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5,15-A_2B_2- and 5,15-A_2BC-Type Porphyrins with Donor and Acceptor Groups for Use in Nonlinear Optics and Photodynamic Therapy[‡]

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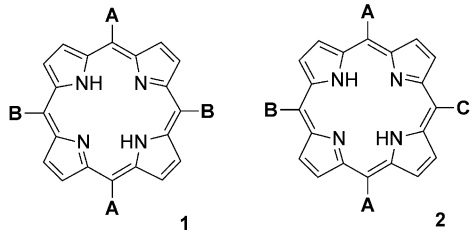
Dedicated to Professor Gerhard Bringmann on the occasion of his 60th birthday

Keywords: Porphyrinoids / Nitrogen heterocycles / C–C coupling / Nonlinear optics / Donor–acceptor systems / Photodynamic therapy

Development of efficient new synthetic strategies leading to more diversified substitution patterns of porphyrin rings is of great importance as it expands the potential applicability of these compounds and provides a more accurate way of tailoring their properties for a specific application. Changes in the electronic and conformational structures induced by different substituents are manifested by unique properties which are of interest for many applications ranging from amphiphilic porphyrins for photodynamic therapy, push–pull systems for optical applications, chiral systems useful in catalysis, to donor–acceptor systems suitable for electron transfer studies. Different chemical strategies were demonstrated for access to unsymetrically substituted porphyrins with nonequivalent β or *meso* substituents. For the latter we have adopted the functionalization of preformed porphyrins in order to obtain a diverse range of porphyrin structures with 5,15-A_2B_2 and 5,15-A_2BC *meso* substitution patterns suitable for applications in optical limiting and photodynamic therapy. The functionalization of A_2-type starting materials by organolithium and palladium-catalyzed cross-coupling reactions is an efficient means to enable the introduction of almost any desired *meso* substituent. We report the nonlinear absorptive properties of our A_2B_2 and A_2BC porphyrins and show that there is strong correlation between structural features and the optical limiting efficiency. The nonlinear optical studies indicate that the 5,15-A_2B_2 substitution pattern provides more promising candidates for use in optical limiting.

Introduction

Current developments for the introduction of *meso* substituents into porphyrins have given access to molecules with induced permanent dipole moments whose strength can be fine tuned by the electron-donating or -withdrawing character of the incorporated groups. In these terms A_2B_2 (**1**) and A_2BC (**2**) compounds have emerged as interesting candidates for application in optics[1] and for electron transfer (ET)[2] studies. Push–pull molecules in general constitute an important class of compounds for nonlinear optical (NLO) studies for applications in photonics.[3] Better access to macrocyclic dyes with push–pull character will expand the range of accessible materials and advance these applications. Likewise, tailoring the nature of the electron-donating and -withdrawing *meso* substituents is crucial for the efficient generation of ET, which mimics natural processes and is related to solar energy conversion. Further progress in both research areas requires easy access to varied structures, which necessitates the development of appropriate synthetic strategies leading to unsymetrically substituted porphyrins.



Different synthetic approaches leading to A_2BC- and A_2B_2-type porphyrins have been reported. The simplest way to obtain 5,15-A_2B_2 systems involves the acid-catalyzed condensation of dipyromethane with aldehyde.[4] Others involve self-condensation of dipyrromethane-1-carbinoles or

[‡] Synthesis of Unsymmetrical *meso*-Substituted Porphyrins, 1. Part 2: Ref.[21]

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the elegant 1-acyldipyrromethane route developed by Lindsey et al.[5] In practial terms, the acid-catalyzed condensation of dipyrromethane with two aldehyde units or two dipyromethane units with aldehyde is still the simplest way to access 5,15-A_2BC compounds.[6] Condensation of dipyrromethanedicarbinole with dipyrromethane has also been reported but turned out not to be an efficient way to access this substitution pattern.[7] Other pathways to both substitution patterns used a step-wise approach where preformed 5,15-A_2 compounds were subjected to further functionalization.[8]

Progress in the use of organometallic reactions has made it possible to prepare large sets of samples for quantitative structure–activity relationship (QSAR) studies in optics.[9] This approach accelerates the progress of optical and biomedical uses of porphyrins as it enables identification of key structural features enhancing certain physicochemical properties and allows the prediction of more promising candidates for specific applications. Currently QSAR approaches are being developed for biomedical studies, i.e. to predict the toxicity or biological activity of porphyrin-based drugs for photodynamic therapy.[10,11] Naturally, the number of possible structures expands drastically with access to more diversified substitution patterns.

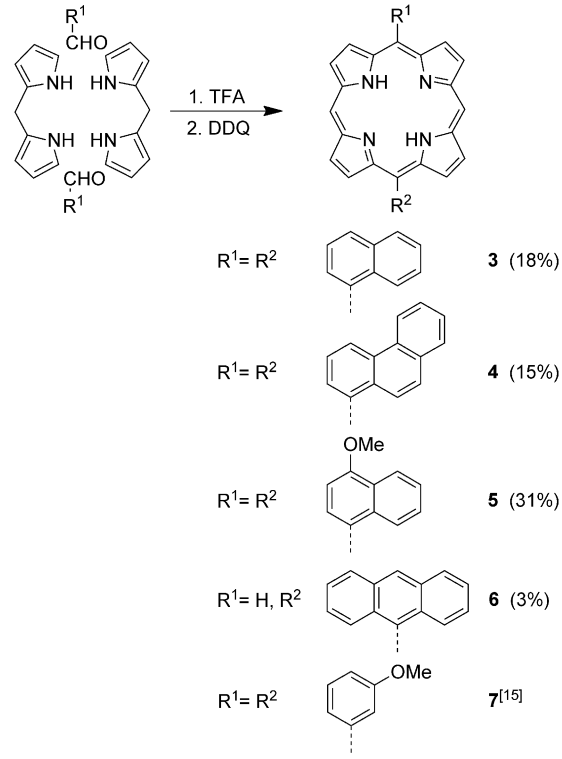
Using our recently developed ABCD approach[12] we describe here systematic studies on the applicability of organolithium and palladium-catalyzed cross-coupling reactions for the functionalization of 5,15-A_2 porphyrins to access a range of 5,15-A_2B_2 and 5,15-A_2BC target compounds. We demonstrate that a rational design of the chemical pathway enables the preparation of almost any desired compound. In additioin, we report the nonlinear absorptive (NLA) properties of our compound library and correlate those properties to structural features.

Results and Discussion

The preparation of A_2B_2- or A_2BC-type porphyrins through functionalization reactions requires a step-wise approach, i.e. starting from A_2-porphyrins and subsequent introduction of the B and C residues.[12]

Synthesis of A_2-Type Porphyrins

A_2-type porphyrins are easily prepared by a [2+2] condensation using dipyrromethane and the respective aldehyde with the *meso* substituent.[6,13] In terms of target compounds we focused here on the introduction of larger aryl residues. As shown in Scheme 1 porphyrins with 1-naphthyl (**3** and **5**) and 9-phenanthrenyl (**4**) substituents were obtained in 18–31% yield. Attempts to prepare the related bisanthracenylporphyrin gave only the monosubstituted scrambling product **6** in low yield.[14] For comparative purposes we also included the well known 3-methoxy derivative **7** in our investigations.[15]



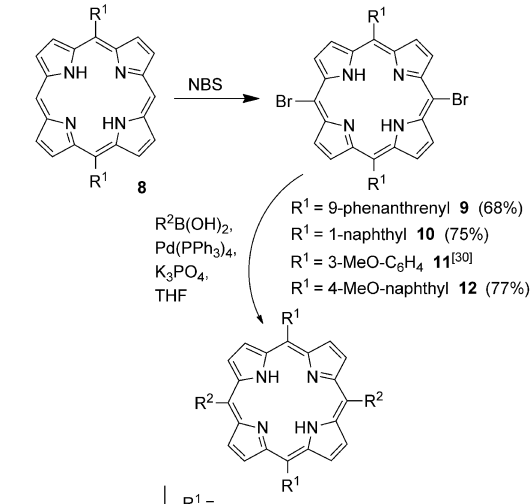
Scheme 1. Synthesis of A_2-porphyrins by condensation reactions.

Synthesis of 5,15-A_2B_2-Type Porphyrins

We first investigated the application of the Suzuki reaction, currently the most widely used organometallic coupling reaction in porphyrin chemistry.[16] This requires preparation of the dibromoporphyrins **9**–**12** from the precursor porphyrins **8**, a reaction easily achieved by treatment with *N*-bromosuccinimide (NBS).[17] Next, reaction of the bromoporphyrins with various boronic acids and catalysis by $Pd(PPh_3)_4$ and K_3PO_4 gave the Suzuki-coupled products in good yields (Scheme 2).

The arylboronic acids used ranged from electron poor phenyl systems to N and S heterocycles. Although the 9-phenanthrenyl derivatives **21**–**25** were synthesized in acceptable yields their solubility is rather low, which limited their use. The lowest yield was observed for the reaction of **10** with 2-benzothiophenylboronic acid. However, in this case, formation of the disubstituted product **20** (21%) was accompanied by formation of the monosubstituted, debrominated **33** (28%). Two other boronic acids showed no reactivity with the porphyrins investigated. Reaction with (10-bromoanthracen-9-yl)boronic acid with **10** gave complete consumption of starting material but only debrominated **3** could be isolated. In the case of (5-bromothiophen-2-yl)-boronic acid no reaction occurred.

Next we prepared the zinc(II) porphyrins **34**–**37** by standard metallation reactions.[18] These compounds were precursors for use in a Heck-type coupling reaction, a versatile method for the introduction of olefinic residues into porphyrins.[19] As shown in Scheme 3 the reaction is suitable for the preparation of 5,15-A_2B_2-type porphyrins and gave

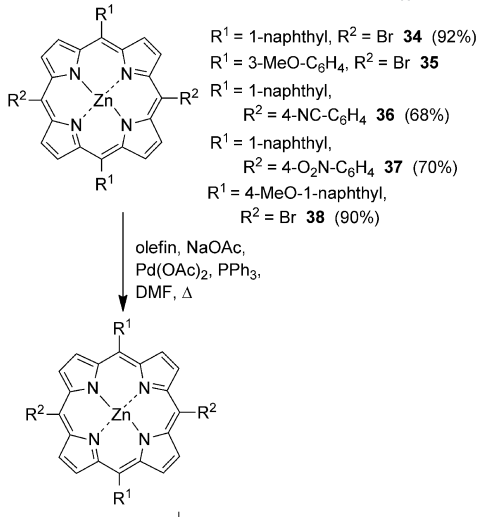


R² =	R¹ = 1-naphthyl	R¹ = 9-phenanthrenyl	R¹ = 3-MeO-C$_6$H$_4$
CO$_2$Me	**13** (30%)	**21** (56%)	**26** (78%)
CN	**14** (66%)	**22** (62%)	**27** (73%)
NO$_2$	**15** (71%)	**23** (55%)	**28** (63%)
Br	**16** (82%)		
OH			**29** (32%)
S	**17** (65%)	**24** (45%)	
	18 (48%)	**25** (40%)	**30** (47%)
Me, N	**19** (45%)		**31** (66%)
S	**20** (21%)		**32** (70%)

Scheme 2. Synthesis of A_2B_2 porphyrins by Suzuki coupling.

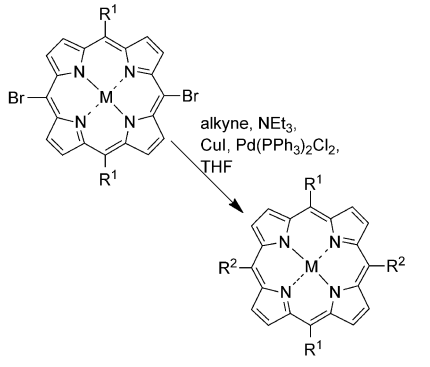
the target materials in moderate to good yields. The reactivity of the (3-methoxyphenyl)porphyrin **35** was higher than that of the 1-naphthylporphyrin **34** and the best yields were obtained with diethylvinyl phosphonate. All products showed exclusive formation of *E*-isomers.

Last, but not least, the target compounds can be prepared by Sonogashira coupling,[20] which allows the direct cross-coupling of terminal alkynes with aryl halides under mild conditions through the use of catalytic [Pd(PPh$_3$)$_2$Cl$_2$] with CuI as the cocatalyst in the presence of an aliphatic amine. This method works well with the respective bromoporphyrins either in free base form or as zinc(II) complexes. As shown in Scheme 4, the yields for the metal complexes and the free base porphyrins are comparable. Trimethylsilyl-protected alkynylporphyrins serve as precursors for the preparation of conjugated oligoporphyrins.[21] Thus, **51** bearing a TMS-protected acetylene group was subjected to removal of TMS by treatment with tetrabutylammonium fluoride (TBAF) in dichloromethane solution. The reaction worked smoothly and gave porphyrin **52** in quantitative yield.



R² =	R¹ = 1-naphthyl	R¹ = 3-MeO-C$_6$H$_4$
NO$_2$	**39** (40%)	**44** (42%)
Br	**40** (38%)	
CO$_2$Me	**41** (30%)	**45** (49%)
CO$_2$Et	**42** (40%)	**46** (83%)
OEt, P=O, OEt	**43** (58%)	**47** (75%)

Scheme 3. Synthesis of A_2B_2 porphyrins by Heck coupling.



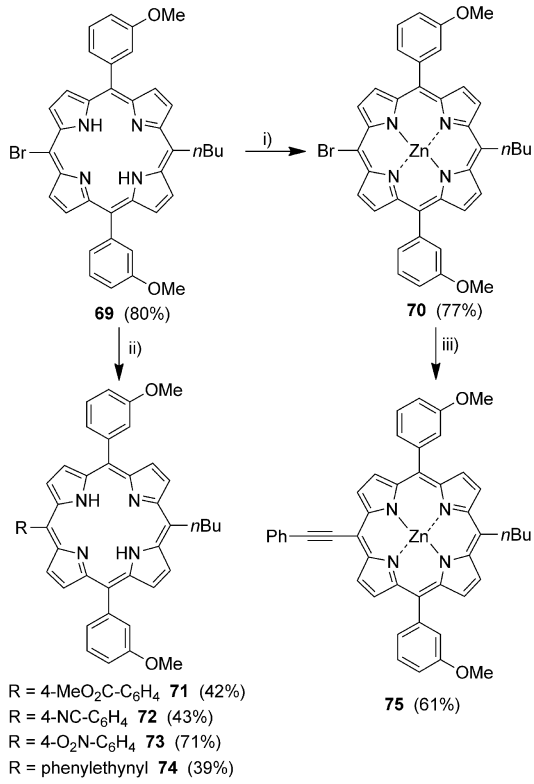
M =	R² =	R¹ = 1-naphthyl	R¹ = 3-MeO-C$_6$H$_4$
2H		**48** (43%)	**53** (38%)
Zn(II)		**49** (60%)	**54** (65%)
2H	SiMe$_3$	**50** (58%)	**55** (42%)
Zn(II)	SiMe$_3$	**51** (48%)	**56** (60%)
		Bu$_4$NF	
Zn(II)	H	**52** (94%)	

Scheme 4. Synthesis of A_2B_2 porphyrins by Sonogashira coupling.

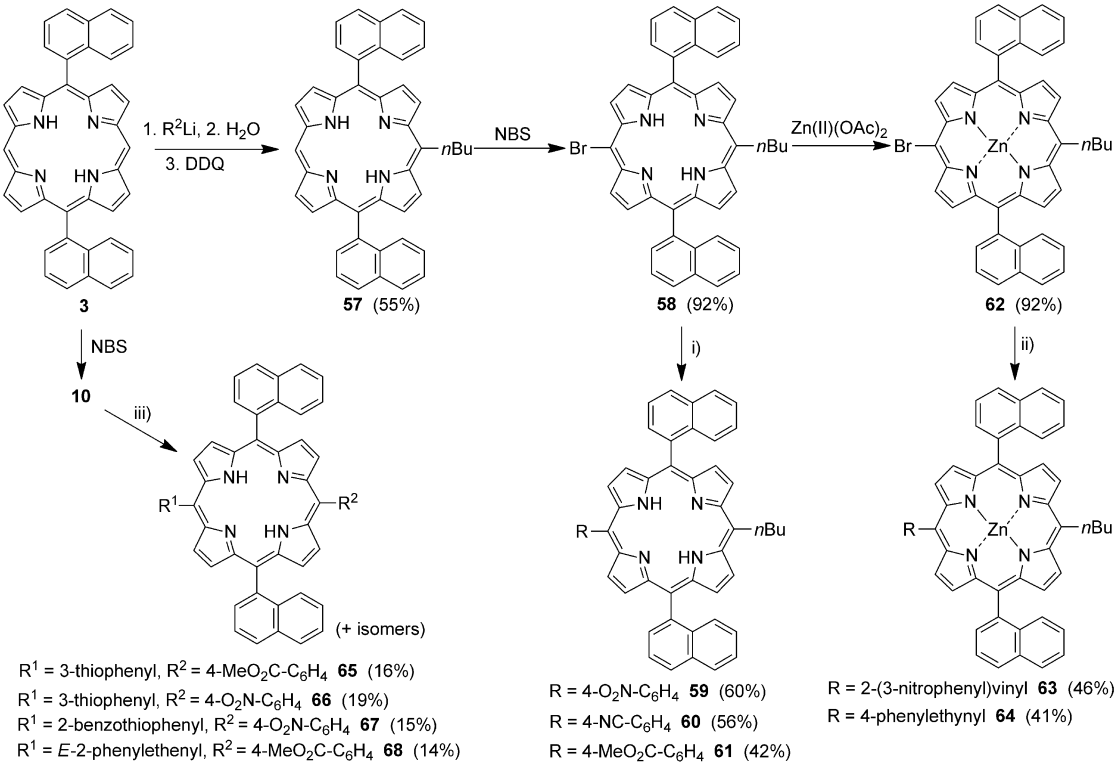
Synthesis of 5,15-A_2BC-Type Porphyrins

Push–pull porphyrins require a strong intramolecular dipole moment. Thus, 5,15-A_2BC-type porphyrins **2** where B is electron-donating and C an electron-withdrawing group have frequently been used for this purpose.[22] We used organolithium chemistry for the introduction of B.[23] As expected, substitution of the free base **3** with *n*BuLi was easily achieved to yield **57**. Reaction with NBS gave **58**, which readily underwent Suzuki coupling to yield the porphyrins **59**–**61** with electron-withdrawing C residues. Zinc(II) insertion into **58** to yield **62** allowed the preparation of **63** by the Heck reaction and **64** by Sonogashira coupling (Scheme 5).

