Porphyrin Amino Acids – Amide Coupling, Redox and Photophysical Properties of Bis(porphyrin) amides

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Supporting Information

Experimental Section

Porphyrins 1a, 2a, Boc-3a and 3a were prepared by published procedures and characterised as follows.^{[S1][S2]}

10,20-Bis(2,4,6-trimethylphenyl)-5,15-bis[4-(methoxycarbonyl)] porphyrin (1a)^{[S1][S2]}



¹**H-NMR (CDCl₃):** $\delta = -2.63$ (s, 2 H, H^{pyrrole-NH}), 1.83 (s, 12 H, H¹⁰₅), 2.63 (s, 6 H, H¹⁰₆), 4.11 (s, 6 H, H⁵₆), 8.31 (d, ³*J*_{HH} = 8.1 Hz, 4 H, H⁵₂), 8.43 (d, ³*J*_{HH} = 8.1 Hz, 4 H, H⁵₃), 8.71 (d, ³*J*_{HH} = 4.7 Hz, 4 H, H^{pyrrole}), 8.74 (d, ³*J*_{HH} = 4.7 Hz, 4 H, H^{pyrrole}) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3425 (b, NH), 2922 (w, CH), 2850 (w, CH), 1722 (vs, CO), 1608 (s), 1386 (vs), 1278 (vs, C-O-C), 1114 (s), 800 (w).

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 419 (36.88), 516 (1.99), 548 (1.13), 593 (0.82), 651 (1.38).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 654 (1.00), 716 (0.20).

Quantum yield: $\Phi = 0.0774$.

Lifetime: τ [ns] = 9.87 (100%).

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.020, -1.670, 0.600, 1.030.

5-(4-Carboxyphenyl)-15-(4-carbomethoxyphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrin (2a)^{[S1][S2]}



UV/Vis (CH₂Cl₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 419 (13.58), 515 (0.70), 549 (0.34), 592 (0.24), 650 (0.30). Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 652 (1.00), 716 (0.26). Quantum yield: Φ = 0.1187. CV (Fc/Fc⁺, 100 mV s⁻¹, CH₂Cl₂): $E_{\frac{1}{2}}$ [V] = -2.090, -1.705, 0.600, 1.060.

15-(4-Carbomethoxyphenyl)-5-(*N-tert*-butoxycarbonyl-4-aminophenyl)-10,20-bis(2,3,4,5,6-pentafluorophenyl) porphyrin (Boc-3a)^{[S1][S2]}



UV/Vis (CH₂Cl₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 420 (68.60), 516 (3.48), 550 (1.91), 594 (1.36), 651 (2.25). Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 654 (1.00), 719 (0.20).

Quantum yield: $\Phi = 0.1112$.

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [**V**] = -2.130, -1.745, 0.535, 0.945.

15-(4-Carbomethoxyphenyl)-5-(4-aminophenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrin (3a)^{[S1][S2]}



UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 421 (34.07), 517 (1.91), 552 (1.10), 593 (0.74), 651 (1.01). **Fluorescence** (**CH**₂**Cl**₂): λ [nm] (relative intensity) = 654 (1.00), 719 (0.21).

Quantum yield: $\Phi = 0.0882$.

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.100, -1.760, 0.455, 0.600.

10,20-Bis(**2,3,4,5,6-pentafluorophenyl**)-**5,15-bis**[**4**-(**methoxycarbonylphenyl**)] **porphyrin** (**1b**). Following a standard procedure^[S3] a solution of pentafluorophenyldipyrromethane (2.00 g, 6.4 mmol) and methyl 4formylbenzoate (1.02 g, 6.4 mmol) in CH₂Cl₂ (700 mL) was treated with TFA (1.2 mL, 15.6 mmol) at room temperature. After 40 min, DDQ (2.1 g, 9.57 mmol) was added and after further 60 min TEA (1.2 mL) was added. The reaction mixture was concentrated under reduced pressure and chromatographed [silica, CH₂Cl₂/petroleum ether b.p. 40/60 (5:1), $R_f = 0.32$] affording a purple powder (200 mg, 0.22 mmol, 7%). C₄₈H₂₄F₁₀N₄O₄ (910.71).



¹**H-NMR (CDCl₃):** $\delta = -2.86$ (s, 2 H, H^{pyrrole-NH}), 4.13 (s, 6 H, H⁵₆), 8.31 (d, ³J_{HH} = 8.2 Hz, 4 H, H⁵₂), 8.47 (d, ³J_{HH} = 8.2 Hz, 4 H, H⁵₃), 8.83 (d, ³J_{HH} = 4.7 Hz, 4 H, H^{pyrrole}), 8.90 (d, ³J_{HH} = 4.8 Hz, 4 H, H^{pyrrole}) ppm.

¹**H-NMR** (**d**₈-**THF**): $\delta = -2.80$ (s, 2 H, H^{pyrrole-NH}), 4.07 (s, 6 H, H⁵₆), 8.37 (d, ³*J*_{HH} = 8.2 Hz, 4 H, H⁵₂), 8.47 (d, ³*J*_{HH} = 8.2 Hz, 4 H, H⁵₃), 8.93 (d, ³*J*_{HH} = 4.7 Hz, 4 H, H^{pyrrole}), 9.05 (d, ³*J*_{HH} = 4.8 Hz, 4 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): $\delta = 52.7$ (s, C⁵₆), 121.4 (s, C⁵), 129.1 (s, C⁵₃), 131.4 (s, C⁵₄), 131.4, 133.3 (m, C^{2,3,7,8,12,13,17,18}), 135.6 (s, C⁵₂), 147.1 (s, C⁵₁), 167.3 (s, C⁵₅) ppm. C¹⁰₁ - C¹⁰₄ are not observed.

¹⁹**F-NMR (d₈-THF):** $\delta = -162.9$ (ddd, ${}^{3}J_{FF} = 23$ Hz, ${}^{3}J_{FF} = 21$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{3/3}$,), -153.4 (t, ${}^{3}J_{FF} = 21$ Hz, 2 F, $F^{10/20}_{4/4}$), -138.0 (dd, ${}^{3}J_{FF} = 24$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{2/2}$) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3435 (w, crystal water), 3327 (w, NH), 2923 (w, CH), 2850 (w, CH), 1718 (s, CO), 1605 (w), 1519 (vs), 1496 (m), 1281 (s, C-O-C), 1114 (m, CF), 987 (s), 804 (w).

MS (FD): m/z (%) = 909.7 (100), 910.7 (55) [M]⁺.

MS (ESI): m/z (%) = 911.17 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 911.1700; calcd. for [M+H]⁺ 911.1716.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 415 (55.69), 510 (3.09), 543 (0.73), 587 (0.95), 641 (0.34).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 645 (1.00), 711 (0.62).

Quantum yield: $\Phi = 0.0520$.

Lifetime: τ [ns] = 10.05 (100%).

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.750, -1.350, 0.890, 1.140.

5-(4-Carboxyphenyl)-15-(4-carbomethoxyphenyl)-10,20-bis(2,3,4,5,6-pentafluorophenyl) porphyrin (2b). Porphyrin 1b (400 mg, 0.447 mmol) was dissolved in 80 mL TFA and 160 mL concentrated HCl_{aq}. The mixture was heated to 60°C. When TLC indicated beginning formation of the diacid the reaction was cooled down, diluted with CH₂Cl₂ (100 mL) and neutralised with a saturated aqueous solution of NaHCO₃. The organic layer was washed with water (3×), dried over Na₂SO₄ and concentrated under reduced pressure. Porphyrins 1b (289 mg) and 2b (101 mg, 25% yield, purple powder, C₄₇H₂₂F₁₀N₄O₄ (896.69)) were isolated by column chromatography [silica, CH₂Cl₂/MeOH (20:1), $R_f = 1.0$ (1b) and $R_f = 0.29$ (2b)].



¹**H-NMR** (**CD**₂**Cl**₂ + 1 drop MeOD): $\delta = -2.94$ (s, 2 H, H^{pyrrole-NH}), 4.07 (s, 3 H, H¹⁵₆), 8.29 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.30 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H⁵₂), 8.43 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H¹⁵₃), 8.44 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H⁵₃), 8.86 (br. s, 4 H, H^{pyrrole}), 8.91 (br. s, 4 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CD₂Cl₂ + 1 drop MeOD): $\delta = 52.6$ (s, C¹⁵₆), 120.6 (s, C⁵), 120.8 (s, C¹⁵), 128.2 (s, C¹⁵₃), 128.5 (s, C⁵₃), 130.3 (s, C¹⁵₄), 130.7 (s, C⁵₄), 134.8 (s, C¹⁵₂), 134.8 (s, C⁵₂), 136.3, 138.8, 145.3, 147.8 (m, C^{10,20/10}

¹⁹**F-NMR** (**CD**₂**Cl**₂ + 1 drop MeOD): $\delta = -162.1$ (ddd, ${}^{3}J_{FF} = 23$ Hz, ${}^{3}J_{FF} = 21$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{3/3}$,), -153.3 (t, ${}^{3}J_{FF} = 21$ Hz, 2 F, $F^{10/20}_{4/4}$), -137.2 (dd, ${}^{3}J_{FF} = 24$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{2/2}$) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3431 (b, OH), 3314 (w, NH), 2925 (w, CH), 2856 (w, CH), 1725 (s, CO), 1698 (s, CO), 1524 (m), 1489 (vs), 1281 (m, C-O-C), 1108 (s, CF), 990 (s), 920 (s).

MS (FD): m/z (%) = 895.58 (100) [M]⁺.

MS (ESI): m/z (%) = 897.17 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 897.1547; calcd. for $[M+H]^+ 897.1560$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 415 (13.74), 510 (0.83), 543 (0.25), 587 (0.30), 641 (0.15).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 645 (1.00), 712 (0.63).

Quantum yield: $\Phi = 0.0604$.

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.810, -1.380, 0.890, 1.120.

15-(4-Carbomethoxyphenyl)-5-(*N-tert*-butoxycarbonyl-4-aminophenyl)-10,20-bis(2,3,4,5,6-

pentafluorophenyl) **porphyrin (Boc-3b).** Porphyrin **2b** (100 mg, 0.11 mmol) was dissolved in 15 mL of dry *tert*-butyl alcohol and 22 μ L (0.16 mmol) TEA. Diphenylphosphoryl azide (DPPA) (29 μ L (0.14 mmol)) was added and this solution was heated to 80°C for two days. The mixture was diluted with 50 mL CH₂Cl₂, washed with diluted aqueous citric acid, a saturated solution of NaHCO₃, and water (3×). After drying with Na₂SO₄ the solvent was evaporated under reduced pressure and the product isolated by column chromatography as purple powder [silica, toluene/ethyl acetate (20:1), *R*_f = 0.47]. Yield 40% (43.2 mg, 0.045 mmol). C₅₁H₃₁F₁₀N₅O₄ (967.81).



¹**H-NMR (CDCl₃):** $\delta = -2.84$ (s, 2 H, H^{pyrrole-NH}), 1.65 (s, 9 H, H²³), 4.13 (s, 3 H, H¹⁵₆), 6.86 (s, 1 H, H^{Boc-NH}), 7.81 (d, ³*J*_{HH} = 8.3 Hz, 2 H, H⁵₃), 8.14 (d, ³*J*_{HH} = 8.3 Hz, 2 H, H⁵₂), 8.30 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.47 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.81 (pt, ³*J*_{HH} = 4.5 Hz, 4 H, H^{pyrrole}), 8.89 (d, ³*J*_{HH} = 4.8 Hz, 2 H, H^{pyrrole}), 9.00 (d, ³*J*_{HH} = 4.8 Hz, 2 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 28.5$ (s, C²³), 52.6 (s, C¹⁵₆), 81.1 (s, C²²), 116.9 (s, C⁵₃), 119.8 (s, C¹⁵), 121.5 (s, C⁵), 128.1 (s, C¹⁵₃), 129.8, 132.3, 132.5 (C^{2,3,7,8,12,13,17,18}), 130.0 (s, C¹⁵₄), 134.6 (s, C¹⁵₂), 135.2 (s, C⁵₂), 136.3, 138.8, 145.3, 147.8 (4 C), (m, C¹⁰₁, C¹⁰₂, C¹⁰₃, C¹⁰₄), 135.7 (s, C⁵₁), 138.6 (s, C⁵₂), 146.0 (s, C¹⁵₁), 153.0 (s, C²¹), 167.2 (s, C¹⁵₅) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -162.3 \text{ (ddd, } {}^{3}J_{FF} = 23 \text{ Hz}, \, {}^{3}J_{FF} = 21 \text{ Hz}, \, {}^{5}J_{FF} = 7 \text{ Hz}, \, 4 \text{ F}, \, \mathrm{F}^{10/20}_{3/3},), \, -152.6 \text{ (t, } {}^{3}J_{FF} = 21 \text{ Hz}, \, 2 \text{ F}, \, \mathrm{F}^{10/20}_{4/4}), \, -137.19 \text{ (dd, } {}^{3}J_{FF} = 24 \text{ Hz}, \, {}^{5}J_{FF} = 8 \text{ Hz}, \, 4 \text{ F}, \, \mathrm{F}^{10/20}_{2/2}) \text{ ppm.}$

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3435 (b w,NH^{Boc}), 3320 (w, NH^{pyrrole}), 2928 (w, CH), 2862 (w, CH), 1724 (m, CO), 1708 (m, CO), 1520 (m), 1494 (m), 1282 (m, C-O-C), 1151 (s, CF), 807 (vs).

MS (FD): m/z (%) = 866.8 (12) [M-COOC(CH₃)₃]⁺, 966.7 (100) [M]⁺.

MS (ESI): m/z (%) = 968.24 (100) [M+H]⁺, 1936.49 (4) [2M+H]⁺.

HR-MS (ESI): obs. m/z = 968.2295; calcd. for $[M+H]^+ 968.2336$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 417 (62.07), 511 (1.56), 545 (1.01), 588 (1.46), 643 (0.68).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 648 (1.00), 713 (0.50).

Quantum yield: $\Phi = 0.0377$.

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [**V**] = -1.820, -1.410, 0.820, 1.020.

15-(4-Carbomethoxyphenyl)-5-(4-aminophenyl)-10,20-bis(2,3,4,5,6-pentafluorophenyl) porphyrin (3b). Porphyrin **Boc-3b** (40 mg, 0.041 mmol) was dissolved in 10 mL of CH_2Cl_2 and 10 mL of TFA was added. The solution was stirred at room temperature for 40 min. The solution was neutralised with saturated solution of NaHCO₃ and diluted with 10 mL CH_2Cl_2 . The organic layer was separated, washed with water (3×), dried with Na₂SO₄ and concentrated under reduced pressure. The yield of **3b** was 95% (33.8 mg, 0.039 mmol, purple powder). $C_{46}H_{23}F_{10}N_5O_2$ (867.69).



¹**H-NMR (CDCl₃):** $\delta = -2.82$ (s, 2 H, H^{pyrrole-NH}), 4.06 (s, 2 H, H^{amine-NH}), 4.10 (s, 3 H, H¹⁵₆), 7.08 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H⁵₂), 8.28 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H¹⁵₂), 8.44 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H¹⁵₃), 8.76 (pt, ³*J*_{HH} = 4.5 Hz, 4 H, H^{pyrrole}), 8.85 (d, ³*J*_{HH} = 4.8 Hz, 2 H, H^{pyrrole}), 9.04 (d, ³*J*_{HH} = 4.8 Hz, 2 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 113.6 \text{ (s, } C_{3}^{5}\text{)}, 52.5 \text{ (s, } C_{6}^{15}\text{)}, 122.7 \text{ (s, } C_{5}^{5}\text{)}, 119.5 \text{ (s, } C_{1}^{15}\text{)}, 128.1 \text{ (s, } C_{3}^{15}\text{)}, 129.6, 132.2, 133.1 (C^{2,3,7,8,12,13,17,18}), 130.0 \text{ (s, } C_{4}^{15}\text{)}, 131.2 \text{ (s, } C_{1}^{5}\text{)}, 134.6 \text{ (s, } C_{2}^{15}\text{)}, 135.9 \text{ (s, } C_{2}^{5}\text{)}, 146.1 \text{ (s, } , C_{1}^{15}\text{)}, 146.5 \text{ (s, } C_{4}^{5}\text{)}, 167.2 \text{ (s, } C_{5}^{15}\text{)} \text{ ppm.}$

¹⁹**F-NMR (CDCl₃):** $\delta = -162.0 \text{ (ddd, } {}^{3}J_{\text{FF}} = 23 \text{ Hz}, \, {}^{3}J_{\text{FF}} = 21 \text{ Hz}, \, {}^{5}J_{\text{FF}} = 8 \text{ Hz}, \, \mathrm{F}^{10/20}_{3/3}), -152.3 \text{ (t, } {}^{3}J_{\text{FF}} = 21 \text{ Hz}, \, 2 \text{ F}, \, \mathrm{F}^{10/20}_{4/4}), -137.19 \text{ (dd, } {}^{3}J_{\text{FF}} = 24 \text{ Hz}, \, {}^{5}J_{\text{FF}} = 8 \text{ Hz}, \, 4 \text{ F}, \, \mathrm{F}^{10/20}_{2/2}) \text{ ppm.}$

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3417 (b m, NH^{amine}), 3314 (w, NH^{pyrrole}), 2919 (w, CH), 2849 (w, CH), 1725 (m, CO), 1614 (m), 1517 (vs), 1496 (vs), 1274 (s, C-O-C), 1108 (s, CF), 990 (vs), 920 (m), 802 (m).

MS (FD): m/z (%) = 867.27 (100) [M]⁺.

MS (ESI): m/z (%) = 868.17 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 868.1777; calcd. for $[M+H]^+ 868.1770$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 419 (73.13), 513 (2.59), 549 (0.95), 590 (0.98), 645 (0.43).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 654 (1.00), 717 (0.42).

Quantum yield: $\Phi = 0.0802$.

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}[V] = -1.82$ (qrev.), -1.39 (qrev.), 0.65 (irr.), 0.79 (irr.).

N-(4-trifluoromethylbenzoyl)morpholine was prepared according to the literature.^[S4]

N-(4-fluorobenzoyl)morpholine was synthesised according to a general procedure for the preparation of *N*-arylmorpholines^[S4]. 33.6 g (0.24 mol) of 4-fluorobenzoic acid was dissolved in 38 mL (0.48 mol) thionyl chloride and heated under reflux overnight. The excess of thionyl chloride was removed under reduced pressure. The residue was dissolved in 100 mL dry CH_2Cl_2 and cooled down to 0°C. A solution of morpholine (60.00 g, 0.70 mol) in 70 ml CH_2Cl_2 was added slowly to the acid chloride solution, so that the temperature remains below 5°C. The colourless suspension was warmed to room temperature and stirred for 10 min. The mixture was washed with water (3×), 2M HCl (3×) and again with water (3×). The organic layer was dried with Na₂SO₄ and the solvent was removed under reduced pressure giving the product as yellow liquid (28.3 g, 0.135 mol, 56%). $C_{11}H_{12}FNO_2$ (209.22).



