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Synthesis and Electrochemical Properties of a Novel Mono-*meso*-ferrocenyl Porphyrin

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Abstract: A synthetic route to mono-*meso*-ferrocenyl porphyrins using a MacDonald-type 2+2 condensation is described. In this method, the substituted diformyldipyrrylmethane **4** is treated with the dicarboxydipyrrylmethane **6**. The 5-ferrocenyldipyrrylmethane was obtained by condensation of benzyl 3-methyl-4-ethylpyrrol-2-carboxylate with ferrocenecarboxaldehyde in the presence of *p*-toluenesulfonic acid. The unequivocal assignment of all proton resonances in the new porphyrin was achieved by means of a detailed analysis of its H–H NOESY correlations. Interestingly, we noticed that the ferrocenyl group introduces an element of asymmetry in the molecule. The corresponding Co(II) and Ni(II) complexes were also prepared. In cyclic voltammograms of the free base and the Co or Ni complexes all voltammetric peaks disappear after four consecutive scans. This result suggests no film formation in any of them.

Key words: porphyrin synthesis, *meso*-ferrocenyl porphyrin, electrochemistry

The electropolymerization of vinyl-substituted metalloporphyrins gave rise to an extended discussion in literature.[2–7] This method, originally described by Macor and Spiro,[8] produces adherent films on electrode surfaces and increases the lifetime of the resulting modified electrodes. We reported a variety of electrochemical sensors prepared by electropolymerization of metalloprotoporphyrin IX dimethyl ester for different analytical applications.[9,10] The polymerization process only occurs with metalloporphyrins and is highly dependent on the nature of the central metal.[8] In this work, we report the synthesis of a novel porphyrin (H_2FP) with two vinyl moieties and a ferrocenyl group, which is very well known for its electrochemical properties.[11–14] With the idea that direct linkage of the ferrocenyl group to the porphyrin *meso*-carbon would induce strong electronic coupling between both systems, we prepared the corresponding Co(II) and Ni(II) complexes to be polymerized.

Synthesis of porphyrins containing four ferrocenyl groups at the *meso*-carbons was first reported in 1977 and was achieved via the reaction of ferrocenecarboxaldehyde with pyrrole in refluxing propionic acid.[15] A few years later, Lindsey and co-workers observed the beneficial effects of salts on an acid-catalyzed condensation leading to porphyrin formation with higher yields.[16] Syntheses of mono- and di-*meso*-ferrocenyl porphyrins employing ferrocenecarboxaldehyde and alkyldipyrrylmethanes[11,17,18] were described for the first time in 1999 and used milder procedures.[19,20] Chandrashekar and co-workers reported in 2000 the synthesis of different *meso*-substituted porphyrins obtained via *meso*-ferrocenyldipyrrylmethane in the presence of trifluoroacetic acid or *p*-toluenesulfonic acid in dichloromethane, followed by oxidation with chloranil.[13,21] Bucher et al. obtained different ferrocene-substituted porphyrin derivatives via MacDonald-type condensations, but the desired tri-*meso*-phenyl mono-*meso*-ferrocenyl porphyrin was isolated from mixtures of derivatives resulting from a scrambling process.[14,22]

We found that the most direct approach to obtain a mono-*meso*-substituted porphyrin **1** in a pure form was to resort to MacDonald's original method[23] in its simplified form,[24–26] that is, the condensation of diformyldipyrrylmethane with a dicarboxydipyrrylmethane (Scheme 1). This method yields unequivocally one of the three possible isomers of this mono-*meso*-ferrocenylporphyrin, avoiding the isolation and purification of mixtures of porphyrins. Although this strategy is well known in porphyrin synthesis, it has never been used to introduce only one ferrocene fragment on a porphyrin *meso*-carbon.

