SYNTHESIS OF LONG-WAVELENGTH ABSORBING PORPHYRIN
m-BENZOIC ACIDS AS MOLECULAR TECTONS FOR SURFACE
STUDIES

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Abstract – Porphyrins are becoming increasingly important building blocks in material science. This is due in part to several favorable characteristics; such as strong absorption into the infrared region, tunable electronic properties and the possibility to modify and define the porphyrin core in multiple ways. Herein we report synthetic methodologies for porphyrin-based molecular tectons for surface studies. The study aims to generate porphyrins with directional anchoring groups of different length and we report a library of long-wavelength absorbing porphyrins with a special focus on organometallic coupling reactions for the introduction of benzoic acid moieties as anchor groups.

INTRODUCTION

Functionalized nanomaterials with defined shapes and sizes are gaining more and more popularity for applications such as electronics, light-energy conversion and photonics. Porphyrins represent very promising materials for such applications due to their strong absorption bands in the visible region, tunable electronic properties and scope of possible modifications. Materials exhibiting strong absorption in the infrared region are especially of interest. Even though there are many porphyrin-based nanomaterials current studies target composite 2D and 3D materials. One example is the use of suitably functionalized porphyrins as molecular tectons in SMOFs, MOFs, DSSCs and for binding to surfaces. Such applications require porphyrin building blocks where: (1) tailored functionalization of the porphyrin core can be used to optimize key performance for different applications and (2) suitable functional groups can direct their spatial arrangement in a given environment or facilitate the assembly to nano-networks of these compounds. Molecular porphyrin tectons can be described as building blocks on a molecular level. These building blocks interact with reciprocal counterparts in a specific manner to form...
molecule-substrate or -surface interactions. Interactions are based on different means such as ionic self-assembly, re-precipitation or coordination polymerization. Notably, the use of weak binding forces offers a facile approach, e.g., to 3D supramolecular networks stabilized by hydrogen bonding or electrostatic forces. Very dense packing can be achieved by porphyrins with unreactive meso-substituents (e.g., phenyl-groups) or porphyrin itself due to Van der Waals interactions. Introducing functional groups to the porphyrin such as pyridyl, alkoxy or carboxyphenyl helps to fine-tune the strength, selectivity and direction of these intermolecular interactions. Thus, porphyrins provide valuable tools to form molecular constructs such as porous networks, aggregates or closed-packed arrays.\(^2\)

H-Bonds are a suitable ‘construction principle’ which can be tuned by varying the number of H-bonds in the material and the strategic placement of hydrogen bonding groups on a porphyrin can be used to design specific nanoarchitectures based on the orientation of the H-bonds.\(^3\) A classic example for porphyrins is the formation of right angular structures when H-bonding groups are attached at the meso-5,10-positions opposed to a linear arrangement derived from H-bonding groups in the meso-5,15-positions.\(^3\)\(^^4\) Similarly, ortho- and para-carboxyphenyl groups have been shown to impact the nanomaterial structure, for example via different orientations in the interspace of layered double hydroxide.\(^5\) Notably, carboxyphenylporphyrins were key components of some of the earliest mesoporous porphyrin-based MOFs\(^6\) and have been widely used in surface chemistry as chemosensors, coordination polymers and catalysts.\(^7\) Other applications of carboxylic acid porphyrins include use in photodynamic therapy\(^8\) or DSSCs,\(^1\)\(^a\)\(^9\) and they present a suitable means to create molecular tectons.

![Figure 1. Illustration of porphyrin carboxylic acids as directional molecular tectons](image)

In the context of exploratory studies on the use of surface-bound porphyrins as biosensors we were interested in providing porphyrins with unique optical properties capable of binding to surface materials in a directional manner. One possible avenue would be the attachment of porphyrins via π-π-interactions to a graphene surface and then using COOH groups for the attachment of bioconjugates. This requires the COOH anchors to point towards one side of the system away from the porphyrin plane, similar to the orientation utilized by Collman in his picket-fence porphyrins as models for oxygen binding heme proteins.\(^1\)\(^0\) A simple means to achieved different directionalities and spacings is provided by using
meso-benzoic acid residues as directional anchor groups (Figure 1). Various syntheses have been reported to generate porphyrins with different aryl-carboxylic acid groups in the past and range from Sonogashira\textsuperscript{1a,9b,11} and Suzuki\textsuperscript{12} couplings to nucleophilic substitution reactions.\textsuperscript{13a} Herein we give a brief account of synthetic studies aimed to synthesize porphyrins with directional anchoring groups of different length. We were especially interested in testing organometallic coupling reactions for the introduction of Ar-COOH and the generation of long-wavelength absorbing meso-β-β-triply–linked surface binding molecular tectons.

RESULTS AND DISCUSSION
SYNTHESIS OF AN A\textsubscript{4}-TYPE TETRACARBOXYLIC ACID PORPHYRIN

Our first target compound was the tetrasubstituted \textit{m}-benzoic acid porphyrin which was deemed to be a good starting point for our synthetic studies due to its ease of synthesis. Furthermore, it provides a very useful reference for comparison with other more complex carboxylic acid porphyrins. Therefore, our investigations began with the synthesis of tetrasubstituted porphyrin 1 using standard condensation procedures.\textsuperscript{13b} Further modification included the insertion of nickel into the porphyrin core \textit{via} reaction with Ni(acac)\textsubscript{2} to give 2 with a yield of 94%. Next, the acid was generated by deprotection of the carboxylic ester under standard base hydrolysis conditions. The reaction required a large excess of base and long reaction times until the starting material was completely consumed. After acidification and extraction the free carboxylic acid 3 was obtained in a yield of 81% after recrystallization (Scheme 1).

Scheme 1. Synthesis of simple, A\textsubscript{4}-type \textit{m}-benzoic acid porphyrins. a) (i) 3-carbomethoxybenzaldehyde, pyrrole, CH\textsubscript{2}Cl\textsubscript{2}, BF\textsubscript{3}·OEt\textsubscript{2}, rt, 16 h, (ii) DDQ, rt, 1 h; b) Ni(II)(acac)\textsubscript{2} (2.5 equiv.), toluene, 120 °C, 18 h; c) KOH (400 equiv.) in H\textsubscript{2}O, THF/MeOH (1:1), 66 °C, 72 h.
Scheme 2. Synthesis of a triply-fused bisporphyrin with two $m$-benzoic acid residues. a) Pd(PPh$_3$)$_4$ (20 mol%), K$_3$PO$_4$ (10 equiv.), THF, 66 °C, 18 h; b) (i) Zn(OAc)$_2$ (5 equiv.), MeOH, CHCl$_3$, 70 °C, 1 h; or (ii) Ni(acac)$_2$ (2.5 equiv.), toluene, 120 °C, 3 h; c) DDQ (5 equiv.), Sc(OTf)$_3$ (5 equiv.), toluene, 50 °C, 18 h; d) KOH (excess) in H$_2$O, THF/MeOH (1:1), 70 °C, 3 h; e) NBS (1 equiv.), CHCl$_3$, pyridine, rt, 2 h; f) CuI (20 mol%), PdCl$_2$(PPh$_3$)$_2$ (10 mol%), THF/TEA (3:1, v/v), 66 °C, 18 h; g) TBAF, THF; h) AsPh$_3$ (1.1 equiv.), Pd$_2$(dba)$_3$ (15 mol%), THF/TEA (3:1, v/v), 66 °C 18 h.

Synthesis of $\pi$-extended biscardoxycilic acid porphyrins

While A$_4$-type systems are easily accessible, they are not that interesting, nor unique. In light of current reports on the use of $\pi$-conjugated and triply-fused systems and related materials for the solubilization of and aggregation with carbon nanotubes$^{14}$ we aimed to access related species capable of further bioconjugation and for the use as molecular tectons as illustrated in Figure 1. Triply-fused dimers offer a range of very interesting and promising properties, notably as optical nonlinear materials due to comprehensive $\pi$-electron delocalization throughout the molecules.$^{15}$ Furthermore, they exhibit large
absorptivities for visible light and a significant red-shift of the absorption spectra into the IR region.\textsuperscript{16} Their prominent electron transport properties make them possible candidates for organic semiconductors or photovoltaic materials.\textsuperscript{17} For these reasons, we decided to synthesize two related bis-carboxylic acid porphyrin dimers, the directly fused compound 7b and, for comparison, the ethyne-bridged dimer 6f (Scheme 2).

For the synthesis of the triply-fused dimer starting material 4a was subjected to Suzuki conditions with a boronate ester either containing an ethyl group at the ester to yield porphyrin 5a in 74% or with a methyl group to yield 5c in 90%. Metal coordination of 5a with zinc resulted in compound 6a in 85%. The metal insertion was performed prior to the next step as the central metal ion plays an important part in oxidative fusing and zinc(II) is typically the metal ion of choice in such reactions.\textsuperscript{16b} Subsequent oxidative fusing using DDQ/Sc(OTf)\textsubscript{3} generated the bisporphyrin product 7a from 6a in a yield of 71%. To obtain target compound 7b porphyrin 7a was deprotected via hydrolysis using NaOH. Compounds such as 5c/d can also be used as starting materials for Pd-catalyzed cross-coupling reactions to yield bisporphyrin carboxylic acids with different linker units. This is exemplified by sequence 5d to 6f (Scheme 2) which gives the target 6f in an overall yield of 29%. Such compounds are of interest in photonics as two-photon absorbers and subsequent studies on this will be reported elsewhere. To obtain the porphyrin monomer with two carboxylic ester groups the dibromoporphyrin 4b was subjected to Suzuki cross-coupling conditions. This reaction gave compound 5b in 78% yield.

