Supporting Information: Ultrafast Energy Transfer in Biomimetic Multistrand Nanorings

Patrick Parkinson,[†] Christiane E. I. Knappke,[‡] Nuntaporn Kamonsutthipaijit,[‡] Kanokkorn Sirithip,[‡] Jonathan D. Matichak,[‡] Harry L. Anderson[‡] and Laura M. Herz[†]

[†] Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, and

[‡] Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Oxford, OX1 3TA

Table of Contents

Geometry of associated complexes

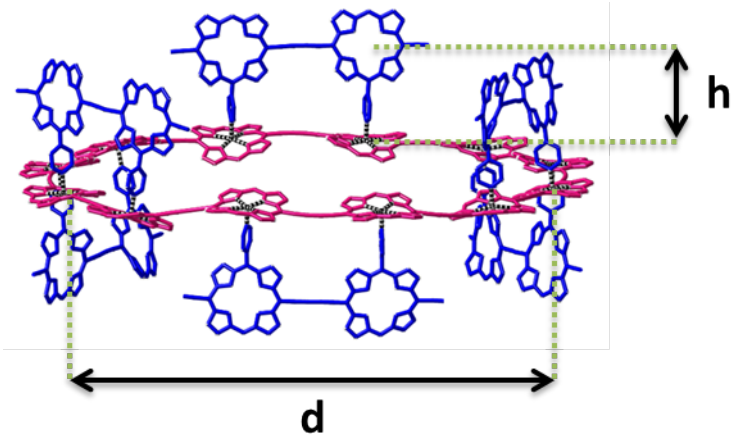


Figure S1: Dimensions of ring-dimer complex, ***c-P12***·(***P2Py2***)$_6$ *where h is the dimer-nanoring distance and d is the nanoring diameter. Energy minimized geometries calculated using the mm+ forcefield in HyperChem©.*

Calculation of energy transfer rates within the Förster formalism are extremely sensitive to length scales (because of the R^{-6} factor). The critical dimensions of the complex are the distance from the center of the dimer porphyrin to the mean plane of the ***c*-P12** nanoring porphyrin (indicated by *h* in Figure S1) and the diameter of the nanoring (indicated by *d*). The diameter of the nanoring has been previously measured to be 47 Å using small-angle X-ray scattering (SAXS) and STM imaging (Reference S1). The distance *h* between the donor dimer porphyrin center and the adjacent ***c*-P12** acceptor porphyrin center was estimated by analyzing several related crystal structures. A search in the Cambridge Structural Database (CSD) resulted in 7 structures that fulfilled the requirement that a free-base porphyrin with a 4-pyridyl-substituent in the meso-position is bound to a zinc-porphyrin (see Figure S2). Table S1 shows the distance h between the centroid A calculated from the coordinates of the four nitrogen atoms of the free-base porphyrin and the centroid B of the four nitrogen atoms of the zinc-porphyrin unit (using the program Mercury). Structures no. 1 and no. 5 were not taken into consideration since the angle formed between the centroid A, the pyridyl-nitrogen atom and centroid B is strongly deviating from 180°. Taking the remaining structures into account gives an arithmetic mean of *h* = 10.16 Å (standard deviation = 0.09 Å).

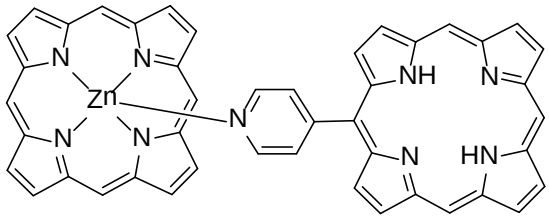


Figure S2: Crystal structures that contained this motif were used for the determination of h.

Table S1 : Data used to obtain a value for *h*. (Structure no. 2 contains the motif shown in Figure S2 twice, each with different parameters.)

Structure No.	***h (centroid A-centroid B)***	***angle (centroid A-N-centroid B)***	***Reference***
1	9.84 Å	141°	D. V. Konarev, A. L. Litvinov, I. S. Neretin, N. V. Drichko, Y. L. Slovokhotov, R. N. Lyubovskaya, J. A. K. Howard, D. S. Yufit, *Cryst. Growth Des.* **2004**, *4*, 643.
2	10.06 Å	175°	E. Iengo, E. Zangrando, R. Minatel, E. Alessio, *J. Am. Chem. Soc.* **2002**, *124*, 1003.
	10.07 Å	173°	
3	10.12 Å	173°	E. Iengo, E. Zangrando, E. Alessio, J.-C. Chambron, V. Heitz, L. Flamigni, J.-P. Sauvage, *Chem. Eur. J.* **2003**, *9*, 5879.
4	10.33 Å	175°	A. K. Burrell, B. M. Jones, S. B. Hall, D. L. Officer, D. C. W. Reid, K. Y. Wild, *J. Inclusion Phenom. Macrocyclic Chem.* **1999**, *35*, 185.
5	9.71 Å	143°	R. K. Kumar, I. Goldberg, *Angew. Chem. Int. Ed.* **1998**, *37*, 3027.
6	10.20 Å	177°	M. Beyler, V. Heitz, J.-P. Sauvage, B. Ventura, L. Flamigni, K. Rissanen, *Inorg. Chem.* **2009**, *48*, 8263.
7	10.18 Å	177°	S. Anderson, H. L. Anderson, A. Bashall, M. McPartlin, J. K. M. Sanders, *Angew. Chem. Int. Ed.* **1995**, *34*, 1096.

Time-resolved photoluminescence measurements and experimental detail

Both steady-state and time-resolved fluorescence (photoluminescence, PL) measurements were carried out on the same experimental apparatus. Approximately 25 µL of 0.1 mM concentration solution in toluene was used for each experiment, which was renewed regularly to avoid photo-degradation. Excitation was provided by a frequency-doubled (450 nm) 100 fs pulse from a Ti:Sapphire laser oscillator (operating at 80 MHz repetition rate). Excitation fluences of 16–800 nJ cm^{-2} $pulse^{-1}$ were used, for steady-state and time-resolved experiments. The power and polarization of the excitation pulse was controlled using a half-wave plate and polarizer. Photoluminescence was collected using off-axis parabolic mirrors and the laser line removed using a colored glass filter. Steady-state measurements used a second polarizer to measure emission whose polarization was parallel to that of the excitation pulse, before the photoluminescence was measured using a spectrometer and liquid-nitrogen cooled CCD.

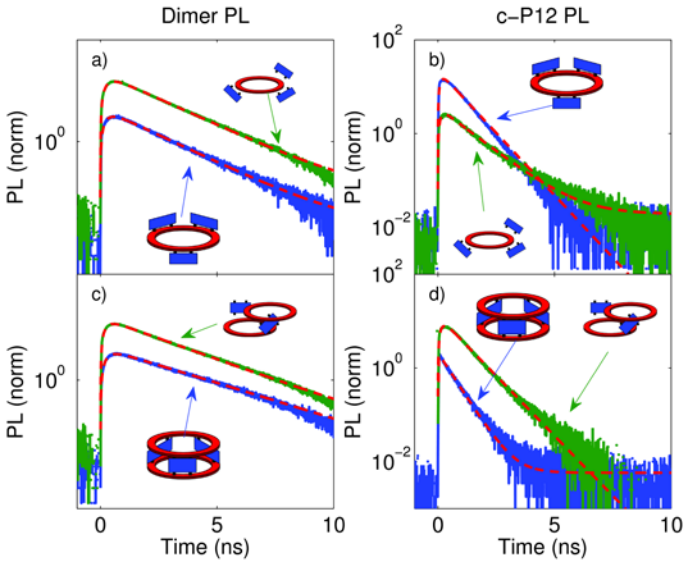


Figure S3: Time-resolved photoluminescence measured using the TCSPC technique for (a,b) the ring-dimer ***c-P12·(P2Py2)$_6$*** *and (c,d) ring-dimer-ring complex* ***(c-P12)$_2$·(P2Py4)$_6$****. (a,c) Emission from the dimer component, (b,d) from the nanoring component. Photoluminescence is shown for the associated (blue line) and dissociated complex state formed by addition of excess pyridine (green line), along with mono-exponential fits (red dashed line). The ultrafast (sub-picosecond) energy transfer dynamic reported in the main manuscript is not visible here, due to the lower time resolution of the TCSPC technique (40 ps). Excitation wavelength: 450 nm; detection wavelengths: 735 nm (a), 721 nm (c) and 866 nm (b,d).*

Time-resolved photoluminescence was measured using either time-correlated single photon counting (TCSPC, Becker and Hickl SPC-130) or photoluminescence up-conversion (PLUC). TCPSC has a temporal resolution of 40 ps and measurement range of 12 ns, while PLUC has a resolution of around 200 fs. PLUC signals were measured using up-conversion in a 1 mm thick β-barium borate (BBO) crystal with an intense delayed 900 nm gate pulse, and the resulting signal was spatially and spectrally filtered before measurement using the spectrometer and CCD.

The PL emission was measured using TCSPC as function of time for both dimer and nanoring components, in both complexes and in each association state; the resultant PL signal is directly proportional to the exciton population. Figure S3 shows the measured PL along with fits of the form

$$PL(t) = (t > 0)\left[A\left(1 - e^{-\frac{t}{\tau_r}}\right)e^{-\frac{t}{\tau}} + B\right] \quad \textbf{S1}$$

Where *A* is the peak emission, τ_r is the signal rise time, τ is a mono-exponential decay constant, and *B* is a baseline offset. A summary of the mono-exponential decay constants is given in Table S2; these values represent the natural lifetime of the chromophores and are used in the energy transfer model.

Table S2: Photoluminescence lifetimes for both complexes in the associated/disassociated state.

	Dimer PL (735 nm/721 nm)		*Nanoring PL (866 nm)*	
	$\tau_{associated}$	$\tau_{dissociated}$	$\tau_{associated}$	$\tau_{dissociated}$
Ring-dimer ***c*-P12·(P2Py2)$_6$**	1760 ps	1820 ps	820 ps	1150 ps
Ring-dimer-ring (**c-P12**)$_2$·(**P2Py4**)$_6$	2610 ps	2210 ps	560 ps	850 ps

Fluorescence titrations

We titrated the donor dimer **P2Py2** into a solution of the acceptor nanoring ***c*-P12** to reach the stoichiometric ratio in the 6:1 complex (see Manuscript Figure 2). However, due to the strength of the association constant, at thermodynamic equilibrium it is expected that a sub-population (<0.2%) of unbound dimers will exist in the solution even at the stoichiometric 6:1 mole ratio. The influence of this population on the energy transfer dynamics was measured using stoichiometric and super-stoichiometric (excess dimer) mixtures of the ring-dimer complex. Figure S4 shows the photoluminescence dynamics for both of these cases. Figure S4c demonstrates the effect of changing this ratio; in both cases, identical energy transfer constants are observed, with a variable baseline depending upon the free-dimer concentration (indicated by *B* in Equation S1).

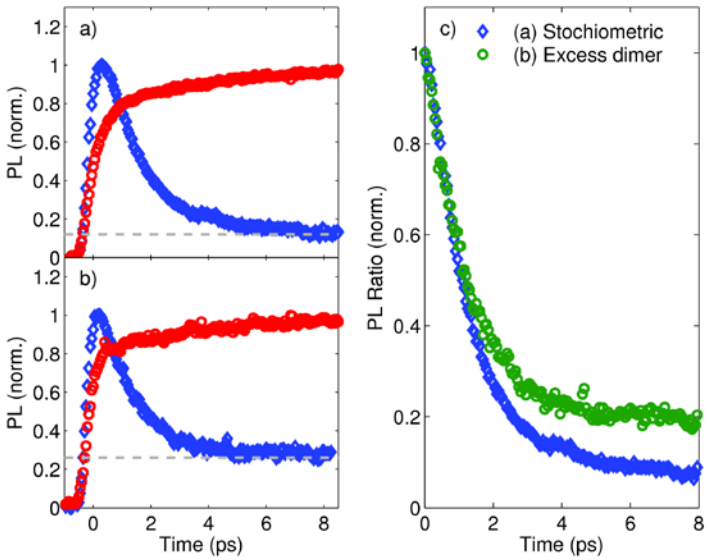


*Figure S4: Dimer photoluminescence dynamics for (a) stoichiometric **c-P12**·(**P2Py2**)$_6$ and (b) super-stoichiometric mixtures of the ring-dimer complex, which excess **P2Py2**. Dynamics for both associated complex (blue diamonds) and dissociated states formed by adding pyridine (red circles) are shown; the baseline is indicated by a dashed grey line. (c) The ratio of photoluminescence emission (indicating energy transfer from dimer to nanoring) is shown for both cases. Excitation wavelength: 450 nm; emission wavelength: 735 nm.*

UV-visible absorption titrations

The binding constant of the dimer **P2Py2** to the nanoring ***c*-P12** was determined by UV-visible titration. The dimer was added to the 12-ring and the concentration of the 12-ring was kept constant during the titration. The data (Figure S5) were analyzed by global fitting with the software Specfit assuming a 1:1 binding situation, i.e. the dimer molecules behave independently in their binding to the 12-ring and the 12-ring is treated as 6 dimer sites. If this assumption were fulfilled in the actual system, isosbestic behavior would be expected. The actual titration shows minor deviation from isosbestic behavior, which may be due to slight initial aggregation of the 12-ring. Nevertheless using the described 1:1 model an acceptable fit (Figure S6) is obtained and a binding constant of log*K* = 6.7 results. This binding constant compares well with the binding constant (log*K* = 7.4) measured for a dimer-dimer system; as expected the binding to the curved system is slightly weaker than that of a linear one.

