Supporting Information

**Tuning the Circumference of Six-Porphyrin Nanorings**

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1 General Methods

Dry toluene, CHCl₃, CH₂Cl₂, THF, NEt₃ and pyridine were obtained from the solvent drying system MBraun MB-SPS-5-BenchTop under nitrogen atmosphere (H₂O content < 20 ppm as determined by Karl-Fischer titration). N,N-Diisopropylamine (i-Pr₂NH) was distilled from CaH₂ and kept over activated molecular sieves (3 Å, 8–12 mesh). Unless specified otherwise, all other solvents were used as commercially supplied. Flash chromatography was carried out using SiO₂ (60 Å, 230–400 mesh) under positive pressure. Analytical thin-layer chromatography was carried out on aluminum-backed silica gel 60 F254 plates. Petroleum ether (PE) 40–60°C was used unless specified otherwise.

All UV-vis-NIR spectra were recorded in solution using a Perkin-Lambda 20 spectrometer (1 cm path length quartz cell). Chloroform (containing ca. 0.5% ethanol as stabilizer) or toluene was used for all titrations without any further purification (HPLC grade). Fluorescence lifetimes were obtained from time correlated single-photon counting (TCSPC) using a single-photon avalanche diode detector with a time-resolution of 40 ps.¹

Unless stated otherwise, ¹H and ¹³C NMR spectra were recorded at 298 K using a Bruker AVIII HD 400, a Bruker AVII 500 or a Bruker AVIII 700 instrument. ¹H and ¹³C NMR spectra are reported in ppm; coupling constants are given in Hertz, to the nearest 0.1 Hz. The solvent used was CDCl₃ which was calibrated to residual CHCl₃ at 7.26 ppm. Diffusion coefficients were measured at 298 K in CDCl₃ using a double stimulated echo sequence for convection compensation. The hydrodynamic radius was estimated from the diffusion coefficient using the Stoke-Einstein equation with a viscosity for CDCl₃ at 298 K of 5.28 × 10⁻⁴ Kg m⁻¹ s⁻¹.

MALDI-ToF spectra were measured at the EPSRC UK National Mass Spectrometry Facility (NMSF, Swansea) using the Applied Biosystems Voyager DE-STR or at the University of Oxford using a Waters Micro MX spectrometer utilizing dithranol or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix.

Size exclusion chromatography (SEC) was carried out using Bio-Rad Bio-Beads S-X1 (40–80 µm bead size). Analytical GPC was carried out using JAIGEL-3H-A (8φ×500) and JAIGEL-4H-A (8φ×500) columns in THF + 1% pyridine as eluent with a flow rate of 1.0 mL/min. Semi-preparative GPC was carried out on a Shimadzu Recycling GPC system equipped with a LC-20 AD pump, SPD-20A UV detector and a set of JAIGEL 3H (20 × 600 mm) and JAIGEL 4H (20 × 600 mm) columns in toluene + 1% pyridine as the eluent at a flow rate of 3.5 mL/min. Where indicated NEt₃-deactivated silica was used, which was prepared by stirring a slurry of silica in PE₄O₆0/3% NEt₃ at 20 °C overnight before removing the solvents under reduced pressure.
2 Compound Naming System

The compounds discussed in this manuscript are systematically labeled according to the following naming system:

Porphyran monomers: \( \text{R-P1-R} \)

Linear Porphyrin oligomers: \( \text{R-}l\text{-PN}[b,e_x]\text{-R} \) in which
\( l \) : denotes linear.
\( N \) : number of porphyrin units in the linear oligomer.
\( b \) : \( x \) is the number of butadiyne [b] links between the porphyrin units in the linear oligomer.
\( e_x \) : \( y \) is the number of ethyne [e] links between the porphyrin units in the linear oligomer.
\( R = H, Br, TMS \) (denoting \( \text{Me}_3\text{Si-acetylene} \)), \( \text{CPDMS} \) (denoting \( \text{CN(CH}_2)_3\text{Me}_2\text{Si-acetylene} \)), \( \text{CPDIPS} \) (denoting \( \text{CN(CH}_2)_3\text{(i-Pr)_2Si-acetylene} \)), \( \text{HC}_2 \) (denoting unprotected acetylene).

Cyclic porphyrin hexamers: \( \text{c-P6}[b,e_x] \) in which
\( c \) : denotes cyclic.
\( b \) : \( x \) is the number of butadiyne [b] links between the porphyrin units in the cyclic oligomer.
\( e_x \) : \( y \) is the number of ethyne [e] links between the porphyrin units in the cyclic oligomer.

The schematic representation of the nanorings (Figure S1), shows the porphyrin units as black spheres interconnected by either butadiyne (in black) or ethynyl linkages (in red).

Templates are labeled T6 and T6* having phenyl or acetylene links between the hexasubstituted central benzene moiety and the pyridine arms, respectively:

Peak assignments in \textsuperscript{1}H are labeled according to the following conventions:
\( a1^{(#)}/a2^{(#)} \) (belongs to EITHER \( a1^{(#)} \) or \( a2^{(#)} \))
\( a1^{(#)}\cdot a2^{(#)} \) (belongs to BOTH \( a1^{(#)} \) and \( a2^{(#)} \))
\( a1\cdot3 \) (belongs to \( a1, a2, a3 \), with and without #)

Correlations in 2D \textsuperscript{1}H NMR are labeled according to the following conventions:
\( s \) : strong correlation
\( w \) : weak correlation
\( o \) : overlap
Figure S1: Chemical structures, compound labels and schematic representations of the compounds used in this study. Ar = 3,5-bis(triethylsilyl)phenyl.

3 Synthetic Procedures

Monomers Br-P1-Br,\(^2\) Br-P1-H,\(^3\) CPDIPS-P1-H,\(^3\) and CPDIPS-P1-C,\(^\text{H},\(^4\) templates T6,\(^5\) and T6*,\(^3\) and porphyrin nanorings c-P6[8]-T6,\(^6\) and c-P6[e6]-T6*,\(^3\) were prepared as reported previously.
3.1 Synthesis of c-P6[b₅e]-T6 and c-P6[b₅e]

We also prepared CPDMS-1-P6[b₅e]-CPDMS by coupling H₂C-I-P2[e]-C₂H with excess H₂C-I-P2[b]-CPDMS but we found that c-P6[b₅e]-T6 prepared by this more direct route was always contaminated by small amounts of c-P6[b₅e-T6].

Scheme S1: Synthesis of c-P6[b₅e]-T6. We also prepared CPDMS-1-P6[b₅e]-CPDMS by coupling H₂C-I-P2[e]-C₂H with excess H₂C-I-P2[b]-CPDMS but we found that c-P6[b₅e]-T6 prepared by this more direct route was always contaminated by small amounts of c-P6[b₅e]-T6.
Br-P1-CPDMS:

Br-P1-Br (1.40 g, 0.77 mmol), Pd₂(dba)₃ (70 mg, 0.077 mmol), Cul (15 mg, 0.077 mmol) and triphenylphosphine (40 mg, 0.15 mmol) were added and the mixture was deoxygenated by freeze-pump-thaw cycles. Cyanopropyldimethylsilylacetylene (97 μL, 0.62 mmol) was added and the reaction mixture was stirred at 50 °C for 40 min after which TLC (PE₄₀-₆₀/CH₂Cl₂ 4:1) showed the desired statistical distribution of products. The volatiles were removed in vacuo and the residue was purified by column chromatography (SiO₂; gradient of PE₄₀-₆₀/CH₂Cl₂ 100:0 to 1:1) affording the desired product Br-P1-CPDMS (332 mg, 23%) as a green solid. Furthermore, starting material Br-P1-Br (559 mg, 40%) and the bis-acetylene substituted product CPDMS-P1-CPDMS (230 mg, 16%, for characterization see below) were obtained.

¹H NMR (400 MHz, CDCl₃, 298 K): δ: 9.72 (d, J = 4.5 Hz, 2H, a1/a1²), 9.67 (d, J = 4.5 Hz, 2H, a1/a1²), 8.94 (d, J = 4.5 Hz, 2H, b1/b1²), 8.91 (d, J = 4.5 Hz, 2H, b1/b1²), 8.24 (d, J = 1.2 Hz, 4H, a), 8.01 (t, J = 1.2 Hz, 2H, p), 2.08 (t, J = 7.0 Hz, 2H, CPDMS-CH₂), 2.04 (m, 2H, CPDMS-CH₂), 1.49–0.90 (m, 156H, THS), 1.18 (m, 2H, CPDMS-CH₂), 0.61 (s, 6H, CPDMS-CH₃) ppm. ¹³C NMR (125 MHz, CDCl₃, 298 K): δ: 153.0, 151.5, 150.6, 149.6, 140.6, 140.3, 139.4, 135.2, 133.7, 133.4, 133.2, 131.2, 124.0, 119.8, 108.9, 106.8, 99.9, 99.4, 33.7, 31.8, 24.2, 22.8, 21.1, 20.9, 16.3, 14.3, 13.0, 12.8, 12.6 ppm. MALDI-ToF m/z 1883.77 (calculated for [C₁₁₂H₁₈₂BrN₅Si₅Zn]⁺: 1894.17).

CPDMS-P1-CPDMS:

Br-P1-Br (454 mg, 0.25 mmol), Pd(PPh₃)₂Cl₂ (35 mg, 0.05 mmol) and Cul (9.5 mg, 0.05 mmol), were placed in a 250-mL two-necked flask. Dry toluene (25 mL), i-Pr₃NH (4.5 mL) and pyridine (0.6 mL) were injected to the Schlenk tube. 3-Cyanopropyldimethylsilylecetylene (151 mg, 0.16 mL, 1.00 mmol) was added by syringe. The reaction mixture was stirred at 50 °C under argon atmosphere for 2.5 h. The solvents were removed in vacuo and the residue was purified by column chromatography (SiO₂; gradient of PE₄₀-₆₀/CH₂Cl₂ 10:1 to 5:1 to 2:1) affording the desired product CPDMS-P1-CPDMS (419 mg, 79% yield) as an oily green solid.

¹H NMR (400 MHz, CDCl₃, 298 K): δ: 9.63 (d, J = 4.5 Hz, 4H, a1), 8.88 (d, J = 4.5 Hz, 4H, b1), 8.22 (d, J = 1.2 Hz, 4H, o), 7.99 (t, J = 1.2 Hz, 2H, p), 2.55 (t, J = 7.0 Hz, 4H, CPDMS-CH₂), 2.13 (m, 4H, CPDMS-CH₂), 1.46–0.89 (m, 156H, THS), 1.19 (m, 4H, CPDMS-CH₂), 0.59 (s, 12H, CPDMS-CH₃) ppm. ¹³C NMR (125 MHz, CDCl₃, 298 K): δ: 152.2, 150.8, 140.5, 140.2, 139.4, 135.2, 133.3, 131.1, 124.3, 119.8, 108.9, 101.0, 99.7, 77.4, 77.2, 76.9, 33.7, 31.8, 24.2, 22.8, 21.1, 20.9, 16.3, 14.3, 13.0, 12.8, 12.6, –1.3 ppm. MALDI-ToF m/z 1953.10 (calculated for [C₁₂₀H₁₉₄N₅Si₅Zn]⁺: 1953.33).
Br-P1-C₂H:

K₂CO₃ (140 mg, 1.0 mmol) was added to a solution of Br-P1-CPDMS (95 mg, 0.051 mmol) in THF (5 mL), MeOH (5 mL) and pyridine (0.1 mL). The suspension was stirred at room temperature for 30 min before the mixture was passed through a plug (SiO₂; PE₄₀-₆₀/CH₂Cl₂ 2:1 + 1% pyridine). The volatiles were removed in vacuo yielding Br-P1-C₂H (90.3 mg 100%) as a green solid.

¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.75 (t, J = 5.0 Hz, 4H, a₁/a₁¹), 8.97 (d, J = 4.7 Hz, 2H, b₁/b₁¹), 8.94 (d, J = 4.7 Hz, 2H, a₂/a₂¹), 8.26 (d, J = 0.8 Hz, 4H, o), 8.02 (t, J = 0.8 Hz, 2H, p), 4.19 (s, 1H, c), 1.51–0.91 (m, 156H, THS) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ 153.2, 151.5, 150.7, 149.5, 140.5, 140.3, 139.4, 135.2, 133.7, 133.4, 133.2, 131.4, 123.9, 106.7, 99.2, 86.0, 83.9, 33.7, 31.8, 24.2, 22.8, 14.3, 12.8 ppm. MALDI-ToF m/z 1758.62 (calculated for [C₁₀₀H₁₇₁BrN₄Si₄Zn⁺]: 1759.11).

Br-P1-TMS:

Zn(OTf)₂ (1.20 g, 3.3 mmol) was placed in a Schlenk flask under argon atmosphere. CH₂Cl₂ (7.5 mL) and NEt₃ (0.9 mL) were added and this mixture was stirred for 30 min. Br-P1-C₂H (287 mg, 0.16 mmol) in CH₂Cl₂ (3 mL) was added and the reaction mixture was stirred for 1 h before trimethylsilyl chloride (41 μL, 0.33 mmol) was added. The mixture was stirred overnight after which MALDI-ToF analysis confirmed completion. Saturated aqueous NH₄Cl was added and the organic layer was extracted and washed with H₂O. The organic layer was dried over MgSO₄ and the volatiles were removed in vacuo. The residue was purified by column chromatography (SiO₂; PE₄₀-₆₀/CH₂Cl₂ 15:1) affording the desired product Br-P1-TMS (220 mg, 75%) as a green solid.