For compound 6a single crystals suitable for X-ray crystallographic analysis were obtained. The structure shows a classic A\textsubscript{2}B Zn(II)-porphyrin structure bearing aryl substituents, in which the porphyrin ring is almost planar and the aryl substituent are held in a nearly orthogonal position (Figure 2). The angles between the aryl ring and 24-atom mean plane of the porphyrin macrocycle are 78.8(4)° (C10), 81.3(4)° (C20) and 118.6(3)° (C15), respectively. Compared to literature examples of tetracoordinated Zn(II) A\textsubscript{2}B-porphyrins [angles of 56.1–85.2° for the C10 and C20 positions (A\textsubscript{2}), and 101.3–121.0° for the C5

![Figure 2. View of the molecular structure of 6a in the crystal. Hydrogen atoms have been removed for clarity; thermal ellipsoids give 50% probability. Selected bond angles [°] and lengths [Å]: Zn-N21 2.034(9), Zn-N22 2.015(8), Zn-N23 2.037(1), Zn-N24 2.0276(9), C4-C5 1.405(8), C5-C6 1.390(7), C9-C11 1.395(5), C10-C11 1.399(5), C14-C15 1.384(7), C15-C16 1.388(7), C19-C20 1.382(5), C20-C1 1.400(5), C4-C5-C6 125.5(3), C9-C10-C11 125.0(3), C14-C15-C16 127.1(3), C19-C20-C1 126.2(3).]
position], these values fall within the expected range for such tetracoordinated complexes. This is also reflected in the structure of the A₃-porphyrin [5,10,15-tris(4-methoxyphenyl)porphyrinato]zinc(II), which shows similar angles of 83.5° for the 5,15-A groups and an angle of 117.0° for the A group opposite the free meso-position. Considering the angles around the meso-positions, C4-C5-C6 [125.5(3)°], C9-C10-C11 [125.0(3)°], C14-C15-C16 [127.1(3)°], and C19-C20-C1 [126.2(3)°], there is an obvious effect of the substitution of the pattern, namely, a flattening of the angle around the free meso-position and contraction of the substitution around the B-group. This is within the range expected for related literary compounds of 126.2–127.7°. In the packing arrangement of compound 6a, a head-to-head interaction is noted with the free meso-positions lining up to face one another. However, there are no notable close contacts between the molecules.

**Extending the ‘arm length’ of peripheral residues**

Moving forward in our approach we decided to extend the length of the peripheral anchor groups. Biosensors utilizing 11-mercaptoundecanonic acid as binding sites for various receptors have been previously reported in the literature. These long chains provide suitable anchor groups for specific bioconjugation and have shown to give good results for different biosensors. Therefore we decided to attempt building porphyrins with longer side arms to mimic the properties of 11-mercaptoundecanonic acid based sensors (Scheme 3). Besides that, supramolecular porphyrin tectons with longer acid chains could be useful for porphyrin hybrid nanoarchitectures and could result in a larger interspace between a layered double hydroxide. This would provide an additional means to sculpt and design nanomaterials. In practical terms we decided to apply an approach for the functionalization of 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin, recently developed by us. Initially, we decided to use a monosubstituted derivative for test reactions to explore the feasibility of this approach for longer chains. Suzuki coupling methodologies were applied

![Scheme 3](image)

**Scheme 3.** Synthesis of monofunctionalized porphyrins via arm attachment. a) 3-Hydroxyphenylboronic acid Pd(PPh₃)₄ (20 mol%), K₃PO₄ (10 equiv.), THF, 66 °C, 18 h; b) (i) K₂CO₃, DMF, 0.5 h, (ii) 1,6-dibromohexane (10) or 1,6-diiodohexane (11), rt, 18 h; c) potassium thioacetate (excess), DMF, rt, 18 h; d) Zn(OAc)₂ (5 equiv.), MeOH, CHCl₃, 70 °C, 1 h.
using 3-hydroxyphenylboronic acid with a bromoporphyrin 8 followed by two consecutive S_N2 reactions (Scheme 3). Installation of the phenol group using standard Suzuki coupling conditions proceeded in excellent yields of up to 84% giving porphyrin 9. The subsequent S_N2 reaction of this phenol porphyrin 9 with both diiodo- and dibromohexane proceeded in excellent yields of 73% (11) and 69% (10) respectively. Another S_N2 reaction using excess potassium thioacetate yielded the desired thioacetate in 86% yield (12). Subsequent metallation with Zn(II) was also carried out in good yield of 74% to give the final target compound 13.

Utilizing the same methodology arm extension was achieved for the tetrasubstituted porphyrin 14 (Scheme 4). Compound 15 was synthesized using K_2CO_3 and methyl-5-bromovalerate in DMF and the desired porphyrin was isolated in 77%. Subsequent metallation utilizing Zn(OAc)_2 gave porphyrin 16 in 89% yield. A slight variation in the reaction sequence of the same methodology was used to obtain target compounds 24 and 25. Here compound 14 was first metallated with Ni(acac)_2 yielding porphyrin 17 in 80%. For the S_N2 reaction, the bromocarboxylic acids 18 and 19 were used with standard esterification methodology and the protected compounds 20 and 21 were isolated in 76 and 82% yields, respectively. These porphyrins were then used for the subsequent S_N2 reaction to synthesize 22 in 56% and 23 in 62% yield. Base hydrolysis of the ester groups yielded the desired targets 24 and 25 in good yields of 65 and 71%, respectively. This methodology proved to be a straightforward approach to introduce longer chains to the meta-aryl-position of the porphyrin. Furthermore, this strategy is compatible with either mono- or tetrasubstitution.

Scheme 4. Synthesis of A4-type porphyrins with extended carboxylic acid residues. a) K_2CO_3 (12 equiv.), methyl 5-bromovalerate (12 equiv.), rt, DMF, 24 h; b) Zn(OAc)_2 (5 equiv.), MeOH, CHCl_3, 70 °C, 1 h; c) Ni(acac)_2 (2.5 equiv.), toluene/DMF (10:1, v/v), 120 °C, 24 h; d) acetyl chloride, MeOH, 70 °C, 24 h; e) K_2CO_3 (12 equiv.), bromoester 20 or 21 (12 equiv.), rt, DMF, 24 h; f) KOH (excess) in H_2O, THF/MeOH (1:1, v/v), 66 °C, 24 h.
For compound 13 single crystals suitable for X-ray crystallographic analysis were obtained. The structure contained one molecular unit associated with two solvent chloroform molecules (Figure 3). As with compound 6a, porphyrin 13 exhibited an almost planar macrocycle ring with meso-aryl substituents orientated orthogonal to the 24-atom mean plane of the porphyrin system. The angles between the aryl ring and the 24-atom mean plane were 103.7° [C5, 73.2(3)°, C10, 82.9(3)°, C15, and 85.6(3)° C20] with the largest angle associated with the B group of the A3B system. Other reported Zn(II) A3B systems,18d show a large range of aryl ring rotation from the 24-atom mean plane at 77.7–83.4° for A groups and 62.6–105.0° for B groups, suggesting that the rotations are quite liberal in such compounds.22 The overall molecular packing features an interesting axial ligand coordination of atom O2 to the Zn(II) metal center of the nearest neighbor forming a penta-coordinated structure (not shown). Features like this have been previously reported by Gomes et al. in which the axial ligand is being provided by the meso-substituted B-group.22a Additionally, one hydrogen bond [C64-H64B···N24] with a donor-acceptor distance of 3.361(9) Å was noted, due of this axial ligand. This feature gives a packing pattern in the unit cell of head-to-tail orientation and solvent chloroform molecules sandwiched between the planes of porphyrin rings. The structure contains several hydrogen bonds between solvent chloroform molecules and the porphyrin structure.

Synthesis of triply-fused biscarboxylic acid porphyrins with extended ‘arms’

Methodologies similar to those outlined in the preceding section were employed for the synthesis of the ‘fused-dimer’ derivative 31 (Scheme 5). The phenol substituted porphyrin 26 was subjected to nucleophilic substitution with a bromo ester to form 27 in good yield. Subsequent metallation with zinc(II) and oxidation with Sc(OTf)₃ gave the fused dimer 29 in a yield of 54%, along with
meso-meso-linked porphyrin dimer 30. Deprotection gave the desired free carboxylic acid substituted porphyrin 31 in 86% yield.

\[ \text{Scheme 5. Synthesis of a triply-fused bisporphyrin with elongated arms for the carboxylic acid residues.} \]

\[ \text{a)} \quad \text{K}_2\text{CO}_3 \text{ (12 equiv.)}, \text{ bromoester (12 equiv.)}, \text{rt, DMF, 24 h}; \text{b)} \quad \text{Zn(OAc)}_2 \text{ (5 equiv.), MeOH, CHCl}_3, 70 \degree \text{C}, 1 \text{ h}; \text{c)} \quad \text{DDQ (5 equiv.), Sc(OTf)}_3 \text{ (5 equiv.), toluene, 50 \degree \text{C}, 18 \text{ h}; d)} \quad \text{NaOH (excess), THF/MeOH, 80 \degree \text{C}, 18 \text{ h.}} \]

**UV/vis studies**

In addition, we investigated the absorption properties of these molecular porphyrin tectons (Figure 4). When the monomeric species 28 is compared to the fused dimer 29 a very distinctive red shift can be observed. As expected the monomer 28 shows the characteristic absorption pattern of a metal porphyrin. In addition to the significant bathochromic shift of the triply-fused dimer 29 a broad splitting of the Soret band can be observed too, which is due to excitonic coupling between the two porphyrin units. The directly-linked dimer 30 is less red shifted than the fused-dimer 29 but more red shifted than the monomer 28.
Again, a split in the Soret band can be observed due to excitonic coupling of the two porphyrin moieties. Our findings correlate with results that have already been reported before in literature for similar compounds. Similar trends were also observed for compounds 6a and 7a.

Furthermore, we were interested if the two series of triply-fused porphyrin dimers show any difference in the absorption spectra. Therefore, we compared compound 7a, which has the carboxylic acid directly on the aromatic ring with compound 29 where the acid is attached on an extended ‘arm’ further away from the porphyrin core. As expected, there was no significant impact on the absorption spectrum.

**CONCLUSION**

Herein we reported the synthesis of a series of different m-benzoic acid porphyrins for possible application as (supra)molecular tectons for surface binding studies. Our approach is based on a logical and straightforward step-wise functionalization of the porphyrin core to achieve the desired substituent pattern and orientations necessary for surface binding studies. The compounds vary from monomeric compounds with one to four carboxylic acid moieties to π-extended biscarboxylic acid porphyrin dimers which prominently feature long-wavelength absorbance. Furthermore, we explored the option to increase the length of the peripheral acid residues to broaden the possible application of these materials for specific bioconjugation in biosensors.

**EXPERIMENTAL**

General experimental conditions and instrumentations were as described before. Compounds 1, 4a, 4b, 4c, 8, 9, 10, 14, and 17 were prepared according to literature procedures.

