Supporting Information:

Transient EPR reveals triplet state delocalization in a series of cyclic and linear π-conjugated porphyrin oligomers

Claudia E. Tait, Patrik Neuhaus, Martin D. Peeks, Harry L. Anderson, and Christiane R. Timmel

†Department of Chemistry, Centre for Advanced Electron Spin Resonance, University of Oxford, South Parks Road, Oxford OX1 3QR, UK.
‡Department of Chemistry, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford OX1 3TA, UK.

Table of Contents:

Experimental Methods
Sample preparation

Time-resolved EPR

Pulse EPR

Spectral analysis

Computational methods

Additional figures

General chemical synthesis details

Synthetic Procedures and Characterization

References

Experimental Methods

Sample preparation
The zinc porphyrin oligomers (P1 to P6) and the porphyrin ring (c-P6) depicted in Figure 1 of the main text were synthesized as described below. The EPR measurements were performed on 50–200 μM solutions in MeTHF: pyridine 10:1. The measurements on the oligomers bound to the template were performed in toluene, since coordinating solvents interfere with the binding of the template. The solutions were degassed by several freeze-pump-thaw cycles and frozen in liquid N2.

Time-resolved EPR
The time-resolved EPR experiments were performed at X-band on a Bruker Elexsys 680 spectrometer equipped with a helium gas-flow cryostat from Oxford Instruments. Laser excitation at 532 nm was provided by the second harmonic of an Nd:YAG laser (Surelite Continuum) with a repetition rate of 10 Hz. Light depolarized with an achromatic depolarizer was used unless otherwise stated. TR-EPR experiments were performed by direct detection with the transient recorder without lock-in amplification; the microwave power was 0.2 mW. The laser background signal was removed by 2D baseline-correction determined based on the off-resonance transients. The spectra were integrated over the first 2 μs after the laser flash. Experiments were typically performed at 20 K, but no changes in the spectra were observed at temperatures between about 100 and 5 K.

Experiments with different excitation wavelengths were performed with an Optotek Opolette Optoparametric Oscillator (OPO) tunable laser (20 Hz repetition rate) at wavelengths corresponding to the region of the Q-bands in the UV-Vis spectra (see Figure S1). For the magnetophotoselection measurements the light was polarized with a Glan-Thompson polarizer.

Pulse EPR
X-band pulse EPR measurements were performed on a Bruker Elexsys 680 spectrometer with a Bruker EN 4118X-MD4 resonator. The measurements were performed at 20 K and with laser excitation as previously described.

The repetition rate of the pulse experiments was determined by the laser repetition rate of 10 Hz (20 Hz for measurements with the OPO). Radical signals were removed with the use of a saturating microwave pulse preceding the laser flash.

1H Mims ENDOR spectra were recorded with the pulse sequence \( \frac{\pi}{2} - \tau - \frac{\pi}{2} - T - \frac{\pi}{2} - \tau - \text{echo} \) with mw pulse lengths of \( t_{\pi/2} = 24 \text{ ns} \), \( T = 120, 160, 200 \text{ ns} \) and a radiofrequency pulse length of 15 μs; the RF power was adjusted based on a nutation experiment. The ENDOR spectra were recorded at the canonical field positions of the triplet state EPR spectrum; spectra were recorded for three different \( \tau \) values (120, 160 and 200 ns) and summed to prevent distortions by blind spots.

Spectral Analysis
The spin-polarized powder triplet state spectra were simulated using EasySpin’s pepper routine. The zero-
field splitting parameters $D$ and $E$ as well as the relative population probabilities at zero-field were determined by least-square fitting of the experimental transient EPR data. The energy ordering of the triplet sublevels was chosen as $|Z|>|X|>|Y|$.

The relative orientations of the zero-field splitting tensor orientations and the optical transition dipole moments was determined based on the polarization ratio calculated from the magnetophotoselection data. The polarization ratio is defined as:\(^2\)\(^3\)

\[ P_i = \frac{I_{1/2} - I_{1/2}^\perp}{I_{1/2} + I_{1/2}^\perp} \]  

where $I_{1/2}$ and $I_{1/2}^\perp$ are the intensities of the derivative EPR signal for excitation with light polarized parallel or perpendicular to the magnetic field at the field positions corresponding to the $X$, $Y$ or $Z$ orientation of the ZFS tensor. The polarization ratio was calculated by integration of the low and high field canonical regions of the derivative spectra; standard deviations were estimated by considering different regions for the integration (derivative signal maximum ±0.05-0.40 mT).

The values of the proton hyperfine couplings along the principal axes of the ZFS tensor were determined by Gaussian deconvolution of the ENDOR spectra.

