FULL PAPER

DOI: 10.1002/ejoc.200((will be filled in by the editorial staff))

Published as:
Ryan, A.; Gehrold, A.; Perusitti, R.; Pintea, M.; Fazekas, M.; Locos, O. B.; Blaikie, F.; Senge, M. O. (2011):
Synthesis of Unsymmetrical meso-Substituted Porphyrins. 2. Porphyrin Dimers and Arrays.
European Journal of Organic Chemistry, 5817–5844.

Synthesis of Unsymmetrical meso Substituted Porphyrins 2. Porphyrin Dimers and Arrays

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Keywords: Porphyrinoids / C–C coupling / nonlinear optics / Tetrapyrroles / bisporphyrins / photodynamic therapy

Current applications of porphyrins in medicine and optics, such as photodynamic therapy or nonlinear absorbers, increasingly require the use of far-red absorbing dyes. Modifications of the porphyrin structure to accommodate these conditions can be achieved by extending the conjugation of the porphyrin π-system, which causes a bathochromic shift in the absorption spectrum. Thus, conjugated porphyrin oligomers have found widespread use. However, past synthetic strategies have mainly targeted symmetric porphyrin dimers, trimers, and oligomers which limit the practical use of such chromophores. Here, a series of symmetric and unsymmetric dimeric and trimeric porphyrin systems which are connected via conjugated linkers, namely alkyne and phenylacetylene, were synthesized via palladium catalyzed C-C coupling reactions. Adopting two approaches, firstly, a series of novel unsymmetric dimers was synthesized via the incorporation of all substituents on the monomeric components prior to coupling. The second was the synthesis of novel symmetric dimers and trimers with free meso positions enabling further chemistry to be carried out. The majority of these conjugated arrays exhibited a bathochromic shift in their UV/vis absorption, in particular the alkyne linked arrays which showed absorption greater than 720 nm. The mass spectrometry spectra for phenylacetylene and diphenylbutadiene linked zinc arrays exhibited detachment of zinc from the porphyrin core in their spectra. These unusual results are both linker and metal dependent, usually only seen for more labile metals.

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Introduction

Multiporphyrin arrays have a wide range of potential applications in areas such as light-harvesting, non-linear optics (NLO), organic light emitting diodes (OLED's) and photodynamic therapy (PDT). Hence, these systems have been investigated widely.[1-5] Despite the vast knowledge and investigations of such arrays, the majority of work involves studies of symmetric multiporphyrin systems. Whilst these are also of interest to our area of research, the main focus was on unsymmetric arrays, through which amphiphilicity for PDT could be enhanced or, with respect to NLO, push-pull systems could be arranged via this unsymmetry. An example for the latter strategy has been given in a preceeding paper.[6]

We are interested in nonlinear optical materials[2a,e] and have initiated a program aimed at the development of new photosensitizers for PDT.[5d,7] Currently commercially available photosensitizers show absorption in 530 to 630 nm range, which limits the penetration of tissue by light.[8,9] Increasing the absorption wavelength of the photosensitizer may enable a deeper penetration and therefore the targeting of deeper tumors. Here conjugated dimers and trimers are ideal potential photosensitizer candidates as their absorption maximum should exhibit a bathochromic shift to this region. The type of linkage in the porphyrin arrays will influence the structure and properties of the system, so by extending the conjugation of the porphyrin π-system, and hence increasing the wavelength absorption, these oligomers could be used as potential photosensitizers for PDT or for other optical applications. Recent work by Anderson *et al.* displays this concept, whereby butadiyne linked dimers were synthesized and tested for *in vitro* PDT.[10] Our aim was to synthesize novel alkyne and phenylacetylene linked arrays and further develop the synthetic chemistry for unsymmetrical array systems. As the delocalization of electrons extends into this alkyne spacer group, these arrays are linear and sterically non-demanding.[11] Hence, the communication between the chromophores should be efficient making them attractive for not only for PDT but also for NLO, OLED and other light harvesting applications.

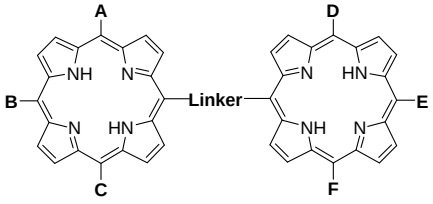


Figure 1. Model for conjugated unsymmetric dimers.

Our approach incorporated two ideas: the first was the synthesis of unsymmetric dimers, namely alkyne linked arrays. These unsymmetric dimers can contain both hydrophilic and hydrophobic entities at the various meso positions (Figure 1), whereby the amphiphilicity is enhanced, thus, in theory, assisting with the entry of the photosensitizer into the cell target.[12] The second approach was to synthesize symmetric conjugated porphyrin dimers and

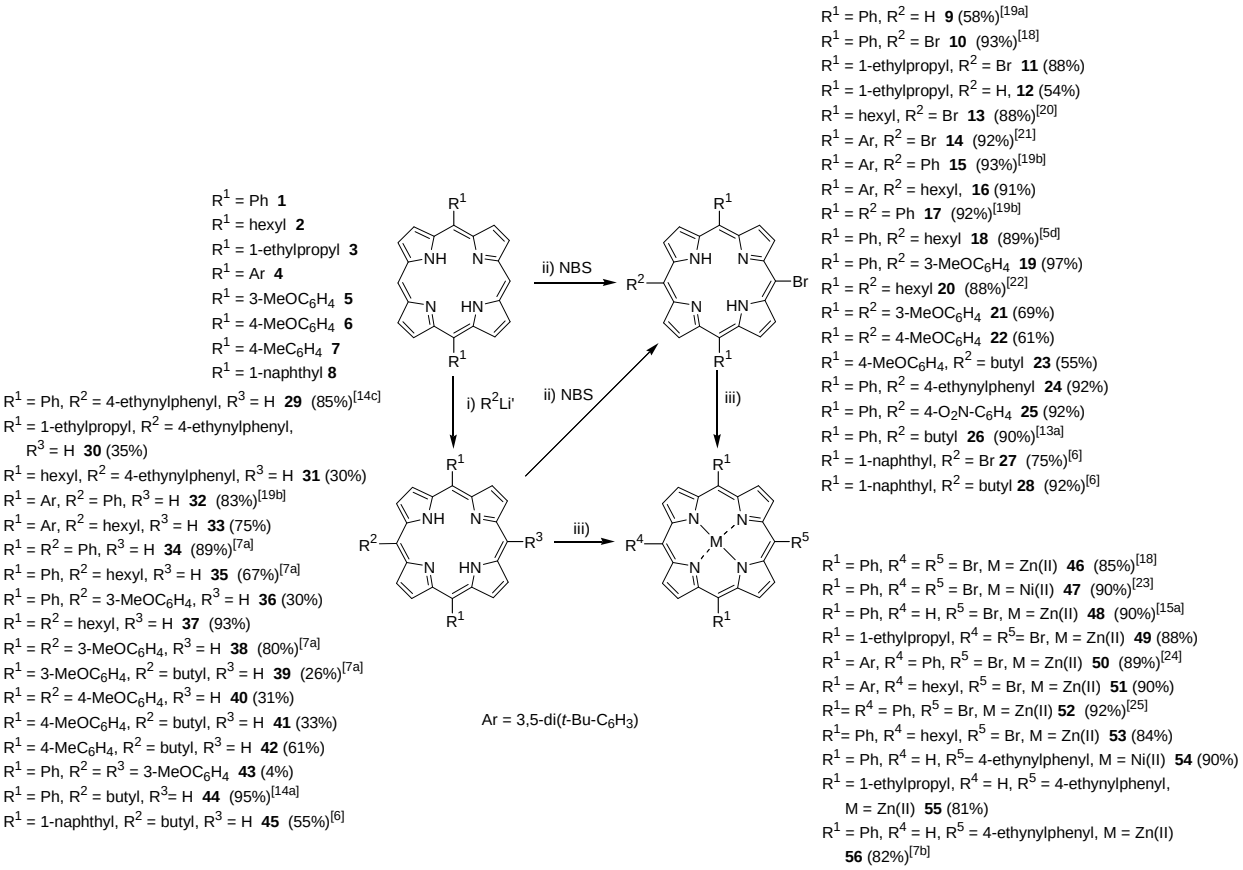
trimers with free meso positions. Linear, trimeric arrays with such linkers, in particular the phenylacetylene linker, have not been investigated to a great extent, with only two such compounds previously synthesized.[13] Once appropriate lead structures are identified further modifications, e.g., the introduction of water solubilizing groups, are possible at the free meso positions to further optimize their biological utility. Here, we outline the basic chemistry of this approach using model compounds.

Results and Discussion

As outlined in the introduction, the synthetic strategy for the synthesis of conjugated porphyrin oligomers was two-fold, incorporating both the synthesis of symmetric dimers and trimers with free meso positions and also the synthesis of unsymmetric arrays. Both strategies utilized Pd-catalyzed cross-coupling reactions and the free meso positions on the symmetric arrays allow subsequent chemical modifications to be carried out. Also, for a mass spectrometric comparative study, some diphenylbutadiyne and butadiyne symmetric dimers were synthesized using a Pd-mediated Glaser coupling method. These arrays can also be further modified due to their free meso positions. Both of these approaches utilize the organolithium methods, developed by us,[14] to introduce the phenylacetylene linker and the substituents on the porphyrin core. Sonogashira coupling was used to introduce the alkyne linker and also for the coupling reactions.[15] Some directly linked dimers were also synthesized via Suzuki coupling[16] to compare their properties to those oligomers which contain conjugated linkers.

Synthesis of porphyrin monomers

5,15-Disubstituted porphyrins[17] were chosen as the starting monomers (Scheme 1) to yield linear oligomers with free meso positions to enable further chemical modifications, enhancing their possible NLO and PDT effects. Porphyrins **1-8** were brominated following a standard procedure[18] forming **9-13**[19a,18,20] in yields ranging from 60-95%, the lower yields being those of monobrominated porphyrins **9**[19] and **12**. Monobromination of the 5,15-disubstituted porphyrins is quite difficult to achieve in a good yield due to the fact that dibrominated porphyrins are formed as side products. However, these monobrominated porphyrin monomers are vital in subsequent coupling reactions to form the linear oligomers, with dibrominated porphyrins being used for trimeric array synthesis. Surprisingly, the dibromo-dihexyl porphyrin **13**[20] proved quite insoluble in many solvents and thus was not used for further reactions. Hence the 1-ethylpropyl derivative **11** was used as this proved more soluble in organic solvents.



Scheme 1. Synthesis of porphyrin precursors: *Reagents and conditions:* i) R^2Li, THF, -70 °C to r.t., NH_4Cl, DDQ. ii) NBS (0.8-2.1 eq.), $CHCl_3$, pyridine, 1-3 h. iii) a) $Zn(OAc)_2$ in MeOH, $CHCl_3$, 60 °C; b) $Ni(acac)_2$, toluene, 120 °C, 0.5 h.

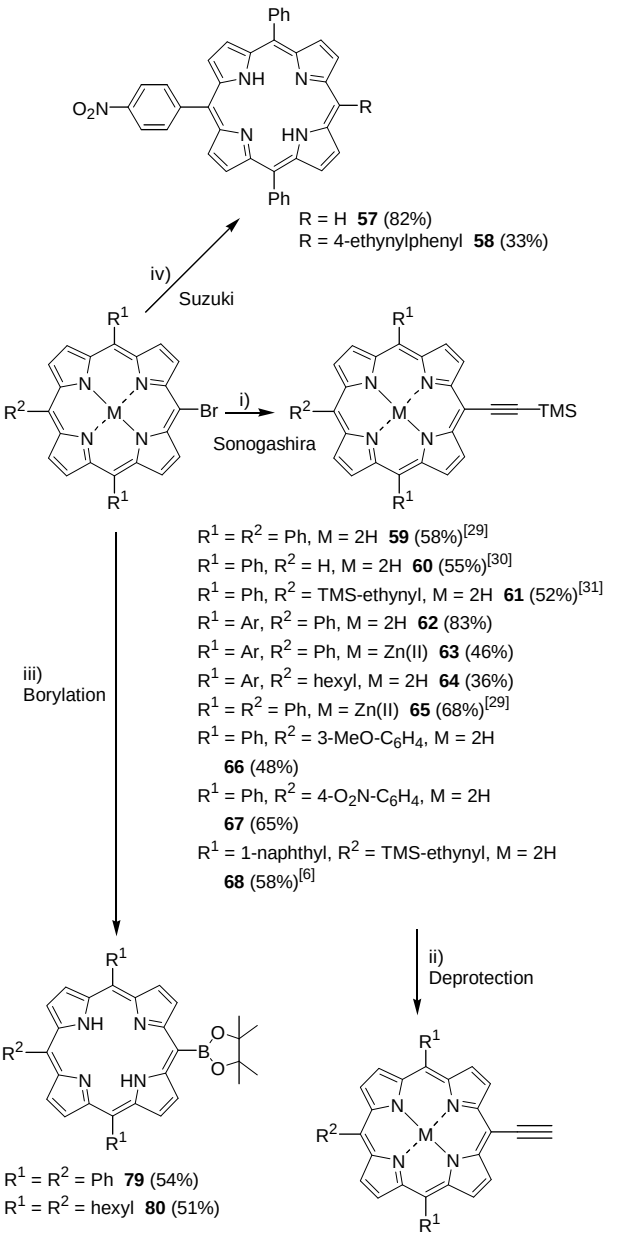
In order to introduce the desired conjugating linker groups, two approaches were used: 1) arylation (organolithium reaction)[14] to introduce the phenylacetylene linker and 2) Sonogashira coupling to introduce the alkyne linker.[14,26] Organolithium reactions were

carried out on 5,15-disubstituted porphyrins **1-3**, to introduce the phenylacetylene linker, and also on porphyrins **1**, **2**, and **4-8** to introduce various substituents at the meso positions. Substituents such as methoxyphenyl have been shown to be beneficial for the localization of photosensitizers in tumors,[27] so it was envisaged that the introduction of such substituents would be advantageous. Unless the organolithium reagent was commercially available it was generated *in situ* and then used to attack the porphyrin at a free meso position to form the desired trisubstituted product.[14a,b] For phenylacetylene introduction, the reaction proceeds quite well with phenyl substituted porphyrins, forming **29**[14a] in 74% yield. However, this was not the case for the alkyl substituted porphyrins, which formed **30** and **31** in yields of 30 and 35%, respectively. The best yield for **30** was obtained when the reaction was left overnight. This appeared initially to be a solubility problem of **3** in THF, however, when the solvent volume was increased no improvement was seen. Other alterations such as adjusting the BuLi equivalents and altering reaction time had no positive effect on the reaction yield. Starting materials **2** and **3** were recovered in approximate yields of 30 and 28%, respectively.

For porphyrins **1**, **2** and **4-8** the trisubstituted porphyrins **32**,[19b] **33**, **34** and **35**,[7a] **36**, **37** and **38**,[7a] **40**, **42**, **44**[14a] and **45**[6] were synthesized in yields ranging from 30-84%. Porphyrins **5** and **6** yielded the butylated side-products **39**[6a] and **41** in yields of 26 and 23%, respectively, along with the desired trisubstituted compounds **38**[7a] and **40** in yields of 65 and 71%, respectively. Also, in the synthesis of **36**, the tetrasubstituted product **43** was formed as a side product in 4% yield. These butylated side-products were also used in subsequent reactions for the synthesis of unsymmetric dimers. The trisubstituted porphyrins **29** and **32-41**, **44, 45** and **57** were also brominated according to standard procedure,[18] with yields ranging from 55 to 92 % for the compounds **14-28**.[21,19b,5d,13a,6] Both free base and metallated porphyrin oligomers were desired and thus porphyrins **9-11**, **15-17**, **29** and **30** were metallated with either zinc(II) or nickel(II),[28] yielding porphyrins **46-56**[18,23,15a,24,25] in yields of 78-92%.

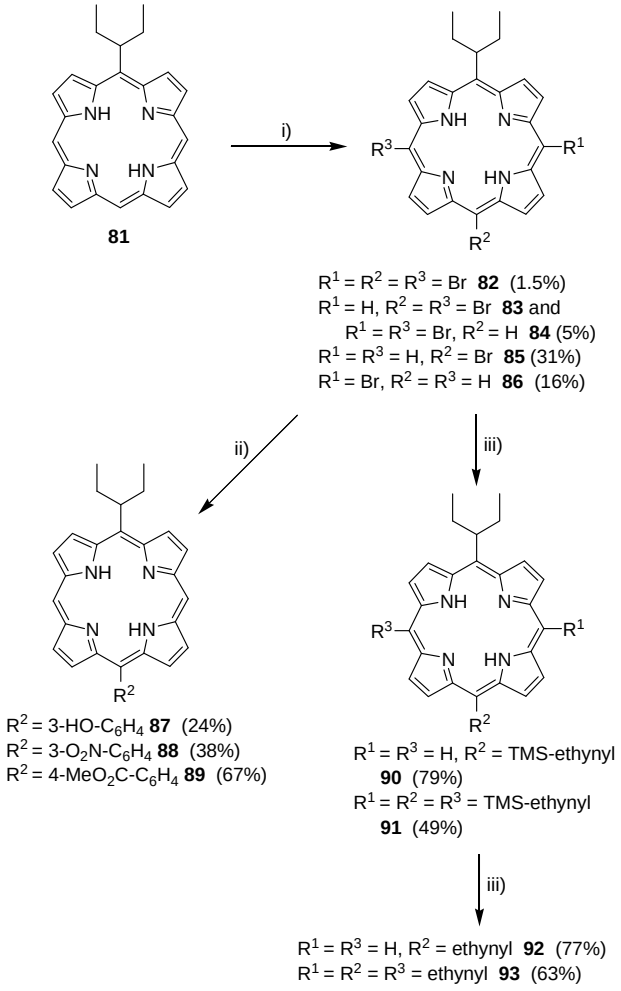
Porphyrins **9, 10, 15-17, 19, 25, 27, 50** and **52** were subjected to Sonogashira coupling[15] conditions (Scheme 2) to form the mono and disubstituted trimethylsilyl acetylenes **59-68**[29-31,6] in yields of 36-83%. An alternative method for this synthesis is a one-step condensation reaction.[29] This, however, is not applicable for the unsymmetric targets, thus the stepwise approach was used. With free base porphyrins **10**, **15-17**, **19**, **25** and **27** there was an inevitable insertion of copper into the core as a side product, thus leading to slightly lower yields of the desired materials. Metallated porphyrins are usually used under these conditions to avoid this formation, although for **63** this did not increase the yield significantly. In addition, there is evidence that zinc insertion can increase the PDT efficacy.[32] Porphyrins **59-68** were subsequently deprotected using TBAF forming the free alkynyl porphyrins **69-78**[33,29,6] in yields of 61-94%, the lowest yield being that for hexyl substituted porphyrin **73**, where much product was lost through recrystallization. Porphyrins **17** and **20** were borylated to form the trisubstituted porphyrinyl boronates **79** and **80** via a palladium catalyzed coupling reaction developed by Lin *et al.*[15a] and Hasobe *et al.*[34] These porphyrinyl boronates were subsequently used to form directly linked dimers via Suzuki coupling as shown in Scheme 4.

In addition Suzuki coupling was used to introduce the 4-nitrophenyl substituent, forming prophyrins **57** and **58** in yields of 82% and 33% from bromoporphyrins **9** and **24** respectively.



Scheme 2. Synthesis of porphyrin precursors via Suzuki or Sonogashira coupling and Miyaura borylation. *Reagents and conditions:* i) TMS-ethyne, $PdCl_2(PPh_3)_2$, CuI, TEA, THF, 40-60 °C, 16 h. ii) TBAF (1M in THF), CH_2Cl_2, 0.5 h, r.t. iii) pinacolborane, $Pd(PPh_3)_2$, DCE, TEA, 80 °C, 16 h. iv) 4-nitrophenyl boronic acid pinacol ester, $Pd(PPh_3)_4$, THF, K_3PO_4, 65°C, 16 h.

In order to construct building blocks for multiporphyrin array we choose 5-monosubstituted porphyrins as starting materials.[35] Of the various possibilities the 1-ethylpropyl derivative **81** is quite soluble.[35a] As shown in Scheme 3 and Table 1 (see experimental section), this compound allows an entry into meso bromosubstituted porphyrins **82-86** with different regiochemical arrangements. The selective bromination of porphyrins with several unsubstituted meso positions is difficult, but can be controlled to some degree depending on the number of NBS equivalents used.[13a] This gives an entry into mono- to tribrominated porphyrins. The 'trans' 15-position relative to the alkyl residue appears to be more reactive then the 10-position.



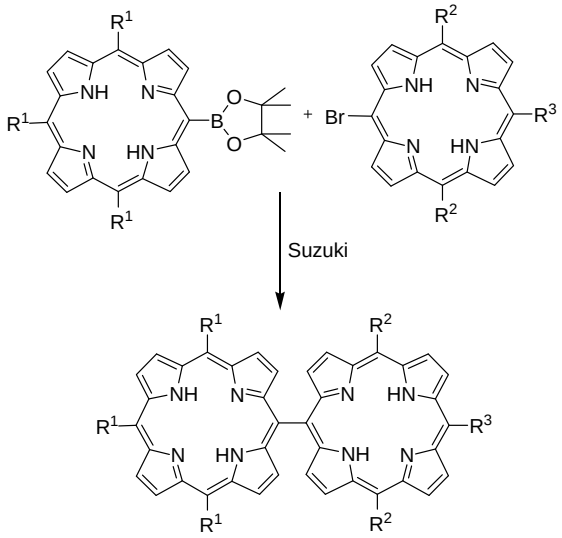
Scheme 3. Synthetic elaboration of a monosubstituted porphyrin. *Reagents and conditions*: i) NBS, pyridine, $CHCl_3$, 0 °C. ii) $R^1B(OH)_2$, K_3PO_4, $Pd(PPh_3)_4$, THF, 12 h. iii) ethynyltrimethylsilane, CuI, $Pd(PPh_3)_2Cl_2$. iv) 1M TBAF solution in THF, CH_2Cl_2.

The 15-brominated derivative **85** was converted into a range of acceptor substituted porphyrins **87-89** in yields of 24 to 67 % using Suzuki coupling conditions. Similar to the other reactions described above Sonogashira reaction with ethynyltrimethylsilane followed by deprotection with TBAF gave the ethynyl substituted porphyrins **92** and **93** in good yields (Scheme 3). The latter is a key intermediate for the preparation of tetrameric porphyrin arrays.

Synthesis of porphyrin oligomers

Depending on the type of oligomer/linker desired, different well established palladium-catalyzed coupling methods were adopted for their synthesis. The most utilized method was copper-free Sonogashira coupling and the others were Suzuki coupling (for the directly linked dimers), Sonogashira coupling (as a comparative to the copper free method) and also Pd-mediated Glaser coupling for homocoupled dimers.[15,16,36,37]

Directly linked dimers: Directly meso-meso linked dimers were synthesized for comparison to investigate what effect the linker has on the absorption wavelength. Using Suzuki coupling methods,[16,34] directly linked amphiphilic dimers **94-97** were synthesized in yields of 29-51% (Scheme 4). Porphyrinyl boronates **79** and **80** provided the hydrophobic entity whilst bromoporphyrins **21**, **22** and **23** provided the hydrophilic entity. Yields for the 3-methoxyphenyl substituted dimers **94** and **97** were lower than those for 4-methoxyphenyl substituted dimers **95** and **96**, most likely due to the stronger electron donating effects of the *para* methoxy group over the *meta* group on the porphyrin macrocycle. Easier purification of hexyl substituted dimers **96** and **97** was observed due to larger differences in polarity. Whilst these arrays do not show much promise as candidates for PDT due to the lack of a bathochromic shift in their absorption profile (see UV section), they were of interest for comparison with the conjugated linked arrays, i.e., to observe the linker effect on the photophysical properties of the array.

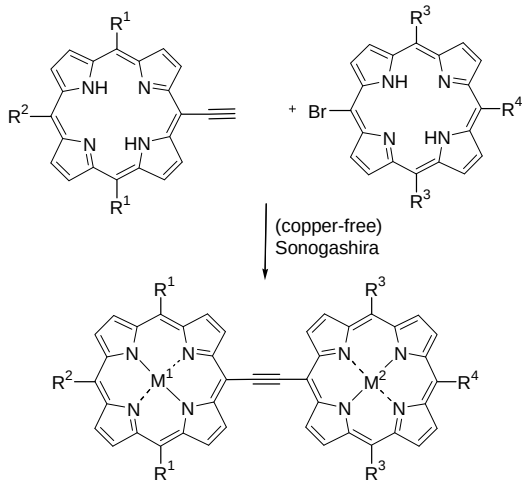


Scheme 4. Synthesis of directly linked porphyrins via Suzuki coupling: *Reagents and conditions:* $Pd(PPh_3)_4$, Cs_2CO_3, toluene, DMF, 80 °C.

Alkyne linked dimers: The first approach mentioned was to synthesize unsymmetric dimers, without any free meso positions, i.e., the introduction of all substituents prior to the coupling reaction to form the oligomer. Unsymmetric alkyne linked dimers were synthesized to yield larger π-systems, resulting in better absorption in the red region and hence the possible use as PDT agents.

These unsymmetric alkyne linked dimers were initially synthesized via original Sonogashira coupling conditions,[15,26] using Pd(II) and CuCl as a co-catalyst. However, formation of the

homocoupled product **118** as an undesirable side product (see Scheme 11) was observed. This homocoupling takes place during the reduction of palladium(II) to palladium(0), thus it was decided to use a copper-free/Pd(0) Sonogashira approach.[36] This coupling protocol yielded the unsymmetric dimers **98-116** in moderate to good yields ranging from 25-68% (Scheme 5). Generally these dimers exhibited good solubility in most organic solvents. However, depending on substituents and in some cases, upon metallation with zinc, this solubility was somewhat diminished. This was particularly noticeable for the phenyl substituted dimers **110** and **111**.

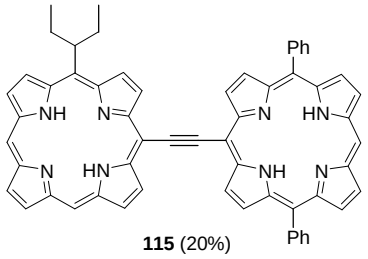


R^1	R^2	M^1	R^3	R^4	M^2	Yield %	#
Ph	Ph	2H	4-MeO-C_6H_4	butyl	2H	29	**98**
Ph	Ph	2H	3-MeO-C_6H_4	3-MeO-C_6H_4	2H	29	**99**
Ar	Ph	2H	4-MeO-C_6H_4	4-MeO-C_6H_4	2H	64	**100**
Ar	Ph	2H	hexyl	hexyl	2H	45	**101**
Ar	Ph	2H	Ph	Ph	2H	45	**102**
Ar	Ph	2H	Ar	hexyl	2H	34	**103**
Ar	Ph	2H	Ar	Ph	2H	43	**104**
Ar	Ph	2H	Ph	Ph	Zn(II)	54	**105**
Ar	Ph	Zn(II)	Ph	Ph	Zn(II)	52	**106**
Ar	Ph	Zn(II)	hexyl	hexyl	Zn(II)	68	**107**
Ph	Ph	2H	Ph	3-MeO-C_6H_4	2H	38	**108**
Ph	Ph	2H	Ph	hexyl	2H	39	**109**
Ph	Ph	2H	Ph	Ph	2H	48	**110**
Ph	Ph	Zn(II)	Ph	Ph	Zn(II)	47	**111**
Ph	4-O_2N-C_6H_4	2H	Ph	butyl	2H	31	**112**
Ph	4-O_2N-C_6H_4	2H	1-naphthyl	butyl	2H	25	**113**
H	1-ethylpropyl	2H	Ph	H	2H	29	**114**

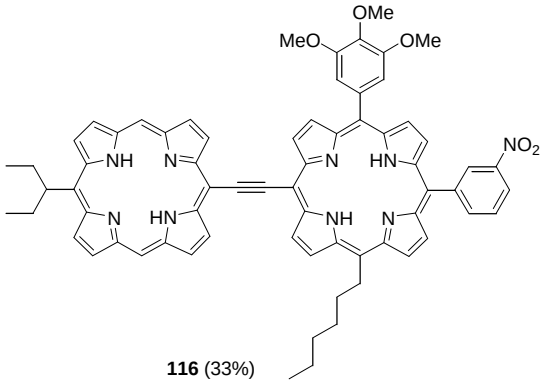
where Ar = (3,5-di-*t*-Bu)C_6H_3

Scheme 5. Synthesis of unsymmetric alkyne linked dimers. *Reagents and conditions:* Sonogashira - $PdCl_2(PPh_3)_2$, CuI, TEA, THF, 40-60 °C, 16 h; copper-free Sonogashira - $Pd_2(dba)_3$, $AsPh_3$, THF, TEA, 60 °C, 16 h.

Compound **105** shows that this can be used to prepare heterobismetallated systems. The bromoprecursor for **113** (25%) was described before.[6] A comparison of **114** (29%) with **115** shows that both the 5,10 and 5,15 linkages can easily be achieved. The latter was prepared by reaction of **68** with **86** in 20% yield.



115 (20%)

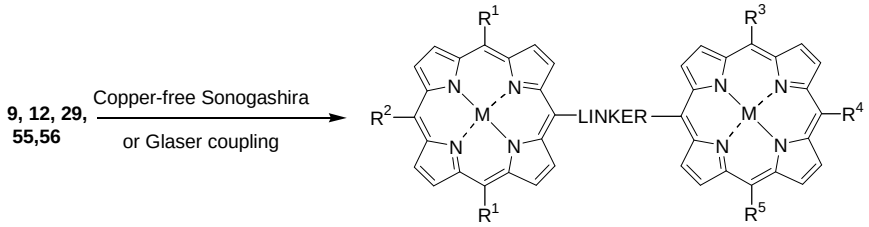


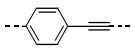
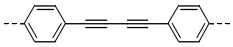
116 (33%)

Phenylacetylene and butadiyne linked dimers: The phenylacetylene linked symmetric and unsymmetric dimers were prepared in a similar manner to dimers **98-116**. In general, the copper-free method worked quite well giving porphyrins **117-125** in yields of 8-44% (Scheme 6). In these cases the desired dimer was the main product and they exhibited good solubility in organic solvents.

