Complexes of aryl-substituted porphyrins and naphthalene diimide: investigations by synchrotron X-ray diffraction and ¹H NMR spectroscopy

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Porphyrin syntheses

5,15-Bis(3,4,5-trimethoxyphenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (1): The title compound was prepared according to the general procedure with the use of 3,4,5-trimethoxybenzaldehyde (0.64 g, 3.27 mmol). Reaction time of 16 h was allowed before the addition of DDQ. Zinc metallation was conducted as described above. The reaction mixture was purified by column chromatography on silica gel eluted with CH₂Cl₂, followed by recrystallisation from toluene layered with hexane to afford **1** as red crystals (0.99 g, 55 %). ¹H NMR (500 MHz, CDCl₃) δ 10.26 (s, 2H, *meso*), 7.39 (s, 4H, ArH), 4.22 (s, 6H, *p*-OCH₃), 4.03 (t, ³J = 8.0, 8H, Por-CH₂), 3.96 (s, 12H, *m*-OCH₃), 2.69 (s, 12H, CH₃), 2.27–2.19 (m, 8H, Por-CH₂-CH₂), 1.83–1.75 (m, 8H, Por-(CH₂)₂-CH₂), 1.57–1.49 (m, 8H, Por-(CH₂)₃-CH₂), 1.47–1.39 (m, 8H, Por-(CH₂)₄-CH₂), 0.95 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 152.6, 147.7, 146.6, 143.7, 139.0, 138.8, 138.2, 119.1, 111.7, 97.8, 61.7, 56.5, 33.3, 32.0, 30.1, 26.9, 22.8, 15.0, 14.1; HRMS ESI [(M+H)⁺] calcd. 1097.6074; found 1097.6046; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ε/M¹ cm⁻¹] 5.62, 4.38, 4.14); elemental analysis for C₆₆H₈₈N₄O₆Zn: calcd. C 72.14, H8.07, N 5.10; found C 72.19, H 8.08, N 5.21.

5,15-Bis(3,5-dimethoxyphenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (2): The title compound was prepared according to the general procedure with the use of 3,5-dimethoxybenzaldehyde (0.54 g, 3.27 mmol). Reaction time of 16 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with $CHCl_3$ /hexane (5/1), followed by recrystallisation from CH_2Cl_2 layered with MeOH to afford 2 as purple crystals (0.16 g, ¹H NMR (500 MHz, CDCl₃) δ 10.24 (s, 2H, meso), 7.32 (d, ⁴J = 2.3, 4H, ArH), 9 %). 6.95 (t, ${}^{4}J = 2.3$, 2H, Ar*H*), 4.02 (t, ${}^{3}J = 7.9$, 8H, Por-C*H*₂), 3.96 (s, 12H, OC*H*₃), 2.69 (s, 12H, C*H*₃), 2.26–2.18 (m, 8H, Por-C*H*₂-C*H*₂), 1.80–1.74 (m, 8H, Por-(C*H*₂)₂-C*H*₂), 1.55– 1.48 (m, 8H, Por-(CH₂)₃-CH₂), 1.45–1.38 (m, 8H, Por-(CH₂)₄-CH₂), 0.94 (t, ${}^{3}J = 7.3$, 12H, Por-(CH₂)₅-CH₃); 13 C NMR { 1 H}(125 MHz, CDCl₃) δ 160.1, 147.4, 146.5, 145.3, 143.6, 138.2, 119.1, 112.6, 100.8, 97.7, 55.7, 33.3, 32.0, 30.1, 26.8, 22.8, 15.0, 14.2; HRMS ESI [(M+H)⁺] calcd. 1037,5862; found 1037.5835; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, cm^{-1}] 5.61, 538, 572 $(\log [\epsilon/M^{-1}])$ 4.32, 4.08); elemental analysis for C₆₄H₈₄N₄O₄Zn·1CH₃OH: calcd. C 72.91 H 8.28, N 5.23; found C 72.79, H 8.08, N 5.23. Single crystals suitable for structure determination were obtained from CHCl₃ solution layered with MeOH.

5,15-Bis(3-methoxyphenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (3): The title compound was prepared according to the general procedure with the use of 3-methoxybenzaldehyde (0.40 mL, 3.27 mmol). Reaction time of 16 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CH₂Cl₂/hexane (1/1), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **3** as purple crystals (0.31 g, 19 %). ¹H NMR (500 MHz, CDCl₃) δ 10.22 (s, 2H, *meso*), 7.74–7.63 (m, 3H, Ar*H*), 7.39–7.36 (m, 1H, Ar*H*), 4.00 (t, ³*J* = 9.0, 8H, Por-CH₂), 2.57 (s, 6H, CH₃), 2.25–2.17 (m, 8H, Por-CH₂-CH₂), 1.81–1.73 (m, 8H, Por-(CH₂)₂-CH₂), 1.56–1.48 (m, 8H, Por-(CH₂)₃-CH₂), 1.45–1.36 (m, 8H, Por-(CH₂)₄-CH₂), 0.94 (t, ³*J* = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 159.1, 147.6, 146.4, 144.9, 143.5, 138.2, 128.4, 126.5, 119.1, 114.2, 97.6, 55.6, 33.3, 32.0, 30.0, 26.8, 22.8, 15.1, 14.2; HRMS ESI [(M+H)⁺] calcd. 977.5651; found 977.5665; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ε/M⁻¹ cm⁻¹] 5.62, 4.33, 4.09); elemental analysis for C₆₂H₈₀N₄O₂Zn: calcd. C 76.09, H 8.24, N 5.72; found C 75.95, H 8.36, N 5.67.