Next, we attempted a mixed Suzuki reaction of **10** with two different boronic acids. The first attempt involved reaction of **10** with (4-methoxycarbonylphenyl)boronic acid and (thiophen-3-yl)boronic acid in equimolar amounts. This gave a mixture of the two A_2B_2 porphyrins (5% **13** and 7% **17**) and the A_2BC porphyrin **65** (16%). Likewise, similar mixtures were obtained through reaction with 3-thiophene boronic acid and (4-nitrophenyl)boronic acid (3% **15**, 8% **17**, 19% **66**), (2-benzothiophenyl)boronic acid and (4-nitrophenyl)boronic acid (3% **20**, 4% **15**, 15% **67**), or (2-phenylethenyl)boronic acid and [4-(methoxycarbonyl)-phenyl]boronic acid (9% **18**, 6% **13**, 14% **68**). Although separation of the three compounds was easily achieved by column chromatography, the low yields make this method suitable only as a "quick and dirty" approach.



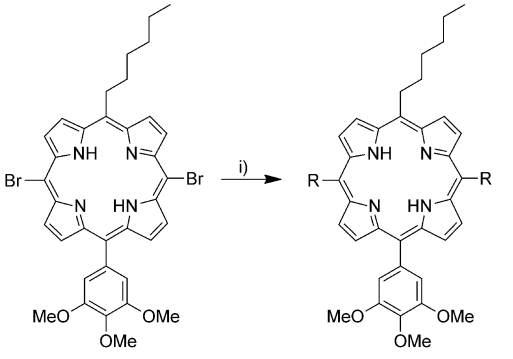
Scheme 6. Reactions of 5,15-bis(3-methoxyphenyl)porphyrins. i) $Zn^{II}(OAc)_2$, ii) Suzuki or Sonogashira, iii) phenylacetylene, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, r.t.



Scheme 5. Synthesis of A_2BC porphyrins. i) Suzuki reaction, ii) Sonogashira or Heck reaction, iii) mixed Suzuki reaction with two boronic acids.

Reaction sequences similar to those shown in Scheme 5 were also used with 3-methoxyphenyl **7**. This porphyrin was butylated through reaction with *n*BuLi and then brominated in 80% yield to **69**. As shown in Scheme 6, this compound can undergo Suzuki or Sonogashira reaction to yield the porphyrins **71**–**74** in acceptable yields. Likewise, metallation with zinc(II) acetate yielded **70**, which allowed the generation of the phenylacetylene substituted porphyrin **75** in better yields compared to the free base **74**.

Finally, we prepared 5,15-A_2BC porphyrins from already available 5,15-BC-type porphyrins.[12a] Such syntheses are easily accomplished as the two free *meso* positions can be quickly brominated with NBS followed by any of the outlined organometallic coupling reactions. As a test compound we choose 5,15-dibromo-10-hexyl-20-(3,4,5-trimethoxyphenyl)porphyrin **76**.[12a] As shown in Scheme 7, Suzuki coupling reactions gave the respective A_2BC-type porphyrins **77**–**80** in good to excellent yields.



Scheme 7. Reactions of 5,15-dibromo-10-hexyl-20-(3,4,5-trimethoxyphenyl)porphyrin. i) $RB(OH)_2$, K_3PO_4, $Pd(PPh_3)_4$, THF, 12 h.

NLO Properties

The newly synthesized compounds were investigated for their NLA properties at 532 nm with the open Z-scan technique. All of the compounds studied exhibited a drop in transmission with intensity, which we attributed to reverse saturable absorption.[25a] Such behavior, which is of interest for optical limiting (OL), arises in macrocyclic dyes upon resonant or close to resonant excitation wavelength due to a sequential two-photon absorption process.[24] The magnitude of the transmission drop varied between compounds, which implies structure–NLA relationships. The typical open Z-scan data obtained for the compounds studied are presented in Figure 1. Details concerning data manipulation follow standard methods reported in the literature.[25] For the comparative studies described in the following paragraphs, we used the effective intensity dependent NLA coefficient, β_{eff}, which is a parameter derived from data fitting (see Table 1).

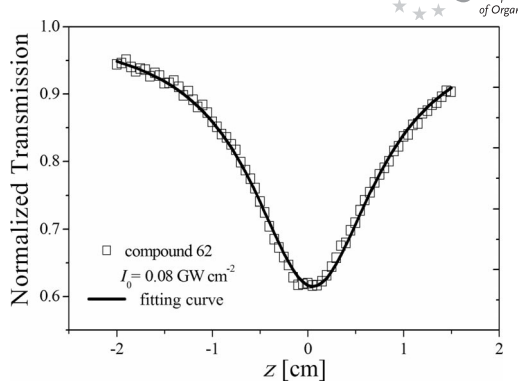


Figure 1. An example of open-aperture Z-scan data obtained for **62**. I_0 stands for onfocus intensity.

Firstly we looked at the OL efficiency of 5,15-A_2B_2 systems where the A substituent was 1-naphthyl and the other substituent was directly linked to porphyrin by a single bond. The following trend in β_{eff} was observed with regard to substituent B: 4-MeOOC–C_6H_4 ≈ 4-NC–C_6H_4 > 3-thiophene ≈ 2-benzothiophene > 1-Me–indole (**13** ≈ **14** > **17** ≈ **20** > **19**). This tendency reveals that NLA is enhanced for compounds with strong electron-withdrawing groups. Compounds with substituent B linked by multiple bonds revealed better OL efficiency in reference to previously discussed compounds and this related to both free base systems and zinc porphyrins. Compound **43** is an exception, which provided a very weak response. This may be related to the particular electronic character of the $PO(OEt)_2$ group. In our considerations on the enhanced NLA in the compounds where substituents were linked by multiple bonds we referred to observations made by McEwan et al.[26] who reported that compounds in which Soret band maxima are closer to the experimental wavelength gave a stronger NLO response. The same is true for our compounds where porphyrins with substituents linked by multiple bonds have Soret band maxima shifted towards longer wavelengths, thus situated closed to the experimental wavelength, gave a stronger signal than similar compounds with singly bonded substituents.

For 5,15-A_2B_2 compounds with a 3-methoxyphenyl group as the A substituent, **56** provided the strongest response of all the compounds studied. Compound **27** with a 4-cyanophenyl B substituent provided a comparable response to analogous **14** with 1-naphthyl instead of the 3-methoxy phenyl group, although the NLA coefficient for the former was smaller. This makes this compound a more promising candidate for OL applications. Put into other words, the same rate of NLA could be achieved at higher transparency at ambient light for **27**. Next we compared compounds with 3-methoxyphenyl and 1-naphthyl groups as the A substituent, but now in a 5,15-A_2BC substitution pattern. Here **72** and **73** with 3-methoxyphenyl residues outperformed those with 1-naphthyl groups **60** and **59** (Figure 2).

Amongst the 5,15-A_2BC compounds with 1-naphyl as the A substituent (**59**–**62**), **62** provided the best response,

Table 1. Comparison of the experimental data for the porphyrins studied, a_0 = linear absorption coefficient; λ_{max} = Soret band maximum; β_{eff} = effective intensity dependent nonlinear absorption coefficient; $Im[\chi^{(3)}_{eff}]$ = imaginary part of the third-order susceptibility $\chi^{(3)}$.

5,15-A_2B_2	A[a]	B	a_0 [cm^{-1}]	λ_{max} [nm]	β_{eff} [$cm\,W^{-1}$] $\times10^{-8}$	$Im[\chi^{(3)}_{eff}]$ [esu] $\times10^{-12}$
13	*af*	4-MeOOC-C_6H_4	0.49	421	1.7 ± 0.1	5.8 ± 0.3
14	*af*	4-NC-C_6H_4	0.79	422	1.6 ± 0.0	5.6 ± 0.0
17	*af*	3-thiophene	0.65	422	1.2 ± 0.0	4.0 ± 0.0
18	*af*	styrene	0.78	437	2.3 ± 0.1	7.9 ± 0.5
19	*af*	1-Me-indole	0.67	427	0.5 ± 0.0	1.7 ± 0.0
20	*af*	2-benzothiophene	0.98	420	1.1 ± 0.1	3.7 ± 0.5
48	*af*	C_6H_4-ethynyl	0.54	445	2.1 ± 0.1	7.3 ± 0.4
39	*am*	3-O_2N-C_6H_4-ethenyl	0.58	439	2.1 ± 0.1	7.1 ± 0.3
43	*am*	$PO(OEt)_2$-ethenyl	0.15	437	0.8 ± 0.1	3.2 ± 0.3
27	*bf*	4-NC-C_6H_4	0.43	420	1.6 ± 0.2	5.5 ± 0.5
56	*bm*	TMS-ethynyl	0.32	449	5.3 ± 0.1	18.0 ± 0.0
5,15-A_2BC, B = *n*-C_4H_9	A[a]	C				
59	*af*	4-O_2N-C_6H_4	0.63	423	0.8 ± 0.0	2.7 ± 0.1
60	*af*	4-NC-C_6H_4	0.20	422	0.5 ± 0.0	1.5 ± 0.1
61	*af*	4-MeOOC-C_6H_4	0.76	422	0.7 ± 0.0	2.3 ± 0.2
62	*am*	Br	0.62	425	1.8 ± 0.1	6.1 ± 0.4
72	*bf*	4-NC-C_6H_4	0.70	419	2.1 ± 0.1	7.1 ± 0.4
73	*bf*	4-O_2N-C_6H_4	0.80	420	1.9 ± 0.2	6.5 ± 0.5

[a] *a* = 1-naphthyl, *b* = 3-MeO–C_6H_4, *f* = free base compound, *m* = zinc-metallated compound.

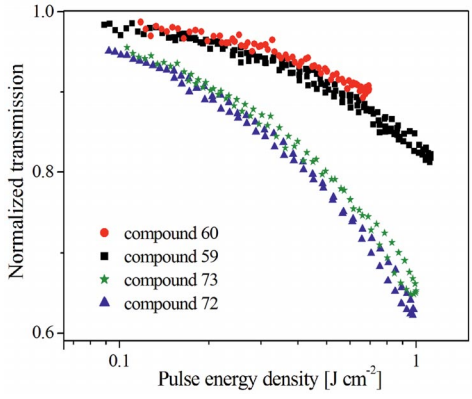


Figure 2. Optical limiting curves plotted as normalized transmission vs. pulse energy density for **59**, **60**, **72**, and **73**.

which we attribute to the presence of zinc. Closed shell metals were reported to have a favorable effect on the NLA as they produce an increase in the intersystem crossing rate resulting in higher quantum yields for the triplet states.[27] Interestingly, compounds with very similar structural features in a 5,15-A_2BC substitution pattern (**59**, **60**, and **61**) revealed slightly different OL efficiency. This indicates a strong correlation between the structural features and the NLA of a compound. The same observation relates to **72** and **73**. A similar finding was reported by McEwan et al., where variation of a substituent at the *para*-position of phenyl rings in tetrasubstituted porphyrins resulted in a variation of their NLA but did not induce major changes to ground state absorption features.[28]

Finally we compared the responses of similar compounds from both substitution patterns. Compounds **13** and **14** with a 5,15-A_2B_2 substitution pattern were compared with 5,15-A_2BC **61** and **60**. Substitution of one of the 4-MeOOC–C_6H_4 groups in **13** or one of the 4-CN–C_6H_4 groups in **14** with *n*-C_4H_9 gave compounds **61** and **60**, respectively. Both compounds with 4-MeOOC–C_6H_4 substituents (**13** and **61**) exhibited stronger NLA than those with 4-CN–C_6H_4 substituents (**14** and **60**). Moreover, compounds with a 5,15-A_2B_2 substitution pattern outperform the respective 5,15-A_2BC compounds.

In summary, our NLO studies revealed that NLA is highly dependent not only on the nature of the *meso* substituents but also on the substitution pattern. Some initial trends concerning the structure–OL efficiency relationships were established, although further studies on unsymetrically substituted compounds are necessary in order to fully understand the correlations observed.

The development of synthetic strategies for unsymmetrically *meso*-substituted porphyrins also provides building blocks to construct more complex structures such as porphyrin oligomers. A series of porphyrin dimers and trimers possessing substituents similar to the previously discussed monomers were synthesized[21] and their NLA investigated.[25a] In these compounds we varied both the *meso* substituents and the linker groups. In addition, for trimers both possible regiochemical configuration patterns (with 5,10- or 5,15-linkages, respectively) gave linear and L-shaped arrays.

No apparent change in the NLO response was observed upon addition of further porphyrin units in reference to monomers. β_{eff} values of the dimers studied were comparable to those of the most promising monomers, though not exceeding that of the best monomer **56**. The same was true for the L-shaped trimers. The NLA of linear trimers was relatively poor. The better studied dimers showed that both the type of linker and the *meso* substituent has an effect on the ground state and excited state absorption. Apart from the influence of the particular *meso* substituent on the NLA, the mutual position of these substituents contributed

to the NLO response and this became evident during the comparison of constitutional isomers. Theses studies again highlight the strong structure–NLO properties relationship.

Conclusions

We demonstrated that the step-wise approach, where preformed porphyrins are subjected to further functionalization by organolithium or palladium-catalyzed cross coupling reactions is an efficient and very flexible way to prepare 5,15-A_2B_2- and 5,15-A_2BC-type compounds for optical applications. The approach outlined provides access to a great range of possible structures and enables fine tuning of the properties that are crucial for the specific application. As shown, NLO studies carried out on the compound library revealed that 5,15-A_2B_2 porphyrins are more promising materials for OL devices than similar 5,15-A_2BC compounds. Some initial trends concerning the relationship between NLA and the structural features were established for the porphyrins studied. A similar approach to that described here for OL is possible for the construction and analysis of potential photosensitizers for photodynamic cancer therapy and indication and is currently in progress in our laboratory.

Experimental Section

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

Starting Materials: Dipyrromethane,[29] 5,15-bis(3-methoxyphenyl)porphyrin[15] (**7**), 5,15-dibromo-10,20-bis(3-methoxyphenyl)porphyrin[30] (**11**), 5-butyl-10,20-bis(3-methoxyphenyl)porphyrin,[15] and 5,15-dibromo-10-hexyl-20-(3,4,5-trimethoxyphenyl)porphyrin[12a] (**76**) were prepared following published procedures.

General Procedure A. Condensation Method for 5,15-A_2 Porphyrins: Dry CH_2Cl_2 (1 L) was placed in a three-necked flask equipped with magnetic stirrer and gas inlet (argon). Dipyrromethane (1 equiv.) and the appropriate aldehyde (1.05–1.75 equiv.) were added. The flask was shielded from ambient light followed by addition of TFA (0.1 equiv.), and the reaction mixture was stirred for 18 h at room temperature. After this time 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 3 equiv.) was added and the mixture was stirred for 1 h. The reaction was terminated by addition of triethylamine (1 mL), and concentrated in vacuo. Typically, the reaction mixture was filtered through a short silica gel column, eluting with CH_2Cl_2. The solution was concentrated in vacuo and the residue purified by column chromatography.

General Procedure B. Bromination of Porphyrins: The porphyrin was dissolved in $CHCl_3$ and cooled to 0 °C. Pyridine and NBS were added directly to the flask (TLC control). After 10–20 min, the reaction reached completion and was quenched with acetone. The solvents were evaporated and the product was washed with several portions of CH_3OH to yield a reddish purple solid.

General Procedure C. Suzuki Coupling: To a Schlenk flask was charged with K_3PO_4 (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere were added porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10–12.5 equiv.), and $Pd(PPh_3)_4$ (0.1 equiv.). The reaction was heated to reflux for 7–10 h (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 dried with Na_2SO_4. The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallization from CH_2Cl_2/CH_3OH to give the desired compound.

General Procedure D. Zinc(II) Insertion with $Zn(ac)_2$: The porphyrin (1 equiv.) was dissolved in dry CH_2Cl_2 (20 mL) and treated with zinc acetate dihydrate (6 equiv.) dissolved in CH_3OH. The reaction was monitored by TLC. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with H_2O. The solvent was removed under reduced pressure and the residues solved in CH_2Cl_2 and filtered through a short silica gel column followed by recrystallization from CH_2Cl_2/CH_3OH.

General Procedure E. Zinc(II) Insertion with ZnO: The free base porphyrin was dissolved in dry CH_2Cl_2 (20 mL) and treated with zinc oxide. After the addition of four drops of trifluoroacetic acid (TFA), the reaction mixture turned green and a change of color back to red indicated completion of the reaction. The product was separated from ZnO and most of the TFA by filtration through a short silica column. Remaining traces of TFA were removed by washing with H_2O. After drying with Na_2SO_4, the solvent was removed in vacuo and the product was purified by column chromatography (silica gel, CH_2Cl_2).

