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Supporting Information

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Enhanced π-Conjugation around a Porphyrin[6] Nanoring

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Materials and Methods

Fluorescence Spectra and Time-Resolved Fluorescence Decays

Emission spectra were recorded on a Spex Fluorolog 3 equipped with a xenon lamp and a NIR sensitive photomultiplier tube (R2658). Due to the low fluorescence quantum yield for the cyclic structures, a small amount of highly fluorescent impurities caused distortion of the emission spectra. The compounds **1a·3** and **1a** were hence measured with excitation at longer wavelengths than the impurity absorption. Time-resolved fluorescence measurements were done by time-correlated single photon counting. The excitation pulse was provided by a Tsunami Ti:Sapphire laser (Spectra-Physics) which was pumped by a Millennia Pro X (Spectra-Physics). The Tsunami output was tuned between 920 nm and 1000 nm and subsequently frequency doubled to wavelengths between 460 nm - 500 nm. The emitted photons were collected by a thermoelectrically cooled micro-channel plate photomultiplier tube (R3809U-50, Hamamatsu). The signal was digitalized using a multi-channel analyzer with 4096 channels (SPC-300, Edinburgh Analytical Instruments). The emission was collected at 780 nm for **4** and at 890 nm for **4·3, 1a·3** and **1a.** The fluorescence decay curves were then fitted to either one or two-exponential expressions by the program FluoFit Pro v.4 (PicoQuant GmbH). The time-resolved fluorescence decay curves are shown in Figure S1. Fitted parameters are listed in Table S1 where τ_1 represents the intrinsic fluorescence life time. **4** was fitted to a double-exponential model where the short life time corresponds to the previously observed conformational relaxation from twisted to planar conformation in the exited state of conjugated porphyrin oligomers.[1] Due to overlapping fluorescence from an impurity (presumably an aggregated linear oligomer) and weak detector sensitivity above 850 nm, the fitting procedure of the circular hexamers where difficult and **4·3** and **1a** could only be fitted using two exponentials where the short life time was attributed to the impurity emission.

Table S1. Fitted life times (τ_1 and τ_2) and pre-exponential factors (a_1 and a_2) from the fluorescence decays of **4**, **4·3**, **1a·3** and **1a** such as those plotted in Figure S1.

	τ_1(ps)	a_1	τ_2(ps)	a_2	X^2_{red}
4	650	0.2	190	0.8	1.1
4·3	500	0.4	200	0.6	1.1
1a·3	340	1	-	-	1.2
1a	460	0.5	170	0.5	1.1

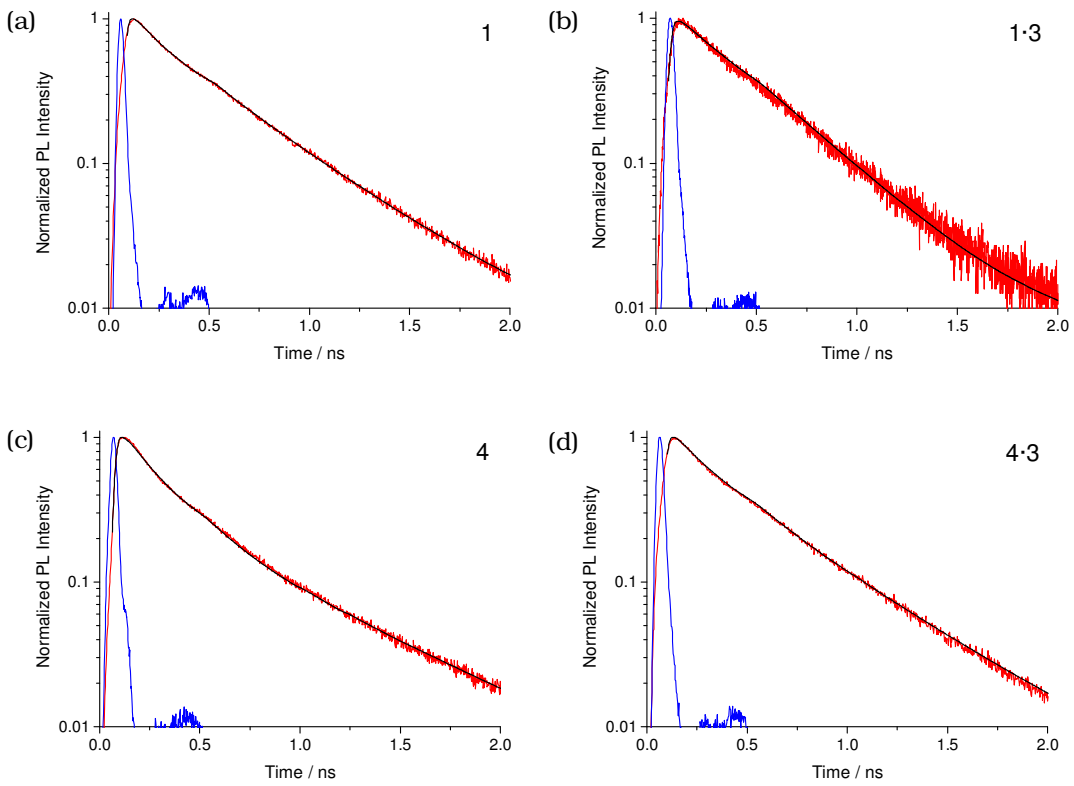


Figure S1. PL decay curves for ***(a)*** **1a**, ***(b)*** **1a·3**, ***(c)*** **4**, and ***(d)*** **4·3** in toluene (the solvent for **1a** and **4** contained 1% pyridine to prevent aggregation). Black lines show the fitted curves corresponding to the parameters listed in Table S1, and blue lines are instrument response functions.

Quantum Mechanical Calculations

The Gaussian 03 program suite[2] was used for the quantum mechanical calculations. The five lowest electronic transitions of a linear, planar and a circular, butadiyne linked, porphyrin hexamer, similar to **1a/b** and **4** but without any substituents on the porphyrins, were computed using Time Dependent Density Functional Theory (TD-DFT) with the B3LYP functional[3-5] and the 6-31G(d) basis set.[6] The structures were geometry optimized with PM3 prior to the TD-DFT calculation.

Table S2. Wavelength, λ, and oscillator strengths, *f*, of the five lowest electronic transitions of a linear (**4**) and a cyclic porphyrin hexamer (**1**) computed from TD-DFT calculations.

	Linear Hexamer		**Cyclic Hexamer**	
Transition	λ (nm)	*f*	λ (nm)	*f*
1	881	6.94	987	0
2	762	0.00	765	2.99
3	745	0.00	765	2.99
4	692	0.97	761	0.0629
5	683	0.0091	761	0.0629

