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Synthesis of *meso*-Substituted ABCD-Type Porphyrins by Functionalization Reactions

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Considerable progress has been made in recent years in the search for synthetic methods leading to functionalized porphyrins, especially for modification of either the β- or *meso* positions. For the latter, total synthesis based on condensation methods or partial synthesis through functionalization of preformed porphyrin have emerged as possible methods. The increasing number of possible technical and medicinal applications for unsymmetrically *meso*-substituted porphyrins requires straightforward methods for the preparation of the so-called ABCD-porphyrins, i.e., porphyrins with up to four different *meso* substituents. Here, we describe new strategies for the synthesis of ABCD-type porphyrins based on porphyrin reactions with organolithium reagents and the use of Pd-catalyzed coupling reactions. With the whole repertoire of contemporary functionalization methods, a comprehensive analysis and comparison of the various strategies for A-, AB-, A_2B-, ABC-, A_2BC- and ABCD-type porphyrins is given. In addition, we report on the synthesis of new functionalized derivatives for some of these porphyrin classes. In practical terms and taking an applied-science-oriented approach, the synthesis of unsymmetrically *meso*-substituted porphyrins is best accomplished by a combination of well-developed condensation methods with subsequent functionalization by organolithium compounds or transition-metal-catalyzed coupling protocols. The methods described are suitable for the preparation of porphyrins for many divergent applications ranging over amphiphilic porphyrins for photodynamic therapy, push-pull systems for optical applications and chiral systems useful in catalysis to donor–acceptor systems suitable for electron-transfer studies.

Introduction

Porphyrins are a unique class of compounds that are ubiquitous in nature and function in a wide variety of roles ranging from oxygen transport, electron transfer and oxidation catalysts to photosynthesis. Thus, these widely distributed and important tetrapyrrolic cofactors play crucial roles in many biochemical and technical processes. These range from impaired biosynthesis (porphyrias), photodynamic cancer therapy (PDT), malaria, neuropsychiatric disorders to industrial applications as sensors, optical materials, oxidation catalysis and in supramolecular chemistry. Overall, porphyrins are probably the most widely studied class of natural products whose studies have impacted almost any modern scientific field.[1] From a chemical viewpoint, their importance is related to their chemical properties, i.e., their photochemical (energy and exciton transfer), redox (electron transfer, catalysis), and coordination properties (metal and axial ligand binding), and their conformational flexibility (functional control).[2]

The various applications and their biochemical relevance are related by a common denominator in the underlying chemistry of these compounds. Current applications require the synthesis of unsymmetrically substituted porphyrins, i.e. systems with different substituents in a regiochemically defined manner. Next to the naturally occurring β-substituted porphyrins (e.g., the chlorophylls and hemes) typical examples are the so-called ABCD-porphyrins (**1**), where four different *meso* substituents are present (**2**).[3] The type and arrangement of these substituents then defines different applications. To name a few, residues with functional groups suitable for small molecule binding may be used for catalysis, a mixture of polar and nonpolar residues yields amphiphilic porphyrins suitable for photodynamic therapy and a mix of electron donating and withdrawing groups will give push-pull porphyrins for applications in nonlinear optics.[4]

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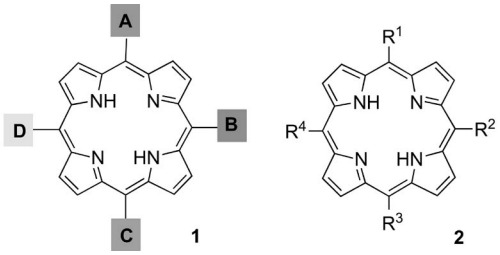
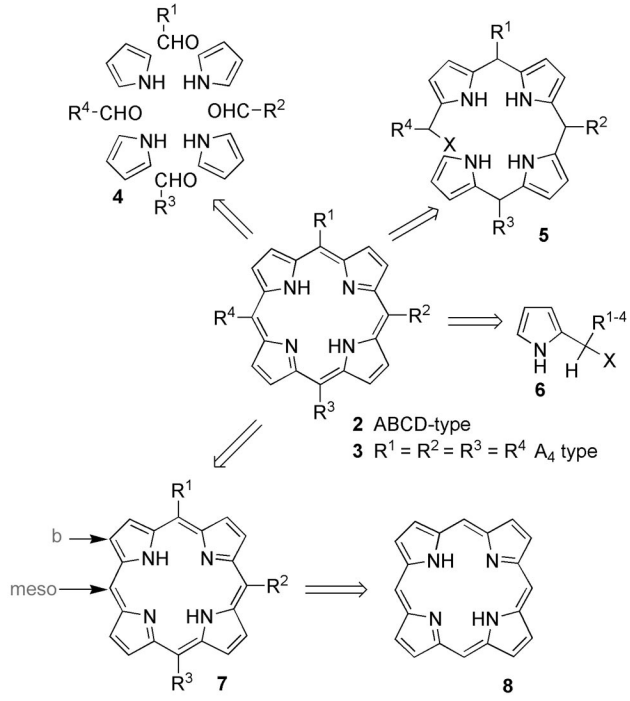


Future progress in this area obviously depends on the synthetic accessibility of porphyrins. While – theoretically – almost any desired β-substituted porphyrin can be prepared based on historical contributions from eminent chemists such as Willstätter, Fischer, Woodward, Eschenmoser and Smith[5a] there were still limitations in the preparation of *meso*-substituted porphyrins. Due to their symmetry and simple preparation most of the applications currently under study use 5,10,15,20-tetrasubstituted porphyrins (**3**) and a significant body of methods has been developed for the modification of the β-positions in such systems.[5b]

In principle, there are three ways to access the more interesting unsymmetrical ABCD-type compounds (Scheme 1). These are the disconnection into a bilane **5** or any combination of pyrrole building blocks **6** that can be used in [2+2] or [3+1] condensation reactions.[6] Theoretically possible is also a mixed condensation using pyrrole **4** and various aldehydes which is still used by many researchers for systems with lower symmetry. Here, the number of regioisomers formed is too large and the necessary purification and separation workup is too cumbersome if possible at all. Note, that most of these reactions involve acid-catalyzed condensation reactions, often resulting in significant scrambling of the pyrrole units thus limiting the type of substituents that can be used.

The most significant contributions in this area of ABCD-porphyrin "total synthesis" were made by the group of Lindsey.[6b] Examples for new developments are the synthesis of 1-bromo-19-acylbilanes by acid-catalyzed condensation of 1-acyldipyrromethanes and 9-bromodipyrromethane-1-carbinols followed by intramolecular cyclization of the 1-bromo-19-acylbilanes in the presence of a metal salt in a noncoordinating solvent and the synthesis of 1-protected 19-acylbilanes by acid-catalyzed condensation 1-acyldipyrromethanes and 9-protected dipyrromethane-1-carbinols with subsequent transformation of the 1-protected 19-acylbilane under basic, metal-templating conditions to give the corresponding metalloporphyrins.[7]

We have taken an alternative approach focusing on partial synthesis starting with preformed porphyrins, i.e. envisioning a step-wise introduction of the four *meso* substituents in **2**. The last decades have seen a surge in novel functionalization reactions of porphyrins, many based on C–C coupling reactions which has put this approach within possibility.[8] By now many A_2BC- and A_3B-type porphyrins have been prepared starting with the easily accessible 5,15-disubstituted porphyrins[3,9–12] and from brominated precursor compounds often based on Heck-type reactions. In this context we have developed the use of organolithium reagents for the synthesis of various tetrapyrrole classes.[13–16]



Scheme 1. Retrosynthetic analysis of ABCD-type porphyrins.

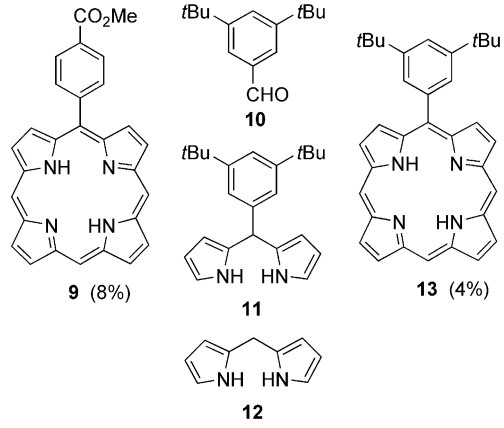
In a strategic sense the preparation of ABCD-type porphyrins by functionalization requires the use of the less-substituted precursors, e.g. **7**, and ultimately use of unsubstituted porphyrin **8**. The latter then allows for preparation of a mono-substituted A-type porphyrin (**7**, $R^2 = R^3 = H$) followed by subsequent regiochemical introductions of the B-, C- and D-type residues. With recent advances in the synthesis of **8**[17] and the preparation of A-type porphyrins through condensation and functionalization reactions[18] all necessary parts for partial synthesis of ABCD-porphyrins are now in hand. Based on our current interest in the application of porphyrins for photodynamic cancer therapy (PDT) and optical applications[19] we here present a comprehensive analysis of the application of the currently available synthetic strategies for the *meso* functionalization of porphyrins. This study aims to evaluate the applicability and limitations of these methods for the preparation of ABCD-type porphyrins in general. We also report on the synthesis of new functionalized derivatives for some of the different ABCD-porphyrin classes.

Results and Discussion

A preparation of ABCD-type porphyrins through functionalization requires a step-wise approach, i.e., starting from A-porphyrins and through sequential introduction of more residues going to the ABCD-type systems. Thus, for practical purposes, we start in our discussion with the least substituted systems.

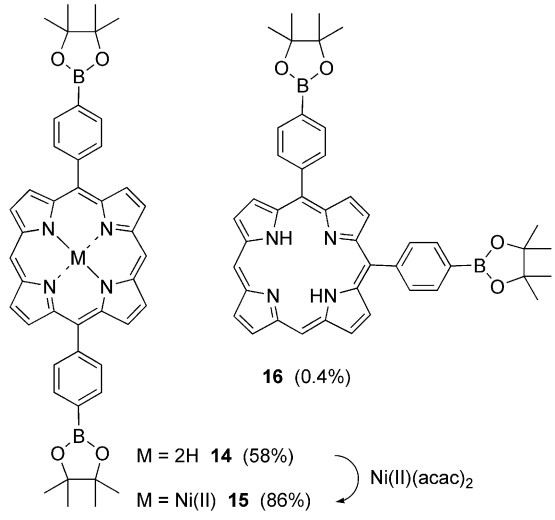
Synthesis of A-Type Porphyrins

These porphyrins are accessible either by substitution of porphyrin ("porphine") with RLi or by mixed condensation.[18] One example for the latter is the mixed condensation of dipyrromethane, 2-hydromethylpyrrole and methyl 4-formylbenzoate to give **9** in 8% yield. Another example is the preparation of compound **13** by condensation of the 5-substituted dipyrromethane **11** (derived from the aldehyde **10**) with dipyrromethane **12** and trimethyl orthoformiate in 4% yield. Typically such condensations give 2–12% yield and the formation of the A-type porphyrin is accompanied by the respective 5,15-A_2-type system, which can be easily removed by chromatography.[18] Preparation from in situ generated porphyrin and reaction with RLi is attractive but works well best for reactions involving ca. 100 mg of starting material. Large scale syntheses are still best performed via mixed condensations.



Synthesis of A_2-Type Porphyrins

The synthesis of 5,15-disubstituted A_2-type porphyrins is well established by now. Their preparation is easily accomplished by a [2+2] condensation using dipyrromethane **12** and the respective aldehyde carrying the *meso* substituent.[3,9–11,20] An example for the synthesis of a 5,15-disubstituted porphyrin with new functional groups is the synthesis of the bisdioxaborolan porphyrin **14** from dipyrromethane and the respective aldehyde in 58% yield. Metallation with nickel acetylacetonate gave the respective metal complex **15**. The related 5,10-disubstituted derivatives are accessible via similar methods but typically give much lower yields.[21] Here compound **16** could be prepared in very low yield (0.4%). Total syntheses have been reported for example 5,10-diphenylporphyrin.[22] 5,15-Disubstituted porphyrins are also often derived from mixed condensation such as AB-type porphyrin syntheses (vide infra).



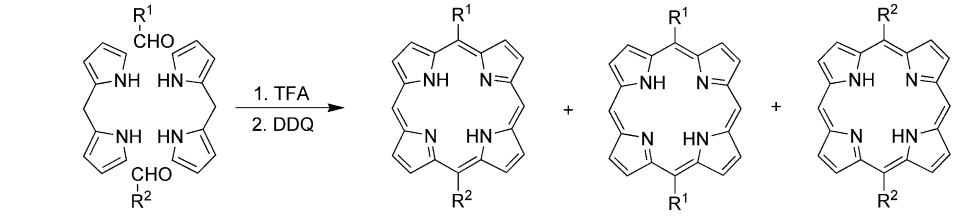
Synthesis of AB-Type Porphyrins

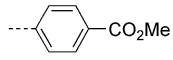
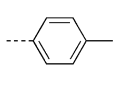
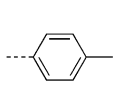
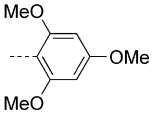
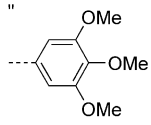
Two possibilities exist for the preparation of 5,15-AB porphyrins. One involves classic mixed condensation reactions. In practical terms this is still a facile reaction and for certain residues allows quick generation of the desired compounds and can even be controlled to give only the target compound as the main product.[11,23] In simple approaches, often product mixtures are encountered. Nevertheless, the different polarities mostly allow for a quick chromatographic separation of the compounds. For example, the preparation of **17** from dipyrromethane and aldehyde gives a yield of 23% but is accompanied by formation of **18** (14%) and **19** (14%). In a similar manner use 2-methoxybenzaldehyde and tolylaldehyde gave **20** in 22% yield while tolylaldehyde and 2,4,6-trimethoxybenzaldehyde gave the 5,15-AB porphyrin **21** in 15% yield. Further examples are illustrated in Scheme 2.

More elegant might be a synthesis using C–C coupling reactions. The use of Heck-type coupling reactions is still problematic due to limited access to the necessary monobromo derivatives.[24] An alternative might be the use of reactions with LiR. However, initially we were not too convinced, as studies with 2,3,7,8,12,13,17,18-octaethylporphyrin and other systems had shown a preference for formation of the 5,10-AB derivatives over the 5,15-AB regioisomers.[13–16] Nevertheless, we attempted some reactions of 5-substituted aryl and alkylporphyrins with LiR reagents under our standard conditions (Scheme 3).

Reaction of the sterically hindered *tert*-butylporphyrin **32** with *n*BuLi gave a mixture of the two possible regioisomers **38** and **39** accompanied by higher alkylated products. Variations of the reaction conditions did not change this situation. With hexyllithium the 5,15-regioisomer **40** was isolated as the main product in low yield. Using dimethylaminophenyllithium again the 5,15-regioisomer **41** was isolated in better yield but was accompanied by small amounts of the respective butyl derivative **38**.

The ethylpropyl porphyrin **33** gave quite satisfactory yields with hexyl (59%) and phenyllithium (69%) but showed a clear preference for the formation of the 5,10-regioisomer (**42** and **43**, respectively). We tried to optimize the synthesis of **42** by variation of the number of equiva-



R^1	R^2			
hexyl		**17** (23%)	**18** (18%)	**19** (14%)
		**20** (22%)		
		**21** (15%)		
*n*Bu	"	**22** (14%)	**23** (16%)	**24** (11%)
pentyl	"	**25** (9%)	**26** (5%)	**24** (2%)
hexyl	"	**27** (17%)	**18** (12%)	**24** (9%)
*n*Bu		**28** (8%)	**23** (6%)	**29** (2%)
pentyl	"	**30** (6%)	**26** (5%)	**29** (2%)
hexyl	"	**31** (17%)	**18** (6%)	**29** (9%)

Scheme 2. Synthesis of AB-porphyrins via condensation reagents.

lents of hexyllithium. Depending on the number of equivalents used (1.5, 2.5, 3.5, 4.5, 5.5) the yields varied over a broad range (42, 52, 59, 29, 44%, respectively) with 3.5 equiv. being the optimum which makes sense as 2 equiv. will be required to neutralize the N-H. Use of the aryllithium reagent 4-(dimethylamino)phenyllithium gave a mixture of the two regioisomers **44** and **45** accompanied by the higher substituted porphyrins **46** and **47**. Similarly, in the case of the 5-arylporphyrins **34** and **35** the formation of both regioisomers was observed with a clear preference for the 5,10 isomer.

Clearly, the reaction of porphyrins with RLi for the preparation of AB-type porphyrins is difficult to control and offers advantages only for very specific cases. Note, that for the reaction of 5-alkylporphyrins with RLi the yields are comparable to those obtained from mixed condensations. Here, the latter offer the advantage of larger scale and easier chromatographic separation. The main benefit of the present method lies in an easier access to the otherwise inaccessible 5,10-regioisomer. Alternatively, use of an excess of alkyllithium reagent offers an entry into A_2B-porphyrins from the monosubstituted precursors. E.g., reaction of **36** with hexyllithium gave the trisubstituted porphyrin **55** in 54% yield. A similar reactivity was observed for **37**, although in this case only the 5,15-A_2B porphyrin **57** could be isolated from the product mixture.

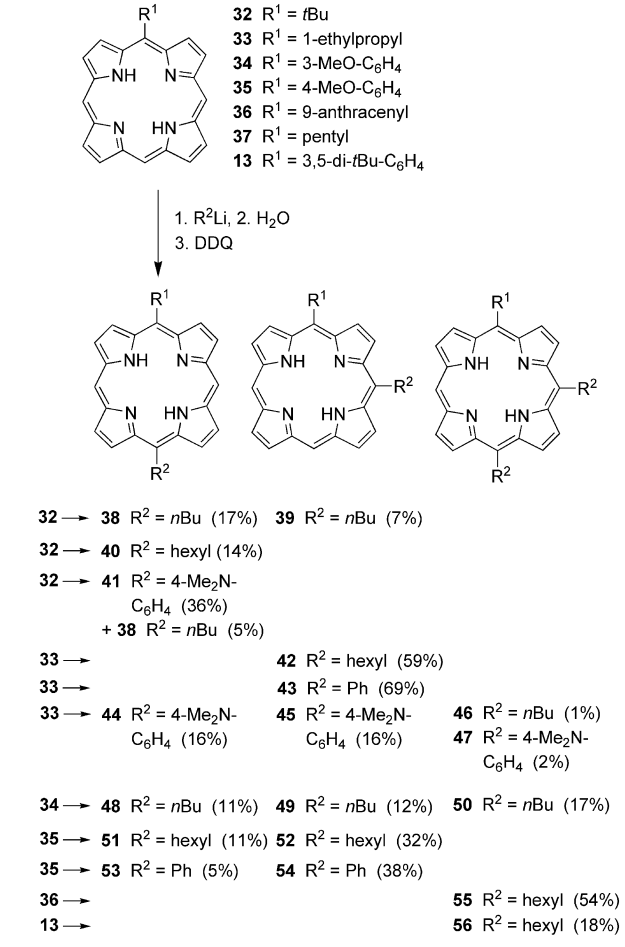
Synthesis of A_2B-Type Porphyrins

5,15-A_2-type porphyrins are conveniently prepared from aldehydes and dipyrromethanes and present useful starting materials for the investigation of reactions at the *meso* position.[9] Using S_NAr reactions they can easily be converted into the respective A_2B-porphyrins without any regiochemical problems.[13b,15] For example, using **58**[11] as starting material the two porphyrins **59** and **60** could be prepared easily in 71 and 77% yield, respectively (Scheme 4).

