Electronic Supplementary Information

Noncovalent interactions in acid-porphyrin complexes

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General experimental information:

Solution state NMR spectra were recorded on Bruker DRX-400 (400 MHz for ^{1}H), Bruker Avance 500 (500 MHz for ^{1}H), Bruker Avance 500 Cryo (125 MHz for ^{13}C) and Bruker Avance QNP (400 MHz for ^{19}F) spectrometers. Where high resolution was required ^{1}H NMR spectra were acquired as 32 K FIDs and zero filled to 64 K points (accuracy to within the third decimal place). Unless otherwise stated, NMR spectra were recorded in deuterated chloroform ($CDCl_3$) at 298 K ± 3 K. In preparing freebase porphyrin samples for NMR spectroscopy acid titration studies the *d*-chloroform was filtered through alumina to remove traces of acid and reduce the water content.

Two dimensional spectra were acquired using standard Burker pulse programs. Gradient double quantum filtered COSY spectra were typically recorded with 640 slices in F_1 and 2048 points in F_2. NOESY spectra (1.2 seconds mixing time) were typically recorded with 800 slices in F_1 and 2048 points in F_2.

In the solution state porphyrin ^{1}H and ^{13}C NMR assignments were made by comparison with previously assigned similarly substituted porphyrin species and were labelled according to the systems shown. Chemical shifts (δ) were quoted in ppm, the downfield direction being positive, and were referenced to the solvent resonances. Coupling constants (*J*) were given in Hz and uncertainties quoted as ± 0.05 Hz. For convenience, the following abbreviations were used: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets, m, multiplet; br, broad; C_q, quaternary carbon.

For NMR titration experiments, porphyrin solutions were typically made up in the 8 x 10^{-3} M concentration range in *d*-chloroform or d_2-dichloromethane. Stoichiometric quantities of acid prepared in *d*-chloroform were added to the NMR sample with shaking to generate at least 10 spectra over the course of the titration experiment.

Column chromatography was performed on either 60 mesh silica gel (Breckland Scientific) or alumina (Al_2O_3), basic, grade (Aldrich). Thin layer chromatography was performed on Kiesel silica gel 60 PF_{254} (Merck) 0.2 mm glass plates.

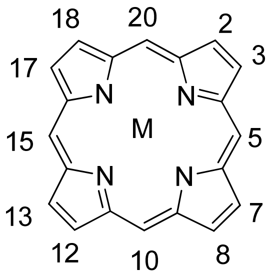
With the exception of chloroform, freshly distilled solvents were used in all preparations. Dry solvents were obtained from solvent stills in accordance with literature procedures.

MALDI TOF mass spectra were recorded on 4700 Proteomics analyser (Applied Biosystems) with TOF/TOF optics. The spectra were acquired in reflector mode and 1000 laser shots were averaged together.

UV-Visible spectra were recorded on a Cary 100 Bio UV-Visible diode array spectrophotometer using a 1 cm path length quartz cell versus a pure solvent reference.

IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer Spectrum RX 1 using a 0.5 mL NaCl cell with 0.5 mmol solutions prepared in chloroform.

Synthetic procedures:



Preparation of tetra *meso* substituted porphyrins[1]

Aldehyde (20.0 mmol) was added to propionic acid (100 mL) and heated to 145 ˚C. Once at this temperature, pyrrole (1.4 mL, 20.0 mmol) was added and the mixture refluxed at this temperature for ninety minutes. After this time, the flask was allowed to cool to room temperature before methanol (~ 5 mL) was added, the mixture was then left to stand overnight. The contents of the flask was filtered, and the filtrate washed with methanol (3 x 100 mL). Purification was performed by way re-crystallisation by layered addition of methanol onto a solution of the product in the minimum amount of dichloromethane.

H_2 Tetrakis-5,10,15,20-(3,5-di-*tert*-butylphenyl)porphyrin[2] 1

5-15 % yield; δ_H (400 MHz, $CDCl_3$) -2.67 (s, 2H, NH), 1.53 (s, 72H, *tert*-butyl H), 7.79 (t, 4H, p-*tert*-butyl *aryl* H), 8.10 (d, 8H, *o-tert*-butyl *aryl* H), 8.90 (s, 8H, β-pyrrolic H); δ_C (125 MHz, $CDCl_3$) 31.7, 35.0, 120.9, 121.2, 129.7, 131.0 (br) 141.3, 148.6. MS: MALDI-TOF-MS (*m/z*) 1062.77 λ_{max} ($CHCl_3$)/ nm 421, 518, 554, 593, 648.

H_2 Tetrakis-5,10,15,20-(phenyl)porphyrin[1] 6

5-15 % yield; δ_H (400 MHz, $CDCl_3$) (228 K) -2.97 (s, 2H, NH), 7.80 (m, 12H, *m and p-aryl* H), 8.24 (d, 8H, *o-aryl* H), 8.81 (s, 4H, β-pyrrolic *pyrrolenine* H) 9.00 (s, 4H, β-pyrrolic *pyrrole* H); δ_C (125 MHz, $CDCl_3$) 120.12 (*meso C*), 126.66 (*aryl C*H), 127.69 (*aryl C*H), 131 (br 2 x β-pyrrolic)[3] 134.54 (*aryl C*H), 142.16 (*aryl* C_q); MS: MALDI-TOF-MS (*m/z*) 614.17; λ_{max} ($CHCl_3$)/ nm 418, 515, 549, 590, 648.

H_2 Tetrakis-5,10,15,20-(3, 4, 5-trimethoxyphenyl)porphyrin[4] 9

11 % yield; δ_H (400 MHz, $CDCl_3$) -2.78 (s, 2H, NH),3.98 (s, 24H, *m*-methoxy), 4.19 (s, 12H, *p*-methoxy), 7.48 (s, 8H, *o*-methoxy *aryl* H), (s, 8H, β-pyrrolic H); δ_C (125 MHz, $CDCl_3$) 56.36, 61.30, 112.78, 120.04, 130.95 (br), 137.52, 137.87, 151.39; MS: MALDI-TOF-MS (*m/z*) 974.28; λ_{max} ($CHCl_3$)/ nm 420, 517, 553, 591 and 647.

H_2 Tetrakis-5,10,15,20-(2, 3, 4, 5, 6-pentafluorophenyl)porphyrin 10

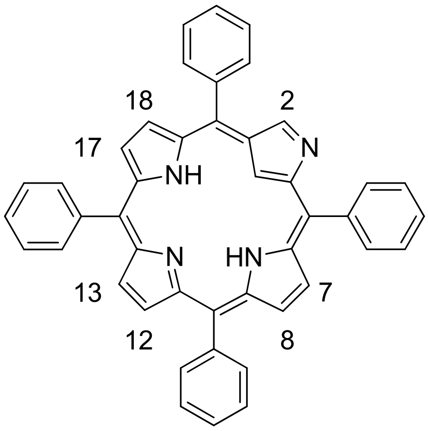
Porphyrin was used as obtained (Aldrich) without further purification.

δ_H (400 MHz, $CDCl_3$) -2.90 (s, 2H, NH), 8.92 (s, 8H, β-pyrrolic H).

H_2 Tri-5,10,15-(4-methylphenyl)-20-(4-pyridyl)porphyrin[5] 13

4-methylbenzaldehyde (1.18 mL, 10.0 mmol) was added to propionic acid (100 mL) and heated to 145 ˚C. Once at this temperature 4-pyridine carboxaldehyde (0.94 mL, 10.0 mmol) and pyrrole (1.4 mL, 20.0 mmol) were added and the mixture refluxed at this temperature for ninety minutes. After this time the flask was allowed to cool to room temperature before methanol (~ 5 mL) was added and the mixture left to stand overnight. The contents of the flask was then filtered and the filtrate washed with methanol (3 x 100 mL). Purification was performed by way of column chromatography on silica, initially using dichloromethane to elute the tetrakis-5,10,15,20-(4-methylphenyl)porphyrin before more polar conditions were employed (2% methanol/ dichloromethane) to elute the desired product. Finally, the desired porphyrin product was re-crystallised by layered addition of methanol onto a solution of the product in the minimum amount of dichloromethane.

2 % yield; δ_H (400 MHz, $CDCl_3$) -2.79 (s, 2H, core NH), 2.71 (s, 9H, *Methyl*), 7.56 (d, ^3J = 8.0 Hz, 6H, *aryl*), 8.10 (d, ^3J = 8.0 Hz, 6H, *aryl*), 8.17 (d, ^3J = 6.0 Hz, 2H, β-pyridyl), 8.77 (d, ^3J = 4.8 Hz, 2H, β-pyrrolic), 8.87 (s, 4H, β-pyrrolic), 8.90 (d, ^3J = 4.8 Hz, 2H, β-pyrrolic), 9.17 (d, ^3J = 6.0 Hz, 2H, α-pyridyl); δ_C (125 MHz, $CDCl_3$) 21.51 (*Me*), 115.94 (C_q), 120.57 (C_q), 121.04 (C_q), 127.43 (*pyridyl*), 127.47 (*C*H), 129.49 (*C*H), 131.5 (br *C*), 134.49 (*C*H), 137.47 (C_q), 137.49 (C_q), 139.00 (C_q), 139.07 (C_q), 148.20 (*pyridyl*), 150.62 (C_q); MS: MALDI-TOF-MS (*m/z*) 657.29; λ_{max} ($CHCl_3$)/ nm 419, 516, 552, 590, 647.



N-Confused Tetrakis-5,10,15,20-(phenyl)porphyrin[6] 2

Pyrrole (1.04 mL, 15.0 mmol) and benzaldehyde (1.52 mL, 15.0 mmol) were added to a round bottom flask (2 L) containing dry dichloromethane (1.5 L). The solution was degassed for ~ 60 minutes before the reaction was initiated by the addition of methane sulfonic acid (0.681 mL, 10.5 mmol). The reaction mixture was stirred at room temperature under nitrogen for 30 minutes before DDQ (3.00 g, 13.2 mmol) was added and the mixture stirred for 30 minutes under air. After this time the mixture was filtered through a column containing 300 g activity III basic alumina, the filtrate was collected. The column was then washed with dichloromethane containing ~ 1% TEA (1 L) and the filtrate was combined with the previous before all the solvent was removed *in vacuo* whilst the crude material was adsorbed onto 15 g of activity III basic alumina. A second column was prepared with 300 g of activity III basic alumina loaded in hexane/ dichloromethane (3:1). The adsorbed crude material was then added to the top of the column. Elution of tetraphenylporphyrin was achieved first, initially with hexane/ dichloromethane (3:1) then with hexane/ dichloromethane (1:1) to completely remove the product. Solvent conditions of hexane/ dichloromethane (1:2) facilitated the elution of the n-confused tetraphenylporphyrin though pure dichloromethane to maybe required to remove the material completely. The necessary fractions were then combined and the solvent removed *invacuo* before the material was recrystalised from dichloromethane layered with methanol.

28 % yield; δ_H (400 MHz, $CDCl_3$) (223 K) -5.09 (s, 1H, core CH), -2.65 and -2.57 (2s, 2H, core NH), 7.80 – 7.87 (m, 8H, *aryl* H), 7.93 (t, 4H, *aryl* H); 8.20 – 8.24 (m, 4H, *aryl* H), 8.42 – 8.46 (m, 4H, *aryl* H), 8.61 – 8.64 (m, 3H, β-pyrrolic H), 8.67 (d, J_{AB} = 3.6 Hz) 1H, β-pyrrolic H), 8.75 (s, 1H, β-pyrrolic H_2), 8.97 – 9.07 (AX dd, J_{AX} = 3.6 Hz, 2H, β-pyrrolic H); δ_C (125 MHz, $CDCl_3$) 117.58 (C_q), 119.10 (C_q), 125.68 (br *C*H), 126.50 (*C*H), 126. 99 (*C*H), 127.01 (*C*H), 127.56 (*C*H), 127.66 (*C*H), 127.81 (*C*H), 127.87 (*C*H), 128.34 (br *C*H), 128.44 (br *C*H), 134.55 (*C*H), 134.63 (*C*H), 135.12 (*C*H), 136.90 (C_q), 136.92 (*C*H), 137.19 (C_q), 139.51 (C_q), 141. 66 (C_q); MS: MALDI-TOF-MS (*m/z*) 615.10; λ_{max} ($CHCl_3$)/ nm 440, 542, 585 and 728.

Preparation of metallated tetra *meso* substituted porphyrins

Copper insertion of freebase porphyrins

Copper (II) acetate hydrate (~ 5 equivalents) was added to the porphyrin mixture in a 30% methanol/chloroform solution. The reaction mixture was refluxed for 90 minutes before complete insertion had been achieved as confirmed by t.l.c (silica; 30% hexane/dichloromethane). After this time the solvent was removed *in vacuo*. Purification of the crude product was performed by way of recrystalisation from chloroform layered with methanol.

Sn insertion into freebase tetra aryl porphyrins

Freebase porphyrin (up to 500 mg) was stirred and refluxed with finely ground anhydrous tin(II) chloride (2.4 equivalents) in pyridine (to give a porphyrin concentration of 0.01 M) for one hour, the solution was then allowed to cool to room temperature. Complete Sn insertion was confirmed by UV spectroscopic examination of a drop of reaction mixture diluted with chloroform. The crude product was precipitated by the addition of water (typically mL quantities) and collected by vacuum filtration on celite. Methanol (typically mL quantities) was washed through the celite plug to remove excess water, followed by chloroform to elute the porphyrin. The chloroform filtrate was washed with aqueous hydrochloric acid (6 M) (typically 2 x 10 mL), water (3 x equal volume to organic solution), and dried over anhydrous sodium sulphate. Evaporation of the organic solution under educed pressure gave a purple solid in high yield.

$SnCl_2$ porphyrin (100 mg) was dissolved in the minimum volume of chloroform and stirred with basic alumina (activity V, 1.6 g per 0.1 mmol of porphyrin) overnight. The resulting slurry was filtered, and the filtrate dried over sodium sulphate, the solvent was evaporated and the residue recrystallised by the layered addition of hexane to a concentrated dichloromethane solution. Purple powders were obtained in good yields.

Ruthenium insertion into freebase tetra aryl porphyrins

H_2Tetrakis 5,10,15,20-3,5-di-*tert*-butyl phenyl porphyrin (120 mg, 0.11 mmol) and tris ruthenium dodecacarbonyl (250 mg, 3.5 equivalents) were added to decalin (15 mL) previously degassed for one hour in a Schlenk flask. The mixture was then refluxed under nitrogen for 72 h. After this time time the mixture was allowed to cool to room temperature before being filtered through a plug of neutral alumina. Elution of the unreacted ruthenium dodecacarbonyl was facilitated by the washing of the alumina with hexane. Finally the crude product was washed off the column by dichloromethane and the solvent was removed *in vacuo*. Purification of the crude product was performed by way of column chromatography on silica using 40 % dichloromethane /hexane to elute the pure product.

$Sn(OH)_2$ Tetrakis-5,10,15,20-(phenyl)porphyrin 4

79 % yield; δ_H (400 MHz, $CDCl_3$) -7.44 (br s, 2H, SnOH), 7.81 (m, 12H, *aryl*), 8.34 (m, 8H, *aryl*), 9.13 (s, 8H, β-pyrrolic H, Sn_{Sat} ^4J (Sn-H) 10.1 Hz); δ_C (125 MHz, $CDCl_3$) 121.23, 127.07 (CH), 128.40 (CH), 132.69 (CH), 135.12 (CH), 141.26, 146.66; MS: MALDI-TOF-MS (*m/z*) 766.10 and 749.03 (-OH); λ_{max} ($CHCl_3$)/ nm 421, 521, 561, 600 and 625.

Ru(CO) Tetrakis-5,10,15,20-(3,5-di-*tert*-butylphenyl)porphyrin 12

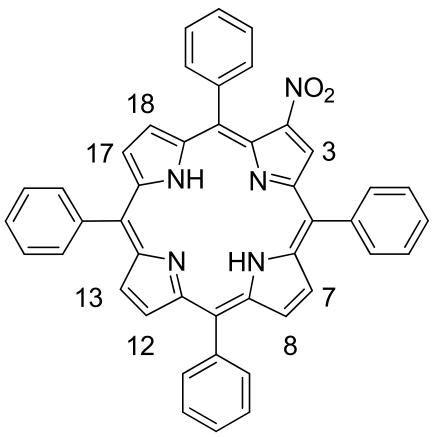
71 % yield; δ_H (400 MHz, $CDCl_3$) 1.54 (s, 72H, *tert*-butyl H), 7.78 (t, 4H, p-*tert*-butyl *aryl* H), 8.07 (d, 8H, *o-tert*-butyl *aryl* H), 8.77 (s, 8H, β-pyrrolic H); δ_C (125 MHz, $CDCl_3$) 24.23 (*C*H), 24.34 (*C*H), 31.75 (*C*H), 35.03 (C_q), 120.60 (*C*H), 123.00 (C_q), 128.99 (*C*H), 129.59 (*C*H), 131.85 (*C*H), 141.52 (C_q), 144.17 (C_q), 148.35 (C_q), 148.58 (C_q), 206.96 (CO ligand); MS: MALDI-TOF-MS (*m/z*) 1162.64 (-C=O) and 2325.29 (2 x RuP – C=O); λ_{max} ($CHCl_3$)/ nm 416, 530 and 563.

Preparation of β-pyrrolic substituted porphyrins

H_2 2,3,7,8,12,13,17,18-(β-Octaethyl)porphyrin 5

Porphyrin was used as obtained (Aldrich) without further purification.