**Computational methods**

DFT geometry optimizations of the triplet excited state structures for $P_1$ to $P_6$ and for $P_2\cdot T_6$ to $P_4\cdot T_6$ were performed in ORCA \(^4\)\(^5\) with the BP86 functional and the SV(P) basis set using the RI approximation with the auxiliary SV/C basis set. The Si(C\(_6\)H\(_{13}\))\(_3\) groups were replaced by hydrogen atoms and the resulting structures were optimized without symmetry constraints. Calculations of the zero-field splitting interaction were performed according to a procedure published by Sinnecker et al.,\(^6\) using the B3LYP functional and the EPRII basis set and calculating the spin-spin contribution to the ZFS using UNO determinants. Calculations could only be performed for systems with up to four porphyrin units, calculations on the larger systems were computationally not feasible. The results were compared to calculations with the BP86 and BHLYP functional to evaluate the extent of the self-interaction error and no significant difference was found. The spin density distributions for the linear oligomers are shown in Figure S2.

The hyperfine parameters were calculated with the B3LYP functional and the EPRII basis set, purposely developed for the calculation of EPR hyperfine interaction values, for the C, N and H nuclei\(^7\)\(^-\)\(^9\) and the 6-31G(d) basis set for Zn.

The DFT calculations for $P_3$ predict an uneven spin density distribution with increased spin density on the central porphyrin unit. The predicted ratio of spin densities on the three porphyrin units depends on the amount of exact Hartree-Fock exchange included in the DFT functional. A calculation with the GGA (generalized gradient approximation) functional BP86 predicts a spin density distribution of 0.26:0.48:0.26 over the three porphyrin units, while the hybrid functional B3LYP, containing 20% of exact exchange and 80% of DFT exchange, predicts a distribution of 0.19:0.62:0.19. Variation of the contribution of exact exchange in the B3LYP functional in the range from 10% to 40% leads to variations of the relative spin density on the central porphyrin unit from 0.54 to 0.74. The best agreement of calculated and experimental hyperfine couplings is obtained for 20% exact exchange, corresponding to the standard B3LYP functional. This amount of exact exchange almost corresponds to the optimal mixing ratio of exact and DFT exchange believed to yield results close to chemical accuracy (25%).\(^10\)

DFT also predicts uneven spin density distributions for $P_4$, $P_5$ and $P_6$, with the spin density mainly localized on the two central porphyrin units for even $N$ and on the central porphyrin unit for odd $N$. The ratios of spin densities resulting from B3LYP/EPRII calculations (20% exact exchange) correspond to 0.10 : 0.40 : 0.40 : 0.10 for $P_4$, 0.04 : 0.19 : 0.54 : 0.19 : 0.04 for $P_5$ and 0.02 : 0.38 : 0.38 : 0.10 : 0.02 for $P_6$. The BP86 functional again predicts different spin density distributions, which are slightly more spread out over the porphyrin array due to the self-interaction error affecting DFT calculations with functionals only containing DFT exchange.\(^1\)\(^1\)

The changes in ZFS parameters for different geometries of the linear oligomers were investigated by considering the SOMOs. The quasi-restricted molecular orbitals from single-point calculations performed at B3LYP/EPRII level for the porphyrin monomer, dimer, trimer and tetramer are shown in Figure S3. The corresponding orbitals of the templated oligomers are shown in Figure S4. The SOMOs localized using the Pipek-Mezey scheme\(^1\)\(^2\) are also shown and were used to separate the Coulomb and exchange contribution to the $D$-value.
Figure S2. Spin density distributions in the first excited triplet state calculated at B3LYP/EPRII level for the optimized geometries of P1 to P6.

Figure S3. Plots of the frontier quasi-restricted molecular orbitals and of the localized SOMOs calculated with B3LYP/EPRII for P1, P2, P3 and P4. The populations of the SOMOs on the different porphyrin units are indicated as percentages. The arrows indicate the electrons occupying each orbital. The small differences in population distributions in the two SOMOs for each molecule arise from deviations of the optimized geometry from symmetry, identical populations are obtained from calculations on symmetrized geometries.
Figure S4. Plots of the frontier quasi-restricted molecular orbitals and of the localized SOMOs calculated with B3LYP/ERPII for P2·T6, P3·T6 and P4·T6. The populations of the SOMOs on the different porphyrin units are indicated as percentages. The arrows indicate the electrons occupying each orbital.