¹**H-NMR (CDCl₃):** δ = 3.63 (br. m, 2 H, H^{7,8,9,10}), 7.03 (m, ³*J*_{HH/FH} = 8.6 Hz, 2 H, H³), 7.69 (dd, ³*J*_{HH} = 8.4 Hz, ³*J*_{FH} = 5.4 Hz, 2 H, H²) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 66.6$ (s, C^{7,8,9,10}), 115.4 (d, ${}^{2}J_{FH} = 21.8$ Hz, C³), 129.2 (d, ${}^{3}J_{FH} = 8.5$ Hz, C²), 131.1 (d, ${}^{4}J_{FH} = 3.4$ Hz, C¹), 163.2 (d, ${}^{1}J_{FH} = 250.0$ Hz, C⁴), 169.2 (s, C⁶) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -110.0$ (tt, ${}^{3}J_{\text{FH}} = 8.6$ Hz, ${}^{4}J_{\text{FH}} = 5.4$ Hz) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3064 (w, CH), 2967 (w, CH), 2918 (w, CH), 2856 (w, CH), 1635 (vs, CO), 1510 (w), 1433 (s), 1281 (s, C-O-C), 1121 (s), 1108 (s, CF), 837 (s), 754 (s).

MS (FD): m/z (%) = 209.3 (100) [M]⁺.

MS (ESI): m/z (%) = 210.09 (21, [M]⁺), 210.09 (100, [M+H]⁺).

HR-MS (ESI): obs. m/z = 210.0930; calcd. for [M+H]⁺ 210.0930.

General procedure for the preparation of 1,9-diacyldipyrromethanes.^[S4] *N*-aroylmorpholine (1 eq.) and phosphorous oxytrichloride (2 eq.) were heated at 65°C under nitrogen for 3 h. The dark solution was cooled to room temperature and diluted with 1,2-dichloroethane. 5-(4-nitrophenyl)dipyromethane^[S6] (0.25 eq.) was added and the solution was stirred under reflux for 2 h and quenched by addition of a saturated aqueous solution of sodium acetate and heated to reflux for 1 h. After cooling to room temperature the mixture was diluted with CH₂Cl₂ and the organic layer was separated. After washing with water (3×) and drying with Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by chromatography [silica, CH₂Cl₂/ethyl acetate (15:1), $R_f = 0.60$].

1,9-bis(4-fluorobenzoyl)-5-(4-nitrophenyl)dipyrromethane. 28.30 g, (0.14 mol) *N*-(4-fluorobenzoyl)morpholine, 41.5 g, (0.28 mol) phosphorous oxytrichloride, 200 mL 1,2-dichloroethane, 18.70 (0.07 mol) 5-(4-nitrophenyl)dipyromethane^[S6], 150 mL CH₂Cl₂ and 360 mL saturated aqueous solution of sodium acetate. Yield 16.90 g (0.033 mol, 47%), red-brown solid. $C_{29}H_{21}F_2N_3O_4$ (511.49).



¹**H-NMR (CDCl₃):** δ = 5.83 (s, 1H, H⁵), 5.93 (ps. t, ³*J*_{HH} = 3.0 Hz, 2 H, H⁷), 6.48 (dd, ³*J*_{HH} = 3.8 Hz, ⁴*J*_{HH} = 2.3 Hz, 2 H, H⁸), 7.08 (t, ³*J*_{HH} = 8.6 Hz, 4 H, H¹³), 7.74 (dd, ³*J*_{HH} = 8.8 Hz, ³*J*_{HF} = 5.4 Hz, 4 H, H¹²), 7.80 (d, ³*J*_{HH} = 8.7 Hz, 2 H, H³), 8.24 (d, ³*J*_{HH} = 8.7 Hz, 2 H, H²), 12.18 (br. s, 2 H, NH) ppm.

¹³C{¹H}-NMR (CDCl₃): δ = 44.8 (s, C⁵), 111.5 (s, C⁷), 115.3 (d, ²*J*_{FH} = 21.7 Hz, C¹³), 120.8 (s, C⁸), 124.1 (s, C²), 129.8 (s, C³), 131.1 (s, C⁹), 132.0 (d, ²*J*_{FH} = 9.0 Hz, C¹²), 133.9 (d, ⁴*J*_{FH} = 2.9 Hz, C¹¹), 139.6 (s, C⁶), 147.4 (s, C⁴), 147.6 (s, C¹), 165.4 (d, ¹*J*_{FH} = 253.9 Hz, C¹⁴), 183.2 (s, C¹⁰) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -106.6$ (tt, ³ $J_{\text{FH}} = 8.6$ Hz, ⁴ $J_{\text{FH}} = 5.4$ Hz) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3230 (b, NH), 3099 (w, CH), 1611 (vs), 1600 (vs), 1517 (m, NO), 1476 (vs), 1344 (vs, NO), 1232 (s, C-O-C), 1149 (s, CF), 886 (m), 754 (m).

MS (FD): m/z (%) = 511.3 (100) [M]⁺, 255.8 (1.07) [M]²⁺.

MS (ESI): m/z (%) = 512.14 (16, [M+H]⁺), 1023.30 (5) [2M+H]⁺.

HR-MS (ESI): obs. m/z = 512.1406; calcd. for $[M+H]^+ 512.1422$.

1,9-bis(4-trifluoromethylbenzoyl)-5-(4-nitrophenyl)dipyrromethane. 50.0 g, (0.24 mol) *N*-(4-trifluoromethylbenzoyl)morpholine, 76.7 g, (0.58 mol) phosphorous oxytrichloride, 350 mL 1,2-dichloroethane, 16.0 (0.06 mol) 5-(4-nitrophenyl)dipyromethane^[S6], 150 mL CH₂Cl₂ and 360 mL saturated aqueous solution of sodium acetate. Yield 27.0 g (0.044 mol, 74%), red-brown solid. $C_{31}H_{19}F_6N_3O_4$ (611.49).



¹**H-NMR (CDCl₃):** δ = 5.86 (s, 1H, H⁵), 6.03 (m, 2 H, H⁷), 6.57 (m, 2 H, H⁸), 7.68 (d, ³J_{HH} = 8.0 Hz, 4 H, H¹²), 7.80 (m, 6 H, H^{3/13}), 8.28 (d, ³J_{HH} = 8.5 Hz, 2 H, H²), 12.09 (s, 2 H, NH) ppm.

¹³C{¹H}-NMR (CDCl₃): δ = 44.8 (s, C⁵), 112.0 (s, C⁷), 121.5 (s, C⁸), 122.1 (s, C¹¹), 124.3 (s, C²), 125.3 (s, C¹²), 129.8 (s, C^{3/13}), 131.1 (s, C⁹), 133.6 (q, ¹*J*_{CF} = 32.7 Hz, C¹⁵), 140.1 (s, C⁶), 140.6 (s, C¹⁴), 147.0 (s, C⁴), 147.6 (s, C¹), 183.4 (s, C¹⁰) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -62.9$ (s) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3255 (b, NH), 3107 (w, CH), 1708 (w, CO), 1618 (s), 1528 (m, NO), 1331 (vs, NO), 1249 (w, C-O-C), 1169 (m, CF), 889 (m), 767 (m).

MS (FD): m/z (%) = 611.22 (100) [M]⁺.

MS (ESI): m/z (%) = 610.15 (9, [M–H]⁺).

HR-MS (ESI): obs. m/z = 610.1175; calcd. for $[M-H]^+ 610.1166$.

General procedure for the preparation of porphyrins 2c and 2d.^[S5] To a stirred solution of 1,9diacyldipyrromethane in THF/methanol (10 : 1) NaBH₄ (20 eq.) was added under nitrogen at room temperature and the mixture was stirred until TLC indicated consumption of starting material. The reaction was quenched with a saturated solution of NH₄Cl_{aq} and diluted with CH₂Cl₂. The organic layer was separated, washed with water (3×) and dried with NaSO₄. After removing the solvent the dipyrromethane-dicarbinol was obtained as a foamlike solid. То this brown residue was added 5-(4-benzoic acid methylester)dipyrromethane^[S6] (1.2 eq.) and acetonitrile. The suspension was dipped in an ultrasonic bath to dissolve the compounds. This solution was added to a pre-cooled solution of DMF and TFA in acetonitrile (0°C) in small portions over 30 min. After stirring for 10 min 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) was added and the mixture was stirred for 1 h. TEA was added to quench the reaction and the mixture was concentrated under reduced pressure. The products were purified by column chromatography [silica, $CH_2Cl_2].$

4-[15-(4-nitro-phenyl)-10,20-di-(4-fluoro)phenylporphyrin-5-yl]methyl benzoate (2c). 6.81 g (180 mmol) NaBH₄, 440 mL THF/methanol (10:1), 9.37 g (0.033 mol) 1,9-bis(4-fluorobenzoyl)-5-(4-nitrophenyl)dipyrromethane, 17.09 g (0.040 mol) 5-(4-methyl benzoate)dipyrromethane, 2 L acetonitrile, 22 mL DMF, 30.8 mL TFA, 28.60 g (0.13 mol) DDQ, 31 mL TEA. [silica, CH_2Cl_2 , $R_f = 0.78$]. Yield 2.37 g (3.14 mmol, 9.5%), purple powder. $C_{46}H_{29}F_2N_5O_4$ (753.75).



¹**H-NMR (CDCl₃):** $\delta = -2.81$ (s, 2 H, H^{pyrrole-NH}), 4.12 (s, 3 H, H¹⁵₆), 7.47 (t, ³*J*_{HH} = 8.6 Hz, 4 H, H^{10/20}_{3/3}), 8.17 (dd, ³*J*_{HH} = 8.4 Hz, ³*J*_{HF} = 3.1 Hz, 4 H, H^{10/20}_{2/2}), 8.30 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.39 (d, ³*J*_{HH} = 8.5 Hz, 2 H, H⁵₂), 8.46 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.65 (d, ³*J*_{HH} = 8.6 Hz, 2 H, H⁵₃), 8.76 (d, ³*J*_{HH} = 4.7 Hz, 2 H, H^{pyrrole}), 8.85 (m, 6 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 52.5$ (s, C¹⁵₆), 113.9 (d, ²*J*_{CF} = 21.3 Hz , C^{10/20}_{3/3}), 117.4 (s, C⁵), 119.6 (s, C^{10/20}), 119.6 (s, C¹⁵) 121.9 (s, C⁵₃), 128.0 (s, C¹⁵₃), 129.8 (s, C¹⁵₄), 134.5 (s, C¹⁵₂), 131.8 (br. S, C^{pyrrole}), 135.1 (s, C⁵₂), 135.7 (d, ³*J*_{CF} = 8.8 Hz , C^{10/20}_{2/2}), 137.6 (d, ⁴*J*_{CF} = 3.4 Hz, C^{10/20}_{1/1}), 146.6 (s, C¹⁵₁), 147.4 (s, C⁵₁), 147.8 (s, C⁵₄), 148.9 (s, C^{pyrrole}), 165.7 (d, ¹*J*_{FH} = 248.1 Hz, C^{10/20}_{4/4}), 167.2 (s, C¹⁵₅) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -114.2$ (tt, ³ $J_{\text{FH}} = 8.6$ Hz, ⁴ $J_{\text{FH}} = 5.4$ Hz).

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3433 (w, NH), 3315 (w, CH), 1724 (s, CO), 1504 (s), 1525 (s, NO), 1348 (vs, NO), 1282 (s, C-O-C), 1105 (s, CF), 798 (vs).

MS (FD): m/z (%) = 753.4 (100) [M]⁺.

MS (ESI): m/z (%) = 754.25 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 754.2260; calcd. for $[M+H]^+ 754.2266$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 421 (29.55), 517 (1.35), 553 (0.58), 592 (0.41), 648 (0.32).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 652 (1.00), 716 (0.36).

Quantum yield: $\Phi = 0.1024$.

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.150, -1.445 (2e), 0.690, 0.950.

4-[15-(4-nitro-phenyl)-10,20-di-(4-trifluoromethyl)phenylporphyrin-5-yl]methyl benzoate (2d). 1.96 g, (51.80 mmol) NaBH₄, 30.8 mL THF/methanol (10:1), 1.00 g (1.64 mmol) 1,9-bis(4- trifluoromethylbenzoyl)-5-(4-nitrophenyl)dipyrromethane, 21.22 g (2.38 mmol) 5-(4-methyl benzoate)dipyrromethane, 568 mL acetonitrile, 2.4 mL DMF, 3.4 mL TFA, 3.12 g (13.74 mmol) DDQ, 3.6 mL TEA. [silica, CH₂Cl₂, $R_f = 0.68$]. Yield 308 mg (0.37 mmol, 22%), purple powder. C₄₈H₂₉F₆N₅O₄ (853.77).



¹**H-NMR** (**CDCl**₃): $\delta = -2.82$ (s, 2 H, H^{pyrrole-NH}), 4.13 (s, 3 H, H¹⁵₆), 8.05 (d, ³*J*_{HH} = 8.0 Hz, 4 H, H^{10/20}_{3/3}), 8.30 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.34 (d, ³*J*_{HH} = 8.3 Hz, 4 H, H^{10/20}_{2/2}), 8.41 (d, ³*J*_{HH} = 8.4 Hz, 2 H, H⁵₂), 8.47 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.66 (d, ³*J*_{HH} = 8.5 Hz, 4 H, H⁵₃), 8.78 (s, ³*J*_{HH} = 4.6 Hz, 2 H, H^{pyrrole}), 8.91 (m, 4 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 52.5$ (s, C¹⁵₆), 117.6 (d, C⁵), 119.2 (s, C^{10/20}), 120.0 (s, C¹⁵), 122.0 (s, C⁵₃), 123.9 (d, ${}^{4}J_{CF} = 3.3$ Hz, C^{10/20}_{3/3}), 125.9 (s, C^{10/20}_{4/4}), 128.1 (s, C¹⁵₃), 129.9 (s, C¹⁵₄), 130.6 (q, ${}^{1}J_{CF} = 32.6$ Hz, C^{10/20}_{5/5}), 131.5 (br. s, C^{pyrrole 2,3,7,8,12,13,17,18}), 134.5 (s, C¹⁵₂), 134.6 (s, C^{10/20}_{2/2}), 135.1 (s, C⁵₂), 145.4 (s, C^{10/20}_{1/1}), 146.4 (s, C¹⁵₁), 147.9 (s, C⁵₄), 148.7 (s, C⁵₁), 167.2 (s, C¹⁵₅) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -62.0$ (s) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3433 (w, NH), 3320 (w, CH), 2925 (w, CH), 2849 (w, CH), 1718 (w, CO), 1504 (s), 1524 (w, NO), 1322 (vs, NO), 1274 (w, C-O-C), 1164 (w, CF), 1066 (s), 796 (vs).

MS (FD): m/z (%) = 853.4 (100) [M⁺].

MS (ESI): m/z (%) = 854.25 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 854.2200; calcd. for $[M+H]^+ 854.2202$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 419 (15.1), 515 (0.42), 549 (0.17), 589 (0.13), 644 (0.07).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 650 (1.00), 715 (0.44).

Quantum yield: $\Phi = 0.0608$

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.020, -1.470 (2e), 0.750, 1.030.

General procedure for the prepation of porphyrins 3c and $3d^{[S5]}$. Under nitrogen 1 eq. nitro-porphyrin 2c or 2d was suspended in conc. aqueous HCl and SnCl₂ (14 eq.) was added. The mixture was stirred under reflux for 1 – 2 h until TLC indicated consumption of starting material. After cooling to room temperature the solution was neutralised with conc. aqueous ammonia and extracted with ethyl acetate. The combined organic phases ware dried with NaSO₄ and the solvent was removed under reduced pressure. The products were purified by column chromatography [silica, toluene : ethyl acetate = 20 : 1].

15-(4-Carbomethoxyphenyl)-5-(4-aminophenyl)-10,20-bis-(4-fluorophenyl)porphyrin (3c). 1.00 g (1.33 mmol) porphyrin **1c**, 424 mL conc. aquaeous HCl, 4.33 g (0.019 mol) SnCl₂. [silica, toluene : ethyl acetate = $20 : 1, R_f = 0.36$]. Yield 470 mg (0.65 mmol, 49%), purple powder. C₄₆H₃₁F₂N₅O₂ (723.77).



¹**H-NMR (CDCl₃):** $\delta = -2.79$ (s, 2 H, H^{pyrrole-NH}), 4.11 (s, 3 H, H¹⁵₆), 7.02 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H⁵₃), 7.44 (ps. t, ³*J*_{HH} = 8.6 Hz, 4 H, H^{10/20}_{3/3}), 7.99 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H⁵₂), 8.17 (dd, ³*J*_{HH} = 8.3 Hz, ³*J*_{HF} = 5.4 Hz, 4 H, H^{10/20}_{2/2}), 8.29 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.44 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.80 (m, 6 H, H^{pyrrole}), 8.96 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 52.4$ (s, C¹⁵₆), 113.5 (s, C⁵₃), 113.7 (d, ²*J*_{CF} = 21.4 Hz , C^{10/20}_{3/3}), 118.3 (s, C¹⁵), 118.9 (s, C^{10/20}), 121.5 (s, C⁵), 127.9 (s, C¹⁵₃), 128.5 (s, C^{pyrrole}), 129.6 (s, C¹⁵₄), 131.0 (br. s, C^{pyrrole}), 132.1 (s, C⁵₁), 134.6 (s, C¹⁵₂), 135.7 (d, ³*J*_{CF} = 8.8 Hz , C^{10/20}_{2/2}), 135.7 (s, C⁵₂), 138.0 (d, ⁴*J*_{CF} = 3.2 Hz, C^{10/20}_{1/1}), 146.2 (s, C⁵₄), 146.9 (s, C¹⁵₁), 162.9 (d, ¹*J*_{FH} = 247.3 Hz, C^{10/20}_{4/4}), 167.3 (s, C¹⁵₅) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -114.7$ (tt, ³ $J_{FH} = 8.6$ Hz, ⁴ $J_{FH} = 5.4$ Hz) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3452 (b, NH^{amine}), 3386 (b, NH^{amine}), 3315 (b, NH^{pyrrole}), 1724 (s, CO), 1504 (s), 1280 (vs, C-O-C), 1155 (s, CF), 802 (vs).

MS (FD): m/z (%) = 723.4 (100) [M]⁺.

MS (ESI): m/z (%) = 724.2 (100) [M+H]⁺, 1448.5 (1) [2M+H]⁺.

HR-MS (ESI): obs. m/z = 724.2522; calcd. for $[M+H]^+ 724.2524$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 421 (30.42), 517 (1.54), 554 (0.90), 593 (0.51), 649 (0.44).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 656 (1.00), 719 (0.29).

Quantum yield: $\Phi = 0.1405$.

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.980, -1.650, 0.51 (irr.).

15-(4-carbomethoxyphenyl)-5-(4-aminophenyl)-10,20-bis-(4-trifluoromethylphenyl) porphyrin (3d).