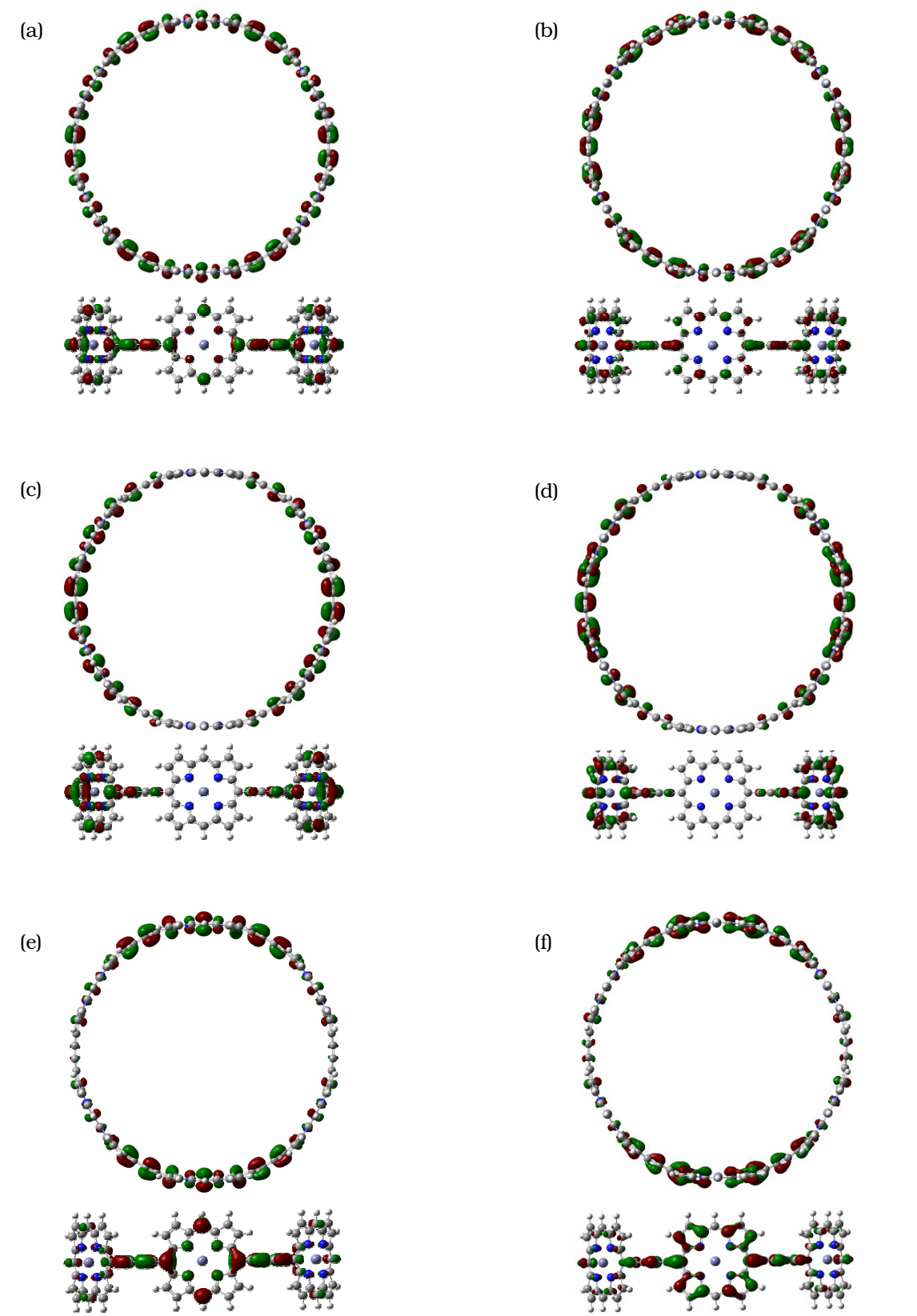


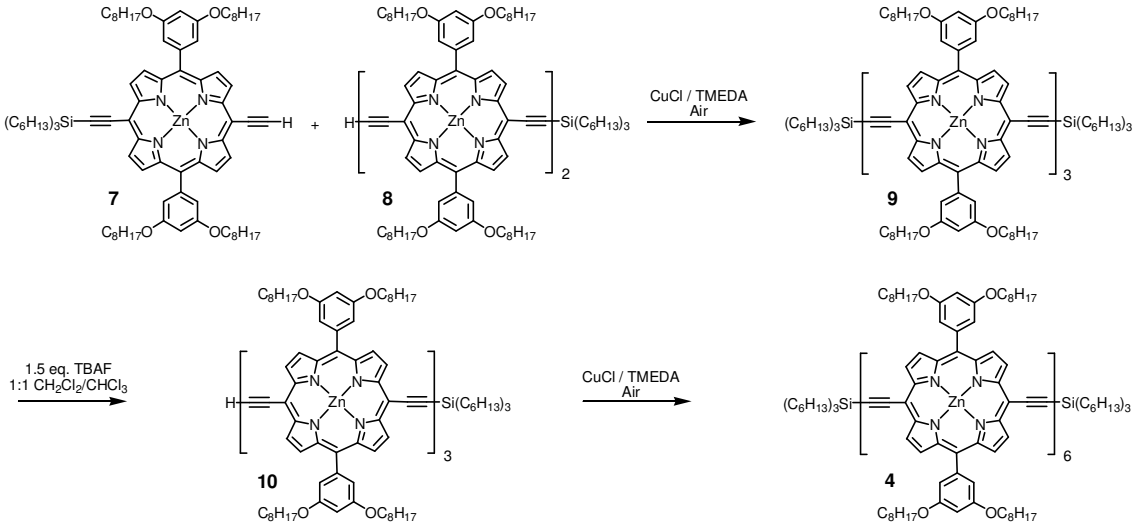
Figure S2. Molecular orbital representations of **1** calculated by DFT for ***(a)*** HOMO, ***(b)*** LUMO, ***(c)*** HOMO-1, ***(d)*** LUMO+1, ***(e)*** HOMO-2, and ***(f)*** LUMO+2.

Synthetic Procedures

All reagents were purchased from commercial sources. Manipulation of all air and/or water sensitive compounds was carried out using standard high vacuum techniques. Porphyrins, **2a/b**, **7** and **8** were synthesized by adapting a published procedure.[7]

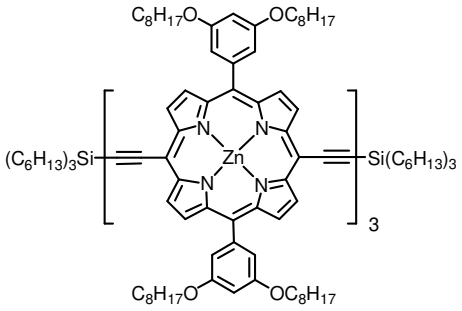
Column chromatography was carried out on Merck® silica gel 60 using a positive pressure of nitrogen. Where mixtures of solvents were used, ratios reported are by volume.

UV-visible spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. NMR spectra were recorded on Bruker instruments, DPX-400 or AV II-500 with cryoprobe. 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 Service, Swansea, UK. Computational chemistry was carried out using the MM+ force-field in HyperChem™, Hypercube Inc. A correction factor of 4% was applied to compensate the underestimation of distances obtained by the molecular mechanics method. This correction factor was determined by comparison with X-ray crystal date for a range of closely related structures. UV-visible spectra were analyzed by fitting the experimental data to the theoretically expected curve using Origin™ or SPECFIT™ software.



Scheme S1. Synthesis of linear porphyrin hexamer **4**.

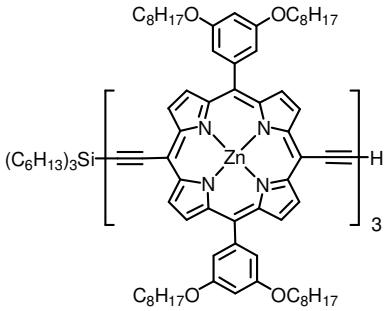
THS$_2$-Porphyrin Trimer (**9**)



Porphyrin monomer **7** (128 mg, 93.7 µmol) and porphyrin dimer **8** (230 mg, 93.7 µmol) were dissolved in dry dichloromethane (73 mL). The mixture was vigorously stirred in a flame dried flask equipped with a $CaCl_2$ drying tube for 25 min. Copper(I) chloride (556 mg, 5.62 mmol) and *N,N,N',N'*-tetramethylethylenediamine (650 µL, 5.62 mmol) were added and vigorous stirring was continued for 1 hour. The reaction mixture was filtered over a short plug of silica using dichloromethane and solvents were removed under vacuum. Size exclusion chromatography on Biobeads SX-1 using tetrahydrofuran gave the trimer as a brown solid (109 mg, 30%); porphyrin dimer (20%) and porphyrin tetramer (20%) were isolated as byproducts.

^{1}H NMR (400 MHz, $CDCl_3$ / 1% d_5-pyridine): δ_H 9.89-9.87 (m, 8H), 9.65 (d, J = 4.5 Hz, 4H), 9.08-9.07 (m, 8H), 8.97 (d, J = 4.5 Hz, 4H), 7.42 (d, J = 2.0 Hz, 4H), 7.39 (d, J = 2.0 Hz, 8H), 6.94-6.91 (m, 6H), 4.21-4.16 (m, 24H), 1.94-1.87 (m, 24H), 1.81-1.75 (m, 12H), 1.58-1.50 (m, 36H), 1.45-1.29 (m, 120H), 1.06-1.01 (m, 12H), 0.94-0.86 (m, 54H). UV-Vis ($CHCl_3$ / 1% Pyridine): λ_{max} (ε) 462 nm (5.3×10^5), 500 nm (2.5×10^5), 590 nm (3.3×10^5), 755 nm (1.9×10^5).

