The synthesis and properties of bis-1,1′-(porphyrinyl)ferrocenes†

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Ferrocene-bridged bisporphyrins have been synthesized by the condensation of corresponding dipyrromethane-derived diols with a bisdipyrromethane. Purification of the final compounds has been achieved without chromatography. The specific geometry of these bisporphyrins makes them valuable starting points for building complex molecular and supramolecular structures. In particular it provides a core to which multiple sites of attractive intermolecular interactions can be attached thereby creating compounds predisposed to form complex networks by association. We have studied the structure of bis-1,1′-(porphyrinyl)ferrocenes by ^{1}H NMR, UV-Vis and electrochemistry. Results have shown that complex dynamic processes occur in these molecules (which may involve conformers, formation of H-aggregates and tautomers) and that they have non-typical electrochemical behaviour.

Introduction

The development of supramolecular chemistry in the past years has relied on the availability of simple components possessing suitable molecular architectures.[1] Multiporphyrin structures have recently attracted enormous attention due to their potential material properties in the fields of sensors, artificial photosynthesis, *etc*.[2] Their spatial orientation could either be totally fixed or absolutely flexible. We have become interested in studying a possible compromise between completely rigid and flexible spacer linking porphyrin moieties, in particular linkers, which would allow for limited hinge-like molecular flexibility. Such molecules bearing various chemical handles in suitable positions are excellent building blocks for the construction of elaborate supramolecular assemblies. We have chosen ferrocene as a candidate for the linker, since the two cyclopentadienyl (Cp) rings are oriented parallel to each other and rotate almost freely even at low temperature (an iron atom constitutes a 'molecular ball bearing').[3] Ferrocene and its derivatives are also attracting much attention nowadays from the viewpoint of supramolecular chemistry, *e.g.* as redox-active ionophores and molecular receptors,[4,5] and 1,1′-disubstitued ferrocenes have been utilized to construct several molecular devices of unique functions.[6] The specific geometry of the ferrocene system might allow the adoption of unusual conformations of molecules bearing bulky groups on their peripheries.[7] In particular, a ferrocene moiety directly attached to the porphyrin ring would cause special orientations of both fragments. Many examples of this type of structure have been synthesized within the past 20 years,[8] and have found applications, for example, in molecular memory studies.[8h] An architectural scheme in which two porphyrins are connected by a ferrocene hinge is very intriguing and we are interested in the effect of such a molecular arrangement on the conformation of these molecules and their properties. The objective of this work was to develop a efficient synthetic route to 1,1′-(porphyrinyl)ferrocenes and to study their fundamental properties. The ultimate goal of this project is to utilize and fine tune possible electronic interaction between the *electro-* and *photo*-active subunits by possible π–π stacking interactions with a specific geometry in molecular electronics and in particular to construct an electrochemically tunable ferrocene–porphyrin supramolecular polymeric system. Covalent polymeric systems encompassing ferrocenyl units within photonic crystals have been recently shown to have interesting material properties.[9]

Results and discussion

The simple retrosynthetic analysis revealed that bis-1,1′-(porphyrinyl)ferrocenes could be synthesized from the respective ferrocene-derived bisdipyrromethane (DPM) **2**, which in turn could be synthesized from the respective 1,1′-diformylferrocene **1** [10] using the general procedure of Lindsey and co-workers.[11] The reaction of **1** performed in the presence of 50 equiv. of pyrrole gave rise to the desired DPM **2** in 40% yield (Scheme 1).
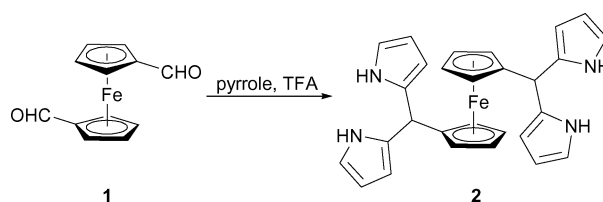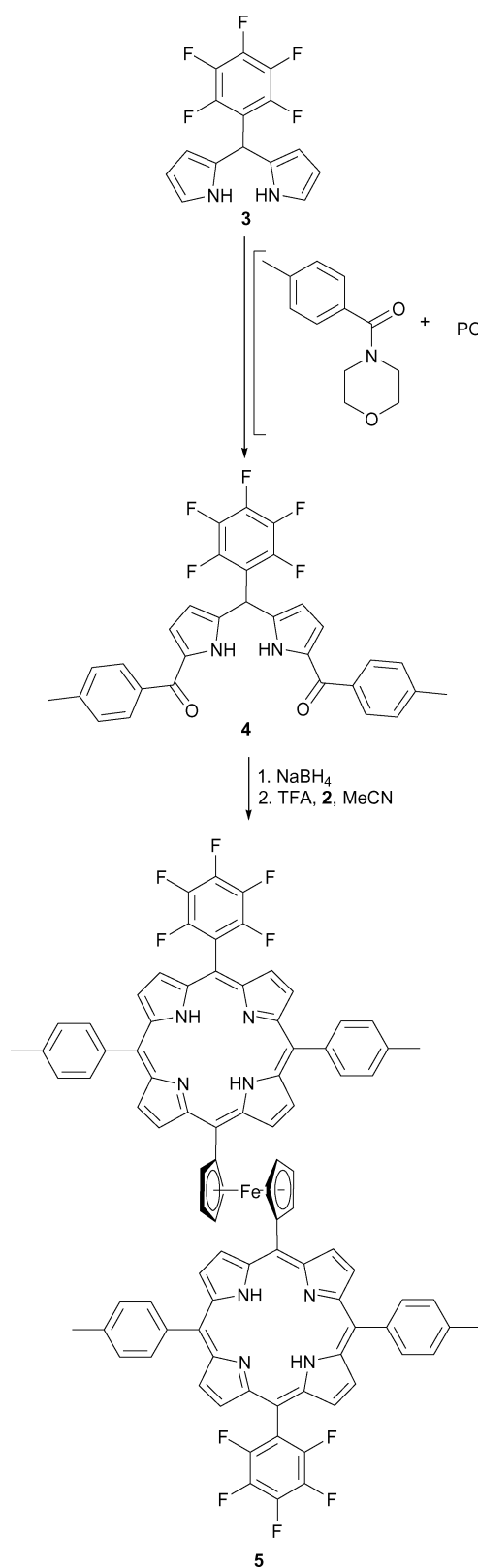