General Procedure F. Heck Reaction: The porphyrin was dissolved in DMF (50 mL) under an argon atmosphere. The olefin, NaOAc, $Pd(OAc)_2$ and triphenylphosphane were added and the temperature was raised to 120 °C for 16 h (TLC control). The crude product was extracted into CH_2Cl_2 and washed with H_2O. The product was purified by silica gel column chromatography.

General Procedure G. Sonogashira Reaction: A degassed solution of triethylamine (15 mL) and THF (5 mL) was cooled to 0 °C. Porphyrin (1 equiv.), alkynyl substrate, CuI, and $Pd(PPh_3)_2Cl_2$ were added. After 10 min, the cold bath was removed and the reaction mixture was stirred for another 2–5 h. 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 CH_2Cl_2/CH_3OH.

General Procedure H. 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 min by syringe. The cold bath was removed and stirring continued for 1.5 h at room temperature. H_2O (0.5 mL) was added and stirring continued for 15 min. DDQ (6 equiv.) in THF (10 mL) was added 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.

5,15-Bis(1-naphthyl)porphyrin (3): Following general procedure A, dipyrromethane (1 g, 6.84 mmol), 1-naphthaldehyde (1 mL, 7.52 mmol), and TFA (0.2 mL) were added to a solution of CH_2Cl_2 (1 L). The reaction mixture was stirred for 24 h at room temperature, followed by addition of DDQ (4.65 g, 21 mmol), and stirring for 1 h at room temp. The crude product was purified by recrystallization from CH_2Cl_2/CH_3OH to give 360 mg (0.51 mmol, 18%) of a purple product; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.87 (s, 2 H, N*H*), 7.16 (m, 4 H, Ar-*H*), 7.54 (t, ^3J = 8.7, 6.4 Hz, 2 H, Ar-*H*), 7.95 (m, 2 H, Ar-*H*), 8.20 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.36 (m, 4 H, Ar-*H*), 8.82 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.32 (d, ^3J = 4.1 Hz, 4 H, H_β), 10.3 (s, 2 H, H_{meso}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 105.12, 124.19, 125.58, 126.07, 127.74, 128.37, 130.93, 131.49, 132.73, 136.69 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 408 (5.02), 501 (3.81), 540 (3.21), 575 (3.37), 629 nm (2.94). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{40}H_{27}N_4$] [M + H$^+$]: 563.2236; found 563.2250.

5,15-Bis(9-phenanthrenyl)porphyrin (4): Following general procedure A, dipyrromethane (1 g, 6.84 mmol), phenanthrene-9-carbaldehyde (1.48 g, 7.18 mmol), and TFA (0.2 mL) were added to a solution of CH_2Cl_2 (1 L). The reaction mixture was stirred for 24 h at room temperature, followed by addition of DDQ (4.8 g, 21 mmol), and stirring for 1 h at room temp. The crude product was purified by recrystallization from CH_2Cl_2/CH_3OH to give 340 mg (0.51 mmol, 15%) of a purple product; m.p. >300 °C; R_f = 0.66 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.81 (s, 2 H, N*H*), 7.18 (m, 4 H, Ar-*H*), 7.54 (s, 2 H, Ar-*H*), 7.69 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 7.86 (m, 2 H, Ar-*H*), 7.97 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.17 (d, ^3J = 6.4 Hz, 2 H, Ar-*H*), 8.65 (m, 4 H, Ar-*H*), 8.93 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.08 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.32 (d, ^3J = 5.3 Hz, 2 H, H_β), 10.32 (s, 2 H, H_{meso}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 411 (4.98), 502 (3.85), 542 (3.38), 575 (3.48), 637 nm (3.08). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{48}H_{31}N_4$] [M + H$^+$]: 663.2549; found 663.2578.

5,15-Bis(4-methoxy-1-naphthyl)porphyrin (5): Following general procedure A, dipyrromethane (1.2 g, 8 mmol), 4-methoxynaphthaldehyde (2.7 g, 14 mmol), and TFA (0.3 mL) were added to a solution of CH_2Cl_2 (1 L). The reaction mixture was stirred for 24 h at room temperature, followed by addition of DDQ (4.8 g, 24 mmol), and stirring for 1 h at room temp. The crude product was purified by recrystallization from CH_2Cl_2/CH_3OH to give 800 mg (1.28 mmol, 31%) of a purple product; m.p. >300 °C; R_f = 0.3 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.89 (s, 2 H, N*H*), 4.35 (s, 6 H, OCH_3), 7.14 (m, 6 H, Ar-*H*), 7.55 (m, 2 H, Ar-*H*), 8.22 (d, ^3J = 8.2 Hz, 1 H, Ar-*H*), 8.26 (d, ^3J = 7.6 Hz, 1 H, Ar-*H*), 8.62 (d, ^3J = 8 Hz, 2 H, Ar-*H*), 8.66 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.30 (d, ^3J = 4.7 Hz, 4 H, H_β), 10.28 (s, 2 H, H_{meso}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.14), 505 (4.16), 541 (3.81), 577 (3.86), 637 nm (3.58). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{42}H_{31}N_4O_2$] [M + H$^+$]: 623.2447; found 623.2444.

5-(9-Anthracenyl)porphyrin (6): Following general procedure A, dipyrromethane (1 g, 6.84 mmol), 9-anthracenecarbaldehyde (1.55 g, 7.52 mmol), and TFA (0.2 mL) were added to a solution of CH_2Cl_2 (1 L). The reaction mixture was stirred for 24 h at room temperature, followed by addition of DDQ (4.65 g, 21 mmol), and stirring for 1 h at room temp. The crude product was purified by recrystallization from CH_2Cl_2/CH_3OH to give 50 mg (0.102 mmol, 3%) of the monosubstituted scrambling product **6**; m.p. >300 °C; R_f = 0.7 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –3.26 (s, 2 H, N*H*), 7.02 (m, 4 H, Ar-*H*), 7.48 (m, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.52 (d, ^3J = 4.1 Hz, 2 H, H_β), 9.00 (s, 1 H, Ar-*H*), 9.26 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.55 (s, 4 H, H_β), 10.34 (s, 2 H, H_{meso}), 10.36 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.97, 104.54, 114.53, 124.90, 125.60, 127.91, 128.10, 130.79, 131.54, 135.24 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 403 (4.92), 501 (3.76), 569 (3.36), 623 nm (2.87). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{34}H_{23}N_4$] [M + H$^+$]: 487.1923; found 487.1921.

5,15-Dibromo-10,20-bis(9-phenanthrenyl)porphyrin (9): Following general procedure B, 5,15-bis(9-phenanthrenyl)porphyrin (**4**) (100 mg, 0.121 mmol) and NBS (80 mg, 0.45 mmol) gave 83 mg (0.101 mmol, 68%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.4 (CH_2Cl_2/*n*-hexane = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.32 (s, 2 H, N*H*), 7.15 (t, ^3J = 8.8 Hz, 2 H, Ar-*H*), 7.22 (t, ^3J = 7.8, 2 H, 6.8 Hz, Ar-*H*), 7.71 (t, ^3J = 7.8, 2 H, 6.8 Hz, Ar-*H*), 7.85 (t, ^3J = 7.8, 2 H, 6.8 Hz, Ar-*H*), 7.96 (t, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.13 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.56 (d, ^3J = 5.9 Hz, 2 H, Ar-*H*), 8.74 (d, ^3J = 4.9 Hz, 4 H, H_β), 9.05 (t, ^3J = 7.8 Hz, 4 H, Ar-*H*), 9.52 (d, ^3J = 4.9 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.29, 103.85, 118.45, 122.77, 123.08, 124.16, 126.69, 126.75, 126.91, 129.63, 131.07, 132.49, 132.71, 135.72, 136.58 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 429 (5.14), 528 (4.03), 566 (3.80), 605 (3.68), 666 nm (3.50). HRMS: *m*/*z* calcd. for [$C_{48}H_{28}N_4Br_2$]: 818.0681; found 818.0638. $C_{48}H_{28}N_4Br_2$ (820.59): calcd. C 70.26, H 3.44, N 6.83; found C 70.45, H 3.66, N 6.74.

5,15-Dibromo-10,20-bis(1-naphthyl)porphyrin (10): Following general procedure B, 5,15-bis(1-naphthyl)porphyrin (**3**) (260 mg, 0.46 mmol) and NBS (205 mg, 1.15 mmol) gave 250 mg (0.35 mmol, 75%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.25 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.40 (s, 2 H, N*H*), 7.09 (t, ^3J = 7.6, 2 H, 8.2 Hz, Ar-*H*), 7.15 (m, 2 H, Ar-*H*), 7.55 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 7.92 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 8.20 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.26 (m, 2 H, Ar-*H*), 8.36 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.61 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.53 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.24, 118.57, 123.80, 125.40, 125.43, 126.02, 127.49, 127.98, 128.58, 132.02, 132.33, 132.37, 132.44, 136.26, 136.28, 138.07 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 426 (5.08), 522 (3.93), 556 (3.67), 601 (3.49), 658 nm (3.43). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{40}H_{25}N_4Br_2$] [M + H$^+$]: 719.0446; found 719.0430.

5,15-Dibromo-10,20-bis(4-methoxy-1-naphthyl)porphyrin (12): Following general procedure B, 5,15-bis(4-methoxy-1-naphthyl)porphyrin (**5**) (360 mg, 0.58 mmol) and NBS (258 mg, 1.445 mmol) gave 350 mg (0.45 mmol, 77%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.41 (s, 2 H, NH), 4.34 (s, 6 H, OCH_3), 7.05 (m, 2 H, Ar-*H*), 7.17 (m, 2 H, Ar-*H*), 7.25 (m, 2 H, Ar-*H*), 7.53 (t, ^3J = 7.6, 2 H, 7 Hz, Ar-*H*), 8.15 (t, ^3J = 7.6, 2 H, 7 Hz, Ar-*H*), 8.62 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.66 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.52 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.73, 102.52, 119.08, 121.73, 124.62, 126.73, 128.13, 130.60, 132.70, 137.46, 156.02 ppm.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 428 (4.98), 523 (3.97), 559 (3.70), 603 (3.50), 661 nm (3.47). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{42}H_{29}N_4O_2Br_2$] [M + H$^+$]: 781.0637; found 781.0599.

5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(1-naphthyl)porphyrin (13): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)porphyrin (**10**) (40 mg, 0.055 mmol), (4-methoxycarbonylphenyl)boronic acid (198 mg, 1.1 mmol), $Pd(PPh_3)_4$ (6.4 mg, 0.0055 mmol), and K_3PO_4 (471 mg, 2.22 mmol) in THF (30 mL) gave 14 mg (0.016 mmol, 30%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.59 (s, 2 H, N*H*), 4.02 (s, 6 H, COOC*H*$_3$), 7.05 (m, 4 H, Ar-*H*), 7.44 (t, ^3J = 7.3, 2 H, 7.8 Hz, Ar-*H*), 7.82 (t, ^3J = 8.3, 2 H, 6.8 Hz, Ar-*H*), 8.08 (t, ^3J = 8.3 Hz, 2 H, Ar-*H*), 8.22 (m, 8 H, Ar-*H*), 8.34 (d, ^3J = 7.8 Hz, 4 H, Ar-*H*), 8.54 (d, ^3J = 4.9 Hz, 4 H, H_β), 8.63 (d, ^3J = 4.9 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 52.43, 118.16, 118.97, 119.04, 124.26, 125.76, 126.34, 127.27, 127.93, 128.46, 128.59, 128.85, 129.62, 129.70, 130.23, 131.42, 132.75, 132.80, 132.90, 134.51, 136.78, 136.81, 139.11, 144.37, 146.69, 146.79, 166.83, 167.28 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.19), 515 (3.89), 553 (3.41), 594 (3.38), 645 nm (3.15). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{56}H_{39}N_4O_4$] [M + H$^+$]: 831.2971; found 831.2957.

5,15-Bis(4-cyanophenyl)-10,20-bis(1-naphthyl)porphyrin (14): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)-porphyrin (**10**) (100 mg, 0.138 mmol), (4-cyanophenyl)boronic acid (254 mg, 1.725 mmol), $Pd(PPh_3)_4$ (16 mg, 0.0138 mmol), and K_3PO_4 (737 mg, 3.47 mmol) in THF (50 mL) gave 70 mg (0.092 mmol, 66%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.52 (s, 2 H, N*H*), 7.13 (m, 4 H, Ar-*H*), 7.54 (m, 2 H, Ar-*H*), 7.92 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.05 (d, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.33 (m, 8 H, Ar-*H*), 8.67 (s, 8 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.42, 102.06, 111.54, 117.46, 118.15, 124.62, 125.93, 127.99, 128.00, 131.46, 132.33, 132.45, 136.29, 138.36, 146.26, 146.37 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.20), 515 (3.95), 548 (3.45), 592 (3.41), 646 nm (3.13). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{54}H_{33}N_6$] [M + H$^+$]: 765.2767; found 765.2790.

5,15-Bis(1-naphthyl)-10,20-bis(4-nitrophenyl)porphyrin (15): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)porphyrin (**10**) (25 mg, 0.035 mmol), (4-nitrophenyl)boronic pinacol ester (87 mg, 0.35 mmol), $Pd(PPh_3)_4$ (4 mg, 0.0035 mmol), and K_3PO_4 (148 mg, 0.70 mmol) in THF (20 mL) gave 20 mg (0.024 mmol, 71%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.50 (s, 2 H, N*H*), 7.12 (m, 4 H, Ar-*H*), 7.54 (t, ^3J = 6.4 Hz, 2 H, Ar-*H*), 7.92 (t, ^3J = 7.6, 2 H, 8.2 Hz, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.30 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.40 (m, 4 H, Ar-*H*), 8.62 (m, 4 H, Ar-*H*), 8.68 (m, 8 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.09), 516 (3.87), 552 (3.38), 592 (3.40), 648 nm (3.19). HRMS: *m*/*z* calcd. for [$C_{52}H_{32}N_6O_4$]: 804.2485; found 804.2511. $C_{52}H_{32}N_6O_4$ (804.86): calcd. C 77.60, H 4.01, N 10.44; found C 77.35, H 3.75, N 10.13.

5,15-Bis(4-bromophenyl)-10,20-bis(1-naphthyl)porphyrin (16): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)-porphyrin (**10**) (50 mg, 0.07 mmol), (4-bromophenyl)boronic acid (176 mg, 0.875 mol), $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), and K_3PO_4 (367 mg, 1.73 mmol) in THF (30 mL) gave 49 mg (0.056 mmol, 82%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.60 (s, 2 H, N*H*), 7.15 (m, 4 H, Ar-*H*), 7.53 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.89 (m, 6 H, Ar-*H*), 8.08 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.18 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.32 (m, 4 H, Ar-*H*), 8.63 (d, ^3J = 4.7 Hz, 4 H, H_β), 8.75 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 117.56, 118.20, 122.03, 123.79, 124.74, 125.28, 126.92, 127.45, 128.37, 129.45, 130.54, 131.65, 132.27, 132.43, 135.34, 136.32, 138.69, 140.35 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.22), 515 (3.97), 548 (3.53), 592 (3.46), 644 nm (3.22). HRMS: *m*/*z* calcd. for (MS ES$^+$) [$C_{52}H_{33}N_4Br_2$] [M + H$^+$]: 873.1051; found 873.1013.

5,15-Bis(1-naphthyl)-10,20-bis(3-thiophenyl)porphyrin (17): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)porphyrin (**10**) (100 mg, 0.138 mmol), (thiophen-3-yl)boronic acid (221 mg, 1.725 mol), $Pd(PPh_3)_4$ (16 mg, 0.0138 mmol), and K_3PO_4 (737 mg, 3.47 mmol) in THF (50 mL) gave 65 mg (0.089 mmol, 65%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.43 (s, 2 H, N*H*), 7.15 (m, 4 H, Ar-*H*), 7.52 (t, ^3J = 7.2, 2 H, 7.5 Hz, Ar-*H*), 7.70 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 7.91 (t, ^3J = 6, 2 H, 6.4 Hz, Ar-*H*), 8.00 (m, 4 H, Ar-*H*), 8.18 (d, ^3J = 8.3 Hz, 2 H, Ar-*H*), 8.32 (m, 4 H, Ar-*H*), 8.61 (d, ^3J = 4.7 Hz, 4 H, H_β), 8.90 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.93, 22.48, 31.42, 114.50, 117.58, 123.33, 124.06, 125.53, 126.07, 127.70, 128.12, 128.55, 132.58, 132.74, 134.26, 136.66, 139.21, 141.83 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.11), 516 (3.93), 552 (3.67), 592 (3.60), 649 nm (3.52). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{48}H_{31}N_4S_2$] [M + H$^+$]: 727.1990; found 727.1981.

5,15-Bis(1-naphthyl)-10,20-bis(2-phenylethenyl)porphyrin (18): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)-porphyrin (**10**) (40 mg, 0.055 mmol), *trans*-β-styrylboronic acid (82 mg, 0.55 mmol), $Pd(PPh_3)_4$ (6.4 mg, 0.0055 mmol), and K_3PO_4 (235 mg, 1.11 mmol) in THF (30 mL) gave 20 mg (0.026 mmol, 48%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –1.93 (s, 2 H, N*H*), 7.15 (m, 4 H, Ar-*H*), 7.39 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*), 7.46 (t, ^3J = 7.5, 2 H, 7.3 Hz, Ar-*H*), 7.55 (m, 6 H, Ar-*H*), 7.92 (d, ^3J = 7 Hz, 6 H, Ar-*H*), 8.20 (d, ^3J = 8 Hz, 2 H, Ar-*H*), 8.33 (m, 4 H, Ar-*H*), 8.62 (d, ^3J = 4.8 Hz, 4 H, H_β), 9.38 (d, ^3J = 4.8 Hz, 4 H, H_β), 9.58 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 116.98, 118.07, 124.30, 125.73, 126. 28, 126.93, 127.91, 128.64, 129.04, 131.51, 132.62, 132.92, 136.76, 137.92, 139.50, 143.22 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 440 (5.11), 585 (4.01), 677 nm (3.82). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{56}H_{39}N_4$] [M + H$^+$]: 767.3175; found 767.3159.