5,15-Bis(4-methoxyphenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (4): The title compound was prepared according to the general procedure with the use of 4-methoxybenzaldehyde (0.40 mL, 3.27 mmol). Reaction time of 16 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (5/1), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **4** as purple crystals (0.23 g, 14 %). ¹H NMR (500 MHz, CDCl₃) δ 10.11 (s, 2H, *meso*), 7.94 (d, ³*J* = 8.3, Ar*H*), 7.28 (d, ³*J* = 8.3, Ar*H*), 4.13 (s, 6H, OCH₃), 3.93 (t, ³*J* = 7.9, 8H, Por-CH₂), 2.50 (s, 12H, CH₃), 2.23–2.15 (m, 8H, Por-CH₂-CH₂), 1.81–1.73 (m, 8H, Por-(CH₂)₂-CH₂), 1.56–1.48 (m, 8H, Por-(CH₂)₃-CH₂), 1.47–1.39 (m, 8H, Por-(CH₂)₄-CH₂), 0.96 (t, ³*J* = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 159.8, 148.2, 146.4, 143.3, 138.2, 136.3, 134.1, 119.0, 112.9, 97.5, 55.6, 33.3, 32.0, 30.0, 26.8, 22.8, 15.4, 14.2; HRMS ESI [(M+H)⁺] calcd. 977.5651; found 977.5627; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ϵ/M^{-1} cm⁻¹] 5.58, 4.29, 4.03); elemental analysis for C₆₂H₈₀N₄O₂Zn·1MeOH: calcd. C 74.94, H 8.29, N 5.55; found C 74.73, H 8.26, N 5.53.

5,15-Diphenyl-2,8,12,18-tetra-*n***-hexyl-3,7,13,17-tetramethylzincporphyrin (5):** The title compound was prepared according to the general procedure with the use of benzaldehyde (0.35 mL, 3.27 mmol). Reaction time of 4 h was allowed before the addition of DDQ. Zinc metallation was conducted as described above. The reaction mixture was purified by column chromatography on silica gel eluted with ethyl acetate/hexane (1/10), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **5** as purple crystals (0.98 g, 66 %). ¹H NMR (500 MHz, CDCl₃) δ 10.19 (s, 2H, *meso*), 8.11–8.08 (m, 4H, ArH), 7.84–7.81 (m, 2H, ArH), 7.78–7.75 (m, 4H, ArH), 3.97 (t, ³J = 7.9, 8H, Por-CH₂), 2.47 (s, 12H, pyrrolic-CH₃), 2.23–2.15 (m, 8H, Por-CH₂-CH₂), 1.80–1.72 (m, 8H, Por-(CH₂)₂-CH₂), 1.55–1.47 (m, 8H, Por-(CH₂)₃-CH₂), 1.45–1.37 (m, 8H, Por-(CH₂)₄-CH₂), 0.93 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 147.8, 146.4, 143.8, 143.5, 138.1, 133.3, 128.1, 127.5, 119.4, 97.6, 33.3, 32.0, 30.0, 26.8, 22.8, 15.2, 14.1; HRMS ESI [(M+H)⁺] calcd. 917.5440; found 917.5414; UV-Vis λ_{max} (CH₂Cl₂)/nm 408, 536, 574 (log [ϵ/M^{-1} cm⁻¹] 5.25, 4.20, 4.03); elemental analysis for C₆₀H₇₆N₄Zn: calcd. C 78.44, H 8.34, N 6.10; found C 78.27, H 8.25, N 6.03.

5,15-Diphenyl-2,8,12,18-tetra-*n***-hexyl-3,7,13,17-tetramethylporphyrin** (6): The freebase porphyrin **6** was obtained from **5** by washing its dichloromethane solution of zincmetallated analogue several times with 3N aqueous HCl, followed by washes with H₂O until a neutral pH of the wash is obtained. The solution was dried over Na₂SO₄ and the solvent was removed under reduced pressure. Recrystallisation using a combination of solvents in layered fashion could yield material of high purity. Demetallation generally proceeds in very good yield (< 95%). Recrystallisation from CH₂Cl₂ layered with MeOH yielded **7** as red needles. ¹H NMR (500 MHz, CDCl₃) δ 10.26 (s, 2H, *mesq*), 8.13–8.07 (m, 4H, ArH), 7.84–7.80 (m, 2H, ArH), 7.78–7.74 (m, 4H, ArH), 4.01 (t, ³J = 7.9, 8H, Por-CH₂), 2.51 (s, 12H, CH₃), 2.25–2.17 (m, 8H, Por-CH₂-CH₂), 1.80–1.72 (m, 8H, Por-(CH₂)₂-CH₂), 1.53–1.46 (m, 8H, Por-(CH₂)₃-CH₂), 1.44–1.36 (m, 8H, Por-(CH₂)₄-CH₂), 0.93 (t, ³J = 7, 12H, Por-(CH₂)₅-CH₃), -2.36 (s, 2H, NH); ¹³C NMR {¹H} (125 MHz, CDCl₃) δ 145.1, 143.3, 142.4, 141.4, 136.2, 133.0, 128.2, 127.6, 118.0, 97.0, 33.3, 32.0, 30.0, 26.8, 22.8, 14.6, 14.1; HRMS ESI [(M+H)⁺] calcd. 855.6305; found 855.6300; UV-Vis λ_{max} (CH₂Cl₂)/nm 408, 506, 540, 574, 626 (log [ϵ /M⁻¹ cm⁻¹] 5.36, 4.31, 3.82, 3.96, 3.32); elemental analysis for C₆₀H₇₈N₄: calcd. C 84.26, H 9.19, N 6.55; found C 84.29, H 9.19, N 6.57.

