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Supporting Information

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Template-Directed Synthesis of a Conjugated Cyclic Porphyrin Octamer

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Synthetic Procedures

Materials and Methods

All reagents were purchased from commercial sources. Manipulation of all air and/or water sensitive compounds was carried out using standard high vacuum techniques.

Column chromatography was carried out on Merck® silica gel 60 using a positive pressure of nitrogen. Where mixtures of solvents were used, ratios reported are by volume.

NMR spectra were recorded on Bruker instruments, DPX-400, AV II-500 with cryprobe or DRX-500 with TBI probe. Chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane and coupling constants (*J*) are quoted in Hertz (Hz). MALDI-ToF mass spectra were acquired by the EPSRC Mass Spectrometry Sevice, Swansea, UK. UV-visible spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. Computational chemistry was carried out using CAChe 4.1, Oxford Molecular Ltd. UV-Vis spectrophotometric titration curves were analyzed by fitting the experimental data to the theoretically expected curve using a simplex nonlinear curve-fitting program[1], using a combination of bisection and the Newton-Raphson method to iteratively solve polynomial equilibrium expressions.

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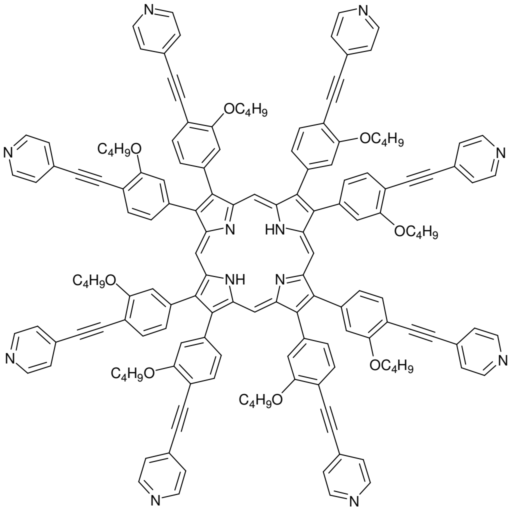
[1] W. H. Press, B. P. Flannery, S. A. Tenkolsky and W. T. Vetterling, *Numerical Recipes in Pascal* **1989**, Cambridge University Press.