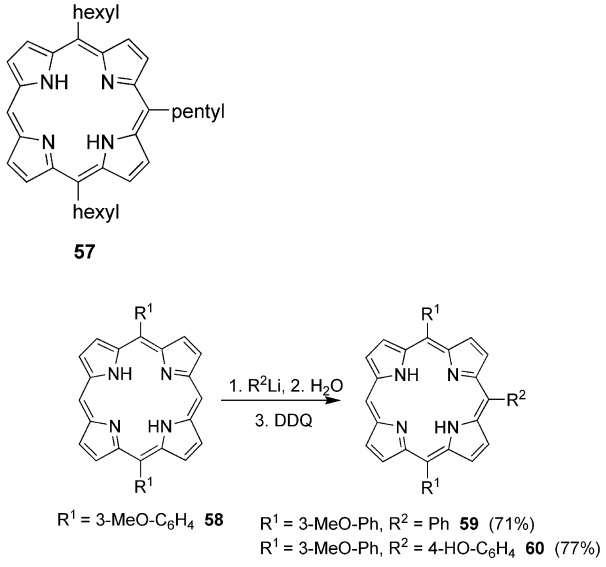
Synthesis of ABC-Type Porphyrins

First we investigated the reaction of 5,15-AB-type porphyrins with RLi reagents to yield ABC-porphyrins (Scheme 5). Similar to the situation for A_2B-porphyrins only one product can be formed and the reactions typically proceeded in very good yields. Using various alkyl and aryllithium reagents the ABC-porphyrins **61**–**64** and **67**–**71** were obtained in yields ranging from 47 to 90%. Some of these free bases were converted into the respective manganese(III) complexes for later oxidation catalyst studies.[25] As one example for possible applications we prepared the 5,10-*meso*-*meso*-strapped porphyrin derivative **72** in good yields through reaction of **20** with 2-methoxyphenyllithium, deprotection of the methyl ether with BBr_3 followed by reaction with 1,12-dibromododecane.

Obviously, 5,10-type AB-porphyrins can be used for the preparation of ABC-porphyrins as well. A comparison of the reactivity of **44** and **45** shows that the 5,10-AB porphyrins do react but give lower yields in line with the stability of the intermediate anion.[16] Note, that such porphyrins could also be derived from the attempted syntheses of ABCD-type porphyrins through reaction of AB-porphyrins with R^1Li/R^2I (vide infra).



Scheme 3. Synthesis of AB-porphyrins by reaction with LiR reagents.



Scheme 4. Synthesis of A_2B-porphyrins via S_NAr.

An alternative approach to ABC-porphyrins is the use of AB-type systems, attempt a selective monobromination of one *meso* position and then use Pd-catalyzed reactions for introduction of the C-residue. Both iodination and bromination reactions have been applied to the *meso* position of porphyrins.[26] In order to access the monobromo derivatives of the AB-type porphyrins we used 1.1 equiv. of NBS for the bromination. Nevertheless, as shown in Scheme 6 the reaction is difficult to control and both the mono- and dibrominated derivatives were formed roughly in a 1:1 ratio with overall yields of 80–90%. However, their polarities are quite different and they are easily separated by column chromatography.

Pd-catalyzed reactions have found widespread use in porphyrin chemistry. These coupling reaction offers several advantages: availability of the reagents, mild reaction conditions, tolerance for a broad range of functional groups, small amount of catalysts and application in one pot synthesis and appropriate conditions have been developed for porphyrins.[27]

[4-(Carboxymethyl)phenyl]boronic acid was treated with porphyrins **22** and **31** and afforded the desired products **82** and **86** in 87% and 89% yield, respectively. Likewise, the styrene-type derivative **84** was prepared in 46% yield. Reaction of **31** with 3-nitrophenylboronic acid gave **85** in 82% yield. Reaction of the same boronic acid with porphyrin **27** yielded product **83** in 46% yield. Note, that 3-nitrophenyl residues in AB-diarylporphyrins have recently been identified by Banfi et al. as having potential for PDT and thus appropriate systems were ABCD-type targets for us.[28] Note, that the 5,15-dibromo derivatives **77**, **79**, and **81** offer an additional entry into 5,15-A_2BC compounds, which show promise as push-pull systems for optical applications.[19b]

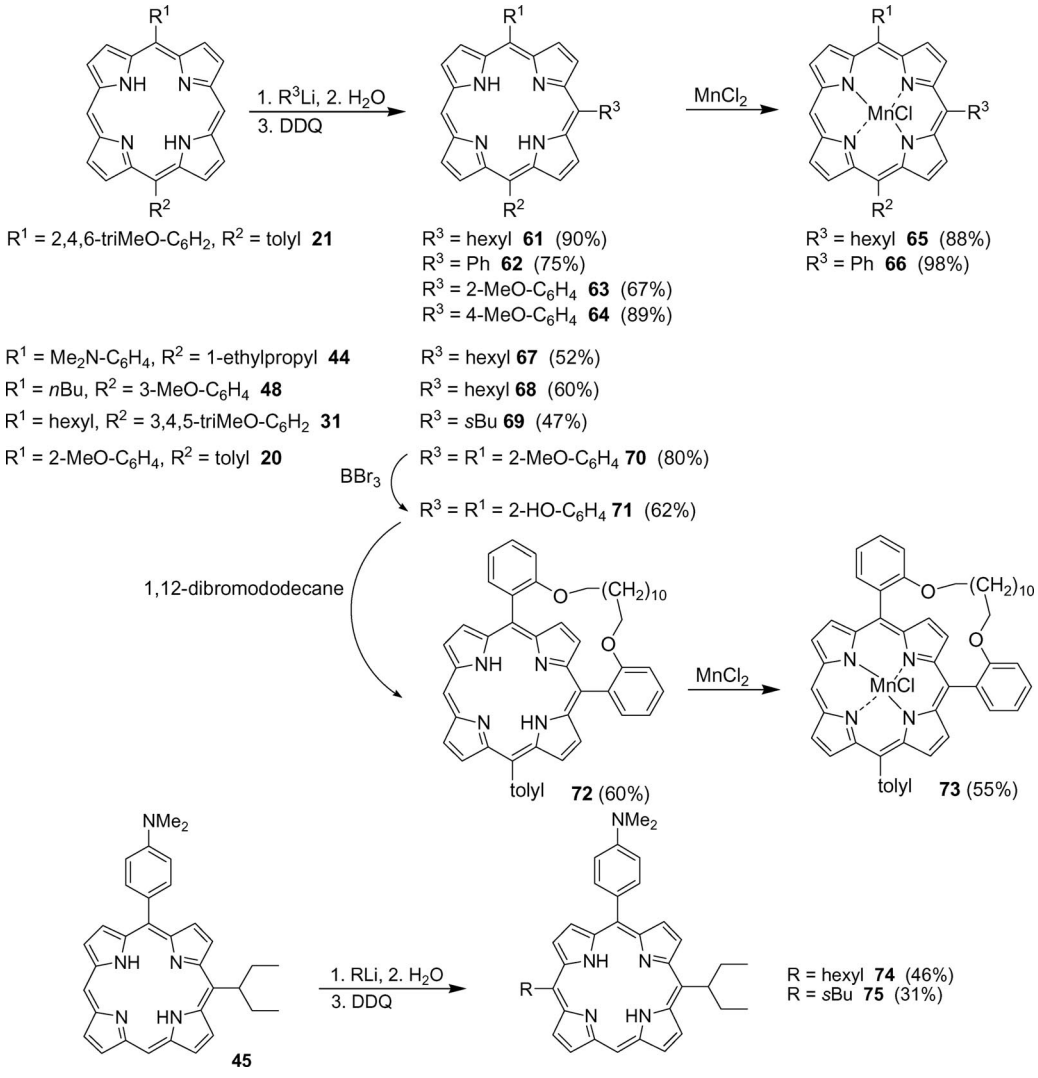
Synthesis of A_2BC-Type Porphyrins

Use of A_2B-porphyrins as starting materials offers again two possibilities: Pd-type couplings of the bromo derivatives and direct substitution with LiR reagents. The latter strategy has been employed quite successfully before.[11,12,14]

Reaction of A_2B-Porphyrins with RLi

In extension of our earlier studies we investigated some additional reagents and A_2B-type porphyrins (Scheme 7). While porphyrin **90** reacted in good to excellent yields with various alkyl- and aryllithium reagents attempts to use RLi with electron-withdrawing groups such as *p*-nitro- and *p*-bromophenyllithium only recovered starting material. Likewise, *p*-methoxyaryllithium or use of the in situ prepared lithiated ester of ethyl 4-bromobutyrate gave no reaction. Similar results were found for porphyrin **89** and additionally, we could show that reaction with 4-ethynylphenyllithium gave the porphyrin **91** in low yield.

Porphyrins such as **89** bearing a *p*-ethynyl group have potential uses in superstructured materials, porphyrin arrays, light-harvesting systems and porphyrin-based materials such as push-pull porphyrins via Glaser or Heck coupling.[29,30] For example, reaction of **94** under Glaser conditions gave the bisporphyrins **95** in excellent yield (Scheme 8). Couplings of compounds such as **94** and *trans*-diiodides could give new unsymmetrical, linear trisubsti-

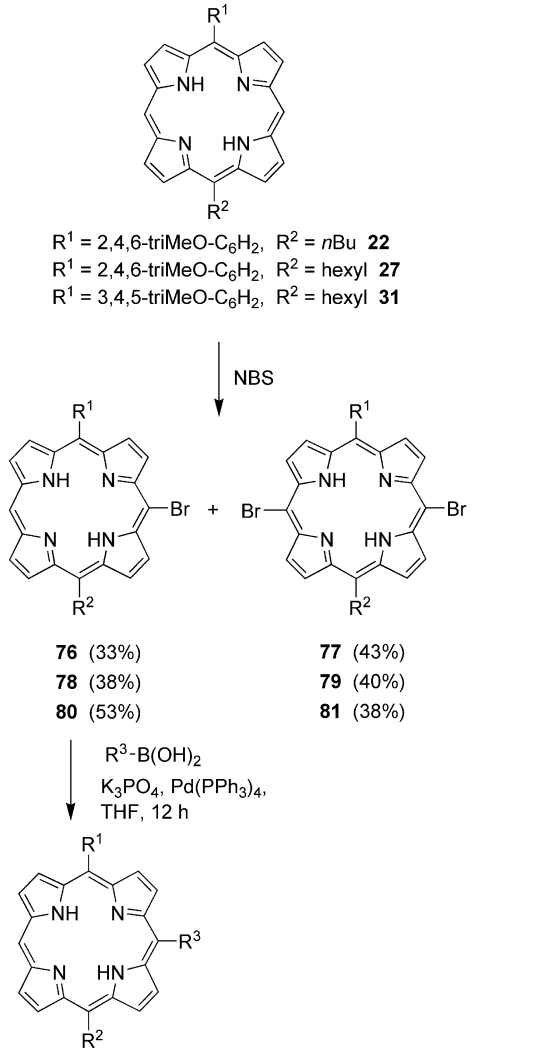


Scheme 5. Synthesis of ABC-porphyrins via S_NAr.

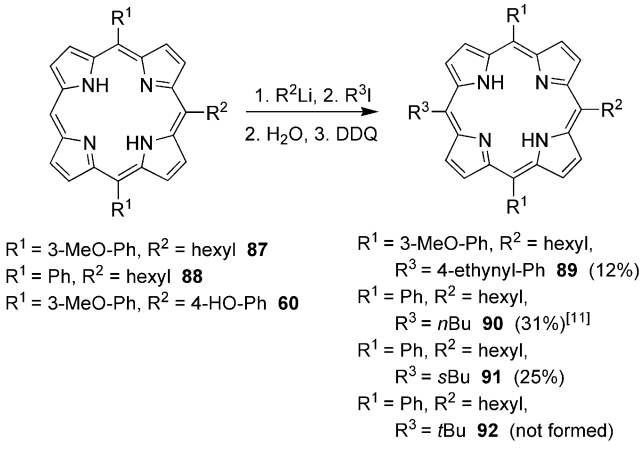
tuted porphyrins which may be used as model compounds for investigations of larger array systems.

The studies shown in Scheme 7 were then extended to the utilization of *meso*-trisubstituted porphyrin **88** to carry different alkyl residues in the "C" position using butyllithium reagents with an increasing degree in steric demand. Reactions of *n*-, *sec*-, and *tert*-butyllithium reagents with **88** were utilized to study the scope of their reactivity towards the *meso* position under the same reaction conditions. *n*- and *sec*-butyllithium reacted in a similar manner to form the unsymmetrical porphyrins **90**[11] and **91** in yields of 31 and 25%, respectively. Reaction with the more hindered *tert*-butyllithium proceeded in a different manner although the attack was still directed to the more reactive *meso* position. Here, phlorin **96** was formed in 20% yield instead of porphyrin **92**. The NMR spectroscopic data are typical for a nonaromatic conjugated system with pyrrolic signals in the δ = 6–7 ppm range. The formation of phlorin **96** indicates that the free *meso* position in **88** is more reactive towards *t*BuLi than β-positions as no chlorin was separated in this case. A similar behaviour was found for **59** which gave the phlorin **98** in 28%. These results are in line with results described by Krattinger and Callot.[32] The phlorins are stable against oxidants and this reaction opened a route for the conversion of free base porphyrins to phlorins with a variety of different *meso* substituents.[33]

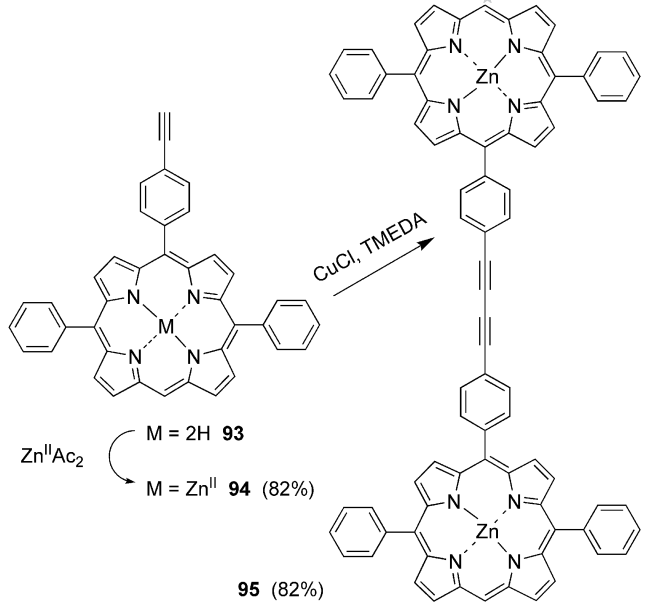
Next we investigated the reactivity of A_2B-porphyrins with aryl groups in the B position. Typically, attacking a *meso* position opposite to one carrying an aryl group is difficult due to steric hindrance of the mesomeric benzylic anion stabilization.[16] While the synthesis of some A_2BC-type porphyrins by this method was successful the yields obtained of these A_2BC-porphyrins were lower than those of A_2BC-porphyrins formed when B was an alkyl group. For example, porphyrin **60** did not react with *p*-ethynylphenyllithium or *n*-butyllithium. Likewise, the use of electron-rich porphyrins gave mixed results. For example, 5-(4-aminophenyl)-10,20-diphenylporphyrin reacted readily with 4-(dimethylamino)phenyl or butyllithium[11] while 5-(4-aminophenyl)-10,20-bis(3-methoxyphenyl)porphyrin reacted only with butyllithium[11] but not with *p*-hydroxyphenyllithium or 2-methoxyphenyllithium.



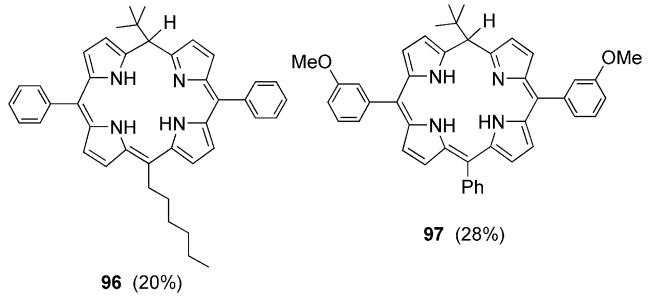
Scheme 6. Synthesis of ABC-porphyrins via Suzuki reactions.



Scheme 7. Synthesis of A_2BC-porphyrins via S_NAr.



Scheme 8. Glaser coupling of **94** to **95**.

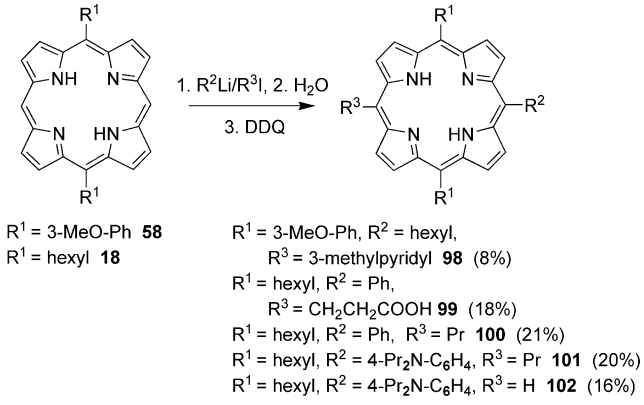


Reaction of A_2-Porphyrins with R^1Li/R^2I

Earlier we had shown that the nickel(II) complexes of A2-porphyrins can be accomplished through the addition of electrophilic reagents such as alkyl iodide "after the hydrolysis step" of the RLi reaction followed by oxidation with atmospheric oxygen permits the preparation of functionalized unsymmetric tetrasubstituted porphyrins.[14] This method was then extended to the respective free base porphyrins.[12] While the yields were low to moderate in the range of 20–45%, the method is still advantageous when compared to related mixed condensations or multi-step syntheses. Attempts to extend the reaction to 5,15-dialkylporphyrins confirmed these limitations (Scheme 9).

