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## **Experimental Procedures**



5-Hydroxymethyl-3,4-dimethylpyrrole-2-carbaldehyde (**11a**). А solution of 3.4dimethylpyrrole-2,5-dicarbaldehyde<sup>S1</sup> (564 mg, 3.73 mmol) in methanol (18 mL) was cooled to 0 °C with the aid of a salt-ice bath. Sodium borohydride (36 mg, 0.93mmol) was then added and the mixture was stirred for 10 min. Brine (21 mL) was added and stirring was continued for an additional 15 min. The mixture was exhaustively extracted with ethyl acetate and the combined organic phases were dried over magnesium sulfate. The drying reagent was removed by suction filtration and the solvent was removed under reduced pressure. The solid residue was recrystallized from chloroform-hexane to give the monoaldehyde (560 mg, 3.66 mmol, 98% yield) as a brown solid, mp 118-128 °C. The product was approximately 97% pure by proton NMR spectroscopy. Further purification by column chromatography on grade 3 alumina, eluting with 20% chloroform-hexanes, gave an analytical sample as a yellow-brown solid, mp 125-126 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.95 (3H, s), 2.25 (3H, s), 3.90 (1H, br s), 4.73 (2H, s), 9.42 (1H, s), 10.40 (1H, br s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 8 8.4, 9.0, 56.6, 117.7, 128.5, 133.7, 139.0, 176.9. Anal. Calcd for C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>: C, 62.73; H, 7.24; N, 9.14. Found: C, 63.16; H, 6.99; N, 9.14.



**5-Acetoxymethyl-3,4-dimethylpyrrole-2-carbaldehyde** (**11b**). Acetic anhydride (7.5 mL) was added to a solution of the foregoing pyrrole carbinol (350 mg, 2.28 mmol) in pyridine (7.5 mL) at -3 °C using a salt-ice bath, and the mixture was stirred for 1 h. The mixture was dispersed between dichloromethane and water, and the organic layer was separated. The aqueous layer was further extracted with dichloromethane (x 3) and the combined organic solutions were dried over sodium sulfate. The solvent was removed under reduced pressure and the dark brown residue was recrystallized from chloroform-hexane to give the acetoxymethylpyrrole (380 mg, 1.94

mmol, 85% yield) as a light brown solid, mp 121-122 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.01 (3H, s, 4-CH<sub>3</sub>), 2.08 (3H, s, OCOCH<sub>3</sub>), 2.26 (3H, s, 3-CH<sub>3</sub>), 5.04 (2H, s, 5-CH<sub>2</sub>), 9.17 (1H, br s, NH), 9.62 (1H, s, CHO); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  8.5 (4-CH<sub>3</sub>), 8.9 (3-CH<sub>3</sub>), 21.0 (OCOCH<sub>3</sub>), 57.2 (5-CH<sub>2</sub>), 120.4, 129.3, 131.0, 131.3, 171.4 (acetate C=O), 177.7 (CHO); EI MS (70 eV): m/z (% relative intensity) 195 (31, M<sup>+</sup>), 153 (28, [M – CH<sub>2</sub>=C=O]<sup>+</sup>), 136 (100, [M – C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>); HR MS (EI) calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>3</sub>: 195.0895, found 195.0893.