**[5,10,15,20-Tetrakis(3’-carboxymethyl)phenylporphyrinato]nickel(II) (2).** The free base porphyrin 1 (260 mg, 0.31 mmol) was reacted with nickel(II) acetate (197 mg, 0.77 mmol) in toluene (30 mL) for 18 h at 120 °C and the crude product purified via column chromatography on silica gel (CH₂Cl₂/MeOH, 9:1, v/v) followed by recrystallization from CH₂Cl₂/MeOH. Yield: 260 mg (0.29 mmol, 94%) of red crystals. Mp >300 °C; Rf: 0.61 (CH₂Cl₂/n-hexane/MeOH, 1:1:0.05, v/v/v, silica gel, 6×3 cm);
1H NMR (400 MHz, CDCl3) δ (ppm): 3.95 (s, 12H, CH3), 7.76 (t, J = 7.6 Hz, 4H, Ar-H), 8.19 (d, J = 7.6 Hz, 4H, Ar-H), 8.39 (d, J = 7.6 Hz, 4H, Ar-H), 8.67-8.71 (m, 12H, Ar-H); 13C NMR (100 MHz, CDCl3) δ (ppm): 167.1, 142.8, 141.0, 137.6, 134.2, 132.3, 129.2, 129.0, 127.1, 118.1, 52.3; UV/vis (CH2Cl2) λmax (log ε): 414 (5.1), 527 nm (4.14); LRMS (MALDI) m/z (%): 902 (30) [M+], 842 (36) [M–C2H3O2], 783 (52) [M+ – C8H16O4], 708 (100) (M+ – C10H10O4), 514 (24) [M+ – C20H20O8]; HRMS (EI) m/z: 846.1274 (Calcd. for C48H28N4O8Ni: 846.1461).

5,10,15,20-Tetrakis(3'-carboxy)phenylporphyrinato]nickel(II) (3). Compound 2 (250 mg, 0.28 mmol) in THF/MeOH (100 mL, 1:1, v/v) was heated to 60 °C, followed by reaction with KOH (6.2 g, 111.80 mmol) at 66 °C for 3 days in the absence of light. The reaction was cooled to rt and acidified to pH 4 using 1M HCl. The organic layer was extracted using CH2Cl2 and dried over Na2SO4, filtered and solvent removed in vacuo. The residue was suspended in n-hexane and filtered. Yield: 190 mg (0.22 mmol, 81%) of a red solid. Mp > 300 °C; Rf: 0.25 (CH2Cl2/n-hexane/MeOH, 1:1:0.1, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3/pyridine-d5, 30:1) δ (ppm): 7.73 (t, J = 7.6 Hz, 4H, Ar-H), 8.13 (d, J = 7.6 Hz, 4H, Ar-H), 8.45 (d, J = 7.6 Hz, 4H, Ar-H), 8.77-8.75 (m, 12H, Ar-H); 13C NMR (100 MHz, CDCl3) δ (ppm): 169.3, 143.9, 140.7, 137.4, 134.7, 133.6, 130.7, 129.2, 126.9, 118.6; UV/vis (CH2Cl2/MeOH, 99:1) λmax (log ε): 411 (5.29), 525 (4.08), 557 nm (3.10); LRMS (MALDI) m/z (%): 846 (16) [M+], 800 (47) [M+ – CHO2], 726 (36) [M+ – C7H5O2], 680 (100) [M+ – C8H6O4], 634 (49) [M+ – C9H7O6], 514 (21) [M+ – C16H12O8]; HRMS (MALDI) m/z: 846.1274 (Calcd. for C48H28N4O8Ni: 846.1461).

10,20-Bis(3,5-di-tert-butyl)phenyl-5-(3'-carboxyethyl)phenylporphyrin (5a). 5-Bromo-10,20-(3,5-di-tert-butyl)phenylporphyrin 4a (175 mg, 0.23 mmol) was heated to 66 °C in the presence of K3PO4 (472 mg, 2.23 mmol), Pd(PPh3)4 (53 mg, 0.05 mmol) and ethyl 3-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)benzoate (252 mg, 0.91 mmol) under argon for 18 h. The solvent was removed in vacuo and the residue dissolved in CH2Cl2 before being washed with saturated aqueous NaHCO3 and water. The organic layer was dried over Na2SO4, filtered and solvent removed in vacuo. The crude product was purified via column chromatography on silica gel (CH2Cl2/n-hexane, 1:2, v/v) followed by recrystallization from CH2Cl2/n-hexane. Yield: 140 mg (0.17 mmol, 74%) of red crystals. Mp >300 °C; Rf: 0.53 (CH2Cl2/n-hexane, 1:1, v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3) δ (ppm): –2.93 (s, 2H, NH), 1.34 (t, J = 7.2 Hz, 3H, CH3), 1.54 (s, 36H, CHtBu), 4.43 (q, J = 7.2 Hz, 4H, CH2), 7.80-7.81 (m, 2H, Ar-H), 8.09-8.10 (m, 4H, Ar-H), 8.38 (d, J = 7.6 Hz, 1H, Ar-H), 8.46 (d, J = 7.6 Hz, 1H, Ar-H), 8.77 (d, J = 4.6 Hz, 2H, Hβ), 8.87-8.88 (m, 1H, Ar-H), 8.92 (d, J = 4.6 Hz, 2H, Hβ), 9.06 (d, J = 4.6 Hz, 2H, Hβ), 9.33 (d, J = 4.6 Hz, 2H, Hβ), 10.22 (s, 1H, Hmeso); 13C NMR (100 MHz, CDCl3) δ (ppm): 166.9, 149.0, 148.9, 143.1, 140.6, 138.1, 134.6, 132.6, 131.7, 131.2, 131.0, 130.1, 130.0, 129.0, 128.9, 126.6, 121.2, 121.1, 118.7, 104.9,
10,20-Bis(3,5-di-tert-butyl)phenyl-5,15-bis(3′-carboxyethyl)phenylporphyrin (5b). Reaction of 5,15-dibromo-10,20-(3,5-di-tert-butyl)phenylporphyrin 4b (200 mg, 0.24 mmol), K$_3$PO$_4$ (502 mg, 2.37 mmol), Pd(PPh$_3$)$_4$ (55 mg, 0.05 mmol) and ethyl 3-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)benzoate (654 mg, 2.37 mmol) following the procedure given for 5a gave 180 mg (0.18 mmol, 78%) of purple crystals. Mp >300 °C; $R_f$: 0.29 (CH$_2$Cl$_2$/n-hexane, 1:1, v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): –2.73 (s, 2H, N$_H$), 1.38 (t, $J$ = 7.2 Hz, 6H, C$_7$H$_3$), 1.46 (s, 36H, H$_t$Bu), 4.41 (q, $J$ = 7.2 Hz, 4H, C$_2$H$_2$), 7.71-7.77 (m, 4H, Ar-$H$), 7.86-7.87 (m, 4H, Ar-$H$), 8.20 (d, $J$ = 7.3 Hz, 2H, Ar-$H$), 8.38 (d, $J$ = 7.3 Hz, 2H, Ar-$H$), 8.66 (d, $J$ = 4.6 Hz, 4H, H$_\beta$), 8.69 (m, 2H, Ar-$H$), 8.66 (d, $J$ = 4.6 Hz, 4H, H$_\beta$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 166.8, 148.8, 142.6, 140.9, 138.2, 134.7, 131.5, 129.9, 129.1, 128.9, 128.2, 126.7, 123.4, 121.8, 121.1, 118.6, 61.2, 35.0, 31.7, 14.3; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$): 420 (5.62), 517 (4.10), 553 (3.66), 593 (3.48), 647 nm (3.55); LRMS (MALDI) m/z (%): 982 (83) [M$^+$], 954 (100) [M$^+$ – C$_2$H$_5$], 895 (40) [M$^+$ – C$_6$H$_{14}$], 853 (17) [M$^+$ – C$_7$H$_{14}$O$_2$]; HRMS (MALDI) m/z: 982.5369 (Calcd for C$_60$H$_{70}$N$_4$O$_4$: 982.5397).

