Electronic Supporting Information

From thioether substituted porphyrins to sulfur linked porphyrin dimers: an unusual $S_NAr$ via thiolate displacement?
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1. General information

All commercial chemicals used were of analytical grade and were supplied by Sigma Aldrich and used without further purification unless otherwise stated. 2-Ethylhexyl-3-mercaptopropionate was purchased from TCI chemicals. Anhydrous toluene was supplied by Acros chemicals. \(^1\)H and \(^{13}\)C NMR spectra were recorded on an Agilent 400-MR (400 MHz for \(^1\)H NMR; 100.6 MHz for \(^{13}\)C NMR) and/or Bruker AV 600 (600 MHz for \(^1\)H NMR; 150.9 MHz for \(^{13}\)C NMR). Chemical shifts are reported in ppm locked on the signal of CDCl\(_3\) solvent. The assignment of signals was confirmed by 2D spectra (COSY, HSQC) except for those porphyrins with low solubility. Photophysical measurements were performed in CH\(_2\)Cl\(_2\). UV-vis absorption measurements were performed with a Specord 250 spectrophotometer. HRMS spectra were measured on MALDI-Q-Tof Premier Micromass and Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray ionisation source (ESI). Melting points were acquired on a Stuart SMP-10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 (fluorescence indicator F254; Merck) pre-coated aluminium sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230-400 mesh). Bromoporphyrins 1a/d\(^1\), 1b\(^2\), 1c\(^3\), 1e\(^4\), 1f\(^5\), 1g/i\(^6\) and 1h\(^7\) were synthesised by known methodologies and had analytical data consistent with the literature.

2. General procedures

2.1 General procedure A: Synthesis of thiol surrogates

A 100 mL Schlenk tube was charged with Argon to which bromoporphyrin 1a-i (1 eq.) was added and dried under high vacuum for 30 min. Anhydrous toluene (10-20 mL) and \(N, N\)-diisopropylethylamine (3-5 eq.) were added and the solution was degassed via three freeze-pump-thaw cycles. 2-Ethylhexyl-3-mercaptopropionate (1.1 eq.), Xantphos (5-8 mol \%) and Pd\(_2\)(dba)\(_3\) (2.5-4 mol \%) were added and the flask was heated to 110 °C for 4-24 h, monitoring the reaction via TLC analysis. The solution was cooled to room temperature and the solvent was removed in vacuo. The crude residue was dissolved in CH\(_2\)Cl\(_2\) and purified through a plug of silica. The solvents were removed in vacuo and the product was purified by column chromatography (silica, CH\(_2\)Cl\(_2\)/n-hexane).

2.2 General procedure B: Synthesis of S-linked porphyrin dimers

A 100 mL Schlenk flask was charged with Argon and the thiol surrogate porphyrin, 2a-g was added and dissolved in anhydrous toluene (10-15 mL). NaOEt (21 % solution in EtOH, 2 eq.) was added dropwise and the mixture was stirred at ambient temperature for 4-24 h. Upon completion, the reaction mixture was poured onto H\(_2\)O. The organic layer was extracted with CH\(_2\)Cl\(_2\) and washed with H\(_2\)O (3 x 50 mL). The organic extracts were dried over Na\(_2\)SO\(_4\), filtered and solvents were removed in vacuo. The residue was purified via filtration through a plug of silica using CH\(_2\)Cl\(_2\)/n-hexane as eluent and/or via column chromatography (silica, CH\(_2\)Cl\(_2\)/n-hexane). The isolated product(s) were recrystallized from CH\(_2\)Cl\(_2\)/MeOH.
3. Synthesis and Characterisation of Substrates and Products

\[ \text{[5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)-15-phenylporphyrinato]zinc(II) 2a:} \]

Synthesized via general procedure A from bromoporphyrin 1a (110 mg, 0.155 mmol), Pd\(_2\)(dba)\(_3\) (4 mg, 0.004 mmol), Xantphos (5 mg, 0.008 mmol), N,N-diisopropylethylamine (0.465 mmol, 0.08 mL) and 2-ethylhexyl-3-mercaptopropionate (0.04 mL, 0.171 mmol) in anhydrous toluene (10 mL). The reaction was stirred at 120 °C for 24 h. Following work-up, the product was purified via filtration through silica plug using (n-hexane:CH\(_2\)Cl\(_2\), 3:1 – 2:1 v/v) as eluent. Solvents were removed in vacuo and the residue was recrystallized from CH\(_2\)Cl\(_2\)/MeOH to yield 2a as purple crystals (112 mg, 0.132 mmol, 85 %); M.p. = 135-137 °C; R\(_f\) = 0.59 (CH\(_2\)Cl\(_2\) : n-hexane = 2:1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta = 0.73\) (m, 6H, alkyl-CH\(_3\)), 1.12-1.30 (m, 8H, alkyl-CH\(_2\)), 1.36-1.38 (m, 1H, alkyl-CH) 2.51 (t, J = 7.2 Hz, 2H, SCH\(_2\)CH\(_2\)COO), 2.71 (s, 6H, tolyl-CH\(_3\)), 3.68 (t, J = 7.2 Hz, 2H, SCH\(_2\)CH\(_2\)COO), 3.80-3.83 (m, 2H, COOCH\(_2\)CH), 7.55 (d, J = 7.8 Hz, 4H, tolyl-o-CH), 7.70-7.74 (m, 3H, phenyl-o-p-CH), 8.07 (d, J = 7.8 Hz, 4H, tolyl-m-CH), 8.16-8.18 (m, 2H, phenyl-m-CH), 8.71 (dd, J = 11.4, 4.7 Hz, 4H, H\(_9\)), 9.03 (d, J = 4.7 Hz, 2H, H\(_9\)), 10.04 ppm (d, J = 4.7 Hz, 2H, H\(_9\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C): \(\delta = 10.8, 13.9, 21.5, 22.8, 23.6, 28.8, 30.2, 34.8, 37.5, 38.5, 67.0, 110.6, 121.6, 122.5, 126.5, 127.3, 127.5, 131.9, 132.2, 133.1, 134.3, 134.4, 137.2, 139.5, 142.6, 149.8, 150.7, 150.8, 154.7, 172.1 ppm; UV/Vis (CH\(_2\)Cl\(_2\)) : \(\lambda_{\text{max}}\) (log \(\epsilon\)) = 423 (5.65), 533 (4.27), 593 nm (3.64); HRMS (MALDI) m/z calcd. for C\(_{51}\)H\(_{46}\)N\(_4\)O\(_{2}\)S\(_2\)Zn [M\(^+\)]: 844.2789, found 844.2787.

\[ \text{[5-(2-Ethylhexyl-3-mercaptopropanoate)-10,15,20-triphenylporphyrinato]zinc(II) 2b:} \]

