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PAPER

Influencing the Electronic Interaction in Diferrocenyl-1-Phenyl-1*H*-Pyrroles†

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Functionalised diferrocenyl-1-phenyl-1*H*-pyrroles were synthesised using Negishi *C*,*C* cross-coupling reactions. The influence of different substituents at the phenyl moiety on the electronic interaction was studied using electrochemistry (cyclic and square-wave voltammetry) and spectro-electrochemistry (*in situ* UV/Vis-NIR spectroscopy). The ferrocenyl moieties gave rise to two sequential, reversible redox processes in each of the diferrocenyl-1-phenyl-1*H*-pyrroles. The observed $\Delta E_{1/2}$ values ($\Delta E_{1/2}$ = difference between first and second oxidation) range between 420 and 480 mV. A linear relationship between the Hammett constants σ of the substituents and the separation of the redox potentials exists. The NIR measurements confirm electronic communication between the iron centers as intervalence charge transfer (IVCT) absorptions were observed in the corresponding mixed-valent monocationic species. All compounds were classified as class II systems according to Robin and Day (M. B. Robin and P. Day, *Adv. Inorg. Chem.*, 1967, **10**, 247–423). The oscillator strength of the charge transfer transition highly depends on the electron donating or electron withdrawing character of the phenyl substituents. This enables direct tuning of the intermetallic communication by simple modification of the molecule's functional group. Hence, this series of molecules may be regarded as model compounds for single molecule transistors.

Introduction

Molecules possessing at least two redox active metal centres combined by π-conjugated connections offer the possibility to generate mixed-valent compounds by oxidising one of the metals, resulting in molecules in which the transition metals have different oxidation states.[1] Mixed valency has attracted interest during recent decades as such species can be used as model systems to study electron transfer properties of, for example, molecular wires and conducting polymers.[2] Moreover, these π-conjugated redox active compounds may be suitable for the design of novel electro-active materials.[3] In this respect, the use of the ferrocene Fe(II)/Fe(III) redox couple, as electron reservoir in conjugated organometallics, is often beneficial due to its high degree of reversibility and stability.[4] Therefore, mixed-valent complexes bearing two equivalent ferrocenyl substituents in different oxidation states are excellent candidates for studying intramolecular electron transfer.[5]

Comparison of the electrochemical behaviour of diferrocenyl thiophene, which has been studied by Iyoda in 1997[6] and the corresponding benzo[*c*]thiophenes of Ogawa and Sato,[7] showed that modification of the π-system in the bridging units between the ferrocenyl moieties can have a significant impact on the electrochemical behaviour of such diferrocenyl heterocycles. The difference between the 1st and the 2nd ferrocenyl based oxidation ($\Delta E_{1/2}$) increases from 150 mV in the 2,5-diferrocenyl thiophene to 280 mV in the appropriate 1,3-diferrocenyl benzo[*c*]thiophene.[6,7] Despite using different electrolytes in those studies, which hinders the comparability, these results clearly show that a modification in the electronic structure of the bridging systems can dramatically change the interaction between the redox-active termini.

Recently, we reported on the synthesis and characterisation of a series of ferrocenyl substituted five-membered heterocycles revealing that the electronic properties of the $^{c}C_4E$ rings (E = S, O, NR; $R = CH_3, C_6H_5$) have strong influence on the intervalence charge transfer in these systems.[8–10] It was found that electron rich pyrroles show much higher intermetallic interactions than, for example, electron poor thiophenes.[8–10] In continuation of this work, we here report the synthesis and characterisation, as well as the electro- and spectro-electrochemial behaviour, of substituted 2,5-diferrocenyl-1-phenyl-1*H*-pyrroles. Modifying the substituent at the phenyl ring enables variation of the electronic properties of the pyrrole core without changing the $^{c}C_4N$ setup. Bobula and Kotora have shown the direct relation between the redox properties of substituted phenylferrocenes and the σ Hammett constants of the substituents.[11] We herein show that the influence of such substituents is not limited to the electrochemical characteristics but also affects the electron transfer properties.

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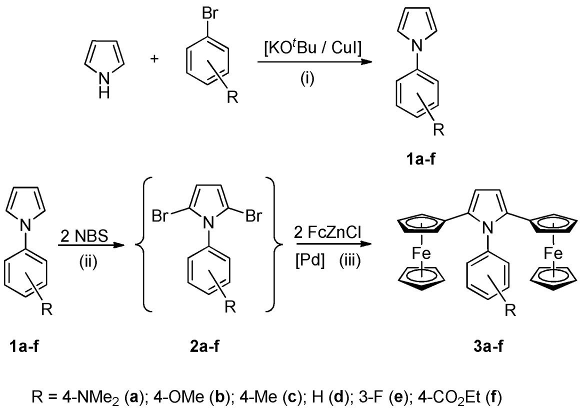
† Electronic supplementary information (ESI) available: NMR-simulation and 2D-Spectra of **3e**, NIR-Spectra of **3a**, **3b**, **3e** and **3f**. See DOI: 10.1039/c1dt10997a

