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A Convenient Synthesis of Trimeric Porphyrins with Systematically Variable Geometry

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Abstract: A facile synthesis of trimeric porphyrins is reported. The geometry of the terminal porphyrins relative to the central macrocycle can be varied without significant changes to the synthetic procedure. This procedure also enables systematic control over the metallation states of the trimeric porphyrins.

INTRODUCTION

The extensive investigations into the primary events occurring within the reaction centers of photosynthetic bacteria have served to elucidate the mechanisms and dynamics of electron transfer within these membrane-bound proteins.[1] These investigations have been greatly assisted by a number of model studies incorporating derivatized porphyrins.[2] As a direct result of the continued search for realistic model systems many new synthetic routes to functionalized porphyrins have been developed. Of particular note are the advances reported in the synthesis of covalently-assembled multiporphyrin arrays.[3]

The synthesis of dimeric porphyrins represents major synthetic achievement in porphyrin chemistry. Yet today, thanks to the efforts of a number of research groups, dimeric porphyrins are becoming relatively common. Indeed, many much larger porphyrin arrays have been reported in recent years.[3] However, even the preparation of dimeric porphyrins can require long and difficult synthetic procedures that result in the isolation of only small amounts of material. Nonetheless the chemistry displayed by the metal complexes of dimeric porphyrins is so intriguing that the laborious procedures are often worth the effort. Reactions such as the electrocatalytic reduction of oxygen to water by dicobalt face-to face porphyrins[4] and of dioxygen by diruthenium cofacial diporphyrins[5] give some indication of the potential of these systems.

To date, explorations of the chemistry of trimeric or larger porphyrin arrays has been severely limited by the complex procedures that are required for their synthesis. Porphyrin arrays with specific metallation sites could be useful for a variety of tasks such as light harvesting, small molecule activation, catalysis and molecular recognition. Here we report a convenient route to trimeric porphyrins that can be prepared in good yield, with a minimal number of steps. The methodology described gives good control over the metallation states of the trimeric porphyrin and enables simple control of the overall trimer geometry.[6]

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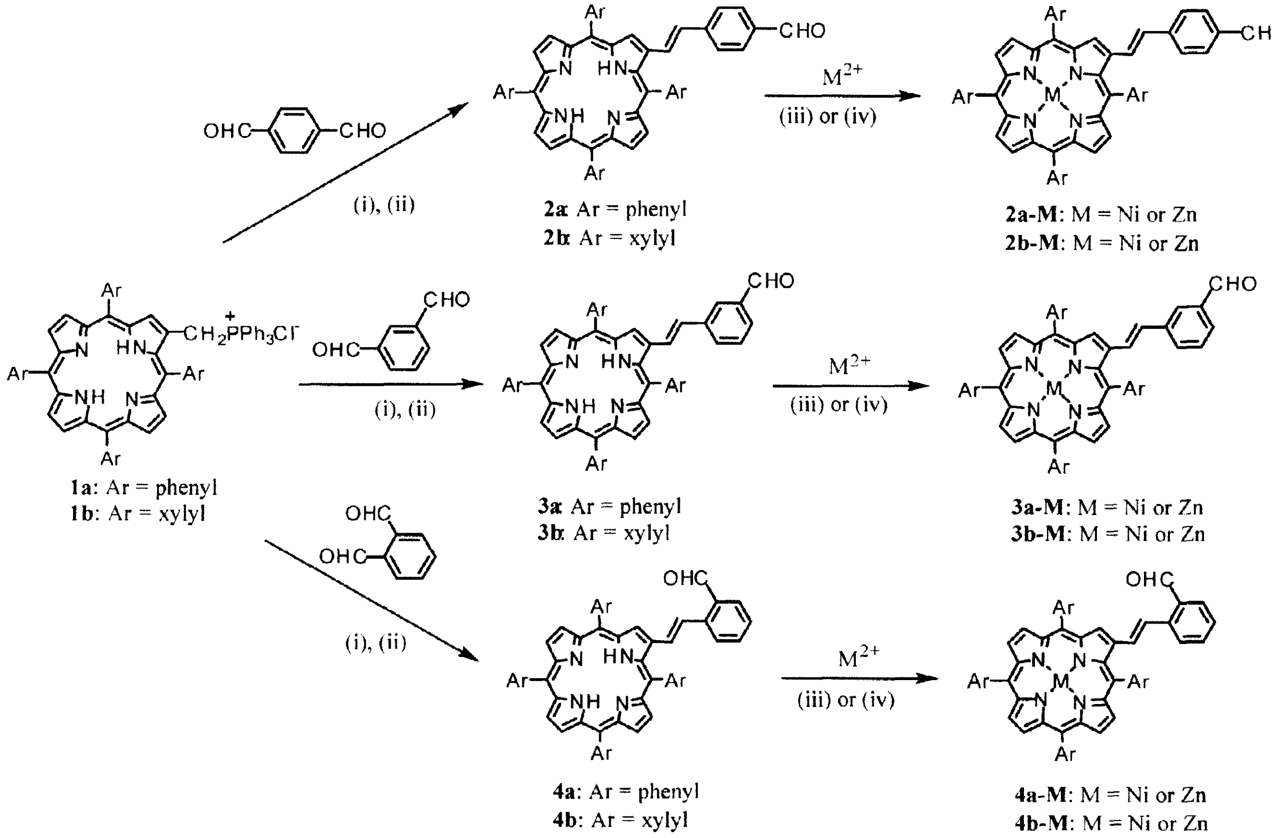
RESULTS AND DISCUSSION

Synthesis of Monomeric Porphyrins

The major advantage of the synthetic route to trimeric porphyrins described here over those currently in the literature lies in the facile and high yielding formation of a series of monomeric porphyrin building blocks.[6,7] Most trimer preparations in the literature proceed *via* the condensation of two equivalents of a porphyrin aldehyde with two equivalents of dipyrrylmethane, forming a new linking central porphyrin.[2c, 3a,b] The problem with these syntheses has traditionally been the complex and low yielding routes to the formation of the porphyrin aldehyde. The key feature of our synthesis lies in the use of a porphyrin phosphonium salt as a crucial intermediate in the formation of the desired porphyrin aldehydes.[8]

These phosphonium salts are readily prepared from tetraarylporphyrins in few steps and high yield (>85% from tetraphenylporphyrin (TPP), (**1a**, Scheme 1)) and may be made on a gram scale. Formation of the monomeric porphyrin aldehyde building blocks from this material was achieved as previously communicated for TPP[6,7] and by an analogous method[9] from tetraxylylporphyrin (TXP). Reactions of the phosphonium salts with *o*-, *m*- or *p*-benzenedicarboxaldehydes under standard Wittig conditions give *cis/trans* mixtures of the desired building blocks which are readily isomerized to the *trans*-isomers (**2**-**4**) in good yield with iodine (Scheme 1).[7] These building blocks can then be metallated under standard conditions to give Ni and Zn metalloporphyrins allowing further variation of the final trimeric products.[6,7]



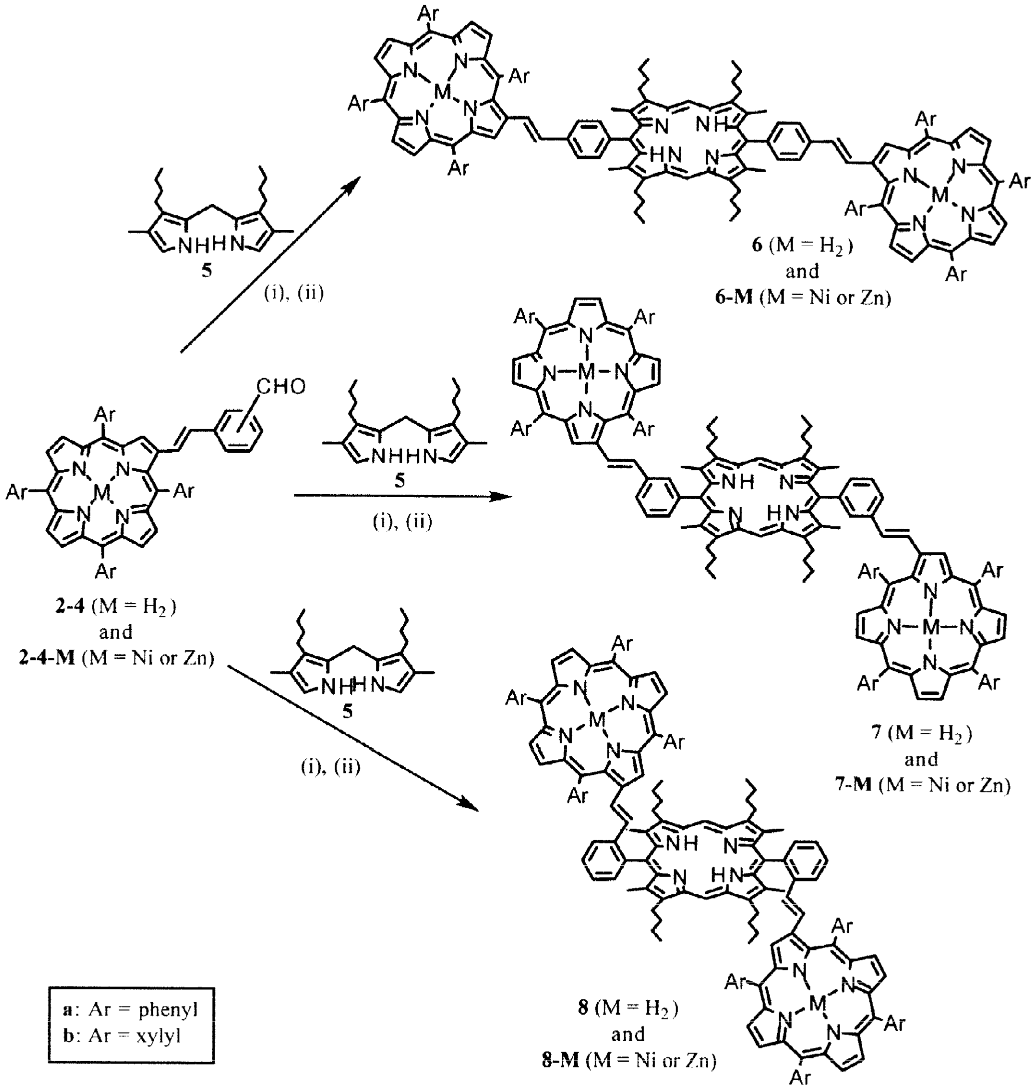
(i) DBU, CH_2Cl_2, R.T.; (ii) I_2, CH_2Cl_2, R.T.; (iii) $Zn(OAc)_2$, MeOH, CH_2Cl_2; (iv) $NiBr_2$, DMF.

