SUPPORTING INFORMATION

Cooperative Assembly of H-bonded Rosettes Inside a Porphyrin Nanoring

Petr Motloch,^a Pernille S. Bols,^b Harry L. Anderson,^{b,*} and Christopher A. Hunter ^{a,*}

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW (UK). ^b Department of Chemistry, Chemistry Research Laboratory, Oxford University, Oxford OX1 3TA (UK)

Email: herchelsmith.orgchem@ch.cam.ac.uk , harry.anderson@chem.ox.ac.uk

Table of Contents

S1: General experimental	2
S2: Synthesis	3
S3: UV-vis-NIR titrations	44
S4: DOSY Spectrum	72
S5: Molecular Modelling	73
S6: References	

S1: General experimental

The syntheses of **B**, **C**, **A** and *c*-P6 were described previously.^{1,2} The chemicals were purchased from commercial suppliers and used without further purifications unless stated otherwise. Solvents were either distilled before use or used as obtained. For chromatography, automatic chromatography systems CombiFlash R_{f}^{+} and CombiFlash R_{f}^{+} Lumen (with UV light detection at 254 nm and 280 nm and evaporative light scattering detector for Lumen) with pre-packed puriFlash columns from Interchim (silica, 25 µm) with a loading of mixtures on Celite were used. The microwave used was Biotage Initiator⁺. The reactions were monitored either by glass TLC plates coated with silica gel 60 F₂₅₄ (Merck) and the plates were inspected by UV light (254 nm) or by LCMS Waters Acquity H-class UPLC coupled with a single quadrupole Waters SQD2 with the conditions as follows: UPLC Column (see below), solvent A: Water + 0.1% formic acid; solvent B: acetonitrile or THF (see below) + 0.1% formic acid; gradient and flow rate (see below); column temperature of 40 °C, the signal was monitored at 254 nm and 280 nm.

Columns

Col1: ACQUITY UPLC CSH C18 Column, 130Å, 1.7 μm, 2.1 mm X 50 mm Col3: ACQUITY UPLC HSS T3 Column, 100Å, 1.8 μm, 2.1 mm X 50 mm

Methods

MeCN-FAST: Gradient: 0 – 2 minutes 5% – 100%B + 1 minute 100%B Flow rate: 0.6 ml/min

MeCN-SLOW: Gradient: 0 – 4 minutes 5% – 100%B + 1 minute 100%B Flow rate: 0.6 ml/min

THF-FAST: Gradient: 0 – 2 minutes 5% – 80%B + 1 minute 80%B Flow rate: 0.4 ml/min

THF-SLOW: Gradient: 0 – 4 minutes 5% – 80%B + 1 minute 80%B Flow rate: 0.4 ml/min

THF_FAST_5%-35%: Gradient of 0-2 minutes 5% – 35%B + 1 minute 100%B Flow rate: 0.4 ml/min

¹H and ¹³C NMR spectra were recorded on Bruker 400 MHz Avance III HD SmartProbe Spectrometers at 400 MHz for ¹H, 128 MHz for ¹¹B, 101 MHz for ¹³C or on a Bruker 500 MHz AVIII HD SmartProbe Spectrometer at 500 MHz for ¹H and 126 MHz for ¹³C. All chemicals shift are quoted in ppm and were referenced to the residual peaks of used solvents: CDCl₃ (¹H: 7.26 ppm; ¹³C: 77.00 ppm), CD₃OD (¹H: 3.31 ppm; ¹³C: 49.00 ppm), d⁶-DMSO (¹H: 2.50 ppm; ¹³C: 39.52 ppm). Coupling constants *J* are stated in Hz. FT-IR spectra were measured on a Bruker Alpha spectrometer. HR-MS spectra were obtained on a Waters Xevo G2-S, Waters Vion IMS Qtof or Waters LCT Premier by electrospray-ionisation of samples. Melting points were recorder on a Mettler-Toledo MP90 system. Elemental analysis was performed by the Microanalysis facility at the Department of Chemistry at the University of Cambridge.

S2: Synthesis

Synthesis of 1



A mixture of 4,6-dichloropyrimidin-2-amine (689 mg, 4.20 mmol), 3-picolylamine (1 mL, 1 g, 9.8 mmol), K_2CO_3 (437 mg, 3.17 mmol) and *t*BuOH (15 mL) were heated at 50 °C for 4 days. The mixture was evaporated and water (20 mL) was added. The mixture was then sonicated for 2 minutes. The obtained solid was collected by suction and dried overnight in vacuum oven at 40 °C to provide the title compound (831 mg, 84% yield) as a white solid.

¹H NMR (CD₃OD/CDCl₃, 400 MHz, 298 K): δ 8.47 (d, J = 1.5 Hz, 1H), 8.39 (d, J = 3.5 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.0, 5.0 Hz, 1H), 5.85 (s, 1H), 4.53 (s, 2H). ¹³C NMR (d⁶-DMSO, 126 MHz, 298 K): δ 164.0, 163.0, 157.6, 149.0, 148.2, 135.4, 135.2, 123.6, 92.8, 41.08.

HR-MS (ESI): Calculated for $C_{10}H_{11}N_5Cl [M+H]^+ 236.0703$, found: 236.0693 ($\Delta = 4.2$ ppm)

FT-IR (thin film): 1640, 1575, 1551, 1469, 1427, 1369, 1331, 1150 cm⁻¹.

MP: 198 – 200 °C





A mixture of 4,6-dichloropyrimidin-2-amine (776 g, 4.64 mmol), 3-(2-aminoethyl)pyridine (1 mL, 1 g, 7.5 mmol), K_2CO_3 (490 mg, 3.55 mmol) and *t*BuOH (18 mL) were heated at 50 °C for 2 days. The mixture was evaporated and water (20 mL) was added. The mixture was then sonicated for 30 minutes. The obtained solid was collected by suction and dried overnight in vacuum oven at 40 °C to provide the title compound (840 mg, 73% yield) as a pale yellow solid.

¹**H** NMR (CD₃OD, 400 MHz, 298 K): δ 8.41 (d, *J* = 2.0 Hz, 1H), 8.37 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.74 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.36 (dd, J = 8.0, 5.0 Hz, 1H), 5.78 (s, 1H), 3.59 (s, 2H), 2.92 (t, J = 7.0 Hz, 2H).

¹³C NMR (d⁶-DMSO, 126 MHz, 298 K): δ 164.1, 163.1, 157.3, 150.0, 147.5, 136.5, 135.1, 123.6, 92.8, 41.3, 32.0.

HR-MS (ESI): Calculated for $C_{11}H_{13}N_5Cl [M+H]^+ 250.0859$, found: 250.0850 ($\Delta = 3.6$ ppm)

FT-IR (thin film): 3276, 2371, 1575, 1478, 1425, 1362 cm⁻¹.

MP: 152 – 157 °C





A mixture of 4,6-dichloropyrimidin-2-amine (800 mg, 4.88 mmol), 4-picolylamine (3 mL, 3.18 g, 29 mmol), K₂CO₃ (676 mg, 4.89 mmol) and *t*BuOH (15 mL) were heated at 60 °C overnight. The mixture was evaporated and water (30 mL) was added. The mixture was then sonicated for 30 minutes and the mixture dissolved. After standing, the form solid was collected and dried in the vacuum oven overnight to provid the title compound (727 mg, 63% yield) as a pale yellow solid.

¹H NMR (CD₃OD, 400 MHz, 298 K): δ 8.44 (d, J = 6.0 Hz, 2H), 7.35 (d, J = 6.0 Hz, 2H), 5.90 (s, 1H), 4.60 (s, 2H).
¹³C NMR (d⁶-DMSO, 126 MHz, 298 K): δ 164.2, 163.0, 157.8, 149.6, 148.9, 122.3, 92.8, 42.3.