THS-Porphyrin Trimer (**10**)

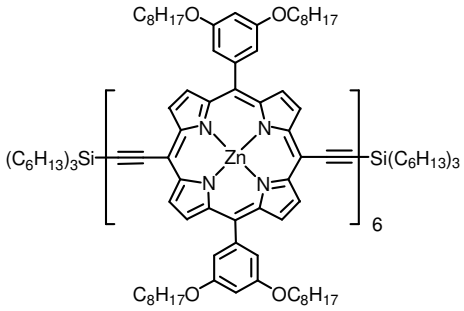


Tetrabutylammonium fluoride (1.0 M in THF, 39.0 µL, 39.0 µmol) was added to a deoxygenated solution of porphyrin trimer **9** (100 mg, 26.2 µmol) in dichloromethane (2.3

mL) and chloroform (2.3 mL). The progress of the reaction was followed by TLC (15% pyridine in petrol 40-60 as eluent). The reaction was quenched with acetic acid (40 µL, 700 µmol) and passed through a short plug of silica using dichloromethane. Chromatography on flash silica gel using 15% pyridine / petrol 40-60 as eluent afforded the desired product as brown solid (36.1 mg, 39%).

^{1}H NMR (400 MHz, $CDCl_3$ / 1% d_5-pyridine): δ_H 9.90-9.86 (m, 8H), 9.66-9.63 (m, 4H), 9.08-9.06 (m, 8H), 8.99-8.96 (m, 4H), 7.41-7.37 (12H), 6.93-6.91 (m, 6H), 4.20-4.15 (m, 24H), 1.94-1.86 (m, 24H), 1.82-1.74 (m, 6H), 1.59-1.49 (m, 30H), 1.44-1.28 (m, 108H), 1.05-1.00 (m, 6H), 0.93-0.83 (m, 45H). MALDI-TOF MS+: *m/z* 3539 ($[M+H]^+$, $C_{222}H_{286}N_{12}O_{12}SiZn_3$, requires 3539);

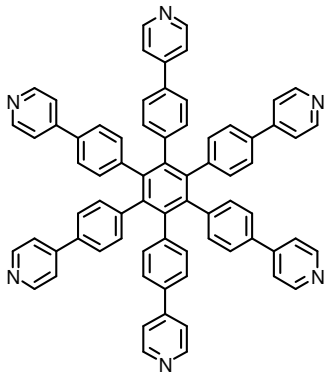
THS$_2$-Porphyrin Hexamer (**4**)



Porphyrin trimer **10** (30.0 mg, 8.48 µmol) was dissolved in dry dichloromethane (5.2 mL). The mixture was vigorously stirred in a flame dried flask equipped with a $CaCl_2$ drying tube for 15 min. Copper(I) chloride (25.2 mg, 254 µmol) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (29 µL, 254 µmol) were added and vigorous stirring was continued for 2.5 hours. The reaction mixture was filtered over a short plug of silica using dichloromethane and solvents were removed under vacuum. Size exclusion chromatography on Biobeads SX-1 using tetrahydrofuran gave porphyrin hexamer as a brown solid (24.3 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$ / 1% d_5-pyridine): δ_H 9.91-9.87 (m, 20H), 9.65 (d, J = 4.5 Hz, 4H), 9.10-9.07 (m, 20H), 8.97 (d, J = 4.5 Hz, 4H), 7.44-7.42 (m, 16H), 7.39-7.38 (m, 8H), 6.95-6.94 (m, 8H), 6.92-6.91 (m, 4H), 4.20-4.16 (m, 48H), 1.94-1.89 (m, 60H), 1.81-1.75 (m, 12H), 1.58-1.50 (m, 72H), 1.42-1.26 (m, 192H), 1.05-1.01 (m, 12H), 0.94-0.86 (m, 90H). MALDI-TOF MS+: *m/z* 7076 ($[M+H]^+$, $C_{444}H_{570}N_{24}O_{24}Si_2Zn_6$, requires 7076); λ_{max} (ε) in $CHCl_3$: 439 nm (2.2×10^5), 519 nm (3.6×10^5), 813 nm (3.6×10^5); λ_{max} (ε) in Toluene/ 1% Pyridine: 466 nm (5.7×10^5), 804 nm (2.9×10^5).

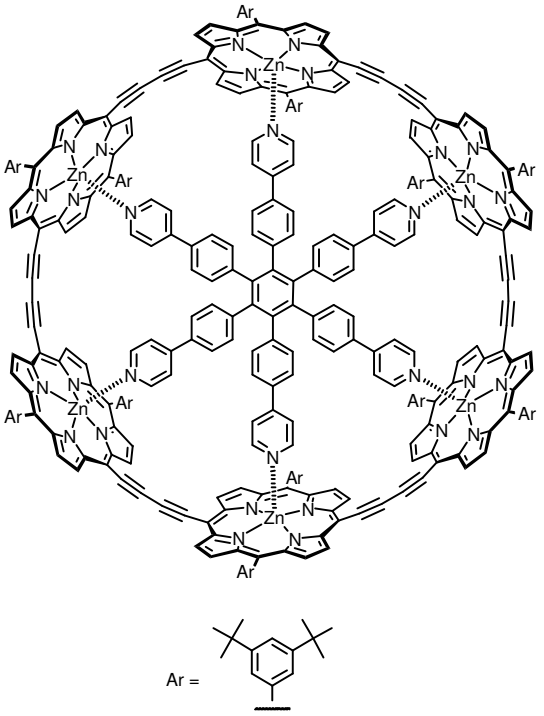
Hexadentate Template (**3**)



To a solution of hexa-(4-bromophenyl)benzene[8] (300.0 mg, 297 µmol) in dimethyleneglycol (9 mL) and tetrahydrofuran (21 mL) was added dichlorobis(triphenylphosphine)-palladium(II) (40.0 mg, 57.0 µmol). After addition of water (12 mL), $NaHCO_3$ (450 mg, 5.36 mmol) and 4-pyridineboronic acid (882 mg, 7.18 mmol), the mixture was deoxygenated and stirred at 70 °C for 5 days. Solvents were removed and the crude product was purified by column chromatography on flash silica gel (dichloromethane : methanol : triethylamine = 10 : 1 : 0.05) to give the template as a white solid (148 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.36 (d, J = 5.5 Hz, 12H), 7.29 (d, J = 5.5 Hz, 12H), 7.18 (d, J = 8.5 Hz, 12H), 6.96 (d, J = 8.5 Hz, 12H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_C 149.17, 147.99, 141.04, 139.85, 134.54, 131.86, 125.37, 121.26. MALDI-TOF MS+: m/z 997.4 ($[M+H]^+$, $C_{72}H_{48}N_6$, requires 997.4); UV-vis ($CHCl_3$): λ_{max} (ε) 278 nm (1.1×10^5).

Cyclic ^{t}Bu-Hexamer · Hexadentate Template (**1a·3**)

