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Template-Directed Assembly of a Macrocyclic Porphyrin Tetramer Using Olefin Metathesis

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A macrocyclic porphyrin tetramer was prepared in 52% yield by olefin metathesis employing a 5,10,15,20-tetrapyridylporphyrin template.

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A bottom-up approach to the construction of discrete nanoscaled assemblies has important implications for several nanotechnologies.[1,2] Multiporphyrin systems in which the porphyrin sub-units are interlinked by self-assembly or covalent means have produced an array of elegant and geometric[3–5] nanometer-scaled structures designed to address aspects of photosynthetic mimicry, host–guest complexation, or catalysis.[6–9] We recently reported a strategy for preparing cubic porphyrin architectures based on the interplay of Sn^{IV}–O and Ru^{II}–N interactions and suggested that linking *meso* positions within the heptaporphyrin array would lead to novel supramolecular hosts.[10] Inspired by the recent work of Kobuke and coworkers,[11] we embarked on the synthesis of tetraporphyrinic macrocycles as a pseudo two-dimensional model to the more complicated cube structure, by employing olefin metathesis and a coordinative template-directed strategy to achieve our goal.[12]

The preparation of the 5,15-substituted metalloporphyrin diene **1** is outlined in Scheme 1. This porphyrin, which contains heptyl and methyl side chains on alternating β-pyrrolic positions, was chosen over other candidates to negate potential problems with solubility within the macrocycle and associated supramolecular constructs. A [2+2] dipyrrolic route was chosen as the synthetic pathway to **1**, by adapting the procedures of Sanders and coworkers and Johnson et al.[13] Alkylation of pentane-2,4-dione with 1-iodoheptane (K_2CO_3, MeCN) produced the monoalkylated product **2** in 88% yield after distillation. Reaction of **2** with the oxime **3**[13*c*] under reducing conditions (Zn, HOAc) yielded the pyrrole **4** as a white solid in 45% yield. Oxidation of **4** ($Pb(OAc)_4$, Ac_2O, HOAc),* and the acid-catalyzed dimerization of **5** gave the dipyrrole **6** in 67% yield on a gram scale. Catalytic hydrogenation (H_2, Pd/C, NEt_3) of the bis(benzyl ester) **6** at ambient temperature yielded the dicarboxylic acid **7** in 80% yield. In situ decarboxylation of **7** in the presence of the butenyl benzaldehyde **8**[15] (TFA, MeOH) gave the corresponding porphyrinogen, which was oxidized to yield the free base porphyrin **9** in a very acceptable 24% yield for the final one-pot multi-step process. Metallation by the standard $Zn(OAc)_2$ method[16] produced the zinc(II) analogue **1**, the metathesis precursor, in high yield.

Reaction of **1** (millimolar concentration) in the presence of 0.25 equivalents of 5,10,15,20-tetrapyridylporphyrin **10** with Grubbs' first generation catalyst (40 mol-%) gave a new band by thin layer chromatography (TLC) analysis.[12*f*] After further catalyst addition (57 mol-%), reaction completion (48 h) was indicated by the loss of **1**, and the template was removed by acid workup. The free base tetraporphyrin macrocycle **11** was isolated by column chromatography in 52% yield (Scheme 2).†

In our hands, olefin metathesis using Grubbs' first-generation catalyst seems unaffected by the presence of **10**, despite the presence of the four pyridine, two pyrrolic, and two pyrrolenic nitrogens. This was verified by performing a ring closure metathesis of diethyl diallyl malonate in the presence of template **10** under the conditions shown in Scheme 3. Conversion of the malonate into the corresponding cyclopentene was achieved in >95% yield.

The ^1H NMR spectrum of the macrocycle **11** (Fig. 1*b*) is consistent with the expected structure and is clearly different

* Oxidation of **4** to form **5** did not occur with $Pb(OAc)_4$ in CH_3CO_2H as outlined in the procedures of ref. [13]. Upon addition of catalytic quantities of Ac_2O to $Pb(OAc)_4/CH_3CO_2H$ we obtained pyrrole **5** in high yields, as adopted from ref. [14]. We also observed formation of pyrrole **5** in good yield in the absence of Ac_2O however the reaction was heated at 80°C for 1.5 h to achieve this.

