S.1 Synthesis and Characterisation of Triply-Fused Diporphyrins

Melting points were recorded on a Stanford Research Systems OptiMelt automated melting point system and are uncorrected. Attenuated Total Reflection (ATR) infrared spectroscopy was performed using a Bruker Alpha-E ATR spectrometer equipped with a zinc selenide crystal. Electronic absorption spectra were recorded on Varian Cary 4000 (900-200 nm) and Cary 5 (1500-200 nm) UV-Vis-NIR spectrophotometers at 25 °C, using spectroscopic-grade solvents. 1H NMR and 13C NMR spectra were recorded on Bruker Avance DPX 200 (200 MHz) and DPX 400 (400 MHz) spectrometers and signals are quoted in ppm relative to tetramethylsilane (TMS, 1H and 13C = 0 ppm) or the solvent residue peak (CDCl3; 1H = 7.26 and 13C = 77.16 ppm) as the internal standard. Deuterated chloroform was dried and deacidified by filtration through basic alumina prior to use. Routine Electrospray Ionization (ESI) mass spectra were recorded on a ThermoQuest Finnigan LCQ ion trap mass spectrometer. High resolution ESI and Matrix-Assisted Laser Desorption/Ionisation Fourier Transform Ion Cyclotron Resonance (LDI-FTICR) mass spectra were recorded on a Bruker Daltonics 7T FTICR mass spectrometer. LDI-FTICR-MS on porphyrins did not require the use of a matrix. Alumina refers to Merck aluminium oxide 90 active I, Type 1077 (63200 mesh), neutral or basic as specified. Column chromatography was routinely carried out using either gravity feed or flash chromatography on Davisiol LC60A 40–63 micron chromatographic silica. Analytical thin layer chromatography (TLC) analyses were performed on Merck silica gel 60 F254 pre-coated sheets (0.2 mm).

15,15'-Dibutyl-10,10',20,20'-tetrakis(3,5-di-tert-butylphenyl)-5,5'-diporphine (H-1DP)

A dry 50 mL Schlenk tube was charged with meso-5,15-bis(3,5-di-tert-butylphenyl)porphine (76 mg, 0.11 mmol), purged with argon and then anhydrous THF (20 mL) was added. The dark purple solution was cooled to −78 °C, then purged under vacuum and backfilled with dry argon three times. Butyllithium (1.43 M in hexane, 300 µL, 0.43 mmol) was added to the solution drop-wise with stirring over 5 min, resulting in a colour change to dark green. Once the addition was complete, the
cold bath was removed and stirring continued for 15 min. A solution of DDQ (96 mg, 0.42 mmol) in anhydrous THF (6 mL) was then cannulated into the reaction mixture and stirring continued for a further 30 min. The solvents were removed from the reaction mixture to afford a crude brown solid, which was chromatographed on silica eluting with light petroleum/dichloromethane (3:1). The initial yellow-brown fraction contained diporphyrin H-1DP and a second red/pink fraction contained 5-butyl-10,20-bis(3,5-di-tert-butylphenyl)porphyrin.

Removal of the solvents gave H-1DP as a dark brown-purple microcrystalline solid (73 mg, 89%), mp > 300 °C. HRMS (LDI-FTICR) (m/z) found: [M+H]+ 1483.98337; C_{104}H_{123}N_8 requires: 1483.98652. IR (ATR, dry film) \( \nu_{\text{max}} \) cm\(^{-1} \): 3317w (NH), 2958s, 1591m, 1472m, 1362m, 1243m, 970w, 914w, 792m. UV-Vis (CHCl_3) \( \lambda_{\text{max}} \) (log \( \varepsilon \) ) nm: 420 (5.2), 450 (5.1), 526 (4.5), 561 (3.9), 597 (3.7), 655 nm (3.7).

1H NMR (Figure S1, 200 MHz, CDCl_3-TMS, \( \delta \)): 9.50 (4H, d, J = 6.0 Hz, \( \beta \)-pyrrolic H), 9.00 (4H, d, J = 6.0 Hz, \( \beta \)-pyrrolic H), 8.48 (4H, d, J = 6.0 Hz, \( \beta \)-pyrrolic H), 8.00–7.92 (12H, m, phenyl H_\( \text{o} \)+\( \beta \)-pyrrolic H), 7.63 (4H, s, phenyl H_p), 5.05 (4H, m, butyl \( \alpha \)-CH_2), 2.56 (4H, m, butyl \( \beta \)-CH_2), 1.1 (4H, m, butyl \( \gamma \)-CH_2), 1.37 (72H, s, tert-butyl H), 1.18–1.10 (6H, m, butyl CH_3), −2.20 (4H, s, pyrrolic inner NH). 13C NMR (125 MHz, CDCl_3-TMS, \( \delta \)): 148.5, 141.2, 129.5, 129.0, 128.2, 125.3, 121.7, 121.3, 120.9, 116.7, 41.0, 35.5, 34.9, 31.7, 23.8, 14.3. MS (m/z) (LDI-FTICR): 1483.98 (100%, [M+H]+), 1440.93 (50%, [M−(C_3H_6)]+).