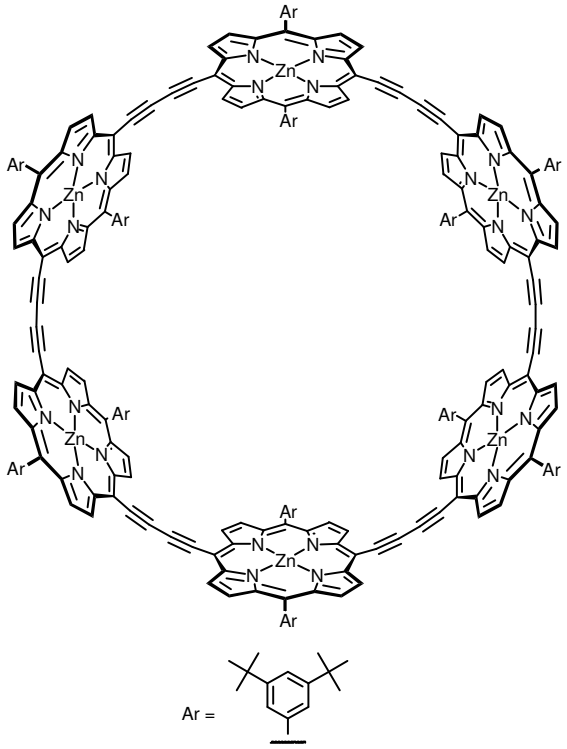


Hexadentate-template **3** (5.4 mg, 5.4 µmol) and diethynyl porphyrin dimer **2a** (27.0 mg, 16.9 µmol) were dissolved in dichloromethane (1 mL) and solvents were removed. A catalyst solution was prepared by dissolving dichlorobis(triphenylphosphine)-palladium(II) (8.2 mg, 12 µmol), copper(I) iodide (4.2 mg, 22 µmol) and iodine (24 mg, 95 µmol) in toluene (12.5 mL) and diisopropylamine (0.9 mL). Part of this catalyst solution (8.8 mL) was added to the dry residue of hexadentate template and porphyrin dimer. The reaction mixture was stirred vigorously at 60 °C under air. UV-Vis spectroscopy showed the reaction to be complete after 1.5 hours. The mixture was diluted with dichloromethane (20 mL), and washed with a saturated aq. $Na_2S_2O_3$ solution (2 × 40 mL) and water (60 mL). Solvents were removed under vacuum. The residue was redissolved in tetrahydrofuran (2 mL) and passed through a 0.45 µm membrane filter. Preparative size exclusion chromatography on Biobeads SX-1 in tetrahydrofuran afforded the hexamer nanoring **1a·3** as a brownish-red solid (13.7 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.59 (d, J = 4.5 Hz, 24H), 8.81 (d, J = 4.5 Hz, 24H), 8.05 (s, 12H), 7.86 (s, 12H), 7.81 (s, 12H), 5.52 (d, J = 9.0 Hz, 12H), 5.48 (d, J = 9.0 Hz, 12H), 5.00 (d, J = 7.0 Hz, 12H), 2.33 (d, J = 7.0 Hz, 12H), 1.58 (s, 108H), 1.54 (s, 108H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.33, 150.04, 148.95, 148.31, 146.19, 142.91, 141.18, 139.88, 138.66,

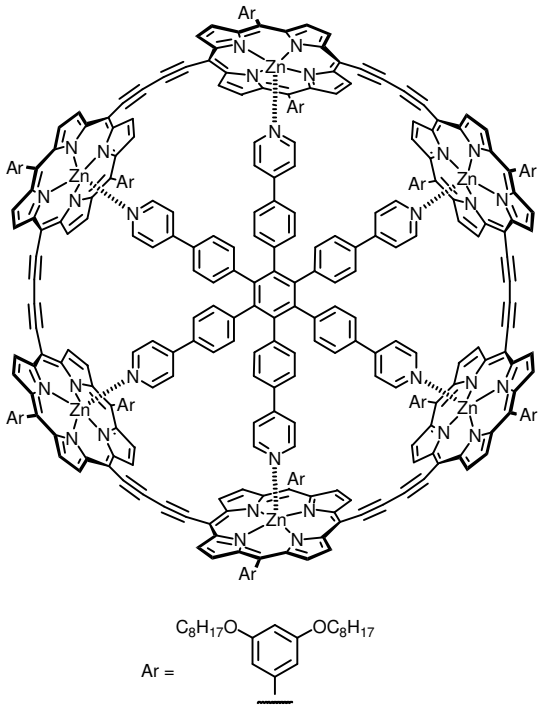
132.84, 132.07, 130.35, 129.46, 125.31, 123.77, 120.92, 119.04, 99.94, 96.50, 89.32, 35.05, 34.97, 31.79, 31.70. MALDI-TOF MS+: *m/z* 5775.4 ($[M]^{\bullet+}$, $C_{384}H_{348}N_{30}Zn_6$, requires 5775.4); UV-vis ($CHCl_3$): λ_{max} (ε) 483 (4.8×10^5), 774 (3.2×10^5), 810 (4.1×10^5), 852 (3.3×10^5).

Cyclic ^{t}Bu-Hexamer (**1a**)



Cyclic hexamer · template complex **1a·3** (3.7 mg, 0.64 µmol) was passed through a size exclusion column (Biobeads SX-1) containing a (100 mg mL^{-1}) solution of DABCO in THF. The crude product mix was dissolved in chloroform and recrystallized by layer addition with methanol. The precipitate was isolated by passing the mix through a 200 nm membrane filter to afford the template-free nanoring as a brownish solid (2.5 mg, 81%). MALDI-TOF MS+: *m/z* 4778 ($[M]^{\bullet+}$, $C_{312}H_{300}N_{24}Zn_6$, requires 4778); UV-vis ($CHCl_3$): λ_{max} (ε) 475 (4.3×10^5), 788 (2.3×10^5); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.62 (d, J = 4.5 Hz, 24 H) 8.79 (d, J = 4.5 Hz, 24 H) 7.90 (d, J = 1.5 Hz, 24 H) 7.75 (d, J = 1.5 Hz, 12 H) 1.49 (s, 216 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 151.93, 150.06, 148.51, 141.26, 133.15, 130.41, 129.58, 125.07, 120.85, 100.36, 94.75, 88.38, 34.96, 31.69.

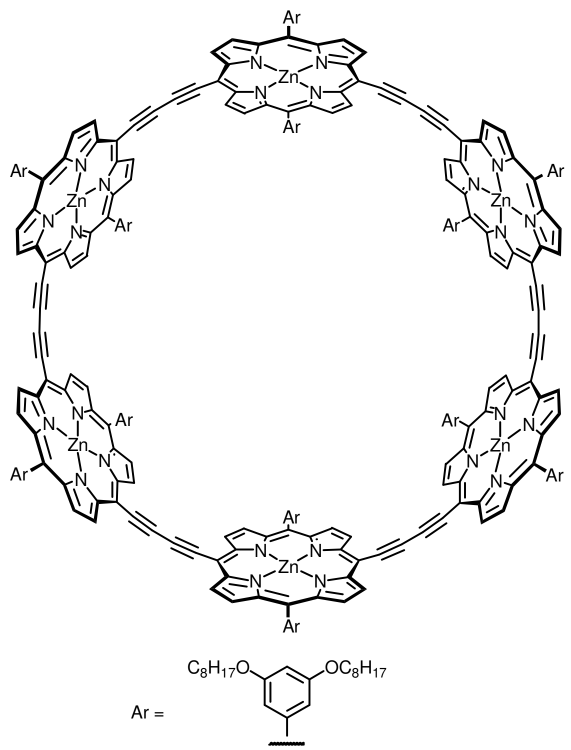
Cyclic Octyloxy-Hexamer · Hexadentate Template (**1b·3**)



Hexadentate-template **3** (2.55 mg, 2.54 µmol) and diethynyl porphyrin dimer **2b** (16.6 mg, 7.64 µmol) were dissolved in dichloromethane (1 mL) and solvents were removed. A catalyst solution was prepared by dissolving dichlorobis(triphenylphosphine)-palladium(II) (8.2 mg, 12 µmol), copper(I) iodide (4.2 mg, 22 µmol) and iodine (24 mg, 95 µmol) in toluene (12.5 mL) and diisopropylamine (0.9 mL). Part of this catalyst solution (3.8 mL) was added to the dry residue of hexadentate template and porphyrin dimer. The reaction mixture was stirred vigorously at 60 °C under air for 2 hours. UV-Vis spectroscopy showed the reaction to be complete. The mixture was diluted with CH_2Cl_2 (10 mL), and washed with $Na_2S_2O_3$ aq. and water. Solvents were removed under vacuum. The mixture was redissolved in THF (2 mL) and passed through a 0.45 µm membrane filter. Preparative size exclusion chromatography on Biobeads SX-1 in tetrahydrofuran afforded the nanoring **1b·3** as a brownish-red solid (6.3 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (d, J = 4.5 Hz, 24H), 8.85 (d, J = 4.5 Hz, 24H), 7.38 (s, 12H), 7.11 (s, 12H), 6.89 (s, 12H), 5.55 (d, J = 8.5 Hz, 12H), 5.47 (d, J = 8.5 Hz, 12H), 5.00 (d, J = 6.5 Hz, 12H), 4.20 (t, J = 6.5 Hz, 24H), 4.09 (t, J = 6.5 Hz, 24H), 2.26 (d, J = 6.5 Hz, 12H), 1.94–1.83 (m, 48H), 1.56–1.26 (m, 240H), 0.90–0.85 (m, 72H). MALDI-TOF MS+: *m/z* 7507.5 ($[M]^{\bullet+}$, $C_{480}H_{540}N_{30}O_{24}Zn_6$, requires 7506.0); UV-vis ($CHCl_3$): λ_{max} (ε) 486 (4.0×10^5), 765 (2.4×10^5), 800 (3.2×10^5), 841 (2.8×10^5).