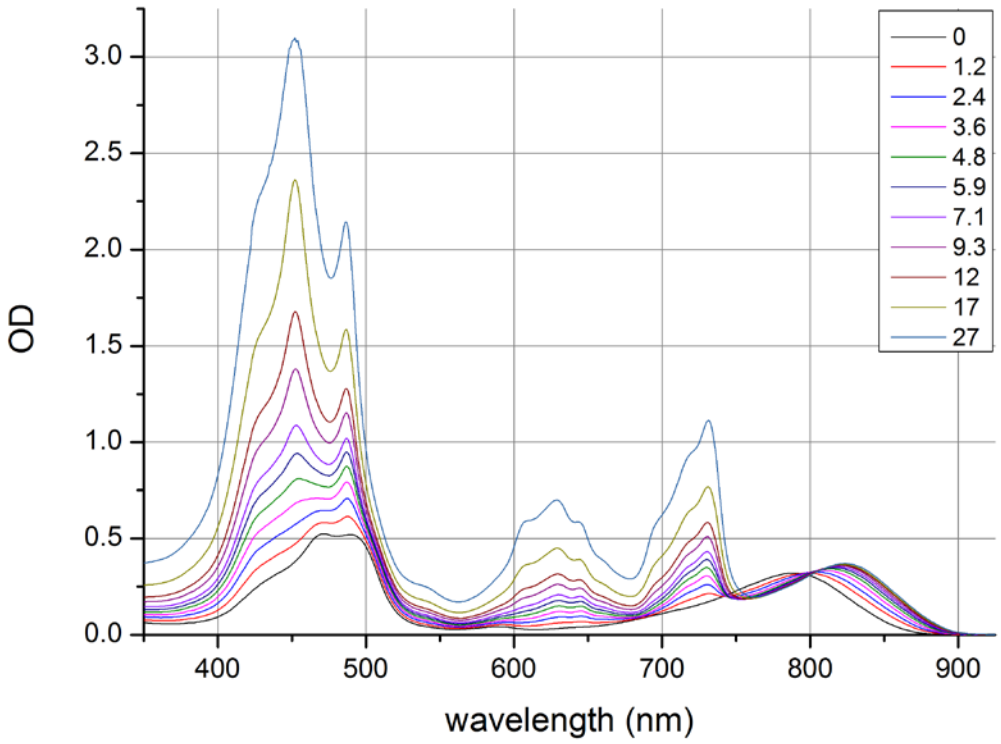


*Figure S5: UV-Visible titration of **c-P12** with **P2Py2**. The concentration of **c-P12** is kept constant during the titration (4.26 x 10^{-7} mol/L). Values in the legend indicate the molar ratio of **P2Py2** to **c-P12**.*

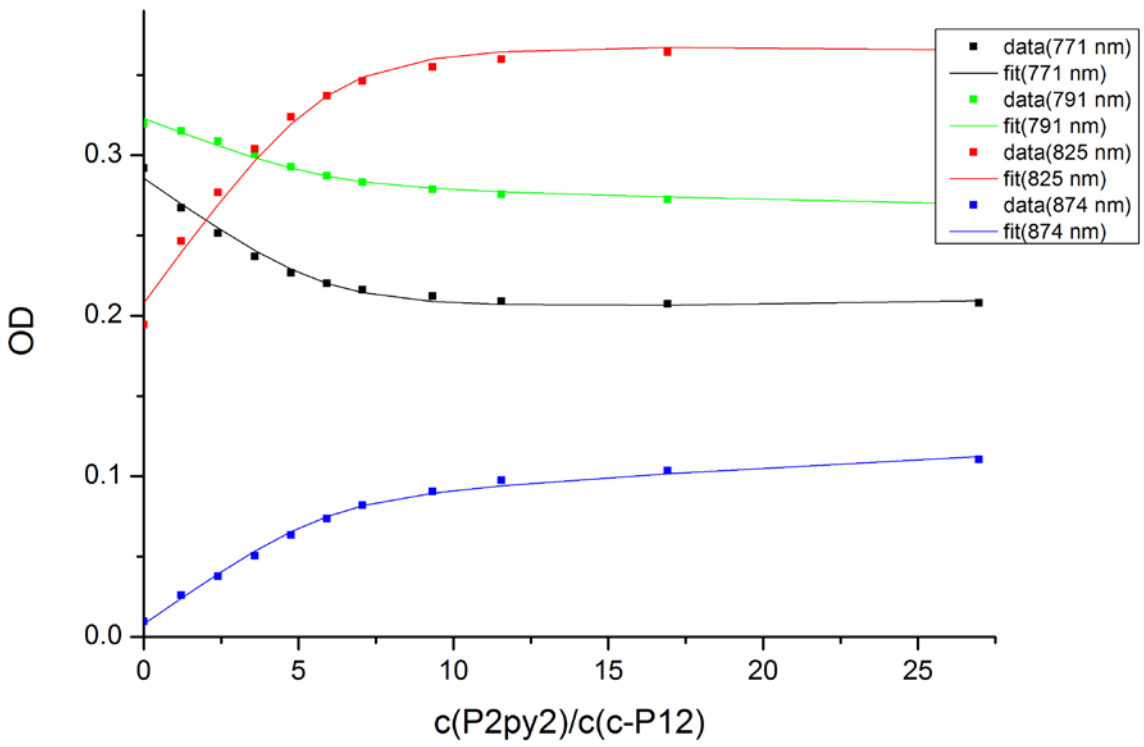


*Figure S6: Plot of the molar concentration ratio of dimer **P2py2** to 12-ring **c-P12** against optical density at various wavelength. Data is from the UV-Visible titration as shown in Figure S5. Fittings were at various wavelengths, obtained by global analysis with Specfit using a 1:1 model.*

Photoluminescence quantum yield

Photoluminescence quantum yield measurements were carried out on both dimer types, for calculation of the radiative rate required for Förster modeling. Optical excitation of dilute solutions (0.25–0.5 µM) of the dimer in toluene/1% pyridine solvent was provided by a continuous 532 nm laser; here, low concentrations were used to avoid reabsorption effects. The samples were positioned inside an integrating sphere, and the signal was measured using a calibrated fiber coupled spectrometer. The efficiency was calibrated against previously measured linear porphyrin hexamer (***l*-P6**) with a known 8% efficiency.[S2] The final quantum efficiency was calculated following the technique presented in Reference S3.

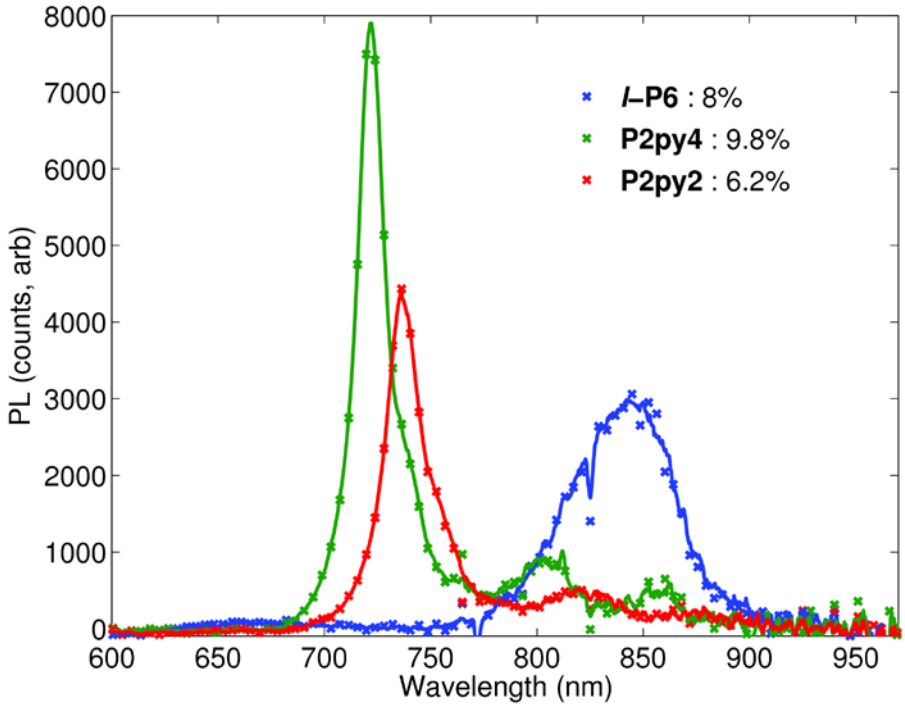


Figure S7: Calibrated dimer photoluminescence taken using quantum yield apparatus. The values for PLQY are calculated using the linear-hexamer as a reference. All compounds were dissolved in toluene containing 1% pyridine; excitation: 532 nm.

General chemical synthesis details

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Dry THF, CH_2Cl_2, chloroform and toluene were obtained by passing through alumina under N_2 pressure. Diisopropylamine (DIPA) was dried over calcium hydride, distilled and stored under nitrogen over molecular sieve. All manipulations of air- or water-sensitive compounds were performed using standard high-vacuum techniques. Flash column chromatography was performed on Merck silica gel 60 (40–63 µm). For TLC Merck silica gel 60 F_{254} aluminum sheets were used. Aluminum oxide, activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å from Sigma Aldrich was used. For size exclusion chromatography Biobeads SX1 (crosslinked polystyrene) were used under gravity elution. "Petrol ether" (PE) always refers to petrol ether 40/60. ^{1}H and ^{13}C NMR spectra were recorded on a BrukerAvance 400 (400.13 and 100.64 MHz), a Bruker DQX 400 (400.13 and 100.64 MHz), a Bruker DRX 500 and BrukerAvance II 500 (500.13 and 125.77 MHz) at 298 K unless otherwise stated. TopSpin (Version 2.1) and Spinworks was used. Chemical shifts (δ in ppm) are referenced to solvent residual peaks ($CDCl_3$ at δ_H 7.24, δ_C 77.0). Abbreviations for ^{1}H-NMR data: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, "t" = pseudo triplet, br = broad. Abbreviations for ^{13}C-DEPTQ-NMR data: *u* = up (CH_3 or CH), *d* = down (CH_2 or C_q). Peaks were assigned based on H,H-COSY, H,C-HMQC and H,C-HMBC correlation spectra. MALDI-TOF-MS were measured with a Waters MALDI Micro MX or by Swansea National Mass Spectrometry Service. Absorption spectra were recorded at 25 °C with a Perkin–Elmer Lambda 20 photospectrometer using quartz 1 cm cuvettes (3 mL).

For GPC the following systems were used:

a) Analytical System: VWR Hitachi Lachrom Elite (pump L-2130, Autosampler L-2200, Diode Array Detector L-2450, Column oven L-2350)

b) Recycling System: Shimadzu (prominence communication bus module CBM-20A, prominence UV-Vis detector SPD-20A, prominence liquid chromatograph LC-20AD, prominence degassing unit DGU-$20A_{3R}$, Shimadzu valve unit FCV-$20AH_2$), detection wavelengths: 371 nm and 500 nm

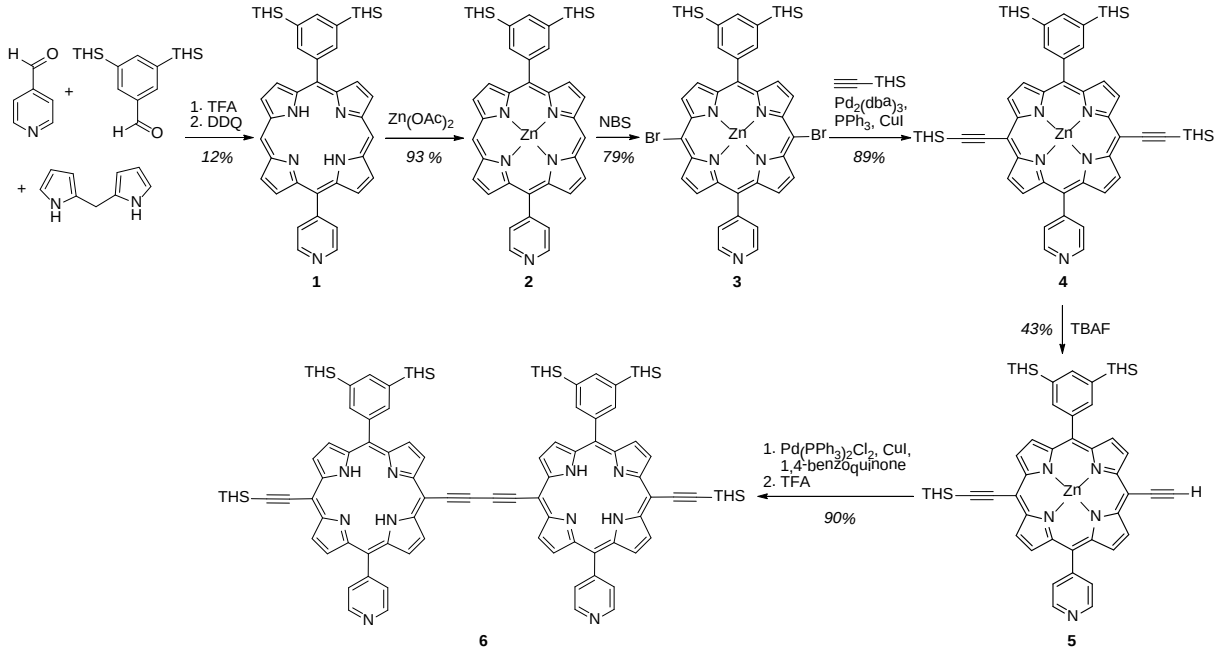
The following GPC column systems were used:

a) Analytical: PL columns in sequence: precolumn PLgel, PLgel 3 µm MIXED-E (2 x 30 cm), PLgel 5 µm MIXED-D (2 x 30 cm), PLgel 5 µm 1000 Å (30 cm)

b) Preparative (recycling): Japan Analytical Industry columns in sequence: precolumn JAIGEL-H-P, JAIGEL-3H, JAIGEL-4H

c) Analytical: Japan Analytical Industry columns in sequence: precolumn JAIGEL-H-P, JAIGEL-3H-A, JAIGEL-4H-A

Synthesis of free-base pyridyl-substituted porphyrin dimer



*Scheme S1: Overview of the synthesis of free-base pyridyl-substituted porphyrin dimer **P2Py2** (THS = $Si(C_6H_{13})_3$). The starting aldehyde, 3,5-bis(trihexylsilyl)benzaldehyde, was synthesized according to Ref. [S4].*

5-(4-pyridyl)-15-(3,5-bis(trihexylsilyl)phenyl)-porphyrin (1)

In a 3-L round-bottom-flask, equipped with a stir bar DCM (1900 mL) was placed. The flask was sealed with a subaseal and evacuated down to 1 mbar followed by backfilling with nitrogen three times. Light was excluded by wrapping the flask with aluminum foil. 3,5-Bis-(trihexylsilyl)-benzaldehyde (3.04 g, 4.51 mmol, 1.0 equiv.) was dissolved in some of the DCM and added. Dipyrromethane (2.02 g, 13.8 mmol, 3.06 equiv.) was added. The flask was sealed again and flushed with nitrogen. 4-Pyrridylcarbaldehyde (0.85 mL, 9.02 mmol, 2.0 equiv.) was added. The mixture was deoxygenated again by evacuating and backfilling with nitrogen. Trifluoroacetic acid (2.14 mL, 28.0 mmol, 6.20 equiv.) was added over a period of 10 min under vigorous stirring. Stirring was continued for 3 h. DDQ (3.89 g, 17.1 mmol, 3.8 equiv.) was added. After 30 min stirring, triethylamine (11.4 mL, 81 mmol, 18 equiv.) was added. After stirring for 30 min, the volume was reduced and the remaining dark solution filtered over a plug of silica eluting with DCM/MeOH (98:2). The solvent was removed from the filtrate. The dark residue was purified by column chromatography on silica initially eluting with petrol ether/DCM 19:1 collecting a red fraction, that consists of 5,15-bis-(3,5-bis(trihexylsilyl)phenyl)-porphyrin (662 mg, 0.416 mmol, 18%). Eluent was changed to DCM/Et_3N (99:1) and then DCM/MeOH/Et_3N (97:2:1). A dark fraction was collected that contained the desired product. After removing the solvent this fraction was subjected again to flash chromatography (silica, eluent: DCM/Et_3N 99:1). A red fraction was collected containing pure **1** (444 mg, 0.432 mmol, 10%). Another fraction that contained **1** was again purified by column chromatography, allowing the separation of additional product (129 mg, 0.126 mmol, 3%; contains minor impurities). Total yield: 573 mg (12%). TLC: R_f (DCM/MeOH 98:2) = 0.42; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 10.35 (s, 2H, *meso*-H), 9.43 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.40 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.10 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.08 (m, 2H, py-H), 9.03 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.34 (s,

2H, *o*-H), 8.22 (m, 2H, py-H), 8.02 (s, 1H, *p*-H), 1.57–1.47 (m, 12H, alkyl-H), 1.45–1.25 (m, 36H, alkyl-H), 1.01–0.93 (m, 12H, alkyl-H), 0.93–0.86 (m, 18H, alkyl-H), –3.10 (s, 1H, N*H*), –3.12 (s, 1H, N*H*); ^{13}C-DEPTQ-NMR (125 MHz, $CDCl_3$): δ = 149.8 (d, 1C, py-C), 148.5 (u, 2C, py-C), 147.5 (d, 2C, α-C), 146.1 (d, 2C, α-C), 145.4 (d, 2C, α-C), 145.2 (d, 2C, α-C), 141.0 (u, 2C, *o*-C), 139.4 (u, 1C, *p*-C), 139.3 (d, 1C, *ipso*-C), 135.5 (d, 2C, *m*-C), 132.2 (u, 2C, β-C), 131.6 (u, 2C, β-C), 131.5 (u, 2C, β-C), 130.1 (u, 2C, β-C), 129.8 (u, 2C, py-C), 121.4 (d, 1C, *meso*-C), 115.0 (d, 1C, *meso*-C), 105.6 (u, 2C, *meso*-C), 33.5 (d, 6C, alkyl-C), 31.6 (d, 6C, alkyl-C), 24.1 (d, 6C, alkyl-C), 22.7 (d, 6C, alkyl-C), 14.2 (u, 6C, alkyl-C), 12.7 (d, 6C, alkyl-C); *m/z* (MALDI-TOF): 1028.4 ($C_{67}H_{97}N_5Si_2$ requires 1028.74).

