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Lead structures for applications in photodynamic therapy. Part 1: Synthesis and variation of *m*-THPC (Temoporfin) related amphiphilic A_2BC-type porphyrins

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Abstract—Photodynamic therapy (PDT) is a developing modality for the treatment of certain tumorous and other diseases. Considerable progress has been made in recent years in the search for new photosensitizers, in particular elucidating the role of localization of the photosensitizer. Known successful photosensitizers of the tetrapyrrole type are amphiphilic molecules, preferably localizing in cellular membrane structures. Thus, the quest for new photosensitizers requires the synthesis of unsymmetrically substituted (amphiphilic) tetrapyrroles. In this article, we describe strategies for the de novo synthesis of amphiphilic tetrapyrroles using a 3-hydroxyphenyl substituted tetrapyrrolic system (Temoporfin) as the lead structure. From an applied science-oriented approach, such a set of amphiphilic porphyrins is best synthesized by combining well-developed condensation methods with subsequent functionalization via organolithium compounds or transition metal catalyzed coupling protocols. Starting from simple A_2- or AB-porphyrins, the synthesis of A_2B-, A_3-, A_3B-, and A_2BC-porphyrins with a mixed hydrophilic/hydrophobic substitution pattern is described. Because of the versatility of this approach to unsymmetrically substituted porphyrins it is also applicable to other areas where porphyryns with a tailor-made substitution patterns are needed, for example, catalysts or molecular electronic devices based on tetrapyrroles.

1. Introduction

Photodynamic therapy (PDT) is a method of medicinal treatment that uses the combination of a dye (a photosensitizer) and light to generate reactive oxygen species, most prominently singlet oxygen, to damage unwanted tissue or cells.[1] Originally applied for the treatment of tumors,[2] PDT has gained an increasing number of potential applications, for example, antiviral and antibacterial PDT,[3] for the treatment of psoriasis[4] or for certain forms of the age-related macular degeneration (AMD).[5] Numerous substances have been tested for their suitability as photosensitizers but until today only a few photosensitizers have gained approval of the legal authorities in Europe and/or the United States, namely Photofrin® (or similar mixtures of hematoporphyrin derivatives), Verteporfin® (benzoporphyrin derivative), ALA (δ-amino levulinic acid), and Temoporfin [5,10,15,20-tetrakis(3-hydroxyphenyl)chlorin **1**].[6] All of these are tetrapyrrolic systems (or—as ALA—a biosynthetic precursor of a porphyrin, that is, protoporphyrin **2**), and indeed tetrapyrrolic systems are the most widely tested class of photosensitizers.[7]

Another property shared by these drugs is their amphiphilic structure, as the molecular frameworks have hydrophilic and hydrophobic parts. This amphiphilicity has been identified as an important criterion for the action of photosensitizers in vivo as it facilitates localization in membrane structures of the cells. It is here, where the reactive oxygen species generated initiate the complex reaction cascade eventually leading to cell death via necrosis and/or apoptosis.[8] Strongly hydrophilic photosensitizers have been shown to lack high PDT efficacy, most probably due to the fact that the singlet oxygen is generated in an aqueous environment, too far away from sensitive cellular structures, given the lifetime of singlet oxygen (2 μs) and the resulting low diffusion distance.[7]

Thus, when developing new photosensitizers for PDT, the

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target should be a series of compounds differing in the extent of hydrophilic/hydrophobic substitution but related to a common lead structure. This will allow a systematic assessment of membrane affinity to establish quantitative structure activity relationships (QSAR). Such an approach has already been successfully applied to compounds of the pheophorbide or hypocrellin series.[9]

Taking these requirements into account, the search for new photosensitizers requires the synthesis of unsymmetrically substituted tetrapyrrolic systems with mixed hydrophilic/hydrophobic substitution pattern (**3**, Fig. 1). One possibility to obtain such systems is to modify the ubiquitous occurring natural tetrapyrroles (chlorophylls, heme), the other possibility is the complete de novo synthesis of appropriate tetrapyrrolic systems. In the quest for potential new photosensitizer structures, both have been employed intensively. Among the approved PDT drugs, Verteporfin is an example for the first approach, the latter is exemplified by 5,10,15,20-tetrakis(3-hydroxyphenyl)-chlorin (**1**, Temoporfin). Additionally, from an industrial perspective the syntheses should be simple, facile, involve only a few synthetic steps, and be simple enough to easily pass the regulatory approval process. In order to simplify the optimization of and search for lead structures the synthetic methodology used in the development process should be simple and versatile to allow the preparation of series of compounds with minimal changes in the reaction conditions. In order to test how much present synthetic methods allow improvements on compounds that have already given promising medicinal results we decided to use Temoporfin, that is, a 3-hydroxyphenyl substituted tetrapyrrolic system as lead structure for our initial studies.

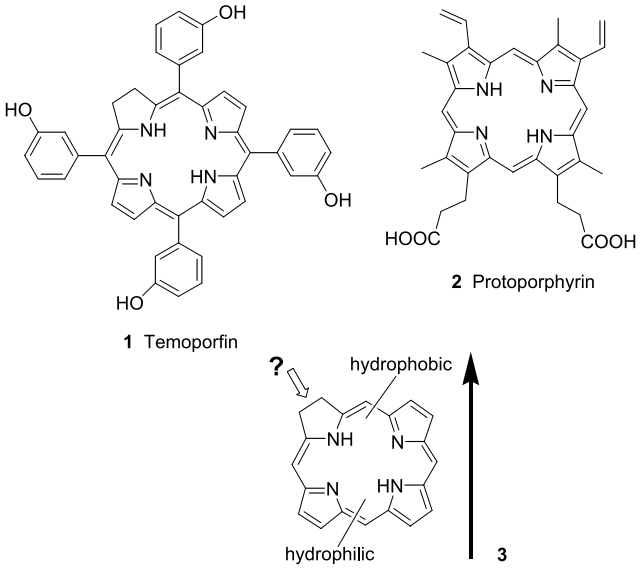


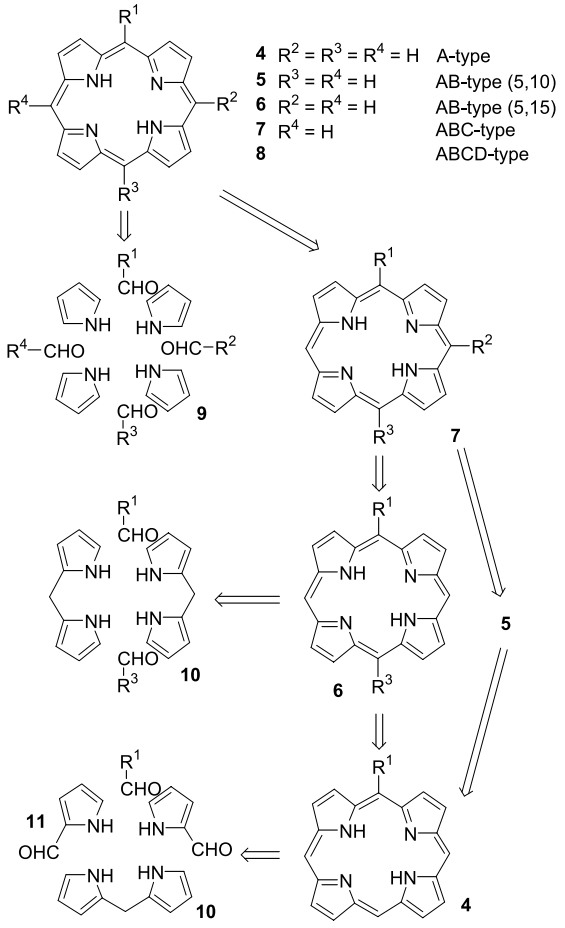
Figure 1. Temoporfin **1** and protoporphyrin **2** as typical photosensitzers and schematic illustration of the basic structure of porphyrins suitable for PDT.

The de novo synthesis of unsymmetrically substituted (amphiphilic) tetrapyrroles may in principle be achieved by condensation of pyrroles or dipyrromethanes with different aldehydes. But, of course, this 'combinatorial' approach results in complex product mixtures, which require tedious chromatographic workup procedures. Thus, more promising is the combination of those classical condensation reactions with subsequent functionalization via organometallic compounds or transition metal catalyzed coupling protocols. In the present work we exemplify how this combination of synthetic methods can be used to obtain—in a straightforward way—unsymmetrically substituted porphyrins with two, three or four substituents. Though the present examples focuses on tetrapyrroles for amphiphilicity studies in PDT, this combination of methods is also suited for preparing unsymmetrically substituted porphyrins for other application protocols, for example, push–pull porphyrins for nonlinear optics, chiral oxidation catalysts, etc.

2. Results and discussion

2.1. Synthetic rational

The most basic retrosynthetic approach for various unsymmetrically substituted porphyrins (**5**–**8**) is the disconnection into pyrrole **9** and aldehydes, where the latter provide the *meso* substitutents (Scheme 1). However, this approach is only successful when the differences in polarity of the individual porphyrins formed are large enough to allow chromatographic separation and it fails for ABC **7** or ABCD **8** porphyrins due to the large number of regioisomers



Scheme 1. Retrosynthetic analysis of ABCD-type porphyrins.

formed. Thus, while easily performed this strategy it is limited to selected types of substituents.[10,11]

A more general approach towards ABCD porphyrins is currently under development by Lindsey's group.[12] However, at present this approach has mainly been elaborated for the synthesis of porphyrins with *meso*-aryl substituents and not for *meso*-alkyl-substituted porphyrins a requirement for us to yield amphiphilic porphyrins. In addition, these methods require more synthetic steps and thus will be more suitable for large-scale synthesis when suitable candidates for further testing have been identified. Additionally, the mixed alkyl/aryl-substituted porphyrins resulting from the mixed-aldehyde–pyrrole condensation reactions usually differ strongly in their polarity, thus making chromatographic separation feasible.

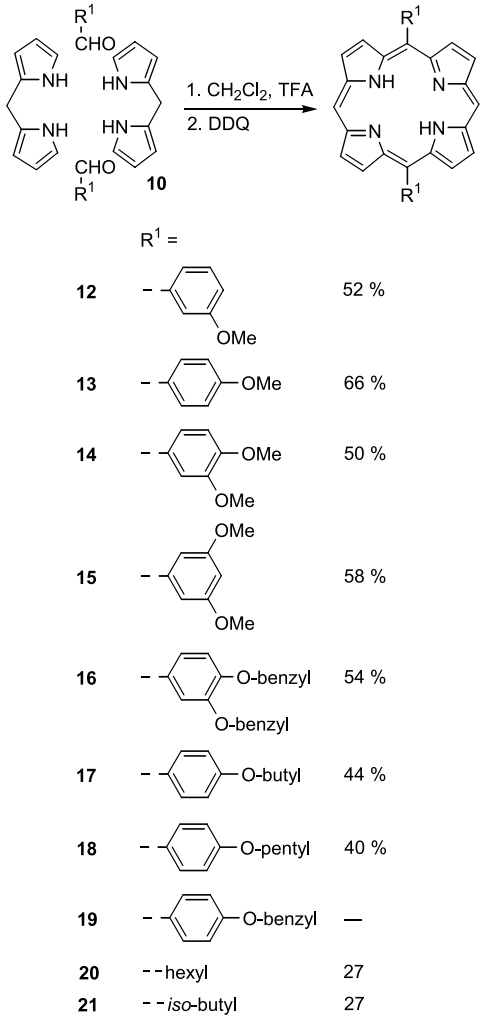
Therefore we decided to utilize a mix of the well-developed condensation reactions and newer methods like our nucleophilic substitution reactions[13] for the preparation of the target compounds. The individual syntheses will be discussed in order of increasing number of substituents and complexity.

2.2. Starting materials—A_2- and AB-porphyrins via condensation reactions

A rational synthesis of A_2BC porphyrins has to start with the respective mono- or disubstituted porphyrins. The easiest approach is the use of A_2-type porphyrins as starting materials for subsequent modifications. A_2-type porphyrins are easily accessible via a 2+2 condensation reaction using dipyrromethane **10** and an appropriate aldehyde.[14]

First, a number of compounds with methoxy groups was prepared (**12**–**15**) in yields of 50–66% using standard type condensation reactions (Scheme 2). As these compounds often had a low solubility, we also prepared the ether derivatives **16**–**19** with longer alkyl chains in order to improve the solubility. Yields ranged from 40 to 54%. However, the benzyl ether **19** proved to be so insoluble to preclude characterization. In order to later introduce individual methoxy residues we also prepared the two dialkylporphyrins **20** and **21** in yields of 27%, each.

Using similar condensation methods we also prepared a number of 5,15-AB-type porphyrins (Scheme 3). While different methods have been described for these[15] we chose mixed condensations for the initial generation of starting materials and prepared compounds **22**–**24** in 14–17% yield. Formation of these compounds was always accompanied by formation of the two symmetric A_2 porphyrins. In the case of using 4-methoxy- or 3,5-dimethoxybenzaldehyde separation of the mixtures is quite easy as the low solubility of the respective A_2-type disubstituted porphyrins retains these on the column. For subsequent functionalization reactions some of the 5,15-AB- and A_2-type porphyrins were converted into the respective nickel(II) complexes. Metallation was performed using the DMF-method[16] to yield compounds **25**–**29** mostly in quantitative yields (Scheme 4).

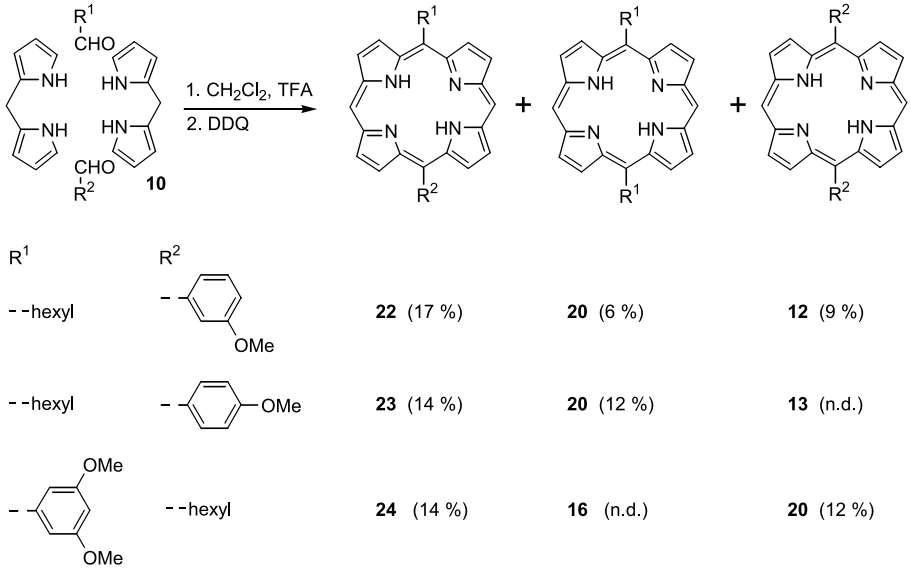


Scheme 2. Synthesis of A_2-type porphyrins.

2.3. A_2B- and A_3-type porphyrins via S_NAr reactions

The first series of target compounds related to *m*-THPC and suitable for biological studies were compounds carrying both precursors for hydroxyphenyl groups and alkyl chains in various combinations. As outlined in Scheme 2 the method of choice for the preparation of porphyrins with three *meso* substituents is the functionalization of the A_2- and AB-type porphyrins described above via electrophilic or nucleophilic substitution reactions.

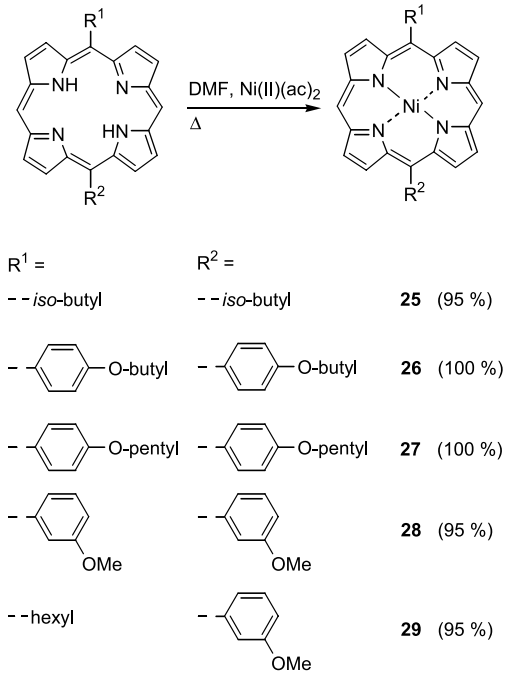
As we have developed the latter method over the last years[17,18] and the present study was intended as a test case of its applicability for a medicinal problem, we reacted a number of free base porphyrins with organolithium reagents as shown in Scheme 5. The reaction works well for both the introduction of aryl or alkyl residues and the A_3 porphyrin **30** and a wide range of A_2B-type porphyrins **32**–**40** could be prepared in yields from 50 to 91%. Only the reaction of bis(4-methoxyphenyl)porphyrin **13** with *n*-hexyl lithium (yielding compound **31**) gave an unsatisfactory yield of 35%, presumably, due to the low solubility of the starting material. This method can also be applied towards the synthesis of 5,10-A_2B-type porphyrins. For example, the



Scheme 3. Synthesis of AB-type porphyrins.

5,15-AB porphyrin **24** was reacted with *n*-hexyl lithium to yield the 5,10-A_2B porphyrin **38** in 60% yield. Alternatively, this compound could be prepared in 80% yield by direct disubstitution of the monosubstituted porphyrin **41**[19] using a method developed for the synthesis of 5,10-disubstituted porphyrins.[20] Thus, S_NAr reactions are useful methods for the preparation of both 5,15- and 5,10-A_2B-type porphyrins.

Again, some porphyrins were converted into the nickel(II) complexes (e.g., **42** and **43**); compound **44** was obtained as side product during the syntheses of **30**.



Scheme 4. Synthesis of metalloporphyrins.

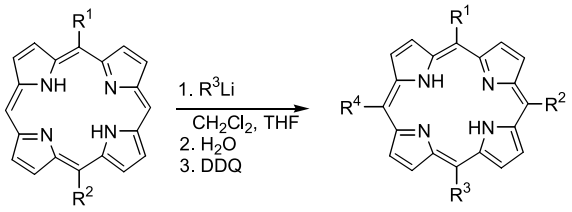
2.4. A_3B-type porphyrins via condensation reactions

The next series involved the mixing of *meso* alkyl and hydroxyphenyl precursor residues at all four *meso* positions to yield A_3B porphyrins. While we had already shown that such compounds can be prepared via reaction of 5,15-disubstituted nickel(II) porphyrins with RLi/RI combinations,[21] this reaction is yet only applicable to metalloporphyrins. As condensations have been utilized for the preparation of tetraarylporphyrins with different aryl residues[22] we investigated the utility of mixed condensation for this purpose.

As shown in Scheme 6, mixed condensation of an aliphatic and aromatic aldehyde yields a mixture of tetrasubstituted A_xB_y porphyrins. All possible combinations are formed, however, the different solubilities of the products allow separation via a single chromatographic column to yield the A_3B target compounds in yields of 6 to 10%. Purification is simpler when the aliphatic aldehyde is utilized as the A, that is, the major component. In this case, the A_4 and A_3B porphyrin show higher solubility and elute first. Thus, for **53** and **58** only the target compounds and the A_4 porphyrins **52** and **57** were isolated, making this a practical method for mixed A_3B porphyrins.

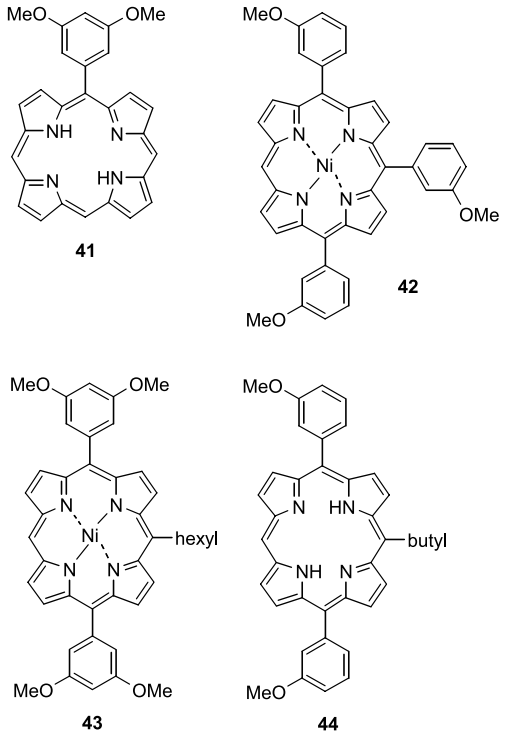
2.5. A_2BC-type porphyrins via S_NAr reactions

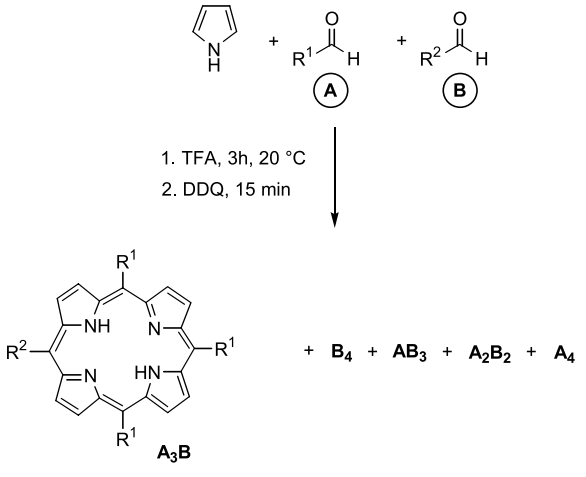
A_2BC free base porphyrins can be prepared via reaction of *meso* trisubstituted porphyrins (A_2B) with an appropriate organolithium reagent introducing the 'C' group. While this reaction often gives excellent yields with lithium aryl reagents and β substituted porphyrins,[13] utilization of *meso* trisubstituted porphyrins **7** as starting materials gave mixed results (Scheme 7). If **7** carries an alkyl residue in the B (R^2) position reaction with LiAr generally gives better yields than alkyl lithium reagents. Likewise, attacking a *meso* position opposite to one carrying an aryl group generally gives lower yields, due to steric hindrance of the mesomeric benzylic anion stabilization, as established by earlier



R^1 =	R^2 =	R^3 =	R^4 =		
3-MeO-Ph	3-MeO-Ph	3-MeO-Ph	H	**30**	(79 %)
hexyl	4-MeO-Ph	H	4-MeO-Ph	**31**	(35 %)
3-MeOPh	hexyl	3-MeO-Ph	H	**32**	(65 %)
4-Butyloxy-Ph	hexyl	4-Butyloxy-Ph	H	**33**	(51 %)
hexyl	4-Pentyloxy-Ph	H	4-Pentyloxy-Ph	**34**	(91 %)
3,5-DiMeO-Ph	hexyl	3,5-DiMeO-Ph	H	**35**	(58 %)
hexyl	*iso*-butyl	H	*iso*-butyl	**36**	(50 %)
hexyl	hexyl	4-MeO-Ph	H	**37**	(53 %)
hexyl	hexyl	3,5-DiMeO-Ph	H	**38**	(60 %)
4-NH_2-Ph	3-MeO-Ph	H	3-MeO-Ph	**39**	(73 %)
hexyl	Ph	H	Ph	**40**	(71 %)

Scheme 5. Synthesis of A_3- and A_2B-type porphyrins via S_NAr reactions.





R^1 =	R^2 =						
3-MeO-Ph	pentyl	**45**	(9 %)	**46**	**47**	**48/49**	**50**
3-MeO-Ph	hexyl	**51**	(8 %)	**52**	**53**	**54/55**	**50**
hexyl	3-MeO-Ph	**53**	(8 %)	-	-	-	**52**
3-MeO-Ph	heptyl	**56**	(10 %)	**57**	**58**	**59/60**	**50**
heptyl	3-MeO-Ph	**58**	(6 %)	-	-	-	**57**

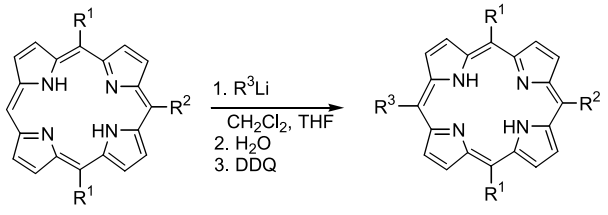
Scheme 6. Synthesis of A_3B-type porphyrins via condensation reactions.

mechanistic studies.[17b] Nevertheless, this method allows the preparation of the target compounds **61–68** in acceptable yields and two steps from the respective A_2 porphyrins. We are currently investigating improvements of these reactions by using various cocatalysts.

The most significant result is, that hydroxyphenyl residues can be introduced directly and in good to excellent yields using the respective dilithio species. For example, the *m*-hydroxyphenylporphyrin **63** could be prepared in 83% yield. As discussed in Section 2.8 currently most strategies involve first preparation of, for example, methoxyarylporphyrins and then demethylation to the desired hydroxyphenylporphyrins. The ease of the direct substitution reaction indicates that the use of protected alcohols followed by deprotection can be circumvented. Bonnett and Martinez recently described a method that allows the conversion of *m*-hydroxyphenyl groups into 3,5-dihydroxyphenyl groups in *m*-THPC derivatives via sensitization reactions offering the possibility to further increase the polarity of such compounds.[23]

2.6. Vinylogous formylation reactions

Alternatively, electrophilic substitution reactions have been utilized for a long time for the modification of porphyrins and as an entry into more elaborate photosensitizer structures.[24] One such example are the benzochlorins,[25] which can be prepared via acid-catalyzed cyclization of

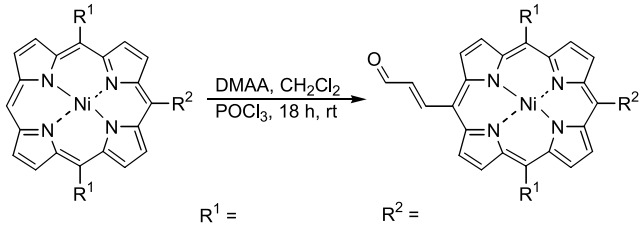


R^1 =	R^2 =	R^3 =		
Ph	hexyl	butyl	**61**	(31 %)
Ph	hexyl	4-Me_2N-Ph	**62**	(54 %)
Ph	hexyl	3-HO-Ph	**63**	(83 %)
Ph	hexyl	4-HO-Ph	**64**	(65 %)
Ph	hexyl	2-MeO-Ph	**65**	(40 %)
Ph	hexyl	2,5-DiMeO-Ph	**66**	(29 %)
Ph	4-H_2N-Ph	4-Me_2N-Ph	**67**	(20 %)
3-MeO-Ph	4-H_2N-Ph	hexyl	**68**	(44 %)

Scheme 7. Synthesis of A_2BC-type porphyrins via S_NAr reactions.

meso acrolein substituted porphyrins.[26,27] In order to test, whether this method is also applicable to the unsymmetric porphyrins targeted here, a number of nickel(II) porphyrins were subjected to a vinylogous Vilsmeier formylation to yield the acroleinporphyrins.

Like classic formylation reactions,[28] the vinylogous Vilsmeier reactions proceed quite well with A_2- and A_2B-type porphyrins. As shown in Scheme 8 the trisubstituted porphyrins **69–71** were accessible in about 60% yield from the respective A_2 porphyrins. The disubstitution products **72–74** were formed in small amounts during these reactions. Likewise the A_2BC porphyrins **75** and **76** could be prepared in good yields. Most vinylogous formylation reactions of porphyrins found in the literature have been performed with β-substituted porphyrins, namely octaethylporphyrin and its derivatives. Yields are in general quite good, often exceeding 80%. Vinylogous formylation reactions on β-unsubstituted porphyrins have — to the best of our knowledge — been described only twice with yields between 29 and 55%.[27,28a] This is in line with our findings which also gave lower yields for β-unsubstituted porphyrins. One reason for this may be a higher reactivity of the β-unsubstituted porphyrins, resulting in side-reactions. This higher reactivity is also supported by the occurrence of bis-vinylogously formylated products for all 5,15-disubstituted porphyrins.



