolic starting materials are combined to form tetrapyrroles. Dipyrromethenes, dipyrryl ketones, and dipyrrylmethanes (DPMs) have been used in these "2 + 2" synthetic methodologies. In 1960, MacDonald and co-workers published the first dipyrrylmethane-based porphyrin syntheses (Scheme 3).[56] The condensations were catalyzed by acid and the interme-

diate tetrapyrroles oxidized by exposure to air to give the desired porphyrins. In a variation of the Mac-Donald synthesis, "3 + 1" synthetic methodologies have been developed in which tripyrrolic species (or tripyrranes) are condensed with 2,5-diformylpyrroles to form a cyclic tetrapyrrole.[65]

Alternative 2 + 2 methods involve the acid-catalyzed condensation of α-free dipyrrylmethanes with aldehydes to form porphyrinogens, which are then chemically oxidized to give porphyrins (Scheme 4).

This methodology is considerably more versatile for array formation, especially of larger assemblies as it is frequently higher yielding and produces more soluble products as well as allows control over substitution at the *meso* positions. There is however a trade off, the time and resources required to make the precursor dipyrrylmethane molecules. Nonethe-

Scheme 9. Synthesis of the Ru-Centered Pentaporphyrin 13[a] of Sanders et al.[71]
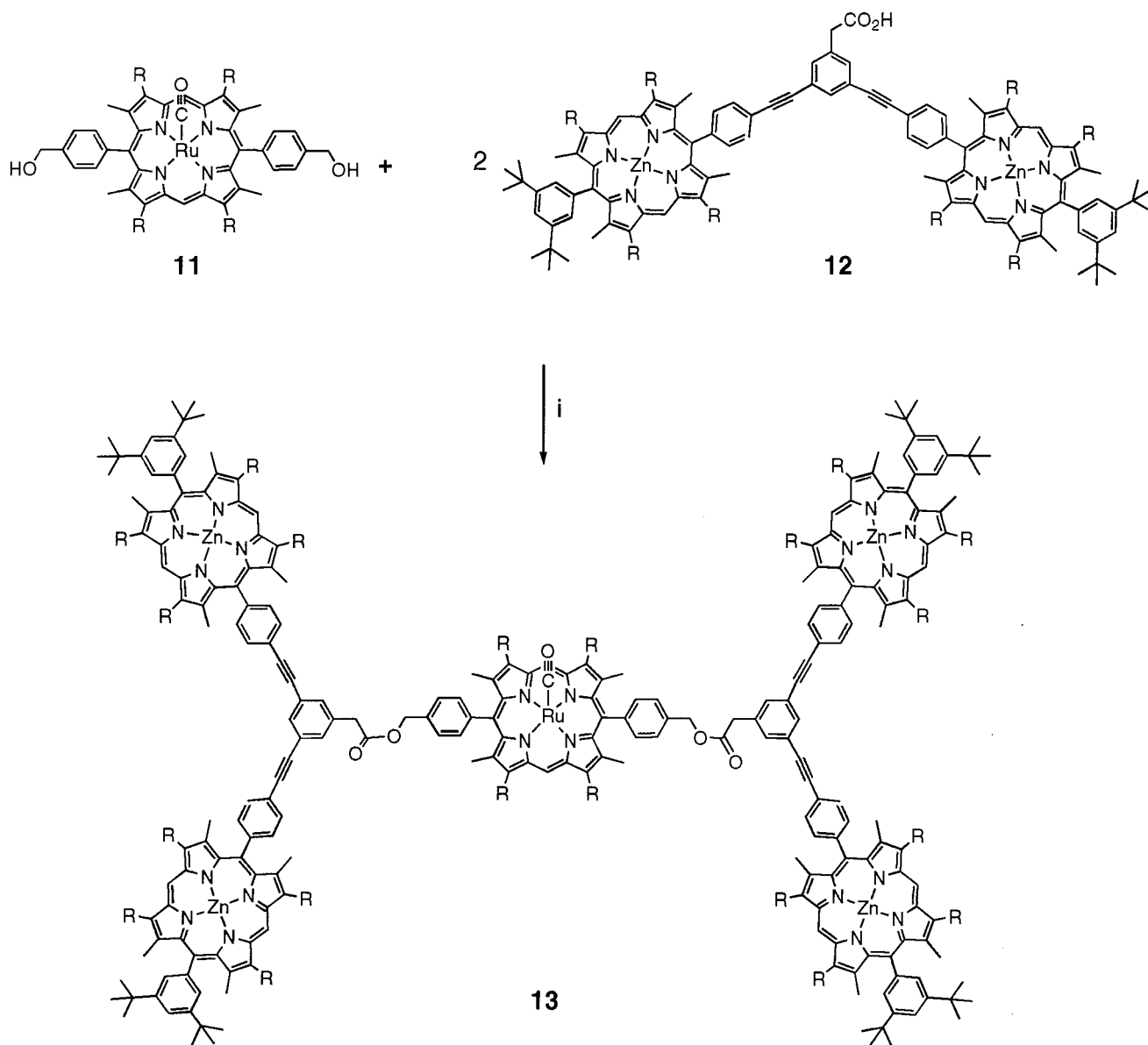

[a] (i) No details given.

less, since the development of efficient methods for the preparation of the required α-free dipyrrylmethanes,[66] this methodology has been used extensively in the synthesis of a wide variety of porphyrins.

B. Porphyrin Assembly Formation

There are two fundamental strategies to porphyrin array construction. By far the majority of porphyrin assemblies have been made using strategy A (Scheme 5), in which the array is developed from the functionalization of the porphyrin monomer. In this case, either a linkage or porphyrin is generated as the array is constructed. The second strategy (B) is an increasingly popular method for array construction and involves the direct coupling of porphyrin moieties.

In strategy A an array will be formed if the derivatized porphyrin (II) is either coupled with a second functionalized porphyrin to form the array linkage or if a new porphyrin is created from the functional group (X), for example, an aldehyde condensation with a pyrrole. The functionalization of the monomeric porphyrin can be achieved in two ways (Scheme 5). Starting with the monomeric porphyrin (I), it is possible to first functionalize it at either the β-pyrrolic or *meso* positions. Another approach is to introduce the functionalization during the porphyrin formation, via a number of alternative procedures, for example, statistical condensation using various aldehyde starting materials. Each functionalization method has advantages and disadvantages, for instance, statistical condensation is an inefficient way of forming functionalized monomeric precursors, giving low yields and requiring careful separation. In some instances however, it is still preferable to the alternative "2 + 2" and "3 + 1" strategies, which give excellent control over functionalization yet require lengthy syntheses of the precursor aldehydes and

Scheme 10. Synthesis of the Amide-Linked Tetraporphyrin 18[a] of Dubowchik and Hamilton[34]
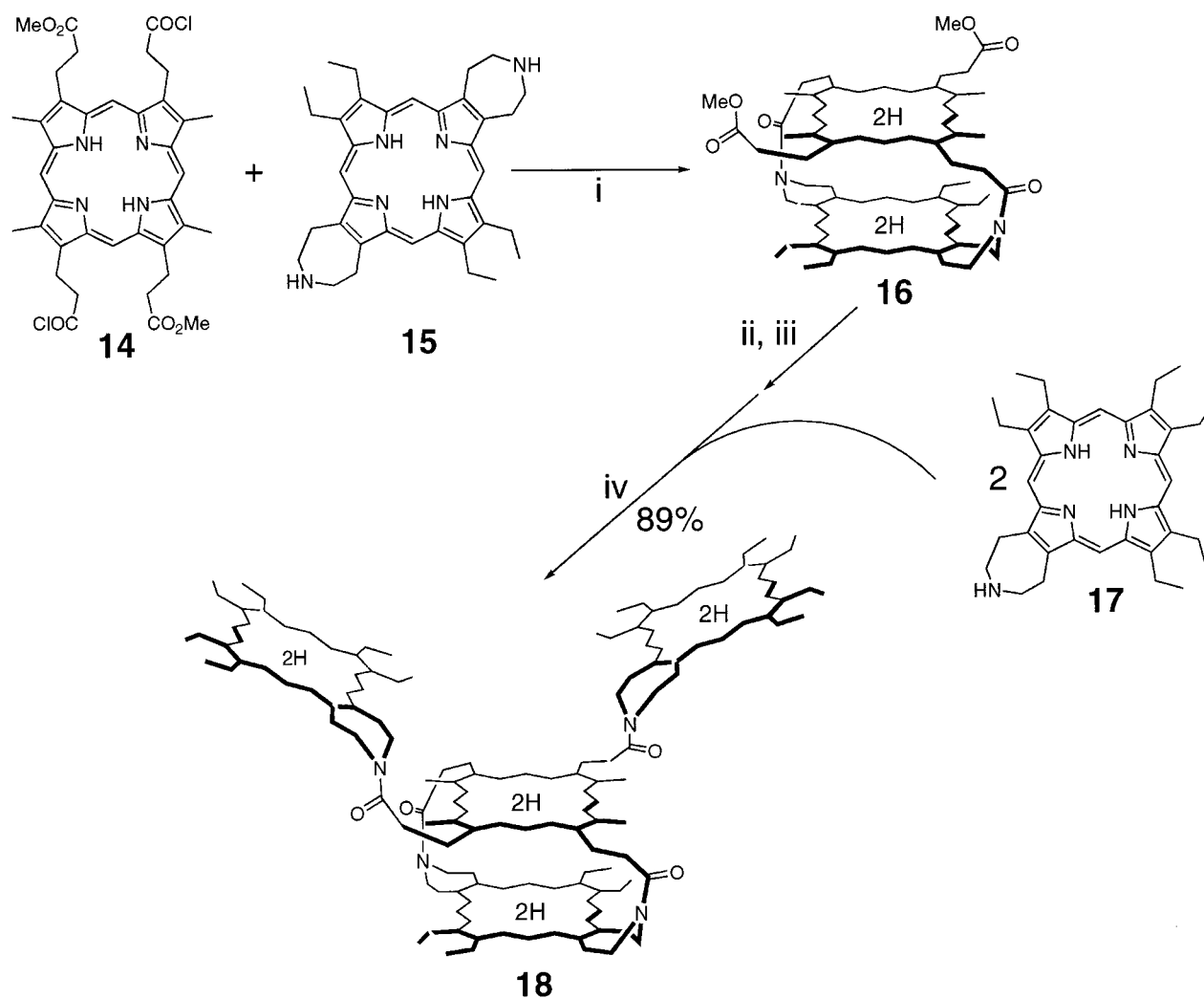
[a] (i) Et₃N, CH₂Cl₂. (ii) KOH, THF, MeOH. (iii) ClCOCOCl. (iv) Et₃N, CH₂Cl₂.

pyrroles. The direct functionalization of a preformed monomeric porphyrin is relatively straightforward but often limited by the small number of electrophilic aromatic substitution reactions that can be easily effected on the porphyrin nucleus. These are the most common methodologies used to form porphyrin ar-
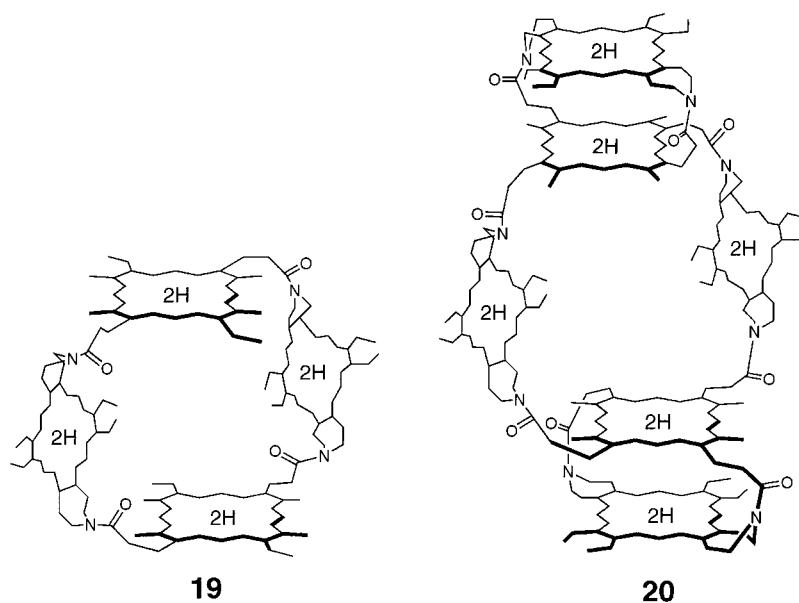

Figure 1. Cyclic tetra- and hexaporphyrins of Dubowchik and Hamilton.[35]

Scheme 11. Synthesis of the "Radial" Pentaporphyrin Zn-23[a] of Milgrom[36]

Zn-**21**

22

i
70%

Zn-**23**

where Tol = §—⟨◯⟩—CH₃
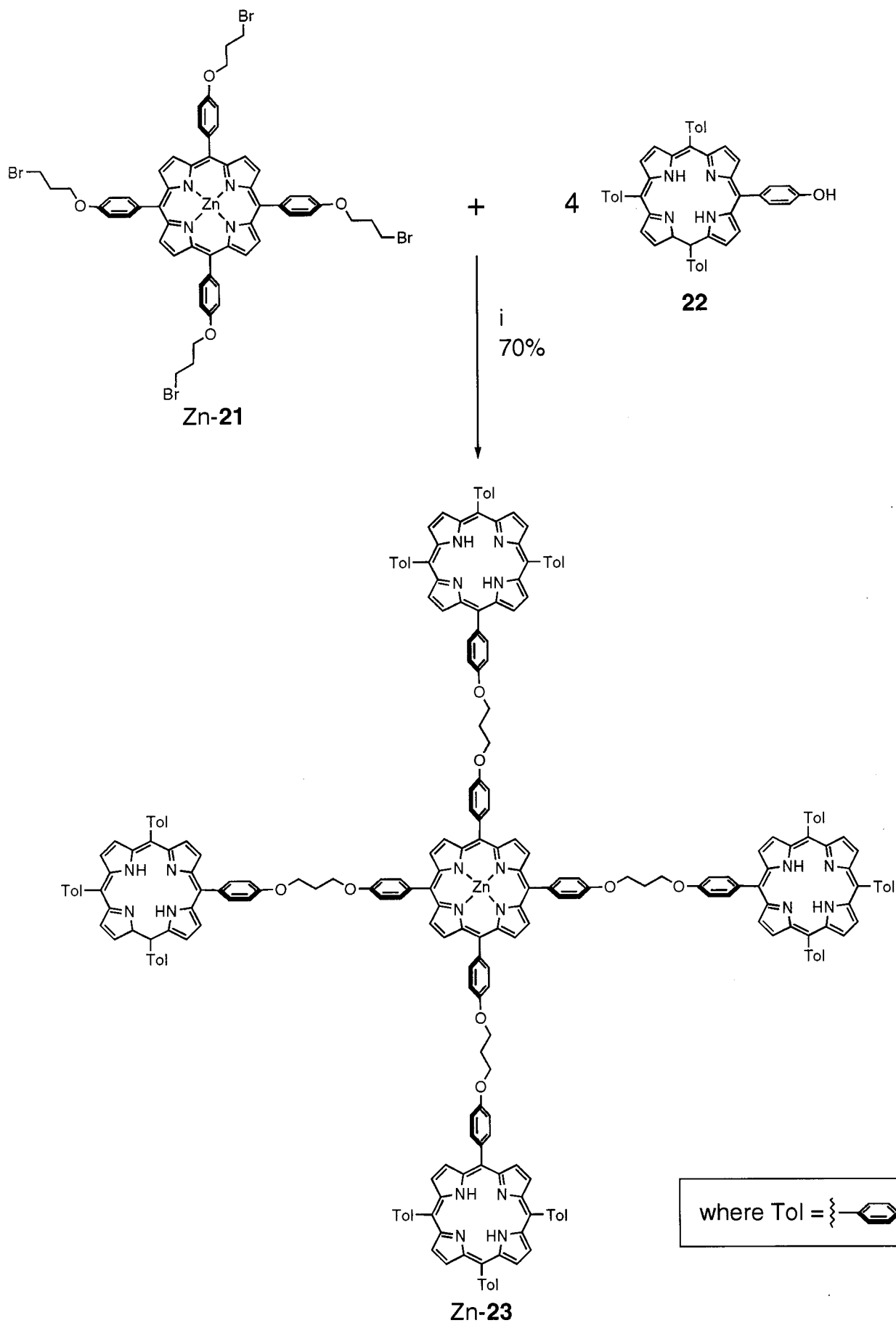
[a] (i) K₂CO₃, DMF, room temperature, 5 days.

Scheme 12. Synthesis of Polymer 25[a] of Scamporrino and Vitalini[84]

24

$$Cl(CH_2)_6Cl$$
$$\xrightarrow{\text{i}}$$
$$40\%$$

25
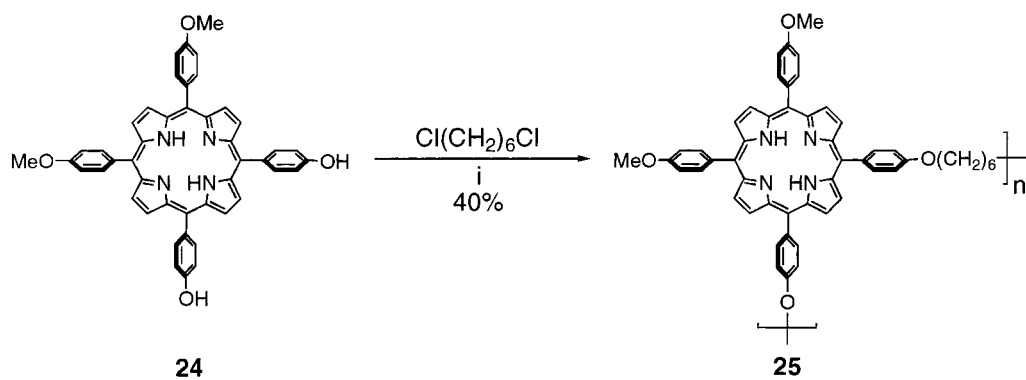
[a] (i) NaOH, TBAB, toluene, H_2O, 100 °C, 1 day.

Scheme 13. Synthesis of the Ether-Linked Pentaporphyrin 28[a] of Norsten and Branda[87]

26 + **27**

i

28
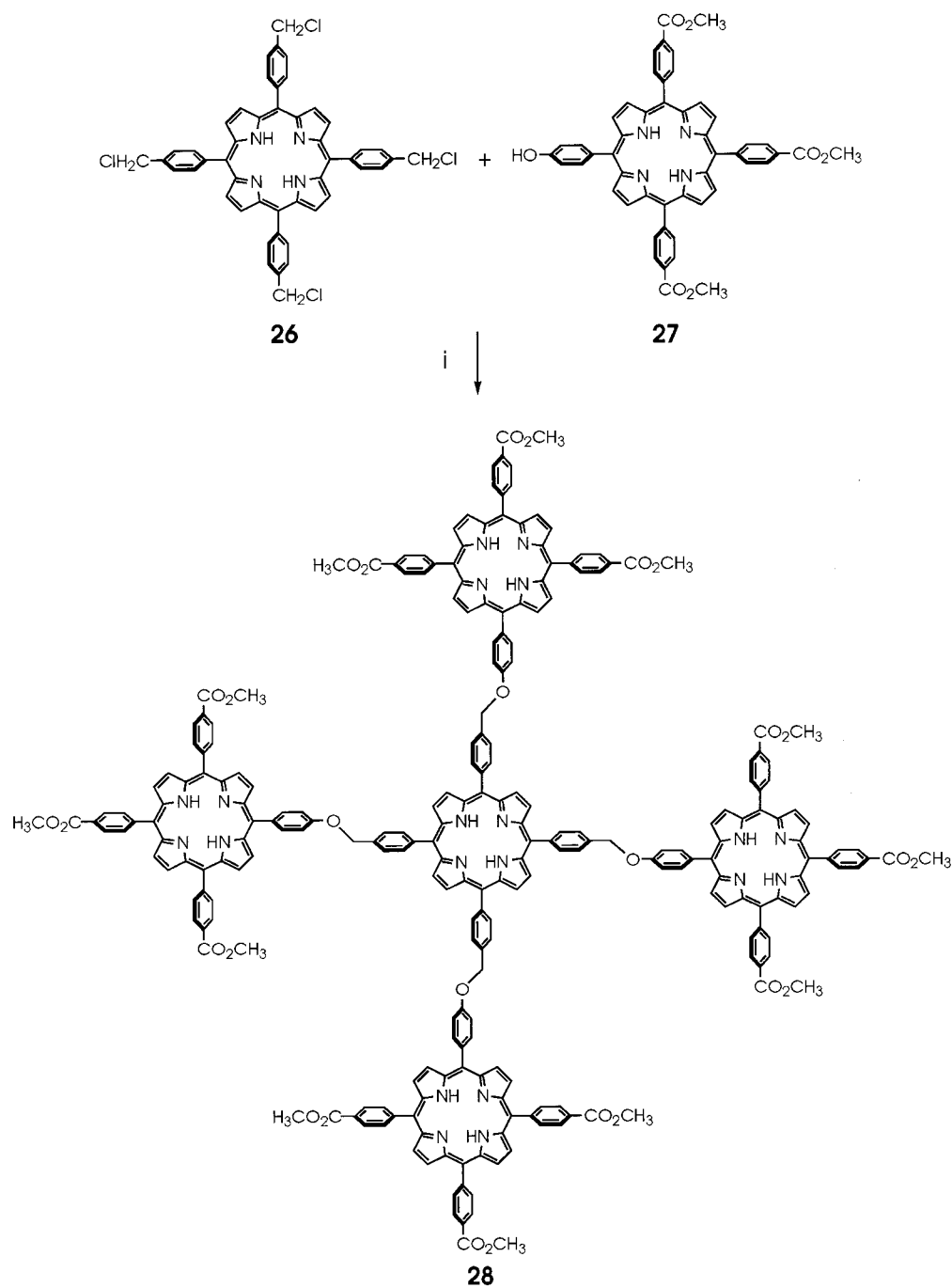
[a] (i) NaOH, DMF, 80−100 °C.

Scheme 14. Synthesis of the Ether-Linked Hexaporphyrin Arrays 31 and 32[85]

29   R = CH₃

30   R = OC₁₆H₃₃

31   R = CH₃

32   R = OC₁₆H₃₃
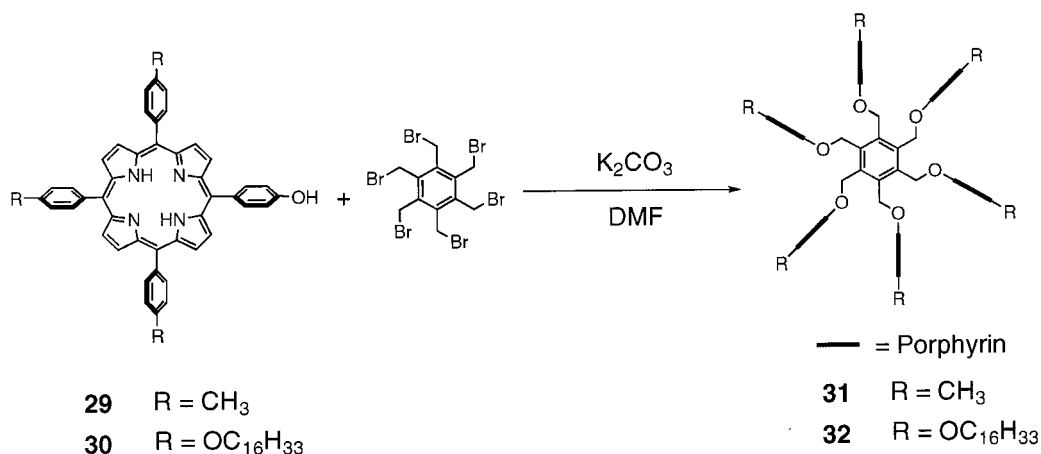
Scheme 15. Synthesis of Ether-Linked Cofacial Triporphyrin Zn₃-36[a] **of Osuka et al.**[38]
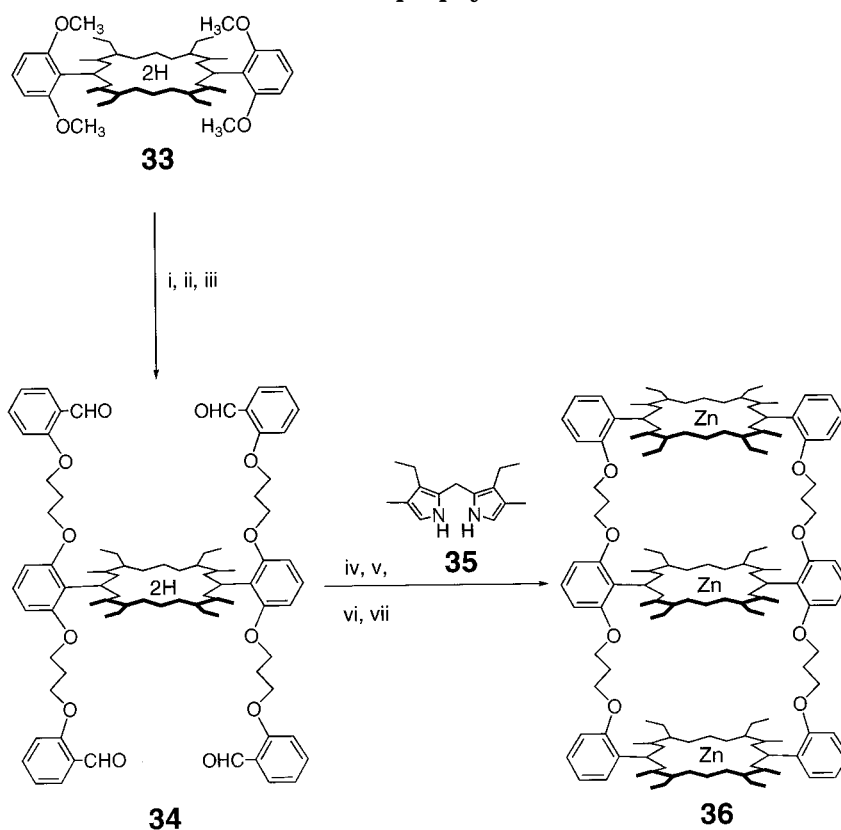
[a] (i) BBr₃, CH₂Cl₂, −78 °C. (ii) 3-(Aryloxy)propyl iodide, K₂CO₃, acetone, reflux, 2 days. (iii) TFA, H₂O, CH₂Cl₂, 8 h. (iv) Zn(OAc)₂. (v) TFA, CH₃CN, room temperature, 12 h. (vi) p-Chloranil, THF, room temperature, o/n. (vii) Zn(OAc)₂.

rays and cover the bulk of the literature examples on the synthesis of porphyrin arrays.

In a few yet steadily growing number of cases, strategy B has been employed to construct porphyrin arrays.[67] By utilizing oxidative coupling via the unsubstituted *meso*-positions of monomeric porphyrins and continuely cycling the products back into the reaction, very large arrays can be generated. This process is quite clean experimentally, but by nature of the reaction only one type of linker is generated, namely, a direct carbon−carbon link between porphyrins.

Another issue that provides an extra layer of complexity is the incorporation of metalloporphyins into the array. In many cases, metalloporphyrins

have desirable characteristics which are important to the utility of a given porphyrin array. However, the stability of metalated porphyrins vary greatly, and this will dictate the time at which the metal should be inserted during the array synthesis. For example, strongly bound nickel and copper porphyrins will readily tolerate most conditions in forming an array from porphyrin I in Scheme 5. Nonetheless, some methodologies will simply fail in the presence of these metals. It is often difficult to predict the success of a given reaction in the presence of different metalloporphyrins. In contrast, porphyrins containing the more labile zinc metal ion will not stand many of the array-forming reactions in Scheme 5. Therefore, the introduction of zinc into a porphyrin

Scheme 16. Synthesis of the Ether-Linked Triporphyrin 39[a] of Osuka et al.[38]
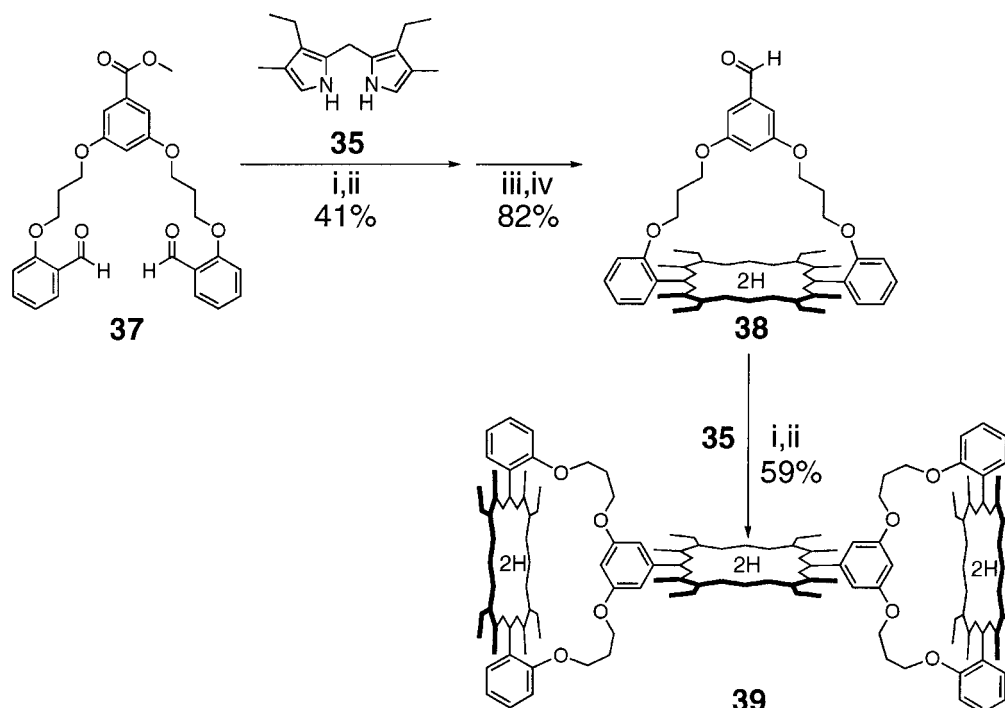
[a] (i) TCA, CH$_3$CN, room temperature, 5 h. (ii) *p*-Chloranil, THF, room temperature, 16 h. (iii) LiAlH$_4$, THF, room temperature, 4 h. (iv) MnO$_2$, CHCl$_3$, reflux, 2 days.