Octadentate porphyrin template 2



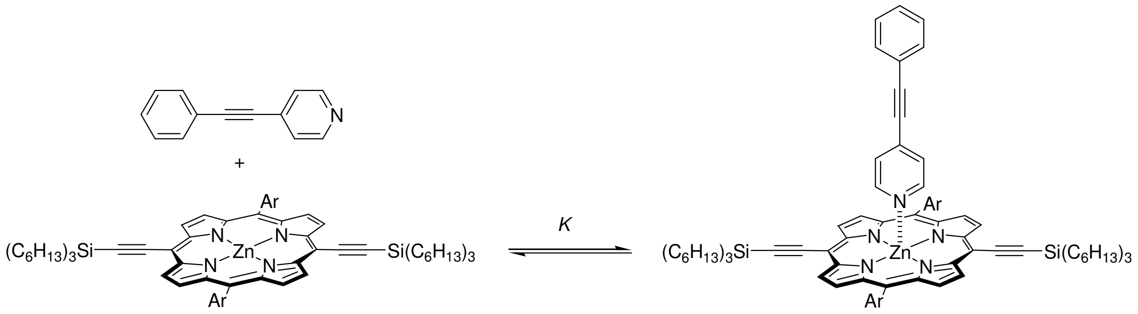
Lithium aluminium hydride (1.0 M in THF, 2.0 eq., 1.51 mL, 1.51 mmol) was added dropwise to a solution of *tert*-butyl 3,4-bis(3-butoxy-4-(pyridin-4-ylethynyl)phenyl)-1*H*-pyrrole-2-carboxylate **9** (500 mg, 0.75 mmol) in dry THF (19 mL) cooled in an ice bath. The reaction mixture was stirred 0.5 hr at 0 ºC before NaOH $_{(aq)}$ (1.0 M, 25 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was separated and washed with water (2 × 25 mL) and solvents removed. Dry CH_2Cl_2 (50 mL) and $CH_3OCH_2OCH_3$ (194 µL, 2.25 mmol) were added and the solution degassed. *para*-Toluene sulfonic acid (572 mg, 3.00 mmol) was added and the reaction mixture stirred for 16 hrs in the dark. DDQ (131 mg, 0.577 mmol) was added and the reaction stirred 10 min before washing with Na_2CO_3 $_{(aq)}$ (sat., 2 × 50 mL) and water (2 × 25 mL). Column chromatography (100:1:1 to 100:2:2 CH_2Cl_2 : MeOH : NEt_3) followed by recrystallisation by layer addition (CH_2Cl_2 / MeOH) gave a brown powder (39 mg, 9%): Found: C 79.87, H 5.52, N 7.22%, Calc for $C_{156.5}H_{135}N_{12}O_8Cl$ [M•0.5CH_2Cl_2]: C 80.08, H 5.80, N 7.16% m.p. >250 ºC; λ_{max} (CH_2Cl_2) / nm (log ε) 317 (5.17), 440 (5.62), 525 (4.55), 563 (4.39), 590 (4.25), 644 (3.96); δ_H (400 MHz, $CDCl_3$) 10.57 (s, 4H), 8.66 (d, 16H, J = 5.0 Hz), 7.81 (d, 1H, J = 7.8 Hz), 7.61 (m, 8H), 7.54 (d, 8H, J = 2.1 Hz), 7.45 (d, 16H, J = 5.0 Hz), 3.92 (t, 16H, J = 6.3 Hz), 1.90-1.77 (m, 16H), 1.67-1.49 (m, 16H), 1.00 (t, 24H, J = 7.3 Hz), -2.88 (s, 2H); δ_C (100 MHz, $CDCl_3$) 160.33, 149.84, 137.22, 133.73, 131.76, 125.42, 124.59, 116.11, 111.58, 103.36, 92.00, 90.59, 68.83, 31.16, 19.31, 13.94; *m/z* (MALDI ToF MS+) 2305.51 ($[M+H]^{\bullet+}$, $C_{156}H_{135}N_{12}O_8$, requires 2304.05).

Cyclic octamer-template complex **2·1**

Template **2** (3.7 mg, 1.6 μmol) was added to porphyrin octamer **3** (12.8 mg, 1.5 μmol) and 2.0 mL of a solution of dichlorobis(triphenylphosphine)-palladium(II) (8.2 mg, 12 μmol), copper(I) iodide (3.4 mg, 18 μmol) and iodine (26 mg, 102 μmol) in toluene (12.5 mL) and diisopropylamine (1.0 mL) was added. The reaction mixture was stirred vigorously at 60 ºC under air for 2 hours. UV-Vis spectroscopy showed the reaction to be complete. The mixture was diluted with CH_2Cl_2 (10 mL), washed with $Na_2S_2O_3$ aq., washed with water, evaporated, redissolved in THF (2 mL) and filtered (0.45 μm membrane). Preparative GPC using a 600 mm (25 mm ID) PLgel column (Polymer Laboratories Ltd.) at 9 mL min^{-1}, collecting the peak at 12.3 min, gave **2·1** as a brown solid (2.2 mg, 14%). MALDI-TOF MS+: *m/z* 10988 ($[M]^{\bullet+}$, $C_{700}H_{790}N_{44}O_{40}Zn_8$, requires 10983); UV-vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$ 441 (3.1×10^5), 498 (3.4×10^5), 757 (1.1×10^5), 798 (1.5×10^5), 848 nm (3.4×10^5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.88 (s, 4H), 9.78 (m, 32H), 9.02 (m, 32H), 7.55 (s, 16H), 7.22 (s, 16H), 6.95 (s, 16H), 6.80–6.76 (m, 16H), 6.51 (s, 8H), 5.38 (d, *J* = 6.5 Hz, 16H), 4.24 (t, *J* = 6.0 Hz, 32H), 4.17 (t, *J* = 6.0 Hz, 32H), 3.34 (t, *J* = 6.0 Hz, 16H), 2.52 (d, *J* = 6.5 Hz, 16H), 1.93–1.91 (m, 80H), 1.56–1.26 (m, 336H), 1.03 (t, *J* = 7.0 Hz, 24H), 0.92–0.89 (m, 96H), –3.57 (s, 2H).