Figure S5. Comparison of the transient and echo-detected EPR spectra of c-P6·T6. The central part of the field sweep was removed due to the presence of a residual radical signal not completely removed by the pre-saturation pulse. The canonical field positions identified from the field sweep are indicated by arrows.
General chemical synthesis details

Unless stated otherwise, all reagents were obtained from commercial sources and used as received without further purification. Diethyl ether, chloroform and toluene were dried by passing through activated alumina columns using a positive pressure of dry N$_2$. Diisopropylamine (DIPA) was dried by distillation from CaH$_2$. All uses of petroleum ether refer to the 40–60 °C fraction. Analytical gel permeation chromatography (GPC) was performed on a JAIGEL H-P precolumn, a JAIGEL 3H-A (8 mm x 500 mm) and a JAIGEL 4H-A column (8 mm x 500 mm) in series with toluene/pyridine 100/1 as eluent. Preparative gel permeation chromatography (GPC) was performed using a line of PLGel 600 mm 10 μm 500 Å, 300 mm 10 μm 500 Å, and 300 mm 10 μm 1000 Å columns (all with 25 mm ID) (Polymer Laboratories Ltd) at a flow rate of 8.5 mL min$^{-1}$. Preparative recycling GPC was performed on a JAIGEL H-P precolumn, a JAIGEL 3H (20 mm x 600 mm) and a JAIGEL 4H column (20 mm x 600 mm) in series with toluene/pyridine 100/1 as eluent. Flash column chromatography was performed on Merck silica gel 60 (40–63 μm). Alumina columns were performed using aluminum oxide, activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å from Sigma Aldrich. For TLC, Merck silica gel 60 F$_{254}$ aluminum-backed sheets were used. Size exclusion chromatography (SEC) was carried out using Bio-Beads SX-1, 200–400 mesh (Bio Rad).

Hexakis-(4-[4-phenylpyridine]benzene$^{13}$ (T6), [5,15-bis(3,5-trihexylsilyl)phenyl]-10,20-dibromoporphyrinato] zinc(II)$^{14}$ (I) and trihexylsilylacetylene$^{15}$ were synthesized according to literature procedures.

NMR spectra were recorded on a Bruker AVIII400 or Bruker AVIII400 (400 MHz) spectrometer. The residual solvent peak was used as internal reference (chloroform, $^1$H δ = 7.26 ppm, $^{13}$C δ = 77.2 ppm). Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constant(s) were reported whenever possible. MALDI-TOF-MS spectra were measured using a Waters MALDI Micro MX or at the EPSRC National Mass Spectrometry service (Swansea, Wales, UK) using the Applied Biosystems Voyager DE-STR. UV-vis absorption spectra were recorded at ambient temperature with a Perkin-Elmer Lambda 20 using quartz 1 cm cuvettes. Absorptions appearing as shoulders are annotated “sh”.

Schemes S1–S3 describe the synthetic strategies for the preparation of porphyrin oligomers (Scheme S1), preparation of cyclic oligomers (Scheme S2) and preparation of free-base linear oligomers (Scheme S3).
Scheme S1. Preparation of linear porphyrin oligomers P1–P6.

Reagents and conditions: (i) trihexylsilylacetylene, Pd(dba)$_3$, CuI, PPh$_3$, toluene, DIPA, 50 °C, 2 h, 92%; (ii) TBAF, CHCl$_3$, CH$_2$Cl$_2$, pyridine, 20 °C; (iii) PdCl$_2$(PPh$_3$)$_2$, CuI, 1,4-benzoquinone, toluene, DIPA, 20 °C, 16 h; (iv) TBAF, CHCl$_3$, pyridine, 20 °C; (v) PdCl$_2$(PPh$_3$)$_2$, CuI, 1,4-benzoquinone, toluene, DIPA, 20 °C, 2 h; (vi) PdCl$_2$(PPh$_3$)$_2$, CuI, 1,4-benzoquinone, toluene, DIPA, 40 °C, 1.5 h.
**Scheme S2.** Preparation of porphyrin nanoring c-P6-T6 and its derivatives.

**Reagents and conditions:**
(i) hexapyridyl template T6,\(^{13}\) Pd(PPh)_3Cl_2, CuI, 1,4-benzoquinone, CHCl_3, DIPA, 20 °C, 16 h, 36%; (ii) TFA, CH_2Cl_2, 20 °C, 5 min, quant.; (iii) Zn(OAc)_2·2H_2O, CHCl_3, MeOH, 20 °C, 6 h, quant.

