Synthesis and properties of directly linked corrole–ferrocene systems†

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Meso-substituted corroles bearing directly linked ferrocene unit have been synthesized for the first time. Among various methods studied, only the condensation of pentafluorophenyldipyrromethane with a formylferrocene led to this type of product. A triad containing corrole and porphyrin bridged with ferrocene has been obtained by a convergent approach. Bilanes were used as crucial substrates in the porphyrin-forming step. For the first time it was shown that H_2O–MeOH–HCl conditions are suitable for preparation of various 10-(formylaryl)corroles *via* the direct condensation of aromatic dialdehydes with dipyrromethanes. Electrochemical studies of 10-ferrocenyl-5,15-bis(pentafluorophenyl)corrole support the possibility of intramolecular electron transfer from the corrole to the ferrocene system after the electrode oxidation of the ferrocene to a ferrocenium cation. We have studied the structure of 1-(corrolyl)-1′-(porphyrinyl)ferrocene by ^{1}H NMR and UV-Vis. NMR spectra show that this compound has more conformational freedom than analogous, previously studied bis-porphyrinylferrocenes. Absorption spectra suggest the lack of strong electronic interaction between ferrocene and porphyrinoids for dyads and significant conjugation for the triad.

Introduction

Multiporphyrin structures have recently attracted enormous attention due to their potential material properties in the fields of sensors, artificial photosynthesis *etc.*[1,2] The spatial orientation of the porphyrins could be either totally fixed or absolutely flexible. We became interested in studying a possible compromise between completely rigid and flexible spacers 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. Ferrocene as a candidate for the linker has been chosen, 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] The specific geometry of the ferrocene system might allow the adoption of unusual conformations of molecules bearing bulky groups on their peripheries.[4] In particular, a ferrocene moiety directly attached to the porphyrin ring would induce special orientations of both fragments. Many examples of ferrocene–porphyrins have been synthesized within the last 20 years, some of them possessing a direct linkage between these two chromophores.[5] Along these lines, we have recently described the synthesis and properties of 1,1′-bis(porphyrinyl)ferrocenes.[6] It was found that complex dynamic processes occur in these molecules (which may involve conformers, formation of H-aggregates and tautomers), and that they exhibit non-typical electrochemical behaviour. An architectural scheme in which two different porphyrinoids are connected by a ferrocene hinge is very intriguing. We were interested in the effect of such a molecular arrangement on the conformation of these molecules and on their properties. Among many different counterpart chromophores we decided to focus on corroles—one carbon short analogs of porphyrins.[7] These aromatic tetrapyrrolic macrocycles exhibit some interesting properties in comparison with porphyrins: smaller cavity, higher fluorescence quantum yield, no phosphorescence, more intense absorption of red light. Moreover, corroles have one additional advantage—they are easily available after recent developments.[7] Their availability is steadily increasing since 1999 to challenge the supreme position of porphyrins.[8] The only known examples of dyads comprised of metallocene and contracted porphyrinoids are ferrocene–oxacorroles, bearing a ferrocene unit in 5-*meso* position, recently obtained and characterized Chandrashekar and co-workers.[9] On the other hand, many rigidly linked cofacial bis(porphyrins) were prepared and investigated as synthetic models of heme/copper terminal oxidases.[10] Guilard, Kadish and co-workers recently extended these studies to Pacman-type cofacial cobalt bis-corroles and porphyrin–corroles.[7c,11] These face-to-face complexes possess simultaneously Co(II) and Co(III) metal ions. Consequently, they are good catalysts for the 4e reduction of O_2 to water.[12a] Investigation of

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† Electronic supplementary information (ESI) available: Fig. S1: Absorption of partly purified *trans*-A_2B-corrole prepared from ferrocenecarbaldehyde (**2**) and 5-(4-methylphenyl)dipyrromethane as a function of time. See DOI: 10.1039/b618631a

porphyrin(Zn(II))–corroles linked by dibenzofuran, dimethylxanthene and (offering significantly greater flexibility) diphenyl ether moieties, led to interesting conclusions regarding the rate of through-space energy transfer.[12b] Recently, we have also started a broad project aiming to explore the possibilities offered by corroles as a part of multicomponent systems.[6,13,14] The objective of this work was to develop an efficient synthetic route to 1-(corrolyl)-1′-(porphyrinyl)ferrocenes and to study their fundamental properties. The ultimate goal of this project was 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.

