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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.[1] 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.[1g] 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,[1a,9] and they present a suitable means to create molecular tectons.

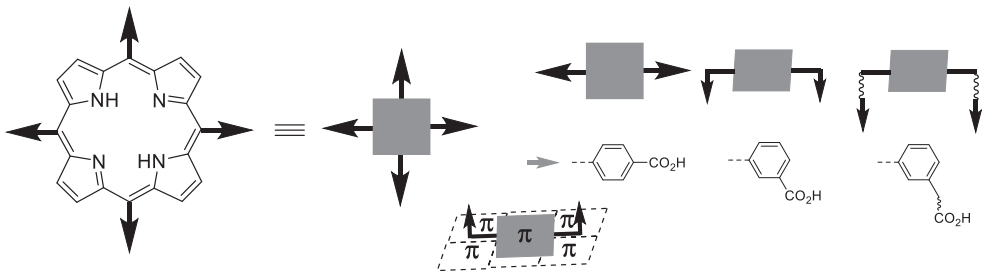


Figure 1. Illustration of porphyrin carboxylic acids as directional molecular tectons

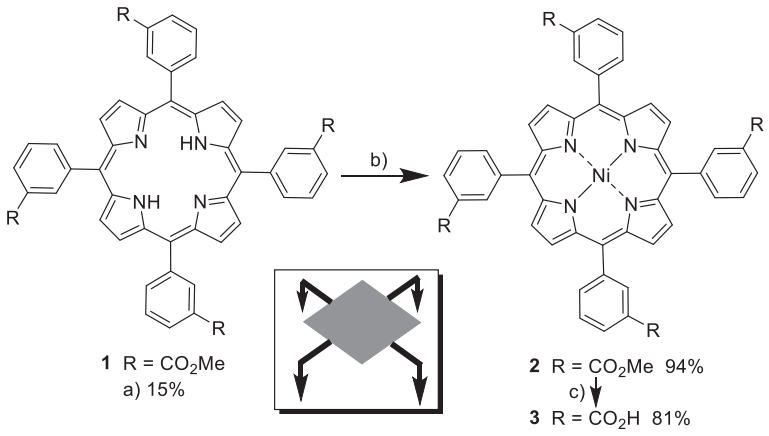
In the context of exploratory studies on the use of surface-bound porphyrins as biosensors we were interested in providing porphyrins with unique optical properties capable of binding to surface materials in a directional manner. One possible avenue would be the attachment of porphyrins *via* π-π-interactions 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.[10] 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[1a,9b,11] and Suzuki[12] couplings to nucleophilic substitution reactions.[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.