Results and discussion

Synthesis and Characterisation

1-Phenyl-1*H*-pyrroles **1a–f** were synthesised using Ullmann-type cross-coupling reactions of the appropriate bromobenzenes and pyrrole according to procedures known in the literature (Scheme 1).[12] Reacting molecules **1a–f** with two equivalents of N-bromosuccinimide leads to the formation of the 2,5-dibromo-1-phenyl-1*H*-pyrroles **2a–f**,[13] which were used in the next reaction step without further purification. Treatment of **2a–f** with FcZnCl (Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) in the presence of catalytic amounts of [Pd(PPh_3)$_4$] gave diferrocenes **3a–f** in 60 to 80% yield (Experimental). A threefold excess of ferrocenyl zinc chloride is required to reach complete conversion of the reactants.



Scheme 1 Syntheses of **3a–f** by consecutive Ullmann-type coupling, dibromination and Negishi-ferrocenylation reactions. (i): In dimethylsulfoxide, 18 h, 110 °C; (ii) in tetrahydrofuran, 2 h, 0 °C, NBS (= *N*-bromo-succinimide); (iii) in tetrahydrofuran, [Pd] = [Pd(PPh_3)$_4$], 48 h, 60 °C.

Diferrocenyl pyrroles **3a–f** are stable to air and moisture in the solid state as well as in solution. They have been identified by elemental analysis, IR, UV/Vis and NMR (^{1}H, ^{13}C{^{1}H}) spectroscopy as well as high resolution ESI TOF mass spectrometry (Experimental). The electrochemical behaviour of all compounds was determined by cyclic voltammetry (CV), square-wave voltammetry (SWV) and *in situ* NIR experiments.

In ^{1}H NMR spectroscopy the expected signals for all compounds were observed. However, **3e** shows a more complex signal pattern, as the protons of the phenyl ring are coupling to each other and to the fluoro atom resulting in four doublets-of-doublets-of-doublets-of-doublets (dddd). The protons for **3e** were assigned by simulation of the spectrum and 2D experiments (Experimental, Supporting Information†). For the cyclopentadienyl groups two pseudo-triplets with J_{HH} = 1.9 Hz (C_5H_4) centred at 3.90 and 4.02 ppm are found as expected for AA′XX′ spin systems.[14] In most cases the pseudo-triplet at 4.02 ppm is overlapping with the singlet for the C_5H_5 protons. Within this series of compounds the pyrrole protons are observed at increasing chemical shifts: 6.34 (**3a**), 6.36 (**3b**), 6.36 (**3c**), 6.39 (**3d**), 6.40 (**3e**), 6.43 (**3f**). More accurately, this trend could be shown by the ^{13}C{^{1}H} NMR shifts of the respective C–H carbon atoms at the pyrrole ring. As it can be seen from Fig. 1, the chemical shifts of this atoms are increasing from **3a** to **3f** indicating that the electron-withdrawing and electron-donating nature of the substituents R at the phenyl moiety, described by the σ Hammett parameter,[15] strongly influence the electronic properties of the pyrrole system. Similar relations are described in the literature, showing linear slopes.[16]

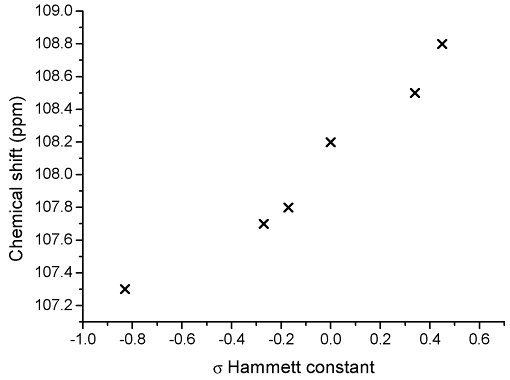


Fig. 1 Correlation of the ^{13}C{^{1}H} NMR shifts of the CH carbon atoms of the pyrrole core and the σ Hammett parameter of the substituents at the phenyl ring in **3a–f**.