5,15-Diphenyl-2,8,12,18-tetra*n***-hexyl-3,7,13,17-tetramethylnickelporphyrin** (7): The free base porphyrin **6** in mixed CHCl₃/MeOH solvent was refluxed with excess (>5 eq) Ni(OAc)₂·4H₂O overnight. After cooling the solution was filtered, washed with H₂O, dried over Na₂SO₄. The solvent was removed under reduced pressure. Recrystallisation from CH₂Cl₂ layered with MeOH yielded **7** as purple crystals. Metallation generally proceeds in good yield (< 90%). ¹H NMR (500 MHz, CDCl₃) δ 9.46 (s, 2H, *meso*), 7.89–

7.85 (m, 4H, Ar*H*), 7.72–7.68 (m, 2H, Ar*H*), 7.67–7.61 (m, 4H, Ar*H*), 3.67 (t, ${}^{3}J$ = 7.9, 8H, Por-C*H*₂), 2.48 (s, 12H, C*H*₃), 2.07–1.99 (m, 8H, Por-C*H*₂-C*H*₂), 1.68–1.60 (m, 8H, Por-(C*H*₂)₂-C*H*₂), 1.50–1.33 (m, 16H, Por-(C*H*₂)₃-C*H*₂) and Por-(C*H*₂)₄-C*H*₂), 0.93 (t, ${}^{3}J$ = 7.2, 12H, Por-(C*H*₂)₅-C*H*₃); ${}^{13}C$ NMR { ${}^{1}H$ }(125 MHz, CDCl₃) δ 144.0, 141.4, 140.4, 139.4, 139.0, 133.1, 128.1, 127.4, 116.4, 96.4, 32.8, 31.9, 29.8, 26.3, 22.7, 15.2, 14.1; HRMS ESI [(M+Na)⁺] calcd. 933.5321; found 933.5318; UV-Vis λ_{max} (C*H*₂C*l*₂)/nm 408, 526, 564 (log [ϵ/M^{-1} cm⁻¹] 5.32, 4.16, 4.29); elemental analysis for C₆₀H₇₆N₄Ni: calcd. C 79.02, H 8.40, N 6.14; found C 78.96, H 8.29, N 6.17.

5,15-Bis(3-fluorophenyl)-2,8,12,18-tetra*-n***-hexyl-3,7,13,17-tetramethylzincporphyrin** (8): The title compound was prepared according to the general procedure with the use of 3-fluorobenzaldehyde (0.35 mL, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (1/2), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **8** as purple crystals (0.53 g, 34 %). ¹H NMR (400 MHz, CDCl₃) δ 10.11 (s, 2H, *meso*), 7.91–7.87 (m, 2H, ArH), 7.85–7.80 (m, 2H, ArH), 7.76–7.69 (m, 2H, ArH), 7.59–7.52 (m, 2H, ArH), 3.92 (t, ³J = 7.9, 8H, Por-CH₂), 2.50 (s, 12H, CH₃), 2.23–2.13 (m, 8H, Por-CH₂-CH₂), 1.82–1.73 (m, 8H, Por-(CH₂)₂-CH₂), 1.57–1.48 (m, 8H, Por-(CH₂)₃-CH₂), 1.47–1.37 (m, 8H, Por-(CH₂)₄-CH₂), 0.96 (t, ³J = 7.2, 12H, Por-(CH₂)₅-CH₃); ¹C NMR {¹H}(125 MHz, CDCl₃) δ 162.4 (d, J_{CF} = 245.4), 147.3, 146.4, 145.8 (d, J_{CF} = 7.8), 143.7, 137.7, 129.5, 128.8 (d, J_{CF} = 8.3), 120.6 (d, J_{CF} = 20.3), 117.6 (d, J_{CF} = 1.4), 115.0 (d, J_{CF} = 20.8), 97.7, 33.2, 32.0, 30.0, 26.7, 22.7, 15.2, 14.1; ¹⁹F NMR {¹H}(376 MHz, CDCl₃) δ -115.2; HRMS ESI [(M+H)⁺] calcd. 953.5251; found 953.5279; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ϵ /M⁻¹ cm⁻¹] 5.61, 4.34, 4.18); elemental analysis for C₆₀H₇₄N₄F₂Zn: calcd. C 75.49, H 7.81, N 5.87; found C 75.59, H 7.76, N 5.84.