Synthesized via general procedure A from bromoporphyrin 1b (200 mg, 0.294 mmol), Pd\(_2\)(dba)\(_3\) (8 mg, 0.008 mmol), Xantphos (9 mg, 0.016 mmol), N,N-diisopropylethylamine (0.15 mL, 0.883 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.08 mL, 0.353 mmol) in anhydrous toluene (20 mL). The reaction was stirred at 120 °C for 24 h. Following work-up, the product was purified by column chromatography (n-hexane:CH\(_2\)Cl\(_2\), 3:1, v/v) and recrystallized from CH\(_2\)Cl\(_2\)/MeOH to yield 2b as purple crystals (183 mg, 0.224 mmol, 76 %); M.p. = 183-185 °C; R\(_f\) = 0.54 (CH\(_2\)Cl\(_2\) : n-hexane = 2:1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\); pyridine-D\(_5\), 50:1, 25 °C): \(\delta = 0.74-0.77\) (m, 6H, alkyl-CH\(_3\)), 1.13-1.21 (m, 8H, alkyl-CH\(_2\)), 1.37-1.41 (m, 1H, alkyl-CH), 2.37 (t, J = 7.3 Hz, 2H, SCH\(_2\)CH\(_2\)COO), 3.63 (t, J = 7.3 Hz, 2H, SCH\(_2\)CH\(_2\)COO), 3.81-3.86 (m, 2H, COOCH\(_2\)CH), 7.65-7.75 (m, 9H, phenyl-o-p-CH), 8.13-8.16 (m, 6H, phenyl-m-CH), 8.77-8.81 (m, 4H, H\(_9\)), 8.90 (d, J = 4.6 Hz, 2H, H\(_9\)), 9.95 ppm (d, J = 4.6 Hz, 2H, H\(_9\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\); pyridine-D\(_5\), 50:1, 25 °C): \(\delta = 10.8, 13.9, 22.8, 23.6, 28.8, 30.2, 34.7, 37.6, 38.5, 66.9, 109.2, 121.0, 122.3, 126.2, 126.3, 127.2, 127.8, 131.4, 131.8, 131.9, 132.7, 134.4, 134.5, 143.2, 149.7, 150.3, 150.5, 154.8, 172.1 ppm; UV/Vis (CH\(_2\)Cl\(_2\)) : \(\lambda_{\text{max}}\) (log \(\epsilon\)) = 422 (5.70), 552 (4.32), 592 nm (3.65); HRMS (MALDI) m/z calcd. for C\(_{49}\)H\(_{44}\)N\(_4\)O\(_2\)S\(_2\)Zn [M\(^+\)]: 816.2476, found 816.2468.
5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-diphenylporphyrinate)zinc(II) 2c:

Synthesized via general procedure A from bromoporphyrin 1c (130 mg, 0.228 mmol), Pd2(dbaz)3 (6 mg, 0.007 mmol), Xantphos (7 mg, 0.012 mmol), N,N-diisopropylethylamine (0.12 mL, 0.693 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.06 mL, 0.277 mmol) in anhydrous toluene (15 mL). The reaction was stirred at 120 °C for 24 h. Following work-up, the product was purified via filtration through silica plug using (n-hexane:CH2Cl2, 3:1 – 2:1 v/v) as eluent. Solvents were removed in vacuo and the residue was recrystallized from CH2Cl2/MeOH to yield a purple solid 2c (130 mg, 0.175 mmol, 76 %); M.p. = 190-191 °C; Rf = 0.43 (CH2Cl2 : n-hexane = 2:1, v/v); 1H NMR (600 MHz, CDCl3, 25 °C): δ = 0.73-0.81 (m, 6H, alkyl-CH3), 1.12-1.30 (m, 8H, alkyl-CH2), 1.37-1.40 (m, 1H, alkyl-CH) 2.46 (t, J = 7.1 Hz, 2H, SCH2CH2COO), 3.65 (t, J = 7.1 Hz, 2H, SCH2CH2COO), 3.75-3.80 (m, 2H, COOCH2CH), 7.79-7.84 (m, 6H, phenyl-CH), 8.23 (d, J = 7.1 Hz, 4H, phenyl-CH), 9.02 (d, J = 4.2 Hz, 2H, Hβ), 9.03 (d, J = 4.2 Hz, 2H, Hβ), 9.30 (d, J = 4.2 Hz, 2H, Hβ), 10.07 (d, J = 4.7 Hz, 2H, Hβ), 10.13 ppm (s, 1H, Hmeso); 13C NMR (150 MHz, CDCl3, 25 °C): δ = 10.8, 13.8, 22.9, 23.5, 28.7, 30.1, 34.8, 37.5, 38.5, 67.0, 107.2, 108.0, 111.3, 120.9, 126.6, 127.6, 131.9, 132.3, 132.4, 132.9, 134.5, 142.4, 149.4, 150.4, 150.6, 154.3, 172.0 ppm; UV/Vis (CH2Cl2): λmax (log ε) = 416 (5.52), 546 nm (4.20); HRMS (MALDI) m/z calcd. for C43H40N4O2SZn [M+]': 740.2163, found 740.2185.