Scheme 1

Synthesis of Trimeric Porphyrin Arrays

Recently, a number of research groups have taken advantage of the "moderate dilution" synthetic strategy developed by Lindsey, in preparing trimeric porphyrin arrays. Lindsey showed that pyrrole and a range of sensitive aldehydes react reversibly in the presence of an acid catalyst to give porphyrinogens at room temperature.[10] These may then be irreversibly oxidized to give the desired porphyrin. Sessler extended this chemistry to the reaction between dipyrrylmethanes and aldehyde-substituted aryl porphyrins affording trimeric porphyrins routinely in >50% yields.[3c,d]

By utilizing Lindsey's conditions, trimeric porphyrin arrays (**6-8**) and (**6-8-M**) may be formed from the condensation of the above porphyrin aldehyde building blocks (**2-4**) and (**2-4-M**) with dipyrrylmethane (**5**) (Scheme 2). These reactions proceed cleanly and in good yield using trifluoroacetic acid (TFA) as the acid catalyst. The porphyrinogen initially formed is oxidized to give the desired porphyrin by the addition of *o*-chloranil to the reaction mixture. Notably, the integrity of the zinc metallated trimers is retained under these conditions.



a: Ar = phenyl
b: Ar = xylyl

(i) CF_3CO_2H, CH_2Cl_2; (ii) *o*-chloranil.

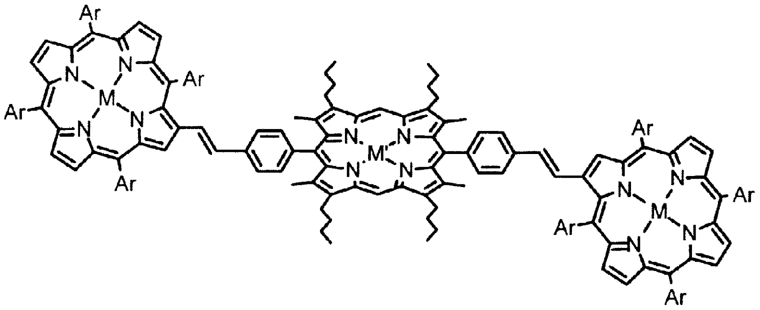
Scheme 2

Full metallation of these trimers may be achieved by insertion of a metal into all porphyrins of the free base trimers (**6-8**) or the central free base porphyrin of the bismetalloporphyrin trimers (**6-8-M**) described above.

Para *Trimeric Porphyrin Arrays*

The condensation of *para* porphyrin aldehyde building blocks (**2a**, **2b**, **2a-Ni**, **2b-Ni**, **2a-Zn**, **2b-Zn**) with dipyrrylmethane (**5**) give the corresponding trimeric porphyrin arrays (**6a**, **6b**, **6a-Ni$_2$**, **6b-Ni$_2$**, **6a-Zn$_2$**, **6b-Zn$_2$**) in approximately 70% yields, under Lindsey's conditions (Scheme 2).

Further metallation of (**6b-Ni$_2$**) and (**6b-Zn$_2$**) is easily carried out using zinc(II) acetate and nickel(II) acetate respectively to give the novel heterotrimetallic complexes (**6b-Ni$_2$Zn**) and (**6b-Zn$_2$Ni**).



6b-Ni$_2$Zn: M=Ni, M'=Zn, Ar=xylyl
6b-Zn$_2$Ni: M=Zn, M'=Ni, Ar=xylyl

The ^{1}H NMR spectrum of (**6b-Ni$_2$Zn**) (Figure 1) shows a number of features common to the spectra of all of these trimeric products. The *meso* protons on the central porphyrin are observed as a singlet at around 10.30 ppm for the *ortho* and *para* isomers and at about 10.45 ppm for the *meta* isomers. The β-pyrrolic protons appear as a complex multiplet around 8.80-9.00 ppm with the lone β-pyrrolic proton adjacent to the site of substitution commonly shifted downfield past 9.00 ppm. The vinyl protons resonate as 16 Hz coupled doublets between 7 and 8 ppm, but are often masked by the aromatic protons which give a complex series of signals in this region. The signals due to the protons of the butyl groups on the central porphyrin are complex multiplets at around 4.00, 2.25 and 1.80 ppm with a triplet at about 1.20 ppm for the terminal methyl group. The methyl protons on the central porphyrin ring appear between 2.65-2.70 ppm, as do the singlets for the remaining aromatic methyls in the TXP trimers. Finally, the highly shielded NH protons of the pyrrole rings, where present, are attributed to the broad singlets around -2.50 ppm.

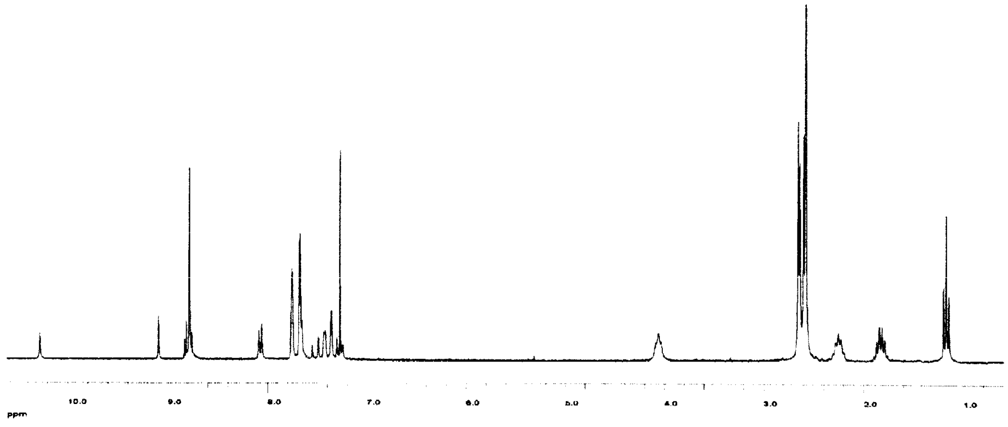


Fig. 1: ^{1}H NMR spectrum of (**6b-Ni$_2$Zn**)

After repeated attempts, small red crystals of (**6b-Ni$_2$Zn**) were obtained. These crystals were of poor quality and diffracted weakly so only a low resolution structure was obtained. The structure is shown in Figure 2 although the quality of this refinement is such that only the gross structure and atom connectivity can be obtained. Given the near planarity of the styryl substituent and the porphyrin core in a previous structure of this type, it was anticipated that the terminal porphyrin rings might lie orthogonal to the central porphyrin plane.[6] However, it is likely that the favourable crystal packing of the all planar porphyrin arrangement overcomes any energy advantage associated with increased conjugation resulting in a near planar structure.