HR-MS (ESI): Calculated for $C_{10}H_{11}N_5Cl [M+H]^+ 236.0697$, found: 236.0694 ($\Delta = 1.5$ ppm)

FT-IR (thin film): 3312, 3200, 2387, 1573, 1556, 1496, 1475, 1417, 1360, 1314, 1249 cm⁻¹.

MP: $> 136 \,^{\circ}$ C (carbonisation)





A mixture of 4,6-dichloropyrimidin-2-amine (1.06 g, 6.46 mmol), 4-(2-aminoethyl)pyridine (1.2 mL, 1.2 g, 10 mmol), K_2CO_3 (0.76 g, 5.5 mmol) and *t*BuOH (15 mL) were heated at 50 °C for 3 days. The mixture was evaporated and water (30 mL) was added. The mixture was then sonicated for 20 minutes. The obtained solid was collected by suction and dried overnight in vacuum oven at 40 °C to provide the title compound (1.43 g, 89% yield) as a yellow solid.

¹H NMR (CD₃OD, 400 MHz, 298 K): δ 8.43 – 8.42 (m, 2H), 7.33 (d, *J* = 6.0 Hz, 2H), 5.79 (s, 1H), 3.61 (s, 2H), 2.93 (t, *J* = 7.0 Hz, 2H). ¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 165.7, 164.4, 162.8, 151.7, 149.9, 126.1, 94.8, 41.9, 35.8.

HR-MS (ESI): Calculated for $C_{11}H_{13}N_5Cl [M+H]^+ 250.0854$, found: 250.0850 ($\Delta = 1.4$ ppm)

FT-IR (thin film): 3277, 2397, 1574, 1481, 1420, 1362 cm⁻¹.

MP: 157 °C (carbonisation)



Synthesis of mA1



1 (337 mg, 1.43 mmol) was flushed with nitrogen in a MW vial. *n*-Pentylamine (1 mL, 0.9 g, 10 mmol) was added and the mixture was heated in microwave at 160 °C for 2 hours. A saturated solution of NaHCO₃ (15 mL) was added and the mixture was extracted with CH₂Cl₂/MeOH(20:1, 2 × 50mL) and CH₂Cl₂(2 × 50 mL). The organic phase was dried over MgSO₄, evaporated and loaded to Celite. A combiflash of the residue on silica (CH₂Cl₂/MeOH: MeOH 0% \rightarrow 20%) provided the title compound (253 mg, 62% yield) as yellowish oil.

¹**H** NMR (CD₃OD, 400 MHz, 298 K): δ 8.50 (s, 1H), 8.38 (d, J = 4.0 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.34 (dd, J = 7.0, 5.0 Hz, 1H), 4.89 (s, 1H), 4.46 (s, 2H), 3.08 (t, J = 7.0 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.29 (d, J = 2.5 Hz, 4H), 0.88 (t, J = 6.0 Hz, 3H). ¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 165.2, 165.1, 164.0, 149.1, 148.4, 137.7, 137.1, 125.1, 74.0, 43.2, 42.3, 30.3, 30.1, 23.5, 14.4.

HR-MS (ESI): Calculated for $C_{15}H_{23}N_6$ [M+H]⁺ 287.1979, found: 287.1976 ($\Delta = 0.98$ ppm)

FT-IR (thin film): 3309, 2955, 2928, 2858, 1575, 1505, 1455, 1424, 1355 cm⁻¹.



Synthesis of mA2



2 (123 mg, 0.493 mmol) was flushed with nitrogen in a MW vial. *n*-Pentylamine (1 mL, 0.9 g, 10 mmol) was added and the mixture was heated in microwave at 150 °C for 7 hours. A saturated solution of NaHCO₃ (10 mL) was added and the mixture was extracted with dichloromethane (4 × 30 mL). The organic phase was dried over MgSO₄, evaporated and loaded to Celite. A combiflash of the residue on silica (CH₂Cl₂/MeOH: MeOH 0% \rightarrow 10%) provided the title compound (124 mg, 84% yield) as orange dense oil.

¹**H** NMR (CD₃OD, 400 MHz, 298 K): δ 8.41 (s, 1H), 8.36 (d, J = 4.0 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.33 (dd, J = 7.5, 5.0 Hz, 1H), 3.45 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 7.0 Hz, 2H), 2.88 (t, J = 7.0 Hz, 2H), 1.56 – 1.53 (m, 2H), 1.35 – 1.30 (m, 4H), 0.91 (t, J = 6.0 Hz, 3H).

¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 165.1, 165.0, 163.9, 150.4, 147.9, 138.7, 137.4, 125.1, 73.6, 43.2, 42.3, 33.8, 30.3, 30.2, 23.5, 14.4.

HR-MS (ESI): Calculated for $C_{16}H_{25}N_6$ [M+H]⁺ 301.2141, found: 301.2142 ($\Delta = 0.3$ ppm)

FT-IR (thin film): 3310, 3189, 2953, 2928, 2858, 1573, 1526, 1458, 1429, 1358 cm⁻¹.



Synthesis of pA1



3 (105 mg, 0.45 mmol) was flushed with nitrogen in a MW vial. *n*-Pentylamine (1 mL, 0.9 g, 10 mmol) was added and the mixture was heated in microwave at 160 °C for 3 hours. A saturated solution of NaHCO₃ (15 mL) was added and the mixture was extracted with CH₂Cl₂/MeOH (20:1, 2×50 mL) and CH₂Cl₂(2×50 mL). The organic phase was dried over MgSO₄, evaporated and loaded to Celite. A combiflash of the residue on silica (CH₂Cl₂/MeOH: MeOH 0% \rightarrow 20%) provided the title compound (71 mg, 55% yield) as orange dense oil.

¹**H** NMR (CD₃OD, 400 MHz, 298 K): δ 8.42 (d, J = 5.5 Hz, 2H), 7.35 (d, J = 5.0 Hz, 2H), 4.86 (s, 1H), 4.47 (s, 2H), 3.08 (t, J = 7.0 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.29 (d, J = 3.0 Hz, 4H), 0.88 (t, J = 6.5 Hz, 3H).

¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 165.2, 165.2, 163.9, 152.3, 149.9, 123.6, 74.0, 44.7, 42.3, 30.3, 30.1, 23.5, 14.4.

HR-MS (ESI): Calculated for $C_{15}H_{23}N_6$ [M+H]⁺ 287.1979, found: 287.1975 ($\Delta = 1.26$ ppm)

FT-IR (thin film): 3302, 3175, 2953, 2926, 2587, 1572, 1497, 1446, 1355, 1312, 1219, 1204 cm⁻¹.



Synthesis of pA2



4 (100 mg, 0.40 mmol) was flushed with nitrogen in a MW vial. *n*-Pentylamine (1 mL, 0.9 g, 10 mmol) was added and the mixture was heated in microwave at 160 °C for 5 hours. A saturated solution of NaHCO₃ (10 mL) and water (10 mL) were added and the mixture was extracted with CH₂Cl₂/MeOH (20:1, 50 mL) and CH₂Cl₂(3×50 mL). The organic phase was dried over MgSO₄, evaporated and loaded to Celite. A combiflash of the residue on silica (CH₂Cl₂/MeOH: MeOH 0% \rightarrow 10%) provided the title compound (97 mg, 81% yield) as yellow oil.