5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)-15-phenylporphyrin 2d: Synthesized via general procedure A from bromoporphyrin 1d (200 mg, 0.310 mmol), Pd2(dbaz)3 (10 mg, 0.011 mmol), Xantphos (15 mg, 0.026 mmol), N,N-diisopropylethylamine (0.21 mL, 1.241 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.08 mL, 0.341 mmol) in anhydrous toluene (20 mL). The reaction was stirred at 120 °C for 24 h. Following work-up, the product was purified via filtration through silica plug using (n-hexane:CH2Cl2, 3:1 – 2:1 v/v) as eluent. Solvents were removed in vacuo and the residue was recrystallized from CH2Cl2/MeOH to yield 2d as purple crystals (169 mg, 0.215 mmol, 70 %); M.p. = 160-161 °C; Rf = 0.68 (CH2Cl2 : n-hexane = 1:1, v/v); 1H NMR (400 MHz, CDCl3, 25 °C): δ = -2.74 (s, 2H, N-H) 0.74-0.77 (m, 6H, alkyl-CH3), 1.11-1.12 (m, 8H, alkyl-CH2), 1.39-1.40 (m, 1H, alkyl-CH), 2.49 (t, J = 7.2 Hz, 2H, SCH2CH2COO), 2.72 (s, 6H, tolyl-CH3), 3.69 (t, J = 7.2 Hz, 2H, SCH2CH2COO), 3.84-3.87 (m, 2H, COOCH2CH), 7.56 (d, J = 7.7 Hz, 4H, tolyl-CH), 7.71-7.78 (m, 3H, phenyl-CH), 8.08 (d, J = 7.7 Hz, 4H, tolyl-CH), 8.16-8.18 (m, 2H, phenyl-CH), 8.78-8.82 (m, 4H, Hβ), 8.95 (d, J = 4.7 Hz, 2H, Hβ), 9.93 ppm (d, J = 4.7 Hz, 2H, Hβ); 13C NMR (100 MHz, CDCl3, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.5, 28.8, 30.2, 34.7, 37.4, 38.5, 67.0, 109.5, 120.7, 121.7, 126.7, 127.4, 127.8, 134.4, 134.5, 137.5, 139.0, 141.9, 172.0 ppm; UV/Vis (CH2Cl2): λmax (log ε) = 421 (5.56), 519 (4.19), 555 (3.89), 595 (3.70), 650 nm (3.54); HRMS (ESI) m/z calcd. for C51H51N4O2S [M+H]+: 783.3733, found 783.3732.
5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)porphyrin 2e. Synthesized via general procedure A from bromoporphyrin 1e (130 mg, 0.228 mmol), Pd₂dba₃ (6 mg, 0.007 mmol), Xantphos (8 mg, 0.014 mmol), N,N-diisopropylethylamine (0.12 mL, 0.684 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.07 mL, 0.274 mmol) in anhydrous toluene (15 mL). The reaction was stirred at 120 °C for 24 h. Following work-up, the product was purified via filtration through silica plug using (n-hexane:CH₂Cl₂, 3:1 – 2:1 v/v) as eluent. Solvents were removed in vacuo and the residue was recrystallized from CH₂Cl₂/MeOH to yield purple crystals 2e (109 mg, 0.154 mmol, 68%); M.p. = 175-177 °C; R₁ = 0.72 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = -3.03 (s, 2H, NH), 0.71-0.79 (m, 6H, alkyl-CH₃), 1.09-1.15 (m, 8H, alkyl-CH₂), 1.35-1.37 (m, 1H, alkyl-CH) 2.48 (t, J = 7.2 Hz, 2H, SCH₂CH₂COO), 2.74 (s, 6H, tolyl-CH₃), 3.34 (t, J = 7.4 Hz, 2H, SCH₂CH₂COO), 3.84-8.87 (m, 2H, COOCH₂CH), 7.60 (d, J = 7.7 Hz, 4H, tolyl-OC₆H₆), 8.12 (d, J = 7.7 Hz, 4H, tolyl-m-CH₃), 8.99-9.02 (m, 4H, H₆), 9.30 (d, J = 4.6 Hz, 2H, H₅), 10.03 (d, J = 4.9 Hz, 2H, H₆), 10.21 ppm (s, 1H, Hmeso); ¹³C NMR (100 MHz, CDCl₃): δ = 10.8, 13.9, 21.5, 22.3, 22.8, 23.5, 28.8, 30.2, 34.7, 37.6, 38.5, 67.0, 106.3, 110.2, 120.2, 127.6, 131.4, 132.1, 135.6, 137.5, 138.6, 172.0 ppm; UV/Vis (CH₂Cl₂): λmax (log ε) = 417 (5.60), 513 (4.29), 548 (3.76), 588 (3.78), 642 nm (3.33); HRMS (MALDI) m/z calcld. for [C₄H₅NO₄S][M⁺]: 706.3341, found 706.3347.

5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)porphyrinato)nickel(II) 2f: Synthesized via general procedure A from bromoporphyrin 1f (200 mg, 0.319 mmol), Pd₂dba₃ (14 mg, 0.016 mmol), Xantphos (19 mg, 0.032 mmol), N,N-diisopropylethylamine (0.17 mL, 0.958 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.15 mL, 0.641 mmol) in anhydrous toluene (20 mL). The product was purified by column chromatography (n-hexane:CH₂Cl₂, 2:1, v/v) and recrystallized (CH₂Cl₂/MeOH) to yield purple crystals 2f (175 mg, 0.230 mmol, 72%); M.p. 138-140 °C; R₁ = 0.31 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.69-0.77 (m, 6H, alkyl-CH₃), 1.09-1.15 (m, 9H, alkyl-CH₂/CH), 2.22 (t, J = 7.2 Hz, 2H, SCH₂CH₂COO), 2.66 (s, 6H, tolyl-CH₃), 3.34 (t, J = 7.2 Hz, 2H, SCH₂CH₂COO), 3.77-3.79 (m, 2H, COOCH₂CH), 7.48 (d, J = 7.7 Hz, 4H, tolyl-OC₆H₆), 7.87 (d, J = 7.7 Hz, 4H, tolyl-m-CH₃), 8.83-8.86 (m, 4H, H₆), 9.06 (d, J = 4.9 Hz, 2H, H₅), 9.74 ppm (s, 1H, Hmeso), 9.82 ppm (d, J = 4.9 Hz, 2H, H₅); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.5, 28.7, 30.1, 34.7, 35.8, 38.5, 66.9, 105.5, 109.5, 118.9, 127.6, 132.3, 132.4, 132.6, 133.2, 133.6, 137.5, 137.6, 142.4, 143.0, 143.2, 146.5 and 171.8 ppm; UV/Vis (CH₂Cl₂): λmax (log ε) = 413 (5.45), 526 (4.30), 556 nm (3.98); HRMS (MALDI) m/z calcld. for C₄H₅NO₄NiO₂S [M⁺]: 762.2546, found 762.2538.

5-(2-Ethylhexyl-3-mercaptopropanoate)-10,20-bis(4-methylphenyl)-15-phenylporphyrinato)nickel(II) 2g: Synthesized via general procedure A from bromoporphyrin 1g (250 mg, 0.355 mmol), Pd₂dba₃ (16 mg, 0.018 mmol), Xantphos (21 mg, 0.036 mmol), N,N-diisopropylethylamine (0.18 mL, 1.067 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.16 mL, 0.710 mmol) in anhydrous toluene (20 mL). Product purified by column chromatography (n-hexane:CH₂Cl₂, 3:1, v/v) and recrystallized (CH₂Cl₂/MeOH) to yield purple crystals 2g (190 mg, 0.226 mmol, 63%); M.p. = 154-156 °C; R₁ = 0.50 (CH₂Cl₂ : n-
hexane = 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 0.72-0.80 (m, 6H, alkyl-CH$_3$), 1.11-1.30 (m, 9H, alkyl-CH$_2$/CH), 2.21 (t, J = 7.2 Hz, 2H, SCH$_2$CH$_2$COO), 2.65 (s, 6H, tolyl-CH$_3$), 3.32 (t, J = 7.2 Hz, 2H, SCH$_2$CH$_2$COO), 3.80-3.82 (m, 2H, COOCH$_2$CH), 7.47 (d, J = 7.7 Hz, 4H, tolyl-o-CH), 7.64-7.67 (m, 3H, phenyl-ω-p/CH), 7.87 (d, J = 7.7 Hz, 4H, tolyl-m/CH), 7.96-7.99 (m, 2H, phenyl-ω-m/CH), 8.69-8.73 (m, 4H, H$_p$), 8.83 (d, J = 4.9 Hz, 2H, H$_p$), 9.78 ppm (d, J = 4.9 Hz, 2H, H$_p$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 10.8, 13.9, 21.5, 22.8, 23.5, 28.8, 30.2, 34.7, 35.6, 38.5, 66.9, 108.9, 119.3, 120.0, 126.9, 127.6, 127.7, 127.8, 132.2, 132.4, 132.5, 133.3, 133.5, 133.6, 137.5, 140.6, 142.3, 143.0, 146.7, 171.8 ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log ε) = 419 (5.39), 535 (4.27), 565 nm (3.88); HRMS (MALDI) m/z calcd. for C$_{51}$H$_{48}$N$_4$NiO$_2$S [M]$^+$: 838.2851, found 838.2833.