Methyl 4,5'-diformyl-3',4'-dimethyl-1,2'-dipyrrylmethane-2-carboxylate (12b). Sodium hydride (60% in mineral oil, 48mg, 0.50 mmol) was added to a solution of methyl 4formylpyrrole-2-carboxylate<sup>S2</sup> (144 mg, 0.94 mmol) in DMF (30 mL) and the mixture was stirred at room temperature for 30 min. A solution of acetoxymethylpyrrole **11b** (171 mg, 0.94 mmol) in DMF (15 mL) was then added dropwise over 10 min and the resulting mixture was stirred for 18 h at 30 °C. The mixture was diluted with ether and washed with water, and the aqueous solution was back extracted with ether (x 3). The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure. Recrystallization from ethanol gave the neo-confused dipyrrylmethane (205 mg, 0.71 mmol, 75%) as a white solid, mp 194 °C, dec; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.08 (3H, s, 3'-CH<sub>3</sub>), 2.25 (3H, s, 4'-CH<sub>3</sub>), 3.91 (3H, s, OCH<sub>3</sub>), 5.46 (2H, s, bridge-CH<sub>2</sub>), 7.36 (1H, d, J = 1.8 Hz, 5-H), 7.43 (1H, d, J = 1.8 Hz, 3-H), 9.60 (1H, s, 5'-CHO), 9.64 (1H, br s, NH), 9.74 (1H, s, 4-CHO); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  8.8 (3'-CH<sub>3</sub>), 9.0 (4'-CH<sub>3</sub>), 44.0 (bridge-CH<sub>2</sub>), 52.4 (OCH<sub>3</sub>), 118.5 (3-CH), 119.9, 124.1, 125.5, 129.3, 130.98, 131.02, 132.5 (5-CH), 162.4 (ester C=O), 177.8 (5'-CHO), 185.3 (4-CHO); EI MS (70 eV): m/z (% relative intensity) 288 (18, M<sup>+</sup>), 256 (28, [M – CH<sub>3</sub>OH]<sup>+</sup>), 227 (25), 213 (31), 153 (10), 136 (100,  $[C_8H_{10}NO]^+$ ); HR MS (EI) calcd for  $C_{15}H_{16}N_2O_4$ : 288.1110, found 288.1106. Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.13; H, 5.51; N, 9.58.



**MacDonald "2 + 2" synthesis of neo-confused porphyrin 13**. *p*-Toluenesulfonic acid (56 mg) in methanol (6 mL) was added dropwise to a stirred mixture of dialdehyde **12b** (29 mg, 0.10 mmol) and dipyrrylmethane dicarboxylic acid **7a**<sup>S3</sup> (31 mg, 0.10 mmol) in dichloromethane (50 mL) and methanol (6 mL). The resulting mixture was allowed to stir for 16 h at room temperature. The solution was shaken with a 0.2% aqueous ferric chloride solution for 20 min to oxidize the phlorin intermediate. The organic phase was separated and the aqueous solution back extracted with dichloromethane. The combined organic solutions were washed with water and 5% aqueous sodium bicarbonate solution, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on grade 3 alumina eluting with dichloromethane and hexane (1:1 to 3:1). The neo-confused porphyrin was collected as a pink-purple fraction, followed by a green band corresponding to the dihydroporphyrin **15**. Recrystallization from chloroform-hexane gave the neo-confused porphyrin (26.4 mg, 0.055 mmol, 55%) as a purple powder, mp >300 °C. The green fraction was recrystallized from chloroform-hexane to give **15** (10 mg, 0.013 mmol, 26%) as a green powder, mp >300 °C.



8,12-Diethyl-2-methoxycarbonyl-7,13,17,18-tetramethyl-1-aza-21-carbaporphyrin (13). UV-vis (1% Et<sub>3</sub>N-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) 329 (4.46), 390 (4.72), 486 (sh, 3.63), 525 (sh, 3.85), 549 (3.98), 562 (sh, 3.96), 604 nm (3.75); UV-vis (3 equiv TFA-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) 298

