Electronic Supplementary Information

Host-Guest 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 (376 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. Unless otherwise stated, NMR spectra were recorded in deuterated chloroform ($CDCl_3$) at 298 K ± 3 K. In preparation of 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. ^{1}H and ^{13}C NMR spectra were referenced relative to residual solvent peaks, and ^{19}F NMR spectra were referenced to $CFCl_3$.

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 dimer solutions were typically prepared in the 4.0 mM concentration range in *d*-chloroform. Stoichiometric quantities of acid prepared in *d*-chloroform were added to the NMR sample with shaking before spectral acquisition.

Nano-electrospray mass spectra were recorded on a LCT MS instrument (Micromass, Manchester, U.K.) equipped with nanoflow Z-spray source. Gold-coated nano-ES capillaries were prepared in-house using a micropipette puller (Flaming/Brown P-97, Sutter Instruments, Novato, CA) and borosilicate glass tubes (Harvard Apparatus, Holliston, MA) as described previously.[1] Stock solutions of the appropriate acid-porphyrin dimer complexes were prepared (1 mM) in dichloromethane (approximate stoichiometries were used rather than an excess of acid) before the samples were further diluted to 55 μM in chloroform before spraying. The spectra were obtained with the following parameters: capillary voltage = 1.4 kV, sample cone voltage = 30 V, extraction cone = 5 V and ion transfer stage pressure = 5.5 mbars. External calibration of the spectra and calibration of the LCT mass spectrometer were achieved using a 100 mg mL^{-1} solution of caesium iodide. Data were acquired and processed using Masslynx 4.0 software (Waters, Manchester, U.K.). All spectra are shown with minimal smoothing and without background subtraction. 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.

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.

Synthetic procedures:

Zinc insertion of freebase porphyrins

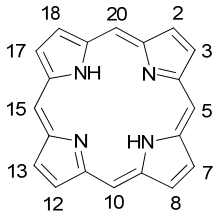
The quantitative conversion of free base porphyrins to their Zn complexes was achieved by stirring a 30 % methanol/chloroform solution of the porphyrin with excess zinc acetate dihydrate (~ 10 equivalents). Complete conversion was achieved in a matter of minutes and confirmed by t.l.c. The reaction mixture was then washed with water three times (equal volume to organic solution) before the organic fraction was dried over anhydrous sodium sulphate and the solvent removed *in vacuo*. The product was then recrystalised from dichloromethane layered with methanol.

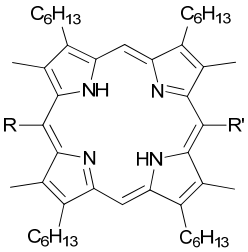
Removal of zinc and copper metal centres

The metallated porphyrin was dissolved in dichloromethane (100 mL), to which concentrated sulphuric acid (2-3 mL) was added and stirred at room temperature until the reaction mixture appeared as a dark green solution. After this time the reaction mixture was transferred to a separating funnel and washed carefully with sodium bicarbonate (2 x 250 mL or until neutralised – at which point the solution returned to the colour of the freebase porphyrin) and finally with water (1 x 250 mL). The solution was dried over anhydrous sodium sulphate and the solvent removed *in vacuo*.

Deprotection of TMS protected acetylenes

TMS protected material was dissolved in methanol or dichloromethane /methanol solution before potassium carbonate (2.5 equivalents) was added. The mixture was stirred overnight at room temperature. After this time the solvent was removed *in vacuo*. The product was then extracted into dichloromethane and washed with water three times (equal volume to organic fraction), dried over anhydrous sodium sulphate and the solvent removed *in vacuo*.





Synthesis of *meso* substituted porphyrins *via* dipyrromethane (General Method)[2]

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 0 °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-iodo phenyl)-2,8,12,18-tetra methyl- 3,7,13,17-tetra hexyl porphyrin (2)

Purification was performed by way of column chromatography on silica using 30 % dichloromethane/hexane to elute, the product was further purified by recrystalisation from dichloromethane layered with methanol.

20 - 40 % yield; δ_H (400 MHz, $CDCl_3$) -2.46 (s, 2H, NH), 0.92 (m, 12 H, $(CH_2)_5$-C*H*$_3$), 1.40 (m, 8H, $(CH_2)_4$-C*H*$_2$-CH_3), 1.50 (m, 8H, $(CH_2)_3$-C*H*$_2$-CH_2CH_3), 1.75 (m, 8H, $(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 2.20 (m, 8H, CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 2.54 (s, 12 H, *Me*), 3.99 (t, 8H, C*H*$_2$-$(CH_2)_4$-CH_3), 7.48 (t, 2H, *aryl* H), 8.05 (d, 2H, *aryl* H), 8.15 (d, 2H, *aryl* H), 8.50 (t, 2H, *aryl* H), 10.25 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.11, 15.00, 22.72, 26.76, 29.97, 31.95, 33.28, 93.55, 116.12, 129.15, 132.21, 132.23, 135.88, 137.33, 141.55, 141.70, 143.67, 144.55, 144.78. MS: MALDI (*m/z*) 1107.45 λ_{max} ($CHCl_3$)/ 411, 508, 542, 574, 626nm

H_2 5,15-*bis*-(3-trimethylsilylethynyl phenyl)-2,8,12,18-tetra methyl- 3,7,13,17-tetra hexyl porphyrin (3)

Reaction flask was charged with porphyrin **2,** tris(dibenzylidene acetone)dipalladium (0) (0.1 equivalents) and triphenylarsine (0.2 equivalents) before it was subjected to five vacuum/nitrogen cycles. Dry dichloromethane and triethylamine (1:1) were added *via* cannula before trimethylsilylacetylene (3 equivalents) was added. The reaction mixture was then stirred overnight (~ 16 hours) at room temperature. After this time the solvent was removed *in vacuo*. Purification was performed by way of column chromatography on silica, using hexane/dichloromethane with 1% methanol to elute.

48 % yield; δ_H (400 MHz, $CDCl_3$) -2.41 (s, 2H, core NH), 0.29 (s, 18H, *TMS*), 0.93 (t, 12 H, $(CH_2)_5$-C*H*$_3$), 1.40 (m, 8H, $(CH_2)_4$-C*H*$_2$-CH_3), 1.51 (m, 8H, $(CH_2)_3$-C*H*$_2$-CH_2CH_3), 1.76 (m, 8H, $(CH_2)_2$-C*H*$_2$-

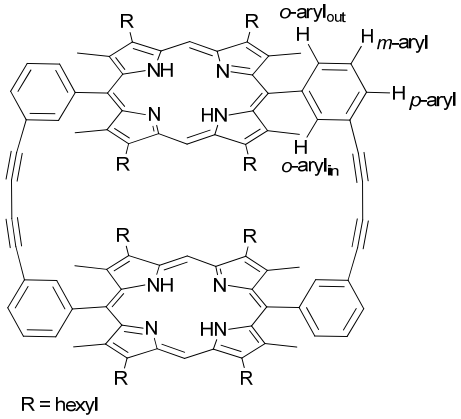
$(CH_2)_2$-CH_3), 2.21 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.54 (s, 12 H, *Me*), 4.00 (t, 8H, CH_2-$(CH_2)_4$-CH_3), 7.70 (td, 2H, *aryl* H), 7.93 (dt, 2H, *aryl* H), 8.06 (tt, 2H, *aryl* H), 8.21 (dt, 2H, *aryl* H), 10.25 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 0.00 (*TMS*), 14.13 ($(CH_2)_5$-CH_3), 15.05 (*Me*), 22.75 ($(CH_2)_4$-CH_2CH_3), 26.79 (CH_2-$(CH_2)_4$-CH_3), 30.01 ($(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 32.00 ($(CH_2)_3$-CH_2-CH_2CH_3), 33.32 ($CH_2CH_2(CH_2)_3$-CH_3), 94.51 (C≡C), 97.10 (*meso* CH), 105.14 (C≡C), 116.77 (C_q *meso*), 122.60 (C_q *aryl*), 127.55, 131.87 and 133.02 (*aryl* CH), 136.00 (*pyrrole*), 136.15 (*aryl* CH), 141.51 (*pyrrole*), 142.42 (*aryl* C_q), 143.48 and 144.95 (*pyrrole*); MS: MALDI (*m/z*) 1047.76; λ_{max} ($CHCl_3$)/ nm 411, 508, 542, 574 and 626.

H_2 5,15-*bis*-(3-ethynyl phenyl)-2,8,12,18-tetra methyl- 3,7,13,17-tetra hexyl porphyrin (4)

95% yield; δ_H (400 MHz, $CDCl_3$) -2.40 (s, 2H, core NH), 0.29 (s, 18H, *TMS*), 0.93 (t, 12 H, $(CH_2)_5$-CH_3), 1.38 (m, 8H, $(CH_2)_4$-CH_2-CH_3), 1.50 (m, 8H, $(CH_2)_3$-CH_2-CH_2CH_3), 1.75 (m, 8H, $(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 2.20 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.53 (s, 12 H, *Me*), 3.19 (s, 2H, C≡C*H*), 3.99 (t, 8H, CH_2-$(CH_2)_4$-CH_3), 7.72 (t, 2H, *aryl* H), 7.95 (dt, 2H, *aryl* H), 8.08 (m, 2H, *aryl* H), 8.26 (m, 2H, *aryl* H), 10.26 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.13 ($(CH_2)_5$-CH_3), 14.98 (*Me*), 22.74 ($(CH_2)_4$-CH_2CH_3), 26.78 (CH_2-$(CH_2)_4$-CH_3), 30.00 ($(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 31.99 ($(CH_2)_3$-CH_2-CH_2CH_3), 33.30 ($CH_2CH_2(CH_2)_3$-CH_3), 77.53 (C≡C), 83.76 (C≡C), 97.12 (*meso* CH), 116.59 (C_q *meso*), 121.52 (C_q *aryl*), 127.68, 132.01 and 133.38 (*aryl* CH), 135.94 (*pyrrole*), 136.36 (*aryl* CH), 141.54 (*pyrrole*), 142.55 (*aryl* C_q), 143.58 and 144.93 (*pyrrole*); MS: MALDI (*m/z*) 903.68; λ_{max} ($CHCl_3$)/ nm 410, 508, 542, 574 and 626.