R^1 =	R^2 =		
4-butyloxy-Ph	H	**69**	(63 %)
4-pentyloxy-Ph	H	**70**	(63 %)
3-MeO-Ph	H	**71**	(56 %)
4-butyloxyphenyl	-CH=CH-CHO	**72**	side prod.
4-pentyloxyphenyl	-CH=CH-CHO	**73**	side prod.
3-MeO-Ph	-CH=CH-CHO	**74**	side prod.
3-MeO-Ph	3-MeO-Ph	**75**	(77 %)
3,5-DiMeO-Ph	hexyl	**76**	(55 %)

Scheme 8. Vinylogous formylation reactions.

An interesting feature of the vinylogously formylated porphyrins is a strong bathochromic shift (~35 nm) in the long-wavelength absorption band, most probably due to the extension of the conjugated system. The bathochromic shift is nearly the same starting from 5,15-di- as well as from 5,10,15-trisubstituted porphyrins. As a bathochromically shifted absorption is a prerequisite for a promising photosensitizer (cf. also Section 2.7), these vinylogously formylated porphyrins - after removal of the central metal ion by standard methods - themselves could have potential as photosensitizers.

Unfortunately, we were unable to accomplish subsequent acid-catalyzed cyclization reactions in a rational manner. Although the synthesis of benzochlorins has been widely used with β-substituted porphyrins,[25] only one compound derived from β-unsubstituted 5,15-disubstituted porphyrins has been reported.[28] However, in all present cases complex product mixtures (>10 compounds) were obtained, that could not be separated. Spectroscopic evidence points towards the formation of different cyclization products, the occurrence of dealkylation reactions and a general instability of the products formed.[29a] Such an anomalous cyclization behavior has also been observed for *meso* 3-methoxyphenyl-substituted β-formyl porphyrins.[29b]

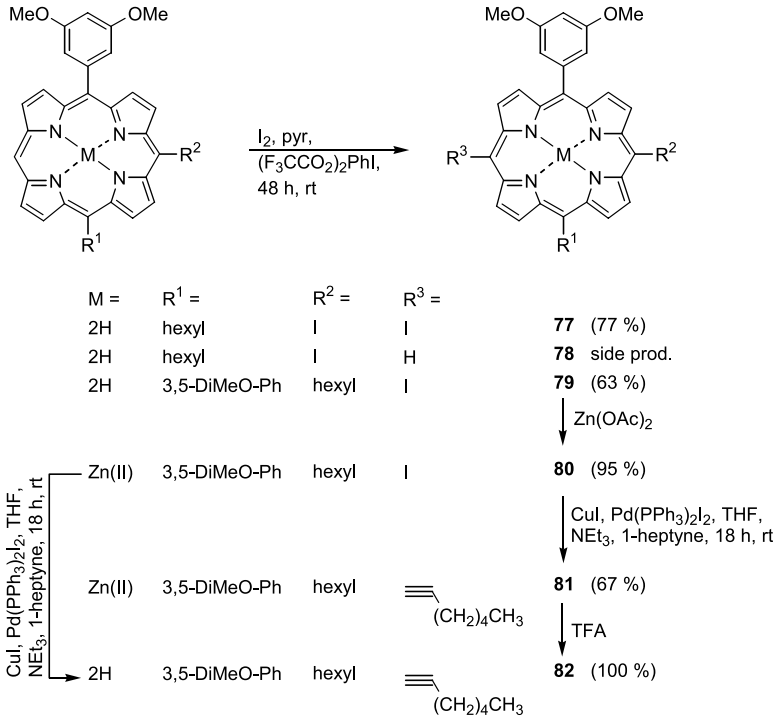
2.7. Alkynyl substituted porphyrins

Another approach for facile *meso* modifications is the preparation of *meso* halogenoporphyrins followed by subsequent coupling reactions.[24b] We were especially interested in functionalization methods that allowed both a modulation of amphiphilicity and the electronic properties of the target compounds. Porphyrins carrying ethynyl residues exhibit bathochromically shifted absorption bands, with each alkynyl system typically accounts for a 15 nm shift.[30] This is a desirable effect for photosensitizers in PDT due to the deeper tissue penetration of the exciting light.

As reasoned above, the basic framework of the porphyrin system should contain both potentially polar and apolar side chains to assure amphiphilicity. As the polar groups are provided here by the hydroxyphenyl groups related to the original Temoporfin framework, this required introduction of the C≡C group in a long aliphatic chain to maintain an amphiphilic system.

Using the A_2B porphyrin **35** as a test bed this compound was *meso* iodinated[31] to give **79** in 63% yield on a 100 mg scale. Longer reaction times led to an increase in yield. However, this was accompanied by the formation of more side products. Metallation with zinc(II) acetate gave the corresponding metalloporphyrin **80** in almost quantitative yield and this compound was then subjected to a palladium-catalyzed coupling[32] with 1-heptyne to give the alkynylated porphyrin **81** in 67% yield (Scheme 9). The reaction sequence was completed by quantitative demetallation of **81** to **82**. For practical purposes the reaction sequence coupling–demetallation (e.g., **80**→**81**→**82**) can be performed in a one-pot procedure by addition of TFA to the crude mixture of the coupling reaction. This gave **82** in 50% yield with respect to **80**. Similar reactions using diiodinated AB porphyrins (e.g., **77**) as starting materials are possible and will be reported elsewhere.

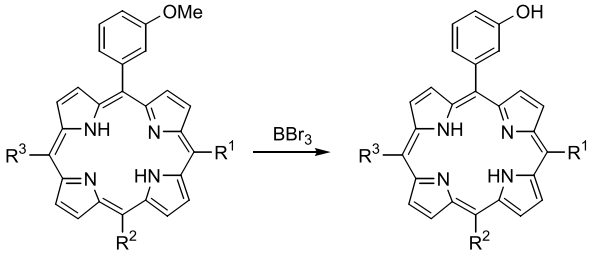
Compounds derived from **82** possessing free hydroxyl groups and the alkynyl chain are very promising candidates as photosensitizers by combining a bathochromically shifted absorption with an amphiphilic molecular structure. Moreover, the alkynyl chain is chemically more stable than, for example, simple chlorin structures, which are easily reoxidized to the corresponding porphyrins, thus loosing their decisive absorption features. As discussed below (cf. Section 2.8) such compounds possessing three free hydroxyl groups and a lipophilic carbon chain also exhibit special features in a biomimetic environment such as liposomes.



Scheme 9. Synthesis of alkynyl substituted porphyrins.

2.8. Hydroxyphenylporphyrins and preliminary biological studies

In order to have truly amphiphilic porphyrins a number of A_2-, AB-, A_3-, A_2B-, and A_3B-type porphyrins carrying methoxyphenyl groups were converted into the respective hydroxyphenyl porphyrins **83**–**92**. The results are summarized in Scheme 10. Demethylation with BBr_3[33] generally proceeds well in yields of 80–90%. Only **83** gave a very low isolated yield, presumably due to the very low solubility of the compound.



R^1 =	R^2 =	R^3 =		
H	3-HO-Ph	H	**83**	(21 %)
H	hexyl	H	**84**	(83 %)
3-HO-Ph	3-HO-Ph	H	**85**	(81 %)
hexyl	3-HO-Ph	H	**86**	(84 %)
3-HO-Ph	3-HO-Ph	pentyl	**87**	(85 %)
hexyl	3-HO-Ph	3-HO-Ph	**88**	(89 %)
heptyl	3-HO-Ph	3-HO-Ph	**89**	(86 %)
hexyl	hexyl	hexyl	**90**	(92 %)
heptyl	heptyl	heptyl	**91**	(87 %)
3-HO-Ph	3-HO-Ph	3-HO-Ph	**92**	(90 %)

Scheme 10. Preparation of hydroxyphenylporphyrins.

In order to test the influence of an amphiphilic substitution pattern on the PDT properties detailed in vitro and in vivo tests are currently ongoing. Initial results on the PDT-related photophysical properties for a number of selected porphyrins were determined in isotropic solution and in liposome membrane model systems and have already been communicated.[34] Absorption, fluorescence, and singlet oxygen quantum yields were determined in isotropic solution and in DPPC liposomes.

In isotropic ethanol solution, the compounds showed properties typical for *meso* substituted porphyrins, that is, fluorescence lifetimes of about 8–9 ns, singlet oxygen quantum yields of 0.6–0.7, and singlet oxygen luminescence lifetimes of 14 μs. Only the *p*-aminophenyl substituted porphyrins **39** and **68** exhibited a smaller singlet oxygen quantum yield. Due to the differences in solubility, with the *m*-hydroxyphenyl-substituted porphyrins having a much higher solubility. As expected, high concentrations in liposomes could only be achieved with compounds having free hydroxy or amino groups. The highest concentration in liposomes was obtained with compounds **87**–**89** (i.e., those that have three 3-hydroxyphenyl substituents and one alkyl chain) and for 5,10,15,20-tetrakis(3-hydroxyphenyl)-porphyrin **92**.

In addition, compounds **87**–**89** exhibited a striking difference to all other compounds studied. Their fluorescence lifetime in liposomes was significantly reduced as was the singlet oxygen quantum yield. Both parameters are indicators of the localization of the dyes in the lipid bilayer and we concluded that the amphiphilic *m*-THPC congeners with one hydrophobic alkyl chain and three 3-hydroxyphenyl residues differ in their localization behavior in the

liposome bilayer from all other compounds studied. Most likely is a preferable localization at the hydrophobic/hydrophilic interface of the liposomes indicating that, compared to Temoporfin, a more specific in vivo localization of unsymmetrically substituted amphiphilic photosensitizers may be achieved using this strategy. Indeed, for related chlorins (not shown) the increasing amphiphilicity of the sensitizer molecules could be correlated with an increased uptake into lysosomes and an increased ratio of necrotic versus apoptotic cells.[35]

3. Conclusions

Starting from an applied-science oriented approach, we have shown how the present tools of synthetic porphyrin chemistry can be combined to obtain a wide variety of unsymmetrically substituted amphiphilic porphyrins as potential photosensitizers and as probes for assessing membrane affinity.

The porphyrin starting materials (such as A_2- or AB-porphyrins) are best prepared by simple condensation reactions of dipyrromethane and suitable aldehydes. These porphyrins are then easily functionalized by an S_NAr reaction with organolithium compounds, allowing the introduction of, for example, alkyl chains, protected phenolic functions, free hydroxyphenyl residues, or aminophenyl substituents. Other methods were complementarily used to further tune the properties of the tetrapyrrolic system, for example, introduction of alkynyl-substituents that exert a bathochromic shift, thus, improving the absorption properties.

Future work will be concentrated on utilizing these principles for the synthesis of photosensitizers with optimized membrane affinity and targeting properties. In particular, the direct introduction of *m*, *o*, and *p*-hydroxyphenyl groups into the tetrapyrrolic system via organolithium chemistry (thus, circumventing deprotection procedures) poses a promising route to compounds with a tailored degree of hydrophilicity. We are currently investigating the synthesis of ABCD porphyrins carrying up to four hydroxyphenyl groups via direct S_NAr reactions.

Further work will be directed towards the construction of combinatorial libraries with these multi-functionalized porphyrins and their extension to chlorin systems. An unsymmetrically substituted chlorin of this type has already been shown to give promising results in Jurkat cell suspensions.[35]

4. Experimental

4.1. General methods

All chemicals used were of analytical grade and were purchased from Aldrich Co. unless stated otherwise. Reactions with organolithium reagents were performed using standard Schlenk techniques and glassware. Melting points were measured on a Reichert Thermovar apparatus and are uncorrected. Silica gel 60 (0.04–0.063 mm, 230–400 mesh ASTM, Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with and without fluorescence indicator F254) or alumina plates (Alox 60, Machery & Nagel). Alternatively, neutral alumina (60 mesh, Alfa), normally deactivated with water (7%= Brockmann grade III), was used for column chromatography. Proton NMR spectra were recorded at a frequency of 250 MHz (AC 250) or 500 MHz (Bruker, AMX 500), ^{13}C NMR spectra at a frequency of 125 MHz. All chemical shifts are given in ppm, referenced on the δ scale downfield from the TMS signal as internal standard. Electronic absorption spectra were recorded on a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane 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. Elemental analyses were performed with a Perkin–Elmer 240 analyzer. Preparative HPLC was performed with columns (23×15 and 23×30 mm, respectively) filled with silica gel [Merck, Nucleosil 50 (5 μm)] using a Knauer-pump (Knauer MPLC Pump and Knauer HPLC Pump 64, respectively). The solvent flow rate was 64 mL/min (P= 23 bar$=23\times10^5$ Pa). UV detection (Knauer Variable Wavelength Monitor) was performed at 420 nm for the porphyrins. Analytical HPLC was performed using a Spectra Physics pump (SP 8810) and an analytical column (4×250 mm) filled with silica gel (Merck, Nucleosil 50, 5 μm). The solvent flow rate was 1 mL/min, with UV/vis detection typically at 420 nm for the porphyrins.

4.2. Starting materials

5-(3,5-Dimethoxyphenyl)porphyrin **41**[19] 5,15-diphenylporphyrin,[14a] 5-(*p*-aminophenyl)-10,20-diphenylporphyrin,[18b] dipyrromethane **10**[12b] and 5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin **50**[36] (which is also obtained as a by-product in the synthesis of **45**, **51**, and **56**) were prepared according to published procedures. Pyrrole-2-carbaldehyde **11** was obtained from Fluka. 4-Pentyloxybenzaldehyde was obtained from Lancaster.

4.3. A_2-type porphyrins

4.3.1. 5,15-Bis(3-methoxyphenyl)porphyrin (12). Dry dichloromethane (1 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (Ar) and a reflux condenser. Dipyrromethane **10** (593 mg, 4.06 mmol) and 3-methoxybenzaldehyde (530 μL, 4.35 mmol) were added. The flask was shielded from ambient light and then 70 μL (0.9 mmol) of TFA were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h, followed by addition of 15 mL of triethylamine. The reaction mixture was concentrated in vacuo to about 100 mL and filtered through 600 mL of silica (column diameter 5 cm), washing with dichloromethane. The eluate was evaporated to dryness and the residue resuspended in 100 mL of dichloromethane and then layered with a 2-fold excess of methanol. After 24 h, the precipitated solid was

removed by suction filtration through a D3 frit and dried in vacuo. Yield: 550 mg (1.05 mmol; 52%) of purple crystals: mp >350 °C, sublimation >300 °C; R_f=0.58 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.16 (s, br., 2H, N*H*), 4.01 (s, 6H, OCH_3), 7.35 (m, 2H, Ph-*H*), 7.67 (m, 2H, Ph-*H*), 7.84 (m, 4H, Ph-*H*), 9.11 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 9.38 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 10.31 ppm (s, 2H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.57, 105.26, 113.55, 120.82, 127.78, 127.92, 131.05, 131.58, 142.75, 145.30, 147.10, 153.64, 158.29 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 (4.30), 361 (4.49), 390 (4.95), 410 (5.57), 474 (3.77), 502 (4.30), 536 (3.88), 575 (3.84), 628 nm (3.56); MS (EI, 80 eV, 250 °C) *m/z* (%): 522 (100) [M^+], 507 (2) [M^+-CH_3], 491 (3) [M^+-CH_3O], 261 (7) [M^{2+}]; HRMS (EI) [$C_{34}H_{26}N_4O_2$]: calcd 522.20558, found 522.20642; [$C_{34}H_{26}N_4O_2$, 522.61 g mol^{-1}]. Anal. Calcd C 78.14, H 5.01, N 10.72. Anal. Calcd for [$C_{34}H_{26}N_4O_2\cdot0.5H_2O$, 531.62 g mol^{-1}]. Anal. Calcd C 76.82, H 5.12, N 10.54, found C 76.80, H 4.90, N 10.53.

4.3.2. 5,15-Bis(4-methoxyphenyl)porphyrin (13). Dry dichloromethane (2 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and 4-methoxybenzaldehyde (1 mL, 8.2 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of trifluoroacetic acid were added and the reaction mixture stirred for 18 h at 20 °C. Subsequently, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 6 mL of triethylamine were added and the reaction mixture was concentrated in vacuo to about 150 mL. Methanol (150 mL) was added and the reaction mixture was filtered through a D3 frit. The residue in the frit was thoroughly washed with acetone and methanol until the washing solution becomes nearly colorless. Finally it was washed with 100 mL of dichloromethane. The filtrate was discarded and the residue in the frit was dried in vacuo to yield 1.42 g (2.7 mmol; 66%) of the title compound as a purple amorphous solid: mp >330 °C; R_f=0.54 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.11 (s, br., 2H, N*H*), 4.12 (s, 6H, OCH_3), 7.34 (m, 4H, phenyl-*H*), 8.18 (m, 4H, phenyl-*H*), 9.09 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 9.38 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 10.29 ppm (s, 2H, *meso-H*); UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 (4.26), 391 (4.86), 410 (5.54), 505 (4.22), 540 (3.93), 577 (3.82), 634 nm (3.56); MS (EI, 80 eV, 300 °C) *m/z* (%): 522 (100) [M^+], 507 (6) [M^+-CH_3], 416 (2) [$M^+-C_6H_7O$], 261 (10) [M^{2+}]; HRMS (EI) [$C_{34}H_{26}N_4O_2$]: calcd 522.20558, found 522.20392; [$C_{34}H_{26}N_4O_2$, 522.61 g mol^{-1}]. Anal. Calcd C 78.14, H 5.01, N 10.72, found C 77.80, H 4.98, N 10.63.

4.3.3. 5,15-Bis(3,4-dimethoxyphenyl)porphyrin (14). Dry dichloromethane (2 L) was placed in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and 3,4-dimethoxybenzaldehyde (1.35 g, 8.1 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of trifluoroacetic acid were added and the reaction mixture was stirred for 18 h at 20 °C. After this time 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 6 mL of triethyl amine were added and the reaction mixture was stirred for 15 min. The reaction mixture was filtered through 100 g of silica, washing with dichloromethane (approximately 4 L). The eluted porphyrin fractions were evaporated to dryness. The porphyrin was resuspended in 100 mL of dichloromethane and then layered with a 2-fold excess of methanol. After 48 h, the precipitated purple solid was removed by suction filtration through a D4 frit and dried in vacuo to yield 1.23 g of a purple amorphous solid (2.1 mmol; 50%): mp >340 °C; R_f=0.65 (SiO_2, CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); ^{1}H NMR (250 MHz, $CDCl_3$) δ=−3.10 (s, 2H, N*H*), 4.03 (s, 6H, OCH_3), 4.19 (s, 6H, OCH_3), 7.31 (m, 2H, phenyl-*H*), 7.81 (m, 4H, phenyl-*H*), 9.12 (d, *J*=5 Hz, 4H, β-pyrrole-*H*), 9.38 (d, *J*=5 Hz, 4H, β-pyrrole-*H*), 10.30 ppm (s, 2H, *meso-H*); UV/vis (CH_2Cl_2): λ_{max} (log ε)=411 (5.60), 505 (4.24), 541 (3.87), 577 (3.74), 633 nm (3.32); MS (EI, 80 eV, 240 °C) *m/z* (%): 582 (100) [M^+], 567 (5) [M^+-CH_3], 551 (6) [M^+-CH_3O], 445 (1) [$M^+-C_8H_9O_2$], 291 (5) [M^{2+}]; HRMS (EI) [$C_{36}H_{30}N_4O_4$]: calcd 582.22668, found 582.22745; [$C_{36}H_{30}N_4O_4$, 582.66 g mol^{-1}]. Anal. Calcd C 74.21, H 5.19, N 9.62, found C 74.11, H 5.05, N 9.97.

4.3.4. 5,15-Bis(3,5-dimethoxyphenyl)porphyrin (15). Dry dichloromethane (2 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (Ar) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and 3,5-dimethoxybenzaldehyde (1.4 g, 8.4 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of TFA were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 6 mL of triethylamine were added and the reaction mixture was concentrated in vacuo to about 200 mL. Methanol (50 mL) was added and the reaction mixture was filtered through a D3 frit. The residue in the frit was thoroughly washed with dichloromethane, acetone, and methanol until the washing solution became nearly colorless. The wash solutions were discarded and the residue in the frit was dried in vacuo to yield 1.4 g (2.4 mmol; 58%) of a purple amorphous solid: mp >340 °C; R_f=0.5 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.16 (s, br., 2H, N*H*), 4.01 (s, 12H, OCH_3), 6.94 (m, 2H, phenyl-H_{para}), 7.46 (m, 4H, phenyl-H_{ortho}), 9.18 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 9.39 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 10.32 ppm (s, 2H, *meso-H*); UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 (4.37), 361 (4.52), 391 (4.96), 407 (5.36), 502 (4.33), 533 (3.93), 573 (3.93), 628 nm (3.61); MS (EI, 80 eV, 250 °C) *m/z* (%): 582 (100) [M^+], 567 (3) [M^+-CH_3], 531 (4) [M^+-CH_3O], 446 (2) [$M^+-C_8H_8O_2$], 291 (11) [M^{2+}]; HRMS (EI) [$C_{36}H_{30}N_4O_4$]: calcd 582.22671, found 582.22833; [$C_{36}H_{30}N_4O_4$, 582.66 g mol^{-1}]. Anal. Calcd C 74.21, H 5.19, N 9.62, found C 74.55, H 5.18, N 9.78.

4.3.5. 5,15-Bis(3,4-dibenzyloxyphenyl)porphyrin (16). Dry dichloromethane (2000 mL) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and 3,4-dibenzyloxybenzaldehyde (2.58 g, 8.1 mmol) were added. The flask was shielded from ambient

light and then 140 μL (1.8 mmol) of TFA were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 6 mL of triethylamine were added and the reaction mixture was stirred for 15 min. The reaction mixture was filtered through 100 g of silica, washing with dichloromethane (~1 L). The eluted porphyrin fractions were evaporated to dryness. The porphyrin was resuspended in 100 mL of dichloromethane and then layered with a twofold excess of methanol. After 24 h, the precipitated purple solid was removed by suction filtration through a D3 frit. This solid was thoroughly washed with dichloromethane (the filtrate was discarded) and then dried in vacuo. Yield: 1967 mg of a purple amorphous solid (2.2 mmol; 54%); mp 319–321 °C; R_f=0.65 (SiO_2, CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.44 (SiO_2, CH_2Cl_2/C_6H_{14}, 2:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.16 (s, 2H, N*H*), 5.36 (s, 4H, OCH_2), 5.48 (s, 4H, OCH_2), 7.33–7.55 (m, 12H, phenyl-*H*), 7.65–7.75 (m, 6H, phenyl-*H*), 7.88 (m, 2H, phenyl-*H*), 8.95 (d, *J*=5 Hz, 4H, β-pyrrole-*H*), 9.31 (d, *J*=5 Hz, 4H, β-pyrrole-*H*), 10.25 ppm (s, 2H, *meso*-*H*); UV/vis (CH_2Cl_2): λ_{max} (log ε)=412 (5.66), 505 (4.13), 542 (3.78), 578 (5.39), 633 nm (3.14); MS (FAB+, CH_2Cl_2/*m*-NO_2-Bzl-OH/Xe), *m/z* (%): 887 (6) [(M+H)$^+$], 796 (1) [(M+H)$^+$−C_7H_7], 443 (0.2) [M^{2+}]; HRMS (EI) [$C_{60}H_{38}N_4O_4$]: calcd 886.35191, found 886.35134; [$C_{60}H_{38}N_4O_4$, 887.05 g mol^{-1}]. Anal. Calcd C 81.24, H 5.23, N 6.32, found C 81.21, H 5.29, N 6.45.

4.3.6. 5,15-Bis(4-butyloxyphenyl)porphyrin (17). Dry dichloromethane (2 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and 4-butyloxybenzaldehyde (1.4 mL, 8.25 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of TFA were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. After addition of 6 mL of triethylamine the reaction mixture was filtered through 50 g of silica (washing with dichloromethane) and then concentrated in vacuo to about 150 mL. The flask was ultrasonicated for 2 min and then layered with a 2-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 1.1 g (1.81 mmol; 44%) of the title porphyrin as a purple amorphous powder: mp >340 °C; R_f=0.60 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.09 (s, br., 2H, N*H*), 1.11 (t, 6H, *J*=7 Hz, $OCH_2CH_2CH_2CH_3$), 1.68 (m, 4H, $OCH_2CH_2CH_2$-CH_3), 1.99 (m, 4H, $OCH_2CH_2CH_2CH_3$), 4.28 (t, 4H, *J*=6 Hz, $OCH_2CH_2CH_2CH_3$), 7.32 (m, 4H, phenyl-*H*), 8.15 (m, 4H, phenyl-*H*), 9.09 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 9.38 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 10.28 ppm (s, 2H, *meso*-H); UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 nm (4.36), 360 (4.44), 391 (4.93), 410 (5.50), 474 (3.85), 505 (4.29), 541 (4.03), 578 (3.89), 633 (3.65); MS (EI, 80 eV, 320 °C) *m/z* (%): 606 (100) [M^+], 549 (5) [M^+−C_4H_9], 458 (12) [M^+−$C_{10}H_{12}O$], 303 (1) [M^{2+}]; HRMS (EI) [$C_{40}H_{38}N_4O_2$]: calcd 606.29948, found 606.29663; [$C_{40}H_{38}N_4O_2$, 606.77 g mol^{-1}]: C 79.18, H 6.31, N 9.23, [$C_{34}H_{26}N_4O_2\cdot 1H_2O$, 615.78 g mol^{-1}]. Anal. Calcd C 76.90, H 6.45, N 8.97, found C 76.36, H 6.05, N 8.81.

4.3.7. 5,15-Bis(4-pentyloxyphenyl)porphyrin (18). Dry dichloromethane (2 L) was placed in a three-necked-flask equipped with magnetic stirrer, gas inlet (Ar) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and 4-pentyloxybenzaldehyde (1.56 mL, 8.25 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of TFA acid were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h, followed by addition of 6 mL triethylamine. The reaction mixture was concentrated in vacuo to about 200 mL, ultrasonicated for 2 min and then filtered through 600 mL of silica (column diameter 5 cm), washing with dichloromethane (ca. 2 L). The eluate was evaporated to dryness and the residue resuspended in 100 mL of dichloromethane and then layered with a 2-fold excess of methanol. After 24 h the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo. Yield: 1.05 g (1.65 mmol; 40%) of purple crystals: mp 314–316 °C; R_f=0.64 (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.48 (CH_2Cl_2/C_6H_{14}, 2:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.08 (s, br., 2H, N*H*), 1.04 (t, 6H, *J*=7 Hz, $OCH_2CH_2CH_2CH_2$-CH_3), 1.45–1.70 (m, 8H, $OCH_2CH_2CH_2CH_2CH_3$ and $OCH_2CH_2CH_2CH_2CH_3$), 2.01 (m, 4H, $OCH_2CH_2CH_2CH_2$-CH_3), 4.27 (t, 4H, *J*=6 Hz, $OCH_2CH_2CH_2CH_2CH_3$), 7.32 (m, 4H, phenyl-*H*), 8.15 (m, 4H, phenyl-*H*), 9.09 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 9.38 (d, 4H, *J*=5 Hz, β-pyrrole-*H*), 10.28 ppm (s, 2H, *meso*-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.13, 22.62, 28.44, 29.25, 68.44, 105.12, 113.15, 118.96, 131.03, 131.46, 133.60, 135.87, 145.12, 147.58, 159.14 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 nm (4.33), 360 (4.40), 391 (4.91), 410 (5.54), 474 (3.69), 505 (4.23), 541 (3.93), 578 (3.74), 633 (3.36); MS (EI, 80 eV, 320 °C) *m/z* (%): 634 (100) [M^+], 563 (6) [M^+−C_5H_{11}], 472 (2) [M^+−$C_{11}H_{14}O$], 317 (1) [M^{2+}]; HRMS (EI) [$C_{42}H_{42}N_4O_2$]: calcd 634.330777, found 634.33423; [$C_{42}H_{42}N_4O_2$, 634.82 g mol^{-1}]. Anal. Calcd C 79.47, H 6.67, N 8.83, found C 78.95, H 6.56, N 8.80.