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.53 (d, J = 6.0 Hz, 2H), 7.15 (d, J = 6.0 Hz, 2H), 4.80 (s, 1H), 4.60 – 4.41 (m, 3H), 3.51 (dd, J = 13.0, 7.0 Hz, 2H), 3.13 (dd, J = 13.0, 7.0 Hz, 2H), 2.89 (t, J = 7.0 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.39 – 1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 164.1, 163.8, 162.2, 150.0, 148.0, 124.1, 72.5, 41.7, 41.7, 35.1, 29.1, 29.0, 22.4, 14.0.

HR-MS (ESI): Calculated for $C_{16}H_{25}N_6$ [M+H]⁺ 301.2135, found: 301.2131 (Δ = 1.30 ppm)

FT-IR (thin film): 3310, 2954, 2927, 2857, 2421, 1555, 1494, 1455, 1430, 1417, 1357, 1219 cm⁻¹.





To a solution of 3-(pyridin-3-yl)propan-1-ol (1 mL, 1.06 g, 7.7 mmol) and NEt₃ (3 mL) in CH_2Cl_2 (50 mL) was added methanesulfonyl chloride (0.8 mL, 10.3 mmol, 1.4 eq) at 0 °C in small parts over the period of 90 minutes. The reaction mixture was stirred at 0 °C for additional 30 minutes and then diluted with CH_2Cl_2 (50 mL). The still-cool solution was washed with H_2O (2×30 mL) and brine (30 mL), dried with MgSO₄ and solvents were removed under reducer pressure (at no more than 30 °C). A combiflash of the residue on silica gel (PE/EtOAc, EtOAc: 0%→100%) provided the title compound as yellowish liquid (1.65 g; quant.)

(This compound is quite unstable even when stored in fridge.)

¹**H NMR (CDCl₃, 400 MHz, 298 K**): δ 8.53 – 8.42 (m, 2H), 7.52 (dt, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.23 (dd, J = 8.0, 5.0 Hz, 1H), 4.24 (t, *J* = 6.0 Hz, 2H), 3.01 (s, 3H), 2.80 – 2.74 (t, *J* = 7.0 Hz, 2H), 2.13 – 2.05 (m, 2H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): 149.9, 147.9, 135.9, 135.6, 123.4, 68.6, 37.4, 30.4, 28.8.



Synthesis of 5-BH₃



5 (2.41 g, 11.1 mmol) was flushed with nitrogen. Then THF (20 mL) was added, which produced slurry solution. The reaction mixture was cooled to -78 °C. To this solution, BH₃•SMe₂(6.0 mL, 2.0M solution in THF, 12 mmol) was added dropwise at -78 °C. After 30 minutes of stirring, the cooling bath was removed. After stirring at RT for 1 hour, the conversion was checked by TLC (10:1 EtOAc/MeOH) and additional BH₃•SMe₂(1.0 mL, 2.0M solution in THF, 2 mmol; altogether 14 mmol) was added dropwise at -78 °C. The solution was stirred for 15 minutes and the cooling bath was removed. After additional 30 minutes of stirring, the mixture was cooled again to -78 °C and methanol (9 mL) was added dropwise. After 15 minutes, the cooling bath was removed and the mixture was allowed to heat to room temperature and then solvents were removed under reduced pressure. A combiflash of the residue on silica (Celite loading, PE/EtOAc; EtOAc: $0\% \rightarrow 100\%$) provided the title compound (2.25 g, 88% yield) as transparent oil, which crystalise upon standing in a freezer over a couple of days/weeks to form a white solid.

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.45 – 8.43 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.25 (td, *J* = 6.0, 1.0 Hz, 2H), 3.02 (d, *J* = 1.0 Hz, 3H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.75 – 2.15 (br, 3H), 2.16 – 2.02 (m, 2H).

¹**H** NMR (CDCl₃, 400 MHz, 298 K, ¹¹B decoupled): δ 8.45 – 8.43 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.45 (dd, J = 8.0, 6.0 Hz, 1H), 4.24 (t, J = 6.0 Hz, 2H), 3.02 (d, J = 1 Hz, 3H), 2.83 (t, J = 8.0 Hz, 2H), 2.55 (s, 3H), 2.16 – 2.02 (m, 2H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 147.2, 145.4, 139.2, 138.5, 125.2, 68.11, 37.4, 29.9, 28.6.

¹¹**B** NMR (CDCl₃, 128 MHz, 298 K, normal glass): δ –12.4 (d, *J* = 88 Hz)

HR-MS (ESI): Calculated for C₉H₁₅BNO₃S [M–H]⁺ 228.0866, found: 228.0865 ($\Delta = 0.4$ ppm)

FT-IR (thin film): 2936, 2360, 2310, 2271, 1620, 1585, 1486, 1443, 1346, 1331, 1164.

MP: 51 – 53 °C

LCMS Method: Col1-MeCN-FAST





Synthesis of 6-BH₃ and 6



NaH (60% in mineral oil, 255 mg, 6.38 mmol) was flushed with nitrogen. THF (10 mL) was added and the mixture was cooled to 0 °C. Then diethyl-2-butylmalonate (1.45 mL, 6.52 mmol) was added dropwise (the solution became clear after the addition). **5-BH**₃ (718 mg, 3.13 mmol) was added as a solid. After 1 hour of stirring, the cooling bath was removed. The mixture was heated at 60 °C for 4 hours and after cooling to RT, water (20 mL) was added and the mixture was extracted with dichloromethane (4 × 30 mL). The organic phase was dried over MgSO₄ and the solvents were removed under reduced pressure. A combiflash of the residue on silica (Celite loading, PE/EtOAc, EtOAc: 0%→50%) provided after drying in vacuum oven overnight products **6-BH**₃ (655 mg, 60% yield) and **6** (219 mg, 21% yield) as transparent dense liquids (**6-BH**₃ crystalise upon storage in freezer over a couple of weeks).

LCMS Method: Col1-MeCN-SLOW

Compound **6-BH**₃:

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.42 – 8.40 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.21 – 4.06 (m, 4H), 3.00 – 2.11 (br, 3H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.91 – 1.78 (m, 4H), 1.59 – 1.46 (m, 2H), 1.32 – 1.23 (m, 2H), 1.20 (t, *J* = 7.0 Hz, 6H), 1.11 – 1.03 (m, 3H), 0.85 (t, *J* = 7.0 Hz, 3H).

¹**H** NMR (CDCl₃, 400 MHz, 298 K, ¹¹B decoupled): δ 8.42 – 8.40 (m, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 8.0, 6.0 Hz, 1H), 4.21 – 4.08 (m, 4H), 2.66 (t, J = 8.0 Hz, 2H), 2.55 (s, 3H), 1.92 – 1.77 (m, 4H), 1.60 – 1.45 (m, 2H), 1.34 – 1.23 (m, 2H), 1.20 (t, J = 7.0 Hz, 6H), 1.15 – 1.01 (m, 2H), 0.86 (t, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 171.4, 147.1, 145.1, 139.6, 138.8, 124.9, 61.1, 57.2, 32.8, 32.2, 31.7, 26.1, 25.1, 22.8, 14.00, 13.8.

¹¹**B** NMR (CDCl₃, 128 MHz, 298 K, normal glass): δ –12.4 (d, *J* = 79 Hz)

HR-MS: Calculated for $C_{21}H_{34}BN_2O_4$ [M+CH₃CN-H]⁺ 389.2612, found: 389.2627 ($\Delta = 3.9$ ppm)

FT-IR (thin film): 2959, 2935, 2872, 2371, 1725, 1619, 1484, 1463, 1444 cm⁻¹.