Scheme 1

The following macrocyclization reaction was carried out using Lindsey's procedure for the synthesis of *meso*-substituted porphyrins bearing up to four different substituents.[12] The reduction of readily available diacyldipyrromethanes[12,13] with NaBH₄ afforded unstable diols which could be transformed into porphyrins using a catalytic amount of trifluoroacetic acid (TFA).

The first ferrocenylbisporphyrin **5** was synthesized in 18% yield using the above procedure starting from diketone **4**, the yield of which should be considered as high given that two porphyrin rings were simultaneously closed (Scheme 2). The choice of substituents was based on the option to further functionalise the *para* position in the C_6F_5 group.[14]

During our attempts to purify compound **5** we found that it behaves in an unusual way during column chromatography. Compound **5** could not be eluted from the column unless a small amount of THF was added, although the polarity of **5** is very low. While trying to solve this problem we found that bisporphyrin **5** could be purified by crystallization directly from

† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of porphyrins **6** and **7** and molecular modelling of porphyrin **7**. See http://www.rsc.org/suppdata/ob/b5/b505366h/

Scheme 2

In order to check the generality of the procedure for the synthesis of bisporphyrinylferrocenes we decided to prepare two additional compounds bearing different substituents. The simplicity of the purification of **5** provided us with additional motivation to check if this is a general behaviour for this class of compounds. Thus, *via* an analogous process we synthesized bisporphyrins **6** and **7** (Fig. 1) possessing different substituents. We found that these compounds strongly resembled porphyrin **5** (both bisporphyrins could not be purified on silica or alumina), and that both of them were easily purified *via* double crystallization. Bisporphyrins were obtained in yields of 17 and 10% respectively. Bisporphyrin **7** was subsequently metallated with Zn(OAc)$_2$ under standard conditions to afford **Zn-7** in 86% yield (Fig. 1).
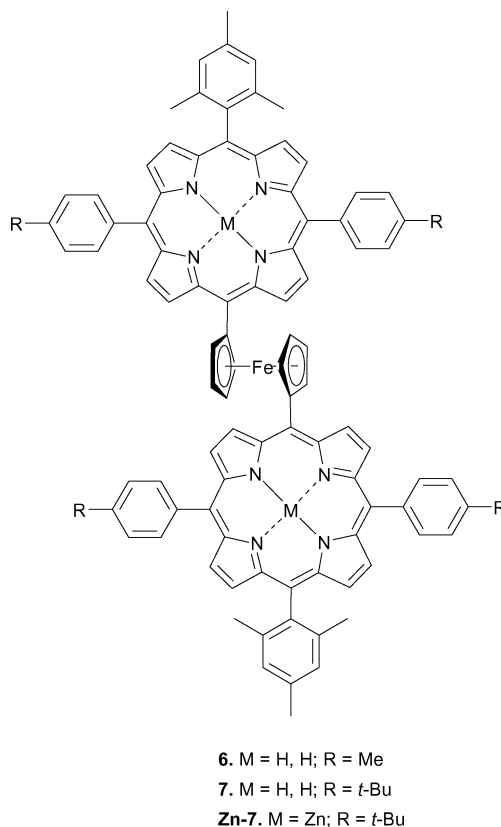

6. M = H, H; R = Me
7. M = H, H; R = *t*-Bu
Zn-7. M = Zn; R = *t*-Bu

Fig. 1 Structure of bisporphyrins **6**, **7** and **Zn-7**.