Results and discussion

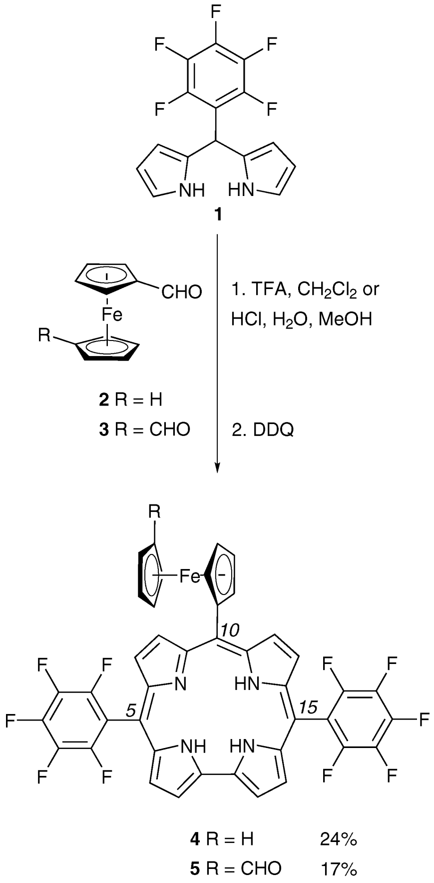
Design and synthesis

Since even simple directly linked ferrocene–corroles are unknown until now we decided to start by preparation of these simple dyads. We build up on our experience in the synthesis of *meso*-substituted *trans*-A_2B-corroles from dipyrromethanes and aldehydes.[8a,15] Thanks to this methodology we could introduce the desired ferrocenyl substituent at the 10 position of the macrocycle core. The two remaining identical substituents at the positions 5 and 15 would allow to control other properties of the system such as solubility, stability and redox properties.

In the light of above considerations the simplest idea was to perform acid-catalyzed condensation of dipyrromethanes with ferrocenecarbaldehyde (**2**). We performed this reaction using different dipyrromethanes under classical conditions (TFA, CH_2Cl_2) developed a few years ago.[15] However only *trans*-A_2B_2-porphyrins were observed as a sole macrocyclic product. The lack of the expected *trans*-A_2B-corrole was confirmed by ESI-MS. Changing the reaction conditions did not alter the results. With a new method for the synthesis of *meso*-substituted corroles in H_2O–MeOH–HCl system[8a] this option was considered as an alternative. The reaction of ferrocenecarbaldehyde (**2**) with 5-(4-methylphenyl)dipyrromethane was performed under these conditions. The formation of the expected *trans*-A_2B-corrole in this reaction was confirmed by ESI-MS, however, all attempts to purify this compound were unsuccessful. We found that partly purified corrole decomposed rapidly, even in the refrigerator. Unfortunately 2,6-dichlorophenyldipyrromethane also gave a highly unstable corrole. It is well known that corroles are generally less stable in solution than their porphyrin analogues.[16–18] It was suggested that the cleavage of the direct C–C bond occurs *via* the formation of dioxetane intermediate leading eventually to biliverdin species.[16] Moreover, recently Guilard, Gros, Barbe and Espinosa reported the first case of room-temperature autoconversion of *meso*-substituted free-base corroles to AB_2C-porphyrins.[18] Also in this case an open-chain bilverdin type structure is postulated as key intermediate. Our studies of partly purified corrole synthesized from ferrocenecarbaldehyde (**2**) and 5-(4-methylphenyl)dipyrromethane revealed the gradual changes in the absorption spectra (ESI†). The intensity of the Soret band decreased rather quickly upon exposure of the sample to light and air.[17b] All attempts to purify and identify products of decomposition failed, but probably the pathway follows the previously proposed one.[16] We decided to switch to dipyrromethane **1** bearing strongly electron-withdrawing groups. Previously it was proved that corroles bearing two such units are stable.[15d]

A combination of a C_6F_5 group and ferrocene moieties in one corrole creates a synthetic problem. It originates from the fact that DDQ can oxidize ferrocenes to radical cations. On the other hand transformation of bilanes bearing two pentafluorophenyl substituents into corroles proved impossible with *p*-chloranil only.[8a] Since neither option was really promising, we decided to try to use *p*-chloranil in the second step of this synthesis. However, the condensation of **1** with ferrocenecarbaldehyde (**2**) did not result in corrole **4** when quenched with *p*-chloranil. The same condensation followed by *in situ* oxidation with DDQ led to the formation of corrole **4** in 24% yield (Scheme 1).