MP: 37 – 40 °C

Compound **6**:

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.38 – 8.36 (m, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.13 (dd, J = 8.0, 5.0 Hz, 1H), 4.09 (q, J = 7.0 Hz, 4H), 2.56 (t, J = 7.5 Hz, 2H), 1.91 – 1.71 (m, 4H), 1.55 – 1.37 (m, 2H), 1.28 – 1.17 (m, 2H), 1.14 (t, J = 7.0 Hz, 6H), 1.06 – 0.98 (m, 2H), 0.81 (t, J = 7.5 Hz, 3H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 171.5, 149.8, 147.3, 136.8, 135.6, 123.1, 60.9, 57.2, 32.9, 31.9, 31.5, 25.9, 25.4, 22.7, 13.9, 13.7.

HR-MS: Calculated for $C_{19}H_{30}NO_4$ [M+H]⁺ 336.2175, found: 336.2173 ($\Delta = 0.6$ ppm)

FT-IR (thin film): 2958, 2935, 2872, 1725, 1575, 1478, 1463, 1423 cm⁻¹.







Synthesis of mB3-BH₃ and mB3



NaH (60% in mineral oil, 300 mg, 7.5 mmol) was flushed with nitrogen and DMF (6 mL) was added. The mixture was cooled to 0 °C and urea (1.18 g, 19.6 mmol) was added. After 2 hours of stirring, **6-BH₃** (646 mg, 1.85 mmol) in DMF (7 mL) was added at 0 °C. The mixture was stirred overnight at RT and a saturated solution of NH₄Cl (5 mL) was added with cooling to 0 °C. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 × 40 mL). The collected organic phase was dried over MgSO₄ and the solvents were removed under reduced pressure (60 °C, <14 mBar). A combliflash of residue on silica (Celite loading, PE/EtOAc, EtOAc: 0%→100%) provided after drying in vacuum oven overnight products **mB3-BH₃** (350 mg, 60% yield) and **mB3** (117 mg, 21% yield) as white crystalline solids.

LCMS Method: Col3-MeCN-FAST

Compound **mB3-BH**₃:

¹**H** NMR (CD₃OD, 400 MHz, 298 K): δ 8.42 (s, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.0, 6.0 Hz, 1H), 2.95 – 2.09 (br, 3H), 2.69 (t, J = 7.5 Hz, 2H), 1.97 – 1.86 (m, 4H), 1.58 – 1.50 (m, 2H), 1.32 – 1.22 (m, 2H), 1.22 – 1.13 (m, 2H), 0.87 (t, J = 7.0 Hz, 3H).

¹**H** NMR (CD₃OD, 400 MHz, 298 K, ¹¹B decoupled): δ 8.42 (s, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.0, 6.0 Hz, 1H), 2.69 (t, J = 7.5 Hz, 2H), 2.54 (s, 3H), 1.97 – 1.86 (m, 4H), 1.58 – 1.51 (m, 2H), 1.32 – 1.22 (m, 2H), 1.22 – 1.13 (m, 2H), 0.87 (t, J = 7.0 Hz, 3H).

¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 174.9, 151.2, 148.4, 146.4, 141.0, 140.6, 126.5, 56.7, 40.1, 38.6, 33.1, 28.1, 27.1, 23.6, 14.0.

¹¹B NMR (CD₃OD, 128 MHz, 298 K, normal glass): δ –12.6

HR-MS: Calculated for $C_{16}H_{23}BN_3O_3$ [M–H]⁺ 316.1832, found: 316.1844 ($\Delta = 3.8$ ppm)

FT-IR (thin film): 3326, 3104, 2959, 2931, 2860, 2368, 1753, 1699, 1619, 1585, 1486, 1441, 1421, 1384, 1335, 1336, 1321 cm⁻¹.

MP: > 161° C (decompose and produce gas)

Compound **mB3**:

This product is characterised below.





Synthesis of mB3



To a mixture of **mB3-BH**₃ (274 mg, 0.86 mmol) and methanol (15 mL) [note: *not dissolved even at* RT] at 0 °C, HCl (*conc.*, 100 µL, 1.2 mmol) was added. After 15 minutes, the cooling bath was removed and the mixture was stirred at RT until full conversion was reached (2 hours), which was checked by LCMS. A saturated solution of NaHCO₃ (4 mL) was added (pH > 8) and then a saturated solution of NH₄Cl (30 mL) was added (pH < 7). The mixture was extracted with dichloromethane (4 × 50 mL), dried over MgSO₄, the solvents were removed under reducer pressure. A combiflash of the residue on silica (Celite loading, PE/EtOAc, EtOAc: 0%→100%) provided after drying in vacuum oven overnight the title compound (170 mg, 65% yield) as a white crystalline solid.

¹**H** NMR (CD₃OD, 400 MHz, 298 K): $\delta 8.37 - 8.35$ (m, 2H), 7.67 - 7.64 (m, 1H), 7.35 (ddd, J = 8.0, 5.0, 1.0 Hz, 1H), 2.64 (t, J = 7.5 Hz, 2H), 2.00 - 1.85 (m, 4H), 1.58 - 1.50 (m, 2H), 1.33 - 1.22 (m, 2H), 1.21 - 1.10 (m, 2H), 0.86 (t, J = 7.0 Hz, 3H). ¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 175.0, 151.4, 150.0, 147.8, 139.0, 138.2, 125.2, 56.9, 40.0, 39.0, 33.4, 28.1, 27.4, 23.7, 14.0.

HR-MS (ESI): Calculated for $C_{16}H_{22}N_3O_3$ [M+H]⁺ 304.1661, found: 304.1668 ($\Delta = 2.3$ ppm)

FT-IR (thin film): 3222, 3103, 2959, 2930, 2859, 1698, 1596, 1580, 1413, 1385, 1357, 1325 cm⁻¹.

MP: 184 – 186 °C

EA: Required for C₁₆H₂₁N₃O₃: C 63.35, H 6.98, N 13.85; found: C 62.92, H 7.09, N 13.66.

LCMS Method: Col3-MeCN-FAST





To a solution of 3-(pyridin-4-yl)propan-1-ol (1.29 g, 9.4 mmol) and NEt₃ (4 mL) in CH₂Cl₂ (50 mL) was added methanesulfonyl chloride (1.2 mL, 15.5 mmol, 1.6 eq) at 0 °C in small parts over the period of 90 minutes. The still-cool solution was washed with H₂O (50 mL) and brine (25 mL), dried with MgSO₄ and solvents were removed under reducer pressure (at no more than 30 °C). A combiflash of the residue on silica gel (PE/EtOAc, EtOAc: $0\% \rightarrow 100\%$) provided the title compound as transparent oil (1.53 g, 77% yield).

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.50 (dd, J = 4.5, 1.5 Hz, 2H), 7.11 (d, J = 6.0 Hz, 2H), 4.22 (t, J = 6.0 Hz, 2H), 2.99 (s, 3H), 2.76 – 2.72 (m, 2H), 2.11 – 2.04 (m, 2H). ¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 149.9, 149.2, 123.7, 68.5, 37.4, 30.9, 29.6.



Synthesis of 7-BH₃

$$\begin{array}{c} & & & \\ & &$$

7 (1.53 g, 7.11 mmol) was flushed with nitrogen. Then THF (10 mL) was added and the reaction mixture was cooled to -78 °C. To this solution, BH₃•SMe₂(4.0 mL, 2.0M solution in THF, 8 mmol) was added dropwise at -78 °C. After 30 minutes of stirring, the cooling bath was removed. After stirring at RT for 2.5 hours, the mixture was cooled again to -78 °C and methanol (3 mL) was added dropwise. After 10 minutes, the cooling bath was removed and the mixture was allowed to heat to room temperature and then solvents were removed under reduced pressure. A combiflash of the residue on silica (Celite loading, PE/EtOAc; EtOAc: $0\% \rightarrow 100\%$) provided the title compound (1.44 g, 88% yield) as transparent oil, which crystalise upon standing in the freezer over a couple of days/weeks to form a white solid.