10,20-Bis(3,5-di-tert-butyl)phenyl-5-(3′-carboxymethyl)phenylporphyrin (5c). Porphyrin 4a (300 mg, 0.39 mmol) was dissolved in THF (20 mL). The solution was then degased via three freeze-pump-thaw cycles and the flask was purged with argon. 3-Methoxycarbonylphenylboronic acid (282 mg, 1.57 mmol), Pd(PPh$_3$)$_4$ (68 mg, 0.06 mmol) and K$_3$PO$_4$ (831 mg, 3.92 mmol) were added. The mixture was stirred at 66 °C for 16 h. The solvent was removed in vacuo and the crude product was washed with NaHCO$_3$ and H$_2$O. The solvent was removed and the residue was dissolved in CH$_2$Cl$_2$ and filtered through silica gel. The porphyrin was purified with column chromatography using CH$_2$Cl$_2$:petroleum ether (1:1). The target was obtained in 90% yield (291 mg, 0.35 mmol) after recrystallization from CH$_2$Cl$_2$:MeOH. Mp >300 °C; $R_f$: 0.39 (CH$_2$Cl$_2$/n-hexane = 1:1 + 1 drop MeOH, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): –2.93 (s, 2H, N$_H$), 1.53 (s, 6H, H$_{tBu}$), 1.55 (s, 30H, H$_{tBu}$), 3.97 (s, 3H, OCH$_3$), 7.82 (m, 6H, J = 4.5 Hz, Ar-$H$), 7.85 (s, 1H, Ar-$H$), 8.21 (d, 4H, J = 1.7 Hz, Ar-$H$), 8.40 (d, 1H, J = 7.5 Hz, Ar-$H$), 8.48 (d, 1H, J = 7.9 Hz, H$_\beta$), 8.78 (d, 2H, J = 4.8 Hz, H$_\beta$), 8.90 (s, 1H, Ar-$H$), 8.96 (d, 2H, J = 4.7 Hz, H$_\beta$), 9.08 (d, 2H, J = 4.6 Hz, H$_\beta$), 9.35 (d, 2H, J = 4.6 Hz, H$_\beta$), 10.24 (s, 1H, H$_{meso}$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm): 148.8, 143.0, 142.5, 140.5, 138.1, 134.5, 132.2, 131.5, 131.0, 129.9, 128.8, 128.5, 126.5, 126.0, 121.0, 120.9, 118.4, 105.0, 104.7, 99.8, 52.2, 34.9, 31.9, 31.6, 29.5; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$): 415 (5.69), 511 (4.28), 545 (3.85), 584 (3.77), 639 nm (3.49); HRMS (MALDI) m/z: 820.4742 (Calcd. for [C$_{56}$H$_{60}$N$_4$O$_2$]: 820.4716).
5-(3'-Carboxymethyl)phenyl-10,20-diphenylporphyrin (5d). Compound 4c (300 mg, 0.55 mmol) was dissolved in THF (20 mL). The solution was degassed via freeze-pump-thaw cycles, before the flask was purged with argon. K$_2$PO$_4$ (1.175 g, 5.54 mmol), Pd(PPh$_3$)$_4$ (96 mg, 0.08 mmol) and 3-methoxycarbonylphenylboronic acid (399 mg, 2.22 mmol) were added. The reaction was stirred for 16 h at 66 °C. The end of the reaction was monitored by TLC. The solvent was removed in vacuo. The residue was washed with a saturated sodium bicarbonate solution and water. The solvent was removed in vacuo and the residue recrystallized using CH$_2$Cl$_2$/MeOH (260 mg, 78%, 0.43 mmol). Mp >300 °C; R$_f$: 0.12 (CH$_2$Cl$_2$/n-hexane = 1:1 + 2 drops MeOH, v/v); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): –3.02 (s, 2H, NH), 3.96 (s, 3H, OC$_3$H$_3$), 7.74-7.81 (m, 6H, Ph-H), 7.83 (d, 1H, J = 7.8 Hz, Ar-H), 8.23 (d, 1H, J = 7.6 Hz, Ar-H), 8.38 (d, 1H, J = 7.5 Hz, Ar-H), 8.77 (d, 2H, J = 4.7 Hz, H$_{β}$), 8.88 (s, 1H, Ar-H), 8.90 (d, 2H, J = 4.8 Hz, H$_{β}$), 9.03 (d, 2H, J = 4.5 Hz, H$_{β}$), 9.36 (d, 2H, J = 4.5 Hz, H$_{β}$), 10.25 (s, 1H, H$_{meso}$); 13C NMR (100 MHz, CDCl$_3$): δ (ppm): 167.5, 143.1, 141.8, 138.6, 134.9, 134.8, 131.2, 129.2, 128.9, 127.9, 127.0, 126.9, 120.0, 119.1, 105.2, 52.5; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$): 412 (5.44), 509 (4.09), 543 (3.55), 582 (3.58), 651 nm (3.25); HRMS (MALDI) m/z: 596.2223. (Calcd. for C$_{40}$H$_{28}$N$_4$O$_2$: 596.2212).

[10,20-Bis(3,5-di-tert-butyl)phenyl-5-(3’-carboxyethyl)phenylporphinato]zinc(II) (6a). The free base porphyrin 5a (220 mg, 0.26 mmol) was reacted with zinc(II) acetate and the crude product purified via column chromatography on silica gel (CH$_2$Cl$_2$) followed by recrystallization from CH$_2$Cl$_2$/MeOH. Yield: 201 mg (0.22 mmol, 85%) of pink crystals. Mp >300 °C; R$_f$: 0.39 (CH$_2$Cl$_2$/n-hexane, 1:1, v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 1.34 (t, J = 7.2 Hz, 3H, CH$_3$), 1.54 (s, 36H, H$_{tBu}$), 4.43 (q, J = 7.2 Hz, 2H, CH$_2$), 7.80-7.81 (m, 2H, Ar-H), 8.09-8.10 (m, 4H, Ar-H), 8.38 (d, J = 7.6 Hz, 1H, Ar-H), 8.46 (d, J = 7.6 Hz, 1H, Ar-H), 8.77 (d, J = 4.6 Hz, 2H, H$_{β}$), 8.87-8.88 (m, 1H, Ar-H), 8.92 (d, J = 4.6 Hz, 2H, H$_{β}$), 9.06 (d, J = 4.6 Hz, 2H, H$_{β}$), 9.33 (d, J = 4.6 Hz, 2H, H$_{β}$), 10.22 (s, 1H, H$_{meso}$); 13C NMR (100 MHz, CDCl$_3$): δ (ppm): 166.9, 150.6, 150.5, 149.9, 149.4, 138.7, 138.6, 143.3, 141.5, 138.0, 134.5, 133.0, 132.4, 131.7, 131.5, 129.9, 129.8, 128.8, 128.7, 126.5, 122.2, 120.9, 119.7, 106.0, 61.1, 35.1, 31.7, 14.3; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$): 416 (5.76), 543 nm (4.23); LRMS (MALDI) m/z (%): 896 (55) [M$^+$], 868 (100) [M$^+$ – C$_2$H$_3$], 824 (23) [M$^+$ – C$_3$H$_5$O$_2$], 796 (37) [M$^+$ – C$_3$H$_11$O$_2$]; HRMS (MALDI) m/z: 896.3989 (Calcd for C$_{57}$H$_{60}$N$_4$O$_2$Zn: 896.4008).

5-Bromo-15-(3’-carboxymethyl)phenyl-10,20-diphenylporphyrin (6c). Porphyrin 5d (450 mg, 0.75 mmol) was dissolved in CHCl$_3$ (200 mL). NBS (201 mg, 1.13 mmol) and pyridine (0.15 mL) were added. The mixture was cooled in an ice bath and stirred for 1 h. The solvent was removed in vacuo after completion and the residue was filtered through silica gel using CH$_2$Cl$_2$. The solvent was evaporated and the desired porphyrin was obtained in 94% yield (478 mg, 0.71 mmol). Mp >300 °C; R$_f$: 0.35 (CH$_2$Cl$_2$/n-hexane = 1:1 + 2 drops MeOH, v/v); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): –2.75 (s, 2H, NH), 2.82 (s, 3H, OC$_3$H$_3$), 7.74-7.81 (m, 6H, Ph-H), 7.83 (d, 1H, J = 7.8 Hz, Ar-H), 8.23 (d, 1H, J = 7.6 Hz, Ar-H), 8.38 (d, 1H, J = 7.5 Hz, Ar-H), 8.77 (d, 2H, J = 4.7 Hz, H$_{β}$), 8.88 (s, 1H, Ar-H), 8.90 (d, 2H, J = 4.8 Hz, H$_{β}$), 9.03 (d, 2H, J = 4.5 Hz, H$_{β}$), 9.36 (d, 2H, J = 4.5 Hz, H$_{β}$), 10.25 (s, 1H, H$_{meso}$); 13C NMR (100 MHz, CDCl$_3$): δ (ppm): 166.9, 150.6, 150.5, 149.9, 149.4, 138.7, 138.6, 143.3, 141.5, 138.0, 134.5, 133.0, 132.4, 131.7, 131.5, 129.9, 129.8, 128.8, 128.7, 126.5, 122.2, 120.9, 119.7, 106.0, 61.1, 35.1, 31.7, 14.3; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$): 416 (5.76), 543 nm (4.23); LRMS (MALDI) m/z (%): 896 (55) [M$^+$], 868 (100) [M$^+$ – C$_2$H$_3$], 824 (23) [M$^+$ – C$_3$H$_5$O$_2$], 796 (37) [M$^+$ – C$_3$H$_11$O$_2$]; HRMS (MALDI) m/z: 896.3989 (Calcd for C$_{57}$H$_{60}$N$_4$O$_2$Zn: 896.4008).
OCH₃), 7.77 (d, J = 6.6 Hz, 6H, Ph-H), 7.83 (s, 1H, Ar-H), 8.19 (d, J = 6.6 Hz, 4H, Ph-H), 8.35 (d, J = 6.1 Hz, 1H, Ar-H), 8.46 (d, J = 8.3 Hz, 1H, Ar-H), 8.72 (d, J = 3.0 Hz, 2H, Hβ), 8.80 (d, J = 4.3 Hz, 2H, Hβ), 8.85 (s, 1H, Ar-H), 8.91 (d, J = 4.3 Hz, 2H, Hβ), 9.68 (d, J = 4.3 Hz, 2H, Hβ); ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 167.1, 142.0, 141.5, 138.2, 134.6, 134.4, 129.0, 128.8, 127.8, 126.8, 126.6, 120.8, 119.2, 103.1, 52.2; UV/vis (CH₂Cl₂): λmax (log ε) = 420 (5.53), 518 (4.16), 553 (3.87), 595 (3.65), 651 nm (3.59); HRMS (MALDI) m/z: 674.1351. (Calcd. for C₄₀H₂₇N₄O₂Br: 674.1317).

5-(3'-Carboxymethyl)phenyl-10,20-diphenyl-15-(trimethylsilyl)ethynyl)porphyrin (6d). Compound 6c (200 mg, 0.30 mmol) was dissolved in THF (20 mL) The solution was degassed via three freeze-pump-thaw cycles, before the flask was purged with argon. PdCl₂(PPh₃)₂ (31.2 mg, 0.04 mmol), CuI (11.3 mg, 0.06 mmol) and trimethylsilylacetylene (1.4 mL, 0.02 mmol) were added. The reaction was stirred at 45 °C for 16 h and the solvent was removed in vacuo. The residue was dissolved in CH₂Cl₂ and filtered through silica gel. After evaporation of the solvent the residue was again filtered through silica gel with CH₂Cl₂:petroleum ether (1:1, v/v). Following this the product was eluted from the silica gel with CH₂Cl₂ and the solvent was evaporated. The crude product was purified by recrystallization from CH₂Cl₂:MeOH giving porphyrin 6d in 127 mg (62%, 0.18 mmol). Mp >300 °C; Rf: 0.26 (CH₂Cl₂/n-hexane = 1:1 + 2 drops MeOH, v/v); ¹H NMR (400 MHz, CDCl₃) δ (ppm): –2.43 (s, 2H, NH), 0.61 (s, 9H, TMS-C₃H₇), 3.98 (s, 3H, OCH₃), 7.73-7.81 (m, 6H, Ph-H), 7.83 (d, J = 7.8 Hz, 1H, Ar-H), 8.19 (d, J = 7.7 Hz, 4H, Ph-H), 8.35 (d, J = 7.6 Hz, 1H, Ar-H), 8.47 (d, J = 7.9 Hz, 1H, Ar-H), 8.69 (d, J = 4.7 Hz, 2H, Hβ), 8.77 (d, J = 4.7 Hz, 2H, Hβ), 8.85 (s, 1H, Ar-H), 8.90 (d, J = 4.7 Hz, 2H, Hβ), 9.67 (d, J = 4.7 Hz, 2H, Hβ); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 168.0, 142.3, 139.1, 139.0, 135.4, 135.2, 129.9, 128.6, 127.5, 53.1; UV/vis (CH₂Cl₂): λmax (log ε) = 428 (5.66), 527 (4.25), 565 (4.35), 604 (3.83), 661 nm (3.96); HRMS (MALDI) m/z: 629.2635 (Calcd. for C₄₅H₃₆N₄O₂Si: 692.2608).