¹H NMR (400 MHz, CDCl₃ + 1% pyridine-d₅, 298 K): δ 9.63 (d, J = 1.2 Hz, 2H, a₁/a₁¹), 9.62 (d, J = 1.2 Hz, 2H, a₁/a₁¹), 8.84 (t, J = 4.8 Hz, 4H, b₁/b₁¹), 8.27 (d, J = 1.0 Hz, 4H, a₂/a₂¹), 7.97 (s, 2H, p), 1.49–0.87 (m, 156H, THS), 0.56 (s, 9H, TMS) ppm. ¹³C NMR (100 MHz, CDCl₃ + 1% pyridine-d₅, 298 K): δ 153.0, 151.2, 150.5, 149.3, 140.9, 140.8, 139.0, 134.7, 133.2, 132.9, 132.6, 131.0, 123.4, 106.2, 100.5, 99.3, 95.6, 33.7, 31.7, 24.2, 22.8, 14.3, 12.8, 0.44 ppm. MALDI-ToF m/z 1831.08 (calculated for [C₁₀₉H₁₇₉BrN₄Si₅Zn⁺]: 1831.15).
HC₂-P1-CPDMS:

CPDMS-P1-CPDMS (980 mg, 0.50 mmol) was dissolved in CHCl₃ (130 mL, with 1.3 mL EtOH) and cooled to 0 °C. TBAF (1.0 M in THF, 0.25 mL, 0.25 mmol) was added and the reaction was monitored by TLC (PE₄₀:₆₀/CH₂Cl₂ 4:1). After 20 min, the reaction was warmed to room temperature. After 50 min total reaction time, the reaction was quenched by adding acetic acid (0.05 mL, 0.9 mmol) and passed through a short plug (SiO₂; CH₂Cl₂ + 1% pyridine). Solvents were removed and the residue was purified by column chromatography (SiO₂; gradient of PE₄₀:₆₀/CH₂Cl₂ 4:1) as a green solid, and starting material CPDMS-P1-CPDMS (200 mg, 20% as a green solid).

¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.65 (d, J = 4.5 Hz, 2H, a1/a1'), 9.59 (d, J = 4.5 Hz, 2H, a1/a1'), 8.86 (d, J = 4.5 Hz, 4H, b1), 8.21 (s, 4H, o), 7.97 (s, 2H, p), 4.14 (s, J = 1H, c), 2.55 (t, J = 7.0 Hz, 2H, CPDMS-CH₃), 2.13 (m, 2H, CPDMS-CH₃), 1.49–0.90 (m, 156H, TMS), 1.18 (m, 2H, CH₂), 0.59 (s, 6H, CPDMS-CH₃), ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 152.3, 152.1, 150.7, 150.6, 140.9, 140.7, 139.1, 136.0, 134.8, 133.0, 132.9, 130.9, 130.7, 123.9, 122.5, 119.9, 110.0, 100.0, 99.5, 98.6, 86.9, 83.3, 33.7, 31.8, 24.2, 22.8, 21.1, 20.9, 16.4, 14.3, 12.8, −1.27 ppm. MALDI-ToF m/z 1829.08 (calculated for [C₁₁₄H₁₈₃N₅Si₂Zn]⁺: 1828.26).

TMS-/P2[e]-CPDMS:

Br-P1-TMS (130 mg, 71.0 μmol), HC₂-P1-CPDMS (140 mg, 76.5 μmol), Pd₃(dbą)₃ (14.6 mg, 14.2 μmol), AsPh₃ (17.3 mg, 56.8 μmol) were added into a flask, and placed under argon atmosphere by three vacuum cycles. Dry THF (5 mL) and NEt₃ (1 mL) were injected to the flask. The reaction mixture was stirred at 60 °C for 17 h under argon atmosphere. The solvents were removed and the residue was purified by SEC (toluene + 1% pyridine) and further purified by column chromatography (SiO₂; gradient of PE₄₀:₆₀/CH₂Cl₂ 10:1 to 10:3) to afford TMS-/P2[e]-CPDMS (163 mg, 64%) as a green solid.

¹H NMR (400 MHz, CDCl₃, 298 K): δ 10.35 (d, J = 4.5 Hz, 2H, a1/a2), 10.33 (d, J = 4.5 Hz, 2H, a1/a2), 9.71 (d, J = 4.5 Hz, 2H, a1/a2), 9.66 (d, J = 4.5 Hz, 2H, a1/a2), 9.06 (d, J = 4.5 Hz, 2H, b1/b1'/b2/b2'), 8.90 (d, J = 4.5 Hz, 2H, b1/b1'/b2/b2'), 8.31 (m, 8H, o), 8.01 (m, 4H, p), 2.58 (t, J = 6.9 Hz, 2H, CPDMS-CH₃), 2.15 (m, 2H, CPDMS-CH₃), 1.50–0.82 (m, 312H, THS), 1.18 (m, 2H, CPDMS-CH₃), 0.62 (s, 6H, CPDMS-CH₃), 0.60 (s, 9H, TMS) ppm. ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 152.6, 152.6, 152.5, 152.4, 150.6, 150.6, 150.6, 150.5, 144.6, 141.0, 140.9, 140.7, 140.6, 136.0, 134.8, 134.7, 133.0, 132.9, 130.9, 130.8, 130.7, 130.5, 129.2, 128.4, 124.3, 124.2, 122.7, 122.2, 119.9, 110.1, 108.6, 103.2, 102.7, 100.9, 100.0, 100.5, 99.7, 98.5, 53.6, 41.5, 33.7, 33.7, 31.8, 31.7, 29.2, 24.2, 22.8, 21.1, 20.9, 20.6, 19.6, 16.4, 14.3, 13.0, 12.8, 12.6, 11.6, 0.5, −1.2 ppm. MALDI-ToF m/z 3579.58 (calculated for [C₂₂₃H₃₆₃N₅Si₂Zn₂]⁺: 3579.48). UV-vis-NIR (toluene + 1% pyridine) λ_max (log ε): 754 (4.92), 580 (4.28), 495 (5.51), 430 (5.28).
HC₂-P2[e]-C₂H:

TMS-I-P2[e]-CPDMS (109 mg, 30.5 μmol) was dissolved in CH₂Cl₂ (10 mL) and pyridine (0.1 mL). TBAF (1.0 M in THF, 0.46 mL, 0.46 mmol) was added and the reaction was stirred for 20 min at room temperature before passing through a plug (SiO₂; CHCl₃ + 1% pyridine). The volatiles were removed in vacuo to afford HC₂-I-P2[e]-C₂H (97 mg, 94%) as a green solid.

¹H NMR (500 MHz, CDCl₃, 298 K): δ₁ 10.31 (d, J = 4.5 Hz, 4H, a1), 9.66 (d, J = 4.5 Hz, 4H, a¹), 8.99 (d, J = 4.5 Hz, 4H, b₁/b₁¹), 8.86 (d, J = 4.5 Hz, 4H, b₁/b₁²), 8.28 (s, 8H, o), 7.97 (s, 4H, p), 4.16 (s, 2H, c), 1.49–0.90 (m, 312H, THS) ppm. ¹³C NMR (125 MHz, CDCl₃, 298 K): δ₂ 152.6, 150.7, 150.6, 145.5, 141.1, 140.7, 139.1, 136.0, 134.8, 133.05, 132.97, 130.8, 130.7, 124.1, 122.9, 102.9, 100.7, 98.9, 87.1, 83.2, 33.7, 31.8, 24.2, 22.8, 14.3, 12.8 ppm. MALDI-ToF m/z 3378.77 (calculated for [C₂₁₂H₃₄₂N₈Si₈Zn₂]⁺: 3382.38).

CPDMS-I-P4[b₂e]-CPDMS:

HC₂-P2[e]-C₂H (96 mg, 29 μmol) and HC₂-P1-CPDMS (417 mg, 0.23 mmol) were dissolved in dry toluene (25 mL). Pd(PPh₃)₂Cl₂ (10 mg, 14 μmol), Cul (27 mg, 0.14 mmol), and 1,4-benzoquinone (61 mg, 0.57 mmol) were dissolved in a mixture of dry toluene (25 mL) and dry i-Pr₂NH (5 mL) and this catalyst solution was added to the porphyrin solution. The reaction was stirred at room temperature and monitored by TLC. After 1 h, the mixture was passed through a plug (SiO₂; CHCl₃ + 1% pyridine). The solvents were removed and the residue was purified by SEC (toluene + 1% pyridine) and further purified by recycling GPC (toluene + 1% pyridine) to afford CPDMS-I-P4[b₂e]-CPDMS (103 mg, 50%) as a yellow-brown solid.

¹H NMR (400 MHz, CDCl₃, 298 K): δ₃ 10.34 (d, J = 4.5 Hz, 4H, a1), 9.89 (overlapping doublets, J = 4.5 Hz, J = 4.5 Hz, 8H, a¹), 9.61 (d, J = 4.5 Hz, 4H, a²), 9.01 (d, J = 4.5 Hz, 4H, b₁), 8.96 (overlapping doublets, J = 4.5 Hz, J = 4.5 Hz, 8H, b₁²), 8.87 (d, J = 4.5 Hz, 4H, b₁³), 8.34 (s, 8H, o), 8.27 (s, 8H, o), 8.02 (m, 8H, p), 2.58 (t, J = 7.0 Hz, 4H, CPDMS-CH₂), 2.16 (m, 4H, CPDMS-CH₂), 1.52–0.83 (m, 624H), 1.22 (m, 4H, CPDMS-CH₂), 0.62 (s, 12H, CPDMS-CH₃) ppm. ¹³C NMR (125 MHz, CDCl₃, 298 K): δ₄ 153.4, 153.1, 152.7, 152.2, 150.8, 150.8, 150.5, 150.5, 143.8, 140.9, 140.7, 139.3, 136.1, 135.0, 134.9, 133.4, 133.3, 133.1, 133.0, 130.9, 130.8, 124.5, 122.6, 119.9, 109.9, 103.5, 101.1, 100.2, 99.5, 98.9, 88.5, 88.2, 82.7, 82.5, 33.7, 31.8, 24.2, 22.8, 21.1, 20.9, 16.4, 14.4, 14.3, 12.8, –1.3 ppm. MALDI-ToF m/z 7037.81 (calculated for [C₄₄₂H₇₀₄N₈Si₈Zn₁₂]⁺: 7036.87). UV-vis-NIR (toluene + 1% pyridine) λₘₐₓ (log ε): 816 (5.28), 659 (4.75), 483 (5.53), 460 (5.61).
HC<sub>2</sub>-P4[<sub>b2</sub>e]-C<sub>2</sub>H:

CPDMS-I-P4[<sub>b2</sub>e]-CPDMS (88 mg, 12 µmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and pyridine (0.05 mL). TBAF (1.0 M in THF, 0.18 mL, 0.18 mmol) was added and the reaction was stirred for 20 min at room temperature before the mixture was passed through a plug (SiO<sub>2</sub>; CHCl<sub>3</sub> + 1% pyridine). The solvents were removed to afford HC<sub>2</sub>-I-P4[<sub>b2</sub>e]-C<sub>2</sub>H (84 mg, 100%) as a brown solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>1</sub> 10.33 (d, J = 4.5 Hz, 4H, a1), 9.91 (d, J = 4.5 Hz, 4H, a1<sup>g</sup>/a2), 9.89 (d, J = 4.5 Hz, 4H, a1<sup>g</sup>/a2), 9.67 (d, J = 4.5 Hz, 4H, a2<sup>g</sup>), 9.01 (d, J = 4.5 Hz, 4H, b1), 8.96 (d, J = 4.5 Hz, 4H, b1<sup>g</sup>/b2), 8.95 (d, J = 4.5 Hz, 4H, b1<sup>g</sup>/b2), 8.88 (d, J = 4.5 Hz, 4H, b2<sup>g</sup>), 8.33 (s, 8H, o), 8.27 (s, 8H, o), 8.01 (m, 8H, p), 4.17 (s, 2H, c), 1.54–0.82 (m, 624H, THS) ppm. MALDI-ToF m/z 6785.39 (calculated for [C<sub>436</sub>H<sub>682</sub>N<sub>15</sub>Si<sub>15</sub>Zn<sub>4</sub>]<sup>+</sup>: 6786.74).

