Supporting Information for: Breaking the Symmetry in Molecular Nanorings

Juliane Q. Gong,† Ludovic Favereau,§ Harry L. Anderson,§ and Laura M. Herz*†*

Department of Physics, University of Oxford, Clarendon Laboratory,
Parks Road, Oxford, OX1 3PU, United Kingdom
Department of Chemistry, University of Oxford, Chemistry Research Laboratory,
Oxford OX1 3TA, United Kingdom

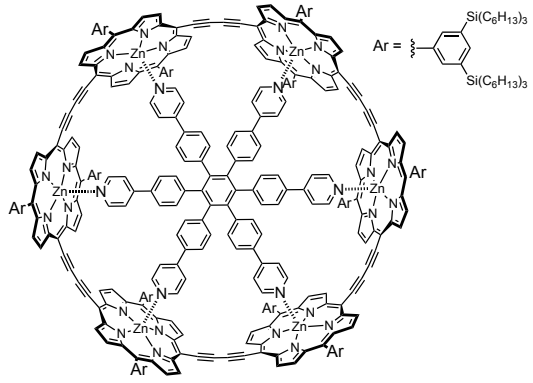
E-mail: juliane.gong@physics.ox.ac.uk; laura.herz@physics.ox.ac.uk

* To whom correspondence should be addressed
† Oxford Physics
§ Oxford Chemistry

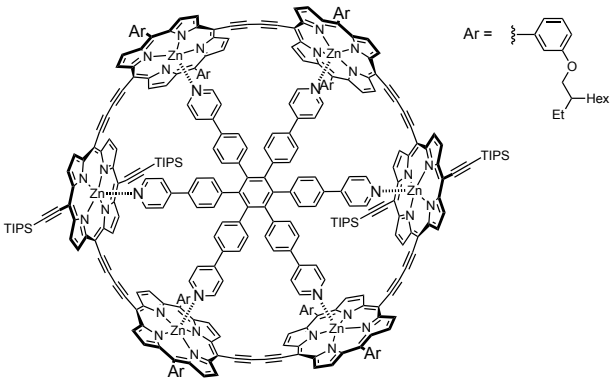
Synthesis and Characterization of Porphyrin Nanorings

All reagents were purchased from commercial sources and solvents were used as supplied unless otherwise noted. Dry solvents ($CHCl_3$, CH_2Cl_2 and toluene) were obtained by passing through alumina under N_2. Diisopropylamine (DIPA) was dried over calcium hydride, distilled and stored under N_2 over molecular sieves. NMR data were recorded at 500 MHz using a Bruker AVII500 (with cryoprobe) or DRX500, or at 400 MHz using a Bruker AVII400 or AVIII400 at 298 K. Chemical shifts are quoted as parts per million (ppm) relative to residual $CHCl_3$ (δ_H 7.27 ppm for ^1H NMR and at δ_C 77.2 ppm for ^{13}C NMR) and coupling constants (*J*) are reported in Hertz. MALDI-ToF spectra were measured at the EPSRC National Mass Spectrometry service (Swansea) using the Applied Biosystems Voyager DE-STR or at the University of Oxford using Waters MALDI Micro MX spectrometer. Size exclusion chromatography (SEC) was carried out using Bio-Beads S-X1, 200–400 mesh (Bio Rad). Analytical and semi-preparative GPC were carried out on Shimadzu Recycling GPC system equipped with LC-20 AD pump, SPD-M20A UV detector and a set of JAIGEL 3H (20 × 600 mm) and JAIGEL 4H (20 × 600 mm) columns in toluene/1% pyridine as eluent with a flow rate of 3.5 mL/min.

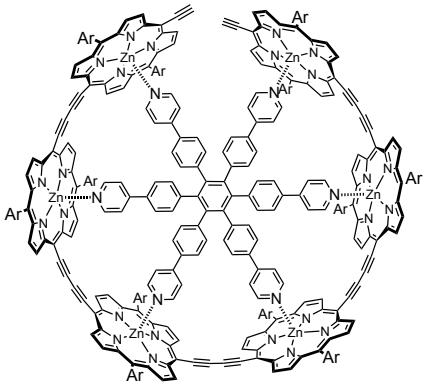
Scheme S1 shows detailed structures of the porphyrin oligomers used in this study. Cyclic porphyrin hexamer template complex ***c*-P6·T6**, spiro-fused nanorings ***s*-P11·(T6)$_2$** and ***s*$_{Et}$-P11·(T6)$_2$**, monomer ***x*-P1** and template **T6** were synthesized and characterized according to reported procedures.[1-4] The linear porphyrin hexamer template complex, ***l*-P6·T6**, was prepared from the protected linear porphyrin hexamer, ***l*-P6$_{TIPS}$**, also reported in reference S1. The cyclic porphyrin hexamer template complex with two opposite tetra(alkyne)-porphyrins, ***c*-P6$_X$·T6**, was synthesized from the corresponding porphyrin trimer, ***l*-P3x**, and template **T6** as described in Scheme S2.



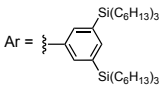
***c*-P6·T6**

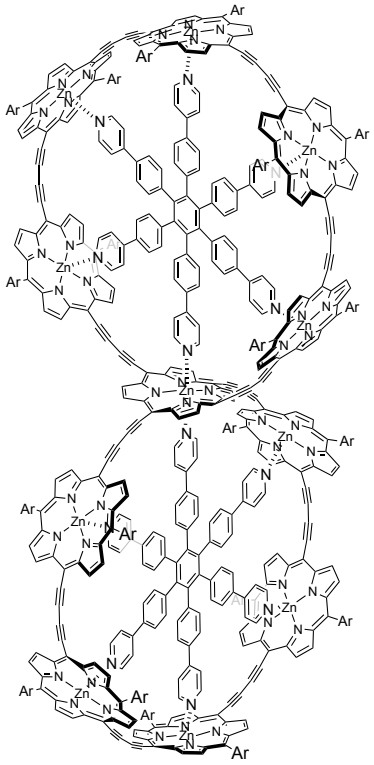


***c*-P6$_x$·T6**

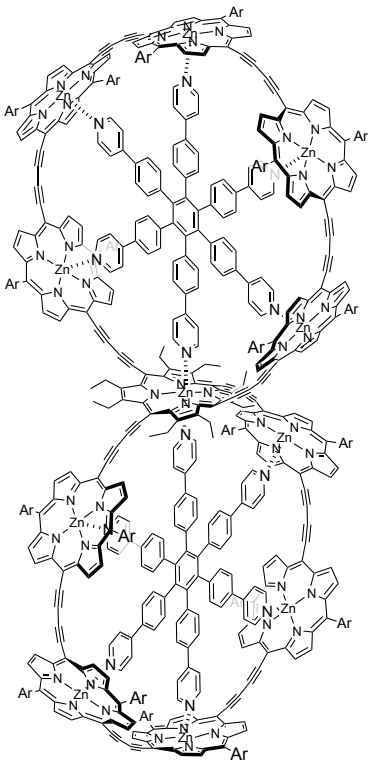


***l*-P6·T6**





***s*-P11·(T6)$_2$**



***s*$_{Et}$-P11·(T6)$_2$**

Scheme S1: Detailed chemical structures of the porphyrin oligomers used in this study. The sidechain [trihexylsilyl, $Si(C_6H_{13})_3$ or 3-((2-ethylhexyl)alkoxy)] has no significant effect on the absorption or photoluminescence spectra of the compounds, but it influences the solubility, aggregation behavior and ease of purification. TIPS = triisopropyl silyl.