5,15-Bis(4-fluorophenyl)-2,8,12,18-tetra*n***-hexyl-3,7,13,17-tetramethylzincporphyrin** (9): The title compound was prepared according to the general procedure with the use of 4-fluorobenzaldehyde (0.35 mL, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (2/3), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **9** as purple needles (0.53 g, 34 %). ¹H NMR (400 MHz, CDCl₃) δ 10.10 (s, 2H, *meso*), 8.03–7.97 (m, 4H, ArH), 7.47–7.41 (m, 4H, ArH), 3.90 (t, ³J = 7.9, 8H, Por-CH₂), 2.44 (s, 12H, CH₃), 2.20–2.10 (m, 8H, Por-CH₂-CH₂), 1.78–1.68 (m, 8H, Por-(CH₂)₂-CH₂), 1.53–1.44 (m, 8H, Por-(CH₂)₃-CH₂), 1.43–1.32 (m, 8H, Por-(CH₂)₄-CH₂), 0.91 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 163.2 (d, J_{CF} = 245.6), 147.8, 146.4, 143.6, 139.7 (d, J_{CF} = 3.3), 137.9, 134.5 (d, J_{CF} = 7.6), 118.0, 114.4 (d, J_{CF} = 21.0), 97.7, 33.3, 32.0, 30.0, 26.7, 22.7, 15.4, 14.1; ¹⁹F NMR {¹H}(376 MHz, CDCl₃) δ -114.7; HRMS ESI [(M+H)⁺] calcd. 953.5251; found 953.5280; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ϵ /M⁻¹ cm⁻¹] 5.64, 4.35, 4.16); elemental analysis for C₆₀H₇₄N₄F₂Zn: calcd. C 75.49, H 7.81, N 5.87; found C 75.41, H 7.74, N 5.75.

5,15-Bis(3,5-difluorophenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (10): The title compound was prepared according to the general procedure with the use of 3,5-difluorobenzaldehyde (0.47 g, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CH₂Cl₂/hexane (1/3), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford 10 as purple crystals (0.41 g, 25 %). ¹H NMR (400 MHz, CDCl₃) δ 10.08 (s, 2H, *meso*), 7.65–7.58 (m, 4H, ArH), 7.29 (tt, ³J = 9.1, ⁴J = 2.4, 2H, ArH), 3.89 (t, ³J = 7.9, 8H, Por-CH₂), 2.53 (s, 12H, CH₃), 2.20–2.09 (m, 8H, Por-CH₂-CH₂), 1.78–1.68 (m, 8H, Por-(CH₂)₂-CH₂), 1.54–1.45 (m, 8H, Por-(CH₂)₃-CH₂), 1.44–1.33 (m, 8H, Por-(CH₂)₄-CH₂), 0.92 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 162.3 (dd, J_{CF} = 248.3, 12.9), 146.9, 146.5,

144.1, 137.3, 117.1 (dd, J_{CF} = 18.3, 5.5), 116.4, 103.7 (t, J_{CF} = 25.0), 98.0, 32.3, 31.9, 30.0, 26.7, 22.7, 15.2, 14.1; ¹⁹F NMR {¹H}(376 MHz, CDCl₃) δ -111.81; HRMS ESI [(M+H)⁺] calcd. 989.5063; found 989.5081; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ϵ/M^{-1} cm⁻¹] 5.54, 4.25, 4.13); elemental analysis for C₆₀H₇₂N₄F₄Zn: calcd. C 72.75, H 7.33, N 5.66; found C 72.60, H 7.25, N 5.61. Single crystals suitable for structure determination were obtained from CH₂Cl₂ solution layered with MeOH.

5,15-Bis(3,4,5-trifluorophenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (11): The title compound was prepared according to the general procedure with the use of 3,4,5-trifluorobenzaldehyde (0.37 mL, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (2/3), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford 11 as purple needles (0.32 g, 19 %). ¹H NMR (400 MHz, CDCl₃) δ 10.10 (s, 2H, *meso*), 7.74–7.65 (m, 4H, ArH), 3.90 (t, ³J = 7.9, 8H, Por-CH₂), 2.53 (s, 12H, CH₃), 2.20–2.12 (m, 8H, Por-CH₂-CH₂), 1.79–1.69 (m, 8H, Por-(CH₂)₂-CH₂), 1.54–1.44 (m, 8H, Por-(CH₂)₃-CH₂), 1.43–1.34 (m, 8H, Por-(CH₂)₄-CH₂), 0.92 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 150.5 (m), 147.1, 146.6, 144.3, 139.5 (m), 137.2, 117.9 (dd, J_{CF}= 14.9, 4.3), 115.6, 98.1, 33.3, 31.9, 30.0, 26.7, 22.7, 15.5, 14.1; ¹⁹F NMR {¹H}(376 MHz, CDCl₃) δ - 136.2 (d, ³J = 18.8); HRMS ESI [(M+H)⁺] calcd. 1025.4874; found 1025.4879; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ε/M⁻¹ cm⁻¹] 5.57, 4.28, 4.18); elemental analysis for C₆₀H₇₀N₄F₆Zn: calcd. C 70.20, H 6.87, N 5.46; found C 70.03, H 6.86, N 5.44.