Standard ^{1}H NMR spectra of all three bisporphyrins **5**–**7** showed significant line broadening. In particular, signals derived from β-pyrrole protons and NH protons were broadened. One has to note that there is no such effect for simple mono-ferrocenylporphyrins at room temperature.[8b,g,16] These intriguing results, which indicated some complex dynamic processes taking place, prompted us to study the variable-temperature ^{1}H NMR spectra. The most interesting regions are shown in Figs. 2 and 3, and full spectra are given in the ESI.† For both porphyrins studied (**6** and **7**), coalescence of the NH resonances occurred at 333 K (500 MHz, $\Delta\delta$ 0.6–0.8 ppm). For both **6** and **7**, the spectra recorded at 273 K show the presence of two NH signals. The only difference between **6** and **7** is the peripheral substituents at the phenyl ring (Me for **6**, *t*-Bu for **7**, Fig. 1). Yet, there was a striking difference in their variable-temperature ^{1}H NMR spectra. While porphyrin **6** gave narrow lines of the β-pyrrole resonances at 333 K, spectra recorded for porphyrin **7** even at 363 K still had broad lines. The other striking difference could be found in the signals of the Fc protons (see ESI†). For compound **6**, lines were pretty narrow even at 273 K, whereas for **7** line broadening is remarkably significant at this temperature. In general, this kind of spectrum suggested the presence of an equilibrium of two conformers with slow exchange relative to the NMR
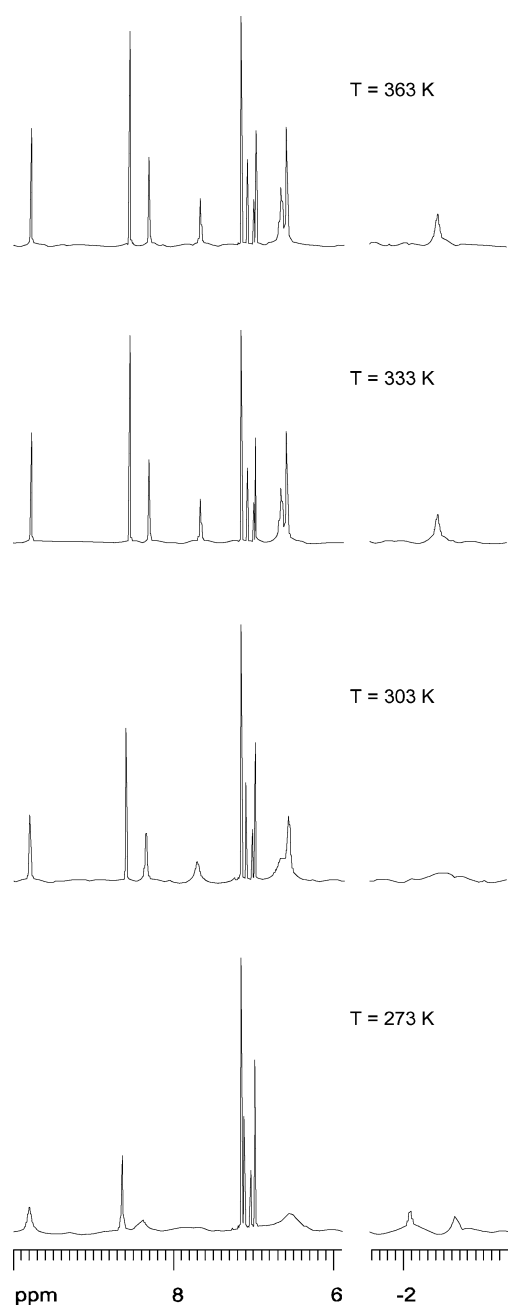
the reaction mixture. Double crystallization gave pure materials. Purification of porphyrins in such a way without at least silica pad filtration is very rare (generally, chromatographic separation is the typical bottleneck in the porphyrin synthesis).[15]

Needless to say that such exceptionally simple purification procedure greatly expands the preparative possibilities due to the fact that it allows for increasing the scale of the experiments. Amounts of bisporphyrin **5** which could be easily obtained in this manner were in the range 300–500 mg.

Fig. 2 Variable-temperature ^{1}H NMR spectra of **6** (aromatic and NH regions).