Porphyrin Monomer P1

Dipyrromethane (3.00 g, 20.5 mmol) and 3-((2-ethylhexyl)oxy)benzaldehyde (4.81 g, 20.5 mmol) were dissolved in oxygen-free CH_2Cl_2 (2.5 L) in the dark. TFA (0.90 mL, 28.7 mmol) was added and the reaction was stirred in the dark for 3 h. Then, DDQ (6.81 g, 30.0 mmol) was added and the mixture stirred for 20 mins before Et_3N (7.5 mL, 54 mmol) was added. The volume was reduced and the mixture passed through a short silica gel column (CH_2Cl_2) to partially remove the side products. The product was carried forward to the next step without further purification.

$Zn(OAc)_2{\cdot}2H_2O$ (4.7 g, 22 mmol) was dissolved in MeOH (30 mL) and added to a solution of free-base 5,15-bis-(3-((2-ethylhexyl)oxy)-phenyl)-porphyrin (3.1 g, 4.3 mmol) in $CHCl_3$ (150 mL). The reaction mixture was stirred at room temperature for 1 h. The volume was reduced and the mixture passed through a short silica gel column (CH_2Cl_2) to remove the excess of $Zn(OAc)_2$. The product was finally recrystallised by layer addition of MeOH in a CH_2Cl_2 solution of zinc porphyrin monomer to give an oily red solid (3.4 g, 43 % over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H (ppm) 10.30 (s, 2H), 9.43 (d, J = 4.4 Hz, 4H), 9.20 (d, J = 4.4 Hz, 4H), 7.87–7.80 (m, 4H), 7.68 (t, J = 7.9 Hz, 2H), 7.37 (dd, J^3 = 7.9 Hz and J^5 = 1.7 Hz, 2H), 4.07 (d, J = 5.3 Hz, 4H), 1.92–1.80 (m, 2H), 1.67–1.44 (m, 8H), 1.42–1.29 (m, 8H), 0.99 (t, J = 7.4 Hz, 6H), 0.91 (t, J = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ_C (ppm) 157.0, 150.1, 149.6, 143.9, 132.7, 131.8, 127.7, 127.5, 121.4, 120.1, 114.1, 106.3, 71.0, 39.7, 30.8, 29.3, 24.1, 23.2, 14.3, 11.3.

MALDI-TOF: m/z = 779.9 ($C_{48}H_{52}N_4O_2Zn$, M^+ requires 780.3).

Dibromo zinc porphyrin monomer

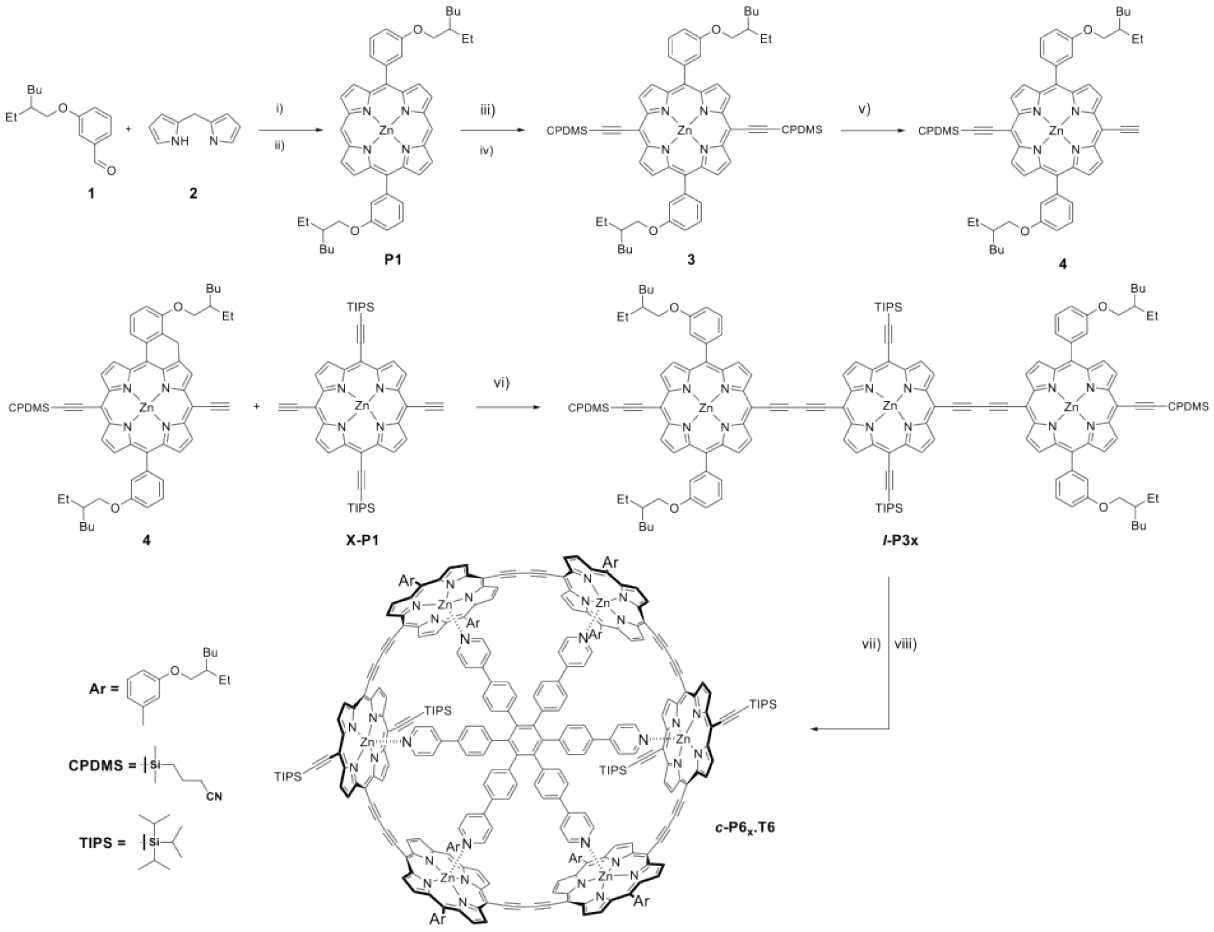
A solution of *N*-bromosuccinimide (1.52 g, 8.56 mmol) in $CHCl_3$ (50 mL) was added dropwise to a solution of zinc 5,15-bis-((2-ethylhexyl)oxy-phenyl)-porphyrin, **P1** (3.35 g, 4.28 mmol) in $CHCl_3$ (150 mL) and pyridine (3 mL) in the dark. The reaction was stirred for 5 min and then quenched with acetone (5 mL). The product was precipitated ($CHCl_3$ / MeOH) to give a purple powder (4.01 g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$ +1% pyridine-d^5, 298 K): δ_H (ppm) 9.66 (d, J = 4.7 Hz, 4H), 8.94 (d, J = 4.7 Hz, 4H), 7.75–7.69 (m, 4H), 7.62 (t, J = 8.0 Hz, 2H), 7.33 (dd, J^3 = 7.8 Hz and

J^5 = 1.7 Hz, 2H), 4.06 (d, J = 5.8 Hz, 4H), 1.90–1.79 (m, 2H), 1.66–1.44 (m, 8H), 1.44–1.29 (m, 8H), 0.99 (t, J = 7.4 Hz, 6H), 0.92 (t, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ_C (ppm) 157.7, 150.8, 150.2, 144.0, 143.7, 136.1, 133.4, 132.9, 127.3, 122.7, 121.9, 121.5, 113.9, 104.9, 71.0, 39.7, 30.7, 29.3, 24.1, 23.2, 14.3, 11.4.

MALDI-TOF: m/z = 940.4 ($C_{48}H_{50}Br_2N_4O_2Zn$, M^+ requires 938.2).