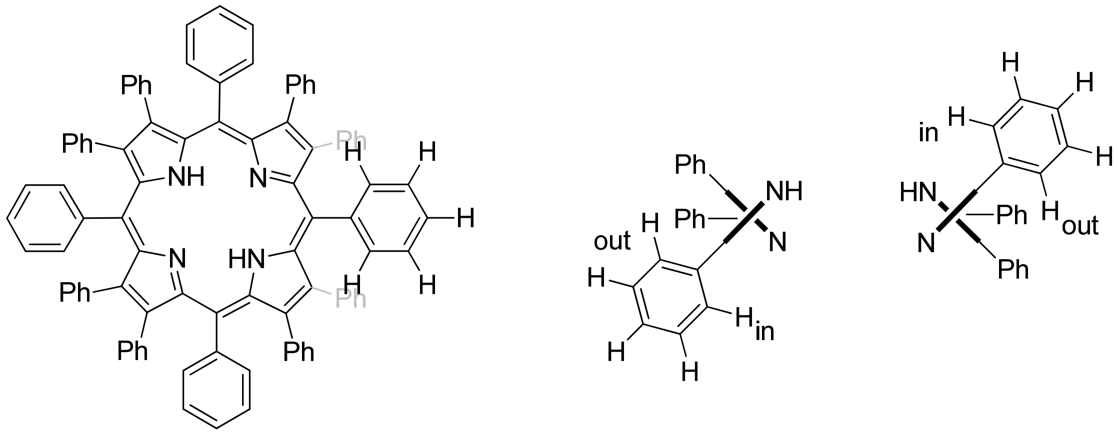
δ_H (400 MHz, $CDCl_3$) -3.97 (s, 2H, NH), 1.89 (t, 24H, CH_2CH_3), 4.04 and 4.12 (br d, 16H, CH_2CH_3), 10.13 (s, 4H, *meso* H).



H_2 2-nitro-Tetrakis-5,10,15,20-(phenyl)porphyrin[7] 3

Under an N_2 atmosphere Cu^{II} tetrakis-5,10,15,20-(phenyl)porphyrin (0.2 mmol) was dissolved in dichloromethane (50 mL) and stirred at room temperature. To this solution was added NO_2 (pre-prepared petroleum ether (40:60) stock solution) (0.2 mmol). The reaction was followed by TLC (30 % dichloromethane /petroleum ether (40:60)) – reaction time < 10 mins. Once the reaction was determined to be complete the crude mixture was filtered through a plug of silica and washed through with petroleum ether (40:60) before the solvent was removed *in vacuo*. Purification was performed by way of column chromatography on silica initially using 30 % dichloromethane/petroleum ether (40:60) to elute small quantities of Cu^{-}tetrakis-5,10,15,20-(phenyl)porphyrin before 50 % dichloromethane/petroleum ether (40:60) was used to elute the desired nitro-substituted product.

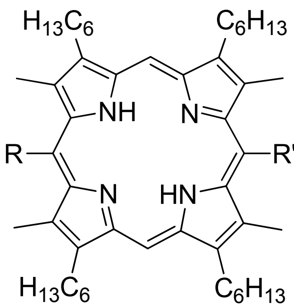
20 % yield; δ_H (400 MHz, $CDCl_3$) -2.61 (s, 2H, core NH), 7.7-7.82 (m, 12H, *m and p-aryl* H), 8.19-8.22 (m, 6H, *o-aryl* H), 8.25-8.27 (m, 2H, *o-aryl* H), 8.72 (AB q, J_{AB} = 4.8 Hz, 2H, β-pyrrolic $H_{12,13}$), 8.90 and 9.02 (AB q, J_{AB} = 4.8 Hz, 2H, β-pyrrolic $H_{17,18}$) 8.90 and 9.94 (AB q, J_{AB} = 4.8 Hz, 2H, β-pyrrolic $H_{7,8}$), 9.05 (s, 1H, β-pyrrolic H_3); δ_C (125 MHz, $CDCl_3$) 44 possible signals, 120.09, 120.57, 120.83, 123.00, 126.87 (CH), 126.91 (CH), 126.96 (CH), 127.07 (CH), 128.01 (CH), 128.22 (CH), 128.40 (CH), 128.54 (CH), 128.91 (CH), 129.45 (CH), 129.90 (CH), 131.86 (CH), 134.56 (CH), 134.70 (CH), 135.02 (CH), 135.04 (CH), 135.41 (CH), 137.95 (br), 139.32 (br), 140.20, 140.30 (br), 141.10, 141.33, 141.56, 142.50 (br), 146.02, 153.06, 156.35 (br), 156.55 (br); MS: MALDI-TOF-MS (*m/z*) 659.14; λ_{max} ($CHCl_3$)/ nm 427,528, 607, 665 and 719.



H_2 - 5, 7, 8, 10, 12, 13, 15, 17, 18, 20, 22, 23 –(dodecaphenyl)porphyrin[8] 8

Benzaldehyde (280 µL, 2.76 mmol) and diphenylpyrrole (605 mg, 2.76 mmol) were added to freshly distilled dichloromethane (275 mL) in a round bottom flask (500 mL). The mixture was degassed for 30 minutes by flushing nitrogen through the stirred solution. After this time, boron trifluoride diethyl etherate (35 µL, 0.276 mmol) was added to the reaction mixture under nitrogen. The flask was then left stirring at room temperature for 90 minutes under an nitrogen atmosphere. After this, DichloroDicyanobenzoQuinone (DDQ) (627 mg, 2.76 mmol) was added to the reaction mixture in order to oxidise the porphrynogen to the desired porphyrin. The mixture was refluxed under air for 30 minutes. Once completed the solvent was removed *in vacuo*. Purification of the desired product was performed by way of column chromatography on basic grade alumina. Partial purification of the green porphyrin dication was achieved using elution conditions of 40 % dichloromethane in hexane however a second column using toluene to elute was required to isolate pure material. The free base porphyrin was isolated by recrystalisation from dichloromethane and 1% potassium hydroxide in ethanol (added until the green solution turned brown, indicating free base formation) and finally layered with ethanol. The product was filtered off after several days and dried under high vac.

1.5 % yield; δ_H (400 MHz, $CDCl_3$) (298 K) -0.92 (br s, 2H, core NH), 6.72 – 6.88 (m, 52H, *aryl* H), 7.66 (d, 8H, *aryl* H); δ_H (500 MHz, CD_2Cl_2) (193 K) -1.45 (s, 2H; core NH), 5.67 (d, ^3J = 6 Hz, 2H, β-pyrrolic *ortho aryl*$_{in}$), 6.06 (d, ^3J = 6 Hz, 2H, β-pyrrolic *ortho aryl*$_{in}$), 6.49 (t, 4H, *aryl*), 6.53 (t, 4H, *aryl*), 6.70 (t, 4H, *aryl*), 6.75 (t, 4H, *aryl*), 6.79 (t, 4H, *aryl*), 6.84 (m, 8H, *aryl*), 7.03 (br t, 8H, *aryl*), 7.51 (d, ^3J = 6 Hz, 2H, β-pyrrolic *ortho aryl*$_{out}$), 7.72 (d, ^3J = 6 Hz, 2H, *meso ortho aryl*), 7.94 (d, ^3J = 6 Hz, 2H, *meso ortho aryl*), 7.97 (d, ^3J = 6 Hz, 2H, β-pyrrolic *ortho aryl*$_{out}$); δ_C (125 MHz, $CDCl_3$) 121.35 (C_q), 121.70 (C_q), 125.05 (br *C*H), 125.70 (*C*H), 126.03 (*C*H), 126.19 (*C*H), 126.33 (*C*H), 126.80 (*C*H), 126.86 (*C*H), 128.44 (*C*H), 131.34 (br *C*H), 131.65 (*C*H), 133.12 (*C*H), 136.57, 137.78 (*C*H), 137.86 (C_q), 138.36 (C_q), 138.80 (C_q), 146.67 (C_q); MS: MALDI-TOF-MS (*m/z*) 1222.30; λ_{max} ($CHCl_3$)/nm 465, 562, 611, 716.



Preparation of *meso* substituted porphyrins *via* dipyrromethane (General Method)[9]

Dibenzyl-3,3'-dihexyl-4,4'-dimethyl-dipyrromethane-5,5'-dicarboxylate (Fig.5.1) (2.00 g, 3.44 mmol) was dissolved in dry tetrahydrofuran (100 mL) containing triethylamine (1 mL). To this mixture was added, whilst stirring, palladium on charcoal (100 mg, 10 %). The reaction flask was evacuated and saturated with hydrogen three times before being left under a hydrogen atmosphere for two hours with continuous stirring. After this time, t.l.c was performed (hexane/ethyl acetate, 5:1) in order to confirm the absence of starting material and therefore completion of the reaction. Removal of the solid palladium on charcoal was achieved by filtration of the reaction mixture through a plug of celite. The solvent and triethylamine were removed initially, in part, by rotary evaporation and subsequently completely, by exposure to high vacuum for two hours.

TFA (20 mL) was added to the dried dipyrrole under nitrogen at O °C. The reaction was maintained at this temperature for 30 minutes before it was allowed to warm to room temperature over 30 minutes (or until all the solid had dissolved). Throughout this time the reaction vessel was intermittently evacuated to remove the carbon dioxide generated. After this time, dichloromethane (50 mL) was added to the reaction flask before transferring the mixture to a separating funnel. The deprotected dipyrromethane was then neutralised with sodium bicarbonate solution (2 x 250 mL) and washed with water (2 x 250 mL). The organic fraction was then dried over anhydrous sodium sulphate and the solvent removed *in vacuo*. The dipyrromethane was then dissolved in dry methanol/dry dichloromethane (1:1) under nitrogen before the aldehyde (3.44 mmol) was added. The reaction mixture was stirred at room temperature for 6 hours.

DDQ (1.18 g, 5.20 mmol) was then added to the reaction mixture and, whilst open to air, was stirred for 30 minutes. Chloroform (100 mL) was added to the reaction mixture. The reaction mixture was washed with a mix of saturated sodium bicarbonate solution and brine (4:1) (2 x 250 mL) (to neutralise the reaction), followed by distilled water (2 x 250 mL). The organic fractions were collected, dried over anhydrous sodium sulphate and the solvent removed *in vacuo*. Purification was performed by way of column chromatography on silica using specified solvent conditions to elute.

H_2 5,15-*bis*-(3,5-di-*tert*-butylphenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin[10] 7

Purification was performed by way of column chromatography on silica using chloroform, hexane and methanol (9:1:2) to elute. Further purification by recrystalisation from chloroform layered with methanol was performed.

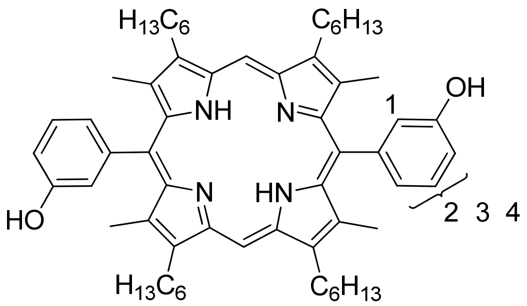
20 – 40 % yield; δ_H (400 MHz, $CDCl_3$) -2.38 (s, 2H, NH), 0.91 (m, 12 H, $(CH_2)_5$-C*H_3*), 1.38 (m, 8H, $(CH_2)_4$-C*H_2*-CH_3), 1.49 (m, 8H, $(CH_2)_3$-C*H_2*-CH_2CH_3), 1.52 (s, 36H, *tert*-butyl H), 1.75 (m, 8H, $(CH_2)_2$-C*H_2*-$(CH_2)_2$-CH_3), 2.21 (m, 8H, CH_2-C*H_2*-$(CH_2)_3$-CH_3), 2.47 (s, 12 H, *Me*), 3.99 (t, 8H, C*H_2*-$(CH_2)_4$-CH_3), 7.81 (t, 2H, *p-tert*-butyl *aryl* H), 7.94 (d, 4H, *o-tert*-butyl *aryl* H), 10.24 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.12 ($(CH_2)_5$-*C*H_3), 14.27 (Me), 22.78 ($(CH_2)_4$-*C*H_2CH_3), 26.80 (*C*H_2-$(CH_2)_4$-CH_3), 29.99 ($(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 31.66 (*tert*-butyl), 31.97 ($(CH_2)_3$-*C*H_2-CH_2CH_3), 33.31 (CH_2*C*$H_2(CH_2)_3$-CH_3), 35.14 (C_q *tert*-butyl), 96.78 (*meso C*), 119.11 (*meso-tert*-butyl *aryl*), 121.01 (*tert*-butyl *aryl*), 127.61 (*o-tert*-butyl *aryl*), 136.43 (*porph-tert*-butyl *aryl*), 141.03 (*m-tert*-butyl *aryl*), 141.30, 142.99, 145.12 and 149.81 (*pyrrole*); MS: MALDI-TOF-MS (*m/z*) 1078.89; λ_{max} ($CHCl_3$)/ nm 411, 508, 542, 574 and 717.

H_2 5-(4-carboxy phenyl)-15-(3, 5-di-*tert*-butyl phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 11

A 1:1 mixture of 3,5-di-*tert*-butylbenzaldyde (1.72 mmol) and 4-carboxy aldehyde (1.72 mmol) was used. Purification of 5-(4-carboxy phenyl)-15-(3,5-di tertiary butyl phenyl) porphyrin **11** from 5,15-*bis*-(3,5-di tertiary butyl phenyl) porphyrin **7** and 5,15-*bis*-(4-carboxy phenyl) porphyrin and the remaining crude material was by way of several silica columns using a mixture of chloroform (9), hexane (1) and methanol (2) to elute. The porphyrin was then re-crystallised by layered addition of methanol onto a solution of the product in the minimum amount of dichloromethane.

< 20 % yield; δ_H (400 MHz, $CDCl_3$) 0.86 (m, unsymmetrical, 12 H, $(CH_2)_5$-C*H_3*), 1.32 (m, 8H, $(CH_2)_4$-C*H_2*-CH_3), 1.42 (m, 8H, $(CH_2)_3$-C*H_2*-CH_2CH_3), 1.47 (s, 36H, *tert*-butyl H), 1.70 (m, 8H, $(CH_2)_2$-C*H_2*-$(CH_2)_2$-CH_3), 2.14 (m, 8H, CH_2-C*H_2*-$(CH_2)_3$-CH_3), 2.42 and 2.44 (s, 12 H, *Me*), 3.94 (m, 8H, C*H_2*-$(CH_2)_4$-CH_3), 7.77 (t, 1H, *p-tert*-butyl *aryl* H), 7.87 (d, 2H, *o-tert*-butyl *aryl* H), 8.14 (d, 2H, *m*-acid *aryl* H), 8.42 (d, 2H, *o*-acid *aryl* H), 10.19 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.06 and 14.08 ($(CH_2)_5$-*C*H_3), 14.26 and 14.92 (*Me*), 22.64 and 22.74 ($(CH_2)_4$-*C*H2CH3), 26.66 and 26.73 (*C*H_2-$(CH_2)_4$-CH_3), 29.83 and 29.94 ($(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 31.65 (*tert*-butyl), 31.87and 31.92 ($(CH_2)_3$-*C*H_2-CH_2CH_3), 33.20 and 33.29 (CH_2-*C*H_2-$(CH_2)_3CH_3$), 35.14 (*C_q tert-butyl*), 97.02 (*meso* CH), 116.16 and 119.67 (*meso-aryl* acid *and tert*-butyl), 121.11 (*p-tert*-butyl *aryl*), 127.53 (*o-tert*-butyl *aryl*), 129.43 (*o*-acid *aryl*), 133.35 (*m*-acid *aryl*), 135.19 (*porph*-acid *aryl*) 136.68 (*tert*-butyl *aryl-porph*),

missing *p*-acid *aryl*), 140.87 (*m-tert*-butyl *aryl*) 141.32, 141.49, 143.17, 143.55, 144.37, 145.29 and 149.90 (*pyrrole*), ~ 171 (*C*OOH); MS: MALDI-TOF-MS (*m/z*) 1010.74; λ_{max} ($CHCl_3$)/ nm 412, 508, 542, 574 and 626.



H_2 5,15-*bis*-(3-hydroxy phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin[11] (SP1)

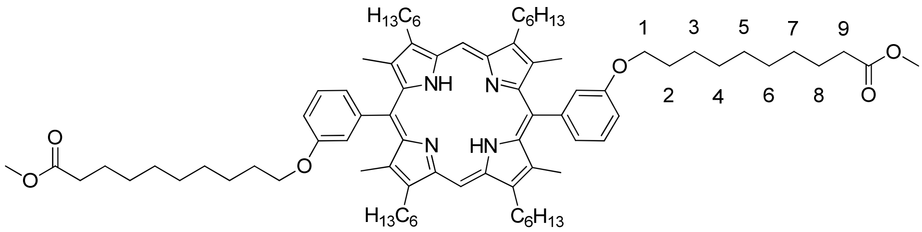
Purification was performed by way of column chromatography on silica using 20 - 40 % hexane/20% methanol in dichloromethane to elute the product.

18% yield; δ_H (400 MHz, $CDCl_3$) not observed (s, 2H, NH), 0.91 (t, 12 H, $(CH_2)_5$-C*H*$_3$), 1.36 (m, 8H, $(CH_2)_4$-C*H*$_2$-CH_3), 1.48 (m, 8H, $(CH_2)_3$-C*H*$_2$-CH_2CH_3), 1.73 (m, 8H, $(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 2.18 (m, 8H, CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 2.54 (s, 12 H, *Me*), 3.98 (t, 8H, C*H*$_2$-$(CH_2)_4$-CH_3), 7.20 - 7.22 (m, 2H, *aryl* H), 7.39 (t *br*, 2H, *aryl* H), 7.56 (t, 2H, *aryl* H), 7.62 (d, 2H, *aryl* H), 10.23 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.11 ($(CH_2)_5$-*C*H_3), 14.47 (Me), 22.72 ($(CH_2)_4$-*C*H_2CH_3), 26.77 (*C*H_2-$(CH_2)_4$-CH_3), 29.96 ($(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 31.97 ($(CH_2)_3$-*C*H_2-CH_2CH_3), 33.26 (CH_2*C*$H_2(CH_2)_3$-CH_3), 96.94 (*meso C*H), 115.12 (OH *aryl* C_1), 117.23 (*meso* C_q OH *aryl*), 120.33, 126.07, 128.74 (OH *aryl* $C_{2,3,4}$), 136.14, 141.36 and 143.31 (*pyrrole*), 143.65 (*meso* OH *aryl*), 144.84 (*pyrrole*), 154.99 (*aryl C*-OH); MS: MALDI-TOF-MS (*m/z*) 886.33; λ_{max} ($CHCl_3$)/ nm 409, 508, 540, 573 and 625.