5-(3'-Carboxymethyl)phenyl-15-(ethynyl)-10,20-diphenylporphyrin (6e). Porphyrin 6d (90 mg, 0.13 mmol) was dissolved in CH₂Cl₂ and TBAF (1 mL) was added. The mixture was stirred and the reaction was monitored by TLC. Upon completion the product was filtered through silica gel using CH₂Cl₂ and the solvent was removed in vacuo yielding the target compound in quantitative yield (80 mg, 0.13 mmol). Mp >300 °C; Rf: 0.26 (CH₂Cl₂/n-hexane = 1:1 + 2 drops MeOH, v/v); ¹H NMR (400 MHz, CDCl₃) δ (ppm): –2.49 (s, 2H, NH), 3.98 (s, 3H, OCH₃), 4.20 (s, 1H, ethynyl-H), 7.79 (m, 6H, Ph-H), 7.84 (d, J = 7.6 Hz, 1H, Ar-H), 8.20 (d, J = 6.9 Hz, 4H, Ph-H), 8.36 (d, J = 7.3 Hz, 1H, Ar-H), 8.47 (d, J = 8.2 Hz, 1H, Ar-H), 8.70 (d, J = 4.6 Hz, 2H, Hβ), 8.78 (d, J = 4.4 Hz, 2H, Hβ), 8.85 (s, 1H, Ar-H), 8.92 (d, J = 4.4 Hz, 2H, Hβ), 9.70 (d, J = 4.7 Hz, 2H, Hβ); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 167.4, 142.4, 141.7, 138.4, 135.1, 134.8, 134.6, 129.3, 128.5, 128.1, 127.0, 122.5, 121.3, 98.1, 89.8, 85.7, 84.8, 84.3, 52.5; UV/vis (CH₂Cl₂): λmax (log ε) = 425 (5.82), 524 (4.48), 560 (4.40), 600 (4.06), 657 nm (4.05); HRMS (MALDI) m/z: 620.2181 (Calcd. for
C₄₂H₂₈N₄O₂: 620.2212.

5,5-(1,2-Ethynediyl)bis[15-(3’-carboxymethyl)phenyl-10,20-diphenylporphyrin] (6f). A Schlenk tube was purged with argon and charged with compound 6e (62 mg, 0.10 mmol in 12 mL THF) followed by addition of 6c (67.5 mg, 0.10 mmol), TEA (5 mL), AsPh₃ (34 mg, 0.11 mmol) and Pd₂(dba)₃ (9 mg, 0.01 mmol). The reaction mixture was stirred at 66 °C for 16 h. The solvent was removed in vacuo and the residue was filtered through silica gel. CH₂Cl₂:petroleum ether (1:1, v/v) was used to remove impurities and then the product was eluted with CH₂Cl₂. The crude product was purified by recrystallization from CH₂Cl₂:MeOH and 6f was obtained in 50% yield (60 mg, 0.05 mmol). Mp >300 °C; Rf: 0.23 (CH₂Cl₂); 1H NMR (400 MHz, CDCl₃) δ(ppm): –2.01 (s, 4H, NH), 4.00 (s, 6H, OCH₃), 7.82 (d, J = 5.5 Hz, 12H, Ph-H), 7.87 (d, J = 7.7 Hz, 2H, Ar-H), 8.29 (d, J = 7.3 Hz, 8H, Ph-H), 8.40 (d, J = 7.2 Hz, 2H, Ar-H), 8.50 (d, J = 7.8 Hz, 2H, Ar-H), 8.73 (d, J = 4.6 Hz, 4H, Hβ), 8.83 (d, J = 4.6 Hz, 4H, Hβ), 8.90 (s, 2H, Ar-H), 9.10 (d, J = 4.5 Hz, 4H, Hβ), 10.35 (d, J = 4.6 Hz, 4H, Hβ); 13C NMR (150 MHz, CDCl₃) δ(ppm): 167.4, 142.4, 141.8, 138.5, 134.9, 134.7, 129.4, 129.1, 128.1, 127.1, 127.0, 121.9, 120.6, 112.0, 52.5; UV/vis (CH₂Cl₂): λmax (log ε) = 406 (5.26), 441 (5.18), 473 (5.47), 520 (4.54), 619 (4.69), 713 nm (4.77); HRMS (MALDI) m/z: 1214.4248 (Calcd. for C₸₂H₅₄N₈O₄: 1214.4268).

Bis[{5-(3’-carboxyethyl)phenyl}-10,20-bis(3,5-di-tert-butyl)phenylporphyrin-13,15,17-triylato]zinc(II) (7a). Porphyrin 6a (20 mg, 0.02 mmol) was dissolved in anhydrous toluene (20 mL) under argon. The reaction mixture was heated to 50 °C upon the addition of DDQ (25 mg, 0.11 mmol) and Sc(OTf)₃ (55 mg, 0.11 mmol) with stirring in the absence of light for 18 h. The reaction was cooled to 0 °C and THF (10 mL) was added and stirred for 1 h. The reaction mixture was purified via column chromatography on alumina (CH₂Cl₂). The solvents were removed in vacuo. Yield: 14 mg (0.01 mmol, 71%) of dark purple solid. Mp >300 °C; Rf: 0.76 (CH₂Cl₂/n-hexane/MeOH, 1:1:0.05, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl₃) δ(ppm): 1.35 (t, J = 7.1 Hz, 6H, CH₃), 1.45 (s, 72H, HtBu), 4.36 (q, J = 7.1 Hz, 4H, CH₂), 7.33 (s, 4H, Hβ), 7.58-7.65 (m, 18H, Ar-H/Hβ), 7.68 (d, J = 4.6 Hz, 4H, Hβ), 7.96 (d, J = 7.5 Hz, 2H, Ar-H), 8.23 (d, J = 7.5 Hz, 2H, Ar-H), 8.44 (s, 2H, Ar-H); 13C NMR not obtained due to low solubility of sample; UV/vis (CH₂Cl₂): λmax (log ε) = 406 (5.26), 441 (5.18), 473 (5.47), 520 (4.54), 619 (4.69), 713 nm (4.77); HRMS (MALDI) m/z: 1214.4248 (Calcd. for C₸₂H₅₄N₈O₄: 1214.4268).

Bis[5-(3’-carboxyethyl)phenyl]-10,20-bis(3,5-di-tert-butyl)phenylporphyrin-13,15,17-triylato]zinc(II) (7b). Porphyrin 7a (20 mg, 0.01 mmol) was dissolved in THF (25 mL) and MeOH (25 mL). The reaction mixture was heated to 70 °C upon the addition of KOH (0.5 g) in H₂O (3 mL) with stirring for 3 h. The reaction was cooled to rt and the solvents removed in vacuo. The residue was suspended in CH₂Cl₂ (100 mL) and the solution was acidified with 1 M HCl. The product was extracted via CH₂Cl₂ and 1% MeOH,
dried over Na$_2$SO$_4$, and filtered. The solvents were removed \textit{in vacuo} and the residue suspended in $n$-hexane. The suspension was filtered to give the title compound. Yield: 12 mg (0.01 mmol, 63%) of a dark purple solid. Mp $>300$ °C; $R_f$: 0.66 (CH$_2$Cl$_2$/$n$-hexane/MeOH, 1:1:0.66, v/v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$ + drop of pyridine) $\delta$ (ppm): 1.41 (s, 72H, H$_{t}$Bu), 7.07 (s, 4H), 7.50-7.62 (m, 22H, Ar-$H$/H$\beta$), 7.92 (d, $J$ = 8.5 Hz, 2H, Ar-$H$), 8.29 (d, $J$ = 6.7 Hz, 2H, Ar-$H$), 8.52 (s, 2H, Ar-$H$); No $^{13}$C NMR spectroscopy was possible due to low solubility; UV/vis (THF) $\lambda_{max}$ (log $\varepsilon$): 420 (4.89), 471 (4.50), 563 (4.83), 960 (4.00), 1099 nm (4.35); LRMS (MALDI) m/z (%): 1730 (100) [M$^+$]; HRMS (MALDI) m/z: 1730.6956 (Calcd for C$_{110}$H$_{106}$N$_8$O$_4$Zn$_2$: 1730.6920).

\{5-[3-(6’-Iodohexyl)oxy]phenyl\}10,15,20-triphenyl|porphyrin (11). [5-(3’-Phenol)-10,15,20-triphenyl]porphyrin 9 (150 mg, 0.24 mmol) was dissolved in anhydrous DMF (10 mL). K$_2$CO$_3$ (327 mg, 2.38 mmol) was added and the solution was stirred at rt for 0.5 h. 1,6-Diiodohexane (0.39 mL, 2.38 mmol) was added and the reaction was left to stir for a further 18 h. The solvents were removed \textit{in vacuo} and the residue dissolved in CH$_2$Cl$_2$ (100 mL), washed with saturated aqueous NaHCO$_3$, brine and H$_2$O (2×100 mL, each), dried over Na$_2$SO$_4$ and filtered. The crude product was purified via column chromatography on silica gel (CH$_2$Cl$_2$) followed by recrystallization from $n$-hexane. Yield: 145 mg (0.17 mmol, 73%) of purple crystals. Mp. 125-126 °C; $R_f$: 0.71 (CH$_2$Cl$_2$/$n$-hexane, 1:1, v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): –2.79 (br. s, 2H, N$H$), 1.44-1.54 (m, 4H, C$H_2$), 1.80-1.90 (m, 4H, C$H_2$), 3.17 (t, $J$ = 7.0 Hz, 2H, C$H_2$), 4.13 (t, $J$ = 6.3 Hz, 2H, C$H_2$), 7.30 (d, $J$ = 8.3 Hz, 1H, Ar-$H$), 7.61 (t, $J$ = 7.9 Hz, 1H, Ar-$H$), 7.71-7.80 (m, 11H, Ar/Ph-$H$), 8.19 (d, $J$ = 7.1 Hz, 6H, Ph-$H$), 8.83 (app. s, 6H, H$\beta$), 8.88 (d, $J$ = 4.8 Hz, 2H, H$\beta$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 157.4, 143.4, 142.1, 134.5, 127.7, 127.6, 126.7, 121.0, 120.2, 120.1, 119.8, 114.1, 68.0, 33.4, 30.3, 29.2, 25.1 6.91; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$): 418 (5.48), 516 (4.07), 550 (3.65), 590 (3.55), 646 nm (3.44); HRMS (MALDI) m/z: 840.2324 (Calcd for C$_{50}$H$_{41}$N$_4$OI: 840.2325. 