**Scheme S3.** Demetallation of linear porphyrin oligomers.

**Reagents and conditions:** (i) TFA, CH_2Cl_2, 20 °C.
Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin (P1)

[Zinc 5,15-bis(3,5-(trihexylsilyl)phenyl)-10,20-dibromoporphyrinato]zinc(II)\(^{14}\) 1 (1.42 g, 0.78 mmol), copper(I) iodide (30 mg, 156 μmol) and triphenylphosphine (41 mg, 156 μmol) were dissolved in a mixture of toluene (35 mL) and DIPA (35 mL) and the solution was degassed by several freeze-pump-thaw cycles. Trihexylsilylacetylene\(^{15}\) (0.91 mL, 2.3 mmol) was added by syringe and the mixture was stirred at 50 °C for 2 h. TLC indicated full conversion. The reaction mixture was filtered over a plug of silica eluting with PE/DCM 4:1. Purification by column chromatography on silica gel (gradient of petroleum ether/CH\(_2\)Cl\(_2\) 100:0 to 100:6) yielded P1 (1.64 g, 92%) as a green oil. 1H NMR (400 MHz, CDCl\(_3\)): δ = 9.74 (d, \(^3J = 4.7\) Hz, 4H; ArH\(_\beta\)), 8.90 (d, \(^3J = 4.7\) Hz, 4H; ArH\(_\beta\)), 8.25 (m, 4H; ArH ortho), 8.00 (m, 2H; ArH para), 1.82–1.69 (m, 12H; CH\(_2\)), 1.59–1.44 (m, 36H; CH\(_2\)), 1.44–1.25 (m, 96H; CH\(_2\)), 1.06–0.98 (m, 12H; CH\(_2\)), 0.98–0.91 (m, 24H; CH\(_2\)), 0.91–0.83 (m, 54H; CH\(_3\)); MS (MALDI-TOF) m/z: calcd. M\(^+\) for C\(_{144}\)H\(_{248}\)N\(_4\)Si\(_6\)Zn: 2269.49; found: 2270.6; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\varepsilon\)): 625 (44,000), 578 (18,000), 446 (323,000), 437 (490,000).

Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10-ethynyl-20-trihexylsilanylethynyl-porphyrin (\{Si,H\}-P1) and Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-ethynyl-porphyrin (\{H,H\}-P1)

P1 (863 mg, 0.380 mmol) was dissolved in CH\(_2\)Cl\(_2\) (60 mL), chloroform (30 mL) and pyridine (7 mL). The solution was deoxygenated by bubbling argon through the solution. The solution was cooled in a water-ice bath and TBAF (570 μL, 1.0 M in THF, 0.57 mmol) was added. The mixture was stirred and frequently monitored by TLC (petroleum ether/CH\(_2\)Cl\(_2\) 20/1). As soon as the preferred ratio of deprotection was reached the reaction was quenched with acetic acid (4.2 μL) and the mixture was filtered through a short column of silica gel (CH\(_2\)Cl\(_2\) with 1% pyridine). Separation by column chromatography on silica gel (gradient of petroleum ether to petroleum ether/CH\(_2\)Cl\(_2\) 10/1, always with 1% pyridine) yielded starting material P1 (133 mg, 15.4%), \{Si,H\}-P1 (370 mg, 48%), and \{H,H\}-P1 (232 mg, 35%), each as green waxy solids.

\{Si,H\}-P1: 1H NMR (400 MHz, CDCl\(_3\)): δ = 9.73 (m, 4H; ArH\(_\beta\)), 8.93 (m, 4H; ArH\(_\beta\)), 8.26 (m, 4H; ArH ortho), 4.18 (s, 1H; CH), 1.76 (m, 6H; CH\(_3\)), 1.59–1.43 (m, 30H; CH\(_3\)), 1.43–1.22 (m, 84H; CH\(_3\)), 1.06–0.98 (m, 6H; CH\(_3\)), 0.98–0.90 (m, 24H; CH\(_3\)), 0.90–0.84 (m, 45H; CH\(_3\)); MS (MALDI-TOF) m/z: calcd. M\(^+\) for C\(_{126}\)H\(_{210}\)N\(_4\)Si\(_5\)Zn: 1986.9; found: 1989.0.

\{H,H\}-P1: 1H NMR (400 MHz, CDCl\(_3\)): δ = 9.75 (d, \(^3J = 4.8\) Hz, 4H), 8.96 (d, \(^3J = 4.8\) Hz, 4H), 8.27 (s, 4H), 8.01 (s, 2H), 4.19 (s, 2H), 0.86–1.50 (m, 156H); 13C NMR (100 MHz, CDCl\(_3\)): δ = 152.3, 150.7, 140.6, 140.2, 139.2, 135.1, 131.2, 123.9, 100.1, 85.9, 83.9, 33.6, 31.7, 24.1, 22.7, 14.2, 12.7, 0.30; MS (MALDI-TOF) m/z: calcd. M\(^+\) for C\(_{108}\)H\(_{172}\)N\(_4\)Si\(_4\)Zn: 1704.31; found: 1703.02; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\varepsilon\)): 430 (5.53), 438 (5.47), 578 (4.23), 612 (4.26).

Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin dimer (P2)

\{Si,H\}-P1 (20 mg, 9.9 μmol) was dissolved in dry toluene (1 mL). PdCl\(_2\)(PPh\(_3\))\(_2\) (0.4 mg, 0.5 μmol), copper(I) iodide (1.0 mg, 5 μmol), and 1,4-benzoquinone (2.2 mg, 20 μmol) were dissolved in a mixture of dry toluene (1 mL) and dry DIPA (0.5 mL) and added. The reaction was monitored by TLC. After 45 min, all \{Si,H\}-P1 had reacted. The volume was reduced and the mixture was filtered through a short column of silica gel (CH\(_2\)Cl\(_2\) and 1% pyridine). The mixture was passed through a SEC column (toluene). Recrystallization of the dimer by layer addition (CH\(_2\)Cl\(_2\)/methanol) yielded P2 (17 mg, 87%). 1H NMR (400 MHz, CDCl\(_3\)): δ = 9.94 (d, \(^3J = 4.7\) Hz, 4H; ArH\(_\beta\)), 9.72 (d, \(^3J = 4.7\) Hz, 4H; ArH\(_\beta\)), 9.00 (d, \(^3J = 4.7\) Hz, 4H; ArH\(_\beta\)), 8.92 (d, \(^3J = 4.7\) Hz, 4H; ArH\(_\beta\)), 8.30 (m, 8H; ArH ortho), 8.02 (m, 4H; ArH ortho), 1.83–1.70 (m, 12H; CH\(_2\)), 1.57–1.46 (m, 60H; CH\(_2\)), 1.44–1.23 (m, 168H; CH\(_2\)), 1.08–1.00 (m, 12H; CH\(_2\)), 1.00–0.92 (m, 48H; CH\(_3\)), 0.92–0.85 (m, 90H; CH\(_3\)); MS (MALDI-TOF) m/z: calcd. M\(^+\) for C\(_{252}\)H\(_{418}\)N\(_8\)Si\(_{10}\)Zn\(_2\): 3971.78; found: 3974.4; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\varepsilon\)): 625 (44,000), 578 (18,000), 446 (323,000), 437 (490,000).
Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis(ethynyl-phenyl)-porphyrin dimer ([H,H]-P2)

TBAF (100 μL, 1.0 M in THF, 100 μmol) was added to a solution of [H,H]-P2 (45 mg, 11 μmol) in CH2Cl2 (20 mL) and the mixture was stirred for 1 h at room temperature. The reaction was monitored by TLC. After the deprotection was complete, acetic acid (1 mL) was added and the mixture was passed through a short column of silica gel (CH2Cl2). Removing the solvent yielded [H,H]-P2 (39 mg, 99%) as a green waxy solid. 1H NMR (400 MHz, CDCl3): δ = 9.97 (d, J= 4.7 Hz, 4H; ArHδ), 9.75 (d, J= 4.7 Hz, 4H; ArHδ), 9.04 (d, J= 4.7 Hz, 4H; ArHδ), 8.96 (d, J= 4.7 Hz, 4H; ArHδ), 8.13 (m, 8H; ArHortho), 8.02 (m, 4H; ArHpara), 4.22 (s, 2H, CH), 1.57–1.46 (m, 48H, CH2), 1.44–1.23 (m, 144H, CH2), 1.00–0.92 (m, 48H, CH2), 0.91–0.85 (m, 72H, CH3); MS (MALDI-TOF) m/z: calcd. M+ for C213H334N8Si8Zn2: 3406.61; found: 3406.6.

Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-ethynyl-porphyrin trimer ([H,H]-P3)

TBAF (50 μL, 1.0 M in THF, 50 μmol) was added to a solution of [H,H]-P3 (21 mg, 3.7 μmol) in CH2Cl2 (21 mL) and the mixture was stirred for 1 h at room temperature. The reaction was monitored by TLC. After the deprotection was complete acetic acid (1 mL) was added and the mixture was passed through a short column of silica gel (CH2Cl2). Removing the solvent yielded [H,H]-P3 (17 mg, 89%) as an olive green solid. 1H NMR (400 MHz, CDCl3): δ = 9.99 (d, J= 4.7 Hz, 4H; ArHδ), 9.97 (d, J= 4.7 Hz, 4H; ArHδ), 9.76 (d, J= 4.7 Hz, 4H; ArHδ), 9.06 (d, J= 4.7 Hz, 4H; ArHδ), 8.97 (d, J= 4.7 Hz, 4H; ArHδ), 8.36 (m, 4H; ArHortho), 8.05 (m, 4H; ArHpara); MS (MALDI-TOF) m/z: calcd. M+ for C210H330N8Si8Zn3: 3986.50; found: 3986.5.
Ar$_{ortho}$), 8.32 (m, 8H; Ar$_{ortho}$), 8.05 (m, 2H; Ar$_{para}$), 8.04 (m, 4H; CH$_2$), 1.45–1.24 (m, 12H; CH$_2$), 0.93–0.85 (m, 108H; CH$_3$); MS (MALDI-TOF) m/z: calcd. M$^+$ for C$_{324}$H$_{512}$N$_{12}$Si$_{12}$Zn$_3$: 5108.90; found: 5108.4.