(4.34), 396 (4.72), 511 (3.67), 550 (3.82), 584 (3.90), 614 (3.99), 662 nm (3.96); UV-vis (1% TFA-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) 302 (4.31), 357 (sh, 4.50), 409 (4.81), 528 (3.73), 571 (3.77), 619 (sh, 3.84), 669 nm (3.94); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.23 (1H, s, 21-H), 1.56 (3H, t, J = 7.6 Hz, 8-CH<sub>2</sub>CH<sub>3</sub>), 1.61 (3H, t, J = 7.6 Hz, 12-CH<sub>2</sub>CH<sub>3</sub>), 1.69 (1H, br s, NH), 2.87 (3H, s, 17-CH<sub>3</sub>), 2.95 (6H, s, 7,18-CH<sub>3</sub>), 3.04 (3H, s, 13-CH<sub>3</sub>), 3.38 (2H, q, J = 7.6 Hz, 8-CH<sub>2</sub>), 3.51 (2H, q, J =7.6 Hz, 12-CH<sub>2</sub>), 4.17 (3H, s, OCH<sub>3</sub>), 8.20 (1H, s, 15-H), 8.30 (1H, s, 10-H), 8.60 (1H, d, J = 1.6 Hz, 3-H), 8.74 (1H, s, 5-H), 10.57 (1H, s, 20-H); <sup>1</sup>H NMR (dication 13H<sub>2</sub><sup>2+</sup>, 500 MHz, TFA-CDCl<sub>3</sub>):  $\delta$  -0.66 (1H, s, 21-H), 1.51 (3H, t, J = 7.6 Hz), 1.53 (3H, t, J = 7.6 Hz) (8,12-CH<sub>2</sub>CH<sub>3</sub>), 3.04 (3H, s, 17-CH<sub>3</sub>), 3.06 (3H, s, 13-CH<sub>3</sub>), 3.14 (3H, s, 7-CH<sub>3</sub>), 3.17 (3H, s, 18-CH<sub>3</sub>), 3.49-3.54 (4H, 2 overlapping quartets, 8,12-CH<sub>2</sub>), 4.16 (3H, s, OCH<sub>3</sub>), 8.25 (1H, d, J = 1.5 Hz, 3-H), 8.69 (1H, s, 15-H), 8.75 (1H, s, 10-H), 9.44 (1H, s, 5-H), 10.99 (1H, s, 20-H); <sup>13</sup>C NMR (125 MHz. CDCl<sub>3</sub>):  $\delta$  10.8, 10.9, 11.03, 11.05, 16.6, 16.8, 19.2, 19.3, 52.1, 93.0, 93.7, 113.4, 113.5, 121.0, 124.9, 125.7, 127.2, 134.2, 135.3, 140.1, 141.4, 142.0, 142.6, 142.9, 144.4, 145.3, 154.7, 162.0, 162.6, 163.2; <sup>13</sup>C NMR (dication  $13H_2^{2+}$ , 125 MHz, TFA-CDCl<sub>3</sub>):  $\delta$  11.0, 11.2, 11.3, 11.7, 15.7, 19.3, 19.5, 53.0, 93.4, 95.1, 112.7, 116.9, 118.5, 122.5, 122.9, 126.0, 134.0, 135.3, 139.3, 141.5, 142.4, 143.3, 145.7, 146.6, 149.8, 152.1, 152.7, 156.0, 161.0; HR MS (EI) calcd for C<sub>30</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>: 480.2525, found 480.2521.



**13,17-Diethyl-5(4-formyl-2-methoxycarbonyl-1-pyrrolyl)-7(4-formyl-2-methoxycarbonyl-1-pyrrolylmethyl)-2,3,7,8,12,18-hexamethyl-5,6-dihydroporphyrin** (**15**). UV-vis (1% Et<sub>3</sub>N-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log ε) 334 (4.35), 385 (4.58), 472 (sh, 3.80), 644 (3.81), 709 nm (3.90); UV-vis (5 equiv TFA-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log ε) 390 (4.66), 642 (sh, 3.71), 717 (3.98), 791 nm (4.00); UV-vis (5% TFA-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log ε) 428 (4.84), 732 (sh, 3.55), 826 nm (3.88); <sup>1</sup>H NMR (500 MHz,