Figure S1: \(^1\)H NMR spectrum of H-1DP in CDCl_3 at 200 MHz. Impurities are marked with an asterisk.

5-Butyl-10,20-bis(3,5-di-tert-butylphenyl)porphyrin was obtained as a purple solid (6 mg, 7%), mp > 300 °C. \(^1\)H NMR analysis was in agreement with the literature. \(^4\) \(^1\)H NMR (200 MHz, CDCl_3-TMS, \( \delta \)): 10.07 (1H, s, meso H), 9.55 (2H, d, J = 6.0 Hz, \( \beta \)-pyrrolic H), 9.25 (2H, d, J = 4.0 Hz, \( \beta \)-pyrrolic H), 9.02 (2H, d, J = 4.0 Hz, \( \beta \)-pyrrolic H), 8.99 (2H, d, J = 6.0 Hz, \( \beta \)-pyrrolic H), 8.11 (4H, d, J = 2.0 Hz, phenyl H_p), 7.83 (2H, t, J = 2.0 Hz, phenyl H_p), 5.09 (2H, t, J = 7.5 Hz, butyl \( \alpha \)-CH_2), 2.70–2.50 (2H, m, butyl \( \beta \)-CH_2), 1.95–1.75 (2H, m, butyl \( \gamma \)-CH_2), 1.56 (36H, s, tert-butyl H), 1.13 (3H, t, J = 7.5 Hz, butyl CH_3), −2.91 (2H, br s, inner NH). MS (ESI) (m/z): 743.67 (100%, [M+H]+);
C\textsubscript{52}H\textsubscript{63}N\textsubscript{4} requires 743.51).

15,15'-Dibutyl-10,10',20,20'-tetrakis(3,5-di-tert-butylphenyl)-5,5'-diporphinatodizinc(II) (Zn-1DP)

A saturated solution of zinc(II) acetate dihydrate in methanol (5 mL) was added to a solution of H-1DP (29.9 mg, 20.1 nmol) in chloroform (30 mL) and the mixture was stirred at room temperature for 5 min. The reaction mixture was worked-up in the usual manner and the resulting purple solid purified on a short silica column eluting with light petroleum/dichloromethane (3:1), which afforded zinc(II) diporphyrin Zn-1DP as a purple solid (32.4 mg, 99%), mp > 300 °C. HRMS (LDI-FTICR) (m/z) found: [M]\textsuperscript{+} 1611.80423; C\textsubscript{104}H\textsubscript{119}N\textsubscript{8}Zn\textsubscript{2} requires: 1611.80461. IR (ATR, dry film) \(\nu\)\textsubscript{max}: 3123w, 3062w, 2960s, 2869m, 1592m, 1363m, 1295w, 1247w, 999s, 823m, 791s cm\textsuperscript{-1}. \(\lambda\)\textsubscript{max} (CHCl\textsubscript{3}) (log\textsubscript{10} \(\epsilon\)): 561 (4.9), 456 (5.5), 424 nm (5.7).

1H NMR (Figure S2, 200 MHz, CDCl\textsubscript{3}-TMS, \(\delta\)): 9.69 (4H, d, \(J = 4.8\) Hz, \(\beta\)-pyrrolic H), 9.10 (4H, d, \(J = 4.8\) Hz, \(\beta\)-pyrrolic H), 8.65 (4H, d, \(J = 4.8\) Hz, \(\beta\)-pyrrolic H), 8.10–8.05 (12H, m, phenyl H\textsubscript{o} + \(\beta\)-pyrrolic H [overlapping]), 7.70 (4H, s, phenyl H\textsubscript{p}), 5.18 (4H, m, butyl \(\alpha\)-CH\textsubscript{2}), 2.72 (4H, m, butyl \(\beta\)-CH\textsubscript{2}), 1.93 (4H, m, butyl \(\gamma\)-CH\textsubscript{2}), 1.48 (72H, s, tert-butyl H), 1.23 (6H [buried], m, butyl CH\textsubscript{3}). 13C NMR (125 MHz, CDCl\textsubscript{3}-TMS, \(\delta\)): 154.9, 150.4, 150.0, 149.7, 148.4, 141.8, 133.6, 132.4, 132.2, 129.7, 129.6, 128.9, 122.7, 122.2, 122.7, 120.7, 118.8, 41.2, 35.0, 31.7, 23.9, 14.3. MS (LDI-FTICR) (m/z): 1611.80 (100%, [M]\textsuperscript{+}), 1568.8 (30%, [M–C\textsubscript{3}H\textsubscript{7}]\textsuperscript{+}).