Scheme S2. Syntheses of linear trimer ***l*-P3$_X$** and cyclic porphyrin hexamer template complex ***c*-P6$_X$•T6**. Conditions and reagents: i) TFA, DDQ, CH_2Cl_2, r.t. 43%; ii) $Zn(OAc)_2$, $CHCl_3$, MeOH, r.t., 99%; iii) NBS, $CHCl_3$, pyridine, r.t., 99%; iv) CPDMSacetylene, $Pd_2(dba)_3$, CuI, PPh_3, toluene, DIPA, 50 °C, 95%; v) TBAF, $CHCl_3$, r.t., 40%; vi) $Pd(PPh_3)_2Cl_2$, CuI, toluene, DIPA, r.t., 27%; vii) TBAF, CH_2Cl_2, r.t., 99%; viii) **T6**, $Pd(PPh_3)_2Cl_2$, CuI, $CHCl_3$, DIPA, r.t., 70%. TIPS = triisopropysilyl, CPDIPS = cyanopropyldiisopropylsilyl, Ar = 3-((2-ethylhexyl)oxy)phenyl.

Zinc porphyrin monomer 3

Zinc 5,15-bis-((2-ethylhexyl)oxy-phenyl)-10,20-dibromo-porphyrin (2.00 g, 2.13 mmol), tris-(dibenzylideneacetone)-di-palladium(0) [$Pd_2(dba)_3$] (195 mg, 0.213 mmol), PPh_3 (168 mg, 0.640

mmol) and CuI (122 mg, 0.64 mmol, 30 mol%) were placed in a pre-dried Schlenk tube before dry toluene (70 mL) and DIPA (70 mL) were added. The mixture was degassed by freeze-pump-thaw and 4-(ethynyldimethylsilyl)butanenitrile (0.966 g, 6.38 mmol) was added. Then, the reaction was stirred at 50 °C for 2 h. The volume was reduced and the mixture passed through a short silica gel column (5:5:0.1 / 40–60 petrol ether: CH_2Cl_2: pyridine) to give a dark green solid (2.1 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$+1% pyridine-d_5, 298 K): δ_H (ppm) 9.65 (d, J = 4.6 Hz, 4H), 8.99 (d, J = 4.6 Hz, 4H), 7.77 (d, J = 7.7 Hz, 2H), 7.75 (s, 2H), 7.65 (t, J = 7.7 Hz, 2H), 7.33 (dd, J^3 = 8.1 Hz and J^5 = 1.8 Hz, 2H), 4.05 (d, J = 5.8 Hz, 4H), 2.25 (t, J = 6.8 Hz, 4H), 2.20-2.08 (m, 4H), 1.91–1.79 (m, 2H), 1.67–1.44 (m, 8H), 1.44–1.31 (m, 8H), 1.21–1.13 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H), 0.94 (t, J = 6.9 Hz, 6H), 0.63 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ_C (ppm) 157.8, 152.3, 150.4, 143.6, 143.2, 133.0, 131.0, 127.6, 127.5, 122.8, 122.5, 121.4, 119.8, 114.1, 109.4, 100.6, 99.4, 71.0, 39.7, 30.7, 29.3, 24.1, 23.2, 21.1, 20.8, 16.3, 14.2, 11.3, –1.3.

MALDI-TOF: m/z = 1079.3 ($C_{64}H_{74}N_6O_2Si_2Zn$, M^+ requires 1078.5).

Monoprotected zinc porphyrin monomer 4

Fully protected porphyrin monomer **3** (800 mg, 0.74 mmol) was dissolved in $CHCl_3$ (80 mL) and pyridine (1 mL) was added. Tetra-*n*-butylammonium fluoride (0.1 mL, 1.0 M solution in THF, 0.15 mmol) was added to the stirred solution. The progress of the reaction was monitored by TLC until an optimal product mixture was reached between the fully protected and the mono-deprotected porphyrin monomer. The reaction was then quenched with CH_3CO_2H (0.1 mL, 1.7 mmol) and passed immediately through a short plug of silica gel (CH_2Cl_2) to give the titled compound in 40% yield as a dark green solid (308 mg, 0.322 mmol). This compound was directly used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H (ppm) 9.68 (d, J = 4.6 Hz, 2H), 9.63 (d, J = 4.6 Hz, 2H), 8.97 (d, J = 4.6 Hz, 4H), 7.77–7.71 (m, 4H), 7.63 (t, J = 8.1 Hz, 2H), 7.34 (dd, J^3 = 7.9 Hz and J^5 = 1.7 Hz, 2H), 4.17 (s, 1H), 4.04 (d, J = 5.8 Hz, 4H), 2.59 (t, J = 6.9 Hz, 2H), 2.22–2.11 (m, 2H), 1.90–1.79 (m, 2H), 1.65–1.43 (m, 8H), 1.43–1.25 (m, 8H), 1.22–1.15 (m, 2H), 0.99 (t, J = 7.5 Hz, 6H), 0.91 (t, J = 7.2 Hz, 6H), 0.62 (s, 6H).

Porphyrin trimer *l*-P3$_x$

Mono-deprotected porphyrin monomer **4** (257 mg, 0.268 mmol) and porphyrin monomer ***x*-P1** (35 mg, 0.045 mmol) were dissolved in toluene (10 mL). Then a catalyst solution of $Pd(PPh_3)_2Cl_2$ (3.1 mg, 4.5 μmol), CuI (4.3 mg, 0.025 mmol) and 1,4-benzoquinone (9.7 mg, 0.090 mmol) in a mixture of toluene (5 mL) and distilled DIPA (5 mL) was added and the reaction mixture was stirred at room temperature for 1 h. The solution was passed through a short silica plug (100:1 CH_2Cl_2:pyridine). The crude mixture was purified by column chromatography (3:7 / 40–60 petrol ether: CH_2Cl_2 with 1% of pyridine), size-exclusion chromatography (BioBeads SX-1, toluene+1% pyridine) and finally precipitated (CH_2Cl_2/MeOH) to yield ***l*-P3$_X$** (33 mg, 27%) as a dark red solid.

^{1}H NMR (500 MHz, $CDCl_3$+1% pyridine-d_5, 298 K): δ_H (ppm) 9.95 (bd, J = 4.5 Hz, 4H), 9.78 (d, J = 4.4 Hz, 4H), 9.64 (d, J = 4.5 Hz, 4H), 9.09 (d, J = 4.5 Hz, 4H), 8.98 (d, J = 4.5 Hz, 4H), 7.86–7.79 (m, 8H), 7.69 (t, J = 8.2 Hz, 4H), 7.38 (dd, J^3 = 7.7 Hz and J^5 = 1.6 Hz, 4H), 4.12 (d, J = 5.5 Hz, 8H), 2.61 (t, J = 6.9 Hz, 4H), 2.24–2.15 (m, 4H), 1.95–1.83 (m, 4H), 1.70–1.48 (m, 58H), 1.48–1.34 (m, 16H), 1.25–1.19 (m, 4H), 1.03 (t, J = 7.5 Hz, 12H), 0.95 (t, J = 7.0 Hz, 12H), 0.65 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ_C (ppm) 157.9, 153.2, 153.1, 152.5, 152.3, 150.6, 150.2, 143.8, 136.3, 133.3, 133.0, 132.3, 131.8, 131.0, 129.2, 128.4, 127.5, 125.4, 121.5, 119.9, 114.0, 109.8, 109.2, 103.9, 102.0, 100.9, 99.7, 99.3, 99.2, 88.9, 87.7, 83.0, 82.3, 71.0, 39.7, 30.8, 29.3, 24.1, 23.2, 21.2, 20.9, 19.3, 16.4, 14.3, 12.1, 11.4, –1.2.