5,15-Bis(1-methyl-1*H*-indol-5-yl)-10,20-bis(1-naphthyl)porphyrin (19): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)porphyrin **10** (30 mg, 0.041 mmol), (1-methylindol-5-yl)-boronic acid (106 mg, 0.41 mmol), $Pd(PPh_3)_4$ (5 mg, 0.0041 mmol), and K_3PO_4 (176 mg, 0.832 mmol) in THF (30 mL) gave 15 mg (0.018 mmol, 45%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.37 (s, 2 H, N*H*), 4.05 (s, 6 H, C*H*$_3$), 6.69 (m, 2 H, Ar-*H*) 7.14 (m, 2 H, Ar-*H*), 7.22 (m, 2 H, Ar-*H*), 7.32 (d, ^3J = 7.3 Hz, 2 H, Ar-*H*), 7.50 (m, 2 H, Ar-*H*), 7.62 (d, ^3J = 8.3 Hz, 2 H, Ar-*H*), 7.88 (t, ^3J = 7.5 Hz, 2 H, Ar-*H*), 8.13 (m, 4 H, Ar-*H*), 8.30 (d, ^3J = 7.8 Hz, 4 H, Ar-*H*), 8.44 (s, 2 H, Ar-*H*), 8.55 (d, ^3J = 4.8 Hz, 4 H, H_β), 8.79 (d, ^3J = 4.8 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 33.17, 101.08, 106.75, 117.09, 121.30, 124.03, 126.00, 127.02, 127.61, 128.35, 128.86,

129.77, 130.46, 132.70, 133.01, 136.18, 136.70, 139.59 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 427 (5.15), 519 (4.04), 555 (3.78), 592 (3.73), 645 nm (3.56). HRMS (MS ES$^+$) *m/z* calcd. for [$C_{58}H_{41}N_6$] [M + H$^+$]: 821.3393; found 821.3373.

5,15-Bis(1-naphthyl)-10,20-bis(2-thianaphthyl)porphyrin (20): Following general procedure C, 5,15-dibromo-10,20-bis(1-naphthyl)-porphyrin (**10**) (30 mg, 0.041 mmol), (thianaphthen-2-yl)boronic acid (73 mg, 0.41 mol), $Pd(PPh_3)_4$ (5 mg, 0.0041 mmol), and K_3PO_4 (176 mg, 0.832 mmol) in THF (30 mL) gave two compounds after column chromatography on silica gel. The title compound **20** was obtained as 7 mg (0.008 mmol, 21%) of purple a solid after recrystallization from CH_2Cl_2/CH_3OH accompanied by the mono-substituted compound **33**; m.p. >300 °C; R_f = 0.66 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.36 (s, 2 H, N*H*), 7.13–7.16 (m, 4 H, Ar-*H*), 7.54 (m, 2 H, Ar-*H*) 7.61 (dd, ^3J = 7.6, 8.2 Hz, 4 H, Ar-*H*), 7.90 (t, ^3J = 8.8, 2 H, 6.4 Hz, Ar-*H*), 8.08 (t, ^3J = 7.6, 4 H, 6.4 Hz, Ar-*H*), 8.14 (s, 2 H, Ar-*H*), 8.18 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.31 (dd, ^3J = 8.2, 7 Hz, 4 H, Ar-*H*), 8.61 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.07 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 111.49, 118.50, 121.49, 123.83, 124.08, 124.73, 124.92, 125.60, 126.19, 127.74, 128.70, 130.73, 132.58, 132.75, 136.59, 138.85, 139.17, 141.74, 142.80 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 428 (4.95), 519 (3.87), 557 (3.66), 592 (3.58), 648 nm (3.45). HRMS (MS ES$^+$) *m/z* calcd. for [$C_{56}H_{35}N_4S_2$] [M + H$^+$]: 827.2303; found 827.2303.

5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(9-phenanthrenyl)-porphyrin (21): Following general procedure C, 5,15-dibromo-10,20-bis(9-phenanthrenyl)porphyrin (**9**) (40 mg, 0.048 mmol), (4-methoxycarbonylphenyl)boronic acid (87 mg, 0.48 mmol), $Pd(PPh_3)_4$ (5.5 mg, 0.0048 mmol), and K_3PO_4 (206 mg, 0.974 mmol) in THF (30 mL) gave 25 mg (0.026 mmol, 56%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.2 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.42 (s, 2 H, N*H*), 4.01 (s, 6 H, COOCH_3), 7.20 (m, 4 H, Ar-*H*), 7.72 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.84 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 7.94 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 8.12 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.16 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.31 (m, 3 H, Ar-*H*), 8.43 (m, 3 H, Ar-*H*), 8.60 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.73 (d, ^3J = 4.7 Hz, 4 H, H_β), 8.77 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.05 (t, ^3J = 8.2 Hz, 4 H, Ar-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.96, 117.58, 118.56, 122.13, 122.42, 125.95, 126.30, 126.93, 127.00, 128.66, 129.76, 133.23, 134.01, 135.82, 137.14, 143.89, 146.16, 166.36, 166.79 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 424 (5.18), 516 (4.08), 549 (3.77), 592 (3.75), 645 nm (3.62). HRMS: *m/z* calcd. for [$C_{64}H_{42}N_4O_4$]: 906.3207; found 906.3189.

5,15-Bis(4-cyanophenyl)-10,20-bis(9-phenanthrenyl)porphyrin (22): Following general procedure C, 5,15-dibromo-10,20-bis(9-phenanthrenyl)porphyrin (**9**) (50 mg, 0.0611 mmol), (4-cyanophenyl)boronic acid (112 mg, 0.763 mmol), $Pd(PPh_3)_4$ (7 mg, 0.00611 mmol), and K_3PO_4 (325 mg, 1.53 mmol) in THF (30 mL) gave 26 mg (0.030 mmol, 62%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.46 (s, 2 H, N*H*), 7.14–7.20 (m, 4 H, Ar-*H*), 7.70 (t, ^3J = 8.2, 2 H, 7 Hz, Ar-*H*), 7.85 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 7.95 (t, ^3J = 7 Hz, 2 H, Ar-*H*), 8.05 (m, 4 H, Ar-*H*), 8.12 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.35 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.59 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.68 (d, ^3J = 4.7 Hz, 4 H, H_β), 8.80 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.06 (t, ^3J = 7.6, 4 H, 8.2 Hz, Ar-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 30.26, 111.57, 117.52, 118.04, 122.21, 122.46, 126.02, 126.33, 127.07, 128.65, 129.24, 129.42, 130.13, 130.35, 133.34, 134.42, 135.78, 136.87, 146.20 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 424 (4.98), 516 (3.85), 552 (3.51), 590 (3.49), 648 nm (3.32). HRMS: *m/z* calcd. for [$C_{62}H_{36}N_6$] [M + H$^+$]: calcd. 840.3001; found 840.3124.

5,15-Bis(4-nitrophenyl)-10,20-bis(9-phenanthrenyl)porphyrin (23): Following general procedure C, 5,15-dibromo-10,20-bis(9-phenanthrenyl)porphyrin (**9**) (50 mg, 0.0611 mmol), (4-nitrophenyl)-boronic acid pinacol ester (190 mg, 0.763 mmol), $Pd(PPh_3)_4$ (7 mg, 0.00611 mmol), and K_3PO_4 (325 mg, 1.53 mmol) in THF (30 mL) gave 30 mg (0.033 mmol, 55%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.42 (s, 2 H, N*H*), 7.18 (m, 4 H, Ar-*H*), 7.71 (t, ^3J = 6.4, 2 H, 7.02 Hz, Ar-*H*), 7.85 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 7.95 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.12 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.41 (d, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.61 (m, 6 H, Ar-*H*), 8.69 (d, ^3J = 4.1 Hz, 4 H, H_β), 8.82 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.07 (t, ^3J = 7.6 Hz, 4 H, Ar-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 117.11, 118.18, 121.47, 122.22, 126.04, 126.87, 127.09, 128.65, 129.25, 130.36, 131.33, 133.36, 134.56, 135.76, 136.81, 147.32, 148.16 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 426 (5.16), 517 (3.98), 552 (3.40), 592 (3.36), 646 nm (2.82). HRMS: *m/z* calcd. for [$C_{60}H_{36}N_6O_4$]: 880.2798; found 880.2532.

5,15-Bis(9-phenanthrenyl)-10,20-bis(3-thiophenyl)porphyrin (24): Following general procedure C, 5,15-dibromo-10,20-bis(9-phenanthrenyl)porphyrin (**9**) (40 mg, 0.048 mmol), (thiophen-3-yl)-boronic acid (62 mg, 0.48 mmol), $Pd(PPh_3)_4$ (5.5 mg, 0.0048 mmol), and K_3PO_4 (206 mg, 0.974 mmol) in THF (30 mL) gave 18 mg (0.021 mmol, 45%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.38 (s, 2 H, N*H*), 7.19–7.23 (m, 4 H, Ar-*H*), 7.69 (t, ^3J = 7.8 Hz, 4 H, Ar-*H*), 7.84 (t, ^3J = 7.5 Hz, 2 H, Ar-*H*), 7.92 (t, ^3J = 7.3 Hz, 2 H, Ar-*H*), 8.00 (d, ^3J = 7.3 Hz, 2 H, Ar-*H*), 8.12 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.59 (t, ^3J = 7.8 Hz, 4 H, Ar-*H*), 8.75 (d, ^3J = 4.5 Hz, 4 H, H_β), 8.90 (d, ^3J = 4.5 Hz, 4 H, H_β), 9.05 (t, ^3J = 8.3 Hz, 4 H, Ar-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.69, 22.21, 31.14, 114.27, 117.17, 122.09, 122.42, 123.10, 125.89, 126.25, 126.95, 127.87, 128.67, 129.55, 130.44, 133.15, 133.96, 135.86, 137.38, 141.46 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 424 (5.28), 517 (4.03), 552 (3.58), 592 (3.51), 650 nm (3.22). HRMS (MS ES$^+$) *m/z* calcd. for [$C_{56}H_{35}N_4S_2$] [M + H$^+$]: 827.2303; found 827.2288.

5,15-Bis(9-phenanthrenyl)-10,20-bis(2-phenylethenyl)porphyrin (25): Following general procedure C, 5,15-dibromo-10,20-bis(9-phenanthrenyl)porphyrin (**9**) (40 mg, 0.048 mmol), *trans*-β-styrylboronic acid (71 mg, 0.48 mmol), $Pd(PPh_3)_4$ (5.5 mg, 0.0048 mmol), and K_3PO_4 (203 mg, 0.96 mmol) in THF (30 mL) gave 22 mg (0.025 mmol, 40%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –1.87 (s, 2 H, N*H*), 7.23 (m, 4 H, Ar-*H*), 7.39 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*), 7.44 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 7.56 (t, ^3J = 7.6, 4 H, 8.2 Hz, Ar-*H*), 7.70 (m, 2 H, Ar-*H*), 7.85 (t, ^3J = 7.6, 2 H, 7 Hz, Ar-*H*), 7.91 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 7.96 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.15 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.61 (d, ^3J = 11.1 Hz, 2 H, Ar-*H*), 8.75 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.06 (t, ^3J = 8.8 Hz, 4 H, Ar-*H*), 9.52 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.57 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 122.12, 122.43, 125.92, 126.27, 126.95, 127.88, 128.12, 128.57, 128.70, 129.52, 133.01, 142.80 ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 439 (4.79), 582 (3.67), 672 nm (3.38). HRMS (MS ES$^+$) *m/z* calcd. for [$C_{64}H_{43}N_4$] [M + H$^+$]: 867.3488; found 867.3465.

5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (26): Following general procedure C, **11** (50 mg, 0.073 mmol), (4-methoxycarbonylphenyl)boronic acid (164 mg,

0.91 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (390 mg, 1.837 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10:1, v/v) followed by recrystallisation from CH_2Cl_2/CH_3OH afforded the title compound (45 mg, 0.056 mmol, 78%) as purple crystals; m.p. > 300 °C; R_f = 0.7 (*n*-hexane/ethyl acetate = 2:1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.77 (s, 2 H, N*H*), 4.02 (s, 6 H, OCH_3), 4.15 (s, 6 H, OCH_3), 7.37 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.68 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.83 (m, 4 H, Ar-*H*), 8.34 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.48 (d, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.83 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta3,7,13,17}$), 8.95 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta2,8,12,18}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.4, 55.5, 113.6, 118.9, 120.3, 120.5, 127.5, 127.6, 127.9, 129.6, 134.5, 143.1, 146.9, 157.9, 167.3 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 419 (5.16), 516 (3.73), 550 (3.73), 594 (2.90), 646 nm (2.42). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{39}N_4O_6$] [M + H$^+$]: 791.2870; found 791.2892.

5,15-Bis(4-cyanophenyl)-10,20-bis(3-methoxyphenyl)porphyrin (27): Following general procedure C, **11** (50 mg, 0.073 mmol), (4-cyanophenyl)boronic acid (134 mg, 0.912 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (390 mg, 1.837 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel using *n*-hexane/ethyl acetate (6:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave the product (39 mg, 0.052 mmol, 73%) as purple crystals; m.p. > 300 °C; R_f = 0.22 (*n*-hexane/ethyl acetate = 6:1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.81 (s, 2 H, N*H*), 4.02 (s, 6 H, OCH_3), 7.08 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.69 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.81 (m, 4 H, Ar-*H*), 8.10 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.36 (d, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.76 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta3,7,13,17}$), 8.97 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta2,8,12,18}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.3, 111.8, 113.5, 117.7, 118.8, 120.5, 120.6, 127.5, 130.4, 134.8, 142.8, 146.8, 157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 420 (5.13), 515 (3.87), 550 (3.40), 591 (3.26), 645 nm (2.96). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{48}H_{32}N_6O_2$] [M + H$^+$]: 791.2870; found 791.2892.

5,15-Bis(3-methoxyphenyl)-10,20-bis(4-nitrophenyl)porphyrin (28): Following general procedure C, **11** (50 mg, 0.073 mmol), (3-nitrophenyl)boronic acid (152 mg, 0.912 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (390 mg, 1.837 mmol) in THF (50 mL) were used. Purification by column chromatography (silica gel, *n*-hexane/CH_2Cl_2 = 1:2, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave the desired compound (35 mg, 0.045 mmol, 63%) as purple crystals; m.p. > 300 °C; R_f = 0.42 (*n*-hexane/CH_2Cl_2 = 1:2, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.79 (s, 2 H, N*H*), 3.99 (s, 6 H, OCH_3), 4.20 (s, 3 H, OCH_3), 7.38 (m, 2 H, Ar-*H*), 7.68 (m, 2 H, Ar-*H*), 7.83 (m, 2 H, Ar-*H*), 7.99 (t, ^3J = 7.6, 2 H, Hz, Ar-*H*), 8.58 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.72 (m, 2 H, Ar-*H*), 8.76 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta3,7,13,17}$), 8.98 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta2,8,12,18}$), 10.11 (m, 2 H, Ar-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 77.2, 113.7, 120.4, 120.6, 123.0, 127.7, 128.3, 139.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 421 (5.16), 549 (3.88), 549 (3.29), 590 (3.25), 647 nm (2.48). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{46}H_{33}N_6O_6$] [M + H$^+$]: 765.2462; found 765.2428.

5,15-Bis(4-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (29): Following general procedure C, **11** (50 mg, 0.073 mmol), (4-hydroxyphenyl)boronic acid (126 mg, 0.9125 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (390 mg, 1.837 mmol) in THF (50 mL) were used. Purification by two consecutive column chromatographies (1. *n*-hexane/ethyl acetate = 6:1, 2. *n*-hexane/ethyl acetate = 2:1, v/v) and recrystallization from CH_2Cl_2/CH_3OH afforded the desired product (17 mg, 0.024 mmol, 32%) as purple crystals; m.p. > 300 °C; R_f = 0.37 (*n*-hexane/ethyl acetate = 2:1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.76 (s, 2 H, N*H*), 4.01 (s, 6 H, OCH_3), 5.80 (br. s, 2 H, O*H*), 7.21 (d, ^3J = 8.8 Hz, 4 H, Ar-*H*), 7.36 (m, 2 H, Ar-*H*), 7.66 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.83 (m, 2 H, Ar-*H*), 8.08 (d, ^3J = 9 Hz, 4 H, Ar-*H*), 8.90 (m, 8 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 53.2, 55.3, 113.4, 113.5, 119.5, 119.6, 120.3, 127.3, 127.5, 134.6, 135.5, 143.4, 155.3, 157.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 420 (5.03), 517 (4.72), 552 (3.53), 593 (3.42), 647 nm (3.36). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{46}H_{35}N_4O_4$] [M + H$^+$]: 707.2658; found 707.2658.