Fig. 3 Variable-temperature ^{1}H NMR spectra of **7** (aromatic and NH regions).

time scale. In unsubstituted ferrocene, the barrier of internal rotation of the Cp rings is estimated to be only one third of that in ethane.[17] This means that in the usual temperature range for NMR investigation the Cp rings rotate freely. It is worthy to emphasize that variable-temperature ^{1}H NMR experiments allowed us to observe two distinct conformational processes for β,β′-fused ferrocene–porphyrins, one of them arising from ferrocene rotations.[18]

Additionally, for this type of *trans*-A$_2$BC-porphyrin the slowing down of the tautomery should give two distinct N–Hs with different environments. This process might have an energy of activation causing a significant deceleration at lower temperatures. Burrell and Officer's group have shown that the presence of β-alkyl substituents hampers the free rotation of ferrocene around a single bond.[8f] For such hindered ferrocene–porphyrins Kim and co-workers showed that coalescence of two distinct NH signals was unobserved up to the higher temperature limit of 373 K.[19] On the other hand, ferrocene–porphyrins lacking these substituents can freely rotate. The question remains if there is still such free rotation around
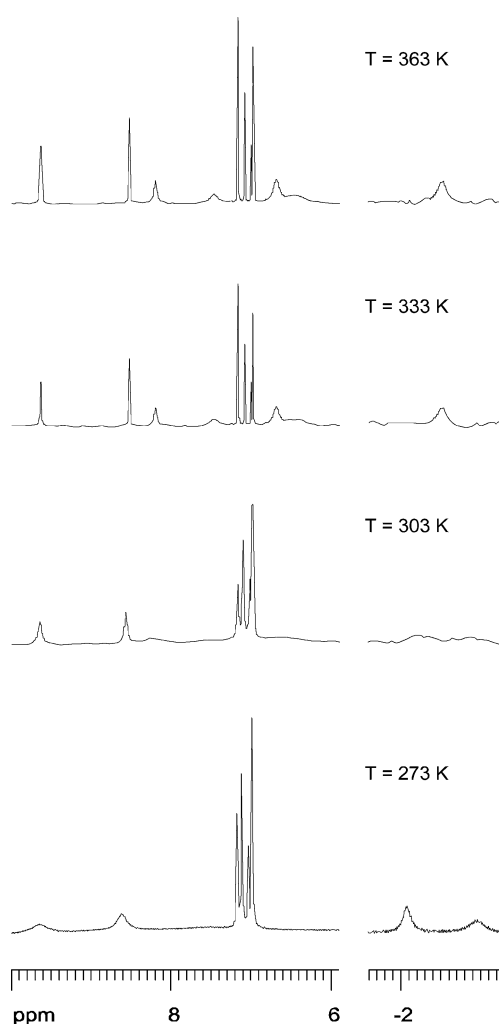
this bond for bis-1,1′-(porphyrinyl)ferrocenes. Free rotation of the ferrocene moiety with the attached porphyrin over the second porphyrin should be rather difficult. On the other hand, simple 1,1′-disubstituted ferrocenes with the possibility of π-stacking interactions between aromatic substituents can posses a π-stacking conformation.[20] We may assume that for bis-1,1′-(porphyrinyl)ferrocenes free rotation of the substituted cyclopentadienyl ligands is not possible, presumably due to their restricted conformation (Fig. 1). This complex picture could be clarified to a certain extent by X-ray analysis. However, so far it has not been possible to obtain crystals of any bisporphyrins suitable for an X-ray crystal structure analysis.

UV-Vis data showed a small blue shift for the Soret band in comparison with directly-bonded mono-ferroceneporphyrins (410–418 nm *vs.* 422 nm). A hypsochromic shift of the Soret band of these porphyrins could result in the formation of H-aggregates.[21] Molecular modelling using Hyperchem was performed to test this hypothesis (see ESI†). The results obtained showed a clear preference for a linear monomer (dihedral angle Por–Cp–Cp′–Por′ of 180°) in comparison to a kinked conformation (*e.g.* with a dihedral angle of *ca.* 104°). Estimations of dimer formation again show a strong preference for an 'open dimer',[22] which as in H-aggregates should have a blue-shifted absorption. Extension of the open dimers to oligomers readily explains the broad NMR spectra and the sharpening of the signals upon increasing the temperature which correlates with deaggregation.