MALDI-TOF: m/z = 2681 ($C_{162}H_{174}N_{14}O_4Si_4Zn_3$, M^+ requires 2686).

λ_{max} ($CHCl_3$) / nm (log e): 435 (5.46), 454 (5.39), 510 (5.34), 633 (4.74), 747 (5.11).

c-P6$_X$·T6

Trimer ***l*-P3$_X$** (33 mg, 0.012 mmol) was dissolved in a mixture of THF (7.5 mL) and MeOH (3.5 mL), and K_2CO_3 (12 mg, 0.086 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. The crude mixture was passed through a short silica plug ($CHCl_3$) to give the fully deprotected trimer which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$+1% pyridine-d_5, 298 K): δ_H (ppm) 9.93 (d, J = 4.6 Hz, 4H), 9.89 (d, J = 4.4 Hz, 4H), 9.76 (d, J = 4.4 Hz, 4H), 9.68 (d, J = 4.6 Hz, 4H), 9.06 (d, J = 4.6 Hz, 4H), 8.96 (d, J = 4.6 Hz, 4H), 7.84–7.76 (m, 8H), 7.67 (t, J = 8.3 Hz, 4H), 7.37 (dd, J^3 = 7.5 Hz and

J^5 = 1.8 Hz, 4H), 4.19 (s, 2H), 4.11 (d, J = 5.7 Hz, 8H), 1.93–1.82 (m, 4H), 1.70–1.46 (m, 58H), 1.48–1.31 (m, 16H), 1.01 (t, J = 7.6 Hz, 12H), 0.93 (t, J = 6.9 Hz, 12H).

Fully deprotected trimer ***l*-P3$_{Xa}$** (30 mg, 12 μmol) and porphyrin monomer ***x*-P1** were dissolved in $CHCl_3$ (10 mL) and DIPA (0.2 mL). Then, hexadentate template **T6** (6.1 mg, 6.2 μmol) was added and the resulting mixture was sonicated for 0.5 h. A catalyst solution was prepared by dissolving $Pd(PPh_3)_2Cl_2$ (2.6 mg, 3.7 μmol), CuI (7 mg, 37 μmol) and 1,4-benzoquinone (5.3 mg, 49 μmol) in dry $CHCl_3$ (8 mL) and freshly distilled DIPA (0.2 mL). This solution was added to the reaction mixture, which was stirred vigorously at room temperature for 3 h. The crude reaction solution was purified by silica column chromatography (1:8 / 40–60 petrol ether:CH_2Cl_2 with 1% of pyridine), size exclusion column on Biobeads SX-1 (toluene, 1% pyridine) and finally precipitated (CH_2Cl_2/MeOH) to yield ***c*-P6$_X$·T6** as a red solid (28 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H (ppm) 9.61–9.63 (m, 16H), 9.48 (bs, 16H), 8.87–8.77 (m, 16H), 7.79 (bs, 4H), 7.75 (d, J = 6.9 Hz, 4H), 7.69–7.53 (m, 16H), 7.34 (d, J = 7.8 Hz, 8H), 5.58–5.49 (m, 12H), 5.46 (d, J = 8.0 Hz, 8H), 5.42 (d, J = 8.0 Hz, 4H) , 5.06–4.99 (m, 8H), 4.98 (d, J = 6.6 Hz, 4H), 4.13 (bs, 8H), 4.05 (d, J = 5.3 Hz, 8H), 2.34–2.23 (m, 12H), 1.93–1.88 (m, 8H), 1.64–1.53 (m, 32H), 1.53–1.46 (m, 84H), 1.46–1.31 (m, 32H), 1.07–0.97 (m, 24H), 0.97–0.89 (m, 24H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ_C (ppm) 158.0, 157.8, 151.9, 151.8, 151.7, 151.4, 149.9, 146.5, 146.4, 143.6, 143.0, 142.9, 140.1, 140.0, 138.8, 132.7, 132.3, 132.0, 131.7, 131.5, 130.7, 130.5, 127.9, 127.7, 127.3, 127.2, 123.9, 123.8, 122.1, 121.0, 119.4, 119.2, 114.4, 113.0, 109.1, 103.7, 101.9, 100.5, 100.0, 99.1, 96.5, 89.4, 71.1, 39.7, 30.7, 29.3, 24.1, 23.2, 19.3, 14.3, 12.1, 11.4.

MALDI-TOF: m/z = 5806 ([***c*-P6$_X$·T6**] – C_3H_7 (isopropyl group from TIPS), $C_{372}H_{348}N_{30}O_8Si_4Zn_6$, [$M^+$ – C_3H_7] requires 5827), m/z = 4829.5 ([***c*-P6$_X$**] – C_3H_7, $C_{297}H_{293}N_{24}O_8Si_4Zn_6$, [$M^+$ – C_3H_7 – **T6**] requires 4829.8).

λ_{max} ($CHCl_3$) / nm (log ε): 489 (5.68), 761 (5.50), 797 (5.68), 837 (5.67).