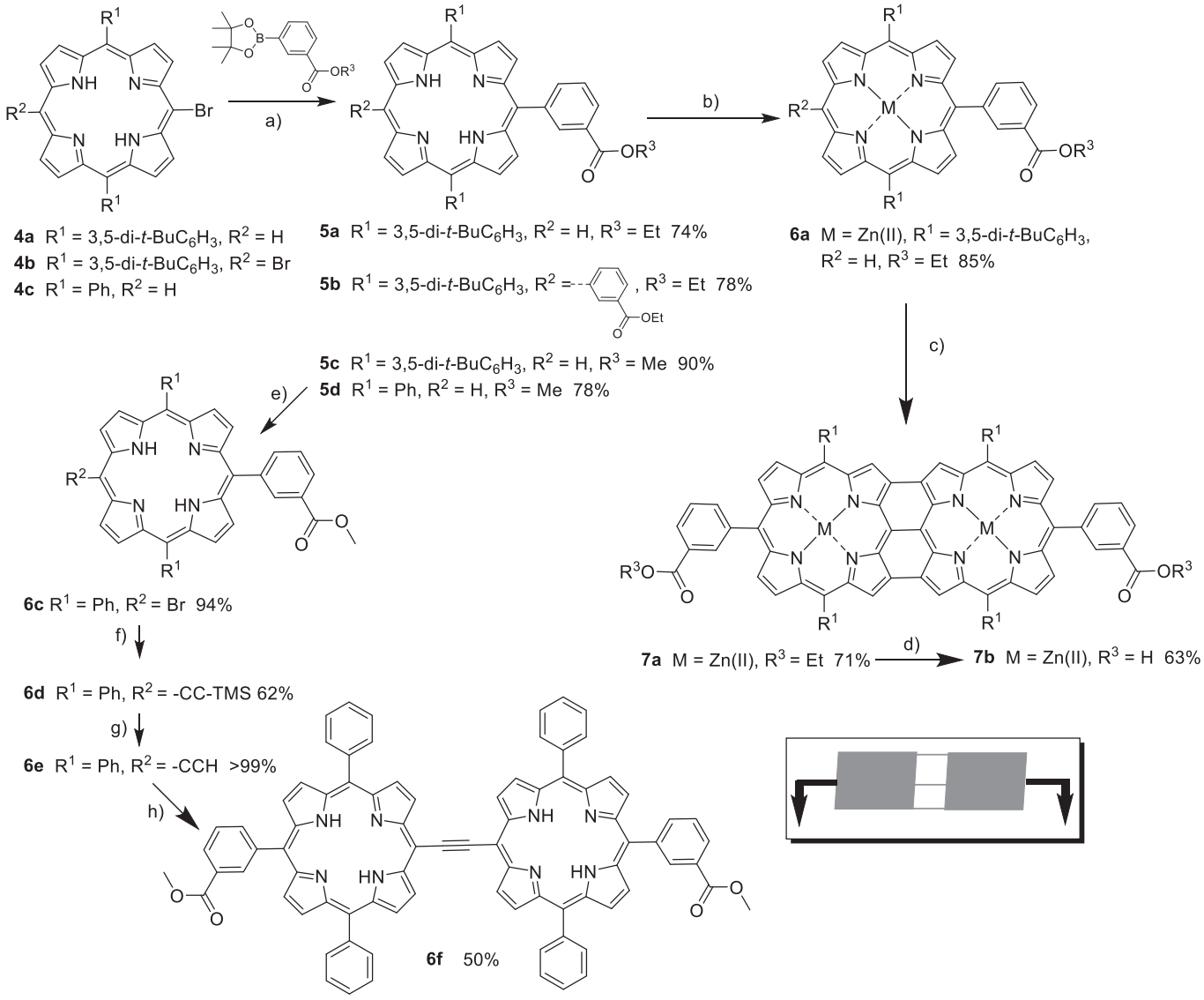
RESULTS AND DISCUSSION

SYNTHESIS OF AN A_4-TYPE TETRACARBOXYLIC ACID PORPHYRIN

Our first target compound was the tetrasubstituted *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.[13b] Further modification included the insertion of nickel into the porphyrin core *via* reaction with $Ni(acac)_2$ 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_4-type *m*-benzoic acid porphyrins. a) (i) 3-carbomethoxybenzaldehyde, pyrrole, CH_2Cl_2, $BF_3{\cdot}OEt_2$, rt, 16 h, (ii) DDQ, rt, 1 h; b) Ni(II)$(acac)_2$ (2.5 equiv.), toluene, 120 °C, 18 h; c) KOH (400 equiv.) in H_2O, 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_3PO_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_2O, 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 π-extended biscarboxylic 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 π–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 π-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.[16] Their prominent electron transport properties make them possible candidates for organic semiconductors or photovoltaic materials.[17] For these reasons, we decided to synthesize two related biscarboxylic acid porphyrin dimers, the directly fused compound **7b** and, for comparison, the ethyne-bridged dimer **6f** (Scheme 2).

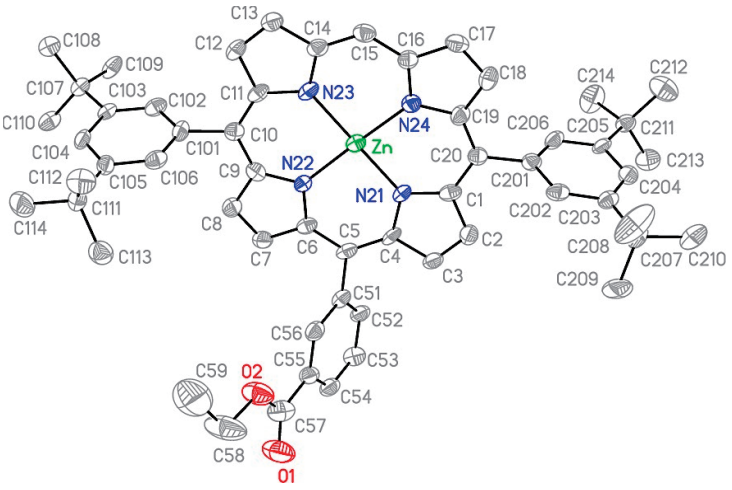


Figure 2. View of the molecular structure of **6a** in the crystal. Hydrogen atoms have been removed for clarity; thermal ellipsoids give 50% probability. Selected bond angles [°] and lengths [Å]: Zn-N21 2.034(9), Zn-N22 2.015(8), Zn-N23 2.037(1), Zn-N24 2.0276(9), C4-C5 1.405(8), C5-C6 1.390(7), C9-C1) 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).

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.[16b] Subsequent oxidative fusing using DDQ/$Sc(OTf)_3$ 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.

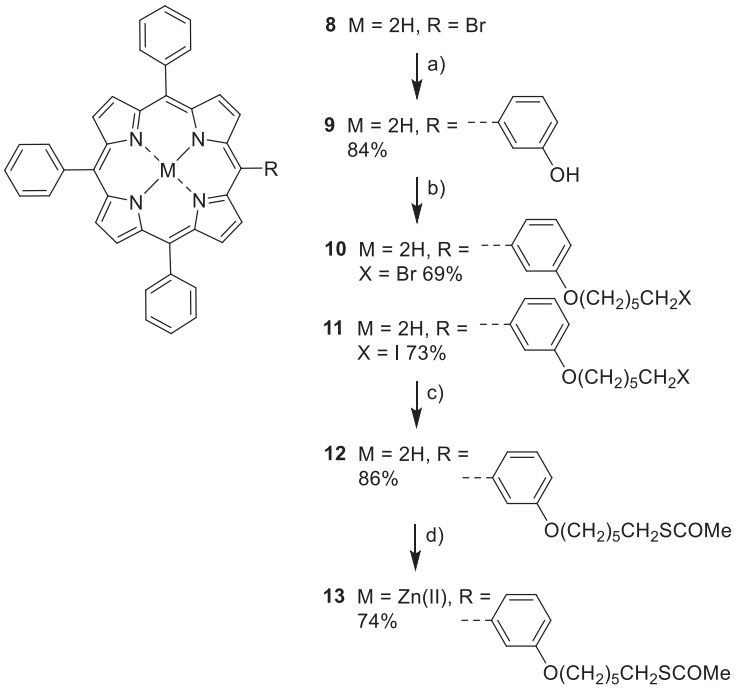
For compound **6a** single crystals suitable for X-ray crystallographic analysis were obtained. The structure shows a classic A_2B Zn(II)-porphyrin structure bearing aryl substituents, in which the porphyrin ring is almost planar and the aryl substitutent are held in a nearly orthogonal position (Figure 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_2B-porphyrins [angles of 56.1–85.2° for the C10 and C20 positions (A_2), and 101.3–121.0° for the C5

position], these values fall within the expected range for such tetracoordinated complexes.[18] This is also reflected in the structure of the A_3-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.[19] 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°.[18a-c] 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.[20] These long chains provide suitable anchor groups for specific bioconjugation and have shown to give good results for different biosensors.[20] 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.