5,15-Bis(3-methoxyphenyl)-10,20-bis(2-phenylethenyl)porphyrin (30): Following general procedure C, **11** (50 mg, 0.073 mmol), *trans*-β-styrylboronic acid (135 mg, 0.912 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (389 mg, 1.837 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afforded the desired compound (25 mg, 0.0534 mmol, 47%) as purple crystals; m.p. > 300 °C; R_f = 0.62 (*n*-hexane/ethyl acetate = 6:1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.24 (s, 2 H, N*H*), 4.03 (s, 6 H, OCH_3), 7.38 (m, 2 H, Ar-*H*), 7.40 (d, ^3J = 16.2 Hz, 2 H, CH=C*H*), 7.49 (m, 2 H, Ar-*H*), 7.61 (m, 4 H, Ar-*H*), 7.61 (m, 4 H, Ar-*H*), 7.69 (m, 2 H, Ar-*H*), 7.83 (m, 4 H, Ar-*H*), 7.97 (m, 4 H, Ar-*H*), 8.91 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.47 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.64 (d, ^3J = 16.4 Hz, 2 H, C*H*=CH) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 29.5, 55.3, 113, 116.8, 120.1, 120.3, 126.8, 127.3, 127.4, 128.1, 128.7, 128.9, 37.8, 143.1, 143.4, 157.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 435 (4.94), 530 (3.43), 581 (3.78), 672 nm (3.42). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{39}N_4O_2$] [M + H$^+$]: 727.3073; found 727.3087.

5,15-Bis(1-methyl-1*H*-indol-5-yl)-10,20-bis(3-methoxyphenyl)-porphyrin (31): Following general procedure C, **11** (50 mg, 0.073 mmol), (1-methylindol-5-yl)boronic acid pinacol ester (235 mg, 0.912 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (390 mg, 1.837 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 6:1, v/v) followed by recrystallisation from CH_2Cl_2/CH_3OH afforded the title compound (38 mg, 0.048 mmol, 66%) as purple crystals; m.p. > 300 °C; R_f = 0.42 (*n*-hexane/ethyl acetate = 6:1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.63 (s, 2 H, N*H*), 4.00 (s, 6 H, OCH_3), 4.10 (s, 6 H, CH_3), 6.75 (d, ^3J = 2.9 Hz, 2 H, Ar-*H*), 7.35 (m, 4 H, Ar-*H*), 7.66 (m, 4 H, Ar-*H*), 7.84 (m, 4 H, Ar-*H*), 8.14 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.47 (s, 2 H, Ar-*H*), 8.88 (dd, ^3J = 4.7 Hz, 8 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.0 55.3, 101.1, 106.7, 113.3, 119.3, 120.2, 121.2, 127.0, 127.5, 128.9, 133.2, 136.2, 143.6, 157.7 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 424 (4.94), 518 (3.52), 555 (3.22), 593 (3.06), 648 nm (3.06). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{52}H_{41}N_6O_2$] [M + H$^+$]: 781.3291; found 781.3284.

5,15-Bis(2-benzothiophenyl)-10,20-bis(3-methoxyphenyl)porphyrin (32): Following general procedure C, **11** (50 mg, 0.073 mmol), (thianaphthalen-2-yl)boronic acid (152 mg, 0.91 mmol), $Pd(PPh_3)_4$ (10.5 mg, 0.009 mmol), and K_3PO_4 (390 mg, 1.837 mmol) in THF (50 mL) were used. Purification by filtration through a silica gel column eluting with *n*-hexane/CH_2Cl_2 (2:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afforded purple crystals (40 mg, 0.05 mmol, 70%); m.p. > 300 °C; R_f = 0.41 (*n*-hexane/ethyl acetate = 6:1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = –2.65 (s, 2 H, N*H*), 4.01 (s, 6 H, OCH_3), 7.36 (m, 2 H, Ar-*H*), 7.6 (m, 6 H, Ar-*H*), 7.8 (m, 4 H, Ar-*H*), 8.13 (t, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.18 (s, 2 H, Ar-*H*), 8.92 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta3,7,13,17}$), 9.17 (d, ^3J = 4.7 Hz, 4 H, $H_{\beta2,8,12,18}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 113.7, 120.4, 121.7, 124.0, 124.9, 125.1, 127.6, 130.8, 143.0 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 425 (4.95), 518 (3.64), 556 (3.38), 593 (3.21), 648 nm (3.1). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{35}N_4O_2S_2$] [M + H$^+$]: 787.2201; found 787.2178.

5,15-Bis(1-naphthyl)-10-(2-thianaphthyl)porphyrin (33): This compound was obtained from the reaction described for **20** as 8 mg (0.011 mmol, 28%) of purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.4 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.69 (s, 2 H, N*H*), 7.14–7.17 (m, 4 H, Ar-*H*), 7.55 (m, 2 H, Ar-*H*), 7.63 (m, 2 H, Ar-*H*), 7.92 (t, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.09 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.16 (t, ^3J = 7.8 Hz, 4 H, Ar-*H*), 8.20 (s, 2 H, Ar-*H*), 8.35 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.67 (d, ^3J = 4.9 Hz, 2 H, H_β), 8.74 (d, ^3J = 4.9 Hz, 2 H, H_β), 9.09 (d, ^3J = 4.9 Hz, 2 H, H_β), 9.27 (d, ^3J = 4.9 Hz, 2 H, H_β), 10.24 (s, 1 H, H_{meso}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (4.71), 514 (3.57), 549 (3.22), 588 (3.25), 644 nm (3.08). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{48}H_{31}N_4S$] [M + H$^+$]: 695.2269; found 695.2264.

[5,15-Dibromo-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (34): Following general procedure D, **10** (200 mg, 0.277 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and treated with a saturated solution of zinc acetate dihydrate dissolved in CH_3OH. The reaction mixture was stirred for 1 h and then washed with H_2O. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 and filtered through a short silica gel column to yield 200 mg (0.191 mmol, 92%) of a purple solid after recrystallization from CH_2Cl_2/MeOH; m.p. >300 °C; R_f = 0.3 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (m, 2 H, Ar-*H*), 7.12 (m, 2 H, Ar-*H*), 7.53 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 7.92 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.26 (d, ^3J = 6.4 Hz, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.69 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.62 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 428 (4.99), 558 (3.74), 598 nm (3.48). $C_{40}H_{22}N_4Br_2Zn$ (783.83): calcd. C 61.29, H 2.83, N 7.15; found C 61.55, H 3.05, N 7.43.

[5,15-Bis(4-cyanophenyl)-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (36): Following general procedure E, **14** (40 mg, 0.052 mmol) was treated with zinc oxide (400 mg) to yield 38 mg (0.009 mmol, 68%) of desired the product after recrystallization from CH_2Cl_2/MeOH; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.13 (m, 4 H, Ar-*H*), 7.53 (m, 2 H, Ar-*H*), 7.92 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.04 (d, ^3J = 8.8 Hz, 4 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.34 (m, 8 H, Ar-*H*), 8.76 (m, 8 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 429 (5.19), 560 (3.99), 601 nm (3.45). $C_{54}H_{30}N_6Zn$ (828.25): calcd. C 78.31, H 3.65, N 10.15; found C 78.05, H 3.74, N 9.87.

[5,15-Bis(1-naphthyl)-10,20-bis(4-nitrophenyl)porphyrinato]zinc(II) (37): Following general procedure E, **15** (20 mg, 0.024 mmol) was treated with zinc oxide (300 mg) to give 15 mg (0.0170 mmol, 70%) of the desired product after recrystallization from CH_2Cl_2/MeOH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06–7.14 (m, 4 H, Ar-*H*), 7.52 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.92 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.31 (m, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.41 (dd, ^3J = 7 Hz, 4 H, Ar-*H*), 8.62 (m, 4 H, Ar-*H*), 8.77 (dd, ^3J = 4.7 Hz, 8 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 431 (4.98), 561 (3.78), 606 nm (3.27). $C_{52}H_{30}N_6O_4Zn$ (868.23): calcd. C 71.94, H 3.48, N 9.68; found C 72.15, H 3.54, N 9.78.

[5,15-Dibromo-10,20-bis(4-methoxy-1-naphthyl)porphyrinato]zinc(II) (38): Following general procedure D, **12** (150 mg, 0.192 mmol) was dissolved in dry CH_2Cl_2 (30 mL) and treated with a saturated solution of zinc acetate dihydrate solved in CH_3OH. The reaction mixture was stirred for 1 h and then washed with H_2O. The solvent was removed under reduced pressure and the residues dissolved in CH_2Cl_2 and filtered through a short silica gel column to give 150 mg (0.177 mmol, 90%) of a purple solid after recrystallization from CH_2Cl_2/MeOH. R_f = 0.36 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.33 (s, 6 H, OCH_3), 6.99 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 7.13 (m, 2 H, Ar-*H*), 7.24 (m, 2 H, Ar-*H*), 7.52 (t, ^3J = 8.2, 2 H, 7 Hz, Ar-*H*), 8.15 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.60 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.75 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.62 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 430 (5.04), 559 (3.87), 598 nm (3.23). HRMS: *m*/*z* calcd. for [$C_{42}H_{26}N_4Br_2O_2Zn$]: 839.9714; found 839.9747.

[5,15-Bis(1-naphthyl)-15,20-bis{(*E*)-2-(3-nitrophenyl)vinyl}porphyrinato]zinc(II) (39): Following general procedure F, **34** (50 mg, 0.063 mmol), 3-nitrostyrene (0.62 mL, 4.46 mmol), NaOAc (29 mg, 0.352 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0063 mmol), and PPh_3 (6.6 mg, 0.0252 mmol) were added to a solution of DMF (50 mL) and heated at 120 °C for 18 h. The crude product was purified by column chromatography using CH_2Cl_2 with 10% *n*-hexane as eluent to yield 23 mg (0.024 mmol, 40%) of a purple solid after recrystallization from CH_2Cl_2/*n*-hexane; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (m, 4 H, Ar-*H*), 7.41 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*), 7.53 (m, 2 H, Ar-*H*), 7.74 (t, ^3J = 7.6, 2 H, 8.2 Hz, Ar-*H*), 7.95 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 8.20 (t, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.30 (t, ^3J = 5.3, 2 H, 9.9 Hz, Ar-*H*), 8.35 (t, ^3J = 7.6, 4 H, 6.4 Hz, Ar-*H*), 8.76 (d, ^3J = 4.7 Hz, 4 H, H_β), 8.78 (s, 2 H, Ar-*H*), 9.48 (d, ^3J = 3.5 Hz, 4 H, H_β), 9.80 (d, ^3J = 16.4 Hz, 2 H, alkene-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 116.54, 119.34, 121.09, 122.39, 124.11, 125.52, 126.01, 127.79, 128.51, 129.79, 130.06, 132.36, 136.67, 139.31, 139.68, 148.88, 149.36, 150.45 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 439 (4.96), 565 (3.82), 615 nm (3.85). $C_{56}H_{34}N_6O_4Zn$ (920.30): calcd. C 73.09, H 3.72, N 9.13; found C 73.28, H 3.66, N 9.27.

[5,15-Bis{(*E*)-2-(4-bromophenyl)vinyl}-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (40): Following general procedure F, **34** (50 mg, 0.063 mmol), 3-nitrostyrene (0.62 mL, 4.46 mmol), NaOAc (29 mg, 0.352 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0063 mmol), and PPh_3 (6.6 mg, 0.0252 mmol) were added to a solution of DMF (50 mL) and heated at 120 °C for 18 h. The crude product was purified by column chromatography using CH_2Cl_2 with 10% *n*-hexane as eluent to yield 24 mg (0.023 mmol, 38%) of a purple solid after recrystallization from CH_2Cl_2/*n*-hexane; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.13 (m, 4 H, Ar-*H*), 7.29 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*), 7.53 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.68 (d, ^3J = 8.7 Hz, 4 H, Ar-*H*), 7.78 (d, ^3J = 8.7 Hz, 4 H, Ar-*H*), 7.93 (t, ^3J = 8.7 Hz, 2 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.34 (t, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.72 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.47 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.67 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 117.32, 119.02, 121.83, 124.10, 125.49, 125.97, 127.76, 128.15, 128.47, 130.15, 131.98, 132.10, 132.34, 132.77, 136.74, 139.74, 141.10, 149.49, 150.30 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 441 (5.13), 567 (3.86), 601 nm (3.94). $C_{56}H_{34}Br_2N_4Zn$ (988.10): calcd. C 68.07, H 3.47, N 5.67; found C 67.84, H 3.72, N 5.51.

[5,15-Bis[(*E*)-2-methoxycarbonylethenyl]-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (41): Following general procedure F, **34** (50 mg, 0.063 mmol), methyl acrylate (0.4 mL, 4.46 mmol), NaOAc (29 mg, 0.352 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0063 mmol), and PPh_3 (6.6 mg, 0.0252 mmol) were added to a solution of DMF (50 mL) and heated at 120 °C for 18 h. The crude product was purified by column chromatography using CH_2Cl_2 with 10% *n*-hexane as eluent to give 15 mg (0.018 mmol, 30%) of a purple solid after recrystallization from CH_2Cl_2/*n*-hexane; m.p. >300 °C; R_f = 0.2 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 6 H, CH_3), 6.66 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*), 7.04 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.11 (d,

^3J = 7, 2 H, 8.8 Hz, Ar-*H*), 7.53 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 7.94 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.20 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.36 (m, 4 H, Ar-*H*), 8.74 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.42 (d, ^3J = 5.3 Hz, 4 H, H_β), 10.16 (d, ^3J = 15.8 Hz, 2 H, alkene-*H*) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 435 (4.93), 565 (3.76), 611 nm (3.70). $C_{48}H_{32}N_4O_4Zn$ (794.19): calcd. C 72.59, H 4.06, N 7.05; found C 72.66, H 3.89, N 7.21.

[5,15-Bis[(*E*)-2-ethoxycarbonylethenyl]-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (42): Following general procedure F, **34** (50 mg, 0.063 mmol), ethyl acrylate (0.5 mL, 4.46 mmol), NaOAc (29 mg, 0.352 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0063 mmol), and PPh_3 (6.6 mg, 0.0252 mmol) were added to a solution of DMF (50 mL) and heated at 120 °C for 18 h. The crude product was purified by column chromatography (ethyl acetate) to yield 20 mg (0.023 mmol, 40%) of purple solid after recrystallization from CH_2Cl_2/*n*-hexane; m.p. >300 °C; R_f = 0.2 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, ^3J = 6.4 Hz, 6 H, CH_2CH_3), 4.07 (m, 4 H, CH_2CH_3), 6.23 (d, ^3J = 15.2 Hz, 2 H, alkene-*H*), 7.09 (m, 4 H, Ar-*H*), 7.52 (d, ^3J = 6.4 Hz, 2 H, 7, Ar-*H*), 7.93 (t, ^3J = 7, 2 H, 8.2 Hz, Ar-*H*), 8.21 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.34 (m, 4 H, Ar-*H*), 8.69 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.27 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.83 (d, ^3J = 15.7 Hz, 2 H, alkene-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.80, 60.29, 113.81, 119.58, 123.79, 124.26, 125.24, 125.73, 126.17, 127.49, 128.07, 128.24, 129.67, 130.01, 132.31, 136.33, 139.17, 145.86, 148.63, 150.37, 150.87 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 435 (4.92), 566 (3.66), 613 nm (3.63). $C_{50}H_{36}N_4O_4Zn$ (822.24): calcd. C 73.04, H 4.41, N 6.81; found C 73.28, H 4.26, N 6.66.

[5,15-Bis[(*E*)-diethylprop-1-enyl phosphonate]-10,20-bis(1-naphthyl)-porphyrinato]zinc(II) (43): Following general procedure F, **34** (50 mg, 0.063 mmol), diethyl vinylphosphonate (0.6 mL, 4.46 mmol), NaOAc (29 mg, 0.352 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0063 mmol), and PPh_3 (6.6 mg, 0.0252 mmol) were added to a solution of DMF (50 mL) and heated at 120 °C for 18 h. The crude product was purified by column chromatography using ethyl acetate/*n*-hexane = 4:1 (v/v) as eluent to yield 23 mg (0.023 mmol, 58%) of a purple solid after recrystallization from CH_2Cl_2/*n*-hexane; m.p. >300 °C; R_f = 0.23 (ethyl acetate/*n*-hexane = 4:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 12 H, OCH_2CH_3), 3.28 (m, 8 H, OCH_2CH_3), 5.31 (br., 2 H, alkene-*H*), 7.14 (m, 2 H, Ar-*H*), 7.19 (m, 2 H, Ar-*H*), 7.51 (t, ^3J = 7, 2 H, 7.6 Hz, Ar-*H*), 7.95 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.21 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.36 (t, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.60 (d, ^3J = 4.7 Hz, 4 H, H_β), 8.79 (br., 6 H, overlapping alkene-*H*, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 15.84, 61.39, 124.02, 125.44, 125.78, 127.73, 128.26, 128.64, 129.30, 132.22, 132.75, 136.96, 140.31, 148.39, 150.74 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 433 (4.98), 568 (3.89), 614 nm (3.80).

[5,15-Bis(3-methoxyphenyl)-10,20-bis{(*E*)-2-(3-nitrophenyl)-vinyl}porphyrinato]zinc(II) (44): Following general procedure F, **35** (40 mg, 0.0538 mmol), 3-nitrostyrene (0.52 mL, 3.76 mmol), NaOAc, (24.7 mg, 0.3 mmol), $Pd(OAc)_2$ (1.2 mg, 0.00538 mmol), and PPh_3 (5.6 mg, 0.0215 mmol) in DMF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1, v/v) afforded purple crystals (20 mg, 0.022 mmol, 42%); m.p. > 300 °C; R_f = 0.33 (*n*-hexane/ethyl acetate = 6:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 6 H, OCH_3), 7.29 overlap (m, ^3J = 15.7 Hz, 2 H, Ar-*H*, d, 2 H, CH=C*H*), 7.58–7.73 (m, 8 H, Ar-*H*), 8.11 (d, ^3J = 8.3 Hz, 2 H, Ar-*H*), 8.71 (s, 2 H, Ar-*H*), 8.92 (d, ^3J = 4.4 Hz, 4 H, H_β), 9.41 (d, ^3J = 4.4 Hz, 4 H, H_β), 9.68 (d, ^3J = 15.7 Hz, 2 H, C*H*=CH) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 437 (5.00), 565 (3.75), 615 nm (3.84).