CDCl<sub>3</sub>):  $\delta$  1.09 (3H, t, J = 7.6 Hz, 17-CH<sub>2</sub>CH<sub>3</sub>), 1.16 (3H, t, J = 7.6 Hz, 13-CH<sub>2</sub>CH<sub>3</sub>), 1.44 (3H, br q, <sup>5</sup>J = 1.0 Hz, 8-CH<sub>3</sub>), 1.85 (3H, br q, <sup>5</sup>J = 1.0 Hz, 7-CH<sub>3</sub>), 1.88 (3H, s, 3-CH<sub>3</sub>), 1.91 (3H, s, 12-CH<sub>3</sub>), 1.92 (3H, s, 2-CH<sub>3</sub>), 2.01 (3H, s, 18-CH<sub>3</sub>), 2.35-2.46 (4H, m, 2 x CH<sub>2</sub>CH<sub>3</sub>), 3.80 (3H, s, 6-pyrrole-CO<sub>2</sub>CH<sub>3</sub>), 3.88 (5-pyrrole-CO<sub>2</sub>CH<sub>3</sub>), 4.30 (1H, d, J = 14.0 Hz, 6-CH<sub>2</sub>), 4.90 (1H, s, 10-H), 5.58 (1H, s, 15-H), 5.79 (1H, d, J = 14.0 Hz, 6-CH<sub>2</sub>), 6.19 (1H, s, 20-H), 6.96 (1H, s, 5-H), 7.04 (1H, d, J = 1.8 Hz, 6-pyrrole 3-H), 7.26 (1H, d, J = 1.8 Hz, 5-pyrrole 3-H), 7.99 (1H, d, J = 1.8 Hz, 6-pyrrole 5-H), 8.46 (1H, d, J = 1.8 Hz, 5-pyrrole 5-H), 9.37 (1H, s, 6-pyrrole-CHO), 9.71 (1H, s, 5-pyrrole-CHO), 13.37 (2H, br s, 2 x NH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  8.8, 9.2, 9.4, 9.6, 9.8, 11.5, 14.9, 15.2, 17.6, 17.9, 50.7, 51.6, 52.0 (2), 87.0, 87.1, 95.6, 115.0, 115.8, 116.3, 121.6, 122.8, 124.3, 124.5, 124.6, 128.6, 131.6, 133.1, 136.05, 136.07, 136.6, 138.1, 139.7, 141.8, 148.2, 150.5, 152.0, 154.3, 161.7, 162.0, 175.1, 185.0, 185.6; HR MS (ESI) calcd for C4<sub>45</sub>H<sub>48</sub>N<sub>6</sub>O<sub>6</sub> + H: 769.3714, found 769.3707.



**Neo-confused phlorin 14**. *p*-Toluenesulfonic acid (56 mg) in methanol (6 mL) was added dropwise to a stirred mixture of dialdehyde **12b** (29 mg, 0.10 mmol) and dipyrrylmethane dicarboxylic acid **7a**<sup>S3</sup> (31 mg, 0.10 mmol) in dichloromethane (50 mL) and methanol (6 mL). The resulting mixture was allowed to stir for 16 h at room temperature. The solution was washed with water and 5% aqueous sodium bicarbonate solution, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on grade 3 alumina eluting with chloroform and hexane (1:1) and a deep blue fraction was collected. The solvent was evaporated under reduced pressure to give the neo-confused phlorin (31.1 mg, 0.069 mmol, 69%) as a purple powder, mp >300 °C; UV-vis (1% Et<sub>3</sub>N-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) 368 (4.53), 562 (4.15), 598 nm (4.15); UV-vis (1% TFA-CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) 327 (4.38), 392 (4.54), 552 (sh, 3.97), 600 (4.19), 669 nm (4.05); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.21 (3H, t, *J* = 7.6 Hz, 12-CH<sub>2</sub>CH<sub>3</sub>), 1.28 (3H, t, *J* = 7.6 Hz, 8-CH<sub>2</sub>CH<sub>3</sub>), 2.27 (3H, s, 7-CH<sub>3</sub>), 2.30 (3H, s, 13-CH<sub>3</sub>), 2.32

(3H, s, 17-CH<sub>3</sub>), 2.35 (3H, s, 18-CH<sub>3</sub>), 2.68 (2H, q, J = 7.6 Hz, 12-CH<sub>2</sub>), 2.72 (2H, q, J = 7.6 Hz, 8-CH<sub>2</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 5.56 (1H, d, J = 1.8 Hz, 21-H), 5.68 (2H, s, 20-CH<sub>2</sub>), 6.06 (1H, s, 10-H), 6.39 (1H, s, 5-H), 6.98 (1H, s, 15-H), 7.04 (1H, d, J = 1.8 Hz, 3-H), 7.67 (1H, br s), 8.27 (1H, v br) (2 x NH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  9.3, 9.7, 10.0, 10.2, 15.0, 15.5, 18.0, 18.5, 44.2, 51.5, 86.1, 98.5, 109.0, 118.2, 118.5, 120.4, 121.6, 122.5, 124.5, 127.2, 129.4, 133.0, 138.83, 138.85, 139.4, 143.9, 149.2, 150.8, 161.9, 165.8; HR MS (EI) calcd for C<sub>30</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>: 482.2682, found 482.2673.