Cyclic Octyloxy-Hexamer (**1b**)



Cyclic hexamer · template **1b·3** (2.7 mg, 0.36 μmol) was passed through a size exclusion column (Biobeads SX-1) containing a (40 mg mL^{-1}) solution of DABCO in toluene. The crude product mix was dissolved in chloroform and recrystallized by layer addition with methanol. The precipitate was isolated by passing the mix trough a 200 nm membranefilter to afford the template-free nanoring as a brownish solid (2.1 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (d, J = 4.5 Hz, 24H), 8.87 (d, J = 4.5 Hz, 24H), 7.22 (s, 24H), 6.84 (s, 12H), 4.08 (t, J = 6.5 Hz, 48H), 1.94–1.83 (m, 48H), 1.56–1.26 (m, 240H), 0.90–0.85 (m, 72H). UV-vis ($CHCl_3$): λ_{max} (ε) 473 (4.3×10^5), 783 (2.3×10^5).

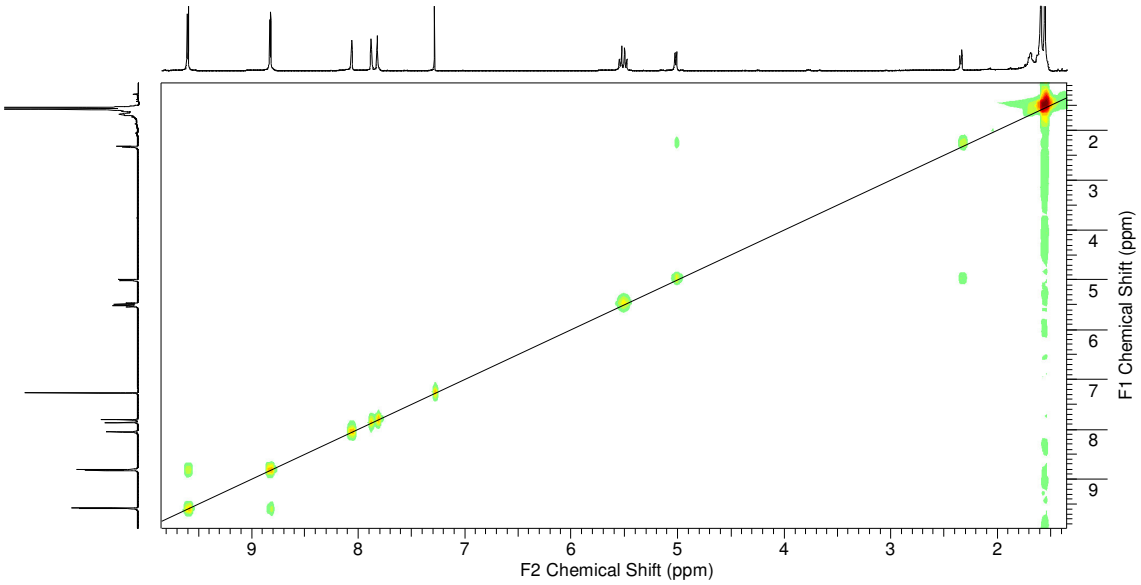


Figure S3. ^{1}H-^{1}H COSY spectrum of cyclic hexamer·template, **1a·3** (400 MHz, $CDCl_3$).

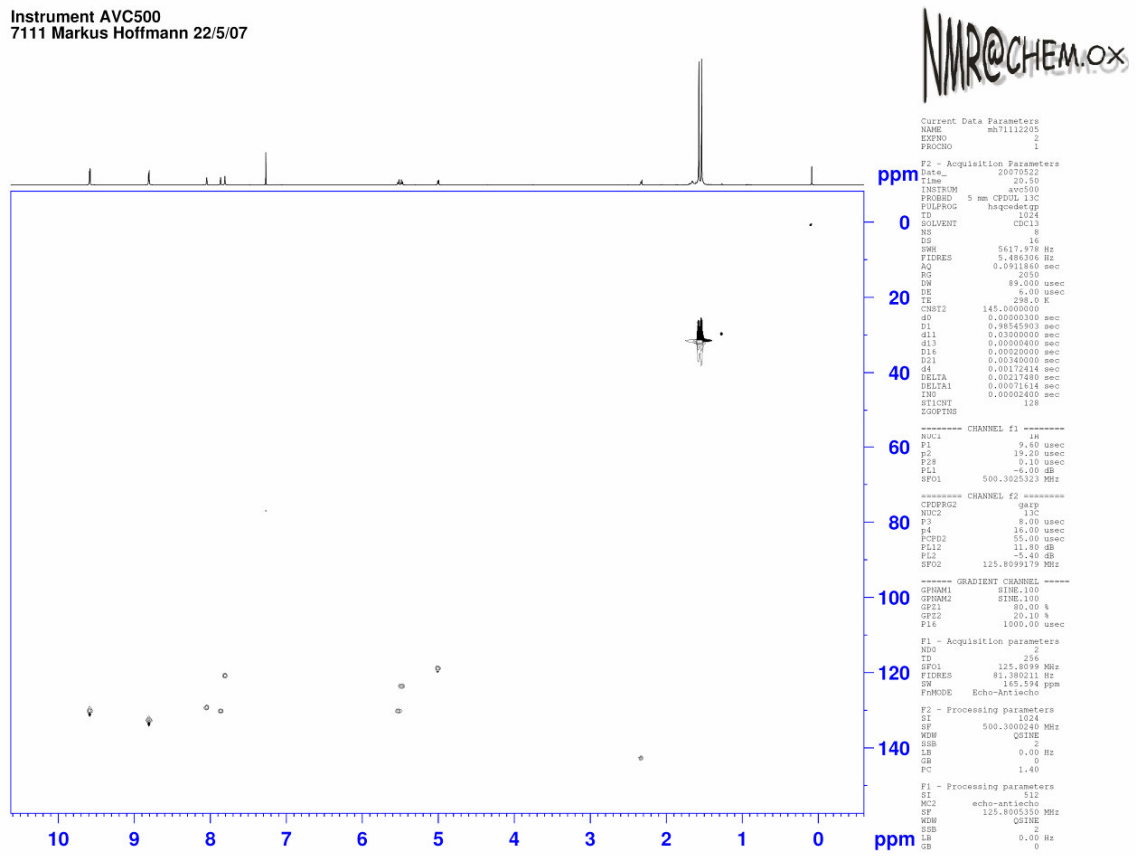


Figure S4. ^{1}H-^{13}C HSQC spectrum of cyclic hexamer·template, **1a·3** (500 MHz, 125 MHz, $CDCl_3$).

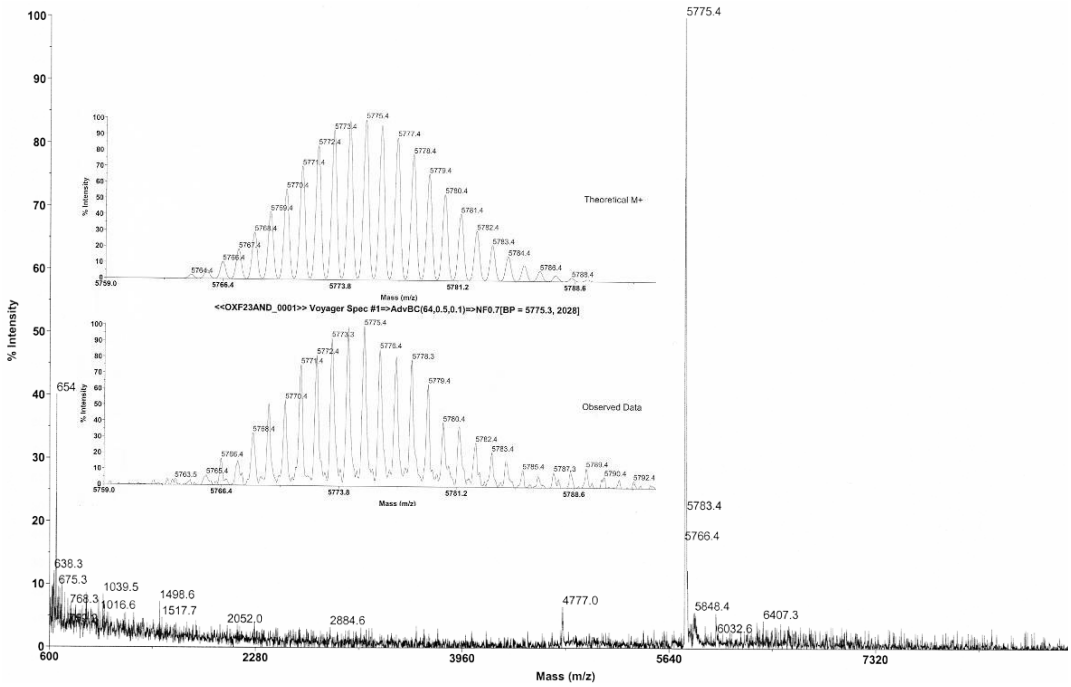


Figure S5. MALDI-TOF mass spectrum of cyclic hexamer·template, **1a·3** (matrix: DCTB, mode: pos. refl.). Expansion insert: Theoretical and observed isotope pattern.