H_2 5-(3-hydroxy phenyl)-15-(3,5-di-*tert*-butyl phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin (SP2)

< 20 % yield; δ_H (400 MHz, $CDCl_3$) -2.38 (s, 2H, NH), 0.90 (t, 12 H, $(CH_2)_5$-C*H*$_3$), 1.37 (m, 8H, $(CH_2)_4$-C*H*$_2$-CH_3), 1.49 (m, 8H, $(CH_2)_3$-C*H*$_2$-CH_2CH_3), 1.52 (s, 18H, di-*tert*-butyl), 1.73 (m, 8H, $(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 2.19 (m, 8H, CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 2.47 (s, 6 H, *Me*), 2.54 (s, 6 H, *Me*), 4.00 (t, 8H, C*H*$_2$-$(CH_2)_4$-CH_3), 7.15 (d, 2H, hydroxy *aryl* H), 7.37 (t *br*, 2H, hydroxy *aryl* H), 7.54 (t, 2H, hydroxy *aryl* H), 7.63 (d, 2H, hydroxy *aryl* H), 7.81 (t, 2H, *p-tert*-butyl *aryl* H), 7.93 (d, 4H, *o-tert*-butyl *aryl* H), 10.23 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.10 and 14.12 ($(CH_2)_5$-*C*H_3), 14.26 and 14.45 (*Me*), 22.72 and 22.77 ($(CH_2)_4$-*C*H_2CH_3), 26.78 (*C*H_2-$(CH_2)_4$-CH_3), 29.96 and 29.98 ($(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 31.65 (*tert*-butyl), 31.95 and 31.99 ($(CH_2)_3$-*C*H_2-CH_2CH_3), 33.28 (CH_2*C*$H_2(CH_2)_3$-CH_3), 35.13 (C_q *tert*-butyl), 96.81 (*meso C*H), 115.03 (OH *aryl C*H), 116.94 (*meso* C_q OH *aryl*), 119.41 (*meso* C_q di-*tert*-butyl *aryl*), 120.31 (OH *aryl C*H), 121.06 (di-*tert*-butyl *aryl C*H), 126.06 (OH *aryl CH*), 127.56 (di-*tert*-butyl *aryl C*H), 128.66 (OH *aryl C*H), 136.01 (OH *aryl pyrrole*), 136.55 (di-*tert*-butyl *aryl* C_q), 140.94 (di-*tert*-butyl *aryl* C_q), 141.32 (di-*tert*-butyl *pyrrole*), 141.38 (OH *aryl pyrrole*), 143.06 (di-*tert*-butyl *pyrrole*), 143.23 (OH *aryl pyrrole*), 143.69 (OH *aryl* C_q), 144.78 (OH *aryl pyrrole*), 145.18 (di-*tert*-butyl *pyrrole*), 149.85 (di-*tert*-butyl *pyrrole*), 154.93 (*aryl C*-OH); MS: MALDI-TOF-MS (*m/z*) 982.39; λ_{max} ($CHCl_3$)/ nm 409, 508, 541, 573 and 624.

Preparation of ester and acid appended porphyrins (Section 10)

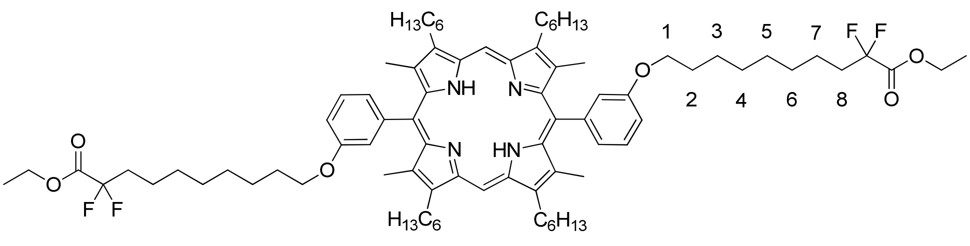


Preparation of H_2Bis-5,15-(3-O-$C_9H_{18}CO_2Me$ phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 18

To a round bottom flask (25 mL) containing anhydrous DMF (10 mL) was added H_2 5,15-*bis*-(3-hydroxy phenyl)-2,8,12,18-tetra methyl- 3,7,13,17-tetra hexyl porphyrin (SP1) (50 mg, 0.06 mmol) and anhydrous potassium carbonate powder (8 equivalents). Finally the methyl 10-iododecanoate (3 equivalents) was added to the reaction mixture (Care must be taken to perform the reaction under anhydrous conditions). Under nitrogen the reaction was heated to 50 °C and stirred. The mixture was t.l.c'd each hour using dichloromethane/hexane with 1 % methanol.

After 3 h the di-ester substituted porphyrin **18** appeared as the major band on the t.l.c. The DMF was removed under high vacuum and the crude reaction mixture was taken up in dichloromethane and washed with water (2 x 150 mL), dried over anhydrous sodium sulphate and the solvent removed *in vacuo*. Purification was performed by way of column chromatography on silica initially using 10 - 20 % dichloromethane/hexane to elute the unreacted methyl 10-iododecanoate before dichloromethane/hexane with 1 % methanol was used to elute the product.

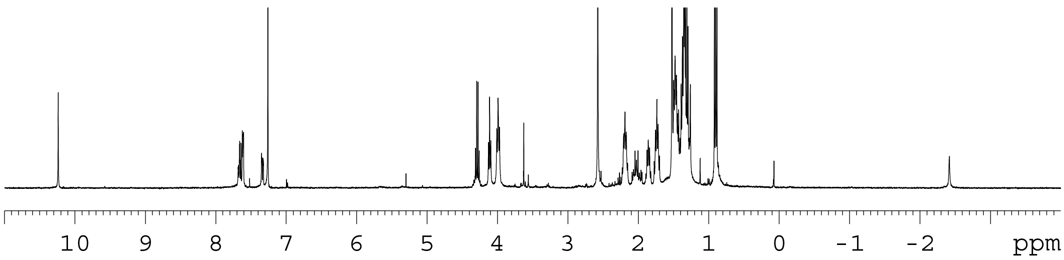
50-60 % yield; δ_H (400 MHz, $CDCl_3$) -2.40 (s, 2H, core NH), 0.92 (t, 12 H, $(CH_2)_5$-CH_3), 1.27 - 1.33 (m, 16H, Arm $H_{4,5,6,7}$), 1.38 (m, 8H, $(CH_2)_4$-CH_2-CH_3), 1.50 (m, 12H, Arm H_3, $(CH_2)_3$-CH_2-CH_2CH_3), 1.61 (m, 4H, Arm H_8), 1.75 (m, 8H, $(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 1.87, (m, 4H, Arm H_2), 2.21 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.28 (t, 4H, Arm H_9), 2.60 (s, 12 H, *Me*), 3.64 (s, 6H, CO_2Me), 4.00 (t, 8H, CH_2-$(CH_2)_4$-CH_3), 4.12 (t, 4H, Arm H_1), 7.35 (d, 2H, *aryl* H), 7.62 – 7.70 (m, 6H, *aryl* H), 10.25 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.12 ($(CH_2)_5$-CH_3), 14.45 (*Me*), 22.74 ($(CH_2)_4$-CH_2CH_3), 24.90 (Arm C_8), 26.01 (Arm C_3), 26.73 (CH_2-$(CH_2)_4$-CH_3), 29.08, 29.15, 29.33, 29.35 and 29.36 (Arm $C_{2,4,5,6,7}$), 29.98 ($(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 31.98 ($(CH_2)_3$-CH_2-CH_2CH_3), 33.29 ($CH_2CH_2(CH_2)_3$-CH_3), 34.05 (Arm C_9), 51.42 (CO_2Me), 68.34 (Arm C_1), 96.86 (*meso* CH), 115.03 (*aryl*), 117.75 (*meso* C_q), 119.24, 125.85 and 128.47 (*aryl* CH), 136.22, 141.37 and 143.23 (*pyrrole*), 143.39 (*aryl* C_q), 144.93 (*pyrrole*), 158.62 (*aryl* C-O-Arm), 174.27 (C=O); MS: MALDI-TOF-MS (*m/z*) 1255.94; λ_{max} ($CHCl_3$)/ nm 410, 508, 542, 573 and 654. $\varepsilon = 3.64 \times 10^5$ M^{-1} cm^{-1} at 410 nm.



Preparation of H_2Bis-5,15-(3-O-$C_9H_{16}F_2CO_2Et$ phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 20

Prepared and purified as for porphyrin **18** substituting ethyl 10-iodo-α,α-difluorodecanoate for the methyl 10-iododecanoate.

40 - 60 % yield; δ_H (400 MHz, $CDCl_3$) -2.40 (s *br,* 2H, core NH), 0.91 (t, 12 H, $(CH_2)_5$-C*H₃*), 1.27 - 1.38 (m, 26H, $(CH_2)_4$-C*H₂*-CH_3, Arm $H_{4,5,6,7}$, $CO_2CH_2CH_3$), 1.47 - 1.51 (m, 12H, $(CH_2)_3$-C*H₂*-CH_2CH_3, Arm H_3), 1.75 (m, 8H, $(CH_2)_2$-C*H₂*-$(CH_2)_2$-CH_3), 1.87, (m, 4H, Arm H_2), 2.06 (m, 4H, Arm H_8), 2.20 (m, 8H, CH_2-C*H₂*-$(CH_2)_3$-CH_3), 2.59 (s, 12 H, *Me*), 4.00 (t, 8H, C*H₂*-$(CH_2)_4$-CH_3), 4.12 (t, 4H, Arm H_1), 4.28 (q, 4H, CO_2C*H₂*CH_3), 7.35 (d, 2H, *aryl* H), 7.61 – 7.60 (m, 6H, *aryl* H), 10.25 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 13.89 (CO_2CH_2C*H₃*), 14.12 ($(CH_2)_5$-CH_3), 14.44 (*Me*), 21.38 (t, Arm C_7), 22.73 ($(CH_2)_4$-*C*H_2CH_3), 25.97 (Arm C_3), 26.78 (*C*H_2-$(CH_2)_4$-CH_3), 28.96, 29.14, 29.18 and 29.33 (Arm $C_{2,4,5,6}$), 29.97 ($(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 31.98 ($(CH_2)_3$-*C*H_2-CH_2CH_3), 33.28 ($CH_2CH_2(CH_2)_3$-CH_3), 34.42 (t, Arm C_8), 62.65 (CO_2*C*H_2CH_3), 68.28 (Arm C_1), 96.94 (*meso C*H), 115.00 (*aryl*), 116.33 (t, Arm C_9), 117.72 (*meso* C_q *aryl*), 119.22, 125.87 and 128.48 (*aryl*), 136.21, 141.36 and 143.23 (*pyrrole*), 143.39 (*aryl* C_q), 144.92 (*pyrrole*), 158.59 (*aryl C*-O-Arm), 164.40 (t, *C*=O); δ_F (400 MHz, $CDCl_3$) -106.16 (F_2CO_2Et); MS: MALDI-TOF-MS (*m/z*) 1355.8639; λ_{max} ($CHCl_3$)/ nm 410, 508, 542, 574 and 654. $\varepsilon = 3.86 \times 10^5$ M^{-1} cm^{-1} at 410 nm.



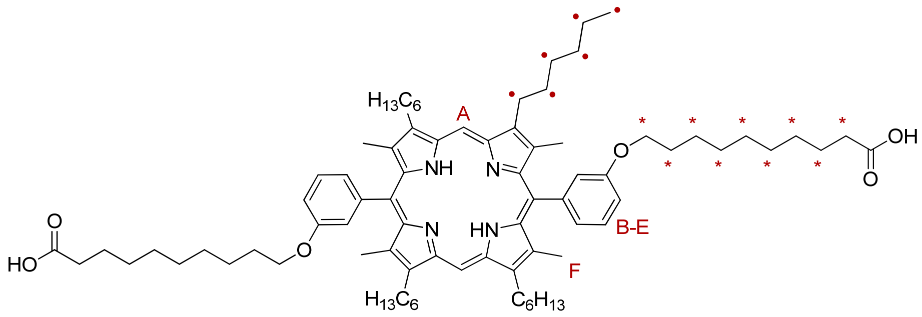
The ^{1}H NMR spectrum (400 MHz) of porphyrin **20** in *d*-chloroform at 298 K.

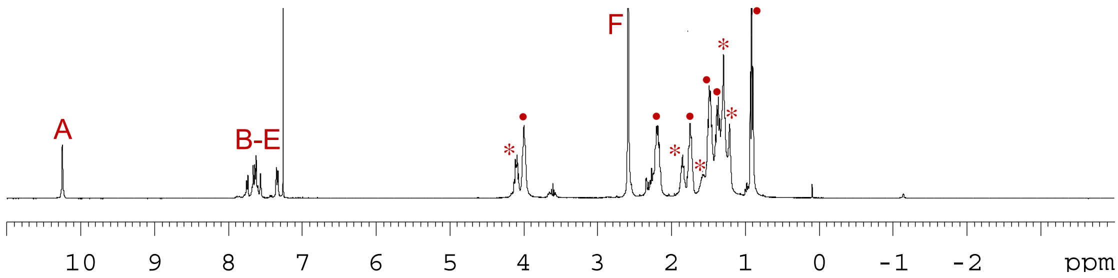
Preparation of H_2Bis-5,15-(3-O-$C_9H_{18}CO_2H$ phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 19

Porphyrin **18** (30 mg, 0.024 mmol) was dissolved in 30 % isopropanol/toluene with potassium hydroxide (8 equivalents) and refluxed for 2 h. After this time the solvent was removed *in vacuo* before the crude mixture was taken up in dichloromethane and washed with 3 M HCl (1 x 250 mL) and water (2 x 250 mL), the organic fraction was dried over anhydrous sodium sulphate and the solvent removed *in vacuo*.

95 % yield; δ_H (400 MHz, $CDCl_3$) not observed (2H, core NH), 0.90 (t, 12 H, $(CH_2)_5$-C*H₃*), 1.27 - 1.33 (m, 16H, Arm H), 1.38 (m, 8H, $(CH_2)_4$-C*H₂*-CH_3), 1.45 (m, 12H, $(CH_2)_3$-C*H₂*-CH_2CH_3), 1.61 (m, 4H, Arm H), 1.75 (m, 8H, $(CH_2)_2$-C*H₂*-$(CH_2)_2$-CH_3), 1.85, (m, 4H, Arm H), 2.21 (m, 8H, CH_2-C*H₂*-$(CH_2)_3$-CH_3), 2.28 (t, 4H, Arm H), 2.60 (s, 12 H, *Me*), 4.00 (t, 8H, C*H₂*-$(CH_2)_4$-CH_3), 4.13 (t, 4H, Arm H_1), 7.35 (d, 2H, *aryl* H), 7.56 – 7.68 (m, 4H, *aryl* H), 7.74 (d, 2H, *aryl* H), 10.25 (s, 2H, *meso* H); MS:

MALDI-TOF-MS (*m/z*) 1227.92; λ_{max} ($CHCl_3$)/ nm 410, 508, 542, 574 and 625. ε = 3.41 x 10^5 M^{-1} cm^{-1} at 410 nm.



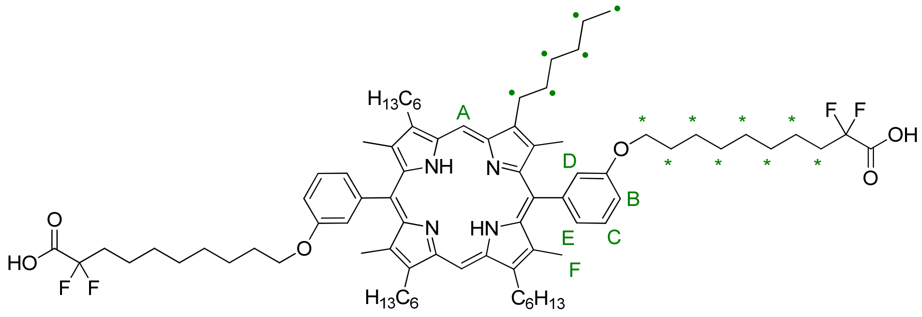


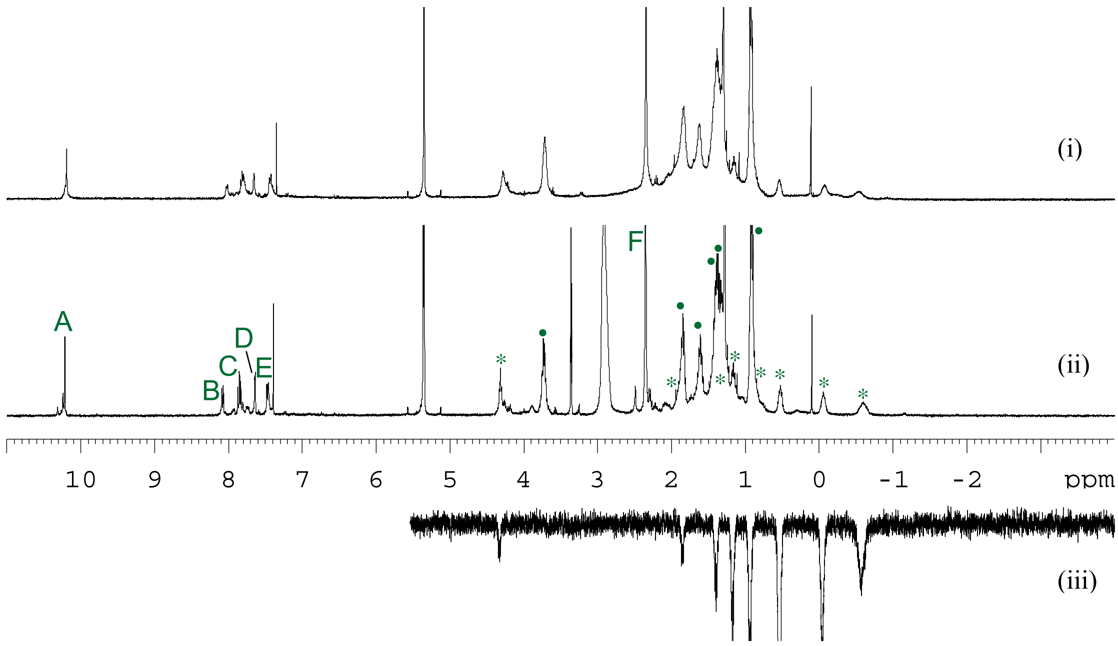
^{1}H NMR spectrum (400 MHz) of porphyrin **19** in *d*-chloroform at 293 K.
Due to significant overlap of several CH_2 (*) groups in the alkyl chains of the appended acids not all the signals could be resolved.