5,15-Bis(2,3,5,6-tetrafluorophenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (12): The title compound was prepared according to the general procedure with the use of 2,3,5,6-tetrafluorobenzaldehyde (0.38 mL, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (1/2), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **12** as purple crystals (0.48 g, 28 %). ¹H NMR (400 MHz, CDCl₃) δ 10.23 (s, 2H, *meso*), 7.63–7.53 (m, 2H, ArH), 3.99 (t, ³J = 7.9, 8H, Por-CH₂), 2.71 (s, 12H, CH₃), 2.25–2.15 (m, 8H, Por-CH₂-CH₂), 1.80–1.70 (m, 8H, Por-(CH₂)₂-CH₂), 1.54–1.45 (m, 8H, Por-(CH₂)₃-CH₂), 1.44–1.33 (m, 8H, Por-(CH₂)₄-CH₂), 0.91 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 147.6 (m), 147.1, 147.0, 145.6 (m), 144.8, 136.1, 124.0 (t, ³J_{CF}= 19.7), 106.6 (t, ³J = 22.3), 101.0, 98.6, 33.4, 31.9, 30.0, 26.8, 22.7, 14.2, 14.1; ¹⁹F NMR {¹H}(376 MHz, CDCl₃) δ -138.0 (dd, ³J = 24.5, ⁵J = 15.1), -139.7 (dd, ³J = 24.5, ⁵J = 15.1); HRMS ESI [(M+H)⁺] calcd. 1061.4686; found 1061.4652; UV-Vis λ_{max} (CH₂Cl₂)/nm 408, 538, 578 (log [ε/M⁻¹ cm⁻¹] 5.53, 4.24, 4.35); elemental analysis for C₆₀H₆₈N₄F₈Zn: calcd. C 67.82, H 6.45, N 5.27; found C 67.67, H 6.51, N 5.18.

5,15-Bis(2,3,4,5,6-pentafluorophenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-

tetramethylzincporphyrin (13): The title compound was prepared according to the general procedure with the use of 2,3,4,5,6-pentafluorobenzaldehyde (0.40 mL, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (2/1), followed by recrystallisation from CHCl₃ layered with hexane to afford 13 as purple crystals (0.37 g, 21 %). ¹H NMR (400 MHz, CDCl₃) δ 10.28 (s, 2H, *meso*), 4.00 (t, ³J = 7.9, 8H, Por-CH₂), 2.71 (s, 12H, CH₃), 2.23–2.15 (m, 8H, Por-CH₂-CH₂), 1.78–1.71 (m, 8H, Por-(CH₂)₂-CH₂), 1.55–1.48 (m, 8H, Por-(CH₂)₃-CH₂), 1.42–1.35 (m, 8H, Por-(CH₂)₄-CH₂), 0.91 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 147.4, 147.1, 145.0, 136.0, 99.7, 98.8, 33.4, 31.9, 29.9, 26.8, 22.7, 14.4, 14.1; ¹⁹F NMR {¹H}(376 MHz, CDCl₃) δ -137.4 (dd, ³J = 22.6, ⁴J = 7.5), -153.7 (t, ³J = 18.8), -162.8

(m); HRMS ESI $[(M+H)^+]$ calcd. 1097.4498; found 1097.4462; UV-Vis λ_{max} (CH₂Cl₂)/nm 408, 538, 578 (log $[\epsilon/M^{-1} \text{ cm}^{-1}]$ 5.53, 4.27, 4.40); elemental analysis for C₆₀H₆₆N₄F₁₀Zn: calcd. C 65.60, H 6.06, N 5.10; found C 65.47, H 5.97, N 5.07. Single crystals suitable for structure determination were obtained from CHCl₃ solution layered with hexane.

5,15-Bis(3-allyloxyphenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-

tetramethylzincporphyrin (14):

The title compound was prepared according to the general procedure with the use of 3allyloxybenzaldehyde (0.53 g, 3.27 mmol). Reaction time of 16 h was allowed before the addition of DDQ. Zinc metallation was conducted as described above. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (1/1), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **15** as red needles (0.45 g, 26 %). ¹H NMR (500 MHz, CDCl₃) δ 10.22 (s, 2H, *meso*), 7.74–7.63 (m, 3H, ArH), 7.43–7.38 (m, 1H, ArH), 6.19–6.11 (m, 1H, OCH₂CH=CH₂), 5.51 (br dd, 1H, OCH₂CH=CH₂ *trans*), 5.35 (br dd, 1H, OCH₂CH=CH₂ *cis*) and 4.73 (br d, 2H, OCH₂CH=CH₂), 4.00 (t, ³J = 7.8, 8H, Por-CH₂), 2.57 (s, 6H, CH₃), 2.25–2.17 (m, 8H, Por-CH₂-CH₂), 1.82–1.74 (m, 8H, Por-(CH₂)₂-CH₂), 1.56–1.48 (m, 8H, Por-(CH₂)₃-CH₂), 1.46–1.36 (m, 8H, Por-(CH₂)₄-CH₂), 0.94 (t, ³J = 7.3, 12H, Por-(CH₂)₅-CH₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 158.1, 147.6, 146.5, 145.0, 143.5, 138.2, 133.4, 128.4, 126.7, 120.0, 119.1, 117.6, 115.2, 97.6, 69.0, 33.3, 32.0, 30.0, 26.8, 22.7, 15.1, 14.1; HRMS ESI [(M+H)⁺] calcd. 1029.5964; found 1029.5997; UV-Vis λ_{max} (CH₂Cl₂)/nm 410, 538, 574 (log [ϵ /M⁻¹ cm⁻¹] 5.54, 4.29, 4.05); elemental analysis for C₆₆H₈₄N₄O₂Zn: calcd. C 76.90, H 8.21, N 5.44; found C 76.41, H 8.16, N 5.33.