Accordingly, synthesis of porphyrin **3** was carried out via condensation of the diformyldipyrrylmethane **4** with the known dicarboxydipyrrylmethane **7**.[27] A very convenient method to synthesize dipyrrylmethane **5** is the condensation of the benzyl-3-methyl-4-ethylpyrrol-2-carboxylate[28] with ferrocene carboxaldehyde in the presence of *p*-toluenesulfonic acid. Hydrogenolysis of the benzyl-ester group in **5** afforded the corresponding dicarboxydipyrrylmethane**,** which was formylated with trimethyl orthoformate (TMO) to yield **4**.[29]

Unfortunately, the synthesis of porphyrin **2** by treatment of 2-hydroxyethyl porphyrin **3** with mesyl chloride–pyridine at 75 °C failed, due to decomposition of the starting material. Exchange of the 2-hydroxyethyl substituents for 2-chloroethyls, using a milder procedure (triphenylphosphine/tetrachloromethane at room temperature),[30] was also unsuccessful. The synthesis of the desired porphyrin in good yields was achieved by an alternative route, which involved the direct preparation of the 2chloroethyl-substi-

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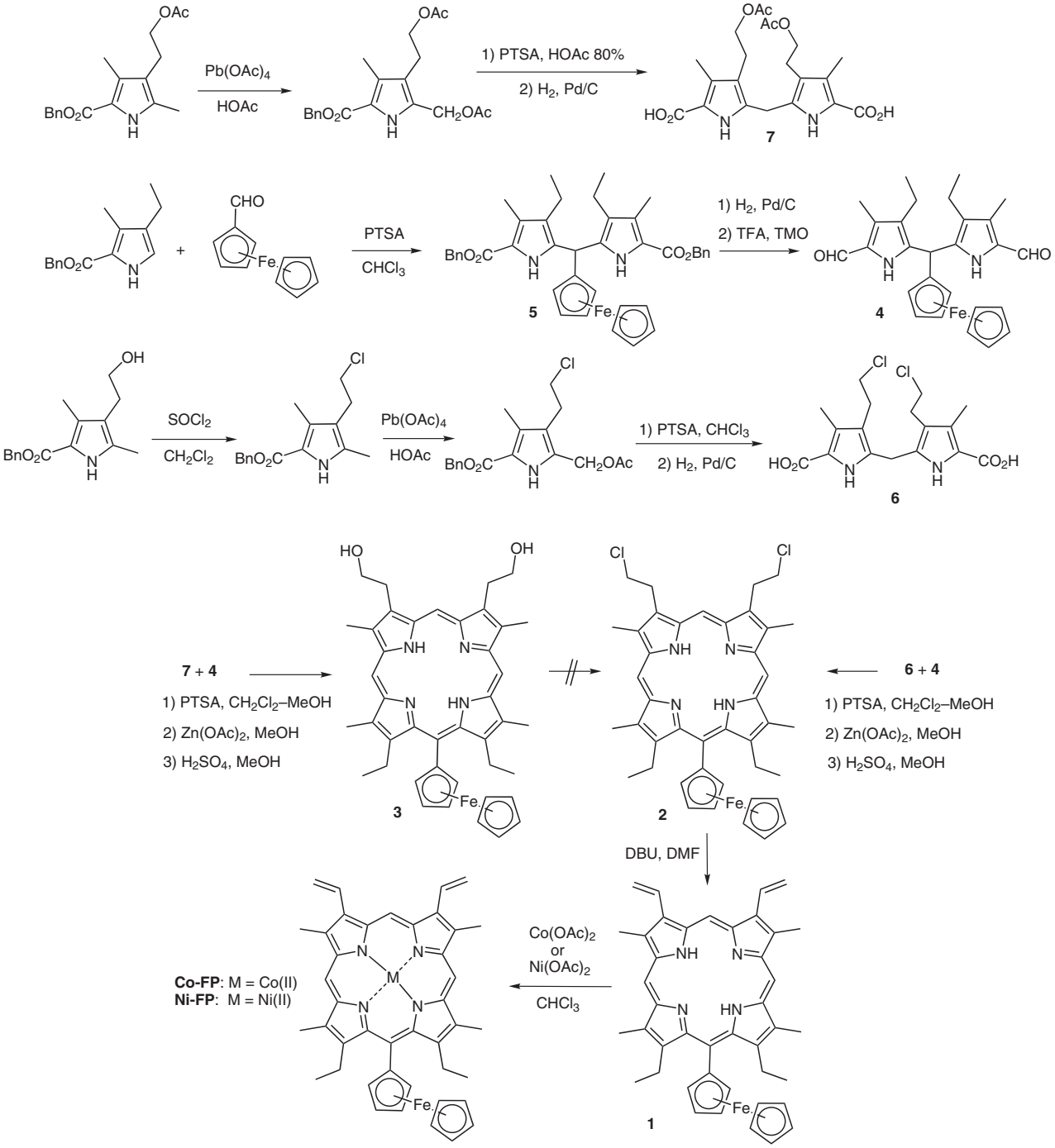