Zn 5,15-*bis*-(3-ethynyl phenyl)-2,8,12,18-tetra methyl- 3,7,13,17-tetra hexyl porphyrin (5)

96% yield; δ_H (400 MHz, $CDCl_3$) 0.92 (m, 12 H, $(CH_2)_5$-CH_3), 1.40 (m, 8H, $(CH_2)_4$-CH_2-CH_3), 1.50 (m, 8H, $(CH_2)_3$-CH_2-CH_2CH_3), 1.75 (m, 8H, $(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 2.18 (m, 8H, CH_2-CH_2-$(CH_2)_3$-CH_3), 2.48 (s, 12 H, *Me*), 3.16 (s, 2 H, C≡CH), 3.95 (t, 8H, CH_2-$(CH_2)_4$-CH_3), 7.71 (t, 2H, *aryl* H), 7.94 (d, 2H, *aryl* H), 8.08 (d, 2H, *aryl* H), 8.25 (t, 2H, *aryl* H), 10.17 (s, 2H, *meso* H).



Porphyrin Dimer[3] (1)

TMEDA (1.7 mL, 11.2 mmol) was added to a stirred solution of **5** (150 mg, 0.16 mmol), 4,4'-bipyridyl (146 mg, 0.9 mmol) and freshly prepared copper (I) chloride (1.1 g, 11.2 mmol) in dichloromethane (380 mL). The reaction mixture was stirred vigorously under air over night. After this time, the mixture was washed with water (4 x 250 mL), methanolic TFA (2 x (5 mL TFA in 100 mL methanol and 250 mL water)) and again with water (3 x 250 mL). The organic fraction was then

dried over anhydrous sodium sulphate, and the solvent removed *in vacuo*. Isolation of the cyclic porphyrin dimer was achieved by column chromatography on silica using dichloromethane/chloroform (1:1) to elute. Further purification by recrystallisation from dichloromethane layered with methanol.

49% yield; δ_H (400 MHz, $CDCl_3$) -2.64 (s, 4H, NH), 0.80 (m, 24 H, $(CH_2)_5$-C*H*$_3$), 1.24 (m, 16H, $(CH_2)_4$-C*H*$_2$-CH_3), 1.35 (m, 16H, $(CH_2)_3$-C*H*$_2$-CH_2CH_3), 1.58 (m, 16H, $(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 1.96 (m, 16H, CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 2.32 (s, 24 H, *Me*), 3.76 (t, 16H, C*H*$_2$-$(CH_2)_4$-CH_3), 7.11 (t, 4H, *aryl* H), 7.70 (d, 4H, *aryl* H), 7.71 (d, 4H, *aryl* H), 8.50 (m, 4H, *aryl* H), 9.95 (s, 4H, *meso* H); δ_C (100 MHz, $CDCl_3$) 14.02 ($(CH_2)_5$-*C*H_3), 14.89 (Me), 22.64 ($(CH_2)_4$-*C*H_2-CH_3), 26.57 (*C*H_2-$(CH_2)_4$-CH_3), 29.90 ($(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 31.82 ($(CH_2)_3$-*C*H_2-CH_2CH_3), 33.07 (CH_2-*C*H_2-$(CH_2)_3$- CH_3), 74.53 (C≡C), 83.72 (C≡C), 96.94 (*meso C*H), 115.82 (*meso* C), 121.12 (C_q), 127.13 (CH); 129.71 (CH), 132.40 (CH), 134.44 (C_q), 135.74 (C_q), 139.39 (CH), 141.76 (C_q), 142.46 (C_q), 144.71 (C_q); MS: MALDI (*m/z*) 1801.15; λ_{max} ($CHCl_3$)/ nm 409, 509, 543, 575 and 628.

H_2 5,15-*bis*-(phenyl)-2,8,12,18-tetra methyl- 3,7,13,17-tetra hexyl porphyrin (M1)

Purification was performed by way of column chromatography on silica using 30 % dichloromethane/hexane to elute, the product was further purified by recrystalisation from dichloromethane layered with methanol.

20 - 40 % yield; δ_H (400 MHz, $CDCl_3$) -2.46 (s, 2H, NH), 0.92 (m, 12 H, $(CH_2)_5$-C*H*$_3$), 1.40 (m, 8H, $(CH_2)_4$-C*H*$_2$-CH_3), 1.50 (m, 8H, $(CH_2)_3$-C*H*$_2$-CH_2CH_3), 1.75 (m, 8H, $(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 2.20 (m, 8H, CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 2.54 (s, 12 H, *Me*), 3.99 (t, 8H, C*H*$_2$-$(CH_2)_4$-CH_3), 7.48 (t, 2H, *aryl* H), 8.05 (d, 2H, *aryl* H), 8.15 (d, 2H, *aryl* H), 8.50 (t, 2H, *aryl* H), 10.25 (s, 2H, *meso* H); δ_C (125 MHz, $CDCl_3$) 14.11, 15.00, 22.72, 26.76, 29.97, 31.95, 33.28, 93.55, 116.12, 129.15, 132.21, 132.23, 135.88, 137.33, 141.55, 141.70, 143.67, 144.55, 144.78. MS: MALDI (*m/z*) 1107.45 λ_{max} ($CHCl_3$)/ 411, 508, 542, 574, 626nm

(1) Hernández, H.; Robinson, C. V. *Nat. Protocol.* **2007**, *2*, 715.
(2) Gunter, M. J.; Mander, L. N. *The Journal of Organic Chemistry* **1981**, *46*, 4792.
(3) Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Journal of the Chemical Society, Perkin Transactions 1* **1995**, 2247.

Computational analysis:

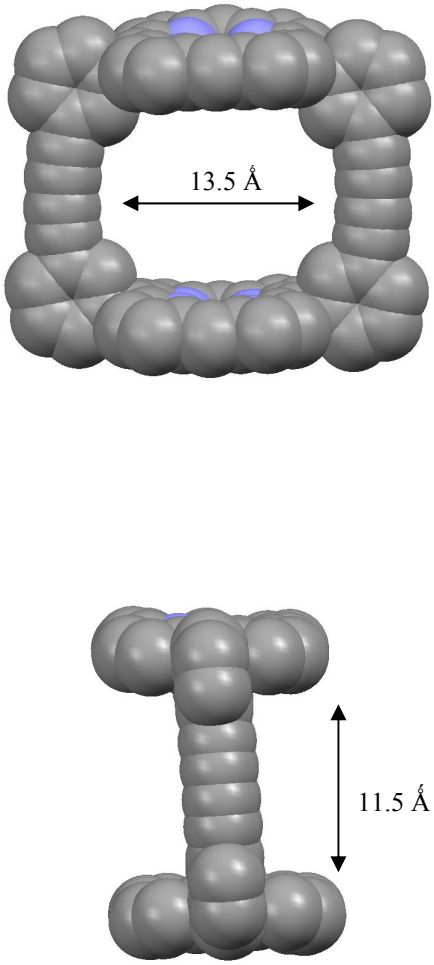


Figure S1. Computationally minimised freebase porphyrin dimer **1** structures. Calculations made using HyperChem molecular modelling package. Hydrogen atoms and β-pyrrolic hexyl and methyl groups have been omitted for clarity.

Modelling

Computational modelling of dimer **1** was undertaken in order to gain familiarity with the size of the cavity, flexibility and shape of the cyclic host molecule. Geometry optimisation was achieved using the HyperChem© molecular modelling package. Semi-empirical calculations were made using the RM-1 method with a convergence criterion of 0.01 Kcal mol^{-1} $Å^{-1}$. In each case the starting point for the modelling came from the coordinates of a modified porphyrin crystal structure.

Spectroscopic analysis:

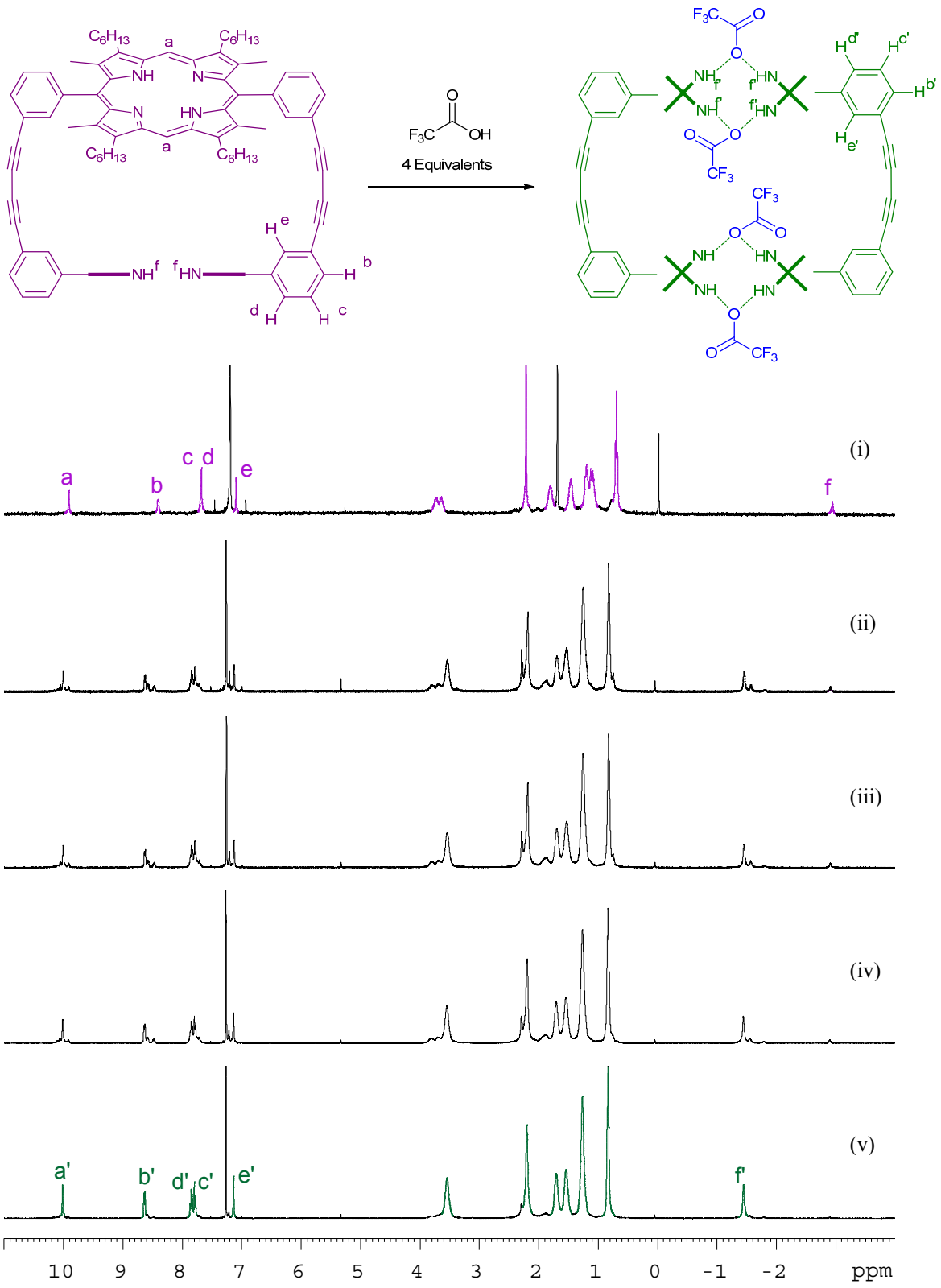


Figure S2. ^{1}H NMR spectra (400 MHz) of freebase porphyrin dimer **1** titration with TFA in *d*-chloroform at 253 K. Dimer **1** with (i) 0.0, (ii) 1.0, (iii) 2.0, (iv) 3.0 and (v) 4.0 equivalents of TFA.