**Scheme 17. Synthesis of Triporphyrin 42[a] of Susumu et al.[96]**
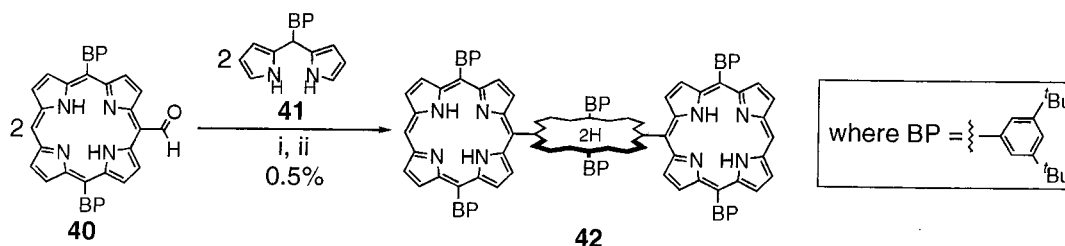
[a] (i) BF$_3$.Et$_2$O, CH$_2$Cl$_2$, room temperature. (ii) Chloranil, room temperature.

array will usually be the final step in the synthesis. Adding to this is the sensitivity of many linkers, which may not be compatible with the conditions necessary to achieve the metallopoprhyrin. The combination of these problems will continue to challenge the imagination and skill of those involved in the synthesis of porphyrin arrays.

IV. Synthesis of Arrays Based on Linker Type

Linkers in porphyrin arrays play a number of roles. They may simply hold the porphyrins together or hold them in a rigid conformation or orientation. They can act to isolate each porphyrin from one another or conversely promote communication between the individual porphyrins. The nature and position of the linker can have a strong influence on the overall properties of the porphyrin array, for example, physical properties such as the solubility and chemical or thermal stability of the assemblies can be affected by both the placement and type of linker.

Many different types of linker have been used to connect porphyrins, and these linkages fall into three broad categories: nonmetallic covalent linkers (e.g.,

Scheme 18. Synthesis of Bispyro-pheophorbideporphyrin 45[a] of Zheng et al.[97]
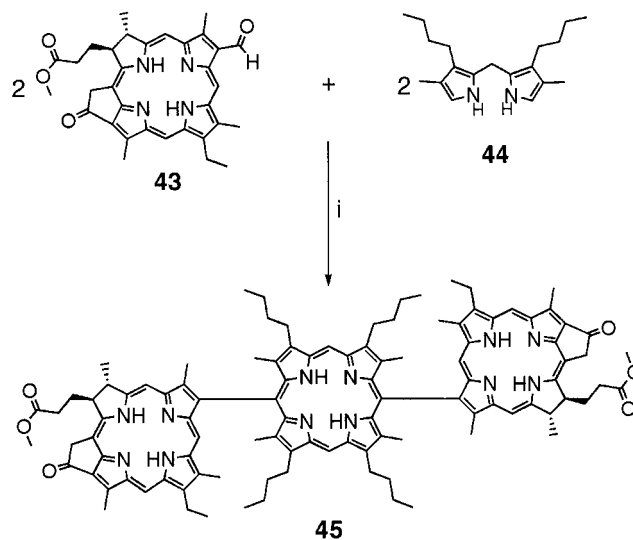
[a] (i) MacDonald reaction conditions.

carbon–nitrogen, carbon–oxygen, and carbon–carbon bonds), metal–ligand coordination (e.g., metal–oxygen and metal–nitrogen), and noncovalent linkers

Scheme 19. Synthesis of Diporphyrin 48[a] of Khoury et al.[98]
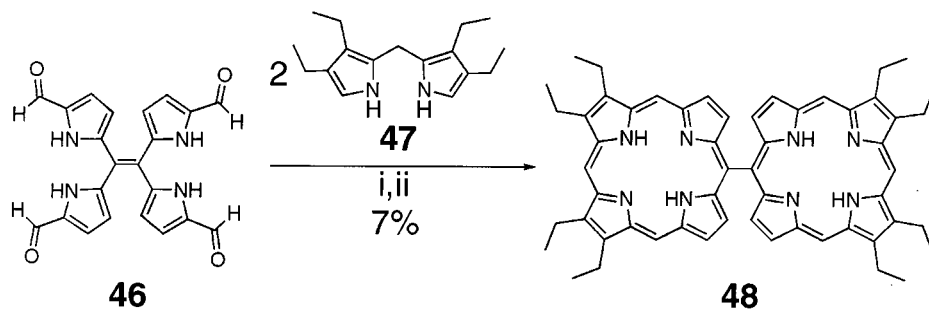
[a] (i) Acid-catalyzed condensation. (ii) DDQ.

Scheme 20. Synthesis of Tetraporphyrin 52[a] of Khoury et al.[99]
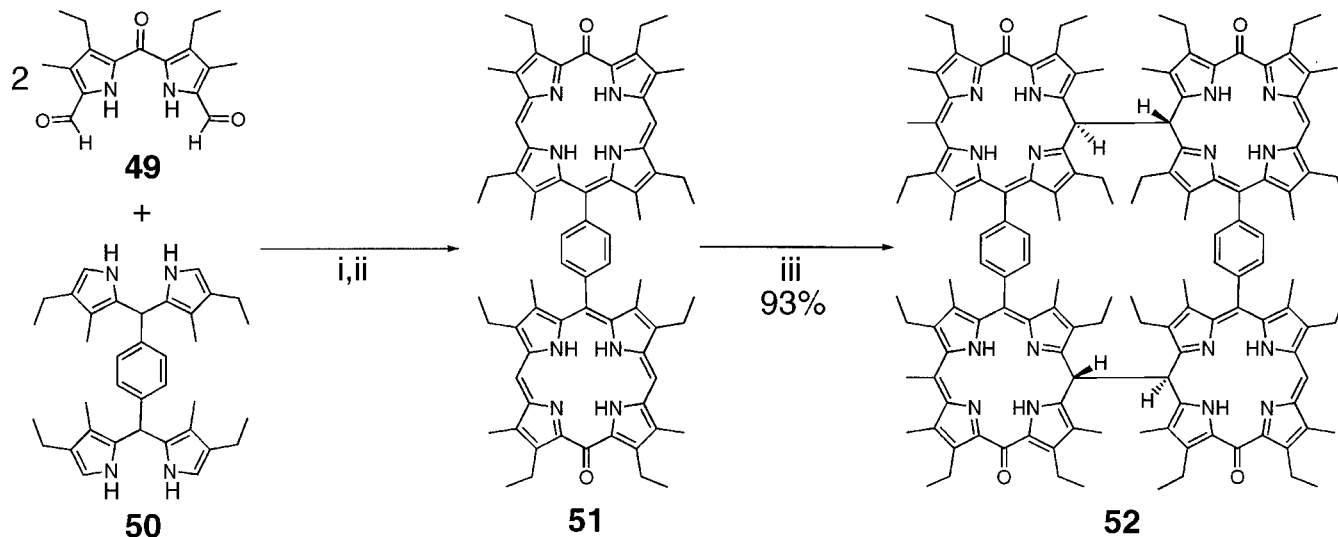
[a] (i) Acid-catalyzed condensation. (ii) Base. (iii) O_2, $h\nu$.

Scheme 21. Synthesis of Porphyrin Arrays Zn_2-54, Zn_3-42, and Zn_4-55[a] of Osuka and Shimidzu[100] and Ogawa[102]
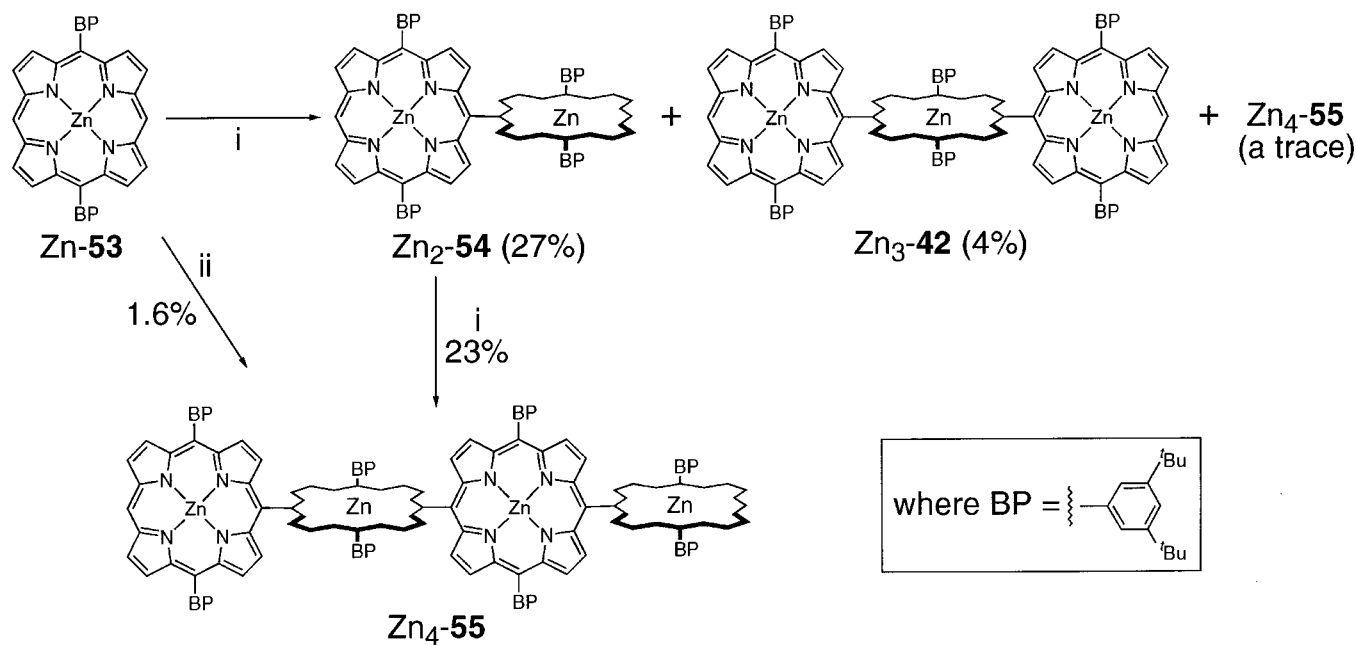
[a] (i) AgPF$_6$, CHCl$_3$, CH$_3$CN, room temperature. (ii) +0.54V vs Ag/AgNO$_3$ (1.65 mF), benzonitrile, Nbu$_4$ClO$_4$ as supporting electrolyte.

(e.g., hydrogen bonding, electrostatic, hydrophobic, hydrophilic, $\pi-\pi$, and van der Waals interactions). The linkages can be created between *meso-* or *β-* pyrrolic carbons of each porphyrin or between sub-

stituents at these positions. For metal−ligand coordination type arrays, the linkage is created by coordination of a metal (which can be contained in the porphyrin core or existing as an external complex)

Scheme 22. Synthesis of the Porphyrin Arrays 58 and 59[a] of Osuka et al.[39]
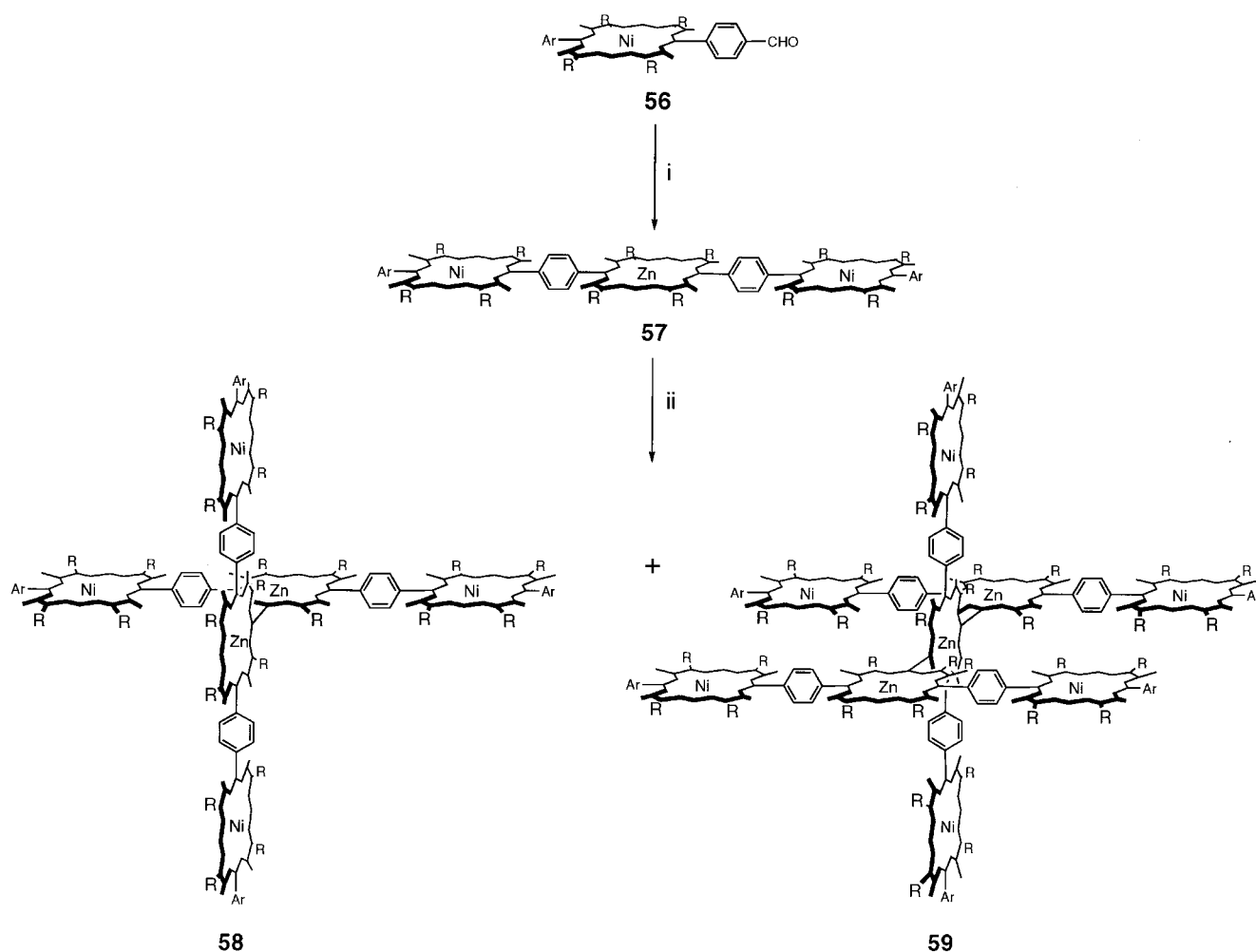
[a] (i) No details given, Lindsey conditions. (ii) AgPF$_6$, CHCl$_3$/CH$_3$CN, room temperature, 22 h.

and ligand (which may or may not be part of another porphyrin). Similarly, the noncovalent interactions can occur through ligands or substituents or directly between porphyrins.

In the initial work in this area, the syntheses of porphyrin dimers, the most readily formed linkages such as amides and esters were utilized. Subsequently, with the development of a wide variety of porphyrin-forming chemistries and substitution methodologies, many different types of linkers have been used to connect porphyrins, allowing significantly greater control over assembly geometry.

## A. Heteroatom Linkers

1. Esters and Amides

Ester bonds have featured in a number of porphyrin assemblies. Traditionally these linkages are synthetically easy to form, which compensates somewhat for the low yields that generally occur. Some of the earliest examples were those of Anton et al., who synthesized ester-linked, heterometalated diporphyrins and triporphyrins for studies of biological electron- and energy-transfer processes.[33] Triporphyrin Cu-**3** was prepared by refluxing diol Cu-**2** and acid chloride **1** in benzene (Scheme 6). A similar

overall approach was used to make diporphyrins from **1** and monoalcohol-substituted porphyrins.

Boxer and Bucks prepared arrays containing two or three pyropheophorbides as structural models for photosynthetic reaction centers (Scheme 7).[68,69] Starting materials **4** and **5** were obtained by extraction from spinach followed by derivatization. Carboxylic acid **4** was coupled to alcohol **5** to form dichlorin **6**. Reduction and metalation of **6** followed by a second coupling reaction with **4** gave trichlorin **7**.

The Sanders group prepared ester-linked arrays of various sizes.[37,70,71] Nonamer porphyrin **10** was synthesized in 69% yield from the Mitsunobu condensation of tetraacid **8** with 4 equiv of alcohol **9** (Scheme 8).[37] A significant advantage of this method lies with the simultaneous Mitsunobu couplings, which once performed allow any incompletely coupled polar products to be easily separated from the desired nonpolar product. The versatility of this methodology was demonstrated using the Mitsunobu condensation in the reverse sense to generate ester-linked pentaporphyrins.[71] In one such example, the acid analogue of **9** was reacted with ruthenium porphyrin diol **11** to form the ruthenium-centered pentaporphyrin **13** but only in 21% yield (Scheme 9).[71]

Linkers containing an amide moiety have been used extensively for the formation of diporphyrin

Scheme 23. Synthesis of Diporphyrin Ni$_2$-61^a of Arnold et al.[103]
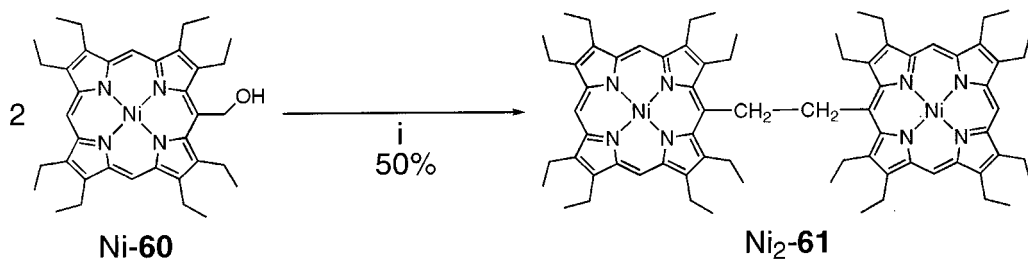
^{a} (i) Concentrated H$_2$SO$_4$, DMF, reflux, 1 h.

Scheme 24. Synthesis of Ethene-Linked Diporphyrins *cis*- and *trans*-62^a of Ponomarev et al.[106]
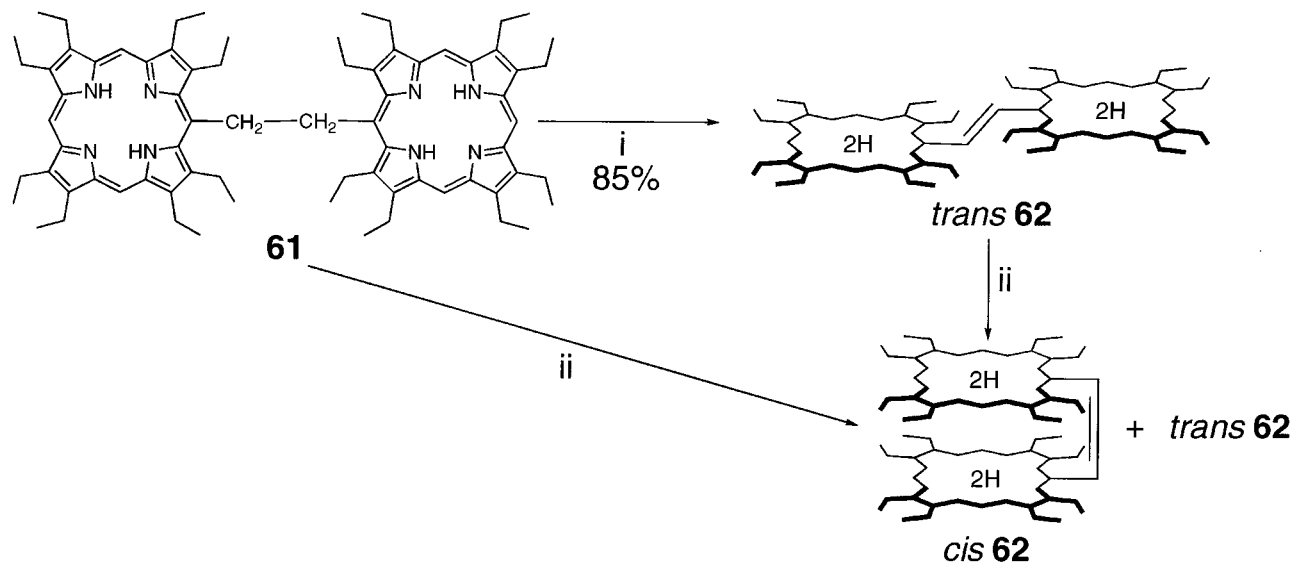
^{a} (i) AcOH, 60−70 °C, 20 min. (ii) AcOH, reflux.

arrays,[3,72−74] sometimes in conjunction with other moieties.[75−79] This reflects the relative ease of formation of amide-type bonds.

In addition to diporphyrins, there are also a few examples of larger amide-linked arrays. In their studies of model systems for photosynthetic reaction centers, Dubowchik and Hamilton prepared diporphyrins,[80,81] triporphyrins,[81] tetraporphyrins,[34,35] and hexaporphyrins[35] with amide linkages between the porphyrins. The synthesis of tetraporphyrin **18** illustrates the basic approach used to construct these arrays (Scheme 10). Diacid chloride **14** and diamine **15** were coupled under high dilution conditions to give diester **16**. Diester **16** was converted to a diacid chloride and then coupled to amine **17** to give tetraporphyrin **18** in 89% yield. By maintaining an excess of diamine **15** at the beginning of the reaction (and using a modified form of **14**), it was possible to favor the 2 + 2 condensation resulting in the formation of the tetraporphyrin **19** in 25% yield (Figure 1). Substituting the diacid form of **16** for **14** under similar conditions resulted in the formation of hexaporphyrin **20** in 35% yield (Figure 1).[35]
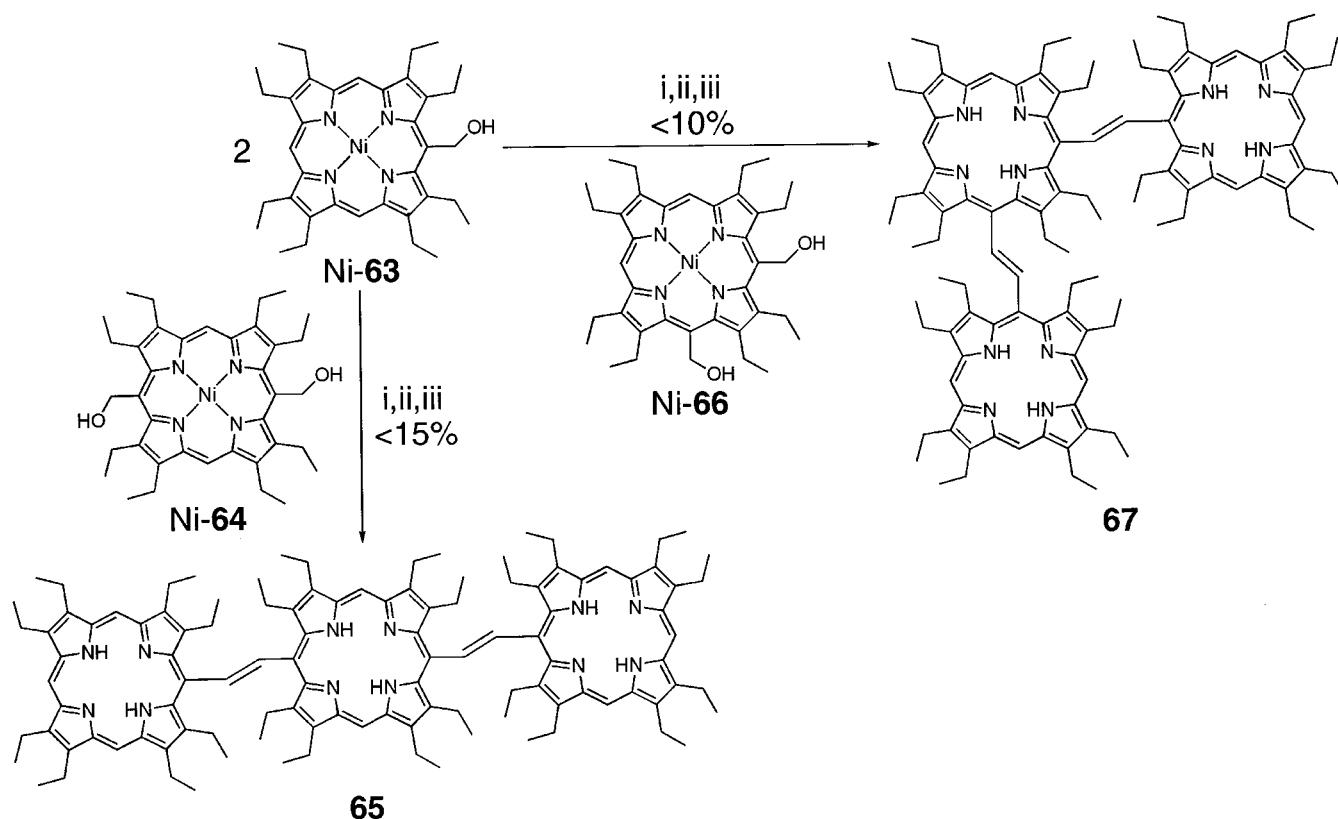
2. Ethers

Ether linkages appear in a wide variety of porphyrin arrays. In 1983, Milgrom published the synthesis of the first large porphyrin array, ether-linked radial pentaporphyrin Zn-**23**, as part of his studies of synthetic porphyrin arrays for light harvesting

(Scheme 11).[36] Coupling of Zn-**21** with excess hydroxyphenylporphyrin **22** (made by a mixed aldehyde condensation) gave pentaporphyrin Zn-**23** in 70% yield. For spectroscopic studies, variously metalated pentaporphyrins were prepared such as Zn$_4$-**23** (free base central porphyrin) and Zn$_5$-**23**.[82] Pandian and Chandrashekar used similar coupling chemistry to make linear diporphyrins from porphyrinyl and thiaporphyrinyl starting materials.[83]

Scamporrino and Vitalini made flexible, ether-linked backbone polymers of TAPs (Scheme 12).[84] Di(hydroxyphenyl)porphyrin **24** was prepared by partial methylation of a tetra(hydroxyphenyl)porphyrin in ~10% yield. Polymer **25** was then formed in ~40% yield by coupling **24** with 1,6-dichlorohexane. Different polymers were prepared by using a variety of substituted starting materials.

Branda and Norsten used a base-catalyzed coupling reaction between **26** and 4 equiv of **27** to form the ether-linked star pentaporphyrin **28** in 48% yield (Scheme 13).[85] While the coupling reaction yield is good, porphyrin **27** is generated from a low-yielding acid-catalyzed statistical condensation of pyrrole with an equimolar mixture of 4-methoxycarbonyl benzaldehyde and 4-hydroxybenzaldehyde.

The efficacy of ether formation is illustrated by the preparation of hexaporphyrins **31** and **32**. Coupling of hexakis(bromomethyl)benzene with **29** and **30** afforded the hexaporphyrins in commendable yields of 30% and 34%, respectively (Scheme 14).[87]

Scheme 25. Synthesis of Ethene-Linked Triporphyrins 65 and 67[a] of Higuchi et al.[107,108]

[a] (i) Concentrated H_2SO_4, DMF, reflux, 3 h. (ii) Concentrated H_2SO_4, room temperature, 5 h. (iii) AcOH, 65 °C, 1 h.

By utilizing short carbon chain ether straps between *meso*-phenyl substituents, Osuka et al. prepared a number of cofacial triporphyrins.[38] These straps restricted the conformational freedom of the porphyrins in the arrays. However, the ether linkages were put in place before the array was completed. Thus, the cofacial triporphyrin **36** was prepared in 35% yield by employing 5,15-bis(2,6-dimethoxyphenyl)etioporphyrin **33** as the starting material. This was demethylated using BBr$_3$, and all of the resulting hydroxyl groups were alkylated with 3-(aryloxy)propyl iodide. Hydrolysis of the acetal groups gave the intermediate porphyrin **34** (Scheme 15). Zinc metalation followed by condensation with DPM **35** and subsequent oxidation with *p*-chloranil resulted in the stacked triporphyrin **36** (Scheme 15).

A similar approach was also used for the preparation of triporphyrins with orthogonal components.[38] TCA-catalyzed condensation of dialdehyde **37** with dipyrrylmethane **35** followed by oxidation gave a strapped porphyrin in 41% yield (Scheme 16). Conversion of the ester to aldehyde **38** followed by a second TCA-catalyzed condensation with dipyrrylmethane and then oxidation gave triporphyrin **39** in 59% yield.

Ether-linked arrays containing up to nine porphyrins have been synthesized in a convenient one-pot proton-transfer polymerization procedure by Fréchet and co-workers. [88]

3. Other Heteroatom Linkers

There are a number of examples of aza-bridged diporphyrin arrays exemplified by the work of Book-

ser and Bruice.[89] Crossley and co-workers made diazocine-bridged diporphyrins in their investigations into potential chiral receptors.[90,91] Tsuchiya prepared a mixture of electron-rich and electron-poor diporphyrins linked by an azobenzene moiety in an attempt to develop new materials for molecular electronics.[92] This linker has not been used, however, to make larger arrays.