For the diphenylbutadiyne and butadiyne homocoupled arrays, Pd-mediated Glaser homo-coupling was used.[37] However, this method proved less successful with yields of 25 and 35% for dimers **127**,[7b] and **129**,[38] the latter of which was synthesized for a mass spectrometry comparison. Reactions were carried out under dry air and reported results for these conditions show good yields.[39] A more oxidative environment is most likely needed to improve yields but as these dimers were only used for a mass spectrometry study; thus, further reaction optimization was not carried out. The other homocoupled dimers **126** and **128** resulted as side product from the synthesis of **135** and **101**, respectively.

Porphyrin oligomers: In order to synthesize the targeted porphyrin trimers, a dibrominated porphyrin was reacted with a mono-'linker'-substituted porphyrin to form the desired trimer *via* the previously described copper-free Sonogashira coupling. This method was initially developed by Lindsey and coworkers.[36a] The free base phenyl substituted trimers **130** and **131** proved to be quite insoluble in most organic solvents, although this made their purification easy via filtration using DCM as solvent. Any remaining monomer or other side products were removed and pure trimers **130** and **131** were obtained in yields of 40 and 32%, respectively (Scheme 7).



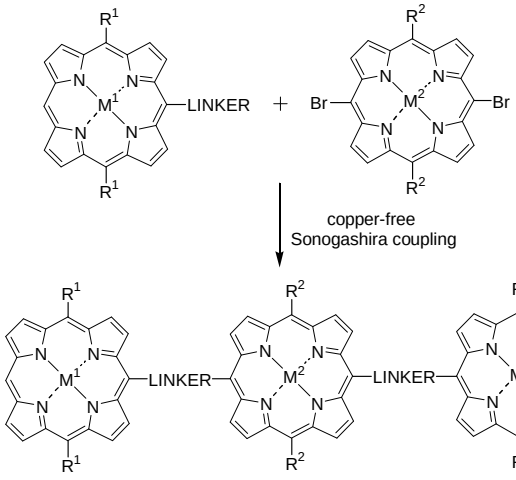
R^1	R^2	R^3	R^4	R^5	M	Yield %	#	Linker
Ph	H	Ph	H	Ph	2H	46	**117**	
Ph	H	Ph	H	Ph	Zn(II)	44	**118**	
Ph	H	1-ethylpropyl	H	1-ethylpropyl	2H	45	**119**	
Ph	4-O_2N-C_6H_4	Ph	butyl	Ph	2H	42	**120**	
Ph	H	Ph	4-O_2N-C_6H_4	Ph	2H	43	**121**	
Ph	H	1-naphthyl	butyl	1-naphthyl	2H	42	**122**	
Ph	4-O_2N-C_6H_4	1-naphthyl	butyl	1-naphthyl	2H	21	**123**	
Ph	H	H	1-ethylpropyl	H	2H	8	**124**	
Ph	H	1-ethylpropyl	H	H	2H	26	**125**	
1-ethylpropyl	H	1-ethylpropyl	H	1-ethylpropyl	Zn(II)	21	**126**	
Ph	H	Ph	H	Ph	Zn(II)	25	**127**	
Ar	H	Ar	H	Ar	2H	22	**128**	
Ph	H	Ph	H	Ph	Zn(II)	35	**129**	

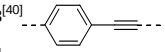
where Ar = 3,5(di-*t*-Bu)C_6H_3

Scheme 6. *Reagents and conditions:* copper-free Sonogashira coupling - $Pd_2(dba)_3$, THF, TEA, 60 °C, 16 h. Pd-Glaser coupling - toluene, $Pd(PPh_3)_2Cl_2$ (0.01 eq.), CuI (0.05 eq.), I_2 (0.5 eq.).

In order to improve solubility to enable full characterizations to be carried out and to minimize possible Pd insertion, zinc(II) was introduced into the monomer porphyrin core, yielding **132** (26%), with dimer **118** being isolated as a side product in a yield of 23%. In addition, to improve solubility, 5,15-dibromo-10,20-bis(3,5-di-*t*-butyl-C_6H_3)porphyrin **14** was coupled to **56,** producing **134** in a 28% yield. Whilst these efforts improved the solubility of the desired product, the column chromatographic purification remained problematic. Much streaking was observed as the trimers were only partially soluble in DCM/hexane and hence there was an inevitable loss of desired product. Increasing the equivalents of palladium(0) catalyst used also had no positive effect on yields as Pd inserted into the porphyrin core and these Pd products appeared as very slow moving fractions, whose presence was determined by mass spectrometry but these were not isolated. Another approach to improve yields was to introduce different substituents on the porphyrin periphery.

Initially dihexylporphyrin monomers were used, but, as stated in a previous section, the dibromo-dihexyl porphyrin **13** is highly insoluble in THF and thus not appropriate for the copper-free Sonogashira coupling. Thus, *neo*-pentyl disubstituted porphyrins **11**, **12**, **30**, **49** and **55** were chosen as starting materials. Initially, reactions with these porphyrins gave many side products and UV data indicated the formation of directly linked oligomers (see UV section). However, on repeating the reaction using the zinc monomers **49** and **55**, followed by purification *via* preparative TLC the desired trimer **135** was isolated in a 46% yield as the main fraction. For the synthesis of **136**, full characterization could not be obtained, although mass spectrometry results showed its formation. The naphthyl substituted trimer **137** exhibited similar solubility problems which is reflected in the low coupling yield of 22%.

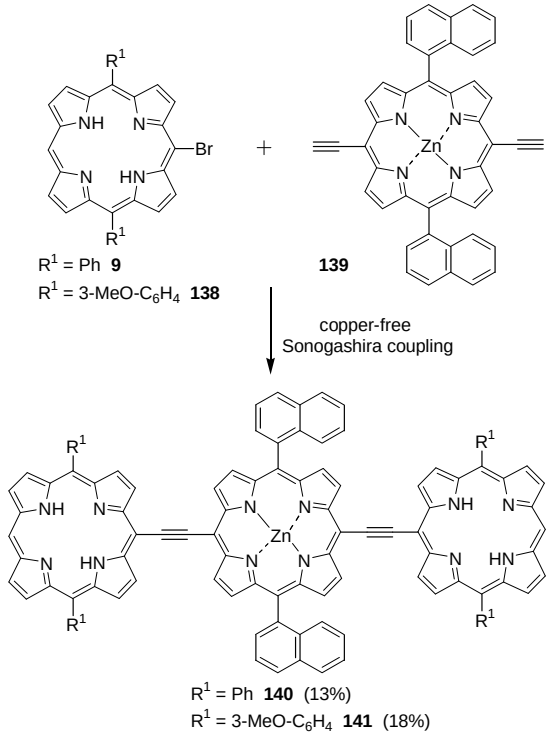


R^1	R^2	M^1	M^2	Yield %	#	Linker
Ph	Ph	2H	2H	40	**130**	
Ph	Ph	2H	2H	38	**131**	
Ph	Ph	Zn(II)	Zn(II)	26	**132**	
Ph	Ph	Ni(II)	Ni(II)	n/d	**133**[40]	
Ph	Ar	Zn(II)	2H	28	**134**	
1-ethylpropyl	1-ethylpropyl	Zn(II)	Zn(II)	44	**135**	
Ph	1-ethylpropyl	Zn(II)	Zn(II)	21	**136**	
Ph	1-naphthyl	2H	2H	22	**137**	

where Ar = 3,5(di-*t*-Bu)C_6H_3

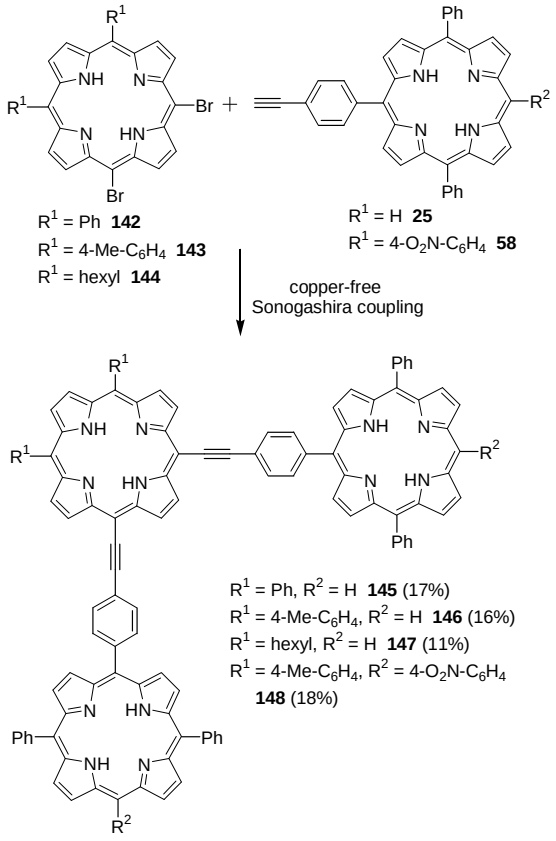
Scheme 7. Synthesis of linear trimers. *Reagents and conditions:* Copper-free Sonogashira coupling - $Pd_2(dba)_3$, $AsPh_3$, THF, TEA, 60 °C, 16 h.

The reverse strategy, i.e. having a diethynyl central unit and reacting it with monobromo sides can also be used (Scheme 8). Trimers **140** and **141** were synthesized in yields of 13 and 18% respectively. These yields are however, lower than those observed for the other synthetic strategy.



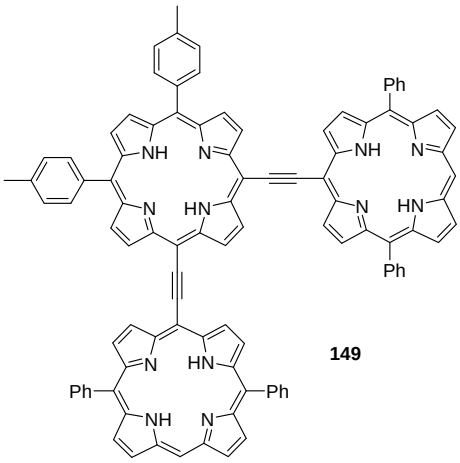
Scheme 8. Synthesis of linear trimers. *Reagents and conditions:* Copper-free Sonogashira coupling - $Pd_2(dba)_3$, $AsPh_3$, THF, TEA, 65 °C, 16 h.

Next we turned our attention to the synthesis of "L-shaped" trimers, i.e. porphyrin systems with connecting linkers in the 5,10 substitutent pattern. The synthesis of these compounds is outlined in Scheme 9. The low yields for trimers **145-148** can again be attributed to solubility problems. An attempt to resolve this by the introduction of hexyl substituents, forming trimer **147**, had no positive effect on the reaction yield.

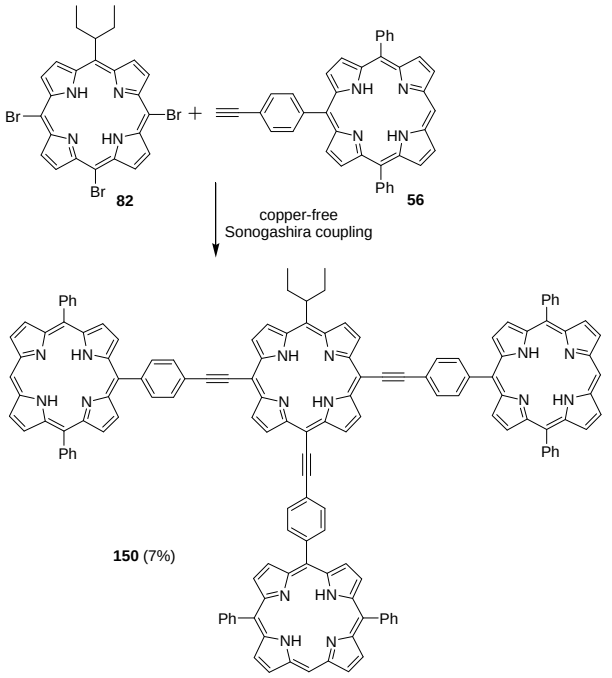


Scheme 9. Synthesis of "L-shaped" trimers. *Reagents and conditions:* Copper-free Sonogashira coupling - $Pd_2(dba)_3$, $AsPh_3$, THF, TEA, 65 °C, 16 h.

A similar coupling of **143**[6] with **77** gave the ethynyl-linked trimer **149** in 7% yield.

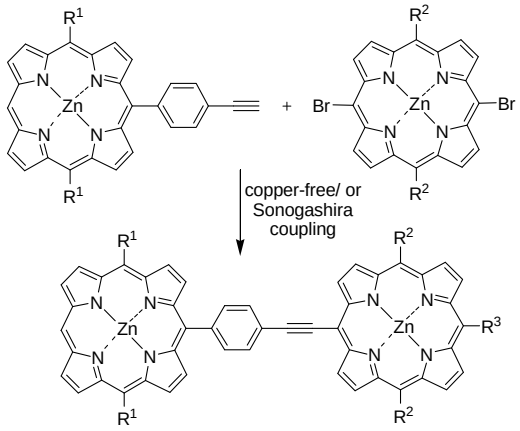


Lastly, we used the tribromo precursor **82** to construct a tetrameric porphyrin array with both 5,15 and 5,10 linkages (**150**). Reaction of **82** with **29** under copper-free Sonogashira conditions gave **150** in low yield (Scheme 10).



Scheme 10. Synthesis of a porphyrin tetramer. *Reagents and conditions:* Copper-free Sonogashira coupling - $Pd_2(dba)_3$, $AsPh_3$, THF, TEA, 65 °C, 5 h.

Side products: A number of side products were isolated during the trimer syntheses (Scheme 11). For the synthesis of **131**, the Glaser coupled dimer **126** was a side product of this reaction, perhaps due to trace copper presence and also the dimer side product **118**, due to incomplete reaction. For the synthesis of trimers **135** and **136** using Sonogashira conditions, the bromo dimer "side products" **151** and **152** proved to be the main products isolated showing an incomplete reaction, with no trimer formation. This suggests that the reaction conditions are not 'forceful' enough for the trimer to form. The Glaser coupled product **126** was also a side product here due to the presence of CuI. Addition of more copper/Pd, increasing the temperature and reaction time gave no improvement on the outcome as the trimers were not formed, only more side products.



Scheme 11. Side product formation during the synthesis of trimers. *Reagents and conditions:* Sonogashira coupling - $PdCl_2(PPh_3)_2$, CuI, TEA, THF, 40-60 °C, 16 h. Copper-free Sonogashira coupling - $Pd_2(dba)_3$, $AsPh_3$ THF, TEA, 60 °C, 16 h.

NMR studies

Noteworthy NMR spectra resulted from the analysis of the oligomers synthesized. Depending on the linker between the porphyrin units, different chemical shift patterns were observed (Figure 2).

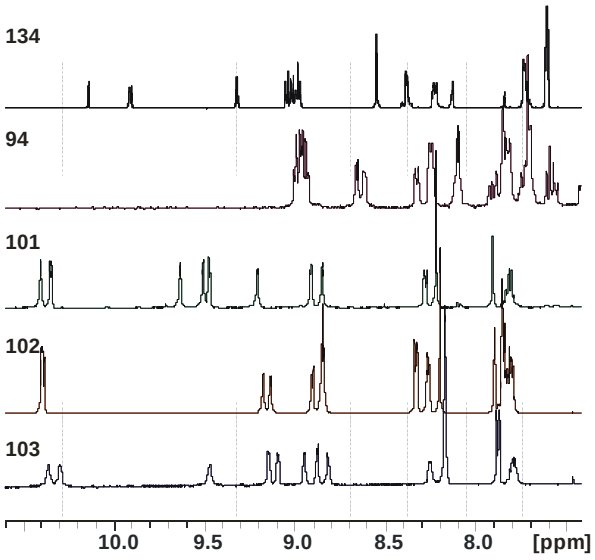


Figure 2. ^{1}H-NMR spectra of oligomers **94, 101, 102, 103** and **134** in $CDCl_3$ showing β and aryl regions.

With the directly linked dimer **94**, a large upfield shift to approximately 9 ppm of the β protons was observed, in comparison with the monomeric porphyrins, where the last set of β signals was observed at approximately 9.8 ppm. In contrast, the alkyne linked oligomers exhibited a different pattern with the β protons being deshielded downfield. Some of these shifts occur at around 10.4 ppm, a shift of approximately 0.7 ppm with respect to monomeric components. Also, these β protons exhibit signals over a wider range than those of the directly linked dimers. With the phenylacetylene linked trimers, a downfield shift was also observed for the meso and β protons, being more pronounced for the β protons. Using ^{1}H-^{1}H COSY NMR analysis (Figure 3), a correlation between the β and aryl protons on trimer **134** and dimer **101** was shown. It is interesting to note that with trimer **134**, the meso proton signal overlaps with that of the β signals. In addition, the signals are quite broad for this alkyl substituted trimer, most likely due to aggregation. The overlap was also seen for the alkyl substituted monomers **49** and **55**, indicating that it is a result of the substitution pattern on the array and independent of the linker.

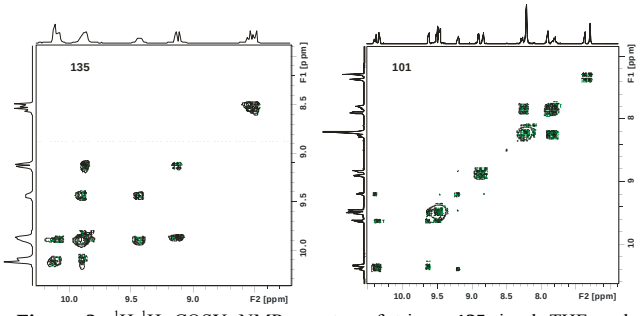


Figure 3. ^{1}H-^{1}H COSY NMR spectra of trimer **135** in d_8-THF and unsymmetric dimer **101** in $CDCl_3$.

UV/vis spectroscopy

The extension of the porphyrin π-conjugation results in the decrease in the HOMO-LUMO gap and this is due to the change in the electron density distribution on the porphyrin.[15,41] The absorption spectra of the porphyrin oligomers depend on the type of linker used and the substituents on the porphyrin macrocycle. With the porphyrin oligomers, most showed a significant split in the Soret band,[42] indicating strong conjugation between the porphyrin units, except for the diphenylbutadiyne linked dimers where a small split was seen, indicating here that the communication between porphyrin subunits is not very efficient. Likewise, in the case of directly linked dimers **94-97**, a split in the Soret band was observed due to excitonic coupling,[2c] but no bathochromic shift was observed as there is no conjugation between the units. The dimer behaves like its monomeric component and thus these systems are not of interest with respect to PDT and NLO but useful as a comparative against the conjugated systems. On the other hand, the phenylacetylene linked dimers and trimers showed a significant split, in particular with trimer **135** (Figure 4). This shows that there is efficient interaction between all porphyrin units in the array.[41b] Additionally, in comparison to monomer Q-band values, there is a large bathochromic shift due to increase in conjugation, into the 700-800 nm region for some trimers. A strong broad Q-band absorbance intensity was also observed with these arrays, in particular for alkyl trimer **135**.

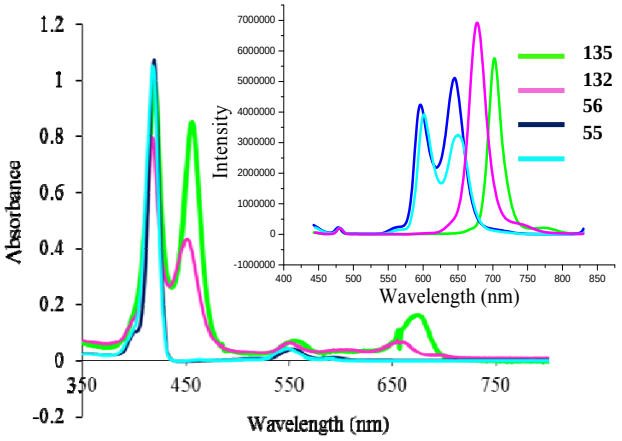


Figure 4. UV/vis absorbance spectrum of trimers **132** and **135** versus monomers **56** and **55** in CH_2Cl_2. Inset: Emission spectrum of trimer **132** versus monomer **56** excited at 443 nm and trimer **135** versus monomer **56**, excited at 445 nm. Concentration: 1.7 x 10^{-7} M in THF.

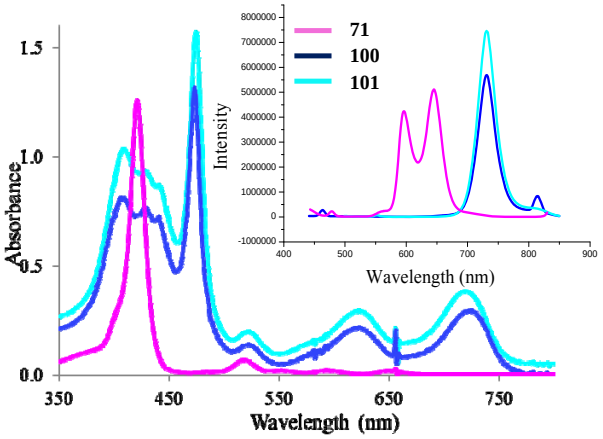


Figure 5. a) Absorbance spectrum of unsymmetric dimers **100** and **101** versus monomer **71**. Inset: Emission spectrum of **100** and **101** excited at both Soret bands versus monomer **71**. Concentration: 1.7 x 10^{-7} M in THF.

Emission studies also showed a bathochromic shift for these oligomers when compared against their monomeric components. This is expected due to the increase in π-conjugation, thus these oligomers are possible leads for applications in NLO and PDT.

With the unsymmetric alkyne linked dimers, again there was a Soret band split and also a significant bathochromic shift to approximately 730 nm (Figure 5). The split differs from that of the phenylacetylene linked arrays due to the less rigid geometry of the alkyne linker, thus allowing the dimer to adopt many different conformations. Also, as seen with the trimeric arrays, the Q-band absorbance of these dimers was more intense in comparison to their monomeric porphyrins. Emission spectra exhibited a significant bathochromic shift, again due to the increase in π-conjugation. Hence, these unsymmetrical dimeric arrays also have to potential to be used in optical applications.

Mass spectrometry

Mass spectrometry provides a useful tool for the structural elucidation of porphyrins.[43] The mass spectrometric analysis of compounds **118, 127, 132, 136, 151** and **152** gave unusual results. As shown in Figure 6, the spectra for dimer **127** and trimer **132** contained signals due to the parent ions of the compounds at m/z 1250 and 1773 respectively, confirming the elemental composition. However, the spectra also showed peaks due to the demetallated species which is not usually observed. Signals at 1187 and 1124 for dimer **127** and at 1711, 1647 and 1584 for trimer **132** correspond to sequential loss of zinc from the oligomers.

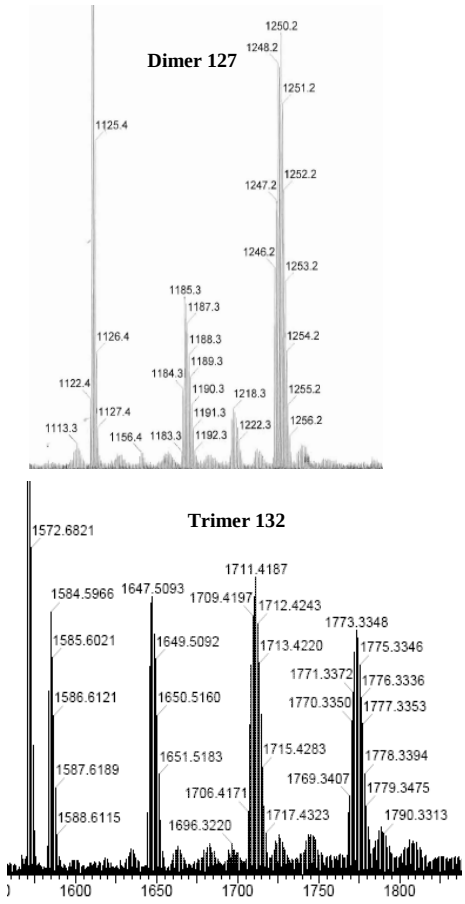


Figure 6. Mass spectra of **127** and **132** showing the loss of zinc from the porphyrin core.

Fragmentation of metalloporphyrins typically proceeds without loss of the metal ion, except in rare cases.[44] Studies utilizing MALDI-tof mass spectrometry showed loss of magnesium only for magnesium porphyrins which are considered the most labile metalloporphyrins. Studies on zinc porphyrin arrays, in particular, also show that there is no significant demetallation of the compounds.[45] A similar fragmentation was observed with dimers **118, 151** and **152**. Note, that this demetallation was not observed in the mass spectra of the butadiyne linked dimer **121**[38] and neither in the case of trimer **135**. This indicates that demetallation is affected both by the linker and the substituents on the porphyrin rings. Also, the nickel(II) trimer **133** did not exhibit any loss of nickel from its core, thereby illustrating that this fragmentation process is also metal dependent. The purity of all arrays was confirmed by ^{1}H-NMR analysis which shows that there is no demetallation in the analytes as no inner N-H signals were observed. This eliminates any possibility that losses in zinc were due to the presence of partially demetallated products in the analyte.

NLO properties

Similar to the concept outlined in the preceeding paper[6] selected dimers and trimers were investigated with regard to their NLO properties. Overall, the β_{eff} of dimers and trimers were in the same range as for the A_2BC-type monomers. For about 20 dimer and trimers investigated the range was β_{eff} 0.5–2.7×10^{-8} cm.W^{-1}. A detailed discussion of these data and comparison with the monomers has been given.[13b]

Conclusions

Porphyrin dimers and trimers were synthesized in moderate to good yields using Pd-mediated Glaser coupling reactions and copper-free Sonogashira coupling reactions. These provide a useful route towards the synthesis of such oligomers. Introduction of alkyl substituents into the periphery greatly enhanced the solubility and hence the yields. The uncapped oligomers with free meso positions allow for subsequent chemical modifications of the free meso positions.[14,46] All dimers and trimers exhibited a red shift in their UV/vis absorption and emission spectra compared to the monomers. In particular, the alkyne linked dimers showed strong absorption around 720 nm, making them good candidates for use as, e.g., possible photosensitizers in PDT and in other optical applications. With unsymmetrical dimers and trimers, amphiphilicity can be enhanced through the alteration of substitution patterns, and they also allow for the fine-tuning of optical properties which would enhance either their PDT or NLO effect. Unsymmetrical arrays are advantageous in that they may be constructed with both hydrophilic and lipophilic components for applications in PDT, or electron withdrawing and electron donating groups can be introduced to enhance NLO effects. In addition, the mass spectrometry of the phenylacetylene linked and diphenylbutadiyne linked oligomers exhibited an unusual demetallation pattern for the zinc(II) compounds. This novel fragmentation process is metal and substituent dependent.

Experimental Section

General methods: Solvents used, preparation of starting materials, spectroscopic instrumentation and analyses were performed as described in the preceeding paper.[6]

General procedure A – Bromination of porphyrins: This procedure was adapted from Boyle and coworkers.[19a] The porphyrin (1 eq.) was dissolved into $CHCl_3$ and NBS (0.8 - 2.1 eq.) and pyridine (0.1 mL) were added. The reaction progression was monitored by TLC using chloroform: hexane (1:1). The reaction was stopped when all the starting material was consumed. The mixture was then filtered through a silica gel plug and recrystallized using CH_2Cl_2/MeOH.

General procedure B – Zinc(II) insertion: Adapting a method by Buchler[28] porphyrin (1 eq.) was dissolved in $CHCl_3$ (25 - 50 mL) and heated to reflux at 60 °C for 10 min. Zinc(II) acetate (5 eq.) in MeOH (1 mL) was added and the reaction heated under reflux for 30 min. Following reaction completion, solvents were removed *in vacuo* and the residue was redissolved in CH_2Cl_2. This solution was passed through a plug of silica using CH_2Cl_2 as eluent. Solvents were removed *in vacuo* to give a pink/purple solid followed by recrystallization CH_2Cl_2/MeOH.

General Procedure C – Borylation of haloporphyrins: The borylation of haloporphyrins was carried out adapting a procedure by Fukuzumi and coworkers.[34] Bromoporphyrin (1 eq.) and $Pd(PPh_3)_4$ (0.2 eq.) were charged to a Schlenk flask and dried under high vacuum. 1,2-Dichloroethane (10 mL) and NEt_3 (180 µL) were then added and the solution was degassed via three freeze-pump-thaw cycles, before the flask was purged with argon. Pinacolborane (15 eq.) was then added and the flask was sealed and stirred at 90 °C. The reaction was followed by TLC using CH_2Cl_2:hexane (2:1, v/v). Once the starting material was consumed, the reaction was quenched with a saturated KCl solution (10 mL), washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was subjected to column chromatography using CH_2Cl_2:hexane (1:1).

General procedure D – Suzuki coupling: A Schlenk flask was charged with K_3PO_4 (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) were added. The reaction was heated to reflux for 7-10 hours (TLC control) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. This mixture was washed with saturated $NaHCO_3$, H_2O, and brine and then dried over Na_2SO_4. The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallization from dichloromethane/methanol to give the desired compound.

General procedure E – Suzuki coupling for the synthesis of directly-linked dimers: A Schlenk tube was charged with bromoporphyrin (1 eq.), porphyrinyl boronate (1 eq.) and Cs_2CO_3 (1.5 eq.) and dried under high vacuum. Dry DMF (1 mL) and dry toluene (2 mL) were then added, and the mixture was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (0.2 eq.) was then added, the flask sealed and stirred at 80 °C. The reaction was followed by TLC. Once the starting material was consumed, the reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over $MgSO_4$, evaporated to dryness, and subjected to column chromatography.