Cyclic octamer 1

2·1 (2.2 mg, 200 nmol) was passed through a size exclusion column (Bio-Beads S-X1, Bio-Rad Laboratories, Ltd.) using chloroform / 20% pyridine. Template-free cyclic octamer **1** was isolated as a brown solid (1.8 mg, 193 nmol, 97%). UV-vis ($CHCl_3$, 1% C_5H_5N): $\lambda_{max}(\varepsilon)$ 464 (4.4×10^5), 490 (3.9×10^5), 802 nm (1.8×10^5); ^{1}H NMR (500 MHz, 328K, $CDCl_3$): δ 9.72 (d, *J* = 4.5 Hz, 32H), 8.95 (d, *J* = 4.5 Hz, 32H), 7.32 (s, 32H), 6.88 (s, 16H), 4.14 (t, *J* = 6.5 Hz, 64H), 1.89–1.84 (m, 64H), 1.55–1.26 (m, 320H), 0.83 (t, *J* = 6.8 Hz, 96H).



Scheme S1 Binding of 10,20-bis-trimethylsilanylethynyl-zinc-porphyrin with 4-(2-phenylethynyl)pyridine, **L**.

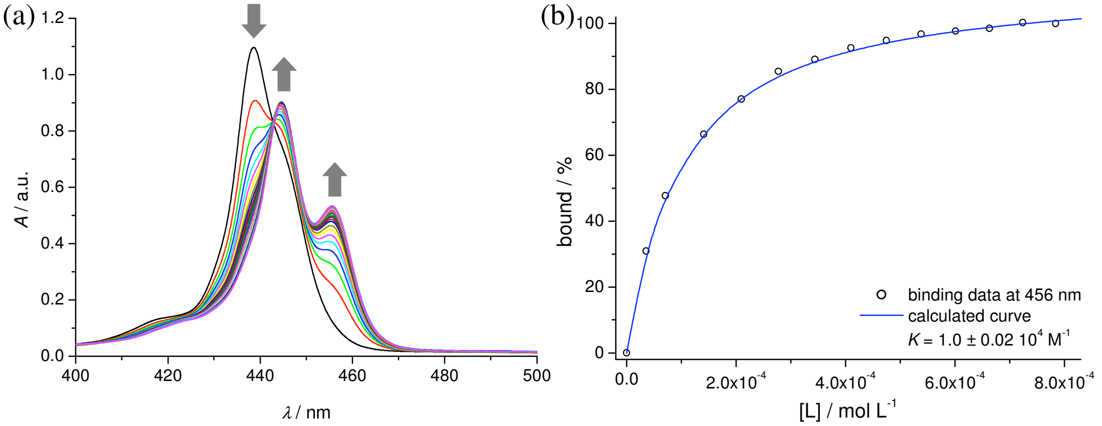


Figure S1 ***(a)*** UV-vis titration of 4-(2-phenylethynyl)pyridine, **L** with 10,20-bis-trimethylsilanylethynyl-zinc-porphyrin, (conc. 3.02 μM, 298 K, $CHCl_3$). The data at 456 nm were fitted to a 1:1 binding isotherm ***(b)*** to give a binding constant of K_0 = 1.0 ± 0.02 10^4 M^{-1}. Arrows indicate areas of increasing and decreasing absorption during the titration.