Scheme 1 Synthesis of mono-*meso*-ferrocenyl porphyrin **1**

tuted dipyrrylmethane **6**[31] and its subsequent MacDonald condensation, followed by vinylation with DBU–DMF.[25,32]

Interestingly, we noticed that the ferrocenyl group introduces an element of asymmetry in porphyrin **1**, because its free rotation is blocked because of steric hindrance. This asymmetry was only observed in the neighborhood of the ferrocenyl moiety, resulting in the non-equivalency of methylenes 7^1 and 3^1 in the ^{1}H NMR spectrum (δ = 4.17–4.32 and 3.45–3.60 ppm, respectively). The unequivocal assignment of porphyrin **1** proton resonances was achieved by means of a detailed analysis of its H–H NOESY correlations (Figure 1 and Experimental Section). A probable geometry of the molecule was obtained by performing a geometry optimization with the semiempirical method ZINDO/1 (Hyperchem 7.0) (Figure 2).

The cyclic voltammograms of the ferrocenyl porphyrin free base (H_2FP) **1** and its metal complexes Co(II)-FP and Ni(II)-FP are displayed in Figure 3. The peak at 0.55–0.58 V corresponds to the ferrocenyl moiety in all cases, but it is important to point out that it was only reversible for Ni-FP. The other two peaks correspond to the monocation

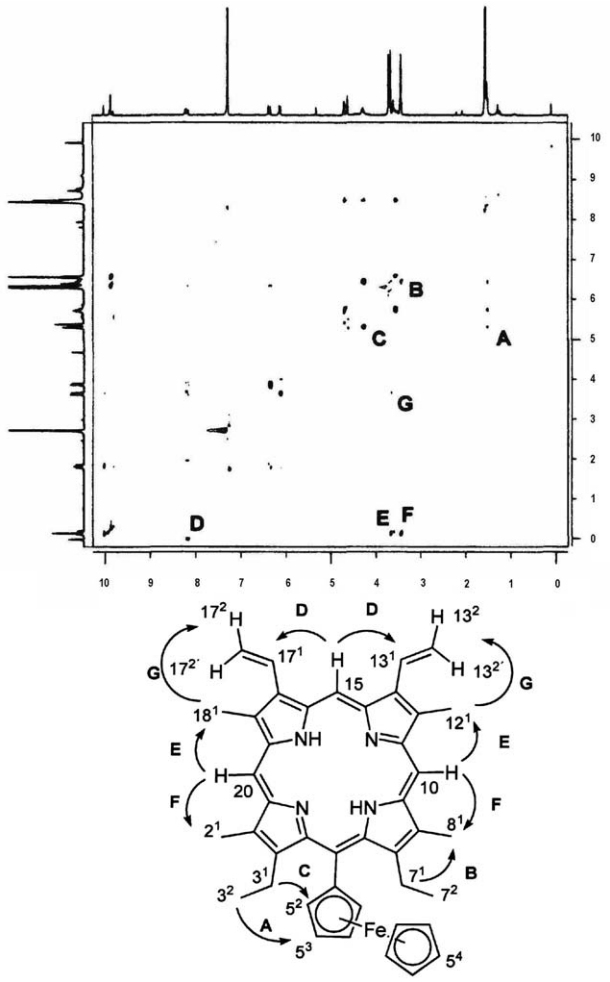

Figure 1 H–H NOESY correlations of porphyrin **1**. No equivalence of methylenes 7^1 and 3^1 (δ = 4.17–4.32 and 3.45–3.60 ppm) can be observed.