Figure S2: \(^1\)H NMR spectrum of Zn-1DP in CDCl\textsubscript{3} at 200 MHz. Impurities are marked with an asterisk. No peaks corresponding to the inner NH environment were observed, indicating successful and quantitative metatllation of both porphyrin centres.

15,15'-Dibutyl-10,10',20,20'-tetrakis-(3,5-di-tert-butylphenyl)-3–3',5–5',7–7'-diporphyrinatodizinc(II) (Zn-3DP)

Zn-1DP (50 mg, 31 nmol), scandium(III) triflate (61 mg, 124 nmol) and DDQ (28 mg, 124 nmol) were combined in a flame-dried flask containing a magnetic stirrer under an atmosphere of argon. Anhydrous toluene (20 mL) was added and the mixture degassed under a stream of argon for 15 min. The
reaction mixture was heated at 100°C for 2 h, then THF (5 mL) was added to quench the reaction. Stirring was continued for a further 1 h before the reaction mixture was filtered through a plug of alumina (basic, Brockmann Grade III). The alumina was flushed with toluene to remove unreacted starting material, then with chloroform/methanol (20:1) to obtain the remaining purple fraction. Removal of the solvent from the purple fraction yielded a dark blue solid, which was recrystallised from methanol-dichloromethane to afford triply-fused diporphyrin Zn-3DP as very fine purple/brown needles (31.7 mg, 64%), mp > 300°C. HRMS (LDI-FTICR, Figure S3) (m/z) found: [M]+ 1605.77566; C_{104}H_{114}N_{8}Zn_{2} requires: 1605.77445. IR (ATR, dry film) ν_{max}: 2955s, 2922s, 2868m, 2854m, 1711w, 1591m, 1457m, 1203s, 999s, 947s, 881m, 788m, 752s cm^{-1}. UV-Vis-NIR (CHCl_{3}) λ_{max} (log_{10} ϵ): 420 (5.0), 471 (4.6), 579 (4.9), 935 (4.06), 1065 nm (4.29). {^1}HNMR (Figure S4, 200 MHz, CDCl_{3}-TMS + 0.1% d5-pyridine, δ): 8.40 (4H, d, J = 6.0 Hz, β-pyrrolic H), 7.80 (4H, d, J = 6.0 Hz, β-pyrrolic H), 7.67 (8H, s, phenyl H_{o}), 7.64 (4H, s, phenyl H_{p}), 7.36 (4H, s, β-pyrrolic H), 4.08–3.98 (4H, m, butyl α-CH₂), 2.20–2.00 (4H, m, butyl β-CH₂), 1.80–1.50 (4H, m, butyl γ-CH₂), 1.45 (72H, s, tert-butyl H), 1.05 (6H, t, J = 8.0 Hz, butyl CH₃). MS (LDI-FTICR) (m/z): 1606 (100%, [M]+), 1563 (54%, [M–C₃H₇]+), 1547 (5%, [M–C₃H₁₀]+), 1519 (5%, [M–C₆H₁₄]+).
Figure S3: Measured and calculated LDI-FTICR spectra of Zn-3DP.
Concentrated sulfuric acid (1 mL) was added to a solution of Zn-3DP (30.4 mg, 18.9 nmol) in chloroform (30 mL) and the mixture stirred, monitoring the progress of demetalation by TLC. The reaction was complete within 1 h. The organic layer was subsequently washed with aqueous Na₂CO₃ (10%, 2 × 50 mL) followed by the usual workup. The crude product was purified by silica gel chromatography eluting with light petroleum/dichloromethane (1:2). The product, H-3DP, eluted as a single dark purple band. Removal of the solvents afforded a purple-black solid (28.3 mg, 99%), mp > 300 °C.