[5-(4-pyridyl)-15-(3,5-bis(trihexylsilyl)phenyl)-porphyrinato]zinc(II) (2)

Porphyrin **1** (251 mg, 0.244 mmol, 1.0 equiv.) was dissolved in chloroform (21 mL). Methanol (3 mL) and zinc acetate-dihydrate (270 mg, 1.23 mmol, 5.0 equiv.) were added. The mixture was stirred at 40 °C for 2 h. The mixture was filtered over a plug of silica eluting with DCM/pyridine (99:1). The solvent was removed from the pink filtrate. The pink residue was dried in high vacuum yielding the desired product **2**, that coordinates one molecule of pyridine. Yield: 0.264 g (93 %). ^{1}H-NMR (500 MHz, $CDCl_3$+1% pyridine-d_5): δ = 10.22 (s, 2H, *meso*-H), 9.36 (d, $^3J_{HH}$ = 4.3 Hz, 2H, β-H), 9.35 (d, $^3J_{HH}$ = 4.2 Hz, 2H, β-H), 9.07 (d, $^3J_{HH}$ = 4.4 Hz, 2H, β-H), 8.89 (d, $^3J_{HH}$ = 4.4 Hz, 2H, β-H), 8.42 (br, 2H, py-H), 8.29 (d, $^4J_{HH}$ = 0.8 Hz, 2H, *o*-H), 8.03 (m, 2H, py-H), 7.98 (t, $^4J_{HH}$ = 1.0 Hz 1H, *p*-H), 1.52–1.43 (m, 12H, CH_2), 1.39–1.31 (m, 12H, CH_2), 1.31–1.22 (m, 24H, CH_2), 0.95–0.89 (m, 12H, CH_2), 0.87-0.81 (m, 18H, CH_3); ^{13}C-DeptQ-NMR (125 MHz, $CDCl_3$+1% pyridine-d_5): δ = 151.8 (d, 1C, py-C), 150.4 (d, 2C, α-C), 149.6 (d, 2C, α-C), 149.3 (d, 2C, α-C), 148.6 (d, 2C, α-C), 147.1 (u, 2C, py-C), 141.1 (d, 1C, *ipso*-C), 140.9 (u, 2C, *o*-C), 138.8 (u, 1C, *p*-C), 134.5 (d, 2C, *m*-C), 132.7 (u, 2C, β-C), 131.9 (u, 2C, β-C), 131.4 (u, 2C, β-C), 131.0 (u, 2C, β-C), 129.8 (u, 2C, py-C), 121.7 (d, 1C, *meso*-C), 115.1 (d, 1C, *meso*-C), 106.0 (u, 2C, *meso*-C), 33.5 (d, 6C, *C*H_2), 31.6 (d, 6C, *C*H_2), 24.0 (d, 6C, *C*H_2), 22.6 (d, 6C, *C*H_2), 14.1 (u, 6C, *C*H_3), 12.6 (d, 6C, *C*H_2); *m/z* (MALDI-TOF): 1090.7 ($C_{67}H_{95}N_5Si_2Zn$ requires 1090.65).

[5,15-dibromo-10-(4-pyridyl)-20-(3,5-bis(trihexylsilyl)phenyl)-porphyrinato]zinc(II) (3)

Porphyrin **2** (0.230 g, 0.196 mmol, 1.0 equiv.) was dissolved in chloroform (6.6 mL). Pyridine (0.13 mL) was added. *N*-Bromosuccinimide (69.0 mg, 0.388 mmol, 1.98 equiv.) was dissolved in chloroform (9.5 mL) and added to the stirred red solution of the porphyrin **2** via a dropping funnel over a period of 15 min. The reaction mixture turned green during the addition. The mixture was stirred for further 10 min. Acetone (0.2 mL) was added. The mixture was filtered over a plug of silica eluting with DCM/pyridine (99:1). The solvent was removed from the filtrate. The product **3** was precipitated by dissolving in in DCM and layering with MeOH. The green precipitate was washed with methanol and dried in high vacuum. Yield: 194 mg (79%). ^{1}H-NMR (500 MHz, $CDCl_3$+1% pyridine-d_5): δ = 9.57 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 9.56 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.84 (m, 2H, py-H), 8.77 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.67 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 8.10 (s, 2H, *o*-H), 7.94 (m, 2H, py-H), 7.90 (s, 1H, *p*-H), 1.42–1.33 (m, 12H, CH_2), 1.29–1.22 (m, 12H, CH_2), 1.21–1.13 (m, 24H, CH_2), 0.85–0.79 (m, 12H, CH_2), 0.77–0.71 (m, 18H, CH_3); ^{13}C-DeptQ-NMR (125 MHz, $CDCl_3$+1% pyridine-d_5): δ = 150.8 (d, 2C, α-C), 150.7 (d, 1C, py-C), 150.1 (d, 2C, α-C), 149.8 (d, 2C, α-C), 149.2 (d, 2C, α-C), 147.7 (u, 2C, py-C), 140.4 (u, 2C, *o*-C), 140.3 (d, 1C, *ipso*-C), 138.8 (u, 1C, *p*-C), 134.5 (d, 2C, *m*-C), 133.4 (u, 2C, β-C), 133.2 (u, 2C, β-C), 132.6 (u, 2C, β-C), 132.1 (u, 2C, β-C), 129.3 (u, 2C, py-C), 123.8 (d, 1C, *meso*-C), 117.5 (d, 1C, *meso*-C), 104.8 (d, 2C, *meso*-C), 33.2 (d, 6C, *C*H_2), 31.3 (d, 6C, *C*H_2), 23.7 (d, 6C, *C*H_2), 22.3 (d, 6C, *C*H_2), 13.9 (d, 6C, *C*H_3), 12.4 (d, 6C, *C*H_2); *m/z* (MALDI-TOF): 1249.3 ($C_{67}H_{93}Br_2N_5Si_2Zn$ requires 1250.47).

[5-(4-pyridyl)-10,20-bis(trihexylsilylethynyl)-15-(3,5-bis(trihexylsilyl)-phenyl)-porphyrinato]zinc(II) (4)

Porphyrin **3** (0.182 g, 0.146 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (13.8 mg, 0.0151 mmol, 10 mol%), PPh_3 (11.5 mg, 0.0438 mmol, 30 mol%) and CuI (8.3 mg, 0.0438 mmol, 30 mol%) were placed in a heat-dried 2-neck 50 mL round-bottom-flask equipped with a tap and a stir bar. The second opening was sealed with a suba seal and the flask was evacuated and backfilled with nitrogen three times. In a heat-dried 2-neck round-bottom-flask with nitrogen inlet and septum dry toluene (10 mL), dry diisopropylamine (12 mL) and THS-acetylene (170 µL, 0.438 mmol, 3.0 equiv.) were freeze-pump-thaw degassed. The solution was cannulated to the solids. The reaction mixture was heated under nitrogen to 50 °C and kept at this temperature for 2.3 h. The reaction mixture was filtered over a plug of silica eluting with DCM/pyridine (99:1). The solvents were removed from the green filtrate under reduced pressure. The residue was subjected to column-chromatography on silica eluting with petrol ether/EtOAc/pyridine (10:1:1). The desired product **4** (232 mg, 89 %) (contains one equivalent of pyridine) was isolated in form of a dark purple semi-solid. TLC: R_f (petrol ether/EtOAc/pyridine 10:1:1) = 0.50; ^{1}H-NMR (500 MHz, $CDCl_3$+1% pyridine-d_5): δ = 9.65 (d, $^3J_{HH}$ = 4.5 Hz, 2H, β-H), 9.62 (d, $^3J_{HH}$ = 4.5 Hz, 2H, β-H), 8.80 (d, $^3J_{HH}$ = 4.5 Hz, 2H, β-H), 8.69 (d, $^3J_{HH}$ = 4.5 Hz, 2H, β-H), 8.61 (br s, 2H, py-H), 8.18 (d, $^4J_{HH}$ = 0.7 Hz, 2H, *o*-H), 8.00 (d, $^3J_{HH}$ = 5.4 Hz, 2H, py-H), 7.96 (br s, 1H, *p*-H), 1.78–1.69 (m, 12H, alkyl-CH_2), 1.55–1.41 (m, 24H, alkyl-CH_2), 1.41–1.21 (m, 60H, alkyl-CH_2) 1.03–0.95 (m, 12H, alkyl-CH_2), 0.94–0.79 (m, 48H, alkyl-CH_2 and alkyl-CH_3); ^{13}C-deptQ-NMR (125 MHz, $CDCl_3$+1% pyridine-d_5): δ = 152.4 (d, 2C, α-C), 152.3 (d, 2C, α-C), 151.2 (d, 1C, py-C), 150.5 (d, 2C, α-C), 148.7 (d, 2C, α-C), 147.5 (u, 2C, py-C), 140.7 (d, 1C, *ipso*-C), 140.3 (u, 2C, *o*-C), 139.0 (u, 1C, *p*-C), 134.6 (d, 2C, *m*-C), 132.8 (u, 2C, β-C), 131.5 (u, 2C, β-C), 131.3 (u, 2C, β-C),131.0 (u, 2C, β-C), 129.5 (u, 2C, py-C), 124.3 (d, 1C, *meso*-C), 118.1 (d, 1C, *meso*-C), 109.2 (d, 2C, *meso*-C), 101.2 (d, 1C, ethynyl-C), 99.7 (d, 1C, ethynyl-C), 33.5 (d, 6C, *C*H_2), 33.3 (d, 6C, *C*H_2), 31.6 (d, 6C, *C*H_2), 31.5 (d, 6C, *C*H_2), 24.3 (d, 6C, *C*H_2), 24.0 (d, 6C, *C*H_2), 22.6 (d, 6C, *C*H_2), 22.6 (d, 6C, *C*H_2), 14.1 (u, 6C, *C*H_3), 14.1 (u, 6C, *C*H_3), 13.8 (d, 6C, *C*H_2), 12.6 (d, 6C, *C*H_2); *m/z* (MALDI-TOF): 1705.1 ($C_{107}H_{171}N_5Si_4Zn$ requires 1705.20); UV-Vis: λ_{max} [nm] ($CHCl_3$+1% pyridine) = 440, 577, 629.

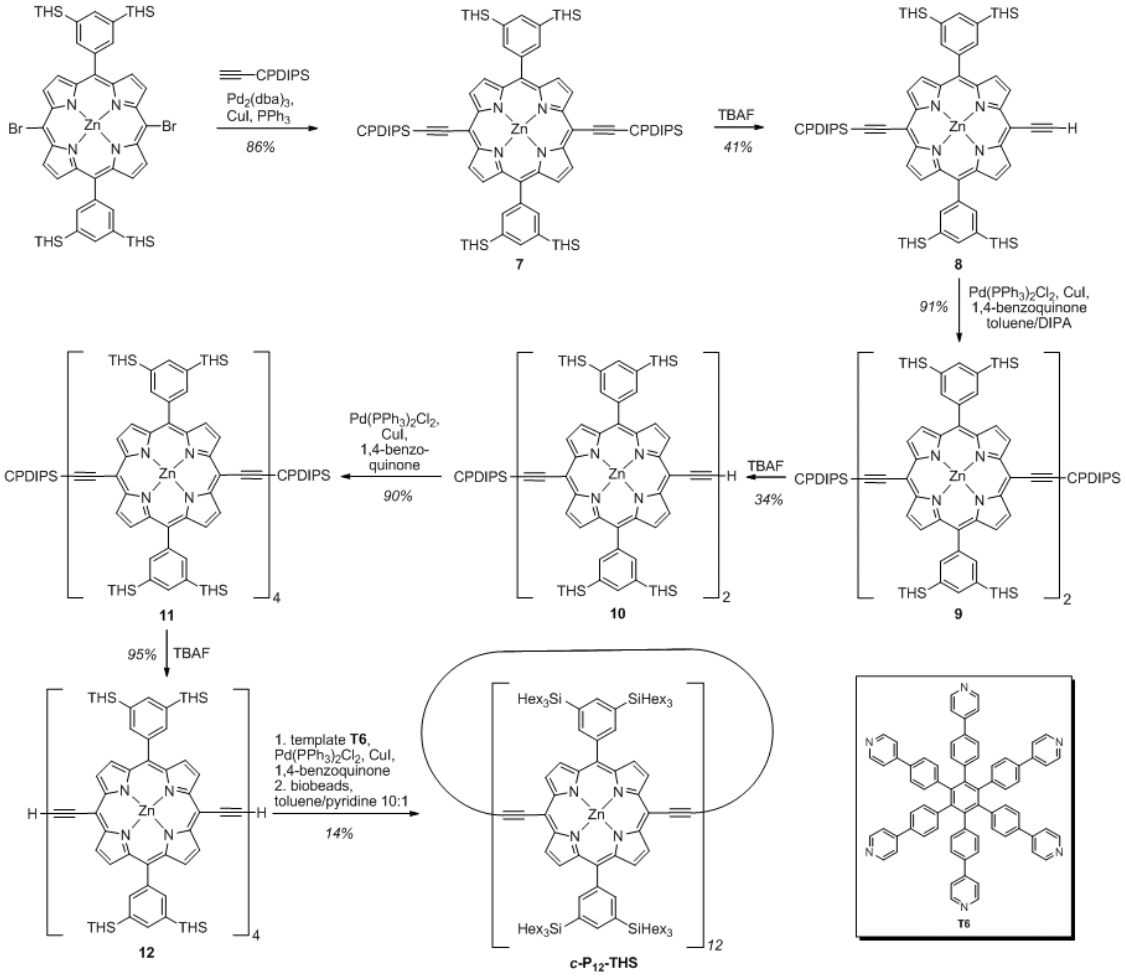
[5-ethinyl-10-(4-pyridyl)-15-trihexylsilylethynyl-20-(3,5-bis(trihexylsilyl)phenyl)-porphyrinato]zinc(II) (5)