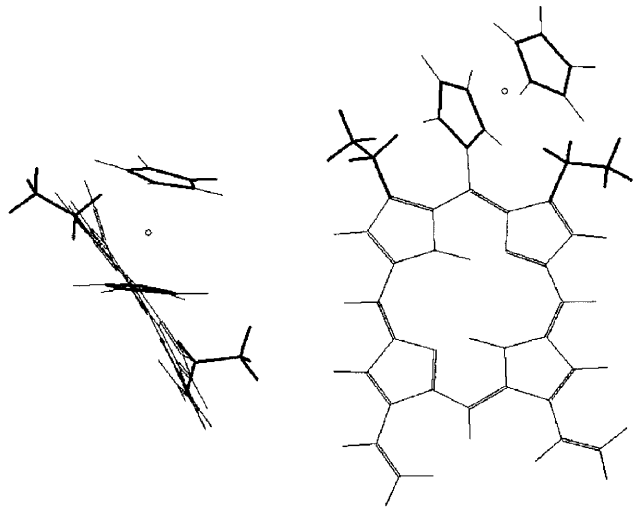

Figure 2 Two views of porphyrin **1**, obtained by a semiempirical method, ZINDO/1 geometry optimization (Hyperchem 7.1). The different environments of the two ethyl residues (bold) can be observed.

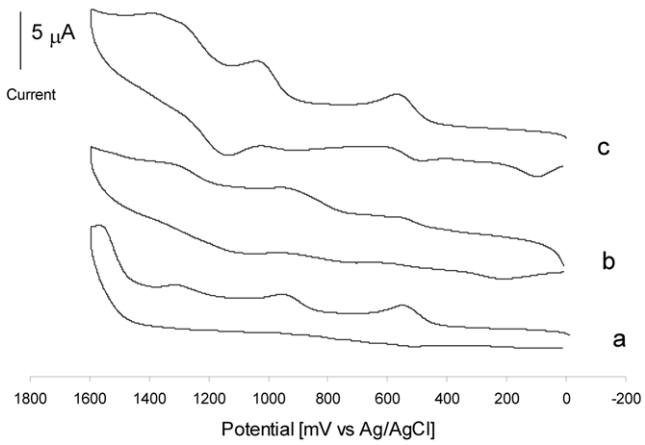

Figure 3 Cyclic voltammograms of (a) free base ferrocenyl porphyrin H_2FP; (b) Co-FP; and (c) Ni-FP (0.4 mM) at glassy carbon electrode in 0.1M TBAP/CH_2Cl_2. Scan rate: 50 mV s^{-1}

radical and dication radical at 0.95 V and 1.3 V, respectively. Here again, Ni-FP shows a more reversible peak at 1.04 V. All peaks disappeared after four consecutive scans. These results suggest that steric hindrance or a lack of porphyrin planarity inhibits intercalation of monomers, defavoring film formation.

UV and visible spectra were recorded on a Jasco 7850 spectrophotometer. 1D and 2D ^{1}H NMR spectra were determined in $CDCl_3$ and recorded by means of a Bruker MSL-300 spectrometer. Electron Impact MS were obtained with a Shimadzu QP 5000-GC 17A and Electrospray-Ion Trap MS (positive ion mode) in a Finnigan LCQ DUO. Melting points were measured on a Fischer–Jones apparatus and are uncorrected.

Cyclic voltammetries were performed with a homemade electrochemical analyser, microprocessor-controlled, with digital signal generator for implementation of different electrochemical techniques. A glassy carbon working electrode, 7 mm^2 area, and a platinum-wire auxiliary electrode were used for all voltammetric experiments.

Coating of the glassy carbon electrode: Solutions of ferrocenylporphyrin (1 mg) and tetra-butylammonium perchlorate (144 mg) in CH_2Cl_2 (4 mL) were cycling through the metalloporphyrin oxidation waves (0 to 1.6 V vs. Ag/AgCl, at 50 mV s^{-1}). Prior to its coating, the electrode was polished with 0.3 μm and 0.05 μm alumina particles and finally rinsed with deionized H_2O.

Co(II) Complex of 3,7-Diethyl-5-ferrocenyl-13,17-divinyl-2,8,12,18-tetramethylporphyrin (Co-FP)

3,7-Diethyl-5-ferrocenyl-13,17-divinyl-2,8,12,18-tetramethylporphyrin (20 mg, 30 μmol) was dissolved in anhyd $CHCl_3$ (40 mL), and a sat. methanolic soln of $Co(CH_3COO)_2 \cdot 4\,H_2O$ (2 mL) was added. The mixture was stirred and refluxed for 30 min and was then diluted with $CHCl_3$ (20 mL). The mixture was washed with H_2O (25 mL), dried over Na_2SO_4, and evaporated to dryness at 40 °C. The residue was crystallized from CH_2Cl_2–hexane to yield 11 mg (50%) of the complex; mp >300 °C.