\{5-[3-(6’-Thioacetate)hexyloxy)phenyl\}10,15,20-triphenyl|porphyrin (12). a) {5-(3’-Bromo-hexyloxy)phenyl}-10,15,20-triphenyl|porphyrin 10 (120 mg, 0.15 mmol) was reacted with potassium thioacetate (104 mg, 0.91 mmol) in anhydrous DMF (10 mL) and the crude product was purified \textit{via} column chromatography on silica gel (CH$_2$Cl$_2$) followed by recrystallization from isopropyl alcohol. Yield: 102 mg (0.13 mmol, 86%) of purple solid. b) Alternatively, the same procedure was used with \{3-[3-(6’-iodohexyl)oxy)phenyl\}10,15,20-triphenyl|porphyrin 11 (120 mg, 0.14 mmol) and potassium thioacetate (98 mg, 0.86 mmol) to yield 12. Mp 112-115 °C; $R_f$: 0.40 (CH$_2$Cl$_2$/$n$-hexane, 1:1, v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): –2.79 (br. s, 2H, NH), 1.21-1.29 (m, 2H, CH$_2$), 1.41-1.47 (m, 2H, CH$_2$), 1.54-1.63 (m, 2H, CH$_2$), 1.81-1.88 (m, 4H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.85 (t, $J$ = 7.1 Hz, 2H, CH$_2$), 4.12 (t, $J$ = 6.4 Hz, 2H, CH$_2$), 7.30 (app. d, $J$ = 8.3 Hz, 1H, Ar-$H$), 7.61 (t, $J$ = 7.9 Hz, 1H, Ar-$H$), 7.70-7.80 (m,
1H, Ar/Ph-H), 8.20 (d, J = 6.1 Hz, 6H, Ph-H), 8.83 (app. s, 6H, Hβ), 8.88 (d, J = 4.8 Hz, 2H, Hβ); 13C NMR (100 MHz, CDCl3) δ (ppm): 196.0, 157.4, 143.4, 142.2, 133.6, 131.3, 127.7, 127.6, 127.4, 126.7, 121.0, 120.2, 120.1, 119.9, 114.1, 109.9, 68.0, 30.6, 29.4, 29.2, 29.0, 28.5, 25.6; UV/vis (CH2Cl2) λmax (log ε): 418 (5.50), 516 (4.07), 550 (3.65), 590 (3.57), 646 nm (3.49); LRMS (MALDI) m/z (%): 788 (100) [M+], 745 (23) [M+ – C2H3O], 713 (13) [M+ – C2H3OS], 630 (32) [M+ – C8H15OS]; HRMS (MALDI) m/z: 788.3171 (Calcd for C52H44N4O2S).

[5{3-(6’-Thioacetate)hexyloxy)phenyl}10,15,20-triphenylporphyrinato]zinc(II) (13). The free base porphyrin 12 (200 mg, 0.25 mmol) was reacted with zinc(II)acetate in MeOH and the crude product purified via column chromatography on silica gel (CH2Cl2) followed by trituation with isopropyl alcohol. Yield: 160 mg (0.12 mmol, 74%) of purple solid. Mp 125-127 °C; Rf: 0.53 (CH2Cl2/n-hexane/MeOH, 1:1:0.1, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3) δ (ppm): 1.21-1.28 (m, 2H, C12H2), 1.40-1.46 (m, 2H, C12H2), 1.54-1.61 (m, 2H, C12H2), 1.81-1.88 (m, 4H, C12H2), 2.23 (s, 3H, C12H3), 2.81 (t, J = 7.1 Hz, 2H, C12H2), 4.11 (t, J = 6.4 Hz, 2H, C12H2), 7.29 (d, J = 8.1 Hz, 1H, Ar-H), 7.60 (t, J = 8.0 Hz, 1H, Ar-H), 7.71-7.80 (m, 11H, Ar/Ph-H), 8.20 (d, J = 6.9 Hz, 6H, Ph-H), 8.93 (s, 6H, Hβ), 8.98 (d, J = 4.6 Hz, 2H, Hβ); 13C NMR (100 MHz, CDCl3) δ (ppm): 195.9, 157.3, 150.2, 150.1, 144.0, 134.4, 132.0, 131.9, 127.5, 127.4, 126.5, 121.1, 121.0, 120.9, 114.0, 68.0, 30.5, 29.4, 29.2, 29.0, 28.5, 25.6; UV/vis (CH2Cl2) λmax (log ε): 420 (5.62), 548 (4.18), 586 nm (3.42); LRMS (MALDI) m/z (%): 850 (100) [M+], 775 (5) [M+ – C2H3OS], 692 (11) [M+ – C8H15OS]; HRMS (MALDI) m/z: 850.2289 (Calcd for C52H42N4O2SZn: 850.2320).

5,10,15,20-Tetrakis[methyl-5’-(m-phenoxy)pentanoate]porphyrin (15). 5,10,15,20-Tetrakis(3’-hydroxy)phenylporphyrin 14 (400 mg, 0.59 mmol) was dissolved in anhydrous DMF (12 mL) under argon. K2CO3 (976 mg, 7.07 mmol) was added and the solution was stirred at rt for 0.5 h. Methyl 5-bromovalerate (1.01 mL, 7.072 mmol) was added and the reaction was stirred for 24 h at room temperature. The solvents were removed in vacuo, the residue dissolved in CH2Cl2, washed with saturated aqueous NaHCO3 (4×100 mL), brine (2×100 mL) and water (2×100 mL), dried over Na2SO4, and filtered. The solvents were removed in vacuo and the residue purified via column chromatography on silica gel (CH2Cl2). The solvents were removed to yield an oil-like, purple product. Yield: 512 mg (0.45 mmol, 77%). Mp 83-85 °C; Rf: 0.48 (CH2Cl2/n-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3) δ (ppm): -2.76 (br. s, 2H, NH), 1.94-1.96 (m, 16H, C12H2), 2.47 (t, J = 6.8 Hz, 8H, CH2), 3.70 (s, 12H, C12H3), 4.21 (t, J = 5.8 Hz, 8H, CH2), 7.35 (dd, J = 8.3, 1.8 Hz, 4H, Ar-H), 7.67 (t, J = 8.0 Hz, 4H, Ar-H), 7.81 (app. s, 4H, Ar-H), 7.85 (d, J = 7.4 Hz, 4H, Ar-H), 8.94 (s, 8H, Hβ); 13C NMR (100 MHz, CDCl3) δ (ppm): 173.9, 157.3, 143.5, 127.7, 127.5, 121.0, 119.9, 114.1, 67.6, 51.6, 33.8, 28.8, 21.8; UV/vis (CH2Cl2) λmax (log ε): 420 (5.60), 516 (4.20), 550 (3.76), 590 (3.68), 648 nm.
(3.58); LRMS (MALDI) m/z (%): 1134 (100) [M⁺]; HRMS (MALDI) m/z: 1134.4949 (Calcd for C₆₈H₇₀N₄O₁₂: 1134.4990).

[5,10,15,20-Tetrakis{methyl-5’-(m-phenoxy)pentanoate}porphyrinato]zinc(II) (16). 5,10,15,20-Tetrakis[methyl-5’-(m-phenoxy)-pentanoate]porphyrin 15 (200 mg, 0.18 mmol) was reacted with zinc(II) acetate in MeOH and the crude product was purified via column chromatography on silica gel (CH₂Cl₂/MeOH, 99:1, v/v). Yield: 187 mg (0.16 mmol, 89%) of a purple oil. Mp 83-85 °C; Rf: 0.40 (CH₂Cl₂/n-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); ¹H NMR (400 MHz, CDCl₃) δ(ppm): 1.90-1.98 (m, 16H, C₆H₂), 2.45 (t, J = 7.0 Hz, 8H, C₆H₂), 3.67 (s, 12H, C₆H₃), 4.18 (t, J = 5.6 Hz, 8H, C₆H₂), 7.34 (dd, J = 8.4, 1.8 Hz, 4H, Ar-H), 7.65 (t, J = 8.0 Hz, 4H, Ar-H), 7.80 (app. s, 4H, Ar-H), 7.84 (d, J = 7.3 Hz, 4H, Ar-H), 9.02 (s, 8H, Hβ); ¹³C NMR (100 MHz, CDCl₃) δ(ppm): 173.9, 157.2, 150.1, 144.1, 132.0, 127.5, 127.4, 120.9, 114.0, 67.6, 51.6, 33.7, 28.8, 21.7; UV/vis (CH₂Cl₂) λmax (log ε): 420 (5.71), 550 (4.29), 584 nm (3.49); LRMS (MALDI) m/z (%): 1196 (100) [M⁺], 736 (7) [M⁺ – C₂₄H₄₄O₈]; HRMS (MALDI) m/z: 1196.4116 (Calcd for C₆₈H₆₈N₄O₁₂Zn: 1196.4125).

