

Disulfide Strapped Porphyrins for Monolayer Formation on Gold

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Supporting Information

Advancing and receding water contact angles were recorded with a Krüss contact angle goniometer using the sessile drop method. Angles were calculated by the G40 software (Krüss) by automatic analysis of images of the drop as it was slowly advanced or receded on the sample. Measurements were made on three different areas of each sample, and at least two independently prepared samples were examined.

Electrochemistry was carried out in a 3 electrode cell in which the gold sample comprised the working electrode with a geometric area of 0.44 cm^2 . A Pt disc was used as a counter electrode with a $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode with KCl salt bridge solution (Radiometer). Potentials are quoted with respect to this electrode.

Experiments were controlled by an Autolab potentiostat and frequency response analyser (EcoChemie BV) interfaced to a computer running the GPES 4.5 and FRA software. The differential double layer capacitance was measured by cyclic voltammetry in 0.1 M NaClO_4 aqueous solution, scanning over the range $-0.3\text{ }-\text{ }-0.4\text{ V}$ at a rate of 0.1 Vs^{-1} . The capacitance was calculated as the sum of the current at -0.35 V in both scan directions divided by $2 \times \text{scan rate} \times \text{geometric electrode area}$. Heterogeneous electron transfer between the modified electrodes and the external redox couple $\text{Fe}(\text{CN})_6^{3-4-}$ was measured by cyclic voltammetry in a solution 1 mM in both $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.1 M in K_2SO_4 scanning over the range $0\text{ }-\text{ }-7\text{ V}$ at 0.1 Vs^{-1} . The solution was purged with N_2 prior to measurement. Faradaic impedance spectra were recorded using the same electrolyte solution. A sinusoidal excitation of 5 mV was applied to the open cell potential of -0.2 V . Impedance was measured at 40 frequencies between 0.1 Hz and 10 kHz . The spectra were analysed with the program Equivalent Circuit (B. A. Boukamp, University of Twente).

All glassware and glass slides used for preparation of monolayers were cleaned by immersion in freshly prepared piranha solution (*conc.* $\text{H}_2\text{SO}_4/30\text{ \% H}_2\text{O}_2$, 7/3) (**caution** - reacts violently with organic material. Contact with metals may cause rapid decomposition) followed by rinsing extensively with distilled water and finally with ultrapure water.

Gold substrates prepared by electron beam evaporation of Ti (5 nm) and Au (200 nm) onto 25 mm diameter glass discs were stored under nitrogen in Fluoroware containers and cleaned prior to use by treatment with oxygen plasma for 5 min followed by soaking in EtOH for 10 min.²⁹

Typical monolayer preparations. Plasma cleaned gold substrates were immersed into a solution of thiol or disulfide at a concentration of $0.1\text{ }-\text{ }1\text{ mM}$ in THF for $\sim 12\text{ h}$ at room temperature. Care was taken to minimize exposure of the porphyrin solutions to light. After incubation samples were rinsed extensively with the same solvents before blowing dry with a stream of nitrogen.

Synthesis

Materials. THF, hexane, EtOAc and Et_2O were distilled before use. When stated as anhydrous, solvents were distilled from an appropriate drying agent immediately prior

to use. Et_3N was freshly distilled from CaH_2 . Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Merck or Fluorochem 60 mesh silica gel was used for column chromatography. 5,5'-Dibenzylloxycarbonyl-3,3'-dihexyl-4,4'-dimethyl-2,2'-dihdropyrrin was prepared according to a standard procedure.²⁰ All other chemicals were purchased as reagent grade or better and used without further purification unless specified otherwise.

General procedure for Zn metalation of porphyrins. Zn metalation was carried out by boiling a solution of free-base porphyrin in chloroform and ~5 % MeOH with excess $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{OAc})_2$ for several minutes. The solution was filtered, washed with water, dried (MgSO_4) and evaporated.

3-(11-Hydroxy-undecyloxy)-benzaldehyde (1)

Typical procedure. 3-Hydroxybenzaldehyde (5.00 g, 41 mmol), 11-bromoundecanol (6.85 g, 27 mmol) and Cs_2CO_3 (14.4 g, 44 mmol) were stirred in DMF (anhydrous, 36 mL) under N_2 for 3 d at rt. Water (50 mL) was added to the dark suspension, which was extracted with Et_2O (2×100 mL). The combined extracts were washed with brine (30 mL), dried (MgSO_4) and evaporated to an orange oil which was redissolved in EtOH (several mL). Water (200 mL) was added, followed by cooling in a refrigerator to precipitate a pink solid which was collected by filtration. The solids were dissolved in Et_2O (70 mL), washed with NaOH (10 %, 3×20 mL), dried (MgSO_4) and evaporated to afford the product as a pink solid (7.30 g, 92 %). This was used without further purification, although could be recrystallized from hexane/EtOAc mixture. R_f 0.19 (hexane/EtOAc, 3/1).