Porphyrin **4** (467 mg, 0.262 mmol, 1.0 equiv.) was dissolved in dry DCM (8 mL) and $CHCl_3$ (8 mL). Pyridine (0.21 mL) was added. Under stirring TBAF solution (1.0 M in THF; 0.18 mL, 0.18 mmol, 0.7 equiv.) was added drop-wise. The reaction was monitored by TLC. After 20 min a good product ratio was reached. Calcium chloride (50 mg) was added and the mixture was filtered over a plug of silica eluting with DCM/pyridine (50:1). The solvent was removed from the green filtrate and the residue was subjected to column-chromatography on silica eluting with petrol ether/EtOAc/pyridine 20:2:1 → 20:8:1. Recovered starting material **4** (108 mg, 23%), desired product **5** (170 mg, 43%), and fully deprotected material (87.3 mg, 27%) were isolated in form of their pyridyl-complexes as dark purple semi-solids. TLC: R_f (petrol ether/EtOAc/pyridine 10:1:1) = 0.34; ^{1}H-NMR (400 MHz, $CDCl_3$+1% pyridine-d_5): δ = 9.66 (d, $^3J_{HH}$ = 4.6 Hz, 1H, β-H), 9.65 (d, $^3J_{HH}$ = 4.6 Hz, 1H, β-H), 9.62 (d, $^3J_{HH}$ = 4.6 Hz, 1H, β-H), 9.61 (d, $^3J_{HH}$ = 4.6 Hz, 1H, β-H), 8.97 (m, 2H, py-H), 8.81 (d, $^3J_{HH}$ = 4.5 Hz, 1H, β-H), 8.80 (d, $^3J_{HH}$ = 4.5 Hz, 1H, β-H), 8.76 (d, $^3J_{HH}$ = 4.6 Hz, 1H, β-H), 8.75 (d, $^3J_{HH}$ = 4.6 Hz, 1H, β-H), 8.16 (d, $^4J_{HH}$ = 0.8 Hz, 2H, *o*-H), 8.08 (m, 2H, py-H), 7.94 (br, 1H, *p*-H), 4.12 (s, 1H, ethynyl-H), 1.77–1.67 (m, 6H, alkyl-H), 1.54–1.19 (m, 66H, alkyl-H), 1.01–0.94 (m, 6H, alkyl-H), 0.92–0.79 (m, 39H); *m/z* (MALDI-TOF): 1422.3 ($C_{89}H_{133}N_5Si_3Zn$ requires 1422.9).

Dimerization of 5-ethinyl-10-(4-pyridyl)-15-trihexylsilylethynyl-20-(3,5-bis(trihexylsilyl)-phenyl)-porphyrin (Synthesis of porphyrin dimer 6, P2Py2)

$Pd(PPh_3)_2Cl_2$ (2.0 mg, 2.9 µmol, 8.1 mol%), copper(I) iodide (3.3 mg, 17 µmol, 0.49 equiv.) and 1,4-benzoquinone (7.8 mg, 72 µmol, 2.1 equiv.) were dissolved in dry toluene (3 mL) and dry DIPA at 20 °C The yellow solution was added to porphyrin **5** (52.6 mg, 35.0 µmol, 1.0 equiv.). The reaction mixture was stirred at 20 °C for 3 h. The reaction mixture was filtered over a plug of silica eluting with DCM/pyridine (50:1). Solvents were removed from the filtrate under reduced pressure. The resulting dark purple/green solid was dissolved in chloroform (5 mL). TFA (0.15 mL, 1.9 mmol, 100 equiv.) was added dropwise under stirring. After 10 min pyridine (0.4 mL) was added and the green mixture was directly filtered over a plug of silica eluting with DCM/pyridine (99:1). Solvents were removed from the filtrate under reduced pressure. The dark purple residue was dissolved in chloroform and filtered. The volume was reduced and the product was precipitated by layering methanol. The dark purple precipitate was washed with methanol and dried in high vacuum affording dimer **6**, **P2Py2** (42.8 mg, 90 %). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.87 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 9.82 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 9.65 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 9.61 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.08 (d, $^3J_{HH}$ = 4.8 Hz, 4H, py-H), 8.90 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 8.86 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.81 (d, $^3J_{HH}$ = 4.4 Hz, 2H, β-H), 8.75 (d, $^3J_{HH}$ = 4.5 Hz, 2H, β-H), 8.26 (s, 4H, *o*-H), 8.18 (m, 4H, py-H), 8.01 (s, 2H, *p*-H), 1.80–1.69 (m, 12H, alkyl-H), 1.52–1.19 (m, 132H, alkyl-H), 1.05–0.98 (m, 12H, alkyl-H), 0.97–0.76 (m, 78H, alkyl-H), –1.91 (s, 4H, N-*H*); ^{13}C-deptQ-NMR (125 MHz, $CDCl_3$): δ = 149.5 (d, 2C, py-C), 148.5 (u, 4C, py-C), 140.5 (u, 4C, *o*-C), 139.6 (u, 2C, *p*-C), 139.2 (d, 2C, *ipso*-C), 135.5 (d, 4C, *m*-C), 129.3 (u, 4C, py-C), 124.4 (d, 2C, *meso*-C), 118.3 (d, 2C, *meso*-C), 107.5 (d, 2C, *meso*-C), 102.5 (d, 2C, *meso*-C or ethynyl-C), 102.4 (d, 2C, *meso*-C or ethynyl-C), 99.5 (d, 2C, ethynyl-C), 87.3 (d, 2C, ethynyl-C), 82.9 (d, 2C, ethynyl-C), 33.5 (d, 12C, CH_2), 33.3 (d, 6C, CH_2), 31.6 (d, 18C, CH_2), 24.3 (d, 6C, CH_2), 24.0 (d, 12C, CH_2), 22.7 (d, 18C, CH_2), 14.2 (u, 18C, CH_3), 13.7 (d, 6C, CH_2), 12.6 (d, 12C, CH_2) [Signals for α- and β-carbons are not visible due to the chemical exchange of the N-H protons]. *m/z* (MALDI-TOF): 2715.1 ($C_{178}H_{268}N_{10}Si_6$ requires 2717.0); UV-Vis: λ_{max} [nm] (ε/mol^{-1} L cm^{-1}) (DCM) = 419 (144,000), 449 (285,000), 483 (141,000), 538 (16,300), 606 (45,200), 626 (59,000), 641 (47,700), 729 (81,200); λ_{max} [nm] (ε/mol^{-1} L cm^{-1}) (toluene) = 451 (336,000), 486 (137,000), 608 (54,700), 628 (59,700), 732 (84,000); Fluorescence: λ_{max} [nm] ($CHCl_3$) = 732 (excitation λ_{ex} = 475 nm).

Synthesis of *c*-P12-THS



Scheme S2: Overview of the synthesis of ***c-P12-THS*** *(THS = $Si(C_6H_{13})_3$, CPDIPS = $Si(C_3H_6CN)(CH(CH_3)_2)_2$). The starting dibromoporphyrin was synthesized according to Ref. [S5]. The template* ***T6*** *was synthesized according to Ref. [S6]*

[5,15-bis-((3-cyanopropyl)diisopropylsilyl)ethynyl-10,20-bis-(3,5-bis-(trihexylsilyl)-phenyl)porphyrinato]zinc (II) (7)

Dibromoporphyrin (646 mg, 0.356 mmol, 1.0 equiv. synthesized according to Ref. [S5]), $Pd_2(dba)_3$ (34.8 mg, 0.038 mmol, 0.11 equiv.), triphenylphosphine (28.0 mg, 0.107 mmol, 0.30 equiv.) and copper(I) iodide (21.4 mg, 0.112 mmol, 0.32 equiv.) were placed in a heat-dried Schlenk flask equipped with a magnetic stirrer bar. The flask was sealed and evacuated and backfilled with nitrogen three times. Dry, freeze-pump-thaw degassed toluene (27 mL) was added. CPDIPS-acetylene (259 mg, 1.24 mmol, 3.5 equiv. synthesized according to Ref. [S4]) was dissolved in dry DIPA (22.5 mL). The mixture was degassed by bubbling through nitrogen. The degassed solution was added to the reaction mixture. The resulting mixture was stirred at 50 °C for 2 h. The reaction mixture was filtered over a plug of silica eluting with DCM. The solvent was removed from the filtrate. The residue was purified be column chromatography on silica eluting with PE/DCM 2:1 →3:2. The product **7** was obtained in form of a green-purple oil (631 mg, 86%). TLC: R_f (PE/DCM 2:1) = 0.23; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.67 (d,

$^3J_{HH}$ = 4.5 Hz, 4H, β-H), 8.89 (d, $^3J_{HH}$ = 4.6 Hz, 4H, β-H), 8.20 (s, 4H, *o*-H), 7.97 (s, 2H, *p*-H), 2.52 (t, $^3J_{HH}$ = 6.9 Hz, 4H, propyl-CH_2), 2.21–2.13 (m, 4H, propyl-CH_2), 1.51–1.22 (m, 124H, CH_2, isopropyl-C*H* and isopropyl-CH_3), 1.17–1.12 (m, 4H, propyl-CH_2), 0.94–0.87 (m, 24H, CH_2), 0.87–0.81 (m, 36H, CH_3); ^{13}C-deptQ-NMR (125 MHz, $CDCl_3$): δ = 152.2 (d, 4C, α-C), 150.6 (d, 4C, α-C), 140.2 (d, 2C, ipso-C), 140.1 (u, 4C, *o*-C), 139.3 (u, 2C, *p*-C), 134.9 (d, 4C, *m*-C), 133.1 (u, 4C, β-C), 130.9 (u, 4C, β-C), 124.1 (d, 2C, meso-C), 119.6 (d, 2C, *C*N), 110.0 (d, 2C, alkyl-C), 101.1 (d, 2C, meso-C), 97.0 (d, 2C, alkyl-C), 33.5 (d, 12C, *C*H_2), 31.6 (d, 12C, *C*H_2), 24.0 (d, 12C, *C*H_2), 22.6 (d, 12C, *C*H_2), 21.6 (d, 2C, propyl-*C*H_2), 21.0 (d, 2C, propyl-*C*H_2), 18.6 (u, 4C, isopropyl-*C*H_3), 18.3 (u, 4C, isopropyl-*C*H_3), 14.1 (u, 12C, *C*H_3), 12.6 (d, 12C, *C*H_2), 12.3 (u, 4C, isopropyl-*C*H), 10.1 (d, 2C, propyl-*C*H_2); *m/z* (MALDI-TOF): 2066.2 ($C_{128}H_{210}N_6Si_6Zn$ requires 2066.46).

[5-((3-cyanopropyl)diisopropylsilyl)ethynyl-15-ethynyl-10,20-bis-(3,5-bis-(trihexylsilyl)-phenyl)porphyrinato]zinc (II) (8)

Porphyrin **7** (140 mg, 0.067 mmol, 1.0 equiv.) was dissolved in DCM (8 mL), chloroform (8 mL) and pyridine (1.3 mL). The solution was cooled in an ice-water bath. TBAF solution, 1.0 M in THF, (0.054 mL, 0.054 mmol, 0.8 equiv.) was added and the reaction monitored by TLC (silica, eluent: PE/DCM 2:1). When a good product ratio had been reached the mixture was filtered over a plug of silica eluting with DCM+1% pyridine. The solvent was removed from the filtrate. The residue was purified by column chromatography on silica eluting with PE/chloroform + 0.5% pyridine 20:1 →1:1, providing di-deprotected product (18 mg, 15%), desired product **8** (54.9 mg, 41%) and, after additional precipitation from chloroform/methanol, starting material (54.8 mg, 0.0222 mmol, 33%). (The fraction obtained from column chromatography that contained the starting material also contained CPDIPSF, which was easily removed by precipitation from chloroform with methanol.) TLC: R_f (PE/DCM 2:1) = 0.52; ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 9.63 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.61 (d, $^3J_{HH}$ = 4.5 Hz, 2H, β-H), 8.84 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 8.82 (d, $^3J_{HH}$ = 4.7 Hz, 2H, β-H), 8.18 (s, 4H, *o*-H), 7.95 (s, 2H, *p*-H), 4.12 (s, 1H, ethynyl-H), 2.51 (t, $^3J_{HH}$ = 6.9 Hz, 2H, propyl-CH_2), 2.24–2.09 (m, 2H, propyl-CH_2), 1.51–1.21 (m, 110H, CH_2, isopropyl-C*H* and isopropyl-CH_3), 1.18–1.08 (m, 2H, propyl-CH_2), 0.95–0.78 (m, 60H, CH_2 and CH_3); *m/z* (MALDI-TOF): 1884.6 ($C_{118}H_{191}N_5Si_5Zn$ requires 1884.33).

Dimerization of [5-((3-cyanopropyl)diisopropylsilyl)ethynyl-15-ethinyl-10,20-bis-(3,5-bis-(trihexylsilyl)-phenyl)porphyrinato]zinc (II) (Synthesis of porphyrin dimer 9)

$Pd(PPh_3)_2Cl_2$ (1.5 mg, 2.1 µmol, 0.16 equiv.), copper(I) iodide (3.3 mg, 17 µmol, 1.3 equiv.) and 1,4-benzoquinone (5.5 mg, 51 µmol, 3.8 equiv.) were dissolved in dry toluene (2.4 mL) and dry DIPA (0.75 mL). The solution was added to porphyrin **8** (54 mg, 27 µmol, 2.0 equiv.). The mixture was stirred at RT for 40 min (TLC-control (silica, eluent PE/DCM 2:1) indicated full conversion after 20 min). The reaction mixture was filtered over a plug of silica eluting with chloroform+1% pyridine. The solvent was removed from the filtrate. The residue was purified by passing over a SEC eluting with toluene producing a dark green product (48.2 mg, 91%). TLC: R_f (PE/DCM 2:1) = 0.41; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.91 (d, $^3J_{HH}$ = 4.6 Hz, 4H, β-H), 9.66 (d, $^3J_{HH}$ = 4.6 Hz, 4H, β-H), 8.96 (d, $^3J_{HH}$ = 4.6 Hz, 4H, β-H), 8.90 (d, $^3J_{HH}$ = 4.6 Hz, 4H, β-H), 8.26 (s, 8H, *o*-H), 7.99 (s, 4H, *p*-H), 2.54 (t, $^3J_{HH}$ = 6.9 Hz, 4H, propyl-CH_2), 2.23–2.14 (m, 4H, propyl-CH_2), 1.53–1.22 (m, 220H, CH_2, isopropyl-C*H* and isopropyl-CH_3), 1.19–1.13 (m, 4H, propyl-CH_2), 0.96–0.89 (m, 48H, CH_2), 0.88–0.83 (m, 72H, CH_3); ^{13}C-deptq-NMR (125

MHz, $CDCl_3$): δ = 153.0 (d, 4C, α-C), 152.2 (d, 4C, α-C), 150.7 (d, 4C, α-C), 150.4 (d, 4C, α-C), 140.4 (u, 8C, *o*-C), 140.2 (d, 4C, *ipso*-C), 139.2 (u, 4C, *p*-C), 135.0 (d, 8C, *m*-C), 133.3 (u, 4C, β-C), 133.1 (u, 4C, β-C), 130.9 (u, 8C, β-C), 124.5 (d, 4C, meso-C), 119.7 (d, 2C, *C*N), 110.3 (d, 2C, alkynyl-C), 101.4 (d, 2C, meso-C), 100.2 (d, 2C, meso-C), 97.0 (d, 2C, alkynyl-C), 87.5 (d, 2C, alkynyl-C), 82.5 (d, 2C, alkynyl-C), 33.5 (d, 24C, *C*H_2-hexyl), 31.6 (d, 24C, *C*H_2-hexyl), 24.0 (d, 24C, *C*H_2-hexyl), 22.7 (d, 24C, *C*H_2-hexyl), 21.6 (d, 2C, *C*H_2-cyanopropyl), 21.0 (d, 2C, *C*H_2-cyanopropyl), 18.6 (u, 4C, *C*H_3-isopropyl), 18.3 (u, 4C, *C*H_3-isopropyl), 14.2 (u, 24C, *C*H_3-hexyl), 12.6 (d, 24C, *C*H_2-hexyl), 12.3 (u, 4C, *C*H-isopropyl), 10.1 (d, 2C, *C*H_2-cyanopropyl); *m/z* (MALDI-TOF): 3765.2 ($C_{236}H_{380}N_{10}Si_{10}Zn_2$ requires 3768.6).