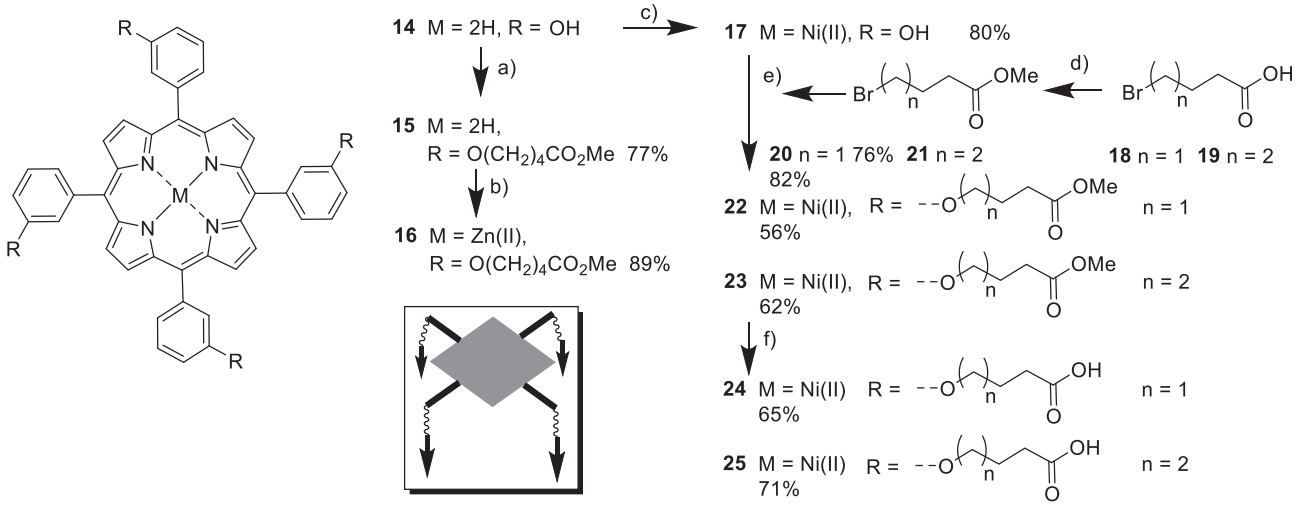
In practical terms we decided to apply an approach for the functionalization of 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin, recently developed by us.[21] Initially, we decided to use a monosubstituted derivative for test reactions to explore the feasibility of this approach for longer chains. Suzuki coupling methodologies were applied



Scheme 3. Synthesis of monofunctionalized porphyrins *via* arm attachment. a) 3-Hydroxyphenylboronic acid $Pd(PPh_3)_4$ (20 mol%), K_3PO_4 (10 equiv.), THF, 66 °C, 18 h; b) (i) K_2CO_3, 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, $CHCl_3$, 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 A_4-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 A_3B system. Other reported Zn(II) A_3B 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.

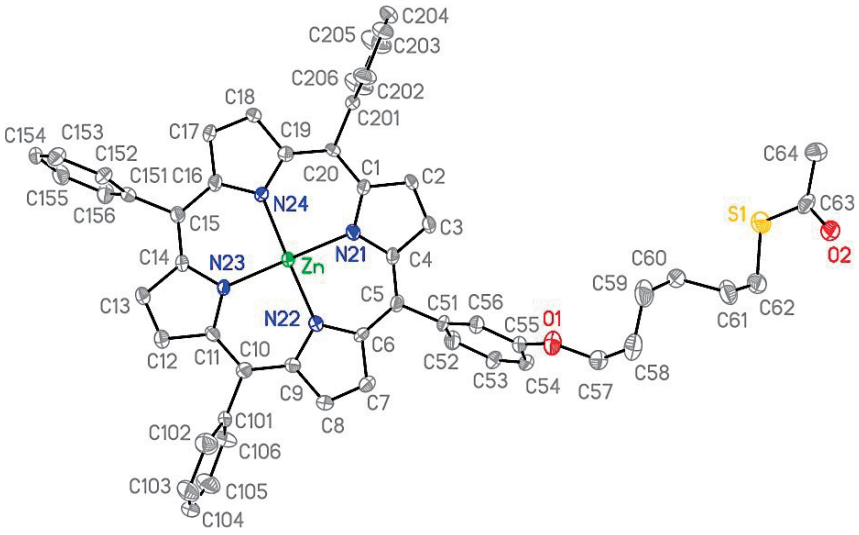
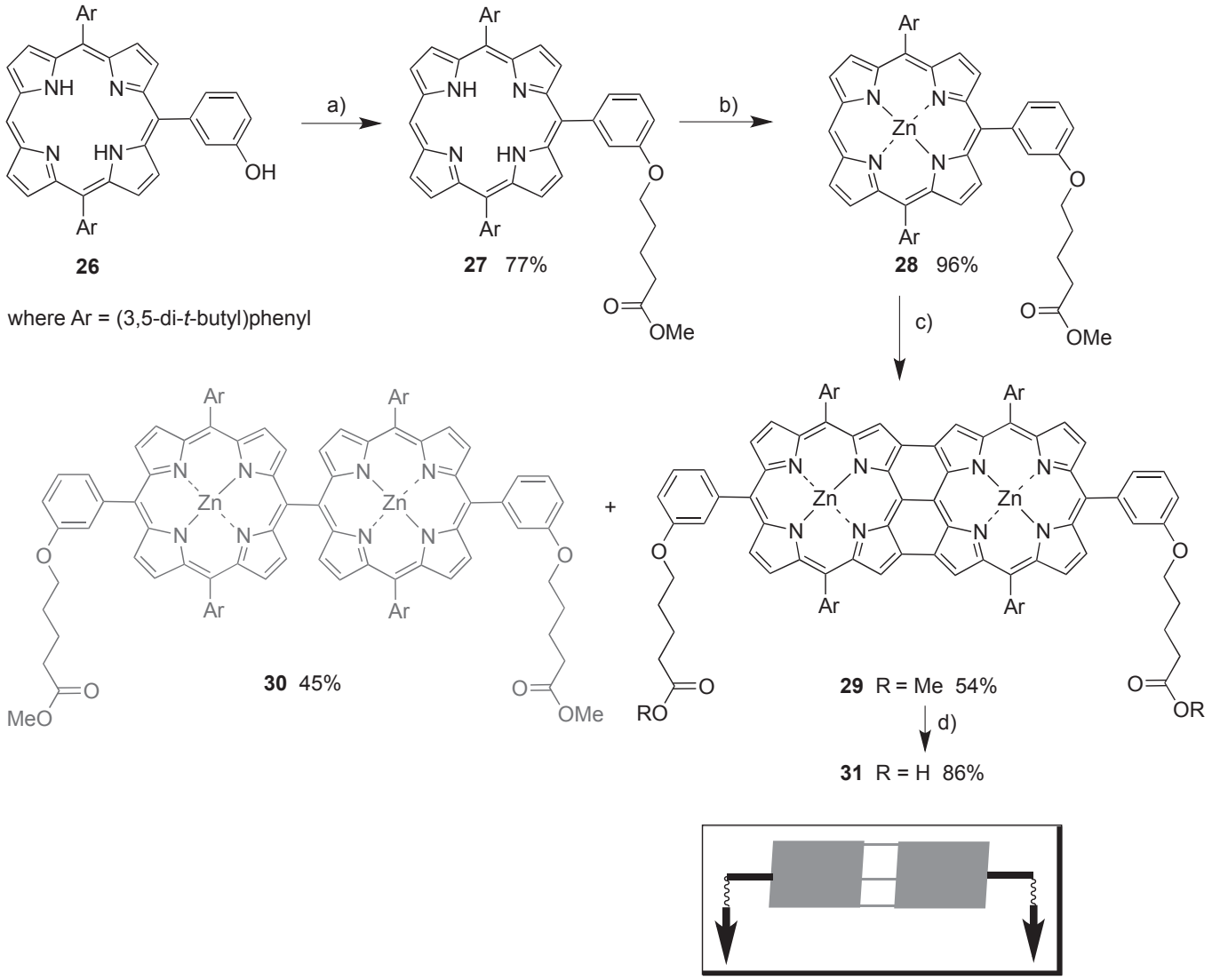