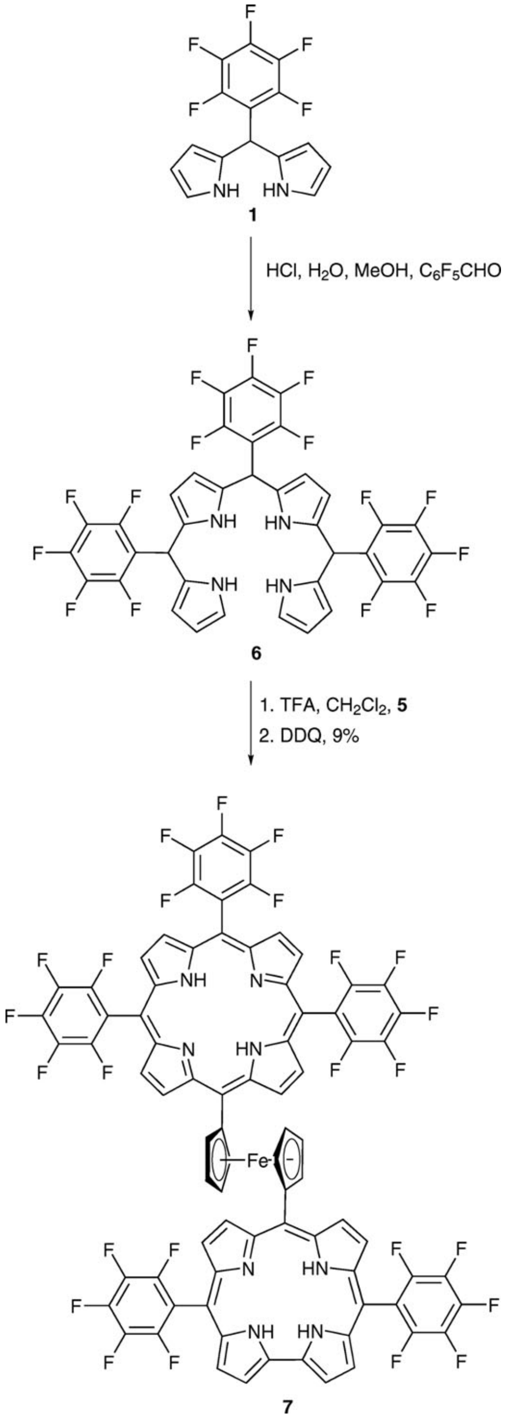
Several issues merit particular consideration when contemplating the synthesis of (corrolyl)(porphyrinyl)ferrocenes. From the view of synthetic efficiency two general strategies ought to be considered. The first starts with the synthesis of formylcorrole followed by assembly of the porphyrin ring. The second strategy starts with the preparation of an elaborated formylporphyrin which would then be used in the corrole forming reaction. The latter strategy was successfully implemented by Guilard *et al.* in the synthesis of face-to-face



Scheme 1

porphyrin–corroles.[11c,12b] An interesting modification of this approach *via* protection/deprotection of 1,1′-diformylferrocene was utilized in preparation of metalloporphyrin–ferrocene–alkylammonium conjugates.[5j,k] Given the moderate stability of corroles it is desirable to gain significant reduction of corrole manipulations. On the other hand the preparation of formylphenylporphyrin requires a multistep synthesis.

Given that relatively high yields of bilanes could be achieved in the reactions of dipyrromethanes with aldehydes under H_2O–MeOH–HCl conditions, we came to the conclusion that it might be possible to perform the reaction of an aromatic dialdehyde with pentafluorophenyldipyrromethane (**1**) under these conditions. Kinetic control of the formation of the bilane *via* precipitation secures that the second formyl group would not further react with the next molecule of dipyrromethane. In such a way we could generate the pivotal ferrocene–corrole core, endowed with an aldehyde functionality for the next step. 1,1′-Diformylferrocene[19] (**3**) reacted with dipyrromethane **1** to form corrole **5** in 17% yield (Scheme 1). With formylcorrole **5** in hand, the best way to efficiently close the porphyrin would be to condense it with bilanes. This strategy was not extensively studied, since, until recently, bilanes were very difficult to synthesize in a straightforward manner. Our corrole synthesis[8a] is in fact based on the very efficient formation of bilanes. When a condensation of bilane bearing three 4-cyanophenyl substituents at 'meso' positions was performed in CH_2Cl_2 in the presence of TFA it led to the formation of the respective (corrolyl)(porphyrinyl)ferrocene (confirmed by ESI-MS). However this molecule was very unstable and could not be purified. In this light we decided to carry out experiments with formation of a bilane bearing only pentafluorophenyl groups **6**. Compound **6** has been prepared *in situ* from dipyrromethane **1** and pentafluorobenzaldehyde and directly reacted with aldehyde **5** (Scheme 2) to give **7** (9%). This compound was stable enough for purification by extensive column chromatography and fully characterized.