^1H NMR (250 MHz, CDCl_3): δ 9.96 (s, 1H, CHO), 7.42 (m, 2H, Ar), 7.37 (m, 1H, Ar), 7.16 (m, 1H, Ar), 4.00 (t, $J = 7$ Hz, 2H, ArOCH_2), 3.63 (br t, $J = 6$ Hz, 2H, CH_2OH), 1.79 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.50 - 1.29 (m, 15H, CH_2 , OH); ^{13}C NMR (62.9 MHz, CDCl_3): δ 192.2, 159.7, 137.8, 130.0, 123.3, 122.0, 112.8, 68.3, 63.1, 32.8, 3 \times 29.5, 29.4, 29.3, 29.1, 26.0, 25.7; FAB MS: m/z [M+H]⁺ calcd 293.2117, found 293.2146; IR (CCl₄): ν_{max} 3638 (w), 2929 (s), 2855 (s), 2724 (w), 1702 (s), 1599 (m), 1262 (s) cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3$: C 73.93, H 9.65. Found: C 73.86, H 9.66; mp 41 - 42 °C.

3-(11-p-Toluenesulfonyloxy-undecyloxy)-benzaldehyde (2)

To a solution of **1** (7.30 g, 25.0 mmol) and Et_3N (5.3 mL) in DCM (anhydrous, 25 mL) at 0 °C under N_2 was added dropwise TsCl (12.2 g, 37.5 mmol) in DCM (anhydrous, 25 mL) over 30 min. After stirring at rt for 17 h under N_2 , additional portions of TsCl (1.00 g, 3.07 mmol) and Et_3N (1.0 mL) were added. Stirring was continued for a further 5 h. The pink solution was washed with water (4×20 mL), dried over MgSO_4 and evaporated onto silica gel which was loaded onto a silica column. The column was eluted first with hexane/EtOAc/CHCl₃ (10/1/1) to elute unreacted starting materials, then with hexane/EtOAc (3/1) to elute the product which was obtained as a white crystalline solid (9.40 g, 84 %). R_f 0.46 (hexane/EtOAc, 3/1).

^1H NMR (400 MHz, CDCl_3): δ 9.96 (s, 1H, CHO), 7.78 (d, $J = 8$ Hz, 2H, Ts), 7.43 (m, 2H, Ar), 7.37 (d, $J = 2$ Hz, 1H, Ar), 7.33 (d, $J = 8$ Hz, 2H, Ts), 7.16 (m, 1H, ArH), 4.01, 4.00 ($2 \times$ t, $J = 7$ Hz, 4H, ArOCH_2 , CH_2OSO_2), 2.44 (s, 3H, CH_3), 1.79 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.35 - 1.22 (m, 12H, $(\text{CH}_2)_6$); ^{13}C NMR (62.9 MHz, CDCl_3): δ 192.1, 159.7, 144.5, 137.7, 133.2, 129.9, 129.7,

127.8, 123.2, 121.9, 112.7, 70.6, 68.2, 29.4, 2 \times 29.3, 29.0, 28.8, 28.7, 25.9, 25.3, 21.6; FAB MS: m/z [M+H]⁺ calcd 447.2205, found 447.2228; IR (CCl₄): ν_{max} 2928 (s), 2956 (m), 2725 (w), 1703 (s), 1599 (m), 1371 (s), 1261 (s), 1189 (s), 1178 (s) cm⁻¹; Anal. Calcd for C₂₅H₃₄O₅S: C 67.24, H 7.67. Found: C 67.06, H 7.70; mp 55 - 57 °C.

3-(11-Thioacetyl-undecyloxy)-benzaldehyde (3)

2 (9.40 g, 21.0 mmol) was finely ground and PEG 400 (65 mL) added. The mixture was sonicated and stirred at 50 °C until dissolution was complete. To this was added KSCOCH₃ (3.13 g, 27.4 mmol). The solution was stirred under N₂ at 40 - 50 °C for 75 min. Water (300 mL) was added to form a white precipitate which was solubilized by shaking with Et₂O (200 mL). The organic phase was separated, and the aqueous layer extracted with further portions of Et₂O (6 \times 100 mL). The combined Et₂O extracts were washed with brine (50 mL), dried (MgSO₄) and evaporated to a pale yellow solid which was recrystallized from hexane to afford the pure product as a white powder (6.27 g, 85 %). R_f 0.43 (hexane/CHCl₃/EtOAc, 10/1/1).

¹H NMR (250 MHz, CDCl₃): δ 9.96 (s, 1H, CHO), 7.45 (m, 2H, Ar), 7.37 (m, 1H, Ar), 7.16 (m, 1H, Ar), 4.00 (t, J = 7 Hz, 2H, OCH₂), 2.85 (t, J = 7 Hz, 2H, CH₂S), 2.30 (s, 3H, SCOCH₃), 1.79 (m, 2H, CH₂), 1.58 - 1.27 (m, 16H, (CH₂)₈); ¹³C NMR (62.9 MHz, CDCl₃): δ 196.0, 192.1, 159.7, 137.7, 129.9, 123.2, 121.9, 112.7, 68.2, 30.6, 29.4, 29.3, 29.1, 28.7, 25.9; FAB MS: m/z [M+H]⁺ calcd 351.1979, found 351.1994; IR (CCl₄): ν_{max} 2928 (s), 2854 (m), 1697 (s), 1262 (s) cm⁻¹; Anal. Calcd for C₂₀H₃₀O₃S: C 68.53, H 8.63. Found: C 68.50, H 8.60; mp 42 - 44 °C.