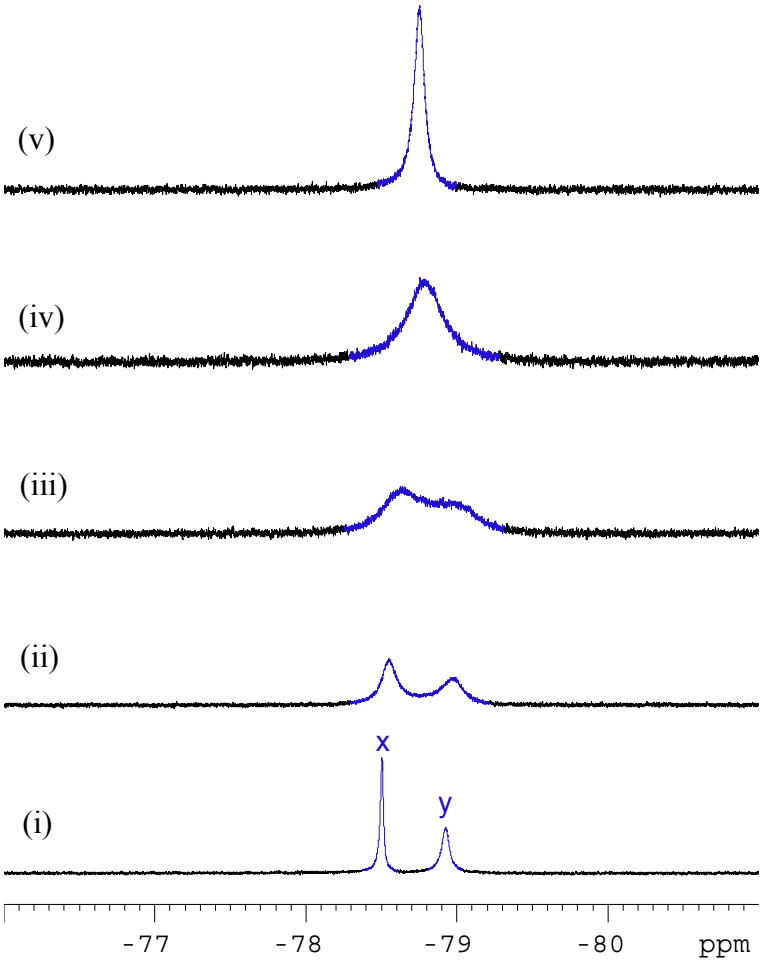


Figure S3. ^{19}F NMR spectra (400 MHz, d-chloroform) of bis acid-porphyrin dimer complex (**1**·**TFA$_4$**) at: (i) 253 K, (ii) 263 K, (iii) 273 K, (iv) 283 K and (v) 298 K (peak width at half height ~ 4 Hz).

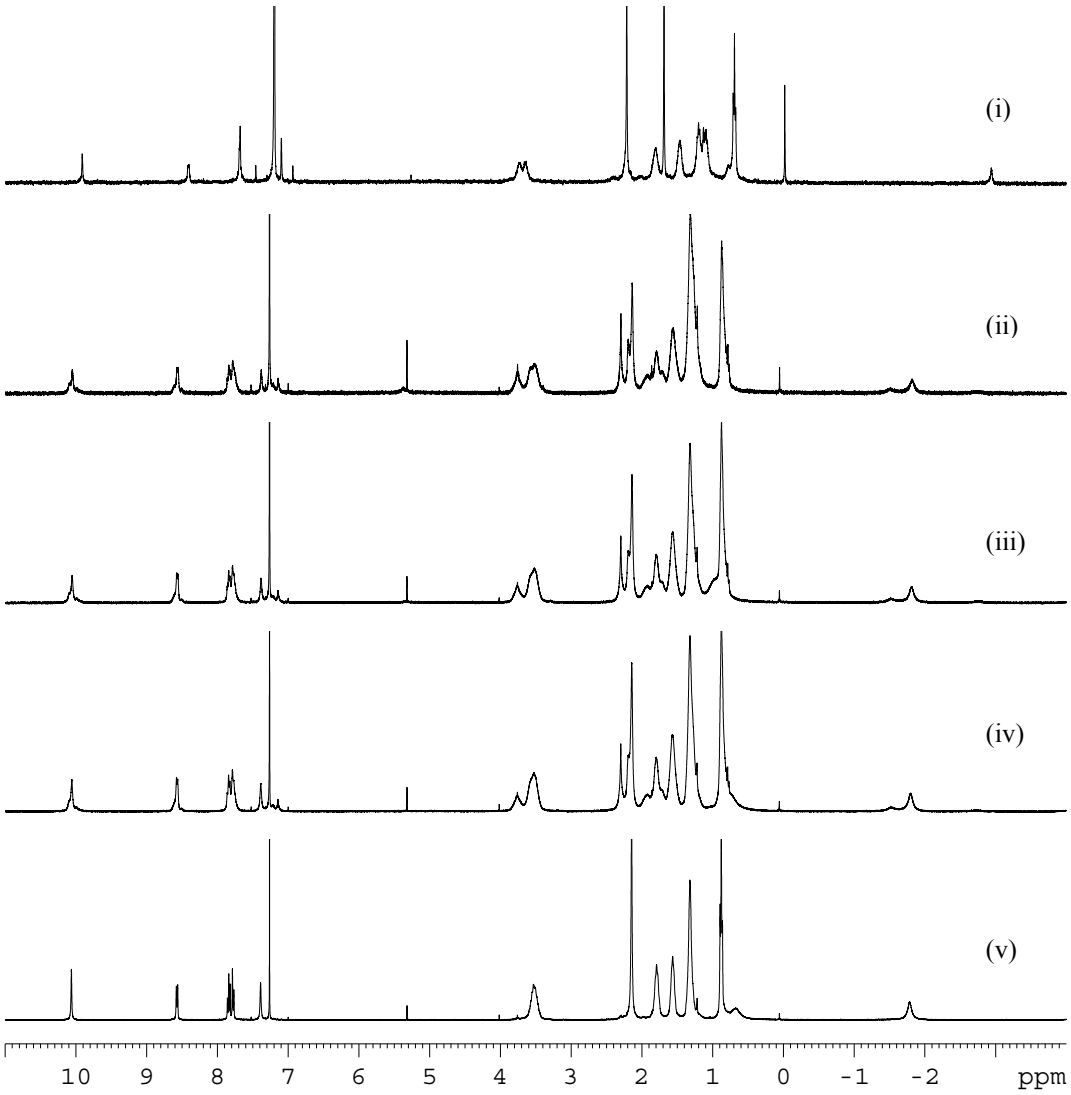


Figure S4. The ^{1}H NMR spectra (400 MHz) of porphyrin dimer **1** titration with PFPA in *d*-chloroform at 253 K. (i) 0.0, (ii) 1.0, (iii) 2.0, (iv) 3.0 and (v) 4.0 equivalents of PFPA.