Spectra Confirming Purity and Identity of New Compounds

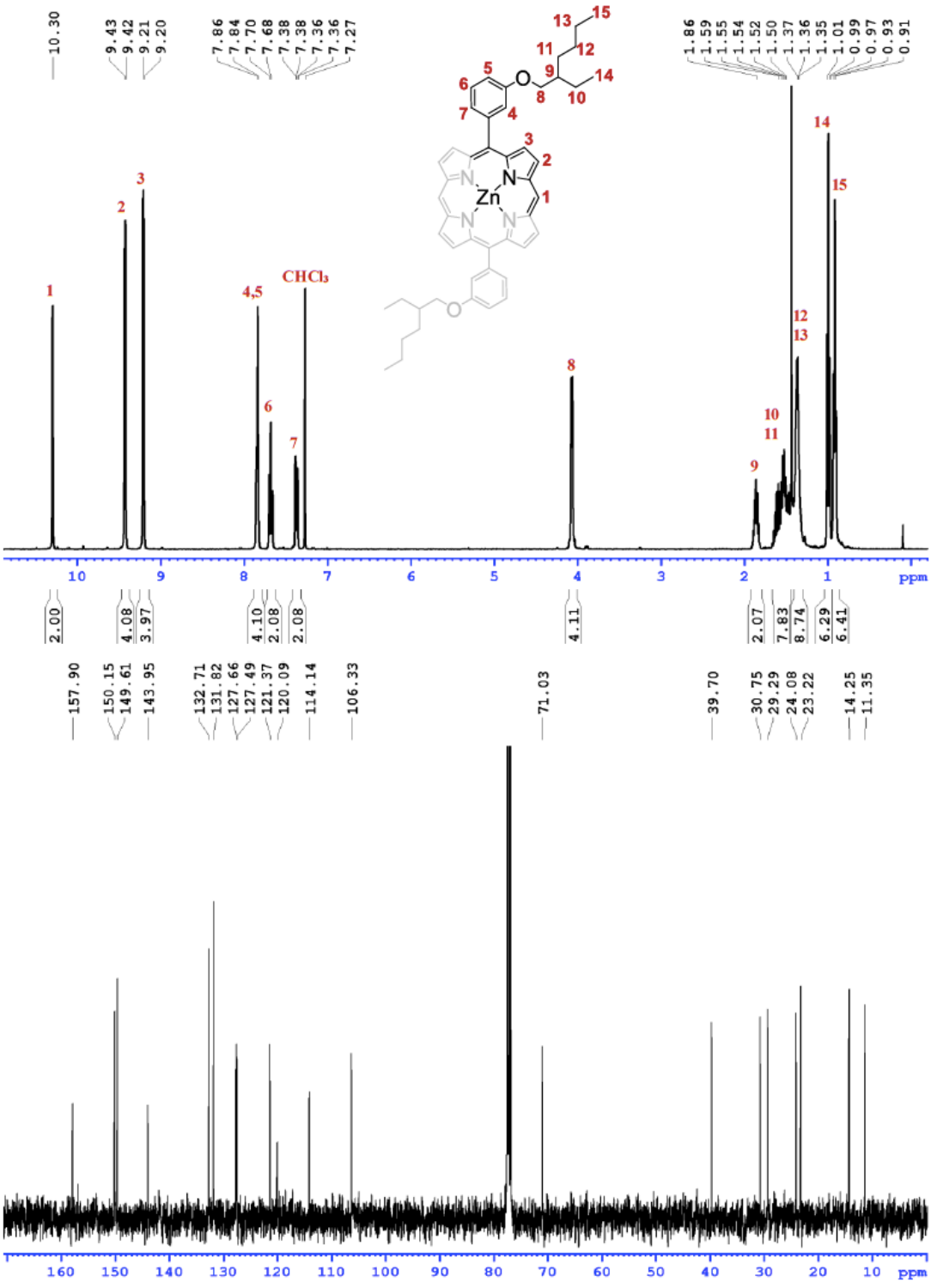


Figure S1: ^{1}H (top) and ^{13}C NMR (bottom) spectra of zinc porphyrin monomer **P1** (400 MHz (100 MHz for ^{13}C), $CDCl_3$, 298 K).

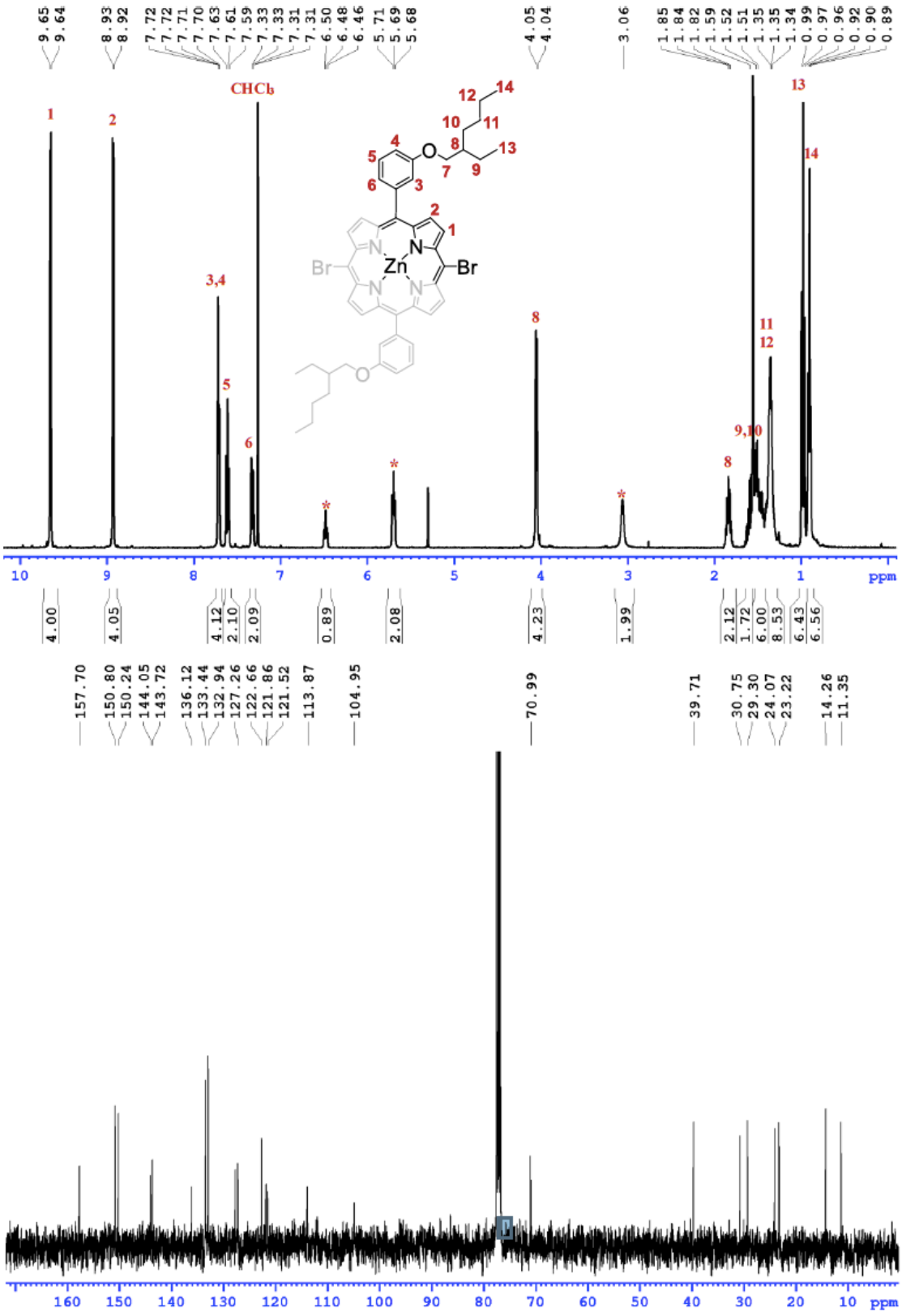


Figure S2. ^{1}H (top, * for pyridine) and ^{13}C NMR (bottom) spectra of dibromo zinc porphyrin monomer (400 MHz (100 MHz for ^{13}C), $CDCl_3$, 298 K).