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.47 (d, J = 6.5 Hz, 2H), 7.34 (d, J = 6.5 Hz, 2H), 4.25 (t, J = 6.0 Hz, 2H), 3.02 (s, 3H), 2.90 – 2.86 (m, 2H), 2.63 (br, 3H), 2.14 – 2.07 (m, 2H). ¹**H** NMR (CDCl₃, 400 MHz, 298 K, ¹¹B decoupled): δ 8.47 (d, J = 6.0 Hz, 2H), 7.34 (d, J = 6.0 Hz, 2H), 4.25 (t, J = 6.0 Hz, 2H), 3.03 (s, 3H), 2.90 – 2.86 (m, 2H), 2.54 (s, 3H), 2.14 – 2.07 (m, 2H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 153.7, 147.3, 125.3, 68.0, 37.5, 31.0, 29.2. ¹¹B NMR (CDCl₃, 128 MHz, 298 K, normal glass): δ –12.7 (d, *J* = 86 Hz).

HR-MS (ESI): Calculated for C₉H₁₅BNO₃S [M–H]⁺ 228.0866, found: 228.0855 (Δ = 4.7 ppm)

FT-IR (thin film): 3021, 2938, 2361, 2312, 2282, 1631, 1349, 1170 cm⁻¹.

MP: 58 °C (melts and decomposes)




Synthesis of 8-BH₃ and 8



NaH (60% in mineral oil, 334 mg, 8.35 mmol) was flushed with nitrogen. THF (10 mL) was added and the mixture was cooled to 0 °C. Then diethyl-2-butylmalonate (1.9 mL, 8.54 mmol) was added dropwise. After 30 minutes of stirring **7-BH**₃ (631 mg, 2.76 mmol) was added as a solid. The mixture was heated at 60 °C for 5 hours and then after cooling to RT, water (20 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). The organic phase was dried over MgSO₄ and the solvents were removed under reduced pressure. A combiflash of the residue on silica (Celite loading, PE/EtOAc, EtOAc: 0%→50%) provided after drying in vacuum oven overnight products **8-BH**₃ (472 mg, 49% crude yield) as transparent oil and **8** (110 mg, 23% crude yield) as yellowish oil. (*Both products contained an additional impurity and were used in the next reactions without further purification*.)

LCMS Method: Coll-MeCN-SLOW

Compound **8-BH**₃:

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.46 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 6.5 Hz, 2H), 4.22 – 4.10 (m, 4H), 2.73 (t, J = 7.5 Hz, 2H), 1.90 – 1.83 (m, 4H), 1.62 – 1.54 (m, 2H), 1.33 – 1.25 (m, 2H), 1.22 (t, J = 7.0 Hz, 6H), 1.13 – 1.05 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H).

¹**H** NMR (CDCl₃, 400 MHz, 298 K, ¹¹B decoupled): δ 8.46 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 6.0 Hz, 2H), 4.21 – 4.10 (m, 4H), 2.73 (t, J = 7.5 Hz, 2H), 2.56 (s, 3H), 1.90 – 1.83 (m, 4H), 1.62 – 1.53 (m, 2H), 1.33 – 1.27 (m, 2H), 1.22 (t, J = 7.0 Hz, 6H), 1.12 – 1.05 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H).

¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 171.5, 155.0, 147.2, 146.8, 125.2, 121.7, 61.2, 57.2, 35.2, 32.3, 31.8, 26.1, 24.3, 22.8, 14.1, 13.8.

¹¹**B** NMR (CDCl₃, 128 MHz, 298 K, normal glass): δ -13.0 (d, *J* = 93 Hz).

MS: 389.26 [M+CHC₃CN-H]⁺

FT-IR (thin film): 2959, 2935, 2872, 2362, 2308, 2280, 1725, 1630, 1562, 1504, 1463, 1439, 1367, 1258, 1200, 1169, 1086, 1024 cm⁻¹.

Compound 8:

¹**H** NMR (CDCl₃, 400 MHz, 298 K): δ 8.48 (d, J = 5.5 Hz, 2H), 7.09 (d, J = 6.0 Hz, 2H), 4.19 – 4.12 (m, 4H), 2.61 (t, J = 7.5 Hz, 2H), 1.91 – 1.83 (m, 4H), 1.57 – 1.49 (m, 2H), 1.34 – 1.24 (m, 2H), 1.21 (t, J = 7.0 Hz, 6H), 1.11 – 1.03 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H). ¹³C NMR (CDCl₃, 101 MHz, 298 K): δ 171.7, 150.7, 149.7, 123.8, 61.1, 57.3, 35.2, 32.0, 31.6, 26.1, 24.6, 22.9, 14.1, 13.9.

MS: 336.22 [M+H]⁺

FT-IR (thin film): 2958, 2936, 2872, 1728, 1601, 1464, 1415, 1367, 1257, 1200, 1160 cm⁻¹.





Synthesis of pB3

NaH (60% in mineral oil, 57 mg, 1.4 mmol) was flushed with nitrogen and DMF (2 mL) was added. The mixture was cooled to 0 °C and urea (197 mg, 3.28 mmol) was added. After 90 minutes of stirring, **8** (102 mg, 0.30 mmol) in DMF (4 mL) was added at 0 °C. The mixture was stirred for 5 days at RT and a saturated solution of NH₄Cl (5 mL) was added with cooling to 0 °C. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). The collected organic phase was dried over MgSO₄ and the solvents were removed under reduced pressure (60 °C, <14 mBar). A combliflash of residue on silica (Celite loading, PE/EtOAc, EtOAc: 0%→100%) provided after drying in vacuum oven at 40 °C overnight the title product (350 mg, 50% yield) as a white crystalline solid.

¹**H** NMR (CD₃OD, 400 MHz, 298 K): δ 8.40 (dd, J = 4.5, 1.5 Hz, 2H), 7.25 (dd, J = 4.5, 1.5 Hz, 2H), 2.65 (t, J = 7.5 Hz, 2H), 1.95 – 1.92 (m, 2H), 1.90 – 1.85 (m, 2H), 1.60 – 1.51 (m, 2H), 1.33 – 1.23 (m, 2H), 1.20 – 1.12 (m, 2H), 0.87 (t, J = 7.0 Hz, 3H). ¹³C NMR (CD₃OD, 101 MHz, 298 K): δ 175.0, 153.3, 149.9, 125.6, 56.9, 40.1, 39.0, 35.6, 28.1, 26.5, 23.7, 14.0.

HR-MS (ESI): Required for $C_{16}H_{22}N_3O_3$ [M+H]⁺ 304.1656, found: 304.1644 (Δ = 3.91 ppm).

FT-IR (thin film): 3226, 3100, 2959, 2930, 2858, 1723, 1701, 1607, 1417, 1384, 1357, 1260, 1217 cm⁻¹.

MP: 174 − 176 °C

EA: Required for C₁₆H₂₁N₃O₃: C 63.35, H 6.98, N 13.85; found: C 62.67, H 7.01, N 13.44.