Scheme 2

Electrochemistry

Typical cyclic voltammetric curves of the compound under study in CH_3CN solutions containing 0.1 M TBAP recorded at the scan rate 0.1 V s^{-1} at a platinum electrode are presented in Fig. 1. The electrochemical behavior observed is reminiscent of that observed previously for similar corrole macrocycles, $(Cor)H_3$, investigated in benzonitrile solutions.[13,20] In particular, a comparison with three compounds with the same corrole macrocycle as in **4** but with naphthalenedicarboxylic imide groups[13] or the pentafluorophenyl group[20] attached instead of the ferrocene moiety, is useful for an identification of reactions corresponding to each peak. Of course, small differences in peak potentials E_p are expected due to a different effect of the ferrocene moiety and a stronger ability of CH_3CN to solvate ions, in particular anions. Irreversible reduction of the corrole macrocycle $(Cor)H_3$ in a parent molecule to a radical anion (peak I_{red} in Fig. 1) occurs at $E_p = -0.58$ V and the further reduction II_{red} was found at $E_p = -0.91$ V. This second peak decreases at the higher scan rate of 1 V s^{-1} indicating the formation of a reactant in a relatively slow chemical reaction, most likely the conversion of a radical anion formed in the first reduction step into the $[(Cor)H_2]^-$ anion, as established for similar compounds.[20] At the reverse potential scan (dotted curve in Fig. 1) the reduction products are oxidized (the peak III_{ox} at $E_p = 0.22$ V), resembling a behavior of similar compounds ($E_p = 0.31$–0.32 V).[13,20] However, a small oxidation peak III_{ox} is also evident on anodic curves (solid and dashed curves in Fig. 1) started at the potential −0.5 V, *i.e.*, before the reduction I_{red} of a corrole system. Most probably this indicates the formation of $[(Cor)H_2]^-$ anions by the proton dissociation of a parent

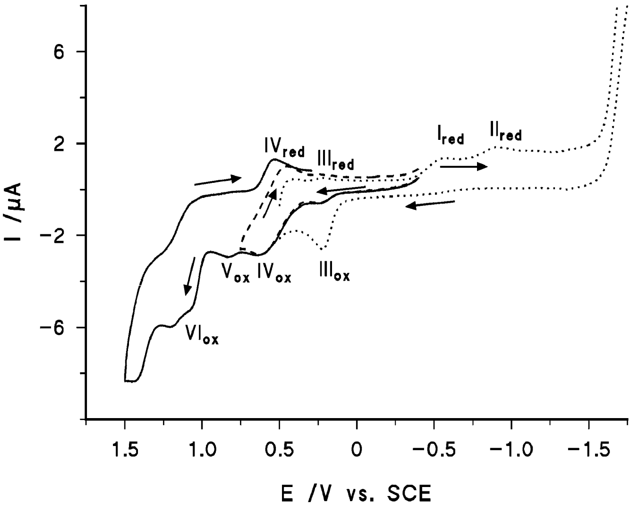


Fig. 1 Cyclic voltammetric curves for the reduction (dotted line) and oxidation (solid and dashed lines) of 0.5 mM solutions of corrole **4** in CH_3CN with 0.1 M TBAP at scan rate 0.1 V s^{-1}

molecule, as observed for some corrole macrocycles in pyridine, but not in PhCN.[20] However, due to a stronger solvation of ions, the dissociation can be more favored in CH_3CN than in PhCN solutions.

The small oxidation peak V_{ox} at E_p = 0.82 V (solid curve in Fig. 1) corresponds to the oxidation of a parent molecule (E_p = 0.84–0.86 V for similar compounds in PhCN)[13,20] and the next two peaks at 1.1 and 1.2 V (VI_{ox}) can be probably related to the oxidation of $[(Cor)H_4]^+$ and $(Cor)H_2$ formed in solution from a primary oxidation product, a radical cation, as established for similar systems (E_p = 1.04–1.2 V).[13,20]