Crystallographic Experimental Details for 15•CHCl<sub>3</sub>. X-ray quality crystals of the chloroform solvate of 15 ( $C_{45}H_{48}N_6O_6$  · CHCl<sub>3</sub>) were obtained by vapor diffusion of hexanes into a chloroform solution of the compound. The crystals were suspended in mineral oil at ambient temperature and a suitable crystal was selected. A mineral oil coated dark green irregular block thereby obtained of approximate dimensions 0.23 mm x 0.31 mm x 0.38 mm was mounted on a 50 µm MicroMesh MiTeGen Micromount and transferred to a Bruker AXS SMART APEX CCD X-ray diffractometer. The X-ray diffraction data were collected at -173°C using Mo-K<sub> $\alpha$ </sub> ( $\lambda$ = 0.71073 Å) radiation. A total of 3672 frames were collected. The total exposure time was 10.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.<sup>S4</sup> The integration of the data using a triclinic unit cell yielded a total of 92328 reflections to a maximum  $\theta$  angle of 31.81° (0.67 Å resolution), of which 15250 were independent (average redundancy 6.055, completeness = 96.2%,  $R_{int} = 2.02\%$ ,  $R_{sig} = 1.47\%$ ) and 12861 (84.33%) were observed with  $F_{a}^{2} > 2 \sigma(F_{a}^{2})$ . The final cell constants of a = 12.2119(3) Å, b = 14.9841(3) Å, c = 15.3037(3) Å,  $\alpha = 63.927(1)^{\circ}$ ,  $\beta = 73.114(1)^{\circ}$ ,  $\gamma = 69.089(1)^{\circ}$ , volume = 2319.71(9) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9254 reflections above 20  $\sigma(I)$  with 5.054° < 2 $\theta$  < 63.51°. Limiting indicies were as follows: -17 ≤ h ≤ 17, -21 ≤ k ≤ 21, -22  $\leq l \leq 22$ . Data were corrected for absorption effects using the multi-scan method (SADABS).<sup>S4</sup> The ratio of minimum to maximum apparent transmission was 0.952 with minimum and maximum SADABS generated transmission coefficients of 0.7105 and 0.7463. Solution and data analysis were performed using the WinGX software package.<sup>S5</sup> The structure was solved and refined in the space group P-1 (no. 2) with Z = 2.<sup>S6</sup> The solution was achieved by chargeflipping methods using the program SUPERFLIP<sup>S7</sup> and the refinement was completed using the program SHELX2013.<sup>S8,S9</sup> All non-H atoms were refined anisotropically. With the exception of H atoms attached to N, all H atoms were included in the refinement in the riding-model approximation (C--H = 0.95, 0.98, and 0.99 Å for Ar-H, CH<sub>3</sub>, and CH<sub>2</sub>;  $U_{iso}(H) = 1.2U_{eq}(C)$  except for methyl groups, where  $U_{iso}(H) = 1.5U_{eq}(C)$ ). H atoms attached to N were identified through the difference Fourier and freely refined isotropically. Full-matrix least-squares refinement on  $F^2$  led to convergence,  $(\Delta/\sigma)_{max} = 0.001$ ,  $(\Delta/\sigma)_{mean} = 0.0000$ , with  $R_I = 0.0542$  and  $wR_2 = 0.1564$  for 12861 data with  $F_o^2 > 2\sigma(F_o^2)$  using 1 restraint and 589 parameters. A final difference Fourier synthesis showed features in the range of  $\Delta\rho_{max} = 0.931 \text{ e}^2/\text{Å}^3$  to  $\Delta\rho_{min} = -1.097 \text{ e}^2/\text{Å}^3$ , which were close to the solvent Cl atoms and are best attributed to unmodelable disorder of the solvent. All residual electron away from the solvent was within accepted norms and was deemed of no chemical significance. Molecular diagrams were generated using ORTEP-3.<sup>S10</sup> CCDC 941797 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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Figure S1. ORTEP III drawing (50% probability level, hydrogen atoms drawn arbitrarily small) of compound **15**.