Electrochemistry and Spectro-electrochemistry

The redox characteristics of **3a–f** were studied by cyclic voltammetry (CV), square-wave voltammetry (SWV) (Fig. 2) and UV/Vis-NIR spectroscopy (Fig. 4 and Fig. 5). As supporting electrolyte 0.1 mol L^{-1} dichloromethane solutions of [N^{n}Bu$_4$][B(C_6F_5)$_4$] were used.[17] The cyclovoltammetric studies were carried out at a scan rate of 100 mV s^{-1} and are summarized in Table 1. All potentials were referenced to the FcH/FcH$^+$ redox couple (E^0 = 0.0 mV).[18]

Compounds **3a–f** show reversible redox events and the ferrocenyl moieties could be oxidised step-wise. Depending on the compound the 1st oxidation occurs between −305 and −190 mV, while the 2nd oxidation can be observed in the range of 170 and 230 mV. A special feature of **3a** is an additional reversible redox event at 890 mV (ΔE_p = 75 mV) which is due to the oxidation of the NMe$_2$ group.[19] The potential of the 1st oxidation (E_1^0) increases when the substituent functionality changes from electron-donating (4-NMe$_2$: **3a**, 4-OMe: **3b**, 4-Me: **3c**) to electron-withdrawing (3-F: **3e**, 4-COOEt: **3f**). Therefore, we can conclude that the nature of the substituent strongly affects the electron density at the iron centers. Plotting the E_1^0 values *versus* the Hammett parameter of the substituents reveals a linear slope

Table 1 Cyclic voltammetry data (potentials *vs.* FcH/FcH$^+$), scan rate 100 mV s^{-1} at a glassy-carbon electrode of 0.5 mmol L^{-1} solutions of **3a–f** in dry dichloromethane containing 0.1 mol L^{-1} of [N(^{n}Bu)$_4$][B(C_6F_5)$_4$] as supporting electrolyte at 25 °C

Compd.	E_1^0 in mV (ΔE_p in mV)^a	E_2^0 in mV (ΔE_p in mV)^a	$\Delta E_{1/2}$ in mV	σ^b
3a	−305 (61)	175 (68)	480	−0.83
3b	−255 (60)	205 (69)	460	−0.27
3c	−250 (71)	205 (75)	455	−0.17
3d	−240 (68)^c	210 (75)^c	450^c	0
3e	−210 (61)	215 (65)	425	0.34
3f	−190 (62)	230 (69)	420	0.45

[a] E_1^0 = Potential of the 1st oxidation; E_2^0 = Potential of the 2nd oxidation. [b] σ = Hammett parameter of the substituent on the phenyl ring.[15] [c] Values have previously been published, see ref. 11

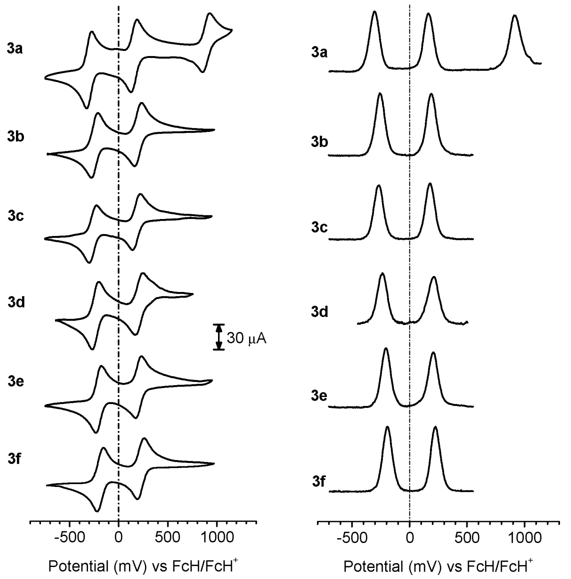


Fig. 2 Left: Cyclic voltammograms of **3a–f**; scan rate: 100 mV. Right: Square-wave voltammograms of **3a–f**. Measurement conditions: dichloromethane, analyte concentration 1.0 mmol L^{-1}, 25 °C, supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol L^{-1}). For $\Delta E_{1/2}$ values see Table 1.

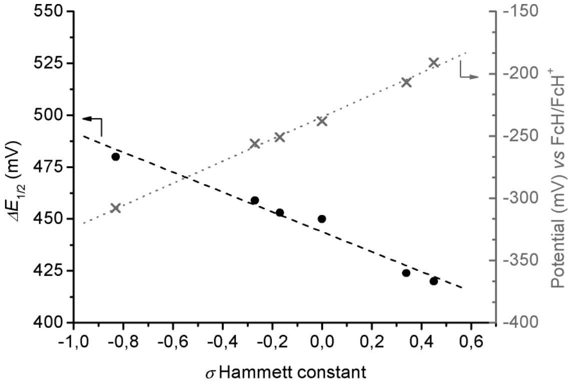


Fig. 3 Left ordinate (black): correlation of the $\Delta E_{1/2}$ values and the σ Hammett constant of **3a–f**, linear fit (R^2 = 0.978, dashed line). Right ordinate (grey): correlation of E_1^0 and the σ Hammett constant of **3a–f**, linear fit (R^2 = 0.995, dotted line).