![Diagram](image1.png)

**[5-(2-Ethylhexyl-3-mercaptopropanoate)-10,15,20-triphenylporphyrinato]nickel(II) 2h:** Synthesized via general procedure A from bromoporphyrin 1h (200 mg, 0.296 mmol), Pd$_2$(dba)$_3$ (14 mg, 0.015 mmol), Xantphos (18 mg, 0.030 mmol), N,N-diisopropylethylamine (0.16 mL, 0.889 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.14 mL, 0.592 mmol) in anhydrous toluene (20 mL). Product purified by column chromatography (n-hexane:CH$_2$Cl$_2$, 3:1, v/v) and recrystallized (CH$_2$Cl$_2$/MeOH) to yield 2h as purple crystals (165 mg, 0.204 mmol, 68%); M.p. = 166-167 °C; R$_f$ = 0.44 (CH$_2$Cl$_2$): n-hexane = 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 0.69-0.77 (m, 6H, alkyl-CH$_3$), 1.11-1.33 (m, 9H, alkyl-CH$_2$/CH), 2.20 (t, J = 7.2 Hz, 2H, SCH$_2$CH$_2$COO), 3.30 (t, J = 7.2 Hz, 2H, SCH$_2$CH$_2$COO), 3.78-3.82 (m, 2H, COOCH$_2$CH), 7.64-7.67 (m, 9H, phenyl-ω-p/CH), 7.96-7.98 (m, 6H, phenyl-ω-m/CH), 8.68-8.69 (m, 4H, H$_p$), 8.79 (d, J = 4.9 Hz, 2H, H$_p$), 9.78 ppm (d, J = 4.9 Hz, 2H, H$_p$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 10.8, 13.9, 22.8, 23.5, 28.7, 30.1, 34.7, 35.6, 38.5, 66.9, 109.1, 119.2, 120.1, 126.8, 126.9, 127.8, 132.2, 132.5, 132.6, 133.3, 133.5, 133.6, 140.4, 140.5, 142.3, 142.8, 146.7, 171.8 ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log ε) = 418 (5.42), 534 (4.27), 566 nm (3.84); HRMS (MALDI) m/z calcd. for C$_{49}$H$_{44}$N$_4$NiO$_2$S [M]$^+$: 810.2538, found 810.2545.

![Diagram](image2.png)

**[5-Butyl-10,20-bis(2-ethylpropyl)-15-(2-ethylhexyl-3-mercaptopropanoate)porphyrinato]nickel(II) 2i:** Synthesized via general procedure A from bromoporphyrin 1i (200 mg, 0.321 mmol), Pd$_2$(dba)$_3$ (14 mg, 0.016 mmol), Xantphos (18 mg, 0.032 mmol), N,N-diisopropylethylamine (0.17 mL, 0.963 mmol) and 2-ethylhexyl-3-mercaptopropionate (0.14 mL, 0.620 mmol) in anhydrous toluene (20 mL). Product purified by column chromatography (n-hexane:CH$_2$Cl$_2$, 5:1, v/v) and recrystallized (CH$_2$Cl$_2$/MeOH) to yield 2i as purple crystals (159 mg, 0.206 mmol, 65%); M.p. = 137-138 °C; R$_f$ = 0.53 (CH$_2$Cl$_2$): n-hexane = 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 0.73-0.81 (m, 6H, ethylhexyl-CH$_3$), 0.90 (t, J = 7.4 Hz, 12H, ethylpropyl-CH$_3$), 1.01 (t, J = 7.8 Hz, 3H, butyl-CH$_3$), 1.15-1.20 (m, 9H, ethylhexyl-CH$_2$/CH), 1.50-1.56 (m, 2H, butyl-CH$_2$/CH$_3$), 2.13-2.19 (m, 4H, SCH$_2$CH$_2$COO/butyl-CH$_2$/CH$_2$CH$_2$), 2.59-2.67 (m, 8H, ethylpropyl-CH$_2$/CH), 3.16 (t, 2H, J = 7.2 Hz, SCH$_2$CH$_2$COO), 3.82-3.84 (m, 2H, COOCH$_2$CH), 4.24-4.27 (m, 2H, ethylpropyl), 4.45 (t, J = 7.6 Hz, 2H, butyl-CH$_2$/CH$_2$CH$_2$), 9.21 (d, J = 5.1 Hz, 2H, H$_p$), 9.31 (d, J = 5.1 Hz, 4H, H$_p$), 9.63 ppm (d, J = 5.1 Hz, 2H, H$_p$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 10.8, 13.9, 22.8, 23.3, 23.5, 28.8, 30.2, 33.5, 33.6, 34.7, 34.9, 38.5, 39.1, 49.3, 66.9, 106.8, 119.0, 121.1, 130.0, 130.8, 131.7, 132.5, 139.9, 141.7, 144.5, 171.9 ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log ε) = 423 (5.35), 546 (4.20), 583 nm (3.69); HRMS (MALDI) m/z calcd. for C$_{45}$H$_{60}$N$_4$NiO$_2$S [M]$^+$: 778.3790, found 778.3821.
[Bis[10,20-bis(4-methylphenyl)-15-phenyl-porphyrinato-5-yl]zinc(II)]sulfide 3a. Synthesized via general procedure B from thiol surrogate 2a (50 mg, 0.059 mmol) and NaOEt (21% solution, 0.1 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (n-hexane:CH₂Cl₂, 1:1, v/v) and recrystallized (CH₂Cl₂/n-hexane) to yield purple crystals (24 mg, 0.019 mmol, 63%); M.p. > 300 °C; R₁ = 0.57 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃: pyridine-d⁵, 30:1, 25 °C): δ = 2.56 (s, 12H, tolyl-CH₃), 7.33 (d, J = 7.8 Hz, 8H, tolyl-α-CH), 7.6-7.7 (m, 6H, phenyl-α/p-CH), 7.82 (d, J = 7.7 Hz, 8H, tolyl-m-CH), 8.10 (d, J = 7.4 Hz, 4H, phenyl-m-CH), 8.52 (d, J = 4.7 Hz, 4H, H₉), 8.65 (d, J = 4.7 Hz, 4H, H₉), 8.69 (d, J = 4.7 Hz, 4H, H₉), 10.35 ppm (d, J = 4.8 Hz, 4H, H₉); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 21.3, 107.5, 120.0, 120.8, 121.4, 126.2, 126.8, 127.1, 131.3, 131.4, 132.9, 134.1, 134.3, 136.6, 140.2, 143.3, 149.4, 149.8, 150.4, 153.9 ppm; UV/Vis (CH₃Cl₂): λmax (log ε) = 410 (5.44), 419 (5.41), 566 (4.47), 621 nm (4.52); HRMS (MALDI) m/z calcd. for C₆₀H₃₄N₉SZn₂ [M]⁺: 1286.2775, found 1286.2770.