Aromatic heterocycles have also been used to link porphyrins through the heteroatom. Ruhlmann et al. synthesized a tetra-*meso*-bipyridine-linked pentaporphyrin via the electrochemical oxidation of zinc octaethylporphyrin (OEP) in the presence of 4,4′-bipyridine.[93]

On rare occasions, other heteroatoms have been used in the linking of porphyrins. One notable example is the use of phosphorus by Ruhlmann and Giraudeau.[94]

B. Carbon–Carbon Linkers

1. Direct Links

A number of arrays have been made in which the porphyrins are directly connected by a single bond, generally through *meso* positions. However, the procedures are commonly low yielding. Nonetheless, these systems are of interest because they invariably display electronic interactions between the coupled porphyrins. To date, the record for the longest covalently linked porphyrin array, a staggering 128 *meso-meso*-linked porphyrins of Osuka and co-workers, belongs to this class of linker.[95]

Scheme 26. Synthesis of Butadiene-Linked Diporphyrins M-70[a] of Bonfantini and Officer[110]

68

+

M-69

$\xrightarrow{\text{i}}$
M = 2H or Ni

M-70
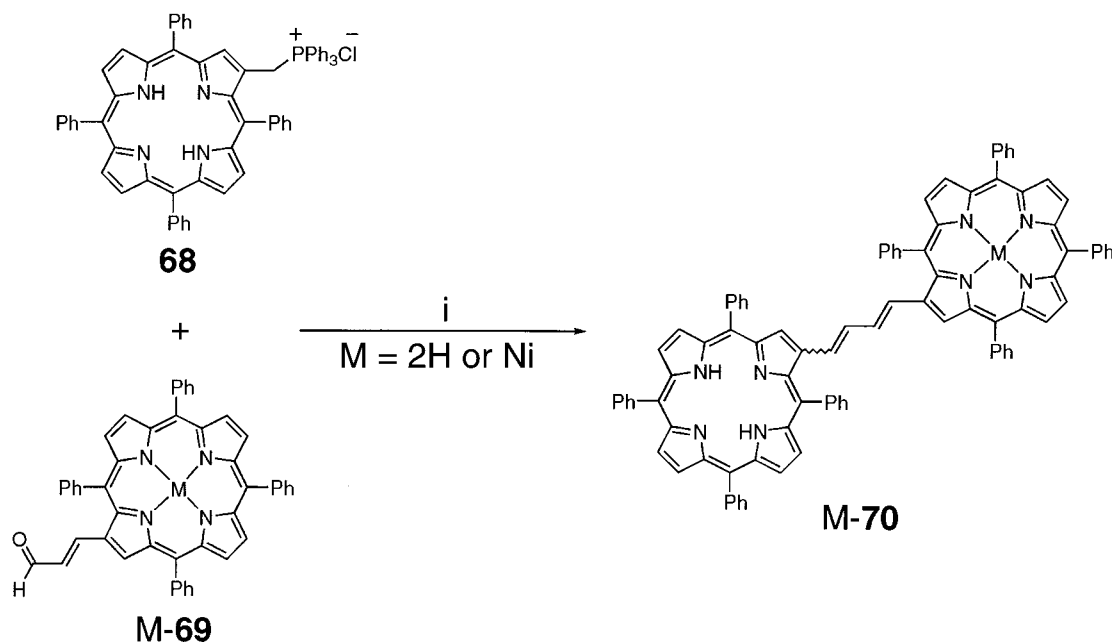
[a] (i) 25−40% aq NaOH, CH₂Cl₂, room temperature.

Many of these arrays were prepared using dipyrrylmethane-based syntheses such as the triporphyrin **42**[96] (Scheme 17) and bispyropheophorbide−porphyrin **45**[97] (Scheme 18), one of the few examples of a β to *meso* linkage. Triporphyrin **42** was prepared in 0.5% yield by condensation of aldehyde **40** and dipyrrylmethane **41**, followed by oxidation. The low yield was attributed to steric hindrance about the aldehyde group of **40**. Bispyropheophorbide−porphyrin **45** was obtained by condensing pyropheophorbide **43** and dipyrrylmethane **44** under MacDonald reaction conditions followed by oxidation (Scheme 18). These compounds were useful for investigating the interactions of directly linked porphyrins.

Analogous *meso* linked diporphyrins such as **48** were also prepared by the same research group, employing a combination of McMurry ketone coupling and dipyrrylmethane chemistry (Scheme 19).[98]

Similar chemistry was used to prepare the interesting oxophlorin square array **52** (Scheme 20).[99] Dipyrryl ketone **49** and bis(dipyrrylmethane) **50** were condensed to give phenyl-bridged di(oxophlorin) **51**. Radical dimerization of **51** yielded 93% of the array **52**. Treatment of **52** with acid regenerated the oxophlorin species **51**, which indicated that formation of the *meso* bonds was reversible. Overall, **52** was unique in that it was a self-assembling oxophlorin array which contained reversible covalent linkages.

In an effort to study the electronic interactions between directly linked porphyrins, Osuka and Shimidzu constructed linear *meso*-linked porphyrin arrays containing up to four porphyrins through chemical oxidative coupling of diarylporphyrin Zn-**53** (Scheme 21).[100,101] The Ag[I]-promoted coupling of Zn-**53** gave a distribution of diporphyrin Zn₂-**54** (27%), triporphyrin Zn₃-**42** (4%), and tetraporphyrin Zn₄-**55** (a trace only) along with unreacted Zn-**53**. Diporphyrin Zn₂-**54** was subjected to the same oxidative coupling process, and tetraporphyrin Zn₄-**55** was thus obtained in 23%

yield. Tetraporphyrin Zn₄-**55** has been made independently via the electrochemical oxidation of diarylporphyrin Zn-**53**. Linear *meso*-linked porphyrin arrays of up to 128 porphyrins have been synthesized in this manner.[95,102]

The Osuka group further expanded on both the number and size of their arrays. The porphyrins **58** and **59** were isolated in 50% and 3% yields, respectively, from the oxidative coupling of the triporphyrin **57**, followed by preparative size exclusion chromatography (Scheme 22).[39] Remarkably, using this methodology they prepared and isolated grid complexes of up to 48 porphyrins.[67]

2. Alkane

One of the earliest alkane-bridged porphyrin arrays was the ethane-linked linear diporphyrin Ni₂-**61** of Arnold et al. prepared by sulfuric acid-catalyzed self-coupling of alcohol Ni-**60** (Scheme 23).[103] The Dolphin group prepared cofacial diporphyrins with β-pyrrolic alkane linkages containing 5, 6, 8, or 10 methylene carbons.[104] Diporphyrins with an ethane linker between *meso* aryl substituents have also been made.[105] To date, no larger arrays with alkane bridges have been reported.

3. Alkene

As a first-generation model of the primary charge separation process in photosynthesis, Ponomarev et al. made ethene-linked diporphyrins[106] from Arnold's ethane-linked diporphyrin **61** (Scheme 24). Warming of **61** to 60−70 °C in acetic acid gave diporphyrin *trans*-**62** in 85% yield, while heating **61** or **62** to reflux in acetic acid (~110 °C) gave a mixture of *cis*- and *trans*-**62**, which were separable by chromatography.

Ponomarev's synthetic approach was extended to make linear and bent triporphyrin arrays (Scheme 25).[107,108] A mixture of ethane- and ethene-bridged

**Scheme 27. Synthesis of Nonaporphyrin 74[a] of Officer et al.[40]**
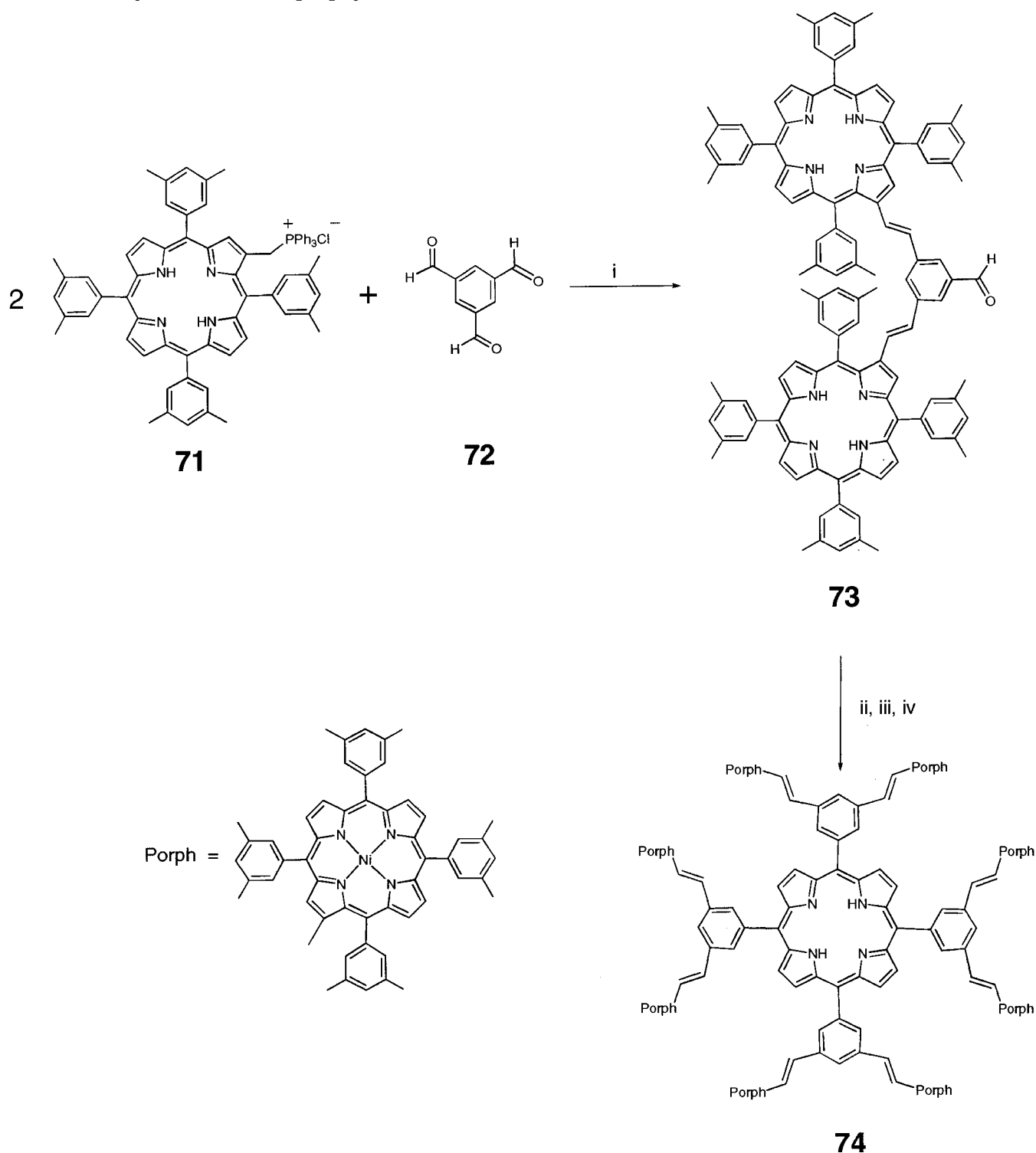
[a] (i) DBU, CH_2Cl_2 then I_2, CH_2Cl_2. (ii) $NiBr_2$, DMF. (iii) pyrrole, TFA, CH_2Cl_2, room temperature, 36 h. (iv) o-Chloranil, CH_2Cl_2, reflux, 3 h.

linear triporphyrins was obtained in approximately 15% yield by coupling diol Ni-**64** to alcohol Ni-**63** using Arnold's method. The crude mixture was demetalated and heated with acetic acid to give all-*trans* triporphyrin **65**. The bent triporphyrin **67** was prepared in analogous fashion (<10% yield) (Scheme 25).

Wittig chemistry has been used to construct porphyrin arrays with alkene bridges between β-pyrrolic carbons. The earliest example of this is that of

Johnson et al., who prepared an ethene-linked dichlorin in 12% yield.[109] Bonfantini and Officer subsequently employed porphyrinyl phosphonium salt **68** in a two-phase Wittig reaction with aldehyde **69** to give butadiene-linked diporphyrin **70** in 62% yield (Scheme 26).[110]

The flexibility of this chemistry has now been well demonstrated by Burrell and Officer, who prepared a variety of triporphyrins,[111,112] pentaporphyrins,[40] and nonaporphyrins.[40] For example, nonaporphyrin

Scheme 28. Synthesis of Diporphyrin Zn₂-77 and Triporphyrin Zn₃-79[a] of Gauler and Risch[114,115]
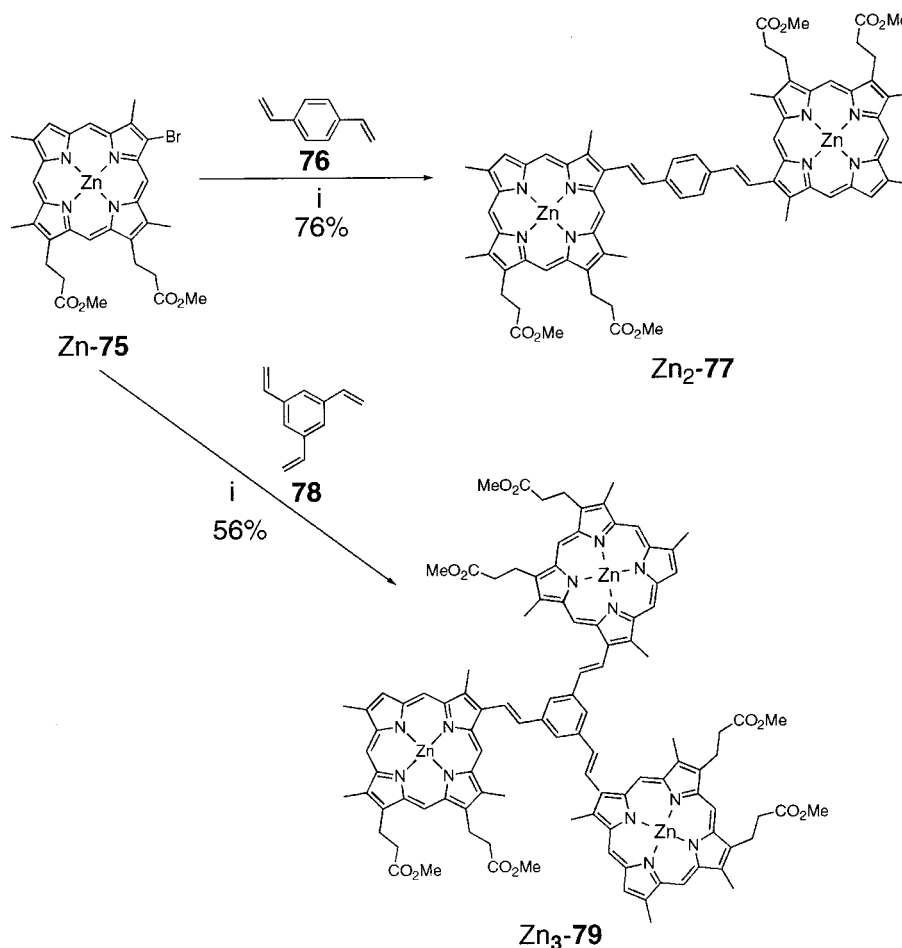
[a] (i) 10% Pd(OAc)₂, TBAB, K₂CO₃, LiCl, DMF, 85 °C, 8–15 h.

74 was prepared in 29% yield from diporphyrin aldehyde Ni-**73** and pyrrole under Lindsey conditions.[53] Aldehyde **73** was, in turn, synthesized from phosphonium salt **71** and trialdehyde **72** using the Wittig chemistry (Scheme 27).[40] Further examples of porphyrin array syntheses employing the Wittig reaction have been summarized in a recent account by Burrell and Officer.[113]

Palladium-catalyzed coupling has been used extensively in the construction of porphyrin arrays; yet only a few examples of its use for the preparation of alkene-linked arrays have been reported. Gauler and Risch employed Heck couplings in their syntheses of diporphyrin Zn₂-**77** and triporphyrin Zn₃-**79** (Scheme 28).[114] Bromoporphyrin Zn-**75** was coupled to diene **76** by heating with 10% palladium acetate in *N,N*-dimethylformamide under phase-transfer conditions, forming Zn₂-**77** in 76% yield. Triporphyrin Zn₃-**79** was produced (56% yield) from the trisalkene **78** in an analogous fashion.[115]

4. Alkyne

A number of research groups have constructed porphyrin arrays with alkyne bonds between porphyrins. The earliest example was a *meso–meso* butadiyne-linked diporphyrin of Arnold et al.[116] This work has been subsequently extended to provide a variety of alkyne-linked diporphyrins with aromatic bridges.[117–119]

Anderson and co-workers developed the use of Glaser–Hay coupling to produce a number of butadiyne-linked linear porphyrin arrays and porphyrin polymers.[120–122] For example, Zn-**80** was deprotected and subjected to oxidative coupling by treatment with copper(I) chloride and *N,N,N',N'*-tetramethylene-diamine (TMEDA) to give polymer Znₙ-**81** (*n* > 10) in 58% yield (Scheme 29). Control over the outcome of the coupling was achieved by coupling monoprotected dialkyne Zn-**80** with trimethylsilylacetylene **82** followed by oxidative coupling. This gave dimer Zn₂-**84** in 28% yield over two steps.[120] Anderson observed that Zn₂-**84** formed bimolecular aggregates in dichloromethane at concentrations down to 10⁻⁶ mol L⁻¹. Within these aggregates, the porphyrin rings of each diporphyrin were determined to be coplanar by NMR and UV–vis absorption spectroscopy. These molecules are of interest because of their highly polarizable, conjugated, and extended π-systems and have potential application in organic semiconductors, near-IR dyes, and electrooptical materials. Anderson elegantly modified this approach to allow a stepwise synthesis of oligomers of up to six porphyrins, which are structurally analogous to Zn₂-**84**.[122]

Therien et al. prepared diporphyrins and triporphyrins containing *meso–meso* alkyne linkages as models for light-harvesting antenna systems (Scheme 30).[123,124] Key alkyne Zn-**88** was made from bromoporphyrin Zn-**85** in two high-yielding steps. Pal-

Scheme 29. Synthesis of Oligoporphyrin Zn$_n$-81 and Diporphyrin Zn$_2$-84[a] of Anderson et al.[120,121]
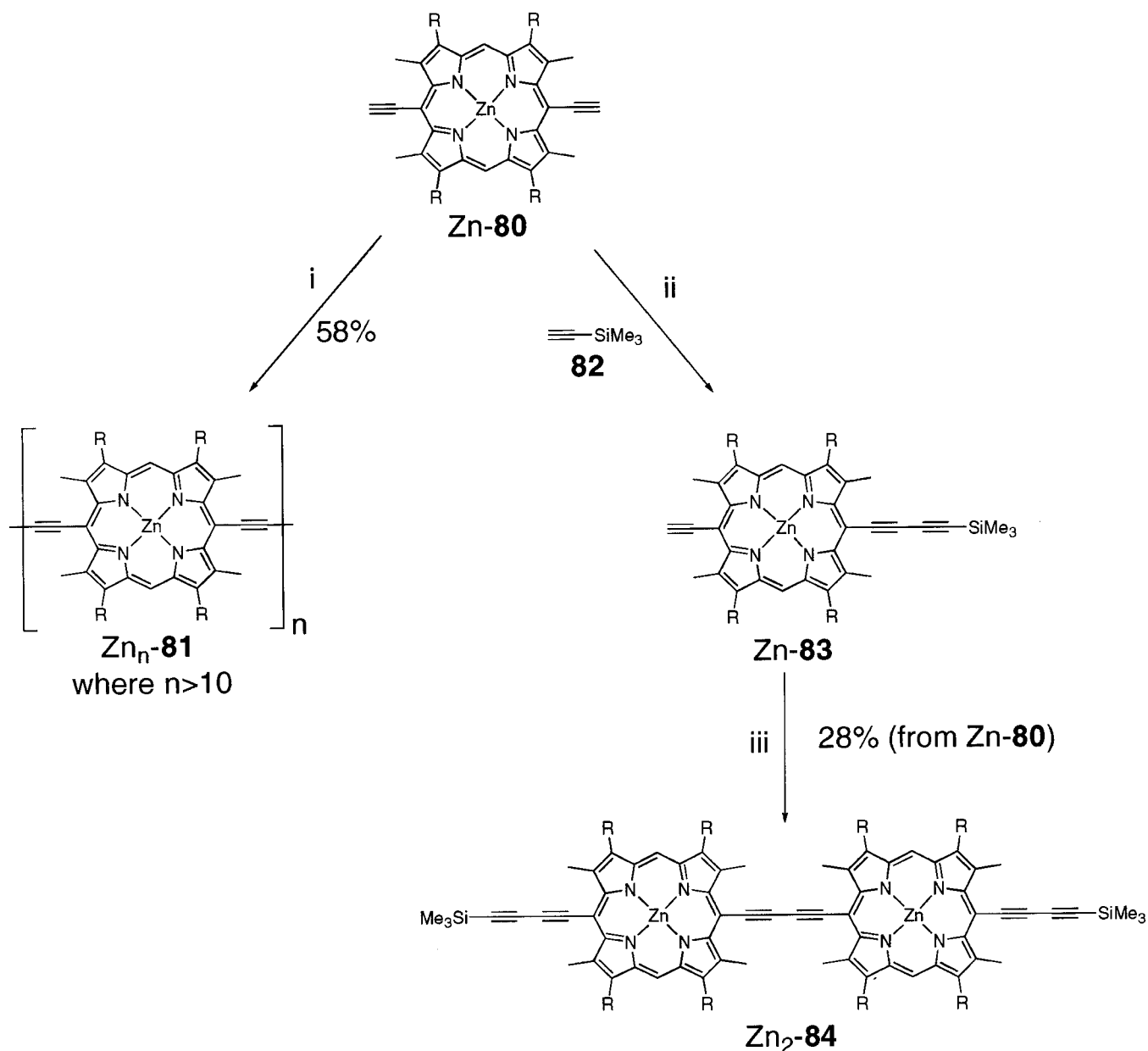
^{a} (i) CuCl, TMEDA, CH$_2$Cl$_2$, air, room temperature, 30 min. (ii) CuCl, TMEDA, CH$_2$Cl$_2$, air, room temperature, 20 min. (iii) CuCl, TMEDA, CH$_2$Cl$_2$, air, room temperature, 25 min.

ladium-catalyzed cross-coupling of Zn-**88** with Zn-**85** gave ethyne-bridged diporphyrin Zn$_2$-**89** in 72% yield (Scheme 30a). Butadiyne-linked diporphyrin Zn$_2$-**90** was obtained in a similar yield from a homocoupling of alkyne Zn-**88** using Eglinton coupling conditions. An identical synthetic approach was used to prepare the TPP equivalents of these diporphyrins, linked through the β positions. Mixed diphenylporphyrin–TPP systems with *meso–β* pyrrolic linkages were synthesized by coupling the appropriate bromoporphyrins and alkynylporphyrins. Triporphyrin Zn$_3$-**92** was prepared in a yield of 33% over three steps, commencing with dibromoporphyrin Zn-**91** and following a similar series of reactions to those used to make diporphyrin Zn$_2$-**89** (Scheme 30b).

The Sanders group created an extensive family of alkyne–aryl-bridged porphyrin arrays for molecular recognition studies. Cyclic and/or linear diporphyrins,

triporphyrins, tetraporphyrins, and octaporphyrins have been made using specific pyridine-based templates to direct the outcome of the coupling reactions through coordination of the zinc porphyrin starting materials.[125] The starting point for their initial syntheses was dialkyne Zn-**93**, which was prepared by condensation of dipyrrylmethane with the appropriate aldehyde followed by zinc insertion.[126] Glaser-type oxidative coupling using copper(I) chloride and TMEDA in the presence of bipyridine **94** as a template gave cyclic diporphyrin **95** in 65–75% yield after demetalation (Scheme 31). Substituting tripyridyltriazine **96** for bipyridine **94** led to the formation of triporphyrin **97** in 50–55% yield. Cyclic trimers of this kind have been used to catalyze acyl transfer reactions[127] and accelerate bimolecular Diels–Alder reactions[128] and in mass spectrometry binding studies[129] of polyoxometalate anions.

Scheme 30. Synthesis of (A) Diporphyrins Zn$_2$-89 and Zn$_2$-90 and (B) Triporphyrin Zn$_3$-92^a of Therien et al.[123,124]
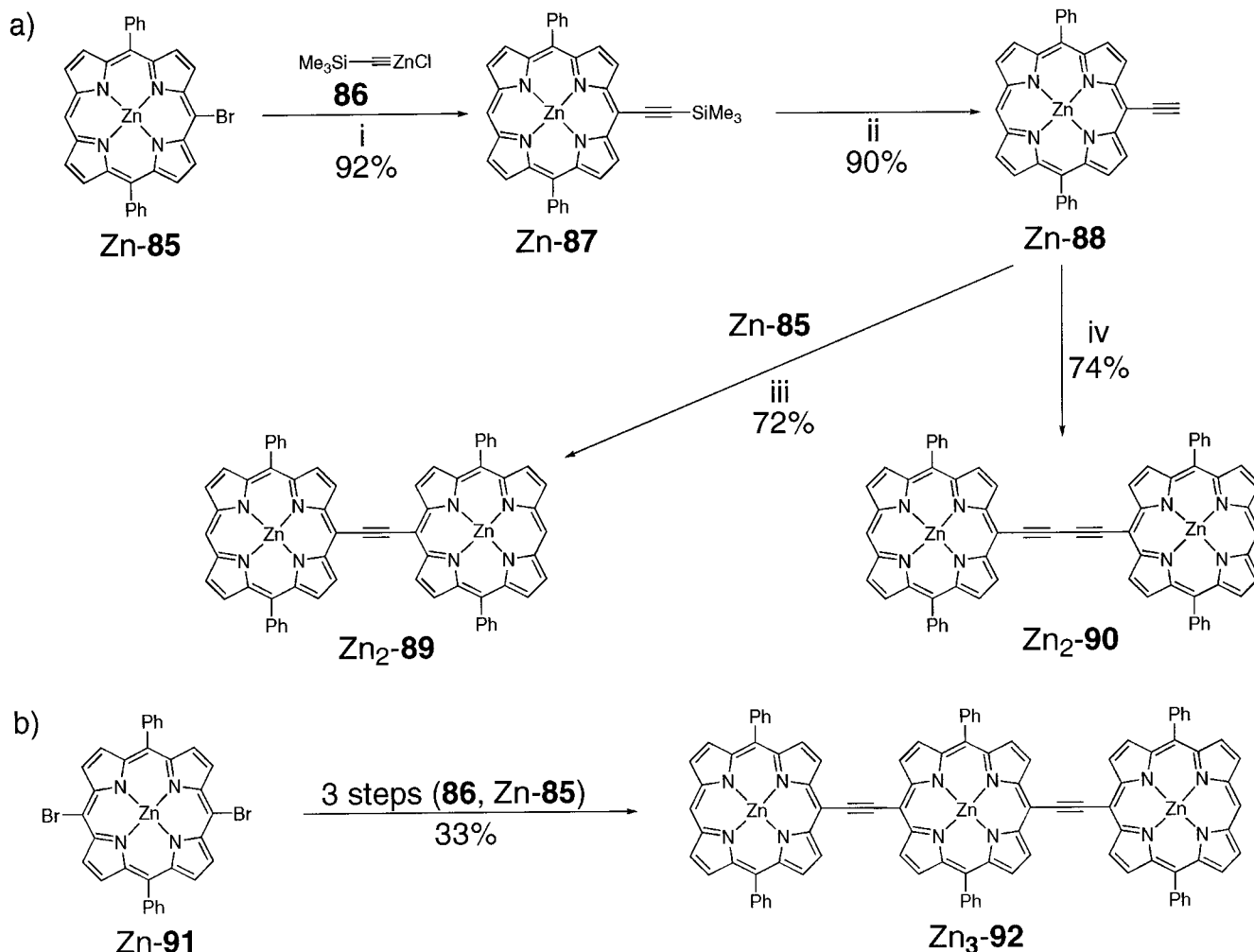
^{a} (i) Pd(PPh$_3$)$_4$, THF, N$_2$, 60 °C. (ii) TBAF/THF, CH$_2$Cl$_2$, N$_2$, room temperature, 50 min. (iii) Pd(PPh$_3$)$_4$, LiN(SiMe$_3$)$_2$, THF. (iv) Cu(OAc)$_2$, C$_5$H$_5$N, 90 °C, 1 h.

A variety of linear porphyrin arrays were made using diprotected dialkyne Zn-**98** and similar coupling procedures (Scheme 32).[125] Oxidative coupling of Zn-**99**, obtained by partial deprotection of Zn-**98**, formed diprotected diporphyrin Zn$_2$-**100** in 34% yield. In a similar fashion, tetraporphyrin Zn$_4$-**101** was obtained by partial deprotection of Zn$_2$-**100** followed by coupling.

However, since chromatography of the mixture resulting from deprotection proved to be difficult, the coupling reaction was carried out in the presence of bipyridine **94** as a scavenger template. The desired diprotected linear tetraporphyrin Zn$_4$-**101** was obtained in 29% yield, while any fully deprotected diporphyrin starting material was converted to cyclic dimer Zn$_2$-**95** through binding to the template, instead of forming higher oligoporphyrins. Linear octaporphyrin Zn$_8$-**102** was then made (15%) from Zn$_4$-**101** using an identical approach but with tetrapyridylporphyrin (TPyP) as the scavenger template.

A second cyclic array, tetraporphyrin **103**, was synthesized using analogous methodology. Full deprotection of linear tetraporphyrin Zn$_4$-**101** followed by oxidative coupling in the presence of TPyP as a template, and then acid demetalation, gave the cyclic

tetraporphyrin **103** in 45% yield (Scheme 33).[125] A crystal structure of tetraporphyrin **103** encapsulating TPyP was obtained which to date is the largest porphyrin array characterized by X-ray crystallography.[130] The complex formed between TPyP and Zn$_4$-**103** was found to be photoactive, the fluorescence of both components being strongly quenched.[130] Similar behavior was observed for Zn-TPyP encapsulated in Zn$_4$-**103**. These systems were proposed as models for the photosynthetic reaction center and/or antenna complexes.