[5,15-Bis[(*E*)-2-methoxycarbonylethenyl]-10,20-bis(3-methoxy)-phenylporphyrinato]zinc(II) (45): Following general procedure F, **35** (40 mg, 0.0538 mmol), methyl acrylate (0.33 mL, 3.76 mmol), NaOAc (24.7 mg, 0.3 mmol), $Pd(OAc)_2$ (1.2 mg, 0.00538 mmol), and PPh_3 (5.6 mg, 0.0215 mmol) in DMF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1, v/v) gave a purple solid (20 mg, 0.026 mmol, 49%); m.p. > 300 °C; R_f = 0.33 (*n*-hexane/ethyl acetate = 6:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 6 H, OCH_3), 3.89 (s, 6 H, OCH_3), 6.39 (d, ^3J = 15.7 Hz, 2 H, CH=C*H*), 7.28 (m, 2 H, Ar-*H*), 7.61 (m, 2 H, Ar-*H*), 7.73 (m, 2 H, Ar-*H*), 8.92 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.08 (d, ^3J = 4.9 Hz, 4 H, H_β), 9.91 (d, ^3J = 15.7 Hz, 2 H, C*H*=CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 22.2, 28.9, 31.1, 50.2, 51.4, 55.0, 112.9, 113.7, 120.0, 121.7, 127.0, 129.4, 132.4, 143.2, 146.3, 148.5, 157.4, 166.1 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 433 (4.98), 564 (3.71), 613 nm (3.76).

[5,15-Bis[(*E*)-2-ethoxycarbonylethenyl]-10,20-bis(3-methoxy)-phenyl)porphyrinato]zinc(II) (46): Following general procedure F, **35** (40 mg, 0.0538 mmol), ethyl acrylate (0.4 mL, 3.76 mmol), NaOAc (24.7 mg, 0.3 mmol), $Pd(OAc)_2$ (1.2 mg, 0.00538 mmol), and PPh_3 (5.6 mg, 0.0215 mmol) in DMF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1, v/v) followed by recrystallization from CH_2Cl_2/*n*-hexane afforded the desired product (35 mg, 0.044 mmol, 83%) as purple crystals; m.p. > 300 °C; R_f = 0.35 (*n*-hexane/ethyl acetate = 6:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, ^3J = 7 Hz, 6 H, CH_2CH_3), 3.93 (s, 6 H, OCH_3), 4.07 (m, 4 H, CH_2CH_3), 6.22 (d, ^3J = 15.2 Hz, 2 H, CH=C*H*), 7.34 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.69 (m, 4 H, Ar-*H*), 7.82 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 9.00 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.34 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.80 (d, ^3J = 15.2 Hz, 2 H, C*H*=CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.0, 60.2, 112.9, 113.7, 120.1, 121.7, 127.0, 127.1, 129.4, 129.9, 132.3, 143.2, 145.9, 148.5, 149.6, 157.3, 165.6 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 433 (4.96), 564 (3.38), 611 nm (3.44).

[5,15-Bis[(*E*)-diethylprop-1-enyl phosphonate)-10,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) (47): Following general procedure F, **35** (40 mg, 0.0538 mmol), diethyl vinylposphonate (0.58 mL, 3.76 mmol), NaOAc (24.7 mg, 0.3 mmol), $Pd(OAc)_2$ (1.2 mg, 0.00538 mmol), and PPh_3 (5.6 mg, 0.0215 mmol) in DMF (50 mL) were used. Recrystallization from CH_2Cl_2/*n*-hexane afforded the desired product (37 mg, 0.040 mmol, 75%) as purple crystals; m.p. > 300 °C; R_f = 0.35 (*n*-hexane/ethyl acetate = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (br. s, 12 H, OCH_2CH_3), 3.21 (br. s, 8 H, OCH_2CH_3), 4.09 (s, 6 H, OCH_3), 5.21 (br. s, 2 H, CH=C*H*), 7.44 (m, 2 H Ar-*H*), 7.77 (t, ^3J = 7.8 Hz, 2 H, Ar-*H*), 7.91 (m, 4 H, Ar-*H*), 8.59 (br. s, 2 H, C*H*=CH), 8.87 (br. s, 4 H, H_β), 9.01 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 55.1, 61.1, 112.5, 113.8, 120.5, 113.8, 120.5, 123.4, 125.2, 126.9, 127.4, 131.9, 144.4, 148.0, 149.9, 150.0, 157.4 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 430 (5.01), 569 (3.64), 630 nm (4.65). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{46}H_{47}N_4O_8P_2Zn$] [M + H$^+$]: 909.2161; found 909.2202.

5,15-Bis(1-naphthyl)-5,15-bis(phenylethynyl)porphyrin (48): Following general procedure G, **10** (50 mg, 0.069 mmol), phenylacetylene (0.17 mL, 0.152 mmol), CuI (3.3 mg, 0.01725 mmol), and Pd)-$(PPh_3)_2Cl_2$ (4.8 mg, 0.0069 mmol) were added to a mixture of THF (5 mL) and triethylamine (15 mL). After 10 min, the cold bath was removed and the reaction mixture was stirred for 3 h at room temp. The crude product was purified by flash column chromatography eluting with CH_2Cl_2/*n*-hexane = 1:3 (v/v) to give 23 mg (0.030 mmol, 43%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.6 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –1.68 (s, 2 H, N*H*), 7.18 (m, 4 H, Ar-*H*), 7.50 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.56 (t, ^3J = 6.4,

6 H, 7.6 Hz, Ar-*H*), 7.94 (t, ^3J = 8.2, 2 H, 7 Hz, Ar-*H*), 8.00 (t, ^3J = 7 Hz, 4 H, Ar-*H*), 8.20 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.31 (t, ^3J = 7, 2 H, 8.8 Hz, Ar-*H*), 8.36 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.60 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.61 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 91.16, 96.85, 100.79 119.03, 123.29, 123.88, 125.38, 125.94, 127.46, 128.48, 132.18, 132.49, 136.18, 138.06 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 445 (5.16), 598 (4.25), 689 nm (3.83). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{56}H_{35}N_4$] [M + H$^+$]: 763.2862; found 763.2887.

[5,15-Bis(1-naphthyl)-10,20-bis(phenylethynyl)porphyrinato]zinc(II) (49): Following general procedure G, **34** (50 mg, 0.063 mmol), phenylacetylene (0.15 mL, 0.140 mmol), CuI (3 mg, 0.016 mmol), and $Pd(PPh_3)_2Cl_2$ (4.4 mg, 0.0063 mmol) were added to a mixture of THF (5 mL) and triethylamine (15 mL). The cold bath was removed after 10 min and the reaction mixture was stirred for 24 h at room temp. The crude product was purified by flash column chromatography eluting with CH_2Cl_2/*n*-hexane = 1:2 (v/v) to yield 32 mg (0.038 mmol, 60%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (m, 2 H, Ar-*H*), 7.13 (m, 4 H, Ar-*H*), 7.54 (t, ^3J = 6.9 Hz, 5 H, Ar-*H*), 7.94 (m, 5 H, Ar-*H*), 8.20 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.29 (t, ^3J = 6.9, 2 H, 8.8 Hz, Ar-*H*), 8.36 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.69 (m, 4 H, H_β), 9.62 (d, ^3J = 4.9 Hz, 2 H, Ar-*H*), 9.69 (d, ^3J = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 91.59, 96.13, 104.77, 119.66, 123.80, 125.28, 125.83, 127.48, 128.23, 131.02, 131.16, 132.18, 132.27, 132.69, 132.83, 133.01, 136.37, 138.81, 149.22, 149.86, 150.32, 151.08 ppm. 152.37. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 440 (4.70), 567 (3.52), 614 nm (3.54). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{56}H_{33}N_4Zn$] [M + H$^+$]: 827.2153; found 827.2155.

5,15-Bis(1-naphthyl)-10,20-bis(trimethylsilanylethynyl)porphyrin (50): Following general procedure G, **10** (50 mg, 0.069 mmol), ethynyltrimethylsilane (0.2 mL, 0.152 mmol), CuI (3.3 mg, 0.01725 mmol), and $Pd(PPh_3)_2Cl_2$ (4.8 mg, 0.0069 mmol) were added to a mixture of THF (5 mL) and triethylamine (15 mL). After 10 min the cold bath was removed and the reaction mixture was stirred for 3 h at room temp. The crude product was purified by flash column chromatography eluted with CH_2Cl_2/*n*-hexane = 1:2 (v/v) to give 30 mg (0.040 mmol, 58%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.7 (CH_2Cl_2/*n*-hexane = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –1.91 (s, 2 H, N*H*), 0.57 [s, 18 H, SiC(CH_3)$_3$], 7.13 (m, 4 H, Ar-*H*), 7.54 (m, 2 H, Ar-*H*), 7.92 (t, ^3J = 8.2, 2 H, 7 Hz, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.27 (d, ^3J = 6.4 Hz, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.58 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.52 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.58, 29.26, 100.43, 102.27, 106.07, 118.88, 123.85, 125.35, 125.91, 127.44, 128.46, 132.17, 132.48, 136.20, 138.01 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 436 (4.86), 542 (3.51), 582 (3.91), 616 (3.19), 678 nm (3.45). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{43}N_4Si_2$] [M + H$^+$]: 755.3026; found 755.3024.

[5,15-Bis(1-naphthyl)-10,20-bis(trimethylsilanylethynyl)porphyrin)-ato]zinc(II) (51): Following general procedure G, **34** (40 mg, 0.051 mmol), ethynyltrimethylsilane (0.15 mL, 0.112 mmol), CuI (2.5 mg, 0.01275 mmol), and $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.0051 mmol) were added to a mixture of THF (5 mL) and triethylamine (15 mL). After 10 min, the cold bath was removed and the reaction mixture was stirred for 3 h at room temp. The crude product was purified by flash column chromatography eluting with CH_2Cl_2/*n*-hexane = 1:2 (v/v) to yield 20 mg (0.024 mmol, 48%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.8 (CH_2Cl_2/*n*-hexane = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 [s, 18 H, SiC(CH_3)$_3$], 7.08 (m, 4 H, Ar-*H*), 7.53 (t, ^3J = 8.2, 2 H, 6.4 Hz, Ar-*H*), 7.93 (t, ^3J = 8.2, 2 H, 7 Hz, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.29 (t, ^3J = 6.4 Hz, 2 H, Ar-*H*), 8.34 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.67 (d, ^3J = 4. 7 Hz, 4 H, H_β), 9.62 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 448 (5.04), 577 (3.70), 636 nm (4.15). HRMS: *m*/*z* calcd. for [$C_{50}H_{40}N_4Si_2Zn$]: calcd. 816.2083; found 816.2068.

[5,15-Diethynyl-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (52): TBAF (0.1 mL of a 1 M solution in THF) was added to a solution of **51** (20 mg, 0.024 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 20 min, and the crude product was filtered through a short silica gel column and purified by recrystallization from CH_2Cl_2/CH_3OH to give 16 mg (0.023 mmol, 94%) of a purple solid; m.p. >300 °C; R_f = 0.4 (CH_2Cl_2/*n*-hexane = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.09 (s, 2 H, C≡C*H*), 7.13 (m, 4 H, Ar-*H*), 7.43 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.54 (t, ^3J = 7 Hz, 2 H, Ar-*H*), 7.83 (t, ^3J = 7 Hz, 2 H, Ar-*H*), 8.20 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.70 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.62 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 432 (4.99), 568 (3.65), 609 nm (3.66). $C_{44}H_{24}N_4Zn$ (674.08): calcd. C 78.40, H 3.59, N 8.32; found C 78.59, H 8.02, N 8.52.

5,15-Bis(3-methoxyphenyl)-10,20-bis(phenylethynyl)porphyrin (53): Following general procedure G, **11** (50 mg, 0.0734 mmol), phenylacetylene (0.176 mL, 0.161 mmol), CuI (3.5 mg, 0.0146 mmol), and $Pd(PPh_3)_2Cl_2$ (5.2 mg, 0.00734 mmol) were added to triethylamine (15 mL) and THF (5 mL). Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1, v/v) gave purple crystals (20 mg, 0.027 mmol, 38%); m.p. > 300 °C; R_f = 0.6 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –1.96 (s, 2 H, N*H*), 4.05 (s, 6 H, OCH_3), 7.40 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.53 (m, 4 H, Ar-*H*), 7.60 (m, 4 H, Ar-*H*), 7.71 (t, ^3J = 8.2, 2 H, Hz, Ar-*H*), 7.82 (m, 2 H, Ar-*H*), 8.05 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.92 (d, ^3J = 4.1 Hz, 4 H, H_β), 9.71 (d, ^3J = 4.9 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 52.9, 54.3, 55.8, 57.2, 91.4, 96.8, 100.7, 112.5, 114.1, 120.7, 121.1, 123.3, 126.2, 126.3, 127.4, 127.9, 128.0, 129.2, 130.4, 132.0, 142.1, 142.2, 157.6 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 442 (4.94), 554 (3.33), 598 (4.06), 627 (3.22), 689 nm (3.76). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{35}N_4O_2$] [M + H$^+$]: 723.2760; found 723.2783.

[5,15-Bis(3-methoxyphenyl)-10,20-bis(phenylethynyl)porphyrinato])zinc(II) (54): Following general procedure G, **35** (40 mg, 0.053 mmol), phenylacetylene (2.5 mg, 0.01325 mmol), CuI (3.7 mg, 0.0053 mmol), and $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.0053 mmol) were added to triethylamine (15 mL) and THF (5 mL). Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1, v/v) gave the desired compound (27 mg, 0.034 mmol, 65%) as purple crystals; m.p. > 300 °C; R_f = 0.55 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.03 (s, 6 H, OCH_3), 7.39 (m, 2 H, Ar-*H*), 7.53 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 7.60 (t, ^3J = 7.8 Hz, 4 H, Ar-*H*), 7.70 (t, ^3J = 7.8 Hz, 2 H, Ar-*H*), 7.79 (s, 4 H, Ar-*H*), 7.83 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.04 (d, ^3J = 6.9 Hz, 2 H, Ar-*H*), 9.01 (d, ^3J = 3.9 Hz, 4 H, H_β), 9.78 (d, ^3J = 4.9 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 225, 29.5, 55.3, 92.1, 96.6, 113.4, 120.1, 122.3, 127.3, 130.9, 131.5, 132.6, 149.8, 151.6, 157.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 446 (491), 583 (3.31), 635 nm (3.93).

5,15-Bis(3-methoxyphenyl)-10,20-bis(trimethylsilanylethynyl))-porphyrin (55): Following general procedure G, **11** (40 mg, 0.0587 mmol), ethynyltrimethylsilane (0.179 mL, 0.129 mmol), CuI (2.8 mg, 0.0146 mmol), and $Pd(PPh_3)_2Cl_2$ (4.1 mg, 0.00587 mmol) were added to triethylamine (15 mL) and THF (5 mL). Purification

was carried out by column chromatography on silica using (*n*-hexane/CH_2Cl_2 = 1:1, v/v) and afforded purple crystals (17.5 mg, 0.024 mmol, 42%); m.p. > 300 °C; R_f = 0.6 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.16 (s, 2 H, N*H*), 0.62 [s, 18 H, Si(CH_3)$_3$], 4.03 (s, 6 H, OCH_3), 7.38 (m, 2 H, Ar-*H*), 7.69 (m, 2 H, Ar-*H*), 7.76 (s, 2 H, Ar-*H*), 7.80 (d, ^3J = 7.2 Hz, 2 H, Ar-*H*), 8.89 (d, ^3J = 4.9 Hz, 4 H, H_β), 9.62 (d, ^3J = 4.9 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.1, 29.5, 55.3, 100.6, 102.5, 106.6, 113.6, 120.2, 127.5, 130.3, 131.6, 142.4, 157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 433 (4.99), 541 (3.97), 581 (4.02), 617 (3.06), 677 nm (3.59). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{44}H_{43}N_4O_2Si_2$] [M + H$^+$]: 715.2925; found 715.2924.

[5,15-Bis(3-methoxyphenyl)-10,20-bis(trimethylsilanylethynyl)-porphyrinato]zinc(II) (56): Following general procedure G, **35** (40 mg, 0.053 mmol), ethynyltrimethylsilane (0.163 mL, 0.1183 mmol), CuI (2.5 mg, 0.01325 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (3.7 mg, 0.0053 mmol) were added to triethylamine (15 mL) and THF (5 mL). Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1:1, v/v) gave 25 mg (0.032 mmol, 60%) of a purple solid; m.p. > 300 °C; R_f = 0.47 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.63 (s, 18 H, CH_3), 3.98 (s, 6 H, OCH_3), 7.34 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.67 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.73 (s, 2 H, Ar-*H*), 7.79 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.98 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.71 (d, ^3J = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.3, 29.5, 55.3, 101.8, 107.2, 113.4, 122.2, 127.4, 132.6, 149.9, 152.1, 157.7 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 446 (5.07), 583 (3.41), 653 nm (4.09).