[Bis[10,15,20-triphenyl-porphyrinato-5-yl]zinc(II)]sulfide 3b. Synthesized via general procedure B from thiol surrogate 2b (50 mg, 0.061 mmol) and NaOEt (21% solution, 0.15 mL) in anhydrous toluene (15 mL). Following aqueous work-up, the product was purified by filtration through a silica plug using n-hexane:CH₂Cl₂ (2:1-1:1, v/v) as eluent and recrystallized from CH₂Cl₂/MeOH to yield purple crystals (21 mg, 0.016 mmol, 56%); M.p. > 300 °C; R₁ = 0.46 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃: pyridine-d⁵, 50:1, 25 °C): δ = 7.51-7.58 (m, 12H, phenyl-α/p-CH), 7.63-7.67 (m, 6H, phenyl-α/p-CH), 7.94 (d, J = 7.3 Hz, m, 8H, phenyl-m-CH), 8.10 (d, J = 7.3 Hz, m, 4H, phenyl-m-CH), 8.49 (d, J = 4.6 Hz, 4H, H₉), 8.62 (d, J = 4.2 Hz, 4H, H₉); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 106.3, 116.8, 117.1, 120.3, 120.7, 121.6, 126.1, 126.2, 127.0, 127.2, 131.4, 131.6, 131.9, 132.9, 134.2, 134.3, 143.2, 149.3, 149.9, 150.3, 153.8 ppm; UV/Vis (CH₃Cl₂): λmax (log ε) = 410 (5.34), 420 (5.34), 564 (4.72), 625 nm (4.74); HRMS (MALDI) m/z calcd. for C₇₆H₅₄N₉S₃Zn₂ [M]⁺: 1230.2149, found 1230.2196.

[Bis[10,20-bis(4-methylphenyl)porphyrinato-5-yl]zinc(II)]sulfide 3c: Synthesized via general procedure B from thiol surrogate 2c (40 mg, 0.054 mmol) and NaOEt (21% solution, 0.15 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (n-hexane:CH₂Cl₂, 2:1-1:1, v/v) and recrystallized (CH₂Cl₂/MeOH) to yield a purple solid 3c (16 mg, 0.015 mmol, 55%); M.p. > 300 °C; R₁ = 0.56 (CH₂Cl₂ : n-hexane = 2:1, v/v); ¹H NMR (600 MHz, CDCl₃: pyridine-d⁵, 50:1, 25 °C): δ = 7.55-7.59 (m, 8H, phenyl-CH₂), 7.61-7.64 (m, 4H, phenyl-CH), 7.99 (d, J = 7.1 Hz, m, 8H, phenyl-CH), 8.55 (d, J = 4.6 Hz, 4H, H₉), 8.82 (d, J = 4.4 Hz, 4H, H₉), 9.21 (d, J = 4.4 Hz, 4H, H₉), 10.03 (s, 2H, H₉eso), 10.38 ppm (d, J = 4.6 Hz, 4H, H₉); ¹³C NMR (150 MHz CDCl₃: pyridine-d⁵, 50:1, 25 °C): δ = 106.4, 120.2, 120.9, 126.1, 127.0, 131.4, 131.9, 132.0, 132.8, 134.1, 134.3, 149.7, 150.3, 153.5 ppm; UV/Vis (CH₃Cl₂): λmax (log ε) = 416[br] (5.31), 559 (4.42), 612 nm (4.23); HRMS (MALDI) m/z calcd. for C₆₄H₃₈N₉S₃Zn₂ [M]⁺: 1078.1523, found 1078.1522.
**Bis[10,20-bis(4-methylphenyl)porphyrinato-5-yl]nickel(II)sulfide 3f**: Synthesized via general procedure B from thiol surrogate 2f (50 mg, 0.065 mmol) and NaOEt (21% solution, 0.1 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (n-hexane:CH₂Cl₂, 1:1, v/v) and recrystallized (CH₂Cl₂/n-hexane) to yield purple crystals (0.023 mmol, 26 mg, 72%); M.p. > 300 °C; Rᵣ = 0.52 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 2.52 (s, 12H, tolyl-CH₃), 7.27 (d, J = 7.6 Hz, 8H, tolyl-CH₂), 7.57 (d, J = 7.7 Hz, 8H, tolyl-m-CH), 8.47 (d, J = 5.0 Hz, 4H, Hₜ), 8.56 (d, J = 4.7 Hz, 4H, Hₜ), 8.79 (d, J = 4.7 Hz, 4H, Hₜ), 9.43 ppm (s, 2H, Hₜmeso), 9.79 ppm (d, J = 5.0 Hz, 4H, Hₜ), ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 21.3, 104.9, 115.4, 118.6, 127.4, 131.7, 131.9, 132.3, 133.4, 133.5, 133.7, 137.2, 142.1, 142.7, 144.8 ppm; UV/Vis (CH₂Cl₂): λ_max (log ε) = 405 (4.92), 452 [sh] (4.59), 539 (3.66), 587 nm (3.66); HRMS (MALDI) m/z calcd. for C₆₈H₄₀N₆S₂Ni₂Zn [M⁺]: 1122.2273, found 1122.2277.