† Attempts to image the free base of square **11** using STM techniques have not been successful. We have attributed this to the more flexible nature of **11** and the heptyl side chains. This view is supported by ref. [12*f*] where STM of a tetraphenylporphyrin analogue on highly ordered pyrolytic graphite was possible when the template porphyrin was complexed, providing a more rigid structure.

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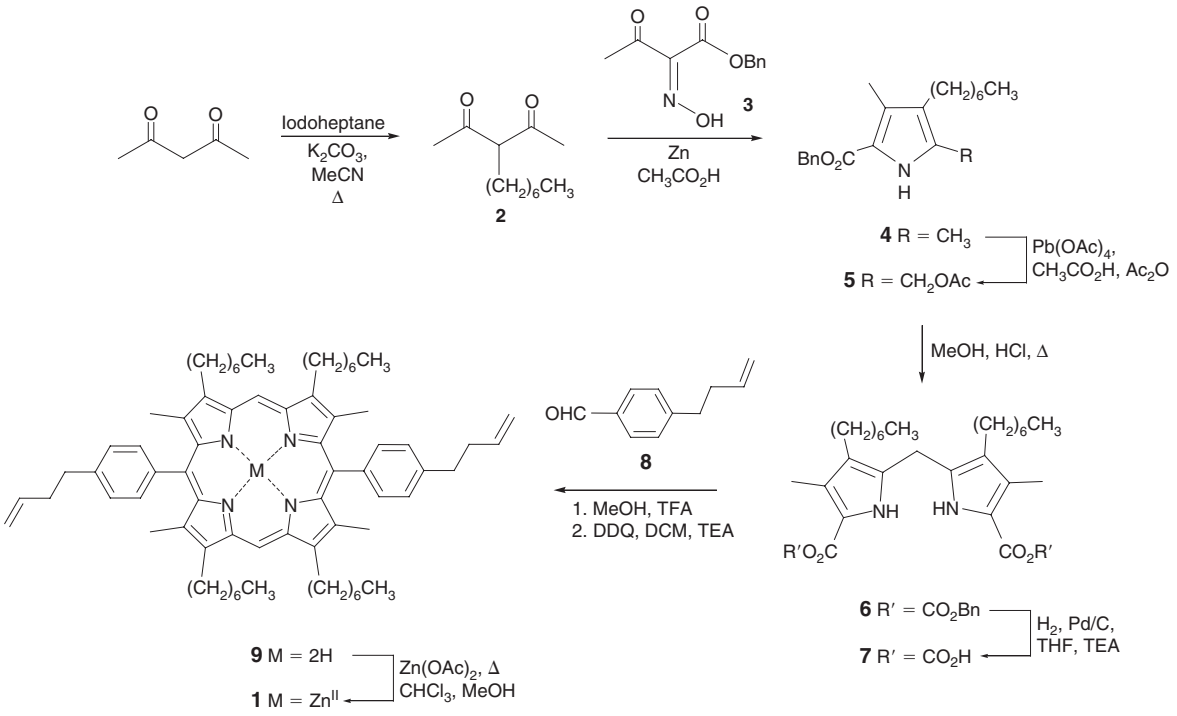
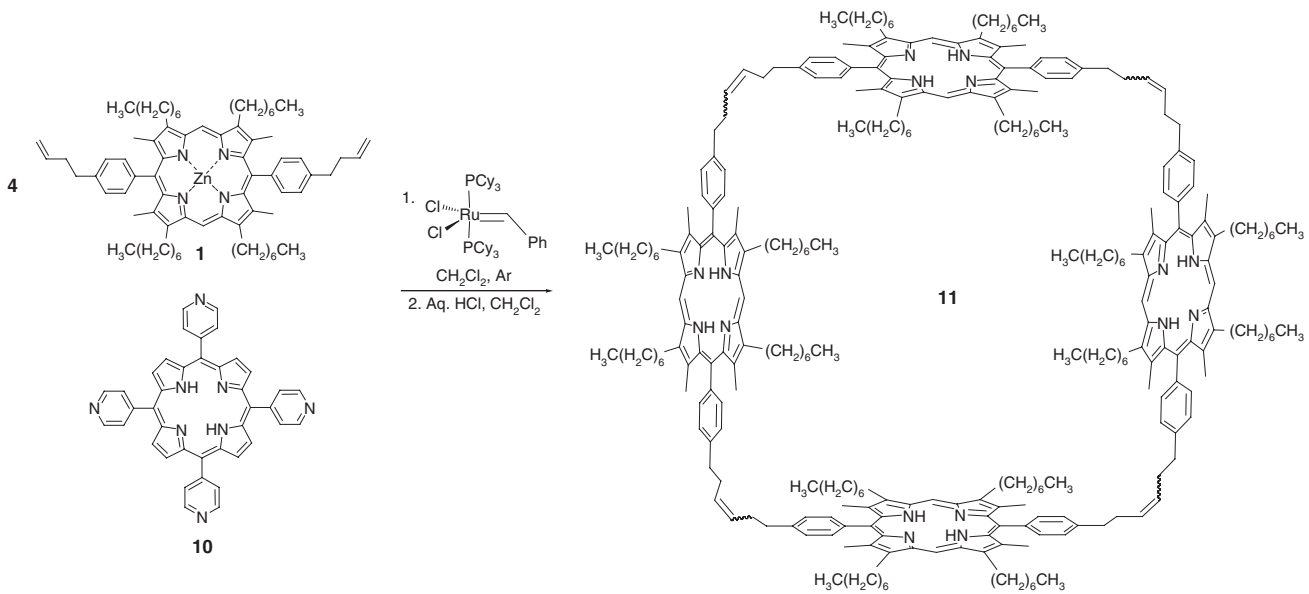
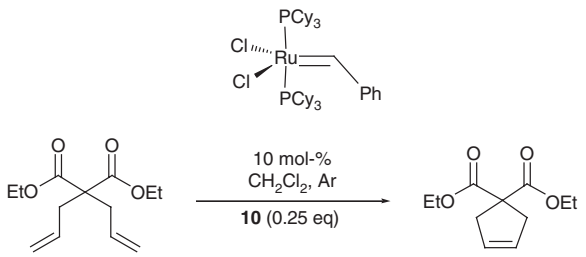