CPDMS-I-P6[<sub>b2</sub>e]-CPDMS:

HC<sub>2</sub>-P4[<sub>b2</sub>e]-C<sub>2</sub>H· (60 mg, 7.8 µmol) and HC<sub>2</sub>-P1-CPDMS (156 mg, 78 µmol) were dissolved in dry toluene (15 mL). Pd(PPh<sub>3</sub>)<sub>2</sub>C1 (8.4 mg, 12 µmol), Cul (23 mg, 0.12 mmol), and 1,4-benzoquinone (92 mg, 0.85 mmol) were dissolved in a mixture of dry toluene (15 mL) and dry i-Pr<sub>2</sub>NH (2 mL). The porphyrin solution was added to the catalyst solution. The mixture was stirred at room temperature and monitored by TLC. After 3 h, the mixture was filtered through a plug (SiO<sub>2</sub>; CHCl<sub>3</sub> + 1% pyridine). The solvents were removed and the residue was purified by SEC (toluene + 1% pyridine) and further purified by recycling GPC (toluene + 1% pyridine) to afford CPDMS-I-P6[<sub>b2</sub>e]-CPDMS (57 mg, 68%) as a brown solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>1</sub> 10.38 (d, J = 4.5 Hz, 4H, a1), 9.98 (m, 16H, a1<sup>g</sup>,2.2<sup>g</sup>,3), 9.68 (d, J = 4.5 Hz, 4H, a3<sup>g</sup>), 9.10 (d, J = 4.5 Hz, 4H, b1), 9.03 (m, 16H, b1<sup>g</sup>,2.2<sup>g</sup>,3), 8.94 (d, J = 4.5 Hz, 4H, b3<sup>g</sup>), 8.39 (s, 8H, o), 8.37 (s, 8H, o), 8.31 (s, 8H, o), 8.05 (m, 12H, p), 2.58 (t, J = 6.9 Hz, 4H, CPDMS-CH<sub>2</sub>), 2.15 (m, 4H, CPDMS-CH<sub>2</sub>), 1.52–0.83 (m, 936H, THS), 1.21 (m, 4H, CPDMS-CH<sub>2</sub>), 0.63 (s, 12H, CPDMS-CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>c</sub> 153.5, 13.2, 152.8,152.3, 151.0, 150.8, 150.7, 143.6, 140.9, 140.7, 140.3, 139.5, 135.4, 135.3, 133.6, 133.3, 131.2, 125.2, 124.7, 122.6, 119.8, 101.4, 100.9, 96.3, 87.6, 82.7, 33.7, 31.8, 24.2, 22.9, 21.1, 20.9, 16.3, 14.4, 14.3, 12.8, –1.3 ppm. MALDI-ToF m/z 10441 (calculated for [C<sub>653</sub>H<sub>1044</sub>N<sub>38</sub>S<sub>26</sub>Zn<sub>16</sub>]<sup>+</sup>: 10441). UV-vis-NIR (toluene + 1% pyridine) λ<sub>max</sub> (log ε): 832 (5.53), 593 (4.72), 493 (5.76), 464 (5.81).
HC$_2$-P6[b$_4$e]-C$_2$H:

CPDMS-/P6[b$_4$e]-CPDMS (18 mg, 1.7 μmol) was dissolved in CH$_2$Cl$_2$ (2 mL) and pyridine (0.05 mL). TBAF (1.0 M in THF, 26 μL, 26 μmol) was added. The reaction mixture was stirred for 20 min at room temperature before it was passed through a plug (SiO$_2$; PE$_{40-60}$/CH$_2$Cl$_2$ 3:1 + 1% pyridine). The solvents were removed in vacuo to afford HC$_2$-P6[b$_4$e]-C$_2$H (17 mg, 100%) as a brown solid.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): δ$_i$ 10.34 (d, J = 4.5 Hz, 4H, a1), 9.90 (m, 16H, a1*,2,2*,3), 9.67 (d, J = 4.5 Hz, 4H, a3*), 9.03 (d, J = 4.5 Hz, 4H, b1), 8.97 (m, 16H, b1*,2,2*,3), 8.89 (d, J = 4.5 Hz, 4H, b3*), 8.35 (s, 8H, o), 8.32 (s, 8H, o), 8.01 (m, 12H, p), 4.18 (s, 2H, c), 1.53–0.83 (m, 936H) ppm. MALDI-ToF m/z 10191.76 (calculated for [C$_{646}$H$_{1022}$N$_{24}$Si$_{24}$Zn$_{6}$]+: 10191.10)

c-P6[b$_4$e]-T6:

HC$_2$-P6[b$_4$e]-C$_2$H (13 mg, 1.3 μmol) was dissolved in dry CHCl$_3$ (14 mL) and dry i-Pr$_2$NH (1.2 mL). T6 (2.6 mg, 2.6 μmol) was dissolved in CHCl$_3$ (3 mL) and added to the porphyrin hexamer solution under inert atmosphere. Complex formation was confirmed by UV-vis-NIR spectroscopy. A catalyst mixture of Pd(PPh$_3$)$_2$Cl$_2$ (90 mg, 0.13 mmol), Cul (24 mg, 0.13 mmol) and 1,4-benzoquinone (14 mg, 0.13 mmol) was added as solids and the reaction progress was monitored by UV-vis-NIR spectroscopy. After 4 h, the mixture was passed through a plug (SiO$_2$; CHCl$_3$ + 1% pyridine). The solvents were removed and the residue was purified by SEC (toluene + 1% pyridine) and further purified by recycling GPC (toluene + 1% pyridine) to afford c-P6[b$_4$e]-T6 (5.4 mg, 37%) as a red-brown solid.

$^1$H NMR (500 MHz, CDCl$_3$, 298 K): δ$_i$ 10.02 (d, J = 4.4 Hz, 4H, a1), 9.43 (m, 16H, a2–3), 9.37 (d, J = 4.4 Hz, 4H, a1*), 8.79 (d, J = 4.4 Hz, 4H, b1), 8.67 (m, 16H, b2–3), 8.59 (d, J = 4.4 Hz, 4H, b1*), 8.31 (s, 8H, o′2,3), 8.28 (s, 4H, o), 8.01 (m, 12H, p), 4.18 (s, 2H, c), 1.53–0.83 (m, 936H) ppm. MALDI-ToF m/z 11184 (calculated for [C$_{718}$H$_{1058}$N$_{24}$Si$_{24}$Zn$_{6}$]+: 11186). UV-vis-NIR (toluene) $\lambda_{\text{max}}$ (log $\varepsilon$): 967 (4.88), 874 (5.78), 831 (5.83), 790 (5.69), 505 (6.04), 441 (5.77).
A solution of freshly recrystallized DABCO in toluene (260 mg/mL) was prepared. A SEC column (toluene) was eluted with DABCO solution (20 mL) such that the top of the column was saturated with DABCO. *c*-P6[b5e]-T6 (4.0 mg, 0.36 μmol) was dissolved in DABCO solution (0.5 mL) and loaded onto the SEC column. The column was eluted with DABCO solution (8 mL) and subsequently with toluene. The collected material was diluted to 40 mL in toluene and washed with water (4 × 50 mL). The toluene fraction was dried over MgSO4 and concentrated. The material was purified on a short plug (SiO2; PE40-60/CH2Cl2 4:1 + 1% pyridine). This procedure was repeated twice to ensure complete template removal from the nanoring to yield *c*-P6[b5e] (3.0 mg, 83%) as a brown solid.

1H NMR (500 MHz, CDCl3 + 1% pyridine-d5, 298 K): δH 10.01 (d, J = 4.4 Hz, 4H, a1), 9.52 (m, 20H, a1–a2–a3), 8.74 (d, J = 4.4 Hz, 4H, b1), 8.67 (m, 20H, b1–b2–b3), 8.07 (s, 24H, o1–o2–o3), 7.91 (s, 12H, p1–p3), 1.47–0.72 (m, 936H, THS) ppm. MALDI-ToF m/z 10192.86 (calculated for [C646H1020N24Si24Zn6]$: 10189.09). UV-vis-NIR (toluene + 1% pyridine) λmax (log ε): 803 (5.62), 610 (4.68), 502 (5.93), 442 (5.73).
3.2 Synthesis of c-P6[be$_5$]-T6* and c-P6[be$_5$]

Scheme S2: Synthetic overview of linear precursor HC$_2$-L-P6[be$_5$]-C$_2$H
Br-P1-Br:

A solution of NBS (0.35 g, 2.0 mmol) in dry CHCl₃ (76 mL) was added to a solution of porphyrin H-P1-H (1.5 g, 0.9 mmol) in dry pyridine (14 mL) and dry CHCl₃ (60 mL) at −78 °C under inert atmosphere. The reaction mixture was stirred at −41 °C for 1 h before acetone (10 mL) was added to quench the excess of NBS. The solution was concentrated under reduced pressure, and passed through a short plug (SiO₂; PE₄₀–₆₀/CH₂Cl₂ 5:1). The solvent was removed under reduced pressure to give Br-P1-Br (1.58 g, 96%) as a red oil.

Characterization data matched those previously reported.[2]

CPDIPS-P1-CPDIPS:

Porphyrin Br-P1-Br (0.83 g, 0.46 mmol) was placed in an argon flushed Schlenk flask. Dry toluene (7 mL) and dry i-Pr₂NH (7 mL) were added. 3-Cyanopropylisopropylsilylacetylene (0.48 g, 0.49 mL, 2.3 mmol) was added. The solution was freeze-pump-thaw degassed (3 cycles). While frozen, catalysts Pd(PPh₃)₂Cl₂ (65 mg, 0.093 mmol) and CuI (9.0 mg, 0.046 mmol) were added under a stream of argon, before performing three additional freeze-pump-thaw cycles. The solution was stirred at 50 °C for 2 h before cooling to room temperature and removing the solvents under reduced pressure. The residue was subjected to a plug (SiO₂; gradient of PE₄₀–₆₀/CH₂Cl₂ 5:1 to 1:1) giving target porphyrin CPDIPS-P1-CPDIPS (0.90 g, 95%) as a green-purple oily solid.

Characterization data matched those previously reported.[4]

HC₂-P1-H:

To a solution of CPDIPS-P1-H (1.35 g, 0.72 mmol) in dry CH₂Cl₂ (13 mL) was progressively added TBAF (1.0 M in THF, 2.50 mL, 2.50 mmol) under inert atmosphere over 15 min at room temperature until full deprotection was indicated by TLC. The reaction mixture was directly passed through a short plug (NEt₃-deactivated SiO₂; CH₂Cl₂) and the solvents removed under reduced pressure. Purification by SEC (toluene) yielded HC₂-P1-H (1.13 g, 93%) as a dark green oily solid.

Characterization data matched those previously reported.[3]
To a dried, argon flushed Schlenk-tube was added Br-P1-Br (0.28 mg, 0.15 mmol) and HC$_2$-P1-H (0.65 mg, 0.38 mmol) together with dry THF (40 mL) and dry NEt$_3$ (5 mL) before performing two consecutive freeze-pump-thaw cycles. While frozen, Pd$_2$(dba)$_3$ (13.5 mg, 15 µmol) and AsPh$_3$ (69 mg, 0.22 mmol) were added under a stream of argon, before performing three additional freeze-pump-thaw cycles. The solution was heated to 60 °C for 2 d before cooling to room temperature and removing the solvents under reduced pressure. A short plug (SiO$_2$; PE$_{40-60}$/CH$_2$Cl$_2$ 5:1) followed by SEC (toluene + 1% pyridine) yielded H-l-P3[e$_2$]-H (580 mg, 75%) as a dark brown oily solid.

Characterization data matched those previously reported.$^{[3]}$

Br-l-P3[e$_2$]-Br:

H-l-P3[e$_2$]-H (100 mg, 20 µmol) was placed in a round-bottom flask. Argon-degassed dry ethanol-stabilized CHCl$_3$ (4 mL), and dry pyridine (1.5 mL) were added before cooling to −78 °C. In a second flask, a solution of NBS (8.0 mg, 44 µmol) in argon-degassed dry ethanol-stabilized CHCl$_3$ (9 mL) was prepared and subsequently added to the first solution over 30 min at −78 °C. Stirring was continued for an additional 10 min at −78 °C. The solution was allowed to warm to −41 °C in a dry ice/MeCN bath, and stirred for 1 h. Finally, the reaction mixture was placed in an ice bath at 0 °C for 45 min. The course of the reaction was monitored by $^1$H NMR of reaction aliquots. The reaction mixture was subjected directly to a short plug (SiO$_2$; PE$_{40-60}$/CH$_2$Cl$_2$ 5:1) yielding Br-l-P3[e$_2$]-Br (78 mg, 76%) as a dark brown oily solid.

Characterization data matched those previously reported.$^{[3]}$
CPDIPS-/P5[e₄]-CPDIPS:

To a dried, argon flushed Schlenk tube was added Br-P3[e₄]-Br (68 mg, 13 µmol) and HC₂-P1-CPDIPS (100 mg, 53 µmol) together with dry THF (3.5 mL) and dry NEt₃ (0.5 mL) before performing two consecutive freeze-pump-thaw cycles. While frozen, Pd₂(dba)₃ (1.2 mg, 1.3 µmol) and AsPh₃ (6.0 mg, 19.5 µmol) were added under a stream of argon, before performing three additional freeze-pump-thaw cycles. The solution was heated to 60 °C for 2 d before cooling to room temperature and removing the solvents under reduced pressure. A short plug (NEt₃-deactivated SiO₂; gradient of PE₄₀–₆₀/CH₂Cl₂ 50:1 to 5:1), and subsequent short SEC (toluene + 1% pyridine) and recycling GPC (toluene + 1% pyridine) yielded CPDIPS-/P5[e₄]-CPDIPS (82 mg, 71%) as a dark brown oily solid.