5,15-Bis(4-nitrophenyl)-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-tetramethylzincporphyrin

(15): The title compound was prepared according to the general procedure with the use of 4-nitrobenzaldehyde (0.49 g, 3.27 mmol). Reaction time of 6 h was allowed before the addition of DDQ. Zinc metallation was conducted as previously described. The reaction mixture was purified by column chromatography on silica gel eluted with CHCl₃/hexane (2/3), followed by recrystallisation from CH₂Cl₂ layered with MeOH to afford **15** as purple needles (0.33 g, 20 %). ¹H NMR (500 MHz, CDCl₃) δ 10.19 (s, 2H, *meso*), 8.67 (b, 4H, Ar*H*), 7.25 (b, 4H, Ar*H*), 4.11 (t, ³*J* = 7.8, 8H, Por-C*H*₂), 2.44 (s, 12H, C*H*₃), 2.28 (m, 8H, Por-CH₂-C*H*₂), 1.66 (broad m, 8H, Por-(CH₂)₂-C*H*₂), 1.54 (broad m, 8H, Por-(CH₂)₃-C*H*₂), 1.40 (broad m, 8H, Por-(CH₂)₄-C*H*₂), 0.94 (t, ³*J* = 7.4, 12H, Por-(CH₂)₅-C*H*₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) δ 165.3, 148.5, 146.2, 134.5, 130.0, 125.2, 105.5, 114.5, 40.3, 32.3, 30.1, 26.5, 23.3, 16.3, 14.5; HRMS MALDI-TOF [M⁺] calcd. 1006.5100; found 1006.1811; UV-Vis λ_{max} (CH₂Cl₂)/nm 444, 474, 578 (log [ϵ /M⁻¹ cm⁻¹] 4.64, 4.22, 3.92).

N,N'-**Di**-(**2'**,**6'**-**di**-*iso*-**propylphenyl**)-**naphthalene-1,4,5,8-tetracarboxylic diimide (II):** Naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.40 g, 1.50 mmol) was suspended in acetic acid (20 mL) and heated at reflux. Into this mixture 2,6-di-*iso*-propylaniline (1.88 mL, 10 mmol) was added and the mixture was kept at reflux at 120 °C for 1 h. The solution was concentrated in *vacuo* and the remaining residue was poured into MeOH (20 mL). The precipitated solid was filtered, dried to afford **II** as light pink solid (0.77 g, 87%). ¹H NMR (500 MHz, CDCl₃) 8.91 (s, 4 H, Ar*H*), 7.55 (t, ${}^{3}J$ = 7.8, 2H, Ar*H*), 7.39 (d, ${}^{3}J$ = 7.8, 2H, Ar*H*), 2.74 (septet, ${}^{3}J$ = 6.9, 4H, ${}^{i}Pr$ -*H*), 1.20 (d, ${}^{3}J$ = 6.9, 24H, ${}^{i}Pr$ -*CH*₃); ¹³C NMR {¹H}(125 MHz, CDCl₃) 162.9, 145.6, 131.6, 130.1, 130.0, 127.7, 126.9, 124.3, 29.3, 24.0; elemental analysis for C₃₈H₃₈N₂O₄: calcd. C 77.79, H 6.53, N 4.77; found C 77.50, 6.58, N 4.77. Single crystals suitable for structure determination were obtained from CH₂Cl₂ solution layered with MeOH.

Crystallographic information

Data for the porphyrins 2, 8, 10, 12 and 13 and the diimide II were collected on a Nonius Kappa CCD with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). Crystallographic data of extremely small crystals of porphyrin 16 was collected using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer.

All structures were solved by direct methods using the program SIR92.¹ The refinement and graphical calculations were performed using the CRYSTALS² program suite. Crystallographic details are summarised in Tables S1 and S2.

Figure S1. The molecular structure of porphyrin **2**. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, red = oxygen, purple = zinc). The Zn atom is placed on an inversion centre.



Figure S2. The molecular structure of porphyrin **8**. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, yellow = fluorine, purple = zinc). The Zn atom is placed on an inversion centre.



Figure S3. The molecular structure of porphyrin 10. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, yellow = fluorine, purple = $\frac{1}{2}$



zinc)

Figure

S4. The molecular structure of porphyrin **12**. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, orange = fluorine, red = oxygen, purple = zinc). The Zn(II) centre is coordinated to a (disordered) MeOH molecule, modeled over two positions each with ca. 50% occupancy. The Zn atom is placed on an inversion centre.



Figure S5. The molecular structure of porphyrin **13**. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, yellow = fluorine, purple = zinc). The Zn atom is placed on an inversion centre.



Figure S6. The molecular structure of porphyrin **16**. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, purple = zinc). There are two independent molecules of Compound **16** in this system and in each case the Zn atoms lie on inversion centres.