*Crystal data* for **15•CHCl<sub>3</sub>**: C<sub>45</sub>H<sub>48</sub>N<sub>6</sub>O<sub>6</sub>•CHCl<sub>3</sub>, M = 888.3, triclinic, a = 12.2119(3), b = 14.9841(3), c = 15.3037(3) Å,  $\alpha = 63.927(1)^{\circ}$ ,  $\beta = 73.114(1)^{\circ}$ ,  $\gamma = 69.089(1)^{\circ}$ , V = 2319.72(9) Å<sup>3</sup>, T = 100 K, space group *P*-1 (no. 2), Z = 2, 92328 reflections measured, 15250 unique ( $R_{int} = 0.0202$ ), final  $R_1 = 0.0542$ ,  $wR_2(F^2) = 0.1564$  for 589 parameters and 12861 data with  $F_0^2 > 2\sigma(F_0^2)$ . CCDC 941797.



Figure S2. Color POV-Ray rendered ORTEP III drawing (50% probability level, hydrogen atoms drawn arbitrarily small; Me and Et groups rendered as sticks for clarity) of compound **15**. Selected bond lengths: C(1)-C(2) 1.5210(15), C(2)-C(3) 1.3437(17), C(3)-C(4) 1.4788(16), C(4)-C(5) 1.4348(16), C(4)-N(21) 1.3174(14), N(21)-C(1) 1.4710(14), C(5)-C(6) 1.3670(17), C(6)-C(7) 1.4614(16), C(6)-N(22) 1.3691(15), C(7)-C(8) 1.3572(18), C(8)-C(9) 1.4609(17), C(9)-C(10) 1.3638(18), C(9)-N(22) 1.3769(16), C(10)-C(11) 1.4314(18), C(11)-C(12) 1.4688(18), C(11)-N(23) 1.3376(16), C(12)-C(13) 1.3584(19), C(13)-C(14) 1.4597(17), C(14)-C(15) 1.3683(17), C(14)-N(23) 1.3999(15), C(15)-C(16) 1.4188(16), C(16)-C(17) 1.4038(16), C(16)-N(24) 1.3765(14), C(17)-C(18) 1.4081(17), C(18)-C(19) 1.3963(15), N(24)-C(19) 1.3641(14), C(19)-C(20) 1.4962(15), C(20)-C(1) 1.5629(15), C(1)-C(25) 1.5509(16), C(25)-N(26) 1.4623(14), N(26)-C(27) 1.3960(14), C(27)-C(28) 1.3738(15), C(28)-C(29) 1.4178(16), C(29)-C(30) 1.3905(16), C(30)-N(26) 1.3516(14), C(20)-N(37) 1.4903(14), N(37)-C(38) 1.3961(14), C(38)-C(39) 1.3773(17), C(39)-C(40) 1.4114(18), C(40)-C(41) 1.3853(17), C(41)-N(37) 1.3523(15).



Figure S3. UV-vis spectrum of neo-confused porphyrin 13 in 1% Et<sub>3</sub>N-CH<sub>2</sub>Cl<sub>2</sub>.



Figure S4. UV-vis spectrum of neo-confused porphyrin 13 in CH<sub>2</sub>Cl<sub>2</sub>.



Figure S5. UV-vis spectra of neo-confused porphyrin **13** in CH<sub>2</sub>Cl<sub>2</sub> (red line), and with 0.5 equiv TFA (orange line), 1 equiv TFA (green line), 2 equiv TFA (blue line) and 3 equiv TFA (purple line).



Figure S6. UV-vis spectrum of neo-confused porphyrin 13 with 3 equiv TFA in  $CH_2Cl_2$ .



Figure S7. UV-vis spectra of neo-confused porphyrin **13** in CH<sub>2</sub>Cl<sub>2</sub> with 200 equiv TFA (red line), 300 equiv TFA (orange line), 500 equiv TFA (green line), 1000 equiv TFA (blue line) and 2000 equiv TFA (purple line).



Figure S8. UV-vis spectrum of neo-confused porphyrin 13 with 2000 equiv TFA in CH<sub>2</sub>Cl<sub>2</sub>.



Figure S9. UV-vis spectrum of neo-confused porphyrin 13 in 5% TFA-CH<sub>2</sub>Cl<sub>2</sub>.



Figure S10. UV-vis spectrum of dihydroporphyrin **15** in 1% Et<sub>3</sub>N-CH<sub>2</sub>Cl<sub>2</sub>.