0.66 g (0.77 mmol) porphyrin **2d**, 100 mL conc. aqueous HCl, 3.00 g (13.2 mmol) SnCl₂. [silica, toluene : ethyl acetate = 20 : 1, $R_f = 0.41$]. Yield 310 mg (0.38 mmol, 49%), purple powder. C₄₈H₃₁F₆N₅O₂ (823.75).



¹**H-NMR (CDCl₃):** $\delta = -2.78$ (s, 2 H, H^{pyrrole-NH}), 4.07 (br. s, 2 H, H^{amine-NH}), 4.12 (s, 3 H, H¹⁵₆), 7.09 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H⁵₂), 8.03 (d, ³*J*_{HH} = 8.0 Hz, 4 H, H^{10/20}_{3/3}), 8.29 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.34 (d, ³*J*_{HH} = 7.8 Hz, 4 H, H^{10/20}_{2/2}), 8.45 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.78 (m, 6 H, H^{pyrrole}), 8.98 (d, ³*J*_{HH} = 4.7 Hz, 2 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (CDCl₃): $\delta = 52.5$ (s, C¹⁵₆), 113.5 (s, C⁵₃), 118.5 (d, C^{10/20}), 118.7 (s, C¹⁵), 121.9 (s, C⁵), 123.7 (d, ${}^{4}J_{CF} = 3.2$ Hz, C^{10/20}_{3/3}), 125.9 (s, C^{10/20}_{4/4}), 128.0 (s, C¹⁵₃), 129.7 (s, C¹⁵₄), 130.1 (q, ${}^{1}J_{CF} = 32.6$ Hz, C^{10/20}_{5/5}), 130.9 (br.s, C^{2,3,7,8,12,13,17,18}), 131.9 (s, C⁵₁), 134.6 (s, C^{10/20/15}_{2/2/2}), 135.7 (s, C⁵₂), 145.8 (s, C^{10/20}_{1/1}), 146.3 (s, C⁵₄), 146.7 (s, C¹⁵₁), 167.3 (s, C¹⁵₅) ppm.

¹⁹**F-NMR (CDCl₃):** $\delta = -62.0$ (s) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3460 (b, NH^{amine}), 3386 (b, NH^{amine}), 3321 (b, NH^{pyrrole}), 1724 (s, CO), 1609 (s), 1315 (vs), 1274 (vs, C-O-C), 1167 (s, CF), 807 (vs).

MS (FD): m/z (%) = 823.4 (100) [M]⁺.

MS (ESI): m/z (%) = 824.30 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 824.2468; calcd. for $[M+H]^+ 824.2460$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 421 (19.9), 517 (0.38), 553 (0.20), 592 (0.11), 650 (0.10).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 656 (1.00), 719 (0.28).

Quantum yield: $\Phi = 0.1189$.

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}[V] = -1.900, -1.560, 0.53$ (irr.).

$[15-(4-Carbomethoxyphenyl)-5-(4-aminophenyl)-10, 20-bis-(4-fluorophenyl)\ porphyrinato] zinc(II)\ (Zn-interval)-10, 20-bis-(4-fluorophenyl)\ porphyrinato] zinc(II)\ porphyrinato] zinc(I$

3c). Porphyrin **3c** (94 mg, 0.13 mmol) and zinc acetate dihydrate (110.2 mg, 0.65 mmol) were stirred overnight in of CH₂Cl₂ (10 mL). After concentration under reduced pressure the product was isolated by column chromatography [silica, toluene : ethyl acetate = 20 : 1, R_f = 0.36]. Yield 102 mg (0.13 mmol, 97%), purple powder. C₄₆H₂₉F₂N₅O₂Zn (787.16).



¹**H-NMR** (**d**₈-**THF**): δ = 4.05 (s, 3 H, H¹⁵₆), 4.90 (s, 2 H, NH₂), 6.96 (d, ³J_{HH} = 8.1 Hz, 4 H, H⁵₃), 7.48 (ps. t, ³J_{HH} = 8.6 Hz, 4 H, H^{10/20}_{3/3}), 7.86 (d, ³J_{HH} = 8.1 Hz, 2 H, H⁵₂), 8.20 (dd, ³J_{HH} = 8.1 Hz, ³J_{HF} = 5.6 Hz, 4 H, H^{10/20}_{2/2}), 8.30 (d, ³J_{HH} = 8.0 Hz, 2 H, H¹⁵₂), 8.41 (d, ³J_{HH} = 8.0 Hz, 2 H, H¹⁵₃), 8.82 (m, 6 H, H^{pyrrole}), 9.00 (d, 2 H, ³J_{HH} = 4.6 Hz H^{pyrrole}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): δ = 52.5 (s, C¹⁵₆), 113.3 (s, C⁵₃), 114.2 (d, ²*J*_{CF} = 21.4 Hz , C^{10/20}_{3/3}), 119.7 (s, C¹⁵), 120.3 (s, C^{10/20}), 123.9 (C⁵), 128.5 (s, C¹⁵₃), 130.5 (s, C¹⁵₄), 131.9, 131.9, 132.4, 133.2, (8 C), (s, C^{pytrole 2,3,7,8,12,13,17,18}), 132.3 (s, C⁵₁), 135.6 (s, C¹⁵₂), 136.5 (s, C⁵₂), 136.8 (d, ³*J*_{CF} = 7.9 Hz, C^{10/20}_{2/2}), 140.8 (d, ⁴*J*_{CF} = 3.2 Hz, C^{10/20}_{1/1}), 149.2 (s, C⁵₄), 149.5 (s, C¹⁵₁), 150.6, 151.0, 151.3, 152.2 (8 C), (s, C^{1,4,6,9,11,14,16,19}), 163.9 (d, ¹*J*_{FH} = 245.6 Hz, C^{10/20}_{4/4}), 167.5 (s, C¹⁵₅) ppm.

¹⁹**F-NMR (d₈-THF):** $\delta = -118.7$ (m, ³ $J_{\text{FH}} = 8.6$ Hz, ⁴ $J_{\text{FH}} = 5.4$ Hz).

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3438 (b, NH^{amine}), 3386 (b, NH^{amine}), 2918 (w, CH), 2849 (w, CH), 1725 (vs, CO), 1607 1503 (m), 1274 (vs, C-O-C), 1156 (s, CF), 1109 (m), 802 (s).

MS (FD): m/z (%) = 785.4 (100) [M]⁺.

MS (ESI): m/z (%) = 785.17 (100) [M]⁺.

HR-MS (ESI): obs. m/z = 785.1579; calcd. for [M]⁺ 785.1581.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 424 (38.11), 551 (2.00), 593 (0.53).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 606 (1.00), 652 (0.63).

Quantum yield: $\Phi = 0.0194$.

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.060, -1.730, 0.415 (irr.).

[10,20-Bis(2,4,6-trimethylphenyl)-5,15-bis[4-(methoxycarbonyl)] porphyrinato]zinc(II) (Zn-1a). Porphyrin 1a (35 mg, 0.042 mmol) and zinc acetate dihydrate (46.67 mg, 0.21 mmol) were stirred overnight in CH₂Cl₂ (5 mL). After concentration under reduced pressure the product was isolated by column chromatography [silica, CH₂Cl₂, $R_f = 0.80$]. Yield 30 mg (0.034 mmol, 81%), purple powder. C₅₄H₄₄N₄O₄Zn (878.35).



¹**H-NMR** (**d**₈-**THF**): $\delta = 1.84$ (s, 12 H, H¹⁰₅), 2.61 (s, 6 H, H¹⁰₆), 4.04 (s, 6 H, H⁵₆), 7.30 (s, 4 H, H^{10/20}_{3/3}), 8.31 (d, ³*J*_{HH} = 6.8 Hz, 4 H, H⁵₂), 8.39 (d, ³*J*_{HH} = 7.9 Hz, 4 H, H⁵₃), 8.68 (d, ³*J*_{HH} = 4.4 Hz, 4 H, H^{pyrrole}), 8.75 (d, ³*J*_{HH} = 4.3 Hz, 4 H, H^{pyrrole}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): $\delta = 21.7$ (s, C^{10/20}_{6/6}), 22.1 (s, C^{10/20}_{5/5}), 52.5 (s, C⁵₆), 119.9 (s, C⁵), 128.4 (s, C⁵₃), 128.7 (s, C^{10/20}_{3/3}), 130.5 (C⁵₄), 131.3, 132.6 (C^{2,3,7,8,12,13,17,18}), 135.5 (s, C⁵₂), 138.4 (C^{10/20}_{4/4}), 140.0 (C^{10/20}_{2/2}), 140.7 (C^{10/20}_{1/1}), 149.4 (C⁵₁), 150.5, 150.9 (C^{1,4,6,9,11,14,16,19}), 167.5 (s, C⁵₅) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3425 (b, NH^{pytrole}), 2922 (w, CH), 2850 (w, CH), 1722 (vs, CO), 1608 (s), 1386 (vs), 1278 (vs, C-O-C), 1114 (s), 800 (w).

MS (ESI): m/z (%) = 877.33 (29) [M+H]⁺.

HR-MS (ESI): obs. m/z = 877.2725; calcd. for $[M]^+ 877.2732$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 421 (44.4), 548 (1.88), 590 (0.36).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 598 (0.97), 647(1.00).

Quantum yield: $\Phi = 0.1001$.

Lifetime: τ [ns] = 2.53 (100%).

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.150, -1.780, 0.439, 0.739.

General procedure for *N*-acylation^[S7]: To a mixture of the amino porphyrin (1 eq.) and acetyl chloride (35 eq.) iodine (1 eq.) was added and the mixture was stirred at room temperature over night. The iodine was destroyed by addition of a saturated aqueous $Na_2S_2O_3$ solution. CH_2Cl_2 was added and the organic phase was separated, washed with saturated aqueous $NaHCO_3$ solution (2×), brine (1×), water (2×) and dried with Na_2SO_4 . The solvent was removed under reduced pressure and the residue was filtered over a silica pad.

5-(4-(*N*-Acetylaminophenyl))-10,20-bis(2,4,6-trimethylphenyl)-15-(4-(methoxycarbonyl-phenyl))

porphyrin (Ac-3a). 40.0 mg (0.052 mmol) Porphyrin 3a, 12.9 mL (0.182 mol) acetyl chloride, 13.1 mg (0.052 mmol) iodine. [silica, toluene : ethyl acetate = 1 : 1, $R_f = 0.38$]. Yield: 34 mg (0.042 mmol, 81%), purple powder. $C_{54}H_{47}N_5O_3$ (813.98).



¹**H-NMR** (**d**₈-**THF**): $\delta = -2.50$ (s, 2 H, H^{pyrrole-NH}), 1.83 (s, 12 H, H^{10/20}_{5/5}), 2.19 (s 3H, H⁵₆), 2.59 (s, 6 H, H^{10/20}_{6/6}), 4.04 (s, 3 H, H¹⁵₆), 7.30 (s, 4 H, H^{10/20}_{3/3}), 8.03 (d, ³*J*_{HH} = 8.4 Hz, 2 H, H⁵₃), 8.10 (d, 2 H, ³*J*_{HH} = 8.4 Hz, H⁵₂), 8.32 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H¹⁵₂), 8.41 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.66 (ps. t, ³*J*_{HH} = 4.5 Hz, 4 H, H^{pyrrole}), 8.74 (d, ³*J*_{HH} = 4.6 Hz, 2 H, H^{pyrrole}), 8.84 (d, ³*J*_{HH} = 4.6 Hz, 2 H, H^{pyrrole}), 9.40 (s, 1 H, H^{amide-NH}) ppm. ¹³C{¹H}-NMR (**d**₈-**THF**): $\delta = 21.2$ (s, C^{10/20}_{5/5}), 21.7 (s, C^{10/20}_{6/6}), 24.4 (s, C⁵₆), 52.5 (s, C¹⁵₆), 118.2 (s, C⁵₃), 119.0 (s, C¹⁵), 119.3 (s, C^{10/20}, 121.1 (C⁵), 128.8 (s, C¹⁵₃), 128.9 (s, C^{10/20}_{3/3}), 130.9 (C¹⁵₄), 135.6 (C⁵₂), 135.7 (s, C¹⁵₂), 137.4, (C⁵₁), 138.8 (s, C^{10/20}_{4/4}), 139.6 (s, C^{10/20}_{2/2}), 140.1 (s, C^{10/20}_{1/1}), 141.0 (C⁵₄) 148.0 (s, C¹⁵₁), 167.4 (s, C¹⁵₅) 168.8 (s, C⁵₅) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3406 (b, NH^{pyrrole}, NH^{amide}), 2954 (m, CH), 2921 (m, CH), 1723 (s, CO), 1702 (s, CO), 1513 (vs), 1381 (m), 1276 (vs, C-O-C), 968 (m).

MS (FD): m/z (%) = 814.2 (100) [M]⁺.

MS (ESI): m/z (%) = 407.69 (2) [M+H]²⁺, 814.37 (100) [M]⁺.

HR-MS (ESI): obs. m/z = 814.3725; calcd. for $[M+H]^+ 814.3757$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 420 (36.29), 516 (1.24), 550 (0.37), 593 (0.28), 652 (0.55).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 654 (1.00), 718 (0.21).

Quantum yield: $\Phi = 0.0778$.

Lifetime: τ [ns] = 10.90 (100%).

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [**V**] = -2.060, -1.710, 0.540, 0.960.

5-(4-(N-Acetylaminophenyl))- 10,20-bis(2,3,4,5,6-pentafluorophenyl)-15-(4-(methoxycarbonyl-phenyl))

porphyrin (Ac-3b). 27.5 mg (0.046 mmol) Porphyrin 3b, 11.4 mL (0.159 mol) acetyl chloride, 5.8 mg (0.046 mmol) iodine. [silica, toluene : ethyl acetate = 1 : 1, $R_f = 0.32$]. Yield: 27 mg (0.030 mmol, 65%), purple powder. $C_{48}H_{25}F_{10}N_5O_3$ (909.73).



¹**H-NMR** (**d**₈-**THF**): $\delta = -2.78$ (s, 2 H, H^{pyrrole-NH}), 2.21 (s, 3H, H⁵₆), 4.05 (s, 3 H, H¹⁵₆), 8.08 (m, 2 H, ³J_{HH} = 8.3 Hz H⁵₃), 8.14 (d, 2 H, ³J_{HH} = 8.3 Hz, H⁵₂), 8.36 (d, 2 H, ³J_{HH} = 8.0 Hz, H¹⁵₂), 8.46 (d, 2 H, ³J_{HH} = 8.0 Hz, H¹⁵₃), 8.91 (d, 2 H, ³J_{HH} = 4.5 Hz, H^{pyrrole}), 9.01 (m, 6 H, H^{pyrrole}), 9.43 (s, 1 H^{amide-NH}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): $\delta = 24.4 (C_{6}^{5}), 52.6 (C_{6}^{15}), 118.2 (C_{3}^{5}), 120.9 (C_{15}^{15}), 122.9 (C_{5}^{5}), 129.0 (C_{3}^{15}), 131.0 (8 C) (br. s, C^{2/3/7/8/12/13/17/18}), 131.3 (C_{4}^{15}), 135.6 (C_{2}^{15}), 135.9 (C_{2}^{5}), 136.7 (C_{1}^{5}), 141.4 (C_{4}^{5}), 137.7, 140.2, 146.6, 149.1 (m, C^{10/20}_{1/1/2/2/3/3/4/4}), 147.2 (C_{11}^{15}), 167.3 (C_{5}^{15}), 168.9 (C_{5}^{5}) ppm.$

¹⁹**F-NMR (d₈-THF):** $\delta = -166.7$ (ddd, ${}^{3}J_{FF} = 23$ Hz, ${}^{3}J_{FF} = 21$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{3/3}$,), -157.8 (t, ${}^{3}J_{FF} = 21$ Hz, 2 F, $F^{10/20}_{4/4}$), -141.3 (dd, ${}^{3}J_{FF} = 24$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{2/2}$) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3417 (b, NH^{amide}, NH^{pyrrole}), 2924 (w, CH), 1719 (m, CO), 1699 (m, CO), 1518 (vs), 1496 (vs), 1276 (m), 1109 (w, CF), 1044 (w, CF), 1037 (w, CF), 987 (vs), 918 (s).

MS (FD): m/z (%) = 909.67 (100) [M]⁺.

MS (ESI): m/z (%) = 910.21 (100) [M]⁺, 1820.41 (49) [2M+H]⁺.

HR-MS (ESI): obs. m/z = 910.1898; calcd. for $[M+H]^+ 910.1876$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 418 (39.31), 512 (2.38), 545 (0.84), 587 (0.93), 642 (0.56).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 647 (1.00), 713 (0.50).

Quantum yield: $\Phi = 0.0696$.

Lifetime: τ [ns] = 9.83 (100%)

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}[V] = -1.810, -1.410, 0.820, 1.030$

5-(4-(*N*-Acetylaminophenyl))-10,20-bis(4-fluorophenyl)-15-(4-(methoxycarbonylphenyl)) porphyrin

(Ac-3c). 33.0 mg (0.046 mmol) Porphyrin 3c, 11.4 mL (0.159 mol) acetyl chloride, 5.8 mg (0.046 mmol) iodine. [silica, toluene : ethyl acetate = 1 : 1, $R_f = 0.35$]. Yield: 24 mg (0.031 mmol, 70%), purple powder. $C_{48}H_{33}F_2N_5O_3$ (765.80).



¹**H-NMR (d₈-THF):** $\delta = -2.71$ (s, 2 H, H^{pyrrole-NH}), 2.21 (s, 3 H, H⁵₆), 4.05 (s, 3 H, H¹⁵₆), 7.53 (t, ³*J*_{HH} = 8.6 Hz, 4 H, H^{10/20}_{3/3}), 8.06 (d, ³*J*_{HH} = 8.4 Hz, 2 H, H⁵₃), 8.10 (d, ³*J*_{HH} = 8.4 Hz, 2 H, H⁵₂), 8.21 (dd, ³*J*_{HH} = 7.9 Hz, ³*J*_{HF} = 2.3 Hz, 4 H, H^{10/20}_{2/2}), 8.32 (d, ³*J*_{HH} = 8.0 Hz, 2 H, H¹⁵₂), 8.44 (d, ³*J*_{HH} = 7.9 Hz, 2 H, H¹⁵₃), 8.82 (m, 6 H, H^{pyrrole}), 8.91(d, ³*J*_{HH} = 4.3 Hz, 2 H, H^{pyrrole}), 9.46 (s, 1 H, H^{amide-NH}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): $\delta = 24.4$ (s, C⁵₆), 52.6 (s, C¹⁵₆), 114.7 (d, ${}^{2}J_{CF} = 21.6$ Hz , C^{10/20}_{3/3}), 118.1 (s, C⁵₃), 119.7 (s, C¹⁵), 120.1 (s, C^{10/20}), 121.8 (s, C⁵), 128.9 (s, C¹⁵₃), 131.0 (s, C¹⁵₄), 131.9 (br. s C^{pyrrole}), 135.6 (s, C¹⁵₂), 135.8 (s, C⁵₂), 136.9 (d, ${}^{3}J_{CF} = 8.1$ Hz, C^{10/20}_{2/2}), 137.5 (s, C⁵₁), 139.4 (d, ${}^{4}J_{CF} = 3.1$ Hz, C^{10/20}_{1/1}), 141.1 (s, C⁵₄), 148.0 (s, C¹⁵₁), 164.1(d, ${}^{1}J_{FH} = 246.5$ Hz, C^{10/20}_{4/4}), 167.4 (s, C¹⁵₅), 168.9 (s, C⁵₅) ppm.