4.3.8. 5,15-Bis(4-benzyloxyphenyl)porphyrin (19). Synthetic procedure similar to that for compound **18** (Section 4.3.7). However, the crude product obtained was completely insoluble in common solvents. Although roughly 300 mg crude material were obtained, no characterization could be performed.

4.3.9. 5,15-Dihexylporphyrin (20). Dry dichloromethane (2 L) was placed in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol) and heptanal (1.17 mL, 8.4 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of trifluoroacetic acid were added and the reaction mixture was stirred for 18 h at 20 °C. After this time 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 3 mL of triethylamine were added and the reaction mixture was concentrated in vacuo to about 150 mL. The reaction mixture was filtered through

600 mL of silica (column diameter 5 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated purple needles were removed by suction filtration through a D3 frit and dried in vacuo. Yield: 534 mg (1.1 mmol; 27%). Purple needles: mp 214–216 °C; R_f=0.87 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.90 (s, br., 2H, N*H*), 0.96 (t, J=7 Hz, 6H, 5^6-CH_3 and 15^6-CH_3), 1.43 (m, 4H, 5^5-CH_2 and 15^5-CH_2), 1.54 (m, 4H, 5^4-CH_2 and 15^4-CH_2), 1.84 (m, 4H, 5^3-CH_2 and 15^3-CH_2), 2.57 (m, 4H, 5^2-CH_2 and 15^2-CH_2), 5.02 (t, J=8 Hz, 4H, 5^1-CH_2 and 15^1-CH_2), 9.41 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.58 (d, J=5 Hz, 4H, β-pyrrole-*H*), 10.17 ppm (s, 2H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.12, 22.73, 29.70, 30.24, 31.93, 34.65, 38.59, 48.33, 104.22, 118.82, 127.77, 131.83, 144.21, 147.49, 153.08 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 (4.21), 360 (4.41), 388 (4.91), 404 (5.45), 475 (3.34), 504 (4.19), 535 (3.56), 578 (3.59), 633 nm (3.18); MS (EI, 80 eV, 220 °C), *m/z* (%): 478 (100) [M^+], 407 (65) [$M^+-C_5H_{11}$], 336 (29) [$M^+-2\times C_5H_{11}$], 239 (4) [M^{2+}]; HRMS (EI) [$C_{32}H_{38}N_4$]: calcd 478.30965, found 478.30755; [$C_{32}H_{38}N_4$, 478.68 g mol^{-1}]. Anal. Calcd C 80.29, H 8.00, N 11.70, found C 80.10, H 7.85, N 11.66.

4.3.10. 5,15-Di(*iso*-butyl)porphyrin (21). The reaction was performed using the conditions given in Section 4.3.9 using 3-methyl butanal (920 μL, 8.5 mmol). After concentration of the reaction mixture it was filtered through 600 mL of silica (column diameter 5 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness and the residue redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated purple needles were removed by suction filtration through a D3 frit and dried in vacuo to yield 470 mg of purple crystals (1.1 mmol; 27%) of the title compound: mp 265–267 °C; R_f=0.57 (CH_2Cl_2/C_6H_{14}, 2:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.91 (s, br., 2H, N*H*), 1.22 (d, 12H, J=6 Hz, $CH_2CH(CH_3)_2$), 2.82 (m, 2H, $CH_2CH(CH_3)_2$), 4.86 (d, 4H, J=8 Hz, $CH_2CH(CH_3)_2$), 9.38 (d, 4H, J=5 Hz, β-pyrrole-*H*), 9.54 (d, 4H, J=5 Hz, β-pyrrole-*H*), 10.17 ppm (s, 2H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=22.37, 36.73, 43.04, 104.35, 117.64, 128.28, 131.71, 144.13, 148.00 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)= 300 nm (4.22), 342 (4.34), 360 (4.45), 402 (5.44), 475 (3.41), 504 (4.22), 535 (3.66), 577 (3.69), 632 (3.33); MS (EI, 80 eV, 230 °C), *m/z* (%): 422 (67) [M^+], 379 (100) [$M^+-C_3H_7$], 336 (47) [$M^+-2\times C_3H_7$], 211 (4) [M^{2+}]; HRMS (EI) [$C_{28}H_{30}N_4$]: calcd 422.24705, found 422.24734; [$C_{28}H_{30}N_4$, 422.57 g mol^{-1}]. Anal. Calcd C 79.59, H 7.16, N 13.26, found C 79.13, H 6.96, N 13.30.

4.3.11. [5,15-Di(*iso*-butyl)porphyrinato]nickel(II) (25). 5,15-Di(*iso*-butyl)porphyrin **21** (200 mg, 0.47 mmol) was placed in a round-bottomed flask equipped with a reflux condenser. DMF (100 mL) and nickel(II) acetate (1.2 g, 6.8 mmol) were added and the flask was heated at 150 °C (bath temperature) for 2 h. The solvent was evaporated to dryness and the residue taken up in dichloromethane. The mixture was ultrasonicated for 2 min and then filtered through silica (50 g), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness and the residue redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated crystals were removed by suction filtration through a D3 frit and dried in vacuo to yield 210 mg (0.44 mmol, 93%) of the title compound as red needles: mp 226 °C; R_f=0.81 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); HPLC (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/C_6H_{14}, 1:1; v/v, flow rate: 1 mL/min, detection at 420 nm): retention time: 2.95 min (90.0%), (same conditions but detection at 254 nm) retention time: 3.02 min (94.4%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.95 (d, 12H, J= 6 Hz, $CH_2CH(CH_3)_2$), 2.42 (m, 2H, $CH_2CH(CH_3)_2$), 4.62 (d, 4H, J=7 Hz, $CH_2CH(CH_3)_2$), 9.14 (d, 4H, J=5 Hz, β-pyrrole-*H*), 9.41 (d, 4H, J=5 Hz, β-pyrrole-*H*), 9.68 ppm (s, 2H, *meso-H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ=23.11, 34.97, 42.43, 103.94, 116.11, 130.19, 132.09, 141.38, 143.09 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=292 (4.08), 322 (3.95), 402 (5.32), 518 (4.16), 549 nm (3.70); MS (EI, 80 eV, 300 °C) *m/z* (%): 478 (88) [M^+], 435 (100) [$M^+-C_3H_7$], 392 (79) [$M^+-2\times C_3H_7$], 239 (6) [M^{2+}]; HRMS (EI) [$C_{28}H_{28}N_4Ni$]: calcd 478.16674, found 478.16619; [$C_{28}H_{28}N_4Ni$, 479.25 g mol^{-1}]. Anal. Calcd C 70.17, H 5.89, N 11.69, found C 69.88, H 5.71, N 11.79.

4.3.12. [5,15-Bis(4-butyloxyphenyl)porphyrinato]-nickel(II) (26). The free base **17** (100 mg, 0.16 mmol) was placed in a round-bottomed flask equipped with a reflux condenser. DMF (50 mL) and 600 mg (3.4 mmol) of nickel(II)acetate were added and the flask was heated at 150 °C (bath temperature) for 1.5 h. The solvent was evaporated to dryness and the residue was taken up in dichloromethane. The mixture was ultrasonicated for 2 min and then filtered through silica (30 g), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness and the residue resuspended in 50 mL of dichloromethane and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated red crystals were removed by suction filtration through a D3 frit and dried in vacuo and gave the title porphyrin in quantitative yield: mp 325 °C; R_f=0.74 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.09 (t, J=7 Hz, 6H, $OCH_2CH_2CH_2CH_3$), 1.66 (m, 4H, $OCH_2CH_2CH_2CH_3$), 1.96 (m, 4H, $OCH_2CH_2CH_2CH_3$), 4.23 (t, J=6 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 7.20 (m, 4H, phenyl-*H*), 7.95 (m, 4H, phenyl-*H*), 8.96 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.16 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.90 ppm (s, 2H, *meso-H*); UV/vis (CH_2Cl_2): λ_{max} (log ε)=323 (4.25), 404 (5.37), 516 (4.28), 547 nm (3.94); MS (EI, 80 eV, 290 °C), *m/z* (%): 662 (100) [M^+], 605 (4) [$M^+-C_4H_9$], 549 (2) [$M^+-C_4H_9$-C_4H_8], 514 (17) [$M^+-C_{10}H_{12}O$], 331 (1) [M^{2+}]; HRMS (EI) [$C_{40}H_{36}N_4NiO_2$]: calcd 662.21917, found 662.21679; [$C_{40}H_{36}N_4NiO_2$, 663.44 g mol^{-1}]. Anal. Calcd C 72.42, H 5.47, N 8.44, [$C_{40}H_{36}N_4NiO_2\cdot\frac{1}{2}H_2O$, 672.45 g mol^{-1}] C 71.45, H 5.55, N 8.33, found C 71.32, H 5.26, N 8.37.

4.3.13. [5,15-Bis(4-pentyloxyphenyl)porphyrinato]-nickel(II) (27). The free base **18** (100 mg, 0.16 mmol) was treated in a similar manner as described in Section 4.3.12. After workup the compound was obtained in quantitative yield; mp 302–304 °C; R_f=0.76 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: C_6H_{14}/CH_2Cl_2, 60:40, v/v, flow: 1 mL/min, detection at

420 nm) retention time: 5.36 min (93.6%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.02 (t, J=7 Hz, 6H, OCH_2CH_2-$CH_2CH_2CH_3$), 1.45–1.66 (m, 8H, $OCH_2CH_2CH_2CH_2CH_3$ and $OCH_2CH_2CH_2CH_2CH_3$), 1.97 (m, 4H, $OCH_2CH_2CH_2$-CH_2CH_3), 4.22 (t, J=6 Hz, 4H, $OCH_2CH_2CH_2CH_2CH_3$), 7.21 (m, 4H, phenyl-*H*), 7.94 (m, 4H, phenyl-*H*), 8.95 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.15 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.89 ppm (s, 2H, *meso*-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.10, 22.58, 28.40, 29.19, 68.36, 104.94, 112.97, 118.15, 131.85, 132.43, 133.20, 134.86, 142.52, 143.30, 159.03 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=323 (4.10), 404 (5.36), 516 (4.25), 547 nm (3.83); MS (EI, 80 eV, 280 °C), *m*/*z* (%): 690 (100) [M^+], 619 (4) [$M^+-C_5H_{11}$], 528 (12) [$M^+-C_{11}H_{14}O$], 345 (1) [M^{2+}]; HRMS (EI) [$C_{42}H_{40}N_4NiO_2$]: calcd 690.25047, found 690.25433; [$C_{42}H_{40}N_4NiO_2$, 691.50 g mol^{-1}]. Anal. Calcd C 72.95, H 5.83, N 8.10, found C 72.68, H 5.66, N 8.09.

4.3.14. [5,15-Bis(3-methoxyphenyl)porphyrinato]-nickel(II) (28). The free base **12** (200 mg, 0.38 mmol) was treated in a similar manner as described in Section 4.3.11 to yield 210 mg red crystals (0.36 mmol, 95%): mp 340 °C; R_f=0.51 (SiO_2, CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.69 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.95 (s, 6H, OCH_3), 7.23–7.32 (m, 2H, phenyl-*H*), 7.57–7.68 (m, 6H, phenyl-*H*), 8.96 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.17 (d, J=5 Hz, 4H, β-pyrrole-*H*), 9.92 ppm (s, 2H, 10-*meso*-*H* and 20-*meso*-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.48, 105.08, 113.55, 119.85, 126.90, 127.71, 132.00, 132.43, 142.37, 142.64, 142.79, 153.49, 158.17 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=317 (3.93), 400 (5.34), 514 (4.19), 546 nm (3.90); MS (EI, 80 eV, 400 °C), *m*/*z* (%): 578 (100) [M^+], 289 (3) [M^{2+}]; HRMS (EI) [$C_{34}H_{24}N_4NiO_2$]: calcd 578.125273, found 578.12732; [$C_{34}H_{24}N_4NiO_2$, 579.28 g mol^{-1}]. Anal. Calcd C 70.50, H 4.18, N 9.67, found C 70.78, H 4.48, N 9.73.

4.4. 5,15-AB-type porphyrins

4.4.1. 5-Hexyl-15-(3-methoxyphenyl)porphyrin (22). Dry dichloromethane (2 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **10** (1.2 g, 8.2 mmol), 3-methoxybenzaldehyde (0.56 mL, 4.6 mmol), and heptanal (0.64 mL, 4.6 mmol) were added. The flask was shielded from ambient light and then 140 μL (1.8 mmol) of TFA were added and the reaction mixture was stirred for 18 h at 20 °C. After this time, 2.77 g (12.2 mmol) of DDQ suspended in 100 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 6 mL of triethylamine were added and the reaction mixture was concentrated in vacuo to about 200 mL. The reaction mixture was filtered through 500 mL of silica (column diameter 5 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The porphyrins were separated by column chromatography on silica (3×60 cm) using dichloromethane/hexane (3:1, v/v) as eluent. The first fraction was 5,15-dihexylporphyrin **20** (120 mg, 0.25 mmol, 6%), the second fraction 5-hexyl-15-(3-methoxyphenyl)porphyrin **22** (370 mg, 0.7 mmol, 17%), and the third fraction 5,15-bis(3-methoxyphenyl)porphyrin **12** (200 mg, 0.38 mmol, 9%). The porphyrins were redissolved/suspended in dichloromethane and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated purple crystals were removed by suction filtration through a D3 frit and dried in vacuo. Title compound: mp 215 °C; R_f=0.39 (SiO_2, CH_2Cl_2/C_6H_{14}, 3:1, v/v); R_f=0.69 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.06 and −3.03 (each s, 1H, N*H*), 0.94 (t, J=7 Hz, 3H, 5^6-CH_3), 1.33–1.59 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.83 (m, 2H, 5^3-CH_2), 2.57 (m, 2H, 5^2-CH_2), 4.00 (s, 3H, 15-OCH_3), 5.02 (t, J=8 Hz, 2H, 5^1-CH_2), 7.34 (m, 1H, phenyl-*H*), 7.68 (m, 1H, phenyl-*H*), 7.81–7.86 (m, 2H, phenyl-*H*), 9.07 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.33 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.41 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.59 (d, J=5 Hz, 2H, β-pyrrole-*H*), 10.21 ppm (s, 2H, 10- and 20-*meso*-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.15, 22.74, 30.28, 31.92, 34.81, 38.75, 55.51, 104.75, 113.38, 117.94, 119.78, 120.73, 127.78, 127.86, 127.99, 130.69, 131.64, 131.78, 142.71, 144.53, 144.77, 147.20, 147.25, 158.24 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=301 (4.10), 366 (4.21), 3.88 (4.68), 406 (5.29), 475 (3.19), 503 (3.99), 536 (3.55), 576 (3.47), 631 nm (3.07); MS (EI, 80 eV, 220 °C), *m*/*z* (%): 500 (100) [M^+], 429 (70) [M^+-71 (C_5H_{11})], 250 (8) [M^{2+}]; MS (FAB+, CH_2Cl_2/*m*-NO_2-Bzl-OH/Xe), *m*/*z* (%): 501 (6) [$(M+H)^+$], 430 (2) [$\{M+H\}^+-C_5H_{11}$]; HRMS (EI) [$C_{33}H_{32}N_4O$]: calcd 500.25761, found 500.25473; [$C_{33}H_{32}N_4O$, 500.64 g mol^{-1}]. Anal. Calcd C 79.17, H 6.44, N 11.19, found C 79.04, H 6.31, N 11.18.

4.4.2. 5-Hexyl-15-(4-methoxyphenyl)porphyrin (23). Dry dichloromethane (2 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. The reaction flask was charged with dipyrromethane **10** (1.2 g, 8.2 mmol), 4-methoxybenzaldehyde (500 μL, 4.15 mmol), and heptanal (580 μL, 4.15 mmol). Further reaction conditions were as described in Section 4.4.1. After concentration the reaction mixture was filtered through a D3 frit. The filtrate was filtered through 600 mL of silica (column diameter 5 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The residue in the frit was thoroughly washed with dichloromethane, acetone, and methanol and then dried in vacuo. It consisted largely of 5,15-bis(4-methoxyphenyl)-porphyrin **13** and was discarded. The eluted porphyrin fractions were separated by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. The first fraction was 5,15-dihexylporphyrin **20** (240 mg, 0.5 mmol, 12%), the second fraction the title compound **23**. Each of the two porphyrins was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated crystals were removed by suction filtration through a D3 frit and dried in vacuo. Yield 5-hexyl-15-(4-methoxyphenyl)porphyrin **23**: 300 mg (0.6 mmol; 14%) of purple crystals: mp 238–240 °C; R_f=0.52 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.11 and −3.07 (each s, 1H, N*H*), 0.93 (t, J=7 Hz, 3H, 5^6-CH_3), 1.41 (m, 2H, 5^5-CH_2), 1.52 (m, 2H, 5^4-CH_2), 1.82 (m, 2H, 5^3-CH_2), 2.56 (m, 2H, 5^2-CH_2), 4.10 (s, 3H, OCH_3), 5.01 (t, J=8 Hz, 2H, 5^1-CH_2), 7.32 (m, 2H, phenyl-*H*), 8.14 (m, 2H, phenyl-*H*), 9.04 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.33 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.40 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.58 (d, J=5 Hz, 2H, β-pyrrole-*H*), 10.30 (s, 2H, *meso*-*H*); UV/vis (CH_2Cl_2): λ_{max} (log ε)=301 (4.05), 360

(4.35), 390 (4.91), 406 (5.53), 474 (3.28), 505 (4.20), 539 (3.70), 578 (3.69), 632 (3.17); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.13, 22.75, 30.28, 31.94, 34.82, 38.74, 55.61, 104.70, 112.60, 118.19, 119.54, 127.97, 130.73, 131.54, 131.82, 133.77, 135.81, 144.54, 144.77, 147.32, 147.70, 159.49; MS (EI, 80 eV, 250 °C), *m/z* (%): 500 (100) [M^+], 429 (66) [$M^+-C_5H_{11}$], 250 (8) [M^{2+}]; HRMS (EI) [$C_{33}H_{32}N_4O$]: calcd 500.257612, found 500.25561; [$C_{33}H_{32}N_4O$, 500.64 g mol^{-1}]. Anal. Calcd C 79.17, H 6.44, N 11.19, found C 78.85, H 6.10, N 11.03.

4.4.3. 5-(3,5-Dimethoxyphenyl)-15-hexylporphyrin (24). Reaction and workup of dipyrromethane (**10**) (1.2 g, 8.2 mmol), 3,5-dimethoxybenzaldehyde (700 mg, 4.1 mmol), and heptanal (580 μL, 4.1 mmol) as described in Section 4.4.2. Yields: 240 mg (0.5 mmol, 12%) purple needles of 5,15-dihexylporphyrin (**20**) and 300 mg purple crystals (0.6 mmol, 14%) of the title compound **24**: mp 295–297 °C; R_f=0.78 (CH_2Cl_2), 0.44 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2 with 0.1% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm) retention time: 2.99 min (97.9%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.04 (s, br., 2H, N*H*), 0.93 (t, *J*=7 Hz, 3H, 5^6-C*H*$_3$), 1.41 (m, 2H, 5^5-C*H*$_2$), 1.52 (m, 2H, 5^4-C*H*$_2$), 1.83 (m, 2H, 5^3-C*H*$_2$), 2.57 (m, 2H, 5^2-C*H*$_2$), 3.98 (s, 6H, OC*H*$_3$), 5.03 (t, *J*=8 Hz, 2H, 5^1-C*H*$_2$), 6.91 (m, 1H, phenyl-*H*$_{para}$), 7.42 (m, 2H, phenyl-*H*$_{ortho}$), 9.11 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.33 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.41 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.60 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.21 (s, 2H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.12, 22.72, 30.25, 31.90, 34.77, 38.70, 55.63, 100.06, 104.71, 105.26, 114.05, 117.90, 119.79, 127.93, 130.67, 131.62, 131.71, 143.34, 144.54, 144.85, 147.17, 159.20; UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 (4.22), 360 (4.40), 390 (4.93), 404 (5.54), 474 (3.38), 504 (4.17), 535 (3.61), 578 (3.69), 633 (3.05); MS (EI, 80 eV, 250 °C), *m/z* (%): 530 (100) [M^+], 459 (57) [$M^+-C_5H_{11}$], 429 (3) [$M^+-C_5H_{11}-2\times CH_3$], 265 (11) [$M^{2+}$]; HRMS (EI) [$C_{34}H_{34}N_4O_2$]: calcd 530.268177, found 530.26574; [$C_{34}H_{34}N_4O_2$, 530.67 g mol^{-1}]. Anal. Calcd C 76.95, H 6.46, N 10.56, found C 77.03, H 6.35, N 10.49.

4.4.4. [5-Hexyl-15-(3-methoxyphenyl)porphyrinato]-nickel(II) (29). 5-Hexyl-15-(3-methoxyphenyl)porphyrin **22** (150 mg, 0.3 mmol) was placed in a round-bottomed flask equipped with a reflux condenser. DMF (50 mL) and 900 mg (5.1 mmol) of nickel(II) acetate were added and the flask was heated at 150 °C (bath temperature) for 1.5 h. The solvent was evaporated to dryness and the residue was taken up in dichloromethane. The mixture was filtered through silica (30 g), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The porphyrin was resuspended in 50 mL of dichloromethane and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated red crystals were removed by suction filtration through a D3 frit and dried in vacuo to give the title compound in quantitative yield: mp 228 °C; R_f=0.68 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.93 (t, *J*=7 Hz, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.29–1.51 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 1.66 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.37 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.94 (s, 3H, OCH_3), 4.58 (t, *J*=7 Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.28 (m, 1H, phenyl-*H*), 7.60 (m, 3H, phenyl-*H*), 8.89 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.05 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.09 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.38 ppm (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.69 ppm (s, 2H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.11, 22.69, 30.15, 31.80, 34.36, 37.74, 55.42, 104.42, 113.43, 117.25, 118.07, 119.80, 126.84, 127.68, 129.40, 131.85, 132.12, 141.87, 142.03, 142.39, 142.52, 142.71, 158.16; MS (EI, 80 eV, 305 °C), *m/z* (%): 556 (100) [M^+], 485 (65) [$M^+-C_5H_{11}$], 278 (2) [M^{2+}]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=401 (5.11), 516 (3.94), 548 nm (3.55); HRMS (EI) [$C_{33}H_{28}N_4NiO$]: calcd 554.16166, found: 554.16169.

4.5. A_3- and A_2B-type porphyrins via S_NAr

4.5.1. 5,10,15-Tris(3-methoxyphenyl)porphyrin (30). 3-Methoxybromobenzene (760 μL, 6 mmol) was dissolved in diethyl ether in a septum equipped Schlenk flask under argon. The flask was cooled in an ice-bath and 4 mL of a 2.5 M solution of *n*-butyl lithium (6 mmol) were added through the septum via a syringe. The solution was stirred for 1 h in the ice bath. The solution gradually becomes turbid. The solution of the lithio-3-methoxybenzene was then cooled to −70 °C. At the same time, in a second Schlenk flask 200 mg (0.38 mmol) of 5,15-bis(3-methoxyphenyl)porphyrin **12** were dried in vacuo for 2 h. THF (40 mL, abs.) was added under argon. The porphyrin suspension was cooled to −70 °C and poured all at once into the flask containing the lithio-3-methoxybenzene. The cold bath was removed and the reaction mixture was stirred for 60 min at 20 °C. The solution gradually changed its color from red to green-brown. Water (3 mL) was added and the solution was stirred for 20 min. On addition of water the reaction mixture changed its color to dark-green. After this time, 3 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 0.78 mmol) were added, upon which the solution became dark red again. The reaction mixture was filtered through silica (3×50 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/hexane (7:3, v/v) as eluent. As the first fraction, a small amount (~15 mg) of 5-butyl-10,20-bis(3-methoxyphenyl)porphyrin **44** was isolated, which was identified by ^{1}H NMR and mass spectrometry (Section 4.5.14). The title compound was eluted as the second fraction. The porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo: 190 mg (0.3 mmol; 79%) purple crystals; mp 253–255 °C; R_f=0.15 (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.44 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.04 (s, br., 2H, N*H*), 3.96 (s, 3H, 10-OC*H*$_3$), 3.99 (s, 6H, 5-OC*H*$_3$ and 15-OC*H*$_3$), 7.30–7.60 (m, 3H, phenyl-*H*), 7.64 (m, 3H, phenyl-*H*), 7.76–7.84 (m, 6H, phenyl-*H*), 8.91 (m [AB-spectrum], 4H, β-pyrrole-*H*), 9.04 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.32 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.20 ppm (s, 1H, 20-*meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.52, 104.83, 113.58, 119.37, 120.24, 120.53, 120.65, 127.34, 127.62, 127.77, 130.70, 131.25, 131.38, 143.12, 143.90, 145.98, 146.87, 157.89, 158.15 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.22), 374 (4.43), 395 (4.89), 413 (5.60), 478 (3.34), 508 (4.27),

541 (3.60), 582 (3.66), 637 nm (3.05); MS (EI, 80 eV, 290 °C), *m/z* (%): 628 (100) [M^+], 613 (3) [M^+-CH_3], 597 (2) [M^+-CH_3O], 314 (14) [M^{2+}]; HRMS (EI) [$C_{41}H_{32}N_4O_3$]: calcd 628.24744, found 628.24714; [$C_{41}H_{32}N_4O_3$, 628.73 g mol^{-1}]. Anal. Calcd C 78.32, H 5.13, N 8.91, found C 78.05, H 4.82, N 8.71.

4.5.2. 5-Hexyl-10,20-bis(4-methoxyphenyl)porphyrin (31). 5,15-Bis(4-methoxyphenyl)porphyrin **13** (220 mg, 0.42 mmol) was dried in vacuo in a septum equipped Schlenk flask for 2 h and then abs. THF (50 mL) was added under argon. The porphyrin suspension was cooled to −70 °C and *n*-hexyl lithium (1100 μL of a 2.5 M solution, 2.75 mmol) was added via a syringe. The cold bath was removed and the reaction mixture was stirred for 15 min at 20 °C. The solution changed its color from red to green-brown. Water (8 mL) was added in two portions and the solution was then stirred for 60 min. Upon addition of water the reaction mixture changed its color to dark-green. Next, 6 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 1.6 mmol) were added in two portions, upon which the solution turned dark-red again. The mixture was stirred for 15 min at 20 °C followed by filtration through silica (column diameter 3 cm, filling height 50 cm), washing with dichloromethane. The filtrate was evaporated to dryness and the product purified by column chromatography on silica (3×70 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. To remove a small amount of a yellow-brown by-product, the porphyrin was again chromatographed on silica (3×70 cm) using dichloromethane as eluent. After evaporation of the solvent the porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 90 mg (0.15 mmol; 35%) of brown microcrystals: mp 251–252 °C; R_f=0.31 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.99 (s, br., 2H, N*H*), 0.91 (t, *J*=7 Hz, 3H, 5^6-C*H*$_3$), 1.38 (m, 2H, 5^5-C*H*$_2$), 1.50 (m, 2H, 5^4-C*H*$_2$), 1.84 (m, 2H, 5^3-C*H*$_2$), 2.55 (m, 2H, 5^2-C*H*$_2$), 4.10 (s, 6H, OC*H*$_3$), 5.05 (t, *J*=8 Hz, 2H, 5^1-C*H*$_2$), 7.30 (m, 4H, phenyl-*H*), 8.12 (m, 4H, phenyl-*H*), 8.97 (m, 4H, β-pyrrole-*H*), 9.24 (d, *J*=4 Hz, 2H, β-pyrrole-*H*), 9.52 (d, *J*=4 Hz, 2H, β-pyrrole-*H*), 10.06 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.10, 22.71, 30.28, 31.91, 35.99, 38.99, 55.61, 103.86, 112.30, 118.75, 121.07, 128.12, 130.79, 131.18, 131.43, 134.49, 135.61, 146.27, 159.47 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.18), 369 (4.35), 397 (4.92), 415 (5.56), 484 (3.56), 511 (4.25), 547 (3.93), 587 (3.73), 642 nm (3.60); MS (EI, 80 eV, 300 °C), *m/z* (%): 606 (100) [M^+], 535 (55) [$M^+-C_5H_{11}$], 303 (10) [M^{2+}]; HRMS (EI) [$C_{40}H_{38}N_4O_2$]: calcd 606.29948, found 606.29742; [$C_{40}H_{38}N_4O_2$, 606.77 g mol^{-1}]. Anal. Calcd C 79.18, H 6.31, N 9.23, found C 79.12, H 6.25, N 9.10.

