Self-Assembly of Pyrrole – Ferrocene Hybrids, Determined Inter Alia by a New Chemically Induced Electrospray Mass Spectrometry Technique

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Abstract: A new approach to organic superstructure self-assembly, based on the use of pyrrole – ester-substituted ferrocenes, is described. Specifically, di- and tetrapyrrole-substituted ferrocenes have been prepared. These species are found to form ribbon-like infinite chains in the solid state. In the case of the tetra-substituted system, self-association takes place in solution to produce small but well-defined oligomers. These oligomers were characterized in solution by VPO analysis and in the solution/gas phase by electrospray mass spectrometric methods. In the latter instance the ferrocene moiety was subjected to selective oxidation prior to analysis, a technique we term *oxidative* electrospray mass spectrometry (O-ESMS).

Keywords: electrospray mass spectrometry · ferrocenes · pyrroles · self-assembly

Introduction

Self-assembly plays a critical role in regulating the formation of many essential biological superstructures, including DNA – protein complexes, cell membranes, viral capsids and multicomponent enzymes.[1] The facile, and often precisely controlled, formation of these highly defined structures in nature derives from a range of recognition and/or self-association processes that are dictated by the chemical information (size and shape) contained in the constituent structural elements. This information, amongst other things, provides the basis for the recognition or nonrecognition of a given substrate.

Recently, considerable effort has been focused on the use of simple synthetic systems to probe the determinants of natural self-assembly. Indeed, a number of elegant organic self-assembling systems are now known.[2, 3a–g] In these, a full range of noncovalent forces, including π – π stacking, hydrogen bonding, and hydrophobic interactions, have been used as recognition motifs. Both inorganic[4] and organometallic[5] recognition interactions have also been employed in this context.

In our own work, we have recently found that expanded porphyrins[6a] and calix[4]pyrroles,[6b] which are both excellent anion-binding receptors, can be used to assemble noncovalent supramolecular aggregates.[6c] This success led us to question whether it might be possible to use nonmacrocyclic (i.e., open-chain) polypyrrolic systems to generate novel self-assembled superstructures. In this paper we wish to report that this can in fact be done. Specifically, we show that the tetrapyrrolylferrocene system **4** self-assembles through hydrogen-bonding interactions both in solution and in the solid state.

As a potential recognition subunit, pyrrole offers only one hydrogen-bond-donating group (i.e., the N-H functionality) in contrast to, for example, nucleobase-derived subunits.[3a] Therefore, we reasoned that if we were to be able to study the self-assembly behavior of pyrrolic receptors, it would be necessary to design subunits containing at least two independent pyrrolic functions. Accordingly, we considered it worthwhile to attach two separate pyrrole units to a ferrocene moiety, a group recently introduced as an easy-to-study molecular ball bearing by Gokel et al.[7] The resulting systems would possess an inherent redox-active element that could be used to facilitate the sometimes tricky process of establishing the occurance of self-assembly.

Results and Discussion

Although the choice of a ferrocene spacer was viewed as attractive for the reasons outlined above, one clearly recognized drawback associated with such an approach centers around the fact that, prior to this work, di- or tetrapyrrolicferrocenes were unknown. In fact, only a few papers describing five-membered-heterocycle-substituted ferrocenes have appeared in the literature.[8a,b] Of the published reports in the

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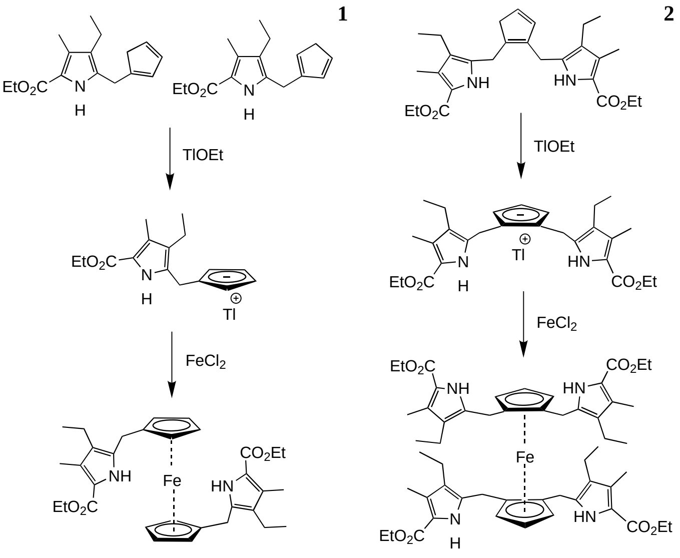
area, only one describes a 1,1′-disubstituted ferrocene, specifically, a 1,1′-dithiopheneferrocene.[8d] This material was synthesized starting from an already functionalized 1,1′-disubstituted ferrocenyl precursor and building the heterocycle onto the ferrocene scaffold. In contrast, we recently succeeded in synthesizing the novel cyclopentadiene-substituted pyrroles **1** and **2** using a substitution-type strategy that involves the reaction between NaCp and an α-acetoxymethylpyrrole.[9] Thus, with precursors **1** and **2** in hand, we were able to generate the desired pyrrole-substituted ferrocenes **3** and **4**. This was done by 1) effecting a specific TlOEt-mediated deprotonation followed by 2) a metathesis process involving the reaction of the Tl-cyclopentadienyls generated in situ with $FeCl_2$ (see Scheme 1).