General Procedure F – Preparation of ethyne porphyrins via Sonogashira coupling: Bromoporphyrin (1 eq.), $PdCl_2(PPh_3)_2$ (0.2 eq.) and CuI (0.3 eq.) were added to a Schlenk flask and dried under high vacuum. The vacuum was released under argon to allow the addition of triethylamine (40 mL) and THF (10 mL). Argon was bubbled through the stirring solution for 10 min to deoxygenate via syringe. Trimethylsilylacetylene (10 eq.) was added, the flask was sealed and allowed to stir at room temperature. The reaction was followed by TLC using $CHCl_3$:hexane (1:2, v/v). Once the starting material was consumed, the solvent was removed *in vacuo* and the residue was dry-loaded onto silica using $CHCl_3$:hexane (1:3, v/v) as an eluant. The desired compound was collected and recrystallized using CH_2Cl_2/MeOH.

General procedure G – Sonogashira reaction: A degassed solution of 15 mL triethylamine and 5 mL THF was cooled to 0 °C. Porphyrin (1 equiv.), alkynyl substrate, CuI and $Pd(PPh_3)_2Cl_2$ were added. After 10 minutes, the cold bath was removed and the reaction mixture was stirred for another additional 2-5 hours. The reaction mixture was filtered through silica gel. The solvent was evaporated and the crude product was purified by flash column chromatography and recrystallization from dichloromethane and methanol.

General procedure H – Deprotection of trimethylsilyl alkynylporphyrins: Trimethylsilylethynylporphyrin (1 eq.) was dissolved in CH_2Cl_2 and TBAF (1M, 1 mL) was added. The reaction was followed by TLC using dichloromethane:hexane (1:1, v/v). Upon completion, the solution was filtered through a plug of silica using CH_2Cl_2 as eluent. Solvent was removed *in vacuo* and the residue recrystallized using $CHCl_3$/MeOH.

General procedure I – Reaction with organolithium reagents: The porphyrin was dissolved in 80 mL dry THF under an argon atmosphere and

the reaction mixture was cooled to -78 °C. *n*-BuLi (6 equiv.) was added dropwise over 15 minutes *via* syringe. The cold bath was removed and stirring continued 1.5 hours at room temperature. Next 0.5 mL H_2O was added and stirring continued for 15 min. Then DDQ (6 equiv.) was added in 10 ml THF and the reaction mixture was stirred for an additional hour. The reaction mixture was filtered through silica gel, followed by evaporation of the solvent. The crude reaction mixture was purified by column chromatography.

General procedure J – Copper-free Sonogashira coupling of porphyrin dimers: This procedure was adapted from a method by Wagner *et al*.[36a] Bromoporphyrin (1 eq.), ethynylporphyrin (1 eq.), $Pd_2(dba)_3$ (0.4 eq.) and $AsPh_3$ (1 eq.) were added to a Schlenk tube and dried under high vacuum. The flask was purged with argon and dry THF (10 mL) and NEt_3 (1 mL) were added. Argon was bubbled through the stirring solution for 10 min to deoxygenate via a syringe. The flask was sealed, and the reaction heated to 65 °C. The reaction was followed by TLC using dichloromethane:hexane (1:1, v/v). Once the starting material was consumed, the solvent was removed and the residue dry-loaded onto silica.

General procedure K – Copper-free Sonogashira coupling for porphyrin arrays: This procedure was adapted from a method by Wagner *et al.* [36a] For the synthesis of dimers **117-125** a 1:1 ratio of phenylethynylporphyrin : monobromoporphyrin was used. For the trimers **130-137** synthesis, mono-functionalized porphyrin (2.1 eq.) and difunctionalized porphyrin (1 eq.) were added to a Schlenk tube. To this $AsPh_3$ (2.1 eq.) and $Pd_2(dba)_3$ were added and the contents dried under high vacuum for 30 minutes and the flask was purged with argon. Dry THF (12 mL) and dry TEA (4 mL) were added and the solution was degassed *via* three freeze-pump-thaw cycles. The flask was then purged with argon, stirred, sealed and heated to 67 °C and left to stir overnight. The reaction was monitored by TLC analysis using CH_2Cl_2/*n*-hexane (1:1, v/v) as eluent. On consumption of starting materials the heat source was removed and the solvents removed *in vacuo*. The crude mixture was passed through a silica plug and solvents removed *in vacuo*. Column chromatography was then carried out using different eluents to yield the desired oligomer.

5,15-Dibromo-10,20-bis(1-ethylpropyl)porphyrin (11): Produced from porphyrin **3** (300 mg, 0.493 mmol) and NBS (184 mg, 1.036 mmol) following general procedure A, to yield purple the product **11** (356 mg, 0.585 mmol, 88%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = -2.34 (s, 2H, N*H*), 0.97 (t, 12H, $^3J_{H\text{-}H}$ = 9.9 Hz, CH_3), 2.81 (m, 4H, CH_2), 2.89 (m, 4H, CH_2), 4.92 (m, 2H, C*H*), 9.57 (d, 4H, $^3J_{H\text{-}H}$ = 2.9 Hz, H_β), 9.75 ppm (d, 4H, $^3J_{H\text{-}H}$ = 3.2 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.8, 24.4, 34.4, 50.0, 67.0, 124.4, 129.8, 133.1 ppm; UV/vis (THF): λ_{max} (log ε) = 422 (5.55), 524 (4.16), 558 (4.05), 606 (3.60), 664 nm (3.84); HRMS (Maldi) *m/z* calcd. for $C_{30}H_{33}N_4Br_2$ $[M+H]^+$ 607.1072 found 607.1066.

5-Bromo-10,20-bis(1-ethylpropyl)porphyrin (12): Produced from porphyrin **3** (300 mg, 0.665 mmol) and NBS (95 mg, 0.532 mmol) in 250 mL $CHCl_3$, following general procedure A to yield purple product **12** (190 mg, 0.358 mmol, 54%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = -2.48 (s, 2H, N*H*), 0.96 (t, 3H, $^3J_{H\text{-}H}$ =14.6 Hz, CH_3), 2.82 (m, 4H, CH_2), 3.05 (m, 4H, CH_2), 5.00 (m, 2H, C*H*), 9.34-9.35 (d, 2H, $^3J_{H\text{-}H}$ = 3.1 Hz, H_β), 9.66 (m, 4H, H_β), 9.87 (d, 4H, $^3J_{H\text{-}H}$ = 3.4 Hz, H_β), 10.11 ppm (s, 1H H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 14.0, 34.7, 50.4, 77.2, 124.8, 132.7 ppm; UV/vis: λ_{max} (log ε) = 414 (5.44), 514 (4.14), 546 (3.64), 592 (3.54), 648 nm (3.42); HRMS (Maldi) *m/z* calcd. for $C_{30}H_{34}N_4Br$ $[M+H]^+$ 529.1967, found 529.1967.

5-Bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-hexylporphyrin (16) Produced from **33** (75 mg, 0.097 mmol) and NBS (20 mg, 0.112 mmol) in 150 mL $CHCl_3$, following the general procedure A. After 50 min the solvent was removed *in vacuo* and the residue purified by column chromatography (silica, CH_2Cl_2/hexane, 1:2) to yield a purple solid. Yield: 75 mg (0.088 mmol, 91%). M.p.: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.64 (s, 2H, N*H*), 0.94-0.98 (t, 3H, $^3J_{H\text{-}H}$ = 14.5 Hz, CH_3), 1.41 (m, 2H, CH_2), 1.57 (s, 36H, *t*-butyl-*H*), 1.66 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 2.57 (m, 2H, CH_2), 4.99 (m, 2H, CH_2), 7.85 (m, 2H, Ph-*H*), 8.05-8.07 (d, 4H, $^3J_{H\text{-}H}$ = 1.5 Hz, Ph-*H*), 8.92 (m, 4H, H_β), 9.46-9.47 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 9.62-9.63 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.5, 20.9, 30.2, 34.9, 35.2, 38.7, 101.5, 121.0, 121.3, 121.4, 123.5, 124.7, 127.7, 128.3, 128.6, 128.7, 129.6, 134.2, 138.9, 140.9, 144.0, 146.5, 146.6, 148.6, 150.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.86), 486 (4.39), 557 (4.52), 659 nm (4.42); HRMS (ESI) *m/z* calcd. for $C_{54}H_{66}BrN_4$ $[M+H]^+$ 849.4471, found 849.4436.

5-Bromo-15-(3-methoxyphenyl)-10,20-diphenyl-porphyrin (19): Produced from **36** (100 mg, 0.176 mmol) and NBS (47 mg, 0.263 mmol) in 60 mL $CHCl_3$, following general procedure A to give purple product **19** (110 mg, 97%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.74 (2H, s, N*H*) 4.00 (3H, s, OCH_3), 7.34-7.36 (m, 1H, *p*-PhOMe-*H*), 7.66 (m, 1H, *m*-PhOMe-*H*) 7.76 (m, 8H, Ph-*H*), 8.21-8.23 (d, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, Ph-*H*) 8.81-8.83 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 8.87-8.88 (d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H_β), 8.92-8.93 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 9.69-9.71 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.3, 102.8, 113.5, 120.3, 130.5, 120.6, 126.6, 127.7, 134.4, 141.6, 143.0, 157.9 ppm. UV/Vis (THF): λ_{max} (log ε) = 419 (5.46), 517 (4.09), 550 (3.81), 595 (3.64), 655 nm (3.77); HRMS (Maldi) *m/z* calcd. for $C_{39}H_{27}BrON_4$ $[M]^+$ 646.1368, found 646.1368.

5-Bromo-10,15,20-tris(3-methoxyphenyl)porphyrin (21): Produced from **38** (157 mg, 0.25 mmol) and NBS (93 mg, 0.52 mmol) following general procedure A. Purple crystals were isolated as **21** (122 mg, 0.172 mmol, 69%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.75 (s, 2H, N*H*), 4.00 (s, 3H, OCH_3), 4.02 (s, 6H, OCH_3), 7.36 (m, 4H, Ph-*H*), 7.67 (m, 4H, Ph-*H*), 7.79 (m, 4H, Ph-*H*), 8.86 (s, 4H, H_β), 8.97 (d, 2H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.69 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.4, 55.5, 102.9, 113.6, 113.7, 120.4, 120.5, 120.6, 127.5, 127.6, 127.7, 131.9, 143.1, 143.2, 158.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.46), 517 (4.11), 553 (3.76), 595 (3.57), 652 nm (3.47); HRMS (ESI) *m/z* calcd. for $C_{41}H_{31}BrN_4O_3$ $[M+H]^+$ 707.1658, found 707.1655.

5-Bromo-10,15,20-tris(4-methoxyphenyl)porphyrin (22): Following general procedure A, **22** was produced from **40** (164 mg, 0.26 mmol) and NBS (70 mg, 0.39 mmol). Purple crystals were isolated (112 mg, 0.159 mmol, 61%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.74 (s, 2H, N*H*), 4.09 (s, 3H, OCH_3), 4.11 (s, 6H, OCH_3), 7.30 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 6H, Ph-*H*), 8.09 (m, 6H, Ph-*H*), 8.82 (s, 4H, H_β), 8.92 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.66 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.4, 55.5, 102.4, 112.2, 120.3, 120.7, 120.5, 134.1, 134.2, 135.2, 135.4, 135.5, 159.3, 159.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.56), 522 (4.20), 556 (4.02), 599 (3.71), 655 nm (3.81); HRMS (ESI) *m/z* calcd. for $C_{41}H_{31}BrN_4O_3$ $[M]^+$ 707.1658, found 707.1671.

5-Bromo-15-butyl-10,20-bis(4-methoxyphenyl)porphyrin (23): Produced from **41** (79 mg, 0.13 mmol) and NBS (46 mg, 0.26 mmol) using general procedure A. Purple crystals were isolated (50 mg, 0.070 mmol, 55%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.70 (s, 2H, N*H*) 1.12 (t, 3H, $^3J_{H\text{-}H}$ = 7.34 Hz, 5-CH_3), 1.80 (m, 2H, 3-CH_2), 2.50 (m, 2H, 2-CH_2), 4.12 (s, 6H, OCH_3), 4.97 (m, 2H, 1-CH_2), 7.30 (d, 5H, $^3J_{H\text{-}H}$ = 8.43 Hz, Ph-*H*), 8.09 (d, 5H, $^3J_{H\text{-}H}$ = 8.34 Hz, Ph-*H*), 8.88 (m, 4H, H_β), 9.44 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.59 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 23.6, 35.3, 40.8, 55.5, 55.6, 101.8, 112.2, 119.9, 121.5, 134.4, 135.4, 135.5, 159.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.33), 522 (4.01), 557 (3.79), 600 (3.45), 656 nm (3.57); HRMS (ESI) *m/z* calcd. for $C_{38}H_{33}BrN_4O_2$ $[M+H]^+$ 657.1865, found 657.1854.

5-Bromo-15-(4-ethynylphenyl)-10,20-diphenylporphyrin (24): Following the general procedure A, 10-(4-ethynylphenyl)-5,15-diphenylporphyrin **29** (100 mg, 0.177 mmol) and NBS (33 mg, 0.186 mmol) gave 105 mg (0.16 mmol, 92 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH; M.p. >300 ºC; R_f = 0.2 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.74 (s, 2H, N*H*), 3.34 (s, 1H, C≡C*H*), 7.81 (m, 6H, Ar-*H*), 7.91 (d, 2H, ^3J = 7.6 Hz, Ar-*H*), 8.17 (d, 2H, ^3J = 7.6 Hz, Ar-*H*), 8.21 (d, 4H, ^3J = 7.1 Hz, Ar-*H*), 8.82 (m, 4H, H_β), 8.93 (d, 2H, ^3J = 4.1 Hz, H_β), 9.70 ppm (d, 2H, ^3J = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 83.6, 103.2, 119.8, 120.9, 121.8, 126.7, 127.9, 130.6, 134.5, 141.7, 142.5 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 420 (4.87), 518 (3.45), 555 (3.13), 598 (2.69), 651 nm (2.57); HRMS (MS ES+) *m/z* calcd. for $[C_{40}H_{26}N_4Br]$ $(M+H^+)$: 641.1341; found 641.1343.

5-Bromo-15-(4-nitrophenyl)-10,20-diphenylporphyrin (25): Following the general procedure A, 10-(4-nitrophenyl)-5,15-diphenylporphyrin **57** (100 mg, 0.171 mmol) and NBS (32 mg, 0.179 mmol) gave 105 mg (0.16 mmol, 92 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. >300 ºC; R_f = 0.24 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.73 (s, 2H, N*H*), 7.82 (m, 6H, Ar-*H*), 8.21 (d, 4H, ^3J = 7.0 Hz, Ar-*H*), 8.38 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.65 (d, 2H, ^3J = 8.2 Hz, Ar-*H*), 8.72 (d, 2H, ^3J = 4.1 Hz, H_β), 8.87 (d, 2H, ^3J = 4.7 Hz, H_β), 8.94 (d, 2H, ^3J = 4.7 Hz, H_β), 9.71 ppm (d, 2H, ^3J = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.7, 104.1, 107.9, 117.3, 121.1, 121.8, 126.7, 127.9, 132.1, 134.4, 134.8, 141.3, 147.7, 148.7 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 421 (4.98), 518 (3.75), 555 (3.57), 599 (3.35), 651 nm (3.33); HRMS (MS ES+) *m/z* calcd. for $[C_{38}H_{25}N_5O_2Br]$ $(M+H^+)$: 662.1192; found 662.1179.

5,15-Bis(1-ethylpropyl)-10-(4-ethynylphenyl)porphyrin (30): A 100 ml Schlenk flask containing *p*-bromophenylethyne (0.91 g, 5.0 mmol) was dried under high vacuum and purged with argon. Dry diethyl ether (10 mL) was added to this solution and it was cooled down to -70 °C using a cold bath. *n*-BuLi (4 mL of a 2.5M solution in *n*-hexane, 10 mmol) was added

drop-wise to the flask over a period of one hour. The reaction mixture was then warmed to -40 °C and dry THF was added drop-wise until a white-pink suspension formed. A solution of 5,15-bis(1-ethylpropyl)porphyrin **3** (200 mg, 0.43 mmol) in dry THF (80 mL) was added rapidly to the vigorously stirred reaction mixture under argon. The reaction was left to stir for approximately 16 hours, forming a brown solution. Saturated NH_4Cl (2 mL) was then added and the solution turned bright green. DDQ was added and the solution turned red and was left to stir for a further one hour. The crude mixture was then filtered through a silica plug using CH_2Cl_2 as eluent. Solvents removed in vacuo and crude residue subjected to column chromatography using CH_2Cl_2:hexane (1:7, v/v) as eluent. Three fractions were obtained, the first being starting material **3**, the second was the desired product **30**, whilst the third was an inseparable mixture of mono and disubstituted butylated starting material **3**. Recrystallization of product **30** from CH_2Cl_2/MeOH yielded purple crystals (86 mg, 0.156 mmol, 35%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.46 (s, 2H, N*H*), 0.96-1.00 (t, 12H, CH_3), 2.83 (m, 4H, CH_2), 2.97 (m, 4H, CH_2), 3.37 (s, 1H, C≡C*H*), 5.05 (m, 2H, C*H*), 7.90-7.92 (d, 2H, $^3J_{H\text{-}H}$ = 5.2 Hz, Ph-*H*), 8.19-8.20 (d, 2H, $^3J_{H\text{-}H}$ = 5.2 Hz, Ph-*H*), 8.85-8.86 (d, 2H, $^3J_{H\text{-}H}$ = 2.2 Hz, H_β), 9.39-9.40 (d, 2H, $^3J_{H\text{-}H}$ = 2.2 Hz, H_β), 9.59-9.60 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 9.69-9.71 (d, 2H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_β), 10.16 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 29.6, 34.4, 49.8, 77.9, 83.7, 121.3, 122.5, 129.9, 131.4, 131.7, 134.0, 144.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 410 (5.51), 510 (4.26), 542 (3.70), 588 (3.66), 644 nm (3.38); HRMS (ESI) *m/z* calcd. for $C_{38}H_{39}N_4$ $[M+H]^+$ 551.3175, found 551.3170.

5-(4-Ethynylphenyl)-10,20-dihexylporphyrin (31): Following the procedure given for **30**, using *p*-bromophenylethyne (0.91 g, 5.0 mmol), *n*-BuLi (4 mL of a 2.5M solution in *n*-hexane, 10 mmol) and 5,15-dihexylporphyrin **2** (200 mg, 0.418 mmol) as the starting material. The desired product was isolated following column chromatography (CH_2Cl_2:hexane, 1:6, v/v) to yield two fractions, the starting material **2** and the desired product **31**, which upon recrystallization from CH_2Cl_2/MeOH gave purple crystals (72 mg, 0.125 mmol, 30%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.84 (s, 2H, N*H*), 0.90-0.92 (t, 6H, CH_3),1.42 (m, 4H, CH_2), 1.53 (m, 4H, CH_2), 2.55 (m, 4H, CH_2), 3.36 (s, 1H, C≡C*H*), 5.01 (m, 4H, C*H*), 7.91-7.93 (d, 2H, $^3J_{H\text{-}H}$ = 6.4 Hz, C_6H_4-*H*), 8.18-8.19 (d, 2H, $^3J_{H\text{-}H}$ = 6.2 Hz, C_6H_4-*H*), 8.89 (s, 2H, H_β), 9.40 (s, 2H, H_β), 9.48 (s, 2H, H_β), 9.59 (s, 2H, H_β), 10.11 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 25.6, 29.6, 30.1, 34.8, 38.5, 78.0, 83.7, 118.0, 119.4, 121.3, 127.4, 128.0, 130.1, 131.4, 131.6, 134.2, 143.7, 144.7, 147.2 ppm; UV/vis (THF): λ_{max} (log ε) = 411 (5.43), 511 (4.12), 542 (3.54), 592 (3.38), 644 nm (3.19); HRMS (ESI) *m/z* calcd. for $C_{40}H_{43}N_4$ $[M+H]^+$ 579.3488, found 579.3463.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-hexylporphyrin (33): 5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrin **4** (100 mg, 0.145 mmol) was dissolved in THF (40 mL) and cooled to -78 °C. *n*-Hexyllithium (2.5 M in hexane, 1.0 mL, 2.5 mmol) was added drop-wise over 30 min. After addition, the solution was stirred for 15 min at -78 °C before warming to room temperature. H_2O/THF (1:1, 5 mL) was added and stirring continued for 10 min. DDQ (329 mg, 1.45 mmol) was added and the solution stirred for 20 min. All solvents were removed, the brown residue dissolved in CH_2Cl_2 (20 mL) and filtered through a plug of silica. The purple solution was purified by column chromatography (silica, CH_2Cl_2/hexane, 1:2, v/v) to yield a purple solid. Yield: 84.1 mg (0.109 mmol, 75%). M.p. > 300 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = -2.91 (s, 2H, N*H*), 0.94-1.00 (t, 3H, CH_3), 1.49 (m, 4H, CH_2), 1.60 (s, 36H, *t*-butyl-*H*), 1.88 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 5.13 (m, 2H, CH_2), 7.82 (m, 2H, Ar-*H*), 8.14 (m, 4H, Ar-*H*), 9.04-9.08 (dd, 4H, $^3J_{H\text{-}H}$ = 12.3 Hz, H_β), 9.30-9.31 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.59-9.60 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.13 ppm (s, 1H, H_{meso}); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 13.9, 14.0, 30.2, 30.3, 34.9, 35.2, 121.1, 121.3, 128.6, 128.7, 128.9, 129.6, 134.2, 138.9, 140.8, 140.9, 144.0, 145.3, 146.5, 148.6, 148.7, 150.5 ppm; UV/Vis (THF): λ_{max} (log ε) = 413 (5.48), 510 (4.04), 544 (3.62), 588 (3.63), 644 nm (3.70); HRMS (ESI) *m/z* calcd. for $C_{94}H_{82}N_8$ $[M+H]^+$ 771.5366, found 771.5360.

5,15-Diphenyl-10-(3-methoxyphenyl)porphyrin (36): *n*-BuLi (12.97 mmol, 5.2 mL) was added slowly to a cooled (0 °C) solution of 3-bromoanisole (12.97 mmol, 1.64 mL) in freshly distilled diethyl ether (8 mL). After the addition was complete the reaction mixture was allowed to warm to room temperature. This mixture was then transferred to a cooled (-20 °C) solution of 5,15-diphenylporphyrin **1** (1.08 mmol, 500 mg), in freshly distilled THF (20 mL). The suspension was allowed to warm to room temperature and stirred for 19 hours. Water (6 mL) was added carefully and after 30 min DDQ (5.40 mmol, 1.23 g) was added. The mixture continued to stir for 1.5 h after which time the suspension was passed through a short column of silica gel and the product mixture was eluted with DCM. The solvents were removed under reduced pressure and the residue was purified using silica gel column chromatography (hexane/CH_2Cl_2, 1:1, v/v) to give purple solid after removal of solvents. Yield: (187 mg, 0.329 mmol, 30%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.97 (s, 2H, N*H*), 4.01 (s, 3H, OCH_3), 7.35-7.38 (m, 1H, *p*-PhOCH_3), 7.65-7.69 (t, 1H, $^3J_{H\text{-}H}$ = 15.6 Hz, *m*-PhOCH_3), 7.83 (m, 8H, Ph-*H*), 8.28 (m, 4H, Ph-*H*), 8.93-8.96 (m, 4H, H_β), 9.04-9.05 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.36-9.38 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β) 10.26 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.7, 21.3, 22.2, 28.9, 29.3, 31.1, 31.5, 55.0, 104.4, 113.1, 119.2, 119.7, 120.0, 126.4, 126.9, 127.3, 130.3, 131.0, 134.3, 141.3, 143.4, 146.7, 157.4 ppm; UV/Vis (THF): λ_{max} (log ε) = 411 (5.65), 508 (4.20), 541 (3.44), 581 (3.77), 640 nm (3.50); HRMS (ESI) *m/z* calcd. for $C_{39}H_{29}N_4O$ $[M]^+$ 568.2263, found 568.2254.

5,10,20-Tris(4-methoxyphenyl)porphyrin (40): *n*-BuLi (12.97 mmol, 5.2 mL) was added slowly to a cooled (0 °C) solution of 3-bromoanisole (12.97 mmol, 1.64 mL) in freshly distilled diethyl ether (8 mL). After the addition was complete the reaction mixture was allowed to warm to room temperature. This mixture was then transferred to a cooled (-20 °C) solution of 5,15-bis(4-methoxyphenyl)porphyrin **6** (1.08 mmol, 500 mg), in freshly distilled THF (20 mL). The suspension was allowed to warm to room temperature and stirred for 19 hours. Water (6 mL) was added carefully and after 30 min DDQ (5.40 mmol, 1.23 g) was added. The mixture continued to stir for 1.5 h after which time the suspension was passed through a short column of silica gel and the product mixture was eluted with CH_2Cl_2. The solvents were removed under reduced pressure and the residue was purified using silica gel column chromatography (hexane/ CH_2Cl_2, 1:1, v/v) to give purple solid **40** after removal of solvents (187 mg, 0.297 mmol, 31%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = -2.99 (s, br., 1H, N*H*), 4.04 (m, 6H, OCH_3) 4.13 (s, 3H, OCH_3), 7.37-7.39 (d, 2H, $^3J_{H\text{-}H}$ = 8.5 Hz, Ph-*H*), 7.70 (m, 2H, Ph-*H*), 7.83 (m, 4H, Ph-*H*), 8.14 (m, 4H, Ph-*H*), 8.92-8.93 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 8.96-8.97 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.08-9.09 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.36-9.37 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 10.24 ppm (s, 1H, H_{meso}); NMR data were in agreement with the literature.[47] UV/Vis (THF): λ_{max} (log ε) = 413 (5.58), 509 (4.14), 544 (3.50), 585 (3.69), 639 nm (3.54); HRMS (Maldi) *m/z* calcd. for $C_{41}H_{32}O_3N_4$ $[M]^+$ 628.2474, found 628.2482.

5-Butyl-10,20-bis(4-methoxyphenyl)porphyrin 41. This compound was isolated from the synthesis of **40**. It is a side-product coming from the direct reaction of butyllithium on **6**, to give a purple powder of **41.** Yield (183 mg, 0.316 mmol, 33%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.99 (s, br., 1H, N*H*), 1.14 (d, 3H, $^3J_{H\text{-}H}$ = 7.4 Hz, CH_3), 1.87-1.79 (m, 2H, CH_2), 2.59-2.51 (m, 2H, CH_2), 4.13 (s, 6H, OCH_3), 5.14-5.05 (m, 2H, CH_2), 7.32 (d, 3H, $^3J_{H\text{-}H}$ = 8.5 Hz, Ph-*H*), 8.15 (d, 3H, $^3J_{H\text{-}H}$ = 8.5 Hz, Ph-*H*), 8.99 (t, 3H, $^3J_{H\text{-}H}$ = 5.1 Hz, H_β), 9.29-9.23 (m, 2H, H_β), 9.57-9.52 (m, 2H, H_β), 10.09 ppm (s, 1H, H_{meso}); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.5, 23.8, 29.9, 31.8, 35.6, 41.1, 55.6, 112.4, 118.8, 134.2, 135.6, 135.7, 159.6 ppm; HRMS (ESI) *m/z* calcd. for $C_{41}H_{33}N_4O_3$ $[M+H]^+$ 629.2553, found 629.2541.

5-Butyl-10,20-bis(4-methylphenyl)porphyrin (42): Following the general procedure I, 5,15-bis(4-methylphenyl)porphyrin **7** (245 mg, 0.49 mmol), *n*-BuLi (1.19 mL, 2.99 mmol), H_2O 0.5 mL and DDQ (445 mg, 1.96 mmol) were used. The crude reaction mixture was purified by column chromatography using *n*-hexane : ethyl acetate = 20 : 1 (v/v), and gave the desired product (267 mg, 0.44 mmol, 61 %) as purple crystals. M.p. > 300 ºC; R_f = 0.5 (*n*-hexane : ethyl acetate = 20 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, 3H, $^3J_{H\text{-}H}$ = 7.1 Hz, $CH_2CH_2CH_2CH_3$), 1.90 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.60 (m, 2H, $CH_2CH_2CH_2CH_3$), 5.13 (t, 2H, $^3J_{H\text{-}H}$ = 5.3 Hz, $CH_2CH_2CH_2CH_3$), 7.65 (d, 4H, $^3J_{H\text{-}H}$ = 8.2 Hz, Ar-*H*), 8.14 (d, 4H, $^3J_{H\text{-}H}$ = 7.6 Hz, Ar-*H*), 9.08 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.10 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.39 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.69 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.18 ppm (s, 1H, H_{meso}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 21.3, 23.6, 35.4, 41.0, 104.8, 119.8, 121.7, 127.9, 128.6, 131.1, 131.9, 132.4, 136.8, 139.2, 149.5, 149.6, 149.7, 149.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε)= 415 (5.07), 452 (3.39), 544 nm (3.73); HRMS (MS ES+) *m/z* calcd. for $[C_{38}H_{32}N_4Zn]$ $(M+H^+)$: 608.1891; found 608.1918.