The Sanders group was also able to produce a number of variations on these cyclic and linear arrays by virtue of relatively simple changes to their starting materials. For example, the central metal was changed from zinc to ruthenium, which drastically increased the binding strength between the host array and guest.[131] In addition, a range of "R group" substituents were used instead of methyl esters, such as alkyl groups and isodecyl esters, with the latter offering improved solubility for larger arrays.[125,132] The use of dioxoporphyrins—where the two nonsubstituted meso positions of the porphyrin now contain a carbonyl functional group—instead of porphyrins led to zinc complexes that bound their templates more

Scheme 31. Synthesis of Cyclic Diporphyrin 95 and Triporphyrin 97[a] of Anderson et al.[126]
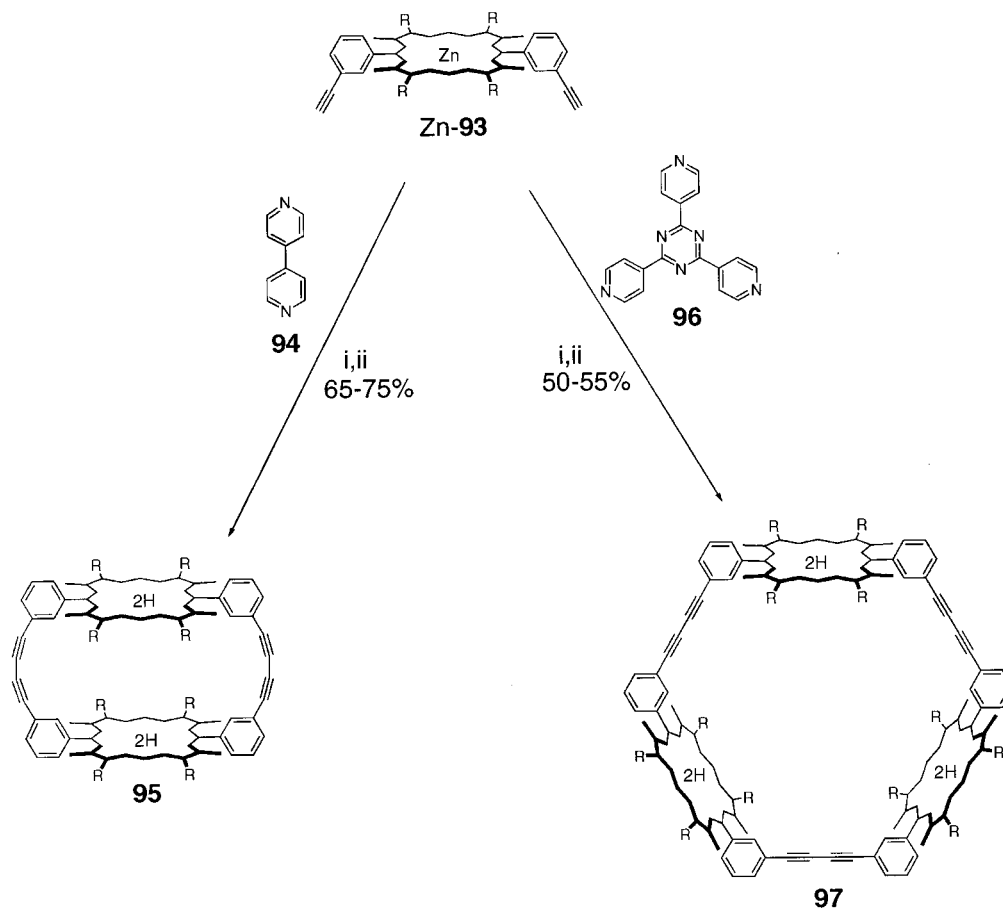
[a] (i) CuCl, TMEDA, CH_2Cl_2, air, 24 h. (ii) 10% TFA/MeOH.

strongly, which was reflected in higher yields for the templated syntheses of cyclic diporphyrins, triporphyrins, and tetraporphyrins.[133] Dioxoporphyrins have also recently been utilized in molecular guest recognition studies.[134]

The cavity size of these cyclic arrays was also increased by utilizing a longer linker length between porphyrins. This was achieved by not only including a platinum complex in the dialkyne linker,[135] but also by using bis(butadiyne)-functionalized porphyrin starting materials instead of dialkynes.[132] Smaller cavity sizes were accessed using a different synthetic approach that involved no oxidative coupling of porphyrins. Acid-catalyzed condensation of dipyrrylmethane **104** and dialdehyde **105** gave a mixture of products including cyclic diporphyrin **106** and cyclic triporphyrin **107**, both in very low yield (Scheme 34).[136] The low yield reflected the simultaneous formation of two or more porphyrinogen rings during the first phase of acid-catalyzed condensations.

Less symmetrical cyclic arrays were obtained through stepwise syntheses (Scheme 35). Iodoarylporphyrin Zn-**108** was prepared by mixed aldehyde condensation with dipyrrylmethane **104**, followed by zinc insertion.[137] Palladium-catalyzed coupling of Zn-**108** to dialkyne Zn-**93** afforded linear triporphyrin Zn₃-**109** in 84% yield. Deprotection and oxidative coupling of the terminal alkynes of Zn₃-**109**, in the presence of tripyridyltriazine **96** as a template, gave a 62% yield of cyclic triporphyrin Zn₃-**110**. Using

similar procedures, nickel and zinc mixed-metal trimers have also been synthesized and used to investigate the binding of various pyridyl ligands.[138]

The Lindsey research group made a wide variety of porphyrin assemblies, with similar alkyne–aryl connectivity to those of the Cambridge researchers, and investigated the potential of the arrays as light harvesters and molecular devices. A modular approach was used to construct diporphyrins,[62,139] linear and bent triporphyrins,[140–143] linear and branched tetraporphyrins,[21,22,144] radial pentaporphyrins,[145,146] and nonaporphyrins.[147]

The linkages were formed by palladium-catalyzed coupling of iodo- and alkyne-functionalized TAPs, the simplest example of which is the preparation of diporphyrin Zn-**113** (Scheme 36).[62] Both alkyne Zn-**111** and iodide **112** were prepared in low yields by mixed-aldehyde condensations. A high-yielding coupling of Zn-**111** and **112** in the presence of a palladium catalyst gave diporphyrin Zn-**113** (87%) as well as small amounts of the homocoupled, butadiyne product and higher molecular weight materials. Diporphyrins of this kind were chiefly used as model compounds for investigation of the spectroscopic and photophysical properties of larger arrays.

Triporphyrin arrays were synthesized by similar coupling procedures (Scheme 37).[140,141] Coupling of *trans*-diiodide **114**, prepared using dipyrrylmethane chemistry, and alkyne Zn-**111** in the presence of a palladium catalyst and triphenylarsine gave linear

Scheme 32. Synthesis of Diporphyrin Zn$_2$-100, Tetraporphyrin Zn$_4$-101, and Octaporphyrin Zn$_8$-102^a of Anderson et al.[125]


where R = -CH$_2$CH$_2$CO$_2$Me
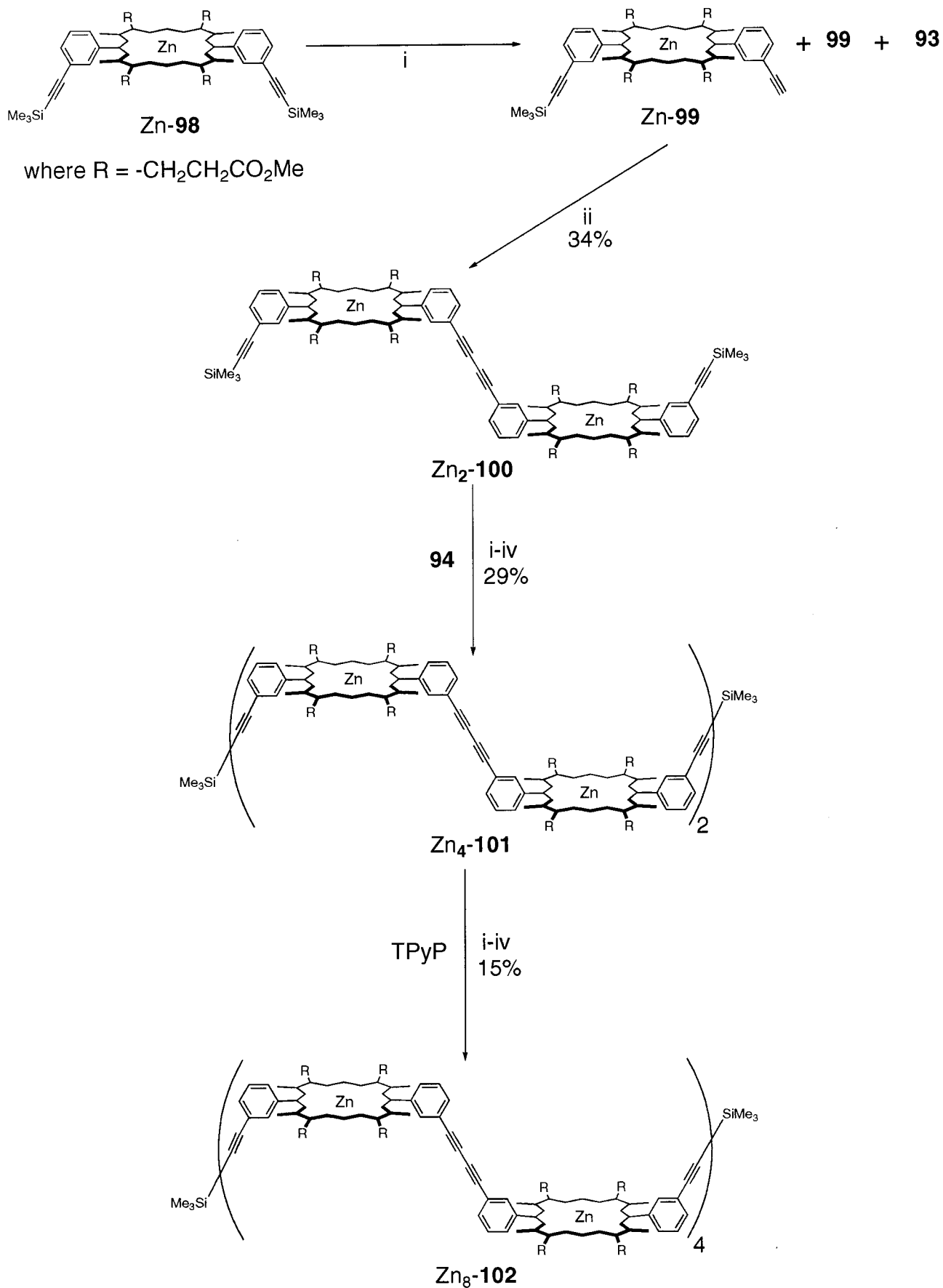
^{a} (i) TBAF/THF, CH$_2$Cl$_2$, room temperature. (ii) CuCl, TMEDA, CH$_2$Cl$_2$, room temperature, 15−30 min. (iii) 10% TFA/MeOH. (iv) Zn(OAc)$_2$, CHCl$_3$.

Scheme 33. Synthesis of Cyclic Tetraporphyrin 103[a] of Anderson et al.[125]

Zn₄-**101**

where R = -CH₂CH₂CO₂Me

i 84%

TPyP | ii,iii 54%

103
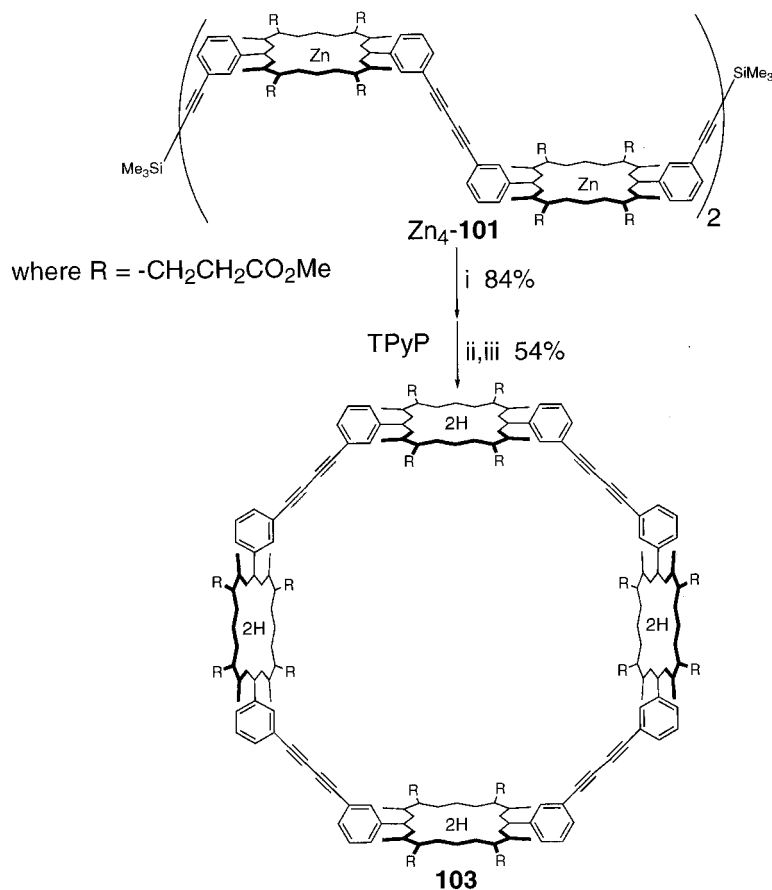
a (i) TBAF/THF, CH₂Cl₂, room temperature, 20 min. (ii) CuCl, TMEDA, CH₂Cl₂, air, room temperature, 30 min. (iii) 10% TFA/MeOH.

Scheme 34. Synthesis of Cyclic Diporphyrin 106 and Triporphyrin 107[a] of Vidal-Ferran et al.[136]

104   **105**

where R = -CH₂CH₂CO₂Me

i,ii

106
3-4%

+

107
1-2%
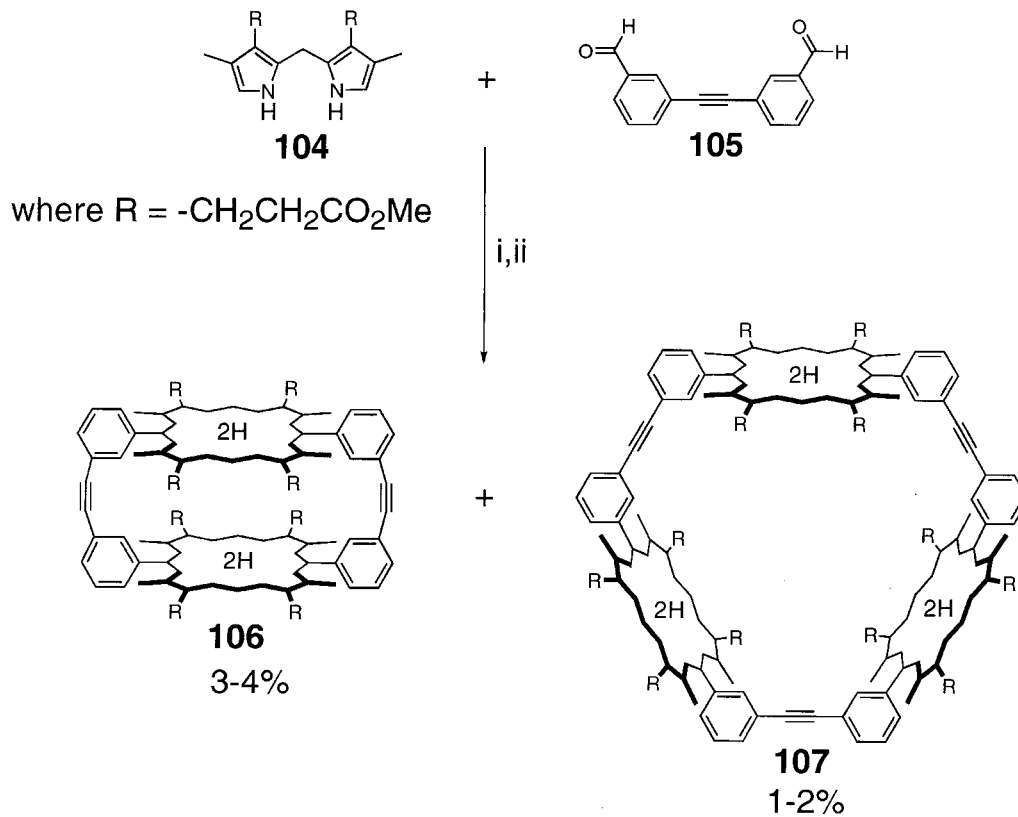
a (i) TFA, CH₂Cl₂. (ii) Oxidation conditions unspecified.

Scheme 35. Synthesis of Triporphyrins Zn₃-109 and Zn₃-110[a] of Vidal-Ferran et al.[137]

where R = -CH₂CH₂CO₂Me

Zn-**108**

Zn-**93**

i
84%

96
iii
65%

ii
95%

Zn₃-**110**

Zn₃-**109**
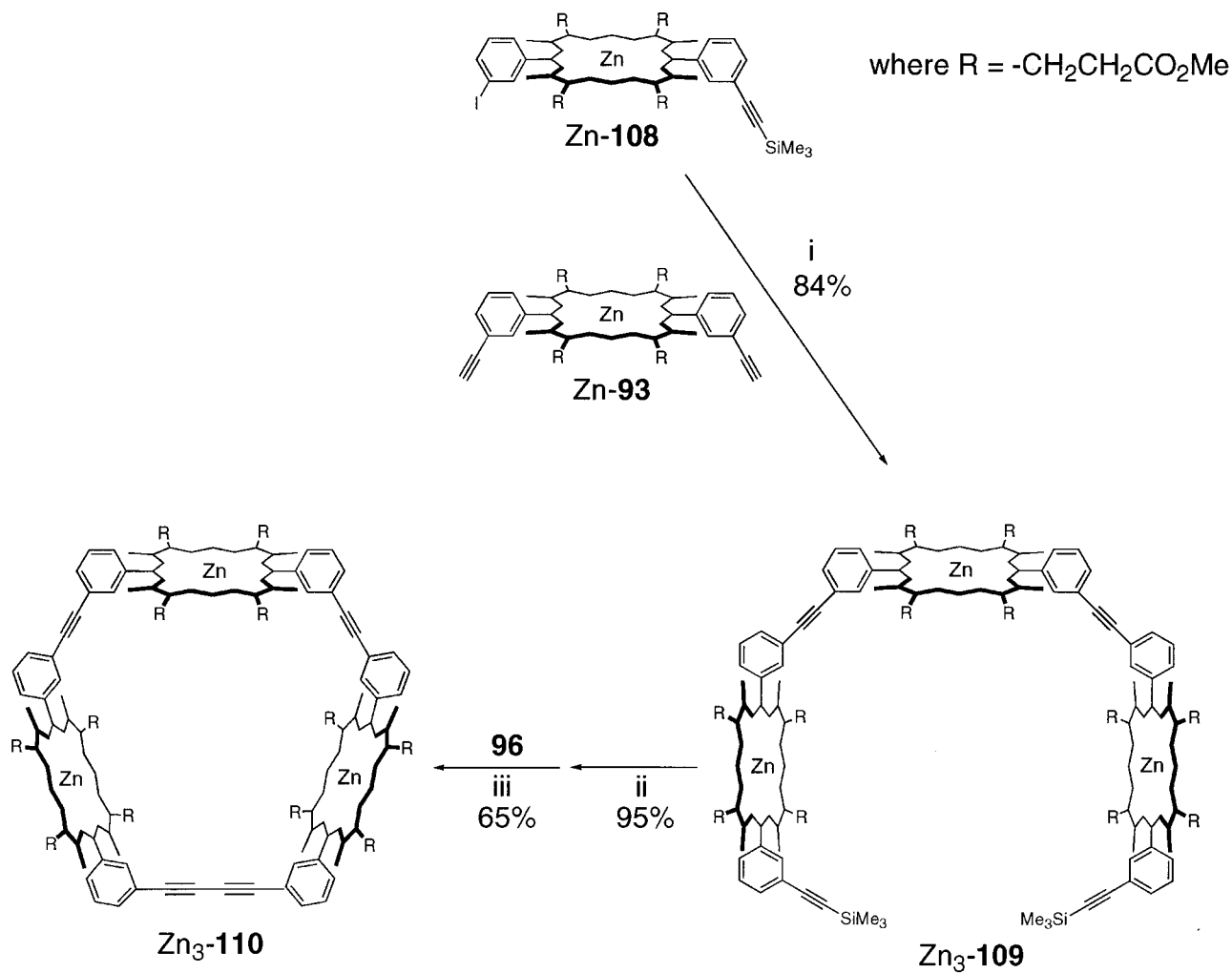
[a] (i) Pd(PPh₃)₄, CuI, Et₃N, THF. (ii) TBAF/THF, CH₂Cl₂. (iii) CuCl, TMEDA, CH₂Cl₂, room temperature.

Scheme 36. Synthesis of Alkyne-Linked Diporphyrin Zn-113[a] of Lindsey et al.[62]

Zn-**111**

+

112

where Ar = H₃C ─ CH₃ / H₃C

i
87%

Zn-**113**
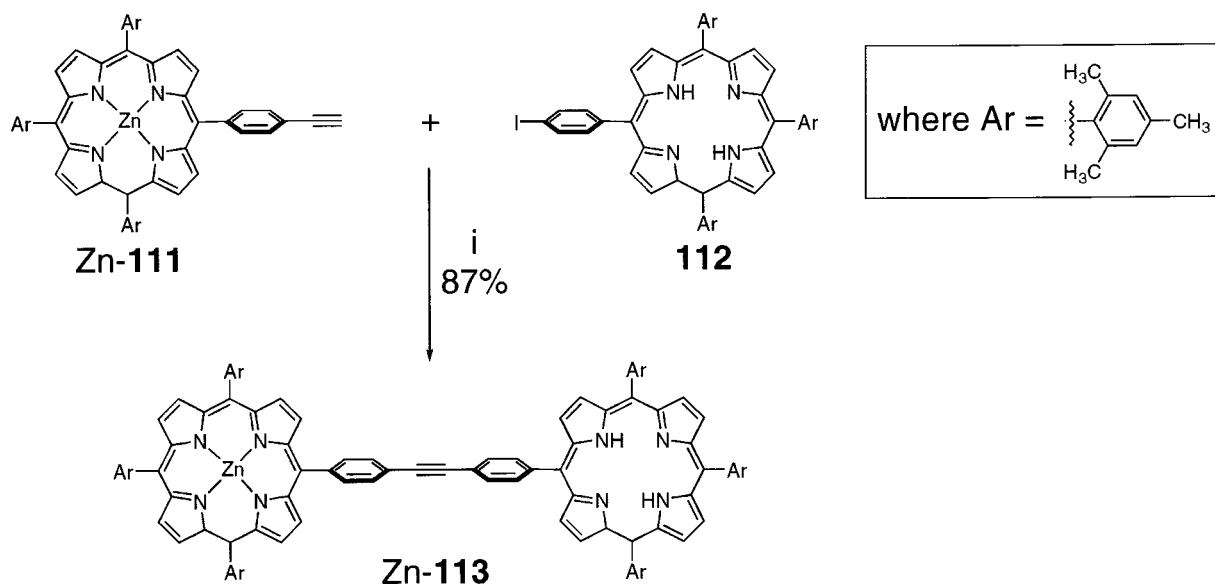
[a] (i) Pd(PPh₃)₄, toluene, Et₃N, argon, 40−50 °C, 24 h.

triporphyrin Zn₂-**115** in 79% yield.[141] The bent tri-porphyrin Zn₂-**117** was obtained in excellent yield via an analogous coupling of c*is*-diiodide **116** with Zn-**111**.[140] This methodology provided a means by which the trimer could be metalated selectively, demonstrating its utility for the control of metalation. These

Scheme 37. Synthesis of Triporphyrins Zn$_2$-115 and Zn$_2$-117[a] of Lindsey et al.[140,141]
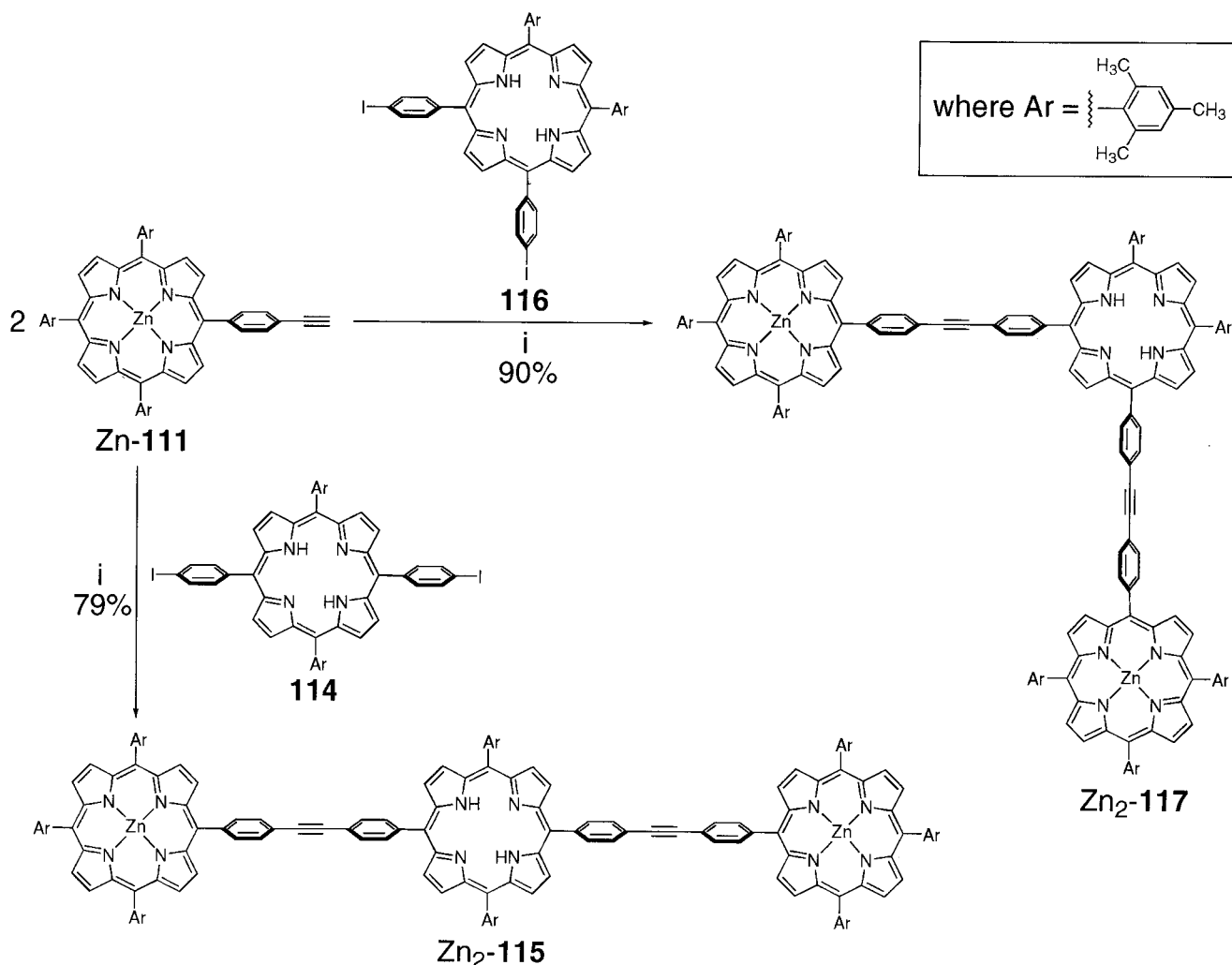
^{a} (i) Pd$_2$(dba)$_3$, AsPh$_3$, toluene, Et$_3$N, argon, 35 °C, 2 h.

triporphyrins were used as model compounds for investigations of larger array systems. Amphipathic triporphyrins capable of energy transfer were prepared in this manner and incorporated into vesicles for the study of transmembrane charge separation, electron transport, and signal transduction.[142]

The value of this methodology has been demonstrated with the synthesis of a number of larger arrays. Radial pentaporphyrin Zn$_4$-120 was prepared in 50% yield through the palladium-catalyzed coupling of alkyne Zn-118 and tetraiodide 119 (Scheme 38).[145] This pentamer was shown to efficiently transfer energy from the peripheral porphyrins to the central free base porphyrin. A modification of this work included the introduction of magnesium into the peripheral porphyrins of closely related diporphyrin and pentaporphyrin arrays. This change resulted in a subtle variation to the energy-transfer properties of these arrays as compared to their zinc analogues.[148]

Lindsey used this modular approach to assemble larger arrays containing eight or nine porphyrins. The details of these syntheses have yet to be fully reported, but the arrays have been the subject of a mass spectrometry study.[149]

More elaborate and unsymmetrical arrays have been made both in a stepwise manner using the template methodology developed by Sanders. The iodide 121, prepared by mixed aldehyde condensation with dipyrrylmethane, was used in a sequence of couplings and desilylations to give the linear tetraporphyrins such as Zn$_3$-122 (Scheme 39).[140] This linear array has been proposed as a molecular photonic wire since energy is transferred from the boron–dipyrromethene dye through the zinc porphyrins to the free base porphyrin upon illumination. Linear and bent triporphyrins of a similar construction to Zn$_3$-122 were also designed as molecular optoelectronic gates where inclusion of a magnesium porphyrin as a redox-switched site, either terminally or adjacently, allowed gating of the energy migration.[22] In an extension to this work, buckminsterfullerene was tethered to a free-base porphyrin, which was in turn attached to an X-shaped tetrazinc porphyrin antenna. This resulted in an artificial photosynthetic antenna–reaction center complex.[150]

Cyclic hexaporphyrin Zn$_6$-126 was synthesized in ∼5% yield via the Pd-mediated coupling of M-123 and 124, using the tripyridine 125 as a template, followed by metalation (Scheme 40).[151] During the course of

Scheme 38. Synthesis of Radial Pentaporphyrin Zn₄-120[a] of Prathapan et al.[145]


Zn-**118**

+

119

where Ar =

Zn₄-**120**
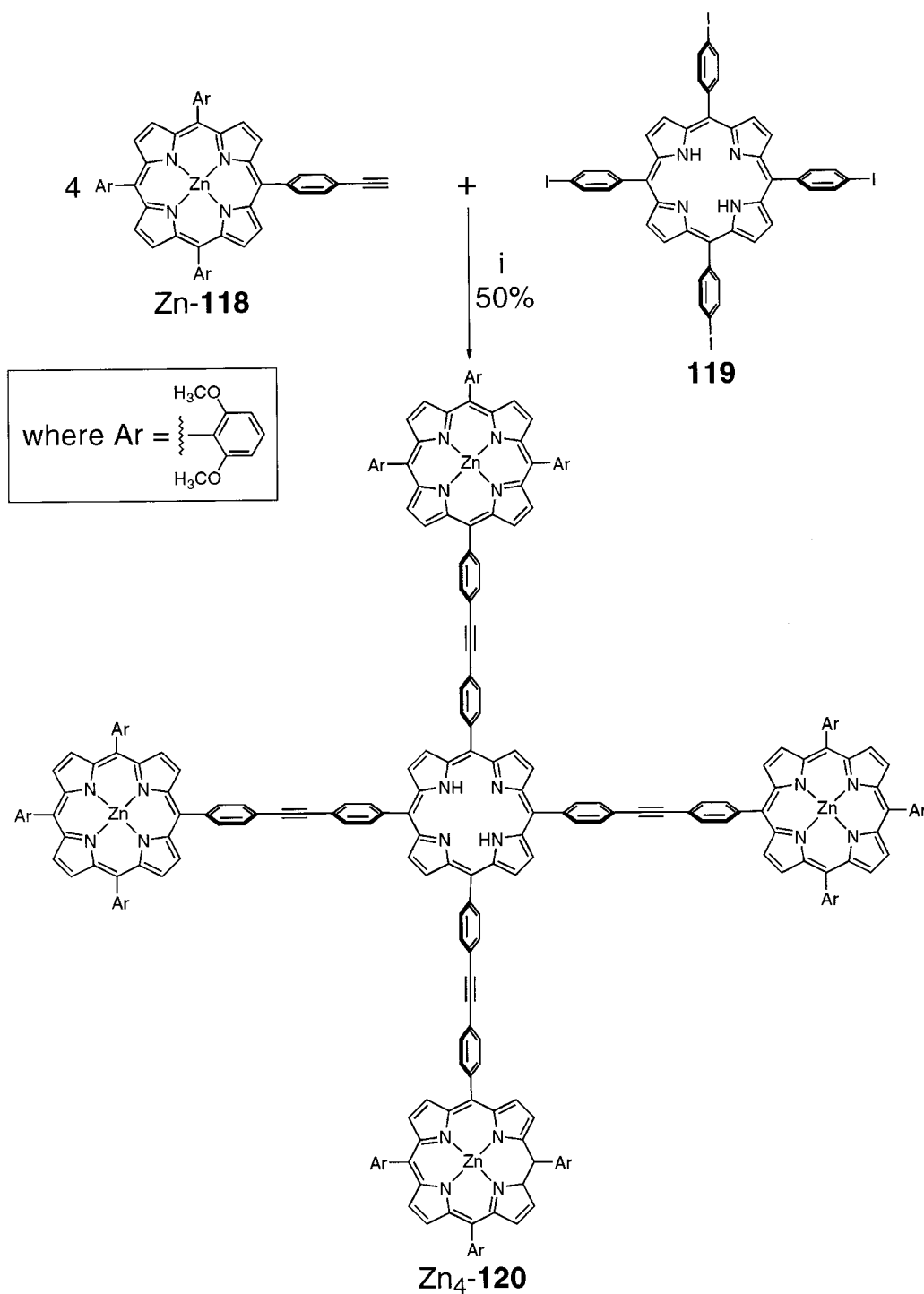
[a] (i) Pd(PPh₃)₄, C₅H₅N, Et₃N, 100 °C, 12 h.

this work, various factors were investigated such as the choice and concentration of the template as well as the complementary reaction where **123** is coupled to M-**124**.