Preparation of H_2Bis-5,15-(3-O-$C_9H_{16}F_2CO_2H$ phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 21

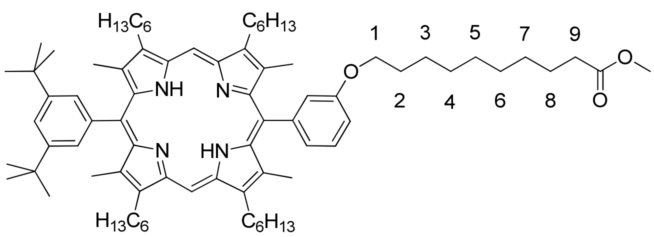
Porphyrin **20** (30 mg, 0.022 mmol) was dissolved in 30 % isopropanol/toluene with potassium hydroxide (8 equivalents) and stirred at room temperature for 24 h. After this time the solvent was removed *in vacuo* before the crude mixture was taken up in dichloromethane and washed with 3 M HCl (1 x 250 mL) and water (2 x 250 mL), the organic fraction was dried over anhydrous sodium sulphate and the solvent removed *in vacuo*.

95 % yield; δ_H (400 MHz, CD_2Cl_2 + MeOD) not observed (2H, core NH), -0.62 (br m, 4H, Arm H_8), -0.08 (br m, 4H, Arm H_7), 0.50 (m, 4H, Arm H_6), 0.87 (m, 4H, Arm H_5), 0.90 (t, 12 H, $(CH_2)_5$-CH_3), 1.13 (m, 4H, Arm H_4), 1.30 - 1.38 (m, 20H, $(CH_2)_4$-CH_2-CH_3, $(CH_2)_3$-CH_2-CH_2CH_3, Arm H_3), 1.58 (m, 8H, $(CH_2)_3$-CH_2-CH_2CH_3), 1.83 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.32 (s, 12 H, *Me*), 3.69 (t, 8H, CH_2-$(CH_2)_4$-CH_3), 4.30 (t, 4H, Arm H_1), 7.44 (d, 2H, *aryl* H), 7.61 (br s, 2H, *aryl* H), 7.82 (t, 2H, *aryl* H), 8.05 (d, 2H, *aryl* H), 10.21 (s, 2H, *meso* H); δ_C (125 MHz, CD_2Cl_2) 159.42 (t, *C*=O); δ_F (400 MHz, CD_2Cl_2) -109.50 (F_2CO_2H); MS: MALDI-TOF-MS (*m/z*) 1299.54; λ_{max} ($CHCl_3$)/ nm 437, 576 and 623. ε = 2.89 x 10^5 M^{-1} cm^{-1} at 437 nm.





[1]H NMR spectra (500 MHz) of porphyrin **21**.
(i) in d_2-dichloromethane at 293 K.
(ii) in *d*-chloroform with d_4-methanol (a few drops) at 293K.
(iii) 1D selective TOCSY of (ii) at 298 K.

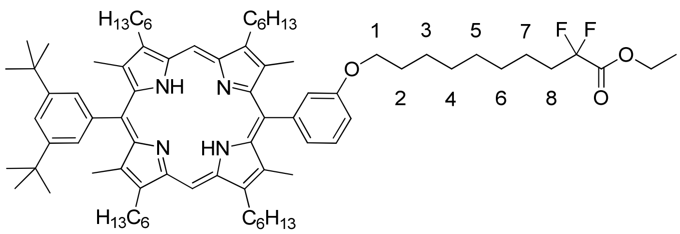


Preparation of H$_2$-5-(3-O-C$_9$H$_{18}$CO$_2$Me phenyl)-15-(3,5-di-*tert*-butyl phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 14

Prepared and purified as for porphyrin **18** substituting 1.5 equivalents of methyl 10-iododecanoate and four equivalents of anhydrous potassium carbonate.

> 80 % yield; δ_H (400 MHz, CDCl$_3$) -2.39 (d, 2H, core NH), 0.91 (t, 12 H, (CH$_2$)$_5$-C*H$_3$*), 1.30 (m, 8H, Arm H$_{4,5,6,7}$), 1.37 (m, 8H, (CH$_2$)$_4$-C*H$_2$*-CH$_3$), 1.50 (m, 10H, Arm H$_3$, (CH$_2$)$_3$-C*H$_2$*-CH$_2$CH$_3$), 1.52 (s, 18H, *tert*-butyl), 1.60 (m, 2H, Arm H$_8$), 1.75 (m, 8H, (CH$_2$)$_2$-C*H$_2$*-(CH$_2$)$_2$-CH$_3$), 1.87, (m, 2H, Arm H$_2$), 2.21 (m, 8H, CH$_2$-C*H$_2$*-(CH$_2$)$_3$-CH$_3$), 2.28 (t, 2H, Arm H$_9$), 2.47 (s, 6H, *Me*), 2.60 (s, 6 H, *Me*), 3.64 (s,

3H, CO_2*Me*), 4.00 (m, 8H, C*H₂*-$(CH_2)_4$-CH_3), 4.12 (t, 2H, Arm H_1), 7.35 (d, 2H, *aryl* H), 7.62 – 7.70 (m, 6H, *aryl* H), 7.82 (t, 1H, *p-tert*-butyl *aryl*), 7.93 (t, 2H, *o-tert*-butyl *aryl*), 10.24 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.12 and 14.13 ($(CH_2)_5$-CH_3), 14.26 and 14.46 (*Me*), 22.74 and 22.77 ($(CH_2)_4$-CH_2CH_3), 24.90 (Arm C_8), 26.02 (Arm C_3), 26.80 (CH_2-$(CH_2)_4$-CH_3), 29.09, 29.15, 29.34, 29.35 and 29.36 (Arm $C_{2,4,5,6,7}$), 29.98 ($(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 31.65 (*tert*-butyl), 31.96 and 32.00 ($(CH_2)_3$-CH_2-CH_2CH_3), 33.30 ($CH_2CH_2(CH_2)_3$-CH_3), 34.06 (Arm C_9), 35.13 (C_q *tert*-butyl), 51.40 (CO_2CH_3), 68.34 (Arm C_1), 96.80 (*meso* CH), 115.07 (Arm *aryl* CH), 117.53 (*meso* C_q arm *aryl*), 119.23 (Arm *aryl* CH), 119.33 (*meso* C_q di-*tert*-butyl *aryl*), 121.05 (di-*tert*-butyl *aryl* CH), 125.90 (Arm *aryl* CH), 127.57 (di-*tert*-butyl *aryl* CH), 128.45 (Arm *aryl* CH), 136.13 (Arm *pyrrole*), 136.51 (di-*tert*-butyl *aryl* C_q), 140.97 (di-*tert*-butyl *aryl* C_q), 141.32 (di-*tert*-butyl *pyrrole*), 141.35 (Arm *pyrrole*), 143.03 (di-*tert*-butyl *pyrrole*), 143.19 (Arm *pyrrole*), 143.46 (arm *aryl* C_q), 144.90 (Arm *pyrrole*), 145.15 (di-*tert*-butyl *pyrrole*), 149.84 (di-*tert*-butyl *pyrrole*), 158.61 (*aryl* C-O-Arm), 174.27 (C=O); MS: MALDI-TOF-MS (*m/z*) 1167.88; λ_{max} ($CHCl_3$)/ nm 410, 508, 541, 574 and 654. $\varepsilon = 3.88 \times 10^5$ M^{-1} cm^{-1} at 410 nm.

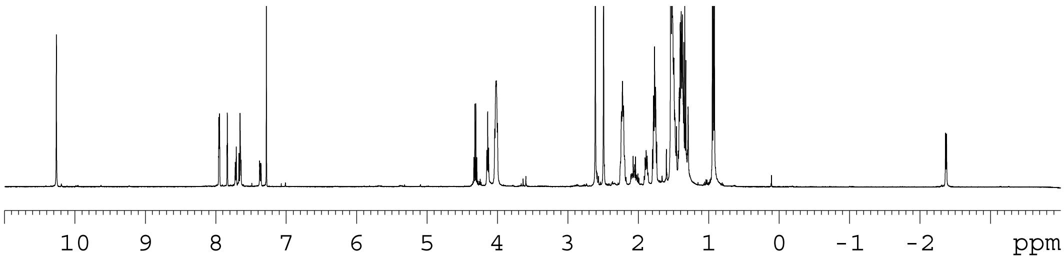


Preparation of H_2-5-(3-O-$C_9H_{16}F_2CO_2Et$ phenyl)-15-(3,5-di-*tert*-butyl phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 16

Prepared and purified as for porphyrin **18** substituting 1.5 equivalents of methyl 10-iodo-α,α-difluorodecanoate and four equivalents of anhydrous potassium carbonate.

> 60 % yield; δ_H (400 MHz, $CDCl_3$) -2.39 (d, 2H, core NH), 0.91 (t, 12 H, $(CH_2)_5$-CH_3), 1.30 (t, 3H, $CO_2CH_2CH_3$), 1.33 (m, 8H, Arm $H_{4,5,6,7}$), 1.37 (m, 8H, $(CH_2)_4$-CH_2-CH_3), 1.49 (m, 10H, Arm H_3, $(CH_2)_3$-CH_2-CH_2CH_3), 1.52 (s, 18H, *tert*-butyl), 1.75 (m, 8H, $(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 1.89, (m, 2H, Arm H_2), 2.02 (m, 2H, Arm H_8), 2.21 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.47 (s, 6H, *Me*), 2.60 (s, 6 H, *Me*), 4.00 (m, 8H, CH_2-$(CH_2)_4$-CH_3), 4.12 (t, 2H, Arm H_1), 4.30 (q, 2H, $CO_2CH_2CH_3$), 7.35 (d, 2H, *aryl* H), 7.62 – 7.70 (m, 6H, *aryl* H), 7.82 (t, 1H, *p-tert*-butyl *aryl*), 7.93 (t, 2H, *o-tert*-butyl *aryl*), 10.25 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 13.90 ($CO_2CH_2CH_3$), 14.11 and 14.12 ($(CH_2)_5$-CH_3), 14.26 and 14.45 (*Me*), 21.39 (t, Arm C_7), 22.73 and 22.77 ($(CH_2)_4$-CH_2CH_3), 25.98 (Arm C_3), 26.80 (CH_2-$(CH_2)_4$-CH_3), 28.96, 29.15, 29.18 and 29.34 (Arm $C_{2,4,5,6}$), 29.98 ($(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 31.65 (*tert*-butyl), 31.96 and 31.99 ($(CH_2)_3$-CH_2-CH_2CH_3), 33.30 ($CH_2CH_2(CH_2)_3$-CH_3), 34.43 (t, Arm C_8), 35.13 (C_q *tert*-butyl), 62.65 (Arm C_1), 68.28 ($CO_2CH_2CH_3$), 96.80 (*meso* CH), 115.05 (Arm *aryl* CH), 116.34 (t, Arm C_9), 117.50 (*meso* C_q arm *aryl*), 119.22 (Arm *aryl* CH), 119.34 (*meso* C_q *tert*-butyl *aryl*), 121.05 (di-*tert*-butyl *aryl* CH), 125.92 (Arm *aryl* CH), 127.57 (di-*tert*-butyl *aryl* CH), 128.45 (Arm *aryl* CH), 136.12 (Arm *pyrrole*), 136.53 (di-*tert*-butyl C_q *aryl*), 140.96 (di-*tert*-butyl *aryl* C_q), 141.32 (di-*tert*-butyl *pyrrole*), 141.35 (Arm *pyrrole*), 143.04 (di-*tert*-butyl *pyrrole*), 143.19 (Arm *pyrrole*), 143.48

(Arm *aryl* C_q), 144.90 (Arm *pyrrole*), 145.16 (di-*tert*-butyl *pyrrole*), 149.84 (di-*tert*-butyl *pyrrole*), 158.59 (*aryl* *C*-O-Arm), 164.41 (t, *C*=O); δ_F (400 MHz, $CDCl_3$) -106.14 (F_2CO_2Et); MS: MALDI-TOF-MS (*m/z*) 1217.55; λ_{max} ($CHCl_3$)/ nm 410, 508, 541, 574 and 654. $\varepsilon = 3.68 \times 10^5$ M^{-1} cm^{-1} at 410 nm.

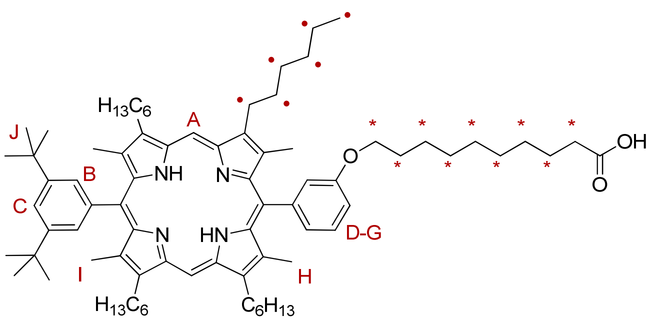


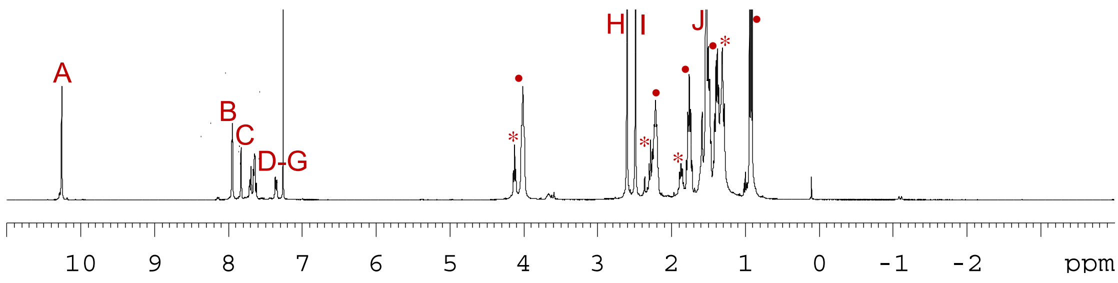
The ^1H NMR spectrum (400 MHz) of porphyrin **16** in *d*-chloroform at 298 K.

Preparation of H_2-5-(3-O-$C_9H_{18}CO_2H$ phenyl)-15-(3,5-di-*tert*-butyl phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 15

Porphyrin **14** (30 mg, 0.026 mmol) was dissolved in 30 % isopropanol/toluene with potassium hydroxide (4 equivalents) and refluxed for 2 h. After this time the solvent was removed *in vacuo* before the crude mixture was taken up in dichloromethane and washed with 3 M HCl (1 x 250 mL) and water (2 x 250 mL), the organic fraction was dried over anhydrous sodium sulphate and the solvent removed *in vacuo*.

95 % yield; δ_H (400 MHz, $CDCl_3$) not observed (2H, core NH), 0.91 (t, 12 H, $(CH_2)_5$-CH_3), 1.25 – 1.65 (m, 44H, Arm H x 5, $(CH_2)_4$-CH_2-CH_3, $(CH_2)_3$-CH_2-CH_2CH_3 and *tert*-butyl), 1.75 (m, 8H, $(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 1.87, (m, 2H, Arm H_2), 2.22 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.28 (t, 2H, Arm H), 2.49 (s, 6H, *Me*), 2.60 (s, 6 H, *Me*), 4.01 (m, 8H, CH_2-$(CH_2)_4$-CH_3), 4.12 (t, 2H, Arm H_1), 7.37 (d, 1H, *aryl* H), 7.60 – 7.70 (m, 6H, *aryl* H), 7.82 (t, 1H, *p*-*tert*-butyl *aryl*), 7.95 (d, 2H, *o*-*tert*-butyl *aryl*), 10.26 (s, 2H, *meso* H); MS: MALDI-TOF-MS (*m/z*) 1153.88; λ_{max} ($CHCl_3$)/ nm 410, 508, 542, 574 and 625. $\varepsilon = 3.29 \times 10^5$ M^{-1} cm^{-1} at 410 nm.



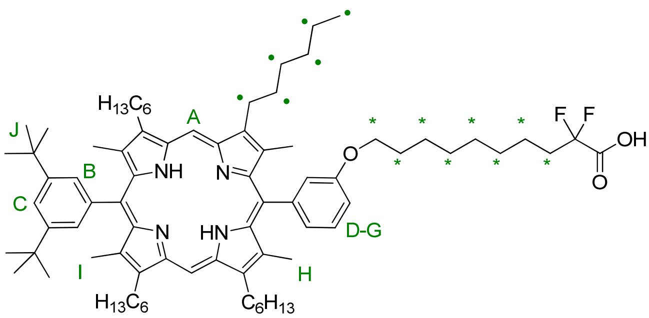


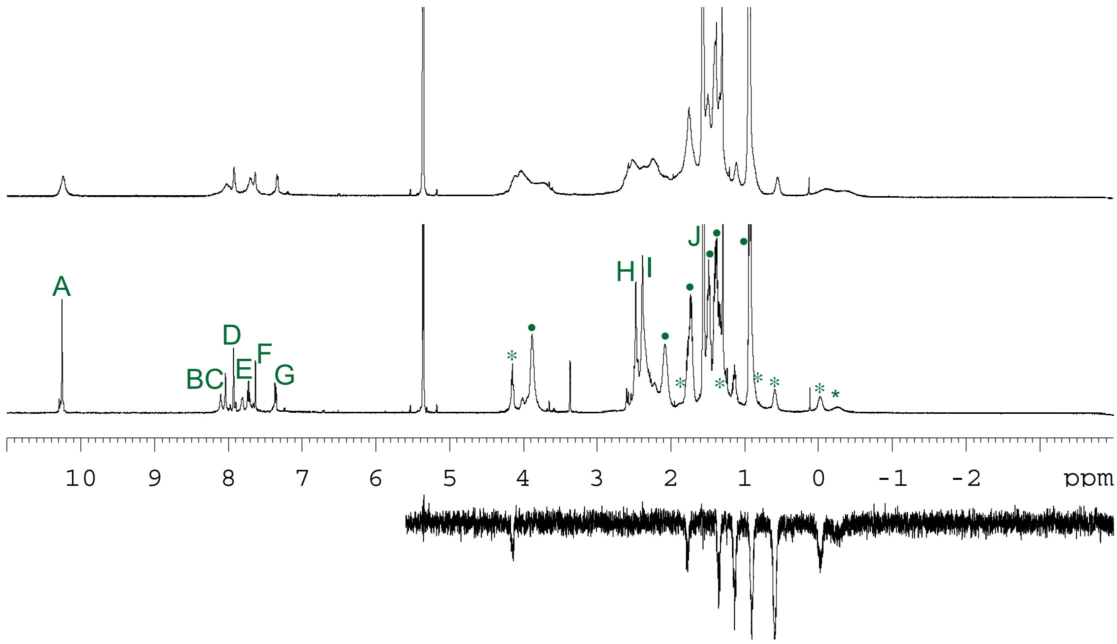
^{1}H NMR spectrum (400 MHz) of porphyrin **15** in *d*-chloroform at 293 K.
Due to significant overlap of several CH_2 (*) groups in the alkyl chains of the appended acids not all the signals could be resolved.