5,15-Bis(3-methoxyphenyl)-10,20-diphenylporphyrin (43): This compound was isolated as a tetrasubstituted side product from the organolithium reaction to synthesize **36**, as a purple powder (21 mg, 0.031 mmol, 4%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.77 (s, 2H, N*H*), 4.01 (s, 6H, OCH_3), 7.34-7.35 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, *p*-PhOCH_3), 7.36-7.37 (d, 1H, $^3J_{H\text{-}H}$ = 2.4 Hz, *p*-PhOCH_3), 7.65-7.69 (t, 2H, $^3J_{H\text{-}H}$ = 15.2 Hz, *m*-PhOCH_3), 7.79 (m, 10H, Ph-*H*), 8.24-8.25 (d, 4H, $^3J_{H\text{-}H}$ = 5.8 Hz, *o*-Ph-*H*), 8.86-8.87 (d, 4H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 8.91-8.92 ppm (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.3, 55.8, 113.6, 115.6, 120.3, 122.2, 122.4, 124.2, 126.5, 127.3, 127.7, 127.8, 128.2, 128.9, 129.8, 131.7, 134.4, 138.8, 139.7, 143.3, 145.8, 145.9, 157.8, 159.1 ppm; UV/Vis (THF): λ_{max} (log ε) = 417 (5.41), 513 (4.05), 547 (3.73), 588 (3.71), 647 nm (3.66); HRMS (ESI) *m/z* calcd. for $C_{39}H_{29}N_4O$ $[M+H]^+$ 675.2760, found 675.2748.

{5,15-Dibromo-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (49): Produced from porphyrin **11** (200 mg, 0.329 mmol) dissolved in $CHCl_3$ (40 mL) and $Zn(OAc)_2$ (301 mg, 1.645 mmol), following general procedure B to yield pink crystals (194 mg, 0.289 mmol, 88%,). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.93 (t, 12H, C*H*$_3$), 2.81 (m, 4H, C*H*$_2$), 2.96 (m, 4H, C*H*$_2$), 5.06 (m, 2H, C*H*), 9.57 (m, 4H, H_β), 9.69 ppm (m, 4H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 34.4, 50.4, 77.2, 124.8, 131.2 132.7 ppm; UV/vis (THF): λ_{max} (log ε) = 428 (5.58), 566 (4.02), 614 nm (3.94); HRMS (Maldi) *m/z* calcd. for $C_{30}H_{30}N_4ZnBr_2$ $[M]^+$ 668.0129, found 668.0136.

{5-Bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-hexylporphyrinato}zinc(II) (51): Produced from **16** (110 mg, 0.132 mmol) dissolved in $CHCl_3$ (25 mL) and zinc(II)acetate (130 mg, 0.6 mmol) dissolved in methanol (2 mL), following general procedure **B,** to give a bright purple solid (106 mg, 0.117 mmol, 90%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 1.54 (s, 36H, *t*-butyl-*H*), 7.81-7.83 (m, 2H, Ph-*H*), 8.03-8.09 (m, 4H, Ph-*H*), 9.02-9.03 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.05-9.06 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.59-9.60 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.74-9.75 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 22.7, 29.7, 30.5, 31.5, 31.8, 39.1, 46.5, 119.4, 120.9, 122.4, 122.5, 123.3, 128.8, 129.1, 129.7, 130.8, 132.4, 132.9, 133.5, 136.8, 141.6, 148.7, 149.7, 150.2, 150.5, 150.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 426 (5.62), 557 (4.44), 642 nm (4.12); HRMS (ESI) *m/z* calcd. for $C_{54}H_{63}BrN_4Zn$ $[M+H]^+$ 911.3606, found 911. 3769.

{5-Bromo-10,20-diphenyl-15-hexylporphyrinato}zinc(II) (53): Produced from **18**[5d] (100 mg, 0.159 mmol) dissolved in $CHCl_3$ (25 mL) and zinc(II)acetate (170 mg, 0.795 mmol) dissolved in methanol (2 mL), according to standard procedure B to give a purple solid (92 mg, 0.133 mmol, 84%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.94 - 0.97 (t, 3H, $^3J_{H\text{-}H}$ = 12.8 Hz, C*H*$_3$), 1.40 (m, 2H, C*H*$_2$), 1.51 (m, 2H, C*H*$_2$), 1.82 (m, 2H, C*H*$_2$), 2.54 (m, 2H, C*H*$_2$), 4.98 (m, 2H, C*H*$_2$), 7.81 (m, 6H, Ph-*H*), 8.19-8.21 (d, 4H, $^3J_{H\text{-}H}$ = 7.9 Hz, Ph-*H*), 8.88 (m, 4H, H_β), 9.46-9.47 (d, 2H, $^3J_{H\text{-}H}$ = 3.3 Hz, H_β), 9.61-9.62 ppm (d, 2H, $^3J_{H\text{-}H}$ = 3.2 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 22.8, 29.8, 30.4, 31.9, 35.4, 38.9, 120.9, 122.1, 126.6, 127.6, 128.8, 132.3, 132.4, 133.0, 134.5, 142.4, 149.5, 149.6, 149.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.33), 557 (3.79), 646 nm (3.57); HRMS (Maldi) *m/z* calcd. for $C_{38}H_{31}BrN_4Zn$ $[M]^+$ 686.1024, found 686. 1027.

{5-(4-Ethynylphenyl)-10,20-diphenylporphyrinato}nickel(II) (54): Porphyrin **29**[14a] (100 mg, 0.178 mmol) and $Ni(acac)_2$ (49 mg, 0.191 mmol) were dissolved in toluene (75 mL) in a 100 mL flask and heated at reflux for 3 hours. The solvent was then removed *in vacuo* and product isolated after filtering the redissolved residue through a plug of silica gel using CH_2Cl_2 as eluent. Recrystallization of the product using CH_2Cl_2/MeOH yielded red-purple crystals (199 mg, 90%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31 (s, 1H, C≡C*H*), 7.74 (m, 6H, Ph-*H*), 7.83-7.85 (d, 2H, $^3J_{H\text{-}H}$ = 7.9 Hz, C_6H_4-*H*), 8.01-8.03 (d, 2H, $^3J_{H\text{-}H}$ = 8.0 Hz, C_6H_4-*H*), 8.05-8.07 (d, 2H, $^3J_{H\text{-}H}$ = 7.0 Hz, Ph-*H*), 8.77-8.78 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 8.82-8.83 (d, 2H, $^3J_{H\text{-}H}$ = 5.0 Hz, H_β), 8.91-8.92 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 9.15-9.16 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 9.85 ppm (s, 1H, H_{meso}); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 83.4, 104.6, 118.2, 121.5, 126.7, 127.6, 130.5, 131.6, 132.1, 132.3, 132.5, 133.5, 140.7, 141.6, 141.9, 142.7, 142.8 ppm; UV/vis (THF): λ_{max} (log ε) = 407 (5.46), 521 (4.29), 557 nm (3.60); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{24}N_4Ni$ $[M]^+$ 618.1354, found 618.1380.

{5,15-Bis(1-ethylpropyl)-10-(4-ethynylphenyl)porphyrinato}zinc(II) (55): Produced from porphyrin **30** (100 mg, 0.181 mmol) dissolved in $CHCl_3$ and $Zn(OAc)_2$ (166 mg, 0.907 mmol), following standard procedure B to yield purple crystals (90 mg, 0.147 mmol, 81%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.98-1.02 (t, 12H, $^3J_{H\text{-}H}$ = 14.6 Hz, C*H*$_3$), 2.88 (m, 4H, C*H*$_2$), 3.05 (m, 4H, C*H*$_2$), 3.37 (s, 1H, C≡C*H*), 5.21 (m, 2H, C*H*), 7.94-7.96 (d, 2H, $^3J_{H\text{-}H}$ = 8.0 Hz, Ph-*H*), 8.24-8.26 (d, 2H, $^3J_{H\text{-}H}$ = 6.1 Hz, Ph-*H*), 9.01-9.03 (d, 2H, $^3J_{H\text{-}H}$ = 7.4 Hz, H_β), 9.37 (d, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, H_β), 9.85 (m, 4H, H_β), 10.19 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 29.7, 34.9, 50.5, 77.2, 77.8, 86.5, 123.0, 131.0, 131.3, 131.5, 134.3 ppm; UV/vis (THF): λ_{max} (log ε) = 420 (5.73), 554 (4.31), 594 nm (3.64); HRMS (Maldi) *m/z* calcd. for $C_{38}H_{37}N_4Zn$ $[M+H]^+$ 613.2310, found 613.2297.

5-(4-Nitrophenyl)-10,20-diphenylporphyrin (57): Following the general procedure D, 5-bromo-10,20-diphenylporphyrin **9** (150 mg, 0.277 mmol), K_3PO_4 (1469 mg, 6.92 mmol), 4-nitrophenyl boronic pinacol ester (862 mg, 3.462 mmol) and $Pd(PPh_3)_4$ (32 mg, 0.028 mmol) gave 138 mg (0.236 mmol, 85 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. > 300 ºC; R_f = 0.42 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -3.00 (s, 2H, N*H*), 7.83 (m, 6H, Ar-*H*), 8.27 (d, 4H, ^3J = 7.0, 8.8 Hz, Ar-*H*), 8.42 (d, 2H, ^3J = 8.2, 8.8 Hz, Ar-*H*), 8.65 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.79 (d, 2H, ^3J = 4.7 Hz, H_β), 8.98 (d, 2H, ^3J = 4.7 Hz, H_β), 9.07 (d, 2H, ^3J = 4.7 Hz, H_β), 9.39 (d, 2H, ^3J = 4.7 Hz, H_β), 10.29 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 105.2, 116.6, 117.0, 120.7, 120.9, 121.5, 125.4, 126.4, 127.2, 127.6, 130.1, 131.2, 134.7, 141.1, 144.4, 145.4, 146.3, 147.3, 148.5, 149.2 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 414 (4.88), 511 (3.66), 544 (3.22), 581 (3.23), 637 nm (2.71); HRMS (MS ES+) *m/z* calcd. for $[C_{38}H_{26}N_5O_2]$ $(M+H^+)$: 584.2087; found 584.2093.

5-(4-Ethynylphenyl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin (58): Following the general procedure D, 5-bromo-15-(4-ethynylphenyl)-10,20-diphenylporphyrin **24** (100 mg, 0.155 mmol), K_3PO_4 (827 mg, 3.896 mmol), 4-nitrophenyl boronic pinacol ester (480 mg, 1.93 mmol) and $Pd(PPh_3)_4$ (18 mg, 0.0155 mmol) gave 35 mg (0.051 mmol, 33 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. >300 ºC; R_f = 0.42 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.77 (s, 2H, N*H*), 3.35 (s, 1H, C≡C*H*), 7.80 (m, 6H, Ar-*H*), 7.93 (d, 2H, ^3J = 8.19 Hz, Ar-*H*), 8.22 (t, 6H, ^3J = 8.2 Hz, Ar-*H*), 8.42 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.67 (d, 2H, ^3J = 8.2 Hz, Ar-*H*), 8.77(d, 2H, ^3J = 4.7 Hz, H_β), 8.86 (d, 2H, ^3J = 4.7 Hz, H_β), 8.91 ppm (m, 4H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 83.6, 121.9, 126.7, 127.8, 128.5, 130.0, 130.6, 131.8, 134.4, 134.7, 135.1 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 419 (4.91), 515 (3.69), 551 (3.48), 592 (3.36), 645 nm (3.31); HRMS (MS ES+) *m/z* calcd. for $[C_{46}H_{30}N_5O_2]$ $(M+H^+)$: 684.2400; found 684.2391.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-trimethylsilanylethynylporphyrin (62): Produced from 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylprophyrin **15** (180 mg, 0.214 mmol), $PdCl_2(PPh_3)_2$ (10.0 mg, 0.143 mmol), CuI (4.0 mg, 5.3 mmol) and ethynyl(trimethyl)silane (0.20 g, 2.04 mmol) according to procedure F. All solvents were removed and the brown residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:2, v/v) to yield a purple solid (154 mg, 0.179 mmol, 83%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.32 (s, 2H, N*H*), 0.60 (s, 9H, Si(C*H*$_3$)$_3$), 1.54 (s, 36H, *t*-Bu*H*), 7.76 (m, 3H, Ph-*H*), 7.84 (m, 2H, Ar-*H*), 8.09 (d, 4H, $^3J_{H\text{-}H}$ = 1.5 Hz, Ar-*H*), 8.20-8.21 (d, 2H, $^3J_{H\text{-}H}$ = 6.6 Hz, Ph-*H*), 8.78-8.79 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 8.83-8.84 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 8.95-8.96 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 9.69-9.70 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.6, 34.9, 98.5, 101.5, 107.2, 121.0, 121.8, 122.3, 126.6, 127.7, 129.7, 134.1, 140.6, 142.1, 148.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 428 (5.12), 529 (3.73), 566 (3.88), 602 (3.35), 663 nm (3.51); HRMS (ESI) *m/z* calcd. for $C_{59}H_{67}N_4Si$ $[M+H]^+$ 859.5135, found 859.5145.

{5,15-Bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-trimethylsilanylethynylporphyrinato}zinc(II) (63): Produced from **{**5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrinato}zinc(II) **50** (50.0 mg, 55.2 µmol), $PdCl_2(PPh_3)_2$ (20.0 mg, 28.6 µmol), CuI (5.0 mg, 26.2 µmol) and ethynyl(trimethyl)silane (0.20 g, 2.04 mmol) following general procedure F. All solvents were removed and the brown residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:3, v/v) to yield a purple solid (23.2 mg, 25.4 µmol, 46%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 0.64 (s, 9H, Si(C*H*$_3$)$_3$), 1.58 (s, 36H, *t*-Bu*H*), 7.77 (m, 3H, Ar-*H*), 7.85 (m, 2H, Ar-*H*), 8.10-8.11 (d, 4H, $^3J_{H\text{-}H}$ = 1.7 Hz, Ph-*H*), 8.21-8.22 (d, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, Ph-*H*), 8.90-8.91 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 8.95-8.96 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.06-9.07 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.80-9.81 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.7, 35.0, 120.9, 122.7, 123.4, 126.5, 127.5, 129.7, 130.9, 132.1, 133.2, 134.2, 141.4, 148.7, 149.8, 150.3, 150.8, 152.5 ppm; UV/vis (THF): λ_{max} (log ε) = 433 (5.49), 569 (4.09), 613 nm (4.13); HRMS (Maldi) *m/z* calcd. for $C_{59}H_{64}N_4SiZn$ $[M]^+$ 920.4192, found 920.4191.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-hexyl-20-(trimethylsilyl)ethynylporphyrin (64): Following general procedure F**,** using bromoporphyrin **15** (65 mg, 0.076 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.029 mmol), CuI (10.0 mg, 0.052 mmol) and ethynyl(trimethyl)silane (0.20 g, 2.04 mmol). The solution was stirred for 20 h at 50 °C. All solvents were removed and the brown residue purified by column chromatography (silica gel, CH_2Cl_2:hexane, 1:3, v/v) to yield a purple solid (23 mg, 25.4 µmol, 36%). Mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.29 (s, 2H, N*H*), 0.61 (s, 9H, Si(C*H*$_3$)$_3$), 0.94-0.98 (t, 3H, $^3J_{H\text{-}H}$ = 14.6 Hz, C*H*$_3$), 1.43 (m, 4H, C*H*$_2$), 1.57 (s, 36H, *t*-Bu*H*), 1.85 (m, 2H, C*H*$_2$), 2.56 (m, 2H, C*H*$_2$), 4.99 (t, 2H, $^3J_{H\text{-}H}$ = 16.4 Hz, C*H*$_2$), 7.84 (m, 2H, Ar-*H*), 8.78-8.81 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, Ar-*H*), 8.90 (m, 4H, H_β), 9.44-9.45 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.60-9.61 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 14.4, 22.6, 30.3, 31.6, 34.8, 38.9, 97.6, 101.1, 107.2, 120.9, 121.5, 121.9, 122.5, 129.5, 134.0, 141.0, 148.3, 150.6 ppm; UV/vis (THF): λ_{max} (log ε) = 424 (5.15), 527 (3.71), 565 (3.78), 607 (3.33), 665 nm (3.53); HRMS (Maldi) *m/z* calcd. for $C_{59}H_{74}N_4Si$ $[M]^+$ 866.5683, found 866.5677.

5-(3-Methoxyphenyl)-10,20-diphenyl-15-trimethylsilanylethynylporphyrin (66): Following general procedure F**,**

using bromoporphyrin **19** (120 mg, 0.185 mmol), $PdCl_2(PPh_3)_2$ (19.5 mg, 0.028 mmol), CuI (8.8 mg, 0.047 mmol) and ethynyl(trimethyl)silane (0.26 mL, 1.85 mmol). The solution was stirred for 12 h at 50 °C. All solvents removed and residue purified via column chromatography (silica, CH_2Cl_2:hexane, 1:2, v/v) to yield a purple product as the main fraction. Yield 59.2 mg (0.089 mmol, 48%). Mp: > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = -2.39 (s, 2H, N*H*), 0.65 (s, 9H, Si(CH_3)$_3$) 4.00 (s, 3H, OCH_3), 7.34-7.36 (dd, 1H, $^3J_{H\text{-}H}$ = 2.5 Hz, Ar-*H*), 7.64-7.67 (t, 2H, $^3J_{H\text{-}H}$ = 15.8 Hz, Ar-*H*), 7.81 (m, 8H, Ar-*H*), 8.23-8.24 (d, 4H, $^3J_{H\text{-}H}$ = 6.5 Hz, Ph-*H*), 8.79-8.80 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 8.85-8.86 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 8.92-8.93 (d, 2H, $^3J_{H\text{-}H}$ = 4.4 Hz, H_β), 9.69-9.70 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 13.9, 22.5, 29.6, 31.4, 55.3, 98.9, 101.8, 106.9, 113.5, 120.2, 120.9, 121.5, 126.6, 127.4, 127.7, 130.9, 134.4, 141.5, 143.1, 157.8 ppm; UV/vis (THF): λ_{max} (log ε) = 427 (5.27), 525 (3.90), 563 (4.02), 602 (3.43), 654 nm (3.35); HRMS (ESI) *m/z* calcd. for $C_{44}H_{37}N_4OSi$ $[M+H]^+$ 665.2737, found 665.2759.

5-(4-Nitrophenyl)-15-trimethylsilanylethynyl-10,20-diphenylporphyrin (67): Following the general procedure G, 5-bromo-15-(4-nitrophenyl)-10,20-diphenylporphyrin **25** (60 mg, 0.090 mmol), ethynyltrimethylsilane (0.14 mL, 0.1 mmol), CuI (4 mg, 0.023 mmol) and $Pd(PPh_3)_2Cl_2$ (6 mg, 0.009 mmol) gave 40 mg (0.058 mmol, 65 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. >300 ºC; R_f = 0.2 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.44 (s, 2H, N*H*), 0.63 (s, 9H, Si(CH_3)$_3$), 7.81 (m, 6H, Ar-*H*), 8.21 (d, 4H, ^3J = 7.8 Hz, Ar-*H*), 8.38 (d, 2H, ^3J = 7.8 Hz, Ar-*H*), 8.65 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.69 (d, 2H, ^3J = 4.9 Hz, H_β), 8.83 (d, 2H, ^3J = 4.7 Hz, H_β), 8.93 (d, 2H, ^3J = 4.9 Hz, H_β), 9.70 ppm (d, 2H, ^3J = 4.9 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.2, 99.5, 102.1, 117.9, 121.0, 121.4, 126.4, 127.6, 134.1, 134.5, 140.9, 147.3, 148.5 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 429 (4.87), 528 (3.55), 566 (3.70), 605 (3.30), 661 nm (3.40); HRMS (MS ES+) *m/z* calcd. for $[C_{43}H_{34}N_5O_2Si]$ $(M+H^+)$: 680.2482; found 680.2493.

5-Ethynyl-10,15,20-triphenylporphyrin (69): Produced from **59** (43 mg, 0.08 mmol) following general procedure H. Purple crystals were isolated (27 mg, 0.05 mmol, 61%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.49 (s, 2H, N*H*), 4.19 (s, 1H, C*H*), 7.76 (m, 9H, Ph-*H*), 8.25-8.14 (m, 6H, Ph-*H*), 8.78 (d, 4H, $^3J_{H\text{-}H}$ = 5.7 Hz, H_β), 8.91 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 9.69 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 53.2, 83.8, 85.4, 97.3, 120.9, 122.1, 126.5, 126.6, 127.7, 130.8, 134.2, 134.3, 141.5, 141.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 425 (5.56), 525 (4.28), 560 (4.17), 599 (3.73), 655 nm (3.71); HRMS (ESI) *m/z* calcd. for $C_{40}H_{27}N_4$ $[M+H]^+$ 563.2236, found 563.2231.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin (71): Produced from 5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-(trimethylsilyl)ethynylporphyrin **62** (130 mg, 0.151 mmol) in CH_2Cl_2 (80 mL) and TBAF in THF (1 M, 0.5 mL, 0.5 mmol) following general procedure H. After 20 min, the solution was filtered through a plug of silica and washed with CH_2Cl_2 (50 mL). All solvents were removed to yield a purple solid. Yield: 112 mg (0.142 mmol, 94%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = -2.37 (s, 2H, N*H*), 1.51 (s, 36H, *t*-Bu*H*), 4.19 (s, 1H, C≡C-*H*), 7.70-7.80 (m, 3H, Ph-*H*), 7.81-7.83 (m, 2H, Ph-*H*), 8.05-8.09 (m, 4H, Ph-*H*), 8.18-8.21 (m, 2H, Ph-*H*), 8.79 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.82 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.97 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.70 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.6, 34.9, 83.6, 85.7, 121.1, 121.8, 122.3, 126.5, 127.7, 129.8, 134.2, 140.5, 142.0, 148.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 427 (5.79), 527 (4.39), 562 (4.36), 602 (3.93), 659 nm (4.00); HRMS (ESI) *m/z* calcd. for $C_{56}H_{59}N_4$ $[M+H]^+$ 787.4727, found 787.4740.

{5,15-Bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrinato}zinc(II) (72): Following general procedure H, **72** was produced from {5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-(trimethylsilyl)ethynylporphyrinato}zinc(II) **63** (100 mg, 0.117 mmol) in CH_2Cl_2 (30 mL) and TBAF in THF (1 M, 0.5 mL, 0.500 mmol). After stirring for 20 min the solution was filtered through a plug of silica and washed with CH_2Cl_2. All solvents were removed *in vacuo* to yield a purple solid. Yield: 86 mg (0.109 mmol, 94%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 1.59 (s, 36H, *t*-Bu*H*), 4.09 (s, 1H, C≡C-*H*), 7.78 (m, 3H, Ph-*H*), 7.86 (m, 2H, Ar-*H*), 8.12-8.13 (d, 4H, $^3J_{H\text{-}H}$ = 1.7 Hz, Ar-*H*), 8.22-8.23 (d, 2H, $^3J_{H\text{-}H}$ = 6.5 Hz, Ph-*H*), 8.93-8.94 (d, 2H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 8.97-8.98 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.08-9.09 (d, 2H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.76-9.77 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.0, 29.5, 30.2, 31.6, 34.9, 83.1, 86.0, 97.8, 120.8, 122.7, 123.2, 125.4, 126.4, 127.4, 128.1, 129.6, 130.6, 132.0, 133.3, 134.1, 135.6, 141.3, 142.5, 148.6, 149.7, 150.2, 150.8, 151.4, 152.5 ppm; UV/Vis (THF): λ_{max} (log ε) = 429 (5.31), 566 (3.91), 608 nm (3.76); HRMS (ESI) *m/z* calcd. for $C_{56}H_{59}N_4$ $[M]^+$ 848.3796, found 848.3836.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-hexylporphyrin (73): Produced from 5,15-bis(3,5-di-*tert*-butylphenyl)-10-hexyl-20-(trimethylsilyl)ethynylporphyrin **64** (23 mg, 0.025 mmol) in CH_2Cl_2 (10 mL) and TBAF in THF (1 M, 0.1 mL, 0.1 mmol) following general procedure H. After stirring for 20 min, the solution was filtered through a plug of silica and washed with CH_2Cl_2 (50 mL). All solvents were removed to yield a purple solid. Yield: 20 mg (0.023 mmol, 93%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.33 (s, 2H, N*H*), 0.94-0.98 (t, 3H, $^3J_{H\text{-}H}$ = 14.5 Hz, CH_3), 1.42 (m, 4H, CH_2), 1.58 (s, 36H, *t*-Bu*H*), 1.86 (m, 2H, CH_2), 2.57 (m, 2H, CH_2), 4.17 (s, 1H, C≡C*H*), 5.00 (m, 2H, CH_2), 7.84 (s, 4H, Ar-*H*), 8.07 (m, 2H, Ar-*H*), 8.91 (m, 4H, H_β), 9.45-9.46 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.63-9.64 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 13.9, 22.6, 30.2, 31.7, 34.9, 35.7, 38.7, 83.3, 35.6, 96.2, 120.9, 121.7, 122.7, 129.5, 129.6, 140.8, 148.7 ppm; UV/vis (THF): λ_{max} (log ε) = 428 (5.48), 525 (4.10), 562 (4.14), 603 (3.69), 661 nm (3.79); HRMS (ESI) *m/z* calcd. for $C_{56}H_{67}N_4$ $[M+H]^+$ 795.5366, found 795.5378.

5,15-Diphenyl-10-ethynyl-20-(3-methoxyphenyl)porphyrin (75): Produced from trimethylsilylethynyl porphyrin **66** (25 mg, 0.038 mmol) following the general procedure H to yield a purple solid (20 mg, 0.034 mmol, 90%). Mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.45 (s, 2H, N*H*), 4.00 (s, 3H, OCH_3), 4.22 (s, 1H, C≡C*H*), 7.35-7.37 (m, 3H, Ar-*H*), 7.64-7.68 (m, 2H, Ar-*H*), 7.81 (m, 6H, Ph-*H*), 8.22-8.24 (d, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, Ph-*H*), 8.79-8.80 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.85-8.86 (d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H_β), 8.93-8.94 (d, 2H, $^3J_{H\text{-}H}$ = 4.0 Hz, H_β), 9.71-9.72 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.1 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.5, 29.6, 30.2, 34.1, 55.6, 37.8, 83.8, 85.4, 97.4, 112.5, 120.3, 120.9, 121.7, 125.4, 126.7, 127.4, 127.7, 131.1, 134.4, 135.7, 141.5, 143.1, 157.8 ppm; UV/vis (THF): λ_{max} (log ε) = 423 (5.58), 523 (4.19), 558 (4.13), 601 (3.66), 662 nm (3.38); HRMS (ESI) *m/z* calcd. for $C_{41}H_{29}N_4O$ $[M+H]^+$ 593.2327, found 593.2341.

5-Ethynyl-15-(4-nitrophenyl)-10,20-diphenylporphyrin (76): Following the procedure H 0.1 mL of 1 M solution of TBAF in THF was added to a solution of 5-(4-nitrophenyl)-15-trimethylsilanylethynyl-10,20-diphenylporphyrin **67** (40 mg, 0.059 mmol) in 20 mL CH_2Cl_2. The reaction mixture was stirred for 20 minutes and the crude product was purified by recrystallization from CH_2Cl_2/MeOH to give 33 mg (0.054 mmol, 92 %) of a purple solid. M.p. >300 ºC; R_f = 0.4 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.49 (s, 2H, N*H*), 4.24 (s, 1H, C≡C*H*), 7.82 (m, 6H, Ar-*H*), 8.22 (d, 4H, ^3J = 6.4 Hz, Ar-*H*), 8.39 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.65 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.70 (d, 2H, ^3J = 4.7 Hz, H_β), 8.85 (d, 2H, ^3J = 4.7 Hz, H_β), 8.96 (d, 2H, ^3J = 4.9 Hz, H_β), 9.73 ppm (d, 2H, ^3J = 4.9 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 84.3, 98.3, 107.8, 112.9, 118.4, 121.3, 121.7, 126.4, 126.7, 127.8, 130.3, 134.8, 141.2, 147.7, 148.8 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 426 (4.85), 524 (3.56), 561 (3.54), 599 (3.23), 673 nm (2.83); HRMS *m/z* calcd. for $[C_{40}H_{23}N_5O_2]$: 605.1852, found 605.1994.

5-Ethynyl-10,20-diphenylporphyrin (77): Following the general procedure H, 0.2 mL (0.0002 mmol) of 1 M solution of TBAF in THF was added to a solution of 10-trimethylsilanylethynyl-5,15-diphenylporphyrin **60** (75 mg, 0.133 mmol) in 20 mL CH_2Cl_2. The reaction mixture was stirred for 20 minutes. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 and filtered over a short silica gel column. Recrystallization from CH_2Cl_2/MeOH gave purple crystals (60 mg, 0.123 mmol, 92 %). M.p. > 300 ºC; R_f = 0.5 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ= -2.7 (s, 2H, N*H*), 4.23 (s, 1H, C≡C*H*), 7.83 (m, 6H, Ar-*H*), 8.26 (m, 4H, Ar-*H*), 8.98 (d, 2H, ^3J = 4.1 Hz, H_β), 9.01 (d, 2H, ^3J = 4.7 Hz, H_β), 9.33 (d, 2H, ^3J = 4.7 Hz, H_β), 9.79 (d, 2H, ^3J = 4.7 Hz, H_β), 10.27 ppm (s, 1H, H_{meso}); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 83.7, 85.7, 97.8, 106.6, 120.3, 126.7, 127.7, 130.5, 131.0, 131.4, 131.6, 134.4, 141.1 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 420 (4.76), 517 (3.38), 552 (3.28), 592 (3.28), 649 nm (2.98); HRMS (MS ES+) *m/z* calcd. for $[C_{34}H_{23}N_4]$ $(M+H^+)$: 487.1910; found 487.1923.

5,10,15-Triphenyl-20-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)porphyrin (79): Produced from **17** (63 mg, 0.102 mmol) with $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) and pinacolborane (1.530 mmol, 0.20 mL) following general procedure C. After purification using column chromatography, **79** was obtained as a purple solid (37 mg, 0.056 mmol, 54%,). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.80 (br s, 2H, N*H*), 1.84 (s, 12H CH_3), 7.76 (m, 9H, *m, p*-Ph-*H*), 8.20 (m, 6H, *o*-Ph-*H*), 8.81 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 8.84 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 8.97 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.86 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 28.9, 84.8, 119.6, 121.3, 126.2, 127.2, 127.3, 134.1, 134.1, 141.6, 141.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.40), 513 (4.03), 547 (3.76), 587 (3.49), 641 nm (3.40); HRMS (ESI) *m/z* calcd. for $C_{44}H_{37}N_4O_2B$ $[M]^+$ 665.3088, found 665.3081.