Figure S7. The molecular structure of known nickel porphyrin 7 showing the severely distorted framework.³ Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, green = nickel)



Figure S8. The molecular structure of di-*iso*-propylphenyl substituted naphthalene diimide **III**. Hydrogen atoms have been omitted for clarity. (Key: grey = carbon, blue = nitrogen, red = oxygen)



Compound	2	8	10	12
Empirical formula	$C_{64}H_{84}N_4O_4Zn$	$C_{60}H_{71}F_2N_4Zn$	$C_{60}H_{72}F_4N_4Zn$	$C_{62}H_{74}F_8N_4O_2Zn$
Temperature (K)	180	180	150	180
Colour	Red	red	Red	red
Crystal size (mm ³)	0.10×0.10×0.20	0.07x 0.23x 0.46	0.10×0.20×0.30	0.08x0.25x0.50
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a (Å)	8.2430(2)	5.71690(10)	5.7210(3)	8.2012(2)
b (Å)	13.0858(3)	14.8893(3)	14.9720(7)	12.8303(4)
c (Å)	13.5204(4)	15.0975(4)	15.1570(14)	13.6161(4)
α (°)	76.6654(11)	95.7726(10)	96.580(2)	73.4069(16)
β (°)	85.1757(11)	100.8123(11)	100.950(3)	84.6669(16)
γ (°)	79.9850(16)	96.9559(12)	96.3100(16)	89.6182(12)
$V(Å^3)$	1395.98 (6)	1242.94(5)	1254.64 (15)	1366.83(7)
Z	1	1	1	1
$D_{calcd} (Mg/m^3)$	1.236	1.271	1.311	1.366
Absorption coefficient	0.491	0.545	0.548	0.520
F ₍₀₀₀₎	558	507	526	592
No. of data measured	12448	13167	18411	11767
No. of unique data	5049	5607	8204	4987
No. of observed data	4025 (I>3.00σ(I))	4463 (I>3.00σ(I))	2404 (I>3.00σ(I))	3681 (I>3.00σ(I))
No. of parameters, p	331	349	314	335
R	0.0439	0.0920	0.0696	0.0580
R_w	0.0522	0.1026	0.0736	0.0676
S(GOF)	1.0937	1.0860	1.0782	0.9926
Largest difference peak and hole (e $Å^3$)	1.04, -0.49	2.22, -1.17	0.66, -0.43	0.45, -1.10

Table S1. Crystallographic data for the porphyrins 2, 8, 10 and 12.

Compound	13	16	II
Empirical formula	$C_{60}H_{66}F_{10}N_4Zn$	C ₇₆ H ₁₀₈ N ₄ Zn	$C_{38}H_{38}N_2O_4$
Temperature (K)	180	200	180
Colour	Red	red	Off-white
Crystal size (mm ³)	0.07×0.23×0.27	0.05x 0.05x 0.20	0.46×0.23×0.10
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	Pca21
a (Å)	8.1034(2)	13.9065(11)	16.017(1)
b (Å)	13.3167(3)	16.3006(13)	8.561(1)
c (Å)	13.5586(4)	17.908(2)	22.982(1)
α (°)	106.0538(10)	105.980(2)	90
β (°)	95.4992(10)	94.520(2)	90
γ (°)	105.8473(15)	115.1360(10)	90
$V(Å^3)$	1329.18 (6)	3442.5(5)	3151.3(3)
Z	1	2	4
D_{calcd} (Mg/m ³)	1.372	1.103	1.237
Absorption coefficient	0.541	0.400	0.08
F ₍₀₀₀₎	574	1244	1248
No. of data measured	10193	30113	16259
No. of unique data	4802	13920	3661
No. of observed data	3977 (I>3.00σ(I))	8468 I>3.00u(I)	3661 (I>3.00σ(I))
No. of parameters, p	340	760	405
R	0.0445	0.1012	0.0523
R _w	0.0544	0.1117	0.1196
S(GOF)	1.2213	1.1307	1.101
Largest difference peak and hole (e $Å^3$)	0.56, -0.61	1.12 , -1.06	0.383, -0.219

Table S2. Crystallographic data for the porphyrins 13, 16 and the naphthyl diimide II.

Figure S9. a) The dilution curves: plot of meso chemical shifts of porphyrins 1 and 13 as a function of concentration (500 MHz, 298K, CDCl₃); b) Typical plot of *meso* chemical shift *versus* number of equivalents of the acceptor molecule. Acceptor I was added to porphyrin 1.



a)

b)



Figure S10. Representative examples of fitted titration curves (EQNMR, using a 1:1 fitting models)

a) Fitted titration curve of *meso* chemical shift of porphyrin 1 *versus* concentration of the acceptor I; b) Fitted titration curve of *meso* chemical shift of porphyrin 11 *versus* concentration of the acceptor I added; c) Fitted titration curve of *meso* chemical shift of *bis*-(4-nitrophenyl) substituted zinc porphyrin 15 *versus* concentration of the acceptor I added; d) Fitted titration curve of of *meso* chemical shift of *bis*-(3,5-di-*tert*-butylpheny) substituted zinc porphyrin 16 *versus* concentration of the acceptor I added.



a)







c)





Figure S11. A plot of *meso* chemical shift of the nickel porphyrin **7** versus number of equivalents of the di-*N*-substituted naphthalene diimide **I** acceptor added.