4.5.3. 10-Hexyl-5,15-bis(3-methoxyphenyl)porphyrin (32). 5,15-Bis(3-methoxyphenyl)porphyrin **12** (160 mg, 0.31 mmol) was dried in vacuo in a septum-equipped Schlenk-flask for 2 h. THF (30 mL, abs.) was then added under argon. The porphyrin suspension was cooled to −70 °C. *n*-Hexyl lithium (550 μL of a 2.5 M solution, 1.35 mmol) was added via a syringe through the septum. The cold bath was removed and the reaction mixture was stirred for 15 min at 20 °C. The solution changed its color from red to green-brown. Water (4 mL) was added and the solution was then stirred for 60 min. On addition of water the reaction mixture changed its color to dark-green. After this time, 3 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 0.78 mmol) were added, upon which the solution became dark red again. The reaction mixture was filtered through silica (3×50 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. The porphyrin was again dissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 120 mg (0.2 mmol; 65%) of red-brown microcrystals: mp 226–227 °C; R_f=0.32 (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.55 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.03 (s, 2H, N*H*), 0.91 (t, *J*=7 Hz, 3H, 5^6-C*H*$_3$), 1.30–1.56 (m, 4H, 5^5-C*H*$_2$ and 5^4-C*H*$_2$), 1.81 (m, 2H, 5^3-C*H*$_2$), 2.55 (m, 2H, 5^2-C*H*$_2$), 4.00 (s, 6H, 10-OC*H*$_3$ and 20-OC*H*$_3$), 5.06 (t, *J*=8 Hz, 2H, 5^1-C*H*$_2$), 7.34 (m, 2H, phenyl-*H*), 7.66 (m, 2H, phenyl-*H*), 7.78–7.83 (m, 4H, phenyl-*H*), 9.00 (m [AB-spectrum], 4H, β-pyrrole-*H*), 9.24 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.52 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.07 ppm (s, 1H, 15-*meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.13, 22.72, 30.29, 31.92, 35.97, 39.04, 55.54, 103.99, 113.49, 118.76, 120.56, 121.24, 127.53, 127.72, 143.39, 158.04 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.17), 372 (4.39), 393 (4.87), 413 (5.53), 478 (3.39), 509 (4.24), 543 (3.74), 584 (3.67), 639 nm (3.40); MS (EI, 80 eV, 310 °C), *m/z* (%): 606 (22) [M^+], 535 (9) [$M^+-C_5H_{11}$], 303 (2) [M^{2+}], 18 (100) [H_2O^+, cf. elem. anal.]; HRMS (EI) [$C_{40}H_{38}N_4O_2$]: calcd 606.29948, found 606.29907; [$C_{40}H_{38}N_4O_2$, 606.77 g mol^{-1}]. Anal. Calcd C 79.18, H 6.31, N 9.23, [$C_{40}H_{38}N_4O_2\cdot\frac{1}{2}H_2O$, 615.78 g mol^{-1}]. Anal. Calcd C 78.02, H 6.38, N 9.10, found C 78.37, H 6.07, N 8.79.

4.5.4. 5,15-Bis(4-butyloxyphenyl)-10-hexylporphyrin (33). Reaction and workup as described in Section 4.5.3 using 5,15-bis(4-butyloxyphenyl)porphyrin **17** (240 mg, 0.4 mmol) as starting material. Yield 140 mg (0.2 mmol; 51%) of brown microcrystals: mp 203 °C; R_f=0.54 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.99 (s, br., 2H, N*H*), 0.91 (t, *J*=7 Hz, 3H, 10^6-C*H*$_3$), 1.11 (t, *J*=7 Hz, 6H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.33–1.55 (m, 4H, 10^4-C*H*$_2$ and 10^5-C*H*$_2$), 1.67 (m, 4H, OCH$_2$CH$_2$C*H*$_2$-CH$_3$), 1.81 (m, 2H, 10^3-C*H*$_2$), 1.99 (m, 4H, OCH$_2$C*H*$_2$CH$_2$-CH$_3$), 2.55 (m, 2H, 10^2-C*H*$_2$), 4.26 (t, *J*=6 Hz, 4H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 5.05 (t, *J*=8 Hz, 2H, 10^1-C*H*$_2$), 7.28 (m, 4H, phenyl-*H*), 8.10 (m, 4H, phenyl-*H*), 8.98 (m, 4H, β-pyrrole-*H*), 9.24 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.52 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.06 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=13.98, 14.11, 9.46, 22.71, 30.29, 31.61, 31.92, 35.99, 68.09, 103.83, 112.85, 118.64, 121.02, 128.07, 130.73, 131.17, 131.47, 134.26, 135.62, 146, 159.04 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.24), 367 (4.33), 397 (4.90), 415 (5.52), 485 (3.53), 511 (4.23), 548 (3.92), 587 (3.69), 644 nm (3.56); MS (EI, 80 eV, 270 °C), *m/z* (%): 690 (100) [M^+], 633 (3) [$M^+-C_4H_9$], 619 (24) [$M^+-C_5H_{11}$], 345 (3) [M^{2+}]; HRMS (EI) [$C_{46}H_{50}N_4O_2$]: calcd 690.39338, found 690.39654;

[$C_{46}H_{50}N_4O_2$, 690.93 g mol^{-1}]. Anal. Calcd C 79.97, H 7.29, N 8.11, [$C_{46}H_{50}N_4O_2 \cdot ½H_2O$]. Anal. Calcd C 78.94, H 7.34, N 8.00 found C 78.48, H 7.33, N 7.99.

4.5.5. 5-Hexyl-10,20-bis(4-pentyloxyphenyl)porphyrin (34). 5,15-Bis(4-pentyloxyphenyl)porphyrin **18** (270 mg, 0.45 mmol) was dried in vacuo in a septum equipped Schlenk flask for 2 h. THF abs. (40 mL) was then added under argon and the suspension was cooled to −70 °C. *n*-Hexyl lithium (1100 μL of a 2.5 M solution, 2.75 mmol) was added via a syringe through the septum, the cold bath removed, and the reaction mixture was stirred for 20 min at 20 °C. The solution changed its color from red to green-brown and water (8 mL) was added in two portions and the solution was stirred for 60 min. Upon addition of 10 mL water the reaction mixture changed its color to dark-green and was stirred for 45 min. Subsequently, 5 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 1.3 mmol) were added in two portions and the solution turned dark-red again. Further workup was as described in Section 4.5.3 to yield 300 mg (0.41 mmol; 91%) of brown microcrystals: mp 174 °C; R_f=0.56 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.98 (s, br., 2H, N*H*), 0.91 (t, J=7 Hz, 3H, 5^6-C*H*$_3$), 1.04 (t, J=7 Hz, 6H, OCH$_2$CH$_2$-CH$_2$CH$_2$C*H*$_3$), 1.33–1.70 (m, 12H, 5^4-C*H*$_2$, 5^5-C*H*$_2$, OCH$_2$-CH$_2$C*H*$_2$CH$_2$CH$_3$, and OCH$_2$CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.81 (m, 2H, 5^3-C*H*$_2$), 2.01 (m, 4H, OCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.55 (m, 2H, 5^2-C*H*$_2$), 4.26 (t, J=6 Hz, 4H, OC*H*$_2$CH$_2$CH$_2$CH$_2$-CH$_3$), 5.06 (t, J=8 Hz, 2H, 5^1-C*H*$_2$), 7.28 (m, 4H, phenyl-*H*), 8.10 (m, 4H, phenyl-*H*), 8.98 (m, 4H, β-pyrrole-*H*), 9.24 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.52 (d, J=5 Hz, 2H, β-pyrrole-*H*), 10.06 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.11, 22.61, 22.71, 28.42, 29.24, 30.29, 31.92, 35.99, 38.99, 68.40, 103.83, 112.85, 118.86, 121.02, 128.07, 130.80, 131.19, 131.46, 134.26, 135.62, 146.82, 159.03 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.34), 370 (4.45), 398 (4.90), 415 (5.59), 482 (3.71), 511 (4.28), 548 (3.99), 587 (3.79), 643 nm (3.56); MS (EI, 80 eV, 270 °C), *m*/*z* (%): 718 (100) [M$^+$], 647 (26) [M$^+$−C_5H_{11}], 359 (1) [M^{2+}]; HRMS (EI) [$C_{48}H_{54}N_4O_2$]: calcd 718.42468, found 718.42767; [$C_{48}H_{54}N_4O_2$, 718.98 g mol^{-1}]. Anal. Calcd C 80.19, H 7.57, N 7.79, [$C_{48}H_{54}N_4O_2 \cdot ½H_2O$]. Anal. Calcd C 79.19, H 7.62, N 7.70, found C 79.36, H 7.56, N 7.80.

4.5.6. 5,15-Bis(3,5-dimethoxyphenyl)-10-hexylporphyrin (35). 5,15-Bis(3,5-dimethoxyphenyl)porphyrin **15** (240 mg, 0.41 mmol) was suspended in 60 mL THF and reacted with *n*-hexyl lithium (1.1 mL of a 2.5 M solution, 2.75 mmol) in a similar manner as described in Section 4.5.3. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. The porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 160 mg (0.24 mmol; 58%) of brown microcrystals: mp 319–320 °C; R_f=0.25 (CH_2Cl_2/C_6H_{14}, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.02 (s, br., 2H, N*H*), 0.92 (t, J=7 Hz, 3H, 5^6-C*H*$_3$), 1.40 (m, 2H, 5^5-C*H*$_2$), 1.51 (m, 2H, 5^4-C*H*$_2$), 1.82 (m, 2H, 5^3-C*H*$_2$), 2.56 (m, 2H, 5^2-C*H*$_2$), 3.98 (s, 12H, OC*H*$_3$), 5.06 (t, J=8 Hz, 2H, 5^1-C*H*$_2$), 6.91 (m, 2H, phenyl-H_{para}), 7.41 (m, 4H, phenyl-H_{ortho}), 9.04 (m, 4H, β-pyrrole-*H*), 9.23 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.52 (d, J=5 Hz, 2H, β-pyrrole-*H*), 10.06 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.14, 22.72, 30.30, 31.91, 35.95, 39.04, 55.65, 100.12, 103.98, 113.93, 118.73, 121.21, 128.24, 131.25, 143.98, 146.23, 158.96 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.07), 370 (4.39), 396 (4.92), 414 (5.39), 480 (3.45), 509 (4.25), 543 (3.60), 584 (3.65), 640 nm (3.41); MS (EI, 80 eV, 270 °C), *m*/*z* (%): 666 (100) [M$^+$], 595 (41) [M$^+$−C_5H_{11}], 565 (2) [M$^+$−C_5H_{11}−2×CH_3], 333 (20) [M^{2+}]; HRMS (EI) [$C_{42}H_{42}N_4O_4$]: calcd 666.32061, found 666.32360; [$C_{42}H_{42}N_4O_4$, 666.82 g mol^{-1}]. Anal. Calcd C 75.65, H 6.35, N 8.40, found C 75.61, H 6.31, N 8.39.

4.5.7. 5-Hexyl-10,20-di(*iso*-butyl)porphyrin (36). 5,15-Di(*iso*-butyl)porphyrin **21** (100 mg, 0.24 mmol) was dried in vacuo in a septum equipped Schlenk flask for 2 h and 25 mL dry THF abs. were then added under argon. The porphyrin solution was cooled to −60 °C and *n*-hexyl lithium (520 μL of a 2.5 M solution, 1.29 mmol) was added via a syringe. The cold bath was removed and the reaction mixture was stirred for 15 min at 20 °C accompanied by a color change from red to green-brown. Water (3 mL) was added and the solution was then stirred for 30 min. Upon addition of water the reaction mixture turned dark-green. Next, 3 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 0.78 mmol) were added, upon which the solution changed color to dark-red again. The mixture was stirred for 15 min at 20 °C and filtered through silica (column diameter 3 cm, filling height 30 cm), washing with dichloromethane. The filtrate was evaporated to dryness and the residue purified by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. The porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield: 60 mg (0.12 mmol; 50%) of brown microcrystals: mp 201–203 °C; R_f=0.72 (CH_2Cl_2/*n*-hexane, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.87 (s, br., 2H, N*H*), 0.95 (t, J=7 Hz, 3H, 5^6-C*H*$_3$), 1.19 (d, J=6 Hz, 12H, CH$_2$CH(C*H*$_3$)$_2$), 1.43 (m, 2H, 5^5-C*H*$_2$), 1.56 (m, 2H, 5^4-C*H*$_2$), 1.86 (m, 2H, 5^3-C*H*$_2$), 2.57 (m, 2H, 5^2-C*H*$_2$), 2.77 (m, 2H, CH$_2$C*H*(CH$_3$)$_2$), 4.83 (d, J=8 Hz, 4H, C*H*$_2$CH(CH$_3$)$_2$), 5.05 (t, J=8 Hz, 2H, 5^1-C*H*$_2$), 9.27 (d, J=4 Hz, 2H, β-pyrrole-*H*), 9.50 (m, 4H, β-pyrrole-*H*), 9.58 (d, J=4 Hz, 2H, β-pyrrole-*H*), 9.95 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.16, 22.79, 23.37, 30.40, 31.95, 36.36, 36.71, 39.08, 43.40, 103.07, 117.49, 120.03, 128.33, 128.53, 128.74, 131.17, 145.14, 147.16 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 (4.23), 363 (4.34), 394 (4.79), 412 (5.64), 479 (3.44), 512 (4.18), 545 (3.85), 589 (3.74), 645 nm (3.66); MS (EI, 80 eV, 250 °C), *m*/*z* (%): 506 (100) [M$^+$], 463 (76) [M$^+$−C_3H_7], 435 (6) [M$^+$−C_5H_{11}], 392 (3) [M$^+$−C_3H_7−C_5H_{11}], 253 (4) [M^{2+}]; HRMS (EI) [$C_{34}H_{42}N_4$]: calcd 506.34095, found 506.34353; [$C_{34}H_{42}N_4$, 506.73 g mol^{-1}]. Anal. Calcd C 80.59, H 8.35, N 11.06, [$C_{34}H_{42}N_4$×½CH_3OH]. Anal. Calcd C 79.27, H 8.48, N 10.72, found C 79.76, H 8.09, N 10.72.

4.5.8. 5,10-Dihexyl-15-(4-methoxyphenyl)porphyrin (37). 5-Hexyl-15-(4-methoxyphenyl)porphyrin **23** (210 mg, 0.42 mmol) was suspended in 50 mL THF and

reacted with *n*-hexyl lithium (1100 μL of a 2.5 M solution, 2.75 mmol) in a similar manner as described in Section 4.5.3. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. After recrystallization from CH_2Cl_2/CH_3OH 130 mg (0.22 mmol; 53%) of brown microcrystals were obtained: mp 131–132 °C; R_f=0.58 (CH_2Cl_2/*n*-hexane, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.93 (s, br., 2H, N*H*), 0.94 (m, 6H, 5^6-C*H*$_3$ and 10^6-C*H*$_3$), 1.35–1.59 (m, 8H, 5^5-C*H*$_2$, 10^5-C*H*$_2$, 5^4-C*H*$_2$, and 10^4-C*H*$_2$), 1.85 (m, 4H, 5^3-C*H*$_2$ and 10^3-C*H*$_2$), 2.55 (m, 4H, 5^2-C*H*$_2$ and 10^2-C*H*$_2$), 4.10 (s, 3H, OC*H*$_3$), 5.02 (m, 4H, 5^1-C*H*$_2$ and 10^1-C*H*$_2$), 7.27 (m, 2H, phenyl-*H*), 8.09 (m, 2H, phenyl-*H*), 8.92 (m, 2H, β-pyrrole-*H*), 9.21 (d, *J*=5 Hz, 1H, β-pyrrole-*H*), 9.29 (d, *J*=5 Hz, 1H, β-pyrrole-*H*), 9.48–9.61 (m, 4H, β-pyrrole-*H*), 9.98 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ= 14.12, 22.75, 30.32, 31.93, 35.31, 36.11, 38.77, 39.02, 55.59, 103.42, 112.32, 118.07, 119.39, 120.49, 127.96, 128.26, 128.45, 130.88, 131.12, 134.41, 135.57, 159.41 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 (4.18), 364 (4.35), 395 (4.89), 413 (5.53), 480 (3.50), 511 (4.22), 547 (3.85), 591 (3.66), 644 nm (3.55); MS (EI, 80 eV, 250 °C), *m*/*z* (%): 584 (100) [M^+], 513 (65) [$M^+-C_5H_{11}$], 442 (9) [$M^+-2\times C_5H_{11}$], 292 (8) [M^{2+}]; HRMS (EI) [$C_{39}H_{44}N_4O$]: calcd 584.351512, found 584.35431; [$C_{39}H_{44}N_4O$, 584.80 g mol^{-1}]. Anal. Calcd C 80.10, H 7.58, N 9.58, found C 79.89, H 7.64, N 9.36.

4.5.9. 5,10-Dihexyl-15-(3,5-dimethoxyphenyl)porphyrin (38). *Method a.* 5-(3,5-Dimethoxyphenyl)porphyrin 41[19] (100 mg, 0.22 mmol) was dried in vacuo in a septum equipped Schlenk-flask for 2 h and then treated with 25 mL abs. THF. The porphyrin suspension was cooled to −70 °C and *n*-hexyl lithium (550 μL of a 2.5 M solution, 1.38 mmol) was added via a syringe through the septum. The cold bath was removed and the reaction mixture was stirred for 20 min at 20 °C. The solution changed its color from red to green-brown and then to dark-blue. Water (5 mL) was added and the solution was then stirred for 60 min resulting in a color change to dark-green. Next; 5 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 1.3 mmol) were added, upon which the solution turned dark-red again. The mixture was stirred for 15 min at 20 °C and then filtered through silica (3×20 cm), washing with dichloromethane. The filtrate was evaporated to dryness and the product purified by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. After evaporation of the solvent the porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 110 mg (0.18 mmol; 80%) of brown microcrystals.

Method b. 5-(3,5-Dimethoxyphenyl)-15-hexylporphyrin **24** (100 mg, 0.19 mmol) was dried in vacuo in a septum equipped Schlenk flask for 2 h. THF abs. (25 mL) was then added under argon and the porphyrin suspension was cooled to −70 °C. *n*-Hexyl lithium (520 μL of a 2.5 M solution, 1.29 mmol) was added via a syringe, the cold bath was removed and the reaction mixture was stirred for 15 min at 20 °C. The solution changed its color from red to green-brown. Water (4 mL) was added and the solution was then stirred for 30 min. Upon addition of water the reaction mixture changed its color to dark-green. Subsequently, 3 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 0.78 mmol) were added, upon which the solution turned dark-red again. Subsequent purification steps were as described before. To remove a small amount of a yellow-brown by-product, the porphyrin was chromatographed a second time on silica (3×70 cm) using the same conditions as before. After recrystallization from CH_2Cl_2/CH_3OH 70 mg of brown crystals (0.11 mmol, 60%) of the title compound were obtained. Mp 133–134 °C; R_f=0.48 (CH_2Cl_2/*n*-hexane, 3:1, v/v), 0.75 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.93 (s, br., 2H, N*H*), 0.96 (m, 6H, 5^6-C*H*$_3$ and 10^6-C*H*$_3$), 1.35–1.60 (m, 8H, 5^5-C*H*$_2$, 10^5-C*H*$_2$, 5^4-C*H*$_2$, and 10^4-C*H*$_2$), 1.83 (m, 4H, 5^3-C*H*$_2$ and 10^3-C*H*$_2$), 2.55 (m, 4H, 5^2-C*H*$_2$ and 10^2-C*H*$_2$), 3.97 (s, 6H, OC*H*$_3$), 5.00 (m, 4H, 5^1-C*H*$_2$ and 10^1-C*H*$_2$), 6.93 (m, 1H, phenyl-H_{para}), 7.42 (m, 2H, phenyl-H_{ortho}), 9.03 (m, 2H, β-pyrrole-*H*), 9.21 (d, *J*=5 Hz, 1H, β-pyrrole-*H*), 9.27 (d, *J*=5 Hz, 1H, β-pyrrole-*H*), 9.48–9.62 (m, 4H, β-pyrrole-*H*), 9.98 ppm (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ= 14.14, 22.75, 30.30, 31.93, 35.29, 36.05, 38.77, 39.02, 55.63, 100.08, 103.47, 113.91, 117.80, 119.68, 120.55, 127.97, 128.41, 130.92, 131.07, 131.21, 143.98, 145.88, 159.02 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 (4.20), 366 (4.38), 394 (4.89), 413 (5.51), 479 (3.59), 510 (4.23), 544 (3.80), 586 (3.72), 642 nm (3.56); MS (EI, 80 eV, 310 °C), *m*/*z* (%): 614 (100) [M^+], 543 (53) [$M^+-C_5H_{11}$], 307 (9) [M^{2+}]; HRMS (EI) [$C_{40}H_{46}N_4O_2$]: calcd 614.36208, found 614.36262; EA [$C_{40}H_{46}N_4O_2$, 614.83 g mol^{-1}]. Anal. Calcd C 78.14, H 7.54, N 9.11, found C 77.81, H 7.51, N 9.10.

4.5.10. 5-(4-Aminophenyl)-10,20-bis(3-methoxyphenyl)-porphyrin (39). 4-Bromoaniline (1 g, 5.8 mmol) was dissolved in 20 mL of absolute diethylether in a septum-equipped Schlenk flask under argon. The solution was cooled in an ice bath. *n*-Butyl lithium (7 mL of a 2.5 M solution, 17.5 mmol) was added dropwise via a syringe through the septum over a period of approximately 1 h. The reaction mixture was stirred for 1 h in the ice bath and then for 45 min at 20 °C. The ethereal solution of this organometallic compound was cooled to −70 °C. To this solution was added, under argon, a cooled (−70 °C) suspension of 210 mg (0.4 mmol) of 5,15-bis(3-methoxyphenyl)porphyrin **12** in 30 mL of absolute THF. The cold bath was removed and the reaction mixture was stirred for 60 min at 20 °C. The solution gradually changed its color from red to green-brown. Water (4 mL) was added and the solution was then stirred for 20 min. On addition of water the reaction mixture changed its color to dark-green. After this time, 3 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 0.78 mmol) were added, upon which the solution became dark red again. After 15 min, the reaction mixture was filtered through silica (3×50 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated until a viscous brown oil was obtained which was then dried in vacuo at 75 °C for 3 h to remove aniline. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/methanol (20:1, v/v) as eluent. The porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated

solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 180 mg (0.29 mmol; 73%) of an amorphous purple solid: mp 271–272 °C; R_f=0.7 (CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.01 (s, 2H, N*H*), 3.98 (s, 6H, OCH_3), 4.80 (s, br., 2H, NH_2), 7.02 (m, 2H, 5-phenyl-*H*), 7.31 (m, 2H, 10,20-phenyl-*H*), 7.63 (m, 2H, 10,20-phenyl-*H*), 7.83 (m, 2H, 10,20-phenyl-*H*), 7.97 (m, 2H, 5-phenyl-*H*), 8.91 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 8.95 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.03 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.29 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.16 ppm (s, 1H, 15-*meso*-H); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.50, 104.41, 105.30, 113.28, 113.52, 119.21, 120.63, 121.30, 127.57, 127.78, 130.47, 131.09, 131.34, 131.64, 132.76, 135.58, 143.22, 146.01, 146.66, 152.81, 153.61, 158.09 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=369 (4.44), 397 (4.97), 415 (5.53), 483 (3.55), 511 (4.25), 546 (3.80), 585 (3.72), 638 nm (3.42); MS (EI, 80 eV, 280 °C), *m*/*z* (%): 613 (100) [M^+], 307 (%) [M^{2+}]; HRMS (EI) [$C_{40}H_{31}N_5O_2$]: calcd 613.24778, found 613.24682; [$C_{40}H_{31}N_5O_2$, 613.72 g mol^{-1}]. Anal. Calcd C 78.28, H 5.09, N 11.41, found C 78.26, H 4.87, N 11.27.

4.5.11. 5-Hexyl-10,20-diphenylporphyrin (40). *n*-Hexyl lithium (1.7 mL of a 2.5 M solution in hexane, 3.4 mmol) was added under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of 5,15-diphenylporphyrin (220 mg, 0.47 mmol) in 40 mL of dry THF at −80 °C. The color of the mixture changed from deep purple to brown within 30 min. 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 (0.06 M) was added and the reaction mixture was stirred for another 60 min at room temperature. The mixture was filtered through silica gel (Merck) 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 (1:7, v/v) yielding the title compound (185 mg, 0.34 mmol, 71%) as purple crystals, mp >300 °C; R_f=0.62 (ethyl acetate/*n*-hexane, 1:4, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=−2.95 (s, 2H, 2×N*H*), 0.92 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.38 (m, 2H, $CH_2CH_2CH_2CH_2$-CH_2CH_3), 1.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.83 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.52 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.02 (t, 2H, *J*=8.1 Hz, CH_2-$CH_2CH_2CH_2CH_2CH_3$), 7.78 (m, 6H, *o*,*p*-Ph-H), 8.23 (m, 2H, *m*-Ph-H), 8.26 (m, 2H, *m*-Ph-H), 8.91 (m, 4H, β-pyrrole-H), 9.24 (d, 2H, *J*=5.0 Hz, β-pyrrole-H), 9.59 (d, 2H, *J*=5.0 Hz, β-pyrrole-H), 10.18 (s, 1H, *meso*-H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=14.54 (5^6-C), 23.13 (5^5-C), 28.16 (5^4-C), 30.11 (5^3-C), 32.33 (5^2-C), 39.45 (5^1-C), 119.45, 121.64, 127.14, 128.07, 135.03, 142.49 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=412 (5.02), 510 (3.69), 544 (3.23), 583.59 (3.28), 655 nm (3.41); MS (EI, 80 eV): *m*/*z* (%): 546 (90) [M^+], 475 (100) [$M^+-C_5H_{11}$], 273 (26) [M^{++}]; HRMS [$C_{46}H_{43}N_5$]: calcd 546.2783, found 546.2759.

4.5.12. [5,10,15-Tris(3-methoxyphenyl)porphyrinato]-nickel(II) (42). 5,10,15-Tris(3-methoxyphenyl)porphyrin **30** (150 mg, 0.24 mmol) was placed in a round-bottomed flask equipped with a reflux condenser. DMF (70 mL) and nickel(II) acetate (1.07 g, 6.1 mmol) were added and the flask was heated at 150 °C (bath temperature) for 2 h. The solvent was evaporated to dryness and the residue was taken up in dichloromethane. The mixture was ultrasonicated for 2 min and then filtered through silica (50 g), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The porphyrin was again dissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated red crystals were removed by suction filtration through a D3 frit and dried in vacuo: 135 mg (0.2 mmol, 83%); mp 239 °C; R_f=0.43 (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.61 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.91 (s, 3H, 10-OCH_3), 3.93 (s, 6H, 5-OCH_3 and 15-OCH_3), 7.20–7.28 (m, 3H, phenyl-*H*), 7.51–7.65 (m, 6H, phenyl-*H*), 8.81 (m, 4H, β-pyrrole-*H*), 8.91 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.11 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.82 ppm (s, 1H, 20-*meso*-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.45, 86.18, 104.65, 113.57, 118.42, 119.16, 119.68, 119.76, 126.79, 126.82, 127.64, 127.72, 132.10, 132.57, 142.31, 142.38, 142.44, 142.66, 142.77, 142.87, 158.08, 158.15 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=317 (4.04), 407 (5.39), 520 (4.97), 551 nm (3.77); MS (EI, 80 eV, 400 °C), *m*/*z* (%): 684 (100) [M^+], 562 (8) [$M^+-(C_7H_7O+CH_3)$], 342 (19) [M^{2+}]; HRMS (EI) [$C_{41}H_{30}N_4NiO_3$]: calcd 684.16713, found 684.16773; [$C_{41}H_{30}N_4NiO_3$, 685.40 g mol^{-1}]. Anal. Calcd C 71.85, H 4.41, N 8.17, found C 71.71, H 4.29, N 7.95.