LCMS Method: Col3_ MeCN_FAST_5%-35%

S3: UV-vis-NIR titrations

S3.1 General

The UV-vis-NIR titrations were recorded on a Cary 60 UV-Vis machine (Agilent Technologies) at 298 K. Freshly opened CHCl₃ (HPLC quality, stabilised with amylene) was used as a solvent and was filtered over basic alumina plug before use. A host solution with known concentration was prepared and fraction of this solution was transferred into a glass cuvette. Then, a guest solution with known concentration was prepared. A change of UV-vis-NIR absorption upon addition of aliquots of guest solution was followed. The observed changes of UV-vis-NIR absorbance were analysed using a purpose-written fitting macro in Microsoft Excel. A 1:1 binding isotherm was used to fit the experimental data assuming that all six porphyrin units of **c-P6** coordinate a pyridine ligand and act identically and independently. The experiments were measured at least two times on at least two different days with freshly prepared solutions in order to eliminate possible systematic errors. The results are stated as average values and errors are quoted as two times the standard deviation.

S3.2 Two component titrations

Figure S1. UV-vis-NIR titration (CHCl₃, 298 K) of **pPy** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 833 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S2. UV-vis-NIR titration (CHCl₃, 298 K) of **mB3** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 842 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S3. UV-vis-NIR titration (CHCl₃, 298 K) of **pB3** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S4. UV-vis-NIR titration (CHCl₃, 298 K) of mA1 to c-P6. UV-vis-NIR spectra are shown on the left with the spectrum of unbound c-P6 in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of c-P6 act identically and independently.

Figure S5. UV-vis-NIR titration (CHCl₃, 298 K) of **mA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 836 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S6. UV-vis-NIR titration (CHCl₃, 298 K) of **pA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 852 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently. A 1:1 binding isotherm struggles to describe the experimental data correctly, but the concentration of ligand for half bound is 7 μ M and the best fit for a 1:1 binding isotherm was used to compare this ligand with other systems.

Figure S7. UV-vis-NIR titration (CHCl₃, 298 K) of **pA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 843 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S8. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **A** and **mB3** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S9. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **A** and **pB3** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S10. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **B** and **mA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S11. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **B** and **mA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 836 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S12. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **B** and **pA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 852 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S13. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **B** and **pA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 843 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S14. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of C and mA1 to c-P6. UV-vis-NIR spectra are shown on the left with the spectrum of unbound c-P6 in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of c-P6 act identically and independently.

Figure S15. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of C and mA2 to c-P6. UV-vis-NIR spectra are shown on the left with the spectrum of unbound c-P6 in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 836 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of c-P6 act identically and independently.

Figure S16. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of C and **pA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 852 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S17. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of C and **pA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 843 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S18. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **mB3** and **mA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 835 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S19. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **mB3** and **mA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 838 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S20. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **mB3** and **pA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S21. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **mB3** and **pA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 842 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S22. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **pB3** and **mA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 831 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S23. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **pB3** and **mA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 837 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S24. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **pB3** and **pA1** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 834 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

Figure S25. UV-vis-NIR titration (CHCl₃, 298 K) of a 1:1 mixture of **pB3** and **pA2** to **c-P6**. UV-vis-NIR spectra are shown on the left with the spectrum of unbound **c-P6** in thick black line and the end spectrum in red thick line. On the right are shown the experimental data at 835 nm (circles) and calculated values (line) based on a 1:1 binding isotherm assuming that the six porphyrin units of **c-P6** act identically and independently.

S3.4 Three component titrations fitted with an All-or-Nothing 1:3:3 isotherm

The titrations were analysed via non-linear regression using a global analysis multiple regression to model the entire spectrum simultaneously (ReactLab EQUILIBRIA software by Jplus Consulting). This allowed us to determine both the binding constants directly (expressed as $log(K_f)$) and the spectra of the species involved in the equilibrium processes (if not already known). The absorption spectra in the window 600-950 nm was used. The titrations were fit to a model where all ligands bind in one step (all-or-nothing) and one model where the ligands bind stepwise in pairs (stepwise). Graphical illustrations of the fits to both models at multiple wavelengths are shown below.

Reaction **Parameters** Fit þ Reactants Products Label ± Туре logK/β M+3A+3B = MA3B3 38.29 0.011 2.00E-01 1.80E-01 Y_meas 740 1.60E-01 Y meas 800 0 Δ 1.40E-01 Y_meas 838 Δ ^ Y meas 0 1.20E-01 X Y_meas 0 +1.00E-01 F Y_calc 740 8.00E-02 Y_calc 800 6.00E-02 Y_calc 838 4.00E-02 Y_calc 0 2.00E-02 Y_calc 0 0.00E+00 0 0.000001 0.000002 0.000003 0.000004 0.000005

mB3+mA1

mB3+mA2

mB3+pA1

mB3+pA2

pB3+mA1

pB3+mA2

S3.5 Three component titrations fitted with a Stepwise 1:3:3 isotherm

ReactLab EQUILIBRIA software was also used to fit the titration data to a model where the ligands bind stepwise in pairs as indicated below (stepwise). Graphical illustrations of the fits at multiple wavelengths are shown below.

	Reactants	Reaction Type	Products	Label	Parameters logK/β	±	Fit þ
	M+A+B	=	MAB		13.55	0.034	TRUE
	MAB+A+B	=	MA2B2		12.56	0.003	TRUE
	MA2B2+A+B	=	MA3B3		11.16	0.053	TRUE
2.00E-01	T						
1.80E-01				→		□ Y_r	neas 740
1.60E-01			5 ° ° °			♦ Y_r	neas 800
1.40E-01				<u>A</u>	_	∆ Y_r	neas 838
1.20E-01			<u>z -</u>			× Y_r	neas 0
1.00E-01						+ Y_r	neas 0
8.00E-02				; U	÷.	—Y_c	alc 740
6.00E-02						<u> </u>	alc 800
4.00E-02						<u> </u>	alc 838
2.00E-02						—Y_c	alc 0
0.00E+00]	—Y_c	alc 0
	0 0.000	0.000 0.000	002 0.000	003 0.000	004 0.00000	5	

mB3+mA1

mB3+mA2

mB3+pA1

mB3+pA2

pB3+mA1

pB3+mA2

S3.6 Statistical Analysis of Quality of Fit to Different 1:3:3 Models

The statistical significance of the difference in the quality of the fit to the two different 1:3:3 models was tested using two statistical analyses: the extra sum-of-squares F-test and Akaike's information criterion.³ The F-test compares the difference in sum-of-squares (SSQ) between a null-hypothesis and an alternative hypothesis with respect to the number of data points and the number of variable parameters used to fit the model. The sum-of-squares is calculated by taking all the deviations of the fit from the data points at each wavelength (residuals), squaring them, and adding them all together. The simpler model is used as the null-hypothesis and can then only be rejected if the alternative hypothesis with more variable parameters gives a significant improvement. The two models have to be nested, meaning that the null hypothesis is a special case of the alternative hypothesis. In this analysis, the number of data points minus the number of fitted parameters is called degrees of freedom (DoF). The value of F is calculated as the relative difference in SSQ divided by the relative difference in DoF using equation S1.

$$F = \frac{\text{SSQ}_{\text{null}} - \text{SSQ}_{\text{alternative}}}{\text{SSQ}_{\text{alternative}}} / \frac{\text{DoF}_{\text{null}} - \text{DoF}_{\text{alternative}}}{\text{DoF}_{\text{alternative}}}$$
(S1)

The closer the ratio F is to 1, the more likely it is that the null hypothesis is correct and the improvement of the SSQ value in the alternative hypothesis is simply due to the higher flexibility of the fit. To interpret the significance of the F-test, its p-value has to be calculated.