[5,10,15,20-Tetrakis{methyl-4’-(m-phenoxy)butanoate}porphyrinato]nickel(II) (22). [5,10,15,20-Tetrakis(3’-hydroxy)phenylporphyrinato]nickel(II) 17 (200 mg, 0.27 mmol) was dissolved in anhydrous DMF (10 mL) under argon. K₂CO₃ (450 mg, 3.26 mmol) was added and the reaction mixture stirred for 0.5 h at rt. The reaction was stirred for a further 24 h upon the addition of methyl 4-bromobutanoate 20 (0.41 mL, 3.26 mmol). The solvents were removed in vacuo, the residue dissolved in CH₂Cl₂ (100 mL), followed by washing with saturated aqueous NaHCO₃, brine and H₂O (3×100 mL, each). The organic extracts were combined, dried over aqueous Na₂SO₄ and filtered. The solvents were removed in vacuo and the residue purified via column chromatography on silica gel (CH₂Cl₂) followed by recrystallization from CH₂Cl₂/MeOH. Yield: 173 mg (0.15 mmol, 56%) of purple crystals. Mp 86-88 °C; Rf: 0.56 (CH₂Cl₂/n-hexane/MeOH, 1:1:0.4, v/v/v, silica gel, 6×3 cm); ¹H NMR (400 MHz, CDCl₃) δ(ppm): 2.12-2.19 (m, 8H, C₆H₂), 2.56 (t, J = 7.2 Hz, 8H, C₆H₂), 3.65 (s, 12H, C₆H₃), 4.12 (t, J = 6.0 Hz, 8H, C₆H₂), 7.20-7.23 (m, 4H, Ar-H), 7.50-7.57 (m, 8H, Ar-H), 7.59-7.61 (m, 4H, Ar-H), 8.76 (s, 8H, Hβ); ¹³C NMR (100 MHz, CDCl₃) δ(ppm): 173.6, 157.3, 142.5, 142.2, 132.0, 127.5, 127.4, 121.7, 114.0, 66.9, 51.6, 30.6, 24.7; UV/vis (CH₂Cl₂) λmax (log ε): 414 (5.41), 550 (4.29), 584 nm (3.49); LRMS (MALDI) m/z (%): 1134 (100) [M⁺]; HRMS (MALDI) m/z: 1134.3539 (Calcd for C₆₆H₆₆N₄O₁₂Ni: 1134.3561).

[5,10,15,20-Tetrakis{methyl-5’-(m-phenoxy)pentanoate}porphyrinato]nickel(II) (23). [5,10,15,20-Tetrakis(3’-hydroxy)phenylporphyrinato]nickel(II) 17 (200 mg, 0.27 mmol), K₂CO₃ (450 mg, 3.26 mmol), and methyl 5-bromovalerate 21 (0.47 mL, 3.26 mmol) were reacted as described for compound 22 to yield 202 mg (0.17 mmol, 62%) of purple crystals. Mp 82-84 °C; Rf: 0.52.
(CH2Cl2/n-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3) δ (ppm): 1.85-1.87 (m, 16H, CH2), 2.40 (t, J = 6.8 Hz, 8H, CH2), 3.64 (s, 12H, CH3), 4.08 (t, J = 5.8 Hz, 8H, CH2), 7.20-7.23 (m, 4H, Ar-H), 7.51-7.61 (m, 12H, Ar-H); 13C NMR (100 MHz, CDCl3) δ (ppm): 173.8, 157.4, 142.5, 142.2, 132.1, 127.7, 126.7, 120.1, 118.8, 114.1, 67.5, 51.5, 33.7, 28.7, 21.7; UV/vis (CH2Cl2) λmax (log ε): 416 (5.13), 528 nm (3.99); LRMS (MALDI) m/z (%): 1190 (100) [M+]; HRMS (MALDI) m/z: 1190.4165 (Calcd for C68H68N4O12Ni: 1190.4187).

[5,10,15,20-Tetrakis{4′(m-phenoxy)butanoic acid}porphyrinato]nickel(II) (24). [5,10,15,20-Tetrakis{methyl-4′(m-phenoxy)butanoate}porphyrinato]nickel(II) 22 (100 mg, 0.09 mmol) was dissolved in THF (50 mL). NaOH (16 g in 50 mL EtOH) was added and the solution was heated to reflux with stirring for 24 h. 1 M HCl was added after the reaction was cooled to rt. The organic layer was extracted with CH2Cl2, washed with H2O (2×250 mL) and dried over Na2SO4. After filtration, the solvent was removed in vacuo and the residue was recrystallized from CH2Cl2/MeOH. Yield: 62 mg (0.06 mmol, 65%) of red crystals. Mp 145-147 °C; Rf: 0.67 (CH2Cl2/n-hexane/MeOH, 2:1:0.6, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3/pyridine-d5, 30:1, v/v) δ (ppm): 2.16-2.24 (m, 8H, CH2), 2.58 (t, J = 7.0 Hz, 8H, CH2), 4.16 (t, J = 6.1 Hz, 8H, CH2), 7.20-7.23 (m, 4H, Ar-H), 7.49-7.60 (m, 12H, Ar-H), 8.76 (s, 8H, Hβ), 11.06 (br. S, 4H, COO); 13C NMR (100 MHz, CDCl3/pyridine-d5, 30:1, v/v) δ (ppm): 176.1, 157.5, 142.8, 142.1, 132.5, 127.7, 126.7, 120.3, 118.8, 114.1, 67.2, 31.0, 24.9; UV/vis (CH2Cl2) λmax (log ε): 414 (5.40), 528 nm (4.26); LRMS (MALDI) m/z (%): 1078 (100) [M+]; HRMS (MALDI) m/z: 1078.2903 (Calcd for C60H52N4O12Ni: 1078.2935).

[5,10,15,20-Tetrakis{5′-(m-phenoxy)pentanoic acid}porphyrinato]nickel(II) (25). [5,10,15,20-Tetrakis{methyl-4′-(m-phenoxy)pentanoate}porphyrinato]nickel(II) 23 (150 mg, 0.13 mmol) treated under the conditions given for 24 gave 102 mg (0.09 mmol, 71%) of red crystals. Mp 130-131 °C; Rf: 0.68 (CH2Cl2/n-hexane/MeOH, 1:1:0.6, v/v/v, silica gel, 6×3 cm); 1H NMR (400 MHz, CDCl3/pyridine-d5, 30:1, v/v) δ (ppm): 1.81-1.89 (m, 16H, CH2), 2.42 (t, J = 6.9 Hz, 8H, CH2), 4.09 (t, J = 5.8 Hz, 8H, CH2), 7.19-7.22 (d, J = 6.9 Hz, 4H, Ar-H), 7.48-7.57 (m, 12H, Ar-H), 8.76 (s, 8H, Hβ); 13C NMR (100 MHz, CDCl3/pyridine-d5, 30:1, v/v) δ (ppm): 176.2, 157.5, 142.7, 142.1, 132.3, 127.6, 126.6, 120.1, 188.8, 114.1, 67.7, 34.1, 28.8, 21.8; UV/vis (CH2Cl2) λmax (log ε): 414 (5.40), 528 nm (4.26); LRMS (MALDI) m/z (%): 1078 (100) [M+]; HRMS (MALDI) m/z: 1078.2903 (Calcd for C64H60N4O12Ni: 1078.2935).

[10,20-Bis(3,5-di-tert-butyl)phenyl-5-{methyl-5′-(m-phenoxy)pentanoate}porphyrin (27). [10,20-Bis(3,5-di-tert-butyl)phenyl-5′-(3′-hydroxy)phenyl]porphyrin 26 (240 mg, 0.31 mmol) was reacted with K2CO3 (213 mg, 1.54 mmol) in anhydrous DMF (10 mL) for 0.5 h, followed by the addition of methyl 5-bromovalerate (0.22 mL, 1.54 mmol) and subsequent stirring for 18 h. The crude product was purified via column chromatography on silica gel (CH2Cl2/n-hexane, 1:1, v/v) followed by
recrystallization from CH$_2$Cl$_2$/n-hexane. Yield: 211 mg (0.24 mmol, 77%) of purple crystals. Mp >300 °C; $R_f$: 0.80 (CH$_2$Cl$_2$/n-hexane/MeOH, 1:1:0.05, v/v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$) δ(ppm): –2.89 (br. s, 2H, N$_2$H), 1.59 (s, 36H, H$_{t}$Bu), 2.04-2.06 (m, 4H, CH$_2$), 2.58 (t, J = 6.8 Hz, 2H, CH$_2$), 3.78 (s, 3H, CH$_3$), 4.31 (t, J = 5.3 Hz, 2H, CH$_2$), 7.28 (m, 1H, Ar-H), 7.30 (m, 1H, Ar-H), 7.84-7.85 (m, 2H, Ar-H), 8.14-8.16 (m, 6H, Ar-H), 8.94 (d, J = 4.7 Hz, 2H, H$_β$), 8.98 (d, J = 4.8 Hz, 2H, H$_β$), 9.10 (d, J = 4.8 Hz, 2H, H$_β$), 9.37 (d, J = 4.8 Hz, 2H, H$_β$), 10.24 (s, 1H, H$_{meso}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 174.2, 158.7, 148.9, 140.8, 135.5, 135.2, 130.1, 121.0, 120.9, 120.2, 112.5, 104.5, 67.7, 51.7, 35.1, 33.8, 31.8, 28.9, 21.9; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$): 416 (5.54), 512 (4.10), 548 (3.67), 586 (3.63), 642 nm (3.57); LRMS (MALDI) m/z (%): 892 (100) [M$^+$], 747 (18) [M$^+$ – C$_7$H$_{14}$O$_3$], 731 (28) [M$^+$ – C$_8$H$_{17}$O$_3$], 717 (32) [M$^+$ – C$_9$H$_{20}$O$_3$]; HRMS (MALDI) m/z: 892.5264 (Calcd for C$_{60}$H$_{68}$N$_4$O$_3$: 892.5291).

[10,20-Bis(3,5-di-tert-butyl)phenyl-5-{methyl-5'-(m-phenoxy)pentanoate}porphyrinato]zinc(II) (28).