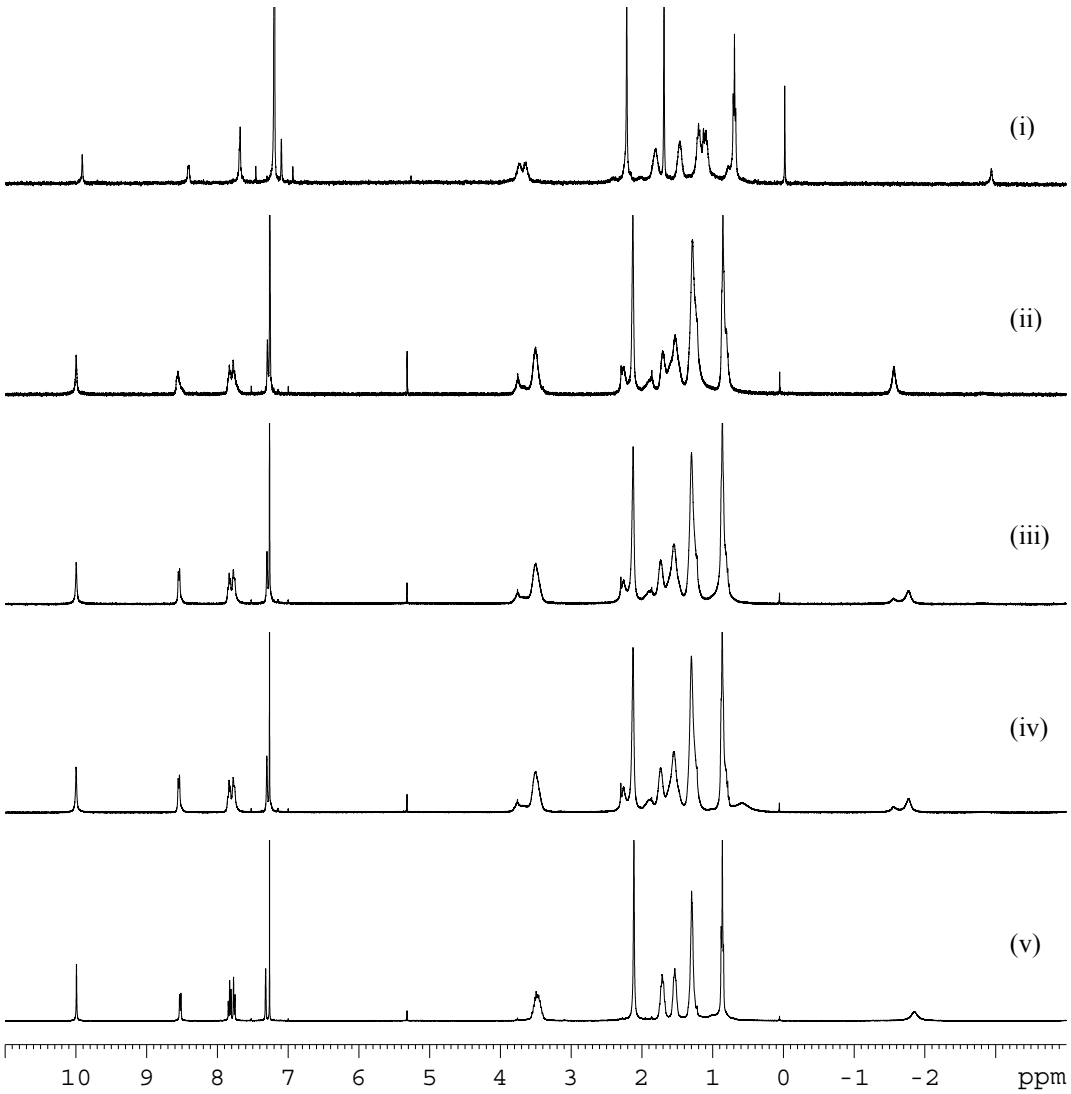


Figure S5. The ^{1}H NMR spectra (400 MHz) of porphyrin dimer **1** titration with HFBA in *d*-chloroform at 253 K. (i) 0.0, (ii) 1.0, (iii) 2.0, (iv) 3.0 and (v) 4.0 equivalents of HFBA.

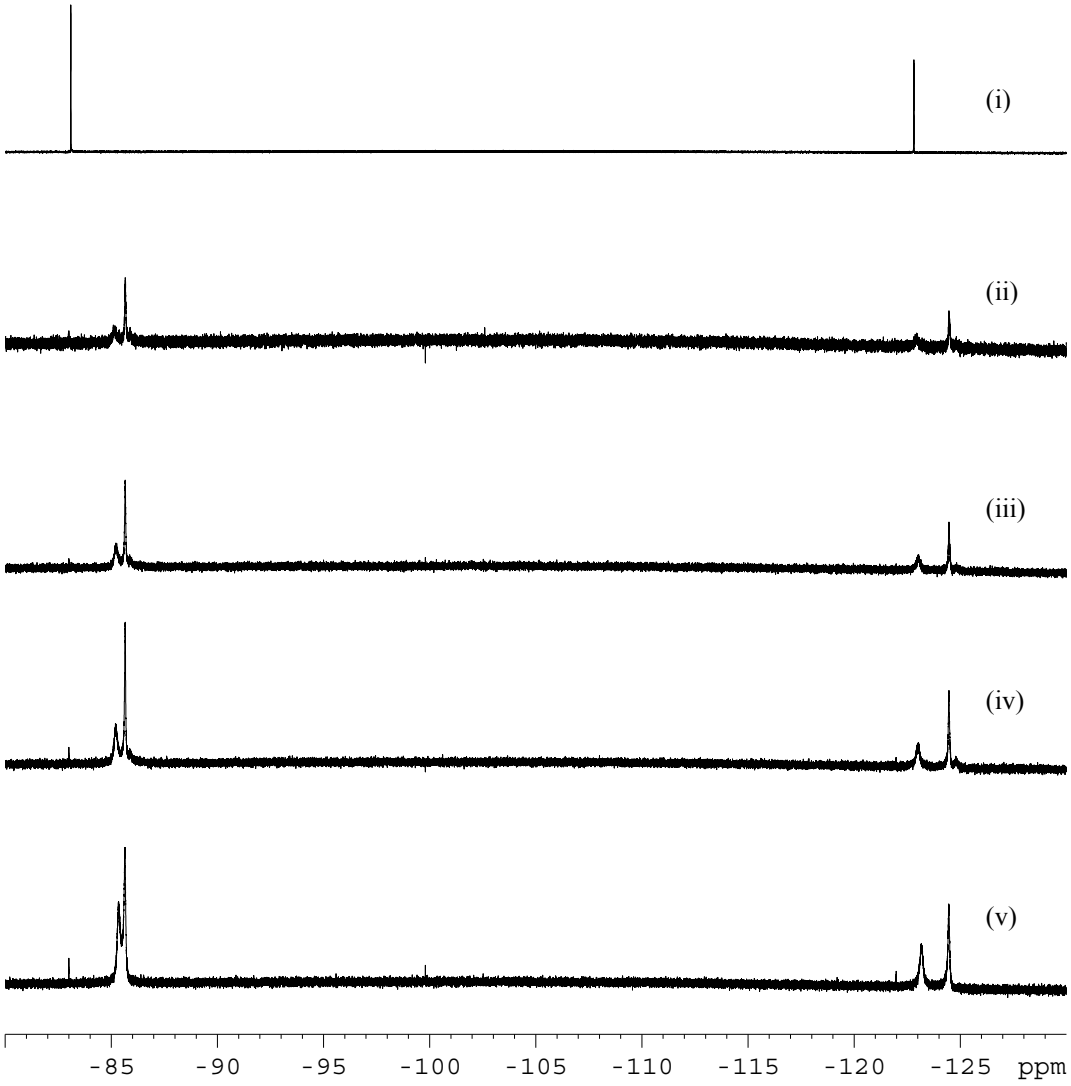


Figure S6. The ^{19}F NMR spectra (400 MHz) of porphyrin dimer **1** titration with PFPA in *d*-chloroform at 253 K. (i) 'free' PFPA, (ii) 1.0, (iii) 2.0, (iv) 3.0 and (v) 4.0 equivalents of PFPA. Figure S8 provides a schematic representation of the chemical shifts of the PFPA complex in comparison with other acids.

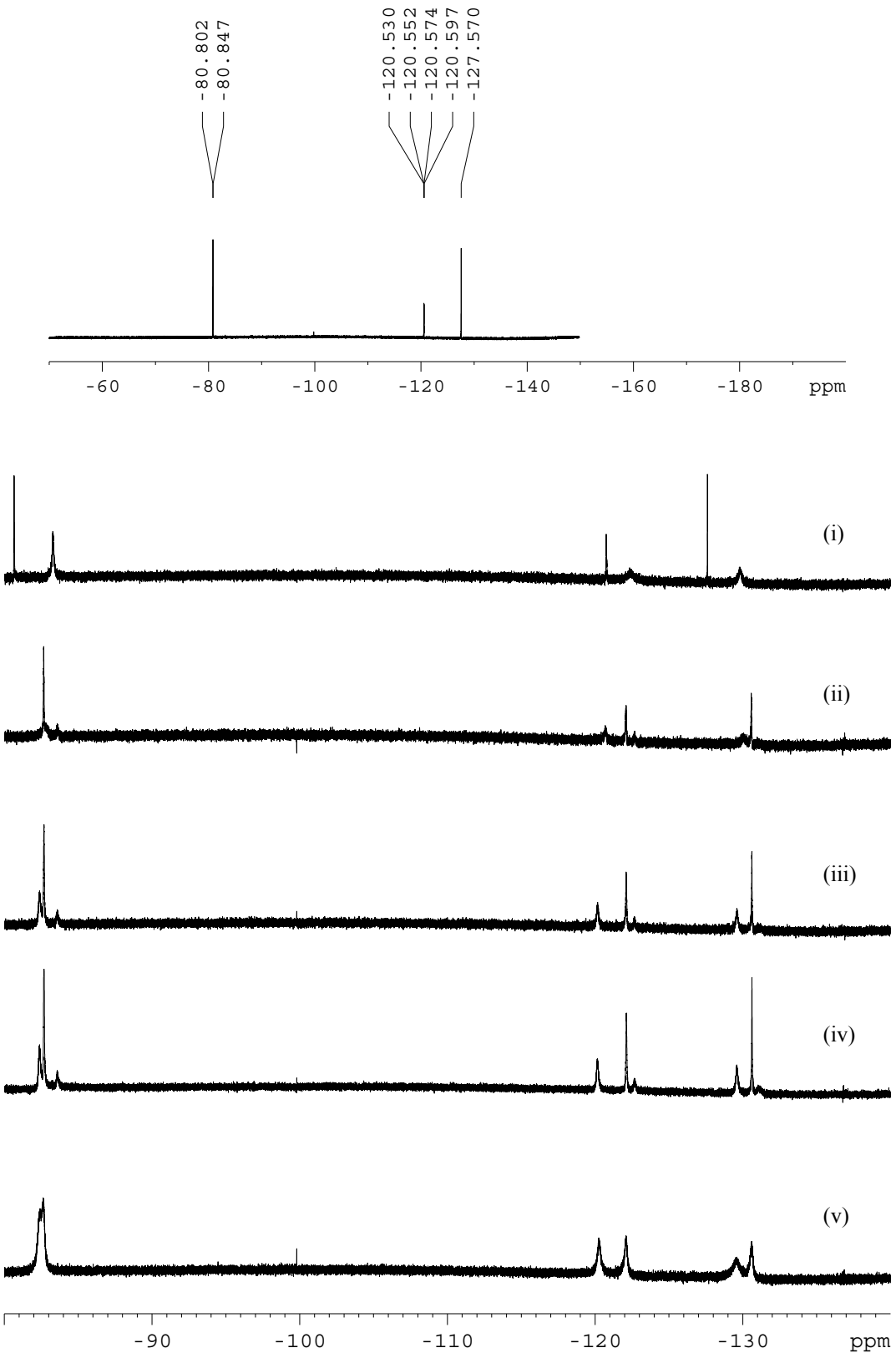


Figure S7. The ^{19}F NMR spectra (400 MHz) of porphyrin dimer **1** titration with HFBA in *d*-chloroform at 253 K. (i) 0.5, (ii) 1.0, (iii) 2.0, (iv) 3.0 and (v) 4.0 equivalents of HFBA. The ^{19}F NMR spectrum (400 MHz) of HFBA in *d*-chloroform at 298 K is shown above for comparison. Figure S8 provides a schematic representation of the chemical shifts of the HFBA complex in comparison with other acids.