For the oxidation processes (solid and dashed curves in Fig. 1) the most interesting difference is the additional pair of peaks: IV_{ox} at E_{pa} = 0.63 V and IV_{red} (E_{pc} = 0.45 V, on a dashed curve, *i.e.*, if the potential scan is reversed just after the oxidation peak). These peaks were not observed for other corrole macrocycles[13,20] and can thus be ascribed to electrode reactions of the ferrocene system. The process is quasi-reversible, with the same heights of anodic and cathodic peaks, but the peak separation ΔE_p = 180 mV is much higher than for a reversible behavior. However, if the potential scan is reversed at a more positive value of 1.5 V (solid curve in Fig. 1), *i.e.*, after the oxidation of the corrole system (peak V_{ox}), the reduction peak IV_{red} has lower height (60% of the corresponding anodic peak), but shifts to the potential E_{pc} = 0.53 V, indicating an increase in the reversibility. This behavior is interesting in respect to the electrochemistry of bis-1,1′-(porphyrinyl)ferrocene,[6] for which the direct electron transfer from the electrode to a ferrocene moiety is unlikely because of steric reasons. However, an anodic and cathodic pair of peaks for the ferrocene system was observed in CH_2Cl_2 solutions, but only at a low scan rate of 0.01 V s^{-1}, whereas the reduction peak was not observed at 0.1 V s^{-1}. It was suggested[6] that for 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. Results shown in Fig. 1 support the possibility of the intramolecular electron transfer between ferrocene and macrocycle units. Namely, for anodic curves (solid curve in Fig. 1) the peak V_{ox} corresponding to the oxidation of corrole unit is very small (0.2 μA), but the peak VI_{ox} for a further oxidation of secondary products has a similar height (2.4 μA) as for the oxidation of ferrocene moiety (2.2 μA). Moreover, the peak IV_{red} corresponding to the reduction of ferrocene cation decreases substantially, if the potential scan was reversed after the peak V_{ox}. Most probably this behavior indicates that the ferrocene cation formed in the heterogeneous oxidation process IV_{ox} oxidizes next a corrole unit, decreasing electrode concentrations of the ferrocene cation and the neutral corrole and thus, results in the decrease of both peaks: V_{ox} and IV_{red}. A smaller irreversibility of processes IV for a longer time of experiment (solid curve) supports also the interpretation given for bis-1,1′-(porphyrinyl)ferrocene[6] that the intramolecular electron transfer is related to some slow structural changes of a molecule.

Spectroscopic and photophysical properties

A standard ^1H NMR spectrum of triad **7** showed certain line broadening, especially signals derived from corrole β-pyrrole protons and corrole NH protons. One has to note that for previously studied bis(porphyrinyl)ferrocenes the line broadening was more significant.[6] These intriguing results, which indicated some complex dynamic processes taking place prompted us to study the variable-temperature ^1H NMR spectra of **7**. The most interesting regions are shown on Fig. 2.

The spectra recorded at 303 K showed the presence of two NH signals: one sharp resonance at δ −2.39 ppm derived from porphyrin and one extremely broad signal (δ −3.50 ppm) derived from corrole. Yet, there was a striking difference in variable-temperature ^1H NMR spectra of triad **7** and previous bis(porphyrinyl)ferrocenes. While compound **7** gave narrow lines of the β-pyrrole porphyrin resonances at 303 K, spectra recorded for bis-porphyrin at the same temperature had broad lines.[6] The other striking difference could be found in the signals of the NH protons (porphyrin). For bis(porphyrinyl)ferrocenes porphyrin-NH signals are broad even at 363 K, while for compound **7** the analogous signal (one line) is pretty narrow even at 303 K. In unsubstituted ferrocene, the barrier of internal rotation of the Cp rings is estimated to be only one third of that in ethane.[21] This means that in the usual temperature range for NMR investigations the Cp rings rotate freely. It is worth emphasizing that variable-temperature ^1H NMR experiments allowed to observe two distinct conformational processes for 1,1′-fused ferrocene–porphyrins, one of them arising from ferrocene rotations.[22]

Ferrocene–porphyrins lacking β-alkyl substituents could freely rotate. The question remains if there is still such free rotation around this bond in (corrolyl)(porphyrinyl)ferrocene **7**. Free rotation of the ferrocene moiety with attached corrole over the porphyrin should be rather difficult (as in the case of bis(porphyrinyl)ferrocenes). On the other hand simple 1,1′-disubstituted ferrocenes with possibility of π-stacking interaction between aromatic substituents could occupy π-stacking conformations.[23] We may assume that for (corrolyl)(porphyrinyl)ferrocene **7** free rotation of the substituted cyclopentadienyl ligands is not possible, presumably due to their steric