Figure S11. UV-vis spectrum of 15 in CH<sub>2</sub>Cl<sub>2</sub>.



Figure S12. UV-vis spectra of **15** in CH<sub>2</sub>Cl<sub>2</sub> (red line), and with 0.5 equiv TFA (orange line), 1 equiv TFA (yellow line), 2 equiv TFA (green line), 5 equiv TFA (light blue line), 10 equiv TFA (dark blue line) and 30 equiv TFA (purple line).



Figure S13. UV-vis spectra of **15** in CH<sub>2</sub>Cl<sub>2</sub> with 500 equiv TFA (red line), 1000 equiv TFA (orange line), 2000 equiv TFA (green line), 3000 equiv TFA (light blue line), 5000 equiv TFA (dark blue line) and 10000 equiv TFA (purple line).



Figure S14. UV-vis spectrum of **15** in CH<sub>2</sub>Cl<sub>2</sub> with 50 equiv TFA.



Figure S15. UV-vis spectrum of 15 in 1% TFA-CH<sub>2</sub>Cl<sub>2</sub>.

0.5

0.4





Figure S16. UV-vis spectrum for neo-confused phlorin 14 in 1% Et<sub>3</sub>N-CH<sub>2</sub>Cl<sub>2</sub>.



Figure S17. The UV-vis spectra for phlorin 14 underwent complex changes upon addition of TFA. In figure A, an overlay of spectra for 14 in CH<sub>2</sub>Cl<sub>2</sub> is shown for 1% Et<sub>3</sub>N (red line), CH<sub>2</sub>Cl<sub>2</sub> only (green line), 0.5 equiv TFA (blue line) and 1 equiv TFA (purple line). Figure B shows further changes going from 1 equiv TFA (red line) to 2 equiv (green), 5 equiv (blue) and 10 equiv TFA (purple). Figure C shows the spectra with 10 equiv (red), 20 equiv (green), 50 equiv (blue) and 100 equiv (purple) TFA. In figure D, spectra were run with 200 equiv (red), 300 equiv (orange), 500 equiv (yellow), 2000 equiv (green), 5000 equiv (light blue), 10000 equiv (dark blue) and 20000 equiv (purple) TFA.



Figure S18. UV-vis spectrum for neo-confused phlorin 14 in 1% TFA-CH<sub>2</sub>Cl<sub>2</sub>.



Figure S19. UV-vis spectrum for neo-confused phlorin 14 in 5% TFA-CH<sub>2</sub>Cl<sub>2</sub>.



Figure S21. DEPT-135 NMR spectrum of hydroxymethylpyrrole 11a in CDCl<sub>3</sub>.



Figure S22. 125 MHz carbon-13 NMR spectrum of hydroxymethylpyrrole 11a in CDCl<sub>3</sub>.



Figure S23. HSQC NMR spectrum of hydroxymethylpyrrole 11a in CDCl<sub>3</sub>.



Figure S24. 500 MHz proton NMR spectrum of acetoxymethylpyrrole **11b** in CDCl<sub>3</sub>.



Figure S25. DEPT-135 NMR spectrum of acetoxymethylpyrrole **11b** in CDCl<sub>3</sub>.



Figure S26. 125 MHz carbon-13 NMR spectrum of acetoxymethylpyrrole 11b in CDCl<sub>3</sub>.



Figure S27. HSQC NMR spectrum of acetoxymethylpyrrole 11b in CDCl<sub>3</sub>.



Figure S28. 500 MHz proton NMR spectrum of 1,2'-dipyrrylmethane 12b in CDCl<sub>3</sub>.



Figure S29. DEPT NMR spectrum of 1,2'-dipyrrylmethane 12b in CDCl<sub>3</sub>.



Figure S30. 125 MHz carbon-13 NMR spectrum of 1,2'-dipyrrylmethane 12b in CDCl<sub>3</sub>.



Figure S31. Selected nOe difference proton NMR spectra for dipyrrole 12b in CDCl<sub>3</sub>.



Figure S32. HSQC NMR spectrum of 1,2'-dipyrrylmethane **12b** in CDCl<sub>3</sub>.





Figure S33. Partial assignments for the proton (upper figure) and carbon-13 (lower figure) NMR spectra of **12b** based on the foregoing data.