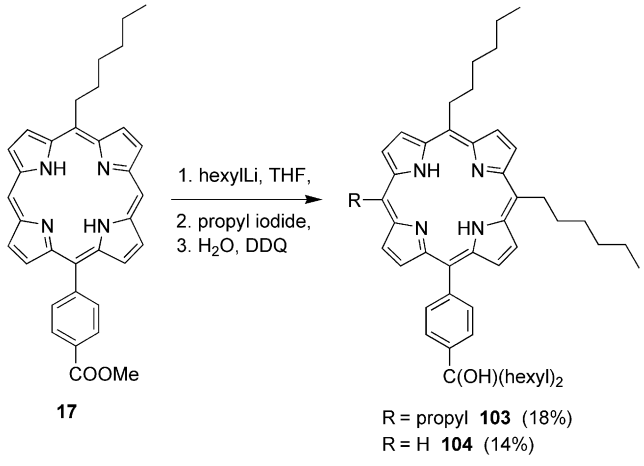
Porphyrin **98** was formed in only 8% yield, while **99** and **100** were obtained in 18 and 21%, respectively. In all three cases the target compounds were formed as the minor product. The main products (24–28%) were the respective trisubstituted A_2B-porphyrins formed by substitution with only R^2 from the organolithium reagent. A similar reaction was observed for reaction of **18** with 4-aminophenyllithium and propyl iodide. Here the A_2BC-porphyrin **101** was formed in 20% yield accompanied by porphyrin **102** in 16% yield. Clearly, this reaction is only useful in certain cases.

Use of a 5,15-AB-type porphyrin also allowed the formation of a 5,10-A_2BC-type porphyrin porphyrin in low yield.



Scheme 9. Synthesis of A_2BC-porphyrins via anion trapping.

Here, reaction of hexyllithium at the *meso* position and the carbonyl position of **17** followed by reaction with propyl iodide gave the porphyrin **103** (18%) accompanied by **104** (14%) (Scheme 10).



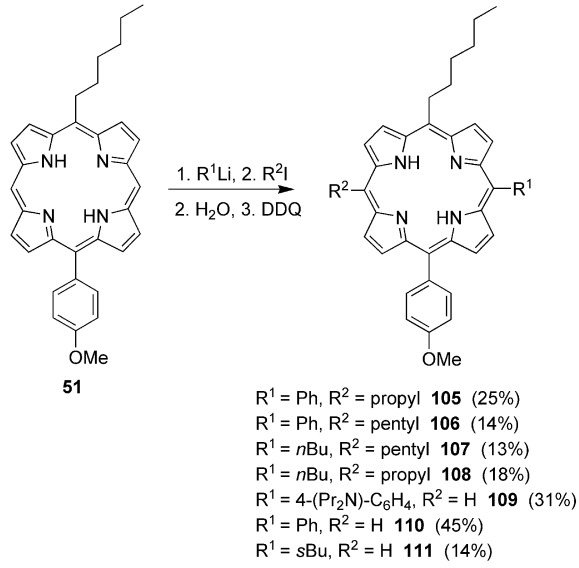
Scheme 10. Synthesis of an 5,10-A_2BC-porphyrin via anion trapping.

Synthesis of ABCD-Type Porphyrins

On the basis of the outline given above three approaches were investigated. These include one-pot anion trapping reactions, sequential RLi reactions and Pd-catalyzed reactions of bromoporphyrins.

One-Pot Reactions

First we investigated the synthesis of ABCD-type porphyrins through a one pot reaction. As described, this was based on the reaction of porphyrins with RLi with formation of an anionic intermediate[16] that can be trapped with electrophiles followed by oxidation.[12,14] For example, the 5,15-disubstituted AB-type porphyrin [5-hexyl-15-(4-methoxyphenyl)porphyrin] (**51**) was treated with phenyllithium in dry THF with formation of an anion that could be trapped with alkyl iodides (*n*-propyl iodide or *n*-pentyl iodide) to yield the tetra-*meso*-substituted free base ABCD-porphyrins **105** and **106** in yields of 25 and 14%, respectively (Scheme 11). In a similar manner, reaction of **51** with *n*-butyllithium/*n*-propyl iodide gave porphyrin **108** and reaction with *n*-butyllithium/*n*-pentyl iodide gave compound **107** in 13 and 18% yield, respectively (Scheme 11).



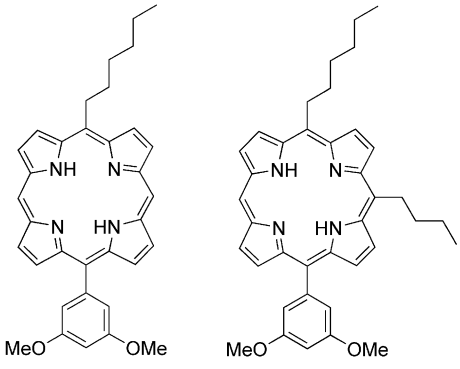
Scheme 11. Reactions of **51** with R^1Li/R^2I combinations.

Typically, three to five equivalents of the organolithium reagents were used and more than ten equivalents of alkyl iodides. Complete trapping of the anionic complex formed with electrophiles required long reaction times under heating (12–24 h at 70 °C) after addition of RI. Nevertheless, the reaction appears difficult to control. Reaction of **51** with *sec*-butyllithium/*n*-propyl iodide or with *sec*-butyllithium/*n*-pentyl iodide in dry THF and subsequently hydrolysis with water and oxidation with DDQ yielded the new free base ABC-porphyrin **111** in 14% yield without formation of the *meso*-tetrasubstituted porphyrin. Similarly, **51** reacted with phenyllithium in dry THF followed by addition of 3-iodopropionic acid or with phenyllithium followed by addition of 3-(iodomethyl)pyridine hydrogen iodide under the same conditions to the ABC-porphyrin **110** in 45% yield, again without any formation of ABCD-porphyrins. Mechanistically the formation of the ABC-porphyrins can be explained by a shift in the equilibrium from the carbanionic intermediate to a phlorin-type intermediate. This is more easily hydrolyzed and oxidized to the ABC-porphyrin than undergoing an electrophilic attack.

Treatment of **51** with *p*-hydroxyphenyllithium/*n*-pentyl iodide or with *p*-hydroxyphenyllithium/*n*-propyl gave no reaction. In contrast reaction with phenyllithium/5-iodouracil (dissolved in 2 mL DMF) or with *p*-hydroxyphenyllithium/3-(iodomethyl)pyridine hydrogen iodide in dry THF and boiling the reaction mixture resulted in the formation of polar blue and black materials, indicating ring-opening reactions.

Similar observations were made with porphyrin **112**. For example, reaction with *n*-butyllithium/*n*-propyl iodide or with *n*-butyllithium/*n*-pentyl iodide gave only the ABC-porphyrin **113** in 15% yield. Various other combinations of

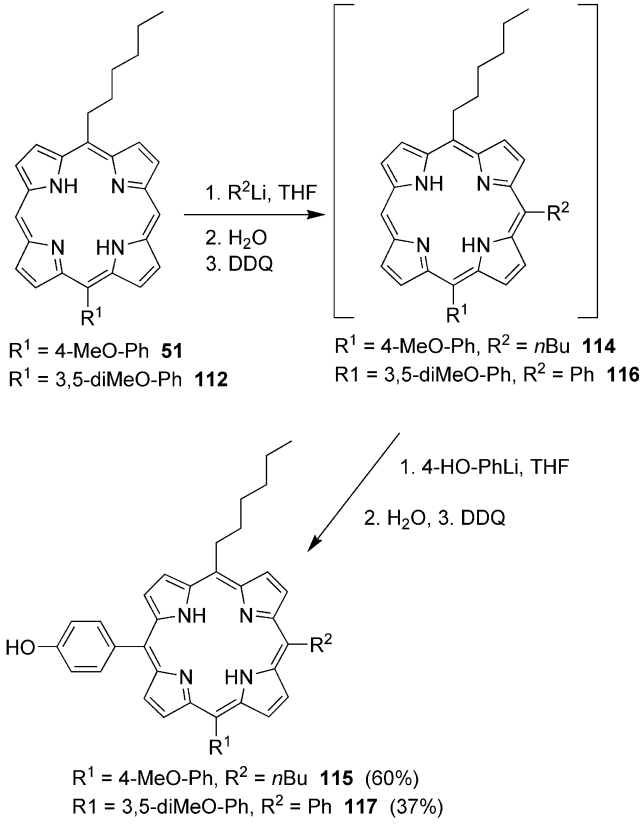
organolithium reagents and alkyl, aryl or heterocyclic iodides together with a wide varity of AB-porphyrins with different functional groups were tested for the synthesis of ABCD-porphyrins but failed to do so. In some cases this is probably due to the inability of the in situ formed ABC-porphyrin intermediate to react with the electrophilic iodide reagents.



112 **113**

Sequential Reactions with RLi

Next, we attempted the preparation of ABCD-type porphyrins by a two-step synthesis through functionalization of the respective AB-porphyrins by two S_NAr reactions with organolithium reagents, first to the ABC-porphyrins (see above) and then to ABCD-type porphyrins. Target compounds were biologically relevant ABCD-porphyrins carrying both precursors for *p*-hydroxyphenyl groups and various alkyl chains.

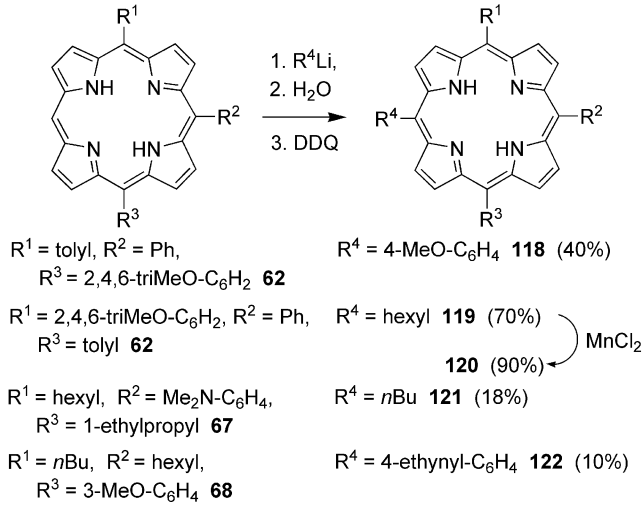


Scheme 12. Transformation of AB-porphyrins to ABCD-porphyrins.

Here, porphyrin **51** was reacted to the ABC-porphyrin **114** by the addition of *n*-butyllithium. The compound was not characterized but added directly to a solution of *p*-hydroxyphenyllithium followed by addition of water and DDQ to form the ABCD-porphyrin 5-butyl-10-hexyl-15-*p*-hydroxyphenyl-20-(4-methoxyphenyl)porphyrin (**115**) in 60% yield (Scheme 12). Using a similar sequence with porphyrin **112**, PhLi and 4-hydroxyphenyllithium, porphyrin **117** was obtained in 37% yield. Similar results were obtained when using ABC-type porphyrins for conversion to the respective ABCD-type systems (see below). The results indicate that the two-step synthesis might be the method of choice for the preparation of functionalized ABCD-porphyrin in acceptable yields as the complete synthetic pathway gave higher overall yields compared to the one-pot procedure.

Reaction of ABC-Porphyrins with RLi

Obviously another possibility is the use of ABC-type porphyrins for reactions with RLi, formally as the last step in a sequence of four reactions starting with porphyrin to yield ABCD-porphyrins. Scheme 13 outlines some of the results. For example, preparation of the ABCD-type porphyrin **118** was possible through reaction of **62** with 4-methoxyphenyllithium in 40% yield. In a similar manner the porphyrins **119** to **122** were accessible in varying yields. In order to prevent β-addition reactions the number of RLi equivalents has to be kept at a minimum for the conversion ABC → ABCD. To some extent, this accounts for the relatively low yields encountered in these reactions.



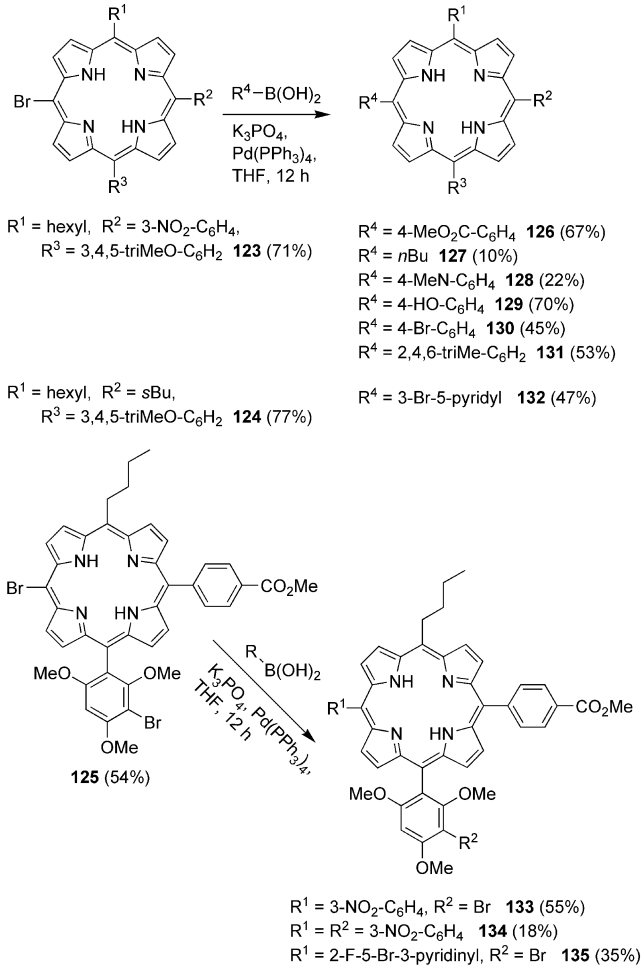
Scheme 13. Transformation of ABC-porphyrins to ABCD-porphyrins via S_NAr.

Nevertheless, these reactions show that, in principle, it is possible to sequentially substitute porphyrin with four different residues using RLi reagents. Admittedly, this method works much better, i.e. with higher yields, for the more soluble octaethylporphyrins where introduction of the

first three *meso* residues can be accomplished in quantitative yield and only introduction of the D residue gives lower yields.[34]

Synthesis of ABCD-Porphyrins Through Pd-Catalyzed Reactions

Having the ABC-type porphyrins in hand, another possibility for the construction of ABCD-type porphyrins was obvious. This involved bromination of the ABC-porphyrins, followed by Pd-catalyzed C–C couplings. The bromination of ABC-porphyrins was achieved easily in good yields. For example, compounds **123** and **124** were obtained in 71 and 77% yield, respectively (Scheme 14). Upon reaction of **82** with NBS a new reaction was observed. The product **125** showed that both *meso* bromination and bromination of the 2,4,6-trimethoxyphenyl residue had occurred in 54% yield. Similar reactions have been observed in the literature for other systems.[35]



Scheme 14. Transformation of ABC-porphyrins to ABCD-porphyrins via Suzuki reactions.

The bromo-ABC-porphyrins were then subjected to Suzuki coupling conditions similar to those used for the preparation of ABC-porphyrins from AB-type systems (see above). As shown in Scheme 14 the reactions works well, although the yields vary significantly and depend on the porphyrin and boron coupling partner used. In some cases (e.g. **127**) debromination of the starting material (to **85**) was observed. The dibromo derivative **125** was also subjected to the coupling conditions to investigate the reactivity of the two different bromo residues. Reaction with 3-nitrophenylboronic acid gave a mixture of the doubly substituted product **134** and compound **133** where only the porphyrin *meso* bromo residue had reacted.

Structural Studies

Despite many attempts only two crystals of sufficient quality for single-crystal X-ray determination could only be grown for two compounds. These were the closely related 5,15-dibromo compounds **79** (Figure 1) and **81** (Figure 2) which differ only in the steric demand of one meso aryl residue (2,4,6-trimethoxyphenyl in **79** vs. 3,4,5-trimethoxyphenyl in **81**). As expected for an unsymmetrical compound[36] **79** forms weakly π-stacked dimers in the crystal with a hexyl chain on the same face as a neighbouring aryl group, i.e. antiparallel layers. In compound **81** the intermolecular separation is much larger and parallel layers are formed. The closest contact observed is a Br–CH_2 interaction (Br2···H10G, 2.883 Å). As shown in Table 1 both structures exhibit only very minor deviations from planarity. The largest deviations are observed for the b-positions (0.03–

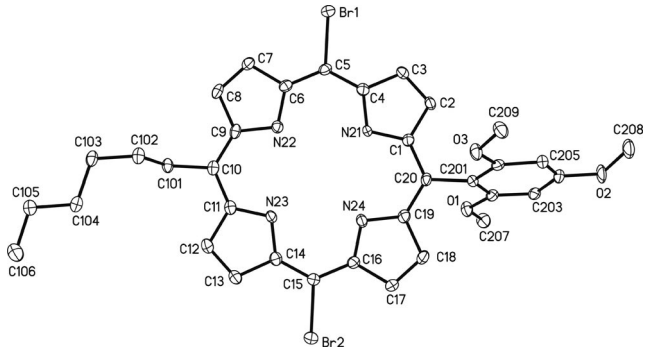


Figure 1. View of the molecular structure of **79** in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are for 50% occupancy.

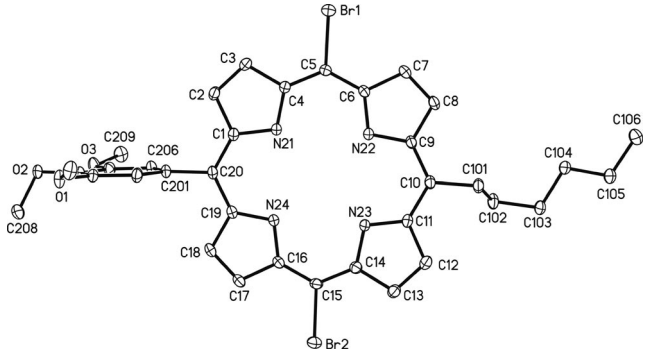


Figure 2. View of the molecular structure of **81** in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are for 50% occupancy.

0.27 Å in 77 and 0.15–0.32 Å in 81). These deviations are in line with crystal packing and minor steric effects to be expected for this class of compounds.[38]

Table 1. Selected structural and conformation parameters [Å] for **79** and **81**.

Compound	**79**	**81**
[times][a]	2.064	2.056
Ξ[b]	0.013	0.039
Δ24[c][37]	0.06	0.15
ΔC_m[d]	0.06	0.09
δC-5[e]	0.04	0.11
δC-10[e]	0.11	0.08
δC-15[e]	0.07	0.09
δC-20[e]	0.02	0.07

[a] Core size, average vector length from the geometric centre of the four nitrogen atoms to the nitrogen atoms. [b] Core elongation parameter defined as the difference between the vector lengths (|N21–N22| + |N23–N24|)/2 – (|N22–N23| + |N21–N24|)/2. [c] Average deviation of the 24 macrocycle atoms from their least-squares plane. [d] Average deviation of the C_m carbon atoms from the 4N-plane. [e] Average deviation of the C_m carbon atom from the 4N-plane.