Figure 3. View of the molecular structure of 13 in the crystal. Hydrogen atoms and solvent molecules have been removed for clarity; thermal ellipsoids give 50% probability. Selected bond angles [°] and lengths [Å]: Zn-N21 2.063(6), Zn-N22 2.042(5), Zn-N23 2.060(6), Zn-N24 2.056(5), C4-C5 1.401(4), C5-C6 1.404(4), C9-C10 1.404(5), C10-C11 1.393(3), C14-C15 1.391(4), C15-C16 1.413(4), C19-C20 1.392(5), C20-C1 1.416(3), C4-C5-C6 125.2(2), C9-C10-C11 125.7(2), C14-C15-C16 125.7(2), C19-C20-C1 125.1(2).

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.



Scheme 5. Synthesis of a triply-fused bisporphyrin with elongated arms for the carboxylic acid residues. a) K_2CO_3 (12 equiv.), bromoester (12 equiv.), rt, DMF, 24 h; b) $Zn(OAc)_2$ (5 equiv.), MeOH, $CHCl_3$, 70 °C, 1 h; c) DDQ (5 equiv.), $Sc(OTf)_3$ (5 equiv.), toluene, 50 °C, 18 h; d) NaOH (excess), THF/MeOH, 80 °C, 18 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.[16b] 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.

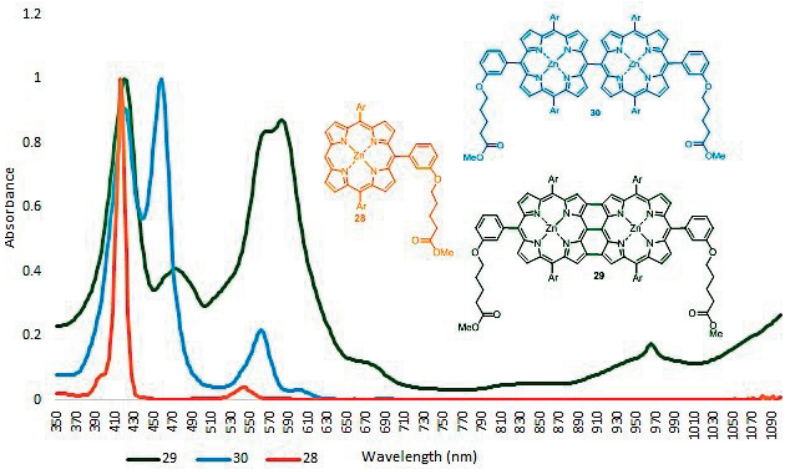


Figure 4. UV/vis absorption spectra of monomer **28** (orange), directly-linked dimer **30** (blue), and fused dimer **29** (green) in CH_2Cl_2.

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.[23] Compounds **1**,[13b,24] **4a**,[25] **4b**,[25] **4c**,[26] **8**,[27] **9**,[28] **10**,[29] **14**,[30] and **17**[31] 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 (CH_2Cl_2/MeOH, 9:1, v/v) followed by recrystallization from CH_2Cl_2/MeOH. Yield: 260 mg (0.29 mmol, 94%) of red crystals. Mp >300 °C; *Rf*: 0.61 (CH_2Cl_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): 3.95 (s, 12H, C*H*$_3$), 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*, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (CH_2Cl_2) λ_{max} (log ε): 414 (5.1), 527 nm (4.14); LRMS (MALDI) *m/z* (%): 902 (30) [M^+], 842 (36) [$M^+ - C_2H_3O_2$], 783 (52) [$M^+ - C_4H_6O_4$], 708 (100) ($M^+ - C_{10}H_{10}O_4$), 648 (80) ($M^+ - C_{12}H_{13}O_6$), 514 (24) [$M^+ - C_{20}H_{20}O_8$); HRMS (EI) *m/z*: 902.1901 (Calcd. for $C_{52}H_{36}N_4O_8Ni$: 902.1887).

[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 CH_2Cl_2 and dried over Na_2SO_4, 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; R_f: 0.25 (CH_2Cl_2/*n*-hexane/MeOH, 1:1:0.1, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5, 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*, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.3, 143.9, 140.7, 137.4, 134.7, 133.6, 130.7, 129.2, 126.9, 118.6; UV/vis (CH_2Cl_2/MeOH, 99:1) λ_{max} (log ε): 411 (5.29), 525 (4.08), 557 nm (3.10); LRMS (MALDI) *m/z* (%): 846 (16) [M^+], 800 (47) [$M^+ - CHO_2$], 726 (36) [$M^+ - C_7H_5O_2$], 680 (100) [$M^+ - C_8H_6O_4$], 634 (49) [$M^+ - C_9H_7O_6$], 514 (21) [$M^+ - C_{16}H_{12}O_8$]; HRMS (MALDI) *m/z*: 846.1274 (Calcd. for $C_{48}H_{28}N_4O_8Ni$: 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 K_3PO_4 (472 mg, 2.23 mmol), $Pd(PPh_3)_4$ (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 CH_2Cl_2 before being washed with saturated aqueous. $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4, filtered and solvent removed *in vacuo*. The crude product was purified *via* column chromatography on silica gel (CH_2Cl_2/*n*-hexane, 1:2, v/v) followed by recrystallization from CH_2Cl_2/*n*-hexane. Yield: 140 mg (0.17 mmol, 74%) of red crystals. Mp >300 °C; R_f: 0.53 (CH_2Cl_2/*n*-hexane, 1:1, v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.93 (s, 2H, N*H*), 1.34 (t, J = 7.2 Hz, 3H, C*H*$_3$), 1.54 (s, 36H, *H*$_{t\text{Bu}}$), 4.43 (q, J = 7.2 Hz, 4H, C*H*$_2$), 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*$_\beta$), 8.87-8.88 (m, 1H, Ar-*H*), 8.92 (d, J = 4.6 Hz, 2H, *H*$_\beta$), 9.06 (d, J = 4.6 Hz, 2H, *H*$_\beta$), 9.33 (d, J = 4.6 Hz, 2H, *H*$_\beta$), 10.22 (s, 1H, *H*$_{meso}$); ^{13}C NMR (100 MHz, $CDCl_3$) 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,