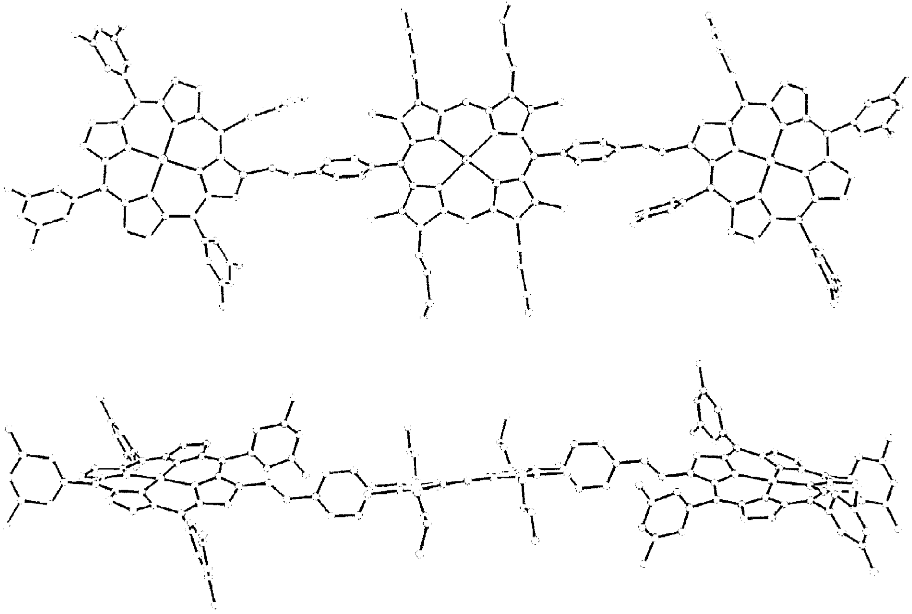
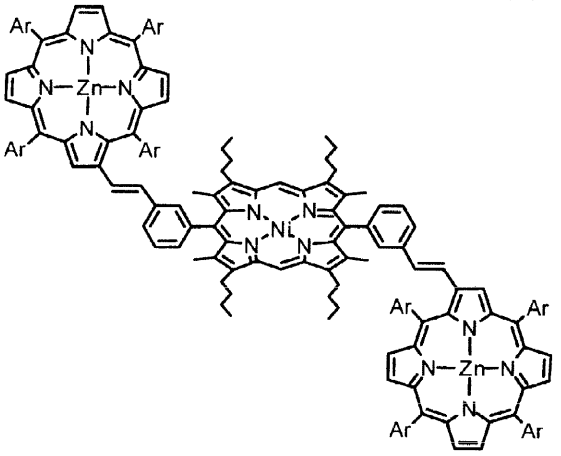


Fig. 2: Crystal structure of *p*-trimer (**6b-Ni$_2$Zn**). Top view and side view with protons removed.

Meta *Trimeric Porphyrin Arrays*

The condensation of *meta* porphyrin aldehyde building blocks (**3a**, **3b**, **3a-Ni**, **3b-Ni**, **3a-Zn**, **3b-Zn**) with dipyrrylmethane (**5**) give the corresponding trimeric porphyrin arrays (**7a**, **7b**, **7a-Ni$_2$**, **7b-Ni$_2$**, **7a-Zn$_2$**, **7b-Zn$_2$**) in approximately 70% yields, under Lindsey's conditions (Scheme 2).

Full metallation of the meta trimeric arrays is exemplified by the novel *meta* heterotrimetallic complex (**7b-Zn$_2$Ni**) which is readily obtained by the treatment of (**7b-Zn$_2$**) with nickel(II) acetate.



7b-Zn$_2$Ni: Ar = xylyl

Again the ^{1}H NMR spectra of these species contain similar features to those described for the *para* species above. However, all of the *meta* trimers exhibit upfield shifts for the protons on one of the aromatic rings of the two terminal porphyrins. Of particular note is that two isomers are observed in the ^{1}H NMR spectra for all the *meta* trimers and both of the isomers exhibit these upfield-shifted signals.

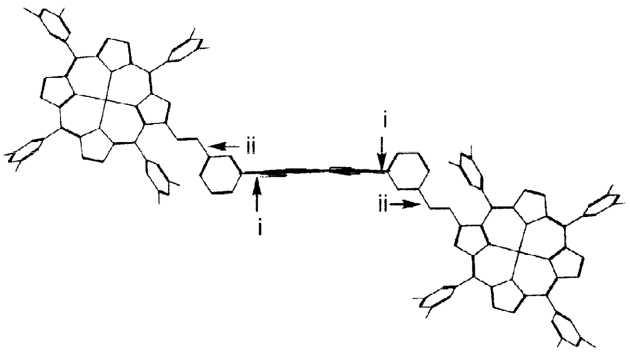
Thus, in the ^{1}H NMR spectrum of *meta* xylyl trimer (**7b**) two singlets at 1.35 ppm and 1.49 ppm, in a ratio of 2:1, are observed for four *meta* methyl groups on each isomer; the remaining xylyl methyl groups resonate around 2.5 ppm. The signals for two *para* aromatic protons are clearly identifiable for each isomer at 5.09 and 5.53 ppm, shifted upfield by 2 ppm. In addition, two sets of singlets are observed for two of the β-pyrrolic and the *meso*-protons. Evidence for these assignments was obtained from the COSY spectrum.

Upfield shifts of this magnitude are consistent with two of the xylyl groups pointing into the center of the central porphyrin ring and thus being affected by anisotropy of that ring's π-system. This information allows us to speculate on the geometry of these species.

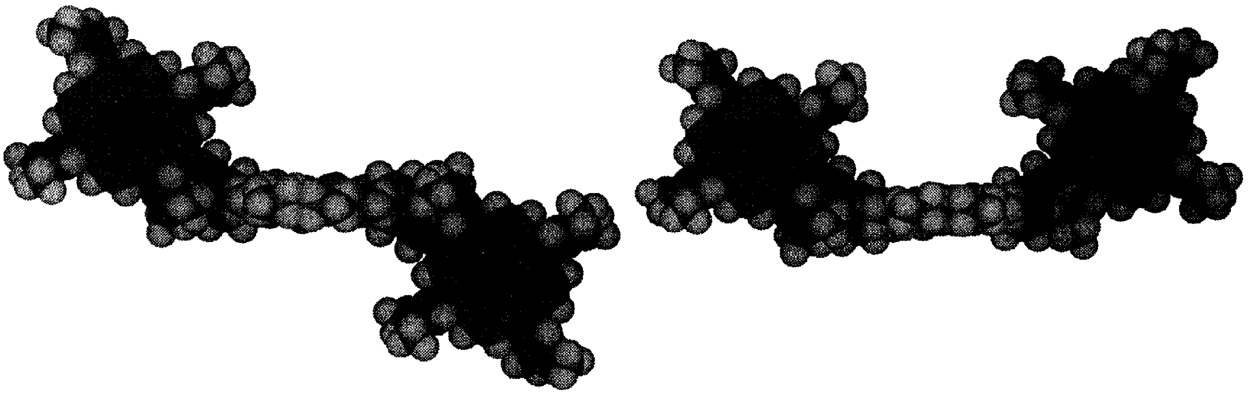
Atropisomers of substituted diphenylporphyrins of this type are well known and result from restricted substituted phenyl ring rotation by the neighbouring methyl groups.[11-13] Thus, it could be presumed that the two isomers are the *anti*- and *syn*-atropisomers represented by structures **A** and **B** in Figure 3. However, these 'open' structures would not appear to provide an explanation for the significant shielding effects observed in all of the *meta*-trimer ^{1}H NMR spectra. Rotation about the σ-bonds adjacent to the alkene linkage (**ii**, Figure 3) brings one aromatic substituent into the shielding cone of the central porphyrin (structures **C** and **D**) which would lead to large upfield shifts of those aromatic protons. Given the apparent unhindered rotation about σ-bond **ii**, the ^{1}H NMR spectra can be rationalised on the basis that the data results from an equilibrium mixture of conformations of which structure **C** is a significant contributor to the *anti*-atropisomer and **D** to the *syn*-atropisomer.

These models also account for the difference in chemical shifts of the anisotropically-affected atropisomer resonances. Given the normal symmetry relationships of atropisomers, their ^{1}H NMR spectra are usually identical.[11] In this case it is clear from structure **D** that, given the steric interactions of the tetraxylylporphyrins, the aromatic protons of the *syn*-atropisomer will be affected to a different degree by the anisotropy of the central ring. In addition, there will be additional ring current effects resulting from having two porphyrins on the same side of the trimer.

Confirmation of this atropisomer mixture appeared to come from the clean isolation of two bands on chromotography of the *meta* trimer products. Both of these bands have identical ^{1}H NMR spectra in all cases, the spectra showing resonances consistent with the two atropisomers as detailed above. When re-chromatographed, these 'pure' fractions also give rise to two bands. It would appear, then, that each of the isolated atropisomers is undergoing a rapid atropisomeric re-equilibration in solution. However, it has been reported[12] that there is a significant barrier to the rotation (60-70 kJ mol^{-1}) of substituted *meso* phenyl substituents on porphyrins with neighbouring methyl substituents; this barrier is even larger[13] (>100 kJ mol^{-1}) when *ortho*-substituted phenyls are involved. Variable temperature ^{1}H NMR spectroscopy over a 100°C range (-30°C to 70°C) has been performed on trimer (**7b**). Over this temperature range two species are always observed and no change is visible in the spectra. This is consistent with a high barrier to substituted phenyl ring rotation, indicative of an activation energy of greater than 70 kJ mol^{-1} for the thermal interconversion of these two atropisomers.[10] Therefore, it would appear that an alternative explanation for this behaviour is required.