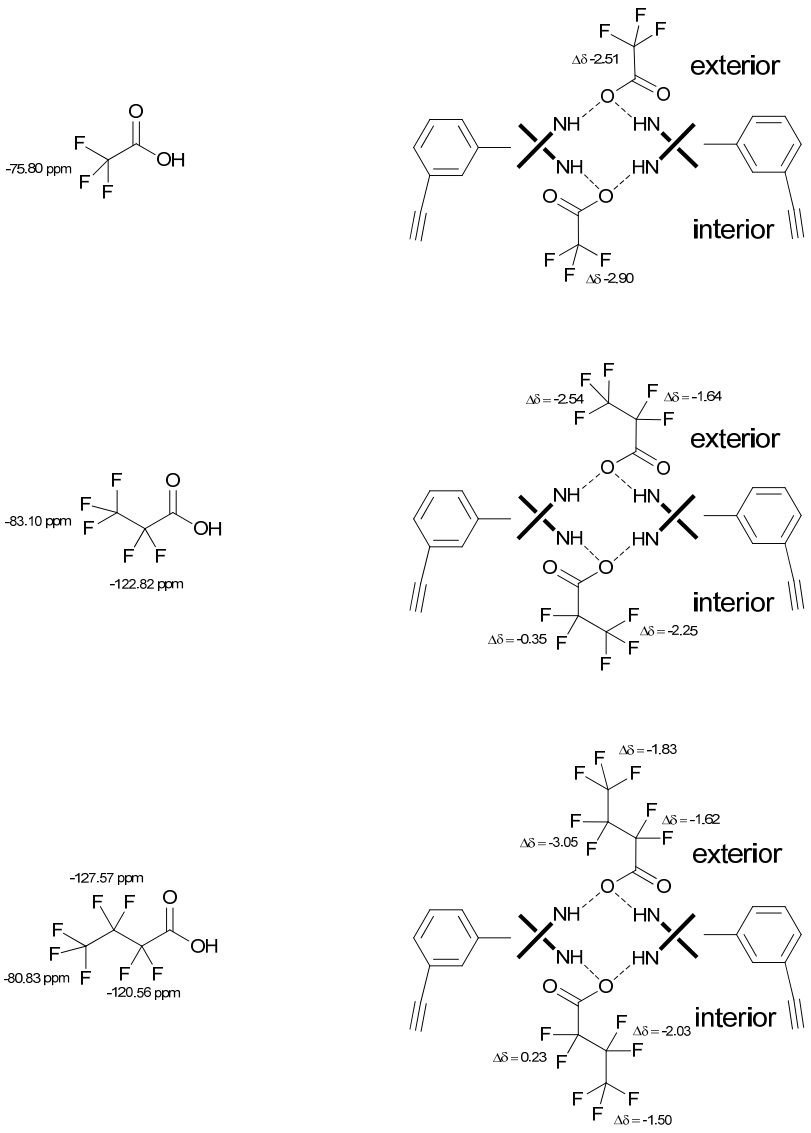


Figure S8. ^{19}F NMR chemical shifts for acid-porphyrin dimer **1** complexes (only half shown for clarity) with (i) TFA, (ii) PFPA and (iii) HFBA anions (right). The free acid chemical shifts are highlighted also (left).

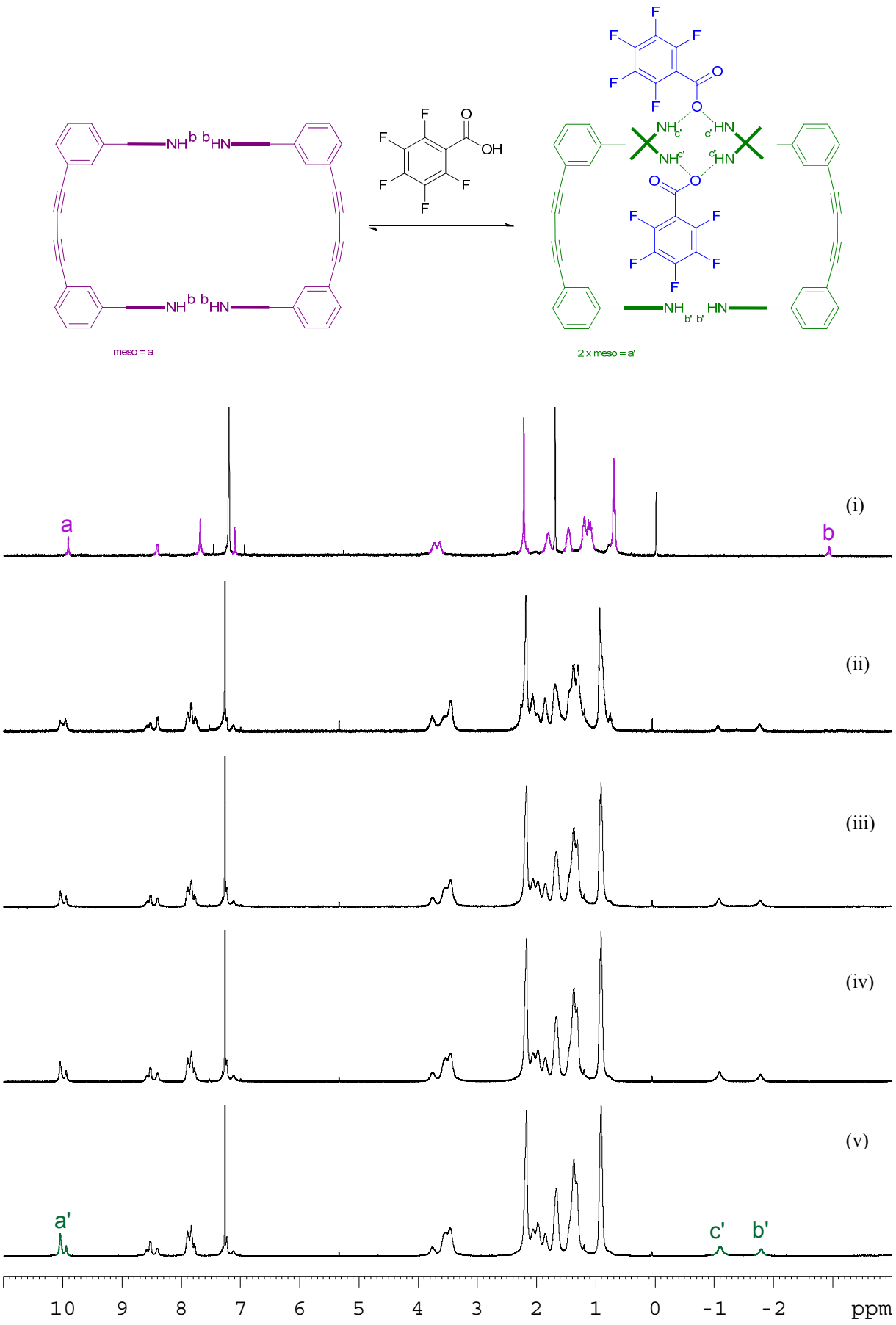
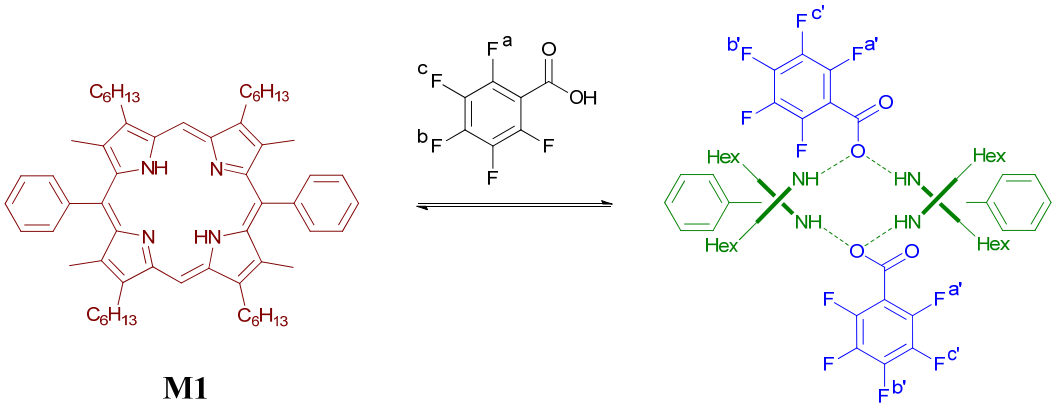


Figure S9. ^{1}H NMR spectra (400 MHz) of freebase porphyrin dimer **1** titration with PFBA in *d*-chloroform at 223 K: 0.0, (ii) 1.0, (iii) 2.0, (iv) 3.0 and (v) 4.0 equivalents of PFBA.