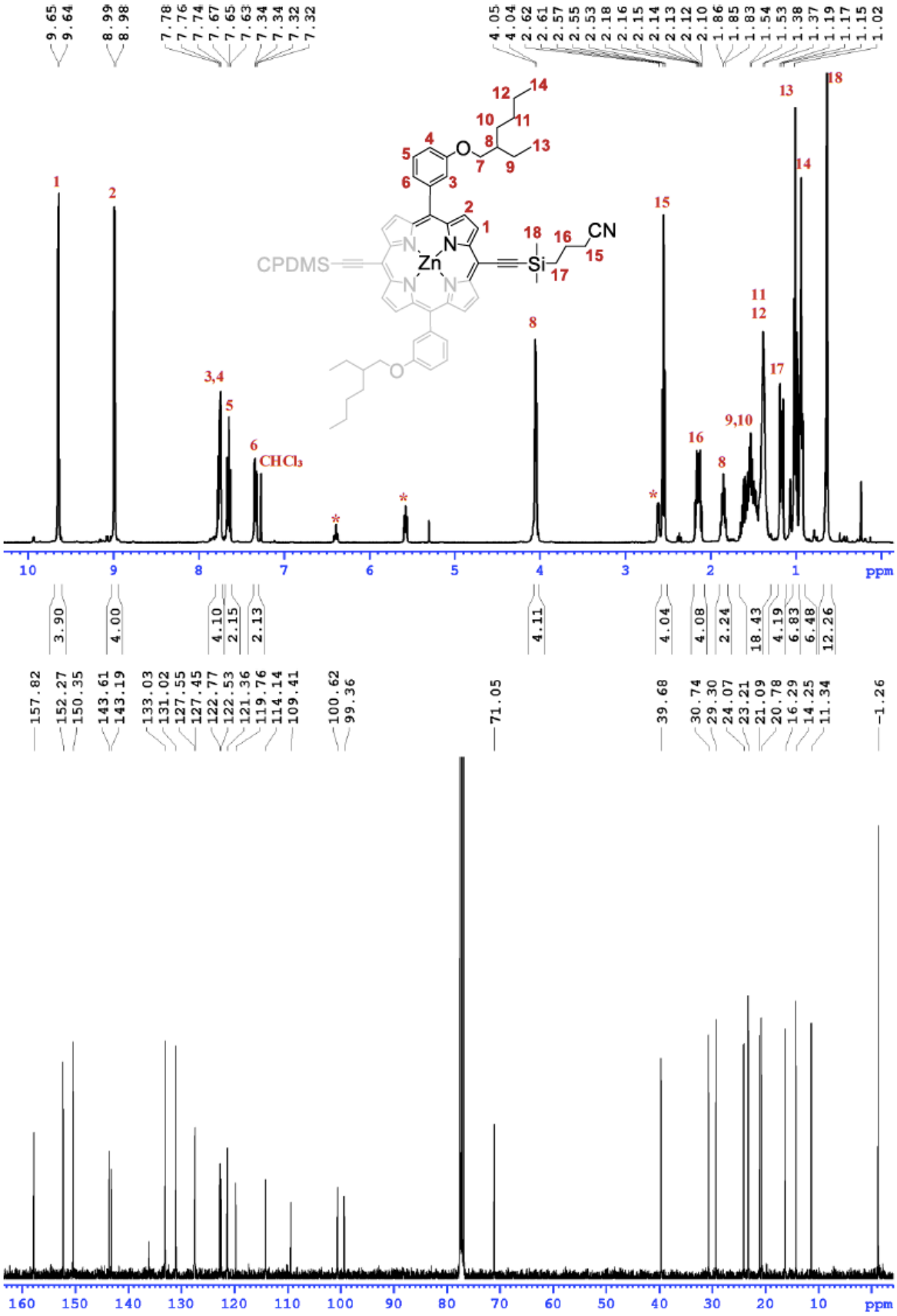


Figure S3: ^{1}H (top, * for pyridine) and ^{13}C NMR (bottom) spectra of zinc porphyrin monomer **3** (400 MHz (100 MHz for ^{13}C), $CDCl_3$, 298 K).

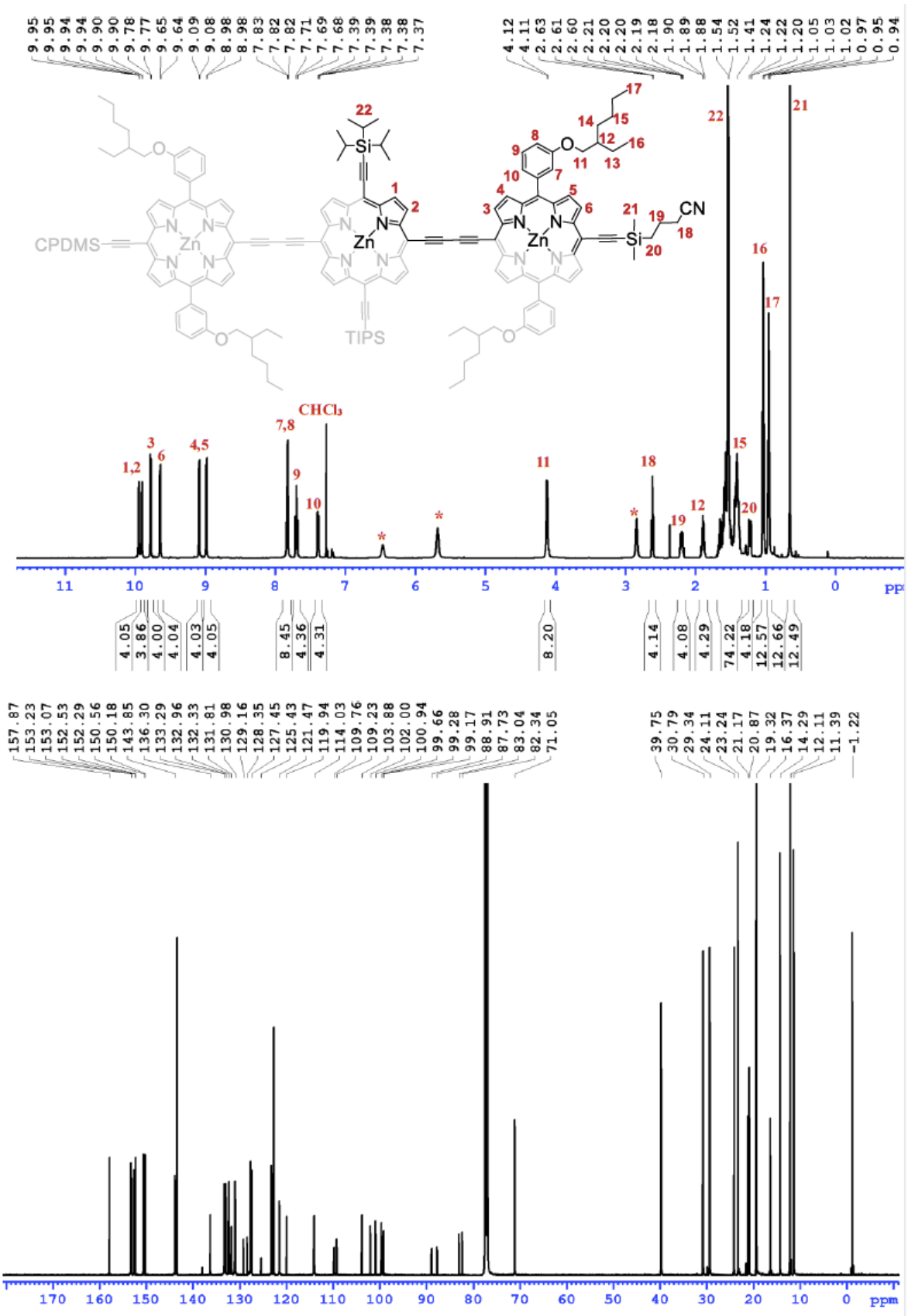


Figure S4. ^{1}H (top, * for pyridine) and ^{13}C NMR (bottom) spectra of zinc porphyrin monomer ***l*-P3x** (500 MHz (125 MHz for ^{13}C), $CDCl_3$, 298 K).