ESI-MS: *m/z* (%) = 715.4 (100) [M^+].

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 419 (5.12), 567 (4.14), 611 nm (4.10).

Anal. Calcd for $C_{42}H_{40}CoFeN_4$: C, 70.50; H, 5.63; N, 7.83. Found: C, 70.53; H, 5.57; N, 7.89.

Ni(II) Complex of 3,7-Diethyl-5-ferrocenyl-13,17-divinyl-2,8,12,18-tetramethylporphyrin (Ni-FP)

3,7-Diethyl-5-ferrocenyl-13,17-divinyl-2,8,12,18-tetramethylporphyrin (15 mg, 23 μmol) was dissolved in anhyd $CHCl_3$ (40 mL), and a sat. methanolic soln of $Ni(CH_3COO)_2 \cdot 4\ H_2O$ (2 mL) was added. The mixture was stirred and refluxed for 30 min and was then diluted with $CHCl_3$ (20 mL). The mixture was washed with H_2O (25 mL), dried over Na_2SO_4, and evaporated to dryness at 40 °C. The residue was crystallized from CH_2Cl_2–hexane; 13 mg of the metal complex was obtained from 15 mg of **1** (80%); mp >300 °C.

ESI-MS: *m*/*z* (%) = 714.4 (100) [M^+].

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (4.26), 517 (3.40), 564 (3.30), 611 (3.30), 668 nm (2.88).

Anal. Calcd for $C_{42}H_{40}FeN_4Ni$: C, 70.52; H, 5.64; N, 7.83. Found: C, 70.45; H, 5.71; N, 7.79.

13,17-Bis(2-chloroethyl)-3,7-diethyl-5-ferrocenyl-2,8,12,18-tetramethylporphyrin (2)

Acid **6** (68 mg, 0.17 mmol) was dissolved in a mixture of anhyd CH_2Cl_2 (60 mL) and MeOH (8.5 mL), containing diformyldipyrrylmethane **4** (82 mg, 0.17 mmol), and PTSA (164 mg, 0.862 mmol) was added. After the mixture was kept in the dark at 20 °C for 24 h, a sat. methanolic soln of $Zn(OAc)_2 \cdot H_2O$ (14 mL) was added. After a further period of 72 h at 20 °C in the dark, the solution was evaporated to dryness at 40 °C, and the residue was dissolved in a 5% soln of H_2SO_4 in MeOH (30 mL). The mixture was kept at 20 °C in the dark for 16 h, was then diluted with $CHCl_3$ (100 mL), washed with H_2O (40 mL) and then with 5% $NaHCO_3$ soln (40 mL), dried over Na_2SO_4, and evaporated to dryness at 40 °C. The residue was dissolved in CH_2Cl_2 and filtered through a column (2 × 10 cm) of TLC silica gel, packed and prewashed with the same solvent. Eluates containing the main band (monitored by its fluorescence) were collected and evaporated to dryness. The residue of porphyrin **2** was crystallized from CH_2Cl_2–hexane and yielded 32 mg (26%) of the complex; mp >300 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 [t, *J* = 7.6 Hz, 6 H, CH_3 (3^2, 7^2)], 3.41 and 3.58 [s, s, 6 H, 6 H, CH_3 (2^1, 8^1, 12^1, 18^1)], 3.50–3.60 [m, 2 H, CH_2 (3^1 or 7^1)], 3.67 [s, 5 H, CH (5^4)], 4.20–4.30 [m, 6 H, CH_2 (13^1, 17^1, 3^1 or 7^1)], 4.32–4.50 [m, 4 H, CH_2 (13^2, 17^2)], 4.59 and 4.65 [m, m, 2 H, 2 H, CH (5^2, 5^3)], 9.60 [s, 1 H, CH (15)], 9.85 [s, 2 H, CH (10, 20)].

ESI-MS: *m*/*z* (%) = 731.3 (100) [M + H]$^+$, 659.3 (30) [M + H – 2HCl]$^+$.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.10), 506 (3.99), 579 (3.79), 603 (3.84), 661 nm (3.54).

Anal. Calcd for $C_{42}H_{44}Cl_2FeN_4$: C, 68.95; H, 6.06; N, 7.66. Found: C, 69.05; H, 6.09; N, 7.57.