Preparation of H_2-5-(3-O-$C_9H_{16}F_2CO_2H$ phenyl)-15-(3,5-di-*tert*-butyl phenyl)-2,8,12,18-(tetra methyl)-3,7,13,17-(tetra hexyl)porphyrin 17

Porphyrin **16** (30 mg, 0.025 mmol) was dissolved in 30 % isopropanol/toluene with potassium hydroxide (4 equivalents) and stirred at room temperature for 24 h. After this time the solvent was removed *in vacuo* before the crude mixture was taken up in dichloromethane and washed with 3 M HCl (1 x 250 mL) and water (2 x 250 mL), the organic fraction was dried over anhydrous sodium sulphate and the solvent removed *in vacuo*.

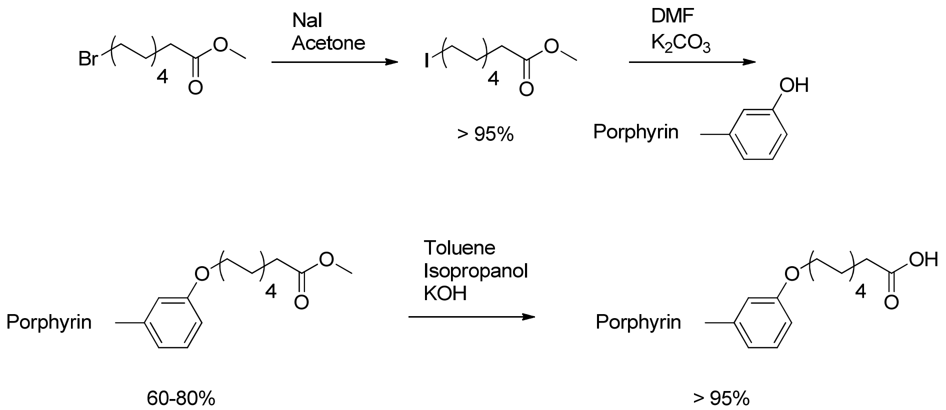
95 % yield; δ_H (400 MHz, CD_2Cl_2 + MeOD) not observed (2H, core NH), -0.40 (br m, 2H, Arm H_8), -0.13 (br m, 2H, Arm H_7), 0.54 (br m, 2H, Arm H_6), 0.92 (br m, 2H, Arm H_5), 0.95 (t, 12 H, $(CH_2)_5$-CH_3), 1.12 (m, 2H, Arm H_4), 1.30 - 1.57 (m, 36H, $(CH_2)_4$-CH_2-CH_3, $(CH_2)_3$-CH_2-CH_2CH_3, Arm H_3, *tert* butyl), 1.75 (m, 10H, Arm H_2, $(CH_2)_3$-CH_2-CH_2CH_3, 2.10 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.40 (s, 6 H, *Me*), 2.48 (s, 6 H, *Me*), 3.89 (br m, 8H, CH_2-$(CH_2)_4$-CH_3), 4.14 (t, 2H, Arm H_1), 7.34 (d, 1H, *aryl* H), 7.64 (s, 1H, *aryl* H), 7.72 (br t, 1H, *aryl* H), 7.81 (br m, 1H, *aryl* H), 7.93 (s, 2H, *aryl* H), 8.05 (br s, 1H, *aryl* H), 10.24 (s, 2H, *meso* H); δ_C (125 MHz, CD_2Cl_2) 159.20 (*C*=O); δ_F (400 MHz, CD_2Cl_2) -108.65 (br s, F_2CO_2H); MS: MALDI-TOF-MS (*m/z*) 1189.57; λ_{max} ($CHCl_3$)/ nm 410, 508, 542, 573 and 625. $\varepsilon = 2.52 \times 10^5$ M^{-1} cm^{-1} at 411 nm.



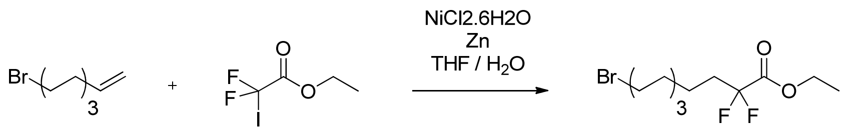


^{1}H NMR spectrum (500 MHz) of porphyrin **17**.
(i) in d_2-dichloromethane at 293 K.
(ii) in *d*-chloroform with d_4-methanol (a few drops) at 293K.
(iii) 1D selective TOCSY of (ii) at 298 K.

Preparation of fluorinated and non-fluorinated ester arms



Basic synthetic route to desired acid appended porphyrins using Finkelstein[12] and Williamson[13] ether coupling reactions.



α,α-fluorinated ester *via* bromoalkene.[14]

Methyl 10-bromodecanoate

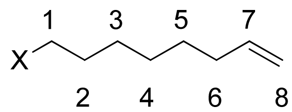
Methyl 10-bromodecanoate was used as obtained (Aldrich) without further purification.

δ_H (400 MHz, $CDCl_3$) 1.30 (m, 8H, $H_{3,4,5,6}$), 1.42 (m, 2H, H_2), 1.62 (m, 2H, H_7), 1.85 (m, 2H, H_8), 2.30 (t, 2H, H_9), 3.41 (t, 2H, H_1), 3.67 (s, 3H, CO_2Me).

Methyl 10-iododecanoate

Methyl 10-bromodecanoate (1g, 3.77 mmol) was dissolved in acetone (100 mL) before sodium iodide (5 equivalents) was added and the mixture refluxed for 48 h. After this time the solvent was removed *in vacuo*. The crude residue was then taken up in dichloromethane, washed with water (3 x 250 mL), the organic phase dried over anhydrous sodium sulphate and the solvent removed *in vacuo*. The product was comprehensively dried under a high vacuum overnight.

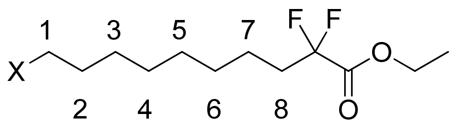
95 % yield; δ_H (400 MHz, $CDCl_3$) 1.29 (m, 8H, $H_{3,4,5,6}$), 1.38 (m, 2H, H_2), 1.62 (m, 2H, H_7), 1.82 (q, 2H, H_8), 2.30 (t, 2H, H_9), 3.20 (t, 2H, H_1), 3.67 (s, 3H, CO_2Me); δ_C (125 MHz, $CDCl_3$) 7.27 (C_1), 24.89 (CH_2), 28.42 (CH_2), 29.05 (CH_2), 29.10 (CH_2), 29.17 (CH_2), 30.43 (CH_2), 33.49 (CH_2), 34.06 (CH_2), 51.43 (CO_2Me), 174.27 (CO_2Me).



8-bromo-1-octene

8-bromo-1-octene was used as obtained (Aldrich) without further purification.

δ_H (400 MHz, $CDCl_3$) 1.35 – 1.44 (m, 6H, $H_{3,4,5}$), 1.86 (q, 2H, H_2), 2.05 (m, 2H, H_6), 3.41 (t, 2H, H_1), 4.93 and 4.95 (d, J_{AB} = 2.0 Hz and J_{AX} = 10.4 Hz, 1H, $H_{8(cis)}$), 4.98 and 5.02 (d, J_{AB} = 2.0 Hz and J_{AX} = 17.2 Hz, 1H, $H_{8(trans)}$), 5.80 (m, 1H, H_7).



Ethyl-10-bromo-2,2-difluoroacetate[14]

THF (3 mL) was added to a round bottom flask (10 mL) and flushed with nitrogen for 10 minutes. After this time zinc powder (342 mg, 5.23 mmol), nickel chloride hexahydrate (52 mg, 0.22 mmol) and water (1 drop) were added under nitrogen. The mixture was stirred at room temperature for 15 minutes. To the flask was then added 8-bromo-1-octene (1g, 5.23 mmol) and iododifluoroacetate (770 µL, 5.23 mmol). The flask was sealed and the mixture stirred at room temperature under an atmosphere of nitrogen. The reaction mixture was regularly t.l.c'd using 10 % ethylacetate/hexane to elute. The starting material and product were identified using potassium permanganate and 2,4-dinitrophenyl hydrazine (Brady's test)[15] staining agents respectively.

60 – 70 % yield; δ_H (400 MHz, $CDCl_3$) 1.33 – 1.40 (m, 8H, $H_{3,4,5,6}$), 1.35 (t, 3H, $CO_2CH_2CH_3$), 1.46 (m, 2H, H_7), 1.85 (q, 2H, H_2), 2.05 (m, 2H, H_8), 3.40 (t, 2H, H_1), 4.32 (q, 2H, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 13.96 ($CO_2CH_2CH_3$), 21.36 (C_7), 28.02, 28.47, 28.90 and 29.00 ($C_{3,4,5,6}$), 32.70 (C_2), 33.91 (C_1), 34.42 (t, C_8), 62.70 ($CO_2CH_2CH_3$), 116.33 (t, C_{10}), 164.41 (t, C=O); δ_F (400 MHz, $CDCl_3$) -106.16 (F_2CO_2Et).

Ethyl-10-iodo-2,2-difluoroacetate

Ethyl 10-bromo-2,2-decanoate (0.5 g, 1.59 mmol) was dissolved in acetone (50 mL) before sodium iodide (5 equivalents) was added and the mixture refluxed for 48 h. After this time the solvent was removed *in vacuo*. The crude residue was then taken up in dichloromethane, washed with water (3 x 250 mL), the organic phase dried over anhydrous sodium sulphate and the solvent removed *in vacuo*. The product was comprehensively dried under a high vacuum overnight.

> 95 % yield; δ_H (400 MHz, $CDCl_3$) 1.32 – 1.39 (m, 8H, $H_{3,4,5,6}$), 1.35 (t, 3H, $CO_2CH_2CH_3$), 1.45 (m, 2H, H_7), 1.83 (m, 2H, H_2), 2.04 (m, 2H, H_8), 3.18 (t, 2H, H_1), 4.33 (q, 2H, CH_2CH_3); δ_C (125 MHz, $CDCl_3$) 7.15 (C_1), 13.96 ($CO_2CH_2CH_3$), 21.35 (t, C_7), 28.25, 28.91 and 28.99 ($C_{4,5,6}$), 30.35 (C_3), 33.41 (C_2), 34.41 (t, C_8), 62.70 ($CO_2CH_2CH_3$), 116.33 (t, C_9), 164.41 (t, C=O).

Synthesis references:

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Spectroscopic analysis:

Porphyrin NMR features at various temperatures and concentrations, showing a small variation in chemical shift as a function of temperature.

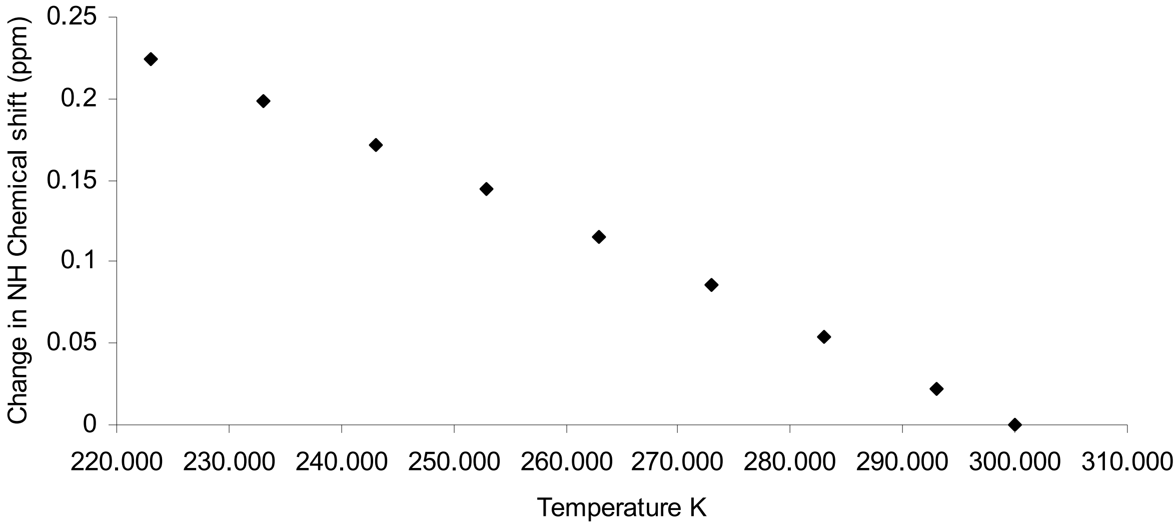


Figure S1. Graph highlights the relationship between the core NH signal of freebase porphyrin **1** (4.6 mmol) and temperature.

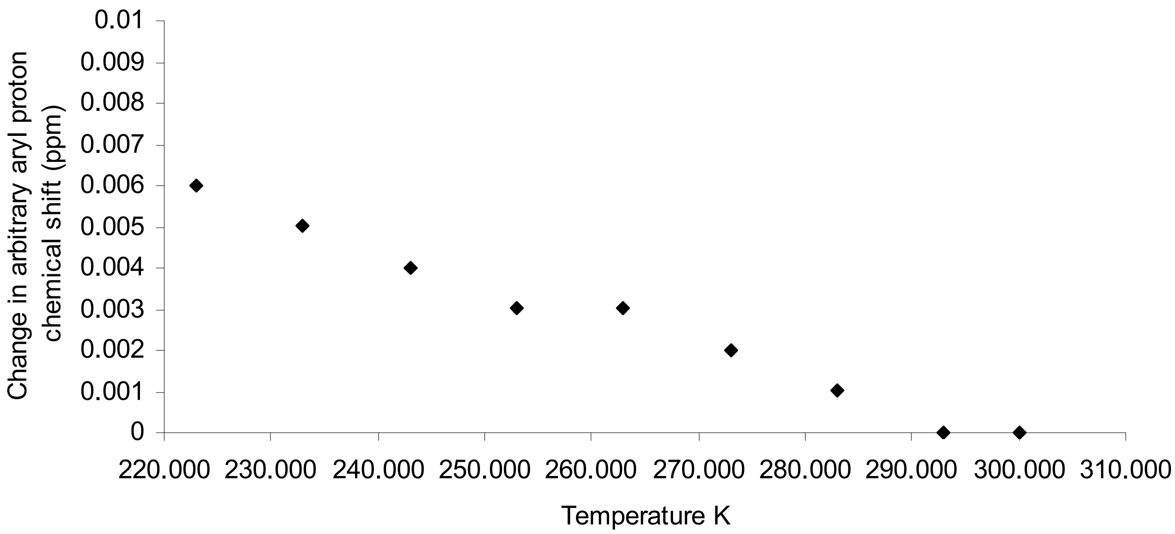


Figure S2. Graph highlights the relationship between an arbitrary aryl proton signal on freebase porphyrin **1** (4.6 mmol) and temperature.

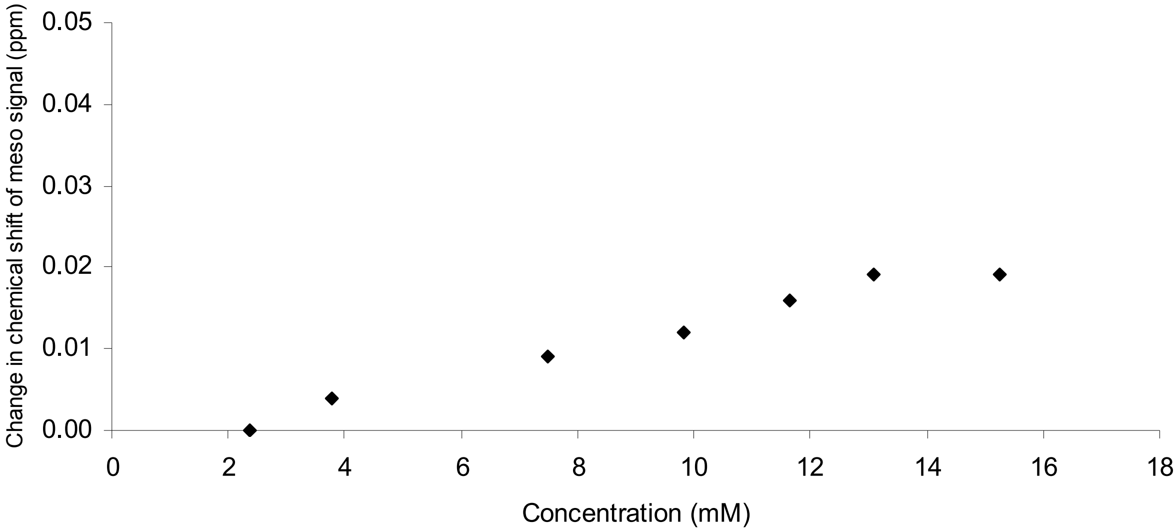
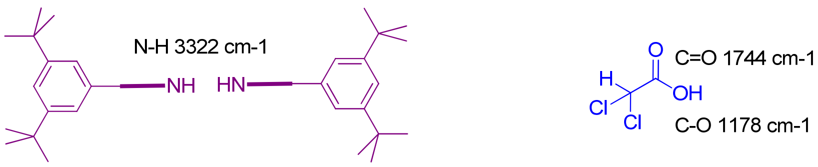


Figure S3. Graph highlights the relationship between the chemical shift of the meso resonance of porphyrin **7** and concentration at 298 K.



Characteristic IR stretching frequencies for porphyrin **1** and DCA.

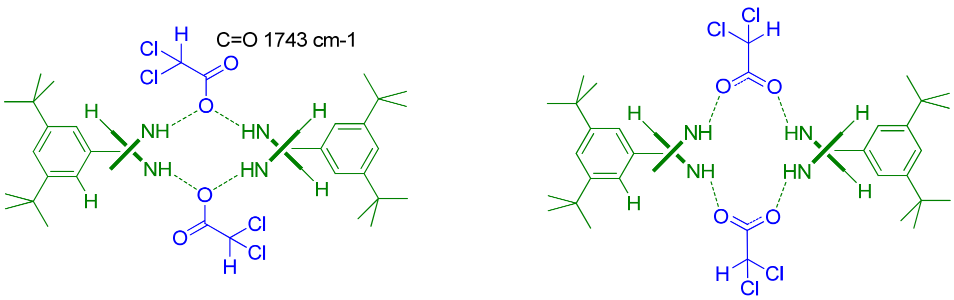


Figure S4. Mono- (left) and bidentate (right) carboxylate anion binding motifs for acid-porphyrin complexes and the C=O IR stretching frequency observed for the porphyrin **1** acid-porphyrin complex.

