**Free base tripyrrins**

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**Supplementary information: Preparation and spectroscopic data for 2 and 5.**

3,8,9,13-Tetraethyl-2,4,13,15-tetramethyltripyrrin (2). Isocyanatonickel(II)tripyrrin 1 (49 mg, 0.1 mmol) is dissolved in diethylether (40 ml) and treated with a saturated KCN solution (10 ml) at ambient temperature in an ultrasound bath for 2 hours. During this time the colour of the mixture changes from green to red. After phase separation the organic layer is washed with water (2 × 20 ml) and dried with sodium sulfate, resulting in a tripyrrin solution. The solvent can be removed in vacuo to leave the free base ligand 2 (35 mg, 90%) as a red solid (calculated for C<sub>26</sub>H<sub>35</sub>N<sub>3</sub>: C 80.16, H 9.05, N 10.79; found: C 79.98, H 9.01, N 11.07%).

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.00 (t, J = 7.6 Hz, 6H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 1.10 (t, J = 7.6 Hz, 6H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 2.04 (s, 6H, 2 × CH<sub>3</sub>), 2.31 (q, J = 7.6 Hz, 4H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 2.32 (s, 6H, 2 × CH<sub>3</sub>), 2.53 (q, J = 7.6 Hz, 4H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 6.50 (s, 2H, 2 × H<sub>meso</sub>), 12.84 (br, 1H, NH).

<sup>13</sup>C-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.5, 14.3, 17.1, 17.4, 17.5, 18.4, 113.2, 133.1, 133.3, 138.9, 139.2, 151.4, 172.6.

**MS** (70 eV, EI): m/z = 389 (M<sup>+</sup>).

**UV/Vis** (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε) = 260 (21000), 330 (57000), 358sh (23000), 530sh (37000), 549 (38000), 601sh (10000), 660 nm (16000 L mol<sup>−1</sup> cm<sup>−1</sup>).

**IR** (Nujol): 3243 (ν<sub>NH</sub>), 1616 cm<sup>−1</sup> (ν<sub>C=C</sub>).

2,15-Di-tert-butyl-3,4,8,9,13,14-hexaethyltripyrrin (5). 2-tert-Butyl-3,4-diethylpyrrole (4) (575 mg, 3.21 mmol) and 3,4-diethyl-2,5-diformylpyrrole (3) (288 mg, 1.61 mmol) are dissolved in trifluoroacetic acid (20 ml) and heated to reflux for 10 hours. After evaporation of all volatiles a solution of sodium acetate (5.0 g, 61 mmol) in methanol (150 ml) is added, and the mixture is subjected to column chromatography on silica with diethylether/pentane (1/9). The blue fraction is collected and treated with a saturated solution of sodium acetate in water (30 ml), whereupon a colour change from blue to red is observed. The phases are separated, the organic layer is washed twice with water (200 ml), dried with sodium sulfate, and the solvent is removed in vacuo to leave the title compound (233 mg, 29%) as
a red powder (calculated for C$_{34}$H$_{51}$N$_3$: C 81.38, H 10.24, N 8.37; found: C 81.21, H 9.98, N 8.40%).

$^1$H-NMR (CD$_2$Cl$_2$): $\delta = 1.14$ (t, $J = 7.6$ Hz, 6H, 2 × CH$_2$CH$_3$), 1.18 (t, $J = 7.6$ Hz, 6H, 2 × CH$_2$CH$_3$), 1.23 (t, $J = 7.6$ Hz, 6H, 2 × CH$_2$CH$_3$), 1.35 (s, 18H, 2 × tBu), 2.56 (q, $J = 7.6$ Hz, 4H, 2 × CH$_2$CH$_3$), 2.57 (q, $J = 7.6$ Hz, 4H, 2 × CH$_2$CH$_3$), 2.61 (q, $J = 7.6$ Hz, 4H, 2 × CH$_2$CH$_3$), 6.65 (s, 2H, $H_{meso}$), 11.70 (br, 1H, NH).

$^{13}$C-NMR (CD$_2$Cl$_2$): $\delta = 14.8, 17.1, 17.4, 17.5, 18.0, 18.3, 22.5, 28.7, 113.4, 133.2, 133.3, 138.2, 145.8, 150.2, 172.7$.

MS (MALDI-TOF): $m/z = 502 ([M + H]^+)$.  

UV/Vis (CH$_2$Cl$_2$): $\lambda_{max} (\varepsilon) = 261$ (22000), 334 (53000), 362sh (22000), 522 (41000), 547 (39000), 671 nm (15000 L mol$^{-1}$ cm$^{-1}$).  

IR (Nujol): 3251 (v$_{NH}$), 1609 cm$^{-1}$ (v$_{C=C}$).