Monodeprotected porphyrin dimer 10

Dimer **9** (48.2 mg, 12.3 µmol, 1.0 equiv.) was dissolved in chloroform (1.6 mL), DCM (1.6 mL) and pyridine (0.25 mL). The mixture was cooled in an ice-water bath. TBAF solution, 1.0 M in THF, (0.01 mL, 10 µmol, 0.8 equiv.) was added. The reaction was monitored by TLC (silica, eluent: PE/DCM 3:1). Once a good product ratio had been reached the mixture was filtered over a plug of silica eluting with chloroform+1% pyridine. The solvent was removed from the filtrate. The residue was purified by column chromatography on silica eluting with PE/chloroform + 0.5% pyridine 20:1→1:1. This afforded di-deprotected dimer (5.3 mg, 12%), desired mono-deprotected dimer **10** (16 mg, 34%) and starting material **9** (18 mg, 37%). TLC: R_f (PE/DCM 3:1) = 0.38; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.86 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.85 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.65 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 9.61 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.93 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.90 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.85 (d, $^3J_{HH}$ = 4.8 Hz, 2H, β-H), 8.84 (d, $^3J_{HH}$ = 4.6 Hz, 2H, β-H), 8.24 (s, 4H, *o*-H), 8.23 (s, 4H, *o*-H), 7.97 (s, 4H, *p*-H), 4.15 (s, 1H, alkynyl-H), 2.53 (t, $^3J_{HH}$ = 6.9 Hz, 2H, propyl-CH_2), 2.23–2.13 (m, 2H, propyl-CH_2), 1.51–1.21 (m, 206H, CH_2, isopropyl-C*H* and isopropyl-CH_3), 1.17–1.11 (m, 2H, propyl-CH_2), 0.96–0.78 (m, 120H, CH_2 and CH_3); *m/z* (MALDI-TOF): 3584.7 ($C_{226}H_{361}N_9Si_9Zn_2$ requires 3587.5).

Protected porphyrin tetramer 11

$Pd(PPh_3)_2Cl_2$ (1.0 mg, 1.4 µmol, 0.3 equiv.), copper(I) iodide (1.4 mg, 7.4 µmol, 1.8 equiv.) and 1,4-benzoquinone (1.8 mg, 17 µmol, 4.0 equiv.) were dissolved in dry toluene (0.5 mL) and dry DIPA (0.15 mL). The solution was added to porphyrin dimer **10** (16 mg, 4.2 µmol, 1.0 equiv.). The mixture was stirred at 20 °C for 3.5 h. The reaction mixture was filtered over a plug of silica eluting with chloroform+1% pyridine. The solvent was removed from the filtrate. The residue was dissolved in chloroform and filtered over a microfilter. The volume of the filtrate was reduced and the product precipitated by layering methanol. The precipitate was washed with methanol and dried in vacuum affording the desired product **11** (14 mg, 90%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.97–9.95 (m, 12H, β-H), 9.71 (d, $^3J_{HH}$ = 4.5 Hz, 4H, β-H), 9.04–9.03 (m, 8H, β-H), 9.00 (d, $^3J_{HH}$ = 4.5 Hz, 4H, β-H), 8.94 (d, $^3J_{HH}$ = 4.7 Hz, 4H, β-H), 8.35 (s, 8H, *o*-H), 8.29 (s, 8H, *o*-H), 8.04 (s, 4H, *p*-H), 8.02 (s, 4H, *p*-H), 2.55 (t, $^3J_{HH}$ = 6.7 Hz, 4H, propyl-CH_2), 2.24–2.17 (m, 4H, propyl-CH_2), 1.55–1.15 (m, 416H, CH_2, isopropyl-C*H*, isopropyl-CH_3 and propyl-CH_2), 1.01–0.79 (m, 240H, CH_2 and CH_3); ^{13}C-deptq-NMR (125 MHz, $CDCl_3$): δ = 153.1 (d, 12C, α-C), 152.3 (d, 4C, α-C), 150.8 (d, 4C, α-C), 150.7 (d, 8C, α-C), 150.5 (d, 4C, α-C), 140.7 (u, 8C, *o*-C), 140.4 (u, 8C, *o*-C), 140.1 (d, 4C, *ipso*-C), 140.0 (d, 4C, *ipso*-C), 139.4 (u, 4C, *p*-C), 139.3 (u, 4C, *p*-C), 135.2 (d, 8C, *m*-C), 135.1 (d, 8C, *m*-C), 133.5 (u, 16C, β-C), 133.2 (u, 4C, β-C), 131.1 (u, 4C, β-C), 131.0 (u, 8C, β-C), 125.0 (d, 4C, meso-C), 124.6 (d, 4C, meso-C), 119.7 (d, 2C, *C*N), 110.0 (d, 2C, alkynyl-C), 101.6 (d, 2C, meso-C), 100.9 (d, 2C, meso-C), 100.8 (d, 2C,

meso-C), 100.3 (d, 2C, meso-C), 97.3 (d, 2C, alkynyl-C), 87.5 (d, 4C, alkynyl-C), 87.4 (d, 2C, alkynyl-C), 82.8 (d, 4C, alkynyl-C), 82.5 (d, 2C, alkynyl-C), 33.6 (d, 24C, *C*H_2-hexyl), 33.5 (d, 24C, *C*H_2-hexyl), 31.7 (d, 24C, *C*H_2-hexyl), 31.6 (d, 24C, *C*H_2-hexyl), 24.1 (d, 24C, *C*H_2-hexyl), 24.0 (d, 24C, *C*H_2-hexyl), 22.8 (d, 24C, *C*H_2-hexyl), 22.7 (d, 24C, *C*H_2-hexyl), 21.6 (d, 2C, *C*H_2-cyanopropyl), 21.1 (d, 2C, *C*H_2-cyanopropyl), 18.6 (u, 4C, *C*H_3-isopropyl), 18.4 (u, 4C, *C*H_3-isopropyl), 14.2 (u, 48C, *C*H_3-hexyl), 12.7 (d, 48C, *C*H_2-hexyl), 12.3 (u, 4C, *C*H-isopropyl), 10.1 (d, *C*H_2-cyanopropyl); *m/z* (MALDI-TOF): 7164.1 ($C_{452}H_{720}N_{18}Si_{18}Zn_4$ requires 7174.0); UV-Vis: λ_{max} [nm] (rel. intensity) (toluene) = 441 (0.68, shoulder), 466 (1.0), 491 (0.69, shoulder), 592 (0.07), 773 (0.44), 805 (0.40, shoulder).

Deprotected porphyrin tetramer 12

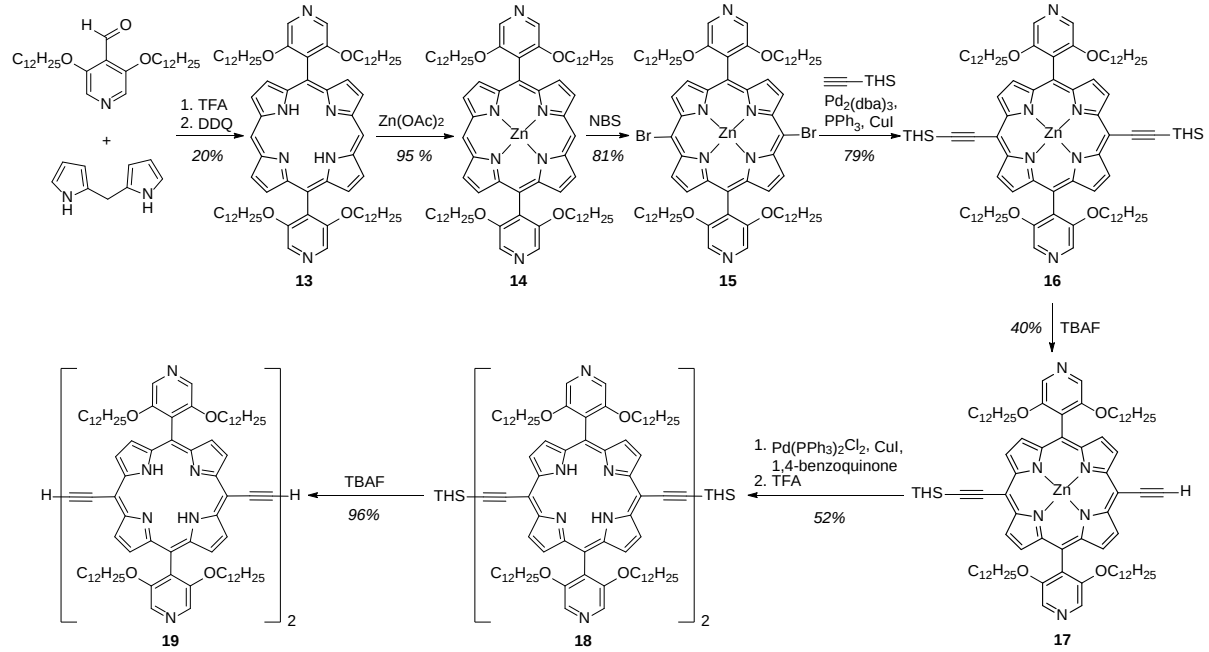
Protected porphyrin tetramer **11** (43.3 mg, 5.78 µmol, 1.0 equiv.) was dissolved in DCM (3 mL) and pyridine (0.07 mL). Under stirring TBAF-solution (1.0 M in THF, 0.015 mL, 15 µmol, 2.5 equiv.) was added. The reaction was monitored by TLC (eluent: PE/DCM 3:1). After 15 min the mixture was filtered over silica eluting with DCM+1% pyridine. The solvent was removed from the filtrate. The residue was dissolved and filtered over a plug of silica eluting with PE/DCM 10:1 +0.5% pyridine (to remove CPDIPS-fluoride). Yield: 39 mg (95%). TLC: R_f (PE/DCM 3:1) = 0.97; ^{1}H-NMR (400 MHz, $CDCl_3$): 9.90–9.87 (m, 12H, β-H), 9.67 (d, $^3J_{HH}$ = 4.7 Hz, 4H, β-H), 8.97–8.94 (m, 12H, β-H), 8.88 (d, $^3J_{HH}$ = 4.5 Hz, 4H, β-H), 8.30 (s, 8H, *o*-H), 8.26 (s, 8H, *o*-H), 8.00 (s, 4H, *p*-H), 7.98 (s, 4H, *p*-H), 4.16 (s, 2H, alkynyl-H), 1.55–1.20 (m, 384H, C*H*$_2$), 0.99–0.82 (m, 240H, C*H*$_2$ and C*H*$_3$); UV-Vis: λ_{max} [nm] ($CHCl_3$) = 457, 584, 755.

Porphyrin nanoring *c*-P12-THS

The template **T6**[12] (3.7 mg, 3.7 µmol, 1.0 equiv.) was dissolved in chloroform (3.6 mL) and methanol (20 µL) under sonication. The clear solution was added to the porphyrin tetramer **12** (39.3 mg, 5.51 µmol, 1.5 equiv.), which had been dissolved in chloroform (8.5 mL). The mixture was sonicated for 20 min. The solvent was removed and the residue dried under vacuum. Afterwards the complex was dissolved in dry chloroform (33.5 mL). $Pd(PPh_3)_2Cl_2$ (5.5 mg, 7.8 µmol, 2.1 equiv.), copper(I) iodide (7.2 mg, 38 µmol, 10 equiv.) and 1,4-benzoquinone (15.7 mg, 145 µmol, 40 equiv.) were dissolved in dry chloroform (3.6 mL) and dry DIPA (0.1 mL) under sonication. The solution was added to the porphyrin/template mixture. The reaction mixture was stirred at 20 °C and monitored by UV-Vis. After 2 h more catalyst ($Pd(PPh_3)_2Cl_2$ (5.6 mg, 8.0 µmol, 2.2 equiv.), copper(I) iodide (7.2 mg, 38 µmol, 10 equiv.) and 1,4-benzoquinone (15.3 mg, 142 µmol, 39 equiv.) dissolved in dry chloroform (3.6 mL) and dry DIPA (0.1 mL)) was added. After 50 min no change was observed so the mixture was heated to 50 °C for 70 min. Then more catalyst ($Pd(PPh_3)_2Cl_2$ (5.7 mg, 8.1 µmol, 2.2 equiv.), copper(I) iodide (7.0 mg, 37 µmol, 10 equiv.) and 1,4-benzoquinone (16.8 mg, 155 µmol, 42 equiv.) dissolved in dry chloroform (3.6 mL) and dry DIPA (0.1 mL)) was added and the reaction mixture stirred at 50 °C for 2 h. Subsequently the reaction mixture was stirred at 20 °C over night. Since further change was observed by UV-Vis catalyst ($Pd(PPh_3)_2Cl_2$ (5.7 mg, 8.0 µmol, 2.2 equiv.), copper(I)iodide (7.3 mg, 38 µmol, 10 equiv.) and 1,4-benzoquinone (16.4 mg, 152 µmol, 41 equiv.) dissolved in dry chloroform (3.6 mL) and dry DIPA (0.1 mL)) was added again and the reaction mixture heated to 50 °C for 2.75 h. The reaction mixture was filtered over a plug of silica eluting with PE/chloroform 9:1. The solvent was removed from the filtrate. The residue was dissolved in PE/chloroform 10:1 and passed over a plug of silica eluting with PE/chloroform 10:1. The solvent was removed from the filtrate. The resulting brown solid was dissolved in toluene/pyridine 9:1 and passed over a SEC column eluting with tolu-

ene/pyridine 9:1. The brown band was collected and the solvent removed. The brown residue was dissolved in toluene+1%pyridine, filtered over a microfilter and purified by recycling GPC. The product was precipitated from chloroform by layering methanol repeatedly to remove residual pyridine to yield **c-P12** (5.3 mg, 14%). TLC: R_f (PE/$CHCl_3$/py 8:1:1) = 0.83; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.85 (d, $^3J_{HH}$ = 4.6 Hz, 48H, β-H), 8.93 (d, $^3J_{HH}$ = 4.4 Hz, 48H, β-H), 8.27 (s, 48H, *o*-H), 7.99 (s, 24H, *p*-H), 1.51–1.44 (m, 288H, CH_2), 1.38–1.24 (m, 864H, CH_2), 0.94–0.90 (m, 288H, CH_2), 0.85–0.82 (m, 432H, CH_3); ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 152.8 (48C, α-C), 150.5 (48C, α-C), 140.6 (48C, *o*-C), 140.1 (24C, *ipso*-C), 139.3 (24C, *p*-C), 135.0 (48C, *m*-C), 133.3 (48C, β-C), 130.9 (48C, β-C), 124.9 (24C, *meso*-C), 100.7 (24C, *meso*-C), 89.3 (24C, alkynyl-C), 84.0 (24C, alkynyl-C); *m/z* (MALDI-TOF): 20597 ($C_{1296}H_{2040}N_{48}Si_{48}Zn_{12}$ requires 20425); UV-Vis: λ_{max} [nm] (toluene) = 471, 489, 588, 779; λ_{max} [nm] (toluene+1% pyridine) = 473, 489, 597, 822.