**Bis[10,20-bis(4-methylphenyl)-15-phenylporphyrinato-5-yl]nickel(II)sulfide 3g**: Synthesized via general procedure B from thiol surrogate 2g (50 mg, 0.060 mmol) and NaOEt (21% solution, 0.1 mL) in anhydrous toluene (15 mL). Product purified by column chromatography (n-hexane:CH₂Cl₂, 5:2, v/v) and recrystallized (CH₂Cl₂/n-hexane) to yield purple crystals (0.020 mmol, 26 mg, 68%); M.p. > 300 °C; Rᵣ = 0.27 (CH₂Cl₂ : n-hexane = 2.5:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 2.53 (s, 12H, tolyl-CH₃), 7.30 (d, J = 7.4 Hz, 8H, tolyl-o-CH), 7.57-7.62 (m, 14H, tolyl-m-CH/phenyl-o/p-CH), 7.84-7.85 (m, 4H, phenyl-m-CH), 8.48-8.51 (m, 12H, Hₜ), 9.75 ppm (d, J = 4.8 Hz, 4H, Hₜ), ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 21.3, 119.0, 119.5, 126.8, 127.4, 127.6, 131.8, 132.0, 132.1, 133.4, 133.5, 133.6, 137.2, 137.3, 140.4, 141.9, 142.0, 142.7 and 145.1 ppm; UV/Vis (CH₂Cl₂): λ_max (log ε) = 409 (5.44), 457 [sh] (5.06), 547 (4.55), 596 nm (4.21); HRMS (MALDI) m/z calcd. for C₃₀H₂₄N₁₈S₂Ni₂Zn [M⁺]: 1274.2947, found 1274.2947.

**5,15-Bis(4-methylphenyl)-10-methylthio-20-phenylporphyrinato]zinc(II) 4a**: Thiol surrogate 2a (50 mg, 0.059 mmol) was dissolved in anhydrous toluene (15 mL) together with methyl iodide (0.08 mL, 1.3 mmol) in a 50 mL Schlenk flask under argon. NaOEt (21% solution, 0.2 mL) was added dropwise and the purple solution turned a green colour, before reverting to purple after 5 min. The solution was left to stir at room temperature for 20 h. The reaction was quenched by adding H₂O (20 mL) and the aqueous layer was extracted three times with CH₂Cl₂. The organic layer was dried over Na₂SO₄, filtered and solvents were removed in vacuo. The residue was filtered through a short plug of silica using CH₂Cl₂ as eluent. Solvents were removed in vacuo and the title compound was obtained via recrystallisation from CH₂Cl₂/MeOH to yield purple crystals (31 mg, 0.046 mmol, 78%); M.p. >300 °C; Rᵣ = 0.61 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 2.73 (s, 6H, tolyl-CH₃), 3.04 (s, 3H, SCH₃), 7.57 (d, J = 7.8 Hz, 4H, tolyl-o-CH), 7.72-7.79 (m, 3H, phenyl-o/p-CH), 8.09 (d, J = 7.8 Hz, 4H, tolyl-m-CH), 8.18-8.20 (m, 2H, phenyl-m-CH), 8.92 (dd, J = 11.0, 4.6 Hz, 2H, Hₜ), 9.04 (d, J = 4.6 Hz, 2H, Hₜ), 10.06 ppm (d, J = 4.6 Hz, 2H, Hₜ); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 21.5, 26.8, 113.7, 121.5, 122.4, 126.5, 127.3, 127.5, 131.9, 132.0, 132.1, 133.1, 134.3, 134.4, 137.2, 139.6, 142.7, 149.8, 150.6, 150.8, 154.2 ppm; UV/Vis
(CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 422 (5.69), 552 (4.32), 593 nm (3.64); HRMS (MALDI) \( m/z \) calcld. for C₄₁H₃₀N₄SZn [M]+: 674.1483, found 674.1492.

**[5-Butyl-10,20-bis(1-ethylpropyl)-15-methylthioporphyrinato]nickel(II) 4f**: Thiol surrogate 2i (100 mg, 0.128 mmol) was dissolved in anhydrous toluene (20 mL) together with methyl iodide (0.08 mL, 1.304 mmol). NaOEt (21% solution, 0.2 mL) was added dropwise and the solution left to stir at room temperature for one hour. Reaction was quenched by adding H₂O (20 mL) and the aqueous layer was extracted three times with CH₂Cl₂. Title compound was obtained via recrystallisation (CH₂Cl₂/MeOH) to yield purple crystals (77 mg, 0.121 mmol, >95%); M.p. 215-216 °C; Rₚ = 0.63 (CH₂Cl₂: n-hexane = 1:4, v/v); \(^1^H\) NMR (400 MHz, CDCl₃, 25 °C): \( \delta = 0.89 \) (t, \( J = 7.4 \) Hz, 12H, ethylpropyl-CH₃), 1.00 (t, \( J = 7.4 \) Hz, 3H, butyl-CH₃), 1.50-1.56 (m, 3H, 2H, butyl-CH₂CH₂CH₂), 2.15-2.23 (m, 2H, butyl-CH₂CH₂CH₂), 2.55-2.69 (m, 8H, ethylpropyl-CH₂), 2.61 (s, 3H, SCH₂), 4.22-4.29 (m, 2H, ethylpropyl-CH₂), 4.44 (t, \( J = 8.0 \) Hz, 2H, butyl-CH₂CH₂CH₂), 9.19 (d, \( J = 5.1 \) Hz, 2H, Hₐ), 9.29-9.31 (m, 4H, Hₘ), 9.63 ppm (d, \( J = 5.1 \) Hz, 2H, Hₐ); \(^{13}\)C NMR (100 MHz, CDCl₃, 25 °C): \( \delta = 13.9 \), 23.3, 24.5, 33.4, 33.6, 39.2, 49.3, 109.8, 118.8, 120.9, 129.9, 130.7, 131.7, 132.1, 139.9, 141.7, 143.9 ppm; UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 423 (5.29), 546 (4.14), 585 nm (3.60); HRMS (MALDI) \( m/z \) calcld. for C₃₅H₃₅N₅S [M]+: 608.2484, found 608.2509.