The experience of the Lindsey research group in palladium coupling reactions has been illustrated by a recent thorough investigation into the optimization of coupling conditions for porphyrin arrays.[152] This study has resulted in the development of simplified reaction conditions leading to products that are more easily purified.

Other groups have adopted the palladium-catalyzed coupling methodology of Lindsey. Osuka et al. prepared tetraporphyrin **128** and diporphyrin **129** in 16% and 28% yields, respectively, via coupling of **127** with 1,2,4,5-tetraiodobenzene (Scheme 41).[153]

Mongin and Gossauer constructed tetraporphyrins with alkyne−aryl bridges that they termed tripodaphyrins (Scheme 42).[154,155] These nanometer-sized materials were prepared with nanofabrication in mind. Palladium-catalyzed coupling of Zn-**130** with tetraalkyne **131** gave tetraporphyrin Zn₄-**132** in 58%

Scheme 39. Construction of Linear Tetraporphyrin Zn$_3$-122 of the Lindsey Group[21]
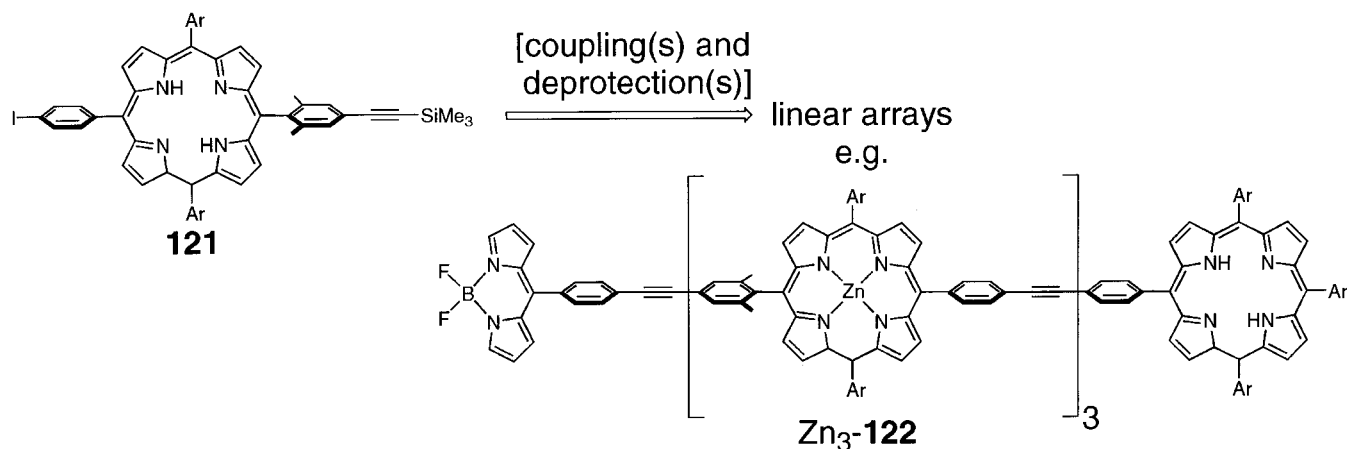
Scheme 40. Synthesis of the Cyclic Hexaporphyrin Zn$_3$-126^a of Li et al.[151]
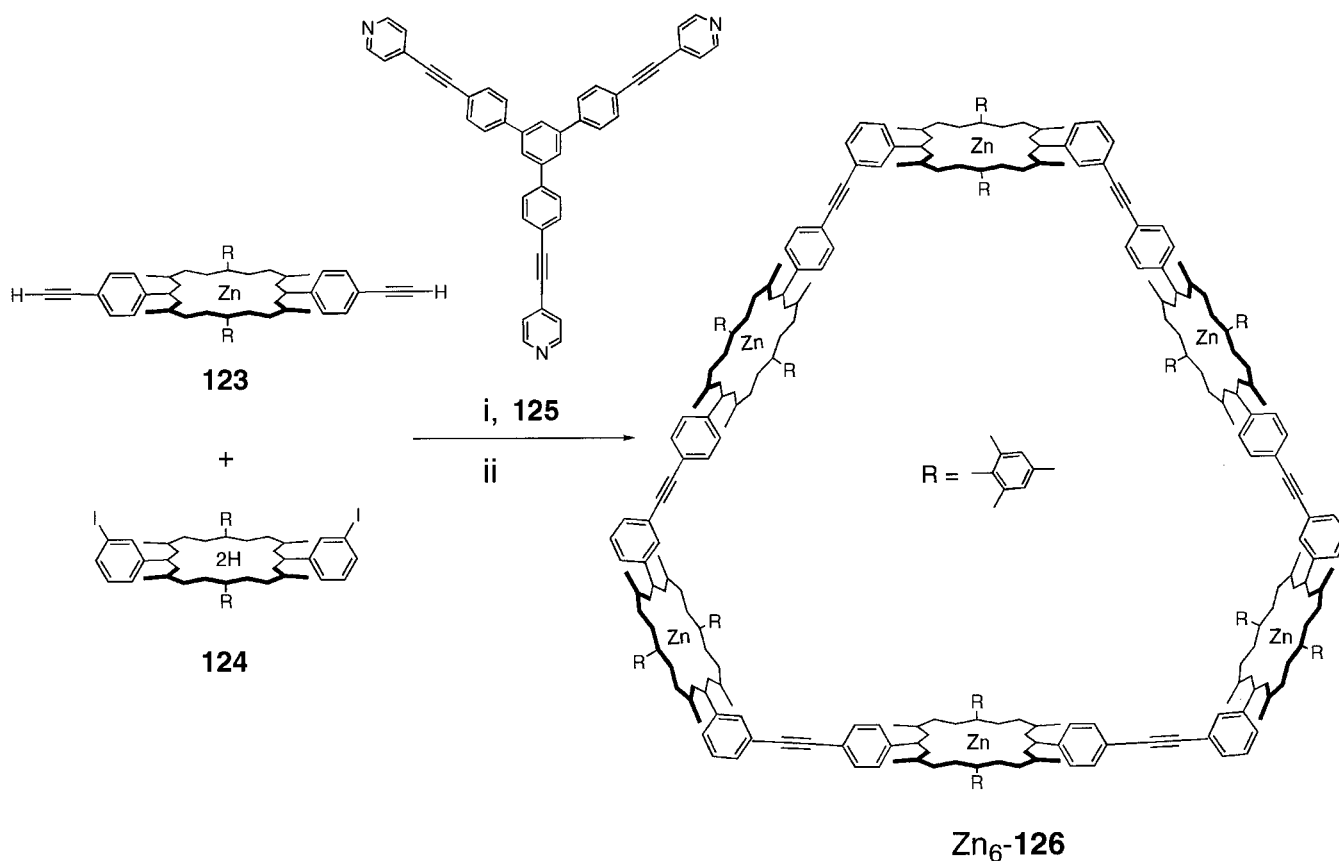
^{a} (i) Pd$_2$(dba)$_3$, AsPh$_3$, toluene, Et$_3$N, 35 °C, o/n. (ii) Zn(Oac)$_2$2H$_2$O, CHCl$_3$, MeOH.

yield. Indeed, the reverse approach, i.e., coupling an alkynylporphyrin to a tetraiodide, was more successful, giving a 89% yield of the tetraporphyrin. In addition, analogous unsymmetrical tetraporphyrin arrays were prepared by a stepwise synthesis.[155] Triple silyl protection of **131** allowed the coupling of one porphyrin moiety before deprotection and coupling of three different porphyrins or phenylacetylene "legs".

Gossauer et al. extended their work to include examples of phenylethynyl-linked triporphyrins and hexaporphyrins[156] and investigated the electronic energy-transfer dynamics of these and other multiporphyrin arrays.[157]

A unique cyclic hexaporphyrin has also been reported by the Swiss research group (Scheme 43).[158] The authors utilized the building block Zn-**133**, which could be reacted selectively to form the desilylated complex Zn-**134** or the iodo complex Zn-**135**. Introduction of free base porphyrins into the final product Zn$_6$-**137** could be achieved by demetalating the monomer Zn-**135** with TFA before the first porphyrin coupling step. The diporphyrin Zn$_2$-**136** was prepared via the palladium-catalyzed coupling of Zn-**134** and Zn-**135**. Successive manipulations using these reactions resulted in the formation of a straight chain hexaporphyrin, which was cyclized by coupling the two ends together using a palladium catalyst to form

Scheme 41. Synthesis of the Tetraporphyrin 128 and Diporphyrin 129[a] of Osuka et al.[153]
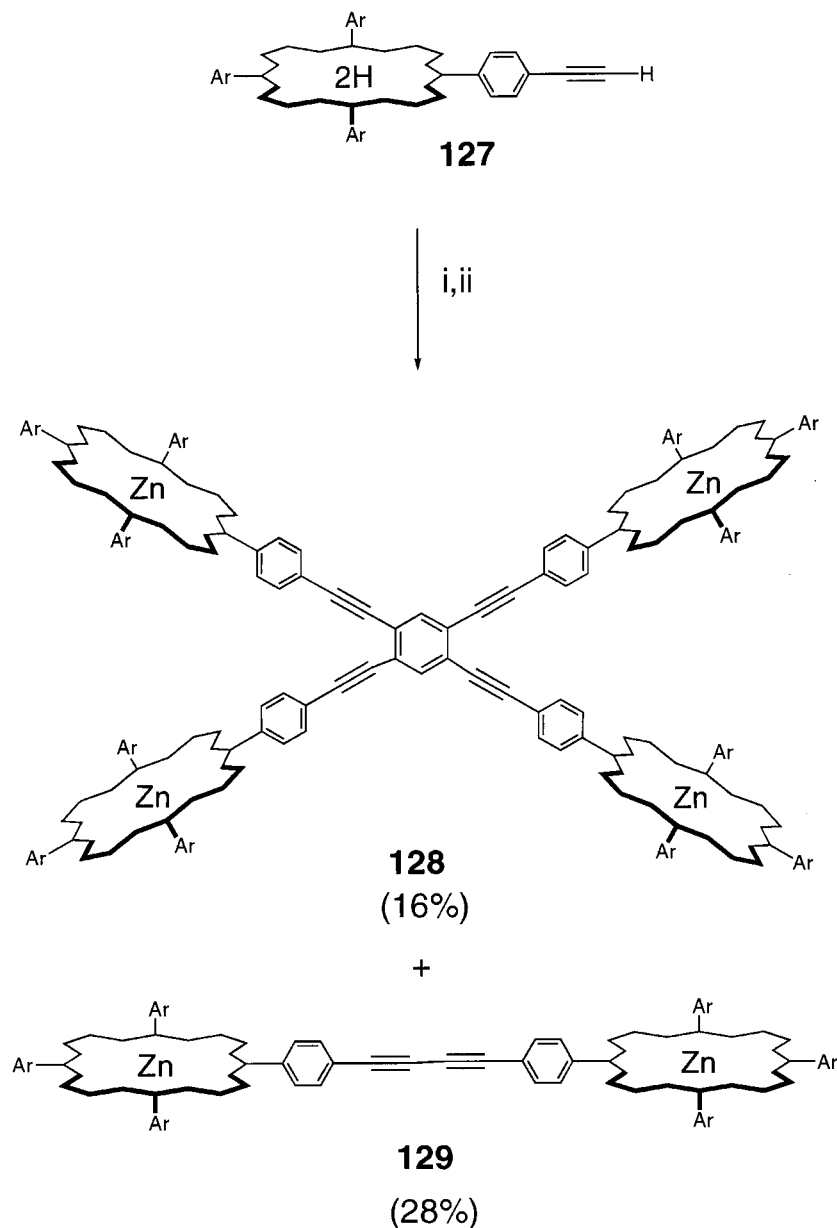
[a] (i) Zinc insertion, no details given. (ii) $Pd_2(dba)_3$, $AsPh_3$, toluene, Et_3N, room temperature, 7 days.

the final product Zn_6-**137** in 20−30% yield.[158] This is the first example of the formation of a large cyclic porphyrin array in the absence of a template.

Mongin et al. have since added a new class of hexamer porphyrin array, which they termed nipha-phyrins, employing the methodologies utilized in the construction of hexaporphyrin **137**. These new arrays are structurally very similar to the tetraporphyin **128** of Osuka and show good energy transfer between zinc and free base porphyrins in the same array.[159]

A number of other research groups have utilized palladium-catalyzed or Glaser copper-mediated couplings to synthesize various porphyrin arrays. König and Zieg prepared a triporphyrin through the reaction of a β-pyrrolic alkyne-substituted TPP with 1,3,5-triiodobenzene.[160] Jones and his researchers synthesized soluble metalloporphyrin polymers through the reaction of dialkyne-substituted porphyrins with long

chain substituted diiodobenzenes.[161] The Diederich group formed a triporphyrin connected at the meso positions by *trans*-enediynediyl linkers.[162] Crossley and McDonald used Glaser-type cross couplings to form imidazole-fused arene-linked di- and tripor-phyrins.[163] Sugiura et al. also used Glaser copper-mediated coupling to form the square-shaped di-acetylene-linked porphyrin tetramer **138** (Figure 2). The yield for their final coupling step (in the absence of a template) was a healthy 22%; however, the key intermediate 5,10-bis(3,5-di-*tert*-butylphenyl)por-phyrin could only be prepared in 3%.[164]

Most of these coupling reactions require an acetyl-enic and a halogenated porphyrin. In contrast, Bea-vington and Burn created a tetrameric porphyrin array by coupling a dimer of a Crossley-type bis-pyrazineporphyrin using a palladium-catalyzed bis-Stille coupling in an excellent 76% yield.[165]

Scheme 42. Synthesis of Tetraporphyrin Zn$_4$-132^a of Mongin and Gossauer[154]

Zn-**130**

i
58%

131

Zn$_4$-**132**
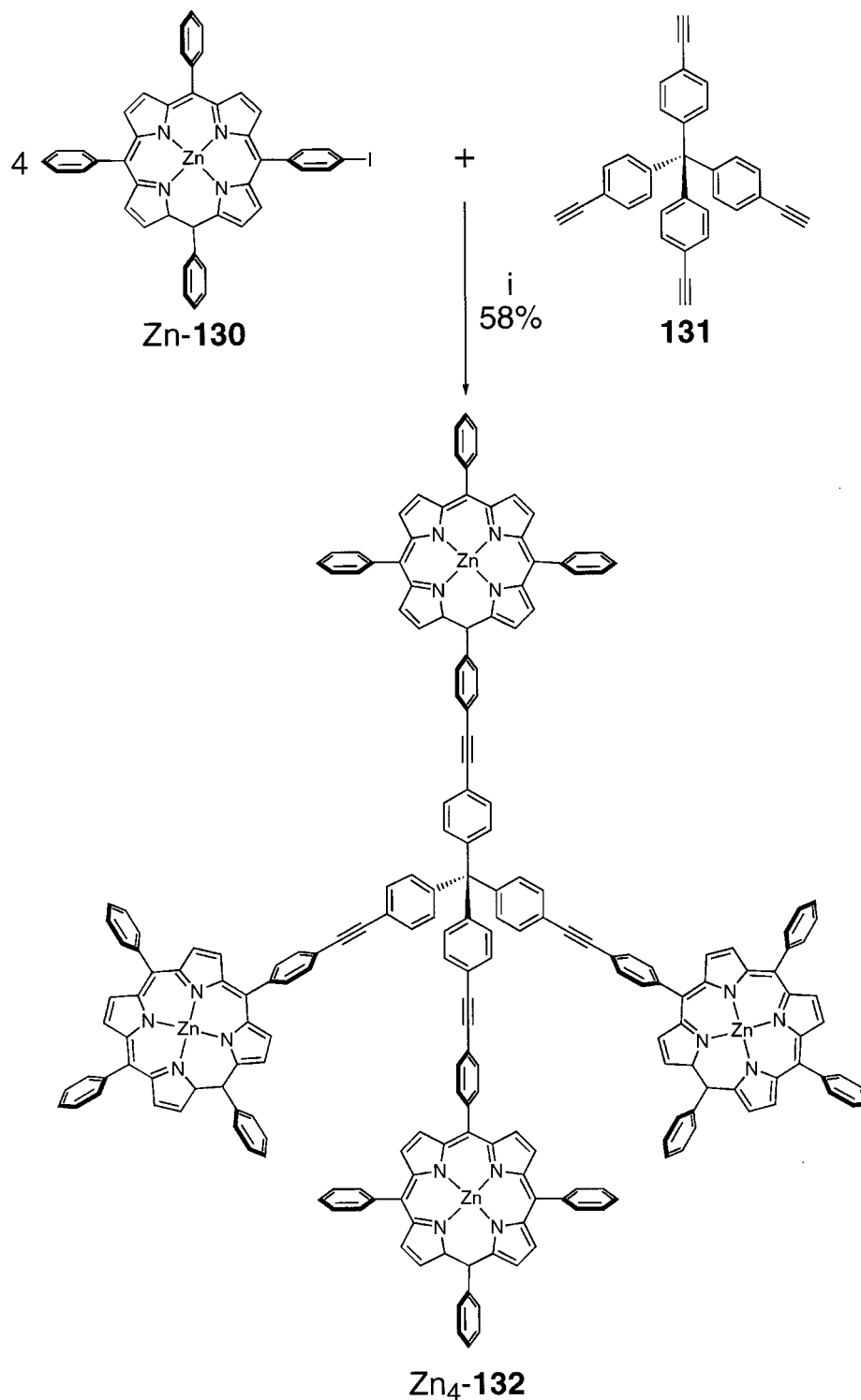
^{a} (i) Pd(PPh$_3$)$_4$, DMF, argon, 40 °C, 15 h.

5. Aromatic

A large number of porphyrin arrays, many of which are diporphyrins, have been made in which the porphyrin components are linked by aromatic rings of various types. These linkages are most often between the *meso* carbons of adjacent porphyrins, and thus, the linking moiety is usually orthogonal to the attached porphyrins. The majority of these systems are constructed using dipyrrylmethane-based syntheses. This general approach was pio-

neered by Chang and Abdalmuhdi, who made an anthracene-linked cofacial diporphyrin.[166] Like Collman's diporphyrins,[3] the cobalt derivatives of these diporphyrins were found to catalyze the electroreduction of oxygen.[167] Chang and Abdalmuhdi then extended the methodology to synthesize the anthracene-linked cofacial triporphyrin **140** via the acid-catalyzed condensation of aldehyde **139** with dipyrrylmethane **35** followed by oxidation (Scheme 44).[168]

Scheme 43. General Synthetic Procedure To Form Macrocyclic Hexaporpyrin Zn₆-137ᵃ of Mongin et al.[158]

Zn-**133**

i

ii

Zn-**134**

Zn-**135**

III

Zn₂-**136**

Linear Hexaporphyrin

Zn₆-**137**
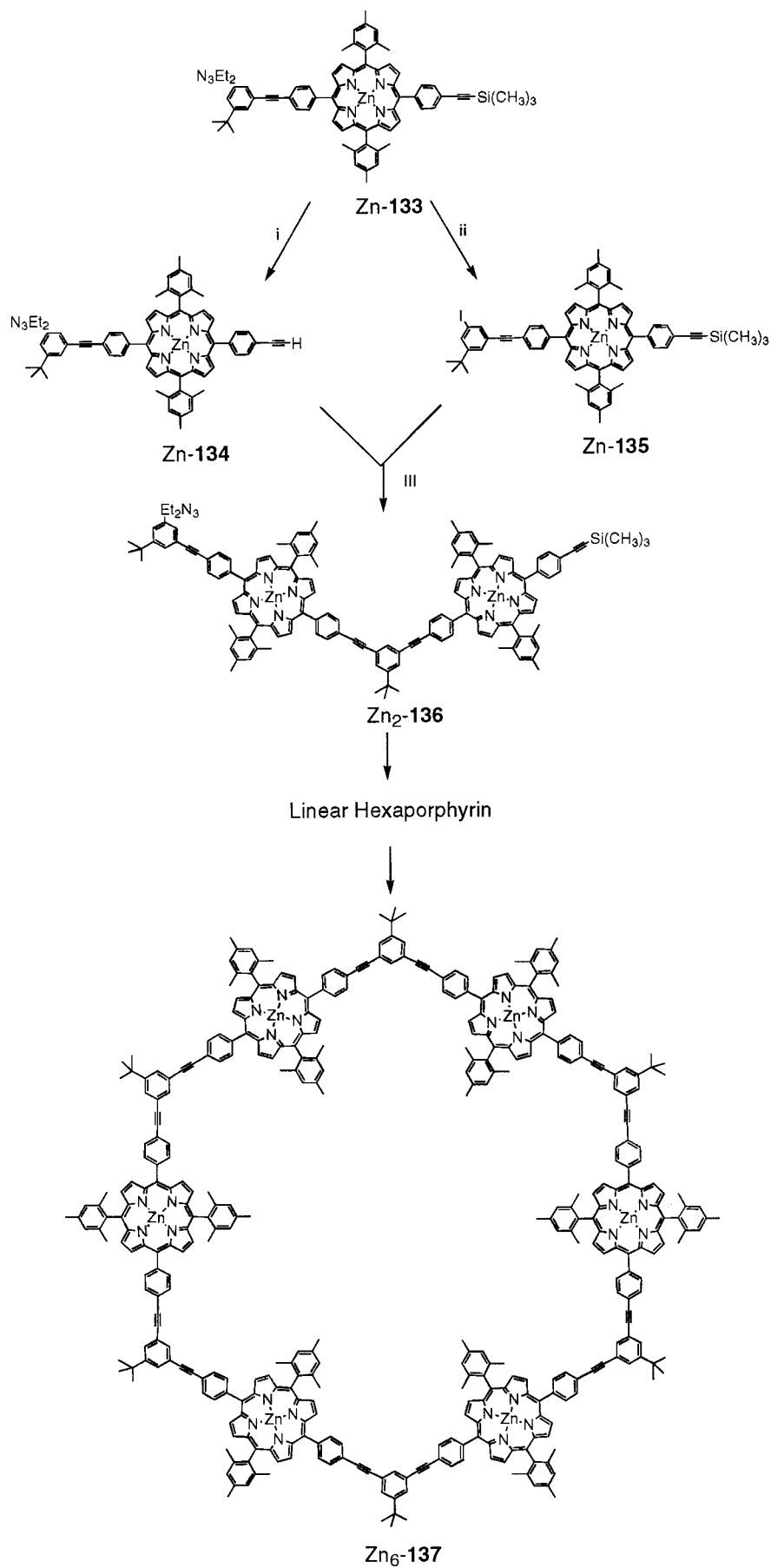
ᵃ (i) 1M NaOH, THF. (ii) CH₃I, 135 °C, 2 h. (iii) Pd(PPh₃)₄ DMF/Et₃N, 40 °C, 14 h.
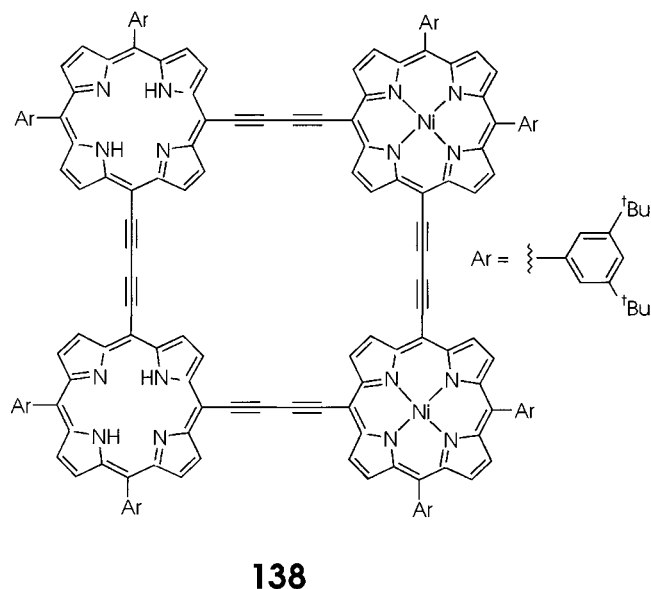
**Figure 2.** Square-shaped porphyrin tetramer of Sugiura et al.[164]

The Texas-based research group of Sessler subsequently exploited this approach to make the first acceptor-substituted porphyrin trimer. Acid-catalyzed

condensation of **141** with dipyrrylmethane **44** afforded triporphyrin **142** (Scheme 45).[169] Unsymmetrical triporphyrins were subsequently obtained by using a mixed-aldehyde condensation of two different porphyrinyl benzaldehydes with **44**.[64] These linear arrays demonstrated rapid energy transfer between porphyrins prior to photon trapping at the redox-active site.[64]

At the same time, Maruyama, Osuka, and co-workers also used Chang's approach to make a multitude of phenylene-bridged porphyrin arrays. They initially constructed a variety of largely linear conformationally constrained triporphyrins and pentaporphyrins with aromatic linkers.[170] Acid-catalyzed condensation of **143** with dipyrrylmethane **35** followed by quinone oxidation gave triporphyrin **144** in 56% yield (Scheme 46). A similar approach was used to make triporphyrins with 1,3-phenyl, biphenyl, diphenylmethyl, and anthracene bridges in place of the 1,4-phenyl linker.