Disulfanyl bis[11-undecyloxy-(3-benzaldehyde)] (4)

3 (3.08 g, 8.79 mmol) was stirred with K₂CO₃ (1.5 g, 11 mmol) in MeOH (60 mL) under air for 17 h to form a white suspension. The solvent was evaporated and water (50 mL) added. This was extracted with Et₂O (3 \times 100 mL), the combined extracts washed with brine (50 mL), dried (MgSO₄) and evaporated to a yellow oil. To a two phase mixture of this oil in CHCl₃ (100 mL) and water (50 mL) was added a saturated solution of I₂ in CHCl₃ until a brown colour persisted. The organic phase was washed with *dil.* sodium thiosulfate (20 mL) and water (50 mL), dried (MgSO₄) and evaporated to a yellow solid. This material was chromatographed on silica twice, eluting with hexane/EtOAc (5/1) then hexane/EtOAc (7/1). Fractions containing a trace of impurity were recrystallized from hot hexane, before recombination with the remaining product. **4** was obtained as a pale cream solid (2.26 g, 84 %). R_f 0.42 (hexane/EtOAc, 5/1).

¹H NMR (250 MHz, CDCl₃): δ 9.95 (s, 2H, CHO), 7.43 (m, 4H, Ar), 7.37 (m, 2H, Ar), 7.16 (m, 2H, Ar), 3.99 (t, J = 7 Hz, 4H, CH₂), 2.67 (t, J = 7 Hz, 4H, SCH₂), 1.79 (m, 4H, CH₂), 1.66 (m, 4H, CH₂), 1.47 - 1.28 (br m, 28H, (CH₂)₇); ¹³C NMR (62.9 MHz, CDCl₃): δ 192.2, 159.1, 137.8, 130.0, 123.3, 121.9, 112.7, 68.3, 39.2, 29.5, 29.3, 29.2, 29.1, 28.5, 26.0; ES MS: m/z [M+Na]⁺ calcd 637.3356, found 637.3373; IR (CCl₄): ν_{max} 2928 (s), 2855 (s), 2722 (w), 1702 (s), 1598 (m) cm⁻¹; Anal. Calcd for C₃₆H₅₄O₄S₂: C 70.31, H 8.85. Found: C 70.40, H 8.90.

2-(11-Hydroxy-undecyloxy)-benzaldehyde (5)

To a suspension of Cs₂CO₃ (9.80 g, 27.8 mmol) and 11-bromoundecanol (5.00 g, 19.9 mmol) in DMF (anhydrous, 30 mL) was added salicylaldehyde (3.2 mL, 30 mmol).

The solution was degassed and stirred under N_2 at rt for 3 d. Water (200 mL) was added and the mixture extracted with Et_2O (5×50 mL). The combined organic extracts were washed with brine (2×30 mL), dried ($MgSO_4$) and evaporated to an oil. This was shaken with water (200 mL) and the resulting emulsion cooled in a refrigerator for 2 h to cause solidification. The cream solids were filtered, washed with water (50 mL) and dried *in vacuo*. Recrystallization from hexane/EtOAc mixture afforded the product as pale yellow crystals after 4 d standing in a refrigerator (4.85 g, 83 %). R_f 0.22 (hexane/EtOAc, 3/1).

1H NMR (400 MHz, $CDCl_3$): δ 10.50 (d, $J = 1$ Hz, 1H, CHO), 7.81 (dd, $J = 2, 8$ Hz, 1H, Ar), 7.51 (m, 1H, Ar), 6.97 (m, 2H, Ar), 4.05 (t, $J = 6$ Hz, 2H, $ArOCH_2$), 3.62 (t, $J = 7$ Hz, 2H, CH_2OH), 1.82 (m, 2H, CH_2), 1.54 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.28 (br m, 13H, $(CH_2)_6$, OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 190.0, 161.6, 135.9, 128.2, 124.9, 120.4, 112.5, 68.5, 63.0, 32.8, 2×29.5 , 2×29.4 , 29.3, 29.1, 26.0, 25.7; EI MS: m/z [M] $^+$ calcd 292.2038, found 292.2036; IR (CCl_4): ν_{max} 3636 (w), 2929 (s), 2856 (s), 1693 (s), 1599 (s), 1457 (s), 1242 (s) cm^{-1} ; Anal. Calcd for $C_{18}H_{28}O_3$: C 73.92, H 9.65. Found: C 74.16, H 9.61; mp 30 - 32 °C.

2-(11-*p*-Toluenesulfonyloxy-undecyloxy)-benzaldehyde (6)

Prepared (from **5**) and purified analogously to **2**. R_f 0.38 (hexane/EtOAc, 3/1). Yellow solid (2.66 g, 87 %).

1H NMR (250 MHz, $CDCl_3$): δ 10.50 (d, $J = 1$ Hz, 1H, CHO), 7.82 (dd, $J = 8, 2$ Hz, 1H, Ar), 7.78 (d, $J = 8$ Hz, 2H, Ts), 7.52 (m, 1H, Ar), 7.33 (d, $J = 8$ Hz, 2H, Ts), 6.98 (m, 2H, Ar), 4.04 (m, 4H, SO_3CH_2 , $ArOCH_2$), 2.44 (s, 3H, CH_3), 1.84 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.29 - 1.08 (m, 14H, $(CH_2)_7$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 189.9, 161.6, 144.6, 135.9, 133.3, 129.8, 128.2, 127.9, 124.9, 120.4, 112.5, 70.7, 68.5, 29.4, 3×29.3 , 29.1, 28.9, 28.8, 26.0, 25.3, 21.6; FAB MS: m/z [M+H] $^+$ calcd 447.2205, found 447.2209; IR ($CDCl_3$): ν_{max} 2929(s), 2856 (s), 1686 (s), 1599 (s), 1177 (s) cm^{-1} ; Anal. Calcd for $C_{25}H_{34}O_5S$: C 67.24, H 7.67, S 7.18. Found: C 66.92, H 7.66, S 6.98.