Electrochemical investigations of bisporphyrin **5** were carried out in both fast-scan (100 mV s^{-1}) and slow-scan (10 mV s^{-1}) modes (Figs. 4 and 5). The CV plots significantly differ from those obtained from ferrocenyl-substituted
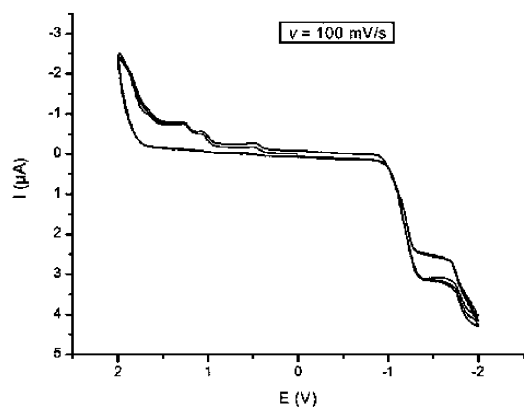
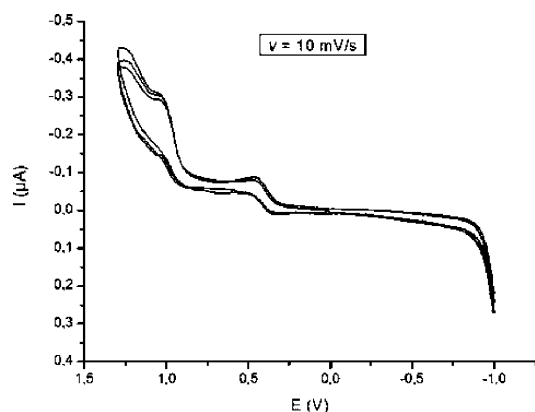**Fig. 4** Fast-scan (100 mV s⁻¹) voltammetry of porphyrin **5**.

Fig. 5 Slow-scan (10 mV s⁻¹) voltammetry of porphyrin **5**.

metalloporphyrins;[5,8f,h] the cyclovoltammograms obtained by Kim's and other groups for ferrocene-substituted hydroporphyrins[20,23] also show a shape quite different from that obtained for **5**. This makes us conclude that the substitution of a ferrocene with porphyrins at either one of the cyclopentadienyl ligands causes significant differences as compared to the previously known mono-substituted porphyrinylferrocenes. One aspect in this context may be the electron transfer between the electrode and the molecule. In contrast to the mono-substituted ferrocenes it seems for obvious steric reasaons unlikely for **5** that an electron transfer directly takes place between the electrode and the ferrocene moiety. It seems more reasonable that the transfer occurs *via* a porphyrin substituent, upon which a transfer to the ferrocene moiety might occur. This, however, would be highly dependent on the conformation of the porphyrin substituent relative to the ferrocene moiety.

The plot obtained for **5** at the fast scan rate (100 mV s⁻¹) shows three irreversible oxidation potentials at $E_A = 0.455$, 1.059 and 1.272 V (*vs.* Fc/Fc⁺). In addition there is possibly a reversible reduction step at $E_A = -1.679$ V, $E_K = -1.326$ V (effective potential is the average value, 1.503). However, the comparatively large difference of 353 mV between these peaks, which strongly exceeds the theoretical value of 59 mV for a perfectly reversible process, raises some doubt in the reversibility of this process. Remarkably, the plot does not show any clearly reversible redox process for the ferrocene moiety in **5**. This suggests that the processes observed most likely takes place at the extended porphyrin π-system and that there is only little electronic communication between these and the ferrocene subunit, presumably because the porphyrin and ferrocene subunits adopt a non-coplanar conformation.

The plot obtained at the slow scan rate (10 mV s⁻¹) shows a reversible oxidation at $E_{1/2} = 0.410$ V. In addition there are less clear signals at $E_A = 1.045$ V and $E_K = 1.050$ V as well as at $E_K = 0.923$ V. Although an interpretation remains somewhat speculative, we suggest that the redox process observed at 0.410 V

is due to the ferrocene moiety, because this value is within the usual range for substituted ferrocenes.[24] The observation, that a reversible process is seen at the slow scan rate but not at the fast scan rate deserves some comment. Usually, a reversible process is observed at a fast scan rate, whereas at a slow scan rate the system often undergoes an EC process, which is a chemical reaction following the electron transfer. The latter requires a certain lifetime of the electrochemically generated species, which is the case at the slower scan rate. In the case of **5**, in contrast to the usual case, a reversible process assigned to the ferrocene unit is observed. A possible explanation is that at the slower scan rate the system has sufficient time to adopt a more coplanar conformation allowing intramolecular electron transfer from the porphyrin unit to the ferrocene. Thus, the CV results can be seen in close connection to the molecular dynamics of **5** and similar systems. Further investigations along these lines, *e.g.* CV measurements at slower scan rates and at variable temperatures, are currently being pursued in our laboratories. In addition, similar investigations with metal coordinated di- and tri-metallic systems are on our agenda.