Diporphyrinyl aldehyde **146** (Scheme 46) was prepared by mixed aldehyde condensation of aldehyde **143**, monoprotected dialdehyde **145**, and dipyrrylmethane **35**, followed by oxidation and deprotection (27% yield over three steps). Condensation of **146** and

Scheme 44. Synthesis of Cofacial Triporphyrin 140[a] of Chang and Abdalmuhdi[168]
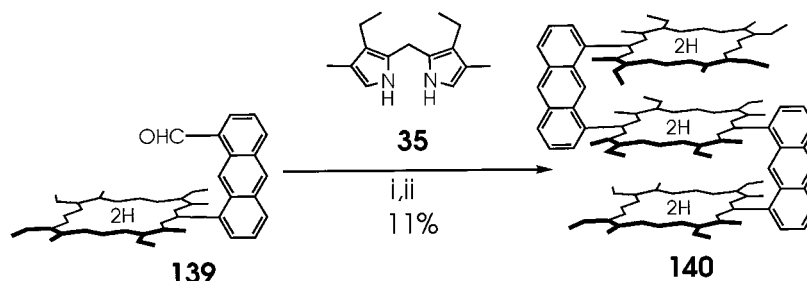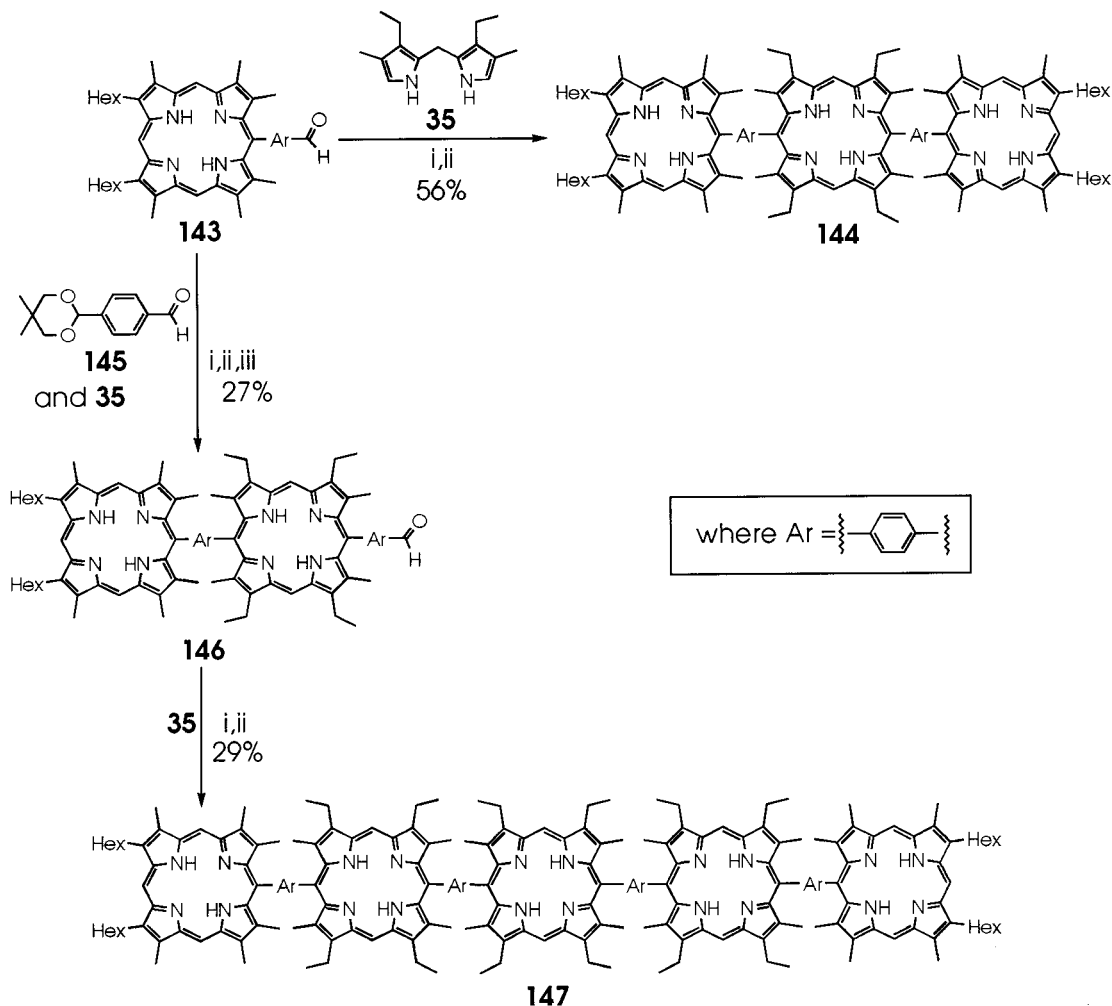

[a] (i) p-TsOH·H₂O, MeOH, 10 h. (ii) o-Chloranil, THF, 1 h.

Scheme 45. Synthesis of Phenyl-Linked Triporphyrin 142[a] of Sessler et al.[169]
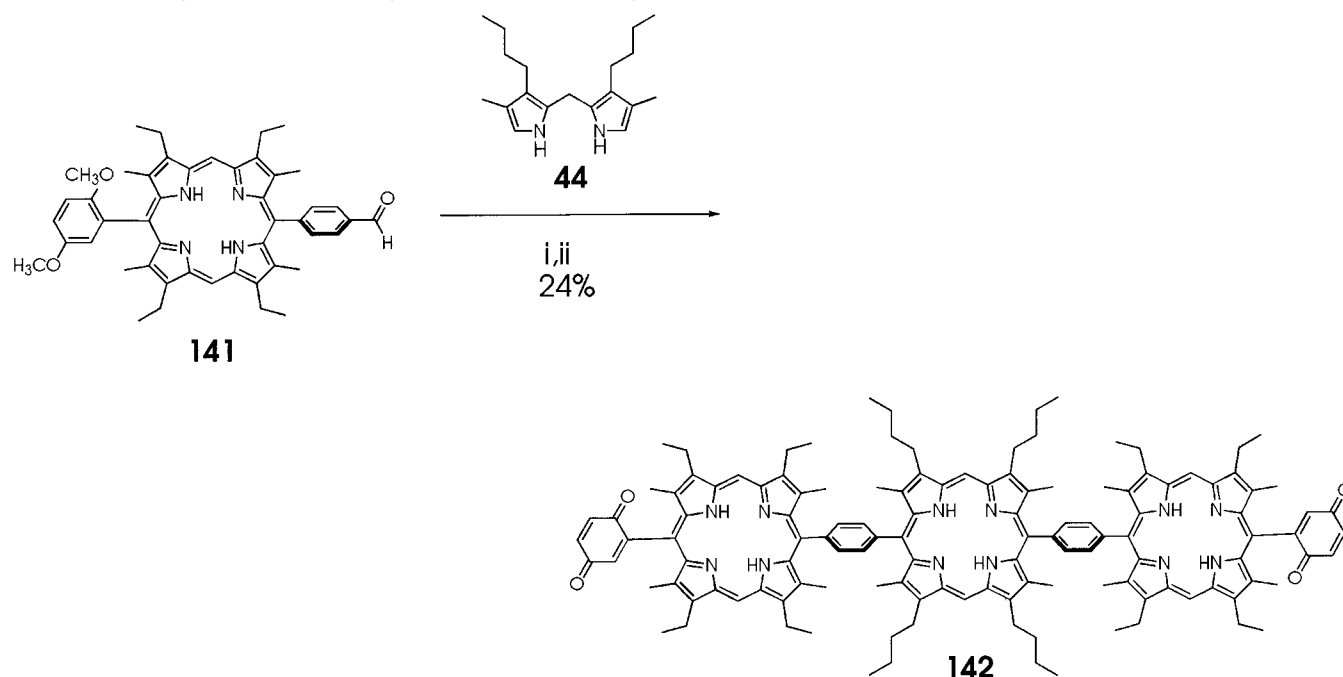
[a] (i) TFA, CH₂Cl₂, argon, 3.5 h. (ii) BI₃, CH₂Cl₂, DDQ.

Scheme 46. Synthesis of Triporphyrin 144 and Pentaporphyrin 147[a] of Nagata et al.[170]

[a] (i) TCA, CH$_3$CN, N$_2$, room temperature. (ii) *p*-Chloranil, THF, room temperature. (iii) TFA, aq H$_2$SO$_4$.
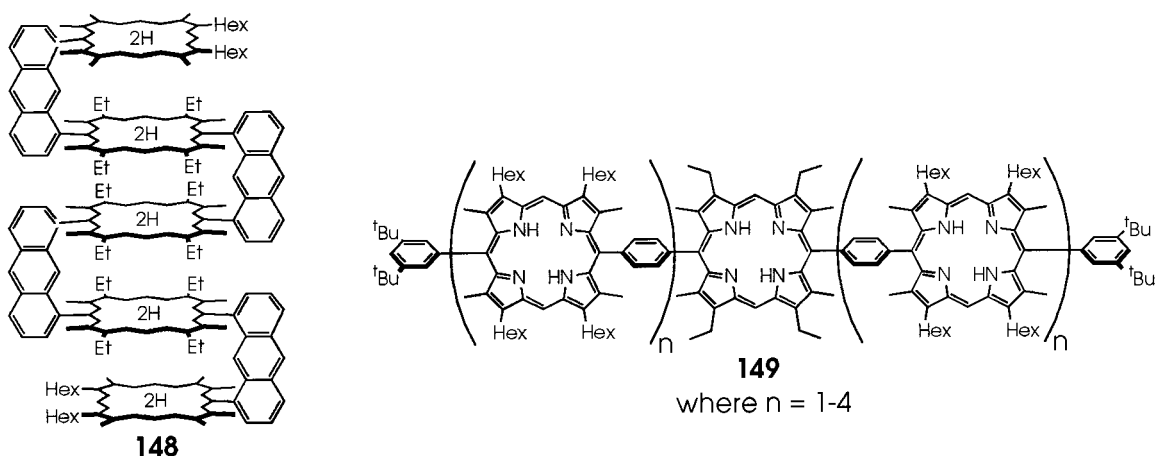

Figure 3. Anthracene-linked pentaporphyrin **148** of Nagata et al.[170] (left) and linear porphyrin arrays **149** of Osuka et al.[63,171] (right).

35 gave pentaporphyrin **147** in 29% yield after oxidation. Anthracene-bridged, stacked pentaporphyrin **148** (Figure 3) was prepared in an analogous manner.

Maruyama and Osuka extended this work, preparing porphyrinyl aldehydes containing up to four porphyrins by using mixed-aldehyde condensations similar to that employed to make diporphyrinyl aldehyde **146**. Condensation of these porphyrinyl

aldehydes with dipyrrylmethane **35** gave linear porphyrin arrays **149** including a nonaporphyrin array, which was at that time the longest porphyrin array reported (Figure 3).[63,171]

This research group also developed strategies for the synthesis of geometrically variable arrays. Thus, they prepared the first *ortho*-phenyl-linked diporphyrin,[172] among many others, and used similar chemistry to construct triporphyrin **152** (Scheme

Scheme 47. Synthesis of Phenyl-Linked Radial Triporphyrin 152[a] of Osuka et al.[173]
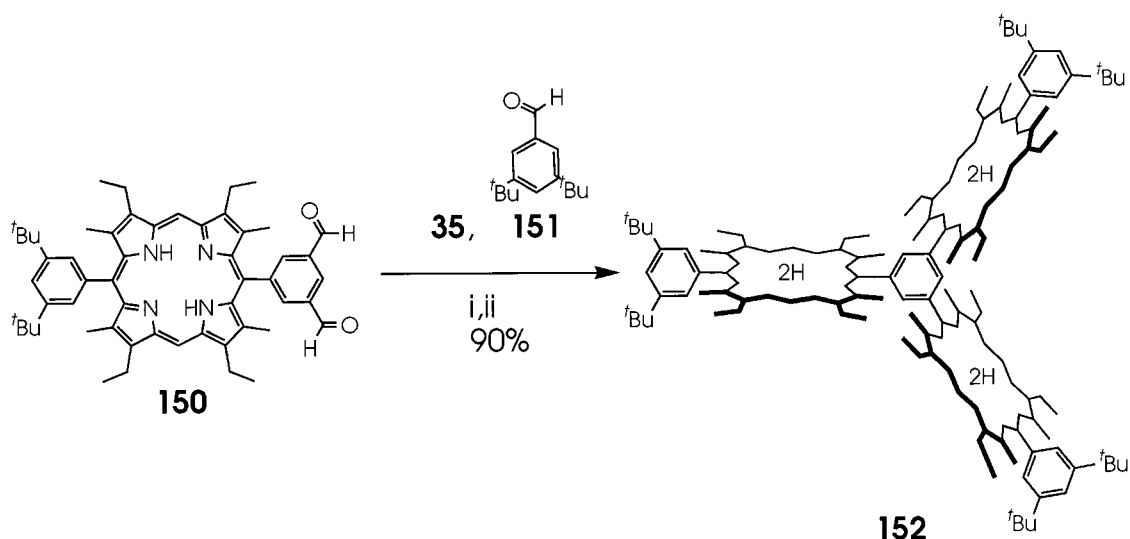

[a] (i) TCA, CH$_3$CN, room temperature, 20 h. (ii) *p*-Chloranil, THF, room temperature, 3 h.

Scheme 48. Synthesis of Tetraporphyrin 156 of Osuka et al.[174]
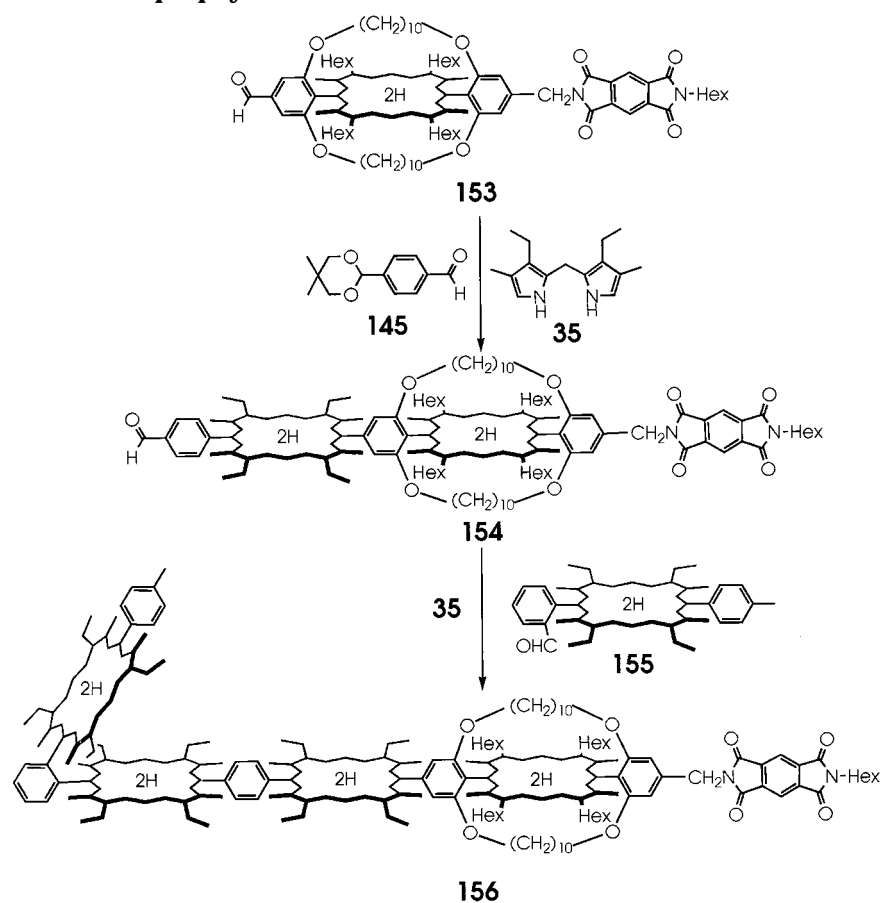
47).[173] The authors noted that the yield for the second phase of condensation reactions was very high (90% based on **150**) and that the analogous reaction to form a *meta*-substituted phenyl-linked diporphyrin also gave a relatively high yield (60%). The increased yields were attributed to enhanced solubility resulting from the 3,5-di-*tert*-butylphenyl substituents at the *meso* positions; the use of tolualdehyde in place of 3,5-di-*tert*-butylbenzaldehyde in the diporphyrin synthesis, resulted in a halving of the yields.

The Osuka group then employed these strategies to construct complex oligoporphyrin molecules with well-defined geometries for the study of electron and energy transfers in multicomponent systems. These molecules were built in a stepwise manner using cycles of mixed aldehyde condensations and protection/deprotection. For example, the important synthetic steps in the preparation of tetraporphyrin **156**[58] are shown (Scheme 48).[174] An acid-catalyzed mixed-aldehyde condensation of **153** with dipyrryl-

Scheme 49. Synthesis of Phenyl-Linked Triporphyrin 159[a] of Hammel et al.[175]
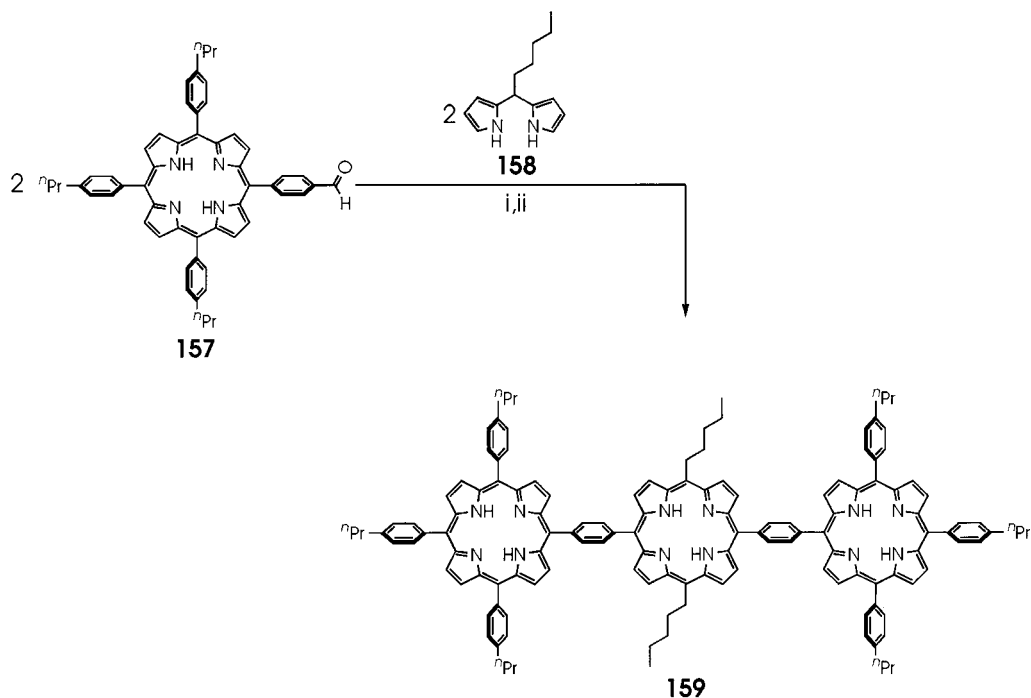
[a] (i) Cl$_2$CHCOOH, CH$_2$Cl$_2$, room temperature, 12 h. (ii) Oxidation.

Scheme 50. Synthesis of Diporphyrin 161 and Pentaporphyrin 162[a] of Wennerstrom et al.[176]
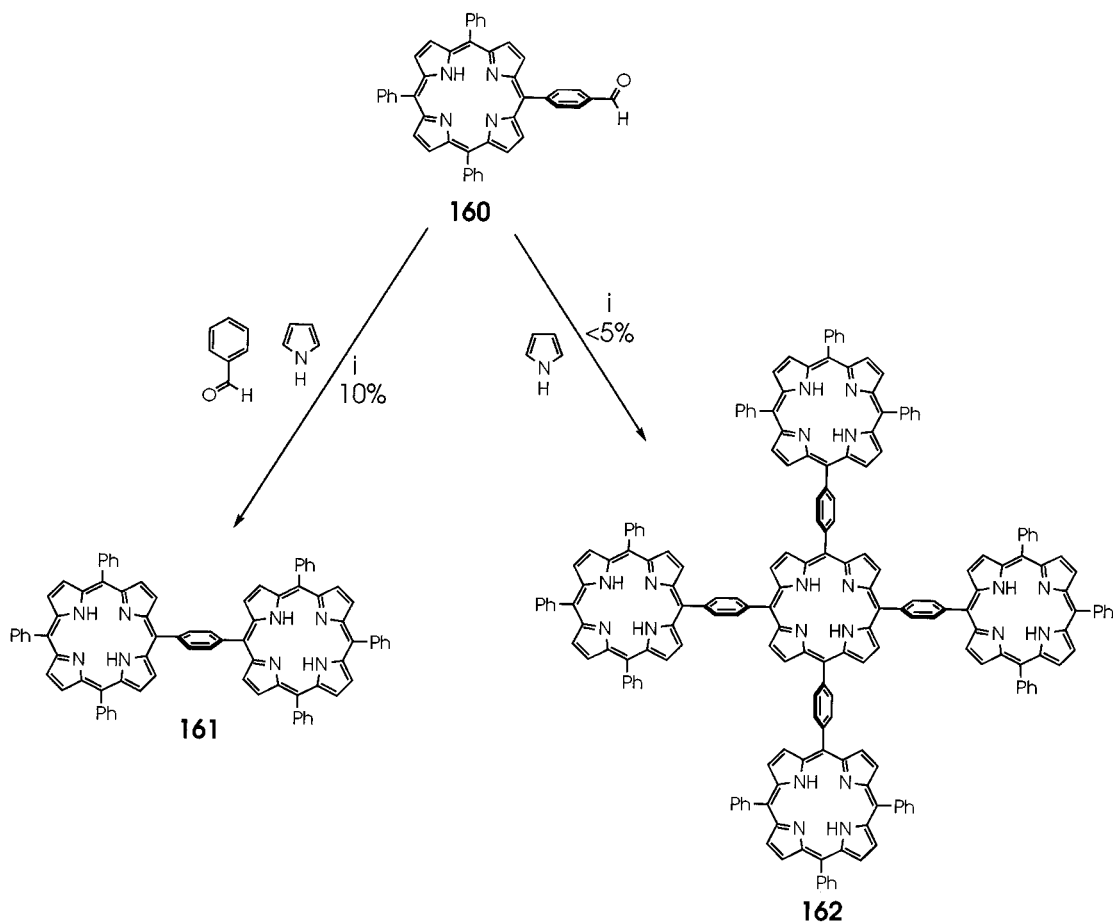
[a] (i) CH$_3$CH$_2$CO$_2$H, reflux.

methane **35** and monoprotected dialdehyde **145** followed by oxidation and deprotection gave diporphyrinyl aldehyde **154** in 60% yield. Another mixed-aldehyde condensation of **154**, dipyrrylmethane **35**, and aldehyde **155** gave tetraporphyrin **156** in 16% yield. Treatment of **156** with zinc acetate gave Zn$_3$-
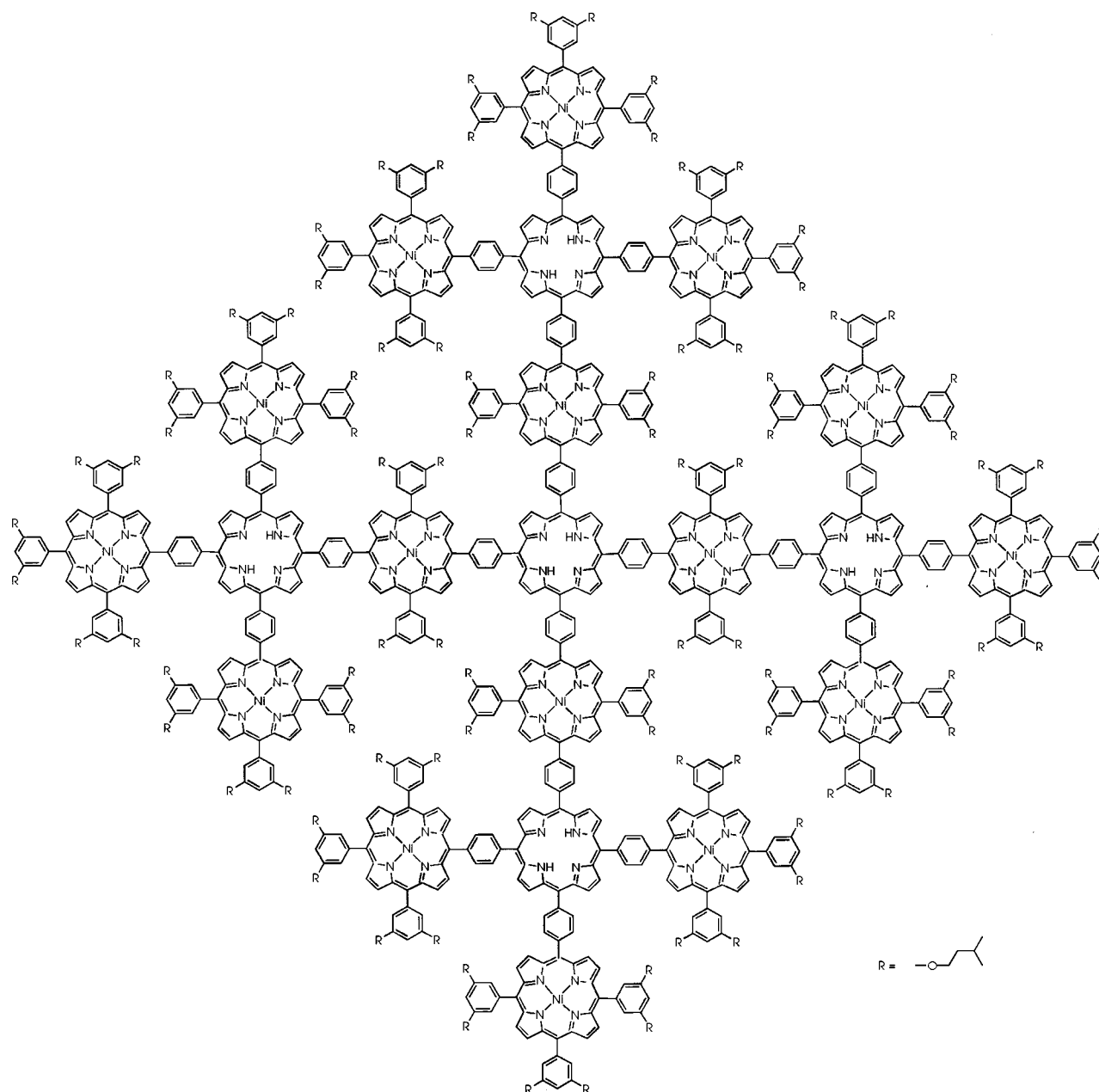
163

**Figure 4.** Porphyrin 21-amer of Sugiura et al.[177]

156, the alkane straps on the porphyrin adjacent to the pyromellitimide preventing metalation at this site. Photophysical studies on Zn$_3$-**156** revealed that stepwise photoinduced charge separation occurred to give a long-lived charge-separated state with a lifetime of 16 μs.[174]

Hammel and co-workers used the readily prepared methylene-substituted dipyrrylmethanes to construct two phenyl-linked linear triporphyrins, only one of which was isolable (Scheme 49).[175] Acid-catalyzed condensation of aldehyde **157** (prepared through a mixed aldehyde condensation) and dipyrrylmethane **158** gave triporphyrin **159** (no oxidation or yield details were given). Treatment with zinc acetate under standard conditions gave the metalated derivative Zn$_3$-**159**, whose redox behavior and charge storage capabilities were investigated.[175]

An Adler condensation was employed to make the first large arene-linked porphyrin array, albeit in low yield. Wennerstrom et al. used a porphyrin aldehyde **160** to make diporphyrin **161**, using a mixed condensation, and radial pentaporphyrin **162** (Scheme 50).[176] Condensation of **160** with excess pyrrole and benzaldehyde in refluxing propanoic acid gave **161** in 10% yield. The pentaporphyrin **162** was obtained in, at best, 5% yield from the condensation of **160** with pyrrole (1 equiv) under the same conditions. The low solubility of **162** made purification very difficult. Ring current effects observed in the NMR spectra of **161** and **162** indicated that the porphyrins were approximately coplanar. The Soret bands of the two arrays were split, which was indicative of electronic interaction between the porphyrin components.

Scheme 51. Synthesis of Diporphyrin 166, Triporphyrins 169 and 171, and Tetraporphyrin 173[a] of Crossley et al.[20,179,180]

Scheme 52. Synthesis of Pentaporphyrins 175 and 176[a] of Vicente et al.[184]

174 i **175** ii **176**
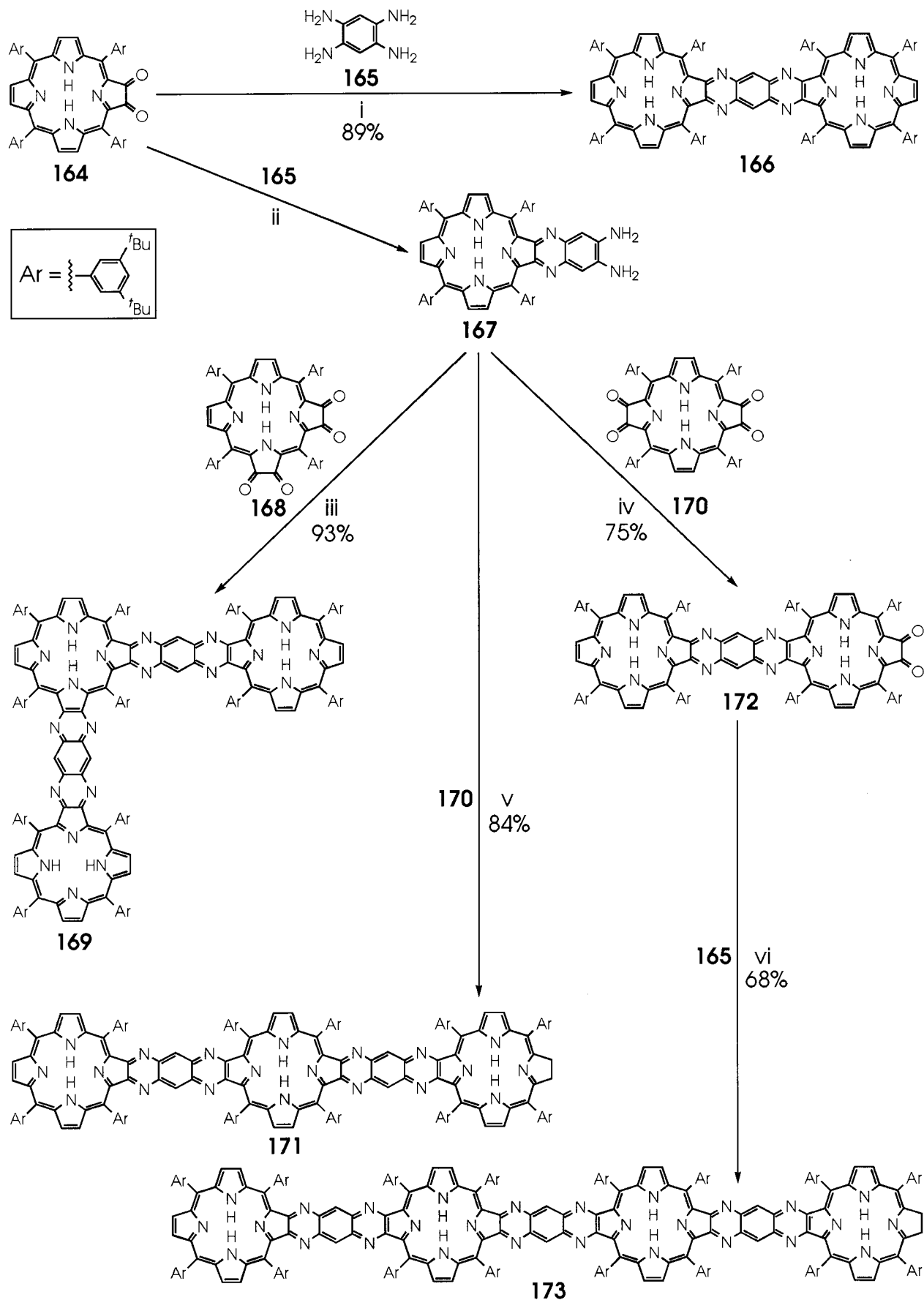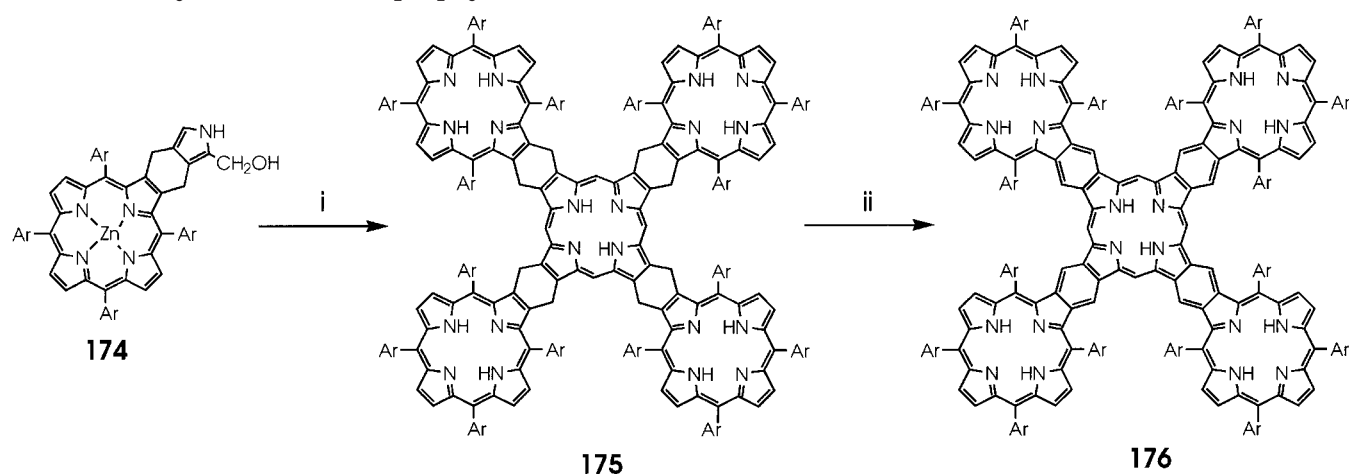
[a] (i,ii) Conditions not published.
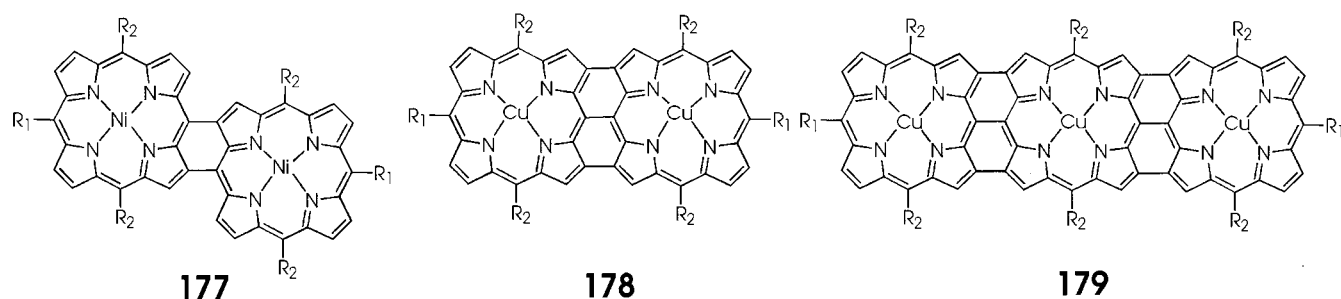

177 **178** **179**

Figure 5. Fused di- and triporphyrins of Osuka et al.[187,188]

Sakata and co-workers synthesized the aryl-linked henicosamer porphyrin array **163** which they termed "a mandala-patterened bandanna" (Figure 4).[177] The final coupling step utilized Lindsey's hindered porphyrin synthesis conditions[178] to give the product in an overall yield of 0.15% over 17 steps.[177] While this is a remarkable achievement, the synthetic route involved two statistical condensation reactions, which are the major contributors to the poor yield.