4.5.13. [5,15-Bis(3,5-dimethoxyphenyl)-10-hexyl-porphyrinato]nickel(II) (43). 5,15-Bis(3,5-dimethoxyphenyl)-10-hexylporphyrin **35** (200 mg, 0.3 mmol) was placed in a round-bottomed flask equipped with a reflux condenser. DMF (70 mL) and 1.2 g (6.8 mmol) of nickel(II) acetate were added and the flask was heated at 150 °C (bath temperature) for 2 h. The solvent was evaporated to dryness and the residue was taken up in dichloromethane. The mixture was ultrasonicated for 2 min and then filtered through silica (50 g), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness and the residue was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated red crystals were removed by suction filtration through a D3 frit and dried in vacuo to yield: 195 mg (0.27 mmol, 90%) of the metalloporphyrin: mp 272 °C; R_f=0.46 (CH_2Cl_2/*n*-hexane, 3:1, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/0.05% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm) retention time: 3.3 min (92.3%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.88 (t, *J*=7 Hz, 3H, 5^6-CH_3), 1.25–1.47 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.62 (m, 2H, 5^3-CH_2), 2.34 (m, 2H, 5^2-CH_2), 3.92 (s, 12H, OCH_3), 4.64 (t, *J*=7 Hz, 2H, 5^1-CH_2), 6.83 (m, 2H, phenyl-H_{para}), 7.20 (m, 4H, phenyl-H_{ortho}), 8.92 (m, 4H, β-pyrrole-*H*), 9.04 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.35 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.68 ppm (s, 1H, *meso*-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.06, 22.62, 30.09, 31.78, 34.53, 37.66, 55.55, 100.10, 103.84, 112.98, 117.34, 119.31, 129.29, 131.93, 132.33, 132.51, 141.90, 141.96, 142.19, 142.91, 159.12 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=325 (3.98), 410 (5.34), 523 (4.17), 551 nm (3.68); MS (EI, 80 eV, 300 °C), *m*/*z* (%): 722 (100) [M^+], 651 (41) [$M^+-C_5H_{11}$], 361 (11) [M^{2+}]; HRMS (EI) [$C_{42}H_{40}N_4NiO_4$]: calcd 722.2403, found 722.24334;

[$C_{42}H_{40}N_4NiO_4$, 723.49 g mol^{-1}]. Anal. Calcd C 69.73, H 5.57, N 7.74, found C 69.41, H 5.31, N 7.54.

4.5.14. 5-Butyl-10,20-bis(3-methoxyphenyl)porphyrin (44). Side product from the synthesis of 5,10,15-tris(3-methoxyphenyl)porphyrin **30** (Section 4.5.1): purple crystals, mp = 272 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -3.01$ (s, 2H, N*H*), 1.14 (t, 3H, $J_{5-6} = 7$ Hz, 6-H), 1.77–1.92 (m, 2H, 5-H), 2.51–2.63 (m, 2H, 4-H), 4.03 (s, 6H, MeO), 5.10 (t, 2H, $J_{3-4} = 7.7$ Hz, 3-H), 7.35–7.39 (m, 2H, Ph), 7.65–7.72 (m, 2H, Ph), 7.81–7.86 (m, 4H, Ph), 9.02 (m, each 2H, 1-H, 8-H), 9.28 (d, 2H, $J_{1-7} = 4.3$ Hz, 7-H), 9.56 (d, 2H, $J_{1-2} = 5.2$, 2-H), 10.11 (s, 1H, *meso-H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta = 14.61$, 24.07, 36.04, 41.51, 55.93, 104.41, 113.91, 119.17, 120.97, 121.57, 127.94, 143.80, 158.45 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 412 (5.19), 439 (3.89), 509 (4.01), 540 (3.75), 586 (3.72), 640 nm (3.68); MS (EI, 80 eV, 300 °C); *m/z* (%): 684 (2.25), 639 (15.68) [$M^+ + Cu$], 595 (10.75) [$M^+ + Cu - C_3H_7$], 578 (100) [M^+], 535 (77.35) [$M^+ - C_3H_7$], 518 (3.96) 495 (5.39), 289 (14.46) [$M^+/2$]; MS (EI, 80 eV, 280 °C); *m/z* (%): 578 (12) [M^+], 535 (34) [$M^+ - C_3H_7$], 289 (20) [M^{++}]; HRMS (EI) [$C_{38}H_{34}N_4O_2$]: calcd 578.268177, found 578.268234.

4.6. A_3B-type porphyrins

4.6.1. 5,10,15-Tris(3-methoxyphenyl)-20-pentylporphyrin (45). Dry dichloromethane (1500 mL) was placed in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Hexanal (0.46 mL, 3.75 mmol), 3-methoxybenzaldehyde (1.37 mL, 11.25 mmol), and pyrrole (1.04 mL, 15 mmol) were added. The flask was shielded from ambient light and then 1.16 mL (15 mmol) of trifluoroacetic acid were added and the reaction mixture was stirred for 3 h at 20 °C. After this time, 2.55 g (11.25 mmol) of DDQ suspended in 200 mL of dry dichloromethane were added and the mixture was stirred for 1 h. Then, 6 mL of triethylamine were added and the reaction mixture was stirred for 15 min. The reaction mixture was filtered through 100 g of silica, washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The eluted porphyrin fractions were separated by column chromatography on silica (3× 60 cm) using gradient elution with dichloromethane/hexane (2:1 to 3:1, v/v). The desired 5,10,15-tris(3-methoxyphenyl)-20-pentylporphyrin was obtained as the fourth fraction, preceded by 5,10,15,20-tetrapentylporphyrin **46** (traces), 5-(3-methoxyphenyl)-10,15,20-tripentylporphyrin **47** (<20 mg) and the (non-separable) isomeric mixture of 5,10-bis(3-methoxyphenyl)-15,20-dipentylporphyrin **48** and 5,15-bis(3-methoxyphenyl)-10,20-dipentylporphyrin **49**. The fifth fraction was 5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin **50** (160 mg, 0.22 mmol, 6%). The title porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated crystals were removed by suction filtration through a D3 frit and dried in vacuo to yield 240 mg (0.34 mmol; 9%) of purple crystals: mp 233–235 °C; $R_f = 0.17$ (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.48 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -2.76$ (s, 2H, N*H*), 0.96 (t, $J = 7$ Hz, 3H, 20^5-CH_3), 1.55 (m, 2H, 20^4-CH_2), 1.78 (m, 2H, 20^3-CH_2), 2.55 (m, 2H, 20^2-CH_2), 3.96 (s, 3H, 10-OCH_3), 3.98 (s, 6H, 5-OCH_3 and 15-OCH_3), 5.00 (t, $J = 8$ Hz, 2H, 20^1-CH_2), 7.28–7.35 (m, 3H, phenyl-*H*), 7.58–7.66 (m, 3H, phenyl-*H*), 7.74–7.82 (m, 6H, phenyl-*H*), 8.82 (s, 4H, β-pyrrole-*H*), 8.94 (d, $J = 5$ Hz, 2H, β-pyrrole-*H*), 9.47 ppm (d, $J = 5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta = 14.12$, 22.78, 32.75, 35.52, 38.55, 55.51, 113.55, 119.00, 119.27, 120.46, 120.80, 127.41, 127.51, 127.64, 127.91, 130.01, 130.76, 131.25, 143.43, 143.78, 146.78, 157.96, 158.03 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 303 (4.25), 374 (4.39), 401 (4.92), 418 (5.61), 484 (3.51), 516 (4.28), 550 (3.89), 592 (3.74), 648 nm (3.64); MS (EI, 80 eV, 250 °C), *m/z* (%): 698 (100) [M^+], 641 (39) [$M^+ - C_4H_9$], 349 (12) [M^{2+}]; HRMS (EI) [$C_{46}H_{42}N_4O_3$]: calcd 698.32569, found 698.32348; [$C_{46}H_{42}N_4O_3$, 698.86 g mol^{-1}]. Anal. Calcd C 79.06, H 6.06, N 8.02, found C 78.77, H 5.87, N 7.80.

4.6.2. 5-Hexyl-10,15,20-tris(3-methoxyphenyl)porphyrin (51). Preparation and workup as described in Section 4.6.1 using heptanal (0.52 mL, 3.75 mmol). Column chromatography gave the desired monohexylated porphyrin **51** as the fourth fraction, preceded by 5,10,15,20-tetrahexylporphyrin **52** (traces), 5,10,15-trihexyl-20-(3-methoxyphenyl)-porphyrin **53** (<20 mg) and the (non-separable) isomeric mixture of 5,10-dihexyl-15,20-bis(3-methoxyphenyl)-porphyrin **54** and 5,15-dihexyl-10,20-bis(3-methoxyphenyl)porphyrin **55**. The fifth fraction was 5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin **50** (170 mg, 0.23 mmol, 6%). The title porphyrin was again dissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated crystals were removed by suction filtration through a D3 frit and dried in vacuo to yield 210 mg (0.29 mmol; 8%) of purple crystals: mp 206–208 °C; $R_f = 0.19$ (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.52 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -2.74$ (s, 2H, N*H*), 0.93 (t, $J = 7$ Hz, 3H, 5^6-CH_3), 1.32–1.57 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.81 (m, 2H, 5^3-CH_2), 2.55 (m, 2H, 5^2-CH_2), 3.97 (s, 3H, 15-OCH_3), 3.99 (s, 6H, 10-OCH_3 and 20-OCH_3), 5.00 (t, $J = 8$ Hz, 2H, 5^1-CH_2), 7.29–7.36 (m, 3H, phenyl-*H*), 7.59–7.68 (m, 3H, phenyl-*H*), 7.76–7.83 (m, 6H, phenyl-*H*), 8.85 (s, 4H, β-pyrrole-*H*), 8.96 (d, $J = 5$ Hz, 2H, β-pyrrole-*H*), 9.47 ppm (d, $J = 5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta = 14.12$, 22.71, 30.25, 31.92, 35.56, 38.85, 55.50, 113.54, 119.01, 119.27, 120.47, 120.81, 127.40, 127.50, 127.64, 131.20, 143.43, 143.78, 157.96, 158.04 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 304 (4.23), 374 (4.39), 401 (4.94), 418 (5.59), 484 (3.48), 516 (4.28), 550 (3.88), 592 (3.72), 648 nm (3.57); MS (EI, 80 eV, 310 °C), *m/z* (%): 712 (100) [M^+], 641 (51) [$M^+ - C_5H_{11}$], 356 (19) [M^{2+}]; HRMS (EI) [$C_{47}H_{44}N_4O_3$]: calcd 712.34134, found 712.34332; [$C_{47}H_{44}N_4O_3$, 712.89 g mol^{-1}]. Anal. Calcd C 79.19, H 6.22, N 7.86, found C 78.83, H 5.93, N 7.69.

4.6.3. 5,10,15,20-Tetrahexylporphyrin (52). Obtained as purple needles (5%, 130 mg, 0.2 mmol) during the synthesis of 5,10,15-trihexyl-20-(3-methoxyphenyl)porphyrin (Section 4.6.4, **53**): mp 120 °C; $R_f = 0.52$ (SiO_2, CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -2.67$ (s, 2H, N*H*), 0.96 (t, $J = 7$ Hz, 12H, $CH_2CH_2CH_2CH_2CH_2$-CH_3), 1.30–1.60 (m, 16H, $CH_2CH_2CH_2CH_2CH_2CH_3$ and

$CH_2CH_2CH_2CH_2CH_2CH_3$), 1.81 (m, 8H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.51 (m, 8H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.90 (t, $J=8$ Hz, 8H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 9.44 ppm (s, 8H, β-pyrrole-H); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=14.14$, 22.76, 30.29, 31.70, 31.95, 32.89, 35.55, 38.66, 118.38, 128.08, ~145 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.04), 349 (4.18), 367 (4.27), 400 (4.86), 418 (5.46), 485 (3.44), 520 (4.14), 555 (3.96), 601 (3.55), 660 nm (3.80); MS (EI, 80 eV, 260 °C): *m/z* (%): 646 (100) [M^+], 575 (27) [M^+-71 (C_5H_{11})], 323 (9) [M^{2+}]; HRMS (EI) [$C_{44}H_{62}N_4$]: calcd 646.49745, found 646.44920; [$C_{44}H_{62}N_4$, 647.01 g mol^{-1}]. Anal. Calcd C 81.68, H 9.66, N 8.66, found C 81.41, H 9.59, N 8.70.

4.6.4. 5,10,15-Trihexyl-20-(3-methoxyphenyl)porphyrin (53). Dry dichloromethane (1500 mL) was placed in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Heptanal (1.57 mL, 11.25 mmol), 3-methoxybenzaldehyde (0.46 mL, 3.75 mmol), and pyrrole (1.04 mL, 15 mmol) were added. Further conditions and workup as described in Section 4.6.1 followed by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (1:1, v/v) as eluent. The desired 5,10,15-trihexyl-20-(3-methoxyphenyl)porphyrin **53** was obtained as the second fraction, preceded by 5,10,15,20-tetrahexylporphyrin **52** (130 mg, 0.2 mmol, 5%). Efforts to recrystallize the 5,10,15-trihexyl-20-(3-methoxyphenyl)porphyrin were unsuccessful; yield: 200 mg (0.3 mmol; 8%) of a purple amorphous solid: mp 91 °C; $R_f=0.48$ (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^1H NMR (250 MHz, $CDCl_3$): $\delta=-2.61$ (s, 2H, N*H*), 1.05 (m, 9H, 5^6-, 10^6-, and 15^6-C*H*$_3$), 1.29–1.63 (m, 12H, 5^5-, 10^5-, and 15^5-C*H*$_2$, 5^4-, 10^4-, and 15^4-C*H*$_2$), 1.85 (m, 6H, 5^3-, 10^3-, and 15^3-C*H*$_2$), 2.56 (m, 6H, 5^2-, 10^2-, and 15^2-C*H*$_2$), 4.02 (s, 3H, OC*H*$_3$), 4.91 (m, 6H, 5^1-, 10^1-, and 15^1-C*H*$_2$), 7.40 (m, 1H, phenyl-*H*), 7.70 (m, 1H, phenyl-*H*), 7.87 (m, 2H, phenyl-*H*), 8.95 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.42 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.47 ppm (m [AB-spectrum], 4H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=14.18$, 22.75, 30.23, 30.28, 31.93, 35.35, 35.72, 38.65, 38.82, 55.44, 113.35, 117.70, 119.06, 119.39, 120.47, 127.36, 127.62, 131.19, 144.08, 145.53, 158.00 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=349 (4.23), 367 (4.30), 398 (4.79), 418 (5.55), 485 (3.39), 519 (4.15), 553 (3.88), 597 (3.64), 655 nm (3.70); MS (EI, 80 eV, 240 °C), *m/z* (%): 668 (100) [M^+], 597 (36) [$M^+-C_5H_{11}$], 334 (4) [M^{2+}]; HRMS (EI) [$C_{45}H_{56}N_4O$]: calcd 668.44541, found 668.44287.

4.6.5. 5-Heptyl-10,15,20-tris(3-methoxyphenyl)porphyrin (56). Preparation and workup as described in Section 4.6.1 using octanal (0.59 mL, 3.75 mmol). Column chromatography gave the desired 5-heptyl-10,15,20-tris(3-methoxyphenyl)porphyrin **56** as the fourth fraction, preceded by 5,10,15,20-tetraheptylporphyrin **57** (traces), 5,10,15-triheptyl-20-(3-methoxyphenyl)porphyrin **58** (<20 mg) and the (non-separable) isomeric mixture of 5,10-diheptyl-15,20-bis(3-methoxyphenyl)porphyrin **59** and 5,15-diheptyl-10,20-bis(3-methoxyphenyl)porphyrin **60**. The fifth fraction was 5,10,15,20-tetrakis(3-methoxyphenyl)-porphyrin **50** (160 mg, 0.22 mmol, 6%). The target fraction was again dissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated crystals were removed by suction filtration through a D3 frit and dried in vacuo to yield 270 mg (0.37 mmol; 10%) of purple crystals: mp 203–205 °C; $R_f=0.23$ (CH_2Cl_2/C_6H_{14}, 3:1, v/v), 0.56 (CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): $\delta=-2.76$ (s, 2H, N*H*), 0.89 (t, $J=7$ Hz, 3H, 5^7-C*H*$_3$), 1.30–1.39 (m, 4H, 5^6-C*H*$_2$ and 5^5-C*H*$_2$), 1.51 (m, 2H, 5^4-C*H*$_2$), 1.80 (m, 2H, 5^3-C*H*$_2$), 2.54 (m, 2H, 5^2-C*H*$_2$), 3.96 (s, 3H, 15-OC*H*$_3$), 3.98 (s, 6H, 10-OC*H*$_3$ and 20-OC*H*$_3$), 5.00 (t, $J=8$ Hz, 2H, 5^1-C*H*$_2$), 7.28–7.35 (m, 3H, phenyl-*H*), 7.59–7.67 (m, 3H, phenyl-*H*), 7.75–7.82 (m, 6H, phenyl-*H*), 8.83 (s, 4H, β-pyrrole-*H*), 8.95 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.47 ppm (d, $J=5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=14.08$, 22.69, 29.37, 30.56, 31.89, 35.56, 38.90, 55.49, 113.52, 118.97, 119.24, 120.42, 120.80, 127.39, 127.49, 127.62, 127.88, 130.68, 131.18, 143.40, 143.75, 145.94, 157.91, 157.99 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=304 (4.17), 373 (4.35), 401 (4.86), 418 (5.59), 485 (3.45), 516 (4.24), 550 (3.84), 592 (3.67), 648 nm (3.56); MS (EI, 80 eV, 250 °C), *m/z* (%): 726 (100) [M^+], 641 (36) [$M^+-C_6H_{13}$], 363 (17) [M^{2+}]; HRMS (EI) [$C_{48}H_{46}N_4O_3$]: calcd 726.35699, found 726.35633; [$C_{48}H_{46}N_4O_3$, 726.92 g mol^{-1}]. Anal. Calcd C 79.31, H 6.38, N 7.71, found C 79.12, H 6.18, N 7.62.

4.6.6. 5,10,15,20-Tetraheptylporphyrin (57). Obtained as purple needles (5%, 140 mg, 0.2 mmol) during the synthesis of 5,10,15-triheptyl-20-(3-methoxyphenyl)porphyrin (Section 4.6.7, **58**): mp 103 °C; $R_f=0.58$ (SiO_2, CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^1H NMR (250 MHz, $CDCl_3$): $\delta=-2.66$ (s, 2H, N*H*), 0.90 (t, $J=7$ Hz, 12H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.35 (m, 16H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.52 (m, 8H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.79 (m, 8H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.50 (m, 8H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 4.91 (t, $J=8$ Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 9.44 ppm (s, 8H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=14.12$, 22.72, 29.41, 30.60, 31.96, 35.56, 38.73, 118.40 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=350 (4.18), 366 (4.27), 400 (4.87), 418 (5.60), 489 (3.40), 520 (4.13), 555 (3.96), 601 (3.54), 660 nm (3.78); MS (EI, 80 eV, 320 °C), *m/z* (%): 702 (100) [M^+], 617 (22) [M^+-85 (C_6H_{13})], 351 (5) [M^{2+}]; HRMS (EI) [$C_{48}H_{70}N_4$]: calcd 702.56005, found 702.56445; [$C_{48}H_{70}N_4$, 703.11 g mol^{-1}]. Anal. Calcd C 82.00, H 10.03, N 7.97, found C 81.95, H 9.95, N 7.69.

4.6.7. 5,10,15-Triheptyl-20-(3-methoxyphenyl)porphyrin (58). Preparation, observations, chromatography and workup as described in Section 4.6.4 using octanal (1.76 mL, 11.25 mmol). Yield of 5,10,15-triheptyl-20-(3-methoxyphenyl)porphyrin **58**: 170 mg (recrystallization unsuccessful, 0.24 mmol; 6%) as a purple amorphous solid; yield of 5,10,15,20-tetraheptylporphyrin **57**: 140 mg (0.2 mmol; 5%) as purple needles. Analytical data for the title compound: mp 144 °C; $R_f=0.52$ (CH_2Cl_2/C_6H_{14}, 1:1, v/v): 0.52; ^1H NMR (250 MHz, $CDCl_3$): $\delta=-2.67$ (s, 2H, N*H*), 0.92 (m, 9H, 5^7-, 10^7-, and 15^7-C*H*$_3$), 1.30–1.41 (m, 12H, 5^6-, 10^6-, and 15^6-C*H*$_2$, 5^5-, 10^5-, and 15^5-C*H*$_2$), 1.53 (m, 6H, 5^4-, 10^4-, and 15^4-C*H*$_2$), 1.79 (m, 6H, 5^3-, 10^3-, and 15^3-C*H*$_2$), 2.51 (m, 6H, 5^2-, 10^2-, and 15^2-C*H*$_2$), 3.98 (s, 3H, OC*H*$_3$), 4.93 (m, 6H, 5^1-, 10^1-, and 15^1-C*H*$_2$), 7.33 (m, 1H, phenyl-*H*), 7.63 (m, 1H, phenyl-*H*), 7.75 (m, 2H, phenyl-*H*), 8.86 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.37 (d, $J=5$ Hz, 2H,

β-pyrrole-*H*), 9.50 (m [AB-spectrum], 4H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.12, 22.72, 29.39, 30.54, 30.59, 31.93, 31.97, 35.39, 35.76, 38.69, 38.86, 55.46, 113.37, 117.68, 119.06, 119.41, 120.44, 127.35, 127.58, 127.79, 131.25, 143.55, 145.71, 157.97 ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.12, 14.15, 22.71, 22.74, 29.39, 29.42, 30.55, 30.64, 31.93, 31.97, 35.41, 35.82, 38.72, 38.93, 55.47, 113.35, 117.65, 119.11, 119.47, 120.33, 127.34, 127.55, ~128.5, ~131.5, 143.97, 157.89 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=349 (4.27), 367 (4.35), 401 (4.86), 418 (5.60), 485 (3.37), 518 (4.20), 553 (3.94), 597 (3.65), 654 nm (3.71); MS (EI, 80 eV, 200 °C), *m*/*z* (%): 710 (100) [M^+], 625 (28) [$M^+-C_6H_{13}$]; HRMS (EI) [$C_{48}H_{62}N_4O$]: calcd 710.49236, found 710.4945.

4.7. A_2BC-type porphyrins via S_NAr

4.7.1. 5-Butyl-15-hexyl-10,20-diphenylporphyrin (61). *n*-Butyl lithium (2 mL of a 2.5 M solution in hexane, 5 mmol) was added under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of 5-hexyl-10,20-diphenylporphyrin **40** (100 mg, 0.18 mmol) in 40 mL of dry THF at −80 °C. The mixture changed from deep purple to brown within 30 min. The reaction mixture was stirred for 1 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 (0.06 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 dichloromethane/*n*-hexane (2:1, v/v) and yielded the title compound (34 mg, 0.05 mmol, 31%) as purple crystals, mp >300 °C; R_f=0.77 (dichloromethane/*n*-hexane, 2:1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=−2.67 (s, 2H, 2×N*H*), 0.94 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.13 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.27 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.52 (m, 2H, $CH_2CH_2CH_2CH_2$-CH_2CH_3),1.81 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 2.48 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.99 (t, 4H, *J*=8.1 Hz, CH_2-$CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.75 (m, 6H, phenyl-*H*), 8.21 (m, 4H, phenyl-*H*), 8.85 (m, 4H, β-pyr-pyrrole-*H*), 9.43 ppm (m, 4H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=13.71 (15^6-C), 22.27 (15^5-C), 23.15 (5^4-C), 29.28 (5^3-C), 29.76 (15^4-C), 31.46 (15^3-C), 34.54 (5^2-C), 34.85 (15^2-C), 38.23 (15^1-C), 40.31 (5^1-C), 118.45, 119.36, 126.08, 127.14, 133.99, 142.26, 143.84, 146.70 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=417 (4.96), 438 (4.03), 515 (3.87), 550 (3.72), 592 (3.59), 651 nm (3.69); MS (EI, 80 eV) *m*/*z* (%): 602 (60) [M^+], 559 (50) [$M^+-C_3H_7$], 531 (64) [$M^+-C_5H_{11}$], 488 (38) [$M^+-C_5H_{11}-C_3H_7$], 301 (26) [M^{++}]; HRMS [$C_{42}H_{42}N_4$]: calcd 602.3409, found 602.3383.

4.7.2. 5-(4-Dimethylaminophenyl)-15-hexyl-10,20-diphenylporphyrin (62). *n*-Butyl lithium (1.2 mL of a 2.5 M solution in hexane, 3 mmol) was slowly added (ca. 1 h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *p*-(dimethylamino)bromobenzene (0.5 g, 2.5 mmol) in 10 mL of dry diethyl ether at 0 °C. After addition of *n*-butyl lithium the cold bath was removed and stirring was continued for another 1 h at room temperature. The solution became yellow and opaque. To the vigorously stirred mixture was added rapidly a solution of 5-hexyl-10,20-diphenylporphyrin **40** (100 mg, 0.18 mmol) in 40 mL of dry THF under an argon atmosphere. The color of the mixture changed from deep purple to brown within 30 min. The reaction mixture was stirred for 3 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 (0.06 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through silica gel (Merck) 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 (1:4, v/v) yielded the title compound (66.1 mg, 0.1 mmol, 54%) as purple crystals, mp >300 °C; R_f=0.42 (ethyl acetate/*n*-hexane, 1:4, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=−2.61 (s, 2H, 2×N*H*), 0.92 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_2CH_2$-CH_3), 1.39 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.79 (m, 2H, $CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 2.53 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.22 (s, 6H, $N(CH_3)_2$), 5.02 (t, 2H, *J*=8.1 Hz, CH_2CH_2-$CH_2CH_2CH_2CH_3$), 7.11 (d, 2H, *J*=7.5 Hz, Ph-H), 7.76 (m, 6H, Ph-H), 8.06 (d, 2H, *J*=7.5 Hz, Ph-H), 8.22 (m, 4H, Ph-H), 8.81 (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*), 8.92 (m, 4H, β-pyrrole-*H*), 9.46 ppm (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=13.72, 22.28, 29.81, 31.47, 35.04, 38.36, 40.25, 110.29, 118.85, 119.64, 126.12, 127.13, 128.33, 134.07, 135.25, 142.18, 149.45 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=419 (4.91), 517 (3.76), 564 (3.47), 595 (3.16), 653 nm (3.33); MS (EI, 80 eV) *m*/*z* (%): 665 (24) [M^+], 594 (25) [$M^+-C_5H_{11}$], 578 (10) [$M^+-C_5H_{12}-CH_3$], 333 (20) [M^{++}]; HRMS [$C_{46}H_{43}N_5$]: calcd 665.3518, found 665.3491.

4.7.3. 5-Hexyl-15-(3-hydroxyphenyl)-10,20-diphenylporphyrin (63). *n*-Butyl lithium (3 mL of a 2.5 M solution in hexane, 7.5 mmol) was added under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *m*-bromophenol (0.87 g, 5 mmol) in 10 mL of dry diethyl ether at 0 °C. After addition of *n*-butyl lithium the cold bath was removed and stirring was continued for 18 h at room temperature. The solution slowly became opaque yellow. To the vigorously stirred mixture was added rapidly a solution of 5-hexyl-10,20-diphenylporphyrin **40** (100 mg, 0.18 mmol) in 40 mL of dry THF under an argon atmosphere. 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 (0.06 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 (1:4, v/v) yielding the title compound (97 mg, 0.15 mmol, 83%) as purple crystals,

mp >300 °C; R_f=0.55 (ethyl acetate/*n*-hexane, 1:3, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=0.96 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.27 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.40 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.72 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.51 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.92 (t, 2H, *J*=8.1 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 6.41 (m, 1H, phenyl-*H*), 6.69 (m, 1H, phenyl-*H*), 6.95 (m, 1H, phenyl-*H*), 7.45 (m, 1H, phenyl-*H*), 7.67 (s, 1H, O*H*), 7.78 (m, 6H, phenyl-*H*), 8.24 (m, 4H, phenyl-*H*), 8.77 (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*), 8.82 (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*), 8.95 (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*), 9.45 ppm (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=13.68, 22.24, 29.75, 31.42, 35.06, 38.37, 113.61, 118.16, 119.20, 120.49, 121.25, 122.13, 123.19, 126.18, 127.22, 130.08, 134.08, 141.90, 142.89, 153.26, 155.77 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε)=417 (4.97), 443 (4.22), 514 (3.76), 549 (3.55), 593 (3.48), 657 nm (3.56); MS (EI, 80 eV): *m*/*z* (%): 638 (16) [M^+], 567 (30) [$M^+-C_5H_{11}$], 319 (18) [M^{++}]; HRMS [$C_{44}H_{38}N_4O$]: calcd 638.3045, found 638.3025; [$C_{44}H_{38}N_4O$, 638.81 g mol^{-1}]. Anal. Calcd C 82.73, H 6.00, N 8.77, found C 82.71, H 5.98, N 8.43.