Scheme 1. Synthesis of *trans*-functionalized alkenyl porphyrin monomer **1**.



Scheme 2. Template-assisted metathesis to form the tetraporphyrin.



Scheme 3. Verification of the use of **10** as a template.

to that seen for the precursor **9**.[12f] Evident within the spectrum of **11** are peaks at δ 5.80 and 5.89 of equal intensity, indicative of *E* and *Z* alkenes, respectively. Their approximate 1 : 1 ratio indicates little steric influence or ring strain from the supramolecular assembly. Future work aims to hydrogenate the alkene linkers of **11** to alleviate the *cis*/*trans* isomerism and produce saturated alkyl linkers.

Electrospray ionization mass spectrometry (ESIMS) provides further evidence for the formation of the macrocyclic porphyrin tetramer **11** (molecular formula: $C_{280}H_{376}N_{16}$). The strong peak within the low-resolution (LR) mass

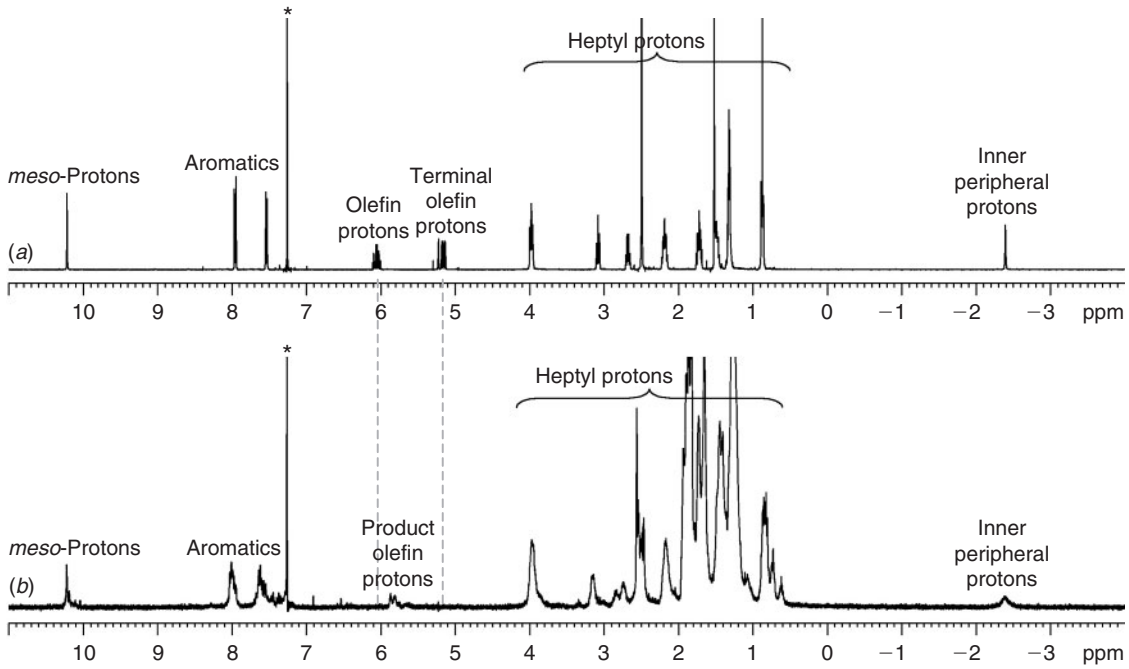


Fig. 1. 300 MHz ^{1}H NMR spectroscopic comparison of (*a*) free base porphyrin **9** and (*b*) square **11**. * represents the residual solvent peak.

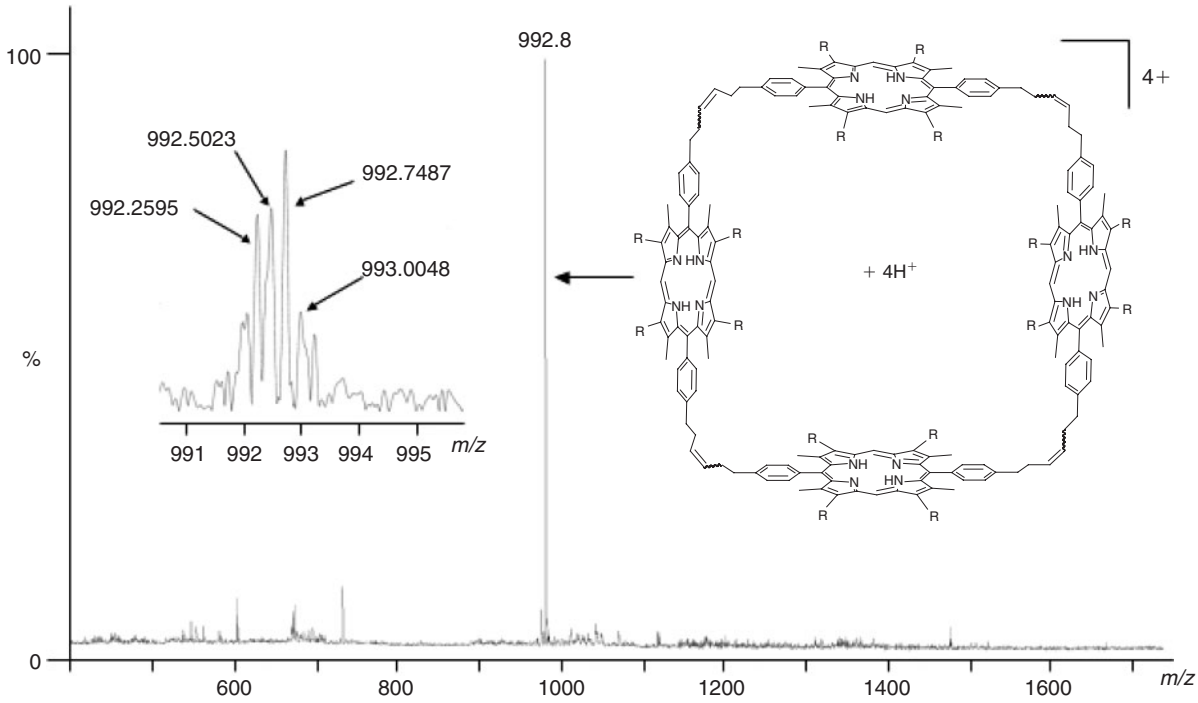


Fig. 2. Positive ion LR-ESIMS of **11**, inset showing HR-ESIMS expansion of the multiply charged *m*/*z* 992 peak.

spectrum at *m*/*z* 992.8, is consistent with the formation of mutiply charged ions but is inconclusive as to which multiply charged ion is present. High-resolution (HR) ESIMS (inset, Fig. 2) was necessary to provide diagnostic information. The incremental 0.25 amu values found for the isotope distribution within the signal at *m*/*z* 992.8 is only consistent with the formula $[\mathbf{11} + 4\mathrm{H}]^{4+}$, i.e. the macrocyclic porphyrin tetramer.