(Fig. 3). This corresponds well with the substituents having a similar influence on the ferrocenyl oxidations in modified ferrocenyl benzenes.[11]

Besides having an influence on the ferrocenyl redox potentials the separation of the redox events ($\Delta E_{1/2}$) also varies depending on the substituent effects. The $\Delta E_{1/2}$ values increase, compared to non-substituted **3d**, when an electron-donating functionality is introduced at the phenyl moiety. Hence, **3a** (480 mV), **3b** (460 mV) and **3c** (455 mV) show a higher separation of the ferrocenyl-based redox processes, while the introduction of electron-withdrawing groups in **3e** (425 mV) and **3f** (420 mV), respectively, leads to a decrease in $\Delta E_{1/2}$. The influence of the substituents can nicely be demonstrated by plotting $\Delta E_{1/2}$ *vs.* σ, revealing a linear relationship (R^2 = 0.978). These results are in good agreement with the observation that electron-rich diferrocenyl heterocycles show a higher degree of intermetallic electron transfer.[10]

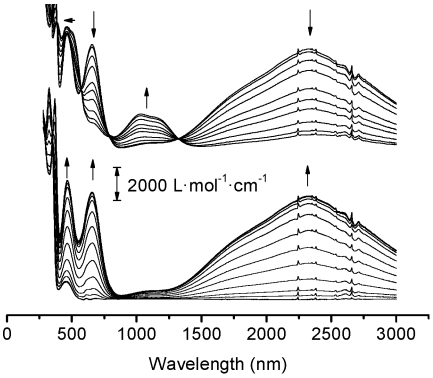


Fig. 4 NIR spectra of **3c** at increasing potentials (bottom: −200 to 300 mV; top: 250 to 900 mV *vs.* Ag/AgCl) at 25 °C, in dichloromethane, supporting electrolyte 0.1 mol L^{-1} [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]. Arrows indicate increasing or decreasing of the absorption.

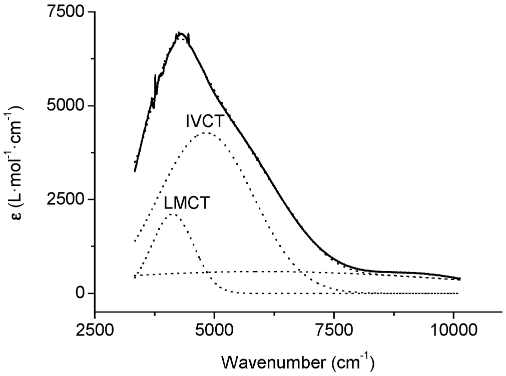


Fig. 5 Deconvolution of the NIR absorption of **3c**$^+$ using three Gaussian-shaped bands determined by spectro-electrochemistry in an Optically Transparent Thin-Layer Electrode (OTTLE) cell.

The spectro-electrochemical studies were conducted by stepwise increase of the potential from −500 to 1500 mV *vs.* Ag/AgCl in an Optically Transparent Thin-Layer Electrode (OTTLE) cell containing dichloromethane solutions of **3a–f** (1.0 mmol L^{-1}) and [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol L^{-1}) as supporting electrolyte. This procedure allows *in situ* generation of **3a–f**$^+$ and **3a–f**$^{2+}$, respectively, and in the case of diferrocenyl-(4-dimethyl-aminophenyl)-pyrrole even the generation of the three-fold charged cation **3a**$^{3+}$. While neutral **3a–f** do not exhibit any absorption in the range between 800 and 3000 nm (NIR region), upon stepwise increase of the potential broad bands are observed indicating the formation of mixed-valent **3a–f**$^+$ species. Further increase of the potential (above 500 mV *vs.* Ag/AgCl) leads to the disappearance of these absorptions and new LMCT bands (LMCT = Ligand-to-Metal Charge Transfer) at *ca.* 1000 and 1150 nm can be observed. The absorptions between 1500 and 2500 nm are characteristic for intervalence transfer exitations.[20] Determination of the physical parameters (wavenumber (ν_{max}), extinction (ε_{max}), Full-Width-at-Half-Maximum (FWHM) ($\Delta\nu_{1/2}$)) was achieved by deconvolution of the NIR data using three Gaussian-shaped overlapping absorptions (Fig. 5, Supporting Information†). The sum of these spectral components closely matches with the measured spectra. In all compounds two transitions were observed contributing to the NIR absorption. Between 4000 and 4150 cm^{-1} a sharp LMCT band was detected. Furthermore, in the range of 4500 to 5100 cm^{-1} a strong

Table 2 NIR data of **3a–f**$^+$ in dry dichloromethane containing 0.1 mol L^{-1} of $[N(^nBu)_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C