¹⁹**F-NMR (d₈-THF):** $\delta = -117.7$ (tt, ${}^{3}J_{\text{FH}} = 8.6$ Hz, ${}^{4}J_{\text{FH}} = 5.4$ Hz) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3419 (b, NH^{amide}), 3321 (w, NH^{pyrrole}), 2927 (w, CH), 2853 (w, CH), 1715 (m, CO), 1593 (m), 1503 (m), 1282 (m, C-O-C), 1151 (s, CF), 800 (vs).

MS (FD): m/z (%) = 765.2 (100) [M]⁺.

MS (ESI): m/z (%) = 766.26 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 766.2621; calcd. for $[M+H]^+$ 766.2630.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 419 (50.42), 515 (2.16), 551 (1.07), 591 (0.72), 647 (0.61).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 652 (1.00), 717 (0.32).

Quantum yield: $\Phi = 0.1003$.

Lifetime: τ [ns] = 9.64 (100%).

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.920, -1.590, 0.590, 0.870.

5-(4-(N-Acetylaminophenyl))-10, 20-bis((4-trifluoromethyl)phenyl)-15-(4-(methoxycarbonylphenyl))-10, 20-bis((4-trifluoromethyl)phenyl)-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl

porphyrin (Ac-3d). 50.0 mg (0.069 mmol) Porphyrin 3d, 17.2 mL (0.240 mol) acetyl chloride, 8.8 mg (0.069 mmol) iodine. [silica, toluene : ethyl acetate = 1 : 1, $R_f = 0.45$]. Yield: 40 mg (0.046 mmol, 67%), purple powder. $C_{50}H_{33}F_6N_5O_3$ (865.82).



¹**H-NMR** (**d**₈-**THF**): $\delta = -2.71$ (s, 2 H, H^{pyrrole-NH}), 2.21 (s, 3 H, H⁵₆), 4.05 (s, 3 H, H¹⁵₆), 8.08 (m, 4 H, H^{5/5}_{2/3}), 8.11 (d, ³*J*_{HH} = 8.1 Hz, 4 H, H^{10/20}_{3/3}), 8.32 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₂), 8.41 (d, ³*J*_{HH} = 7.9 Hz, 4 H, H^{10/20}_{2/2}), 8.44 (d, ³*J*_{HH} = 8.1 Hz, 2 H, H¹⁵₃), 8.81 (m, 6 H, H^{pyrrole}), 8.93 (d, ³*J*_{HH} = 4.5, 2 H, H^{pyrrole}), 9.45 (s, 1 H, H^{amide-NH}) ppm.

¹³C{¹H}-NMR (d₈-THF): $\delta = 23.2$ (s, C⁵₆), 52.7 (s, C¹⁵₆), 118.3 (s, C⁵₃), 119.8 (s, C^{10/20}), 120.2 (s, C¹⁵), 122.3 (s, C⁵), 124.8 (s, C^{10/20}_{4/34}), 124.9 (d, ⁴*J*_{CF} = 3.3 Hz, C^{10/20}_{3/3}), 127.5 (s, C^{10/20}_{4/4}), 129.0 (s, C¹⁵₃), 130.4 (q, ¹*J*_{CF} = 32.2 Hz, C^{10/20}_{5/5}), 131.2 (s, C¹⁵₄), 132.1 (br. s, C^{2,3,7,8,12,13,17,18}), 135.7 (s, C¹⁵₂), 136.0 (m, C^{5/10/20}_{2/2/2}), 137.4 (s, C⁵₁), 141.3 (s, C⁵₄), 147.4 (s, C^{10/20}_{1/1}), 147.9 (s, C¹⁵₁), 167.5 (s, C¹⁵₅), 169.0 (s, C⁵₅) ppm.

¹⁹**F-NMR (d₈-THF):** $\delta = -65.0$ (s).

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3419 (b, NH^{amide}), 3321 (w, NH^{pyrrole}), 2952 (w, CH), 1724 (s, CO), 1609 (m), 1511 (m), 1282 (s, C-O-C), 1127 (s, CF), 808 (s).

MS (FD): m/z (%) = 865.6 (100) [M]⁺.

MS (ESI): m/z (%) = 866.27 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 866.2566; calcd. for $[M+H]^+ 866.2563$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 419 (41.4), 515 (1.78), 550 (0.79), 590 (0.57), 646 (0.40).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 650 (1.00), 716 (0.36).

Quantum yield: $\Phi = 0.1080$.

Lifetime: τ [ns] = 9.98 (100%).

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.900, -1.550, 0.640, 0.890.

[5-(4-(N-Acetylaminophenyl))-10, 20-bis(2, 4, 6-trimethylphenyl)-15-(4-(methoxycarbonyl-phenyl))-10, 20-bis(2, 4, 6-trimethylphenyl-

porphyrinato]zinc(II) (**Zn-Ac-3a).** Porphyrin **Ac-3a** (25 mg, 0.031 mmol) and zinc acetate dihydrate (34 mg, 0.15 mmol) were stirred overnight in CH₂Cl₂ (5 mL). After concentration under reduced pressure the product was isolated by column chromatography [silica, toluene : ethyl acetate = 1 : 1, R_f = 0.50]. Yield 23 mg (0.026 mmol, 85%), purple powder. C₅₄H₄₅N₅O₃Zn (877.35).



¹**H-NMR** (**d**₈-**THF**): $\delta = 1.85$ (s, 12 H, H^{10/20}_{5/5}), 2.20 (s 3H, H⁵₆), 2.61 (s, 6 H, H^{10/20}_{6/6}), 4.04 (s, 3 H, H¹⁵₆), 7.29 (s, 4 H, H^{10/20}_{3/3}), 8.00 (d, ${}^{3}J_{\text{HH}} = 8.2$ Hz, 2 H, H⁵₃), 8.10 (d, 2 H, ${}^{3}J_{\text{HH}} = 8.4$ Hz, H⁵₂), 8.31 (d, ${}^{3}J_{\text{HH}} = 8.2$ Hz, 2 H, H¹⁵₃), 8.66 (ps. t, ${}^{3}J_{\text{HH}} = 4.6$ Hz, 4 H, H^{pyrrole}), 8.74 (d, ${}^{3}J_{\text{HH}} = 4.6$ Hz, 2 H, H^{pyrrole}), 8.84 (d, ${}^{3}J_{\text{HH}} = 4.6$ Hz, 2 H, H^{pyrrole}), 9.38 (s, 1 H, H^{amide-NH}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): $\delta = 21.7$ (s, C^{10/20}_{6/6}), 22.1 (s, C^{10/20}_{5/5}), 24.4 (s, C⁵₆), 52.5 (s, C¹⁵₆), 117.6 (C⁵₃), 119.4 (s, C¹⁵) 119.6 (C^{10/20}), 121.4 (s, C⁵), 128.4 (s, C¹⁵₃), 128.7 (s, C^{10/20}_{3/3}), 130.4 (s, C¹⁵₄), 130.9, 131.2, 132.4, 133.3 (s, C^{2,3,7,8,12,13,17,18}), 135.6 (s, C¹⁵₂), 135.6 (s, C⁵₂), 138.3 (s, C⁵₁), 140.0 (s, C^{10/20}_{2/2}), 140.6 (s, C⁵₄), 140.8 (s, C^{10/20}_{1/1}), 149.6 (s, C¹⁵₁), 150.4, 150.7, 150.9, 151.3 (s, C^{1,4,6,9,11,14,16,19}), 167.5 (s, C¹⁵₅), 168.7 (s, C⁵₅) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3404 (b, NH^{amide}), 2922 (w, CH), 2853 (w, CH), 1732 (m, CO), 1668 (m, CO), 1495 (m), 1398 (m), 1278 (s), 995 (vs), 798 (m).

MS (FD): m/z (%) = 875.79 (100) [M]⁺.

MS (ESI): m/z (%) = 875.31 (88), 877.31 (100), 879.31 (68), [M]⁺.

HR-MS (ESI): obs. m/z = 877.2823; calcd. for $[M]^+ 875.2814$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 423 (45.12), 551 (1.92), 592 (0.45).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 604 (1.00), 652 (0.99).

Quantum yield: $\Phi = 0.1343$.

Lifetime: τ [ns] = 2.17 (100%).

CV (**Fc/Fc⁺**, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.860, 0.335, 0.750.

[5-(4-(*N*-Acetylaminophenyl))-10,20-bis(2,3,4,5,6-pentafluorophenyl)-15-(4-(methoxycarbonyl-phenyl))

porphyrinato]zinc(II) (Zn-Ac-3b). Porphyrin **Ac-3b** (15 mg, 0.016 mmol) and zinc acetate dihydrate (18 mg, 0.08 mmol) were stirred overnight in CH₂Cl₂ (5 mL). After concentration under reduced pressure the product was isolated by column chromatography [silica, toluene : ethyl acetate = 1 : 1, R_f = 0.48]. Yield 14 mg (0.014 mmol, 87%), purple powder. C₄₈H₂₃F₁₀N₅O₃Zn (973.09).



¹**H-NMR** (**d**₈-**THF**): δ = 2.21 (s, 3H, H⁵₆), 4.06 (s, 3 H, H¹⁵₆), 8.05 (m, 2 H, ³J_{HH} = 8.3 Hz H⁵₃), 8.10(d, 2 H, ³J_{HH} = 8.3 Hz, H⁵₂), 8.33 (d, 2 H, ³J_{HH} = 8.0 Hz, H¹⁵₂), 8.43 (d, 2 H, ³J_{HH} = 8.0 Hz, H¹⁵₃), 8.89 (d, 2 H, ³J_{HH} = 4.6 Hz, H^{pyrrole}), 8.98 (m, 6 H, H^{pyrrole}), 9.42 (s, 1 H^{amide-NH}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): $\delta = 24.4 (C_{6}^{5})$, 52.6 (C¹⁵₆), 117.8 (C⁵₃), 121.3 (C¹⁵), 123.2 (C⁵), 128.6 (C¹⁵₃), 131.0, 131.3, 133.6, 134.3 (C^{2,3,7,8,12,13,17,18}), 130.8 (C¹⁵₄), 135.6 (C¹⁵₂), 135.9 (C⁵₂), 138.2 (C⁵₁), 140.9 (C⁵₄), 137.5, 140.0, 146.6, 149.0 (m, C^{10/20}_{1/1/2/2/3/3/4/4}), 148.8 (C¹⁵₁), 150.5, 150.7, 151.3, 152.3 (C^{1,4,6,9,11,14,16,19}), 167.4 (C¹⁵₅), 168.8 (C⁵₅) ppm.

¹⁹**F-NMR (d₈-THF):** $\delta = -167.2$ (ddd, ${}^{3}J_{FF} = 24$ Hz, ${}^{3}J_{FF} = 21$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{3/3}$,), -158.6 (t, ${}^{3}J_{FF} = 21$ Hz, 2 F, $F^{10/20}_{4/4}$), -141.5 (dd, ${}^{3}J_{FF} = 24$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{10/20}_{2/2}$) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3442 (b, NH^{amide}), 2926 (w, CH), 2851 (w, CH), 1720 (m, CO), 1518 (vs), 1493 (vs), 1282 (m), 1114 (w, CF), 1074 (w, CF), 1053 (w, CF), 989 (vs), 918 (vs), 939 (s).

MS (FD): m/z (%) = 971.35 (100) [M]⁺.

MS (ESI): m/z (%) = 971.10 (43) [M]⁺), 972.11 (100) [M+H]⁺.

HR-MS (ESI): obs. m/z = 971.0931; calcd. for $[M]^+ 971.0933$.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 422 (51.09), 552 (2.01), 593 (0.36).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 602 (1.00), 652 (0.92).

Quantum yield: $\Phi = 0.0771$.

Lifetime: τ [ns] = 1.94 (100%).

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -1.980, -1.580, 0.600, 0.940.

[5-(4-(N-Acetylaminophenyl))-10, 20-bis(4-fluorophenyl)-15-(4-(methoxycarbonyl-phenyl))

porphyrinato]zinc(II) (Zn-Ac-3c). Porphyrin **Ac-3c** (12 mg, 0.016 mmol) and zinc acetate dihydrate (15 mg, 0.15 mmol) were stirred overnight in CH₂Cl₂ (5 mL). After concentration under reduced pressure the product was isolated by column chromatography [silica, toluene : ethyl acetate = 1 : 1, R_f = 0.50]. Yield 13 mg (0.015 mmol, 94%), purple powder. C₄₈H₃₁F₂N₅O₃Zn (829.20).



¹**H-NMR** (**d**₈-**THF**): $\delta = 2.20$ (s, 3 H, H⁵₆), 4.05 (s, 3 H, H¹⁵₆), 7.50 (t, ${}^{3}J_{\text{HH}} = 8.6$ Hz, 4 H, H^{10/20}_{3/3}), 8.03 (d, ${}^{3}J_{\text{HH}} = 8.3$ Hz, 2 H, H⁵₃), 8.08 (d, ${}^{3}J_{\text{HH}} = 8.4$ Hz, 2 H, H⁵₂), 8.18 (dvd, ${}^{3}J_{\text{HH}} = 8.1$ Hz, ${}^{3}J_{\text{HF}} = 2.4$ Hz, 4 H, H^{10/20}_{2/2}), 8.30 (d, ${}^{3}J_{\text{HH}} = 8.0$ Hz, 2 H, H¹⁵₂), 8.41 (d, ${}^{3}J_{\text{HH}} = 8.0$ Hz, 2 H, H¹⁵₃), 8.83 (m, 6 H, H^{pyrrole}), 8.92 (d, ${}^{3}J_{\text{HH}} = 4.6$ Hz, 2 H, H^{pyrrole}), 9.41 (s, 1 H, H^{amide-NH}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): δ = 24.4 (s, C⁵₆), 52.5 (s, C¹⁵₆), 114.2 (d, ²*J*_{CF} = 21.4 Hz , C^{10/20}_{3/3}), 117.8 (s, C⁵₃), 120.2 (s, C¹⁵), 120.6 (s, C^{10/20}), 122.3 (s, C⁵), 128.5 (s, C¹⁵₃), 130.5 (s, C¹⁵₄), 132.1, 132.2, 132.5, 132.8 (s, C^{pyrrole 2,3,7,8,12,13,17,18}), 135.6 (s, C¹⁵₂), 135.7 (s, C⁵₂), 136.8 (d, ³*J*_{CF} = 7.9 Hz, C^{10/20}_{2/2}), 138.8 (s, C⁵₁), 140.7 (d, ⁴*J*_{CF} = 2.9 Hz, C^{10/20}_{1/1}), 140.7 (s, C⁵₄), 149.4 (s, C¹⁵₁), 150.7, 151.2, 151.3, 151.6 (s, C^{1,4,6,9,11,14,16,19}), 163.9 (d, ¹*J*_{FH} = 245.7 Hz, C^{10/20}_{4/4}), 167.5 (s, C¹⁵₅), 168.7 (s, C⁵₅) ppm.

¹⁹**F-NMR (d₈-THF):** $\delta = -118.6$ (tt, ³ $J_{\text{FH}} = 8.6$ Hz, ⁴ $J_{\text{FH}} = 5.4$ Hz).

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3432 (b, NH^{amide}), 2926 (w, CH), 1698 (m, CO) 1598 (m), 1507 (m), 1283 (m, C-O-C), 1159 (s, CF), 993 (vs), 802 (vs).

MS (FD): m/z (%) = 827.3 (92) [M]⁺.

MS (ESI): m/z (%) = 828.18 (4) [M+H]⁺.

HR-MS (ESI): obs. m/z = 827.1695; calcd. for [M]⁺ 827.1686.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 420 (41.45), 548 (1.87), 587 (0.50).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 598 (0.97), 646 (1.00).

Quantum yield: $\Phi = 0.0569$.

Lifetime: τ [ns] = 1.85 (100%).

CV (**Fc/Fc**⁺, **100** mV s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.110, -1.750, 0.380, 0.780.

[5-(4-(N-Acetylaminophenyl))-10, 20-bis((4-trifluoromethyl)phenyl)-15-(4-(methoxycarbonylphenyl))-10, 20-bis((4-trifluoromethyl)phenyl)-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyl)phenyl-10, 20-bis((4-trifluoromethyll)phenyl-10, 20-bis((4-trifluoromethyll)phenyl-10, 20-bis((4-trifluoromethyll)phenyl-10, 20-bis((4-trifluoromethyll)phenyl-10, 20-bis((4-trifluoromethyll)phenyl-10, 20-bis((4-trifluoromethyll)phenyl-10, 20-bis((4-t

porphyrinato]zinc(II) (**Zn-Ac-3d).** Porphyrin **Ac-3d** (20 mg, 0.023 mmol) and zinc acetate dihydrate (25 mg, 0.11 mmol) were stirred overnight in CH₂Cl₂ (10 mL). After concentration under reduced pressure the product was isolated by column chromatography [silica, toluene : ethyl acetate = 1 : 1, R_f = 0.40]. Yield 18 mg (0.019 mmol, 82%), purple powder. C₅₀H₃₁F₆N₅O₃Zn (929.18).



¹**H-NMR** (**d**₈-**THF**): $\delta = 2.19$ (s, 3 H, H⁵₆), 4.04 (s, 3 H, H¹⁵₆), 8.02 (d, ${}^{3}J_{\text{HH}} = 8.3$ Hz, 2 H, H⁵₃), 8.08 (m, 6 H, H^{10/20/5}_{3/3/2}), 8.30 (d, ${}^{3}J_{\text{HH}} = 7.99$ Hz, 2 H, H¹⁵₂), 8.40 (m, 4 H, H^{15/10/20}_{3/2/2}), 8.82 (m, 6 H, H^{pyrrole}), 8.93 (d, ${}^{3}J_{\text{HH}} = 4.5$ Hz, 2 H, H^{pyrrole}), 9.40 (s, 1 H, H^{amide-NH}) ppm.