**[5-Hexylthio-10,20-bis(4-methylphenyl)-15-phenylporphyrinato]nickel(II) 4g**: Thiol surrogate 2g (50 mg, 0.060 mmol) was dissolved in anhydrous toluene (20 mL) together with 1-bromohexane (0.1 mL, 0.603 mmol). NaOEt (21% solution, 0.2 mL) was added dropwise and the solution left to stir at room temperature for one hour. Reaction was quenched by adding H₂O (20 mL) and the aqueous layer was extracted three times with CH₂Cl₂. Title compound was obtained via recrystallisation (CH₂Cl₂/MeOH) to yield purple crystals (43 mg, 0.058 mmol, >95%); M.p. 241-243 °C; Rₚ = 0.54 (CH₂Cl₂: n-hexane = 1:4, v/v); \(^1^H\) NMR (400 MHz, CDCl₃, 25 °C): \( \delta = 0.72 \) (t, \( J = 7.2 \) Hz, 3H, hexyl-CH₃), 1.02-1.04 (m, 2H, CH₂CH₂CH₃), 1.08-1.12 (m, 2H, CH₂CH₂CH₃), 1.26-1.32 (m, 4H, hexyl-CH₂), 2.64 (s, 6H, tolyl-CH₃), 3.07 (t, \( J = 7.0 \) Hz, 2H, SCH₂CH₂), 7.48 (d, \( J = 7.4 \) Hz, 4H, tolyl-CH₂), 7.64-7.67 (m, 3H, phennyl-o/p-CH₂), 7.87 (d, \( J = 7.7 \) Hz, 4H, tolyl-m-CH), 7.96-7.98 (m, 2H, phenyl-m-CH), 8.67-8.71 (m, 4H, Hₐ, 8.82 (d, \( J = 5.0 \) Hz, 2H, Hₐ), 9.80 ppm (d, \( J = 5.0 \) Hz, 2H, Hₐ); \(^{13}\)C NMR (100 MHz, CDCl₃, 25 °C): \( \delta = 13.9 \), 21.5, 22.4, 28.2, 29.8, 31.2, 41.5, 119.1, 126.9, 127.3, 127.6, 127.7, 127.9, 131.6, 132.1, 132.3, 132.6, 133.0, 133.2, 133.6, 137.5, 137.6, 140.7, 142.2, 142.8, 142.9 and 146.7 ppm; UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 420 (5.23), 536 (4.15), 569 nm (3.77); HRMS (Malldi) \( m/z \) calcld. for C₄₆H₄₀N₄NiS [M]+: 738.2327, found 738.2364.

**5-(4-bromothiophenyl)-10,20-bis(4-methylphenyl)-15-phenylporphyrin 5c**: 4-Bromothiophenol (80 mg, 0.423 mmol) and K₂CO₃ (200 mg, 1.450 mmol) were dissolved in anhydrous DMF (12 mL) in a 3-necked round bottomed flask. The solution was purged with argon and was heated to 100 °C for 2 h. Thiol surrogate 2d (100 mg, 0.128 mmol) was added and the reaction was allowed to stir at 110 °C for 2h, monitoring the reaction via TLC analysis (CH₂Cl₂/n-hexane 1:1, v/v). Upon completion, the reaction was allowed to cool to room temperature and was washed with H₂O (30 mL x 3) and extraction with CH₂Cl₂. Solvents were removed in vacuo and the residue was purified via column chromatography (CH₂Cl₂/n-hexane 1:2, v/v) to yield 2 main fractions, the first was 5c with fraction two containing dimer 3d (<40 %). Solvents were removed and the title compound was obtained via recrystallisation (CH₂Cl₂/MeOH) to yield purple
crystals (45 mg, 0.060 mmol, 47 %); M.p. >300 °C; Rf = 0.57 (CH₂Cl₂ : n-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = -2.61 (s, 2H, NH), 2.70 (s, 6H, tolyl-CH₃), 6.84 (d, J = 8.6 Hz, 2H, C₆H₄Br-o-H), 7.10 (d, J = 8.6 Hz, 2H, C₆H₄Br-m-H), 7.55 (d, J = 7.6 Hz, 4H, tolyl-o-CH), 7.74-7.79 (m, 3H, phenyl-CH), 8.06 (d, J = 7.6 Hz, 4H, tolyl-m-CH), 8.18 (d, J = 7.5 Hz, 2H, phenyl-CH), 8.80-8.82 (m, 4H, H₂), 8.90 (d, J = 4.7 Hz, 2H, H₀), 9.79 ppm (d, J = 4.7 Hz, 2H, H₀); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 21.5, 105.1, 118.4, 121.9, 122.5, 126.7, 127.5, 127.9, 131.7, 134.4, 134.5, 137.6, 138.7, 141.8, 142.7 ppm; UV/Vis (CH₂Cl₂): λ_max (log ε) = 423 (5.57), 521 (4.29), 557 (4.00), 594 (3.81), 649 nm (3.65); HRMS (MALDI) m/z calcd. for C₄₆H₃₃N₄SBr [M]+: 752.1609, found 752.1591.
4. Note on displacement reactions:

**General procedure for displacement of alkyl/aromatic halide with porphyrin thiolate:**
Thiol surrogate (1 eq.) was dissolved in anhydrous toluene (20 mL) together with alkyl/aryl halide 6-13 (5-10 eq.). NaOEt (21% solution, 0.2 mL) was added dropwise and the solution left to stir at room temperature for one hour. Reaction was quenched by adding H2O (20 mL) and the aqueous layer was extracted three times with CH2Cl2. The title compound and/or S-linked dimer was obtained via recrystallisation (CH2Cl2/MeOH) to yield purple crystals.

**General procedure for displacement porphyrin thioether chain by N- or S-nucleophile:**
Nucleophile 14, 15 or 16 (3 eq.) and K2CO3 (10-11 eq.) were dissolved in anhydrous DMF (12 mL) in a 3-necked round bottomed flask. The solution was purged with argon and was heated to 100 °C for 2 h. Thiol surrogate (1 eq.) was added and the reaction was allowed to stir at 110 °C for 2 h, monitoring the reaction via TLC analysis (CH2Cl2/n-hexane 1:1, v/v). Upon completion, the reaction was allowed to cool to room temperature and was washed with H2O (30 mL x 3) and was extracted with CH2Cl2. Solvents were removed in vacuo and the residue was purified via column chromatography (CH2Cl2/n-hexane 1:2, v/v).

**General procedure for displacement porphyrin thioether chain by organolithium reagent:**
Thiol surrogate (1 eq.) was added to a Schlenk flask under argon and dissolved in anhydrous THF (20-30 mL). The solution was cooled to -78 °C before dropwise addition of organolithium reagent 17 or 18 (6 eq.). Following addition, the reaction was allowed to stir at -78 °C for 10 min before warming to room temperature (over approx. 2 h). H2O (2 mL) was added and the solution stirred for 20 min. DDQ (6 eq.) was added and the reaction was allowed stir open to air for 1 h. The solution was then filtered through a plug of silica using CH2Cl2 as eluent. Solvents were removed in vacuo and the residue was purified via column chromatography (CH2Cl2/n-hexane 1:2, v/v).