In conformational terms the main difference between both compounds is the tilt angle between the trimethoxyphenyl residue and the least-squares-plane of the macrocycle. In compound **81** the tilt angle is 94.4°, i.e. the residue is orthogonal to the molecular plane. In the compound **79** the tilt angle is 70.6° which is more in line with those of other *meso* arylporphyrins.[36a]

Conclusions

A full analysis of the synthesis of all members of the ABCD-type porphyrin series by using porphyrin reactions with organolithium reagents and Pd-catalyzed coupling reactions has been given. As shown, the synthesis of the 5,15-A_2 starting materials is still best accomplished by condensation methods. Reaction of A-porphyrins with RLi works but is somewhat problematic due to the formation of regioisomers and multiple alkylation products. Here additional synthetic developments are required.[24] Nevertheless, the AB-porphyrins are suitable starting materials for ABC-type systems through nucleophilic substitution, and the reactions give good yield. Additionally, Pd-catalyzed reactions of appropriately brominated systems can be used, but they require the separation of the mono- and dibromo starting materials. The ABC-porphyrins can be transformed with RLi reagents to the respective ABCD-type systems, but the yields are somewhat unsatisfactory and for sterically hindered systems side reactions may be observed. Similarly, AB-systems can be converted via RLi/RI to ABCD-porphyrins, again with low yields. Here, use of Pd-catalyzed reactions is preferred although the RLi method gives easier access to alkyl-substituted systems. Monobromination of ABC-porphyrins proceeds well, and the subsequent coupling reactions give acceptable yields. In order to optimize the overall yields, a combination of both methods is necessary. Overall, a use of either method for the individual steps in the sequence A→AB→ABC→ABCD porphyrins can give almost any desired ABCD-porphyrins.

Experimental Section

General Methods: All chemicals used were of analytical grade and purified before use. Dichloromethane was dried with phosphorus pentoxide followed by distillation; THF was dried with sodium followed by distillation. Silica gel 60 (Merck) was used for column chromatography unless otherwise noted. Analytical thin-layer chromatography (TLC) was carried out using silica gel 60 plates (fluorescence indicator F_{254}; Merck). Melting points are uncorrected and were measured with a Reichert Thermovar instrument. NMR spectra were recorded using a Bruker AM 270 instrument (270 MHz), a Bruker DPX 400 (400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR) or a Bruker AV 600 (600.13 MHz for ^{1}H NMR and 150.90 MHz for ^{13}C NMR) instrument. Chemical shifts are given in ppm and referenced to the TMS signal as internal standard. The assignment of the signals was confirmed by 2D spectra (COSY, HMBC, HMQC) except for those porphyrins with low solubility. Electronic absorption spectra were recorded with a Specord S10 instrument (Zeiss) using CH_2Cl_2 as solvent. Mass spectra were recorded using a Varian MAT 711 or MAT 112 S mass spectrometer using the EI technique with a direct insertion probe and an excitation energy of 80 eV. FAB spectra were recorded with CH-5 DF instrument from Varian. HRMS data were determined using a Micromass TOF instrument fitted with an EI probe. Elemental analyses were performed with a Perkin–Elmer 240 analyzer. Data for single-crystal X-ray determinations were collected using Rigaku Saturn-724 system complete with CCD detector utilizing Mo-K_α radiation.

Starting Materials: 5-(*tert*-Butyl)porphyrin (**32**), **33**, **34**, **39**,[18] 5,15-bis(3-methoxyphenyl)porphyrin (**58**),[11] **48**,[11] **87**,[11] **88**,[11] 5-(4-ethynylphenyl)-10,20-diphenylporphyrin (**96**),[15] 5,15-dihexylporphyrin (**18**),[11] 5-hexyl-15-(4-methoxyphenyl)porphyrin (**51**),[11] and 5-hexyl-15-(3,5-dimethoxyphenyl)porphyrin (**112**),[11] were prepared following published procedures.

5-(4-Methoxycarbonylphenyl)porphyrin (9): Dry dichloromethane (2 L) was placed in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane (600 mg, 4 mmol), 2-(hydroxymethyl)pyrrole (680 μL, 7.8 mmol), and methyl 4-formylbenzoate (630 mg, 3.8 mmol) were added. The flask was shielded from ambient light and then 1.40 mL (1.8 mmol) of trifluoroacetic acid were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.72 g (12 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Next, 3 mL of triethylamine were added and the reaction mixture was stirred for 15 min. The reaction mixture was filtered through followed by chromatography on silica using dichloromethane as eluent. The first fraction was porphyrin (≈ 10 mg), followed by the title compound and traces of 5,15-bis-[4-(methoxycarbonyl)phenyl]porphyrin. Recrystallization from CH_2Cl_2/MeOH gave 128 mg of red crystals (0.29 mmol; 8%); m.p. >300 °C. R_f = 0.77 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –3.60 (br. s, 2 H, N*H*), 4.15 (s, 3 H, COO*CH*$_3$), 8.33 (m, 2 H, phenyl-*H*), 8.46 (m, 2 H, phenyl-*H*), 9.06 (d, *J* = 4 Hz, 2 H, β-pyrrole-*H*), 9.41 (d, *J* = 4 Hz, 2 H, β-pyrrole-*H*), 9.50 (m, 4 H, β-pyrrole-*H*), 10.25 (s, 1 H, C15-*H*), 10.33 (s, 2 H, C10-*H* and C20-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 400 (4.85), 422 (3.77), 586 (3.54). MS (EI, 80 eV, 140 °C): *m*/*z* (%) = 444 (100) [M^+], 429 (1) [$M^+ - CH_3$], 413 (1) [$M^+ - CH_3O$], 385 (9) [$M^+ - C_2H_3O_2$], 222 (1) [M^{2+}]. HRMS: calcd. for $C_{28}H_{20}N_4O_2$ 444.15863; found

444.15649. $C_{28}H_{20}N_4O_2$ (444.49): calcd. C 75.66, H 4.54, N 12.60; found C 75.98, H 4.76, N 12.23.

3,5-Bis(*tert*-butyl)benzaldehyde (10): Prepared in 58% yield following the procedure given by Newman and Lee;[39] m.p. 84 °C; lit. 84–85 °C. ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 9.99 (s, 1 H, C*H*O), 7.71 (m, 3 H, Ar-H$_o$, Ar-H_p), 1.35 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 193.16, 151.87, 136.24, 128.87, 124.13, 34.97, 31.31 ppm. MS (40 °C, 80 eV): *m*/*z* = 219 (3) [M + 1]$^{\cdot+}$, 218 (16) [M]$^{\cdot+}$, 203 (100) [M – CH_3]$^{\cdot+}$, 175 (3) [M – C_3H_7]$^{\cdot+}$), 57 (3) [M – $C_{11}H_{13}O$]$^{\cdot+}$).

5-[3,5-Bis(*tert*-butyl)]dipyrromethane (12): Prepared in 48% yield following the procedure given by Beavington and Burn.[40] ^{13}C NMR (63 MHz, $CDCl_3$): δ = 150.80, 140.84, 132.94, 122.67, 120.81, 116.96, 108.25, 107.10, 44.45, 34.79, 31.44 ppm.

5-[3,5-Bis(*tert*-butyl)]porphyrin (13): Dipyrromethane (0.34 g, 2.3 mmol) and the 5-substituted dipyrromethane **12** (2.3 mmol) were dissolved in 1.2 L dichloromethane and degassed under Ar for 10 min. Next, trimethyl formiate (38 mL, 0.35 mmol) was added and the solution treated dropwise with a solution of trichloroacetic acid (17.65 g, 108 mmol) in 460 mL dichloromethane. The mixture was stirred for 4 h at room temp. and then mixed with pyridine (31.2 mL, 0.39 mol) and stirring was continued for another 17 h. The solution was purged with oxygen for 10 min for oxidation and filtered through silica gel. After removal of the solvent in vacuo column chromatography (*n*-hexane/ethyl acetate; 5:1, v/v) gave a purple solid as the main fraction after removal of the solvent (23 mg, 0.05 mmol, 4%); m.p. 273 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 10.32 (s, 2 H, *meso*-$H^{10,20}$), 10.24 (s, 1 H, *meso*-H^{15}), 9.49 (AB, $^3J_{12,13}$ = 4.6, $^3J_{17,18}$ = 4.6 Hz, 2 H, β-pyrrole-$H^{12,18}$), 9.46 (AB, $^3J_{12,13}$ = 4.6, $^3J_{17,18}$ = 4.6 Hz, 2 H, β-pyrrole-$H^{13,17}$), 9.41 (AB, $^3J_{2,3}$ = 4.6, $^3J_{7,8}$ = 4.6 Hz, 2 H, β-pyrrole-$H^{2,8}$), 9.14 (AB, $^3J_{2,3}$ = 4.6, $^3J_{7,8}$ = 4.6 Hz, 2 H, β-pyrrole-$H^{3,7}$), 8.12 (m, 2 H, Ar-H_o), 7.83 (m, 1 H, Ar-H_p), 1.55 [s, 18 H, C(CH_3)$_3$], –3.58 (bs, 2 H, N*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.00, 140.70, 131.71, 131.17, 130.99, 130.10, 121.15, 104.56 (C10, C20), 103.30 (C15), 35.08 (C31, C35), 31.76 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 401 (5.33), 497 (4.19), 528 (3.44), 569 (3.70), 623 (2.78). MS (160–170 °C, 80 eV): *m*/*z* = 499 (36) [M + 1]$^{\cdot+}$, 498 (100) [M]$^{\cdot+}$. HRMS: calcd. for $C_{34}H_{34}N_4$ 498.27835; found 498.27444.

5,15-Bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]porphyrin (14): Dipyrromethane (1.38 g, 9.25 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2.25 g, 9.71 mmol) were added to a 2 L three-necked flask containing dichloromethane (1 L) under Ar. After 30 min TFA (0.1 g, 0.925 mmol) was added and the mixture was stirred for 12 h. Next two equiv. DDQ (4.2 g, 18.5 mmol) were added and stirring was continued for 60 min at room temp. followed by addition of 1 mL triethylamine. Without evaporation of solvent, the crude reaction mixture was passed through a filter containing silica gel, using dichloromethane as eluent. The solvent was evaporated and the resulting residue was recrystallized from dichloromethane/methanol to give purple crystals (1.92 g, 58.2%); m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 10.35 (s, 2 H, *meso*-*H*), 9.42 (d, *J* = 4.64 Hz, 4 H, β-pyrrole-*H*), 9.1 (d, *J* = 4.64 Hz, 4 H, β-pyrrole-*H*), 8.3 (dd, *J* = 9.065 Hz, 8 H, Ph-*H*), 1.55 (s, 24 H, CH_3), –3.1 (br. s, 2 H, N*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 133.97, 132.86, 131.24, 130.57, 104.90, 83.70, 28.91, 24.62, 24.42 ppm. UV/Vis (THF): $\lambda_{max.}$ (log ε) = 406 (4.42), 502 (4.21), 535 (3.95), 576 (3.84), 631 nm (364). HRMS: calcd. for $C_{44}H_{44}B_2N_4O_4$ 714.4666; found 715.3600.

{5,15-Bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]porphyrinato}nickel(II) (15): Free base porphyrin **14** (626.5 mg, 0.877 mmol) and nickel acetylacetonate (900 mg, 3.51 mmol) were dissolved in toluene (200 mL) and stirred for 4 d at 110 °C. The crude reaction mixture was passed through a filter containing silica gel, using CH_2Cl_2 as eluent. The solvent was evaporated and the resulting residue was recrystallized from dichloromethane/methanol to yield purple crystals (0.75 mmol, 86%); m.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 9.97 (s, 2 H, *meso*-*H*), 9.21 (m, 2 H, β-pyrrole-*H*), 8.95 (m, 2 H, β-pyrrole-*H*), 8.2 (d, *J* = 7 Hz, 2 H, β-pyrrole-*H*), 8.11 (d, *J* = 7 Hz, 2 H, β-pyrrole-*H*), 7.97 (d, *J* = 7.6 Hz, 2 H, Ph-*H*), 7.89 (d, *J* = 7.6 Hz, 2 H, Ph-*H*), 1.53 (s, 24 H, CH_3) ppm. UV/Vis(THF): $\lambda_{max.}$ (log ε) = 400 (5.2), 515 (4.17), 546 nm (3.94). HRMS: calcd. for $C_{44}H_{42}B_2N_4O_4Ni$ 770.2746; found 770.2750.

5,10-Bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]porphyrin (16): Tripyrrane (2 g, 8.8 mmol), pyrrole (0.6 g, 8.88 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (4.22 g, 18.2 mmol) were added under Ar at room temperature to a 2 L three-necked flask containing 1 L of dichloromethane. After 30 min, TFA (0.127 g, 0.888 mmol) was added, and mixture was stirred for 12 h. Then four equiv. of DDQ (8 g, 35.2 mmol) were added and stirring was continued for 60 min at room temp. followed by addition of 1 mL NEt_3. The crude reaction mixture was passed through a filter containing silica gel, eluting with CH_2Cl_2. The solvent was evaporated to near dryness and then absorbed onto 5 g of silica gel. The absorbed sample was added to the top of the column containing silica gel and with *n*-hexane/acetone (1:1, v/v). The product was isolated as purple crystals in 0.4% yield (27 mg); m.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 10.27 (s, 2 H, *meso*-*H*), 9.49 (s, 2 H, β-pyrrole-*H*), 9.37 (d, *J* = 4.08 Hz, 2 H, β-pyrrole-*H*), 9.04 (d, *J* = 4.68 Hz, 2 H, β-pyrrole-*H*), 8.93 (s, 2 H, β-pyrrole-*H*), 8.26 (dd, *J* = 7.6 Hz, 8 H, Ph-*H*), 1.58 (s, 24 H, CH_3), –3.34 (br. s, 2 H, N*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 24.61, 29.27, 83.7, 119.5, 103.84, 132.57, 133.73, 144.58 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 407 (4.55), 503 (3.28), 576 (2.79), 630 nm (2.30). HRMS: calcd. for $C_{44}H_{44}B_2N_4O_4$ 714.4666; found 715.3685.

General Procedure for the Synthesis of AB-Type Porphyrins (Mixed Condensation): A three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser was charged with 2 L dichloromethane. Dipyrromethane (1200 mg, 8.2 mmol), the appropriate aldehyde (4.14 mmol), and the other appropriate aldehyde (4.15 mmol) were added. Then 140 µL (1.8 mmol) TFA were added and the reaction mixture was stirred for 16 h at 20 °C. Next DDQ (2.77 g, 12.2 mmol) in 100 mL of dry dichloromethane was added and the mixture was stirred for 1 h. Subsequently, 6 mL of NEt_3 were added and the reaction mixture was filtered through 600 mL of silica, eluting with dichloromethane. Column chromatography eluting with dichloromethane gave the fractions which were recrystallized from CH_2Cl_2/MeOH to yield purple crystals.

5-Hexyl-15-(4-methoxycarbonylphenyl)porphyrin (17): The procedure followed that given above using dipyrromethane (1200 mg, 8.2 mmol), methyl 4-formylbenzoate (680 mg, 4.14 mmol), and heptanal (0.580 mL, 4.15 mmol). Column chromatography eluting with dichloromethane gave three fractions which were recrystallized from CH_2Cl_2/MeOH to yield purple crystals. The first fraction was 5,15-dihexylporphyrin (**18**), 181 mg, 0.378 mmol, 18%), the second fraction 5-hexyl-15-(4-methoxycarbonylphenyl)porphyrin (**17**, 525 mg, 0.99 mmol; 23%), and the third fraction 5,15-bis(4-methoxycarbonylphenyl)porphyrin (**19**, 168 mg, 0.29 mmol, 14%). **17:** M.p. 256 °C. R_f = 0.37 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –3.05, –3.04 (each s, 1 H, N*H*), 0.92 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 1.41 (m, 2 H, CH_2CH_3), 1.53 (m, 2 H, $CH_2CH_2CH_3$),

1.80 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.59 (m, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 4.11 (s, 3 H, $COOCH_3$), 5.01 (t, J = 8 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 8.33 (m, 2 H, Ph-*H*), 8.43 (m, 2 H, Ph-*H*), 8.93 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 9.36 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 9.43 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 9.61 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 10.22 (s, 2 H, *meso*-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 407 (5.18), 503 (4.07), 536 (3.63), 576, 640 nm (3.55). HRMS: calcd. for $C_{34}H_{32}N_4O_2$ 528.2525; found 528.2749. $C_{34}H_{32}N_4O_2$ (528.65): calcd. C 77.25, H 6.10, N 10.60; found C 77.21, H 6.49, N 10.99.

5,15-Bis(4-methoxycarbonylphenyl)porphyrin (19): Obtained from the synthesis of **17**; m.p. >300 °C. R_f = 0.11 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –3.13 (s, 2 H, N*H*), 4.12 (s, 6 H, $COOCH_3$), 8.37 (m, 4 H, Ph-*H*), 8.45 (m, 4 H, Ph-*H*), 9.13 (d, J = 5 Hz, 4 H, β-pyrrole-*H*), 9.38 (d, J = 5 Hz, 4 H, β-pyrrole-*H*), 10.18 (s, 2 H, *meso*-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ = 405, 506, 534, 574, 639 nm. HRMS: calcd. for $C_{36}H_{26}N_4O_4$ 578.1954; found 578.2314. $C_{36}H_{26}N_4O_4$ (578.63): calcd. C 74.73, H 4.53, N 9.68; found C 74.51, H 4.78, N 9.57.

General Procedure for the Synthesis of 5,15-AB-Type Porphyrins (Organolithium Reaction): For example, 5-(*tert*-butyl)porphyrin (**32**, 100 mg, 0.272 mmol) was dissolved in 80 mL dry THF under argon and the reaction mixture was cooled to –78 °C. *n*BuLi (0.435 mL, 1.088 mmol) was added dropwise over 15 min via syringe. The cold bath was removed and stirring continued 1.5 h at room temperature. 0.5 mL H_2O was added and stirring continued 15 min. Then DDQ (243.3 mg, 1.088 mmol) was added in 10 mL THF and the reaction mixture was stirred for an additional hour. The reaction mixture was filtered through silica gel, followed by evaporation of the solvent.