3,7-Diethyl-5-ferrocenyl-13,17-bis(2-hydroxyethyl)-2,8,12,18-tetramethylporphyrin (3)

Dipyrrylmethane diacid **7** (61 mg, 0.14 mmol) was condensed with diformyldipyrrylmethane **4** (66 mg, 0.14 mmol) following the same procedure as described for **2**. Final purification of porphyrin **3** was achieved by filtration through a column (2 × 10 cm) of TLC silica gel using CH_2Cl_2–MeOH (95:5) as eluent. Crystallization of the porphyrin from CH_2Cl_2–hexane yielded 20 mg (20%); mp >300 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 [t, *J* = 7.4 Hz, 6 H, CH_3 (3^2, 7^2)], 3.42 and 3.46 [s, s, 6 H, 6 H, CH_3 (2^1, 8^1, 12^1, 18^1)], 3.49–3.60 [m, 2 H, CH_2 (3^1 or 7^1)], 3.67 [s, 5 H, CH (5^4)], 4.17–4.30 [m, 6 H, CH_2 (13^1, 17^1, 3^1 or 7^1)], 4.38 [t, *J* = 6.5 Hz, 4 H, CH_2 (13^2, 17^2)], 4.60–4.65 [m, 4 H, CH (5^2, 5^3)], 9.74 [s, 1 H, CH (15)], 9.85 [s, 2 H, CH (10, 20)].

ESI-MS: *m*/*z* (%) = 695.5 (100) [M + H]$^+$.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (4.97), 504 (3.98), 531 (3.84), 573 (3.74), 599 (3.68), 659 nm (3.36).

Anal. Calcd for $C_{42}H_{46}FeN_4O_2$: C, 72.62; H, 6.67; N, 8.07. Found: C, 72.40; H, 6.69; N, 8.06.

3,7-Diethyl-5-ferrocenyl-13,17-divinyl-2,8,12,18-tetramethylporphyrin (1)

DBU (0.65 mL) was added to a solution of porphyrin **2** (25 mg) in anhyd DMF (18 mL), and the mixture was stirred for 72 h at r.t. in the dark. The solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 15 mL), dried over Na_2SO_4, and evaporated. The residue was dissolved in CH_2Cl_2 and filtered through a column as for **2**. Crystallization of porphyrin **1** from CH_2Cl_2–hexane yielded 13.6 mg (60%); mp >300 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 [t, *J* = 7.5 Hz, 6 H, CH_3 (3^2, 7^2)], 3.41 [s, 6 H, CH_3 (2^1, 8^1)], 3.65 [s, 6 H, CH_3 (12^1, 18^1)], 3.45–3.60 [m, 2 H, CH_2 (3^1 or 7^1)], 3.70 [s, 5 H, CH (5^4)], 4.17–4.32 [m, 2 H, CH_2 (3^1 or 7^1)], 4.60–4.67 [m, 4 H, CH (5^2, 5^3)], 6.11 [dd, *J* = 1.6, 11.5 Hz, 2 H, CH (13^2, 17^2)], 6.34 [dd, *J* = 1.6, 17.7 Hz, 2 H, CH ($13^{2'}$, $17^{2'}$)], 8.17 [dd, *J* = 11.5, 17.7 Hz, 2 H, CH (13^1, 17^1)], 9.85 [s, 2 H, CH (10, 20)], 10.00 [s, 1 H, CH (15)].

ESI-MS: *m*/*z* (%) = 659.3 (100) [M + H]$^+$.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.14), 509 (4.06), 588 (3.89), 606 (3.90), 667 nm (3.59).

Anal. Calcd for $C_{42}H_{42}FeN_4$: C, 76.59; H, 6.43; N, 8.51. Found: C, 76.63; H, 6.45; N, 8.48.