¹³C{¹H}-NMR (**d**₈-THF): δ = 24.6 (s, C⁵₆), 52.7 (s, C¹⁵₆), 117.9 (s, C⁵₃), 120.3 (s, C^{10/20}), 120.7 (s, C¹⁵), 122.8 (s, C⁵), 124.5 (d, ⁴*J*_{CF} = 3.4 Hz, C^{10/20}_{2/2}), 127.6 (s, C^{10/20}_{4/4}), 128.7 (s, C¹⁵₃), 130.5 (q, ¹*J*_{CF} = 38.2 Hz, C^{10/20}_{5/5}), 130.8 (s, C⁵₄), 132.3, 132.6, 132.6, 133.3 (s, C^{pyrrole 2,3,7,8,12,13,17,18}), 135.7 (s, C⁵₂), 135.9 (s, C¹⁵₂), 136.0 (m, C^{10/20}_{2/2}), 138.7 (s, C⁵₄) 140.9 (s, C⁵₄), 148.8 (m, C^{10/20}_{1/1}), 149.3 (s, C¹⁵₁), 150.8, 150.9, 151.0, 151.9 (s, C^{pyrrole 1,4,6,9,11,14,16,19}), 167.6 (s, C¹⁵₅), 168.9 (s, C⁵₅) ppm.

¹⁹**F-NMR (d₈-THF):** $\delta = -64.9$ (s) ppm.

IR (**KBr**): $\tilde{\nu}$ [cm⁻¹] = 3433 (b, NH^{amide}), 2929 (w, CH), 2854 (w, CH), 1724 (w, CO), 1703 (w, CO), 1610 (m), 1517 (w), 1387 (w), 1283 (m, C-O-C), 1163 (m, CF), 1126 (s), 997 (s), 792 (s).

MS (FD): m/z (%) = 927.2 (100) [M]⁺.

MS (ESI): m/z (%) = 927.19 (40) [M]⁺, 950.17 (97) [M+Na]⁺.

HR-MS (ESI): obs. m/z = 950.1512; calcd. for [M+Na]⁺ 950.1512.

UV/Vis (**CH**₂**Cl**₂): λ [nm] (ε / [10⁴ M⁻¹cm⁻¹]) = 420 (28.3), 548 (1.17), 588 (0.21).

Fluorescence (CH₂Cl₂): λ [nm] (relative intensity) = 597 (0.81), 645 (1.00).

Quantum yield: $\Phi = 0.0838$.

Lifetime: τ [ns] = 2.07 (100%).

CV (**Fc/Fc**⁺, **100 mV** s⁻¹, **CH**₂**Cl**₂): $E_{\frac{1}{2}}$ [V] = -2.010, -1.560, 0.420, 0.850.

General synthesis of bis(porphyrins) 4a, 4b, 4c, 4d, Zn^2 -4d: The porphyrin acid component was dissolved in anhydrous CH₂Cl₂, 1-chloro-*N*,*N*,2-trimethylpropenylamine (Ghosez' reagent) was added and the reaction mixture was stirred under nitrogen for 3h at room temperature. After the acid chloride formed (TLC control) excess of Ghosez' reagent and solvent were removed by evaporation under reduced pressure. In order to remove the *N*,*N*-dimethyl amide byproduct anhydrous CH₂Cl₂ was added and the volatiles were again evaporated. The acid chloride was dissolved in CH₂Cl₂ (with 1 drop of triethylamine) and the solution was added dropwise to a solution of the porphyrin amino component in CH₂Cl₂ (with 1 drop of triethylamine). The reaction mixture was stirred for 12h at room temperature, washed with water and the organic phase was concentrated under reduced pressure. After column chromatography (silica, CH₂Cl₂/ethyl acetate 100:1) the respective dyad was isolated.



4a: 2a (10.0 mg, 0.012 mmol), CH₂Cl₂ (3×5 mL), 1-chloro-*N*,*N*,2-trimethylpropenylamine (7 µL, 0.048 mmol), triethylamine (2×1 drop), **3b** (8.7 mg, 0.010 mmol). Yield: 6.1 mg (0.0037 mmol, 37%), purple powder. C₉₉H₆₅F₁₀N₉O₅ (1650.61). *R*_f = 0.35 (silica, CH₂Cl₂/ethyl acetate 100:1). ¹H NMR (CDCl₃): δ = -2.80 (s, 2 H, H^{C6F5-pyroleNH}), -2.56 (s, 2 H, H^{Mes-pyroleNH}), 1.87 (s, 12 H, H^{26/36}_{5/5}), 2.65 (s, 6 H, H^{26/36}_{6/6}), 4.12 (s, 3 H, H³¹₆), 4.14 (s, 3 H, H¹⁵₆), 7.31 (s, 4 H, H^{26/36}_{3/3}), 8.22 (d, ³*J*_{HH} = 8.3 Hz, 2 H, H⁵₃), 8.34 (m, 6 H, H^{5/15/31}_{2/2/2}), 8.44 (d, ³*J*_{HH} = 8.2 Hz, 2 H, H²¹₂), 8.47 (m, 6 H, H^{15/21/31}_{3/3/3}), 8.72 (d, ³*J*_{HH} = 4.8 Hz, 2 H, H^{pyrole}), 8.74 (m, 4 H, H^{pyrrole}), 8.85 (d, ³*J*_{HH} = 4.7 Hz, 2 H, H^{pyrrole}), 8.89 (d, ³*J*_{HH} = 4.5 Hz, 2 H, H^{pyrrole}), 8.92 (d, ³*J*_{HH} = 4.7 Hz, 4 H, H^{pyrrole}), 9.00 (d, ³*J*_{HH} = 4.7 Hz, 2 H, H^{pyrrole}) ppm; H^{amide-NH} not observed. ¹³C{¹H} NMR (CDCl₃): δ = 21.5 (C^{10/20}_{6/6}), 21.7 (C^{10/20}_{5/5}), 52.4, 52.5 (C^{15/31}_{6/6}), 118.6, 119.0, 120.0 (C^{5/10/15/20/21/26/31/36}), 118.6 (C⁵₃), 127.8, 127.9, 128.1 (C^{15/21/31}_{3/3/3}), 127.8 (C^{26/36}_{3/3}), 130.2, 137.8 (C^{15/31}_{4/4}), 130.2 (C^{pyrrole 2.3.7.8,12,13,17.18}), 134.6, 135.0, 135.3, (C^{5/15/31/21}_{2/2/2}), 138.3 (C^{26/36}_{1/1}), 138.6 (C⁵₁), 139.4 (C^{26/36}_{2/2}), 145.8 (C⁵₄), 147.0 (C²¹₄), 165.9 (C²¹₅), 167.1, 167.4 (C^{15/31}_{5/5}) ppm. ¹⁹F NMR (CDCl₃): δ = -162.0 (ddd, ³*J*_{FF} = 24 Hz, ⁵*J*_{FF} = 21 Hz, ⁵*J*_{FF} = 8 Hz, 4 F, F^{10/20}_{3/3}), -152.0 (t, ³*J*_{FF} = 21 Hz, 2 F, F^{10/20}_{4/4}), -136.7 (dd, ³*J*_{FF} = 24 Hz, ⁵*J*_{FF} = 25

= 8 Hz, 4 F, $F^{10/20}_{2/2}$ ppm. MS (FD): m/z (%) = 1650.1 (100) [M]⁺. MS (ESI): m/z (%) = 825.8 (83) [M+H]²⁺, 1650.1 (87) [M]⁺, 1651.5 (100) [M+H]⁺. HR-MS (ESI): obs. m/z = 1650.4983; calcd. for [M+H]⁺ 1650.5027. IR (KBr): \tilde{v} [cm⁻¹] = 3439 (b, NH^{amide}/NH^{pyrrole}), 2924 (s, CH), 2850 (m, CH), 1730 (m, CO), 1517 (s), 1281 (m, C-O-C), 1109 (s, CF). UV/Vis (CH₂Cl₂): λ (ε / M⁻¹ cm⁻¹) = 421 (684600), 513 (38500), 549 (14100), 590 (12500), 649 (9500).



4b: 2b (35 mg, 0.039 mmol), CH₂Cl₂ (3×10 mL), 1-chloro-*N*,*N*,2-trimethylpropenylamine (20 μ L, 0.156 mmol), triethylamine (2×1 drop), **3a** (27.0 mg, 0.035 mmol). Yield: 28.4 mg (0.017 mmol, 49%), purple powder. C₉₉H₆₅F₁₀N₉O₅ (1650.61). $R_{\rm f} = 0.34$ (silica, CH₂Cl₂/ethyl acetate 100:1). ¹H NMR (CDCl₃): $\delta = -2.80$ (s, 2 H, H^{C6F5pyrroleNH}), -2.59 (s, 2 H, H^{MespyrroleNH}), 1.87 (s, 12 H, H^{10/20}_{5/5}), 2.65 (s, 6 H, $H^{10/20}_{6/6}$), 4.12 (s, 3 H, H^{15}_{6}), 4.14 (s, 3 H, H^{31}_{6}), 7.31 (s, 4 H, $H^{10/20}_{3/3}$), 8.27 (d, ${}^{3}J_{HH} =$ 8.5 Hz, 2 H, H⁵₃), 8.32 (m, 6 H, H^{5/15/31}_{2/2/2}), 8.44 (d, ${}^{3}J_{HH} = 7.3$ Hz, 4 H, H^{15/21}_{3/2}), 8.48 (d, 4 H, ${}^{3}J_{HH}$ = 7.9 Hz, $H^{21/31}_{3/3}$), 8.54 (s, 1 H, $H^{\text{amide-NH}}$), 8.74 (d, ${}^{3}J_{\text{HH}}$ = 4.7 Hz, 2 H, H^{pyrrole}), 8.78 (m, 4 H, H^{pyrrole}), 8.84 (d, ${}^{3}J_{\text{HH}} = 4.3$ Hz, 4 H, H^{pyrrole}), 8.87 (d, ${}^{3}J_{\text{HH}} = 4.5$ Hz, 2 H, H^{pyrrole}), 8.91 (d, ${}^{3}J_{\text{HH}} = 4.7$ Hz, 2 H, H^{pyrrole}), 9.09 (d, ${}^{3}J_{HH} = 4.7$ Hz, 2 H, H^{pyrrole}) ppm. ${}^{13}C{}^{1}H$ NMR (CDCl₃): $\delta = 21.5$ $(C^{10/20}_{6/6}), 21.7 (C^{10/20}_{5/5}), 52.4, 52.5 (C^{15/31}_{6/6}), 117.9, 118.3, 118.8, 118.9, 120.0, 121.2$ $(C^{5/10/15/20/21/26/31/36})$, 118.8 (C^{5}_{3}) , 125.6, 128.1 $(C^{15/21/31}_{3/3/3})$, 127.8 $(C^{10/20}_{3/3})$, 127.9, 134.6, 134.6 $(C^{5/15/31}_{2/2/2})$, 129.6, 130.0, 135.4, 138.3 $(C^{15/21/31}_{4/4/4})$, 134.2, 136.3, 137.9, 146.0 $(C^{15/21/31/26/36}_{1/1/1/1})$, 135.0 (C^{21}_{2}), 137.5 (C^{5}_{1}), 138.2 ($C^{10/20}_{1/1}$), 139.4 ($C^{10/20}_{2/2}$), 146.2 (C^{5}_{4}), 146.8 (C^{21}_{4}), 145.4, 147.7 $(C_{26/36}^{26/36})_{2/2}, C_{3/3}^{26/36})_{3/3}, C_{4/4}^{26/36}), 166.2 (C_{5}^{21}), 167.2, 167.3 (C_{5/31}^{15/31}) ppm.$ ¹⁹F NMR (CDCl₃): $\delta = -162.0$ (ddd, ${}^{3}J_{FF} = 23$ Hz, ${}^{3}J_{FF} = 21$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F^{26/36}_{3/3}$), -152.0 (t, ${}^{3}J_{FF} = 21$ Hz, 2 F, $F^{26/36}_{4/4}$), -136.7 (dd, ${}^{3}J_{\text{FF}} = 24$ Hz, ${}^{5}J_{\text{FF}} = 8$ Hz, 4 F, $F^{26/36}_{2/2}$) ppm. MS (FD): m/z (%) = 1649.8 (50) [M]⁺, 1651.9 (100) $[M+2H]^+$. MS (ESI): m/z (%) = 826.3 (100) $[M+H]^{2+}$, 1650.5 (50) $[M]^+$, 1651.5 (82) $[M+H]^+$. HR-MS (ESI): obs. m/z = 1650.5067; calcd. for $[M+H]^+ 1650.5027$. IR (KBr): $\tilde{v} [cm^{-1}] =$ 3441 (b, NH^{amide}), 3324 (w, NH^{pyrrole}), 2926 (s, CH), 2860 (m, CH), 1723 (m, CO), 1515 (m), 1503

(m), 1266 (m, C-O-C), 1109 (s, CF). UV/Vis (CH₂Cl₂): λ (ε / M⁻¹ cm⁻¹) = 420 (787000), 513 (46700), 549 (18000), 590 (15500), 649 (11200).



4c: 2a (23.4 mg, 0.026 mmol), CH₂Cl₂ (3×10 mL), 1-chloro-N,N,2-trimethylpropenylamine (14 μ L, 0.104 mmol), triethylamine (2×1 drop), 3d (17.2 mg, 0.021 mmol). Yield: 6.1 mg (0.0145 mmol, 69%), purple powder. C₉₅H₅₁F₁₆N₉O₅ (1702.45). $R_{\rm f} = 0.32$ (silica, CH₂Cl₂/ethyl acetate 100:1). ¹H NMR (CDCl₃): $\delta = -2.81$ (s, 2 H, H^{C6F5pyrroleNH}), -2.76 (s, 2 H, H^{CF3pyrroleNH}), 4.13, 4.14 (2s, 2×3 H, $H^{15/31}_{6/6}$), 8.06 (d, ${}^{3}J_{HH} = 8.0$ Hz, 4 H, $H^{10/20}_{3/3}$), 8.26 (d, ${}^{3}J_{HH} = 8.4$ Hz, 2 H, H^{5}_{3}), 8.32 (m, 6 H, $H^{5/15/31}_{2/2/2}$), 8.37 (d, ${}^{3}J_{HH} = 8.0, 4 H, H^{10/20}_{2/2}$), 8.48 (m, 8 H, $H^{15/21/21/31}_{3/2/3/3}$), 8.54 (s, 1H, $H^{amide-NH}$), 8.84 (m, 8 H, H^{pyrrole}), 8.90 (d, ${}^{3}J_{HH} = 4.7$ Hz, 2 H, H^{pyrrole}), 8.93 (d, ${}^{3}J_{HH} = 4.8$ Hz, 2 H, H^{pyrrol}), 9.01 (pt, ${}^{3}J_{\text{HH}} = 6.3 \text{ Hz}, 4 \text{ H}, \text{H}^{\text{pyrrole}}$) ppm. ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (CDCl₃): $\delta = 52.5, 52.6$ (C ${}^{15/31}_{6/6}$), 118.7 (C ${}^{5}_{3}$), 118.8, 119.2, 120.0, 120.4, 123.2 ($C^{5/10/15/20/21/26/31/36}$), 123.8 (d, ${}^{1}J_{CF} = 3.3$ Hz, $C^{10/20}_{3/3}$), 134.6 $(C^{10/20}_{3/3})$, 125.8 $(C^{10/20}_{4/4})$, 125.8, 125.9, 128, 128.2 $(C^{5/15/21/31}_{3/3/3})$, 130.1 (q, ${}^{1}J_{CF} = 32.2$ Hz, $C^{10/20}_{5/5}$, 130.1, 130.9, 131.2 ($C^{2,3,7,8,12,13,17,18}$), 134.6, 135.0, 135.4 ($C^{5/15/21/31}_{2/2/2/2}$), 134.6, 134.8, 138.0 ($C^{15/21/31}_{4/4/4}$), 136.3, 138.8, 145.4, 147.8 ($C^{26/36}_{2/2}$, $C^{26/36}_{3/3}$, $C^{26/36}_{4/4}$), 138.3 (C^{5}_{1}), 145.2, 145.7, 145.8, 146.6 ($C^{5/10/20/15/21/31}_{4/1/1/1/1}$), 166.0 (C^{21}_{5}), 167.2, 167.3 (C^{15}_{5} , C^{31}_{5}) ppm. ¹⁹F NMR (CDCl₃): δ $= -162.6 \text{ (ddd, } {}^{3}J_{\text{FF}} = 23 \text{ Hz}, {}^{3}J_{\text{FF}} = 23 \text{ Hz}, {}^{5}J_{\text{FF}} = 8 \text{ Hz}, 4 \text{ F}, \text{F}^{10/20}_{3/3}, \text{)}, -152.32 \text{ (t, } {}^{3}J_{\text{FF}} = 21 \text{ Hz}, 2 \text{ F},$ $F_{4/4}^{10/20}$, -137.19 (dd, ${}^{3}J_{FF} = 24$ Hz, ${}^{5}J_{FF} = 8$ Hz, 4 F, $F_{2/2}^{10/20}$, -62.0 (s, 6 F, $F_{5/5}^{10/20}$) ppm. MS (FD): m/z (%) = 1703.3 (100) [M+H]⁺. MS (ESI): m/z (%) = 851.7 (72) [M+H]²⁺, 1702.4 (75) [M]⁺, 1703.4 (100) $[M+H]^+$. HR-MS (ESI): obs. m/z = 1702.3815; calcd. for $[M+H]^+$ 1702.3836. IR (KBr): \tilde{v} [cm⁻¹] = 3443 (b, NH^{amide}), 3320 (w, NH^{pyrrole}), 2952 (w, CH), 2927 (w, CH), 2854 (w, CH), 1724 (m, CO), 1609 (w), 1494 (m), 1266 (s, C-O-C), 1102 (s, CF). UV/Vis (CH₂Cl₂): $\lambda (\varepsilon / M^{-1} cm^{-1}) =$ 420 (745000), 512 (16100), 549 (5300), 590 (5000), 645 (2600).