M1

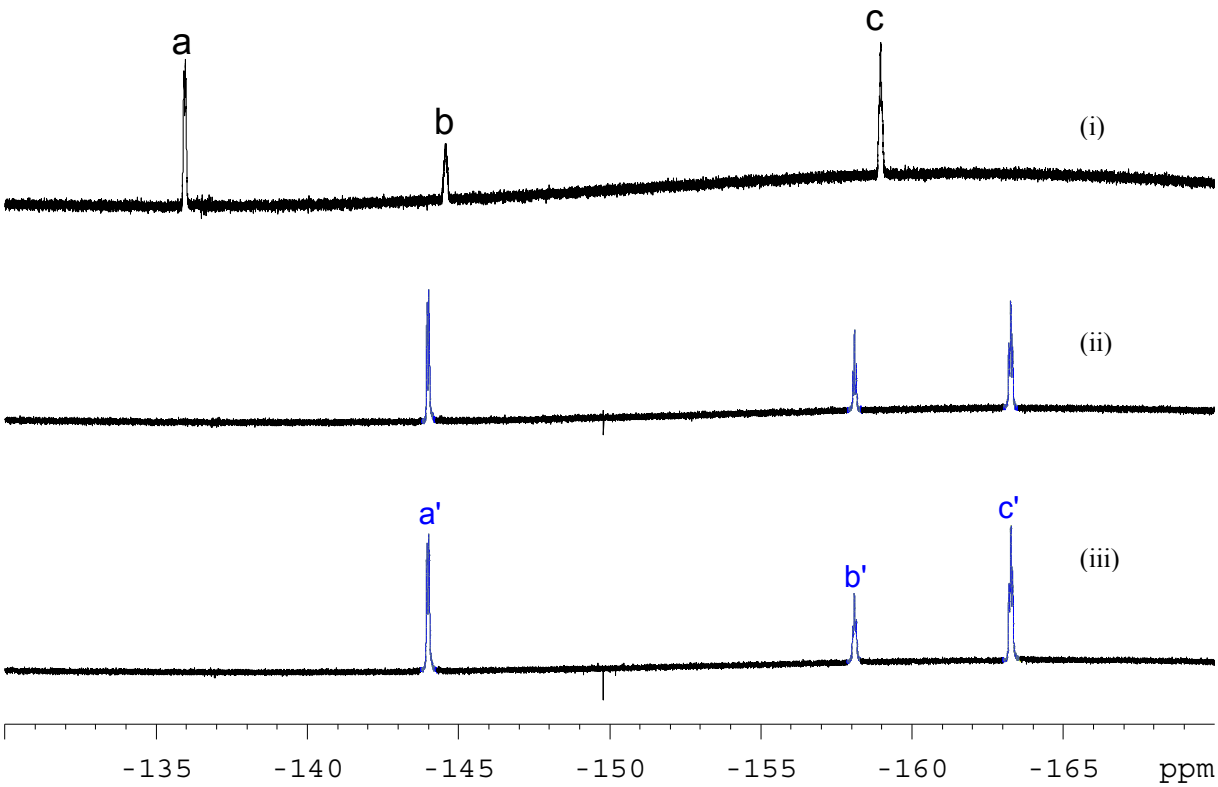


Figure S10. ^{19}F NMR spectra (400 MHz) of the titration between porphyrin monomer **M1** (above) and PFBA in *d*-chloroform at 228 K. (i) PFBA, (ii) porphyrin **M1** with 1.0 equivalents of PFBA, and (iii) porphyrin **M1** with 2.0 equivalents of PFBA.

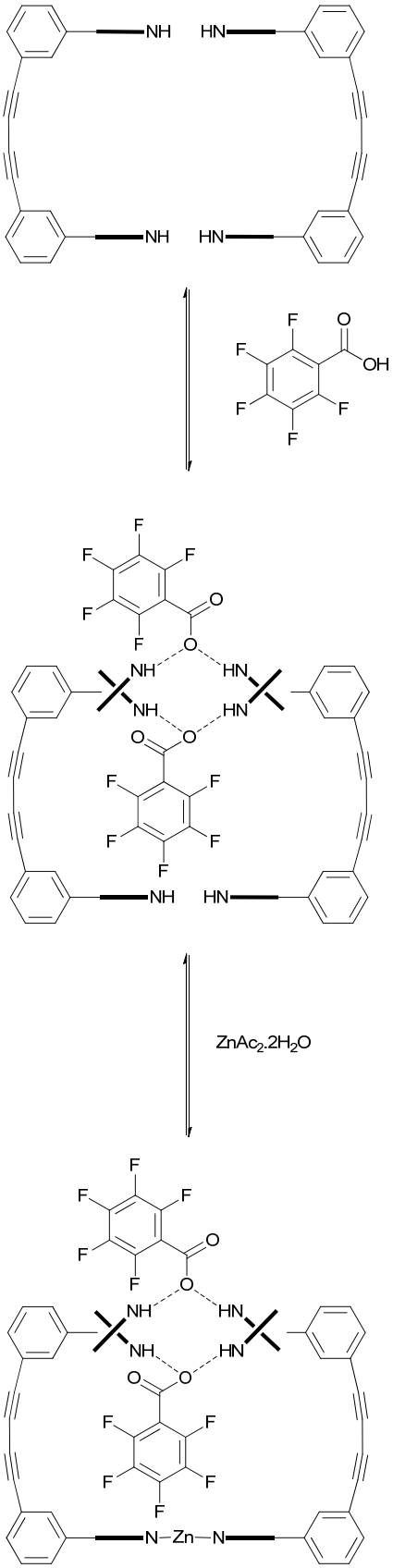
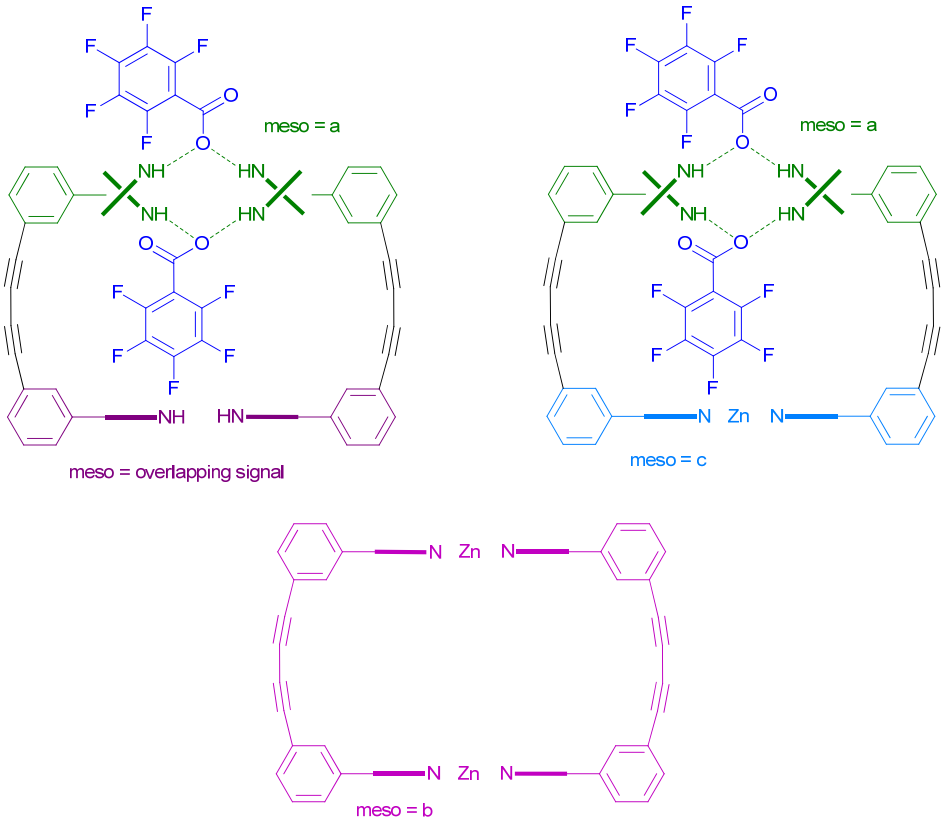


Figure S11. Scheme representing possible selective core NH protecting group application for PFBA within porphyrin dimer **1**.



A schematic representation of the products obtained from the porphyrin dimer **1** core NH protecting group experiment with PFBA and zinc acetate dihydrate.

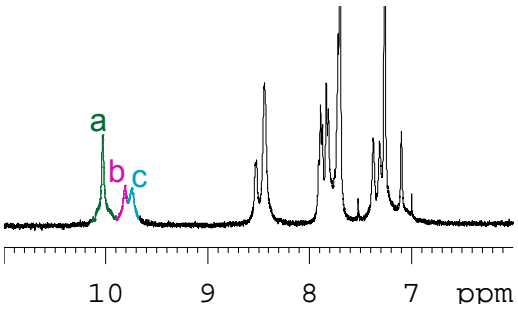
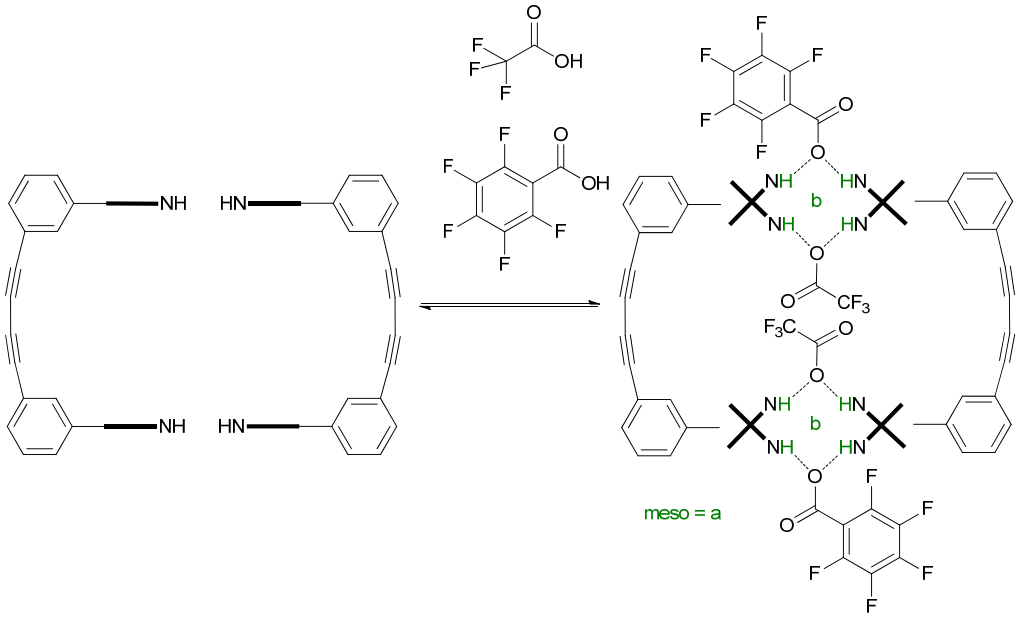


Figure S12. Partial ^{1}H NMR spectrum (400 MHz) of the porphyrin dimer **1** core NH protecting group experiment with 2 equivalents PFBA and 1 equivalent of zinc acetate dihydrate. The spectrum highlights the meso signals of the three species identified in the figure above, which were characterised by tracking the change in the relative ratios as a function of added PFBA and zinc acetate. The overlapping meso resonance is expected at 9.9 ppm (Figure S9), however, this signal is likely to have been consumed by the base of resonance a.



Schematic representation of a *possible* acid-porphyrin dimer complex with TFA and PFBA biased in its formation by the size restrictions of the dimer system.

