Supplementary Material (ESI) for Chemical Communications

Inclusion of C_{60} into an adjustable porphyrin dimer generated by dynamic disulfide chemistry

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Instrumentation

^{1}H NMR spectra were recorded on Bruker DRX-500, DRX-400 or DPX-250 instruments or on a DRX instrument fitted with a cryoprobe.[†] ^{13}C NMR spectra were recorded on Bruker DPX-400 (100 MHz) or DRX-500 (125 MHz) instrument. Chemical shifts are quoted in parts per million with reference to residual protons of the deuterated solvent for the ^{1}H and the ^{13}C resonances of the solvent for ^{13}C NMR.

MALDI TOF mass spectra were recorded on a Kratos Kompact 4, and electrospray mass spectra were recorded on a Micromass Quattro-LC triple quadrupole apparatus (QUATTRO).

Solution state IR spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer at 4 cm^{-1} resolution or better.

Uv-vis absorption spectra were recorded on a Hewlett Packard 8452A diode array spectrometer.

HPLC analyses were carried out on a Hewlett Packard 1050 system coupled to a UV analyser and the data were processed using HP Chemstation software. Separations were achieved in the reverse phase using a Jupiter Phenomemex column (300 Å, 25.0 cm × 4.6 mm, 5 μm particle size), a C18 phase. All separations were achieved by the gradient elution of MeOH and THF mixtures tabulated below with a flow rate of 1 ml min^{-1} and an injection volume of 2 μl. Assignments were made in the first instance by isolation and mass spectrometric analysis, and then by comparison with known

[†] A cryoprobe is a NMR probe, which is cooled to approximately 26 K. This gives a greatly improved signal to noise ratio, making it ideal for the measurement of NMR spectra of species at low concentration.

samples. The chromatography was carried out at 20 °C in a HP oven, to minimise temperature fluctuations which lead to variable retention times.

HPLC Gradients:

Time (min)	% MeOH	% THF
0	80	20
15	40	60
20	40	60

The isothermal calorimetry measurements (microcalorimetry) were conducted by using a thermostated and fully computer-operated MCS-ITC calorimeter from MicroCal, LLC, Northampton, MA, USA. Aliquots of 10 μl were titrated into the calorimetric cell every 3 mins over a one and a half hour period. Data analysis using the customised ITC module of the Origin 5.0 software package and a least squares fitting procedure to fit the data to the appropriate binding model. All measurements were carried out at 25 °C. For each system studied a blank run was carried out in which the titrant was titrated into the cell containing solvent only to allow corrections for the heat effects due to dilution to be made.

Thin Layer Chromatography was carried out on Kieselgel 60 F_{24} (Merck) 0.2 mm plates. Porphyrins were inspected initially by sight and then visualised by UV light. Other organic compounds were visualised by UV absorption, or developed with phosphomolybdic acid in 20 % aqueous ethanol or vanillin. Column chromatography was carried out using neutral alumina (Aldrich) or Kieselgel 60 (Merck) 230-400 mesh and using distilled solvents.

All chemicals were purchased from Acros, Aldrich, Avocado or Fluka in reagent grade quality or better and used without further purification. All solvents were distilled prior to use and dry solvents were freshly distilled from CaH_2 under argon. Ultrapure water was obtained from a Millipore water purification system. HPLC grade $CHCl_3$ and MeOH (Aldrich) and THF (Fisher) were filtered with a 0.45 μm Millipore filter and used without further purification.

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Preparation of analytical libraries

All analytical scale reactions were carried out at RT on a 0.5 ml or 1 ml scale. The monomer(s) were dissolved to give a solution of 20 mM. The stock solution was then diluted to give the required concentration for cyclisation (5 mM unless otherwise stated) to give the correct volume. DBU was added to the reaction to initiate exchange at a concentration such that ca. 20 – 40 μl were added to give the required equivalents of DBU (0.1 equivalents with respect to thiol equivalents). HPLC or MS analysis was performed by removal of 10 – 50 μl aliquots from the reaction mixture. All templates were solids: for the higher MW templates, the required mass was simply weighed out and added. For the low MW templates, highly concentrated solutions of the template were made up, so that less than 10 μl of solution was added to give the correct equivalents. All cyclisations were stirred at RT and followed by HPLC analysis every 24 hours for up to seven days.