4d: 2a (21.0 mg, 0.029 mmol), CH₂Cl₂ (3×10 mL), 1-chloro-N,N,2-trimethylpropenylamine (15 μL, 0.116 mmol), triethylamine (2×1 drop), 3c (20.0 mg, 0.027 mmol). Yield: 25.0 mg (0.017 mmol, 63%), purple powder. C₉₉H₇₃F₂N₉O₅ (1506.69). $R_{\rm f} = 0.41$ (silica, CH₂Cl₂/ethyl acetate 100:1). ¹H NMR (CDCl₃): $\delta = -2.76$ (s, 2 H, H^{PhFpyrroleNH}), -2.58 (s, 2 H, H^{MespyrroleNH}), 1.87 (s, 12 H, H^{26/36}_{5/5}), 2.65 (s, 6 H, $H^{26/36}_{6/6}$), 4.12, 4.13 (2 s, 2 × 3 H, $H^{15/36}_{6/6}$), 7.31 (s, 4 H, $H^{26/36}_{3/3}$), 7.47 (t, ${}^{3}J = 8.6$ Hz, 4 H, $H^{10/20}_{3/3}$), 8.20 (dd, ${}^{3}J = 8.5$ Hz, ${}^{3}J = 5.4$ Hz, 4 H, $H^{10/20}_{2/2}$), 8.24 (d, ${}^{3}J_{HH} = 8.4$ Hz, 2 H, H^{5}_{3}), 8.32 (m, 6 H, $H^{5/15/31}_{2/2/2}$), 8.46 (m, 8 H, $H^{15/21/21/31}_{3/2/3/3}$), 8.52 (s, 1 H, $H^{\text{amide-NH}}$), 8.74 (d, ${}^{3}J_{\text{HH}} = 4.8$ Hz, 2 H, H^{pyrrole}), 8.78 (m, 4 H, H^{pyrrole}), 8.82 (d, ${}^{3}J_{HH} = 4.7$ Hz, 2 H, H^{pyrrole}), 8.85 (m, 4 H, H^{pyrrole}), 8.89 (d, ${}^{3}J_{\text{HH}} = 4.7 \text{ Hz}, 2 \text{ H}, \text{H}^{\text{pyrrole}}$), 9.00 (d, ${}^{3}J_{\text{HH}} = 4.7 \text{ Hz}, 4 \text{ H}, \text{H}^{\text{pyrrole}}$) ppm. ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (CDCl₃): δ = 52.5 ($C_{6/6}^{15/31}$), 113.8 (d, ${}^{2}J_{CF}$ = 21.3 Hz , $C_{3/3}^{10/20}$), 118.6 (C_{3}^{5}), 117.9, 118.3, 118.8, 118.9, 119.2, 120.1 ($C^{5/10/15/20/21/26/31/36}$), 125.6, 128.0, 128.0, 135.0 ($C^{15/21/21/31}_{3/2/3/3}$), 127.9 ($C^{26/36}_{3/3}$), 129.7, 134.3, 138.0 (C^{15/26/36/31}_{4/1/1/4}), 131.0 (C^{2,3,7,8,12,13,17,18,23,24,28,29,33,34,38,39}), 134.6 (d, ${}^{4}J_{CF} = 3.2$ Hz, C^{10/20}_{1/1}), 134.6, 135.0, 135.4 ($C^{5/15/31}_{2/2/2}$), 135.7 (d, ${}^{3}J_{CF} = 8.0$ Hz, $C^{10/20}_{2/2}$), 138.4 (C^{5}_{1}), 138.2 ($C^{26/36}_{1/1}$), 139.4, 146.1 146.8, 146.9 ($C^{15/21/21/31}_{1/1/4/1}$), 162.9 (d, ${}^{1}J_{CF} = 247.4$ Hz, $C^{10/20}_{4/4}$), 166.2 (C^{21}_{5}), 167.3, 167.4 (C_{5}^{15} , C_{5}^{31}) ppm. ¹⁹F NMR (CDCl₃): $\delta = -114.5$ (tt, ³ $J_{HF} = 8.6$ Hz, ⁴ $J_{HF} = 5.4$ Hz) ppm. MS (FD): m/z (%) = 1506.9 (100) [M]⁺. MS (ESI): m/z (%) = 753.8 (90) [M+H]²⁺, 754.3 (100) $[M+2H]^{2+}$, 1506.6 (37) $[M]^+$. HR-MS (ESI): obs. m/z = 1506.5826; calcd. for $[M]^+$ 1506.5781. IR (KBr): \tilde{v} [cm⁻¹] = 3443 (b, NH^{amide}), 3320 (w, NH^{pyrrole}), 2927 (w, CH), 2853 (w, CH), 1724 (m, CO), 1609 (m), 1512 (s), 1274 (s, C-O-C), 1103 (s, CF). UV/Vis (CH₂Cl₂): λ (ε / M⁻¹ cm⁻¹) = 421 (459800), 513 (23400), 550 (11600), 592 (73000), 649 (8000).



Zn²-4d: 2a (26.0 mg, 0.033 mmol), CH₂Cl₂ (3×10 mL), 1-chloro-*N*,*N*,2-trimethylpropenylamine (17 µL, 0.132 mmol), triethylamine (2×1 drop), Zn-3c (22.0 mg, 0.028 mmol). Yield: 17.0 mg (0.011 mmol, 40%), purple powder. $C_{99}H_{71}F_2N_9O_5Zn$ (1570.07). $R_f = 0.41$ (silica, CH₂Cl₂/ethyl acetate 100:1). ¹H NMR (d₈-THF): $\delta = -2.47$ (s, 2 H, H^{MespyrroleNH}), 1.87 (s, 12 H, H^{26/36}_{5/5}), 2.63 (s, 6 H, $H^{26/36}_{6/6}$, 4.06 (s, 6 H, $H^{15/31}_{6/6}$), 7.35 (s, 4 H, $H^{26/36}_{3/3}$), 7.52 (t, ${}^{3}J = 8.5$ Hz, 4 H, $H^{10/20}_{3/3}$), 8.22 (dd, ${}^{3}J = 8.2$ Hz, ${}^{3}J = 5.9$ Hz, 4 H, H ${}^{10/20}_{2/2}$), 8.25 (d, ${}^{3}J_{\text{HH}} = 8.6$ Hz, 2 H, H ${}^{5}_{3}$), 8.39 (m) and 8.54 (d, ${}^{3}J_{\text{HH}}$ = 7.9 Hz, 14 H / 2 H, H^{5/15/15/21/21/31/31}_{2/2/3/2/3/}), 8.71 (d, ${}^{3}J_{HH}$ = 4.6 Hz, 2 H, H^{pyrrole}), 8.75 (d, ${}^{3}J_{HH}$ = 4.6 Hz, 2 H, H^{pyrrole}), 8.78 (d, ${}^{3}J_{HH} = 4.5$, 2 H, H^{pyrrole}), 8.84 (d, ${}^{3}J_{HH} = 4.5$ Hz, 2 H, H^{pyrrole}), 8.86 (d, ${}^{3}J_{\text{HH}} = 4.7 \text{ Hz}, 2 \text{ H}, \text{H}^{\text{pyrrole}}), 8.89 \text{ (d, }{}^{3}J_{\text{HH}} = 4.3 \text{ Hz}, 4 \text{ H}, \text{H}^{\text{pyrrole}}), 9.03 \text{ (d, }{}^{3}J_{\text{HH}} = 4.6 \text{ Hz}, 2 \text{ H}, \text{H}^{\text{pyrrol}}),$ 10.16 (s, 1 H, H^{amide-NH}) ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 21.7$ (C^{26/36}_{6/6}), 21.9 (C^{26/36}_{5/5}), 52.5 $(C^{15/31}_{6/6}), 114.2 \ (d, {}^{2}J_{CF} = 21.5 \ Hz, C^{10/20}_{3/3}), 119.0 \ (C^{5}_{3}), 119.6, 119.9, 120.2, 120.6$ $(C^{5/10/15/20/21/26/31/36})$, 128.9 (4 C, $C^{26/36}_{3/3}$), 136.8 (d, ${}^{3}J_{CF} = 7.9$ Hz, $C^{10/20}_{2/2}$), 128.5, 128.8, 128.9, 135.6, 135.9, 136.8, 136.9 ($C^{5/15/15/21/21/31/31}_{2/2/3/2/3}$), 130.6, 131.0, 132.2, 132.3, 132.5, 132.9 $(C^{2,3,7,8,12,13,17,18,23,24,28,29,33,34,38,39}), 150.7, 151.2, 151.4, 151.6 (C^{1/4/6/9/11/14/16/19}), 139.5 (C^{26/36}_{1/1}), 149.5 (C^{26/3$ 139.0, 139.8, 136.6, 140.1, 140.7, 146.3, 147.8, 149.4 ($C^{5/5/15/15/21/21/31/31}_{1/4/1/4/1/4}$), 140.7 ($C^{10/20}_{1/1}$), 163.9 (d, ${}^{1}J_{CF} = 245.8$ Hz, $C^{10/20}_{4/4}$), 166.7 (C^{21}_{5}), 167.4, 167.5 ($C^{15/31}_{5/5}$) ppm. 19 F NMR (d₈-THF): δ = -114.5 (m) ppm. MS (FD): m/z (%) = 1568.2 (100) [M]⁺. MS (ESI): m/z (%) = 784.8 (34) $[M+H]^{2+}$, 1568.6 (17) $[M]^+$, 1569.6 (21) $[M+H]^+$. HR-MS (ESI): obs. m/z = 1568.4926; calcd. for $[M-H]^+$ 1568.4916. IR (KBr): \tilde{v} [cm⁻¹] = 3435 (b, NH^{amide}/NH^{pyrrole}), 2919 (w, CH), 2853 (w, CH), 1724 (m, CO), 1602 (m), 1511 (m), 1274 (s, C-O-C), 1103 (s, CF). UV/Vis (CH₂Cl₂): $\lambda (\varepsilon / M^{-1} cm^{-1})$ ¹) = 423 (816300), 515 (27000), 549 (32500), 593 (11800), 651 (15300).



Synthesis of Zn¹Zn²-4d: To porphyrin 4d (7.0 mg, 0.0045 mmol) in CH₂Cl₂ (5 mL) was added zinc acetate dihydrate (9.88 mg, 0.045 mmol) and the solution was stirred for 12 h at room temperature. The mixture was concentrated in vacuum. After column chromatography (silica, toluene/ethyl acetate 20:1) $\mathbf{Zn^{1}Zn^{2}-4d}$ was isolated as purple powder. Yield: 6.4 mg (0.0039 mmol, 88%). $C_{99}H_{69}F_2N_9O_5Zn_2$ (1633.44). $R_f = 0.37$ (silica, toluene/ethyl acetate 20:1). ¹H NMR (d₈-THF): $\delta =$ 1.88 (s, 12 H, $H^{26/36}_{5/5}$), 2.63 (s, 6 H, $H^{26/36}_{6/6}$), 4.05 (s), 4.06 (s, $H^{15/31}_{6/6}$), 7.32 (s, 4 H, $H^{26/36}_{3/3}$), 7.52 (t, ${}^{3}J = 8.7$ Hz, 4 H, H ${}^{10/20}_{3/3}$), 8.22 (dd, ${}^{3}J = 8.4$ Hz, ${}^{3}J = 5.6$ Hz, 4 H, H ${}^{10/20}_{2/2}$), 8.25 (d, ${}^{3}J_{HH} = 8.6$ Hz, 2 H, H⁵₃), 8.32 (m, 4 H); 8.41 (m, 8 H,); 8.51 (d, ${}^{3}J_{HH} = 8.1$ Hz, 2 H) (H^{5/15/15/21/2131/31}_{2/2/3/2/3/2}), 8.71 (d, ${}^{3}J_{HH} = 4.6$ Hz, 2 H, H^{pyrrole}), 8.74 (d, ${}^{3}J_{HH} = 4.6$ Hz, 2 H, H^{pyrrole}), 8.77 (d, ${}^{3}J_{HH} = 4.6$ Hz, 2 H, H^{pyrrole}), 8.84 (d, ${}^{3}J_{\text{HH}} = 4.6$ Hz, 2 H, H^{pyrrole}), 8.87 (d, ${}^{3}J_{\text{HH}} = 4.7$ Hz, 2 H, H^{pyrrole}), 8.88 (d, ${}^{3}J_{\text{HH}} = 4.6$ Hz, 2 H, H^{pyrrole}), 8.89 (d, ${}^{3}J_{HH} = 4.6$ Hz, 2 H, H^{pyrrole}), 9.04 (d, ${}^{3}J_{HH} = 4.6$ Hz, 2 H, H^{pyrrole}), 10.15 (s, 1 H, H^{amide-NH}) ppm. ¹³C{¹H} NMR (d₈-THF): $\delta = 21.8$ (C^{26/36}_{6/6}), 22.2 (C^{26/36}_{5/5}), 52.5 (C^{15/31}_{6/6}), 114.2 (d, ${}^{2}J_{CF} = 21.5$ Hz , $C_{3/3}^{10/20}$, 119.0 (s, 1 C, C_{3}^{5}), 119.9, 120.3, 120.6, 122.3 $(C^{5/10/15/20/21/26/31/36})$, 126.7, 128.4, 128.5, 135.6, 135.6, 135.9, 138.4, 139.6 $(C^{5/15/15/21/21/31/31}_{2/2/3/2/3/2})$, 128.7 ($^{26/36}_{3/3}$), 130.5 (d, $^{4}J_{CF} = 3.2$ Hz, $C^{10/20}_{1/1}$), 131.3, 131.3, 140.7, 140.8, 147.9, 149.4 $(\mathbf{C}^{5/5/15/15/21/21/31/31}_{1/4/1/4/1/4/1/4}),$ 132.7, 132.2, 132.3. 132.6, 132.8, 132.9 $(C^{2,3,7,8,12,13,17,18,23,24,28,29,33,34,38,39})$, 136.9 (d, ${}^{3}J_{CF} = 7.9$ Hz, $C^{10/20}_{2/2}$), 150.6, 150.7, 150.7, 151.0, 151.0, 151.2, 151.4, 151.6 ($C^{1/4/6/9/11/14/16/19/22/25/27/30/32/35/37/40}$), 163.1 (d, ${}^{1}J_{CF} = 245.2$ Hz, $C^{10/20}_{4/4}$), 166.8 (C^{21}_{5}), 167.5 (C^{15}_{5} , C^{31}_{5}) ppm. ¹⁹F NMR (d₈-THF): $\delta = -118.7$ (br.s) ppm. MS (FD): m/z (%) = 1632.6 (100) $[M]^+$. HR-MS (ESI): obs. m/z = 1630.4067; calcd. for $[M+H]^+$ 1630.4051. IR (KBr): \tilde{v} $[cm^{-1}] = 3425$ (b, NH^{amide}), 2925 (s, CH), 2856 (w, CH), 1726 (m, CO), 1602 (m), 1512 (m), 1278 (m, C-O-C), 1101 (s, CF). UV/Vis (CH₂Cl₂): $\lambda (\varepsilon / M^{-1} \text{ cm}^{-1}) = 423$ (806700), 549 (45600), 588 (13000).

Discussion of relevant NMR data of bis(porphyrins): The pyrrole NH proton resonances are indicative of the electron withdrawing nature of the porphyrin substituents: $\delta = -2.80 (C_6F_5)$, $-2.76 (4-C_6H_4CF_3)$, $-2.76 (4-C_6H_5F)$, $-2.6 (2,4,6-C_6H_2(CH_3)_3)$. Their correct integral ratio confirms the composition of **4a** – **4d**. The presence of two methyl ester groups is confirmed by the presence of two resonances of the CH₃ groups again in the correct integral ratio at $\delta = 4.12 - 4.14$ ppm. Particularly informative is the ¹⁹F NMR spectrum of **4c** which displays the expected ¹⁹F resonances of the C₆F₅ and C₆H₄CF₃ substituents in the correct intensity ratio (Supporting Information, Figure S1).

The zinc porphyrins $\mathbf{Zn^2-4d}$ and $\mathbf{Zn^1Zn^2-4d}$ are less soluble in chloroform than their parent free-base bis(porphyrin) 4d. In tetrahydrofuran their amide protons resonate at $\delta = 10.1$ ppm due to hydrogenbonding to the solvent. In the bis(metalated) complex $\mathbf{Zn^1Zn^2-4d}$ pyrrole-NH resonances are absent as expected. $\mathbf{Zn^2-4d}$ shows a single resonance at $\delta = -2.5$ ppm corresponding to the pyrrole-NH nuclei of the mesityl substituted free-base porphyrin proving the presence of the correct isomer $\mathbf{Zn^2-4d}$.

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DFT Section

Fig. S2 DFT calculated spin densities of radical ions $4c^+$ and $4c^-$ (isosurface value at 0.01 a.u.; B3LYP/LANL2DZ, PCM CH₂Cl₂).



Fig. S3 Frontier orbitals of 4b isosurface value at 0.05 a.u.; B3LYP/LANL2DZ, PCM CH₂Cl₂.



Fig. S4 Frontier orbitals of 4c isosurface value at 0.05 a.u.; B3LYP/LANL2DZ, PCM CH₂Cl₂.



Fig. S5 Frontier orbitals of Zn²-4d isosurface value at 0.05 a.u.; B3LYP/LANL2DZ, gasphase.



Fig. S6 EPR spectra of $4b^{+/-}$, $Zn^2-4d^{+/-}$ and their reference compounds in CH₂Cl₂ at 77 K (9.4 GHz).



Fig. S7. Normalised Soret bands of 4a - 4d, Zn^2-4d and Zn^1Zn^2-4d and their constituent reference porphyrins

in CH_2Cl_2 .



Fig. S8. Normalised (to Q(0,0)) emission spectra of Ac-3a – Ac-3d in CH₂Cl₂.



Fig. S9. Normalised (logarithmic) fluorescence decays of $Zn^{1}Zn^{2}$ -4d, Zn-1a and Zn-Ac-3c in $CH_{2}Cl_{2}$.



Fig. S10. X-band EPR spectra of radical ions $\mathbf{Zn}^{1}\mathbf{Zn}^{2}-4\mathbf{d}^{+/-}$ and reference radicals in CH₂Cl₂ at 295 K (9.4 GHz).