6. Fused Aromatic

In 1991 Crossley and Burn prepared the first benzo-fused large porphyrin array[20] following on from their earlier dimer synthesis.[179] This methodology has now led to a variety of porphyrin arrays containing up to four porphyrins (Scheme 51). These arrays are rigid and the porphyrins coplanar by virtue of tetraazaanthracene bridges between pairs of β-pyrrolic carbons. These linkages were created by coupling porphyrinyl diones or tetraones to diamines or tetraamines. Condensation of tetraamine **165** with excess dione **164** gave diporphyrin **166** in 89% yield.[179] Alternatively, control of the reaction conditions using 1 equiv of **164** gave diaminoporphyrin **167**.[180] Coupling of excess **167** with *cis*- and *trans*-porphyrinyl tetraones **168** and **170** (which were prepared in an analogous manner to **164**) gave bent triporphyrin **169** (93% yield) and linear triporphyrin **171** (84%), respectively. Diporphyrin dione **172** could be prepared in an analogous fashion in 75% yield. Condensation of excess **172** with tetraamine **165** gave tetraporphyrin **173** (68%). Tetraporphyrin **173** was

originally prepared by forming the antipodal tetraone of diporphyrin **166** and coupling it to **165** and **164**.[20]

The bridges are conjugated to the porphyrin macrocycles, affording a large delocalized π system that could conduct electrons, and thus, these linear arrays have been proposed as molecular wires. Solubility of the arrays is maintained by the *tert*-butyl aryl substituents, which also provide a layer of "insulation" for the wires. This overall synthetic approach has been used by Crossley to prepare a variety of other molecules.[181–183]

An alternative approach to fused arrays has been developed by Vicente et al., who prepared rigid pentamer **176** via the oxidation of pentaporphyrin **175** in quantitative yield (Scheme 52).[184] Pentaporphyrin **175** was formed from the cyclizing of alcohol **174** and subsequent oxidation.

The synthesis and crystal structure of a pyrrole-fused trimer has also been reported by Smith and co-workers.[185,186]

In an extension to their directly linked *meso*–*meso* arrays, Osuka and co-workers formed the doubly *meso*–β-linked diporphyrin **177** (Figure 5)[187] and the fully fused $(\beta$-$\beta)_2$–(*meso*–*meso*)-linked dimer and trimer arrays **178** and **179** (Figure 5).[188] In a simple yet elegant procedure, the triporphyrin **179** was formed in 33% yield via a one-pot oxidation (over 3 days) of the corresponding tricopper directly linked *meso*–*meso* triporphyrin array.

Using a TeCl$_4$ *meso*-substituted nickellated monoporphyrin as their starting material, Sugiura et al.

Scheme 53. Synthesis of the Pentamer 182 and Nonamer 187[a] of the Lindsey Group[190,191]
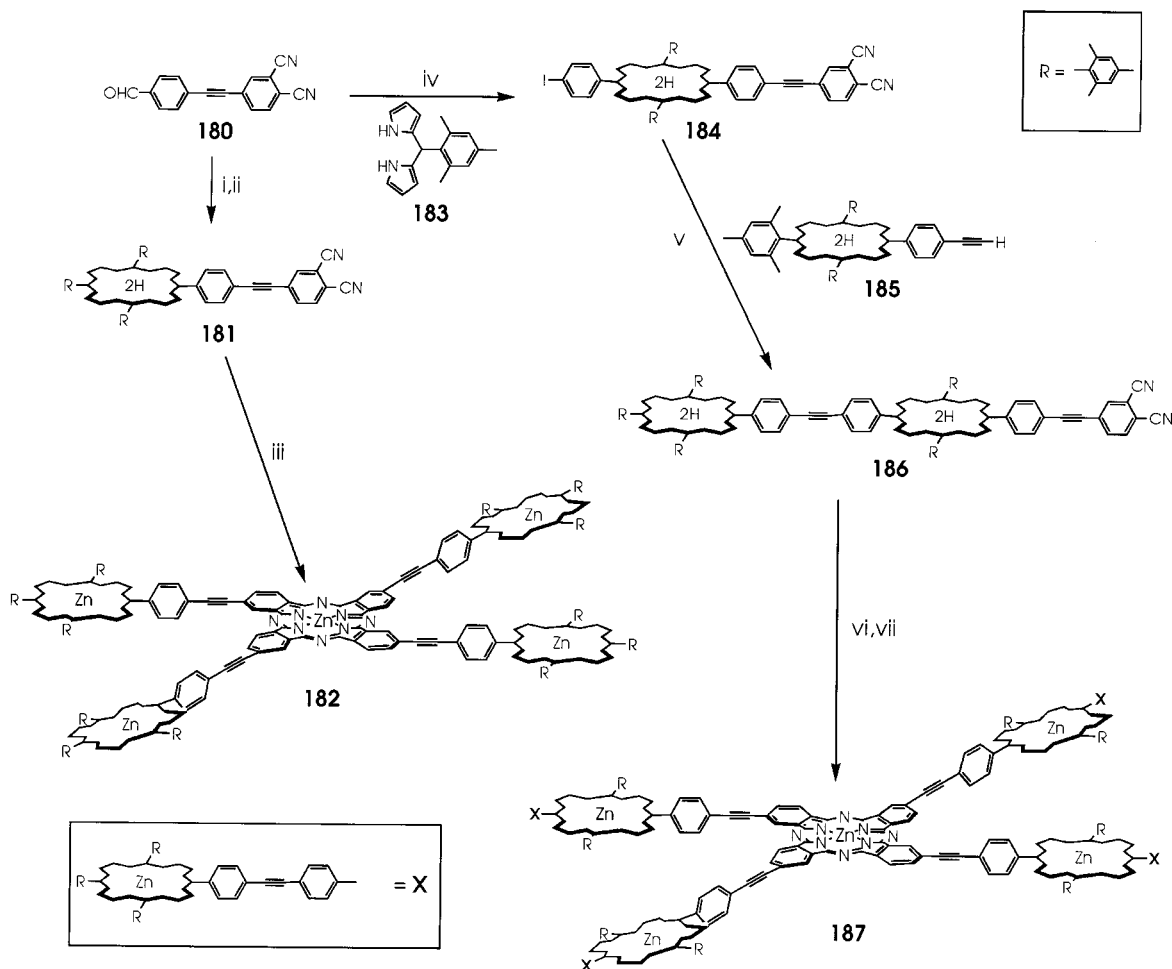
[a]Both **182** and **187** are composed of a mixture of regioisomers. (i) mesitaldehyde, pyrrole, $BF_3 \cdot O(Et)_2$, $CHCl_3$, room temperature, 1 h. (ii) DDQ, room temperature, 1h. (iii) $Zn(OAc)_2$, DBU, 1-Pentanol, reflux, 36 h. (iv) 4-iodobenzaldehyde, CH_2Cl_2, TFA, DDQ. (v) $Pd_2(dba)_3$, tri-o-tolylphosphine, toluene/TEA 5:1, 35 °C, 3.5 h. (vi) $LiO(CH_2)_4CH_3$, 145 °C, 2 h. (vii) $Zn(OAc)_2 \cdot 2H_2O$, 80 °C, 2h.

also prepared **177** as well as further $TeCl_4$ dimer derivatives.[189]

7. Other Aromatic Linkers

There are very few examples of porphyrin arrays constructed around other aromatic moieties such as phthalocyanines. The Lindsey group prepared pentaporphyrins and nonaporphyrins in which a phthalonitrile cyclotetramerization strategy has been employed in the final step (Scheme 53).[190,191] Mixed condensation of **180** with mesitaldehyde and pyrrole gave porphyrinyl phthalonitrile **181**, which was subsequently cyclized under Shiraishi conditions to form the phthalocyanine-centered pentaporphyrin **182** in 15% yield.[190] In a subsequent paper, the Lindsey group found that by utilizing lithium pentoxide for the phthalocyanine formation, the yield of **182** could be increased to 58%.[191] The phthalocyanine-centered nonaporphyrin **187** was prepared in a similar fashion. Condensation of **180** with the mesitylene substituted dipyrrylmethane **183** and 4-iodobenzaldehyde gave the *trans*-substituted porphyrin **184**. Palladium-mediated coupling of alkyne **185** to **184** gave alkyne-linked diporphyrin **186** in 51% yield. Lithium pentoxide coupling and subsequent zinc metalation gave nonaporphyrin **187** in 28% yield.

C. Miscellaneous Linkers

1. Metal–Metal Bonding

A number of diporphyrins have been made in which two metalloporphyrins are held in a very close, cofacial orientation by metal-to-metal bonding.[192] The bond orders may be one (e.g., rhodium, iridium), two (ruthenium, osmium), three (rhenium), or four (molybdenum, tungsten). These diporphyrins are of interest as tools in the study of the nature of discrete metal-to-metal bonds.

The only reported example of a larger array containing a number of metal-to-metal bonds is that of Collman's anthracene-linked tetraporphyrin containing two sets of Ru−Ru bonds.[193]

2. Metal–Ligand Coordination

Metal−ligand coordination of porphyrins and porphyrin arrays and related supramolecular chemistry has become a fast-growing and vibrant area of interest in recent years. However, the following section takes only a brief look at this type of linker. For a more comprehensive examination of the use of coordination chemistry in the construction of porphyrin arrays, readers are referred to the excellent reviews by Sanders[32] and Aida.[194]
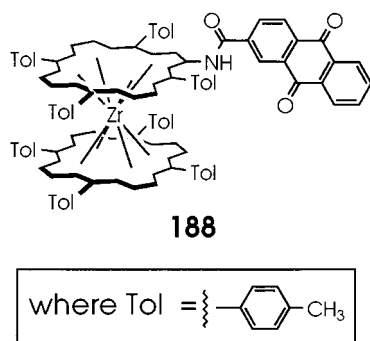
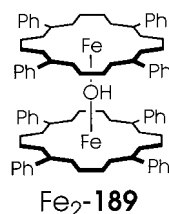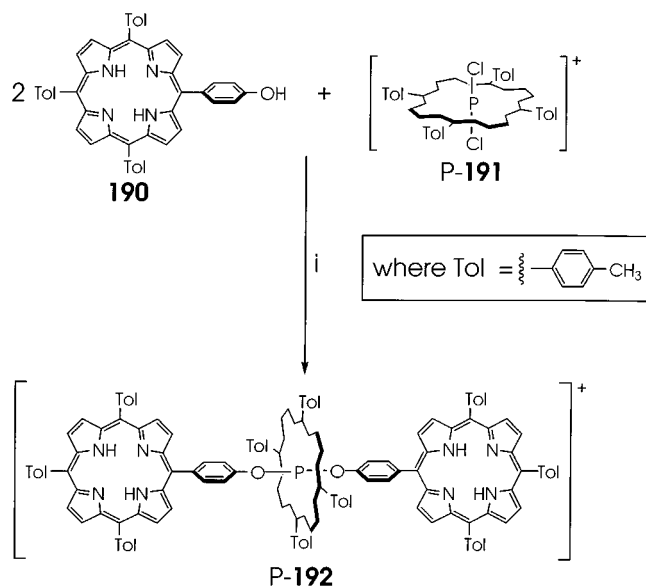**Figure 6.** Zirconium double-decker diporphyrin **188** of Girolami et al.[195]

Figure 7. μ-Oxo diporphyrin Fe$_2$-**189**[198]

Scheme 54. Synthesis of Triporphyrin P-192^a of Rao and Maiya[200]

^{a} (i) C$_5$H$_5$N, reflux, 5 h.

Perhaps the simplest metal−ligand porphyrin array constructions are the "sandwich" or "double-decker" compounds where the eight nitrogens of two porphyrin dianions sandwich metal ions such as zirconium, tantalum, or some lanthanide metals. An example of this type of compound is the zirconium double-decker diporphyrin **188** of Girolami et al.[195] (Figure 6). "Triple-deckers" that sandwich two metal ions between three porphyrin dianions, as well as sandwich compounds that contain two or three different porphyrins or phthalocyanines, have also been made.[196] The close proximity of the porphyrin rings in the sandwiches has seen these types of arrays explored as potential models for the special pair.

Metal−oxygen axial coordination has been used to build porphyrin arrays. Simple examples are the
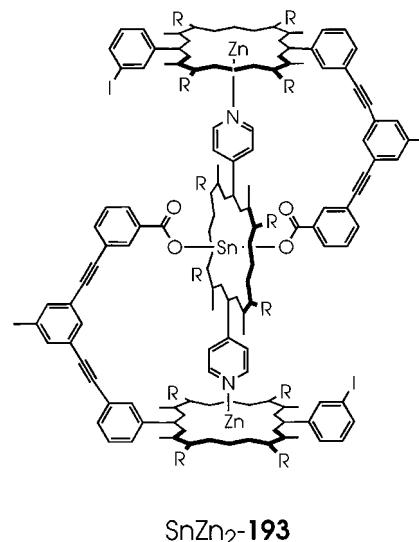
SnZn$_2$-**193**

Figure 8. Triporphyrin SnZn$_2$-**193** of Kim, Bampos, and Sanders.[202]
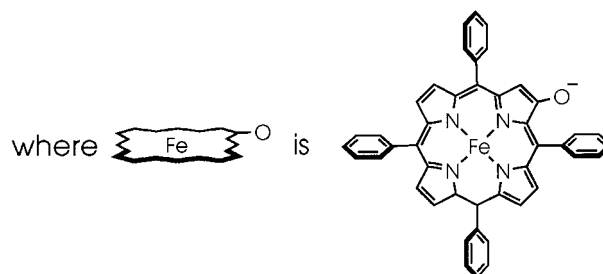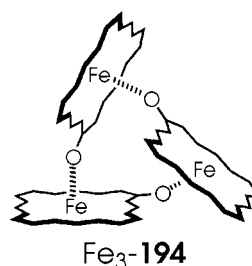
Fe$_3$-**194**

Figure 9. Cyclic triporphyrin Fe$_3$-**194** of Wojaczynski and Latos-Grazynski.[203]

μ-oxo diporphyrins in which the metal centers of two metalloporphyrins are axially bound to a common oxygen atom.[197] The metals are typically transition metals such as iron, e.g., Fe$_2$-**189**[198] (Figure 7), ruthenium, or manganese. These complexes are of interest because of their relevance to biological systems.

Porphyrin assemblies have been made in which axial phosphorus−oxygen bonds connect the components of the array.[199−201] The initial one-pot approach by Shimidzu and his research group afforded mixtures of ethylene glycol-linked phosphorus(V) porphyrin arrays of up to four porphyrins.[199] The first controlled synthesis gave the triporphyrin P-**192** in ~50% yield (Scheme 54) by refluxing phosphorus porphyrin P-**191** with hydroxyphenylporphyrin **190** in pyridine.[200] A similar series of center-to-edge phosphorus(V) triporphyrins have been synthesized and their photophysical properties studied.[201]

Another approach to coordinated center-to-edge triporphyrins has been reported by Sanders et al.,

Figure 10. Pentaporphyrin Os₄-**195** of Kariya et al.[207]

which elegantly demonstrates how porphyrin arrays can be constructed using selective metal−ligand binding and preorganized geometries.[202] For example, the triporphyrin SnZn₂-**193** was prepared quantitatively using stoichiometric amounts of the two metalated porphyrins (Figure 8).

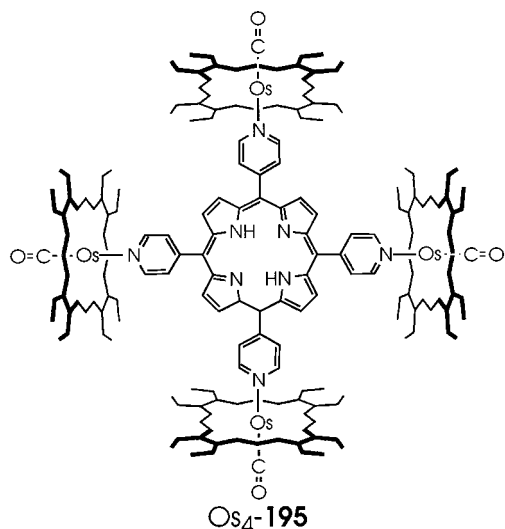A number of cyclic oligoporphyrins have been made in which an oxygen-containing *meso-* or *β*-pyrrolic substituent of a metalloporphyrin axially binds to a neighboring metalloporphyrin. An example of this is triporphyrin Fe₃-**194** of Wojaczynski and Latos-Grazynski in which a *β*-pyrrolic alkoxide substituent of an iron porphyrin binds to the iron of an adjacent metalloporphyrin (Figure 9).[203] Manganese and gallium derivatives have also been synthesized.[204−206]

Metal−nitrogen axial coordination has been used more extensively to construct synthetic porphyrin arrays. Oligoporphyrins containing up to five porphyrins in a number of geometries have been assembled by coordinating suitable metalloporphyrins to TAPs bearing one, two, three, or four *meso*-pyridyl substituents. This approach was employed by Kariya et al. to make a family of porphyrin arrays, including pentaporphyrin Os₄-**195**, that contain OsOEP(C=O) entities coordinated to a central TPyP (Figure 10).[207] Arrays with similar coordination architectures were prepared by Alessio et al.,[208,209] Kumar and Goldberg,[210] Kuan-Jiuh Lin,[211] Fleischer and Shachter,[212] Wilson and Anderson,[213] Funatsu et al.,[214] and Chernook et al.[215]

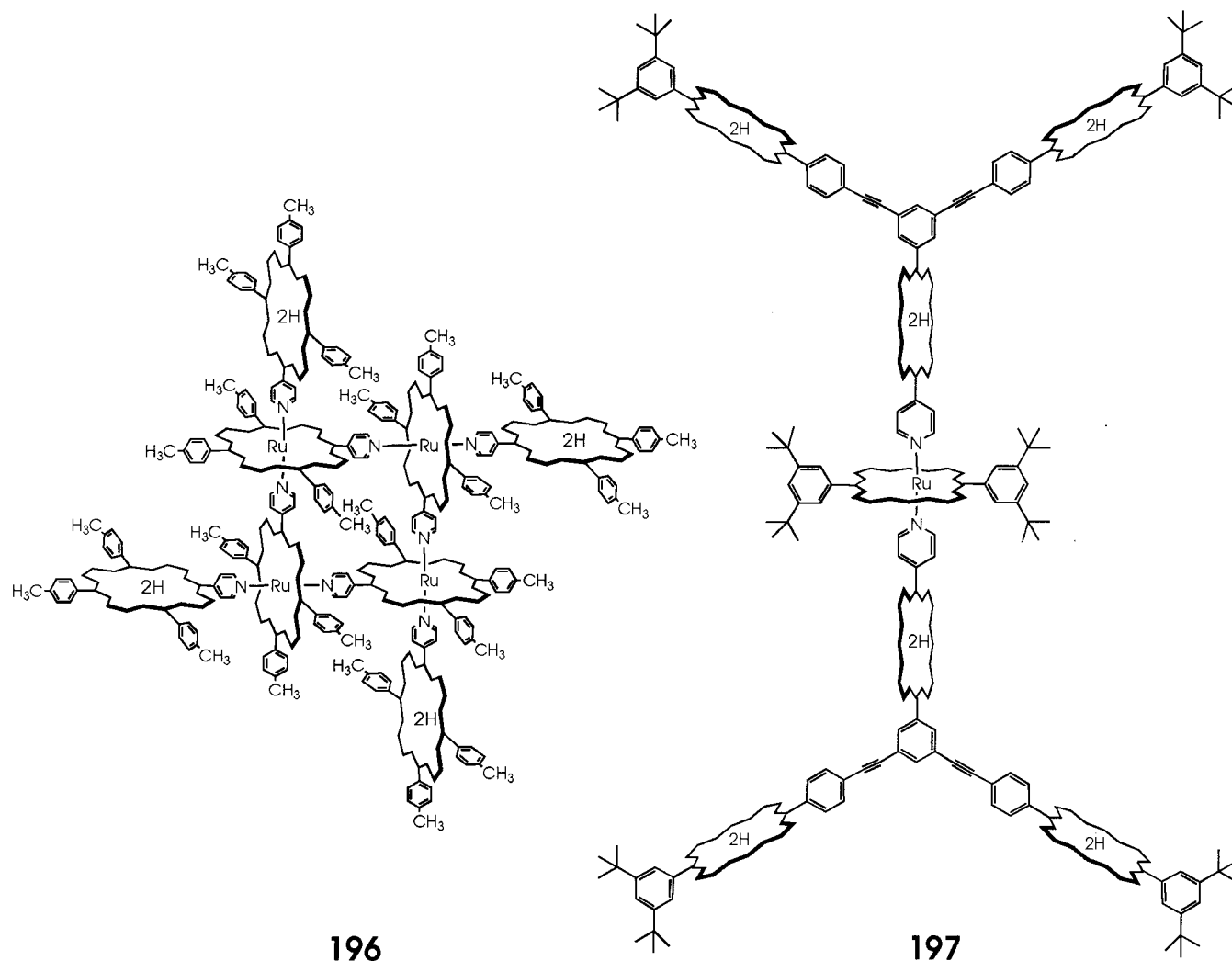There has been intense interest in ruthenium−pyridyl coordination to form large porphyrin arrays

Figure 11. (a) Octaporphyrin **196** of Okumura et al.[216] (b) Heptaporphyrin **197** of the Sanders group.[217]
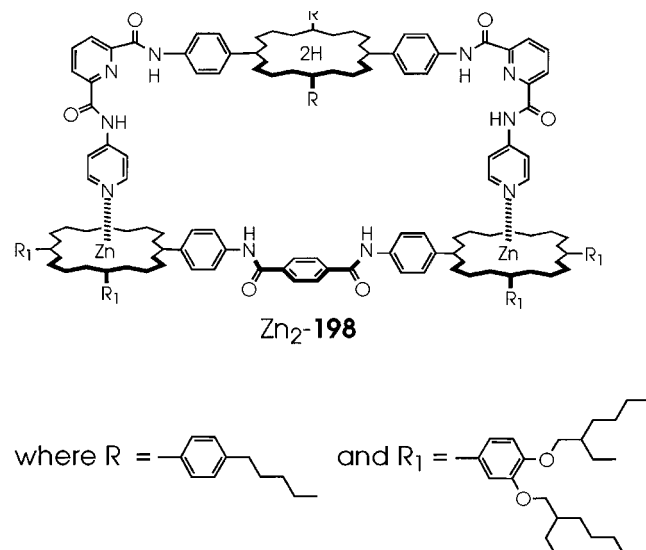
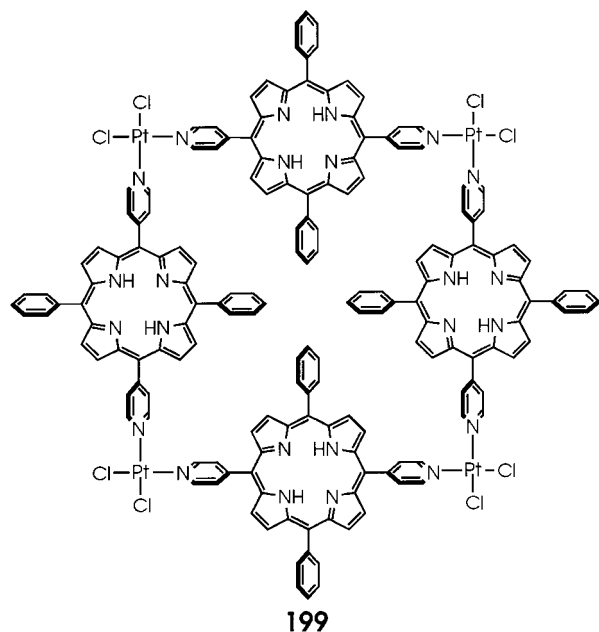**Figure 12.** Triporphyrin Zn$_2$-**198** of Hunter et al.[222]

Figure 13. Tetraporphyrin **199** of Drain and Lehn.[223]

in recent years, since the essentially irreversible bond formed with this type of coordination linker allows for a myriad of array geometries. Two representative examples are those of Okumura et al. (Figure 11a)[216] and the Sanders group (Figure 11b).[217]

More sophisticated arrays have been accessed by synthesizing porphyrins with elaborate pyridine substituents. As part of their studies of photoactive supramolecular assemblies, Hunter et al. constructed self-assembling cyclic diporphyrins,[218] triporphyrins and tetraporphyrins,[219] and higher[220,221] as well as elegant triporphyrin Zn$_2$-**198** (Figure 12).[222]

The coordinated metal does not have to be part of a metalloporphyrin. In their general studies of molecular electronic devices, the Drain group prepared self-assembling cyclic di-, tetra-, and nonaporphyrin arrays, such as tetraporphyrin **199**, by coordination of four dipyridylporphyrins to four platinum or palladium centers (Figure 13).[223,224] Similar cyclic assemblies were made by Stang et al.,[225,226] while Slone

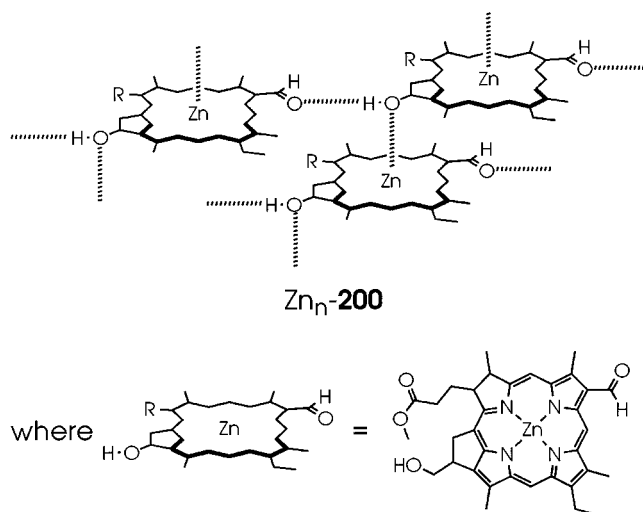**Figure 14.** Diagram of a segment of the aggregate Zn$_n$-**200** of Jesorka et al. showing the hydrogen and coordination bonding.[235]

et al. employed rhenium bridges in their tetraporphyrins and pentaporphyrins.[227] Huck et al. formed arrays containing up to 12 porphyrins through a succession of palladium–nitrile and palladium–pyridine coordination.[228] Yuan et al. constructed bent diporphyrins and radial tetraporphyrins from mono-pyridylporphyrins and platinum and palladium centers.[229] Abrahams et al. crystallized copper and palladium TPyP with copper(I) and cadmium metal centers, respectively, thus obtaining solid state, infinite polymeric arrays of porphyrins.[230,231] Sharma et al. crystallized network arrays containing both free base and metalloporphyrins using TPyP with various metals.[232]

3. Hydrogen Bonding

Chlorosomes in green bacteria contain aggregates of magnesium bacteriochlorophylls that serve as light-harvesting systems.[233] These aggregates do not have an associated protein scaffold and are held together by various noncovalent interactions. These natural systems have been modeled by Tamiaki et al., who prepared aggregates of 50–100 zinc chlorins, such as Zn$_n$-**200** (Figure 14).[234,235] These types of aggregates self-assemble and are held together by coordination and hydrogen bonding between hydroxy substituents, carbonyl substituents, and chelated zinc ions of neighboring chlorins.[235] The researchers incorporated a covalent dichlorin that contained a zinc chlorin and a free base chlorin into an aggregate at a ratio of 1:50 dichlorin:monomer.[234] Absorption of light by the aggregate resulted in the observation of rapid singlet energy transfer from the aggregate to the free base component of the dichlorin.