4.7.4. 5-Hexyl-15-(4-hydroxyphenyl)-10,20-diphenylporphyrin (64). *n*-Butyl lithium (3 mL of a 2.5 M solution in hexane, 7.5 mmol) was added under an argon atmosphere 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. Further reaction and work-up followed the procedure given in Section 4.7.3 to yield the title compound (76 mg, 0.12 mmol, 65%) as purple crystals, mp >300 °C; R_f=0.33 (ethyl acetate/*n*-hexane, 1:4, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=0.94 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.36 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.51 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.81 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.99 (t, 2H, *J*=8.1 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 6.46–6.49 (m, 3H, Ph-H), 6.99 (d, 2H, *J*=7.5 Hz, Ph-H), 7.23–7.26 (m, 3H, Ph-H), 7.76 (m, 2H, Ph-H), 7.78 (s, 1H, O*H*), 7.98 (d, 2H, *J*=7.5 Hz, Ph-H), 8.20–8.23 (d, 2H, *J*=7.5 Hz, Ph-H), 8.82 (m, 4H, β-pyrrole-*H*), 8.95 (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*), 9.48 ppm (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.54 (5^6-C), 23.11 (5^5-C), 30.65 (5^4-C), 32.29 (5^3-C), 35.58 (5^2-C), 39.26 (5^1-C), 113.10, 117.45, 120.03, 121.16, 127.05, 128.10, 132.71, 134.95, 136.06, 142.72, 154.81 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=417 nm (4.96), 445 (4.51), 514 (4.28), 595 (4.14), 653 nm (4.15); MS (EI, 80 eV) *m*/*z* (%): 638 (18) [M^+], 567 (34) [$M^+-C_5H_{11}$], 319 (17) [M^{++}]; HRMS [$C_{44}H_{38}N_4O$]: calcd 638.3045, found 638.3027; [$C_{44}H_{38}N_4O$, 638.81 g mol^{-1}]. Anal. Calcd C 82.73, H 6.00, N 8.77, found C 82.58, H 6.15, N 8.85.

4.7.5. 5-Hexyl-15-(2-methoxyphenyl)-10,20-diphenylporphyrin (65). *n*-Butyl lithium (2 mL of a 2.5 M solution in hexane, 5 mmol) was added under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *o*-bromoanisole (0.5 g, 2.7 mmol) in 10 mL of dry THF at −78 °C. After addition of *n*-butyl lithium the cold bath was removed and stirring was continued for 1 h at room temperature. To the vigorously stirred mixture was added rapidly a solution of 5-hexyl-10,20-diphenylporphyrin **40** (50 mg, 0.09 mmol) in 40 mL of dry THF under an argon atmosphere. The mixture changed from deep purple to brown within 30 min. The reaction mixture was 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 (0.06 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 (1:4, v/v) yielding the title compound (24 mg, 0.04 mmol, 40%) as purple crystals, mp >300 °C; R_f=0.25 (ethyl acetate/*n*-hexane, 1:4, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=−2.64 (s, 2H, 2×N*H*), 0.96 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.28 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.85 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.56 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.8 (s, 3H, OCH_3), 5.04 (t, 2H, *J*=8.1 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.01 (m, 1H, phenyl-*H*), 7.37 (m, 2H, phenyl-*H*), 7.79 (m, 6H, phenyl-*H*), 8.01 (m, 1H, phenyl-*H*), 8.22 (m, 4H, phenyl-*H*), 8.76 (m, 4H, β-pyrrole-*H*), 8.92 (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*), 9.49 ppm (d, 2H, *J*=5.0 Hz, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.14, 22.71, 30.23, 31.90, 35.58, 38.81, 55.66, 111.06, 115.18, 119.23, 120.74, 126.54, 127.55, 128.58, 130.88, 131.44, 135.56, 157.01, 159.42 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=416 (4.93), 443 (4.20), 514 (4.00), 565 (3.86), 594 (3.63), 649 nm (3.86); MS (EI, 80 eV): *m*/*z* (%): 652 (20) [M^+], 581 (35) [$M^+-C_5H_{11}$], 489 (18) [$M^+-C_5H_{11}-C_6H_5-CH_3$], 326 (15) [$M^{++}$]; HRMS [$C_{45}H_{40}N_4O$]: calcd 652.3202, found 652.3176.

4.7.6. 5-(2,5-Dimethoxyphenyl)-15-hexyl-10,20-diphenylporphyrin (66). *n*-Butyl lithium (2 mL of a 2.5 M solution in hexane, 5 mmol) was added under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of 1-bromo-2,5-dimethoxybenzene (0.5 g, 2.4 mmol) in 10 mL of dry THF at −80 °C. After addition of *n*-butyl lithium the cold bath was removed and stirring was continued for 1 h at room temperature. To the vigorously stirred mixture was added rapidly a solution of 5-hexyl-10,20-diphenylporphyrin **40** (50 mg, 0.09 mmol) in 40 mL of dry THF under an argon atmosphere. The mixture changed from deep purple to brown within 30 min. 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 (0.06 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 and washed with enough *n*-hexane. Final purification was achieved by column chromatography and elution with ethyl acetate/*n*-hexane (1:4, v/v) yielded the title compound (18 mg, 0.03 mmol, 29%) as purple crystals, mp >300 °C; R_f=0.22 (ethyl acetate/*n*-hexane, 1:4, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=−2.66 (s, 2H, 2×N*H*), 0.95 (t, 3H, *J*=7.2, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.26 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.52 (m,

2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.89 (m, 2H, $CH_2CH_2CH_2$-$CH_2CH_2CH_3$), 2.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.50–3.91 (m, 6H, $2\times OCH_3$), 5.05 (t, 2H, $J=8.1$ Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 6.77 (m, 1H, phenyl-*H*), 7.28 (m, 1H, phenyl-*H*), 7.58 (m, 1H, phenyl-*H*), 7.77 (m, 6H, phenyl-*H*), 8.20 (m, 4H, phenyl-*H*), 8.77 (m, 4H, β-pyrrole-*H*), 8.89 (d, 2H, $J=5.0$ Hz, β-pyrrole-*H*), 9.49 ppm (d, 2H, $J=5.0$ Hz, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=$ 13.71, 22.28, 29.83, 31.48, 35.58, 38.41, 55.48, 56.27, 111.60, 114.37, 117.30, 118.85, 120.96, 126.13, 127.15, 131.50, 134.00, 142.02, 151.99, 153.69 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=417 (4.97), 440 (3.97), 514 nm (3.83), 545 (3.61), 590 (3.57), 649 nm (3.61); MS (EI, 80 eV) *m/z* (%): 682 (20) [M^+], 611 (36) [$M^+-C_5H_{11}$], 341 (14) [M^{++}]; HRMS [$C_{45}H_{40}N_4O$]: calcd 682.3307, found 682.3275.

4.7.7. 5-(4-Aminophenyl)-15-(4-dimethylaminophenyl)-10,20-diphenylporphyrin (67). *n*-Butyl lithium (0.6 mL of a 2.5 M solution in hexane, 0.6 mmol) was slowly added (ca. 1 h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *p*-(dimethylamino)bromobenzene (0.25 g, 1.25 mmol) in 10 mL of dry diethylether at 0 °C. After addition of *n*-butyl lithium the cold bath was removed and stirring was continued for another 1 h at room temperature. The solution became bright yellow and opaque. To the vigorously stirred mixture was added rapidly a solution of 5-(*p*-aminophenyl)-10,20-diphenylporphyrin (50 mg, 0.09 mmol) in 40 mL of dry THF under an argon atmosphere. The mixture changed from deep purple to brown within 30 min. The reaction mixture was stirred for 4 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 (0.06 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 (1:2, v/v) yielded the title compound (12 mg, 0.017 mmol, 20%) as purple crystals, mp >300 °C; $R_f=0.72$ (ethyl acetate/*n*-hexane, 1:1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=-2.65$ (s, 2H, 2×NH), 3.23 (s, 6H, $N(CH_3)_2$), 7.02 (d, 2H, $J=7.5$ Hz, Ph-H), 7.11 (d, 2H, $J=7.5$ Hz, phenyl-*H*), 7.77 (m, 6H, phenyl-*H*), 7.97 (d, 2H, $J=7.5$ Hz, phenyl-*H*), 8.07 (d, 2H, $J=7.5$ Hz, phenyl-*H*), 8.24 (m, 4H, phenyl-*H*), 8.83 (d, 2H, $J=5.0$ Hz, β-pyrrole-*H*), 8.84 (d, 2H, $J=5.0$ Hz, β-pyrrole-*H*), 8.92 (d, 2H, $J=5.0$ Hz, β-pyrrole-*H*), 8.95 ppm (d, 2H, $J=5.0$ Hz, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=40.27$, 110.28, 113.01, 119.31, 120.54, 126.183, 127.14, 134.13, 142.03, 145.52, 149.54 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=421 (5.09), 518 (4.03), 560 (3.90), 597 (3.79), 655 nm (3.97); MS (EI, 80 eV) *m/z* (%): 658 (4) [M^+-CH_2], 336 (6) [M^{++}], 149 (100) [4-Me_2N–C_6H_4–CHO]; [$C_{46}H_{36}N_6$ 672.83 g mol^{-1}]. Anal. Calcd C 82.11, H 6.15, N 8.85, found C 82.45, H 6.52, N 8.71.

4.7.8. 5-(4-Aminophenyl)-15-hexyl-10,20-bis(3-methoxyphenyl)porphyrin (68). 5-(4-Aminophenyl)-10,20-bis(3-methoxyphenyl)porphyrin **39** (65 mg, 0.11 mmol) was dried in vacuo in a septum-equipped Schlenk-flask for 2 h. 20 mL of abs. THF were then added under argon. The porphyrin solution was cooled to −70 °C. *n*-Hexyl lithium (250 μL of a 2.5 M solution, 6.25 mmol) was added via a syringe through the septum. The cold bath was removed and the reaction mixture was stirred for 15 min at 20 °C. The solution changed its color from red to green-brown. Water (4 mL) was added and the solution was then stirred for 20 min. Upon addition of water the reaction mixture changed its color to dark-green. After this time, 3 mL of a solution of DDQ (0.6 g DDQ in 10 mL THF, ca. 0.78 mmol) were added, upon which the solution becomes dark red again. The reaction mixture was filtered through silica (column 3×50 cm), washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/methanol (20:1, v/v) as eluent. The porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 33 mg (0.047 mmol; 44%) of purple microcrystals; mp 129–130 °C; $R_f=0.74$ ($CH_2Cl_2/CH_3C(O)OCH_2CH_3$, 95:5, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=-2.74$ (s, 2H, N*H*), 0.91 (t, $J=7$ Hz, 3H, 15^6-CH_3), 1.30–1.52 (m, 4H, 15^5-CH_2 and 15^4-CH_2), 1.80 (m, 2H, 15^3-CH_2), 2.53 (m, 2H, 15^2-CH_2), 3.98 (s, 6H, OCH_3), 4.99 (t, $J=8$ Hz, 2H, 15^1-CH_2), 7.02 (m, 2H, 5-phenyl-*H*), 7.32 (m, 2H, 10,20-phenyl-*H*), 7.63 (m, 2H, 10,20-phenyl-*H*), 7.80 (m, 2H, 10,20-phenyl-*H*), 7.94 (m, 2H, 5-phenyl-*H*), 8.81 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 8.86 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 8.93 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.45 ppm (d, $J=5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): $\delta=14.14$, 22.72, 30.26, 31.92, 35.51, 38.82, 55.50, 113.48, 119.05, 120.00, 120.29, 120.38, 127.36, 127.62, ~130, 132.29, 135.60, 143.87, 145.95, 157.88 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=370 (4.35), 401 (4.84), 420 (5.52), 489 (3.61), 518 (4.22), 555 (3.93), 594 (3.65), 651 nm (3.65); MS (EI, 80 eV, 200 °C), *m/z* (%): 697 (100) [M^+], 349 (18) [M^{2+}]; HRMS (EI) [$C_{46}H_{43}N_5O_2$]: calcd 697.34168, found 697.34424.

4.8. Vinylogous formylation reactions

4.8.1. [5,15-Bis(4-butyloxyphenyl)-10-(2-formylethenyl)-porphyrinato]nickel(II) (69). 3-Dimethylamino acrolein (1.2 mL, 12 mmol) together with 12 mL of dry dichloromethane were placed in a 100 mL three-necked flask equipped with magnetic stirrer and gas inlet and cooled in an ice-bath. Then, 1.2 mL (12.8 mmol) of $POCl_3$ were added dropwise via a syringe under argon. Initially, a white precipitate formed upon addition of $POCl_3$, which dissolved again on further addition of the reagent. At the end a viscous, red-brown solution was formed which was stirred for 15 min at 0 °C. This solution was then transferred to a second flask (also cooled in an ice bath) containing 220 mg (0.33 mmol) [5,15-bis(4-butyloxyphenyl)porphyrinato]-nickel(II) **26** dissolved in 200 mL of dry dichloromethane. The cold bath was removed and the reaction mixture stirred for 18 h at 20 °C. After this time, 200 mL of a saturated sodium carbonate solution were added and the mixture was stirred for 12 h. Then, the phases were separated and the organic phase was washed with brine (3×200 mL) and then with water (4–5×200 mL) up to neutral reaction of the

water phase. The organic phase was dried with sodium sulfate and then evaporated to dryness. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/acetic acid ethylester (50:1, v/v) as eluent. The red-green product was eluted first, followed by a second fraction containing the doubly formylated product (72, <5%). The target porphyrin fractions were evaporated to dryness and redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated green-purple crystals were removed by suction filtration through a D4 frit and dried in vacuo to yield 150 mg (0.21 mmol, 63%) of the title compound: mp 211 °C; R_f=0.64 (CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/0.05% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm) retention time: 6.5 min (95%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.08 (t, J=7 Hz, 6H, $OCH_2CH_2CH_2CH_2CH_3$), 1.54–1.71 (m, 4H, $OCH_2CH_2CH_2CH_3$), 1.96 (m, 4H, $OCH_2CH_2CH_2CH_3$), 4.20 (t, J=7 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 6.59 (dd, J_1=15 Hz, J_2=8 Hz, 1H, 10^2-C*H*), 7.19 (m, 4H, phenyl-*H*), 7.82 (m, 4H, phenyl-*H*), 8.76 (d, J=5 Hz, 2H, β-pyrrole-*H*), 8.83 (d, J=5 Hz, 2H, β-pyrrole-*H*), 8.99 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.24 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.59 (d, J=15 Hz, 1H, 10^1-C*H*), 9.63 (s, 1H, *meso-H*), 10.01 ppm (d, J=8 Hz, 1H, 10^3-C*H*O); ^{13}C NMR (60 MHz, $CDCl_3$): δ=13.96, 19.42, 31.53, 68.05, 106.29, 108.67, 113.16, 119.45, 130.37, 132.27, 132.66, 132.76, 133.83, 134.68, 140.91, 141.40, 142.19, 142.25, 143.57, 151.82, 159.23, 192.03 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=318 (4.49), 430 (5.24), 542 (4.10), 587 (4.06) nm; MS (EI, 80 eV, 300 °C), *m/z* (%): 716 (100) [M^+], 688 (20) [M^+-CO], 631 (2) [$M^+-CO-C_4H_9$], 358 (1) [M^{2+}]; HRMS (EI) [$C_{43}H_{38}N_4NiO_3$]: calcd 716.22974, found 716.22766; [$C_{43}H_{38}N_4NiO_3$, 717.49 g mol^{-1}]. Anal. Calcd C 71.98, H 5.34, N 7.81, found C 71.51, H 5.22, N 7.67.

4.8.2. [5-(2-Formylethenyl)-10,20-bis(4-pentyloxyphenyl)porphyrinato]nickel(II) (70). 3-(Dimethylamino)acrolein (0.6 mL, 6 mmol) and 6 mL of dry dichloromethane were placed in a 100 mL three-necked flask equipped with magnetic stirrer and gas inlet and cooled in an ice-bath. Then, 0.6 mL (6.4 mmol) of $POCl_3$ were added dropwise via a syringe under argon. Upon addition of the $POCl_3$ a white precipitate formed, which dissolved again on further addition of the reagent. Eventually, a viscous, red-brown solution was formed which was stirred for 15 min at 0 °C. This solution was then transferred to a second flask (also cooled in an ice bath) containing 120 mg (0.17 mmol) [5,15-bis(4-pentyloxyphenyl)porphyrinato]-nickel(II) **27** dissolved in 100 mL dry dichloromethane. Further conditions and workup were similar to those given in Section 4.8.1. Yield: 80 mg (0.11 mmol, 63%) of green-purple crystals: mp 160 °C; R_f=0.67 (CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/0.05% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm) retention time 5.80 min (96.5%), (same conditions but detection at 254 nm) retention time 5.87 min (94.9%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.01 (t, J=7 Hz, 6H, $OCH_2CH_2CH_2CH_2CH_3$), 1.43–1.66 (m, 8H, $OCH_2CH_2CH_2CH_2CH_3$ and $OCH_2CH_2CH_2CH_2CH_3$), 1.96 (m, 4H, $OCH_2CH_2CH_2CH_2CH_3$), 4.19 (t, J=7 Hz, 4H, $OCH_2CH_2CH_2CH_2CH_3$), 6.63 (dd, J_1=15 Hz, J_2=8 Hz, 1H, 5^2-C*H*), 7.19 (m, 4H, phenyl-*H*), 7.85 (m, 4H, phenyl-*H*), 8.77 (d, J=5 Hz, 2H, β-pyrrole-*H*), 8.86 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.01 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.29 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.65 (d, J=15 Hz, 1H, 5^1-C*H*), 9.65 (s, 1H, *meso-H*), 10.05 ppm (d, J=8 Hz, 1H, 5^3-C*H*O); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.09, 22.57, 28.38, 29.16, 68.36, 106.27, 108.65, 113.15, 119.42, 130.35, 132.26, 132.65, 132.74, 133.80, 134.66, 140.87, 141.38, 142.17, 142.23, 143.55, 151.79, 159.21, 192.02 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=317 (4.24), 429 (5.18), 544 (3.98), 590 nm (3.91); MS (EI, 80 eV, 300 °C), *m/z* (%): 744 (100) [M^+], 716 (27) [M^+-CO], 673 (10) [$M^+-C_5H_{11}$], 645 (9) [$M^+-CO-C_5H_{11}$], 574 (5) [$M^+-CO-2\times C_5H_{11}$], 545 (12) [$M^+-CO-2\times C_5H_{11}-CHO$], 372 (2) [$M^{2+}$]; HRMS (EI) [$C_{45}H_{42}N_4NiO_3$]: calcd 744.261039, found 744.26446; [$C_{45}H_{42}N_4NiO_3$, 745.54 g mol^{-1}]. Anal. Calcd C 72.50, H 5.68, N 7.51, found C 72.22, H 5.23, N 7.43.

4.8.3. [5-(2-Formylethenyl)-5,15-bis(3-methoxyphenyl)porphyrinato]nickel(II) (71). 3-(Dimethylamino)acrolein (600 μL, 6 mmol) together with 6 mL of dry dichloromethane were placed in a 100 mL-three-necked-flask equipped with magnetic stirrer and gas inlet. The flask was cooled in an ice-bath. Then, 600 μL (6.4 mmol) of phosphoroxytrichloride were added dropwise via a syringe under argon. At first, a white precipitate was formed on addition of the phosphoroxytrichloride, which dissolved again on further addition of the reagent. Eventually, a viscous, red-brown solution was formed which was stirred for 15 min at 0 °C. This solution was then transferred to a second flask (also cooled in an ice bath) containing 100 mg (0.17 mmol) [5,15-bis(3-methoxyphenyl)porphyrinato]-nickel(II) **28** dissolved in 100 mL of dry dichloromethane. The cold bath was removed and the reaction mixture stirred for 18 h at 20 °C. After this time, 100 mL of a saturated sodium carbonate solution were added and the mixture was stirred for 12 h. Then, the phases were separated and the organic phase was washed with brine (3×100 mL) and then with water (4–5×100 mL) up to neutral reaction of the water phase. The organic phase was dried with sodium sulfate and then evaporated to dryness. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/acetic acid ethylester (50:1, v/v) as eluent. First, the red-green product was eluted. As a second fraction, a small amount (~10 mg) of the doubly formylated product **74** was isolated. The eluted porphyrin fractions were evaporated to dryness. The monoformylated porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of methanol. After 24 h, the precipitated crystals were removed by suction filtration through a D4 frit and dried in vacuo to yield 60 mg (0.09 mmol, 56%) of green-purple crystals; mp 233 °C; R_f=0.6 (CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.94 (s, 6H, OCH_3), 6.58 (dd, J_1=15 Hz, J_2=8 Hz, 1H, 5^2-C*H*), 7.23–7.30 (m, 2H, phenyl-*H*), 7.49–7.61 (m, 6H, phenyl-*H*), 8.77 (d, J=5 Hz, 2H, β-pyrrole-*H*), 8.83 (d, J=5 Hz, 2H, β-pyrrole-*H*), 8.97 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.21 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.55 (d, J=15 Hz, 1H, 5^1-C*H*), 9.60 (s, 1H, *meso-H*), 10.01 ppm (d, J=8 Hz, 1H, 5^3-C*H*O); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.46, 106.31, 108.85, 113.62, 119.21, 119.72, 126.59, 127.91, 130.47, 132.76, 133.77, 140.91, 141.46, 141.49, 141.67, 142.35, 142.99,

151.66, 158.26, 191.97 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=313 (4.25), 370 (4.16), 427 (5.18), 538 (4.03), 584 nm (3.95); MS (EI, 80 eV, >300 °C), *m/z* (%): 632 (55) [M^+], 630 (100) [M^+-2H], 602 (50) [M^+-CH_2O, 523 (14) [$M^+-2H-C_7H_7O$], 495 (15) [$M^+-CH_2O-C_7H_7O$], 315 (9) [$(M\text{-}2H)^{2+}$]; MS (FAB+, CH_2Cl_2/*m*-NO_2-Bzl-OH/Xe), *m/z* (%): 633 (1) [$(M+H)^+$]; HRMS (EI) [$C_{37}H_{26}N_4NiO_3$]: calcd 632.13584, found 632.13579; [$C_{37}H_{26}N_4NiO_3$, 633.33 g mol^{-1}]: calcd C 70.17, H 4.14, N 8.85, found C 69.75, H 3.97, N 9.26.

4.8.4. [5,15-Bis(4-butyloxyphenyl)-10,20-bis(2-formylethenyl)porphyrinato]nickel(II) (72). Obtained in trace amounts during the synthesis of [5,15-bis(4-butyloxyphenyl)-10-(2-formylethenyl)porphyrinato]nickel(II) **69** (Section 4.8.1): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.02 (t, *J*=7 Hz, 6H, $OCH_2CH_2CH_2CH_3$), 1.52–1.65 (m, 4H, $OCH_2CH_2CH_2CH_3$), 1.88 (m, 4H, $OCH_2CH_2CH_2CH_3$), 4.13 (t, *J*=7 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 6.52 (dd, J_1=15 Hz, J_2=8 Hz, 1H, 10^2-*H*), 7.12 (m, 4H, phenyl-*H*), 7.72 (m, 4H, phenyl-*H*), 8.66 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.12 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.42 (d, *J*=15 Hz, 1H, 10^1-*H*), 9.96 ppm (d, *J*=8 Hz, 1H, 10^3-C*H*O); MS (EI, 80 eV, 320 °C), *m/z* (%): 770 (100) [M^+], 742 (40) [M^+-CO], 714 (38) [$M^+-2\times CO$]; HRMS (EI) [$C_{46}H_{40}N_4NiO_4$]: calcd 770.24030, found 578.25138.

4.8.5. [5,15-Bis(2-formylethenyl)-10,20-bis(4-pentyloxyphenyl)porphyrinato]nickel(II) (63). Obtained in traces during the synthesis of [5-(2-formylethenyl)-10,20-bis(4-pentyloxyphenyl)porphyrinato]nickel(II) **70** (Section 4.8.2). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.00 (t, *J*=7 Hz, 6H, $OCH_2CH_2CH_2CH_2CH_3$), 1.43–1.66 (m, 8H, $OCH_2CH_2CH_2CH_2CH_3$ and $OCH_2CH_2CH_2CH_2CH_3$), 1.95 (m, 4H, $OCH_2CH_2CH_2CH_2CH_3$), 4.18 (t, *J*=7 Hz, 4H, $OCH_2CH_2CH_2CH_2CH_3$), 6.57 (dd, J_1=15 Hz, J_2=8 Hz, 2H, 10^2-*H*), 7.17 (m, 4H, phenyl-*H*), 7.77 (m, 4H, phenyl-*H*), 8.71 (d, *J*=5 Hz, 4H, β-pyrrole-*H*), 9.17 (d, *J*=5 Hz, 4H, β-pyrrole-*H*), 9.48 (d, *J*=15 Hz, 1H, 10^1-*H*), 10.00 ppm (d, *J*=8 Hz, 2H, 10^3-C*H*O); HRMS (EI) [$C_{48}H_{44}N_4NiO_4$]: calcd 798.27160, found 578.27377.

4.8.6. [5,15-Bis(2-formylethenyl)-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) (74). Obtained in traces during the synthesis of [5-(2-formylethenyl)-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) **71** (Section 4.8.3). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.95 (s, 6H, OCH_3), 6.63 (dd, 1H, J_{2-3}=15.4 Hz, J_{1-2}=7.7 Hz, –CH=C*H*–CHO), 7.25–7.30 (m, 2H, phenyl-*H*), 7.46 (m, 2H, phenyl-*H*), 7.52–7.64 (m, 4H, phenyl-*H*), 8.79 (d, 4H, J_{4-5}=5.2 Hz, β-pyrrole-*H* 2), 9.25 (d, 4H, J_{4-5}=5.2 Hz, β-pyrrole-*H* 3), 9.57 (d, 1H, J_{2-3}=15.4 Hz, –C*H*=CH–CHO), 10.08 (d, 1H, J_{1-2}=7.7 Hz, -C*H*O).