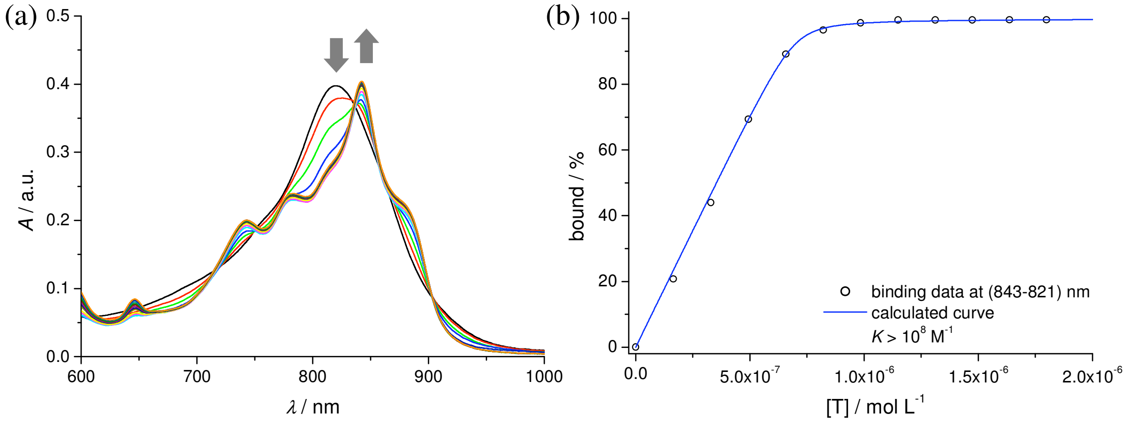


Figure S2 ***(a)*** UV-vis titration of Template, **2** with linear porphyrin octamer, **3** ([**3**] = 1.8 μM, 298 K, $CHCl_3$). ***(b)*** Binding isotherm obtained from the absorbance data at (843-821) nm. The data at (843-821) nm were fitted to a 1:1 binding isotherm ***(b)*** to give a binding constant of $K > 10^8$ M^{-1}. Arrows indicate areas of increasing and decreasing absorption during the titration.