In summary, we have demonstrated a useful method for preparing a macrocyclic porphyrin tetramer. Research currently underway in our laboratories is exploring the host–guest possibilities of the metalloporphyrin square, including rotaxane applications, and a systematic approach to using Type I and II olefins for more elaborate structures.[17] Such results will be published in due course.

Experimental

All chemicals were used as supplied from Aldrich. Solvents were obtained as AR grade reagents and were used as received. LR-ESIMS

were recorded on a Micromass Platform II API QMS-quadrupole electrospray mass spectrometer. HR-ESIMS were recorded on a Bruker BioApex 47e Fourier-transform mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX 300 MHz spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C) or a Bruker DRX 400 MHz spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C), as solutions in $CDCl_3$. Chemical shifts (δ) were calibrated against the residual solvent peak. UV-Visible spectra were recorded on a Varian model Cary 100 Bio UV-Visible Spectrophotometer in the specified solvent system.

Compounds **2**–**7** and **9** were prepared by modifying the procedures reported previously by Sanders and coworkers and Johnson et al.[13] The major change to that documented was the use of 1-iodoheptane in the alkylation to achieve dione **2** rather than 1-iodohexane. However, two other minor differences were the addition of acetic anhydride to assist in producing the acetoxypyrrole **5**[14] and the one-pot decarboxylation, acid catalyzed condensation, and oxidation from **7** to afford the free base porphyrin **9**.

Dione **2**: (48.53 g, 88%). δ_H (300 MHz) 3.51 (t, *J* 7.2, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.73 (q, *J* 7.4, 2H), 1.16 (s, 10H), 0.79 (t, *J* 6.05, 3H). δ_C (50 MHz) 203.9, 68.5, 31.4, 30.4, 29.1, 28.6, 28.0, 27.2, 13.6. *m/z* (LR-ESI, +ve, $C_{12}H_{22}O_2$) calc. 198.2, found 199.0 $[M+H]^+$, 221.0 $[M+Na]^+$, 238.6 $[M+K]^+$.

Oxime **3**: (19.6 g, quant.). δ_H (300 MHz) 9.12 (s, 1H), 7.31 (m, 5H), 5.29 (s, 2H), 2.33 (s, 3H). δ_C (75 MHz) 194.2, 176.8, 161.7, 134.4, 128.5, 128.4, 128.1, 67.7, 25.1. ν_{max} (nujol)/cm^{-1} 3422m (br), 1728m, 1681m, 1456m. *m/z* (LR-ESI, +ve, $C_{11}H_{11}NO_4$) calc. 221.1, found 244.1 $[M+Na]^+$.

Pyrrole **4**: (5.4 g, 45%). δ_H (300 MHz) 8.51 (s, 1H), 7.37 (m, 5H), 5.28 (s, 2H), 2.33 (t, *J* 7.5, 2H), 2.27 (s, 3H), 2.18 (s, 3H), 1.28 (m, 10H), 0.87 (t, *J* 6.6 Hz, 3H). δ_C (75 MHz) 161.5, 137.0, 130.0, 128.7, 128.3, 128.2, 127.9, 122.8, 116.6, 65.5, 32.1, 31.1, 29.6, 29.4, 24.2, 22.9, 14.3, 11.7, 11.9. ν_{max} (nujol)/cm^{-1} 3290s, 3090w, 1657s. λ_{max}/nm (ε/M^{-1} cm^{-1}) ($CHCl_3$) 259 (4.71), 282 (4.58). *m/z* (LR-ESI, +ve, $C_{21}H_{29}NO_2$) calc. 327.2, found 328.4 $[M+H]^+$, 350.3 $[M+Na]^+$, 366.6 $[M+K]^+$.

Acetoxypyrrole **5**: (1.1 g, 85%). δ_H (300 MHz) 8.97 (s, 1H), 7.38 (m, 5H), 5.31 (s, 2H), 5.00 (s, 2H), 2.42 (t, *J* 11.0, 2H), 2.28 (s, 3H), 2.06 (s, 3H), 1.43 (m, 2H), 1.28 (m, 8H), 0.88 (t, *J* 9.6, 3H). δ_C (100 MHz) 171.1, 162.4, 136.7, 128.8, 128.4, 128.3, 127.4, 125.7, 123.7, 119.1, 65.9, 57.3, 32.1, 31.5, 29.6, 29.4, 24.1, 22.9, 21.1, 14.3, 10.7. ν_{max} (nujol)/cm^{-1} 3301m, 1670s, 1464m, 1377m. λ_{max}/nm (ε/M^{-1} cm^{-1}) ($CHCl_3$) 259 (4.82), 276 (4.69). *m/z* (LR-ESI, +ve, $C_{23}H_{31}NO_4$) calc. 385.23, found 386.3 $[M+H]^+$, 408.3 $[M+Na]^+$.