Scheme 1. Synthesis of the pyrrole substituted ferrocenes **3** and **4**.

Solid-state structure: The first evidence that systems **3** and **4** could self-assemble came from X-ray diffraction studies. X-ray quality crystals of both derivatives were obtained from CH_2Cl_2/hexanes. In the case of **3** this was done by storing the relevant samples at −30 °C for several days, whereas in the case of **4** it was achieved by allowing the solution to evaporate slowly at room temperature. The resulting structures revealed that the ferrocene ball bearings adopt a *trans* geometry in both cases (Figure 1).

These same structural analyses also revealed that strong intermolecular H-bond interactions between the pyrrolic NH and ester functionalities result in the formation of infinite ribbons (Figure 2). While there is no obvious evidence of interaction between the chains, the contacts within the chain (leading to the observed long-range order) appear to be extremely well defined. For instance, in the case of **3** the intermolecular separation between the pyrrole nitrogens and the ester oxygens was found to be 2.95 Å, a distance consistent with the proposed intermolecular hydrogen bonds. Interestingly, presumably as a result of a need to accommodate two intermolecular H-bridges between the two noncovalently linked pyrrole units, the N–H⋯O angle of 164° deviates considerably from the ideal value of 180°.

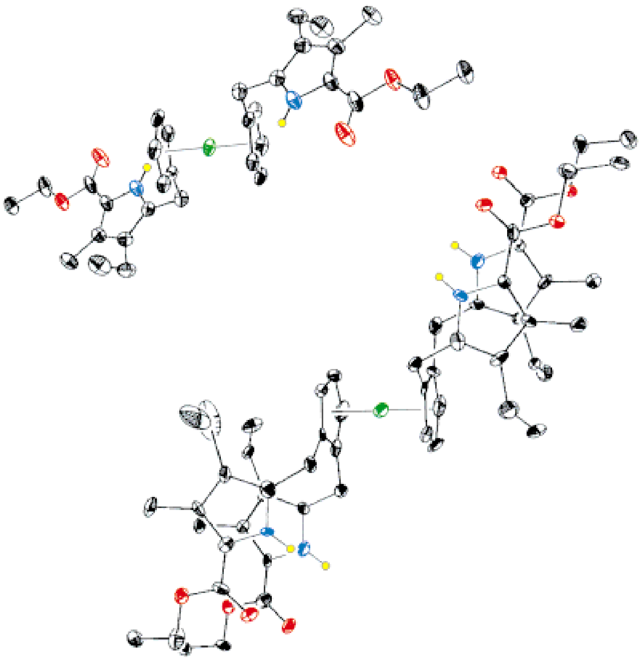


Figure 1. Molecular structures of **3** (above) and **4** (below) as determined by X-ray crystallography (thermal ellipsoids are scaled to the 30 % probability level). C: black; H: yellow; N: dark blue; O: red; Fe: green.

Similar features are seen in the solid-state structure of **4**. In this instance, the individual tetrapyrrolic ferrocene subunits are linked by eight hydrogen bonds. Since this is twice the number of intermolecular contacts found in the ribbons of **3**, it was expected that the monomer-to-monomer separation might be smaller in **4** than in **3**. This indeed proved to be the case. In fact an average N(pyrrole)-to-O(ester) distance of 2.89 Å was found in the solid structure of **4**.[10] This is 0.06 Å shorter than in the structure of **3** (vide supra). Further, in the case of **4**, the need to accomodate a greater number of hydrogen bonds than **3** leads to a further deviation from linearity of the N–H⋯O angle (averaged value 145°).