Compd.	Transition	ν_{max} (cm^{-1}) (ε_{max} (L mol^{-1} cm^{-1}))	$\Delta\nu_{1/2}$ (cm^{-1})	$(\Delta\nu_{1/2})_{theo.}$(cm^{-1})	Γ	$f\times10^3$ (cm^{-1})
3a$^+$	IVCT	5055 (4678)	2358	3417	0.31	50.72
	LMCT	4134 (2789)	1099			
3b$^+$	IVCT	4870 (4296)	2360	3354	0.30	46.64
	LMCT	4050 (2205)	1100			
3c$^+$	IVCT	4825 (4279)	2337	3339	0.30	46.00
	LMCT	4130 (2112)	1037			
3d$^+$	IVCT	4820 (4200)[a]	2369[a]	3340	0.30	45.76
	LMCT	4256 (1805)[b]	690[b]			
3e$^+$	IVCT	4586 (3584)	2413	3254	0.26	39.76
	LMCT	4056 (1527)	1045			
3f$^+$	IVCT	4554 (3445)	2438	3243	0.25	38.63
	LMCT	4027 (1023)	962			

[a] Values have previously been published, see ref. 9. [b] See ref. 10.

absorption with $\Delta\nu_{1/2}$ values typical for IVCT absorption was found (Table 2). For all compounds **3a–f** the FWHM is in the same range (2337–2438 cm^{-1}), the extinction increases with the electron donating capabilities of the phenyl substituent. This tendency supports the results which were observed in the voltammetric studies (*vide supra*).

The strength of the intervalence charge transfer (IVCT) absorption is expressed by the oscillator strength f, which can be calculated from ε_{max} and $\Delta\nu_{1/2}$ (FWHM) assuming Gaussian-shaped transitions (eqn (1)).[21]

$$f = 4.6\times10^{-9}\times\varepsilon_{max}\times\Delta\nu_{1/2} \tag{1}$$

Due to their similar structures, the electrostatic interactions of the ferrocenyls in this series of molecules are very similar. We previously have shown that these conditions enable a direct correlation of the electrochemical and the spectro-electrochemical results.[10] A plot of f *vs.* the $\Delta E_{1/2}$ values shows a linear relation (R^2 = 0.9899, Fig. 6) proving that **3a–f**$^+$ can be classified as class II mixed-valent species. This relationship confirms similar observations in a series of diferrocenyl heterocycles.[10] Furthermore, the classification criterion of Brunschwig, Creutz and Sutin[22] derived from the theoretical and the experimental FWHM (eqn (2) and eqn 3) confirm that these are moderately to strongly coupled class II systems. It is noteworthy that Γ also increases when the σ Hammett parameter decreases, showing that the electronic coupling increases with the electron-donating capability of the substituents.

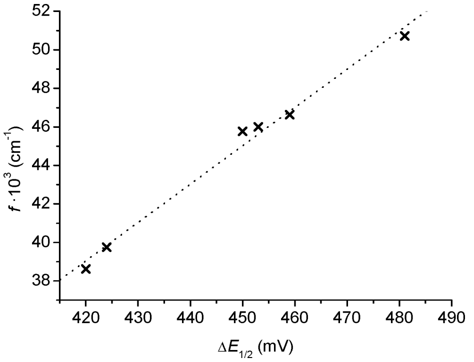


Fig. 6 Correlation of the oscillator strength f of the IVCT absorption and the $\Delta E_{1/2}$ values of **3a–f**$^+$ determined by NIR and cyclic voltammetry, respectively.

$$(\Delta\nu_{1/2})_{theo.} = (2310\nu_{max})^{1/2} \tag{2}$$

$$\Gamma = 1 - ((\Delta\nu_{1/2})/(\Delta\nu_{1/2})_{theo.}) \tag{3}$$

Conclusions

A series of phenyl-substituted 2,5-diferrocenyl-1*H*-pyrroles was synthesised using palladium-catalysed Negishi *C*,*C* cross-coupling reactions. Within this series a systematic change from electron-donating (R = NMe$_2$, OMe, Me) to electron neutral (R = H) to electron-withdrawing (R = F, CO$_2$Et) functionalities was realized. NMR studies confirmed that the substituents R have a significant effect on the electron density in the pyrrole core system which could be monitored nicely by the $^{13}C\{^1H\}$ shift of the pyrrolic carbon atoms. Electrochemical studies (cyclic voltammetry and square-wave voltammetry) were performed to investigate the redox behaviour of the ferrocenyl-substituted heterocyclic compounds. The electron-donating or electron-withdrawing character of the substituents affects the redox potentials of the ferrocenyl oxidations, as a linear relationship between the σ Hammett constants and the appropriate E_1^0 values was observed. In addition, the electronic influence is not limited to the redox potentials but the separation of the redox events $\Delta E_{1/2}$ also correlates linearly with the Hammett constants. *In situ* UV/Vis-NIR measurements revealed significant electron transfer in the mixed valence oxidation state for all compounds in this series, which allows their classification as class II systems according to Robin and Day.[23] Furthermore, the electron transfer properties are tuneable as the oscillator strength f of the IVCT absorption varies with the substituent on the phenyl group. It is obvious that the pyrrole core has to be electron-rich to achieve a high degree of intermetallic communication as the highest f values were observed in compounds with electron-donating functionality (**3a–c**). Due to the possibility to adjust the electron transfer, and hence the "conductivity" of the heterocyclic core, this series of compounds can be regarded as a model system for single molecule transistors. For substituted diferrocenyl-1-phenyl-1*H*-pyrroles a linear relationship between $\Delta E_{1/2}$ and f (IVCT) was found which is in agreement with the theoretical hypothesis for a series of molecules with similar geometries and hence, similar electrostatic properties.