Akaike's information criterion (AIC) is an alternative approach to comparing models which does not require the models to be nested and does not rely on p-values or the concept of statistical significance. The logic is not one of hypothesis testing, so you do not state a null hypothesis. Rather, the method lets you determine which model is more likely to be correct and quantify how much more likely. For each model, an AICc score is calculated using equation S2.

$$AIC_c = N \cdot \ln\left(\frac{SSQ}{N}\right) + 2K + \frac{2K(K+1)}{N-K-1}$$
(S2)

Where N is the number of data points and K is the number of variable parameters. The model which has the lowest AICc score is more likely to be correct. How much more likely it is to be correct depends on the absolute difference and can be calculated as the evidence ratio (equation S3).

evidence ratio =
$$\frac{1}{e^{-0.5 \cdot \Delta AIC_c}}$$
 (S3)

The evidence ratio is the probability that the model with the lower AICc value is correct divided by the probability that the model with the higher AICc value is correct.

The number of data points is the total number of recorded spectra and the number of fitted parameters is the sum of the number of fitted spectra of species in solution and the number of fitted binding constants. For the all-or-nothing model there is one binding constant and two fitted spectra (c-P6 and c-P6·A_{mB3}), so the number of variable parameters is 3. For the stepwise model, there are three binding constants and four fitted spectra (c-P6, c-P6·AB, c-P6·A₂B₂ and c-P6·A_{mB3}), so the number of variable parameters is 7.

For the F-test analysis, the all-or-nothing model was used as the null hypothesis and the stepwise model was used as the alternative hypothesis. The p-values were calculated using an automatic calculator on the website https://www.socscistatistics.com/pvalues/fdistribution.aspx.

https://www.socscistatistics.com/pvalues/fdistribution.aspx.

The details are provided below. In all cases, the p-value is less than 0.0015 and the evidence ratio is greater than 80 indicating that the stepwise model is most appropriate and that the increase in goodness of fit cannot be explained by the increase in parameters.

mB3+mA1	F-test			Akaike's Criterion	Information
	SSQ	DoF	var. para.		AICc
all-or-nothing	1.76E-02	13	3		-101.01
stepwise	2.90E-03	9	7		-109.85
difference	1.47E-02	4			8.84
relative difference	5.06	0.44			
Ν	16.00				
F	11.40				
p-value	0.001426			evidence ra	atio 83
mB3+mA2	F-test			Akaike's	Information
	550	DeE		Criterion	AICa
all an nothing	550	12 00	var. para.		
an-or-notning	5.26E-02	12.00	3		-/6.60
stepwise	2.54E-03	8.00	1		-100.27
	5.01E-02	4.00			23.66
relative difference	19.74	0.50			
N E	15.00	12.00			
F	39.48				
p-value	0.000026			evidence ra	atio 137455
	E tost			Abaikala	Information
mB3+pA1	r-test			Criterion	mommation
mB3+pA1	SSQ SSQ	DoF	var. para.	Criterion	AICc
mB3+pA1 all-or-nothing	SSQ 2.14E-02	DoF 13.00	var. para. 3	Criterion	AICc -97.87
mB3+pA1 all-or-nothing stepwise	SSQ 2.14E-02 2.84E-03	DoF 13.00 9.00	var. para. 3 7	Criterion	AICc -97.87 -110.21
all-or-nothing stepwise difference	SSQ 2.14E-02 2.84E-03 1.86E-02	DoF 13.00 9.00 4.00	var. para. 3 7	Criterion	AICc -97.87 -110.21 12.34
mB3+pA1 all-or-nothing stepwise difference relative difference	SSQ 2.14E-02 2.84E-03 1.86E-02 6.55	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Criterion	AICc -97.87 -110.21 12.34
mB3+pA1 all-or-nothing stepwise difference relative difference N	SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Criterion	AICc -97.87 -110.21 12.34
mB3+pA1 all-or-nothing stepwise difference relative difference N F	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Criterion	AICc -97.87 -110.21 12.34
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value	SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	evidence r	AICc -97.87 -110.21 12.34
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	evidence ra	AICc -97.87 -110.21 12.34
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion	AICc -97.87 -110.21 12.34 atio 477 Information
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 477 477 Information AICc
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055	DoF 13.00 9.00 4.00 0.44	var. para. 3 7 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 atio 477 Information AICc -74.91
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055	DoF 13.00 9.00 4.00 0.44 0.44	var. para. 3 7 Var. para. 3 7	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 477 477 Information AICc -74.91 -115.32
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2 all-or-nothing stepwise difference	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055 F-test SSQ 5.89E-02 9.31E-04 5.80E-02	DoF 13.00 9.00 4.00 0.44	var. para. 3 7 4 4 7 4 7 7	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 477 477 Information AICc -74.91 -115.32 40.40
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2 all-or-nothing stepwise difference relative difference	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055 F-test SSQ 5.89E-02 9.31E-04 5.80E-02	DoF 13.00 9.00 4.00 0.44 DoF 13 9 4 0.44	var. para. 3 7 4 var. para. 3 7	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 AICc AICc -74.91 -115.32 40.40
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2 all-or-nothing stepwise difference relative difference N	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055 F-test SSQ 5.89E-02 9.31E-04 5.80E-02 62.31 15.00	DoF 13.00 9.00 4.00 0.44 DoF 13 9 4 0.44	var. para. 3 7 Var. para. 3 7	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 477 Information AICc -74.91 -115.32 40.40
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2 all-or-nothing stepwise difference relative difference N F	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055 F-test SSQ 5.89E-02 9.31E-04 5.80E-02 62.31 15.00	DoF 13.00 9.00 4.00 0.44 5 13 9 4 0.44	var. para. 3 7 	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 477 477 Information AICc -74.91 -115.32 40.40
mB3+pA1 all-or-nothing stepwise difference relative difference N F p-value mB3+pA2 all-or-nothing stepwise difference relative difference N F	F-test SSQ 2.14E-02 2.84E-03 1.86E-02 6.55 16.00 14.73 0.00055 F-test SSQ 5.89E-02 9.31E-04 5.80E-02 62.31 15.00 124.62	DoF 13.00 9.00 4.00 0.44 DoF 13 9 4 0.44	var. para. 3 7 	Akaike's Criterion evidence ra Akaike's Criterion	AICc -97.87 -110.21 12.34 477 Information AICc -74.91 -115.32 40.40