61.2, 35.1, 31.7, 14.3; UV/vis (CH_2Cl_2) λ_{max} (log ε): 414 (5.65), 510 (4.20), 545 (3.64), 585 (3.64), 639 nm (3.50); LRMS (MALDI) *m/z* (%): 835 (53) [M^+], 806 (100) [$M^+ - C_2H_5$], 791 (78) [$M^+ - C_3H_8$], 775 (82) [$M^+ - C_3H_8O$], 734 (32) [$M^+ - C_6H_{14}O$]; HRMS (MALDI) *m/z*: 834.4846 (Calcd for $C_{57}H_{62}N_4O_2$: 834.4873).

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_3PO_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; *Rf*: 0.29 (CH_2Cl_2/*n*-hexane, 1:1, v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.73 (s, 2H, N*H*), 1.38 (t, *J* = 7.2 Hz, 6H, C*H*$_3$), 1.46 (s, 36H, $H_{t\text{Bu}}$), 4.41 (q, *J* = 7.2 Hz, 4H, C*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_β), 8.69 (m, 2H, Ar-*H*), 8.66 (d, *J* = 4.6 Hz, 4H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) δ (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_2Cl_2) λ_{max} (log ε): 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) [$M^+ - C_2H_5$], 895 (40) [$M^+ - C_6H_{14}$], 853 (17) [$M^+ - C_7H_{14}O_2$]; HRMS (MALDI) *m/z*: 982.5369 (Calcd for $C_{60}H_{70}N_4O_4$: 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_3PO_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_2O. The solvent was removed and the residue was dissolved in CH_2Cl_2 and filtered through silica gel. The porphyrin was purified with column chromatography using CH_2Cl_2:petroleum ether (1:1). The target was obtained in 90% yield (291 mg, 0.35 mmol) after recrystallization from CH_2Cl_2: MeOH. Mp >300 °C; *Rf*: 0.39 (CH_2Cl_2/*n*-hexane = 1:1 + 1 drop MeOH, v/v); ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): –2.93 (s, 2H, N*H*), 1.53 (s, 6H, $H_{t\text{Bu}}$), 1.55 (s, 30H, $H_{t\text{Bu}}$), 3.97 (s, 3H, OC*H*$_3$), 7.82 (m, 6H, *J* = 4.5 Hz, Ar-*H*), 7.85 (s, 1H, Ar-*H*), 8.21 (d, 4H, *J* = 1.7Hz, Ar-*H*), 8.40 (d, 1H, *J* = 7.5 Hz, Ar-*H*), 8.48 (d, 1H, *J* = 7.9Hz, H_β), 8.78 (d, 2H, *J* = 4.8 Hz, H_β), 8.90 (s, 1H, Ar-*H*), 8.96 (d, 2H, *J* = 4.7 Hz, H_β), 9.08 (d, 2H, *J* = 4.6 Hz, H_β), 9.35 (d, 2H, *J* = 4.6 Hz, H_β), 10.24 (s, 1H, H_{meso}); ^{13}C NMR (150 MHz, $CDCl_3$): δ (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_2Cl_2): λ_{max} (log ε) = 415 (5.69), 511 (4.28), 545 (3.85), 584 (3.77), 639 nm (3.49); HRMS (MALDI) *m/z*: 820.4742 (Calcd. for [$C_{56}H_{60}N_4O_2$]: 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_3PO_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_2Cl_2/MeOH (260 mg, 78%, 0.43 mmol). Mp >300 °C; R_f: 0.12 (CH_2Cl_2/ *n*-hexane = 1:1 + 2 drops MeOH, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –3.02 (s, 2H, N*H*), 3.96 (s, 3H, OC*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 = 4.6 Hz, H_β), 10.25 (s, 1H, H_{meso}); ^{13}C NMR (150 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_2Cl_2): λ_{max} (log ε) = 412 (5.44), 509 (4.09), 543 (3.55), 582 (3.58), 651 nm (3.25); HRMS (MALDI) *m/z*: 596.2223. (Calcd. for $C_{40}H_{28}N_4O_2$: 596.2212).

[10,20-Bis(3,5-di-*tert*-butyl)phenyl-5-(3'-carboxyethyl)phenylporphyrinato]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_2Cl_2) followed by recrystallization from CH_2Cl_2/MeOH. Yield: 201 mg (0.22 mmol, 85%) of pink crystals. Mp >300 °C; R_f: 0.39 (CH_2Cl_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, C*H*$_3$), 1.54 (s, 36H, $H_{t\text{Bu}}$), 4.43 (q, J = 7.2 Hz, 2H, C*H*$_2$), 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}); ^{13}C 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_2Cl_2) λ_{max} (log ε): 416 (5.76), 543 nm (4.23); LRMS (MALDI) *m/z* (%): 896 (55) [M^+], 868 (100) [$M^+ - C_2H_5$], 824 (23) [$M^+ - C_3H_5O_2$], 796 (37) [$M^+ - C_5H_{11}O_2$]; HRMS (MALDI) *m/z*: 896.3989 (Calcd for $C_{57}H_{60}N_4O_2Zn$: 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_2Cl_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_2Cl_2/ *n*-hexane = 1:1 + 2 drops MeOH, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.75 (s, 2H, N*H*), 2.82 (s, 3H,