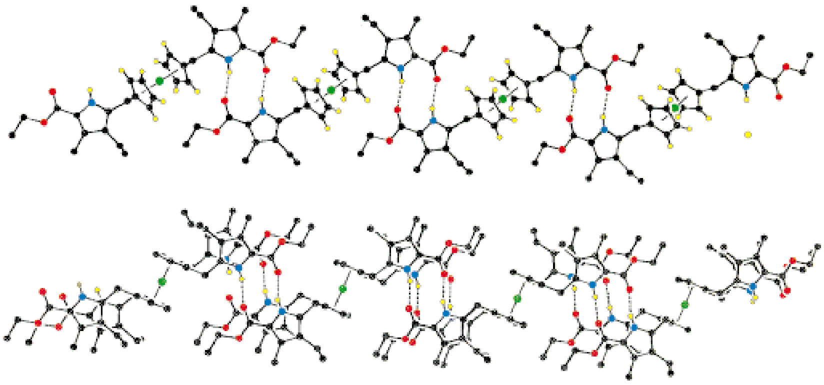


Figure 2. Side views of representative tetrameric subunits found in the infinite ribbon structures formed by **3** (above) and **4** (below) in the solid state.

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In both complexes the individual ferrocene units within a given supramolecular chain lie parallel to each other. In the case of **3** the ferrocene units form an angle of 62° with regard to the mean ribbon plane. By contrast, the analogous angle is 29° in the case of **4**. The larger angle found in **3** is in agreement with the smaller pyrrole-to-Cp twist seen in this system as compared to **4**. In **4** the individual pyrroles of each dipyrrolecyclopentadienyl unit are seen to stack on top of each other (distance: 3.45 Å).[11] This leads to the suggestion that $\pi-\pi$ stacking effects could play a role in defining the overall self-assembled structure.

Solution-state structure: The well-defined long-range order observed in the solid-state structures of both **3** and **4** led us to question whether a similar self-assembly process might occur either in solution or in other less well defined media. In this context, we were particularly keen to determine whether **4**, with its greater number of hydrogen-bonding groups and structurally defined potential for $\pi-\pi$ stacking, would be more likely to form aggregates than **3**. In a first effort to address this issue, vapor pressure measurements (VPO) were conducted in toluene. From these it was determined that the average molecular weight of **4** in solution is that of a trimer ($M_{\text{found}} = 2897$, $M_{\text{calcd}}(\text{monomer}) = 959$).[12] By contrast, the average molecular weight of **3** was found to be that of a monomer ($M_{\text{found}} = 587\,\text{g}\,\text{mol}^{-1}$, $M_{\text{calcd}}(\text{monomer}) = 572\,\text{g}\,\text{mol}^{-1}$). These results lead us to conclude that **4**, but not **3**, undergoes self-assembly in solution, even under conditions of high dilution (10^{-4} to 8×10^{-4} M) required for the VPO measurements.

In an attempt to define more rigorously the nature of the solution-phase self-assembly seen with **4**, ^{1}H NMR spectroscopic dilution studies were carried out in $CDCl_3$. Interestingly, no observable spectroscopic changes could be seen over the studied concentration range (1 mM – 10 mM). Thus, little could be concluded from these studies. Further, efforts to break any putative self-assembled aggregates by adding [D$_4$]MeOH proved unsuccessful as a result of the very poor solubility of **4** in this solvent.

Given the above, an alternative means of characterizing the solution-phase behavior of **4** was sought. To this end we turned to mass spectrometry (MS). While, strictly speaking, MS gives information only about species present in the gas phase, there is often a good correlation between what occurs in solution and what is observed using electrospray ionization mass spectrometry (ESI-MS).[13] Indeed, this technique has been used recently to analyze a range of aggregation processes in solution.[14] It has seen limited application, however, in the area of organic self-assembly. This is because many noncovalently linked superstructures are uncharged and thus not detectable by ESI-MS techniques. Furthermore, attempts to generate protonated species by the addition of acids are expected to lead to the collapse of aggregates based on H-bonding. Facing this problem, Lehn and coworkers developed a method, called *ion-labeling* ESMS (IL-ESMS), which offers the detection of originally neutral species.[15] In this technique, a K$^+$-binding crown ether is appended synthetically to a less relevant binding site of the supermolecule, thereby introducing the requisite charge into the self-assembled structures. While this approach is elegant, in the case of **3** and **4** we reasoned that the ferrocene subunit, were it oxidized to its corresponding ferrocenium form, would serve as the sought-after charged functionality. To the best of our knowledge such an approach, which we term *oxidative* electrospray mass spectrometry (O-ESMS), has not hitherto been tried.