4.8.7. [5-(2-Formylethenyl)-10,15,20-tris(3-methoxyphenyl)porphyrinato]nickel(II) (75). 3-(Dimethylamino)-acrolein (600 μL, 6 mmol) together with 6 mL of dry dichloromethane were placed in a 100 mL three-necked flask equipped with magnetic stirrer and gas inlet. The flask was cooled in an ice bath. Then, 600 μL (6.4 mmol) of $POCl_3$ were added dropwise via a syringe under argon. At first, a white precipitate was formed on addition of the phosphoroxytrichloride, which dissolves again on further addition of the reagent. At the end a viscous, red-brown solution was formed which was stirred for 15 min at 0 °C. This solution was then transferred to a second flask (also cooled in an ice bath) containing 100 mg (0.15 mmol) [5,10,15-tris(3-methoxyphenyl)porphyrinato]nickel(II) **42** dissolved in 100 mL of dry dichloromethane. Further conditions and workup were similar to those given in Section 4.8.3. Yield 80 mg (0.11 mmol, 72%) of purple-green crystals: mp 163 °C; R_f=0.6 (CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.90 (s, 3H, OCH_3), 3.92 (s, 6H, OCH_3), 6.66 (dd, J_1=15 Hz, J_2=8 Hz, 1H, 5^2-C*H*), 7.18–7.28 (m, 3H, phenyl-*H*), 7.45–7.50 (m, 3H, phenyl-*H*), 7.51–7.62 (m, 6H, phenyl-*H*), 8.66 (m [AB-spectrum], 4H, β-pyrrole-*H*), 8.85 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.29 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.45 (d, *J*=15 Hz, 1H, 5^1-C*H*), 10.07 (d, *J*=8 Hz, 1H, 5^3-C*H*O); ^{13}C NMR (60 MHz, $CDCl_3$): δ=55.46, 108.44, 113.72, 119.56, 119.62, 119.76, 120.86, 126.53, 127.89, 127.97, 130.80, 132.43, 133.01, 134.06, 141.40, 141.47, 142.23, 143.03, 151.45, 158.30, 192.03 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=315 (4.18), 434 (5.14), 548 (3.99), 593 nm (3.94); MS (EI, 80 eV, 350 °C), *m/z* (%): 738 (58) [M^+], 736 (100) [M^+-2H], 708 (36) [M^+-CH_2O], 629 (9) [$M^+-2H-C_7H_7O$)], 601 (11) [$M^+-CH_2O-C_7H_7O$)], 368 (11) [$(M-2H)^{2+}$]; MS (FAB+, CH_2Cl_2/*m*-NO_2-Bzl-OH/Xe), *m/z* (%)=739 (1) [$(M+H)^+$]; HRMS (EI) [$C_{44}H_{32}N_4NiO_4$]: calcd 738.17770, found 738.17779.

4.8.8. [5,15-Bis(3,5-dimethoxyphenyl)-10-(2-formylethenyl)-20-hexylporphyrinato]nickel(II) (76). Reaction of 3-dimethylaminoacrolein (1.2 mL, 12 mmol) in 12 mL of dry dichloromethane, 1.2 mL (12.8 mmol) $POCl_3$, and 240 mg (0.33 mmol) [5,15-bis(3,5-dimethoxyphenyl)-10-hexylporphyrinato]nickel(II) **43** dissolved in 200 mL of dry dichloromethane as described in Section 4.8.1. Yield 140 mg (0.18 mmol, 55%) of green-purple crystals: mp 223 °C; R_f=0.58 (CH_2Cl_2/$CH_3C(O)OCH_2CH_3$, 95:5, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/0.05% CH_3OH, v/v, flow: 2 mL/min, detection at 420 nm) retention time: 11.39 min (100%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.88 (t, *J*=7 Hz, 3H, 15^6-CH_3), 1.23–145 (m, 4H, 15^5- and 15^4-CH_2), 1.54 (m, 2H, 15^3-CH_2), 2.22 (m, 2H, 15^2-CH_2), 3.93 (s, 12H, OCH_3), 4.48 (t, *J*=7 Hz, 2H, 15^1-CH_2), 6.63 (dd, J_1=15 Hz, J_2=8 Hz, 1H, 5^2-C*H*), 6.83 (m, 2H, phenyl-H_{para}), 7.14 (m, 4H, phenyl-H_{ortho}), 8.76 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 8.86 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.19 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.25 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.58 (d, *J*=15 Hz, 1H, 5^1-C*H*), 10.01 ppm (d, *J*=8 Hz, 1H, 5^3-C*H*O); ^{13}C NMR (60 MHz, $CDCl_3$): δ=13.96, 22.50, 29.86, 31.61, 33.99, 37.15, 55.49, 100.09, 107.52, 112.67, 119.21, 121.58, 130.24, 130.62, 132.57, 134.00, 140.56, 140.78, 141.48, 141.84, 141.96, 142.13, 151.29, 153.26, 158.26, 159.20, 191.98 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=320 (4.26), 437 (5.22), 555 (4.01), 598 nm (4.00); MS (EI, 80 eV, 280 °C), *m/z* (%): 776 (100) [M^+], 748 (31) [M^+-CO], 705 (31) [$M^+-C_5H_{11}$], 677 (23) [$M^+-CO-C_5H_{11}$], 662 (8) [$M^+-CO-CH_3-C_5H_{11}$], 639 (7) [$M^+-C_8H_9O_2$], 568 (3) [$M^+-C_8H_9O_2-C_5H_{11}$], 388 (6) [M^{2+}]; HRMS (EI) [$C_{45}H_{42}N_4NiO_5$]: calcd 776.25087, found 776.25433; [$C_{45}H_{42}N_4NiO_5$, 777.54 g mol^{-1}]. Anal. Calcd C 69.51, H 5.44, N 7.21, found C 69.50, H 5.15, N 7.02.

4.9. Alkynyl substituted porphyrins

4.9.1. 5-(3,5-Dimethoxyphenyl)-15-hexyl-10,20-diiodoporphyrin (77). 5-(3,5-Dimethoxyphenyl)-5-hexylporphyrin **24** (53 mg, 0.1 mmol) was dissolved in 80 mL of dry chloroform under argon. Iodine (36 mg, 0.14 mmol) and 4 drops of pyridine were added, followed by 42 mg (0.1 mmol) of [bis(trifluoroacetoxy)iodo]benzene. The reaction flask was then shielded from ambient light and the reaction mixture was stirred for 48 h at 20 °C, followed by filtration through silica (40 g), washing with dichloromethane. The filtrate was evaporated to dryness. The recovered solvent was red-colored, due to the presence of unreacted iodine. The product was purified by column chromatography on silica (3×60 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. The diiodinated porphyrin was isolated as the first fraction, as the second fraction a small amount of the monoiodinated porphyrin **78** (Section 4.9.2). The title porphyrin was dissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of hexane. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield: 60 mg (0.077 mmol; 77%) of purple crystals: mp 204 °C; R_f=0.86 (CH_2Cl_2/*n*-hexane, 3:1, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: C_6H_{14}/CH_2Cl_2, 75:25, v/v, flow: 1 mL/min, detection at 420 nm) retention time: 3.66 min (95.9%), (same conditions but detection at 254 nm) retention time 3.01 min (97.9%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.89 (s, br., 2H, N*H*), 0.92 (t, J=7 Hz, 3H, 5^6-CH_3), 1.31–1.51 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.75 (m, 2H, 5^3-CH_2), 2.37 (m, 2H, 5^2-CH_2), 3.96 (s, 6H, OCH_3), 4.67 (t, J=8 Hz, 2H, 5^1-CH_2), 6.89 (m, 1H, phenyl-H_{para}), 7.30 (m, 2H, phenyl-H_{ortho}), 8.82 (d, J=4 Hz, 2H, β-pyrrole-*H*), 9.24 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.53 (d, J=4 Hz, 2H, β-pyrrole-*H*), 9.57 ppm (d, J=5 Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.09, 22.67, 30.17, 31.80, 35.55, 38.96, 55.63, 100.21, 113.87, 120.31, 122.36, 143.31, 158.87 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=295 (4.28), 378 (4.40), 407 (4.89), 426 (5.58), 494 (3.63), 526 (4.18), 562 (4.13), 605 (3.63), 664 nm (3.87); MS (EI, 80 eV, 270 °C), *m/z* (%): 782 (2) [M^+], 711 (1) [$M^+-C_5H_{11}$], 656 (4) [M^+-I], 530 (100) [$M^+-2\times I$], 459 (66) [$M^+-2\times I-C_5H_{11}$], 265 (10) [$(M-2\times I)^{2+}$]; MS (FAB+, CH_2Cl_2/*m*-NO_2-Bzl-OH/Xe), *m/z* (%): 783 (6) [$(M+H)^+$], 711 (2) [$M^+-C_5H_{11}$], 656 (2) [M^+-I], 585 (1) [$M^+-I-C_5H_{11}$], 530 (0.4) [$M^+-2\times I$]; HRMS (EI) [$C_{34}H_{32}I_2N_4O_2$] calcd 782.06148, found 782.06445; [$C_{34}H_{32}I_2N_4O_2$, 782.46 g mol^{-1}]. Anal. Calcd C 52.17, H 4.12, N 7.16, found C 52.38, H 4.39, N 7.45.

4.9.2. 5-(3,5-Dimethoxyphenyl)-15-hexyl-10-iodoporphyrin (78). Obtained in traces during the synthesis of 5-(3,5-dimethoxyphenyl)-15-hexyl-10,20-diiodoporphyrin **77** (Section 4.9.1). R_f=0.77 (CH_2Cl_2/*n*-hexane, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.22 (s, br., 2H, N*H*), 0.93 (t, J=7 Hz, 3H, 5^6-CH_3), 1.31–1.51 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.77 (m, 2H, 5^3-CH_2), 2.42 (m, 2H, 5^2-CH_2), 3.97 (s, 6H, OCH_3), 4.75 (t, J=8 Hz, 2H, 5^1-CH_2), 6.92 (m, 1H, phenyl-H_{para}), 7.38 (m, 2H, phenyl-H_{ortho}), 8.98 (m, 2H, β-pyrrole-*H*), 9.17 (m, 2H, β-pyrrole-*H*), 9.33 (m, 2H, β-pyrrole-*H*), 9.71 (m, 2H, β-pyrrole-*H*), 9.94 ppm (s, 1H, *meso*-*H*).

4.9.3. 5,15-Bis(3,5-dimethoxyphenyl)-10-hexyl-20-iodoporphyrin (79). 5,15-Bis(3,5-dimethoxyphenyl)-10-hexylporphyrin **32** (134 mg, 0.2 mmol) was dissolved in 160 mL of dry chloroform under argon and treated with iodine (72 mg, 0.28 mmol), 8 drops of pyridine, and 84 mg (0.2 mmol) of [bis(trifluoroacetoxy)iodo]benzene. The reaction flask was then shielded from ambient light and the reaction mixture was stirred for 48 h at 20 °C. The reaction mixture was filtered through silica (40 g), washing with dichloromethane. The recovered solvent was red-colored, due to the presence of unreacted iodine. The filtrate was evaporated to dryness and the residue was purified by column chromatography on silica (3×50 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. After evaporation of the solvent, the porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of hexane. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit, dried in vacuo and yielded 100 mg (0.13 mmol; 63%) of green-purple microcrystals: mp 251 °C; R_f=0.43 (CH_2Cl_2/*n*-hexane, 3:1, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/0.1% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm), retention time: 3.01 min (98.1%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.67 (s, br., 2H, N*H*), 0.91 (t, J=7 Hz, 3H, 5^6-CH_3), 1.38 (m, 2H, 5^5-CH_2), 1.50 (m, 2H, 5^4-CH_2), 1.78 (m, 2H, 5^3-CH_2), 2.49 (m, 2H, 5^2-CH_2), 3.96 (s, 12H, OCH_3), 4.91 (t, J=8 Hz, 2H, 5^1-CH_2), 6.91 (m, 2H, phenyl-H_{para}), 7.35 (m, 4H, phenyl-H_{ortho}), 8.90 (d, J=5 Hz, 2H, β-pyrrole-*H*), 8.94 (d, J=4 Hz, 2H, β-pyrrole-*H*), 9.40 (d, J=4 Hz, 2H, β-pyrrole-*H*), 9.57 ppm (d, J=5 Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.12, 22.69, 30.22, 31.87, 35.44, 38.77, 55.63, 100.19, 113.84, 119.99, 121.98, 143.97, 158.79 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=306 (4.20), 380 (4.38), 407 (4.93), 424 (5.56), 485 (3.68), 521 (4.24), 556 (3.97), 597 (3.74), 654 nm (3.63); MS (EI, 80 eV, 270 °C), *m/z* (%): 792 (12) [M^+], 666 (100) [M^+-I], 595 (38) [$M^+-I-C_5H_{11}$], 333 (12) [$(M-I)^{2+}$]; MS (FAB+, CH_2Cl_2/*m*-NO_2-Bzl-OH/Xe), *m/z* (%): 793 (100) [$(M+H)^+$], 721 (25) [$M^+-C_5H_{11}$], 667 (11) [$(M+H)^+-I$], 595 (11) [$M^+-I-C_5H_{11}$]; HRMS (EI) [$C_{42}H_{41}IN_4O_4$]: calcd 792.21726, found 792.21924; [$C_{42}H_{41}IN_4O_4$, 792.72 g mol^{-1}]. Anal. Calcd C 63.64, H 5.21, N 7.07, [$C_{42}H_{41}IN_4O_4\cdot\frac{1}{2}H_2O$]: C 62.92, H 5.28, N 6.99, found C 62.66, H 4.94, N 6.65.

4.9.4. [5,15-Bis-(3,5-dimethoxyphenyl)-10-hexyl-20-iodoporphyrinato]zinc(II) (80). The corresponding free base porphyrin **79** (90 mg, 0.11 mmol) was dissolved in 70 mL of dichloromethane and treated with a solution of zinc(II) acetate (230 mg, 1.25 mmol) in methanol. The mixture was stirred until the reaction was complete (TLC control, dichloromethane/*n*-hexane, 3:1, v/v, approximately 15 min). The reaction mixture was transferred to a separatory funnel and washed with water (3×100 mL). The organic phase was filtered through 100 g of silica, washing with dichloromethane, and then evaporated to dryness. The residue was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of hexane. After 24 h, the precipitated dark-purple microcrystals were removed by suction filtration through a D3 frit and dried in vacuo to yield 90 mg (0.105 mmol, 95%) of the zinc(II) complex: mp >280 °C (dec.); R_f=0.42 (CH_2Cl_2); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2, flow: 1 mL/

min, detection at 420 nm) retention time: 4.86 min (99.8%), (same conditions but detection at 254 nm) retention time: 4.93 min (100%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.92 (t, J=7 Hz, 3H, 5^6-CH_3), 1.28–1.56 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.82 (m, 2H, 5^3-CH_2), 2.52 (m, 2H, 5^2-CH_2), 3.93 (s, 12H, OCH_3), 4.95 (t, J=7 Hz, 2H, 5^1-CH_2), 6.86 (m, 2H, phenyl-H_{para}), 7.33 (m, 4H, phenyl-H_{ortho}), 8.99 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.03 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.51 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.70 ppm (d, J=5 Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.12, 22.71, 30.35, 31.90, 35.83, 39.04, 55.62, 100.12, 113.81, 120.97, 122.88, 129.32, 132.59, 133.48, 137.50, 144.39, 149.73, 150.56, 150.63, 152. 33, 158.75 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=312 (4.19), 350 (4.02), 406 (4.63), 424 (5.60), 518 (3.38), 554 (4.29), 592 nm (3.61); MS (EI, 80 eV, 305 °C), *m/z* (%): 854 (26) [M^+], 783 (18) [$M^+-C_5H_{11}$], 728 (100) [M^+-I], 657 (89) [$M^+-I-C_5H_{11}$], 364 (4) [$(M-I)^{2+}$]; HRMS (EI) [$C_{42}H_{39}IN_4O_4Zn$]: calcd 854.13063, found 854.13021.

4.9.5. [5,15-Bis(3,5-dimethoxyphenyl)-10-(hept-1-ynyl)-20-hexylporphyrinato]zinc(II) (81). [5,15-Bis(3,5-dimethoxyphenyl)-10-hexyl-20-iodoporphyrinato]zinc(II) **80** (28 mg, 0.033 mmol) was dissolved in 20 mL of dry THF (filtered through basic alumina) under argon. Copper(I) iodide (6 mg, 0.032 mmol), dichlorobis(triphenylphosphine)palladium(II) (3 mg, 0.0042 mmol), triethylamine (50 μL, 0.3 mmol), and 1-heptyne (50 μL, 0.38 mmol) were added and the reaction mixture was stirred for 18 h at 20 °C in the dark. The reaction mixture was filtered through silica (50 g), washed with dichloromethane and the filtrate evaporated to dryness. The product was purified by column chromatography on silica (3×50 cm) using dichloromethane/*n*-hexane (3:1, v/v), as eluent. First a small non-uniform red fraction (according to TLC) was obtained whose NMR-spectrum showed complicated multiplets for the porphyrin β-protons and inequivalent methoxy groups, suggesting the presence of phenyl-ring substituted products. The alkyne-substituted porphyrin was obtained as the second fraction. After evaporation of the solvent the porphyrin was redissolved in as little dichloromethane as possible and then layered with a 2–3-fold excess of hexane. After 24 h, the precipitated solid was removed by suction filtration through a D3 frit and dried in vacuo to yield 18 mg (0.022 mmol; 67%) of green-purple microcrystals: mp 274 °C; R_f=0.49 (CH_2Cl_2); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/0.1% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm) retention time: 3.41 min (100%), (same conditions but detection at 254 nm) retention time: 3.48 min (100%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.92 (t, J=7 Hz, 3H, 15^6-CH_3), 1.05 (t, J=7 Hz, 3H, 5^7-CH_3), 1.32–1.64 (m, 6H, 15^4-CH_2, 15^5-CH_2, and 5^6-CH_2), 1.81 (m, 4H, 15^3-CH_2 and 5^5-CH_2), 2.04 (m, 2H, 5^4-CH_2), 2.53 (m, 2H, 15^2-CH_2), 2.99 (t, J=7 Hz, 2H, 5^3-CH_2), 3.95 (s, 12H, OCH_3), 4.97 (t, J=8 Hz, 2H, 15^1-CH_2), 6.87 (m, 2H, phenyl-H_{para}), 7.36 (m, 4H, phenyl-H_{ortho}), 9.01 (m, 4H, β-pyrrole-*H*), 9.49 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.65 ppm (d, J=5 Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.14, 20.50, 22.46, 22.73, 28.99, 30.38, 31.58, 31.93, 35.86, 38.99, 55.64, 82.88, 97.21, 100.11, 113.72, 120.77, 122.88, 128.98, 130.95, 132.14, 132.52, 144.62, 149.24, 149.56, 150.14, 152.81, 158.83 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=311 (4.22), 348 (4.05), 409 (4.69), 428 (5.60), 432 (5.55), 523 (3.60), 562 (4.29), 598 nm (4.03); MS (EI, 80 eV, 300 °C), *m/z* (%): 822 (19) [M^+], 751 (6) [$M^+-C_5H_{11}$], 694 (1) [$M^+-C_4H_9$], 411 (1) [M^{2+}], 44 (100) [CO_2^+]; HRMS (EI) [$C_{49}H_{50}N_4O_4Zn$]: calcd 822.31235, found 822.31567.

4.9.6. 5,15-Bis(3,5-dimethoxyphenyl)-10-(hept-1-ynyl)-20-hexylporphyrin (82). The zinc(II) complex of 5,15-bis(3,5-dimethoxyphenyl)-10-hexyl-20-iodoporphyrin **80** (28 mg, 0.033 mmol) was dissolved in 20 mL of dry THF (filtered through basic alumina) under argon and initially reacted using the conditions and reagents given in Section 4.9.5. The product fraction was evaporated to dryness, dissolved again in 15 mL of dichloromethane, 13 drops of TFA were added (from a 1 mL syringe) and the mixture was stirred for 2 min. After this time, 20 mL of water were added and the mixture was transferred to a separatory funnel. The phases were separated and the organic phase was washed with water (2×15 mL), saturated sodium bicarbonate solution (1×15 mL), and again with water (1×15 mL). The organic phase was dried over sodium sulfate and then evaporated to dryness, followed by chromatography on silica (2×30 cm) using dichloromethane/*n*-hexane (3:1, v/v) as eluent. The eluted porphyrin fraction was evaporated to dryness, recrystallized from dichloromethane/hexane, removed by suction filtration through a D3 frit and dried in vacuo to yield 12 mg (0.016 mmol; 50%) of green-purple microcrystals. Alternatively, the present free base can be obtained from the respective zinc(II) complex **81** by stirring with TFA for a few minutes in quantitative yield: mp 217 °C; R_f=0.45 (CH_2Cl_2/*n*-hexane, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.39 (s, br., 2H, N*H*), 0.97 (t, J=7 Hz, 3H, 15^6-CH_3), 1.11 (t, J=7 Hz, 3H, 5^7-CH_3), 1.33–1.70 (m, 6H, 15^4-CH_2, 15^5-CH_2, and 5^6-CH_2), 1.86 (m, 4H, 15^3-CH_2 and 5^5-CH_2), 2.10 (m, 2H, 5^4-CH_2), 2.55 (m, 2H, 15^2-CH_2), 3.05 (t, J=7 Hz, 2H, 5^3-CH_2), 4.02 (s, 12H, OCH_3), 4.99 (t, J=8 Hz, 2H, 15^1-CH_2), 6.95 (m, 2H, phenyl-H_{para}), 7.41 (m, 4H, phenyl-H_{ortho}), 8.96 (m, 4H, β-pyrrole-*H*), 9.44 (d, J=5 Hz, 2H, β-pyrrole-*H*), 9.60 ppm (d, J=5 Hz, 2H, β-pyrrole-*H*); MS (EI, 80 eV, 305 °C), *m/z* (%): 760 (100) [M^+], 689 (44) [$M^+-C_5H_{11}$], 380 (4) [M^{2+}]; HRMS (EI) [$C_{49}H_{52}N_4O_4$]: calcd 760.39886, found 760.39827.

4.10. Preparation of hydroxyphenyl porphyrins

4.10.1. 5,15-Bis(3-hydroxyphenyl)porphyrin (83). 5,15-Bis(3-methoxyphenyl)porphyrin **12** (100 mg, 0.19 mmol) was suspended in 150 mL of dry dichloromethane in a three-necked flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 25 mL-dropping funnel. The mixture was cooled to −50 °C. The flask was shielded from ambient light and the dropping funnel was charged with 7 mL (7 mmol) of a 1 M solution of boron tribromide. The BBr_3 solution was added dropwise to the porphyrin solution over a period of approximately 15 min. Then, the reaction mixture was stirred for 18 h and slowly warmed to 20 °C. After this time, the reaction mixture was cooled again to −30 °C and 3 mL of an acetone/water-mixture (2:1, v/v) were added dropwise. The mixture was slowly warmed to 20 °C and then 10 g of sodium bicarbonate were added. The mixture was stirred for 2 h until it changed its color from green to red. Then, 0.5 mL of triethylamine and 10 g of

anhydrous sodium sulfate were added and the mixture was stirred for 18 h at 20 °C. After this time, the mixture was filtered. Despite intensive washing, a large amount of the deprotected porphyrin could not be isolated due its extremely low solubility. The isolated porphyrin was finally purified by column chromatography on silica (3×40 cm) using dichloromethane/methanol (10:1, v/v) as eluent to yield 20 mg (0.04 mmol; 21%) of a purple amorphous solid: mp >340 °C; R_f=0.49 (CH_2Cl_2/CH_3OH, 9:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−3.12 (s, 1H, N*H*), 7.35 (m, 1H, phenyl-*H*), 7.67 (m, 1H, phenyl-*H*), 7.75 (m, 2H, phenyl-*H*), 9.14 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.57 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.54 (s, 2H, *meso-H*); UV/vis (CH_2Cl_2):[37] λ_{max} (rel. int.)=365 (0.11), 389 (0.26), 406 (1.00), 503 (0.06), 536 (0.03), 574 (0.02), 631 (0.01); MS (EI, 80 eV, 310 °C), *m/z* (%): 494 (100) [M^+], 477 (2) [M^+−17 (OH)], 401 (2) [M^+−93 (C_6H_5O)], 247 (11) [M^{2+}]; HRMS (EI) [$C_{32}H_{22}N_4O_2$]: calcd 494.17428, found 494.17743.

4.10.2. 5-Hexyl-15-(3-hydroxyphenyl)porphyrin (84). 5-Hexyl-15-(3-methoxyphenyl)porphyrin **22** (100 mg, 0.2 mmol) was dissolved in 90 mL of dry dichloromethane in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 25 mL-dropping funnel. The mixture was cooled to −50 °C. The flask was shielded from ambient light and the dropping funnel was charged with 3.6 mL (3.6 mmol) of a 1 M solution of boron tribromide. The boron tribromide solution was added dropwise to the porphyrin solution over a period of approximately 5 min. Then, the reaction mixture was stirred for 18 h and slowly warmed to 20 °C. After this time, the reaction mixture was cooled again to −30 °C and 3 mL of an acetone/water-mixture (2:1, v/v) were added dropwise. The mixture was slowly warmed to 20 °C and then 10 g of sodium bicarbonate were added. The mixture was stirred for 2 h until it changed color from green to red. Then, 0.5 mL of triethylamine and 10 g of anhydrous sodium sulfate were added and the mixture was stirred for 18 h at 20 °C. After this time, the mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved again in a mixture of acetic acid ethylester and water (2:1, v/v). The organic phase was washed with brine (1×50 mL), and with water (2×50 mL). The organic phase was dried over anhydrous sodium sulfate and then evaporated to dryness. Final purification was achieved by column chromatography on silica (3×40 cm) using dichloromethane/methanol (10:1, v/v) as eluent. Yield: 80 mg (0.16 mmol; 83%) of a purple, amorphous solid; mp 193 °C; R_f=0.15 (SiO_2, CH_2Cl_2/CH_3OH, 9:1, v/v), 0.41 (CH_2Cl_2); ^{1}H NMR (250 MHz, acetone-d_6): δ=−3.03 (s, 2H, N*H*), 0.89 (t, *J*=7 Hz, 3H, 5^6-CH_3), 1.38 (m, 2H, 5^5-CH_2), 1.52 (m, 2H, 5^4-CH_2), 1.83 (m, 2H, 5^3-CH_2), 2.56 (m, 2H, 5^2-CH_2), 5.11 (t, *J*=8 Hz, 2H, 5^1-CH_2), 7.31 (m, 1H, phenyl-*H*), 7.60–7.74 (m, 3H, phenyl-*H*), 9.00 (s, br., 1H, O*H*), 9.06 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.49 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.57 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.78 ppm (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.41 (s, 2H, 10- and 20-*meso-H*); ^{13}C NMR (60 MHz, acetone-d_6): δ=14.33, 23.37, ∼30 (superposition with solvent signal), 32.65, 35.12, 39.73, 105.67, 115.77, 119.04, 120.69, 123.02, 127.33, 128.87, 129.25, 131.35, 132.84, 133.08, 143.34, 145.67, 148.05, 148.27, 157.20 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=301 (4.13), 364 (4.38), 3.88 (4.87), 406 (5.47), 474 (3.33), 503 (4.16), 536 (3.62), 576 (3.65), 631 nm (3.05); MS (EI, 80 eV, 250 °C), *m/z* (%): 486 (100) [M^+], 415 (97) [M^+−71 (C_5H_{11})], 243 (5) [M^{2+}]; HRMS (EI) [$C_{32}H_{30}N_4O$]: calcd 486.24196, found 486.24533.

4.10.3. 5,10,15-Tris(3-hydroxyphenyl)porphyrin (85). 5,10,15-Tris(3-methoxyphenyl)porphyrin **30** (105 mg, 0.17 mmol) was dissolved in 90 mL of dry dichloromethane in a three-necked flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 25 mL-dropping funnel. The mixture was cooled to −50 °C. The flask was shielded from ambient light and the dropping funnel was charged with 9 mL (9 mmol) of a 1 M solution of boron tribromide. The BBr_3 solution was added dropwise to the porphyrin solution over a period of approximately 15 min. Then, the reaction mixture was stirred for 18 h and slowly warmed to 20 °C. After this time, the reaction mixture was cooled again to −30 °C and 3 mL of an acetone/water-mixture (2:1, v/v) were added dropwise. The mixture was slowly warmed to 20 °C and then 10 g of sodium bicarbonate were added. The mixture was stirred for 2 h until it changed its color from green to red, followed by addition of 0.5 mL of triethylamine and 10 g of anhydrous sodium sulfate and stirring for 18 h at 20 °C. After this time, the mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved again in a mixture of acetic acid ethylester and water (2:1, v/v). The organic phase was washed with brine (1×50 mL), and with water (2×50 mL). The organic phase was dried over anhydrous sodium sulfate and then evaporated to dryness. Final purification was achieved by column chromatography on silica (3×40 cm) using dichloromethane/methanol (10:1, v/v) to yield 80 mg (0.14 mmol; 81%) of a purple amorphous solid: mp 233–235 °C; R_f=0.29 (CH_2Cl_2/CH_3OH, 9:1, v/v); ^{1}H NMR (250 MHz, acetone-d_6): δ=−3.02 (s, 2H, N*H*), 7.33 (m, 3H, phenyl-*H*), 7.58–7.75 (m, 9H, phenyl-*H*), 8.97 (m [AB-spectrum], 4H, β-pyrrole-*H*), 9.07 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.51 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 10.44 ppm (s, 1H, 20-*meso-H*); ^{13}C NMR (60 MHz, acetone-d_6): δ=115.87, 120.40, 121.25, 122.94, 127.27, 128.41, 128.70, ∼132, 143.73, 144.54, 156.73, 156.98 ppm; UV/vis (CH_2Cl_2): λ_{max} (log εlog ε)=371 (4.18), 392 (4.58), 413 (5.29), 480 (3.27), 508 (3.95), 542 (3.41), 581 (3.44), 637 nm (3.01); MS (EI, 80 eV, 320 °C), *m/z* (%): 586 (100) [M^+], 569 (1) [M^+−OH], 493 (1) [M^+−C_6H_5O], 293 (12) [M^{2+}]; HRMS (EI) [$C_{38}H_{26}N_4O_3$]: calcd 586.20049, found 586.20001.