OC*H*$_3$), 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, *H*$_\beta$), 8.80 (d, *J* = 4.3 Hz, 2H, *H*$_\beta$), 8.85 (s, 1H, Ar-*H*), 8.91 (d, *J* = 4.3 Hz, 2H, *H*$_\beta$), 9.68 (d, *J* = 4.3 Hz, 2H, *H*$_\beta$); ^{13}C NMR (150 MHz, $CDCl_3$): 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 (CH_2Cl_2): λ_{max} (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 $C_{40}H_{27}N_4O_2Br$: 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. $PdCl_2(PPh_3)_2$ (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 CH_2Cl_2 and filtered through silica gel. After evaporation of the solvent the residue was again filtered through silica gel with CH_2Cl_2:petroleum ether (1:1, v/v). Following this the product was eluted from the silica gel with CH_2Cl_2 and the solvent was evaporated. The crude product was purified by recrystallization from CH_2Cl_2:MeOH giving porphyrin **6d** in 127 mg (62%, 0.18 mmol). Mp >300 °C; *R*$_f$: 0.26 (CH_2Cl_2/ *n*-hexane = 1:1+ 2 drops MeOH, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.43 (s, 2H, N*H*), 0.61 (s, 9H, TMS-C*H*$_3$), 3.98 (s, 3H, OC*H*$_3$), 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, *H*$_\beta$), 8.77 (d, *J* = 4.7 Hz, 2H, *H*$_\beta$), 8.85 (s, 1H, Ar-*H*), 8.90 (d, *J* = 4.7 Hz, 2H, *H*$_\beta$), 9.67 (d, *J* = 4.7 Hz, 2H, *H*$_\beta$); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 168.0, 142.3, 139.1, 139.0, 135.4, 135.2, 129.9, 128.6, 127.5, 53.1; UV/vis (CH_2Cl_2): λ_{max} (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 $C_{45}H_{36}N_4O_2Si$: 692.2608).

5-(3'-Carboxymethyl)phenyl-15-(ethynyl)-10,20-diphenylporphyrin (6e). Porphyrin **6d** (90 mg, 0.13 mmol) was dissolved in CH_2Cl_2 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 CH_2Cl_2 and the solvent was removed *in vacuo* yielding the target compound in quantitative yield (80 mg, 0.13 mmol). Mp >300 °C; *R*$_f$: 0.24 (CH_2Cl_2/ *n*-hexane =1:1 + 2 drops MeOH, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.49 (s, 2H, N*H*), 3.98 (s, 3H, OC*H*$_3$), 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, *H*$_\beta$), 8.78 (d, *J* = 4.4 Hz, 2H, *H*$_\beta$), 8.85 (s, 1H, Ar-*H*), 8.92 (d, *J* = 4.4 Hz, 2H, *H*$_\beta$), 9.70 (d, *J* = 4.7 Hz, 2H, *H*$_\beta$); ^{13}C NMR (150 MHz, $CDCl_3$) 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 (CH_2Cl_2): λ_{max} (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

$C_{42}H_{28}N_4O_2$: 620.2212).

5,5-(1,2-Ethyndiyl)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), $AsPh_3$ (34 mg, 0.11 mmol) and $Pd_2(dba)_3$ (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. CH_2Cl_2:petroleum ether (1:1, v/v) was used to remove impurities and then the product was eluted with CH_2Cl_2. The crude product was purified by recrystallization from CH_2Cl_2:MeOH and **6f** was obtained in 50% yield (60 mg, 0.05 mmol). Mp >300 °C; *Rf*: 0.23 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.01 (s, 4H, N*H*), 4.00 (s, 6H, OCH_3), 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, H_β), 8.83 (d, J = 4.6 Hz, 4H, H_β), 8.90 (s, 2H, Ar-*H*), 9.10 (d, J = 4.5 Hz, 4H, H_β), 10.35 (d, J = 4.6 Hz, 4H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$) 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 (CH_2Cl_2): λ_{max} (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 $C_{82}H_{54}N_8O_4$: 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 (CH_2Cl_2). The solvents were removed *in vacuo*. Yield: 14 mg (0.01 mmol, 71%) of dark purple solid. Mp >300 °C; *Rf*: 0.76 (CH_2Cl_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): 1.35 (t, J = 7.1 Hz, 6H, CH_3), 1.45 (s, 72H, $H_{t\text{Bu}}$), 4.36 (q, J = 7.1 Hz, 4H, CH_2), 7.33 (s, 4H, H_β), 7.58-7.65 (m, 18H, Ar-*H*/H_β), 7.68 (d, J = 4.6 Hz, 4H, H_β), 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*); ^{13}C NMR not obtained due to low solubility of sample; UV/vis (CH_2Cl_2) λ_{max} (log ε): 416 (4.98), 456 (4.54), 578 (4.91), 920 (4.14), 1043 nm (4.36); LRMS (MALDI) *m/z* (%): 1786 (100) [M^+], 1762 (12) [$M^+ - C_2H_5$], 1734 (3) [$M^+ - C_2H_5$]; HRMS (MALDI) *m/z*: 1786.7614 (Calcd for $C_{114}H_{114}N_8O_4Zn_2$: 1786.7546).

Bis[5-(3'-benzoic acid)-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 H_2O (3 mL) with stirring 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 the solution was acidified with 1 M HCl. The product was extracted *via* CH_2Cl_2 and 1% MeOH,

dried over Na_2SO_4, and filtered. The solvents were removed *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_2Cl_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) δ (ppm): 1.41 (s, 72H, $H_{t\mathrm{Bu}}$), 7.07 (s, 4H), 7.50-7.62 (m, 22H, Ar-*H*/H_β), 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) λ_{max} (log ε): 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 $C_{110}H_{106}N_8O_4Zn_2$: 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_2CO_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 *in vacuo* and the residue dissolved in CH_2Cl_2 (100 mL), washed with saturated aqueous $NaHCO_3$, brine and H_2O (2×100 mL, each), dried over Na_2SO_4 and filtered. The crude product was purified *via* column chromatography on silica gel (CH_2Cl_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_2Cl_2/*n*-hexane, 1:1, v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.79 (br. s, 2H, N*H*), 1.44-1.54 (m, 4H, CH_2), 1.80-1.90 (m, 4H, CH_2), 3.17 (t, J = 7.0 Hz, 2H, CH_2), 4.13 (t, J = 6.3 Hz, 2H, CH_2), 7.30 (d, J = 8.3 Hz, 1H, Ar-*H*), 7.61 (t, J = 7.5 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_β), 8.88 (d, J = 4.8 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) δ (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_2Cl_2) λ_{max} (log ε): 418 (5.48), 516 (4.07), 550 (3.65), 590 (3.55), 646 nm (3.44); HRMS (MALDI) *m/z*: 840.2324 (Calcd for $C_{50}H_{41}N_4OI$: 840.2325.