Dipyrrole **6**: (1.7 g, 67%). δ_H (300 MHz) 8.54 (s, 2H), 7.34 (m, 10H), 5.28 (s, 4H), 3.82 (s, 2H), 2.34 (t, *J* 5.85, 4H) 2.27 (s, 6H), 1.34 (m, 4H), 1.27 (s, 16H), 0.87 (m, 6H). δ_C (100 MHz) 161.7, 136.7, 129.7, 128.7, 128.4, 128.2, 128.1, 123.3, 117.8, 65.8, 32.1, 31.2, 29.8, 29.5, 24.2, 22.8, 14.5, 11.6, 11.0. *m/z* (LR-ESI, +ve, $C_{41}H_{54}N_2O_4$) calc. 638.41, found 661.5 $[M+Na]^+$.

Dicarboxylic acid dipyrrole **7**: (0.61 g, 80%). δ_H (300 MHz) 11.27 (s, 2H), 9.74 (s, 2H), 3.83 (s, 2H), 3.02 (m, 6H), 2.44 (t, *J* 7.3, 4H), 2.27 (s, 6H), 1.32 (m, 16H), 0.88 (m, 6H). δ_C (100 MHz) 160.1, 130.4, 125.2, 121.6, 120.8, 32.2, 31.7, 30.2, 29.5, 24.9, 22.9, 14.3, 10.9, 8.9. *m/z* (LR-ESI, +ve, $C_{27}H_{42}N_2O_4$) calc. 458.31, found 481.5 $[M+Na]^+$, 497.5 $[M+K]^+$.

Aldehyde **8**: prepared by adapting the reported method of Wilcox and coworkers.[15a] The 4-(4-bromophenyl)but-1-ene precursor was prepared as per the procedure described by Kabalka and coworkers.[15b] A solution of 4-(4-bromophenyl)but-1-ene (10 g, 47.4 mmol) in tetrahydrofuran (THF) (100 mL) was cooled to −78°C and *n*-butyllithium (2.5 M solution in hexane, 20.4 mL, 52.2 mmol) was added slowly to maintain a temperature below −70°C. The solution was stirred for 30 min and *N*,*N*-dimethylformamide (DMF) (8.8 mL, 111.8 mmol) was added at −78°C followed by a further 30 min stirring. The solution was then warmed to 0°C, quenched with H_2O (150 mL), extracted with Et_2O (3 × 100 mL), washed with H_2O (3 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a crude yellow residue. Column chromatography (silica, 8/1 hexane/EtOAc) gave **8** (5.23 g, 69%) as a colourless liquid. δ_H (300 MHz) 9.95 (s, 1H), 7.78 & 7.32 (ABq, *J* 8.4, 4H), 5.81 (m, 1H), 5.00 (m, 2H), 2.78 (t, *J* 8.2, 2H), 2.38 (m, 2H). δ_C (75 MHz) 192.0, 149.4, 137.4, 134.8, 130.0, 129.3, 115.6, 35.7, 35.1. *m/z* (LR-ESI, +ve, $C_{11}H_{12}O$) calc. 160.08, found 160.9 $[M+H]^+$.