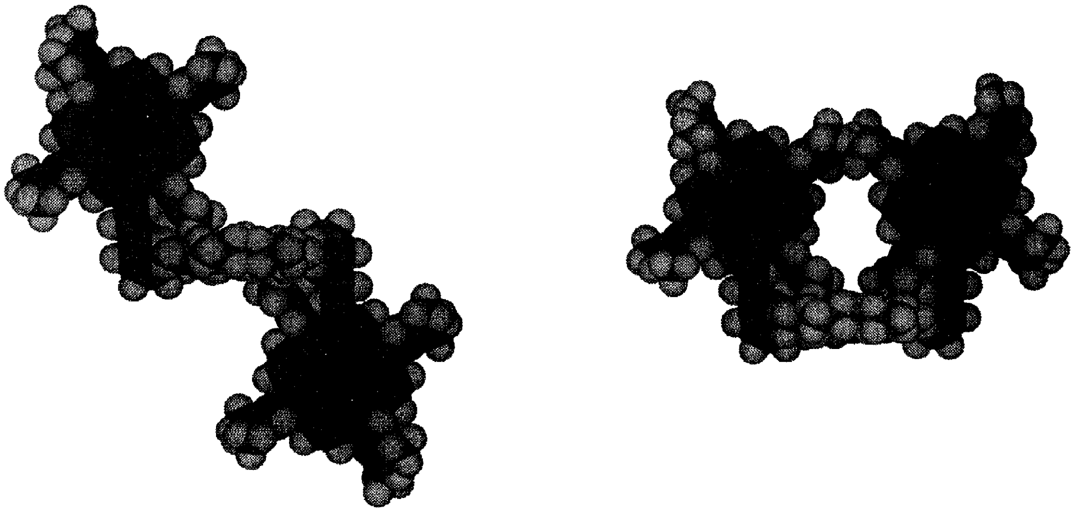


Carbon skeleton of *meta* trimer (Isomer A) showing σ-bonds rotated.



Isomer A

Isomer B
(By rotation about σ-bond i of Isomer A)



Isomer C
(By rotation about σ-bonds ii of Isomer A)

Isomer D
(By rotation about σ-bonds ii of Isomer B)

Figure 3: Computer-generated* CPK models of some conformations of *meta* trimer (**7b-Ni$_2$**).

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[*] These structures were generated in Chem3D Pro® from crystallographic data of published porphyrin structures. No energy minimisations were carried out.

It would seem likely then that these two chromatography bands result from solid-state surface effects; two stable conformations formed as a result of binding to silica gel which reform the atropisomer mixture in solution as observed by ^{1}H NMR spectroscopy. Preferential binding of porphyrin derivatives on silica gel has been observed by Lindsey during chromatography of atropisomers of *meso*-tetrakis(*o*-aminophenyl)porphyrin.[12]

Ortho *Trimeric Porphyrin Arrays*

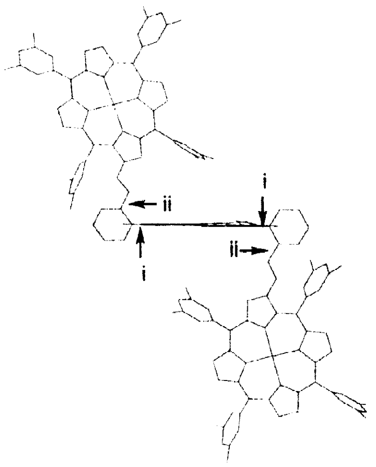
The condensations of *ortho* porphyrin aldehyde building blocks (**4a**, **4b**, **4a-Ni**, **4b-Ni**, **4a-Zn**, **4b-Zn**) with dipyrrylmethane (**5**) give the corresponding trimeric porphyrin arrays (**8a**, **8b**, **8a-Ni$_2$**, **8b-Ni$_2$**, **8a-Zn$_2$**, **8b-Zn$_2$**) in 40-50% yields, under Lindsey's conditions (Scheme 2). These yields are consistently 20% lower than those obtained for the analogous *meta* and *para* reactions. This lower yield may be explained in terms of the increased steric hindrance of the *ortho* aldehydes over their *meta* and *para* equivalents.

The ^{1}H NMR spectra of these *ortho* species contain the common features described for the *para* species above. Like the *meta*-trimers, all of the *ortho* isomers for these trimers also show upfield shifts for the protons on one of the aromatic rings of the two terminal porphyrins in each case. However, unlike the *meta*-trimers, only one set of signals is evident in the ^{1}H NMR spectra. For example, in the ^{1}H NMR spectrum of xylyl trimer (**8b**) the signals for the protons on one of the phenyl groups are observed as a singlet at 6.52 ppm due to the *ortho* protons and one at 4.46 ppm due to the *para* protons. A singlet at 0.27 ppm is observed for the methyl groups at the *meta* positions on these phenyl rings. Evidence for these assignments was obtained from the appropriate COSY spectra. Again, shifts of this magnitude are consistent with central porphyrin ring anisotropic effects.

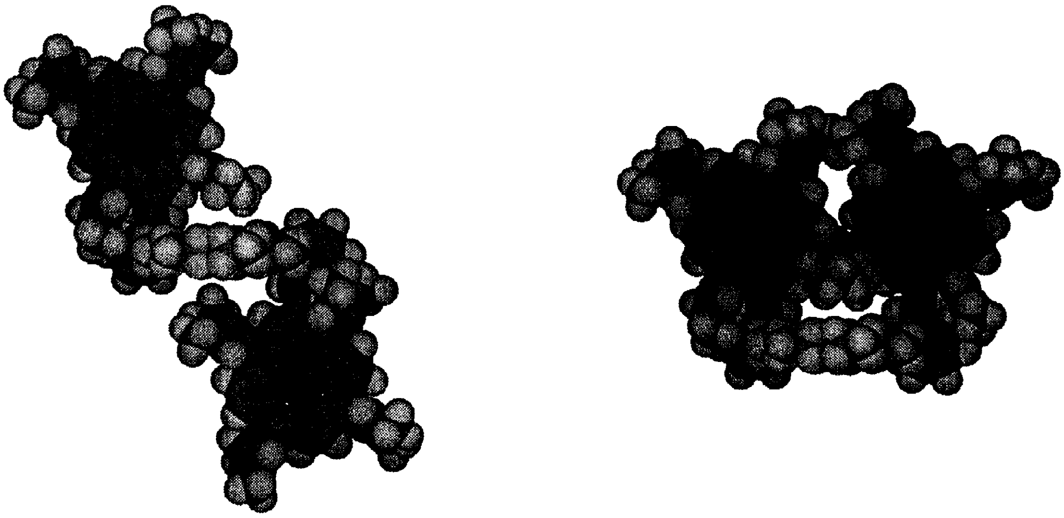
Examination of molecular models (Figure 4) would again seem to account for this observation of the formation of a single atropisomer. The 'open' conformers for the *ortho*-trimer *anti*- and syn-atropisomers are depicted in figure 4, structures **A** and **B**, respectively. It is quite clear that structure **B** is much more sterically congested than the analogous *meta*-trimer structure (B, Figure 3). Furthermore, rotation around σ-bond **ii** must be restricted as it leads to even greater steric interactions as shown in structure **D**. Therefore, it is not unreasonable to expect that the *syn*-atropisomer of the *ortho*-trimers will not be formed.

Notwithstanding this observation of only one isomer by ^{1}H NMR spectroscopy, the *ortho* trimers behave on chromatography in a completely analogous fashion to the *meta*-trimers, with the clean separation of two bands from silica gel columns. As before, these bands have identical ^{1}H NMR spectra and when re-chromatographed, these pure fractions also give rise to two separate bands. This provides compelling evidence for the existence of solid-state surface effects as previously postulated for the *meta*-trimers.

The degree and nature of metallation of the trimers reported above can be followed by UV-vis spectroscopy. Since the Soret band and Q bands of the free base central porphyrin are generally masked by the bands of the outer porphyrins, the free base or dimetallated trimer UV-vis spectrum is similar to that of the analogous building block. Thus, the UV-vis spectrum of *para*-trimer (**6b**) is typical of a free base porphyrin with a single Soret band and four Q bands in the visible region (Table 1) and compares favourably with that of the free base building block (**2b**). The spectrum of the dimetallated trimer (**6b-Ni$_2$**) is typical of a metallated porphyrin with two major Q bands (compare (**2b-Ni**)). The third Q band (508 nm) can be attributed to the free base central porphyrin, the band no longer masked by a Q band of the outer porphyrins. As expected, this band is lost on insertion of zinc into the trimer to give (**6b-Ni$_2$Zn**) (Table 1).