Characterization data matched those previously reported.[³]

HC₂-/P5[e₄]-CPDIPS:

To a solution of CPDIPS-/P5[e₄]-CPDIPS (0.151 g, 17.2 µmol) in dry CH₂Cl₂ (9 mL), dry ethanol-stabilized CHCl₃ (4.5 mL) and dry pyridine (0.1 mL) was progressively added TBAF (1.0 M in THF, 0.17 mL, 0.17 mmol) under inert atmosphere over 15 min at 0 °C. The course of the reaction was monitored by TLC. The reaction mixture was subjected directly to a short plug (NEt₃-deactivated SiO₂; CHCl₃) to quench the excess of TBAF and purified by flash column chromatography (NEt₃-deactivated SiO₂; gradient: PE₄₀–₆₀, PE₄₀–₆₀/CH₂Cl₂ 40:1 to 10:1) yielding HC₂-/P5[e₄]-CPDIPS (78 mg, 53%) as a dark brown oily solid.

Characterization data matched those previously reported.[³]
Br-/P6[ε2]-CPDIPS:

To a dried, argon flushed Schlenk-tube was added HC2-/P5[ε4]-CPDIPS (97 mg, 11.3 µmol) and Br-P1-Br (102 mg, 56.4 µmol) together with dry THF (3.5 mL) and dry NEt3 (0.5 mL) before performing two consecutive freeze-pump-thaw cycles. While frozen, Pd2(dba)3 (1.0 mg, 1.1 µmol) and AsPh3 (5.2 mg, 17 µmol) were added under a stream of argon, before performing three additional freeze-pump-thaw cycles. The solution was heated to 60 °C for 3 d before cooling to room temperature and removing the solvents under reduced pressure. A short plug (NEt3-deactivated SiO2; CH2Cl2), and subsequent short SEC (toluene) and recycling GPC (toluene + 1% pyridine) yielded Br-/P6[ε2]-CPDIPS (67 mg, 58%) as a dark brown oily solid.

Characterization data matched those previously reported.[3]

CPDIPS-/P6[ε2]-CPDIPS:

To a dried, argon flushed Schlenk-tube was added Br-/P6[ε2]-CPDIPS (13.0 mg, 1.26 µmol) and acetylene-CPDIPS (1.30 mg, 6.29 µmol) together with dry toluene (2 mL) and dry i-Pr2NH (1 mL) before performing three consecutive freeze-pump-thaw cycles. While frozen, Pd(PPh3)2Cl2 (177 µg, 20 mol%), and CuI (30 µg, 10 mol%) were added under a stream of argon, before performing three additional freeze-pump-thaw cycles. The solution was heated to 50 °C for 2 h before cooling to room temperature and removing the solvents under reduced pressure. The residue was subjected to a plug (NEt3-deactivated SiO2; PE40-60/CH2Cl2 1:1) giving target CPDIPS-/P6[ε2]-CPDIPS (12.5 mg, 95%) which was directly used in the next step.

1H NMR (400 MHz, CDCl3, 298 K): δH 10.36–10.31 (m, 20H, a1–2,a3), 9.64 (d, J = 4.4 Hz, 4H, a3#), 9.03–8.99 (m, 20H, b1–2,b3), 8.87 (d, J = 4.4 Hz, 4H, b3#), 8.38 (s, 8H, o), 8.36 (s, 8H, o), 8.29 (s, 8H, o), 8.02–8.00 (m, 12H, p), 2.57 (t, J = 7.2 Hz, 4H, CPDIPS-CH2), 2.26–2.18 (m, 4H, CPDIPS-CH), 1.54–0.70 (m, 968H, THS, CPDIPS) ppm.

MALDI-ToF m/z 10453 (calculated for [C658H1082N26Si26Zn6 ]+: 10458). UV-vis-NIR (toluene + 1% pyridine) λmax (log ε): 873 (4.88), 498 (5.15), 440 (5.01).
HC$_2$↓-P6[e$_5$]-C$_2$H:

To a solution of **CPDIPS↓-P6[e$_5$]-CPDIPS** (12.5 mg, 1.20 μmol) in dry CH$_2$Cl$_2$ (2.0 mL) and dry pyridine (20 μL) was progressively added TBAF (1.0 M in THF, 7.2 μL, 7.2 μmol) at room temperature and stirred for 15 min. The course of the reaction was monitored by TLC. The reaction mixture was subjected directly to a short plug (NEt$_3$-deactivated SiO$_2$; CH$_2$Cl$_2$) yielding **HC$_2$↓-P6[e$_5$]-C$_2$H** (12 mg, 96%) as a dark brown meta-solid. Due to the tendency to homo-couple in the presence of oxygen, the target is best directly subjected to cyclization.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$H 10.37–10.33 (m, 20H, a1–2,a3), 9.68 (d, $J = 4.4$ Hz, 4H, a3$^3$), 9.04–9.01 (m, 20H, b1–2,b3), 8.89 (d, $J = 4.4$ Hz, 4H, b3$^3$), 8.38 (s, 8H, o), 8.37 (s, 8H, o), 8.31 (s, 8H, o), 8.03–8.01 (m, 12H, p), 4.18 (s, 2H, c), 1.56–0.71 (m, 936H, THS) ppm.
Scheme S3: Synthetic overview of c-P6[be5].

\[ \text{Pd(PPh}_3)_2\text{Cl}_2, \text{ Cul 1,4-benzoquinone} \]

\[ \text{then SEC tol/py} \]

\[ \text{25\%} \]
To a dried, argon flushed Schlenk-tube was added HC$_2$-P6[be$_3$]-C$_2$H (12.0 mg, 1.19 μmol) and T6* (2.44 mg, 3.57 μmol) together with dry i-Pr$_2$NH (0.5 mL) before degassing by a stream of argon and stirring for 15 min at room temperature. Under counter-flow, 1,4-benzoquinone (10 mg, 92 μmol), Pd(PPh$_3$)$_2$Cl$_2$ (10 mg, 14 μmol) and CuI (10 mg, 52 μmol) were added and degassing continued for 5 min. The solution stirred at room temperature for 1.5 h before removing the solvents under reduced pressure. The residue was subjected to a short plug (NEt$_3$-deactivated SiO$_2$, PE$_{40-60}$/CH$_2$Cl$_2$ 1:1), and subsequent short SEC (toluene) and recycling GPC (toluene + 1% pyridine) giving target ring c-P6[be$_3$]-T6* (3.2 mg, 25%) as a brown solid.

$^1$H NMR (700 MHz, CDCl$_3$, 298 K): δ$_H$ 9.93 (d, J = 4.2 Hz, 4H, a$_1$), 9.90 (dd, J = 8.9, 4.4 Hz, 16H, a$_2$–3), 9.36 (d, J = 4.3 Hz, 4H, a1), 8.66 (d, J = 4.2 Hz, 4H, b1$^b$), 8.61 (d, J = 4.8 Hz, 16H, b2–3), 8.49 (d, J = 4.3 Hz, 4H, b1), 8.06 (s, 8H, o’2,3), 8.02 (s, 4H, o’1), 7.92–7.90 (m, 20H, a1–3,p2,3), 7.88 (s, 4H, p1), 4.40 (d, J = 6.1 Hz, 4H, β1), 4.21 (d, J = 6.4 Hz, 8H, β2,3), 2.00 (t, J = 6.1 Hz, 8H, a2,3), 1.94 (d, J = 5.8 Hz, 4H, a1), 1.58–0.46 (m, 936H, THS) ppm.

MALDI-ToF m/z 10774 (calculated for [C$_{686}$H$_{1044}$N$_{30}$Si$_{24}$Zn$_6$]$^+$: 10778). UV-vis-NIR (toluene + 1% pyridine) $\lambda_{max}$ (log ε): 436 (5.39), 500 (5.74), 853 (5.45), 899 (5.40), 955 (5.15).
To remove the template, c-P6[be₃]-T6* (3.2 mg, 0.30 μmol) was dissolved in pyridine/toluene (100:1) and subjected to repeated SEC (pre-saturated with pyridine/toluene 100:1, 4×) and another plug (NE₃-deactivated SiO₂; PE₄₀–₆₀/CH₂Cl₂ 1:1) yielding desired template-free c-P6[be₃] (2.9 mg, 99%) as a brown solid.

¹H NMR (700 MHz, CDCl₃, 298 K): δ, 9.94–9.90 (m, 20H, a₁⁺,a₂–3), 9.43 (d, J = 4.3 Hz, 4H, a₁), 8.71–8.69 (m, 20H, b₁⁺,b₂–3), 8.62 (d, J = 4.4 Hz, 4H, b₁), 8.02 (br s, 24H, o), 7.91–7.90 (m, 12H, p), 1.48–0.38 (m, 936H, THS) ppm. MALDI-ToF m/z 10097 (calculated for [C₆₃₈H₁₁₀₂₀N₂₄Si₂₄Zn₆]⁺: 10094). UV-vis-NIR (toluene + 1% pyridine) λₘₐₓ (log ε): 428 (5.45), 494 (5.81), 780 (5.36).
4 ¹H-NMR Assignment of c-P6[b₅e]·T6, c-P6[b₅e], c-P6[be₅]·T6* and c-P6[be₅]

In the following section, the full assignments of the ¹H-NMR spectra of the nanorings c-P6[b₅e] and c-P6[be₅], with and without the template T6(*), are described. All ¹H-NMR spectra were recorded at 298 K using a Bruker AVIII 700 instrument with CDCl₃ as the solvent. The 2D-NMR techniques COSY and NOESY were used to achieve full assignment of the signals. COSY correlations are indicated in blue, NOESY correlations are indicated in red. The assignment of the nanostructure will be discussed systematically.

4.1 Assignment of c-P6[b₅e]·T6

Assignment of Porphyrin 1
We can assign the 4H-doublet at 10.02 ppm with confidence to proton a₁, on the basis of its unusual chemical shift; this enables us to assign b₁ through a COSY correlation (Figure S2). The other distinct COSY correlation in this region between two 4H-doublets is assigned to a₁* and b₁* (supported by NOE correlations as discussed below).
Figure S2: Region of the COSY correlation spectrum (500 MHz, CDCl₃, 298 K) of c-P6[b₅e]-T6, indicating the COSY correlation between proton a₁ and proton b₁ and proton a₁# and b₁#.

NOESY correlations from proton a₁ to o₁, o’₁, a₁ and β₁ (Figures S3 and S4) enable the assignment of these protons. Protons α₁ and β₁ exhibit a COSY correlation (not shown), confirming their assignment.

Figure S3: Region of the NOESY spectrum (500 MHz, CDCl₃, 298 K) of c-P6[b₅e]-T6, indicating the NOEs between proton a₁ and protons o₁ and o’₁.
Figure S4: Region of the NOESY spectrum (500 MHz, CDCl₃, 298 K) of c-P6[b₂e]-T6, indicating the NOEs between proton α₁ and protons α₁ and β₁.

NOE cross-peaks correlating o₁/o₁' and a₁º and b₁º confirm their assignment (Figure S5). NOEs between o₁/o₁' and p₁ could not be distinguished due to the overlap between o₁ and p₁.

Figure S5: Region of the NOESY spectrum (500 MHz, CDCl₃, 298 K) of c-P6[b₂e]-T6, indicating the NOEs between protons o₁/o₁' and protons α₁, a₁º, b₁ and b₁º.
Finally, NOEs from $\alpha_1$ and $\beta_1$ to $\gamma_1$ and $\delta_1$ (Figure S6) (and a COSY correlation from $\gamma_1$ to $\delta_1$; not shown), complete the assignment of porphyrin 1.

**Figure S6:** Region of the NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of c-P6[b$_5$e]-T6, indicating the NOEs between protons $\alpha_1$ and $\beta_1$ and protons $\gamma_1$ and $\delta_1$. 
Assignment of Porphyrins 2 and 3

The assignment of porphyrins 2 and 3 follows from the assignment of porphyrin 1 using the COSY correlations and NOEs from the template. There are NOEs from δ₁ to δ₂ (Figure S7) enabling the identification of δ₂, which has NOEs to β₂,3 and α₂,3 (both the α and β signals for porphyrins 2 and 3 overlap at 1.95 ppm and 4.81 ppm, respectively).

Figure S7: Region of the NOESY spectrum (500 MHz, CDCl₃, 298 K) of c-P6[b₃e]-T6, indicating the NOEs between protons δ₁ and δ₂ and subsequently protons δ₂ and β₂,3 and α₂,3.
Proton δ2 has a COSY correlation to γ2 at 5.33 ppm (Figure S8). There is another pair of template protons displaying a COSY correlation which is assigned to δ3 (5.50 ppm) and γ3 (5.35 ppm). This assignment is further confirmed by NOEs from γ2 and γ3 to the overlapping signal β2,3 (Figure S7).

Figure S8: Region of the COSY correlation spectrum (500 MHz, CDCl3, 298 K) of c-P6[b5e]-T6, indicating the COSY correlation between proton δ3 and proton γ3 and proton δ2 and γ2.
The signal at 8.31 ppm can be assigned to $\text{o'2}$ and $\text{o'3}$ as there is a strong NOE between the signal at 8.31 ppm and the $\text{a2,3}$ signal at 1.95 ppm and a very weak NOE between the signal at 8.31 ppm and the $\text{b2,3}$ signal at 4.81 ppm (Figure S9).