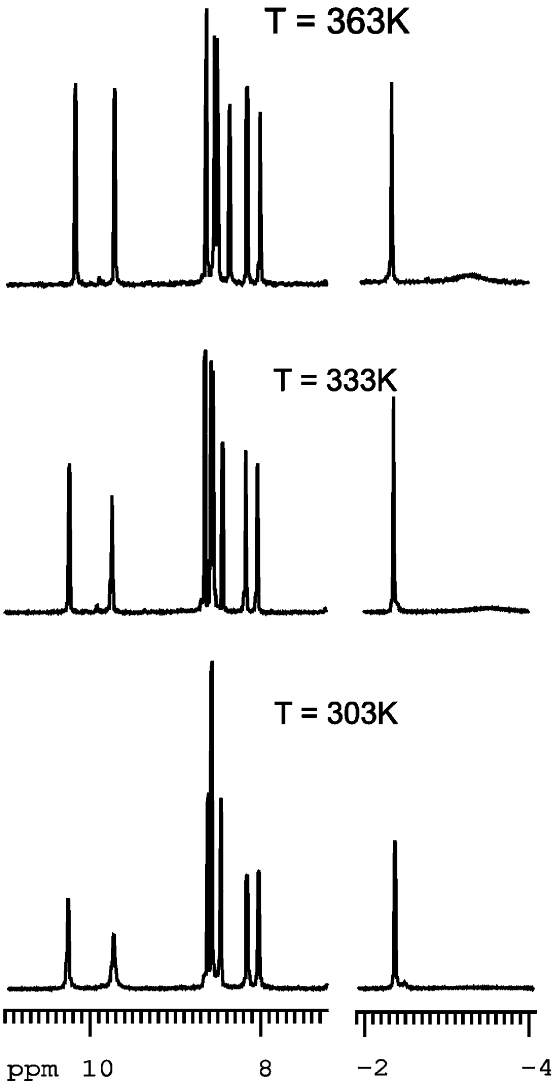


Fig. 2 Variable-temperature ^{1}H NMR spectra of **7** (aromatic and NH regions)

hindrance (Scheme 2). However the comparison of VT-NMR of compound **7** with previously studied bis(porphyrinyl)ferrocenes suggests a higher degree of conformational freedom. It is worth mentioning that β-substituted bis-porphyrins linked by diphenyl ether crystallize in face-to-face conformation.[12b]

A UV-Vis spectroscopic investigation was carried out on corroles **4**, **5** and **7** in order to obtain more information about the nature of the unique π systems of the compounds prepared. The absorption spectra of corroles **4** and **5** in acetonitrile were nearly identical and display bands at 428–439, 554–557, 589–593 and 636–641 nm. UV-Vis data showed a small red shift for the Soret band in comparison with 5,15-bis(pentafluorophenyl)-10-*p*-tolylcorrole[15d] λ_{abs} (428–439 *vs.* 419 nm). A bathochromic shift of the Soret band of corroles **4** and **5** could result from the formation of H-aggregates.[24] In contrast to ferroceneoxacorrole studied by Chandrashekar *et al.*[9] who observed a significant decrease in ε values *vs.* *meso*-substituted corroles with aryl substituents, in our case the ε values are almost identical. This might indicate that there is not a strong electronic interaction between both chromophores (*i.e.* corrole and ferrocene).

The electronic spectrum of compound **7** is more complex. It displays a shoulder Soret-band and one additional intriguing Q-band. This band located at 500 nm has no equivalent in spectra of corroles **4** and **5** or in spectra of any classical porphyrins or corroles. In contrast to spectra of corroles **4** and **5** molar absorption coefficients for triad **7** are much smaller than expected from superimposition of spectra of the parent macrocycles which suggests a high degree of electronic interaction. The same was previously observed for 1,1′-bis-(porphyrinyl)ferrocenes.

Experimental

Synthesis

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes, cyclohexane) were distilled prior to use. All reported ^{1}H NMR spectra were recorded on a Bruker AM 500 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV-Vis spectra were recorded in toluene (Cary). Chromatography was performed on silica (Kieselgel 60, 200–400 mesh). Mass spectra were obtained *via* EI or electrospray MS (ESI-MS). The purity of all new corroles was established based on ^{1}H NMR spectra. All dipyrromethanes[25] and 1,1′-diformylferrocene[19] were prepared according to literature procedures.