5,10,15-Trihexyl-20-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-porphyrin (80): Produced from **20** (64 mg, 0.100 mmol) with $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) and pinacolborane (1.500 mmol, 0.13 mL), following general procedure C. The flask was stirred for 7 h to avoid degradation of products. After purification, **80** was obtained as a purple solid (35 mg, 0.051 mmol, 51%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.65 (s, 2H, NH) 0.95 (m, 12H, 5-CH_2), 1.42 (m, 6H, 5-CH_2), 1.53 (m, 6H, 4-CH_2), 1.85-1.75 (m, 6H, 3-CH_2), 1.87 (s, 12H, CH_3), 2.54 (d, 6H, $^3J_{H\text{-}H}$ = 7.0 Hz, 2-CH_2), 4.95 (s, 6H, 1-CH_2), 9.46 (d, 2H, , $^3J_{H\text{-}H}$ = 4.3 Hz, H_β), 9.58-9.48 (m, 4H, H_β), 9.84 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.1 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.1, 30.1, 30.2, 31.8, 35.4, 35.7, 38.5, 38.7, 84.9, 118.7, 121.2, 128.1 ppm; UV/vis: λ_{max} (log ε) = 421(5.46), 517 (4.11), 553 (3.76), 595 (3.57), 652 nm (3.47); HRMS (ESI) *m/z* calcd. for $C_{44}H_{62}N_4O_2B$ $[M+H]^+$ 689.4966, found 689.4977.

5,10,15-Tribromo-20-(1-ethylpropyl)porphyrin (82): Following the general procedure A 5-(1-ethylpropyl)porphyrin **81** (80 mg, 0.21 mmol), NBS (56.13 mg, 0.315 mmol), pyridine (1.0 mL) acetone (10 mL) in 70 mL of $CHCl_3$ were used. The products were separated on column chromatography using silica gel (*n*-hexane : ethyl acetate = 10 : 1, v/v) followed by a second column eluting with the same solvents. The first fraction was 5,10,15-tribromo-20-(1-ethylpropyl)porphyrin **82** (2 mg, 0.0032 mmol, 1.5 %) as purple crystals, the second fraction 5,15-dibromo-10-(1-ethylpropyl)porphyrin **84** and 5,10-dibromo-20-(1-ethylpropyl)porphyrin **83** (6 mg, 0.011 mmol, 5 %) as purple crystals, the third fraction 5-bromo-15-(1-ethylpropyl)porphyrin **85** (30 mg, 0.065 mmol, 31 %) as purple crystals, and the fourth fraction gave 5-bromo-10-(1-ethylpropyl)porphyrin **86** (15 mg, 0.032 mmol, 15.5 %) as purple crystals. For optimization of the yields of individual compounds see Table 1. M.p. > 300 ºC; R_f = 0.8 (*n*-hexane : ethyl acetate = 10 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.69 (s, 1H, N*H*), -2.53 (s, 1H, N*H*), 0.97 (t, 6H, *J* = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.78 (m, 2H, CH(CH_2CH$_3$)$_2$), 2.90 (m, 2H, CH(CH_2CH$_3$)$_2$), 4.96 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.56 (d, 2H, *J* = 4.7 Hz, H_β), 9.60 (m, 2H, H_β), 9.65 (d, 2H, *J* = 4.7 Hz, H_β), 9.7 ppm (m, 2H, H_β); UV/vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.05), 526 (3.69), 561 (3.65), 609 (3.27), 667 nm (3.40); HRMS (MS ES+) *m/z* calcd. for $[C_{25}H_{22}N_4Br_3]$ $(M+H^+)$: 614.9395; found 614.9385. See Table 1 for the optimum conditions for each compound.

Table 1. Bromination of 5-(1-ethylpropyl)porphyrin **81**.

	Equivalents of NBS			
Entry	**3**	**1.5**	**1**	**0.8**
82	93	1.5	–	–
83/84	–	5.3	4.1	4
85	–	31	60	41
86	–	15.5	21.4	13.8
81	–	–	5	10

5,10-Dibromo-15-(1-ethylpropyl)porphyrin (83): The compound was obtained from the synthesis of **82** by purification of a small amount of the mixed fraction **83/84** via chromatography. M.p. > 300 ºC; R_f = 0.57 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -3.04 (s, 1H, N*H*), -2.77 (s, 1H, N*H*), 1.00 (t, 6H, *J* = 7.3 Hz, CH(CH_2CH_3)$_2$), 2.83 (m, 2H, CH(CH_2CH$_3$)$_2$), 2.95 (m, 2H, CH(CH_2CH$_3$)$_2$), 4.99 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.16 (d, 1H, *J* = 4.4 Hz, H_β), 9.28 (br s, 1H, H_β), 9.49 (d, 1H, *J* = 4.4 Hz, H_β), 9.52 (d, 1H, *J* = 4.4 Hz, H_β), 9.64 (br s, 2H, H_β), 9.69 (d, 1H, *J* = 4.0 Hz, H_β), 9.82 (br s, 1H, H_β), 9.93 ppm (br s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ =13.9, 29.5, 31.7, 34.5, 50.1, 97.3, 101.2, 103.6, 105.3, 107.1, 129.3, 131.8, 132.1, 133.1, 133.7, 145.3, 146.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.07), 515 (3.84), 548 (3.50), 593 (3.36), 652 nm (3.21); HRMS (MS ES+) *m/z* calcd. for $[C_{25}H_{23}N_4Br_2]$ $(M+H^+)$: 537.0289; found 537.0289.

5-Bromo-15-(1-ethylpropyl)porphyrin (85): Obtained from the synthesis of **82** as purple crystals (30 mg, 0.065 mmol, 31 %). M.p. >300 ºC; R_f = 0.45 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.90 (s, 1H, N*H*), -2.69 (s, 1H, N*H*), 1.00 (t, 6H, *J* = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.89 (m, 2H, CH(CH_2CH$_3$)$_2$), 3.01 (m, 2H, CH(CH_2CH$_3$)$_2$), 5.08 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.38 (d, 2H, *J* = 4.4 Hz, H_β), 9.42 (m, 2H, H_β), 9.69 (d, 2H, *J* = 4.4 Hz, H_β), 9.72 (br s, 1H, H_β), 9.77 (br s, 1H, H_β), 10.18 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 34.5, 49.9, 99.9, 105.0, 105.4, 123.8, 128.7, 129.1, 130.8, 131.1, 132.0, 132.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (4.69), 505 (3.32), 537 (2.71), 580 (3.54), 640 nm (2.13); HRMS (MS ES+) *m/z* calcd. for $[C_{25}H_{24}N_4Br]$ $(M+H^+)$: 459.1184; found 459.1193.

5-Bromo-10-(1-ethylpropyl)porphyrin (86): The compound was obtained from the synthesis of **82** (15 mg, 0.032 mmol, 16 %) as purple crystals. M.p. >300 ºC; R_f = 0.37 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -3.22 (br s, 2H, N*H*), 0.98 (t, 6H, *J* = 7.3 Hz, CH(CH_2CH_3)$_2$), 2.86 (m, 2H, CH(CH_2CH$_3$)$_2$), 3.00 (m, 2H, CH(CH_2CH$_3$)$_2$), 5.13 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.33 (m, 2H, H_β), 9.39 (m, 2H, H_β), 9.76 (m, 2H, H_β), 9.82 (d, 1H, *J* = 4.4 Hz, H_β), 9.90 (br s, 1H, H_β), 10.02 (s, 1H, H_{meso}), 10.18 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 34.9, 50.5, 103.1, 103.9, 104.5, 104.7, 124.8, 129.1, 129.6, 130.8, 131.7, 133.4, 145.3, 148.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 (4.72), 505 (3.65), 539 (3.32), 581 (3.42), 656 nm (3.36); HRMS *m/z* calcd. for (MS ES+) $[C_{25}H_{24}N_4Br]$ $(M+H^+)$: 459.1184; found 459.1180.

5-(1-Ethylpropyl)-15-(3-hydroxyphenyl)porphyrin (87): Following the general procedure D 5-bromo-15-(1-ethylpropyl)porphyrin **85** (20 mg, 0.0435 mmol), 3-hydroxyphenyl boronic acid (75 mg, 0.543 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) and K_3PO_4 (231 mg, 1.087 mmol) in THF (50 mL) were used. Purification via column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 4 : 1, v/v) followed by a second column using CH_2Cl_2 : *n*-hexane = 2 : 1 (v/v) and recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (5 mg, 0.010 mmol, 24 %). M.p. >300 ºC; R_f = 0.5 (CH_2Cl_2 : *n*-hexane = 4 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.77 (s, 2H, N*H*), 0.99 (m, 6H, CH(CH_2CH_3)$_2$), 2.88 (m, 2H, CH(CH_2CH$_3$)$_2$), 3.04 (m, 2H, CH(CH_2CH$_3$)$_2$), 5.5 (s, 1H, O*H*), 5.13 (m, 1H, -C*H*(CH_2CH_3)$_2$, 7.67 (t, 1H, *J* = 7.6 Hz, Ar-*H*), 7.74 (s, 2H, Ar-*H*), 7.84 (m, 1H, Ar-*H*), 9.26 (s, 2H, H_β), 9.39 (d, 2H, *J* = 4.7 Hz, H_β), 9.48 (m, 2H, H_β), 9.80 (m, 2H, H_β), 10.29 ppm (s, 2H, H_{meso}); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (4.64), 503 (3.28), 545 (2.90), 575 (2.91), 629 nm (2.60); HRMS (MS ES+) *m/z* calcd. for $[C_{31}H_{29}N_4O]$ $(M+H^+)$: 473.2341; found 473.2336.

5-(1-Ethylpropyl)-15-(3-nitrophenyl)porphyrin (88): Following the general procedure D 5-bromo-15-(1-ethylpropyl)porphyrin **85** (20 mg, 0.044 mmol), 3-nitrophenyl boronic acid (91 mg, 0.543 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) and K_3PO_4 (231 mg, 1.087 mmol) in THF (50 mL) were used. Purification via column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 1 : 2, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple cyrstals (8 mg, 0.0159 mmol, 38 %). M.p. >300 ºC; R_f = 0.5 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.61 (s, 1H, N*H*), -2.45 (s, 1H, N*H*), 0.99 (t, 6H, *J* = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.87 (m, 2H, CH(CH_2CH$_3$)$_2$), 3.00 (m, 2H, CH(CH_2CH$_3$)$_2$), 4.22 (s, 1H, C*H*), 5.08 (m, 1H, C*H*(CH_2CH_3)$_2$), 8.01 (d, 1H, *J* = 7.5 Hz, Ar-*H*), 8.60 (d, 2H, *J* = 7.2 Hz, Ar-*H*), 8.71 (d, 1H, *J* = 7.5 Hz, Ar-*H*), 8.97 (d, 2H, *J* = 3.8 Hz, H_β), 9.16 (s, 1H, H_β), 9.44 (d, 2H, *J* = 4.5 Hz, H_β), 9.49 (m, 2H, H_β), 9.79 (br s, 1H, H_β), 9.84 (br s, 1H, H_β), 10.33 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 29.8, 49.9, 104.9, 105.3, 114.3, 123.9, 128.7, 129.1, 131.8, 132.3, 140.0, 142.9, 146.6, 147.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 407 (4.74), 505 (3.70), 538 (3.39), 577 (3.30), 637 nm (3.00); HRMS (MS ES+) *m/z* calcd. for $[C_{31}H_{28}N_5O_2]$ $(M+H^+)$: 502.2243; found 502.2237.

5-(1-Ethylpropyl)-15-(4-methoxycarbonylphenyl)porphyrin (89): Following the general procedure D 5-bromo-15-(1-ethylpropyl)porphyrin **85** (20 mg, 0.044 mmol), 4-methoxycarbonylphenyl boronic acid (86 mg, 0.435 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) and K_3PO_4 (185 mg, 0.870 mmol) in THF (50 mL) was used. Purification via column chromatography on silica gel (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afforded purple crystals (5 mg, 0.001 mmol, 67 %). M.p. >300 ºC; R_f = 0.5 (CH_2Cl_2 : *n*-hexane = 1 : 2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.81 (s, 1H, N*H*), -2.73 (s, 1H, N*H*), 1.00 (t, 6H, *J* = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.89 (m, 2H, CH(CH_2CH$_3$)$_2$), 3.02 (m, 2H, CH(CH_2CH$_3$)$_2$), 4.16 (s, 6H, OCH_3), 5.13 (m, 1H, C*H*(CH_2CH_3)$_2$), 8.37 (d, 2H, *J* = 8.2 Hz, Ar-*H*), 8.51 (d, 2H, *J* = 8.2 Hz, Ar-*H*), 9.03 (d, 2H, *J* = 4.1 Hz, H_β), 9.42 (d, 2H, *J* = 4.7 Hz, H_β), 9.49 (m, 2H, H_β), 9.78 (m, 1H, H_β), 9.83 (d, 1H, H_β), 10.32 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 29.0, 34.5, 52.2, 53.2, 104.7, 116.5, 128.1, 129.2, 131.9, 134.7, 145.9, 146.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (5.14), 504 (4.01), 537 (3.71), 576 (3.41), 633 nm (3.21); HRMS (MS ES+) *m/z* calcd. for $[C_{33}H_{31}N_4O_2]$ $(M+H^+)$: 515.2447; found 515.2447.

5-(1-Ethylpropyl)-15-trimethylsilanylethynylporphyrin (90): Following procedure G 5-bromo-15-(1-ethylpropyl)porphyrin **85** (46 mg, 0.1 mmol), ethynyltrimethylsilane (0.152 mL, 0.11 mmol), CuI (5 mg, 0.025 mmol) and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) were added to 15 mL triethylamine and 5 mL THF. Purification via column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 1 : 2, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afford purple crystals (38 mg, 0.008 mmol, 79 %). M.p. >300 ºC; R_f = 0.48 (*n*-hexane : CH_2Cl_2 = 4 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.48 (s, 2H, N*H*), 0.66 (s, 9H, Si(CH_3)$_3$), 0.98 (t, 6H, *J* = 7.01 Hz, CH(CH_2CH_3)$_2$), 2.83 (m, 2H, CH(CH_2CH$_3$)$_2$), 2.99 (m, 2H, CH(CH_2CH$_3$)$_2$), 5.05 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.39 (d, 4H, *J* = 4.4 Hz, H_β), 9.72 (d, 4H, *J* = 4.8 Hz, H_β), 10.20 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 34.6, 50.1, 97.1, 101.6, 105.6, 106.0, 125.2, 128.8, 129.7,

129.8, 131.5, 131.7, 132.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (4.75), 505 (3.67), 537 (3.37), 580 (3.28), 634 nm (3.15); HRMS (MS ES+) *m/z* calcd. for [$C_{30}H_{33}N_4Si$] ($M+H^+$): 477.2467; found 477.2475.

5-(1-Ethylpropyl)-10,15,20-tris(trimethylsilanylethynyl)porphyrin (91): Following the general procedure G 5,10,15-tribromo-20-(1-ethylpropyl)porphyrin **82** (150 mg, 0.243 mmol), ethynyltrimethylsilane (1.1 mL, 0.8 mmol), CuI (12 mg, 0.06 mmol) and $Pd(PPh_3)_2Cl_2$ (17 mg, 0.024 mmol) in 15 mL triethylamine and 5 mL THF were used. Purification via column chromatography on silica gel using (CH_2Cl_2 : *n*-hexane = 1 : 2, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (80 mg, 0.012 mmol, 49 %). M.p. >300 °C; R_f = 0.84 (*n*-hexane : CH_2Cl_2 = 4 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -1.82 (s, 1H, N*H*), -1.74 (s, 1H, N*H*), 0.64 (s, 27H, Si(*CH*$_3$)$_3$), 0.95 (t, 6H, *J* = 7.3 Hz, CH(CH_2CH_3)$_2$), 2.77 (m, 2H, CH(CH_2CH_3)$_2$), 2.90 (m, 2H, CH(CH_2CH_3)$_2$), 4.95 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.53 (m, 3H, H_β), 9.57 (br s, 1H, H_β), 9.62 (d, 2H, *J* = 4.8 Hz, H_β), 9.67 ppm (m, 2H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 34.5, 50.3, 99.9, 102.4, 102.5, 105.7, 106.8, 127.6, 129.2, 130.3, 131.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε)= 445 (4.77), 556 (3.12), 595 (3.90), 636 (2.52), 696 nm (3.30); HRMS (MS ES+) *m/z* calcd. for [$C_{40}H_{49}N_4Si_3$] ($M+H^+$): 669.3295; found 669.3265.

5-Ethenyl-15-(1-ethylpropyl)porphyrin (92): Following the general procedure H, 5-(1-ethylpropyl)-15-trimethylsilanylethynylporphyrin **90** (35 mg, 0.073 mmol), 1 M solution TBAF (0.2 mL, 0.0002 mmol) in THF and CH_2Cl_2 (20 mL) were used. Recrystallization gave purple crystals (23 mg, 0.056 mmol, 77 %). M.p. >300 ºC; R_f = 0.6 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.61 (s, 1H, N*H*), -2.45 (s, 1H, N*H*), 0.99 (t, 6H, *J* = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.87 (m, 2H, CH(CH_2CH_3)$_2$), 3.00 (m, 2H, CH(CH_2CH_3)$_2$), 4.22 (s, 1H C*H*), 5.08 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.41 (d, 4H, *J* = 4.7 Hz, H_β), 9.72 (d, 4H, *J* = 4.7 Hz, H_β), 10.22 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.7, 29.2, 34.2, 49.7, 83.2, 84.2, 105.5, 125.0, 128.4, 128.8, 129.1, 129.3, 131.1, 132.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 411 (4.70), 512 (3.43), 548 (3.44), 584 (3.11), 640 nm (3.00); HRMS (MS ES+) *m/z* calcd. for [$C_{27}H_{25}N_4$] ($M+H^+$): 405.2068; found 405.2069.

5-(1-Ethylpropyl)-10,15,20-triethynylporphyrin (93): Following the general procedure H, 5-(1-ethylpropyl)-10,15,20-tris(trimethylsilanylethynyl)porphyrin **91** (70 mg, 0.104 mmol), 1 M TBAF solution in THF (0.3 mL, 0.0003 mmol) dissolved in 20 mL CH_2Cl_2 were used. Recrystallization from CH_2Cl_2/MeOH gave purple crystals (30 mg, 0.070 mmol, 63 %). M.p. >300 ºC; R_f = 0.66 (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.04 (s, 1H, N*H*), -1.94 (s, 1H, N*H*), 0.98 (t, 6H, *J* = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.80 (m, 2H, CH(CH_2CH_3)$_2$), 2.92 (m, 2H, CH(CH_2CH_3)$_2$), 4.18 (s, 2H, C*H*), 4.23 (s, 1H, C*H*), 4.99 (m, 1H, C*H*(CH_2CH_3)$_2$), 9.55-9.65 ppm (m, 8H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.7, 29.7, 30.0, 31.9, 34.6, 50.4, 84.6, 127.9, 129.5, 129.8, 130.8, 131.8, 146.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log *ε)* = 436 (4.70), 541 (4.70), 581 (3.80), 621 (3.32), 684 nm (3.50); HRMS (MS ES+) *m/z* calcd. for [$C_{31}H_{25}N_4$] ($M+H^+$): 453.2094; found 453.2079.

5-(10',15',20'-Triphenylporphyrin-5'-yl)-10,15,20-tris(3-methoxyphenyl)porphyrin (94): Produced from **79** (5 mg, 0.0075 mmol), **20** (5 mg, 0.007 mmol), Cs_2CO_3 (6 mg, 0.03 mmol) and $Pd(PPh_3)_4$ (1 mg, 0.0008 mmol) following general procedure E**.** After purification, a dark purple solid was isolated (3 mg, 0.003 mmol, 29%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.24-2.28 (m, 4H, N*H*), 3.94 (s, 3H, OC*H*$_3$), 4.07 (s, 3H, OC*H*$_3$), 7.57 (m, 3H, Ph-*H*), 7.71 (m, 8H, Ph-*H*), 7.83 (m, 8H, Ph-*H*), 7.89-7.83 (m, 3H, Ph-*H*), 8.09-8.10 (d, 4H, $^3J_{H-H}$ = 4.8 Hz, H_β), 8.24-8.26 (d, 4H, $^3J_{H-H}$ = 6.8 Hz, Ph-*H*), 8.31-8.34 (d, 4H, $^3J_{H-H}$ = 5.5 Hz, Ph-*H*), 8.61-8.62 (d, 2H, $^3J_{H-H}$ = 4.0 Hz, H_β), 8.65-8.66 (d, 2H, $^3J_{H-H}$ = 4.8 Hz, H_β), 8.97 ppm (m, 8H, H_β). ^{13}C NMR (150 MHz, $CDCl_3$): δ= 14.1, 22.7, 29.4, 31.9, 41.0, 126.6, 126.7, 127.7, 128.8, 134.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 406 (5.20), 503 (3.94), 533 (3.53), 574 nm (3.48); HRMS (Maldi) *m/z* calcd. for $C_{79}H_{56}N_8O_3$ $[M]^+$ 1165.4554, found 1165.4497.

5-Butyl-10,15-bis(4-methoxyphenyl)-20-(10',15',20'-triphenylporphyrin-5'-yl)porphyrin (95):[48] Produced from **79** (10 mg, 0.015 mmol), **23** (10 mg, 0.015 mmol), Cs_2CO_3 (10 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (2 mg, 0.002 mmol), following general procedure E to give a green solid (9 mg, 0.008mmol, 48%). Mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.23 (s, 2H, N*H*) -2.15 (s, 2H, N*H*), 1.18-1.22 (t, 3H, $^3J_{H-H}$ = 14.7 Hz, *CH*$_3$), 1.87 (m, 2H, *CH*$_2$), 2.60 (m, 2H, *CH*$_2$), 4.05 (s, 6H, OC*H*$_3$), 5.13 (m, 2H, *CH*$_2$), 7.23-7.35 (d, 4H, $^3J_{H-H}$ = 8.8 Hz, Ar-*H*), 7.71 (m, 6H, Ph-*H*), 7.84 (m, 2H, Ph-*H*), 8.04-8.05 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, Ph-*H*), 8.12 (d, 6H, $^3J_{H-H}$ = 8.6 Hz, Ar-*H*), 8.23 (m, 4H, H_β), 8.31-8.33 (d, 2H, $^3J_{H-H}$ = 5.4 Hz, Ph-*H*), 8.60 (m, 4H, H_β), 8.91 (m, 4H, H_β), 9.02-9.03 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β), 9.61-9.62 ppm (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β); UV/vis: λ_{max} (log ε) = 430 (4.90), 522 (3.58), 558 (3.60), 605 nm (3.65); HRMS (Maldi) *m/z* calcd. for $C_{76}H_{59}N_8O_2$ $[M+H]^+$ 1115.4761, found 1115.4783.

5-(10',15',20'-Trihexylporphyrin-5'-yl)-10,15,20-tris(4-methoxyphenyl)porphyrin (96): Produced from **80** (10 mg, 0.015 mmol), **22** (12 mg, 0.02 mmol), Cs_2CO_3 (4 mg, 0.02 mmol) and $Pd(PPh_3)_4$ (3 mg, 0.003 mmol) following general procedure E, to give green solid (6 mg, 0.005 mmol, 37%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.14 (s, 2H, N*H*), -2.05 (s, 2H, N*H*), 0.91-0.82 (m, 12H, *CH*$_2$), 1.38 (m, 6H *CH*$_2$), 1.45 (m, 6H, *CH*$_2$), 1.76 (m, 4H, *CH*$_2$), 1.92 (m, 2H, *CH*$_2$), 2.54 (m, 4H, *CH*$_2$), 2.63 (m, 2H, *CH*$_2$), 4.04 (s, 6H, OC*H*$_3$), 4.18 (s, 3H, OC*H*$_3$), 4.94 (m, 4H, *CH*$_2$), 5.11-5.15 (t, 2H, $^3J_{H-H}$ = 15.6 Hz, *CH*$_2$), 7.24-7.25 (d, 4H, $^3J_{H-H}$ = 8.3 Hz, Ph-*H*), 7.38-7.39 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ph-*H*), 8.05-8.06 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β), 8.08-8.09 (d, 2H, $^3J_{H-H}$ = 4.4 Hz, H_β), 8.16-8.18 (d, 4H, $^3J_{H-H}$ = 8.8 Hz, Ph-*H*) 8.25-8.26 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ph-*H*) 8.63-8.64 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β), 8.96-8.97 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β), 9.00-9.01 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β), (m, 4H, H_β), 9.13-9.14 (d, 2H, $^3J_{H-H}$ = 4.4 Hz, H_β), 9.58-9.60 (d, 2H, $^3J_{H-H}$ = 4.0 Hz, H_β), 9.66-9.67 ppm (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 14.0, 22.5, 22.7, 29.5, 29.6, 30.1, 30.2, 31.7, 31.9, 38.5, 55.3, 112.0, 112.1, 135.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 410 (5.67), 450 (5.01), 507 (4.48), 567 (3.95), 599 (3.87), 666 nm (3.49); HRMS (Maldi) *m/z* calcd. for $C_{79}H_{81}N_8O_3$ $[M+H]^+$ 1189.6432, found 1189.6428.

5-(10',15',20'-Trihexylporphyrin-5'-yl)-10,15,20-tris(3-methoxyphenyl)porphyrin (97): Produced from **80** (10 mg, 0.015 mmol), **21** (8 mg, 0.01 mmol), Cs_2CO_3 (4 mg, 0.02 mmol) and $Pd(PPh_3)_4$ (2 mg, 0.002 mmol) following general procedure E to give a purple solid. Yield = 8 mg (0.007 mmol, 51%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.16 (s, 2H, N*H*) -2.07 (s, 2H, N*H*), 0.86 (m, 12H, *CH*$_3$), 1.00 (m, 6H *CH*$_2$), 1.36-1.30 (m, 8H, *CH*$_2$), 1.77 (m, 4H, *CH*$_2$), 1.92-1.86 (m, 2H, *CH*$_2$) 2.50 (m, 4H, *CH*$_2$), 2.62 (m, 2H, *CH*$_2$), 4.01 (s, 6H, OC*H*$_3$), 4.14 (s, 3H, OC*H*$_3$), 4.94-4.85 (m, 4H, *CH*$_2$), 5.14-5.06 (m, 2H, *CH*$_2$), 7.21 (d, 4H, $^3J_{H-H}$ = 8.6 Hz, Ph-*H*), 8.03 (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β), 8.07 (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β), 8.14 (d, 4H, $^3J_{H-H}$ = 8.6 Hz, Ph-*H*), 8.22 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, H_β), 8.61 (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β), 8.96 (dd, 4H, $^3J_{H-H}$ = 13.2, 4.7 Hz, H_β), 9.11 (d, 2H, $^3J_{H-H}$ = 4.9 Hz, H_β), 9.56 (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β), 9.63 ppm (d, 2H, $^3J_{H-H}$ = 4.8 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 14.0, 22.8, 29.6, 30.1, 30.3, 38.6, 55.7, 110.0, 112.0, 113.4, 134.1, 135.3, 137.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 413 (4.97), 452 (4.10), 525 (4.34), 564 (3.96), 601 (3.87), 661 nm (3.79); HRMS (Maldi) *m/z* calcd. for $C_{79}H_{81}N_8O_3$ $[M+H]^+$ 1189.6432, found 1189.6471.

5-Butyl-15-(5'-ethynyl-10',15',20'-triphenylporphyrin)-10,20-bis(4-methoxyphenyl)porphyrin (98): Produced from **69** (10 mg, 0.018 mmol), **23** (12 mg, 0.018 mmol), $AsPh_3$ (4 mg, 0.013 mmol) and $Pd_2(dba)_3$ (5 mg, 0.001 mmol) following procedure J. After purification dark green crystals were isolated (5 mg, 0.004 mmol, 29%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ= -2.02 (s, 2H, N*H*), -1.93 (s, 2H, N*H*), 1.15 (t, 6H, $^3J_{H-H}$ = 7.4 Hz, *CH*$_3$), 1.88-1.81 (m, 2H, *CH*$_2$), 2.57-2.51 (m, 2H, *CH*$_2$), 4.14 (s, 6H, OC*H*$_3$), 4.98 (m, 2H, *CH*$_2$), 7.35 (m, 4H, Ar-*H*), 7.80 (m, 9H, Ph-*H*), 8.17 (m, 4H, Ar-*H*), 8.22 (m, 2H, Ph-*H*), 8.29 (m, 4H, Ph-*H*), 8.80 (m, 4H, H_β), 8.90-8.91 (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β), 9.07 (m, 4H, H_β), 9.44 (d, 2H, $^3J_{H-H}$ = 4.8 Hz, H_β), 10.24 (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β), 10.32 ppm (d, 2H, $^3J_{H-H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.5, 29.2, 29.6, 29.9, 31.8, 55.5, 112.2, 120.7, 127.8, 128.2, 128.7, 128.8, 130.3, 134.3, 134.4, 134.7, 135.4, 141.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 415 (4.73), 470 (4.72), 518 (3.89), 620 (3.93), 717 nm (4.00); HRMS (Maldi) *m/z* calcd. for $C_{78}H_{58}N_8O_2$ $[M]^+$ 1138.4683, found 1138.4803.