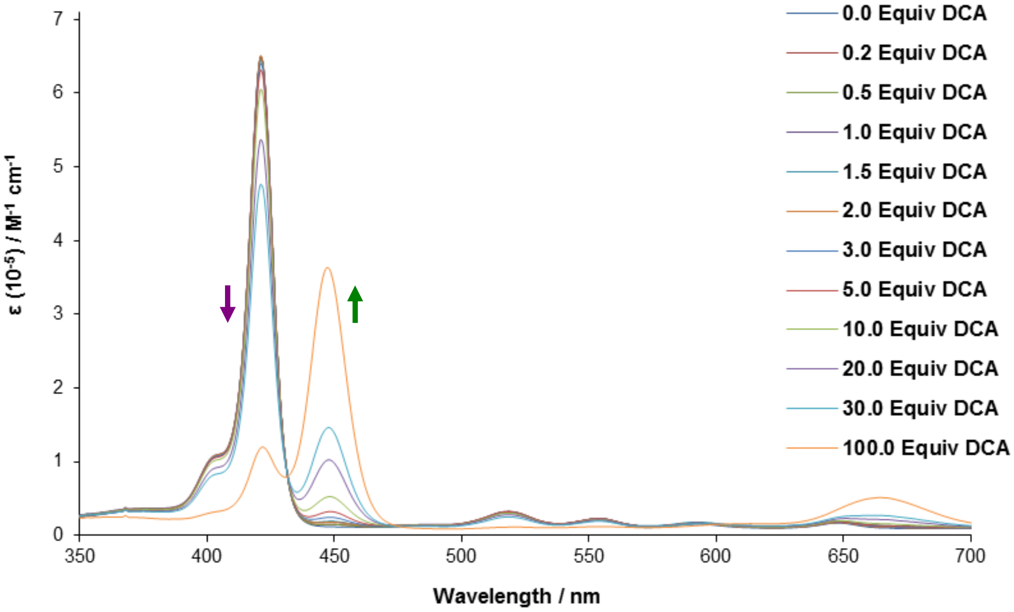
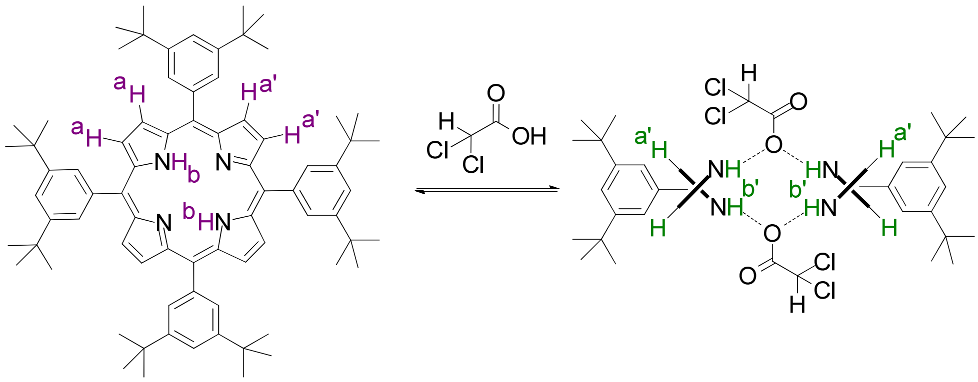


Figure S5. UV/Vis Spectra following the titration of porphyrin **1** with DCA in chloroform. The spectra show a single isosbestic point between the Soret bands of the freebase porphyrin **1** at 421 nm and the acid-porphyrin complex at 447 nm.



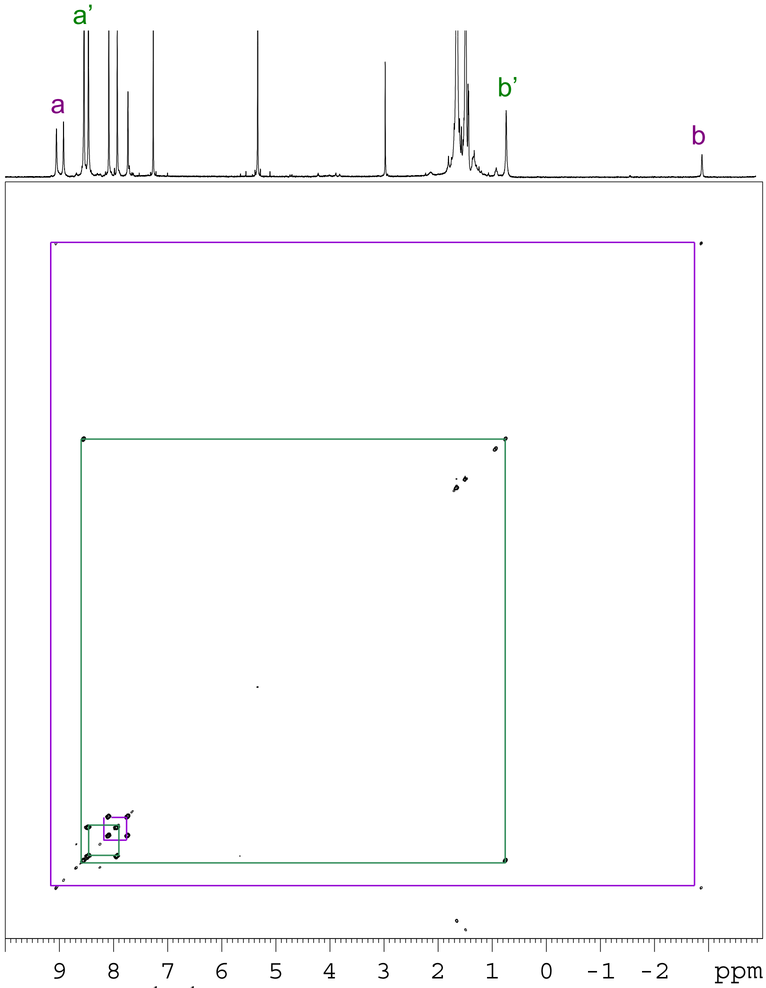


Figure S6. 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of 1:1 mixture of porphyrin **1** and DCA in *d*-chloroform at 228 K. The spectrum highlights the signals present as a result of the long range coupling between the core NH protons and the respective pyrrolic resonances of the freebase porphyrin and the acid-porphyrin complex.

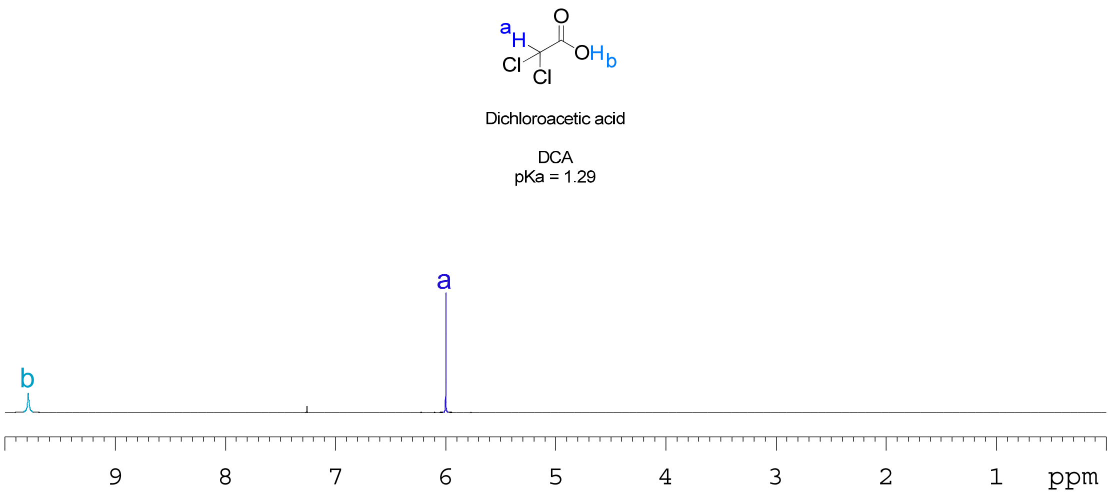
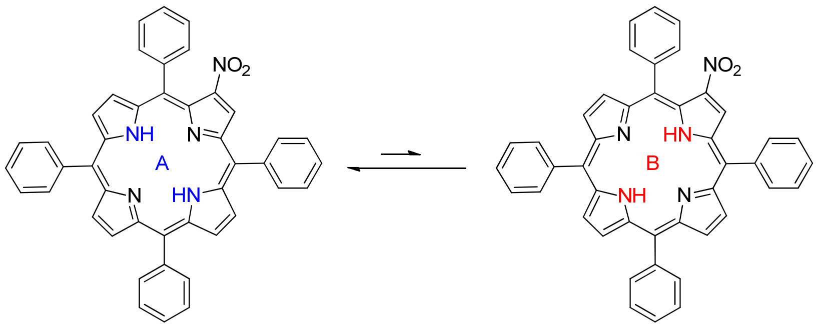


Figure S7. ^{1}H NMR spectrum (400 MHz) of dichloroacetic acid (DCA) in *d*-chloroform at 298 K.



Tautomers of porphyrin **3**.

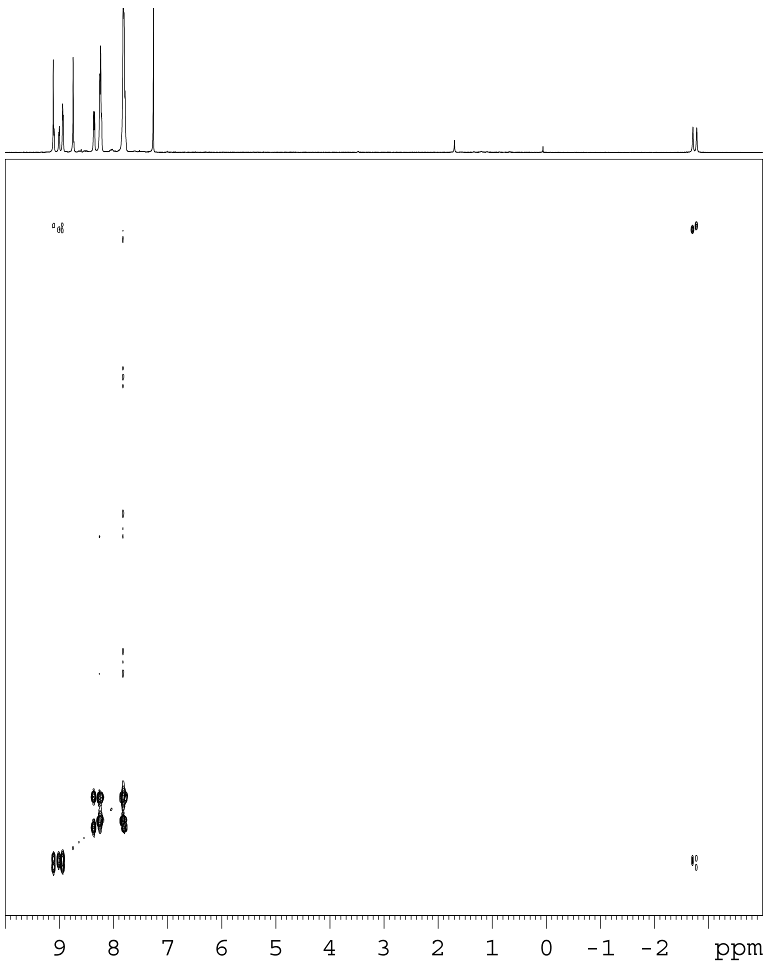
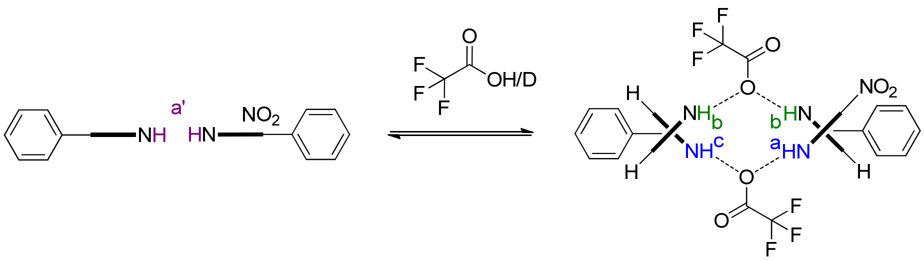


Figure S8. 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of porphyrin **3** in *d*-chloroform at 228 K. The two distinct inner-NH peaks of the major tautomer (near -3ppm) show correlations to the β-pyrrolic resonances above 9ppm.



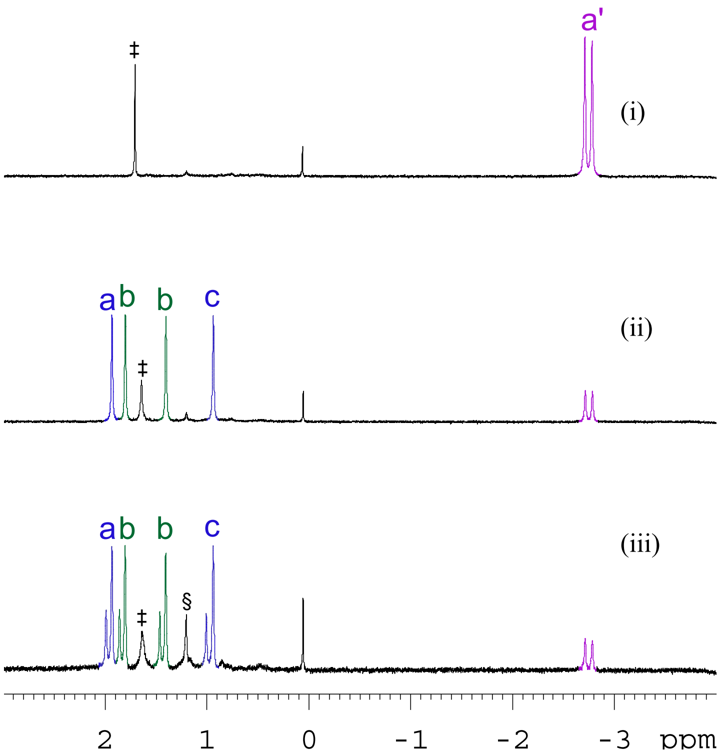


Figure S9. Highfield region of the ^{1}H NMR spectrum (400 MHz) in *d*-chloroform at 228 K of (i) porphyrin **3**, (ii) porphyrin **3** and two equivalents of TFA, and (iii) porphyrin **3** and two equivalents of *d*-TFA (‡ H_2O § DHO).

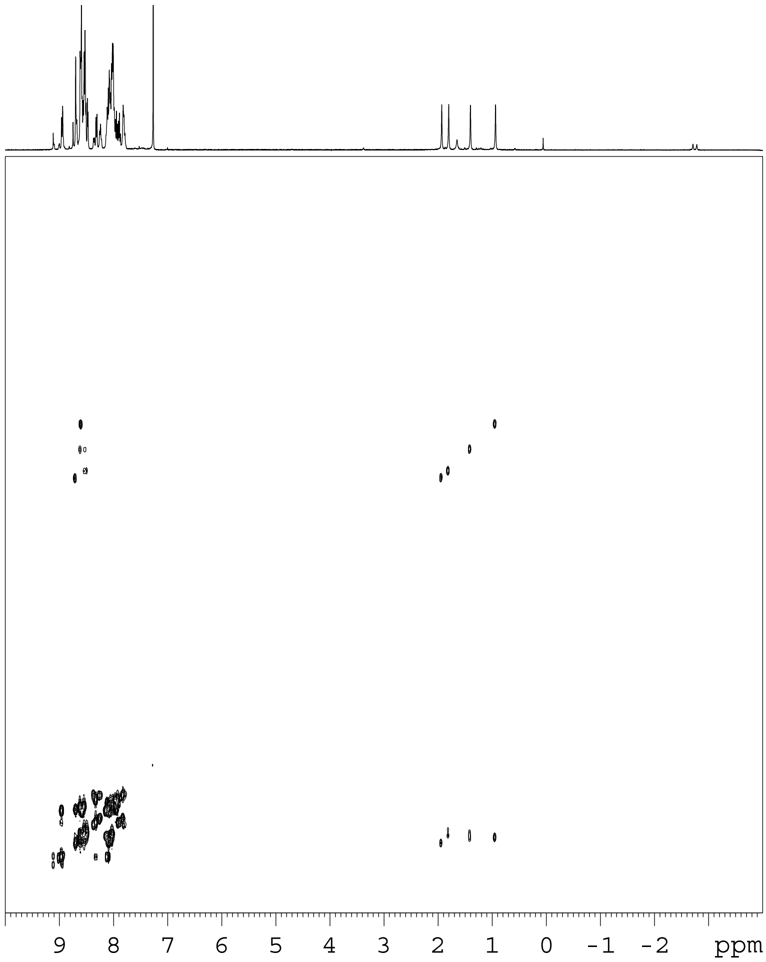
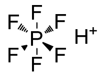
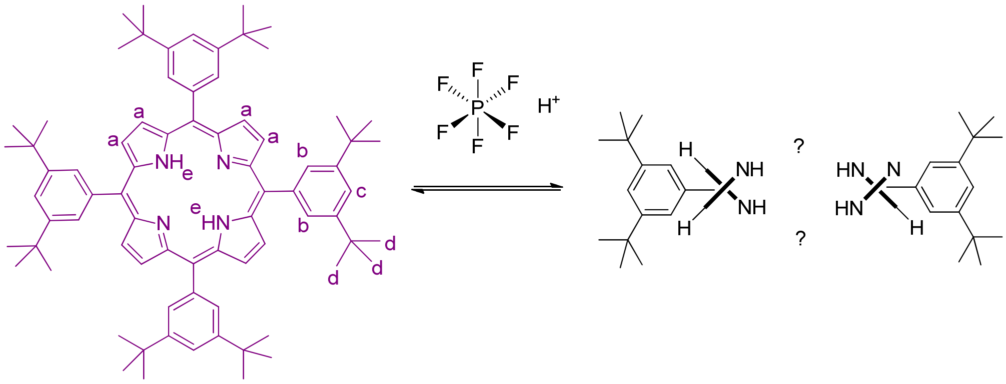


Figure S10. 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of porphyrin **3** with two equivalents of TFA in *d*-chloroform at 228 K. The resonances between 1-2 ppm show correlations to the β-pyrrolic resonances above 8.5 ppm.