5-(*n*-Butyl)-15-(*tert*-butyl)porphyrin (38): Prepared according to the general procedure using 5-(*tert*-Butyl)porphyrin (**32**, 100 mg, 0.272 mmol), *n*BuLi (0.435 mL, 1.088 mmol) and DDQ (243.3 mg, 1.088 mmol). The crude reaction mixture was purified by column chromatography eluting with *n*-hexane/CH_2Cl_2 (2:1, v/v). The first fraction was 5-(*n*-butyl)-15-(*tert*-butyl)porphyrin (**38**, 20 mg, 0.047 mmol, 17%) as purple crystals, the second fraction 5-(*n*-butyl)-10-(*tert*-butyl)porphyrin (**39**, 8 mg, 0.018 mmol, 7%) as purple crystals, followed by starting material (10 mg, 0.027 mmol, 10%). Compound **38**: M.p. > 300 °C. R_f = 0.6 (*n*-hexane/CH_2Cl_2, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –1.97 (s, 2 H, N*H*), 1.15 (t, J = 7.0 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.81 (m, 2 H, $CH_2CH_2CH_2CH_3$) 2.50 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.61 [s, 9 H, $C(CH_3)_3$], 4.94 (t, J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 9.24 (d, J = 4.68 Hz, 2 H, β-pyrrole-*H*), 9.34 (d, J = 4.1 Hz, 2 H, β-pyrrole-*H*), 9.50 (d, J = 4.68 Hz, 2 H, β-pyrrole-*H*), 9.86 (d, J = 4.68 Hz, 2 H, β-pyrrole-*H*), 10.06 (s, 2 H, *meso*-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.7, 23.1, 29.2, 33.4, 39.8, 40.0, 40.3, 103.9, 119.1, 127.1, 129.7, 130.7, 131.0, 141.4, 143.0, 146.6, 147.7 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 405 (4.68), 509 (3.62), 542 (3.52), 542 (3.52), 636 nm (3.22). MS (EI, 250 °C, 80 eV): m/z = 450 (100) $[M]^{\cdot+}$, 435 (72) $[M - CH_3]^+$, 394 (10) $[M - C_4H_9 + H]^{\cdot+}$, 379 (7) $[M - C_5H_{11}]^+$, 323 (17) $[M - C_4H_9 + H - C_5H_{11}]^+$, 225 (3) $[M]^{2+}$. HRMS: calcd. for $C_{28}H_{31}N_4$ 423.2549; found 423.2551.

5-(*n*-Butyl)-10-(*tert*-butyl)porphyrin (39): Derived from the synthesis of **38**; m.p. > 300 °C. R_f = 0.4 (*n*-hexane/CH_2Cl_2, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.41 (s, 2 H, N*H*), 1.15 (t, J = 7.01, Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.81 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.52 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.46 [s, 9 H, $C(CH_3)_3$], 4.93 (t, J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 9.11 (d, J = 4.67 Hz, 1 H, β-pyrrole-*H*), 9.2 (d, J = 4.67 Hz, 1 H, β-pyrrole-*H*), 9.25 (m, 3 H, β-pyrrole-*H*), 9.5 (d, J = 4.68 Hz, 1 H, β-pyrrole-*H*), 9.69 (d, J = 5.26 Hz, 1 H, β-pyrrole-*H*), 9.79 (m, J = 4.68 Hz, 2 H, β-pyrrole-*H*, *meso*-*H*), 10.06 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.6, 13.7, 19.2, 22.2, 22.5, 23.2, 26.6, 28.9, 29.2, 29.7, 30.5, 31.4, 32.3, 35.0, 36.6, 36.9, 40.2, 102.0, 103.3, 120.2, 125.5, 127.4, 128.3, 129.1, 129.2, 130.0, 130.4, 130.7, 131.0, 167.2 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 412 (4.81), 513 (3.80), 551 (3.32), 591 (3.47), 645 nm (3.10). HRMS: calcd. for $C_{28}H_{31}N_4$ 423.2549; found 423.2553.

5-*tert*-Butyl-15-[4-(dimethylamino)phenyl]porphyrin (41): A 250-mL Schlenk flask was charged with 4-bromo-*N*,*N*-dimethylaniline (11 equiv.) dissolved in 20 mL diethyl ether. A 2.5 M solution of *n*BuLi in hexane (1 equiv.) was added dropwise over 45 min under Ar at –78 °C. The cold bath was removed and the solution stirred for 2 h at room temp. A 100-mL Schlenk flask was charged with a solution of the porphyrin **32** (53 mg, 0.14 mmol, 1 equiv.) in 50 mL THF and cooled to –70 °C. This solution was then added to the solution of the in situ generated LiR reagent (cooled to –40 to –70 °C, 11 equiv.). The colour changed from red to green-brown. The cold bath was removed and the solution stirred for 2 h at room temp. Next 5 mL water in 5 mL THF was added and this was accompanied by a colour change to green. The solution was stirred for 30 min followed by addition of 10 equiv. DDQ which resulted in a colour change to red. The mixture was filtered through silica gel and then neutral alumina eluting with dichloromethane followed by removal of the solvent in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane = 1:3, v/v and CH_2Cl_2/*n*-hexane = 1:7, v/v) gave 5-*n*-butyl-15-*tert*-butylporphyrin (**38**) (2 mg, < 0.01 mmol, 5%) as the first fraction. The title compound **41** followed as the second fraction to yield purple crystals after recrystallization from CH_2Cl_2/MeOH (19 mg, 0.04 mmol, 36%); m.p. 270 °C (decomp.). R_f = 0.4 (CH_2Cl_2/*n*-hexane, 9:1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 10.07 (s, 2 H, *meso*-*H*), 9.85 (AB, ^3J = ^3J = 4.8 Hz, 2 H, β-pyrrole-$H^{3,7}$), 9.26 (AB, ^3J = ^3J = 4.7 Hz, 2 H, β-pyrrole-$H^{12,18}$), 9.23 (AB, ^3J = ^3J = 4.8 Hz, 2 H, β-pyrrole-$H^{2,8}$), 9.10 (AB, ^3J = ^3J = 4.7 Hz, 2 H, β-pyrrole-$H^{13,17}$), 8.12 (AB, ^3J = ^3J = 8.2 Hz, 2 H, Ar-H_o), 7.15 (AB, ^3J = ^3J = 8.2 Hz, 2 H, Ar-H_m), 3.23 [s, 6 H, $N(CH_3)_2$], 2.60 [s, 9 H, $C(CH_3)_3$], –1.93 (br. s, 2 H, N*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.04, 148.10, 147.61, 143.90, 142.10, 135.96, 131.09, 131.06, 130.62, 130.13, 128.78, 126.66, 120.14, 111.38, 104.69, 40.90, 40.73, 40.41 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 413 (4.78), 513 (4.07), 554 (4.07), 581 (3.89), 641 nm (3.70). MS (250 °C, 80 eV): m/z = 485 (92) $[M]^{\cdot+}$, 470 (100) $[M - CH_3]^+$, 429 (25) $[M - CH_3 - C_2H_3N]^+$, 243 (23) $[M]^{2+}$, 295 (30) $[M - CH_3]^{2+}$. HRMS: calcd. for $C_{32}H_{31}N_5$ 485.2579; found 485.2562.

General Procedure for the Synthesis of 5,10-AB-Type Porphyrins: A 250-mL Schlenk flask was charged with the porphyrin (1 equiv.) in 50 mL THF under Ar and cooled to –70 °C. The LiR reagent (hexylllithium, 3.5 equiv. of a 2.5 M solution in hexane) was added dropwise over 15 min and the colour changed from red to green-brown. The cold bath was removed and the solution stirred for 30 min at room temp. Next water (1 mL in 5 mL THF) was added and the colour changed to green. The solution was stirred for 15 min and then oxidized with DDQ followed by stirring for a further 30 min accompanied by a colour change to red. The mixture was fitered through silica gel eluting with dichloromethane and the solvents removed in vacuo.

5-(1-Ethylpropyl)-10-hexylporphyrin (42): Prepared using the general procedure given above using porphyrin **33** (1 equiv.) and hexyllithium (3.5 equiv. of a 2.5 M solution in hexane). Column chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (1:1, v/v) gave a first fraction containing a mixture of di- and higher

alkylated species followed by the title compound as purple crystals after recrystallization from CH_2Cl_2/MeOH/H_2O (37.1 mg, 0.08 mmol, 59%); m.p. 135 °C. R_f = 0.46 (*n*-hexane/CH_2Cl_2, 1:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.06 (s, 1 H, *meso*-*H*^{15}), 10.01 (s, 1 H, *meso*-*H*^{20}), 9.79 (m, 1 H, β-pyrrole-*H*^{7}), 9.73 (m, 1 H, β-pyrrole-*H*^{3}), 9.65 (m, 1 H, β-pyrrole-*H*^{8}), 9.62 (AB, $^3J_{H12,H13}$ = 4.7 Hz, 1 H, β-pyrrole-*H*^{12}), 9.33 (m, 4 H, β-pyrrole-*H*^{2,13,17,18}), 5.14 [m, 1 H, *m*, C*H*(CH$_2$)$_2$], 5.09 (t, ^3J = 8.2 Hz, 2 H, C*H*$_2$C$_5$H$_{11}$), 3.00, 2.84 [m, 4 H, CH(C*H*$_2$)$_2$], 2.60 (m, 2 H, CH$_2$C*H*$_2$C$_4$H$_9$), 1.87 (m, 2 H, C$_2$H$_4$C*H*$_2$C$_3$H$_7$), 1.55 (m, 2 H, C$_3$H$_6$C*H*$_2$C$_2$H$_5$), 1.43 (m, 2 H, C$_4$H$_8$CH$_2$C*H*$_3$), 0.97 (t, ^3J = 7.4 Hz, 3 H, C$_5$H$_{10}$C*H*$_3$), 0.96 (t, ^3J = 7.3 Hz, 6 H, CH$_2$C*H*$_3$), –3.22 (br. s, 2 H, N*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): $\delta \approx$ 130 (C2, C3, C7, C8, C12, C13, C17, C18), 123.21 (C5), 120.14 (C10), 103.11 (C15), 102.84 (C20), 50.53, 39.06, 36.10, 34.83, 31.94, 30.40, 22.78, 14.13 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 406 (5.58), 504 (4.14), 534 (3.37), 579 (3.60), 634 nm (3.08). MS (EI, 80 eV): *m*/*z* = 464 (100) [M]$^{\cdot+}$, 435 (93) [M – C$_2$H$_5$]$^+$, 393 (20) [M – C$_5$H$_{11}$]$^+$, 364 (11) [M – C$_5$H$_{11}$ – C$_2$H$_5$]$^{\cdot+}$, 335 (10) [M – C$_5$H$_{11}$ – 2C$_2$H$_5$]$^+$, 232 (11) [M]$^{2+}$. HRMS: calcd. for $C_{31}H_{37}N_4$ 465.3018; found 465.3035.

General Procedure for the Synthesis of 5,15-AB$_2$/A$_2$-Type Porphyrins: A 25-mL Schlenk flask was charged with dried porphyrin (0.05 mmol) dissolved in 10 mL THF. The solution was cooled to –80 °C and treated with 0.2 mmol of a 2.5 M solution of hexyllithium (80 μL). The colour changed from red to green-brown and after 10 min changed to purple. The cold bath was removed and the solution stirred for 15 min at room temp. Next water (1 mL) was added and stirring was continued for 15 min. This was accompanied by a colour change to yellow-brown. Then DDQ (0.1 mmol, 23 mg) in 0.4 mL THF was added and the mixture stirred for 15 min until the colour had changed to dark red. The mixture was filtered through silica gel and the solvent removed in vacuo.

5-(3,5-Di-*tert*-butylphenyl)-10,15-dihexylporphyrin (56): Prepared following the above general procedure using porphyrin **13** (23 mg, 0.05 mmol) and a 2.5 M solution of hexyllithium(80 μL, 0.2 mmol). Column chromatography eluting with *n*-hexane/CH_2Cl_2 (1:1, v/v) gave a purple solid (6 mg, 0.01 mmol, 18%); m.p. 192 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.00 (s, 1 H, *meso*-*H*^{20}), 9.61, 9.57 (AB, ^3J = 4.8 Hz, 2 H, β-pyrrole-*H*^{12,13}), 9.54 (AB, ^3J = 4.6 Hz, 1 H, β-pyrrole-*H*^{17}), 9.50 (AB, ^3J = 4.6 Hz, 1 H, β-pyrrole-*H*^{8}), 9.31 (AB, ^3J = 4.6 Hz, 1 H, β-pyrrole-*H*^{18}), 9.21 (AB, ^3J = 4.7 Hz, 1 H, β-pyrrole-*H*^{2}), 8.95 (AB, ^3J = 4.7 Hz, 2 H, β-pyrrole-*H*^{3,7}), 8.05 (d, *J* = 1.9 Hz, 2 H, Ar-*H*$_o$), 7.79 (t, *J* = 1.9 Hz, 1 H, Ar-*H*$_p$), 5.05, 5.00 (t, *J* = 8.1 Hz, 4 H, -C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.57 (m, 4 H, -CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.84 (m, 4 H, -CH$_2$CH$_2$C*H*$_2$CH$_2$-CH$_2$CH$_3$), 1.55 (m, 4 H, -CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.53 [s, 9 H, C(C*H*$_3$)$_3$], 1.41 (m, 4 H, -CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.94 (t, *J* = 7.3 Hz, 6 H, -CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$), –2.91 (s, 2 H, N*H*) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, TMS): δ = 148.85, 140.93, 132.52, 131.27, 130.80, 129.85, 128.47, 127.91, 127.91, 128.24, 120.96, 120.42, 119.29, 103.38, 39.06, 38.80, 36.17, 35.33, 35.06, 31.76, 30.34, 22.77, 14.14 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 413 (5.50), 511 (4.19), 545 (3.78), 588 (3.65), 644 nm (3.54). MS (EI, 80 eV): *m*/*z* = 668 (46) [M + 1]$^{\cdot+}$, 667 (100) [M]$^{\cdot+}$, 610 (9) [M – C$_4$H$_9$]$^{\cdot+}$, 596 (14) [M – C$_5$H$_{11}$]$^{\cdot+}$, 539 (12) [M – C$_9$H$_{20}$]$^{\cdot+}$, 525 (30) [M – C$_{10}$H$_{22}$]$^{\cdot+}$. HRMS: calcd. for $C_{41}H_{48}N_4$ 596.38790; found 596.38421.

5,15-Bis(3-methoxyphenyl)-10-phenylporphyrin (59): Phenyllithium (2 mL of a 1.8 M solution in hexane, 0.06 mmol) was slowly added (ca. 1 h) under argon to a 100-mL Schlenk flask charged with a solution of 5,15-bis(*m*-methoxyphenyl)porphyrin (**58**, 200 mg, 0.38 mmol) in 40 mL of dry THF at –80 °C. The reaction mixture was stirred for 5 h (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:4, v/v) yielding the title compound (163 mg, 0.27 mmol, 71%) as purple crystals; m.p. >300 °C. R_f = 0.52 (ethyl acetate/*n*-hexane, 1:4, v/v). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = –2.91 (s, 2 H, N*H*), 4.02 (s, 6 H, OC*H*$_3$), 7.41 (m, 2 H, Ph-*H*), 7.71–7.92 (m, 9 H, Ph-*H*), 8.29 (m, 2 H, Ph-*H*), 8.96 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.02 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.12 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.33 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 10.19 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 55.06, 104.34, 113.09, 118.94, 120.21, 126.12, 127.19, 130.96, 134.05, 142.11, 142.64, 157.66 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 413 nm (5.17), 441 (3.94), 508 (4.23), 541 (3.73), 582 (3.77), 637 nm (3.52). MS (EI, 80 eV): *m*/*z* (%): 598 (100) [M$^+$], 567 (10) [M$^+$ – 2CH$_3$ – H], 522 (8) [M$^+$ – C$_6$H$_4$], 491 (8) [M$^+$ – 2CH$_3$ – C$_6$H$_5$], 299 (86) [M^{++}]. HRMS: calcd. for $C_{40}H_{30}N_4O_2$ 598.2368; found 598.2356.

5-(4-Hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (60): *n*-Butyllithium (4 mL of a 2.5 M solution in hexane, 10 mmol) was added under argon to a 100-mL Schlenk flask charged with a solution of *p*-bromophenol (0.87 g, 5 mmol) in 10 mL of dry diethyl ether at 0 °C. After addition of *n*-butyllithium the cold bath was removed and stirring was continued for 18 h at room temperature. To the vigorously stirred mixture was added rapidly a solution of 5,15-bis(3-methoxyphenyl)porphyrin (**58**, 200 mg, 0.38 mmol) in 40 mL of dry THF under argon. Further workup followed the procedure for **59**. Final purification by column chromatography on silica gel and elution with ethyl acetate/*n*-hexane (1:1, v/v) gave the title compound (182 mg, 0.29 mmol, 77%) as purple crystals; m.p. >300 °C. R_f = 0.54 (ethyl acetate/*n*-hexane, 2:1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 4.01 (s, 6 H, OCH$_3$), 6.89 (d, *J* = 7.5 Hz, 2 H, Ph-*H*), 7.37 (d, *J* = 7.5 Hz, 2 H, Ph-*H*), 7.66 (t, 2 H, Ph-*H*), 7.88 (m, 4 H, Ph-*H*), 7.90 (s, 1 H, O*H*), 7.97 (d, *J* = 7.5 Hz, 2 H, Ph-*H*), 8.91 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.00 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.12 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.32 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 10.17 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 55.06, 104.22, 112.95, 118.91, 120.25, 127.38, 131.01, 134.33, 135.06, 142.67, 154.87, 157.62 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 414 (5.17), 445 (4.06), 508 (4.17), 542 (3.61), 582 (3.64), 655 nm (3.39). MS (EI, 80 eV): *m*/*z* (%): 614 (38) [M$^+$], 307 (40) [M^{++}]. HRMS: calcd. for $C_{40}H_{30}N_4O_3$ 614.2317; found 614.2288.

General Procedure for the Synthesis of ABC-Type Porphyrins: Porphyrin (0.1 mmol) was dissolved in THF and cooled to –78 °C. Hexyllithium was added dropwise over the course of 15 min. The cold bath was removed and stirring was continued for another 15 min. This was followed by addition of 0.5 mL water in 5 mL THF, stirring for 15 min and addition of 6 mL of a solution of DDQ in THF. The mixture was stirred for 20 min and then filtered through neutral alumina washing with dichloromethane.

5-Hexyl-10-(4-methylphenyl)-20-(2,4,6-trimethoxyphenyl)porphyrin (61): Prepared following the above standard procedure using porphyrin **21** (55 mg, 0.1 mmol). Column chromatography eluting with neat dichloromethane gave the title compound as the single product as a purple solid (59 mg, 0.09 mmol, 90%); m.p. >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.09 (s, 1 H, *meso*-*H*), 9.60

(m, 2 H, β-pyrrole-*H*), 9.30 (m, 2 H, β-pyrrole-*H*), 8.90 (m, 4 H, β-pyrrole-*H*), 8.21 (d, ^3J = 7.35 Hz, 2 H, tolyl-H_m), 7.56 (d, ^3J = 7.35 Hz, 2 H, tolyl-H_o), 6.68 (s, 2 H, Ar-H_o), 5.04 (t, ^3J = 8.09 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.11 (s, 3 H, *p*-OCH_3), 3.50 (s, 6 H, *m*-OCH_3), 2.70 (s, 3 H, C_6H_4-CH_3), 2.56 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.83 (m, 2 H, $CH_2CH_2CH_2CH_2$-CH_2CH_3), 1.54 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.43 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.00 (t, ^3J = 7.30 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), –3.05 (*bs*, 2 H, N*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.99, 161.12, 148.41–145.14, 142.371, 139.80, 137.14, 134.50, 131.02–130.50, 127.25, 119.12–118.56, 104.00, 102.87, 91.00, 56.06, 55.64, 38.81, 35.51, 31.93, 30.34, 22.75, 21.51, 14.14 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 413 (5.45), 511 (4.53), 543 (4.09), 585 (4.03), 641 nm (3.81). MS (270 °C, 8 kV): *m*/*z* = 650.0 (100.00) $[M]^{\cdot+}$, 579.0 (71.47) $[M - C_5H_{11}]^+$, 325.0 (10.91) $[M]^{2+}$. HRMS: calcd. for $C_{42}H_{42}N_4O_3$ 650.32569; found 650.32575.