[5{3-(6'-Thioacetate)hexyloxy)phenyl}10,15,20-triphenyl]porphyrin (12). a) {5-(3'Bromo-hexyl)oxy)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 *via* column chromatography on silica gel (CH_2Cl_2) followed by trituration with 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_2Cl_2/*n*-hexane, 1:1, v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.79 (br. s, 2H, N*H*), 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,

11H, Ar/Ph-*H*), 8.20 (d, *J* = 6.1 Hz, 6H, Ph-*H*), 8.83 (app. s, 6H, H_β), 8.88 (d, *J* = 4.8 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.0, 157.4, 143.4, 142.2, 134.5, 131.6, 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 (CH_2Cl_2) λ_{max} (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) [$M^+ - C_2H_3O$], 713 (13) [$M^+ - C_2H_3OS$], 630 (32) [$M^+ - C_8H_{15}OS$]; HRMS (MALDI) *m/z*: 788.3171 (Calcd for $C_{52}H_{44}N_4O_2S$: 788.3185).

[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 (CH_2Cl_2) followed by trituation with isopropyl alcohol. Yield: 160 mg (0.12 mmol, 74%) of purple solid. Mp 125-127 °C; R_f: 0.53 (CH_2Cl_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): 1.21-1.28 (m, 2H, CH_2), 1.40-1.46 (m, 2H, CH_2), 1.54-1.61 (m, 2H, CH_2), 1.81-1.88 (m, 4H, CH_2), 2.23 (s, 3H, CH_3), 2.81 (t, *J* = 7.1 Hz, 2H, CH_2), 4.11 (t, *J* = 6.4 Hz, 2H, CH_2), 7.29 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 7.60 (t, *J* = 8.1 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, H_β), 8.98 (d, *J* = 4.6 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.9, 157.3, 150.2, 150.1, 144.0, 134.4, 132.0, 131.9, 127.5, 127.4, 127.3, 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 (CH_2Cl_2) λ_{max} (log ε): 420 (5.62), 548 (4.18), 586 nm (3.42); LRMS (MALDI) *m/z* (%): 850 (100) [M^+], 775 (5) [$M^+ - C_2H_3OS$], 692 (11) [$M^+ - C_8H_{15}OS$]; HRMS (MALDI) *m/z*: 850.2289 (Calcd for $C_{52}H_{42}N_4O_2SZn$: 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. K_2CO_3 (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 CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ (4×100 mL), brine (2×100 mL) and water (2×100 mL), dried over Na_2SO_4, and filtered. The solvents were removed *in vacuo* and the residue purified *via* column chromatography on silica gel (CH_2Cl_2). The solvents were removed to yield an oil-like, purple product. Yield: 512 mg (0.45 mmol, 77%). Mp 83-85 °C; R_f: 0.48 (CH_2Cl_2/*n*-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): –2.76 (br. s, 2H, N*H*), 1.94-1.96 (m, 16H, CH_2), 2.47 (t, *J* = 6.8 Hz, 8H, CH_2), 3.70 (s, 12H, CH_3), 4.21 (t, *J* = 5.8 Hz, 8H, CH_2), 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, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (CH_2Cl_2) λ_{max} (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 $C_{68}H_{70}N_4O_{12}$: 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 (CH_2Cl_2/MeOH, 99:1, v/v). Yield: 187 mg (0.16 mmol, 89%) of a purple oil. Mp 83-85 °C; R_f: 0.40 (CH_2Cl_2/*n*-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.90-1.98 (m, 16H, C*H*$_2$), 2.45 (t, *J* = 7.0 Hz, 8H, C*H*$_2$), 3.67 (s, 12H, C*H*$_3$), 4.18 (t, *J* = 5.6 Hz, 8H, C*H*$_2$), 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, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (CH_2Cl_2) λ_{max} (log ε): 420 (5.71), 550 (4.29), 584 nm (3.49); LRMS (MALDI) *m/z* (%): 1196 (100) [M$^+$], 736 (7) [M$^+$ – $C_{24}H_{44}O_8$]; HRMS (MALDI) *m/z*: 1196.4116 (Calcd for $C_{68}H_{68}N_4O_{12}Zn$: 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. K_2CO_3 (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 CH_2Cl_2 (100 mL), followed by washing with saturated aqueous $NaHCO_3$, brine and H_2O (3×100 mL, each). The organic extracts were combined, dried over aqueous Na_2SO_4 and filtered. The solvents were removed *in vacuo* and the residue purified *via* column chromatography on silica gel (CH_2Cl_2) followed by recrystallization from CH_2Cl_2/MeOH. Yield: 173 mg (0.15 mmol, 56%) of purple crystals. Mp 86-88 °C; R_f: 0.56 (CH_2Cl_2/*n*-hexane/MeOH, 1:1:0.4, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.12-2.19 (m, 8H, C*H*$_2$), 2.56 (t, *J* = 7.2 Hz, 8H, C*H*$_2$), 3.65 (s, 12H, C*H*$_3$), 4.12 (t, *J* = 6.0 Hz, 8H, C*H*$_2$), 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, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.6, 157.3, 142.5, 142.2, 132.1, 27.7, 126.8, 120.2, 118.7, 114.0, 66.9, 51.6, 30.6, 24.7; UV/vis (CH_2Cl_2) λ_{max} (log ε): 414 (5.41), 528 nm (4.27); LRMS (MALDI) *m/z* (%): 1134 (100) [M$^+$]; HRMS (MALDI) *m/z*: 1134.3539 (Calcd for $C_{64}H_{60}N_4O_{12}Ni$: 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), K_2CO_3 (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; R_f: 0.52