Large scale cyclisation under templating conditions

Large scale cyclisations were carried out at 5 mM concentration on the 50 – 100 mg scale. Stoichiometric addition of template, and 0.1 equivalents of DBU with respect to thiol equivalents were set up as described above. The reactions were stirred at RT until thermodynamic equilibrium was reached, as ascertained by HPLC analysis of 10 – 50 μl aliquots removed from the mixture. On equilibrium being reached, the solvent was removed by rotaevaporation, and the resulting residue dissolved in a 20 ml of CH_2Cl_2. This was washed with water 1 × 20 ml, dried over $MgSO_4$, and the solvent removed. The solid was then dissolved in $CHCl_3$, and subjected to flash filtration over alumina, eluting with $CHCl_3$.

General Procedure for Synthesis of Porphyrins

Palladium on carbon (10 %, usually 0.1 g per every 1 g of dihydropyrrin used) was added to a solution of 5,5'-dibenzyloxycarbonyl-3,3'-dihexyl-4,4'-dimethyl-2,2'-dihydropyrrin (1 eq.) in THF (50 ml, containing 2% NEt_3 and 2% MeOH). The resulting black suspension was degassed and placed under an atmosphere of hydrogen. The solution was stirred for 3 hours, the catalyst filtered off and the filtrate concentrated to give an off-white solid that was dried under vacuum. To this solution

of diacid, trifluoroacetic acid (ca. 17 ml, degassed by three freeze-pump cycles) was added via cannula and the mixture stirred for 30 mins at 0 °C all under Ar in darkness, with periodic degassing to remove the incipient CO_2. The appropriate aldehyde (1 eq) was dissolved in dry degassed MeOH (20 ml) and added via cannula to the decarboxylated dihydropyrrin solution at –15 °C (ice/NaCl bath). After 2 hours, and on warming to RT, DDQ (20 fold excess) was added and the solution stirred for 30 mins. Triethylamine (ca.15 ml) was added dropwise to ensure neutralisation of the solution. The solvent was removed, and the residue dissolved in CH_2Cl_2, then washed with H_2O (3 × 100 ml) with a few drops of NH_3, and dried over Na_2SO_4. This was concentrated to give a thick dark red solution that was purified by column chromatography (alumina, CH_2Cl_2). Most porphyrins were then re-crystallised by layered addition of either MeOH or hexane to a saturated $CHCl_3$ or CH_2Cl_2 solution of the porphyrin.

Zinc metallation of Free Base Porphyrins

Free base porphyrins were converted to zinc complexes in essentially quantitative yield by treatment with excess $Zn(OAc)_2$ in $CHCl_3$ at RT, with gentle heating and agitation for 2-3 mins. After 30 mins, the solution was evaporated to dryness, and the residue taken up in CH_2Cl_2. This was then filtered through a sintered glass funnel to remove the excess $Zn(OAc)_2.2H_2O$, the filtrate was washed with water, dried over Na_2SO_4, evaporated to dryness and recrystallised by addition of either MeOH or hexane to a saturated $CHCl_3$ or CH_2Cl_2 solution of the porphyrin.

Synthetic procedure for Zn-1

3-(2-Bromoethoxy)benzaldehyde

3-Hydroxybenzaldehyde (5 g, 41 mmol) was dissolved in dry DMF (36 ml) under N_2 and K_2CO_3 (6.07 g, 44 mmol) was added. After 30 mins of stirring, 1,2-dibromobutane (14.66 ml, 170 mmol) was added. The reaction mixture was then heated to 60 °C for 3 days. H_2O (50 ml) was added to the suspension, which was then extracted with Et_2O (3 × 100 ml). The combined extracts were washed with brine (30 ml), dried over $MgSO_4$ and evaporated to an oil. This was subjected to vacuum pressure for 12 hours, after which time a pink/white solid precipitated. This was filtered off and identified as unreacted 3-hydroxybenzaldehyde. Column

chromatography over silica was performed on the oily residue (CH_2Cl_2:MeOH 100:2 up to 100:6) to yield a pale yellow oil. Yield: 3.72 g (40%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.97 (s, 1H, C*H*O), 7.47 (m, 2H, Ar-*H*), 7.37 (s, 1H, *o*-Ar-*H*), 7.18 (d, *J* = 6.5 Hz, 1H, Ar-*H*), 4.33 (t, *J* = 6 Hz, 2H, OCH_2), 3.65 (t, *J* = 6 Hz, 2H, CH_2Br);