5-(5',10',20'-Triphenylporphyrin)-ethynyl-10,15,20-tris(3-methoxyphenyl)porphyrin (99): Produced from **69** (10 mg, 0.018 mmol), **21** (13 mg, 0.018 mmol), $AsPh_3$ (5 mg, 0.020 mmol) and $Pd(PPh_3)_4$ (2 mg, 0.001 mmol) following procedure J. After purification dark green crystals were isolated (3 mg, 0.002 mmol, 29%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.03 (s, 2H, N*H*) -2.01(s, 2H, N*H*), 3.98 (s, 3H, OC*H*$_3$), 4.01 (s, 6H, OC*H*$_3$), 7.10 (d, $^3J_{H-H}$ = 15.9 Hz, 4H, Ar-*H*), 7.63 (m, 6H, Ph-*H*), 7.75 (d, 4H, $^3J_{H-H}$ = 15.9 Hz, Ar-*H*), 7.91-7.87 (m, 3H, Ph-*H*), 8.24-8.20 (m, 3H, Ph-*H*), 8.32-8.27 (m, 4H, Ph-*H*), 8.83-8.81 (m, 3H, H_β), 8.87-8.85 (m, 3H, H_β), 8.95-8.90 (m, 3H, H_β), 9.11-9.08 (m, 2H, H_β), 9.15-9.12 (m, 2H, H_β), 9.35-9.32 (m, 1H, H_β), 10.37-10.32 ppm (m, 4H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 22.5, 22.6, 29.2, 29.7, 29.9, 31.8, 55.5, 125.3, 126.7, 127.5, 127.9, 128.2, 128.8, 130.3, 134.3, 134.4, 136.7, 143.2 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 412 (4.91), 473 (4.88), 517 (4.01), 620 (4.09), 713 nm (4.19); HRMS (Maldi) *m/z* calcd. for $C_{81}H_{56}N_8O_3$ $[M]^+$ 1188.4475, found 1188.4490.

5-{5',10',20'-Tris(4-methoxy)phenyl}ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin (100): Following procedure J 5,15-bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **71** (20.0 mg,

0.025 mmol), 5-bromo-10,15,20-tri(p-methoxy)phenylporphyrin **22** (18 mg, 0.025 mmol), $AsPh_3$ (10 mg, 0.033 mmol) and $Pd_2(dba)_3$ (2 mg, 0.003 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 14 h at 65 °C. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:4 to 2:1, v/v) to yield a red-green solid. Yield: 23 mg (0.016 mmol, 64%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -1.92 (s, 2H, N*H*), -1.89 (s, 2H, N*H*), 1.59 (s, 36H, *t*-Bu-*H*), 4.11 (s, 3H, CH_3), 4.14 (s, 6H, CH_3), 7.31 (d, 2H, $^3J_{H\text{-}H}$ = 8.2 Hz, Ph-*H*), 7.31 (d, 4H, $^3J_{H\text{-}H}$ = 8.8 Hz, Ph-*H*), 7.74-7.80 (m, 3H, Ph-*H*), 7.85-7.89 (m, 4H, Ph-*H*), 8.15 (d, 2H, $^3J_{H\text{-}H}$ = 8.2 Hz, Ph-*H*), 8.17-8.21 (m, 4H, Ph-*H*), 8.23 (d, 4H, $^3J_{H\text{-}H}$ = 8.8 Hz, Ph-*H*), 8.84-8.93 (m, 8H, H_β), 9.17 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β) 9.20 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β) 10.40 ppm (m, 4H, H_β); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 35.2, 55.6, 55.6, 99.9, 100.2, 100.3, 100.3, 112.3, 112.4, 121.2, 121.3, 121.8, 122.9, 126.7, 129.8, 134.3, 134.3, 135.5, 135.6, 140.8, 149.0, 159.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 (4.77), 475 (4.95), 522 (4.05), 623 (4.22), 719 nm (4.34); HRMS (ESI) *m/z* calcd. for $C_{97}H_{88}N_8O_3$ $[M+H]^+$ 1413.7086, found 1413.7058.

5-(5',10',20'-Trihexylporphyrin)ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin (101): Following procedure J 5,15-bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **71** (21 mg, 0.027 mmol), 5-bromo-10,15,20-trihexylporphyrin **20** (17 mg, 0.027 mmol), $AsPh_3$ (25 mg, 0.082 mmol) and $Pd_2(dba)_3$ (16 mg, 0.028 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 4 h at 65 °C and then for 15 h at room temperature. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:4 to 1:1, v/v) to yield a red-green solid. Yield: 16 mg (0.012 mmol, 45%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -1.93 (s, 2H, N*H*), -1.89 (s, 2H, N*H*), 0.94-1.00 (m, 9H, CH_3), 1.38-1.49 (m, 6H, CH_2), 1.51-1.60 (m, 6H, CH_2), 1.59 (s, 36H, *t*-Bu-*H*), 1.81-1.91 (m, 6H, CH_2), 2.51-2.61 (m, 6H, CH_2), 4.91-4.98 (m, 6H, CH_2), 7.72-7.80 (m, 3H, Ph-*H*), 7.83-7.86 (m, 2H, Ph-*H*), 8.13-8.16 (m, 4H, Ph-*H*), 8.21-8.25 (m, 2H, Ph-*H*), 8.81 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.88 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.17 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.45 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β) 9.49 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.61 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.32 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.37 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β);. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.7, 22.8, 29.7, 29.8, 30.3, 30.4, 31.8, 31.9, 35.1, 35.4, 36.0, 98.4, 99.4, 100.3, 100.7, 120.8, 121.3, 121.6, 121.8, 122.8, 126.7, 127.8, 128.4, 128.9, 129.9, 133.7, 134.3, 140.9, 142.2, 149.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 410 (4.61), 473 (4.82), 522 (3.85), 623 (4.04), 723 nm (4.17); HRMS (ESI) *m/z* calcd. for $C_{94}H_{106}N_8$ $[M+H]^+$ 1347.8606, found 1347.8619.

5-(5',10',20'-Triphenylporphyrin)ethynyl-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin (102): Following procedure J 5,15-bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **71** (20 mg, 0.025 mmol), 5-bromo-10,15,20-triphenylporphyrin **17** (16 mg, 0.025 mmol), $AsPh_3$ (10 mg, 0.033 mmol) and $Pd_2(dba)_3$ (2 mg, 0.002 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 4 h at 65 °C and then for 15 h at room temperature. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:3 to 1:1, v/v) to yield a red-green solid. Yield: 15 mg (0.012 mmol, 45%). M.p. > 300 °C. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ = -2.00 (s, 2H, N*H*), -1.94 (s, 2H, N*H*), 1.58 (s, 36H, *t*-Bu-*H*), 7.74-7.85 (m, 12H, Ph-*H*), 7.83-7.86 (m, 2H, Ph-*H*), 8.15-8.18 (m, 4H, Ph-*H*), 8.21-8.26 (m, 4H, Ph-*H*), 8.28-8.34 (m, 4H, Ph-*H*), 8.80-8.90 (m, 8H, H_β), 9.11 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.15 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.36 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.37 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 35.1, 53.4, 99.7, 100.1, 100.4, 100.7, 121.3, 121.5, 121.9, 122.0, 123.0, 126.7, 126.8, 126.9, 127.8, 127.9, 129.8, 134.3, 134.4, 134.6, 140.8, 141.8, 142.0, 142.2, 149.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (4.80), 474 (4.99), 521 (4.31), 624 (4.37), 719 nm (4.42); HRMS (ESI) *m/z* calcd. for $C_{94}H_{82}N_8$ $[M+H]^+$ 1323.6749, found 1323.6741.

5-(5',15'-Bis(3,5-di-*tert*-butylphenyl)-10'-phenylporphyrin)ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-hexylporphyrin (103): Following procedure J 5,15-bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-hexylporphyrin **73** (30 mg, 0.039 mmol), 5-bromo-10,20-bis-(3,5-di-tert-butylphenyl)-15-phenylporphyrin **15** (33 mg, 0.039 mmol), $AsPh_3$ (10 mg, 0.033 mmol) and $Pd_2(dba)_3$ (4 mg, 0.004 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 6 h at 65 °C. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:4 to 2:1, v/v) to yield a red-green solid. Yield: 20 mg (0.013 mmol, 34%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -1.95 (s, 2H, N*H*), -1.88 (s, 2H, N*H*), 1.57 (s, 36H, *t*-Bu-*H*), 1.59 (s, 36H, *t*-Bu-*H*), 0.94-0.98 (m, 3H, CH_3), 1.41-1.47 (m, 2H, CH_2), 1.64-1.70 (m, 2H, CH_2), 1.83-1.90 (m, 2H, CH_2), 2.55-2.60 (m, 2H, CH_2), 4.94-5.02 (m, 2H, CH_2), 7.72-7.80 (m, 3H, Ph-*H*), 7.83-7-87 (m, 2H, Ph-*H*), 7.83-7.86 (m, 2H, Ph-*H*), 8.12-8.16 (m, 4H, Ph-*H*), 8.20-8.24 (m, 2H, Ph-*H*), 8.79 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, Ph-*H*), 8.84 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, Ph-*H*), 8.92 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.06 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.11 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.44 (s, 2H, H_β), 10.27 (s, 4H, H_β), 10.33 ppm (s, 4H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.5, 29.3, 29.4, 29.6, 30.2, 30.3, 34.9, 121.1, 122.2, 122.7, 124.7, 125.4, 126.5, 129.5, 129.6, 134.2, 135.5, 140.7, 140.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 408 (4.94), 474 (5.13), 521 (4.24), 622 (4.38), 721 nm (4.50); HRMS (ESI) *m/z* calcd. for $C_{110}H_{114}N_8$ $[M]^+$ 1546.9166, found 1546.9181.

Bis{10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin-5-yl)ethynyl (104): Following procedure J 5,15-bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **71** (18 mg, 0.023 mmol), 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrin **15** (19 mg, 0.023 mmol), $AsPh_3$ (10 mg, 0.033 mmol) and $Pd_2(dba)_3$ (1 mg, 0.002 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 6 h at 65 °C. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:4 to 2:1, v/v) to yield a red-green solid. Yield: 15 mg (0.010 mmol, 43%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -1.93 (s, 4H, N*H*), 1.58 (s, 72H, *t*-Bu-*H*), 7.72-7.81 (m, 6H, Ph-*H*), 7.83-7.87 (m, 4H, Ph-*H*), 8.13-8.18 (m, 8H, Ph-*H*), 8.21-8.26 (m, 4H, Ph-*H*), 8.79 (s, 4H, H_β), 8.86 (s, 4H, H_β), 9.14 (s, 4H, H_β), 10.36 ppm (s, 4H, H_β); ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 35.0, 53.3, 99.8, 100.2, 121.1, 121.6, 122.7, 126.6, 127.6, 129.7, 134.2, 140.7, 142.0, 148.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (4.59), 474 (4.72), 523 (3.87), 622 (3.99), 718 nm (4.09); HRMS (ESI) *m/z* calcd. for $C_{110}H_{114}N_8$ $[M+H]^+$ 1547.9292, found 1547.9245.

{5-(10',20'-Bis(3,5-di-*tert*-butylphenyl)-15'-phenylporphyrin-5-yl}ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (105): Following procedure J, 5,15-bis(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **71** (32 mg, 0.040 mmol), bromoporphyrin **52** (27 mg, 0.040 mmol), $AsPh_3$ (20.2 mg, 0.066 mmol) and $Pd_2(dba)_3$ (9.0 mg, 0.010 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred for 4 h at 65 °C and then for 15 h at room temperature. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:4 to 1:1, v/v) to yield a red-green solid. Yield: 30 mg (0.022 mmol, 54%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -1.93 (s, 2H, N*H*), 1.58 (s, 36H, *t*-Bu-*H*), 7.70-7.83 (m, 12H, Ph-*H*), 7.85-7.87 (m, 4H, Ph-*H*), 8.15-8.18 (m, 4H, Ph-*H*), 8.22-8.25 (m, 2H, Ph-*H*), 8.29-8.32 (m, 4H, Ph-*H*), 8.80 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.87 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.88 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.92 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.13 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.19 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.33 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β) 10.43 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.7, 35.0, 99.7, 100.0, 100.3, 101.8, 121.1, 121.6, 121.9, 122.3, 122.7, 126.4, 126.6, 127.6, 129.7, 130.8, 131.9, 132.2, 133.2, 134.1, 134.2, 134.3, 140.7, 142.4, 148.8, 149.9, 150.1, 150.5, 152.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (4.86), 473 (4.99), 521 (4.31), 624 (4.37), 716 nm (4.42); HRMS (ESI) *m/z* calcd. for $C_{94}H_{80}N_8Zn$ $[M+H]^+$ 1385.5930, found 1385.5876.

{5-[(10',20'-Bis(3,5-di-*tert*-butylphenyl)-15'-phenylporphyrinato-5-yl]zinc(II)}ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (106): Following procedure J, ethynyl porphyrin **72** (28 mg, 0.033 mmol), bromoporphyrin **52** (22 mg, 0.033 mmol), $AsPh_3$ (15 mg, 0.049 mmol) and $Pd_2(dba)_3$ (5 mg, 0.005 mmol) were dried *in vacuo* and dissolved in degassed NEt_3 (1 mL) and THF (4 mL). The solution was stirred at 65 °C for 16 h. All solvents were removed and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:4 to 1:1, v/v) to yield a red-brown solid. Yield: 25 mg (0.017 mmol, 52%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 1.59 (s, 36H, *t*-Bu-*H*), 7.70-7.83 (m, 14H, Ph-*H*), 8.15-8.22 (m, 8H, Ph-*H*), 8.29-8.32 (m, 4H, Ph-*H*), 8.89 (s, 2H, H_β), 8.92 (s, 4H, H_β), 8.97 (s, 2H, H_β), 9.18 (s, 2H, H_β), 9.23 (s, 2H, H_β), 10.43 ppm (s, 4H, H_β). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.8, 35.1, 121.0, 122.4, 122.8, 123.9, 126.6, 126.7, 127.7, 129.7, 130.7, 131.0, 132.0, 132.3, 132.3, 133.3, 133.6, 134.2, 134.3, 134.4, 141.5, 142.5, 148.8, 150.0, 150.1, 150.3, 150.3, 150.6, 150.9, 152.8, 152.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (4.63), 480 (4.92), 559 (4.22), 690 nm (4.35); HRMS (ESI) *m/z* calcd. for $C_{94}H_{78}N_8Zn_2$ $[M+H]^+$ 1447.4935, found 1447.5011.

{5-[(5',10',20'-Trihexylporphyrinato-5-yl)zinc(II]ethynyl-10,20-bis(3,5-di-*tert*-butylphenyl)-15-phenylporphyrinato}zinc(II) (107): Dimer **101** (11 mg, 0.008 mmol) was dissolved in $CHCl_3$ (10 mL) and heated to reflux for 10 min. Zinc(II)acetate (100 mg, 0.406 mmol) was dissolved in methanol (2 mL) and both solutions were combined. The mixture was heated to reflux for 30 min. All solvents were removed *in vacuo*, the residue dissolved in CH_2Cl_2 (5 mL) and filtered through a plug of silica. All solvents were removed to yield a red/brown solid. Yield: 8 mg (0.006 mmol, 68%). M.p. > 300 °C. ^{1}H NMR (600 MHz, THF-d_8, TMS): δ = 0.94-

0.99 (m, 9H, CH_3), 1.42-1.48 (m, 6H, CH_2), 1.54-1.60 (m, 6H, CH_2), 1.61 (s, 36H, *t*-Bu-*H*), 1.86-1.94 (m, 6H, CH_2), 2.54-2.65 (m, 6H, CH_2), 5.03-5.12 (m, 6H, CH_2), 7.74-7.78 (m, 3H, Ph-*H*), 7.93-7.95 (m, 2H, Ph-*H*), 8.19-8.25 (m, 6H, Ph-*H*), 8.78 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.84 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.16 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.57 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β) 9.59 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.77 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.43 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.49 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, THF-d$_8$, TMS): δ = 14.5, 23.7, 30.7, 31.2, 32.1, 33.0, 35.8, 40.0, 121.7, 122.0, 122.8, 124.0, 125.9, 127.2, 129.4, 130.6, 130.7, 131.3, 132.5, 133.6, 135.2, 138.2, 143.5, 149.5, 150.2, 150.5, 15.1, 151.2, 151.6, 153.2, 153.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 432 (4.45), 479 (4.78), 557 (4.21), 696 nm (4.38); HRMS (ESI) *m/z* calcd. for $C_{94}H_{102}N_8Zn_2$ $[M+H]^+$ 1471.6903, found 1471.6889.

5-(5',10',20'-Triphenylporphyrin-5-yl)ethynyl-15-(3-methoxyphenyl)-10,20-diphenylporphyrin (108):[48] Obtained from ethynyl porphyrin **75** (25 mg, 0.042 mmol), bromoporphyrin **10** (26 mg, 0.042 mmol), $AsPh_3$ (27 mg, 0.089 mmol) and $Pd_2(dba)_3$ (3.8 mg, 0.004 mmol) using general procedure J to yield a dark green solid following column chromatography CH_2Cl_2:Hex (1:3, v/v). Yield (18 mg, 0.016 mmol, 38%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.09 (s, 2H, N*H*), -1.99 (s, 2H, N*H*), 4.02 (s, 3H, OCH_3), 7.54 (m, 4H, Ar-*H*), 7.84 (m, 16H, Ar-*H*), 8.27 (8H, m, Ph-*H*), 8.82 (m, 8H, H_β), 9.03-9.04 (d, 2H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.11-9.12 (d, 2H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.95-9.96 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 10.36-10.37 ppm (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); UV/vis (THF): λ_{max} (log ε) = 407 (4.89), 471 (5.13), 520 (4.22), 625 (4.40), 712 nm (4.48); HRMS (ESI) *m/z* calcd. for $C_{79}H_{52}N_8O$ $[M+H]^+$ 1128.4264, found 1128.4277.

5-(5'-Hexyl-10',20'-diphenyl-5-yl)ethynyl-10,15,20-triphenylporphyrin (109): Produced from ethynyl porphyrin **69** (30 mg, 0.053 mmol), bromoporphyrin **18** (33 mg, 0.053 mmol), $AsPh_3$ (34 mg, 0.111 mmol) and $Pd_2(dba)_3$ (5 mg, 0.004 mmol) using general procedure J to yield a dark solid following column chromatography (silica, CH_2Cl_2:hexane, 1:3, v/v) (23 mg, 0.340 mmol, 39%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -1.99 (s, 2H, N*H*) -1.93 (s, 2H, N*H*) 0.91 (t, 3H, CH_3), 1.76-1.81 (m, 4H, CH_2), 1.84-1.88 (m, 2H, CH_2), 2.58 (m, 2H, CH_2), 5.00 (m, 2H, CH_2), 7.82 (m, 16H, Ph-*H*), 8.30 (m, 12H, Ph-*H*), 8.23-8.36 (m, 4H, H_β), 8.90-8.91 (d, 2H, H_β), 9.05-9.06 (d, 2H, H_β), 9.09-9.11 (d, 2H, H_β), 9.46-9.48 (d, 2H, H_β), 10.27-10.29 (d, 2H, H_β), 10.33-10.34 ppm (d, 2H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 22.8, 29.4, 29.7, 31.9, 126.8, 126.9, 127.9, 134.4, 134.5, 134.6, 141.9 ppm; UV/Vis (THF): λ_{max} (log ε) = 427 (4.79), 472 (5.02), 519 (4.11), 620 (4.24), 714 nm (4.34); HRMS (ESI) *m/z* calcd. for $C_{78}H_{58}N_8$ $[M+H]^+$ 1107.4904, found 1107.4863.

1,2-Bis(5,10,15-triphenylporphyrin-20-yl)ethine (110): Produced from ethynyl porphyrin **69** (80 mg, 0.142 mmol), bromoporphyrin **10** (76 mg, 0.142 mmol), $AsPh_3$ (48 mg, 0.156 mmol) and $Pd_2(dba)_3$ (13 mg, 0.014 mmol) using general procedure J. The solvent was removed *in vacuo* and the residue filtered through a plug of silica using CH_2Cl_2/TEA as eluant (99:1, v/v), giving a green fraction. After removal of the solvent and recrystallization from CH_2Cl_2/MeOH a dark powder was obtained (75 mg, 0.068 mmol, 48%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ_H = -1.96 (s, 2H, N*H*) 7.81 (m, 18H, Ph-*H*), 8.23 (m, 6H, Ph-*H*), 8.32 (m, 8H, Ph-*H*), 8.84 (m, 8H, H_β), 9.11-9.13 (d, 4H, H_β), 10.36-10.38 (d, 4H, H_β) ppm. ^{13}C NMR (150 MHz, THF-d$_8$): δ = 29.5, 53.3, 126.6, 126.9, 128.0, 134.2, 134.5 141.6 ppm; UV/Vis (THF): λ_{max} (log ε) = 407 (5.04), 472 (5.24), 519 (5.29), 619 (4.44), 712 nm (4.53); HRMS (ESI) *m/z* calcd. for $C_{78}H_{46}N_8$ $[M+H]^+$ 1099.4255, found 1099.4237.

1,2-Bis[5,10,15-triphenylporphyrin-20-ylato}zinc(II)]ethine (111): Produced from ethynyl porphyrin **74** (70 mg, 0.112 mmol), bromoporphyrin **52** (67 mg, 0.112 mmol), $AsPh_3$ (38 mg, 0.123 mmol) and $Pd_2(dba)_3$ (10 mg, 0.011 mmol) using general procedure J. The solvent was removed *in vacuo* and the residue filtered through a plug of silica using CH_2Cl_2/TEA as eluent (99:1, v/v), to yield a green fraction. Recrystallization from CH_2Cl_2/MeOH gave a dark powder (75 mg, 0.068 mmol, 47%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.83 (m, 20H, Ph-*H*), 8.26 (m, 4H, Ph-*H*), 8.33 (m, 6H, Ph-*H*), 8.95-8.96 (d, 8H, H_β), 9.23-9.24 (d, 4H, H_β), 10.51-10.52 ppm (d, 4H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 98.8, 99.2, 120.3, 120.7, 124.6, 124.6, 125.7, 128.5, 129.6, 129.8, 130.8, 132.6, 132.8, 141.6, 141.7, 148.1, 148.4, 148.8, 151.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 412 (5.18), 479 (5.44), 548 (4.36), 685 nm (4.74); HRMS (ESI) *m/z* calcd. for $C_{78}H_{46}N_8Zn_2$ $[M]^+$ 1222.2428, found 1222.2468.

1-[(10',20'-Diphenyl)-15'-(4-nitrophenyl)porphyrin-5-yl]-2-(5-butyl-10,20-diphenylporphyrin-5-yl]ethine (112): Following the general procedure J, 5-ethynyl-15-(4-nitrophenyl)-10,20-diphenylporphyrin **76** (21 mg, 0.033 mmol), 5-bromo-15-butyl-10,20-diphenylporphyrin **26** (20 mg, 0.033 mmol), $AsPh_3$ (20 mg, 0.066 mmol) and $Pd_2(dba)_3$ (8 mg, 0.008 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and heated at 65 ºC for 16 hours. The crude product was been purified by column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 2:1, v/v) to give 11 mg (0.009 mmol, 31 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. >300 ºC; R_f = 0.36 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.02 (s, 2H, N*H*), -1.92 (s, 2H, N*H*), 1.16 (t, 3H, ^3J = 7.6 Hz, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.53 (m, 2H, $CH_2CH_2CH_2CH_3$), 5.01 (t, 2H, ^3J = 8.2, 7.6 Hz, $CH_2CH_2CH_2CH_3$), 7.84 (m, 12H, Ar-*H*), 8.30 (d, 8H, ^3J = 7.0 Hz, Ar-*H*), 8.42 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.67 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.71 (d, 2H, ^3J = 4.7 Hz, H_β), 8.89 (dd, 4H, ^3J = 4.7 Hz, H_β), 9.05 (d, 2H, ^3J = 4.1 Hz, H_β), 9.11 (d, 2H, ^3J = 4.7 Hz, H_β), 9.48 (d, 2H, ^3J = 5.3 Hz, H_β), 10.26 (d, 2H, ^3J = 4.7 Hz, H_β), 10.35 ppm (d, 2H, ^3J = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.7, 22.5, 30.7, 40.7, 99.1, 100.5, 101.5, 121.0, 121.8, 126.6, 127.7, 134.3, 134.8, 141.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 (5.03), 428 (5.04), 472 (5.20), 519 (4.37), 622 (4.47), 713 nm (4.54); HRMS (MS ES+) *m/z* calcd. for $[C_{76}H_{54}N_9O_2]$: 1124.4384; found 1124.4400.

1-[(10',20'-Diphenyl)-15'-(4-nitrophenyl)porphyrin-5-yl]-2-[(5-butyl-10,20-dinaphthylporphyrin-5-yl]ethine (113): Following the general procedure J, 5-ethynyl-15-(4-nitrophenyl)-10,20-diphenylporphyrin **76** (18 mg, 0.029 mmol), 5-bromo-15-butyl-10,20-dinaphthylporphyrin **28** (20 mg, 0.029 mmol), $AsPh_3$ (18 mg, 0.057 mmol) and $Pd_2(dba)_3$ (7 mg, 0.007 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and heated at 65 ºC for 14 hours. The crude product was been purified by column chromatography (CH_2Cl_2 : *n*-hexane = 2:1, v/v) to give 9 mg (0.007 mmol, 25 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. >300 ºC; R_f = 0.5 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.02 (s, 2H, N*H*), -1.62 (s, 2H, N*H*), 1.15 (t, 3H, ^3J = 7.0 Hz, $CH_2CH_2CH_2CH_3$), 1.86 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.55 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.95 (t, 2H, ^3J = 8.8, 7.6 Hz, $CH_2CH_2CH_2CH_3$), 7.18-7.26 (m, 4H, Ar-*H*), 7.57 (m, 2H, Ar-*H*), 7.79-7.84 (m, 8H, Ar-*H*), 7.96 (m, 2H, Ar-*H*), 8.22 (d, 2H, ^3J = 8.7 Hz, Ar-*H*), 8.26 (d, 4H, ^3J = 6.4 Hz, Ar-*H*), 8.38 (dd, 6H, ^3J = 8.3 Hz, Ar-*H*), 8.65 (m, 2H, H_β), 8.68 (d, 2H, ^3J = 4.5 Hz, H_β), 8.80 (m, 2H, H_β), 8.85 (d, 2H, ^3J = 4.5 Hz, H_β), 9.04 (d, 2H, ^3J = 4.1 Hz, H_β), 9.37 (d, 2H, ^3J = 3.4 Hz, H_β), 10.14 (d, 2H, ^3J = 4.5 Hz, H_β), 10.27 ppm (d, 2H, ^3J = 4.1 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 23.5, 35.1, 40.7, 99.2, 100.2, 101.4, 118.1, 121.7, 122.9, 124.1, 125.6, 126.2, 127.8, 128.7, 129.8, 132.5, 134.8, 136.7, 139.0, 141.3, 147.7, 148.8 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 409 (4.92), 430 (4.93), 473 (5.16), 520 (4.22), 620 (4.37), 714 nm (4.45); HRMS (MS ES+) *m/z* calcd. for $[C_{84}H_{57}N_9O_2]$: 1224.4655; found 1224.4662.

1-[(5-(1-Ethylpropyl)porphyrin-15-yl)-2-[(10,20-diphenylporphyrin-5-yl)ethine (114): Following the general procedure J, 5-ethynyl-10,20-diphenylporphyrin **77** (30 mg, 0.065 mmol), 5-bromo-15-(1-ethyl-propyl)porphyrin **85** (32 mg, 0.065 mmol), $AsPh_3$ (40 mg, 0.13 mmol) and $Pd_2(dba)_3$ (15 mg, 0.016 mmol) in a mixture of THF (15 mL) and NEt_3 (5 mL) were used. Purification of the product was carried out by two column chromatographies on silica gel (1. *n*-hexane : CH_2Cl_2 = 4 : 1, 2. 1:1, v/v) and recrystallization from CH_2Cl_2/CH_3OH to give purple crystals (16 mg, 0.018 mmol, 29 %). M.p. >300 ºC; R_f = 0.57 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.27 (s, 2H, N*H*), -2.12 (s, 2H, N*H*), 1.04 (t, 6H, ^3J = 7.0 Hz, $CH(CH_2CH_3)_2$), 2.89 (m, 2H, $CH(CH_2CH_3)_2$), 3.04 (m, 2H, $CH(CH_2CH_3)_2$), 5.08 (m, 1H, $CH(CH_2CH_3)_2$), 7.87 (m, 6H Ar-*H*), 8.34 (m, 4H, Ar-*H*), 9.01 (d, 2H, ^3J = 4.7 Hz, H_β), 9.22 (d, 2H, ^3J = 4.7 Hz, H_β), 9.31 (d, 2H, ^3J = 4.7 Hz, H_β), 9.42 (d, 2H, ^3J = 4.7 Hz, H_β), 9.52 (d, 2H, ^3J = 4.7 Hz, H_β), 9.75 (m, 2H, ^3J = 4.7 Hz, H_β), 10.18 (s, 1H, H_{meso}), 10.25 (s, 2H, H_β); 10.32 (d, 2H, ^3J = 3.5 Hz, H_β), 10.49 (s, 1H, H_{meso}), 10.50 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 34.5, 50.7, 98.3, 98.9, 100.8, 120.7, 126.8, 127.7, 131.8, 132.5, 134.5, 141.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε)= 398 (4.70), 417 (4.66), 432 (4.65), 464 (4.96), 509 (4.19), 609 (4.24), 696 nm (4.27); HRMS (MS ES+) *m/z* calcd. for $[C_{59}H_{45}N_8]$ $(M+H^+)$: 865.3767; found 865.3757.

1-[5-(1-Ethylpropyl)porphyrin-10-yl)]-2-(10,20-diphenylporphyrin-5-yl)ethine (115): Following the general procedure J, 5-ethynyl-10,20-diphenylporphyrin **77** (30 mg, 0.065 mmol), 5-bromo-10-(1-ethylpropyl)porphyrin **86** (37 mg, 0.065 mmol), $AsPh_3$ (40 mg, 0.131 mmol) and $Pd_2(dba)_3$ (15 mg, 0.016 mmol) in a mixture of THF (15 mL) and NEt_3 (5 mL) were used. Purification via two colum chromatograpies on silica gel (1. CH_2Cl_2 : *n*-hexane = 1 : 2, 2. CH_2Cl_2 : *n*-hexane = 1 : 2, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (10 mg, 0.011 mmol, 20 %). M.p. >300 ºC, R_f = 0.37 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 400 (4.94), 433 (4.86), 466 (5.16), 510 (4.40), 605 (4.40), 695 nm (4.41); HRMS (MS ES+) *m/z* calcd. for $[C_{59}H_{45}N_8]$ $(M+H^+)$: 865.3767; found 865.3763.