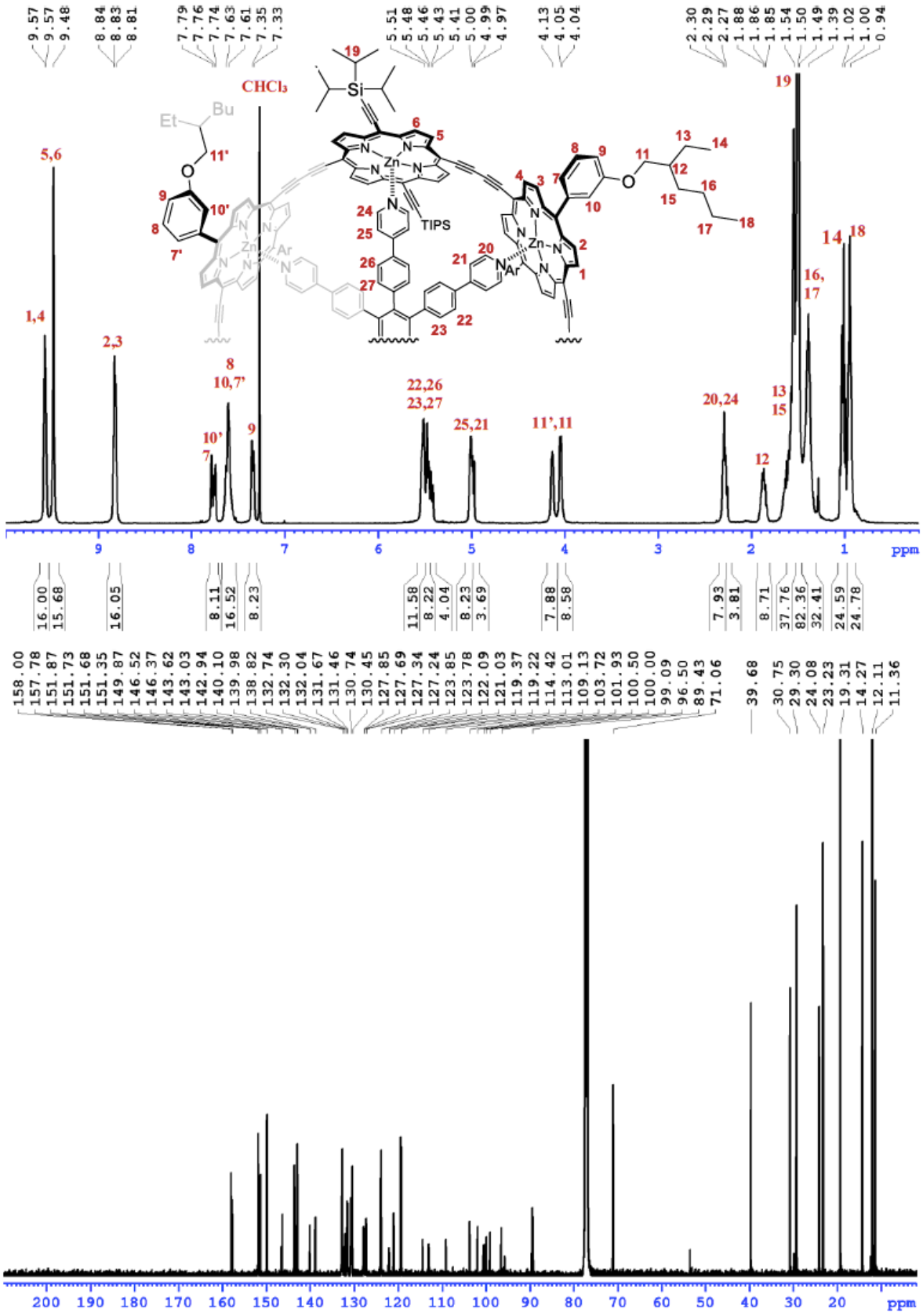


Figure S5. ^{1}H (top) and ^{13}C NMR (bottom) spectra of cyclic porphyrin hexamer template complex ***c*-P6$_X$·T6** (500 MHz (125 MHz for ^{13}C), $CDCl_3$, 298 K).

Absorption and Emission Spectra

Figure S6 shows extinction coefficient and PL emission spectra at room temperature for all porphyrin nanorings under investigation. Extinction coefficient spectra were measured over the range of 350–1000 nm and the emission spectra were measured in the range of 800–1500 nm at an excitation wavelength of 500nm corresponding to the Soret band.

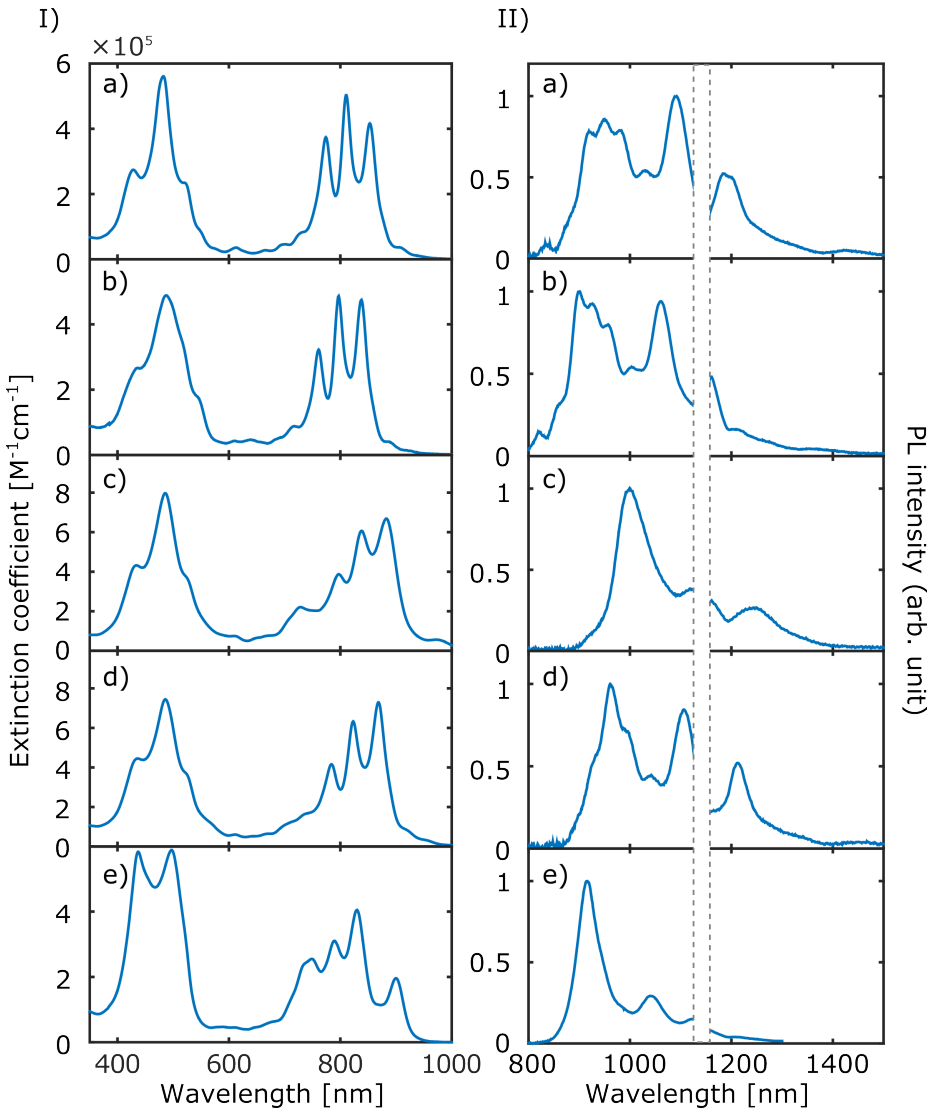


Figure S6: Extinction coefficient (I) and PL intensity (II) spectra of a) ***c*-P6·T6**, b) ***c*-P6$_X$·T6**, c) fused ring with ethyl, d) fused ring and e) ***l*-P6·T6**. Data points between dotted lines in PL intensity spectrum are excluded because of solvent absorption effects.

Time-Resolved Photoluminescence Spectroscopy

The photoluminescence (PL) upconversion technique was engaged to investigate the PL dynamics of sample solutions held in quartz cuvettes. An excitation pulse was generated by a mode-locked Ti:Sapphire laser with pulse duration of 100 fs and a repetition rate of 80 MHz. PL is collected and optically gated in a beta-barium-borate (BBO) crystal by a vertically polarized time-delayed gate beam. The upconverted signal, which consists of sum-frequency photons from the gate pulse and the vertical component of the PL, was collected, dispersed in a monochromator and detected using a nitrogen-cooled CCD. Using a combination of a half-wave plate and a Glan-Thompson polarizer, the polarization of the excitation pulse was varied and the PL intensity dynamics were recorded separately for components polarized parallel ($I_{||}$) and perpendicular ($I_{\perp}$) to the excitation pulse polarization as shown in Figure S7a) for ***l*-P6·T6** as an example. The PL anisotropy is defined using $\gamma = \frac{I_{||} - I_{\perp}}{I_{||} + 2I_{\perp}}$ and calculated from the measured components.[2,5,6] The full-width-half-maximum of the instrumental response function was measured to be ~270 fs, which gives the time-resolution limit of the system. The anisotropy dynamics are constant within at least 15ps after excitation, as shown for ***l*-P6·T6** in Figure S7b) as an example for such traces. To obtain a representative value for the PL anisotropy as a function of excitation wavelength, eight PL intensity values were independently recorded at 5 ps delay for each polarization direction, averaged and the equation above was applied. The concentration of the sample solutions was on the order of 10^{-4} mol/L. To achieve a good signal-to-noise ratio and comparability, the detection wavelength was chosen to be near the emission peak for each sample and kept constant for all excitation wavelengths.