10-Butyl-5,15-bis(1-naphthyl)porphyrin (57): Following general procedure H, **3** (300 mg, 0.533 mmol) was dissolved in dry THF (80 mL) under an argon atmosphere and the reaction mixture was cooled down to –78 °C. *n*BuLi (2.13 mL, 5.33 mmol) was added dropwise over 15 min by syringe. The cold bath was removed and stirring continued for 14 h at room temperature, followed by addition of H_2O (0.5 mL). Stirring continued for 15 min and then DDQ (1.2 g, 5.33 mmol) was added in THF (10 mL). The reaction mixture was stirred for an additional hour to give 180 mg (0.29 mmol, 55%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.42 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.70 (s, 2 H, N*H*), 1.13 (t, ^3J = 7.6, 3 H, 6.4 Hz, CH_2CH_2CH_2CH_3), 1.82 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 2.55 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 5.06 (m, 2 H, CH_2CH$_2$CH$_2$CH$_3$), 7.13–7.19 (m, 4 H, Ar-*H*), 7.54 (t, ^3J = 8.2. 8.8, 6.4 Hz, 2 H, Ar-*H*), 7.93 (m, 2 H, Ar-*H*), 8.20 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.32 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.36 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.72 (m, 4 H, H_β), 9.19 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.47 (d, ^3J = 4.7 Hz, 2 H, H_β), 10.07 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.19, 23.70, 35.53, 41.09, 104.04, 116.56, 121.26, 124.28, 125.69, 126.19, 127.87, 128.68, 131.11, 132.73, 136.87, 139.28 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 414 (5.11), 509 (3.90), 545 (3.42), 584 (3.48), 640 nm (3.18). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{44}H_{35}N_4$] [M + H$^+$]: 619.2862; found 619.2859.

5-Bromo-15-butyl-10,20-bis(1-naphthyl)porphyrin (58): Following general procedure B, **57** (150 mg, 0.242 mmol) and NBS (46 mg, 0.254 mmol) gave 155 mg (0.22 mmol, 92%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.4 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.39 (s, 2 H, N*H*), 1.11 (t, ^3J = 7.6, 3 H, 7 Hz, CH$_2$CH$_2$CH$_2$CH_3), 1.81 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 2.51 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 4.93 (t, ^3J = 7.6, 2 H, 7 Hz, CH_2CH$_2$CH$_2$CH$_3$), 7.13 (t, ^3J = 8.2 Hz, 4 H, Ar-*H*), 7.54 (m, 2 H, Ar-*H*), 7.92 (m, 2 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.29 (m, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.62 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.36 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.51 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.96, 23.45, 34.97, 40.64, 101.73, 117.61, 121.50, 124.05, 125.58, 126.14, 127.73, 128.44, 132.52, 132.74, 136.69, 139.08 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 424 (5.01), 519 (3.76), 555 (3.42), 598 (3.33), 651 nm (3.16). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{44}H_{34}N_4Br$] [M + H$^+$]: 697.1967; found 697.1951.

5-Butyl-10,20-bis(1-naphthyl)-15-(4-nitrophenyl)porphyrin (59): Following general procedure C, **58** (40 mg, 0.057 mmol), K_3PO_4 (303 mg, 1.425 mmol), (4-nitrophenyl)boronic pinacol ester (178 mg, 0.7125 mmol), and Pd(PPh$_3$)$_4$ (6.6 mg, 0.0057 mmol) in THF (40 mL) gave 25 mg (0.033 mmol, 60%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2: *n*-hexane = 1:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ = –2.39 (s, 2 H, N*H*), 1.13 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH$_2$CH$_2$CH_3), 1.83 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 2.55 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 5.00 (t, ^3J = 7.9 Hz, 2 H, CH_2CH$_2$CH$_2$CH$_3$), 7.12–7.16 (m, 2 H, Ar-*H*), 7.53 (m, 2 H, Ar-*H*), 7.92 (m, 2 H, Ar-*H*), 8.19 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.29 (d, ^3J = 6.8 Hz, 2 H, Ar-*H*), 8.32 (d, ^3J = 6.8 Hz, 2 H, Ar-*H*), 8.36 (m, 4 H, Ar-*H*), 8.59 (d, ^3J = 8.6 Hz, 2 H, Ar-*H*), 8.61 (s, 4 H, H_β), 8.69 (d, ^3J = 4 Hz, 2 H, H_β), 9.42 (d, ^3J = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.14, 23.65, 35.19, 40.96, 115.86, 117.65, 121.79, 124.21, 125.72, 126.27, 127.90, 128.61, 131.94, 132.67, 132.90, 135.04, 136.85, 139.36, 147.63, 148.95 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 423 (4.97), 518 (3.80), 552 (3.48), 594 (3.36), 647 nm (3.27). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{38}N_5O_2$] [M + H$^+$]: 740.3026; found 740.3006.

5-Butyl-15-(4-cyanophenyl)-10,20-bis(1-naphthyl)porphyrin (60): Following general procedure C, **58** (40 mg, 0.057 mmol), K_3PO_4 (303 mg, 1.425 mmol), (4-cyanophenyl)boronic acid (105 mg, 0.7125 mmol), and Pd(PPh$_3$)$_4$ (6.6 mg, 0.0057 mmol) in THF (40 mL) gave 23 mg (0.031 mmol, 56%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.32 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.42 (s, 2 H, N*H*), 1.16 (m, 3 H, CH$_2$CH$_2$CH$_2$CH_3), 1.81 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 2.54 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 4.98 (t, ^3J = 7.6, 2 H, 8.18 Hz, CH_2CH$_2$CH$_2$CH$_3$), 7.13 (m, 4 H, Ar-*H*), 7.53 (m, 2 H, Ar-*H*), 7.91 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.03 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.20 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.32 (m, 6 H, Ar-*H*), 8.61 (s, 4 H, H_β), 8.69 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.42 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.73, 23.22, 30.51, 34.74, 40.52, 111.25, 115.94, 117.11, 118.61, 121.21, 123.78, 125.28, 127.99, 128.15, 129.77, 130.08, 131.40, 132.23, 134.47, 136.36, 138.91, 146.47 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 424 (4.91), 516 (3.78), 552 (3.43), 590 (3.44), 648 nm (3.25). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{51}H_{38}N_5$] [M + H$^+$]: 720.3127; found 720.3121.

5-Butyl-15-(4-methoxycarbonylphenyl)-10,20-bis(1-naphthyl)-porphyrin (61): Following general procedure C, **58** (40 mg, 0.057 mmol), K_3PO_4 (303 mg, 1.425 mmol), (4-methoxycarbonylphenyl)boronic acid (128 mg, 0.7125 mmol), and Pd(PPh$_3$)$_4$ (6.6 mg, 0.0057 mmol) in THF (40 mL) gave 18 mg (0.023 mmol, 42%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.32 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.41 (s, 2 H, N*H*), 1.13 (t, ^3J = 7 Hz, 3 H, CH$_2$CH$_2$CH$_2$CH_3), 1.83 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 2.55 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 4.10 (s, 3 H, COOCH_3), 4.99 (t, ^3J = 7.6, 2 H, 8.2 Hz, CH_2CH$_2$CH$_2$CH$_3$), 7.14 (m, 4 H, Ar-*H*), 7.53 (t, ^3J = 7.6, 2 H, 6.4 Hz, Ar-*H*), 7.91 (m, 2 H, Ar-*H*), 8.19 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.30 (m, 4 H, Ar-*H*), 8.34 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.41 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.59 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.68 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.42 (d, ^3J = 4.7 Hz, 2 H,

H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.00, 23.50, 35.01, 40.77, 52.19, 117.17, 121.08, 124.05, 125.53, 126.09, 127.71, 128.54, 129.31, 132.51, 132.74, 134.34, 136.69, 139.39, 146.61 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (4.90), 518 (3.70), 552 (3.40), 593 (3.41), 646 nm (3.22). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{52}H_{41}N_4O_2$] [M + H$^+$]: 753.3230; found 753.3226.

[5-Bromo-15-butyl-10,20-bis(1-naphthyl)porphyrinato]zinc(II) (62): Following general procedure D, **58** (100 mg, 0.143 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and zinc acetate dihydrate (188 mg, 0.860 mmol) dissolved in CH_3OH was added to the reaction mixture to yield 98 mg (0.129 mmol, 90%) after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2: *n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.6 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.55 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.98 (t, ^3J = 7.6, 2 H, 8.2 Hz, $CH_2CH_2CH_2CH_3$), 7.07 (m, 4 H, Ar-*H*), 7.52 (m, 2 H, Ar-*H*), 7.92 (m, 2 H, Ar-*H*), 8.19 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.29 (m, 2 H, Ar-*H*), 8.34 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.67 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.45 (d, ^3J = 3.5 Hz, 2 H, H_β), 9.59 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.21, 23.78, 35.54, 41.24, 118.45, 122.42, 124.06, 125.60, 126.07, 127.85, 128.26, 128.74, 129.43, 131.63, 132.65, 132.99, 136.94, 140.17, 149.82, 150.54, 150.79 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 425 (4.81), 555 (3.53), 597 nm (2.92). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{44}H_{31}N_4BrZn$] (M$^+$): 758.1072; found 758.1057.

[5-Butyl-10,20-bis(1-naphthyl)-15-{2-(3-nitrophenyl)vinyl}porphyrinato]zinc(II) (63): Following general procedure F, **62** (50 mg, 0.065 mmol), 3-nitrostyrene (0.3 mL, 2.3 mmol), NaOAc (30 mg, 0.364 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0065 mmol), and PPh_3 (6.8 mg, 0.026 mmol) were added to DMF (50 mL) and heated at 120 °C for 16 h. The crude product was purified by column chromatography (CH_2Cl_2/*n*-hexane = 2:1, v/v) to give 25 mg (0.030 mmol, 46%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.23 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 7.6 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.87 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.57 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.99 (t, ^3J = 7.6, 2 H, 8.7 Hz, $CH_2CH_2CH_2CH_3$), 7.04–7.15 (m, 4 H, Ar-*H*), 7.37 (d, ^3J = 15.8 Hz, 1 H, alkene-*H*), 7.50–7.55 (m, 2 H, Ar-*H*), 7.68 (t, ^3J = 8.2 Hz, 1 H, Ar-*H*), 7.93 (t, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.14 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.25 (d, ^3J = 6.4 Hz, 1 H, Ar-*H*), 8.30 (d, ^3J = 6.4 Hz, 1 H, Ar-*H*), 8.34 (m, 3 H, Ar-*H*), 8.73 (m, 4 H, H_β), 9.42 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.49 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.74 (d, ^3J = 15.8 Hz, 1 H, alkene-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.03, 23.63, 35.33, 40.98, 115.24, 118.36, 121.02, 122.22, 124.06, 125.46, 127.73, 128.35, 128.55, 129.18, 129.70, 132.16, 132.75, 136.73, 139.15, 139.84, 148.84, 149.38, 150.25 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 430 (5.09), 560 (3.86), 604 nm (3.53). MS (ES$^+$): *m*/*z* (%) = 827 (100%), [$C_{52}H_{37}N_5O_2Zn$] (M$^+$).

[5-Butyl-10,20-bis(1-naphthyl)-15-(phenylethynyl)porphyrinato]zinc(II) (64): Following general procedure G, **62** (50 mg, 0.065 mmol), phenylacetylene (0.08 mL 0.072 mmol), CuI (3 mg, 0.016 mmol), and $Pd(PPh_3)_2Cl_2$ (4.6 mg, 0.0065 mmol) were added to a mixture of THF (5 mL) and triethylamine (15 mL). After 10 min, the cold bath was removed and the reaction mixture was stirred for 24 h at room temp. The crude product was purified by flash column chromatography eluting with CH_2Cl_2/*n*-hexane = 1:2 (v/v) to give 21 mg (0.026 mmol, 41%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.5 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 6.9, 3 H, 8.8 Hz, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.55 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.99 (t, ^3J = 7.8, 2 H, 8.8 Hz, $CH_2CH_2CH_2CH_3$), 7.11 (m, 4 H, Ar-*H*), 7.38 (m, 2 H, Ar-*H*), 7.55 (m, 5 H, Ar-*H*), 7.94 (m, 2 H, Ar-*H*), 7.99 (d, ^3J = 7.8 Hz, 2 H, Ar-*H*), 8.20 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.35 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.70 (d, ^3J = 3.9 Hz, 4 H, H_β), 9.45 (d, ^3J = 3.9 Hz, 2 H, H_β), 9.71 (d, ^3J = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.00, 23.60, 35.37, 40.93, 92.17, 95.80, 118.87, 124.05, 125.46, 125.96, 127.70, 128.27, 128.48, 129.17, 130.75, 131.98, 132.34, 132.61, 136.69, 139.66, 150.00, 150.47, 152.43 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 438 (4.98), 566 (3.74), 606 nm (3.69). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{52}H_{36}N_4Zn$]: 828.2231; found 828.2270.

5-(4-Methoxycarbonylphenyl)-10,20-bis(1-naphthyl)-20-(3-thiophenyl)porphyrin (65): Following general procedure C, **10** (50 mg, 0.07 mmol), (4-methoxycarbonylphenyl)boronic acid (63 mg, 0.35 mol), (thiophen-3-yl)boronic acid (45 mg, 0.35 mmol), $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), and K_3PO_4 (293 mg, 1.38 mmol) in THF (40 mL) gave 7 mg (0.009 mmol, 16%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.2 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.12 (s, 2 H, N*H*), 4.14 (s, 3 H, $COOCH_3$), 7.16–7.23 (m, 4 H, Ar-*H*), 7.56 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.71 (t, ^3J = 8.2, 2 H, 6.4 Hz, Ar-*H*), 7.86 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 7.90 (s, 1 H, Ar-*H*), 7.95 (t, ^3J = 7 Hz, 2 H, Ar-*H*), 8.14 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.62 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.75 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.06 (t, ^3J = 8.2 Hz, 4 H, Ar-*H*), 9.38 (d, ^3J = 5.3 Hz, 2 H, H_β), 9.50 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.04), 515 (3.81), 551 (3.47), 592 (3.44), 645 nm (3.30). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{52}H_{35}N_4O_2S$] [M + H$^+$]: 779.2481; found 779.2508.

5,15-Bis(1-naphthyl)-10-(4-nitrophenyl)-20-(3-thiophenyl)porphyrin (66): Following general procedure C, **10** (50 mg, 0.07 mmol), pinacol (4-nitrophenyl)boronate (120 mg, 0.483 mmol), (thiophen-3-yl)boronic acid (62 mg, 0.487 mmol), $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), and K_3PO_4 (368 mg, 1.735 mmol) in THF (40 mL) gave 10 mg (0.013 mmol, 19%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.2 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.39 (s, 2 H, N*H*), 7.13 (t, ^3J = 6.4 Hz, 4 H, Ar-*H*), 7.53 (m, 2 H, Ar-*H*), 7.72 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.92 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.01 (m, 1 H, Ar-*H*), 8.03 (m, 1 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.30 (d, ^3J = 7.6 Hz, 1 H, Ar-*H*), 8.34 (d, ^3J = 8.2 Hz, 3 H, Ar-*H*), 8.40 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.64 (m, 7 H, overlapped Ar-*H*, H_β), 8.93 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 115.45, 116.78, 118.26, 121.86, 123.67, 124.26, 125.76, 126.33, 127.93, 128.52, 128.88, 131.46, 132.74, 134.42, 135.05, 136.77, 139.05, 141.76, 147.68, 148.95 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.02), 517 (3.75), 553 (3.23), 592 (3.14), 646 nm (2.30). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{50}H_{32}N_5O_2S$] [M + H$^+$]: 766.2277; found 766.2278.

5-(2-Benzothiophenyl)-10,20-bis(1-naphthyl)-15-(4-nitrophenyl)-porphyrin (67): Following general procedure C, **10** (50 mg, 0.07 mmol), (4-nitrophenyl)boronic acid (120 mg, 0.483 mol), (thianaphthenyl)boronic acid (86 mg, 0.483 mmol), $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), and K_3PO_4 (368 mg, 1.735 mmol) in THF (40 mL) gave 8 mg (0.010 mmol, 15%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.3 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.42 (s, 2 H, N*H*), 7.14 (m, 4 H, Ar-*H*), 7.54 (m, 2 H, Ar-*H*), 7.61 (t, ^3J = 8.8, 2 H, 7.6 Hz, Ar-*H*), 7.91 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.09 (t, ^3J = 6.4 Hz, 2 H, Ar-*H*), 8.14 (s, 1 H, Ar-*H*), 8.19 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.29 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.34 (d, ^3J = 8.8 Hz,

2 H, Ar-*H*), 8.40 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.63 (m, 8 H, Ar-*H*, H_β), 9.08 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 425 (4.98), 516 (3.68), 555 (3.29), 590 (3.18), 648 nm (2.46). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{54}H_{34}N_5O_2S$] [M + H$^+$]: 816.2433; found 816.2467.

5,15-Bis(1-naphthyl)-10-(4-methoxycarbonylphenyl)-20-[(*E*)-2-phenylethenyl]porphyrin (68): Following general procedure C, **10** (60 mg, 0.083 mmol), (4-methoxycarbonylphenyl)boronic acid (75 mg, 0.415 mol), *trans*-β-styrylboronic acid (62 mg, 0.415 mmol), $Pd(PPh_3)_4$ (10 mg, 0.0083 mmol), and K_3PO_4 (352 mg, 1.66 mmol) in THF (40 mL) gave 8 mg (0.010 mmol, 14%) of a purple solid after recrystallization from CH_2Cl_2/CH_3OH; m.p. >300 °C; R_f = 0.2 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.24 (s, 2 H, N*H*), 4.09 (s, 3 H, COOCH_3), 7.12–7.16 (m, 4 H, Ar-*H*), 7.41 (d, ^3J = 15.8 Hz, 1 H, alkene-*H*), 7.53 (t, ^3J = 7, 2 H, 6.4 Hz, Ar-*H*), 7.58 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.93 (m, 4 H, Ar-*H*), 8.18 (d, ^3J = 8.7 Hz, 2 H, Ar-*H*), 8.28 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.33 (t, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.41 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.58 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.67 (d, ^3J = 4.7 Hz, 4 H, H_β), 9.44 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.62 (d, ^3J = 15.8 Hz, 1 H, alkene-*H*) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 424 (5.01), 516 (3.78), 553 (3.44), 591 (3.37), 647 nm (3.31). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{56}H_{39}N_4O_2$] [M + H$^+$]: 799.3073; found 799.3064.