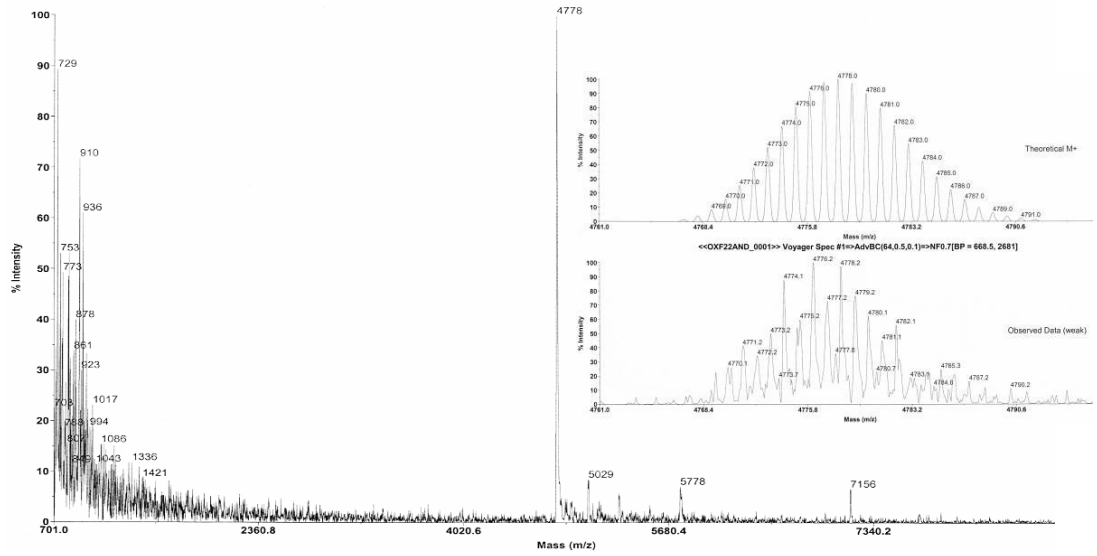


Figure S6. MALDI-TOF mass spectrum of cyclic hexamer, **1a** (matrix: DCTB, mode: pos. linear). Expansion insert: Theoretical and observed isotope pattern.

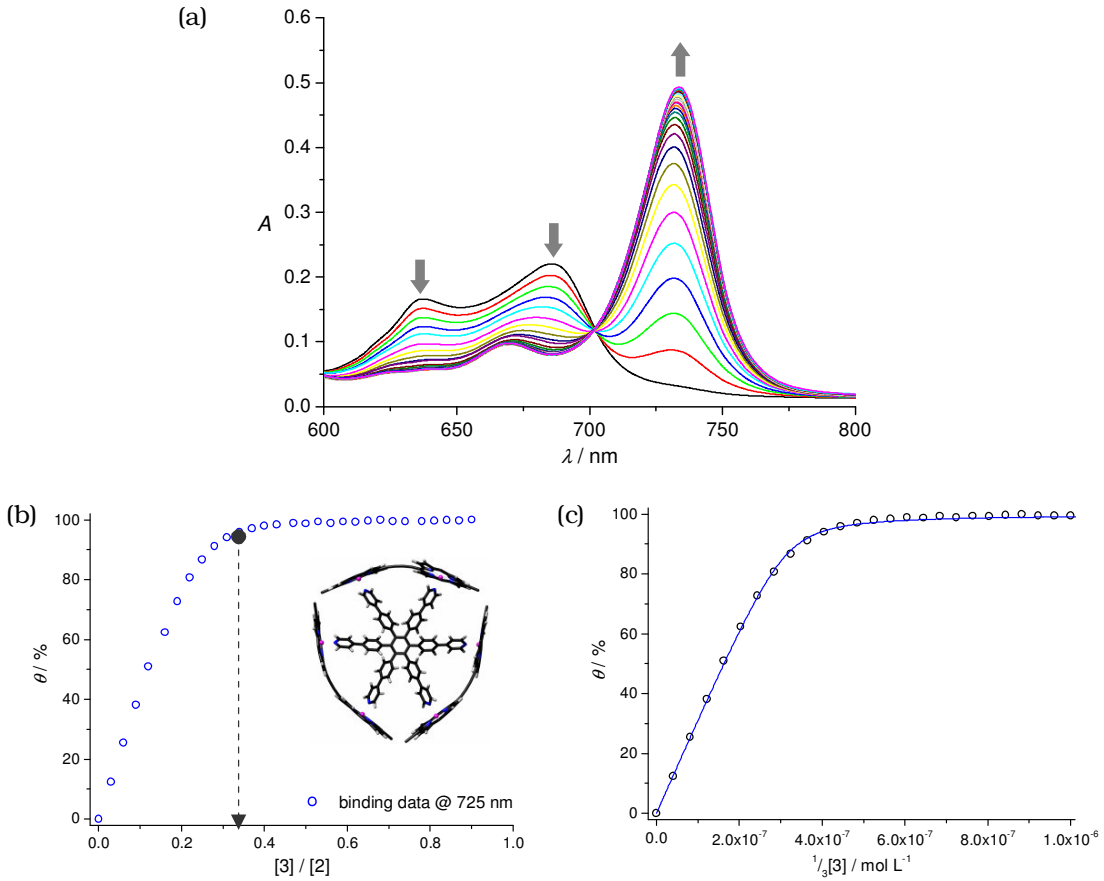


Figure S7. (a) UV-vis titration of hexadentate template, **3** to 10,20-bis-ethynyl-5,15-bis-octyloxy-zinc-porphyrin dimer, **2b**, (conc. 8.9 µM, 298 K, $CHCl_3$). Arrows indicate areas of increasing and decreasing absorption during the titration. ***(b)*** The strong binding event gives the correct stoichiometry (3:1) for the complex $\mathbf{2b_3}$**·3**. ***(c)*** The binding data at 725 nm were fitted to a 3:1 binding isotherm to give a binding constant of K_f =1.6 ± 0.1 × 10^8 M^{-1}, assuming that the three molecules of **2b** bind independently.

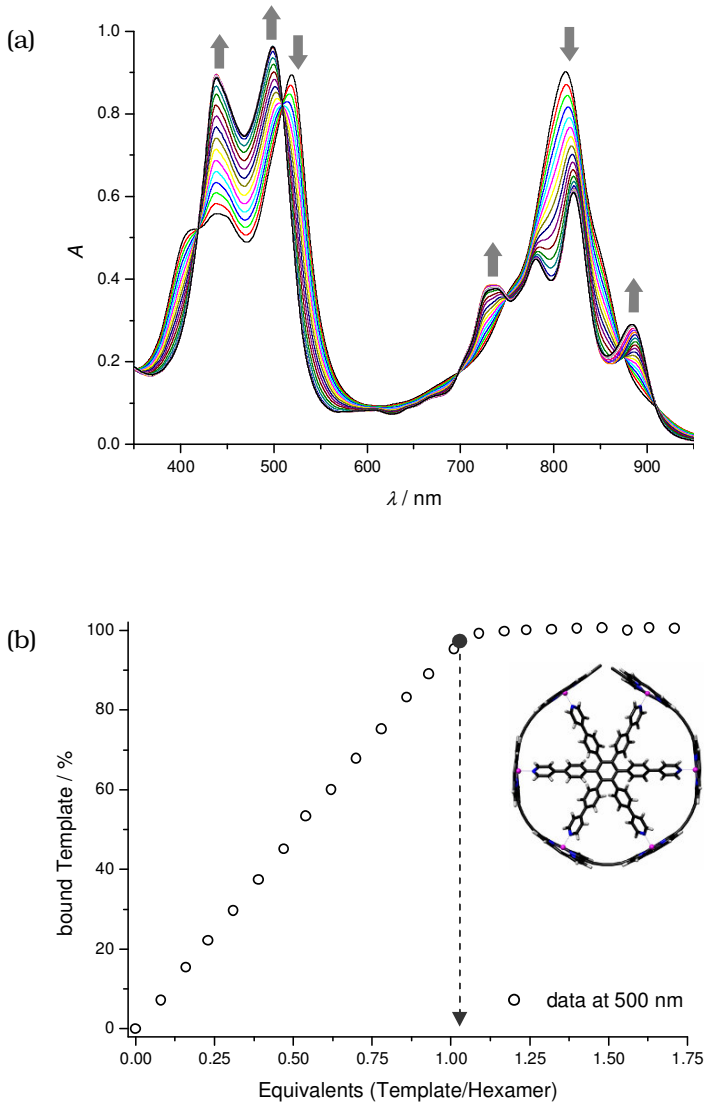


Figure S8. (a) UV-vis titration of hexadentate-template, **3** with linear porphyrin hexamer, **4** ([**4**] = 2.6 μM, 298 K, $CHCl_3$). ***(b)*** Binding isotherm obtained from the absorbance data at 500 nm. The strong binding event gives the correct stoichiometry (1:1) for the complex **4·3**. Arrows indicate areas of increasing and decreasing absorption during the titration.