5-(2-Methoxyphenyl)-10-(4-methylphenyl)-20-(2,4,6-trimethoxyphenyl)porphyrin (63): The free base porphyrin **21** (113 mg, 0.2 mmol) was dissolved in 40 mL abs. THF and cooled to –40 °C. The LiR reagent was added under vigorous stirring, the cold bath removed and the mixture stirred for 1 h. The LiR reagent was prepared by dissolving 1 g bromoanisol (5.4 mmol) in 15 mL abs. ethyl ether in a Schlenk tube. Next 2.2 mL BuLi (2.5 M in *n*-hexane, 5.5 mmol) were added dropwise over 30 min at –78 °C. The cold bath was removed and the mixture stirred for 1 h at room temp. After mixing the two components the red mixture slowly turned brown. Next, 5 mL water in 5 mL THF were added and stirring continued for 30 min. Oxidation was achieved by stirring under air for 16 h. The mixture was filtered through neutral alumina and washed with dichloromethane. Column chromatography eluting with CH_2Cl_2/*n*-hexane (1:2, v/v) yielded the target compound as purple crystals after recrystallization from CH_2Cl_2/MeOH (90 mg, 0.13 mmol, 67%); m.p. > 320 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.23 (s, 1 H, *meso*-*H*), 9.33 (m, 4 H, β-pyrrole-*H*), 9.08 (d, ^3J = 4.54 Hz, 2 H, β-pyrrole-*H*), 9.02 (d, ^3J = 4.54 Hz, 2 H, β-pyrrole-*H*), 8.16 (d, ^3J = 7.81 Hz, 2 H, tolyl-H_o), 7.61 (d, ^3J = 7.45 Hz, 2 H, tolyl-H_m), 6.63 (s, 2 H, OMe-Ar-H_m), 4.12 (s, 3 H, *p*-OH_3), 3.53 (s, 6 H, *o*-OH_3), 2.71 (s, 3 H, C_6H_4-CH_3), –3.05 (bs, 2 H, N*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.03, 161.21, 159.29, 148.84–146.42, 139.13, 137.20, 135.42, 134.60, 131.56–130.08, 127.46, 119.62, 111.95, 104.02, 91.09, 56.00, 55.59, 55.47, 21.47 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 407 (5.23), 504 (4.03), 539 (3.60), 575 (3.55), 630 nm (3.01). MS (FAB^+, 3 eV): *m*/*z*. = calcd. for $C_{43}H_{36}N_4O_4$ 672.27366; found 673.0 (100.00) $[M + H]^+$. $C_{43}H_{36}N_4O_4$ (672.78): calcd. C 76.77, H 5.39, N 8.33; found C 76.55, H 5.70, N 8.57.

General Procedure for the Metallation with Manganese Chloride: Free base porphyrin (100 mg, 0.14 mmol) was dissolved together with 150 mg $MnCl_2 \cdot 4H_2O$ in 25 mL acetic acid (96%) and 7 mL acetic anhydride. The solution was heated for 4 h at 110 °C. After cooling to room temp. dichloromethane was added and the organic phase washed several times with water. The organic solvent was evaporated and the residue dried under high vacuum.

Chloro[5-hexyl-10-(4-methylphenyl)-20-(2,4,6-trimethoxyphenyl)porphyrinato]manganese(III) (65): Prepared following the above general procedure using porphyrin **61** (100 mg, 0.14 mmol) and $MnCl_2 \cdot 4H_2O$ (150 mg). Column chromatography eluting with dichloromethane gave a minor compound followed by the metal complex. Evaporation of the solvent gave a gree-red residue (99 mg, 0.12 mmol, 88%); m.p. >300 °C. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 370 (4.38), 405 (4.40), 479 (4.60), 581 (3.71), 614 (3.66), 643 nm (3.55). MS (FAB^+, 3 kV) = : *m*/*z* = calcd. for $C_{42}H_{40}ClMnN_4O_3$ 738.21694; found 738.0 (9.0) $[M]^{\cdot+}$, 703.0 (100.0) $[M - Cl]^+$.

5,10-Bis(2-hydroxyphenyl)-15-(4-methylphenyl)porphyrin (71): A solution of **70** (200 mg of the atropisomeric mixture, 0.33 mmol) in 500 mL dichloromethane was treated dropwise with 1.3 mL BBr_3 solution (13 mmol) over the course of 1 h. The mixture was stirred for 16 h at room temp. and then poured onto ice and treated with $NaHCO_3$ until neutral. The solution was diluted with dichloromethane and the organic phase extracted three times with water. After drying of Na_2SO_4 the solvent was removed in vacuo. Column chromatography on silica gel eluting with neat dichloromethane gave one product fraction which yielded a red-brown solid (120 mg, 0.21 mmol, 62%); m.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.14 (s, 1 H, *meso*-*H*), 9.29 (m, 2 H, β-pyrrole-$H^{2,18}$), 8.99 (m, 1 H, β-pyrrole-H^{17}), 8.90 (m, 5 H, β-pyrrole-$H^{3,7,8,12,13}$), 8.27 (m, 2 H, tolyl-H_o), 8.10 (m, 2 H, Ar-H_o), 7.90 (m, 2 H, Ar-H_p), 7. 06 (m, 2 H, tolyl-H_m), 7.21 (m, 4 H, Ar-H_m), –2.70 (bs, 2 H, N*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 413 (5.21), 509 (3.81), 544 (3.12), 584 (3.05), 639 nm (2.42). MS (290 °C, 80 eV): *m*/*z* = 584.0 (100.00) $[M]^{\cdot+}$). HRMS: calcd. for $C_{39}H_{28}N_4O_2$ 584.22123; found 584.22125.

5,10-[2,2′(-Dodecamethyleneoxy)diphenyl]-15-(4-methylphenyl)porphyrin (72): A solution of 100 mg of the dihydroxyporphyrin **71** (0.2 mmol) and 400 mg K_2CO_3 in 25 mL DMF was heated to 100 °C. Over the course of 4 h 81.5 mg 1,12-dibromodecane (0.25 mmol dissolved in 10 mL DMF) were added dropwise and heating continued for another 3 h. The solution was cooled and treated with saturated aq. ammonium chloride. After addition of 50 mL dichloromethane the organic phase was washed three times with water and dried with Na_2SO_4. The solvent was removed in high vacuum and column chromatography with CH_2Cl_2/*n*-hexane (1:2, v/v) gave the title compound as a purple solid (90 mg, 0.12 mmol, 60%); m.p. 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.14 (s, 1 H, *meso*-*H*), 9.26 (m, 2 H, β-pyrrole-$H^{2,18}$), 8.97 (AB, ^3J = 4.41 Hz, 1 H, β-pyrrole-H^{17}), 8.89 (AB, ^3J = 5.50 Hz, 1 H, β-pyrrole-H^{13}), 8.83 (AB, ^3J = 4.41 Hz, 2 H, β-pyrrole-$H^{3,12}$), 8.75 (AB, ^3J = 4.41 Hz, 2 H, β-pyrrole-$H^{7,8}$), 8.09 (m, 4 H, Ar-H_o), 7.76 (m, 2 H, Ar-H_p), 7.56, (d, ^3J = 8.09 Hz, 2 H, tolyl-H_m), 7.34 (m, 4 H, Ar-H_m), 3.86 (m, 4 H, alkyl chain), 0.86 (m, 6 H, alkyl chain), –0.81 (m, 8 H, alkyl chain), –1.11 (m, 6 H, alyl chain), –2.92 (*bs*, 2 H, N*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 415 (5.39), 511 (4.22), 545 (3.82), 582 (3.71), 635 nm (3.36). MS (300 °C, 80 eV): *m*/*z* = 750.0 (100.00) $[M]^+$, 375.0 (9.62) $[M]^{2+}$. HRMS: calcd. for $C_{51}H_{50}N_4O_2$ 750.39338; found 750.39341. $C_{51}H_{50}N_4O_2$ (750.98): calcd. C 81.57, H 6.71, N 7.46; found C 81.23, H 6.80, N 7.59.

Chloro{5,10-[2,2′-(dodecamethyleneoxy)diphenyl]-15-(4-methylphenyl)porphyrinato}manganese(III) (73): The free base porphyrin **72** (100 mg, 0.13 mmol) was dissolved in 50 mL DMF and heated with 60 mg $MnCl_2 \cdot 4H_2O$ to reflux. After coolinig to room temp. the mixture was filtered through neutral alumina (Brockman grade III). Column chromatography eluting with dichloromethane gave several minor fractions and the metal complex as the main fraction. Evaporation of the solvent followed by column chromatography eluting with neat dichloromethane gave the title compound (60 mg, 0.07 mmol, 55%); m.p. >300 °C. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 380 (4.40), 405 (3.77), 487 (4.90), 597 (3.95), 629 nm (2.91). MS (FAB^+, 3 kV): *m*/*z* = calcd. for $C_{51}H_{48}ClMnN_4O_2$ 838.28463; found 838.0 (7.0) $[M]^{\cdot+}$, 803.0 (100.0), $[M - Cl]^+$.

General Procedure for Bromination of 5,15-AB-Type Porphyrins: The porphyrin (1 equiv.) was dissolved in 100 mL of chloroform and cooled to 0 °C. Pyridine (1.0 mL) was added to act as an acid

scavenger. NBS (1.1 equiv.) was added directly to the flask, and the reaction was followed by TLC. When the reaction reached completion it was quenched with 10 mL of acetone. The solvents were evaporated under reduced pressure, and the product was dissolved in CH_2Cl_2 followed by filtration through silica gel.

5,15-Dibromo-10-(*n*-butyl)-20-(2,4,6-trimethoxyphenyl)porphyrin (77): Prepared following the general bromination procedure given above using 5-butyl-15-(2,4,6-trimethoxyphenyl)porphyrin (**22**, 160 mg, 0.3 mmol), NBS (58.51 mg, 0.33 mmol) and acetone (10 mL). The products were separated using column chromatography (*n*-hexane/CH_2Cl_2, 2:1, v/v). The first fraction was 5,15-dibromo-10-butyl-20-(2,4,6-trimethoxyphenyl)porphyrin (**77**, 90 mg, 0.13 mmol, 43%) as purple crystals, the second fraction gave 5-bromo-10-butyl-20-(2,4,6-trimethoxyphenyl)porphyrin (**76**, 60 mg, 0.098 mmol, 33%) as purple crystals. Data for **77**: M.p. > 300 °C. R_f = 0.5 (*n*-hexane/CH_2Cl_2, 1:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = –2.75 (s, 2 H, N*H*), 1.13 (t, *J* = 7.53 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.77 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.41 (m, 2 H, $CH_2CH_2CH_2CH_3$), 3.57 (s, 6 H, OCH_3), 4.15 (s, 3 H, *p*-OCH_3), 4.72 (t, *J* = 8.28, Hz, 2 H, $CH_2CH_2CH_2CH_3$), 6.62 (s, 2 H, Ar-*H*), 8.82 (s, 2 H, β-pyrrole-*H*), 9.31 (s, 2 H, β-pyrrole-*H*), 9.56 (d, *J* = 4.52 Hz, 2 H, β-pyrrole-*H*), 9.59 (d, *J* = 4.15 Hz, 2 H, β-pyrrole-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 23.4, 29.5, 34.9, 40.7, 55.4, 55.8, 56.2, 90.6, 91.4, 91.8, 102.5, 111.4, 112.6, 121.7, 157.3, 160.3, 160.8, 162.0 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 422 (4.95), 522 (4.14), 556 (4.01), 603 (3.53), 661 nm (3.74). HRMS (ES^+): calcd. for $C_{33}H_{31}N_4O_3Br_2$ $[M + H]^+$ 691.0740; found 691.0742.

General Procedure for Suzuki Coupling: A Schlenk flask was charged with K_3PO_4 (20 equiv.) and anhydrous THF (60 mL) under argon. Then the porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) were added. The reaction was heated at reflux temperature for 12–24 h (TLC control) and protected from light. After completion, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$, H_2O, and brine and then dried with Na_2SO_4. The organic solvent was evaporated and the crude product was purified by flash chromatography.

5-(*n*-Butyl)-10-(4-methoxycarbonylphenyl)-15-(2,4,6-trimethoxyphenyl)porphyrin (82): Using the above general Suzuki coupling procedure 5-bromo-10-(*n*-butyl)-20-(2,4,6-trimethoxyphenyl)porphyrin **76** (150 mg, 0.245 mmol), 4-methoxycarbonylphenyl boronic acid (440.9 mg, 2.45 mmol), $Pd(PPh_3)_4$ (28.31 mg, 0.0245 mmol) and K_3PO_4 (1041 mg, 4.9 mmol) in THF (50 mL) were used. Silica gel column chromatography (*n*-hexane/CH_2Cl_2, 1:1, v/v) afforded the product as purple crystals (145 mg, 0.217 mmol, 89%); m.p. > 300 °C. R_f = 0.42 (*n*-hexane/ethyl acetate, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.83 (s, 2 H, N*H*), 1.15 (t, *J* = 7.02 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.56 (m, 2 H, $CH_2CH_2CH_2CH_3$), 3.54 (s, 6 H, OCH_3), 4.13 (s, 3 H, *p*-OCH_3), 4.14 (s, 3 H, OCH_3), 5.06 (t, *J* = 8.18 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 6.62 (s, 2 H, Ar-*H*), 8.31 (d, *J* = 8.18 Hz, 2 H, Ar-*H*), 8.45 (d, *J* = 8.19 Hz, 2 H, Ar-*H*), 8.73 (d, *J* = 5.26 Hz, 1 H, β-pyrrole-*H*), 8.86 (d, *J* = 4.68 Hz, 2 H, β-pyrrole-*H*), 8.96 (d, *J* = 4.1 Hz, 1 H, β-pyrrole-*H*), 9.11 (m, 2 H, Ar-*H*), 9.27 (d, *J* = 4.1 Hz, 1 H, β-pyrrole-*H*), 9.38 (d, *J* = 4.67 Hz, 1 H, β-pyrrole-*H*), 9.51 (d, *J* = 4.68 Hz, 1 H, β-pyrrole-*H*), 9.61 (d, *J* = 4.68 Hz, 1 H, β-pyrrole-*H*), 10.10 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 23.2, 29.2, 34.5, 40.4, 51.9, 55.2, 90.4, 103.7, 110.6, 111.4, 117.2, 119.8, 126.8, 127.1, 127.7, 128.8, 129.7, 133.9, 147.5, 160.6, 161.5, 167.0 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 414 (5.00), 510 (4.00), 544 (3.52), 584 (3.60), 640 nm (3.42). HRMS (ES^+): calcd. for $C_{41}H_{39}N_4O_5$ $[M + H]^+$ 667.2920; found 667.2938.

5-(4-Ethynylphenyl)-15-hexyl-10,20-bis(3-methoxyphenyl)porphyrin (89): *n*-Butyllithium (2 mL of a 2.5 M solution in *n*-hexane, 2.5 mmol) was added under argon to a 50-mL Schlenk flask charged with a solution of *p*-bromophenylethyne (0.45 g, 2.5 mmol) in 10 mL of dry diethyl ether at –70 °C. The reaction mixture was then warmed to –40 °C and THF was added dropwise until the aryllithium was formed as a white-bright pink suspension. To this vigorously stirred mixture was added rapidly a solution of 5-hexyl-10,20-bis(3-methoxyphenyl)porphyrin (**87**, 50 mg, 0.082 mmol) in 30 mL of dry THF under argon. The mixture changed from deep purple to brown within 30 min. The reaction mixture was stirred for 2 h (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum or washed with enough *n*-hexane. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:10, v/v) and yielded the title compound (7 mg, 0.1 mmol, 12%) as purple crystals; m.p. >300 °C. R_f = 0.49 (ethyl acetate/*n*-hexane, 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.72 (s, 2 H, N*H*), 0.94 (t, *J* = 7.2 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.28 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.56 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.84 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.61 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.34 (s, 1 H, *H*C≡C), 4.02 (s, 6 H, OCH_3), 5.05 (t, *J* = 8.1 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.38 (m, 2 H, Ph-*H*), 7.69 (m, 2 H, Ph-*H*), 7.82 (m, 4 H, Ph-*H*), 7.89 (d, *J* = 7.6 Hz, 2 H, Ph-*H*), 8.19 (d, *J* = 7.6 Hz, 2 H, Ph-*H*), 8.78 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{2,8}$), 8.88 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{12,18}$), 8.98 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{3,7}$), 9.51 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{13,17}$) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 449 (5.10), 440 (3.97), 486 (3.32), 560 (2.15), 581 (3.05), 656 nm (4.29). HRMS: calcd. for $C_{48}H_{42}N_4O_2$ 706.3308; found [M + 1] 707.3365. $C_{48}H_{42}N_4O_2$ (706.89): calcd. C 81.56, H 5.99, N 7.93; found C 81.41, H 6.35, N 8.17.

5-(*sec*-Butyl)-15-hexyl-10,20-diphenylporphyrin (91): *sec*-Butyllithium (1 mL of a 2.5 M solution in hexane, 2.5 mmol) was added under argon to a 50-mL Schlenk flask charged with a solution of 5-hexyl-10,20-diphenylporphyrin (**88**, 50 mg, 0.09 mmol) in 30 mL of dry THF at –80 °C. The mixture changed from deep purple to brown within 30 min. The reaction mixture was stirred for 3 h (TLC control). Further workup followed the procedure for **89** and column chromatography and elution with ethyl acetate/*n*-hexane (1:8, v/v) yielded the title compound (13 mg, 0.02 mmol, 25%) as purple crystals; m.p. >300 °C. R_f = 0.75 (ethyl acetate/*n*-hexane, 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.56 (s, 2 H, N*H*), 0.91 (t, *J* = 7.6 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.10–1.31 [m, 5 H, $CH(CH_3)(CH_2CH_3)$, $CH_2CH_2CH_2CH_2CH_2CH_3$], 1.44 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.88 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.42 [d, *J* = 7.4 Hz, 3 H, $CH(CH_3)(CH_2CH_3)$], 2.52 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.75 [m, 2 H, $CH(CH_3)(CH_2CH_3)$], 4.98 (t, *J* = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.32 [m, 1 H, $CH(CH_3)(CH_2CH_3)$], 7.77 (m, 6 H, Ph-*H*), 8.22 (m, 4 H, Ph-*H*), 8.86 (d, *J* = 5.0 Hz, 4 H, β-pyrrole-$H^{2,8,12,18}$), 9.43 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{13,17}$), 9.57 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{3,7}$) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 441 (5.08), 486 (3.38), 514 (3.15), 581 (3.42), 656 nm (4.17). HRMS: calcd. for $C_{42}H_{42}N_4$ 602.3409; found [M + 1]

603.3487. $C_{42}H_{42}N_4$ (602.82): calcd. C 83.68, H 7.02, N 9.29; found C 83.17, H 7.20, N 9.50.