2-(11-Thioacetyl-undecyloxy)-benzaldehyde (7)

Prepared from **6** analogously to **3**. Column chromatography on silica eluted with hexane/EtOAc/ $CHCl_3$ (10/1/1) afforded the product as a colourless oil (1.31 g, 71 %). R_f 0.30 (hexane/EtOAc/ $CHCl_3$, 10/1/1).

1H NMR (250 MHz, $CDCl_3$): δ 10.51 (d, $J = 1$ Hz, 1H, CHO), 7.82 (dd, $J = 8, 2$ Hz, 1H, Ar), 7.52 (m, 1H, Ar), 6.98 (m, 2H, Ar), 4.06 (t, $J = 6$ Hz, 2H, OCH_2), 2.85 (t, $J = 7$ Hz, 2H, SCH_2), 2.31 (s, 3H, $COCH_3$), 1.84 (m, 2H, CH_2), 1.58 - 1.27 (m, 16H, $(CH_2)_8$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 189.9, 161.6, 135.9, 128.2, 124.9, 120.4, 112.5, 68.5, 30.6, 29.5, 29.3, 2×29.1 , 28.8, 26.0; FAB MS: m/z [M+H] $^+$ calcd 351.1974, found 351.1994; IR ($CDCl_3$): ν_{max} 2929 (s), 2856 (m), 1685 (s), 1599 (s) cm^{-1} ; Anal. Calcd for $C_{20}H_{30}O_3S$: C 68.53, H 8.63. Found: C 68.35, H 8.64.

Disulfanyl bis[11-undecyloxy-(2-benzaldehyde)] (8)

Prepared from **7** using a modification of the procedure used for **4**. $CHCl_3$ was used instead of Et_2O for the extraction step in the work-up. The $CHCl_3$ extracts were treated with I_2 , washed with KI (aq), sodium thiosulfate (aq), dried ($MgSO_4$) and evaporated to a yellow oil. Some solid material failed to dissolve during the extraction,

and this was treated directly with I_2 in $CHCl_3$ which resulted in dissolution. This solution was worked up as described, to afford a black oil. Both portions of oil were combined and chromatography on silica eluted with hexane/EtOAc (6/1) afforded the product as a cream solid (887 mg, 49 %). R_f 0.38 (hexane/EtOAc, 5/1).

1H NMR (400 MHz, $CDCl_3$): δ 10.51 (d, J = 1 Hz, 2H, CHO), 7.82 (dd, J = 8, 2 Hz, 2H, Ar), 7.52 (m, 2H, Ar), 6.99 (m, 4H, Ar), 4.07 (t, J = 6 Hz, 4H, OCH_2), 2.68 (t, J = 6 Hz, 4H, SCH_2), 1.84 (m, 4H, CH_2), 1.67 (m, 4H, CH_2), 1.48 (m, 4H, CH_2), 1.39 - 1.29 (m, 24H, $(CH_2)_6$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 189.9, 161.6, 135.9, 128.2, 124.9, 120.4, 112.5, 68.5, 39.2, 29.5, 29.3, 29.2, 29.1, 28.5, 26.0; ES MS: m/z $[M+Na]^+$ calcd 637.3356, found 637.3339; IR ($CDCl_3$): ν_{max} 2929 (s), 2856 (s), 1686 (s) cm^{-1} ; Anal. Calcd for $C_{36}H_{54}O_4S_2$: C 70.31, H 8.85. Found: C 70.18, H 8.78.

2,8,12,18-Tetrahexyl-5,15-bis[3-(11-thioacetyl-undecyloxy)-phenyl]-3,7,13,17-tetramethyl porphyrin (9)

Prepared according to a standard procedure from **3**.²⁰ Purification by chromatography on silica eluted with hexane/EtOAc (10/1) followed by recrystallization twice from $CHCl_3$ layered with MeOH afforded the product as purple crystals (2.30 g, 70 %). R_f 0.51 (hexane/EtOAc, 10/1).

1H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 2H, *meso*), 7.63 (m, 6H, Ar), 7.33 (dt, J = 8, 1 Hz, 2H, Ar), 4.10 (t, J = 7 Hz, 4H, OCH_2), 3.98 (t, J = 8 Hz, 8H, hex H^1), 2.81 (t, J = 7 Hz, 4H, SCH_2), 2.57 (s, 12H, CH_3), 2.28 (s, 6H, $SCOCH_3$), 2.18 (m, 8H, hex H^2), 1.85 (m, 4H, CH_2), 1.73 (m, 8H, hex H^3), 1.55 - 1.24 (m, hex $H^{4,5}$, 48H, $(CH_2)_8$), 0.89 (t, J = 7 Hz, 12H, hex H^6), -2.44 (s, 2H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 196.0, 158.7, 145.0, 143.5, 143.3, 141.5, 136.3, 128.5, 125.9, 119.4, 117.8, 115.1, 97.0, 68.5, 33.4, 32.1, 30.6, 30.1, 29.6, 2 \times 29.5, 29.2, 29.1, 28.8, 26.9, 26.1, 22.8, 14.5, 14.2; UV/vis (DCM): λ_{max} 408, 506, 540, 572 nm; FAB MS: m/z $[M+H]^+$ calcd 1343.9298, found 1343.9393; IR (CCl_4): ν_{max} 2928 (s), 2856 (s), 1694 (s), 1595 (m), 1467 (m), 1137 (m) cm^{-1} . Anal. Calcd for $C_{86}H_{126}N_4O_4S_2$: C 76.85, H 9.45, N 4.17. Found: C 76.89, H 9.53, N 4.20.