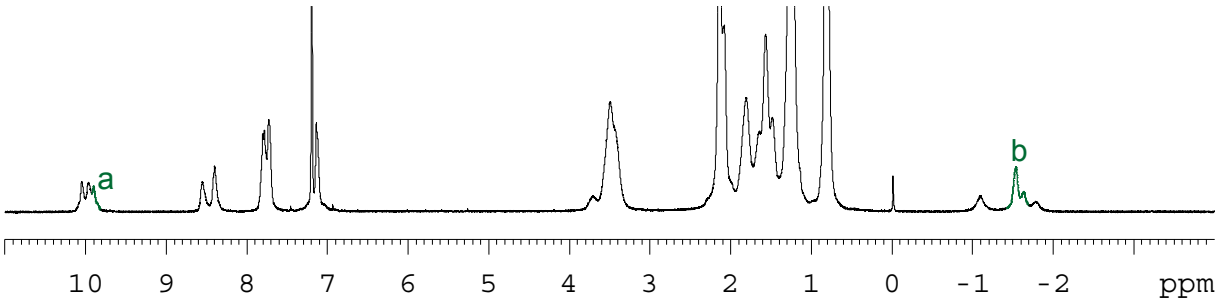


Figure S13. ^{1}H NMR spectrum (400 MHz) of porphyrin dimer with 4 equivalents of a 1:1 mixture of TFA and PFBA in *d*-chloroform at 228 K. The broad spectrum and multiple core NH and meso proton resonances suggests that the different sized anions have no particular binding preference for inside or outside the dimer.

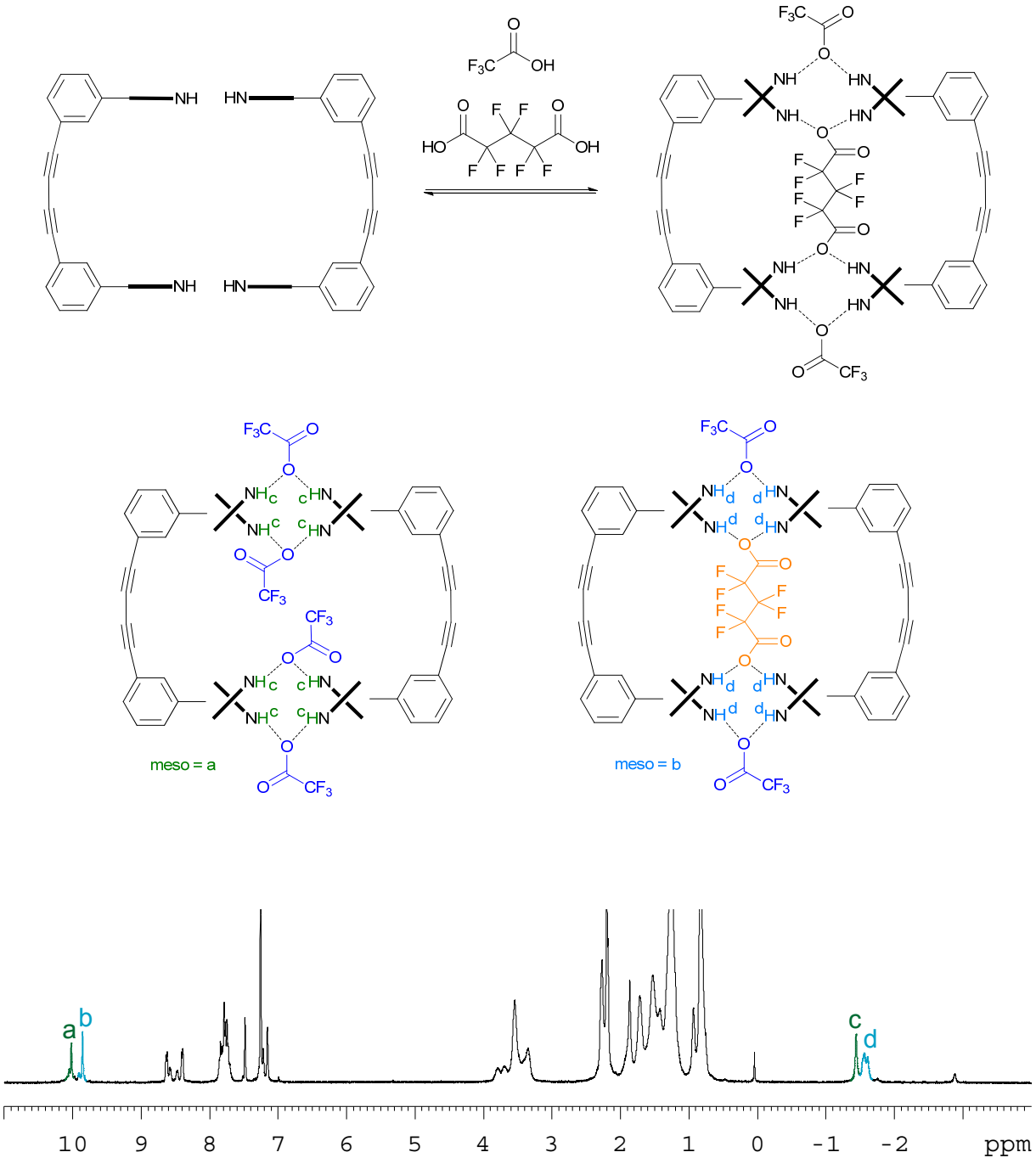


Figure S14. ^{1}H NMR spectrum (400 MHz) of *acid-porphyrin* dimer **1** assemblies with TFA and HFGA in *d*-chloroform at 233 K. Two major species were identified as highlighted above.

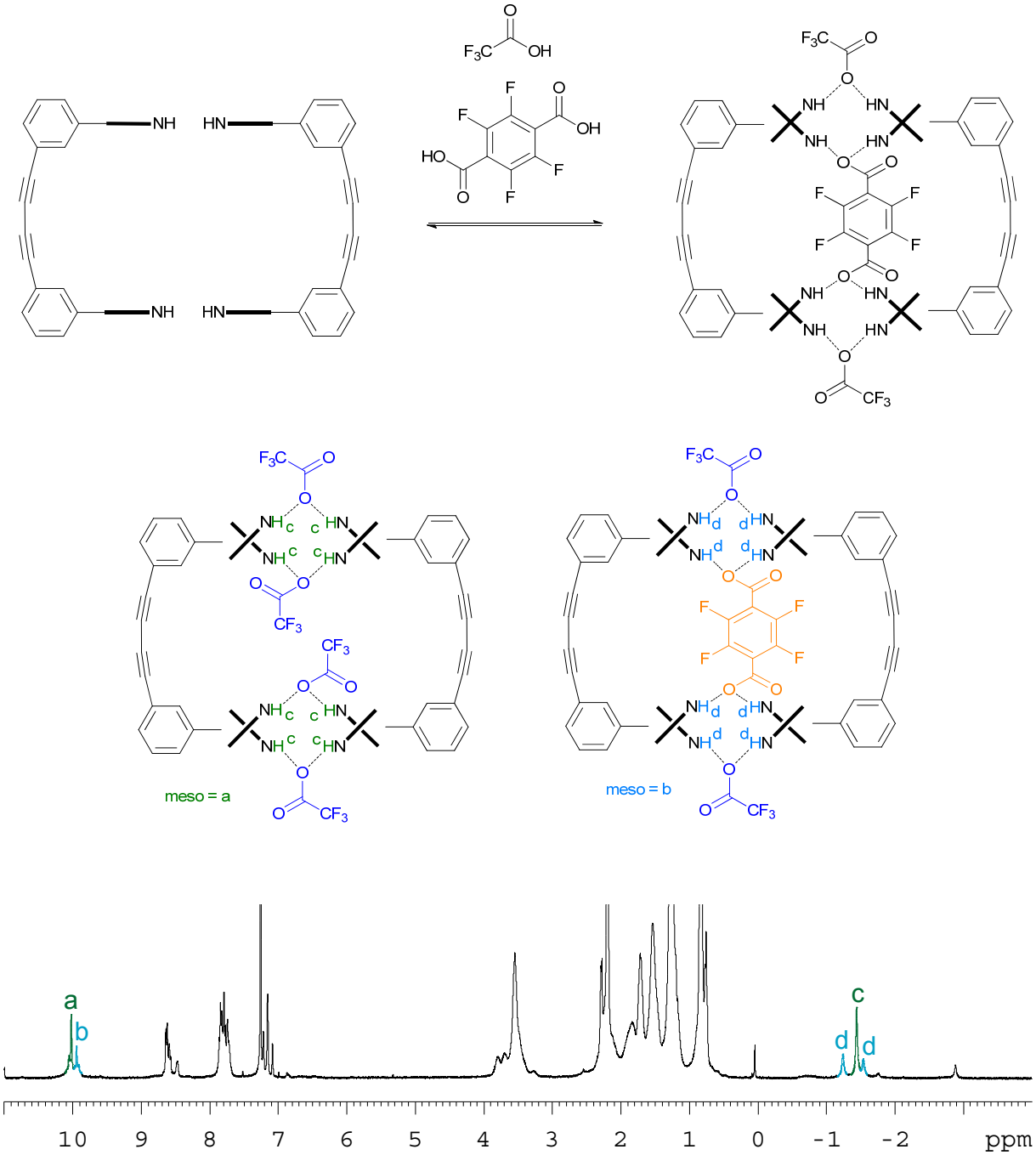


Figure S15. ^{1}H NMR spectrum (400 MHz) of acid-porphyrin dimer **1** assemblies with TFA and TFTA in *d*-chloroform at 233 K. Two major species were identified as highlighted by the structures above.