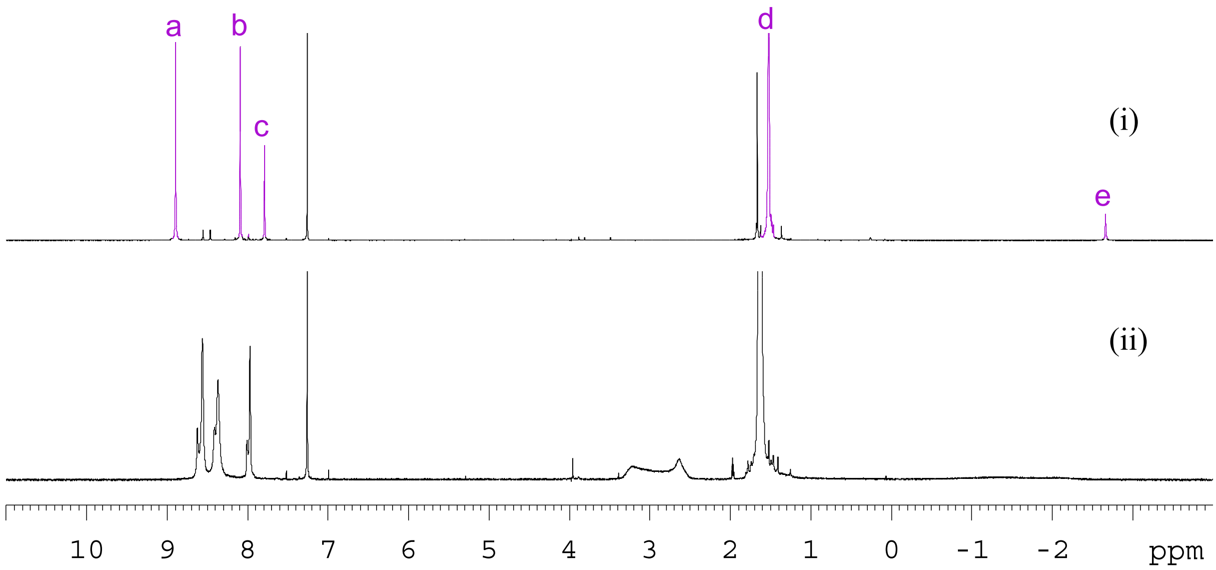
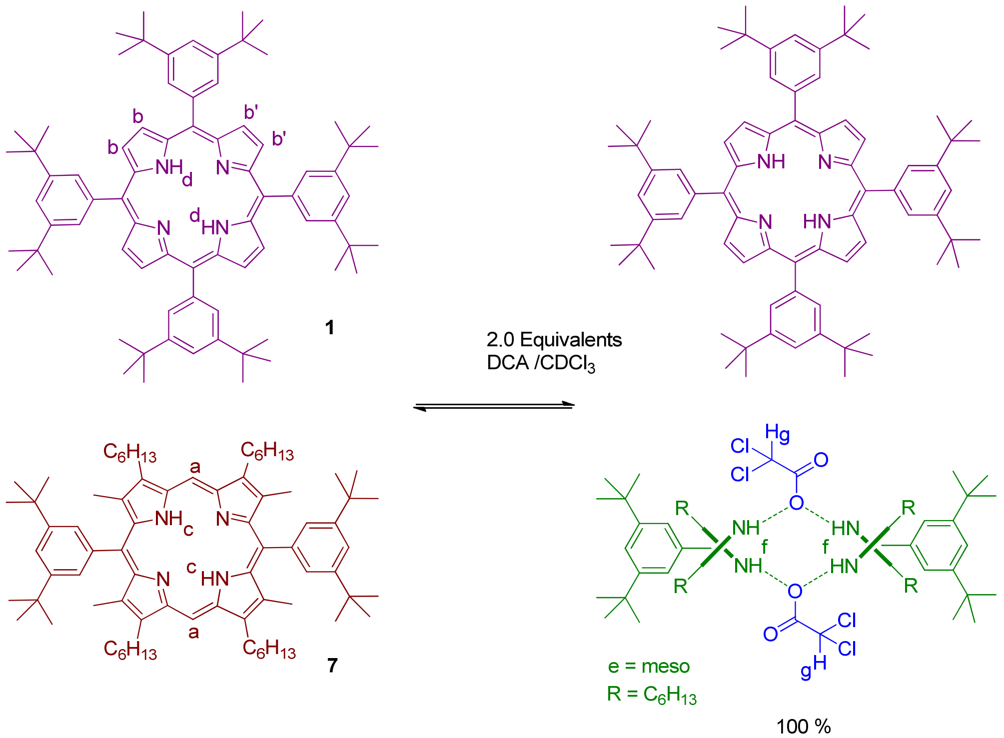


Figure S11. ^{1}H NMR spectra (400 MHz) in *d*-chloroform and *d*$_3$-acetonitrile at 298 K of (i) porphyrin **1** (small amount of water present ~1.7 ppm), and (ii) porphyrin **1** with one equivalent of HFPA.

In this example the absence of any readily identifiable signals (i.e. single core NH resonance or a single β-pyrrolic resonance) as observed in all our previous examples was sufficient enough to support the claim that in the absence of a coordinating anion the system does not behave in the same predictable manner. The broad resonance observed in spectrum (ii) (2.6 - 3.3 ppm) could not be assigned definitively so we chose not to speculate.



Scheme representing the competition between porphyrins **1** and **7** for two equivalents of DCA.

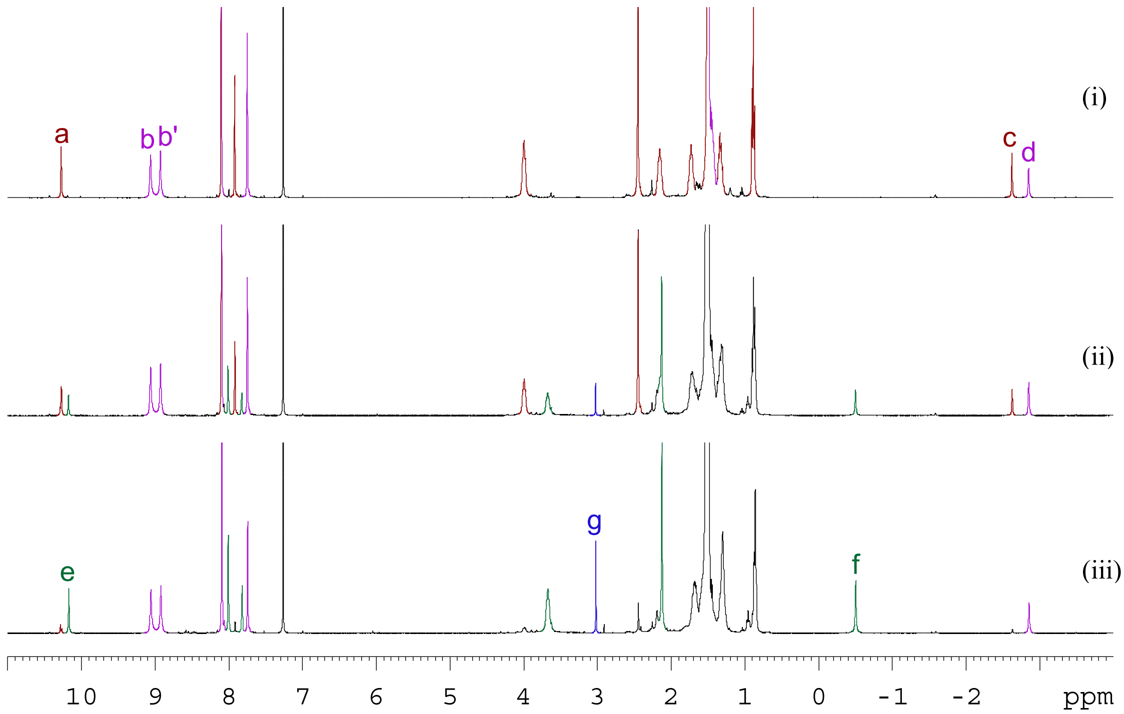
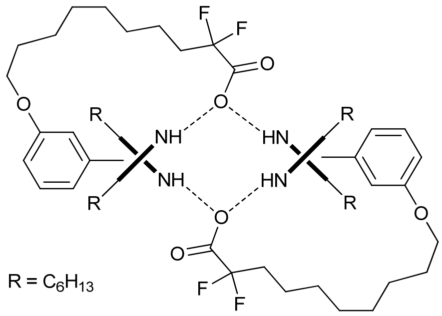
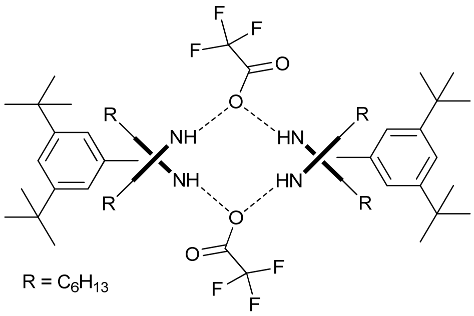


Figure S12. [1]H NMR spectra (400 MHz) of the competition between porphyrins **1** and **7** for 2 equivalents of DCA in *d*-chloroform at 223 K: (i) a 1:1 mixture of porphyrins **1** and **7** in the absence of DCA, (ii) a 1:1 mixture of porphyrins **1** and **7** with one equivalent of DCA, and (iii) a 1:1 mixture of porphyrins **1** and **7** with two equivalents of DCA.



21



7

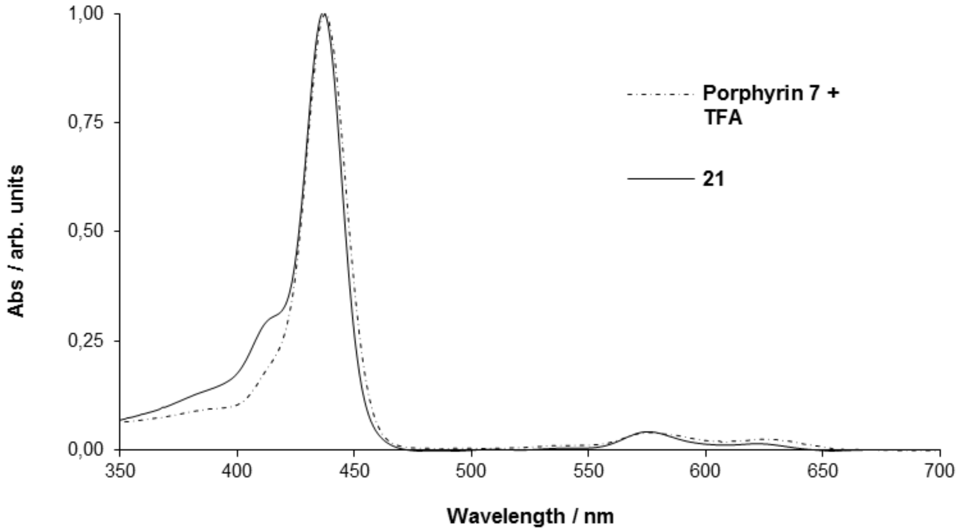
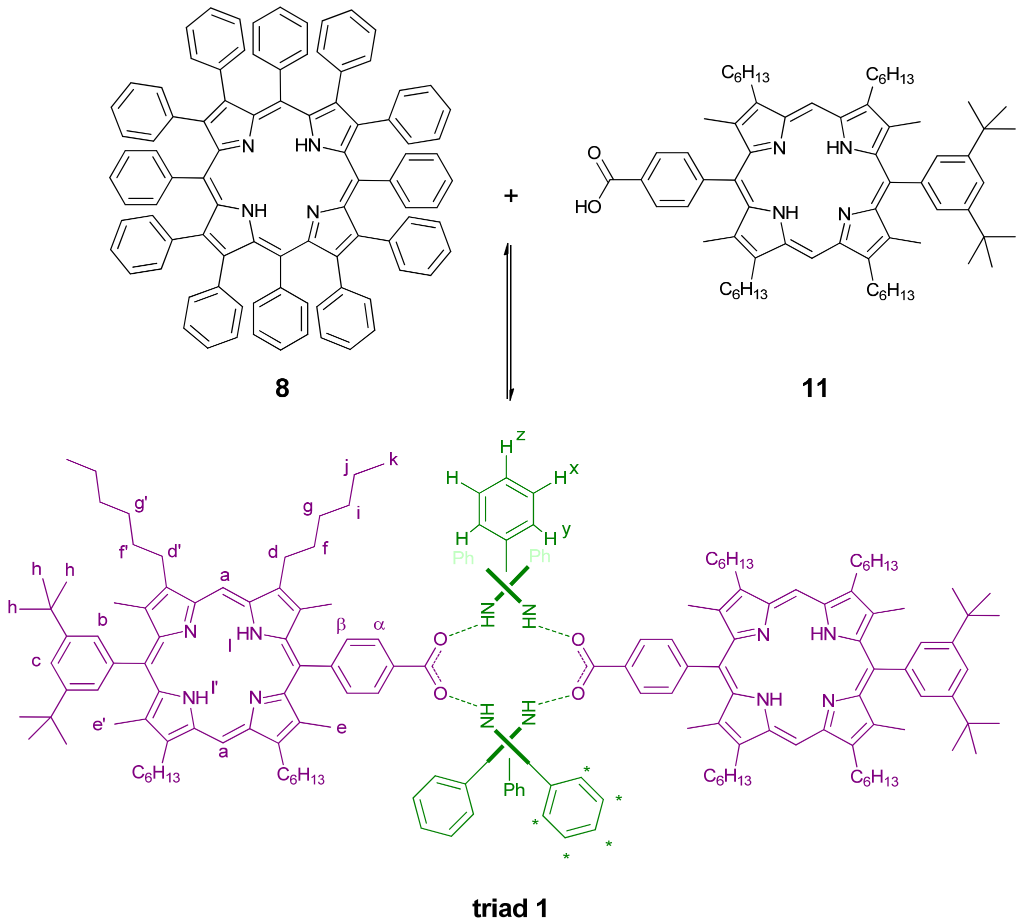


Figure S13. Normalised UV/Vis Spectra of porphyrin **21** compared to the TFA acid-porphyrin **7** complex (**7·TFA$_2$**). The two protonated porphyrins have comparable Soret bands at 437 and 438 nm respectively.



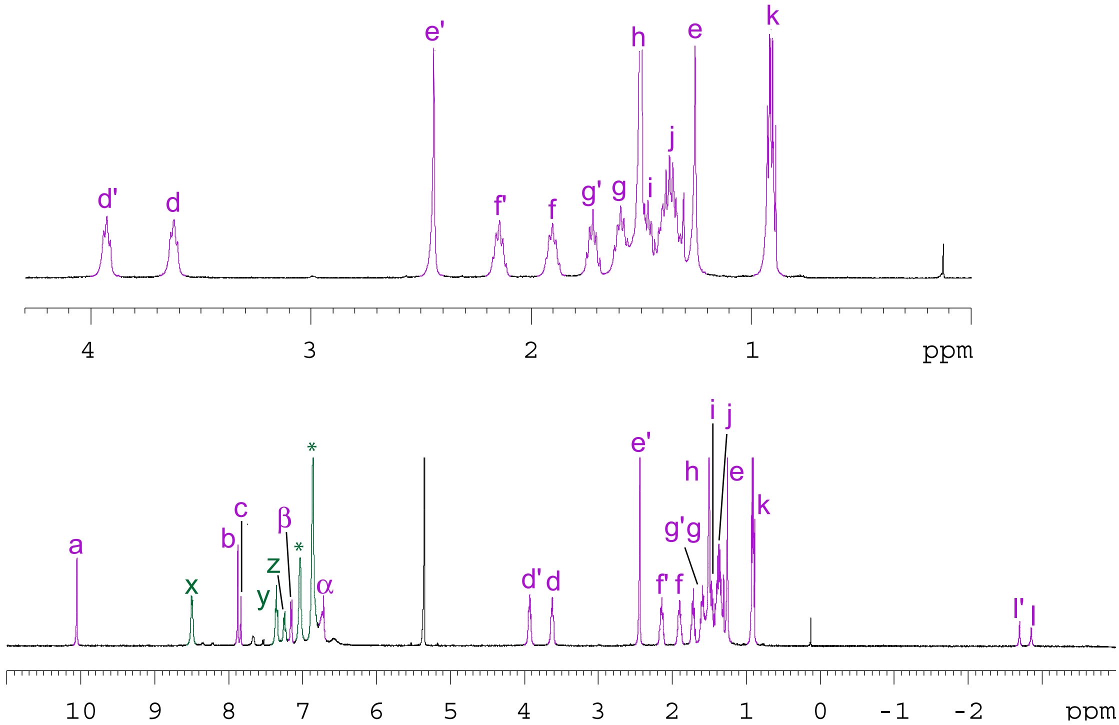


Figure S14. ^{1}H NMR spectrum (500 MHz) of porphyrin **triad 1** in d_2-dichloromethane at 298 K and an expansion of the aliphatic region shown above.