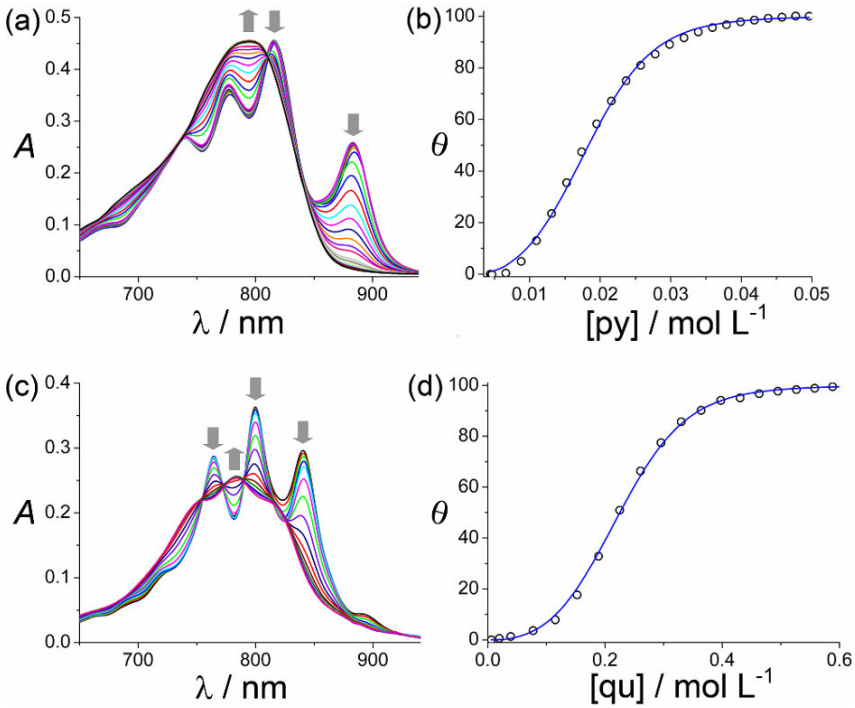


Figure S9. Vis/NIR titration spectra and binding curves for **4·3** + pyridine (a and b), and **1b·3** + quinuclidine (c and d), in $CHCl_3$ at 298 K (*A* is absorption; θ is % fraction bound; [**4·3**] = 1.8 µM; [**1b·3**] = 1.2 µM) ○: data at b) 878 nm and d) 850 nm; —: calculated curve (Equations S1-S5). Arrows indicate areas of increasing and decreasing absorption during the titration.

Calculation of Equilibrium Constants

The curves in Figure S9 (b) and (d) were fitted with the following equations S1-S5, where **M** is either **1b** or **4**, **T** is hexadentate template **3**, and **L** is either quinuclidine or pyridine.

$$K_b = ([\mathbf{M}\cdot\mathbf{L}_6][\mathbf{T}]) / ([\mathbf{M}\cdot\mathbf{T}][\mathbf{L}]^6) \quad \text{(S1)}$$

$$[\mathbf{M}]_0 = [\mathbf{M}\cdot\mathbf{T}]+[\mathbf{M}\cdot\mathbf{L}_6] \quad \text{(S2)}$$

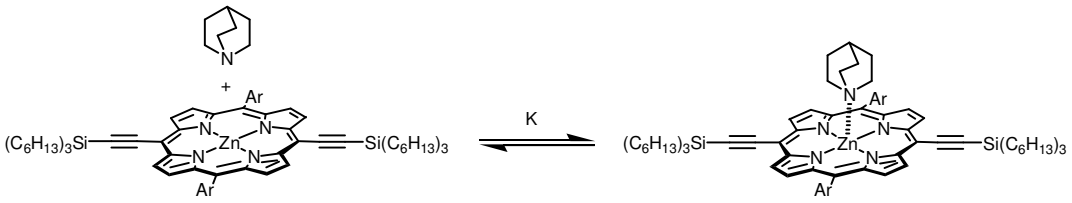
$$[\mathbf{L}]_0 = [\mathbf{L}] \quad \text{(S3)}$$

$$[\mathbf{T}] = [\mathbf{M}\cdot\mathbf{L}_6] \quad \text{(S4)}$$

$$K_b[\mathbf{M}\cdot\mathbf{T}][\mathbf{L}]_0^6 - ([\mathbf{M}]_0 - [\mathbf{M}\cdot\mathbf{T}])^2 = 0 \quad \text{(S5)}$$

Equilibrium constants K_f as occurring for the formation of **1b·3** and **4·3** were evaluated by measuring how easily a competing ligand displaces the template (K_b), as shown by a thermodynamic cycle described in Equation S6. K_L is the binding constant of the competing ligand (quinuclidine or pyridine) for one zinc center of the porphyrin hexamer.

$$K_f = K_L^6 / K_b \quad \text{(S6)}$$



Scheme S2. Binding of 10,20-bis-tritrihexylsilanylethynyl-5,15-bis-octyloxy-zinc-porphyrin with quinuclidine, **Qu**.

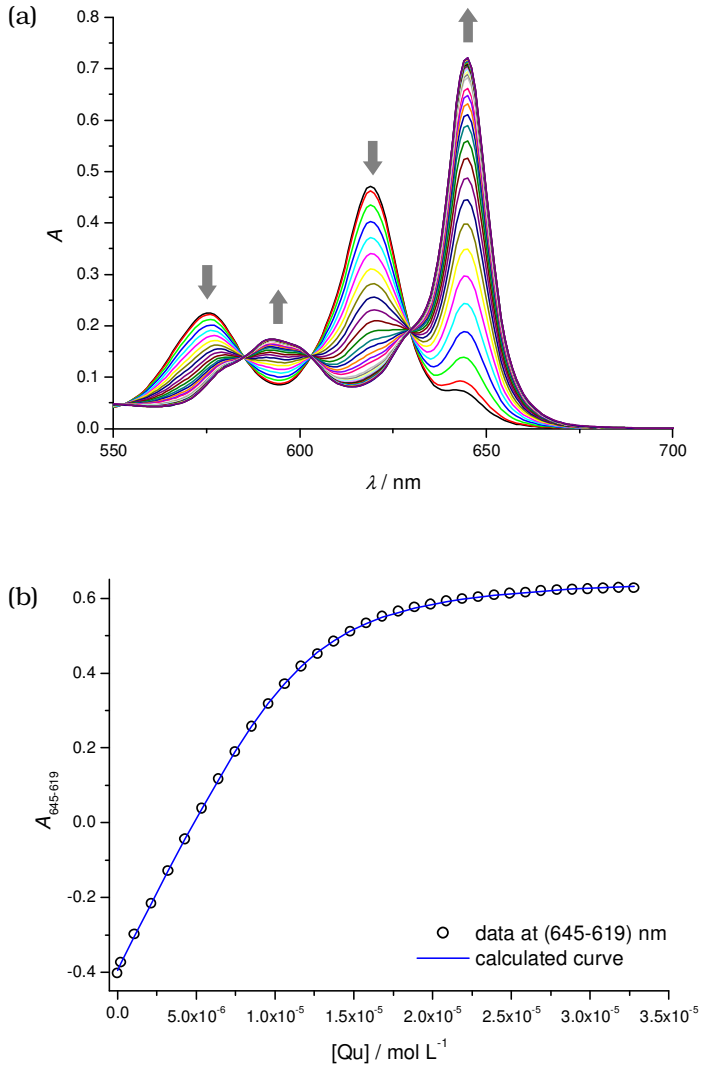
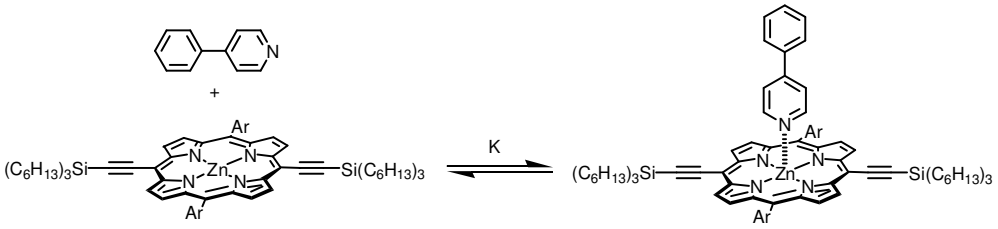