[5-(4-Ethynylphenyl)-10,20-diphenylporphyrinato]zinc(II) (94): The free base porphyrin 5-(4-ethynylphenyl)-10,20-diphenylporphyrin (**93**, 100 mg, 0.18 mmol) was dissolved in 100 mL dichloromethane. At room temperature 5 mL MeOH (dry) and 0.6 g of zinc(II) acetate were added and the mixture stirred for 30 min. After washing three times with water the organic phase was dried with Na_2SO_4, concentrated in vacuo and chromatography on alumina (dichloromethane/*n*-hexane, 1:5, v/v) to give 98 mg of **94** (1.5 mmol, 82%) after recrystallization from CH_2Cl_2/MeOH; m.p. > 300 °C. R_f = 0.43 (dichloromethane/*n*-hexane, 1:5, v/v, alumina). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 3.30 (s, 1 H, *H*C≡C), 7.65–7.75 (m, 6 H, Ph-*H*), 7.85 (d, ^3J = 7.4 Hz, 2 H, Ph-*H*), 8.20–8.30 (m, 6 H, Ph-*H*), 8.80–9.0 (each *d*, ^3J = 5.0 Hz, 4 H, β-pyrrole-*H*), 9.20 (d, ^3J = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.40 (d, ^3J = 5.0 Hz, 2 H, β-pyrrole-*H*), 10.20 (s, 1 H, *meso*-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 413 (5.31), 539 (3.93), 562 nm (4.10). MS (EI, 80 eV, 170 °C), *m*/*z* (%): 626 (100) [M^+], 313 (7) [M^{2+}]. HRMS: calcd. for $C_{40}H_{24}N_4Zn$ 626.1449; found 626.1452.

1,4-Bis[(4-phenyl-10,20-diphenylporphyrinato-5-yl)zinc(II)]butane-1,3-diyne (95): Porphyrin **94** (50 mg, 0.08 mmol) was dissolved in 30 mL dichloromethane and CuCl (457 mg, 44.57 mmol) and 0.6 mL TMEDA were added slowly. The reaction mixture was stirred for 3 h at room temperature and washed 5 times with water (100 mL each). The organic phase was dried with Na_2SO_4 and the solvent removed in vacuo. Chromatographic work-up on alumina eluting with dichloromethane gave the dimer (41 mg pink crystals, 0.033 mmol, 82% after recrystallization from CH_2Cl_2/MeOH); m.p. > 300 °C. R_f = 0.76 (dichloromethane/THF: 10:1, v/v, silica gel). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 7.60–7.65 (d, *J* = 7.6 Hz, 4 H, Ph-*H*), 7.70–7.80 (m, 12 H, Ph-*H*), 7.90–7.95 (d, *J* = 7.6 Hz, 4 H, Ph-*H*), 8.20–8.25 (d, *J* = 7.4 Hz, 8 H, Ph-*H*), 8.80 (m, 8 H, β-pyrrole-*H*), 9.05 (d, β-pyrrole-*H*, ^3J = 5.0 Hz, 4 H), 9.40 (d, β-pyrrole-*H*, ^3J = 5.0 Hz, 4 H), 10.25 (s, 2 H, *meso*-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 416 (5.23), 460 (3.89), 544 nm (4.00). MS (EI, 80 eV, 170 °C), *m*/*z* (%): 1250 (43) [M^+], 600 (52) [M^{2+} – C_2H_2], 524 (64) [M^{2+} – C_8H_6]. FAB(+) calcd. for $C_{80}H_{47}N_8Zn_2$ 1251.57; found 1251.

5-(*tert*-Butyl)-15-hexyl-5,24-dihydro-10,20-diphenylporphyrin (96): *tert*-Butyllithium (1 mL of a 2.5 M solution in hexane, 2.5 mmol) was added under argon to a 50-mL Schlenk flask charged with a solution of 5-hexyl-10,20-diphenylporphyrin (**88**, 50 mg, 0.09 mmol) in 30 mL of dry THF at –80 °C. The reaction mixture was stirred for 5 h (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equivalents of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:6, v/v) yielding the title compound (11 mg, 0.02 mmol, 20%) as purple crystals; m.p. 227 °C. R_f = 0.43 (ethyl acetate/*n*-hexane, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.91 (t, *J* = 6 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.09 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.28 [s, 9 H, $C(CH_3)_3$] 1.44 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.88 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.47 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.13 (t, *J* = 6 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.32 (s, 1 H, 5-*H*), 6.04–6.47 (m, 4 H, β-pyrrole-*H*), 6.51–6.85 (m, 4 H, β-pyrrole-*H*), 7.14–7.59 (m, 6 H, Ph-*H*), 7.87–7.96 (m, 4 H, Ph-*H*), 10.39, 10.57 and 10.94 (s each, 3 H, N*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 376 (5.03), 435 (4.82), 578 (4.84), 656 (4.17) nm.[31]

5-(*tert*-Butyl)-5,24-dihydro-10,20-bis(3-methoxyphenyl)-15-phenylporphyrin (97): *tert*-Butyllithium (2 mL of a 1.8 M solution in hexane, 0.06 mmol) was slowly added (ca. 1 h) under argon to a 50-mL Schlenk flask charged with a solution of 5-phenyl-10,20-bis(3-methoxyphenyl)porphyrin (**59**, 35 mg, 0.06 mmol) in 30 mL of dry THF. The mixture was heated to 50 °C and stirred for 30 min. Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.02 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum or washed with *n*-hexane. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:8, v/v) and gave the title compound (11 mg, 0.016 mmol, 28%) as purple crystals; m.p. 226 °C. R_f = 0.47 (ethyl acetate/*n*-hexane, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.28 [s, 9 H, $C(CH_3)_3$], 3.91 (s, 6 H, OCH_3), 5.33 (s, 1 H, H^5), 6.01–6.43 (m, 4 H, β-pyrrole-*H*), 6.53–6.66 (m, 4 H, β-pyrrole-*H*), 6.87 (m, 2 H, Ar-*H*), 7.06–7.15 (m, 4 H, Ar-*H*), 7.37 (m, 3 H, Ar-*H*), 7.51 (m, 4 H, Ar-*H*), 9.88, 10.02 and 10.65 (each s, 3 H, N*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 350 (4.85), 453 (4.69), 577 (5.11), 656 (4.15) nm.[31]

5-Hexyl-10,20-bis(3-methoxyphenyl)-15-[(3-pyridyl)methyl]porphyrin (98): *n*-Hexyllithium (1 mL of a 2.5 M solution in hexane) was slowly added under argon to a 100-mL Schlenk flask charged with a solution of 5,15-bis(3-methoxyphenyl)porphyrin (**58**, 100 mg, 0.19 mmol) in 40 mL of dry THF at –80 °C under argon. After 15 min the solution was treated with a solution of 300 mg (0.86 mmol) 3-(iodomethyl)pyridine hydrogen iodide dissolved in 4 mL DMF and stirred for 24 h and heated to 75 °C (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.04 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography on silica gel and elution with ethyl acetate/*n*-hexane (1:8, v/v) and yielded the title compound (8 mg, 0.01 mmol, 6%) as purple crystals and the trisubstituted porphyrin (28%). Data for **98**: M.p. >300 °C. R_f = 0.35 (ethyl acetate/*n*-hexane, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.62 (s, 2 H, N*H*), 0.91 (t, *J* = 7.2 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.23 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.54 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.83 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.55 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.03 (s, 6 H, OCH_3), 4.99 (t, *J* = 8.1 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 6.38 (s, 2 H, pyridyl-CH_2), 7.01 (m, 2 H, pyridyl-*H*), 7.35 (m, 3 H, 2 Ar-*H*, 1 pyridyl-*H*), 7.66 (m, 2 H, Ar-*H*), 7.79 (m, 4 H, Ar-*H*), 8.38 (s, 1 H, pyridyl-*H*), 8.95 (m, 4 H, β-pyrrole-$H^{2,8,12,18}$), 9.33 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{13,17}$), 9.48 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{3,7}$) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 420 (5.07), 485 (3.74), 516 (3.62), 551 (2.92), 593 (3.04), 655 nm (4.00). HRMS: calcd. for $C_{46}H_{43}N_5O_2$ 697.3416; found [M + 1] 698.3516. $C_{46}H_{43}N_5O_2$ (697.88): calcd. C 79.17, H 6.21, N 10.04; found C 79.44, H 6.51, N 9.92.

3-(5,15-Dihexyl-10-phenylporphyrin-20-yl)propionic Acid (99): Phenyllithium (0.6 mL of a 1.8 M solution in hexane, 0.018 mmol) was slowly added under argon to a 50-mL Schlenk flask charged with a solution of 5,15-dihexylporphyrin (**18**, 80 mg, 0.167 mmol) in 30 mL of dry THF at r.t. under argon. After 15 min the solution

was treated with a solution of 200 mg (1 mmol) 3-iodopropionic acid dissolved in 5 mL THF and stirring for 24 h (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography on silica gel and elution with ethyl acetate/*n*-hexane (1:10, v/v) yielded the title compound (19 mg, 0.03 mmol, 18%) as purple crystals and the respective trisubstituted porphyrin (27%). Data for **99**: M.p. >300 °C. R_f = 0.47 (ethyl acetate/*n*-hexane, 1:7, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.65 (s, 2 H, N*H*), 0.91 (t, *J* = 7.2 Hz, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.20 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.55 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.86 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.57 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, CH_2CH_2COOH), 3.72 (t, *J* = 6.4 Hz, 2 H, CH_2CH_2COOH), 4.98 (t, *J* = 8.1 Hz, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.77 (m, 3 H, Ph-*H*), 8.21 (m, 2 H, Ph-*H*), 8.88 (m, 4 H, β-pyrrole-$H^{3,7,13,17}$), 9.44 (m, 4 H, β-pyrrole-$H^{2,8,12,18}$), 10.56 (s, 1 H, COO*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 418 (5.08), 440 (3.94), 517 (3.79), 552 (3.91), 593 (3.88), 655 nm (4.09). HRMS: calcd. for $C_{41}H_{46}N_4O_2$ 626.3621; found 626.4512. $C_{41}H_{46}N_4O_2$ (626.84): calcd. C 78.56, H 7.40, N 8.94; found C 78.76, H 7.80, N 9.21.

5,15-Dihexyl-10-[4-(dipropylamino)phenyl]-20-propylporphyrin (101) and 5,15-Dihexyl-10-[4-(dipropylamino)phenyl]porphyrin (102): *n*-Butyllithium (4 mL of a 2.5 M solution in hexane, 10 mmol) was added under argon to a 100-mL Schlenk flask charged with a solution of *p*-bromoaniline (1 g, 5 mmol) in 10 mL of dry diethyl ether at 0 °C. After addition of *n*-BuLi the cold bath was removed and stirring was continued for another 2 h at room temperature. To the vigorously stirred mixture was added rapidly a solution of 5,15-dihexylporphyrin (**18**, 150 mg, 0.313 mmol) in 40 mL of dry THF. The mixture changed from deep purple to brown within 30 min. After 1 h the solution was treated with 1 mL propyl iodide (10 mmol) and stirred for 12 h and heated to 70 °C (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography on silica gel and elution with ethyl acetate/*n*-hexane (1:10, v/v). The first fraction consisted of 101 (43 mg, 0.06 mmol, 20%) and the second fraction of **102** (34 mg, 0.05 mmol, 16%). Data for **101**: purple crystals; m.p. >300 °C. R_f = 0.63 (ethyl acetate/*n*-hexane, 1:6, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.57 (s, 2 H, N*H*), 0.92 (t, *J* = 7.2 Hz, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.11 [m, 6 H, $N(CH_2CH_2CH_3)_2$], 1.25 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.37–1.51 (m, 7 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 1.84–1.93 [m, 8 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $N(CH_2CH_2CH_3)_2$], 2.56 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 3.55 [m, 4 H, $N(CH_2CH_2CH_3)_2$], 4.99 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 7.04 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 8.05 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 9.02–9.11 (m, 4 H, β-pyrrole-*H*), 9.45 (m, 4 H, β-pyrrole-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.22, 13.76, 14.59, 20.13, 20.24, 22.34, 29.22, 29.85, 31.27, 31.52, 32.63, 34.56, 35.03, 37.15, 38.16, 38.21, 50.71, 52.74, 109.24, 109.44, 117.84, 118.35, 118.57, 126.48, 127.55, 128.86, 146.52 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 436 (5.10), 486 (4.32), 511 (4.29), 581 (3.64), 656 nm (4.28). HRMS: calcd. for $C_{47}H_{61}N_5$ 695.4926; found [M + 1] 696.5008. $C_{47}H_{61}N_5$ (696.03): calcd. C 81.09, H 8.84, N 10.07; found C 81.29, H 8.59, N 9.98. Data for 102: purple crystals; m.p. >300 °C. R_f = 0.55 (ethyl acetate/*n*-hexane, 1:6, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.75 (s, 2 H, N*H*), 0.92 (t, *J* = 7.2 Hz, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.14 [m, 6 H, $N(CH_2CH_2CH_3)_2$], 1.28 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.37–1.51 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.85–1.94 [m, 8 H, $CH_2CH_2CH_2CH_2CH_3$, $N(CH_2CH_2CH_3)_2$], 2.58 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.56 [m, 4 H, $N(CH_2CH_2CH_3)_2$], 5.02 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.04 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 8.04 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 8.99 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.34 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 8.44 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.56 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-*H*), 10.03 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.22, 13.74, 20.23, 22.31, 29.29, 29.82, 31.51, 34.55, 38.15, 52.75, 102.72, 109.26, 118.57, 120.45, 126.46, 127.58, 129.33, 130.91, 131.91, 135.36, 144.73, 147.23 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 434 (5.11), 585 (3.78), 656 nm (4.11). HRMS: calcd. for $C_{44}H_{55}N_5$ 653.4457; found [M + 1] 653.4491. $C_{44}H_{55}N_5$ (653.95): calcd. C 80.81, H 8.48, N 10.71; found C 81.09, H 8.71, N 10.43.

5,10-Dihexyl-15-[4-(dihexyl-hydroxymethyl)phenyl]-20-propylporphyrin (103) and 5,10-Dihexyl-15-[4-(dihexyl-hydroxymethyl)phenyl]-porphyrin (104): *n*-Hexyllithium (2 mL of a 2.5 M solution in hexane, 5 mmol) was added under argon to a 100-mL Schlenk flask charged with a solution of 5-hexyl-15-(4-methylcarboxyphenyl)porphyrin (**17**, 40 mg, 0.07 mmol) in 40 mL of dry THF under argon. The mixture changed from deep purple to brown within 30 min. After 1 h the solution was treated with 0.5 mL propyl iodide (0.52 mmol) and stirring for 12 h and heating to 70 °C (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.02 M) was added and the reaction mixture was stirred for another 60 min at room temperature. The mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography and elution with acetone/*n*-hexane (1:5, v/v). The first fraction consisted of **103** (11 mg, 0.013 mmol, 18%) and the second fraction of **104** (8 mg, 0.01 mmol, 14%). Data for **103**: Purple crystals; m.p. >300 °C. R_f = 0.31 (acetone/*n*-hexane, 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.60 (s, 2 H, N*H*), 0.96–1.15 [t, *J* = 7.2 Hz, 12 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$], 1.23 [m, 8 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$], 1.41–1.65 [m, 16 H, $CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$], 1.81–1.91 (m, 7 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 2.12 [m, 4 H, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$], 2.55 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 4.98 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 7.78 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 8.17 (m, 6 H, Ar-*H*), 8.87 (d, *J* = 5.0 Hz, 2 H, β-pyrrole-$H^{13,17}$), 9.43 (m, 2 H, β-pyrrole-$H^{2,18}$), 9.54 (m, 4 H, β-pyrrole-$H^{3,7,8,12}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 22.20, 22.38, 23.29, 28.99, 29.31, 31.52, 35.01, 35.38, 36.84, 38.28, 38.47, 42.82, 117.61, 118.28, 118.68, 118.90, 123.10, 126.83, 127.35, 127.88, 133.74, 140.02, 145.33 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 418 (5.18), 519 (3.50), 553 (3.78), 601 (3.88), 655 nm (3.75). HRMS: calcd. for $C_{54}H_{74}N_4O$ 794.5862; found 794.5725. Data for **104**: Purple crystals; m.p. >300 °C. R_f = 0.31 (acetone/*n*-hexane, 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.88 (s, 2 H, N*H*), 0.93–1.15 [t, *J* = 7.2 Hz, 12 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$], 1.23 [m, 8 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $C(OH)$-

$CH_2CH_2CH_2CH_2CH_2CH_3$], 1.41–1.73 [m, 16 H, $CH_2CH_2CH_2$-$CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2$-$CH_2CH_2CH_2CH_3$, $C(OH)CH_2CH_2CH_2CH_2C$-H_2CH_3], 1.82–1.90 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.09 [m, 4 H, $C(OH)$-$CH_2CH_2CH_2CH_2CH_2CH_3$], 2.57 (m, 4 H, $CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 5.06 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.79 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.21 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.87 (d, J = 5.0 Hz, 2 H, β-pyrrole-$H^{13,17}$), 9.34 (d, 2 H, β-pyrrole-$H^{2,18}$), 9.54 (m, 4 H, β-pyrrole-$H^{3,7,8,12}$), 10.03 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.66, 22.18, 29.29, 29.88, 29.90, 31.31, 34.87, 35.66, 38.37, 38.64, 42.80, 103.03, 117.77, 119.06, 120.08, 123.29, 127.81, 130.38, 133.91, 138.72, 139.38, 145.41 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ ($\log\varepsilon$) = 435 (5.10), 486 (3.11), 514 (2.57), 581 (3.42), 656 nm (3.72). HRMS: calcd. for $C_{51}H_{68}N_4O$ 752.5393; found 752.4981.