^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3, 163.2, 136.4, 130.3, 124.3, 121.9, 113.9, 68.3, 28.1;

MS (ES): *m/z* 230.0 [MH^+].

Thioacetic acid *S*-[2-(3-formylphenoxy)-ethyl] ester

To a solution of 3-(2-bromoethoxy)benzaldehyde (3.5 g, 15 mmol) in acetone (40 ml) was added potassium thioacetate (3.4 g, 30 mmol) with stirring, and then the mixture was refluxed for 5 hrs, until no starting material was visible by TLC. On cooling to RT, water (80 ml) was added, and the mixture was extracted with EtOAc (6 × 15 ml), and the solvent removed. Column chromatography (Et_2O/hexane 1:1) gave the product as a light brown oil. Yield: 3.5 g (95%).

^{1}H NMR (250 MHz, $CDCl_3$): δ 9.93 (s, 1H, C*H*O), 7.43 (m, 1H, Ar-*H*), 7.40 (s, 1H, Ar-*H*), 7.135 (dd, 1H, Ar-*H*), 4.12 (t, *J* = 6 Hz, 2H, OCH_2), 3.25 (t, *J* = 6 Hz, 2H, CH_2S), 2.34 (s, 3H, CH_3);

^{13}C NMR (63 MHz, $CDCl_3$): δ 194.8, 191.7, 158.8, 137.8, 130.0, 123.3, 121.5, 113.3, 66.6, 30.4, 28.1;

MS (ES): *m/z* 225.6 [MH^+].

5,15-Di[3-(2-acetylsulfanylethoxy)phenyl]-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrin

This was synthesised according to the general procedure for the preparation of porphyrins using thioacetic acid *S*-[2-(3-formylphenoxy)ethyl]ester (1.56 g, 6.98 mmol) and 5,5'-dibenzyloxycarbonyl-3,3'-dihexyl-4,4'-dimethyl-2,2'-dihydropyrrin (3 g, 6.98 mmol) and recrystallised from CH_2Cl_2:MeOH. Yield: 2 g (53 %).

^{1}H NMR (250 MHz, $CDCl_3$): δ 10.26 (s, 2H, *meso*), 7.71 (m, 2H, Ar), 7.65 (s, 2H, Ar*H*), 7.62 (m, 2H, Ar*H*), 7.36 (d, *J* = 8 Hz, 2H, Ar*H*), 4.27 (t, *J* = 6 Hz, 4H, OCH_2), 4.00 (t, 8H, hex-^{1}CH_2), 3.38 (t, *J* = 6 Hz, 4H, OCH_2), 2.57 (s, 12H, pyrrolic-CH_3), 2.36 (s, 6H SCOCH_3), 2.20 (m, 8H, hex-^{2}CH_2), 1.75 (m, 8H, hex-^{3}CH_2), 1.50 (m, 8H,

hex-^{4}CH_2), 1.39 (m, 8H, hex-^{5}CH_2), 0.91 (t, J = 7 Hz, 12H, hex-^{6}CH_3), -2.42 (s, 2H, N*H*);

^{13}C NMR (125 MHz, $CDCl_3$): δ 195.1, 158.0, 145.5, 146.3, 145.0, 143.8, 138.0, 129.1, 127.0, 119.5, 118.6, 114.5, 95.9, 66.7, 33.4, 31.7, 30.3, 28.4, 26.8, 22.5, 14.6, 14.1;

MS (MALDI): *m/z* 1090.8 [M^+].