Synthesis of free-base tetrapyridyl-substituted porphyrin dimer



Scheme S3 : Overview of the synthesis of free-base tetrapyridyl-substituted porphyrin dimer (THS = Si(C_6H_{13})$_3$). The starting aldehyde, 3,5-bis-(dodecyloxy)isonicotinaldehyde, was synthesized according to Ref. [S7,8].

3,5-Bis(dodecyloxy)isonicotinaldehyde

A solution of 3,5-bis(dodecyloxy)pyridine (0.500 g, 1.12 mmol) in dry THF (6 mL) was degassed by pumping and feeding N_2 back three times and then *n*-BuLi (2.5 M in hexane, 0.600 mL, 1.45 mmol) was added slowly at 0 °C under N_2. (Do not let the solution freeze while adding the BuLi). The reaction mixture was stirred for 30 min at room temperature. Dry DMF was added (0.13 mL, 1.68 mmol). After stirring for 24 h, water (0.2 mL) was added to stop the reaction. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with water (2 × 5 mL) and dried over $MgSO_4$ and then the solvent was removed under reduced pressure. Chromatography through a short silica column and recrystallization from hot methanol afforded the desired product as a white solid (269 mg, 50% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 10.52 (s, 1H, C*H*O), 8.10 (s, 2H, py-H), 4.15 (t, $^3J_{HH}$ = 6.4 Hz, 4H, OCH_2), 1.87–1.80 (m, 4H, alkyl-H), 1.50 –1.43 (m, 4H, alkyl-H), 1.31–1.20 (m,

32H, alkyl-H), 0.87 (t, $^{3}J_{HH}$ = 6.4 Hz, 6H, alkyl-H); $^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$): δ = 181.8 (1C, *C*HO), 154.6 (2C, py-C), 128.6 (2C, py-C), 69.9 (2C, O*C*H_2), 31.9-22.6 (40C, *C*H_2), 14.1 (4C, *C*H_3).

5,15-bis-(3,5-bis(dodecyloxy)pyridyl)-porphyrin (13)

Dipyrromethane (307 mg, 2.10 mmol, 1.0 equiv.) and 3,5-bis-(dodecyloxy)-isonicotinaldehyde (1.0 g, 2.1 mmol, 1.0 equiv.) were dissolved in CH_2Cl_2 (375 mL). The reaction mixture was deoxygenated by evacuating and feeding back N_2. Trifluoroacetic acid (0.50 mL, 6.30 mmol, 3.0 equiv.) was added. After stirring in the dark for 3 h DDQ (906 mg, 3.99 mmol, 1.90 equiv.) was added and the mixture stirred for 20 min before Et_3N (1.14 mL, 8.19 mmol, 3.90 equiv.) was added to quench the acid. The mixture was passed through a short silica gel column eluting with CH_2Cl_2/pyridine (90: 10) to separate the tarry side products. The solvent was removed from the filtrate under reduced pressure. The residue was subjected to column-chromatography on silica eluting with petrol ether/CH_2Cl_2/pyridine (60:40:2→50:50:2). The product was recrystallized by layer addition (CH_2Cl_2/MeOH) to give a bright purple powder (256 mg, 20%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.21 (s, 2H, *meso*-H), 9.31 (d, $^{3}J_{HH}$ = 4.4 Hz, 4H, β-H), 8.94 (d, $^{3}J_{HH}$ = 4.4 Hz, 4H, β-H), 8.52 (s, 4H, py-H), 3.97 (t, $^{3}J_{HH}$ = 6.4 Hz, 8H, OC*H*$_2$), 1.37– 0.47 (m, 92H, alkyl-H), –3.11 (s, 2H, N*H*); $^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$): δ = 155.6 (4C, py-C), 146.5 (4C, α-C), 145.2 (4C, α-C), 131.5 (4C, β-H), 130.1 (4C, β-H), 128.9 (4C, py-C), 127.0 (2C, py-C), 108.4 (2C, *meso*-C), 104.6 (2C, *meso*-C), 69.5 (4C, O*C*H_2), 31.9–22.6 (40C, *C*H_2), 14.1 (4C, *C*H_3); *m/z* (MALDI-TOF): 1202.44 ($C_{78}H_{114}N_6O_4$ requires 1201.91).

[5,15-bis-(3,5-bis(dodecyloxy)pyridyl)-porphyrinato]zinc(II) (14)

A solution of $Zn(OAc)_2{\cdot}2H_2O$ (214 mg, 1.17 mmol, 5.00 equiv.) in methanol (1 mL) was added to a solution of 5,15-bis-(3,5-bis-(dodecyloxy)pyridyl)-porphyrin (**13**) (280 mg, 0.233 mmol, 1.0 equiv.) in $CHCl_3$ (25 mL). The mixture was stirred at 50 °C for 5 h. The solvent was removed and the residue purified by passing over a short silica plug, eluting with CH_2Cl_2/pyridine 99:1. Precipitation from CH_2Cl_2 by layering MeOH afforded the desired product as a bright purple powder (281 mg, 95% yield). The product was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$+1% pyridine-d_5): δ = 10.03 (s, 2H, *meso*-H), 9.25 (d, $^{3}J_{HH}$ = 4.4 Hz, 4H, β-H), 8.92 (d, $^{3}J_{HH}$ = 4.4 Hz, 4H, β-H), 8.36 (s, 4H, py-H), 3.89 (t, $^{3}J_{HH}$ = 6.4 Hz, 8H, OC*H*$_2$), 1.27–0.40 (m, 92H, alkyl-H); *m/z* (MALDI-TOF): 1264.96 ($C_{78}H_{116}N_6O_4Zn$ requires 1263.83).

[5,15-dibromo-10,20-(3,5-bis(dodecyloxy)pyridyl)-porphyrinato]zinc(II) (15)

A solution of *N*-bromosuccinimide (78.8 mg, 0.44 mmol, 2.0 equiv.) in $CHCl_3$ (12 mL) was added dropwise to a solution of porphyrin **14** (281 mg, 0.221 mmol, 1.0 equiv.) in $CHCl_3$ (10 mL) and pyridine (0.17 mL) under exclusion of light. After the addition, the reaction mixture was stirred for further 10 min before acetone (0.2 mL) was added to quench the reaction. The mixture was filtered over a plug of silica eluting with PE:EtOAc:pyridine 10:1:1. The solvent was removed under reduced pressure. The product was precipitated from chloroform by layer addition of methanol to give a purple powder (256 mg, 81% yield). ^{1}H-NMR (400 MHz, $CDCl_3$+1% pyridine-d_5): δ = 9.54 (d, $^{3}J_{HH}$ = 4.7 Hz, 4H, β-H), 8.73 (d, $^{3}J_{HH}$ = 4.7 Hz, 4H, β-H), 8.47 (s, 4H, py-H), 3.94 (t, $^{3}J_{HH}$ = 6.4 Hz, 8H, OC*H*$_2$), 1.22–1.06 (m, 24H, C*H*$_2$), 0.99–0.78 (m, 40H, C*H*$_2$), 0.75–0.66 (m, 10H, C*H*$_2$), 0.54–0.39 (m, 18H, C*H*$_2$, C*H*$_3$). $^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$): δ = 155.5 (4C, py-C), 150.0 (4C, α-C), 149.8 (4C, α-C), 133.1 (4C, β-H), 131.8 (4C, β-H), 128.7 (4C, py-C), 128.4 (2C, py-C), 110.8 (2C, *meso*-C), 104.1 (2C, *meso*-C), 69.3 (4C, O*C*H_2), 31.8-22.6 (40C, *C*H_2), 14.0 (4C, *C*H_3); *m/z* (MALDI-TOF): 1422.67 ($C_{78}H_{112}Br_2N_6O_4Zn$ requires 1423.65).

[5,15-bis-(3,5-bis(dodecyloxy)-pyridyl)-10,20-trihexylsilylethynyl-porphyrinato]zinc(II) (16)

Porphyrin **15** (255 mg, 0.179 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (16.5 mg, 0.018 mmol, 10 mol%), PPh_3 (14.2 mg, 0.054 mmol, 30 mol%) and CuI (10.3 mg, 0.054 mmol, 30 mol%) were combined in a heat dried 2-neck round bottom flask and then evacuated and back filled with N_2 three times. Dry toluene (15 mL) and pyridine (0.7 mL) were added and freeze-pump-thaw degassed 3 times. Dry DIPA (18 mL) and THS-acetylene (0.17 mL, 0.448 mmol, 2.50 equiv.) were added at 20 °C. The reaction mixture was stirred at 50 °C for 2.5 h, then filtered over a plug of silica eluting with CH_2Cl_2/pyridine 99:1. The solvent was removed under reduced pressure. The residue was subjected to column-chromatography on silica eluting with petroleum ether: EtOAc: pyridine 15:1:0.5 to afford the desired product as a green solid (265 mg, 79% yield). ^{1}H-NMR (400 MHz, $CDCl_3$+1% pyridine-d_5): δ = 9.52 (d, $^3J_{HH}$ = 4.4 Hz, 4H, β-H), 8.68 (d, $^3J_{HH}$ = 4.4 Hz, 4H, β-H), 8.46 (s, 4H, py-H), 3.90 (t, $^3J_{HH}$ = 6.4 Hz, 8H, OCH_2), 1.50–1.43 (m, 8H, CH_2), 1.36–1.29 (m, 66H, CH_2), 1.17–0.75 (m, 66H, CH_2), 0.68–0.43 (m, 44H, CH_2, CH_3). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 155.6 (4C, py-C), 152.1 (4C, α-C), 149.3 (4C, α-C), 131.2 (4C, β-H), 130.9 (4C, β-H), 128.9 (4C, py-C), 128.7 (2C, py-C), 111.2 (2C, *meso*-C), 109.5 (2C, *meso*-C), 100.3 (2C, ethynyl-C), 98.3(2C, ethynyl-C), 69.6 (4C, OCH_2), 33.4–22.6 (64C, CH_2), 14.1 (4C, CH_3), 13.8 (6C, CH_3), 13.0 (6C, SiCH_2); *m/z* (MALDI-TOF): 1877.25 ($C_{118}H_{190}N_6O_4Si_2Zn$ requires 1878.4).

[5,15-bis-(3,5-bis(dodecyloxy)pyridyl)-10-ethynyl-20-trihexylsilylethynyl–porphyrinato]-zinc(II) (17)

TBAF (1.0 M in THF, 0.097 mL, 0.097 mmol, 0.70 equiv.) was added to a solution of protected pyridyl porphyrin monomer **16** (260 mg, 0.138 mmol, 1.0 equiv.) in 1:1 CH_2Cl_2:$CHCl_3$ (10 mL). The reaction mixture was stirred at 20 °C and monitored by TLC. Upon completion (1 h), the reaction mixture was passed immediately over a short plug of silica (DCM/pyridine 99:1). Purification by column chromatography (petrol ether:EtOAc:pyridine 10:1:0.5) provided the desired product as a green solid (220 mg, 43% yield). ^{1}H-NMR (400 MHz, $CDCl_3$+1% pyridine-d_5): δ = 9.56 ("t", $^3J_{HH}$ = 4.4 Hz, 4H, β-H), 8.72 (dd, $^3J_{HH}$ = 4.4 Hz, 4H, β-H), 8.48 (s, 4H, py-H), 4.03 (s, 1H, ethynyl-H), 3.90 (m, 8H, OCH_2), 1.73–1.71 (m, 6H, CH_2), 1.55–1.47 (m, 6H, CH_2), 1.40–1.04 (m, 38H, CH_2), 0.99–0.80 (m, 47H, CH_2, CH_3), 0.74–0.60 (m, 6H, CH_2), 0.57–0.46 (m, 28H, CH_2, CH_3); *m/z* (MALDI-TOF): 1596.10 ($C_{100}H_{152}N_6O_4SiZn$ requires 1595.18).

Dimerization of 5,15-bis-(3,5-bis(dodecyloxy)pyridyl)-10-ethynyl-20-trihexylsilylethynyl–porphyrin (Synthesis of porphyrin dimer 18)

$Pd(PPh_3)_2Cl_2$ (3.3 mg, 4.7 µmol, 8.1 mol%), CuI (4.1 mg, 0.03 mmol, 0.49 equiv.) and benzoquinone (13.4 mg, 0.124 mmol, 2.10 equiv.) were combined. The reagents were dissolved in dry toluene (5.5 mL) and dry DIPA (1.25 mL) and then added into a stirred solution of monodeprotected porphyrin monomer **17** (94.0 mg, 0.06 mmol, 1.0 equiv.) in dry toluene (5.5 mL) and dry DIPA (1.25 mL). The reaction mixture was stirred at 20 °C and monitored by TLC (10:1:0.5 PE:EtOAc:pyridine). Upon completion (2 h), the mixture was passed over a plug of silica (CH_2Cl_2/pyridine 99:1). Solvents were removed from the filtrate under reduced pressure. The residue was further purified by chromatography on SEC-column eluting with toluene producing a green solid. The green solid

was dissolved in chloroform (8.0 mL). TFA (0.34 mL, 4.46 mmol, 100 equiv.) was added under stirring. The mixture was stirred for 10 min, and then quenched with pyridine (0.5 mL). The mixture was filtered directly over a plug of silica eluting with chloroform. The solvent was removed from the filtrate and the residue dried in vacuum to obtain the desired product as green solid (47 mg, 52% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.79 (d, $^{3}J_{HH}$ = 4.8 Hz, 4H, β-H), 9.57 (d, $^{3}J_{HH}$ = 4.8 Hz, 4H, β-H), 8.81 (d, $^{3}J_{HH}$ = 4.8 Hz, 4H, β-H), 8.71 (d, $^{3}J_{HH}$ = 4.8 Hz, 4H, β-H), 8.53 (s, 8H, py-H), 4.01 (t, $^{3}J_{HH}$ = 5.6 Hz, 16H, OCH_2), 1.81–1.78 (m, 12H, CH_2), 1.60–1.36 (m, 40H, CH_2), 1.01–0.81 (m, 128H, CH_2), 0.76–0.73 (m, 34H, CH_2, CH_3), 0.68–0.57 (m, 48H, CH_2, CH_3). ^{13}C-deptQ-NMR (125 MHz, $CDCl_3$): δ = 155.5 (d, 8C, py-C), 128.9 (u, 8C, py-C), 126.9 (d, 4C, py-C), 111.8 (d, 4C, *meso*-C), 107.7 (d, 2C, *meso*-C), 101.5 (d, 2C, *meso*-C or ethynyl-C), 101.1 (d, 2C, *meso*-C or ethynyl-C), 98.8 (d, 2C, ethynyl-C), 87.0 (d, 2C, ethynyl-C), 82.4 (d, 2C, ethynyl-C), 69.7 (d, 8C, OCH_2), 33.4–22.6 (d, 128C, CH_2), 14.2 (u, 8C, CH_3), 14.0 (u, 6C, CH_3), 12.6 (d, 6C, SiCH_2) [Signals for α- and β-carbons are not visible due to the chemical exchange of the N-H protons]. *m/z* (MALDI-TOF): 3062.00 ($C_{100}H_{152}N_6O_4SiZn$ requires 3063.36); λ_{max} [nm] (ε/mol^{-1} L cm^{-1}) (toluene) = 453 (3.33×10^5), 486 (1.94×10^5), 533 (2.38×10^4), 606 (6.75×10^4), 625 (7.60×10^4), 641 (6.42×10^4), 726 (1.05×10^5).