2,8,12,18-Tetrahexyl-5,15-bis[3-(11-thioacetyl-undecyloxy)-phenyl]-3,7,13,17-tetramethyl porphyrinato zinc(II) (Zn-9)

9 was Zn metalated according to the general procedure. An attempt at recrystallization from $CHCl_3$ layered with MeOH afforded **Zn-9** as a pink oil which was dried *in vacuo* (1.79 g, 97 %).

1H NMR (400 MHz, $CDCl_3$): δ 10.18, 10.15 (2 \times s, 2H, *meso*), 7.68 (m, 6H, Ar), 7.39 (m, 2H, Ar), 4.15 (m, 4H, OCH_2), 3.98 (m, 8H, hex H^1), 2.75 (m, 4H, SCH_2), 2.60, 2.59 (2 \times s, 12H, CH_3), 2.23 (m, 14H, hex H^2 , $COCH_3$), 1.90 (m, 4H, CH_2), 1.81 (m, 8H, hex H^3), 1.58 - 1.29 (m, 48H, hex $H^{4,5}$, $(CH_2)_8$), 0.98 (t, J = 7 Hz, hex H^6); ^{13}C (100.6 MHz, $CDCl_3$): δ 195.9, 158.6, 2 \times 147.6, 146.4, 146.3, 144.9, 2 \times 143.4, 2 \times 138.1, 128.4, 126.3, 119.8, 119.7, 2 \times 119.2, 115.0, 97.5, 68.4, 33.4, 32.1, 2 \times 30.5, 30.1, 2 \times 29.5, 29.4, 2 \times 29.1, 28.8, 26.8, 26.1, 22.8, 2 \times 15.1, 14.2; MALDI MS: m/z $[M]^+$ 1406. UV/vis (DCM): λ_{max} 410, 538, 574 nm; Anal. Calcd for $C_{86}H_{124}N_4O_2S_2Zn$: C 73.39, H 8.88, N 3.98. Found: C 73.40, H 8.96, N 4.09.

2,8,12,18-Tetrahexyl-5,15-bis[2-(11-thioacetyl-undecyloxy)-phenyl]-3,7,13,17-tetramethyl porphyrin (10)

Prepared from **7** according to the standard procedure.²⁰ The porphyrin was separated from the crude material by chromatography on silica eluted with hexane/EtOAc/CHCl₃ (20/1/1) gradient to hexane/EtOAc (10/1) and recrystallization from CHCl₃ layered with MeOH. This afforded a purple solid (1.26 g, 52 %) consisting of a mixture of atropisomers which could not be separated.

ES MS: *m/z* [M+H]⁺ 1344; Anal. Calcd for C₈₆H₁₂₆N₄O₄S₂: C 76.85, H 9.45, N 4.17.

Found: C 76.89, H 9.44, N 4.25.

Free-base *meta* strapped porphyrin (**11**)

Et₃N (2 mL) was added to a suspension of Pd/C (10 %, 0.04 g) and 5,5'-dibenzoyloxycarbonyl-3,3'-dihexyl-4,4'-dimethyl-2,2'-dihdropyrrin (397 mg, 0.65 mmol) in THF (50 mL). After degassing, the mixture was stirred under H₂ for 2 h, filtered through celite and evaporated to a grey solid which was dried *in vacuo*. To this was added TFA (degassed, 15 mL) and stirred under N₂ at 0 °C for 10 min, followed by 30 min at rt with periodic exposure to vacuum. After cooling to -20 °C a solution of **4** (200 mg, 0.33 mmol) in THF (degassed, 100 mL) at 0 °C was added by cannula. The solution was cooled to -25 °C, and stirred in the dark under N₂, allowing to warm to -7 °C over 4 h. DDQ (192 mg, 0.85 mmol) was added, and stirring continued at rt for 20 min. Et₃N (30 mL) was added followed by CHCl₃ (200 mL). The solution was washed with portions (100 mL) of water until the washings were colourless. The organic phase was dried (MgSO₄) and evaporated to a brown tar. Column chromatography on silica eluted with hexane/EtOAc (20/1) afforded a red oil which was chromatographed a second time eluting with hexane/CHCl₃/EtOAc (40/1/1) to yield the product as a red foam (215 mg, 53 %). *R*_f 0.34 (hexane/EtOAc, 10/1).