HRMS (LDI-FTICR) (m/z) found: [M]+ 1479.95559; C₁₀₄H₁₁₈N₈ requires: 1479.95079. IR (ATR, dry film) νmax: 3322w (NH), 2957s, 2921s, 2854m, 1592m, 1468m, 1362m, 1247w, 1093w cm⁻¹. UV-Vis (CHCl₃) λmax (log₁₀ ε): 409 (5.08), 561 (5.03), 1086 nm (4.48). ¹H NMR (Figure S5, 200 MHz, CDCl₃-TMS, δ): 8.27 (4H, s, β-pyrrolic H), 7.75–7.60 (20H, m, overlapping 2 × β-pyrrolic H and phenyl H₀/p), 3.97 (4H, m, butyl α-CH₂), 2.11 (4H, m, butyl β-CH₂), 1.63 (4H, m, butyl γ-CH₂), 1.46 (72H, s, tert-butyl H), 1.04 (6H, t, J = 8.0 Hz, butyl CH₃). MS (LDI-FTICR) (m/z): 1479.95 (100%, [M]+), 1436.89 (45%, [M−(C₃H₆)]⁺), 1393.84 (5%, [M−(C₆H₁₃)]⁺).

Figure S4: ¹H NMR spectrum of Zn-3DP in CDCl₃ + 0.1% d⁵-pyridine at 200 MHz. Impurities are marked with an asterisk.

15,15'-Dibutyl-10,10',20,20'-tetrakis-(3,5-di-tert-butylphenyl)-3–3',5–5',7–7'-diporphine (H-3DP)
Chemical Shift δ (ppm) 
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

Figure S5: $^1$H NMR spectrum of H-3DP in CDCl$_3$ at 200 MHz. Impurities are marked with an asterisk.

15,15$'$.Dibutyl-10,10$'$.20,20$'$.tetrakis-(3,5-di-tert-butylphenyl)-3–3$'$.5–5$'$.7–7$'$.diporphyrinatodipalladium(II) (Pd-3DP)

A methanol solution of palladium(II) acetate (15 mg, 67 nmol) and sodium acetate (16 mg, 0.20 mmol) was added to a solution of H-1DP (15 mg, 10 nmol) in chloroform (20 mL) and the mixture stirred under nitrogen for 2 days, protected from light. Once the metalation had gone to completion, as evidenced by TLC, the mixture was worked up as usual to give a crude solid that was purified by silica gel chromatography eluting with light petroleum/dichloromethane (2:1). The product eluted as a single dark purple fraction. Removal of the solvents afforded the product as a dark blue solid (16 mg, 95%), mp > 300$^\circ$C. HRMS (LDI-FTICR, Figure S6) ($m/z$) found: [M]$^+$ 1688.71720; C$_{104}$H$_{114}$N$_8$Pd$_2$ requires: 1688.72847. IR (ATR, dry film) $\nu_{\text{max}}$: 2959s, 2922s, 2869m, 1591m, 1503w, 1459m, 1362m, 1247w, 1012m, 786m cm$^{-1}$. UV-Vis (CHCl$_3$) $\lambda_{\text{max}}$ (log$\epsilon$): 408 (5.2), 567 (5.3), 930 nm (4.5).

$^1$H NMR (Figure S7, 200 MHz, CDCl$_3$-TMS, δ): 8.48–8.46 (4H, br m, β-pyrrolic H), 7.94–7.92 (4H, br m, β-pyrrolic H), 7.74–7.69 (12H, br m, phenyl H$_{o/p}$), 7.39 (4H, br s, β-pyrrolic H), 4.11–4.09 (4H, br m, butyl α-CH$_2$), 2.19–2.11 (4H, br m, butyl β-CH$_2$), 1.52–1.51 (4H, br m, butyl γ-CH$_2$, partially buried), 1.49 (72H, s, tert-butyl H), 1.10–1.07 (6H, t, $J = 8.0$ Hz, butyl CH$_3$). MS (LDI-FTICR) ($m/z$): 1688.72 (100%, [M]$^+$), 1644.66 (65%, [M–(C$_3$H$_6$)]$^+$), 1604.69 (10%, [M–(C$_6$H$_{13}$)]$^+$), 1539.78 (38%, [M–(C$_3$H$_6$)-Pd]$^+$).
Figure S6: Measured and calculated LDI-FTICR spectra of Pd-3DP.
Figure S7: $^1$H NMR spectrum of Pd-3DP in CDCl$_3$ at 200 MHz. Impurities are marked with an asterisk.
Figure S8: Ultrafast transient absorption dynamics of **Pd-3DP** in CHCl₃, pumping at 920 nm and probing every 10 nm between 560 and 660 nm. Grey line depicts the experimental data, bolded black curve describes the fitted decay model (biexponential for probes at 580 and 590 nm; monoexponential for all other probe wavelengths). The sharp negative spike within the first 2 ps of measurement in all of traces displaying excited-state absorption is a coherent artifact, which we believe to arise from rapid $S_2 \rightarrow S_1$ internal conversion following population of $S_2$ due to two-photon absorption of the pump beam.
References