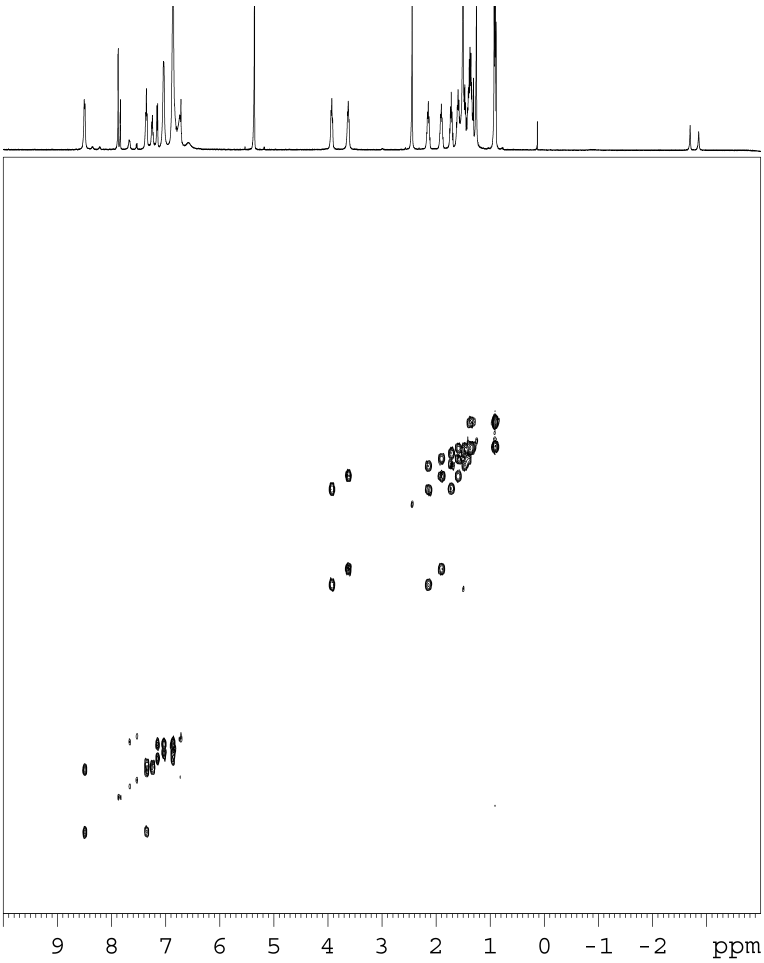


Figure S15. 2D ^{1}H-^{1}H COSY NMR spectrum (500 MHz) of **triad 1** in d_2-dichloromethane at 298.

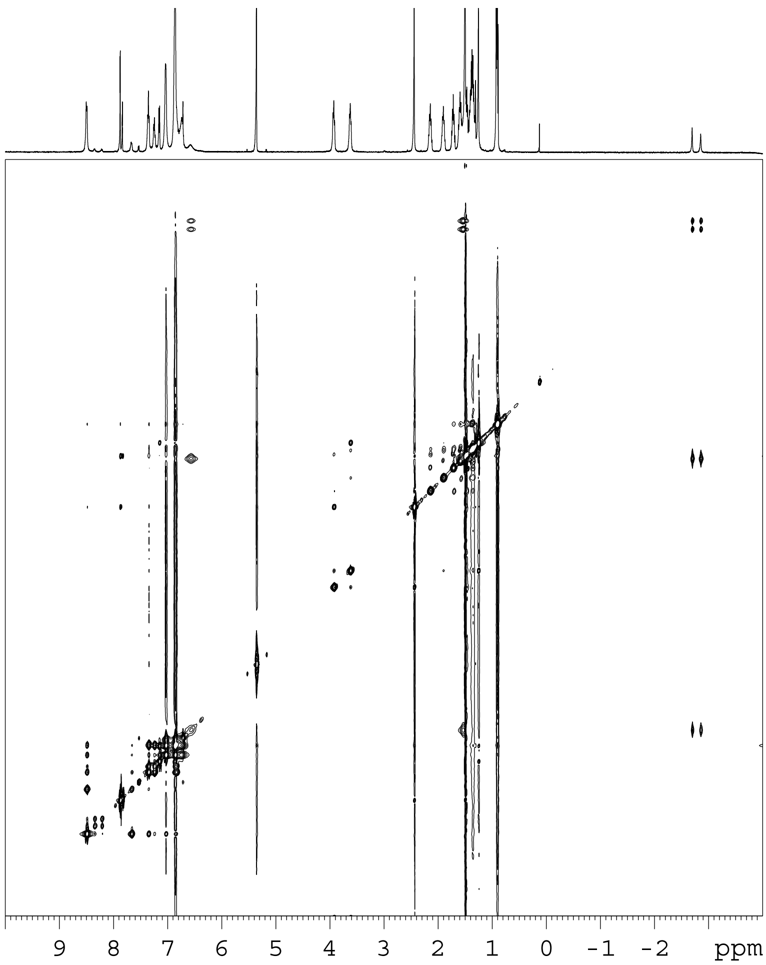


Figure S16. 2D ^{1}H-^{1}H NOESY NMR spectrum (500 MHz) of **triad 1** in d_2-dichloromethane at 298 K.

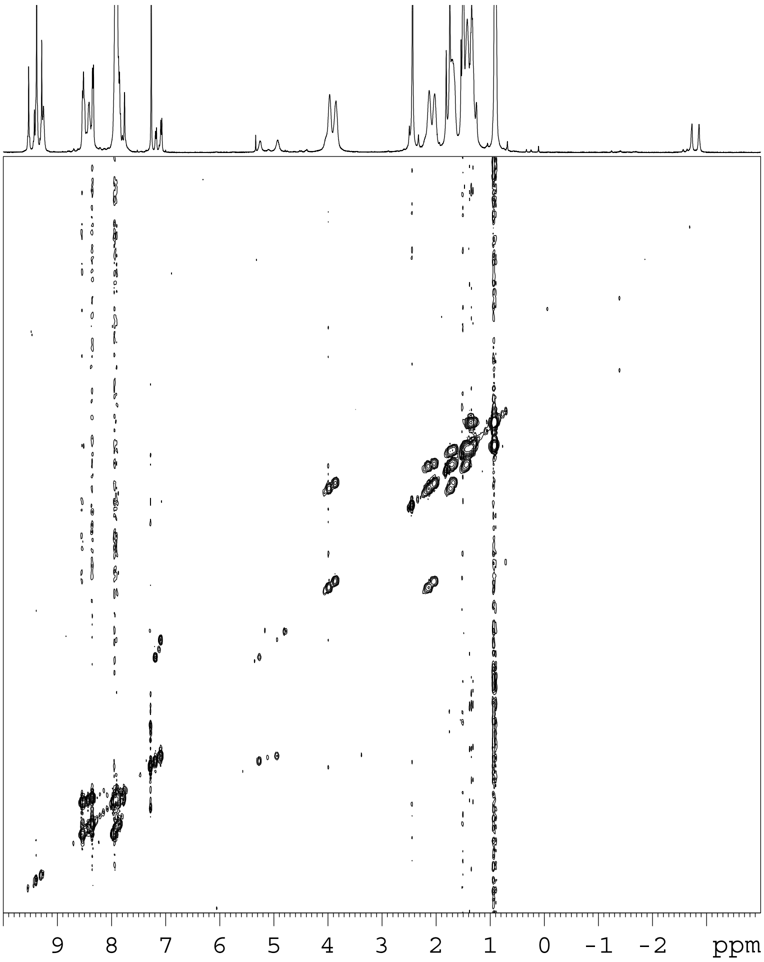
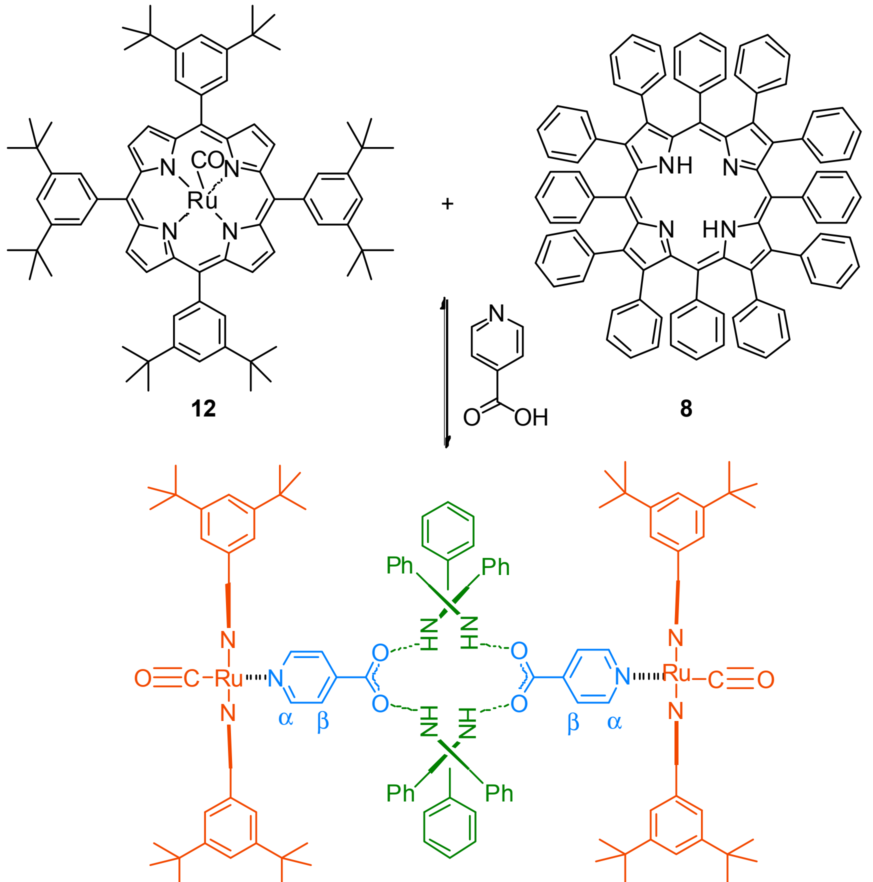


Figure S17. 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of **triad 2** prior to the addition of DCA in *d*-chloroform at 298 K.



Schematic representation of the possible self-assembly of porphyrin **triad 3** from porphyrin **8**, two equivalents of porphyrin **12** and isonicotinic acid.

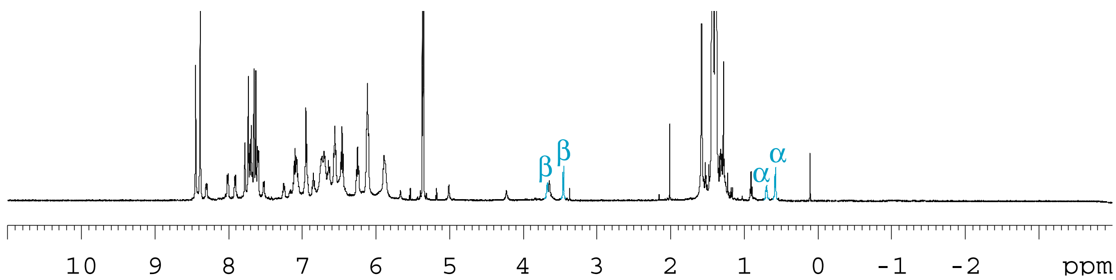


Figure S18. ^{1}H NMR spectrum (500 MHz) of attempt to generate porphyrin **triad 3** from porphyrin **8**, two **12** porphyrins and isonicotinic acid in d_2-dichloromethane at 298 K.

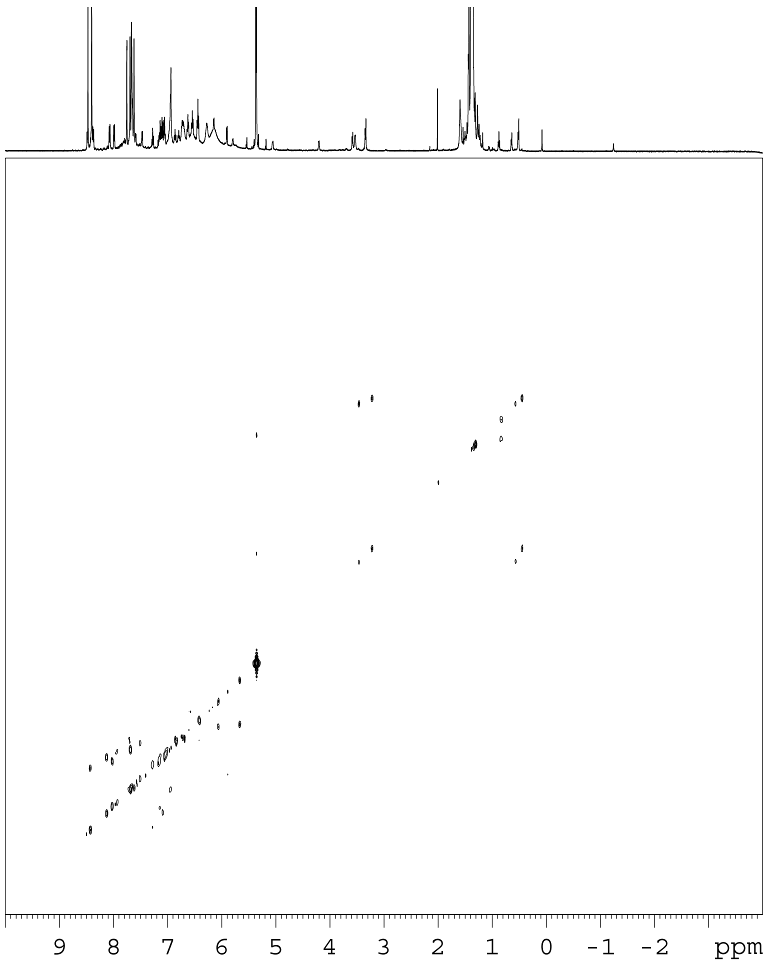


Figure S19. 2D ^{1}H-^{1}H COSY NMR spectrum (500 MHz) of **triad 3** in d_2-dichloromethane at 298 K. Diagnostic cross-peaks are identified between the β-protons just above 3 ppm and the α-protons in the aliphatic region. Both appear at higher field due to the effect of the Ru porphyrins on either side of the complex.

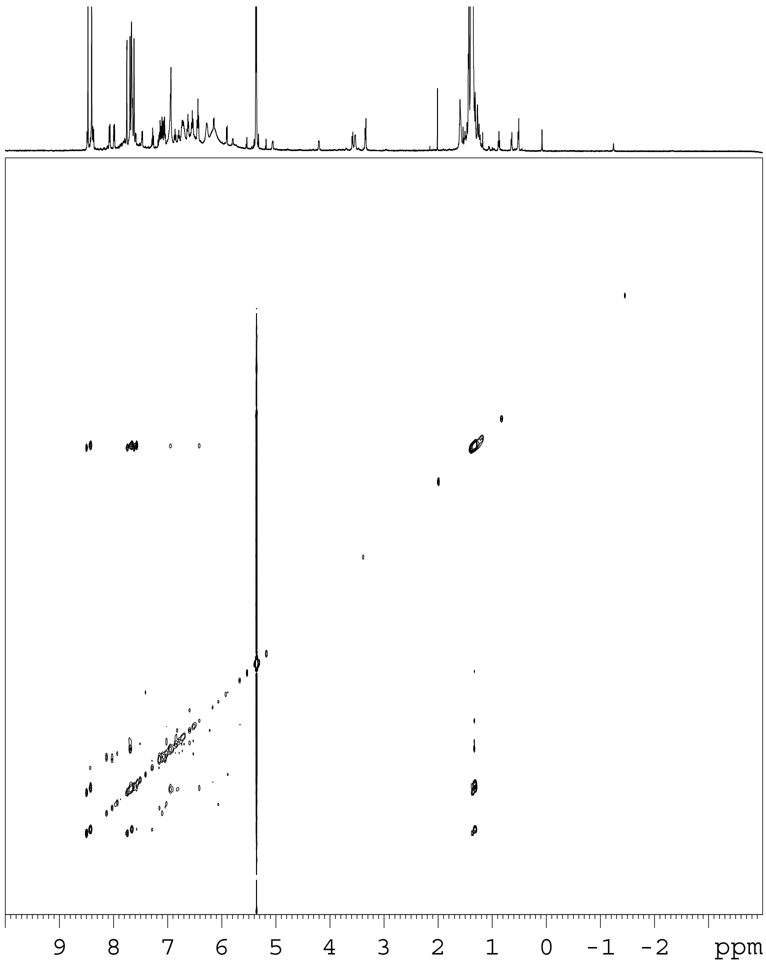


Figure S20. 2D ^{1}H-^{1}H NOESY NMR spectrum (500 MHz) of **triad 3** in d_2-dichloromethane at 298 K.

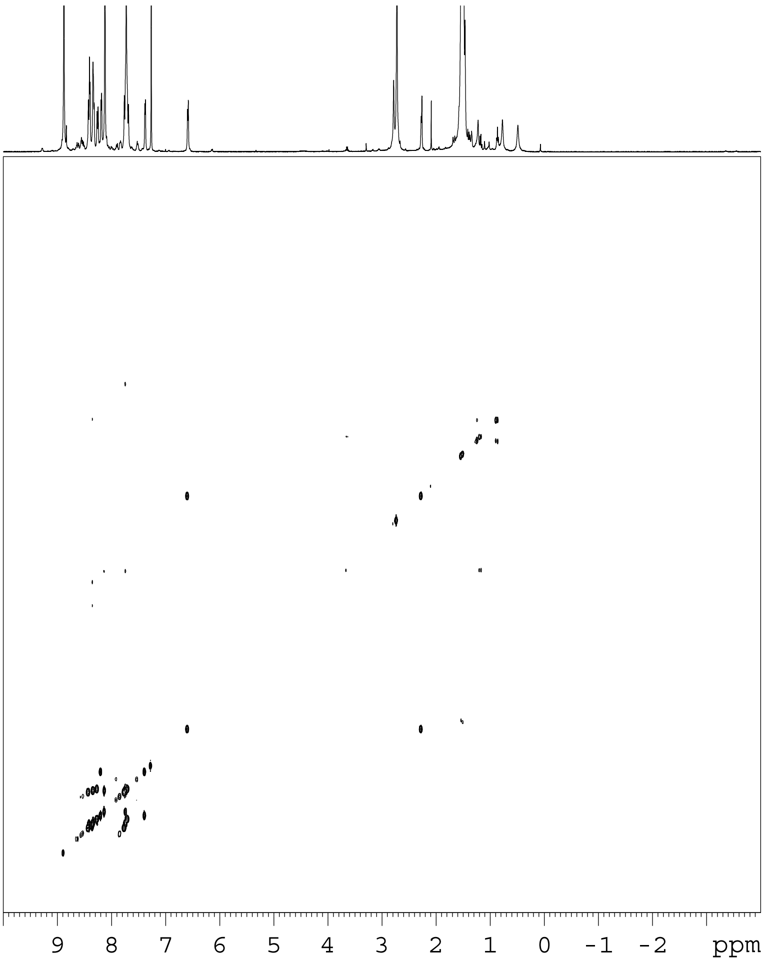


Figure S21. 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of **dyad 1·DCA$_2$** in *d*-chloroform at 298 K. Diagnostic cross-peaks are identified between the β-protons near 6.5 ppm and the α-protons in the aliphatic region (just above 2ppm). These resonances feel the effect of only one bound Ru porphyrin in the complex.