¹H NMR (400 MHz, CDCl₃): δ 10.25 (s, 2H, *meso*), 7.83 (d, *J* = 7 Hz, 2H, Ar), 7.66 (t, *J* = 8 Hz, 2H, Ar), 7.46 (t, *J* = 2 Hz, 2H, Ar), 7.33 (dd, *J* = 8, 2 Hz, 2H, Ar), 4.06 - 3.93 (t, *J* = 7 Hz, 12H, OCH₂, hex H¹), 2.58 (s, 12H, CH₃), 2.21 (m, 12H, CH₂, hex H²), 1.83 (m, 4H, CH₂), 1.75 (m, 8H, hex H³), 1.52 - 0.89 (m, 60H, hex H⁴⁻⁶, (CH₂)₈), -2.42 (s, 2H, NH); ¹³C NMR (100.6 MHz, CDCl₃): δ 158.6, 145.0, 143.4, 143.3, 141.4, 136.3, 128.5, 125.7, 119.0, 117.8, 115.8, 97.0, 68.4, 38.6, 33.3, 32.0, 30.0, 29.4, 29.2, 29.0, 28.9, 28.2, 26.9, 25.7, 22.8, 14.5, 14.2; UV/vis (DCM): λ_{max} 406, 506, 540, 574 nm; ES MS: *m/z* [M+H]⁺ calcd 1257.8925, found 1257.8930; Anal. Calcd for C₈₂H₁₂₀O₂N₄S₂: C 78.26, H 9.61, N 4.45. Found: C 78.07, H 9.63, N 4.55.

Zn *meta* strapped porphyrin (**Zn-11**)

Prepared from **4** using the same procedure as **11** except the product was Zn metalated according to the general procedure after chromatography. **Zn-11** was obtained as a pink foam (356 mg, 41 %).

¹H NMR (400 MHz, CDCl₃): δ 10.18 (s, 2H, *meso*), 7.84 (d, *J* = 7 Hz, 2H, Ar), 7.67 (t, *J* = 8 Hz, 2H, Ar), 7.48 (s, 2H, Ar), 7.36 (d, *J* = 8 Hz, 2H, Ar), 4.07 (t, *J* = 7 Hz, 4H, OCH₂), 3.97 (m, 8H, hex H¹), 2.57 (s, 12H, CH₃), 2.20 (m, 8H, hex H²), 2.07 (t, *J* = 7 Hz, SCH₂), 1.85 (m, 12H, hex H³, CH₂), 1.54 - 0.94 (m, 60H, hex H⁴⁻⁶, (CH₂)₈); ¹³C (100.6 MHz, CDCl₃): δ 158.6, 147.6, 146.4, 144.8, 143.5, 138.2, 128.3, 126.2, 119.4, 119.2, 115.5, 97.6, 68.4, 38.4, 33.3, 32.0, 30.1, 29.2, 29.1, 2 × 28.9, 2 × 28.8, 28.1, 26.8, 25.7, 22.8, 15.1, 14.2; UV/vis (DCM): λ_{max} 344, 410, 538, 574 cm; ES MS: *m/z* [M+H]⁺ calcd 1318.7982, found 1318.7958; Anal. Calcd for C₈₂H₁₁₈O₂N₄S₂Zn: C 74.53, H 9.00, N 4.24. Found: C 74.56, H 9.00, N 4.24.

Zn *trans* *ortho* strapped porphyrin (*trans*-Zn-12)

Zn *cis* *ortho* strapped porphyrin (*cis*-Zn-12)

Prepared from **8** using the same procedure as for **11** except the solution temperature was maintained in the range -25 - -20 $^{\circ}\text{C}$ for 210 min instead of allowing to warm. A mixture of **trans-12** and **cis-12** was separated from the crude product by column chromatography on silica eluted with hexane/EtOAc (20/1) (R_f 0.4). This mixture was Zn metalated according to the general procedure. The individual atropisomers were separated by preparative TLC on silica plates eluted twice with hexane/EtOAc (40/1). Two major red bands were observed, the upper being **cis-Zn-12**, the lower being **trans-Zn-12**.

Data for **trans-Zn-12**: Purple crystals (116 mg, 14 %).

^1H NMR (400 MHz, CDCl_3): δ 10.15 (s, 2H, *meso*), 7.83 (dd, J = 7, 2 Hz, 2H, Ar), 7.75 (td, J = 8, 2 Hz, 2H, Ar), 7.37 (t, J = 7 Hz, 2H, Ar), 7.27 (d, J = 8 Hz, 2H, Ar), 4.00 (m, 12H, OCH_2 , hex H^1), 2.88 (t, J = 7 Hz, 4H, SCH_2), 2.58 (s, 12H, CH_3), 2.23 (m, 8H, hex H^2), 1.82 (m, 12H, hex H^3 , CH_2), 1.53 (m, 8H, hex H^4), 1.44 (m, 12H, hex H^5 , CH_2), 1.22 (m, 4H, CH_2), 1.15 (m, 4H, CH_2), 0.96 (m, 16H, hex H^6 , CH_2), 0.73 (br m, 4H, CH_2), 0.54 (br m, 4H, CH_2), 0.39 (br m, 8H, $(\text{CH}_2)_2$); ^{13}C NMR (100.6 MHz, CDCl_3): δ 159.1, 148.0, 142.9, 137.6, 135.0, 133.1, 129.8, 120.6, 115.3, 111.9, 97.1, 67.8, 40.1, 33.6, 32.2, 30.2, 30.0, 29.8, 29.6, 29.5, 29.4, 29.1, 28.8, 28.7, 27.0, 25.4, 22.9, 14.7, 14.3; UV/vis (DCM): λ_{max} 338, 412, 538, 574 nm; MALDI MS: m/z [M] $^+$ 1324; Anal. Calcd for $\text{C}_{82}\text{H}_{118}\text{O}_2\text{N}_4\text{S}_2\text{Zn}$: C 74.53, H 9.00, N 4.24. Found: C 74.32, H 8.97, N 4.31.