Prior to the ESMS experiments, a small amount of I_2 (10% of a molar equiv) was added to dichloromethane solutions of **3** and **4**.[16] Complexes **3** and **4** activated in this way gave spectra such as those reproduced in Figure 3. No signals ascribable to decomposition products were detected, leading us to suggest that the oxidation process involves the ferrocene units exclusively. The dominant O-ESMS signal observed for **4** (Figure 3b) corresponds to the dimeric species (*m*/*e* 1916.9) whereas the spectrum of **3** (Figure 3a) is strongly dominated

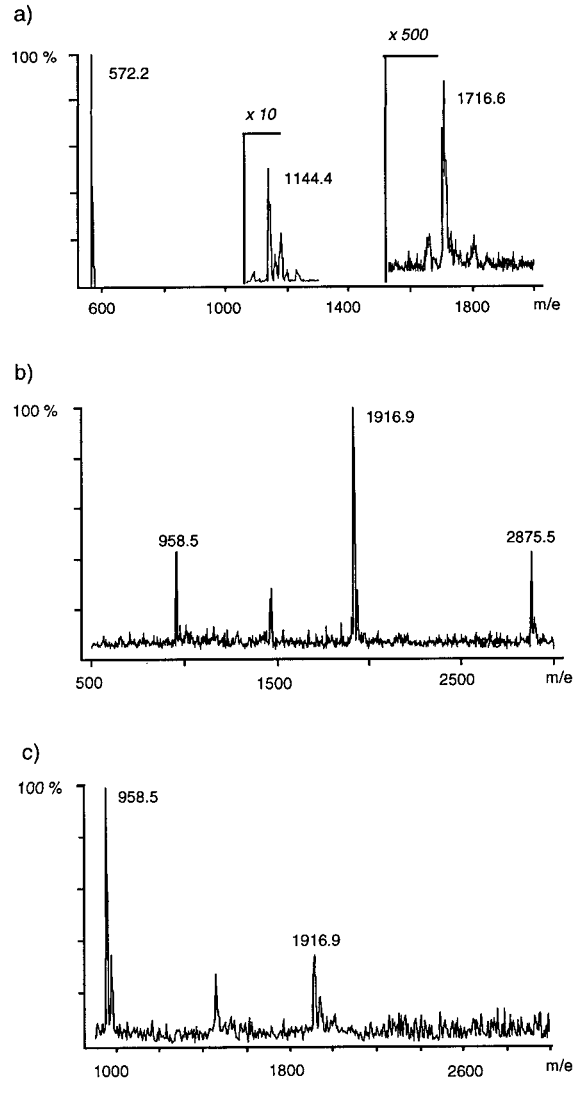

Figure 3. O-ESMS mass spectra of a) **3** and b) **4** dissolved in CH_2Cl_2. A solution of I_2 in CH_2Cl_2 (10 μL; 10^{-2} M) was added to solutions of **3** and **4** (0.2 mL total volume; 5×10^{-3} M) one hour prior to analysis. The resulting solutions were then diluted eighty times with CH_2Cl_2. c) O-ESMS of the solution used to produce trace b) reanalyzed after the addition of an identical amount (v/v) of a mixture consisting of 47% MeOH, 47% H_2O, and 6% AcOH.

by a peak that is easily assignable to the monomer (*m*/*e* 572.2). This latter signal is characterized by an intensity approximately 700 times larger than that of the corresponding trimer peak (*m*/*e* 1716.6). By contrast, the trimer peak observed in the O-ESMS spectrum of **4** (*m*/*e* 2875.5), while not dominant, is actually more intense than the corresponding monomer signal (*m*/*e* 958.5).