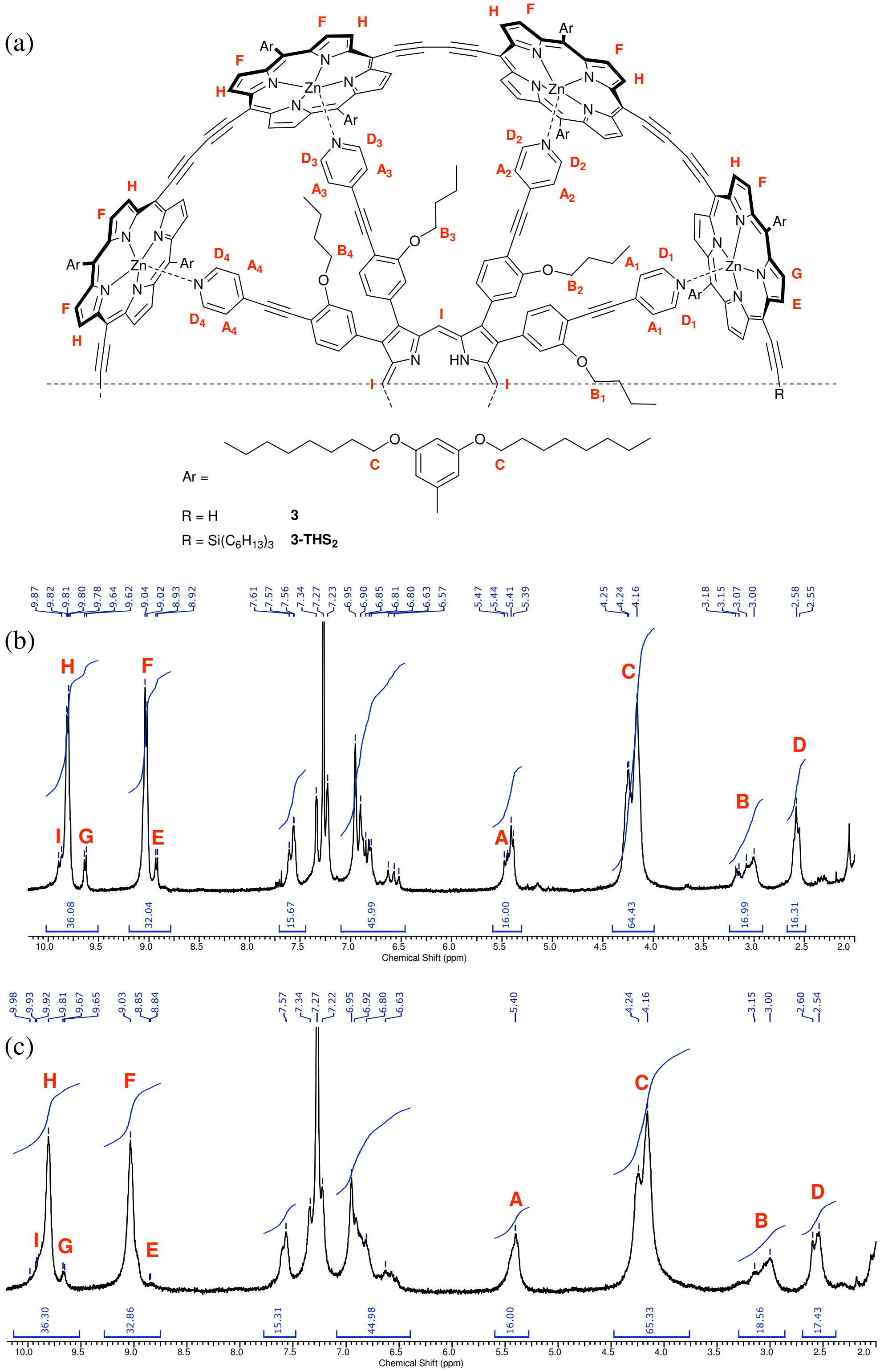
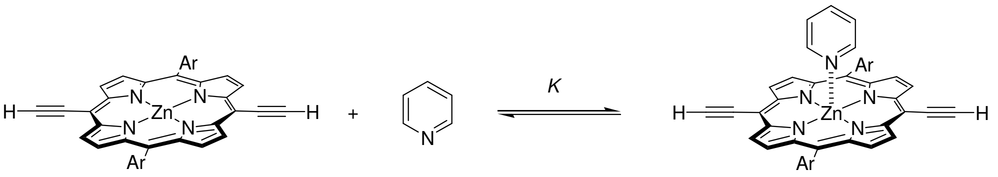


Figure S3 (a) Structure of template complex with deprotected octamer **2·3** and trihexylsilyl-protected octamer **2·3-THS$_2$**, respectively. The dashed line represents a plane of symmentry. Selected ^{1}H NMR spectra from titration of template, **2** with ***(b)*** linear trihexylsilyl-protected porphyrin octamer, **3-THS$_2$** and ***(c)*** linear octamer, **3** (500 MHz, 298 K, CDCl$_3$). The integrations shown on these spectra confirm the 1:1 stoichiometry of both complexes.



Scheme S2 Binding of 10,20-bis-ethynyl-zinc-porphyrin with pyridine, **Py**.