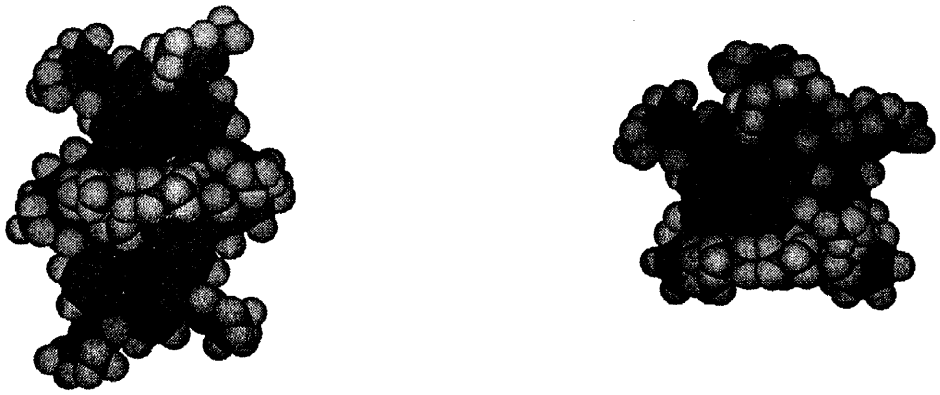


Carbon skeleton of *ortho*-trimer (Isomer A) showing σ-bonds rotated.



Isomer A

Isomer B
(By rotation about σ-bond i of Isomer A)



Isomer C
(By rotation about σ-bonds ii of Isomer A)

Isomer D
(By rotation about σ-bonds ii of Isomer B)

Figure 4: Computer-generated[*] CPK models of some conformations of *ortho* trimer (**8b-Ni$_2$**).

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[*] These structures were generated in Chem3D Pro® from crystallographic data of published porphyrin structures. No energy minimisations were carried out.

Table 1: UV-vis Spectral Data for Selected Building Blocks and Trimers

Compound	Soret Band	Q Bands			
2b*	430	526	568	601	658
6b	428	522	568	599	655
2b-Ni*	432		540	580	
6b-Ni$_2$	431	508	539	576	
6b-Ni$_2$Zn	432 and 412		540	575	

*Data taken from ref. 9.

Thus, not only can we make major variations in the state of metallation of these trimers, we can also monitor these variations simply using UV-vis spectroscopy.

CONCLUSION

In summary, this report shows that by using new synthetic strategy, porphyrin trimers may be formed simply and in good yield using methodologies well suited to scaling up.[15] A large degree of control over the geometry and metallation of the products is achieved. Therefore, this method shows great promise for the formation of further diverse trimeric porphyrin arrays and for extension to larger arrays that have traditionally proven even more synthetically challenging. Both of these are areas of current interest in our research.

EXPERIMENTAL

General methods

^{1}H NMR spectra were recorded on a JEOL GX270 spectrometer at 270 MHz. ^{1}H NMR data are expressed in ppm downfield from tetramethylsilane (TMS), referenced to TMS or $CHCl_3$ and are reported as position (δ_H), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet and m = multiplet), coupling constant (J Hz), relative integral and assignment. Fast atom bombardment mass spectra (FAB MS) were determined using a Varian VG70-250S double focusing magnetic sector mass spectrometer with an ionization potential of 70 eV. Merck type 60 (230-400 mesh) silica gel was used for column chromatography. Thin layer chromatography (TLC) was performed on precoated silica gel plates (Merck Kieselgel 60F$_{254}$). The synthesis of aldehydes (**2-4**)[7], (**2-4-M**)[9] and dipyrrylmethane (**5**)[12] have been described previously.

5,15-*bis*(1'-(4'-(*trans*-1"-(2"-(2"'-(5"',10"',15"',20"'-Tetraphenylporphyrin)yl)ethen)yl)phenyl))-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**6a**)

Dipyrrylmethane (**5**) (14 mg, 49 μmol) and aldehyde (**2a**) (37 mg, 50 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (3.9 μL, 51 μmol) was added by syringe and the reaction mixture stirred for 4 h at room temperature. *o*-Chloranil (19 mg, 77 μmol) was added and the reaction heated at reflux for 8 h. The solvent was removed under reduced pressure and the resulting solid purified by flash column chromatography (silica gel, $CHCl_3$/hexane 2:1). Trimer (**6a**) was obtained as a purple solid (33 mg, 69%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ_H = -2.51 (br s, 4H, $N\underline{H}_{terminal}$), -2.31 (br s, 2H, $N\underline{H}_{central}$), 1.15 (t, ^3J = 7.3 Hz, 12H, $-CH_2CH_2CH_2C\underline{H}_3$), 2.00-2.05 (m, 8H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.22-2.30 (m, 8H, $-CH_2C\underline{H}_2CH_2CH_3$), 2.65 (s, 12H, $-C\underline{H}_3$), 4.00-4.11 (m, 8H, $-C\underline{H}_2CH_2CH_2CH_3$), 7.30 (d, ^3J = 16.2 Hz, 2H, $H_{ethenyl}$), 7.64 (d, ^3J = 16.2 Hz, 2H, $H_{ethenyl}$), 7.68 (d, ^3J = 7.9 Hz, 4H, H_{Ar}), 7.79-7.88 (m, 24H, $H_{m,p}$), 8.06 (d, ^3J = 7.9 Hz, 4H, H_{Ar}), 8.24-8.36 (m, 16H, H_o), 8.82-8.87 (m, 12H, H_β), 9.18 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max} (log ε): 426 (5.63), 518 (4.70), 566 (4.47), 598 (4.23), 654 (3.68) nm. MS (FAB): 2022 ((M + 3H)$^+$, 100). HRMS calcd. for MH$^+$ ($C_{144}H_{123}N_{12}$): 2019.9994. Found: 2019.9927.

5,15-*bis*-(4'-(*trans*-1"-(2"-(2'''-(5''',10''',15''',20'''-Tetraphenylporphyrinato nickel(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**6a-Ni$_2$**)

Dipyrrylmethane (**5**) (6.4 mg, 22 µmol) and aldehyde (**2a-Ni**) (18 mg, 22 µmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (1.8 µL, 23 µmol) was added by syringe and the reaction mixture stirred for 4 h at room temperature. *o*-Chloranil (9 mg, 37 µmol) was added and the reaction heated at reflux for 5 h. The solvent was removed under reduced pressure and the resulting solid purified by flash column chromatography (silica gel, $CHCl_3$/hexane 2:1). Trimer (**6a-Ni$_2$**) was obtained as a purple solid (16 mg, 68%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ_H = -2.34 (br s, 2H, $N\underline{H}_{central}$), 1.15 (t, 12H, ^3J = 7.3 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.75-1.86 (m, 8H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.18-2.33 (m, 8H, $-CH_2C\underline{H}_2CH_2CH_3$), 2.64 (s, 12H, $-C\underline{H}_3$), 3.99-4.14 (m, 8H, $-C\underline{H}_2CH_2CH_2CH_3$), 7.16 (d, 2H, ^3J = 15.9 Hz, $H_{ethenyl}$), 7.46 (d, 2H, ^3J = 15.9 Hz, $H_{ethenyl}$), 7.59 (d, 4H , ^3J = 8.2 Hz, H_{Ar}), 7.68-82 (m, 24H, $H_{m,p}$), 8.01-8.15 (m, 20H, H_o and H_{Ar}), 8.73-8.78 (m, 12H, H_β), 9.07 (s, 2H, H_β), 10.31 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max} (log ε): 428 (5.62), 508 (4.73), 538 (4.74), 576 (4.69) nm. MS (FAB): 2134 ((M + 3H)$^+$, 100). HRMS calcd. for MH$^+$ ($C_{144}H_{121}N_{12}Ni_2$): 2133.8544. Found: 2133.8511.

5,15-*bis*(1'-(3'-(*trans*-1"-(2"-(2'''-(5''',10''',15''',20'''-Tetraphenylporphyrin)yl)ethen)yl)phenyl))-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**7a**)

Dipyrrylmethane (**5**) (13 mg, 45 µmol) and aldehyde (**3a**) (34 mg, 46 µmol) were dissolved in CH_2Cl_2 (4.6 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (3.5 µL, 45 µmol) was added by syringe and the reaction mixture stirred for 12 h at room temperature. *o*-Chloranil (18 mg, 73 µmol) was added and the reaction heated at reflux for 16 h. The solvent was removed under reduced pressure and the resulting solid purified by flash column chromatography (silica gel, $CHCl_3$/hexane 2:1). Trimer (**7a**) was obtained as a purple solid (14 mg, 82%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ_H = -2.59 (br s, 4H, $N\underline{H}_{terminal}$), -2.15 (br s, 2H, $N\underline{H}_{central}$), 1.19 (t, ^3J = 7.3 Hz, 12H, $-CH_2CH_2CH_2C\underline{H}_3$), 1.81-1.92 (m, 8H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.30-2.38 (m, 8H, $-CH_2C\underline{H}_2CH_2CH_3$), 2.71 (s, 12H, $-C\underline{H}_3$), 4.15-4.20 (m, 8H, $-C\underline{H}_2CH_2CH_2CH_3$), 6.11 (t, ^3J = 6.4 Hz, 2H, H_p - isomer **a**), 6.47 (t, ^3J = 6.4 Hz, 2H, H_p - isomer **b**), 7.06 (t, ^3J = 6.4 Hz, 4H, H_m - isomer **a**), 7.22 (t, ^3J = 6.4 Hz, 4H, H_m - isomer **b**), 7.60-8.34 (m, $H_{o,m,p}$ and $H_{Ar,\,ethenyl}$), 8.52 (d, ^3J = 4.9 Hz, H_β - isomer **a**), 8.57 (d, ^3J = 4.9 Hz, H_β - isomer **b**), 8.67 (d, ^3J = 5.2 Hz, H_β - isomer **a**), 8.69 (d, ^3J = 5.2 Hz, H_β - isomer **b**), 8.80-8.89 (m, H_β), 9.16 (s, H_β - isomer **b**), 9.17 (s, H_β - isomer **a**), 10.46 (s, 1H, H_{meso} - isomer **b**), 10.47 (s, 1H, H_{meso} - isomer **a**). UV-vis (CH_2Cl_2) λ_{max} (log ε): 406(sh) (5.51), 424 (5.64), 516 (4.63), 568 (4.42), 598 (4.24), 653 (4.04) nm. MS (FAB): 2021 ((M + 2H)$^+$, 100%). HRMS calcd. for MH$^+$ ($C_{144}H_{123}N_{12}$): 2019.9994. Found: 2019.9946.