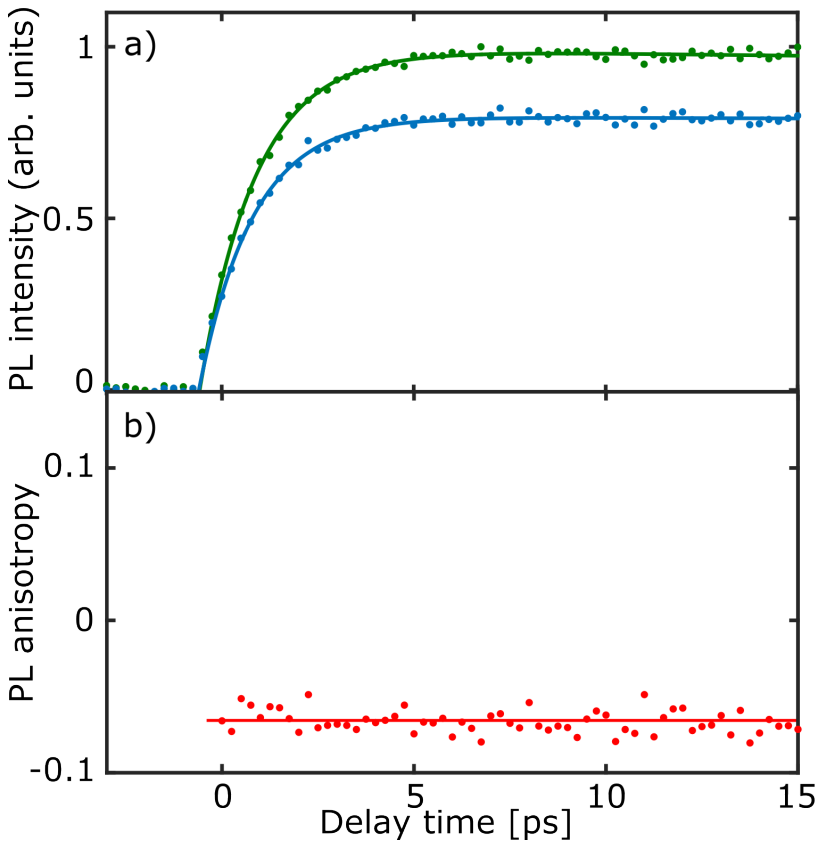


Figure S7: a) Time-resolved PL dynamics of ***l*-P6·T6**. The sample was excited by 810 nm pulses polarized either parallel (blue dots) or perpendicular (green dots) to the detection polarization and the PL at 915 nm was detected. b) PL anisotropy dynamics of ***l*-P6·T6**. The lines serve as a guide to the eye.

To investigate PL decay dynamics at longer delay time after excitation electronic gating through time-correlated single-photon counting (TCSPC) technique was used (Becker&Hickl module). Here, the emission was detected with a silicon single-photon avalanche diode, yielding a temporal resolution of around 40 ps. By fitting the PL intensity (I) decay to a single exponential decay model, $I = Ae^{-t/\tau}$, the lifetime τ of the excitation was extracted.

Quantum Yield and Radiative Rate

As quantum yield measurements had been carried out on porphyrin nanorings in previous studies,[7] a relative approach was adopted in this study using ***l*-P6** as a reference:

$$QY_{sample} = \frac{I_{sample}}{I_{ref}} \times \frac{Abs_{ref}(\lambda_{ext})}{Abs_{sample}(\lambda_{ext})} \times QY_{ref},$$

where I is the integrated area of PL emission spectrum at the excitation wavelength λ_{ext} and $Abs(\lambda_{ext})$ is the absorbance at λ_{ext}. The QY of the reference compound ***l*-P6** is 28%. The quantum yields for each compound was independently measured three times and the average was taken.

Steady-state absorption and time-integrated PL spectra at room temperature were recorded using a PerkinElmer Lambda 1050 UV/VIS/NIR spectrometer and a Horiba FluoroLog fluorimeter respectively.

Using the obtained quantum yield and the overall decay rate Γ_{total} extracted from the PL transients ($\Gamma_{total} = 1/\tau$), the radiative (Γ_r) and non-radiative (Γ_{nr}) rate were extracted using:

$$\Gamma_{rad} = QY \times \Gamma_{total} \quad \text{and} \quad \Gamma_{total} = \Gamma_r + \Gamma_{nr}.$$

The non-radiative rate is approximately a factor of ten larger than the radiative rate for all compounds except the symmetry-broken ***l*-P6·T6**, where Γ_{nr} is only larger by a factor of four. The observed PL transients are dominated by the contribution from the non-radiative decay.

References

(1) Tait, C. E.; Neuhaus, P.; Peeks, M. D.; Anderson, H. L.; Timmel, C. R. Triplet State Delocalization in a Conjugated Porphyrin Dimer Probed by Transient EPR Techniques. *J. Am. Chem. Soc.* **2015** *137*, 8284–8293.

(2) Favereau, L.; Cnossen, A.; Kelber, J. B.; Gong, J. Q.; Oetterli, R. M.; Cremers, J.; Herz, L. M.; Anderson, H. L. Six-Coordinate Zinc Porphyrins for Template-Directed Synthesis of Spiro-Fused Nanorings. *J. Am. Chem. Soc.* **2015** *137*, 14256–14259.

(3) Hoffmann, M.; Kärnbratt, J.; Chang, M.-H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. Enhanced π Conjugation Around a Porphyrin[6] Nanoring. *Angew. Chem. Int. Ed.* **2008**, *47*, 4993–4996.

(4) Screen, T. E. O.; Lawton, K. B.; Wilson, G. S.; Dolney, N.; Ispasoiu, R.; Goodson, T.; Martin, S. J.; Bradley, D. D. C.; Anderson, H. L. Synthesis and Third Order Nonlinear Optics of a New Soluble Conjugated Porphyrin Polymer. *J. Mater. Chem.* **2001**, *11*, 312–320.

(5) Chang, M.-H.; Hoffmann, M.; Anderson, H. L.; Herz, L. M. Dynamics of Excited State Conformational Relaxation and Electronic Delocalization in Conjugated Porphyrin Oligomers. *J. Am. Chem. Soc.* **2008**, *130*, 10171–10178.

(6) Sprafke, J. K.; Kondratuk, D. V.; Wykes, M.; Thompson, A. L.; Hoffmann, M.; Drevinskas, R.; Chen, W.-H. et al. Belt-Shaped π-Systems: Relating Geometry to Electronic Structure in a Six-Porphyrin nanoring. *J. Am. Chem. Soc.* **2011**, *133*, 17262–17273.

(7) Yong, C.-K.; Parkinson, P.; Kondratuk, D. V.; Chen, W.-H.; Stannard, A.; Summerfield, A.; Sprafke, J. K.; O'Sullivan, M. C.; Beton, P. H.; Anderson, H. L. et al. Ultrafast Delocalization of Excitation in Synthetic Light-Harvesting Nanorings. *Chem. Sci.* **2015**, *6,* 181–189.