5,15-Di[3-(2-acetylsulfanylethoxy)phenyl]-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrin zinc(II)

This was zinc metallated according to the general procedure, and recrystallised from $CHCl_3$:hexane.

^{1}H NMR (250 MHz, $CDCl_3$): δ 10.19 (s, 2H, *meso*), 7.73 (t, J = 6 Hz, 2H, Ar), 7.64 (m, 4H, Ar*H*), 7.37 (d, J = 6 Hz, 2H, Ar*H*), 4.25 (t, J = 5 Hz, 4H, OCH_2), 3.99 (t, 8H, hex-^{1}CH_2), 3.35 (t, J = 5 Hz, 4H, OCH_2), 2.54 (s, 12H, pyrrolic-CH_3), 2.34 (s, 6H SCOCH_3), 2.12 (m, 8H, hex-^{2}CH_2), 1.75 (m, 8H, hex-^{3}CH_2), 1.50 (m, 8H, hex-^{4}CH_2), 1.38 (m, 8H, hex-^{5}CH_2), 0.92 (t, J = 7 Hz, 12H, hex-^{6}CH_3);

^{13}C NMR (125 MHz, $CDCl_3$): δ 195.2, 157.9, 145.6, 146.4, 145.0, 143.5, 138.1, 128.5, 126.9, 120.0, 118.9, 114.9, 97.7, 66.9, 33.3, 32.0, 30.5, 28.5, 26.8, 22.8, 15.1, 14.2;

MS (MALDI): *m/z* 1154.6 [M^+].

5,15-Di[3-(2-mercaptoethoxy)phenyl]-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrin zinc(II)

5,15-Di[3-(2-acetylsulfanylethoxy)phenyl]-2,8,12,18-tetra-hexyl-3,7,13,17-tetramethyl-porphyrin zinc(II) (0.5 g, 0.43 mmol) was dissolved in degassed CH_2Cl_2 (50 ml), and hydrazine monohydrate (1 ml) was added. This solution was stirred under Ar for 12 hours, before the solvent was removed under reduced pressure. The residue was redissolved in degassed DCM (50 ml) and washed with degassed H_2O (100ml) under Ar. The porphyrin was dried over Na_2SO_4 and used without further purification.

^{1}H NMR (250 MHz, $CDCl_3$): δ 10.20 (s, 2H, *meso*), 7.75 (t, J = 6 Hz, 2H, Ar), 7.66 (m, 4H, Ar*H*), 7.38 (d, J = 6 Hz, 2H, Ar*H*), 4.30 (t, J = 5 Hz, 4H, OCH_2), 3.99 (t, 8H, hex-^{1}CH_2), 2.99 (q, J = 6, 7.5 Hz, 4H, OCH_2), 2.57 (s, 12H, pyrrolic-CH_3), 2.21 (m, 8H, hex-^{2}CH_2), 2.07 (t, J = 7.5Hz, 2H, S*H*), 1.75 (m, 8H, hex-^{3}CH_2), 1.54 (m, 8H, hex-^{4}CH_2), 1.42 (m, 8H, hex-^{5}CH_2), 0.93 (t, J = 7 Hz, 12H, hex-^{6}CH_3);

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 145.5, 146.2, 144.7, 143.5, 138.3, 128.5, 126.7, 119.8, 118.9, 114.7, 97.6, 67.0, 35.4, 32.1, 30.5, 28.4, 26.7, 22.6, 14.1;
MS (MALDI): *m/z* 1070.4 [M^+].

Synthetic procedure for Zn-2⋅BPy

The large scale cyclisation of the Zn *meta* long monomer (50 mg, 0.05 mmol) was carried out in the presence of BPy (3.5 mg, 0.025 mmol) in 8 ml $CHCl_3$ with 3 μl DBU, according to the general procedure. Yield: 25 mg (50 %).