10-(Ferrocenyl)-5,15-bis(pentafluorophenyl)corrole (4). Ferrocenecarbaldehyde (107 mg, 0.5 mmol) and pentafluorophenyldipyrromethane (**1**) (312 mg, 1 mmol) were dissolved in MeOH (50 mL), and a mixture of H_2O (50 mL) with HCl aq (36%, 2.5 mL) was added. The reaction was stirred at 25 °C for 3 h. Subsequently, the reaction mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 300 mL with $CHCl_3$. DDQ (227 mg, 1 mmol) was added to this mixture followed after 10 min with hydrazine (5 μL of solution in anhydrous THF). After 1 h solvent was partially evaporated and the residue was chromatographed (silica, hexane–CH_2Cl_2 4 : 1 then 3 : 2, 1 : 1). Pure product was obtained after crystallization from CH_2Cl_2–hexane (97 mg, 24%); R_f = 0.61 (silica, CH_2Cl_2–hexane 3 : 2); δ_H (500 MHz; $CDCl_3$; Me_4Si) −2.43 (br s, 2H, NH-cor) 4.25 (s, 5H, Fc), 4.82 (m, 2H, *J* = 1.8 Hz, Fc), 5.58 (m, 2H, *J* = 1.8 Hz, Fc), 8.49 (d, 2H, *J* = 4.1 Hz, β-H), 8.68 (d, 2H, *J* = 4.7 Hz, β-H), 9.02 (d, 2H, *J* = 4.2 Hz, β-H), 9.87 (br d, 2H, *J* = 4.5 Hz, β-H); ESI-HR obs. 815.0913 [M + H^+], calc. exact mass 815.0951 ($C_{41}H_{21}N_4F_{10}Fe$); λ_{max}(acetonitrile)/nm ($10^{-3}\varepsilon$) 428 (103.2), 554 (9.2), 593 (10.3), 641 (26.9).

1-Formyl-1′-{10-[5,15-bis(pentafluorophenyl)corrolyl}ferrocene (5). 1,1′-Diformylferrocene (312 mg, 1 mmol) and pentafluorophenyldipyrromethane (**1**) (624 mg, 2 mmol) were dissolved in MeOH (50 mL), and a mixture of H_2O (50 mL) with HCl (aq) (36%, 2.5 mL) was added. Subsequently, the reaction mixture was stirred at 25 °C for 2 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with

H_2O, dried (Na_2SO_4), filtered, and diluted to 300 mL with $CHCl_3$. DDQ (681 mg, 3 mmol) was added to the reaction mixture. After 10 min the reaction mixture was concentrated to 1/4 of the initial volume and filtered through a silica pad (CH_2Cl_2) to collect two fractions. The fraction containing pure corrole was evaporated to dryness and immediately crystallized (CH_2Cl_2–hexane). The fraction containing corrole **5**, accompanied with some unidentified impurities, was filtered through silica pad once more (CH_2Cl_2) and crystallized in the same way. Totally 189 mg (17.4%) of dark green–brown crystals of corrole **5** was obtained. R_f = 0.38 (silica, CH_2Cl_2–hexane 4 : 1) (Found: C, 59.81; H, 2.30; N, 6.56. $C_{42}H_{20}N_4F_{10}FeO$ requires C, 59.88; H, 2.39; N, 6.65%); δ_H (500 MHz; $CDCl_3$; Me_4Si) −2.24 (br s, 2H, NH-cor), 4.58 (m, 2H, J = 1.9 Hz, Fc), 4.90 (m, 2H, J = 1.9 Hz, Fc), 4.93 (m, 2H, J = 1.9 Hz, Fc), 5.7 (m, 2H, J = 1.9 Hz, Fc), 8.52 (d, 2H, J = 4.2 Hz, β-H), 8.7 (d, 2H, J = 5.0 Hz, β-H), 9.05 (d, 2H, J = 4.4 Hz, β-H), 9.73 (br d, 2H, J = 4.6 Hz, β-H), 9.92 (s, 1H, CHO). ESI-HR obs. 843.0936 [M + H^+] calc. exact mass 843.0899 ($C_{42}H_{21}N_4F_{10}FeO$);. λ_{max}(acetonitrile)/nm ($10^{-3}\varepsilon$) 439 (103.6), 557 (10.3), 589 (10.8), 636 (24.1).