In conclusion, a new and interesting type of supramolecular building block, 1,1′-bis(porphyrinyl)ferrocenes, has been prepared very efficiently on a large scale avoiding chromatographic purification.[25] Variable-temperature-dependent ¹H NMR spectra showed that the equilibrium between 'open dimers', oligomers, tautomers and possibly also conformers is rather complex. The electrochemistry showed that some kind of conjugative interactions occur between both subunits which are different from those in directly-bonded mono-ferroceneporphyrins. These observations suggested that further exploration of bis-1,1′-(porphyrinyl)ferrocenes would be highly productive. Work on the utilization of this scaffold in the construction of electrochemically tunable ferrocene–porphyrin supramolecular polymeric systems and metal–organic frameworks is in progress in our laboratory.

Experimental

General

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. ¹H NMR: Bruker AM 500 MHz or 200 MHz spectrometer. *J* values are given in Hz. UV-VIS spectra were recorded in toluene (Cary). ESI-MS: (Mariner) the purity of all new compounds was established based on ¹H NMR spectra, elemental analyses and ESI-MS spectra. All dipyrromethanes,[26] 1,1′-diformylferrocene,[10] *N*-methylbenzoylmorpholine[13] and diacyldipyrromethanes[12,13] were prepared according to literature procedures.

1,9-Bis(4-methylbenzoyl)-5-mesityldipyrromethane (8). *N*-(4-Methylbenzoyl)morpholine (5.125 g, 25 mmol) and phosphorus oxytrichloride (4.66 mL, 50 mmol) were mixed under an inert atmosphere and kept at 65 °C for 3 h. After cooling to room temperature, the mixture was dissolved in dry 1,2-dichloroethane (12.5 mL) and 5-mesityldipyrromethane (1.65 g, 6.25 mmol) was added in a single batch. The reaction mixture was stirred at reflux for 2 h before quenching with saturated aqueous CH_3COONa (50 mL) and heated for an additional hour at 60 °C. The mixture was cooled to 25 °C, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic phases were extracted with water to remove CH_3COOH, dried (Na_2SO_4) and chromatographed (silica; hexane–ethyl acetate, 9 : 1, then 4 : 1). Subsequent chromatography (silica; hexane–ethyl acetate, 95 : 5, then 9 : 1) afforded a solid which was crystallized (ethyl acetate–hexane, 1 : 4) to give off-white crystals (1.85 g, 59%). All physicochemical properties concur with literature data.[11]

1,1′-Bis[bis-(2,2′-pyrryl)methyl]ferrocene (2). A mixture of pyrrole (20 mL, 0.3 mol) and 1,1′-diformylferrocene **1**[9] (1.40 g, 6.0 mmol) was flushed with argon for 5 min and treated with TFA (92 μL, 1.2 mmol). The mixture was stirred for 25 min at 25 °C, and triethylamine (170 μL, 1.2 mmol) was added. The excess pyrrole was removed under reduced pressure. The resulting oil was dissolved in ethyl acetate, washed with water and then dried (Na$_2$SO$_4$). The solvent was removed under reduced pressure to afford a brown oil. The crude product was purified by column chromatography (silica; hexane–ethyl acetate, 4 : 1). The resulting solid was crystallized (Et$_2$O–hexane 1 : 1) afforded crystals (mp 182–184 °C) (882 mg, 40%). R_f = 0.55 (silica; ethyl acetate–hexane, 1 : 4); ^{1}H NMR (200 MHz, CDCl$_3$): δ 3.96 (br s, 4H, Fc), 4.05 (br s, 4H, Fc), 5.01 (s, 2H, CH), 5.95 (br s, 4H, CH–pyrrole), 6.14 (br d, 4H, J = 2.6 Hz, CH–pyrrole), 6.64 (br s, 4H, CH–pyrrole), 7.86 (br s, 4H, NH); MS(ESI): m/z 474.15 [M + H$^+$]. A satisfactory elemetal analysis could not be obtained on this substance.

General procedure for the preparation of porphyrins

A sample of NaBH$_4$ (1.89 g, 50 mmol) was added in small portions (every 10 min) to a stirred solution of a diacyl dipyrromethanes (1 mmol) in THF–methanol (3 : 1, 80 mL) in a flask open to the atmosphere. The progress of the reduction was monitored by TLC (alumina; CH$_2$Cl$_2$–ethyl acetate, 3 : 2). After the reaction was completed (about 1 h), the reaction mixture was poured into a stirred mixture of saturated aqueous NH$_4$Cl (80 mL) and CH$_2$Cl$_2$ (100 mL). The organic phase was isolated, washed with water (2 × 100 mL), and dried (Na$_2$SO$_4$). Removal of the solvent in a rotary evaporator under reduced pressure ($T \leqslant 30$ °C) yielded the dicarbinol as an oil. Diol and bisdipyrromethane **2** (240 mg, 0.5 mmol) were dissolved in acetonitrile (400 mL) and TFA (930 μL, 12 mmol) was added with vigorous stirring. After 25 min DDQ (680 mg, 3 mmol) was added. The reaction mixture was stirred for 1 h at room temperature, triethylamine (1.68 mL, 12 mmol) was added, before being evaporated and purified by crystallization.