Data for **cis-Zn-12**: Red foam (217 mg, 25 %).

^1H NMR (400 MHz, CDCl_3): δ 10.14 (s, 2H, *meso*), 7.74 (m, 4H, Ar), 7.29 (m, 4H, Ar), 3.98 (m, 12H, OCH_2 , hex H^1), 2.55 (s, 12H, CH_3), 2.48 (t, J = 7 Hz, 4H, SCH_2), 2.21 (m, 8H, hex H^2), 1.77 (m, 8H, hex H^3), 1.52 (m, 8H, hex H^4), 1.43 (m, 12H, hex H^5 , CH_2), 1.14 - 1.03 (m, 8H, $(\text{CH}_2)_2$), 0.94 (t, J = 7 Hz, 12H, hex H^6), 0.89 (m, 4H, CH_2), 0.78 (m, 4H, CH_2), 0.68 - 0.53 (m, 16H, $(\text{CH}_2)_4$); ^{13}C NMR (100.6 MHz, CDCl_3): δ 159.1, 148.0, 146.2, 142.9, 137.7, 134.9, 133.1, 129.7, 120.5, 115.4, 111.7, 97.0, 68.3, 39.4, 33.5, 32.1, 30.1, 29.8, 28.9, 2 × 28.8, 2 × 28.6, 27.9, 26.9, 25.4, 22.8, 14.5, 14.2; UV/vis (DCM): λ_{max} 338, 412, 538, 574 nm; MALDI MS: m/z [M] $^+$ 1321; Anal. Calcd for $\text{C}_{82}\text{H}_{118}\text{O}_2\text{N}_4\text{S}_2\text{Zn}$: C 74.53, H 9.00, N 4.24. Found: C 74.35, H 8.98, N 4.37.

Free-base *trans* *ortho* strapped porphyrin (*trans*-12)

A solution of **trans-Zn-12** (5.5 mg, 4.1 μmol) in CHCl_3 (30 mL) was washed with HCl (3 N, 10 mL), water (3 × 30 mL), dried (MgSO_4) and evaporated to a red solid (4.3 mg, 83 %).

^1H NMR (500 MHz, CDCl_3): δ 10.13 (s, 2H, *meso*), 7.80 (dd, J = 7, 1 Hz, 2H, Ar), 7.73 (m, 2H, Ar), 7.34 (m, 2H, Ar), 7.28 (m, 2H, Ar), 4.00 (m, 8H, hex H^1 , OCH_2), 3.93 (m, 4H, hex H^1), 2.87 (t, J = 7 Hz, SCH_2), 2.55 (s, 12H, CH_3), 2.16 (m, 8H, hex H^2), 1.83 (m, 4H, CH_2), 1.70 (m, 8H, hex H^3), 1.44 (m, 12H, hex H^4 , CH_2), 1.35 (m, 8H, hex H^5), 1.26 (m, 4H, CH_2), 1.12 - 1.05 (m, 8H, $(\text{CH}_2)_2$), 0.88 (m, 16H, hex H^6 , CH_2), 0.58 (m, 4H, CH_2), 0.52 (m, 4H, CH_2), 0.44 (m, 4H, CH_2), -2.31 (s, 2H, NH); ES MS: m/z [M] $^+$ 1258.

Free-base *cis ortho strapped porphyrin (cis-12)*

TFA (several drops) was added to a solution of **cis-Zn-12** (125 mg, 95 μ mol) in CHCl_3 (50 mL). The green solution was washed with water (2×20 mL), Et_3N was added until a red colour was observed followed by washing with further portions of water (3×20 mL). The solution was dried (MgSO_4) and evaporated to afford the product as a red foam (97 mg, 82 %).

^1H NMR (400 MHz, CDCl_3): δ 10.18 (s, 2H, *meso*), 7.73 (m, 4H, Ar), 7.29 (m, 4H, Ar), 3.98 (m, 12H, OCH_2 , hex H^1), 2.55 (s, 12H, CH_3), 2.49 (t, $J = 7$ Hz, 4H, SCH_2), 2.19 (m, 8H, hex H^2), 1.74 (m, 8H, hex H^3), 1.50 - 1.34 (m, 20H, hex H^4 , $(\text{CH}_2)_3$), 1.09 (m, 8H, hex H^5), 0.91 (m, 16H, hex H^6 , CH_2), 0.82 (m, 4H, CH_2), 0.72 - 0.63 (m, 16H, $(\text{CH}_2)_4$), -2.34 (s, 2H, NH); ^{13}C NMR (100.6 MHz, CDCl_3): δ 158.9, 145.3, 142.6, 141.1, 135.8, 134.7, 131.5, 129.9, 120.5, 114.0, 111.6, 96.3, 68.3, 39.4, 33.4, 32.0, 30.0, 28.9, 28.8, 2×28.7 , 28.6, 27.9, 26.8, 25.5, 22.8, 14.1, 13.8; ES MS: m/z [M] $^+$ 1258.