Deprotected porphyrin dimer 19

The protected porphyrin dimer **18** (10.0 mg, 3.26 μM, 1.0 equiv.) was dissolved in CH_2Cl_2 (2 mL). TBAF (1.0 M in THF, 0.013 mL, 0.013 mmol, 4.0 equiv.) was added to the solution. The mixture was stirred for 30 min. Methanol (4 mL) was added, which resulted in the precipitation of the product that was filtered off and washed with methanol. The desired product was afforded as a green solid (7.8 mg, 96% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.80 (d, $^{3}J_{HH}$ = 4.6 Hz, 4H, β-H), 9.59 (d, $^{3}J_{HH}$ = 4.6 Hz, 4H, β-H), 8.83 (d, $^{3}J_{HH}$ = 4.6 Hz, 4H, β-H), 8.75 (d, $^{3}J_{HH}$ = 4.6 Hz, 4H, β-H), 8.53 (s, 8H, py-H), 4.17 (s, 2H, ethynyl-H), 4.02 (t, $^{3}J_{HH}$ = 6.4 Hz, 16H, OCH_2), 1.16–0.56 (m, 184H, CH_2, CH_3); ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 155.5 (8C, py-C), 128.0 (12C, py-C), 111.6 (4C, *meso*-C), 99.7 (2C, *meso*-C or ethynyl-C), 99.1 (2C, *meso*-C or ethynyl-C), 87.0 (2C, ethynyl-C), 85.2 (2C, *meso*-C or ethynyl-C), 84.4 (2C, *meso*-C or ethynyl-C), 82.5 (2C, ethynyl-C), 69.8 (8C, OCH_2), 31.8–22.6 (80C, CH_2), 14.1 (8C, CH_3) [Signals for α- and β-carbons are not visible due to the chemical exchange of the N-H protons]. λ_{max} [nm] (ε/mol^{-1} L cm^{-1}) (toluene) = 450 (2.62×10^5), 483 (1.79×10^5), 530 (2.28×10^4), 719 (7.64×10^4). *m/z* (MALDI-TOF): 2498.30 ($C_{164}H_{230}N_{12}O_8$ requires 2497.81).

Analytical GPC of 12-porphyrin ring and free-base porphyrin dimers

Analytical GPC was carried out on the 12-porphyrin ring, ***c*-P12** and both dimers (**P2Py2** and **P2Py4**) to confirm the purities of these precursors for the formation of the double- and triple-strand complexes (Figure S8). Analytical GPC traces of all species were measured at 450 nm eluting with toluene/1% pyridine.

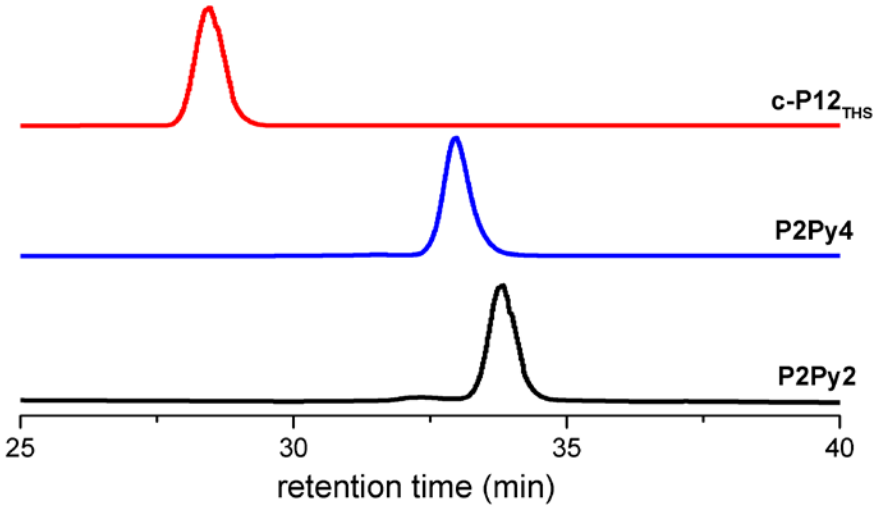


*Figure S8: Analytical GPC traces of 12-ring **c-P12** (red) at 28.45 min, free-base porphyrin dimers **P2Py2** (blue) and **P2Py4** (black) at 32.96 and 33.81 min, respectively (absorption signal at 450 nm; toluene/1%pyridine; flow rate 1 mL min^{-1}; 313 K; Japan Analytical Industry columns in sequence: precolumn JAIGEL-H-P, JAIGEL-3H-A, JAIGEL-4H-A).*

^{1}H-NMR titrations

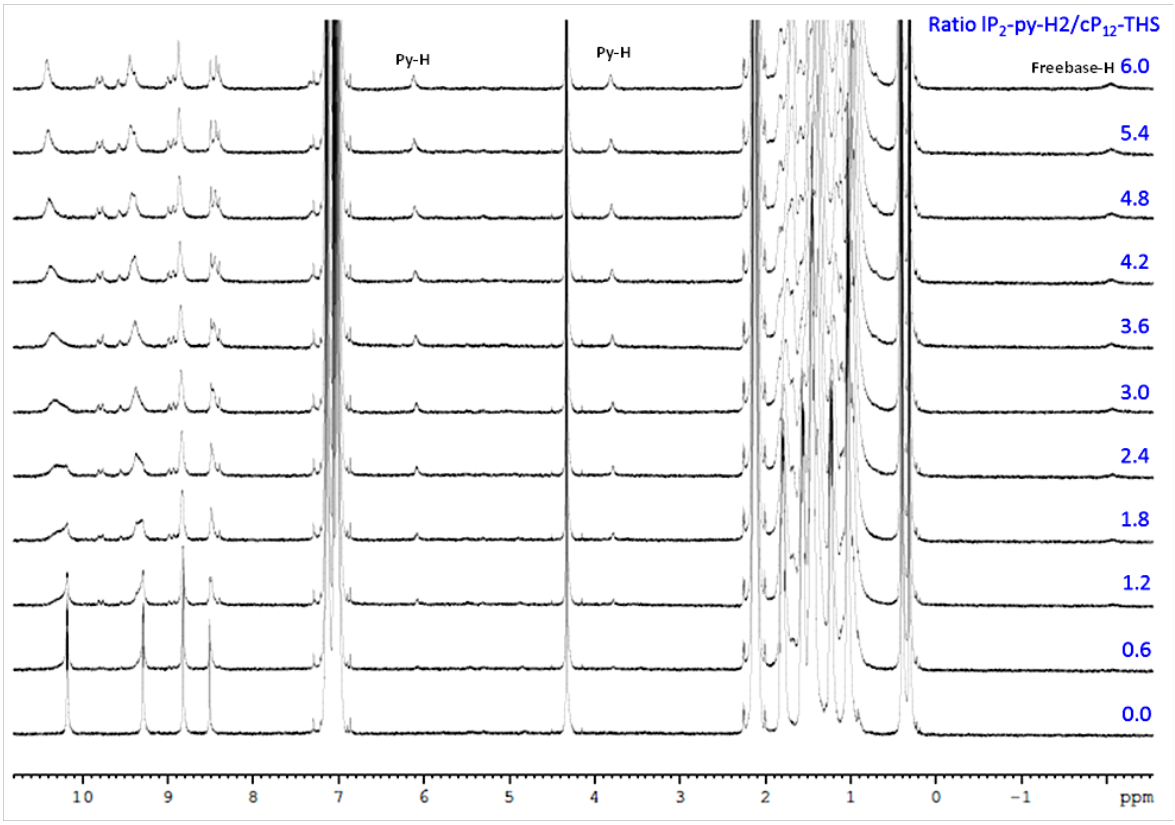


*Figure S9: ^{1}H-NMR titration of **c-P12** with **P2Py2** (toluene-d8, 298 K, 500 MHz, [**c-P12**] = 0.08 mM) and assignment of ratio of **P2Py2/c-P12***

^{1}H-NMR titration analysis was performed to confirm the self-assembly of the complexes. Upon adding dimer **P2Py2** to 12-ring **c-P12**, the appearance of new species was observed (Figure S10). The protons of the pyridyl substituent of the freebase-dimer display tremendous high-field shifts: $\Delta\delta$ = 5.27 and = 2.06, compared to the resonances at 7.66 and 8.91 ppm of the corresponding protons in the pure dimer. This shift is consistent with the coordination of the pyridyl groups to the Zn centers of the porphyrin. The porphyrin system possesses a strong ring-current that leads to the high field shift of the bound pyridyl-protons.

MALDI-ToF of the ring-dimer-ring $(c\text{-}P12)_2\cdot(P2Py4)_6$ complex

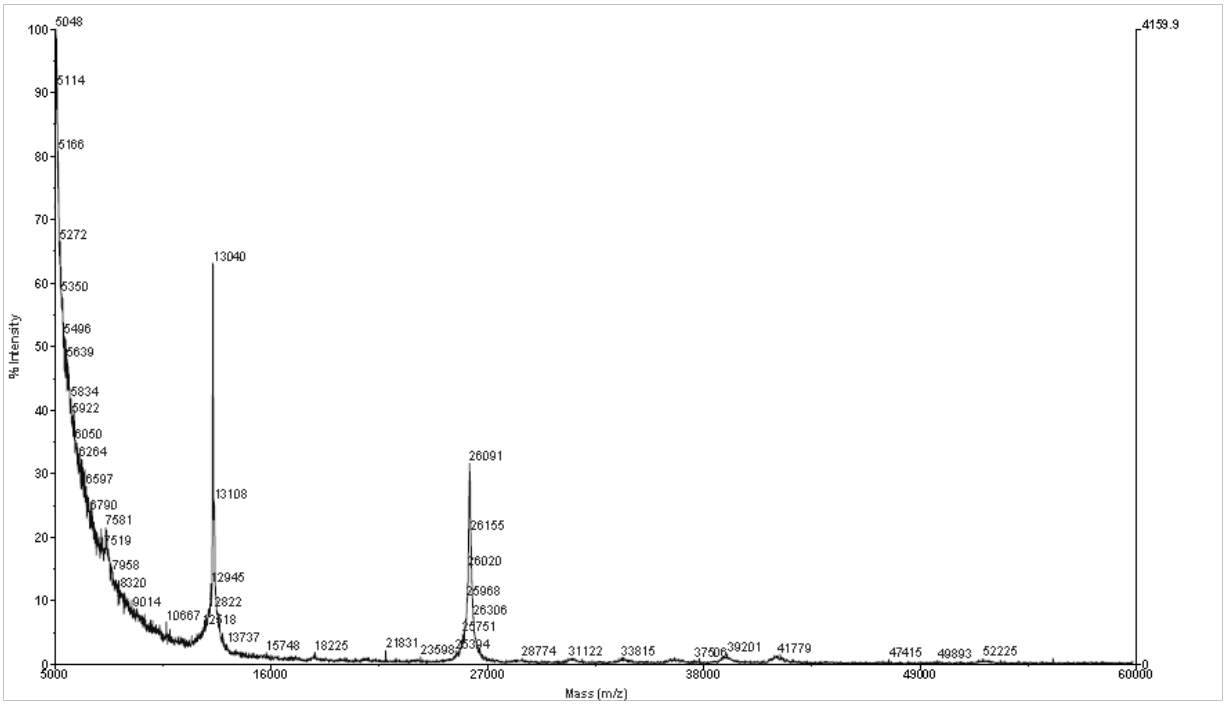


Figure S10: MALDI-ToF analysis of the ***(c-P12)$_2$·(P2Py4)$_6$*** *complex; full range (spectrum acquired by the EPSRC National Mass Spectrometry Center at Swansea University).*

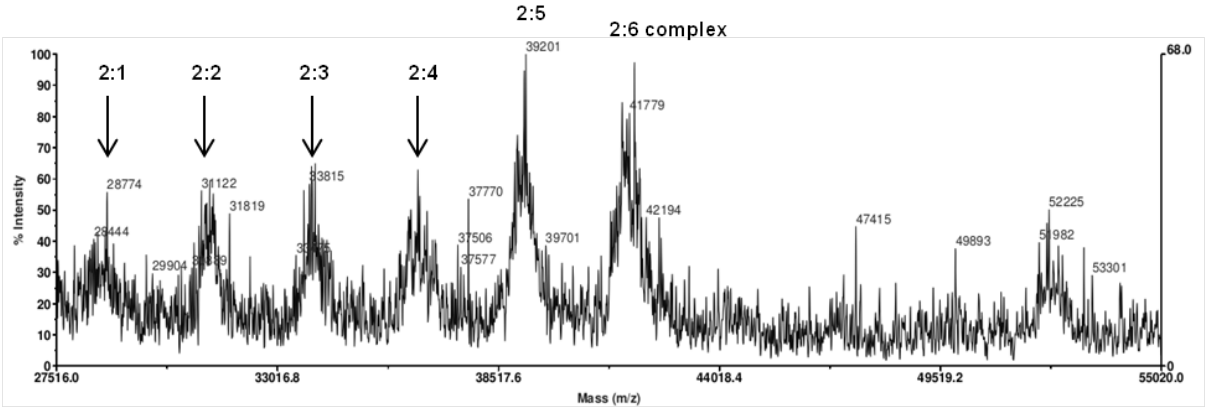
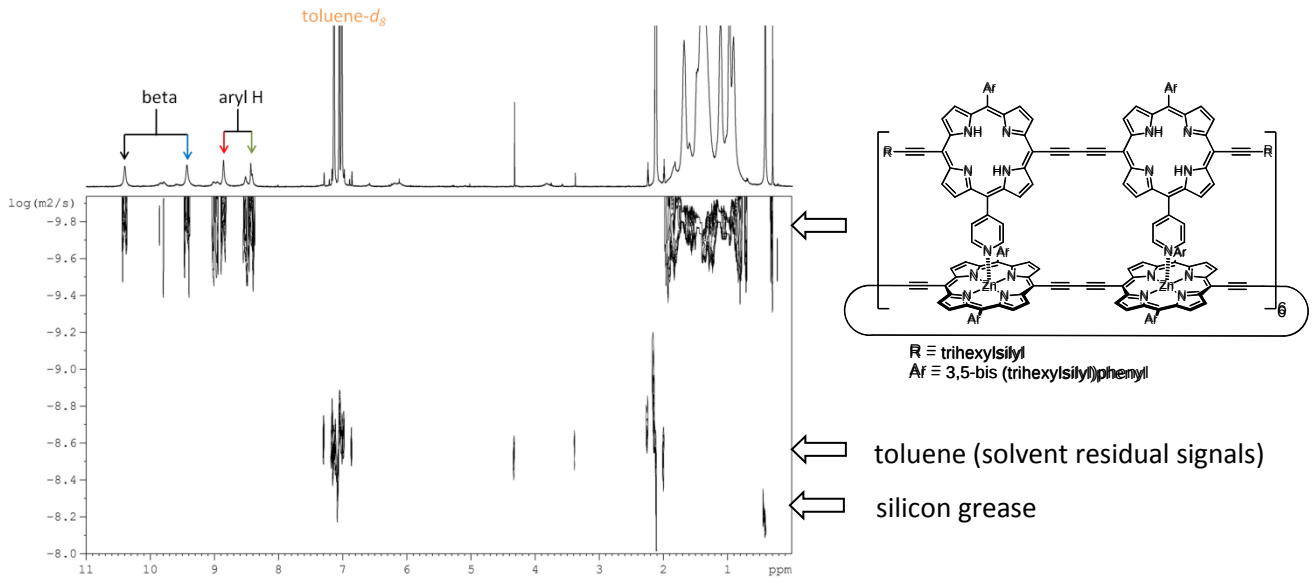


Figure S11: MALDI-ToF analysis of the (c-P12)$_2$·(P2Py4)$_6$ complex; zoom in (spectrum acquired by EPSRC National Mass Spectrometry Center at Swansea University).