pB3+mA1	F-test			Akaike's Criterion	Information
	SSQ	DoF	var. para.		AICc
all-or-nothing	4.02E-02	13.00	3		-87.80
stepwise	1.51E-03	9.00	7		-120.29
difference	3.87E-02	4.00			32.50
relative difference	25.61	0.44			
Ν	16.00				
F	57.61				
p-value	< 0.00001			evidence ratio	11397107
pB3+mA2	F-test			Akaike's Criterion	Information
	SSQ	DoF	var. para.		AICc
all-or-nothing	3.46E-02	12.00	3		-82.92
stepwise	2.42E-03	8.00	7		-101.00
difference	3.21E-02	4.00			18.08
relative difference	13.30	0.50			
Ν	15.00				
F	26.59				
p-value	0.000113			evidence ratio	8442
pB3+pA1	F-test			Akaike's Criterion	Information
pB3+pA1	F-test SSQ	DoF	var. para.	Akaike's Criterion	Information AICc
pB3+pA1 all-or-nothing	F-test SSQ 4.06E-02	DoF 13.00	var. para. 3	Akaike's Criterion	Information AICc -87.61
pB3+pA1 all-or-nothing stepwise	F-test SSQ 4.06E-02 2.48E-03	DoF 13.00 9.00	var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38
pB3+pA1 all-or-nothing stepwise difference	F-test SSQ 4.06E-02 2.48E-03 3.82E-02	DoF 13.00 9.00 4.00	var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77
pB3+pA1 all-or-nothing stepwise difference relative difference	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77
pB3+pA1 all-or-nothing stepwise difference relative difference N	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion	AICc -87.61 -112.38 24.77
pB3+pA1 all-or-nothing stepwise difference relative difference N F	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77 238747
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value pB3+pA2	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test	DoF 13.00 9.00 4.00 0.44	var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77 238747 Information
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value pB3+pA2	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ	DoF 13.00 9.00 4.00 0.44	var. para. 3 7 Var. para.	Akaike's Criterion	AICc -87.61 -112.38 24.77 238747 Information AICc
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value pB3+pA2 all-or-nothing	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ 3.86E-02	DoF 13.00 9.00 4.00 0.44	var. para. 3 7 var. para. 3	Akaike's Criterion	AICc -87.61 -112.38 24.77 238747 Information AICc AICc -88.42
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value pB3+pA2 all-or-nothing stepwise	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ 3.86E-02 2.81E-03	DoF 13.00 9.00 4.00 0.44 0.44	var. para. 3 7 Var. para. 3 7	Akaike's Criterion	AICc -87.61 -112.38 24.77 238747 Information AICc -88.42 -110.38
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value pB3+pA2 all-or-nothing stepwise difference	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ 3.86E-02 2.81E-03 3.58E-02	DoF 13.00 9.00 4.00 0.44 0.44 1 1 1 1 1 3.00 9.00 4.00	var. para. 3 7 Var. para. 3 7	Akaike's Criterion	AICc -87.61 -112.38 24.77 238747 Janformation AICc -88.42 -110.38 21.96
pB3+pA1 all-or-nothing stepwise difference relative difference N F p-value bB3+pA2 all-or-nothing stepwise difference relative difference	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ 3.86E-02 2.81E-03 3.58E-02 12.77	DoF 13.00 9.00 4.00 0.44 DoF 13.00 9.00 4.00 0.44	var. para. 3 7 var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77 238747 Information AICc -88.42 -110.38 21.96
pB3+pA1 all-or-nothing stepwise difference relative difference p-value blab-pA2 losepwise difference stepwise difference N N	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ 3.86E-02 2.81E-03 3.58E-02 12.77 16.00	DoF 13.00 9.00 4.00 0.44 0.44	var. para. 3 7 Var. para. 3 7	Akaike's Criterion	AICc -87.61 -112.38 24.77 238747 Janformation AICc -112.38 238747 AICc -110.38 -110.38 21.96
pB3+pA1 all-or-nothing bitsepwise difference relative difference N bitsepwise bitsepwise all-or-nothing bitsepwise difference lifference liffe	F-test SSQ 4.06E-02 2.48E-03 3.82E-02 15.41 16.00 34.67 0.000018 F-test SSQ 3.86E-02 2.81E-03 3.58E-02 12.77 16.00 28.74	DoF 13.00 9.00 4.00 0.44 DoF 13.00 9.00 4.00 0.44	var. para. 3 7 var. para. 3 7	Akaike's Criterion	Information AICc -87.61 -112.38 24.77 238747 Information AICc -112.38 238747 10.38 21.96

S4: DOSY Spectrum

Figure S26. ¹H NMR DOSY spectrum (500 MHz, CDCl₃, 298 K) of a 1:3:3 mixture of *c*-P6 (0.16 mM), **pB3** and **mA2** (0.48 mM).
S5: Molecular Modelling

The structure of **T** from the X-ray structure of **c-P6•T** was used as a template to determine the positions of the six pyridines when they are bound to the porphyrin nanoring. The side chain H-bonding groups required for rosette formation were then built onto the six pyridine fragments. A conformational search was carried out using the OPLS3 force field in MacroModel implemented in the Schrödinger Suite 2016-4. Calculations were carried out with no solvent and with no cut-off for non-covalent interactions, but the coordinates of the nitrogen atoms and carbon atoms in the position 4 were constrained, allowing the pyridine units to rotate around their axes but not to move (Figure S27). Figure S28 shows an example of the outcome: the lowest energy structure obtained for $mB3_3 \cdot mA2_3$ is the H-bonded rosette.



Figure S27. Using T as a framework for construction of rosette models. The coordinated of the atoms in red were constrained for the calculations.



Figure S28. Top and side views of the lowest energy structure of $mB3_3 \cdot mA2_3$ rosette system from a conformational search, where the coordinates of the nitrogen atoms and carbon atoms in the position 4 of pyridine units were constrained (the alkyl groups of both barbituratepyridines and pyrimidine-pyridines were replaced by hydrogen atoms in the calculations). Hydrogen atoms that do not contribute to H-bonding are not shown for clarity; colouring: mB_3 in red, mA_2 in blue, green dashed line is the H-bond.

The pyridine groups from the lowest energy structure obtained using molecular mechanics were superimposed on the positions of the pyridine groups in the X-ray crystal structure of **c**-**P6•T**, and the resulting structure was optimised using the semi-empirical PM6 method as implemented in Gaussian 09.⁴ In this way, it was possible to find structures of the rosette motif bound inside the porphyrin nanoring for several ligand combinations, and the results are shown in Figure S29.



Figure S29. Top and side views of the PM6-optimised structures of H-bonded rosettes bound inside the porphyrin nanoring (a) c-P6•mB3₃•mA1₃, (b) c-P6•mB3₃•mA2₃, (c) c-P6•mB3₃•pA1₃, (d) c-P6•mB3₃•pA2₃ (alkyl groups on barbiturate-pyridines and pyrimidine-pyridines and 3,5-bis(t-butyl)phenyl on c-P6 were replaced by hydrogen atoms in the calculations). Hydrogen atoms that do not contribute to H-bonding are not shown for clarity. Colouring: c-P6 in black with highlighted Zn atoms in yellow, barbiturate-pyridines in red, pyrimidine-pyridines in blue, green dashed line is the H-bond.



It was also possible to obtain a model of rosette-like structure of **c-P6•mB3**₆ using the same approach (Figure S30).

Figure S30. Top and side views of the PM6-optimised structure of **c-P6•mB3**₆ (zinc centres in yellow and H-bonding interactions in green). Alkyl groups on **mB3** and the 3,5-bis(t-butyl)phenyl groups on **c-P6** were replaced by hydrogen atoms in the calculations, and hydrogen atoms that do not contribute to H-bonding are not shown for clarity.

S6: References

- 1) Motloch, P., Hunter, C. A. Org. Biomol. Chem. 2020, 18, 1602–1606.
- 2) (a) Hoffmann, M.; Kärnbratt, J.; Chang, M.-H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. *Angew. Chem. Int. Ed.* 2008, *47*, 4993-4996. (b) Sprafke, J. K.; Kondratuk, D. V.; Wykes, M.; Thompson, A. L.; Hoffmann, M.; Drevinskas, R.; Chen, W.-H.; Yong, C. K.; Kärnbratt, J.; Bullock, J. E.; Malfois, M.; Wasielewski, M. R.; Albinsson, B.; Herz, L. M.; Zigmantas, D.; Beljonne, D.; Anderson, H. L. *J. Am. Chem. Soc.* 2011, *133*, 17262-17273.
- Motulsky, H. J.; Christopoulos, A. *Fitting models to biological data using linear and nonlinear regression. A practical guide to curve fitting.* (Chapters 21-23). 2003, GraphPad Software Inc., San Diego CA, <u>www.graphpad.com</u>.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford, CT, USA, 2009.