As part of their research into photoinduced energy transfers, Sessler's group prepared triporphyrin Zn$_2$-**201** (Figure 15).[236] Porphyrins with covalently attached, complementary nucleic acid base-pair substituents were synthesized and allowed to assemble in solution. Multiple hydrogen bonds held the triporphyrin in a rigid conformation.

Replacement of a single TAP aryl group by a single imidazole substituent has led to the formation of a
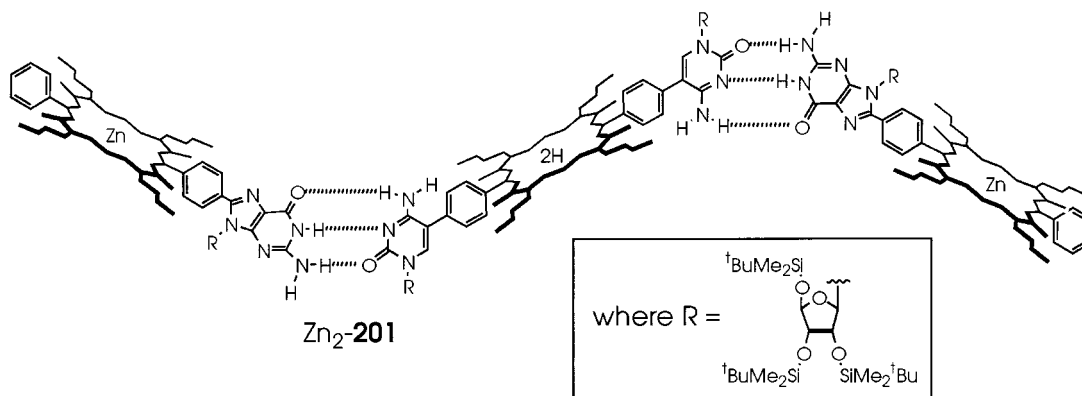
Figure 15. Triporphyrin Zn$_2$-**201** of Sessler et al.[236]
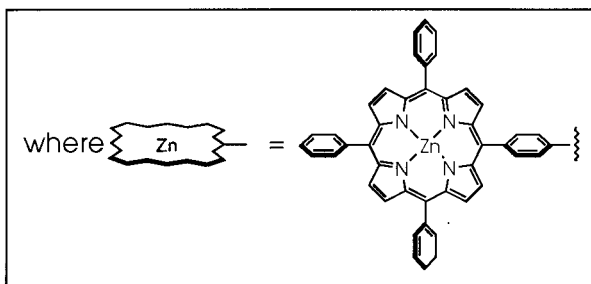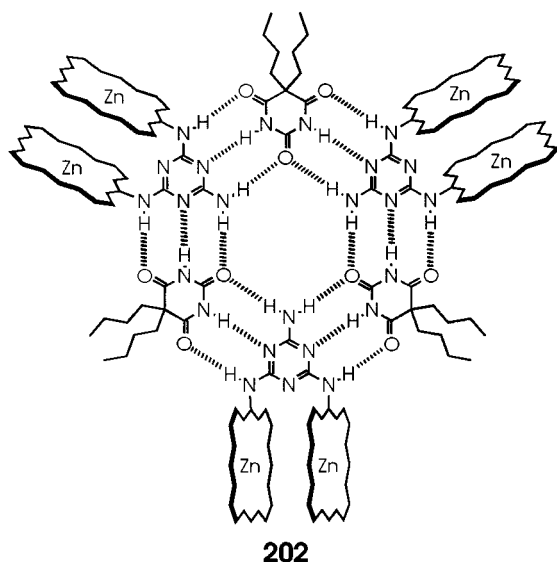

202

Figure 16. Hydrogen-bonded hexaporphyrin **202** of Drain et al.[238]

dimer and tetramer via imidazole dimerization or tetramerization.[237]

In a remarkable example of multicomponent self-assembly, Drain et al. formed supramolecular hexameric porphyrin array **202** through multiple hydrogen bonding of three triaminotriazine units bearing two appended TPPs, each with three complimentary dialkylbarbituric acids (Figure 16).[238]

V. Conclusion

In the 25 years of literature covered by this review, it is clear that the most progress in large array formation has occurred in the last five years. Up until 1996, the largest arrays reported contained nine porphyrins and only two examples were known. Since that time (five years), the porphyrin array size has gone from 9 to a remarkable 128 porphyrins with numerous examples of varying sizes in between. This can be directly attributed to the development of synthetic methodology for porphyrin chemistry.

Currently, the dominant methodology for porphyrin array synthesis is metal-mediated coupling of alkyne-substituted porphyrins. Unfortunately this methodology is often hindered by difficulties in purification, but this is balanced by its utility in other areas, such as controlling spatial geometry.

The oxidative coupling method of metalated porphyrins of the Osuka group provides the most exciting potential for dramatically increasing the size of porphyrin arrays with a very simple procedure.[95] Moreover, their arrays can be easily converted to materials with potential utility in molecular electronics.[188] There is still a need however to continue to develop other array coupling methodologies such that a wider variety of linkages can be introduced into larger arrays with increased control. In particular, if porphyrin arrays are to be anything more that a curiosity, procedures that require the formation of statistical mixtures need to be avoided. For example, the impressive 21-porphyrin assembly of Sakata requires a significant effort to prepare but with an overall yield of <1% is unlikely to be of practical use.[177]

One of the major challenges that await research groups in this area is the development of applications for these unique materials. While many potential applications are on the horizon, there are several issues that need to be addressed before any commercial development of porphyrin assemblies can be considered. The most relevant to this review is the efficiency of any desired synthesis. As with everything, new developments are likely to replace the current most common synthetic procedures. In particular, the continued progress in the self-assembly of porphyrin arrays looks like it is set to have a significant influence over the next few years.

Ultimately, it is the vision and daring of porphyrin researchers that have created and so dramatically advanced this stimulating area. Thanks to the work described in this review, we are now in a revolution in the preparation of porphyrin arrays. There are sufficient different synthetic methodologies now known that developments of materials that have commercial

application seem inevitable, and we hope this review will encourage even more exciting future endeavors.

VI. References

(1) Tetrapyrroles refer to molecules containing the fully conjugated porphin nucleus (porphyrins) as well as reduced derivatives such as chlorins and bacteriochlorins, phlorins, and porphyrinogens.
(2) Zheng, J.-Y.; Konishi, K.; Aida, T. *Tetrahedron* **1997**, *53*, 9115.
(3) Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537.
(4) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198.
(5) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.
(6) Gust, D. *Nature* **1997**, *386*, 21.
(7) Rabanal, F.; Gibney, B. R.; DeGrado, W. F.; Moser, C. C.; Dutton, P. L. *Inorg. Chim. Acta* **1996**, *243*, 213.
(8) Arai, T.; Takei, K.; Nishino, N.; Fujimoto, T. *J. Chem. Soc., Chem. Commun.* **1996**, 2133.
(9) Arai, T.; Kobata, K.; Mihara, H.; Fujimoto, T.; Nishino, N. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1989.
(10) Geier, G. R., III; Sasaki, T. *Tetrahedron Lett.* **1997**, *38*, 3821.
(11) Konishi, K.; Kimata, S.; Yoshida, K.; Tanaka, M.; Aida, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2823.
(12) Moan, J. *Photochem. Photobiol.* **1986**, *43*, 681.
(13) Kahl, S. B.; Li, J. *Inorg. Chem.* **1996**, *35*, 3878.
(14) An, J. M.; Yang, S. J.; Yi, S.-Y.; Jhon, G.-J.; Nam, W. *Bull. Korean Chem. Soc.* **1997**, *18*, 117.
(15) Mehta, G.; Muthusamy, S.; Maiya, B. G.; Arounaguiri, S. *Tetrahedron Lett.* **1997**, *38*, 7125.
(16) Ao, R.; Kummerl, L.; Haarer, D. *Adv. Mater.* **1995**, *7*, 495.
(17) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341.
(18) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147.
(19) Perry, J. W.; Mansour, K.; Lee, I.-Y. S.; Wu, X.-L.; Bedworth, P. V.; Chen, C.-T.; Ng, D.; Marder, S. R.; Miles, P.; Wada, T.; Tian, M.; Sasabe, H. *Science* **1996**, *273*, 1533.
(20) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569.
(21) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.
(22) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996.
(23) In this review, the terms assembly and array are used interchangeably and refer to a system containing two or more porphyrins linked together by any means.
(24) Dolphin, D.; Hiom, J.; Paine, J. B., III *Heterocycles* **1981**, *16*, 417.
(25) Vicente, M. G. H.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1999**, 1771.
(26) Arnold, D. P. *Synlett* **2000**, *3*, 296.
(27) Shinmori, H.; Osuka, A. *J. Synth. Org. Chem. Jpn.* **1999**, *57*, 749.
(28) Blanco, M.-J.; Jiménez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293.
(29) Anderson, H. L. *Chem. Commun.* **1999**, 2323.
(30) Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113.
(31) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133.
(32) Sanders, J. K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 3, p 347.
(33) Anton, J. A.; Kwong, J.; Loach, P. A. *J. Heterocyl. Chem.* **1976**, *13*, 717.
(34) Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1391.
(35) Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 293.
(36) Milgrom, L. R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2535.
(37) Mak, C. C.; Pomeranc, D.; Montalti, M.; Prodi, L.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1083.
(38) Osuka, A.; Kobayashi, F.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1213.
(39) Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3023.
(40) Officer, D. L.; Burrell, A. K.; Reid, D. C. W. *J. Chem. Soc., Chem. Commun.* **1996**, 1657.
(41) Kosal, M. E.; Suslick, K. S. *J. Solid State Chem.* **2000**, *152*, 87.
(42) Smith, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 1, p 1.
(43) Smith, K. M. *J. Porphyrins Phthalocyanines* **2000**, *4*, 319.
(44) Vicente, M.; Graca, H.; Smith, K. M. *Curr. Org. Chem.* **2000**, *4*, 139.
(45) Shanmugathasan, S.; Edwards, C.; Boyle, R. W. *Tetrahedron* **2000**, *56*, 1025.
(46) Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 1, p 45.
(47) Paine, J. B., III In *Porphyrins*; Dolphin, D., Ed.; Academic: New York, Vancouver, 1978; Vol. 1, p 101.
(48) Kim, J. B.; Adler, A. D.; Longo, F. R. In *Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978.
(49) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323.
(50) Rothemund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1941**, *63*, 267.
(51) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
(52) Lindsey, J. S.; Hsu, H. C.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, *27*, 4969.
(53) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.
(54) Lindsey, J. S.; MacCrum, K. A.; Tyhonas, J. S.; Chuang, Y.-Y. *J. Org. Chem.* **1994**, *59*, 579.
(55) Li, F.; Yang, K.; Tyhonas, J. S.; MacCrum, K. A.; Lindsey, J. S. *Tetrahedron* **1997**, *53*, 12339.
(56) Arsenault, G. P.; Bullock, E.; MacDonald, S. F. *J. Am. Chem. Soc.* **1960**, *82*, 4384.
(57) Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9310.
(58) Osuka, A.; Tanabe, N.; Kawabata, S.; Yamazaki, I.; Nishimura, Y. *J. Org. Chem.* **1995**, *60*, 7177.
(59) Onaka, M.; Shinoda, T.; Izumi, Y.; Nolen, E. *Tetrahedron Lett.* **1993**, *34*, 2625.
(60) Gradillas, A.; del Campo, C.; Sinisterra, J. V.; Llama, E. F. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2611.
(61) Drain, C. M.; Gong, X. *J. Chem. Soc., Chem. Commun.* **1997**, 2117.
(62) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941.
(63) Osuka, A.; Tanabe, N.; Nakajima, S.; Maruyama, K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 199.
(64) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618.
(65) Lash, T. D. *Chem. Eur. J.* **1996**, *2*, 1197.
(66) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427.
(67) Nakano, A.; Yamazaki, T.; Nishimura, Y.; Yamazaki, I.; Osuka, A. *Chem. Eur. J.* **2000**, *6*, 3254.
(68) Boxer, S. G.; Bucks, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 1883.
(69) Bucks, R. R.; Boxer, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 340.
(70) Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3020.
(71) Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1085.
(72) Collman, J. P.; Elliott, C. M.; Halbert, T. R.; Tovrog, B. S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 18.
(73) Collman, J. P.; Bencosme, C. S.; Barnes, C. E.; Miller, B. D. *J. Am. Chem. Soc.* **1983**, *105*, 2704.
(74) Gust, D.; Moore, T. A.; Moore, A. L.; Macpherson, A. N.; Lopez, A.; DeGraziano, J. M.; Gouni, I.; Bittersmann, E.; Seely, G. R.; Gao, F.; Nieman, R. A.; Ma, X. C.; Demanche, L. J.; Hung, S.-C.; Luttrull, D. K.; Lee, S.-J.; Kerrigan, P. K. *J. Am. Chem. Soc.* **1993**, *115*, 11141.
(75) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63.
(76) Tamiaki, H.; Suzuki, S.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2633.
(77) Tamiaki, H.; Nomura, K.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1863.
(78) Ema, T.; Nemugaki, S.; Tsuboi, S.; Utaka, M. *Tetrahedron Lett.* **1995**, *36*, 5905.
(79) Flores, V.; Nguyen, C. K.; Sindelar, C. A.; Vasquez, L. D.; Shachter, A. M. *Tetrahedron Lett.* **1996**, *37*, 8633.
(80) Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1985**, 904.
(81) Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1986**, 665.
(82) Davila, J.; Harriman, A.; Milgrom, L. R. *Chem. Phys. Lett.* **1987**, *136*, 427.
(83) Pandian, R. P.; Chandrashekar, T. K. *Inorg. Chem.* **1994**, *33*, 3317.
(84) Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 1625.
(85) Norsten, T.; Branda, N. *Chem. Commun.* **1998**, 1257.
(86) Milgrom, L. R.; O'Neill, F. *Tetrahedron* **1995**, *51*, 2137.
(87) Biemans, H. A. M.; Rowan, A. E.; Verhoeven, A.; Vanoppen, P.; Latterini, L.; Foekema, J.; Schenning, A. P. H. J.; Meijer, E. W.; de Schryver, F. C.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1998**, *120*, 11054.
(88) Hecht, S.; Emrick, T.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 313.
(89) Booksser, B. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 4208.
(90) Crossley, M. J.; Hambley, T. W.; Mackay, L. G.; Try, A. C.; Walton, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1077.

(91) Allen, P. R.; Reek, J. N. H.; Try, A. C.; Crossley, M. J. *Tetrahedron: Asymmetry* **1997**, *8*, 1161.
(92) Tsuchiya, S. *J. Am. Chem. Soc.* **1999**, *121*, 48.
(93) Ruhlmann, L.; Lobstein, S.; Gross, M.; Giraudeau, A. *J. Org. Chem.* **1999**, *64*, 1352.
(94) Ruhlmann, L.; Giraudeau, A. *J. Chem. Soc., Chem. Commun.* **1996**, 2007.
(95) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458.
(96) Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399.
(97) Zheng, G.; Pandey, R. K.; Forsyth, T. P.; Kozyrev, A. N.; Dougherty, T. J.; Smith, K. M. *Tetrahedron Lett.* **1997**, *38*, 2409.
(98) Khoury, R. G.; Jaquinod, L.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1997**, 1057.
(99) Khoury, R. G.; Jaquinod, L.; Nurco, D. J.; Pandey, R. K.; Senge, M. O.; Smith, K. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2496.
(100) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135.
(101) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Angew. Chem., Int. Ed. Engl.* **1999**.
(102) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Chem. Commun.* **1998**, 337.
(103) Arnold, D.; Johnson, A. W.; Winter, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1643.
(104) Hiom, J.; Paine, J. B., III; Zapf, U.; Dolphin, D. *Can. J. Chem.* **1983**, *61*, 2220.
(105) Lee, D. A.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1215.
(106) Ponomarev, G. V.; Borovkov, V. V.; Sugiura, K.; Sakata, Y.; Shul'ga, A. M. *Tetrahedron Lett.* **1993**, *34*, 2153.
(107) Higuchi, H.; Shimizu, K.; Ojima, J.; Sugiura, K.; Sakata, Y. *Tetrahedron Lett.* **1995**, *36*, 5359.
(108) Higuchi, H.; Shimizu, K.; Takeuchi, M.; Ojima, J.; Sugiura, K.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1923.
(109) Johnson, D. G.; Svec, W. A.; Wasielewski, M. R. *Isr. J. Chem.* **1988**, *28*, 193.
(110) Bonfantini, E. E.; Officer, D. L. *Tetrahedron Lett.* **1993**, *34*, 8531.
(111) Burrell, A. K.; Officer, D. L.; Reid, D. C. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 900.
(112) Belcher, W. J.; Burrell, A. K.; Campbell, W. M.; Officer, D. L.; Reid, D. C. W.; Wild, K. Y. *Tetrahedron* **1999**, *55*, 2401.
(113) Burrell, A. K.; Officer, D. L. *Synlett* **1998**, 1297.
(114) Gauler, R.; Risch, N. *Tetrahedron Lett.* **1997**, *38*, 223.
(115) Gauler, R.; Risch, N. *Eur. J. Org. Chem.* **1998**, 1193.
(116) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366.
(117) Arnold, D. P.; James, D. A. *J. Org. Chem.* **1997**, *62*, 3460.
(118) Arnold, D. P.; James, D. A.; Kennard, C. H. L.; Smith, G. *J. Chem. Soc., Chem. Commun.* **1994**, 2131.
(119) Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron* **1992**, *48*, 8781.
(120) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972.
(121) Anderson, H. L.; Martin, S. J.; Bradley, D. D. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 655.
(122) Taylor, P. N.; Huuskonen, J.; Rumbles, G.; Aplin, R. T.; Williams, E.; Anderson, H. L. *Chem. Commun.* **1998**, 909.
(123) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.
(124) Lin, V. S.-Y.; Therien, M. J. *Chem. Eur. J.* **1995**, *1*, 645.
(125) Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2247.
(126) Anderson, H. L.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1400.
(127) Mackay, L. G.; Wylie, R. S.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1994**, *116*, 3141.
(128) Walter, C. J.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1993**, 458.
(129) Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 946.
(130) Anderson, S.; Anderson, H. L.; Bashall, A.; McPartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1096.
(131) Marvaud, V.; Vidal-Ferran, A.; Webb, S. J.; Sanders, J. K. M. *J. Chem. Soc., Dalton Trans.* **1997**, 985.
(132) Anderson, H. L.; Walter, C. J.; Vidal-Ferran, A.; Hay, R. A.; Lowden, P. A.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2275.
(133) McCallien, D. W. J.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1995**, *117*, 6611.
(134) Clyde-Watson, Z.; Bampos, N.; Sanders, J. K. M. *New J. Chem.* **1998**, 1135.
(135) Mackay, L. G.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 43.
(136) Vidal-Ferran, A.; Clyde-Watson, Z.; Bampos, N.; Sanders, J. K. M. *J. Org. Chem.* **1997**, *62*, 240.
(137) Vidal-Ferran, A.; Muller, C. M.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2657.
(138) Vidal-Ferran, A.; Bampos, N.; Sanders, J. K. M. *Inorg. Chem.* **1997**, *36*, 6117.
(139) Clausen, C.; Gryko, D. T.; Yasseri, A. A.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7371.
(140) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166.
(141) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266.
(142) Nishino, N.; Wagner, R. W.; Lindsey, J. S. *J. Org. Chem.* **1996**, *61*, 7534.
(143) Clausen, C.; Gryko, D. T.; Dabke, R. B.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7363.
(144) Wagner, R. W.; Seth, J.; Yang, S. I.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1998**, *63*, 5042.
(145) Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519.
(146) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578.
(147) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. 42nd ASMS Conference on Mass Spectrometry, 1994; p 949.
(148) Li, F.; Gentemann, S.; Kalsbeck, W. A.; Seth, J.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Mater. Chem.* **1997**, *7*, 1245.
(149) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93.
(150) Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604.
(151) Li, J.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927.
(152) Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974.
(153) Osuka, A.; Ikeda, M.; Shiratori, H.; Nishimura, Y.; Yamazaki, I. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1019.
(154) Mongin, O.; Gossauer, A. *Tetrahedron Lett.* **1996**, *37*, 3825.
(155) Mongin, O.; Gossauer, A. *Tetrahedron* **1997**, *53*, 6835.
(156) Mongin, O.; Papamicaël, C.; Hoyler, N.; Gossauer, A. *J. Org. Chem.* **1998**, *63*, 5568.
(157) Brodard, P.; Matzinger, S.; Vauthey, E.; Mongin, O.; Papamicaël, C.; Gossauer, A. *J. Phys. Chem. A* **1999**, *103*, 5858.
(158) Mongin, O.; Schuwey, A.; Vallot, M.-A.; Gossauer, A. *Tetrahedron Lett.* **1999**, *40*, 8347.
(159) Mongin, O.; Hoyler, N.; Gossauer, A. *Eur. J. Org. Chem.* **2000**, 1193.
(160) König, B.; Zieg, H. *Synthesis* **1998**, 171.
(161) Jiang, B.; Yang, S.-W.; Barbini, D. C.; Jr., W. E. J. *Chem. Commun.* **1998**, 213.
(162) Wytko, J.; Berl, V.; McLaughlin, M.; Tykwinski, R. R.; Schreiber, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1998**, *81*, 1964.
(163) Crossley, M. J.; McDonald, J. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2429.
(164) Sugiura, K.; Fujimoto, Y.; Sakata, Y. *Chem. Commun.* **2000**, 1105.
(165) Beavington, R.; Burn, P. L. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1231.
(166) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388.
(167) Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725.
(168) Abdalmuhdi, I.; Chang, C. K. *J. Org. Chem.* **1985**, *50*, 410.
(169) Sessler, J. L.; Capuano, V. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1134.
(170) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054.
(171) Osuka, A.; Tanabe, N.; Zhang, R.; Maruyama, K. *Chem. Lett.* **1993**, 1505.
(172) Osuka, A.; Nakajima, S.; Nagata, T.; Maruyama, K.; Toriumi, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 582.
(173) Osuka, A.; Liu, B.; Maruyama, K. *J. Org. Chem.* **1993**, *58*, 3582.
(174) Osuka, A.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Mataga, N. *Tetrahedron Lett.* **1995**, *36*, 5781.
(175) Hammel, D.; Erk, P.; Schuler, B.; Heinze, J.; Mullen, K. *Adv. Mater.* **1992**, *4*, 737.
(176) Wennerstrom, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* **1989**, *30*, 1129.
(177) Sugiura, K.; Tanaka, H.; Matsumoto, T.; Kawai, T.; Sakata, Y. *Chem. Lett.* **1999**, 1193.
(178) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.
(179) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1987**, 39.
(180) Crossley, M. J.; Govenlock, L. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 2379.
(181) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921.
(182) Crossley, M. J.; Try, A. C.; Walton, R. *Tetrahedron Lett.* **1996**, *37*, 6807.
(183) Reek, J. N. H.; Rowan, A. E.; de Gelder, R.; Beurskens, P. T.; Crossley, M. J.; De Feyter, S.; de Schryver, F.; Nolte, R. J. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 361.
(184) Vicente, M. G. H.; Cancilla, M. T.; Lebrilla, C. B.; Smith, K. M. *Chem. Commun.* **1998**, 2355.

(185) Jaquinod, L.; Siri, O.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1261.
(186) Paolesse, R.; Jaquinod, L.; Sala, F. D.; Nurco, D. J.; Prodi, L.; Montalti, M.; Natale, C. D.; D'Amico, A.; Carlo, A. D.; Lugli, P.; Smith, K. M. *J. Am. Chem. Soc.* **2000**, *122*, 11295.
(187) Tsuda, A.; Nakano, A.; Furuta, H.; Yamochi, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 558.
(188) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549.
(189) Sugiura, K.; Matsumoto, T.; Ohkouchi, S.; Naitoh, Y.; Kawai, T.; Takai, Y.; Ushiroda, K.; Sakata, Y. *Chem. Commun.* **1999**, 1957.
(190) Li, J.; Diers, J. R.; Seth, J.; Yang, S. I.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 9090.
(191) Li, J.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 9101.
(192) Collman, J. P.; Arnold, H. J. *Acc. Chem. Res.* **1993**, *26*, 586.
(193) Collman, J. P.; Fish, H. T. *Inorg. Chem.* **1996**, *35*, 7922.
(194) Aida, T.; Jiang, D.-L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 3, p 369.
(195) Girolami, G. S.; Hein, C. L.; Suslick, K. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1223.
(196) Chabach, D.; De Cian, A.; Fischer, J.; Weiss, R.; El Malouli Bibout, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 898.
(197) Buchler, J. W. In *Porphyrins and Metalloporphyrins*, 2nd ed.; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 5.
(198) Evans, D. R.; Mathur, R. S.; Heerwegh, K.; Reed, C. A.; Xie, Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1335.
(199) Segawa, H.; Kunimoto, K.; Susumu, K.; Taniguchi, M.; Shimidzu, T. *J. Am. Chem. Soc.* **1994**, *116*, 11193.
(200) Rao, T. A.; Maiya, B. G. *J. Chem. Soc., Chem. Commun.* **1995**, 939.
(201) Susumu, K.; Tanaka, K.; Shimidzu, T.; Takeuchi, Y.; Segawa, H. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1521.
(202) Kim, H.-J.; Bampos, N.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1999**, *121*, 8120.
(203) Wojaczynski, J.; Latos-Grazynski, L. *Inorg. Chem.* **1995**, *34*, 1044.
(204) Wojaczynski, J.; Latos-Grazynski, L. *Inorg. Chem.* **1995**, *34*, 1054.
(205) Wojaczynski, J.; Latos-Grazynski, L. *Inorg. Chem.* **1996**, *35*, 4812.
(206) Wojaczynski, J.; Latos-Grazynski, L.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1997**, *36*, 4548.
(207) Kariya, N.; Imamura, T.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 833.
(208) Alessio, E.; Macchi, M.; Heath, S.; Marzilli, L. G. *J. Chem. Soc., Chem. Commun.* **1996**, 1411.
(209) Alessio, E.; Macchi, M.; Heath, S. L.; Marzilli, L. G. *Inorg. Chem.* **1997**, *36*, 5614.
(210) Kumar, R. K.; Goldberg, I. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3027.
(211) Lin, K.-J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2730.
(212) Fleischer, E. B.; Shachter, A. M. *Inorg. Chem.* **1991**, *30*, 3763.
(213) Wilson, G. S.; Anderson, H. L. *Chem. Commun.* **1999**, 1539.
(214) Funatsu, K.; Kimura, A.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 1625.
(215) Chernook, A. V.; Rempel, U.; von Borczyskowski, C.; Shulga, A. M.; Zenkevich, E. I. *Chem. Phys. Lett.* **1996**, *254*, 229.
(216) Okumura, A.; Funatsu, K.; Sasaki, Y.; Imamura, T. *Chem. Lett.* **1999**, 779.
(217) Darling, S. L.; Mak, C. C.; Bampos, N.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *New J. Chem.* **1999**, *23*, 359.
(218) Hunter, C. A.; Sarson, L. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2313.
(219) Chi, X.; Guerin, A. J.; Haycock, R. A.; Hunter, C. A.; Sarson, L. D. *J. Chem. Soc., Chem. Commun.* **1995**, 2567.
(220) Michelsen, U.; Hunter, C. A. *Angew. Chem., Int. Ed.* **2000**.
(221) Haycock, R. A.; Hunter, C. A.; James, D. A.; Michelsen, U.; Sutton, L. R. *Org. Lett.* **2000**, *2*, 2435.
(222) Hunter, C. A.; Hyde, R. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1936.
(223) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313.
(224) Drain, C. M.; Nifiatis, F.; Vasenko, A.; Batteas, J. D. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2344.
(225) Stang, P. J.; Fan, J.; Olenyuk, B. *J. Chem. Soc., Chem. Commun.* **1997**, 1453.
(226) Fan, J.; Whiteford, J. A.; Olenyuk, B.; Levin, M. D.; Stang, P. J.; Fleischer, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 2741.
(227) Slone, R. V.; Hupp, J. T. *Inorg. Chem.* **1997**, *36*, 5422.
(228) Huck, W. T. S.; Rohrer, A.; Anilkumar, A. T.; Fokkens, R. H.; Nibbering, N. M. M.; Veggel, F. C. J. M. v.; Reinhoudt, D. N. *New J. Chem.* **1998**, 165.
(229) Yuan, H.; Thomas, L.; Woo, L. K. *Inorg. Chem.* **1996**, *35*, 2808.
(230) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606.
(231) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727.
(232) Sharma, C. V. K.; Broker, G. A.; Huddleston, J. G.; Baldwin, J. W.; Metzger, R. M.; Rogers, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 1137.
(233) Tamiaki, H. *Coord. Chem. Rev.* **1996**, *148*, 183.
(234) Tamiaki, H.; Miyatake, T.; Tanikaga, R.; Holzwarth, A. R.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 772.
(235) Jesorka, A.; Balaban, T. S.; Holzwarth, A. R.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2861.
(236) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 7, 704.
(237) Ikeda, C.; Nagahara, N.; Motegi, E.; Yoshioka, N.; Inoue, H. *Chem. Commun.* **1999**, 1759.
(238) Drain, C. M.; Russell, K. C.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 337.