The self-assembly between the 12-ring **c-P12$_{C8}$** and **P2Py4** was analyzed by MALDI-ToF. The two major peaks correspond to ***c*-P12$_{C8}$** (*m/z* 13040, expected 13018) and **(*c*-P12$_{C8}$)$_2$** aggregate (*m/z* 26091, expected 26036). When looking at the magnified spectrum, six minor peaks were found, corresponding to the expected mass for **(*c*-P12$_{C8}$)$_2$·(P2Py4)$_6$** (*m/z* 41779, expected 41024), **(*c*-P12$_{C8}$)$_2$·(P2Py4)$_5$** (*m/z* 39201, expected 38526), **(*c*-P12$_{C8}$)$_2$·(P2Py4)$_4$** (*m/z* 36508, expected 36028), **(*c*-P12$_{C8}$)$_2$·(P2Py4)$_3$** (*m/z* 33815, expected 33530), **(*c*-P12$_{C8}$)$_2$·(P2Py4)$_2$** (*m/z* 31122, expected 31032) and **(*c*-P12$_{C8}$)$_2$·(P2Py4)** (*m/z* 28444, expected 28534), respectively.

^{1}H-DOSY of *c*-P12$_{THS}$·(P2py2)$_6$, *c*-P12$_{THS}$ and P2py2

a)



b)

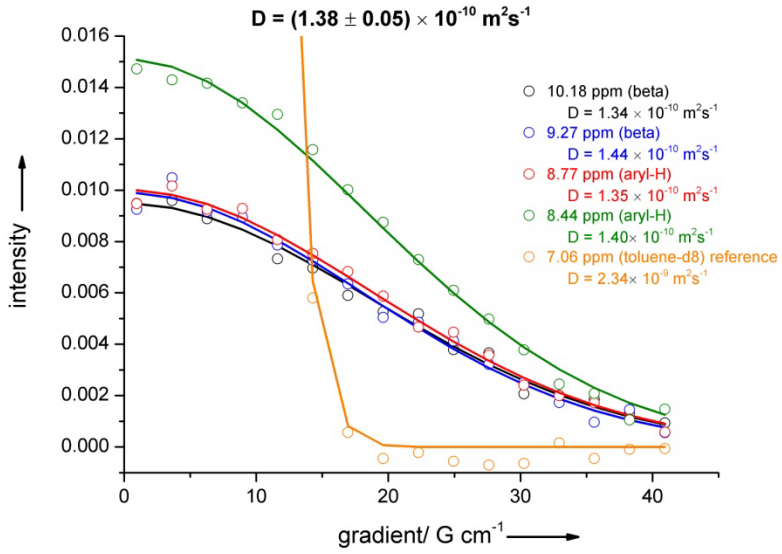
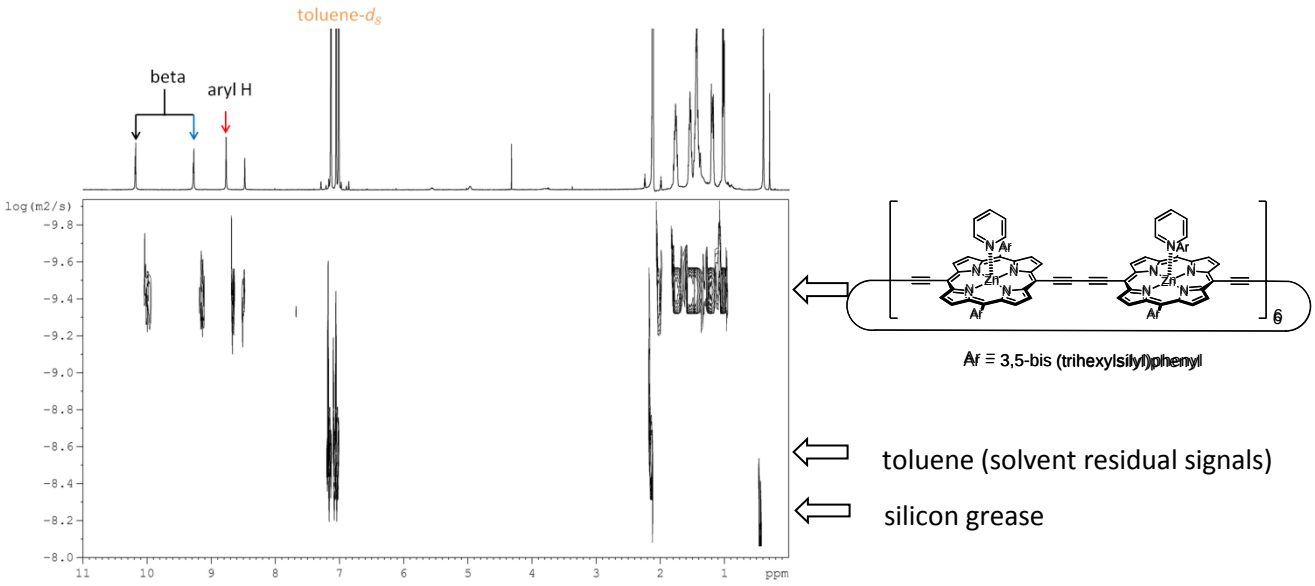


*Figure S12: ^{1}H-DOSY of **c-P12$_{THS}$·(P2py2)$_6$** in toluene-d8 at 298 K measured at 500 MHz with Δ = 100 ms, δ = 4 ms and g = 0.96–41 G cm^{-1}. a) DOSY plot (made by TOPSPIN software version 2.1) b) Fitted diffusion decay curves and resulting diffusion coefficients. The diffusion coefficients from four proton resonances at the core of the molecule (two porphyrin-beta-protons and two aryl protons of the **c-P12$_{THS}$** part) were used to calculate the diffusion coefficient.*

The DOSY plot of ***c*-P12$_{THS}$·(P2py2)$_6$** shows that all protons corresponding to the complex diffuse at the same rate, which verifies the integrity of the complex. As expected, the diffusion coefficients obtained from the 1:6

complex show that the complex diffuses less rapidly than either ***c*-P12$_{THS}$** or **P2py2**, implying that the hydrodynamic radius of the complex is larger than the radii of its components.

a)



b)

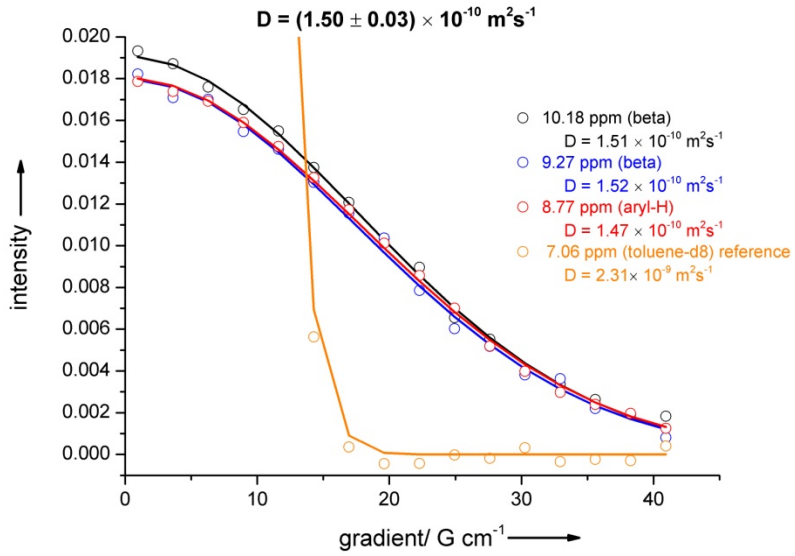
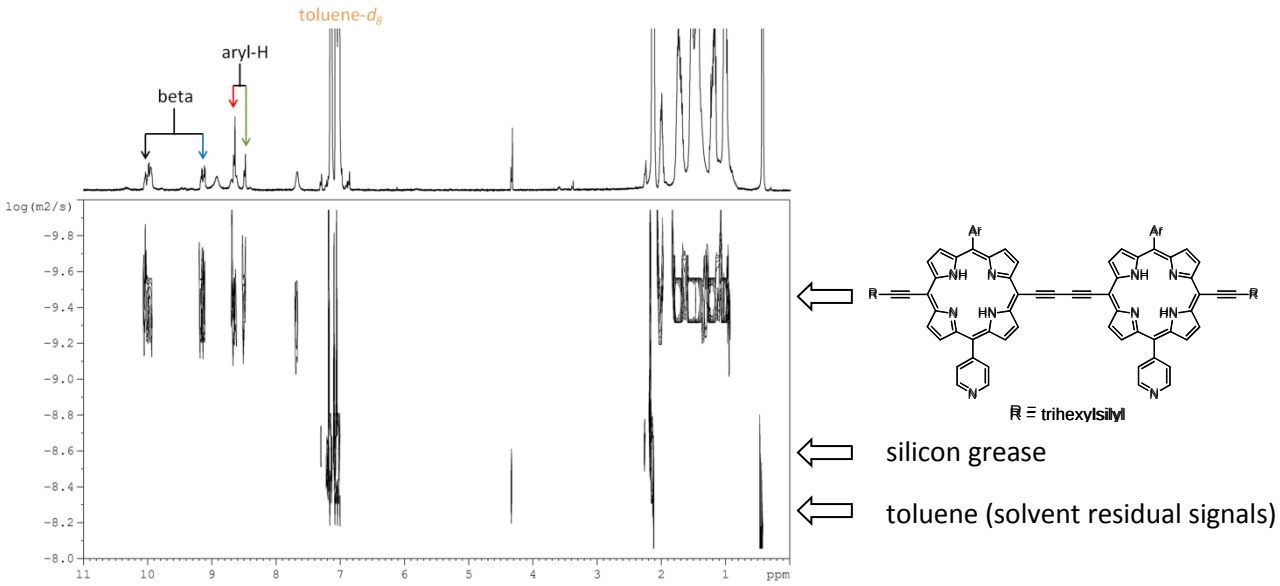


*Figure S13: ^{1}H-DOSY of **c-P12$_{THS}$** in toluene-d8 at 298 K measured at 500 MHz with Δ = 100 ms, δ = 4 ms and g = 0.96–41 G cm^{-1}. a) DOSY plot was made by TOPSPIN software version 2.1 b) Fitted diffusion decay curves and resulting diffusion coefficients. Diffusion coefficients from four proton resonances at the core of the molecule (two porphyrin-beta protons and aryl protons) were used to calculate the diffusion coefficient.*

a)



b)

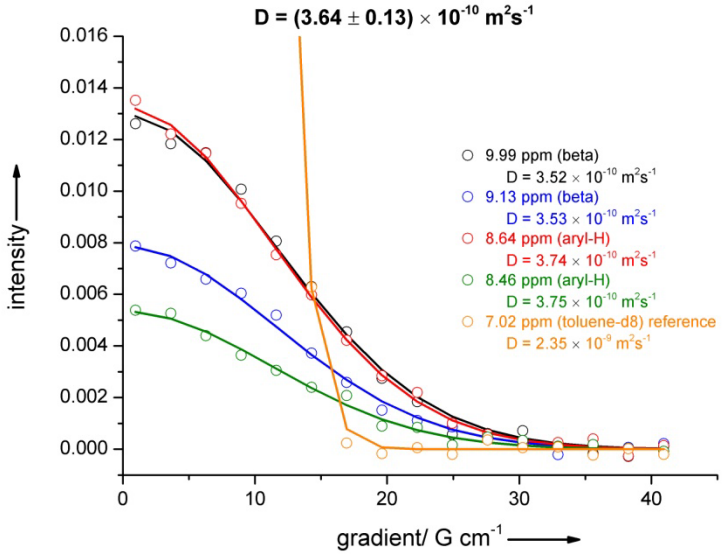


*Figure S14: ^{1}H-DOSY of **P2py2** in toluene-d8 at 298 K measured at 500 MHz with Δ = 100 ms, δ = 4 ms and g = 0.96–41 G cm^{-1}. a) DOSY plot was made by TOPSPIN software version 2.1 b) Fitted diffusion decay curves and resulting diffusion coefficients. Diffusion coefficients from four proton resonances at the core of the molecule (two porphyrin-beta protons and two aryl protons) were used to calculate the diffusion coefficient.*

References

(1) O'Sullivan, M. C.; Sprafke, J. K.; Kondratuk, D. V.; Rinfray, C.; Claridge, T. D. W.; Saywell, A.; Blunt, M. O.; O'Shea, J. N.; Beton, P. H.; Malfois, M.; Anderson, H. L. *Nature* **2011**, *469*, 72.

(2) Hoffmann, M.; Karnbratt, J.; Chang, M.-H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 4993.

(3) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.

(4) Gaefke, G.; Höger, S. *Synthesis* **2008**, *2008*, 2155.

(5) Grozema, F. C.; Houarner-Rassin, C.; Prins, P.; Siebbeles, L. D. A.; Anderson, H. L. *J. Am. Chem. Soc.* **2007**, *129*, 13370.

(6) Hoffmann, M.; Kärnbratt, J.; Chang, M. H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. *Angew. Chem. Int. Ed.***2008**, *47*, 4993.

(7) Kiriya, D.; Chang, H.-C.; Kitagawa, S. *J. Am. Chem. Soc.* **2008**, *130*, 5515.

(8) Féau, C.; Klein, E.; Kerth, P.; Lebeau, L. *Synth. Commun.* **2010**, *40*, 3033.