Adding methanol to a dichloromethane solution of **4** (prior to the I_2 treatment) did not result in a great change in the ESI-MS spectrum, a result we take to reflect the stability of these aggregates. By contrast, when samples of **4** in CH_2Cl_2 were combined with a similar quantity (v/v) of a solution consisting of 47% MeOH, 47% H_2O, and 6% AcOH prior to the I_2 treatment, the peak assigned to the trimer was seen to vanish (Figure 3c). Under these conditions the intensity of the dimer peak also decreases while that of the monomer increases. This deaggregation process is not ascribed to simple protonation; rather, it is thought to reflect the fact that the added acetic acid acts as a hydrogen-bond donor. Thus it competes successfully with the pyrrole NH group for the carbonyl lone pairs. This prevents aggregation both in solution and in the gas phase. This explanation is consistent with the fact that, under these conditions, we observed monomer peaks ascribable to M^+ and $[M{+}H_2O]^+$ rather than to $[M{+}H]^+$ species.

Several control studies were carried out in order to confirm that the observed ions are actually present in solution prior to the ESI-MS experiment and not caused by, for instance, proton-mediated ion-molecule reactions in the gas phase. The first of these consisted of dilution studies carried out in the context of the O-ESMS analyses. These revealed that in the case of both **3** and **4**, similar aggregate-to-monomer ratios were observed independent of the sample concentration employed. While not a proof, such findings are consistent with the postulate that the aggregation behavior observed reflects events taking place in solution rather than those occurring in the gas phase subsequent to ionization.

The second set of control experiments involved high-resolution oxidative electrospray ionization analyses of the monomer and dimer signals associated with the ferrocenium forms of **3** and **4**.[17] These studies confirmed that no additional hydrogen atoms were present in the detected ion. This result provides good support for the contention that the signals assigned to the self-assembled forms of **3** and **4** are those of ferrocenium cations. These same high-resolution experiments also served to rule out the presence of doubly charged positive ions. In particular, the observation of a unit mass separation between the ^{12}C- and ^{13}C-isotope peaks served to confirm the singly charged nature of the species assigned to monomeric and aggregated forms of **3** and **4**. Thus, while not bearing directly on the issue of solution-phase versus gas-phase chemistry, these studies do confirm the reliability of the data discussed above and their relevance in the context of self-assembly.

In addition to the above experiments, we studied dichloromethane samples of **3** and **4** under alternative soft ionization conditions, namely those of fast atom bombardment ionization (FAB) using nitrobenzyl alcohol as the matrix.[18] Here, significantly weaker dimer and trimer peaks were found for both **3** and **4** than in the corresponding O-ESMS experiments (the ratios of monomer:dimer:trimer were found to be of the order of 1:0.02:$\leq$0.003 in both cases). While these small peaks could reflect aggregation processes occuring in the gas phase, the general lack of higher order signals under the FAB-MS conditions appears consistent with the proposal that the O-ESMS measurements reflect self-assembly processes occuring in solution.

Conclusion

In this paper we have described a new approach to generating self-assembling structures containing organometallic subunits. The two prototypic systems we report here, the di- and tetrapyrrole-substituted ferrocenes **3** and **4**, both crystallize in the form of infinite ribbons and show the expected intermolecular interactions in the solid state. On the basis of VPO and O-ESMS analyses, it is also clear that system **4** undergoes self-assembly in solution and/or the gas phase. Interestingly, the O-ESMS experiments, to the extent that they reflect chemical processes occurring in solution, reveal a lower percentage of self-assembled trimer than might be expected on the basis of the VPO analyses. However, such differences, although noteworthy, could simply reflect the fact that it is a cationic (i.e., ferrocenium) material that is being studied by O-ESMS, whereas VPO measurements are carried out with neutral species. Certainly, it could be expected that cation–cation repulsions would serve to restrict the size of the aggregates formed by self-assembly.[19] In any event, we propose that the O-ESMS method detailed in this report is one that could prove useful in analyzing the solution and/or gas phase aggregation properties of appropriately designed self-assembling systems.

Experimental Section

Material and methods: For the characterization of synthetic intermediates, low-resolution CI mass spectra were obtained on a Finnigan MAT TSQ70 mass spectrometer. High-resolution CI mass spectra were obtained on a VG ZAB-E mass spectrometer. ^1H and ^{13}C NMR spectra were measured at 25°C on a GE QE-300 spectrometer at 300 and 75.5 MHz or on a Bruker WM-250 spectrometer at 250 and 75.5 MHz, respectively. Tetrahydrofuran (THF) was dried by distillation from a sodium melt under nitrogen. All other solvents and reagents were obtained from commercial sources and used as received unless indicated otherwise.