Cartesian coordinates of DFT optimised geometries (B3LYP/LANL2DZ, PCM CH₂Cl₂):

4a			
7	-7.760541000	-1.506887000	-0.095645000
7	-7.869162000	-1.4/0/15000	-0.340637000
7	-10.850728000	1.394218000	0.051896000
6	-6.399478000	-1.282692000	0.094849000
6	-6.724828000	-3.529929000	-0.199270000
6	-8.003542000	-2.860279000	-0.284222000
1	-4.696712000	-2.740595000 -4 595405000	0.165983000
6	-9.255157000	-3.465572000	-0.511793000
6	-5.782529000	-0.032953000	0.322807000
6	-11.768728000	-3.522755000	-0.857824000
6	-12.120395000	-1.303257000	-0.481603000
6	-10.512160000	-2.821146000	-0.557692000
1	-11.8/1228000	-4.5/412/000	-1.085257000
6	-12.825830000	-0.080913000	-0.352078000
6	-8.097138000	2.709325000	0.506629000
6 6	-6.827704000	2 496204000	0.663428000
6	-6.487774000	1.192515000	0.428139000
1	-6.715034000	4.501993000	0.780790000
6	-12.873044000	2.439135000	0.093859000
6	-11.902697000	3.392354000	0.333151000
6	-10.613102000	2.737885000	0.307777000
6 1	-12.215855000	2 593066000	-0.093324000
1	-12.062127000	4.443981000	0.519693000
6	-9.359337000	3.346724000	0.503198000
6 6	-9.23//12000	-4.952010000	-0./29661000
6	-8.861452000	-6.898688000	-2.183598000
6	-9.208739000	-7.765607000	-1.143414000
6	-9.569993000	-7.241943000	0.101388000
6 6	-3.662256000	-0.018643000	1.662417000
6	-2.263805000	0.372061000	1.797962000
6	-1.450699000	0.014934000	0.696551000
6	-2.067435000	-0.361610000	-0.520989000
1	-4.273994000	0.628245000	2.519254000
1	-1.805075000	0.647983000	2.737352000
1	-3.914208000	-0.666772000	-1.582809000
6 6	-9.331258000	4.832304000 5.388258000	2.016194000
6	-9.348082000	6.769083000	2.240866000
6	-9.413579000	7.643392000	1.151934000
6	-9.462860000	7.128443000	-0.146/92000
6	-14.320065000	-0.095904000	-0.498179000
6	-15.128523000	-0.782431000	0.438371000
6 6	-16.524253000	-0.125262000	-0 775786000
6	-16.341656000	0.559224000	-1.717831000
6	-14.945883000	0.576061000	-1.574398000
1	-14.663041000	-1.292499000	1.276809000
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۲ ۲	4 55010000	1.371421000 5 00/737000	-0 500/02000
6	10 250602000	5 86/65/000	0.355402000
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6 6	9.831193000 6.346053000 12.362724000 13.325326000 12.648351000 11.088165000	3.525040000 0.124815000 3.474597000 2.504840000 1.263573000 2.834429000	-0.591751000 0.307773000 -0.980193000 -0.908343000 -0.508122000 -0.625101000
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6 6 1 1	6.346053000 12.362724000 13.325326000 12.648351000 11.088165000 12.491884000 14.378526000	3.525040000 0.124815000 3.474597000 2.504840000 1.263573000 2.834429000 4.507824000 2.605888000	-0.591751000 0.307773000 -0.980193000 -0.908343000 -0.508122000 -0.625101000 -1.266202000 -1.124112000
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6 6 1 1 6 6 6 6	9.851195000 6.346053000 12.362724000 12.648351000 11.088165000 12.491884000 13.324835000 8.581588000 7.285333000 6.321058000	3.525040000 0.124815000 2.504840000 1.263573000 2.834429000 4.507824000 2.605898000 0.030179000 -2.685416000 -3.368955000 -2.401330000	-0.591751000 0.307773000 -0.980193000 -0.908343000 -0.625101000 -1.266202000 -1.124112000 -0.330196000 0.554608000 0.663027000 0.580939000
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6	9.412069000	5.856362000	0.214873000
6	14.202267000	-0.091643000	-0.807443000
6	14.697215000	-0.834172000	-1.906074000
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6	16.982574000	-0.169199000	-1.366251000
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6	18.431816000	-0.235164000	-1.695541000
8	18.918203000	-0.873524000	-2.655136000
1	8.485562000	-0.673800000	0.463848000
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7	-11.506645000	-1.501405000	-0.500016000
7	-8.569261000	-1.428646000	-0.214511000
7	-11.523763000	1.378473000	0.100710000
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6	-13.530987000	-0.028607000	-0.420203000
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1	-10.210293000	7.564554000	1 100615000
1	-9.780331000	7 205294000	2 971479000
1	-9 611854000	-7 829735000	1 339806000
5	-10 126825000	9 309801000	1 11//17000
1	0.572014000	9.309001000	0.227270000
1	-11 17/935000	9.636123000	1 0/9358000
1	-9 7/191/000	9.630123000	2 085446000
±	-10 112363000	4 676320000	3 196089000
1	-10 953217000	3 973254000	3 134251000
1	-9 205203000	4 073408000	3 334366000
1	-10.249436000	5.289351000	4.093297000
6	-9.610517000	5.236435000	-1.874158000
1	-8 691244000	4 641514000	-1 955256000
1	-10.442617000	4.570947000	-2.138396000
1	-9.563958000	6.033200000	-2.624251000
6	-9.189473000	-9.253030000	-0.972526000
1	-8.926499000	-9.761903000	-0.037934000
1	-10.164302000	-9.645310000	-1.296577000
1	-8.455554000	-9.537922000	-1.736098000
6	-9.828485000	-5.221506000	2.051174000
1	-9.030182000	-4.538353000	2.368723000
1	-10.766207000	-4.651194000	2.086409000
1	-9.897449000	-6.027943000	2.789084000
6	-8.946937000	-4.584635000	-2.957482000
1	-9.821161000	-3.944407000	-3.134145000
1	-8.085283000	-3.915895000	-2.832144000
1	-8.780359000	-5.184889000	-3.858363000
1	10.352505000	-5.397360000	-1.442684000
1	8.731815000	-4.841783000	2.523187000
1	8.645431000	-7.326437000	2.834634000
1	10.261326000	-7.882020000	-1.130530000
1	8.856/63000	4.926233000	-2.681452000
	8 946951000	/.40468/000	-3.034070000
1	11 025254000	7 0 6 5 0 0 0 0 0	0 70010000
1	11.025354000	7.865893000	0.722130000
1	11.025354000 10.939825000	7.865893000 5.387289000	0.722130000
1 1 7	11.025354000 10.939825000 0.471563000	7.865893000 5.387289000 0.362146000	0.722130000 1.075299000 0.465717000
1 1 7 1	11.025354000 10.939825000 0.471563000 0.031752000	7.865893000 5.387289000 0.362146000 0.618958000	0.722130000 1.075299000 0.465717000 -0.411641000
1 1 7 1 6 8	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.044144000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000
1 1 7 1 6 8 30	11.025354000 10.939825000 0.471563000 -0.373046000 0.044144000 9.722576000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023664000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000
1 1 7 1 6 8 30	11.025354000 10.939825000 0.471563000 -0.373046000 0.044144000 9.722576000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023964000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000
1 1 7 1 6 8 30 Zn² -	11.025354000 10.939825000 0.471563000 0.031752000 0.034144000 9.722576000 -4d ⁺	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023964000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000
$\frac{1}{1}$ $\frac{1}{7}$ $\frac{1}{6}$ $\frac{30}{2n^2}$	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.044144000 9.722576000 -4dd+ 8.190726000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023964000	0.72213000 1.075299000 0.465717000 -0.411641000 1.53786000 2.717273000 -0.100346000 1.032478000
1 1 7 1 6 8 30 Zn² -	11.025354000 10.939825000 0.471563000 0.031752000 0.034144000 9.722576000 -4d 8.190726000 11.106162000	7.865893000 5.387289000 0.362146000 0.618958000 -0.055401000 0.023964000 -1.243385000 -1.276361000	0.72213000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000
1 1 7 1 6 8 30 Zn² -	11.025354000 10.939825000 0.471563000 0.031752000 0.04144000 9.722576000 9.722576000 4dt ⁺ 8.190726000 11.106162000 8.082738000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023964000 -1.243385000 -1.276361000 1.419580000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000
1 1 7 1 6 8 30 Zn² •	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.044144000 9.722576000 1.106162000 8.082738000 11.006335000	7.86593000 5.387289000 0.362146000 0.142280000 -0.055401000 0.023964000 -1.276361000 1.419580000 1.403738000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000
1 1 7 1 6 8 30 Zn² -	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.044144000 9.722576000 -4dd ⁺ 8.190726000 11.106162000 8.082738000 11.006335000 6.826014000	7.865893000 5.387289000 0.362146000 0.142280000 -0.055401000 0.023964000 -1.276361000 1.419580000 1.403738000 -1.017070000	0.72213000 1.075299000 0.465717000 -0.411641000 1.537860000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.113989000 -0.713526000 1.184498000
1 1 7 1 6 8 30 Zn² -	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.04144000 9.722576000 1.106162000 11.006335000 6.826014000 6.268048000	7.865893000 5.387289000 0.362146000 0.618958000 0.023964000 -0.055401000 -1.243385000 -1.276361000 1.419580000 1.403738000 -1.017070000 -2.223932000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.84498000 0.753681000
1 1 7 1 6 8 30 Zn² - 7 7 7 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.044144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.297484000	7.86593000 5.387289000 0.362146000 0.142280000 -0.05540100 0.023964000 -1.276361000 1.419580000 1.403738000 -1.017070000 -2.22332000 -3.127203000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 1.13989000 1.84498000 1.753681000 1.941358000
1 1 7 1 6 8 30 Zn² - 7 7 7 6 6 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.044144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.297484000 8.525133000	7.865893000 5.387289000 0.362146000 0.142280000 -0.055401000 0.023964000 -1.276361000 1.419580000 1.403738000 -1.017070000 -2.223932000 -3.127203000 -2.517412000	0.722130000 1.075299000 0.465717000 -0.411641000 2.717273000 -0.100346000 0.394282000 -0.113989000 -0.113989000 -0.713526000 1.184498000 1.753681000 1.941358000 1.485120000
1 1 7 1 6 8 30 Zn² 7 7 7 7 6 6 6 6 1	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.04144000 9.722576000 1.106162000 11.106162000 11.006335000 6.826014000 7.297484000 8.525133000 5.223270000	7.865893000 5.387289000 0.362146000 0.618958000 0.023964000 -0.055401000 -1.276361000 1.419580000 1.419580000 1.403738000 -1.017070000 -2.223932000 -3.127203000 -2.517412000 -2.374383000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.184498000 1.941358000 1.941358000 1.947717000 1.977717000
1 1 7 1 6 8 30 Zn² - 7 7 7 7 6 6 6 6 6 1	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.04414000 9.722576000 1.106162000 8.082738000 11.006335000 6.826014000 6.826014000 6.268048000 7.297484000 8.525133000 5.223270000 7.227455000 0.0445000 0.0455000 0.25513000 0.227455000 0.227455000 0.0445000 0.0445000 0.0445000 0.04550000 0.04550000 0.0455000000000000000000000000000000000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 -1.276361000 1.419580000 1.403738000 -1.017070000 -2.22332000 -3.127203000 -2.517412000 -2.374383000 -4.125475000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 -0.113989000 -0.713526000 1.84498000 1.941358000 1.941358000 1.485120000 2.346647000 2.346647000
1 1 7 1 6 8 30 Zn² 7 7 7 7 6 6 6 6 1 1 6	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.044144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.237484000 8.525133000 5.223270000 7.227455000 9.802445000	7.86593000 5.387289000 0.362146000 0.142280000 -0.055401000 0.023964000 -1.276361000 1.419580000 -1.017070000 -2.223932000 -3.127203000 -2.517412000 -2.517412000 -3.113466000 -3.113466000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.84498000 1.753681000 1.941358000 1.941358000 1.9477717000 2.34647000 1.502492000 1.502492000
1 1 7 6 8 30 Zn² - 7 7 7 7 6 6 6 6 6 6 1 1 6 6	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.04144000 9.722576000 11.106162000 8.082738000 11.00635000 6.826014000 6.268048000 7.227484000 5.223270000 7.22748000 5.223270000 7.22745000 9.802445000 6.134436000 12.007325000	7.865893000 5.387289000 0.362146000 0.618958000 0.023964000 -0.055401000 0.023964000 -1.276361000 1.419580000 1.419580000 1.403738000 -2.223932000 -3.127203000 -2.517412000 -2.374383000 -4.125475000 -3.113466000 0.162093000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.184498000 1.753681000 1.941358000 1.941358000 1.977717000 2.346647000 1.502492000 0.828000000 1.82400000
1 1 7 1 6 8 30 Zn² - 7 7 6 6 6 6 6 1 1 6 6 6 6	1.025354000 1.025354000 1.939825000 0.471563000 0.031752000 0.04414000 9.722576000 1.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.297484000 8.525133000 5.223270000 7.227455000 9.802445000 6.134436000 12.297975000 12.297975000	7.865893000 5.387289000 0.362146000 0.618958000 0.023964000 -1.243385000 -1.276361000 1.419580000 -1.276361000 1.419580000 -1.27338000 -3.127203000 -2.223932000 -3.127203000 -2.517412000 -2.374383000 -4.125475000 -3.179251000 -3.2772051000 -3.2772051000 -3.2772051000 -3.2772051000 -3.277200 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000 -3.2772000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.84498000 1.941358000 1.941358000 1.941358000 1.977717000 2.346647000 1.502492000 0.828000000 1.085122000 0.65122000
1 1 7 8 30 Zn² 7 7 7 7 6 6 6 6 1 1 6 6 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.044144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.297484000 8.525133000 5.22370000 9.802445000 6.134436000 12.297975000 13.203533000 12.455248000	7.86593000 5.387289000 0.362146000 0.142280000 -0.055401000 -1.273364000 -1.273361000 1.419580000 1.419580000 -1.419580000 -2.22332000 -2.517412000 -2.517412000 -2.517412000 -2.5174383000 -1.125475000 -3.113466000 0.162093000 -2.330674000 -1.14482000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 -0.113989000 -0.713526000 1.753681000 1.941358000 1.485120000 1.97777000 2.346647000 1.502492000 0.82800000 1.085122000 0.507473000 0.057473000
1 1 7 1 6 8 30 Zn² - 7 7 7 7 7 7 7 7 6 6 6 6 6 1 1 6 6 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.04144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.237484000 8.525133000 5.223270000 7.227455000 9.802445000 6.134436000 12.297975000 13.203533000 12.452549000 10.988488000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023964000 -1.276361000 1.419580000 1.419580000 1.419580000 -2.223932000 -2.517412000 -2.374383000 -4.125475000 0.162093000 -3.113466000 0.162093000 -3.179251000 -1.144982000 -2.51467000 -1.144982000 -2.51467000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.184498000 1.753681000 1.941358000 1.941358000 1.941358000 1.941358000 1.9242000 0.52492000 0.82800000 1.085122000 0.507473000 0.069041000 1.06941000
$\sum_{i=1}^{1} \sum_{j=1}^{1} \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{i$	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.04144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.297484000 8.525133000 7.227455000 9.80245000 13.203533000 12.452549000 10.988488000 12.483173000	7.865893000 5.387289000 0.362146000 0.618958000 0.023964000 -1.276361000 -1.276361000 1.419580000 1.403738000 -1.017070000 -2.217412000 -2.374383000 -4.125475000 -3.117425000 -3.11746000 0.162093000 -1.144982000 -2.519467000 -4.147269000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.184498000 1.941358000 1.941358000 1.947717000 2.346647000 1.502492000 0.828000000 1.05122000 0.507473000 0.069041000 1.009587000 1.527775000
1 1 7 1 6 8 30 Zn² 7 7 7 7 7 6 6 6 6 6 6 6 6 6 6 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.04144000 9.722576000 1.106162000 8.082738000 11.006335000 6.826014000 6.26048000 7.297484000 8.525133000 5.223270000 9.802445000 6.134436000 12.297975000 13.203533000 12.452549000 10.988488000 12.483173000 14.268216000	7.865893000 5.387289000 0.362146000 0.0142280000 -0.055401000 -1.276361000 1.419580000 1.403738000 -1.276361000 1.419580000 -3.127203000 -2.22332000 -3.127203000 -2.517412000 -2.374383000 -4.125475000 -3.179251000 -2.330674000 -1.144982000 -2.519467000 -2.476329000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.844980000 1.941358000 1.941358000 1.941358000 1.977717000 2.346647000 1.502492000 0.629492000 0.629492000 0.69041000 1.09587000 1.527775000 0.40298001
$\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i$	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.031752000 0.044144000 9.722576000 11.106162000 8.082738000 11.006335000 6.826014000 6.268048000 7.297484000 8.525133000 5.223270000 7.227455000 9.802445000 6.134436000 12.297975000 13.203533000 12.45254000 13.203533000 12.48173000 14.268216000 13.049529000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 -1.276361000 1.419580000 1.419580000 1.419580000 -2.223932000 -2.517412000 -2.374383000 -4.125475000 -3.113466000 0.162093000 -3.179251000 -1.144982000 -2.519467000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.4753257000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.184498000 1.941358000 1.941358000 1.941358000 1.92492000 0.82800000 1.502492000 0.507473000 0.69041000 1.527775000 0.400298000 -0.57169000
1 1 7 1 6 8 30 Zn² 7 7 7 6 6 6 6 6 6 1 1 6 6 6 6 1 1 6 6 6 6 6 1 1 6 6 6 6 6 6 6 6 6 6 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.04144000 9.722576000 11.106162000 11.006335000 6.826014000 7.297484000 8.525133000 7.227455000 9.80245000 13.203533000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.452549000 10.988488000 12.45249000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.989000 10.9990000 10.999000 10.99000 10.99000 10.99000 10.990000 10.990000 10.990000 10.990000 10.990000 10.990000 10.990000 10.990000 10.990000 10.9900000 10.990000000000000000000000000000000000	7.865893000 5.387289000 0.362146000 0.618958000 0.023964000 -1.276361000 -1.276361000 1.419580000 1.419580000 1.403738000 -1.017070000 -2.223932000 -3.127203000 -2.517412000 -2.374383000 -4.125475000 -3.113466000 0.162093000 -3.1792511000 -2.5194671000 -2.5194671000 -2.476329000 -0.0281570000 2.70684000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.184498000 1.941358000 1.941358000 1.941358000 1.941358000 1.941522000 0.828000000 1.052492000 0.68941000 1.059473000 0.66941000 1.05987000 1.527775000 0.400298000 -0.570169000 -0.541522001
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$\sum_{j=1}^{n-1} \sum_{j=1}^{n-1} $	11.025354000 10.939825000 0.471563000 0.031752000 0.031752000 0.031752000 0.031752000 0.04144000 9.722576000 11.106162000 8.082738000 11.006335000 6.266048000 7.297484000 8.525133000 7.227455000 9.802445000 6.134436000 12.297975000 13.203533000 12.452549000 13.049529000 8.220498000 6.024864000 6.743361000 13.049529000 8.220498000 6.024864000 6.743361000 13.868272000 10.664432000 12.356216000 13.93520000 11.924783000 9.89727000 10.98478000 9.89727000 10.98478000 9.89727000 10.98478000 9.89727000 10.98478000 9.89727000 10.974187000 9.86600000 4.55698000 3.74382000 2.359361000 1.845550000 2.75221000 4.136550000 4.121593000 1.703399000	7.865893000 5.387289000 0.362146000 0.618958000 0.142280000 -0.055401000 0.023964000 -1.276361000 1.419580000 1.419580000 1.419580000 -2.223932000 -2.517412000 -2.374383000 -2.517412000 0.162093000 -3.179251000 -2.330674000 -1.144982000 -2.330674000 -1.144982000 -2.319467000 -2.319467000 -2.476329000 -2.51888000 1.302454000 4.427080000 2.551888000 1.302454000 4.427080000 2.551888000 1.302454000 4.427080000 2.551888000 1.302454000 4.427080000 2.55188000 1.47386000 2.5957401000 -7.10662000 -4.95687000 0.497461000 -4.95687000 0.497461000 -4.95687000 0.497461000 -3.280959000 -4.25687000 0.191296000 0.321915000 0.321915000 0.32397000 0.123803000 0.101405000 0.383563000 0.44569000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 -0.113989000 -0.713526000 1.84498000 1.941358000 1.941358000 1.941358000 0.52492000 0.52492000 0.52492000 0.52492000 0.52492000 0.52775000 0.66941000 1.09587000 1.02775000 0.641522000 0.577159000 -0.641522000 0.577159000 -0.54152000 -0.57795000 -0.54152000 -1.576431000 0.242840000 -1.56441000 -1.5641000 -1.26729000 -0.934104000 -1.976430000 2.247915000 -1.97626000 3.494970000 4.03328000 3.222621000 1.84058000 1.082613000 0.232091000 1.545891000 2.395658000 -1.08178000 2.395658000 -0.62252000
1 1 1 7 1 6 8 30 2 n ² - 7 7 7 7 6 6 6 6 6 1 1 6 6 6 6 6 6 6 6 6	11.025354000 10.939825000 0.471563000 0.031752000 -0.373046000 0.04144000 9.722576000 11.106162000 11.006335000 6.826014000 7.297484000 8.268048000 7.297484000 8.223270000 7.227455000 9.80245000 12.452549000 13.203533000 12.452549000 13.203533000 12.452549000 13.203533000 14.268216000 13.20353000 6.937360000 6.024864000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.890866000 12.9927000 9.89572000 9.89572000 10.06443200 10.074187000 9.89572000 10.9848200 10.9727000 10.98482000 10.9727000 10.98482000 10.9727000 10.98428000 10.9727000 10.84255000 10.975221000 10.84555000 2.752521000 1.3558000 4.121593000 1.70399000 4.817884000	7.865893000 5.387289000 0.362146000 0.142280000 0.023964000 -1.276361000 1.419580000 1.419580000 1.419580000 1.403738000 -2.223932000 -3.127203000 -2.517412000 -2.374383000 -4.125475000 -3.113466000 0.162093000 -3.179251000 -2.519467000 -2.519467000 -2.476329000 -2.519467000 -2.476329000 -2.519467000 2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.476329000 -2.519467000 -2.407182000 2.50568000 2.65681000 -4.497861000 -4.497861000 -4.925687000 0.191296000 0.323915000 0.321915000 0.321915000 0.323963000 0.101405000 0.383633000 0.444569000 0.03415000	0.722130000 1.075299000 0.465717000 -0.411641000 1.537860000 2.717273000 -0.100346000 1.032478000 0.394282000 0.113989000 -0.713526000 1.84498000 1.753681000 1.971717000 2.346647000 0.82800000 1.85122000 0.65941000 1.085122000 0.65941000 1.52775000 0.40298000 0.59775000 0.40298000 0.59775000 0.40298000 0.59775000 0.40298000 0.59775000 0.44522000 0.59775000 0.44522000 0.59775000 0.44522000 0.59775000 0.44522000 0.59775000 0.44522000 1.52775000 0.432232000 0.59775000 0.432232000 0.59775000 0.242840000 0.242840000 0.242840000 0.242840000 0.34104000 1.206729000 1.4617692000 1.46833000 2.097626000 3.494970000 1.82633000 0.07551000 0.23291000 1.545891000 2.62449000 0.232958000 -0.626252000 3.237988000