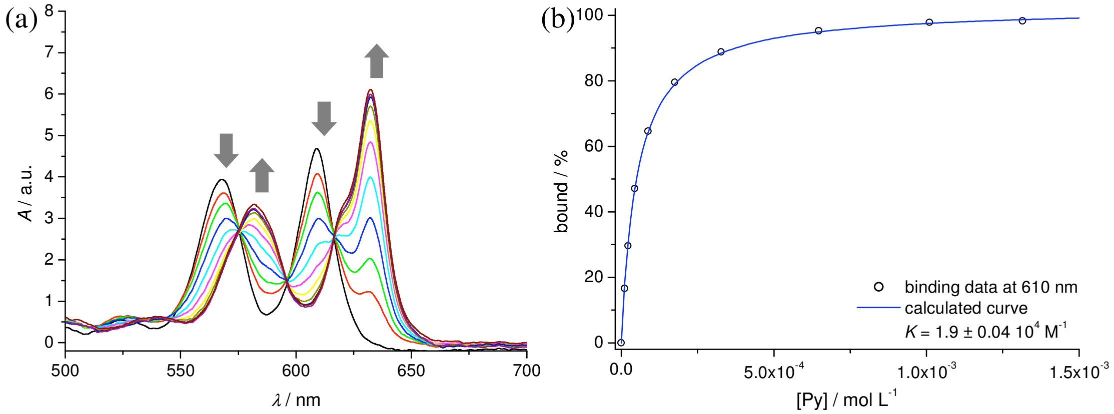


Figure S4 (a) UV-vis titration of pyridine, **Py** with 10,20-bis-ethynyl-zinc-porphyrin (conc. 2.8 μM, 298 K, $CHCl_3$). The data at 610 nm were fitted to a 1:1 binding isotherm ***(b)*** to give a binding constant of $K = 1.9 \pm 0.04$ 10^4 M^{-1}. Arrows indicate areas of increasing and decreasing absorption during the titration.

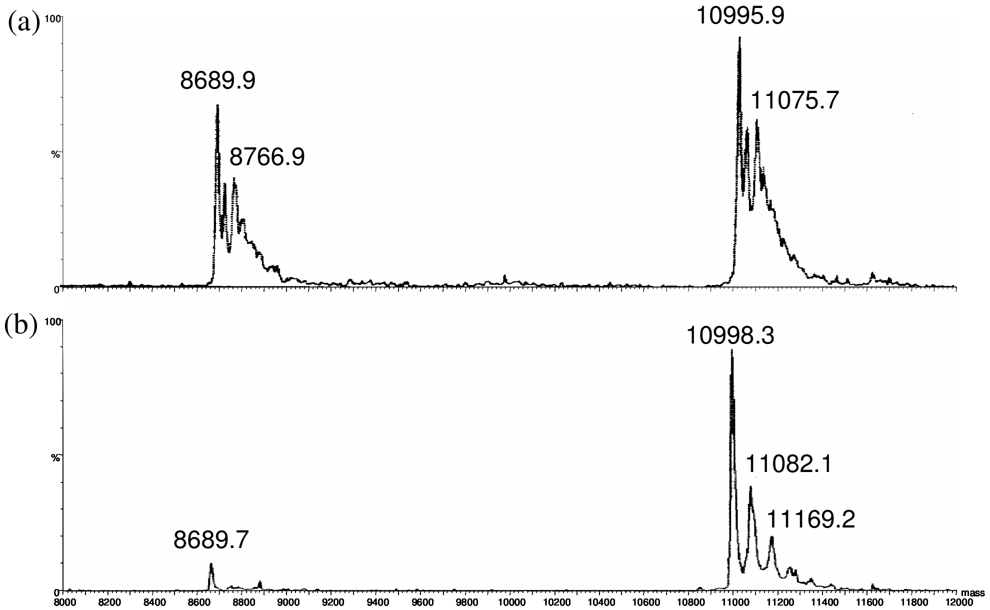


Figure S5 MALDI-ToF mass spectra of ***(a)*** **2·3** (expected mass **2·3** 10985.2, found 10995.9; expected mass **3** 8680.4, found 8689.9) and ***(b)*** **2·1** (expected mass **2·1** 10983.2, found 10998.3; expected mass **1** 8678.3, found 8689.7), recorded in positive linear mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as matrix.