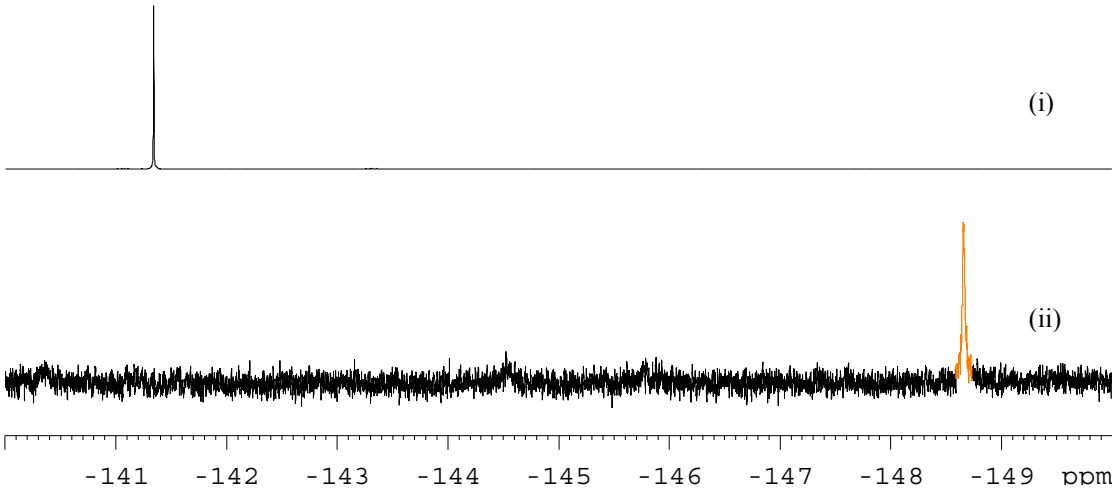


Figure S16. ^{19}F NMR spectra (400 MHz) of (i) TFTA in d_4-methanol at 298 K and (ii) the TFTA signal in the presence of porphyrin dimer **1** in *d*-chloroform at 233 K.

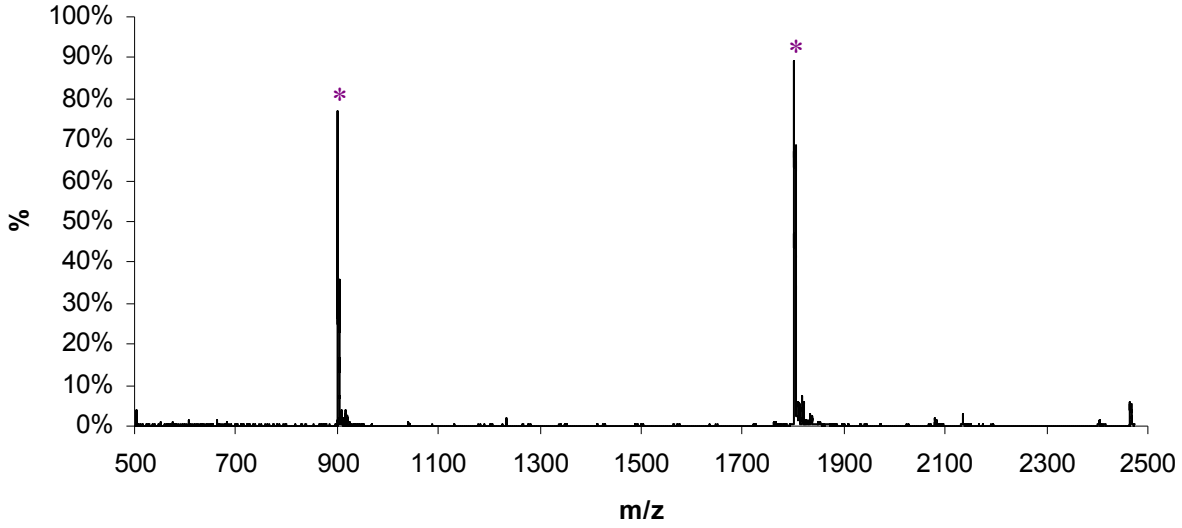


Figure S17. Nano-electrospray spectrum of freebase porphyrin dimer **1**. The two main peaks at 902and 1803 *m/z* are assigned to the 2+ and 1+ charge states of the dimer *.

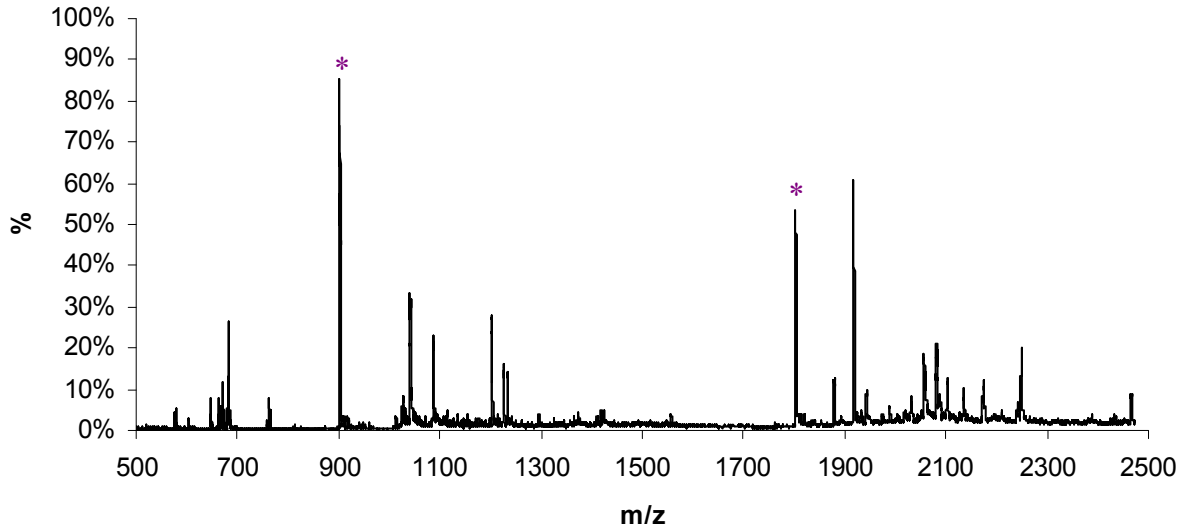


Figure S18. Nano-electrospray spectrum of porphyrin dimer **1** with TFA. Three main peaks were observed. Those at 902 and 1803 *m/z* are assigned to the 2+ and 1+ charge states of the freebase dimer *.

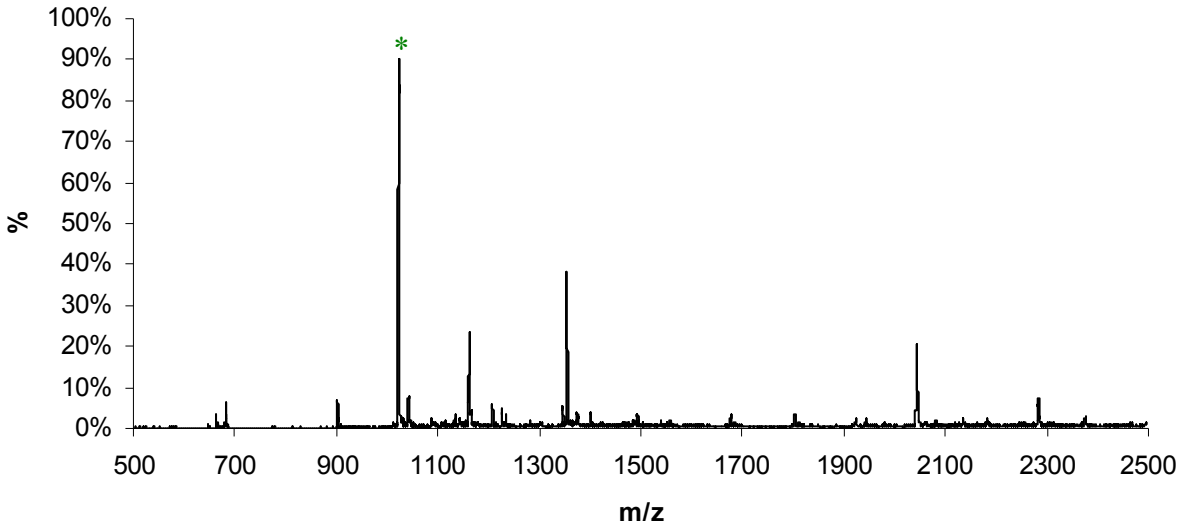


Figure S19. Nano-electrospray spectrum of porphyrin dimer **1** with HFGA. The major peak at 1022 *m/z* was assigned to the 2+ charge state of a non-covalent complex between dimer and HFGA *.

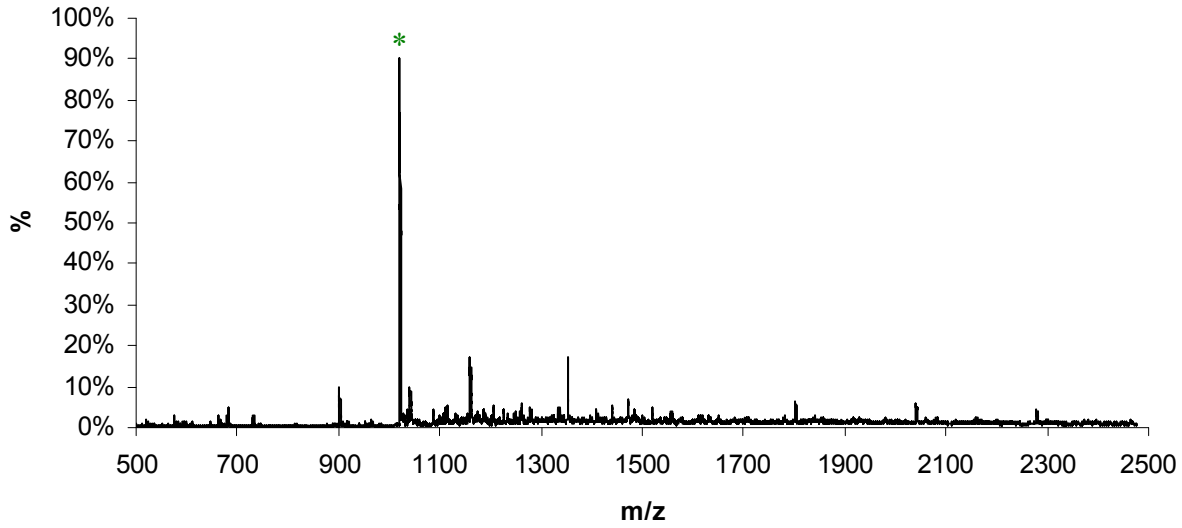


Figure S20. Nano-electrospray spectrum of porphyrin dimer **1** with TFTA. The major peak at 1021 *m/z* was assigned to the 2+ charge state of a non-covalent complex between dimer and TFTA *.