Zinc 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin pentamer (P5)

A solution of PdCl$_2$(PPh$_3$)$_2$ (10 mg, 14 $\mu$mol), copper(I) iodide (28 mg, 147 $\mu$mol) and 1,4-benzoquinone (22 mg, 200 $\mu$mol) in toluene (10 mL) and DIPA (1.5 mL) was added to a stirred mixture of {Si,H}-P1 (65 mg, 33 $\mu$mol) and {H,H}-P3 (15 mg, 3 $\mu$mol) in toluene (10 mL). The mixture was stirred for 2 h at room temperature, then the solvent was removed and the mixture was filtered over a short column of silica gel (CH$_2$Cl$_2$/petroleum ether 1/1). Purification by preparative GPC (toluene/pyridine 10/1) and subsequent recrystallization by layer addition (CH$_2$Cl$_2$/methanol) yielded P2 (37 mg, 28% relative to {Si,H}-P1) and P5 (8 mg, 30% relative to {H,H}-P3).

P5:

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.97 (m, 16H; Ar$_{ortho}$), 9.73 (d, $^3$J = 4.6 Hz, 4H; Ar$_{ortho}$), 9.05 (m, 12H; Ar$_{para}$), 9.02 (d, $^3$J = 4.6 Hz, 4H; Ar$_{ortho}$), 8.92 (d, $^3$J = 4.6 Hz, 4H; Ar$_{para}$), 8.37 (m, 12H; Ar$_{ortho}$), 8.31 (m, 8H; Ar$_{ortho}$), 8.06 (m, 6H; Ar$_{para}$), 8.03 (m, 4H; Ar$_{para}$), 1.83–1.70 (m, 12H; CH$_2$), 1.60–1.46 (m, 12H; CH$_2$), 1.45–1.24 (m, 384H; CH$_2$), 1.07–0.94 (m, 12H; CH$_2$), 0.94–0.85 (m, 198H; CH$_3$); MS (MALDI-TOF) m/z: calcd. M$^+$ for C$_{576}$H$_{928}$N$_{20}$Si$_{22}$Zn$_5$: 9078.67; found: 9083; UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ [nm] ($\epsilon$ [M$^{-1}$ cm$^{-1}$]): 769 (320,000), 581 (499,000), 491 (636,000), 453 (698,000).

Zinc (3,5-bis-trihexylsilanyl-phenyl)-porphyrin[6] nanoring–template complex (c-P6•T6)

{H,H}-P1 (200 mg, 0.120 mmol) and template T6$^{13}$ (29 mg, 29 $\mu$mol) were dissolved in chloroform (133 mL) by sonication for 2 h A solution of Pd(PPh$_3$)$_2$Cl$_2$ (27 mg, 39 $\mu$mol), copper(I) iodide (37 mg, 0.19 mmol) and 1,4-benzoquinone (89 mg, 0.80 mmol) in chloroform (18 mL) and DIPA (0.25 mL) was added to the porphyrin mixture, at room temperature. The mixture was stirred at room temperature overnight, open to air. The reaction mixture was partially concentrated and passed over a plug of alumina (CHCl$_3$). Purification by SEC (toluene) and preparative recycling GPC (toluene + 1% pyridine) afforded c-P6•T6 (78 mg, 36%) as a brown solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.54 (d, $^3$J = 4.4 Hz, 24H; Ar$_{ortho}$), 8.72 (d, $^3$J = 4.4 Hz, 24H; Ar$_{ortho}$), 8.37 (m, 12H; Ar$_{ortho}$), 8.32 (m, 12H; Ar$_{ortho}$), 8.06 (m, 12H; Ar$_{ortho}$), 5.52 (m, 12H; AA’ phenyl), 5.45 (m, 12H; BB’ phenyl), 4.99 (m, 12H; AA’ pyridine), 2.41 (m, 12H; AB’ pyridine).
XX’ pyridine), 1.56–1.41 (m, 144H; CH₂), 1.41–1.17 (m, 432H; CH₂), 1.00–0.75 (m, 360H; CH₂, CH₃); MS (MALDI-TOF) m/z: calcd. M⁺ for C₇₂H₁₀₆₈N₃₀Si₂₄Zn₆: 1121; found: 11207. UV-vis (CH₂Cl₂) λₘₐₓ [nm] (ε [M⁻¹ cm⁻¹]): 850 (404,000), 808 (496,000), 772 (374,000), 612 (39,000), 482 (570,000).