(CH_2Cl_2/*n*-hexane/MeOH, 1:1:0.5, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.85-1.87 (m, 16H, C*H*$_2$), 2.40 (t, *J* = 6.8 Hz, 8H, C*H*$_2$), 3.64 (s, 12H, C*H*$_3$), 4.08 (t, *J* = 5.8 Hz, 8H, C*H*$_2$), 7.20-7.23 (m, 4H, Ar-*H*), 7.51-7.61 (m, 12H, Ar-*H*), 8.77 (s, 8H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (CH_2Cl_2) λ_{max} (log ε): 416 (5.13), 528 nm (3.99); LRMS (MALDI) *m/z* (%): 1190 (100) [M$^+$]; HRMS (MALDI) *m/z*: 1190.4165 (Calcd for $C_{68}H_{68}N_4O_{12}Ni$: 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 CH_2Cl_2, washed with H_2O (2×250 mL) and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo* and the residue was recrystallized from CH_2Cl_2/MeOH. Yield: 62 mg (0.06 mmol, 65%) of red crystals. Mp 145-147 °C; R_f: 0.67 (CH_2Cl_2/*n*-hexane/MeOH, 2:1:0.6, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5, 30:1, v/v) δ(ppm): 2.16-2.24 (m, 8H, C*H*$_2$), 2.58 (t, *J* = 7.0 Hz, 8H, C*H*$_2$), 4.16 (t, *J* = 6.1 Hz, 8H, C*H*$_2$), 7.20-7.23 (m, 4H, Ar-*H*), 7.49-7.60 (m, 12H, Ar-*H*), 8.76 (s, 8H, *H*$_\beta$), 11.06 (br. S, 4H, COO*H*); ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-d_5, 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 (CH_2Cl_2) λ_{max} (log ε): 414 (5.40), 528 nm (4.26); LRMS (MALDI) *m/z* (%): 1078 (100) [M$^+$]; HRMS (MALDI) *m/z*: 1078.2903 (Calcd for $C_{60}H_{52}N_4O_{12}Ni$: 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; R_f: 0.68 (CH_2Cl_2/*n*-hexane/MeOH, 1:1:0.7, v/v/v, silica gel, 6×3 cm); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5, 30:1, v/v) δ (ppm): 1.81-1.89 (m, 16H, C*H*$_2$), 2.42 (t, *J* = 6.9 Hz, 8H, C*H*$_2$), 4.09 (t, *J* = 5.8 Hz, 8H, C*H*$_2$), 7.19-7.22 (d, *J* = 6.9 Hz, 4H, Ar-*H*), 7.48-7.57 (m, 12H, Ar-*H*), 8.76 (s, 8H, *H*$_\beta$); ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-d_5, 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 (CH_2Cl_2) λ_{max} (log ε): 416 (5.29), 528 nm (4.15); LRMS (MALDI) *m/z* (%): 1134 (100) [M$^+$]; HRMS (MALDI) *m/z*: 1134.3508 (Calcd for $C_{64}H_{60}N_4O_{12}Ni$: 1134.3561).

[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 K_2CO_3 (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 (CH_2Cl_2/*n*-hexane, 1:1, v/v) followed by

recrystallization from CH_2Cl_2/*n*-hexane. Yield: 211 mg (0.24 mmol, 77%) of purple crystals. Mp >300 °C; R_f: 0.80 (CH_2Cl_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*H*), 1.59 (s, 36H, $H_{t\text{Bu}}$), 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_2Cl_2) λ_{max} (log ε): 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$^+$ – $C_7H_{14}O_3$], 731 (28) [M$^+$ – $C_8H_{17}O_3$], 717 (32) [M$^+$ – $C_9H_{20}O_3$]; HRMS (MALDI) *m/z*: 892.5264 (Calcd for $C_{60}H_{68}N_4O_3$: 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_2Cl_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_2Cl_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, $H_{t\text{Bu}}$), 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*), 7.83 (app. s, 2H, 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, 131.1, 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_2Cl_2) λ_{max} (log ε): 416 (5.69), 544 (4.28), 582 nm (3.48); LRMS (MALDI) *m/z* (%): 954 (100) [M$^+$]; HRMS (MALDI) *m/z*: 954.4426 (Calcd for $C_{60}H_{66}N_4O_3Zn$: 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_2Cl_2/*n*-hexane, 1:1, v/v), followed by isolation of the triply-fused dimer using CH_2Cl_2/2% MeOH. Yield: 56 mg (0.03 mmol, 54%) of purple crystals. Mp >300 °C; R_f: 0.66 (CH_2Cl_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, $H_{t\text{Bu}}$), 1.88-1.91 (m, 8H, CH_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_2Cl_2) λ_{max} (log ε): 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); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.42 (s, 72H, $H_{t\text{Bu}}$), 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*), 8.11 (d, J = 4.7 Hz, 4H, H_β), 8.18 (d, J = 8.4 Hz, 4H, Ar-*H*), 8.68 (d, J = 4.7 Hz, 4H, H_β), 9.00 (d, 4H, J = 4.7 Hz, H_β), 9.04 (d, J = 4.7 Hz, 4H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$) 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) λ_{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); ^{1}H NMR (400 MHz, $CDCl_3$/pyridine-d_5, 20:1, v/v) δ(ppm): 1.42 (s, 72H, $H_{t\text{Bu}}$), 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*); ^{13}C NMR (100 MHz, $CDCl_3$/pyridine-d_5, 20:1, v/v) 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) λ_{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.[32] Diffraction data for the compound was collected on a Bruker APEX 2 DUO CCD diffractometer using Incoatec IμS CuK$_\alpha$ (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.[33] The structure was solved with Direct Methods and refined against $|F^2|$ with the program OLEX^2 using all data.[34a] 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 SHELXTL.[34b,c] $C_{57}H_{60}N_4O_2Zn$ (M = 898.46 g.mol^{-1}): monoclinic, space group $P2_1/n$, a = 26.0025(13) Å, b = 5.7174(3) Å, c = 33.5335(19) Å, β = 100.215(4), V = 4906.3(5) Å^3, Z= 4, T = 99.97K, μ(CuKα) = 1.040 mm^{-1}, D_{calc} = 1.216 g cm^{-3}, 27214 reflections measured (3.976° ≤ 2θ≤ 122.518°), 5281 unique (R_{int} = 0.1159, R_{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**. $C_{53}H_{43}Cl_3N_4O_2SZn$ (M =971.69 g.mol^{-1}): triclinic, space group P1, α = 10.7348(4) Å, b = 10.9532(4) Å, c = 11.2018(4) Å, α = 73.7480(10)°, β = 80.1710(10)°, γ = 74.9300(10)°, V = 1214.16(8) Å^3, Z = 1, T= 100.0K, μ(CuKα) = 2.971 mm^{-1}, D_{calc} = 1.329 g.cm^{-3}, 29482 reflections measured (8.268° ≤ 2θ≤ 137.262°), 8543 unique (R_{int} = 0.0312, R_{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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