5-Bromo-15-butyl-10,20-bis(3-methoxyphenyl)porphyrin (69): Following general procedure B, 5-butyl-10,20-bis(3-methoxyphenyl)porphyrin (60 mg, 0.094 mmol), NBS (20.2 mg, 0.11 mmol), pyridine (1.0 mL) and acetone (10 mL) in dry CH_2Cl_2 were used. Purification of the product was carried out by filtration through a silica gel column using CH_2Cl_2 followed by recrystallization from CH_2Cl_2/CH_3OH afforded the desired compound (50 mg, 0.76 mmol, 80%) as purple crystals; m.p. > 300 °C; R_f = 0.8 (*n*-hexane/CH_2Cl_2 = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.73 (s, 2 H, N*H*), 1.14 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.83 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.52 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.03 (s, 6 H, OCH_3), 4.98 (t, ^3J = 8 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.38 (m, 2 H, Ar-*H*), 7.68 (t, ^3J = 8 Hz, 2 H, Ar-*H*), 7.79 (m, 4 H, Ar-*H*), 8.93 (t, ^3J = 5.5 Hz, 4 H, H_β), 9.46 (d, ^3J = 4.5 Hz, 2 H, H_β), 9.62 (d, ^3J = 4.5 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.7, 23.1, 34.8, 40.4, 55.0, 113.1, 119.4, 119.9, 121.1, 127.0, 142.8, 157.4 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 421 (4.73), 518 (3.40), 554 (3.17), 596 (3.01), 657 nm (2.96). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{38}H_{34}N_4O_2Br$] [M + H$^+$]: 657.1865; found 657.1862.

[5-Bromo-15-butyl-10,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) (70): Following general procedure D, **69** (100 mg, 0.152 mmol) and zinc acetate dihydrate (167 mg, 0.912 mmol) in dry CH_2Cl_2 (20 mL) gave a purple solid after recrystallization from CH_2Cl_2/MeOH (85 mg, 0.117 mmol, 77%); m.p. > 300 °C; R_f = 0.16 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.5 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.86 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.53 (m, 2 H, $CH_2CH_2CH_2CH_3$), 3.99 (s, 6 H, OCH_3), 4.94 (t, ^3J = 8 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.34 (m, 2 H, Ar-*H*), 7.68 (t, ^3J = 7.8 Hz, 2 H, Ar-*H*), 7.79 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.99 (dd, ^3J = 2.5 Hz, 4 H, H_β), 9.51 (d, ^3J = 4.8 Hz, 2 H, H_β), 9.70 (d, ^3J = 4.8 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 23.7, 35.4, 41.1, 55.5, 113.4, 120.3, 120.7, 127.3, 127.5, 129.2, 132.5, 133.1, 143.8, 149.7, 150.0, 150.5, 157.7 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 422 (5.19), 553 (3.93), 593 nm (3.46). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{38}H_{31}N_4O_2BrZn$] (M$^+$): 718.0936; found 718.0922.

5-Butyl-15-(4-methoxycarbonylphenyl)-10,20-bis(3-methoxyphenyl)porphyrin (71): Following general procedure C, **69** (32.8 mg, 0.05 mmol), (4-methoxycarbonylphenyl)boronic acid (112 mg, 0.625 mmol), $Pd(PPh_3)_4$ (7.2 mg, 0.00625 mmol), and K_3PO_4 (265 mg, 1.25 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afforded the desired compound (15 mg, 0.021 mmol, 42%) as purple crystals; m.p. > 300 °C; R_f = 0.25 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.72 (s, 2 H, N*H*), 1.15 (t, ^3J = 7.6 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.56 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.02 (s, 6 H, OCH_3), 4.13 (s, 3 H, OCH_3), 5.06 (t, ^3J = 8.2 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.37 (m, 2 H, Ar-*H*), 7.6 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.81 (m, 4 H, Ar-*H*), 8.30 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.45 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.75 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.88 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.99 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.52 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 23.2, 29.2, 34.8, 40.5, 55.0, 113.0, 117.2, 119.9, 120.7, 127.0, 127.1, 127.5, 128.9, 134.1, 143.1, 157.4, 166.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 419 (4.92), 516 (3.57), 551 (3.30), 593 (3.22), 648 nm (3.18). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{46}H_{38}N_5O_2$] [M + H$^+$]: 713.3107; found 713.3128.

5-Butyl-15-(4-cyanophenyl)-10,20-bis(3-methoxyphenyl)porphyrin (72): Following general procedure C, **69** (32.8 mg, 0.05 mmol), (4-cyanophenyl)boronic acid (91.8 mg, 0.625 mmol), $Pd(PPh_3)_4$ (7.2 mg, 0.00625 mmol), and K_3PO_4 (265 mg, 1.25 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afforded the desired compound (7 mg, 0.025 mmol, 43%) as purple crystals; m.p. > 300 °C; R_f = 0.15 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.73 (s, 2 H, N*H*), 1.16 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.56 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.02 (s, 6 H, OCH_3), 5.06 (t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.38 (d, ^3J = 8.3 Hz, 2 H, Ar-*H*), 7.68 (t, ^3J = 7.6 Hz, 1 H, Ar-*H*), 7.81 (m, 4 H, Ar-*H*), 8.08 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.33 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.69 (d, ^3J = 4.1 Hz, 2 H, H_β), 8.90 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.99 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.53 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 18.4, 35.3, 41.0, 55.5, 11.7, 113.5, 116.3, 119.7, 120.4, 121.6, 127.4, 130.5, 134.9, 143.4, 145.2, 154.6, 157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 419 (4.98), 516 (3.63), 551 (3.34), 592 (3.28), 648 nm (3.21). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{45}H_{38}N_5O_2$] [M + H$^+$]: 680.3026; found 680.2999.

5-Butyl-10,20-bis(3-methoxyphenyl)-15-(4-nitrophenyl)porphyrin (73): Following general procedure C, **69** (32.8 mg, 0.05 mmol), pinacol (4-nitrophenyl)boronate (156 mg, 0.625 mmol), $Pd(PPh_3)_4$ (7.2 mg, 0.00625 mmol), and K_3PO_4 (265 mg, 1.25 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (25 mg, 0.035 mmol, 71%); m.p. > 300 °C; R_f = 0.42 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.71 (s, 2 H, N*H*), 1.16 (t, ^3J = 7.6 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.56 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.02 (s, 6 H, OCH_3), 5.06 (t, ^3J = 7.6, 2 H, Hz, $CH_2CH_2CH_2CH_3$), 7.38 (m, 2 H, Ar-*H*), 7.68 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.81 (m, 4 H, Ar-*H*), 8.39 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.65 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 8.70 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.91 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.0 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.53 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 23.6, 35.3, 41.0, 53.5, 113.5, 115.8, 119.8, 120.4, 121.9, 127.5, 127.9, 135.1, 143.4, 147.6, 149.1, 157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 420 (5.08), 516 (3.8), 552 (3.47), 592 (3.34), 648 nm (3.20). HRMS (MS ES$^+$) *m*/*z* calcd. for [$C_{44}H_{38}N_5O_4$] [M + H$^+$]: 700.2924; found 700.2908.

5-Butyl-10,20-bis(3-methoxyphenyl)-15-(phenylethynyl)porphyrin (74): Following general procedure G, **69** (40 mg, 0.060 mmol), ethynylbenzene (0.072 mL, 0.066 mmol), CuI (2.9 mg, 0.015 mmol), and $Pd(PPh_3)_2Cl_2$ (4.2 mg, 0.0060 mmol) were added to triethylamine (15 mL) and THF (5 mL). Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1, v/v) afforded the desired compound (16 mg, 0.0235 mmol, 39%) as purple crystals; m.p. > 300 °C; R_f = 0.37 (*n*-hexane/CH_2Cl_2 = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.24 (s, 2 H, N*H*), 1.15 (t, ^3J = 7.3, 3 H, Hz, $CH_2CH_2CH_2CH_3$), 1.83 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.53 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.04 (s, 6 H, OCH_3), 4.98 (t, ^3J = 8 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.39 (m, 2 H, Ar-*H*), 7.53 (m 1 H, Ar-*H*), 7.60 (t, ^3J = 7.5 Hz, 2 H, Ar-*H*), 7.70 (t, ^3J = 7.5 Hz, 2 H, Ar-*H*), 7.83 (m, 4 H, Ar-*H*), 8.07 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.91 (d, ^3J = 4.8 Hz, 2 H, H_β), 8.94 (d, ^3J = 4.8 Hz, 2 H, H_β), 9.44 (d, ^3J = 5 Hz, 2 H, H_β), 9.71 (d, ^3J = 4.8 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 23.6, 29.7, 35.3, 40.8, 55.5, 91.9, 96.4, 98.6, 120.3, 127.5, 128.5, 131.6, 143.3,157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 433 (4.78), 532 (3.36), 575 (3.67), 610 (3.05), 668 nm (3.25). HRMS (MS ES$^+$) *m*/*z* calcd. for $[C_{46}H_{39}N_4O_2]$ [M + H$^+$]: 679.3073; found 670.3082.

[5-Butyl-10,20-bis(3-methoxyphenyl)-15-(phenylethynyl)porphyrinato]zinc(II) (75): Following general procedure G, **70** (40 mg, 0.055 mmol), phenylacetylene (0.066 mL, 0.0605 mmol), CuI (2.6 mg, 0.01375 mmol), and $Pd(PPh_3)_2Cl_2$ (3.8 mg, 0.0055 mmol) were added to triethylamine (15 mL) and THF (5 mL). Purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1, v/v) afforded the title compound as purple crystals (25 mg, 0.033 mmol, 61%); m.p. > 300 °C; R_f = 0.2 (*n*-hexane/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.86 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.54 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.01 (s, 6 H, OCH_3), 4.99 (t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.36 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.50 (m, 1 H, Ar-*H*), 7.58 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 7.68 (t, ^3J = 8.2 Hz, 2 H, Ar-*H*), 7.77 (s, 2 H, Ar-*H*), 7.82 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.03 (d, ^3J = 7 Hz, 2 H, Ar-*H*), 8.99 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.01 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.52 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.78 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.7, 29.2, 35.0, 55.0, 92.0, 95.4, 98.9, 113.0, 119.8, 120.7, 126.9, 127.8, 128.2, 130.2, 131.1, 132.3, 143.4, 148.8, 149.3, 149.5, 152.0, 157.4 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 436 (4.70), 566 (3.24), 608 nm (3.33).

5-Hexyl-10,20-bis(4-methoxycarbonylphenyl)-15-(3,4,5-trimethoxyphenyl)porphyrin (77): Following general procedure C, **76** (50 mg, 0.0696 mmol), (4-methoxycarbonylphenyl)boronic acid (157 mg, 0.87 mmol), $Pd(PPh_3)_4$ (10.1 mg, 0.0087, mmol), and K_3PO_4 (221 mg, 1.739 mmol) in THF (50 mL) were used. Purification of the product was carried out by column chromatography on silica gel using *n*-hexane/ethyl acetate (10:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH to give the desired compound (40 mg, 0.048 mmol, 69%) as purple crystals; m.p. > 300 °C; R_f = 0.14 (*n*-hexane/ethyl acetate = 6:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.72 (s, 2 H, N*H*), 0.95 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.42 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$) 1.52 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.65 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.98 (s, 6 H, OCH_3), 4.15 (s, 3 H, OCH_3), 4.19 (s, 6 H, OCH_3), 5.05 (t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 8.32 (d, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.48 (d, ^3J = 8.2 Hz, 4 H, Ar-*H*), 8.77 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.89 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.94 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.54 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 19.0, 24.8, 29.5, 31.7, 35.4, 52.2, 56.2, 60.1, 65.0, 112.7, 118.2, 127.0, 130.0, 147.0, 151.3, 167.1 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (4.91), 516 (4.09), 553 (3.92), 592 (3.61), 647 nm (3.39). HRMS (MS ES$^+$) *m*/*z* calcd. for $[C_{51}H_{49}N_4O_7]$ [M + H$^+$]: 829.3601; found 829.3629.

5,15-Bis(4-cyanophenyl)-10-hexyl-20-(3,4,5-trimethoxyphenyl)-porphyrin (78): Following general procedure C, **76** (30 mg of 0.0417 mmol), (4-cyanophenyl)boronic acid, (75.6 mg, 0.521 mmol), $Pd(PPh_3)_4$ (6 mg, 0.00521 mmol), and K_3PO_4 (221 mg, 1.739 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 5:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (16 mg, 0.02 mmol, 50%); m.p. > 300 °C; R_f = 0.15 (*n*-hexane/ethyl acetate = 6:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.75 (s, 2 H, N*H*), 0.96 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.42 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.52 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.58 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.99 (s, 6 H, OCH_3), 4.20 (s, 3 H, OCH_3), 5.06 (t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 8.11 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.36 (d, ^3J = 7.6 Hz, 4 H, Ar-*H*), 8.72 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.84 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.97 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.57 (d, ^3J = 4.1 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 30.2, 31.9, 35.6, 39.0, 56.3, 61.3, 111.9, 112.8, 117.3, 119.0, 119.9, 121.9, 130.5, 134.9, 137.0, 137.9, 147.2, 151.5 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (4.89), 516 (3.78), 551 (3.62), 592 (3.52), 647 nm (3.17). HRMS (MS ES$^+$) *m*/*z* calcd. for $[C_{49}H_{43}N_6O_3]$ [M + H$^+$]: 763.3397; 763.3386.

5-Hexyl-10,20-bis(3-nitrophenyl)-15-(3,4,5-trimethoxyphenyl)-porphyrin (79): Following general procedure C, **76** (30 mg, 0.0417 mmol), (3-nitrophenyl)boronic acid (87 mg, 0.521 mmol), $Pd(PPh_3)_4$ (6 mg, 0.00521 mmol), and K_3PO_4 (221 mg, 1.739 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH afforded the desired compound (32 mg, 0.039 mmol, 96%) as purple crystals; m.p. > 300 °C; R_f = 0.14 (*n*-hexane/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.73 (s, 2 H, N*H*), 0.95 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.42 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.53 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.85 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.57 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.99 (s, 6 H, OCH_3), 4.19 (s, 3 H, OCH_3), 5.05 (t, ^3J = 7 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.46 (s, 2 H, Ar-*H*), 8.00 (t, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.57 (d, ^3J = 7.6 Hz, 2 H, Ar-*H*), 8.72 (m, 4 H, Ar-*H*), 8.84 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.98 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.10 (s, 2 H, H_β), 9.61 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 22.5, 30.0, 31.7, 35.4, 38.8, 56.2, 61.1, 116.4, 199.8, 121.8, 127.5, 128.1, 136.8, 137.8, 139.4, 143.8, 146.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (4.97), 517 (3.76), 552 (3.43), 591 (3.33), 650 nm (3.32). HRMS (MS ES$^+$) *m*/*z* calcd. for $[C_{47}H_{43}N_6O_7]$ [M + H$^+$]: 803.3193; found 803.3204.

5-Hexyl-10,20-bis(4-hydroxyphenyl)-15-(3,4,5-trimethoxyphenyl)-porphyrin (80): Following general procedure C, **76** (50 mg, 0.0695 mmol), (4-hydroxyphenyl)boronic acid (96 mg, 0.695 mmol), $Pd(PPh_3)_4$ (8 mg, 0.00695 mmol), and K_3PO_4 (295 mg, 1.39 mmol) in THF (50 mL) were used. Purification by column chromatography on silica gel (CH_2Cl_2/CH_3OH = 100:1, v/v) followed by recrystallization from CH_2Cl_2/CH_3OH gave purple crystals (35 mg, 0.046 mmol, 67%); m.p. > 300 °C; R_f = 0.5 (CH_2Cl_2/CH_3OH = 100:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.71 (s, 2 H, N*H*), 0.66 (t, ^3J = 7 Hz, 3 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.41 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.53 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.84 (m, 2 H, $CH_2CH_2CH_2$-

$CH_2CH_2CH_3$), 2.58 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.98 (s, 6 H, OCH_3), 4.19 (s, 3 H, OCH_3), 5.04 (t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.19 (s, 2 H O*H*), 7.24 (d, ^3J = 8.8 Hz, 2 H, Ar-*H*), 7.46 (s, 2 H, Ar-*H*), 8.09 (d, ^3J = 8.2 Hz, 2 H, Ar-*H*), 8.85 (d, ^3J = 5.3 Hz, 2 H, H_β), 8.91 (d, ^3J = 4.7 Hz, 2 H, H_β), 8.96 (d, ^3J = 4.7 Hz, 2 H, H_β), 9.51 (d, ^3J = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.7, 29.7, 31.9, 35.6, 38.9, 56.3, 61.2, 112.6, 113.4, 118.7, 119.0, 120.6, 134.8, 135.4, 137.5, 151.2, 155.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 420 (4.87), 519 (4.04), 542 (3.87), 593 (3.57), 651 nm (3.53). HRMS (MS ES$^+$) *m/z* calcd. for [$C_{47}H_{45}N_4O_5$] [M + H$^+$]: 745.3390; found 745.3363.

Optical Measurements: Measurements of the optical limiting properties were carried out using the open Z-scan technique. A 6 ns Q-switched Nd:YAG laser operating at the second harmonic of 532 nm with a pulse repetition rate of 10 Hz was used. The beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The samples were prepared by dissolving the porphyrin in DMF at 0.01 g L^{-1} followed by gentle agitation for about 30 min in a low power sonic bath. All measurements were performed in a quartz cell with 10 mm path length to enhance the optical limiting response.

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