1,1′-Di(5-ethoxycarbonyl-3-ethyl-4-methylpyrrol-2-yl)ferrocene (**3**): A regioisomeric mixture consisting of 1-(2-ethoxycarbonyl-4-ethyl-3-methylpyrrol-5-yl)cyclopenta-1,3-diene and 2-(2-ethoxycarbonyl-4-ethyl-3-methylpyrrol-5-yl)cyclopenta-1,3-diene[9] (**1**, 1.51 g, 5.8 mmol) was dissolved in dry THF (100 mL) under an Ar blanket. A solution of TlOEt (1.44 g, 5.8 mmol) in dry THF (10 mL) was then added dropwise and the flask covered with Al foil. After two hours, solid iron(II) chloride (365 mg, 2.9 mmol) was added and the resulting slurry was stirred overnight at room temperature under an Ar atmosphere. Subsequently, the precipitated TlCl was filtered off and washed with THF. The solvent was evaporated off with a rotary evaporator and the resulting residue taken up in dichloromethane. Insoluble materials were removed by filtration. The resulting filtrate was collected and taken to dryness. It was then subjected to flash chromatography on a silica gel column (2.5 × 40 cm) with dichloromethane as the eluent. This gave the starting material **1** (560 mg, 2.2 mmol) as the first main fraction and the product **3** (575 mg, 56%) as the second main fraction. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.04$ (t, 6H, CH_2CH_3), 1.28 (t, 6H, OCH_2CH_3), 2.25 (s, 6H, CH_3), 2.39 (q, 4H, CH_2CH_3), 3.59 (s, 4H, CH_2-C_5), 4.12 (m, 8H, Cp), 4.22 (q, 4H, OCH_2CH_3), 8.67 (brs, 2H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 162.07$, 132.13, 126.98, 123.67, 117.51, 85.96, 69.67, 69.36, 60.00, 26.25, 17.58, 15.88, 14.98, 10.76; HRMS (CI +): calcd for $C_{54}H_{70}FeN_4O_8$ 572.2337, found 572.2340; cyclic voltammetry: Fc^+/Fc $E_{1/2} =$ 428 mV, Py^+/Py $E_{pa} = 1500$ mV (100 mVs^{-1}).

1,1′,2,2′-Tetra(5-ethoxycarbonyl-3-ethyl-4-methylpyrrol-2-yl)ferrocene (4): To a solution of 1,2-di(2-ethoxycarbonyl-4-ethyl-3-methylpyrrol-5-yl)cyclopenta-1,3-diene[9] (**2**, 483 mg, 1.07 mmol) in dry THF (50 mL), a solution of thallium ethoxide (266 mg, 1.07 mmol) in dry THF (3 mL) was added dropwise under Ar over a period of 10 mins. The resulting yellow-orange solution was stirred at room temperature for 2 h in the absence of light. At this juncture, solid iron(II) chloride (63 mg, 0.5 mmol) was added all at once. The resulting yellow-to-light-brownish slurry was stirred overnight at room temperature under an Ar blanket. Insoluble materials were then filtered off and washed with THF. The filtrate and washings were combined and taken to dryness in vacuo. The resulting dark residue was then purified by chromatography on a silica gel column (2 × 15 cm) with first dichloromethane and then a mixture of 1.5 % by volume of methanol in dichloromethane used as the eluents. The fraction collected with pure dichloromethane contained the starting material **2** (182 mg, 0.4 mmol), while the first orange fraction eluting with the MeOH/CH_2Cl_2 mixture contained clean **4** (102 mg, 35 %). ^{1}H NMR (250 MHz, CD_2Cl_2): $\delta = 1.01$ (t, 12H, CH_2CH_3), 1.26 (t, 12H, OCH_2CH_3), 2.18 (s, 12H, CH_3), 2.31 (q, 8H, CH_2CH_3), 3.58 (s, 8H, CH_2-C_5), 4.06 (brs, 2H, Cp), 4.13 (brs, 4H, Cp), 4.20 (q, 8H, OCH_2CH_3), 8.13 (brs, 4H, NH); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 161.47$, 130.87, 126.58, 123.52, 117.73, 84.50, 71.69, 69.57, 59.78, 24.63, 17.52, 15.59, 14.68, 10.39; HRMS (CI +): calcd for $C_{54}H_{70}FeN_4O_8$ 959.4542, found 959.4543; cyclic voltammetry: Fc^+/Fc $E_{1/2} = 648$ mV, Py^+/Py $E_{pa} = 1555$ mV (100 mVs^{-1}).