**Figure S9:** Region of the NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of c-P6[5b],[e]-T6, indicating the NOEs between protons $\text{o'2,3}$ and $\text{a2,3}$ and $\text{b2,3}$ and NOEs between protons $\text{a2,3}$ and $\text{b2,3}$ to $\text{a2–3}$ and $\text{b2–3}$. 
The NOE between the signal at 8.31 ppm and the signal at 9.43 ppm identifies the latter as \textit{a}2–3 which itself displays a NOE to the signal at 7.91, identifying this signal as \textit{o}2, 3 (Figure S10). This also enables the assignment of the multiplet at 8.67 as \textit{b}2–3 as this signal shows strong NOEs to \textit{a}2, 3, weak NOEs to \textit{b}2, 3 (Figure S9), strong NOEs to \textit{a}2–3, and strong NOEs to \textit{o}2, 3 and \textit{o}'2, 3 (Figure S10).

\textbf{Figure S10:} Region of the NOESY spectrum (500 MHz, CDCl\textsubscript{3}, 298 K) of \textit{c-P6[b, e]-T6}, indicating the NOEs between protons \textit{o}'2, 3 and \textit{a}2–3 which subsequently shows NOEs to \textit{o}2, 3, and indicating the NOEs between \textit{b}2–3 to \textit{a}2–3, \textit{a}2, 3 and \textit{o}'2, 3.

The remaining signals at 7.96 ppm and 7.94 ppm are assigned to \textit{p}1–3. Since these signals don’t display any NOE or COSY correlations, a specific assignment is not possible.
Table S1: Correlation matrix depicting the COSY and NOE correlations in the $^1$H NMR spectrum of c-P6[b5e]-T6 (labels: $s$: strong correlation, $w$: weak correlation, $o$: overlapping signals).

|          | beta 1 | aryl 1 | template 1 | THS 1 | beta 2 | aryl 2 | template 2 | THS 2 | beta 3 | aryl 3 | template 3 | THS 3 |
|----------|--------|--------|------------|-------|--------|--------|------------|-------|--------|--------|------------|-------|
| a        |        |        |            |       |        |        |            |       |        |        |            |       |
| a#       | $S$    |        |            |       |        |        |            |       |        |        |            |       |
| b        |        |        |            |       |        |        |            |       |        |        |            |       |
| b#       |        |        |            |       |        |        |            |       |        |        |            |       |
| δ        |        |        |            |       |        |        |            |       |        |        |            |       |
| w        |        |        |            |       |        |        |            |       |        |        |            |       |
| w#       |        |        |            |       |        |        |            |       |        |        |            |       |
| o        |        |        |            |       |        |        |            |       |        |        |            |       |
| o#       |        |        |            |       |        |        |            |       |        |        |            |       |
| a·        |        |        |            |       |        |        |            |       |        |        |            |       |
| a·#       |        |        |            |       |        |        |            |       |        |        |            |       |
| template 2 |        |        |            |       |        |        |            |       |        |        |            |       |
| δ        |        |        |            |       |        |        |            |       |        |        |            |       |
| w        |        |        |            |       |        |        |            |       |        |        |            |       |
| w·        |        |        |            |       |        |        |            |       |        |        |            |       |
| o        |        |        |            |       |        |        |            |       |        |        |            |       |
| o·        |        |        |            |       |        |        |            |       |        |        |            |       |
| template 3 |        |        |            |       |        |        |            |       |        |        |            |       |
| δ        |        |        |            |       |        |        |            |       |        |        |            |       |
| w        |        |        |            |       |        |        |            |       |        |        |            |       |
| w·        |        |        |            |       |        |        |            |       |        |        |            |       |
| o        |        |        |            |       |        |        |            |       |        |        |            |       |
| o·        |        |        |            |       |        |        |            |       |        |        |            |       |

COSY

NOESY
4.2 Assignment of c-P6[b₅e]

Assignment of Porphyrins 1, 2 and 3

The $^1$H NMR spectrum of c-P6[b₅e] has more overlapping signals than its template-complex counterpart c-P6[b₅e]-T6 and hence most of the individual signals cannot be assigned. We can assign the 4H-doublet at 10.01 ppm with confidence to proton a₁; this enables us to assign b₁ through a COSY correlation (Figure S11). There is only one other distinct COSY correlation in this region between two 20H-multiplets which are overlapping signals for a₁#,a₂–3 at 9.52 ppm and b₁#,b₂–3 at 8.67 ppm.

Figure S11: Region of the COSY correlation spectrum (500 MHz, CDCl₃ + 1% pyridine-d₅, 298 K) of c-P6[b₅e], indicating the COSY correlation between proton a₁ and b₁ and protons a₁#,a₂–3 and b₁#,b₂–3.
NOESY correlations from the 20H multiplets at 9.52 ppm and 8.67 ppm to the 24H singlet at 8.07 ppm confirms the assignment of the latter as o1–3, o’1–3 (denoted in Figure S12 as o). A weak NOESY correlation between this singlet and the 12H singlet at 7.91 enables the assignment of this signal as p1–3 (denoted as p) and completes the assignment of c-P6[b5e].

Figure S12: Region of the NOESY spectrum (500 MHz, CDCl3 + 1% pyridine-d5, 298 K) of c-P6[b5e], indicating the NOEs between protons a1,o2–3 and b1,o2–3 to o, and the weak NOE from o to p.
**Table S2**: Correlation matrix depicting the COSY and NOE correlations in the $^1$H NMR spectrum of c-P6[β2ε] (labels; s: strong correlation, w: weak correlation, o: overlapping signals).

|       | beta 1 | aryl 1 | THS 1 | beta 2 | aryl 2 | THS 2 | beta 3 | aryl 3 | THS 3 |
|-------|--------|--------|-------|--------|--------|-------|--------|--------|-------|
| a     |        |        |       |        |        |       |        |        |       |
| a#    |        |        |       |        |        |       |        |        |       |
| b     |        |        |       |        |        |       |        |        |       |
| b#    |        |        |       |        |        |       |        |        |       |
| o     |        |        |       |        |        |       |        |        |       |
| o'    |        |        |       |        |        |       |        |        |       |
| p     |        |        |       |        |        |       |        |        |       |
| T     |        |        |       |        |        |       |        |        |       |
| T'    |        |        |       |        |        |       |        |        |       |

|       | beta 1 | aryl 1 | THS 1 | beta 2 | aryl 2 | THS 2 | beta 3 | aryl 3 | THS 3 |
|-------|--------|--------|-------|--------|--------|-------|--------|--------|-------|
| a     |        |        |       |        |        |       |        |        |       |
| a#    |        |        |       |        |        |       |        |        |       |
| b     |        |        |       |        |        |       |        |        |       |
| b#    |        |        |       |        |        |       |        |        |       |
| o     |        |        |       |        |        |       |        |        |       |
| o'    |        |        |       |        |        |       |        |        |       |
| p     |        |        |       |        |        |       |        |        |       |
| T     |        |        |       |        |        |       |        |        |       |
| T'    |        |        |       |        |        |       |        |        |       |

**COSY**

**NOESY**
4.3 Assignment of c-P6[be₃]-T6*

As we can assign the 4H-doublet at 9.36 ppm with confidence to proton a₁, this enables us to assign b₁ through a COSY correlation as the 4H-doublet at 8.49 ppm (Figure S13). The other distinct COSY correlation in this region between two 4H doublets is assigned to a₁# and b₁# (supported by NOE correlations; Figure S14). Unlike the COSY spectrum, the NOESY also shows a weak correlation between the near beta protons b₁ and b₁# (Figure S14).

Assignment of Porphyrin 1

Figure S13: Region of the COSY spectrum (700 MHz, CDCl₃, 298 K) of c-P6[be₃]-T6*, indicating the COSY correlations between protons a₁ and b₁, and protons a₁# and b₁#.
Figure S14: Region of the NOESY spectrum (700 MHz, CDCl₃, 298 K) of c-P₆[be₅]·T₆*, indicating the NOE cross peaks correlating beta protons a₁ and b₁, a₁# and b₁#, and b₁#.

The signals for the aryl protons ortho to the porphyrin are split due to the different environments inside and outside the nanoring. The NOE cross peaks correlating the beta protons (b₁ and b₁#) and the downfield shifted ortho proton at 8.02 ppm allow us to identify this 4H-singlet as o'₁. Along the same lines, the NOE cross peaks correlating the beta protons (b₁ and b₁#) and the upfield shifted ortho proton lead us to locate the proton o₁ as part of a 20H-multiplet between 7.92–7.90 ppm. In addition, the NOE cross peak correlating the proton o'₁ and the corresponding para proton p₁ allowed us to identify the latter as a 4H-singlet at 7.88 ppm (Figure S15).

Figure S16 shows the NOE cross peaks correlating proton o'₁ and the template resonances which enables us to identify protons a₁ at 1.94 ppm (strong correlation) and β₁ at 4.40 ppm (weak correlation). Moreover, the correlation between the template protons, namely a₁ and β₁, is easily observable in both COSY and NOESY spectra (Figure S17).
Figure S15: Region of the NOESY spectrum (700 MHz, CDCl\textsubscript{3}, 298 K) of c-P6[be\textsubscript{5}]-T6*, indicating the NOE cross peaks correlating the beta (b\textsubscript{1} and b\textsubscript{1}\#) and the ortho protons (o\textsubscript{1} and o'\textsubscript{1}). The proton o'\textsubscript{1} also correlates with the p\textsubscript{1}.

Figure S16: Region of the NOESY spectrum (700 MHz, CDCl\textsubscript{3}, 298 K) of c-P6[be\textsubscript{5}]-T6*, indicating the NOE cross peaks correlating proton o'\textsubscript{1} and template resonances (a\textsubscript{1} and b\textsubscript{1}).
Assignments of Porphyrins 2 and 3

The assignment of porphyrins 2 and 3 follows from the assignment of porphyrin 1. We can assign the 16H-doublet of doublets at 9.90 ppm with confidence to protons $\alpha_{2-3}$, which enables us to assign protons $\beta_{2-3}$ through a COSY correlation as a 16H-doublet at 8.61 ppm (Figure S18). Figure S19 shows the NOE cross peaks correlating the beta protons ($\alpha_{2-3}$ and $\beta_{2-3}$) and the aryl protons ortho to the porphyrin. Thus, we easily identified the downfield shifted protons $o'_{2,3}$ as the 8H-singlet at 8.06 ppm and the upfield shifted protons $o_{2,3}$ along with $p_{2,3}$ as part of a 20H-multiplet between 7.92–7.90 ppm.

Figure S20 depicts the NOE cross peaks correlating the aryl ortho protons and the template resonances. Specifically, the protons $o'_{2,3}$ strongly correlates to protons $\alpha_{2,3}$ at 2.00 ppm and $\beta_{2,3}$ at 4.21 ppm, whereas protons $o_{2,3}$ weakly correlates only to protons $\alpha_{2,3}$. As also commented earlier for porphyrin 1, the correlation between the template protons, namely $\alpha_{2,3}$ and $\beta_{2,3}$, is easily observable in both COSY and NOESY spectra (Figure S17).
Figure S18: Region of the COSY spectrum (700 MHz, CDCl₃, 298 K) of c-P6[be₅]·T6⁺, indicating the COSY correlations between protons a2–3 and b2–3.

Figure S19: Region of the NOESY spectrum (700 MHz, CDCl₃, 298 K) of c-P6[be₅]·T6⁺, indicating the NOE cross peaks correlating the beta protons (a2–3 and b2–3) and the aryl ortho protons (o'2,3 and o2,3).
Figure S20: Region of the NOESY spectrum (700 MHz, CDCl₃, 298 K) of c-P6[be₃]-T6*, indicating the NOE cross peaks correlating the aryl ortho protons (o'₂,₃ and o₂,₃) and the template resonances (α₂,₃ and β₂,₃).
Table S3: Correlation matrix depicting the COSY and NOE correlations in the $^1$H NMR spectrum of c-P6[be$_5$]-T6* (labels; s: strong correlation, w: weak correlation, o: overlapping signals).

| beta 1 | THS 1 | template 1 | beta 2 | THS 2 | template 2 | beta 3 | THS 3 | template 3 |
|--------|--------|------------|--------|--------|------------|--------|--------|------------|
| a      |        |            | a      |        |            | a      |        |            |
| a#     |        |            | a#     |        |            | a#     |        |            |
| S      |        |            | S      |        |            | S      |        |            |
|        |        |            |        |        |            |        |        |            |
| b      |        |            | b      |        |            | b      |        |            |
| b#     |        |            | b#     |        |            | b#     |        |            |
| S      |        |            | S      |        |            | S      |        |            |
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4.4 Assignment of c-P6[be₅]

**Assignment of Porphyrin 1**

As we can assign the 4H-doublet at 9.43 ppm with confidence to proton a₁, this enables us to assign b₁ through a NOESY correlation as the 4H-doublet at 8.62 ppm (Figure S21). Unlike the template-based system, here the protons a₁ and b₁ resonate together with the rest of beta protons of the nanoring, namely a₂–3 and b₂–3, respectively.