Description of the Hammett approach

Initially, a Hammett type linear free energy analysis treatment was employed here to describe the electronic contributions of the substituents. A new electronic function P(E) introduced in equation below takes into account of both the nature and positional dependence of each substituent and represents the sum of electronic contribution over all the position on the phenyl ring, where σ_x is the Hammett constant of any substituent X for a given porphyrin *j*. Thus, the Hammett equation to describe the 1:1 complexation process is defined as:

$$\log \frac{K_j}{K_H} = P(E) = 2\sum \sigma_X \rho \tag{1}$$

The sensitivity of the complexation under study to the total electronic contribution of the substituents is measured by a parameter ρ . A factor of 2 is introduced into the equation to take account of both phenyl rings. Hammett constants are taken from the literature.⁴

Table S3. Data used for the Hammett plot for a selected range of porphyrins, where the number of substituents at the phenyl rings could be varied systematically.

Porphyrin	log(<i>K_j / K_H</i>)	Sum of <i>meta</i> contributions [†]	Sum of <i>para</i> contributions [†]	<i>P</i> (E)
1	0.278	0.48	-0.54	-0.12
2	0.134	0.48	0	0.96
3	0.063	0.24	0	0.48
4	0.022	0	-0.54	-1.08
5	0	0	0	0
8	-0.14	0.68	0	1.36
9	-0.031	0	0.12	0.24
10	-0.383	1.36	0	2.72
11	-0.649	1.36	0.12	2.96

[†]Sum of *meta* contributions is given by number of *meta* substituents multiplied by Hammett constant for *meta*-substituted fluorine or methoxy group on each aryl ring. The same applies to *para* contributions using Hammett constants for *para* substituents. Values of σ_{para} for OMe and F are -0.27 and 0.06 respectively.⁴ Values of σ_{meta} for OMe and F are 0.12 and 0.34 respectively.⁴ The plot of log K_{j}/K_{H} against P(E) is shown below. Data points of porphyrins **12** and **13** are not included in the plot since Hammett constant for *ortho* fluorine was not available).



Figure S12. Hammett plot for data collected in Table S3.

Description of the Swain's dual parameter approach

The sigma values for the substituents in the Hammett approach may be broken down into two components, given by equation below:

$$\sigma = a\sigma_I + b\sigma_R \tag{2}$$

The original Swain equation⁵ can be written in the following form:

$$\log \frac{K}{K_{H}} = \rho_{I}\sigma_{I} + \rho_{R}\sigma_{R} = \rho(a\sigma_{I} + b\sigma_{R})$$
(3)

where sigma I (σ_I) and sigma R (σ_R) are known parameters which are position independent and are the same for *meta* and *para* for a given substituent; ρ , *a* and *b* are determined by a fitting algorithm and their value will be known except for a multiplicative constant. Although ρ , *a* and *b* represent a redundant set of constants and since only two are required from equation 2, this notation should describe more accurately the relative contribution of induction and resonance in transmitting the electronic effect. This notation does not introduce any real extra parameters and does not contain any extra information with respect to equation 2. For this reason and without the loss of generality, the value of the parameter *a* in equation 2 can be arbitrarily set to unity. Thus, equation 3 now becomes:

$$\log \frac{K}{K_{H}} = \rho \left(\sigma_{I} + \beta \sigma_{R} \right) \tag{4}$$

To take into an account of the possible positional dependence of the resonance contribution, two sigma parameters sigma *meta* (σ_m) and sigma *para* (σ_p) with different beta values are introduced, therefore:

$$\sigma_m = \sigma_I + \beta_m \sigma_R \tag{5}$$

$$\sigma_p = \sigma_I + \beta_p \sigma_R \tag{6}$$

Also for a given porphyrin *j*, the overall electronic contribution form the peripheral substituents depends also on the total number of *meta* substituents (N_{jm}) and *para* substituents (N_{jp}) . Therefore the Swain equation can be written as follow:

$$\log \frac{K_j}{K_H} = \rho \left[N_{jm} \left(\sigma_I + \beta_m \sigma_R \right) + N_{jp} \left(\sigma_I + \beta_p \sigma_R \right) \right]$$
(7)

Equation 7 was used in the fitting of the experimental data

Table S4. Data corresponding to the linear trend (Figure 8 in main text and also copied below) relevant to the subset of selected Zn(II)-porphyin donors (methoxy- and fluoride-substituted), where the number and size of substituents were carefully modulated to tune the electron density at the porphyrin centre. The trend line shown was fitted for the Swain equation (Denoted *Equation 4* in main text) (MicroMath[®] Scientist[®] 2.01, MicroMath, Inc) implementing a least squares algorithm. The linear fit gives σ the value of -0.43 ± 0.04 with a correlation factor (R²) of 0.94.



Porphyri	n <i>K_j/K_H</i>	$\log(K_j/K_H)$	N _{jm}	Njp	$\sigma_{I}^{[a]}$	$\sigma_{R}^{[a]}$	$N_{jm} (\sigma_I + 0.65\sigma_R) + N_{jp} (\sigma_I + 0.73\sigma_R)$
1	1.897	0.285	4	2	0.25	-0.51	-0.571
2	1.362	0.135	4	0	0.25	-0.51	-0.326
3	1.155	0.066	2	0	0.25	-0.51	-0.163
4	1.051	0.038	0	2	0.25	-0.51	-0.245
5	1	0	0	0	0	0	0
8	0.931	-0.008	2	0	0.52	-0.44	0.398
9	0.724	-0.117	0	2	0.52	-0.44	0.468
10	0.414	-0.325	4	0	0.52	-0.44	0.936
11	0.224	-0.485	4	2	0.52	-0.44	1.334
^a See refe	rence 6 be	low					

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