(5-(1-Ethylpropyl)-porphyrin-15-yl)-ethynyl-(5-hexyl-10-(3-nitrophenyl)-15-(3,4,5-trimethoxyphenyl)porphyrin-20-yl) (116): Following the general procedure J, 5-(1-ethylpropyl)-15-ethynylporphyrin **92** (20 mg, 0.05 mmol) 5-bromo-10-hexyl-15-(3-nitrophenyl)-20-(3,4,5-trimethoxyphenyl)porphyrin[6] (38 mg, 0.05 mmol), $AsPh_3$ (31 mg, 0.1 mmol) and $Pd_2(dba)_3$ (11 mg, 0.013 mmol) in a mixture of THF (15 mL) and NEt (5 mL) were used. Purification of the product was carried out by two column chromatographies on silica gel (1. *n*-hexane : CH_2Cl_2 = 2 : 1, 2. *n*-hexane : ethyl acetate = 3 : 1, v/v) and recrystallization from CH_2Cl_2/CH_3OH to give purple crystals (18 mg, 0.016 mmol, 33 %). M.p. >300 ºC; R_f = 0.5 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.06 (s, 2H, N*H*), -1.97 (s, 2H, N*H*), 1.00 (t, 3H, J = 7.0 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.05 (t, 6H, J = 7.0 Hz, $CH(CH_2CH_3)_2$), 1.47 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.89 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.62 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.90 (m, 2H, $CH(CH_2CH_3)_2$), 3.04 (m, 2H, $CH(CH_2CH_3)_2$), 4.06 (s, 6H, OCH_3), 4.24 (s, 3H, OCH_3), 5.00 (t, 2H, J = 7.0 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.11 (m, 1H, $CH(CH_2CH_3)_2$), 7.56 (s, 2H, Ar-*H*), 7.99 (t, 1H, J = 7.6 Hz, Ar-*H*), 8.56 (d, 1H, J = 7.6 Hz, Ar-*H*), 8.70 (d, 1H, J = 4.7 Hz, H_β), 8.72 (s, 1H, Ar-*H*), 8.75 (d, 1H, J = 4.7 Hz, H_β), 8.96 (d, 1H, H_β), 9.12 (s, 1H, Ar-*H*), 9.26 (d, 1H, J = 4.7 Hz, H_β), 9.43 (br s, 2H, H_β), 9.47 (d, 1H, J = 4.7 Hz, H_β), 9.56 (d, 2H, J = 4.7 Hz, H_β), 9.75 (d, 2H, J = 4.7 Hz, H_β), 9.79 (br s, 1H, H_β), 10.27 (s, 2H, H_{meso}), 10.35 (d, 2H, J = 4.1 Hz, H_β), 10.42 (d, 1H, J = 4.7 Hz, H_β), 10.50 ppm (d, 1H, J = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 22.6, 31.7, 34.5, 35.3, 38.7, 50.0, 56.3, 61.1, 98.1, 99.2, 99.6, 100.7, 105.9, 112.7, 117.4, 120.7, 122.6, 125.2, 127.4, 127.6, 128.0, 128.8, 129.1, 130.7, 131.3, 131.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.09), 437 (4.92), 468 (5.30), 513 (4.35), 553 (4.04), 615 (4.49), 710 nm (3.61); HRMS *m/z* calcd. for (MS ES+) $[C_{68}H_{62}N_9O_5]$ $(M+H^+)$: 1084.4874; found 1084.4926.

4-(10,20-Diphenylporphyrin-5-yl)-phenylethynyl-(10,20-diphenylporphyrin-5-yl) (117): Following the general procedure I, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (30 mg, 0.0533 mmol), 5-bromo-10,20-diphenylporphyrin **9** (32 mg, 0.059 mmol), $AsPh_3$ (33 mg, 0.106 mmol) and $Pd_2(dba)_3$ (12 mg, 0.013 mmol) in a mixture of THF (15 mL) and NEt_3 (5 mL) were used. Purification via column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 1 : 1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (25 mg, 0.0244 mmol, 46 %). M.p. >300 ºC, R_f = 0.25 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.91 (s, 2H, N*H*), -2.44 (s, 2H, N*H*), 7.85 (m, 12H Ar-*H*), 8.31 (m, 8H, Ar-*H*), 8.47 (s, 4H, Ar-*H*), 9.01 (m, 4H, H_β), 9.08 (m, 6H, H_β), 9.33 (d, 2H, J = 4.4 Hz, H_β), 9.39 (d, 2H, J = 4.4 Hz, H_β), 10.05 (d, 2H, J = 4.41 Hz, H_β), 10.22 (s, 1H, H_{meso}), 10.28 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 93.5, 96.6, 96.7, 104.8, 106.4, 119.5, 120.5, 123.4, 126.7, 127.6, 127.7, 128.6, 129.7, 131.1, 134.5, 134.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (4.87), 433 (4.92), 511 (3.76), 571 (3.92), 571 (3.92), 602 (3.43), 662 nm (3.59); HRMS (MS ES+) *m/z* calcd. for $[C_{72}H_{47}N_8]$ $(M+H^+)$: 1023.3910; found 1023.3924.

5-{[(10',20'-Diphenylporphyrinato-5-yl)zinc(II)]-4-phenylethynyl-10,20-diphenylporphyrinato}zinc(II) (118):[49] Following general procedure K, **118** was produced from phenylethynyl porphyrin **56** (20 mg, 0.032 mmol) and bromoporphyrin **48** (19 mg, 0.032 mmol) to yield a purple product (16 mg, 0.014 mmol, 44%). M.p. > 300 °C. ^{1}H NMR (400 MHz $CDCl_3$/pyridine-d^5 10:1, TMS): δ = 7.02 (d, 2H, C_6H_4-*H*), 7.54 (d, 2H, C_6H_4-*H*), 7.25 (m, 2H, Ph-*H*), 7.86 (10H, m, Ph-*H*), 8.32 (8H, m, Ph-*H*), 8.48 (s, 2H, H_β), 9.10 (m, 4H, H_β), 9.17 (m, 4H, H_β), 9.41-9.42 (d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H_β), 9.47-9.48 (d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H_β), 10.11-10.12 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 10.28 (s, 1H, H_{meso}), 10.35 ppm (s, 1H, H_{meso}); UV/vis (CH_2Cl_2): λ_{max} (log ε) = 419 (4.89), 440 (4.62), 552 (3.75), 617 nm (3.61); HRMS (Maldi) *m/z* calcd. for $C_{75}H_{42}N_8Zn_2$ $[M+1]^+$ 1147.2147, found 1147.2135.

5-[4-(10',20'-Diphenylporphyrin-5-yl)phenylethynyl]-10,20-bis(1-ethylpropyl)porphyrin 119. Produced from porphyrin **29** (23 mg, 0.041 mmol) and porphyrin **12** (25 mg, 0.041mmol), following general procedure K to yield a purple powder (green in solution) (19 mg, 0.018 mmol, 45%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.87 (s, 2H, N*H*), -1.89 (s, 2H, N*H*), 1.03 (t, $^3J_{H\text{-}H}$ = 14.7 Hz, 12H, CH_3), 2.88 (m, 4H, CH_2), 3.02 (m, 4H, CH_2), 5.05 (m, 2H, C*H*), 7.85 (m, 6H, Ph-*H*), 8.31-8.34 (m, 2H, Ph-*H*), 8.49 (s, 4H, C_6H_4-*H*), 9.04-9.05 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.09-9.12 (dd, 4H, $^3J_{H\text{-}H}$ = 13.2 Hz, H_β), 9.41-9.42 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.67-9.68 (m, 2H, H_β), 9.78-9.79 (m, 2H, H_β), 10.14 (s, 1H, H_{meso}), 10.15 (s, 2H, H_β), 10.30 ppm (s, 1H, H_{meso});. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 29.2, 29.3, 29.5, 30.2, 31.8, 34.07, 45.6, 119.7, 122.3, 123.6, 123.0, 125.4, 126.7, 127.4, 127.6, 128.3, 129.3, 129.6, 131.2, 131.9, 132.1, 134.6, 134.8, 138.5, 139.5, 139.7, 141.6 ppm; UV/vis (THF): λ_{max} (log ε) = 412 (6.05), 434 (5.99), 508 (4.97), 572 (5.07), 666 nm (4.71); HRMS (Maldi) *m/z* calcd. for $C_{70}H_{58}N_8$ $[M]^+$ 1010.4784, found 1010.4736.

5-[4-(10',20'-Diphenylporphyrin-15'-(4-nitrophenyl)-5-yl)phenylethynyl]-15-butyl-10,20-diphenylporphyrin (120): Following the general procedure J, 5-bromo-15-butyl-10,20-diphenylporphyrin **26** (30 mg, 0.050 mmol), 5-(4-ethynylphenyl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin **58** (34 mg, 0.052 mmol), $AsPh_3$ (31 mg, 0.100 mmol), $Pd_2(dba)_3$ (12 mg, 0.013 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 3 days. The crude product was purified by column chromatography (CH_2Cl_2 : *n*-hexane = 1:2, v/v), followed by a second column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 1:1, v/v) to give 25 mg (0.020 mmol, 42 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. >300 ºC; R_f = 0.3 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.69 (s, 2H, N*H*), -2.14 (s, 2H, N*H*), 1.16 (t, 3H, ^3J = 7.0, 7.6 Hz, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.55 (m, 2H, $CH_2CH_2CH_2CH_3$), 5.02 (t, 2H, ^3J = 7.6 Hz, $CH_2CH_2CH_2CH_3$), 7.45 (m, 2H, Ar-*H*), 7.65 (m, 2H, Ar-*H*), 7.83 (m, 12H, Ar-*H*), 8.28 (m, 8H, Ar-*H*), 8.45 (s, 4H, Ar-*H*), 8.69 (m, 2H, H_β), 8.80 (m, 2H, H_β), 8.89 (m, 2H, H_β), 8.97 (m, 4H, H_β), 9.07 (m, 2H, H_β), 9.48 (m, 2H, H_β), 9.88 ppm (m, 2H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 13.5, 24.5, 34.8, 40.9, 121.7, 125.6, 125.7, 127.1, 127.7, 128.1, 128.7, 129.9, 129.9, 134.1, 134.3, 134.9, 134.9, 135.1, 142.1 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 420 (5.01), 435 (5.08), 516 (3.93), 580 (4.12), 670 nm (3.70); HRMS (MS ES+) *m/z* calcd. for $[C_{82}H_{57}N_9O_2]$: 1200.4655; found 1200.4641.

5-[4-(10',20'-Diphenylporphyrin-5-yl)phenylethynyl]-[10,20-diphenyl-15-(4-nitrophenyl)]porphyrin (121): Follwing the general procedure J, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (34 mg, 0.060 mmol), 5-bromo-15-(4-nitrophenyl)-10,20-diphenylporphyrin **25** (40 mg, 0.060 mmol), $AsPh_3$ (37 mg, 0.12 mmol) and $Pd_2(dba)_3$ (14 mg, 0.015 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and heated at 65 ºC for 24 hours. The crude product was been purified by column chromatography (CH_2Cl_2 : *n*-hexane = 1:1, v/v) to give 30 mg (0.026 mmol, 43 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. >300 ºC; R_f = 0.26 (CH_2Cl_2: *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.91 (s, 2H, N*H*), -2.24 (s, 2H, N*H*), 7.84 (m, 12H, Ar-*H*), 8.29 (m, 8H, Ar-*H*), 8.41 (d, 2H, ^3J = 8.2 Hz, Ar-*H*), 8.50 (s, 4H, Ar-*H*), 8.67 (d, 2H, ^3J = 8.2 Hz, Ar-*H*), 8.71 (d, 2H, ^3J = 4.7 Hz, H_β), 8.87 (d, 2H, ^3J = 4.7 Hz, H_β), 9.03 (t, 4H, ^3J = 4.7 Hz, H_β), 9.07 (m, 4H, H_β), 9.41 (d, 2H, ^3J = 4.1 Hz, H_β), 9.99 (d, 2H, ^3J = 4.7 Hz, H_β), 10.30 ppm (s, 1H, H_{meso}); UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 413 (5.08), 437(5.10), 510 (3.99), 543 (3.71), 579 (4.20), 670 nm (3.81).

5-[4-(10',20'-Diphenylporphyrin-5-yl)phenylethynyl]-15-butyl-10,20-dinaphthylporphyrin (122): Following the general procedure J, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (32 mg, 0.057 mmol), 5-bromo-15-butyl-10,20-dinaphthylporphyrin **28** (40 mg, 0.057 mmol), $AsPh_3$ (35 mg, 0.114 mmol) and $Pd_2(dba)_3$ (13 mg, 0.014 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and heated at 65 ºC for 36 hours. The crude product was been purified by column chromatography on silica gel (CH_2Cl_2 : *n*-hexane = 2:1, v/v), followed by a second column purification (CH_2Cl_2: *n*-hexane = 2:3, v/v) to give 20 mg (0.016 mmol, 37 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. >300 ºC; R_f = 0.36 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.93 (s, 2H, N*H*), -1.87 (s, 2H, N*H*), 1.13 (t, 3H, ^3J = 7.8, 6.9 Hz, $CH_2CH_2CH_2CH_3$), 1.82 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.52 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.94 (t, 2H, ^3J = 7.8 Hz, $CH_2CH_2CH_2CH_3$), 7.20 (m, 4H, Ar-*H*), 7.56 (m, 2H, Ar-*H*), 7.81 (m, 6H, Ar-*H*), 7.95 (t, 2H, ^3J = 7.9, 8.8 Hz, Ar-*H*), 8.22 (d, 2H, ^3J = 7.8 Hz, Ar-*H*), 8.29 (d, 4H, ^3J = 7.8 Hz, Ar-*H*), 8.30-8.42 (m, 8H, Ar-*H*), 8.62 (d, 2H, ^3J = 4.9 Hz, H_β), 8.72 (m, 2H, H_β), 8.99 (d, 2H, ^3J = 3.9 Hz, H_β), 9.04 (dd, 4H, ^3J = 3.9 Hz, H_β), 9.36 (d, 2H, ^3J = 4.9 Hz, H_β), 9.38 (d, 2H, ^3J = 3.9 Hz, H_β), 9.79 (d, 2H, ^3J = 4.9 Hz, H_β), 10.27 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 23.5, 35.1, 40.7, 92.8, 96.4, 98.6, 104.9, 118.1, 119.6, 122.7, 123.4, 124.1, 125.6, 126.2, 127.6, 128.5, 129.7, 130.8, 131.2, 132.5, 134.6, 136.7, 139.1, 141.6, 142.7 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 413 (5.05), 439 (5.12), 510 (4.04), 543 (3.87), 579 (4.20), 671 nm (3.75); HRMS (MS ES+) *m/z* calcd. for $[C_{84}H_{58}N_8]$: 1179.4863; found 1179.4805.

5-[4-(10',20'-Diphenylporphyrin-15'-(4-nitrophenyl)-5-yl)phenylethynyl]-15-butyl-10,20-dinaphthylporphyrin (123): Following the general procedure J, 5-(4-ethynylphenyl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin **26** (25 mg, 0.036 mmol), 5-bromo-15-butyl-10,20-dinaphthylporphyrin **28** (25 mg, 0.036 mmol), $AsPh_3$ (23 mg, 0.073 mmol) and $Pd_2(dba)_3$ (8 mg, 0.009 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and heated at 65 ºC for 3 days. The crude product was purified by column chromatography (CH_2Cl_2 : *n*-hexane = 2:1, v/v/),

followed by a second silica gel column (CH_2Cl_2 : *n*-hexane = 1:2, v/v/) to yield 21 mg (0.016 mmol, 45 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. >300 ºC; R_f = 0.3 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.72 (s, 2H, N*H*), -1.87 (s, 2H, N*H*), 1.13 (t, 3H, ^3J = 7.0, 7.6 Hz, $CH_2CH_2CH_2CH_3$), 1.84 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.55 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.95 (t, 2H, ^3J = 7.6, 8.2 Hz, $CH_2CH_2CH_2CH_3$), 7.20 (m, 4H, Ar-*H*), 7.57 (t, 2H, ^3J = 8.2 Hz, Ar-*H*), 7.82 (m, 6H, Ar-*H*), 7.96 (t, 2H, ^3J = 8.2 Hz, Ar-*H*), 8.22 (d, 2H, ^3J = 8.2 Hz, Ar-*H*), 8.26 (d, 4H, ^3J = 7.6 Hz, Ar-*H*), 8.33-8.45 (m, 10H, Ar-*H*), 8.62 (d, 2H, ^3J = 4.1 Hz, H_β), 8.68 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.71 (m, 2H, H_β), 8.78 (d, 2H, ^3J = 5.3 Hz, H_β), 8.94 (t, 4H, ^3J = 4.1, 4.7 Hz, H_β), 9.03 (d, 2H, ^3J = 4.7 Hz, H_β), 9.37 (d, 2H, ^3J = 5.3 Hz, H_β), 9.78 ppm (d, 2H, ^3J = 4.7 Hz, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 13.7, 23.2, 35.7, 40.4, 95.9, 116.4, 117.8, 120.4, 121.4, 122.5, 123.9, 125.3, 125.9, 126.4, 127.5, 128.2, 129.5, 132.2, 134.1, 134.7, 138.7, 141.4, 147.3 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 419 (5.21), 439 (5.33), 518 (4.26), 579 (4.41), 670 nm (4.03); HRMS (MS ES+) *m/z* calcd. for $[C_{90}H_{62}N_9O_2]$: 1300.5026; found 1300.5034.

4-(10,20-Diphenylporphyrin-5-yl)-phenylethynyl-(1-ethylpropyl-porphyrin-15-yl) (124): Following the general procedure J, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (30 mg, 0.0533 mmol), 5-bromo-15-(1-ethylpropyl)porphyrin **85** (33 mg, 0.05936), $AsPh_3$ (36 mg, 0.118 mmol), $Pd_2(dba)_3$ (13 mg, 0.015 mmol) in a mixture of THF (15 mL) and NEt_3 (5 mL) were used. Purification via column chromatography on silica gel (*n*-hexane : CH_2Cl_2 = 2 : 1, v/v) followed by a second column using *n*-hexane : CH_2Cl_2 (1 : 1, v/v) and recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (5 mg, 0.005 mmol, 8 %). M.p. >300 ºC, R_f = 0.37 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.90 (s, 2H, N*H*), -2.32 (s, 1H, N*H*), -2.24 (s, 1H, N*H*), 1.01 (t, 6H, *J* = 7.0, 7.6 Hz, $CH(CH_2CH_3)_2$), 2.88 (m, 2H, $CH(CH_2CH_3)_2$), 3.03 (m, 2H, $CH(CH_2CH_3)_2$), 5.1 (m, 1H, $CH(CH_2CH_3)_2$), 7.84 (m, 6H Ar-*H*), 8.32 (m, 4H, Ar-*H*), 8.49 (s, 4H, Ar-*H*), 9.04 (d, 2H, *J* = 4.7 Hz, H_β), 9.10 (m, 4H, H_β), 9.41 (d, 4H, *J* = 4.7 Hz, H_β), 9.51 (d, 2H, *J* = 4.7 Hz, H_β), 9.72 (m, 1H, H_β), 9.78 (m, 1H, H_β), 9.99 (m, 2H, H_β), 10.27 (s, 2H, H_{meso}), 10.30 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 34.5, 50.0, 53.2, 67.8, 92.2, 95.9, 96.4, 99.9, 104.1, 105.6, 119.6, 123.4, 125.0, 126.7, 129.8, 131.5, 132.3, 134.5, 141.6, 142.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.01), 425 (5.05), 510 (3.85), 566 (4.09), 595 (3.49), 648 (3.53) nm; HRMS (MS ES+) *m/z* calcd. for $[C_{65}H_{49}N_8]$ ($M+H^+$): 941.4080; found 941.4088.

4-(10,20-Diphenylporphyrin-5-yl)phenylethynyl-(5-ethylpropylporphyrin-10-yl) (125): Following the general procedure J, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (30 mg, 0.053 mmol), 5-bromo-10-(1-ethylpropyl)porphyrin **86** (40 mg, 0.131 mmol), $AsPh_3$ (37 mg, 0.065 mmol) and $Pd_2(dba)_3$ (15 mg, 0.016 mmol) in a mixture of THF (15 mL) and NEt_3 (5 mL) were used. Purification via two column chromatographies on silica gel (each with *n*-hexane : CH_2Cl_2 2 : 1, v/v) and recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (16 mg, 0.017 mmol, 26 %). M.p. >300 ºC; R_f = 0.25 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.89 (s, 2H, N*H*), -2.72 (s, 1H, N*H*), -2.61 (s, 1H, N*H*), 1.04 (t, 6H, *J* = 7.0 Hz, $CH(CH_2CH_3)_2$), 2.9 (m, 2H, $CH(CH_2CH_3)_2$), 3.06 (m, 2H, $CH(CH_2CH_3)_2$), 5.18 (m, 1H, $CH(CH_2CH_3)_2$), 7.85 (m, 6H, Ar-*H*), 8.33 (m, 4H, Ar-*H*), 8.50 (s, 4H, Ar-*H*), 9.04 (d, 2H, *J* = 4.7 Hz, H_β), 9.10 (m, 3H, H_β), 9.38-9.46 (m, 5H, H_β), 9.74 (br s, 1H, H_β), 9.80 (br s, 1H, H_β), 9.85 (br s, 1H, H_β), 9.92 (br s, 1H, H_β), 10.12 (m, 1H, H_β), 10.14 (s, 1H, H_{meso}), 10.19 (b s, 1H, H_β), 10.20 (s, 1H, H_{meso}), 10.30 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.2, 34.6, 50.3, 93.7, 96.3, 100.2, 104.9, 105.7, 119.6, 123.5, 125.0, 126.7, 129.7, 130.9, 131.3, 134.5, 141.6, 142.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 414 (4.90), 510 (3.70), 564 (3.78), 655 nm (3.40); HRMS (MS ES+) *m/z* calcd. for $[C_{65}H_{49}N_8]$ ($M+H^+$): 941.4080; found 941.4088.

4,4'-Bis[{10,15-bis(1-ethylpropyl)porphyrinato}zinc(II)]phenyl]-but-1,3-diyne (126): Homocoupled side product obtained as a purple powder from the synthesis of **135** (11 mg, 0.009 mmol, 21 %). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.02 (t, 24H, $^3J_{H\text{-}H}$ = 14.3 Hz, CH_3), 2.88 (m, 8H, CH_2), 3.06 (m, 8H, CH_2), 5.09 (m, 4H, C*H*), 8.05-8.07 (d, 4H, , $^3J_{H\text{-}H}$ = 7.8 Hz, Ph-*H*), 8.28-8.30 (d, 4H, $^3J_{H\text{-}H}$ = 7.3 Hz, Ph-*H*), 9.13-9.14 (d, 4H, $^3J_{H\text{-}H}$ = 9.1 Hz, H_β), 9.47-9.48 (m, 4H, H_β), 9.86 (m, 8H, H_β), 10.19 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ= 14.1, 22.5, 29.5, 123.8, 128.5, 130.8, 130.9, 134.4 ppm; UV/vis: λ_{max} (log ε) = 420 (5.63), 456 (4.75), 552 (4.40), 592 (3.86), 668 nm (4.00); HRMS (Maldi) *m/z* calcd. for $C_{76}H_{70}N_8Zn_2$ $[M+1]^+$ 1222.4306, found 1222.4417.

Bis[5,5'[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl]porphyrin-but-1,3-diyne (128): Using the original Sonogashira conditions,[18] 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-phenylporphyrin **71** (20 mg, 0.025 mmol), bromo-10,15,20-tris(4-methoxyphenyl)porphyrin **22** (16 mg, 0.025 mmol), CuI (4 mg, 0.020 mmol) and $PdCl_2(PPh_3)_2$ (20 mg, 0.011 mmol) were dried *in vacuo* and then dissolved in degassed NEt_3 (1 mL) and THF (4 mL). After stirring the solution for 15 h at rt all solvents were removed in vacuo and the residue purified by column chromatography (silica, CH_2Cl_2:hexane, 1:1, v/v) to yield a green solid. NMR showed that not the desired product was formed, but **64** had undergone reductive coupling to give **120**. Yield: 9 mg (0.006 mmol, 22%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = -2.00 (s, 4H, N*H*), 1.59 (s, 72H, *t*-Bu-*H*), 7.73-7.81 (m, 6H, Ph-*H*), 7.85-7.87 (m, 4H, Ph-*H*), 8.13-8.16 (m, 8H, Ph-*H*), 8.21-8.24 (m, 4H, Ph-*H*), 8.79 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.84 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.07 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 9.96 ppm (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.7, 35.0, 83.6, 85.7, 121.2, 123.0, 126.5, 128.3, 128.5, 129.8, 133.6, 134.2, 139.5, 140.5, 188.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 446 (4.79), 476 (4.65), 526 (3.76), 610 (4.08), 708 nm (4.19); HRMS (ESI) *m/z* calcd. for $C_{112}H_{114}N_8$ $[M+H]^+$ 1571.9406, found 1571.9456.

5,15-Bis{10,20-diphenylporphyrin-5-yl)ethynyl}-10,20-diphenylporphyrin (130). Trimer **130** was generated from bromoporphyrin **9** (40 mg, 0.074 mmol) and ethynylporphyrin **70** (18.0, 0.035 mmol), following general procedure K to yield a purple/brown powder (20 mg, 0.014 mmol, 40%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/d-TFA 10:1, TMS): δ = 8.16 (m, 12H, Ph-*H*), 8.60 (m, 8H, Ph-*H*), 8.71 (m, 6H, Ph-*H*), 9.09-9.10 (dd, 8H, $^3J_{H\text{-}H}$ = 6.6 Hz, H_β), 9.17-9.18 (d, 4H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β), 9.54-9.55 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.11-10.12 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.20-10.22 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.89 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$ 10:1): δ = 124.6, 125.1, 127.4, 127.6, 128.4, 130.7, 131.2, 137.8, 138.1, 145.9, 146.3 ppm; UV/vis: λ_{max} (log ε) = 410 (4.96), 479 (4.96), 634 (4.57), 673 (4.53), 787 nm (4.45); HRMS (Maldi) *m/z* calcd. for $C_{100}H_{62}N_{12}$ $[M+1]^+$ 1431.5236, found 1431.5240.

5,15-Bis{4-(10',20'-diphenylporphyrin-5-yl)phenylethyne}-10,20-diphenylporphyrin (131): Trimer **131** was obtained from phenylethynylporphyrin **29** (48 mg, 0.086 mmol) and bromoporphyrin **10** (25 mg, 0.040 mmol) to yield a purple powdered product (24 mg, 0.015 mmol, 38%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$/d-TFA 10:1, TMS): δ = 8.10 (m, 18H, Ph-*H*), 8.60 (m, 12H, Ph-*H*), 8.79-8.80 (d, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, C_6H_4-*H*), 8.83-8.85 (d, 4H, $^3J_{H\text{-}H}$ = 4.6 Hz, C_6H_4-*H*), 8.88-8.90 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 8.93-8.95 (m, 8H, H_β), 9.10-9.11 (d, 4H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.50-9.51 (d, 4H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.71-9.72 (d, 4H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 10.75 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$ 10:1): δ = 128.2, 128.5, 128.6, 129.2, 130.3, 130.4, 130.6, 130.8, 132.3, 138.1, 138.3, 138.9 ppm; UV/vis: λ_{max} (log ε) = 412 (5.10), 446 (5.02), 508 (4.70), 602 (4.60), 634 (4.56), 710 nm (4.51); HRMS (Maldi) *m/z* calcd. for $[M]^+$ ($C_{112}H_{70}N_{12}$) 1582.5846, found 1582.5859.

{5,15-Bis[4-(10',20'-diphenylporphyrinato-5-yl)zinc(II)}phenylethyne]-10,20-di[phenylporphyrin-5-ylato}zinc(II) (132): Synthesized from phenylethynylporphyrin **56** (39 mg, 0.061 mmol) and bromoporphyrin **46** (20 mg, 0.029 mmol), following general procedure K to yield a dark purple solid (14 mg, 0.007 mmol, 26%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d^5 10:1, TMS): δ = 7.78 (m, 18H, Ph-*H*), 8.28 (d, 12H, $^3J_{H\text{-}H}$ = 7.3 Hz, Ph-*H*), 8.41 (m, 8H, C_6H_4-*H*), 8.98 (m, 8H, H_β), 9.07 (m, 8H, H_β), 9.36-9.37 (d, 4H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_β), 9.94-9.95 (d, 4H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 10.19 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$/pyridine-d_5 10:1): δ = 45.6, 52.8, 63.2, 123.3, 127.0, 127.1, 129.3, 131.4, 131.6, 131.7, 132.1, 132.2, 132.5, 134.4, 134.6, 143.3, 149.3, 149.6 ppm; UV/vis: λ_{max} (log ε) = 418 (4.05), 451 (3.79), 551 (2.95), 605 (2.75), 659 (2.97), 698 nm (1.94); HRMS (Maldi) *m/z* calcd. for $C_{112}H_{64}N_{12}Zn_3$ $[M+1]^+$ 1769.3372, found 1769.3369.

{5,15-Bis[4-(10',20'-diphenylporphyrinato-5-yl)nickel(II)}phenylethynyl]-{10,20-diphenylporphyrinylato}nickel(II) (133):[40] Synthesized from phenylethynylporphyrin **54** (20 mg, 0.032 mmol) and bromoporphyrin **47** (10 mg, 0.015 mmol), following general procedure K to yield an impure dark solid containing **133**. HRMS (Maldi) *m/z* calcd. for $C_{112}H_{64}N_{12}Ni_3$ $[M]^+$ 1750.3437, found 1750.3448.