**Figure S21:** Region of the NOESY spectrum (700 MHz, CDCl₃, 298 K) of c-P6[be₅], indicating the NOE cross peak correlating protons a₁ and b₁.
Assignment of Porphyrins 2 and 3
We can assign the 20H-multiplet between 9.94–9.90 ppm with confidence to protons \(a_1^\#\) and \(a_2-3\), which enables us to assign protons \(b_1^\#\) and \(b_2-3\) through a NOESY correlation as the 20H-multiplet between 8.71–8.69 ppm (Figure S22).

The signals for the aryl protons ortho to the porphyrin are broader than for the template-based system, thus indicating conformational exchange. Figure S22 also depicts the NOE cross peaks correlating the beta protons (\(a_1, a_1^\#, a_2-3, b_1\) and \(b_1^\#, b_2-3\)) and the aryl ortho protons o as a 24H-broad singlet at 8.02 ppm. Finally, the 12H-multiplet between 7.91–7.90 ppm is assigned to all the aryl para protons p of the system.

**Figure S22:** Region of the NOESY spectrum (700 MHz, CDCl\(_3\), 298 K) of c-P6[be\(_5\)], indicating the NOE cross peaks correlating the beta protons \(a_1, a_1^\#, a_2-3, b_1\) and \(b_1^\#, b_2-3\) and the ortho protons o. The protons \(a_1^\#, a_2-3\) also correlate to \(b_1^\#, b_2-3\).
Table S4: Correlation matrix depicting the NOE correlations in the \(^1\)H NMR spectrum of c-P6[be\(_3\)] (labels; s: strong correlation, w: weak correlation, o: overlapping signals).

|          | beta 1 | asyl 1 | THS 1 | beta 2 | asyl 2 | THS 2 | beta 3 | asyl 3 | THS 3 |
|----------|--------|--------|-------|--------|--------|-------|--------|--------|-------|
| a        | s s    | o'     | p s   | s      | o'     | p s   | s      | o'     | p s   |
| b        | s      | o'     | p s   | s      | o'     | p s   | s      | o'     | p s   |
| b'       | o      | o'     | p o   | o      | o'     | p o   | o      | o'     | p o   |
| o'       | o'     | o'     | p o   | o'     | o'     | p o   | o'     | o'     | p o   |
| p        | o'     | o'     | p o   | o'     | o'     | p o   | o'     | o'     | p o   |
| t        | o o o o| o o o o| p o o o| o o o o| p o o o| p o o o| o o o o| p o o o| p o o o|
| t'       | o o o o| o o o o| p o o o| o o o o| p o o o| p o o o| o o o o| p o o o| p o o o|

Note: The NOESY correlations are indicated in the matrix. The matrix shows the correlation strength between different chemical shifts.
5 Spectra Confirming Identity of New Compounds

Figure S23: $^1$H NMR spectrum of compound Br-P1-CPDMS (400 MHz, CDCl$_3$, 298 K).

Figure S24: $^{13}$C NMR spectrum of compound Br-P1-CPDMS (125 MHz, CDCl$_3$, 298 K).
Figure S25: (top) Simulated MALDI-ToF spectrum of compound \( \text{Br-P1-CPDMS} \) ([C_{112}H_{182}BrN_{5}Si_{5}Zn]^+). (bottom) Measured MALDI-ToF spectrum of compound \( \text{Br-P1-CPDMS} \) (matrix: DCTB).

Figure S26: \(^1\)H NMR spectrum of compound \( \text{CPDMS-P1-CPDMS} \) (400 MHz, CDCl\(_3\), 298 K, * denotes coordinated pyridine).
Figure S27: $^{13}$C NMR spectrum of compound CPDMS-P1-CPDMS (125 MHz, CDCl$_3$, 298 K).

Figure S28: (top) Simulated MALDI-ToF spectrum of compound CPDMS-P1-CPDMS ([C$_{120}$H$_{194}$N$_{6}$Si$_{6}$Zn]$^+$). (bottom) Measured MALDI-ToF spectrum of compound CPDMS-P1-CPDMS (matrix: DCTB).
Figure S29: $^1$H NMR spectrum of compound Br-P1-C$_2$H (400 MHz, CDCl$_3$, 298 K).

Figure S30: $^{13}$C NMR spectrum of compound Br-P1-C$_2$H (100 MHz, CDCl$_3$, 298 K).
Figure S31: (top) Simulated MALDI-ToF spectrum of compound Br-P1-C$_2$H ([C$_{106}$H$_{171}$BrN$_4$Si$_4$Zn]$^+$). (bottom) Measured MALDI-ToF spectrum of compound Br-P1-C$_2$H (matrix: DCTB).

Figure S32: $^1$H NMR spectrum of compound Br-P1-TMS (400 MHz, CDCl$_3$ + 1% pyridine-d$_5$, 298 K).
Figure S33: $^{13}$C NMR spectrum of compound Br-P1-TMS (100 MHz, CDCl$_3$ + 1% pyridine-d$_5$, 298 K).

Figure S34: (top) Simulated MALDI-ToF spectrum of compound Br-P1-TMS ([C$_{109}$H$_{178}$BrN$_4$Si$_5$Zn]$^+$). (bottom) Measured MALDI-ToF spectrum of compound Br-P1-TMS (matrix: DCTB).
Figure S35: $^1$H NMR spectrum of compound HC$_2$-P1-CPDMS (400 MHz, CDCl$_3$, 298 K; * denotes coordinated pyridine).

Figure S36: $^{13}$C NMR spectrum of compound HC$_2$-P1-CPDMS (125 MHz, CDCl$_3$, 298 K).
Figure S37: (top) Simulated MALDI-ToF spectrum of compound **HC$_2$-P1-CPDMS** ([C$_{114}$H$_{183}$N$_5$Si$_5$Zn]$^+$). (bottom) Measured MALDI-ToF spectrum of compound **HC$_2$-P1-CPDMS** (matrix: DCTB).

Figure S38: $^1$H NMR spectrum of compound **TMS-I-P2[e]-CPDMS** (400 MHz, CDCl$_3$, 298 K).
**Figure S39:** $^{13}$C NMR spectrum of compound TMS-l-P2[e]-CPDMS (125 MHz, CDCl$_3$, 298 K).

**Figure S40:** (top) Simulated MALDI-ToF spectrum of compound TMS-l-P2[e]-CPDMS ([C$_{223}$H$_{361}$N$_9$Si$_{10}$Zn$_2$]$^+$). (bottom) Measured MALDI-ToF spectrum of compound TMS-l-P2[e]-CPDMS (matrix: DCTB).
Figure S41: $^1$H NMR spectrum of compound HC$_2$-P2[e]-C$_2$H (500 MHz, CDCl$_3$, 298 K, * denotes coordinated pyridine).

Figure S42: $^{13}$C NMR spectrum of compound HC$_2$-P2[e]-C$_2$H (125 MHz, CDCl$_3$, 298 K).
Figure S43: (top) Simulated MALDI-ToF spectrum of compound HC$_2$-P2[e]-C$_2$H ($[C_{214}H_{342}N_8Si_8Zn_2]^+$). (bottom) Measured MALDI-ToF spectrum of compound HC$_2$-P2[e]-C$_2$H (matrix: DCTB).

Figure S44: $^1$H NMR spectrum of compound CPDMS-I-P4[b$_2$e]-CPDMS (400 MHz, CDCl$_3$, 298 K, * denotes coordinated pyridine).
Figure S45: $^{13}$C NMR spectrum of compound CPDMS-[P4][b2e]-CPDMS (125 MHz, CDCl$_3$, 298 K).

Figure S46: (top) Simulated MALDI-ToF spectrum of compound CPDMS-[P4][b2e]-CPDMS ([C$_{442}$H$_{704}$N$_{18}$Si$_{18}$Zn$_4$]). (bottom) Measured MALDI-ToF spectrum of compound CPDMS-[P4][b2e]-CPDMS (matrix: DCTB).
Figure S47: $^1$H NMR spectrum of compound HC$_2$I-P4[b$_2$e]-C$_2$H (400 MHz, CDCl$_3$, 298 K, * denotes coordinated pyridine).

Figure S48: (top) Simulated MALDI-ToF spectrum of compound HC$_2$I-P4[b$_2$e]-C$_2$H ($[\text{C}_{430}\text{H}_{682}\text{N}_{16}\text{Si}_{16}\text{Zn}_4]$). (bottom) Measured MALDI-ToF spectrum of compound HC$_2$I-P4[b$_2$e]-C$_2$H (matrix: DCTB).
Figure S49: $^1$H NMR spectrum of compound CPDMS-I-P6[b$_{4}e$]-CPDMS (400 MHz, CDCl$_3$, 298 K, * denotes coordinated pyridine).

Figure S50: $^{13}$C NMR spectrum of compound CPDMS-I-P6[b$_{4}e$]-CPDMS (125 MHz, CDCl$_3$, 298 K).
Figure S51: (top) Measured MALDI-ToF spectrum of compound CPDMS-P6[be]-CPDMS (matrix: DCTB). (bottom) Simulated MALDI-ToF spectrum of compound CPDMS-P6[be]-CPDMS ([C_{658}H_{1044}N_{26}Si_{26}Zn_{6}]^{+}).

Figure S52: $^1$H NMR spectrum of compound HC_P6[be]-C_2H (400 MHz, CDCl_3, 298 K, * denotes coordinated pyridine).
Figure S53: (top) Simulated MALDI-ToF spectrum of compound \( \text{HC}_2\text{-I-P6[b,e]H} \) (\([\text{C}_{646}\text{H}_{1022}\text{N}_{24}\text{Si}_{24}\text{Zn}_{6}]^+\)). (bottom) Measured MALDI-ToF spectrum of compound \( \text{HC}_2\text{-I-P6[b,e]H} \) (matrix: DCTB).

Figure S54: \(^1\text{H}\) NMR spectrum of compound \( \text{c-P6[b,e]T6} \) (500 MHz, CDCl\(_3\), 298 K).
Figure S55: (top) Measured MALDI-ToF spectrum of compound c-P6[b₂e]-T6 (matrix: DCTB). (bottom) Simulated MALDI-ToF spectrum of compound c-P6[b₂e]-T6 ([C₇₁H₁₂₀₆N₁₉S₂₄Z₆]⁺).

Figure S56: "H NMR spectrum of compound c-P6[b₂e] (500 MHz, CDCl₃ + 1% pyridine-d₅, 298 K, * denotes residual pyridine signals).
Figure S57: (top) Simulated MALDI-ToF spectrum of compound \( \text{c-P6[b_5e]} \) \([\text{C}_{646}\text{H}_{1020}\text{N}_{24}\text{Si}_{24}\text{Zn}_6]^+\). (bottom) Measured MALDI-ToF spectrum of compound \( \text{c-P6[b_5e]} \) (matrix: DCTB).
Figure S58: $^1$H NMR spectrum of compound CPDIPS-l-P6[e$_5$]-CPDIPS (400 MHz, CDCl$_3$, 298 K, * denotes residual pyridine).

Figure S59: High-resolution MALDI-ToF spectrum of compound CPDIPS-l-P6[e$_5$]-CPDIPS (matrix: DCTB). Insert shows the predicted isotope distribution for CPDIPS-l-P6[e$_5$]-CPDIPS ($[C_{658}H_{1066}N_{50}Si_{15}Zn_6]^{+}$).
Figure S60: $^1$H NMR spectrum of compound HC$_2$-P6[e$_3$]-C$_2$H (400 MHz, CDCl$_3$, 298 K, * denotes residual pyridine).

Figure S61: $^1$H NMR spectrum of compound c-P6[be$_3$]-T6* (700 MHz, CDCl$_3$, 298 K).
Figure S62: High-resolution MALDI-ToF spectrum of compound c-P6[be₅]-T6* (matrix: DCTB). Insert shows the predicted isotope distribution for c-P6[be₅]-T6* ([C₆₁₈₅₁₃₂₄₂₆⁺]).

Figure S63: ¹H NMR spectrum of compound c-P6[be₅] (700 MHz, CDCl₃, 298 K). The ortho resonances are in slow exchange on the NMR timescale and appear broadened.
6 UV-vis-NIR Titrations

6.1 Estimation of Formation Constants

The binding constants of the templates $T_6$ and $T_6^*$ with $c$-$P_6[b_3e]$, $c$-$P_6[b_4e]$, $c$-$P_6[b_5e]$ and $c$-$P_6[e_6]$ were determined by denaturation titrations (break-up titration) with the competing ligands $N$-methylimidazole or pyridine. In order to determine the strain energy of $c$-$P_6[b_3e]$, the binding constant for $HC_2-l$-$P_6[b_4e]$-$C_2H$ was determined using pyridine as a competing ligand.

Using the data from these denaturation titrations ($K_{dn} = \text{denaturation constant}$) and the formation constant of the single site binding event of the competing ligand with a zinc-porphyrin monomer ($K_{\text{ref}} = \text{association constant for } N\text{-methyl imidazole or pyridine to THS-monomer}$), allows us to derive the formation binding constant ($K_f$) between the porphyrin nanorings and the templates using the following equation:

$$K_f = \frac{K_{\text{ref}}^6}{K_{dn}}$$

via the thermodynamic cycle shown in Figure S64.