FAB and O-ESMS mass spectrometry: FAB-MS was carried out with 5.2×10^{-6} M solutions of **3** and **4** in dichloromethane. Spectra were recorded on a VG Analytical ZAB-E/SE instrument with nitrobenzyl alcohol (NBA) as matrix. Positive-ion electrospray ionization experiments were performed using electrospray ionization sources fabricated in-house for a Finnigan MAT TSQ 70 mass spectrometer (San Jose, CA) and a Micromass ZAB-E high-resolution double-sector mass spectrometer (Manchester, UK).[17a,b] Low-resolution mass spectra were obtained with the TSQ 70 and ZAB-E mass spectrometers. High-resolution mass spectra were obtained by means of the ZAB-E mass spectrometer. Both ionization sources used heated capillary tubing for desolvation and for ion transport into the ion sources of the mass spectrometer. For the experiments performed in this study, sample solutions were introduced into the electrospray ionization source with a syringe pump (Harvard Apparatus, Natick, MA; Model 55-111). A sample flow rate of approximately 100 μLmin^{-1} was generally used in order to obtain a stable signal. Ultramark 1621 (PCR, Gainesville, FL) was used as a reference/calibration compound[17c] for the mass range of 800 – 2100 Da, and gramacidin S (Sigma) was used as a calibration compound for the mass range of 500 – 1200 Da.

The following procedure was used for sample preparation: first, solutions of the pyrrole – ferrocene complexes were made up in dichloromethane (0.2 mL volume; 5×10^{-3} M). Next, a solution of iodine in dichloromethane (10 μL; 10^{-2} M) was added. Finally, the resulting solution was diluted with dichloromethane prior to analysis. The dilution factors were 80 and 10 for the low- and high-resolution MS studies, respectively.

X-Ray crystallography: Crystals of **3** grew as yellow prisms by slow evaporation from CH_2Cl_2, while crystals of **4** grew as pale yellow needles by slow evaporation from CH_2Cl_2/hexane solution. The data for both crystals were collected at − 75 °C on a Siemens P3 diffractometer, equipped with a Nicolet LT-2 low-temperature device and with a graphite monochromator with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Details of crystal data, data collection, and structure refinement are listed in Table 1. The data were corrected for Lp effects but not for absorption. Data reduction, decay correction, and structure solution and refinement were performed using the SHELXTL/PC software package.[20] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms bound to carbon were calculated in idealized positions (C–H 0.96 Å) with isotropic displacement parameters set to 1.2 × Ueq of the attached atom (1.5 × Ueq for methyl hydrogen atoms). The hydrogen atoms of nitrogen were observed in a ΔF map and refined with isotropic atomic displacement parameters set at 1.2 × Ueq of the attached nitrogen atom. The function, $\Sigma w(F_o^2 - F_c^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02 \times P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$. The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficients were obtained from ref. [21]. Other computer programs used in this work are listed elsewhere.[22] All figures were generated by means of SHELXTL/PC.[20] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100402. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code + 44 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data,[a] data collection, and refinement parameters.

	3	**4**
formula	$C_{34}H_{44}N_2O_4FeCl_4$	$C_{54}H_{70}N_4O_8Fe$
M_r	742.36	958.99
a, Å	9.089(1)	10.842(3)
b, Å	8.078(1)	12.891(4)
c, Å	25.354(3)	19.568(5)
α, °		71.93(2)
β, °	98.85(1)	77.54(2)
γ, °		82.79(2)
V, Å^3	1841.2(4)	2533.7(13)
Z	2	2
F(000)	776	1024
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
T, °C	− 100	− 75
2θ range, °	4 – 50	4 – 50
scan speed ° min^{-1} [a]	5 – 10	6 – 15
ρ_{calc}, gcm^{-3}	1.34	1.26
reflections measured	4365	9416
unique reflections	3239	8902
decay correction	0.9942 – 1.008	0.9565 – 1.006
R_{int} (F^2)	0.047	0.111
μ, cm^{-1}	7.38	3.55
crystal size, mm	0.17 × 0.25 × 0.46	0.17 × 0.17 × 0.56
transmission factor range	0.7619 – 0.8597	N/A
$R_w(F^2)$ [b]	0.167	0.146
$R(F)$ [c]	0.0749	0.0800
GoF., S [d]	1.021	0.851
parameters	214	616
max $\lvert \Delta/\sigma \rvert$	< 0.1	< 0.1
min, max peaks (e Å^{-3})	− 0.41, 0.51	− 0.44, 0.35