Dibenzyl-3,7-diethyl-5-ferrocenyl-2,8-dimethyldipyrrylmethane-1,9-dicarboxylate (5)

Benzyl 3-methyl-4-ethylpyrrol-2-carboxylate (625 mg, 2.57 mmol) was dissolved in $CHCl_3$ (65 mL), and ferrocenecarboxaldehyde (550 mg, 2.57 mmol) and PTSA (250 mg, 1.285 mmol) were added to this solution. The mixture was refluxed for 4 h and then diluted with H_2O (100 mL). The organic layer was separated and washed with sat. aq $NaHCO_3$ soln (20 mL) and then with H_2O (20 mL). The organic layer was dried over Na_2SO_4, filtered, and the solvent was evaporated at reduced pressure. After purification with a silica-gel column (3 × 30 cm) and CH_2Cl_2 as eluent, the desired product was obtained as a yellow oil with a yield of 613 mg (70%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 [t, *J* = 7.5 Hz, 6 H, CH_3 (3^2, 7^2)], 2.30 [s, 6 H, CH_3 (2^1, 8^1)], 2.36 [m, 4 H, CH_2 (3^1, 7^1)], 3.91–3.92 [m, 2 H, CH (5^2)], 4.21–4.23 [m, 7 H, CH (5^3, 5^4)], 5.09 [s, 1 H, CH (5)], 5.27 [d, *J* = 12.6 Hz, 2 H, CH (9^3, 1^3)], 5.34 [d, *J* = 12.6 Hz, 2 H, CH ($9^{3'}$, $1^{3'}$)], 7.30–7.43 [m, 10 H, CH_2Bn)], 9.44 [br s, 2 H, NH (10, 11)].

MS (EI, 70 eV): *m*/*z* (%) = 682 (7.0) [M^+], 574 (6.5) [M^+ – $OCH_2C_6H_5$], 466 (2.3) [M^+ – $2OCH_2C_6H_5$], 401 (2.2) [466 – C_5H_5], 345 (1.0) [401 – Fe].

Anal. Calcd for $C_{41}H_{42}FeN_2O_4$: C, 72.14; H, 6.20; N, 4.10. Found: C, 72.20; H, 6.17; N, 4.06.

3,7-Diethyl-5-ferrocenyl-2,8-dimethyl-1,9-diformyldipyrrylmethane (4)

A solution of dipyrrylmethane **5** (270 mg, 0.396 mmol) in EtOH (50 mL) was reduced with H_2 at 50 psi over 10% Pd on charcoal (135 mg) for 3 h. The catalyst was filtered, the solvent evaporated to dryness at reduced pressure, and the acid thus obtained was recrystallized from MeOH–H_2O, yielding 142 mg (71%); mp >190 °C (dec).

MS (EI, 70 eV): *m*/*z* (%) = 458 (3.0) [M^+ – CO_2], 414 (3.8) [M^+ – $2CO_2$].

A solution of dicarboxydipyrrylmethane (142 mg), obtained as described above, in trifluoroacetic acid (2.9 mL) was maintained at 0

°C for 20 min, and trimethyl orthoformate (1.4 mL) was added. The mixture was kept at 0 °C for 10 min, and H_2O (10 mL) and 10% aq NH_3 (15 mL) were added successively at 0 °C. The aqueous mixture was extracted twice with CH_2Cl_2 (2 × 30 mL). The organic layer was washed with H_2O (20 mL), dried over Na_2SO_4, and the solvent was evaporated at reduced pressure. The crude product was purified on a column of TLC silica gel and eluted with CH_2Cl_2–MeOH (98:2). The dipyrrylmethane thus obtained was recrystallized from MeOH–10% aq NH_3 and was obtained as a yellow solid with a yield of 53 mg of (40%); mp 206–207 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 [t, *J* = 7.6 Hz, 6 H, CH_3 (3^2, 7^2)], 2.30 [s, 6 H, CH_3 (2^1, 8^1)], 2.49 [m, *J* = 7.6 Hz, 4 H, CH_2 (3^1, 7^1)], 4.05 [s, 5 H, CH (5^4)], 4.14–4.20 [m, 4 H, CH (5^2, 5^3)], 5.30 [s, 1 H, CH (5)], 9.58 [s, 2 H, CHO (1^1, 9^1)], 10.66 [br s, 2 H, NH (10, 11)].

MS (EI, 70 eV): *m*/*z* (%) = 470 (100) [M^+], 404 (9.6) [$M^+ - C_5H_5$], 375 (12.5) [404 – CHO], 361 (3.3) [375 – CH_3].

Anal. Calcd for $C_{27}H_{30}FeN_2O_2$: C, 68.94; H, 6.43; N, 5.96. Found: C, 68.86; H, 6.42; N, 5.93.

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