The free base 27 (180 mg, 0.20 mmol) was reacted with zinc(II) acetate in MeOH. The crude product was purified via column chromatography on silica gel (CH$_2$Cl$_2$/n-hexane, 1:1, v/v). Yield: 185 mg (0.19 mmol, 96%) of pink solid. Mp > 300 °C; $R_f$: 0.73 (CH$_2$Cl$_2$/n-hexane/MeOH, 1:1:0.1, v/v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 1.56 (s, 36H, H$_{t}$Bu), 1.95-2.05 (m, 4H, CH$_2$), 2.53 (t, J = 6.6 Hz, 2H, CH$_2$), 3.74 (s, 3H, CH$_3$), 4.30 (t, J = 5.8 Hz, 2H, CH$_2$), 7.24 (s, 1H, Ar-H), 7.27 (s, 1H, Ar-H), 8.14 (app. s, 6H, Ar-H), 9.04 (dd, J = 4.6 Hz, 4H, H$_β$), 9.17 (d, J = 4.6 Hz, 2H, H$_β$), 9.43 (d, J = 4.8 Hz, 2H, H$_β$), 10.27 (s, 1H, H$_{meso}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 173.6, 158.1, 150.0, 149.6, 149.4, 148.2, 141.2, 134.9, 132.5, 131.6, 131.5, 129.4, 121.5, 120.7, 120.3, 112.0, 105.2, 67.2, 51.2, 34.6, 33.4, 31.3, 28.5, 26.4; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$): 416 (5.54), 548 (3.67), 582 nm (3.48); LRMS (MALDI) m/z (%): 954 (100) [M$^+$]; HRMS (MALDI) m/z: 954.4426 (Calcd for C$_{60}$H$_{68}$N$_4$O$_3$Zn: 954.4426).

Bis[10,20-Bis(3,5-di-tert-butyl)phenyl-5-{methyl-5'-(m-phenoxy)pentanoate}porphyrin-13,15,17-triylato]zinc(II) (29).

Porphyrin 28 (100 mg, 0.10 mmol) was reacted with DDQ (118 mg, 0.52 mmol) and Sc(OTf)$_3$ (258 mg, 0.52 mmol) in anhydrous toluene (30 mL) at 50 °C in the dark for 3 h. The crude product was purified via column chromatography on alumina (CH$_2$Cl$_2$/n-hexane, 1:1, v/v), followed by isolation of the triply-fused dimer using CH$_2$Cl$_2$/2% MeOH. Yield: 56 mg (0.03 mmol, 54%) of purple crystals. Mp >300 °C; $R_f$: 0.66 (CH$_2$Cl$_2$/n-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); $^1$H NMR (400 MHz, CDCl$_3$/pyridine-d$_5$, 20:1, v/v) δ (ppm): 1.38 (s, 72H, H$_{t}$Bu), 1.88-1.91 (m, 8H, H$_2$), 2.44 (t, J = 6.6 Hz, 4H, CH$_2$), 3.67 (s, 6H, CH$_3$), 4.09 (app. m, 4H, CH$_2$), 6.99 (d, J = 8.2 Hz, 4H, Ar-H), 7.04 (s, 4H, H$_β$), 7.47 (d, J = 4.3 Hz, 4H, H$_β$), 7.52 (m, 16H, Ar-H), 7.60-7.63 (m, 4H, H$_β$); $^{13}$C NMR (100 MHz, CDCl$_3$/pyridine-d$_5$, 20:1, v/v) δ (ppm): 173.5, 147.9, 133.3, 129.9, 127.8, 126.2, 120.0, 112.4, 67.0, 51.1, 34.4, 33.3, 31.2, 28.4, 21.3; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$): 420 (5.25), 474 (4.86), 582 (5.19), 966 (4.49),
1100 nm (4.68); LRMS (MALDI) m/z (%): 1902 (100) [M+]; HRMS (MALDI) m/z: 1902.8446 (Calcd for C_{120}H_{126}N_8O_6Zn_2: 1902.8383).

**Bis[10,20-Bis(3,5-di-tert-butyl)phenyl-5-{methyl-5’-(m-phenoxy)pentanoate}porphyrin-15-ylato]zinc(II) (30).** Isolated as fraction 1 during the synthesis of 29. Yield: 45 mg (45%, 0.02 mmol) of a red-purple solid. Mp >300 °C; Rf: 0.69 (CH_2Cl_2/n-hexane/MeOH, 1:1:0.05, v/v/v, silica gel, 6×3 cm); ^1H NMR (400 MHz, CDCl_3) δ(ppm): 1.42 (s, 72H, H_tBu), 2.03-2.04 (m, 8H, CH_2), 2.54 (t, J = 7.0 Hz, 4H, CH_2), 3.74 (s, 6H, CH_3), 4.30 (t, J = 5.3 Hz, 4H, CH_2), 7.29 (d, J = 8.6 Hz, 4H, Ar-H), 7.66-7.67 (m, 4H, Ar-H), 8.06-8.07 (m, 8H, Ar-H); 1H NMR (400 MHz, CDCl_3/pyridine-d_5, 20:1, v/v) δ(ppm): 174.0, 158.6, 154.8, 150.9, 150.3, 150.0, 148.4, 141.7, 135.4, 135.3, 132.2, 132.0, 131.9, 129.6, 123.2, 121.5, 120.7, 119.3, 112.6, 67.7, 51.6, 34.9, 33.8, 31.6, 28.9, 21.8; UV/vis (CH_2Cl_2) ʔ_\text{max} (log ε): 420 (5.45), 458 (5.50), 562 (4.83), 602 nm (4.01); LRMS (MALDI) m/z (%): 1910 (100) [M+]; HRMS (MALDI) m/z: 1906.8774 (Calcd for C_{120}H_{130}N_8O_6Zn_2: 1906.8696).

**Bis[10,20-Bis(3,5-di-tert-butyl)phenyl-5-{5’-(m-phenoxy)pentanoic acid}porphyrin-13,15,17-triylato]zinc(II) (31).** Compound 29 (40 mg, 0.02 mmol) dissolved in THF (25 mL) and MeOH (25 mL) was reacted with KOH (1.2 g, 21.4 mmol) in H_2O (10 mL) at 70 °C for 3 h. The reaction was cooled to rt and the solvents removed in vacuo. The residue was suspended in CH_2Cl_2 (100 mL) and acidified with 1 M HCl. The crude product was extracted using CH_2Cl_2/MeOH (99:1, v/v) and recrystallized from n-hexane. Yield: 34 mg (0.02 mmol, 86%) of purple crystals. Mp >300 °C; Rf: 0.57 (CH_2Cl_2/n-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); ^1H NMR (400 MHz, CDCl_3/pyridine-d_5, 20:1, v/v) δ(ppm): 1.42 (s, 72H, H_tBu), 1.96-1.99 (m, 8H, CH_2), 2.53 (t, J = 6.8 Hz, 4H, CH_2), 4.15 (t, J = 5.6 Hz, 4H, CH_2), 7.01-7.10 (m, 8H, H_β/Ar-H), 7.51-7.63 (s, 24H, H_β/Ar-H); ^13C NMR (100 MHz, CDCl_3) δ(ppm): 176.3, 158.4, 153.3, 148.4, 140.7, 134.3, 133.7, 130.7, 128.2, 126.7, 120.4, 112.8, 67.7, 34.9, 34.3, 31.7, 29.0, 21.9; UV/vis (CH_2Cl_2) ʔ_\text{max} (log ε): 420 (5.20), 474 (4.80), 582 (5.13), 966 (4.42), 1100 nm (4.61); LRMS (MALDI) m/z (%): 1874 (100) [M+]; HRMS (MALDI) m/z: 1874.8044 (Calcd for C_{118}H_{122}N_8O_6Zn_2: 1874.8070).

**Crystal structure determination of 6a.** Crystals were grown following the protocol developed by Hope. Diffraction data for the compound was collected on a Bruker APEX 2 DUO CCD diffractometer using Incoatec μS CuK_α (λ = 1.54178 Å) radiation. Crystals were mounted on a MiTeGen MicroMount and collected at 100(2) K using an Oxford Cryosystems Cobra low-temperature device. Data were collected using omega and phi scans and corrected for Lorentz and polarization effects using the APEX software suite. The structure was solved with Direct Methods and refined against │F^2│ with the program OLEX² using all data. Non-hydrogen atoms were refined with anisotropically thermal
parameters. Hydrogen atoms were generally placed in geometrically calculated positions and refined using a riding model. All images were rendered using XP in SHELXL.\textsuperscript{34b,c} C\textsubscript{57}H\textsubscript{60}N\textsubscript{4}O\textsubscript{2}Zn (M = 898.46 g.mol\textsuperscript{-1}): monoclinic, space group \textit{P2}$_1$/\textit{n}, \(a = 26.0025(13)\) Å, \(b = 5.7174(3)\) Å, \(c = 33.5335(19)\) Å, \(\beta = 100.215(4)\), \(V = 4906.3(5)\) Å\textsuperscript{3}, \(Z = 4\), \(T = 99.97\)K, \(\mu(\text{CuK}\alpha) = 1.040\) mm\textsuperscript{-1}, \(D_{\text{calc}} = 1.216\) g cm\textsuperscript{-3}, 27214 reflections measured (3.976° \(\leq 2\theta \leq 122.518\)°), 5281 unique \((R_{\text{int}} = 0.1159, R_{\text{sigma}} = 0.1053)\) which were used in all calculations. The final \(R_1\) was 0.0615 \((I > 2\sigma(I))\) and \(wR_2\) was 0.1615 (all data).

Crystal structure determination of 13. General details as given for 6a. C\textsubscript{53}H\textsubscript{43}Cl\textsubscript{3}N\textsubscript{4}O\textsubscript{2}SZn (M =971.69 g.mol\textsuperscript{-1}): triclinic, space group \textit{P}1, \(a = 10.7348(4)\) Å, \(b = 10.9532(4)\) Å, \(c = 11.2018(4)\) Å, \(\alpha = 73.7480(10)\)°, \(\beta = 80.1710(10)\)°, \(\gamma = 74.9300(10)\)°, \(V = 1214.16(8)\) Å\textsuperscript{3}, \(Z = 1\), \(T = 100.0\)K, \(\mu(\text{CuK}\alpha) = 2.971\) mm\textsuperscript{-1}, \(D_{\text{calc}} = 1.329\) g.cm\textsuperscript{-3}, 29482 reflections measured (8.268° \(\leq 2\theta \leq 137.262\)°), 8543 unique \((R_{\text{int}} = 0.0312, R_{\text{sigma}} = 0.0299)\) which were used in all calculations. The final \(R_1\) was 0.0564 \((I > 2\sigma(I))\) and \(wR_2\) was 0.1546 (all data). The structure was refined as a refined as a two-component inversion twin. Solvent chloroform molecules were modeled over two positions with a 47:53\% occupancy.

CCDC 1549910 and 1549911 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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REFERENCES