Figure S35. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of **15** in CDCl<sub>3</sub>.



Figure S36. Selected nOe difference proton NMR spectra for 15 in CDCl<sub>3</sub>.



Figure S37. HSQC NMR spectrum of 15 in CDCl<sub>3</sub>.



Figure S38. 125 MHz carbon-13 NMR spectrum of 15 in CDCl<sub>3</sub>.



Figure S39. DEPT-135 NMR spectrum of 15 in CDCl<sub>3</sub>.



\* = 8.8, 9.2 or 9.4

Figure S40. Partial assignments for the proton (upper figure) and carbon-13 (lower figure) NMR spectra of **15** based on the foregoing data.



Figure S41. 500 MHz proton NMR spectrum of neo-confused porphyrin 13 in CDCl<sub>3</sub>.



Figure S42. Selected nOe difference proton NMR spectra for 13 in CDCl<sub>3</sub>.



Figure S43. 500 MHz carbon-13 NMR spectrum of neo-confused porphyrin 13 in CDCl<sub>3</sub>.



Figure S44. DEPT-135 NMR spectrum of neo-confused porphyrin 13 in CDCl<sub>3</sub>.



Figure S45. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of neo-confused porphyrin **13** in CDCl<sub>3</sub>.



Figure S46. HSQC NMR spectrum of neo-confused porphyrin 13 in CDCl<sub>3</sub>.



Figure S47. Partial assignments for the proton (upper figure) and carbon-13 (lower figure) NMR spectra of **13** based on the foregoing data.



Figure S48. 500 MHz proton NMR spectrum of neo-confused porphyrin dication  $13H_2^{2+}$  in TFA-CDCl<sub>3</sub>.



Figure S49.  ${}^{1}$ H- ${}^{1}$ H COSY NMR spectrum of neo-confused porphyrin dication 13H<sub>2</sub><sup>2+</sup> in TFA-CDCl<sub>3</sub>.



Figure S50. Selected nOe difference proton NMR spectra of  $13H_2^{2+}$  in TFA-CDCl<sub>3</sub>.



Figure S51. DEPT-135 NMR spectrum of neo-confused porphyrin dication  $13H_2^{2+}$  in CDCl<sub>3</sub>.



Figure S52. 125 MHz carbon-13 NMR spectrum of neo-confused porphyrin dication  $13H_2^{2+}$  in TFA-CDCl<sub>3</sub>.



Figure 53. HSQC NMR spectrum of neo-confused porphyrin dication  $13H_2^{2+}$  in TFA-CDCl<sub>3</sub>.





Figure S54. Partial assignments for the proton (upper figure) and carbon-13 (lower figure) NMR spectra of  $13H_2^{2+}$  in TFA-CDCl<sub>3</sub> based on the foregoing data.



Figure S55. 500 MHz proton NMR spectrum of neo-confused phlorin 14 in CDCl<sub>3</sub>.



Figure S56. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of neo-confused phlorin **14** in CDCl<sub>3</sub>.



Figure S57. Selected nOe difference proton NMR spectra for 14 in CDCl<sub>3</sub>.



Figure S58. DEPT-135 NMR spectrum of neo-confused phlorin 14 in CDCl<sub>3</sub>.



Figure S59. 125 MHz carbon-13 NMR spectrum of 14 in CDCl<sub>3</sub>.



Figure S60. HSQC NMR spectrum of neo-confused phlorin 14 in CDCl<sub>3</sub>.





Figure S61. Partial assignments for the proton (upper figure) and carbon-13 (lower figure) NMR spectra of neo-confused phlorin **14** in CDCl<sub>3</sub> based on the foregoing data.



Figure S62. Electron impact mass spectrum of acetoxymethylpyrrole 11a.



Figure S63. Electron impact mass spectrum of neo-confused dipyrrylmethane 12b.



Figure S64. Electrospray ionization mass spectrum of hexapyrrolic species 15.



Figure S65. Electron impact mass spectrum of neo-confused porphyrin 13.



Figure S66. Electron impact mass spectrum of neo-confused phlorin **14** (m/z 482). Oxidation to neo-confused porphyrin **13** (m/z 480) has occurred to a considerable extent.