[a] Data were collected by means of ω scans with a scan range of 1° in ω. Lattice parameters were obtained from the least-squares refinement of 33 reflections with $10.4 < 2\theta < 18.0°$ for **3**, and 40 reflections with $15.1 < 2\theta < 18.5°$ for **4**. [b] $R_w = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o)^4\}^{1/2}$ and where the weight, w, is defined as follows: $w = 1/\{\sigma^2(F_o{}^2) + (a \times P)^2 + b \times P\}$; $P = [1/3 \times (\text{maximum of } (0 \text{ or } F_o^2) + 2/3 \times F_c^2]$. The parameters a and b were suggested during refinement and are 0.0409 and 3.6619, respectively, for **3**. [c] The conventional R index based on F where the 1666 and 2230 observed reflections have $F_o > 4(\sigma(F_o))$ for **3** and **4**, respectively. [d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Electrochemistry: Cyclic voltammetry was carried out at room temperature (25 ± 2 °C) under dry Ar using a Bioanalytic Systems (BAS) CV-50 W Version 2 MF 9093 Voltammetric Analyzer. Dry acetonitrile was the solvent in the case of **3**, while a 1:1 mixture of dry acetonitrile and dry dichloromethane was used for **4**. In both cases 0.1 M $[CH_3(CH_2)_3]_4NPF_6$ was the supporting electrolyte, a platinum disk the working electrode (1.6 mm diameter), and a platinum wire the auxiliary electrode. An Ag/AgCl couple, separated from the bulk solution by means of a porous Vycor plug, was used as the reference electrode.

Vapor pressure osmometry (VPO): Measurements were performed using a Corona/Wescan vapor pressure osmometry molecular weight apparatus

(Model 232 A). All materials were measured in toluene with the concentration ranging from 10^{-4} to 8×10^{-4} M. Sublimed benzophenone was used as the instrument standard.

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[10] In contrast to what is seen in the case of **3**, the bond distances of the intermolecular H-bonds formed by the four pyrrolic subunits of **4** are not quite equal. Specifically, for **3**, the geometry of the H-bonding interactions is as follows: N1–H1···O1, N···O 2.947(6) Å, H···O 2.071(6) Å, N–H···O 164.1(5)°. By contrast, for **4**, the relevant geometry of the interactions is: N1–H1N···O3 (related by $2-x$, $1-y$, $-z$), N···O 2.922(9) Å, H···O 2.11(7) Å, N–H···O 151(7)°; N2–H2N···O2 (related by $2-x$, $1-y$, $-z$), N···O 2.877(9) Å, H···O 2.10(7) Å, N–H···O 135(5)°; N1′–H1′N···O3′ (related by $-x$, $1-y$, $1-z$), N···O 2.881(9) Å, H···O 2.15(7) Å, N–H···O 144(7)°; N2′–H2′N···O2′ (related by $-x$, $1-y$, $1-z$), N···O 2.901(9) Å, H···O 2.10(7) Å, N–H···O 150(6)°.

[11] The value of 3.45 Å given for the distance between the two pyrroles of a dipyrrolecyclopentadienyl is an average owing to the four slightly different sets of H-bonds in **4**. It corresponds to the distance measured perpendicular to the plane of one pyrrole unit to the center of the adjacent one.

[12] As a control, the molecular weight of **2** was also determined by VPO. As expected, an average molecular weight typical for a mostly monomeric species was recorded ($M_{found} = 552$, $M_{calcd} = 452$).

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[19] In order to augment our chances of seeing higher-order aggregates in the case of **4**, we also tried carrying out the I_2-mediated reactions at

lower concentrations than those given in the experimental section. However, this led to a significant decrease in the sensitivity of the O-ESMS signals. Likewise, using a higher molar ratio of I_2 led to a substantial reduction in the intensity of those signals ascribable to the aggregated forms of **4**, presumably as the result of charge repulsion effects. Even under these latter conditions, no peaks ascribable to doubly charged ions could be observed.

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