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1 1 1 1 6 1 1 1 6 1 1 1 6 1 1 1 6 1 1 1 6 1 1 1 6 1	21.387798000 21.381184000 10.307287000 9.551696000 8.738647000 10.018763000 10.035278000 9.605706000 11.081068000 9.507832000 0.2260753000 11.095290000 9.370988000 9.370988000 9.364219000 8.453486000 10.484799000 9.352131000 8.85946000 10.369901000 8.805946000 10.369901000 8.805946000 10.327012000 9.446830000 11.133666000 10.426385000 8.699676000 9.516865000 7.830246000 8.456020000 -9.404182000 -9.607534000 -8.133351000	0.33113000 1.190176000 -0.607692000 -6.153570000 -7.772675000 6.544736000 7.976377000 -8.542592000 -9.280320000 -8.829719000 -8.622564000 -2.882923000 -2.882923000 -2.882923000 -2.882923000 -3.860157000 -5.442364000 -4.13628000 8.85310000 -4.13628000 8.85310000 -5.589939000 5.589939000 5.589939000 5.589939000 5.5589939000 5.5589939000 5.5589939000 3.888151000 3.330146000 4.276546000 5.36089000 3.330146000 4.276546000 5.36638000 7.785476000 -7.785476000 -4.100176000	-1.687665000 -1.75025000 5.034630000 1.114017000 -4.263068000 -0.406311000 3.709581000 3.022048000 3.891036000 4.668647000 4.401414000 4.401414000 4.401414000 4.401414000 4.401414000 4.433958000 -0.260033000 -0.260033000 -0.754979000 -0.752654000 -2.917677000 -2.917677000 -3.092476000 -3.865169000 0.864830000 1.421323000 0.86483000 1.421323000 0.86483000 -3.348651000 -3.34865000 -3.34863000 -4.71490200 -0.56880000 3.755178000 4.683294000 0.872449000 -3.598801000
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	-9.630315000 -11.029211000 -8.610706000	5.109838000 7.607241000 7.808556000 -4.985424000	2.274232000 2.437473000 -1.642339000 -2.140491000
1	-9.630315000 -11.029211000 -8.610706000 -8.497988000	7.607241000 7.808556000 -4.985424000 -7.484769000	2.274232000 2.437473000 -1.642339000 -2.140491000 -2.274382000
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1 1 7 1 6 8 30 30 Zn¹Z	-9.630315000 -11.029211000 -8.610706000 -0.752851000 -10.752851000 -0.747353000 -0.288994000 0.080875000 -0.351197000 -9.978056000 9.257174000 Vn²-4d ⁺	5.109838000 7.607241000 -4.985424000 -7.784917000 -5.285772000 0.313405000 0.012119000 0.597245000 0.864448000 0.038433000 0.029571000	2.274252000 2.437473000 -1.642339000 -2.140491000 -2.274382000 1.395512000 1.529363000 0.795727000 -0.057744000 1.866075000 3.025881000 -0.046138000 0.168468000
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1 1 1 7 1 6 8 30 Z n ¹ Z 7 7 7 7 7 6 6 6 6 6 6 6 6 6 6 6 6 6	-9.630315000 -11.029211000 -8.610706000 -8.497988000 -10.752851000 -10.870106000 0.288994000 0.080875000 -0.288994000 0.351197000 9.978056000 9.257174000 7.759470000 10.742205000 6.417251000 5.700660000 6.417251000 6.417251000 6.417251000 5.700400000 6.42210000 4.642210000 6.438895000 9.108669000 5.828876000 11.594957000 12.584487000 11.97078800 11.9707800 11.9707800 11	-1.10838000 7.607241000 7.808556000 -4.985424000 -7.484769000 -7.784917000 -5.285772000 0.313405000 0.12119000 0.597245000 0.864448000 0.038433000 0.029571000 -1.463660000 1.324854000 -0.811487000 -1.989155000 -2.480408000 -2.035018000 -2.035018000 -3.230952000 0.450583000 -3.515230000 -2.70822000 -1.41261800 -1.41261800 -1.41261	2.274222000 2.437473000 -1.642339000 -2.140491000 -2.274382000 1.395512000 1.529363000 -0.057744000 1.866075000 3.025881000 -0.046138000 0.168468000 0.168468000 0.318887000 0.08909000 -0.560181000 1.121863000 1.604650000 1.301858000 0.849765000 0.849765000 0.303273000 -0.009730000 -0.009730000
1 1 1 1 7 7 1 6 8 30 Zn¹Z 7 7 7 7 7 7 7 7 7 6 6 6 6 6 6 6 6 6 6 6 6 6	-9.630315000 -11.029211000 -8.61706000 -8.497988000 -10.752851000 -0.747353000 -0.288994000 0.08875000 -0.351197000 -9.978056000 9.257174000 2.647473 2.64747 7.759470000 10.617473000 7.871979000 10.742205000 6.417251000 5.70060000 6.417251000 5.70060000 6.417039000 7.909402000 4.642210000 6.438895000 9.188695000 9.188695000 1.594957000 12.584487000 11.594957000 12.584487000 11.970788000 10.359472000 11.59472000 11.60042000 11.60042000 11.60042000 11.60042000 11.594957000 12.584487000 11.970788000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 11.594957000 12.584487000 13.59472000 14.6004200 14.6004200 14.6004200 15.59472000 15.59472000 15.59472000 15.59472000 15.59472000 15.59472000 15.59472000 15.59472000 15.5947200 15.594	-1.10838000 7.607241000 7.808556000 -4.985424000 -7.784917000 -5.285772000 0.012119000 0.597245000 0.86448000 0.038433000 0.029571000 -1.463660000 1.629918000 1.324854000 -0.811487000 -1.989155000 -3.008621000 -2.480408000 -2.035018000 -4.022949000 -3.515230000 -3.515230000 -2.741623000 -2.741623000 -2.741623000 -2.741623000	2.274222000 2.437473000 -1.642339000 -2.140491000 -2.274382000 1.395512000 1.529363000 -0.057744000 1.866075000 3.025881000 -0.046138000 -0.046138000 0.168468000 0.168468000 0.168468000 0.318887000 1.121863000 1.604650000 1.301858000 0.849765000 0.849765000 0.804125000 0.814925000
1 1 1 1 7 1 6 8 30 Z n ¹ Z 7 7 7 7 6 6 6 6 6 6 6 6 6 6 6 6 6	-9.630315000 -11.029211000 -8.61070600 -8.497988000 -10.752851000 -0.747353000 -0.288994000 0.08875000 -0.351197000 -9.978056000 9.257174000 Cn²-4d⁺ 7.759470000 10.617473000 7.871979000 10.742205000 6.417251000 5.70060000 6.617039000 7.909402000 4.642210000 6.438895000 9.108669000 5.82876000 11.594957000 12.584487000 11.970788000 10.359472000 11.689811000 13.69326002	-1.10838000 7.607241000 7.808556000 -4.985424000 -7.848769000 -7.784917000 -5.285772000 0.313405000 0.012119000 0.597245000 0.864448000 0.029571000 -1.140578000 -1.463660000 1.629918000 1.324854000 -0.811487000 -1.989155000 -3.008621000 -2.480408000 -2.480408000 -2.480408000 -2.30952000 0.450583000 -2.700822000 -1.412618000 -2.7141623000 -2.537038000 -2.557038000 -2.537038000 -2.55703800 -2.557703800 -2.557703800 -2.557703800 -2.557705800 -2.55	2.274252000 2.437473000 -1.642339000 -2.274382000 1.395512000 1.529363000 0.795727000 -0.057744000 1.866075000 3.025881000 -0.046138000 0.168468000 0.318887000 0.318887000 0.318887000 1.221863000 1.221863000 1.301858000 1.301858000 1.301858000 1.301858000 0.847765000 0.849765000 0.849765000 0.84925000 0.814925000 0.814925000 1.42591000
1 1 1 1 7 1 6 8 30 7 7 7 7 7 7 6 6 6 6 6 6 6 6 6 6 6 1 1 6 6 6 6 6 6 6 6 6 6 6 6 6	-9.630315000 -11.029211000 -8.61706000 -8.497988000 -10.87016600 -0.752851000 -0.288994000 0.288994000 0.288994000 0.28875000 -9.978056000 9.257174000 7.759470000 10.617473000 7.871979000 10.742205000 6.417251000 5.700660000 6.417251000 5.700660000 6.41725000 1.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 11.594957000 12.584487000 11.594957000 11.594957000 11.594957000 12.584487000 11.594957000 12.584487000 13.628036000 13.628036000 12.66540000 13.628036000	-1.10838000 7.607241000 7.808556000 -4.985424000 -7.484769000 -7.784917000 -5.285772000 0.012119000 0.597245000 0.864448000 0.038433000 0.029571000 -1.140578000 -1.463660000 1.324854000 -0.811487000 -1.989155000 -3.008621000 -2.480408000 -2.035018000 -4.0583000 -3.230952000 0.450583000 -2.700822000 -1.412618000 -2.74623000 -2.94515800 -2.9451580	2.274252000 2.437473000 -1.642339000 -2.140491000 -2.274382000 1.395512000 1.529363000 0.795727000 -0.057744000 1.866075000 3.025881000 0.046138000 0.168468000 0.168468000 0.318887000 0.08999000 -0.560181000 1.60465000 1.121863000 1.60465000 1.301858000 0.301858000 0.261287000 0.849765000 0.849755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.84755000 0.8475780000000000000000000000000000000000
1 1 1 7 1 6 8 30 Z n ¹ Z 7 7 7 7 7 6 6 6 6 6 6 6 6 1 1 6 6 6 6 6 6 6 6 6 6 6 6 6	-9.630315000 -11.029211000 -8.610706000 -10.752851000 -10.752851000 -0.28994000 0.080875000 -0.288994000 0.351197000 9.978056000 9.257174000 7.759470000 10.617473000 7.871979000 10.742205000 6.417251000 5.700660000 6.417251000 5.70040000 6.43895000 9.108669000 5.828876000 11.594957000 12.584487000 11.970788000 10.359472000 11.689811000 3.628036000 12.656614000 8.144484000	<pre>>.109838000 7.607241000 7.808556000 -4.985424000 -7.784917000 -5.285772000 0.313405000 0.012119000 0.597245000 0.864448000 0.038433000 0.029571000 -1.463660000 1.629918000 1.324854000 -0.811487000 -1.989155000 -3.230952000 0.450583000 -2.130528000 -4.515230000 -2.741623000 -2.94515800</pre>	2.274252000 2.437473000 -1.642339000 -2.274382000 1.395512000 1.529363000 0.795727000 -0.057744000 1.866075000 3.025881000 -0.046138000 0.168468000 0.168468000 0.08909000 -0.560181000 1.121863000 1.604650000 1.720266000 1.301858000 0.849765000 0.849765000 0.849765000 0.849765000 0.849765000 0.849765000 0.849765000 0.849765000 0.814925000 1.142591000 0.170115000 -0.537778000 -0.427104001

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ю	-3.009326000	0.33/659000	0.443462000
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1 6 8 30 30	-0.301150000 0.072142000 -0.366847000 -9.963017000 9.249436000	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000	-0.084044000 1.789201000 2.916170000 -0.094410000 0.183829000
1 6 8 30 30 7 n ¹ 7	-0.30115000 0.072142000 -0.366847000 -9.963017000 9.249436000	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000	-0.084044000 1.789201000 2.916170000 -0.094410000 0.183829000
1 6 8 30 30 Zn¹Z	-0.30115000 0.072142000 -0.366847000 -9.963017000 9.249436000 Cn²-4d⁻	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000	-0.084044000 1.789201000 2.916170000 -0.094410000 0.183829000
1 6 8 30 30 Zn¹Z 7	-0.301150000 0.072142000 -0.366847000 -9.963017000 9.249436000 Zn²-4d⁻ 7.802952000	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000	-0.084044000 1.789201000 2.916170000 -0.094410000 0.183829000 0.921016000
1 6 8 30 30 Zn¹Z	-0.30115000 0.072142000 -0.366847000 -9.963017000 9.249436000 Cn²-4d 7.802952000 10.663504000	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000 -1.181428000 -1.469913000	-0.084044000 1.789201000 2.916170000 0.183829000 0.921016000 0.285926000
1 6 8 30 30 Zn¹Z 7 7 7	-0.30115000 0.072142000 -0.366847000 -9.963017000 9.249436000 Cn²-4d 7.802952000 10.6663504000 7.891387000	0.128781000 0.872277000 1.23922500 0.022876000 0.089367000 -1.181428000 -1.469913000 1.606338000	-0.08404000 1.789201000 2.916170000 0.094410000 0.183829000 0.921016000 0.285926000 0.037240000
1 6 8 30 30 Zn¹Z 7 7 7 7	-0.301150000 -0.301150000 -0.366847000 -9.963017000 9.249436000 2.49436000 2.49436000 2.49436000 1.663504000 7.891387000 10.763812000	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000 -1.181428000 -1.469913000 1.666338000 1.334053000	-0.08404000 1.789201000 2.916170000 0.094410000 0.183829000 0.921016000 0.285926000 0.037240000 -0.542461000
1 6 8 30 30 Zn¹Z 7 7 7 7 6	-0.301150000 -0.301150000 -0.366847000 -9.963017000 9.249436000 2.0 ² -4d ⁻ 7.802952000 10.663504000 7.891387000 10.763812000 6.456675000	0.128781000 0.872277000 1.23922500 0.022876000 0.089367000 -1.181428000 -1.469913000 1.606338000 1.334053000 -0.86863000	-0.084044000 1.789201000 2.916170000 0.094410000 0.183829000 0.921016000 0.285926000 0.037240000 -0.542461000 1.100360000
1 6 8 30 30 Zn¹Z 7 7 7 7 6 6	-0.301150000 -0.301150000 -0.366847000 -9.963017000 9.249436000 Zn²-4d 7.802952000 10.665504000 7.891387000 10.763812000 6.456675000 5.747692000	0.128781000 0.872277000 1.23922500 0.022876000 0.089367000 -1.181428000 -1.469913000 1.606338000 1.334053000 -0.868603000 -2.064736000	-0.08404000 1.789201000 2.916170000 0.094410000 0.183829000 0.921016000 0.285926000 0.037240000 -0.542461000 1.100360000 1.548544000
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, 6 8 30 30 Zn¹Z 7 7 7 7 6 6 6 6 6	-0.301150000 -0.36847000 -9.963017000 9.249436000 2.1 2.1 2.2 2.4 2.4 0. 663504000 1. 763812000 1. 763812000 6. 456675000 5. 747692000 6. 672979000 7. 862632000	0.128781000 0.872277000 1.23922500 0.022876000 0.089367000 -1.181428000 -1.469913000 1.606338000 1.334053000 -0.868603000 -2.064736000 -3.078691000 -2.528748000	-0.084044000 1.789201000 2.916170000 0.094410000 0.183829000 0.285926000 0.037240000 -0.542461000 1.100360000 1.548544000 1.643327000 1.245387000
1 6 8 30 Zn¹Z 7 7 7 7 6 6 6 6 1	-0.30115000 -0.30115000 -0.36684700 -9.963017000 9.249436000 2n²-4d 7.802952000 10.66350400 10.763812000 6.45675000 5.747692000 6.672979000 7.962632000 4.688857000	0.128781000 0.872277000 1.239225000 0.022876000 0.089367000 -1.469913000 1.606338000 1.334053000 -0.868603000 -2.064736000 -3.078691000 -2.528748000 -2.125739000	-0.08404000 1.789201000 2.916170000 0.094410000 0.183829000 0.285926000 0.037240000 -0.542641000 1.548544000 1.548544000 1.245387000 1.751455000
1 6 8 30 Zn¹Z 7 7 7 7 6 6 6 6 1 1	-0.301150000 -0.301150000 -0.366847000 -9.963017000 9.249436000 2.49436000 2.49436000 2.49436000 10.663504000 10.663504000 10.763812000 6.456675000 5.747692000 6.672979000 7.962632000 4.688857000 6.501297000	0.128781000 0.872277000 1.23922500 0.022876000 0.089367000 -1.469913000 1.606338000 1.334053000 -0.868603000 -2.064736000 -3.078691000 -2.528748000 -2.528748000 -4.102758000	-0.084044000 1.789201000 2.916170000 0.094410000 0.183829000 0.285926000 0.037240000 1.00360000 1.100360000 1.5424514000 1.643327000 1.245387000 1.751455000 1.942279000
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