5-Hexyl-10-phenyl-15-(4-methoxyphenyl)-20-propylporphyrin (105): PhLi (0.8 mL of a 1.8 M solution in hexane, 0.02 mmol) was slowly added (ca. 1 h) under argon to a 100-mL Schlenk flask charged with a solution of 5-hexyl-15-(4-methoxyphenyl)porphyrin (**105**, 100 mg, 0.19 mmol) in 40 mL of dry THF. The mixture was heated to 50 °C and stirred for 30 min. After 1 h the solution was treated with 0.7 propyl iodide (7.1 mmol) and stirring for 20 h and heating to 70 °C (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.06 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica geland the organic solvent was removed under vacuum. Final purification was achieved by column chromatography (ethyl acetate/*n*-hexane = 1:10, v/v) yielded the title compound (31 mg, 0.05 mmol, 25%) as purple crystals, besides the respective trisubstituted porphyrin (14%) and starting material (8%); m.p. >300 °C. R_f = 0.76 (ethyl acetate/*n*-hexane, 1:5, v/v). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.61 (s, 2 H, N*H*), 0.99 (t, J = 8.1 Hz, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 1.34 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.41 (m, 2 H, $CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 1.86 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.57 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 4.09 (s, 3 H, OCH_3), 5.02 (t, J = 8.1 Hz, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 7.25 (d, J = 8 Hz, 2 H, Ph-*H*), 7.79 (m, 3 H, Ph-*H*), 8.15 (d, J = 8 Hz, 2 H, Ph-*H*), 8.27 (m, 2 H, Ph-*H*), 8.81 (m, 2 H, β-pyrrole-$H^{13,17}$), 8.98 (m, 2 H, β-pyrrole-$H^{2,18}$), 9.43 (m, 2 H, β-pyrrole-$H^{3,12}$), 9.56 (m, 2 H, β-pyrrole-$H^{7,8}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.79, 14.58, 22.36, 29.33, 29.88, 31.33, 31.53, 35.25, 37.10, 38.45, 55.12, 111.71, 118.16, 119.24, 119.49, 126.22, 126.75, 127.13, 128.35, 134.07, 135.14, 141.99, 158.86 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ ($\log\varepsilon$) = 444 (4.97), 487 (4.30), 601 (4.03), 657 nm (4.28). HRMS: calcd. for $C_{42}H_{42}N_4O$ 618.3358; found [M + 1] 619.3425. $C_{42}H_{42}N_4O$ (618.82): calcd. C 81.52, H 6.84, N 9.05; found C 81.63, H 7.05, N 8.97.

5-Butyl-10-hexyl-20-(4-methoxyphenyl)-15-pentylporphyrin (107): *n*BuLi (0.4 mL of 2.5 M solution in hexane, 1 mmol) was slowly added under argon to a 100-mL Schlenk flask charged with a solution of 5-hexyl-15-(4-methoxyphenyl)porphyrin (**51**, 100 mg, 0.19 mmol) in 40 mL of dry THF at –80 °C under argon. After 15 min the solution was treated with 0.8 mL *n*-pentyl iodide (6.1 mmol) and stirred for 12 h (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:15, v/v) yielded the title compound (15 mg, 0.023 mmol, 13%) as purple crystals, trisubstituted porphyrin (9%) and starting material (7%); m.p. >300 °C. R_f = 0.57 (ethyl acetate/*n*-hexane, 1:5, v/v). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.63 (s, 2 H, N*H*), 0.87 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$), 1.37 (m, 5 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$), 1.56 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$), 1.86 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2$-CH_3), 2.56 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2$-CH_2CH_3, $CH_2CH_2CH_2CH_3$), 4.13 (s, 3 H, OCH_3), 5.02 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2$-CH_3), 7.33 (d, J = 8 Hz, 2 H, Ar-*H*), 8.11 (d, J = 8 Hz, 2 H, Ar-*H*), 8.85 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 9.40 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 9.52 (d, J = 5 Hz, 2 H, β-pyrrole-*H*), 9.55 (d, J = 5 Hz, 2 H, β-pyrrole-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ ($\lg\varepsilon$) = 442 (5.09), 486 (3.51), 548 (3.27), 581 (3.51), 656 nm (4.27). HRMS: calcd. for $C_{42}H_{50}N_4O$ 626.3984; found [M + 1] 627.4061. $C_{42}H_{50}N_4O$ (626.89): calcd. C 80.47, H 8.04, N 8.94; found C 80.67, H 6.95, N 8.63.

5-[4-(Dipropylamino)phenyl]-10-hexyl-20-(4-methoxyphenyl)porphyrin (109): *n*-Butyllithium (2 mL of a 2.5 M solution in hexane, 5 mmol) was added under argon to a 100-mL Schlenk flask charged with a solution of *p*-bromoaniline (0.5 g, 2.5 mmol) in 10 mL of dry diethyl ether at 0 °C. After addition of *n*BuLi the cold bath was removed and stirring was continued for another 2 h at room temperature. To the vigorously stirred mixture was added rapidly a solution of 5-hexyl-15-(4-methoxyphenyl)porphyrin (**51**, 100 mg, 0.19 mmol) in 40 mL of dry THF under argon at –80 °C. The mixture changed from deep purple to brown within 30 min. After 1 h the solution was treated with 1 mL propyl iodide (10 mmol) and stirring for 12 h and heating to 70 °C (TLC control). Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. The mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:10, v/v) yielding the title compound (41 mg, 0.06 mmol, 31%) as purple crystals; some starting material (13%) was recovered, too; m.p. >300 °C. R_f = 0.54 (ethyl acetate/*n*-hexane, 1:8, v/v). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.81 (s, 2 H, N*H*), 0.92 (t, J = 7.2 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.13 [m, 6 H, $N(CH_2CH_2CH_3)_2$], 1.27 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.57 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.83–1.94 [m, 6 H, $CH_2CH_2CH_2CH_2CH_2CH_3$, $N(CH_2CH_2CH_3)_2$], 2.61 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.54 [m, 4 H, $N(CH_2CH_2CH_3)_2$], 4.12 (s, 3 H, OCH_3), 5.04 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.05 (d, J = 7.5 Hz, 2 H, Ar-*H*), 7.34 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.05 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.15 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.88–9.01 (d, J = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.02–9.13 (d, J = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.28–9.37 (d, J = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.51–9.61 (d, J = 5.0 Hz, 2 H, β-pyrrole-*H*), 10.09 (s, 1 H, *meso*-*H*) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ ($\log\varepsilon$) = 443 (5.09), 486 (3.81), 585 (3.67), 656 nm (4.22). HRMS: calcd. for $C_{45}H_{49}N_5O$ 675.3937; found [M + 1] 676.4039. $C_{45}H_{49}N_5O$ (675.92): calcd. C 79.96, H 7.31, N 10.36; found C 79.65, H 7.05, N 10.01.

5-Hexyl-15-(4-methoxyphenyl)-10-phenylporphyrin (110): Phenyllithium (0.8 mL of a 1.8 M solution in hexane, 0.02 mmol) was slowly added (ca. 1 h) under argon to a 100-mL Schlenk flask charged with a solution of 5-hexyl-15-(4-methoxyphenyl)porphyrin (**51**, 100 mg, 0.19 mmol) in 40 mL of dry THF. The mixture was

heated to 50 °C and stirred for 30 min. Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.06 M) was added and the reaction mixture was stirred for another 60 min at room temperature. The mixture was filtered through silica gel and the organic solvent was removed under vacuum. Column chromatography (ethyl acetate/*n*-hexane, 1:10, v/v) gave the title compound (51 mg, 0.088 mmol, 45%) as purple crystals besides starting material (8%); m.p. >300 °C. R_f = 0.69 (ethyl acetate/*n*-hexane, 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.87 (s, 2 H, N*H*), 0.95 (t, J = 8.1 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.32 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.53 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.56 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.11 (s, 3 H, OCH_3), 5.05 (t, J = 8.1 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.31 (d, J = 8 Hz, 2 H, Ph-*H*), 7.82 (m, 3 H, Ph-*H*), 8.16 (d, J = 8 Hz, 2 H, Ph-*H*), 8.25 (m, 2 H, Ph-*H*), 8.85–8.91 (d, J = 5 Hz, 2 H, β-pyrrole-$H^{13,17}$), 8.96–9.03 (d, J = 5 Hz, 2 H, β-pyrrole-$H^{8,12}$), 9.31–9.39 (d, J = 5 Hz, 2 H, β-pyrrole-$H^{2,18}$), 9.51–9.61 (d, J = 5 Hz, 2 H, β-pyrrole-$H^{3,7}$), 10.14 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.74), 22.31, 29.85, 31.50, 34.73, 38.37, 55.13 (C_{OCH3}), 103.82, 111.93, 118.26, 119.45, 119.61, 126.04, 127.03, 127.20, 127.93, 130.61, 130.75, 131.09, 131.37, 133.63, 134.01, 135.23, 142.43, 142.64, 158.93 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 441 (4.97), 548 (2.76), 596 (3.34), 644 nm (3.95). HRMS: calcd. for $C_{39}H_{36}N_4O$ 576.2889; found [M + 1] 577.2946. $C_{39}H_{36}N_4O$ (576.74): calcd. C 81.22, H 6.29, N 9.71; found C 81.47, H 6.32, N 9.58.

5-Butyl-10-hexyl-15-(4-hydroxyphenyl)-20-(4-methoxyphenyl)porphyrin (115): *n*-Butyllithium (2 mL of a 2.5 M solution in hexane, 10 mmol) was added under argon to a 50-mL Schlenk flask charged with a solution of *p*-bromophenol (0.43 g, 2.5 mmol) in 10 mL of dry diethyl ether at 0 °C. After addition of *n*BuLi the cold bath was removed and stirring was continued for 18 h at room temperature. To the vigorously stirred mixture was added rapidly a solution of 5-butyl-10-hexyl-20-(4-methoxyphenyl)porphyrin (**114**, 40 mg, 0.07 mmol) in 30 mL of dry THF under argon. Subsequently, a mixture of 2 mL of water in 3 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of 10 equiv. of DDQ in THF (0.03 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:8, v/v) yielded the title compound (28 mg, 0.04 mmol, 60%) as purple crystals; 8% starting material were recovered; m.p. >300 °C. R_f = 0.52 (ethyl acetate/*n*-hexane, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.66 (s, 2 H, N*H*), 0.95 (t, J = 7.5 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.15 (t, J = 7.5 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.29 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.53 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.89 (m, 4 H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.57 (m, 4 H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.11 (s, 3 H, OCH_3), 5.01 (t, J = 7.8 Hz, 4 H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.15 (d, J = 7.5 Hz, 2 H, Ar-*H*), 7.30 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.04 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.11 (d, J = 7.5 Hz, 2 H, Ar-*H*), 8.78 (s, 2 H, β-pyrrole-$H^{17,18}$), 8.97 (d, J = 5 Hz, 2 H, β-pyrrole-$H^{2,13}$), 9.45 (d, J = 5 Hz, 2 H, β-pyrrole-$H^{3,12}$), 9.59 (s, 2 H, β-pyrrole-$H^{7,8}$) ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 446 (5.08), 486 (3.36), 581 (3.15), 615 (3.39), 656 nm (4.24). HRMS: calcd. for $C_{43}H_{44}N_4O_2$ 648.3464; found 648.2985. $C_{43}H_{44}N_4O_2$ (648.85): calcd. C 79.60, H 6.84, N 8.63; found C 79.99, H 7.05, N 8.58.

5-(*n*-Butyl)-15-[4-(dimethylamino)phenyl]-10-(1-ethylpropyl)-20-hexylporphyrin (121): The synthesis followed the standard procedures using *n*BuLi (0.03 mL, 0.09 mmol of a 2.5 M solution in *n*-hexane), 5-[4-(dimethylamino)phenyl]-10-(1-ethylpropyl)-20-hexylporphyrin (**67**, 42 mg, 0.07 mmol) and oxidation with air overnight. Column chromatography on silica gel (CH_2Cl_2 with 1% NEt_3) gave only the product after recrystallization from CH_2Cl_2/MeOH as purple crystals (8.3 mg, 0.01 mmol, 18%); m.p. 212 °C. R_f = 0.40 (CH_2Cl_2/*n*-hexane, 2:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 9.67 (m, 1 H, β-pyrrole-H^8), 9.57 (AB, ^3J = ^3J = 4.8 Hz, 2 H, β-pyrrole-$H^{3,7}$), 9.53 (AB, ^3J = ^3J = 4.8 Hz, 4 H, β-pyrrole-$H^{2,12}$), 9.40 (AB, ^3J = 4.7 Hz, 1 H, β-pyrrole-H^{18}), 8.89 (m, 2 H, β-pyrrole-$H^{13,17}$), 8.01 (AB, ^3J = ^3J = 8.6 Hz, 2 H, Ar-H_o), 7.11 (AB, ^3J = ^3J = 8.6 Hz, 2 H, Ar-H_m), 5.02 [m, 3 H, $CH(CH_2)_2$, $CH_2C_3H_7$], 4.93 (t, ^3J = 8.0 Hz, 2 H, $CH_2C_5H_{11}$), 3.23 [s, 6 H, $N(CH_3)_2$], 2.86 [m, 4 H, $CH(CH_2)_2$], 2.58 (m, 2 H, $CH_2CH_2C_2H_5$), 2.52 (m, 2 H, $CH_2CH_2C_4H_9$), 1.90 (m, 2 H, $C_2H_4CH_2CH_3$), 1.82 (m, 2 H, $C_2H_4CH_2C_3H_7$), 1.52 (m, 2 H, $C_3H_6CH_2C_2H_5$), 1.41 (m, 2 H, $C_4H_8CH_2CH_3$), 1.19 (t, ^3J = 7.4 Hz, 3 H, $C_3H_6CH_3$), 0.95 (t, ^3J = ^3J = 7.4 Hz, 6 H, CH_2CH_3), 0.94 (t, ^3J = 7.2 Hz, 3 H, $C_5H_{10}CH_3$), –2.64 (br. s, 2 H, N*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.22, ≈ 145, 135.39, ≈ 131.9, 130.66, ≈ 129.1, ≈ 128.8, ≈ 128.4, ≈ 127.8, 122.10, 119.08, 110.62, 50.26, 41.20, 40.63, 38.77, 35.80, 34.54, 32.02, 30.31, 23.83, 22.83, 13.96 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 420 (4.81), 522 (3.98), 559 (3.88), 600 (3.60), 658 nm (3.72). MS TOF, MS, (ES$^+$, 70 eV): m/z = 640 (10) $[M]^{\cdot+}$, 320 (100) $[M]^{2+}$. HRMS: calcd. for $C_{43}H_{54}N_5$ 640.7379; found 640.4355.

5-Butyl-10-hexyl-20-(4-ethynylphenyl)-15-(3-methoxyphenyl)porphyrin (122): The synthesis followed the standard procedures using 5-butyl-10-hexyl-15-(3-methoxyphenyl)porphyrin (**68**, 60 mg, 0.107 mmol), 4-bromoethynylphenyl (292.47 mg, 1.615 mmol), *n*BuLi (1.3 mL, 3.231 mmol), H_2O (0.5 mL) and DDQ (288.2 mg, 1.26 mmol). Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1, v/v) followed by a second column using *n*-hexane/CH_2Cl_2 (1:1) gave the title compound as purple crystals (7 mg 0.01 mmol, 10%); m.p. >300 °C. R_f = 0.66 (CH_2Cl_2/*n*-hexane, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = –2.69 (s, 2 H, N*H*), 0.96 (t, J = 7.01 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.17 (t, J = 7.01 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.43 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.53 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.86 (m, 4 H, CH_2), 2.57 (m, 4 H, CH_2), 3.34 (s, 1 H, C*H*), 4.00 (s, 3 H, OCH_3), 5.02 (m, 4 H, CH_2), 7.35 (m, 1 H, Ar-*H*), 7.65 (t, J = 7.6 Hz, 1 H, Ar-*H*), 7.78 (m, 2 H, Ar-*H*), 7.90 (d, J = 8.18 Hz, 2 H, Ar-*H*), 8.17 (d, J = 8.18 Hz, 2 H, Ar-*H*), 8.73 (d, J = 4.68 Hz, 1 H, β-pyrrole-*H*), 8.81 (d, J = 4.67 Hz, 1 H, β-pyrrole-*H*), 8.85 (d, J = 4.67 Hz, 1 H, β-pyrrole-*H*), 8.93 (d, J = 4.68 Hz, 1 H, β-pyrrole-*H*), 9.48 (m, 2 H, β-pyrrole-*H*), 9.61 (s, 2 H, β-pyrrole-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 22.6, 23.2, 28.9, 30.5, 31.4, 34.9, 35.2, 38.4, 40.5, 52.9, 55.0, 67.5, 83.3, 112.9, 117.0, 118.0, 119.8, 119.9, 120.9, 127.0, 130.0, 133.9, 142.6, 143.1, 157.4 ppm. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 418 (5.03), 518 (3.57), 553 (3.29), 592 (3.01), 644 nm (3.04). HRMS (ES$^+$): calcd. for $C_{45}H_{45}N_4O$ [M + H]$^+$ 657.3593; found 657.357.

Crystal Structure Determinations: Growth and handling of crystals followed the concept developed by Hope.[41] Intensity data were collected at 108 K with a Rigaku Saturn-724 system complete with CCD detector utilizing Mo-K_α radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz, polarization and extinction effects. The structures were solved with Direct Methods using the SHELXTL PLUS program system[42a] and refined against $|F^2|$ with the program XL from SHELX-97 using all data.[42b] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally placed into geometrically calculated positions

and refined using a ridging model. The N-H hydrogen atoms were located in difference maps and refined using the standard riding model. Crystal data for **77**: $C_{35}H_{34}N_4O_3Br_2$, M = 718.46, triclinic, space group $P\bar{1}$, a = 8.0071(14), b = 11.7648(18), c = 17.446(3) Å, α = 98.114(11), β = 99.002(9), γ = 104.531(10)°, V = 1543.1(5) Å^3, Z = 2, T = 108 K, μ (Mo-K_α) = 2.670 cm^{-1}, 11705 reflections measured, 5398 unique reflections measured (R_{int} = 0.0722), 401 parameters, 4486 reflections with $I > 2.0\sigma(I)$, refinement against $|F^2|$, $R1[I > 2.0\sigma(I)]$ = 0.0339, $wR2$ (all data) = 0.0859, S = 0.957, $\rho_{max.}$ = 0.514. Crystal data for **81**: $C_{35}H_{34}N_4O_3Br_2$, M = 718.46, triclinic, space group $P\bar{1}$, a = 7.9861(11), b = 11.6530(15), c = 17.173(2) Å, α = 90.5430(10), β = 98.012(2), γ = 107.818(2)°, V = 1504.3(3) Å^3, Z = 2, T = 108 K, μ (Mo-K_α) = 2.739 cm^{-1}, 32735 reflections measured, 8937 unique reflections measured (R_{int} = 0.0217), 401 parameters, 8070 reflections with $I > 2.0\sigma(I)$, refinement against $|F^2|$, $R1[I > 2.0\sigma(I)]$ = 0.0338, $wR2$ (all data) = 0.0823, S = 01.046, $\rho_{max.}$ = 0.612.

CCDC-749453 (for **77**) and -749454 (for **81**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Synthetic procedures and analytical data for compounds **20**–**22**, **25**–**28**, **30**, **31**, **40**, **43**–**50**, **52**–**55**, **57**, **62**, **64**, **66**–**70**, **74**–**81**, **83**–**86**, **100**, **106**, **108**, **111**, **113**, **117**–**119**, and **123**–**135**.

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