Experimental

General conditions

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, toluene, n-hexane, and n-pentane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride.

Instrumentation

Infrared spectra were recorded using FT-Nicolet IR 200 equipment. The ^1H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.303 MHz in the Fourier transform mode; the $^{13}C\{^1H\}$ NMR spectra were recorded at 125.800 MHz. Chemical shifts are reported in δ (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: $CHCl_3$, δ 7.26; $^{13}C\{^1H\}$ NMR: $CDCl_3$, δ 77.00). The melting points of analytical purity samples (sealed off in nitrogen-purged capillaries) were determined using Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed using a Thermo FLASHEA 1112 Series instrument. Spectro-electrochemical measurements were carried out in an OTTLE cell similar to that described previously,[24] from dichloromethane solutions containing 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte using a Varian Cary 5000 spectrometer. High resolution mass spectra were recorded using a micrOTOF QII Bruker Daltonite workstation.

Electrochemistry

Measurements on 1.0 mmol L^{-1} solutions of **3a–f** in dry, air-free dichloromethane containing 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilizing a Radiometer Voltalap PGZ 100 electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2) and an Ag/Ag^+ (0.01 mol L^{-1} $[AgNO_3]$) reference electrode mounted on a Luggin capillary was used. The working electrode was pretreated by polishing using a Buehler microcloth first with 1 micron and then with $\frac{1}{4}$ micron diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mol L^{-1} $[AgNO_3]$ and 0.1 mol L^{-1} $[N(^nBu)_4][B(C_6F_5)_4]$ in acetonitrile, in a luggin capillary with a vycor tip. This luggin capillary was inserted into a second luggin capillary with vycor tip filled with a 0.1 mol L^{-1} $[N(^nBu)_4][B(C_6F_5)_4]$ solution in dichloromethane. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Experimental potentials were referenced against an Ag/Ag^+ reference electrode but results are presented referenced against ferrocene as an internal standard as required by IUPAC.[18] To achieve this, since the ferrocene couple FcH/FcH^+ interferes with the ferrocenyl signals of **3a–f**, each experiment was first performed in the absence of any internal standard, and then repeated in the presence of 1 mmol L^{-1} of ferrocene. Data were then manipulated in a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH^+ couple to 0.0 V. Under our conditions the FcH/FcH^+ couple was at 220 mV *vs.* Ag/Ag^+, $\Delta E_p = 61$ mV.[25]

Reagents

1a–f were prepared according to published procedures.[12] All other chemicals were purchased from commercial suppliers and were used as received.

Synthesis

Gerneral Procedure – Synthesis of 2,5-diferrocenyl-1-phenyl-1*H*-pyrroles (3a–f). To 1.5 mmol of the substituted phenylpyrrole **1a–f** dissolved in 50 mL of tetrahydrofuran, and 534 mg (3.0 mmol) of N-bromosuccinimide were added in a single portion at −20 °C. After 1 h of stirring at this temperature the solvent was evaporated and the resulting solid was suspended in tetrachloromethane. Filtration through a pad of Celite and removal of all volatiles in vacuum gave **2a–f** as brown-yellow oils. Without further purification the appropriate oil was dissolved in 30 mL of tetrahydofuran and added in a single portion to a solution of 4.5 mmol ferrocenyl zinc chloride prepared from monolithiated ferrocene and $[ZnCl_2\cdot 2\,thf]$ in tetrahydrofuran.[13] To this mixture 17 mg (0.015 mmol) of $[Pd(PPh_3)_4]$ was added in a single portion. After stirring at 60 °C for 48 h all volatiles were evaporated and the precipitate was dissolved in 100 mL of toluene and washed three times with 50 mL portions of water. The organic phase was dried over $MgSO_4$ and the solvent was evaporated to dryness in oil-pump vacuum. The remaining solid was purified by column chromatography (column size 20 cm × 5 cm) on alumina using a n-hexane-toluene mixture of ratio 1 : 1 (*v*/*v*) as eluent. All volatiles were removed under reduced pressure. The title compounds were obtained as orange solids.