![Thermodynamic cycle](image)

**Figure S64:** (left) Generalized thermodynamic cycle of $c$-$P_6[b_3e]$$T_6(*)$ relating the formation constant of the template complex ($K_f$) to the denaturation constant ($K_{dn}$) and the binding constant of each porphyrin unit for the competing ligand L ($K_{\text{ref}}^6$ and $K_{\text{ref}}^{16}$, respectively). (right) Structure of the THS-monomer, used to determine $K_{\text{ref}}$; THS = trihexylsilyl.

**Table S5:** Summary of UV-vis-NIR reference titrations with THS-monomer.

| Complex                  | $K_{\text{ref}} (M^{-1})$ | $K_a$ | $K_{\text{chem ref}}$ |
|--------------------------|---------------------------|-------|-----------------------|
| $l$-$P1$-pyridine         | $(1.3 \pm 0.1) \times 10^4$ | 2     | $(6.5 \pm 0.6) \times 10^3$ |
| $l$-$P1$-methylimidazole  | $(4.2 \pm 0.4) \times 10^5$ | 2     | $(2.0 \pm 0.2) \times 10^5$ |
| $l$-$P1$-4-phenylpyridine | $(3.4 \pm 0.3) \times 10^4$ | 2     | $(1.7 \pm 0.2) \times 10^4$ |
| $l$-$P1$-(4-phenylethynyl)pyridine | $(6.3 \pm 0.6) \times 10^3$ | 2     | $(3.2 \pm 0.3) \times 10^3$ |
**Figure S65**: UV-vis titration of pyridine and THS-monomer (run 1, toluene, 298 K, [THS-monomer] = 6.7 μM, $K_{ref} = 1.2 \times 10^4$ M$^{-1}$).

**Figure S66**: UV-vis titration of pyridine and THS-monomer (run 2, toluene, 298 K, [THS-monomer] = 6.7 μM, $K_{ref} = 1.4 \times 10^4$ M$^{-1}$).

**Figure S67**: UV-vis titration of 4-phenylpyridine and THS-monomer (run 1, toluene, 298 K, [THS-monomer] = 6.2 μM, $K_{ref} = 3.2 \times 10^4$ M$^{-1}$).
Figure S68: UV-vis titration of 4-phenylpyridine and THS-monomer (run 2, toluene, 298 K, [THS-monomer] = 4.5 μM, $K_{\text{ref}} = 3.6 \times 10^4 \text{ M}^{-1}$).

Figure S69: UV-vis titration of N-methylimidazole and THS-monomer (run 1, toluene, 298 K, [THS-monomer] = 4.2 μM, $K_{\text{ref}} = 4.2 \times 10^5 \text{ M}^{-1}$).

Figure S70: UV-vis titration of N-methylimidazole and THS-monomer (run 2, toluene, 298 K, [THS-monomer] = 4.2 μM, $K_{\text{ref}} = 4.1 \times 10^5 \text{ M}^{-1}$).
Table S6: Summary of denaturation constants and formation constants (measured in toluene at 298 K).

| complex                        | denaturant     | $K_{dn}$ (M$^{-5}$) | $K_{f}$ (M$^{-1}$) | log $K_{f}$ (M$^{-1}$) |
|--------------------------------|----------------|---------------------|-------------------|----------------------|
| $HC_2$-I-P6[e$_5$]-C$_2$H-T6*  | pyridine       | (7.4 ± 0.7) × 10$^8$| (6.5 ± 3.9) × 10$^{15}$| 15.8 ± 0.3          |
| $HC_2$-I-P6[b$_5$e]-C$_2$H-T6  | pyridine       | (5.9 ± 0.7) × 10$^4$| (8.2 ± 5.0) × 10$^{19}$| 19.9 ± 0.3          |
| $HC_2$-I-P6[b$_6$]-C$_2$H-T6   | pyridine       | (7.0 ± 3.0) × 10$^3$| (6.9 ± 5.1) × 10$^{20}$| 20.8 ± 0.3          |
| c-P6[e$_5$]-T6*                | pyridine       | (5.1 ± 0.4) × 10$^{-5}$| (9.5 ± 5.7) × 10$^{18}$| 29.0 ± 0.3          |
| c-P6[be$_5$]-T6*               | N-methylimidazole| (1.9 ± 0.3) × 10$^{-5}$| (2.9 ± 1.8) × 10$^{18}$| 38.5 ± 0.3          |
| c-P6[b$_5$e]-T6                | N-methylimidazole| (1.4 ± 0.1) × 10$^{-2}$| (3.9 ± 2.3) × 10$^{15}$| 35.6 ± 0.3          |
| c-P6[b$_6$]-T6                 | N-methylimidazole| (5.4 ± 0.6) × 10$^{-4}$| (1.0 ± 0.6) × 10$^{17}$| 37.0 ± 0.3          |

Figure S71: UV-vis-NIR titration of pyridine and $HC_2$-I-P6[b$_5$e]-C$_2$H-T6 illustrating the removal of the T6 template (run 1, toluene, 298 K, $[HC_2$-I-P6[b$_5$e]-C$_2$H-T6] = 1.5 μM, $K_{dn}$ = 5.7 × 10$^{4}$ M$^{-5}$).

Figure S72: UV-vis-NIR titration of pyridine and $HC_2$-I-P6[b$_5$e]-C$_2$H-T6 illustrating the removal of the T6 template (run 2, toluene, 298 K, $[HC_2$-I-P6[b$_5$e]-C$_2$H-T6] = 1.5 μM, $K_{dn}$ = 6.0 × 10$^{4}$ M$^{-5}$).
Figure S73: UV-vis-NIR titration of N-methylimidazole and c-P6[b6]·T6 illustrating the removal of the T6 template (run 1, toluene, 298 K, [c-P6[b6]·T6] = 1.5 μM, $K_{on} = 4.6 \times 10^{-5}$ M$^{-1}$).

Figure S74: UV-vis-NIR titration of N-methylimidazole and c-P6[b5]·T6 illustrating the removal of the T6 template (run 2, toluene, 298 K, [c-P6[b5]·T6] = 1.3 μM, $K_{on} = 6.1 \times 10^{-5}$ M$^{-1}$).

Figure S75: UV-vis-NIR titration of N-methylimidazole and c-P6[b5e]·T6 illustrating the removal of the T6 template (run 1, toluene, 298 K, [c-P6[b5e]·T6] = 0.68 μM, $K_{on} = 1.4 \times 10^{-2}$ M$^{-1}$).
Figure S76: UV-vis-NIR titration of N-methylimidazole and c-P6[b₅e]-T6 illustrating the removal of the T6 template (run 2, toluene, 298 K, [c-P6[b₅e]-T6] = 0.68 μM, $K_{dn} = 1.4 \times 10^{-2}$ M⁻¹).

Figure S77: UV-vis-NIR titration of pyridine and HC₂-P6[b₅]-C₂H-T6 illustrating the removal of the T6 template (run 1, toluene, 298 K, [HC₂-P6[b₅]-C₂H-T6] = 2.9 μM, $K_{dn} = 8.4 \times 10^{3}$ M⁻¹).

Figure S78: UV-vis-NIR titration of pyridine and HC₂-P6[b₅]-C₂H-T6 illustrating the removal of the T6 template (run 2, toluene, 298 K, [HC₂-P6[b₅]-C₂H-T6] = 2.9 μM, $K_{dn} = 5.6 \times 10^{3}$ M⁻¹).

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Model: Breakup (User)
Equation: $a = b \cdot (1/K_{dn} + (K_{dn} \cdot (A_{810-A872})^{2}))$
Plot: $A_{810-A872}$
a = -0.1178
b = 0.12058
K = 0.0141
Reduced Chi-Sq = 1.94156
R-Square(COO) = 0.99834
Adj. R-Square = 0.99867
Figure S79: UV-vis-NIR titration of pyridine and HC$_2$I-P6[e$_5$]-C$_2$H-T6* illustrating the removal of the T6* template (run 1, toluene, 298 K, [HC$_2$I-P6[e$_5$]-C$_2$H-T6*] = 1.7 μM, $K_{dn} = 7.0 \times 10^{8}$ M$^{-5}$).

Figure S80: UV-vis-NIR titration of pyridine and HC$_2$I-P6[e$_5$]-C$_2$H-T6* illustrating the removal of the T6* template (run 2, toluene, 298 K, [HC$_2$I-P6[e$_5$]-C$_2$H-T6*] = 1.7 μM, $K_{dn} = 7.8 \times 10^{8}$ M$^{-5}$).

Figure S81: UV-vis-NIR titration of pyridine and c-P6[e$_5$]-T6* illustrating the removal of the T6* template (Run 1, toluene, 298 K, [c-P6[e$_5$]-T6*] = 0.42 μM, $K_{dn} = 4.6 \times 10^{5}$ M$^{-3}$).
Figure S82: UV-vis-NIR titration of pyridine and c-P6[e6]-T6* illustrating the removal of the T6* template (run 2, toluene, 298 K, [c-P6[e6]-T6*] = 0.42 µM, $K_{dn} = 5.5 \times 10^{-5}$ M$^{-5}$).

Figure S83: UV-vis-NIR titration of N-methylimidazole and c-P6[e6]-T6* illustrating the removal of the T6* template (run 1, toluene, 298 K, [c-P6[e6]-T6*] = 0.38 µM, $K_{dn} = 1.2 \times 10^{-4}$ M$^{-5}$).

Figure S84: UV-vis-NIR titration of N-methylimidazole and c-P6[be5]-T6* illustrating the removal of the T6* template (run 1, toluene, 298 K, [c-P6[be5]-T6*] = 1.0 µM, $K_{dn} = 1.9 \times 10^{-5}$ M$^{-5}$).
Figure S85: UV-vis-NIR titration of N-methylimidazole and c-P6[be5]·T6* illustrating the removal of the T6* template (run 2, toluene, 298 K, [c-P6[be5]·T6*] = 0.97 μM, K_d = 1.8 × 10^{-5} M^{-1}).

6.2 Estimation of Statistically-Corrected Effective Molarities

Average effective molarities were calculated using the equation:

\[ \overline{EM} = \frac{5}{K_1^6 K_{chem}} \]

where \( K_{chem} \) is the statistically corrected formation constant of the nanoring-template complex (\( K_{chem} = K/K_0 \)) and \( K_1 \) is the statistically corrected binding constant for a reference ligand (4-phenylpyridine for T6; 4-phenylethynyl pyridine for T6*) from Table S5. Statistical factors (\( K_o \)) were calculated using Benson’s symmetry number method (and it works out that in every case the value is 768).\(^{[7-9]}\)

Table S7: Summary of formation constants and effective molarities.

| complex | log \( K (M^{-1}) \) | log \( K_{chem} (M^{-1}) \) | \( \overline{EM} (M) \) | log\( \overline{EM} \) |
|---------|-----------------|-----------------|----------------|----------------|
| HC2-L-P6[e5]-C4H-T6* | 15.8 ± 0.3 | 12.9 ± 0.3 | 0.024 ± 0.006 | −1.6 ± 0.1 |
| HC2-L-P6[b5e]-C4H-T6 | 19.9 ± 0.3 | 17.0 ± 0.3 | 0.020 ± 0.005 | −1.7 ± 0.1 |
| HC2-L-P6[b5e]-C2H-T6 | 20.9 ± 0.3 | 18.0 ± 0.3 | 0.032 ± 0.007 | −1.5 ± 0.1 |
| c-P6[e5]-T6* | 29.0 ± 0.3 | 26.1 ± 0.3 | 10 ± 2 | 1.0 ± 0.1 |
| c-P6[be5]-T6* | 38.5 ± 0.3 | 35.6 ± 0.3 | 830 ± 190 | 2.9 ± 0.1 |
| c-P6[b5e]-T6 | 35.6 ± 0.4 | 32.7 ± 0.4 | 28 ± 6 | 1.4 ± 0.1 |
| c-P6[b6]-T6 | 37.0 ± 0.4 | 34.1 ± 0.4 | 52 ± 6 | 1.7 ± 0.1 |
6.3 Calculations of experimental strain energies

\[ \Delta G_f = -RT \ln(K_f) \]

where \( K_f \) is the formation constant of the complex from Table S7, \( R \) is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)) and \( T \) is temperature (298 K).