4.10.4. 5-Hexyl-10,20-bis(3-hydroxyphenyl)porphyrin (86). 5-Hexyl-10,20-bis(3-methoxyphenyl)porphyrin **32** (100 mg, 0.16 mmol) was dissolved in 90 mL of dry dichloromethane in a three-necked flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 25 mL-dropping funnel. The mixture was cooled to −50 °C. The flask was shielded from ambient light and the dropping funnel was charged with 6 mL (6 mmol) of a 1 M solution of boron tribromide. The BBr_3 solution was added dropwise to the porphyrin solution over a period of approximately 15 min. Further conditions and purification as described in Section 4.10.3 to yield 80 mg (0.14 mmol; 84%) of a purple amorphous solid: mp 169 °C; R_f=0.64 (CH_2Cl_2/CH_3OH, 9:1, v/v); ^{1}H NMR (250 MHz, acetone-d_6): δ=−3.02 (s,

2H, N*H*), 0.86 (t, $J=7$ Hz, 3H, 5^6-CH_3), 1.30–1.52 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.83 (m, 2H, 5^3-CH_2), 2.51 (m, 2H, 5^2-CH_2), 5.06 (t, $J=8$ Hz, 2H, 5^1-CH_2), 7.32 (m, 2H, phenyl-*H*), 7.58–7.72 (m, 6H, phenyl-*H*), 8.99 (m [AB-spectrum], 6H, β-pyrrole-*H* and 2O*H*), 9.38 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.66 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 10.25 ppm (s, 1H, 15-*meso*-*H*); ^{13}C NMR (60 MHz, acetone-d_6): $\delta=14.13$, 23.34, ~30 (superposition with solvent signal), 32.61, 36.24, 40.00, 104.97, 115.81, 119.79, 122.09, 122.91, 127.22, 128.62, 129.49, 132.08, 144.03, ~147, 156.90 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.13), 372 (4.37), 395 (4.95), 413 (5.54), 480 (3.47), 509 (4.22), 543 (3.70), 584 (3.67), 640 nm (3.36); MS (EI, 80 eV, 315 °C), *m/z* (%): 578 (100) [M^+], 521 (2) [$M^+-C_4H_9$], 507 (95) [$M^+-C_5H_{11}$], 289 (10) [M^{2+}]; HRMS (EI) [$C_{38}H_{34}N_4O_2$]: calcd 578.26818, found 578.26434.

4.10.5. 5,10,15-(3-Hydroxyphenyl)-20-pentylporphyrin (87). 5,10,15-Tris(3-methoxyphenyl)-20-pentylporphyrin **45** (120 mg, 0.17 mmol) was dissolved in 90 mL of dry dichloromethane in a three-necked-flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 25 mL-dropping funnel. The mixture was cooled to −50 °C. The flask was shielded from ambient light and the dropping funnel was charged with 9 mL (9 mmol) of a 1 M solution of boron tribromide. Further conditions and purification as described in Section 4.10.3 to yield 95 mg (0.14 mmol; 85%) of a purple amorphous solid: mp 201 °C; $R_f=0.43$ (CH_2Cl_2/CH_3OH, 9:1, v/v); ^{1}H NMR (250 MHz, acetone-d_6): $\delta=-2.74$ (s, 2H, N*H*), 0.93 (t, $J=7$ Hz, 3H, 20^5-CH_3), 1.51 (m, 2H, 20^4-CH_2), 1.79 (m, 2H, 20^3-CH_2), 2.52 (m, 2H, 20^2-CH_2), 5.01 (t, $J=8$ Hz, 2H, 20^1-CH_2), 7.27–7.34 (m, 3H, phenyl-*H*), 7.55–7.72 (m, 9H, phenyl-*H*), 8.88 (s, 4H, β-pyrrole-*H*), 8.96 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.05 (br s, 3H, O*H*), 9.63 ppm (d, $J=5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, acetone-d_6): $\delta=14.37$, 23.40, 33.27, 35.79, 39.52, 115.79, 120.07, 120.32, 121.70, 122.80, 127.11, 128.49, ~129, ~132, 144.06, 144.41, 156.79, 156.87; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.20), 374 (4.38), 401 (4.89), 418 (5.62), 482 (3.49), 515 (4.26), 550 (3.86), 591 (3.67), 647 nm (3.60); MS (EI, 80 eV, 310 °C), *m/z* (%): 656 (83) [M^+], 599 (70) [$M^+-C_4H_9$], 328 (11) [M^{2+}], 172 (100); HRMS (EI) [$C_{43}H_{36}N_4O_3$]: calcd 656.27874, found 656.27630.

4.10.6. 5-Hexyl-10,15,20-tris(3-hydroxyphenyl)-porphyrin (88). Reaction, workup and chromatography using 5-hexyl-10,15,20-tris(3-methoxyphenyl)porphyrin **51** (120 mg, 0.17 mmol) as described in Section 4.10.5 gave 100 mg (0.15 mmol; 89%) of the title compound as a purple amorphous solid: mp 150–151 °C; $R_f=0.43$ (CH_2Cl_2/CH_3OH, 9:1, v/v); ^{1}H NMR (250 MHz, acetone-d_6): $\delta=-2.73$ (s, 2H, N*H*), 0.86 (t, $J=7$ Hz, 3H, 5^6-CH_3), 1.22–1.41 (m, 4H, 5^5-CH_2 and 5^4-CH_2), 1.76 (m, 2H, 5^3-CH_2), 2.47 (m, 2H, 5^2-CH_2), 4.94 (t, $J=8$ Hz, 2H, 5^1-CH_2), 7.26–7.34 (m, 3H, phenyl-*H*), 7.54–7.75 (m, 9H, phenyl-*H*), 8.88 (s, 4H, β-pyrrole-*H*), 8.95 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.03 (br s, 3H, O*H*), 9.58 ppm (d, $J=5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, acetone-d_6): $\delta=14.30$, 23.30, ~30 (superposition with solvent signal), 32.57, 35.78, 39.75, 115.78, 120.05, 120.30, 121.68, 122.80, 127.09, 128.47, 129.19, 131.48, 144.04, 144.39, 156.77, 156.85 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (3.73), 374 (3.92), 399 (4.44), 418 (5.18), 483 (3.10), 515 (3.79), 550 (3.43), 591 (3.28), 647 nm (3.15); MS (EI, 80 eV, 300 °C), *m/z* (%): 670 (100) [M^+], 599 (50) [$M^+-C_5H_{11}$], 335 (8) [M^{2+}]; HRMS (EI) [$C_{44}H_{38}N_4O_3$]: calcd 670.29439, found 670.29493.

4.10.7. 5-Heptyl-10,15,20-tris(3-hydroxyphenyl)-porphyrin (89). Reaction, workup and chromatography using 5-heptyl-10,15,20-tris(3-methoxyphenyl)porphyrin **56** (125 mg, 0.17 mmol) as described in Section 4.10.5 yielded 100 mg of the title compound as a purple amorphous solid (0.15 mmol; 86%): mp 180 °C; $R_f=0.48$ (CH_2Cl_2/CH_3OH, 9:1, v/v); ^{1}H NMR (250 MHz, acetone-d_6): $\delta=-2.74$ (s, 2H, N*H*), 0.85 (t, $J=7$ Hz, 3H, 5^7-CH_3), 1.25–1.37 (m, 4H, 5^6-CH_2 and 5^5-CH_2), 1.50 (m, 2H, 5^4-CH_2), 1.81 (m, 2H, 5^3-CH_2), 2.53 (m, 2H, 5^2-CH_2), 5.04 (t, $J=8$ Hz, 2H, 5^1-CH_2), 7.27–7.34 (m, 3H, phenyl-*H*), 7.55–7.72 (m, 9H, phenyl-*H*), 8.88 (s, 4H, β-pyrrole-*H*), 8.96 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.04 (s, br., 3H, O*H*), 9.65 ppm (d, $J=5$ Hz, 2H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, acetone-d_6): $\delta=14.26$, 23.29, ~30 (superposition with solvent signal), 31.04, 32.61, 35.84, 39.85, 115.79, 120.05, 120.30, 121.70, 122.79, 127.08, 128.48, 129.14, 131.77, 144.02, 144.38, 156.73, 156.87 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 (4.12), 374 (4.34), 401 (4.85), 418 (5.57), 483 (3.48), 515 (4.22), 550 (3.82), 591 (3.67), 647 nm (3.57); MS (EI, 80 eV, 340 °C), *m/z* (%): 684 (100) [M^+], 599 (66) [$M^+-C_6H_{13}$], 342 (8) [M^{2+}]; HRMS (EI) [$C_{45}H_{40}N_4O_3$]: calcd 684.31004, found 684.31433.

4.10.8. 5,10,15-Trihexyl-20-(3-hydroxyphenyl)porphyrin (90). 5,10,15-Trihexyl-20-(3-methoxyphenyl)porphyrin **53** (100 mg, 0.15 mmol) was dissolved in 60 mL of dry dichloromethane in a three-necked flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 25 mL-dropping funnel. The mixture was cooled to −50 °C. The flask was shielded from ambient light and the dropping funnel was charged with 2.7 mL (2.7 mmol) of a 1 M solution of boron tribromide. The BBr_3 solution was added dropwise to the porphyrin solution over a period of approximately 5 min. Then, the reaction mixture was stirred for 18 h and slowly warmed to 20 °C. After this time the reaction mixture was cooled again to −30 °C and 3 mL of an acetone/water-mixture (2:1, v/v) were added dropwise. The mixture was slowly warmed to 20 °C and 50 mL of water were added. The phases were separated and the organic phase was washed with water (1×50 mL), saturated sodium bicarbonate solution (1×50 mL), brine (2×50 mL), and again with water (1×50 mL). The organic phase was dried over anhydrous sodium sulfate and then evaporated to dryness. Final purification was achieved by column chromatography on silica (3×60 cm) using dichloromethane as eluent to yield 90 mg (0.14 mmol; 92%) of a purple amorphous solid: mp 84 °C; $R_f=0.21$ (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=-2.73$ (s, br., 2H, N*H*), 0.93 (m, 9H, 5^6-, 10^6-, and 15^6-CH_3), 1.29–1.58 (m, 12H, 5^5-, 10^5-, and 15^5-CH_2, 5^4-, 10^4-, and 15^4-CH_2), 1.77 (m, 6H, 5^3-, 10^3-, and 15^3-CH_2), 2.50 (m, 6H, 5^2-, 10^2-, and 15^2-CH_2), 4.89 (m, 6H, 5^1-, 10^1-, and 15^1-CH_2), 7.13 (m, 1H, phenyl-*H*), 7.39 (m, 1H, phenyl-*H*), 7.51 (m, 1H, phenyl-*H*), 7.69 (m, 1H, phenyl-*H*), 8.76 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.31 (d, $J=5$ Hz, 2H, β-pyrrole-*H*), 9.46 ppm (m [AB-spectrum], 4H, β-pyrrole-*H*); ^{13}C NMR (60 MHz,

$CDCl_3$): δ=14.14, 14.16, 22.72, 22.76, 30.22, 30.31, 31.90, 31.93, 35.38, 35.78, 38.65, 38.85, 114.46, 117.24, 119.11, 119.50, 121.62, 127.47, 127.51, 143.96, 153.73 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=350 (4.19), 367 (4.27), 398 (4.80), 418 (5.53), 485 (3.53), 518 (4.14), 553 (3.90), 597 (3.60), 654 nm (3.75); MS (EI, 80 eV, 250 °C), *m/z* (%): 654 (100) [M^+], 583 (35) [$M^+-C_5H_{11}$], 512 (2) [$M^+-(2\times C_5H_{11})$], 327 (6) [M^{2+}]; HRMS (EI) [$C_{44}H_{54}N_4O$]: calcd 654.42976, found 654.42657.

4.10.9. 5,10,15-Triheptyl-20-(3-hydroxyphenyl)-porphyrin (91). Reaction, workup and chromatography using 5,10,15-triheptyl-20-(3-methoxyphenyl)porphyrin **58** (100 mg, 0.14 mmol) as described in Section 4.10.8 yielded 85 mg of the title compound as a purple amorphous solid (0.12 mmol; 87%): mp 98 °C; R_f=0.25 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ=−2.70 (s, 2H, N*H*), 0.91 (m, 9H, 5^7-, 10^7-, and 15^7-CH_3), 1.30–1.39 (m, 12H, 5^6-, 10^6-, and 15^6-CH_2, 5^5-, 10^5-, and 15^5-CH_2), 1.50 (m, 6H, 5^4-, 10^4-, and 15^4-CH_2), 1.76 (m, 6H, 5^3-, 10^3-, and 15^3-CH_2), 2.49 (m, 6H, 5^2-, 10^2-, and 15^2-CH_2), 4.93 (m, 6H, 5^1-, 10^1-, and 15^1-CH_2), 7.17 (m, 1H, phenyl-*H*), 7.47 (m, 1H, phenyl-*H*), 7.53 (m, 1H, phenyl-*H*), 7.70 (m, 1H, phenyl-*H*), 8.78 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.33 (d, *J*=5 Hz, 2H, β-pyrrole-*H*), 9.48 (m [AB-spectrum], 4H, β-pyrrole-*H*); ^{13}C NMR (60 MHz, $CDCl_3$): δ=14.10, 22.70, 29.39, 30.54, 30.62, 31.92, 35.41, 35.82, 38.69, 38.90, 114.52, 117.21, 119.14, 119.54, 121.74, 127.60, ~128, 131.14, 144.14, 153.78; UV/vis (CH_2Cl_2): λ_{max} (log ε)=350 (4.34), 365 (4.40), 401 (4.93), 418 (5.59), 483 (3.49), 518 (4.21), 552 (3.97), 597 (3.69), 655 nm (3.79); MS (EI, 80 eV, 300 °C), *m/z* (%): 696 (100) [M^+], 611 (26) [$M^+-C_6H_{13}$], 348 (8) [M^{2+}]; HRMS (EI) [$C_{47}H_{60}N_4O$]: calcd 696.47671, found 696.47937.

4.10.10. 5,10,15,20-Tetrakis(3-hydroxyphenyl)porphyrin (92).[38] *Modified literature procedure*. 5,10,15,20-Tetrakis(3-methoxyphenyl)porphyrin (400 mg, 0.54 mmol) was dissolved in 200 mL of dry dichloromethane in a three-necked flask equipped with magnetic stirrer, gas inlet (argon), drying tube, and a 100 mL dropping funnel. The mixture was cooled to −50 °C and the flask shielded from ambient light. The dropping funnel was charged with 70 mL (70 mmol) of a 1 M solution of boron tribromide and this was added dropwise to the porphyrin solution over a period of approximately 1 h. The reaction mixture was stirred for 18 h and slowly warmed to room temperature. Subsequently, the reaction mixture was cooled again to −30 °C and 5 mL of an acetone/water mixture (4.5:1) were added dropwise. The mixture was slowly warmed to 20 °C and treated with 25 g of sodium bicarbonate. The mixture was stirred for 3 h until its color changed from green to red. After addition of 2 mL of triethylamine and 25 g of anhydrous sodium sulfate the mixture was stirred for 18 h at 20 °C, filtered and the filtrate evaporated to dryness. The residue was redissolved in a mixture of acetic acid ethylester and water (2:1). The organic phase was washed with brine (2×100 mL), sodium bicarbonate solution (2×100 mL), and with water (2×100 mL), dried over anhydrous sodium sulfate and then evaporated to dryness. to yield 330 mg (0.49 mmol; 90%) of a purple amorphous solid: R_f=0.37 (CH_2Cl_2/CH_3OH, 9:1, v/v); HPLC: (Nucleosil 50, 5 μm, eluent: CH_2Cl_2/10% CH_3OH, v/v, flow: 1 mL/min, detection at 420 nm) retention time: 3.57 min (91.8%), (same conditions but detection at 254 nm) retention time: 3.64 min (90.7%); the ^{1}H NMR was identical with that given in the literature; ^{13}C NMR (60 MHz, acetone-d_6): δ=115.86, 120.91, 122.82, 127.13, 128.57, 131.86, 144.10, 156.83; MS (EI, 80 eV, 320 °C), *m/z* (%): 678 (100) [M^+], 585 (1) [$M^+-C_6H_5O$], 339 (9) [M^{2+}]; HRMS (EI) [$C_{44}H_{30}N_4O_4$]: calcd 678.22677, found 678.22845.

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References and notes

1. (a) Finsen, N. R. *Om Anvendelse i Medicinen af koncentrerede kemiske Lysstraaler* 1896. (b) Macdonald, I. J.; Dougherty, T. J. *J. Porphyrins Phthalocyanines* **2001**, *5*, 105–129. (c) Ackroyd, R.; Kelty, C.; Brown, N.; Reed, M. *Photochem. Photobiol.* **2001**, *74*, 656–669. (d) Hopper, C. *Lancet Oncol.* **2000**, *1*, 212–219.
2. Kelly, J. F.; Snell, M. E. *J. Urol.* **1976**, *115*, 150–151. Bonnett, R. *Rev. Contemp. Pharmacother.* **1999**, *10*, 1–19.
3. (a) Wainwright, M. *J. Antimicrob. Chemother.* **1998**, *42*, 13–28. (b) Das, K.; English, D. S.; Fehr, M. J.; Smirnov, A. V.; Petrich, J. W. *J. Phys. Chem.* **1996**, *100*, 18275–18281.
4. Kirby, B.; Griffiths, C. E. M. *Brit. J. Dermatol., Suppl.* **2001**, *144*, 37–43.
5. Schmidt-Erfurth, U.; Hasan, T. *Surv. Ophthalmol.* **2000**, *45*, 195–214.
6. (a) Dolmans, D. E. J. G. J.; Fukumura, D.; Jain, R. K. *Nat. Rev.* **2003**, *3*, 380–387. (b) Bonnett, R.; White, R. D.; Winfield, U.-J.; Berenbaum, M. C. *Biochem. J.* **1989**, *261*, 277–280. (c) Richter, A. M.; Kelly, B.; Chow, J. K.; Liu, D. J.; Towers, G. M. N.; Dolphin, D.; Levy, J. G. *J. Natl. Cancer Inst.* **1987**, *79*, 1327–1332. (d) Kelly, J. F.; Snell, M. E. *J. Urol.* **1976**, *115*, 150–151. A detailed discussion of the development of Photofrin may be found in Ref. 7. (e) Kennedy, J. C.; Pottier, R. H.; Pross, D. C. *J. Photochem. Photobiol. B. Biol.* **1990**, *6*, 143–148. (f) Kennedy, J. C.; Pottier, R. H. *J. Photochem. Photobiol. B. Biol.* **1992**, *14*, 275–292.
7. Bonnett, R. *Chemical Aspects of Photodynamic Therapy*; Gordon & Breach: Amsterdam, 2000.
8. Granville, D. J.; McManus, B. M.; Hunt, D. W. C. *Histol. Histopathol.* **2001**, *16*, 309–317. Moor, A. C. E. *J. Photochem. Photobiol.* **2000**, *57*, 1–13. Bourre, L.; Rousset, N.; Thibaut, S.; Eleouet, S.; Lajat, Y.; Patrice, T. *Apoptosis* **2002**, *7*, 221–230.
9. He, Y.-Y.; Liu, H.-Y.; An, J.-Y.; Han, R.; Jiang, L.-L. *Dyes Pigm.* **2000**, *44*, 63–67. MacDonald, I. J.; Morgan, J.; Bellnier, D. A.; Paskiewicz, G. M.; Whitaker, J. E.; Litchfield, D. J.; Dougherty, T. J. *Photochem. Photobiol.* **1999**, *70*, 789–797. Potter, W. R.; Henderson, B. W.; Bellnier, D. A.; Pandey, R. K.; Vaughan, L. A.; Weishaupt, K. R.; Dougherty, T. J. *Photochem. Photobiol.* **1999**, *70*, 781–788.

10. Little, R. G.; Anton, J. A.; Loach, P. A.; Ibers, J. A. *J. Heterocycl. Chem.* **1975**, *12*, 343–349. Kong, J. L. Y.; Loach, P. A. *J. Heterocycl. Chem.* **1980**, *17*, 737–744. Little, R. G. *J. Heterocycl. Chem.* **1994**, *50*, 8941–8968.
11. A first systematic approach to ABCD-porphyrins via acyl-substituted dipyrromethanes is described in: Lee, C.-H.; Li, F.; Iwamoto, K.; Dadok, J.; Bothner-By, A. A.; Lindsey, J. S. *Tetrahedron* **1995**, *51*, 11645–11672.
12. (a) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872. (b) Rao, P. D.; Littler, B. J.; Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 1084–1092. (c) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323–7344. (d) Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Org. Proc. Res. Dev.* **2003**, *7*, 799–812. (e) Muthukumaran, K.; Ptaszek, M.; Noll, B.; Scheidt, W. R.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 5354–5364. (f) Tamaru, S.-i.; Lianhe, Y.; Youngblood, W. J.; Muthukumaran, K.; Taniguchi, M.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 765–777.
13. Senge, M. O.; Richter, J. *J. Porphyrins Phthalocyanines* **2004**, *8*, 934–953. Senge, M. O.; Hatscher, S. S.; Wiehe, A.; Dahms, K.; Kelling, A. *J. Am. Chem. Soc.* **2004**, *126*, 13634–16365.
14. (a) Brückner, C.; Posakony, J. J.; Johnson, C. K.; Boyle, R. W.; James, B. R.; Dolphin, D. *J. Porphyrins Phthalocyanines* **1998**, *2*, 455–465. (b) Manka, J. S.; Lawrence, D. S. *Tetrahedron Lett.* **1989**, *30*, 6989–6992. (c) Treibs, A.; Häberle, N. *Liebigs Ann. Chem.* **1968**, *718*, 183–207.
15. Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427–11440.
16. Buchler, J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 157–231.
17. (a) Kalisch, W. W.; Senge, M. O. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1107–1109. (b) Senge, M. O.; Kalisch, W. W.; Bischoff, I. *Chem. Eur. J.* **2000**, *6*, 2721–2738. (c) Feng, X.; Bischoff, I.; Senge, M. O. *J. Org. Chem.* **2001**, *66*, 8693–8700.
18. (a) Senge, M. O.; Feng, X. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3615–3621. (b) Feng, X.; Senge, M. O. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1030–1038.
19. Wiehe, A.; Ryppa, C.; Senge, M. O. *Org. Lett.* **2002**, *4*, 3807–3809.
20. Hatscher, S.; Senge, M. O. *Tetrahedron Lett.* **2002**, *58*, 4375–4381.
21. Feng, X.; Senge, M. O. *Tetrahedron* **2000**, *56*, 587–590.
22. (a) A_3B tetraaryl systems via mixed condensations: Sun, Y.; Martell, A. E.; Tsutsui, M. *J. Heterocycl. Chem.* **1986**, *23*, 561–565. (b) Wiehe, A.; Senge, M. O.; Kurreck, H. *Liebigs Ann. Chem.* **1997**, 1951–1963. (c) Dietel, E.; Hirsch, A.; Zhou, J.; Rieker, A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1357–1364. (d) A_3B systems with both *meso* aryl and alkyl residues: Park, Y. T.; Kim, H. W. *Bull. Kor. Chem. Soc.* **1990**, *11*, 468–470. (e) Park, Y. T.; Yun, Y. S.; Kim, H. W.; Kim, Y. D. *Bull. Kor. Chem. Soc.* **1990**, *11*, 171–173. (f) Atamian, M.; Wagner, R. W.; Lindsey, J. S.; Bocian, D. F. *Inorg. Chem.* **1988**, *27*, 1510–1512. (g) Oulmi, D.; Maillard, P.; Guerquin-Kern, J.-L.; Huel, C.; Momenteau, M. *J. Org. Chem.* **1995**, *60*, 1554–1564. (h) Dieks, H.; Senge, M. O.; Kirste, B.; Kurreck, H. *J. Org. Chem.* **1997**, *62*, 8666–8680.
23. Bonnett, R.; Martinez, G. *Org. Lett.* **2002**, *4*, 2013–2016.
24. (a) Fuhrhop, J.-H. In Dolphin, D., Ed.; The Porphyrins; Academic: New York, 1978; Vol. 1, pp 131–159. (b) Vicente, M. G. H. In Kadish, K. M., Smith, K. M., Guilard, R., Eds.; The Porphyrin Handbook; Academic: New York, 2000; Vol. 1, pp 149–199.
25. (a) Vicente, M. G. H.; Smith, K. M. *J. Org. Chem.* **1991**, *56*, 4407–4418. (b) Senge, M. O.; Vicente, M. G. H.; Parkin, S. R.; Hope, H.; Smith, K. M. *Z. Naturforsch.* **1992**, *47b*, 1189–1202.
26. Gunter, M. J.; Robinson, B. C.; Gulbis, J. M.; Tiekink, E. R. T. *Tetrahedron* **1991**, *47*, 7853–7868.
27. Boyle, R. W.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1994**, 2463–2464.
28. (a) Yeung, M.; Ng, A. C. H.; Drew, M. G. B.; Vorpagel, E.; Breitung, E. M.; McMahon, R. J.; Ng, D. K. P. *J. Org. Chem.* **1998**, *63*, 7143–7150. (b) Balaban, T. S.; Bhise, A. D.; Fischer, M.; Linke-Schaetzel, M.; Roussel, C.; Vanthuyne, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2140–2144.
29. (a) Note, that there is an increasing body of examples for complex *meso* and β fused porphyrins derived from such systems: Callot, H. J.; Ruppert, R.; Jeandon, C.; Richeter, S. *J. Porphyrins Phthalocyanines* **2004**, *8*, 111–119. (b) Barloy, L.; Dolphin, D.; Dupre, D.; Wijesekera, T. P. *J. Org. Chem.* **1994**, *59*, 7976–7985.
30. Wilson, G. S.; Anderson, H. L. *Synlett* **1996**, 1039–1040.
31. Shanmugathasan, S.; Johnson, C. K.; Edwards, C.; Matthews, E. K.; Dolphin, D.; Boyle, R. W. *J. Porphyrins Phthalocyanines* **2000**, *4*, 228–232.
32. Negishi, E.-i.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979–2017. Boyle, R. W.; Johnson, C. K.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1995**, 527–528.
33. Kong, J. L. Y.; Loach, P. A. *J. Heterocycl. Chem.* **1980**, *17*, 737–744. Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249–282. Laville, I.; Pigaglio, S.; Blais, J.-C.; Loock, B.; Maillard, P.; Grierson, D. S.; Blais, J. *Bioorg. Med. Chem.* **2004**, *12*, 3673–3682.
34. For details see: Wiehe, A.; Simonenko, E.; Senge, M. O.; Röder, B. *J. Porphyrins Phthalocyanines* **2001**, *5*, 758–761.
35. Rancan, F.; Wiehe, A.; Nöbel, M.; Senge, M. O.; Al Omari, S.; Böhm, F.; John, M.; Röder, B. *J. Photochem. Photobiol. B: Biol.* **2005**, *78*, 17–28.
36. Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836.
37. Only the relative intensities of the absorption bands are given due to the low solubility of the compound.
38. Syrbu, S. A.; Semeikin, A. S.; Russ *J. Org. Chem.* **1999**, *35*, 1236–1239.