^{1}H NMR (500MHz, $CDCl_3$): δ 9.14 (s, br, 4H, *meso-H*), 7.84 (s, br, 4H, aryl-*H*), 7.36 (s, 4H, br aryl-*H*), 7.25 (s, br, 4H, aryl-*H*), 7.13 (s, br, 4H, aryl-*H*), 4.57 (s, br, 6H, β-*H* pyridyl guest), 4.23 (s, br, 8H, OCH_2CH_2), 3.89 (s, br, 8H, $^1CH_2$), 3.74 (s, br, 8H, $^1CH_2$), 3.14 (s, br, 8H, CH_2CH_2S), 2.38 (s, 24H, Me), 2.01 (s, br, 16H, $^2CH_2$), 1.70 (s, br, 4H, α-*H* pyridyl guest), 1.56 (m, br, 16H, $^3CH_2$), 1.44 (m, br, 16H, $^4CH_2$), 1.35 (m, br, 16H, $^5CH_2$), 0.82 (m, br, 24H, $^6CH_2$);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.8, 145.9, 145.0, 144.5, 142.0, 141.9, 136.2, 127.1, 126.2, 125.8, 118.1, 117.7, 117.0, 116.0, 113.8, 96.0, 65.7, 38.0, 30.8, 28.6, 21.6, 13.9, 13.0;
UV-vis ($CDCl_3$): λ 418, 344, 548, 580 nm;
MS (MALDI): 2138.0 [M^+–guest].

Synthetic procedure for Zn-2⋅DABCO

The large scale cyclisation of the Zn *meta* long monomer (50 mg, 0.05 mmol) was carried out in the presence of DABCO (3 mg, 0.025 mmol) in 8 ml $CHCl_3$ with 3 μl DBU, according to the general procedure.

^{1}H NMR (500MHz, $CDCl_3$): δ 9.58 (s, 4H, *meso-H*), 7.49 (s, 4H, inner *o*-aryl-*H*), 7.41 (dd, *J* = 7.5 Hz, 4H, *m*-aryl-*H*), 7.31 (d, *J* = 7.5 Hz, 4H, *p*-aryl-*H*), 7.08 (d, *J* = 7.5 Hz, 4H, outer *o*-aryl-*H*), 4.53 (t, *J* = 5.1 Hz, 8H, OCH_2CH_2), 3.80 (m, 8H, $^1CH_2$), 3.54 (m, 8H, $^1CH_2$), 3.30 (t, *J* = 5.1 Hz, 8H, CH_2CH_2S), 2.26 (s, 24H, Me), 1.91 (m, 8H, $^2CH_2$), 1.84 (m, 8H, $^2CH_2$), 1.51 (m, 16H, $^3CH_2$), 1.34 (m, 16H, $^4CH_2$), 1.28 (m, 16H, $^5CH_2$), 0.85 (m, 24H, $^6CH_2$), –4.95 (s, 12H, CH_2 DABCO guest);
UV-vis ($CDCl_3$): λ 418, 548, 584, 342 nm;
MS (MALDI): 2137.0 [M^+–guest].

Synthetic procedure for 2H-2 without template

Removal of Zn and template from any of the Zn *meta* long dimer complexes was achieved by treatment with 10 % TFA in MeOH. The porphyrin was extracted into $CHCl_3$ (20 ml) and then washed with water (3 × 50 ml). The solution was dried over Na_2SO_3 and used without further purification.

Major identifiable peaks only reported, dimer exists in a variety of conformations.

^{1}H NMR (500MHz, $CDCl_3$): δ 10.11, 9.85, 9.56, 9.03 (s, br, all *meso-H*), –2.45, –2.95, –3.11 (s, br, all N*H*$_2$);

UV-vis ($CDCl_3$): λ 405, 512, 574, 538 nm;

MS (MALDI): 2010.7 [M^+].

Synthetic procedure for Zn-2 without template

Zn metallation of the free base dimer was achieved according to the general procedure. Alternatively, chromatography of a dimer·ligand complex over silica effected the removal of the guest ligand.

Major identifiable peaks only reported, dimer exists in a variety of conformations.

^{1}H NMR (500MHz, $CDCl_3$): δ 9.23, 9.10, 8.86, 8.60 (s, br, all *meso-H*);

UV-vis ($CDCl_3$): λ 408, 510, 576, 542 nm;

MS (MALDI): 2137.4 [M^+].