Data for 2,5-diferrocenyl-1-(4-dimethylaminophenyl)-1*H*-pyrrole 3a. Yield: 582 mg (1.05 mmol, 70% based on **1a**) Anal. Calc. for $C_{32}H_{30}Fe_2N_2$ (554.28): C, 69.34; H, 5.46; N, 5.05 Found: C, 69.33; H, 5.56.; N, 4.96 Mp.: 224 °C (decomposition). IR data (KBr): 3084 m, 2922 s, 2847 m, 2810 w, 1614 w, 1524 s, 1358 m, 1328 w, 1101 m, 1022 w, 999 m, 815 s, 805 s, 755 m. ^1H NMR ($CDCl_3$, δ); 7.18 (m, 2H, C_6H_4), 6.80 (m, 2H, C_6H_4), 6.34 (s, 2H, $\mathbf{H_2}C_4N$), 4.02 (m, 14 H, C_5H_5/C_5H_4), 3.93 (pt, $J_{HH} = 1.9$ Hz, 4H, C_5H_4), 3.09 (s, 6H, $C\mathbf{H_3}$); $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, δ): 150.4 ($(CH_3)_2N$-$^i\mathbf{C}$-C_6H_4), 132.4 ($^i\mathbf{C}$-C_4H_2N), 130.3 (C_6H_4), 128.7 (N-$^i\mathbf{C}$-C_6H_4), 111.8 (C_6H_4), 107.3 (C_4H_2N), 79.4 ($^i\mathbf{C}$-C_5H_4) 69.3 (C_5H_5), 67.4 (C_5H_4), 66.2 (C_5H_4), 40.6 ($\mathbf{C}H_3$). HR-ESI-MS [*m*/*z*]: calc'd for $C_{32}H_{30}Fe_2N_2$: 554.1103, found: 554.1082 $[M]^+$.

Data for 2,5-diferrocenyl-1-(4-methoxyphenyl)-1*H*-pyrrole 3b. Yield: 540 mg (1.00 mmol, 66% based on **1b**) Anal. Calc. for $C_{31}H_{27}Fe_2NO$ (541.24): C, 68.79; H, 5.03; N, 2.59 Found: C, 68.66; H, 5.10.; N, 2.54 Mp.: 230 °C. IR data (KBr): 3089 m, 3006 w, 2953 m, 2924 w, 2901 w, 2892 w, 2828 m, 1608 m, 1594 s, 1439 m, 1419 m, 1293 m, 1247 s, 1104 s, 1040 s, 1025 s, 1001 s, 836 m, 819 s, 758, m. ^1H NMR ($CDCl_3$, δ); 7.25 (m, 2H, C_6H_4), 7.02 (m, 2H, C_6H_4), 6.36 (s, 2H, $\mathbf{H_2}C_4N$), 4.02 (m, 14 H, C_5H_5/C_5H_4), 3.93 (s, 3H, $C\mathbf{H_3}$), 3.90 (pt, $J_{HH} = 1.9$ Hz, 4H, C_5H_4); $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, δ): 159.6 (CH_3O-$^i\mathbf{C}$-C_6H_4), 132.8 (N-$^i\mathbf{C}$-C_6H_4), 132.4 ($^i\mathbf{C}$-C_4H_2N), 130.8 (C_6H_4), 113.8 (C_6H_4), 107.7 (C_4H_2N), 79.2 ($^i\mathbf{C}$-C_5H_4) 69.4

(C_5H_5), 67.5 (C_5H_4), 66.5 (C_5H_4), 55.5 (**CH_3**). HR-ESI-MS [*m*/*z*]: calcd for $C_{31}H_{27}Fe_2NO$: 541.0787, found: 541.0773 $[M]^+$.

Data for 2,5-diferrocenyl-1-(4-tolyl)-1*H*-pyrrole 3c. Yield: 593 mg (1.13 mmol, 75% based on **1c**) Anal. Calc. for $C_{31}H_{27}Fe_2N$ (525.24): C, 70.89; H, 5.18; N, 2.67 Found: C, 70.67; H, 4.89; N, 2.59 Mp.: 235 °C. IR data (KBr): 3098 m, 3090 m, 3030 w, 2915 w, 1643 w, 1515 s, 1420 s, 1329 m, 1106 s, 1037 w, 1023 m, 1001 s, 821 s, 806 m, 764 s. ^1H NMR ($CDCl_3$, δ); 7.29 (m, 2H, C_6H_4), 7.21 (m, 2H, C_6H_4), 6.36 (s, 2H, $\mathbf{H_2}C_4N$), 4.01 (m, 14 H, C_5H_5/C_5H_4), 3.88 (pt, J_{HH} = 1.9 Hz, 4H, C_5H_4), 2.5 (s, 3H, $\mathbf{CH_3}$); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ): 138.6 (N-$^i\mathbf{C}$-C_6H_4), 137.9 (CH_3-$^i\mathbf{C}$-C_6H_4), 137.4 ($^i\mathbf{C}$-C_4H_2N), 129.6 (C_6H_4), 129.4 (C_6H_4), 107.8 (C_4H_2N), 79.2 ($^i\mathbf{C}$-C_5H_4) 69.4 (C_5H_5), 67.4 (C_5H_4), 66.5 (C_5H_4), 21.4 ($\mathbf{CH_3}$). HR-ESI-MS [*m*/*z*]: calc'd for $C_{31}H_{27}Fe_2N$: 525.0838, found: 525.0821 $[M]^+$.