1,1′-Bis{5,10-bis(4-methylphenyl)-15-(pentafluorophenyl)-porphyrin-20-yl}ferrocene (5). The reaction was performed following the general procedure starting from 1,9-bis(4-methyl-benzoyl)-5-(pentafluorophenyl)dipyrromethane **4** (658 mg, 1.2 mmol) followed by condensation with 1,1′-bis[bis-(2,2′-pyrryl)methyl]ferrocene **2** (288 mg, 0.6 mmol). The reaction mixture was evaporated to dryness and crystallized from THF–Et$_2$O to give dark crystals (mp > 360 °C). The residue was crystallized from THF–CH$_2$Cl$_2$–hexane and afforded pure crystals. In total, 159 mg of porphyrin were obtained (18%). R_f = 0.50 (silica; CH$_2$Cl$_2$–hexane, 1 : 1); ^{1}H NMR (200 MHz, CDCl$_3$): δ −2.82 (br s, 4H, NH), 2.51 (s, 12H, CH$_3$), 4.98 (s, 4H, Fc), 5.65 (s, 4H, Fc), 7.01 (m, 16H, Ar–H), 7.80 (d, 4H, J = 4.8 Hz, β-H), 8.47 (d, 4H, J = 5.0 Hz, β-H), 8.57 (d, 4H, J = 4.8 Hz, β-H), 9.77 (d, 4H, J = 5.0 Hz, β-H); MS(ESI): m/z 1496.4 [M + H$^+$]. Anal. calc. for C$_{90}$H$_{56}$F$_{10}$FeN$_8$: C, 72.29; H, 3.77; N, 7.49. Found: C, 71.88; H, 4.05; N, 7.23%. UV-Vis (toluene): λ_{max}/nm ($\varepsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1}) 418 (314), 506 (22), 591 (13.5), 674 (13).

1,1′-Bis{5,10-bis(4-methylphenyl)-15-mesitylporphyrin-20-yl}ferrocene (6). The reaction was performed following the general procedure starting from 1,9-bis(4-methylbenzoyl)-5-mesityldipyrromethane **8** (500 mg, 1.0 mmol) followed by condensation with 1,1′-bis[bis-(2,2′-pyrryl)methyl]ferrocene **2** (240 mg, 0.5 mmol). The reaction mixture was evaporated to dryness and crystallized from ethyl acetate/hexane to give only impurity. The residue was crystallized from ethyl acetate/hexane and the resulting crystals were recrystallized from THF–ethyl acetate–hexane to give dark crystals (mp > 360 °C) (115 mg, 17%). R_f = 0.53 (silica; CH$_2$Cl$_2$–hexane, 1 : 1); ^{1}H NMR (500 MHz, CDCl$_3$): δ −2.61 (br s, 4H, NH), 1.82 (s,

12H, CH$_3$–Mesyl), 2.52 (s, 12H, CH$_3$), 2.63 (s, 6H, CH$_3$–Mesyl), 4.90 (s, 4H, Fc), 5.65 (s, 4H, Fc), 7.00 (br d, 8H, J = 5.5 Hz Ar–H), 7.21 (br s, 8H, Ar–H), 7.27 (br d, 8H, Ar–H), 7.93 (br s, 4H, β-H), 8.41 (d, 4H, J = 3.0 Hz, β-H), 8.51 (d, 4H, J = 4.5 Hz, β-H), 9.85 (br s, 4H, β-H); MS(ESI): m/z 1400.6 [M + H$^+$]. Anal. calc. for C$_{96}$H$_{78}$FeN$_8$: C, 82.39; H, 5.62; N, 8.01. Found: C, 82.54; H, 5.51; N, 7.74%. UV-Vis (toluene): λ_{max}/nm ($\varepsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1}) 417 (320), 513 (21), 580 (13), 673 (11).