1-[5,15-bis(pentafluorophenyl)corrol-10-yl]-1′-[5,10,15-tris-(pentafluorophenyl)porphyrin-20-yl}ferrocene (7). Pentafluorobenzaldehyde (6 μL, 0.05 mmol) and pentafluorophenyldipyrromethane (**1**) (31 mg, 0.1 mmol) were dissolved in MeOH (5 mL), and a mixture of H_2O (5 mL) with HCl (aq) (36%, 0.5 mL) was added. The reaction was stirred at 25 °C for 3 h and extracted with CH_2Cl_2. Subsequently the organic layer was washed twice with H_2O, dried (Na_2SO_4) and filtered. The residue was dissolved in CH_2Cl_2 (4 mL) and corrole **5** (35 mg, 0.042 mmol) was added followed by TFA (3.2 μL, 0.041 mmol). The mixture was stirred overnight and then was diluted to 12 mL with CH_2Cl_2. DDQ (27 mg, 0.12 mmol) was added and mixture was stirred for several hours. The residue was chromatographed (silica, hexane–CH_2Cl_2 4 : 1 then 3 : 2, 2 : 3, 1 : 4, CH_2Cl_2). THF (300 μl per 100 mL of the eluent) was always added to the solvent mixture to facilitate separation. Collected product was rechromatographed (silica, hexane–CH_2Cl_2 9 : 1) After evaporation, pure triad **7** was dissolved in CH_2Cl_2–hexane, and evaporated again to obtain crystalline product (7.3 mg, 9%). R_f = 0.57 (silica, CH_2Cl_2–hexane 2 : 3); δ_H (500 MHz; toluene-d$_7$; Me_4Si) −3.50 (br s, 3H, NH-cor), −2.39 (s, 2H, NH-por), 4.70 (br s, 2H, Fc), 4.83 (br s, 2H, Fc), 5.58 (br s, 2H, Fc), 5.66 (br s, 2H, Fc), 8.05 (d, 2H, J = 3.5 Hz, β-H-cor), 8.19 (br s, 2H, β-H-cor), 8.50 (d, 2H, J = 4.7 Hz, β-H-por), 8.60 (d, 2H, J = 4.8 Hz, β-H-por), 8.61 (d, 2H, J = 4.8 Hz, β-H-por), 8.65 (d, 2H, J = 4.1 Hz, β-H-por), 9.76 (br s, 2H, β-H-cor), 10.29 (br s, 2H, β-H-cor); ESI-HR obs. 1620.1487 [M + H^+], calc. exact mass 1620.1465 ($C_{79}H_{30}N_8F_{25}Fe$); λ_{max}(acetonitrile)/nm ($10^{-3}\varepsilon$) 309 (24.3), 416 (101.3), 449 (45.3), 505 (11.1) 550 (8.0) 594 (7.9) 639 (13.0).

Electrochemistry

Chemicals. Anhydrous acetonitrile 99.8% from Sigma-Aldrich was used as received. Vacuum-dried tetra-*n*-butylammonium perchlorate (TBAP, electrochemical grade from Fluka) was used as supporting electrolyte (c = 0.1 M). The concentration of the reactant **4** was 0.5 mM.

Instrumentation. Cyclic voltammetry was carried out with a EG&G PAR 273A potentiostat controlled by a PC computer by means of the software M270 from PAR. The positive feedback method of *iR* compensation was applied. A three-electrode cell was used consisting of a platinum-disk working electrode (1.5 mm diameter), a platinum counter electrode and a saturated calomel reference electrode (SCE). All potentials are referred against SCE. The solution was deoxygenated with argon and a blanket of gas was maintained over the solution surface during measurements.

Conclusions

In conclusion, our studies have clearly documented the ability of the dipyrromethane + aldehyde strategy in the H_2O–MeOH–HCl system to assemble complex triads bearing a corrole skeleton. The crucial synthesis of (formylferrocenyl)-corrole was achieved directly from 1,1′-bisformylferocene in high yield. The influence of the ferrocene moiety on the structure of the corrole core seems to be rather significant judging from the extremely low stability of derivatives bearing other than strongly electron withdrawing groups in the remaining *meso*-positions. In some contrast, UV-Vis spectra of simple 10-ferrocenylcorroles indicate that the level of conjugation between both chromophores is rather low.

Variable temperature-dependent ^{1}H NMR spectra showed that the conformational freedom of 1-(corrolyl)-1′-(porphyrinyl)ferrocene is higher than in 1,1′-bis(porphyrinyl)ferrocenes. The electrochemical analysis of 10-ferrocenylcorroles indicated the intramolecular electron transfer from the corrole moiety to the ferrocene unit after the electrode oxidation of the latter to a ferrocene cation, similarly as proposed previously for 1,1′-bis(porphyrinyl)ferrocenes. These observations suggested that further exploration of such triads would be highly productive. Work on utilization of this scaffold in the construction of electrochemically tuneable metal–organic frameworks is in progress in our laboratory.

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