| Table 1: Displacement reactions: a) porphyrin thiol surrogate with alkyl/aromatic halides and b) displacement of thioether chain by nucleophilic base |
|---|---|---|---|---|
| Entry | R2-X | R2-X | M | Product | Yield | | Entry | Nucleophile | R2-X | R2-X | M | Product | Yield |
| 1 | 6 | Tolyli | Ph | Zn | 4a | 71 | 10 | 14 | Tolyli | Ph | Zn | 5a | n/d |
| 2 | 7 | Tolyli | Ph | Zn | 4b | trace | 11 | 15 | Tolyli | Ph | Zn | 5b | n/d |
| 3 | 8 | Tolyli | Ph | Zn | 4c | trace | 12 | 16 | Tolyli | Ph | Zn | 5c | 48 |
| 4 | 9 | Tolyli | Ph | Zn | 4d | n/d | 13 | 17 | Tolyli | Ph | Zn | 5d | <10% |
| 5 | 11 | Tolyli | Ph | Zn | 4e | n/d | 15 | 17 | Tolyli | Ph | Ni | 5e | Trace |
| 6 | 6 | 1-Ethylpropyl | n-Butyl | Ni | 4f | 95 | 16 | 17 | Tolyli | Ph | Ni | 5f | <10% |
| 7 | 7 | Tolyli | Ph | Ni | 4g | 95 | 17 | 18 | Tolyli | Ph | Ni | 5f | n/d |
| 8 | 10 | Tolyli | Ph | Ni | 4h | n/d | 18 | 16 | Tolyli | Ph | Ni | 5g | >30% |
| 9 | 12 | Tolyli | Ph | Ni | 4i | n/d |

* Isolated yield; " Reagents and conditions: R-2X (5-10 eq.), NaOEt (21% in EtOH), toluene, rt, Ar, 3-18 h; * S-linked dimer predominant product; * Reagents and conditions: i) S-N-nucleophile (5 eq.), K2CO3 (10-11 eq.), DMF, 110 °C, 2 h ii) porphyrin (1 eq.), 110 °C, 2-16 h; * Reagents and conditions: i) porphyrin, THF, -78 °C ii) n-BuLi (6 eq.), -78 °C – rt, 2 h; * Predominant product was unreacted starting material.

Table 1 is an expansion of Table 3 in the main text. For alkyl and aryl halides 6-13, numerous halide displacement attempts were made, with most success observed for alkyl derivatives 6 and 7. For aromatic halides, no displacement was observed, with the predominant product being the S-linked dimer. This indicates that for aromatic residues the thioether chain acts as a better leaving group than halides I, Br or F. For nucleophilic displacement of the thioether chain, nucleophiles 14-18 were used. For N-nucleophiles 14 and 15,
the predominant products observed again were S-linked dimers indicating that the nucleophilic strength of the porphyrin thiolate exceeds that of the aforementioned bases. Using organolithium reagents 17 and 18, some success was seen with butylated products 5d and 5e synthesised in <10 % yield. The other products from this reaction were unreacted starting material (~40 %) and higher butylated product (<10 %). Best results were observed using S-nucleophile 16 whereby the thiolate generated from this thiophenol successfully displaced the thioether chain of porphyrin 2d, giving 5c in 48 % yield. This displays the potential applicability of this type of surrogate to act as a leaving group using soft nucleophiles such as 16.

5. References

Electronic Supplementary Material (ESI) for Chemical Communications

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$^1\text{H NMR 2a}$

$^{13}\text{C NMR 2a}$
1H NMR 2d

13C NMR 2d
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$\text{1H NMR 3b}$

$\text{13C NMR 3b}$


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$^{1}$H NMR 3g

$^{13}$C NMR 3g
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$^{1}$H NMR 4c

$^{13}$C NMR 4c
Proposed mechanism for the deprotection of the thioether chain and $S_N Ar$ for sulfur-linked bisporphyrin formation
Distinguishing between sulfide- and disulfide-linked bisporphyrins 3e via HRMS and $^1$H NMR

**Elemental Composition Report**

**Single Mass Analysis**
- Tolerance = 10.0 PPM / DBE: min = -1.5, max = 100.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Odd and Even Electron Ions**
- 33 formula(a) evaluated with 1 results within limits (up to 50 closest results for each mass)
- Elements Used:
  - C: 0-68
  - H: 0-50
  - N: 0-8
  - O: 2-8
  - S: 0-2
  - F: 0-1

**HRMS**
- 1042.3597 (calc. 1042.3600)
- 1042.3360 (-0.3)

**$^1$H NMR of aromatic regions of 2e**
- 2e (protected thiol)
- 3e (mixture of sulfide and disulfide linked porphyrins)

**Mass spectra of 3e**: mixture of disulfide (i) and sulfide (ii) linked porphyrins

**$^1$H NMR of aromatic regions of 2e and 3e**
- 2e (protected thiol)
- 3e (mixture of sulfide and disulfide linked porphyrins) in CDCl$_3$ (400 MHz)
Compound 3e contains an inseperable mixture of sulfide and disulfide linked bisporphyrins. In order to prove the presence of both materials, the HRMS and $^1$H NMR spectra are presented on S-32. The parent ion peak at $m/z$ 1042.3597 represents the disulfide linked dimer, whilst that showing a parent ion peak at $m/z$ 1010.3870 indicates the sulfur linked dimer. Using $^1$H NMR analysis, a comparison with starting material 2e is shown and complete consumption is observed. For S-linked dimer 3e, one set of $\beta$-signals, integrating for 4 protons, appears at 10.1 ppm, downfield from the meso signal and this is a common trait observed for all S-linked dimer bearing a free meso position (see $^1$H NMR spectra of 3e and 3f). These reflect in inner $\beta$-protons and the opposite is observed for the disulfide linked dimer, whereby communication between the porphyrin units is less than that for the S-linked counterpart. Additionally, broad signals are observed for the aromatic signals in contrast to the S-linked dimer, whereby sharp signals were seen in all other compounds.

Crystal data for sulphur-linked bisporphyrin 3b

Crystal data: C$_{79}$H$_{52}$N$_8$O$_2$SZn$_2$•0.5CH$_3$OH, $M = 1326.12$, triclinic, space group $P\bar{1}$, $a = 12.2362(6)$, $b = 15.0184(7)$, $c = 17.9322(9)$ Å, $\alpha = 99.999(2)^\circ$, $\beta = 103.404(1)^\circ$, $\gamma = 93.376(1)^\circ$, $V = 3140.0(3)$ Å$^3$, $Z = 2$, $T = 104$ K, $\mu$ (MoK$_\alpha$) = 0.856 cm$^{-1}$. 26768 reflections measured, 10863 unique reflections measured ($R_{int} = 0.025$), 875 parameters, 8742 reflections with $I > 2.0\sigma(I)$, refinement against $|F^2|$, $R_1(I > 2.0\sigma(I)) = 0.0855$, $wR_2$ (all data) = 0.2226, $S = 1.05$, $\rho_{max} = 5.99$. The structure shows disorder of one axial methanol and one phenyl residue, both of which were refined with 50 % occupancy. A methanol of solvation was refined with 50 % occupancy. The residual electron density is located close to the S atom (0.8 Å). CCDC 951823.