5,15-*bis*(1'-(2'-(*trans*-1"-(2"-(2'"-(5'",10'",15'",20'"-Tetraphenylporphyrin)yl)ethen)yl)phenyl))-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**8a**)

Dipyrrylmethane (**5**) (15 mg, 52 μmol) and aldehyde (**4a**) (39 mg, 52 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (4.1 μL, 53 μmol) was added by syringe and the reaction mixture stirred for 10 h at room temperature. *o*-Chloranil (20 mg, 81 μmol) was added and the reaction heated at reflux for 15 h. The solvent was removed under reduced pressure and the resulting solid purified by flash column chromatography (silica gel, $CHCl_3$/hexane 2:1). Trimer (**8a**) was obtained as a purple solid (11 mg, 56%). ^1H NMR ($CDCl_3$, 270 MHz): δ_H = -2.95 (br s, 4H, $N\underline{H}_{terminal}$), -1.95 (br s, 2H, $N\underline{H}_{central}$), 0.99 (t, ^3J = 7.3 Hz, 12H, $-CH_2CH_2CH_2C\underline{H}_3$), 1.62-1.79 (m, 8H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.07-2.29 (m, 8H, $-CH_2C\underline{H}_2CH_2CH_3$), 2.63 (s, 12H, $-C\underline{H}_3$), 3.95-4.12 (m, 8H, $-C\underline{H}_2CH_2CH_2CH_3$), 5.31-5.46 (m, 6H, $H_{m,p}$), 6.83 (dd, 4H, ^3J = 6.4 Hz, ^4J = 1.5 Hz, H_o), 6.98 (d, ^3J = 16.2 Hz, 2H, $H_{ethenyl}$), 7.09 (d, ^3J = 16.2 Hz, 2H, $H_{ethenyl}$), 7.38 (d, ^4J = 1.5 Hz, 2H, H_{Ar}), 7.54-8.20 (m, 36H, H_{Ar}), 8.20-8.25 (m, 2H, H_β), 8.47-8.51 (m, 2H, H_β), 8.63-8.77 (m, 10H, H_β), 10.37 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max} (log ε): 404(sh) (4.65), 423 (5.65), 520 (4.71), 565 (4.43), 598 (4.33), 656 (4.12) nm. MS (FAB): 2021 ((M + 2H)$^+$, 100%). HRMS calcd. for MH^+ ($C_{144}H_{123}N_{12}$): 2019.9994. Found: 2019.9950.

5,15-*bis*-(4'-(*trans*-1"-(2"-(2'"-(5'",10'",15'",20'"-Tetraxylylporphyrin)yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**6b**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**2b**) (50 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**6b**) was obtained as a purple solid (43 mg, 65%). ^1H NMR ($CDCl_3$, 270 MHz): δ_H = -2.54 (br s, 4H, $N\underline{H}_{terminal}$), -2.31 (br s, 2H, $N\underline{H}_{central}$), 1.16 (t, 12H, ^3J = 7.4 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.78-1.87 (m, 8H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.23-2.29 (m, 8H, $-CH_2C\underline{H}_2CH_2CH_3$), 2.61-2.71 (m, 60H, $-C\underline{H}_3$), 4.06-4.10 (m, 8H, $-C\underline{H}_2CH_2CH_2CH_3$), 7.25-7.53 (m, 10H, $H_{ethenyl,\ p}$), 7.67 (d, 2H, ^3J = 17.5 Hz, $H_{ethenyl}$), 7.75 (d, 4H, H_{Ar}), 7.83-7.98 (m, 16H, H_o), 8.10 (d, 4H, H_{Ar}), 8.83-8.92 (m, 12H, H_β), 9.21 (s, 2H, H_β), 10.34 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max} (log ε): 428 (5.81), 522 (4.84), 568 (4.62), 599 (4.37), 655 (3.98) nm. MS (FAB): 2244 ((M+H)$^+$, 100). HRMS calcd. for M^+ ($C_{160}H_{154}N_{12}$): 2243.2419. Found: 2243.2410.

5,15-*bis*-(4'-(*trans*-1"-(2"-(2'"-(5'",10'",15'",20'"-Tetraxylylporphyrinato zinc(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**6b-Zn₂**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**2b-Zn**) (54 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**6b-Zn$_2$**) was obtained as a purple solid (53 mg, 76%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ_H = -2.27 (br s, 2H, N$\underline{H}_{central}$), 1.16 (t, 12H, ^3J = 7.3 Hz, -$CH_2CH_2CH_2C\underline{H}_3$), 1.78-1.87 (m, 8H, -$CH_2CH_2C\underline{H}_2CH_3$), 2.21-2.29 (m, 8H, -$CH_2C\underline{H}_2CH_2CH_3$), 2.61-2.71 (m, 60H, -$C\underline{H}_3$), 4.05-4.11 (m, 8H, -$C\underline{H}_2CH_2CH_2CH_3$), 7.40 (d, 2H, ^3J = 17.1 Hz, $H_{ethenyl}$), 7.43 (br s, 4H, H_p), 7.52 (br s, 4H, H_p), 7.63 (d, 2H, ^3J = 17.1 Hz, $H_{ethenyl}$), 7.76 (d, 4H, ^3J = 7.8 Hz, H_{Ar}), 7.88 (br s, 8H, H_o), 7.97 (br s, 8H, H_o), 8.10 (d, 4H, ^3J = 7.8 Hz, H_{Ar}), 8.89-9.04 (m, 12H, H_β), 9.31 (s, 2H, H_β), 10.34 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max}: 431, 558, 593, 632 nm. MS (FAB): 2371 ((M+5H)$^+$, 100). HRMS calcd. for M$^+$ ($C_{160}H_{150}N_{12}Zn_2$): 2367.0689. Found: 2367.0634.

5,15-*bis*-(4'-(*trans*-1"-(2"-(2'''-(5''',10''',15''',20'''-Tetraxylylporphyrinato zinc(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrinato nickel(II) (**6b-Zn$_2$Ni**)

Ni(OAc)$_2$·4H$_2$O (2.1 mg, 8.4 μmol) was dissolved in methanol (2 mL) and added to a solution of trimer (**6b-Zn$_2$**) (20 mg, 8.4 μmol) and the reaction mixture heated at reflux for 3 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). The metallated trimer (**6b-Zn$_2$Ni**) was obtained as a purple solid (19 mg, 93%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ_H = 1.17 (t, 12H, ^3J = 7.3 Hz, -$CH_2CH_2CH_2C\underline{H}_3$), 1.80-1.86 (m, 8H, -$CH_2CH_2C\underline{H}_2CH_3$), 2.21-2.27 (m, 8H, -$CH_2C\underline{H}_2CH_2CH_3$), 2.57-2.64 (m, 60H, -$C\underline{H}_3$), 4.03-4.06 (m, 8H, -$C\underline{H}_2CH_2CH_2CH_3$), 7.27 (d, 2H, ^3J = 15.8 Hz, $H_{ethenyl}$), 7.35 (br s, 4H, H_p), 7.43 (br s, 4H, H_p), 7.51 (d, 2H, ^3J = 15.8 Hz, $H_{ethenyl}$), 7.54 (br s, 8H, H_o), 7.67 (d, 4H, ^3J = 7.9 Hz, H_{Ar}), 7.75 (br s, 8H, H_o), 8.07 (d, 4H, ^3J = 7.9 Hz, H_{Ar}), 8.74-8.83 (m, 12H, H_β), 9.09 (s, 2H, H_β), 10.27 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max}: 413, 431, 540, 574 nm. MS (FAB): 2357 ((M+2H)$^+$, 100). HRMS calcd. for M$^+$ ($C_{160}H_{148}N_{12}Zn_2Ni$): 2422.9886. Found: 2422.9875.