Data for 2,5-diferrocenyl-1-(3-fluorophenyl)-1*H*-pyrrole 3e. Yield: 572 mg (1.08 mmol, 72% based on **1e**) Anal. Calc. for $C_{30}H_{24}FFe_2N$ (529.21): C, 68.09; H, 4.57; N, 2.65 Found: C, 68.17; H, 4.56.; N, 2.60 Mp.: 212 °C. IR data (KBr): 3091 m, 2923 m, 1596 m, 1489 s, 1450 m, 1412 s, 1264 m, 1189 m, 1104 m, 879 m, 845 m, 815 s, 773 m. ^1H NMR ($CDCl_3$, δ); 7.41 (dddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{FH}$ = 6.3 Hz, $^5J_{HH}$ = 0.5 Hz, 1H, 5-**H**-C_6H_4), 7.19 (dddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{FH}$ = 8.4 Hz, $^4J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, 4-**H**-C_6H_4), 7.06 (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.9 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, 6-**H**-C_6H_4), 7.03 (dddd, $^3J_{FH}$ = 9.2 Hz, $^4J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 2.1 Hz, $^5J_{HH}$ = 0.5 Hz, 1H, 2-**H**-C_6H_4), 6.40 (s, 2H, $\mathbf{H_2}C_4N$), 4.05 (m, 14 H, C_5H_5/C_5H_4), 3.90 (pt, J_{HH} = 1.9 Hz, 4H, C_5H_4); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ): 162.4 (d, $^1J_{CF}$ = 249 Hz, 3-**C**-C_6H_4F), 141.4 (d, $^3J_{CF}$ = 9.5 Hz, 1-**C**-C_6H_4F), 132.4 ($^i\mathbf{C}$-C_4H_2N), 129.7 (d, $^3J_{CF}$ = 8.9 Hz, 5-**C**-C_6H_4F), 125.8 (d, $^4J_{CF}$ = 3.0 Hz, 6-**C**-C_6H_4F), 117.4 (d, $^2J_{CF}$ = 21.9 Hz, 2-**C**-C_6H_4F), 115.6 (d, $^2J_{CF}$ = 20.8 Hz, 4-**C**-C_6H_4F), 108.5 (C_4H_2N), 78.8 ($^i\mathbf{C}$-C_5H_4) 69.5 (C_5H_5), 67.5 (C_5H_4), 67.0 (C_5H_4). HR-ESI-MS [*m*/*z*]: calcd for $C_{30}H_{24}FFe_2N$: 529.0587, found: 529.0560 $[M]^+$.

Data for ethyl 4-(2,5-diferrocenyl-1*H*-pyrrol-1-yl)benzoate 3f. Yield: 700 mg (1.20 mmol, 80% based on **1f**) Anal. Calc. for $C_{33}H_{29}Fe_2NO_2$ (583.28): C, 67.95; H, 5.01; N, 2.40 Found: C, 67.53; H, 5.06; N, 2.37. Mp.: 267 °C. IR data (KBr): 3093 m, 2923 w, 1718 s, 1653 m, 1606 m, 1419 m, 1411 m, 1272 s, 1114 m, 1105 m, 1097 m, 819 m, 766 m. ^1H NMR ($CDCl_3$, δ); 8.11 (m, 2H, C_6H_4), 7.30 (m, 2H, C_6H_4), 6.43 (s, 2H, $\mathbf{H_2}C_4N$), 4.43 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $C\mathbf{H_2}CH_3$), 4.04 (s, 10 H, C_5H_5), 4.02 (pt, J_{HH} = 1.9 Hz, 4H, C_5H_4), 3.88 (pt, J_{HH} = 1.9 Hz, 4H, C_5H_4), 1.44 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $CH_2\mathbf{CH_3}$); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ): 166.0 (CO), 144.0 (N-$^i\mathbf{C}$-C_6H_4), 132.0 ($^i\mathbf{C}$-C_4H_2N), 130.3 (CO-$^i\mathbf{C}$-C_6H_4), 129.9 (C_6H_4), 129.7 (C_6H_4), 108.8 (C_4H_2N), 78.9 ($^i\mathbf{C}$-C_5H_4) 69.5 (C_5H_5), 67.6 (C_5H_4), 67.3 (C_5H_4), 61.3 ($\mathbf{CH_2}CH_3$), 14.3 ($CH_2\mathbf{CH_3}$). HR-ESI-MS [*m*/*z*]: calc'd for $C_{33}H_{29}Fe_2NO_2$: 583.0893, found: 583.0846 $[M]^+$.

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