The strain energy of the cyclic complexes can be expressed as the difference in binding energy between corresponding cyclic and linear oligomers, assuming that the major difference in binding strength is related to the strain energy.

\[ \Delta G_{\text{strain}} = \Delta G_{f, \text{cyclic}} - \Delta G_{f, \text{linear}} \]

Table S8: Summary of formation constants, binding energies and estimated strain energies

| complex                  | \( \log K_f (M^{-1}) \) | \( \Delta G_f (kJ \text{ mol}^{-1}) \) | related linear system | \( \Delta G_{\text{strain}} (kJ \text{ mol}^{-1}) \) |
|-------------------------|-------------------------|--------------------------------------|-----------------------|-----------------------------------------------|
| HC\(_2\)-/P6[\(e_3\)]-C\(_2\)H·T6\(* \) | 15.8 ± 0.3              | 90 ± 2                               | –                     | –                                             |
| HC\(_2\)-/P6[\(b_4\)e]-C\(_2\)H·T6                                      | 19.9 ± 0.3              | 113 ± 2                              | –                     | –                                             |
| HC\(_2\)-/P6[\(b_5\)e]-C\(_2\)H·T6                                      | 20.8 ± 0.3              | 119 ± 2                              | –                     | –                                             |
| c-P6[\(e_3\)]·T6\(* \)                                    | 29.0 ± 0.3              | 166 ± 2                              | HC\(_2\)-/P6[\(e_3\)]-C\(_2\)H·T6\(* \) | 76 ± 3\(^a\) |
| c-P6[\(be_5\)]·T6\(* \)                                   | 38.5 ± 0.3              | 220 ± 2                              | HC\(_2\)-/P6[\(e_3\)]-C\(_2\)H·T6\(* \) | 130 ± 3 |
| c-P6[\(b_5\)e]-T6                                            | 35.6 ± 0.3              | 203 ± 2                              | HC\(_2\)-/P6[\(b_4\)e]-C\(_2\)H·T6                                      | 90 ± 3 |
| c-P6[\(b_6\)]·T6                                            | 37.0 ± 0.3              | 211 ± 2                              | HC\(_2\)-/P6[\(b_3\)]-C\(_2\)H·T6                                      | 92 ± 3 |

\(^a\)substantial distortion of the template
7 NMR Binding Competition Experiments

A competition NMR experiment was designed to compare the affinities of \( c\text{-P6}[b_6] \) and \( c\text{-P6}[b_5e] \) for the template \( T6 \) (Figure S86). Although the \( ^1H \)-NMR spectra of \( c\text{-P6}[b_6] \cdot T6, c\text{-P6}[b_5e], c\text{-P6}[b_5e] \cdot T6 \) and \( c\text{-P6}[b_5e] \) overlap, several peaks are unique for \( c\text{-P6}[b_6] \cdot T6 \) and \( c\text{-P6}[b_5e] \cdot T6 \) (Figure S87), particularly the \( \beta \) resonances from bound \( T6 \). Solutions of equal quantities of \( c\text{-P6}[b_6] \) and \( c\text{-P6}[b_5e] \cdot T6 \) (1:1 mole ratio; approximately 1 mg of each; 0.1 \( \mu \)mol) in CDCl\(_3\) (0.5 mL) were mixed in an NMR tube (Figure S87, top). The exchange of the template \( T6 \) proceeds very slowly without presence of a competing ligand to catalyze the de-coordination of \( T6 \), therefore, \( N \)-methylimidazole (40 \( \mu \)L, 500 \( \mu \)mol) as a stronger competing ligand was added. After 1 hour, equilibrium was achieved; the solution was evaporated, and \( N \)-methyl imidazole was removed under vacuum. The solid residue was dissolved in CDCl\(_3\) (0.5 mL). \( ^1H \) NMR integration showed that the mole ratio of \( c\text{-P6}[b_6] \cdot T6 \) and \( c\text{-P6}[b_5e] \cdot T6 \) was 1.25, indicating a marginally higher affinity of \( c\text{-P6}[b_6] \) towards \( T6 \) (Figure S88, bottom). This experiment was also conducted in the complementary order, starting with an equimolar mixture of \( c\text{-P6}[b_5e] \) and \( c\text{-P6}[b_6] \cdot T6 \), yielding a similar result (mole ratio = 1.21, Figure S89). This confirms that the mixture is at equilibrium under these experimental conditions.

![Figure S86: Competitive binding experiment investigating the relative affinity of \( c\text{-P6}[b_6] \) and \( c\text{-P6}[b_5e] \) towards \( T6 \).](image)

\( \begin{align*}
\text{(1) initial} & \quad \begin{array}{c}
\text{1.0 : 1.0}
\end{array} \\
\text{(2) initial} & \quad \begin{array}{c}
\text{1.0 : 1.0}
\end{array} \\
\text{N-methyl imidazole} & \quad \begin{array}{c}
\text{mixture at equilibrium}
\end{array} \\
1.23 & \quad 1.00 \quad : \quad 1.00 \quad : \quad 1.23
\end{align*} \)
Figure S87: $^1$H-NMR spectra (500 MHz, CDCl$_3$, 298 K) of pure compounds (from top to bottom): c-P6[b$_5$]·T6, c-P6[b$_6$], c-P6[b$_5$]·T6 and c-P6[b$_6$]. Resonances a1 and b1 stand out the porphyrin regions providing a measure for the c-P6[b$_5$]·T6 system. T6 $\beta$ resonances in c-P6[b$_5$]·T6 and c-P6[b$_6$]·T6 are split and provide the cleanest measure for the c-P6[b$_5$]·T6 / c-P6[b$_6$]·T6 ratio.
Figure S88: $^1$H-NMR spectra (500 MHz, CDCl$_3$, 298 K) of an initially equimolar mixture c-P6$[b_6]$ and c-P6$[b_5e]$.T6 (top) and after template redistribution catalyzed by N-methylimidazole (bottom).

Figure S89: $^1$H-NMR spectra (500 MHz, CDCl$_3$, 298 K) of initially equimolar mixture c-P6$[b_6]$.T6 and c-P6$[b_5e]$ (top) and after template redistribution catalyzed by N-methylimidazole (bottom).
8 Photophysical Measurements

Fluorescence quantum yields $\Phi_f$ were measured using linear butadiyne-linked porphyrin hexamer as a reference. Its reported $\Phi_f$ of 28% (toluene, 1% pyridine) was further verified using an integrating sphere. The following formula was used for the calculation of the relative $\Phi_f$:

$$\Phi_f(S) = \Phi_f(R) \cdot \frac{1 - 10^{-AR}}{1 - 10^{-AS}} \cdot \frac{\int I_S(\nu)d\nu}{\int I_R(\nu)d\nu} \cdot \frac{n_S^2}{n_R^2}$$

where $A$ is the optical density at the excitation wavelength, $n$ the refractive index of the solvent, $\int I_S(\nu)d\nu$ the integrated spectral fluorescence photon flux which was approximated by the integrated blank and dark-count corrected signals of the emission (in wave-numbers).

The low quantum yield and red-shifted emission of most of the reported compounds prevented us from measuring absolute quantum yields using an integrating sphere. Several accumulated spectra were necessary to obtain emission profiles with acceptable signal-to-noise. All fluorescence samples were prepared with optical densities < 0.1 under ambient conditions. The potential degradation of the samples was assessed by their UV-vis-NIR absorption spectra showing in all cases no observable decomposition even after >300 cycles (5 hours), indicating remarkable stability. Excitation spectra of all compounds were acquired at several different emission wavelengths.

Figure S90: Steady-state absorption (black lines) and fluorescence (dashed lines) spectra at 295 K of (left) c-P6[b$_6$], c-P6[b$_5$e$_1$], c-P6[be$_5$], c-P6[e$_6$] in toluene/1% pyridine and (right) c-P6[b$_6$]-T6, c-P6[b$_5$e$_1$]-T6, c-P6[be$_5$]-T6*, c-P6[e$_6$]-T6* in toluene. Fluorescence quantum yields are given in %. The indentation at 1140 nm of the emission spectra is associated with solvent.
**Fluorescence Lifetimes**

All samples were excited at 810 nm with a power of 20 mW. Fluorescence emission was detected at 1050 nm. The fluorescence lifetimes $\tau$ were extracted by fitting a mono-exponential decay model to the experimentally observed fluorescence intensity: $I_F(t) = A e^{-t/\tau}$. The experimental fluorescence data with fits for each sample are shown in Figure S91 and the resulting lifetimes are given in Table S9. From the fluorescence lifetimes $\tau$ and the fluorescence quantum yields $\phi_f$, the total, radiative and non-radiative decay rates ($k_{tot}$, $k_{rad}$ and $k_{nonrad}$) are calculated for each sample using: $k_{tot} = 1/\tau$ and $k_{tot} = k_{rad} + k_{nonrad}$, with $k_{rad} = \phi_f \cdot k_{tot}$. The rates are given in Table S9. The fluorescence of sample c-P6[be$_5$]·T6$^*$ was too weak ($\phi_f \approx 0.01\%$) to allow the recording of a reliable fluorescence decay.

**Table S9.** Fluorescence lifetimes $\tau$ (detected at 1050 nm, sample excited at 810 nm), total decay rate $k_{tot}$, radiative decay rate $k_{rad}$, non-radiative decay rate $k_{nonrad}$, and fluorescence quantum yields.

| sample          | $\tau$ (ns) | $k_{tot}$ (1/ns) | $k_{rad}$ (1/ns) | $k_{nonrad}$ (1/ns) | $\phi_f$ (%) |
|-----------------|-------------|-----------------|-----------------|---------------------|-------------|
| c-P6[be$_5$]    | 0.51        | 1.96            | 0.035           | 1.93                | 1.8         |
| c-P6[be$_5$]·T6 | 0.34        | 2.91            | 0.011           | 2.89                | 0.38        |
| c-P6[be$_5$]    | 0.44        | 2.27            | 0.023           | 2.24                | 1.00        |
| c-P6[be$_5$]·T6 | 0.32        | 3.17            | 0.012           | 3.16                | 0.39        |
| c-P6[be$_5$]    | 0.28        | 3.61            | 0.0094          | 3.60                | 0.26        |
| c-P6[be$_5$]·T6*| 0.22        | 4.51            | 0.0063          | 4.50                | 0.14        |
| c-P6[e$_6$]     | 0.49        | 2.02            | 0.0026          | 2.02                | 0.13        |
Fig. S91: Experimentally determined fluorescence lifetime decay (blue) and fits of a mono-exponential decay model to the data (red) for c-P6[b₆], c-P6[b₅e], c-P6[be₅], c-P6[e₆] (left) and c-P6[b₅]-T₆, c-P6[b₅e]-T₆, c-P6[be₅]-T₆* (right). The fluorescence decay was measured at 1050 nm.
9 Computational Chemistry

9.1 Geometry Optimization

All DFT calculations were carried out using Gaussian 16/A.03.\cite{11} In all computational models, the aryl side-groups are truncated to –H. All geometries were optimized at the B3LYP\cite{12} level of theory using the 6-31G* basis set.\cite{13-15} Frequency calculations were performed for all structures confirming that geometries represent minima. The calculated Cartesian coordinates can be found in the provided .xyz files.

\[ c-P6[b_6] \]
\[ c-P6[b_6]-T6 \]
\[ c-P6[b_{6e}] \]
\[ c-P6[b_{6e}]-T6 \]

**Fig. S92:** Geometries from DFT calculations.
Fig. S92 (continued): Geometries from DFT calculations.
9.2 Calculation of Strain Energy

The theoretical predicted strain of the DFT calculations \( \Delta H_{\text{strain}} \) was estimated by homodesmotic reactions at the B3LYP/6-31G* level of theory. Subtraction of the relative energies gave the corresponding strain energy according to:

\[
E_{c-P6[e6]} + E_{l-P2[e1]} - E_{l-P8[e7]} = E_{\text{strain}(c-P6[e6])} \tag{1}
\]

\[
E_{c-P6[b6]} + E_{l-P2[b1]} - E_{l-P8[b7]} = E_{\text{strain}(c-P6[b6])} \tag{2}
\]

\[
E_{c-P6[b5e]} + E_{l-P2[e1]} - E_{l-P8[e2b5]} = E_{\text{strain}(c-P6[b5e])} \tag{3}
\]

\[
E_{c-P6[be5]} + E_{l-P2[b1]} - E_{l-P8[e5b2]} = E_{\text{strain}(c-P6[be5])} \tag{4}
\]

Table S10. Electronic and strain energies for the cyclic and linear oligo porphyrin compounds (B3LYP/6-31G*).

| Energy / Hartrees | Strain energy / kJ mol\(^{-1}\) |
|------------------|-----------------|
| c-P6[e6]         | -17055.23727    | 131.2 |
| c-P6[b6]         | -17512.21118    | 99.8  |
| c-P6[b5e]        | -17436.04888    | 105.2 |
| c-P6[be5]        | -17131.39974    | 114.7 |
| l-P2[e1]         | -5762.42020     | -     |
| l-P2[b1]         | -5838.58050     | -     |
| l-P8[e1]         | -22817.70792    | -     |
| l-P8[e2b1]       | -22970.02436    | -     |
| l-P8[be2b1]      | -23350.83010    | -     |
| l-P8[e5b2]       | -23198.50955    | -     |

Table S11. Electronic and binding energies for the cyclic oligo porphyrin compounds (B3LYP/6-31G*).

| Energy / Hartrees | Binding energy / kJ mol\(^{-1}\) |
|------------------|------------------|
| T6               | -3101.117883     | -     |
| T6*              | -2171.730162     | -     |
| c-P6[e6]-T6*     | -19227.07341     | -144.4|
| c-P6[b6]-T6      | -20613.47323     | -275.0|
| c-P6[b5e]-T6     | -20537.30451     | -252.9|
| c-P6[be5]-T6*    | -19303.25692     | -215.5|
Fig. S93: Homodesmotic reactions used for strain calculations.
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