{5,15-Bis[4-[(10',20'-diphenylporphyrinato)zinc(II)]phenylethynyl]-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (134): Produced from phenylethynylporphyrin **56** (31 mg, 0.050 mmol) and bromoporphyrin **14** (20 mg, 0.024 mmol), according to general procedure K, to yield a dark green solid (13 mg, 0.006 mmol, 28%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d^5 10:1, TMS): δ= -1.73 (s, 2H, N*H*), 7.73 (m, 12H, Ph-*H*), 7.84 (m, 4H, C_6H_4-*H*), 8.12-8.13 (d, $^3J_{H\text{-}H}$ = 1.8 Hz, 4H, C_6H_4-*H*), 8.23 (8H, m, Ph-*H*), 8.38 (m, 6H, C_6H_3-*H*), 8.97 (m, 8H, H_β), 9.01-9.02 (d, 4H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.04-9.05 (d, 4H, $^3J_{H\text{-}H}$ = 4.6 Hz, H_β), 9.31-9.32 (d, 4H, $^3J_{H\text{-}H}$ = 4.5 Hz, H_β), 9.90-9.91 (d, 4H, $^3J_{H\text{-}H}$ = 4.7 Hz, H_β), 10.14 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$/pyridine-d_5 10:1): δ = 13.9, 22.4,

31.4, 34.9, 120.0, 126.2, 127.0, 129.4, 129.8, 131.2, 131.4, 131.6, 132.1, 134.5, 134.9, 143.2 ppm; UV/vis: λ_{max} (log ε) = 418 (4.55), 447 (4.39), 551 (3.32), 610 (3.57), 698 nm (3.35); HRMS (Maldi) *m/z* calcd. for $C_{128}H_{98}N_{12}Zn_3$ $[M+1]^+$ 1931.6620, found 1931.662.

{5,15-Bis[4-(10',20'-bis(1-ethylpropyl)porphyrinato-5-yl)zinc(II)]phenylethynyl-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (135): Produced from phenylethynylporphyrin **55** (58 mg, 0.094 mmol) and bromoporphyrin **49** (30 mg, 0.045 mmol) following general procedure K to yield a purple product (green in solution). Yield (34 mg, 0.020 mmol, 44%). M.p. > 300 °C. ^{1}H NMR (600 MHz, THF-d_8, TMS): δ = 1.02 (t, 24H, $^3J_{H-H}$ = 14.6 Hz, C*H*$_3$), 2.93 (m, 12H, C*H*$_2$), 3.16 (m, 12H, C*H*$_2$), 5.35 (m, 6H, C*H*), 8.50-8.51 (d, 4H, $^3J_{H-H}$ = 7.6 Hz, Ph-*H*), 8.54-8.55 (d, 4H, $^3J_{H-H}$ = 7.6 Hz, Ph-*H*), 9.12-9.14 (d, 4H, $^3J_{H-H}$ = 9.2 Hz, H_β), 9.44 (m, 4H, H_β), 9.88-9.90 (m, 12H, H_β), 10.10 (m, 4H, H_β), 10.13 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, THF-d_8): δ = 13.3, 20.2, 28.8, 29.6, 34.7, 45.1, 50.2, 124.9, 129.4, 129.9, 130.2, 130.5, 130.8, 131.1, 131.3, 134.8, 142.1, 144.5, 146.7, 147.7, 148.0, 148.8, 149.1, 149.3, 149.7, 151.6, 152.2, 152.4 ppm; UV/vis: λ_{max} (log ε) = 418 (5.41), 454 (5.32), 554 (4.22), 668 nm (4.59); HRMS (Maldi) *m/z* calcd. for $C_{128}H_{98}N_{12}Zn_3$ $[M]^+$ 1732.6068, found 1732.6035.

{5,15-Bis[4-(10',20'-diphenylporphyrinato-5-yl)zinc(II)]phenylethynyl-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (136): Produced from phenylethynylporphyrin **56** (20 mg, 0.032 mmol) and bromoporphyrin **49** (10 mg, 0.015 mmol) following general procedure K to yield a dark green product (bright green in solution). Yield (6 mg, 0.003 mmol, 21%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.98 (t, 12H, $^3J_{H-H}$ = 14.6 Hz, C*H*$_3$), 2.89 (m, 4H, C*H*$_2$), 3.07 (m, 4H, C*H*$_2$), 5.16 (m, 2H, C*H*), 7.67 (s, 4H, C_6H_4-*H*), 7.80 (m, 12H, Ph-*H*), 8.29 (m, 8H, Ph-*H*), 8.43-8.44 (d, 4H, $^3J_{H-H}$ = 3.5 Hz, C_6H_4-*H*), 9.03-9.04 (d, 4H, $^3J_{H-H}$ = 4.6 Hz, H_β), 9.07-9.08 (d, 4H, $^3J_{H-H}$ = 4.5 Hz, H_β), 9.11-9.13 (d, 4H, $^3J_{H-H}$ = 4.6 Hz, H_β), 9.38-9.39 (d, 4H, $^3J_{H-H}$ = 4.5 Hz, H_β), 9.79 (m, 4H, H_β), 10.00 (m, 4H, H_β), 10.20 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.6, 35.1, 50.8, 106.0, 126.5, 127.3, 129.7, 131.2, 132.0, 132.8, 134.0, 134.8, 135.2 ppm; UV/vis (THF): λ_{max} (log ε) = 422 (5.63), 457 (5.20), 554 (4.14), 673 nm (4.20); HRMS (Maldi) *m/z* calcd. for $C_{110}H_{76}N_{12}Zn_3$ $[M+H]^+$ 1732.6068, found 1732.6035.

5,15-Bis{4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl}-10,20-dinaphthylporphyrin (137): Following the general procedure K 5,15-dibromo-10,20-dinaphthylporphyrin **27** (30 mg, 0.042 mmol), 5-ethynylphenyl-10,20-diphenylporphyrin **29** (49 mg, 0.087 mmol), $AsPh_3$ (26 mg, 0.084 mmol) and $Pd_2(dba)_3$ (10 mg, 0.0105 mmol) gave 15 mg (0.009 mmol, 22 %) of the target compound. M.p. >300 ºC; R_f = 0.54 (CH_2Cl_2: *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.74 (s, 4H, N*H*), -1.49 (s, 2H, N*H*), 7.60 (t, 2H, ^3J = 7.6 Hz, Ar-*H*), 7.83 (s, 12H, Ar-*H*), 8.00 (t, 2H, ^3J = 7.6, 8.2 Hz, Ar-*H*), 8.24 (d, 2H, ^3J = 8.19 Hz, Ar-*H*), 8.30 (s, 8H, Ar-*H*), 8.41 (m, 12H, Ar-*H*), 8.73 (m, 4H, Ar-*H*), 9.00 (d, 4H, ^3J = 4.7 Hz, H_β), 9.06 (dd, 10H, ^3J = 4.7 Hz, H_β), 9.40 (d, 6H, ^3J = 4.1 Hz, H_β), 9.83 (d, 4H, ^3J = 4.7 Hz, H_β), 10.29 (s, 2H, H_{meso}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 93.0, 95.3, 100.1, 101.9, 103.4, 105.5, 107.3, 110.1, 120.1, 120.2, 124.8, 126.3, 126.9, 127.3, 128.2, 129.6, 130.5, 131.1, 131.6, 135.1, 135.4, 142.5 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 412 (5.36), 451 (5.24), 510 (4.56), 545 (4.43), 605 (4.64), 694 nm (3.48); HRMS (MS ES+) *m/z* calcd. for $[C_{120}H_{75}N_{12}]$: 1683.6238; found 1683.6270.

5,15-Bis{10,20-diphenylporphyrin-5-yl)ethynyl}-10,20-dinaphthylporphyrin (140): Following the general procedure K, 5-bromo-10,20-diphenylporphyrin **9** (34 mg, 0.062 mmol), (5,15-diethynyl-10,20-dinaphthylporphyrinato)zinc(II) **139** (20 mg, 0.029 mmol), $AsPh_3$ (18 mg, 0.058 mol) and $Pd_2(dba)_3$ (7 mg, 0.007 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 20 hours. The crude product was been purified by column chromatography using as eluent first CH_2Cl_2 : *n*-hexane (2:1, v/v) followed by elution with neat CH_2Cl_2, then a mixture of THF and methanol to give 6 mg (0.007 mmol, 13 %) of a purple solid. M.p. >300 ºC; R_f = 0.3 (THF : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, d_1-TFA): δ = 7.96 (t, 4H, ^3J = 7.52, 8.04 Hz, Ar-*H*), 8.16 (m, 4H, Ar-*H*), 8.53 (m, 12H, Ar-*H*), 8.76 (m, 4H, Ar-*H*), 9.05 (m, 12H, Ar-*H,* H_β), 9.46 (d, 2H, ^3J = 4.8 Hz, H_β), 9.57 (d, 4H, ^3J = 4.8 Hz, H_β), 9.61 (d, 4H, ^3J = 4.8 Hz, H_β), 10.02 (d, 4H, ^3J = 4.8 Hz, H_β), 10.62 (d, 4H, ^3J = 4.8 Hz, H_β), 10.68 (d, 4H, ^3J = 4.8 Hz, H_β), 11.40 ppm (s, 2H, H_{meso}); UV/vis (DMF): λ_{max} (log ε) = 414 (5.52), 478 (5.25), 569 (4.62), 642 (4.56), 717 nm (4.66).

5,15-Bis{10,20-diphenylporphyrin-5-yl)ethynyl}-10,20-bis(3-methoxyphenyl)porphyrin (141): Following the general procedure K, 5-bromo-10,20-bis(3-methoxyphenyl)porphyrin **138** (28 mg, 0.047 mmol), (5,15-diethynyl-10,20-dinaphthylporphyrinato)zinc(II) **139**[13a] (15 mg, 0.022 mmol), $AsPh_3$ (14 mg, 0.04 mol) and $Pd_2(dba)_3$ (5 mg, 0.006 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 24 h. The crude product was been purified by column chromatography eluting first with CH_2Cl_2 : *n*-hexane (2:1, v/v) then followed by elution with neat CH_2Cl_2 to give 7 mg (0.007 mmol, 18 %) of purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. >300 ºC; R_f = 0.44 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -3.68 (s, 4H, N*H*), 6.00 (s, 12H, OC*H*$_3$), 7.15-7.21 (m, 6H, Ar-*H*), 7.40 (d, 4H, ^3J = 8.3 Hz, Ar-*H*), 7.54 (m, 2H, Ar-*H*), 7.71 (t, 4H, ^3J = 8.8, 7.2 Hz, Ar-*H*), 7.86 (d, 6H, ^3J = 7.2 Hz, Ar-*H*), 7.89 (s, 4H, Ar-*H*), 8.00 (t, 2H, ^3J = 7.2, 8.3 Hz, Ar-*H*), 8.24 (d, 2H, ^3J = 8.8 Hz, Ar-*H*), 8.42 (m, 4H, H_β), 8.81 (m, 4H, H_β), 8.99 (d, 4H, ^3J = 4.4 Hz, H_β), 9.16 (d, 4H, ^3J = 5.0 Hz, H_β), 9.36 (d, 4H, ^3J = 4.4 Hz, H_β), 10.27 (s, 2H, H_{meso}), 10.29 (d, 2H, ^3J = 3.9 Hz, H_β), 10.42 ppm (d, 2H, ^3J = 4.4 Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 52.9, 104.6, 111.8, 118.5, 118.7, 122.9, 125.3, 125.8, 126.6, 127.5, 128.6, 130.7, 135.2, 140.6, 148.9, 149.7, 150.79, 156.6 ppm; UV/vis (DMF): λ_{max} (log ε) = 411 (5.18), 481 (4.92), 567 (4.29), 651 (4.24), 731 nm (4.42).

10,20-Bis{4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl}-5,10-porphyrin (145): Following the general procedure K, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (47 mg, 0.084 mmol), 5,10-dibromo-15,20-diphenylporphyrin **142**[13a] (25 mg, 0.040 mmol), $AsPh_3$ (25 mg, 0.08 mmol) and $Pd_2(dba)_3$ (9 mg, 0.01 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 3 days. The crude product was been purified by column chromatography (CH_2Cl_2 : *n*-hexane = 1:2, v/v) followed by a second chromatographic purification eluting with CH_2Cl_2 : *n*-hexane (1:1, v/v) to give 11 mg (0.007 mmol, 17 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. > 300 ºC; R_f = 0.5 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.92 (s, 4H, N*H*), -1.77 (s, 2H, N*H*), 7.82 (m, 22H, Ar-*H*), 8.26 (m, 4H, Ar-*H*), 8.31 (m, 8H, Ar-*H*), 8.49 (s, 8H, Ar-*H*), 8.78 (s, 2H, Ar-*H*), 9.02 (d, 4H, ^3J = 4.7 Hz, H_β), 9.08 (m, 8H, H_β), 9.38 (d, 4H, ^3J = 4.1 Hz, H_β), 9.90 (d, 2H, ^3J = 5.3 Hz, H_β), 10.06 (s, 2H, H_β), 10.27 ppm (s, 2H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 22.7, 29.7, 92.9, 97.2, 100.5, 105.0, 113.4, 119.8, 122.9, 123.4, 125.4, 126.9, 127.8, 128.3, 128.8, 129.6, 130.0, 130.5, 130.9, 131.1, 134.4, 134.7, 138.7, 139.8, 141.7, 143.2, 143.5, 147.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.33), 454 (5.15), 509 (4.36), 547 (4.13), 598 (4.34), 656 (3.81), 692 nm (3.91); HRMS (MS ES+) *m/z* calcd. for $[C_{112}H_{71}N_{12}]$: 1583.6064; found 1583.6082.

10,20-Bis{4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl}-5,10-di(4-methylphenyl)porphyrin (146): Following the general procedure K, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (46 mg, 0.080 mmol), 5,10-dibromo-15,20-di(4-methylphenyl)porphyrin **143**[13a] (25 mg, 0.038 mmol), $AsPh_3$ (23 mg, 0.076 mmol) and $Pd_2(dba)_3$ (9 mg, 0.0095 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 3 days. The crude product was been purified by column chromatography (CH_2Cl_2 : *n*-hexane = 1:1, v/v) followed by a second chromatographic purification eluting with CH_2Cl_2 : *n*-hexane (2:1, v/v) to give 10 mg (0.006 mmol, 16 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. >300 ºC; R_f = 0.36 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.91 (s, 4H, N*H*), -1.75 (s, 2H, N*H*), 2.78 (s, 6H, C*H*$_3$), 7.63 (d, 4H, ^3J = 7.6 Hz, Ar-*H*), 7.83 (m, 12H, Ar-*H*), 8.15 (d, 4H, ^3J = 8.2 Hz, Ph-*H*), 8.31(m, 8H, Ar-*H*), 8.49 (s, 8H, Ar-*H*), 8.80 (s, 2H, H_β), 9.00 (d, 2H, ^3J = 4.7 Hz, H_β), 9.03 (d, 4H, ^3J = 4.7 Hz, H_β), 9.08 (d, 4H, ^3J = 4.7 Hz, H_β), 9.10 (d, 4H, ^3J = 4.7 Hz, H_β), 9.39 (d, 4H, ^3J = 4.7 Hz, H_β), 9.89 (d, 2H, ^3J = 4.7 Hz, H_β), 10.06 (s, 2H, H_β), 10.28 ppm (s, 2H, H_{meso}); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 21.3, 29.5, 92.7, 96.9, 100.2, 104.9, 119.5, 119.7, 123.0, 123.2, 126.7, 127.4, 127.6, 129.8, 131.3, 134.2, 134.5, 134.8, 137.6, 138.5, 141.5, 143.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.10), 453 (4.91), 510 (4.06), 549 (3.76), 599 (4.03), 692 nm (3.48); HRMS (MS ES+) *m/z* calcd. for $[C_{114}H_{75}N_{12}]$: 1611.6238; found 1611.6305.

10,20-Bis{4-(10',20'-diphenylporphyrin-5-yl)phenylethynyl}-5,10-dihexylporphyrin (147): Following the general procedure I, 5,15-diphenyl-10-(4-ethynylphenyl)porphyrin **29** (46 mg, 0.082 mmol), 15,20-dibromo-5,10-dihexylporphyrin **144**[6] (25 mg, 0.039 mmol), $AsPh_3$ (24 mg, 0.078 mmol) and $Pd_2(dba)_3$ (9 mg, 0.009 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 3 days. The crude product was purified by column chromatography (CH_2Cl_2 : *n*-hexane = 1:2, v/v) to give 7 mg (0.004 mmol, 11 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. >300 ºC; R_f = 0.56 (CH_2Cl_2: *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.90 (s, 4H, N*H*), -2.10 (s, 2H, N*H*), 1.02 (t, 6H, ^3J = 6.4, 7.0 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.44 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.58 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.87 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.56 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.94 (t, 4H, ^3J = 8.2, 6.4 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.84 (m, 12H, Ar-*H*), 8.32 (m, 8H, Ar-*H*), 8.47 (s, 8H, Ar-*H*), 9.04 (d, 4H, ^3J = 4.7 Hz, H_β), 9.10 (dd, 6H, ^3J = 4.7 Hz, H_β), 9.40 (d, 2H, ^3J = 4.7 Hz, H_β), 9.46 (s, 2H, H_β), 9.50 (d, 4H, ^3J = 4.1 Hz, H_β), 9.53 (d, 2H, ^3J = 4.7 Hz, H_β), 9.93 (d, 4H, ^3J = 4.1 Hz, H_β), 10.29 ppm (s,

2H, H_{meso}); UV/vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.05), 436 (5.07), 509 (4.06), 545 (3.89), 583 (4.22), 677 nm (3.96).

10,20-Bis{4-(10',20'-diphenylporphyrin-15'-(4-nitrophenyl)-5-yl)phenylethynyl}-5,10-di(4-methylphenyl)porphyrin (148): Following the general procedure K 5-(4-ethynylphenyl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin **58** (53 mg, 0.077 mmol), 5,10-dibromo-15,20-diphenylporphyrin **142**[13a] (25 mg, 0.038 mmol), $AsPh_3$ (24 mg, 0.077 mmol) and $Pd_2(dba)_3$ (9 mg, 0.009 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 24 hours. The crude product was by column chromatographiy (CH_2Cl_2 : *n*-hexane = 2:1, v/v) to give 13 mg (0.007 mmol, 18 %) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH. M.p. > 300 ºC; R_f = 0.2 (CH_2Cl_2 : *n*-hexane = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = -2.68 (s, 4H, N*H*), -1.74 (s, 2H, N*H*), 2.79 (s, 6H, C*H*$_3$), 7.63 (d, 4H, ^3J = 7.6 Hz, Ar-*H*), 7.80-7.85 (m, 12H, Ar-*H*), 8.15 (d, 4H, ^3J = 7.6 Hz, Ar-*H*), 8.28 (d, 8H, ^3J = 6.4 Hz, Ar-*H*), 8.43 (d, 4H, ^3J = 8.2 Hz, Ar-*H*), 8.49 (s, 8H, Ar-*H*), 8.67 (d, 4H, ^3J = 8.2 Hz, Ar-*H*), 8.79 (t, 6H, ^3J = 4.8, 4.1 Hz, H_β), 8.95 (d, 4H, ^3J = 4.7 Hz, H_β), 8.99 (d, 6H, ^3J = 4.7 Hz, H_β), 9.09 (d, 4H, ^3J = 4.7 Hz, H_β), 9.89 (d, 2H, ^3J = 4.7 Hz, H_β), 10.05 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.4, 29.5, 93.0, 96.8, 100.2, 116.7, 120.0, 121.7, 123.1, 126.7, 127.8, 130.0, 134.2, 135.0, 137.6, 138.5, 141.7, 142.3, 147.6, 149.0 ppm; UV/VIS (CH_2Cl_2): λ_{max} (log ε) = 420 (5.31), 454 (5.12), 517 (4.34), 555 (4.19), 598 (4.26), 692 nm (3.73).

10,20-Bis{(10',20'-diphenylporphyrin-5-yl)ethynyl}-5,10-di(4-methylphenyl)porphyrin (149): Following the general procedure K, 5-ethynyl-10,20-diphenylporphyrin **77** (21 mg, 0.042 mmol), 5,10-dibromo-15,20-di(4-methylphenyl)porphyrin **143**[13a] (10 mg, 0.020 mmol), $AsPh_3$ (13 mg, 0.04 mmol) and $Pd_2(dba)_3$ (4 mg, 0.004 mmol) were added to a mixture of THF (40 mL) and TEA (4 mL) and kept at 65 ºC for 3 days. The crude product was been purified by two consecutive column chromatographies (CH_2Cl_2: *n*-hexane = 1. 1:2, 2. 1:1, v/v) to yield 3 mg (0.027 mmol, 7 %) of a purple solid after recrystallization from CH_2Cl_2/MeOH. M.p. > 300 ºC; R_f = 0.4 (CH_2Cl_2 : *n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, d_8-THF, TMS): δ = -2.22 (s, 4H, N*H*), 1.99 (s, 2H, N*H*), 2.75 (s, 6H, C*H*$_3$), 7.63 (d, 2H, ^3J = 7.3 Hz, Ar-*H*), 7.86 (m, 12H, Ar-*H*), 8.12 (d, 2H, ^3J = 7.8 Hz, Ar-*H*), 8.19 (d, 4H, ^3J = 7.8 Hz, Ar-*H*), 8.34 (m, 8H, Ar-*H*), 8.84 (m, 6H, H_β), 9.02 (d, 6H, ^3J = 4.4 Hz, H_β), 9.12 (d, 2H, ^3J = 4.4 Hz, H_β), 9.17 (d, 2H, ^3J = 4.9 Hz, H_β), 9.34 (d, 4H, ^3J = 4.4 Hz, H_β), 10.23 (s, 2H, H_{meso}), 10.34 (d, 2H, ^3J = 4.9 Hz, H_β), 10.44 ppm (d, 2H, ^3J = 4.9 Hz, H_β); UV/vis (CH_2Cl_2): λ_{max} (log ε) = 403 (5.10), 422 (5.13), 469 (5.29), 514 (4.44), 612 (4.51), 700 nm (4.56).

5-(1-Ethylpropyl)-10,15,20-tris[4-(10,20-diphenylporphyrin-5-yl)phenylethynyl]porphyrin (150): Following the general procedure K, 5-(4-ethynylphenyl)-10,20-diphenylporphyrin **29** (73 mg, 0.129 mmol), 5,10,15-tribromo-20-(1-ethylpropyl)porphyrin **82** (25 mg, 0.040 mmol), $AsPh_3$ (40 mg, 0.129 mmol) and $Pd_2(dba)_3$ (15 mg, 0.016 mmol) in a mixture of THF (15 mL) and NEt_3 (5 mL) were used. Purification via column chromatography on silica gel (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v), followed by recrystallization from CH_2Cl_2/CH_3OH afforded purple crystals (6 mg, 0.002 mmol, 7 %). M.p. >300 ºC; R_f = 0.62 (*n*-hexane : CH_2Cl_2 = 1 : 1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.90 (s, 6H, N*H*), -1.20 (s, 2H, N*H*), 1.04 (t, 6H, J = 7.0 Hz, CH(CH_2CH_3)$_2$), 2.92 (m, 2H, CH(CH_2CH_3)$_2$), 3.01 (m, 2H, CH(CH_2CH_3)$_2$), 5.02 (m, 1H, C*H*(CH_2CH_3)$_2$), 7.85 (m, 18H, Ar-*H*), 8.31 (m, 12H, Ar-*H*), 8.51 (s, 4H, Ar-*H*), 8.50 (s, 8H, Ar-*H*), 9.03-9.11 (m, 19H, H_β), 9.38 (m, 8H, H_β), 9.93 (d, 2H, J = 4.7 Hz, H_β), 10.01 (d, 3H, J = 4.7 Hz, H_β), 10.26 (s, 1H, H_{meso}), 10.28 ppm (s, 2H, H_{meso}); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 412 (3.99), 463 (3.54), 509 (2.99), 547 (2.64), 584 (2.7), 626 (2.74), 714 nm (2.37); HRMS (MS ES+) *m/z* calcd. for [$C_{145}H_{96}N_{16}$] ($M+H^+$): 2061.8082; found 1031.4080 (2+)

{5-Bromo-10,20-bis(1-ethylpropyl)-15-{4-[(10',20'-bis(1-ethylpropyl)porphyrinato)zinc(II)]phenylethynyl]porphyrinato}zinc(II) (151): Produced as a side product from the synthesis of **135**, via Sonogashira conditions (general procedure F). Phenylethynylporphyrin **55** (48 mg, 0.078 mmol), bromoporphyrin **49** (25 mg, 0.037 mmol), CuI, $PdCl_2(PPh_3)_2$ to yield a purple solid (18 mg, 0.015 mmol, 40%). M.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 1.02 (t, 24H, $^3J_{H-H}$ = 14.5 Hz, C*H*$_3$), 2.88 (m, 8H, C*H*$_2$), 3.06 (m, 8H, C*H*$_2$), 5.21 (m, 2H, C*H*), 5.23 (m, 2H, C*H*), 7.55 (s, 1H, Ph-*H*), 7.72 (s, 1H, Ph-*H*), 8.04-8.06 (d, 1H, $^3J_{H-H}$ = 8.3 Hz, Ph-*H*), 8.28-8.30 (d, 1H, $^3J_{H-H}$ = 8.0 Hz, Ph-*H*), 9.18-9.20 (m, 2H, H_β), 9.47-9.48 (m, 2H, H_β), 9.69-9.93 (m, 10H, H_β), 10.07 (m, 2H, H_β), 10.18 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.5, 22.8, 29.5, 34.7, 50.4, 123.4, 123.6, 125.8, 128.7, 129.4, 130.7, 131.3, 131.6, 132.8, 134.3, 134.6, 143.7, 149.4, 152.3 ppm; UV/vis: λ_{max} (log ε) = 418 (5.19), 444 (5.21), 554 (4.03), 640 nm (4.29); HRMS (Maldi) *m/z* calcd. for $C_{68}H_{65}N_8Zn_2Br$ $[M]^+$ 1200.3098, found 1200.3135.

{5-Bromo-10,20-bis(1-ethylpropyl)-15-[4-[10',20'-diphenylporphyrinato-5-yl)zinc(II)]phenylethynyl]porphyrinato}zinc(II) 152. Produced from phenylethynylporphyrin **56** (39 mg, 0.063 mmol) and bromoporphyrin **49** (20 mg, 0.030 mmol) using Sonogashira conditions (procedure F) to yield a purple solid (15 mg, 0.013 mmol, 42%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.97 (t, 12H, $^3J_{H-H}$ = 14.8 Hz, C*H*$_3$), 2.86 (m, 4H, C$_2$), 3.02 (m, 4H, C*H*$_2$), 5.12 (m, 2H, C*H*), 7.82 (m, 6H, Ph-*H*), 8.32 (m, 4H, Ph-*H*), 8.45 (m, 4H, C_6H_4-*H*), 9.02-9.04 (d, 2H, $^3J_{H-H}$ = 4.6 Hz, H_β), 9.07-9.08 (d, 2H, $^3J_{H-H}$ = 4.4 Hz, H_β), 9.11-9.12 (d, 2H, $^3J_{H-H}$ = 4.6 Hz, H_β), 9.37-9.38 (d, 2H, $^3J_{H-H}$ = 4.3 Hz, H_β), 9.71 (m, 6H, H_β), 9.99 (s, 2H, H_β), 10.20 ppm (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 29.5, 34.7, 50.3, 120.2, 126.2, 127.1, 129.3, 130.7, 131.5, 131.7, 132.3, 134.5, 134.8, 143.1, 145.8, 149.1, 149.4, 149.7, 149.9, 150.1 ppm; UV/vis: λ_{max} (log ε) = 420 (5.49), 444 (5.46), 552 (4.33), 640 nm (4.54); HRMS (Maldi) *m/z* calcd. for $C_{70}H_{53}N_8Zn_2Br$ $[M]^+$ 1212.2159, found 1212.2184.

Acknowledgments

This work was supported by grants from Science Foundation Ireland (SFI P.I. 09/IN.1/B2650 and SFI Ureka Supplement 04/RP1/B482UR08) and the Health Research Board (HRB Translational Research Award 2007 TRA/2007/11). We are grateful to the Centre for Synthesis and Chemical Biology (CSCB) for HRMS measurements.

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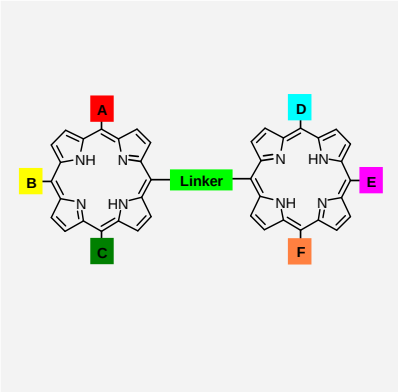
[49] ^{13}C NMR spectrum of compound **84** was not obtained due to pyridine-d_5 overshadowing many signals.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents

((Porphyrin Arrays))

Application of contemporary synthetic methods using organolithium and Pd-catalyzed C–C coupling reactions allows the synthesis of unsymmetrical ADCD-type porphyrins dimers and arrays for optical applications.



Aoife A. Ryan, Andreas Gehrold, Romain Perusitti, Monica Pintea, Marijana Fazekas, Oliver B. Locos, Frances Blaikie, Mathias O. Senge*
Page No. – Page No.

Synthesis of Unsymmetrical meso Substituted Porphyrins 2. Porphyrin Dimers and Arrays

Keywords: Porphyrinoids / C–C coupling / nonlinear optics / Tetrapyrroles / donor-acceptor compounds / photodynamic therapy