Figure S10. (a) UV-vis titration of quinuclidine, **Qu** with 10,20-bis-trihexylsilylethynyl-5,15-bis-octyloxy-zinc-porphyrin, (conc. 1.7 μM, 298 K, $CHCl_3$). The data at 645 and 619 nm were fitted to a 1:1 binding isotherm ***(b)*** to give a binding constant of $K_{Qu} = 1.2 \pm 0.1 \times 10^6$ M^{-1}. Arrows indicate areas of increasing and decreasing absorption during the titration.



Scheme S3. Binding of 10,20-bis-trihexylsilanylethynyl-5,15-bis-octyloxy-zinc-porphyrin with 4-phenyl-pyridine, **PhPy**.

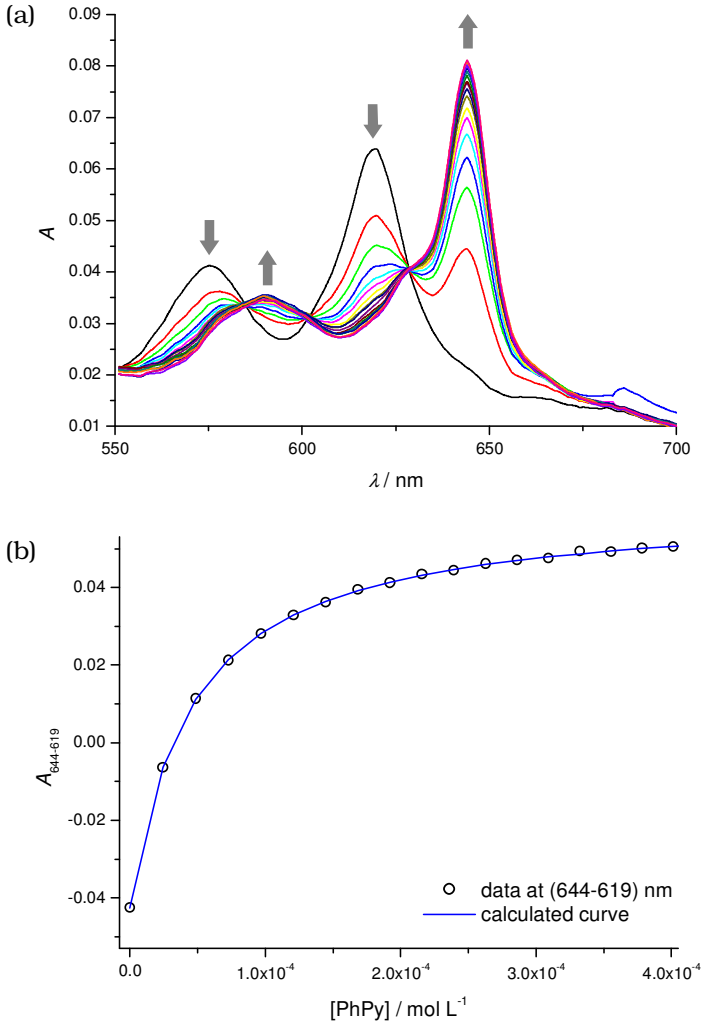
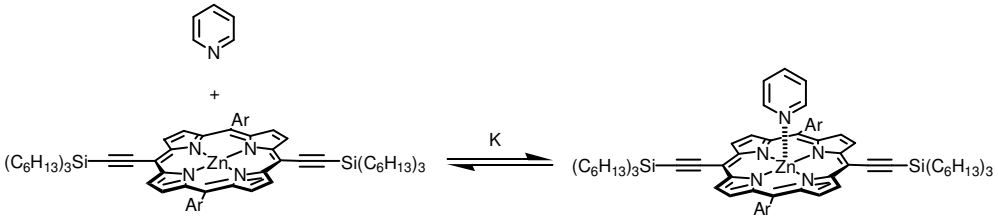


Figure S11. (a) UV-vis titration of 4-phenylpyridine, **PhPy** with 10,20-bis-trihexylsilylethynyl-5,15-bis-octyloxy-zinc-porphyrin, (conc. 2.2 µM, 298 K, $CHCl_3$). The data at 644 and 619 nm were fitted to a 1:1 binding isotherm. ***(b)*** to give a binding constant of $K_0 = 2.3 \pm 0.2 \times 10^4$ M^{-1}. Arrows indicate areas of increasing and decreasing absorption during the titration.



Scheme S4. Binding of 10,20-bis-trihexylsilanylethynyl-5,15-bis-octyloxy-zinc-porphyrin with pyridine, **Py**.

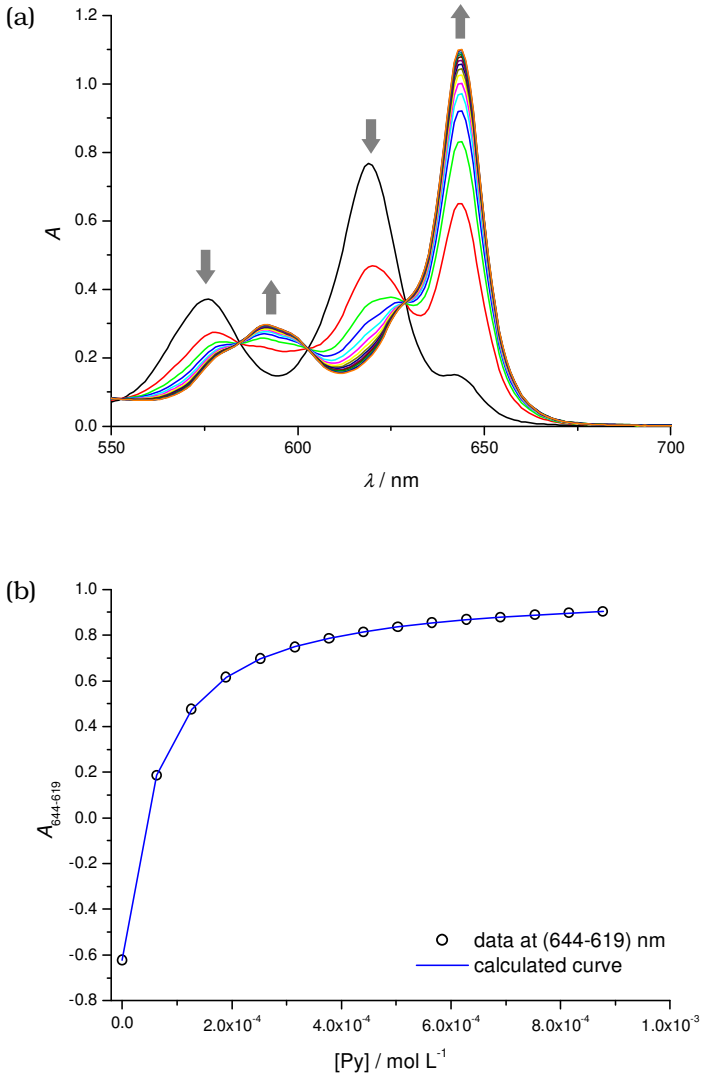


Figure S12. (a) UV-vis titration of pyridine, **Py** with 10,20-bis-trihexylsilylethynyl-5,15-bis-octyloxy-zinc-porphyrin, (conc. 19 µM, 298 K, $CHCl_3$). The data at 644 and 619 nm were fitted to a 1:1 binding isotherm. ***(b)*** to give a binding constant of K_{Py} = 1.8 ± 0.2 × 10^4 M^{-1}. Arrows indicate areas of increasing and decreasing absorption during the titration.

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