2,8,12,18-Tetrahexyl-5,15-bis[3-(11-mercaptop-undecyloxy)-phenyl]-3,7,13,17-tetramethyl porphyrin (13)

To a solution of **9** (1.00 g, 0.74 mmol) in THF (10 mL) was added mercaptoethanol (0.50 mL, 7.13 mmol) and butylamine (1.0 mL, 10.1 mmol). After degassing the solution was refluxed under N_2 for 1 h. TLC indicated incomplete reaction. Additional portions of butylamine (1.0 mL, 10.1 mmol) and mercaptoethanol (0.50 mL, 7.13 mmol) were added, the solution degassed, and refluxed for 2 h under N_2 . Et_2O (100 mL) was added and the solution washed with water (3×50 mL), brine (30 mL), dried (MgSO_4) and evaporated to a red oil. Chromatography on silica gel eluted with hexane/EtOAc/toluene (10/1/1) afforded the product as a viscous purple oil which solidified on standing (785 mg, 84 %). R_f 0.34 (hexane/EtOAc, 15/1). A sample for analysis was obtained by recrystallization from DCM layered with MeOH.

^1H NMR (400 MHz, CDCl_3): δ 10.25 (s, 2H, *meso*), 7.67 (m, 6H, Ar), 7.35 (m, 2H, Ar), 4.12 (t, $J = 7$ Hz, 4H, OCH_2), 4.00 (t, $J = 8$ Hz, 8H, hex H^1), 2.59 (s, 12H, CH_3), 2.47 (q, 4H, $J = 7$ Hz, SCH_2), 2.20 (m, 8H, hex H^2), 1.87 (m, 4H, CH_2), 1.75 (m, 8H, hex H^3), 1.57 - 1.26 (m, 50H, hex $\text{H}^{4,5}$, SH, $(\text{CH}_2)_8$), 0.91 (t, $J = 7$ Hz, 12H, hex H^6), -2.41 (s, 2H, NH); ^{13}C NMR (100.6 MHz, CDCl_3): δ 158.7, 145.0, 143.4, 143.3, 141.4, 136.3, 128.5, 125.9, 119.3, 117.8, 115.1, 97.0, 68.4, 34.0, 33.3, 32.0, 30.0, 29.6, 2×29.5 , 29.4, 29.1, 28.4, 26.8, 26.1, 24.6, 22.8, 14.5, 14.2; UV/vis (DCM): λ_{max} 408, 506, 542, 572 nm; FIB MS: m/z [M+H] $^+$ 1262; IR (CCl₄): ν_{max} 2929 (s), 2857 (s), 1596 (m), 1466 (m) cm^{-1} . Anal. Calcd for $\text{C}_{82}\text{H}_{122}\text{O}_2\text{N}_4\text{S}_2$: C 78.17, H 9.76, N 4.45. Found: C 78.14, H 9.69, N 4.46.

2,8,12,18-Tetrahexyl-5,15-bis[3-(11-mercaptop-undecyloxy)-phenyl]-3,7,13,17-tetramethyl porphyrinato zinc(II) (Zn-13)

Prepared from **Zn-9** similarly to **13**, except DTT (0.20 g, 1.3 mmol) was used instead of mercaptoethanol. Column chromatography on silica eluting with hexane/EtOAc (10/1) followed by a second column eluting with hexane/CHCl₃ (4/1) with a gradient to CHCl₃ afforded the product as a red oil (1.04 g, 62 %) which solidified on storage at -20 °C. R_f 0.40 (hexane/EtOAc, 10/1).

¹H NMR (400 MHz, CDCl₃): δ 10.17, 10.15 (2 \times s, 2H, *meso*), 7.67 (m, 6H, Ar), 7.36 (m, 2H, Ar), 4.11 (m, 4H, OCH₂), 3.96 (m, 8H, hex H¹), 2.57, 2.56 (2 \times s, 12H, CH₃), 2.38 (q, J = 7 Hz, 4H, SCH₂), 2.20 (m, 8H, hex H²), 1.87 (m, 4H, CH₂), 1.77 (m, 8H, hex H³), 1.54 - 1.17 (m, 50H, hex H^{4,5}, SH, (CH₂)₈), 0.95 (t, J = 7 Hz, 12H, hex H⁶); ¹³C NMR (100.6 MHz, CDCl₃): δ 158.6, 147.6, 146.4, 144.9, 143.5, 138.2, 128.4, 126.3, 119.7, 119.2, 115.0, 97.6, 68.4, 34.0, 33.4, 2 \times 32.1, 2 \times 29.5, 29.4, 29.1, 28.4, 26.8, 26.1, 24.6, 22.8, 15.1, 14.2; UV/vis (DCM): λ_{max} 410, 538, 574 nm; ES MS: *m/z* [M+Na]⁺ calcd 1343.8036, found 1343.7914; IR (CCl₄): ν_{max} 2929 (s), 2857 (s), 1596 (m), 1286 (m) cm⁻¹. Anal. Calcd for C₈₂H₁₂₀O₂N₄S₂Zn: C 74.42, H 9.14, N 4.23. Found: C 74.48, H 9.15, N 4.33.

References

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