1,1′-Bis{5,10-bis(4-*tert*-butylphenyl)-15-mesitylporphyrin-20-yl}ferrocene (7). The reaction was performed following the general procedure starting from 1,9-bis(4-*tert*-butylbenzoyl)-5-mesityldipyrromethane (702 mg, 1.2 mmol) followed by condensation with 1,1′-bis[bis-(2,2′-pyrryl)methyl]ferrocene **2** (288 mg, 0.6 mmol). The reaction mixture was evaporated to dryness and crystallized from THF–CH$_2$Cl$_2$–Et$_2$O–hexane to give dark crystals (37 mg). The residue was crystallized from THF–ethyl acetate–hexane afforded pure crystals (mp > 360 °C) (58 mg). In total, 95 mg of porphyrin were obtained (10%). R_f = 0.45 (silica; CH$_2$Cl$_2$–hexane, 1 : 1); ^{1}H NMR (500 MHz, CDCl$_3$): δ −2.84 (br s, 4H, NH), 1.43 (s, 36 H, CH$_3$–t-Bu), 1.73 (s, 12 H, CH$_3$–Mes), 2.62 (s, 6 H, CH$_3$–Mes), 5.01 (s, 4H, Fc), 5.81 (s, 4H, Fc), 6.83 (br s, 16 H, Ar–H), 7.24 (br s, 4 H, Ar–H), 7.65 (br s, 4H, β-H), 8.15 (br s, 4H, β-H), 8.42 (br s, 4H, β-H), 9.72 (br s, 4H, β-H); MS(ESI): m/z 1568.8 [M + H$^+$]. Anal. calc. for C$_{108}$H$_{102}$FeN$_8$: C, 82.73; H, 6.56; N, 7.15. Found: C, 82.46; H, 6.42; N, 7.04%. UV-Vis (toluene): λ_{max}/nm ($\varepsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1}) 410 (245), 513 (18), 580 (11), 673 (8).

1,1′-Bis{Zn(II)-5,10-bis(4-*tert*-butylphenyl)-15-mesitylporphyrin-20-yl}ferrocene (Zn-7). A solution of **7** (20 mg, 0.013 mmol) in CHCl$_3$ (20 mL) was treated overnight with a solution of Zn(OAc)$_2$·2H$_2$O (30 mg, 0.137 mmol) in methanol (5 mL) at room temperature. The solvent was removed and residue was filtered through pads of silica (silica; CH$_2$Cl$_2$) to afford a pure solid which was crystallized from CH$_2$Cl$_2$–hexane to give dark crystals (19 mg, 86%). R_f = 0.67 (silica; CH$_2$Cl$_2$–hexane, 1 : 1); ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.48 (s, 36 H, CH$_3$–t-Bu), 1.83 (s, 12 H, CH$_3$–Mes), 2.65 (s, 6 H, CH$_3$–Mes), 5.00 (s, 4H, Fc), 5.82 (s, 4H, Fc), 6.91 (br s, 8 H, Ar–H), 7.11 (d, 8 H, J = 7.2 Hz, Ar–H), 7.27 (br s, 4 H, Ar–H), 7.79 (br s, 4H, β-H), 8.37 (d, 4H, J = 4.2 Hz, β-H), 8.57 (d, 4H, J = 4.6 Hz, β-H), 10.00 (d, 4H, J = 4.4 Hz, β-H); MS(ESI): m/z 1691.7 [M + H$^+$]. Anal. calc. for C$_{108}$H$_{98}$FeN$_8$Zn$_2$ + 2H$_2$O: C, 74.95; H, 5.94; N, 6.47. Found: C, 74.87; H, 5.82; N, 6.43%. UV-Vis (toluene): λ_{max}/nm ($\varepsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1}) 426 (373), 571 (21), 628 (23).

Electrochemistry

CV measurements were carried out in Hannover and later confirmed in Heidelberg. The measurements were performed using three electrodes: the working electrode was a glass-covered platinum wire (diameter *ca.* 1 mm), the reference electrode was Ag/AgCl, and the counter electrode was a platinum spiral. The supporting electrolyte was tetrabutylammonium hexafluorophosphate. The oven-dried measurement cell was cooled to 25 °C under argon and then filled with the solution of the supporting electrolyte and the sample. The solution was flushed with argon for 5 min. All measurements were performed at 25 °C. A Princeton Applied research potentiostat/galvanostat model 263A was used in Heidelberg; a HEKA Electronik potentiostat model PG 284/IEC was used in Hannover. All potentials are given *vs.* Fc/Fc$^+$.

Measurement 1: solvent CH$_2$Cl$_2$ (3.0 mL), supporting electrolyte Bu$_4$NPF$_6$ (232.4 mg), sample amount 2.2 mg, sweep width −2.0 V to +2.0 V, scan rate 100 mV s^{-1}.

Measurement 2: solvent CH$_2$Cl$_2$ (3.0 mL), supporting electrolyte Bu$_4$NPF$_6$ (231.8 mg), sample amount 1.1 mg, sweep width −1.0 V to +1.3 V, scan rate 10 mV s^{-1}.

Molecular modelling

Calculations were performed within the HyperChem® Package[27] by extensive energy minimizations (Polak–Ribiere conjugate gradient) alternating between molecular mechanics (MM+ force field) and semiempirical calculations (PM3).

Acknowledgements

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