5,15-*bis*-(4'-(*trans*-1"-(2"-(2'''-(*meso*-5''',10''',15''',20'''-Tetraxylylporphyrinato nickel(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**6b-Ni$_2$**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**2b-Ni**) (54 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**6b-Ni$_2$**) was obtained as a purple solid (42 mg, 60%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ_H = -2.30 (br s, 2H, N$\underline{H}_{central}$), 1.16 (t, 12H, ^3J = 7.3 Hz, -$CH_2CH_2CH_2C\underline{H}_3$), 1.77-1.86 (m, 8H, -$CH_2CH_2C\underline{H}_2CH_3$), 2.18-2.32 (m, 8H, -$CH_2C\underline{H}_2CH_2CH_3$), 2.56-2.65 (m, 60H, -$C\underline{H}_3$), 4.05-4.09 (m, 8H, -$C\underline{H}_2CH_2CH_2CH_3$), 7.25 (d, 2H, ^3J = 16.8 Hz, $H_{ethenyl}$), 7.36 (br s, 4H, H_p), 7.44 (br s, 4H, H_p), 7.50 (d, 2H, ^3J = 16.8 Hz, $H_{ethenyl}$), 7.66 (br s, 8H, H_o), 7.67 (d, 4H, ^3J = 7.8 Hz, H_{Ar}), 7.75(br s, 8H, H_o), 8.06 (d, 4H, ^3J = 7.8 Hz, H_{Ar}), 8.76-8.83 (m, 12H, H_β), 9.09 (s, 2H, H_β), 10.32 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max} (log ε): 275 (4.63), 310 (4.63), 431 (5.65), 508 (4.61), 539 (4.63), 576 (4.55) nm. MS (FAB): 2357 ((M+2H)$^+$, 100). HRMS calcd. for M$^+$ ($C_{160}H_{150}N_{12}Ni_2$): 2355.0813. Found: 2355.0823.

5,15-*bis*-(4'-(*trans*-1"-(2"-(2'''-(*meso*-5''',10''',15''',20'''-Tetraxylylporphyrinato nickel(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrinato zinc(II) (**6b-Ni$_2$Zn**)

Zn(OAc)$_2$·2H$_2$O (8.1 mg, 33 μmol) was dissolved in methanol (2 mL) and added to a solution of trimer (**6b-Ni$_2$**) (73 mg, 26 μmol) and the reaction mixture stirred at room temperature for 10 min. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, $CHCl_3$). The product was then precipated out of dichloromethane with methanol. The metallated trimer (**6b-Ni$_2$Zn**) was obtained as a purple solid (59 mg, 94 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ_H = 1.15 (t, 12H, ^3J = 7.3 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.78-1.85 (m, 8H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.17-2.31 (m, 8H, $-CH_2C\underline{H}_2CH_2CH_3$), 2.54-2.64 (m, 60H, $-C\underline{H}_3$), 4.03 (m, 8H, $-C\underline{H}_2CH_2CH_2CH_3$), 7.26 (d, 2H, ^3J = 15.9 Hz, $H_{ethenyl}$), 7.34 (br s, 4H, H_p), 7.40-7.42 (br s, 4H, H_p), 7.50 (d, 2H, ^3J = 15.6 Hz, $H_{ethenyl}$), 7.64-7.74 (m, 20H, H_o and H_{Ar}), 8.05 (d, 4H, ^3J = 7.6 Hz, H_{Ar}), 8.74-8.81 (m, 12H, H_β), 9.07 (s, 2H, H_β), 10.26 (s, 2H, H_{meso}). UV-vis (CH_2Cl_2) λ_{max} (log ε): 285 (4.60), 320 (4.64), 412 (5.60), 432 (5.69), 540 (4.82), 575 (4.61) nm. MS (FAB): 2417 (M^+, 100). HRMS: calcd. for M^+ ($C_{160}H_{148}N_{12}$ Ni_2Zn): 2416.9966. Found: 2416.9878.

5,15-*bis*-(3'-(*trans*-1"-(2"-(2'"-(5'",10'",15'",20'"-Tetraxylylporphyrin)yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**7b**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**3b**) (50 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**7b**) was obtained as a purple solid (48 mg, 73%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ_H = -2.63 (br s, $N\underline{H}_{terminal}$), 1.15 (t, ^3J = 7.3 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.35 (s, $C\underline{H}_3$ - isomer **a**), 1.49 (s, $C\underline{H}_3$ - isomer **b**), 1.77-1.89 (m, $-CH_2CH_2C\underline{H}_2CH_3$), 2.22-2.35 (m, $-CH_2C\underline{H}_2CH_2CH_3$), 2.53-2.68 (m, $-C\underline{H}_3$), 4.08-4.17 (m, $-C\underline{H}_2CH_2CH_2CH_3$), 5.09 (s, H_p - isomer **a**), 5.53 (s, H_p - isomer **b**), 7.26-8.11 (m, $H_{o,m,p}$ and $H_{Ar, ethenyl}$), 8.44 (d, ^3J = 4.9 Hz, H_β - isomer **a**), 8.50 (d, ^3J = 4.9 Hz, H_β - isomer **b**), 8.60 (d, ^3J = 4.9 Hz, H_β - isomer **a**), 8.63 (d, ^3J = 4.9 Hz, H_β - isomer **b**), 8.80-8.85 (m, H_β), 9.18 (s, H_β - isomer **b**), 9.21 (s, H_β -isomer **a**), 10.43 (s, H_{meso} - isomer **b**), 10.47 (s, H_{meso} - isomer **a**). UV-vis (CH_2Cl_2) λ_{max} (log ε): 428 (5.85), 525 (4.83), 570 (4.71), 601 (4.40), 659 (4.01) nm. MS (FAB): 2244 ($(M+H)^+$, 100). HRMS calcd. for M^+ ($C_{160}H_{154}N_{12}$): 2243.2419. Found: 2243.2410.

5,15-*bis*-(3'-(*trans*-1"-(2"-(2'"-(5'",10'",15'",20'"-Tetraxylylporphyrinato zinc(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**7b-Zn$_2$**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**3b-Zn**) (54 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**7b-Zn$_2$**) was obtained as a purple solid (42 mg, 60%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ_H = 1.14 (t, ^3J = 7.3 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.37 (s, $-C\underline{H}_3$ - isomer **a**), 1.53 (s, $-C\underline{H}_3$ - isomer **b**), 1.77-1.85 (m, $-CH_2CH_2C\underline{H}_2CH_3$), 2.21-2.29 (m, $-CH_2C\underline{H}_2CH_2CH_3$), 2.53-2.69 (m, $-C\underline{H}_3$), 4.06-4.14 (m, $-C\underline{H}_2CH_2CH_2CH_3$), 5.16 (s, H_p - isomer **a**), 5.62 (s, H_p - isomer **b**), 7.29-8.07 (m, $H_{o,m,p}$ and $H_{Ar, ethenyl}$), 8.56 (d, ^3J = 4.6 Hz, H_β - isomer **a**), 8.62 (d, ^3J = 4.6 Hz, H_β - isomer **b**), 8.73 (d, ^3J = 4.6 Hz, H_β - isomer **a**), 8.77 (d, ^3J = 4.6 Hz, H_β - isomer **b**), 8.89-8.98 (m, H_β), 9.29 (s, H_β - isomer **b**), 9.32 (s, H_β - isomer **a**), 10.43 (s, H_{meso} - isomer **b**), 10.46 (s, H_{meso} - isomer **a**). UV-vis (CH_2Cl_2) λ_{max}: 431, 508, 559, 594 nm. MS (FAB): 2371 ($(M+5H)^+$, 100). HRMS calcd. for M^+ ($C_{160}H_{150}N_{12}Zn_2$): 2367.0689. Found: 2367.0732.

5,15-*bis*-(3'-(***trans***-1"-(2"-(2'''-(5''',10''',15''',20'''-Tetraxylylporphyrinato nickel(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**7b-Ni₂**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**3b-Ni**) (54 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated under reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**7b-Ni₂**) was obtained as a purple solid (49 mg, 71%). ^1H NMR ($CDCl_3$, 270 MHz): δ_H = -2.05 (br s, $N\underline{H}_{central}$ isomer **b**), -2.04 (br s, $N\underline{H}_{central}$ - isomer **a**), 1.14 (t, ^3J = 7.3 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.31 (s, $-C\underline{H}_3$ - isomer **a**), 1.38 (s, $-C\underline{H}_3$ - isomer **b**), 1.75-1.87 (m, $-CH_2CH_2C\underline{H}_2CH_3$), 2.21-2.33 (m, $-CH_2C\underline{H}_2CH_2CH_3$), 2.47-2.64 (m, $-C\underline{H}_3$), 4.09-4.14 (m, $-C\underline{H}_2CH_2CH_2CH_3$), 5.05 (s, H_p - isomer **a**), 5.36 (s, H_p - isomer **b**), 7.13 (d, ^3J = 15.9 Hz, $H_{ethenyl}$ - isomer **a**), 7.26-8.10 (m, $H_{o,\,m,\,p}$ and $H_{Ar,\,ethenyl}$), 8.42-8.45 (m, H_β), 8.51-8.53 (m, H_β), 8.68-8.73 (m, H_β), 9.02 (s, H_β - isomer **b**), 9.06 (s, H_β - isomer **a**), 10.40 (s, H_{meso} - isomer **b**), 10.43 (s, H_{meso} - isomer **a**). UV-vis (CH_2Cl_2) λ_{max}: 429, 508, 541, 577 nm. MS (FAB): 2357 ($(M+2H)^+$, 100). HRMS calcd. for M^+ ($C_{160}H_{150}N_{12}Ni_2$): 2355.0813. Found: 2355.0858.