Free base (3,5-bis-trihexylsilanyl-phenyl)-porphyrin[6] nanoring (FB-c-P6)

c-P6·T6 (5.4 mg, 0.48 μmol) was dissolved in CH₂Cl₂ (5 mL) and trifluoroacetic acid (50 μL, 0.65 mmol) was added. The mixture was stirred for 5 min. at room temperature then pyridine (0.5 mL) was added and the mixture was immediately filtered over a short column of silica gel (CH₂Cl₂). Removing the solvent yielded FB-c-P6 (4.8 mg, 100%) as a green solid. ¹H NMR (400 MHz, CDCl₃): δ = 9.56 (d, 3J = 4.7 Hz, 24H; ArH), 8.71 (d, 3J = 4.7 Hz, 24H; ArH), 8.15 (m, 24H; ArHortho), 7.96 (m, 12H; ArHpara), 1.52–1.36 (m, 144H; CH₂), 1.36–1.14 (m, 432H; CH₂), 1.07–0.94 (m, 144H; CH₂), 0.94–0.85 (m, 216H; CH₃), –1.29 (s, 12H; NH); MS (MALDI-TOF) m/z: calcd. M⁺ for C₆₄H₁₇₂N₂₄Si₂₄: 9834; found: 9836; UV-vis (CH₂Cl₂) λₘₐₓ [nm] (ε [M⁻¹ cm⁻¹]): 772 (285,000), 748 (307,000), 593 (42,000), 473 (516,000).

Zinc (3,5-bis-trihexylsilanyl-phenyl)-porphyrin[6] nanoring (c-P6)

FB-c-P6 (4.8 mg, 0.48 μmol) was dissolved in CH₂Cl₂ (10 mL) and a solution of Zn(OAc)₂·2H₂O (50 mg, 228 μmol) in methanol (2 mL) was added. The mixture was stirred over night at room temperature then filtered through a short column of silica gel (CH₂Cl₂). Recrystallization by layer addition (CH₂Cl₂/methanol) yielded c-P6 (4.9 mg, 100%) as a brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 9.67 (d, 3J = 4.6 Hz, 24H; ArH), 8.81 (d, 3J = 4.6 Hz, 24H; ArH), 8.16 (m, 24H; ArHortho), 7.91 (m, 12H; ArHpara), 1.50–1.37 (m, 144H; CH₂), 1.37–1.12 (m, 432H; CH₂), 0.94–0.84 (m, 144H; CH₂), 0.84–0.72 (m, 216H; CH₃); MS (MALDI-TOF) m/z: calcd. M⁺ for C₆₄H₁₇₂N₂₄Si₂₄Zn₆: 10214; found: 10211; UV-vis (CH₂Cl₂) λₘₐₓ [nm] (ε [M⁻¹ cm⁻¹]): 772 (285,000), 748 (307,000), 593 (42,000), 473 (516,000).
General Procedure 1: TFA demetallation of zinc porphyrin oligomers

TFA (100 eq. per Zn, ~0.5 vol% vs. CHCl3) was added to a solution of porphyrin substrate (1 eq.) in CHCl3 (~0.1–0.5 mM). The reaction mixture was monitored by UV-vis spectroscopy, diluting aliquots in CH2Cl2/1% pyridine. Upon completion, the reaction mixture was quenched by addition of pyridine and was immediately passed through a SiO2 plug (CH2Cl2 + 1% pyridine). Purification by flash chromatography on SiO2 (petroleum ether) afforded the free-base oligomer.

Free-base 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin FB-P1

P1 (10 mg, 4.4 μmol) was subject to general procedure 1 to afford FB-P1. 1H NMR (400 MHz, CDCl3): δ = 9.59 (d, 3J = 4.7 Hz, 4H; ArHβ), 8.76 (d, 3J = 4.6 Hz, 4H; ArHβ), 8.22 (s, 4H; ArHortho), 7.99 (s, 2H; ArHpara), 1.78–1.67 (m, 11H), 1.57–1.21 (m, 132H), 1.04–0.80 (m, 92H), –2.11 (s, 2H; NH); MS (MALDI-TOF) m/z: calcd. M+ for C144H250N4Si6: 2206.12; found 2206.64; UV-vis (CH2Cl2) λmax [nm]: 433, 442, 583, 677.