Porphyrin **9**: Dipyrrole **7** (79.2 mg, 172.7 μmol), aldehyde **8** (27.7 mg, 172.9 μmol), and MeOH (5 mL) were combined and degassed by three freeze–thaw cycles. Trifluoroacteic acid (TFA) was separately degassed under the same conditions. In a dark, Ar atmosphere, TFA (1 mL) was added to the dipyrrole mixture at about −50°C. The solution was allowed to warm to ambient temperature and stirring continued for a further 4 h. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; 0.9 g, 3.96 mmol) was added followed by $CHCl_3$ (25 mL), and the mixture was stirred for 2 h before triethylamine (TEA; 8 mL) was added. The mixture was stirred overnight. The solution was washed with H_2O (×3) and concentrated. Purification by column chromatography (silica, $CHCl_3$) yielded **9**. Recrystallization from CH_2Cl_2/MeOH gave (20.8 mg, 24%) of dark red coloured product. δ_H (400 MHz) 10.21 (s, 2H), 7.96 and 7.54 (ABq, *J* 7.8, 8H), 6.06 (m, 2H), 5.18 (m, 4H), 3.97 (t, *J* 7.6, 8H), 3.08 (t, *J* 7.4, 4H), 2.70 (q, *J* 7.2, 4H), 2.49 (s, 12H), 2.18 (p, *J* 7.4, 8H), 1.72 (p, *J* 7.5, 8H), 1.50 (m, 8H), 1.31 (m, 16H), 0.87 (t, *J* 6.8, 12H), −2.40 (s, 2H). λ_{max}/nm (ε/M^{-1} cm^{-1}) ($CHCl_3$) 409 (4.92), 508 (4.01), 541 (3.56), 574 (3.68). *m/z* (LR-ESI, +ve, $C_{72}H_{98}N_4$) calc. 1018.78, found 1019.8 $[M+H]^+$.

Zinc porphyrin **1**: Zinc(II) was inserted into free base porphyrin **10** using the acetate method.[16] (38 mg, 84%). δ_H (400 MHz) 10.15 (s, 2H), 7.96 and 7.53 (ABq, *J* 7.9, 8H), 6.07 (m, 2H), 5.18 (m, 4H), 3.95 (t, *J* 7.7, 8H), 3.09 (t, *J* 7.5, 4H), 2.69 (q, *J* 7.1, 4H), 2.46 (s, 12H), 2.18 (m, 8H), 1.72 (m, 8H), 1.50 (m, 8H), 1.34 (m, 16H), 0.89 (t, *J* 6.9, 12H). δ_C (100 MHz) 147.9, 146.4, 143.3, 141.7, 141.2, 138.2, 138.0, 133.1, 127.6, 119.4, 115.4, 97.5, 36.2, 35.6, 33.4, 32.0, 30.3, 29.5, 26.8, 22.7, 15.2, 14.1. λ_{max}/nm (ε/M^{-1} cm^{-1}) ($CHCl_3$) 409 (5.05), 536 (3.91), 572 (3.82). *m/z* (HR-ESI, +ve, $C_{72}H_{96}N_4Zn$) calc. 1080.692, found 1080.6919 $[M]^+$.

Square **11**: Zinc porphyrin **1** (13.4 mg, 12.4 μmol) and template porphyrin **10** (2 mg, 3.2 μmol) were stirred in CH_2Cl_2 (15 mL, degassed) in the dark under an Ar atmosphere. Grubbs first-generation catalyst (4.1 mg, 4.98 μmol) was added and the reaction was monitored by TLC. Further catalyst additions were made (5.8 mg, 7.05 μmol) and stirring was maintained. When TLC analysis showed that **1** was predominately consumed, the solution was washed consecutively with 30 mL HCl (3 M), H_2O (×2), $NaHCO_3$ (sat. soln.), H_2O (×2), and dried ($MgSO_4$). After the sample was concentrated, it was purified by column chromatography (silica, $CHCl_3$) and residual solvent was removed under high vacuum to obtain the square **11** as a purple-red solid (6.4 mg, 52%). δ_H (300 MHz) 10.18 (br m, 8H), 8.01 (br m, 16H), 7.64 (br m, 16H), 5.87 (br m, 4H), 5.81 (br m, 4H), 3.94 (br m, 32H), 3.15–0.82 (br m, 288H), −2.38 (br s, 8H). λ_{max}/nm (ε/M^{-1} cm^{-1}) ($CHCl_3$) 413 (5.56), 509 (4.46), 542 (4.06), 575 (4.09). *m/z* (LR-ESI, +ve, $C_{280}H_{376}N_{16}$) calc. 3966.2, found 992.8 $[M+4H]^{4+}$.

Accessory Materials

A scheme describing the template-directed assembly of four equivalents of alkenyl porphyrin **1** with the free base porphyrin **10** to give the desired square geometry in preparation for metathesis, and the corresponding time-averaged ^{1}H NMR spectroscopic changes of **1** and **10** during the assembly are available from the author or, until November 2010, the *Australian Journal of Chemistry*.

Acknowledgements

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