5,15-*bis*-(3'-(*trans*-1"-(2"-(2'''-(5''',10''',15''',20'''-Tetraxylylporphyrinato zinc(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrinato nickel(II) (**7b-Zn₂Ni**)

$Ni(OAc)_2{\cdot}4H_2O$ (2.1 mg, 8.4 μmol) was dissolved in methanol (2 mL) and added to a solution of trimer (**7b-Zn₂**) (20 mg, 8.4 μmol) and the reaction mixture heated at reflux for 3 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). The metallated trimer (**7b-Zn₂Ni**) was obtained as a purple solid (14 mg, 69%). ^1H NMR ($CDCl_3$, 270 MHz): δ_H = 1.14 (t, ^3J = 7.3 Hz, $-CH_2CH_2CH_2C\underline{H}_3$), 1.22 (s, $-C\underline{H}_3$ isomer **a**), 1.30 (s, $-C\underline{H}_3$ isomer **b**), 1.79-1.83 (m, $-CH_2CH_2C\underline{H}_2CH_3$), 2.23-2.27 (m, $-CH_2C\underline{H}_2CH_2CH_3$), 2.46-2.61 (m, $-C\underline{H}_3$), 4.07-4.13 (m, $-C\underline{H}_2CH_2CH_2CH_3$), 4.93 (s, H_p - isomer **a**), 5.27 (s, H_p - isomer **b**), 7.08 (d, ^3J = 16.0 Hz, $H_{ethenyl}$ - isomer **a**), 7.25-8.08 (m, $H_{o,\,m,\,p}$ and $H_{Ar,\,ethenyl}$), 8.41-8.43 (m, H_β), 8.48-8.50 (m, H_β), 8.68-8.72 (m, H_β), 8.97 (s, H_β - isomer **b**), 9.04 (s, H_β - isomer **a**), 10.32 (s, H_{meso} - isomer **b**), 10.35(s, H_{meso} - isomer **a**). UV-vis (CH_2Cl_2) λ_{max}: 410, 431, 540, 575 nm. MS (FAB): 2357 ($(M+2H)^+$, 100). HRMS calcd. for M^+ ($C_{160}H_{148}N_{12}Zn_2Ni$): 2422.9886. Found: 2422.9912.

5,15-*bis*-(2'-(*trans*-1"-(2"-(2'''-(5''',10''',15''',20'''-Tetraxylylporphyrin)yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**8b**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**4b**) (54 mg, 59 μmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture bubbled with N_2 for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1). Trimer (**8b**) was obtained as a purple solid

(34 mg, 51%).^{1}H NMR (CDCl$_3$, 270 MHz): δ_H = -2.93 (br s, 4H, N$\underline{H}_{terminal}$), -1.96 (br s, 2H, N$\underline{H}_{central}$), 0.27 (s, 12H, -C$\underline{H}_3$), 0.99 (t, 12H, ^3J = 7.3 Hz, -CH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.67-1.78 (m, 8H, -CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 2.10-2.20 (m, 8H, -CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 2.58 (s, 12H, -C$\underline{H}_3$), 2.62 (s, 12H, -C$\underline{H}_3$), 2.65 (s, 12H, -C$\underline{H}_3$), 2.80 (s, 12H, -C$\underline{H}_3$), 4.01-4.07 (m, 8H, -C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 4.46 (s, 2H, H$_p$), 6.52 (s, 4H, H$_o$), 7.14 (d, 2H, ^3J = 16.2 Hz, H$_{ethenyl}$), 7.25-7.41 (m, 6H, H$_p$), 7.66-7.86 (m, 22H ,H$_{o,\ Ar,\ ethenyl}$), 8.26 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.51 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.75-8.80 (m, 10H, H$_\beta$), 10.33 (s, 2H, H$_{meso}$). UV-vis (CH$_2$Cl$_2$) λ_{max} (log ε): 428 (5.50), 523 (4.58), 568 (4.31), 600 (4.12), 658 (3.65) nm. MS (FAB): 2244 ((M+H)$^+$, 100). HRMS calcd. for (M+H)$^+$ (C$_{160}$H$_{155}$N$_{12}$): 2244.2453. Found: 2244.2449.

5,15-*bis*-(2'-(*trans*-1"-(2"-(2"'-(5"',10"',15"',20"'-Tetraxylylporphyrinato zinc(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**8b-Zn$_2$**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**4b-Zn**) (54 mg, 59 μmol) were dissolved in CH$_2$Cl$_2$ (5 mL) and the mixture bubbled with N$_2$ for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH$_2$Cl$_2$/hexane 2:1). Trimer (**8b-Zn$_2$**) was obtained as a purple solid (25 mg, 36 %). ^{1}H NMR (CDCl$_3$, 270 MHz): δ_H = -2.00 (br s, 2H, N$\underline{H}_{central}$), 0.27 (s, 12H, -C$\underline{H}_3$), 1.00 (t, 12H, ^3J = 7.3 Hz, -CH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.70-1.79 (m, 8H, -CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 2.18-2.26 (m, 8H, -CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 2.49 (s, 12H, -C$\underline{H}_3$), 2.58 (s, 12H, -C$\underline{H}_3$), 2.65 (s, 12H, -C$\underline{H}_3$), 2.80 (s, 12H, -C$\underline{H}_3$), 4.00-4.05 (m, 8H, -C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 4.53 (s, 2H, H$_p$), 6.51 (s, 4H, H$_o$), 7.10 (d, 2H, ^3J = 16.4 Hz, H$_{ethenyl}$), 7.21-7.45 (m, 6H, H$_p$), 7.66-7.87 (m, 22H ,H$_{o,\ Ar,\ ethenyl}$), 8.40 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.65 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.80-8.90 (m, 10H, H$_\beta$), 10.31 (s, 2H, H$_{meso}$). UV-vis (CH$_2$Cl$_2$) λ_{max}: 430, 542, 579, 628 nm. MS (FAB): 2370 ((M+4H)$^+$, 100). HRMS calcd. for M$^+$ (C$_{160}$H$_{150}$N$_{12}$ Zn$_2$): 2367.0689. Found: 2367.0659.

5,15-*bis*-(2'-(*trans*-1"-(2"-(2"'-(5"',10"',15"',20"'-Tetraxylylporphyrinato nickel(II))yl)ethenyl))phenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-butylporphyrin (**8b-Ni$_2$**)

Dipyrrylmethane (**5**) (17 mg, 59 μmol) and aldehyde (**4b-Ni**) (54 mg, 59 μmol) were dissolved in CH$_2$Cl$_2$ (5 mL) and the mixture bubbled with N$_2$ for 5 min. Trifluoroacetic acid (5.4 μL, 70 μmol) was added by syringe and the reaction mixture stirred for 1 h at room temperature. *o*-Chloranil (26 mg, 105 μmol) was added and the reaction heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, CH$_2$Cl$_2$/hexane 2:1). Trimer (**8b-Ni$_2$**) was obtained as a purple solid (36 mg, 52%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ_H = -2.09 (br s, 2H, N$\underline{H}_{central}$), 0.38 (s, 12H, -C$\underline{H}_3$), 1.00 (t, 12H, ^3J = 7.3 Hz, -CH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.69-1.77 (m, 8H, -CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 2.16-2.19 (m, 8H, -CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 2.44 (s, 12H, -C$\underline{H}_3$), 2.53 (s, 12H, -C$\underline{H}_3$), 2.59 (s, 12H, -C$\underline{H}_3$), 2.73 (s, 12H, -C$\underline{H}_3$), 3.97-4.02 (m, 8H, -C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 4.88 (s, 2H, H$_p$), 6.35 (s, 4H, H$_o$), 6.95 (d, 2H, ^3J = 15.9 Hz, H$_{ethenyl}$), 7.20 (d, 2H, ^3J = 15.9 Hz, H$_{ethenyl}$), 7.23 (s, 2H, H$_p$), 7.30 (s, 2H, H$_p$), 7.32 (s, 2H, H$_p$), 7.46 (s, 4H, H$_o$), 7.57 (s, 4H, H$_o$), 7.61-7.68 (m, 8H, H$_{o,\ Ar}$), 7.81 (t, 2H, H$_{Ar}$), 7.92 (d, 2H, H$_{Ar}$), 8.14 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.42 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.60 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 8.65-8.67 (m, 6H, H$_\beta$), 8.76 (d, 2H, ^3J = 4.9 Hz, H$_\beta$), 10.26 (s, 2H, H$_{meso}$). UV-vis (CH$_2$Cl$_2$) λ_{max}: 430, 507, 541, 577 nm. MS (FAB): 2357 ((M+2H)$^+$, 100). HRMS calcd. for M$^+$ (C$_{160}$H$_{150}$N$_{12}$ Ni$_2$): 2355.0813. Found: 2355.0794.

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15. The trimeric porphyrins **6b**, **6b-Zn$_2$** and **6b-Ni$_2$** have been prepared in 300 mg quantities using scaled-up versions of the procedures reported here.