Free-base 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin dimer FB-P2

P2 (8.0 mg, 2.0 μmol) was subject to general procedure 1 to afford FB-P2. 1H NMR (400 MHz, CDCl3): δ = 9.82 (d, 3J = 4.6 Hz, 4H; ArHβ), 9.61 (d, 3J = 4.7 Hz, 4H; ArHβ), 8.88 (d, 3J = 4.7 Hz, 4H; ArHβ), 8.80 (d, 3J = 4.7 Hz, 4H; ArHβ), 8.28 (s, 8H; ArHortho), 8.02 (s, 4H; ArHpara), 1.81–1.69 (m, 12H), 1.58–1.23 (m, 229H), 1.06–0.82 (m, 149H), –1.83 (s, 4H; NH). MS (MALDI-TOF) m/z: calcd. M+ for C252H422N8Si10: 3845.05; found: 3844.56; UV-vis (CH2Cl2) λmax [nm]: 418, 450, 477, 641, 752, 781.

Free-base 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin trimer FB-P3

P3 (3.0 mg, 0.53 μmol) was subject to general procedure 1 to afford FB-P3. 1H NMR (400 MHz, CDCl3): δ = 9.88–9.79 (m, 8H; ArHβ), 9.61 (d, 3J = 4.4 Hz, 4H; ArHβ), 8.95–8.85 (m, 8H; ArHβ), 8.80 (d, 3J = 4.4 Hz, 4H; ArHβ), 8.33 (s, 4H; ArHortho), 8.28 (s, 8H; ArHortho), 8.04 (s, 2H; ArHpara), 8.02 (s, 4H; ArHpara), 1.82–0.97 (m, 546H), –1.56 (s, 2H; NH), –1.82 (s, 4H; NH). MS (MALDI-TOF) m/z: calcd. M+ for C360H594N12Si14: 5483.99; found: 5482.42; UV-vis (CH2Cl2) λmax [nm]: 428 (sh), 450, 486 (sh), 641, 752, 781 (sh).

Free-base 5,15-bis(3,5-bis-trihexylsilanyl-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin tetramer FB-P4

P4 (3.0 mg, 0.54 μmol) was subject to general procedure 1 to afford FB-P4. 1H NMR (400 MHz, CDCl3): δ = 9.85 (m, 12H; ArHβ), 9.62 (d, 3J = 4.6 Hz, 4H; ArHβ), 8.99–8.87 (m, 12H; ArHβ), 8.81 (d, 3J = 4.2 Hz, 4H; ArHβ), 8.35 (s, 8H; ArHortho), 8.30 (s, 8H; ArHortho), 8.05 (s, 4H; ArHpara), 8.02 (s, 4H; ArHpara), 1.82–0.76 (m, 702H; CH3/CH2), –1.53 (s, 4H; NH), –1.80 (s, 4H; NH). MS (MALDI-TOF) m/z: calcd. M+ for C468H766N16Si18: 7122.92; found: 7124.11; UV-vis (CH2Cl2) λmax [nm]: 450, 477, 642, 770.
References
1. Stoll, S.; Schweiger, A. J. Magn. Reson. 2006, 178, 42-55.
2. Siegel, S.; Judeikis, H. S. J. Phys. Chem. 1966, 70, 2205-2211.
3. Thurnauer, M. C.; Norris, J. R. Biochem. Biophys. Res. Commun. 1976, 73, 501-506.
4. Neese, F. ORCA - an ab initio, Density Functional and Semiempirical program package, 2.9/3.0; 2011.
5. Neese, F. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 73-78.
6. Sinnecker, S.; Neese, F. J. Phys. Chem. A 2006, 110, 12267-12275.
7. Barone, V., In Recent Advances in Density Functional Methods, Part I, Chong, D. P., Ed. World Scientific Publ. Co.: Singapore, 1996.
8. Barone, V. J. Chem. Phys. 1994, 101, 6834-6838.
9. Barone, V. J. Chem. Phys. 1994, 101, 10666-10676.
10. Ernzerhof, M., Hybrid Methods: Combining Density Functional and Wavefunction Theory. In Density Functionals: Theory and Applications, Joubert, D., Ed. Springer: 1998; pp 60-90.
11. Polo, V.; Kraka, E.; Cremer, D. Mol. Phys. 2002, 100, 1771-1790.
12. Pipek, J.; Mezey, P. J. Chem. Phys. 1989, 90, 4916-4926.
13. Hoffmann, M.; Kärnbratt, J.; Chang, M.-H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. Angew. Chem. Int. Ed. 2008, 47, 4993-6.
14. Grozema, F. C.; Houarner-Rassin, C.; Prins, P.; Siebbeles, L. D. A.; Anderson, H. L. J. Am. Chem. Soc. 2007, 129, 13370-13371.
15. Lehnherr, D.; Gao, J.; Hegmann, F. A.; Tykwinski, R. R. Org. Lett. 2008, 10, 4779-4782.